University of Hamburg
Faculty of Chemistry

Synthesis and Characterization of Cyclic Polymers and Biodegradable Networks

Dissertation submitted in partial satisfaction of the
requirements for the degree Doctor of Philosophy
in Technical and Macromolecular Chemistry

by

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Committee members:

1) Prof. Dr. H. R. Kricheldorf
2) Prof. Dr. W. Kaminsky

To my parents

This work was carried out between 2002 and 2004 in the laboratory of Technical and macromolecular chemistry under the supervision of Prof. Dr. H. R. Kricheldorf.

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Hamburg, April 2005 Mazen Garaleh

List of Publications

1. **Macrocycles 32.**

   ``Syntheses of Cyclic Poly(ether ketone)s of Bisphenol-A´´
   Hans R. Kricheldorf, Mazen Garaleeh, Gert Schwarz, Lali Vakhtangishvili, High Perform. Polym. 2004, 16, 137.

2. **Macrocycles 28.**

   ``Cyclic Poly(benzonitrile ether)s Derived from Bisphenol-A´´
   Hans R. Kricheldorf, Mazen Garaleh, Gert Schwarz, Polym. Sci. Part A. Polym. Chem. 2003, 41, 3838.

3. **Macrocycles 30.**

   ``Cyclic Poly(pyridine ether)s by Polycondensation of 2,6-difluoropyridine with Various Diphenols.´´
   Hans R. Kricheldorf, Mazen Garaleh and Gert Schwarz, 2004, submitted.

4. **Polylactones 65.**

   ``Tertiary Amine-Initiated Zwitterionic Polymerization of Pivalolactone´´ (Reinvestigation by Means of MALDI-TOF Mass Spectrometry)
   Hans R. Kricheldorf, Mazen Garaleh, and Gert Schwarz Journal of Macromolecular Science, Pure and Applied Chemistry (2005), A42(2), 139-148.

5. **Polylactones 72.**

   ``Biodegradable Combi-Networks Derived from Poly(ε-caprolactone) and Poly(ethylene glycol)s or Poly(dimethyl siloxane)s´´
   Hans R. Kricheldorf, Mazen Garaleh, 2005, submitted.

6. **Cyclic aromatic polyethers.**

   Hans R. Kricheldorf, Mazen Garaleeh, Gert Schwarz, Lali Vakhtangishvili, 2004, submitted

Abbreviations

ε-CL:	ε-Caprolactone.
C.-F. theory:	Carothers-Flory theory.
Cat:	Catalyst.
CoI:	Coinitiator
DABCO:	1,4-Diazabicyclo[2,2,2]octane.
4,4'-DFBP:	4,4'-difluorobenzophenone.
2,6-DFBP:	2,6-difluorobenzophenone.
2,6-DFP:	2,6-Diflouropyridin.
Da:	Dalton.
DMAP:	Dimethylaminopyridine.
DMF:	Dimethylformamide.
DMSO:	Dimethylsulfoxide.
DSC:	Differential scanning calorimetry.
EOX:	Ethyloxazoline.
FAB:	Fast atom bombardment.
GPC:	Gel-permeation chromatography.
HPLC:	High-performance liquid chromatography.
I:	Initiator.
IR:	Infrared spectroscopy.
J.-S.	Theory: Jacobson-Stockmayer theory.
KCPs:	Kinetic controlled polycondensations.
LD:	Laser desorption.
M:	Monomer.
MALDI-TOF:	Matrix-assisted laser desorption/ionization time to flight mass spectroscopy.
4-MeP:	4-Methylpyridine.
MWD:	Molecular weight distribution.
NCAs:	α-Amino acid N-carboxyanhydrides.
NMP:	N-Methylpyrrolidon.
NMR:	Nuclear magnetic resonance.

PCLs:	Poly(ε-Caprolacton)s.
PEG:	Poly(ethylene glycol).
PEKs:	Poly(ether ketone)s.
PESs:	Poly(ether sulfone)s.
PiL:	Pivalolactone.
PDMS:	Bis(hydroxyprobyl)-terminated poly(dimethylsiloxan)
PS:	Polystyrene.
REP:	Ring-expansion polymerization.
ROP:	Ring-opening polymerization.
RZDM:	Ruggli-Ziegler high dilution principle.
SEC:	size-exclusion chromatography.
$SnOct_2$:	Tin(II)2-ethylhexanoate.
TCPs:	Thermodynamic controlled polycondensations.
TEG:	Tetraethylene glycol.
THF:	Tetrahydrofuran.
VPO :	Vapor pressure osmometry.
X-ray:	Wide-angle X-ray.

Symbols

α:	The ratio of rate of propagation to rate of cyclization.
ΔH:	Reaction enthalpy.
ΔG:	Gibbs-Free energy.
ΔS:	Entropy.
$\overline{DP}$:	Degree of polymerization.
f_f:	The frequency.
η_{inh}:	Inherent viscosity.
Kc:	Equilibrium constant.
m_{DP}:	The mass of a polymer chain with individual ($\overline{DP}$).
m_f:	The mass fraction.

M_{ei}:	Mass where cycles and linear chains show equal peak intensities in the MALDI-TOF ms.
M/I:	Monomer/Initiator ratio.
M_n:	Number average molecular weight.
m.s:	Mass spectra.
M_w:	The Weight Average Molecular Weight.
M/Z:	Mass to chare ratio.
N_t-N_o:	The number of functional groups.
P:	Conversion.
ρ_w:	Weight fraction of rings.
S:	Stoichometric ratio of functional groups.
S:	The flight distance.
t:	The time of flight.
U:	The accelerating voltage.
V_p :	The rate of propagation.
V_c:	The rate of cyclization.
X:	a constant > 1.

Contents

Summary

This work can be subdivided into two parts. In the first part of this work various aromatic polyethers, and aliphatic polyester derived from pivalolacton were synthesized to study the role of cyclization in polycondensations. The second part represents the synthesis of biodegradable networks either from poly(ε-caprolactone) alone or in combination with different polyols with the purpose to separate cycles from linear chains via selective entrapment.

* First part

a) Poly(ether ketone)

Two classes of poly(ether ketone)s were prepared from bisphenol-A through the polycondensation of bisphenol-A with different difluorobenzophenones, namely with 4,4'-difluorobenzophenone or with 2,6-difluorobenzophenone and 4'-tert.butyl-2,6-difluorobenzo-phenone. Two different synthetic methods were compared. Firstly, polycondensations of the free bisphenol-A in DMSO or sulfolane with azeotropic distillation of water. Secondly, polycondensations of bistrimethylsilyl bisphenol-A in N-methylpyrrolidone. The second approach gave higher yields and higher molecular weights (M_ns up to 85 000 Da and M_ws up to 190 000 Da). The MALDI-TOF mass spectra revealed that the fraction of cyclic oligomers and polymers systematically increased with higher molecular weights. A third class of PEKs was synthesized from the reaction between silylated 4-tert.butylcatechol and 4,4'-difluorobenzophenone. This class of PEKs confirmed the trends observed for silylated bisphenol-A. Under optimum conditions cyclic poly(ether ketone)s were detectable in the MALDI-TOF mass spectra up to molecular weights of 18 000 Da.

b) Poly(benzonitrile ether)

Bisphenol-A was polycondensed with 2,6-dichloro-, 2,6-difluoro-, 2,4-difluoro- and 3,5-difluorobenzonitrile in sulfolane. With 2,6- and 2,4-difluorobenzonitrile quantitative conversions were achieved, and the MALDI-TOF mass spectra revealed a nearly quantitative formation of cyclic oligoethers and polyethers. Furthermore, O,O'-Bistrimethylsilyl bisphenol-A was polycondensed with the afore mentioned dihalobenzonitriles in dry NMP (promoted by potassium carbonate). Both temperature and time were optimized. Only with 2,6-difluorobenzonitrile nearly quantitative conversions were achieved with the consequence of high molecular weights and a high content of cycles. The SEC elution curves exhibited a tendency towards a bimodal character, when larger fractions of cycles were present. Calibration with polystyrene standards

indicated number average molecular weights (M_ns) up to 10^5 Da and weight averages (M_ws) up to 2.3 x 10^5 Da.

c) Poly(pyridine ether)

The bis-trimethylsilyl derivatives of six different diphenols were polycondensed with 2,6-difluoropyridine in N-methylpyrrolidone in the presence of K_2CO_3. The reaction conditions were optimized for almost quantitative conversions. The feed ratio was systematically varied to optimize the molecular weight. It was found that a 2 mol% excess of 2,6-difluoropyridine is needed to obtain maximum molecular weights. In the MALDI-TOF mass spectra of the optimized polyethers only cycles were found (detectable up to 5 000 Da). Obviously, the relatively low molecular weights obtained under optimized conditions resulted from limitation of the chain growth by cyclization indicating a high cyclization tendency for poly(pyridine ether)s. The SEC measurements not only proved low molecular weights, but also demonstrated the existence of bimodal mass distributions and high polydispersities. Protonation of the poly(pyridine ether)s required strong acids such as methane or trifluoromethane sulfonic acid. The solubilities of the neutral and protonated polyether derived from bisphenol-A were studied in various solvents. The MALDI-TOF mass spectra proved that protonation at 20-25°C does not cause cleavage of ether bonds.

d) Aliphatic polyester

In zwitterionic polymerization of pivalolactone performed in N-methylpyrrolidone using pyridine, 4-methylpyridine (4-MP) and 4-(N,N-dimethylamino)pyridine (DMAP) as initiators, linear chains having one pyridinium ion and one $CO_2^{\ominus}$ ion as end groups were found to be the main reaction products. The absence of cyclic oligolactones even at temperatures up to 140°C proves that the chain growth of the zwitterionic chains exclusively proceeds by anionic ring-opening polymerization and not by poly/condensation steps. When dichloromethane was used as reaction medium, part of the polylactone chains had $–CO_2CH_2Cl$ end groups due to side reactions with the solvent. With diazabicyclooctane as initiator a clean zwitterionic polymerization was also found in NMP. With triethylamine or 2-ethyloxazolidine as initiators, the zwitterionic/anionic ring-opening polymerization was again the predominant process, but significant side reactions also took place. In the case of 2-ethyloxazolidine, these side reactions included the formation of cyclic oligolactones. In the case of β-propiolactone complete elimination of the pyridinium ions with formation of acrylate chain ends was observed.

* Second part:

Telechelic poly(ε-caprolactone) having two OH-end groups were prepared by ring-opening polymerization of ε-caprolactone (ε-CL) initiated with tetraethylenglycol or 1,4-butanediol and tin(II) 2-ethylhexanoate ($SnOct_2$). By variation of the monomer to coinitiator ratio, poly(ε-caprolactone)s with number average molecular weights (Mns) around 2000, 3000, 4000, and 5000 were prepared. Different classes of networks were synthesized from these polymers using trimesoylchloride and pyridine. The first class was prepared only from telechelic poly(ε-CL) with trimesoylchloride. Two different classes were synthesized from Poly(ε-CL) with PEG or PDMS. Poly(ε-CL) of 2000 was mixed with poly(ethylene glycol), PEG-2000, in various ratios and crosslinked with trimesoylchloride and pyridine. Analogously, a poly(ε-CL) of 4000 was mixed in solution with PEG-4600 and crosslinked. Furthermore, a poly(ε-CL) of 2000 Da was mixed in solution with an OH-functional polysiloxane of similar chain length and this mixture was crosslinked. The isolated gels were characterized by ^{1}H-NMR spectroscopy, DSC measurements X-ray, and swelling measurements in three different solvents. Biodegradable networks were used successfully to trap cyclic aromatic polyethers, whereby the possibility to use the extraction or degradation methods for separation of trapped cyclic polymers from linear one were studied.

1 Introduction

1.1 The Role of Cyclization

Macrocycles have gained a great importance in polymer science not only because they are found in the natural products such as circular DNA molecules, cyclic peptides, and cyclic polysaccharides[1], but they can also be used for the synthesis of high molecular weight polymers using ring-opening polymerization [1,2], as well as in polymer recycling based on chain-ring equilibria [3]. Cyclization reactions represent an inherent, unavoidable component of step-growth polymerization and may be dominant factor for limitation of chain growth [4]. Therefore, many researchers and theories tried to study and elucidate the role of cyclizations, the factors affecting the degree of cyclization and the relation between the conversion and the extent of cyclization. A comprehensive review of these studies as well as a brief representation of the classical theory of polycondensation especially its view related to the role of cyclization is summarized as follows.

1.1.1 The classical theory of polycondensation

The classical theory based on the work of Carothers [5] and Flory [6] describes the polycondensation of difunctional linear monomers as step-growth process, which means the linear monomers react with each other yielding linear oligomers and finally linear polymers. Furthermore, one of the most important hypotheses of this theory is the reactivity of the end groups which is assumed to be independent of the chain length. As a consequence, all reactive species, including monomers and linear oligomers have the chance to react with each other at any time and any concentration. The degree of polymerization ($\overline{DP}$) as given by Carothers's equation (1) was considered as a function of conversion (P), whereby the ($\overline{DP}$) increases with the conversion (P) of functional group.

$$\overline{\mathrm{DP}} = \frac{1}{1-\mathrm{P}} \quad \text{with } \mathrm{P} = \frac{N_o - N_t}{N_o} \tag{1}$$

$\overline{\mathrm{DP}}$ = ***average degree of polymerization***

P = conversion of functional groups

N_o , N_t = ***number of functional groups***

Accordingly, the frequency and mass distribution of a polymer mixture are represented mathematically in Equations 2 and 3. Moreover, the corresponding mass distribution is obtained by multiplication of the frequencies by the molar mass of chains with individual ($\overline{DP}$).

$$f_f = p^{\overline{DP}-1}(1-p) \tag{2}$$

$$W_f = m_{\overline{DP}}\, p^{\overline{DP}-1}(1-p) \tag{3}$$

Where f_f and W_f are the frequency and the mass fraction, respectively, of the polycondensation components having identical degrees of polymerization ($\overline{DP}$), and m_{DP} is the mass of a polymer chain with individual ($\overline{DP}$). These two equations are presented graphically in Figures 1 and 2.

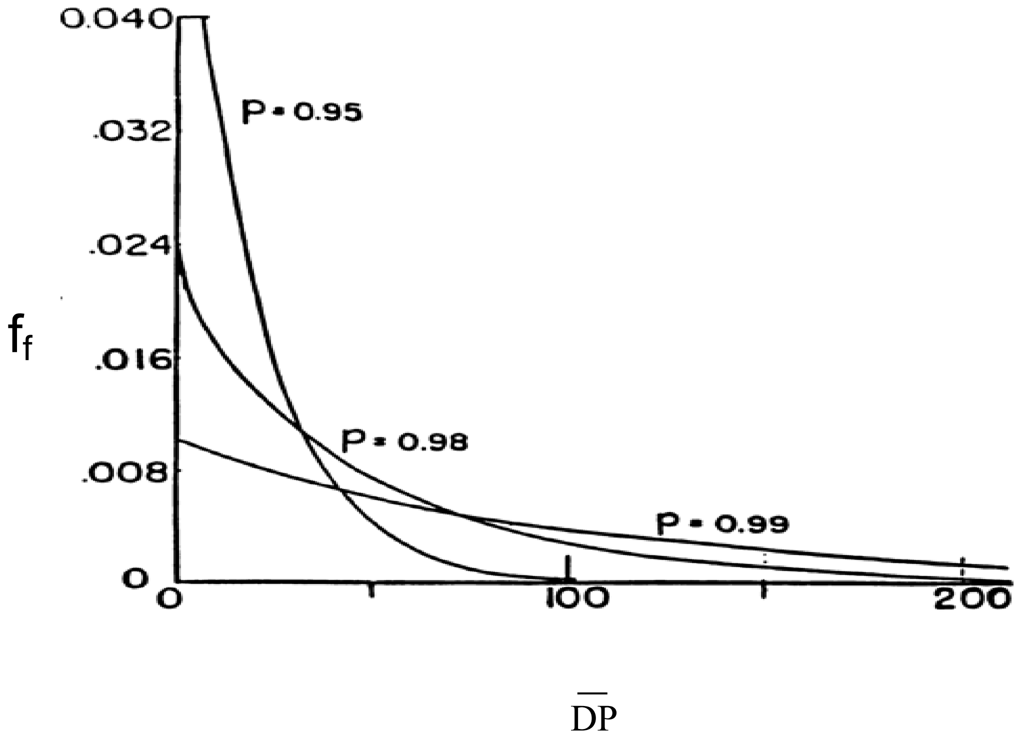


Fig 1. Frequency distribution in the classical theory of step-growth polymerization calculated for three different conversions.

This theory is considered as a greatest worth in polymer science despite it suffers form the following shortcomings [4,7]. Firstly, the relation between the average degree of polymerization and the conversion is given for ideal reaction conditions. These conditions are the absence of side reactions destroying functional group, ideal stoichiometry, and 100% conversion. Secondly, it doesn't differentiate between thermodynamically controlled and kinetically controlled step-growth polymerization. Thirdly, it doesn't consider the significant contribution of cyclization reactions. Furthermore, the classical theory assumes that highest molecular weights could be only obtained with exactly 1:1 stoichiometry (ideal stoichiometry as the theory mean) of the functional groups. In the case of ``a-a`` + ``b-b`` monomers it was found sometimes that an excess amount of one monomer may give higher molecular weights than in the ideal case.

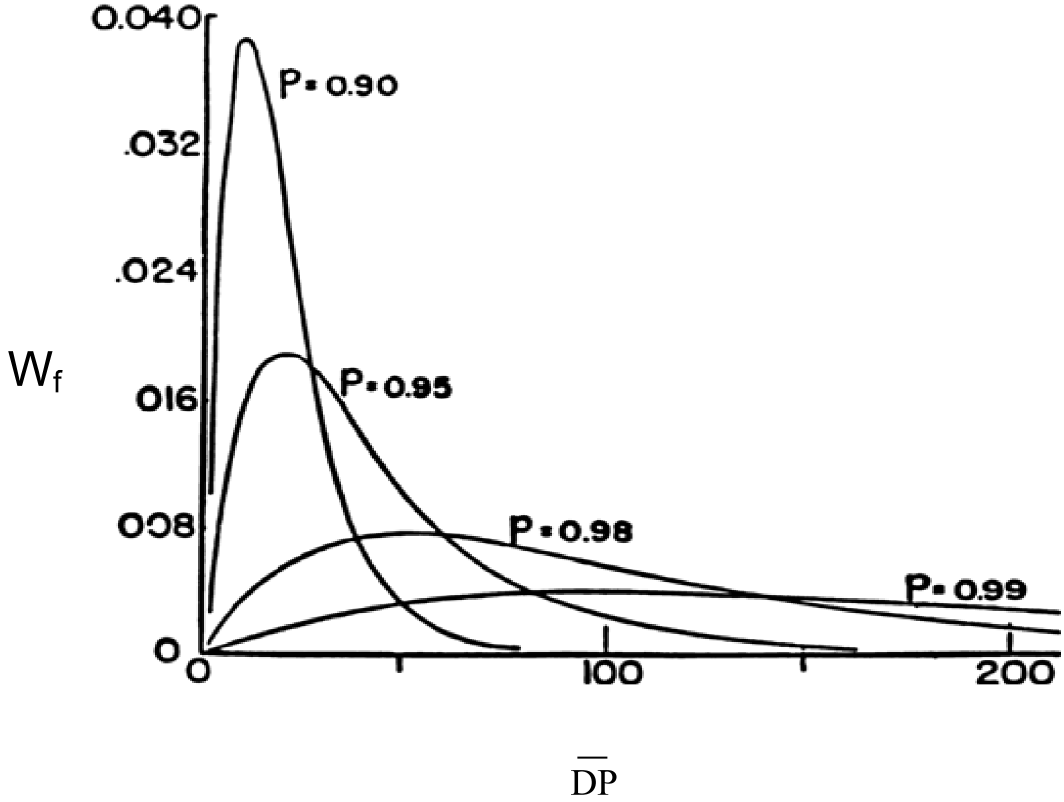


Fig 2. Mass distribution in the classical theory of step-growth polymerization calculated for three different conversions.

According to Kihara et al [8]. the degree of polymerization is enhanced by stoichometric imbalance, if the first condensation of a difunctional monomer enhances the second condensation of the remaining functional groups. This stoichometric imbalance-enhanced polymerization is shown mathematically in Eq.4, and may be accounted for three reasons [7]:

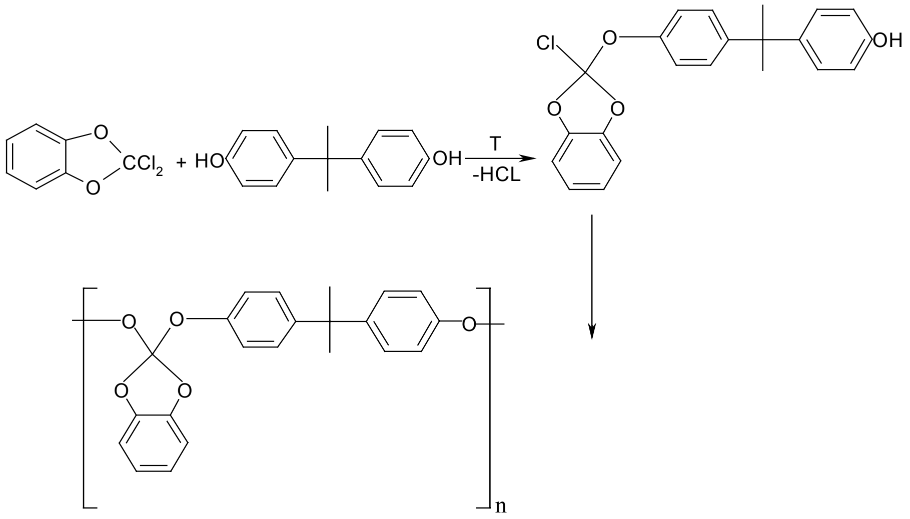
$$\overline{DP} = \frac{(1+S)}{(1+S-2P)} \qquad \textbf{(4)}$$

$S\ (\geqq 1) =$ ***is the stoichometric ratio of functional groups***

a. Side reactions of at least one monomer which doesn’t disturb the step-growth polymerization, as in the case of the hydrolysis of phosgene in the interfacial syntheses of polycarbonates, which is compensated by an excess of phosgene.

b. Physical reasons including: distillation, sublimation, adsorption on solid surface, and complexation with other reaction components may be hindering one monomer to participate completely in the step-growth polymerization process.

c. Two-step propagation with a faster second step: in this case an intermediate is formed with functional groups which are more reactive than one of the starting monomers. Therefore, an excess of the least reactive monomer will be necessary to accelerate the process. A typical example for this phenomena is the polycondensation of 2, 2-dichloro-4, 5-benzodioxolane with diphenols (Scheme 1) [8].



Scheme 1

According to Carothers [9-11] and Flory [12] the polycondensation process goes through two reactions, including intramolecular reaction which is responsible for the formation of simple monomeric ring containing 5-7 atoms and the intermolecular reaction which may lead either to a polymeric ring or a polymeric chain. Moreover as they suggested the intramolecular reaction, which may lead to ring larger than 6 ring system, generally proceeds intremolecularly because the probability of intra- to intermolecular reaction decreases with the addition of one more atom to the chain. This more atom leads to more freedom of rotation, which on the basis of sachse-moher theory [12]: any restriction of freedom of rotation of the chain's atoms increases the chances of ring formation. Consequently the polymeric products would always be open-chains.

As in all fields of chemistry, the polycondensation main product, which could be isolated from the polymer process, is either kinetic control or thermodynamic control product. Unfortunately, the classical theory of polycondensation does not distinguish between kinetic and thermodynamic control of reactions resulting in cyclization. These types of controlled reactions will be discussed below in detail.

1.1.2 Further studies in cyclization

Several publications [13-19], reviews [22-23] and at least on text book [1] report cyclic species produced through the polymerization process. Around 1930 the Ruggli-Ziegler high dilution principle (RZDM) [24] was developed, which states that a possibility of cyclization in polymerization exists due to the ability of the difunctional molecules (monomers, oligomers) to choose between the cyclization and propagation. Despite that high dilution favors the cyclization because of it is intramolecular character, and it was used from hundreds of chemists for the synthesis of macrocycles it wasn't considered in the classical theory to elucidate and prove the existence of cyclization reactions in polymer process.

In 1950 Jacobson and Stockmayer [13,14] studied theoretically and experimentally the role of cyclization at equilibrium and came to the following conclusions: Firstly, the chain ends of the step-growth products are always in equilibrium with cyclic oligomers and open-chain polymers. Secondly, the amount of rings is an increasing function of system volume. Therefore, only small weight fraction of cycles is present in polycondensations conducted in bulk. This small fraction is in agreement with Flory's calculations[6] which suggested that the weight fraction of cycles in equilibrium systems is about 2.5% wt of products at 100% conversion. Thirdly, the J.-S. theory suggested a critical concentration below which the condensing system can be converted entirely into rings, but above which it is not possible [13], so that the average degree of polymerization of these rings never exceeds the number of 4. Fourthly, in the case of 'a-a' and 'b-b' polymer systems larger extent of reaction, or more even balance of monomers increases the yield of rings. The results of Jacobson and Stockmayer studies are presented graphically in Figure 3.

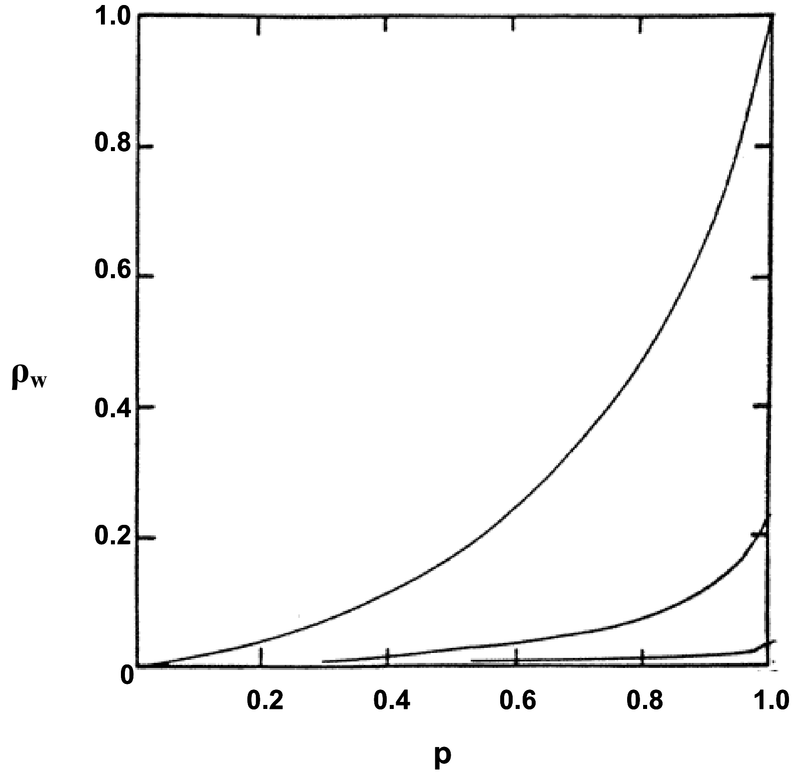


Fig 3. Weight fraction of rings, ρ_w, as a function of the extent of the reaction, p, for 'a-a' and 'b-b' polymer systems at three dilution. Upper curve, $B'/c = 0.5$; middle curve, $B'/c = 0.05$; lower curve, $B'/c = 0.005$.

In 1970 (and later) Stepto and coworkers [15,16] as well as Gordon and Temple [17,18] studied mathematically the kinetically controlled step-growth polymerization. These published treatments concerned low to moderate concentration polycondensations, but not polycondensations in bulk. Their studies assume that under ideal conditions any kinetically-controlled polymerization should yield cyclic reaction products by reaching 100% conversion. This conclusion may be explained based on the following hypothesis: cyclization can compete with propagation at any time and concentration even at high one as shown schematically in Figure 4. With respect to this conclusion, there is a largely deviation from the classical theory of step-growth polymerization. These mathematical treatments take into the account the influence of the concentration, and represent a quantitative version of the RZDM.

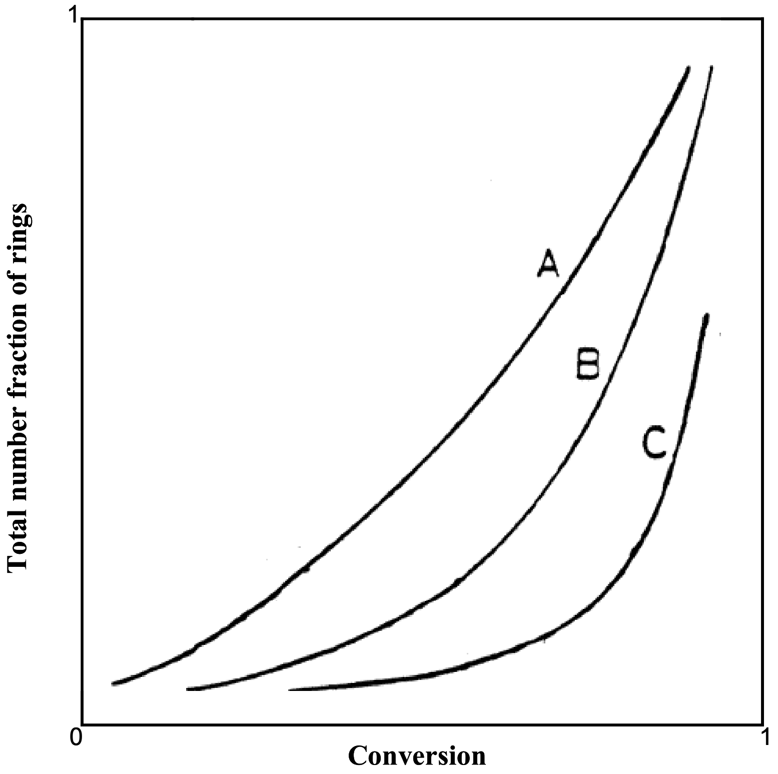


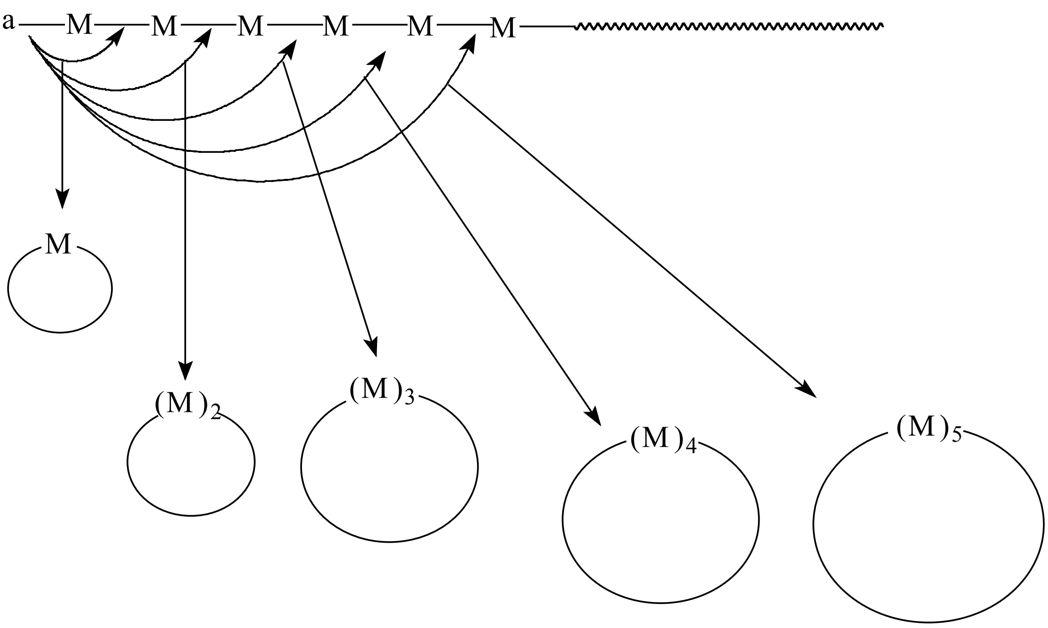
Fig 4. The mass fraction of cycles in kinetically controlled step-growth polymerization (with increasing concentration from A to C).

1.1.3 Kricheldorf's Theory of Polycondensation

Kricheldorf et al. studied intensively the role of cyclization plays in step-growth polymerization [25-31,36-38,40-45]. These studies were based on the differentiation between the role of cyclization played in kinetic or thermodynamic controlled polycondensations. Consequently, Kricheldorf constructed his own theories of step-growth polymerization, which may be considered as the most important modification of the classical theory. As discussed below, this theory simply divides the polycondensation according to the conditions determine the type of products (cycles, linear) into thermodynamic controlled polycondensations (TCPs) and kinetic controlled polycondensations (KCPs).

1.1.3.1 Theory of thermodynamic controlled Polycondensation

Thermodynamically controlled polycondensation (TCP) could be defined as a polycondensation containing equilibration processes, which are responsible for the formation of rings due to the reaction of the reactive end-group with the polymer chain resulting in the so-called `` Back-biting`` (Scheme 2). Moreover, the reaction mixtures represent the thermodynamic optimum at any stage of polycondensation[36]. TCP was studied earlier by Flory [6,12] and Jacobson-Stockmayer[13,14], and according to these studies the population of cyclic products are seemed to be smaller than 3% at 100 % conversion in bulk. Kricheldorf and coworkers [25-31] studied intensively the role of TCP in the formation of cyclic products, and according to the results obtained he constructed the theory of ideal TCPs. TCPs theory based on the following hypotheses [31]. Firstly, cyclizations involving both reactive chain ends of oligomers or polymers occur at any stage of the polymerization. Secondly, since "back-biting" does not prevent cyclization via both chain ends, all reaction products will be cycles at 100% conversion. According to this hypothesis the polycondensation mixture needs to be described as ring-ring equilibrium at high conversion (e.g. > 99.9 %). These hypotheses are in contradiction with the prediction of the C.-F. theory and to the J.-S. theory, which postulated the formation of one giant polymer chain as the main product at 100% conversion [6]. Thirdly, the thermodynamics of the ring-ring equilibrium limits the chain growth. The ring-ring equilibrium depends on the cyclization tendency of individual monomers/polymers, which is an inherent property of their structure. The ring-ring equilibrium is concentration and temperature dependent, because lower concentrations and higher temperatures favour the formation of smaller (strain-free) macrocycles at the expense of larger ones due to a gain in entropy [31]. Therefore, both concentration and temperature have an influence on the maximum molecular weight which can be achieved in an ideal TCP. In this case, the theory of ideal TCP is in agreement with C.-F. theory, which also postulated that formation of large rings is possible under special conditions including high dilution and heating under vacuum in the presence of catalyst [10,12].



Scheme 2

The theoretical treatment of TCP theory represented in Eq.5 based on the hypothesis that the ring-ring equilibrium is exclusively the main equilibration in the polymer process as shown in Eq.6, and the linear chains work as catalyst in this cyclization process.

$$\overline{DP} = \frac{1}{1-P\left(1-\frac{1}{\mathbf{X}}K_c\right)} \qquad \mathbf{(5)}$$

where $$K_c = \frac{\left[c(M)_{x+y}\right]}{\left[c(M)_x\right]\left[c(M)_y\right]}$$

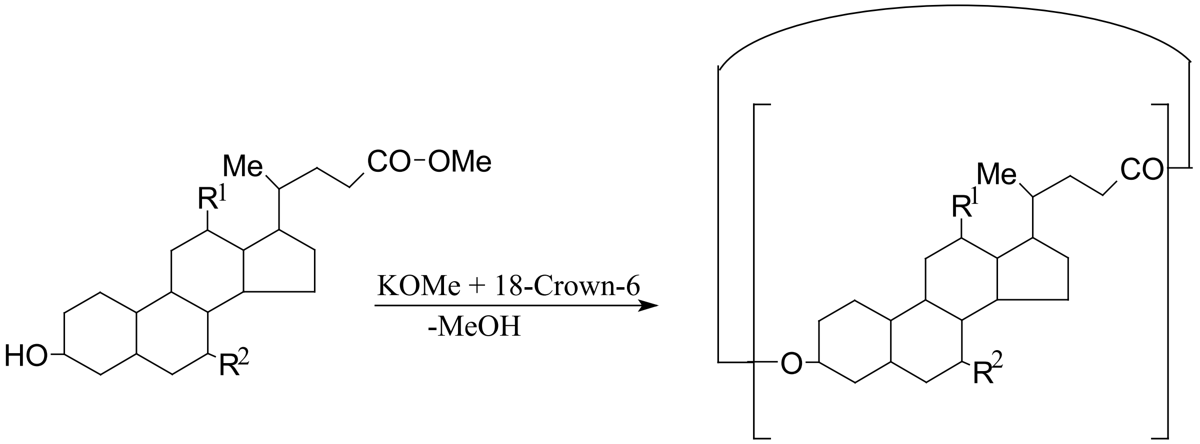
$$c(M)_x + c(M)_y \xrightleftharpoons{cat} c(M)_{x+y} \qquad \mathbf{(6)}$$

Where X is a constant > 1 used for the adjustment of Eq.5 for polycondensations with different concentrations.

Several kinds of cyclic oligomers and polymers were synthesized under the condition of thermodynamic control polymerization including:

a. Polyesters:

Despite the several studies on ring-chain equilibria [20,21,32-35] concerned on the frequency distribution of the cyclic oligoesters, only few examples of cyclic oligo- or polyesters were synthesized to study the relation between the role of cyclization and percent of conversion or the molecular weight distribution[32]. A typical example is cyclic oligoesters derived from methyl cholates **1a-c** as illustrated in Eq.7. According to this experiment Brady et al[32] fund a certain equilibration distribution of cyclic oligoesters (**2a-b**) but no high molecular weight polyesters.



1a-c

a: R^1= $OCH_2C_6H_4C_6H_5$,R^2= H

b: R^1= $OCH_2C_6H_5$,R^2= $OCH_2OCH_2CH_2OMe$

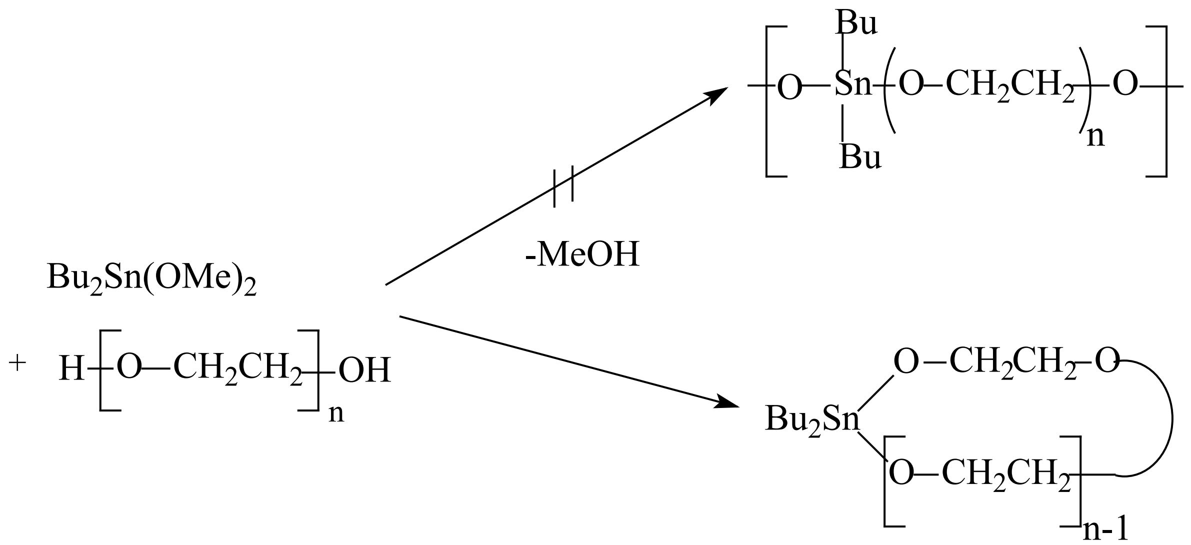
c: R^1= $OCH_2C_6H_4OMe$,R^2= $OCH_2C_6H_4OMe$

2a-c

(7)

b. Polyethers:

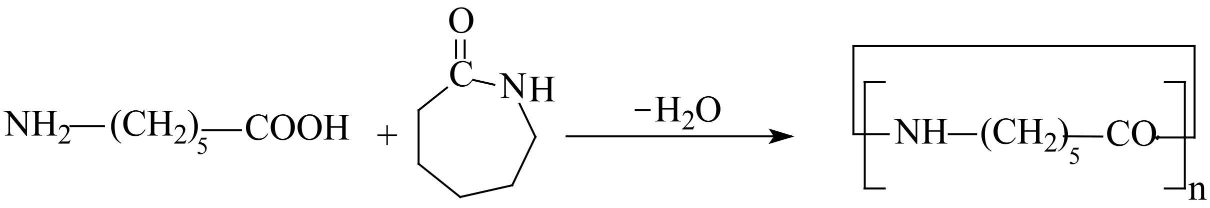
The quite most important group of cyclic polyethers is based on tin alkoxides (either Sn(II) or Sn(IV)) especially $Bu_2Sn(OMe)_2$. Regardless of the length of alkane diols, oligoethylene glycols or oligo(tetrahydrofuran)diols (up to 2000) used as reaction partners, only tin-containing macrocycles were obtained as demonstrated in Scheme 4 [25,26]. The formation of tin containing macrocycles could be discussed taking into account the stability of small cyclic tin compounds (eg. cyclic dimers or trimers) due to the presences of intramolecular donor-acceptor interaction between O atoms and Bu_2Sn. Furthermore it may be concluded from these results that polymers containing Sn-O bonds are thermodynamically unstable above room temperature mainly due to entropy reasons.



Scheme 4

c. Polyamides:

The formation of cyclic polyamides was found to be a byproduct of polyamidation resulting via transamidation reactions taking place during polycondensation in bulk at 260 °C [27]. Based on the experimental analyses used in these studies, cycles with degree of polymerization greater than 10 were not possible to be identified. However, Kricheldorf et al. reinvestigated the polycondensation used in the previous studies, which is based on polyamid-6. Synthesis of polyamid-6 was performed by thermal (co)polymerization of ε-caprolactam and ε-aminocaproic acid as shown in Eq.8. Although it was difficult to obtain good MALDI-TOF spectra of polyamid-6, it was found that the frequency as well as the degree of polymerization of cyclic polyamide-6 increases with conversion. Regardless if a neat polycondensation or mainly ring-opening polymerization is performed, the final reaction products were cycles.

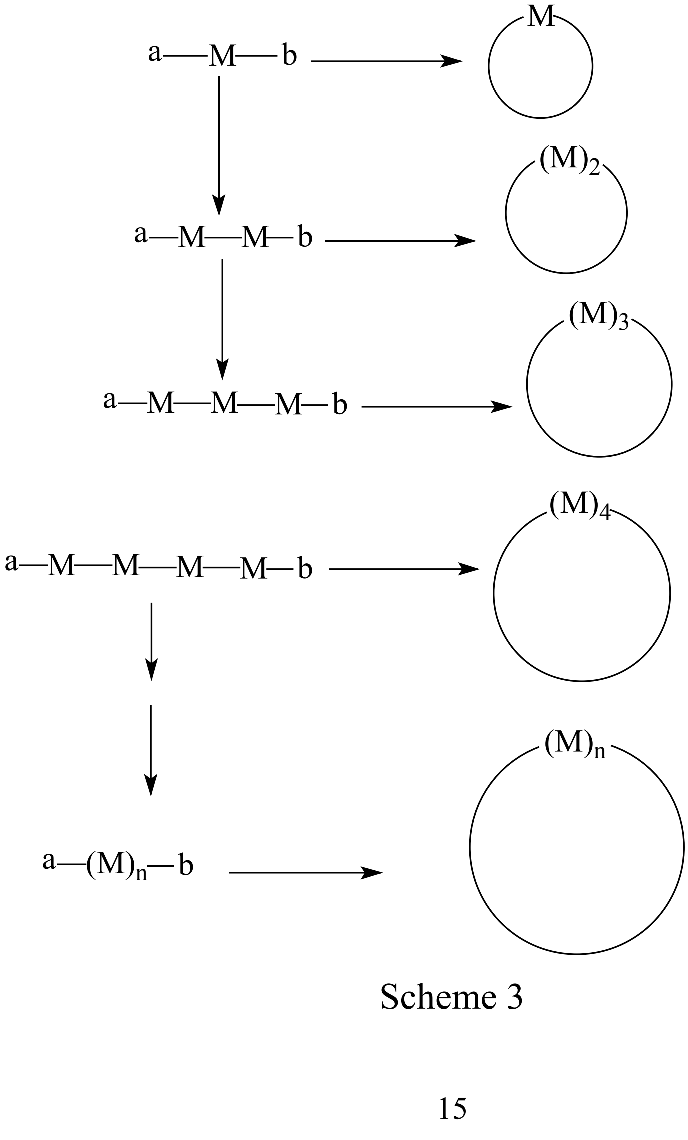


(8)

1.1.3.2 Theory of kinetic controlled Polycondensation

Kinetic control means that equilibration reactions are absent and the reaction mixtures do not represent the thermodynamic optimum of the system studied [36]. In analogy to theory of TCP, the theory of KCP is based on hypotheses, which were obtained from studies dealing with the composition of reaction mixtures in polycondensations under kinetic control.

Firstly, on the basis of MALDI-TOF mass spectra allowing the detection of individual polymer molecules up to masses of around 50 000 Da, it was found that cyclization competes with propagation at any stage of the polycondensation and at any concentration as showen in scheme 3. Consequently the reaction products must be 100% cycles even if the polycondensation was conducted in bulk, because the polycondensation reactions are self-diluting reactions with respect to the functional group (reactive linear species). According to this theory, self-diluting is the most important reason responsible for the formation of cycles, whereby a high probability of cyclization is possible even for high molecular weight chains, in addition to the limitation of the chain growth.



Scheme 3

Secondly, any optimization of the reaction conditions favouring a higher molecular weight automatically enhanced the formation of cycles.

Thirdly, these results agree with calculations by Stepto et al.[15,16], and Gordon et al.[17,18], who postulated that an ideal KCP conducted in solution yields 100% cycles of any size at 100% conversion. Kricheldorf modified Carothers's equation taking into his account the role of propagation and cyclization rates play on degree of polymerization as well as the adaptation of polycondensation at different concentrations as represented by Eq.9.

$$\overline{DP} = \frac{1}{1 - P\left(1 - \frac{1}{X^{\alpha}}\right)} \qquad \mathbf{(9)}$$

With $\alpha = V_p/V_c$ where V_p and V_c are the rate of propagation and cyclization, X is a constant > 1.0, allowing the adjustment of the equation at different concentrations. Figure 5 is a graphical illustration of the different possibilities, which may take place in the polycondensation as considered by Equation 9. The different lines in Fig. 5 represent specific situations, in which either both of V_p and V_c exist in the polymer process or one of them. Curves B to E illustrate the function of both of them as assumed in this theory for the achievement of ideal KCP. Curves A and F illustrate the extreme cases. Where curve A shows the absence of cyclization (V_c = o), moreover it presents the polycondensation assumed by the classical theory for the formation of one giant chain. According to this theory, this extreme case may exist only, if the polymer chains are extremely stiff, have good solubility in inert solvent, and in the absence of side reactions [36]. Curve F represents the absence of propagation (V_p= 0), which corresponds to the rapid cyclization without formation of any high molecular weight cyclic polymers. This case is more realistic than the first one in organic chemistry, and it may be one of the reasons, why Flory and Carothers didn't consider the cyclization in polycondensation.

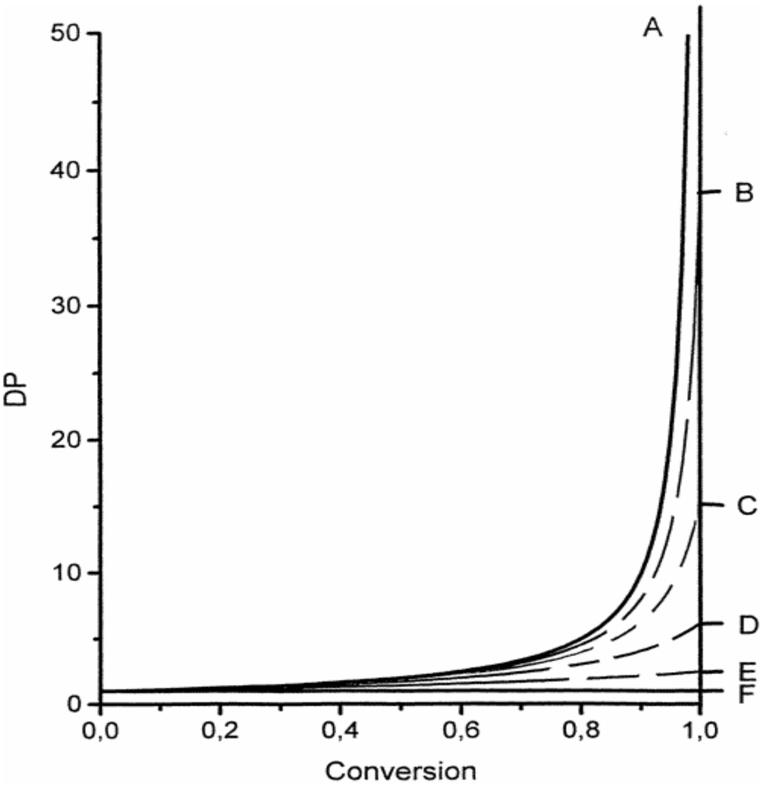
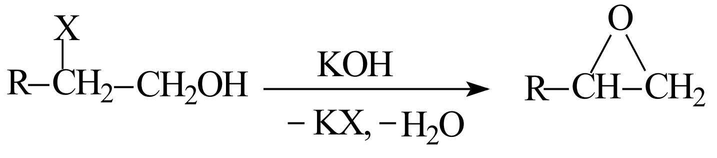


Fig 5. Chain growth / conversion as calculated from equation (9) with X = 1.2 and various V_p / V_c : A) ∞, B) 20, C) 15, D) 5, E) 0.1, and F) 0 .

A typical example of this case is the epoxide formation from the base catalyzed dehydrohalogenation of β–chloro- or bromoalcoholes (Eq.10), where the cyclization takes place under kinetic control. Because epoxides are thermodynamically unstable, cyclization is kinetically favoured over the formation of liner oligomers or polymers.



$$R{-}\overset{X}{\overset{|}{C}}H_2{-}CH_2OH \xrightarrow[-\,KX,\,-\,H_2O]{KOH} R{-}\overset{O}{\overset{/\,\backslash}{CH{-}CH_2}} \qquad \textbf{(10)}$$

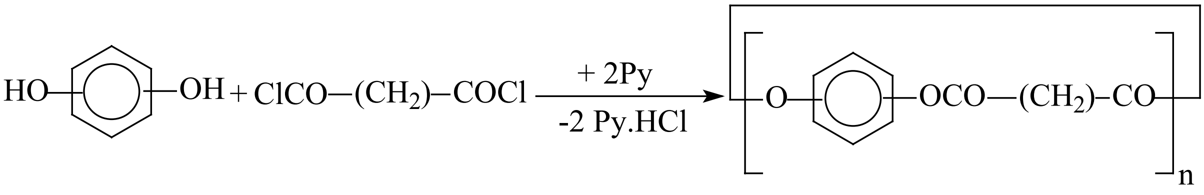
$X = Cl, Br$

To understand obviously the importance of the V_p/V_c ratio as decisive factor for the extent of chain growth or cyclization, it is necessary to take into account the factors affect this ratio. As the theory suggested these factors are [4]: the flexibility of the oligomer and polymer backbones, the stereochemistry, and the building of blocks. Each of these factors play a very important role in determination of the extent of V_p/V_c ratio, and the effect of them could be elucidated as a function of number and kind of conformations. Obviously, increasing the number of conformations to chain length decreases the rate of cyclization (V_p/V_c ratio increases). In example, when comparing aromatic with aliphatic polymers, the number of conformations is higher in later case due to the flexibility of alkyl chain. The rate of cyclization in aliphatic polyethers is found to be greater than in polyesters or polyalkanes. This observation may be explained by the different chain geometry: polyethers are more inclined than polyesters and they favour gauche conformation due to repulsive electron interactions of O-electrons and σ-electrons in β-position, in contrast to alkanes in which trans-conformation are energetically most favourable. Both factors lead to a bended polyethers chain, which favour cyclization [36]. In the case of aromatic chains, the position of the functional groups determines the probability of cyclization. Simply, aromatic polymers containing functional groups in *meta*- or *ortho*-position have higher opportunity for cyclization than in the case of polymers containing *para*-functional groups.

The following paragraph introduces types of different cyclic polymers produced by polymerization under kinetic controll.

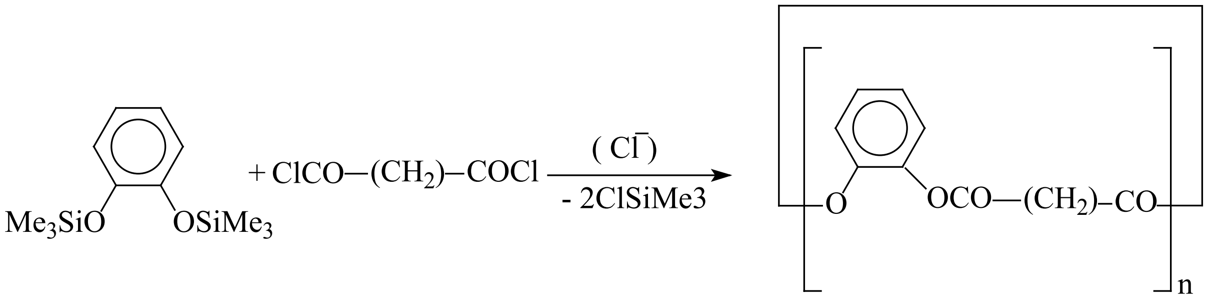
a. Polyesters:

It is well known that polyesterifications at high temperature (e.g. ≤ 250 °C) involve equilibration reactions, so that the definition of KCP can not be considered in this case. Kricheldorf et al. reported the formation of polyesters via KCP [37,38]. They prepared polyesters using two methods, the so called ``pyridine method´´ (working ≤ 20 °C) and the silyl method (working ≤ 200 °C) [37]. In case of the pyridine method (Eq.11) the condition was controlled to prevent side reactions, otherwise could have taken place. With respect to this method, the fraction of cycles and their molar masses increased when the reaction conditions favoured higher molar mass of the entire sample.



(11)

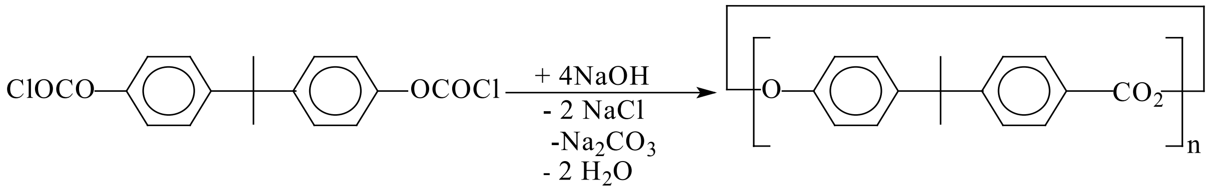
For the silyl method, bis(trimethylsilyl) derivatives of aromatic diols was reacted with diacid chlorides in bulk as shown in Eq.12. the chloride ion needed as catalyst dose not cause transestrification at temperature ≤ 250 °C. MALDI-TOF spectra of reactions products confirm that up to limit of these measurements at 6000 Da, cyclic polyesters are the major products [38].



(12)

b. Polycarbonates:

In 1980 polycarbonates containing high fraction of cycles were reported for the first time. These cyclic polycarbonates were prepared by Horbach et al. [39,40] using interfacial hydrolytic polycondensation of bisphenol-A bischloroformate (Eq.13). However, the experimental identification of cycle's formation was exclusively based on the end group analyses using conventional methods. Kricheldorf et al.[41] studied the same polycondensation of bisphenol-A bischloroformate done by Horbach with intensive reinvestigation of all important parameters, such as temperature, reaction time, NaOH feed ratio, and catalyst concentration, to optimize the condition leading to high molecular weight. This reinvestigation confirmed the result of Horbach and showed the formation of high molecular weight cycles up to 55 000 Da using MALDI-TOF. The presence of high molecular weight cycles supported the theory of KCPs, since it postulates that cyclization competes with propagation at any chain length.



(13)

c. Polyamides:

The role cyclization played in the syntheses of polyamides was studied by Kricheldorf et al. using different synthetic methods [42-45]. According to these studies, the ratio of cyclic oligo- or polyamides produced in these polycondensations was more difficult to be determined than for other polymers. Some examples of these difficulties are:

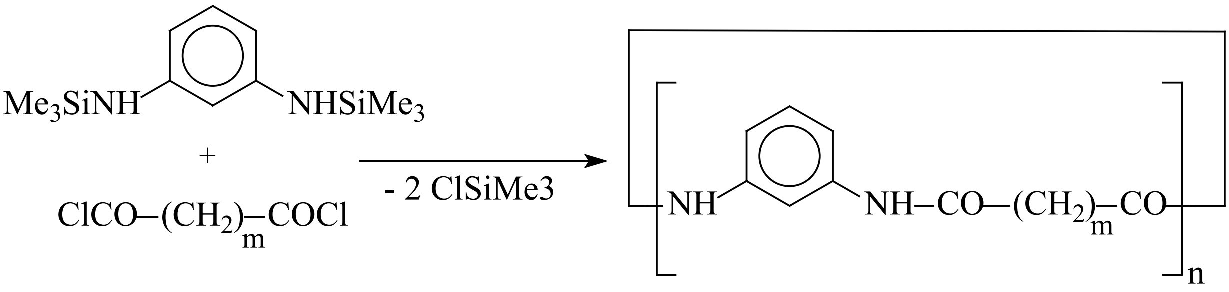
a. It was difficult to measure the MALD-TOF of the some polyamides obey the definition of KCPs. as in the case of poly (p-phenyleneterephthalamide) [42].

b. The synthesis of cyclic polyamides under KC conditions using melt process at temperatures higher than 220 °C was impossible because the possibility of equilibration.

c. The presence of side reactions such as ß-elimination of HCl.

Despite these difficulties the studies led to two important conclusions.

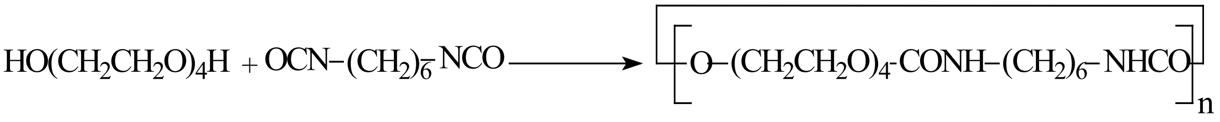
Firstly, no cycles were found in the synthesis of rigid-rod-type polyamides. This means, the synthesis of *para*-functional polymers at low temperature obeys largely the classical theory of polycondensation. Secondly, cyclic oligo and polyamides could be synthesized at low temperature via KCPs, as shown in Eq.14.



(14)

d. Polyurethanes:

The first study of the role of cyclization played in polyurethane synthesis was reported by Stepto et al.[18]. According to the degree of cyclization determined by using the comparison of end group analysis and the absolute molecular weight, Stepto concluded that large amounts of cycles were formed. Kricheldorf et al.[4] reinvestigated the polyaddition of tetraethylene glycol (TEG) and 1,6-diisocyanatohexane by variation of the mol ratio of both monomers. The reaction was preformed in bulk at 60 °C using dibutyltin diacetate (Eq.15). The results based on MALDI-TOF measurements proved the presence of cycles in all samples. Furthermore, it was found that the ratio of cycles increased with the feed ratio of diisocyanate. However, the formation of allophonate groups was also observed.



$$HO(CH_2CH_2O)_4H + OCN-(CH_2)_6-NCO \longrightarrow \left[O-(CH_2CH_2O)_4-CONH-(CH_2)_6-NHCO \right]_n$$

(15)

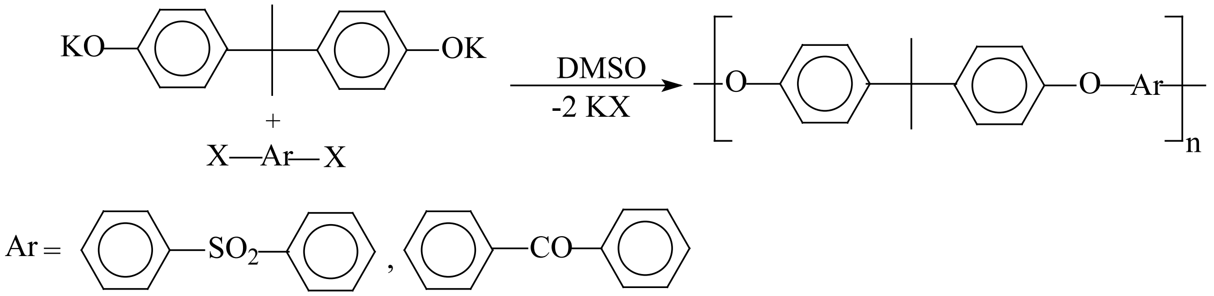
1.2 Aromatic polyethers

Aromatic polyethers are used in industry as, thermostable engineering plastics, resins of high-performance composites, high temperature adhesives, and basis materials for the production of membranes [46]. The industrial importance of aromatic polyethers is the results of their specific properties such as high chemical stability against hydrolysis or oxidation at high temperatures (up to 250 °C), thermostability, and high heat distortion temperatures.

A wide variety of aromatic polyethers has been developed for both, industrial and research applications including: polyethersulfones, polyetherketones, polyetherpyridines, polyethernitriles, polyetherimides, and polyphenylene ethers. Different strategies were successfully used in syntheses of aromatic polyethers depending on the kind of aromatic polyethers. As examples: Polysulfonylation may be used for synthesis of polyethersulfones, and Friedel-Crafts polyacylation for the synthesis of polyetherketones [47,48]. Nucleophilic substitution polycondensation of activated nitro or haloaromatices is the most widely used synthetic method for syntheses of all types of aromatic polyethers. Thereby, the activation of nitro or halo groups toward nucleophilic substitution need activating groups. Well-known activating groups are carbonyl, sulfone, cyano, ester, and aldehyde groups [49]. A brief description of the synthetic methods based on nucleophilic substitution polymerization is represented below.

1.2.1 Condensation of potassium salts of diphenols in an inert aprotic solvent

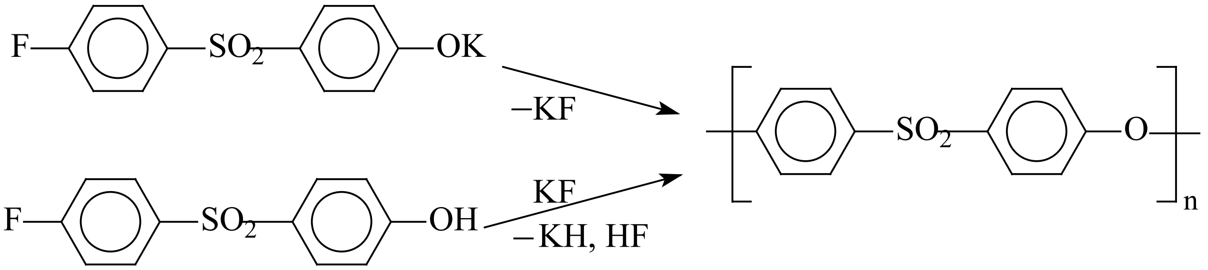
The oldest and most successful synthetic method used extensively in synthesis of aromatic polyethers is based on the condensation of potassium salts of diphenols with dichloro or difluorodiphenyl derivatives in an inert solvent [49,50]. The variation of the electrophilic reaction partner using different activating groups such as SO_2 or CO allowed the preparation of different polyethers. A typical example is shown in Eq.16. Potassium salt of diphenols could be prepared either prior to the polycondensation using a dry suspension (or solution), or in situ using a combination of free diphenols with K_2CO_3 in polar aprotic solvent. High molecular weights could be achieved by optimization of the solvent and temperature.



(16)

1.2.2 Condensation of monomers with two different groups

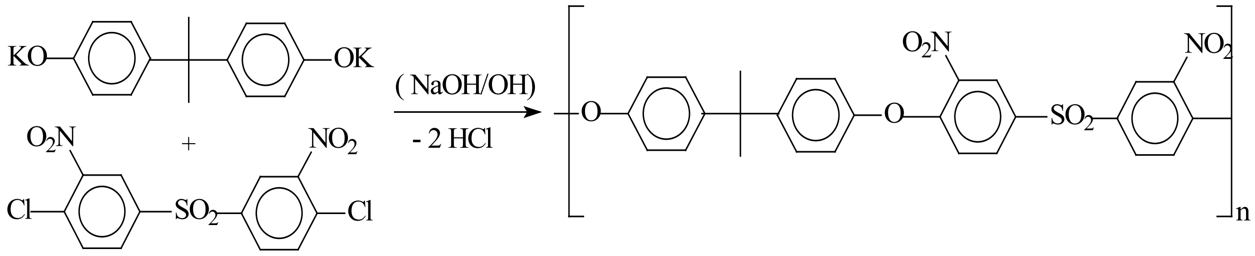
This strategy used the same procedures as strategy one (condensation of potassium salts of diphenols), but in this case only one type of monomer was needed to synthesize aromatic polyethers [50-52] as shown for example in Eq.17.



(17)

1.2.3 Interfacial condensation

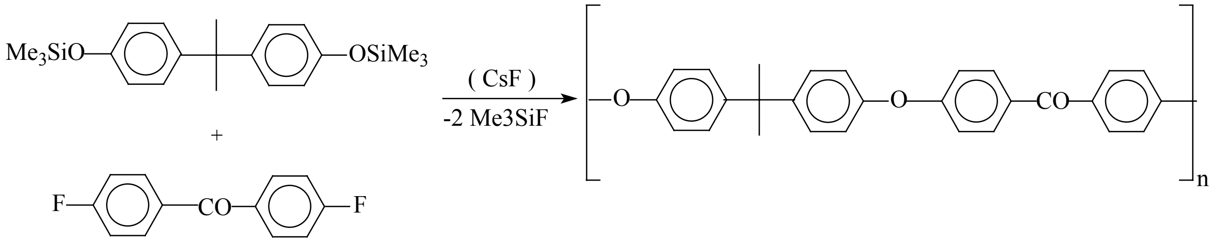
Phase transfer catalysts in dichloromethane or nitrobenzene could be used for the synthesis of aromatic polyethers [49,50]. Interfacial condensation may be used for reactive dihalodiphenyl compounds, when nitro groups are introduced in these compounds (Eq.18), because, nitro groups enhance the reactivity of the C-Cl groups.



(18)

1.2.4 Silyl method

Instead of free diphenols or their potassium salts, silylated bisphenol may be used in synthesis of aromatic polyethers [53-55] (Eq.19). This silyl method may be conducted either in melt or in solution. In both cases difluorodiphenyl compounds are required because dichloroaromatics are not reactive enough [56]. Furthermore, CsF was used as catalyst in melt, while K_2CO_3 was applied in solution.



(19)

The silyl method has the advantage to avoid the formation (or presence) of water, and then, avoids the hydrolysis of C-F groups.

1.3 Biodegradable and Biocompatible Networks

Biocompatible networks may be classified depending on their behavior in water into hydrogel and amphiphilic networks. Hydrogels are polymer networks which absorb and retain water without dissolving [57]. In the last 35 years, the ability of hydrogels for medical applications has been widely investigated [58,59]. For instance, poly(2-hydroxyethyl methacrylate) hydrogels are commercially used as lens materials, and they have potential for design of artificial implants [60], drug delivery system [61], and carriers for immobilization of bioactive species, such as enzymes, cells, and antibiotics [62]. However, hydrogels are not utilizable in all the medical applications, because the mechanical properties of hydrogels do not fit the requirements of structural applications, and they are not suitable for the loading and release of lipophilic drugs [63,64]. Amphiphilic networks are a combination of chemically bonded hydrophilic and hydrophobic chains, able to swell in both water and hydrocarbons [65]. As a rule, these networks results from the cross-linking of hydrophilic main chains, by hydrophobic oligomers end-capped with a polymerizable group at both ends. The free-radical polymerization of hydrophobic comonomers with dimacromonomers results in the expected amphiphilic networks [65]. For example, Jerome et al. have reported the synthesis of amphiphilic networks by free-radical polymerization of a methyacrylate-capped polycaprolactone or polylactide with poly(2-ethoxyethyl methacrylate) [66].

The modification of biodegradable polymers by incorporation of regular network structure is quite interesting in synthesis of new types of biodegradable materials, because it is expected to give better physical and chemical properties, such as resistance to heat distortion and chemicals [67].

Biodegradable networks based on poly(ε-caprolactone) will be explained mainly in this paragraph, because poly(ε-caprolactone) is the main component in all networks prepared in this work.

One of the most important properties of crosslinked polyesters for the medical application is the average pore size. The control of pore size is possible by variation of the segment lengths using a simple synthetic procedure. Two synthetic strategies were used to achieve this goal [68].

a. Two or more steps procedure:

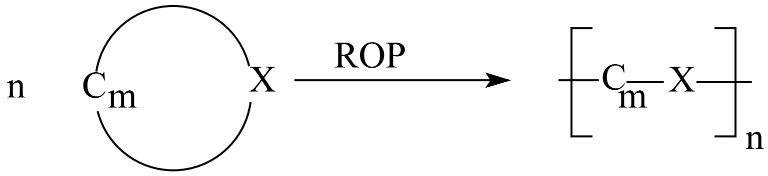
This procedure involves preparation of linear chain segments and cross-linking in separate steps [69-88]. The first step comprises the synthesis of macromonomers characterized by hydroxyl end groups. These macromonomers are either used directly for the synthesis of networks using trifunctional acid chlorides or for the preparation of further macromonomers terminated with double bonds. Acrylic, methacrylic, maleic and itaconic derivatives have been used to prepare such telechelic polyesters. Subsequently, they have been cured by thermal, redox- or photoinitiation to crosslinked polyesters [66,67,69-75]. These unsaturated prepolymers have been prepared by functionalizing hydroxyl terminated oligomers or polymers with corresponding acid chlorides [76-81]. Mostly, acrylic and methacrylic acids were used for the synthesis of bioresorbable networks, due to the good reactivity of their double bonds. For almost all unsaturated systems, the hydrolysis of ester linkages leads to free acids and free alcohols which are easily absorbed.

b. One-pot procedures:

Named also *in situ* procedure, based on the ring-expansion polymerization (REP) of D,L-lactide or lactones initiated either by cyclic tin alkoxides or by a tetrafunctional Sn-containing initiator [68,89,90]. This REP is combined with in situ cross-linking by means of di- or tricarboxylic acid chloride. Also Spirocyclic tin initiators have been utilized for synthesis of crosslinked polyesters using one-pot procedures [91]. REP is defined as polymerization reaction starting from cyclic monomers and cyclic initiators and yielding cyclic polymers [92]. This strategy allows the control of pore size through the variation of the monomer to initiator ratio. Anther advantage of crosslinked polyesters produced by this method is their ability to be degraded and absorbed in the body [89].

1.3.1 Mechanisms of ring-opining polymerization

Polymers have been produced from cyclic monomers through ring-opening polymerization (ROP) as illustrated in Scheme 5. These monomers contained functional groups, able to be polymerizable, such as olefinic groups or functional groups contain one or two of the following elements: O, N, S, P, and Si [93]. In 1863 Wurtz reported the first ring-opening polymerization, where ethylenoxide was polymerized to produce oligoethylenoxide [94].



Scheme 5

Aliphatic polyesters have been synthesized using either polycondensation or ring-opening polymerization In comparison to polycondensation of diols either with dicarboxylic acid or with acid chloride and to polycondensation of hydroxylcarboxylic acid, ROP has the following advantages:

a. The synthesis of high molecular weight polyesters is possible under mild conditions in relative short time. In contract, polycondensation needs high temperatures and long time to produce high molecular weight polyesters [95].

b. In absence of side reactions, the molecular weight can be controlled by the ratio of monomer to initiator. In polycondensation, high molecular weight polyesters are rarely produced because the MW depends on the conversion, where it is difficult to achieved high conversion.

For successful ROP, the free energy change of the reaction ΔG, must be negative under the conditions used [96,97]. Otherwise it is not possible to produce polymers using ROP, as in the case of γ-butyrolactone, where ΔG is positive.

$$\Delta G = \Delta H - T\Delta S$$

As shown in Gibbs-Helmholz equation two factors determine the value of ΔG; reaction enthalpy (ΔH) and the entropy (ΔS). Reactions with negative ΔH and positive ΔS represent the most favored case for ROP to produce high molecular weight polymers. The effect of ring size on the ΔG of a polymerization reaction can be attributed to ring strain. As a consequence of high bond angle distortions in three- and four membered lactone rings, the value of ΔH is negative, which make them polymerizable. For higher membered rings, the angle strain decreases sharply, therefore the important factors determine the value of ΔG is the degree of free rotation. The value of ΔG for all ROP of lactones is negative with exception of 5 ring lactones. For instance, the ΔG value for ROP of ε-caprolactone at room temperature is –15 KJ/mol [98].

Regarding the reactivity of lactones, some generalizations were made as follows [95]:

a. The higher the strain in the ring, the more likely it is to undergo polymerization.

b. Introduction of alkyl or aryl substituents decreases the polymerizability by stability of the reactant and decreasing ΔG of the polymerization reaction.

c. almost all 4-, 7- and 8-membered rings are polymerizable.

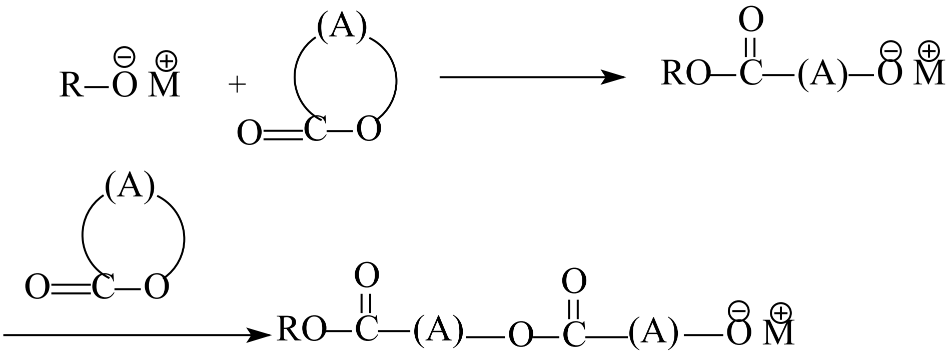
d. The higher the equilibrium constant in alkaline hydrolysis, the greater is the tendency to polymerize.

Three different mechanisms were utilized in the synthesis of polyesters from lactones using ROP, namely anionic [99-110], cationic [99,111-118] and coordination-insertion mechanisms [118-132]. β-lactones behave differently from higher lactones in polymerization process, due to two characteristic features of these monomers that influence their reactivities: high polarity (for β-lactone, D = 46, whereas for ε-caprolactone, D = 40) and the very high internal strain of four-membered β-lactones ring [133].

A brief description of these mechanisms is summarized in the following:

1.3.1.1 Anionic mechanism

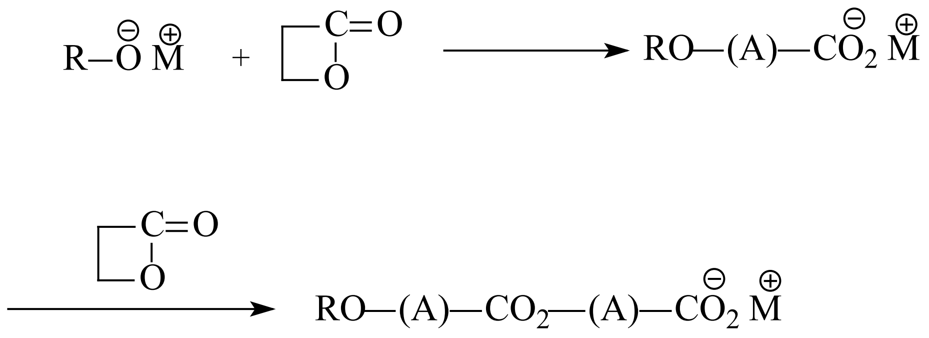
The main initiators have been used in anionic ROP are nucleophiles, either strong one or weak one. This mechanism is based on the nucleophilic attack of the initiator onto the carbonyl group, whereby the intermediate formed depends on wether the lactone is a β-lactone or not. In most lactones [99-103], the intermediates produce through the breaking of the acyl-oxygene bond forming alkyloxide anion intermediate as shown in Scheme 6.



Scheme 6

β-lactones such as pivalolcatone studied in the first part of this dissertation represent a special case, where the intermediate formed by breaking of the alkyl-oxygen bond forming carboxylate anion intermediate as shown in Scheme 7 [103-109].

The intermediates formed in both cases propagate the ROP through the attack on the unreacted lacton monomers.

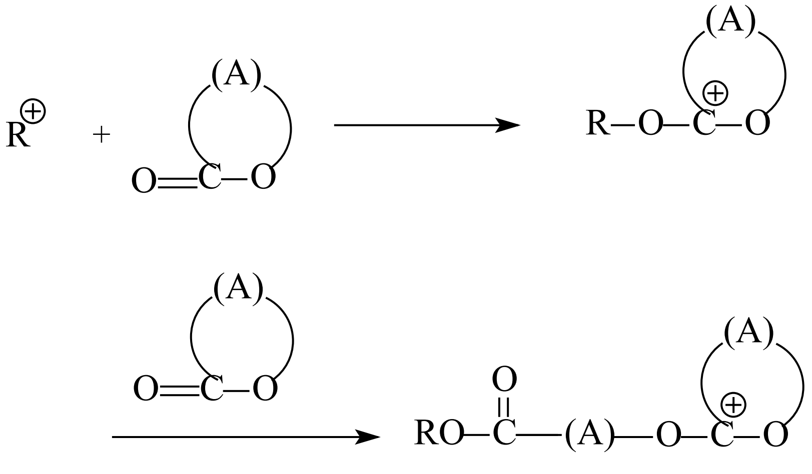


Scheme 7

1.3.1.2 Cationic mechanisms

The typical initiators used in cationic polymerization of lactones are Protonic acids, alkylating agents, acylating agents, and Lewis acids [111, 134]. As a rule, all ROP using these initiators go through the cationic mechanism, with exception of some Lewis acids such as zinc(II)chloride, tin(IV)chloride and aluminum(III)chloride. These initiators were found by Kricheldorf et al. to follow the insertion mechanism [117-119].

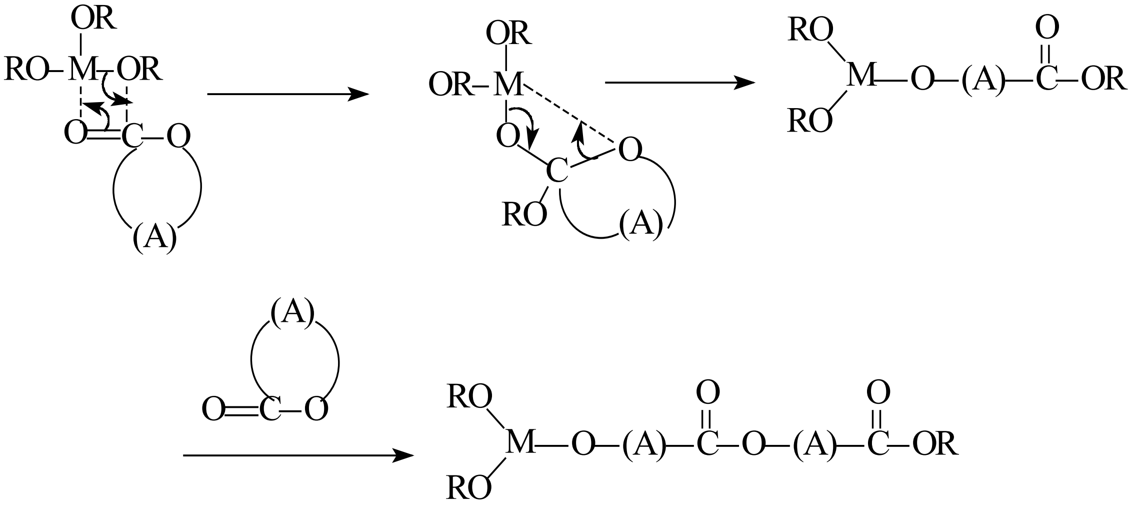
It was conventional until the middle of 80th that cationic polymerization of lactones involve electrophilic attack of initiator on the endo-oxygen atom, followed by the formation of an acylium cation through the cleavage of acyl-oxygen bond [99]. Penczek et al. [112,113] and Kricheldorf et al. [117,118] reinvestigated this mechanism independently using ^{1}H-NMR and IR spectroscopy. When alkylating agents were used as initiators, the spectroscopic analysis proved the formation of methylester end groups. This result could be explained by assuming electrophilic attack of the initiator on the exo-oxygen, followed with the cleavage of alkyl-oxygen bond as illustrated in Scheme 8. The dioxocarbocation formed is electrostaticaly stable due to the delocalization of positive charge. The growth of the polymer chain is accomplished through the continuous attack of exo-oxygen on the formed dioxocarbocation.



Scheme 8

1.3.1.3 Coordination-insertion mechanisms

The prerequisite for initiators to be useful in the insertion mechanism is the presence of free p- or d-orbitals. The most common initiators among this class of initiators are aluminum alkoxides like $Al(OiPr)_3$, as well as Zinc compounds such as $EtZnOCH_3$ and Tin compounds such as Me_3SnOMe [123-129,135-137]. The steps of this mechanism are illustrated in Scheme 9. The first step involve coordination of the lactone to the metal atom (M), followed by ring opening and insertion of the unit into the metal-ligand bond. The subsequent step is the acyl-oxygen cleavage of the intermediate. High molecular weight polyesters are produced through the continuous repeat of all steps with the formed oligomers or polymer chains which contain the metal atom.



Scheme 9

1.4 Characterization of Cyclic Polymers

Unfortunately, cyclic polymers and the role of cyclization played in step-growth polymerization have not been taken into account in polymer science especially in the theoretical background of polycondensations, because no instruments were available to characterize this type of polymers. However, the instruments used were suitable to characterise soluble low molecular weight cyclic oligomers after the separation of the insoluble polymer and the solvent. With respect to this point different chromatographic and spectroscopic methods could be used such as GPC, HPLC, NMR, and IR [1]. The most important success in the field of cyclic polymers as in the determination of molecular weight was achieved after the development of novel mass spectroscopy methods [138,139], namely soft ionisation methods with low fragmentations especially fast atom bombardment (FAB), laser desorption (LD) and matrix-assisted laser desorption/ionization time to flight mass spectroscopy (MALDI-TOF). These soft ionisation techniques allow the determination of molecular weights up to a few thousand Dalton. Currently MALDI-TOF is the most powerful instrument used to characterize cyclic polymers due to the following reasons. Firstly, it allows desorption and ionization of very large molecules even if in complex mixtures. Secondly, it allows direct identification of mass-resolved polymer chains, including intact oligomers within molecular weight distribution [140]. Furthermore, it is suitable to estimate the MW and MWD independent of structure as well as the determination of end groups with very low sample consumption and within short time [141]. For the above reasons MALDI-TOF will be explained in more detail below.

MALDI-TOF mass spectroscopy was developed in 1988 by Hillenkamp and Karas [142,143]. In the beginning it was used only for the analysis of large biomolecules dissolved in water. In 1992 [144] it was used for the first time to analyze synthetic polymers, because synthetic polymers are insoluble in water which was the only solvent used to dissolve the samples. Since the synthetic polymers are polydispers the signal-to-noise ratio was worse [144,145].

In principle, MALDI-TOF mass spectroscopy is based on the production of intact molecule ions by the irradiation of the matrix material, which absorbs the laser energy and is responsible for the transfer of the analyte into the gas phase as shown graphically in Figure 6. The analyte is assumed to be homogenously embedded in the matrix.

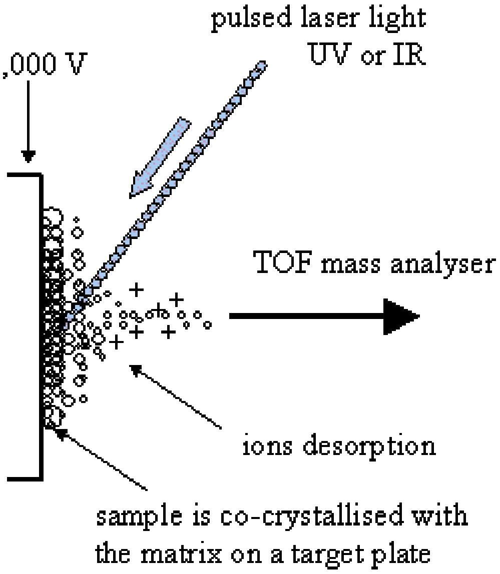


Fig 6. Scheme of the matrix-assisted laser adsorption/ionization process.

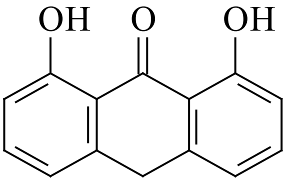
Some of the common used matrixes for the sample preparation of synthetic polymers are dithranol (1,8,9-trihydroxyanthracene) (I), DHB (3,5-dihydroxybenzenoic acid) (II), 3-methoxy-4-hydroxycinamic acid (III), and nicotinic acid (IV). In general, the matrix materials have to meet the following requirements [140]:

a. High electronic absorption at the employed laser wave length (usually 337 nm of nitrogen laser).
b. Good vacuum stability.
c. Good solubility in organic solvent used to dissolve the analyte.
d. Good miscibility with the analyte in the solid phase.

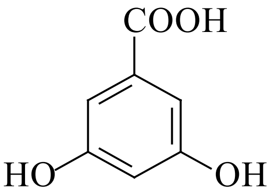
The choice of matrix and the sample preparation are crucial points in MALDI mass spectroscopy. While the selection of the matrix materials is a trial and error process, sample preparation can be achieved as follow [140]: Solutions of matrix and polymer prepared from identical solvents are mixed together in appropriate ratio (usually 1000:1, matrix: polymer). To enhance the cationization, metal ions are often added as their organic or inorganic salts, depending on their solubility. About 1 µl of the whole solution is then applied on the sample holder and allowed to dry. Then the sample is irradiated by a pulse of UV laser. The formed ions are accelerated by statistic electrical field of up to 35 kV. Depending on their mass to charge ratio they have different velocities. Consequently the detector measures the time of flight of each ion by the time difference between the start signal (signal of laser pulse) and the signal caused by each ion. Mass to charge ratio (M/Z) can be evaluated by Eq.20.

$$\frac{m}{z} = \frac{2U\,t^2}{s^2} \qquad \textbf{(20)}$$

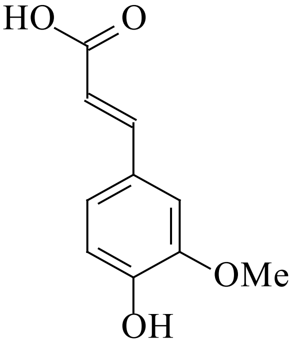
where *m* is the mass of ion, Z is the charge of ion, U is the accelerating voltage, t is the time of flight and s is the flight distance.



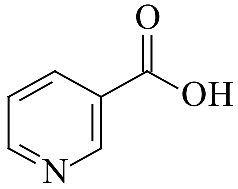
(I)



(II)



(III)



(IV)

The MALDI-TOF mass spectroscopy suffers from some problems summarized in the following points [146,147].

a. The values of M_n and M_w may depend on the laser power used. This dependence causes the poor reproducibility of MALD-TOF analysis of polymers.
b. The high molecular weight part of polymers is always underestimated.
c. MALDI-TOF MS fails to give reliable M_n and M_w values of polydispers polymers with broad molecular weight distribution.
d. The intensity of peaks decrease with increasing molecular weight.

Since condensation polymers is important in our life, it is necessary to study the theoretical background and to improve the classical theory of polycondensation taking into account the new points of view concern in the role of cyclization, especially Kricheldorf's new theory. In order to prove the validity of this theory, it is necessary to investigate the role of cyclization in different type of polycondensation. In this context, the present work represents experimental evidences for the validity of the KCPs theory.

2 The purpose of this work

2.1 Syntheses of cyclic polyethers

Different polycondensations should be studied and the reaction conditions should be optimized for high conversions and molecular weights. The formation of cycles should be studied in order to prove the validity of Kricheldorf's new theory of polycondensation.

Three different polyethers will be synthesized under kinetic control polycondensations. Namely, Poly(ether ketone)s, poly(ether benzonitrile)s and poly(ether pyridine)s should be synthesized to optimize the polycondensation with respect to high molecular weight and conversion. Therefore, different monomers should be synthesized suitable for each kind of polyether. The structure and the reactivity of each monomer have to be studied as a function of cyclization and molecular weight. Furthermore, the influences of synthesis method, temperature, reaction time as well as solvent system on cyclization should be studied in detail.

2.2 Syntheses of cyclic aliphatic polyesters

In the second part of this work cyclic aliphatic polyester should be synthesized from pivalolactone via ring-opening polymerization. The effect of initiators, reaction time, solvent, and temperature should be studied with respect to the cyclization tendency as well as to the reinvestigation of end groups.

2.3 Syntheses of biodegradable networks

This part of the present work is aimed at synthesizing networks from mixtures of two types of chain segments having different chemical structure. OH-terminated poly(ε-caprolactone)s should serve as main component for all syntheses. These biodegradable chains should be synthesized using ring-opening polymerization (ROP) in presence of 1,4-butandiol or tetraethylenglycol as cointiator and tin(II)2-ethylhexanoate ($SnOct_2$) as initiator. In this way, different OH-terminated poly(ε-caprolactone)s should be obtianed either by changing the coinitiator or the ratio of ε-caprolactone to coinitiators. These telechelic PCLs should be crosslinked either alone or in combination with poly(ethylene oxide)s as example of a polar hydrophilic chain segment or with polysiloxanes as examples of non-polar hydrophobic chains. Since poly(ε-caprolactone)s are not compatible with these polymers in the melt, it was hoped that homogeneous solutions of poly(ε-caprolactone)s with each of them can be obtained having sufficiently high concentrations to enable crosslinking. Trimesoyl chloride should be used as crosslinking agent to provide crosslinks based on ester groups allowing for complete hydrolysis or aminolysis of the network. Furthermore, biodegradable networks should be used to trap and separate cyclic aromatic polyethers from linear ones.

The structures and properties of cyclic polymers, telechilic poly(ε-caprolactone)s, and the networks as well as contents and the structures of polymers and monomers will be studied and confirmed using the following analytical methods:

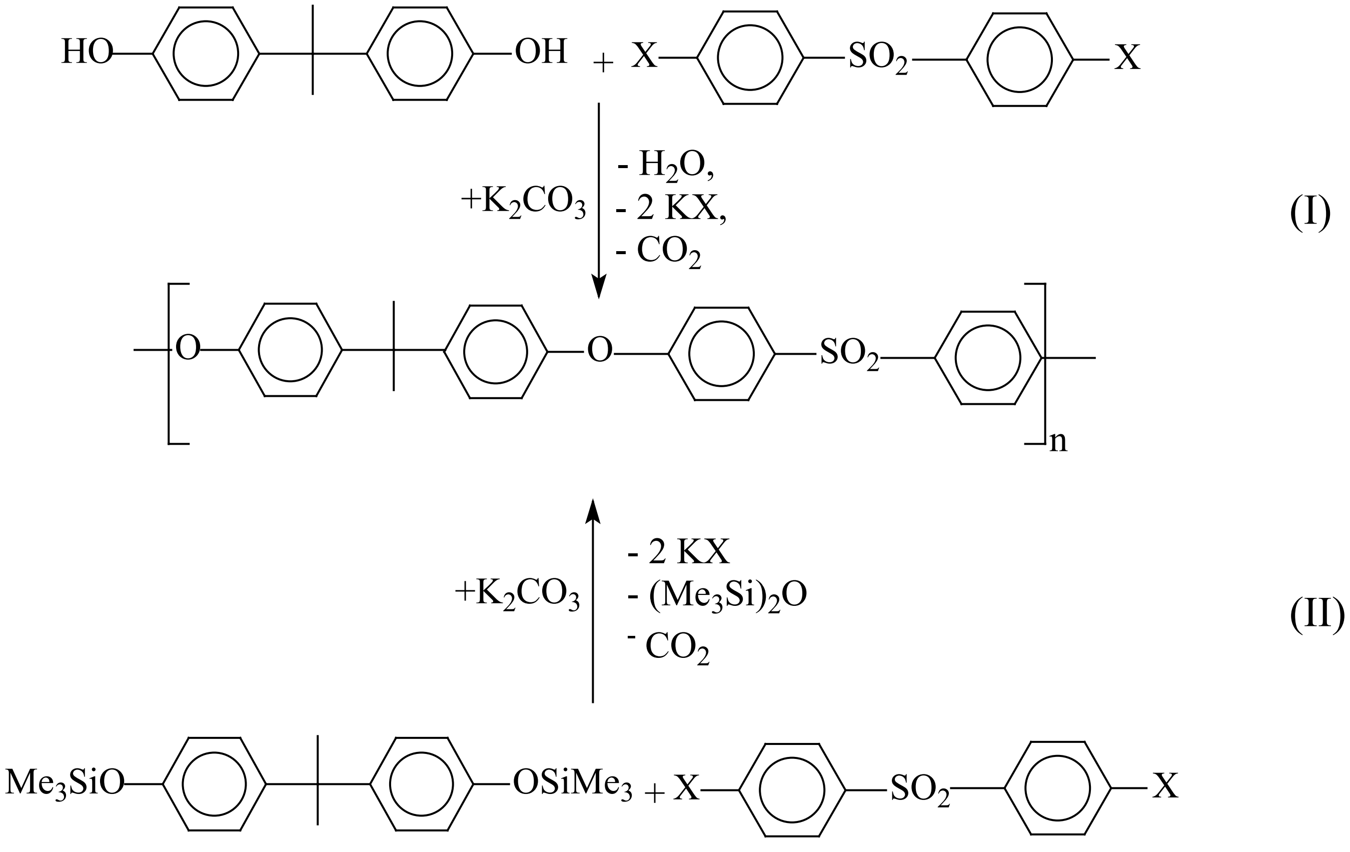
1. ^{1}H-NMR spectroscopy.
2. MALDI-TOF spectroscopy.
3. SEC measurements.
4. DSC measurements.
5. Wide-angle X-ray
6. Viscosity Solution viscosity measurements.
7. Elemental analyses.

3 Results and Discussions

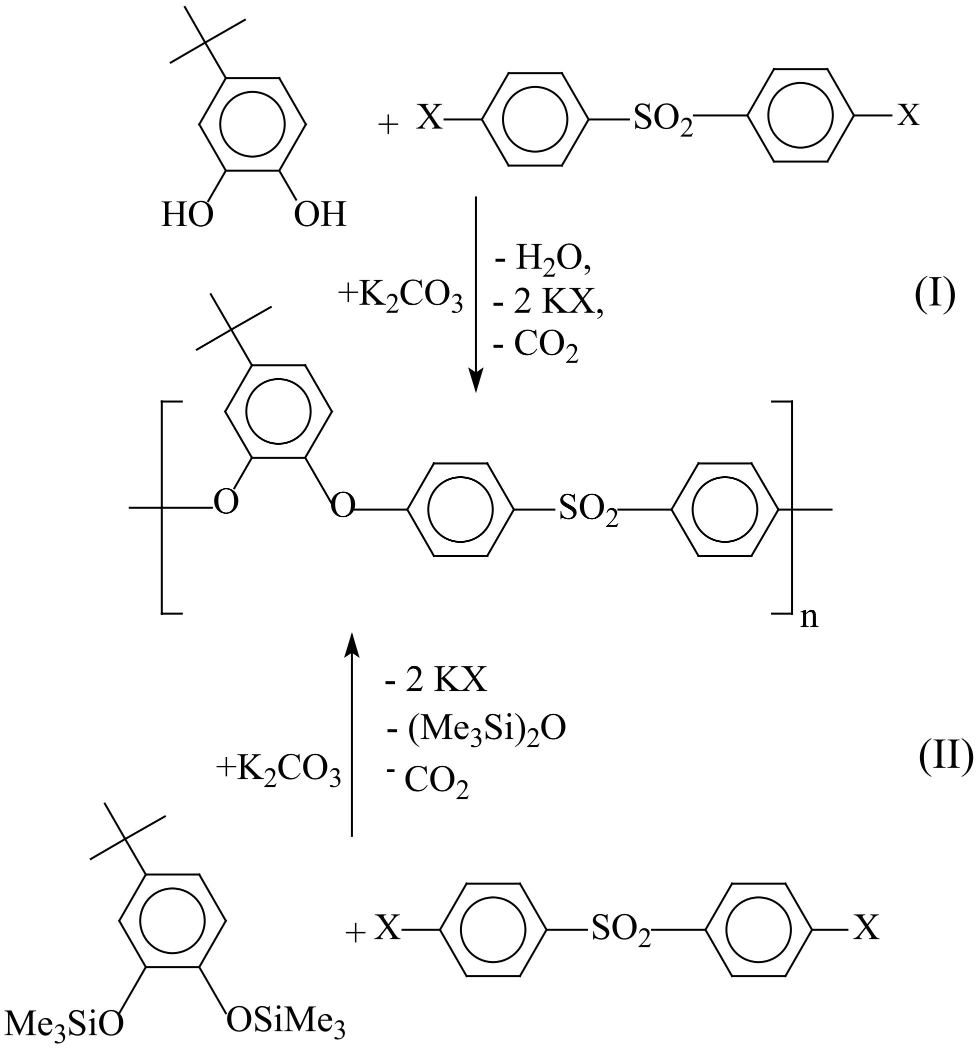
3.1 Syntheses of cyclic polyethers under kinetically controlled polymerization:

Conventional syntheses of cyclic aromatic oligoethers were obtained by ring-chain interconversion based on the fact that activated ether linkages in aromatic polyethers can be reversibly cleaved by fluoride ion in dipolar aprotic solvents [148-151]. This interconversion take places either in melt or in solution under pseudo-high dilution conditions.

Recently Kricheldorf et al. studied [152-154] the synthesis of cyclic poly(ether sulfone)s PESs (Schemes 10 and 11) and allowed the detection of cyclic polymers by MALDI-TOF mass spectrometry up to masses of around 20000 Da without fractionation and up to 27000 Da after fractionation. These cyclic PES's were synthesized using free or silylated bisphenols. The reactivities and the structures of free and silylated bisphenols as well as dihalobenzosulfones were studied with regared to the content and $\overline{DP}$ of cycles.



Scheme 10



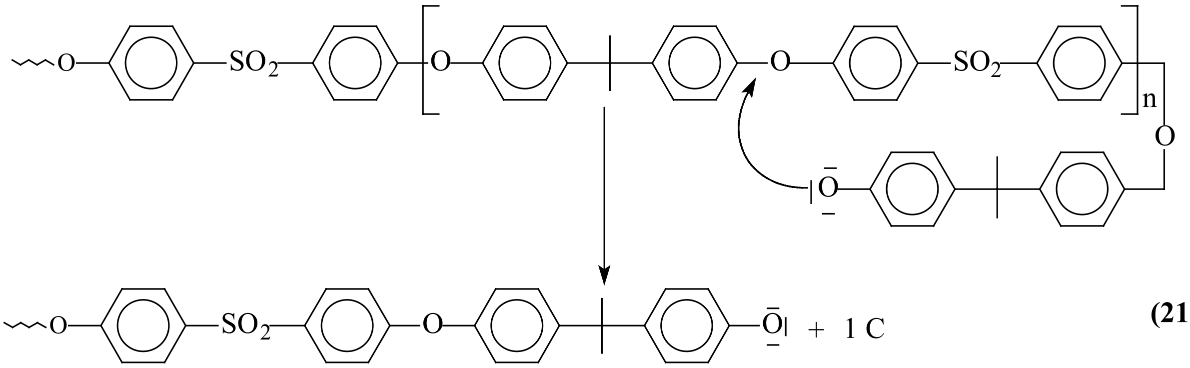
Scheme 11

Both theoretical and experimental results indicate that the extent of cyclization is a sensitive indicator of the perfection of the reaction conditions (no side reactions, perfect stoichiometry, and high conversion).

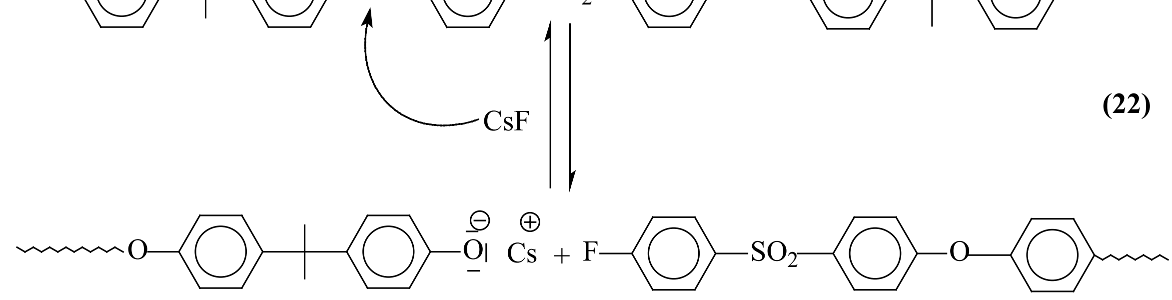
According to the results of poly(ether sulfone)s three different aromatic polyethers were synthesized in this work using two main synthetic methods. Method (**I**) represents the nucleophilic substitution of free bisphenol with K_2CO_3 in polar aprotic solvent with the azeotropic removal of liberated water, while method (**II**) represents the silyl method. The silyl method has more advantages than method **I** [153]. First, the lower reactivity of the silylated bisphenols enables the study of the influence of reaction time and the temperature on the course of polycondensation. Second, the silyl method may be preformed either in bulk or in solution. Third, the hydrolytic cleavage of C-F bonds is avoided because no water is formed. Fourth, distillation of silylated diphenols allows an intensive purification from oxidation products and inorganic salts.

Based on the standard reaction conditions typically used for syntheses of poly(ether sulfone)s via method I [153], DMSO was used as reaction medium in combination with toluene or xylene for the azeotropic removal of water. The main bisphenol used in synthesize of aromatic polyether was Bisphenol-A, because it yielded polymers soluble in several common inert solvents allowing for an easy characterization by various analytical methods.

In the present work, it was necessary to take into account the probability of cycle formation due to ``back-biting degradation``, (Eq.21). According to previous studies dealing with syntheses of cyclic poly(ether sulfone)s under kinetic controlled polycondensation, back-biting degradation could be attributed to the following reasons [153]. First, the capability of CsF to cleave the backbone of PES as illustrated in Eq.22. Second, higher polycondensation temperatures increase the back-biting probability. Based on these studies, the silyl method (method II) was used only in solution using K_2CO_3 as catalyst and at moderate temperatures to decrease the possibility of ring formation via thermodynamic controlled polycondensation.



(21)



(22)

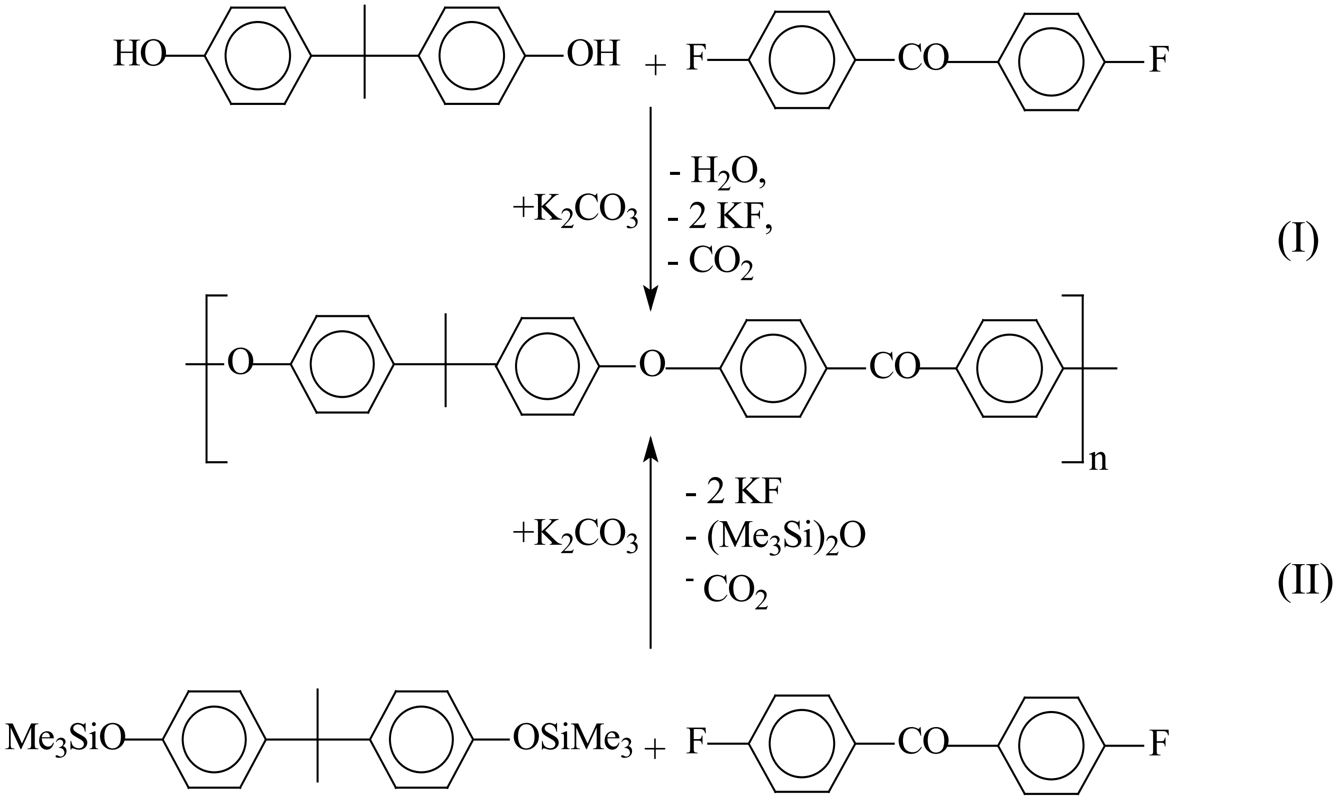
3.1.1 Cyclic Poly(ether ketone)s

3.1.1.1 Introduction

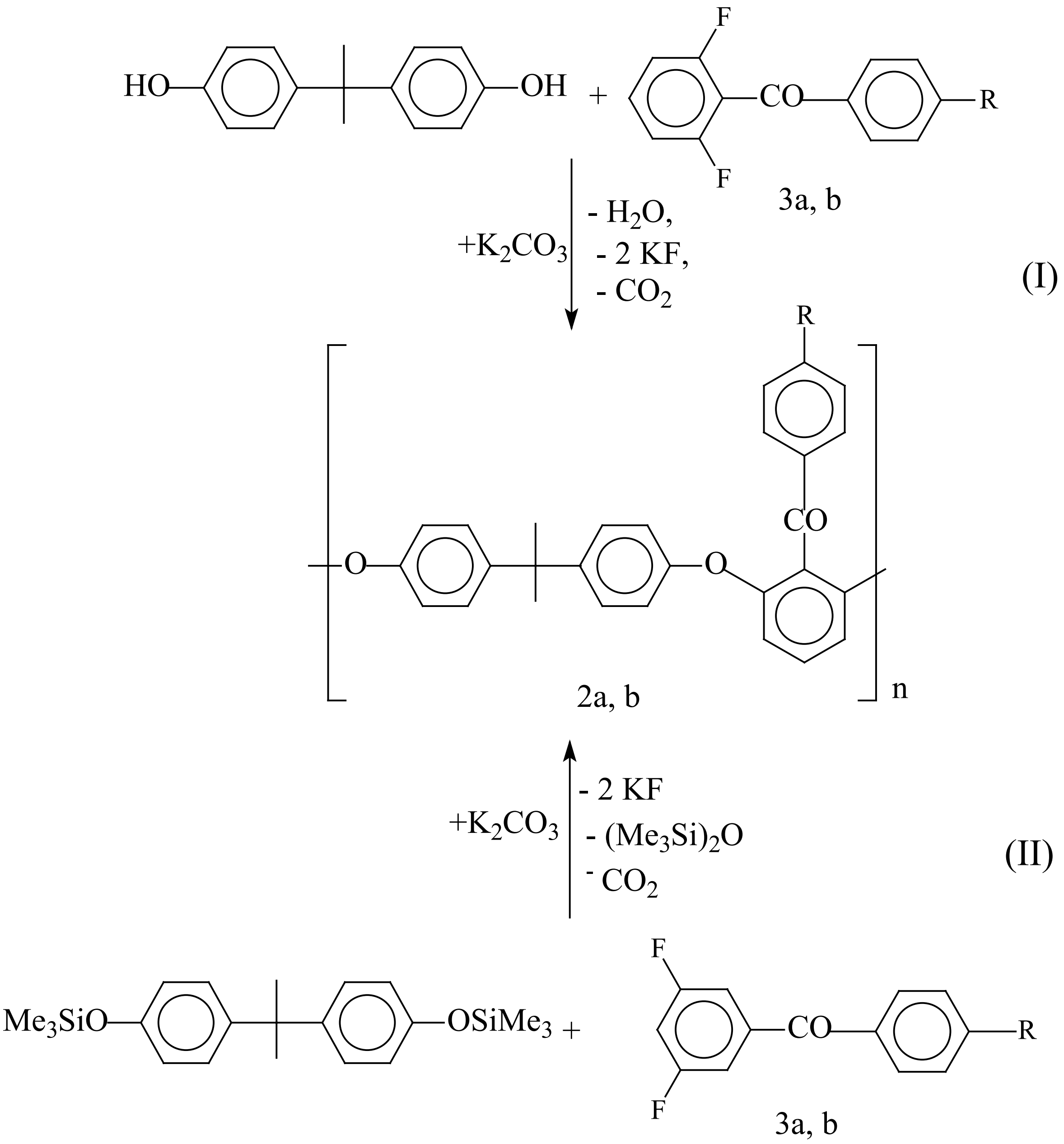
Poly(ether ketone)s PEKs are one important classe of thermostable engineering plastics. The first synthesis of PEKs was described by Bonner [155]. He used Friedel-Crafts polyacylation of aromatic diacid chloride with oxly biphenyl derivatives or aromatic acid chlorides containing phenoxy groups. Moreover, polyacylations can be accomplished in the presence of Lewis acids using normal Friedel-Crafts solvents (such as dichloromethane). Further attempts to prepare PEKs using this strategy were reported in the literature [156-158]. In general, Friedel-Craft reactions yielded low molecular weight products, which were not sufficient for technical applications. Aromatic nucleophilic substitution using halobenzophenones was first investigated by Johnson et el.[159]. However, this strategy sometimes needs high temperatures, halobenzophenones with high electrophilicity and polar aprotic solvents to achieve high molecular weight. Kricheldorf et al. used successfully the silyl method for the first time to synthesize PEKs without solvents in the melt [54,55]. Yet under such conditions equilibration and back-biting takes place.

This experimental work represents the first attempt to investigate the role of cyclization played in the synthesis of poly(ether-ketone)s via the kinetic controlled polycondensation of bisphenol-A and difluorobenzophenone isomers. This work was accomplished according to the following strategy. Poly(ether-ketone)s of bisphenol-A were prepared using two different synthetic methods (I and II) (Schemes 12 + 13). The influence of these methods on cyclization tendency and molecular weight was compared. Furthermore, the reactivity of isomeric difluorobenzophenones (4,4'- versus 2,6-isomers) was compared. The MALDI-TOF measurements of the poly(ether ketone)s improved the chance to detect the presence of cyclic poly(ether-ketone)s.

In this context it should be mentioned that cyclic oligo(ether ketone)s were synthesized by numerous authors either by direct polycondensation using the pseudo-high dilution method or by CsF-catalyzed "back-biting degradation" of preformed poly(ether ketone)s [160-177].


HO
OH
+
F
CO
F
+K2CO3
- H2O,
- 2 KF,
- CO2
(I)
O
O
CO
n
+K2CO3
- 2 KF
- (Me3Si)2O
- CO2
(II)
Me3SiO
OSiMe3
+
F
CO
F

Scheme 12

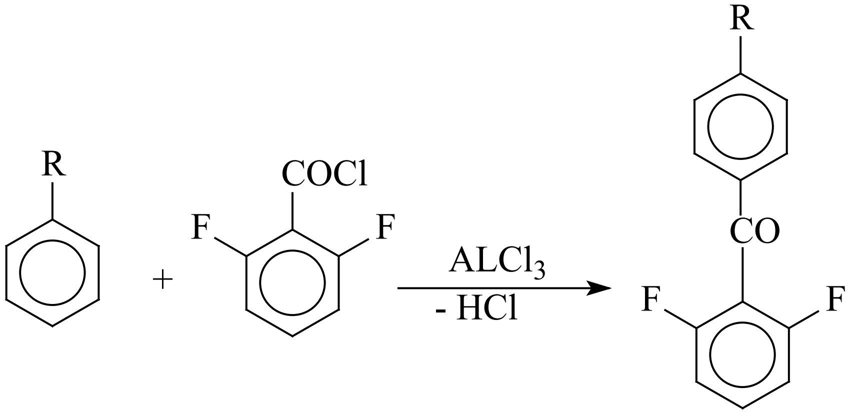


a) R = H b) R = CMe_3

Scheme 13

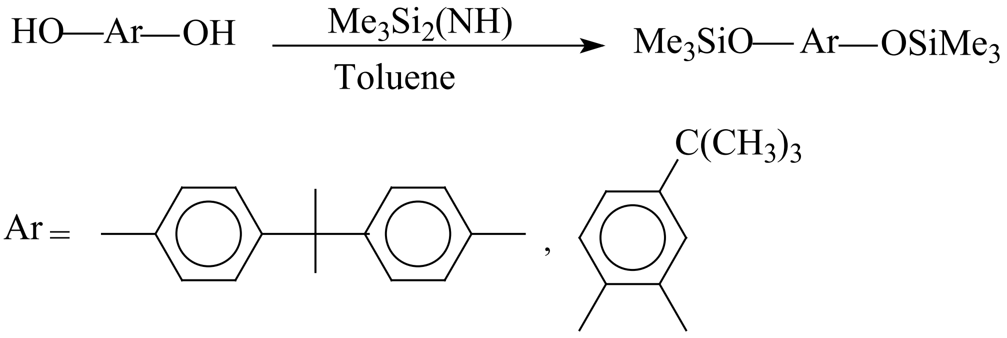
3.1.1.2 Monomer syntheses

Difluorobenzophenones were synthesized by Friedel-Crafts acylation of nucleophilic aromatic compounds with commercially available 2,6-di fluorobenzoyl chloride (Eq.23) in the presence of aluminum chloride as Lewis acid. Since the nucleophilicity of aromatic compounds is very important to give satisfactory results, the aromatic compounds used were nucleophilic enough for the acylations. The yield and properties of the difluorobenzophenones are summarized in the experimental part. The chemical structure of the difluorobenzophenones was proved using ^{1}H-NMR (Fig.7).



(23)

Bisphenol-A and 4-tert.butyl-catechol were silylated by means of hexamethyldisilazane in dry toluene (Eq.24). The yields and properties weresummarized in Table 25 (Exptl. Part).



$$\text{HO—Ar—OH} \xrightarrow[\text{Toluene}]{\text{Me}_3\text{Si}_2\text{(NH)}} \text{Me}_3\text{SiO—Ar—OSiMe}_3$$

(24)

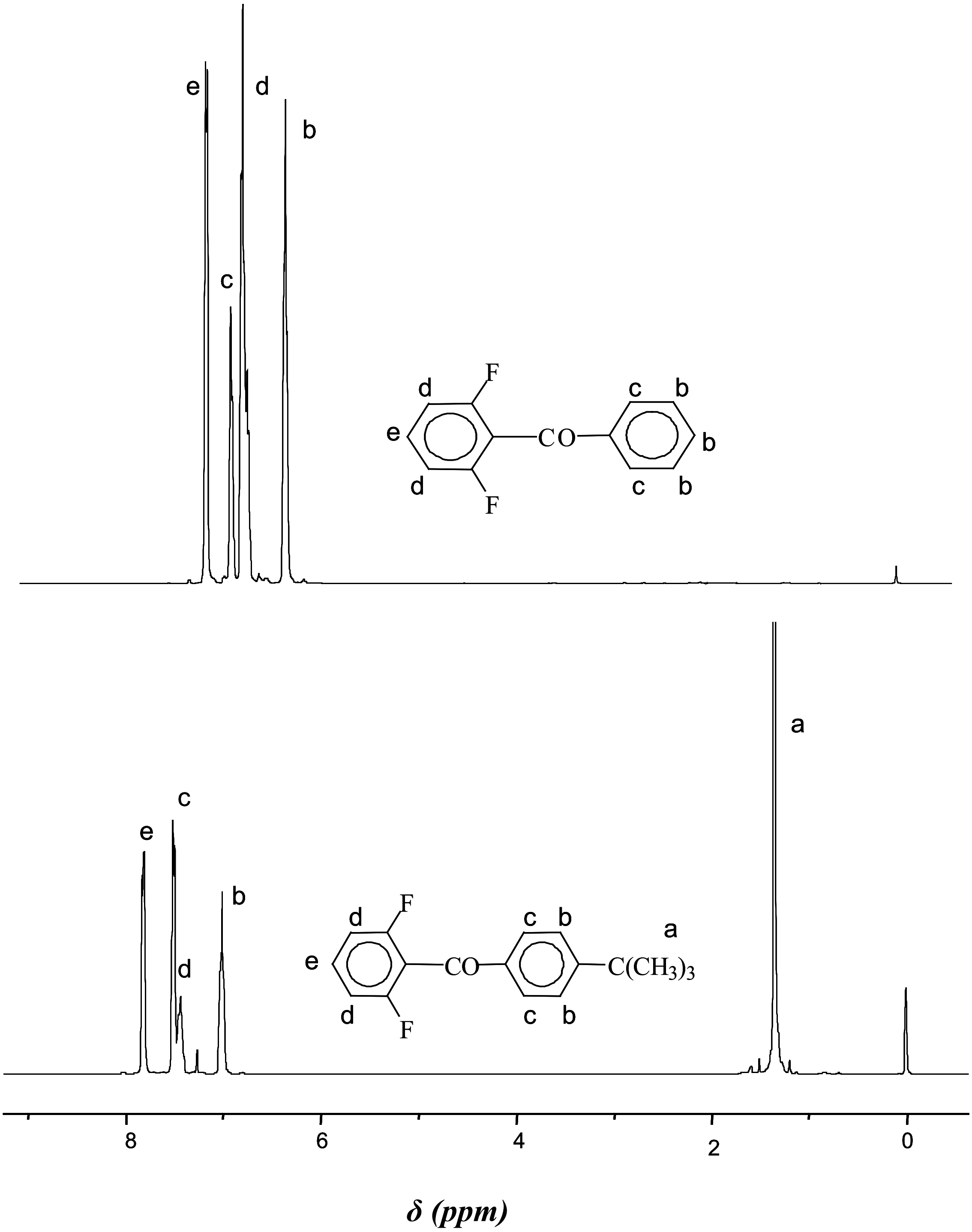


***Fig7.* 400 MHz ^{1}H NMR spectrum of a difluorobenzophenones in deuterated chloroform**

3.1.1.3 Polycondensations of 4,4'-DFBP

Free bisphenol-A was reacted with 4,4'-DFBP using K_2CO_3 as catalyst and F^- acceptor. As indicated by the results listed in Table 1, a high yield, but only a moderate viscosity was obtained (No.1, Table.1). Since 4,4'-DFBP is less reactive than 4,4'-difluorodiphenylsulfone, higher reaction temperatures seemed to be advantageous. However, replacement of DMSO by NMP or sulfolane did not significantly raise the molecular weights (Nos. 2 + 3, Table.1).

Table.1. Polycondensations of 4,4'-difluorobenzophenone with bisphenol-A (method I) or with bistrimethylsilyl bisphenol-A (method II).

Exp. No.	**Method**	**Excess of DFBP**	**Reaction medium**	**Temp. (°C)**	**Time (h)**	**Yield (%)**	**η_{inh}[a] (dL/g)**	**Reaction[b] products**
1	**I**	**0**	**DMSO/Toluene**	**135-140**	**6**	**98**	**0.20**	**C, La, Lb, Lc**
2	**I**	**0**	**NMP/Toluene**	**145-150**	**6**	**97**	**0.23**	**C, La, Lc**
3	**I**	**0**	**Sulfolane/Toluene**	**150-155**	**6**	**98**	**0.22**	**C, La, Lc**
4	**II**	**0**	**NMP (10 mL)**	**140-145**	**48**	**66**	**0.62**	**C (+ few Lb)**
5	**II**	**1%**	**NMP (10 mL)**	**140-145**	**48**	**69**	**0.85[c]**	**C**
6	**II**	**0**	**NMP (60 mL)**	**140-145**	**48**	**70**	**0.42**	**C**
7	**II**	**0**	**NMP (10 mL)**	**165-170**	**48**	**67**	**0.28**	**C, Lb**
8	**II**	**1%**	**NMP (10 mL)**	**165-170**	**48**	**83**	**0.43**	**C, Lb**
9	**II**	**0**	**NMP (60 mL)**	**165-170**	**48**	**41**	**0.18**	**C, Lb**

[a] ***measured at 20°C with c = 2 g/L in CH_2Cl_2***

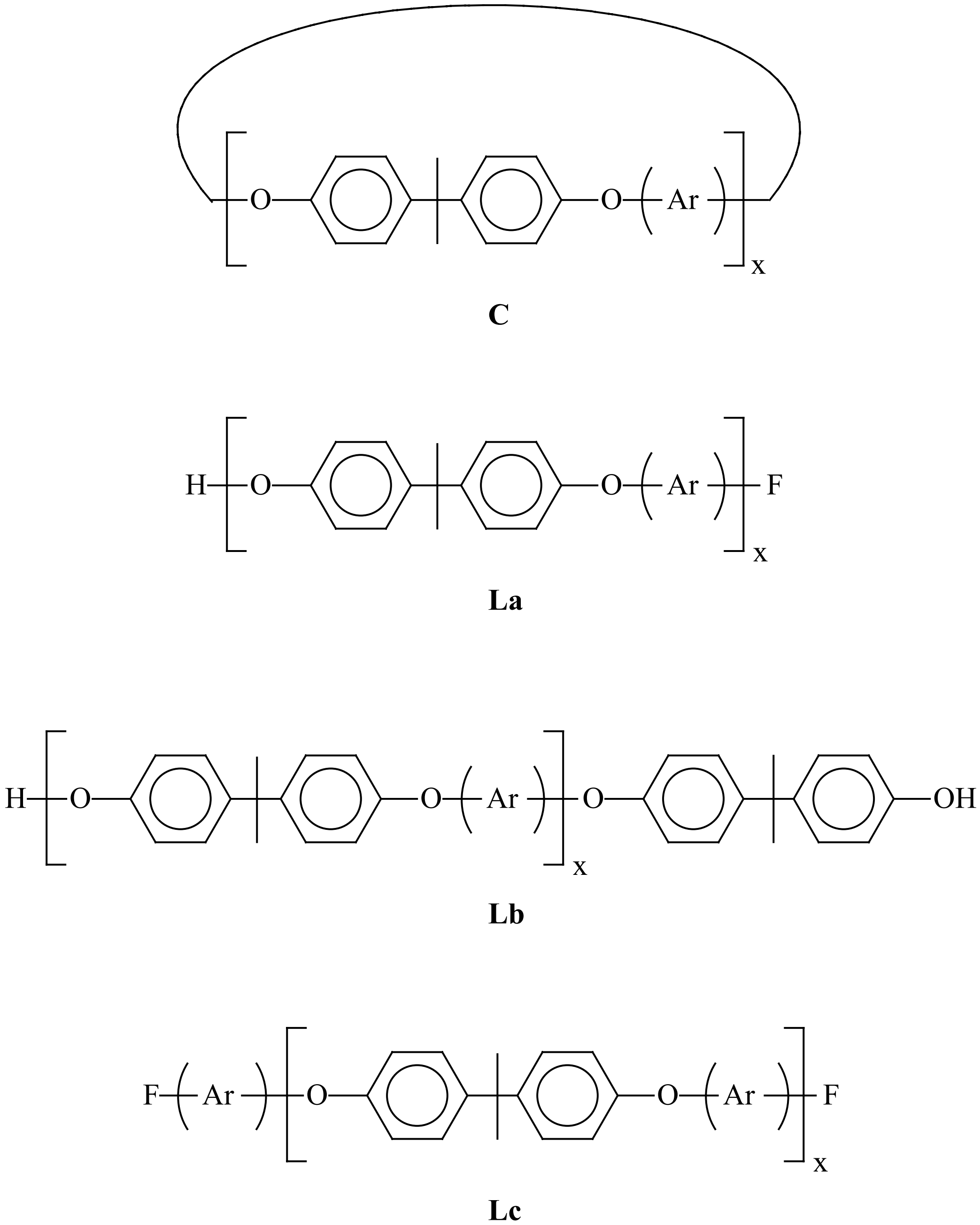
[b] ***as revealed by MALDI-TOF mass spectrometry***

[c] ***M_n = 85 000 Da, M_w = 190 000 Da by PS-calibrated SEC in THF***

The MALDI- TOF mass spectra (m.s.) indicated the formation of large molar quantities of cycles in all three samples. In the case of sample No. 1 (Table.1), the mass peaks of the linear chains **La**, **Lb** and **Lc** were also detectable (Scheme 14), indicating incomplete conversion. The peaks of these linear chains prevailed over those of the cycles above 3500 Da. In agreement with the slightly higher viscosities, higher conversions were achieved for the samples Nos. 2 and 3 (Table.1). In their MALDI-TOF m.s. the peaks of the cycles were predominant up to the technical limits of these measurements around 7000 Da. Figure 8 illustrates the m.s. of the poly(ether ketone) prepared in NMP (No. 2). The high content of cycles suggests that these reaction conditions favored cyclization and the chain growth was severely limited by cyclization.

The polycondensation of silylated bisphenol-A was performed in dry NMP, which is considered as the optimum solvent for the silyl method (method **II**) [178]. According to the procedure previously elaborated for activated dichloroaromatics [178], method **II** gave better results than method **I** (Nos. 4-9, Table 1), because the formation of water and hydrolytic cleavage of C-F groups are avoided. However, polycondensation via method **I** is essentially complete within 3 to 4 h, due to the high concentration of potassium phenoxide.

The functions of K_2CO_3 in method **II** were not only as catalyst and HF acceptor but also as source of the oxygen anion [179] as illustrated in Scheme 15. The higher concentrations, which can be used with method **II**, certainly contribute to the formation of higher molecular weights as illustrated by a comparison of experiments No.4 with 6 or No.7 and 9. However, even when compared at identical concentrations, method **II** gave higher molecular weights than method **I**.



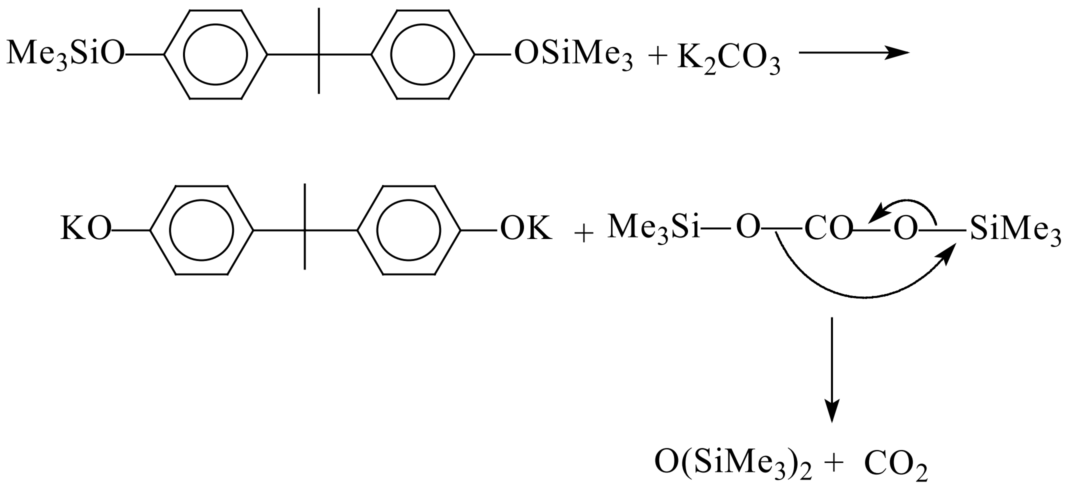
C

La

Lb

Lc

Scheme 14



Scheme 15

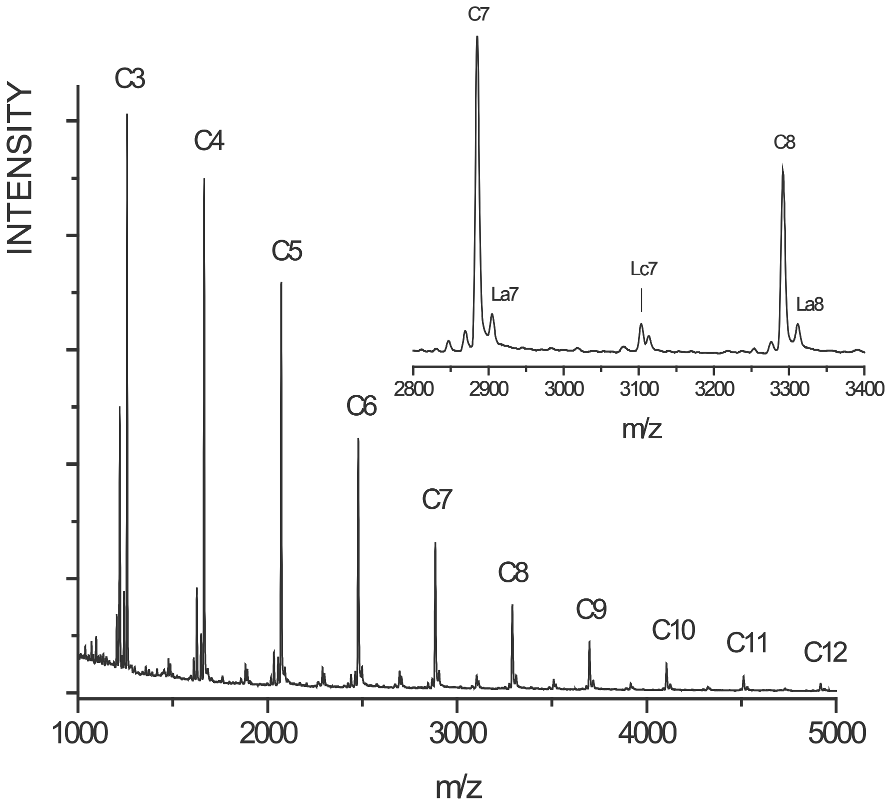
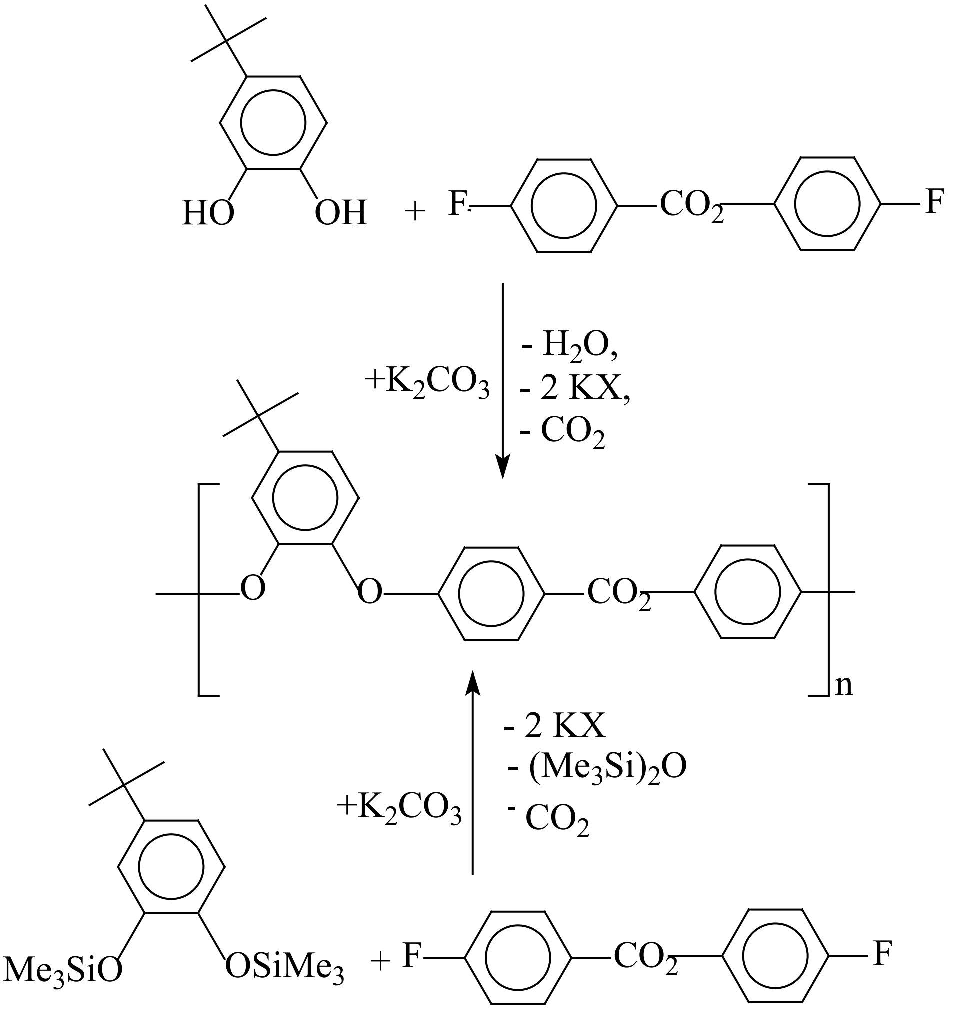


Fig 8. MALDI-TOF mass spectrum of poly(ether ketone) no.2, table 1, prepared from free bisphenol-A and 4,4-difluorobenzophenone.

This progress is supported by the results of the MALDI-TOF measurements which revealed high contents of cycles. As exemplarily illustrated in Figure 8, only cycles were detectable in favorable cases. Unfortunately, most MALDI-TOF m.s. were limited to a mass range up to 5 000 - 6 000 Da. Variation of the matrix material from a cyanocinnamic acid to 2,5-dihydroxybenzoic acid, 2,4,6-trihydroxyacetophenone(hydrate) and dithranol did not bring a substantial progress. However, in the case of sample No. 5, Table 1, which had the highest molar mass, the peaks of cycles (and nothing else) were detectable up to 10 000 Da, when the polymer/matrix ratio and the cut off range were optimized.

When the polycondensations Nos. 4-6 were compared with themselves and with the series Nos. 7-9, the following interesting observations were found. First, in both series the highest molecular weights were obtained with a slight excess of the 4,4'-DFBP. Whether this excess is necessary to compensate for a loss by side reactions or by sublimation was not elucidated, but a similar trend was observed for syntheses involving 2,6-difluorobenzophenones (Tables 3 and 4) and also for syntheses of poly(ether sulfone)s [153]. Second, higher temperature(s) gave lower molecular weights in all three experiments. Third, dilution by a factor of six reduces the molecular weights (Nos. 6 and 9). Hence, it may be concluded that the higher molecular weights obtained by method **II** are at least a consequence of the higher concentration. To find out if the trends resulted from the condensations of free and silylated bisphenol-A are typical or unusual for syntheses of soluble non-crystalline poly(ether ketone)s, a few polycondensations were conducted with silylated 4-tert.butylcatechol (Scheme 16). In unpublished results [180], polycondensations of free 4-tert.butylcatechol with 4,4'-DFBP were reported and only low viscosities ($\eta_{inh} < 0.13$ dL/g) were obtained, regardless if DMSO, NMP or sulfolane were used as reaction medium.

The results listed in Table 2 demonstrate clearly that the "silyl method" (**II**) gave again significantly higher molecular weight. These results also demonstrate that the long reaction time of 48 h is, indeed, necessary to achieve high conversions. As expected from Kricheldorf's theory of step-growth polymerizations [4,37,42,153], the MALDI-TOF m.s. of the high molar mass samples (Nos. 3 + 4, Table 2) exclusively displayed peaks of cycles, and in the optimum case, the cycles were observable up to masses of 18000 Da, proving the cyclization of long chains (Figure 9). Another interesting aspect of these results concerns the point that 4-tert.-butylcatechol does not favour cyclization more than bisphenol-A, despite the *ortho* position of the OH-group. Also in the case of poly(ether sulfone)s, silylated bisphenol-A and 4-tert.butylcatechol gave similar molecular weights.



Scheme 16

Table.2. Polycondensation of 4,4'-difluorobenzophenone with silylated 4-tert.butyl-catechol in NMP at 140-145°C

Exp. No.	**Excess of DFDP**	**Time(h)**	**Yield (%)**	η_{inh}[a)] **(dL/g)**	**Reaction[b)] products**
1	**0%**	**24**	**97**	**0.27**	**C (+ few Lb)**
2	**0%**	**48**	**98**	**0.30**	**C (+ few Lb)**
3	**1%**	**24**	**97**	**0.65**	**C**
4	**1%**	**48**	**88**	**0.68**	**C**

a) measured at 20°C with c = 2 g/L in CH_2Cl_2

b) as revealed by MALDI-TOF mass spectrometry

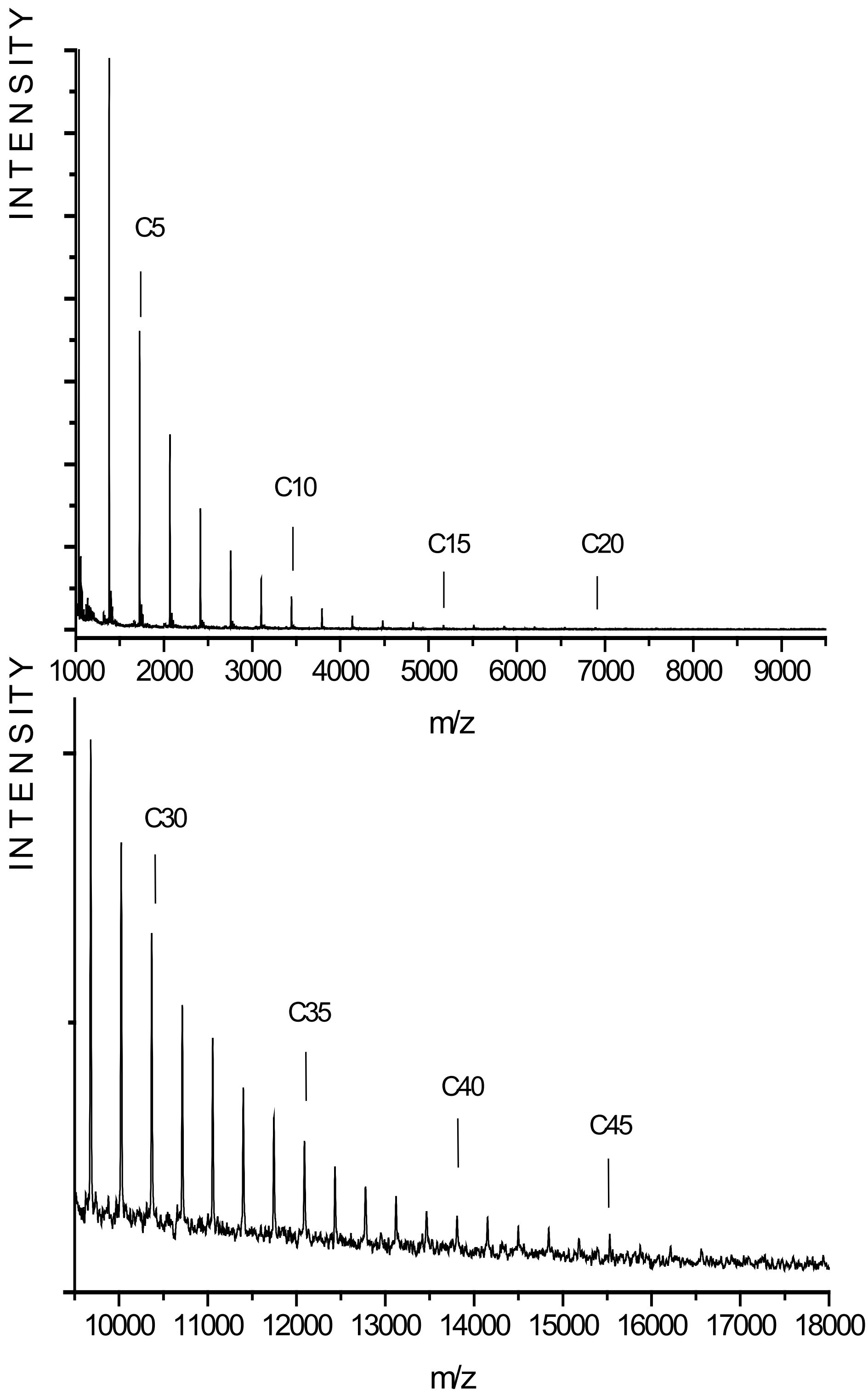


Fig 9. MALDI-TOF mass spectrum of poly(ether ketone) no.4, table 2, prepared from Silylated 4-tert.butylcatechol and 4,4-difluorobenzophenon.

3.1.1.4 Polycondensations of 2,6-DFBP

The polycondensations of free bisphenol-A with 2,6-DFBP (**3a**) or with it's tert.butyl derivative **3b** (Scheme 13) are performed quite analogously to the corresponding polycondensations with 4,4'-DFBP. Both yields and inherent viscosities obtained with **3a** (method **I**, Nos. 1 + 2, Table 3) were extremely low and the MALDI-TOF m.s. confirmed the formation of linear oligomers. The results obtained with the monomer **3b** (Nos. 1-5, Table 4) were slightly better, but all these experiments demonstrate that the 2,6-difluoromonomers are somewhat less reactive than 4,4'-DFBP. Regardless if **3a** or **3b** was used as reaction partner of silylated bisphenol-A, method **II** gave considerably better results than method **I**. Successful polycondensations of silylated diphenols with 2,6-difluorobenzophenones have been already reported previously [55].Yet, in agreement with a lower reactivity of **3a** (or **3b**) relative to 4,4'-DFBP, a higher temperature was needed (165 instead of 140°C) to obtain optimum results (Nos. 5 + 6, Table 3). High fractions of cycles were detectable in all products of method **II**, but only the sample with the highest molecular weight gave a MALDI-TOF m.s. exclusively displaying the mass peaks of cycles. Unfortunately, the mass peaks of cycles were only detectable up to 7000 Da.

Table.3. Polycondensations of 2,6-difluorobenzophenone 3a with bisphenol-A (method I) or with bistrimethylsilyl bisphenol-A (method II)

Exp. No.	Method	Excess of 3a	Reaction medium	Temp. (°C)	Time (h)	Yield (%)	η_{inh} [a] (dL/g)	Reaction [b] Products
1	I	0	DMSO/Toluene	140-145	6	1	—	La, Lb, Lc
2	I	0	Sulfolane/Xylene	170-175	6	18	0.04	La, Lc
3	II	0	NMP	140-145	48	73	0.19	C, La, Lb, Lc
4	II	1%	NMP	140-145	48	85	0.20	C, La, Lb, Lc
5	II	0	NMP	165-170	48	68	0.57	C, La, Lb
6	II	1%	NMP	165-170	48	71	0.81[c]	C

[a] ***measured at 20°C with c = 2 g/L in***

[b] ***as revealed by MALDI-TOF mass spectrometry below 5 000 Da***

[c] ***M_n = 74 000 Da, M_w = 170 000 Da by PS-calibrated SEC in THF***

When **3b** was used as monomer, in average the viscosity values were somewhat lower than those obtained with **3a** due to a slightly lower reactivity. This lower electrophlicity is obviously a result of the positive inductive effect of the tert.butyl group perhaps combined with a somewhat higher steric demand.

However, the trends were the same and the highest viscosity value was found for the sample prepared with 1% excess of the difluoromonomer at 165°C (No. 10, Table 4). Whether the excess of the difluoromonomer is needed to compensate for side reactions or for a higher volatility relative to that of the silylated bisphenol-A is not clear at this time, but this effect was also observed for syntheses of poly(ether sulfone)s from silylated bisphenol-A [153]. The MALDI-TOF m.s. of the poly(ether ketone) **2b** with the highest molecular weight (No. 10, Table 4) still displayed the mass peaks of all three linear species **La**, **Lb** and **Lc** as demonstrated in Figure 10. According to this theory this spectroscopic result confirms that the conversion was far from complete and that the lower molecular weight was not a consequence of more intensive cyclization. Therefore, this result confirms that the reactivity of **3b** was, indeed, lower than that of **3a**. Together with the results of the first section, the order of reactivity of all three electrophilic monomers may be given as:

4,4'-DFBP > 3a > 3b.

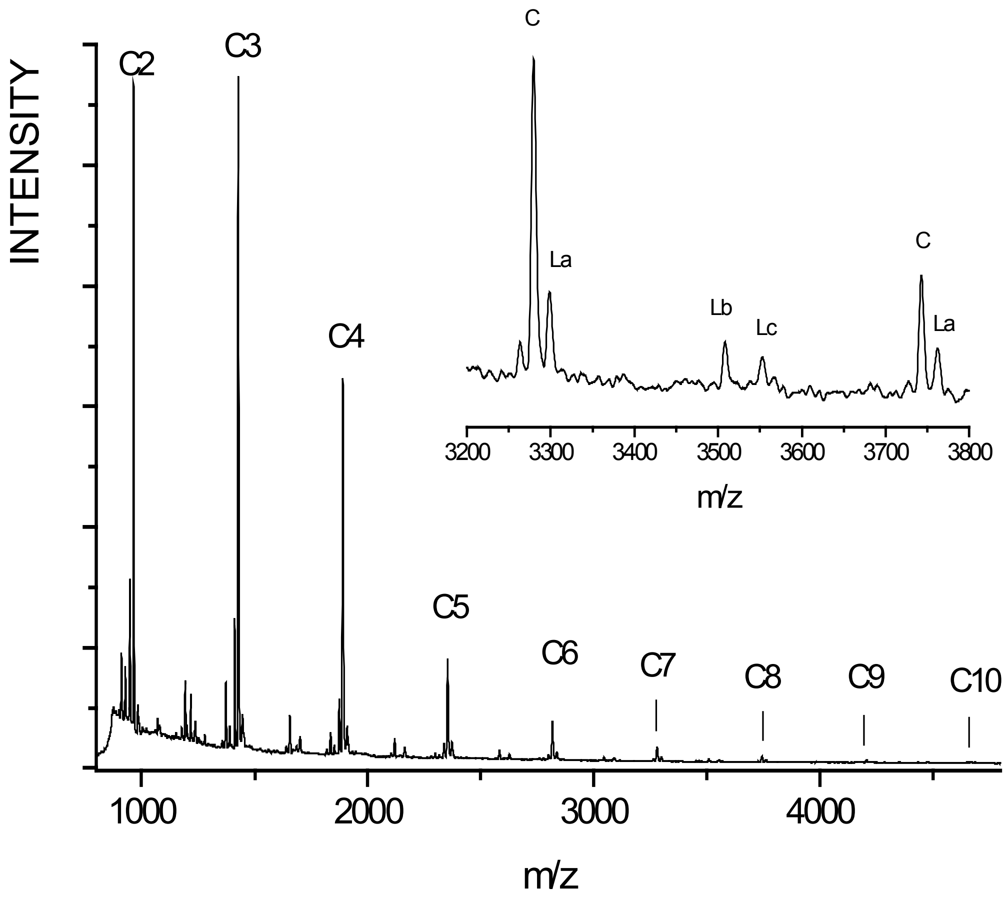


Fig 10. MALDI-TOF mass spectrum of the poly(ether ketone) No. 10, Table 4, prepared from silylated bisphenol-A and 2,6-difluoro-4'-tert.butylbenzophenone.

Table 4. Polycondensations of 2,6-difluoro-4'-t.butylbenzophenone 3b with bisphenol-A (method I) or with bistrimethylsilylbisphenol-A (method II).

Exp. No.	Method	Excess of 3b	Reaction medium	Temp. (°C)	Time (h)	Yield (%)	η_{inh} a) (dL/g)	Reaction b) products
1	**I**	**0**	**DMSO/Toluene**	**140**	**6**	**13**	**—**	**——**
2	**I**	**0**	**DMSO/Xylene**	**170**	**6**	**48**	**0.08**	**C, La, Lb, Lc**
3	**I**	**0**	**Sulfolane/Toluene**	**170**	**6**	**sirupy**	**oligomers**	**——**
4	**I**	**0**	**Sulfolane/Xylene**	**190**	**6**	**sirupy**	**oligomers**	**——**
5	**I**	**0**	**NMP/Toluene**	**140**	**6**	**40**	**0.05**	**——**
6	**II**	**0**	**NMP**	**140-145**	**48**	**68**	**0.14**	**C, La, Lb, Lc**
7	**II** c	**0**	**NMP**	**140-145**	**48**	**77**	**0.38**	**C, La, Lb, Lc**
8	**II**	**1%**	**NMP**	**140-145**	**48**	**66**	**0.15**	**C, La, Lb, Lc**
9	**II**c	**0**	**NMP**	**165-170**	**48**	**77**	**0.35**	**C, La, Lb, Lc**
10	**II**c	**1%**	**NMP**	**165-170**	**48**	**80**	**0.42**d	**C, La, Lb, Lc**

a) measured at 20°C with c = 2 g/L in CH_2Cl_2

b) as revealed by MALDI-TOF mass spectrometry below 5 000 Da

c) the monomer 3b was recrystallized prior to the polycondensation

d) M_n = 43 000 Da, M_w = 81 000 Da by PS-calibrated SEC in THF

3.1.1.5 Molecular weight distributions

Three samples with relatively high molecular weights (No. 5, Table 1, No. 6, Table 3 and No. 10, Table 4) were subjected to SEC measurements in tetrahydrofuran. Calibration with commercial polystyrene standards yielded the high molecular weight data presented in the footnotes of Tables 1, 3 and 4. Even if this calibration is not highly accurate, it confirms the formation of high molecular weights under optimized reaction conditions. Particularly interesting is the finding that all three elution curves display a tendency towards a bimodal mass distribution with a first (weaker) maximum in the mass range of the cyclic oligomers below 5000 Da (Figure 11). Similar and even more pronounced bimodal mass distributions were recently found for various polycondensations under condition favoring cyclization. In kinetically controlled polycondensations the cyclic oligomers are stable over the entire course of the polycondensation and, thus form necessarily a first maximum in the mass distribution. In contrast, the linear oligomers disappear completely when the conversion approaches 100%, regardless if the classical theory or the new theory of step-growth polymerization is considered [4].

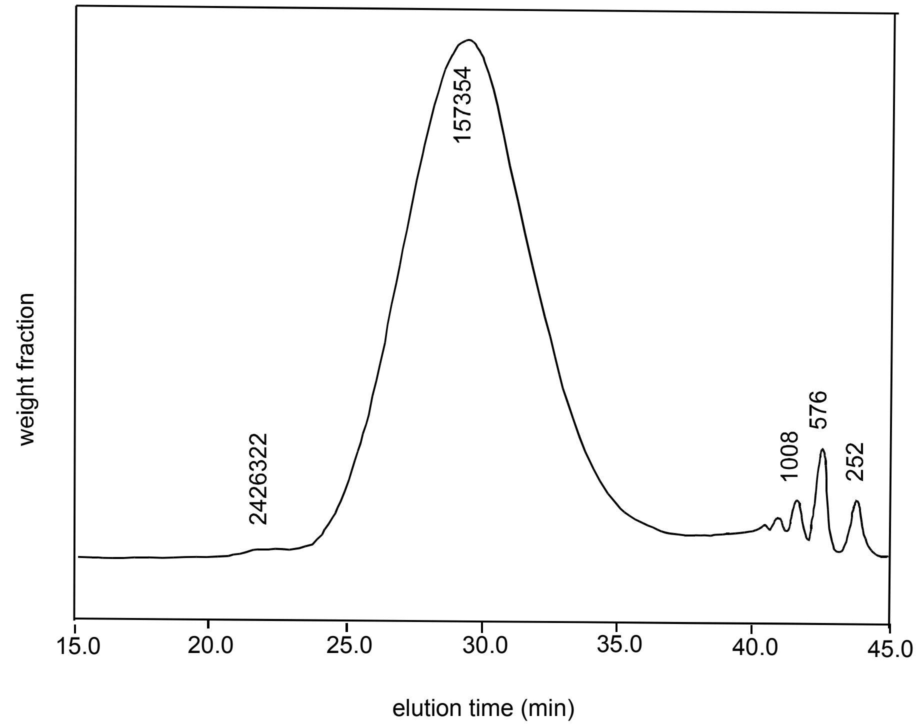


Fig 11. SEC elution curve of the poly(ether ketone) prepared from silylated bisphenol-A and 2,6-DFBP (No. 6, Table 3).

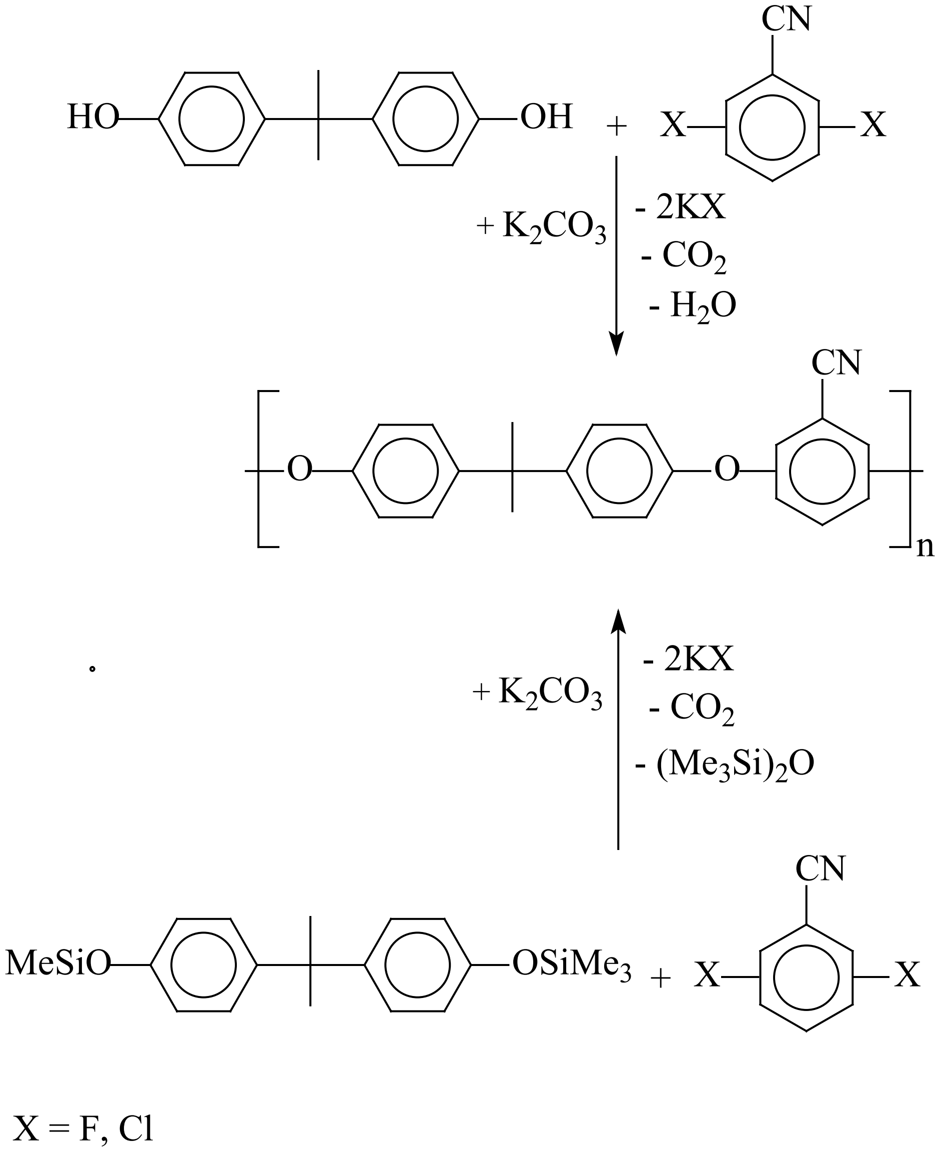
3.1.2 Cyclic poly(benzonitrile ether)s

3.1.2.1 Introduction

Poly(benzonitrile ether)s also named poly(cyanoaryl ether)s represent an interesting class of thermostable aromatic polyethers characterized by pendant nitrile groups. These nitrile groups may interact with polar surfaces and allow a variety of modifications such as alkylation and hydrolysis. The first syntheses of poly(benzonitrile ether)s were disclaimed in a patent [181]. The presence of a strong electron withdrawing group (nitrile group) makes the nucleophilic substitution easier by activation of the neighboring C-F groups. As a consequence, two different synthetic methods have been described so far. The first method (methode I) is the polycondensation of a free diphenol with a dichloro- (or dinitro-) benzonitrile in a polar solvent using K_2CO_3 as catalyst and halogen acceptor [181,182]. The second approach is based on the polycondensation of silylated diphenols with difluorobenzonitriles in the melt using CsF as catalyst [183,184]. In the present work the polycondensation of silylated diphenols was performed in a polar solvent with K_2CO_3 as promoter (method II) . this work had the purpose to compare two synthetic methods (methods I and II) with respect to the formation of cyclic oligoethers and cyclic polyethers (Scheme 17). The polycondensation of free bisphenol-A and silylated bisphenol-A should be compared under similar conditions with respect to the extent of cyclization. Four different dihalobenzonitriles, 2,6-dichloro-, 2,6-difluoro-, 2,4-difluoro- and 3,5-difluorobenzonitrile were used as electrophilic reaction partners and compared with regard to their reactivity and cyclization tendency. Therefore, this work was designed as a further experimental investigation to check validity of the new theory of KCP. Furthermore, the isolation of cyclic poly(benzonitrile ether)s is of interest for a variety of chemical and physical studies.

3.1.2.2 Polycondensation of bisphenol-A in sulfolane

In the above studies dealing with syntheses of poly(ether ketone)s from bisphenol-A or 4-tert.-butylcatechol, it was found that polycondensations in sulfolane have a particularly high tendency to yield cyclic oligomers and cyclic polymers. Rather clean polycondensations were observed yielding low molar mass cyclic poly(ether ketone)s due to the limitation of the chain growth by cyclization. Therefore, a first series of polycondensations was conducted in such a way that sulfolane was used as reaction medium in combination with toluene or xylene for the azeotropic removal of the liberated water. The change from toluene to xylene allow for higher reaction temperature. The results listed in Table 5 indeed demonstrate that slightly higher viscosity values were obtained with xylene, suggesting that the conversion was closer to completion at the higher temperature. A particular problem of small scale experiments is the maintenance of an ideal stoichiometry. In addition to a perfect weighing of the monomers, the different volatilities of the reaction partners may become a problem in experiments conducted at temperatures above 120°C. Nonetheless the MALDI-TOF m.s. of the polyethers listed in Table 5 indicated that the stoichiometry was close to the ideal case. Apparently due to rapid reactions the high volatilities of the dihalobenzonitriles (relative to bisphenol-A) did not significantly affect the stoichiometry.



X = F, Cl

Scheme 17

Table 5. Polycondensations of bisphenol-A with 2,6-dichloro- or 2,6-difluorobenzonitrile in sulfolane

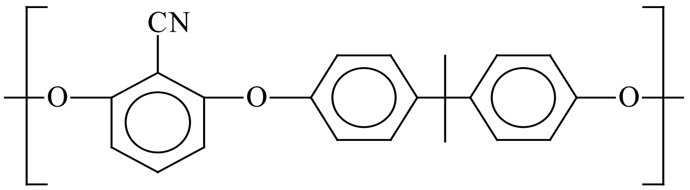
Exp. No.	**Benzonitrile Derivative**	**Cosolvent**	**Temp. (°C)**	**Yield (%)**	**η_{inh} a) (dL(g)**	**M_{ci} b) (Da)**	**M_n c) (Da)**	**M_w c) (Da)**
1	**2,6-Dichloro-**	**Toluene**	**150**	**56**	**0.05**	**< 1 000**	**–**	**–**
2	**2,6-Dichloro-**	**Xylene**	**170**	**55**	**0.13**	**~ 2 500**	**4 000**	**9 000**
3	**2,6-Difluoro-**	**Toluene**	**150**	**80**	**0.41**	**> 7 000**	**30 000**	**58 000**
4	**2,6-Difluoro-**	**Xylene**	**170**	**82**	**0.50**	**> 8 000**	**40 000**	**74 000**
5	**2,4-Difluoro-**	**Xylene**	**170**	**60**	**0.10**	**> 12 000**	**d)**	**d)**
6	**3,5-Difluoro-**	**Xylene**	**170**	**61**	**0.12**	**~ 2 300**	**3 200**	**6 600**

a) ***measured at 20°C with c = 2 g/L in CH_2Cl_2***

b) ***mass where cycles and linear chains show equal peak intensities in the MALDI-TOF ms***

c) ***PS-calibrated SEC measurements in THF***

d) ***Bimodal, see Figure 15b***



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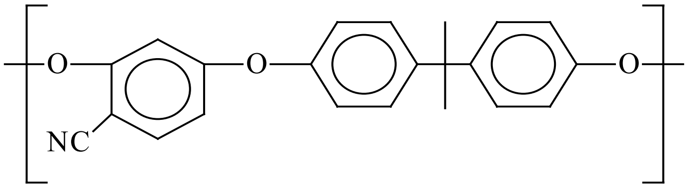

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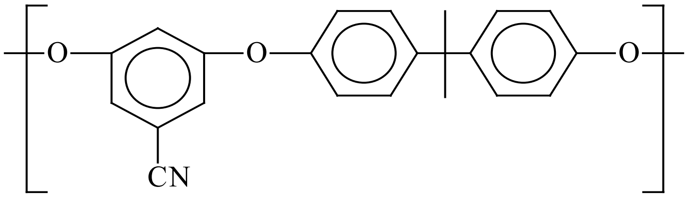

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When 2,6-dichlorobenzonitrile was used as comonomer low inherent viscosities were found (Nos. 1, 2, Table 5). The MALDI-TOF m.s. revealed the reasons for the low molecular weights. As illustrated in the mass spectrum of Figure 12 the peak pattern consists of four peaks representing cycles and the four linear chains **La**, **Lb** and **Lc** (scheme 18). These linear species represent the three possible combinations of end groups which are typical for an incomplete polycondensation of "a-a" and "b-b" monomers. Therefore, the MALDI-TOF m.s. of the polyethers Nos. 1 and 2, Table 5, demonstrate that in these cases the conversions were far from completion.

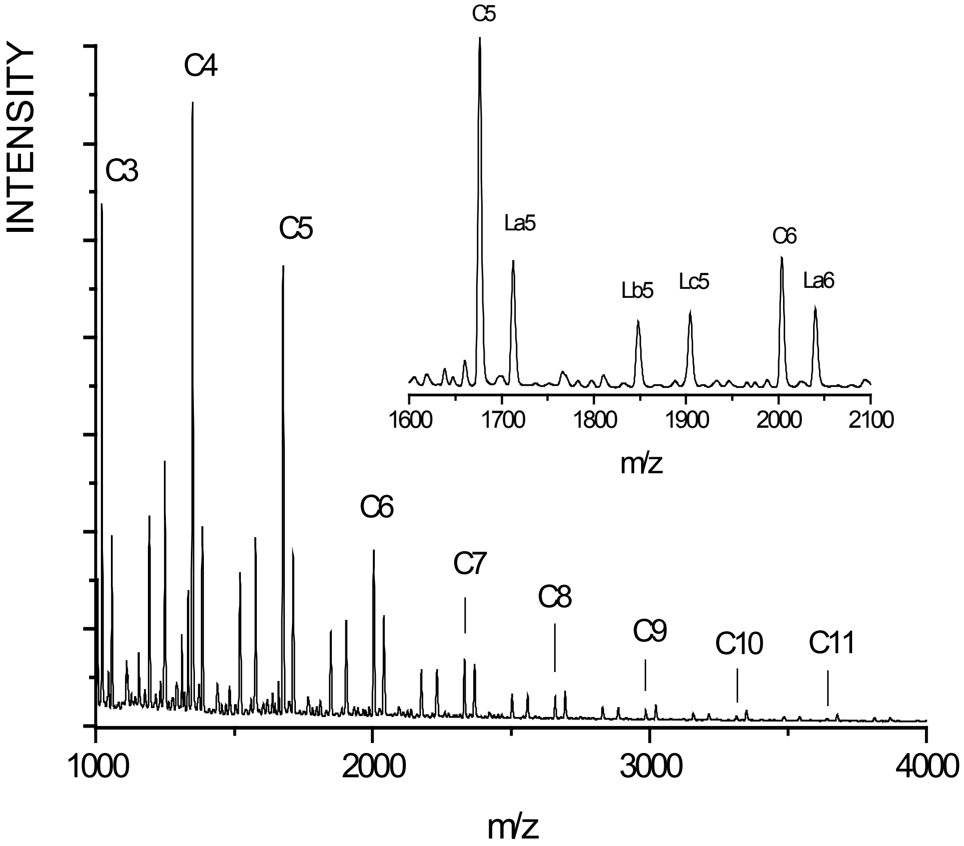
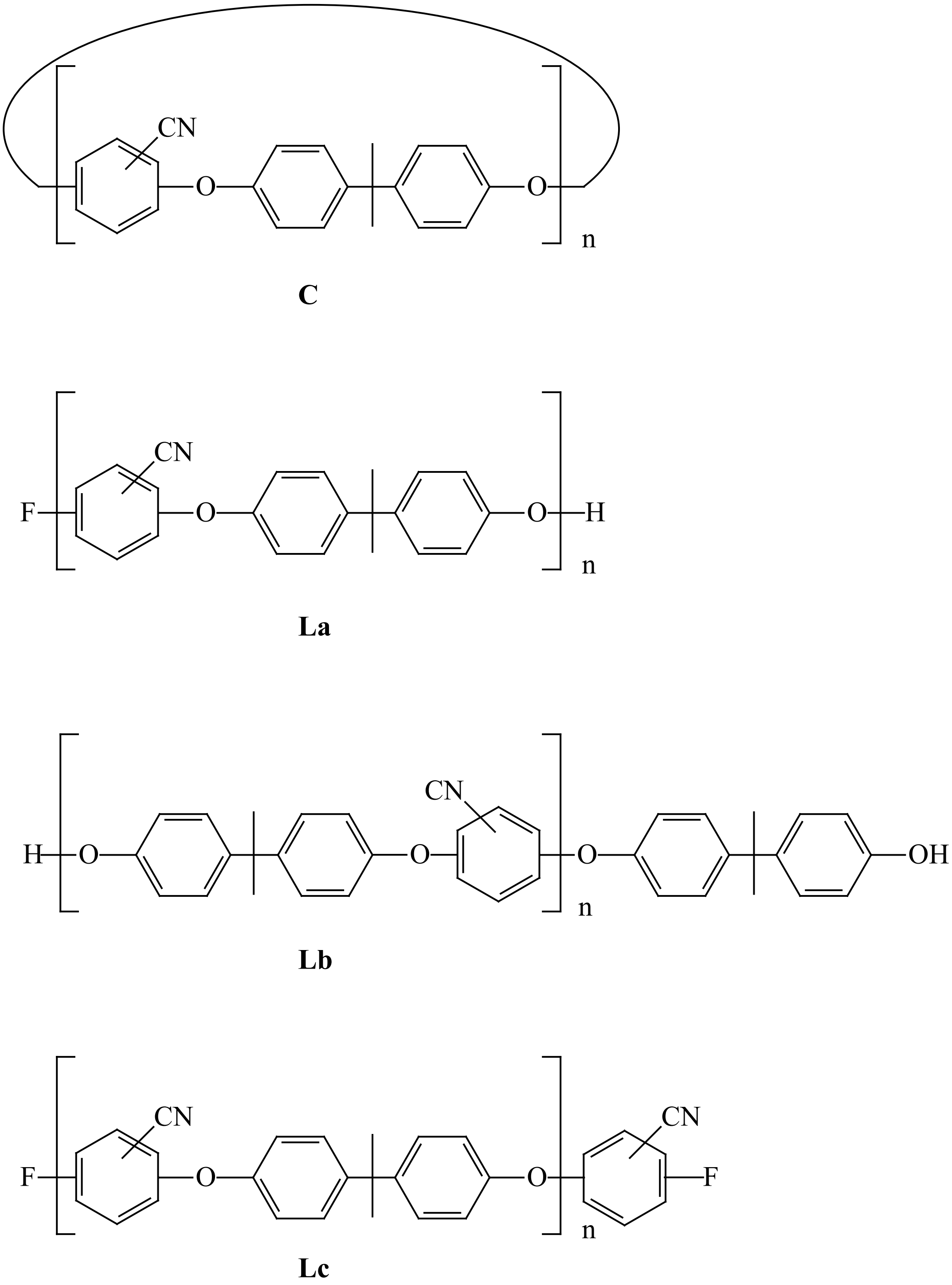


Fig 12. MALDI-TOF mass spectrum of polyether (No. 2, Table 5) prepared from 2,6-dichlorobenzonitrile in sulfolane/xylene



Scheme 18

With the more reactive 2,6-difluorobenzonitrile significantly higher molecular weights were obtained. According to the recent theory of polycondensation [4,37,42,153] higher conversions not only favor higher molecular weights, but also a higher ratio of cyclization. In agreement with this theory the m.s. of Figure 13 demonstrates for experiment No. 4, Table 5, that cycles were the main reaction product up to the technical limit of this spectrum around 11 000 Da. Particularly, interesting results were obtained in comparison with the polycondensation of 2,4-difluorobenzonitrile, because a low molar mass product was obtained in case of 2,4-difluorobenzonitrile, although its reactivity should be considerably higher than that of the 2,6-dichlorobenzonitrile. Nonetheless, the inherent viscosity indicates that the polymers of exp. Nos. 2 and 5 possess similar molar masses. Despite this similarity the MALDI-TOF m.s. presented in Figure 14 proved that the polyether **5** prepared in sulfolane consisted almost completely of cycles. Hence the chain growth was not limited by incomplete conversion, but by intensive cyclization. This finding means that the polycondensation of the 2,4-difluorobenzonitrile involves a much higher cyclization tendency than the polycondensations of the 2,6- or 3,5-isomers, although all three isomers have the fluoro-atoms in meta position relative to each other. A satisfactory explanation of this effect cannot be forwarded at this time. However, this result demonstrates that a proper understanding of correlations between reaction conditions and chain growth requires information about cyclization tendencies. Despite a slightly higher viscosity value relative to the polyether of 2,4-difluorobenzonitrile, the chain growth of the polyether derived from 3,5-difluorobenzonitrile (structure **6**) was limited by incomplete conversion and not so much by cyclization. The MALDI-TOF revealed in addition to the predominant peaks of cycles, the peaks of **Lb** and **Lc** chains. This result is reasonable considering that the reactivity of fluoroatoms in *meta* position to the nitrile group should be lower than those in ortho or para position. In summary, these results demonstrate that when the reactivity of the dihalobenzonitrile suffices for high conversions, high yields of cycles can be obtained in sulfolane as reaction medium.

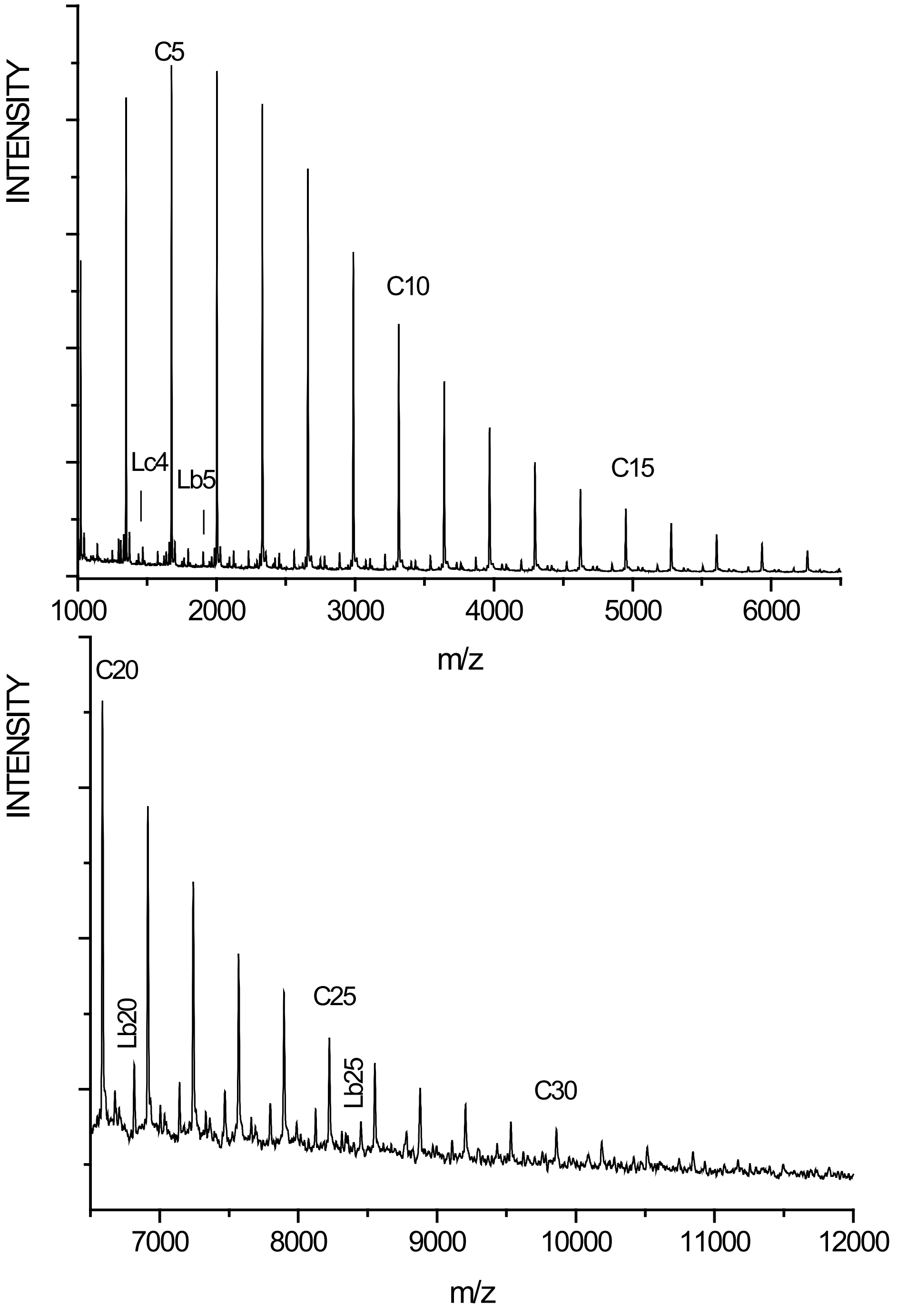


Fig 13. MALDI-TOF mass spectrum of a polyether (4, Table 5) prepared from 2,6- difluorobenzonitrile in sulfolane/xylene

3.1.2.3 Polycondensations of silylated bisphenol-A

The usefulness of silylated bisphenol-A for syntheses of poly(benzonitrile ether)s from 2,6-dichloro- or 2,6-difluorobenzonitrile has been demonstrated in literature [183,184]. With 2,6-difluorobenzonitrile these polycondensations were conducted in bulk at temperatures up to 270°C using CsF as catalyst. Under these conditions, equilibration by CsF-catalyzed cleavage of ether bonds is expected, so that the entire course of the polycondensation and the formation of cycles occur under thermodynamic controlled condition. In the present work, all polycondensations of silylated bisphenol-A were conducted at temperatures $\leq$ 170°C with K_2CO_3 as catalyst to establish a kinetically controlled conditions and to allow for a comparison with the experiments conducted in sulfolane. From numerous syntheses of poly(ether sulfone)s [153,154] and poly(ether ketone)s in the above work , it was concluded that NMP is the best reaction medium for K_2CO_3 promoted polycondensations of silylated diphenols, and thus, all experiments with silylated bisphenol-A studied in this work were performed in NMP. All polycondensations of silylated bisphenol-A conducted with 2,6-dihalobenzonitriles were compiled in Table 6. With 2,6-dichlorobenzonitrile significantly higher molecular weights were obtained than in sulfolane (Nos. 1 + 2, in Tables 5 and 6). This result fits with a previous study [183] where analogous polycondensations were performed in NMP at 180°C, and η_{inh} values up to 0.72 dL/g were determined. In agreement with Kricheldorf new theory of polycondensation the higher molecular weights were combined with higher fractions of cycles. In contrast to the m.s. of Figure 12 only mass peaks of cycles were detectable (up to 6 000 Da) in the m.s. of the samples Nos. 1 and 2, Table 6. Polycondensations of 2,6-difluorobenzonitrile were studied at three different temperatures. At 100°C (Nos. 3 and 4, Table 6) moderate molecular weights were obtained which were comparable to those obtained in sulfolane at 150-170°C (Nos. 3 and 4, Table 5). At higher temperatures even higher molecular weights were achieved with a record at 165°C (No. 8, Table 6). As expected for such high molecular weights, only cycles were detected in the MALDI-TOF m.s. one reason why the experiments with silylated bisphenol-A in NMP yielded higher molecular weights than polycondensations of free diphenols, is certainly the higher concentration of the reaction partners.

Table 6. Polycondensations of silylated bisphenol-A with 2,6-dichloro- or 2,6-difluorobenzonitrile in NMP.

Exp. No.	**Benzonitrile Derivative**	**Excess of Benzonitrile**	**Temp. (°C)**	**Time (h)**	**Yield (%)**	**η_{inh} [a] (dL(g)**	**M_n [b] (Da)**	**M_w [b] (Da)**
1	**2,6-Dichloro-**	—	**165**	**24**	**58**	**0.52**	**30 000**	**57 000**
2	**2,6-Dichloro-**	—	**165**	**48**	**59**	**0.48**	–	–
3	**2,6-Difluoro-**	—	**100**	**48**	**66**	**0.41**	**25 000**	**46 000**
4	**2,6-Difluoro-**	**1 mol%**	**100**	**48**	**68**	**0.57**	**35 000**	**70 000**
5	**2,6-Difluoro-**	—	**145**	**24**	**68**	**1.30**	**130 000**	**310 000**
6	**2,6-Difluoro-**	**1 mol%**	**145**	**24**	**70**	**0.98**	**70 000**	**205 000**
7	**2,6-Difluoro-[c]**	**1 mol%**	**145**	**24**	**50**	**1.17**	–	–
8	**2,6-Difluoro-**	—	**165**	**24**	**70**	**1.40**	**150 000**	**350 000**

[a] ***measured at 20°C with c = 2 g/L in CH_2Cl_2***

[b] ***PS-calibrated SEC measurements in THF***

[c] ***2,6-difluorobenzonitrile was recrystallized from ligroin***

[d] ***60 mL of NMP were used for comparison with experiments Nos. 3 and 4 of Table.5.***

In the case of 2,6-dichlorobenzonitrile, the longer reaction time may also play a positive role. Four polycondensations were conducted with 2,4-difluoro- and 3,5-difluorobenzonitrile (Table 7). The resulting molecular weights were higher than those obtained in sulfolane (Nos. 5+6, Table 5), but they were clearly lower than the best values achieved with the 2,6-isomer under similar conditions (Nos. 4 and 8, Table 6). Interestingly, the polyethers prepared from 2,4-difluorobenzonitrile in NMP (Nos. 1 + 2, Table 7) showed a lower tendency of cyclization than the product isolated from sulfolane (No. 5, Table 5) despite considerably higher molecular weights. As explained above a similar trend was found for syntheses of poly(ether ketone)s. Why polycondensations in sulfolane may involve a particularly high cyclization tendency cannot be explained at this time.

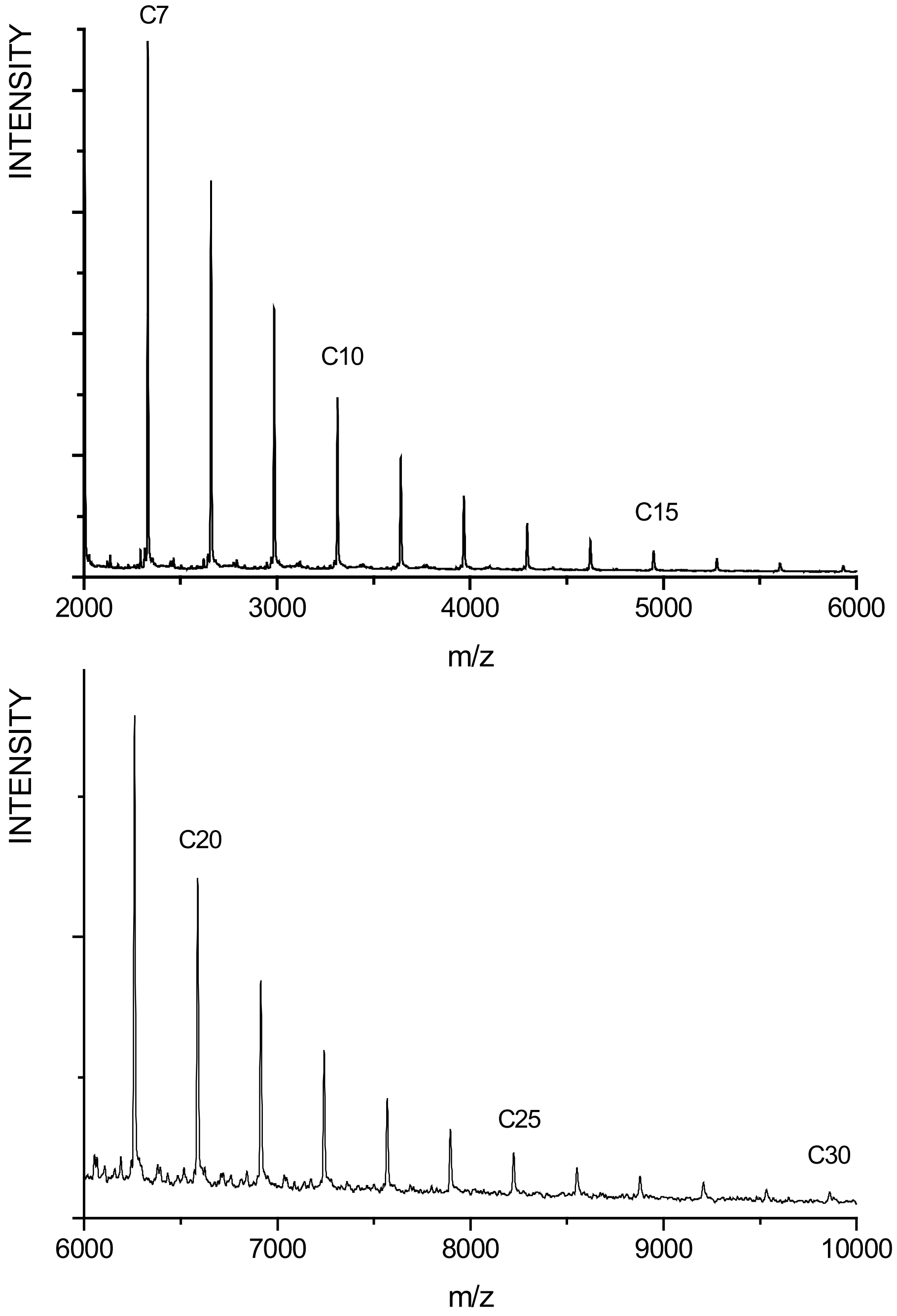


Fig 14. MALDI-TOF mass spectrum **of the polyether (No. 8, Table 6) prepared from 2,6-difluorobenzonitrile in NMP**

Table 7. Polycondensations of silylated bisphenol-A with 2,4-dichloro- or 3,5-difluorobenzonitrile in NMP at 165°C / 24 h

Exp. No.	Benzonitrile Derivative	Excess of Benzonitrile	Yield (%)	η_{inh}[a)] (dL(g)	Composition	M_{ei}[b)] (Da)
1	**2,4- Difluoro-**	**—**	**80**	**0.36**	**C + La + Lc**	**~ 11 000**
2	**2,4- Difluoro-**	**1 mol%**	**65**	**0.56**	**C + Lc**	**> 10 000**
3	**3,5-Difluoro-**	**—**	**83**	**0.48**	**C + La + Lb**	**~ 5 600**
4	**3,5-Difluoro-**	**1 mol%**	**partially**	**crossl.**	**C + Lc**	**(~ 10 000)**

[a)] ***measured at 20°C with c = 2 g/L in CH_2Cl_2***

[b)] ***mass where cycles and linear chains show identical peak intensities***

3.1.2.4 Molecular weight distributions

Number average molecular weights (M_ns) and weight averages (M_ws) were determined via SEC measurements in tetrahydrofuran calibrated with commercial polystyrene standards (Tables 5 and 6). The rather high M_n and M_w values combined with moderate solution viscosities suggest that either the calibration with polystyrene overestimates the real molecular weights or the solutions of the polyethers in dichloromethane are close to the θ-conditions. In the case of poly(ether sulfone)s it was found [153] that M_w values derived from polystyrene calibration are in good agreement with those determined by means of light scattering measurements. Furthermore, it was found that the solutions in CH_2Cl_2 or $CHCl_3$ are indeed close to θ-conditions [179]. Therefore, solutions of poly(benzonitrile ether)s are likely to obey the same trends. More interesting than the accuracy of the M_n and M_w data are molecular weight distributions. According to the classical theory of step growth polymerizations [185] the frequency distribution (eq.(2)) and the mass distribution (eq.(3)) are monomodal. However, recently it was found for polycarbonates[41,186], poly(ether sulfone)s [153] and poly(ether ketone)s that the mass distributions may have a bimodal character when the reaction conditions favor cyclization. In the present work similar trends were observed. The mass distributions as presented by the SEC elution curves had a monomodal character with polydispersities in the range of 1.9-3.0 when the content of cycles was relatively low. However, in cases of high cyclization tendency (what is particularly true for sample No. 7, Table 5) a clear trend towards a bimodal mass distribution was observed (Figure 15a and 15b). Clearly, the first maximum (which is absent in the classical MWD of eq. (2)) is due to the presence of a large fraction of cyclic oligomers. Therefore, it is now obvious for a larger number of polycondensates and polycondensation methods that the classical theories of molecular weight distribution are not valid any more, when intensive cyclization is favored under the given reaction conditions.

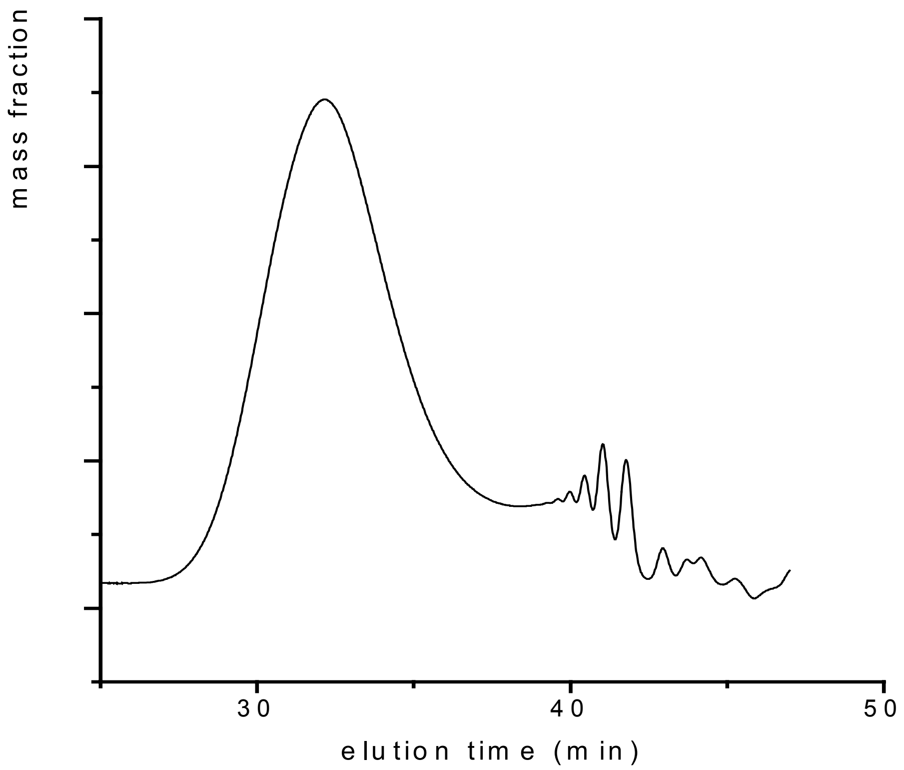


Fig 15a. SEC elution curves of poly(ether) 4 (3, Table 5)

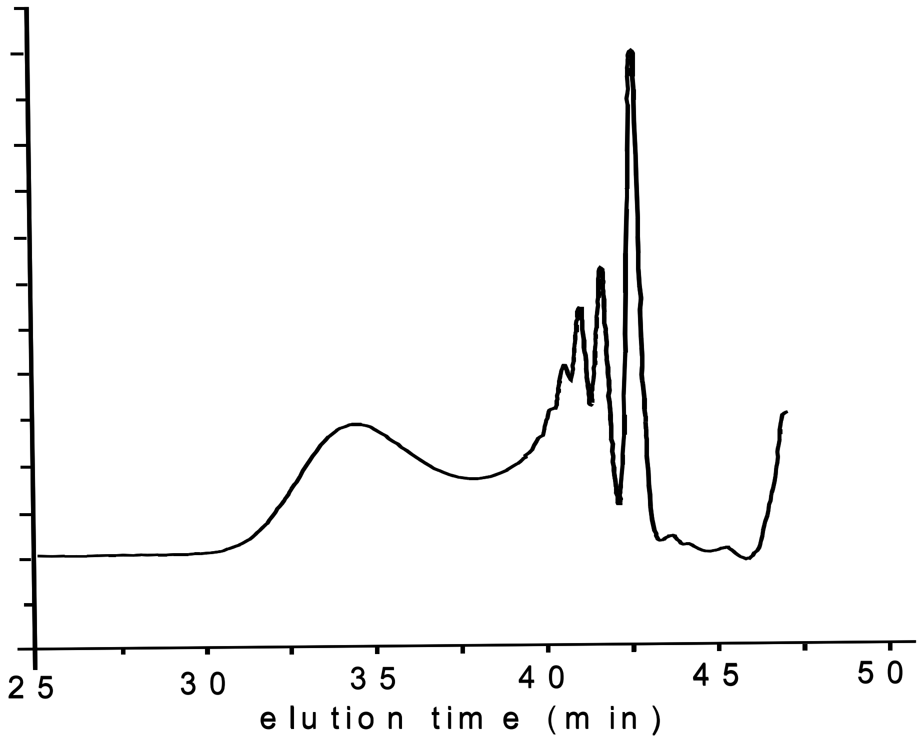


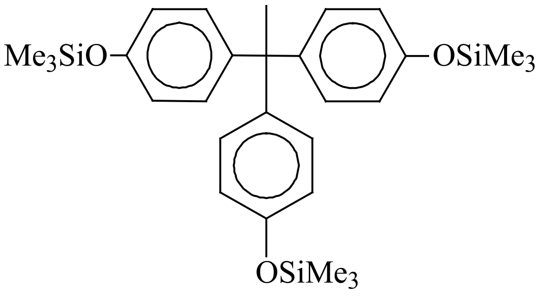
Fig 15b. SEC elution curves of poly(ether) 5 (5, Table 5)

3.1.3 Poly(pyridine ether)s

3.1.3.1 Introduction

Poly(pyridine ether)s could be used for the preparation of membrane, which bases particularly on the fact that pyridine group enables a variation of permeability. In this respect the pyridine units may react as ligands for heavy metal ions, and the hydrophilicity can be varied by protonation or quaternization of pyridine ring. Nevertheless, with the exception of poly(vinyl pyridine)s, polymers containing pyridine units have not attracted much interest, although the high chemical stability and nucleophilicity, which render pyridine moieties attractive as a building blocks. In 1987 the first synthesis and characterization of poly(pyridine ether)s was reported [187] and to the best of our knowledge, two more papers [188,189] have meanwhile appeared. In these papers, the poly(pyridine ether)s were prepared by polycondensation of silylated diphenols with 2,6-dichloro or 2,6-difluoropyridine either in bulk [188] or in solution [189]. The polycondensation in bulk (catalyzed by CsF) yielded moderate to high molecular weights. However, in NMP solution only low viscosities and molecular weights were obtained, despite a relatively high reaction temperature of 180-185 °C [189]. It was believed that the activation of the halo atoms by the pyridine ring does not suffice to reach high conversions. In this context, the present work had the purpose to reinvestigate polycondensations of 2,6-difluoropyridine with various silylated diphenols (structures **7-12**) in NMP as illustrated in Scheme 19. It should be elucidated if the low molecular weights obtained previously [189] were the consequence of low conversions (due to insufficient reactivity), or of extensive side reactions, or of efficient cyclization.

Syntheses of polyethers involving efficient cyclization are of particular interest, because they may allow an extension to "a_2 + b_3" or "a_2 + b_4" type polycondensations. If tri- or tetra functional phenols such as **13** or **14** are polycondensed with reactive difluoro aromats under conditions allowing for efficient cyclization, gelation may be avoided and a novel architecture, namely multicyclic polymers may be obtained. Reports [190,191] on two successful syntheses of multicyclic polyethers have been recently published and stimulate further studies of cyclization tendencies in polycondensations.



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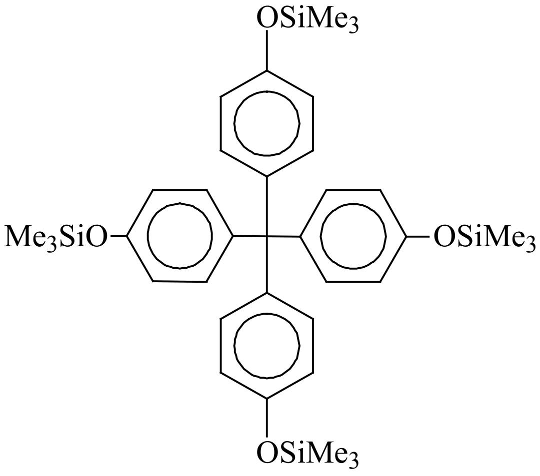

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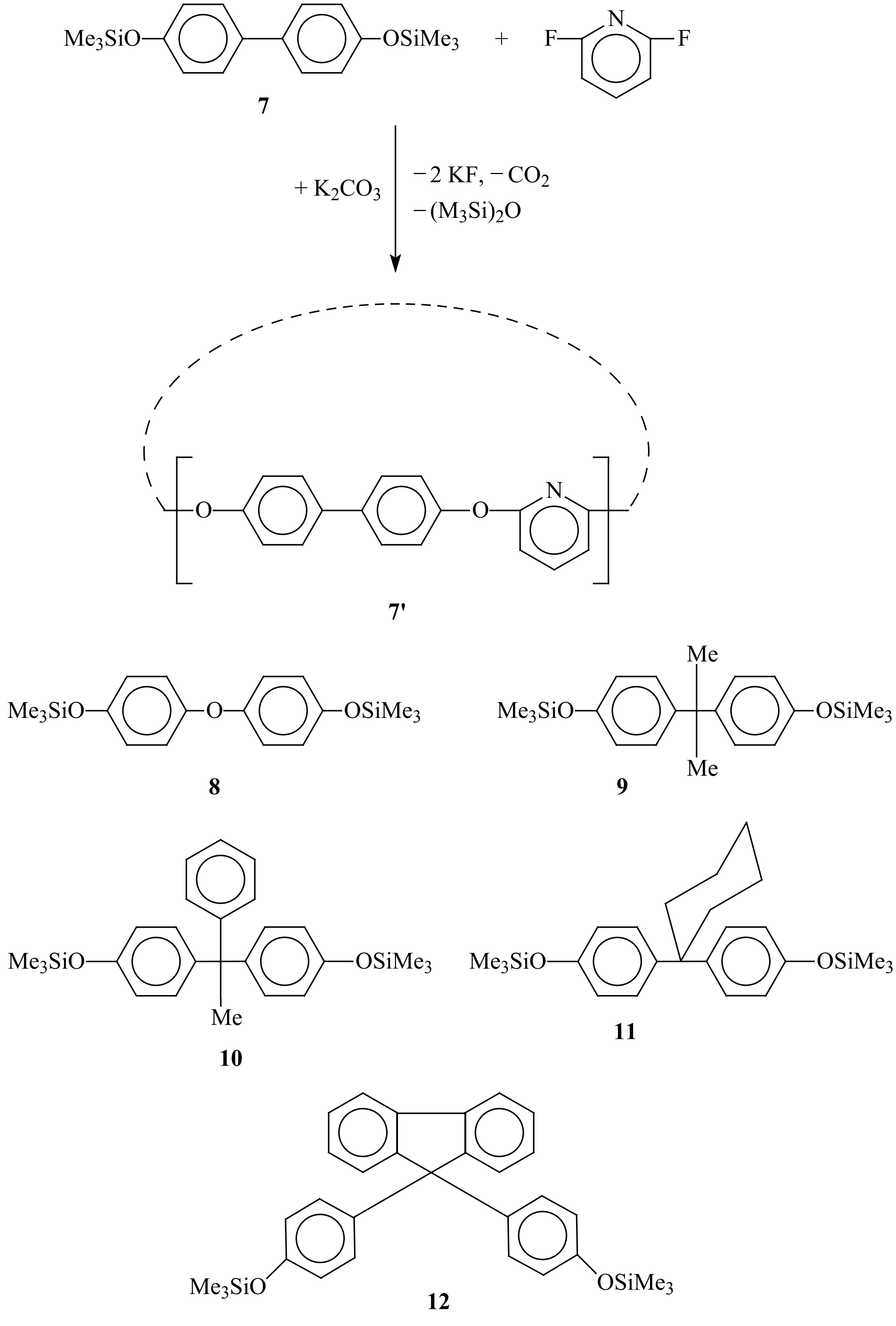
3.1.3.2 Silylation of diphenols

The silylation of diphenols was successfully accomplished in dry xylene using hexamethyldisilazane. The silylated diphenols **7**[188], **8**[188], **9**[188], **11**[192,193] and **12**[194] were mentioned in the literature, but with exception of **12** no characterization was reported. Therefore, elemental analyses and ^{1}H-NMR data of all silylated diphenol used in this work were compiled in Table 23 (exp. Part).

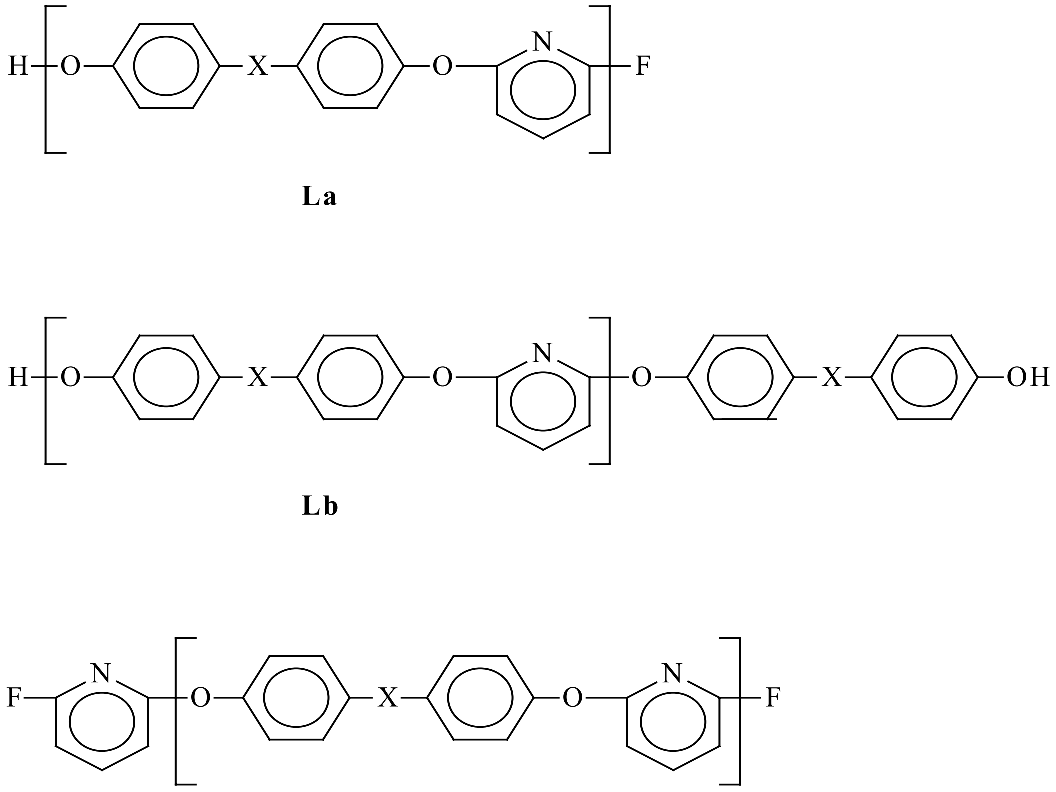
3.1.3.3 Polycondensations of silylated bisphenol-A

It was known [190,195] from numerous syntheses of polyamides, polyesters and polyethers that polycondensations of silylated monomers frequently yield cleaner polycondensation processes than the parent diamines or diphenols. Therefore, only silylated diphenols (**7-12**) were used as reaction partners of 2,6-difluoropyridine. A first series of polycondensations was performed with silylated bisphenol-A (**9**) to optimize the reaction conditions for maximum molecular weights. It was known from the above works and previous studies [152,153] that NMP is the best solvent for polycondensations of silylated diphenols. Previous syntheses of various aromatic poly(ether sulfone)s, poly(benzonitrile ether)s, and poly(ether ketone)s also suggested that a temperature around 160°C in combination with a reaction time of 48 h will suffice to achieve almost 100% conversion. Therefore, the most important parameter which had to be varied and studied systematically was the feed ratio diphenol/2,6-difluoropyridine. From previous syntheses of aromatic poly(ether sulfone)s, poly(benzonitrile ether)s, and poly(ether ketone)s it was learned that the best results were obtained with a 1 mol% excess of the electrophilic reaction partner. This situation prompted us to perform a series of polycondensations of silylated bisphenol-A with variation of the feed ratio starting out from an equimolar ratio. The results summarized in

Table 8 demonstrate that the highest molecular weight was obtained with a 2 mol% excess of 2,6-difluoropyridine (No. 3, Table 8). The MALDI-TOF mass spectra revealed that the polymers prepared without excess or with 1 mol% excess of 2,6-DFP contained considerable amounts of OH-terminated linear chains (**Lb**, Scheme 20). With a larger excess of 2,6-DFP (Nos. 4-6) chains having two C-F end groups (**Lc**) were found in the reaction products. In the mass spectrum of the optimum product (No. 3, Table 8) only peaks of cyclic polyethers were detectable (Figure 16). These results indicate that in the case of the optimum product (No. 3), the chain growth was mainly limited by cyclization and not by side reactions, by an imbalance of the stoichiometry or by incomplete conversion. The absence of **La** chains from all reaction products was another piece of evidence that the reaction condition allowed for quantitative conversions.


Me3SiO
OSiMe3
+
F
N
F
7
+ K2CO3
− 2 KF, − CO2
− (M3Si)2O
O
O
N
7'
Me3SiO
O
OSiMe3
8
Me
Me3SiO
OSiMe3
Me
9
Me3SiO
OSiMe3
Me
10
Me3SiO
OSiMe3
11
Me3SiO
OSiMe3
12

Scheme 19



Lc

Scheme 20

Table 8. Polycondensations$^{a)}$ ***of silylated bisphenol-A (9) with 2,6-difluoropyridine with variation of the feed ratio.***

Exp. No.	$\frac{9}{2{,}6-DFP}$	**Yield (%)**	η_{inh} $^{b)}$ **(dL/g)**	**Reaction products (MALDI-TOF)**
1	**1.0/1.00**	**58**	**0.12**	**C + Lb**
2	**1.0/1.01**	**60**	**0.16**	**C + Lb**
3	**1.0/1.02**	**58**	**0.31** $^{c)}$	**C (Figure 16)**
4	**1.0/1.04**	**61**	**0.22**	**C + Lc**
5	**1.0/1.06**	**59**	**0.12**	**C + Lc**
6	**1.0/1.10**	**65**	**0.06**	**C + Lc**

$^{a)}$ ***performed at 160 °C in NMP for 48 h***

$^{b)}$ ***measured at 20 °C with c = 2 g/L in*** CH_2Cl_2

$^{c)}$ $M_n \approx 2\,600$, $M_w \approx 53\,000$ ***Da from polystyrene-calibrated SEC measurements***

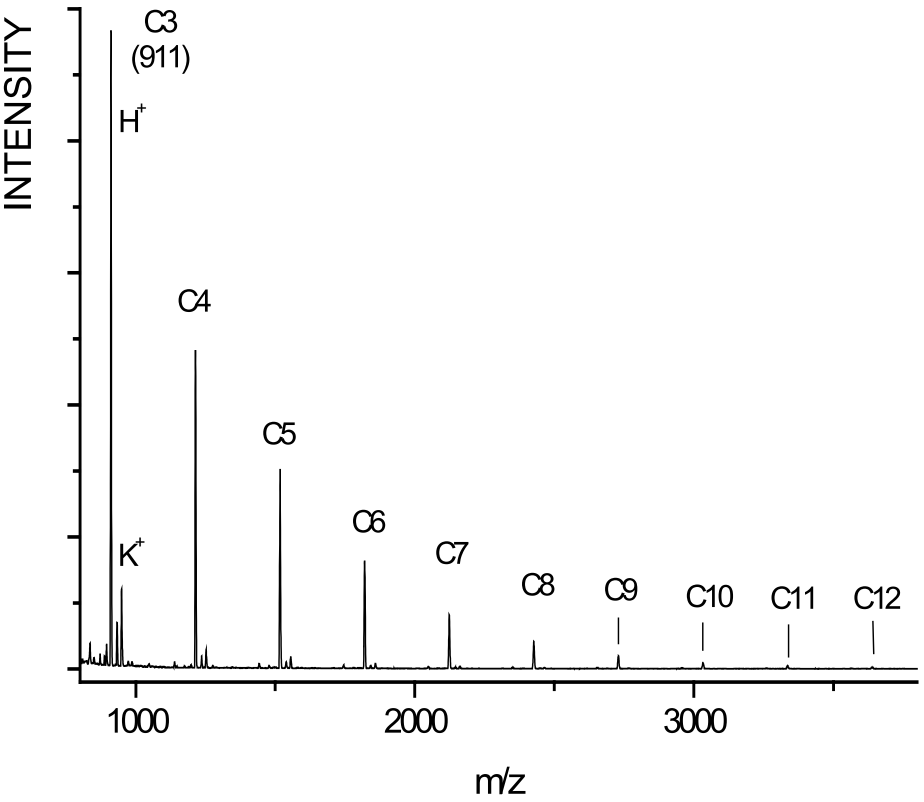


Fig 16. MALDI-TOF mass spectrum of the poly(ether pyridine) 9' (No. 8, Table 8) doped with protons.

3.1.3.4 Polycondensations of various diphenols

On the basis of the results presented above, the silylated diphenols **7**, **8**, **10**, **11** and **12** were polycondensed with 2,6-DFP in such a way that for each diphenol two or three polycondensations were conducted using 1, 2 or 3 mol% excess of 2,6-DFP. The results compiled in Table 9 demonstrated that in most cases the highest molecular weights were obtained with an excess of 2 mol% of 2,6-DFP. The MALDI-TOF mass spectra of the optimized polyethers exclusively displayed mass peaks of cycles as exemplarily illustrated in Figure 17.

Table 9. Polycondensations a) of various silylated diphenols with 2,6-difluoropyridine in NMP

Exp. No.	Silylated Diphenol	$\frac{\text{Diphenol}}{2{,}6-\text{DFP}}$	Yield (%)	η_{inh} b) (dL/g)	Reaction products (MALDI-TOF)
1	***8***	**1.0/1.01**	**66**	**0.15 b)**	**C + Lb**
2	***8***	**1.0/1.02**	**62**	**0.18 b)**	**C**
3	***10***	**1.0/1.01**	**67**	**0.14 c)**	**C d)**
4	***10***	**1.0/1.02**	**68**	**0.13 c)**	**C + Lc**
5	***10***	**1.0/1.03**	**67**	**0.13 c)**	**C + Lc**
6	***11***	**1.0/1.01**	**71**	**0.08 c)**	**C + Lb**
7	***11***	**1.0/1.02**	**73**	**0.12 c)**	**C e)**
8	***11***	**1.0/1.03**	**75**	**0.06 c)**	**C + Lc**
9	***12***	**1.0/1.01**	**74**	**0.02 b)**	**C + Lb**
10	***12***	**1.0/1.02**	**75**	**0.03 b)**	**C + Lb**
11	***12***	**1.0/1.03**	**73**	**0.12 b)**	**C**

a) 48 h at 160-165°C

b) measured at 20°C with c = 2 g/L in THF

c) measured at 20°C with c = 2 g/L in CH_2Cl_2

d $M_n \approx$ 1 550 Da, $M_w \approx$ 20 000 Da from polystyrene-calibrated SEC measurements

e) $M_n \approx$ 1 300 Da, $M_w \approx$ 15 000 Da from polystyrene-calibrated SEC measurements

Polyethers prepared with an excess of 1 mol% of 2,6-DFP contained **Lb** chains, indicating an effective deficit of 2,6-DFP in the reaction mixture. In contrast, C-F terminated **Lc**-chains were found in the reaction products prepared with 3 mol% excess of 2,6-DFP. These observations demonstrate that the mass spectra are sensitive enough to allow for the detection of 1 mol% variation of the stoichiometry. The absence of **La** chains proved again that the conversions were almost quantitative. The inherent viscosities of the optimized poly(pyridine ether)s **8'-12'** (derived from the monomers **8–12**) were measured in two ways (polyether **7'** was excluded, because it proved to be insoluble in all aprotic or weakly acidic solvents). First, a constant mass concentration of 2 g/L was used in agreement with almost all of our previous works. The low inherent viscosities found in all cases indicate low molecular weights. For instance, inherent viscosities in the range of 0.6-1.0 dL/g were obtained for optimized poly(ether sulfone)s [152], and our above work concerned with poly(ether ketone)s and poly(benzonitrile ether)s prepared under quite similar reaction conditions. Second, solutions containing equimolar concentrations of repeating units were measured. This second series of viscosities should allow for rough comparison of the average chain lengths or ring sizes. The comparison suggests that the average ring size decreased in the order

8'> 9'> 10', 11', 12'

Since cyclization was the limiting factor of the chain growth of the optimized polyethers, the order of ring sizes necessarily represents the cyclization tendencies. This order looks reasonable, because the bond angle of the ether group in **9** and **9'** is wider (120-124°) than of the other soluble polyethers (109-111°) and because the cyclic substituents of **11** (**11**') and **12** (**12**') certainly favor cyclization.

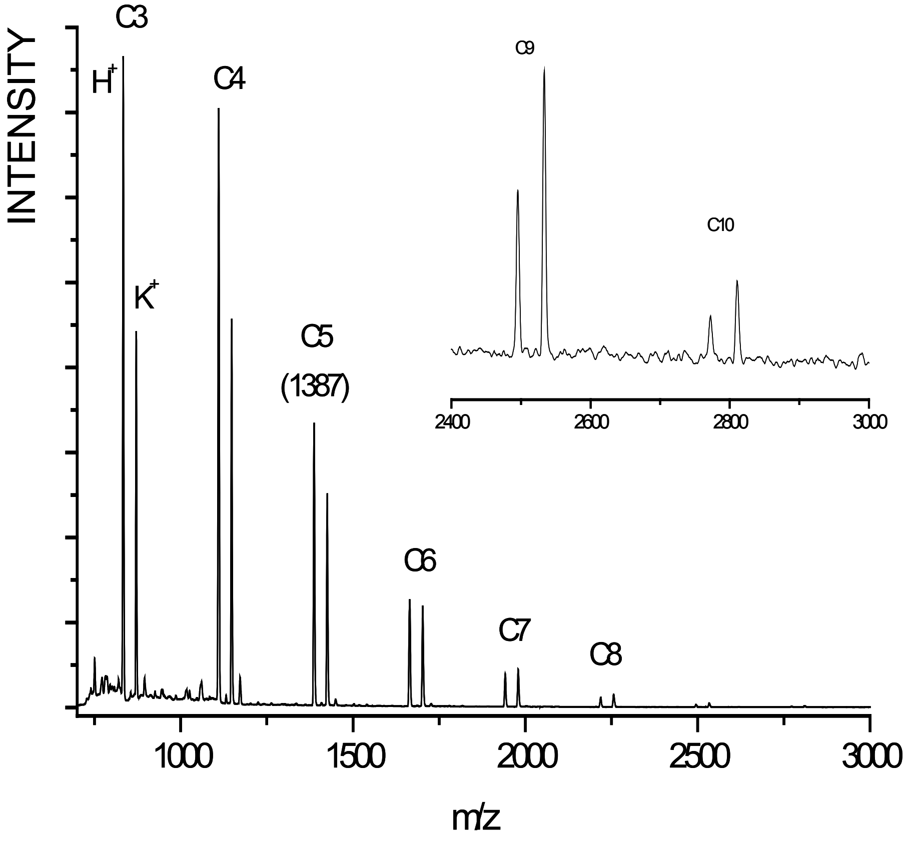


Fig 17. MALDI-TOF mass spectrum of the poly(pyridine ether) 8' (No. 2, Table 9) doped with $K^{\oplus}$ trifluoroacetate.

3.1.3.5 Molecular weight distributions

SEC measurements were conducted of those polyethers soluble in chloroform (**9'**, No. 3, Table 8, **10'**, No. 3, Table 9 and **11'**, No. 7, Table 9). The number average (M_n) and weight average (M_w) molecular weights thus obtained were listed in the footnotes of Tables 8 and 9. Although the calibration with polystyrene is possibly not highly accurate, these SEC measurements contributed two useful of informations. First, the M_n values were low in agreement with the low inherent viscosities. Second, they evidenced bimodal mass distributions with high polydispersities, as exemplarily illustrated in figure 18. Such bimodal mass distributions in combination with monomodal frequency distributions were also found for the other classes of aromatic polethers with a high content of cyclic oligomers and polymers. In his classical theory of polycondensations, Flory [6,12] has calculated monomodal mass distributions along with a polydispersity of 2.0. However, this classical theory ignored the role of cyclization and all oligomers and low molar mass polymers disappear when the conversion approaches 100%. In real kinetically controlled polycondensations (KCPs) cycles are formed which are stable inert species which do not vanish, regardless of the conversion. Therefore, a maximum resulting from the cyclic oligomers appears in both frequency and mass distributions. The second maximum in the mass distribution is a normal consequence of the high molar mass chains as demonstrated by Flory.

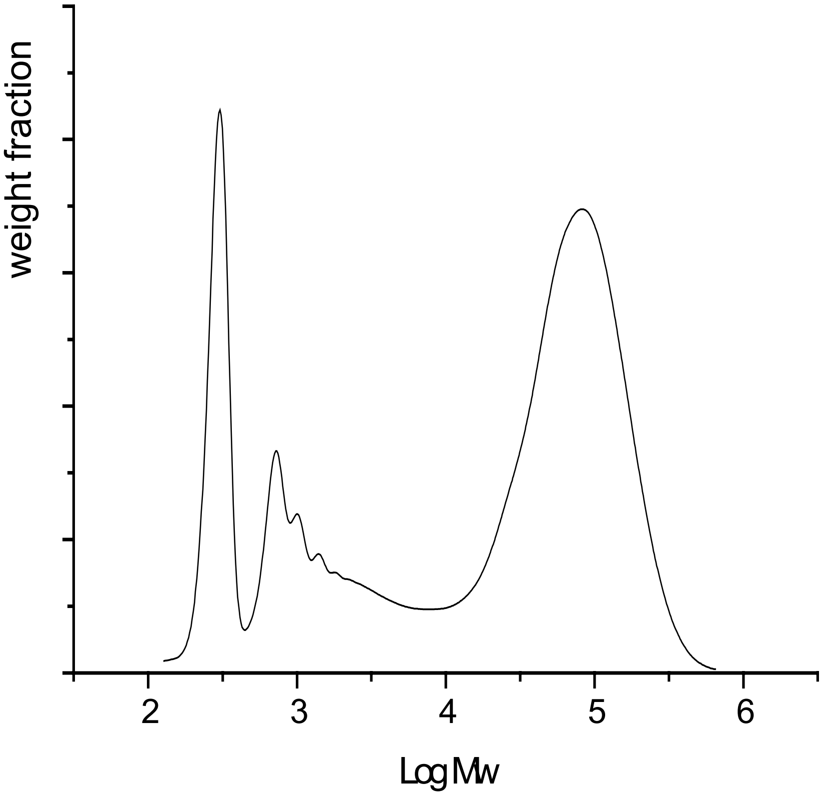


Fig 18. SEC elution curve of the poly(pyridine ether) 9', No. 3, Table 8: $M_n \approx 2\ 6000$ Da, $M_w \approx 53\ 000$ Da (calibrated with polystyrene).

3.1.3.6 Solubilities

For future studies of properties of cyclic poly(pyridine ether)s it was useful to learn more about their solubilities in various organic solvents. Since the pyridine ring is a weakly basic moiety, it allows protonation by strong acids (in contrast to pyridine, 2,6-DFP is neutral in water). It is obvious that protonation will cause a dramatic change of the solubilities. All solubility tests were performed with the polyether **9'** at a concentration of 20 g/L. The results obtained with aprotic solvents were summarized in Table 10. This polyether was found to be insoluble in ethyl acetate and surprisingly in DMSO, whereas it was soluble in all other polar and non-polar solvents. The test with protic solvents (Table 11) proved polyether **9'** to be insoluble in water, methanol or ethanol and in formic acid or acetic acid. Yet, **9'** was soluble in the more acidic solvents dichloroacetic acid, trifluoroacetic acid and methane sulfonic acid. When methane sulfonic acid, which certainly protonates the pyridine units, was added in somewhat more than equimolar quantity to the solution or suspension of **9'** in various solvents, the following observations were made. The protonated polyether precipitated from all solutions in aprotic solvents (Table 11). Furthermore, it remained insoluble in the protic solvents water, methanol, ethanol and acetic acid. However, it dissolved completely in formic acid. This observation suggests that formic acid was not strong enough to protonate the polyether, whereas methane sulfonic acid was sufficiently acidic. For all other poly(pyridine ether)s of this work good solubilities in THF and dichloroacetic acid were found (20 g/L) and a moderate or low solubility in chloroform. Finally, the stability of the cyclic polyether **9'**, No. 3, Table 3 in acidic solution was checked. The solutions in trifluoroacetic acid and in formic acid/methane sulfonic acid were stored for 24 h at 23-25°C. Furthermore, the suspension obtained by addition of triflic acid to the solution of **9'** in nitrobenzene was stored at 23-25°C for 24 h. All three solutions and suspensions respectively were precipitated into methanol containing enough triethylamine to neutralize the acids. The isolated polyethers were then characterized by MALDI-TOF mass spectroscopy. However, the mass spectra were unchanged; no cleavage of cycles was detectable. This means that the poly(pyridine ether)s can be processed former studied in acidic solutions.

Table 10. Solubilities of poly(pyridine ether) 9' (prepared from 9) in various aprotic solvents.

Solvent	Solubility[a)]
THF	**s**
DMF	**s**
$CHCl_3$	**s**
DMSO	**none**
Nitrobenzene	**s**
Ethyl acetate	**none**
Chlorobenzene	**s**

a) measured at 20 °C with 20 g/ L.

Table 11. Solubilities of poly(pyridine ether) 9' (prepared from 9) in various protic solvents.

Neat solvent	Solubility[a)]	with additional methane sulfonic acid[b)]	Solubility[c)]
Water	none	Water	none
Methanol	none	Methanol	none
Ethanol	none	Ethanol	none
m-cresol	s	m-cresol	s
2-Chlorophenol	s	2-Chlorophenol	s
Formic acid	none	Formic acid	s
Acetic acid	none	Acetic acid	none
Dichloroacetic acid	s	Dichloroacetic acid	s
Trifluoroacetic acid	S (95%)	Trifluoroacetic acid	s
methane sulfonic acid	s	-	-

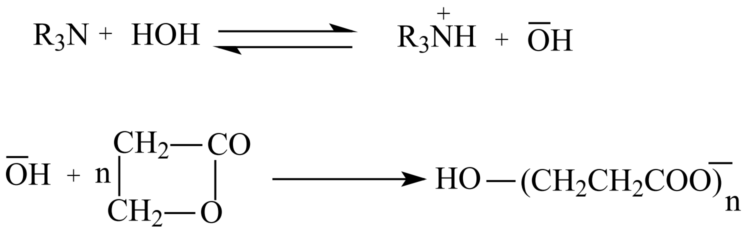
a) measured at 20 °C with 20 g/ L.

b) 10 vol %.

3.2 Synthesis and characterization of Cyclic Polyester by means of Zwitterionic Polymerization of Pivalolactone Initiated with Tertiary Amine:

3.2.1 Introduction

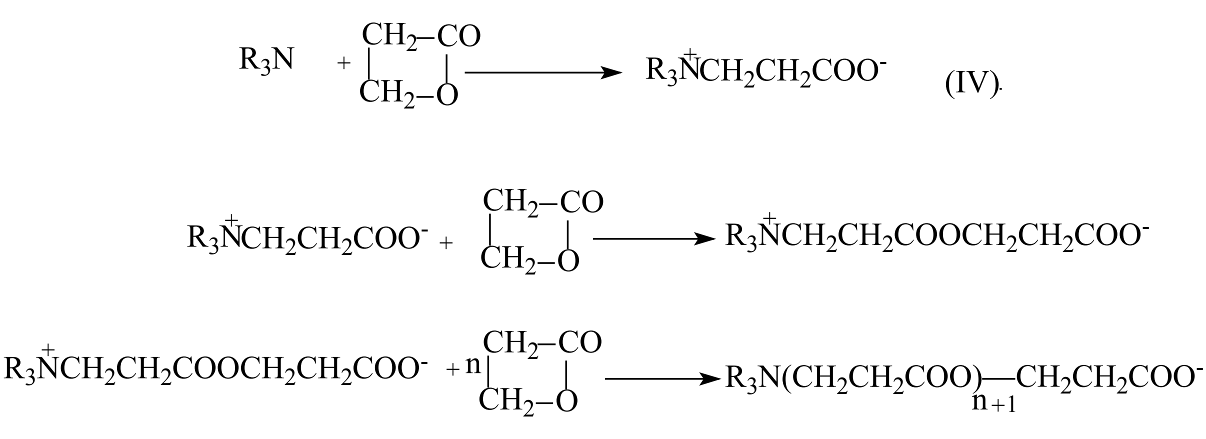
Anionic polymerization of β-lactones initiated by uncharged initiators (tertiary amines) may be performed through two different mechanisms, namely cocatalysis mechanism and zwitterions mechanism [196]. In the cocatalysis mechanism the initiation proceeds by an ionisable cocatalyst such as water and alcohol (Scheme 21). The zwitterion mechanism may be initiated by the direct reaction between monomers and certain initiators (Scheme 22). The initially formed betaine (**IV**) is responsible for the propagation of the polymerization process, in despite of the difficulty to separate the opposite charges of betaine and the decrease of nucleophilicity caused by the inductive effect of the ammonium group. In contrast to initiation with protic nucleophiles the zwitterions mechanism offer the chance to prepare cyclic polyethers.



$$R_3N + HOH \rightleftharpoons R_3\overset{+}{N}H + \overline{O}H$$

$$\overline{O}H + n\begin{array}{l} CH_2-CO \\ | \qquad\quad | \\ CH_2-O \end{array} \longrightarrow HO-(CH_2CH_2COO)^{-}_{n}$$

Scheme 21



$$R_3N + \begin{array}{l} CH_2-CO \\ | \qquad\quad | \\ CH_2-O \end{array} \longrightarrow R_3\overset{+}{N}CH_2CH_2COO^- \quad (IV).$$

$$R_3\overset{+}{N}CH_2CH_2COO^- + \begin{array}{l} CH_2-CO \\ | \qquad\quad | \\ CH_2-O \end{array} \longrightarrow R_3\overset{+}{N}CH_2CH_2COOCH_2CH_2COO^-$$

$$R_3\overset{+}{N}CH_2CH_2COOCH_2CH_2COO^- + n\begin{array}{l} CH_2-CO \\ | \qquad\quad | \\ CH_2-O \end{array} \longrightarrow R_3N(CH_2CH_2COO)_{n+1}-CH_2CH_2COO^-$$

Scheme 22

About three to five decades ago, zwitterionic polymerizations of β-lactones and other heterocycles involving macrozwitterions were intensively studied by several research groups [196-215]. For several reasons, the course of such zwitterionic polymerizations may be very complex. For instance, the chain growth may proceed as an ionic ring-opening polymerization (typically anionic) involving a chain growth kinetic. Alternatively, the zwitterionic monomers or dimers may react with each other by a polycondensation or polyaddition process involving a step-growth kinetic. Furthermore, elimination reactions at the cationic chain end may result in unsaturated, dead endgroups. Moreover, cyclization reactions may take place either physically [196] or chemically with cancellation of both charges. The characterization of isolated polymers in previous studies was based on molecular weight measurements (VPO or SEC) and on IR- and ^{1}H NMR spectroscopy. Neither method allows for a clear cut detection of cyclic oligomers or polymers in complex reaction mixtures. In this context, the present work was designed as a reinvestigation of tertiary amine-initiated polymerizations of β-pivalolactone and β-propiolactone with the purpose to elucidate the chemical sturctur of the polymerization products including the cyclic oligo- and polyesters (if it is found) by means of MALDI-TOF mass spectrometry.

3.2.2 Pyridine-Initiated Polymerization of PiL

The pyridine-initiated polymerizations of PiL were conducted in two solvents of different polarity, namely in dichloromethane and in NMP (Table 12). In addition to pyridine, 4-methylpyridine and DMAP were used as initiators. Both, basicity and nucleophilicity increase in the above given order of the initiators. This variation had the purpose to find out, if these properties have an influence on the structure of the reaction products. The monomer/initiator ratio (M/I) was fixed at 100/1 for all polymerizations, but the temperature was varied.

With pyridine as initiator, a uniform reaction product was obtained which was identified as linear chains of structure **17a** by MALDI-TOF mass spectroscopy (Figure 19). Even when the temperature was raised to 140°C, no formation of cyclic oligo-/polylactones was detectable. This result proves that a zwitterionic polymerization took place in such a way that the initiation step was followed by an anionic ring-opening polymerization (Scheme 23). A polycondensation process (with step-growth kinetic) involving a nucleophilic attack of the $CO_2^{\ominus}$ anion onto the pyridinium group with elimination of pyridine should automatically result in the formation of cyclic oligo- and polylactones. Taking in to account, that ring opening polymerization is considered as polycondensation process, and as demonstrated in the above works concerned with aromatic polyethers; it was found that any kinetically controlled polycondensation (no equilibration) involves a permanent competition between cyclization and chain growth at any concentration and at any stage of the polycondensation. Therefore, the absence of cycles necessarily rules out a significant contribution of condensation steps, and it rules out that “back-biting degradation” occurred. Furthermore, the absence of cyclic polyester could be elucidated according to the formation of cyclic oligo- and polypeptides synthesized from the Zwitterionic polymerization of α-amino acid N-carboxyanhydrides (NCAs) [216-218] to the bond strength , where the ($^+$N-CO) is more weaker than the ($^+$N-CH$_2$) which allow the cyclization with the elimination of initiator.

Table 12. Pyridine-initiated polymerizations of pivalolactone.

Exp. No.	Initiator	Solvent	Temp. (°C)	Time (h)	Yield (%)	η_{inh} ^{a} (dL/g)
1	Pyridine	CH_2Cl_2	20	48	78	0.09
2	Pyridine	NMP	20	48	93	0.09
3	Pyridine	NMP	60	24	100	0.17
4	Pyridine	NMP	100	24	100	0.20
5	Pyridine	NMP	140	24	100	0.63
6	4-Methylpyr.	CH_2Cl_2	20	48	65	0.07
7	4-Methylpyr.	NMP	20	48	76	0.08
8	4-Methylpyr.	NMP	60	24	95	0.10
9	4-Methylpyr.	NMP	100	24	100	0.19
10	4-Methylpyr.	NMP	140	24	100	0.25
11	DMAP	CH_2Cl_2	20	48	93	0.09
12	DMAP	NMP	20	48	87	0.28
13	DMAP	NMP	60	24	95	0.33
14	DMAP	NMP	100	24	98	0.37

a) measured at 20°C with c = 2 g/L in CH_2Cl_2/TFA (8:1).

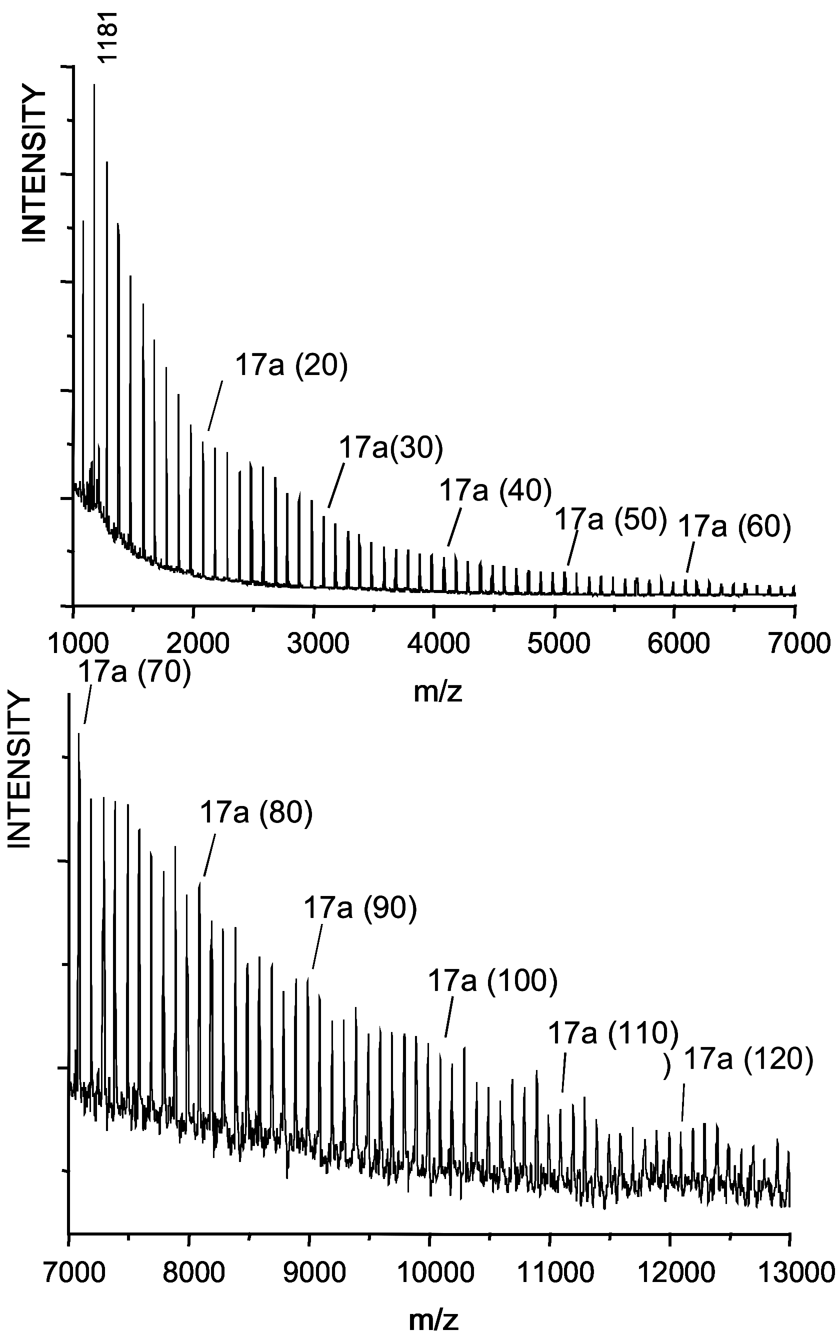
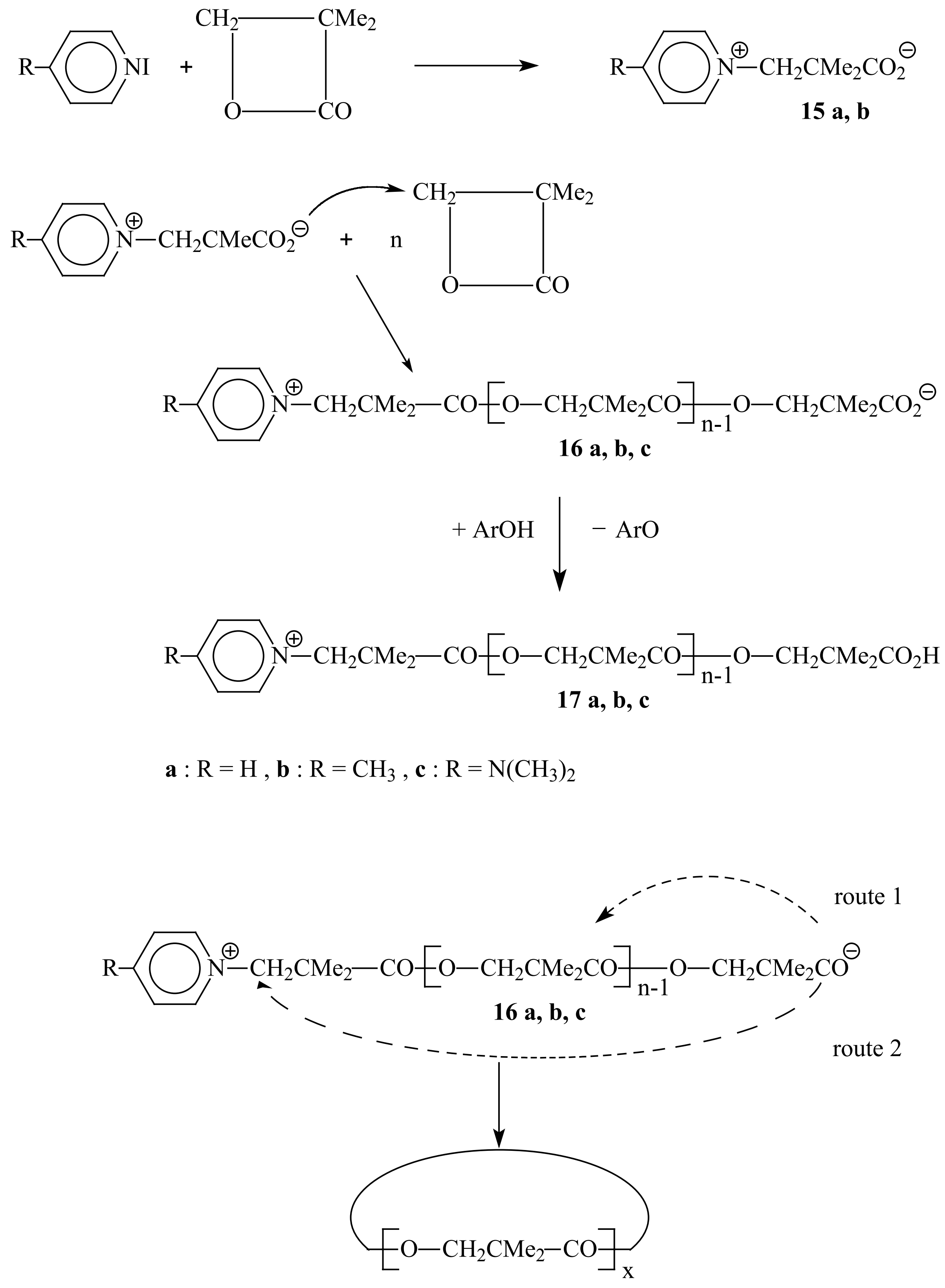


Fig 19. MALDI-TOF mass spectrum of a pyridine-initiated polypivalolactone (12a, No. 3, Table 10) prepared in NMP at 60°C (the number in brackets indicates the DP).



a : R = H , **b** : R = CH_3 , **c** : R = $N(CH_3)_2$

Scheme 18

Perfectly analogous results were found for 4-methylpyridine as initiator (Nos. 6-10, Table 12). Regardless, if pyridine or its 4-methyl derivative was used, the ^{1}H NMR-spectra proved the covalent incorporation of pyridinium endgroups (Figure 20). The formation of a CO_2H endgroup (structure **17b**) indicated by MALDI-TOF m.s (Figure 21) may be explained by proton transfer from the matrix (dithranol) to the $CO_2^{\ominus}$ ion of the zwitterionic chain of structure **16** (Scheme 23). With DMAP as initiator in NMP, polylactone chains of structure **17c** were the only reaction product at 100°C (No. 14, Table 12), and they were the predominant product at 60 or 20°C. From this point of view, the DMAP-initiated polymerizations agreed well with the pyridine and 4-MeP-initiated ones. However, at these lower temperatures chains having an additional mass of 14 Da were also observed. Such mass peaks may either result from $K^{\oplus}$-doped cyclic oligo-/polylactones or from linear chains having one methyl ester endgroup and one dimethylaminopyridinium endgroup. In order to clarify the origin of these mass peaks, the measurements were repeated with $Li^{\oplus}$ doping. In contrast to the linear chains intramolecularly "doped" by pyridinium endgroups, the peaks of the cycles should shift to lower masses by 32 Da ($K^{\oplus}$ - $Li^{\oplus}$). However, such a shift was not observed. Therefore, the MALDI-TOF m.s. with $Li^{\oplus}$ doping suggest that linear chains with methyl ester endgroups are present (structure **18a**). The methyl ester endgroups may be formed when the polylactones precipitated into methanol are heated for drying. When the crude reaction products of repeated syntheses were precipitated into diethyl ether, methyl ester endgroups were indeed absent, and the MALDI-TOF m.s. exclusively displayed the mass peaks of chains with structure **17c**.

Furthermore, it should be mentioned that the MALDI-TOF m.s. of all polylactones prepared in dichloromethane showed a species corresponding to chains of structure **17** with an additional mass of 48-49 Da. This linear species was assigned to structure **18b** resulting from the reaction of the carboxylate anions (structure **16**) with the solvent. Finally, it should be mentioned that the structures **17a**, **17b** and **17c** were confirmed by ^{1}H NMR spectroscopy. The ^{1}H NMR spectra of all polylactones listed in Table 12 displayed the aromatic protons of the pyridinium endgroups as exemplarily illustrated by Figure 20 for a DMAP-initiated polylactone.

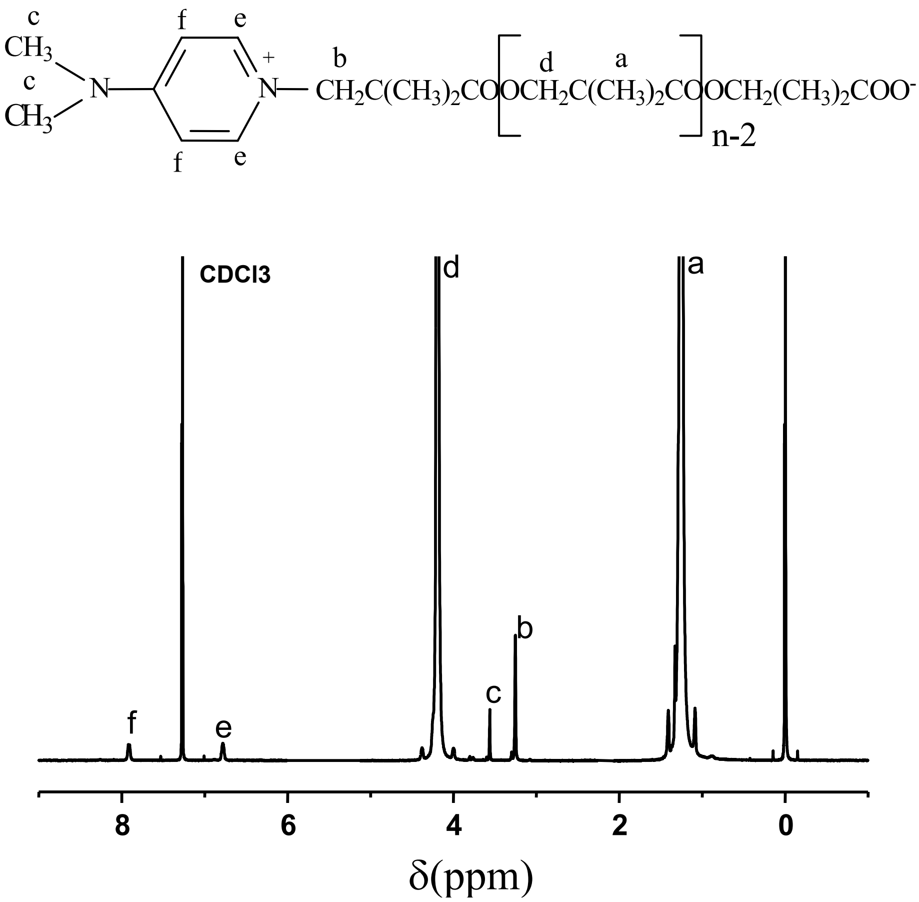


Fig 20. 400 MHz ^{1}H NMR spectrum of a DMAP-initiated polypivalolactone (17c, No. 12, Table 10) prepared in NMP.

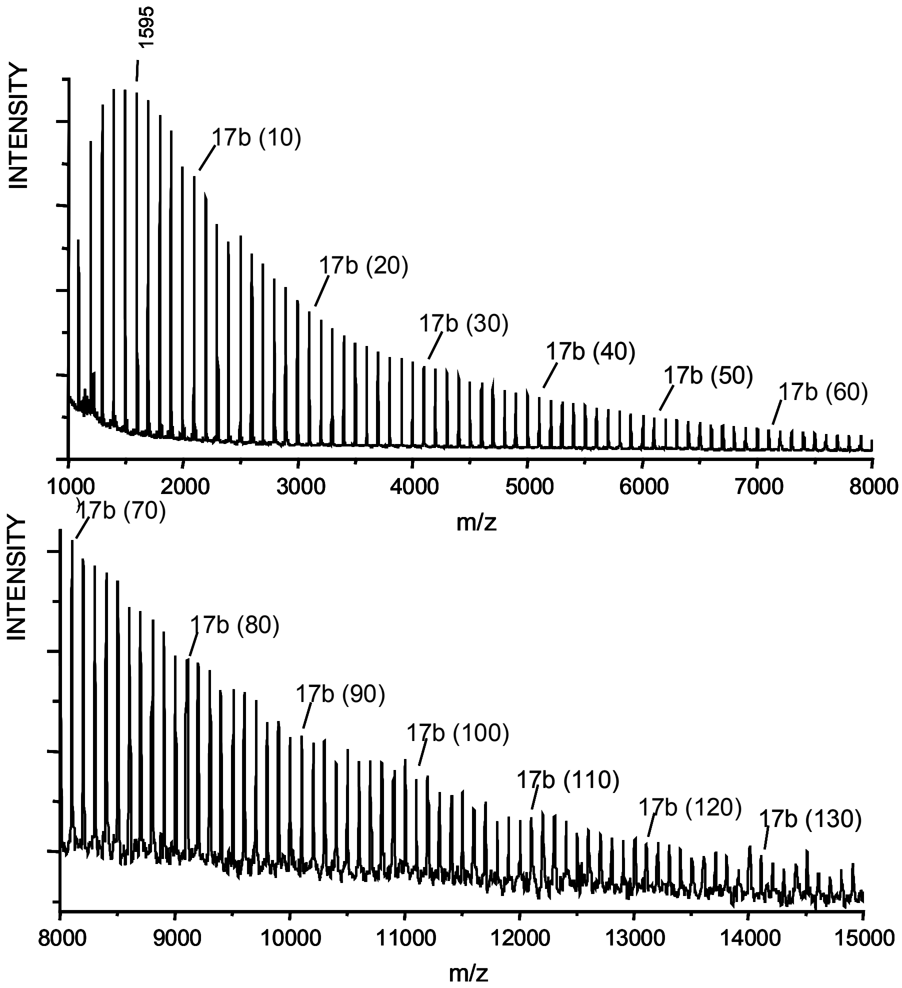


Fig 21. MALDI-TOF mass spectrum of a 4-methylpyridine-initiated polypivalolactone (12b, No. 8, Table 10) prepared in NMP at 60°C (the number in brackets indicates the DP).

3.2.3 Initiation with Tertiary Alkylamines

Three aliphatic tertiary amines of largely different structure were selected as initiators for the second part of this work, namely DABCO, triethylamine and 2-EOX. To avoid side reactions with the solvent, all polymerizations were conducted in NMP (Table 13). The MALDI-TOF m.s of the polylactones initiated by DABCO exclusively displayed mass peaks of linear chains having the structure **19**. This result ruled out that both nitrogens of DABCO started a chain growth in “both directions”. The absence of cyclic oligolactones also proves that no or only few (poly)condensation steps occurred in perfect agreement with the pyridine-initiated polymerizations. With triethylamine rather complex reaction products were obtained. The main product found in the

MALDI-TOF m.s. had the structure **20** resulting from zwitterionic polymerization analogous to the pyridine-initiated polylactones. Cyclic

oligolactones were absent, indicating that frequent condensation steps had not occurred. However, a byproduct was detected having the structure **21** resulting from an initiation by $OH^{\ominus}$. The origin of the traces of water which played the role of coinitiators is not clear at this time, since all reagents were carefully dried. A third type of linear species which was present in small quantities was not identified with regard to its endgroups. From initiation with 2-ethyloxazolidine a complex reaction product was obtained. Both, ^{1}H NMR and IR spectra clearly proved that polypivalolactone was formed and no copolymers. This point needs to be emphasized, because it is known from the work of Saegusa et al.[206-208] that the unsubstituted oxazolidine yields an alternating copolymer when heated with PiL in equimolar ratios. The MALDI-TOF mass spectra prove that chains of structure **22** were the main products in all three samples. In other words, a normal zwitterionic polymerization of PiL has occurred. Furthermore, the $K^{\oplus}$-doped peaks of cyclic oligolactones were detectable in contrast to all other reaction products discussed above. However, in the case of initiation with 2-ethyloxazolidine, an end-to-end cyclization may take place as outlined in Eq.25. Such a cyclization mechanism cannot exist for the other amine initiators studied in this work, and thus the unique formation of cycles (**23**) in 2-ethyloxazolidine-initiated polymerization and the absence of cycles in all other samples have a plausible explanation.

Table13. Zwitterionic polymerization of PiL initiated with various tertiary nucleophiles in NMP.

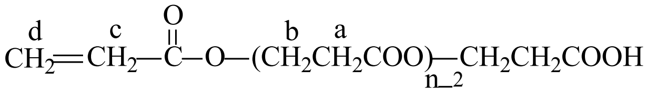
Exp. No.	**Initiator**	**Temperature (°C)**	**Time (h)**	**Yield (%)**	**η_{inh} [a] (dL/g)**
1	**DABCO [b]**	**20**	**48**	**97**	**0.40**
2	**DABCO [b]**	**100**	**24**	**100**	**1.03**
3	**Triethylamine**	**20**	**48**	**3**	**—**
4	**Triethylamine**	**100**	**24**	**98**	**0.58**
5	**2-Ethyloxazoline**	**20**	**48**	**16**	**0.07**
6	**2-Ethyloxazoline**	**100**	**24**	**50**	**0.12**

a)measured at 20°C with c = 2 g/L in CH_2Cl_2/TFA (volume ratio 8:1).

b)diazabicyclooctane.

3.2.4 Pyridine-initiated polymerizations of β-propiolactone

For comparison, two pyridine-initiated polymerizations of β-propiolactone were performed with M/I = 100 in NMP at 20 and 60°C. The MALDI-TOF m.s. of the isolated polylactones displayed a clean course of both polymerizations. Only one kind of polylactones was formed. The mass peaks corresponded to $K^{\oplus}$–doped cycles. Pyridinium endgroups were totally absent. The ^1H NMR spectra displayed the presence of acrylate endgroups (Fig.22). Therefore, these polylactones should have the linear structure **24**, which is isomeric to cyclic oligo- and polylactones. In other words, the initially formed pyridinium groups were quantitatively eliminated and the resulting acrylate ions played the role of initiators. This result is in good agreement with studies of other research groups [199] which were published before MALDI-TOF mass spectroscopy was available.



$$\overset{d}{CH_2}{=}\overset{c}{CH_2}-\overset{\overset{O}{\|}}{C}-O-(\overset{b}{CH_2}\overset{a}{CH_2}COO)_{n-2}-CH_2CH_2COOH$$

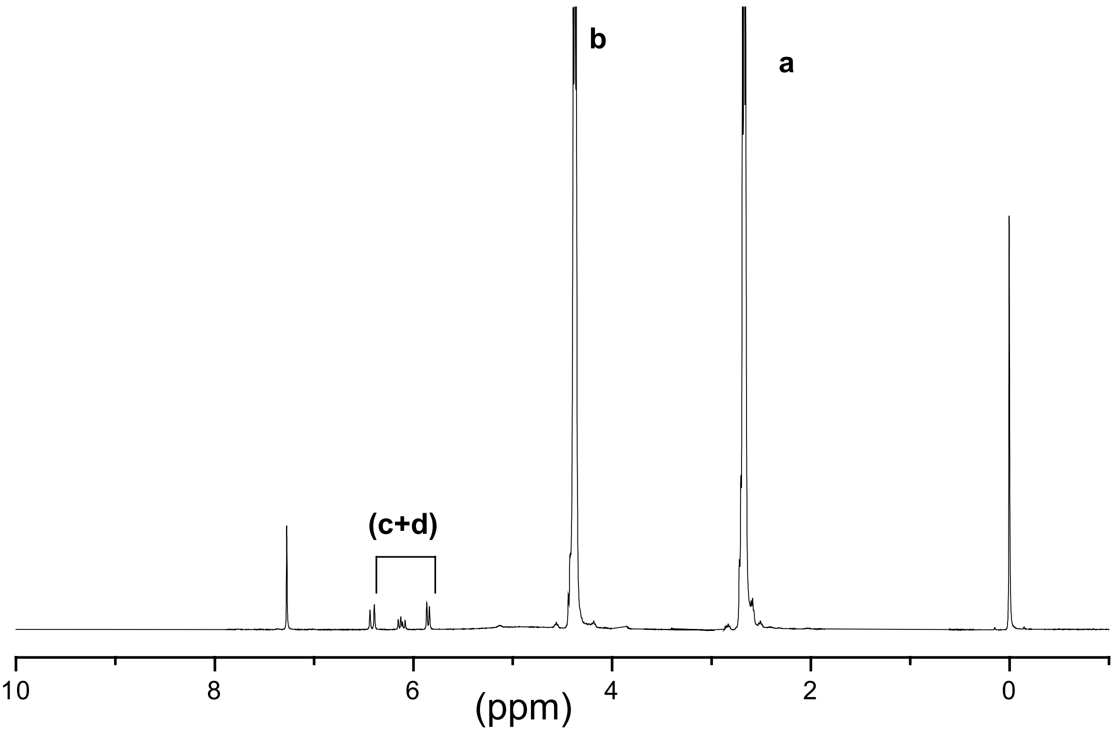
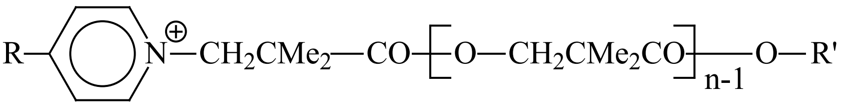
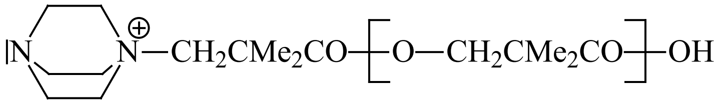


Fig 22. 400 MHz ^1H NMR spectrum of a Py-initiated β-Propiolactone prepared in NMP.



18a : R' = CH_3 **18b** : R' = CH_2Cl



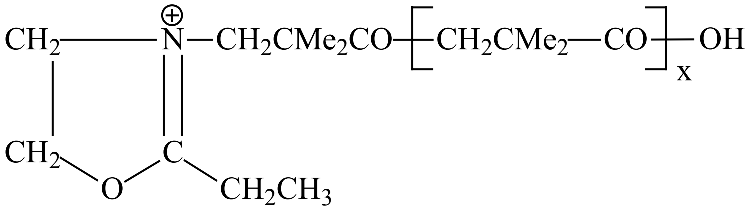
19

$$(CH_3CH_2)_3\overset{\oplus}{N}-CH_2CMe_2CO-\left[O-CH_2CMe_2CO\right]-OH$$

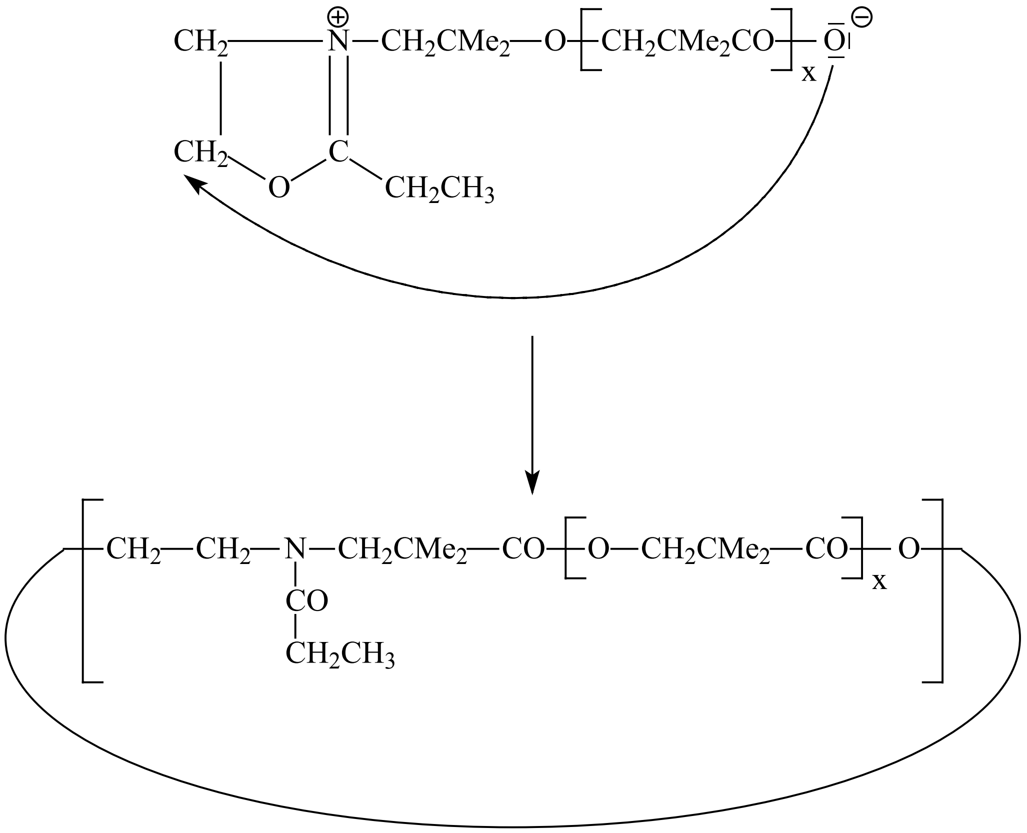
20

$$H-\left[O-CH_2CMe_2-CO\right]-OH$$

21



22



(25)

23

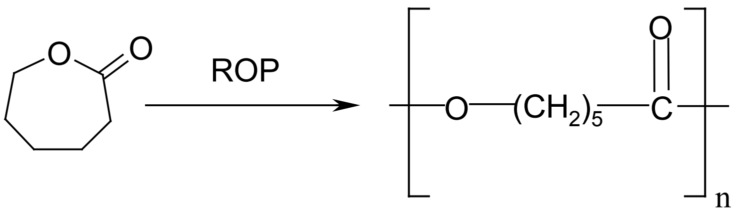
$$CH_2{=}CH{-}CO{-}\left[O{-}CH_2CH_2{-}CO\right]{-}OH$$

24

3.3 Biodegradable polymer networks

3.3.1 Introduction

Poly(ε-caprolacton)s (PCLs) are semicrystalline aliphatic polyesters produced using ROP (Eq.26). The degree of crystallinity and melting point are inversely proportional with PCL molecular weights, while the glass transition temperature is nearly constant with value of – 60 °C [219 ,94]. The melting points of PCLs are in the range of 59-64 °C.



(26)

The most important features of PCLs are:

a. They have good solubility in organic solvents.

b. They are biodegradable

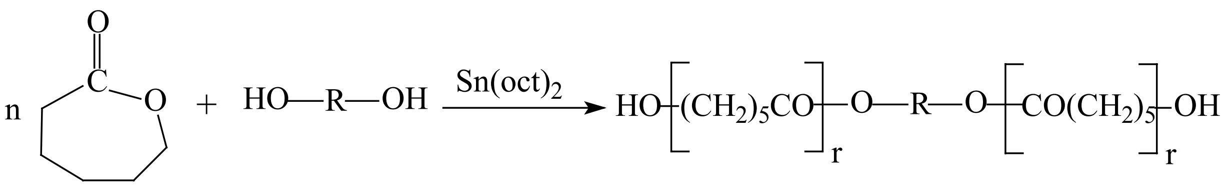
c. Their melting points are low.

d. Their compatibility to blend with different polymers such as polyethylene, nylon-6 and polystyrene [220-222].

PCLs have attracted much attention as implantable carriers for drug delivery systems and as surgical repair materials, because of their excellent mechanical strength, and permeability by drugs [223,224]. However, the high methylene content and crystallinity of the polymers cause a decrease in the rate of biodegradation and in the efficiency of drug encapsulation. Therefore, modification of PCLs is necessary to overcome this problem. PCLs can be modified through the introduction of hydrophilic segments and branched structures [225], copolymerization and the incorporation of PCLs into network structures. The hydrophilicity of these crosslinked polyesters can be improved by the introduction of polyether chains in the chemical structure [226-228]. This chemical introduction of polyether blocks can be accomplished using acrylated poly(ester-ether) precursors containing poly(ethylene glycol) PEG, poly(propylene glycol) or poly(tetramethylene glycol) as the ether block or by copolymerization of monoacrylated PEG with acrylated polyesters. When the PEG content was high, the precursors were water-soluble and the final photocured networks showed water absorption of 80-95% [227-228].

3.3.2 Synthesis and characterization of poly(ε-caprolactone)diols

Different poly(ε-caprolactone)diols (poly(ε-CL)diols), with monomer/coinitiator ratios 20/1, 30/1, 40/1, and 50/1, were prepared by ring-opening polymerization of ε-caprolactone (ε-CL) using a standard procedure already described by Kricheldorf et.al [229]. The polymerization was initiated either with 1,4-butandiol (BD) as hydrophobic cointiator or with tetraethylenglycol (TEG) as hydrophilic cointiator in the presence of $Sn(Oct)_2$ as catalyst (Scheme 24). The good solubility of BD and TEG in ε-caprolactone allows the control of the molecular weight via the M/COI ratio. In addition, the ROP could be performed without solvent. Therefore, BD and TEG were used as coinitiators to make hydroxyl telechelic poly(ε-caprolactone), and to allow for the control of the molecular weight of the oligomers.



$n = 2r = 20, 30, 40, 50$

$HO{-}R{-}OH = HO(CH_2CH_2O)_4H$, $HO(CH_2)_4OH$

Scheme 24

The successful preparation of OH-terminated telechelic poly(ε-caprolactone)s derived from BD were confirmed by ^{1}H-NMR as shown in Fig.23. Because the peaks of BD overlapped with the beaks of ε-CL, the molecular weights of hydroxyl telechelic poly(ε-CL) were calculated from ^{1}H-NMR spectra by determination the ration of the integral areas of methylene hydrogen adjacent to ε-CL carbonyl group around $\delta = 2.30$ ppm to those of methylene protons of ε-CL units adjacent to the hydroxyl end groups around $\delta = 3.65$ ppm. In the case of hydroxyl telechelic poly(ε-CL)s derived from TEG, their was no overlapped between the signals of TEG and poly(ε-CL). Therefore, the molecular weights were determined by measuring the ratio of the integral areas of methylene protons of ε-CL adjacent to carbonyl group around $\delta = 2.30$ ppm to those of (CH_2O) group of TEG around $\delta = 4.23$ ppm (Fig.24).

Table 14. Synthesis of poly(ε-caprolacton)diol derived from tetraethylenglyol and 1,4-butandiol.

polymers	Coinitiator (CoI)	ε-CL/ CoI	ε-CL/I[a]	Yield (%)	η[c] (dl/g)	^{1}H-NMR[d]	MALDI-TOF[d]	Tg [e] (^{0}C)	Tm [e] (^{0}C)
PCL_1	**TEG**	**20**	**500**	**90**	**0.11**	**19**	**21**	**-59.89**	**48.15**
PCL_2	**TEG**	**30**	**500**	**93**	**0.15**	**33**	**32**	**-55.68**	**56.63**
PCL_3	**TEG**	**40**	**500**	**96**	**0.17**	**42**	**39**	**-56.36**	**52.02**
PCL_4	**TEG**	**50**	**500**	**97**	**0.22**	**51**	**48**	**-58.95**	**55.40**
PCL_5	**BD**	**20**	**500**	**90**	**0.13**	**21**	**19**	**-59.26**	**49.81**
PCL_6[b]	**BD**	**20**	**500**	**87**	**0.10**	**24**	**22**	**-43.32**	**53.30**
PCL_7	**BD**	**30**	**500**	**90**	**0.15**	**30**	**32**	**-55.21**	**54.03**
PCL_8	**BD**	**40**	**500**	**92**	**0.18**	**42**	**39**	**-57.54**	**54.42**
PCL_9	**BD**	**50**	**500**	**88**	**0.16**	**48**	**47**	**-54.22**	**56.94**

[a] ***$Sn(oct)_2$ was used as initiator.***

[b] ***$Bi(acetat)_2$ was used as initiator.***

[c] ***inherent viscosity was measured in CH_2Cl_2 at 20 ^{0}C , c = 2g/l.***

[d] ***ratio of ε-CL to cointiator measured by ^{1}H-NMR and MALDI-TOF.***

[e] ***thermal properties were measured with 20^{0}C/min.***

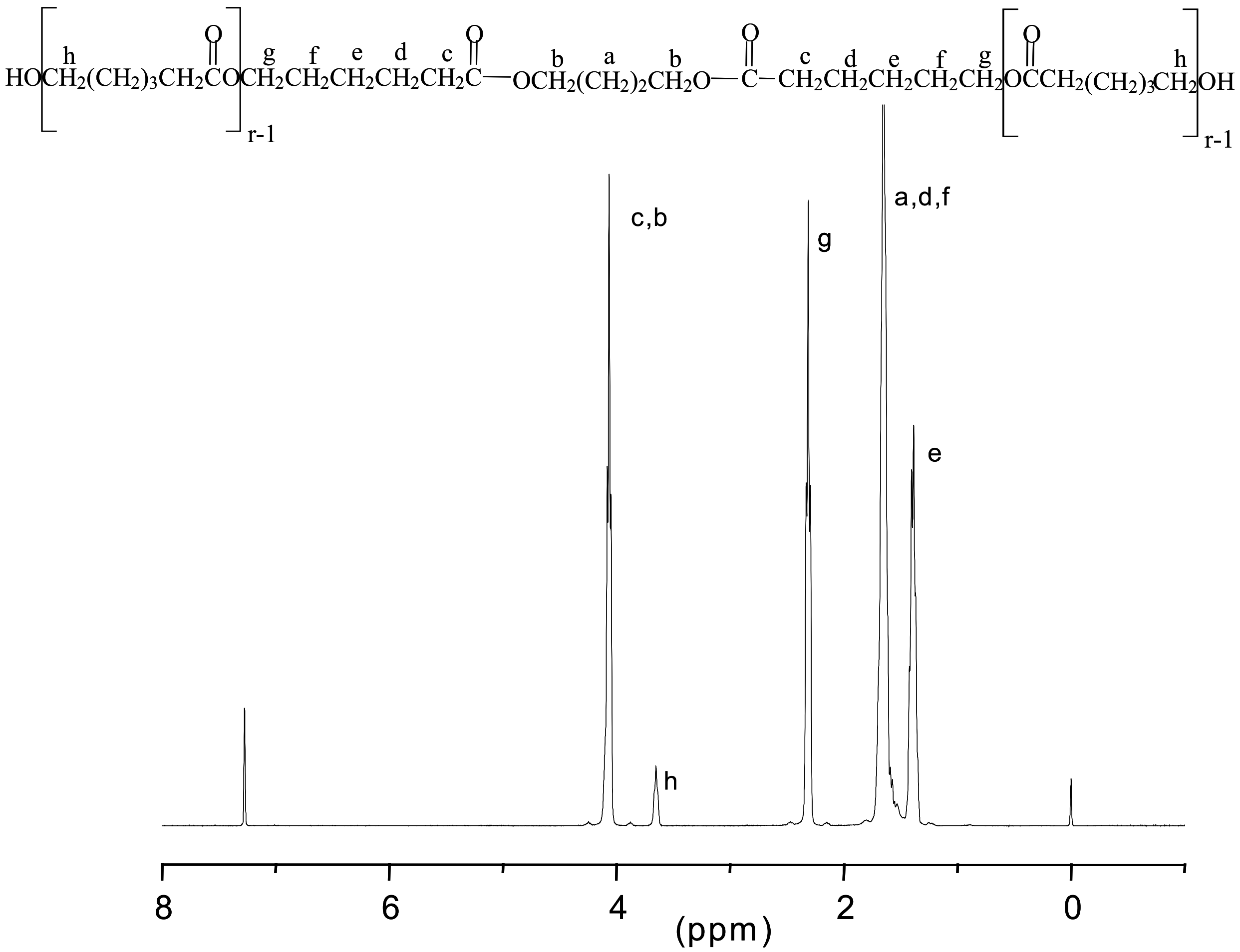
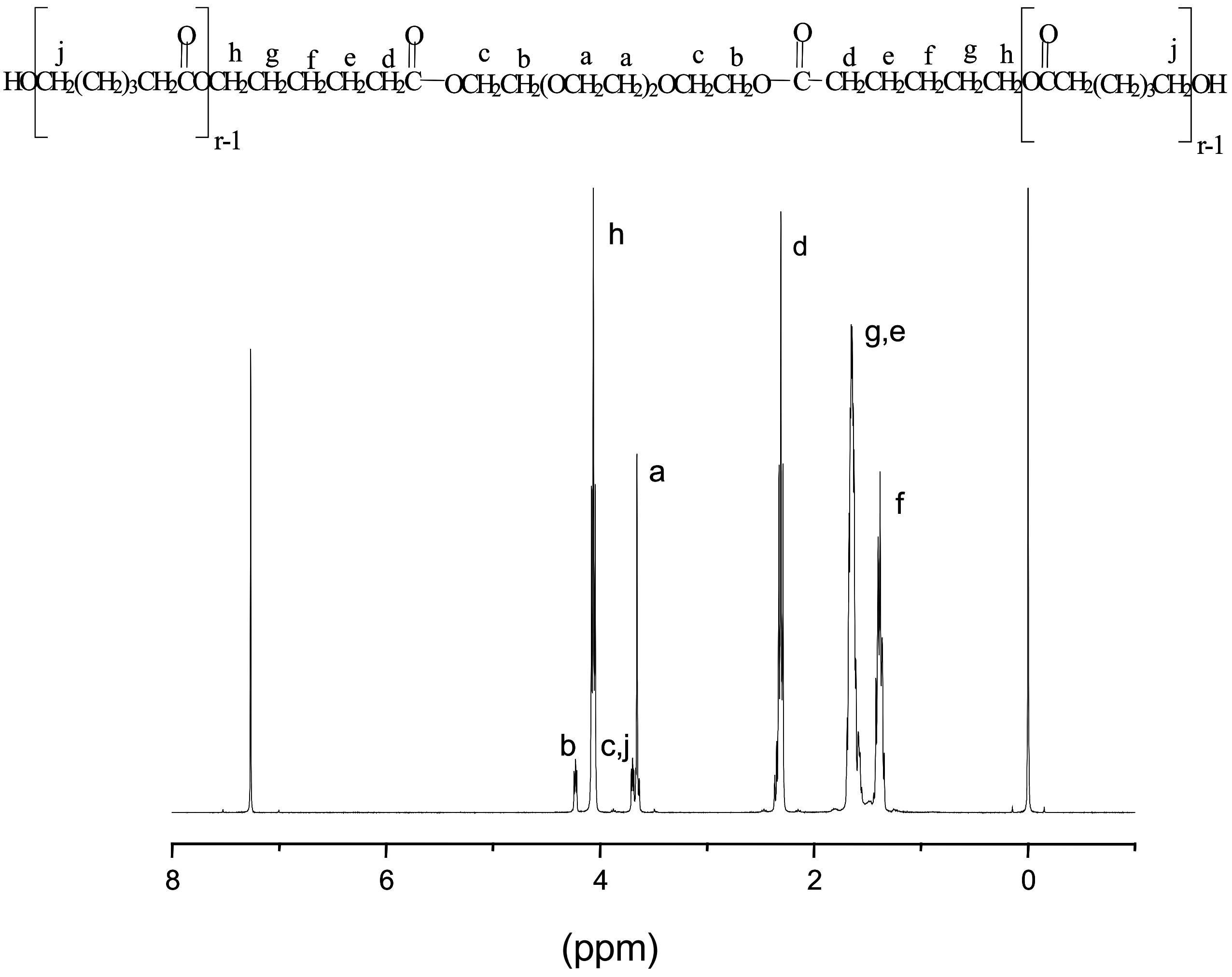


Fig 23. ^{1}H-NMR spectrum of telechelic poly(ε-caprolactone) prepared using 1,4-butandiol (1/20).

Further confirmation of the structure was accomplished by MALDI-TOF mass Spectroscopy as illustrated in Figures 25. The absence of cyclic oligo-caprolacton showed by MALDI-TOF mass spectra proved that the normal transesterification reactions including back-biting degradation were absent at the experimental conditions. High yields and moderate viscosities were obtained from the polymerization as listed in Table 14. It seems to be obviously that viscosities of ε-caprolactone oligomers increase with the ratio of ε-CL to coinitiator.



$$\mathrm{HO}\left[\mathrm{CH_2(CH_2)_3CH_2}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{O}\right]_{r-1}\mathrm{CH_2CH_2CH_2CH_2CH_2}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{-OCH_2CH_2(OCH_2CH_2)_2OCH_2CH_2O-}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{-CH_2CH_2CH_2CH_2CH_2}\left[\mathrm{O}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{CH_2(CH_2)_3CH_2}\right]_{r-1}\mathrm{OH}$$

Fig 24. ^{1}***H-NMR spectrum of telechelic poly(ε-caprolactone) prepared using tetraethylenglycol (1/20).***

As seen in Table 14, and the DSC traces shown in Fig 26, both, T_m and T_g represent the expected thermal values of poly(ε-caprolactone). However, it appears that, increasing the ratio of monomer to coinitiator or changing the coinitiator did not obviously change the values of T_g and T_m. Furthermore, the T_ms of poly(ε-CL)diols derived from BD show slightly higher values than those derived from TEG.

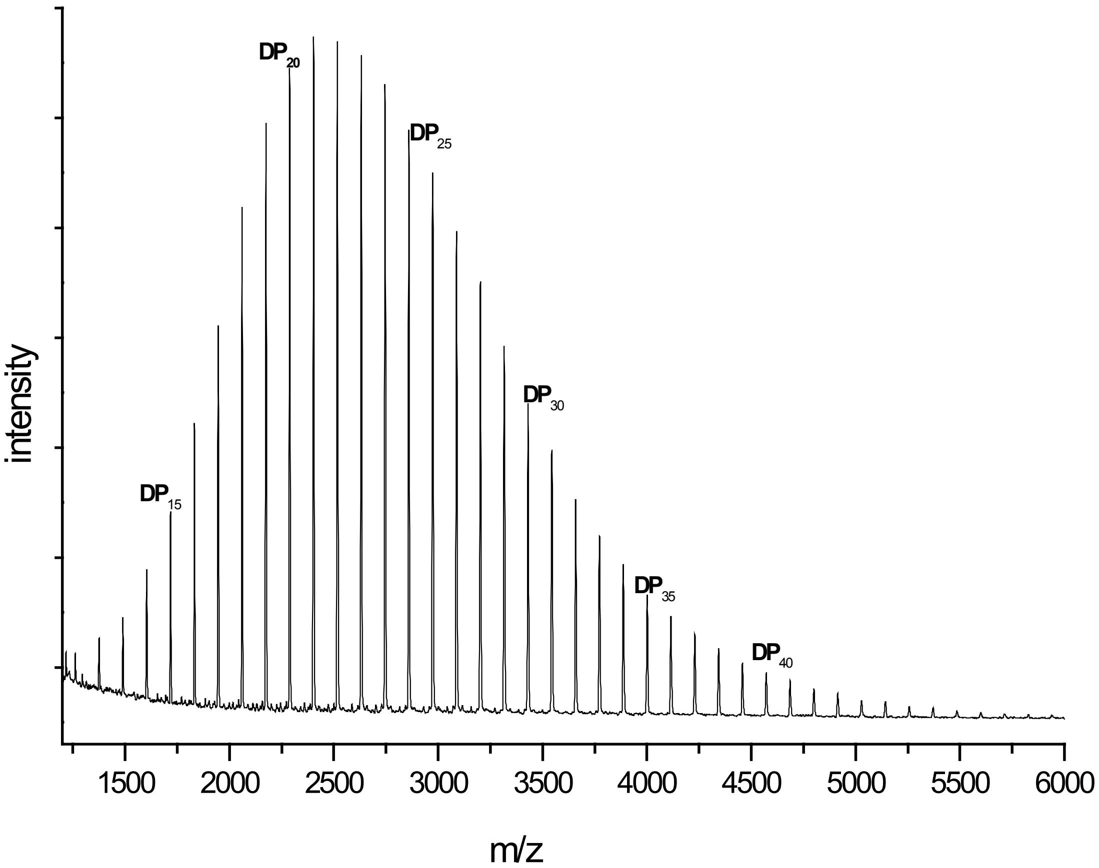


Fig 25. MALDI-TOF mass spectrum of PCL$_1$

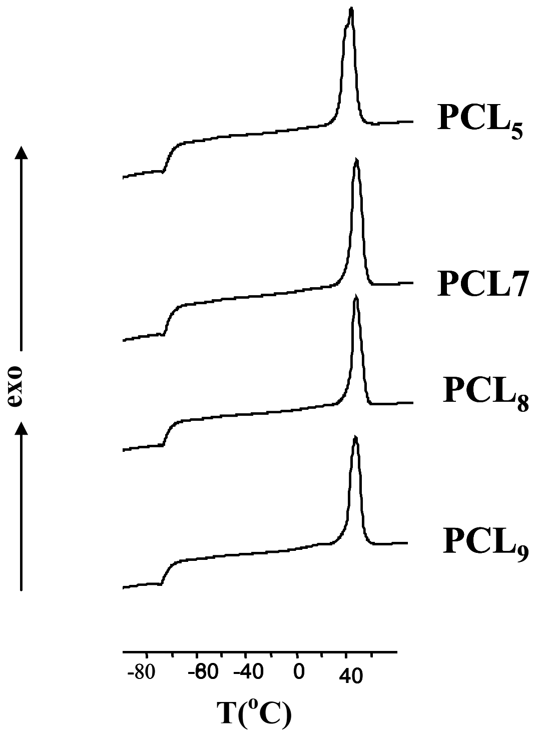


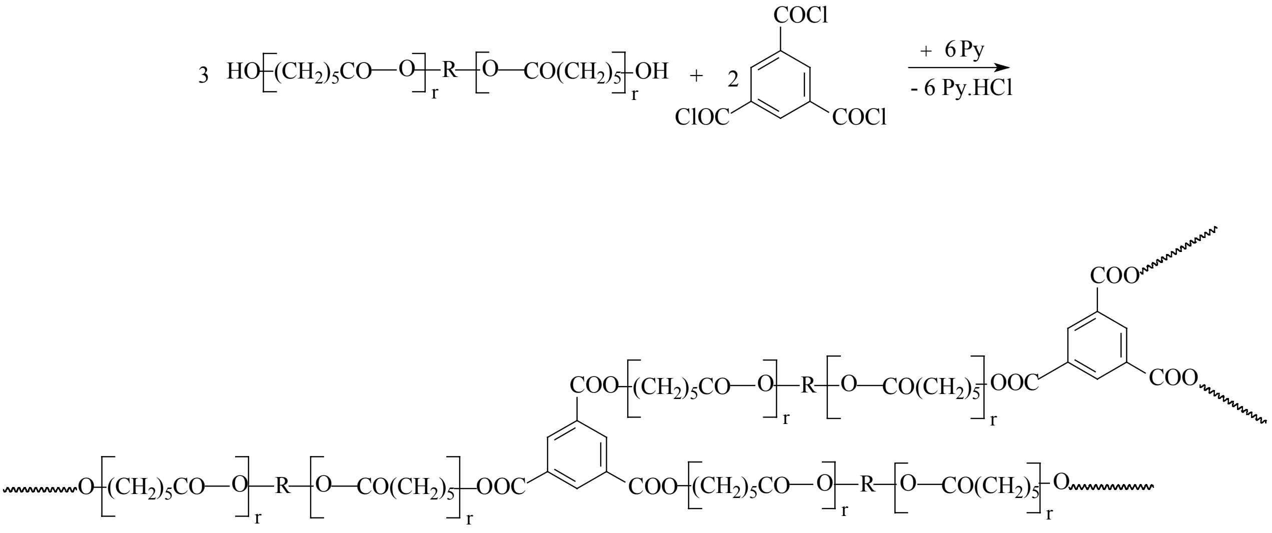
Fig 26. DSC curves of the poly(ε-CL)diols derived from BD

3.3.3 Synthesis and characterization of Network

3.3.3.1 Synthesis and characterization of networks derived from poly(ε-CL)diols

The cross-linking of poly(ε-CL)diols was performed in dichloromethane using trimesoly chloride in presence of pyridine as shown in Scheme 25. After complete addition of pyridine, a rapid increase of viscosity followed by gelation was observed within 5-10 min. Although, the cross-linking occurred to such an extent that the stirrer was stopped, the polymerization was continued for 24 h. The resulting gels were intensively extracted with dichloromethane to remove noncrosslinked (unreacted or cyclic) materials.

Trimesoly chloride was used as cross-linking agent because it is commercial and convenient for a ^{1}H-NMR spectroscopy characterization of the chemical structure [68]. However, as reported in literature [89], this aromatic compound can be replaced by a biodegradable and biocompatible trifunctional acid chloride derived from glutaric acid and glycerol. The results listed in Table 15 show yields of networks in range of 75- 98 %.



R = $(CH_2)_4$, $(CH_2CH_2O)_4$

Scheme 25

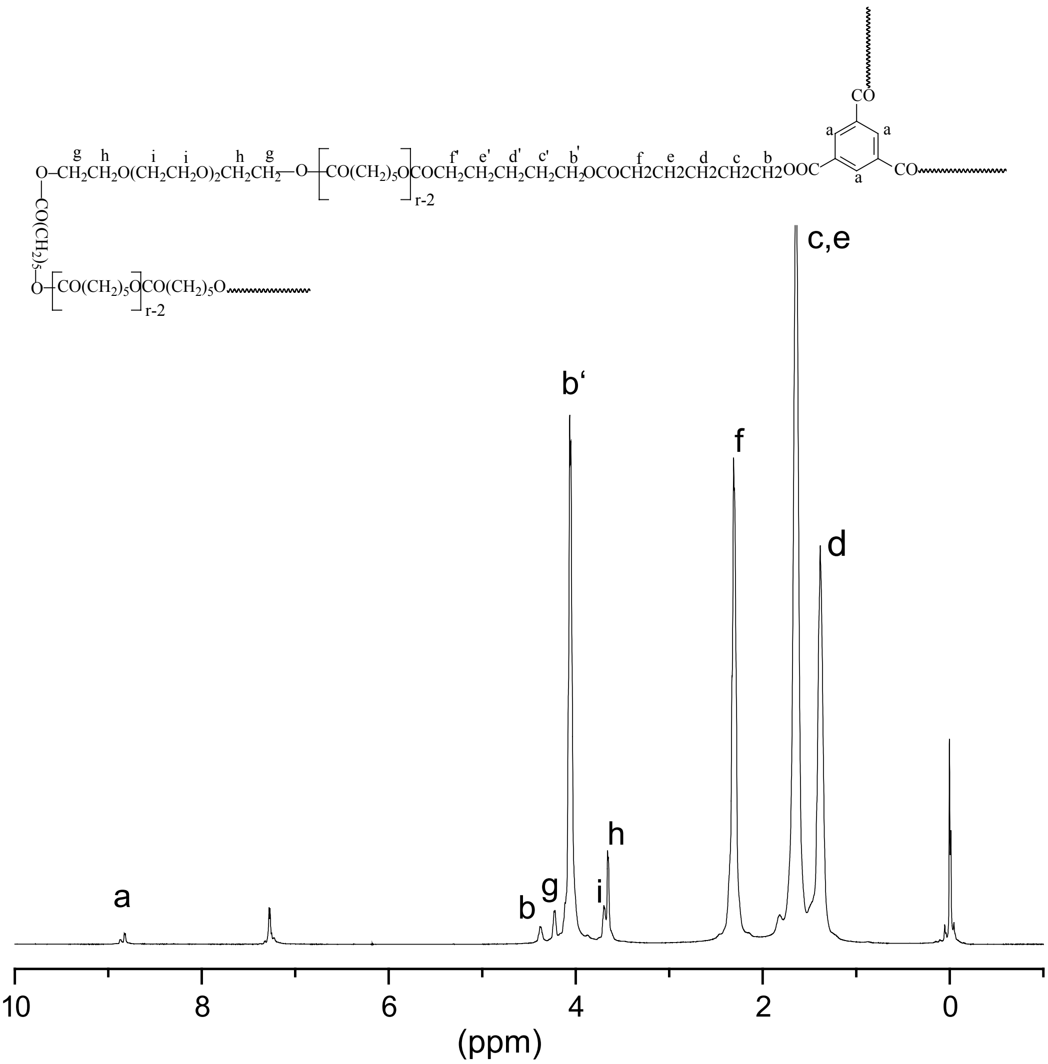


Fig 27. ^{1}H-NMR spectrum of Net3 in Table 19.

As a consequence of good swelling of all networks in $CDCl_3$, it was feasible to record ^{1}H-NMR spectra with narrow signal width as illustrated in Figure 27.

Table 15. Networks synthesized from poly(ε-CL)diols derived from TEG and BD

Network	poly(ε-caprolactone)diols	Yield (%)	SF[a] in CH_2Cl_2	SF[a] in THF	SF[a] in Toluene	T_g [b] (^{0}C)	T_m [b] (^{0}C)
Net_1	**PCL1**	**94**	**13**	**12**	**11**	**-62.7**	**39.2**
Net_2	**PCL2**	**86**	**18**	**15**	**13**	**-61.3**	**45.7**
Net_3	**PCL3**	**82**	**34**	**24**	**20**	**-43.1**	**55.6**
Net_4	**PCL4**	**98**	**27**	**25**	**18**	**-42.5**	**54.2**
Net_5	**PCL5**	**85**	**26**	**20**	**16**	**-51.9**	**49.7**
Net_6	**PCL7**	**75**	**32**	**22**	**18**	**-55.2**	**54.03**
Net_7	**PCL8**	**97**	**30**	**26**	**21**	**-55.2**	**53.95**
Net_8	**PCL9**	**80**	**37**	**28**	**19**	**-54.2**	**56.5**

[a] The swelling factors (SF) are multiplied with Factor of 10
[b] thermal properties were measured with 20^{0}C/min.

As illustrated by DSC traces of Figure 28 and the DSC data listed in Table 15, the linear chain segments were indeed able to crystallize, and the melting temperature (T_m) decreased with lower M/COI ratio or, in other words, with a higher density of cross-links. This consequence was accompanied by a decrease of glass transition temperatures.

Finally the swelling effect of solid gels was studied in different solvents. The data listed in Table 15 exhibit two important results. Firstly, the volume expansion indeed increases with M/COI ratio used for polymerization of ε-CL. Secondly, they also prove that the quality of solvation plays a role with CH_2Cl_2 being the best solvent.

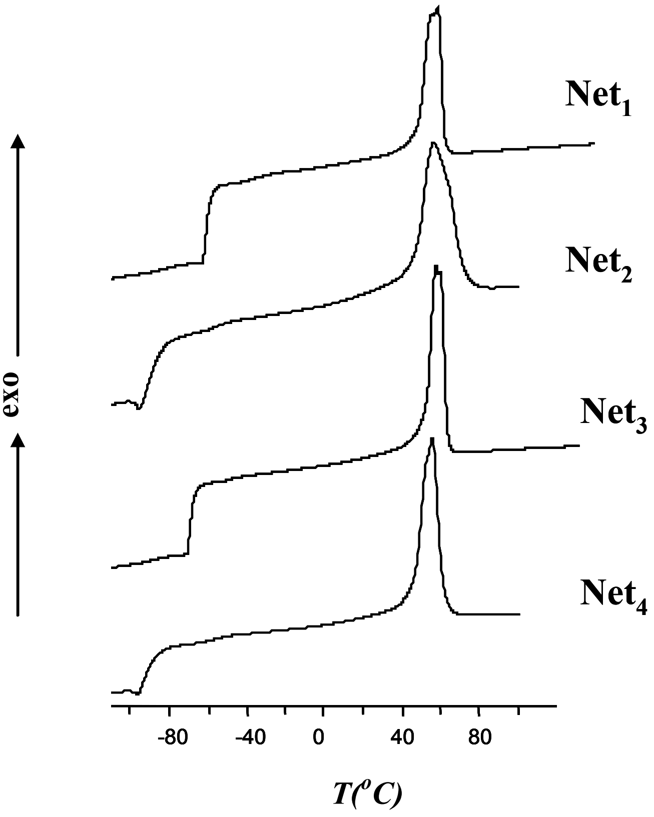
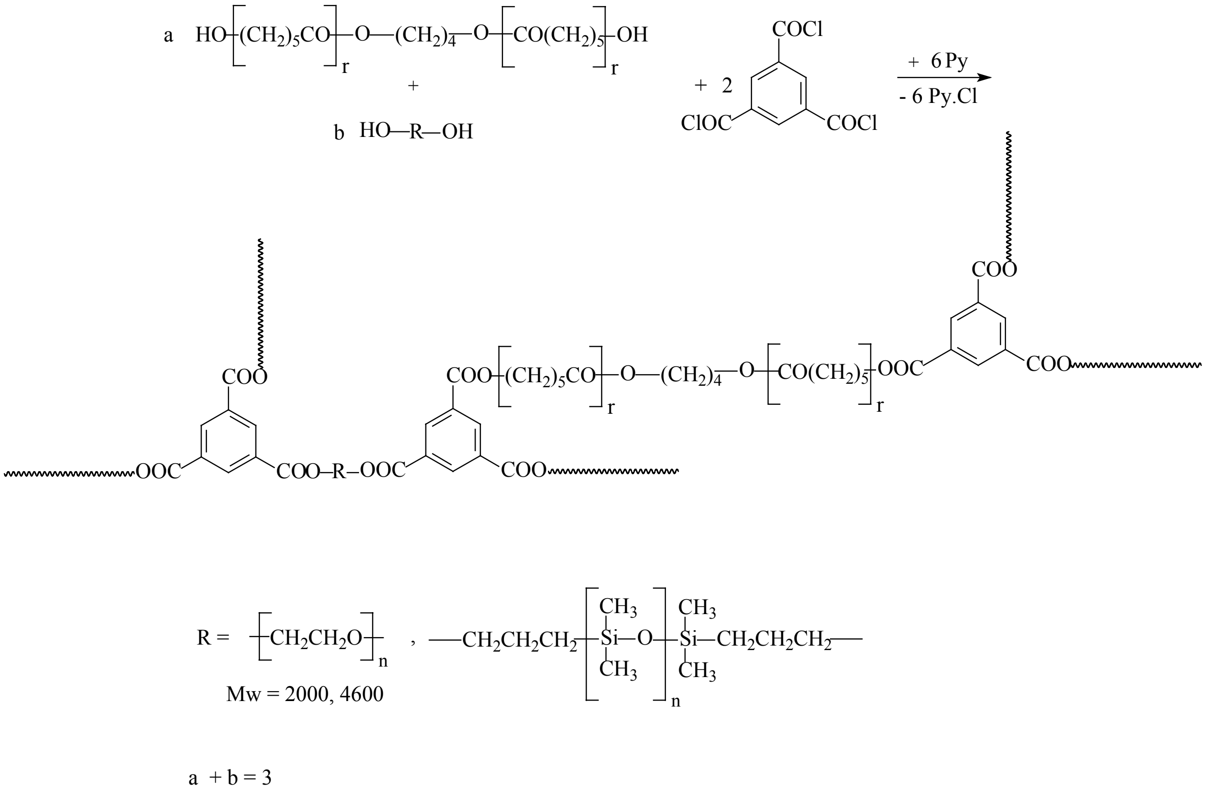


Fig 28. DSC curves of the networks synthesized from poly(ε-CL)diols derived from TEG

3.3.3.2 Synthesis and characterization of combi-networks derived from poly(ε-CL)diols and polyethyleneglecols

Two series of biodegradable combi-networks were synthesized from poly(ε-CL)diols derived from BD with PEGs. Namely, Poly(ethylene glycol) with Mws 2000 and 4600, were mixed with poly(ε-CL)diols have nearly the same Mw. Since PEGs are hydrophilic, they were used to modify the hydrophobic character of poly(ε-CL)diols. For this reason, PEGs were mixed with poly(ε-CL)diols in various ratios and cross-linked with trimesoyl chloride and pyridine as demonstrated in Scheme 26. Produced gels were mechanically removed from the reactor and extracted with hot CH_2Cl_2 prior to their characterization. The yields of the extracted gels after they were dried and weight, were between 74 and 99 % as listed in Tables 16 and 17. Low yield may be attributed to two reasons: first, the mechanical workup procedure and, second, the formation of soluble reaction products which were extracted in CH_2Cl_2. the high ability of these gels to swell in $CDCl_3$ allows the formation of narrow signals even at high highest cross-linked density as shown in Figures 29. Therefore, the poly(ε-CL)diols/PEGs ratio could be easily measured from the integral areas of signals with respect to each components. Taking into account a marginal error of at least ± 5, the experimental ratios showed an acceptable agreement with the feed ratios. The feed ratios and the experimental ratio determined from the isolated networks were listed in Tables 16 and 17.



Scheme 26

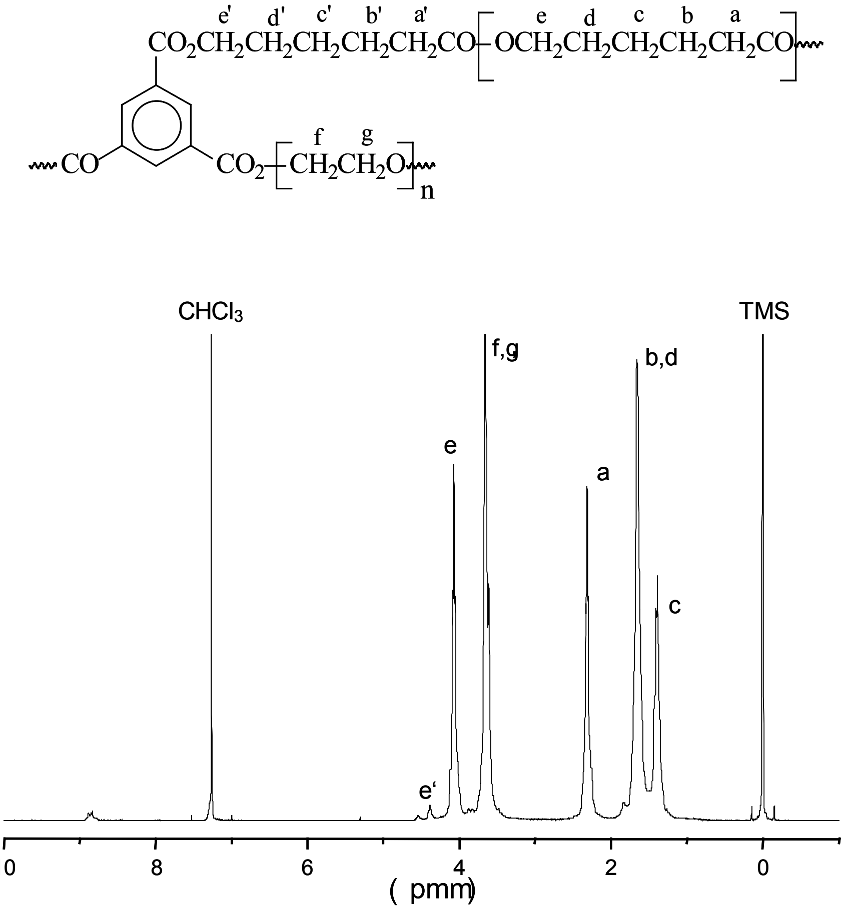


Fig 29. The 400 MHz ^{1}H-NMR spectrum of Net$_{19}$ in Table 21 swelling in CDCl$_3$.

Table 16. Combi-networks synthesized from PCL$_5$with PEG 2000

Network	Feed ratio of PCL5/ PEG2000[a]	Yield (%)	SF[b] in CH_2Cl_2	SF[b] in THF	SF[b] in Toluene	Ratio of PCL5/PEG 2000 Using ^{1}H-NMR	T_g [c] (^{0}C)	T_m [c] (^{0}C)
Net$_5$	100/0	85	26	20	16	100:0.0	-51.87	49.67
Net$_9$	80/20	82	17	13	12	78:22	-54.28	48.50
Net$_{10}$	60/40	76	23	12	10	50:50	-43.43	50.71
Net$_{11}$	50/50	69	27	23	18	47:53	-47.33	47.76
Net$_{12}$	40/60	86	26	12	9	30:70	-54.11	40.16
Net$_{13}$	80/20	93	17	11	8	83:17	-43.43	50.71
Net$_{14}$	0/100	99	23	17	13	0.0:100	-	-

[a] *M.W $_{PEG}$ = 2000 g/mol.*
[b] *the swelling factors (SF) are multiplied with Factor of 10.*
[c] *thermal properties were measured with 20^{0}C/min.*

Table 17. Combi-networks synthesized from PCL_8 with PEG = 4600

Network	Ratio of PCL_8/ PEG4600[a]	Yield (%)	SF[b] in CH_2Cl_2	SF[b] in THF	SF[b] in Toluene	Ratio of PCL_8/PEG 4600 Using H-NMR	T_g[c] (^0C)	T_m[c] (^0C)
Net $_7$	**100/0**	**97**	**30**	**26**	**21**	**100:0.0**	-55.20	53.95
Net $_{15}$	**80/20**	**88**	**20**	**16.6**	**14**	**70:30**	-51.61	52.24
Net $_{16}$	**60/40**	**88**	**30**	**20.6**	**15**	**46:54**	-53.50	52.72
Net $_{17}$	**50/50**	**99**	**15**	**8**	**1.7**	**41:59**	-55.07	53.95
Net $_{18}$	**40/60**	**99**	**17**	**11**	**10.8**	**21:79**	-52.31	52.13
Net $_{19}$	**20/80**	**99**	**16**	**9.4**	**9.4**	**13:87**	-49.64	60.56
Net $_{20}$	**0/100**	**74**	**45**	**23**	**8.6**	**0.0:100**	-56.05	61.52

[a] M.W of PEG = 2000 g/mol.
[b] the swelling factors (SF) are multiplied with Factor of 10.
[c] thermal properties were measured with 20^0C/min.

The swelling of all gels performed in these series was studied in three solvents of different structures: CH_2Cl_2, THF, and toluene as listed in Tables 16 and 17. As in the case of network derived only from poly(ε-CL)diols, the highest swelling factors determined for all gels was found in CH_2Cl_2. Whereas dichloromethane and tetrahydrofuran are good solvents for both PCL and PEG, toluene is a relatively poor solvent for PEG. Therefore, the experiments with toluene show as overriding effect decreasing swelling with higher contents of PEG. The most conspicuous result of all three series of swelling measurements is a maximum of swelling at the 50/50 composition when the chain segments are short (Table 16). Possibly this result is a consequence of a minimum of the total crystallinity of the entire network. Interestingly, the opposite trend is detectable for the networks derived from the longer chain segments (Table 17). This conspicuous difference in the swelling tendencies of both series of networks may be speculatively interpreted as follows. In the case of the long segments, length and mobility possibly suffice for a nearly optimum crystallization of both kinds of chain segments. Optimum crystallization means here that the degree of crystallization of both PCLs and PEG approaches the value typical for the non-crosslinked homopolymers. If this is true, the 50/50 composition represents the maximum of the total crystallinity of the networks, with the consequence of a lower tendency to swell. Regardless of the interpretation, these results demonstrate that the interaction of the PCL/PEG combi-network with solvents (and other low molar mass compounds) depends in a complex manner of segment length and composition.

The thermal behavior of all gels was evaluated by DSC. These results are summarized in tables 16 and 17. Figure 30 and the results listed Tables 16 and 17 shows only one T_m peak probably the melting point of PCL block, because earlier crystallization of PCL block restricted the crystallization of the PEG block. The second probability of Tm is the overlapping of melting peaks of PCL and PEG blocks. Anyway the values of Tm seem to increase with the ratio of PEG, while the values of T_g decrease. DSC data listed in Tables 16 and 17 show the presence of phase separation, which is also demonstrated by the WAXS results shown in Fig 31.

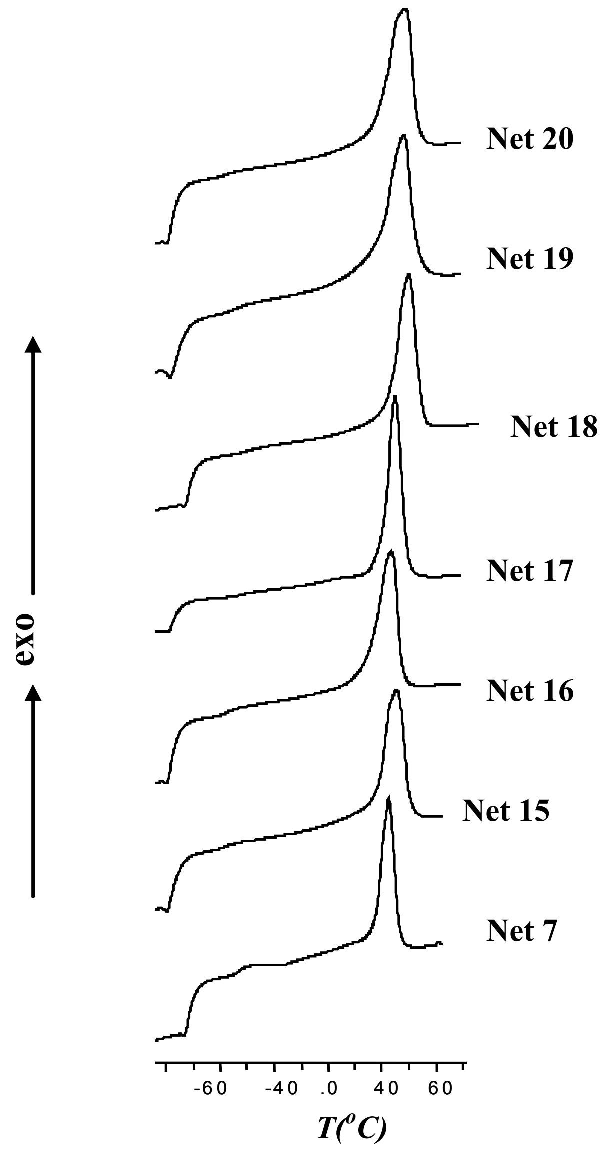


Fig 30. DSC curves of the networks synthesized from PCL$_8$ and PEG with Mw = 4600

Figure 31 shows the WAXS intensity curves of gels synthesized from PEG (Mw ~ 4600) and poly(ε-CL)diols. Sharp diffraction peaks were measured for these films, probably because of crystallization of the PCL components. The crystalline pattern of both PCL and PEG domains were observed clearly in **$\mathbf{Net_{18}}$,** indicating that the melting peaks in DSC profile was contributed by both domains.

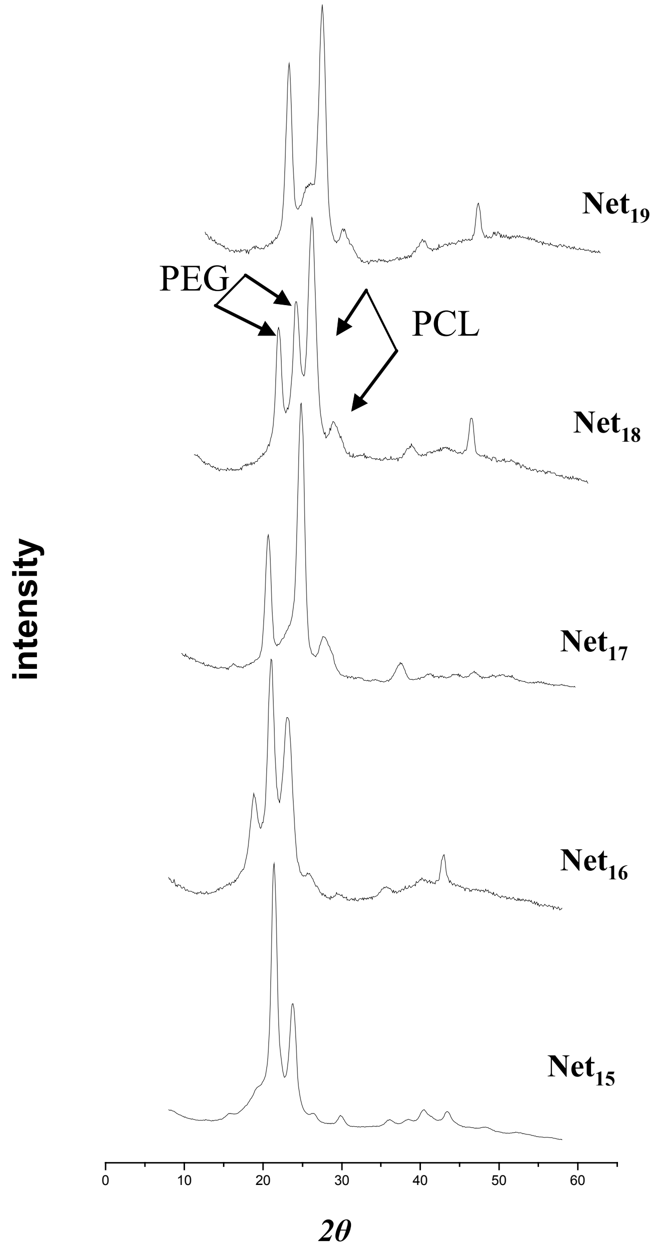


Fig 31. WAXS patterns of gels film synthesized from PCL_8 with PEG = 4600

3.3.3.3 Synthesis and characterization of combi-networks derived from poly(ε-CL)diols and bis(hydroxyprobyl)-terminated poly(dimethylsiloxan)

New series of gels were prepared from poly(ε-CL)diols (Mw ~ 2000) derived from BD with bis(hydroxyprobyl)-terminated poly(dimethylsiloxan) (PDMS) with Mw about 4000. This commercial polysiloxane had a number average molecular weight (M_n) of 4000 Da, what means that its chain lengths were similar to those of the aforementioned PCL. These gels with hydrophobic characters was produced by mixing PDMS in different ratios with poly(ε-CL)diols and cross-linked by mean of trimesoyl chloride and pyridine (Scheme 26). Yields between 42 and 85 were achieved as compiled in Table 18.

Table 18. Combi-networks synthesized from PCL_5 with Polysiloxane.

Network	Feed ratio of PCL_5/ Poly(siloxan)[a] 4000	Yield (%)	SF[b] in CH_2Cl_2	SF[b] in THF	SF[b] in Toluene	Ratio of PCL_5/ Polysiloxane Using ^{1}H-NMR	T_g [c] (°C)	T_m [c] (°C)
Net$_5$	**100/0**	**85**	**26**	**20**	**16**	**100:0.0**	-51.87	49.7
Net$_{21}$	**80/20**	**42**	**32**	**34.7**	**24**	**88.12**	-50.32	45.0
Net$_{22}$	**60/40**	**84**	**26.9**	**26.8**	**19.9**	**63.37**	-39.65	40.1
Net$_{23}$	**50/50**	**80**	**10.5**	**11.9**	**10.3**	**54:46**	-42.08	37.0
Net$_{24}$	**40/60**	**77**	**13.6**	**13.8**	**9.5**	**43:57**	-47.6	39.1
Net$_{25}$	**20/80**	**78**	**9.6**	**11.6**	**9.3**	**27:73**	-52.01	36.9
Net$_{26}$	**0/100**	**84**	**10.3**	**19.6**	**12.7**	**0.0:100**	-	-

[a] ***M.W Polysiloxane = 4000 g/mol***
[b] ***the swelling factors (SF) are multiplied with Factor of 10***
[c] ***thermal properties were measured with 20°C/min.***

The actual mole ratios of PCL to PDMS incorporated in the building of biodegradable networks were successfully measured from the ^{1}H-NMR, where the spectra showed sharp peaks as illustrated in Figure 32. The molar compositions found by ^{1}H NMR spectroscopy roughly agreed with the feed ratios, as exemplarily illustrated in Figure 32. However, in contrast to the PEG-containing networks, the PDMS-containing networks display the trend that PCL was more efficiently incorporated than the polysiloxane.

The swelling behavior of all gels synthesized from PMDS was studied in three solvents of different structures: CH_2Cl_2, THF, and toluene as listed in Tables 18. The highest swelling factors determined for all gels were found in CH_2Cl_2. As it was found in this work, the swelling factor decreased in the following sequences CH_2Cl_2 > THF > toluene. All three liquids are good solvents for both kinds of segments. Therefore, it is difficult to understand why the swelling factor decreases, when the content of siloxane chains increases. For tetrahydrofuran and toluene this trend is not clear. For these solvents the swelling of both homo-networks was stronger than for most combi-networks (with exception of the 80/20 composition). No satisfactory explanation can be offered for this observation at this time. The DSC measurements revealed the following trends: Only Tg and Tm of the PCL segments were detectable because the polysiloxane chains do not crystallize and because their Tg (-120°C for the non-crosslinked homopolymer) was lower than the starting temperature of our measurements. The DSC curves presented in Figure 33 illustrate how Tm and the melting enthalpy depend on the composition of the PDMS-containing networks. The WAXS powder patterns confirmed the crystallization of the PCL segments. Since no other crystallizing component was present, all WAXS powder patterns of the series III networks were uniform.

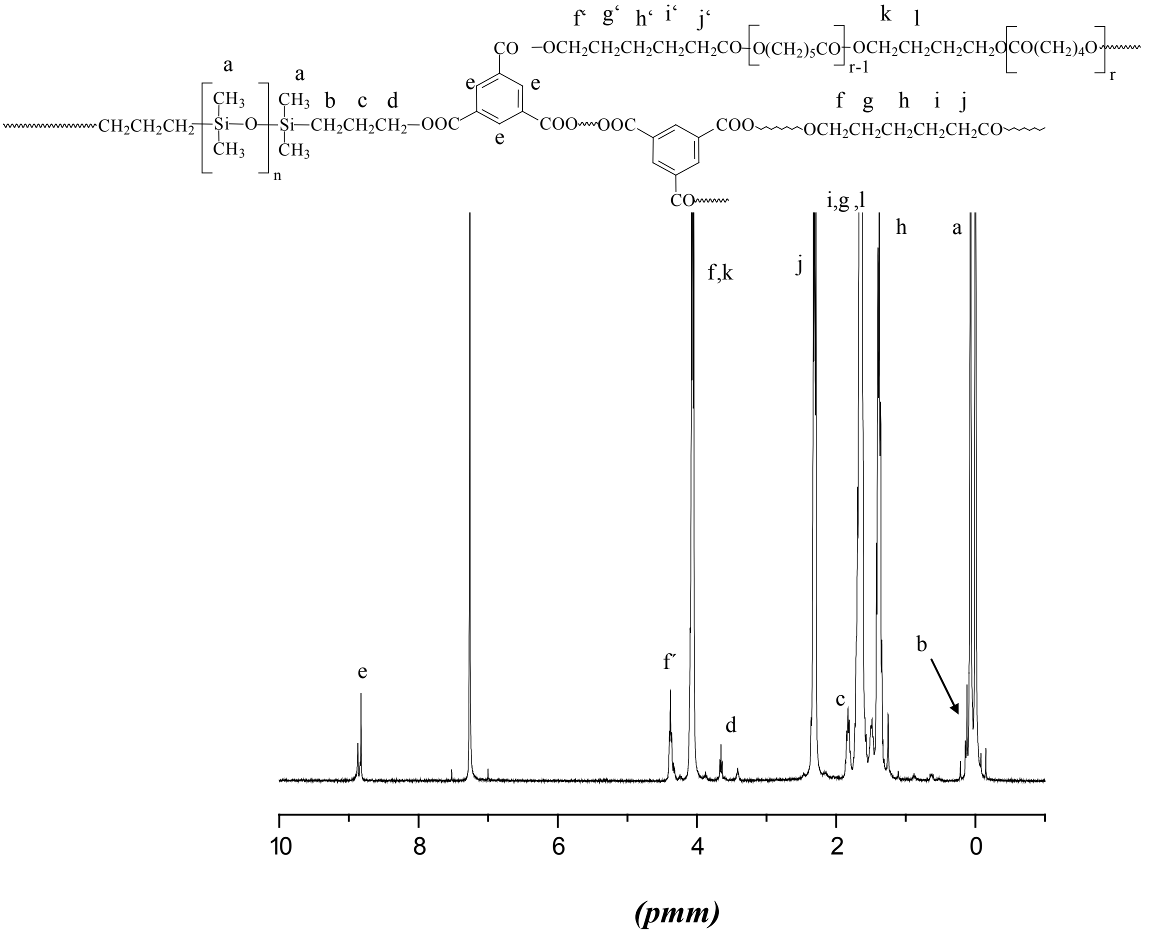


Fig 32. The 400 MHz ^1H-NMR spectrum of Net_{21} in Table 22 swelling in $CDCl_3$.

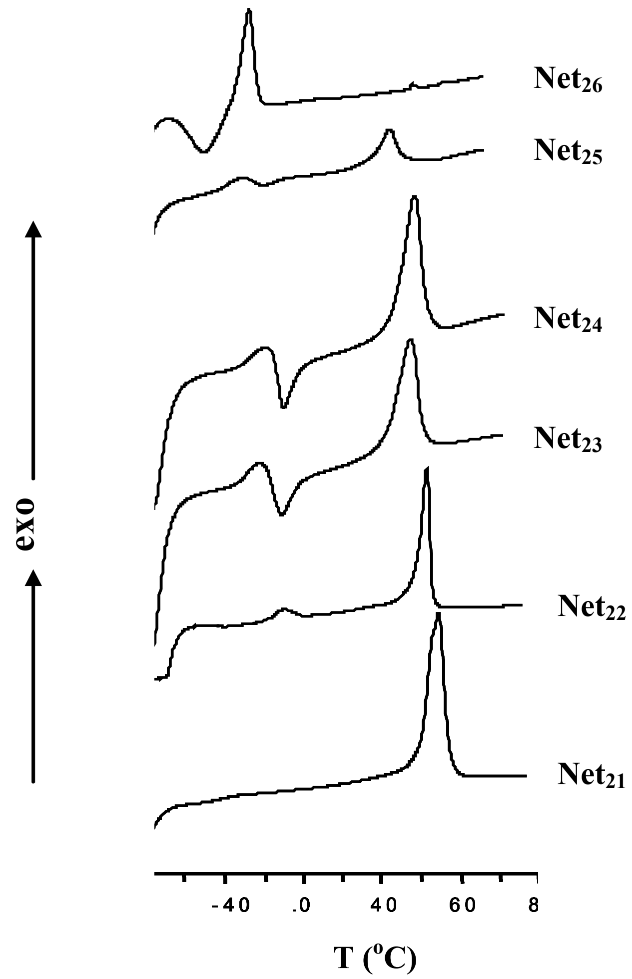


Fig 33. DSC curves of networks synthesized from PCL$_5$ and PDMS with Mw = 4000

3.4 Trapping and purification of cyclic polymers using biodegradable networks:

3.4.1 Introduction

As shown in the previous sections of this thesis polycondensation products contained usually mixture of cyclic and linear polymers. These linear polymers in most cases could be considered as byproducts. The purification of cyclic polymers requires the separation from linear byproducts. Therefore, different methods were used to perform the separation of cyclic products [230-248]. Instrumental methods based on fractionation techniques were utilized to remove linear byproducts [230-239]. One of the most effective methods is liquid chromatography at the critical condition (LCCC). The critical condition is the condition where all linear species elute at the same time regardless of their molecular weight [247], whereby, the separation only depends on chain architecture. The conditions (e.g. solvent quality, temperature, solid phase) are charactirstic for a given polymer to establish this special case. This method is only applicable to mg quantities.

Cyclic materials have also been efficiently separated from charged linear byproducts using a macroporous anion-exchange resin [240]. This method is not applicable to any kind of polymer mixtures because it is restricted to charged linear byproducts. Cyclodextrines (α, β, and γ) were used recently to separate cyclic polymers by inclusion complexation of the linear byproducts with cyclodextrines [241-248].

Different macrocyclic compounds with up to around 100 atoms were successfully trapped either in linear or network structures [249-258]. However, the threading of larger-size flexible cyclic polymers has scarcely been reported [259-263]. These cyclic polymers were exclusively based on poly(dimethylsiloxanes) PDMS. Furthermore, no attempt was made to use this technique in the separation of cyclic polymers from linear byproducts.

The present work aimed to trap and separate cyclic polymers from linear byproducts using biodegradable networks.

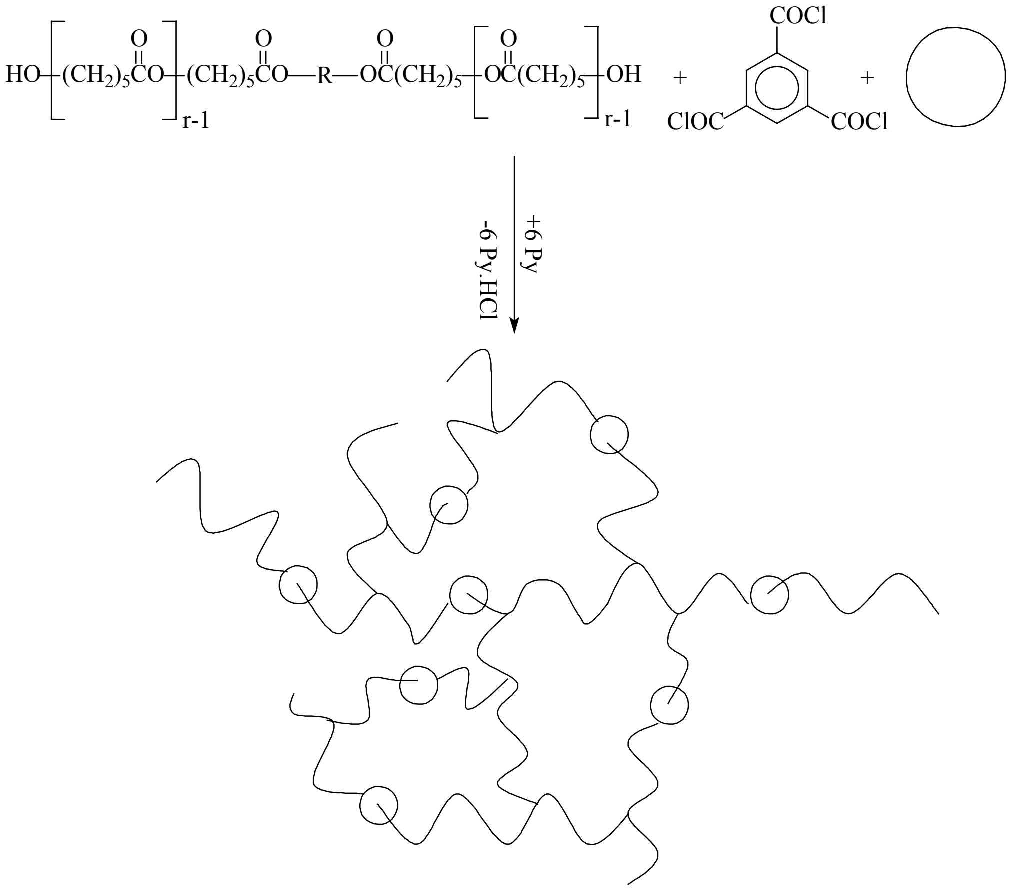
3.4.2 Results and discussions

Different crosslinkable prepolymers mainly based on ε-caprolactone were synthesized as listed in Table 19. These polymers were crosslinked in the presence of either cyclic polymer or mixture of cyclic and linear aromatic polyethers using trimesoylchloride and pyridine as shown in Scheme 27. All the synthesized networks were extracted using dichloromethane to remove all polymer species which were not trapped in the network structure.

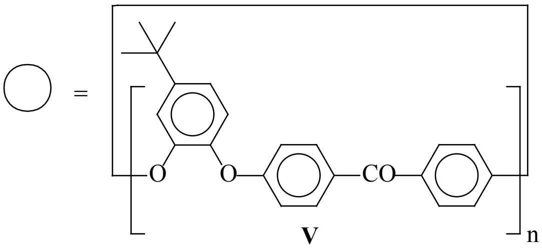
Trapping of cyclic aromatic polyethers in biodegradable networks was achieved by crosslinked poly(ε-caprolactone) using trimesoyl chloride and pyridine in the presence of cyclic aromatic polyethers. The trapping was accomplished by the PCL chain threading through cyclic polymers during the crosslinked process.

Table 19. Synthesis of poly(ε-caprolacton)diol derived from tetraethylenglyol and PEG.

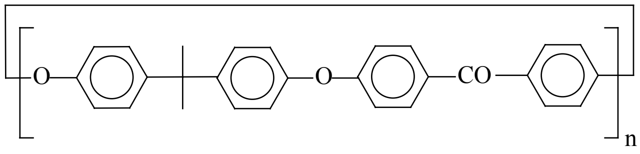
Polymer	**M1**	**COI**	**Feed ratio (M/COI)**	**Actual ratio measured by ^{1}H-NMR**	**yields**
PCL$_1$	**ε-CL**	**TEG**	**1/20**	**19**	**90**
PCL$_3$	**ε-CL**	**TEG**	**1/40**	**42**	**97**
PCL$_{10}$	**ε-CL**	**PEG600**	**1/20**	**18**	**84**
PCL$_{11}$	**ε-CL**	**PEG2000**	**1/20**	**22**	**96**



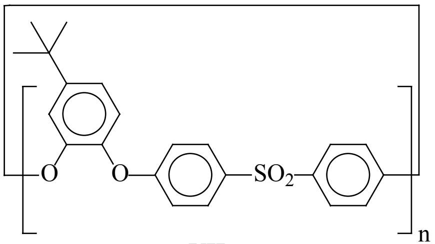
R = TEG, PEG $_{MW=600}$, PEG $_{MW=2000}$



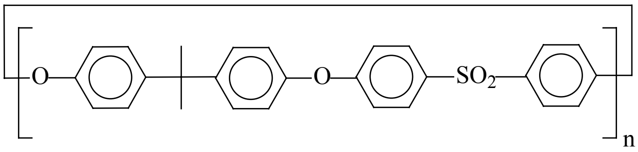
V



VI



VII



VIII

The driving force of this process was the establishment of noncovalent interactions between the cyclic species and poly(ε-caprolactone) chains. The interpenetrating of cyclic species in network structure was proved by ^{1}H-NMR spectroscopy. As illustrated in Figure 34 the chemical shift characteristic for aromatic hydrogens in cyclic polymers are found in the expected range 7-8 ppm. The quantity of cyclic species trapped in network was approximately 25% by weight. Furthermore, the quantity was found to increase with higher poly(ε-caprolactone) diols chain length.

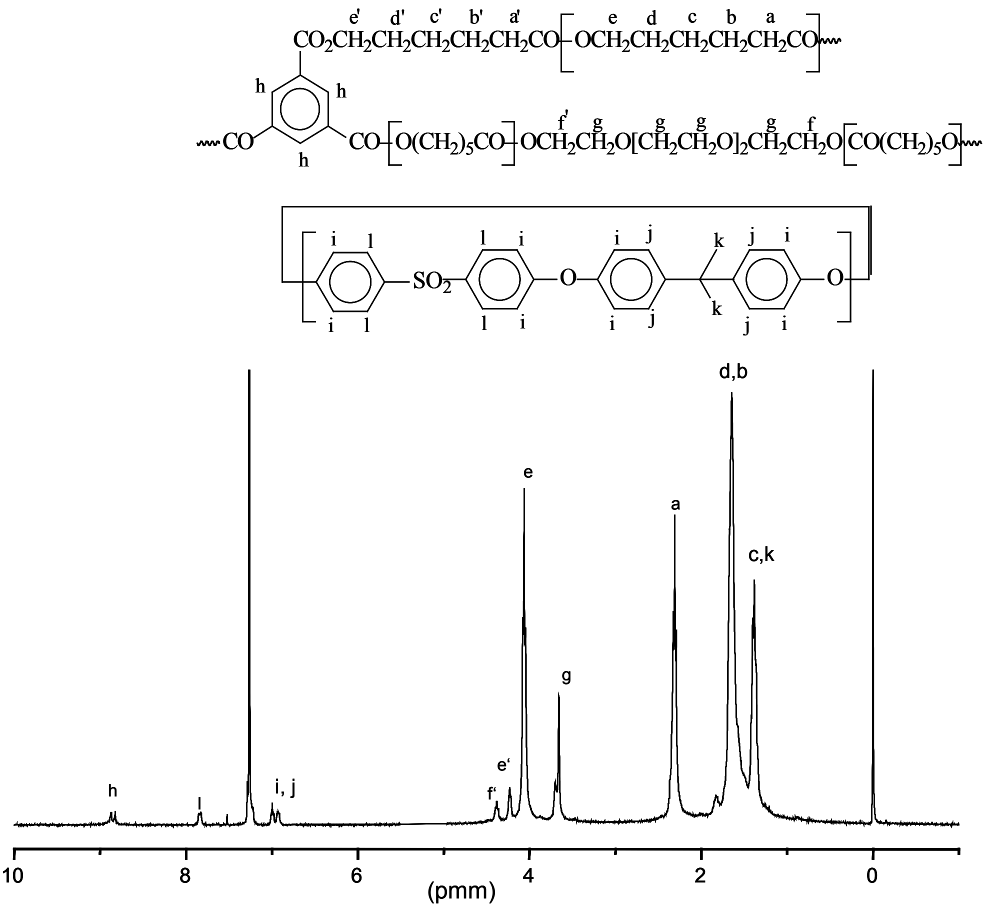


Fig 34. The 400 MHz ^{1}H-NMR spectrum of network synthesized from PCL1 trapped with poly(ether sulfone)(VIII) swelling in $CDCl_3$.

The attempt to separate cyclic aromatic polyethers was performed through the crosslinking of PCL in the presence of mixture of cyclic and linear species. The linear aromatic polyethers used in these experiments were synthesized to produce polymers without –OH terminated groups, which may form covelant bonds in the crosslinking process.

To remove the linear and the non trapped cyclic species, they were extracted using dichloromethane. The extracted species were characterized using MALDI-TOF and as shown in Figure 35 the extract contained both cyclic and linear species. After extraction, the networks were chemically degraded using propylamine to produce soluble low molecular weight compounds (e.g. σ-hydroxyhexanoyl propylamide). After the degradation of networks, the cyclic species were precipitated into methanol, whereby the degradation products were expected to be soluble. However, the degradation products of the networks synthesized from PCL_1 and PCL_2 were not completely soluble in methanol. Therefore, PEG with Mw of 600 and 2000 were used to synthesis poly(ε-caprolactone) diols which increase the solubility of degradation products. All the degradation products were completely soluble which allow the recovery of aromatic polyethers trapped in network structure. The recovered polyether species were characterized using MALDI-TOF spectroscopy as shown in Figure 36. Unfortunately, the recovered species contained cyclic and linear species. When chloroform and tetrachloromethan were used instead of dichloromethan for extraction of nontrapped cyclic species and linear species, same results were found. The presence of linear species may be explained by the strong noncovalent interactions between the aromatic polyether chains and PCL chains.

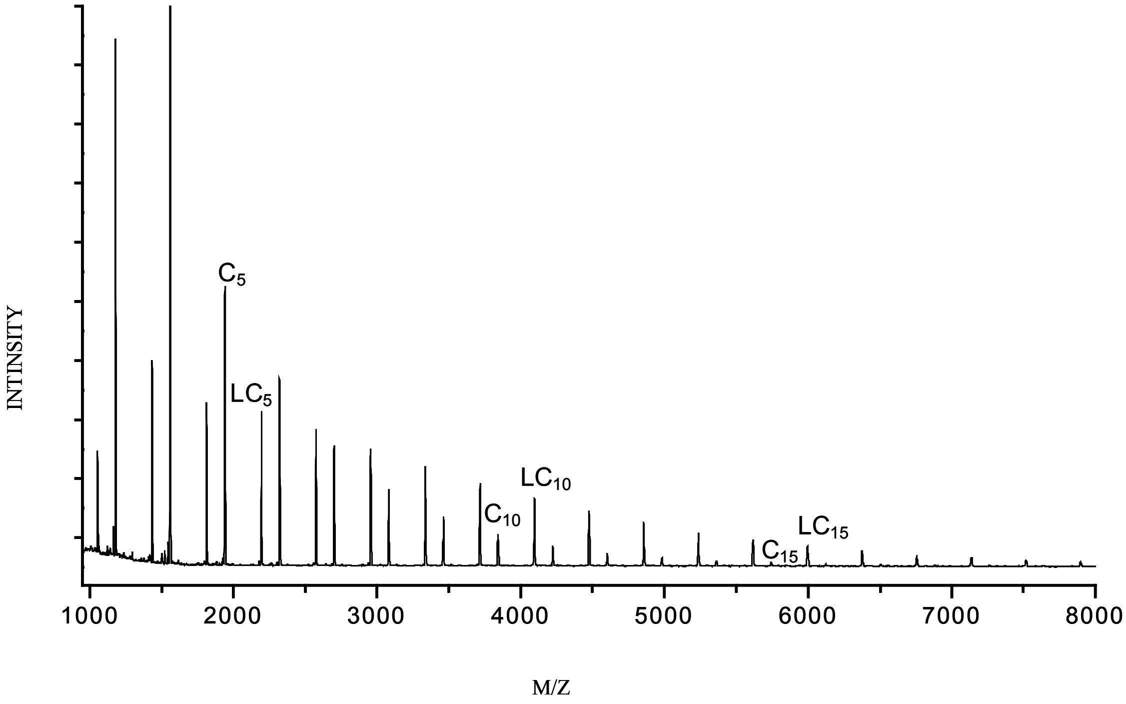


Fig 35. MALDI-TOF mass spectrum of extracted poly(ether slufone)(VII)

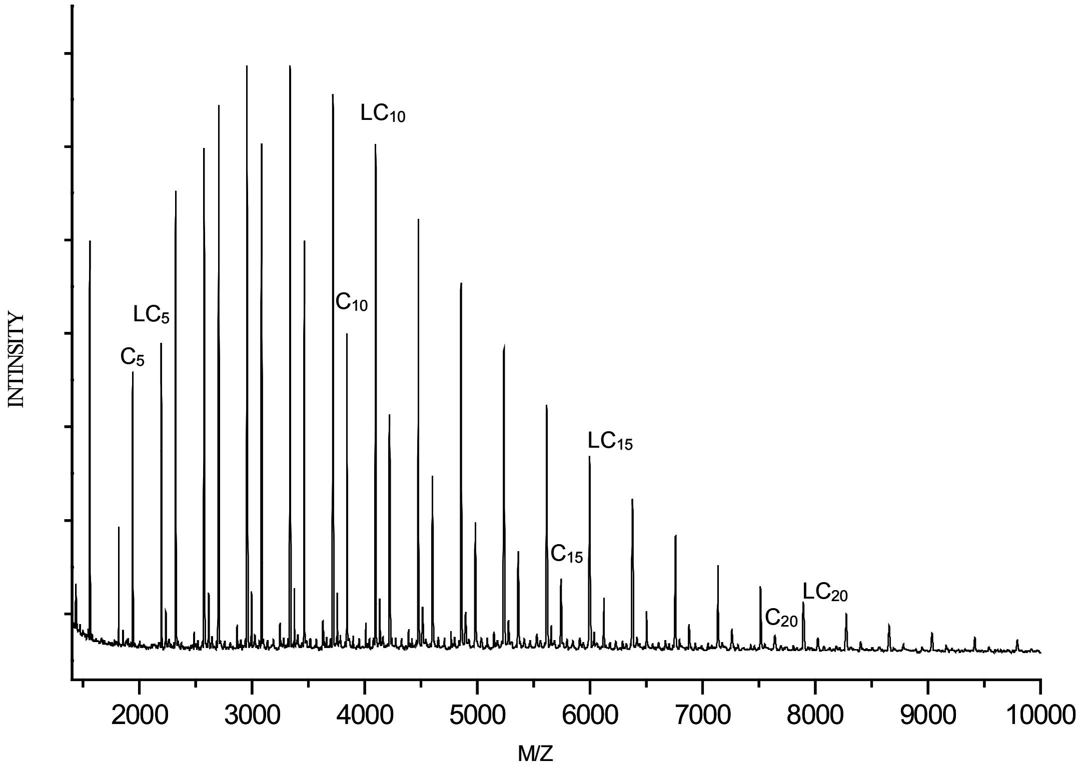


Fig 36. MALDI-TOF mass spectrum of poly(ether slufone) (VII) after the degradation of network with n-propylamine

4 Conclusions

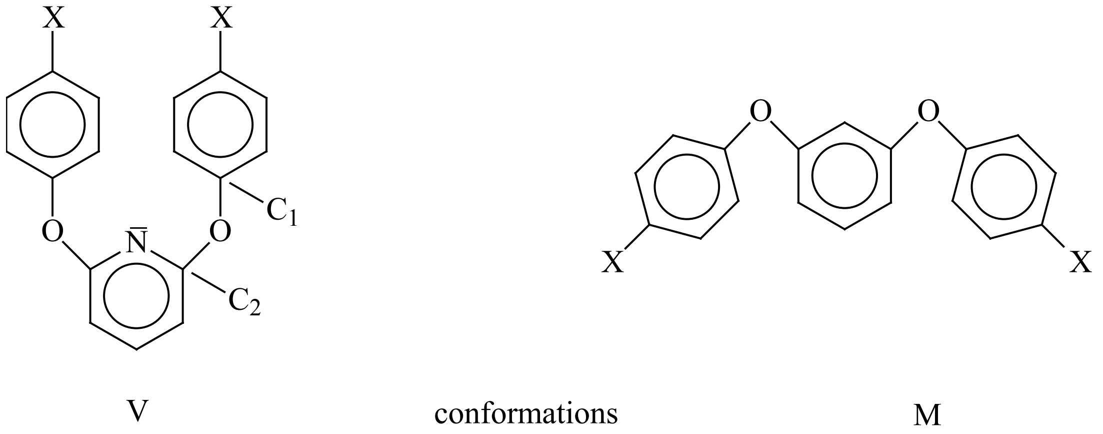
4.1 Synthesis of cyclic aromatic polyethers and aliphatic polyester

Different aromatic polyethers were synthesized under different conditions to prove the validity of Kricheldorf's new theory dealing with polycondensations under kinetic controlled conditions. Additionally, reinvestigation of aliphatic polyester based on pivalolacton was performed using different catalyst to check out the probability of cyclization reactions. The conclusions of this work are summarized in this section with respect to each polymer.

Synthesis of poly(ether ketone)s provide several informative conclusions. First, the quality of MALDI-TOF m.s. has been improved and in favorable cases the mass peaks of cyclic poly(ether ketone)s were detectable up to 18 000 Da, indicating the cyclization of long chains. Secondly, the extent of cyclization proved again to be a useful indicator of perfect reaction conditions. All factors favoring clean polycondensations and high conversions also favored cyclizations. Thirdly, the silyl method proved to be superior to the polycondensation of free bisphenol-A. Fourthly, in agreement to syntheses of poly(ether sulfone)s [152,153], 4-tert.butylcatechol did not favor cyclization when compared to bisphenol-A despite the ortho position of both ether bonds. Fifthly, 2,6-difluoroketones do not favor cyclization when compared to 4,4'-difluorobenzophenone, but higher reaction temperatures may be needed for high conversions.

The syntheses of poly(benzonitrile ether)s studied in this work revealed a couple of unexpected trends in addition to the expected ones. An expected overriding trend is the formation of larger fractions of cyclic oligomers and polymers with increasing conversion, and thus, with increasing reactivity of the dihalobenzonitrile. Another expected result is the lower reactivity of the 3,5-difluorobenzonitrile relative to the 2,4- and 2,6-isomers. Rather unexpected is the high cyclization tendency observed for polycondensations of the 2,6- and even more for the 2,4-difluorobenzonitrile in the sulfolane or xylene system. Unexpected, with respect to the classical theoretical background of step growth polymerizations is the bimodal character of MWDs, whenever the reaction conditions favor cyclization.

Poly(ether pyridine)s synthesized in this work allow the following conclusions: Despite lower reaction temperatures relative to previous studies, the reaction conditions used in this work allowed for almost quantitative conversions of the functional groups. The samples with the highest molecular weights possess the highest content of cyclic polyethers. No side reactions were detectable. Therefore, the chain growth of the optimized samples was limited by cyclization according to Eq.9 since both inherent viscosities and SEC measurements indicate low molecular weights. Hence, it may be concluded that the polycondensations of 2,6-DFP involve a particularly high cyclization tendency. This conclusion was supported by computer simulation of conformations resulting from rotations around the C_1-O and C_2-O bonds in the model compound 2,6-diphenoxypyridine (Scheme 27). This computer simulation indicates that a V-like conformation with nearly parallel (coplanar) phenoxy groups is energetically most favorable. The distance of functional groups in para position (X) amounts to approx 6.5 Å as compared to 13-14 Å in M-like conformations. It is obvious that V-like conformations favor cyclization reactions more than M-like conformations.



Scheme 27

In summary, the present works provided a satisfactory completion of Kricheldorfs et.al. recent studies of other aromatic polyethers [151-153].

The investigation of zwitterionic polymerization of pivalolactone using MALDI-TOF mass spectroscopic measurements evidenced that both pyridine-type initiators and trialkylamine initiate a zwitterionic polymerization of pivalolactone. With exception of initiation with 2-ethyloxazoline, no cyclic oligolactones were found. This finding proves that the chain growth almost exclusively proceeds via an anionic ring-opening polymerization of the lactone. However, it was also observed that the molecular weights increased in NMP at higher temperatures, also the conversions were high at all temperatures. In other words, the molecular weights did not parallel the conversions. This finding suggests that at least a few condensation steps involving the anionic chain ends contributed to the chain growth after the anionic ring-opening polymerization was almost complete. In the case of initiation with 2-ethyloxazoline, cyclization via a special mechanism was also observed.

Based on the polycondensation's results and conclusions of aromatic polyethers, it could be clearly to give the new theory of Kricheldorf preponderance over the classical theory of Flory and Carothres. This preponderance is supported with the following general results and conclusions.

1) With help of MALDI-TOF mass techniques allows the detection of individual polymer molecules up to the technical range, it was found that cycles were the main product.

2) It was found that cyclization competes with propagation at any stage of the polycondensation and at any concentration. As a consequence, the most components of polycondensation products must be cycles.

Taking into account this result, it is necessary to consider the rate of propagation and cyclization in measuring the degree of polymerization. In addition to the adaptation of polycondensation at different concentrations as represented by Eq.9

3) In all polycondensations made in this work, it was found that the optimization of reaction conditions for high conversion, favour the formation of cyclic aromatic polyethers. This conclusion agree with calculations by Stepto et al.[15,16], and Gordon et al.[17,18], who postulated that an ideal KCP yields 100% cycles of any size at 100% conversion.

4) It was found that the chemical structure of monomers did not play important role in the rate of cyclization. It was thought that functional groups in *meta*- or *ortho*-position have higher opportunity for cyclization than in the case of polymers containing *para*-functional groups. In contrary to this expectation, monomers with *para*-functional groups have higher opportunity to produce cycles. This result shown clearly in synthesis of Poly(ether ketone)s , where PEKs derived from **4,4'-DFBP** have higher tendency for cyclization than those synthesized from **3a** or **3b.**

5) GPC measurements performed in this work showed the bimodal character of MWDs, whenever the reaction conditions favor cyclization. This result is in contrary with the classical theoretical background of step growth polymerizations, which suggest the monomodal character.

Considering Kricheldorf's theory and both inverse- and normal Ruggli-Ziegler high dilution principle, these results could be elucidated as follow: the polycondensation reactions are self-diluting reactions with respect to the functional group (reactive linear species). Therefore, a high probability of cyclization is possible even for high molecular weight chains, in addition to the limitation of the chain growth caused by cyclization.

With respect to all the above results and conclusions, it may be generalized that: cyclic polymers can be produced under kinetic controlled step-growth polymerization from any type of polycondensation reaction, by modification of the synthesis method to prevent the formation of side reactions, which may causes any kind of equilibria or destruction of functional groups.

4.2 Synthesis of biodegradable networks

Various biodegradable networks based on aliphatic polyester and trimsoly chloride as cross-linked were prepared. The first classes were prepared from poly(caprolactone)diols with Mws of 2000, 3000, 4000, and 5000. These networks polyester varied in their properties, depending on the Mw of poly(CL)diols, and the chemical structure of the coinitiators used in the synthesis of poly(CL)diols. 1,4-Butandiol and tetraethylenglycol were used successfully in the synthesis of these diols. Another classes of biodegradable networks polyesters were prepared from poly(CL)diols and different polyols. Namely, poly(ethylene glycol)s with Mws 2000 and 4600, and bis(hydroxypropyl)-poly(dimethylsiloxane) with mw of 4000. The reaction sequence of these classes of cross-linked polyesters allowed the control of their properties through the hydrophilicity of the polyols, the ratio of poly(CL)diols to these polyols, and to the Mws of poly(CL)dilos. The ability to vary the properties of these biodegradable networks and the good swelling in several organic solvents suggested that such networks might be useful as matrix of drug-delivery systems. DSC and WAXS measurements showed the presence of phase separation between poly(CL)diols block and PEG or PDMS blocks. The Tm peaks of PEG were not detected due to the earilear crystillization of PCL blocks or to the overlapping of Tm peaks of PCL blocks and PEG blocks. The overlapping of Tm peaks was proved by WAXS which showed the crystalline pattern of both PCL and PEG domains. Despite the results showed that biodegradable network could be successfully used to trap cyclic species, it was difficult to use them for the separation of cyclic species by extraction.

5 Experimental Part:

5.1 Instruments and measurements

5.1.1 Viscosity

The inherent viscosities were measured using an automated Ubbelohde viscometer thermostated at 20°C. The concentration of about 2 g/l was accomplished by dissolving the polymers either in CH_2Cl_2 or in a mixture of CH_2Cl_2 and trifluoroacetic acid (volume ratio 4/1).

5.1.2 ^{1}H-NMR spectroscopy

The 400 MHz ^{1}H-NMR spectra were recorded on a Bruker Avance 400 FT spectrometer in 5 mm o.d. sample tubes using $CDCl_3$ + TMS as solvent and shift reference.

5.1.3 MALDI-TOF

The MALDI-TOF mass spectra were measured with a Bruker Biflex III mass spectrometer equipped with a nitrogen laser (λ = 337 nm). All spectra were recorded in the reflection mode using an acceleration voltage of 20 kV. The irradiation targets were prepared either from solutions in chloroform or solutions in chloroform containing trifluoroacetic acid (volume ratio 8:1) using dithranol as matrix and potassium trifluoroacetate as dopant.

5.1.4 Size-exclusion Chromatography

The SEC measurements were performed with a SEC apparatus of Polymer Laboratories containing a RI detector “Shodex RI 101”. A combination of three PL mixed bed column was used with chloroform as eluent (flow rate 1.0 mL/min). Commercial polystyrene standards served for calibration.

5.1.5 Differential scanning calorimeter (DSC)

The DSC measurements were preformed using Mettler Toledo apparatus of type DSC821e, whereby the date was analyzed using STARE 6.01 software. The heating and cooling rats used in measuring the DSC of polymers were 20 ^{o}C/min. 3-8 mg of polymers were weight in aluminum patella.

5.1.6 Wide angle X-ray

WAXS were measured using Goniometer D500 (Siemens) connected with Siemac V (Siemens). Cu-Kα radiation with $\lambda = 1.54$ Å was used as source of X-ray.

5.1.7 Elemental analysis

Elemental analyses were carried out with a Heraeus CHN-O-Rapid instrument.

5.2 Solvents and chemicals

Table 20. List of solvents and their purification methods:

Solvent	Hazard Codes	R-phrases	S-phrases	Sources	Purification method
Acetic Acid	**C**	**10-20/21/22-35**	**23-26-45**	**Merck, Darmstadt**	**-**
Chlorobenzene	**Xn, N**	**10-20-51/53**	**24/25-61**	**Aldrich, Steinheim**	**-**
Chloroform	**Xn**	**22-38-40-48/20/ 22**	**20/22**	**Merck, Darmstadt**	**-**
Chloroform-d$_1$	**Xn**	**22-38-40-48/20/ 22**	**36/37**	**Aldrich, Steinheim**	**-**
2-Chlorophenol	**Xn, N**	**20/21/22-51/53**	**28-61**	**Fluka**	**-**
Dichloroacetic Acid	**C, N**	**35-50**	**1/2-26-45-61**		**-**
Dichloromethane	**Xn**	**40**	**23/24/25 -36/37**	**Merck, Darmstadt**	**1**
Diethylether	**F+, Xn**	**12-19**	**2-9-16-29-33**	**Merck, Darmstadt**	**2**
Dimethyl sulfoxide	**-**	**-**	**24/25**	**Merck, Darmstadt**	**-**
Dioxan	**F, Xn**	**11-19-36/37-40-66**	***9-16-36/37-46***	**Merck, Darmstadt**	**-**
Ethanol	**F**	**11**	**7-16**	**Merck, Darmstadt**	**-**
Ethyl Acetate	**F, Xi**	**11-36-66-67**	**16-23-29 -33**	**Merck, Darmstadt**	**-**
Formic Acid	**C**	**35**	**23-26-36/ 37-39-45**	**Laucaster**	**-**
m-Cresol	**T**	**24/25-34**	**36/37/39-45**	**Merck, Darmstadt**	**-**

Solvent	Hazard Codes	R-phrases	S-phrases	Sources	Purification method
Methanol	**F, T**	**11-23/24/25-39**	**7-16-36/37-45**	**Merck, Darmstadt**	**-**
Dimethylformamide	**T**	**61-20/21-36**	**53-45**	**Merck, Darmstadt**	**-**
N-methyl pyrrolidone	**Xi**	**36/38**	**41**	**Gift from BASF AG**	**2**
Nitrobenzene	T, N	**23/24/25-40-48/23/24-51/53-62**	**28-36/37-45-61**	**Merck, Darmstadt**	**-**
Petroleum ether (60/70)	**F,Xn,N**	**11-38-48/20-51/53-62-65-67**	**16-33-36/37-60-62**	**Haltermann, Hamburg**	**1**
sulfolane	**Xn**	**22**	**23-25**	**Merck, Darmstadt**	**-**
Sulfonic Acid	**-**	**-**	**-**	**Merck, Darmstadt**	**-**
Tetrahydrofuran	**F,Xi**	**11-19-36/37**	**16-29-33**	**Merck, Darmstadt**	**3**
Trifluoroacetic Acid	**C**	**20-35-52/53**	9-26/27/28-45-61	**Laucaster**	**-**
Toluene	**F,Xi**	11-20	16-25-29-33	**Merck, Darmstadt**	**3**
Xylene	**Xn**	**10-20/21-38**	**25**	**Merck, Darmstadt**	**-**

1) Was distilled over P_4O_{10} at atmospheric pressure

2) Was twice distilled over P4O10 in vacuum.

3) Distillation over sodium.

Table 21. Chemicals and their purifications:

Substance	Hazardes Code	R-phrases	S-phrases	Source	Purification method
1,1-bis(4-hydroxyphenyl) phenyl ethane	**Xi**	**36**	**26-36**	**Aldrich, Milwaukee**	**-**
9,9-bis(4-hydroxyphenyl) fluorene	**Xi,N**	**36/38-50/ 53**	**26-37-60- 61**	**Aldrich, Milwaukee**	**-**
1,1-bis(4-hydroxyphenyl) cyclohexane	**Xi**	**36/37/38**	**26-36**	**Aldrich, Milwaukee**	**-**
Bisphenol-A	**Xi**	36/37/38- 43	24-26-37	**A gift of Bayer AG, Urindingen**	**-**
1,4-Butandiol	**Xn**	**22**	**36**	**Aldrich, Steinheim**	**1, 6**
Calcium hydrid	**F**	**15**	**7/8-24/ 25-43**	**Aldrich, Steinheim**	**-**
ε-Caprolactone	**-**	**23-24/25**	**4**	**Aldrich, Steinheim**	**2**
1,4-Diazabicyclo [2.2.2] octane	**F,Xn**	**11-22- 36/37/38- 52/53**	**26-60**	**Aldrich, Milwaukee**	**-**
2,6-Dichlorobenzonitrile	**Xn,N**	**21-51/53**	**36/37-61**	**Aldrich, Milwaukee**	**-**
2,4-Diflurobenzonitrile	**Xn**	**20/21/22- 36/37/38**	**26-37/ 39**	**Aldrich, Milwaukee**	**-**
3,5-Diflurobenzonitrile	**Xn**	**20/21/22- 36/37/38**	**26-36**	**Aldrich, Milwaukee**	**-**
2,6-Diflurobenzoic acid	**Xi**	**36/37/38**	**26-36**	**Aldrich, Steinheim**	**-**
2,6-Diflurobenzonitrile	**Xn**	**20/21/22- 36/37/38**	**26-36**	**Aldrich, Milwaukee**	
2,6-Difluoropyridine **(minimum purity 99%)**	**Xi**	**10-36/37/ 38**	**16-26- 36/37/39**	**Aldrich, Milwaukee**	**-**

Substance	Hazardes Code	R-phrases	S-phrases	Source	Purification method
4,4'-Dihydroxybiphenyl	**Xn**	**21-36/37/ 38**	**26-36**	**Aldrich, Milwaukee**	**-**
4,4'-Dihydroxybiphenyl ether	**-**	**-**	**-**	**Bayer AG, Urindingen**	**-**
4-N,N-Dimethylaminopyridine	**T+**	**25-27-36/ 37/38**	**26-28-36/ 37/39-45**	**Aldrich, Milwaukee**	**4**
2-Ethyloxazoline	**Xn**	**10-20/21/ 22**	**16-26-28-36/37/39**	**Aldrich, Milwaukee**	**3**
4-Flurobenzoic acid	**Xi**	**37/38**	**22-28**	**Aldrich, Steinheim**	**-**
Hexamethyldisilazane	**F,C**	**11-20/21/ 22-34**	**16-26-36/ 37/39-45**	**Fluka**	**-**
4-Methylpyridine	**T**	**10-20/22-24-36/37/38**	**26-36-45**	**Aldrich, Milwaukee**	**3**
P_4O_{10}	**C**	**35**	**22-26-45**	**Riedel-de Haön**	**-**
PEG 2000	**-**	**-**	**-**	**Aldrich, Steinheim**	**2**
PEG 4600	**-**	**-**	**-**	**Aldrich, Steinheim**	**2**
Pivalolactone	**?**	**?**	**?**	**E.T. DuPont ,Wilmington**	**3**
Poly(dimethylsiloxan) 4000	**-**	**-**	**Wacker**	**-**	**1**
potassium carbonate	**Xn**	**22-36/37/38**	**26-36**	**Merck, Darmstadt**	**5**
β-Propiolactone	**T+**	**45-26-36/ 38**	**53-45**	**Aldrich, Milwaukee**	**3**
Propylamine	**F, C**	**11-20/21/ 22-34**	**16-26-36-45-7/9**	**Aldrich, Milwaukee**	**-**
Pyridine	**F,Xn**	**11-20/21/22**	**26-28**	**Aldrich, Milwaukee**	**3**
Sodium	**F,C**	**14/15-34**	**8-43-45**	**Merck, Darmstadt**	**-**

Substance	Hazardes Code	R-phrases	S-phrases	Source	Purification method
Thionylchloride	**C**	**14-20/22-29-35**	**26-36/37/39-45**	**Merck, Darmstadt**	**6**
4-Tert.butylcatechol	**C**	**21/22-34-43**	**26-36/37/39-45**	**Aldrich, Steinheim**	**-**
tetraethyleneglycol	**-**	**-**	**-**	**Aldrich, Steinheim**	**1, 6**
Tin(II)ethylhexanoat	**Xn**	**63**	**20/21/22**	**Aldrich**	**1+6**
Trimesic acid	**Xi**	**36/37/38**	**26-36/37/39**	**Aldrich, Steinheim**	**-**

1) Azeotropic distillation using absolute toluene.

2) Stirred over freshly powdered calcium hydride (48 h), and then distilled at 60-80 ^oC in vacuum.

3) Were distilled over freshly powdered calcium hydride

4) Was dried in desiccators over P_4O_{10} in vacuum.

5) Was dried at 160°C in vacuum.

6) Vacuum distillation.

R-Statements:

R10 Flammable.

R11 Highly flammable.

R12 Extremely flammable.

R14 Reacts violently with water.

R19 May form explosive peroxides.

R20 Harmful by inhalation.

R21 Harmful in contact with skin.

R22 Harmful if swallowed.

R23 Toxic by inhalation.

R24 Toxic in contact with skin.

R25 Toxic if swallowed.

R27 Very toxic in contact with skin.

R29 Contact with water liberates toxic gas.

R34 Causes burns.

R35 Causes severe burns.

R36 Irritating to eyes.

R37 Irritating to respiratory system.

R38 Irritating to skin.

R39 Danger of very serious irreversible effects.

R40 Limited evidence of a carcinogenic effect.

R43 May cause sensitization by skin contact.

R48 Danger of serious damage to health by prolonged exposure.

R50 Very toxic to aquatic organisms.

R51 Toxic to aquatic organisms.

R52 Harmful to aquatic organisms.

R53 May cause long-term adverse effects in the aquatic environment.

R62 Risk of impaired fertility.

R65 Harmful: may cause lung damage if swallowed.

R66 Repeated exposure may cause skin dryness or cracking.

R67 Vapours may cause drowsiness and dizziness.

S-Statements:

S1 Keep locked up.

S2 Keep out of the reach of children.

S4 Keep away from living quarters.

S7 Keep container tightly closed.

S8 Keep container dry.

S9 Keep container in a well-ventilated place.

S16 Keep away from sources of ignition.

S20 When using, do not eat or drink.

S22 Do not breathe dust.

S23 Do not breathe vapour.

S24 Avoid contact with skin.

S25 Avoid contact with eyes.

S26 In case of contact with eyes, rinse immediately with plenty of water and seek medical advice.

S27 Take off immediately all contaminated clothing.

S28 After contact with skin, wash immediately with plenty of soap-suds.

S29 Do not empty into drains.

S33 Take precautionary measures against static discharges.

S36 Wear suitable protective clothing.

S37 Wear suitable gloves.

S39 Wear eye / face protection.

S41 In case of fire and / or explosion do not breathe fumes.

S42 During fumigation / spraying wear suitable respiratory equipment.

S43 In case of fire use ... (there follows the type of fire-fighting equipment to be used.)

S45 In case of accident or if you feel unwell, seek medical advice immediately (show the label whenever possible.)

S53 Avoid exposure - obtain special instructions before use.

S60 This material and its container must be disposed of as hazardous waste.

S61 Avoid release to the environment. Refer to special instructions / safety data sheets.

S62 If swallowed, do not induce vomitting; seek medical advice immediately and show this container or label.

5.3 Monomer synthesis

5.3.1 Difluorobenzophenones

2,6-difluorobenzoyl chloride (0.3 mol) was added to a suspension of aluminum chloride (0.35 mol) in 500 ml of dry dichloromethane and the solution of a nucleophilic aromatic compound (0.3 mol) in 100 ml of dry dichloromethane was added dropwise under cooling with ice. Then, the reaction mixture was stirred for 5 h without cooling and then refluxed for 1 h. the cold reaction mixture was stirred with 1 L of acidic ice cold water, the organic layer separated, and the water extracted once with 300 ml of dichloromethane. The combined organic phases were washed with water, dried over sodium sulfate and concentrated. The residual product was crystallized from toluene + ligroin.

Table 22. Properties of difluorobenzophenone.

DFBP	Yileds (%)	m.p (°C)	Elem.Analysis			
				C	H	F
4,4'-DFBP	**75**	**103-105**	**Calcd.**	**71.56**	**3.70**	**17.41**
			Found.	**71.40**	**3.79**	**17.56**
2,6-DFBP (*3a*)	62	-	**Calcd.**	**71.56**	**3.70**	**17.41**
			Found.	**71.36**	**3.81**	**16.86**
2,6-DFBP (*3b*)	66	68-70	**Calcd.**	**74.44**	**5.88**	**13.85**
			Found.	**75.20**	**5.19**	**13.77**

5.3.2 Trimesoyl chloride

Trimesoyl acid was converted into the acid chloride by means of refluxing thionylchloride. 1 mol of trimsolyacid was refluxed with exess amount of thionlychloride for 6 h. Unreacted thinolychloride was removed by distillation. Trimsolychloride was purified two times using vacuum distillation. The yield and melting point were 80.7 % and 29-31 °C respectively.

5.3.3 Silylated diphenols

All silylated diphenols used in this work were prepared as follows. A diphenol (0.2 mol) and hexamethyldisilazane (0.25 mol) were refluxed in dry xylene (100 mL) until the evolution had almost ceased. The reaction mixture was then concentrated in vacuo, and the product was distilled over a short path apparatus in a vacuum of 10^{-2} mbar (yields 91-95%). the elemental analyses and ^{1}H NMR data of all silylated diphenols used in this work were compiled in Table 23.

Table 23. Properties of the Silylated Diphenols 7-12.

Monomer Nr.	**Yield (%)**	**Elemental Formula**	**Molecular weight (g/mol)**	**Elem.Analysis**			**^{1}H NMR chemical shift δ (ppm)**
					C	**H**	
7	**71.0**	**$C_{18}H_{26}Si_2O_2$**	**330.57**	**Calcd.** **Found.**	**65.40** **65.65**	**7.93** **7.85**	**7.43-7.40 (d,4H), 6.89-6.86 (d,4H), 0.29 (s,18H)**
8	**85.6**	**$C_{18}H_{26}Si_2O_3$**	**346.57**	**Calcd.** **Found**	**62.38** **62.43**	**7.56** **7.57**	**6.89-6.87 (d,4H), 6.80-6.78 (d,4H), 0.27 (s,18H)**
9	**95.4**	**$C_{21}H_{31}Si_2O_2$**	**371.65**	**Calcd.** **Found**	**67.87** **67.98**	**8.41** **8.55**	**7.12-7.03 (d,4H), 6.77-6.68 (d,4H), 1.62 (s,6H), 0.26 (s,18H)**
10	**87.8**	**$C_{26}H_{34}Si_2O_2$**	**434.73**	**Calcd.** **Found**	**71.84** **71.96**	**7.88** **8.01**	**7.25-7.22 (m,3H), 7.09-0.07(d,2H), 6.92-6.91 (d,4H), 6.72-6.71 (d,4H), 2.13 (s,3H), 0.26 (s,18H)**
11	**91.0**	**$C_{24}H_{36}Si_2O_2$**	**412.72**	**Calcd.** **Found**	**69.85** **70.03**	**8.79** **8.82**	**7.13-7.11 (d,4H), 6.76-6.74 (d,4H), 2.22 (s,4H), 1.56-1.51 (d,6H), 0.28 (s,18H)**
12	**71.0**	**$C_{31}H_{34}Si_2O_2$**	**494.78**	**Calcd.** **Found**	**75.25** **74.96**	**6.93** **7.18**	**7.77-7.75 (d,2H), 7.41-7.40 (d,2H), 7.35-7.30 (m,2H), 7.29-7.27 (t,2H), 7.07-7.04 (d,4H), 6.69-6.67 (d,4H), 0.24 (s,18H)**

5.4 Polycondensations

5.4.1 Polycondensation of bisphenol-A with difluorobenzophenones

5.4.1.1 With free bisphenol-A

Bisphenol-A (20 mmol) and 4,4'-DFBP were dissolved in DMSO (or sulfolane 50 mL) and K_2CO_3 (21 mmol) and toluene (or xylene, 20 mL) were added. The reaction vessel equipped with magnetic stirrer, distillation head and dropping funnel was placed in an oil bath and rapidly heated to 140°C or to a higher temperature (see Tables 1, 2, 3). The slowly distilling toluene was dropwise replaced from the dropping funnel. After 6 h, the remaining toluene was removed in rot. evap. and the reaction mixture was slowly poured into hot water. The precipitated polymer was isolated by filtration, washed with water and dried at 60°C in vacuo.

5.4.1.2 With silylated diphenols

Bis-trimethylsilyl bisphenol-A (20 mmol), 4,4'-DFBP (20 mmol) and dry K_2CO_3 (21 mmol) were weighed into a round-bottom flask, which was finally equipped with a magnetic stirrer. Dry NMP (10 mL) was added and the reaction vessel was placed into an oil bath preheated to 100°C. The temperature was rapidly raised to 140-145°C and then maintained for 24 or 48 h. Finally, the reaction mixture was diluted with 20 mL of NMP and precipitated into hot water.

5.4.2 Polycondensation of bisphenol-A with difluorobenzonitriles

5.4.2.1 In sulfolane

Bisphenol-A (10 mmol), dihalobenzonitrile (10 mmol) and K_2CO_3 (11 mmol) were weighed into a 250 mL three-necked flask which was then equipped with a dropping funnel distillation head and magnetic bar. Sulfolane (50 mL) and xylene (20 mL) were added and the reaction vessel was thermostated in an oil bath at 170-173°C. The xylene which slowly distilled off was replaced from the dropping funnel. After 6 h the xylene was completely removed in vacuo and the remaining sulfolane solution was precipitated into hot water. The isolated polymer was washed with hot water and dried at 80°C in vacuo.

5.4.2.2 In dry NMP

O,O'-Bistrimethylsilyl bisphenol-A (10 mmol), a dihalobenzonitrile (10 mmol) and dry K_2CO_3 (11 mmol) were weighed into a cylindrical glass reactor, which was equipped with a flat-blade glass reactor, gas-inlet and gas-outlet tubes. Dry NMP (10 mL) was added and the reaction vessel was placed into an oil bath preheated to 100°C. Temperature and time were then selected according to the data listed in Table 2. Finally, the reaction mixture was diluted with 10-20 mL of NMP and precipitated into hot water. The isolated polymer was washed (stirred) with hot water and dried in vacuo at 80°C.

5.4.2.3 Pseudo-high dilution method

A solution of O,O'-bistrimethylsilyl bisphenol-A (10 mmol) in dry NMP (20 mL) and a solution of 2,6-difluorobenzonitrile (10 mmol) were added dropwise and simultaneously to a stirred suspension of dry K_2CO_3 (11 mmol) in dry NMP (40 mL) at a bath temperature of 160-165°C. The total addition required approximately 45 min. The reaction mixture was stirred for additional 2 h and poured into water. In an analogous experiment 10.1 mmol of 2,6-difluorobenzonitrile was used (No. 10, Table 6).

5.4.3 Polycondensation of silylated biphenols with difluoropyridines

As a typical example polyether **9'** (No. 3, Table 8) was synthesized as follow. Silylated bisphenol-A (20 mmol), 2,6-difluoropyridine (20.4 mmol), K_2CO_3 (22 mmol) and NMP (30 mL) were weighed into a cylindrical glass reactor equipped with mechanical stirrer, gas-inlet and gas-outlet tubes. The reaction vessel was placed into an oil bath preheated to 100°C. The temperature was rapidly raised to 160-165°C and maintained for 48 h. A very slow stream of dry O_2-free nitrogen was passed over the reaction mixture to remove the liberated hexamethyldisiloxane. Finally, the cold reaction mixture was poured into hot water, and the precipitated polyether was isolated by filtration. All other polycondensations were conducted analogously.

5.4.4 Tertiary Amine-Initiated Zwitterionic Polymerization of Pivalolactone

5.4.4.1 Pyridine-Initiated Polymerization of Pivalolactone

Pivalolactone (40 mmol) was weighed in a 50 mL Erlenmeyer flask having silanized glass walls, the solvent (20 mL) was added and the initiator (0.4 mL of a 1 M solution in CH_2Cl_2 or in dioxane) was injected by means of a syringe. The reaction vessel was closed with glass stopper and steel spring and immersed into a preheated oil bath (see Table 12). Finally, the reaction mixture was poured into methanol and the isolated polylactone was dried at 60°C in vacuo. All experiments listed in Table 12 were performed analogously. However, the DMAP-initiated experiments were repeated and precipitated into diethyl ether.

5.4.4.2 DABCO-Initiated Polymerizations of Pivalolactone

Pivalolactone (40 mmol) was weighed into a 50 mL Erlenmeyer flask having silanized glass walls, dry NMP (20 mL) was added, and pyridine (0.4 mL of a 1

M solution in dry dioxane) was injected by means of a syringe. The reaction vessel was closed with glass stopper and steel spring and thermostated at 20°C (48 h) or 100°C (24 h). Finally, the reaction mixture was poured into methanol, and the isolated polylactone was dried at 60°C in vacuo. The triethylamine-initiated polymerizations were conducted analogously.

5.4.4.3 Polymerization of Pivalolactone with 2-Ethyloxazoline

Pivalolactone (20 mmol) and 2-ethyloxazoline (20 mmol) were weighed into a 50 mL Erlenmeyer flask having silanized glass walls and dry NMP (20 mL) was added. The closed reaction vessel was thermostated at 20 or 100°C. Finally, the reaction mixture was precipitated into diethylether, the product was isolated by centrifugation and dried at 40°C in vacuo.

5.4.4.4 Pyridine-Initiated Polymerizations of β-Propiolactone

β-Propiolactone (40 mmol) was weighed into a 50 mL Erlenmeyer flask having silanized glass walls, and pyridine (0.4 mL of a 1 M solution in dry dioxane) was injected. The reaction vessel was closed with glass stopper and steel spring and thermostated at 20 or 60°C for 48 h. Afterwards the reaction mixture was poured into diethyl ether.

5.5 Biodegradable networks

5.5.1 Silylation of glassware

For the synthesis of telechelic Poly(є-Caprolacton)s, the silylated glassware should be used to prevent the reaction of OH-groups exist at the wall of the glassware. Silylation of glassware was accomplished by filling the glassware with about 50 ml dichlorodimethylsilan, after 3 hours the glass washed two times with absolute diethyl ether, and then allowed to dry in oven.

5.5.2 Telechelic Poly(є-Caprolacton) Oligomers Syntheses

Є-Caprolacton (50 mmol) and TEG (2.5 mmol) were weighed under nitrogen into a cylindrical glass reactor with silanized glass walls and equipped with a flat blade stirrer. The Sn(octat)$_2$ initiator (0.1mmol) was injected by means of a syringe in the form of a 0.5 M solution in dry toluene under . The reaction vessel was placed into an oil bath preheated to 80 °C. After 20 h, the reaction mixture was diluted with dichloromethane and precipitated in cold methanol.

PCLs synthesized from BD were conducted analogously to those described under 5.5.2.

5.5.3 Network Syntheses

5.5.3.1 Based on Telechelic Poly(є-Caprolactone) Oligomers.

Poly(є-Caprolactone) oligomers (3 mmol) and trimesoyl chloride

(2 mmol) was dissolved in dry dichloromethane in round bottle flask and equipped with flatblade stirrer and gas-inlet gas-outlet tubes. Dry pyridine

(6 mmol) was added drop wise at room temperature. After 48h, the resulting network was extracted in a soxlet extractor with dry dichloromethane for 24h.Finally the gel was dried at 40 ºC. The structure of gel was confirmed with ^{1}H -NMR.

5.5.3.2 Based on mixtures of Telechelic Poly(є-Caprolacton) Oligomers and PEGs or Polysiloxane

Poly(є-Caprolactone) oligomers (1.5 mmol), Polysiloxane (1.5 mmol) and trimesoylchloride (2 mmol) was dissolved in dry dichloromethane in round bottle flask and equipped with flat blade stirrer and gas-inlet gas-outlet tubes. Dry pyridine (6 mmol) was added drop wise at room temperature. After 48h, the resulting network was extracted in a soxlet extractor with dry dichloromethane for 24h.Finally the gel was dried at 40 ºC. The structure of gel was confirmed with ^{1}H-NMR.

5.5.4 Trapping of cyclic polymer in network

A mixture of poly(є-Caprolactone) oligomers (3 mmol), cyclic poly(ether ketone) (2mmol with respect to the repeting unit), and 2 mmol of trimesolychloride was dissolved in 40 ml dry dichloromethane in round bottle flask and equipped with flat blade stirrer and gas-inlet gas-outlet tubes. Dry pyridine (6 mmol) was added drop wise at room temperature. After 48h, the resulting network was extracted in a soxlet extractor with dry dichloromethane for 24h.Finally the gel was dried at 40 ºC. The insertion of cycles in network's structure was confirmed with ^{1}H-NMR.

5.5.5 Separation of cyclic polymer using biodegradable network

A mixture of cyclic and linear poly(ether ketone) (2mmol with respect to the repeting unit), poly(є-Caprolactone) oligomers (3 mmol), and 2 mmol of trimesolychloride was dissolved in 40 ml dry dichloromethane in round bottle flask and equipped with flat blade stirrer and gas-inlet gas-outlet tubes. Dry pyridine (6 mmol) was added drop wise at room temperature. After 48h, the resulting network was extracted in a soxlet extractor with dry dichloromethane for 24h. Finally the gel was dried at 40 ºC. As an example of the degradation of networks, 0.5 mmol of network derived from PCL_1 was swelled in 100 ml dioxan. Propylamine (3.5 mmol) was added to swelled gel and heated for 48 h at 110 °C. the produced solution was pricipetated in methanol. After the product was dried under vacum at 60 °C, it was charicterized using MALDI-TOF.

6 Zusammenfassung

Diese Arbeit setzt sich aus zwei Teilen zusammen. Im ersten Teil wurden verschiedene aromatische Polyether und aliphatische Polyester hergestellt, um die Rolle der Zyklisierungsreaktionen bei Polykondensationen zu untersuchen. Der zweite Teil behandelt die Synthese von biologisch abbaubaren Netzwerken aus Poly(ε-caprolacton) bzw. aus einer Mischung von Poly(ε-caprolacton) mit verschiedenen Polyolen mit dem Ziel, zyklische und nichtzyklische Polymere voneinander zu trennen.

Teil I

a) Poly(etherketon)e

Zwei Klassen von Poly(etherketon)en wurden durch Polykondensation von Bisphenol-A mit verschiedenen Difluorbenzophenonen hergestellt, entweder mit 4,4´-Difluorbenzophenon oder mit 2,6-Difluorbenzophenon und 4´-tert-Butyl-2,6-difluorbenzophenon. Dabei wurden zwei verschiedene Synthesemethoden angewandt und verglichen. Zum einen wurde das freie Bisphenol-A in DMSO oder Sulfolan unter azeotroper Entfernung des Wassers polykondensiert. Zum anderen wurde Bis-trimethylsilylbisphenol-A in N-Methylpyrrolidon polykondensiert. Die letztere Methode lieferte höhere Ausbeuten und Molekulargewichte (M_ns bis zu 85 000 Da und M_ws bis zu 190 000 Da). In den MALDI-TOF-Massenspektren konnten mit zunehmendem Molekulargewicht auch zunehmende Anteile an zyklischen Oligomeren und Polymeren beobachtet werden.

Eine dritte Klasse von Poly(etherketon)en wurde aus silyliertem 4-tert-Butylcatechol und 4,4´-Difluorbenzophenon hergestellt. In diesem Fall wurden die Trends, die beim silylierten Bisphenol-A festgestellt wurden, bestätigt. Unter optimierten Bedingungen konnten zyklische Poly(etherketon)e bis zu 18 000 Da im MALDI-TOF-Massenspektrum detektiert werden.

b) Poly(benzonitrilether)

Bisphenol-A wurde mit 2,6-Dichlor-, 2,6-Difluor, 2,4-Difluor und 3,5-Difluorbenzonitril in Sulfolan polykondensiert. Mit 2,6- und 2,4-Difluorbenzonitril konnten quantitative Umsätze erreicht werden, und die Massenspektren zeigten einen nahezu quantitativen Anteil an zyklischen Oligoether und Polyethern. Weiterhin wurde O,O´-Bis-(trimethylsilyl)-

bisphenol-A mit den bereits erwähnten Dihalogenbenzonitrilen in trockenem NMP unter Optimierung von Zeit und Temperatur polykondensiert. Nur im Fall von 2,6-Difluorbenzonitril konnten nahezu quantitative Umsätze mit der Konsequenz hoher Molekulargewichte und hoher Anteile an Zyklen erreicht werden. Die SEC-Kurven wiesen die Tendenz zu einer bimodalen Verteilung auf, wenn ein hoher Anteil an Zyklen im Massenspektrum vorlag. Die Kalibrierung mit einem Polystyrolstandard führte zu Zahlenmitteln bis zu 10^5 Da und Massenmitteln bis zu 2.3×10^5 Da.

c) Poly(pyridinether)

Die Bis-trimethylsilylderivate von sechs verschiedenen Diphenolen wurden mit 2,6-Difluorpyridin in NMP in Gegenwart von K_2CO_3 polykondensiert. Die Reaktionsbedingungen wurden optimiert, um einen quantitativen Umsatz zu erreichen. Die Monomerverhältnisse wurden systematisch variiert, um das Molekulargewicht zu optimieren. Es zeigte sich, dass für maximale Molekulargewichte ein 2-%iger Überschuss an 2,6-Difluorpyridin notwendig ist. Die Massenspektren der optimierten Polyether zeigten ausschließlich Zyklen mit Molekulargewichten bis zu 5 000 Da. Offensichtlich resultieren die niedrigen Molekulargewichte aus der Limitierung des Kettenwachstums durch die hohe Zyklisierungstendenz der Poly(pyridinether). Durch SEC-Messungen konnten nicht nur die niedrigen Molekulargewichte, sondern ebenfalls bimodale Verteilungen mit hohen Polydispersitäten nachgewiesen werden. Die Protonierung der Poly(pyridinether) erfordert starke Säuren wie z.B. Methan- oder Trifluormethansulfonsäure. Die Löslichkeit der neutralen und protonierten Polyether wurde für verschiedene Lösungsmittel untersucht. Die MALDI-TOF-Massenspektren zeigten, dass die Protonierung bei 20 - 25 °C nicht zur Spaltung der Etherbindung führt.

d) Aliphatische Polester aus Pivalolacton

Die Zwitterionische Polymerisation von Pivalolacton in NMP wurde mit Hilfe von Pyridin, 4-Methylpyridin und 4-N,N-Dimethylaminopyridin als Initiatoren durchgeführt mit der Hoffnung, zyklische Polyester zu erhalten. Als Hauptprodukt wurden jedoch lineare Ketten mit einer Pyridiniumion- und einer Carboxylat-Endgruppe gefunden. Die Abwesenheit von Zyklen, sogar bei Reaktionstemperaturen bis zu 140 °C, beweist, dass das Kettenwachstum der zwitterionischen Ketten ausschließlich durch anionische ringöffnende Polymerisation stattfindet. Bei Verwendung von Dichlormethan treten Nebenreaktionen mit demselben auf, die bei Teilen der Polylactonketten zu Chlormethylester-Endgruppen führten. Auch mit Diazabizyklooctan als Initiator wurde in NMP eine saubere zwitterionische Polymerisation gefunden. Bei der

Verwendung von Triethylamin oder 2-Ethyloxazolidin als Initiatoren war die zwitterionische anionische Polymerisation wiederum die Hauptreaktion. Es traten allerdings signifikante Nebenreaktionen auf. Im Fall von 2-Ethyloxazolidin beinhalteten die Nebenreaktionen auch die Bildung von zyklischen Oligolactonen.

Bei der Polymerisation von β-Propiolacton wurde die vollständige Eliminierung des Pyridiniumions unter Bildung von Acrylat-Engruppen beobachtet.

Teil II

Zunächst wurden telechele Poly(ε-caprolacton)e mit zwei OH-Endgruppen durch ringöffnende Polymerisation von ε-Caprolacton hergestellt. Als Initiator bzw. Coinitiator wurde Zinn(II)-2-ethylhexanoat ($SnOct_2$) bzw. Tetraethylenglycol oder 1,4-Butandiol verwendet. Durch Variieren der Monomer/Coinitiator-Verhältnisse wurden Polylactone mit Molekulargewichten von 2000, 3000, 4000 und 5000 Da synthetisiert.

Verschiedene Klassen von Netzwerken wurden aus diesen Polyestern mit Trimesinsäuretrichlorid und Pyridin hergestellt. Die erste Klasse wurde aus dem telechelen Poly(ε-CL) und Trimesinsäuretrichlorid erhalten. Zwei weitere Klassen wurden aus dem Gemisch von Poly(ε-CL) mit PEG oder PDMS synthetisiert. Zum einen wurde Poly(ε-CL)-2000 mit PEG-2000 in verschiedenen Verhältnissen gemischt und mit Trimesinsäuretrichlorid und Pyridin vernetzt. Analog dazu wurde Poly(ε-CL)-4000 mit PEG-4600 gemischt und vernetzt. Zum anderen wurde Poly(ε-CL)-2000 mit einem telechelen Polysiloxan mit OH-Engruppen und ähnlicher Kettenlänge in Lösung vermischt und vernetzt. Die isolierten Gele wurden mit ^{1}H-NMR-Spektroskopie, Quellungsmessungen in drei verschiedenen Lösungsmitteln, DSC und Röntgenstreuung untersucht.

Biologisch abbaubare Netzwerke werden genutzt, um zyklische, aromatische Polyether "einzufangen". Die Abtrennung der linearen von den zyklischen Polymeren kann anschließend durch Extraktion oder durch Degradierung der Netzwerke erfolgen. Beide Methoden wurden hier untersucht, lieferten aber keinen zufriedenstellenden Erfolg.

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I affirm that, the present work was made only by me under supervise of Prof. Dr. H. R. Kricheldorf and it is based on only my experimental work and the literature specified in this work.

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