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Blue-Light-Induced RAFT Polymerization for the Development of Functional Diblock Copolymer Membranes

Dissertation

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Publications

This dissertation is written in cumulative form and includes three first-author articles which have been published in scientific journals prior to this thesis. These publications are listed in the following:

- 1) Blue light-induced iniferter RAFT polymerization in aqueous-alcoholic media as a universal tool for the homopolymerization of various monomer families: kinetic investigations on different scales.
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- 2) Amphiphilic Block Copolymers via Blue-Light-Induced Iniferter RAFT *Ab Initio* Emulsion Polymerization in Water–Alcoholic Media
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- 3) pH-responsive size- and charge-selective block copolymer membrane for the separation of small proteins
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Abbreviations

2VP	<u>2</u> - <u>V</u> inyl <u>p</u> yridine
4VP	<u>4</u> - <u>V</u> inyl <u>p</u> yridine
AC	<u>A</u> ffinity <u>C</u> hromatography
ACPA	4,4'- <u>A</u> zobis(4- <u>c</u> yanopentanoic <u>a</u> cid)
AFM	<u>A</u> tom <u>i</u> c <u>F</u> orce <u>M</u> icroscopy
AFM-IR	<u>A</u> tom <u>i</u> c <u>F</u> orce <u>M</u> icroscope- <u>I</u> nfrared <u>S</u> pectroscopy
AIBN	2,2'- <u>A</u> zobis(isobutyronitrile)
ATR	<u>A</u> ttenuated <u>T</u> otal <u>R</u> eflection
ATRP	<u>A</u> tom <u>T</u> ransfer <u>R</u> adical <u>P</u> olymerization
<i>b</i>	<i>block</i>
BCP	<u>B</u> lock <u>C</u> opolymer
BSA	<u>B</u> ovine <u>S</u> erum <u>A</u> lbumin
BSE	<u>B</u> ackscattered <u>E</u> lectron
C	<u>C</u> ylinders
CC	<u>C</u> ovalent <u>C</u> hromatography
CDSPA	4- <u>C</u> yano-4-[(<u>d</u> odecyl <u>s</u> ulfanylthiocarbonyl)sulfanyl] <u>p</u> entanoic acid
CMC	<u>C</u> ritical <u>M</u> icelle <u>C</u> oncentration
CPDTC	2- <u>C</u> yano-2- <u>p</u> ropyl <u>d</u> odecyl <u>t</u> ri <thio<u>carbonate</thio<u>
Cr	<u>C</u> ritical Point
CRP	<u>C</u> ontrolled <u>R</u> adical <u>P</u> olymerization
CTA	<u>C</u> hain <u>T</u> ransfer <u>A</u> gent
DDMAT	2-(Dodecylthiocarbonothioylthio)-2-methylpropionic acid, also known as S- <u>D</u> odecyl-S'-(α , α' - <u>d</u> imethyl- α'' - <u>a</u> cetic acid) <u>t</u> ri <thio<u>car- bonate</thio<u>
DLS	<u>D</u> ynamic <u>L</u> ight <u>S</u> cattering
DMA	<i>N,N</i> - <u>D</u> imethyl <u>a</u> crylamide
DMAc	<i>N,N</i> - <u>D</u> imethyl <u>a</u> cetamide
DMAEA	2- <u>D</u> imethylamino <u>e</u> thyl <u>a</u> crylate
DMF	<i>N,N</i> - <u>D</u> imethyl <u>f</u> ormamide
DSC	<u>D</u> ifferential <u>S</u> canning <u>C</u> alorimetry
DTRP	<u>D</u> egenerative <u>T</u> ransfer <u>R</u> adical <u>P</u> olymerization

eATRP	<u>E</u> lectrochemically Mediated <u>A</u> tom <u>T</u> ransfer <u>R</u> adical <u>P</u> olymerization
EIPS	<u>E</u> vaporation- <u>I</u> nduced <u>P</u> hase <u>S</u> eparation
EsB	<u>E</u> nergy <u>S</u> elective <u>B</u> ackscattered
Eq	<u>E</u> quivalent
eRAFT	<u>E</u> lectrochemically Mediated <u>R</u> eversible <u>A</u> ddition- <u>F</u> ragmentation Chain <u>T</u> ransfer
FID	<u>F</u> ree <u>I</u> nduction <u>D</u> ecay
FT	<u>F</u> ourier <u>T</u> ransform
FTIR	<u>F</u> ourier <u>T</u> ransform <u>I</u> nfra <u>r</u> ed
G	<u>G</u> yroid
GBL	γ - <u>B</u> utyro <u>l</u> actone
GEP	<u>G</u> el <u>E</u> lectrophoresis
GPC	<u>G</u> el <u>P</u> ermeation <u>C</u> hromatography
HIC	<u>H</u> ydrophobic <u>I</u> nteraction <u>C</u> hromatography
IEC	<u>I</u> on- <u>E</u> xchange <u>C</u> hromatography
IEF	<u>I</u> soelectric <u>F</u> ocusing
IMAC	<u>I</u> mmobilized <u>M</u> etal Ion <u>A</u> ffinity <u>C</u> hromatography
iniferter	<u>I</u> nitator- <u>t</u> ransfer agent- <u>t</u> erminator
IR	<u>I</u> nfra <u>r</u> ed
ISR	<u>I</u> ntermediate <u>S</u> egregation <u>R</u> egime
ITP	<u>I</u> odine <u>T</u> ransfer <u>P</u> olymerization
IUPAC	<u>I</u> nternational <u>U</u> nion of <u>P</u> ure and <u>A</u> ppplied <u>C</u> hemistry
L	Lamellae
LbL	<u>L</u> ayer- <u>b</u> y- <u>L</u> ayer
LED	<u>L</u> ight- <u>E</u> mitting <u>D</u> iode
macroCTA	<u>M</u> acromolecular <u>C</u> hain <u>T</u> ransfer <u>A</u> gent
macroRAFT	<u>M</u> acromolecular <u>R</u> eversible <u>A</u> ddition- <u>F</u> ragmentation Chain <u>T</u> ransfer
MADIX	<u>M</u> acromolecular <u>D</u> esign by <u>I</u> nterchange of <u>X</u> anthate
MAM	<u>M</u> ore <u>A</u> ctivated <u>M</u> onomer
MD	<u>M</u> olecular <u>D</u> ynamics
Med _{ox}	<u>M</u> ediator Species in its <u>O</u> xidated State
Med _{red}	<u>M</u> ediator Species in its <u>R</u> educed State
MF	<u>M</u> icro <u>f</u> iltration
MMM	<u>M</u> ixed <u>M</u> atrix <u>M</u> embrane

MWCO	<u>M</u> olecular <u>W</u> eight <u>C</u> ut- <u>O</u> ff
N	<u>N</u> onsolvent
NF	<u>N</u> anofiltration
NIPAM	<u>N</u> -isopropylacrylamide
NIPS	<u>N</u> onsolvent- <u>I</u> nduced <u>P</u> hase <u>S</u> eparation
NMP	<u>N</u> itroxide <u>M</u> ediated <u>P</u> olymerization
NMR	<u>N</u> uclear <u>M</u> agnetic <u>R</u> esonance
OCRP	<u>O</u> rganocobalt-Mediated <u>R</u> adical <u>P</u> olymerization
ODT	<u>O</u> rders- <u>D</u> isorder <u>T</u> ransition
OHRP	<u>O</u> rganoheteroatom-Mediated <u>R</u> adical <u>P</u> olymerization
OOT	<u>O</u> rders- <u>O</u> rders <u>T</u> ransition
P	<u>P</u> olymer
PDI	<u>P</u> olydispersity <u>I</u> ndex
P2VP	<u>P</u> oly(2- <u>v</u> inylpyridine)
P4VP	<u>P</u> oly(4- <u>v</u> inylpyridine)
PAA	<u>P</u> oly(<u>a</u> crylic <u>a</u> cid)
PAGE	<u>P</u> olyacrylamide <u>G</u> el <u>E</u> lectrophoresis
PBS	<u>P</u> hosphate- <u>B</u> uffered <u>S</u> aline
PDMA	<u>P</u> oly(<u>N,N</u> - <u>d</u> imethylacrylamide)
PDMAEA	<u>P</u> oly(2- <u>d</u> imethylamino <u>e</u> thyl <u>a</u> crylate)
PDMAEMA	<u>P</u> oly(2- <u>d</u> imethylamino <u>e</u> thyl <u>m</u> ethacrylate)
PEC	<u>P</u> olyelectrolyte <u>C</u> omplex
PEO	<u>P</u> oly(<u>e</u> thylene <u>o</u> xide)
PET	<u>P</u> hoto-induced <u>E</u> lectron/ <u>E</u> nergy <u>T</u> ransfer
PET-RAFT	<u>P</u> hoto-induced <u>E</u> lectron/ <u>E</u> nergy <u>T</u> ransfer <u>R</u> eversible <u>A</u> ddition- <u>F</u> ragmentation Chain <u>T</u> ransfer
PFG	<u>P</u> ulsed <u>F</u> ield <u>G</u> radient
pH	<u>P</u> ondus <u>H</u> ydrogenii
PHEMA	<u>P</u> oly(2- <u>h</u> ydroxyethyl <u>m</u> ethacrylate)
photoiniferter	<u>P</u> hoto <u>I</u> nitiator-transfer agent- <u>t</u> erminator
photoRAFT	<u>P</u> hotoinitiated <u>R</u> eversible <u>A</u> ddition- <u>F</u> ragmentation Chain <u>T</u> ransfer
P(HTMB- <i>r</i> -I)	<u>P</u> oly(4-(2- <u>h</u> ydroxyethylthio)-2- <u>m</u> ethyl <u>b</u> utene- <u>r</u> andom-4-(2- hydroxyethylthio)-3-methyl butene- <u>r</u> andom-isoprene)
pI	<u>I</u> soelectric <u>P</u> oint
PI	<u>P</u> olyisoprene

PISA	<u>P</u> olymerization- <u>I</u> nduced <u>S</u> elf- <u>A</u> ssembly
pK	Dissociation Constant at Logarithmic Scale
PMMA	<u>P</u> oly(<u>m</u> ethyl <u>m</u> eth <u>a</u> crylate)
PNaSS	<u>P</u> oly(<u>s</u> odium <u>s</u> tyrene <u>s</u> ulfonate)
PRE	<u>P</u> ersistent <u>R</u> adical <u>E</u> ffect
PS	<u>P</u> ol <u>s</u> tyrene
PSGE	<u>P</u> ulsed <u>G</u> radient <u>S</u> pin <u>E</u> cho
PtBOS	<u>P</u> oly(<u>t</u> ert- <u>b</u> utoxystyrene)
PVP	<u>P</u> oly(<u>v</u> inyl <u>p</u> yridine)
<i>r</i>	<u>r</u> andom
RAFT	<u>R</u> eversible <u>A</u> ddition- <u>F</u> ragmentation Chain <u>T</u> ransfer
RDRP	<u>R</u> eversible- <u>D</u> eactivation <u>R</u> adical <u>P</u> olymerization
Redox-RAFT	<u>R</u> edox-Initiated <u>R</u> eversible <u>A</u> ddition- <u>F</u> ragmentation Chain <u>T</u> ransfer
RF	Radio-Frequency
RI	<u>R</u> efractive <u>I</u> ndex
RITP	<u>R</u> everse <u>I</u> odine <u>T</u> ransfer <u>P</u> olymerization
RO	<u>R</u> everse <u>O</u> smosis
ROMP	<u>R</u> ing- <u>O</u> pening <u>M</u> etathesis <u>P</u> olymerization
RPC	<u>R</u> eversed- <u>P</u> hase <u>C</u> hromatography
S	<u>S</u> elf-Assembly
S	<u>S</u> olvent
S	<u>S</u> pheres
SCMF	<u>S</u> elf- <u>C</u> onsistent <u>M</u> ean <u>F</u> ield
S _{cp}	<u>S</u> pheres (<u>C</u> lose <u>P</u> acked)
SDS-PAGE	<u>S</u> odium <u>D</u> odecyl <u>S</u> ulfate- <u>P</u> oly <u>a</u> crylamide <u>G</u> el <u>E</u> lectrophoresis
SE	<u>S</u> econdary <u>E</u> lectron
SE	<u>S</u> pin- <u>E</u> cho
SEC	<u>S</u> ize <u>E</u> xclusion <u>C</u> hromatography
SEM	<u>S</u> canning <u>E</u> lectron <u>M</u> icroscopy
SNIPS	<u>S</u> elf-Assembly & <u>N</u> onsolvent-Induced <u>P</u> hase <u>S</u> eparation
sono-RAFT	<u>S</u> onochemically initiated <u>R</u> eversible <u>A</u> ddition- <u>F</u> ragmentation Chain <u>T</u> ransfer
SSL	<u>S</u> trong <u>S</u> egregation <u>L</u> imit
STE	<u>S</u> timulated <u>E</u> cho
TCT	<u>T</u> hiocarbonyl <u>t</u> hio

TEM	<u>T</u> ransmission <u>E</u> lectron <u>M</u> icroscopy
Tf	<u>T</u> riflate
TGA	<u>T</u> hermogravimetric <u>A</u> alysis
THF	<u>T</u> etra <u>h</u> ydro <u>f</u> uran
TIPS	<u>T</u> hermally <u>I</u> nduced <u>P</u> hase <u>S</u> eparation
TMS-TMAC	<i>N</i> -[3-(<u>t</u> ri <u>m</u> ethoxy <u>s</u> ilyl)propyl]- <i>N,N,N</i> - <u>t</u> ri <u>m</u> ethylammonium <u>c</u> hloride
TTC	<u>T</u> ri <u>t</u> hiocarbonate
UF	<u>U</u> ltrafiltration
UV	<u>U</u> ltraviolet
UV-VIS	<u>U</u> ltraviolet- <u>v</u> isible
VIPS	<u>V</u> apor- <u>I</u> nduced <u>P</u> hase <u>S</u> eparation
VOC	<u>V</u> olatile <u>O</u> rganic <u>C</u> ompounds
WSL	<u>W</u> eak <u>S</u> egregation <u>L</u> imit

Constants and Variables

a	Segment Length
A	Absorbance
A	Surface Area
a_j	Area per Junction
A_{matrix}	Area of Matrix
A_{pores}	Area of Pores
A_{pores}	Total Area
a_0	Head Group Area
B_0	Magnetic Field Strength
[CTA]	Chain Transfer Agent Concentration
c	Concentration
c	Kozeny Constant
c_f	Concentration in the Feed
c_p	Concentration in the Permeate
c_p	Heat Capacity
C_{tr}	Transfer Constant
D	Diffusion Coefficient
D	Domain Spacing
$\bar{D}$	Dispersity
d	Diameter
E	Energy
E	Electrical Potential
E_{coh}	Cohesion Energy
f	Initiator Efficiency
f_c	Coupling Factor
G	Gibbs Free Energy
G	Gradient Strength
G_{mix}	Gibbs Free Energy of Mixing
G^0	Gibbs Free Energy under Standard Conditions
$g_1(\tau)$	Field Autocorrelation Function
$g_2(\tau)$	Intensity Autocorrelation Function
$G(\Gamma)$	Probability Distribution of Decay Rates

h	Height
H	Enthalpy
H_{mix}	Enthalpy of Mixing
I	Current
I	Light Intensity
$[I]$	Initiator Concentration
J	Flux
J_v	Volumetric Flux
k	Heat Transmission Coefficient
K	RAFT Equilibrium Constant
k_{act}	Rate Constant for Activation
k_{add}	Rate Constant for Addition
k_{addP}	Rate Constant for Addition of a Polymer Chain
k_B	Boltzmann Constant
k_β	Rate Constant for β -elimination
k_d	Rate Constant for Decomposition
k_{deac}	Rate Constant for Deactivation
k_i	Rate Constant for Initiation
K_n	Cumulant n
k_p	Rate Constant for Propagation
k_p^{app}	Apparent First Order Rate Constant
$k_{p,\text{rein}}$	Rate Constant for Propagation by Reinitiation
k_{tr}	Rate Constant for Chain Transfer
k_t	Rate Constant for Termination
$k_{t,\text{comb}}$	Rate Constant for Termination by Recombination
$k_{t,\text{disp}}$	Rate Constant for Termination by Disproportionation
l	Length
L	Domain Spacing
L	Length of the Pore
L	Livingness
l_c	Hydrophobic Tail Length
m	Mass
$[M]$	Monomer Concentration
M_{CTA}	Molecular Weight of the Chain Transfer Agent
M_M	Molecular Weight of the Monomer

$\bar{M}_{n,th}$	Theoretical Number-Averaged Molecular Weight
MW	Molecular Weight
m_{w1}	Mass After 1 st Rinsing
m_{w2}	Mass After 2 nd Rinsing
m_0	Initial Mass
m_1	Mass after Adsorption
n	Number of Equivalent Neighboring Nuclei
$\bar{n}$	Average Number of Radicals Per Particle
N	Degree of Polymerization
N_A	Avogadro's Number
$N_{in\ Atotal}$	Quantity in the Total Area
N_p	Number of Latex Particles Nucleated per Unit Volume of Water
Nu	Nusselt Number
$[P\cdot]$	Concentration of Propagating Chains
p	Conversion
p	Packing Parameter
p	Pressure
p	Transmembrane Pressure
P	Permeance
P	Power
Pr	Prandtl Number
P_{theo}	Theoretical Permeance
q	Scattering Vector
Q	Heat Energy
r	Radius
R	Universal Gas Constant
R	Rejection
R	Resistance
R_C	Core Radius
Re	Reynolds Number
R_F	Flory Radius
R_g	Radius of Gyration
R_h	Hydrodynamic Radius
R_p	Rate of Polymerization
R_{TEM}	Radius observed via TEM
S	Entropy

S	Specific Surface Area
S_{mix}	Entropy of Mixing
t	Time
T	Temperature
T_{air}	Air Temperature
T_g	Glass Transition Temperature
T_m	Melting Temperature
T_{ODT}	Order-to-Disorder Transition Temperature
v	Volume of the Hydrophobic Segment
ν	Flory Exponent
V	Voltage
V	Volume
$\dot{V}$	Volume Flow
V_{mix}	Volume of the Mixture
V_{molar}	Molar Volume
w	Thickness of The Wall
w	Weight
$w(\log M)^f$	Mass Portion of the Respective Molecular Weight in the Feed
$w(\log M)^p$	Mass Portion of the Respective Molecular Weight in the Permeate
$w(\log M)^r$	Mass Portion of the Respective Molecular Weight in the Retentate
z	Number of Nearest Neighbors
Z	Aggregation Number
α	Heat Transfer Coefficient
α	Statistic Segment Length
α	Ratio between Degree of Polymerization of a Homopolymer to Part of the Respective Block of a Block Copolymer
α	Relative Chain Length
γ	Gyromagnetic Ratio
Γ	Decay Rate
$\bar{\Gamma}$	Average Decay Rate
δ	Duration of the Gradient Pulse
δ	Solubility Parameter
Δ	Diffusion Time
δ_D	Dispersive Term of the Hansen Solubility Parameter
δ_H	Hydrogen-Bonding Term of the Hansen Solubility Parameter

δ_P	Polar Term of the Hansen Solubility Parameter
δ_T	Hansen Solubility Parameter
ε	Interaction Energy
ε	Extinction Coefficient
η	Refractive Index
η	Viscosity
θ	Scattering Angle
λ	Heat Conductivity Coefficient
λ	Wavelength
μ	Chemical Potential
μ	Magnetic Moment
Π	Osmotic Pressure
ρ	Density
τ	Delay Time
τ	Transmission
ϕ	Porosity
ϕ	Volume Fraction
ϕ^*	Critical Volume Fraction of Block Copolymer in Solution
χ	Flory–Huggins–Staverman Interaction Parameter
χN	Interaction Parameter
χN_{eff}	Effective Interaction Parameter
ψ	Selectivity
ψ^i	Ideal Selectivity
ψ^t	True Selectivity
ω_0	Larmor-Frequency
$\hbar$	Planck Constant

1 Zusammenfassung

Membranen stellen eine Schlüsseltechnologie der modernen Trenntechnik dar. Insbesondere ladungs- und größenselektive Membranen bieten durch die Kombination physikalischer Siebung mit elektrostatischen Wechselwirkungen ein hohes Maß an Selektivität. Sie eignen sich für Anwendungen in der Wasseraufbereitung,^{1–4} Lebensmitteltechnologie^{5–7} sowie der biotechnologischen^{8–10} und pharmazeutischen^{10–12} Produktion. Besonders bei der Trennung und Aufreinigung empfindlicher Biomoleküle bieten Membranen gegenüber konventionellen Verfahren Vorteile wie einen geringeren Energieverbrauch, einen kontinuierlichen Betrieb und eine hohe Skalierbarkeit.^{13,14} Eine zentrale Anwendung in diesem Bereich ist die Proteinseparation, bei der mithilfe funktionalisierter Membranen Proteine nicht nur nach Größe, sondern auch nach Ladung selektiv getrennt werden können. Darüber hinaus verfügen Membranen mit entgegengesetzt geladenen Kanälen über ein hohes Potenzial für den selektiven Transport geladener Moleküle und Ionen, wodurch beispielsweise Salze oder andere kleine Ionen gezielt aus komplexen Gemischen entfernt werden können — ein Ansatz, der insbesondere in der Aufreinigung oder Entsalzung von Bedeutung ist.¹⁵

Ein vielversprechender Ansatz zur Herstellung solcher funktionalen Membranen liegt im Einsatz von Blockcopolymeren. Diese makromolekularen Materialien können sich zu geordneten Nanostrukturen selbst organisieren und ermöglichen so die Herstellung von Membranen mit enger Porengrößenverteilung, gleichmäßiger Porenmorphologie und hoher Porosität.¹⁶ Die gezielte Einführung funktioneller Gruppen in den porenbildenden Block erlaubt eine Feinabstimmung der Membraneigenschaften, etwa durch lokale Ladungen oder Stimuli-responsive Funktionen.

Die begrenzte kommerzielle Verfügbarkeit von Blockcopolymeren ist jedoch eine Herausforderung, da ihre Synthese komplex ist und spezielle Polymerisationstechniken erfordert. Neben etablierten lebenden Polymerisationen stellen kontrollierte radikalische Methoden, insbesondere die reversible Additions-Fragmentierungs-Kettenübertragungs-Polymerisation (RAFT-Polymerisation), eine attraktive Alternative dar. Sie kombiniert die einfache Handhabung radikalischer Prozesse mit präziser Kontrolle über die Polymerarchitektur. Durch den Einsatz spezifischer Kettentransferreagenzien lassen sich gut definierte Strukturen mit enger Molekulargewichtsverteilung erzeugen. Zudem ermöglicht eine lichtinduzierte Initiierung milde Reaktionsbedingungen und eine präzise, zeitlich steuerbare Polymerisation.

In Anbetracht dessen vereint die vorliegende Dissertation zwei zentrale Fragestellungen: Zum einen die Entwicklung einer nachhaltigen, blaulichtinduzierten RAFT-Polymerisation in grünen Lösungsmitteln zur gezielten Synthese von Diblockcopolymeren in verschiedenen Labormaßstäben, und zum anderen deren Anwendung in anspruchsvollen Membranprozessen für größen- und ladungsselektive Separationen. Diese Arbeit schlägt somit eine Brücke zwischen grundlegender polymerchemischer Forschung und der anwendungsorientierten Entwicklung maßgeschneiderter Membranmaterialien für hochselektive Trennprozesse. Die Dissertation umfasst vier Hauptabschnitte:

Der erste Teil der Arbeit befasst sich mit der lichtinduzierten Polymerisation einer Reihe verschiedener Monomere aus unterschiedlichen Klassen – darunter *N,N*-

Dimethylacrylamid (DMA) als Vertreter der Acrylamide, 2-Dimethylaminoethylacrylat (DMAEA) als Vertreter der Acrylate und Vinylpyridine (VPs) (2- und 4-Vinylpyridin) – in umweltfreundlichen Wasser-Ethanol-Gemischen. Ein im Rahmen der Dissertation konzipierter und gebauter Photoreaktor, optimiert auf die Absorption des RAFT-Agens, ermöglichte eine skalierbare Reaktionsführung (untersucht bis 500 mL) bei kontrollierten Bedingungen und kurzen Reaktionszeiten. Die Methode erwies sich als robust und vielseitig einsetzbar.

Im zweiten Teil der Arbeit wurde die lichtinduzierte RAFT-Polymerisation auf die Synthese amphiphiler Diblockcopolymere, Poly(*N,N*-Dimethylacrylamid)-*block*-Polystyrol (PDMA-*b*-PS) und Poly(4-Vinylpyridin)-*block*-Polystyrol (P4VP-*b*-PS), im Rahmen einer *ab initio* Emulsionspolymerisation übertragen. Ein zweistufiges Verfahren sowie ein Semi-Batch-Ansatz wurden hinsichtlich Partikelbildung, Kinetik und Skalierbarkeit untersucht. Trotz der Trübung war die Methode bis zu einem Reaktionsvolumen von 500 mL (mit einer Polymerausbeute von bis 95 g Polymer) skalierbar. Kinetische Untersuchungen zeigten nur geringfügig verlängerte Reaktionszeiten bei vergleichbarem Umsatz.

Im dritten Teil wurden die synthetisierten PDMA-*b*-PS Diblockcopolymere zur Herstellung von Membranen verwendet. Mithilfe von Selbstorganisation und nichtlösungsmittelinduzierter Phasentrennung (SNIPS) entstanden isoporöse Membranen mit definierter Porenstruktur. Durch eine nachträgliche Salzsäurebehandlung wurden die hydrophilen PDMA-Blöcke in Blöcke aus Polyacrylsäure (PAA) umgewandelt, welche den Membranen eine pH-abhängige negative Ladung verliehen. Diese führten zu einer selektiven Proteinrückhaltung basierend auf Größe und Ladung. Während die ursprünglichen PDMA-*b*-PS Diblockcopolymer Membranen alle getesteten Proteine zurückhielten, ermöglichte die Funktionalisierung eine bevorzugte Permeation positiv geladener Proteine.

Der vierte Teil beschäftigt sich mit der Herstellung und Charakterisierung von Blendmembranen aus PDMA-*b*-PS und P4VP-*b*-PS Diblockcopolymeren. Untersuchungen mit der Transmissionselektronenmikroskopie deuteten auf eine Mikrophasenseparation innerhalb der makrophasenseparierten Membran hin. Eine gezielte Funktionalisierung der Porenwände durch Quaternisierung bzw. Hydrolyse ermöglichte die Erzeugung von positiv und negativ geladenen Porenbereichen. Erste Filtrationstests zeigten das Potenzial für eine vollständige Passage von sowohl ein- als auch zweiwertigen Ionen.

Insgesamt demonstriert diese Arbeit den vollständigen Weg von einer nachhaltigen Polymerisationsmethode bis zur Anwendung funktionalisierter Diblockcopolymere in selektiven Membrantrennprozessen. Die entwickelten Systeme bieten eine vielversprechende Grundlage für zukünftige membranbasierte Anwendungen in der Bioseparation und darüber hinaus.

2 Abstract

Membranes represent a fundamental technology in modern separation science. Particularly, size- and charge-selective membranes offer a high degree of selectivity by combining physical sieving with electrostatic interactions, making them suitable for applications in water and wastewater treatment,^{1–4} food processing,^{5–7} as well as in biotechnological^{8–10} and pharmaceutical^{10–12} production. Especially for the separation and purification of sensitive biomolecules, membranes provide advantages over conventional processes, such as lower energy consumption, continuous operation, and high scalability.^{13,14} A key application in this area is protein separation, where functionalized membranes enable selective separation of proteins not only by size but also by charge. Furthermore, membranes with oppositely charged channels offer great potential for the selective transport of charged molecules and ions, making it possible to selectively remove salts or other small ions from complex mixtures — an approach that is particularly relevant in purification or desalination.¹⁵

The use of block copolymers represents a promising approach for developing functional membranes. These macromolecular materials can self-assemble into well-ordered nanostructures, enabling the production of membranes with narrow pore size distributions, uniform pore morphology, and high porosity.¹⁶ The targeted incorporation of functional groups into the pore-forming block allows fine-tuning of membrane properties, such as introducing localized charges or stimuli-responsive functionalities.

However, the limited commercial availability of block copolymers remains a challenge due to their complex synthesis, which requires specialized polymerization techniques. In addition to established living polymerizations, controlled radical polymerization methods — particularly the reversible addition–fragmentation chain transfer (RAFT) polymerization — present an attractive alternative. RAFT polymerization combines the operational simplicity of radical processes with precise control over polymer architecture. Using specific chain transfer agents, well-defined polymer structures with narrow molecular weight distributions can be obtained. Furthermore, light-induced initiation allows for mild reaction conditions and temporally controlled polymerizations.

In light of this, the present dissertation addresses two principal research questions: first, the development of a sustainable, blue light-induced RAFT polymerization in green solvents for the controlled synthesis of diblock copolymers in different laboratory scales; and second, the application of these polymers in advanced membrane processes for selective size- and charge-selective separations. This work thus bridges the gap between fundamental polymer chemistry and the application-oriented development of tailored membrane materials for highly selective separation processes. The dissertation comprises four main sections:

This dissertation is divided into four main sections, covering the synthesis of homopolymers and diblock copolymers *via* light-induced RAFT polymerization, as well as the fabrication, characterization and application-specific performance tests of diblock copolymer membranes and diblock copolymer blend membranes.

The first part focuses on the light-induced polymerization of a range of monomers from different classes — including *N,N*-dimethylacrylamide (DMA) as a representative acrylamide, 2-dimethylaminoethyl acrylate (DMAEA) as an acrylate, and vinylpyridines

(2- and 4-vinylpyridine) — in environmentally friendly water–ethanol mixtures. A custom-designed photoreactor, optimized for the absorption profile of the RAFT agent, enabled controlled and scalable reactions (tested up to 500 mL) under mild conditions and with short reaction times. The method proved to be robust and versatile.

In the second part, the light-induced RAFT polymerization was extended to the synthesis of amphiphilic block copolymers — poly(*N,N*-dimethylacrylamide)-*block*-polystyrene (PDMA-*b*-PS) and poly(4-vinylpyridine)-*block*-polystyrene (P4VP-*b*-PS) — *via* an *ab initio* emulsion polymerization. Both a two-step and a semi-batch approach were investigated in terms of particle formation, kinetics, and scalability. Despite system turbidity, the process was scalable up to 500 mL (with a polymer yield of up to 95 g), with only marginally extended reaction times at comparable conversions.

In the third part, the synthesized PDMA-*b*-PS diblock copolymers were used for membrane fabrication. By employing self-assembly and non-solvent induced phase separation (SNIPS), isoporous membranes with well-defined pore structures were obtained. Subsequent treatment with hydrochloric acid converted the hydrophilic PDMA blocks into blocks of poly(acrylic acid) (PAA), imparting a pH-dependent negative charge to the membranes. This modification enabled selective protein retention based on both size and charge. While the original PDMA-*b*-PS membranes retained all tested proteins, the functionalization allowed for the preferential permeation of positively charged proteins.

The fourth part addresses the fabrication and characterization of blend membranes composed of PDMA-*b*-PS and P4VP-*b*-PS diblock copolymers *via* the SNIPS process. Investigations by transmission electron microscopy suggested microphase separation within the macroscopically phase-separated membrane structure. Targeted functionalization of the pore walls *via* quaternization and hydrolysis enabled the generation of positively and negatively charged pore domains. Initial filtration experiments revealed the potential for complete transport of both monovalent and divalent ions.

Overall, this work demonstrates the complete pathway from a sustainable polymerization strategy to the application of functionalized diblock copolymers in selective membrane separation processes. The systems developed herein provide a promising foundation for future membrane-based applications in bioseparation and beyond.

3 Introduction

This chapter lays the theoretical background for the publications presented in chapter 5 and the unpublished results presented in chapter 6. It is organized into six key sections, each addressing a distinct topic.

The first section, chapter 3.1, introduces block copolymers, emphasizing their microphase separation behavior in pure block copolymers and their blends. Given that block copolymers are predominantly synthesized using “living” polymerization or controlled radical polymerization methods, chapter 3.2 provides a concise overview of reversible deactivation radical polymerization (RDRP) techniques. Among these, reversible addition-fragmentation chain transfer (RAFT) polymerization stands out as a widely utilized method. It is employed in the synthesis of both the homo- and block copolymers featured in this work (publications 1 and 2). Chapter 3.3 delves deeper into the principles of RAFT polymerization, highlighting its recent advances and developments. Since the block copolymers synthesized through RAFT polymerization in this study are used to fabricate membranes (publication 3 and unpublished results), chapter 3.4 explores the theoretical foundation of membranes, with particular attention to the production of isoporous and multifunctional membranes. As the isoporous diblock copolymer membranes are applied in protein separation (publication 3), chapter 3.5 covers the fundamental concepts of proteins. Finally, chapter 3.6 concludes with an overview of the characterization methods used in this work.

3.1 Block Copolymers

Polymers are a fundamental class of materials consisting of long chains of repeating molecular units. Due to their remarkable versatility, they play an indispensable role in our daily lives. The basic building blocks of polymers are monomers, which are transformed into polymers through polymerization processes. When two or more different types of monomers are involved in a polymerization process, the resulting products are known as copolymers. These copolymers are further classified based on the number of distinct monomers involved, such as binary and ternary copolymers.¹⁷

Copolymers are also categorized according to the specific arrangement of their monomers, resulting in various structures, including random, alternating, gradient, and graft copolymers. Figure 1 illustrates examples of dicopolymers. Depending on the sequence of the repeating units, they are generally categorized into four classes: random, alternating, gradient and graft copolymers. Among these, block copolymers (BCPs) represent an extreme form of gradient copolymers.¹⁷ These macromolecules consist of discrete, chemically distinct blocks that are linked at one or more junction points.^{18,19}

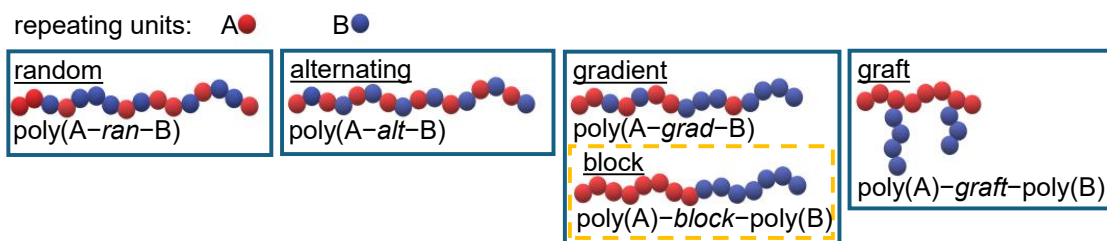


Figure 1. Copolymer sequences of dicopolymers.

3.1.1 Microphase Separation of Block Copolymers

3.1.1.1 Phase Separation of Block Copolymers in Melt State

Block copolymers exhibit unique properties arising from the differing chemical and physical characteristics of their polymer segments (blocks). Although the blocks are inherently incompatible, block copolymers do not undergo macrophase separation like conventional incompatible polymers. This is because their blocks are covalently bonded, preventing large-scale phase separation. Instead, block copolymers undergo microphase separation, self-assembling into a variety of ordered nanostructures, also referred to as microphase morphologies.²⁰ The specific morphology formed depends on several factors, including the number and composition of the blocks, their chemical nature, and their connectivity (e.g., linear, branched, star-like, or cyclic structures).²¹

The microphase separation of block copolymers is governed by various parameters and forces. In general, the miscibility of a multicomponent system is determined by the Gibbs free energy of mixing which incorporates contributions of the enthalpy of mixing ΔH_{mix} , the entropy of mixing ΔS_{mix} and the temperature T , as shown in Equation (1). For the components to be miscible, the change in the free energy of the mixture ΔG_{mix} must be negative.

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T\Delta S_{\text{mix}} \quad (1)$$

From Equation (1) it can be derived that decreasing the temperature enhances the tendency of segregation, leading to the formation of a microphase separated structure. This microphase separation of block copolymers occurs below a critical temperature known as the order-to-disorder transition temperature (T_{ODT}).¹⁸ According to the Flory–Huggins–Staverman theory,^{22–25} the entropic and the enthalpic contributions to mixing are given by the Equations (2) and (3), respectively. The entropy of mixing ΔS_{mix} for a system consisting of the polymers (or blocks) A and B is determined by the degree of polymerization N , their volume fractions ϕ as well as the universal gas constant R . As shown in Equation (2), mixing is inversely proportional to the degree of polymerization of the two polymers (or blocks). Therefore, larger polymers exhibit smaller entropy of mixing compared to smaller polymers, which makes phase separation more likely in high-molecular-weight systems.

$$\Delta S_{\text{mix}} = -R \left(\frac{\phi_A}{N_A} \ln \phi_A + \frac{\phi_B}{N_B} \ln \phi_B \right) \quad (2)$$

$$\Delta H_{\text{mix}} = RT \phi_A \phi_B \chi_{AB} \quad (3)$$

The phase behavior and miscibility of two homopolymers in a blend is described by Flory-Huggins solution theory, which models macroscopic phase separation driven by unfavorable enthalpic interactions. The change in the normalized molar Gibbs free energy ($\Delta G/RT$) is described by the Equation (4):

$$\frac{\Delta G}{RT} = \frac{\phi_A}{N_A} \ln \phi_A + \frac{\phi_B}{N_B} \ln \phi_B + \chi_{AB} \phi_A \phi_B \quad (4)$$

As shown in Equation (3), the enthalpy of mixing ΔH_{mix} depends on the Flory–Huggins–Staverman interaction parameter χ_{AB} . This parameter quantifies the energy cost per contact between the dissimilar repeating units A and B according to Equation (5). According to this Equation, χ_{AB} is influenced by several factors: (i) z which represents the number of nearest neighbors, (ii) the Boltzmann constant k_B , and (iii) the interaction energies between the repeating units A and B, A and A, and B and B (ϵ_{AB} , ϵ_{AA} and ϵ_{BB}), respectively. ϵ_{AB} is positive when there are repulsive (unfavorable) interactions between repeating units A and B, and negative when the interactions are favorable, encouraging miscibility.²⁶

$$\chi_{AB} = \left(\frac{z}{k_B T} \right) [\epsilon_{AB} - 0.5 (\epsilon_{AA} + \epsilon_{BB})] \quad (5)$$

Negative interaction energies — where $\epsilon_{AB} - 0.5 (\epsilon_{AA} + \epsilon_{BB}) < 0$ — correspond to a negative χ_{AB} , implying favorable mixing. Conversely, positive values lead to a positive χ_{AB} , which promotes phase separation. However, for most chemically dissimilar repeating units that lack strong specific interactions (e.g., hydrogen bonding), χ_{AB} is small and positive, and inversely proportional to the temperature.²⁶ Consequently, at elevated

temperatures — such as in high-temperature polymer melts — the effective repulsion between unlike units diminishes, improving miscibility.

The structure of a block copolymer formed by microphase separation is essentially an equilibrium process balancing between the two competing forces, enthalpy and entropy. For a block copolymer with a given composition and molecular weight, the morphology is typically observed that minimizes the free energy of the system.²⁶ The two competing forces, enthalpy and entropy, are commonly expressed by the product of the Flory–Huggins–Staverman segmental interaction parameter and the degree of polymerization, χN .²⁷ The interaction parameter χ represents the interfacial energy between the blocks (enthalpic contribution) while the degree of polymerization N reflects the elastic energy of the blocks (entropic contribution).^{18,26}

This entropic factor opposes microphase separation as it requires the polymer chains to deviate from their preferred random coil conformations and adopt more extended conformations, leading to chain stretching.^{26,28,29} The competition between entropy and enthalpy governs the final morphology of the microphase-separated system, which is further influenced by the volume fractions ϕ of the blocks and the specific polymer architecture.²⁹

The simplest and most extensively studied form of a block copolymer is the linear AB diblock copolymer. In a typical phase diagram of a conformationally symmetric diblock copolymer with an equal statistical segment length, as shown in Figure 2, the degree of segregation between the different blocks is expressed by the product $\chi_{AB}N$ and plotted

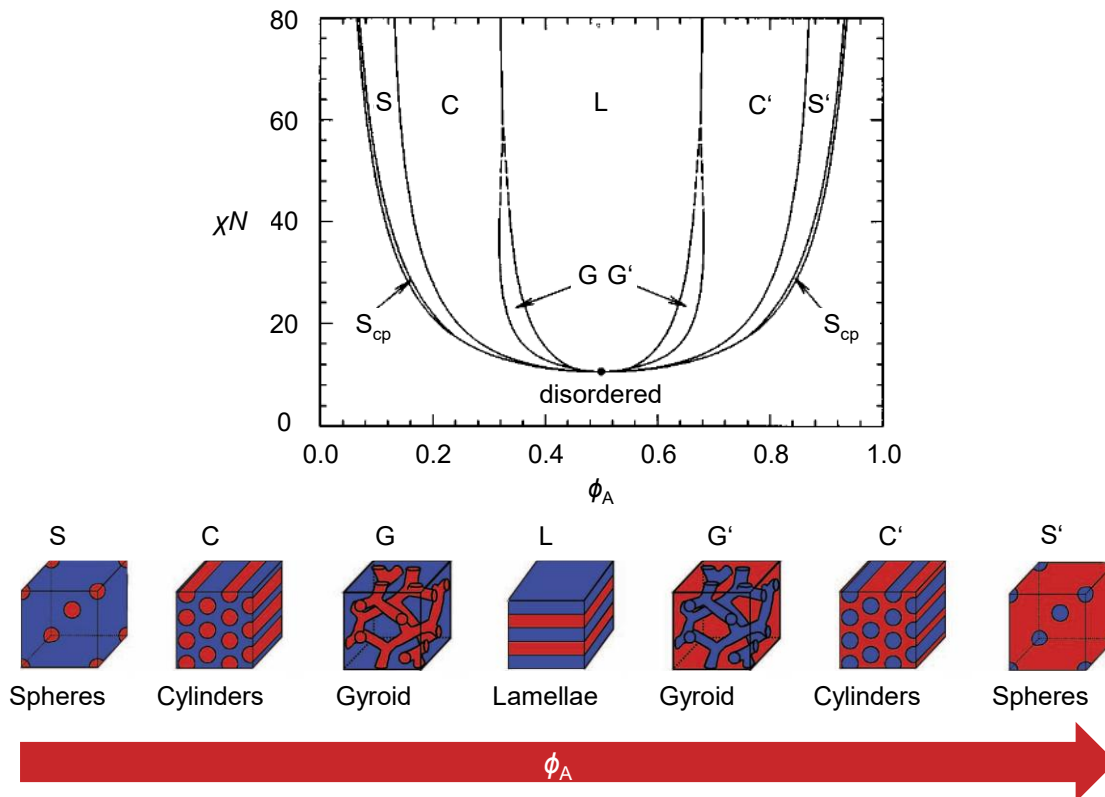


Figure 2. Theoretical phase diagram of a linear diblock copolymer and the morphology of the ordered phases (S_{cp} : close packed spheres, S: spheres, C: cylinders, G: gyroid, L: lamellae). Microdomains for block A are colored red, for block B in blue. Illustration reprinted and modified from ^{27,30}, with the permission of AIP Publishing and from Elsevier.

against the volume fraction of block A ϕ_A . This phase diagram, first presented by Matsen and Bates by using the incompressible Gaussian chain model and self-consistent mean field theory (SCMF), shows that a specific segregation strength $\chi N \geq 10$ is required for phase separation. Below this threshold, the diblock copolymers remain disordered, as entropy dominates the energetic penalty and therefore prevents segregation.²⁷ As χN increases, a transition from the disordered state to an ordered state occurs, resulting in microphase separation. Above the order-disorder transition (ODT) curve, the diblock copolymers segregate into thermodynamically stable ordered microphase-separated structures.

According to the degree of segregation χN , three different regimes can be identified in the phase diagram: the weak segregation limit (WSL) which corresponds to χN close to 10 (generally $10 \leq \chi N \leq 15$) and which is 10.5 for a symmetric diblock copolymer in the mean field limit, the intermediate segregation regime (ISR) ($15 \leq \chi N \leq 100$) and the strong segregation limit (SSL) for values of $\chi N \geq 100$.

The weak segregation limit was first described by Leibler.³¹ In this regime, χN is low, indicating only weak repulsive interaction between different blocks which leads to the formation of broad interfaces between the microdomains. As the name already implies, segregation is weak, and most of the chains remain unperturbed.³² The ordered microscopic density profile is approximately sinusoidally in space (see Figure 3), reflecting the minimal degree of phase separation. Since the polymers adopt a freely-jointed (Gaussian) chain conformation, the domain spacing $D \sim N^{0.5}$.^{32,33}

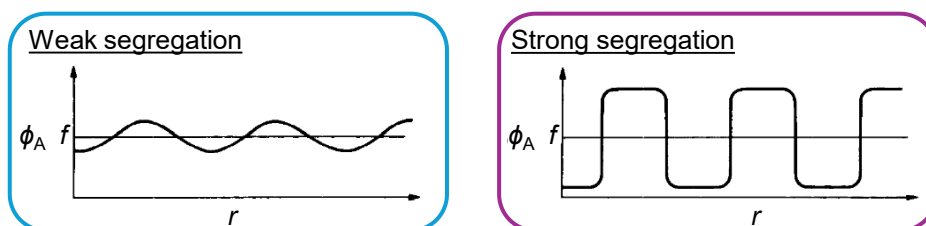


Figure 3. One-dimensional composition profiles of a microphase-separated diblock copolymer in the weak (WSL) and strong (SSL) segregation limits. ϕ_A is the local volume fraction of the block A and f refers to the macroscopic volume fraction of the block A (i.e. 0.5 for the symmetric diblock copolymer). Illustration reprinted and modified from ³², with permission from Annual Reviews, Inc.

In the intermediate segregation regime (ISR), the repulsive interactions between the diverse blocks become stronger, and the polymer chains deviate from their ideal Gaussian conformations. This regime was explored by Matsen and Bates using the incompressible Gaussian chain model and self-consistent field theory.²⁷ Several factors, including the interfacial area, chain stretching, spontaneous mean curvature, packing frustration, and segment distribution phase behavior influence the microphase separation in this region. In the ISR, the chains are perturbed, and the domain spacing scales as $D \sim N^{0.8}$.^{27,34}

In the strong segregation limit (SSL), where χN is high, the interfacial area between the blocks is minimized due to the incompressibility constraint. This leads to significant stretching of the polymer chains, which is entropically unfavorable, but the enthalpic contribution dominates in this regime. Therefore, the chains are perturbed and lead to larger microdomain dimensions $D \sim \alpha N^{2/3} \chi^{1/6}$ where α represents the statistic segment length.^{32,35} In the SSL, the ordered microscopic density profile exhibits sharply defined, discrete microphases, where block A is either fully present or absent in each domain

(see Figure 3). In addition to phase separation in the bulk state, block copolymers can as well self-assemble in selective solvents solution which will be discussed in the next two sections.

3.1.1.2 Selectivity of Solvents Towards Block Copolymers

The selectivity of solvents towards block copolymers is a crucial factor influencing their self-assembly and the formation of micelles.³⁶ This selectivity is based on the different solubility of the distinct blocks of the copolymer in a given solvent. Solubility parameters are often used to predict compatibility of substances, i. a. polymers, and provide a numerical basis for qualitative idea of “like dissolves like.” For this purpose, cohesive and adhesive properties of materials are correlated and predicted only from the properties of the components.³⁷

The Hildebrand solubility parameter³⁸ is a one-component solubility parameter and can be used for solutions without molecular polarity or specific interactions.³⁹ This solubility parameter δ describes the cohesive energy density for nonpolar, non-associating systems according to Equation (6):

$$\delta = \sqrt{\frac{E_{\text{coh}}}{V_{\text{molar}}}} \quad (6)$$

In this Equation, E_{coh} is the cohesion energy and V_{molar} the molar volume. The enthalpy of mixing for a binary mixture, based on semi theoretical grounds by Scatchard^{40,41} and Hildebrand^{42–45} and therefore called the Hildebrand–Scatchard Equation, determines the change in enthalpy per volume unit of the mixture V_{mix} through mixing two components A and B:

$$\frac{\Delta H_{\text{mix}}}{V_{\text{mix}}} = (\delta_A - \delta_B)^2 \phi_A \phi_B \quad (7)$$

In this Equation, it is assumed that the volume remains constant during mixing and the pressure stays unchanged. Additionally, it is presumed that molecular interactions are not influenced by the presence of other molecules, and the mixing process is random and independent of temperature. Furthermore, no chemical reactions, complex formations, or specific molecular associations should occur.³⁷ As indicated by Equation (7), the term $(\delta_A - \delta_B)^2$ represents the squared difference between the solubility parameters of the components. For the components to be miscible, this difference must be minimal.³⁷

Hildebrand's approach was later extended by Hansen and colleagues, who developed a three-dimensional solubility parameter model that accounts for polar interactions and hydrogen bonds.^{46,47} In this model, the Hansen solubility parameter δ_T is composed of three different contributions: the dispersive term δ_D , the polar term δ_P , and the hydrogen-bonding term δ_H according to the Equation (8).

$$\delta_T^2 = \delta_D^2 + \delta_P^2 + \delta_H^2 \quad (8)$$

The theory generally states that the closer the values of the solubility parameters of two components are, the greater their compatibility and the better they will mix. In the case of a diblock copolymer composed of block A and block B, a solvent is considered selective if the difference in the solubility parameter between the solvent and one block is significantly smaller than the difference for the other block. In this scenario, the solvent is selective for the block with the smaller deviation in solubility parameter. Consequently, the choice of solvent plays a crucial role in influencing the self-assembly behavior of block copolymers in solution, as will be discussed in the following section.

3.1.1.3 Phase Separation of Block Copolymers in Solution

In analogy with low molecular weight surfactants, block copolymers can form aggregates known as micelles, through self-assembly in selective solvents, once the concentration exceeds their critical micelle concentration (CMC).^{48,49} The CMC is the concentration at which micelles begin to form.⁵⁰ Below the CMC, only molecularly dissolved block copolymers are present in solution, usually as unimers, as shown Figure 4 (left). As the concentration of block copolymer chains in the solution c_{BCP} increases beyond the CMC, more micelles are formed. However, the concentration of unimers remains approximately constant at the value corresponding to the CMC.⁵⁰ Therefore, a thermodynamic equilibrium between the polymer chains in the micelles and those present as unimers is established (see Figure 4).

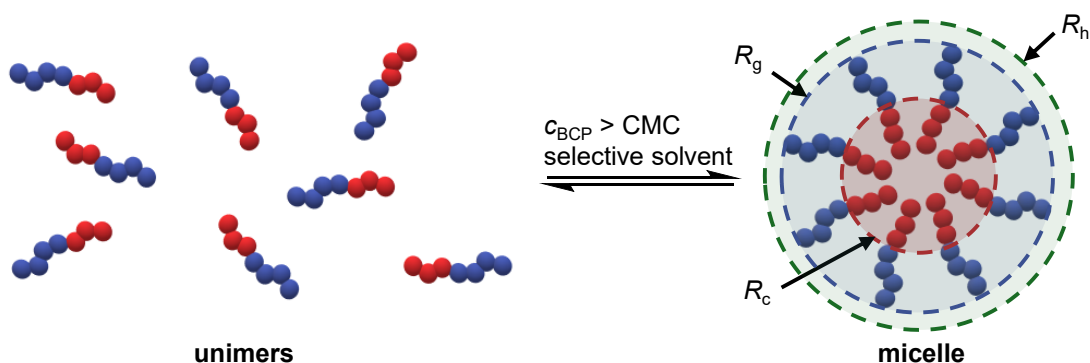


Figure 4. State of the diblock copolymers below the CMC and self-assembly of diblock copolymers above the CMC.

A typical spherical micelle is shown in Figure 4 (right). Such a micelle is characterized by the aggregation of a specific number of block copolymer chains, defined as the aggregation number Z , which is 8 in this example. The micelle has a core with a defined core radius R_c , while its overall size can be characterized by the radius of gyration R_g , and its hydrodynamic radius R_h , also referred as Stokes radius.⁵¹ Both represent the radius of the micelle; however, the value of R_h is typically larger than R_g , because it accounts for the viscous drag at the surface of the micelle, reflecting the interaction with the surrounding solvent.

The block copolymers form the micelles in selective solvents in a so-called closed association process.⁵² Thereby, the rather more insoluble blocks form a micellar core to minimize the unfavorable interactions with the poor solvent. These blocks are surrounded by a corona with the more soluble block to achieve a state of minimum free energy.⁵³ The Gibbs free energy of a micelle is mainly attributed to the interfacial energy of the core-shell interface, the stretching energy of the block copolymer chains, and the

repulsion among the chains in the corona.⁵⁰ The Gibbs free energy of micellization can be calculated in a first approximation according to the following Equation (9) through the critical micelle concentration [CMC], which is expressed in mole fraction units.⁵²

$$\Delta G^0 = RT \ln[\text{CMC}] \quad (9)$$

To describe the micellization of block copolymers, the packing parameter p is often used, first introduced by Israelachvili⁵⁴ to describe the micellization of surfactants. The packing parameter is a dimensionless quantity that describes the relationship between the molecular structure of the surfactant, the curvature of the hydrophobic-hydrophilic interface and the resulting particle morphology according to Equation (10).

$$p = \frac{v}{a_0 \cdot l_c} \quad (10)$$

In this Equation, a_0 is the head group area, l_c presents the hydrophobic tail length and v denotes the volume of the hydrophobic segment. In an aqueous medium, the hydrophobic blocks of the amphiphilic block copolymers form the micelle core, while the hydrophilic blocks constitute the corona. In this context, the hydrophobic block replaces the surfactant tail, the hydrophilic block corresponds to the polar head group, and the hydrophobic-hydrophilic interfacial area per chain represents the surfactant head group area.⁵⁵ This analogy allows for the prediction of the micellar structure — whether spherical, cylindrical, or vesicular micelles will form (see Figure 5).

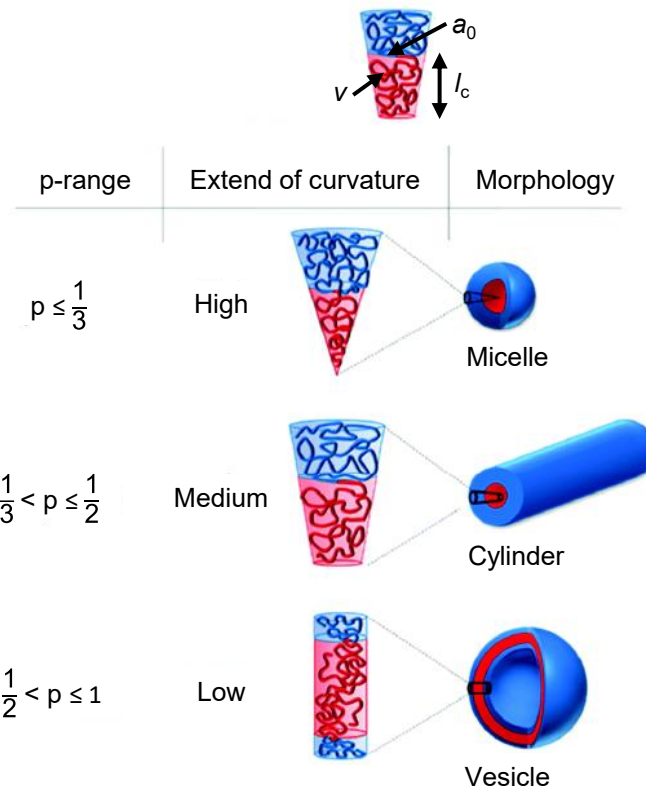


Figure 5. Morphology of self-assembled surfactants in dependence of the packing parameter p . Figure reprinted and modified from ⁵⁵, with permission from John Wiley & Sons, Inc.

However, only the unfavorable stretching of the solvophobic chains within the micellar core and the reduction in interfacial energy between the core-forming block and the solvent are considered. The stretching caused by the repulsive interactions between the solvophilic corona chains should also be taken into consideration but is disregarded here.⁵⁵ On top, even more complex morphologies, e.g. multicompartment micelles, toroids, and helices, have been obtained apart from the previous mentioned when a third block was introduced or the polymer architecture was changed from the conventional linear structure.⁵⁵ In practice, the micelle morphology depends on the molecular weight, the relative block lengths, the solvent composition, and the temperature.⁵⁶

The self-assembly of block copolymers in solution, like in melt, is driven by the minimalization of the free energy (as discussed above), but it is more complicated than their behavior in the bulk.¹⁹ In general, depending on the volume fraction of a block copolymer in solution, block copolymer solutions can be divided into three regimes: dilute, semi-dilute and concentrated.¹⁸

In dilute solutions, the concentration of polymer chains is sufficiently low to prevent significant intermolecular interactions between block copolymers.⁵⁷ Under these conditions, micellization occurs in a selective solvent once the CMC is exceeded. The dilute regime persists until the volume fraction of the block copolymer reaches the point where the swollen polymer coils begin to overlap ϕ^* , as described by Equation (11). Therefore the diluted state is valid up to $\phi < \phi^*$.⁵⁸

$$\phi^* = \frac{a^3 \cdot N}{R_F^3} = N^{1-3\nu} \quad (11)$$

In this Equation, a is the monomer size (also referred to as the segment length or Kuhn length), R_F the Flory radius, and ν the Flory exponent, which equals 0.588 in a good solvent and 0.5 in a theta solvent (where polymer coils behave as ideal chains).

When the concentration of block copolymers increases to the semi-dilute regime, the polymer chains begin to overlap.⁵⁷ Consequently, interactions and entanglements among the polymer chains become increasingly significant. Predictions for the ODT have been made by Olvera de la Cruz,⁵⁹ as well as Fredrickson and Leibler.⁶⁰ The crossover to the concentrated regime typically occurs at $\phi \approx 0.1 - 0.2$.¹⁸ In the concentrated regime, the solution phase behavior follows the 'dilution approximation', assuming that the polymer-solvent interactions remain favorable.⁶¹ The mean-field ODT and order-order transitions (OOT) in this regime resemble those observed in the melt state. In phase diagrams (like Figure 2), the segregation strength χN can be replaced by $\phi_{BCP} \chi N$, where ϕ_{BCP} is the volume fraction of the block copolymer.

3.1.2 Block Copolymer Blends

Blending is a straightforward experimental approach and an effective strategy for designing morphologies.⁶² These mixed materials are referred to as blends. In block copolymer blends, different scenarios can arise:⁶³

- i) One or more blocks from different block copolymers mix to form common microdomains, resulting in formation of superlattices.

- ii) The blocks remain immiscible, leading to macrophase separation between the microphase-separated domains of different block copolymers.
- iii) All blocks become miscible with each other, resulting in a homogeneous disordered phase.

Two primary types of interactions between different blocks influence mixing: entropic and enthalpic. When chemically similar blocks mix, the driving force is primarily entropic. In such cases, the formation of common microdomains by chemically similar blocks increases conformational entropy, lowering the overall energy compared to the energy required to stretch the blocks into separate domains.⁶³ In contrast, chemically dissimilar blocks may mix due to attractive enthalpic interactions, such as hydrogen bonds, which drive miscibility through favorable intermolecular forces.⁶³ The resulting morphology of the blend, however, depends on several factors, including the composition of the raw materials. This involves selecting the type of polymers (e.g., homopolymers or block copolymers) and determining the number of blocks in the block copolymers, as well as the components with which they are blended. The following sections discuss examples of different blend compositions to illustrate these principles.

3.1.2.1 Blends of Diblock Copolymer and Homopolymer (AB/A')

In general, a homopolymer with a significant segregation strength relative to all blocks of a given block copolymer will undergo macrophase separation from the block copolymer, behaving similarly to the separation observed between two incompatible homopolymers.⁶⁴ Therefore, research has primarily focused on blends of block copolymers with chemically similar homopolymers.

In a binary blend of a diblock copolymer AB with a homopolymer A', the phase behavior is preliminary determined by the degree of polymerization of the homopolymer $N_{A',\text{homopolymer}}$ compared to the degree of polymerization of the corresponding block in the block copolymer $N_{A,\text{copolymer}}$.⁶⁵ The parameter α is introduced as the ratio of the degree of polymerization of homopolymer A' to that of the A block in the diblock copolymer AB, as defined in Equation (12).

$$\alpha = \frac{N_{A',\text{homopolymer}}}{N_{A,\text{copolymer}}} \quad (12)$$

This ratio plays a crucial role in determining the extent of mixing between the homopolymer and the block copolymer, influencing the resulting phase behavior and microstructure of the blend. When the degree of polymerization of the homopolymer is significantly larger than that of the corresponding block in the copolymer ($N_{A',\text{homopolymer}} \gg N_{A,\text{copolymer}}$ and therefore $\alpha \gg 1$), macrophase separation occurs (see Figure 6 (a)). In this case, the block copolymer domain spacing L and the interfacial area per junction a_j remain approximately at their equilibrium values and are denoted as L_0 and $a_{j,0}$, respectively.⁶⁴

When the degrees of polymerization of the homopolymer and the A block of the copolymer are approximately equal ($\alpha \approx 1$), the homopolymer is selectively solubilized within the A block domains of the copolymer, as illustrated in Figure 6 (b). In this "dry brush regime," the homopolymer chains remain localized at the center of the A block domains, optimizing the conformational entropy of both the homopolymer and the block

copolymer. The term "dry brush" refers to the analogy with polymer brushes grafted to surfaces, where block copolymer chains extend from domain interfaces, and the homopolymer chains do not penetrate the brush-like structure of the block copolymer. In this regime, the domain spacing L increases; however, the interfacial area per junction $a_{j,0}$ remains unchanged.⁶⁴

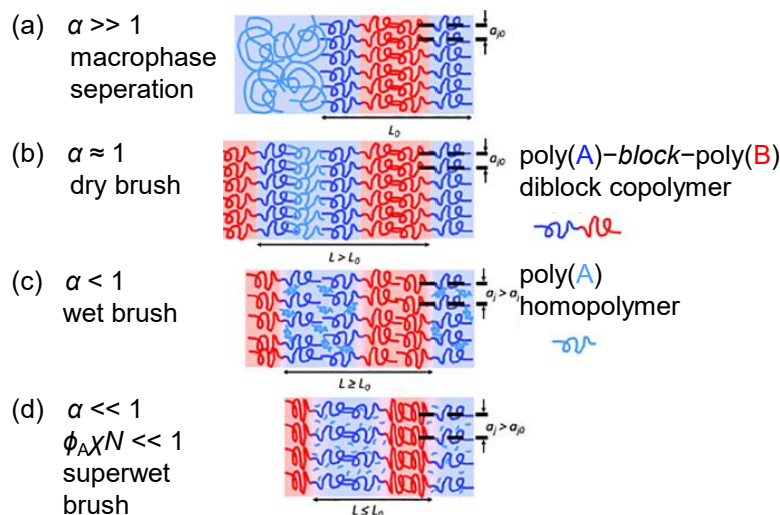


Figure 6. Regimes for binary blend of a AB diblock copolymer and a homopolymer A. Figure reprinted and modified with permission of from by the American Physical Society according to ⁶⁴.

If the degree of the polymerization in the homopolymer is smaller than that of the respective diblock copolymer ($\alpha < 1$), the homopolymer is weakly solubilized in the domain center of the A block domain of the copolymer (see Figure 6 (c)). This causes the A blocks to swell, increasing the interfacial area per block which may lead to morphological transitions. This regime is known as the "wet brush regime," where the homopolymer chains penetrate the block copolymer brush, causing the brush to become "wetted".¹⁸ Through the swelling of the block copolymer chains of the block A, L increases. However, this increase is partly counteracted by an increase in a_j resulting from the compression of opposing block chains due to incompressibility constraints.

In cases where $\alpha \ll 1$ and the segregation strength is low $\phi_A \chi N \ll 1$, the short homopolymer chains distribute uniformly throughout the A domain and up to the domain interface (see Figure 6 (d)). This regime is referred to as the "superwet brush regime," where the block copolymer chains are fully "wetted," leading to a decrease in L compared to L_0 and an increase in a_j . For further insights into homopolymer and block copolymer blends, references provide detailed discussions on these phenomena.^{18,64}

3.1.2.2 Blends of Similar Diblock Copolymers (AB/A'B')

The thermodynamic driving forces for blends of two block copolymers are generally similar to those governing self-assembly in previously discussed blends of diblock copolymers and homopolymers. However, blending block copolymers introduces an additional junction point, adding complexity and frustration to the system.⁶⁴

In the simplest scenario, diblock copolymers with chemically identical blocks but different molecular weights and/ or block weight fractions are blended. If the molecular weights are too dissimilar, the blend typically undergoes macrophase separation. This

occurs because one block must either stretch excessively or compress significantly to achieve mixing.⁶⁶ However, when the molecular weights are more similar, mixing becomes feasible.⁶⁴ Mixing is particularly favorable if the stretching energy of the extended block is sufficiently reduced to offset the compression energy of the less-stretched block.⁶²

When the volume fractions of block A differ significantly, such that the neat block copolymers would form distinct morphologies, coexisting morphologies can sometimes emerge in the blend. This coexistence arises from the relative energies of competing states. In a pure diblock copolymer, a single morphology minimizes the free Gibbs energy. In contrast, block copolymer blends can exhibit multiple morphologies with comparable free energies, resulting in coexisting structures.

In the case of blends with chemically equal block copolymers, but different molecular weights, such as AB/A'B' blends, the two distinct molecular weights introduce an additional degree of freedom, allowing for a spatial redistribution of chains. An example of the coexistence of diverse morphologies is shown in Figure 7 for blends of polystyrene-*block*-poly(methyl methacrylate) diblock copolymers. Similar examples exist for other systems like for polystyrene-*block*-polyisoprene^{67–69} polystyrene-*block*-poly(4-vinylpyridine).⁷⁰ As shown by mixing of polystyrene-*block*-poly(2-vinylpyridine) diblock copolymers with different morphologies, a blend can also lead to a morphology in between.⁷¹ Molecular dynamics (MD) simulations provide valuable insights into the evolution of these morphologies and the associated kinetic effects. Research has shown that blending can stabilize locally defective motifs, leading to the formation of high-energy morphologies that would otherwise be difficult to achieve.^{64,72–75}

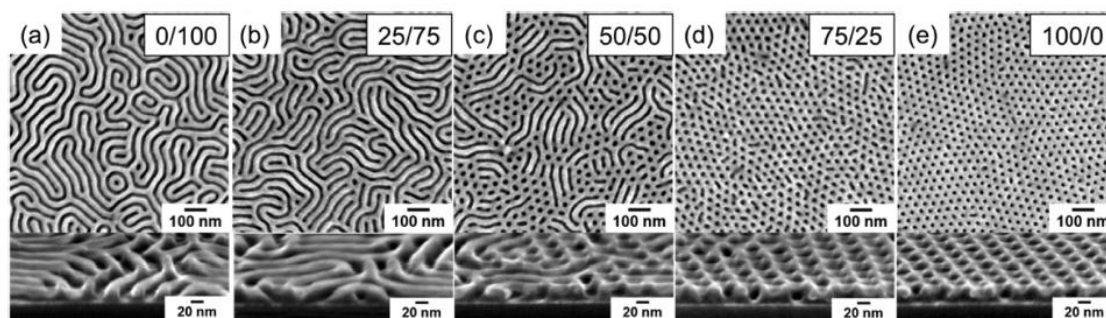


Figure 7. Phase morphology of thin films composed of blended cylinder- and lamellar-forming polystyrene-*block*-poly(methyl methacrylate) (PS-*b*-PMMA) block copolymers. The first number indicates the weight fraction of the cylindrical block copolymer; the second number is the weight fraction of the lamellar block copolymer. Figure reprinted from ⁷⁶, with permission from American Chemical Society.

3.1.2.3 Blends of Dissimilar Diblock Copolymers (AB/A'C)

Blending diblock copolymers with two diblock copolymers with a chemically identical block (A) but chemically distinct second blocks (B and C, respectively) can be an effective strategy to engineer new morphologies with enhanced functionality. Such blends are very interesting since a variety of functional chemical species can be employed.⁷⁷ The morphology and phase behavior in such systems are governed by the Flory-Huggins interaction parameters, which determine whether phase separation occurs between the blocks. If the interaction between blocks B and C is unfavorable

($\chi_{BC} > 0$), the diblock copolymers tend to macrophase separate.⁶⁴ Macroscopic phase-separation is commonly observed in blends of AB and A'C diblock copolymers.⁷⁸ Macrophase separated structures and or kinetically trapped morphologies were observed for binary blends of AB/A'C like polystyrene-*block*-polyisoprene/ polystyrene-*block*-poly(ethylene propylene),⁷⁹ polystyrene-*block*-poly(ethylene propylene)/ polystyrene-*block*-poly(partially hydrogenated polyisoprene)⁸⁰ as well as polystyrene-*block*-polyisoprene/ polyisoprene-*block*-poly(ethylene oxide).⁸¹ The resulting morphologies in these blends are influenced by several factors, including the mass ratios of the blocks of A to B, A' to C as well as the volume fraction and molecular weights of both diblock copolymers.⁸² This complexity makes it challenging to create uniform nanostructures. To achieve well-ordered microphase separation in AB/A'C diblock copolymer blends, the interfacial energy between the B and C blocks must be minimized. Therefore, χ_{BC} must be smaller than χ_{AB} and χ_{AC} , respectively.^{78,80,83} Otherwise even minor repulsive interactions between the B and C blocks will lead to macrophase separation.^{84,85}

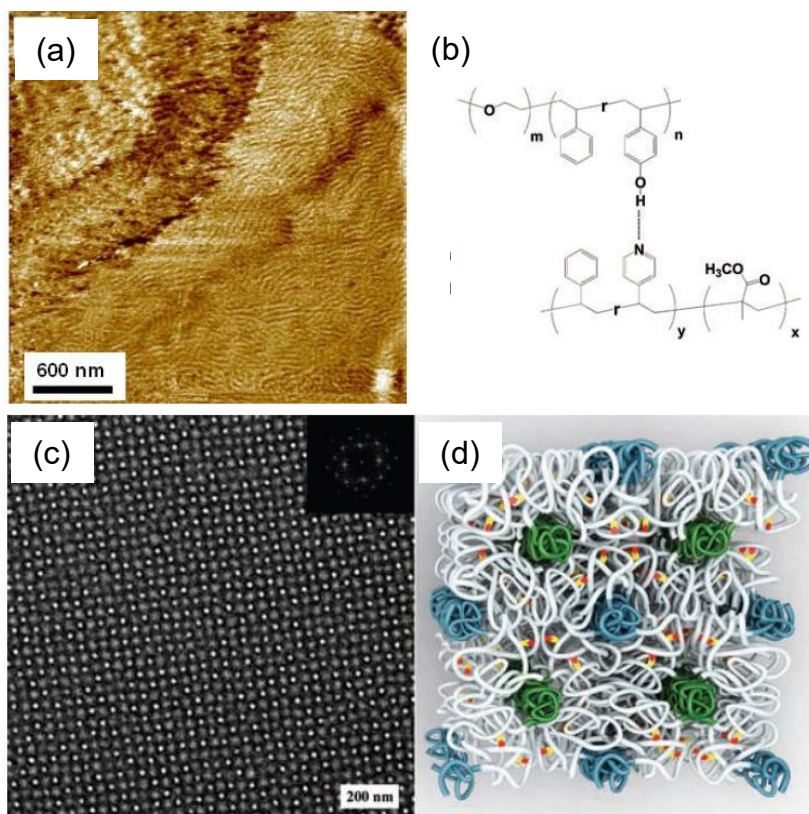


Figure 8. (a) AFM image of the spin-coated and solvent annealed parent poly(ethylene oxide)-*block*-polystyrene/ polystyrene-*block*-poly(methyl methacrylate) blend. (b) Chemical structure of the poly(ethylene oxide)-*block*-poly(styrene-*r*-4-hydroxystyrene)/ poly(styrene-*r*-4-vinylpyridine)-*block*-poly(methyl methacrylate) blend. (c) TEM image and Fourier-transformed image of the solvent-annealed blend film of poly(ethylene oxide)-*block*-poly(styrene-*r*-4-hydroxystyrene)/ poly(styrene-*r*-4-vinylpyridine)-*block*-poly(methyl methacrylate). (d) Proposed chain packings of (c). Images reprinted and adapted from⁸⁶, with permission from AAAS.

A significant challenge in achieving uniform long-range order in binary mixtures of two functional diblock copolymers is overcoming the inherent tendency toward macrophase separation.⁸² Uniform long-range order for two functional diblock copolymer blends through microphase separation still has not been achieved in the absence of

supramolecular interactions due to the overwhelming tendency of macrophase separation.⁸⁷ However, introducing favorable supramolecular interactions, such as hydrogen bonds between the blocks, can profoundly influence microphase separation. For example, this has been observed by blending the diblock copolymers poly(ethylene oxide)-*block*-poly(styrene-*r*-4-hydroxystyrene) / poly(styrene-*r*-4-vinylpyridine)-*block*-poly(methyl methacrylate).⁸⁶ For the parent poly(ethylene oxide)-*block*-polystyrene/ polystyrene-*block*-poly(methyl methacrylate) blend a macrophase-separated structure with no long-range order was observed. Through the incorporation of 4-hydroxystyrene and 4-vinylpyridine units into the major PS blocks A and A', respectively, the supramolecular assembly *via* H-bonds between the phenolic units of the 4-hydroxystyrene and the 4-pyridine units led to the formation of nanoscale morphologies (see Figure 8). With increasing composition of the hydrogen bond components, the observed morphologies transitioned from vertical cylinders with little order to square arrays with poor order, and finally to square arrays with a high degree of in-plane order. These blend experiments show that near stoichiometric ratios of the hydrogen bonding groups enable good order as well as controlled local packing of cylindrical domains.

The effect of hydrogen bonds has as well been investigated in binary mixtures of polystyrene-*block*-poly(4-vinyl pyridine) and poly(ethylene glycol)-*block*-poly(4-hydroxy styrene).⁸⁸ In contrast to previous examples where the major blocks interacted, this study focused on hydrogen bonds between the minor blocks B and C. Through hydrogen bond interactions between the poly(4-vinyl pyridine) and the poly(4-hydroxy styrene), a common cylindrical domain was established. This demonstrates the power of hydrogen bonds to influence phase behavior and domain structure in block copolymer blends.

In a nutshell, blending block copolymers is a powerful technique to tune the morphology. The self-assembly of block copolymer blends is governed by the interplay between entropy, which favors mixing, and enthalpy, which drives phase separation to minimize unfavorable interactions. The resulting nanostructures are determined by this delicate balance and can be tuned by adjusting parameters such as block composition, molecular weight, and temperature. By carefully selecting the type of block copolymer(s) and their chemical composition, blending can create complex nanostructures in a controlled manner, with increased complexity arising from the number of blocks in the system. More exotic morphologies can also be achieved by incorporating other chain architectures.⁶⁴ For further insights, additional information is provided in the literature.^{18,62,64,89-91}

Due to the flexibility in tailoring material properties by adjusting the composition, molecular weight, and sequence of the constituent blocks and therefore adaptable properties of block copolymers and their blends, they received an increasingly important role in the development of innovative materials with multifunctional capabilities. One of them is in the implementation of functional membranes which will be discussed in chapter 3.4. Before, the synthesis to receive such well-defined block copolymers will be discussed in chapter 3.2 and 3.3.

3.2 Reversible-Deactivation Radical Polymerization (RDRP)

Radical polymerization is one of the most widely used mechanisms for synthesizing polymers. In free-radical polymerization, the growing polymer chains are terminated by events such as recombination or disproportionation, rendering them incapable of further growth. These terminated chains are referred to as dead and are unsuitable for the synthesis of block copolymers.⁹² This limitation distinguishes free-radical polymerization from living polymerizations. In living polymerizations, unwanted side reactions, such as chain transfer or termination, are effectively suppressed. All polymer chains are initiated simultaneously, and the active ends of the polymer chains remain reactive indefinitely. This allows for continued chain growth and facilitates the synthesis of block copolymers. An ideally living polymerization system produces polymers with a dispersity index $\bar{D}$ approaching 1.0, signifying uniform chain lengths.⁹³ Living polymerization encompasses several polymerization techniques, including anionic polymerization,^{94,95} cationic polymerization,⁹⁶ ring-opening metathesis polymerization (ROMP),^{97,98} and group-transfer polymerization.⁹⁹

With development of reversible deactivation radical polymerizations, also referred to as controlled radical polymerizations (CRPs), in the 1990's, new opportunities for the fabrication of polymers with controlled molecular weights and terminal groups were provided, while retaining the robustness of the radical process.¹⁰⁰ RDRPs encompass a suite of techniques, including nitroxide mediated polymerization (NMP),^{101–103} atom transfer radical polymerization (ATRP),^{104,105} and RAFT polymerization.¹⁰⁶ These methods have revolutionized polymer synthesis, enabling control over polymer composition, topology, and chain length, and allowing for the precise synthesis of block and graft copolymers.^{100,107}

The defining feature of CRPs is the ability to control the chain growth by the implementation of a reversible deactivation mechanism. The fundamental principle of RDRPs involves establishing a dynamic equilibrium between propagating (i.e., active species) and reversibly deactivated polymer chains (i.e., dormant species).¹⁰⁰ Periodic deactivation of the growing chains by leaving groups prevents uncontrolled chain growth and irreversible termination since the deactivated chains can be reactivated to continue polymerization. The equilibrium strongly favors the dormant state compared to the active, propagating state, minimizing bimolecular termination events and leading to the apparent simultaneous growth of all polymer chains. This is why RDRPs are often called "controlled" or "living" radical polymerizations, although they are not living polymerizations.^{108,109}

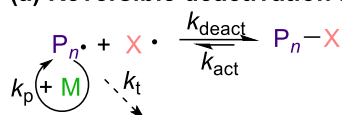
The equilibria in RDRPs are mediated by specific agents or catalysts, which distinguish the various techniques. Three primary deactivation/ activation mechanisms form the basis of CRP methods, as illustrated in Scheme 1:¹⁰⁶

1. Persistent radical effect (PRE)¹¹⁰ (Scheme 1 (a)): This mechanism relies on persistent (thus long-lived) radicals that predominantly terminate through cross-coupling. For example, nitroxide radicals are used as regulators in NMP,^{111,112} while cobalt complexes are employed in organocobalt-mediated radical polymerization (OCRP) to transition between active and dormant species.¹¹³

2. Catalytically mediated PRE (Scheme 1 (b)): This mechanism is similar to the PRE; however, the deactivation/ activation cycles are catalytically mediated by redox-active transition metal catalysts.¹¹⁴ In ATRP, a transition metal-halide complex in its higher oxidation state reacts with propagating radical species to form dormant polymer chains, while regenerating the original metal complex.¹¹⁵

3. Degenerative transfer (Scheme 1 (c)): Unlike PRE-based mechanisms, degenerative transfer radical polymerizations (DTRPs) rely on a high concentration of transfer agents relative to radicals.¹¹⁴ In these systems, active radicals undergo a degenerative exchange with dormant species through a bimolecular transfer process. This exchange can be pursued by atoms like iodine in the (reverse) iodine transfer polymerization ((R)ITP),^{116,117} by group transfer like in the organoheteroatom-mediated radical polymerization (OHRP) (with TeR, SbR₂, BiR₂ etc.) or by addition–fragmentation chemistry (e.g., with dithioesters) like in the reversible addition-fragmentation chain transfer (RAFT) polymerization.¹¹⁸ A specific RAFT variant utilizing xanthates is known as macromolecular design by interchange of xanthate (MADIX).¹¹⁹

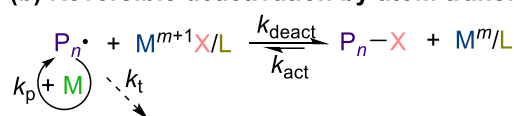
(a) Reversible deactivation by coupling



NMP, OCRP

X = nitroxide, cobalt complex

(b) Reversible deactivation by atom transfer



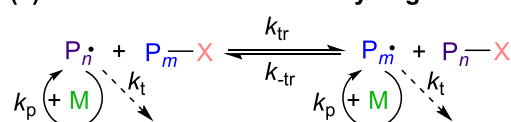
ATRP

X = halide

M = Cu, Ru, Ni, Fe, Mo, ...

L = amines, phosphines, ...

(c) Reversible deactivation by degenerative transfer



RAFT/MADIX, (R)ITP, OHRP

X = S(C=Z), I, TeR, SbR₂, BiR₂

Scheme 1. Dynamic deactivation/ activation equilibria in the mechanisms of various RDRP techniques based on a) reversible deactivation by coupling (NMP, OCRP), b) reversible deactivation by atom transfer (ATRP), and c) reversible deactivation by degenerative transfer (RAFT, (R)ITP, and OHRP).¹²⁰ All techniques rely on a dynamic equilibrium between active propagating radical species ($P_n^\bullet$ / $P_m^\bullet$) and the dormant species (P_n-X / P_m-X). Through the rapid deactivation of growing radicals, a low concentration of the active species is accomplished.

In summary, RDRPs mimic the characteristics of living polymerizations by maintaining active centers that can be reversibly deactivated and reactivated. This activation/ deactivation process enables precise control over composition, and chain length distribution. In contrast to classical living polymerizations such as anionic polymerization, RDRPs are more tolerant to impurities, reducing the need for stringent reaction conditions and simplifying the experimental workload. They offer greater versatility compared to ionic polymerizations, including a broader range of compatible monomers and scalable, user-friendly reaction conditions. RDRPs can be conducted in protic solvents, such as water and alcohols, which opens up opportunities for greener, less toxic, and safer processes. This makes them particularly appealing for environmentally sustainable polymer synthesis.

As a result, RDRP techniques represent a transformative approach to polymer synthesis. Looking ahead, further advancements in this field are expected to drive

industrial applications, leading to the development of a growing number of high-value products derived from RDRPs in the coming decades.^{107,121–123} One of these techniques is RAFT polymerization, which has garnered the most attention among all RDRP methods. This polymerization method is discussed in detail in the following chapter.

3.3 RAFT Polymerization

In the field of RDRPs, RAFT polymerization has emerged as a leading technique, playing a crucial role in the development of precise polymers in both academia and industry.^{122,124,125} Since its first reports in 1998,^{106,126,127} it has become one of the most versatile, widely used and powerful methods for controlled polymerization.^{125,128–131} The appeal of RAFT lies in its ability to achieve exceptional control over polymerization under standard free-radical polymerization conditions, requiring only the addition of a suitable chain transfer agent (CTA) – also commonly denoted as RAFT agent.

RAFT agents are typically thiocarbonylthio (TCT) compounds, as shown in the general structure in Figure 9. Besides the thiocarbonylthio group, these molecules consist of two key substituents: the radical leaving group R and the activating group Z, both of which are critical in governing the polymerization process.^{132,133} The R-group must be an effective homolytic leaving group capable of efficiently reinitiating polymerization, while the Z-group modulates the reactivity of the C=S bond towards monomer addition and controls the fragmentation rate of the intermediate radicals. In addition, it also evaluates the polarity and suitability for specific solvents, which is particularly important in heterogeneous processes such as emulsions and dispersions. Together, these substituents allow for precise control of chain growth and polymer properties. In this work, trithiocarbonates (TTCs) are employed as RAFT agents due to their exceptional ability to control polymerization for a broad range of more activated monomers (MAMs). Examples of such monomers include (meth)acrylates, (meth)acrylamides, vinylpyridines, styrene, and acrylonitrile.¹²⁸

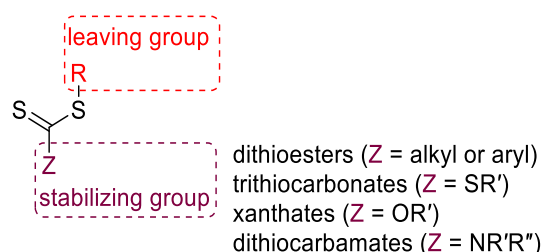


Figure 9. Typical chemical structure of a RAFT agent. In dependence of the Z-group attached to the thiocarbonylthio moiety, the RAFT agents are classified as dithioesters, trithiocarbonates, xanthates and dithiocarbamates.

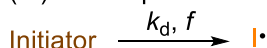
3.3.1 Mechanism and Kinetics of the RAFT Polymerization

Scheme 2 illustrates the mechanism of a conventional RAFT polymerization, which includes initiation, propagation, and termination steps known from those in standard radical polymerization. However, RAFT polymerization is distinguished by two unique equilibria: the pre-equilibrium and the main equilibrium.

Similar to any conventional radical polymerization, the process begins by the generation of a radical from an initiator (Scheme 2, step I). Typically, a thermal initiator such as 2,2'-azobis(isobutyronitrile) (AIBN) is used, although other radical sources can also initiate polymerization, depending on the system. In the second step of initiation, the initiating radicals add monomer units to form propagating chains ($P_n^\bullet$), as in conventional free radical polymerization.

I) Initiation

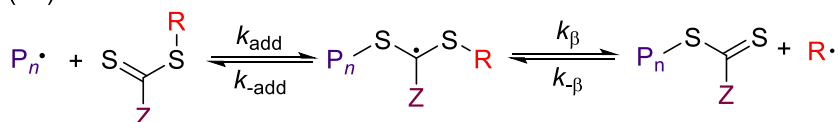
(Ia) Decomposition of the initiator



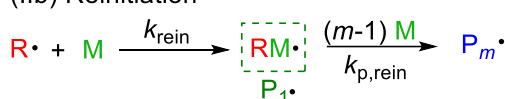
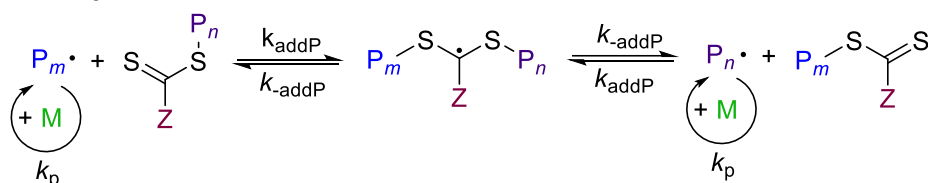
(Ib) Addition of monomer

**II) Preequilibrium**

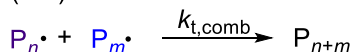
(IIa) Reversible chain transfer



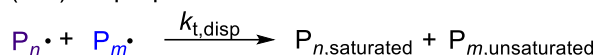
(IIb) Reinitiation

**III) Main equilibrium****IV) Termination**

(IVa) Recombination



(IVb) Disproportionation

**Scheme 2.** Schematic mechanism of the conventional RAFT polymerization with an external initiating source.¹³⁴

The subsequent reactions are unique to RAFT polymerizations. Chain transfer agents play a crucial role by suppressing the chain propagation, as propagating chains are more likely to react with CTAs than with monomers — a key feature of RAFT polymerization.

In the pre-equilibrium stage (Scheme 2, step II), propagating chains undergo reversible chain transfer with the initial RAFT agent, forming an intermediate radical that fragments into a leaving group radical $\text{R}^\bullet$ and a macromolecular RAFT agent (macroRAFT agent). The leaving group radical can reinitiate polymerization by adding to new monomers. Rapid reinitiation is essential to ensure a short pre-equilibrium phase and effective control over polymerization. Slow reinitiation, on the other hand, can cause inhibition or rate retardation. The pre-equilibrium ends when all initial CTAs are consumed and the leaving group radicals reinitiate new propagating chains.^{131,134}

The preequilibrium is followed by the main equilibrium (Scheme 2, step III), in which a degenerative chain transfer between propagating and dormant chains is established. Propagating and dormant chains are in a dynamic equilibrium through reversible fragmentation and addition involving intermediate radicals. Because all chains participate equally in the equilibrium, the time each chain spends propagating before

adding to a macroRAFT agent is consistent, ensuring uniform and controlled growth across all chains.

Although RAFT polymerization is a radical process, irreversible termination events like recombination and disproportionation cannot be entirely avoided. However, proper selection of RAFT agents and reaction conditions minimizes these events. By keeping most chains in a dormant state and minimizing the time spent propagating, the majority of chains retain their thiocarbonylthio end-group. This end-group enables further chain extensions and facilitates the synthesis of multiblock copolymers.¹³⁵

Notably, the RAFT equilibrium neither generates nor consumes radicals. Once a steady state is reached, the RAFT agent acts as an ideal transfer agent, with no impact on the polymerization rate, as radical fragmentation and subsequent reinitiation occur rapidly.¹³⁴ Therefore, the polymerization rate R_p is the same as in a conventional free radical polymerization, following Equation (13):

$$R_p = k_p \sqrt{\frac{f k_d [I]}{k_t}} [M] \quad (13)$$

where k_p is the rate constant for propagation, f the initiator efficiency, k_d the decomposition rate coefficient of the initiator, k_t the rate constant for termination, $[I]$ the initiator concentration, and $[M]$ the monomer concentration.

Monomers with a high propagation rate k_p and initiators with a high decomposition rate k_d lead to an increased polymerization rate. In such systems, the initiator concentration can be kept low while maintaining a high polymerization rate. At the same time, low initiator concentrations are favorable for preserving a high proportion of polymer chains carrying the thiocarbonylthio moiety.

When using typical thermal initiators, the numbers of chains that are dead (i.e., lacking the thiocarbonylthio moiety) corresponds to the number of initiator molecules that have decomposed during the polymerization process.¹²⁸ To maintain a high chain-end livingness L , a low initial initiator to chain transfer agent ratio, $[I]_0/[CTA]_0$, is required. This relationship is described by Equation (14), where f represents the initiator efficiency and f_c the coupling factor. When $f_c = 1$, termination occurs only *via* bimolecular combination; when $f_c = 0$, termination occurs exclusively by bimolecular disproportionation).¹²⁸

$$L = \frac{[CTA]_0}{[CTA]_0 + 2 f [I]_0 (1 - e^{-k_d t}) (1 - \frac{f_c}{2})} \quad (14)$$

Another important parameter for the RAFT polymerization is the initial monomer to chain transfer agent ratio, $[M]_0/[CTA]_0$. This ratio determines the number of RAFT agent molecules in the polymerization system, which in turn dictates the number of chains that carry the thiocarbonylthio moiety. At a given initiator concentration, the number of dead chains remains constant and independent of other parameters. The $[M]_0/[CTA]_0$ also dictates the number-averaged degree of polymerization (N). At higher target degree of polymerization, the fraction of chains obtaining the TCT moiety decreases because the lower RAFT agent concentration reduces the chain-end livingness, as described in Equation (14).

Apart from that, the $[M]_0/[CTA]_0$ ratio, combined with the conversion p , the molecular weight of the monomer M_M and the molecular weight of the CTA M_{CTA} , can be used to calculate the number-averaged theoretical molecular weight *via* Equation (15).^{136,137} This theoretical molecular weight corresponds to the actual number-average molecular weight in the absence of undesired reactions, such as termination or irreversible chain transfer. Consequently, the target molecular weight can be accurately predicted when side reactions play a minor role.¹³⁷

$$\bar{M}_{n,th} = \frac{[M]_0}{[CTA]_0} \cdot p \cdot M_M + M_{CTA} = N \cdot M_M + M_{CTA} \quad (15)$$

Consequently, in a typical RAFT polymerization, the molecular weight increases linearly with the monomer conversion, as in a classical living polymerization.¹³⁸

A third important parameter in RAFT polymerization is the initial ratio between monomer and initiator, $[M]_0/[I]_0$, which significantly impacts the polymerization rate. As previously discussed, higher initiator concentrations generate a greater concentration of radicals, leading to an increased propagation rate.¹³⁷

To analyze the reaction kinetics, a linearized form of the first-order rate law is typically employed, yielding a pseudo-first-order rate plot. This approach allows the steady-state radical concentration to be validated by observing linear progression over time. The underlying equation for this plot is provided in Equation (16).

$$\ln \frac{[M]_0}{[M]_t} = k_p [P\cdot]_t t \quad (16)$$

To summarize, the key to RAFT polymerization lies in the degenerative exchange between the growing polymer chains and dormant species, which ensures precise control over the process. This equilibrium, which favors the dormant chains, maintains a low overall concentration of propagating radicals, thereby reducing the likelihood of irreversible termination events. During the process, the (macro)RAFT agent undergoes numerous activation cycles, adding less than one monomer unit per cycle. This uniform and controlled growth leads to a narrow molecular weight distribution. However, achieving this ideal growth requires strict adherence to optimal polymerization parameters. The initiator concentration, for instance, must be carefully selected. High initiator concentrations compromise the livingness of polymer chains, increasing the ratio of dead chains to thiocarbonylthio-functional dormant chains. Conversely, insufficient initiator concentration can result in rate retardation or an inhibition period, undermining the efficiency of the polymerization. Additionally, selecting an appropriate RAFT agent for the monomer system is essential for achieving effective control over molecular weight and dispersity. The rate of chain addition to the chain transfer agent k_{add} must be sufficiently high, and the fragmentation during preequilibrium k_β must also occur rapidly to ensure quick chain reinitiation $k_{p,rein}$. This avoids inhibition periods and promotes efficient polymerization. Ultimately, the success of RAFT polymerization hinges on the careful optimization of the ratio of the initial concentrations of the initiator, monomer, and chain transfer agent, $[I]_0/[M]_0/[CTA]_0$. These parameters collectively influence the polymerization rate, control over molecular weight distribution, the degree of livingness, and the target molecular weight of the polymer.

3.3.2 Advances in RAFT Polymerization

3.3.2.1 Alternative Initiation Methods

In contrast to NMP and ATRP, the mechanism of RAFT polymerization relies on the degenerate chain transfer of polymer chains, necessitating the continuous addition of (re)initiating radicals.¹²⁵ Traditionally, RAFT polymerizations are conducted using an external thermal initiator, a widely explored and well-understood approach due to the accessibility and simplicity of these initiators.¹²⁵ However, thermal initiation has limitations in terms of application scope. Thermal initiators are hazardous and require proper storage conditions. Moreover, polymerization temperatures must be tailored to match the decomposition rate of the initiator to ensure a consistent radical supply throughout the process and maintain a suitable polymerization rate. Thermal initiation also provides limited temporal and spatial control. At the end of the polymerization, some polymer chains are not in the dormant state and cannot undergo further chain extension, as the radical supply from the initiator determines the number of dead chains.^{125,128}

In addition to thermal initiation, redox reactions are another common method for initiating RAFT polymerization. Redox-initiated RAFT polymerization (redox-RAFT) is advantageous because it uses inexpensive oxidizing and reducing agents, which require low activation energies and allow the polymerizations to proceed at low temperatures. This reduces side reactions and shortens inhibition periods.¹³⁹ One frequently used redox pair is *tert*-butyl hydroperoxide/ ascorbic acid.¹⁴⁰ However, a significant drawback of this approach is that the final product may be contaminated with foreign substances from the redox initiator. In particular, heavy metal ions, such as iron, can be challenging to remove completely.

Beyond these traditional approaches, new initiation methods have been developed. For example, certain monomers, such as styrene, can undergo self-initiation under harsh conditions (e.g., at temperatures above 110 °C).¹⁴¹ Another innovative approach uses enzymes like glucose oxidase in the presence of oxygen to produce hydrogen peroxide through the oxidation of glucose to *D*-glucono- δ -lactone (see Figure 10).¹⁴² This hydrogen peroxide can subsequently participate in a Fenton reaction, generating hydroxyl and hydroperoxyl radicals that initiate RAFT polymerization.¹⁴³ This method has been extended further by using the hydrogen peroxide produced during glucose oxidation as part of a redox pair to generate hydroxyl radicals, which serve as initiators for the RAFT polymerization.¹⁴⁴

Interestingly, besides the way to perform RAFT as a radical polymerization, it has also been adapted for cationic systems. Transfer chain agents were shown to be responsive to cationic activation, enabling cationic RAFT polymerization.¹⁴⁵ In 2010, it was reported that Lewis acids such as EtAlCl₂, SnCl₄, and ZnCl₂ could activate oxygenester bonds.¹⁴⁶ However, the RAFT mechanism's contribution to these Lewis acid-catalyzed systems was found to be minimal.¹⁴⁷ A subsequent approach used direct protonation of monomers with triflic acid to generate cationic propagating species P_n^+ with triflate TfO⁻ as the counterion, resembling the classical RAFT mechanism in a cationic system (see Figure 10).¹⁴⁷ Recently, it has been shown that acids can trigger the RAFT polymerization in the absence of light and exogenous thermal radical initiators.¹⁴⁸

In recent years, there has been a growing focus on initiating RAFT polymerization using external stimuli without introducing additional substances. This approach eliminates

contamination of the resulting polymers with inorganic or organic additives, broadening their usability. For instance, in electrochemically mediated RAFT polymerization (eRAFT), an external electric field is applied to initiate the process. Although the concept of eRAFT builds on prior work in electrochemically mediated ATRP polymerization (eATRP), early attempts at applying electrochemical stimuli to traditional RAFT systems were unsuccessful due to the excessive reduction of CTA-generated fragments into anions. Subsequent studies, such as those by Matyjaszewski's group, demonstrated that thiocarbonylthio compounds could be electro reduced by applying an electric field.¹⁴⁹ However, these experiments yielded low conversions and high dispersities, highlighting the need for further exploration of mediators with sterically hindered structures. In conventional eRAFT polymerizations, radical formation often depends on external electroactive initiators such as benzoyl peroxide or 4-bromobenzenediazonium tetrafluoroborate (see Figure 10).¹⁵⁰ These systems typically involve a mediator species that alternates between its oxidized (Med_{ox}) and reduced (Med_{red}) states.

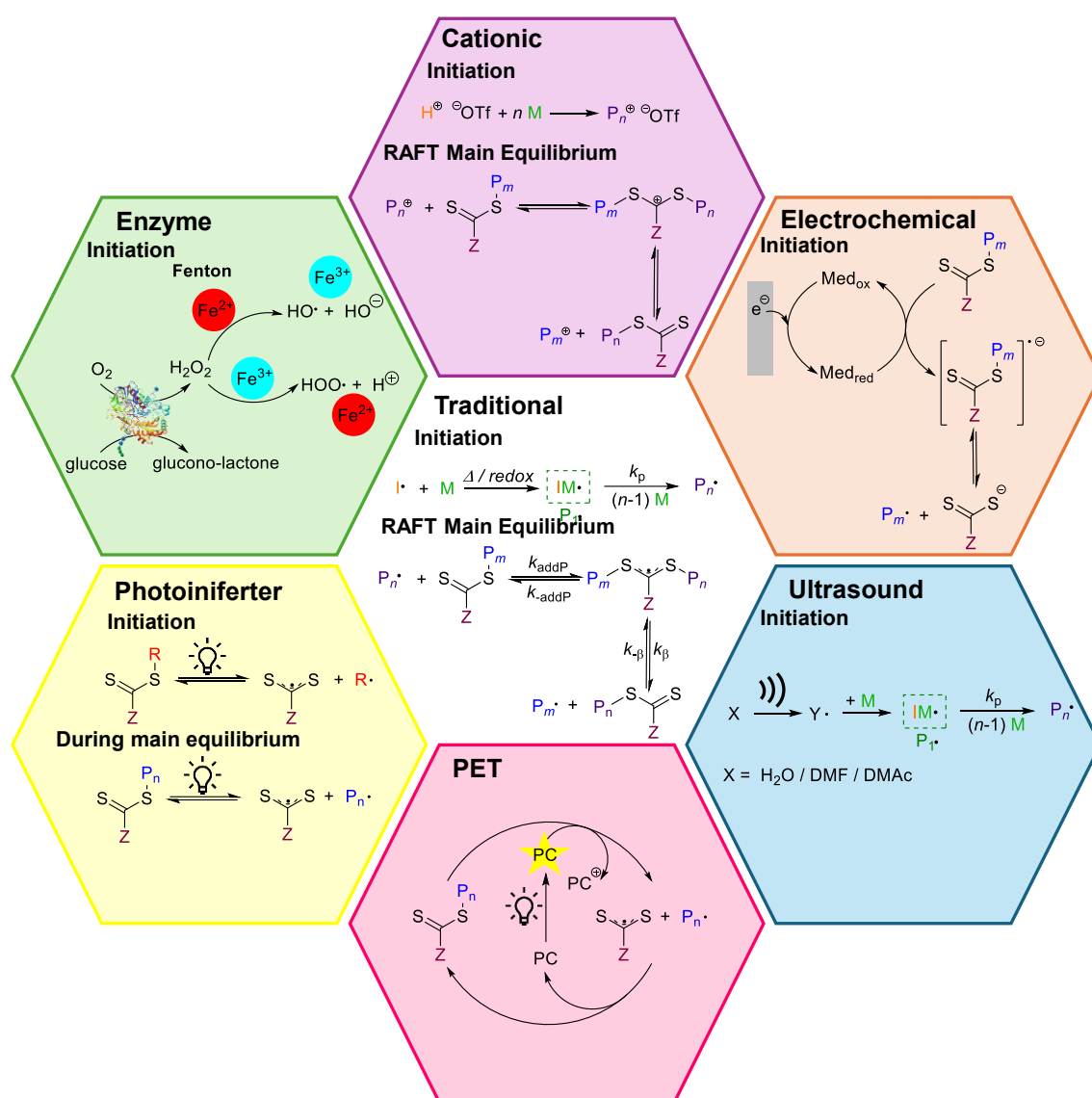


Figure 10. Initiation methods for RAFT polymerization. Illustration reprinted and modified from ¹²⁵, with permission from Wiley-VCH GmbH.

Despite their promise, such processes have not yet provided significant advantages over other initiation methods due to their continued reliance on electroactive mediators.

A greener and more promising approach to initiating RAFT polymerization is the use of ultrasound, which generates radicals directly from the reaction solvent. The first reported sonochemically initiated RAFT polymerization (sono-RAFT) was conducted in an aqueous medium, where high-frequency ultrasound dissociated water molecules into hydrogen and hydroxyl radicals.¹⁵¹ Organic solvents such as dimethylformamide (DMF) and dimethylacetamide (DMAc), known for their low vapor pressure and room-temperature viscosity, have also been successfully used in sono-RAFT polymerization.¹⁵² The adaptability of low-frequency ultrasound for sono-RAFT polymerization was demonstrated by Sumerlin's group.¹⁵³ However, this method currently has limitations regarding achievable molecular weights and monomer conversions.^{125,153}

For activating the RAFT polymerization process, photochemical approaches have garnered the most attention.¹²⁵ Light is an especially attractive regulator due to its low cost, ubiquity, and unparalleled spatial and temporal control.¹⁵⁴ The polymerization process can be easily modulated by switching the light source “on” and “off,” making it probably the most attractive external regulator.^{155,156} Various photochemical strategies for RAFT polymerization have been developed. One common method involves using conventional photoinitiators, which decompose under UV or visible light to generate radicals. While the mechanism remains similar to traditional thermally-initiated RAFT, photoinitiation provides advantages such as high polymerization rates and suitability for temperature-sensitive compounds.¹¹⁸

Another innovative approach is photoinduced electron/ energy transfer RAFT polymerization (PET-RAFT), which uses a photoredox catalyst to drive polymerization *via* electron or energy transfer, depending on the catalyst type.¹⁵⁷ Through the addition of the photocatalyst, the polymerization can be induced by different wavelengths, depending on the initiator used ranging from infrared (IR) to ultraviolet (UV).¹²⁵ The excitation of the photocatalyst to a higher energetic state allows it to transfer energy or an electron to the chain transfer agent, causing fragmentation into propagating species and a persistent thiocarbonylthio radical, participating in the main RAFT equilibrium process (see Figure 10).¹⁵⁸ PET-RAFT polymerization was first reported by Boyer's group using of tris[2-phenylpyridinato-C2,N]iridium(III) ($\text{Ir}(\text{ppy})_3$) under visible light.¹⁵⁷ The process oxidizes the catalyst from Ir^{III} to Ir^{IV} which is later reduced back to its active state to complete the catalytic cycle. Currently, it is still under debate if the photocatalyst in its excited state interacts with the CTA through an electron or an energy transfer process, as certain photocatalysts and CTA combinations indicate more in the direction of energy transfer, while other photocatalysts and CTAs show higher evidence for the electron-transfer pathway.¹⁵⁸ One significant advantage of PET-RAFT is the high degree of livingness of polymer chains compared to thermally initiated RAFT polymerization, as the photocatalyst acts purely as a catalyst and does not directly induce chain termination. Furthermore, PET-RAFT offers a method to remove oxygen through the photocatalyst. Thereby, the photocatalyst can transform from triplet oxygen to singlet oxygen.¹⁵⁹ In the presence of appropriate compounds which can react with the singlet oxygen, oxygen can be fully removed. However, it is still advantageous to previously flush the polymerization medium because otherwise induction periods can be caused. The main disadvantage of PET-RAFT is that – like in all polymerizations triggered by external additives – the

polymer is contaminated with the photocatalyst. However, the polymerizations usually run fast due to high catalytic activity,¹⁵⁴ making it a good spatial and temporal controllable method for all applications where no complete purity of the polymer is required.

An even more elegant photochemical RAFT polymerization method is the direct photoactivation of the chain transfer agent. This polymerization method is called photoiniferter RAFT polymerization, since the RAFT agent serves as the initiator, transfer agent and terminator agent.^{160,161} While the RAFT agent acts as both transfer and terminator agent in the conventional RAFT mechanism, its additional role as an initiator makes this method particularly attractive. The radical generation occurs *via* photolysis of the C–S bond, as shown in Figure 10. Since all thiocarbonyl-containing molecules share similar absorption characteristics due to electronic transitions involving the C=S double bond, the cleavage of this bond can be activated either by a $\pi\text{--}\pi^*$ transition or by a spin forbidden $n\text{--}\pi^*$ transition of the thiocarbonyl group (see Figure 11).^{161,162} These transitions can be triggered by short-wavelength UV light (≈ 320 nm, $\pi\text{--}\pi^*$ transition) or visible light (400 – 550 nm, $n\text{--}\pi^*$ transition), depending on the absorption characteristics of the RAFT agent used. The versatility of this method is evident in the ability to tune excitation wavelengths based on the RAFT agent, with characteristic colors (e.g., yellow for trithiocarbonates, light red for dithiobenzoates) resulting from the absorption band. Although the absorption band for visible light is weaker than for UV, it offers higher quantum yields for β -fragmentation.¹⁶²

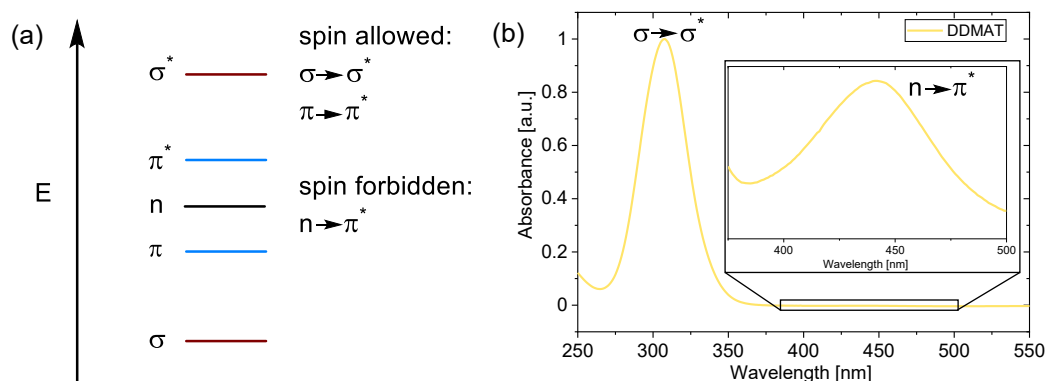


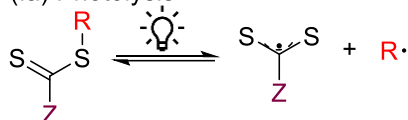
Figure 11. (a) Simplified electronic energy level for thiocarbonyl (C=S) compounds. Image adapted from ¹⁶¹, with permission from the American Chemical Society. (b) UV–VIS absorption spectrum of the RAFT agent 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid (DDMAT) used in this work.

As illustrated in Scheme 3, the mechanism of photoiniferter RAFT polymerization differs slightly from the traditional RAFT mechanism. In this approach, as no external initiator is required, polymerization begins directly in the preequilibrium stage. Upon illumination with light of a suitable wavelength, the chain transfer agent absorbs the incoming light and transitions to an excited state, which is followed by homolytic cleavage of the C–S bond. This process generates a propagating radical and a persistent thiocarbonylthio radical. During the main equilibrium stage, the propagating species are formed similarly to the preequilibrium phase and undergo reversible chain transfer, just as in conventional RAFT polymerization. The deactivated polymer chains can be reactivated by the light source. Radical concentration remains constant throughout the polymerization process, as it is governed solely by the CTA concentration, which does not change during an ideal RAFT polymerization. This steady radical concentration is one of the key advantages of photoinduced RAFT polymerization compared to thermal

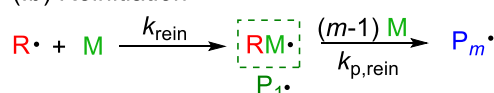
RAFT polymerization, since in the latter the radical concentration decreases over time, leading to slower polymerization rates during extended reactions.¹⁶³

I) Preequilibrium

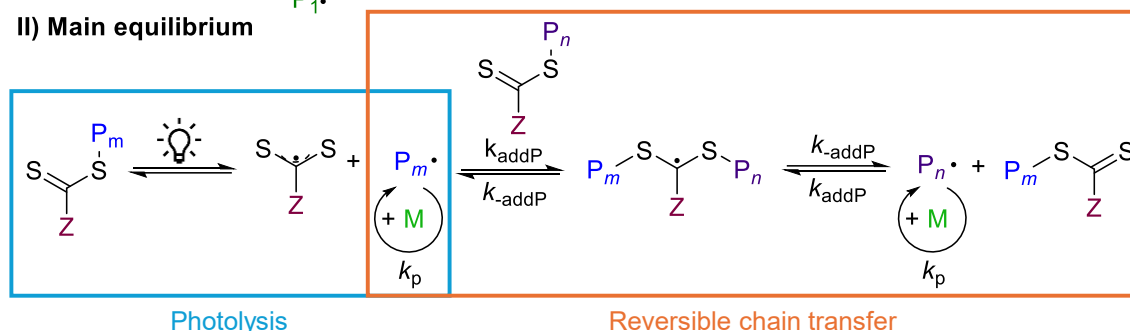
(Ia) Photolysis



(Ib) Reinitiation

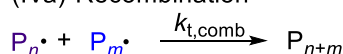


II) Main equilibrium

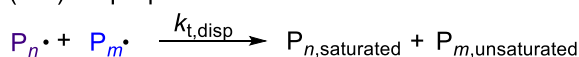


III) Termination

(IVa) Recombination



(IVb) Disproportionation



Scheme 3. Mechanism of the photoiniferter RAFT polymerization.

Since light-induced RAFT polymerization remains a radical polymerization process, undesired irreversible decomposition or termination events can occur. However, these events are typically less frequent compared to techniques relying on exogenous radical sources, resulting in enhanced livingness of the polymer chains.¹⁶⁴ The extent of undesired side products is influenced by the choice of the irradiation source. For instance, UV light causes more irreversible degradation of the thiocarbonylthio compound compared to visible light, leading to reduced control over polymerization and polymers with higher dispersities. Additionally, UV light poses more significant health risks to humans, making visible-light-induced RAFT polymerization a safer and more advantageous alternative.¹⁶⁵

Several decisive steps led to the development of various methods for visible-light-driven RAFT polymerization (see Figure 12). The photoactivity of thio-containing compounds is well known through the initial development of the iniferter process by Otsu already in 1982.^{166,167} In this early work, tetraethylthiuram disulfide was studied for its effect on the polymerization of methyl methacrylate and styrene. However, the original RAFT process was established much later, in 1998.^{106,126,127}

The introduction of effective photocatalysts for visible-light activation came in 2008.^{168–170} These catalysts laid the foundation for the development of PET-RAFT in 2014, where an iridium-based catalyst enabled the polymerization of various

monomers — including (meth)acrylamides, (meth)acrylates, styrene, and vinyl esters — under blue light irradiation.¹⁵⁷ The photoiniferter RAFT approach was independently reported by the groups of Boyer¹⁶⁰ and Qiao¹⁶¹ in 2015. These studies demonstrated the polymerization of diverse monomers under blue or green light without requiring a photoinitiator or photocatalyst. In the same year, cationic RAFT polymerization was introduced.^{145,171} Shortly after, in 2016, visible-light-driven cationic RAFT polymerization in the presence of a photocatalyst was realized.¹⁷²

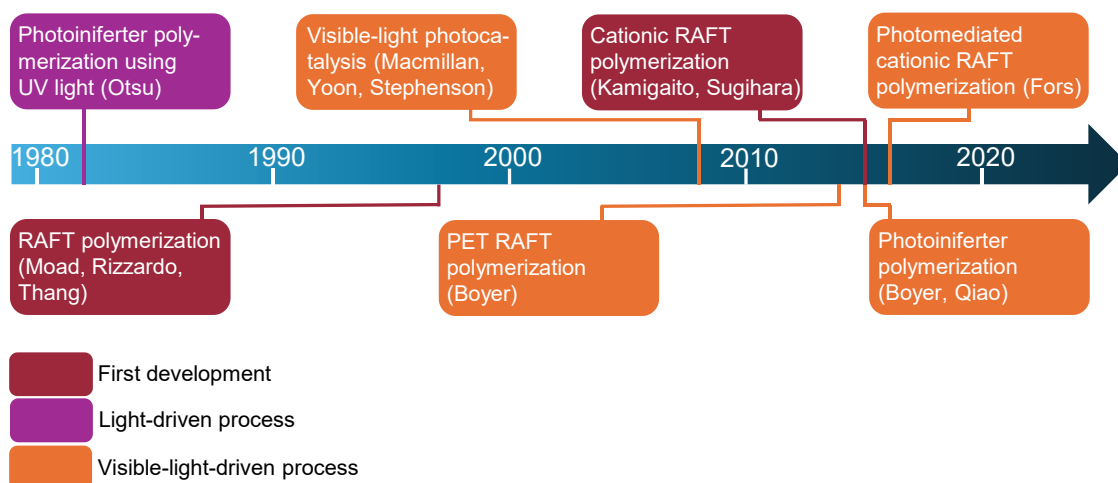


Figure 12. Milestones towards the development of visible-light-regulated RAFT polymerization. Figure adapted according to ¹⁷³, with permission from Royal Society of Chemistry.

In summary, over the past two decades, numerous techniques have been developed for activating RAFT polymerization. Among these, photoregulation stands out as an especially attractive method due to the widespread availability of light and the ability to easily control the polymerization process through its switchable “on”/ “off” behavior. Beyond the use of photoinitiators or photocatalysts to activate the RAFT process, direct excitation of the thiocarbonylthio group of the (macro)RAFT agent using UV or visible light induces homolysis of the C–S bond. While the resulting thiocarbonyl radical remains stable and unreactive with surrounding monomers, the R-radical effectively initiates the polymerization process.

A key advantage of the photoiniferter method is the significant reduction in irreversible termination events, which results in high end-group fidelity as most of the TCT functionalities retain at the end of the polymerization. This enhanced livingness enables the synthesis of multiblock copolymers with precise control. Furthermore, since the RAFT agent itself acts as the polymerization initiator, the reaction temperature is decoupled from the initiation process. This feature is particularly beneficial for controlling the polymerization of high k_p monomers, as it allows for significantly lower reaction temperatures, reducing thermal energy consumption during the polymerization process.

Another major advantage of photoiniferter RAFT polymerization is the purity of the resulting polymers, if high conversions are obtained. Unlike conventional methods, no free catalysts need to be removed, as the RAFT agent functions as the only initiator, simplifying the purification process. In particular, visible-light-driven RAFT polymerization holds great promise in the field of polymer chemistry, offering a greener and more sustainable approach for synthesizing advanced polymers while addressing environmental challenges.¹⁷⁴ However, while this light-based activation process

contributes to sustainability, other critical polymerization parameters, such as the choice of solvent, play a key role in advancing greener and more efficient polymerization techniques. These aspects, along with their potential to drive further progress in sustainable polymer science, are discussed in the following section.

3.3.2.2 RAFT Polymerization in Heterogenous Systems

RAFT polymerization, like free-radical polymerization, can be performed in heterogeneous systems. Unlike homogeneous polymerization, where reactants and products exist within a single phase, heterogeneous polymerization occurs in systems with distinct phases. These heterogeneities within the polymerization medium provide significant advantages for industrial processes. Among the benefits are enhanced heat transfer efficiency, reduced viscosity even at high solid concentrations, the ability to substitute harmful solvents with safer alternatives, and accelerated reaction rates compared to homogeneous polymerizations.¹⁷⁵

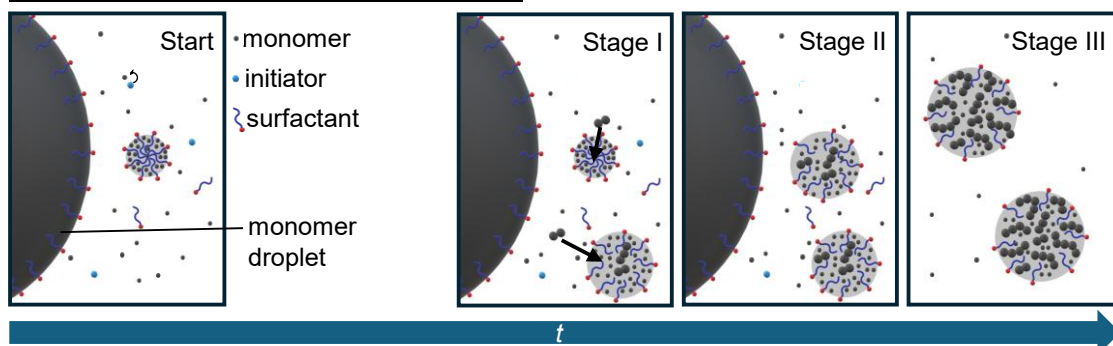
Heterogeneous polymerization encompasses several techniques, with emulsion and dispersion polymerization receiving particular attention. In both methods, the polymer produced during the polymerization process is insoluble in the continuous phase. The primary distinction between emulsion and dispersion polymerization lies in the solubility of the monomer(s) in the solvent(s). In dispersion polymerization, the monomer is fully soluble in the solvent, whereas in emulsion polymerization, the monomer is only sparingly soluble in the continuous phase, with the main part of the monomer molecules forming large aggregates called monomer droplets. Since this study utilizes emulsion polymerization for synthesizing diblock copolymers, the mechanistic details of emulsion polymerization are discussed further.

Emulsion polymerization involves the polymerization of monomers that are insoluble in the continuous phase, typically water. A standard emulsion polymerization system consists of water, a monomer with low water solubility, a surfactant (to reduce surface tension between phases), and a water-soluble initiator.^{176,177} Due to the hydrophobic nature of the monomer, only a small fraction dissolves in the aqueous phase. When the surfactant concentration exceeds its critical micelle concentration (CMC), some monomers reside within the monomer-swollen micelles. However, the main part of the monomer molecules incorporates to large monomer droplets. These monomer droplets are dispersed in the continuous phase. According to the micelle nucleation model, proposed by Harkins^{178–180} and Smith,^{181–183,183} the emulsion polymerization is divided into three stages as following:

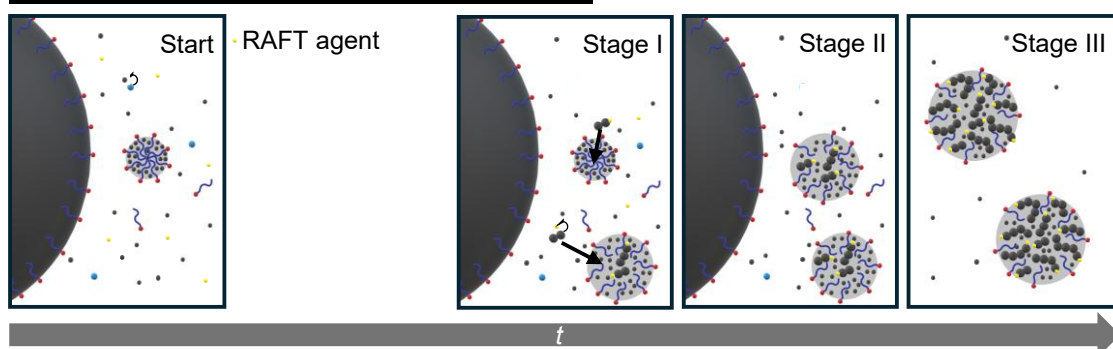
1. Stage I: Particle nucleation: In the first stage, radicals generated by the water-soluble initiator, such as 4,4'-azobis(4-cyanopentanoic acid) (ACPA), react with the small fraction of monomers dissolved in the aqueous phase to form oligomers that are increasingly hydrophobic compared to the monomers (see Figure 13 (a) stage I). Thus, the initial locus of polymerization is in the aqueous phase.¹⁸⁴ Once these oligomers reach a critical chain length, they become sufficiently hydrophobic to migrate into monomer-swollen micelles (micelle nucleation) or nucleate independently (homogeneous nucleation), initiating chain growth. Although propagating chains can also enter larger monomer droplets, this is less likely due to the higher surface area of the micelles.¹⁷⁶ The particle nucleation stage (interval I) concludes when all micelles are converted into latex particles — monomer-swollen particles that serve as reaction loci for

polymerization.¹⁷⁶ During this stage, the polymerization rate is relatively slow due to the limited solubility of the monomer in the aqueous medium.

(a) Emulsion polymerization with a surfactant



(b) RAFT Emulsion polymerization with a surfactant



(c) Surfactant-free RAFT *ab initio* emulsion polymerization

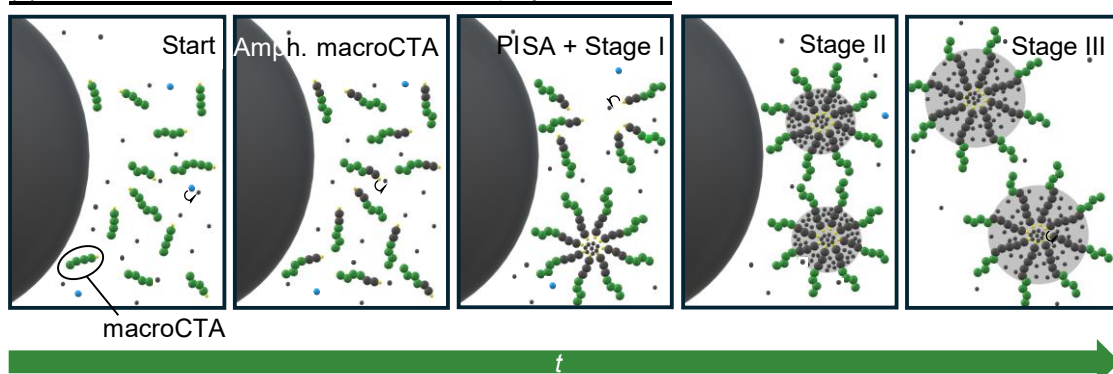


Figure 13. (a) Polymerization course of (a) the conventional emulsion polymerization using a surfactant, (b) RAFT emulsion polymerization with a surfactant (exemplary with a water-soluble RAFT agent) and (c) the surfactant-free RAFT *ab initio* emulsion polymerization.

2. Stage II: Growth stage: Following particle nucleation, the system enters the growth stage (Figure 13 (a) stage II), during which the latex particle concentration remains relatively constant. Polymer chains propagate primarily within the monomer-swollen latex particles, consuming the monomer inside. To maintain the reaction, a concentration equilibrium exists among the monomer in the droplets, the aqueous medium and the latex particles. The monomer droplets act as reservoirs, releasing monomer that diffuses through the aqueous phase into the growing latex particles. This steady supply of monomer maintains a constant polymerization rate during this stage. The local high monomer concentration within the latex particles accelerates the reaction,

making the polymerization rate significantly faster than in the first stage. This growth phase encompasses monomer conversions ranging from approximately 10 % to 60 %, during which the latex particles increase in size.¹⁷⁶

3. Stage III: Monomer depletion: The third and final stage (Figure 13 (a) stage III) begins when the monomer droplets are fully depleted. At this point, the propagating chains within the remaining latex particles consume the residual monomer. As the monomer concentration in the particles gradually decreases, the polymerization rate also declines. This stage, known as the monomer depletion phase, continues until the polymerization is complete.¹⁸⁵

RAFT emulsion polymerization rarely employs conventional approaches involving surfactants. The mechanism is similar to the free-radical emulsion polymerization. In addition to water, the water-soluble initiator, monomer with low water solubility and the surfactant, the RAFT agent is added. The location of the RAFT agent depends on its solubility characteristics. Hydrophobic RAFT agents preferentially dissolve in the monomer droplets or monomer-swollen micelles, and during micellar nucleation, they are transported into the polymer particles as chain growth proceeds. In contrast, water-soluble RAFT agents initially reside in the aqueous phase, where they participate in early radical reactions. As the growing RAFT-controlled chains reach sufficient hydrophobicity, they migrate into polymer particles, where polymerization continues.

Early studies identified several challenges, such as uncontrolled polymerization in monomer droplets,¹⁸⁶ poor colloidal stability,^{186,187} difficulty in controlling molecular weight,^{186–188} sensitivity of certain RAFT agents to water, sluggish transport of hydrophobic RAFT agents through the aqueous medium,¹⁸⁷ and the surface activity of some RAFT agents.^{189,190} These issues led researchers to explore surfactant-free alternatives for RAFT polymerization.

A breakthrough came when Hawket's group demonstrated the first successful surfactant-free RAFT *ab initio* emulsion polymerization by using poly(acrylic acid) macroCTAs in aqueous solution, chain-extended with *n*-butyl acrylate.¹⁹¹ In this approach, hydrophilic poly(acrylic acid) macroCTAs dissolved in water were made amphiphilic by the addition of hydrophobic *n*-butyl acrylate monomers, leading to the synthesis of poly(acrylic acid)-*block*-poly(*n*-butyl acrylate) diblock copolymers. To avoid polymerization in monomer droplets, the hydrophobic *n*-butyl acrylate monomer was added slowly, forming stable micelles. However, subsequent studies revealed that this seeded approach is unnecessary, as the presence of monomer droplets does not compromise the polymerization control.

A typical surfactant-free RAFT *ab initio* emulsion polymerization, as illustrated in Figure 13 (c), begins with the hydrophilic macroCTA chains fully dissolved in the aqueous phase. A water-soluble initiator generates radicals that activate the RAFT macroCTA, forming propagating radicals. As the hydrophobic monomer is introduced, a second, hydrophobic block is chain-extended from the hydrophilic macroCTA. With increasing block length, the resulting block copolymer becomes progressively more amphiphilic. Upon reaching a critical degree of polymerization, these amphiphilic block copolymers spontaneously self-assemble into micellar structures within the aqueous environment. This process is called polymerization-induced self-assembly (PISA).¹⁹² The *in situ* formed stabilizers enable particle nucleation without conventional surfactants. The resulting aggregates typically adopt spherical morphologies, but other structures such

as worm-like micelles or vesicles can also be formed.¹⁹³ Subsequently, the amphiphilic macroCTA participates in the same sequence of reactions described in chapter 3.3.1.

Following nucleation, monomers diffuse into the micelles like in a conventional emulsion polymerization, allowing the latex particles to grow further (Figure 13 (c), stage II). The hydrophilic block stabilizes the particles, while the hydrophobic block continues to extend, integrating into the latex particles.¹⁹⁴ Growth continues until monomer depletion (Figure 13 (c) stage III), where the reaction slows as the remaining monomer is consumed. This surfactant-free approach is versatile, accommodating various combinations of hydrophilic and hydrophobic blocks, enabling the synthesis of multiblock copolymers (e.g. *via* sequential seeded emulsion polymerization).¹⁹⁵

Surfactant-free RAFT *ab initio* emulsion polymerization driven by PISA is a highly efficient and elegant method for particle nucleation through the self-assembly of an amphiphilic macroCTA without the necessity of conventional surfactant.¹⁹⁶ Since no additional surfactant is required, the resulting polymers are of high purity, minimizing the need for extensive purification. Through the speed-up of the reaction rate compared to the homogenous polymerization system, higher molecular weights can be targeted and even low propagating monomers like styrene can be polymerized at higher polymerization rates.¹⁹⁷ The latter point is of enormous importance since many commercial block copolymers involve one or more polystyrene blocks. Their applicability covers a broad spectrum, such as membranes, which are discussed in the subsequent chapter.

3.4 Membranes

According to the International Union of Pure and Applied Chemistry (IUPAC), a membrane is defined as a “structure, having lateral dimensions much greater than its thickness, through which mass transfer may occur under a variety of driving forces.”¹⁹⁸ Another commonly accepted definition describes a membrane as a selective barrier between two phases that restricts the movement of components in a controlled manner.^{3,199,200} Consequently, membranes play a crucial role in separation processes.

Compared to other separation technologies such as, e.g., distillation, membrane technology often requires less energy, leading to a significant reduction in carbon dioxide emissions.^{57,201} Additionally, membrane-based separation operates under milder conditions, making it suitable for the purification of sensitive molecules. These advantages make membranes an attractive choice for a wide range of separation applications.

The membrane separation process is illustrated in Figure 14. In this process, two different volumes are separated, which may exist in the same phase, such as liquid/ liquid or gas/ gas, or in different phases, such as gas/ liquid. Typically, the feed stream enters a module containing the membrane, where it is divided into two streams: the retentate, which remains on the feed side, and the permeate, which passes through the membrane. Separation occurs because one or more components of the feed selectively pass through the membrane to the permeate side faster than the other components.

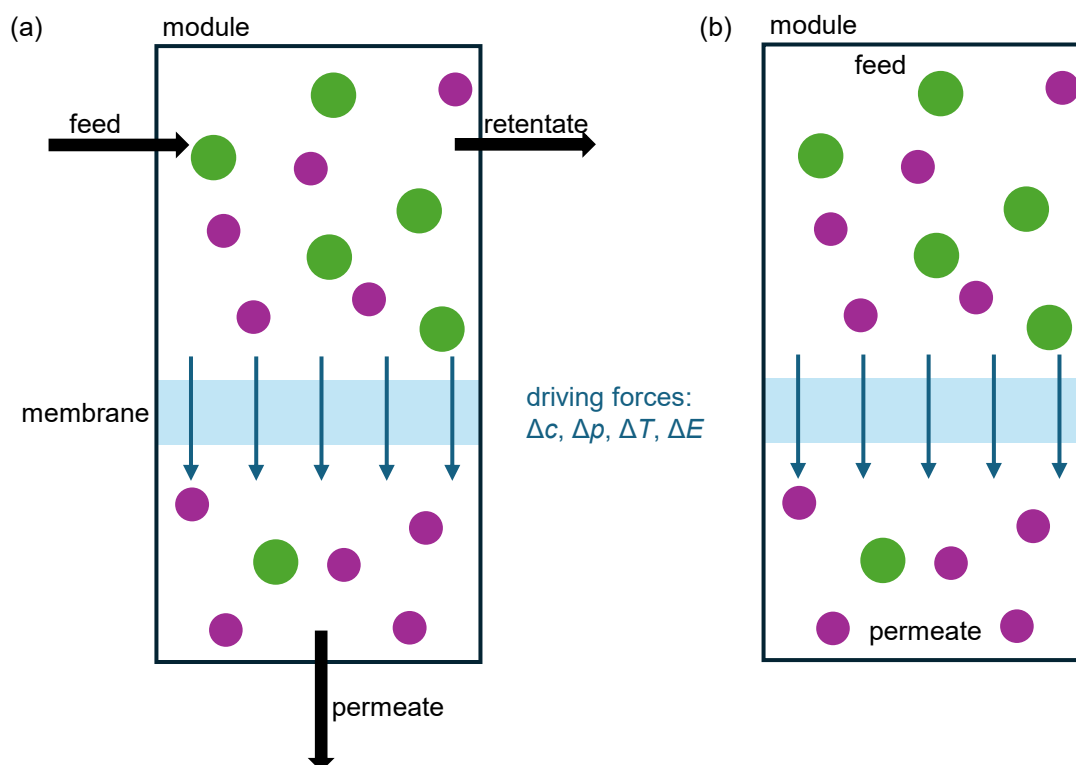


Figure 14. Schematic representation of a membrane separation process. (a) Continuous operation mode (cross-flow) and (b) discontinuous operation mode (dead-end). Figure adapted according to ^{199,202}, with permission from Springer Nature and De Gruyter.

As the feed and the permeate are spatially separated, their compositions differ. For instance, as shown in Figure 14 (a), the membrane may selectively allow molecules of one type with the violet color to pass through more readily than the green ones, resulting in a permeate enriched in violet molecules and a retentate depleted of them. In a continuous process, the retentate leaves the module, as illustrated in Figure 14 (a). Conversely, in a discontinuous so-called dead-end process (Figure 14 (b)), the retentate is not removed, leading to a gradual increase in the concentration of the rejected components in the feed over time.^{199,202,203}

Unlike thermal separation processes, which are governed by thermodynamic equilibrium, membrane-based separation is a rate-driven process that relies on a driving force. Separation occurs through size exclusion or due to differences in diffusion kinetics of the components passing through the membrane. Transport through a membrane is driven by external forces applied to the components in the feed. These external forces comprise concentration gradients Δc , pressure gradients Δp , temperature gradients ΔT and electrical potential difference ΔE created by an electric field. In most membrane processes, the driving force is either a pressure or concentration (or activity) difference across the membrane. The parameters pressure, concentration (or activity) and the temperature can be included into a single thermodynamic parameter, the chemical potential μ .^{200,202,203}

The applicability of membranes largely depends on their properties, which form the basis for their classification. These categories will be explored in the following chapter.

3.4.1 Classification of Membranes

Membranes can be classified based on various aspects. At present, there are several common classifications which are listed in the following:^{3,199,204–207}

(1) Material composition

The material composition of a membrane refers to the chemical nature of its constituent materials. Membranes are broadly categorized as either synthetic or biological. Biological membranes can be further divided into living and non-living membranes. Synthetic membranes are classified as either inorganic (ceramics, metals, zeolites, or silica), organic (natural and synthetic polymer membranes) or organic-inorganic hybrid membranes.

(2) Morphology/ structure

A membrane structure determines its separation mechanism and applications. According to their morphology or structure, membranes can be classified into symmetric (symmetric dense and symmetric porous membranes) and asymmetric membranes (with a dense selective top layer and a more porous sublayer). The symmetric membranes can be further subdivided into isotropic porous membranes and nonporous/ dense membranes (see Figure 15).

(3) Driving forces

Separation in membranes is driven by transmembrane pressure, temperature, concentration gradients, or electrical potential (as previously described). Pressure-driven membrane processes are categorized according to the membrane pore size and the operating pressure into microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) (see Figure 16).

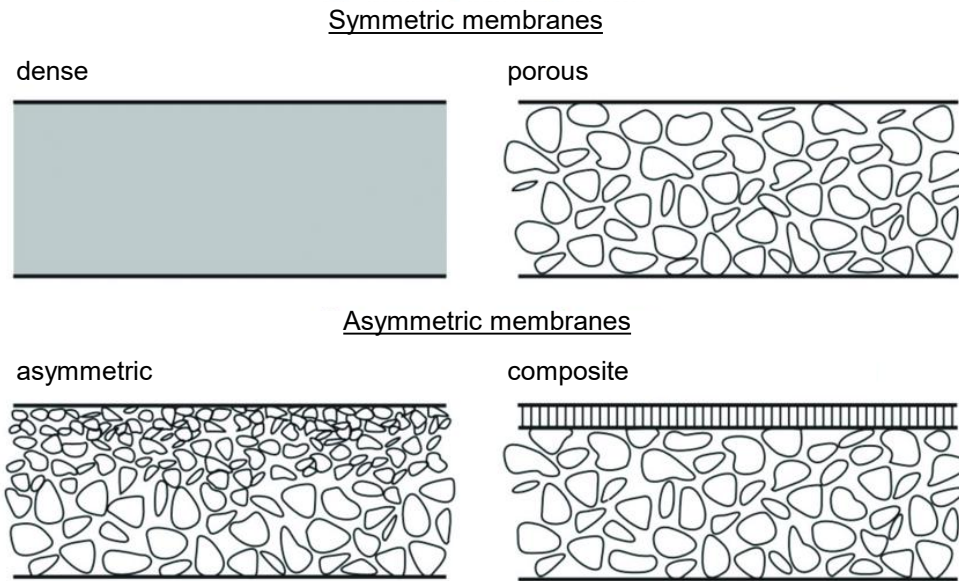


Figure 15. Classification of membranes according to their structure. Figure reprinted and adapted from ²⁰⁸, with permission from MDPI.

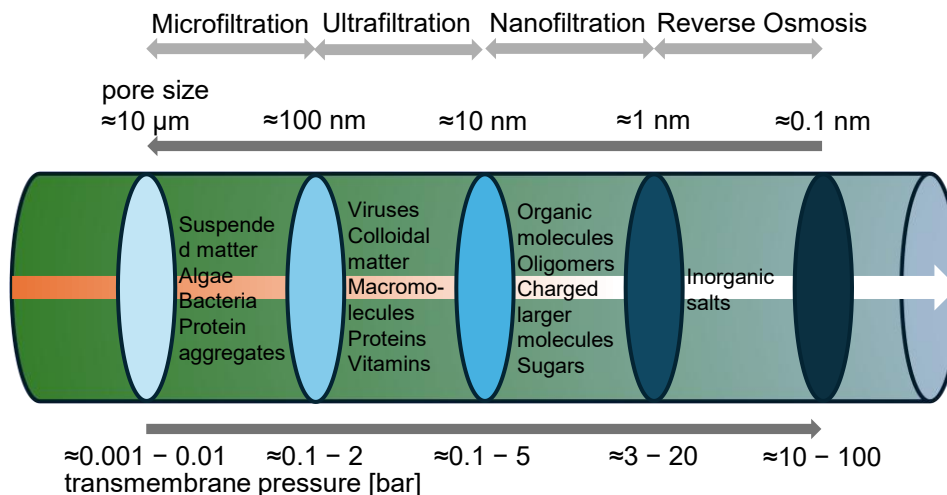


Figure 16. Pressure-driven membrane processes. Figure adapted from ²⁰², with permission from De Gruyter.

(4) Phase of the volumes

Membranes can also be classified based on the phase of the separated substances, such as gas separation membranes, liquid separation membranes, solid-liquid separation membranes and gas-liquid separation membranes.

(5) Transport mechanism

The transport mechanism depends on the membrane structure. Dense membranes follow the solution-diffusion model (see Figure 17), where permeating species first dissolve into the membrane material and then diffuse through it (see Wijmans et. al ²⁰⁵). This mechanism deviates from the facilitated or carrier-mediated transport, where specific carrier molecules enhance the selective transport of certain species. As pore size increases to the molecular scale, molecular sieving and Knudsen diffusion become relevant. These mechanisms

rely on size exclusion and molecular collisions with pore walls, respectively. For membranes with larger pores (in the nanometer to micrometer range), Poiseuille (viscous) flow and particle filtration dominate. Here, transport is pressure-driven, a process described by the pore-flow model, and often involves size-based separation.

(6) Geometry

Depending on the geometry of the membrane, they are divided into flat sheet, hollow fiber, and tubular membranes.

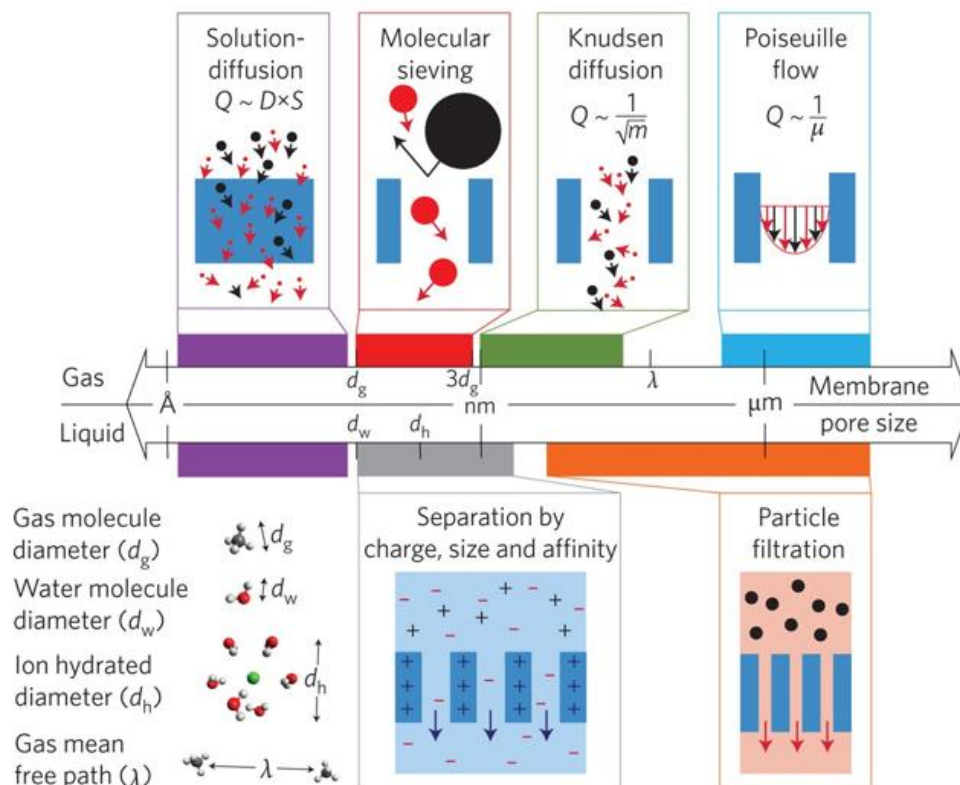


Figure 17. Transport mechanisms through membranes. Figure reprinted from ²⁰⁹, with permission from Springer Nature.

As the membranes discussed in this work are ultrafiltration membranes, the next chapter will discuss their specific properties and parameters in detail.

3.4.2 Ultrafiltration Membranes

Ultrafiltration is a pressure-driven membrane-based separation process that removes particles and dissolved macromolecules smaller than 0.1 μm and larger than about 2 nm from small solutes and solvent.^{210,211} The lower limit of rejected solutes typically corresponds to molecular weights of a few thousand Daltons.¹⁹⁹ Consequently, ultrafiltration membranes are designed to separate molecules with higher molecular weights and suspended solids.²¹² Ultrafiltration is widely used as a mainstream separation technology in water and wastewater treatment applications.²¹³ It is also frequently employed as a pretreatment stage for reverse osmosis processes.

The separation performance of ultrafiltration membranes primarily depends on the size and shape of the solutes relative to the membrane pore size. Secondary factors, such as solute-membrane interactions (e.g., electrostatic effects), also influence performance.^{199,210} Since ultrafiltration is pressure-driven, the volumetric flux J_v is directly proportional to the applied pressure, as shown in Equation (17). In this Equation, P represents the permeability constant, also referred to as permeance.^{199,214} Permeance, which normalizes the flux by the applied pressure, is often used to characterize ultrafiltration membranes and describes the pressure-independent flow rate per unit membrane area.

$$J_v = P \cdot \Delta p \quad (17)$$

Ultrafiltration membranes typically feature an asymmetric structure, with a much denser top layer which is characterized by smaller pore sizes and lower surface porosity compared to the bottom layer (as shown in the bottom-left image in Figure 15). The top layer is usually less than 1 μm thick, while the sublayer, often described as sponge-like, provides mechanical support to the membrane.¹⁹⁹ Since the top layer has the smallest pore size, the separation properties of asymmetric ultrafiltration membranes are determined primarily by this selective layer. The flux of an ultrafiltration membrane depends significantly on the geometry of the pores within the top layer. Two idealized membrane structures are commonly considered: Membranes composed of densely packed spherical particles (Figure 18 (a)), and membranes with arrays of parallel cylindrical pores (Figure 18 (b)).

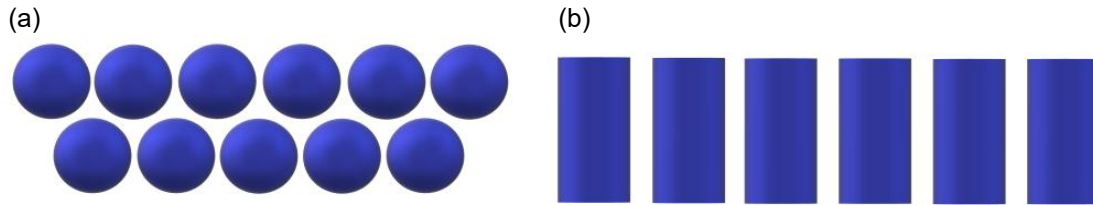


Figure 18. Idealized geometries of the top layer of porous ultrafiltration membranes. (a) Dense package of spherical particles, (b) parallel cylinders.

For membranes with densely packed spherical particles, the permeance can be calculated using the Carman-Kozeny Equation, where c is the Kozeny constant and S is the specific surface area based on the solid volume.^{215,216}

$$P = \frac{\phi^3}{c \cdot (1 - \phi)^2 \cdot S^2} \quad (18)$$

For membranes with a parallel array of uniform cylindrical pores, the permeance is evaluated using the Hagen-Poiseuille Equation (Equation (19)).²¹⁷ This equation is based on two assumptions: 1) the pore length is equal to the thickness of the selective layer, 2) all cylindrical pores obtain the same radius.

$$P = \frac{\phi \cdot r^2}{8 \cdot \eta \cdot L} \quad (19)$$

In the Hagen-Poiseuille Equation, ϕ is the porosity, r the radius of the pores, η the viscosity of the fluid and L the length of the cylindrical pore.

However, since real membrane morphologies often deviate from these idealized models, the applicability of these equations must be carefully considered. Experimentally, the volumetric flux J_v is determined as the volume of fluid flowing through the membrane per unit area per unit time. This is described by Equation (20), where ΔV is the change in volume, A the surface area of the membrane, Δt the time frame, Δw is the change in weight and ρ the density.

$$J_v = \frac{\Delta V}{A \cdot \Delta t} = \frac{\Delta w}{A \cdot \rho \cdot \Delta t} \quad (20)$$

The permeance is determined *via* the volume which passes through the surface area of the membrane per time per transmembrane pressure according to Equation (21).

$$P = \frac{\Delta V}{A \cdot \Delta t \cdot \Delta p} = \frac{\Delta w}{A \cdot \rho \cdot \Delta t \cdot \Delta p} \quad (21)$$

The quality of separation that the membrane provides can be expressed in terms of rejection. The rejection R of a compound can be described by Equation (22) in which c_p is the concentration of the substance in the permeate and c_f the corresponding concentration in the feed. Since R is a dimensionless parameter, it does not depend on the units in which the concentration is expressed. The value of R varies between 1 (complete retention of the solute) and 0 (solute and solvent pass through the membrane freely).^{199,210}

$$R = 1 - \frac{c_p}{c_f} \quad (22)$$

When multiple substances are present in the feed, the selectivity of a membrane to allow a component A to pass through relative to component B is described by the separation factor Ψ , also called selectivity, as defined in Equation (23).¹⁹⁹ In this Equation, $c_p(A)$ and $c_p(B)$ represent the concentrations of components A and B in the permeate, while $c_f(A)$ and $c_f(B)$ are their respective concentrations in the feed.

$$\Psi_{A/B} = \frac{\frac{c_p(A)}{c_p(B)}}{\frac{c_f(A)}{c_f(B)}} \quad (23)$$

Ultrafiltration membranes are characterized by two key performance parameters: permeance and selectivity.²¹⁸ Typically, a trade-off exists between permeability and selectivity,²¹⁴ necessitating a balance between achieving adequate flux and effective separation in terms of rejection and selectivity. It is important to note, however, that these

performance parameters can change over the membrane's lifetime and are highly influenced by external operating conditions.

One of the major challenges in ultrafiltration processes is membrane fouling.²¹⁹ Fouling occurs when substances accumulate on the membrane surface (surface fouling) or within its pores (pore blocking), leading to irreversible performance degradation.²²⁰ Fouling is noticeable by a progressive decline in permeate flux with time during constant pressure operation or by an increase in transmembrane pressure during operation at constant filtration flux.²¹⁹ For this reason, long-term monitoring of membrane performance is essential.

The morphology of an ultrafiltration membrane — particularly its porosity and pore size — is crucial for achieving optimal separation performance. Consequently, the choice of membrane material and the manufacturing method significantly influence membrane properties. Approximately 90% of ultrafiltration membranes are made from polymeric materials.²¹⁸ The most common fabrication techniques for polymeric ultrafiltration membranes are phase inversion and electrospinning. Among these, phase inversion remains the leading method. The four primary types of phase inversion processes are thermally induced phase separation (TIPS), vapor-induced phase separation (VIPS), solvent-controlled evaporation-induced phase separation (EIPS), and nonsolvent-induced phase separation (NIPS). Among these four phase inversion techniques, NIPS is the most widely used technique for producing porous ultrafiltration membranes.²¹⁸ Asymmetric ultrafiltration membranes fabricated using the NIPS process will be discussed in detail in the next chapter.

3.4.3 Nonsolvent Induced Phase Separation (NIPS)

The NIPS process, first developed by Loeb and Sourirajan in the early 1960s,^{221,222} is also referred to as the “Loeb–Sourirajan process” or “wet-phase inversion”. Today, it remains the most widely used method for producing integral asymmetric ultrafiltration membranes. This process requires only three components: a polymer (P), a solvent (S), and a nonsolvent (N). The solvent must completely dissolve the polymer, while the nonsolvent should be a poor solvent for the polymer, causing precipitation, but also be miscible with the solvent.

In a typical NIPS-based membrane fabrication process, the polymer solution, comprising the polymer and solvent, is cast as a thin film on a support material (e.g., a nonwoven fabric) or substrate (e.g., a glass plate) and then immersed in a nonsolvent bath. Due to the miscibility of the solvent and nonsolvent, an exchange occurs between the nonsolvent in the bath and the solvent in the film. This exchange begins at the film's surface and gradually progresses throughout the entire film. As the exchange occurs, phase separation leads to the formation of two distinct phases: a polymer-rich phase which forms the membrane matrix and a polymer-poor phase which becomes the membrane pores.²²³ This phase separation begins at the surface and proceeds at a reduced rate through the thin polymer film. Consequently, the membrane develops an asymmetric structure, characterized by a dense surface layer supported by a more porous, sponge-like sublayer, as described in chapter 3.4.2. This dense top layer is often attributed not only to the phase inversion process but also to partial solvent evaporation prior to immersion in the non-solvent, a common step in the NIPS method. The resulting

top surface structure is denser, while the porosity increases toward the bottom. The morphology of the top surface is mainly influenced by numerous factors, such as the viscosity of the casting solution, the molecular weight, composition and concentration of the polymer, the presence and composition of additives, evaporation rate and evaporation time of the solvent(s), bath temperature as well as environmental parameters such as the temperature and the humidity of the surrounding air.²²⁴

The phase separation process can be represented by a triangular phase diagram consisting of the three components polymer, solvent, and nonsolvent (Figure 19 (a)). Each point on the diagram represents a specific mixture of the three components, with the edges representing binary mixtures. Generally, the phase diagram is divided into diverse regions, in which the regions a), b), c) and d) are stable, e) is the metastable region and f) the unstable region. The binodal curve separates the stable homogenous region from the metastable region, while the spinodal curve delineates the metastable region from the unstable region. In the metastable region, the chemical potential of a component is the same in both coexisting equilibrium phases, the polymer-rich phase and the polymer-lean phase. The intersection between the binodal curve and the spinodal curve is the critical point Cr. The tie lines connect points with equal chemical potential. Hence, the composition of the polymer-rich and polymer-lean phases can be determined at any stage of the phase separation process.^{220,224,225}

During the membrane formation process, the phase separation from a one-phase region into two or more phases with different compositions is induced by the decrease in the free Gibbs free energy.²²⁰ The phase separation can occur in the metastable or unstable region of the phase diagram.²²⁴ By entering the metastable region, the phase separation is kinetically controlled by nucleation and growth of the nuclei, driven by the diffusion of macromolecules into the nucleated domains. To minimize Gibbs free energy, the system tends to demix into two phases with compositions equal to those of the points on the binodal curve (equilibrium compositions). In the unstable region, the Gibbs free energy decreases immediately. Therefore, the phase separation occurs through the spinodal decomposition between polymer (or polymer solution) and the nonsolvent (or precipitant-solvent mixture). The phase separation is initiated by a spontaneous formation of coherent composition/ concentration fluctuations. These fluctuations grow and finally form the coexisting phases with an interpenetrating structure and corresponding equilibrium compositions.^{220,224}

A typical pathway during the NIPS is shown in Figure 19 (b). Initially, the casting solution consists only of the polymer and solvent, represented by the start point t_0 on the phase diagram which is at the edge of the polymer-solvent mixture. During the NIPS process, the composition changes from the initial composition at t_0 to the final composition in the membrane at t_∞ . As the nonsolvent gradually penetrates into the film, the precipitation pathway at the top surface differs from that at the bottom. Through the exchange of the solvent with the nonsolvent, composition changes by losing solvent and gaining nonsolvent. Upon reaching the metastable region at time t_1 , the polymer solution at the top surface enters the two-phase region, initiating phase separation into a polymer poor (micronucleus) phase and a polymer rich continuous phase. Due to the gradual exchange of the nonsolvent towards the bottom of the cast film, the time point at which the precipitation at the bottom occurs is delayed (t_2). At this stage, the polymer-rich phase can still flow or agglomerate. By further exchange of the solvent by the nonsolvent, the viscosity of the precipitated polymer is high enough so that the polymer solidifies (t_3 for

the top surface and t_4 for the bottom surface). When the NIPS process is fully completed (t_∞), this solidified polymer phase forms the membrane matrix, whereas the liquid nonsolvent phase forms the pores of the membrane. The composition of the top and the bottom surface differs from another (see Figure 19). This is induced by the reduced precipitation rate towards the bottom of the cast film. Thereby the asymmetric structure with a more polymer-rich (and therefore denser) top surface, and the increased fraction of the nonsolvent causes a pronounced pore gradient along the cross-section of the membrane.

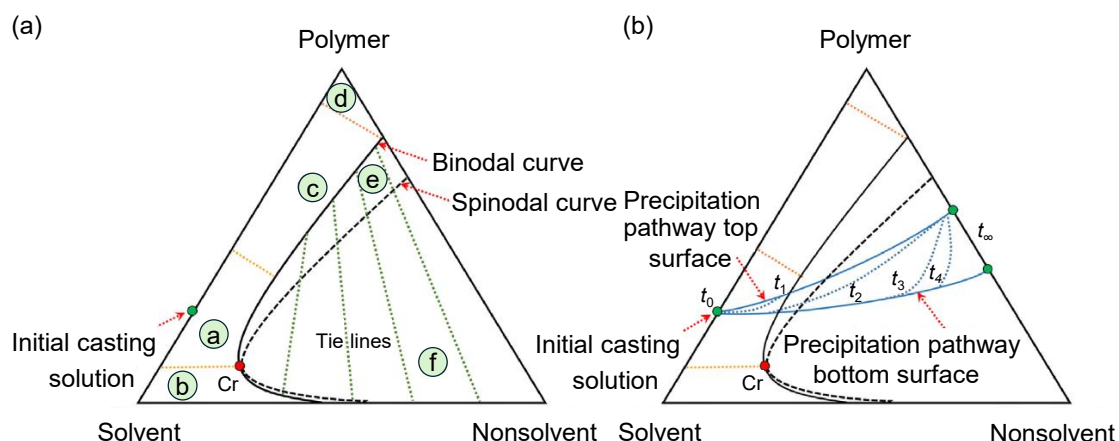


Figure 19. Schematic illustration of a ternary phase diagram of a nonsolvent, solvent and polymer for the fabrication process of membranes by the NIPS process. (a) Stable one-phase region with suitable composition to prepare the initial casting solution, (b) stable one-phase region where the composition is not appropriate to fabricate a membrane, (c) one-phase gel region, (d) glassy region, (e) metastable region, and (f) unstable region. The critical point represents the point where the spinodal and binodal curve touch each other. (b) Precipitation pathways of the top and bottom part. Figure adapted from ²²⁰, with permission from Elsevier.

Nonsolvent-induced phase separation is widely used for the fabrication of ultrafiltration membranes. It can be combined with the self-assembly of block copolymers, as discussed in the next section, to create advanced membranes with tailored properties.

3.4.4 Fabrication of Integral Asymmetric, Isoporous Block Copolymer Membranes

As discussed in chapter 3.1, block copolymers exhibit unique properties due to their ability to self-assemble into uniformly sized microdomains through microphase separation. This makes them highly attractive candidates for the fabrication of membranes with uniform pore sizes, known as isoporous membranes. On the other hand, NIPS remains the most widely utilized and facile method for industrial-scale production of commercial membranes (see chapter 3.4.3).²²⁶ The SNIPS process, introduced by Peinemann, Abetz, and Simon,²²⁷ combines the self-assembly of block copolymers (S) with the NIPS process in a single step. This approach enables the large-scale fabrication of membranes featuring an isoporous surface and an integral asymmetric substructure.²²⁴

Analogous to NIPS, in the SNIPS process, a semi-concentrated polymer solution is cast as a thin film and precipitated into a nonsolvent (as described in chapter 3.4.3).²²⁶ However, the SNIPS process introduces additional factors that significantly influence the final membrane structure. After casting the polymer film, solvent evaporation begins. Thereby, the solvent concentration in the film changes as a function of time and position. The solvent evaporates faster from the top surface than from the bottom, causing a concentration gradient within the polymer film. However, the solvent concentration at the surface rapidly decreases below the order-disorder solvent concentration.²²⁸ Below this threshold, the solvent can no longer sufficiently mediate the unfavorable enthalpic interactions between the two polymer blocks. As a result, the effective segregation strength between the copolymer blocks increases, driving microphase separation. The microphase-separated ordered phase nucleates at the film's surface and grows inward, forming a perpendicular cylindrical structure in the top portion of the membrane. Meanwhile, the lower portion of the polymer film remains disordered until it enters the metastable or unstable region during phase separation.²²⁸

The growth rate of the perpendicular cylinders depends on the product of two terms, the local viscosity of polymer chains (chain relaxation time) and the effective segmental incompatibility between the dissimilar polymer segments (thermodynamic driving force). In regions with high solvent concentration, the polymer chains exhibit higher mobility, resulting in a lower relaxation time. The thermodynamic driving force for microphase separation is small because the solvent mediates interactions between incompatible polymer blocks. Conversely, in regions with low solvent concentration, the thermodynamic driving force for microphase separation increases, but the polymer chain mobility decreases due to higher viscosity. These two factors are not linearly proportional in their dependence from the compositional parameters, which limits the directional growth of the microphase-separated domains to a few hundred nanometers (typically within the range of 100 – 200 nm).^{224,228}

The combination of NIPS and self-assembly of block copolymers results in membranes with exceptionally highly ordered and densely packed pores that have a narrow size distribution on the top surface. Beneath this is a robust sponge-like sublayer, as illustrated in Figure 20. This dual-layer structure combines the superior selectivity of isoporous membranes with the mechanical support provided by the asymmetric substructure.

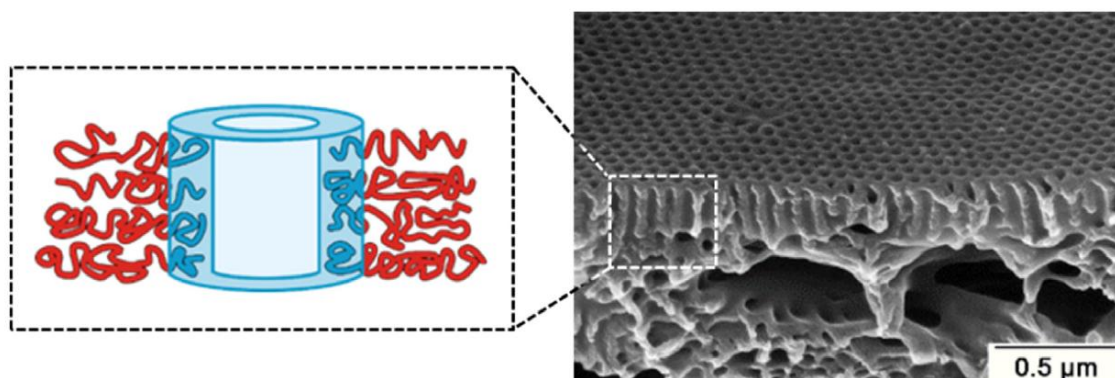


Figure 20. Scanning electron micrograph (SEM image) of an integral asymmetric isoporous membrane fabricated of a block copolymer through the SNIPS process. The left illustration depicts the self-assembled structure of the top surface with the blue parts being the minor blocks and the red parts the major blocks of the block copolymer. Reprinted from ²²⁰, with permission from Elsevier.

Block copolymer membranes prepared *via* the SNIPS process feature a sharp molecular weight cut-off and consequently high selectivity due to the isoporous top surface.²²⁹ By modifying parameters such as composition, block length, and the number of blocks, the properties of these membranes can be fine-tuned to meet specific application requirements. This allows for precise control over key membrane characteristics, including pore size, stimuli responsiveness, and fouling resistance.²³⁰

As a result, block copolymer membranes offer greater versatility in achieving controlled pore sizes and narrow pore size distributions compared to conventional membranes.^{229,231} Due to the thermodynamic principles governing block copolymer self-assembly, most membranes exhibit pore sizes in the range of 10 nm and 100 nm.²³² However, expanding this range to achieve smaller pore diameters in the sub-10 nm range and lower molecular weight cut-offs presents a significant challenge.²²⁴ To address this limitation, post-modification of block copolymer membranes provides a promising avenue to further adjust pore size, introduce specific functionalities, and modify surface charge. This approach will be discussed in the next section.

3.4.5 Post-Modification of Block Copolymer Membranes

Post-modification of block copolymer membranes offers a powerful and convenient way to adjust the membrane properties.²²⁰ An advantage of post-modification is that no further parameters for casting have to be optimized since a given membrane can be used for various post-functionalizations.²²⁴ Through post-treatment using chemical or physical methods, the well-ordered and self-assembled isoporous top layer can be preserved. To keep the structure of the membrane, the chemical reaction or the physical treatment needs to be performed in a heterogenous medium, otherwise rearrangement of the morphology might occur.

A common approach is to modify the block copolymer membrane to obtain unique functionality in the minority block, enabling a selective transport pathway. The main goals of post-treatment of the pore-forming block are to impart stimuli responsive properties (e.g., pH-,^{233–236} temperature-,²³⁷ and redox- responsiveness²³⁸) incorporate charges^{239–241} or desired functional groups,²⁴² and tune the pore size of the selective layer (e.g., by crosslinkage^{240,241,243,244}).

Polystyrene-*block*-poly(4-vinylpyridine) (PS-*b*-P4VP)ⁱ diblock copolymer membranes, probably one of the most extensively studied block copolymer membranes, exhibit pH-responsive behavior. At low pH, the nitrogen atoms in the pyridine rings are protonated, resulting in stretching of the newly formed more hydrophilic segment and a consequent decrease in pore size. At neutral or high pH, deprotonation of the nitrogen moieties causes the polymer chains to collapse.²³¹ However, if the pyridine nitrogen

ⁱ To clarify potential confusion, it is essential to note that PS-*b*-P4VP and P4VP-*b*-PS refer to the same block copolymer. However, in this work, the polymer is consistently referred to as P4VP-*b*-PS, to align with the synthesis method presented herein, where the P4VP block is synthesized first, followed by the synthesis of the PS block. This sequence contrasts with the synthesis route *via* anionic polymerization, where the PS block is typically synthesized first, followed by the P4VP block. The adopted naming convention reflects the sequential nature of the synthesis process used in this study and ensures clarity and consistency throughout the discussion.

moieties of the P4VP block are quaternized, permanent charges are introduced into the membrane. Zhang et. al.²³⁹ demonstrated that chemical modification of the P4VP block with halogenated alkanes like methyl-, ethyl-, and propyl iodide introduces a permanent positive charge. This modification alters the membrane's swelling behavior in aqueous media, resulting in a decrease in pore size and an overall reduction in water permeance. Among the post-modified membranes, a longer alkyl chain length attached to the nitrogen atom of the 4VP units led to an increase in water flux and a corresponding decrease in methylene blue retention.

Conversely, to introduce negative charges within the membrane's pores, the groups of Boudouris and Phillip^{233,234} prepared polyisoprene-*block*-polystyrene-*block*-poly(*N,N*-dimethylacrylamide) (PI-*b*-PS-*b*-PDMA) triblock copolymer membranes, where the initial PDMA block is non-stimuli-responsive. After hydrolysis with hydrochloric acid, the PDMA was converted into a poly(acrylic acid) (PAA) block, imparting the membranes with pH-dependent negative charges and pH-responsive behavior. The post-modified membranes exhibited a reduction in permeance with increasing pH, highlighting the dynamic, tunable nature of their performance.

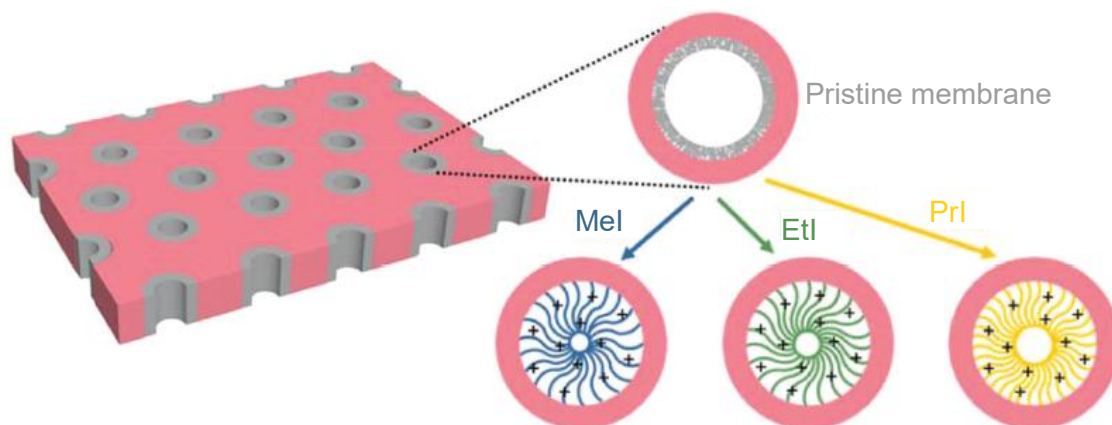


Figure 21. Schematic representation of the pore size in the hydrated state of the quaternized PS-*b*-P4VP diblock copolymer membrane with methyl iodide (Mel), ethyl iodide (Etl) and propyl iodide (Prl) at the same degree of conversion (52 %). Figure adapted from ²³⁹, with permission from John Wiley and Sons.

Thus, post-modification reactions on block copolymers represent a highly promising strategy for developing isoporous membranes with tailored properties.²²⁴ These adaptable properties make block copolymer membranes particularly attractive for a wide range of applications. One notable area is their use in the separation of biological substances such as proteins, which is discussed in chapter 3.5. Furthermore, the potential for significantly broadens the scope of block copolymers, enabling their use in the creation of multifunctional membranes. This aspect will be explored in greater detail in the next section.

3.4.6 Block Copolymer Blend Membranes

Apart from post-modification, blending block copolymers offers a versatile strategy to tailor membrane properties. In the simplest case, AB diblock copolymer is blended with a homopolymer of the pore-forming block. One of the first examples was to blend a polystyrene-*block*-poly(methyl methacrylate) (PS-*b*-PMMA) diblock copolymer with

poly(methyl methacrylate) PMMA homopolymer.²⁴⁵ Thin films of this blend were cast on silicon oxide substrates before being transferred onto a porous polysulfone membrane. The PMMA homopolymer was subsequently removed using acetic acid, yielding an isoporous block copolymer membrane with a PS matrix and PMMA pores. However, this method poses significant challenges for upscale.

Later, the same group adapted this approach by blending a PS-*b*-PMMA diblock copolymer containing a dicarboxylic acid end group with PMMA homopolymer.²⁴⁶ After removing the PMMA homopolymer, the functionalized carboxylic acid groups enabled immobilization of DNA-based molecular recognition agents. Another strategy involves introducing a selectively miscible yet chemically distinct homopolymer for the minority block into a diblock copolymer casting solution. Gamys et al.²⁴⁷ demonstrated this by blending poly(acrylic acid)-*block*-polystyrene (PAA-*b*-PS) diblock copolymer with poly(ethylene oxide) (PEO) homopolymer. Hydrogen bonds between PAA and PEO localized PEO exclusively within the PAA phase. Rinsing with methanol produced nanoporous PAA-*b*-PS thin films. However, despite their novelty, these approaches offer limited practical advantages since the homopolymers are removed after casting.

A more promising method is blending chemically identical block copolymers with varying compositions. Radjabian and Abetz²⁴⁸ blended PS-*b*-P4VP diblock copolymers to create isoporous membranes using the SNIPS process, demonstrating a linear relationship between pore diameter and the weight-averaged degree of polymerization of the blended copolymers. This technique demonstrates fine-tuning of pore diameters by simply adjusting blend composition.

A more complex approach involves the casting of membranes from blended block copolymers with identical matrix-forming block(s) but distinct pore-forming blocks. Yu et al.²⁴⁹ used diblock copolymers with polystyrene as common matrix forming block, by blending PS-*b*-PAA and PS-*b*-P4VP diblock copolymers, to fabricate membranes *via* the SNIPS process. The hydrogen bonds between PAA and P4VP resulted in self-assembly within the same phase. The resultant membranes exhibited small pore diameters of 1.5 nm in aqueous media, effectively rejecting solutes with molecular weights of 600 g·mol⁻¹ — which was to the best of my knowledge previously not obtained by any other method using block copolymers. This demonstrates the potential of blending diblock copolymers to achieve tunable pore sizes from ultrafiltration to nanofiltration regime.

It becomes more complicated when the pore-forming blocks do not interact, as this behavior has been scarcely studied. Wiesner's group²⁵⁰ explored membranes from blends of two triblock terpolymers, polyisoprene-*block*-polystyrene-*block*-poly(4-vinylpyridine) (PI-*b*-PS-*b*-P4VP) and polyisoprene-*block*-polystyrene-*block*-poly(dimethylamino ethyl methacrylate) (PI-*b*-PS-*b*-PDMAEMA), using the SNIPS process. Both terpolymers shared chemically identical matrix-forming blocks (PI and PS), but their pore-forming blocks differed. Unlike PAA and P4VP blends, PDMAEMA and P4VP did not exhibit intermolecular interactions like hydrogen bonds. Solutions predominantly containing PI-*b*-PS-*b*-PDMAEMA triblock copolymer failed to form stable structures using the SNIPS process, while those rich in PI-*b*-PS-*b*-P4VP triblock copolymer formed membranes with a porous top layer ($\approx$ 200 nm skin thickness) and a hierarchically sponge-like porous substructure (see Figure 22). Due to the pH responsiveness of both the P4VP and the PDMAEMA block, the blended membranes displayed mixed intermediate performance compared to pure triblock copolymer

membranes. This "mix-and-match" approach enables the design of more complex, multifunctional materials solely by varying the casting solution composition.²⁵¹ However, to the best of my knowledge it remains unclear whether the SNIPS process produces membranes with mixed pores (P4VP and PDMAEMA co-assembled) or distinct pore species (pure P4VP pores and pure PDMAEMA pores), since no detailed structural investigations were executed (see ^{250,251}). To clarify the structural arrangement of block copolymer blends in membranes and the potential applicability for multifunctional membranes, there is still plenty of scope for further research in this area. Further details about multifunctional membranes will be discussed in the next chapter.

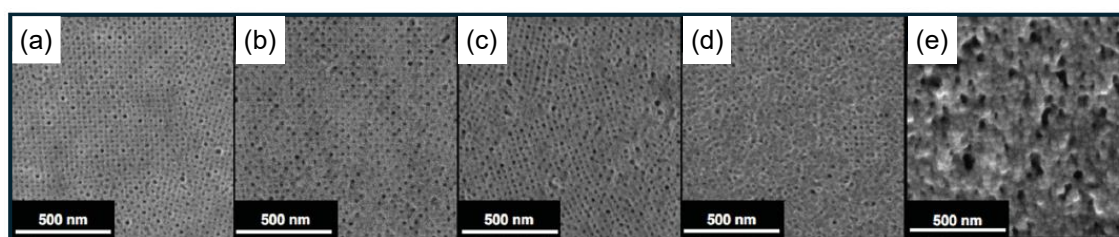


Figure 22. SEM images of the surface structures of pure diblock copolymer and blend membranes consisting of PI-*b*-PS-*b*-P4VP and PI-*b*-PS-*b*-PDMAEMA diblock copolymers. (a) Pure PI-*b*-PS-*b*-P4VP diblock copolymer membrane, (b) 9:1, (c) 7:3 and (d) 6:4 blend of PI-*b*-PS-*b*-P4VP: PI-*b*-PS-*b*-PDMAEMA diblock copolymers, and (e) pure PI-*b*-PS-*b*-PDMAEMA diblock copolymer membrane.

Figure reprinted from ²⁵⁰, with permission from John Wiley and Sons.

3.4.7 Multifunctional and Charge-Mosaic Membranes

Functional membranes have garnered significant interest due to their ability to achieve separation not only through steric hindrance but also *via* additional mechanisms such as charge-selectivity and sorption.²⁵² Incorporating functional moieties along the pore walls allows these membranes to separate molecules of similar size through electrostatic and van der Waals interactions, hence enhancing solute-solute selectivity.^{252,253} For instance, ion-exchange and charge-functionalized nanofiltration membranes rely on electrostatic repulsion through the Donnan²⁵⁴ exclusion mechanism to restrict the passage of co-ions (ions with the same charge as the membrane) while allowing counter-ions (oppositely charged ions) to pass. Such nanofiltration membranes are particularly effective at rejecting multivalent co-ions while allowing monovalent co-ions to pass through, making them valuable for applications like water softening.²⁵⁵

Beyond selective separation, functional membranes offer advanced features such as customized selectivity, adjustable permeability, antifouling, self-cleaning capabilities, and the ability to support *in situ* reactions. These attributes broaden their application potential across diverse fields. Functional nanochannel membranes are categorized into two types based on their mechanisms: physically functional nanochannel membranes, such as conductive membranes and stimuli-responsive membranes like pH-responsive, and thermoresponsive membranes, and chemically functional nanochannel membranes, including photocatalytic, electro-catalytic, and biocatalytic nanochannel membranes.²⁵⁶

By employing various functionalities into the membrane's pore walls, multifunctional membranes with unique chemistry in discrete nano- through microscale domains are obtained. The functionalities in a multifunctional membrane are typically distributed through various strategies. For multifunctional ultrafiltration membranes, key preparation

techniques include, besides the integration of the different functionalities into polymer chains through synthesis, blending, surface coating, and reverse filtration. In reverse filtration, active materials are introduced at the bottom of ultrafiltration membranes through a bottom-up filtration process. Unlike conventional surface filtration, where materials are deposited on the top surface, reverse filtration allows materials to pass through the membrane and accumulate at its base or within inner layers. By contrast, surface coating typically involves applying (or depositing) active materials to the top surface of an ultrafiltration membrane *via* filtration or immersion, followed by a fixation step to secure the materials in place. Blending, another common approach, encompasses the mixing of at least two different components to create a multifunctional membrane. One widely used method for preparing multifunctional ultrafiltration membranes is to blend a polymer matrix with active particles in an organic solvent. The resulting casting solution is then solidified through phase separation, producing mixed matrix membranes (MMMs).²⁵⁷

Apart from these techniques, other techniques were developed for the preparation of multifunctional ultrafiltration membranes. These techniques include spray coating, where thin films are sprayed onto pristine membranes, and layer-by-layer (LbL) assembly, which fabricates alternating layers with diverse properties.²⁵⁷ Block copolymers can also be used to create multifunctional nanopores. For instance, Wiesner's group used a polystyrene-*block*-poly(4-vinylpyridine)-*block*-poly(propylene sulfide) triblock terpolymer with a small very small poly(propylene sulfide) block.²⁵⁸ By incorporating the poly(propylene sulfide) and poly(4-vinylpyridine) blocks in the same pore, a pH-responsive membrane capable of binding target molecules *via* thiol-ene click chemistry was developed. Later, Zhang et. al. used polyisoprene-*block*-polystyrene-*block*-poly(4-vinylpyridine) (PI-*b*-PS-*b*-P4VP) triblock terpolymers and hydroxylated the PI block with mercaptoethanol *via* thiol-ene click chemistry to poly(4-(2-hydroxyethylthio)-2-methyl butene-*random*-4-(2-hydroxyethylthio)-3-methyl butene-*random*-isoprene)-*block*-polystyrene-*block*-poly(4-vinylpyridine) (P(HTMB-*r*-I)-*b*-PS-*b*-P4VP).²⁵⁹ Through the post-functionalization of the membrane, partially positively and negatively charged multifunctional nanochannels were obtained from the both end-blocks which resided within the same pore domain.²⁵⁹

Membranes with obvious spatial charge distribution, the so-called mixed-charged membranes, mainly include dually-charged (Janus) and polyelectrolyte complex (PEC), and charge-mosaic membranes.²⁶⁰ Janus membranes obtain two distinct and contrasting properties on each side, similar to the two-faced Roman god Janus. These opposing properties work collaboratively at the interface of the parts with the distinct properties. Through these contrasting properties, a distinctive transport behavior within the membrane is obtained.²⁶¹ PEC membranes are created through the combination of oppositely charged polyelectrolytes.²⁶² However, charge-mosaic contain parallel arrays of alternating positively (anion-exchange) and negatively (cation-exchange) charged domains (as shown in Figure 23).^{263,264} Unlike homogeneous ion-exchange membranes that transport only one ion type, while retaining the oppositely charged ions, charge-mosaic membranes enable simultaneous transport of anions and cations *via* distinct pathways, maintaining electroneutrality.²⁶⁵ These membranes demonstrate preferential permeability for electrolytes than similarly sized neutral solutes.²⁶⁴ Charge-mosaic membranes exhibit high salt permeability due to their unique microstructure, which combines two factors: (i) the overall high effective concentration of electrolytes within the

membrane (i.e., the typically high, several molar concentrations of cations in the cation exchange elements and anions in the anion exchange elements), and (ii) the short-circuiting of membrane potentials of the individual elements by circulating currents.²⁶⁶

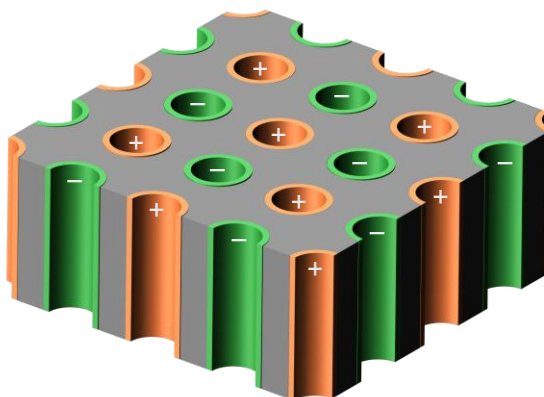


Figure 23. Morphology of an isoporous charge-mosaic membrane. The negatively and positively charged pores alternate.

The unique mass transfer characteristics of charge-mosaic membranes were first predicted by Sollner and colleagues.^{267–270} Subsequently, Kedem and Katchalsky^{271–273} developed a theoretical framework to describe the transport of electrolytes and water through these membranes, which was later extended by Leitz et al.^{274,275} as well as Weinstein et al.^{266,276}

Charge-mosaic membranes consist of distinct anion-selective and cation-selective regions arranged in a mosaic structure. This configuration creates unique transport mechanisms arising from the electrical interactions between the oppositely charged domains.²⁶⁷ In theory, when a charge-mosaic membrane separates two electrolyte solutions with differing concentrations, circular electrical currents develop between the oppositely charged regions, as illustrated in Figure 24.

In homogeneous ion exchange membranes, salts are largely excluded due to the near-complete repulsion of co-ions, resulting in membrane potentials that can closely approach ideal Donnan values. However, when homogeneous regions with opposite fixed charges are arranged in a mosaic structure, the resulting configuration is likely to partially or fully short-circuit these potentials. This facilitates unhindered ion transport through the charged channels, significantly increasing overall salt permeability.¹⁵

The preferential ion transport of charge-mosaic membranes is referred to as negative osmosis,^{266,277} which contrasts with normal osmosis. In normal osmosis, water moves across a semi-permeable membrane from a region of lower solute concentration (lower osmotic pressure) to a region of higher solute concentration (higher osmotic pressure). This process occurs to equalize the solute concentrations on both sides of the membrane, driven by the difference in osmotic pressure. Negative osmosis is reverse to this natural osmotic process. Water flows against the osmotic gradient — from a solution with higher osmotic pressure to one with lower osmotic pressure — without the application of external pressure, unlike reverse osmosis, where pressure is actively applied to reverse the flow.¹⁵

Negative osmosis is driven by electroosmotic effects, where currents generated within the membrane by oppositely charged regions facilitate water movement against the gradient. This is commonly observed with highly asymmetric electrolytes, such as K_2SO_4 ,

MgCl₂ and strong acids, where the mobility of the co-ion (which moves with the solvent) significantly exceeds that of the counterion (which moves against the solvent).¹⁵ However, according to Sollner's predictions, negative osmosis does not strictly require asymmetric electrolytes; the electroosmotic water transport driven by circulating currents alone could be strong enough to overcome normal osmosis.²⁶⁷ Thermodynamic calculations by Kedem and Katchalsky further support this assumption.²⁷¹

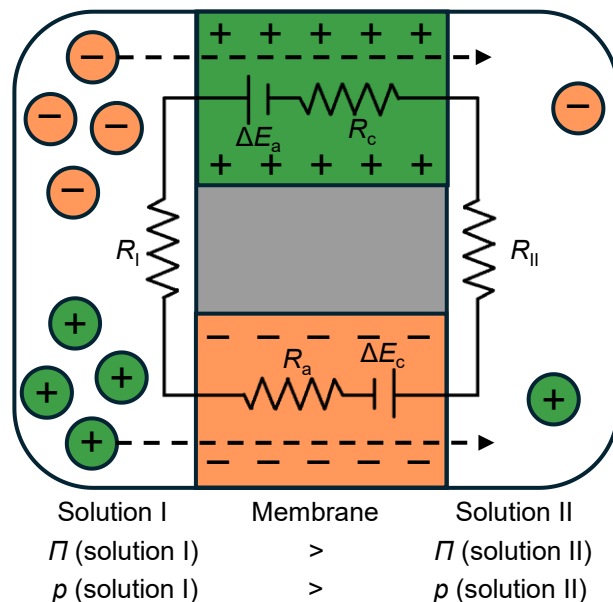


Figure 24. Theoretical transport mechanism of charge-mosaic membranes by negative osmosis. The oppositely charged channel of the charge-mosaic membrane (green: positively charged channel, orange: negatively charged channel) separated by an insulator (grey) cause an electrical circuit. Thereby, the ions permeate through the oppositely charged channels from the solution I with higher osmotic pressure (Π_{high}) to the solution II with a lower osmotic pressure (Π_{low}). R_I and R_{II} are the electrical resistances of the solution I and II, respectively. R_a and R_c are the electrical resistances of the anionic and cationic channels, respectively. ΔE_a and ΔE_c are the membrane potentials of the anionic and cationic channels, respectively. Figure according to ²⁷⁸, with permission from Springer Nature.

The negative osmosis effect — where electroosmotic forces drive water from regions of higher to lower osmotic pressure — makes charge-mosaic membranes effective in separating electrolytes from non-electrolytes *via* dialysis. During dialysis, the ion concentration in the feed solution naturally decreases as the system tends to equalize solute concentrations on both sides of the membrane. Additionally, charge mosaic membranes are promising for the concentration of dilute electrolyte solutions in the presence of hydrostatic pressure and chemical potential gradient by piezo dialysis.²⁷⁸ The term "piezo dialysis" is derived from "piezo," meaning pressure, and "dialysis," which refers to the separation of particles in a liquid. In this process, pressure is applied to drive ions across the semi-permeable membrane, drawing both anions and cations into a low-pressure compartment, thus desalinating the solution on the high-pressure side. This contrasts with reverse osmosis, where a salt-rejecting membrane desalinated the low-pressure side.^{279,280}

For piezo dialysis to work, counterions must move freely across the entire membrane thickness through continuous pathways containing the appropriate fixed-charge groups. Co-ion transport is generally restricted, maintaining selective ion flow and osmotic balance. This free counterion movement is enabled by the cancelation of streaming

potentials in neighboring membrane domains. Charge-mosaic membranes used in piezo dialysis also demonstrate selective permeability, favoring monovalent ions over divalent ions.²⁸⁰

Since Sollner introduced the concept of charge-mosaic membranes, significant efforts have been made to develop highly efficient versions of these membranes. These efforts focus on minimizing the size of both the cation- and anion-exchange regions and, ideally, achieving a homogeneous dispersion of positive and negative charged sites with high densities. Various approaches have been explored to fabricate charge-mosaic membranes from diverse polymeric materials and techniques.

The earliest charge-mosaic membranes were fabricated by embedding strong anion- and cation-exchange resin particles into matrix polymers that are impermeable to ions, such as silicone rubber or poly(vinyl chloride).^{15,281} Equal amounts of small-sized resin particles were used, and these membranes successfully separated ions like potassium chloride from non-electrolytes such as sucrose and glucose.²⁷⁶ Later, polyethylene matrices were modified with copolymers of styrene, vinyl pyridine, and 2-vinyl benzene, which were converted into cation- and anion-exchange entities.²⁸² These membranes demonstrated promising performance in separating monovalent and divalent ions. Another method involved crosslinking P4VP nanospheres of 250 – 350 nm in size with linear poly(sodium styrene sulfonate).²⁸³ Quaternization of P4VP with methyl iodide created the anion-exchange domains, while the sulfonate polymer served as the cation exchanger. The sulfonate polymer was crosslinked around the quaternary ammonium nanospheres, creating an active matrix of cation exchanger surrounding the anion-exchange nanospheres. These membranes effectively separated potassium chloride from glucose or sucrose. This technique was further refined to produce composite membranes with an active layer on a support membrane, enhancing salt transport over water transport.²⁸⁴ A similar approach was used by Hirao et. al.²⁸⁵ This group coated crosslinked poly(4-vinylpyridine) and poly(sodium styrene sulphonate) microspheres which have been incorporated into an active layer on top of a supporting membrane. This membrane was thought to might be potentially used for pressure dialysis.

Block copolymers have emerged as a versatile option for charge-mosaic membrane fabrication. Fujimoto and colleagues developed a BABCB pentablock copolymer system comprising polyisoprene-*block*-polystyrene-*block*-polyisoprene-*block*-poly(4-vinylbenzyltrimethylammonium)-*block*-isoprene pentablock copolymers and selectively introduced anion and cation exchange groups into the microphase separated phases.^{286,287} The amino groups of the poly(4-vinylbenzyltrimethylammonium) were quaternized to create anion-exchange elements, the isoprene blocks were crosslinked, and styrene segments were sulfonated to form cation-exchange elements. The resulting membrane featured a microphase-separated structure with domain sizes of approx. 50 nm, containing striped regions of positive and negative charges provided by the pentablock copolymer. The pentablock products have been commercialized as Desalton® membranes (Tosoh Co. Ltd., Tokyo). These membranes showed significant cation- and anion-exchange capacities, with cation transport numbers close to 0.50 for potassium chloride. Also, they exhibited piezo dialysis effects and negative osmosis, consistent with charge-mosaic membrane predictions.

Another triblock copolymer approach involved polystyrene-*block*-polybutadiene-*block*-poly(4-vinylpyridine) (PS-*b*-PB-*b*-P4VP) triblock copolymers.²⁸⁸ Casting this polymer yielded a three-layer lamellar structure with repeating PS, PB, and P4VP

domains. The PB block was crosslinked using γ -ray irradiation, the P4VP domains were quaternized with diiodomethane, and the PS domains were sulfonated with chlorosulfonic acid. These membranes demonstrated optimal salt flux at pH 6, with no detectable transport of non-electrolytes, such as proteins or sucrose.

Polymer blending has also been investigated. Platt and Schindler blended poly(2-vinylpyridine-*co*-butadiene) with poly(styrene-*co*-butadiene) and a film of this blend was cast from solution in THF.²⁸⁹ Phase separation occurred due to the incompatibility of the two polymers, and P4VP domains were quaternized with methyl bromide, crosslinked with sulfur monochloride, and the polystyrene part sulfonated. The resulting membranes were porous, with modest salt enrichment of 4.8 %.

Higa et al.²⁹⁰ used cut laminated stacks of negatively and positively charged base membranes for establishing multifunctional membranes. For this purpose, charged membranes were obtained by blending poly(vinyl alcohol) with other polymers. The negatively charged base membranes and positively charged base membranes were alternately stacked and physically and chemically cross-linked. The average domain sizes between the positively and negatively charged layers of these membranes were about 10000 times larger than those obtained in the Desalton[®] pentablock copolymer membrane.²⁶³ The process was adjusted 4 years later by blending the raw polymers from the pristine trial. The flux of potassium chloride through the membrane was smaller than through the Desalton[®] membrane, but the permselectivity for electrolytes was increased compared to the Desalton[®] membrane.

Conjugate electrospinning using two oppositely charged nozzles was used to fabricate membranes with poly(sodium styrene sulfonate) (PNaSS) as the anionic exchange component and P4VP as the cationic exchange component, embedded in a poly(vinyl alcohol) matrix.²⁹¹ The composite nanofibers comprised a PNaSS nanofiber paired with a P4VP nanofiber. However, salt rejection tests were not reported.

The group of Philip investigated the generation of charge mosaic membranes using layer-by-layer assembly of polymeric nanotubes on track-etched membranes as sacrificial templates.²⁶⁵ The polymeric nanotubes had pore walls functionalized with either positively charged poly(ethylene imine) or negatively charged poly(styrene sulfonate) moieties. These nanotubes were then deposited onto a porous support to form mixed mosaic membranes. Vertically aligned nanotubes without overlapping between adjacent elements were observed. These mixed mosaic membranes were more permeable to ionic solutes than to similarly sized neutral molecules and showed negative rejection for sodium chloride, indicating that it permeated through the membrane more rapidly than water.

One of the newest trials to receive a charge mosaic membrane is to use inkjet printing.²⁹² Poly(vinyl alcohol)-based composite inks containing poly(diallyl dimethyl-ammonium chloride) or poly(sodium 4-styrenesulfonate) were used to pattern positively charged or negatively charged domains on the surface of a polycarbonate track-etched membrane, obtaining a pore diameter of 30 nm. One membrane exhibited a similar areal coverage of the positive and negative domains and leading to a nearly overall neutral surface charge. A negative salt rejection for single salt systems was observed which is characteristic for a charge mosaic membrane.

Recently, Higa's group reported using screen printing to fabricate thin (20 μ m) striped charge-mosaic membranes with negatively and positively charged layers on a porous support.²⁹³ As inks, aqueous solutions of poly(vinyl alcohol)-*block*-poly(sodium styrene

sulfonate) and poly(vinyl alcohol)–*block*–poly(vinyl benzyl trimethyl ammonium chloride) were used. The printed layers achieved domain sizes of 173 μm and 203 μm for the negatively charged and the positively charged parts, respectively, with nearly equal charge densities for both layers. These membranes demonstrated 25-fold higher electrolyte permselectivity compared to Desalton® membranes and exhibited negative osmosis. In the piezo dialysis test a negative rejection of sodium chloride was noticed.

Despite numerous efforts, the lack of a reliable and scalable fabrication method for charge-mosaic membranes has hindered deeper understanding of their mechanisms and optimization for salt transport.²⁹⁴ New and improved techniques are required to optimize the charge-mosaic membrane fabrication process. One of them might be the combination of blending of block copolymers and block copolymer self-assembly which is investigated in this thesis (chapter 6).

Since proteins are ionizable molecules, possessing both negatively and positively charged groups, charged membranes hold great potential for protein separation. The fundamental properties of proteins are discussed in the following chapter.

3.5 Proteins

Proteins are large complex molecules (macromolecules) made up of one or more chains of amino acids linked together in a specific sequence. They are present in all biological systems, from prokaryotes to higher eukaryotes. Proteins hold a central position in living cells both quantitatively and qualitatively, a distinction reflected in their name, which is derived from the Greek word *protos*, meaning "of primary importance" or "first in rank." They are the most abundant class of biomolecules, accounting for over 50 % of the dry weight of cells, surpassing other major biopolymers such as nucleic acids, polysaccharides, and lipids. The diversity of proteins within an organism is directly linked to the number of genes in its genome, ranging from a few hundred in certain bacteria to several thousand in animals and humans.²⁹⁵

Proteins perform essential roles in virtually all biological processes. Most chemical reactions in living organisms are catalyzed by enzymes — specialized proteins that can dramatically accelerate reaction rates. Proteins also transport and store ions, small molecules, and electrons. They exhibit hormonal activity and, in the form of antibodies, help organisms differentiate between self and non-self, thereby defending against pathogens. Proteins also play a crucial role in signal reception and transmission, both within cells and between them. Furthermore, they regulate the expression of genetic information during transcription and translation, playing key roles in cell growth and differentiation. In addition to their biochemical functions, proteins provide structural support. They form the filamentous architecture within and between cells, which is crucial for maintaining cellular integrity, enabling cellular contraction, and facilitating coordinated movement.²⁹⁵

Proteins are composed of α -amino acids arranged in specific sequences and fold into unique three-dimensional structures that determine their function. These structural and functional aspects will be explored in the following sections.

3.5.1 Amino Acids – Building Blocks of Proteins

Proteins, regardless of their structural or functional roles, are polymers composed of the same fundamental building blocks: α -amino acids. The general structure of an α -amino acid, illustrated in Figure 25 (a), includes an amino group, a carboxyl group, a hydrogen atom, and a unique side chain (R group) attached to a central α -carbon. For this reason, amino acids are also called α -amino acids. The R group varies in size, charge, shape, and chemical composition, which gives each amino acid its unique properties. Among the 20 α -amino found in proteins, 19 share this basic structure. The exception is proline, whose side chain is bonded to the nitrogen atom, forming an imino acid.²⁹⁵

The structure depicted in Figure 25 (a), however, does not fully capture the dynamic nature of amino acids. The ionization of the carboxyl and amino groups depends on the surrounding pH, as shown in see Figure 25 (b). In acidic conditions, the carboxyl group remains non-ionized, while the amino group is ionized and positively charged. At neutral physiological pH, typical for proteins, the carboxyl group is negatively charged, and the amino group is positively charged. At higher pH values, the carboxyl group stays

negatively charged, while the amino group becomes non-ionized. Consequently, amino acids are zwitterions — molecules with both positively and negatively charged groups.

The ionizable nature of amino acids makes them act as weak acids or bases, playing critical roles in protein behavior and reactivity. The amino group, with a basic pKa of approximately 9, becomes protonated ($-\text{NH}_3^+$) beyond this pH, and loses its proton (becoming neutral $-\text{NH}_2$) above this pH. Conversely, the carboxyl group, with an acidic pKa of around 2, remains in its neutral form ($-\text{COOH}$) only at very low pH levels, and becomes negatively charged ($-\text{COO}^-$) at higher pH. This acid-base behavior influences protein properties, helps to identify amino acids, and determines their reactivity.^{295,296}

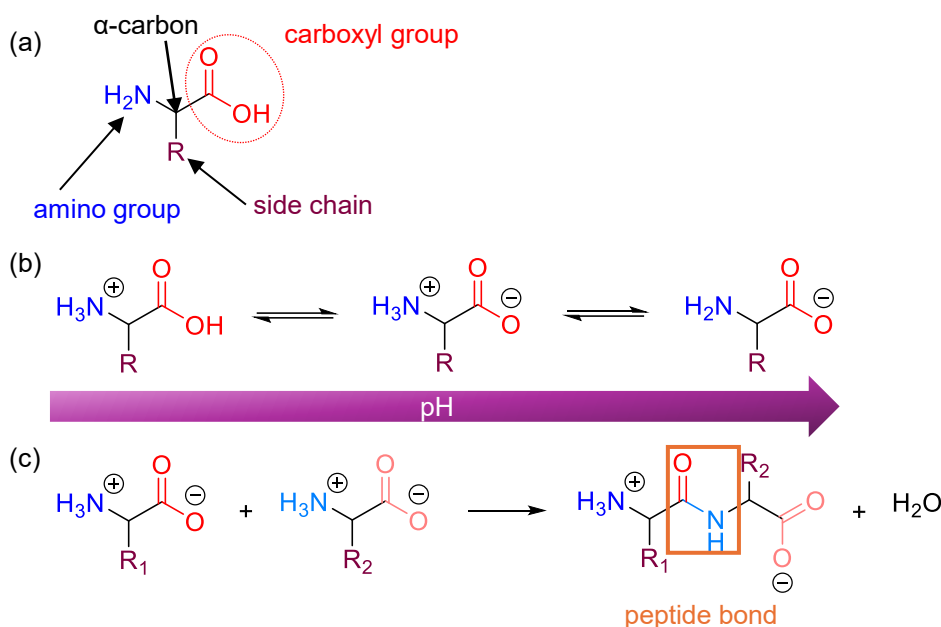


Figure 25. (a) General structure of an α -amino acid. Each amino acid consists of a central α -carbon bonded to an amino group, a carboxyl group, a hydrogen atom, and a distinct R group (side chain). (b) pH-dependent ionization of amino acids. At low pH values ($\approx < 2$), amino acids carry a net positive charge due to the protonation of the amino group. As the pH rises above 2, the carboxyl group is deprotonated, resulting in a zwitterionic structure (a molecule with both a positive and negative charge) that typically exists between pH 2 and 9. At high pH values ($\approx > 9$), the amino group becomes uncharged, leaving the amino acid with a net negative charge due to the deprotonation of the carboxyl group. (c) Formation of a peptide bond. A peptide bond is formed through the reaction between the carboxyl group of one amino acid and the amino group of another. This reaction releases a molecule of water and links the amino acids covalently to form a dipeptide.

In addition to the amino and carboxyl groups in the main chain, the side chains of amino acids can also contain ionizable groups. Amino acids are classified based on the chemical properties of their R groups as follows:

- aliphatic (5 amino acids),
- hydroxylic (2 amino acids),
- acidic or dicarboxylic, and corresponding amides (4 amino acids),
- basic (3 amino acids),
- cyclic (4 amino acids),
- sulfur-containing amino acids (2 amino acids).

For additional details, see references^{295,296}. Except for glycine, whose side chain is a hydrogen atom, the α -carbon in all amino acids is asymmetric. This asymmetry leads to the existence of two optical isomers: the D and L forms. Importantly, only the L isomer

occurs in natural proteins.²⁹⁵ An exception is found in certain microorganisms, such as some fungi and actinomycetes, which can produce D-amino acids — often as components of antibiotics or bacterial cell walls, such as peptidoglycan.

The enormous functional diversity of proteins arises from the linear arrangement of diverse amino acid residues. In all proteins, amino acids are covalently linked by amide bonds, known as peptide bonds (see Figure 25 (c)). Proteins are composed of one or more polypeptide chains and are classified based on their amino acid sequence, composition, and length. In some cases, such as hemoglobin, proteins consist of multiple polypeptide subunits assembled into a functional complex, a higher-order organization known as quaternary structure.^{295–297}

3.5.2 Solubility and Characteristics of Proteins

Proteins primarily exist in aqueous or membrane environments, where their solubility is influenced by several factors. In water, protein solubility is enhanced by polar groups in the side chains of amino acids on the protein's surface, while hydrophobic groups are typically packed inside the protein structure. The addition of salts can significantly affect their solubility. At low ionic strength, solubility increases due to the salting-in effect, whereas at higher ionic strengths, solubility decreases due to the salting-out effect.²⁹⁵

In addition to the ionic strength, protein solubility is also highly dependent on pH, particularly in relation to the protein's isoelectric point (pI) — the pH at which the protein has no net electrical charge. At the pI, the positive and negative charges on the protein surface are balanced, minimizing repulsive electrostatic forces between protein molecules. As a result, protein solubility is lowest at the isoelectric point, which can lead to aggregation or even precipitation due to dominant attractive interactions between protein molecules. At pH values above the pI, proteins carry a net negative charge, while below the pI, they carry a net positive charge. In both cases, the resulting repulsive interactions increase solubility.^{295,296}

Additional factors influencing protein solubility include temperature and the dielectric constant of the solvent, which is a quantitative measure of the solvent's polarity. Proteins are generally insoluble in nonpolar solvents because their solubility primarily depends on interactions between their polar and charged groups and water, which has the highest polarity and dielectric constant among common solvents. When proteins are unfolded or partially denatured, their solubility typically decreases due to the exposure of nonpolar groups, which reduces compatibility with aqueous environments.²⁹⁵

3.5.3 Detection and Quantification of Amino Acids and Proteins

The detection of amino acids and proteins can be achieved using physical, chemical, and biological techniques. The simplest and most direct method for determining protein concentration in solution is to measure absorbance with a UV-VIS spectrometer. Proteins can be identified by the ultraviolet absorbance of the peptide bond at wavelengths below 230 nm. Additionally, proteins containing amino acids with indole rings, such as tryptophan, or aromatic rings, like phenylalanine and tyrosine, exhibit absorbance around 280 nm, which can also be used for detection.²⁹⁵

Protein concentration in solution can be quantified using Beer–Lambert’s law,²⁹⁶ which states that the absorbance A of light passing through a medium is directly proportional to the concentration c of the absorbing substance and the path length l . This relationship is described by the equation:²⁹⁸

$$A = \log \left(\frac{I_0}{I} \right) = \varepsilon \cdot c \cdot l \quad (24)$$

where I_0 is the incoming and I is the transmitted light intensity, and ε the molar extinction coefficient.

In addition, in the range of 25 – 50 % of all proteins found within organisms contain metal ions²⁹⁹ which can introduce specific absorbance features within the UV-VIS spectrum. For example, cytochrome C obtains a central iron ion, which absorbs light at characteristic wavelengths depending on its oxidation state. For Fe^{2+} , absorption occurs at 550 nm, 521 nm and 414 nm, while for Fe^{3+} , absorption occurs at 530 nm and 408 nm.³⁰⁰

Additional methods to determine protein concentration include the Lowry assay, the Bradford assay, and the bicinchoninic acid assay (for more details, refer to reference ³⁰¹).

3.5.4 Structures of Proteins

Proteins are defined by four structural levels: primary, secondary, tertiary, and quaternary structures. The amino group of the first amino acid and the carboxyl group of the last amino acid in a polypeptide chain remain intact, giving the chain two distinct ends: the N-terminus (amino end) and the C-terminus (carboxyl end).³⁰² The primary structure refers to the linear sequence of amino acid residues along a polypeptide chain, resulting from the covalent linkage of individual amino acids *via* peptide bonds. It is the specific arrangement of amino acids from the N-terminus to the C-terminus, and this sequence ultimately dictates the higher-order structures of the protein.²⁹⁶

The secondary structure arises from intramolecular interactions within the polypeptide chain, forming localized conformations. It represents folding patterns within specific regions of the chain, driven by hydrogen bonds between the backbone atoms apart from R groups. The two principal types of secondary structures are the α -helix and the β -sheet. α -helices are regular, spiral-shaped structures stabilized by hydrogen bonds between backbone carbonyl and amide groups, while β -sheets consist of extended strands arranged in parallel or antiparallel formations, also stabilized by hydrogen bonds.^{295–297,303}

The tertiary structure describes the overall three-dimensional shape of a protein, representing its most stable, low-energy conformation. It results from the packing and spatial arrangement of secondary structure elements (e.g., α -helices and β -sheets) into a compact, globular structure. Tertiary structure is primarily determined by interactions between the R groups of amino acids. These interactions are mainly noncovalent, including hydrogen bonds, electrostatic forces, repulsive forces, and hydrophobic interactions. Additionally, covalent bonds, particularly disulfide bridges, contribute to stabilizing the protein’s conformation. The tertiary structure often includes functional units called domains, which contribute to the protein’s specific activity.^{295–297}

Many proteins consist of multiple polypeptide chains, known as subunits or monomers, which can be identical or distinct in their amino acid sequences. The quaternary structure describes the arrangement and interactions of these subunits to form a larger protein complex. Similar to the tertiary structure, quaternary structure is stabilized by hydrogen bonds, electrostatic forces, hydrophobic interactions, and repulsive forces. A subunit is a single protein molecule within the complex, and its interactions with other subunits are essential for the protein's overall function.^{295–297}

Proteins are often purified for various applications, such as functional studies, industrial processes, and diagnostics. To achieve this, diverse purification techniques have been developed, which will be discussed in the next section.

3.5.5 Protein Purification

The advancement of techniques for separating and purifying biological macromolecules, such as proteins, has been a cornerstone of many breakthroughs in bioscience and biotechnology.³⁰⁴ Early research primarily relied on adsorption and precipitation methods to fractionate complex protein mixtures. These methods are still used today for preliminary fractionation or to concentrate protein samples. The development of preparative electrophoretic and chromatographic techniques in the 1950s and 1960s introduced more systematic purification protocols, establishing the foundation for the advanced methods available today.³⁰⁴

To date, a variety of techniques have been established for protein fractionation, based on differences in the physical and chemical properties of proteins (see Table 1). Many of these rely on chromatographic methods, which separate proteins through interactions between the stationary and mobile phases. The specific mechanisms of separation depend on the type of chromatography used.

Size-exclusion chromatography (SEC), also known as gel filtration chromatography (GPC), separates proteins based on their size, more specifically their hydrodynamic radius (Stokes radius). The stationary phase consists of porous beads made of materials like agarose or polyacrylamide. The pores within these beads vary in size and allow molecules to penetrate to different extents based on their size. Larger molecules are excluded from entering the pores and elute first, while smaller molecules enter the pores, traveling a longer, more convoluted path through the column, and elute later.

In reversed-phase chromatography (RPC), the stationary phase is hydrophobic, typically consisting of silica beads coated with long hydrocarbon chains. The mobile phase is more polar, often a mixture of water or aqueous buffer and an organic solvent. Separation is based on hydrophobicity, as proteins interact with the hydrophobic stationary phase. Gradually increasing the concentration of the organic solvent in the mobile phase reduces hydrophobic interactions with the column, causing proteins to elute at different times depending on their hydrophobicity.

Similar to RPC, hydrophobic interaction chromatography (HIC) also separates proteins based on hydrophobicity. However, the mobile phase usually consists of an aqueous solution with a high salt concentration (e.g., ammonium sulfate). Through the addition of salt, the hydrophobic interactions between the protein and the stationary phase are promoted. Gradually decreasing the salt concentration weakens these interactions, allowing proteins to elute.

Table 1. Various common protein fractionation methods and corresponding separation properties.^{304–306}

Fractionation method	Physical/ chemical property
Size-exclusion chromatography (SEC)	Stokes radius
Reversed-phase chromatography (RPC)	Hydrophobicity
Hydrophobic interaction chromatography (HIC)	Hydrophobicity
Ion-exchange chromatography (IEC)	Charge
Affinity chromatography (AC)	Specific biomolecular interaction
Gel electrophoresis (GEP)	Stokes radius
Isoelectric focusing (IEF)	Isoelectric point
Ultrafiltration (UF)	Stokes radius, partially charge

Ion exchange chromatography (IEC) separates proteins based on their charge. The stationary phase consists of a resin or matrix carrying charged groups. In anion exchange chromatography, negatively charged proteins interact with a positively charged stationary phase, while in cation exchange chromatography, positively charged proteins interact with a negatively charged stationary phase. The mobile phase is typically an aqueous buffer. Proteins elute as the ionic strength of the buffer increases through a salt gradient or as the pH changes, which modulates the charge on the proteins.^{304–306}

One of the primary mechanisms for protein separation is adsorption, which forms the basis of affinity chromatography.³⁰⁶ Affinity chromatography is a type of liquid chromatography that relies on the specific interaction between a target protein and a ligand immobilized on particles within a packed column. This method achieves high specificity, as purification is based on the specific binding interactions between the protein and the ligand. A specialized form of affinity chromatography is immobilized metal ion affinity chromatography (IMAC), which is particularly useful for purifying proteins that exhibit affinity for metal ions. Another variant is covalent chromatography (CC), often employed to purify proteins containing specific reactive groups, such as thiol groups on cysteine residues.^{304,306}

Electrophoresis is another widely used laboratory method for separating proteins. Introduced in the early 20th century, electrophoresis relies on the migration of charged particles and molecules in an electric field and is therefore ideally suited for proteins, which are generally charged.³⁰⁶ Since the speed of migration varies depending on both charge and size, the components of a sample separate into distinct zones, forming a characteristic pattern that can be visualized.

The simplest form of protein electrophoresis is gel electrophoresis, with polyacrylamide gel electrophoresis (PAGE) being the most common variant. Particularly often used are sodium dodecyl sulfate-polyacrylamide gel electrophoresis (SDS-PAGE) and native PAGE.³⁰⁴ In SDS-PAGE, the separation of the proteins occurs primarily by size, as the detergent SDS denatures the proteins and imparts a uniform negative charge. Native PAGE preserves the native structure and charge of proteins, enabling separation based on both size and charge.

Another electrophoretic technique is isoelectric focusing (IEF), which separates proteins based on their isoelectric point (pI). Proteins migrate within a continuous pH gradient until they reach their equilibrium position, where their net charge is zero, corresponding to their pI.³⁰⁴

Chromatography, particularly affinity chromatography, is one of the most widely used methods for protein purification due to its high specificity. This specificity stems from the strong interaction between a protein and its ligand, making it suitable for both small-scale laboratory research and large-scale industrial applications. However, affinity chromatography has some notable limitations. The ligands used in affinity chromatography are expensive, causing high cost. Potential ligand leakage can lead to contamination of the target protein, and during elution proteins might be denatured the protein or the activity is affected.

Hence, membranes are an alternative to chromatography for certain applications, offering lower costs and the ability to maintain constant pH during the separation process, reducing the risk of protein denaturation. Ultrafiltration membranes are used to separate and concentrate proteins primarily based on size, specifically the protein's Stokes radius. The pore sizes of ultrafiltration membranes typically range from a few nanometers to 100 nm, allowing them to retain macromolecules like proteins.³⁰⁷ Ultrafiltration membranes have a specific molecular weight cut-off (MWCO), determined by their pore size. The MWCO defines the molecular weight at which a certain percentage of a solute percentage (usually 90 % or 95 %) is retained by the membrane, thus indicating its separation efficiency. MWCO values are typically expressed in kilodaltons (kDa) and reflect the size limit of molecules that can pass through the pores.³⁰⁸

While size exclusion is the primary separation mechanism in ultrafiltration membranes, hydrophobic and electrostatic interactions also influence the separation process.³⁰⁴ For instance, in charged ultrafiltration membranes, exclusion relies on both size- and charge. Positively or negatively charged ultrafiltration membranes can reject similarly charged proteins due to charge repulsion. Conversely, the transport of oppositely charged proteins can be enhanced due to the attractive forces between the protein and the membrane surface.^{308,309}

One of the significant challenges in using ultrafiltration membranes for protein separation is fouling, which can occur in various forms. Proteins are particularly challenging foulants because they readily adsorb onto membrane surfaces and pore walls, leading to both pore blockage and the formation of a cake or deposit, as well as within the membrane's pore structure. Beyond that, denatured or aggregated proteins tend even more to deposit on the membrane surface. The fouling results in a reduced flow rate during constant pressure operation (diminishes permeate flux) and alters solute selectivity. This decrease in permeance negatively impacts the efficiency and cost-effectiveness of protein recovery processes. Therefore, membrane fouling is a critical issue in protein filtration processes that impacts efficiency and operational costs.^{308,309}

To address the challenges of traditional membrane systems, such as fouling, selectivity, and efficiency, new membrane materials, surface modifications, and innovative membranes are explored. However, to fabricate polymers and membranes, a variety of techniques are required to characterize them. These techniques will be discussed in the following section.

3.6 Characterization Methods

This section aims to offer a general overview of the fundamental principles behind the characterization methods employed. For a more comprehensive and detailed explanation, readers are encouraged to consult current literature.

3.6.1 Nuclear Magnetic Resonance (NMR) Spectroscopy

NMR spectroscopy is a powerful spectroscopic technique widely used in the elucidation of molecular structures, dynamics, and interactions.³¹⁰ The physical foundation of NMR spectroscopy lies in the magnetic properties of atomic nuclei. Nuclei that possess nuclear spin also exhibit a magnetic moment μ . However, the magnetic moment of atomic nuclei can only adopt specific orientations in an external magnetic field, as dictated by quantum mechanics. In the absence of an external magnetic field, these spin states are energetically equivalent. When an external magnetic field is applied, energy differences emerge between the spin states, a phenomenon known as the Zeeman effect.³¹¹

In NMR spectroscopy, a sample is placed in an external magnetic field, causing the nuclei to align either with or against the field. When a specific radiofrequency pulse is applied *via* a transmitter, the nuclei are shifted to another energetic state, away from the typical Boltzmann distribution. As they relax back to their ground state, they emit radiofrequency signals that are detected and analyzed. The energy E , required to induce these transitions is directly proportional to both the strength of the external magnetic field B_0 and the gyromagnetic ratio γ of the nucleus as shown in Equation (25), where $\hbar$ represents the Planck constant and ω_0 the Larmor-frequency. The gyromagnetic ratio is a fundamental property unique to each nucleus and determines its resonance frequency in the magnetic field.^{310,312}

$$E = \hbar \cdot \gamma \cdot B_0 = \hbar \cdot \omega_0 \quad (25)$$

The energy is detected by a radiofrequency receiver, recording a spectral line known as the resonance signal. In this way, an NMR spectrum is generated for the substance being analyzed. This technique is applicable to all nuclei that possess a non-zero magnetic moment, including nuclei such as ^1H , ^{19}F , ^{14}N and ^{15}N , among many others. However, in the field of organic chemistry, the ^{12}C isotope, which is abundant, lacks a magnetic moment and cannot be detected by NMR. Only the ^{13}C obtains a magnetic moment and can be observed in NMR spectroscopy. However, the natural abundance of it is only 1.1 %.^{310,312}

However, the resonance frequencies are influenced by the local magnetic fields experienced by individual nuclei. These local magnetic fields can deviate from the main external magnetic field due to factors such as the electronic environment surrounding the nucleus or magnetic interactions with neighboring nuclei. These variations in local fields affect the resonance frequency of each nucleus, providing detailed insights into the molecular structure. Because of this sensitivity to local environments, NMR

spectroscopy is a powerful tool for determining the structure and composition of molecules.

In ^1H -NMR spectroscopy, the applied pulse can be a 90° radiofrequency pulse. This pulse flips the magnetization of the nuclei from the z-axis (aligned with the magnetic field) into the xy-plane. However, the pulse can also vary in size, either smaller or larger, in which case its projection onto the xy-axis is measured. After the pulse is applied and then turned off, the nuclei begin to return to their equilibrium state, emitting energy in the process. This energy emission is detected as a signal, which decays over time. This decaying signal is known as free induction decay (FID). The FID is a time-domain signal, meaning it changes over time. To convert this into a more useful frequency-domain spectrum, a mathematical operation called the Fourier transform (FT) is applied. The FT converts the decaying time-domain FID into a frequency-domain spectrum, where each peak corresponds to a distinct chemical environment of the hydrogen atoms in the sample.

In most spectroscopic methods, absorption (on the y-axis) is plotted against frequency or wavelength (on the x-axis). However, in NMR spectroscopy, the x-axis represents the chemical shift rather than frequency. The chemical shift scale is used because the resonance frequency is directly proportional to the strength of the magnetic field (as shown in Equation (25)). This dependence on the magnetic field strength complicates the direct comparison of spectra obtained from different NMR spectrometers. To address this, the chemical shift is introduced as a dimensionless unit, which normalizes the data and makes it independent of the magnetic field strength, allowing for consistent comparison of spectra across different instruments.³¹²

The chemical shift is established using a standard reference compound that defines a specific point on the chemical shift scale. The position of a peak in the NMR spectrum is determined by measuring its frequency difference from the reference peak and then dividing this difference by the frequency of the reference peak. By using this ratio of frequencies, the dependence on the magnetic field strength is eliminated. As a result, the chemical shift becomes independent of the external magnetic field. Chemical shifts are typically expressed in parts per million (ppm), allowing for consistent comparison across different instruments and conditions.³¹² Empirically, the chemical shifts of specific functional groups in various solvents have been established, providing valuable reference points that aid in interpreting NMR spectra and determining the structures of unknown compounds. The area under each resonance signal is directly proportional to the number of nuclei contributing to that signal. By integrating these signals, the relative number of protons in different chemical environments within the molecule can be quantified, offering insights into the molecular structure and the distribution of atoms.³¹⁰

Not all signals in NMR spectroscopy appear as a single peak; often, signals are split due to a phenomenon known as spin-spin coupling, or J -coupling. This splitting occurs as a result of magnetic interactions between neighboring, non-equivalent nuclei that possess magnetic moments. The pattern of splitting follows the $n + 1$ rule, where n is the number of equivalent neighboring nuclei, and the multiplicity of the signal will be $n + 1$. The separation between the split peaks is called the coupling constant (J -value), measured in Hz. The J -value provides important information about the distance and bonding relationship between the coupled nuclei. A larger J -value indicates stronger coupling, typically observed in nuclei that are closer or separated by fewer chemical bonds.^{310,312}

Among all magnetic nuclei, proton NMR spectroscopy (^1H -NMR) is the most widely used technique in NMR spectroscopy. In addition to its primary role in structural identification, ^1H -NMR is highly effective for monitoring chemical reactions. Changes in the integrals of specific groups can be tracked over time, as the integrals for some signals decrease while others increase, providing insight into reaction progress (as shown in Figure 26 for the RAFT polymerization of DMA). This capability makes ^1H -NMR a standard tool for determining the conversion in reactions like RAFT polymerizations, where monitoring the relative intensities of signals corresponding to different functional groups allows for precise tracking of polymerization kinetics.

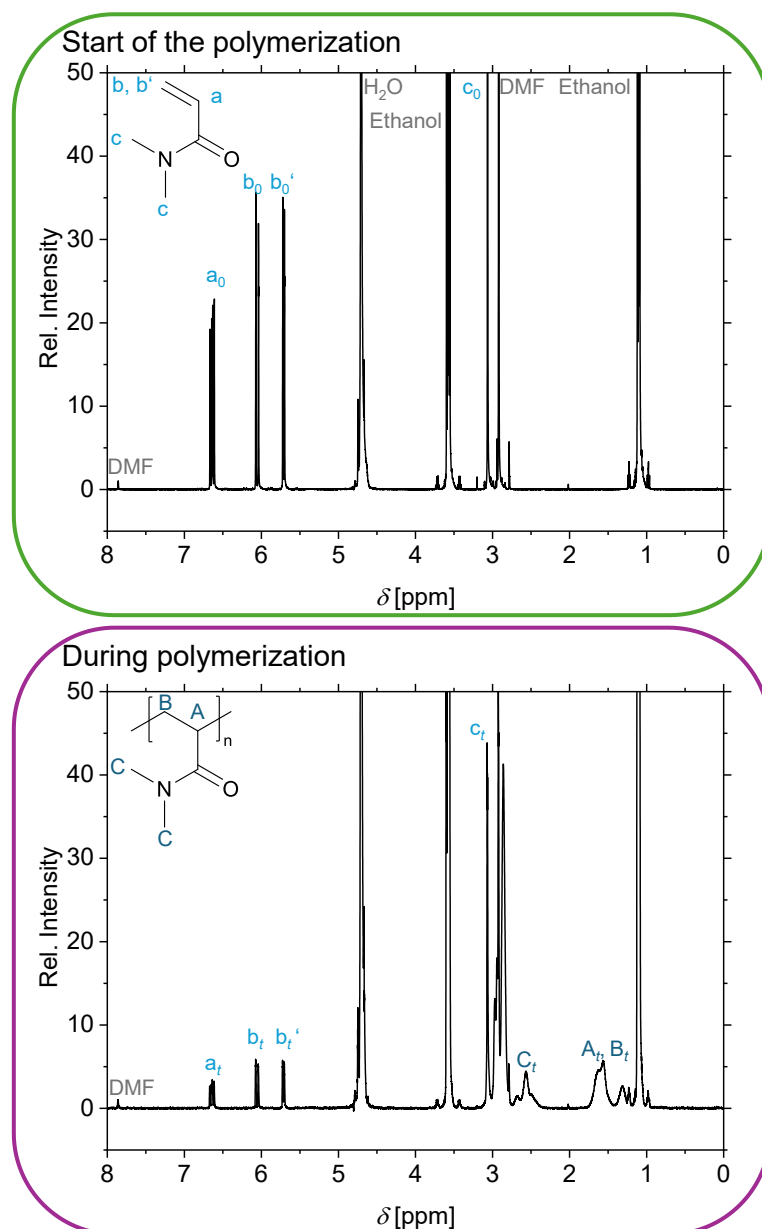


Figure 26. ^1H -NMR spectrum at the beginning (top) and during (bottom) the RAFT polymerization of DMA. The x-axis represents the chemical shift (in ppm), while the y-axis represents the relative intensity, normalized to the *N,N*-dimethylformamide (DMF) signal at approximately 7.9 ppm. A typical NMR spectrum displays chemical shifts decreasing from left to right. While the solvent signals remain unchanged due to their non-reactivity, the monomer signal intensity decreases as polymerization progresses, accompanied by the appearance of new signals corresponding to the polymer PDMA.

3.6.1.1 Pulsed Field Gradient Nuclear Magnetic Resonance (PFG NMR) Spectroscopy

Pulsed field gradient nuclear magnetic resonance (PFG NMR) spectroscopy, also called PSGE NMR (pulsed gradient spin echo nuclear magnetic resonance) spectroscopy, is a specialized NMR technique used to measure molecular diffusion and motion.³¹³ This approach captures the change in position of individual molecules between gradient pulses, reflecting their displacement over the time interval.³¹⁴

In PFG NMR, the standard pulse method used in conventional ¹H-NMR is adapted to include a sequence known as the spin-echo sequence. This sequence consists of an initial 90 ° radiofrequency pulse followed by a 180 ° pulse. The rationale behind this two-pulse sequence is as follows:

- The 90 ° pulse flips the magnetization of the nuclear spins into the transverse plane, initiating precession in the xy plane and signal generation.
- The subsequent 180 ° pulse serves to refocus the dephasing spins, which naturally start to lose coherence due to local magnetic field inhomogeneities after the initial excitation. This pulse effectively reverses the dephasing, rephasing the spins to produce a coherent signal, known as a spin echo.

In PFG NMR, this basic spin-echo sequence is augmented by the addition of magnetic field gradients, which are applied in a controlled manner during the sequence. These pulsed field gradients, typically applied before and after the 180 ° pulse, enable the measurement of molecular diffusion.

The first gradient pulse imposes a spatially dependent phase shift across the sample, effectively encoding the initial positions of the nuclear spins based on their location within the gradient field. After a defined delay, a second gradient pulse is applied. The degree to which the spins refocus after this second gradient depends on whether the molecules have diffused or moved during the delay period.

If the molecules have diffused, the phase shifts induced by the first gradient will not be perfectly refocused by the second gradient, resulting in a reduced echo signal. The extent of this signal attenuation is proportional to the degree of molecular motion. By analyzing the change in signal intensity, it is possible to quantify the diffusion coefficient and gain insights into molecular dynamics and interactions within the sample.^{313–316}

The intensity of the recorded NMR signal depends on the gradient pulse (the gradient strength G and the duration of the gradient pulse δ), the diffusion time between gradient pulses Δ as well as the diffusion coefficient D according to the Stejskal–Tanner equation³¹⁷:

$$I = I_0 \cdot \exp(-D \cdot (\gamma \cdot G \cdot \delta)^2 \cdot (\Delta - \frac{\delta}{3})) \quad (26)$$

where I is the measured signal area, I_0 the maximum signal area and γ the gyromagnetic ratio. By rearranging and taking the logarithm, the following equation is obtained.

$$-\ln\left(\frac{I}{I_0}\right) = DG^2\gamma^2\delta^2\left(\Delta - \frac{\delta}{3}\right) \quad (27)$$

It is important to note that, aside from the diffusion coefficient D , all other parameters in the pulse sequence are either fixed within the pulse sequence (G , δ , and Δ) or measured directly (I and I_0). Hence, during the measurement, the intensity of the pulsed gradients G is systematically varied. Consequently, NMR spectra are recorded as a function of the varying gradient strength G .³¹³ Accordingly, by measuring I at varying gradient strengths, the resulting values are then plotted against the parameters $G^2 \gamma^2 \delta^2 \left(\Delta - \frac{\delta}{3} \right)$. The slope of the linear fit to this plot provides the diffusion coefficient D , as described by the Stejskal–Tanner equation.

3.6.2 Size Exclusion Chromatography (SEC)

Size exclusion chromatography (SEC), also known as gel permeation chromatography (GPC), is the most popular analytical technique for determining the molecular weight and molecular weight distribution (also referred to as dispersity $\mathcal{D}$) of polymers.³¹⁸ It is extensively employed in the analysis of polymers, biopolymers, proteins, and other macromolecules.

The separation process in SEC is governed by the molecular size, more specifically by the hydrodynamic radius or volume, rather by enthalpic interactions with the stationary phase. This distinguishes SEC from other chromatographic methods like adsorption or ion-exchange chromatography, where interactions between the analyte and stationary phase play a larger role.³¹⁸ The two key components of SEC are the stationary and the mobile phase. The stationary phase consists of a column packed with porous beads of defined pore size, while the mobile phase is typically the same solvent used to dilute the sample.³¹⁸

In practice, a sample is dissolved in an appropriate solvent and injected into a column. As the sample elutes through the column, the molecules can penetrate the pores of the network to varying degrees due to their volume, i.e., molecules with a high hydrodynamic volume are too large to penetrate into the pores and elute within short time frames. As the volume of the molecules decreases, the molecules can penetrate into the pores and i.e., take longer to pass through the column and elute later (see Figure 27).³¹⁸ Therefore, the hydrodynamic volume of a molecule determines the elution time point and volume. To analyze the sample's molecular weight distribution, the concentration of molecules in the eluate is monitored. This can be done using a differential refractometer, which detects differences in refractive index between the solvent and solute, or with a UV-VIS spectrometer, which measures differences in absorption.¹⁷ The output is an elugram, in which the detector signal is plotted against the elution volume. In this elugram, molecules with higher molecular weight elute at smaller volumes, while those with lower molecular weight elute at larger volumes.

SEC is a relative method because it does not measure molecular weight directly. Instead, it requires calibration with standards of known molecular weight. For polymers, polystyrene standards with narrow molecular weight distributions are often used. By calibrating the SEC system with a series of standards, a relationship between elution volume and molecular weight can be established.^{17,318} A major advantage of SEC is that it is a non-destructive technique, allowing for the recovery of analytes after separation. This makes it particularly valuable for sensitive or valuable samples.

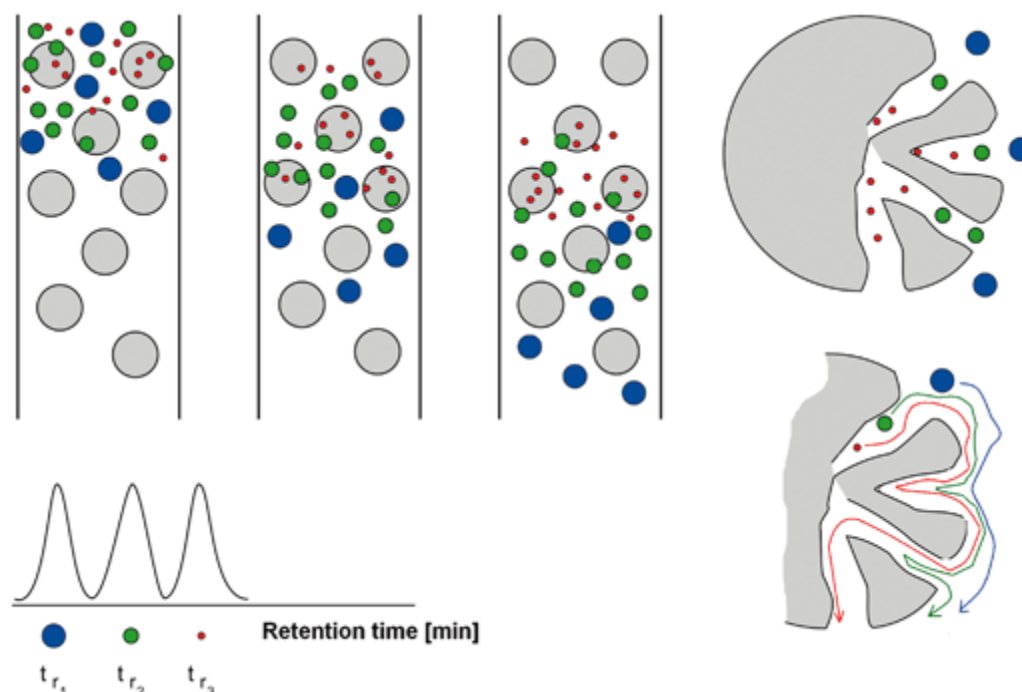


Figure 27. Separation mechanism of molecular mixtures by size exclusion chromatography. Molecules with a small hydrodynamic radius can diffuse into the pores of the beads, slowing their passage through the column and resulting in later retention times. In contrast, molecules with a large hydrodynamic radius are excluded from the pores and elute more quickly. As a result, the elugram displays a characteristic separation pattern, with larger molecules appearing first, followed by progressively smaller molecules. Reprinted with permission from ³¹⁹.

3.6.3 Dynamic Light Scattering (DLS)

Detection of light scattering from matter is a useful technique with applications in numerous scientific disciplines where specific properties of molecules can be studied, depending on the light source and detector.³²⁰ Dynamic Light Scattering (DLS) is a very powerful tool for studying the diffusion behavior of small particles and macromolecules in solution, determining their sizes, size distributions, and (in some cases) the shapes of particles in liquids.^{320,321}

DLS measures the fluctuations in light intensity caused by the Brownian motion of macromolecules and particles in solutions. For the measurement, a laser beam is directed at a sample containing macromolecules or particles, causing the incident light to scatter in all directions. The intensity of the scattered light is recorded by a detector. As the particles or macromolecules are constantly moving due to Brownian motion, the monochromatic incident light experiences Doppler broadening, where the scattered light shifts in frequency according to the motion of the particles in solution. Depending on the phase of the scattered light waves, they can interfere either destructively (canceling each other out) or constructively (amplifying each other), producing a measurable signal. The DLS detector captures these intensity fluctuations, which reflect the random motion of the particles or macromolecules.^{320,321}

A digital autocorrelator is used to analyze the scattered light by correlating the intensity fluctuations over time, typically on the nanosecond to microsecond scale. This correlation provides information about how rapidly the intensity changes, which is directly related to the diffusion behavior of the particles or macromolecules. The key output is

the intensity-correlation function or second-order correlation function, denoted as $g_2(\tau)$. This function describes the temporal evolution of the scattered light intensity and reflects the motion of the macromolecules being studied. Mathematically, $g_2(\tau)$ is an integral over the product of the light intensities at an initial time t and at a delayed time $(t + \tau)$, where τ is the time delay. The normalized function of $g_2(\tau)$ is shown in Equation (28). The braces indicate the averaging of the measured properties over the duration of the experiment.³²⁰

$$g_2(\tau) = \frac{\langle I(t) \cdot I(t + \tau) \rangle}{\langle I(t) \rangle^2} \quad (28)$$

The correlation function tracks the similarity between the scattered signal at an initial time t and a later time $t + \tau$. Initially, the signals are fully correlated, but this correlation decreases over time. Small particles, with faster Brownian motion, exhibit a rapid decay in correlation, while larger particles, moving more slowly, show a slower decline. Hence, the rate of decay in the autocorrelation function directly reflects the particle size and diffusion characteristics.

The relative motion of particles can be understood by analyzing the electric field correlation function, $g_1(\tau)$, also known as the first-order correlation function. This function captures the statistical correlation between the positions of particles at different times, providing insight into their collective motion. By examining $g_1(\tau)$, the patterns of correlated particle movement in the system can be inferred. The normalized version of $g_1(\tau)$ is shown in Equation (29).³²⁰

$$g_1(\tau) = \frac{\langle E(t) \cdot E(t + \tau) \rangle}{\langle E(t) \rangle^2} \quad (29)$$

$g_1(\tau)$, which describes the correlation of the scattered electric field, is not directly measured but is derived from $g_2(\tau)$ using the Siegert relation:³²²

$$g_1(\tau) = \sqrt{g_2(\tau) + 1} \quad (30)$$

For monodisperse particles, the electric field correlation function $g_1(\tau)$ decays exponentially and is characterized by a decay constant Γ , which reflects the Brownian motion of the macromolecules. This decay constant Γ is related to the diffusion behavior of the particles or macromolecules, expressed by the translational self-diffusion coefficient of the particle D and the length of the scattering vector q :^{320,321}

$$g_1(\tau) = e^{-\Gamma\tau} = e^{-q^2 D \tau} \quad (31)$$

The length of the scattering vector depends on the scattering angle θ , the wavelength λ of the light in the scattering medium, and the refractive index of medium η , and is given by:³²⁰

$$q = \frac{4\pi\eta}{\lambda} \sin \frac{\theta}{2} \quad (32)$$

As seen from Equation (31) and (32), DLS directly provides the translational self-diffusion coefficient D of the particle or macromolecule. While in theory, a single measurement at one scattering angle is sufficient to determine D , it can also be determined by measurements at multiple scattering angles. The decay constant of $g_1(\tau)$ is then plotted against q^2 . This plot should yield a straight line, with its slope corresponding to D . D is particularly valuable for calculating other key hydrodynamic parameters. For instance, the hydrodynamic radius R_h , defined as the radius of an equivalent sphere that diffuses at the same rate as the particle being studied, can be determined using the Stokes-Einstein equation:

$$D = \frac{k_B T}{6\pi\eta R_h} \quad (33)$$

For non-spherical molecules, the hydrodynamic radius does not correspond to the actual geometric radius of the particle. Instead, R_h represents the radius of a hypothetical sphere that diffuses at the same rate as the particle in question. The relationship between the translational diffusion coefficient or hydrodynamic radius and the true dimensions of non-spherical particles is highly dependent on the particle's shape, meaning R_h is an approximation that reflects the particle's diffusive behavior rather than its precise geometry.³²¹

In contrast, for a polydisperse system, $g_1(\tau)$ cannot be described by a single exponential decay. Instead, it is expressed as an intensity-weighted integral over a distribution of decay rates, $G(\Gamma)$, which accounts for the range of particle sizes and their respective diffusion behaviors. This representation is crucial for accurately capturing the dynamics of polydisperse samples.³²¹

$$g_1(\tau) = \int_0^\infty G(\Gamma) \cdot e^{-\Gamma\tau} d\Gamma \quad (34)$$

Thus, the first-order time correlation function becomes a sum of exponentials in the case of polydisperse systems. One method to characterize this sum of exponentials is the cumulants method. In this approach, the logarithm of the normalized correlation function $g_1(\tau)$, is expanded into a Taylor expansion according to Equation (35).^{320,321}

$$\ln(g_1(\tau)) = -K_1\tau + \frac{K_2}{2!}\tau^2 + \frac{K_3}{3!}\tau^3 + \frac{K_4}{4!}\tau^4 + \dots \quad (35)$$

The coefficients K_n in this expansion are known as cumulants. The coefficients K_n represent the average, variance, skewness, and kurtosis of the measured distributions for the decay rates, respectively, based on a Gaussian distribution. Notably, the polydispersity index (PDI) can be derived from the following relationship, where $\bar{\Gamma}$ is the average decay rate:³²⁰

$$\text{PDI} = \frac{K_2}{K_1^2} = \frac{K_2}{\bar{\Gamma}^2} \quad (36)$$

3.6.4 Transmission Electron Microscopy (TEM)

Transmission Electron Microscopy (TEM) is an imaging technique that enables the observation of materials with exceptionally high resolution, reaching the sub-nanometer scale. Due to the short wavelength of electrons (approximately 100,000 times shorter than visible light photons), TEM achieves resolutions far beyond those of optical microscopy, making it an indispensable tool for the microstructural characterization of materials. It is frequently used in fields like cell biology and soft-matter materials research.^{323,324}

In TEM, a high-energy electron beam is directed at an ultrathin sample, and the interactions between the electrons and the sample generate highly detailed images. The electrons are accelerated by a high voltage (typically between 100 and 300 kV), which directs them toward the sample. Then, the condenser lenses focus them into a small, uniform beam. When the electron beam interacts with the sample, several outcomes are possible: electrons may either pass through the sample or interact with the atoms *via* elastic or inelastic scattering. Elastic scattering occurs when the electron's kinetic energy and momentum are conserved. This process bends the electron's path due to interactions with the sample's atomic nuclei, with the degree of scattering depending on the atomic number of the elements in the sample. These elastically scattered electrons provide high-resolution information, crucial for imaging. Inelastic scattering, on the other hand, involves a loss of energy, leading to radiation damage and lower image resolution. These processes are less localized than elastic scattering and do not contribute to high-resolution details. Additionally, energy loss causes the electrons to interact differently with the lenses, creating variations in focal lengths. Once the electron beam has passed through the sample, the objective lens focuses the transmitted and scattered electrons to form an intermediate image. This image is then further magnified by a series of additional lenses. The final magnified image is projected onto a fluorescent screen or captured on photographic film for permanent recording. Since electrons cannot carry color information, all TEM images are produced in grayscale.^{324,325}

The degree to which the electron beam is deflected depends on the electron density of the material it encounters. Atoms with higher electron density cause stronger deflection of the beam. Organic specimens are primarily composed of atoms with low electron density, resulting in relatively low contrast in their magnified images. To enhance contrast, heavy metals are often used to increase the electron density which increases the beam deflection, producing clearer, more defined images. This process is called staining.³²⁴

3.6.5 Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM), is one of the most versatile instruments for the examination and analysis of the microstructure morphology and characterization of the chemical composition on a mesoscopic length scale. It is widely utilized across numerous disciplines for the detailed examination of both organic and inorganic materials. It is a highly effective method for analyzing samples at the nanometer to micrometer scale. SEM operates at extremely high magnifications, reaching up to 300 000 and even up to

1000 000 in some modern models, enabling the precise imaging of a wide variety of materials with exceptional detail.^{326,327}

The process begins with the generation of a high-energy electron beam in the electron gun. The incident electrons usually obtain energies of 2 – 40 keV. The electrons are then accelerated toward the sample. Two or three electromagnetic condenser lenses focus and demagnify the electron beam into a fine probe. These lenses precisely control the size and focus of the electron beam, ensuring it remains narrow and focused as it moves toward the sample. Once focussed, the electron beam is directed onto the sample surface and is scanned across a selected area of the specimen surface in a raster pattern using scan coils. The electrons from the beam penetrate the specimen, creating a teardrop-shaped interaction volume whose size depends on several factors, including the beam energy, the atomic mass of the specimen's constituent elements, and the angle of incidence at which the electron beam strikes the surface. The penetration depth of the electrons increases with higher beam energy, larger incidence angles, and lower atomic mass of the specimen's elements.³²⁸

When the primary electron beam scans the sample surface, it interacts with the sample through both elastic and inelastic scattering (like in TEM, see chapter 3.6.4). In elastic scattering, the incident electron is deflected by the specimen's atomic nucleus or outer-shell electrons with minimal energy loss and a significant change in direction. Electrons scattered at angles greater than 90 ° are known as backscattered electrons (BSEs) and provide valuable compositional information. In inelastic scattering, the incident electron transfers substantial energy to the sample, exciting its electrons. The amount of energy loss depends on whether the electrons are excited individually or collectively, and on their binding energy within the atom. This excitation results in the emission of secondary electrons (SE), typically with energies below 50 eV. The secondary electron signal is the most widely used in SEM, generated by the interaction of the primary electron beam. Due to their low energy, averaging around 3 – 5 eV, secondary electrons can only escape from within a few nanometers of the sample surface, allowing for highly accurate beam position marking and topographic information with excellent resolution. SEs are primarily used to provide topographic contrast, visualizing surface texture and roughness. The quality of the topographical image depends on how many secondary electrons reach the detector, and SE signals can resolve surface structures down to around 10 nm or better. Additionally, other signals, such as characteristic X-rays, Auger electrons, and cathodoluminescence, are generated, offering further analytical information.³²⁷

Backscattered electrons are not as numerous as the secondary electrons and obtain significantly higher energy. An energy-selective backscattered (EsB) detector is a specialized detector used in SEM to selectively detect backscattered electrons based on their energy. The EsB detector can filter the backscattered electrons based on their energy, allowing only electrons within a specific energy range to be detected. Since backscattered electron yield depends on the atomic number (higher atomic number elements scatter more electrons), the EsB detector can provide high-contrast images that highlight compositional differences between materials. This is why samples stained with heavy elements like iodine can be analyzed particularly effectively using the EsB detector. Iodine's high atomic number enhances backscattered electron contrast, allowing the EsB detector to better differentiate between areas with varying elemental compositions, resulting in clearer and more detailed images. Additionally, the EsB

detector enhances surface-specific details while minimizing interference from deeper layers, making it useful for surface analysis.³²⁷

3.6.6 Differential Scanning Calorimetry (DSC)

DSC is the most popular thermal analysis and measures the heat flow associated with physical and chemical changes in a material as a function of temperature or time. By comparing the heat flow to a reference material, DSC provides insights into key thermal properties, such as melting points, crystallization, glass transitions, and thermal stability.^{329,330}

In DSC, the sample and an inert reference material (often an empty pan) are placed in separate, thermally isolated pans within the DSC apparatus. A controlled temperature program is applied, which may involve heating, cooling, or maintaining a constant temperature. The temperature changes at a constant rate depending on the experimental objective. As the temperature varies, the sample undergoes physical or chemical transformations, such as melting, crystallization, or phase transitions, which either absorb or release heat. The reference material, however, remains unchanged. When the sample absorbs heat (an endothermic process), more energy is needed to maintain the same temperature as the reference, and this heat flow difference is recorded. Conversely, if the sample releases heat (an exothermic process), less energy is required, and this reduction in heat flow is measured. DSC detects these changes in heat flow as the sample undergoes temperature-induced transformations and records the difference in heat flow caused by internal physical or chemical processes. In the absence of such processes, no significant heat flow difference is observed, except when the ongoing chemical reactions release or absorb heat. The DSC output is a thermogram, a graph plotting heat flow against temperature or time, providing critical insights into the material's thermal behavior. Key events such as melting, glass transition, crystallization, or decomposition appear as peaks or shifts on this graph (see Figure 28).^{329,330}

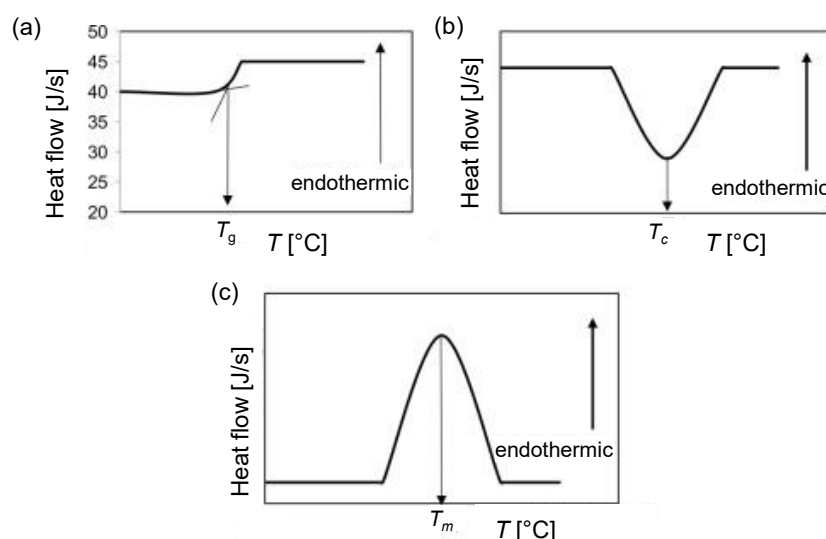


Figure 28. DSC thermograms illustrate (a) the glass transition, (b) crystallization, and (c) melting. Adapted with permission from ³³¹.

In polymer science, DSC is a crucial tool for determining key thermal properties such as the glass transition temperature T_g and melting temperature T_m of polymers. It is also widely used to assess the mixing behavior of amorphous polymers. When block copolymers undergo microphase separation, or when incompatible polymer blends undergo macrophase separation, distinct glass transition temperatures corresponding to the individual homopolymers are observed. In contrast, when polymers are compatible and mix well, a single glass transition temperature is detected, which falls between the T_g values of the pure polymers. This provides valuable insights into polymer miscibility and phase behavior.

4 Objective of This Work

Advanced separation tasks often demand more than simple size-based sieving to achieve the desired selectivity. Functional membranes offer a promising solution by combining traditional size exclusion with additional separation mechanisms based on molecular interactions. These interactions arise from functional groups embedded within the membrane's pores or nanochannels with the respective molecules or ions, enabling enhanced selectivity beyond purely physical filtering. By incorporating charged groups into the pore structures, membranes can also perform charge-selective separations. This dual functionality — size and charge selectivity — makes such membranes particularly effective for separating biomolecules such as proteins. Furthermore, introducing oppositely charged domains within the membrane enables applications beyond biomolecule separation, such as the selective removal of salts and other small ions from complex mixtures — an approach useful in fields like purification or desalination. Block copolymers hold significant promises as advanced materials for fabricating these functional membranes. Their high versatility allows precise tuning of material properties by adjusting the composition, molecular weight, and sequence of their constituent blocks, thereby facilitating the incorporation of diverse functional groups and control over pore size.

The objective of this thesis is to develop and optimize blue-light-induced RAFT polymerization as a versatile and sustainable technique for synthesizing functional homopolymers and, subsequently, tailored block copolymers for the fabrication of advanced isoporous membranes. These membranes are intended to enable specific separation functions, particularly size- and charge-selectivity, for potential advanced separation tasks.

This thesis focuses on four key aspects, as illustrated in Figure 29. It addresses the scalable and environmentally friendly synthesis of homopolymers and diblock copolymers, along with the fabrication, modification, and testing of diblock copolymer membranes and their blend membranes. These topics will be discussed in detail in the following:



Figure 29. Subject areas of the doctoral thesis: Publication 1 focuses on the scalable synthesis of macroCTAs, which serve as precursors for the diblock copolymer synthesis discussed in publication 2.

Publication 3 addresses the development of isoporous PDMA-*b*-PS membranes, their post-functionalization into PAA-*b*-PS membranes, and their application for the separation of small proteins. The fourth part examines the characterization of PDMA-*b*-PS/ P4VP-*b*-PS blends and the development of multifunctional membranes.

Part 1: Light-induced RAFT polymerization for the synthesis of macromolecular chain transfer agents (macroCTAs)

The first part of this work (chapter 5.1) focuses on developing a scalable and environmentally friendly synthesis approach for fabricating homopolymers with diverse functional groups. This research aims to serve as a guide for chemists in RAFT community by providing insights into the optimization and limitations of photoiniferter visible-light-induced RAFT polymerization. It examines monomers with propagation rates ranging from high to low, highlighting the potential of visible light as an initiation source for RAFT polymerization. Additionally, the study evaluates the impact of visible light on synthesizing homopolymers across various laboratory scales, emphasizing its utility for sustainable and scalable polymer production.

Part 2: Light-induced RAFT *ab initio* emulsion polymerization for the synthesis of diblock copolymers

Building on the successful synthesis of homopolymers in different scales using visible light, the second part (chapter 5.2) explores the application of these polymers as macromolecular chain transfer agents for the synthesis of diblock copolymers. This approach employs polymerization-induced self-assembly to enhance the polymerization rate for monomers with slow propagation rates, such as styrene. This *ab initio* emulsion polymerization uses visible light as the initiation source. Despite challenges associated with light penetration in turbid media, this research demonstrates that, with optimized synthesis parameters, the method can be both efficient and scalable in different laboratory scales. Beyond scalability, the study focuses on characterizing the resulting latex particles and evaluating the potential of a semi-batch process to further simplify the synthesis.

Part 3: PDMA-*b*-PS diblock copolymer membranes – post-modification and application for protein separation

This section (chapter 5.3) shifts the focus from polymer synthesis to practical application, highlighting the utility of diblock copolymers in membrane technology. Poly(*N,N*-dimethylacrylamide)-*block*-polystyrene (PDMA-*b*-PS) diblock copolymers were selected for the larger-scale fabrication of isoporous membranes due to their favorable properties. This section provides a comprehensive guide to membrane development, including the fabrication process using the SNIPS method, post-modification strategies to develop pH-responsive, negatively charged poly(acrylic acid)-*block*-polystyrene (PAA-*b*-PS) diblock copolymer membranes with size and charge selectivity, and application testing with model protein substances.

Part 4: PDMA-*b*-PS/ P4VP-*b*-PS blends as candidates for multifunctional membranes

The final part of this thesis (chapter 6) explores the fabrication of multifunctional membranes *via* diblock copolymer blending. The study integrates the diblock copolymers PDMA-*b*-PS and P4VP-*b*-PS, discussed in earlier sections, into polymer blends. Initially, classical characterization methods are employed to analyze the behavior of the two polymers within the blend, providing the foundation for optimizing the resulting membranes.

To develop multifunctional membranes featuring oppositely charged channels, the SNIPS method is applied, and the post-modification techniques developed in part 3 are extended. The PDMA segments are modified to introduce negative charges, while an additional post-modification strategy is applied to the P4VP blocks to introduce positive charges. This chapter highlights the innovative possibilities of diblock copolymer blends to engineer membranes with tailored properties.

5 Cumulative Part

This chapter contains reprints of the three first-author articles that have been published as part of this thesis. Each section includes a synopsis and the full text of the corresponding publication.

5.1 Publication 1

The first publication arising from this work focuses on establishing a universal and scalable tool for synthesizing polymers from various monomer classes. For this purpose, RAFT polymerization was utilized to produce homopolymers from monomers with different functionalities. Specifically, four monomers representing three different monomer classes were selected: an acrylamide (*N,N*-dimethylacrylamide), an acrylate (2-dimethylaminoethyl acrylate), and two vinylpyridines (2- and 4-vinylpyridine). Typically, each of these monomers requires distinctly different polymerization conditions.

This work introduces the use of blue light as the initiation source for the photoiniferter RAFT synthesis of macroCTAs. A key advantage of this approach is the decoupling of radical generation rate from polymerization temperature, significantly reducing thermal energy consumption compared to conventional thermal initiators — a benefit that is particularly relevant for monomers with high propagation rates.

Another important advancement is the use of a water–ethanol mixture (50:50 w/w) as the polymerization medium, providing a more environmentally friendly alternative to traditional solvents used in polymerizations. This is especially significant for vinylpyridines, which are conventionally polymerized in bulk^{332–335} or in petroleum-based organic solvents.^{335–338} Furthermore, the study demonstrates the scalability of the blue-light-induced approach, successfully scaling up the polymerization to a 500 mL scale, yielding approximately 90 g polymer.

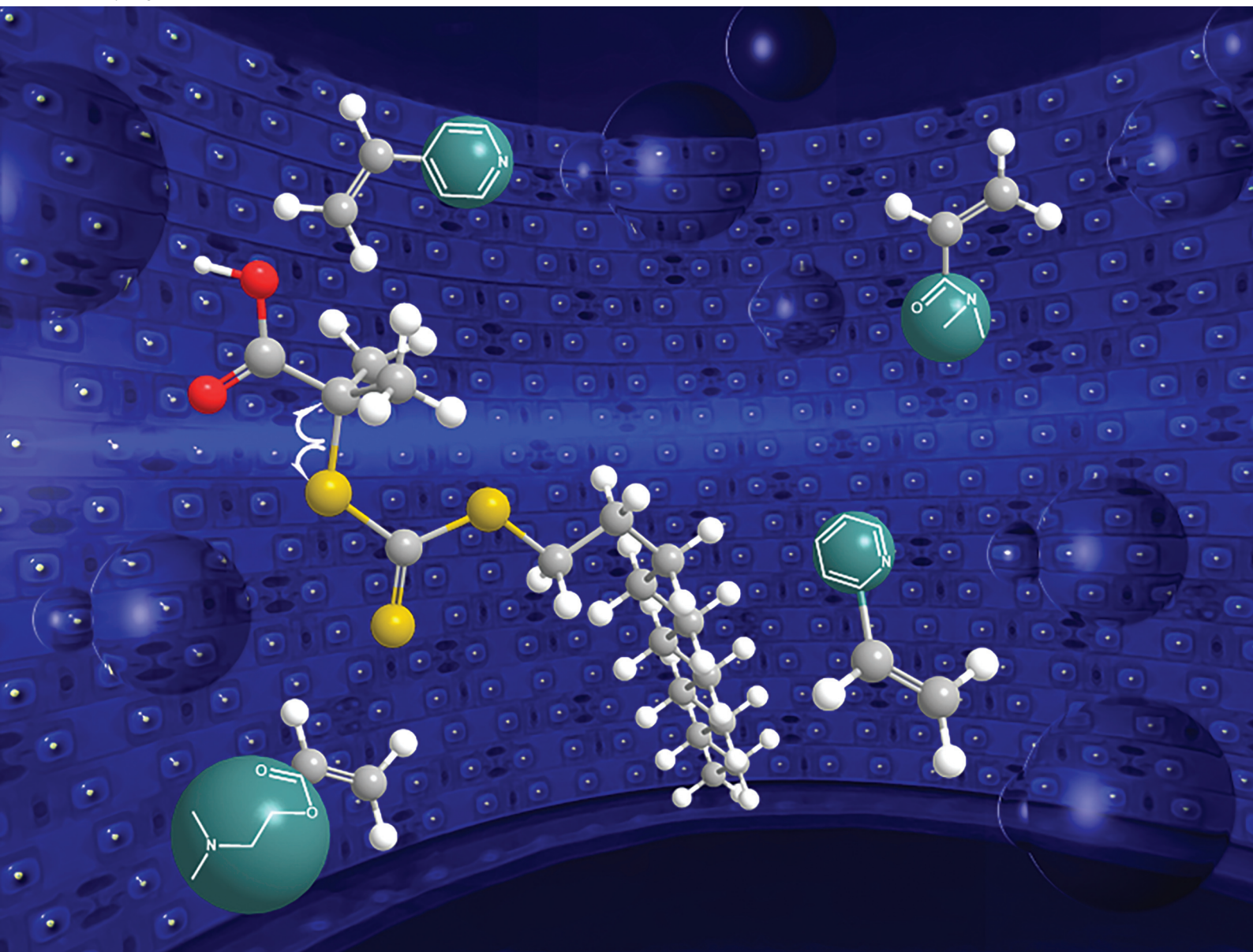
Overall, these findings underscore the potential of this visible-light-induced photoiniferter RAFT polymerization as a practical method for scalable polymer production and highlight the promise of water-ethanol mixture as an eco-friendly solvent for the polymerization of different monomers.

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Blue light-induced iniferter RAFT polymerization in
aqueous-alcoholic media as a universal tool for the
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investigations on different scales



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Blue light-induced iniferter RAFT polymerization in aqueous-alcoholic media as a universal tool for the homopolymerization of various monomer families: kinetic investigations on different scales†

Lara Hub, ^{a,b} Joachim Koll, ^a Maryam Radjabian ^{*a} and Volker Abetz ^{*a,b}

Photo-iniferter RAFT polymerization offers an opportunity to synthesize polymers without the requirements of external initiators. Blue light-induced iniferter RAFT polymerization was performed in a water–ethanol mixture (50 : 50 w/w) as an environmentally friendly, facile and tunable method to prepare well-defined homopolymers of different monomer classes like poly(*N,N*-dimethylacrylamide) (PDMA), poly(2-dimethylamino ethylacrylate) (PDMAEA) and poly(vinylpyridines) (PVPs). Homopolymers were synthesized on different laboratory scales between 1 g and 75 g. The influence of light intensity and temperature on polymerizations on different scales was investigated. Polymerization conditions were optimized and narrow molecular weight-distributed PDMA ($\bar{D}$ = 1.08–1.30), PDMAEA ($\bar{D}$ = 1.21–1.42), P4VP ($\bar{D}$ = 1.07–1.31) and P2VP ($\bar{D}$ = 1.14–1.35) were synthesized on larger laboratory scales and in short polymerization times ($\leq$ 6 h). This study highlights the versatile usability and adaptability of visible light-induced RAFT polymerization for larger polymer production in a batch process.

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Introduction

The development of reversible-deactivation radical polymerization (RDRP) techniques (previously called controlled radical polymerizations (CRPs))^{1,2} like nitroxide-mediated polymerization (NMP),^{3–5} atom transfer radical polymerization (ATRP)^{6,7} and reversible addition–fragmentation chain transfer (RAFT) polymerization⁸ has revolutionized the field of radical polymerization. Since these techniques closely imitate the characteristics of living polymerization,⁹ they provide important improvements over the classical radical polymerization. Tailor-made polymers with predictable molecular weight, low dispersity ($\bar{D}$), high end-group fidelity and capacity for continued chain growth can be obtained. RAFT controls the polymerization of a broad range of functional monomers and is compatible with a wide range of solvents and reaction conditions and is therefore, up to now, the most versatile RDRP technique.¹⁰

Within the last few decades, new methods were established to externally regulate the RAFT polymerization. Apart from tra-

ditional thermal initiation, alternative initiation methods *via* external stimuli have attracted wide interest.¹¹ More recently, photo-induced RAFT polymerization has gained considerable attraction. Most of the criteria for an ideal system are met by photo-initiation since light is a cheap, environmentally friendly, easily and widely accessible, non-invasive source and has no release of volatile organic compounds (VOCs).^{11,12} Moreover, it provides spatiotemporal control and allows to adjust the radical concentration independent of the reaction temperature.¹³ This ability to conduct photo-initiated polymerization under mild reaction conditions makes it so distinctive.¹⁴ Nevertheless, especially for monomers with a small propagation rate constant (k_p) value, sufficient thermal energy must be provided for monomer propagation (according to Arrhenius equation) in order to carry out polymerization efficiently. The often-mentioned polymerization at room temperature is only suitable for fast propagating monomers, otherwise very long polymerization times are required and make the photopolymerization ineffective.

PhotoRAFT benefits from the versatility that the RAFT agent itself can be selectively photoactivated either *via* the usage of a photoredox catalyst such as a transition metal catalyst¹⁵ or an organic dye molecule¹⁶ (photo-induced electron/energy transfer (PET)-RAFT)^{17,18} or *via* the photo-iniferter process. The iniferter (initiator transfer agent-terminator)^{19,20} process is easy to handle since it does only require the chain transfer agent (CTA), monomer and solvent and not any exogenous radical

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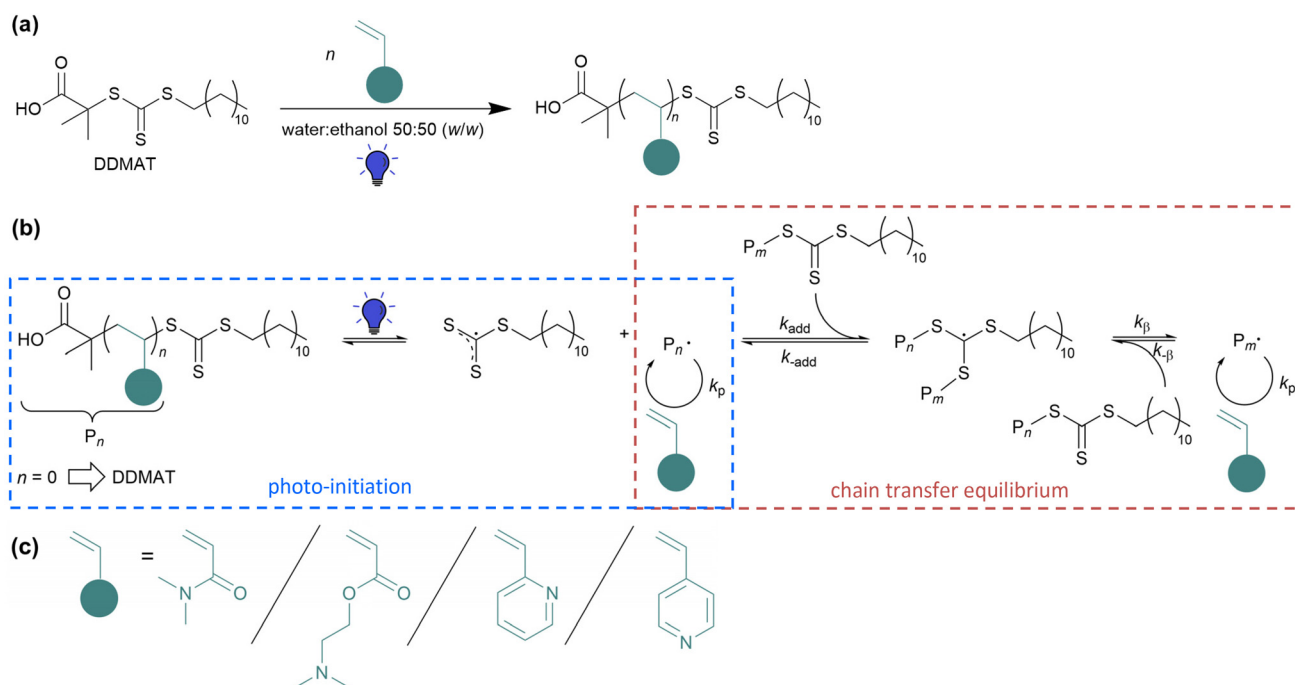
†Electronic supplementary information (ESI) available. See DOI: <https://doi.org/10.1039/d3py00241a>



source or photocatalyst radical (see Scheme 1(a)). By usage of thiocarbonylthio CTAs, initiation occurs *via* direct photoactivation of the CTA, generating a persistent thiocarbonylthio radical which acts as controlling agent and a transient radical which initiates the polymerization²¹ (see Scheme 1(b)), exemplary with 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid (DDMAT). For the light-initiation, an accurate selection of the light emitting source is important since the energy of the emitting photons is related to the wavelength and thus responsible for the electronic transition to higher energetic orbitals.²² However, the light intensity influences the amount of photons and therefore the radical concentration and the propagation rate.²³ The absorption of the thiocarbonylthio (TCT) group of RAFT agent is mainly located in the UV region. Due to the high energy of UV light, unfortunately side reactions like the decomposition of RAFT agent were observed leading to loose living behaviour of the RAFT polymerization.^{24,25} Therefore, to increase chain-end fidelity, the TCT group can be also activated by the second absorption band utilizing visible light sources.²⁶ The absorption band in the visible light region is much weaker and give the TCT RAFT agents the typical yellow colour (see Fig. S1†).²⁷ Herein, light-emitting diodes (LEDs) have been proven as efficient light sources for visible light-initiated RAFT polymerizations. They require low energy and operating costs and exhibit a longer lifetime compared to other light sources. On top, they emit nearly monochromatic light with less harmful UV rays and no IR radiation and therefore less heat is generated.^{12,13,24} First reports on visible

light-induced iniferter RAFT polymerization was conducted by the group of Boyer²⁸ and Qiao²⁶ in the mid 2010s for polymerization of methacrylate, diverse acrylates and *N*-isopropylacrylamide (NIPAM) utilizing a blue LED strip. Followed by blue light-induced iniferter polymerization of vinylacetate,²⁹ visible light-iniferter RAFT polymerization has shown to be an effective tool to synthesize diverse homopolymers. While several groups have already investigated the visible light-induced polymerization of (meth)acrylates and (meth)acrylamides, polymerization of vinylpyridines was rarely studied so far, especially the kinetics and optimization of the synthesis conditions of 2VP and 4VP *via* RAFT polymerization.³⁰ Nieswandt *et al.* synthesized diverse PVP homopolymers *via* traditional thermal RAFT polymerization in bulk.^{31,32} With visible light initiation, so far only Xin and co-workers described the blue light iniferter RAFT polymerization of 2VP and utilized high 2VP weight fractions in the solution and low degree of polymerization.²⁷

Besides blue light, photolysis of several RAFT agents can be as well initiated by green light and provides good control for the polymerization of methacrylates.³³ Recently, Xu and Abetz have shown that graft copolymers can be synthesized *via* the visible-light induced iniferter RAFT polymerization by selective excitation of different RAFT functionalities by green and blue light.^{34,35} Therefore, due to its advantages, visible light-induced iniferter RAFT polymerization has gained increasing interest for the synthesis of well-defined polymers. However, it has been remarked as a disadvantage of photo-initiation that



Scheme 1 (a) Synthetic route towards diverse macroCTAs *via* blue light-induced iniferter RAFT polymerization utilizing a home-made blue LED light source. (b) Mechanism of the blue light-induced RAFT polymerization with the RAFT agent DDMAT. Initiation occurs by the photo-induced cleavage of the C–S bond. The transient radical can propagate and take part in the chain transfer equilibrium. (c) Chemical structure of the monomers *N,N*-dimethylacrylamide (DMA), (2-dimethylamino ethyl)acrylate (DMAEA), 2-vinylpyridine (2VP) and 4-vinylpyridine (4VP).



an increased reactor dimension hinders the polymerization procedure in a scale-up in a batch process.^{36,37} Photo-induced polymerizations are significantly determined by other external factors such as light intensity and reactor dimensions and therefore it is important to study the influence of these parameters for the iniferter RAFT polymerization. Therefore, we investigate the influence of the batch reactor dimensions on a variety of homopolymerizations of fast and slowly propagating monomers.

Herein, we report an initiator- and catalyst-free blue light-induced iniferter RAFT polymerization of poly(*N,N*-dimethylacrylamide) (PDMA), poly(2-dimethylamino ethylacrylate) (PDMAEA), poly(2-vinylpyridine) (P2VP), and poly(4-vinylpyridine) (P4VP) homopolymers (see Scheme 1) in batches with dimensions between 10 mL and 500 mL reaction volume. A home-made blue LED is utilized to initiate the polymerization *via* direct activation of the TCT functionality. In order to make the polymerization procedure more sustainable, a water-ethanol mixture was used as solvent system, also for the rather nonpolar vinylpyridine monomers. This is an improvement towards the conventionally used petroleum-based solvents and demonstrates the versatility of the water-alcoholic mixture (50 : 50 *w/w*) for RAFT homopolymerizations. Synthesis conditions for each polymerization are kinetically investigated and optimized. The effect of dimensions of the glass vial towards the kinetics of the homopolymerization is studied showing the applicability of the batch process up to 500 mL reaction volume.

Experimental

Photoreactor setup

For the blue light-initiated RAFT polymerizations, a self-made cylindrical photoreactor was designed in which two LED strips (each with a length of 500.0 cm and 120 LEDs per m (Seki®)) were attached to the inner lower part of the aluminum cylinder (inner diameter: 18.0 cm, height: 25.0 cm, see Fig. S2†). The light intensity was adjusted by a MiLight® MiBoxer® RGB LED Controller regulated by a MiLight® remote control.

Materials

Ultrapure water (Milli-Q® quality, resistivity >18.2 MΩ cm⁻¹) was obtained from a Milli-Q® water purification system (Siemens Labostar). All other solvents including ethanol (≥99.9%, Merck), *N,N*-dimethylformamide (DMF) (≥99.8%, Merck), tetrahydrofuran (THF) (≥99.8%, Merck), cyclohexane (≥99.5%, Carl Roth) were used as received. Deuterium oxide (D₂O), deuterated methanol (MeOH-*d*₄) and chloroform (CDCl₃) were purchased from Deutero GmbH. As RAFT agent, 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid (DDMAT) (Sigma-Aldrich, stored at 4 °C) was used without further purification. 4-Vinylpyridine (4VP) (Thermo Scientific) was distilled prior polymerization to get de-inhibited and colorless monomer. *N,N*-dimethylacrylamide (DMA) (Sigma Aldrich), 2-dimethylamino ethylacrylate (DMAEA) (Sigma-Aldrich) and 2-vinylpyridine (2VP) (Thermo Scientific) were

de-inhibited over activated basic aluminum oxide (Carl Roth) prior to each polymerization.

Synthesis of PDMA macroCTA *via* blue light-induced iniferter RAFT solution polymerization

In a typical photo-iniferter RAFT polymerization of DMA with a molar ratio of [DMA]₀/[DDMAT]₀ = 500/1, DDMAT (15.0 mg, 41.1 μmol, 1.0 eq.) and DMA (2.12 mL, 20.6 mmol, 500 eq.) were dissolved in ethanol (5.21 mL). While stirring, water (4.11 mL) was added dropwise and *N,N*-dimethylformamide (20 μL) added as an internal reference for ¹H-NMR analysis and an initial sample was taken. The solution was degassed by purging the ice-cooled polymerization vial with argon for 10 min. The polymerization vessel was placed at the centre of the blue LED. Polymerization was carried out under blue light irradiation (λ_{max} = 451 nm) at a water bath temperature of 40 °C under constant stirring (400 rpm). After the desired time of exposure to the blue light, the polymerization was stopped by turning off the irradiation source, quenching in an ice-cooling bath and exposing to air. The solvent was removed by vacuum and the crude polymer was obtained by drying under vacuum at 40 °C for 24 h. Subsequently, the polymer was dissolved in THF, precipitated in cold cyclohexane, filtered and dried under vacuum at 40 °C for 48 h.

The blue light-induced iniferter polymerization of the other monomers is followed by the same protocol and can be found in the ESI.†

General protocol of polymerizations in 250 mL and 500 mL vessels. The molar ratio between the substances and the general protocol were left unchanged apart from the longer argon-purging period of 30 min.

Characterization

NMR spectroscopy. ¹H-NMR spectra were recorded at ambient temperature using a Bruker® AV500 spectrometer with 16 scans per spectrum and a delay of 3 s. The samples from the homopolymerization of DMA were measured in D₂O and of DMAEA, 2VP and 4VP in MeOH-*d*₄. The determination of the monomer conversion and the theoretical molecular weight $\bar{M}_{n,th}$ is explained in the ESI.† Analysis was performed with the program MestReNova® 14.2.

Size exclusion chromatography (SEC). Size exclusion chromatography (SEC) experiments were conducted at 50 °C using dimethylacetamide (DMAc) as solvent with LiCl (0.1 M). Samples were measured at a flow rate of 1.0 mL min⁻¹ using a Hitachi® L2130 pump. A PSS® GRAM pre-column (dimension 8 × 50 mm) and two PSS® GRAM columns (8 × 300 mm, particle size 10 μm) with a porosity of 3000 Å and 1000 Å, respectively, were used. The analysis was conducted with the signal recorded by a Hitachi® L2490 RI refractive index detector as a function of time. The instrumentation was calibrated with the use of polystyrene standards and the data were analyzed using the software PSS® Win GPC UniChrom V8.10.

Light intensity measurement. The light intensity of the blue LED was determined with an Ocean Insight® FLAME-T-UV-VIS spectrometer with QP400-2-SR-BX optical fiber and cosine cor-



rector. The sensor was placed at different positions within the cylinder and the height was varied in 2 cm steps. The light intensity was measured upwards and downwards and was afterwards summed to determine a more precise light intensity. The denoted light intensity is referred to the averaged light intensity at the different high positions.

UV-Vis Spectroscopy. UV-Vis-spectra were recorded using a Cary® 5000 UV-VIS-NIR or a Shimadzu® UVmini-1240 spectrophotometer. Ethanol served as solvent to dilute the RAFT agent.

Results and discussion

Herein, blue light-induced iniferter RAFT solution polymerization of DMA, DMAEA and vinylpyridines using DDMAT as RAFT agent are presented. DDMAT was used as an universal RAFT agent showing good control of the polymerization of more activated monomers (MAMs) like acrylates, acrylamides and aromatic vinyl monomers.^{38–41} The DDMAT RAFT agent absorbs in the UV region (265 nm–365 nm) due to the spin allowed $\pi \rightarrow \pi^*$ electronic transition of the thiocarbonyl group and the absorption in the visible light region (385 nm–545 nm) is caused by the spin forbidden $n \rightarrow \pi^*$ electronic transition (see Fig. S1†). Photo-iniferter RAFT polymerizations were conducted by activating the thiocarbonyl adsorption band of DDMAT in the visible light region by blue light irradiation. For this purpose, a home-made photo reactor was installed. The aluminum basis provides high thermal conductivity to avoid possible overheating of the LEDs. A cylindrical geometry was chosen to achieve an optimal three-dimensional illumination of the polymerization solution. The design is particularly cost-effective, and the light intensity is homogeneous throughout the entire height irradiation area (see Fig. S3†). Additionally, the installed controller allows adjustment of light intensities by switching the voltage of the LED stripes (see Fig. 1(a), exemplary for a position in the center and at a height of 6 cm). The voltage can be tuned in different steps from 13.2 V–23.9 V. The specified light intensity values refer to the averaged values over a height range up to 15 cm. By varying the voltage of the blue LED, same peak emission profiles are observed. The home-made LED device emits light at $\lambda_{\text{max}} = 451$ nm and therefore very close to the absorption maximum of the RAFT agent in the visible light region (see Fig. 1(b)), preserving optimal efficient light initiation conditions. Since photoRAFT polymerizations were performed with different vessel sizes, the distribution of the light intensity within the blue LED was determined. Fig. 1(c) shows the light intensity distribution of the blue light at $\lambda_{\text{max}} = 451$ nm in the relevant area of the photoreactor; the distance of 9 cm constitutes the centre of the photoreactor. Depending on the distance to the LED stripes, height-averaged light intensities between 46 mW cm^{-2} and 55 mW cm^{-2} are preserved by applying a voltage of 19.7 V at the blue LED. The light intensity given in the further course refers to the intensity at the edge of the surface of the vessel. For the polymerizations, an environmentally friendly ethanol-water mixed solvent was used. Ethanol serves as a

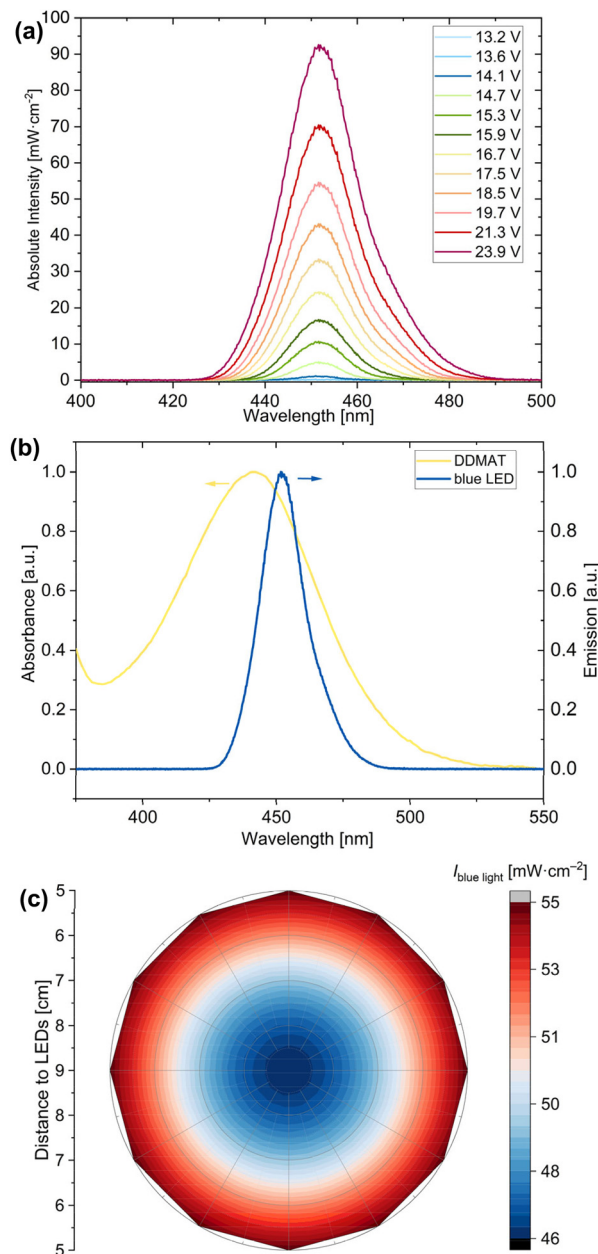


Fig. 1 (a) Light intensity spectrum of the blue LED at a height of 6 cm in dependence of the applied voltage. The maximum emission wavelength is at $\lambda_{\text{max}} = 451$ nm. (b) Comparison of the absorption of the RAFT agent DDMAT (in ethanol) in the visible light range due to the spin forbidden $n \rightarrow \pi^*$ electronic transition of the thiocarbonyl functionality and the emission spectrum of the blue LED. (c) Light intensity distribution of blue light at $\lambda_{\text{max}} = 451$ nm within the blue LED at an applied voltage of 19.7 V. For this purpose, the light intensities were measured up to the height of 15 cm and averaged in each radial position. The centre of the photoreactor is at a distance of 9 cm towards the LED stripes.

cosolvent, is safe and categorized as a recommended solvent in terms of solvent selection.^{42,43} Due to the good solubility of DDMAT, monomers (DMA, DMAEA and the vinylpyridine isomers), as well as resulting homopolymers, all the polymerizations were conducted in a solvent mixture of water-ethanol



(50 : 50, *w/w*). In the following, sample codes are used (e.g., PDMA^z), in which superscripts signify the overall theoretical number average molecular weight (in kDa).

Synthesis of PDMA via blue-light induced iniferter RAFT solution polymerization

Most literature reports the synthesis of PDMA by thermally initiated RAFT polymerization in petroleum based solvents like dioxane,^{44–48} DMAc⁴⁹ or DMF^{50,51} at temperatures ranging from 60 °C–80 °C. The polymerizations of DMA can be conducted in pure water with a water-soluble RAFT agent, however DDMAT is not soluble in water and thus ethanol as a cosolvent is required. Preliminary solubility tests of the RAFT agent in water–ethanol mixtures showed a good solubility of DDMAT in the (50 : 50 *w/w*) mixture. In the systems with higher water content the RAFT agent precipitates.

Herein, the light intensities have been varied to establish the blue light initiated RAFT solution polymerization in the water–ethanol mixture (50 : 50, *w/w*) towards well-defined PDMA macroCTAs without any further catalysts or initiators. The rate of cleavage of sulphur-carbon bonds is light intensity dependent. Therefore, it is expected that the radical concentration increases by applying a higher light intensity of the blue LED. Fig. 2(a) shows the illumination time-dependent conversion of DMA with $[DMA]_0/[DDMAT]_0 = 500$ by varying the light intensity of the blue LED. As expected, the conversion increases by increasing the light intensity. Interestingly, the polymerization conducted at 16 mW cm^{−2} shows a short inhibition time (<30 min) and afterwards, the conversion follows a linear slope by time. Under these conditions, the light intensity is the polymerization-rate determining factor. By increasing the light intensity further to 30 mW cm^{−2} and 49 mW cm^{−2}, high conversions within short polymerization times are reached and no inhibition period is observed. Within the first 2 h – probably even longer – these polymerizations follow pseudo-first-order kinetics (see Fig. 2(b)), indicating a constant concentration of propagating radical species during the polymerization. Noticeably, a sharp increase in conversion is recognized when the light intensity is increased from 16 mW cm^{−2} to 30 mW cm^{−2}. A further increase to 49 mW cm^{−2} slightly influences the conversion. Therefore, it is confirmed that by increasing light intensity of the blue LED a faster reaction is observed. This can be explained by the higher radical concentration obtained by increased light intensity. Apparent propagation rate constants $k_{p,app}$ are determined from the slope of the first order plot in Fig. 2(b) and are calculated to be 0.19 h^{−1}, 0.55 h^{−1} and 0.70 h^{−1}, respectively, and are therefore directly proportional to the light intensity (see Fig. 2(c)). However, in the photo-iniferter RAFT, the light intensity dependence of the apparent rate coefficient differs from that observed in the PET RAFT polymerization with the photocatalyst Ir(ppy)₃ due to the square root dependence of the apparent rate coefficient for the photocatalyst excitation process k_{EX} .⁵²

A linear increase of apparent molecular weight $\bar{M}_{n,app}$ with conversion is observed (see Fig. 2(d)). The discrepancy of different evolution of $\bar{M}_{n,app}$ and $\bar{M}_{n,th}$ is caused by the

different hydrodynamic radii of PDMA and PS standards in DMAc. Dispersities remain low over the complete polymerization (≤ 1.25) and show to be unaffected by the monomer conversion. Furthermore, no influence of light intensity on the dispersity of the PDMA homopolymers can be detected (see Table S1†).

In order to proof the temporal control over the polymerization of DMA, the blue light was periodically switched on and off in 30 min intervals (see Fig. 2(e)). When the light was switched on, polymerization occurred. By switching off the blue light, conversion was almost stopped; however, the pre-formed radicals can slightly react with the present monomers. This experiment confirms that the polymerization occurs only under visible light irradiation and shows the temporal control within this process.

With the aim to perform polymerization on different laboratory scales, 4 different vessels were used to perform the polymerization. In addition to the aforementioned polymerization scale of 20 mL, vessels with 40 mL, 250 mL and 500 mL volume were used. Synthesis of PDMA macroRAFT agent in larger vessels were performed under the same aforementioned conditions ($[DMA]_0/[DDMAT]_0 = 500$, 40 °C, voltage blue LED = 19.7 V). The 20 mL and 40 mL vessels have the same diameter of 2.5 cm. The 250 mL vessel possess a diameter of 6.0 cm and vessel with a volume of 500 mL has a diameter of 7.5 cm. Due to these different dimensions, the kinetics of this polymerization process change. The enlargement of the scale changes the distance to the LED strips and, as shown in Fig. 1(c), the light intensity is slightly altered. Adjusted by a voltage of 19.7 V, light intensity at the surface of each vessel is changed from 49 mW cm^{−2} (20 mL and 40 mL vials) to 52 mW cm^{−2} (250 mL vessel) to 55 mW cm^{−2} (500 mL vessel). Despite the slight increase in light intensity due to the increasing radius of the vessel, the final conversion of the polymerization in the 250 mL vessel decreased by 6% and in the 500 mL vessel decreased by 12% compared to the polymerization in 20 mL vessel (see Fig. 3(a)). However, polymerizations conducted in the vessels with 20 mL and 40 mL volume showed similar conversions. The penetrated light and therefore the radical concentration is determined by the exposed shell surface area $2\pi rh$ of a cylindrical vessel with r as the radius and h as the height. Since a similar intensity distribution in the photo-reactor regardless of the height is dictated (see Fig. S3†), a similar number of photons per area penetrate the solution in all areas of the glass surface. According to our observations, the light intensity and thus the generation of radicals is significantly related to the radius of the vessels. Attributed to Beer-Lambert law $A = \log(I_0/I) = \epsilon cl$ in which A is the absorbance, I_0 is the incoming and I the transmitted intensity, ϵ the molar extinction coefficient, c the molar concentration and l is the path length, in our case the absorption depends proportionally on the path length (all other factors remain constant). Since we have a three-dimensional symmetrical set-up, the path length corresponds to the radius of the vessel. Due to this, the polymerizations in the 20 mL and 40 mL vessels show the same kinetics. A similar observation was made for the PET



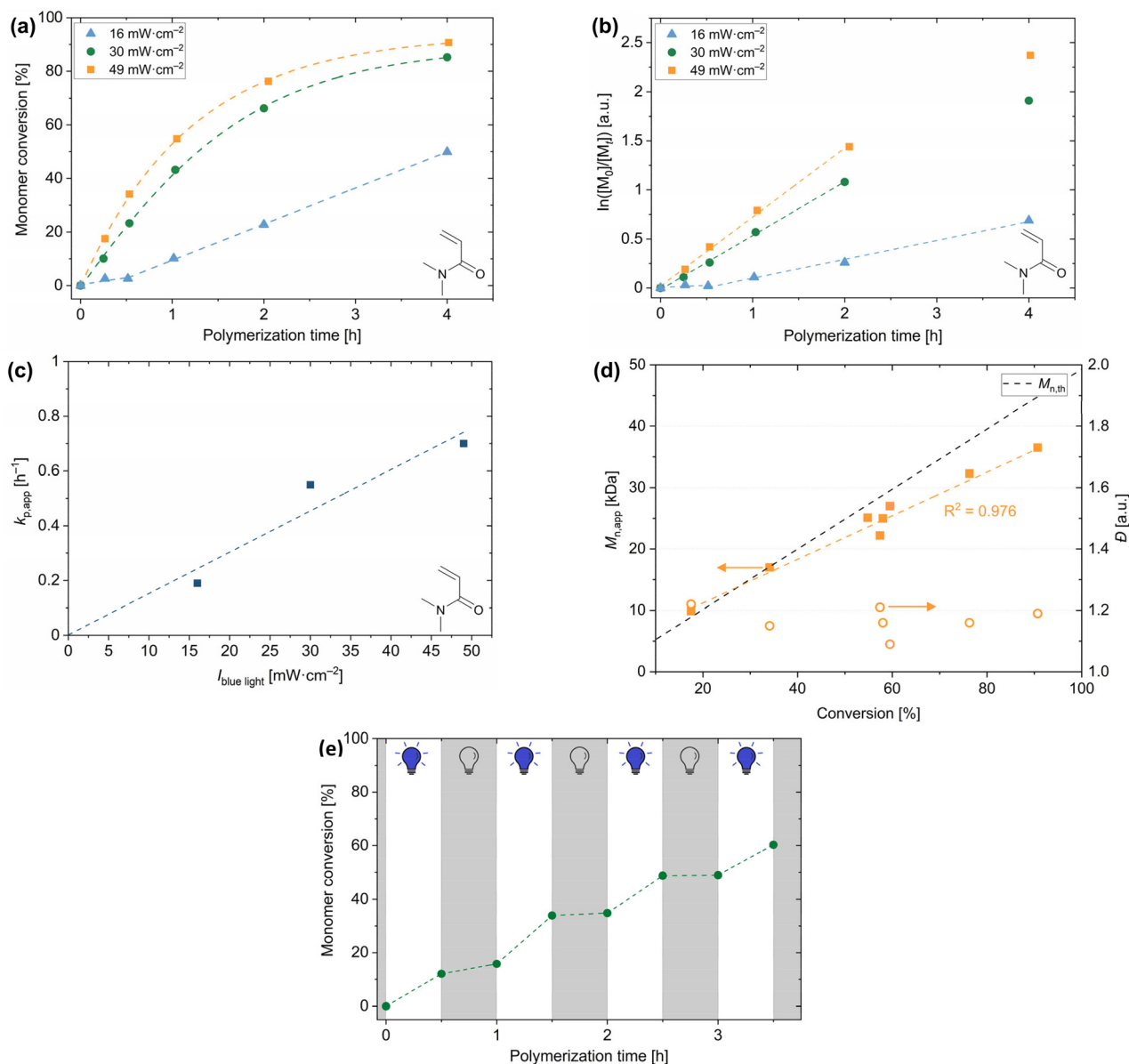


Fig. 2 (a) Monomer conversion and (b) pseudo first-order kinetic plots of blue light-initiated RAFT solution polymerization of DMA ($[DMA]_0/[DDMAT]_0 = 500$) in the water–ethanol mixture (50 : 50 w/w) (20% w/w) at 40 °C with different light intensities (referred to $\lambda_{max} = 451$ nm). (c) Linear dependence of the apparent propagation constant $k_{p,app}$ of the light intensity. (d) Evolution of $\bar{M}_{n,app}$ (solid squares) and dispersity (hollow points) with conversion of the blue-light initiated homopolymerization of DMA synthesized in the 20 mL vessels at 49 mW cm⁻² ($\bar{M}_{n,app}$ and $\bar{D}$ were determined by analysis of SEC curves, eluent: DMAc, poly(styrene) calibration). (e) “On–off” kinetic plot of the blue light-induced DMA homopolymerization at 30 mW cm⁻².

RAFT polymerization of methyl acrylate with PADTC RAFT agent and the photocatalyst Ir(ppy)₃.⁵² By changing the reaction volume but keeping the diameter constant, similar reaction rates were observed. Calculations of the apparent propagation constants show that this constant decreases linearly with increasing vessel radius from 0.70 h⁻¹ (20 mL vessel) to 0.57 h⁻¹ (250 mL vessel) to 0.49 h⁻¹ (500 mL vessel) as shown in Fig. 3(b), regardless of the slight change in light intensity on the surface. Despite the reduction of the conversion by vessel radius, the homopolymerization of DMA in all reaction volumes proceeds in a fast manner without any inhibition

period. Even in the 500 mL vessels, polymers with low dispersity are obtained (see Fig. 3(c)). This shows the adaptability of the blue light-induced iniferter RAFT polymerization even for a larger production of PDMA homopolymers on the laboratory scale up to a yield of about 75 g polymer.

Synthesis of PDMAEA via blue-light induced iniferter RAFT solution polymerization

In order to investigate the efficiency of this synthesis procedure to acrylates, thermo and pH dual-responsive poly(2-(dimethylamino) ethyl acrylate) (PDMAEA) was synthesized. The



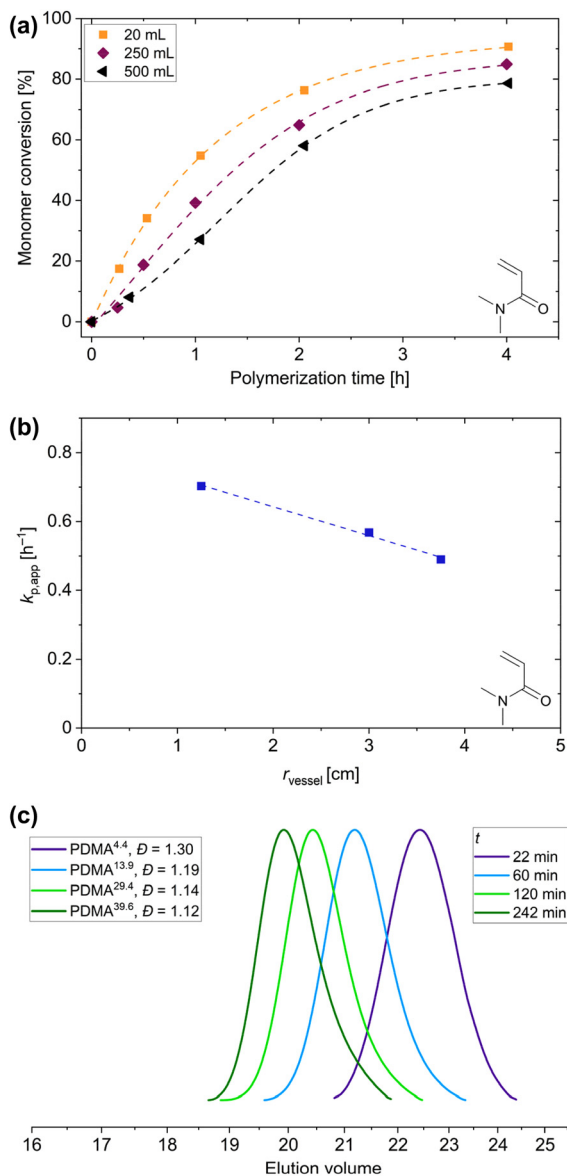


Fig. 3 (a) DMA conversion *via* blue light initiation at 19.7 V in dependence of the vessel size. (b) Dependence of the apparent propagation constant $k_{p,app}$ of the vessel radius. (c) SEC traces of the polymerization of DMA on 500 mL scale at a light intensity of 55 mW cm⁻².

polymerization conditions were adapted from the optimized conditions for DMA. Fig. 4(a) displays the conversion of the blue light-induced polymerization of DMAEA with $[DMAEA]_0/[DDMAT]_0 = 500$ in water-ethanol mixtures (50 : 50, w/w) at 40 °C and an adapted voltage of 19.7 V at the blue LED. Conversion in the small 20 mL vials decreased by almost 30% compared to DMA; the difference in conversion on a larger scale decreased by the same order of magnitude. Apparent propagation rate constants $k_{p,app}$ are determined to be 0.34 h⁻¹ for the DMAEA polymerization in the 20 mL vessel and 0.26 h⁻¹ for the polymerization in the 250 mL vessel. It indicates that DMAEA is slower in propagation than DMA in this photo-iniferter RAFT process. The same observation was made

in the PET-RAFT polymerization by green light irradiation of these two monomers.⁵³ As observed for the polymerization of DMA, light-induced polymerization of DMAEA also proceeds in a first order fashion up to 2 h polymerization time (see Fig. 4(b)).

Synthesis of PVP *via* blue light-induced iniferter RAFT solution polymerization

Compared to the pre-discussed DMA and DMAEA, the vinylpyridine isomers are more slowly propagating in a RAFT process due to the mesomeric stabilization of the formed radicals. Therefore, the synthesis becomes more challenging. Herein, 4-vinylpyridine and 2-vinylpyridine were polymerized in the water-ethanol mixture (50 : 50, w/w) *via* blue light-induced iniferter solution polymerization. To the best of our knowledge, this is the first time to synthesize such VP polymers *via* RAFT in aqueous media under neutral pH conditions.

In order to study the influence of several reaction parameters on the kinetics, photo-iniferter RAFT polymerization of 4VP was systematically investigated with $[4VP]_0/[DDMAT]_0 = 470$. Fig. 5(a) shows the illumination time-dependent conversion of 4VP conducted with different monomer contents at a polymerization temperature of 40 °C. Whereas for the DMA and DMAEA polymerizations no induction period was observed under these synthesis conditions, an inhibition period is observed for the synthesis of 4VP in the small 40 mL polymerization vessel (<30 min) as well as in the 250 mL vessel (<1 h). The pre-equilibrium time frame is extended for the 4-vinylpyridine polymerization probably due to the smaller addition rate coefficient of the monomer to the RAFT agent (see Scheme 1(b)).⁵⁴ This leads to a longer reinitiation time and a slow transition from the pre- to the main equilibrium of the RAFT process and a retardation of the polymerization.

Compared to the above-mentioned monomers, the conversion of 4VP is significantly reduced. At comparable conditions in the small vessels with 20% (w/w) and 4 h polymerization time at 49 mW cm⁻², a conversion of 41% was reached, which is 50% less than for DMA and 21% less than for DMAEA. Apparent propagation constants $k_{p,app}$ are determined to be 0.15 h⁻¹ for the polymerization in the vessel with 40 mL volume and 0.08 h⁻¹ for the polymerization in the 250 mL vessel. Thus, compared to DMA, these values are lower by a factor of 4.7 for the small vessels and by a factor of 7.1 for the reaction in 250 mL vessel. Consequently, synthesis conditions were changed to generate a more effective polymerization. The influence of different key parameters such as temperature, light intensity and monomer concentration were systematically investigated. Due to the photo-iniferter mechanism, the initiation step is independent of temperature. Thus, increasing the reaction temperature assists the monomer addition but might lead to a higher termination rate. Moderately increasing the water bath temperature from 40 °C to 50 °C leads to an increase in conversion of more than 10% after 4 h polymerization time (see Table S8†). It indicates that for the monomer addition of 4-vinylpyridine a higher activation energy barrier must be overcome compared to DMA, although both mono-



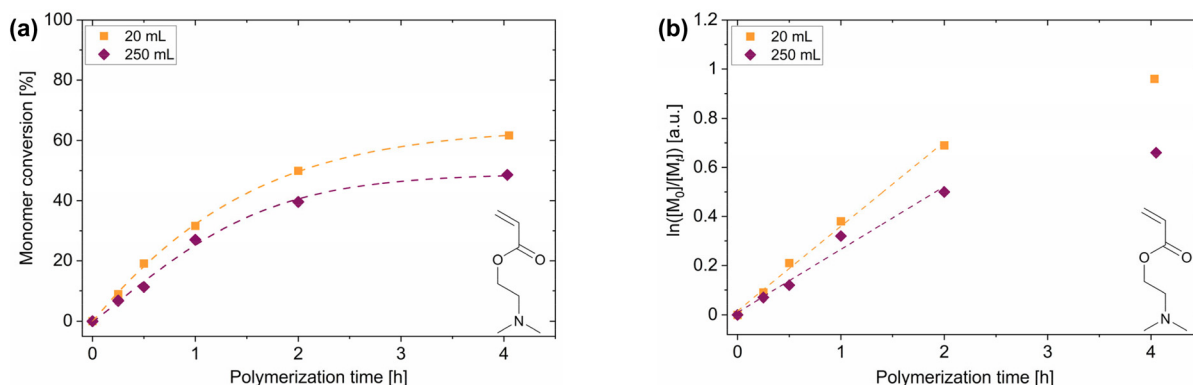


Fig. 4 (a) DMAEA conversion and (b) pseudo first-order kinetic plots of blue light-initiated iniferter RAFT solution polymerization of DMAEA ($[\text{DMAEA}]_0/[\text{DDMAT}]_0 = 500$) in water–ethanol mixtures (50 : 50 w/w) (20% w/w) at 40 °C and an adapted voltage of 19.7 V at the blue LED.

mers are considered as more activated monomers (MAMs).⁹ A higher intensity leads to more frequent fragmentation and therefore to a higher radical concentration. By increasing the light intensity from 52 mW cm⁻² to 86 mW cm⁻², conversion was enhanced by only 5% after 4 h polymerization time (see Table S12†). This shows that the increase in light intensity has little effect on conversion and radical generation is already very effective at 52 mW cm⁻². In order to investigate the influence of monomer concentration on conversion, concentration was increased to 30 (w/w) ($[\text{4VP}]_0/[\text{DDMAT}]_0 = 470$, see Fig. 5(a)). Conversion could be enhanced by 7% after a polymerization time of 4 h compared to the one with 20% (w/w). The solution viscosity was still low enough to guarantee a uniform mixture during the whole polymerization process. No influence of the monomer concentration on the dispersity of the P4VP macroCTAs was observed, neither for the polymers synthesized in the small vessels, nor in the 250 mL vessels (see Tables S8, 9, S11 and 12†). Therefore, executing the polymerization at 30% (w/w) is more attractive compared to 20% (w/w). The polymerization conditions can be adjusted to mitigate the decrease in 4VP conversion.

It has been shown that degradation of the thiocarbonyl functionality by time leads to the formation of dead polymer chains.²⁷ Therefore, in order to ensure high livingness of the P4VP homopolymers, the polymerization was stopped after 6 h. During this time, pseudo first-order kinetic plots show linear slope (see Fig. 5(b)).

By changing a reaction vessel from 40 mL to 250 mL and adapting the same voltage of 19.7 V, conversion decreased more distinctly compared to the previously mentioned monomers (around 25% after 6 h polymerization time at 30% (w/w), see Fig. 5(a)). The apparent propagation rate constant $k_{p,\text{app}}$ is reduced from 0.190 h⁻¹ to 0.109 h⁻¹ by choosing the larger scale. For 4VP as a monomer with a small propagation constant, conversion is strongly effected by scale enlargement. By choosing a light intensity of 86 mW cm⁻² instead of 52 mW cm⁻², conversion increases by 6% after 6 h (see Table S12†). Another way to compensate the conversion decrease is to choose a higher temperature (see Table S12†).

In order to demonstrate the applicability of the light-induced iniferter polymerization to synthesize higher molecular weight polymers, 4VP was synthesized with a molar ratio of $[\text{4VP}]_0/[\text{DDMAT}]_0 = 760$ at 40 °C in a 250 mL vessel (see Table S13†). A P4VP^{42,2} was synthesized with a low dispersity of 1.22. It indicates that the synthesis method is also suitable for higher $[\text{4VP}]_0/[\text{DDMAT}]_0$ ratios and the polymerization is still well controlled, although the DDMAT concentration is significantly decreased.

The effect of temperature on the kinetics of the blue light-induced polymerization of 2VP is even more significant than for 4VP and therefore studied here in detail. Fig. 5(c) illustrates the systematical investigation of the influence of temperature on the conversion of reaction in the small vessel (40 mL) in the temperature range between 40 °C and 70 °C. The position of the pyridinyl nitrogen atom in 2VP and 4VP dramatically influences the propagation rate in RAFT polymerization and therefore the course of the polymerization. When comparing the two polymerizations of 4VP and 2VP at 40 °C and 30% (w/w), an inhibition time prolonged by about 15 min is observed for the photoRAFT polymerization of 2VP. This is probably due to the smaller addition rate constant of 2VP compared to 4VP to the RAFT agent DDMAT. As well, only 35% 2VP conversion was reached after a polymerization of 6 h, whereas under similar reaction conditions a 4VP conversion of 65% was determined. This proves that even more thermal energy is required to promote the light-induced RAFT of polymerization of 2VP compared to 4VP for achieving comparable conversions. By increasing the reaction temperature from 40 °C to 70 °C, the conversion can increase by 23% to 58% after 6 h exposure to the blue light. Due to the temperature increase, apparent propagation rate constants $k_{p,\text{app}}$ enhance from 0.085 h⁻¹ to 0.155 h⁻¹. Thus, the synthesis can be carried out efficiently at low polymerization time. This increase in the propagation constant can be explained by the fact that propagation is driven by thermal energy. At higher temperature, more thermal energy is available and thus more reactive species are above the activation energy level for the monomer addition. Thus, more collisions of the radical of the growing chain with monomer units



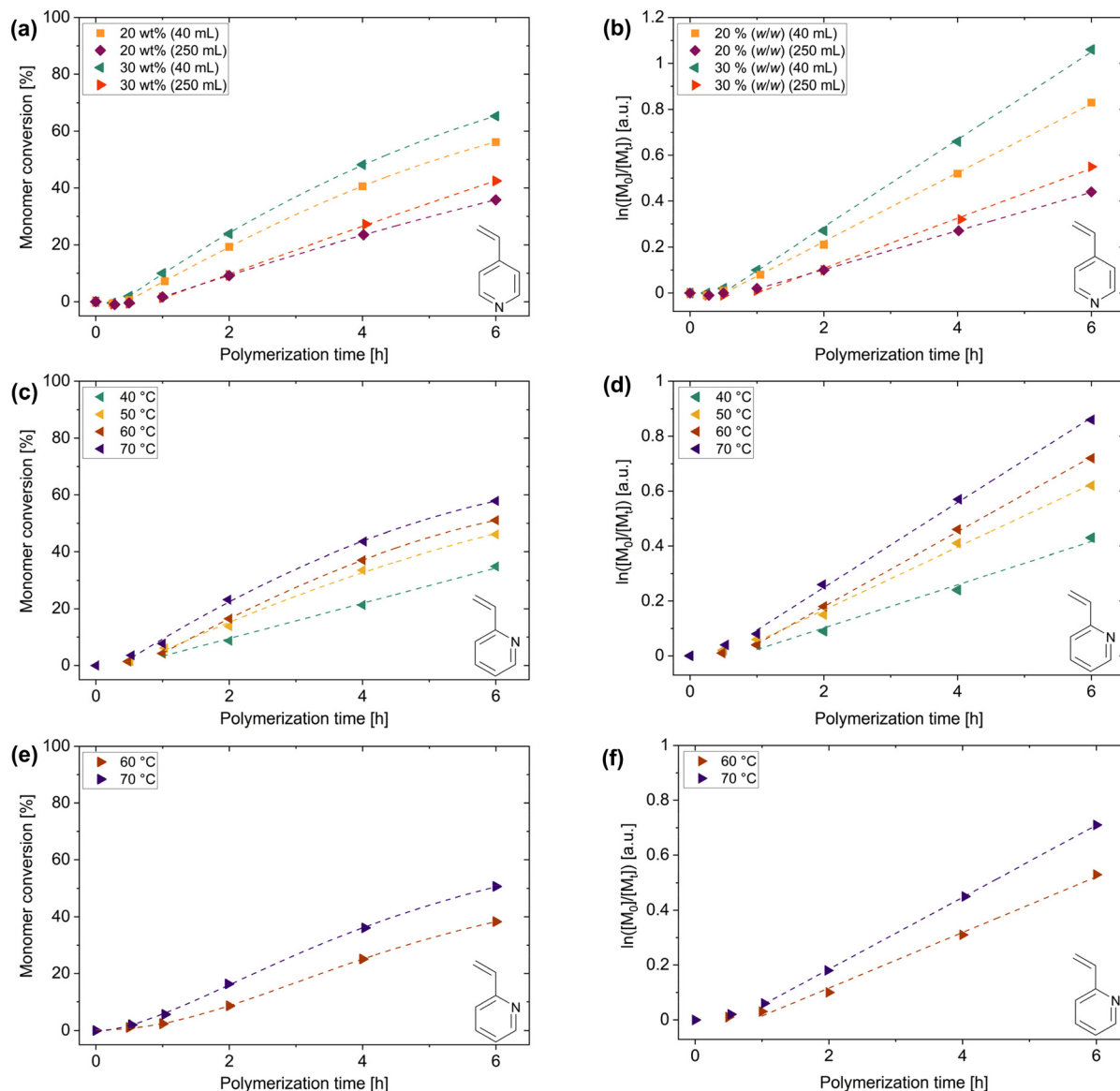


Fig. 5 (a) Monomer conversion and (b) pseudo first-order kinetic plots of blue light-initiated iniferter RAFT solution polymerization of 4VP ($[4VP]_0/[DDMAT]_0 = 470$, 40 °C, 19.7 V). (c) Monomer conversion and (d) pseudo first-order kinetic plots of blue light-initiated RAFT solution polymerization of 2VP on 40 mL scale at temperatures of 40 °C – 70 °C ($[2VP]_0/[DDMAT]_0 = 470$, 19.7 V). (e) Monomer conversion and (f) pseudo first-order kinetic plots of blue light-initiated RAFT solution polymerization of 2VP on 250 mL scale at temperatures of 60 °C and 70 °C ($[2VP]_0/[DDMAT]_0 = 470$, 19.7 V).

lead to chain extension. Pseudo first-order kinetic plots show linear behavior from 2 h (40 °C) or 1 h (50 °C–70 °C) (see Fig. 5(d)), indicating a constant radical concentration. Dispersities of P2VP macroCTAs remain low independent of polymerization temperature ($D = 1.09$ – 1.36 , see Table S14[†]).

From an energy point of view, a temperature increase towards 70 °C is reasonable, as this can significantly shorten the polymerization time. This is particularly important for larger scale applications since previous experiments showed that longer polymerization times are required in order to receive comparable conversions. As already observed for the photo-iniferter RAFT polymerization of 2VP in the small

vessels, a temperature of 40 °C compared to 70 °C is associated with a doubling of the reaction time to reach same conversion. A rough estimation of the energy consumption for both synthesis in the 250 mL vessels in order to reach 50% conversion (see chapter 9[†]) shows an energy consumption of approx. 1.42 MJ for the synthesis at 40 °C and 12 h polymerization time and of 1.05 MJ for the synthesis conducted at 70 °C but only 6 h polymerization time. Therefore, adapting the polymerization conditions to shorter polymerization time and higher temperature leads to a bisection of the polymerization time and decreased energy consumption saving energy and manpower. Due to these findings, P2VP polymerizations in the



250 mL vessels were carried out only at 60 °C and 70 °C. Both polymerizations show a short inhibition period (<1 h) (see Fig. 5(e) and (f)) as observed likewise for the polymerisation in the small vials. After 6 h polymerization time, 2VP conversions of 41% and 51% were determined at polymerization temperatures of 60 °C and 70 °C, respectively, thus reduced by 10% and 7% by using a 250 mL vessel instead of the small ones. Polymers with low dispersities were obtained ($\bar{D}$ = 1.14–1.35, see Table S15†). Therefore, especially the optimized synthesis at a temperature of 70 °C turns out to be robust approach for conducting the polymerization on a larger scale and presents a suitable synthesis procedure for larger production of tailor made P2VP homopolymer.

Conclusions

We developed and optimized routes to synthesize well-defined macroCTAs on different laboratory scales *via* RAFT polymerization induced by blue light without the use of exogenous initiators or catalysts. The switchable and uniform illumination *via* the cylindrical blue LED irradiation offers the possibility to adjust the radical generation and thus to influence the polymerization process. In combination with DDMAT as a suitable RAFT agent to control the polymerization in water–ethanol (50 : 50, *w/w*) solvent system, a versatile and environmentally friendly RAFT polymerization strategy for various monomer families is established. MAM classes encompassing acrylamides, acrylates and even rather nonpolar vinylpyridines (4- and 2-isomer) could be polymerized with good control despite the different apparent propagation constants. Due to the decoupling of the initiation from the thermal conditions, high DMA and DMAEA conversions can be achieved at a low ambient temperature of 40 °C after short polymerization times ($\leq$ 4 h). Furthermore, we have shown that synthesis up to 500 mL scale is possible without significant loss of conversion. Comparably, 4VP as a slower propagating monomer in the RAFT process demonstrated a good control even at 40 °C polymerization temperature. While for DMA and DMAEA the same synthesis conditions can be used for the larger 250 mL scale, it is recommended to adjust the parameters for 4VP polymerization towards higher light intensities and/or temperatures. Visible light-induced polymerization of 2VP showed a strong temperature-dependence of the kinetics. We conclude that it is possible to reach relatively high conversions at 70 °C and a high robustness in terms of scalability. This adaptability of the synthesis conditions to the various monomers, even for the larger scales, is the strength of this polymerization approach.

Author contributions

Lara Hub: conceptualization, data curation, formal analysis, investigation, methodology, validation, visualization, writing – original draft, writing – review & editing; Joachim Koll: investigation, writing – review & editing; Maryam Radjabian: concep-

tualization, project administration, supervision, writing – review & editing; Volker Abetz: funding acquisition, resources, supervision, writing – review & editing.

Conflicts of interest

There are no conflicts to declare.

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5.2 Publication 2

This publication builds upon the blue-light-induced RAFT polymerization method for macroCTA synthesis in solution by extending its applicability to the synthesis of amphiphilic diblock copolymers in a heterogeneous system. This was achieved by integrating the light initiation approach with polymerization-induced self-assembly (PISA), a challenging endeavor due to the presence of monomer droplets and undiluted particles, which hinder light penetration into the polymerization medium. Effective mixing was therefore critical to ensure uniform polymer chain growth throughout the process.

In this section, amphiphilic diblock copolymers, poly(*N,N*-dimethylacrylamide)-*block*-polystyrene (PDMA-*b*-PS) and poly(4-vinylpyridine)-*block*-polystyrene (P4VP-*b*-PS), were successfully synthesized *via ab initio* emulsion polymerization in aqueous-alcoholic media. The polymerization kinetics were systematically investigated, and the resulting latex particles were analyzed using dynamic light scattering (DLS) and transmission electron microscopy (TEM). The study highlighted differences in the chain extension behaviors of PDMA and P4VP macroCTAs with styrene, revealing important insights into their respective polymerization characteristics.

Additionally, semi-batch trials emerged as a highly effective strategy for the synthesis of PDMA-*b*-PS diblock copolymers, specifically for the production of PDMA-*b*-P(DMA-*grad*-S)-*b*-PS block copolymers. This method resulted in a minimal transition region between the pure PDMA and pure PS blocks, simplifying the synthesis process and enabling the production of a complete block copolymer within a single working day.

Furthermore, the scalability of the photoiniferter RAFT polymerization for diblock copolymer synthesis was examined, with experiments conducted at a scale of up to 500 mL. Remarkably, the conversion rates were found to be minimally affected by the different vessel radii, demonstrating the robustness of the method and its suitability for different laboratory scales. The synthesized diblock copolymers exhibited microphase-separated structures in their bulk state, showcasing their potential for applications in advanced material design.

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Amphiphilic Block Copolymers via Blue-Light-Induced Iniferter RAFT *Ab Initio* Emulsion Polymerization in Water–Alcoholic Media

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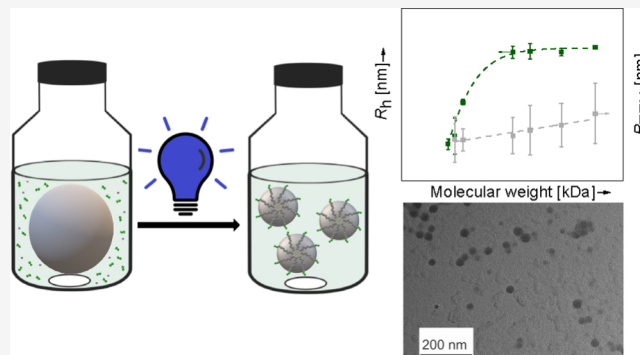


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ABSTRACT: Amphiphilic block copolymers comprise a fascinating class of smart materials due to their unique ability to self-organize, making them attractive candidates for a wide range of applications in materials engineering and medical sciences. The synthesis of these copolymers commonly involves harmful solvents, especially in classical living anionic polymerization. With the development of reversible addition–fragmentation chain transfer (RAFT) and polymerization–induced self-assembly (PISA), an environmentally more friendly and versatile method has been established for the synthesis of such amphiphilic block copolymers. Through the utilization of visible light to initiate polymerization through the so-called photoiniferter process, we emphasize the adaptability of this photopolymerization in different scales although the incident light illuminates only the surface area of the reaction vessels. We describe an easily adjustable, blue-light-initiated RAFT PISA approach to synthesize a series of amphiphilic poly(*N,N*-dimethylacrylamide)–*block*–polystyrene (PDMA–*b*–PS) and poly(4-vinylpyridine)–*block*–polystyrene (P4VP–*b*–PS) diblock copolymers with low molecular weight dispersities. The polymerizations were conducted as both two-step and semibatch processes. Furthermore, the effect of scalability on the polymerization kinetics was investigated, proving the light-induced RAFT polymerization as a scalable polymerization method in a batch process with a reaction volume of up to 500 mL. The bulk morphology of both resulting diblock copolymers having different weight fractions of the minor and major blocks was analyzed. While a cylindrical PDMA microdomain in a PS matrix can be observed at 20–25% by weight of PDMA, the equivalent composition reveals a spherical morphology of P4VP domains in a PS matrix. In essence, the scalable, rather eco-friendly photoinduced synthesis of tailored, nanostructured block copolymers without harmful solvents significantly increases their suitability for applications.



1. INTRODUCTION

Block copolymers (BCPs) are an outstanding class of soft materials due to their unique structural properties that enable the formation of a variety of nanoscale-ordered structures both in pure state^{1–6} and also in blends with other BCPs,^{4,7,8} other polymers,^{9–12} and in solutions.^{13,14} They are composed of at least two or more chemically different blocks, which may be connected in linear,^{1–6} star, or other branched topologies,^{4,15,16} and even cyclic BCPs have been reported.¹⁷ Different chemical compositions among the blocks lead to segmental incompatibilities, which are responsible for their self-assembly behavior, and may lead to long-range ordered mesoscale structures if the compositional and molecular weight dispersity are well-controlled^{1–4} or the self-assembly is guided by interfaces¹⁸ or external fields.¹⁹

Their distinctive architecture imparts a wide range of tunable properties and functionalities, making block copolymers versatile and valuable in various applications like in patterned substrates,^{20,21} nanolithography,²² membranes,^{23,24} and as mesoporous materials for energy storage systems.²⁵

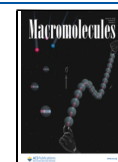
The synthesis of block copolymers requires a controlled process that enables the precise arrangement of different polymer segments within a single macromolecule. In the past, such polymers have been synthesized via living polymerization methods.^{26–35} Through the development of reversible-deactivation radical polymerization (RDRP) techniques like nitroxide-mediated polymerization (NMP),^{36–38} atom transfer radical polymerization (ATRP),^{39,40} and reversible addition–fragmentation chain transfer (RAFT),⁴¹ new synthetic opportunities toward well-controlled block copolymers became available. These techniques are more robust since the radical process provides higher versatility, less potential interference by impurities, and higher tolerance toward functional groups

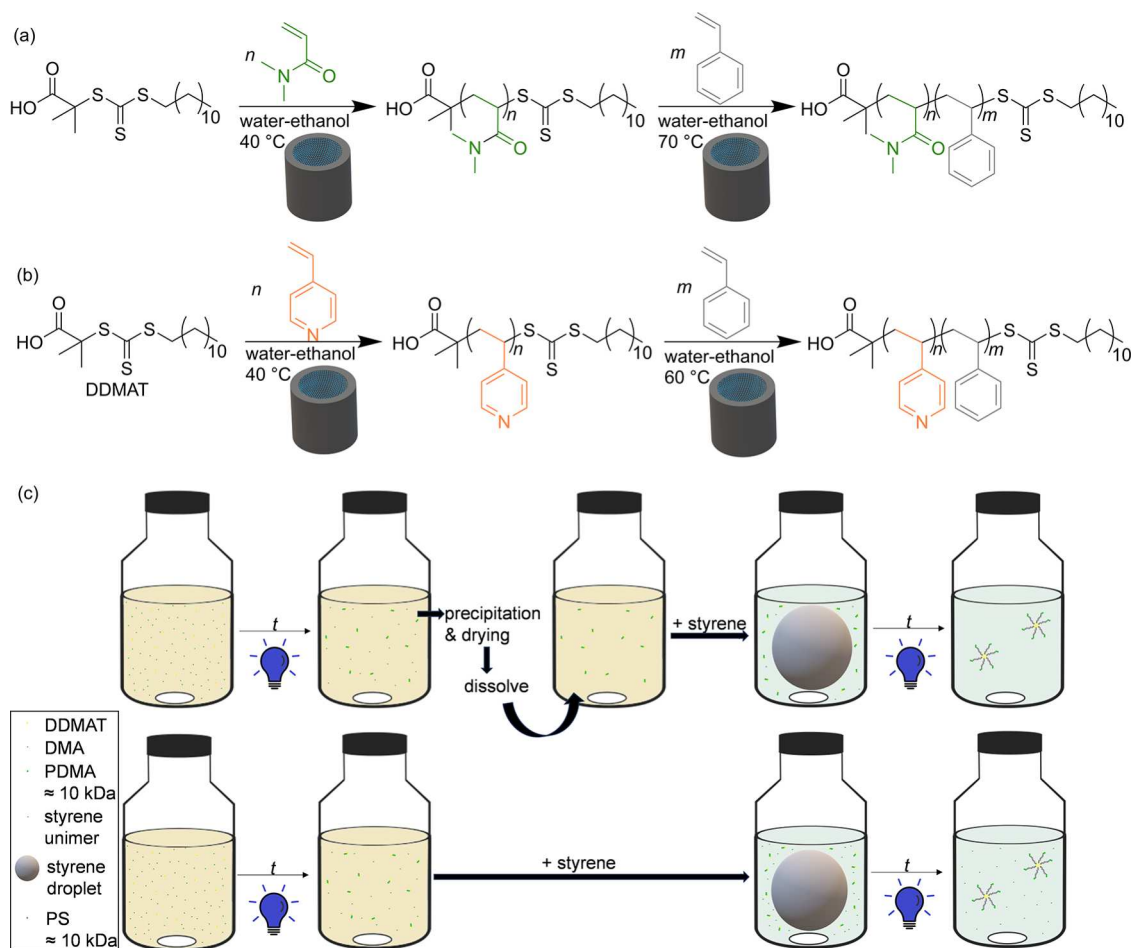
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Scheme 1. Synthetic Routes^a

^aSynthetic routes toward (a) poly(*N,N*-dimethylacrylamide)-*block*-polystyrene (PDMA-*b*-PS) and (b) and poly(4-vinylpyridine)-*block*-polystyrene (P4VP-*b*-PS) amphiphilic diblock copolymers via blue-light-induced iniferter RAFT polymerization utilizing a homemade blue LED light source. Photoiniferter RAFT solution polymerization of DMA and 4VP is conducted first, followed by the *ab initio* emulsion polymerization of styrene. (c) Workflow of the polymerization in the two-step process (top) and in the semibatch process (bottom), exemplary for the synthesis of PDMA-*b*-PS copolymers (not to scale).

and reaction conditions,^{42,43} saving effort and resources for monomer and solvent preparation.

The versatility of RAFT polymerization makes it appropriate for controlled radical polymerization with a wide range of functional monomers.^{43,44} Its applicability to perform in water and alcohols as well as their mixtures, enabling polymerizations in emulsion^{45–47} and dispersion,^{48–52} makes the RAFT method attractive and environmentally sustainable. These heterogeneous polymerization systems provide efficient heat transfer while simultaneously keeping the viscosity low throughout the polymerization.⁵³ Likewise, the polymerization rate is increased compared to homogeneous polymerization systems,^{54,55} enabling the polymerization of slowly propagating monomers like styrene.^{56,57} Within the past few years, the combination of polymerization-induced self-assembly (PISA) and RAFT polymerization has emerged as a novel polymerization approach for amphiphilic block copolymers. Favorably, the PISA process is conducted as surfactant-free polymerization without any additional stabilizer. Herein, a macromolecular chain transfer agent (macroCTA) acts as a steric stabilizer and is chain-extended with a monomer via either dispersion or emulsion polymerization. Hence, the amphiphilic macroCTA is formed *in situ*, and due to the incompatibility of

one of the blocks with the solvent, the polymer chains self-assemble.⁵⁸ PISA enables the synthesis of amphiphilic block copolymers with remarkable precision, leading to the formation of diverse nanostructures including micelles, vesicles, and worms.⁵⁹

New methods to initiate the RAFT polymerization gained wide interest within the past few years. Different external stimuli such as light,⁶⁰ redox catalysts,⁶¹ ultrasound,⁶² electricity,⁶³ or enzymes⁶⁴ were studied to initiate the RAFT polymerization. Photoregulation of polymerizations became a popular initiation method due to its ability to provide highly precise spatiotemporal control, its cost-efficiency, and environmental-friendly features.^{44,65,66} Due to the absorption of RAFT agents, UV- and visible-light-emitting lamps can be used to initiate the iniferter RAFT process. Herein, the RAFT agent acts as an initiator and transfer and reversible terminator agent.⁶⁷ In comparison to UV light, the absorptivity in the visible region is considerably weaker; however, well-defined polymers with high reproducibility can be obtained. When utilizing thiocarbonylthio (TCT) RAFT agents, the absorption maximum is often located in the blue range. First described by the Qiao group,⁶⁸ blue light-emitting diodes (LEDs) are ideally suited for initiating iniferter RAFT polymerization. Low energy

consumption and high lifetimes are some of its advantages.⁶⁶ In addition, for a highly efficient initiation, an LED with a suitable wavelength can be chosen according to the absorption range of the RAFT agent. Recently, we have shown that a homemade blue LED reactor can be effectively used for the excitation of the 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid (DDMAT) RAFT agent for the visible-light-induced iniferter homopolymerizations of monomers of different families.⁶⁹ Good control of the polymerizations and high robustness in terms of scalability were proved.

Compared to the previously investigated homogeneous polymerization systems, conducting the light-induced RAFT polymerization in heterogeneous polymerization systems is more complex. Scattering caused by monomer droplets and undissolved polymer results in a small penetration depth of incident light into the reaction mixture. In recent years, several groups investigated the visible-light-initiated RAFT PISA in dispersion via photoinduced electron/energy transfer (PET)^{70–76} rather than the photoiniferter^{77,78} process. Boyer's group reported the photoPISA dispersion polymerization for synthesizing block copolymers via chain extension of poly(oligo(ethylene glycol) methyl ether methacrylate) macro-CTA with benzyl methacrylate in ethanol. The procedure was conducted without the use of an external catalyst or initiator utilizing blue and green light.⁷⁹ Visible-light-induced emulsion polymerization has been even less frequently addressed. Boyer's group reported the miniemulsion polymerization of styrene via PET-RAFT mediated by a household-grade blue LED⁸⁰ and of butyl methacrylate utilizing green light.⁸¹ Lauterbach and Abetz synthesized poly(*N*-acryloylpyrrolidin)-*block*-polystyrene diblock copolymers via emulsion polymerization induced by UV light and showed the feasibility of the photoiniferter PISA polymerization.⁸²

To date, light-induced RAFT polymerization batch reactions were performed on small lab scales, and only small amounts of polymers (usually in single-digit gram range) were synthesized. However, since photopolymerizations are influenced by spatial parameters such as the distance to the light source or the surface of the reaction vial, the influence of such key parameters on the polymerization kinetics is of particular interest.

Herein, we aim to use an initiator-, catalyst-, and surfactant-free visible-light-induced iniferter *ab initio* emulsion RAFT polymerization to synthesize poly(*N,N*-dimethylacrylamide)-*block*-polystyrene (PDMA-*b*-PS) and poly(4-vinylpyridine)-*block*-polystyrene (P4VP-*b*-PS) diblock copolymers. A homemade blue LED reactor is utilized to generate the radicals directly from the macroCTAs. The synthesis approach consists of the photoiniferter solution polymerization of the initial monomers, DMA and 4VP, in water-ethanol mixtures and subsequent chain extension of these macroCTAs with styrene (see Scheme 1a,b). The courses of the polymerizations were kinetically monitored, and the formed particles were analyzed by transmission electron microscopy (TEM) and dynamic light scattering (DLS). Besides performing these syntheses as a two-step approach (Scheme 1c, top), semibatch polymerizations (Scheme 1c, bottom) were conducted, in which styrene was added as the second monomer after a certain polymerization time of the first monomer. On top, the experiments were conducted on different vessel scales of 20 to 500 mL to investigate the scalability of this technique to synthesize higher amounts of diblock copolymers in a batch process. Finally, the bulk structure of the PDMA-*b*-PS and

P4VP-*b*-PS diblock copolymers with different compositions was investigated and compared.

2. RESULTS AND DISCUSSION

Blue-light-induced iniferter RAFT *ab initio* emulsion polymerization was performed as a surfactant-free polymerization to generate the amphiphilic PDMA-*b*-PS and P4VP-*b*-PS diblock copolymers. This polymerization can be carried out either as a two-step or via a semibatch approach (see Scheme 1c). In both cases, the synthesis of the first block of the diblock copolymer was conducted as a solution polymerization. For the second step, the emulsion polymerization, good stabilization of the emulsion is required. Therefore, DDMAT, a RAFT agent with a dodecyl functionality on the Z-group, was chosen since it interacts with the styrene monomer and stabilizes the styrene droplets.⁸²

In the following, sample codes are used (e.g., PDMA^z and PDMA_x-*b*-PS_y^z), where subscripts signify the weight fraction of the individual block (in wt %) and superscripts indicate the overall theoretical number average molecular weight (in kDa).

2.1. Synthesis of PDMA and P4VP Homopolymers via Blue-Light-Induced Iniferter RAFT Solution Polymerization. Homopolymerizations of DMA and 4VP were conducted as previously reported.⁶⁹ The polymerizations were carried out on a 250 mL scale and were terminated upon reaching approximately 50% conversion. Both PDMA and P4VP macroCTAs were synthesized to achieve a comparable degree of polymerization ($N \approx 200$, see Table 1). The synthesis of all PDMA and P4VP macroCTAs was

Table 1. PDMA and P4VP MacroCTAs Synthesized via Blue-Light-Induced RAFT Solution Polymerization

Polymer ^a	$\bar{M}_{n, th}$ [kDa] ^b	$\bar{M}_{n, app}$ [kDa] ^c	$\bar{D}$ ^d	N^e
PDMA ^{20.4}	20.4	16.7	1.25	202
PDMA ^{21.1}	21.1	18.8	1.13	209
PDMA ^{21.2}	21.2	16.8	1.22	210
P4VP ^{21.5}	21.5	25.9	1.12	201
P4VP ^{22.2}	22.2	27.6	1.09	208
P4VP ^{23.7f}	23.7	32.1	1.11	222

^aSuperscripts denote the theoretical number-average molecular weight determined by ¹H NMR spectroscopy. ^bTheoretical number-average molecular weight determined by ¹H NMR spectroscopy.

^cApparent number-average molecular weight determined by SEC with PS calibration. ^dDispersity determined by SEC with PS calibration.

^eNumber of repeating units determined by ¹H NMR spectroscopy.

^fSynthesized at 50 °C.

carried out under the same conditions, utilizing a ratio of $[DDMAT]_0/[DMA]_0 = 1:500$ and $[DDMAT]_0/[4VP]_0 = 1:470$ on a 250 mL scale at a temperature of 40 °C and illuminated with the blue LED at $\lambda_{max} = 451$ nm and an intensity of 52 mW·cm⁻². Only the synthesis of P4VP^{23.7} was conducted at 50 °C instead of 40 °C, resulting in a slightly larger molecular weight compared to those of the other P4VPs. The deviations of the theoretical molecular weight $\bar{M}_{n, th}$ of the different polymer batches from each other, as determined by ¹H NMR, synthesized under identical conditions, are less than 1 kDa, showing the high reproducibility of this synthesis method. The apparent number-average molecular weights $\bar{M}_{n, app}$ of the PDMA and P4VP macroCTAs deviate from the theoretical ones due to the different hydrodynamic volumes of

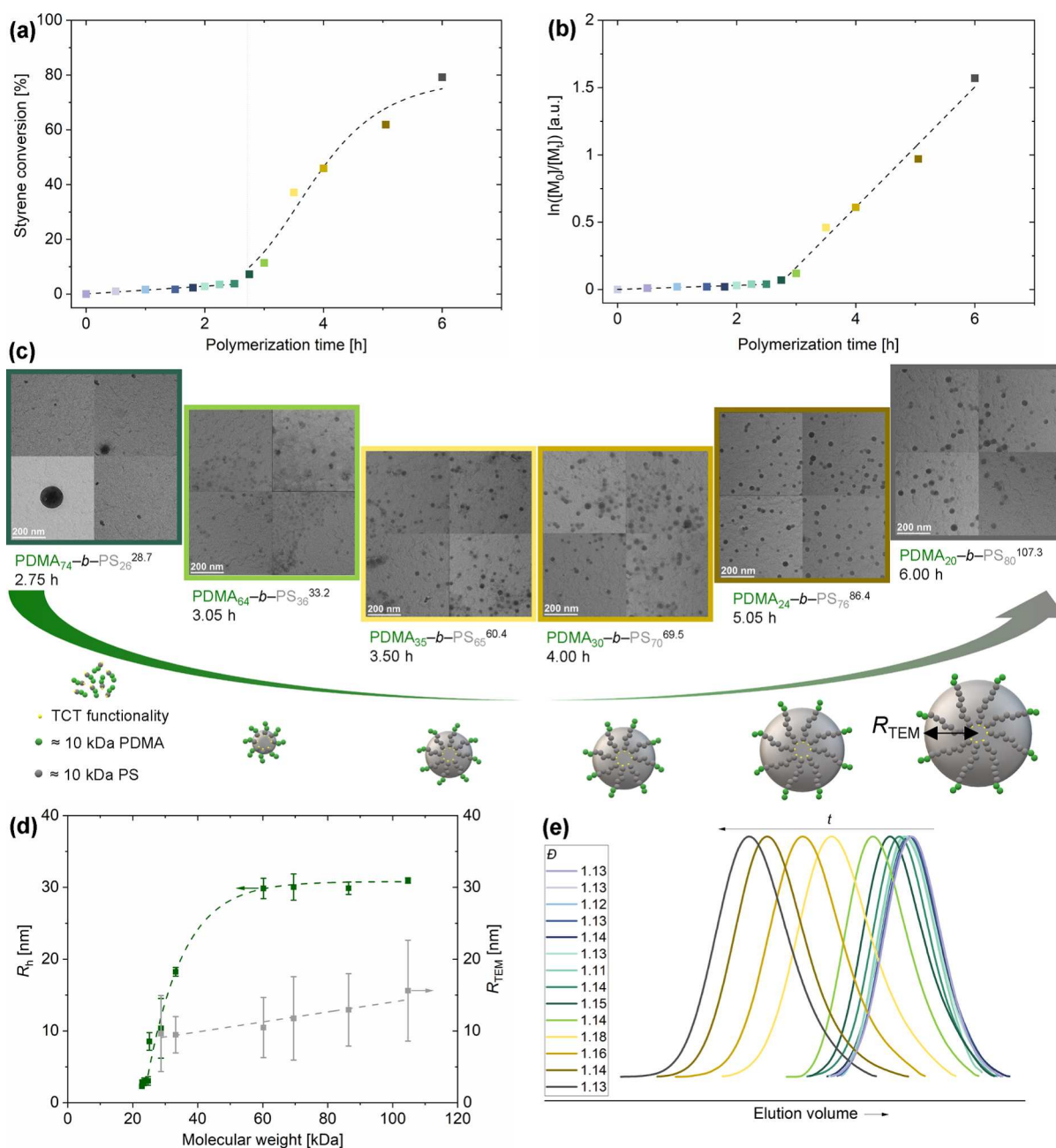


Figure 1. (a) Conversion and (b) pseudo-first-order plot of the blue-light-induced *ab initio* emulsion polymerization of styrene with PDMA^{21.1} macroCTA. (c) TEM images of the diblock copolymers prepared at the different time intervals during the polymerization. (d) Average hydrodynamic radius R_h and radius determined by TEM R_{TEM} of the latex particles as a function of molecular weight. (e) SEC traces of PDMA^{21.1} macroCTA and the PDMA-*b*-PS diblock copolymers of the kinetic study synthesized during the *ab initio* emulsion polymerization. Polymerization conditions: $[PDMA]_0/[styrene]_0 = 1/1000$ (20% w/w) in water–ethanol mixture (50:50 w/w), 70 °C, $I_{blue\ light} = 87\text{ mW}\cdot\text{cm}^{-2}$.

these polymers compared to the polystyrene standard. All polymers showed low dispersities of ≤ 1.25 .

2.2. Synthesis of PDMA-*b*-PS via Blue-Light-Induced Iniferter RAFT Emulsion Polymerization. For the chain extension of PDMA macroCTAs with styrene, experiments were performed on the 250 mL scale in the water–ethanol (50:50 (w/w)) mixture with $[PDMA]_0/[styrene]_0 = 1/1000$ (20% (w/w)). The macroCTA acted as a stabilizer for the formed latex and was intended to prevent coagulation. The incident blue light homolytically cleaved the C–S bond of the thiocarbonyl functionality, leading to the formation of a transient radical that could subsequently react with available styrene.

In the aqueous-alcoholic medium, PDMA macroCTA was fully dissolved. Ethanol as a cosolvent increased the solubility of styrene compared to pure water; however, styrene still had a sufficient low solubility in a water–ethanol (50:50 (w/w)) mixture that the initial polymerization mixture remained milky, even at the higher temperature of 70 °C, see Figure S5. In dispersion polymerization, the initial mixture would be transparent and become turbid during the polymerization process. Furthermore, the presence of the micrometer-sized monomer droplets was confirmed by TEM and DLS and will be discussed in detail. Therefore, we conclude that the polymerization follows the mechanism of an *ab initio* emulsion polymerization.

Due to the low monomer concentration of the diluted styrene in the solvent mixture as well as the low propagation rate of styrene in RAFT polymerization, the monomer addition rate was very slow. The kinetic data shown in Figure 1a demonstrate a marginal increase of the styrene conversion within the first 2.5 h. In this stage, the apparent polymerization rate k_p^{app} , determined via the slope of the first-order plot in Figure 1b, was very low with a value of 0.015 h^{-1} .

As the degree of polymerization N of styrene in the macroCTAs increased, the polystyrene block became insoluble due to its hydrophobic nature. Therefore, the polymer chains formed a micellar structure to minimize the unfavorable contact of polystyrene with the solvent system (PISA process). A core-shell architecture is expected, with the PS block forming the core of the micelle and the PDMA block forming the shell. Due to the hydrophobic environment inside the micelles, the monomer diffused from the monomer droplets through the aqueous-alcoholic phase into the micelles, leading to the formation of latex particles. This process is called micellar nucleation and follows the principles of interval I according to the theory of Harkins.^{83,84} The locally increased concentration of styrene within the latex particles led to a steep rise in styrene conversion (Figure 1a). The transition between these two reaction phases, determined by the interception of the two slopes of the linear fits of the first-order plot (Figure 1b), occurred at 2.73 h, resulting in a conversion of about 4% and a number of styrene units N_{PS} of about 40.

The PISA process can be monitored and characterized by imaging methods like TEM, as well as scattering methods like DLS. For TEM analysis, samples were air-dried to allow evaporation of volatile components such as water, ethanol, and styrene, and only the polymer aggregates remain on the grid. The morphology of the unstained samples is depicted in Figure 1c. At the beginning of polymerization, only spherically shaped agglomerates were detectable in the TEM images. Homopolymers synthesized via RAFT are known to also have a slightly amphiphilic character as the RAFT group chemically differs from the homopolymer. The hydrophobic dodecyl group allowed the chains of the macroCTA to attach to the styrene monomer droplets like surfactants. Therefore, the large, dark agglomerates shown in Figure S14 and Figure 1c at 2.75 h likely present dried monomer droplets with attached polymers, which shrunk due to the drying process. These agglomerates were the only detectable species up to the polymerization time of 2.50 h, and they appeared at 2.75 h simultaneously with the emergence of additional micellar species in the midnanometer range. In the next sample, taken 15 min later, the agglomerates had completely disappeared as the micelle formation was completed. The first micelles were observed at 2.75 h with an average radius R_{TEM} of $9.6 \pm 5.3 \text{ nm}$ (see Figure 1c, 2.75 h). In the DLS measurements, up to 3.05 h, two distinct decays of $g_2(\tau)$ vs time were observed, indicating the presence of two different-sized species. Initially, species around 2 to 3 nm (see Figure 1d), probably macroCTA unimers, and those in the submicrometer range were identified. The latter completely disappeared in the sample of 3.50 h; meanwhile, the macroCTAs continued to grow, and at the onset of the formation of the latex particles via nucleation, an increase of the hydrodynamic radius R_h from $8.5 \pm 1.2 \text{ nm}$ (2.50 h) to $18.2 \pm 0.6 \text{ nm}$ (3.05 h) is observed (as shown in Figure 1d). This value thus deviates by almost 9 nm from the value determined with TEM. The difference between particle radii determined via the two different methods can be attributed to

the difference in the respective preparation and measurement methods. In the TEM preparation process, the emulsion was dropcast and subsequently air-dried, leaving only the polymer on the grid. Thus, the inside of the micelle had considerably shrunk due to the evaporation of styrene. In addition, PDMA-*b*-PS micelles show a low electron density contrast between the blocks and an unclear outer edge. Since in the preparation method water evaporated as the least volatile component and is still a solvent for PDMA, the PDMA corona might not have been part of the visible micelle, causing this indistinct interface between the core of the latex particles and the background. This leads to the assumption that only the PS part is visible in the TEM. On the other hand, in DLS, the *z*-averaged radius of a latex particle in the aqueous-alcoholic medium, in which PDMA swells, is determined. Considering the hydrate shell and the unreacted styrene in the latex particle rationalizes a significantly larger radius than the one determined by using TEM.

After the nucleation phase is completed, it was followed by the steady-state reaction stage. Herein, the rate of polymerization remained constant, since the monomer concentration within the latex particles remained constant. The consumed monomer in the latex particles was replaced by monomer, which diffused from the monomer droplets via the aqueous-alcoholic phase into the latex particles. This phase spanned from approximately 2.75 to 4.0 h with a conversion of 8 to 46%. The apparent propagation rate k_p^{app} increased to 0.447 h^{-1} . It can be observed that all PISA-generated PDMA-*b*-PS latex particles had a spherical shape (see Figure 1c). The latex particle radius determined by TEM further increased with longer polymerization time as more styrene is converted to PS. The hydrodynamic radius R_h increased to $29.9 \pm 1.4 \text{ nm}$ in the molecular weight range between 20 and 60 kDa (see Figure 1d).

Within the last 2.5 h of polymerization, when a molecular weight of 60 kDa was reached, the hydrodynamic latex particle radius remained constant at about 30 nm. The reason might be that within this time interval the monomer inside the monomer droplets was fully consumed and the residual monomer within the latex particles was consumed (monomer depletion). Only one species is observed; neither unimers nor aggregated latex particles are detected. The size distribution of the latex particles does not deviate from the average value by more than 2 nm, and the polydispersity index PDI is about 0.15. This narrow distribution of particle sizes enables similar polymerization conditions for all chains involved in the process and thus uniform growth. This was also reflected in the molecular weight distribution of the polymers (see Figure 1e). The SEC traces of the PDMA-*b*-PS diblock copolymers clearly shift to lower elution volumes per unit of time. Ultimately, diblock copolymers with low molecular weight distributions ($\bar{D} = 1.11\text{--}1.18$) were obtained.

2.3. Synthesis of P4VP-*b*-PS via Blue-Light-Induced Iniferter RAFT Emulsion Polymerization. In contrast to PDMA, P4VP exhibits a significantly lower solubility in water. Although the homopolymerization of 4VP was conducted in the water-ethanol mixture (50:50, *w/w*), the dissolution of P4VP after precipitation and drying proved to be significantly challenging, particularly for higher molecular weights of P4VP. Due to this, the water-ethanol mixture was slightly adjusted by increasing the weight fraction of ethanol to 60% (*w/w*). Furthermore, preliminary tests have shown that the heterogeneous polymerization of styrene with P4VP macroCTAs is

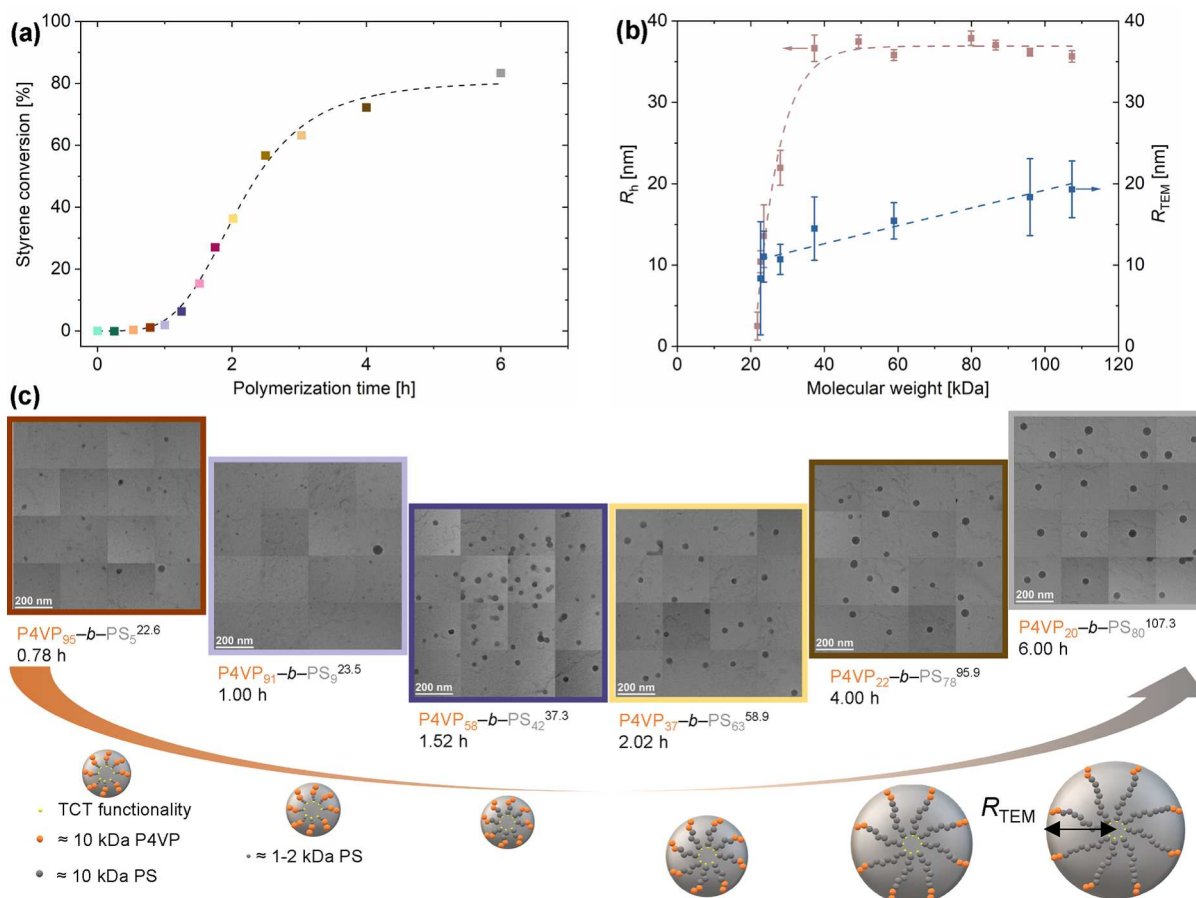


Figure 2. (a) Conversion of the visible-light-induced *ab initio* emulsion polymerization of styrene with P4VP^{21.5} macroCTA. (b) Average hydrodynamic radius of the latex particles determined by DLS, and radius determined by TEM as a function of molecular weight. (c) TEM images of the assembled polymers prepared at different time intervals during the polymerization. Polymerization conditions: $[P4VP]_0/[styrene]_0 = 1/1000$ (20% w/w) in water–ethanol mixture (40:60 w/w), 60 °C, $I_{blue\ light} = 87\text{ mW}\cdot\text{cm}^{-2}$.

significantly faster than that with the PDMA homopolymers. Thus, the polymerization temperature was reduced by 10 to 60 °C.

Similarly, as for PDMA-*b*-PS, samples were collected to determine the kinetics and the evolution of the particle size. Figure 2 (a) shows the styrene conversion in the chain extension of P4VP^{21.5} with styrene with a ratio of $[P4VP]_0/[styrene]_0 = 1/1000$ (20% (w/w)) at a light intensity of $87\text{ mW}\cdot\text{cm}^{-2}$ on a 250 mL scale. Likewise, as shown in Figure 1a, initially a slow conversion of styrene was observed until the latex particles were formed. The slope of the first-order plot (Figure S10) indicates a polymerization rate of 0.019 h^{-1} for the styrene addition, which is comparable to the rate determined for the styrene addition to the PDMA macroCTA. It can be observed that the first polymerization period takes 65 min. Thus, the initial polymerization phase, in which the amphiphilic diblock copolymers were formed and later acted as surfactants for the latex particles, was 2.5 times shorter compared to the polymerization with PDMA discussed earlier. A very low styrene conversion of 1.7% was sufficient to induce the self-assembly of the chains. Therefore, only 17 units of styrene needed to be added to cause micelle formation. For PDMA, which had a similar degree of polymerization as P4VP, it required 2.4 times more styrene units to be added. This may be attributed to the Flory–Huggins interaction parameter $\chi_{P4VP/PS}$ which is 3 times larger for P4VP-*b*-PS than for PDMA-*b*-PS.^{85,86} After the latex particles were formed, the

polymerization rate increased to 0.468 h^{-1} and thus the polymerization rate was approximately as fast as the emulsion polymerization of PDMA-*b*-PS. It can therefore be concluded that the duration of the initial polymerization phase is significantly influenced by the Flory–Huggins interaction parameter of the blocks.

The evolution of the particle size determined via TEM is shown in Figure 2b,c. At a polymerization time of 0.78 h, the first latex particles with a radius of $8.4 \pm 6.9\text{ nm}$ became detectable, accompanied by noticeable agglomerates. These were already before recognizable (see Figure S15a), and the last sample, which exhibited agglomerates, was taken at a polymerization time of 1.25 h (see Figure S15b). It can therefore be assumed that the nucleation period will not have been fully completed by then. An increase of the particle radius to $14.5\text{ nm} \pm 3.9\text{ nm}$ was observed following a polymerization time of 1.52 h when a molecular weight of 37 kDa was reached; after that, the particles showed only slight growth to a final radius of $19.3\text{ nm} \pm 3.5\text{ nm}$ (see Figure 2b). Compared to the PDMA-*b*-PS particles, the P4VP-*b*-PS particles showed a slightly larger radius in TEM. Even after staining the sample with iodine (which marks the P4VP microdomains), no evident difference regarding the appearance of the corona or a larger size between the unstained and stained particles was observed (see Figure S16 and the histograms in Figure S19). The size difference between the stained and unstained samples was found to be smaller than the width of the Gaussian

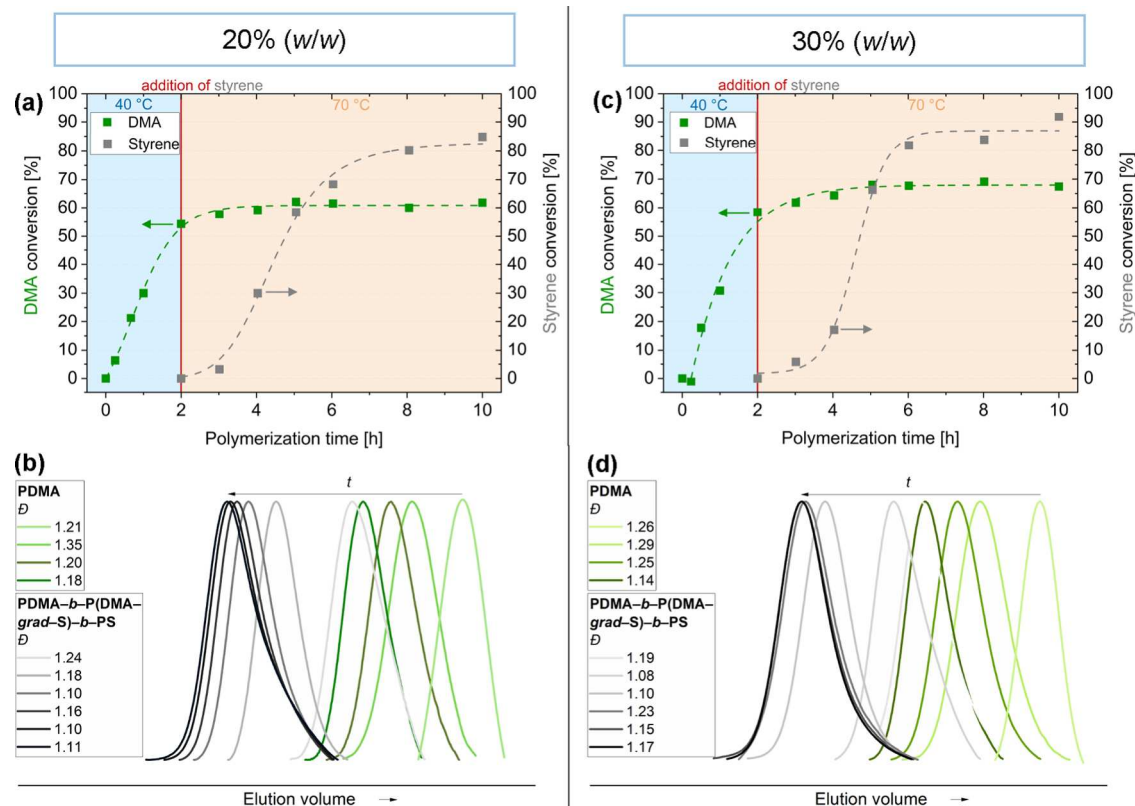


Figure 3. Kinetic investigation of the semibatch RAFT synthesis of PDMA-*b*-P(DMA-*grad*-S)-*b*-PS copolymers performed at different RAFT agent and monomer contents. Evolution of the conversion of DMA and styrene and of the SEC traces at 20% (w/w) (a, b) and 30% (w/w) (c, d) RAFT agent, DMA, and styrene content. Initially, the polymerization was conducted at a ratio of $[DDMAT]_0/[DMA]_0 = 1:500$ in a water-ethanol mixture (50:50 w/w) at 40 °C and $I_{\text{blue light}} = 49 \text{ mW}\cdot\text{cm}^{-2}$; after a polymerization of 2 h, 1000 equiv of styrene was added, the temperature increased to 70 °C, and the light intensity enhanced to $83 \text{ mW}\cdot\text{cm}^{-2}$.

distribution. Therefore, it is likely that the obtained radius in TEM included both blocks, PS and P4VP. Furthermore, a sharper interface between the background and the P4VP-*b*-PS particles compared to the PDMA-*b*-PS particles was observable. Ethanol, as a more volatile solvent than water, evaporated first, and the remaining water was a nonsolvent for P4VP (in contrast to the previously discussed PDMA). This leads to the reasonable assumption that the P4VP chains collapse, and a sharp contrast of the particles is visible.

In DLS, the hydrodynamic radius R_h increased from an initial $2.5 \pm 1.7 \text{ nm}$ (0.53 h, molecular weight of 22 kDa) to $36.6 \pm 1.6 \text{ nm}$ (1.52 h, molecular weight of 37 kDa). From this time point on, the latex particles had reached their maximum size and remained constant over the residual polymerization time. Compared to the PDMA-*b*-PS latex particles, the P4VP-*b*-PS particles showed a slightly higher hydrodynamic radius. Once the nucleation phase had completed, latex particles obtained a small PDI value, indicating favorable prerequisites for uniform chain growth. The diblock copolymer chains exhibited dispersities ranging between 1.09 and 1.22.

In some cases, a small amount of residual P4VP homopolymer remained, which is attributed to the chemical nature of 4VP and the increased termination probability.⁸⁷

The average number of radicals per particle ($\bar{n}_{\text{RAFT}}$) was estimated for both chain extensions of PDMA^{21.1} and P4VP^{21.5}, respectively (see chapter 11†). In both cases, $\bar{n}_{\text{RAFT}}$ values of 0.25 and 0.28, respectively, were determined. It is essential to note that these values should be considered as rough approximations. The specific values are in the same order of

magnitude as determined by Luo's group in seeded RAFT emulsion polymerizations of styrene with macro-RAFT agents and different potassium persulfate concentrations and in the RAFT miniemulsion polymerization of methyl methacrylate.^{88,89} We could expect that the average number of radicals per particle in the synthesis of PDMA-*b*-PS and P4VP-*b*-PS conducted on the same scale should be similar. Since the turbidity in the synthesis of PDMA-*b*-PS is slightly higher (caused by higher water content), a small decrease of the average number of radicals per particle is reasonable.

2.4. Semibatch Synthesis of Copolymers. To facilitate the polymerization process, the light-induced RAFT polymerization for the PDMA-*b*-PS copolymers was conducted using a semibatch process. For this experiment, a smaller scale of 20 mL was chosen. Initially, the PDMA homopolymer was synthesized via a conventional RAFT solution polymerization at a weight fraction of 6.4% (w/w) ($[DDMAT]_0/[DMA]_0 = 1:500$, water-ethanol mixture (50:50 w/w), 40 °C; $I_{\text{blue light}} = 49 \text{ mW}\cdot\text{cm}^{-2}$). To compensate for the reduced weight fraction of RAFT agent and DMA monomer in the solution polymerization compared to the typically used 20% (w/w), the homopolymerization was carried out with an extended polymerization time of 2 h. As shown in Figure 3a, the conversion of DMA proceeded linearly with time within the first 2 h of the polymerization and exceeded a conversion of 54% after 2 h. After 2 h, 1000 equiv of styrene was added as a second monomer and the temperature was increased to 70 °C and the light intensity to $83 \text{ mW}\cdot\text{cm}^{-2}$. Hereby, the total weight fraction of monomer and macroCTA was increased to

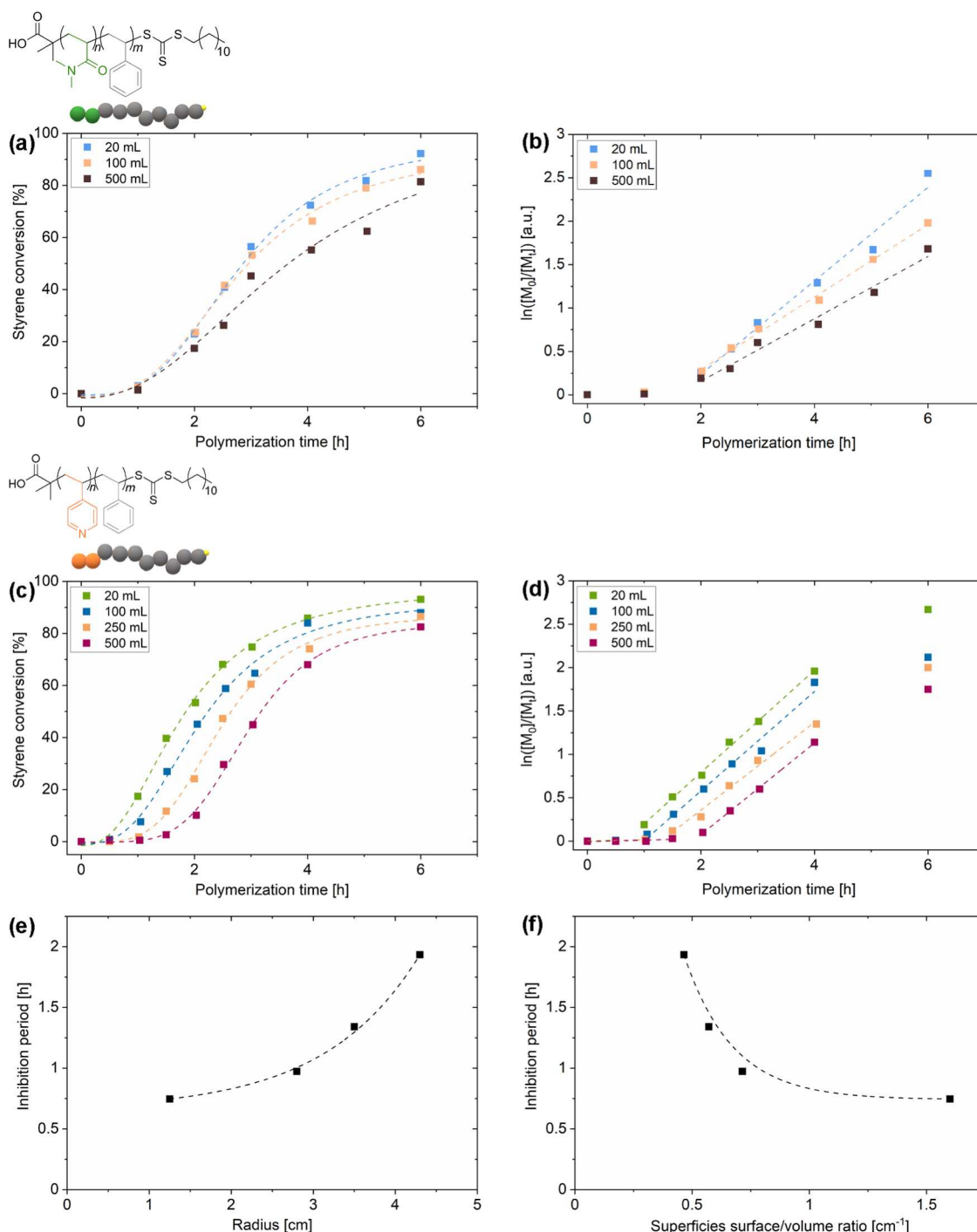


Figure 4. Influence of vessel dimensions on the (a) conversion and (b) pseudo-first-order plot of the blue-light-induced PISA RAFT chain extension of PDMA^{20.6} with styrene ($[PDMA]_0/[styrene]_0 = 1/1000$ (20% (w/w)) in water–ethanol mixture (50:50 w/w), and 70 °C. (c) Conversion and (d) pseudo-first-order plot of the RAFT polymerization of P4VP^{23.7} macroCTA with styrene at a ratio of $[P4VP]_0/[styrene]_0 = 1/1000$ performed at 60 °C in a water–ethanol mixture (40:60 w/w) and 20% (w/w) macroCTA and styrene content.

20% (w/w). After addition, the conversion of DMA slightly increased over the next 2 h and remained steady at 60% conversion. The slope of the first-order kinetic plot is 0.003 h^{-1} between the 4 and 10 h polymerization time (see Figure S12a). Styrene polymerized immediately after addition without inhibition time and the conversion increased rapidly to 74% in the first 4 h. Afterward, the polymerization rate decreased similarly to the emulsion polymerization discussed above due to the monomer depletion. Thus, there is a small time span of

approximately 1.5 h in which DMA and styrene copolymerized (according to the Boltzmann fit of the DMA conversion). However, while only about 25 repetition units of DMA were incorporated per polymer chain into this transition region from PDMA to PS, about 130 units of styrene were incorporated into the chain. Due to the excess of styrene units, self-assembly of the polymer chains occurred despite copolymerization with DMA. The incompatibility of polystyrene in the aqueous-alcoholic medium drove the styrene molecules into the latex

particles. Meanwhile, the aqueous-alcoholic medium is a very good solvent for the residual DMA monomers and thus they likely stayed in the diluted medium. Therefore, a spatial segregation occurred between reaction space, including the growing macroCTA TCT functionality in the inner part of the latex particles with styrene, and DMA. The polymerization rate of styrene increased dramatically, while that of DMA stagnated. At the end of the polymerization, a copolymer with 24 wt % PDMA and a total molecular weight of 111.6 kDa was synthesized. The SEC traces in Figure 3b show a clear shift to a lower elution volume and therefore a higher molecular weight over time. The dispersities are comparable to those obtained by the two-step synthesis process. As a result, the semibatch synthesis provides a suitable alternative since it facilitates the process by eliminating the need for additional purification of the homopolymer.

To enhance the efficiency of the polymerization further, the semibatch polymerization was conducted at a total RAFT agent and monomer content of 30% (*w/w*). In this process, the weight fraction of the RAFT agent and monomer in the homopolymerization increased to 10% (*w/w*). Apart from a small inhibition time of 15 min, the DMA homopolymerization progresses similarly to that described previously. In the initial phase after the addition of styrene, the polymerization proceeded more slowly than the one at 20% (*w/w*) with a rate of 0.020 h⁻¹. Though, after completion of the nucleation phase, the emulsion polymerization advanced much faster. The polymerization rate increased from 0.395 h⁻¹ (observed after nucleation in the emulsion polymerization at 20% (*w/w*)) to 0.762 h⁻¹ (30% (*w/w*)). Thus, the increase in weight fraction makes a significant difference in the kinetics, and high styrene conversions could be obtained after a total polymerization time of 6 h. Therefore, the polymerization time can be further shortened by 2 h, which makes this polymerization method even more effective. Increasing the weight fraction of the RAFT agent and monomer does not affect the dispersity (see Figure 3d). As a product, a copolymer with 26 wt % DMA units and a total molecular weight of 125 kDa with a low dispersity of 1.17 was obtained.

To synthesize the P4VP-*b*-PS copolymers via the semibatch process, 4VP and DDMAT (20% *w/w*) were diluted in the water-ethanol mixture (50:50 *w/w*) with a ratio of [DDMAT]₀/[4VP]₀ = 1:500. The homopolymerization was performed at a light intensity of 49 mW·cm⁻² at 70 °C for 6 h, and thus 4 h longer than for PDMA and at elevated temperature, due to the significantly lower propagation rate of 4VP compared to DMA.⁶⁹ After 6 h, a 4VP conversion of 61% was obtained (see Figure S13). 1000 equiv of styrene was added and the polymerization was performed for further 4 h at an increased light intensity of 83 mW·cm⁻². Meanwhile, in the semibatch synthesis with DMA and styrene, the conversion of DMA remained stagnant, and in the later stages, only styrene was converted; in the semibatch synthesis of 4VP and styrene, 4VP still continues to copolymerize with styrene after the addition of styrene. However, the increase of styrene conversion 30 min after the addition of styrene indicated that polymerization-induced self-assembly occurs, regardless of the copolymerization with 4VP. Therefore, a P4VP-*b*-P(4VP-*grad*-S) copolymer could be synthesized with this approach; however, it does not exhibit such a sharp copolymer boundary as with DMA and styrene.

2.5. Scalability of the Photoiniferter RAFT Polymerization for Diblock Copolymer Synthesis. Since radical

generation occurs solely through the activation of the macroCTA via visible light, the determination of the light intensity is of enormous importance. While in solution polymerization, the light can penetrate deep into the solution, also on a larger scale,⁶⁹ the monomer droplets and self-assembled latex particles in the disperse phase cause significantly greater scattering of the light. Based on this, transmission measurements of the emulsions were carried out. Over the entire polymerization process, the emulsion was very turbid. For the PDMA-*b*-PS RAFT synthesis, absorbance measurements at $\lambda = 451$ nm ranged between 3.39 and 4.32 AU for samples thicknesses of 1.0 cm. For the RAFT synthesis of P4VP-*b*-PS, there was a slight decrease in absorbance between 3.29 and 4.11 AU due to the slightly increased ethanol content in the solvent mixture. Hence, in contrast to solution polymerization, radicals can only be generated close to the surface of the vessel and not inside the vessel. This influences the reaction kinetics of polymerization, and therefore, the impact of scaling on polymerization kinetics was investigated.

Polymerizations were conducted at comparable light intensity, which varied slightly through the experimental setup. Vessels with larger sizes, e.g., larger diameters, are closer to the LED stripes than those with smaller diameters. Therefore, slightly different light intensities at the vessel surface were determined between 83 and 91 mW·cm⁻². Likewise, all other polymerization parameters were kept constant to determine the effect of the polymerization dimensions. Figure 4a shows the styrene conversion of the blue-light-induced chain-extension of PDMA^{20,6} with 1000 equiv of styrene in the water-ethanol mixture (50:50 *w/w*) and 20% (*w/w*) macroCTA and monomer content. The course of the styrene conversion of the polymerizations on the 20 and 100 mL scale is initially very similar; however, after a polymerization time of 2 h, the conversion on the 20 mL scale increased more strongly than on the 100 mL scale. As expected, the final styrene conversions decreased with an increased polymerization volume. According to the slopes of the linear fits in Figure 4b, a slightly reduced polymerization rate with increased vessel size could be observed, ranging from 0.538 h⁻¹ for the polymerization in the 20 mL scale to 0.359 h⁻¹ for the polymerization in 500 mL.

A similar kinetic investigation was conducted for the chain extension of P4VP^{23,7} with styrene ([P4VP]₀/[styrene]₀ = 1000 (20% (*w/w*)) in a water-ethanol mixture (40:60 *w/w*), 60 °C). As shown in Figure 4c, the course of conversion is very similar in all four different scales. Just the first initial phase to obtain the amphiphilic copolymer was prolonged with increased vessel size, and high conversions (>80%) are obtained, even on the 500 mL scale. Polymerization rates k_p^{app} obtained from Figure 4d were on the same order of magnitude and range from 0.590 to 0.503 h⁻¹ with a decelerated rate in higher scales. The onset of the linear increase of the first-order plot after the nucleation shifts to the later polymerization times with an increased scale (from nearly 45 min to almost 2 h). We figured out that this starting time, occurring before the emulsion polymerization (herein called inhibition time), depends exponentially on the radius of the reaction vessel (see Figure 4e). However, the correlation of the inhibition time between vessels with a radius of 2.8 (100 mL), 3.5 (250 mL), and 4.3 cm (500 mL) follows an increasing, superlinear trend. Since the light cannot penetrate deeply into the turbid reaction medium and only the superficial surface of the vessel is illuminated with the blue light, we investigated the

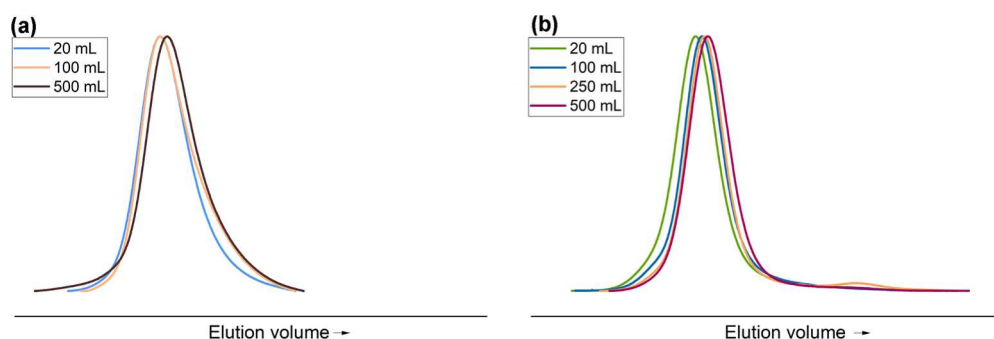


Figure 5. Polymerization scale-dependent molecular weight distribution of the end products of (a) PDMA-*b*-PS and (b) P4VP-*b*-PS diblock copolymer synthesis. ($[\text{PDMA}]_0/[\text{styrene}]_0 = 1/1000$ (20% (w/w)) in water-ethanol mixture (50:50 w/w), and 70 °C; $[\text{P4VP}]_0/[\text{styrene}]_0 = 1/1000$ (20% (w/w)) in water-ethanol mixture (40:60 w/w) at 60 °C).

dependence of the superficies surface/volume ratio on the inhibition time (see Figure 4f). Herein, we observe a decreasing correlation between the inhibition time and the superficies surface/volume ratio. While the trend appears to be linear for low ratios, just the polymerization in the smallest vessel with the highest surface/volume ratio falls out of the line. It is assumed that a linear correlation exists when the polymerization is light-initiation-controlled, while in the case of the smallest vessel, it is likely diffusion-controlled. However, the latter mechanism is irrelevant for practical, large-scale reactors, making the superficies surface/volume ratio the decisive factor for scaling.

The effect of the scalability on the molecular weight distribution of the samples is shown in the SEC traces in Figure 5. For the final PDMA-*b*-PS samples (Figure 5a), a slight increase in dispersity was observed with an increased batch size. This observation is mainly attributed to the low amount of bimolecular end product of the synthesis in the 500 mL scale. Nevertheless, the molecular weight distributions are very similar and have no significant effect on the polymer properties of the diblock copolymers. The P4VP-*b*-PS samples (Figure 5b) showed minor traces of the P4VP macroCTA, with the majority of the chains indicating chain extension. When considering the pure diblock copolymers, small dispersities of 1.13–1.18 were observed, demonstrating no significant effect of the polymerization scale on the molecular weight distribution.

In summary, the challenges introduced by high weight fractions and a turbid emulsion with a small penetration depth of the light are resolved by sufficient mixing, guaranteeing uniform polymer growth. Having further clarified the geometric relationships, we demonstrate the strength of visible-light-induced RAFT emulsion polymerization.

2.6. Bulk Morphology of Diblock Copolymers. While the bulk structure of P4VP-*b*-PS has been well studied in the literature, the bulk morphology of PDMA-*b*-PS has been less investigated.^{51,90,91} To investigate the bulk structure of the diblock copolymers, thin films were obtained from slowly evaporating solutions in chloroform and annealing above the glass transition temperatures. Ultrathin 50 nm sections of P4VP-*b*-PS were stained with iodine to increase the contrast between PS and P4VP, while the TEM was performed on unstained PDMA-*b*-PS since preliminary tests of homopolymer blends showed a good phase contrast between PDMA and PS (PDMA is brighter than PS).

Figure 6 shows the bulk structure of several PDMA-*b*-PS diblock copolymers with different compositions and molecular

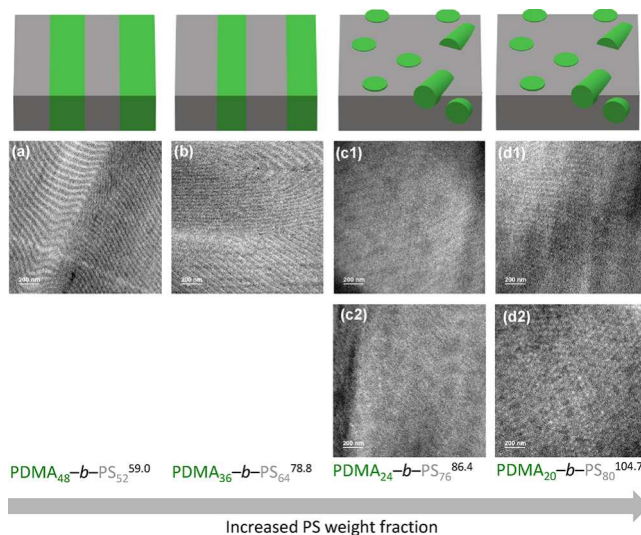


Figure 6. Bulk morphology of PDMA-*b*-PS diblock copolymers with different compositions and molecular weight. The bright areas correspond to the PDMA microphase.

weight. The diblock copolymer with relatively equal weight fractions of both blocks, PDMA₄₈-*b*-PS₅₂^{59.0} (Figure 6a), shows alternating bright PDMA lamellae and dark PS lamellae oriented in different directions. Likewise, PDMA₃₆-*b*-PS₆₄^{78.8} (Figure 6b) shows a similar morphology. By increasing the PS weight fraction further to 75 (Figure 6c) and 80 wt % (Figure 6d), both parallel and perpendicular orientation of PDMA cylinders surrounded by a PS matrix was obtained.

P4VP-*b*-PS diblock copolymers were synthesized with a similar composition and molecular weight as those of the previously discussed PDMA-*b*-PS. Figure 7 illustrates the bulk morphology of (a) P4VP₂₅-*b*-PS₇₅^{86.6} and (b) P4VP₂₀-*b*-PS₈₀^{107.3} diblock copolymers. For both diblock copolymers, P4VP spheres within a PS matrix are observed. The total degrees of polymerization are 626 for P4VP₂₅-*b*-PS₇₅^{86.6} and 825 for P4VP₂₀-*b*-PS₈₀^{107.3} (with $N_{\text{P4VP}} = 201$, $N_{\text{PS}} = 625$, and $N_{\text{PS}} = 824$). By comparing the bulk structure with the PDMA-*b*-PS diblock copolymers with a similar degree of polymerization and composition (Figure 6c,d) with $N_{\text{PDMA}} = 209$ and $N_{\text{PS}} = 627$ and $N_{\text{PS}} = 803$, it is evident that the diblock copolymers segregate in different morphologies.

Since the segregation strength of PDMA-*b*-PS is notably weaker than that of P4VP-*b*-PS (with $\chi_{\text{PDMA/PS}}^{\text{PDMA/PS}}$ being approximately three times smaller than $\chi_{\text{P4VP/PS}}^{\text{P4VP/PS}}$), it was unexpected that, with a similar degree of polymerization and

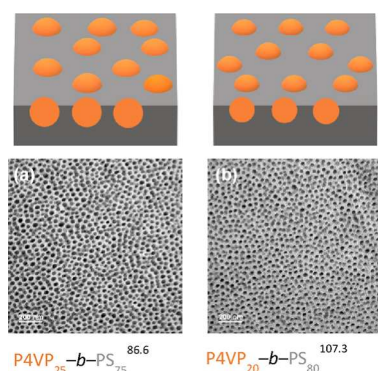


Figure 7. Bulk morphology of two different P4VP-*b*-PS diblock copolymers. The dark areas correspond to the iodine-stained P4VP microphase.

composition, PDMA would form cylindrical microdomains while P4VP formed spherical ones. The unexpected results can be attributed to the film preparation process. During this procedure, the diblock copolymers were diluted in chloroform and the chloroform was allowed to evaporate slowly. Due to the exchange of air between the desiccator and the ambient environment, humidity had the potential to enter the system. Since PDMA is a relatively hygroscopic polymer and water acts as a good solvent for PDMA while being a nonsolvent for PS, it becomes evident that the presence of water can lead to swelling of the PDMA domains. Therefore, the increase in the total volume fraction of PDMA can result in a transition from spherical to cylindrical microdomains. After allowing the samples to dry for several days above the glass transitions, residual water was still observed which was confirmed by TGA and FTIR experiments. This observation implies that water persisted within the polymer.

3. CONCLUSIONS

Visible-light-induced RAFT polymerization was employed to establish easily tailorable and robust pathways for the synthesis of amphiphilic diblock copolymers PDMA-*b*-PS and P4VP-*b*-PS without relying on additional initiators or catalysts. The reaction kinetics for the *ab initio* emulsion polymerization in the synthesis of both diblock copolymers was investigated, revealing distinctions in the reaction course depending on which macroCTA was used to initiate the polymerization. Using macroCTAs with a comparable degree of polymerization for PDMA and P4VP, it was observed that, to produce the amphiphilic diblock copolymer essential for the formation of latex particles, 2.5 times more styrene units are needed to be added to the PDMA macroCTA compared to P4VP. The evolution of latex particle size was investigated, and non-agglomerated latex particles were obtained in this synthesis approach. In addition to the conventional two-step route, which creates well-defined diblock copolymers, the semibatch process has been proven to be a suitable approach for synthesizing copolymers, especially DMA and styrene copolymers, since a sharp transition between the PDMA block and PS block is obtained. Therefore, the semibatch process facilitates the polymerization process, resulting in a notable reduction in the time expenditure within a workday.

Since photopolymerizations are influenced by spatial parameters such as the distance to the light source or the surface of the reaction vial, we investigated the influence of vessel dimensions on the polymerization kinetics. Despite the

turbidity of the reaction medium, high conversions can be obtained in all reaction volumes from 20 to 500 mL. We can primarily identify a time delay in the first polymerization phase, affecting amphiphilic copolymer generation. Therefore, to ensure the same product properties, the polymerization time must be slightly adjusted by choosing a different polymerization scale.

A TEM investigation of the bulk morphology of PDMA-*b*-PS and P4VP-*b*-PS diblock copolymers revealed diverse structures at equivalent compositions of the diblock copolymers. The production of further polymers at high throughput and with reliable outcomes, while keeping the reaction liquid eco-friendly, will enable the application of these diblock copolymers in various fields of material science.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.macromol.3c02256>.

Additional information about the full experimental details, experimental setup of the photoreactor, PDMA and P4VP macroCTAs, emulsions, determination of the conversion via NMR analysis, first-order plot of the synthesis of P4VP-*b*-PS diblock copolymers, additional information on the semibatch synthesis of PDMA-*b*-P(DMA-*grad*-S)-*b*-PS and P4VP-*b*-P(4VP-*grad*-S) copolymers, additional TEM images of the particles, TEM histograms, hydrodynamic and particle radii determined by TEM of the *ab initio* emulsion polymerizations, and estimation of the average number of radicals per particle (PDF)

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Author Contributions

The manuscript was written through the contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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5.3 Publication 3

Building on the foundational work outlined in the previous two publications, which focused on the synthesis of polymers *via* RAFT polymerization, this publication explores the application of amphiphilic PDMA-*b*-PS diblock copolymers in membranes. The corresponding PDMA-*b*-PS diblock copolymers were synthesized as described in publication 2 and subsequently employed to fabricate isoporous membranes using the SNIPS (self-assembly and nonsolvent-induced phase separation) process. The casting solution composition and membrane formation parameters were systematically optimized to enable the production of isoporous membranes on a larger scale.

Following membrane fabrication, a post-modification process was carried out to convert the pore-forming PDMA block into PAA. This modification rendered the membranes pH-responsive, with water permeance decreasing at higher pH levels due to the increased stretching of the negatively charged PAA chains.

Due to the small nanometer-scale pore size of the isoporous PAA-*b*-PS membranes in water, the membranes were evaluated for protein separation. At physiological pH of 7.4, corresponding to the pH of blood, the membrane pores carried a negative charge. This resulted in higher rejection rates for negatively charged proteins compared to positively charged proteins of similar size. In separation experiments involving a mixture of cytochrome C, a positively charged protein with a hydrodynamic radius of 1.6 nm, and other proteins, the PAA-*b*-PS membranes demonstrated selectivity for cytochrome C. This selectivity was attributed to the combined size- and charge-selective properties of the membrane, highlighting its potential for precise protein separation in biotechnological and biomedical applications.

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pH-responsive size- and charge-selective block copolymer membrane for the separation of small proteins

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ABSTRACT

Blue-light-induced RAFT polymerization was utilized to synthesize poly(*N,N*-dimethylacrylamide)-*block*-polystyrene (PDMA-*b*-PS) diblock copolymers to obtain 40 g per batch for membrane fabrication. Using a combination of self-assembly and non-solvent induced phase separation (SNIPS), larger isoporous membranes ($\approx 0.5 \text{ m} \cdot 0.3 \text{ m}$) were fabricated with pore diameters of $\approx 25 \text{ nm}$ in the dry state and around 4 nm in the wet state. These membranes were post-modified with hydrochloric acid to impart negatively charged, pH-responsive poly(acrylic acid)-*block*-polystyrene (PAA-*b*-PS) membranes. While all proteins like cytochrome C, insulin, lysozyme, myoglobin, and ovalbumin were fully rejected by the pristine PDMA-*b*-PS membrane, the PAA-*b*-PS membrane demonstrated selective rejection based on protein size and charge, effectively rejecting the proteins with a hydrodynamic radius $R_h \geq 1.9 \text{ nm}$. The PAA-*b*-PS membrane showed a real selectivity of 4.1 for the positively charged protein cytochrome C compared to the similarly sized, but negatively charged insulin, as well as a real selectivity of 16.1 towards the negatively charged ovalbumin. This illustrates the size- and charge-selective characteristics of the PAA-*b*-PS membrane for protein separation.

1. Introduction

The increasing population and the associated energy consumption are driving the demand of sustainable technologies with low energy consumption, particularly in industrial processes. New materials for the tailor-made separation of components are increasingly needed [1]. Membranes are a preferable choice since the separation requires less energy compared to most separation processes, as no phase transition energy is required [1–3]. Beyond that, choosing selective membranes offers the opportunity to perform the separation process under moderate conditions which is especially important for handling sensitive substances and enables their applicability in biomedical fields [4]. Block copolymers are ideal materials for forming selective membranes with well-defined pore size and functionality due to their ability to form self-organized structures. This makes them promising candidates for various applications primarily in the ultrafiltration regime. Tailorable block copolymer properties such as the Flory–Huggins–Staverman interaction parameter χ (which depends on the selection of the monomers), the overall degree of polymerization N , the volume fraction of the component blocks f and the particular polymer architecture determine

the structure on the nanoscale [5].

A facile and straightforward technique to fabricate integral asymmetric isoporous block copolymer membranes with a selective top layer and a highly porous substructure is the combination of self-assembly (S) and non-solvent induced phase separation (NIPS), known as the SNIPS process [6]. Herein, the minor block acts as the pore-forming block, while the major block forms the matrix of the isoporous layer. The integral asymmetric membranes obtain a selective and rather dense top surface, and underneath a sponge-like substructure with increasing porosity towards the bottom [7]. In addition to flat sheet membranes [8], this technique enables as well the fabrication of hollowfiber membranes [9–11].

There are several strategies to reduce the effective pore size of flat sheet block copolymer membranes from the ultra- to nanofiltration regimes. Integrating stimuli-responsive blocks as pore-forming block of the membrane, triggered by external stimuli like CO_2 [12], temperature [13] or pH-responsiveness [13–15] alters the stretching behavior of the pore forming block from collapsed to stretched state, thereby influencing the pore size over a broad range. Alternatively, techniques such as blending block copolymers [16], selectively swelling hydrophilic

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pore-forming blocks [17], post-functionalization [18–21], as well as cross-linking [22–24] have been developed to fine-tune the effective pore size of block copolymer membranes. These strategies enable separations at length scales which are conventionally unavailable with block copolymer membranes, making them attractive candidates for separations of proteins [20,25,27] and even dyes [22,28,29]. Mainly larger proteins like bovine serum albumin (BSA), hemoglobin, catalase and γ -globulin can be separated by block copolymer membranes [20, 30–34]. Zhang et al. demonstrated that a polystyrene-*block*-poly (4-vinylpyridine) (PS-*b*-P4VP) membrane, after adjusting the pore size by the sequential infiltration synthesis with inorganic compounds and subsequent post-functionalization with a cationic molecule, became suitable for separating similarly sized, but oppositely charged proteins lysozyme and β -lactoglobulin. The membrane exhibited a selectivity for β -lactoglobulin over lysozyme [35].

The scalability of block copolymer synthesis has posed a significant challenge for decades due to the requirement to exclude oxygen and the sensitivity of other ingredients like water, especially in anionic polymerization processes. Through the development of reversible deactivation radical polymerization (RDRP) techniques, the synthesis of such block copolymers can be performed via a radical polymerization process which is less prone to impurities. On top, it enables the polymerization in aqueous media and with external stimuli such as light [36]. These advancements permit polymerizations to be carried out under more environmentally friendly conditions, saving energy and reducing the usage of volatile organic compounds (VOCs).

Herein, via blue-light-induced RAFT polymerization, poly(*N,N*-dimethylacrylamide)-*block*-polystyrene (PDMA-*b*-PS) diblock copolymers were synthesized with polymer batch yields of 40 g each and copolymer composition ranging between 20 wt% and 23 wt% PDMA, and with a total molecular weight around 105 kDa. High reproducibility and scaling-up feasibility of the photoiniferter approach was observed, as previously demonstrated [37,38]. The casting parameters for the fabrication of isoporous membranes using the SNIPS process were optimized. Subsequently, the membrane was post-modified to create the pH-responsive poly(acrylic acid)-*block*-polystyrene (PAA-*b*-PS) membrane. The obtained size- and charge selective membrane showed promising application potential for the separation of small proteins with hydrodynamic radii ranging between 1.5 nm and 2.8 nm.

2. Experimental

2.1. Materials

2-(Dodecylthiocarbonothioylthio)-2-methylpropionic acid (DDMAT) (Sigma-Aldrich, stored at 4 °C) was used as received. *N,N*-dimethylacrylamide (DMA) (Sigma Aldrich) and styrene were deionized over activated basic aluminum oxide (Carl Roth) prior to each polymerization. Ultrapure water (Milli-Q® quality, resistivity > 18.2 M Ω cm⁻¹) was obtained from a Milli-Q® water purification system (Siemens Labostar). Ethanol ($\geq$ 99.9 %, Merck), *N,N*-dimethylformamide (DMF) ($\geq$ 99.8 %, Merck), dioxane ($\geq$ 99.5 %, Carl Roth), and tetrahydrofuran (THF) ($\geq$ 99.8 %, Merck) were used as received. Deuterium oxide (D₂O) and deuterated THF (THF-*d*₈) were purchased from Deutero GmbH. Poly (ethylene oxide) of different molecular weight (1–100 kDa) and low molecular weight distribution were purchased from Sigma Aldrich. The proteins cytochrome C ($\geq$ 95 %, from bovine heart, Sigma Aldrich), lysozyme ($\geq$ 98 %, from chicken egg white, Merck) and myoglobin ($\geq$ 90 %, from equine heart, Sigma Aldrich) were stored at -20 °C. Insulin (human, 99.99 % MedChemExpress), as well as Ovalbumin (from chicken egg white, $\geq$ 80 % Himedia) were stored at 6 °C and used as received.

2.2. Determination of the viscosity of casting solutions

The casting solutions were prepared by dissolving the PDMA-*b*-PS

diblock copolymers in the respective solvent system and the solutions were allowed to rest for several hours before the measurement. The viscosities of the diblock copolymer solutions were measured using an Anton Paar® MCR 502 rheometer with concentric cylinder cup geometry (CC17) at a temperature of 25 °C. The viscosities were determined for shear rates between 0.01 and 100 s⁻¹ (see Fig. S1). The reported viscosities correspond to the values determined at a shear rate of 1 s⁻¹.

2.3. Membrane fabrication

Casting solutions were prepared by dissolving the PDMA-*b*-PS diblock copolymers at a concentration of 33–34 wt% in a ternary solvent mixture (dioxane:THF:DMF 60:20:20 (w/w/w)). The solutions were prepared by stirring at room temperature for a minimum of 48 h before casting and allowed to rest for some hours before the membrane fabrication. Flat sheet membranes were cast using the SNIPS process. A home-made casting machine was used [39]. A gap distance of 100 μ m between the doctor blade and the polyester non-woven support was adjusted. The evaporation time before immersion into the water bath was controlled by the casting speed and optimized to obtain the highest pore uniformity. After casting, the flat sheet membranes stayed in water bath for at least 60 min. Afterwards, the membranes were dried for a minimum of 48 h under vacuum at 60 °C.

2.4. Membrane post-functionalization

PDMA-*b*-PS diblock copolymer membranes were post-modified under acidic conditions with 6 M hydrochloric acid at 80 °C for 24 h. Thereafter, the membranes were washed several times with deionized water to remove the unreacted components and byproducts.

2.5. Membrane characterization

2.5.1. Scanning electron microscopy (SEM)

Scanning electron microscopy investigations were carried out to observe both the membrane's top surface and cross-section morphology on a Merlin (Zeiss, Germany) using an acceleration voltage of 1–5 kV, respectively. A CCU-010 coating device (Safematic Switzerland) was used to coat approx. 1 nm platinum on the sample surface. SEM images were subsequently analyzed using the software IMS (Imagic Bildverarbeitung AG, Switzerland) to determine the average pore size of membranes. The denoted pore size and distribution as well as surface porosity were determined by analyzing 3–5 images, each taken at different positions within the membrane, with a magnification of 100 K.

2.5.2. Attenuated total Reflectance Fourier Transform Infrared (ATR-FTIR) spectroscopy

ATR-FTIR spectroscopy was conducted with a Bruker Alpha (diamond-ATR unit).

2.5.3. Water permeance

Water permeance measurements were performed in dead-end mode using a homemade device. To condition the samples, membranes were immersed in demineralized water overnight. A transmembrane pressure (Δp) of 2 bar was applied and the samples were measured at room temperature. The change in weight of the permeate Δw by time Δt was recorded. Triple determination was carried out. The permeance P was calculated in the following way, with ρ representing the density of the permeate and A the surface area of the membrane:

$$P = \frac{\Delta w}{A \cdot \rho \cdot \Delta t \cdot \Delta p} \quad (1)$$

The pH-dependent permeances were determined in dead-end mode using a homemade device at a transmembrane pressure of 2 bar. To adjust the pH, the solutions were prepared with hydrochloric acid or sodium hydroxide and the pH value of each solution was determined

with a FiveEasy™ pH bench meter with a pH electrode LF410 (Mettler Toledo). The membrane samples were first measured at pH = 1.0, and thereafter the pH was increased by replacing the aqueous solution. After completing the measurement at pH of 11.0, the solutions were stepwise exchanged with aqueous solutions of lower pH. The measurements at each pH were conducted for at least 6 h to ensure the samples were fully equilibrated. The entire protocol was performed in duplicate.

2.5.4. Permeance measurements of a perfluorinated solvent

A homemade measurement device was used to determine the permeances of perfluoro(methylcyclohexane) in a dead-end mode at room temperature. A transmembrane pressure of 1 bar was applied. The change in weight of the permeate Δw by time Δt was recorded. Double determination was carried out. The determination of the permeance followed the same way as described in 2.5.3.

2.5.5. Molecular weight cut-off (MWCO) experiments

For the determination of the molecular weight cut-off, poly(ethylene oxide) (PEO) of different molecular weights ranging from 1 kDa to 100 kDa and low molecular weight distributions were tested individually. Each PEO sample was diluted in deionized water to a concentration of 1 g L⁻¹. A transmembrane pressure of 2 bar was applied and the samples were measured at room temperature. A double determination was carried out. The retention R of the PEO was determined by the following equation:

$$R = 1 - \frac{w(\log M)_p}{\frac{w(\log M)_f + w(\log M)_r}{2}} \quad (2)$$

where $w(\log M)_p$, $w(\log M)_f$ and $w(\log M)_r$ represent the mass portion of PEO of the respective molecular weight in the permeate, feed and retentate, respectively. The concentration of the PEO samples in the feed and the permeate was measured by size exclusion chromatography (SEC). SEC measurements were performed at 25 °C in bidistilled water with 0.5 g L⁻¹ sodium azide. A flow rate of 1.0 mL min⁻¹ was adjusted using a VWR-Hitachi L-2130 pump. Analysis was conducted using a PSS® SUPREMA 10 µm precolumn, and two PSS® SUPREMA 10 µm columns, with a porosity of 3000 Å and 100 Å, respectively. Detection was performed using a Chromaster 5450 RI detector. For the determination, a PEO calibration was used. The correlation of hydrodynamic radius R_h (in nm) and molecular weight MW (in Da) is given by the following equation [40]:

$$R_h = 0.06127 \cdot MW^{0.3931} \quad (3)$$

The herein denoted MWCO value corresponds to a retention of 95 % of the solute.

2.5.6. Protein adsorption

Protein adsorption experiments were conducted using the proteins cytochrome C, insulin, lysozyme, myoglobin, and ovalbumin. Protein solutions were prepared in a phosphate-buffered saline (PBS, pH = 7.4) at a concentration of 1 g L⁻¹ except insulin, whose concentration was decreased to 0.2 g L⁻¹ due to the low solubility in water. Block copolymer membrane samples and pure non-woven samples were immersed in a 2 mL protein solution in a sealed vial and shaken at 90 rpm at room temperature for 24 h to ensure the membrane reached the adsorption equilibrium. Thereafter, membrane samples were rinsed twice with 2 mL of the buffer solution for 30 min at 90 rpm to remove the not adsorbed proteins. The protein concentration was determined by a GENESYS 10S UV-VIS spectrometer (Thermo Scientific). The concentration of the proteins in the PBS solutions can be used to determine the mass of the adsorbed protein according to the following equation:

$$\text{adsorption} = \frac{m_0 - (m_1 + m_{w1} + m_{w2})}{A} \quad (4)$$

where m_0 is the initial mass of each protein, m_1 is the protein mass after

24 h of adsorption experiment, m_{w1} and m_{w2} are the protein masses after the 1st and 2nd rinsing with the PBS buffer, and A is the surface area of the membrane.

2.5.7. Protein retention measurements

2.5.7.1. Dead-end-flow. Protein retention performance was conducted in a dead-end-flow mode with a stirred test cell (EMD Millipore™ XFUF04701) at a transmembrane pressure of 1.9 – 4 bar at room temperature. Initially, diblock copolymer membranes were conditioned with freshly prepared phosphate-buffered saline (PBS, pH = 7.4) for a minimum of 2 h to reach full equilibrium. Thereafter, the feed solution was replaced with the protein solution (1.0 g L⁻¹, except insulin with 0.2 g L⁻¹). Retention of at least 2 different membrane pieces were analyzed, for each of them, a minimum of 4 different samples was measured. Long-term measurements between 2 and 5 days were conducted to obtain steady-state behavior after potential effects such as protein adsorption on the membrane and non-woven. The denoted retention values are derived from the steady-state region of the protein measurements. The protein content of the feed C_f and the permeate C_p was determined by a GENESYS 10S UV-VIS spectrophotometer (Thermo Scientific). The retention R of each protein was determined via the following equation where C_p , C_f and C_r are the concentrations of proteins in permeate, feed and retentate, respectively:

$$R = 1 - \frac{C_p}{\frac{C_f + C_r}{2}} \quad (5)$$

The ideal selectivity (ψ^i) of one protein (x) from another one (y) is expressed by the observed percentage transmissions τ of two different proteins by the following equation [41].

$$\psi_{x/y}^i = \frac{\tau_x}{\tau_y} \quad (6)$$

For the determination of the true selectivity (ψ^t), protein mixtures consisting of cytochrome C and the respective other protein were measured. The respective membrane was first conditioned with PBS puffer as described above and thereafter proteins solutions with 0.5 g L⁻¹ cytochrome C and 0.5 g L⁻¹ of the other protein were prepared (apart from the solution containing insulin, in which the concentration of cytochrome C and insulin were 0.1 g L⁻¹, respectively). The membrane was initially conditioned with PBS puffer as described above. Thereafter, the protein solutions measured in the dead-end mode at a transmembrane pressure of 4 bar. The measurements were performed for 3 days and the samples of the steady-state region of the protein measurements were taken for the analysis of the true selectivity. The true selectivity was determined by the transmission ratio of the two proteins similarly as described in Equation (6).

2.5.7.2. Cross-flow. Cross-flow experiments of protein solutions were performed using a Watson-Marlow 520S pump with a constant flow rate of 40 mL min⁻¹, a cross-flow velocity of 0.025 m s⁻¹, a transmembrane pressure of 1.9 bar and a feed volume of 300 mL. Initially, the membranes were measured for a minimum of 2 h with the PBS buffer solution to reach a fully equilibrated state. Afterwards, the feed solution was exchanged with the PBS-buffered protein solution with a protein concentration of 1 g L⁻¹. Retention of 2 different membrane pieces was analyzed and minimum 8 samples were taken during the measurement. The retention was determined in an analogous way as described in section 2.5.7.1.

3. Results and discussion

3.1. Polymer synthesis

PDMA-*b*-PS diblock copolymers were synthesized using blue-light-

induced RAFT polymerization [37,38]. The scalability of the polymerization process facilitated the synthesis of diblock copolymers up to a 500 mL scale, whereby almost 80 g of polymer can be synthesized. All polymers used herein were synthesized in the 250 mL scale, where the average polymer yield corresponds to 40 g. Well-defined PDMA-*b*-PS diblock copolymers were synthesized with weight fractions of the PDMA block ranging between 20 wt% and 23 wt% and total molecular weight between 102 kDa and 108 kDa (see Table S1). All block copolymers show low molecular weight distributions with $\bar{D} = 1.08 - 1.19$.

3.2. Membrane fabrication optimization via SNIPS

The groups of Boudaris and Philip [42,43] cast the polyisoprene-*block*-polystyrene-*block*-poly(*N,N*-dimethylacrylamide) (PI-*b*-PS-*b*-PDMA) membranes on a glass substrate with a relatively low polymer concentration of 15 wt% in 50:50 (w/w) dioxane:THF mixture. An average pore diameter of $53 \text{ nm} \pm 20 \text{ nm}$ was reported [42]. With the adapted parameters of 70:30 (w/w) dioxane:THF and 15 wt% polymer content, a pore diameter of $\approx 40 \text{ nm}$ in the dry state was observed [14]. To enhance the mechanical stability of the membrane, herein, PDMA-*b*-PS diblock copolymer membranes were cast on a non-woven substrate. Since the initial casting solution with 70:30 (w/w) dioxane:THF and 15 wt% polymer showed a relatively low viscosity of 0.06 Pa·s, a higher polymer concentration of 35 wt% was chosen to increase the viscosity to 16.5 Pa·s, preventing the polymer solution from soaking into the non-woven substrate. In addition, the evaporation time was decreased to form the assembled isoporous layer. These membranes showed an isoporous surface structure with a high pore uniformity compared to the PI-*b*-PS-*b*-PDMA membranes cast on glass [42]. According to the solubility parameters listed in Table S2, both THF and dioxane are expected to be better solvents for PS than for PDMA. Since both solubility parameters are relatively similar, we assume the presence of both solvents in the individual blocks. However, partially closed pores were still observed, with their number decreasing with increased dioxane content in the solution (see Fig. S2). Therefore, with an increased dioxane content, the proportion of volatile THF within the PDMA domains is decreased, thus reducing the chances of pore shrinkage due to evaporation. A further increase of the dioxane content over 70 wt% did not lead to a further improvement of the isoporous top surface; instead, pore connections were observed (see Fig. S3). However, by comparing the top surface structure of membranes cast at 6 s and 15 s evaporation time, shrinkage of the pore size and more closed pores were observed with prolonged evaporation time.

For further optimization, ternary dioxane-THF-DMF solvent systems were used for membrane casting. According to the solubility parameters of the SNIPS components [44,45] (see Table S2), DMF is a less-volatile selective solvent for the PDMA domains compared to the PS matrix domains. Based on the binary 70:30 (w/w) dioxane:THF mixture, replacing 10 wt% of dioxane and THF, respectively, with DMF has led to an isoporous surface structure with highly ordered hexagonally packed cylinders (see Fig. S4). Membranes were cast with 33 wt% to 34 wt% diblock copolymer content (depending on the specific diblock copolymer used) and the viscosities of the optimized casting solutions were $\approx 3 \text{ Pa}\cdot\text{s}$. The membranes exhibited an open substructure, interspersed with macrovoids (see Fig. 1).

We investigated the influence of relative humidity on the membrane morphology while maintaining a fixed evaporation time of 15 s (see Fig. 2). At humidities above 45 %, the membrane top surface exhibits coexistence of less uniform pores with larger pore size and interconnected pores along with the cylindrical/lamellar-like microstructure (see Fig. 2 (c) and (d)). The sensitivity to relative humidity was similarly reported for polystyrene-*block*-poly(2-hydroxyethyl methacrylate) (PS-*b*-PHEMA) membranes [19]. Therefore, air-conditioned environment was essential for casting the isoporous block copolymer membranes.

The use of a membrane casting machine facilitated the reproducible

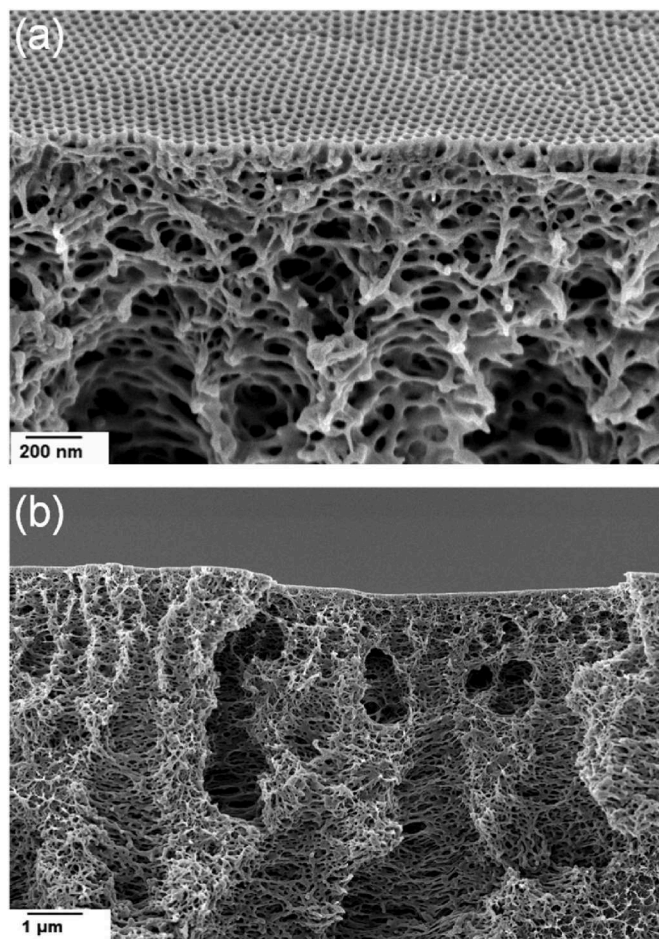


Fig. 1. SEM images of the cross-section of the M1 PDMA₂₃-*b*-PS₁₀₂ diblock copolymer membrane at a polymer concentration of 33.5 % (w/w) at an evaporation time of 15 s in dioxane:THF:DMF 60:20:20 (w/w).

fabrication of block copolymer membranes on larger scales with sizes up to $0.5 \text{ m} \cdot 0.3 \text{ m}$. Different segments of the membrane were examined by SEM and revealed a consistent isoporous surface with regular hexagonal PDMA pore pattern (see Fig. 3). A comparable pore size distribution, averaging $26.5 \text{ nm} \pm 3.7 \text{ nm}$, and a porosity of $25.9 \% \pm 1.4 \%$ were observed (for further details see Table S3). The cross-sections at the different spots within the membrane are displayed in Fig. S5.

With optimized casting parameters and achievement of uniform pore size and distribution across the entire membrane, several diblock copolymer membranes were cast in this larger format. Although the polymer and casting parameters were slightly varied, the resulting membranes exhibited consistency in pore size and porosity even with minor alterations in polymer composition and concentration (see Table 1). The membranes are consecutively numbered for identification. All membranes were cast in air-conditioned environments with relative humidities $\leq 43 \%$ and air temperatures T_{air} between 19°C and 21°C .

3.3. Post-modification

Based on the experiments conducted by Hillmyer's group [46], PDMA-*b*-PS membranes were functionalized with 6 M aqueous hydrochloric acid at 80°C (see Fig. 4 (a)). The course of the modification reaction was followed by ATR-FTIR spectroscopy (see Fig. 4 (b)). In contrast to their observation, a modification time of 24 h was sufficient to convert the amide groups (1630 cm^{-1}) to carboxylic acid groups (1710 cm^{-1}) in our study. Extending the duration to 48 h did not lead to a further significant enhanced conversion. Therefore, all PDMA-*b*-PS

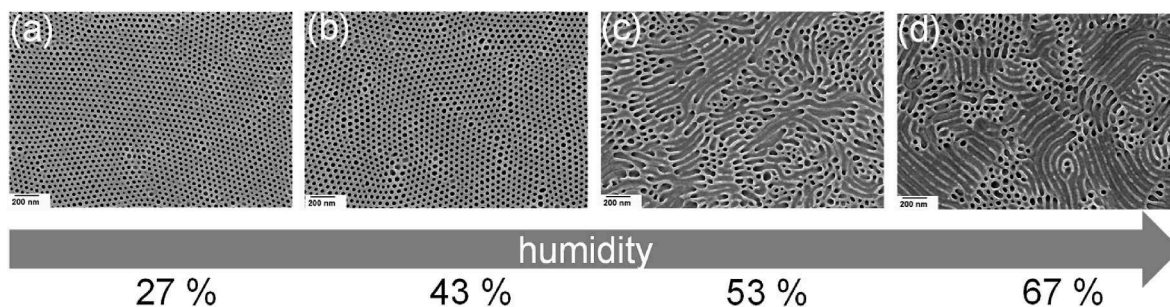


Fig. 2. Effect of humidity on the top surface of the PDMA₂₃-b-PS₁₀₅ diblock copolymer membranes.

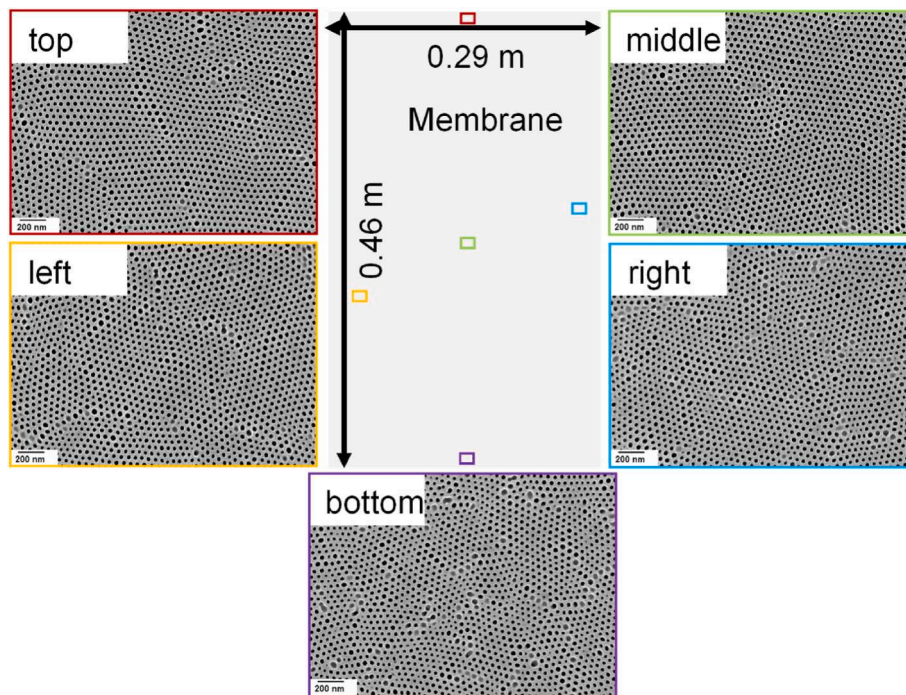


Fig. 3. Top-surface of the M2 PDMA₂₂-b-PS₇₈ membrane at different positions.

Table 1

Process parameters and membrane characteristics of PDMA-*b*-PS membranes.

Membrane	Polymer ^a	<i>c</i> [wt%] ^b	Relative humidity [%]	<i>T</i> _{air} [°C]	Pore size [nm] ^c	Porosity [%] ^c
M1	PDMA ₂₃ - <i>b</i> -PS ₇₇ ¹⁰²	33.5	29	21	25.2 ± 3.4	23.1 ^d
M2	PDMA ₂₂ - <i>b</i> -PS ₇₈ ¹⁰⁸	34	43	20	26.5 ± 3.7	25.9 ± 1.5
M3	PDMA ₂₂ - <i>b</i> -PS ₇₈ ¹⁰⁸	33	42	19	25.2 ± 2.8	22.7 ± 1.0
M4	PDMA ₂₂ - <i>b</i> -PS ₇₈ ¹⁰⁸	34	28	20	23.8 ± 3.3	21.5 ± 1.2
M5	PDMA ₂₀ - <i>b</i> -PS ₈₀ ¹⁰⁵	33	33	20	27.4 ± 6.6	26.5 ± 1.9

^a Subscripts denote the weight percentage of each block in the diblock copolymer, superscripts denote the number-average molecular weight determined by ¹H NMR spectroscopy.

^b Polymer concentration in the casting solution (in wt%).

^c Determined via SEM.

^d Due to the small membrane area analyzed, the standard deviation is not accurate and not denoted.

membranes were modified for 24 h.

After post-functionalization, SEM analysis reveals a slight reduction in the pore size of the membrane from the pristine membrane, measuring 25.2 nm ± 2.8 nm in the pristine membrane and 23.8 nm ± 2.6 nm in the post-modified membrane.

3.4. Permeance measurements

From the SEM images, the areas of the dark region (pores) A_{pores} , and

the bright areas (matrix) A_{matrix} , were determined by setting a critical grey value. The pore areas are defined by their individual surface area $\pi \cdot r^2$ multiplied by their quantity in the total area $N_{\text{in } A_{\text{total}}}$. To calculate the surface porosity Φ , the area of the pores is divided by the total area A_{total} :

$$\Phi = \frac{A_{\text{pores}}}{A_{\text{pores}} + A_{\text{matrix}}} = \frac{A_{\text{pores}}}{A_{\text{total}}} = \frac{\pi \cdot r^2 \cdot N_{\text{in } A_{\text{total}}}}{A_{\text{total}}} \quad (7)$$

Theoretical water flow rates were calculated via the Hagen-Poiseuille

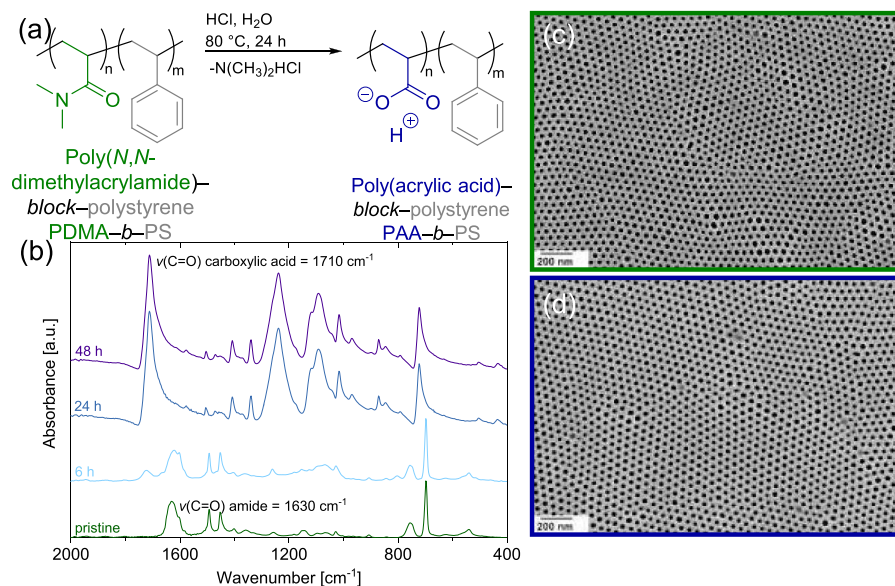


Fig. 4. (a) Schematic representation of the modification reaction of the PDMA-*b*-PS membranes. (b) Reaction monitoring of the modification via ATR-FTIR of the pristine PDMA-*b*-PS sample at 6 h, 24 h and 48 h of modification time. The intensities are normalized to the C-H stretching bond of polystyrene. Top surface structure of the (c) pristine M3 PDMA₂₂-*b*-PS₁₀₈ membrane and (d) the converted membrane after 24 h modification time.

equation which describes the volume flow $\dot{V}$ in a microchannel modeled as a straight cylinder according to the following equation:

$$\dot{V} = \frac{\pi \cdot r^4 \cdot \Delta p}{8 \cdot \eta \cdot L} \quad (8)$$

Herein, r is the average radius of the pores (determined by SEM, see Table 1), Δp is the transmembrane pressure, η denotes the viscosity of the fluid (water: $8.94 \cdot 10^{-4}$ Pa·s at 25 °C) and L is the length of the cylindrical pore (determined by SEM). For the calculation, it is assumed that the permeance is dictated by the selective layer and the spongy substructure is negligible. To determine the theoretical water permeance P_{theo} , the porosity Φ of the top layer must be considered according to the equation:

$$P_{\text{theo}} = \frac{\dot{V} \cdot N_{\text{in}} A_{\text{total}}}{A_{\text{total}} \cdot \Delta p} = \frac{\pi \cdot r^4 \cdot \Delta p \cdot N_{\text{in}} A_{\text{total}}}{A_{\text{total}} \cdot 8 \cdot \eta \cdot L \cdot \Delta p} = \frac{r^2 \cdot \Phi}{8 \cdot \eta \cdot L} \quad (9)$$

In this determination, the theoretical water permeance would be ≈ 900 L/(m² h bar). Water permeance measurements of the pristine PDMA-*b*-PS membranes is shown in Fig. 5 (b). Apart of the membrane M2, all membranes showed water permeances around ≈ 11 L/(m²·h·bar). This is mostly attributed to the swelling of the PDMA segments in aqueous media, as indicated in the scheme in Fig. 5 (a). Water permeance measurements were performed up to a transmembrane pressure of 4 bar. No influence of the pressure on the permeance was observed. To determine the permeance without any interaction with the ultrafiltration membrane, perfluorinated solvents are suitable for

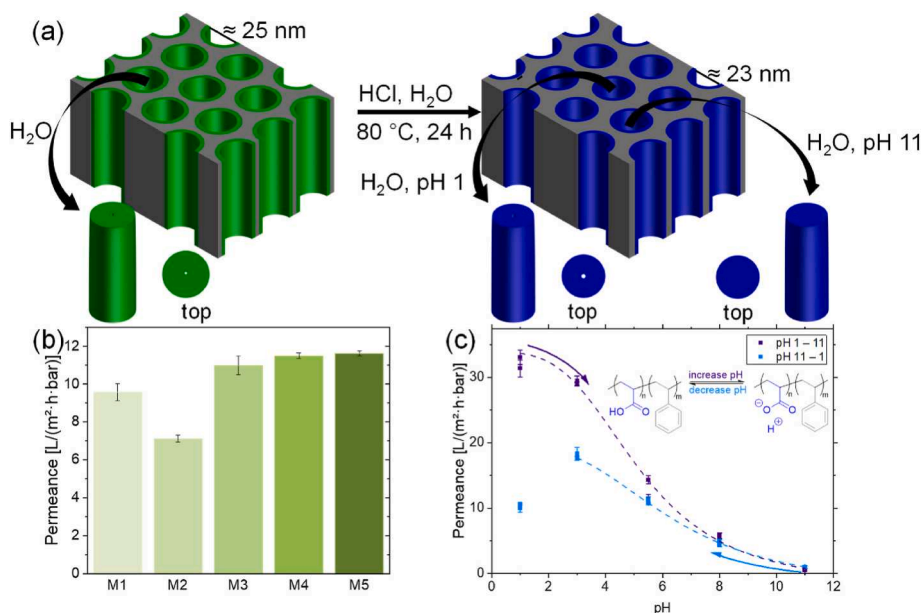


Fig. 5. (a) Schematic illustration of the PDMA-*b*-PS membrane in the dried and wet state (left) and of the PAA-*b*-PS membrane (right). (b) Water permeance of the different PDMA-*b*-PS membranes (M1-M5). (c) pH-dependent water permeance of the PAA-*b*-PS membrane.

comparable data independent of chemical composition [47]. Herein, perfluoro(methylcyclohexane) ($\eta = 1.56 \cdot 10^{-3}$ Pa·s) was used for permeance measurements of the PDMA-*b*-PS membrane. Permeances ranging from 200 – 350 L/(m²·h·bar) were determined.

Since PDMA is a non-stimuli responsive polymer, the water permeance remains unaffected by varying pH, as demonstrated for the PI-*b*-PS-*b*-PDMA membrane of Boudouris' and Phillip's groups [42]. PAA is a weak polyelectrolyte, rendering the membranes responsive to pH through the ionization-induced conformational transition (see scheme in Fig. 5 (c)). However, Swift et al. observed that this transition only occurred for PAA chains with a molar mass greater than 16.5 kDa [48]. At low pH, the protonated PAA units can form hydrogen bonds among each other, leading to a compact conformation of the pore forming block. This hydrogen-bonded network results in a permeance $\approx$ 32 L/(m²·h·bar) and therefore approximately threefold higher water permeance than that of the PDMA-*b*-PS membrane. Increasing the pH prompts the ionization of the PAA segments, resulting in chain stretching due to the repulsion between the negatively charged chains. This leads to a decrease of water permeance. Turning point of the water permeance is approximately at pH 5, consistent with the pK_a of PAA around 4.5 [48]. At a high pH of 11, the PAA segments are extended, so that the pores are nearly closed, resulting in a water permeance <1 L/(m²·h·bar).

By exchanging the highly basic solution with a more acidic one, some of the PAA units are once again protonated. However, compared to the previous cycle from pH 1 to 11, in the cycle from pH 11 to 1 a smaller fraction undergoes reprotonation due to the dominant electrostatic repulsions between the negatively charged chains, decelerating the increase of the pore size and inducing a hysteresis. In contrast to the observation of Weidman et al. [14], we did not observe a complete return to the original permeance, as we did not flush with deionized water after the trials. Therefore, likely more ionic interactions between the deprotonated PAA species and the sodium ions remained and were not fully compensated.

3.5. Molecular weight cut-off (MWCO)

Since pore swelling significantly affects the pore size of the membranes, retention measurements in aqueous media were performed using poly(ethylene oxide) (PEO) with different molecular weights ranging from 1 kDa to 100 kDa. Due to the high impact of the pH on the swelling behavior of the PAA chains, measurements were conducted in deionized water (pH = 5.5) and at a higher pH of 7.5 for applicability in biological systems. As depicted in Fig. 6 (a), the pristine PDMA-*b*-PS membrane showed the sharpest MWCO. While the membrane almost completely rejected only 22 % of PEO with 1 kDa, corresponding to a hydrodynamic radius of 0.9 nm, it fully rejected PEO with 10 kDa, resulting in a hydrodynamic radius of 2.3 nm. The MWCO at 95 % rejection was determined to be a MW_{PEO} of 8.5 kDa, which refers to a

hydrodynamic radius of 2.2 nm. The subsequent post-modification reaction resulted in a rejection shift toward higher molecular weight/solute radius. At pH 5.5, the MWCO of PAA-*b*-PS membrane with 95 % rejection was determined to be a MW_{PEO} of 83.5 kDa, corresponding to a hydrodynamic radius of 4.9 nm. This is in agreement with the higher permeance of the PAA-*b*-PS compared to the PDMA-*b*-PS membrane at pH = 5.5, as the larger PDMA chains than PAA chains result in smaller pores (at low pH). Through the stretching of the PAA segments, the MWCO at pH = 7.5 was determined to be 33.5 kDa, therefore an equivalent hydrodynamic radius of 3.7 nm.

It is obvious that the MWCO of the PAA-*b*-PS membrane, especially at pH = 5.5, is not as sharp as the one of the pristine PDMA-*b*-PS membrane. Initially, a linear increase in retention with increasing molecular weight of the PEO is observed. However, when the retention exceeds roughly 80 %, only marginal increases are observed with higher molecular weight. One feasible reason for this phenomenon could be the hydrogen bonding interaction between the terminal OH groups of the PEO with the carboxylic groups of the PAA. It has been established that both free and intermolecular hydrogen bonds exist in a PAA/PEO blend [49]. These intramolecular interactions could facilitate the passage of PEO through the membrane. Since at the pH of 5.5 more protonated carboxylate groups are present compared to the pH of 7.5, this phenomenon could also explain the more pronounced widening of the retention course at pH of 5.5. Therefore, the real MWCO value might be even smaller than the determined one.

3.6. Protein separation

Herein, five different proteins with different sizes and charges were used as model compounds for protein separation tests. Their characteristics are displayed in Table 2. Proteins pairs with similar size, but opposite charge were chosen: cytochrome C and insulin as well as lysozyme and ovalbumin, respectively. Cytochrome C and lysozyme are

Table 2
Characteristics of the analyzed proteins.

Protein	Molecular weight [kDa]	Isoelectric point	R_h [nm]	Dimensions [nm × nm × nm]	Wavelength [nm]
Cytochrome C	12.5	9.59 [50]	1.6 [51]	2.5 × 2.6 × 3.7 [52]	530
Insulin	5.8	5.4 [53]	1.5 [54]	2.5 × 3.0 × 3.2 [55]	277
Lysozyme	14.3	11.35 [51, 56]	1.9 [57]	3.0 × 3.0 × 5.0 [58]	280
Myoglobin	17.0	7.10 [59]	2.1 [60]	2.1 × 3.5 × 4.4 [61]	280
Ovalbumin	42.8	4.5 [62]	2.8 [63]	3.0 × 3.6 × 7.0 [64]	279

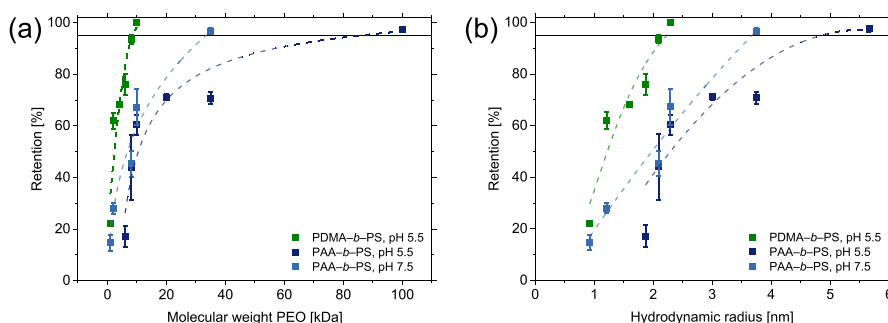


Fig. 6. (a) MWCO and (b) solute rejection curves for the pristine PDMA-*b*-PS membrane and the PAA-*b*-PS membrane using poly(ethylene oxide) (PEO) with different molecular weights. MWCO was determined for both membranes in deionized water (pH = 5.5); additionally, a MWCO of the PAA-*b*-PS membrane was conducted at pH = 7.5 as reference value for the protein measurements.

both positively charged at the pH of 7.4, meanwhile insulin and ovalbumin are negatively charged. Although ovalbumin has a higher hydrodynamic radius than lysozyme, it is in the first two dimensions similar in size to lysozyme. Myoglobin (Myo) serves as the fifth protein since it is relatively uncharged at the examined pH.

The adsorption behavior of the five different proteins was tested to evaluate the fouling behavior, a crucial consideration in practical application. Furthermore, understanding the impact on the effective pore diameter is important as adsorbed proteins can significantly reduce the pore size or even entirely block the pores [65]. In preliminary tests with the non-woven material, it was observed that insulin adsorbs on the non-woven. Therefore, the adsorption of insulin, as shown in Fig. S6, is only induced by the non-woven material and not by the PDMA-*b*-PS or PAA-*b*-PS polymer. None of the investigated proteins were found to adsorb on the PDMA-*b*-PS membrane. However, due to the negative charge on the PAA-*b*-PS membrane, both positively charged proteins, cytochrome C and lysozyme, adsorb on the membrane as illustrated in Fig. S6 (b). This observation was expected due to the electrostatic interaction between the positively charged proteins and the negatively charged PAA units.

Fig. 7 (a) shows the retention of the five different proteins in the PDMA-*b*-PS membrane. Notably, all proteins were almost completely rejected by the pores of the PDMA-*b*-PS membrane. It was expected that both cytochrome C and insulin might permeate through the membrane due to their smaller hydrodynamic radius compared to the hydrodynamic radius of 2.2 nm, determined via MWCO of the PDMA-*b*-PS membrane (size sieving). However, the initial flushing of the membranes with the PBS buffer resulted in the permeance of ≈ 8 L/(m²·h·bar), therefore ≈ 3 L/(m²·h·bar) less than the permeance of the deionized water. Buffer can influence the permeability due to the salt-membrane and salt-analyte interactions, as well as variations in ionic strengths [66]. We hypothesize that the effective pore size of our membranes using the PBS buffer is slightly reduced compared to pure aqueous media.

Through the post-modification, the size of the pores changed as indicated in Fig. 6 (b) and the charge of the PAA-*b*-PS membrane pores shifted from non to negatively charged. As shown in Fig. 7 (b), the proteins myoglobin and ovalbumin were nearly fully rejected, while cytochrome C, insulin and lysozyme can permeate through the membrane. At the isoelectric point of the protein, it becomes uncharged and therefore the transport through the membrane is governed by size exclusion rather than charge interactions. Hence, the high rejection of myoglobin is only induced by size sieving. For the other four proteins, both the charge and the chemical interactions of the protein with the membrane play a major role. While the nanochannels of the modified membrane allowed cytochrome C to permeate through, only 23 % of the similarly sized, but negatively charged insulin could permeate through the membrane. This might be caused by the electrostatic repulsion between the charged insulin molecules with the likewise charged pores. Moreover, the electrostatic repulsion between protein and the

membrane might also enhance the rejection of ovalbumin compared to lysozyme; however, the size sieving is likely the more dominant factor for the high rejections.

Of special interest are the separation performances of cytochrome C and lysozyme. Besides the slightly different hydrodynamic radii, the main difference between these proteins is the number of arginine residues (2 for cytochrome C and 11 for lysozyme) and the number of lysine residues (19 for cytochrome C and 6 for lysozyme) [67]. However, Zydney's group observed that in ultrafiltration and ion exchange chromatography, the protein sieving coefficient through the oppositely charged membranes is determined almost entirely by the net surface charge density of the protein, rather than the charge distribution within the protein [67]. Both proteins exhibit a net protein charge of $\approx +7$ at pH = 7.4 [68]. Likewise, both proteins can form hydrogen bonds along the channels which can facilitate the transport through the membrane [69]. In contrast to the other proteins, a time-dependency of the retention and the permeance was observed for cytochrome C and lysozyme. In the dead-end measurement of cytochrome C, an decrease in permeance (see Fig. 8 (a)) and a decrease in retention (see Fig. 8 (b)) is observed over time. Initially, the proteins adsorb to the membrane, resulting in high rejections. Thereafter, once the membrane becomes fully saturated with protein, the transport through the membrane is governed not only by size-exclusion, but also by electrostatic and chemical interactions. Obviously, it takes some time until an equilibrium is reached. The permeance is significantly reduced by proteins compared to the pure PBS buffer solution, as the effective diffusion coefficient was greatly decreased with the negatively charged nanopores in addition to a steric effect [70]. A similar observation of the time-dependent permeance and rejection was noted for the lysozyme measurement. Therefore, the rejections of cytochrome C and lysozyme as denoted in Fig. 7 (b) correspond to the values in the steady-state region from Fig. 8. The permeance of lysozyme is approx. 9-times smaller than of cytochrome C, and likewise the rejection of 90 % is nearly 30 times higher than of cytochrome C. Since in the experiments with lysozyme the lowest permeance among all protein experiments was observed, we assume that the pores of the membrane are mainly blocked by the lysozyme molecules. Additional experiments of these two proteins in the cross-flow mode were performed (see Fig. 8). A remarkable increase in rejection is observed for cytochrome C compared to the measurements obtained in the dead-end-flow mode. Since the transport through the membrane is promoted by chemical and electrostatic interactions, fewer potential interactions might occur or the interactions might be disrupted by the shear forces of the filtering fluid parallel to the membrane as well as the reduction of concentration polarization in cross-flow mode. This results in slightly higher rejections compared to the dead-end mode measurement. In the case of lysozyme, pore blockage is likely the dominant factor contributing to the low permeance, with a slight, though not significant increase observed in the cross-flow mode measurement. Likewise, the retention appears to be nearly unaffected by the measurement method. However, a significant difference in rejection

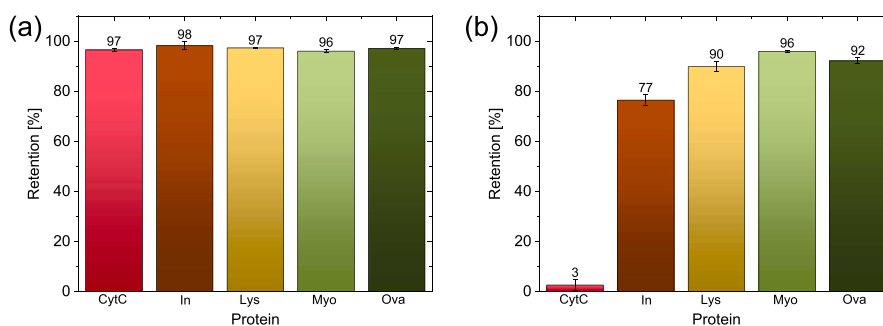


Fig. 7. Protein retention of the (a) pristine PDMA-*b*-PS membrane and (b) PAA-*b*-PS membrane measured in the dead-end mode in the PBS-buffered system at pH = 7.4.

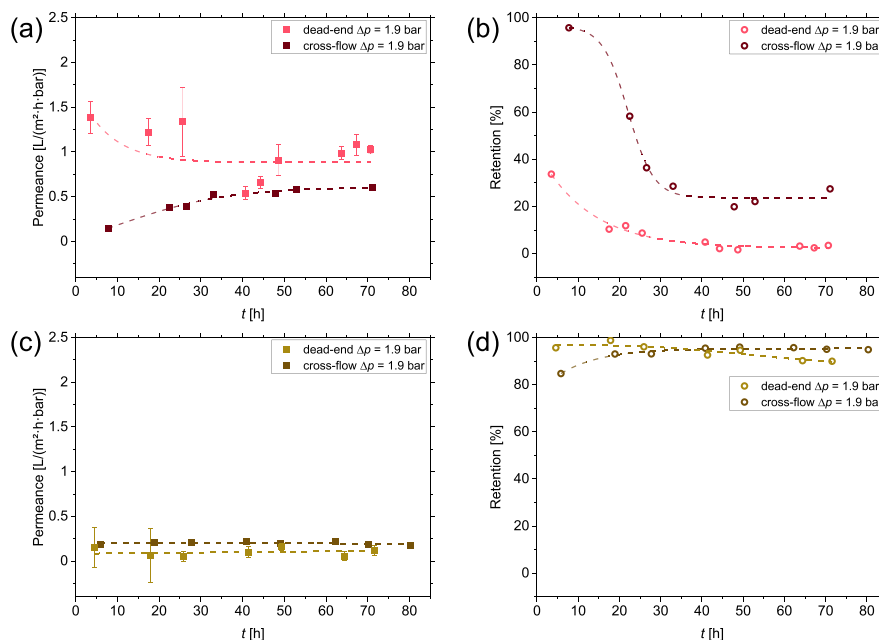


Fig. 8. (a),(c) Permeance and (b),(d) retention of the PAA-*b*-PS membrane in the measurement of cytochrome C (a),(b) and lysozyme (c),(d) in dead-end and cross-flow mode in the PBS-buffered system at pH = 7.4.

between cytochrome C and lysozyme can be observed in both, dead-end and cross-flow mode. Therefore, we assume that the difference in the rejections is mainly due to the differences in adsorption. Lysozyme adsorbs more strongly onto the membrane than cytochrome C (see Fig. S6), leading to greater pore blockage. This increased adsorption combined with the higher molecular weight of lysozyme results in smaller effective pore sizes and consequently higher retention.

Through the described effects of size exclusion, as well as electrostatic and chemical interactions, the investigated PAA-*b*-PS membrane exhibits selectivity for the cytochrome C. The ideal selectivities are provided in Table 3. However, it should be noted that the selectivities of real protein mixtures can significantly deviate from the ideal protein selectivities due to interactions between the proteins. Therefore, measurements of the protein mixtures were performed. Whereas the initially assumed high ideal selectivity of cytochrome C against lysozyme was not confirmed by the real selectivity due to the blockage of the pores caused by lysozyme, the PAA-*b*-PS membrane showed charge selectivity of cytochrome C against the similarly sized insulin. As well, the charge- and size selective properties of the PAA-*b*-PS membrane engendered a true selectivity of 16.6 for cytochrome C compared to ovalbumin, which exceeds the ideal selectivity of 12.4. For larger proteins like myoglobin, we expect an even higher true selectivity for cytochrome C, as already indicated by the ideal selectivity in Table 3. However, the real selectivity

Table 3

Ideal selectivity ψ^i of cytochrome C in comparison to the other proteins from single-solute experiments and real selectivity ψ^r of mixed solutes containing cytochrome C and the respective protein on the PAA-*b*-PS membrane in dead-end mode.

Ideal selectivity ψ^i			
$\psi_{\text{CytC/In}}^i$	$\psi_{\text{CytC/Lys}}^i$	$\psi_{\text{CytC/Myo}}^i$	$\psi_{\text{CytC/Ova}}^i$
4.1	9.6	24.3	12.4
Real selectivity ψ^r			
$\psi_{\text{CytC/In}}^r$	$\psi_{\text{CytC/Lys}}^r$	$\psi_{\text{CytC/Myo}}^r$	$\psi_{\text{CytC/Ova}}^r$
4.0	1.0	— ^a	16.3

^a Could not be determined due to overlapping of both proteins in the UV-VIS spectrum.

could not be determined due to the overlapping of both proteins in the UV-VIS spectrum.

Compared to most other block copolymer membranes, the PAA-*b*-PS membrane effectively separated small-sized proteins that would pass through most other isoporous membranes. Using a PS-*b*-P2VP ultrathin polymer covering film anodic aluminum oxide composite membrane, it obtained a rejection of 95 % ovalbumin, whereas only 22 % cytochrome C was rejected [71]. Polystyrene-*block*-poly(*tert*-butoxystyrene)-*block*-polystyrene (PS-*b*-PtBOS-*b*-PS) copolymer membranes modified with imidazole and pyridine exhibited a cytochrome C rejection of 33 % [69]. Comparable rejections of cytochrome C and ovalbumin were obtained only with a layered mesoporous silica thin membrane [72]. 93.4 % of cytochrome C permeated through the membrane, meanwhile 91.8 % of ovalbumin was intercepted. However, this membrane does not exhibit charge selectivity.

While previously described membranes demonstrated selectivity primarily based on pore size, additional post-modifications can not only reduce the pore size but also introduce charged groups into the pores of membranes. For protein separation, the post-modification of PS-*b*-P4VP with aluminum oxide and the introduction of a cationic group via reaction with *N*-[3-(trimethoxysilyl)propyl]-*N,N,N*-trimethylammonium chloride (TMS-TMAC) showed a selectivity of 5.5 for the negatively charged β -lactoglobulin over the negatively charged lysozyme [35]. Herein, an even smaller pore size was obtained with only one post-modification step, resulting in reverse charge selectivity compared to Zhang et al. [35] with a comparable charge selectivity of 4.1.

Interestingly, compared to our report, PS-*b*-PAA block copolymer micelles-based membranes exhibited compared to our report a similar rejection of 5 % for cytochrome C, but only 12 % rejection of ovalbumin. This shows that in addition to the selection of the block copolymer and post-modification process, the membrane production process also significantly influences to the separation performance. Therefore, the size- and charge-selective characteristics of the PAA-*b*-PS membrane hold promise for protein separation.

4. Conclusion

In this work, PDMA-*b*-PS diblock copolymers were synthesized using blue-light-induced RAFT polymerization in a highly reproducible

way. Optimal casting parameters were identified for the fabrication of PDMA-*b*-PS flat sheet membranes via SNIPS technique, resulting in highly ordered integral asymmetric isoporous membranes. Through a post-modification process, the PDMA domains were successfully converted to PAA, meanwhile preserving the membrane morphology. The PAA-*b*-PS membranes exhibited a pH-dependent water permeance and molecular weight cut-off, with decreasing water permeance at higher pH values. At the examined pH of 7.4, the membrane exhibited charge-selectivity, showing a true selectivity of 4.1 for the positively charged protein cytochrome C over similarly sized negatively charged protein insulin. Furthermore, the membranes showed size-selectivity for the smaller proteins with $R_h \leq 1.9$ nm, demonstrating a true selectivity of 16.1 for cytochrome C over the oppositely-charged and larger ovalbumin. Therefore, we developed a scalable block copolymer membrane with promising applicability in the separation of small proteins.

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CRediT authorship contribution statement

Lara Hub: Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Joachim Koll:** Writing – review & editing, Validation, Investigation. **Kristian Buhr:** Writing – review & editing, Validation, Investigation. **Maryam Radjabian:** Writing – review & editing, Supervision, Project administration, Conceptualization. **Volker Abetz:** Writing – review & editing, Supervision, Resources, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.memsci.2024.123021>.

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6 Unpublished Results

This chapter presents the key findings related to PDMA-*b*-PS/ P4VP-*b*-PS diblock copolymer blend membranes. It begins with a discussion of the preliminary tests conducted on the PDMA-*b*-PS/ P4VP-*b*-PS diblock copolymer blends, focusing on the determination of phase separation using DSC and PFG NMR spectroscopy (chapter 6.1). Subsequently, it details the results of optimizing the membrane fabrication process for these diblock copolymer blends (chapter 6.2). The chapter then explores the outcomes of post-modification efforts applied to the blend membranes (chapter 6.3) and concludes with performance evaluations using salts (chapter 6.4).

6.1 Determination of the Phase Separation of Homopolymer Blends and Diblock Copolymer Blends

To fabricate PDMA-*b*-PS and P4VP-*b*-PS diblock copolymer blend membranes, it is crucial to understand the phase separation behavior of the individual block copolymers and their blends. Microphase separation in both PDMA-*b*-PS and P4VP-*b*-PS block copolymers has already been reported. Notably, P4VP/ PS blends exhibit one of the highest reported Flory-Huggins-Staverman interaction parameters, with $\chi_{\text{P4VP/PS}}$ of 0.30 – 0.35.³³⁹ This strong incompatibility drives pronounced microphase separation in P4VP-*b*-PS diblock copolymers, as evidenced in bulk materials,³³³ thin film morphologies^{340–342} and SNIPS membranes.^{227,343,344}

In contrast, the interaction parameter between PDMA and PS is significantly lower, with $\chi_{\text{PDMA/PS}}$ of 0.096.³⁴⁵ However, it is sufficient to induce microphase separation in emulsion,³⁴⁶ bulk systems^{346,347} and SNIPS membranes.^{233,348,349} However, whether the two polymers PDMA and P4VP — or their respective blocks — phase separate from each other remains unexplored. This understanding is critical for predicting the structure and separation performance of PDMA-*b*-PS/ P4VP-*b*-PS diblock copolymer blend membranes.

Since P4VP is more polar than PS and thus more compatible with PDMA, which typically indicates favorable interactions, it is anticipated that the Flory-Huggins-Staverman interaction parameter $\chi_{\text{PDMA/P4VP}}$ is anticipated to be relatively low (likely < 0.1). To investigate the phase separation behavior between PDMA and P4VP blocks, preliminary tests were conducted using both homopolymer blends and diblock copolymer blends. These tests aim to provide insights into the incompatibility of PDMA and P4VP in the blends and their impact on the microphase-separated morphologies.

6.1.1 Thermal Characterization of Homopolymers and Block Copolymers and Their Blends

The individual homopolymers, along with the diblock copolymers and their blends, were analyzed using differential scanning calorimetry (DSC) (see Figure 30). To prepare the blends, chloroform solutions were used, followed by slow solvent evaporation and subsequent drying (for further details, see chapter 9.4.1). In the following, subscripts indicate the weight percentage of each block in the diblock copolymer, while superscripts denote the number-average molecular weight determined by $^1\text{H-NMR}$ spectroscopy.

To ensure accurate interpretation, the homopolymers were first examined, and their respective glass transition temperatures are shown in Figure 30 (a). Figure 30 (b) displays the DSC thermograms of the $\text{PDMA}_{23}\text{-}b\text{-PS}_{77}^{102.1}$ and $\text{P4VP}_{21}\text{-}b\text{-PS}_{79}^{125.6}$ diblock copolymers, as well as their blend. The glass transitions of the minor blocks, PDMA and P4VP, are barely visible in the thermograms due to the dominant signal from the unshifted glass transition of PS.

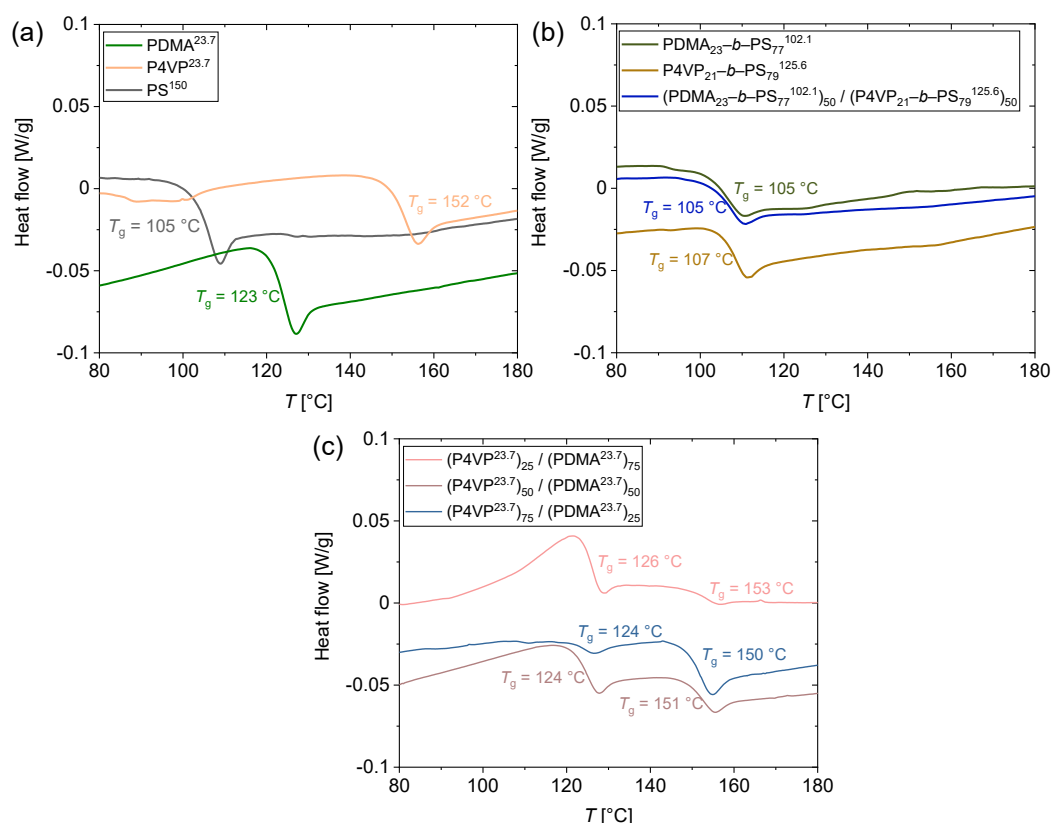


Figure 30. DSC thermogram of (a) the pure PDMA, P4VP and PS homopolymers, (b) the PDMA-*b*-PS and P4VP-*b*-PS diblock copolymers and their blend and (c) the P4VP/ PDMA blends in with varying compositions. In the blends, the composition is expressed as a molar fraction, with the specific molar fraction of each polymer indicated by a subscripted number (in mol%).

Hence, in the individual diblock copolymers as well as the diblock copolymer blend containing equal molar ratios (50 mol% each) of $\text{PDMA}_{23}\text{-}b\text{-PS}_{77}^{102.1}$ and $\text{P4VP}_{21}\text{-}b\text{-PS}_{79}^{125.6}$, the weight fraction of the minor blocks may be too low to detect their individual glass transitions. In addition, although the glass transition temperatures of PS (100 °C) and PDMA (125 °C) differ by about 25 °C, the detection of two distinct

transitions in the thermogram can still be challenging — particularly due to overlapping signals, broad transitions, or compositional effects in the copolymer. To enhance detection, blends of P4VP and PDMA homopolymers with varying compositions were analyzed (see Figure 30 (c)). All blends exhibited two distinct glass transitions, identical to those of the pure homopolymers, indicating minimal miscibility at the molecular level. This observation suggests phase separation of the individual blocks.³⁵⁰

Therefore, it can be concluded that the incompatibility, expressed by the product of the Flory–Huggins–Staverman interaction parameter and the degree of polymerization (χN), among the three polymers — PS, PDMA, and P4VP — is sufficiently high to drive phase separation in the bulk state.

6.1.2 Determination of Diffusion Coefficients in Casting Solutions

Although DSC experiments indicated phase separation between PDMA and P4VP in the bulk — prepared from slowly evaporated chloroform solutions — their behavior in solutions may differ significantly due to variations in solvent selectivity and the distinct conditions during solution preparation. When block copolymers are diluted in solvents, the solvent plays a critical role in influencing the interactions between polymer blocks and the system's thermodynamics. Solvents that preferentially solvate one block enhance phase separation by increasing block incompatibility, while solvents that are favorable for both blocks reduce the driving force for phase separation, promoting a mixed or disordered phase.

To investigate the phase separation behavior of the block copolymer blends in the casting solution, pulsed field gradient (PFG) NMR spectroscopy was employed to measure the diffusion coefficients of solutes — a kinetic parameter that can indirectly reflect microstructural organization and phase separation resulting from thermodynamic incompatibility. The theoretical background and methodology of this characterization are discussed in chapter 3.6.1.1.

For this analysis, polymer casting solutions containing a PDMA₁₉-*b*-PS₈₁^{112.0} diblock copolymer, a P4VP₁₉-*b*-PS₈₂^{135.4} diblock copolymer, and their 50:50 molar ratio blend were prepared using a solvent system of THF, DMF, and dioxane in a 50:30:20 (w/w/w) ratio (see chapter 9.4.2 for further details). A representative ¹H-NMR spectrum of the blend is shown in Figure 31 (a), which includes signals from both the polymers and solvents. Upon applying gradient pulses in PFG NMR, the faster diffusion of the solvent relative to the solute results in a more significant signal decay for the solvent, particularly at higher gradient strengths. Consequently, the solvent signals diminish at high gradient strengths and may even disappear, as shown in Figure 31 (b). Due to overlapping polymer signals, deconvolution was performed using a fitting method, with the deconvoluted NMR signals for the blend illustrated in Figure 31 (c). For determining the diffusion coefficients of the PDMA and P4VP blocks, signals 7 and 1 from the fitted spectra were used, respectively.

Diffusion coefficients were measured for both the pure diblock copolymer solutions and the diblock copolymer blend solution. The polymers were measured in a solvent mixture of THF:DMF:dioxane in a 50:30:20 (w/w/w) ratio. The individual concentrations and diffusion coefficients are listed in Table 2. Notably, the PDMA block in the pure PDMA₁₉-*b*-PS₈₁¹¹² diblock copolymer solution exhibited a lower diffusion coefficient

compared to the same block in the block copolymer blend. This is consistent with the lower total polymer concentration in the blend, which likely leads to decreased intermolecular interactions or entanglements that hinder diffusion. In contrast, the P4VP block showed a slightly higher diffusion coefficient in the blend than in the pure $\text{P4VP}_{19}\text{-}b\text{-PS}_{82}^{135.4}$ diblock copolymer solution.

Table 2. Diffusion coefficients of diblock copolymer and blend solutions.

Polymer	Weight fraction [wt %]	Diffusion coefficient PDMA block [$\text{m}^2\cdot\text{s}^{-2}$]	Diffusion coefficient P4VP block [$\text{m}^2\cdot\text{s}^{-2}$]
$\text{PDMA}_{19}\text{-}b\text{-PS}_{81}^{112.0}$	35	$9.23\cdot 10^{-12} \pm 2.43\cdot 10^{-13}$	-
$\text{P4VP}_{19}\text{-}b\text{-PS}_{82}^{135.4}$	20	-	$9.89\cdot 10^{-12} \pm 1.36\cdot 10^{-12}$
$(\text{PDMA}_{19}\text{-}b\text{-PS}_{81}^{112.0})_{50}/(\text{P4VP}_{19}\text{-}b\text{-PS}_{82}^{135.4})_{50}$	26	$1.06\cdot 10^{-11} \pm 1.23\cdot 10^{-12}$	$6.29\cdot 10^{-12} \pm 6.56\cdot 10^{-13}$

Even when accounting for measurement errors (approximately 10 – 15%), the results demonstrate that the PDMA and P4VP blocks diffuse at distinct rates within the equimolar diblock copolymer blend solution. Specifically, the PDMA block exhibits a higher diffusion rate than the P4VP block. This difference suggests that the PDMA and P4VP blocks are phase-separated, likely residing in distinct micelles within the blend.

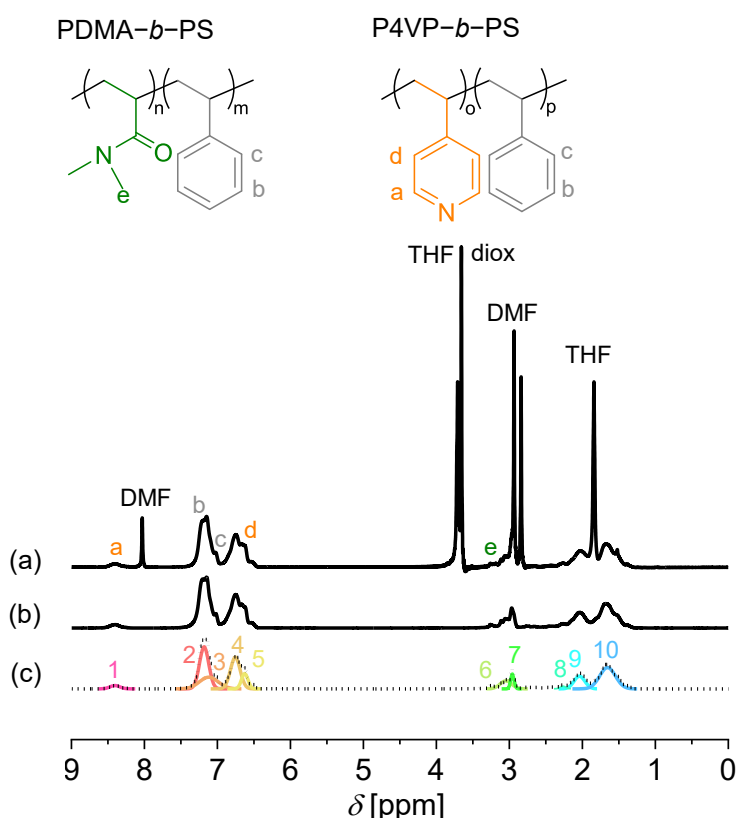


Figure 31. ^1H -NMR spectra of the $(\text{PDMA}_{19}\text{-}b\text{-PS}_{81}^{112.0})_{50}/(\text{P4VP}_{19}\text{-}b\text{-PS}_{82}^{135.4})_{50}$ diblock copolymer blend casting solution. (a) Conventional ^1H -NMR spectrum including the solvent signals. (b) Representative ^1H -NMR spectrum after applying a gradient pulse. The solvent signals disappeared while the polymer signals remained. (c) ^1H -NMR spectrum of (b) with corresponding peak fitting (deconvolution).

In summary, the DSC experiments of the blends in the bulk and the PFG NMR analysis of the casting solutions suggest that the P4VP and PDMA blocks do not form a common domain but are instead phase-separated. However, these findings provide only preliminary evidence of phase separation in the block copolymer membranes, which could involve either microphase separation of the blocks or polymer–nonsolvent demixing during membrane formation. A definitive conclusion requires further investigation directly within the membranes which will be discussed in the following chapter.

6.2 Diblock Copolymer Blend Membrane Formation *via* the SNIPS Process

6.2.1 Optimization of the Casting Process

One of the goals of this work is to implement diblock copolymer blends in the fabrication of isoporous membranes. This requires the identification of suitable casting conditions. For membrane production using the SNIPS process, key factors such as the composition of the solvent system, polymer content in the casting solution, and external conditions like temperature and humidity significantly influence the final membrane morphology. Establishing optimal casting conditions for the PDMA-*b*-PS/ P4VP-*b*-PS diblock copolymer blends is more challenging than for pure diblock copolymers due to the differences in solvent selectivity and solubility behavior of each block. Previous studies identified a 50:50 (w/w)³⁵¹ and a 40:60 (w/w)^{352,353} mixture of THF and DMF as a suitable solvent system for casting P4VP-*b*-PS diblock copolymer membranes. However, also ternary mixture of dioxane, THF, and DMF 33.3:33.3:33.3 (w/w/w)²⁵⁸ were used as suitable casting solutions. In contrast, for PDMA-*b*-PS, a ternary solvent mixture of dioxane, THF, and DMF in a 60:20:20 (w/w/w) ratio was found to produce isoporous membranes.³⁴⁹ However, the casting conditions optimized for each individual diblock copolymer are incompatible with the respective other, preventing the formation of isoporous membranes in either case.

During optimization of the casting conditions, various solvent mixtures were examined, with a focus on ternary combinations of dioxane, THF, and DMF. Initially, solutions of the pure diblock copolymers were prepared separately and then mixed. Later, one solution, including both diblock copolymers, was prepared. As no differences in the morphology of the resulting block copolymer blend membranes were observed between the two approaches, both methods were considered equivalent.

The best results were obtained using the ternary solvent mixture of dioxane, THF, and DMF in a 20:50:30 (w/w/w) ratio. However, a significant challenge arose due to the differing behaviors of the two block copolymers in solutions. For casting pure PDMA-*b*-PS diblock copolymer membranes, relatively high polymer concentrations of around 33 – 34 wt% were necessary to prevent the polymer from excessive penetration into the nonwoven substrate. In contrast, casting pure P4VP-*b*-PS diblock copolymer membranes required significantly lower diblock copolymer concentrations, around 23 wt%. These differences of optimal weight concentrations made it more challenging to form optimized PDMA-*b*-PS/ P4VP-*b*-PS diblock copolymer blend membranes. At lower polymer concentrations (mid- to late- 20s wt%), the block copolymer blend solutions exhibited low viscosity, leading to the polymer solution soaking into the nonwoven material. Conversely, increasing the polymer content above 30 wt% prevented the solution from being absorbed, but resulted in a denser membrane substructure, as seen in Figure 32 (a). This densification is also evident in the water permeance data (Figure 32 (b)). At a polymer concentration of 32 wt%, the membrane became nearly impermeable, indicating that achieving the right polymer concentration was critical for optimizing membrane properties. Thus, one of the main challenges was

finding the ideal optimized content for the solutions to balance structural integrity and permeability.

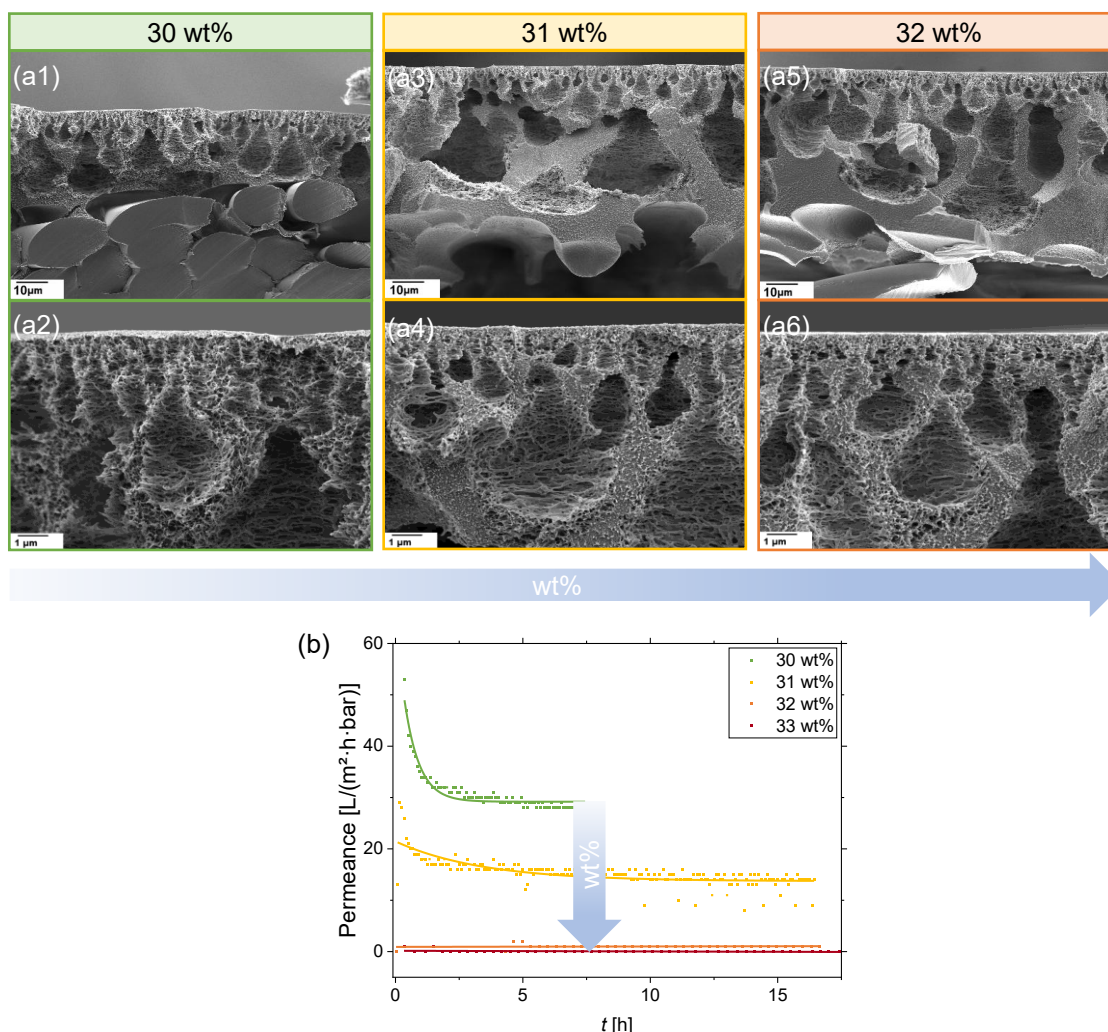


Figure 32. (a) SEM images of the cross-view of the (PDMA₂₀-*b*-PS₈₀¹⁰⁵)₅₀/ (P4VP₁₈-*b*-PS₈₂¹³⁵)₅₀ diblock copolymer blend membranes cast at the different weight fraction of the blended polymers: (a1, a2): 30 wt% polymer, (a3, a4): 31 wt% polymer, (a5, a6): 32 wt% polymer. Images show the membranes cast from dioxane:THF:DMF 20:50:30 (w/w/w) solutions obtained after an evaporation time of 10 s. (b) Water permeance of the blend membranes in dependence of the polymer weight fraction in the solution.

Since conventional blending of the diblock copolymers and dissolving them in solvents did not result in well-defined isoporous membranes with a sponge-like substructure, additional additives were introduced into the casting solution. The incorporation of γ -butyrolactone (GBL), a common membrane structure modifier, did not improve the membrane structure, likely because GBL is not a true non-solvent for all components of the polymer blend. In contrast, the addition of glycerin to the casting solution proved more effective. Even at low concentrations (≤ 3 wt%), glycerin significantly increased the viscosity of the solution. This higher viscosity, induced by the incompatibility with all blocks, inhibited the penetration of the casting solution into the nonwoven substrate, thereby promoting better phase separation and contributing to the formation of a more defined porous substructure. Blend membranes with 2 – 3 wt% glycerin exhibited an isoporous top surface and an open, sponge-like substructure. A PDMA₂₀-*b*-PS₈₀¹⁰⁵/ P4VP₁₈-*b*-PS₈₂¹³⁵ diblock copolymer blend membrane with a 50:50

molar ratio of both diblock copolymers and a total polymer concentration of 26 wt% and 3 wt% glycerin is shown in Figure 33. This is a larger membrane (> DIN A4 size) which was analyzed at different positions. The images reveal variations in the brightness across the top surfaces, creating the impression that some pore assemblies appear more sunken than others. These brightness differences are a result of surface topography, as interactions with electrons — particularly the emission of secondary electrons — are more pronounced in regions with elevated structures. This phenomenon is known as the edge effect.³⁵⁴ Peaks and edges emit a higher number of secondary electrons, making them appear brighter. Surfaces with the shallower angles of a surface exhibit greater interaction with the penetrating electron beam, leading to an increased emission of secondary electrons. Hence, in the SEM images of the diblock copolymer blend membranes, a roughness resulting from surface topography is observed.

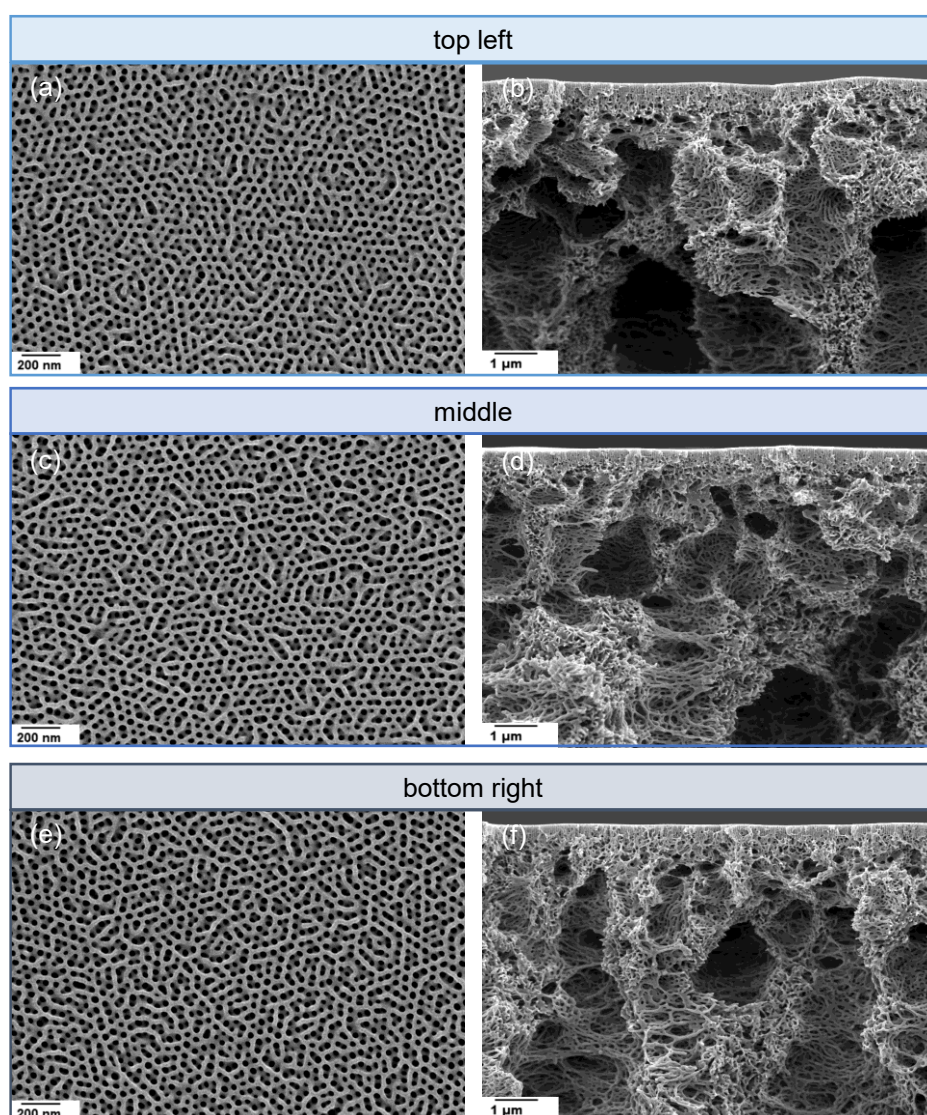


Figure 33. (a), (c), (e) Top surface structure and (b), (d), (f) cross-view of the $(\text{PDMA}_{20}\text{-}b\text{-PS}_{80})_{50} / (\text{P4VP}_{18}\text{-}b\text{-PS}_{82})_{50}$ diblock copolymer blend membrane at different positions in the membrane. The membrane was cast from a solution with a total polymer concentration of 26 wt% in dioxane:THF:DMF 20:50:30 (w/w/w) and 3 wt% glycerin as an additive.

The diblock copolymer blend membrane had an average pore size of 22.2 ± 4.7 nm. Notably, the cylindrical structures on the surface were relatively long, with heights approximately ranging from 200 – 300 nm. The water permeance of the membrane was determined at different positions of the membrane, ranging from 110 – 135 L/(m²·h·bar).

6.2.2 Diblock Copolymer Blend Membrane Characterization

With the successful optimization of casting conditions for PDMA-*b*-PS/ P4VP-*b*-PS diblock copolymer blend membranes, the next step was to analyze the pore composition within the diblock copolymer blend membrane. To achieve this, the diblock copolymer blend membrane was stained with iodine and examined *via* SEM using an energy-selective backscattered (EsB) electron detector. This detector captures backscattered electrons (BSEs) reflected from the sample surface. Since the yield of BSEs increases with atomic numbers, elements such as iodine (with a high atomic number) generate more BSEs than lighter elements, enhancing imaging contrast. In imaging, the stained domains appear brighter than the non-stained domains.

Previous studies have shown that iodine selectively stains P4VP in the presence of PDMA.^{355,356} Therefore, the staining process relies on the premise that iodine interacts with P4VP but not with PDMA (as shown in Figure 34). Consequently, iodine should be localized in the P4VP domains, leaving the PDMA domains unstained.

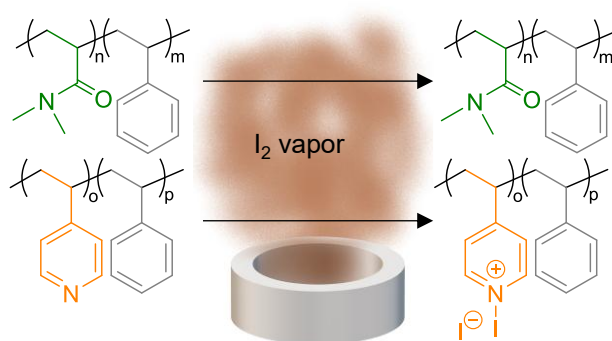


Figure 34. Iodine-staining reaction of both diblock copolymers PDMA-*b*-PS and P4VP-*b*-PS. The PDMA-*b*-PS remains unreacted,^{355,356} meanwhile the nitrogen atom of the P4VP reacts with iodine.

The SEM images of the PDMA₂₀-*b*-PS₈₀¹⁰⁵/ P4VP₁₈-*b*-PS₈₂¹³⁵ diblock copolymer blend membrane, which was cast with 2 wt% glycerin as an additive, are presented in Figure 35 (a) and (b). Like the membrane cast with 3 wt% glycerin (Figure 33), the pores are hexagonally ordered, and the membranes show the same surface roughness. The corresponding images of the positions (a) and (b), obtained using the EsB detector, are shown in Figure 35 (c) and (d). The images reveal regions with varying contrast: some pore walls appear brighter, indicating the presence of iodine through the staining process, while others remain unstained, suggesting an absence of iodine. Assuming that only P4VP is stained with iodine, this implies a non-uniform distribution of P4VP — being concentrated in some areas and absent in others. The spatial distribution of these regions appears random and disordered. This suggests that in some regions PDMA dominates in the pore walls, while in others, P4VP is more prevalent. Interestingly,

certain pores show only partial staining rather than complete white rings, indicating a possible coexistence of both PDMA and P4VP within individual pores. However, further analysis is required to confirm this potential colocalization. A hypothesized morphology, based on the SEM images, is illustrated in Figure 35 (e), where P4VP-filled pores are interspersed with, and sometimes surrounded by, PDMA-filled pores. Hence, a microphase separation in a macrophase-separated structure is observed. A fitting description for this morphology could be a "patchwork-like" or "mosaic" arrangement, where regions dominated by either P4VP or PDMA are interspersed, creating a heterogeneous but interconnected pore network.

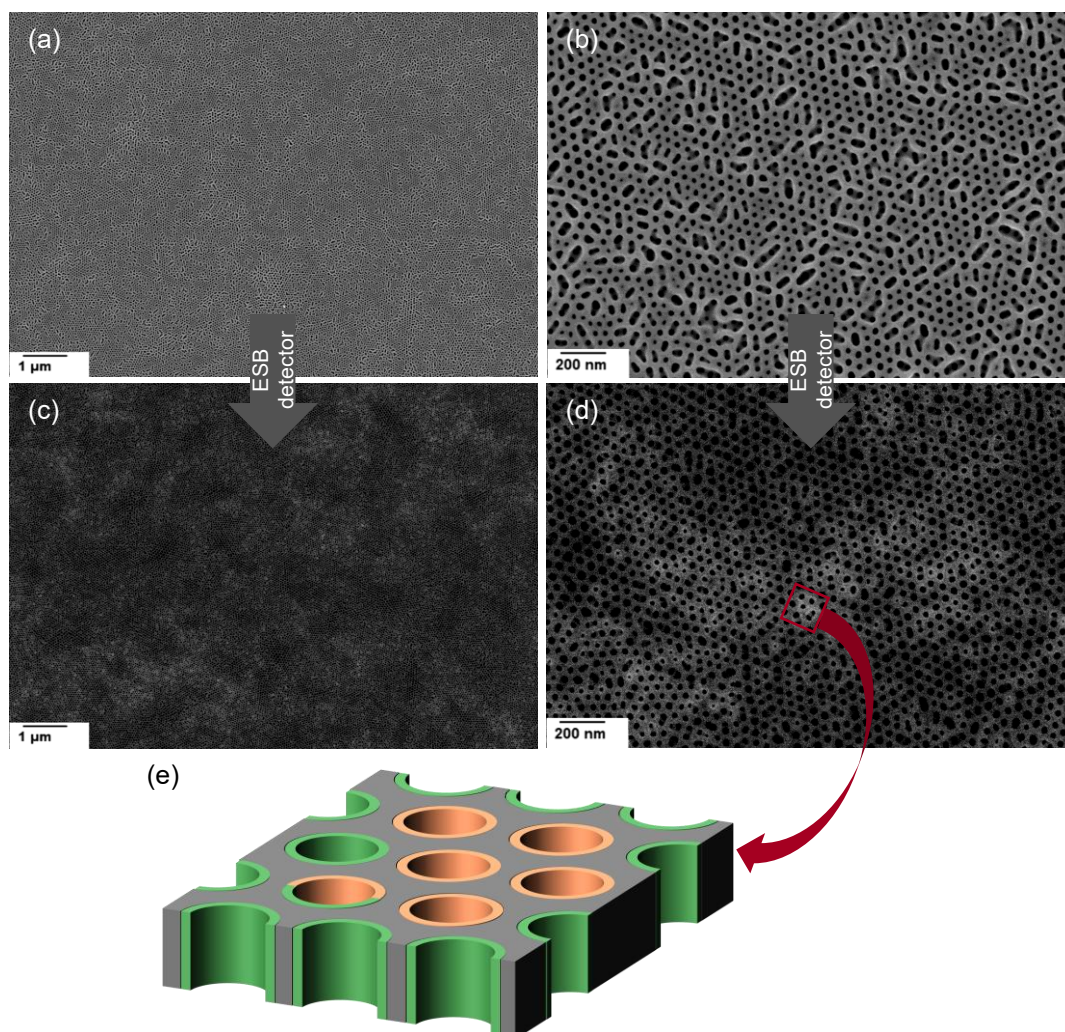


Figure 35. (a), (b) SEM images of a $(\text{PDMA}_{20}\text{-}b\text{-PS}_{80}^{104.7})_{50}/(\text{P4VP}_{18}\text{-}b\text{-PS}_{82}^{135})_{50}$ diblock copolymer blend membrane cast from a solution with a total polymer concentration of 26 wt% and 2 wt% glycerin in dioxane:THF:DMF 20:50:30 (w/w/w). (a) Shows the diblock copolymer blend membrane surface at a 10k magnification, (b) at a 50k magnification. (c), (d) SEM images at the same position of (a) and (b), respectively, using an EsB detector. (e) The proposed structure derived from the SEM images. The PDMA and P4VP pores are randomly distributed over the membrane surface, mostly in larger clusters of some pores of one type.

Since the pores of the diblock copolymer blend membranes are uncharged after casting, post-modification is required to impart opposite charges within the membrane pores. The details of the post-modification reactions are discussed in the next section.

6.3 Post-Modification Reactions of the Diblock Copolymer Membranes

In the next step, the PDMA-*b*-PS/ P4VP-*b*-PS diblock copolymer blend membranes were post-modified to incorporate charges into the membrane. The goal was to convert PDMA into negatively charged PAA (in the same manner as outlined in publication 3, see chapter 5.3) and to quaternize the nitrogen of P4VP to introduce positive charges into the membrane's pores. Hydrochloric acid (HCl) and methyl iodide (MeI) were employed as reactants for these modifications, respectively. The sequence of these modifications was critical to prevent potential side reactions. Since PAA can react with MeI to form poly(methyl acrylate) and HI, the quaternization with MeI was performed first, followed by the conversion of PDMA to PAA using HCl.

To optimize the quaternization of P4VP, the post-modification of the P4VP-*b*-PS membrane with methyl iodide was examined under various conditions, including diluted aqueous solutions, alcoholic solutions, and MeI vapor. While reactions in water and ethanol caused noticeable changes in the membrane morphology, with mainly closed pores and/or reorganization of the membrane's structure, the membrane structure remained intact when exposed to small amounts of MeI vapor. However, vapor-phase reactions proceed significantly more slowly than those in aqueous or alcoholic media.

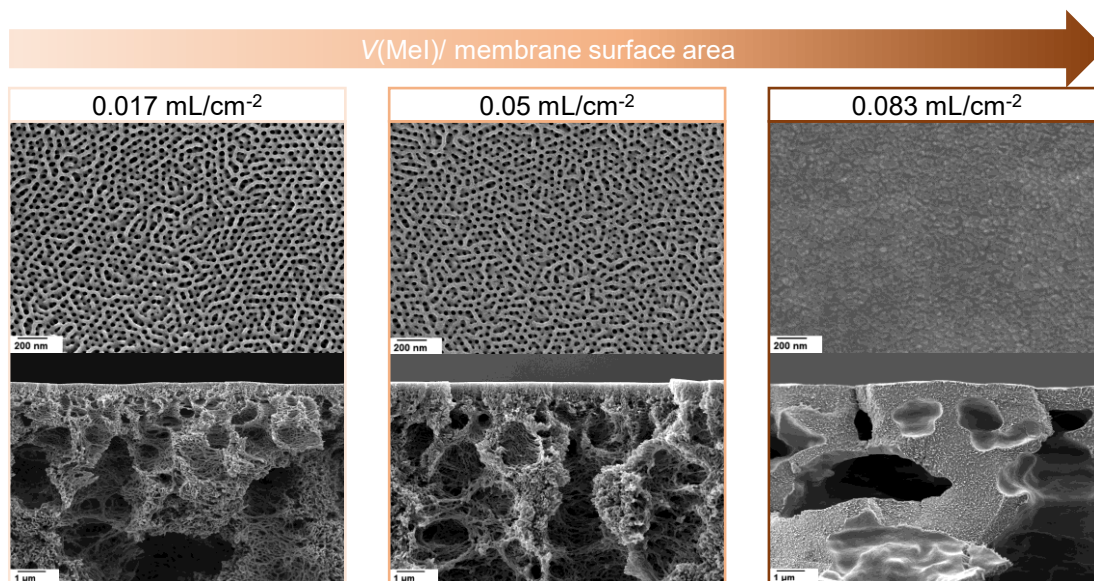


Figure 36. Surface structure (upper images) and cross-sections (bottom pictures) of the (PDMA₂₀-*b*-PS₈₀¹⁰⁵)₅₀/ (P4VP₁₈-*b*-PS₈₂¹³⁵)₅₀ diblock copolymer blend membrane post-modified with different amounts of methyl iodide. The reaction was performed with membranes of similar surface area and in the same chamber.

These optimized reaction conditions were applied to the blend membranes, using varying volumes of methyl iodide to achieve a high degree of functionalization, while maintaining a constant membrane surface area and reaction chamber size. Figure 36 presents top-surface SEM images of the blend membranes modified with different volumes of methyl iodide, normalized to membrane surface area. As shown, up to 0.05 mL of methyl iodide per square centimeter of membrane surface area did not alter the membrane structure. However, increasing the concentration of MeI to 0.083 mL/cm²

to accelerate the reaction showed structural changes in the membrane. The pores were closed, and the substructure became noticeably denser. The excessive use of methyl iodide also affected the membrane performance. It caused the membrane to become not only dense but also more brittle, leading to breakage during water flux measurements.

After treating the diblock copolymer blend membranes with 0.05 mL/cm² methyl iodide, the products were analyzed using infrared (IR) spectroscopy. Unlike the pure P4VP-*b*-PS diblock copolymer membranes, which exhibited a distinct shift of the C=N stretching vibration from ≈ 1600 cm⁻¹ to the C=N⁺ stretching vibration at ≈ 1640 cm⁻¹ after post-modification,²³⁹ no clear shift was observed in the diblock copolymer blend membranes after post-modification. This is due to the overlap with the C=O stretching vibration signal of the PDMA component (see Figure 37).

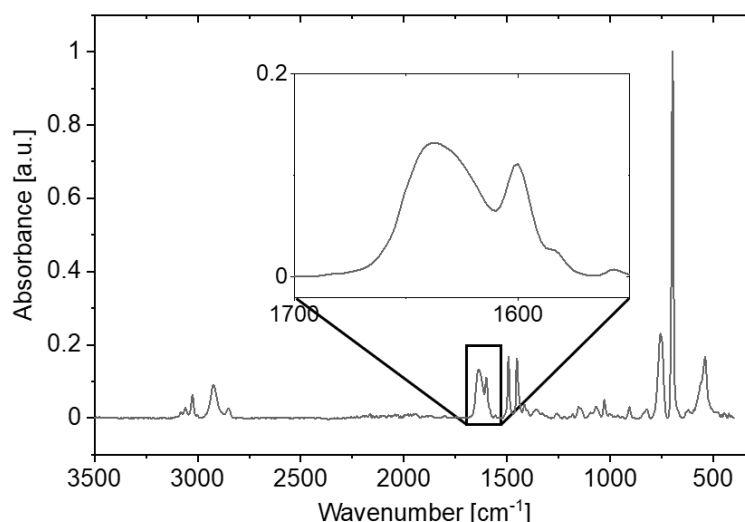


Figure 37. FTIR spectrum of a PDMA-*b*-PS/ P4VP-*b*-PS diblock copolymer blend membrane. The enlarged section shows the region between 1700 cm⁻¹ and 1550 cm⁻¹, with the C=N stretching vibration at ≈ 1600 cm⁻¹ and the C=O stretching vibration at ≈ 1630 cm⁻¹.

Consequently, ¹H-NMR spectroscopy was employed on both the pristine diblock copolymer blend membrane and those post-modified with Mel to assess the conversion of the reaction. Upon diluting the pristine diblock copolymer blend in deuterated chloroform, all signals were clearly identifiable, as shown in Figure 38 (a). However, after the post-modification reaction with Mel, as shown in Figure 38 (b), the signal of P4VP completely disappeared, and the expected signals following the reaction with Mel were also not detectable. It is hypothesized that the interaction parameter between PS and the poly(vinyl methyl pyridinium) is even higher than that between PS and P4VP. Since chloroform may not act as a non-selective solvent, it is possible that the P4VP/ P4VP-Me blocks self-assemble and form micellar cores, leading to the absence of signals in the ¹H-NMR spectrum.

A similar observation was made when using DMF-*d*₈ as solvent, with signals of the partially reacted P4VP block remaining undetectable. To find a solvent system where all signals could be observed, mixtures of deuterated solvents of different selectivity were tested. A mixture of THF-*d*₈ and methanol-*d*₄ (58 vol%:42 vol%), enabled clear signal detection. Figure 39 (a) presents the ¹H-NMR spectrum after the methyl iodide modification reaction in this solvent mixture. In addition to the signal at ≈ 8.25 ppm, responding to the protons labeled 'a' in the P4VP, an additional signal at ≈ 8.75 ppm was

observed, corresponding to the protons a_q of the quaternized P4VP-Me. By analyzing the ratio between these two signals, a conversion of 51 % of the reaction with methyl iodide was determined. Moreover, the signal of the PDMA, located at 3.1 – 2.8 ppm, remained unchanged, confirming that PDMA did not react with methyl iodide as anticipated. The proposed reactions occurring during this modification are shown in Figure 39 (b). Both the membrane surface (Figure 39 (c)) and cross-section (Figure 39 (d)) maintained an open structure throughout the modification process.

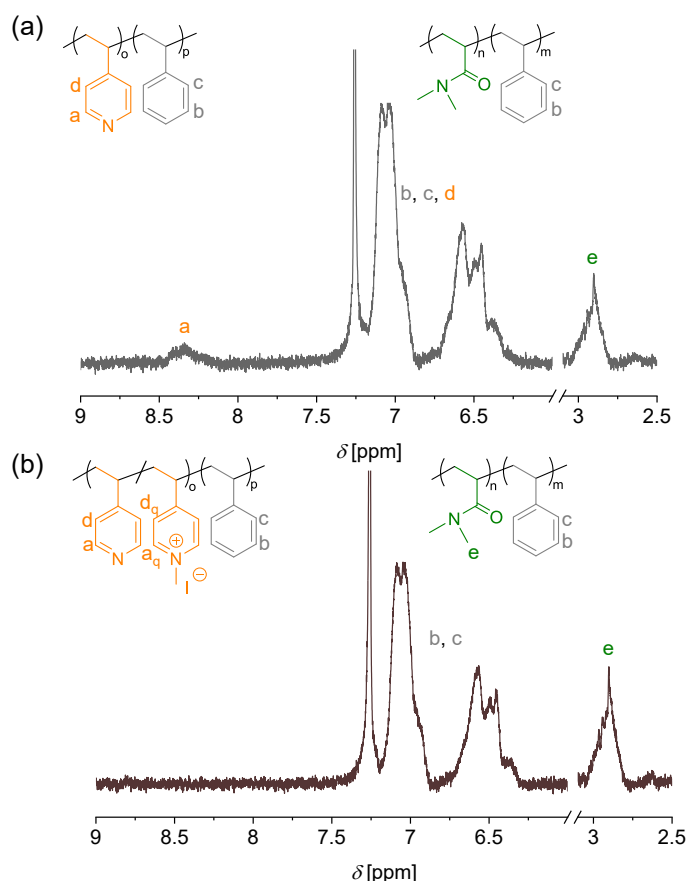


Figure 38. ^1H -NMR spectra in deuterated chloroform of the polymer of (a) the pristine PDMA-*b*-PS/P4VP-*b*-PS diblock copolymer blend membrane, and (b) the blend membrane after modification with 0.05 mL/cm² Mel.

Independent of this, the pristine PDMA-*b*-PS/P4VP-*b*-PS diblock copolymer blend membrane was modified using an aqueous hydrochloric acid solution, following a procedure analogous to that described for the PDMA-*b*-PS diblock copolymer membrane in the publication 3 in section 5.3. After functionalization, the membrane was rinsed with water to remove any residual hydrochloric acid. FTIR spectroscopy was used to analyze the membrane. The resulting IR spectrum, shown in Figure 39 (e), demonstrates a reduction of the C=O stretching vibration of the amide at $\approx 1637\text{ cm}^{-1}$, along with the appearance of a new C=O stretching vibration attributed to carboxylic acid at $\approx 1723\text{ cm}^{-1}$. Given the previously observed near-complete conversion of the pure PDMA-*b*-PS diblock copolymer membrane to PAA-*b*-PS, it is likely that the remaining signal at $\approx 1637\text{ cm}^{-1}$ belongs to the C=N⁺ stretching bond of the protonated P4VP. Notably, this protonation of P4VP is pH-dependent and reversible, as reported in

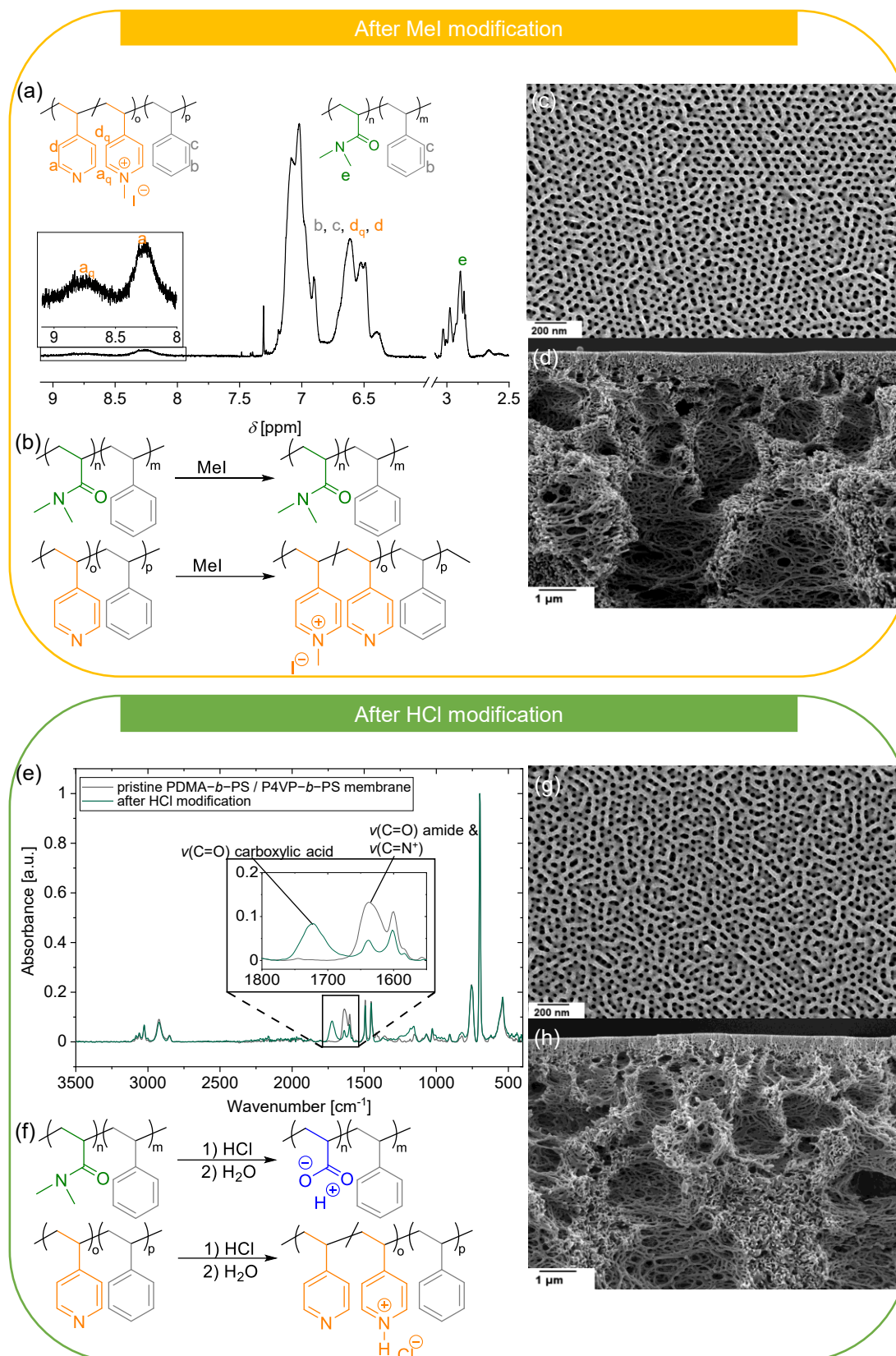


Figure 39. Modification reactions of the (PDMA₂₀-*b*-PS₈₀¹⁰⁵)₅₀/ (P4VP₁₈-*b*-PS₈₂¹³⁵)₅₀ diblock copolymer blend membrane. Top: reaction with methyl iodide (7 d 0.05 mL/cm²); bottom: reaction with hydrochloric acid (24 h 6 M HCl). (a) ¹H-NMR spectrum in mixtures of THF-*d*₈ and methanol-*d*₄ (58 vol%:42 vol%) of the membrane polymer after post-modification. (b), (f) Proposed reactions occurring during the post-modifications. (c), (d), (g), (h) SEM images before and after the post-modification. (e) ATR-FTIR spectrum of the membrane surface before and after the post-modification.

earlier studies.^{357,358} Furthermore, the hydrochloric acid modification did not cause any significant changes to the membrane structure, as evidenced by Figure 39 (g) and (h).

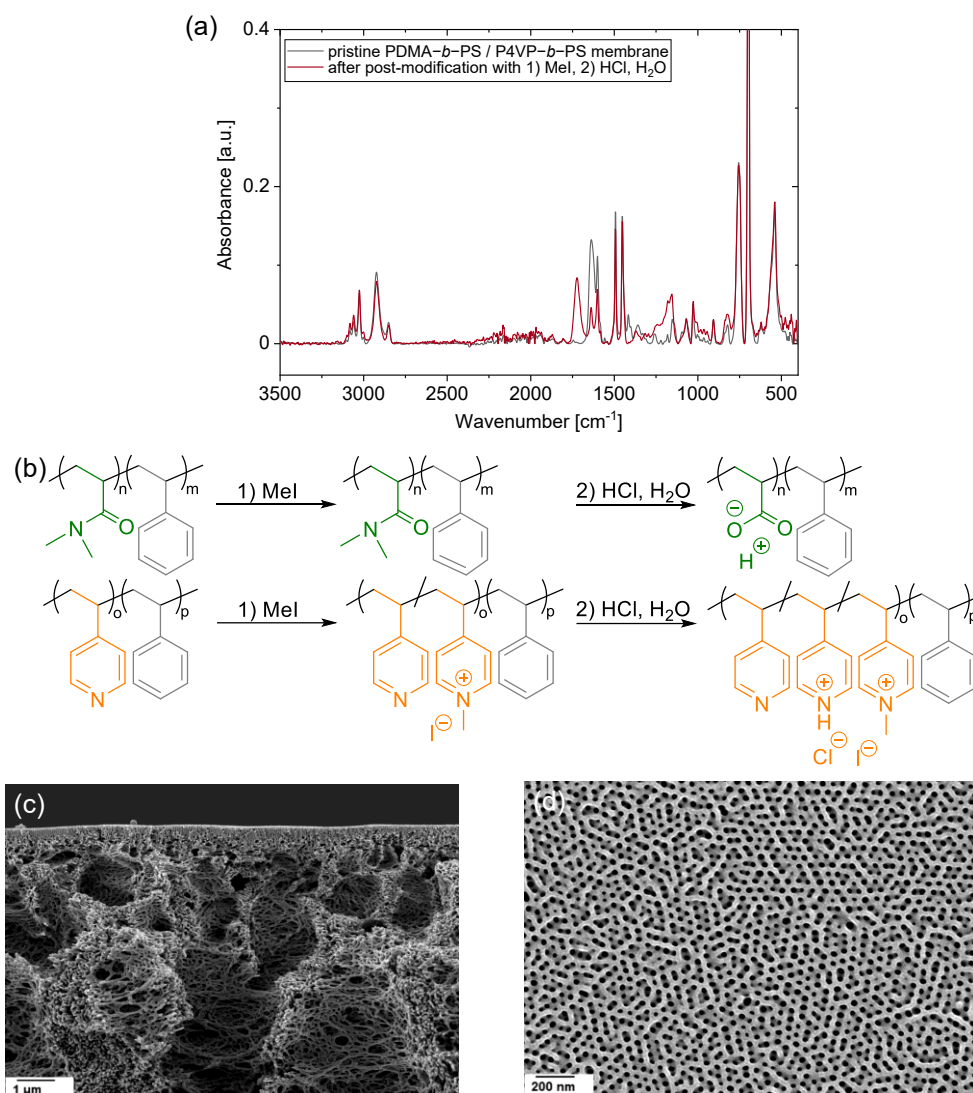


Figure 40. (a) Zoomed-in FTIR spectrum of the pristine PDMA-*b*-PS/ P4VP-*b*-PS diblock copolymer blend membrane and the membrane after the two modification reactions with methyl iodide (0.05 mL/cm²) and hydrochloric acid (6 M aqueous hydrochloric acid at 80 °C). (b) Proposed reactions happening during the modification reactions. (c) Cross-section and (d) top surface of the blend membrane after both modification reactions.

Since both post-modification reactions individually yielded promising results, they were conducted sequentially. The blend membranes were first treated with methyl iodide, followed by hydrochloric acid. Figure 40 (a) presents the FTIR spectra of the blend membrane before and after these two modification steps. A clear shift is observed from the C=O stretching vibration of the amide group to the C=O stretching vibration of the acid, confirming the change from PDMA to PAA. Additionally, the spectrum shows both the C=N stretching band of P4VP and the C=N⁺ stretching band, indicating the presence of unreacted P4VP, as expected from the prior modification reaction. However, it is unclear to what extent P4VP reacted with Mel versus HCl, since both reactions produce the C=N⁺ stretching band. It is likely that the final product contains contributions from both reactions. The proposed mechanisms for these reactions are illustrated in Figure

40 (b). Based on signal integration, it is estimated that approximately 41% of the P4VP underwent reaction. Following the two modification reactions on the blend membrane, the overall structure remained intact, as shown in Figure 40 (c) and (d).

Water permeance measurements were conducted of the pristine and post-modified diblock copolymer blend membranes after each reaction step, with the results presented in Figure 41. The pristine PDMA-*b*-PS / P4VP-*b*-PS diblock copolymer blend membrane exhibited a water permeance of approximately 126 ± 12 L/(m²·h·bar). After modification with methyl iodide, the permeance decreased to 84 ± 9 L/(m²·h·bar). This reduction is expected, as the reaction of P4VP with methyl iodide results in partial charging of the pore-forming P4VP block, causing significant swelling during water flux measurements. However, it is worth noting that this reduction in water permeance is significantly smaller than that observed in pure P4VP-*b*-PS diblock copolymer membranes with similar conversion.²³⁹

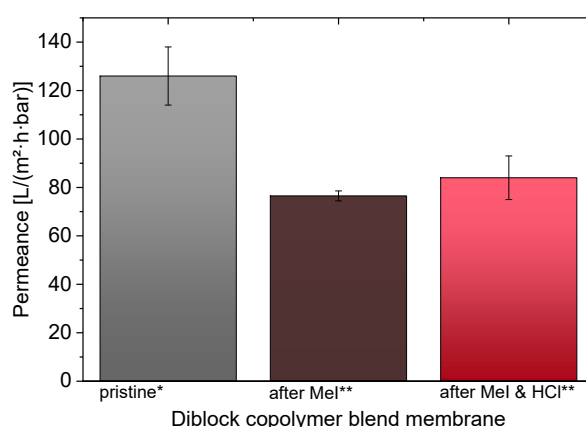


Figure 41. Permeance of the pristine blend membrane and after the reaction with Mel and after both modification reactions. * Quadruple determination, ** due to the small membrane area, only a single determination was conducted; for more precise information, these results have to be repeated.

After the additional modification with hydrochloric acid, a slight increase in water permeance was observed. This effect mirrors the behavior obtained in the post-modification of pure PDMA-*b*-PS diblock copolymer membranes into PAA-*b*-PS diblock copolymer membranes, in which ionization of the pore-forming block reduced stretching, leading to an increase of permeance in deionized water.³⁴⁹ However, it should be noted that measurements after the modification reactions were performed on a single sample per condition, although each measurement included multiple data points — as indicated by the error bars. Therefore, while the initial results are indicative, further investigation with additional replicates would help substantiate the findings and account for potential sample variability.

In summary, the PDMA-*b*-PS / P4VP-*b*-PS diblock copolymer blend membranes were successfully post-modified to introduce opposite charges within the membrane pores. To generate positive charges, the P4VP block was post-modified using Mel. However, only vapor-phase Mel modifications were effective, as solution-based modifications led to changes in the membrane morphology. Even with vapor-phase treatment, only a limited amount of Mel (≤ 0.05 mL·cm⁻²) could be applied to avoid morphological changes or pore blockage. Although the quaternization of P4VP with Mel was successful, complete conversion was not achieved. This reaction rendered the P4VP channels positively charged. To introduce complementary functionality, the PDMA

domains of the membranes were subsequently modified to introduce additional negative charges *via* the ionization of carboxylic acid groups in the PAA. To achieve this, hydrochloric acid was used to convert the PDMA block into PAA, following an approach like that described in publication 3. By the combination of these two post-modifications, neither of these modifications caused structural changes in the membrane morphology. The water flux measurements indicated a decrease in permeance of the post-modified membranes compared to the pristine membrane, which was expected. However, an additional modification to reduce the P4VP-Me/ P4VP pores could be beneficial to decrease the pore size.

Due to the opposite charges within the membrane pores, the membrane is predestinated for enhanced ion transport compared to non-ionic transport. Consequently, in the next step, the oppositely charged block copolymer membrane underwent salt-permeation tests.

6.4 Permeance and Retention Measurements of Post-Modified Diblock Copolymer Blend Membranes with Salts

To evaluate the performance of multifunctional membranes, such as charge-mosaic membranes, which are designed to separate electrolytes from non-electrolytes *via* dialysis, the post-modified double-charged diblock copolymer blend membrane was subjected to salt permeation tests. Sodium chloride (NaCl) was selected to represent monovalent salts, while magnesium sulfate (MgSO_4) was chosen as a representative divalent salt. No asymmetric salts were used for the measurements.

Figure 42 illustrates the salt rejection behavior of monovalent and divalent ions. As shown, all ions permeate through the membrane with little to no rejection. Interestingly, this includes divalent cations such as Mg^{2+} and SO_4^{2-} , but also the monovalent ions Na^+ and Cl^- . There is a slight tendency for cations to be retained more than anions, which would suggest a deviation from electroneutrality. This effect could be attributed to the significantly higher conversion of PDMA to PAA compared to the quaternization of P4VP, resulting in an excess of negative charges within the membrane. Consequently, a mildly increased retention of cations relative to anions may occur due to charge imbalance. However, the error bars fall within the same range as the observed retention values, indicating that the retention of cations and anions is approximately equivalent within experimental uncertainty.

However, in general, large uncharged molecules can be retained depending on the pore size of the membrane, as shown by previous diblock copolymers membranes.³⁴⁹ This suggests a potential application for desalinating a saline solution containing neutral particles by adding fresh water. By fine-tuning the molecular weight of the block copolymers and implementing further post-modification, the pore size and molecular weight cutoff could be optimized for specific applications. Given that the PAA pores are already relatively small due to the significant swelling of PAA in aqueous systems, the next step would be to reduce the size of the P4VP pores in addition to the quaternization. This adjustment might enable the creation of oppositely charged pores with comparable sizes in aqueous media.

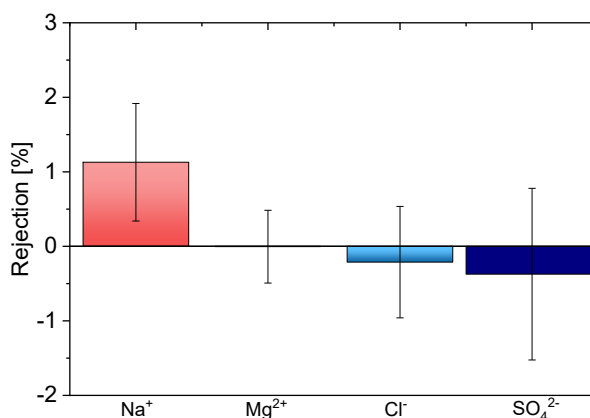


Figure 42. Rejection of monovalent and divalent cations and anions by the double-charged diblock copolymer blend membrane.

7 Discussion and Outlook

This chapter brings together the various components of this thesis, including the research findings published in the three articles reprinted in chapter 5 and the unpublished work detailed in chapter 6, covering the synthesis of homopolymers (chapter 7.1) and diblock copolymers (chapter 7.2), as well as exploring the application of diblock copolymers in the development of isoporous membranes for protein separation (chapter 7.3) and in the development of diblock copolymer blend membranes with oppositely charged channels (chapter 7.4). Additionally, it provides an outlook for future research directions (chapter 7.5).

7.1 Synthesis of Homopolymers *via* Light-Induced RAFT Polymerization

At the outset of this thesis, the high potential of block copolymers for diverse applications was highlighted, particularly due to their remarkable ability to self-assemble into a variety of well-defined morphologies. This self-assembly behavior is especially advantageous for fabrication of isoporous membranes, benefiting from the precise and tunable nanostructures that block copolymers can enable.

Despite these promising features, the synthesis of well-defined block copolymers with a narrow molecular weight distribution remains a significant challenge. Many of these block copolymers commonly used are synthesized *via* living anionic polymerization. However, this method is highly sensitive to impurities, moisture, and other environmental conditions, necessitating strictly anhydrous and oxygen-free environments. These stringent requirements complicate the polymerization process and make it both technically demanding and costly to implement, especially on an industrial scale. Additionally, the range of monomers that can be utilized is relatively limited, as only those capable of stabilizing the propagating anion are suitable. Consequently, there is an ongoing need to develop economically viable and more robust synthetic methods to produce high-quality block copolymers while maintaining precise control over reaction conditions.

RAFT polymerization has become a promising alternative for the synthesis of block copolymers. Unlike living anionic polymerization, RAFT does not require extreme conditions, such as stringent exclusion of oxygen or moisture. It can be carried out under relatively mild and easily controlled conditions, making it more practical for both laboratory and industrial applications.

Publication 1 (chapter 5.1) establishes a strong foundation for the synthesis of block copolymers by detailing the preparation of homopolymer macroRAFT agents using a photo-iniferter approach. This method was chosen over the traditional thermally initiated RAFT mechanism. This choice offers distinct advantages, notably the decoupling of the initiation step from temperature, allowing the polymerization of especially rapidly propagating monomers at lower temperatures like 40 °C instead of the typical 80 °C

required for thermal initiation and short polymerization times (1 – 6 h). A simple, custom-built setup was assembled to ensure optimal irradiation of the polymerization mixture. This setup is highly cost-effective, with an initial investment of approximately 200 €, and offers the flexibility to match the wavelength of the LED strips with the absorption characteristics of the RAFT agent used. It is important to note that the light intensity of LED strips can diminish with frequent use, necessitating periodic checks and replacements to maintain optimal performance. Nevertheless, the LED strips typically have a lifespan of about one year with regular use of several hours per week, and the material replacement cost is only 50 €, making this a highly economical and sustainable solution for ongoing experiments.

The second cornerstone was to select an environmentally friendly solvent system. Aqueous-alcoholic mixtures emerged as the optimal choice due to their compatibility with trithiocarbonate RAFT agents, which maintain high solubility in these media. Furthermore, both the monomers and the resulting polymers demonstrated sufficient solubility in these systems. Ultimately, a 50:50 (w/w) water–ethanol mixture was selected, providing the lowest concentration of ethanol at which all components remained sufficiently dissolved, ensuring effective polymerization while minimizing the use of organic solvent. Ethanol was chosen over other alcohols since it is one of the most recommended organic solvents^{359,360} and can be derived from renewable sources such as biomass or the biodegradable fractions of waste, making it a sustainable and eco-friendly option for polymerization. This selection highlights a commitment to greener chemistry and contributes to a more environmentally sustainable synthesis process.

This polymerization process was successfully adapted for the synthesis of macroCTAs across a range of monomer classes. Specifically, PDMA was synthesized as representative of polyacrylamides, PDMAEA for polyacrylates, and polyvinylpyridines such as P2VP and P4VP for vinyl polymers. Due to the distinct chemical properties of these monomers, different apparent propagation rate constants were observed, with the order: DMA > DMAEA > 4VP > 2VP. As anticipated, the rate of polymerization was highly dependent on the light intensity, a key factor that influences scalability. A rarely investigated but crucial parameter in this context is the geometry of the reaction vessel, which significantly affects the polymerization rate. Specifically, the polymerization rate decreases as the diameter of the vessel increases, with the apparent propagation constants showing a linear decline with a larger vessel radius. This effect is more pronounced for slowly propagating monomers, such as vinylpyridine, compared to rapidly propagating monomers, like DMA, making the system with low propagating monomers more dependent on the continuous emergence of new species to shift the equilibrium toward the propagating chain.

Notably, blue-light-induced RAFT polymerization offers significant advantages by decoupling initiation from temperature. This makes it particularly well-suited for monomers that do not require high activation energies for polymerization, such as (meth)acrylates and (meth)acrylamides. For the vinylpyridines, to achieve a satisfactory space-time yield, additional measures were required, such as increasing the concentration of monomer and RAFT agent or adjusting the temperature to accelerate the polymerization process.

In conclusion, photoiniferter RAFT polymerization has proven to be a scalable and versatile method for synthesizing various macroCTAs across different monomer classes. However, the findings emphasize that fast-propagating monomers, such as acrylates

and acrylamides — which are also more extensively documented in the literature — are particularly well-suited since high conversion rates can be achieved at a low ambient temperature. Furthermore, scalability up to a 500 mL reaction volume was demonstrated without significant loss of conversion or broadening of dispersity, highlighting the robustness and efficiency of visible-light-induced RAFT polymerization.

7.2 Synthesis of Diblock Copolymers *via* Light-Induced RAFT Polymerization

To synthesize PDMA-*b*-PS and P4VP-*b*-PS diblock copolymers, the corresponding macroCTAs were chain-extended with styrene, as detailed in publication 2 (chapter 5.2). A key challenge in synthesis of polystyrene-containing diblock copolymers *via* conventional RAFT solution polymerization is the relatively slow propagation rate of styrene. To overcome this limitation, an *ab initio* emulsion polymerization approach was employed. This strategy offers notable advantages over solvent-based methods, particularly in terms of reaction kinetics and environmental sustainability: i) the heterogeneous distribution of styrene in the emulsion creates high monomer concentrations within the latex particles, accelerating polymerization, and ii) emulsion polymerizations are carried out in aqueous systems, enhancing environmental sustainability. This approach enabled the synthesis of amphiphilic macroCTAs through polymerization-induced self-assembly (PISA) without the need for additional surfactants or stabilizers, ensuring purer final products. Moreover, like the solution polymerizations described in publication 1, these emulsion polymerizations were initiated by blue light.

The reaction kinetics and latex particle formation were thoroughly investigated for both PDMA-*b*-PS and P4VP-*b*-PS systems. For this purpose, PDMA and P4VP macroCTAs with comparable degrees of polymerization were used and subsequently chain-extended with an identical amount of styrene. A detailed comparison revealed faster self-assembly in the synthesis of P4VP-*b*-PS diblock copolymers compared to PDMA-*b*-PS diblock copolymers, probably due to the approximately three times larger Flory-Huggins interaction parameter χ for P4VP-*b*-PS than for PDMA-*b*-PS.^{339,345} Other typical phenomena characteristic of emulsion polymerizations, such as latex particle swelling and monomer depletion, were also observed. The final latex particles of both systems displayed a dry-state radius of approximately 20 nm.

The synthesis of P4VP-*b*-PS diblock copolymers was more complex than that of PDMA-*b*-PS, likely due to the findings from publication 1 regarding the homopolymerization behavior of 4VP. The homopolymerization of 4VP proceeded at a significantly slower rate compared to DMA, requiring approximately six times longer reaction durations to obtain similar conversions. This prolonged reaction time can increase the likelihood of side reactions, including termination events. Additionally, the precipitation and recovery of P4VP were less efficient, often requiring multiple attempts to fully recover the polymer. These challenges underscore the inherent complexities of working with 4VP as a monomer compared to DMA. However, the obtained block copolymers of PDMA-*b*-PS and P4VP-*b*-PS could be synthesized within short polymerization (times ≤ 6 h) and with narrow molecular weight distribution.

A critical factor anticipated to affect the polymerization process was light scattering, which arose from the presence of monomer droplets and latex particles in the emulsion system. In contrast to the previously discussed homogeneous solution polymerization, light scattering in this system could limit the light penetration and potentially hinder radical generation inside the vessel. However, despite these challenges, the polymerization rates remained high, even after the formation of the latex particles by the amphiphilic macroCTAs. This finding highlights its suitability for scalable laboratory synthesis.

Nevertheless, an inverse relationship between inhibition time and the surface-to-volume ratio of the reaction vessel was observed, necessitating adjustments to reaction duration for larger-scale setups. For larger vessel diameters, conversion versus time curves exhibited a shift towards longer reaction times, emphasizing the importance of optimizing reaction conditions during scale-up. However, in all polymerizations, high conversions (> 80 % after 6 h) were achieved. These findings underscore the robustness of the photoiniferter RAFT polymerization process, even under conditions where light penetration is limited.

The findings discussed thus far relate to a two-step process where homopolymers were first synthesized, followed by chain extension with styrene. However, a more practical and efficient approach is the semi-batch process, in which the second monomer is added sequentially. This approach was specifically adapted to streamline the synthesis of PDMA-*b*-PS diblock copolymers.

Since the homopolymerization of PDMA had already been successfully conducted in the same solvent system, adopting a semi-batch strategy was a logical step. In this setup, the RAFT agent and DMA monomer were introduced at the outset, followed by the addition of styrene after 2 h of polymerization. This approach yielded intriguing results. Upon the introduction of styrene, the reaction conversion of DMA subsequently stagnated, likely due to the formation of amphiphilic block copolymers and the onset of the PISA process. The micelle formation increased the local concentration of styrene, leading to the formation of latex particles. Conversely, DMA, which is highly soluble in the water-ethanol mixture, probably lacked the driving force to migrate into the latex particles. This resulted in a localized separation of the reaction environment from the unincorporated DMA. This semi-batch strategy offered distinct advantages compared to the two-step approach: (i) the process eliminated the need for homopolymer purification and (ii) the overall working time to produce the polymers can be reduced by several hours.

In contrast, the semi-batch polymerization of 4VP and styrene did not exhibit stagnation in the conversion of 4VP after adding the styrene. This difference can likely be attributed to the poorer solubility of 4VP in the water-ethanol mixture compared to DMA and its probably increased miscibility with styrene, which encouraged 4VP's incorporation into latex particles during polymerization.

In summary, PDMA-*b*-PS and P4VP-*b*-PS diblock copolymers were successfully synthesized using a combined approach of blue-light-induced RAFT polymerization and the PISA process. This method proved effective for producing block copolymers in substantial quantities under environmentally friendly conditions, establishing blue-light-induced RAFT polymerization as a compelling alternative to traditional anionic polymerization. Moving forward, these block copolymers are used for application in membrane fabrication.

7.3 Charged Isoporous Diblock Copolymer Membranes

The successful synthesis of PDMA-*b*-PS diblock copolymers *via* blue-light-induced RAFT polymerization — synthesized as detailed in publications 1 and 2 — provided sufficient quantities of material for membrane fabrication. Isoporous PDMA-*b*-PS diblock copolymer membranes are particularly attractive due to their potential for post-modification. Specifically, the PDMA block can be converted into PAA, a water-soluble and pH-responsive polymer, thus significantly expanding the functional versatility of these membranes.

A key advantage of diblock copolymer membranes lies in their isoporous surface structure, which provides precise size-selective separation. Incorporating charged functionalities further enhances their performance by introducing charge-selective behavior, crucial for advanced separation applications.

Previous studies by the research groups of Boudouris and Phillip^{233,234,348} predominantly employed PI-*b*-PS-*b*-PDMA triblock copolymers cast onto glass plates using the SNIPS process. However, those membranes exhibited a moderately broad pore size distribution in the dried state. To improve membrane stability and scalability, this work replaced glass plates with non-woven substrates. This adjustment required optimization of casting solution formulation. A ternary dioxane-THF-DMF (60:20:20 w/w/w) solvent system with a high polymer concentration (33 – 34 wt%) resulted in membranes with a pore size of approximately 25 nm in the dried state and a surface porosity of around 23 %. This casting approach produced membranes with enhanced isoporosity compared to earlier reports.^{233,234,348} Moreover, the use of non-woven substrates and a casting machine enabled the fabrication of larger membrane areas, supporting future industrial-scale production.

The influence of humidity during membrane fabrication was also investigated. Due to the hygroscopic nature of both the solvents and the PDMA block, high ambient humidity (> 45 % at room temperature) compromised the isoporous surface, resulting in interconnected pore structures. These findings emphasize the necessity of strict humidity control during processing to maintain structural integrity.

Following successful fabrication, the PDMA-*b*-PS diblock copolymer membranes were successfully post-modified to generate PAA-*b*-PS diblock copolymer membranes, enabling a comparative assessment of their properties. Both membrane types exhibited pore swelling in water, reducing their effective pore size. However, while the PDMA-*b*-PS diblock copolymer membranes showed no pH-dependent change in water permeance, the PAA-*b*-PS diblock copolymer membranes displayed pronounced pH-responsive behavior, with reduced permeance at higher pH values. This effect arises from the ionization state of the PAA chains: at low pH, hydrogen bonding between segments leads to a compact structure, whereas at higher pH, ionization and electrostatic repulsion promote chain stretching, limiting water flux.

Effective pore sizes were characterized using narrow molecular weight-distributed PEOs. The PDMA-*b*-PS diblock copolymer membranes exhibited the smallest pore size, corresponding to an MWCO hydrodynamic radius of 2.2 nm. In contrast, PAA-*b*-PS membranes showed tunable pore sizes depending on pH: at pH 5.5, the MWCO corresponded to 4.9 nm, while at pH 7.5 it was reduced to 3.7 nm. This tunability

is particularly relevant for protein separation, where precise size and charge-based discrimination are required.

Protein separation experiments were conducted at pH 7.8, approximating physiological conditions, in PBS buffer. The PAA-*b*-PS diblock copolymer membranes, featuring negatively charged pores, offered both size- and charge-selective separation. Test proteins included cytochrome C and insulin, with similar hydrodynamic radii but opposite charges at physiological pH, as well as lysozyme and ovalbumin, which have comparable sizes but opposite charges. Myoglobin, near neutral at this pH, served as a control.

The pristine PDMA-*b*-PS membranes demonstrated lower permeance in PBS than in deionized water, likely due to salt-membrane and salt-analyte interactions and the higher ionic strength of the buffer, which effectively reduced pore size. Under these conditions, the pristine membranes rejected all tested proteins. In contrast, the PAA-*b*-PS membranes showed selective rejection. Proteins such as lysozyme, myoglobin, and ovalbumin were predominantly rejected ($\geq 90\%$), whereas cytochrome C and insulin demonstrated differential transport: cytochrome C, a positively charged protein, permeated nearly completely (3 % rejection), while insulin, negatively charged, was largely rejected (77 %). These results can be attributed to favorable electrostatic attraction facilitating cytochrome C transport, while electrostatic repulsion hindered insulin passage.

Tests with protein mixtures provided a more application-oriented perspective. While no clear selectivity emerged between cytochrome C and lysozyme due to pore blockage by lysozyme, a distinct preference for cytochrome C was observed relative to other proteins, with selectivity factors of 4 compared to insulin and 16 compared to ovalbumin. This demonstrates the ability of PAA-*b*-PS diblock copolymer membranes to preferentially facilitate transport of small, positively charged proteins while excluding larger or negatively charged species.

Overall, the PAA-*b*-PS diblock copolymer membranes exhibit significant promise for protein separation applications. Their separation range lies at the interface of ultrafiltration and nanofiltration, making them highly relevant for biomedical and biotechnological uses. Additionally, the possibility of tuning pore size through copolymer composition and molecular weight broadens their potential beyond protein separations to a wide range of targeted separation processes.

Finally, the insights gained from this work serve as a valuable foundation for developing block copolymer blend membranes using PDMA-*b*-PS as a key component. A comprehensive understanding of pore size, permeance, MWCO, and selectivity will be critical in optimizing the next generation of functional membranes for advanced separations.

7.4 Diblock Copolymer Blend Membranes

In the final part of this work, blending of diblock copolymers and post-modifications were used to develop oppositely charged diblock copolymer blend membranes. This effort builds on the expertise gained from the PDMA-*b*-PS diblock copolymer membrane system, as detailed in the previous chapter, combined with knowledge from the well-established PS-*b*-P4VP diblock copolymer system — one of the earliest and most well-established isoporous membrane platforms. The PS-*b*-P4VP diblock copolymer system provides a robust foundation for further structural and chemical modifications and enhancements.^{227,239,241,361,362} However, several challenges needed to be addressed, particularly in optimizing the casting and post-modification process.

Given that these blend membranes had not been manufactured previously, optimizing the casting conditions was essential. Achieving membranes with distinct oppositely charged channels on the top surface, rather than mixed-charge domains, required a comprehensive understanding of the blending behavior of the two block copolymers.

To investigate the structural compatibility and phase separation behavior of the two diblock copolymers, DSC was employed to examine the glass transition temperatures of the individual block copolymers and their blends. In polymer systems, distinct T_g values indicate phase-separated domains, while intermediate T_g values suggest mixed-phase regions. The DSC analysis of the PDMA-*b*-PS/ P4VP-*b*-PS diblock copolymer blend did not reveal distinct glass transitions for either PDMA or P4VP, nor any intermediate T_g . This outcome was likely due to a sensitivity issue of the measurement in consequence of the low weight fractions of the PDMA and P4VP blocks in the blend. To address this limitation, blends of the individual homopolymers PDMA and P4VP, which were used as the macroRAFT agents for the respective diblock copolymers with polystyrene, were analyzed instead. The PDMA/ P4VP blends exhibited two distinct T_g values corresponding to the individual polymers, confirming the presence of discrete, phase-separated domains.

In solution, the structural composition often deviates from that of bulk blends prepared from solutions with unselective solvents or polymer melts, since domain formation is governed by the effective interaction parameter χN_{eff} which is further modulated by solvent interactions and other environmental factors, significantly influence domain formation. To gain further insights, PFG NMR spectroscopy was employed to the diblock copolymer blend casting solution to measure the diffusion coefficients of the PDMA and P4VP blocks. The analysis revealed a higher diffusion rate for the PDMA block compared to the P4VP block in the blend. This difference suggests that the two blocks remained phase-separated and likely formed distinct micellar structures within the casting solution.

As the phase separation behavior of the diblock copolymer blends showed promising results regarding the immiscibility of the PDMA and the P4VP block, the next step was the fabrication of the blend membranes. However, the production of isoporous membranes through the SNIPS process is strongly influenced by factors such as solvent composition, polymer concentration, and external conditions like temperature and humidity. Previous work had established optimal conditions for casting pure PDMA-*b*-PS and P4VP-*b*-PS membranes, respectively, but these conditions were not suitable for the diblock copolymer blend system. Therefore, extensive optimization of SNIPS parameters and fabrication conditions was necessary to achieve well-defined

blend membranes. A ternary solvent system consisting of dioxane, THF, and DMF in a 20:50:30 (w/w/w) ratio proved to be the most suitable for fabricating isoporous PDMA-*b*-PS/ P4VP-*b*-PS diblock copolymer blend membranes. However, the differing optimal polymer concentrations for each copolymer complicated the process. PDMA-*b*-PS diblock copolymers required high polymer concentrations (33 – 34 wt%) to prevent penetration into the nonwoven substrate, whereas P4VP-*b*-PS diblock copolymers required casting at lower concentrations ($\approx$ 23 wt%). Achieving a balance between structural integrity and permeability proved challenging, as polymer concentrations above 30 wt% resulted in dense, nearly impermeable membranes, while lower concentrations led to solution absorption into the substrate. Finally, the addition of glycerin to the casting solution successfully addressed these challenges. Just 2 – 3 wt% glycerin increased solution viscosity, preventing substrate absorption and enabling the formation of membranes with an isoporous top surface and an open, sponge-like substructure.

SEM images of the diblock copolymer blend membranes revealed an isoporous top structure with a consistent surface roughness. SEM imaging, combined with EsB electron detection after iodine staining, indicated a "patchwork-like" morphology, where regions dominated by either PDMA or P4VP were interspersed across the surface. This random distribution suggests microphase separation within a macrophase-separated structure.

To impart opposite charges within the membrane structure, post-modification reactions were conducted. The P4VP block was quaternized using methyl iodide, while the PDMA block was converted into PAA using hydrochloric acid. Methyl iodide vapor-phase reactions maintained the membrane structure integrity but proceeded slowly. SEM analysis showed that small volumes of methyl iodide did not affect membrane morphology, while higher volumes (≥ 0.083 mL/cm²) led to pore closure and densification, negatively impacting membrane performance. FTIR spectroscopy confirmed successful quaternization, though overlapping signals with the PDMA component complicated interpretation. ¹H-NMR analysis in a solvent mixture of THF-*d*₈ and methanol-*d*₄ revealed a 51% conversion of P4VP to its quaternized form, while PDMA remained unreacted.

Subsequent treatment with hydrochloric acid further functionalized the membrane, introducing pH-dependent negatively charged PAA domains. FTIR analysis indicated a shift from amide to carboxylic acid groups, confirming the conversion. Notably, both post-modification reactions preserved the membrane's open structure, as evidenced by SEM imaging.

Water permeance measurements highlighted the impact of post-modification on membrane performance. The pristine blend membrane exhibited a permeance of 126 ± 12 L/(m²·h·bar). Following quaternization with methyl iodide, permeance decreased to 84 ± 9 L/(m²·h·bar) due to swelling of the charged P4VP block. After hydrochloric acid treatment, a slight increase in permeance was observed, likely due to ionization-induced pore stabilization, consistent with previous findings for pure PDMA-*b*-PS diblock copolymer membranes.³⁴⁹

As membranes with distinct positively and negatively charged channels can enable simultaneous transport of anions and cations *via* distinct pathways, salt permeation tests were performed on the charged diblock copolymer membrane. The tests revealed that monovalent and divalent ions passed through the post-modified membranes without

significant rejection. However, based on the pore size of the membranes, larger uncharged molecules can be retained. This suggests potential applications for separating neutral particles from saline solutions. Further optimization, such as reducing the size of P4VP pores prior to quaternization, could enhance selectivity for charged species.

This study successfully developed and optimized PDMA-*b*-PS/ P4VP-*b*-PS diblock copolymer blend membranes with isoporous top surfaces and interconnected substructures. Although the desired regular charge-mosaic structure was not obtained, the integration of post-modification reactions introduced opposite charges within the membrane pores, creating a multifunctional membrane system. The combination of phase-separated pore structures and tailored surface charges makes these membranes promising candidates for advanced separation processes, including the selective removal of charged species and desalination applications.

7.5 Outlook

This work successfully demonstrated the strength of blue light to initiate RAFT polymerizations in solutions and in emulsions. The resulting diblock copolymers enabled the development of functional membranes with advanced separation capabilities. Specifically, PDMA-*b*-PS diblock copolymers proved suitable for fabricating isoporous membranes, which could be further post-modified to achieve charge- and size-selective separation of proteins. Furthermore, the study established important groundwork for the fabrication, post-functionalization, and characterization of diblock copolymer blend membranes, highlighting their potential as multifunctional separation materials featuring oppositely charged domains. Nevertheless, several aspects warrant further optimization and in-depth characterization to fully exploit their capabilities in advanced membrane applications.

One of the primary limitations was the limited investigation of the spatial distribution of charged domains, which was only assessed through staining of pristine PDMA-*b*-PS/P4VP-*b*-PS diblock copolymer membranes. To conclusively determine the final structure, more advanced analytical techniques are recommended. A promising method is AFM-IR (atomic force microscope-infrared spectroscopy), which can map the distribution of PDMA and P4VP domains by scanning the surface while simultaneously recording IR spectra. This technique would provide a clearer understanding of the pore structure and the distribution of functional moieties.

Another challenge lies in the likely size disparity between P4VP/ P4VP-Me block and PAA block pores. While PAA and P4VP-Me swell in aqueous environments, P4VP only swells at very low pH values. Since the P4VP units were only partially post-modified to P4VP-Me units, the pores size of the P4VP/ P4VP-Me pores in neutral aqueous media is probably larger compared to the PAA pores. An additional post-modification step could reduce pore size yielding comparable pore sizes to the PAA domains and achieving a narrow MWCO for the blend membranes. Further improvement could involve further modifying PAA to introduce permanent negative charges, thereby eliminating the membrane's pH-dependent separation characteristics while maintaining its selective functionality.

Future research should prioritize several key areas to further enhance the performance and applicability of these diblock copolymer blend membranes. Advanced structural characterization, particularly through techniques such as AFM-IR and other surface-mapping methods, will provide deeper insights into the nanoscale morphology and chemical distribution of the several blocks within the membranes. Additionally, refining post-modification steps will be crucial to achieve an optimal balance between pore size control and the introduction of stable charges, ensuring both selectivity and functionality. Furthermore, long-term stability evaluations under operational conditions will be necessary to assess membrane durability and overall performance over extended periods. These advancements will be essential for fully realizing the potential of these diblock copolymer blend membranes in advanced separation technologies.

8 References

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9 Appendix

9.1 Supporting Information Publication 1

The supporting information is reprinted with permission from L. Hub, J. Koll, M. Radjabian, V. Abetz, Blue light-induced iniferter RAFT polymerization in aqueous-alcoholic media as a universal tool for the homopolymerization of various monomer families: kinetic investigations on different scales, *Polym. Chem.* **2023**, 14 (26), 3063–3074 – published by The Royal Society of Chemistry.

Supporting information

Blue light-induced iniferter RAFT polymerization in aqueous-alcoholic media as a universal tool for the homopolymerization of various monomer families: kinetic investigations in different scales

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1. Absorption spectrum of the RAFT agent DDMAT

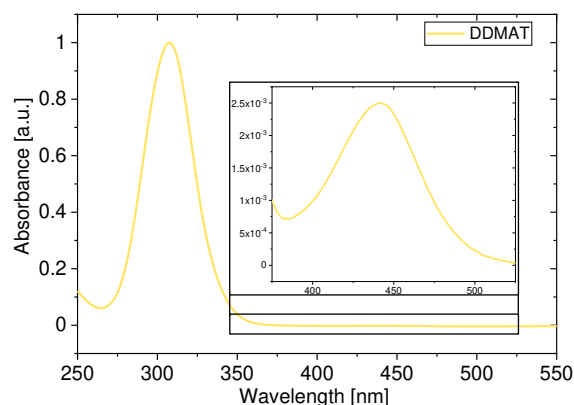


Fig. S 1: UV-Vis absorption spectrum of the RAFT agent DDMAT in ethanol. The signal with the maximum at 308 nm shows the spin-allowed $\pi \rightarrow \pi^*$ electronic transition, the second absorption region with the local maximum at 442 nm is assigned to the spin forbidden $n \rightarrow \pi^*$ electronic transition.

2. Photoreactor set-up

2.1 Experimental set-up

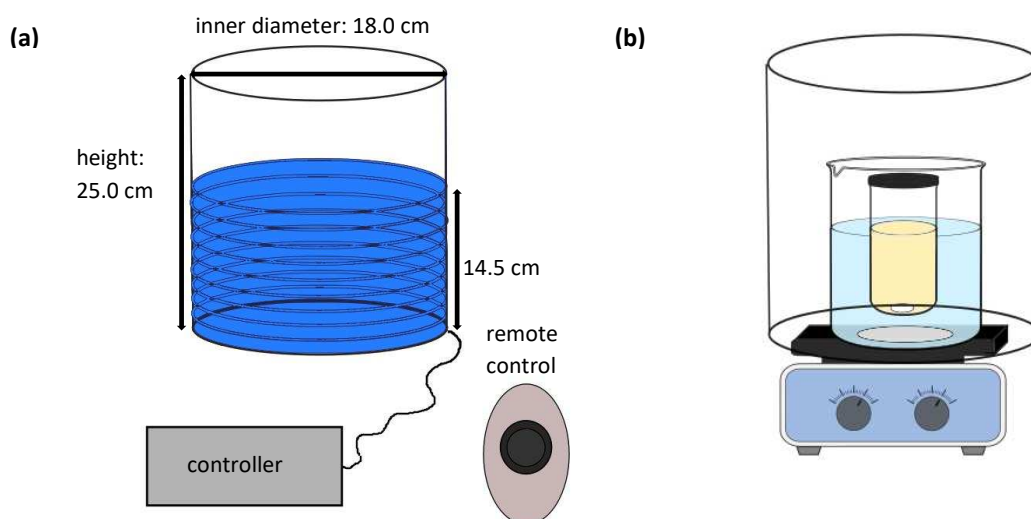


Fig. S 2: (a) Schematic set-up of the photoreactor. (b) Schematic experimental set-up for blue light initiated RAFT polymerizations. The polymerization vessels were placed into a water bath centered on the heating plate (not to scale).

2.2 Light intensity of the photoreactor

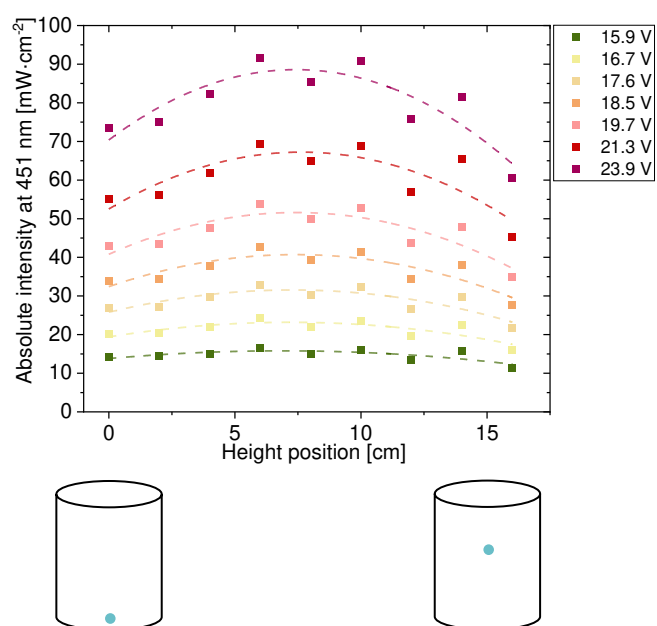


Fig. S 3: Height position dependent light intensity of the blue LED at the maximum emission wavelength of $\lambda_{\text{max}} = 451 \text{ nm}$ at the centre of the blue LED.

3. Synthesis of PDMAEA, P4VP and P2VP macroCTAs *via* blue light-induced iniferter RAFT solution polymerization

Synthesis of PDMAEA macroCTA *via* blue light-induced iniferter RAFT solution polymerization. A typical photo-iniferter RAFT polymerization of DMAEA with a molar ratio of $[DMAEA]_0/[DDMAT]_0 = 500/1$ was conducted as follows: DDMAT (10.0 mg, 27.4 μmol , 1.0 eq.) and DMAEA (2.22 mL, 13.7 mmol, 500 eq.) were dissolved in ethanol (5.34 mL). While stirring the solution, water (4.22 mL) was added dropwise and *N,N*-dimethylformamide (20 μL) added as an internal reference for ^1H -NMR analysis and an initial sample was taken. The solution was degassed by purging the ice-cooled polymerization vial with argon for 10 min. The polymerization vessel was placed in the centre of the photoreactor and the polymerization was carried out under blue light irradiation ($\lambda_{\text{max}} = 451 \text{ nm}$) at a water bath temperature of 40 °C under constant stirring (400 rpm). After the desired time of exposure to the blue light, the polymerization was stopped by turning off the irradiation source, quenching in an ice-cooling bath and exposing to air. The solvent was removed by vacuum and the crude polymer was obtained by drying in vacuum at 40 °C for 24 h. Subsequently, the polymer was dissolved in ethanol, precipitated in cold cyclohexane, filtered and dried under vacuum at 40 °C for 48 h.

Synthesis of P4VP macroCTA *via* blue light-induced iniferter RAFT solution polymerization. A typical RAFT photopolymerization of 4-vinylpyridine with a molar ratio of $[4VP]_0/[DDMAT]_0 = 470/1$ was conducted as follows: DDMAT (30.0 mg, 82.3 μmol , 1.0 eq.) and 4VP (4.19 mL, 38.9 mmol, 471 eq.) were dissolved in ethanol (10.41 mL) and stirred for homogenization. Water (8.23 mL) was added dropwise. The reaction solution was degassed by purging the ice-cooled polymerization vial with argon for 10 min. The polymerization vial was placed in the water bath with a temperature of 40 °C or 50 °C and illuminated with blue light ($\lambda_{\text{max}} = 451 \text{ nm}$). After the desired time of exposure to the blue light, the polymerization was stopped by turning-off the irradiation source, quenching in an ice-cooling bath and exposing to air. The solvent was removed by vacuum and the crude polymer was obtained by drying in vacuum at 40 °C for 24 h. Subsequently, the polymer was dissolved in ethanol, precipitated in cold cyclohexane, filtered and dried under vacuum at 40 °C for 48 h.

Synthesis of P2VP macroCTA *via* blue light-induced iniferter RAFT solution polymerization. In a typical photo-iniferter RAFT polymerization of 2VP with a molar ratio of $[2VP]_0/[DDMAT]_0 = 470/1$, DDMAT (35.0 mg, 96.0 μmol , 1.0 eq.) and 2VP (4.89 mL, 45.3 mmol, 470 eq.) were dissolved in ethanol (7.09 mL). Under stirring conditions, water (5.60 mL) was added. The cooled solution was degassed by purging with argon for 10 min. The polymerization vessel was placed in the centre of the photoreactor and the polymerization was conducted under constant stirring (400 rpm) and started by placing the vial in the water bath (40 °C – 70 °C) and exposing the solution to blue light ($\lambda_{\text{max}} = 451 \text{ nm}$). After the desired time of exposure to the blue light, the polymerization was stopped by turning-off the irradiation source, quenching in an ice-cooling bath and exposing to air. The solvent was removed by vacuum and the crude polymer was obtained by drying in vacuum at 40 °C for 24 h. Subsequently, the polymer was dissolved in ethanol, precipitated in cold cyclohexane, filtered and dried under vacuum at 40 °C for 48 h.

4. NMR analysis

4.1 Determination of the DMA conversion

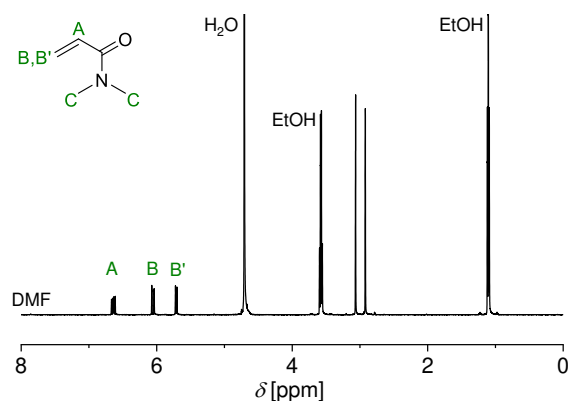


Fig. S 4: Full ¹H-NMR spectrum (in D₂O) of the reaction solution of the blue light-induced iniferter RAFT polymerization of DMA in the water-ethanol mixtures (50:50 w/w) (20% w/w).

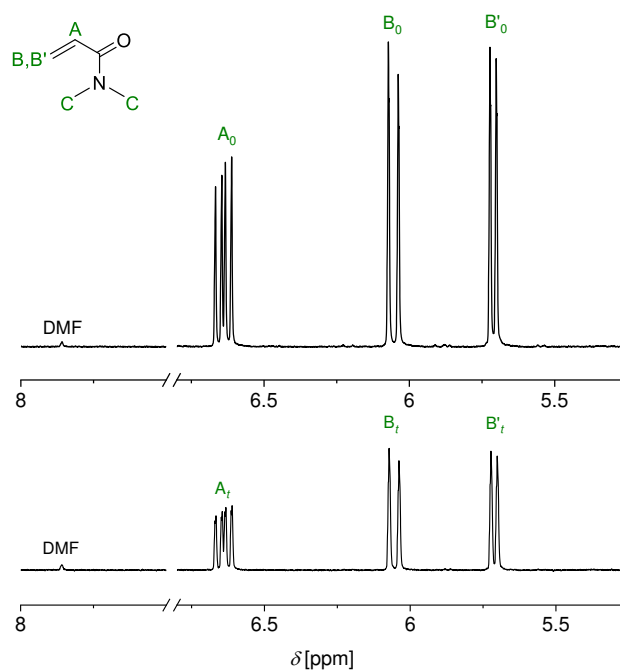


Fig. S 5: ¹H-NMR spectrum (in D₂O) of the reaction solution of the photo-iniferter RAFT polymerization of DMA at the start of the polymerization (top) and at the end of the polymerization (bottom). The protons for the determination of the conversion are assigned to the respective signals.

The monomer conversion p of DMA after normalization to the DMF signal integral is calculated as follows:

$$p_{\text{DMA}} = 1 - \frac{I_{A_t} + I_{B_t} + I_{B'_t}}{I_{A_0} + I_{B_0} + I_{B'_0}} \quad (1)$$

The theoretical molecular weight of the PDMA macroCTAs was calculated in the following way:

$$\bar{M}_{n,\text{th}} = \frac{[\text{DMA}]_0}{[\text{DDMAT}]_0} \cdot p_{\text{DMA}} \cdot M_{\text{DMA}} + M_{\text{DDMAT}} \quad (2)$$

4.2 Determination of the DMAEA conversion

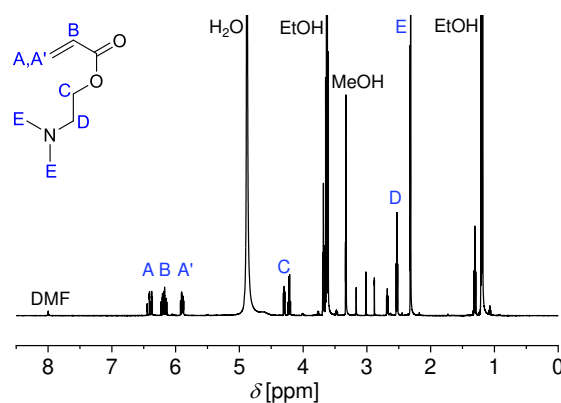


Fig. S 6: Full ^1H -NMR spectrum (in $\text{MeOH-}d_4$) of the reaction solution of the blue light-induced iniferter RAFT polymerization of DMAEA in the water-ethanol mixtures (50:50 w/w) (20% w/w).

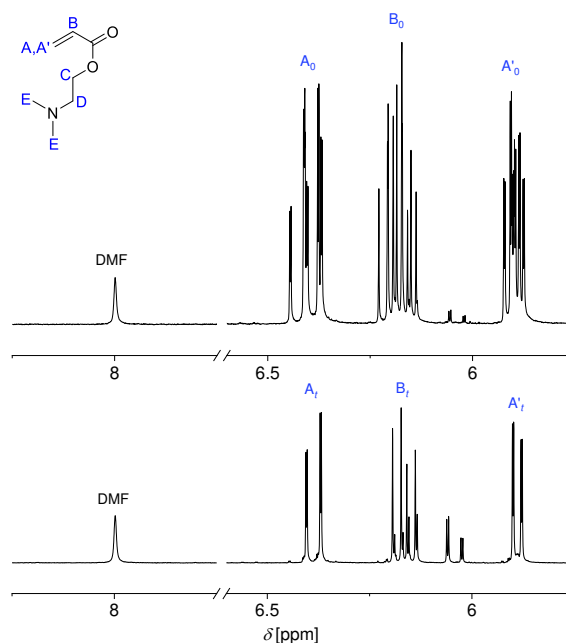


Fig. S 7: ^1H -NMR spectrum (in $\text{MeOH-}d_4$) of the reaction solution of the photo-iniferter RAFT polymerization of DMAEA at the start of the polymerization (top) and at the end of the polymerization (bottom). The protons for the determination of the conversion are assigned to the respective signals.

The monomer conversion p of DMAEA after normalization to the DMF signal integral is calculated as follows:

$$p_{\text{DMAEA}} = 1 - \frac{I_{A_t} + I_{B_t} + I_{A'_t}}{I_{A_0} + I_{B_0} + I_{A'_0}} \quad (3)$$

The theoretical molecular weight of the PDMAEA macroCTAs was calculated in the following way:

$$\bar{M}_{n,\text{th}} = \frac{[\text{DMAEA}]_0}{[\text{DDMAT}]_0} \cdot p_{\text{DMAEA}} \cdot M_{\text{DMAEA}} + M_{\text{DDMAT}} \quad (4)$$

4.3 Determination of the 4VP conversion

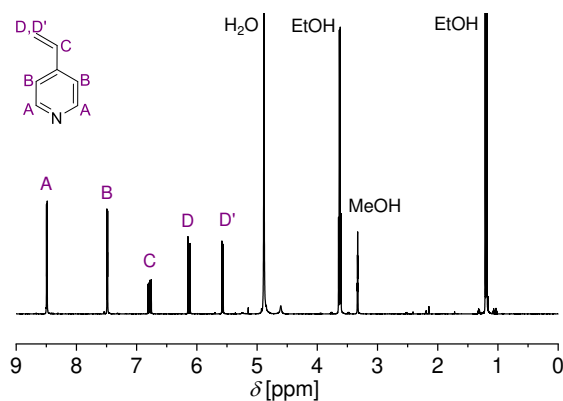


Fig. S 8: Full ^1H -NMR spectrum (in $\text{MeOH-}d_4$) of the reaction solution of the blue light-induced iniferter RAFT polymerization of 4VP in the water-ethanol mixtures (50:50 w/w) (20% w/w).

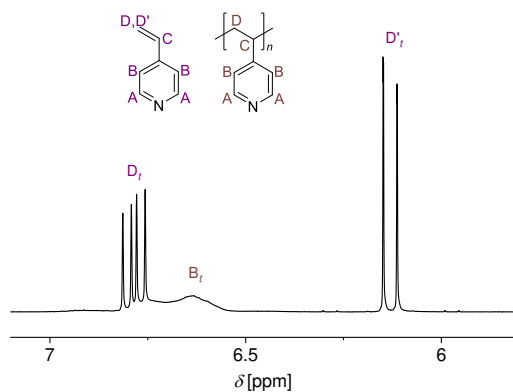


Fig. S 9: ^1H -NMR spectrum ($\text{MeOH-}d_4$) of the reaction solution of the photo-iniferter RAFT polymerization of 4VP at the end of the polymerization. The protons for the determination of the conversion are assigned to the respective signals.

The monomer conversion p of 4VP is calculated as follows:

$$p_{4VP} = \frac{I_{D_t+B_t} - I_{D'_t}}{I_{D'_t} + I_{D_t+B_t}} \quad (5)$$

The theoretical molecular weight of the P4VP macroCTAs was calculated in the following way:

$$\bar{M}_{n,th} = \frac{[4VP]_0}{[DDMAT]_0} \cdot p_{4VP} \cdot M_{4VP} + M_{DDMAT} \quad (6)$$

4.4 Determination of the 2VP conversion

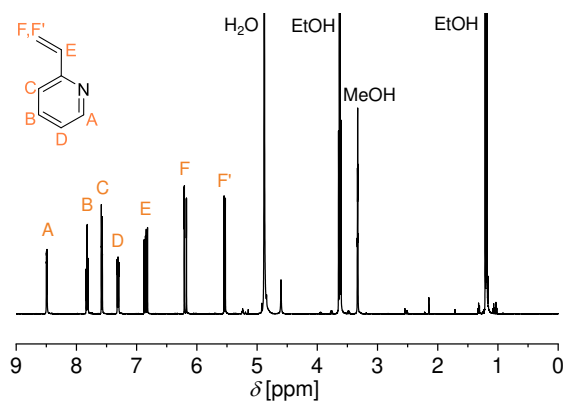


Fig. S 10: Full ^1H -NMR spectrum (in $\text{MeOH-}d_4$) of the reaction solution of the blue light-induced iniferter RAFT polymerization of 2VP in the water-ethanol mixtures (50:50 w/w) (30% w/w).

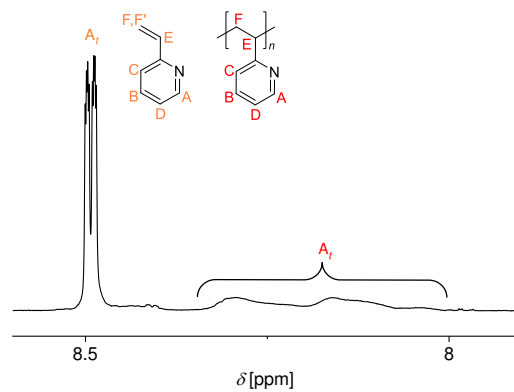


Fig. S 11: ^1H -NMR spectrum (in $\text{MeOH-}d_4$) of the reaction solution of the photo-iniferter RAFT polymerization of 2VP at the end of the polymerization. The protons for the determination of the conversion are assigned to the respective signals.

The monomer conversion p of 2VP is calculated as follows:

$$p_{2VP} = \frac{I_{A_t}}{I_{A_t} + I_{A_p}} \quad (7)$$

The theoretical molecular weight of the P2VP macroCTAs was calculated in the following way:

$$\bar{M}_{n,th} = \frac{[2VP]_0}{[DDMAT]_0} \cdot p_{2VP} \cdot M_{2VP} + M_{DDMAT} \quad (8)$$

5. PDMA homopolymers

5.1 In 20 mL vessels

Table S 1: Synthesized PDMA homopolymers *via* blue light-induced iniferter RAFT solution polymerization with a molar ratio of $[DMA]_0/[DDMAT]_0 = 500$ in water-ethanol mixtures (50:50 w/w) (20% w/w).

T [°C]	I_{light} [mW·cm ⁻²]	Sample code ^{a)}	time [min]	conversion [%] ^{b)}	$\bar{M}_{n,\text{th}}$ [kDa] ^{c)}	$\bar{M}_{n,\text{app}}$ [kDa] ^{d)}	$\bar{D}$ ^{e)}
40	16	PDMA ^{1.5}	31	2.4	1.5	2.4	1.41
		PDMA ^{5.4}	61	10.2	5.4	4.7	1.36
		PDMA ^{11.6}	120	22.8	11.6	11.2	1.24
		PDMA ^{24.8}	240	49.9	24.8	23.1	1.12
40	30	PDMA ^{5.3}	15	10.1	5.3	4.8	1.39
		PDMA ^{11.8}	32	23.3	11.8	10.8	1.20
		PDMA ^{21.6}	62	43.2	21.6	19.7	1.15
		PDMA ^{30.8}	90	62.5	30.8	28.0	1.12
		PDMA ^{32.8}	120	66.2	32.8	28.5	1.14
		PDMA ^{42.1}	240	85.2	42.1	33.2	1.20
40	49	PDMA ^{8.9}	16	17.5	8.9	9.9	1.22
		PDMA ^{17.1}	32	34.1	17.1	17.0	1.15
		PDMA ^{27.2}	63	54.8	27.2	25.1	1.14
		PDMA ^{28.5}	75	57.4	28.5	22.2	1.21
		PDMA ^{28.7}	75	58.0	28.7	25.0	1.16
		PDMA ^{29.8}	80	59.5	29.8	27.0	1.09
		PDMA ^{37.7}	123	76.3	37.7	32.3	1.16
		PDMA ^{44.8}	241	90.7	44.8	36.5	1.19

^{a)} superscripts denote the theoretical number-average molecular weight determined by ¹H-NMR spectroscopy. ^{b)} determined via ¹H-NMR spectroscopy. ^{c)} theoretical number-average molecular weight determined by ¹H-NMR spectroscopy. ^{d)} apparent number-averaged molecular weight determined by SEC with PS calibration. ^{e)} dispersity determined by SEC with PS calibration.

Table S 2: Synthesized PDMA homopolymers *via* blue light-induced iniferter RAFT solution polymerization with a molar ratio of $[DMA]_0/[DDMAT]_0 = 800$ in water-ethanol mixtures (50:50 w/w) (20% w/w).

T [°C]	I_{light} [mW·cm ⁻²]	Sample code ^{a)}	time [min]	conversion [%] ^{b)}	$\bar{M}_{n,\text{th}}$ [kDa] ^{c)}	$\bar{M}_{n,\text{app}}$ [kDa] ^{d)}	$\bar{D}$ ^{e)}
40	49	PDMA ^{31.5}	60	39.9	31.5	26.2	1.16
		PDMA ^{33.8}	60	42.1	33.8	35.9	1.12
		PDMA ^{37.2}	75	46.3	37.2	32.2	1.13
		PDMA ^{43.0}	90	52.7	43.0	36.8	1.15

^{a)} superscripts denote the theoretical number-average molecular weight determined by ¹H-NMR spectroscopy. ^{b)} determined via ¹H-NMR spectroscopy. ^{c)} theoretical number-average molecular weight determined by ¹H-NMR spectroscopy. ^{d)} apparent number-averaged molecular weight determined by SEC with PS calibration. ^{e)} dispersity determined by SEC with PS calibration.

5.2 In 250 mL vessels

Table S 3: Synthesized PDMA homopolymers *via* blue light-induced iniferter RAFT solution polymerization with a molar ratio of $[DMA]_0/[DDMAT]_0 = 500$ in water-ethanol mixtures (50:50 w/w) (20% w/w).

T [°C]	I_{light} [mW·cm ⁻²]	Sample code ^{a)}	time [min]	conversion [%] ^{b)}	$\bar{M}_{n,\text{th}}$ [kDa] ^{c)}	$\bar{M}_{n,\text{app}}$ [kDa] ^{d)}	$\bar{D}$ ^{e)}
40	52	PDMA ^{2.7}	15	4.7	2.7	4.8	1.25
		PDMA ^{9.8}	30	18.8	9.8	9.6	1.20
		PDMA ^{17.1}	30	24.2	12.5	7.9	1.20
		PDMA ^{20.0}	60	39.2	20.0	18.6	1.15
		PDMA ^{25.5}	64	50.1	25.5	17.2	1.12
		PDMA ^{23.5}	70	46.1	23.5	17.8	1.16
		PDMA ^{23.7}	70	46.5	23.7	19.1	1.17
		PDMA ^{31.1}	120	61.3	31.1	29.4	1.08
		PDMA ^{32.9}	120	64.9	32.9	28.5	1.12
		PDMA ^{43.0}	240	84.9	43.0	37.3	1.10

T [°C]	I_{light} [mW·cm ⁻²]	Sample code ^{a)}	time [min]	conversion [%] ^{b)}	$\bar{M}_{n,\text{th}}$ [kDa] ^{c)}	$\bar{M}_{n,\text{app}}$ [kDa] ^{d)}	$\bar{D}$ ^{e)}
		PDMA ^{40.6}	241	80.2	40.6	36.0	1.08

^{a)} superscripts denote the theoretical number-average molecular weight determined by ¹H-NMR spectroscopy. ^{b)} determined via ¹H-NMR spectroscopy. ^{c)} theoretical number-average molecular weight determined by ¹H-NMR spectroscopy. ^{d)} apparent number-averaged molecular weight determined by SEC with PS calibration. ^{e)} dispersity determined by SEC with PS calibration.

5.3 In 500 mL vessels

Table S 4: Synthesized PDMA homopolymers *via* blue light-induced iniferter RAFT solution polymerization with a molar ratio of [DMA]₀/[DDMAT]₀ = 500 in water-ethanol mixtures (50:50 w/w) (20% w/w).

T [°C]	I_{light} [mW·cm ⁻²]	Sample code ^{a)}	time [min]	conversion [%] ^{b)}	$\bar{M}_{n,\text{th}}$ [kDa] ^{c)}	$\bar{M}_{n,\text{app}}$ [kDa] ^{d)}	$\bar{D}$ ^{e)}
40	55	PDMA ^{4.4}	22	8.1	4.4	5.7	1.30
		PDMA ^{13.9}	60	27.1	13.9	14.8	1.19
		PDMA ^{29.4}	120	58.1	29.4	25.2	1.14
		PDMA ^{43.0}	240	78.6	39.6	34.4	1.12

^{a)} superscripts denote the theoretical number-average molecular weight determined by ¹H-NMR spectroscopy. ^{b)} determined via ¹H-NMR spectroscopy. ^{c)} theoretical number-average molecular weight determined by ¹H-NMR spectroscopy. ^{d)} apparent number-averaged molecular weight determined by SEC with PS calibration. ^{e)} dispersity determined by SEC with PS calibration.

6. PDMAEA homopolymers

6.1 In 20 mL vessels

Table S 5: Synthesized PDMAEA homopolymers *via* blue light-induced iniferter RAFT solution polymerization with a molar ratio of $[\text{DMAEA}]_0/[\text{DDMAT}]_0 = 320$ in water-ethanol mixtures (50:50 w/w) (20% w/w).

T [°C]	I_{light} [mW·cm ⁻²]	Sample code ^{a)}	time [min]	conversion [%] ^{b)}	$\bar{M}_{n,\text{th}}$ [kDa] ^{c)}	$\bar{M}_{n,\text{app}}$ [kDa] ^{d)}	$\bar{D}$ ^{e)}
40	49	PDMAEA ^{4.7}	16	8.9	4.7	3.2	1.25
		PDMAEA ^{8.4}	31	16.5	8.4	5.3	1.23
		PDMAEA ^{13.6}	61	27.0	13.6	8.2	1.20
		PDMAEA ^{21.4}	120	43.0	21.4	13.6	1.15
		PDMAEA ^{30.8}	240	62.2	30.8	17.7	1.23

^{a)} superscripts denote the theoretical number-average molecular weight determined by ¹H-NMR spectroscopy. ^{b)} determined via ¹H-NMR spectroscopy. ^{c)} theoretical number-average molecular weight determined by ¹H-NMR spectroscopy. ^{d)} apparent number-averaged molecular weight determined by SEC with PS calibration. ^{e)} dispersity determined by SEC with PS calibration.

Table S 6: Synthesized PDMAEA homopolymers *via* blue light-induced iniferter RAFT solution polymerization with a molar ratio of $[\text{DMAEA}]_0/[\text{DDMAT}]_0 = 500$ in water-ethanol mixtures (50:50 w/w) (20% w/w).

T [°C]	I_{light} [mW·cm ⁻²]	Sample code ^{a)}	time [min]	conversion [%] ^{b)}	$\bar{M}_{n,\text{th}}$ [kDa] ^{c)}	$\bar{M}_{n,\text{app}}$ [kDa] ^{d)}	$\bar{D}$ ^{e)}
40	49	PDMAEA ^{5.6}	15	8.9	7.1	6.8	1.27
		PDMAEA ^{8.1}	17	10.8	8.1	5.0	1.23
		PDMAEA ^{12.2}	30	16.5	12.2	6.1	1.37
		PDMAEA ^{14.7}	30	19.1	14.7	11.7	1.21
		PDMAEA ^{21.5}	60	29.4	21.5	9.4	1.43
		PDMAEA ^{24.1}	60	31.6	24.1	15.0	1.35
		PDMAEA ^{33.4}	120	46.1	33.4	15.9	1.40
		PDMAEA ^{37.6}	120	49.9	37.6	19.8	1.42
		PDMAEA ^{43.2}	240	59.8	43.2	21.7	1.41
		PDMAEA ^{46.7}	243	61.7	46.7	23.0	1.44

^{a)} superscripts denote the theoretical number-average molecular weight determined by ¹H-NMR spectroscopy. ^{b)} determined via ¹H-NMR spectroscopy. ^{c)} theoretical number-average molecular weight determined by ¹H-NMR spectroscopy. ^{d)} apparent number-averaged molecular weight determined by SEC with PS calibration. ^{e)} dispersity determined by SEC with PS calibration.

6.2 In 250 mL vessels

Table S 7: Synthesized PDMAEA homopolymers *via* blue light-induced iniferter RAFT solution polymerization with a molar ratio of $[\text{DMAEA}]_0/[\text{DDMAT}]_0 = 500$ in water-ethanol mixtures (50:50 w/w) (20% w/w).

T [°C]	I_{light} [mW·cm ⁻²]	Sample code ^{a)}	time [min]	conversion [%] ^{b)}	$\bar{M}_{n,\text{th}}$ [kDa] ^{c)}	$\bar{M}_{n,\text{app}}$ [kDa] ^{d)}	$\bar{D}$ ^{e)}
40	52	PDMAEA ^{5.6}	15	6.8	5.6	4.8	1.29
		PDMAEA ^{9.0}	30	11.3	9.0	7.6	1.21
		PDMAEA ^{21.1}	60	27.0	21.1	11.0	1.26
		PDMAEA ^{30.8}	120	39.6	30.8	16.3	1.25
		PDMAEA ^{37.6}	242	48.6	37.6	17.5	1.42

^{a)} superscripts denote the theoretical number-average molecular weight determined by ¹H-NMR spectroscopy. ^{b)} determined via ¹H-NMR spectroscopy. ^{c)} theoretical number-average molecular weight determined by ¹H-NMR spectroscopy. ^{d)} apparent number-averaged molecular weight determined by SEC with PS calibration. ^{e)} dispersity determined by SEC with PS calibration.

7. P4VP homopolymers

7.1 In 40 mL vessels

Table S 8: Synthesized P4VP homopolymers *via* blue light-induced iniferter RAFT solution polymerization with a molar ratio of $[4VP]_0/[DDMAT]_0 = 470$ in water-ethanol mixtures (50:50 w/w) (20% w/w).

T [°C]	I_{light} [mW·cm ⁻²]	Sample code ^{a)}	time [min]	conversion [%] ^{b)}	$\bar{M}_{n,\text{th}}$ [kDa] ^{c)}	$\bar{M}_{n,\text{app}}$ [kDa] ^{d)}	$\bar{D}$ ^{e)}
40	49	P4VP ^{0.6}	30	0.6	0.6	2.2	1.25
		P4VP ^{0.7}	30	0.6	0.7	3.1	1.17
		P4VP ^{5.2}	58	9.8	5.2	6.5	1.21
		P4VP ^{3.9}	62	7.2	3.9	5.7	1.19
		P4VP ^{3.5}	68	6.4	3.5	8.3	1.23
		P4VP ^{8.5}	120	16.5	8.5	13.9	1.19
		P4VP ^{9.7}	120	19.3	9.7	12.1	1.18
		P4VP ^{11.4}	125	22.4	11.4	14.2	1.16
		P4VP ^{18.9}	240	37.6	18.9	23.9	1.22
		P4VP ^{20.0}	240	40.6	20.0	22.9	1.25
		P4VP ^{27.5}	360	56.2	27.5	33.9	1.22
50	49	P4VP ^{2.4}	30	4.2	2.4	6.2	1.23
		P4VP ^{3.5}	59	6.3	3.5	12.1	1.19
		P4VP ^{15.2}	119	30.1	15.2	21.8	1.23
		P4VP ^{25.6}	240	51.3	25.6	34.5	1.34

^{a)} superscripts denote the theoretical number-average molecular weight determined by ¹H-NMR spectroscopy. ^{b)} determined via ¹H-NMR spectroscopy. ^{c)} theoretical number-average molecular weight determined by ¹H-NMR spectroscopy. ^{d)} apparent number-averaged molecular weight determined by SEC with PS calibration. ^{e)} dispersity determined by SEC with PS calibration.

Table S 9: Synthesized P4VP homopolymers *via* blue light-induced iniferter RAFT solution polymerization with a molar ratio of $[4VP]_0/[DDMAT]_0 = 470$ in water-ethanol mixtures (50:50 w/w) (30% w/w).

T [°C]	I_{light} [mW·cm ⁻²]	Sample code ^{a)}	time [min]	conversion [%] ^{b)}	$\bar{M}_{n,\text{th}}$ [kDa] ^{c)}	$\bar{M}_{n,\text{app}}$ [kDa] ^{d)}	$\bar{D}$ ^{e)}
40	49	P4VP ^{1.3}	30	1.9	1.3	3.0	1.26
		P4VP ^{5.5}	60	10.0	5.5	7.6	1.23
		P4VP ^{12.6}	120	23.8	12.6	15.8	1.18
		P4VP ^{25.1}	240	48.2	25.1	29.6	1.35
		P4VP ^{33.8}	360	65.3	33.8	37.8	1.36

^{a)} superscripts denote the theoretical number-average molecular weight determined by ¹H-NMR spectroscopy. ^{b)} determined via ¹H-NMR spectroscopy. ^{c)} theoretical number-average molecular weight determined by ¹H-NMR spectroscopy. ^{d)} apparent number-averaged molecular weight determined by SEC with PS calibration. ^{e)} dispersity determined by SEC with PS calibration.

Table S 10: Synthesized P4VP homopolymers *via* blue light-induced iniferter RAFT solution polymerization with a molar ratio of $[4VP]_0/[DDMAT]_0 = 750$ in water-ethanol mixtures (50:50 w/w) (20% w/w).

T [°C]	I_{light} [mW·cm ⁻²]	Sample code ^{a)}	time [min]	conversion [%] ^{b)}	$\bar{M}_{n,\text{th}}$ [kDa] ^{c)}	$\bar{M}_{n,\text{app}}$ [kDa] ^{d)}	$\bar{D}$ ^{e)}
40	49	P4VP ^{5.7}	60	6.8	5.7	8.8	1.29
		P4VP ^{4.5}	65	5.4	4.5	9.7	1.26
		P4VP ^{8.6}	120	10.7	8.6	16.9	1.22
		P4VP ^{13.3}	121	16.5	13.3	17.3	1.23
		P4VP ^{20.3}	240	26.0	20.3	32.6	1.17
		P4VP ^{21.1}	240	26.5	21.1	29.6	1.26
		P4VP ^{31.6}	361	39.9	31.6	36.2	1.44

^{a)} superscripts denote the theoretical number-average molecular weight determined by ¹H-NMR spectroscopy. ^{b)} determined via ¹H-NMR spectroscopy. ^{c)} theoretical number-average molecular weight determined by ¹H-NMR spectroscopy. ^{d)} apparent number-averaged molecular weight determined by SEC with PS calibration. ^{e)} dispersity determined by SEC with PS calibration.

7.2 In 250 mL vessels

Table S 11: Synthesized P4VP homopolymers *via* blue light-induced iniferter RAFT solution polymerization with a molar ratio of $[4VP]_0/[DDMAT]_0 = 470$ in water-ethanol mixtures (50:50 w/w) (20% w/w).

T [°C]	I_{light} [mW·cm ⁻²]	Sample code ^{a)}	time [min]	conversion [%] ^{b)}	$\bar{M}_{n,\text{th}}$ [kDa] ^{c)}	$\bar{M}_{n,\text{app}}$ [kDa] ^{d)}	$\bar{D}$ ^{e)}
40	52	P4VP ^{1.2}	60	1.7	1.2	3.0	1.23
		P4VP ^{4.9}	120	9.2	4.9	7.6	1.27
		P4VP ^{12.0}	241	23.5	12.0	15.9	1.19
		P4VP ^{18.1}	360	35.8	18.1	22.8	1.21

^{a)} superscripts denote the theoretical number-average molecular weight determined by ¹H-NMR spectroscopy. ^{b)} determined via ¹H-NMR spectroscopy. ^{c)} theoretical number-average molecular weight determined by ¹H-NMR spectroscopy. ^{d)} apparent number-averaged molecular weight determined by SEC with PS calibration. ^{e)} dispersity determined by SEC with PS calibration.

Table S 12: Synthesized P4VP homopolymers *via* blue light-induced iniferter RAFT solution polymerization with a molar ratio of $[4VP]_0/[DDMAT]_0 = 470$ in water-ethanol mixtures (50:50 w/w) (30% w/w).

T [°C]	I_{light} [mW·cm ⁻²]	Sample code ^{a)}	time [min]	conversion [%] ^{b)}	$\bar{M}_{n,\text{th}}$ [kDa] ^{c)}	$\bar{M}_{n,\text{app}}$ [kDa] ^{d)}	$\bar{D}$ ^{e)}
40	52	P4VP ^{1.1}	60	1.4	1.1	2.9	1.27
		P4VP ^{5.0}	120	9.3	5.0	7.1	1.21
		P4VP ^{13.9}	243	27.2	13.9	17.6	1.20
		P4VP ^{19.5}	360	39.1	19.5	22.8	1.13
		P4VP ^{21.5}	360	42.5	21.5	25.7	1.24
40	86	P4VP ^{2.1}	60	3.4	2.1	5.1	1.22
		P4VP ^{7.3}	120	13.8	7.3	12.1	1.14
		P4VP ^{16.7}	240	32.6	16.7	23.8	1.25
		P4VP ^{25.0}	360	49.1	25.0	35.9	1.23
50	526	P4VP ^{2.1}	61	3.5	2.1	4.6	1.29
		P4VP ^{7.3}	120	13.6	7.1	11.2	1.17
		P4VP ^{16.7}	241	31.6	16.1	24.9	1.12
		P4VP ^{25.0}	360	46.9	23.7	37.1	1.11

^{a)} superscripts denote the theoretical number-average molecular weight determined by ¹H-NMR spectroscopy. ^{b)} determined via ¹H-NMR spectroscopy. ^{c)} theoretical number-average molecular weight determined by ¹H-NMR spectroscopy. ^{d)} apparent number-averaged molecular weight determined by SEC with PS calibration. ^{e)} dispersity determined by SEC with PS calibration.

Table S 13: Synthesized P4VP homopolymers *via* blue light-induced iniferter RAFT solution polymerization with a molar ratio of $[4VP]_0/[DDMAT]_0 = 760$ in water-ethanol mixtures (50:50 w/w) (30% w/w).

T [°C]	I_{light} [mW·cm ⁻²]	Sample code ^{a)}	time [min]	conversion [%] ^{b)}	$\bar{M}_{n,\text{th}}$ [kDa] ^{c)}	$\bar{M}_{n,\text{app}}$ [kDa] ^{d)}	$\bar{D}$ ^{e)}
40	86	P4VP ^{2.7}	60	3.0	2.7	60	1.31
		P4VP ^{5.6}	120	6.6	5.6	6.8	1.18
		P4VP ^{22.5}	240	27.9	22.5	37.5	1.08
		P4VP ^{33.1}	360	41.2	33.1	55.4	1.07
		P4VP ^{42.2}	480	52.7	42.2	73.1	1.22

8. P2VP homopolymers

8.1 In 40 mL vessels

Table S 14: Synthesized P2VP homopolymers *via* blue light-induced iniferter RAFT solution polymerization with a molar ratio of $[2VP]_0/[DDMAT]_0 = 470$ in water-ethanol mixtures (50:50 w/w) (30% w/w).

T [°C]	I_{light} [mW·cm ⁻²]	Sample code ^{a)}	time [min]	conversion [%] ^{b)}	$\bar{M}_{n,\text{th}}$ [kDa] ^{c)}	$\bar{M}_{n,\text{app}}$ [kDa] ^{d)}	$\bar{D}$ ^{e)}
40	49	P2VP ^{2.5}	60	4.2	2.5	2.7	1.33
		P2VP ^{4.7}	120	8.7	4.7	6.7	1.27
		P2VP ^{11.0}	240	21.3	11.0	16.6	1.19
		P2VP ^{17.8}	360	34.9	17.8	26.6	1.17
50	49	P2VP ^{1.1}	31	1.6	1.1		
		P2VP ^{3.4}	62	6.1	3.4	5.1	1.24
		P2VP ^{7.2}	120	13.8	7.2	11.7	1.28
		P2VP ^{17.0}	240	33.6	17.0	27.3	1.21
		P2VP ^{23.2}	360	46.1	23.2	42.1	1.14
60	49	P2VP ^{1.0}	29	1.4	1.0		
		P2VP ^{2.5}	60	4.3	2.5	4.3	1.36
		P2VP ^{8.6}	120	16.5	8.6	13.7	1.21
		P2VP ^{18.7}	240	37.1	18.7	33.6	1.23
		P2VP ^{25.7}	360	51.1	25.7	54.3	1.09
70	49	P2VP ^{2.1}	32	3.6	2.1		
		P2VP ^{4.2}	60	7.7	4.2	7.1	1.17
		P2VP ^{11.9}	119	23.2	11.9	17.7	1.21
		P2VP ^{22.0}	241	43.6	22.0	45.6	1.12
		P2VP ^{29.0}	360	57.9	29.0	73.7	1.10

^{a)} superscripts denote the theoretical number-average molecular weight determined by ¹H-NMR spectroscopy. ^{b)} determined via ¹H-NMR spectroscopy. ^{c)} theoretical number-average molecular weight determined by ¹H-NMR spectroscopy. ^{d)} apparent number-averaged molecular weight determined by SEC with PS calibration. ^{e)} dispersity determined by SEC with PS calibration.

8.2 In 250 mL vessels

Table S 15: Synthesized P2VP homopolymers *via* blue light-induced iniferter RAFT solution polymerization with a molar ratio of $[2VP]_0/[DDMAT]_0 = 470$ in water-ethanol mixtures (50:50 w/w) (30% w/w).

T [°C]	I_{light} [mW·cm ⁻²]	Sample code ^{a)}	time [min]	conversion [%] ^{b)}	$\bar{M}_{n,\text{th}}$ [kDa] ^{c)}	$\bar{M}_{n,\text{app}}$ [kDa] ^{d)}	$\bar{D}$ ^{e)}
60	52	P2VP ^{1.6}	60	2.5	1.6	2.2	1.26
		P2VP ^{4.9}	120	9.1	4.9	6.7	1.25
		P2VP ^{13.6}	240	26.9	13.6	19.6	1.19
		P2VP ^{20.6}	360	41.1	20.6	33.0	1.17
70	52	P2VP ^{3.1}	63	5.6	3.1	4.3	1.35
		P2VP ^{8.4}	119	16.3	8.4	11.5	1.25
		P2VP ^{18.1}	242	36.1	18.1	30.4	1.17
		P2VP ^{25.4}	360	50.7	25.4	50.0	1.14

^{a)} superscripts denote the theoretical number-average molecular weight determined by ¹H-NMR spectroscopy. ^{b)} determined via ¹H-NMR spectroscopy. ^{c)} theoretical number-average molecular weight determined by ¹H-NMR spectroscopy. ^{d)} apparent number-averaged molecular weight determined by SEC with PS calibration. ^{e)} dispersity determined by SEC with PS calibration.

9. Determination of required energy for the polymer synthesis

In order to estimate the required energy to perform light-induced iniferter RAFT polymerization at different temperatures some assumptions are made. These assumptions were implemented to determine and compare the energy consumption between the experiments at 40 °C and 70 °C. Due to the fact that the polymerization vessel is immersed in a stirred heat bath, there is a temperature equilibrium between the polymerization solution and the surrounding heat bath. Since the polymer and monomer concentration change with time and not all the required parameters for water/ethanol mixtures are available, therefore, only water (as reaction medium) and the water bath are considered as a model system. In this study, all polymerizations were carried out in a 300 mL water bath and half of the amount of solvent used for the polymerization was water as well. Therefore, it is assumed that a polymerization system including 500 mL water in a 600 mL beaker is on top of a hot plate as a heating source. Heater is required for heating of the water to raise the temperature as well as carrying out the polymerization at a constant temperature in a given period of time.

Due to the heat transfer to the surrounding environment, the energy is consumed to keep the temperature constant (non-isothermal system). The heat is transferred out of the beaker on the one hand through the glass wall and on the other hand through direct contact with air. To keep the temperature constant, the heat loss must be compensated by heating of the plate. Due to this, the net heat transferred into or out of the system consists of two contributions: 1) the heating of the water to the desired temperature ($\Delta Q_{\text{heating-up}}$), and 2) the heating of the water to hold it at a constant temperature in a given time period. The latest term can be estimated using the heat loss through the glass wall (ΔQ_{glass}), and the heat loss through the direct contact of the water surface with the air (ΔQ_{air}) (see Fig. S 11). Other influencing factors for the determination of the energy such as the heat of reaction generated over time and the heat generated by the blue LED were neglected (the aluminum cylinder dissipates most of the heat from the LED lamp). As well, the evaporation of solvent is not considered. All formulas for the calculation as well as material-specific characteristic data were taken from the VDI Heat Atlas.¹

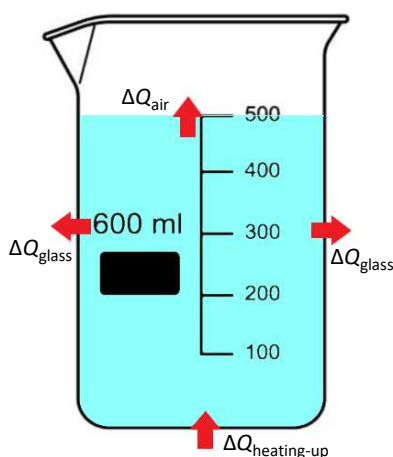


Fig. S 12: Schematic representation of the heat transfer from the model system.

The required energy $\Delta Q_{\text{heating-up}}$ for the heating-up of the water depends on the mass m , the heat capacity c_p and the difference in temperature ΔT and is calculated *via*

$$\Delta Q_{\text{heating-up}} = m \cdot c_p \cdot \Delta T \quad (9)$$

Part of the heat transferred by time from water to surrounding air through the glass wall was determined based on the calculation described in the chapter “Fundamentals of calculation methods for heat conduction, convective heat transfer and thermal radiation” using the example of heat transfer through a plane wall.¹ The heat flow is determined by the heat transmission coefficient k , the lateral surface of the beaker A and the difference in temperature ΔT .

$$\dot{Q}_{\text{glass}} = k \cdot A \cdot \Delta T \quad (10)$$

The heat transmission coefficient k is calculated using the heat transfer coefficient of the water bath α_1 , the thickness of the wall Δw , the heat conductivity coefficient of glass λ_w and the heat transfer coefficient of the surrounding air α_2 .

$$k = \frac{1}{\frac{1}{\alpha_1} + \frac{\Delta w}{\lambda_w} + \frac{1}{\alpha_2}} \quad (11)$$

To determine the heat transfer coefficient α_1 according to equations from the chapter “heat transfer and power consumption in stirred vessels”,¹ the Nusselt number Nu for a beam stirrer was calculated *via* the following equation with the constant C , the Reynolds number Re , the Prandtl number Pr and the dynamic viscosity η in which the viscosity term is negligible.

$$Nu = C \cdot Re^{\frac{2}{3}} \cdot Pr^{\frac{1}{3}} \cdot \left(\frac{\eta}{\eta_w} \right)^{0.14} \quad (12)$$

In order to calculate the constant C , the following equation for a vessel with a blade stirrer and without current breaker is used. In this equation, d stands for diameter and h for height.

$$C = 0.6 \cdot \left(\frac{d_{\text{stirrer}}}{d_{\text{vessel}}} \right)^{-0.25} \cdot \left(\frac{h_{\text{liquid}}}{d_{\text{vessel}}} \right)^{0.15} \cdot \left(\frac{h_{\text{stirrer}}}{h_{\text{fill height}}} \right)^{0.15} \quad (13)$$

The Reynolds number Re from equation 12 was calculated by

$$Re = \frac{n \cdot d_{\text{stirrer}}^2 \cdot \rho}{\eta} \quad (14)$$

Subsequently the heat transfer coefficient α_1 was determined by

$$\alpha = \frac{Nu \cdot \lambda}{d_v} \quad (15)$$

where, λ is the conductivity coefficient and d_v denotes the vessel diameter.

For the determination of α_2 , a heat coefficient of 10 W/(m²·K) is supposed to use for the determination of ΔQ_{wall} and ΔQ_{air} (typical value for a low speed flow of air over a surface).

The heat exchange between the free surface of the water and the ambient air circulating over the surface occurs mainly *via* convection. According to the chapter “Heat Transfer in Free Convection: Fundamentals”, the heat flow $\dot{Q}_{\text{air}}$ was calculated *via*

$$\dot{Q}_{\text{air}} = \alpha_2 \cdot A \cdot \Delta T \quad (16)$$

In order to determine the thermal energy change ΔQ_{glass} and ΔQ_{air} , the heat flow $\dot{Q}_{\text{glass}}$ as well as $\dot{Q}_{\text{air}}$ are multiplied by the duration time of the reaction. For the same 2VP conversion of 50 %, based on the kinetic data, the reaction time of 12 h and 6 h were respectively determined for the reaction temperature of 40 °C and 70 °C.

The required power P of the blue LED lamp for the polymerization was determined by experimental data of the voltage V and current I followed by equation 17.

$$P = V \cdot I \quad (17)$$

The energy ΔE_{LED} is determined by multiplication of the power P with the reaction time.

References

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9.2 Supporting Information Publication 2

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Supporting information

Amphiphilic block copolymers *via* blue-light-induced iniferter RAFT *ab initio* emulsion polymerization in water-alcoholic media

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1. Experimental

1.1 Setup of the blue LED-reactor

As the light source, a self-made cylindrical photoreactor was designed. Two LED strips (each with a length of 500.0 cm and 120 LEDs per meter (Seki®)) were affixed to the inner lower part of the aluminium cylinder (inner diameter: 18.0 cm, height: 25.0 cm). The light intensity was controlled by a MiLight® MiBoxer® RGB LED Controller which was operated using a MiLight® remote control.

1.2 Materials

Ultrapure water (Milli-Q® quality, resistivity $>18.2 \text{ M}\Omega\cdot\text{cm}^{-1}$), was obtained from a Milli-Q® water purification system (Siemens Labostar). Ethanol ($\geq 99.9 \%$, Merck), *N,N*-dimethylformamide (DMF) ($\geq 99.8 \%$, Merck), tetrahydrofuran (THF) ($\geq 99.8 \%$, Merck), 1,4-dioxane ($\geq 99.5 \%$, Carl Roth) and chloroform ($\geq 99 \%$, anhydrous, Sigma Aldrich) were used as received. Deuterium oxide (D_2O), deuterated methanol ($\text{MeOH-}d_4$) and THF ($\text{THF-}d_8$) were purchased from Deutero GmbH. 2-(Dodecylthiocarbonothioylthio)-2-methylpropionic acid (DDMAT) (Sigma-Aldrich, stored at 4°C) was used as received. *N,N*-dimethylacrylamide (DMA) (Sigma Aldrich), and styrene (Sigma Aldrich) were deinhibited over activated basic aluminum oxide (Carl Roth) prior to each polymerization. 4-vinylpyridine (4VP) (Thermo Scientific) was distilled before each polymerization.

1.3 Synthesis of PDMA macroCTAs

The synthesis of PDMA follows the protocol as recently published.¹ A typical photoiniferter RAFT polymerization of DMA was conducted with a molar ratio of $[\text{DMA}]_0/[\text{DDMAT}]_0 = 500/1$. DDMAT (0.280 g, 0.786 mmol, 1.0 eq.) and DMA (39.5 mL, 0.384 mol, 500 eq.) were dissolved in ethanol (97 mL). While stirring, water (77 mL) was added dropwise and *N,N*-dimethylformamide (0.2 mL) added as an internal reference for $^1\text{H-NMR}$ analysis and an initial sample was taken. The solution was degassed by purging with argon for 30 min. The polymerization vessel was placed at the centre of the blue LED. Polymerization was carried out under blue light irradiation ($\lambda_{\text{max}} = 451 \text{ nm}$) at $52 \text{ mW}\cdot\text{cm}^{-2}$ and a water bath temperature of 40°C under constant stirring (400 rpm). After the desired time of exposure to the blue light, the polymerization was stopped by turning off the irradiation source, quenching in an ice-cooling bath and exposing to air. The solvent was removed by vacuum and the crude

polymer was obtained by drying under vacuum at 40 °C for 24 h. Subsequently, the polymer was dissolved in THF, precipitated in cold cyclohexane, filtered, and dried under vacuum at 40 °C for 48 h.

1.4 Synthesis of P4VP macroCTAs

The synthesis of the P4VP macroCTAs was conducted in an analogous way as recently reported.¹ In a typical photoiniferter RAFT of 4-vinylpyridine with a molar ratio of $[4VP]_0/[DDMAT]_0 = 470/1$, DDMAT (0.425 g, 1.17 mmol, 1.0 eq.) and 4VP (59.3 mL, 0.550 mol, 471 eq.) were dissolved in ethanol (86 mL). While stirring, water (68 mL) was added dropwise. The reaction solution was degassed by purging the ice-cooled polymerization vial with argon for 30 min. The vial was placed in the water bath with a temperature of 40 °C and illuminated with blue light ($\lambda_{\text{max}} = 451 \text{ nm}$) at $52 \text{ mW}\cdot\text{cm}^{-2}$. After the desired time of exposure to the blue light, the polymerization was stopped by turning-off the irradiation source, quenching in an ice-cooling bath and exposing to air. The solvent was removed by vacuum and the crude polymer was obtained by drying in vacuum at 40 °C for 24 h. Subsequently, the crude polymer was dissolved in ethanol, precipitated in cold cyclohexane, filtered, and dried under vacuum at 40 °C for 48 h.

1.5 Synthesis of PDMA-*b*-PS via blue-light-induced iniferter RAFT *ab initio* emulsion polymerization.

In a typical photoiniferter RAFT emulsion polymerization of styrene with PDMA macroCTAs with a molar ratio of $[PDMA]_0/[\text{styrene}]_0 = 1/1000$, PDMA^{21.1} (6.000 g, 0.284 mol, 1.00 eq.) was dissolved in ethanol (86 mL) and Milli-Q[®] water (68 mL) was added dropwise under stirring. Subsequently, styrene (30.9 mL, 286.4 mol, 1000 eq.) was added dropwise and the resulting emulsion was homogenized for 30 min at 600 rpm. The ice-cooled emulsion was purged with argon for 30 min. The polymerization vial was immersed into a water bath with a temperature of 70 °C and the emulsion was constantly stirred (600 rpm) and illuminated with blue light ($\lambda_{\text{max}} = 451 \text{ nm}$) at $87 \text{ mW}\cdot\text{cm}^{-2}$. After the desired polymerization time, the photopolymerization was stopped by switching off the blue LED, cooling it with ice and exposing it to air. The solvent was removed by vacuum and the crude polymer was dried under vacuum at 40 °C for 24 h. In the next step, the polymer was dissolved in THF, precipitated in cold water, filtered, and dried under vacuum at 40 °C for 48 h.

1.6 Synthesis of P4VP-*b*-PS via blue-light-induced iniferter RAFT *ab initio* emulsion polymerization.

In a typical photoiniferter RAFT polymerization of P4VP macroCTA with styrene with a molar ratio of $[P4VP]_0/[styrene]_0 = 1/1000$, P4VP^{21.5} (6.000 g, 0.279 mol, 1.00 eq) was dissolved in ethanol (107 mL). By stirring, Milli-Q[®] water (56 mL) was added dropwise. Styrene (32.0 mL, 0.278 mol, 1000 eq.) was added and the emulsion was stirred for 30 min at 600 rpm. The cooled emulsion was purged with argon for 30 min and afterwards immersed into a water bath with a temperature of 60 °C. Polymerization was started by exposing to blue light ($\lambda_{max} = 451\text{ nm}$) at $87\text{ mW}\cdot\text{cm}^{-2}$. The polymerization was stopped by turning off the irradiation source, quenching by ice-cooling and exposing it to air. The solvent was removed by vacuum and the crude polymer was obtained by drying in vacuum at 40 °C for 24 h. The final block copolymer was obtained by dissolving the crude polymer in dioxane, precipitation in water and drying at 40 °C for 48 h.

1.7 Semibatch blue-light-induced iniferter RAFT polymerization of DMA and styrene

In a typical semibatch photoiniferter RAFT polymerization, DDMAT (10.0 mg, 31.1 μmol , 1.00 eq.) and DMA (1.40 mL, 13.6 mmol, 500 eq.) were dissolved in ethanol (10.69 mL). Water (8.45 mL) was added dropwise and *N,N*-dimethylformamide (20 μL) was added as an internal reference for ¹H-NMR analysis. An initial sample was taken, and the solution was degassed by purging the ice-cooled polymerization vial with argon for 10 min. The polymerization vessel was placed at the center of the blue LED reactor and polymerization and illuminated with blue light ($\lambda_{max} = 451\text{ nm}$) at $49\text{ mW}\cdot\text{cm}^{-2}$ and a water bath temperature of 40 °C under constant stirring (600 rpm). Meanwhile, the styrene was prepared separately and flushed with argon for 10 min. After 2 h reaction time, styrene (3.15 mL, 27.5 mmol, 1000 eq.) was transferred to the polymerization vial, the temperature of the water bath was increased to 70 °C and the light intensity of the blue LED was increased to $83\text{ mW}\cdot\text{cm}^{-2}$. After 6 h of exposure to light, the polymerization was stopped by turning off the irradiation source, quenching it in an ice-cooled bath and exposing it to air. The solvent was removed by vacuum and the crude polymer was obtained by drying under vacuum at 40 °C for 24 h. Subsequently, the polymer was dissolved in THF, precipitated in cold water, filtered, and dried under vacuum at 40 °C for 48 h.

1.8 Semibatch blue-light-induced iniferter RAFT polymerization of 4VP and styrene

In a typical semibatch photoiniferter RAFT polymerization, DDMAT (10.0 mg, 31.1 μmol , 1.00 eq.) and 4VP (1.47 mL, 13.7 mmol, 500 eq.) were dissolved in ethanol (10.97 mL). Trioxane was added as an internal reference for ^1H -NMR analysis. Water (8.67 mL) was added dropwise. An initial sample was taken, and the solution was degassed by purging the ice-cooled polymerization vial with argon for 10 min. The polymerization vessel was placed at the center of the blue LED reactor and polymerization and illuminated with blue light ($\lambda_{\text{max}} = 451 \text{ nm}$) at $49 \text{ mW}\cdot\text{cm}^{-2}$. The water bath had a temperature of 40°C and the polymerization was performed under constant stirring (600 rpm). Meanwhile, the styrene was prepared separately and flushed with argon for 10 min. After 6 h reaction time, styrene (3.17 mL, 27.7 mmol, 1000 eq.) was transferred to the polymerization vial, the temperature of the water bath was increased to 70°C and the light intensity of the blue LED was increased to $83 \text{ mW}\cdot\text{cm}^{-2}$. After an additional 4 h exposure to light, the polymerization was stopped by turning off the irradiation source, quenching it in an ice-cooled bath and exposing it to air. The solvent was removed by vacuum and the crude polymer was obtained by drying under vacuum at 40°C for 24 h. Subsequently, the polymer was dissolved in dioxane, precipitated in cold water, filtered, and dried under vacuum at 40°C for 48 h.

1.9 Characterization

1.9.1 Light intensity measurement. The light intensity of the blue LED reactor was determined with an Ocean Insight® FLAME-T-UV-VIS spectrometer with a QP400-2-SR-BX optical fiber and cosine corrector. The sensor was placed at different positions within the cylinder and the height was varied in 2 cm steps. The light intensity was measured upwards and downwards and was afterwards summed up to determine a more precise light intensity. The denoted light intensity refers to the averaged light intensity at the different high positions.

1.9.2 NMR spectroscopy. ^1H -nuclear magnetic resonance (NMR) spectra were recorded at ambient temperature using a Bruker® AV500 spectrometer with 16 scans per spectrum and a delay of 3 s. The determination of the styrene conversion and the theoretical molecular weight $\bar{M}_{\text{n,th}}$ of the block copolymers is explained in Chapter 5. Analysis was realized with the program MestReNova® 14.2.

1.9.3 Size exclusion chromatography (SEC). Size exclusion chromatography (SEC) analysis were conducted at 50 °C using DMAc containing LiCl (0.1 M). Measurements were performed at a flow rate of 1.0 mL·min⁻¹ using a VWR-Hitachi® L2130 pump. A PSS® GRAM pre-column (dimension 8·50 mm) and two PSS® GRAM columns (8·300 mm, particle size 10 µm) with a porosity of 3000 Å and 1000 Å, respectively, were used for the measurements. The analysis was conducted with a Hitachi® L2490 RI refractive index detector. The instrumentation was calibrated with the use of polystyrene standards and the data were analyzed using the software PSS® Win GPC UniChrom V8.10.

The SEC measurements of the end products of the different polymerization scales (Figure 5) have been performed at 50 °C when using DMF containing LiCl (0.05 M) as solvent. Measurements were performed at a flow rate of 0.8 mL·min⁻¹ using an isocratic PSS® SECcurity pump. A PSS® GRAM acid pre-column and a combination of three PSS® GRAM acid columns (each 8·300 mm), 2 with pore sizes of 3000 Å and one with a pore size of 100 Å, were used. The analysis was conducted with a PSS® SECcurity Differential-Refractometer-Detector. PS standards were used as references and the analysis was made with the software PSS® WinGPC UniChrom V8.10.

1.9.4 Dynamic Light Scattering (DLS). DLS-measurements were performed using an ALV®/CGS-3 Compact Goniometer system utilizing an ALV®/LSE-5004 Multiple Tau Digital Correlator (V.1.7.9.) in combination with a Cobolt™ Samba™ 50 laser (Nd:YAG, 532 nm, 400 mW) and the ALV® Digital Correlator Software 3.0. Measurements were conducted at 20 °C at a scattering angle of 90 °. Prior to measurement, the emulsions were diluted with water-ethanol mixtures (50:50 (w/w) for PDMA-*b*-PS and 60:40 (w/w) for P4VP-*b*-PS) to a polymer concentration of 0.2 mg·mL⁻¹. The diluted samples were filled into a quartz glass vial and were placed into a measurement cell filled with toluene. The toluene bath was tempered by a Julabo® F25 thermostat (working with a mixture of water and ethylene glycol providing a temperature accuracy of 0.01 °C). Analysis of all measurements was conducted with data evaluation software developed by F. Lauterbach.² The viscosity of the water-ethanol mixtures (50:50 (w/w)

and 40:60 (w/w)) was determined *via* the DMA 4100 M (Anton Paar®) and was considered for the data evaluation.

1.9.5 Transmission electron microscopy (TEM) of the latex particles. TEM images of the samples of the *ab initio* emulsion polymerization were taken with a Tecnai™ G2 F20 (FEI Thermo Fisher Scientific) transmission electron microscope in bright field mode, operating at an acceleration voltage of 120 kV. The emulsions of PDMA-*b*-PS were diluted with 50:50 (w/w) water-ethanol mixtures and those of P4VP-*b*-PS were diluted with a 40:60 (w/w) mixture to a polymer concentration between 15 mg·mL⁻¹ and 2 mg·mL⁻¹ (lower concentrations for larger micelles) and dropcast onto carbon-coated copper grids (Plano S160-4 Cu-grids with a mesh size of 400 and carbon film). The excess emulsion was blotted with filter paper after 1 min and dried under air. TEM analysis was conducted *via* the software imageJ® *via* grey-value thresholding, denoising *via* “remove outlier pixels” and a circularity cut-off to achieve reliable particle recognition. For 0.78 h, 1.00 h and 1.25 h (P4VP-*b*-PS) and 2.75 h (PDMA-*b*-PS), thresholding did not reveal the micelles. Hence, the size of the micelles and agglomerates was determined manually. The histograms with bins of 1 nm were fit with a Gaussian distribution.

1.9.6 Transmission electron microscopy (TEM) of the bulk morphology. The bulk morphology of the PDMA-*b*-PS and P4VP-*b*-PS diblock copolymers was investigated *via* TEM. A Tecnai™ G2 F20 (FEI Thermo Fisher Scientific) transmission electron microscope was used, operated at an accelerating voltage of 120 kV in the bright field mode. Polymers were diluted in chloroform to 6 % (w/w) and the films were cast and subsequently slowly dried in the presence of chloroform vapor in a desiccator for two weeks. Afterwards, the block copolymer films were stepwise thermally annealed up to 160 °C (P4VP-*b*-PS) or 140 °C (PDMA-*b*-PS) in vacuum. Employing a Leica Ultramicrotome EM UCT (Leica Microsystems) equipped with a diamond knife (Diatome AG), ultrathin sections of approximately 50 nm were cut. PDMA-*b*-PS samples remained unstained meanwhile the P4VP-*b*-PS samples were stained by iodine vapor.

- 1.9.7 Thermogravimetric analysis (TGA).** TGA was conducted with a TG 209 F1 Iris® under argon atmosphere. The temperature was increased from initially 30 °C to 300 °C with a heating rate of 10 K·min⁻¹.
- 1.9.8 Fourier transform infrared spectroscopy (FTIR).** FTIR spectroscopy was conducted with a Bruker Alpha (diamond-ATR unit).

2. Experimental setup of the photoreactor

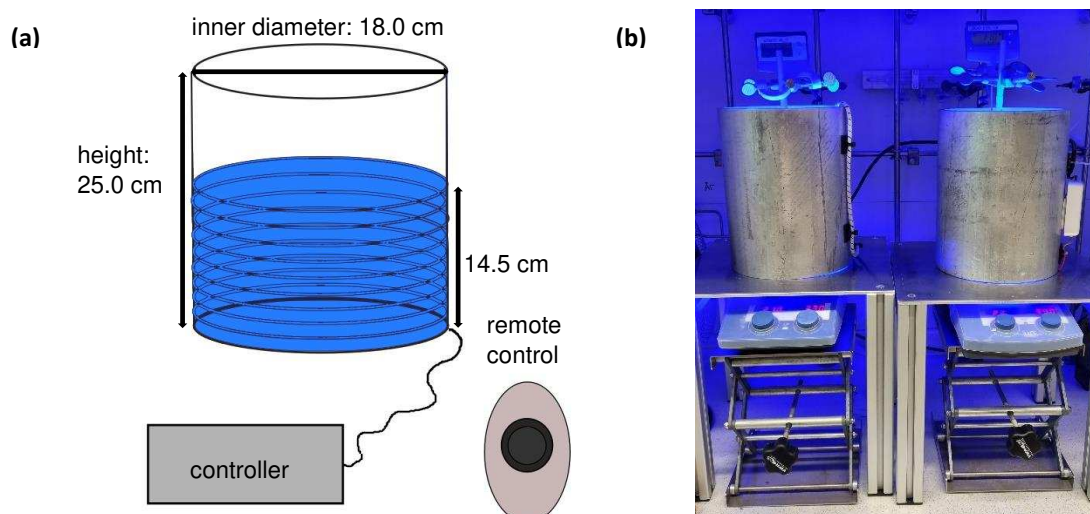


Figure S 1. (a) Schematic setup of the blue LED array. (b) Experimental setups for blue-light-initiated RAFT polymerizations.

3. PDMA and P4VP macroCTAs

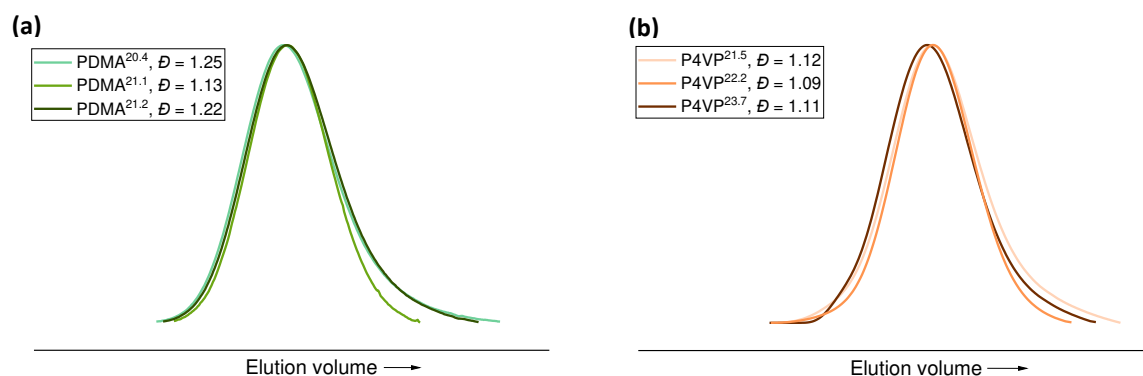


Figure S 2. SEC traces of the (a) PDMA and (b) P4VP macroCTAs synthesized *via* blue-light-induced RAFT solution polymerization.

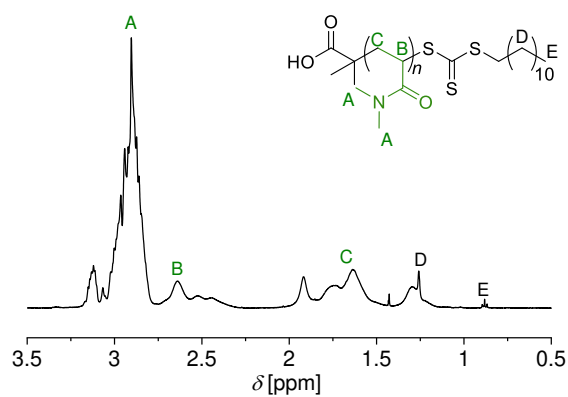


Figure S 3. ¹H-NMR spectrum of the PDMA^{20.4} macroCTA.

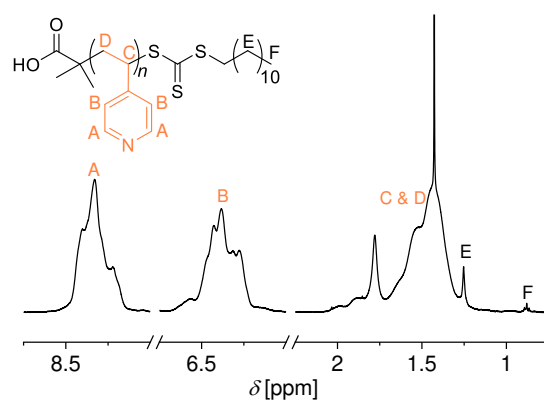


Figure S 4. ^1H -NMR spectrum of the P4VP^{22.2} macroCTA.

4. Emulsions



Figure S 5. Prepared emulsion for the chain extension of PDMA macroRAFT agent with styrene.

5. NMR analysis

5.1 Determination of the styrene conversion for PDMA-*b*-PS diblock copolymers

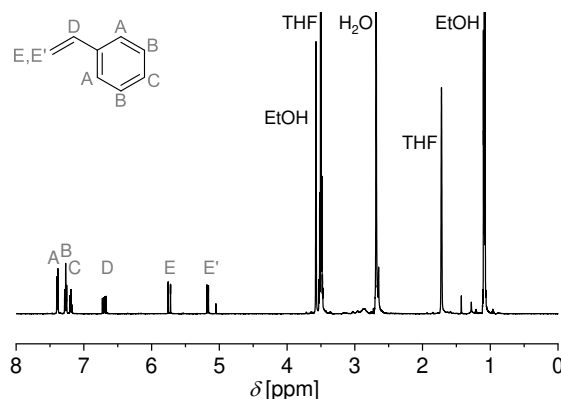


Figure S 6. Complete ^1H -NMR spectrum (in $\text{THF-}d_8$) of the initial reaction emulsion of the photoiniferter RAFT chain extension of PDMA with styrene in the water-ethanol mixture (50:50 (w/w), 20 (w/w)).

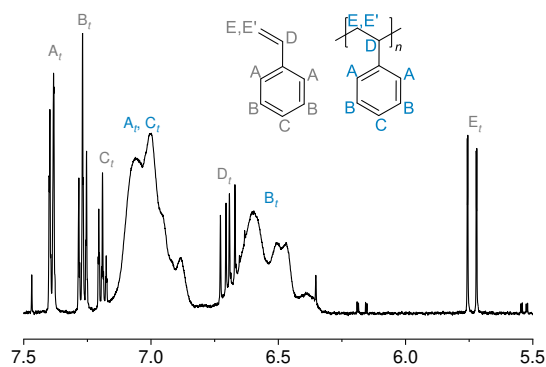


Figure S 7. ^1H -NMR spectrum (in $\text{THF-}d_8$) of the emulsion of the photoiniferter RAFT chain extension of PDMA with styrene at the end of the polymerization. The protons for the determination of the conversion are assigned to the respective signals.

The monomer conversion p of styrene is calculated as follows:

$$p_{\text{styrene}} = \frac{I_{A_t+C_t} + I_{B_t+D_t} - I_{E_t}}{I_{A_t+C_t} + I_{B_t+D_t} - I_{E_t} + I_{A_t} + I_{B_t} + I_{C_t}} \quad (1)$$

The theoretical molecular weight of the PDMA-*b*-PS diblock copolymers was calculated in the following way:

$$\bar{M}_{n,\text{th}} = \frac{[\text{styrene}]_0}{[\text{DDMAT}]_0} \cdot p_{\text{styrene}} \cdot M_{\text{styrene}} + \bar{M}_{n,\text{th}} (\text{PDMA macroCTA}) \quad (2)$$

5.2 Determination of the styrene conversion for P4VP-*b*-PS diblock copolymers

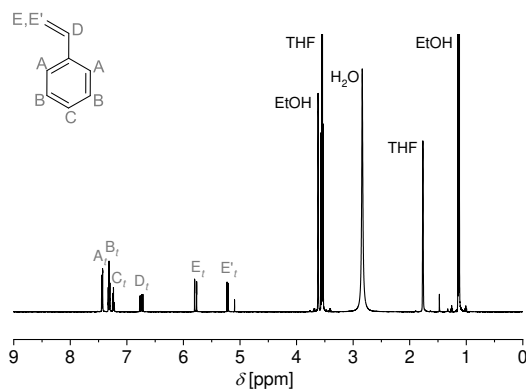


Figure S 8. Complete ^1H -NMR spectrum (in $\text{THF-}d_8$) of the initial reaction emulsion of the photoiniferter RAFT chain extension of P4VP with styrene in the water-ethanol mixture (40:60 (w/w), 20 % (w/w)).

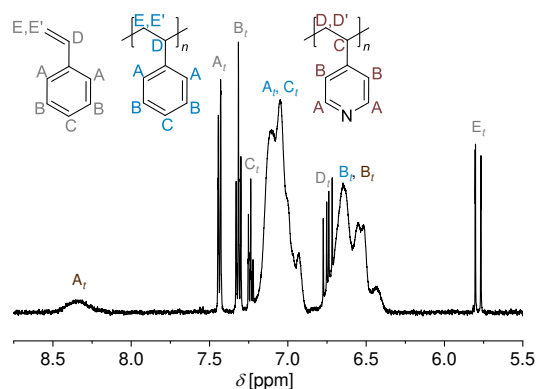


Figure S 9. ^1H -NMR spectrum (in $\text{THF-}d_8$) of the emulsion of the photoiniferter RAFT chain extension of P4VP with styrene at the end of the polymerization. The protons for the determination of the conversion are assigned to the respective signals.

The monomer conversion p of styrene is calculated as follows:

$$p_{\text{styrene}} = \frac{I_{A_t+C_t} + I_{B_t+D_t+B_t} - I_{E_t} - I_{A_t}}{I_{A_t+C_t} + I_{B_t+D_t+B_t} - I_{E_t} - I_{A_t} + I_{A_t} + I_{B_t} + I_{C_t}} \quad (3)$$

The theoretical molecular weight of the P4VP-*b*-PS diblock copolymers was calculated in the following way:

$$\bar{M}_{n,\text{th}} = \frac{[\text{styrene}]_0}{[\text{DDMAT}]_0} \cdot p_{\text{styrene}} \cdot M_{\text{styrene}} + \bar{M}_{n,\text{th}} (\text{P4VP macroCTA}) \quad (4)$$

6. First-order plot of the synthesis of P4VP-*b*-PS diblock copolymers

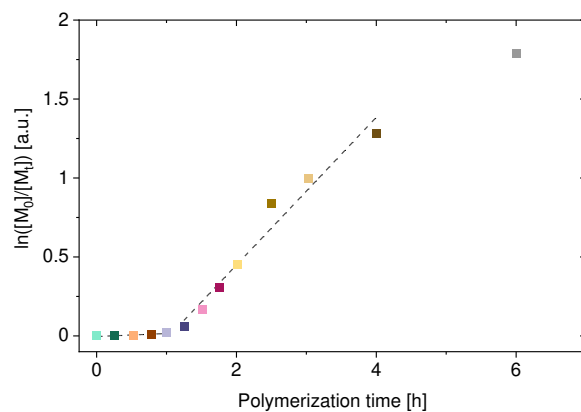


Figure S 10. Pseudo-first-order plot of the blue-light-induced polymerization of $[P4VP]_0/[styrene]_0 = 1:1000$ (20 % w/w) in water-ethanol mixture (40:60 w/w), 60 °C, $I_{blue\ light} = 87\text{ mW}\cdot\text{cm}^{-2}$.

7. Semibatch synthesis

7.1 PDMA-*b*-P(DMA-*grad*-S)-*b*-PS

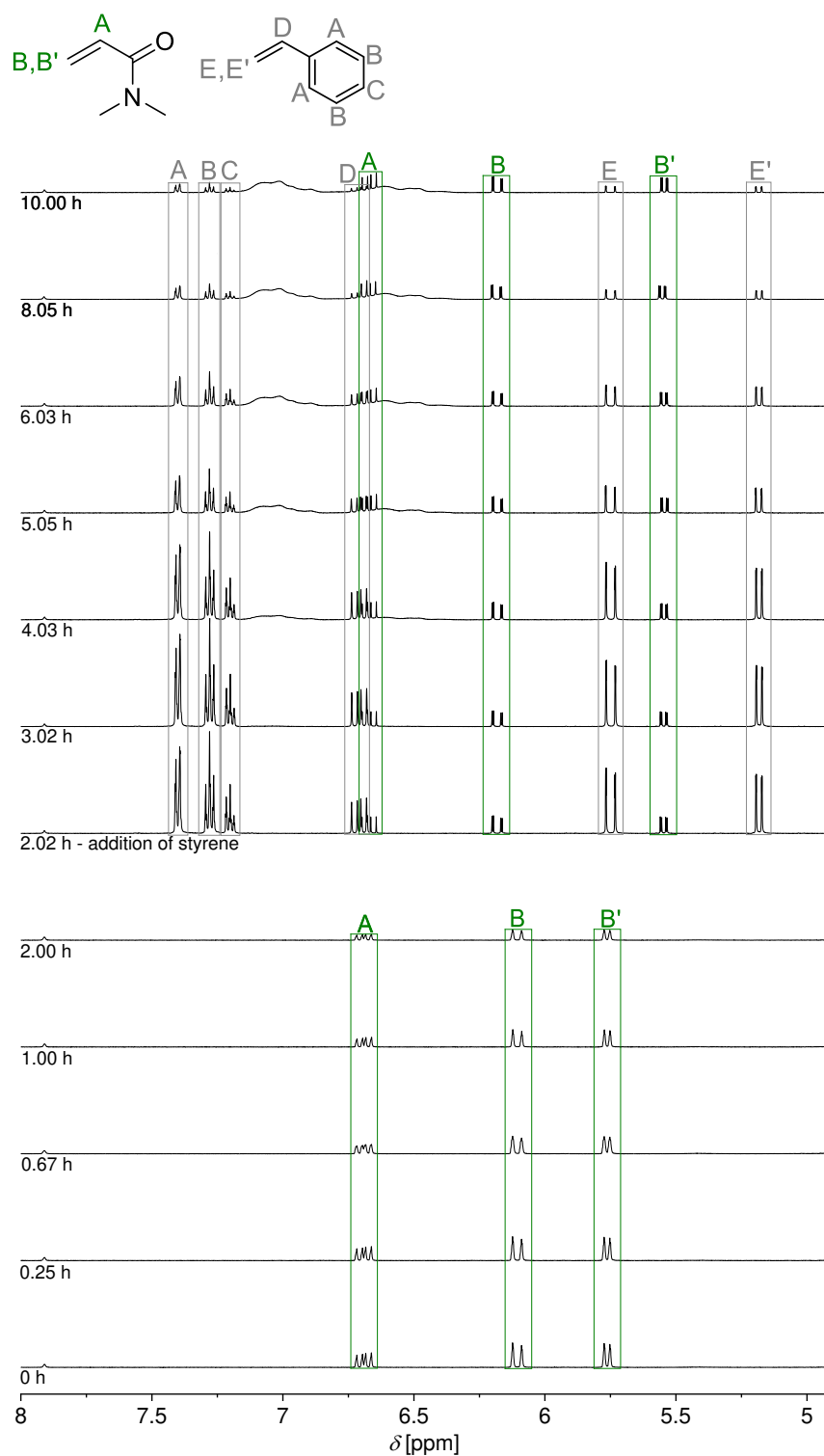


Figure S 11. NMR spectra of the kinetics of the semibatch synthesis of PDMA-*b*-P(DMA-*grad*-S)-*b*-PS with $[\text{DDMAT}]_0/[\text{DMA}]_0/[\text{styrene}]_0 = 1:500:1000$ at 20 % (w/w) (normalized to the DMF signal at 7.91 ppm). The first 5 samples were measured in D_2O , the samples after the addition of styrene were measured in $\text{THF-}d_8$.

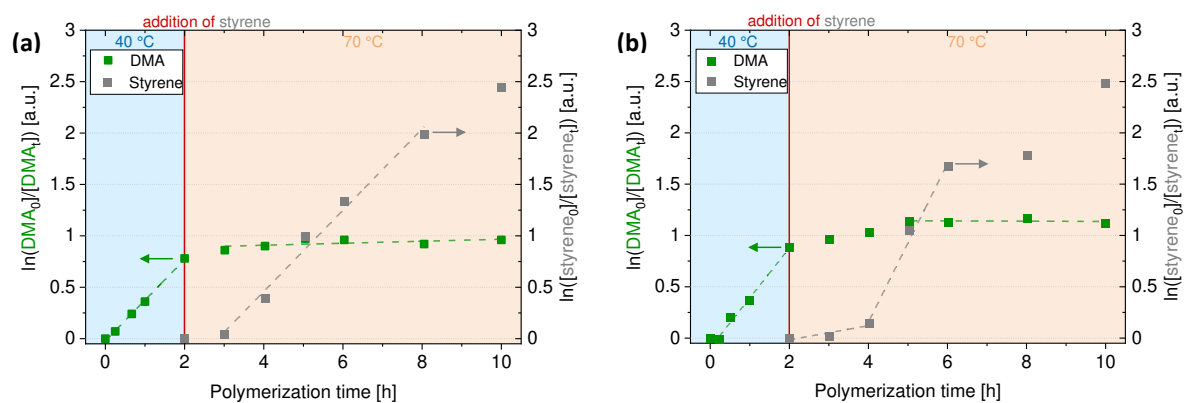


Figure S 12. Pseudo-first-order plots of the blue-light-induced semi batch polymerization of $[DDMAT]_0/[DMA]_0/[styrene]_0 = 1:500:1000$ at (a) 20 % (w/w) and (b) 30 % (w/w) RAFT agent and monomer content.

7.2 P4VP-*b*-P(4VP-*grad*-S) copolymers

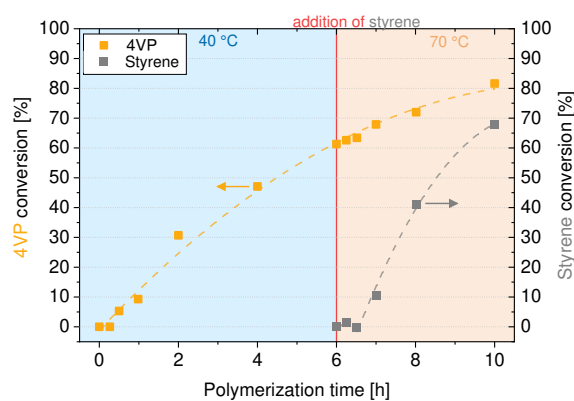
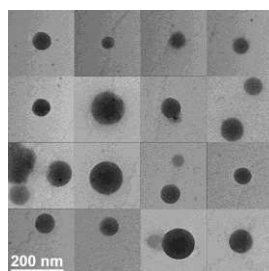


Figure S 13. Conversion of the semibatch polymerization of $[DDMAT]_0/[4VP]_0/[styrene]_0 = 1:500:1000$ at 20 % (w/w).

8. Additional TEM images of the particles

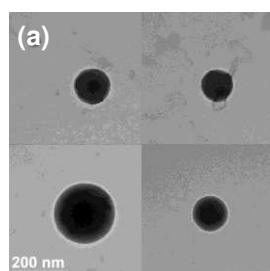
8.1 PDMA-*b*-PS



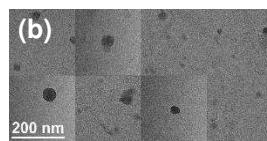
2.50 h

Figure S 14. Particles observed during the synthesis of PDMA-*b*-PS at polymerization time of 2.50 h.

8.2 P4VP-*b*-PS

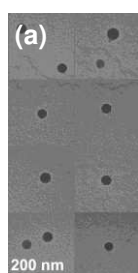


0.53 h

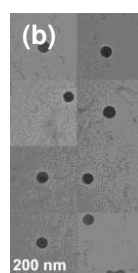


1.25 h

Figure S 15. Particles observed during the synthesis of P4VP-*b*-PS at polymerization time of (a) 0.53 h and (b) 1.25 h.



unstained



stained

Figure S 16. (a) Unstained and (b) iodine-stained particles observed during the synthesis of P4VP-*b*-PS at polymerization time of 6.00 h

9. TEM histograms

9.1 TEM histograms of the particles in the synthesis of PDMA-*b*-PS

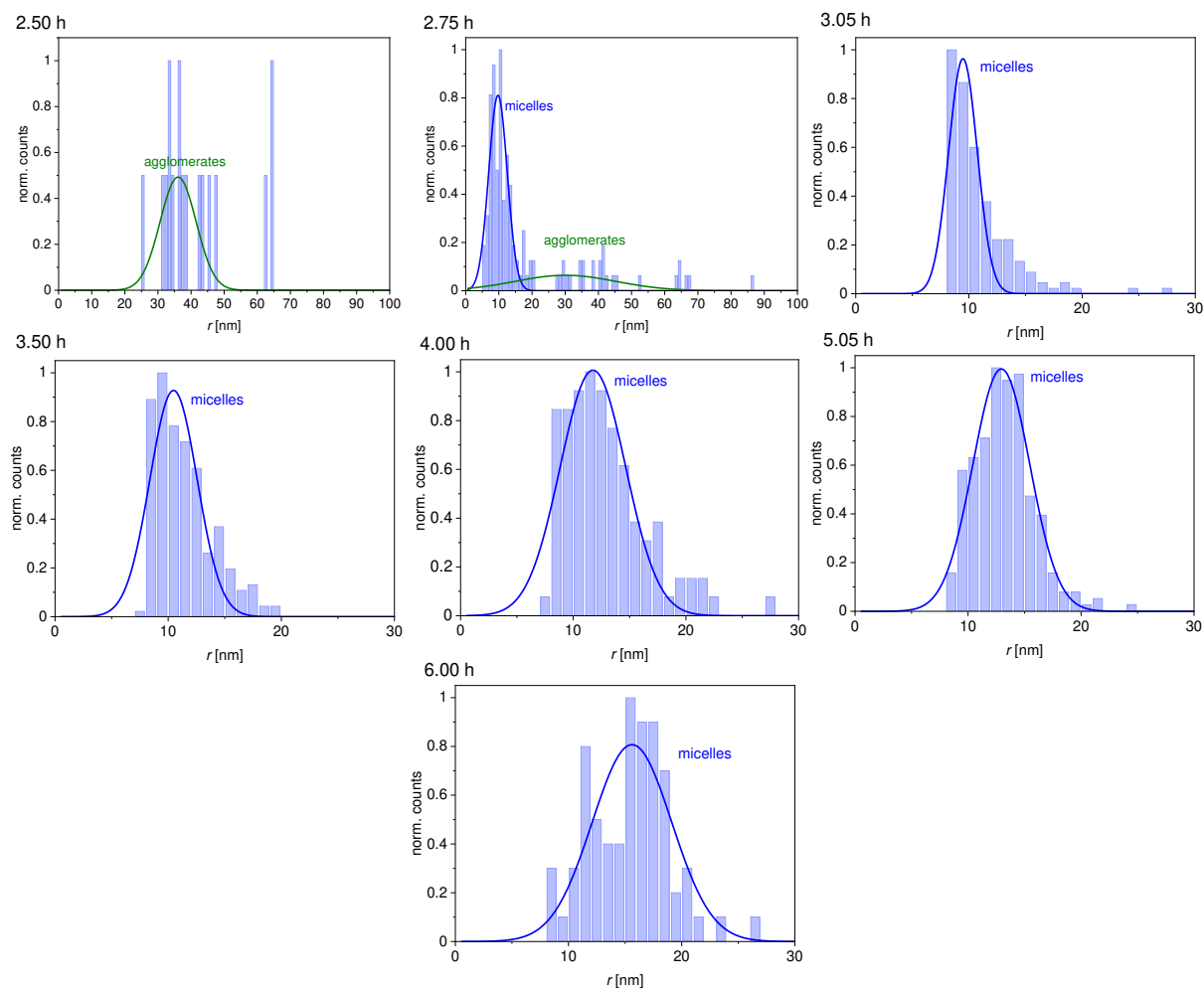


Figure S 17. TEM histograms of the particles observed the in the blue-light-induced RAFT emulsion polymerization of PDMA-*b*-PS.

9.2 TEM histograms of the particles in the synthesis of P4VP-*b*-PS

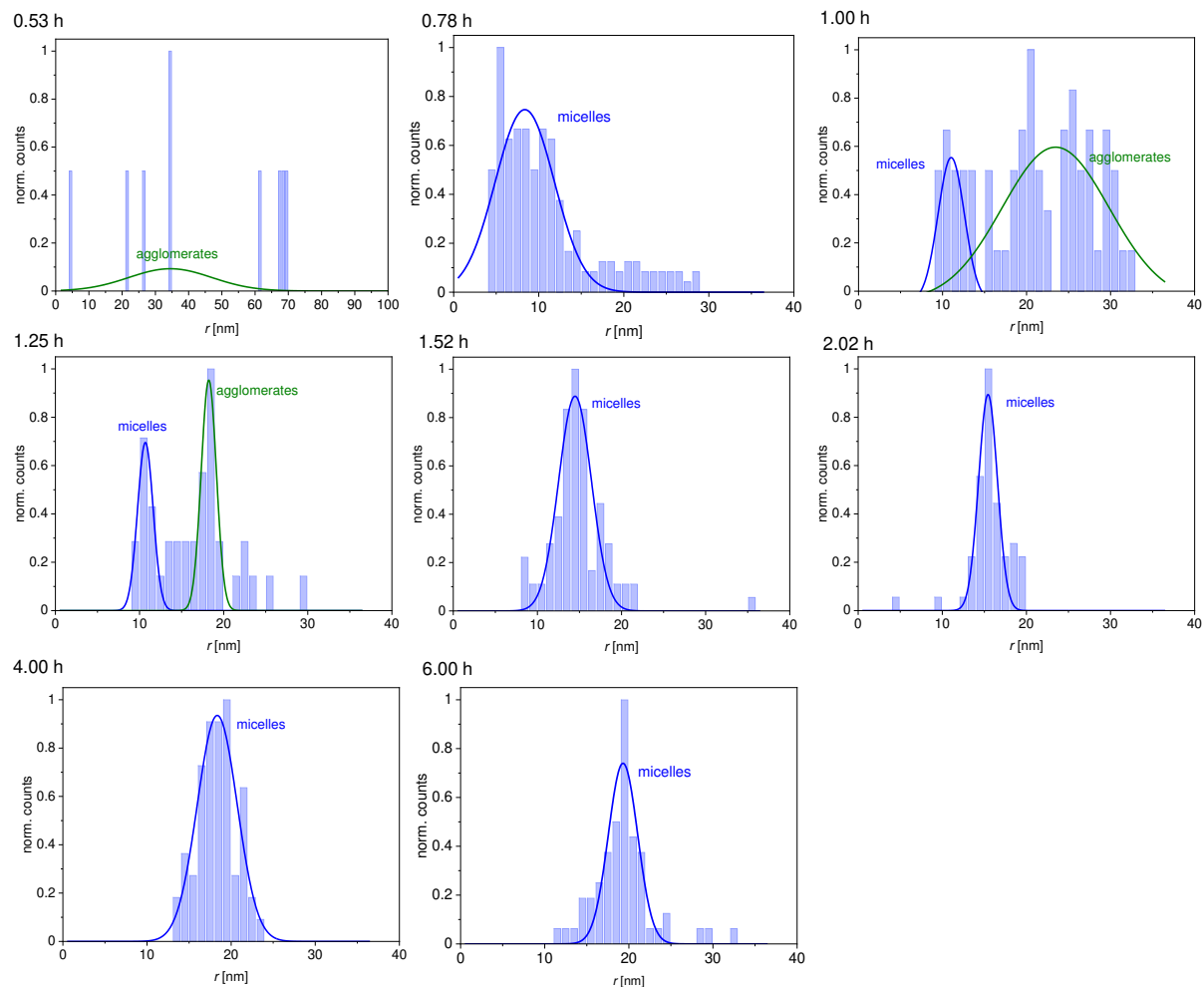


Figure S 18. TEM histograms of the particles observed in the blue-light-induced RAFT emulsion polymerization of P4VP-*b*-PS.

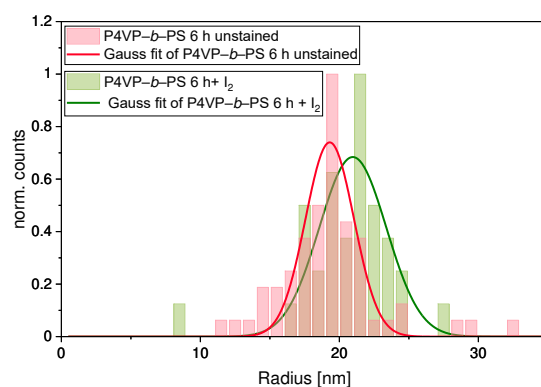


Figure S 19. Unstained and iodine-stained (I_2) TEM histograms of the P4VP-*b*-PS diblock copolymer particles after 6.00 h polymerization.

10. Hydrodynamic and particle radii determined by TEM of the *ab initio* emulsion polymerizations

Table S 1. Polymer samples of the blue-light-induced *ab initio* emulsion polymerization of styrene with PDMA^{21.1} macroCTA ([PDMA]₀/[styrene]₀ = 1/1000 (20 % w/w) in water-ethanol mixture (50:50 w/w), 70 °C, $I_{\text{blue light}} = 87 \text{ mW} \cdot \text{cm}^{-2}$).

Polymer ^{a)}	t [h]	Conversion ^{b)}	R_h [nm] ^{c)}	R_{TEM} [nm] ^{d)}
PDMA ₉₅ - <i>b</i> -PS ₅ ^{22.2}	0.50	1.0		
PDMA ₉₃ - <i>b</i> -PS ₇ ^{22.8}	1.00	1.6	2.3 ± 0.1	
PDMA ₉₂ - <i>b</i> -PS ₈ ^{22.9}	1.50	1.7	2.9 ± 0.3	
PDMA ₉₂ - <i>b</i> -PS ₈ ^{23.5}	1.80	2.3	2.9 ± 0.5	
PDMA ₈₈ - <i>b</i> -PS ₁₂ ^{24.1}	2.00	2.8		
PDMA ₈₅ - <i>b</i> -PS ₁₅ ^{24.7}	2.25	3.5	3.0 ± 0.6	
PDMA ₈₄ - <i>b</i> -PS ₁₆ ^{25.1}	2.50	3.8	8.5 ± 1.2	
PDMA ₇₄ - <i>b</i> -PS ₂₆ ^{28.7}	2.75	7.2	10.4 ± 4.2	9.6 ± 5.3
PDMA ₆₄ - <i>b</i> -PS ₃₆ ^{33.2}	3.05	11.4	18.2 ± 0.6	9.5 ± 2.5
PDMA ₃₅ - <i>b</i> -PS ₆₅ ^{60.4}	3.50	37.1	29.9 ± 1.4	10.5 ± 4.2
PDMA ₃₀ - <i>b</i> -PS ₇₀ ^{69.5}	4.00	45.9	30.1 ± 1.8	11.8 ± 5.8
PDMA ₂₄ - <i>b</i> -PS ₇₆ ^{86.4}	5.05	61.9	29.9 ± 0.9	13.0 ± 5.0
PDMA ₂₀ - <i>b</i> -PS ₈₀ ^{104.7}	6.00	79.2	31.0 ± 0.4	15.6 ± 7.0

^{a)} Subscripts denote the weight fraction of each block and superscripts the theoretical number-average molecular weight determined by ¹H-NMR spectroscopy. ^{b)} Conversion determined by ¹H-NMR spectroscopy. ^{c)} Hydrodynamic radius determined by DLS. ^{d)} Particle radius determined by TEM.

Table S 2. Polymer samples of the blue-light-induced *ab initio* emulsion polymerization of with P4VP^{21.5} macroCTA ([P4VP]₀/[styrene]₀ = 1/1000 (20 % w/w) in water-ethanol mixture (40:60 w/w), 60 °C, $I_{\text{blue light}} = 87 \text{ mW} \cdot \text{cm}^{-2}$).

Polymer ^{a)}	<i>t</i> [h]	Conversion ^{b)}	<i>R_h</i> [nm] ^{c)}	<i>R_{TEM}</i> [nm] ^{d)}
P4VP ₉₉ - <i>b</i> -PS ₁ ^{21.8}	0.53	0.3	2.5 ± 1.7	
P4VP ₉₅ - <i>b</i> -PS ₅ ^{22.6}	0.78	1.1	10.4 ± 1.3	8.4 ± 6.9
P4VP ₉₁ - <i>b</i> -PS ₉ ^{23.5}	1.00	1.9	13.6 ± 3.9	11.0 ± 3.1
P4VP ₇₇ - <i>b</i> -PS ₂₃ ^{28.0}	1.25	6.3	22.0 ± 2.1	10.7 ± 1.9
P4VP ₅₈ - <i>b</i> -PS ₄₂ ^{37.3}	1.52	15.3	36.7 ± 1.6	14.5 ± 3.9
P4VP ₄₄ - <i>b</i> -PS ₅₆ ^{49.3}	1.75	27.0	37.5 ± 0.8	
P4VP ₃₇ - <i>b</i> -PS ₆₃ ^{58.9}	2.02	36.3	35.8 ± 0.7	15.4 ± 2.2
P4VP ₂₇ - <i>b</i> -PS ₇₃ ^{79.9}	2.50	56.7	37.9 ± 0.9	
P4VP ₂₅ - <i>b</i> -PS ₇₅ ^{86.6}	3.03	63.2	37.0 ± 0.6	
P4VP ₂₂ - <i>b</i> -PS ₇₈ ^{95.9}	4.00	72.2	36.2 ± 0.5	18.4 ± 4.7
P4VP ₂₀ - <i>b</i> -PS ₈₀ ^{107.3}	6.00	83.3	35.7 ± 0.7	19.3 ± 3.5

^{a)} Subscripts denote the weight fraction of each block and superscripts the theoretical number-average molecular weight determined by ¹H-NMR spectroscopy. ^{b)} Conversion determined by ¹H-NMR spectroscopy. ^{c)} Hydrodynamic radius determined by DLS. ^{d)} Particle radius determined by TEM.

11. Estimation of the average number of radicals per particle

In a typical free-radical emulsion polymerization, the rate of polymerization R_p is determined *via* the following equation:³

$$R_p = -\frac{d[M]}{dt} = \frac{k_p \cdot [M]_p \cdot \bar{n} \cdot N_p}{N_A} \quad (5)$$

where $[M]$ is the initial molar concentration of monomer, k_p is the propagation rate coefficient, $[M]_p$ is the concentration of monomer in particles, $\bar{n}$ denotes the average number of radicals per particle, N_p is the number of latex particles nucleated per unit volume of water, and N_A is the Avogadro's number.

The rate of polymerization was determined from the slope of the first order plots. Through the readjustment of Equation 5, the average number of radicals per particle could be determined by Equation 6.

$$\bar{n} = \frac{R_p \cdot N_A}{k_p \cdot [M]_p \cdot N_p} \quad (6)$$

The average number of radicals per particle can be calculated from the steady-state region of the conversion versus time kinetic plot ($\frac{dconv}{dt}$) as follows:⁴

$$\bar{n} = \frac{\frac{dconv}{dt} \cdot N_A \cdot [M]_0}{k_p \cdot [M]_p \cdot N_p} \quad (7)$$

where $[M]_0$ is the initial molar concentration of monomer.

Due to the RAFT equilibrium, the average number of radicals per particle in a RAFT emulsion polymerization might differ from the one calculated for a free-radical polymerization. Therefore, the RAFT equilibrium constant K and the initial RAFT agent concentration $[RAFT]_0$ (in our case macroRAFT agent concentration) need to be considered to estimate the number of radicals per particle in a RAFT emulsion polymerization $\bar{n}_{RAFT}$. The calculation follows Equation 8, where $\bar{n}_{blank}$ is the average number of radicals per particle in a RAFT free radical polymerization (in the previous equations denoted as $\bar{n}$).⁵

$$\frac{1}{\bar{n}_{RAFT}} = \frac{1}{\bar{n}_{blank}} + 2K \cdot [RAFT]_0 \quad (8)$$

Table S 3. Parameters for the calculation of the estimation of the number of radicals per particle in the emulsion polymerizations with styrene.

Parameter	Value	Determined at T [°C]	Reference
k_p	480 L mol ⁻¹ s ⁻¹	70	6
$[M]_p$	5.8 mol L ⁻¹	70	6
N_p	1 · 10 ¹⁷ L ⁻¹	50	7
K	314 L mol ⁻¹	75	5

With the specified parameters from Table S 3, average number of radicals per particle $\bar{n}_{blank}$ values of 0.29 and 0.32 for a free radical emulsion polymerization of styrene with PDMA^{21.1} and P4VP^{21.5}, respectively, were calculated. The correction with the RAFT equilibrium in Equation 8 results in $\bar{n}_{RAFT}$ values of 0.25 and 0.28 for a RAFT emulsion polymerization of styrene with PDMA^{21.1} and P4VP^{21.5},

respectively. Due to the assumed parameters from other publications, which do not fully correspond to the analyzed system, the calculated values are subject to errors and are intended only as a rough guide.

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9.3 Supporting Information Publication 3

The supporting information is reprinted with permission from L. Hub, J. Koll, K. Buhr, M. Radjabian, V. Abetz, pH-responsive size- and charge-selective block copolymer membrane for the separation of small proteins. *Journal of Membrane Science* **2024**, 708, 123021 – published by Journal of Membrane Science (Elsevier).

Supporting information

pH-responsive size- and charge-selective block copolymer membrane for the separation of small proteins

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1. Experimental

1.1 Polymer synthesis

1.1.1 Synthesis of PDMA macroCTA

PDMA macroCTAs were synthesized *via* blue-light-induced iniferter RAFT polymerization in an analogous way to that reported previously.[1] DDMAT (280 mg, 0.768 mmol, 1.00 eq.) and DMA (39.5 mL, 384 mmol, 500 eq.) were dissolved in ethanol (97 mL). Then water (77 mL) was added, followed by addition of *N,N*-dimethylformamide (100 μ L) as an internal reference for ^1H -NMR analysis. An initial sample was taken. The solution was degassed by purging the ice-cooled polymerization vessel with argon for 30 min. The polymerization vessel was then placed at the center of the blue LED. Polymerization was carried out under blue light irradiation ($\lambda_{\text{max}} = 451 \text{ nm}$) at a water bath temperature of 40 °C under constant stirring (400 rpm). After 60 min, the polymerization was stopped by turning off the irradiation source, quenching in an ice cooling bath and exposing to air. The solvent was removed by vacuum and the crude polymer was obtained by drying under vacuum at 40 °C for 24 h. Subsequently, the polymer was dissolved in THF, precipitated in cold cyclohexane, filtered, and dried under vacuum at 40 °C for 48 h.

1.1.2 Synthesis of PDMA-*b*-PS diblock copolymers

PDMA-*b*-PS were synthesized *via* the chain extension of the PDMA macroCTAs with styrene as reported previously.[2] PDMA^{21.1} (6.000 g, 0.284 mol, 1.00 eq.) was dissolved in ethanol (86 mL) and water (68 mL) was added dropwise under stirring. Subsequently, styrene (30.9 mL, 286.4 mol, 1000 eq.) was added dropwise and the resulting emulsion was homogenized for 30 min at 600 rpm. The ice-cooled emulsion was purged with argon for 30 min. The polymerization vial was immersed in a water bath at a temperature of 70 °C and the emulsion was stirred constantly (600 rpm) while being illuminated with blue light ($\lambda_{\text{max}} = 451 \text{ nm}$). After 6 h, the photopolymerization was stopped by switching-off the blue LED, cooling with ice and exposing to air. The solvent was removed by vacuum and the crude polymer was dried under vacuum at 40 °C for 24 h. In the next step, the polymer was dissolved in THF, precipitated in cold water, filtered, and dried under vacuum at 40 °C for 48 h.

1.2 Polymer characterization

1.2.1 ^1H -NMR spectroscopy

^1H -nuclear magnetic resonance (NMR) spectra were recorded at ambient temperature using a Bruker® AV500 spectrometer with 16 scans per spectrum and a delay of 3 s. Analysis was realized with the program MestReNova® 14.2.

1.2.2 GPC

Gel permeation chromatography (GPC) measurements were carried out at 50 °C using dimethylacetamide (DMAc) containing LiCl (0.1 M) as solvent. Measurements were performed at a flow rate of 1.0 mL·min⁻¹ using a VWR-Hitachi® L2130 pump. A PSS® GRAM pre-column (dimension 8·50 mm) and two PSS® GRAM columns (8·300 mm, particle size 10 µm) with a porosity of 3000 Å and 1000 Å, respectively, were used for the measurements. A Hitachi® L2490 RI refractive index detector was employed to record the signal. The instrumentation was calibrated with the use of polystyrene (PS) standards and the data were analyzed using the software PSS® Win GPC UniChrom V8.10.

2. PDMA-*b*-PS diblock copolymers

Table S1. PDMA-*b*-PS diblock copolymers synthesized *via* blue-light induced RAFT polymerization.

Polymer ^{a)}	$\bar{M}_n$ [kDa] ^{b)}	$\bar{M}_{n,app}$ [kDa] ^{c)}	$\bar{D}$ ^{d)}
PDMA ₂₃ - <i>b</i> -PS ₇₇ ¹⁰²	102	90	1.19
PDMA ₂₀ - <i>b</i> -PS ₈₀ ¹⁰⁵	105	95	1.11
PDMA ₂₃ - <i>b</i> -PS ₇₇ ¹⁰⁵	105	98	1.17
PDMA ₂₂ - <i>b</i> -PS ₇₈ ¹⁰⁸	108	115	1.08

^{a)} Subscripts denote the weight percentage of each block in the diblock copolymer, superscripts denote the number-average molecular weight determined by ¹H-NMR spectroscopy. ^{b)} Number-average molecular weight determined by ¹H-NMR spectroscopy. ^{c)} Apparent number-average molecular weight determined by SEC with PS calibration. ^{d)} Dispersity determined by SEC with PS calibration.

3. Optimization of the casting parameters

Table S2. Solubility parameters of all components in the SNIPS process.

Component	δ_D (MPa ^{0.5})	δ_P (MPa ^{0.5})	δ_H (MPa ^{0.5})	$\delta = \sqrt{\delta_D^2 + \delta_P^2 + \delta_H^2}$
Dioxane [3]	17.5	1.8	9.0	19.8
THF [3]	16.8	5.7	8.0	19.5
DMF [3]	17.4	13.7	11.3	24.8
Water [3]	15.6	16.0	42.3	47.8
PS [3]	18.5	4.5	2.9	19.3
PDMA [4]				21.7

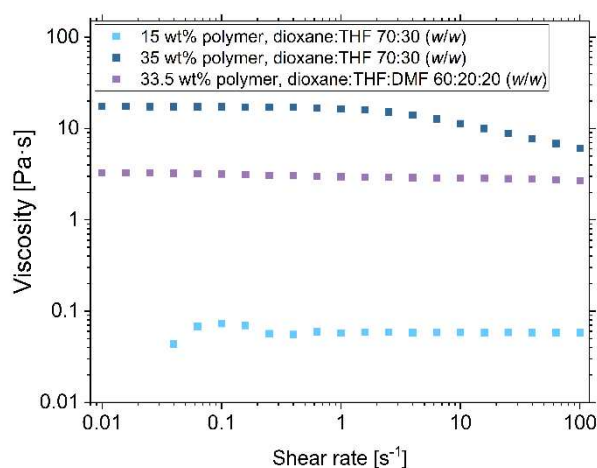


Fig. S1. Shear rate dependent viscosity of the casting solutions in the dioxane:THF 70:30 (w/w) and the dioxane:THF:DMF 60:20:20 (w/w) mixture.

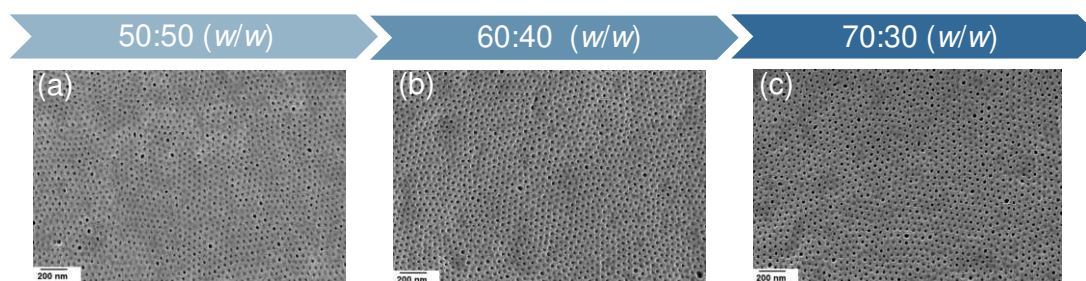


Fig. S2. SEM micrographs of the top surface of PDMA₂₃-*b*-PS₇₇¹⁰² diblock copolymer membranes at a polymer concentration of 35 wt% and an evaporation time of 15 s in different solvent ratios of dioxane:THF of (a) 50:50 (w/w), (b) 60:40 (w/w) and (c) 70:30 (w/w).

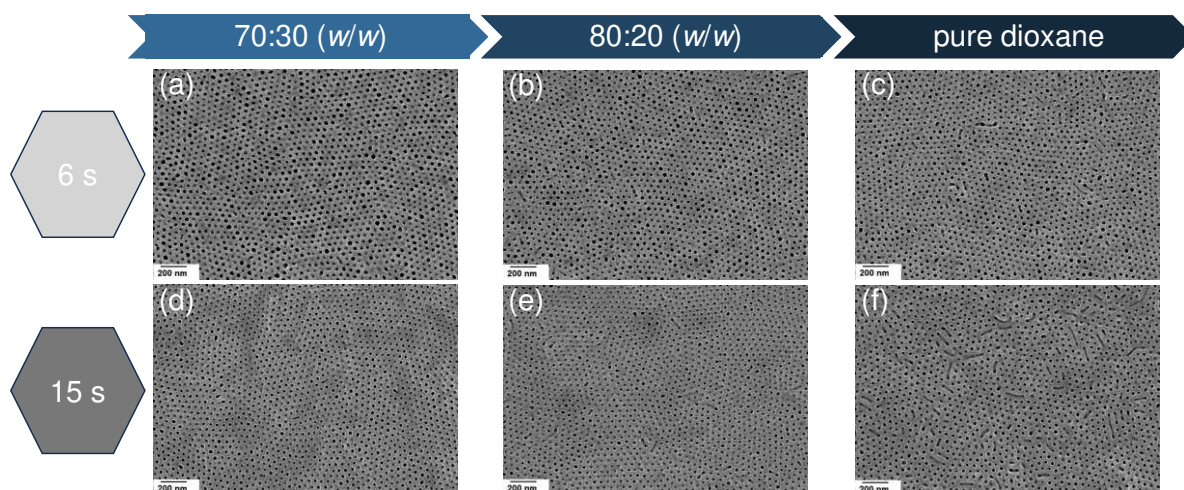


Fig. S3. SEM micrographs of the top surface of PDMA₂₃-*b*-PS₇₇¹⁰² diblock copolymer membranes at a polymer concentration of 33.5 wt% in (a) & (d) dioxane:THF 70:30 (w/w), (b) & (e) dioxane:THF 80:20 (w/w) and (c) & (f) dioxane at an evaporation time of 6 s and 15 s, respectively.

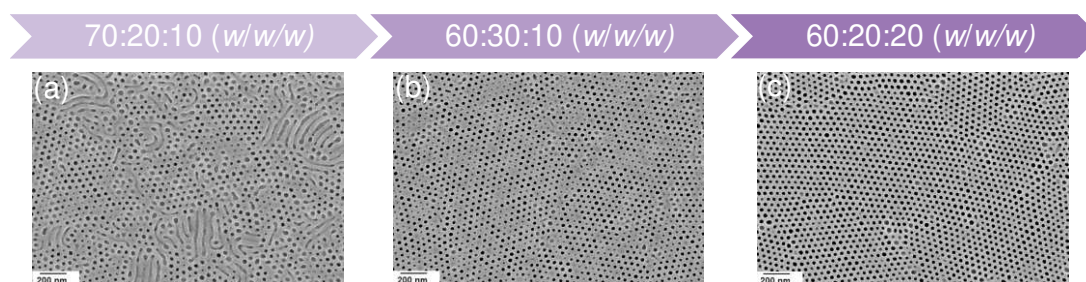


Fig. S4. SEM micrographs of the top surface of PDMA₂₃-*b*-PS₇₇¹⁰² diblock copolymer membranes at a polymer concentration of 33.5 wt% in (a) dioxane:THF:DMF 70:20:10 (w/w/w), (b) dioxane:THF:DMF 60:30:10 (w/w/w), and (c) dioxane:THF:DMF 60:20:20 (w/w/w).

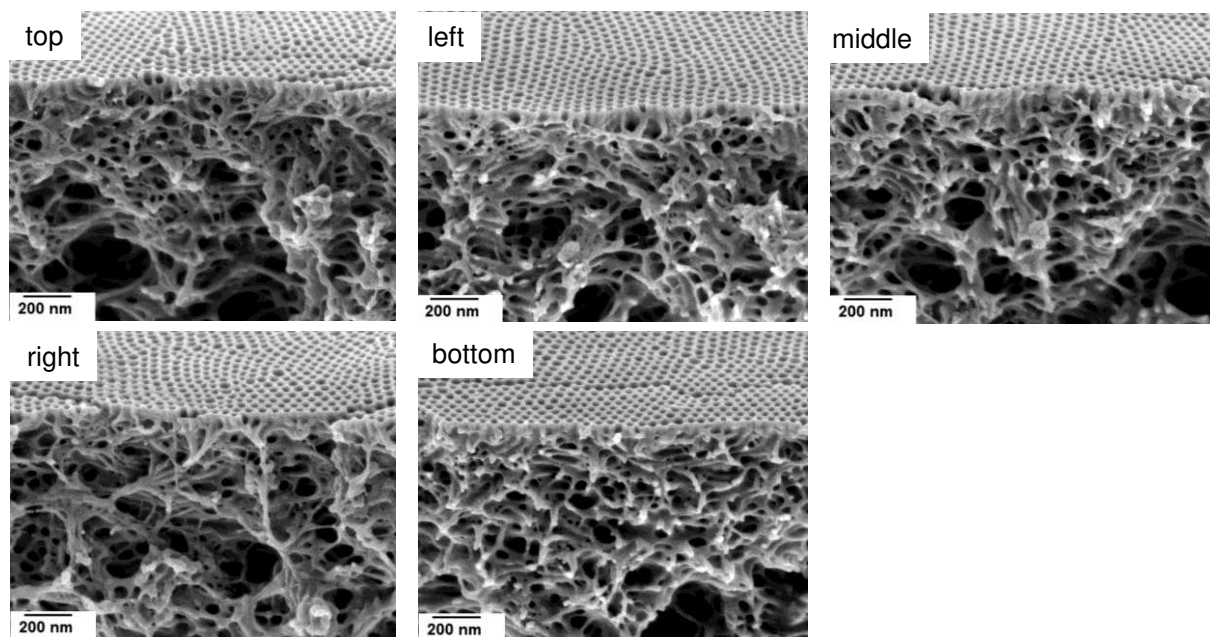


Fig. S5. Cross-view of the M2 PDMA₂₂-*b*-PS₇₈¹⁰⁸ membrane at different positions.

Table S3. Pore size and porosity of the M2 PDMA₂₂-*b*-PS₇₈¹⁰⁸ membrane.

Position in sample	Pore size [nm]	Porosity [%]
top	26.4 ± 3.3	25.5
left	26.9 ± 3.5	26.8
middle	27.3 ± 2.9	27.0
right	27.1 ± 3.7	26.7
bottom	25.0 ± 4.2	23.3
total average	26.5 ± 3.7	25.9 ± 1.4

4. Protein adsorption

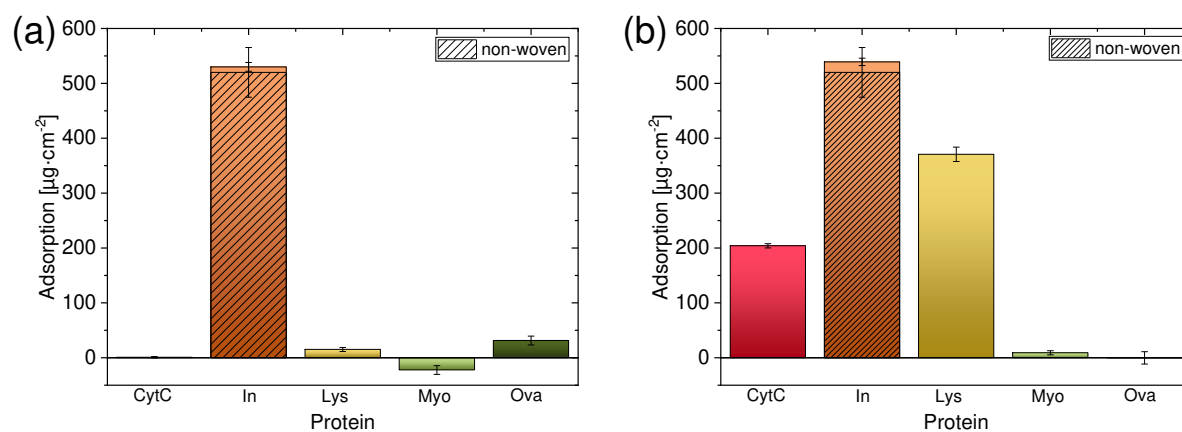


Fig. S6. Protein adsorptions of the proteins cytochrome C (CytC), insulin (In), lysozyme (Lys), myoglobin (Myo) and Ovalbumin (Ova) on the (a) PDMA-*b*-PS and (b) PAA-*b*-PS membrane.

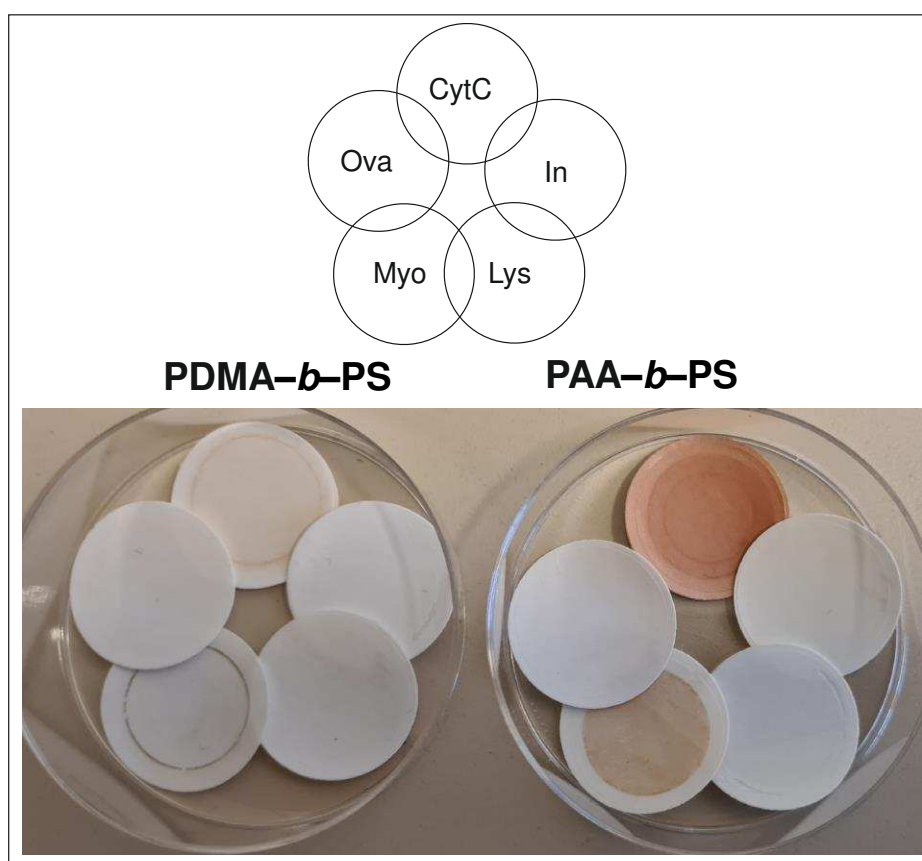


Fig. S7. PDMA-*b*-PS (left) and PAA-*b*-PS (right) membrane samples after the protein separation performance tests of the individual proteins.

References

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9.4 Experimental Section for the Unpublished Results

9.4.1 Determination of the Glass Transition Temperature of Polymers and their Blends *via* DSC

The homo- and diblock copolymers as well the blends were diluted in chloroform. The solvent was slowly evaporated, and the samples were dried at 180 °C for 2 d before the measurement to ensure no contamination and homogeneity of the samples. Differential scanning calorimetry was performed on a DSC 1 (Star system, Mettler-Toledo, Gießen, Germany). The pure polymers and the blends were analyzed in a temperature range from 25 °C to 200 °C. A heating and cooling rate of 10 K·min⁻¹ was exerted using nitrogen as a purge gas stream (60 mL·min⁻¹). Per sample, three heating-cooling cycles were conducted. The third heating trace was used for the interpretation of the results.

9.4.2 Determination Of Diffusion Coefficients Using PFG NMR

For the analysis, casting solutions containing the PDMA₁₉-*b*-PS₈₁^{112.0} diblock copolymer, the P4VP₁₉-*b*-PS₈₂^{135.4} diblock copolymer, and the blend of these two with a molar ratio of 50:50 were prepared in a solvent system of THF:DMF:dioxane with a ratio of 50:30:20 (w/w/w). To receive a relative similar viscosity of the solution, the polymer solutions were prepared with 35 wt% PDMA₁₉-*b*-PS₈₁^{112.0}, 20 wt% P4VP₁₉-*b*-PS₈₂^{135.4}, and the blend with a total polymer concentration of 26 wt%. The blend was established by mixing the two solutions (as shown in Figure 43).

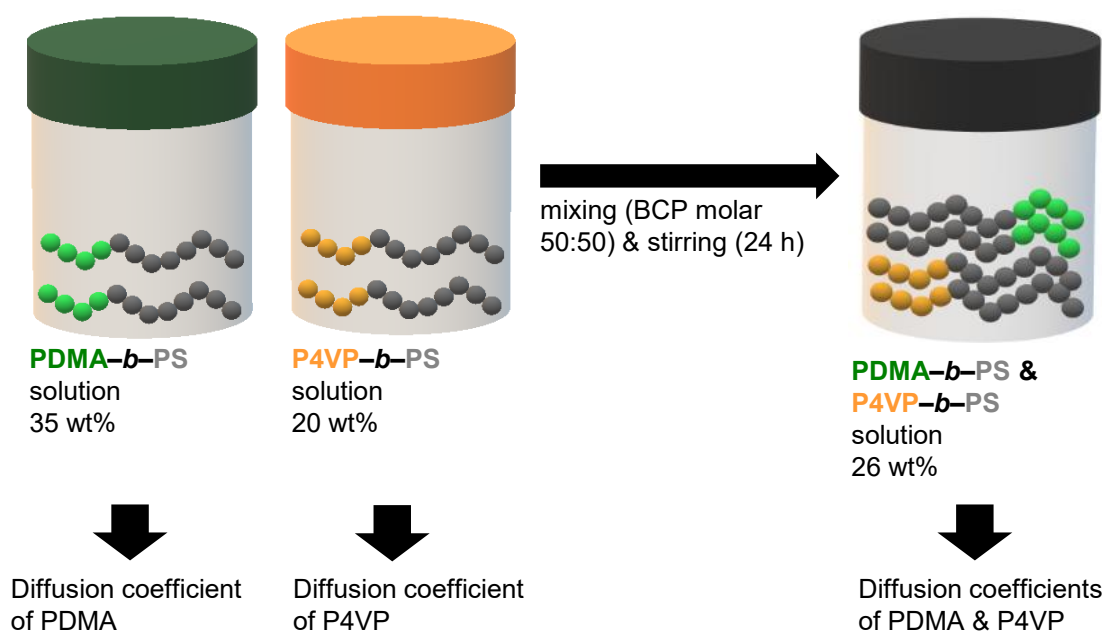


Figure 43. Solutions for the determination of the diffusion coefficients.

The temperature was controlled using 4% methanol in methanol- d_4 (Bruker standard sample). The gradient unit (Bruker GERAT, Diff30 probe head) was calibrated at 25 °C using a known sample (doped water sample, Bruker, $D = 1.91\text{m}^2/\text{s}$). This resulted in a calibration constant of 118.00 G/mm. The following measurements were carried out at 23 °C. The pulse sequence used was the Pulse Gradient Stimulated Echo (diffSte) sequence.^{317,363} A diffusion time of 35 ms and a gradient pulse of 1 ms were used for all measurements. The gradient field strength varied from approx. 58 G/cm up to 1168 G/cm in 16 steps. For each step, 16 scans were recorded. The average heating of the sample was < 0.1 °C. Each measurement was repeated ten times.

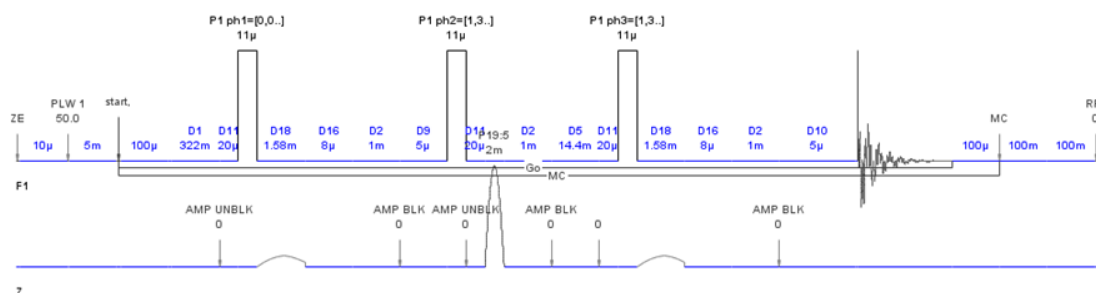


Figure 44. Pulse sequence used for the PFG NMR experiments.

The measurement results were analyzed using the Bruker Dynamics Center software (version 2.7.3). The measured diffusion values for the signal intensity and area were averaged over all measurements of the sample. In principle, 5 – 10 % errors due to convection in the sample, eddy current effects and non-linearities of the transmitters must be taken into account in the measurements; in the case of samples with a high proton density (NMP), radiation damping also occurs. Before the measurement, each sample was tempered in the NMR for at least half an hour until 23 °C was reached. For the evaluation of the diffusion measurements, at least the results of the first two gradient levels were discarded, as the influence of the solvent signals still influences the results. The analysis was conducted by using peak-fitting (deconvolution). The results were subject to DOSY transformation.

9.4.3 Fabrication of PDMA-*b*-PS/ P4VP-*b*-PS Diblock Copolymer Blend Membranes

The diblock copolymer casting solutions were prepared by mixing PDMA-*b*-PS and P4VP-*b*-PS diblock copolymers in a 50:50 molar ratio. The polymer blend was then dissolved in a ternary solvent mixture of dioxane, THF, and DMF (20:50:30 w/w/w) to achieve a concentration of 26 wt%. The solutions were stirred at room temperature for several hours to ensure complete dissolution. Subsequently, 3 wt% glycerin (relative to the total solution weight) was added as a viscosity modifier, and the mixture was stirred for an additional 24 h before casting. The solution was then allowed to rest for several hours prior to membrane fabrication.

Flat sheet membranes were produced using the SNIPS process with a custom-built casting machine. The gap between the doctor blade and the polyester nonwoven support was set to 100 µm. The evaporation time before immersion in the water bath was

carefully controlled by adjusting the casting speed, optimizing it to achieve maximum pore uniformity. After casting, the membranes were submerged in a water bath for at least 60 min. Finally, the membranes were dried under vacuum at 60 °C for a minimum of 48 h to ensure complete drying.

9.4.4 SEM Analysis and Staining of Diblock Copolymer Blend Membranes

SEM was performed to investigate the top surface and cross-section morphology of the membranes using a Merlin SEM (Zeiss, Germany) at an accelerating voltage of 1 – 5 kV. Prior to imaging, the membrane samples were coated with approximately 1 nm of platinum using a CCU-010 coating device (Safematic, Switzerland) to enhance conductivity and image quality. The SEM images were analyzed with IMS software (Imagic Bildverarbeitung AG, Switzerland) to measure the average pore size of the membranes. Pore size, distribution, and surface porosity were determined by analyzing 3 images for each membrane, ensuring statistical reliability and accurate representation of the membrane's morphology.

To analyze the stained membranes, the samples were first coated with 8 nm carbon and then stained with iodine vapor in vacuum for 45 min to selectively stain the P4VP pore-forming block. One sample was stained first, followed by coating, with the same contrast. The images were recorded in a Zeiss Merlin SEM at 1.5 – 2 keV with the energy-selective backscattering (EsB) detector at various energy-section grid voltages and probe currents.

9.4.5 Post-Modification of Diblock Copolymer Blend Membranes

PDMA-*b*-PS/ P4VP-*b*-PS diblock copolymer blend membranes underwent a two-step post-modification process. First, the membranes were exposed to methyl iodide vapor. To achieve this, membranes of known size were placed in a desiccator, and a small vessel containing methyl iodide (0.05 mL/cm² based on membrane surface area) was added. The desiccator was sealed, allowing the vapor to react with the membranes for seven days. Following this, the membranes were dried at 40 °C for two days. To evaluate the conversion, ¹H-NMR spectra were recorded at ambient temperature using a Bruker® AV500 spectrometer with 16 scans per spectrum and a 3 s delay. Samples were analyzed in a solvent mixture of THF-*d*₈ and methanol-*d*₄ (58:42 vol%).

In the second modification step, the membranes were treated under acidic conditions with 6 M hydrochloric acid at 80 °C for 24 h. Afterward, they were thoroughly washed with deionized water to remove unreacted components and byproducts. The conversion was followed *via* attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy using a Bruker Alpha with a diamond-ATR unit.

9.4.6 Water Permeance Measurements

Water permeance measurements were conducted in dead-end filtration mode using a custom-built device. Prior to testing, the membranes were conditioned by soaking them

in demineralized water overnight. A transmembrane pressure (Δp) of 2 bar was applied, and measurements were performed at room temperature. The change in permeate weight (Δw) over time (Δt) was recorded to determine the water permeance. Each sample was measured in triplicate to ensure accuracy and reproducibility. The water permeance P was calculated using Equation (37), where ρ represents the density of the permeate and A is the surface area of the membrane:

$$P = \frac{\Delta w}{A \cdot \rho \cdot \Delta t \cdot \Delta p} \quad (37)$$

9.4.7 Salt Rejection Measurements

The salt rejection performance of the membranes was measured with a 1 g·L⁻¹ aqueous solution of the salts, and samples were analyzed using ion chromatography (Dionex ICS600, Thermofischer Scientific Inc.).

9.5 Used Hazardous Substances According to GHS

The chemicals that were used in this work are listed in Table 3 together with their GHS-Pictograms, Hazard- and Precautionary-Statements, as well as indications for disposal.

Table 3. Used chemicals and their Hazard- and Precautionary-Statements.

Substance	Symbol	Hazard-Statements	Precautionary-Statements
Acetone	 	225, 319, 336	210, 305+351+338, 370+378, 403+235
Activated basic aluminum oxide	 	222, 229, 319, 336	210, 251, 305+351+338, 405, 410+412, 501
Chloroform	 	302, 331, 315, 319, 351, 361d, 336, 372	261, 305+351+338, 311
Chloroform- <i>d</i>	 	302, 315, 319, 331, 351, 361d, 372	260, 280, 301+312+330, 304+340+311, 305+351+338, 403+233
2-Cyano-2-propyldodecyltrithiocarbonate		302	-
4-Cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl]pentanoic acid		302	264, 270, 301+312+330, 501
4-Cyano-4-(phenylcarbo- <i>no</i> thioylthio)-pentanoic acid		317	280
Cyclohexane	   	225, 304, 315, 336, 410	210, 273, 301+310+331, 302+352
Deuterium oxide	-	-	-
2-Dimethylaminoethylacrylate	   	226, 302, 311, 314, 317, 330, 400	210, 273, 280, 303+361+ 353, 304+340+310, 305+351+338

Substance	Symbol	Hazard-Statements	Precautionary-Statements
1,4-Dioxane	  	225, 319, 335, 351	210, 261, 281, 305+351+338
Disodium hydrogen phosphate		-	-
2-(Dodecylthio-carbonothioyl-thio)-2-methylpropionic acid		315, 319, 335	302+352, 305+351+338
<i>N,N</i> -Dimethyl-acetamide	 	312 +332, 319, 360D	202, 280, 302+352+312, 304+340+312, 305+351+338, 308+313
<i>N,N</i> -Dimethyl-acrylamide	 	301+311, 318	280, 301+310, 305+351+338, 312
<i>N,N</i> -Dimethyl-formamide	  	226, 312+332, 319, 360D	201, 280, 305+351+338, 308+313
Ethanol	 	225, 319	210, 240, 305+351+338, 403+233
Hydrochloric acid	 	290, 314, 335	234, 261, 271, 280, 303+361+353, 305+351+338
Lithium chloride		302, 315, 319	264, 270, 280, 301+312, 302+352, 305+351+338
Magnesium sulfate		-	-
Methanol- <i>d</i> ₄	  	225, 301+311+331, 370	210, 233, 280, 301+310, 303+361+353, 304+340+311
Methyl iodide	    	226, 301+331, 312, 315, 318, 335, 351, 410	210, 273, 280, 301+310, 303+361+353, 305+351+338

Substance	Symbol	Hazard-Statements	Precautionary-Statements
Perfluoro(methylcyclohexane)		-	-
Potassium chloride		-	-
Potassium dihydrogen phosphate		-	-
Sodium chloride		-	-
Sodium hydroxide		290, 314	234, 260, 280, 303+361+353, 304+340+310, 305+351+338
Styrene	  	226, 315, 319, 332, 361d, 372	210, 260, 280, 305+351+338, 370+378
Tetrahydrofuran	  	225, 302, 319, 335, 351	210, 280, 301+312+330, 305+351+338, 370+378, 403+235
Tetrahydrofuran- <i>d</i> ₈	  	225, 302, 319, 335, 336, 351	202, 210, 233, 301+312, 305+351+338, 308+313
2-Vinylpyridine	   	226, 302, 311, 314, 317, 411	210, 273, 280, 301+312, 303+361+353, 305+351+338
4-Vinylpyridine	   	226, 301, 314, 317	280, 301+310+330, 303+361+353, 304+340+310, 305+351+338, 333+313

Table 4. Used carcinogenic and mutagenic substances and substances toxic for reproduction.

Substance	CAS-Number	CMR-Classification
Chloroform	67-66-3	1B
Chloroform- <i>d</i> (solvent for NMR)	865-49-6	2
<i>N,N</i> -Dimethylacetamide	127-19-5	1B
<i>N,N</i> -Dimethylformamide	68-12-2	1B
Methyl iodide	74-88-4	2

10 Danksagung

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11 Eidesstattliche Versicherung

Hiermit versichere ich an Eides statt, die vorliegende Dissertationsschrift selbst verfasst und keine anderen als die angegebenen Quellen und Hilfsmittel benutzt zu haben. Sofern im Zuge der Erstellung der vorliegenden Dissertationsschrift generative Künstliche Intelligenz (gKI) basierte elektronische Hilfsmittel verwendet wurden, versichere ich, dass meine eigene Leistung im Vordergrund stand und dass eine vollständige Dokumentation aller verwendeten Hilfsmittel gemäß der Guten wissenschaftlichen Praxis vorliegt. Ich trage die Verantwortung für eventuell durch die gKI generierte fehlerhafte oder verzerrte Inhalte, fehlerhafte Referenzen, Verstöße gegen das Datenschutz- und Urheberrecht oder Plagiate.

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