Partly hydrogenated and functionalized polybutadiene rubber

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All men by nature desire knowledge
Aristoteles

Contents

Acronyms

ABS	acrylonitrile-butadiene-styrene
AFM	atomic force microscopy
ALL	polyallene
ω	angular frequency
a_T	shift factor (TTS)
b	transition parameter
BR	butadiene rubber
BRBr	polyvinyl bromide
BRBr2	polydibromide
n-BuLi	*n*-butyl lithium
CapBR	polybutadiene-polycaprolactone copolymer
c_BR	concentration of polybutadiene rubber
c_cat	catalyst concentration
ϵ-CL	ϵ-caprolactone
cp	crossover point
m-CPBA	*meta*-chloroperoxybenzoic acid
$\dot{\gamma}_\mathrm{c}$	critical shear-rate
DCM	dichloromethane
DIE	polydiene
DSC	differential scanning calorimetry
E_a	flow activation energy
EBR	epoxidized polybutadiene rubber
EPv	epoxide value
F_n	functionality
G	shear modulus
G'	storage modulus
G''	loss modulus
GPC	gel permeation chromatography

G^*	complex modulus
HBR	hydrogenated polybutadiene rubber
ΔH_m	enthalpy of fusion
HTBR	hydroxyl-terminated polybutadiene rubber
I_ct	calculated integral of 1,4-*cis/trans* double bonds
I_cy	calculated integral of 1,2-cyclic double bonds
INE	polyalkyne
IR	infrared spectroscopy
I_v	calculated integral of 1,2-vinyl double bonds
η^*	complex shear viscosity
LBR	liquid polybutadiene rubber
MFC	mass flow controller
M_n	number average molecular weight
m_s	sample mass
M_w	weight average molecular weight
MWD	molecular weight distribution
n	slope of the non-NEWTONIAN region
NMR	nuclear magnetic resonance
NR	natural rubber
OHBR	polybutadiene-based polyol
OHv	hydroxide value
PBAN	polybutadiene acrylonitrile copolymer
PCL	polycaprolactone
PDI	polydispersity index
p_H	hydrogen pressure [bar gauge]
PU	Polyurethane
Q_H	hydrogen consumption
R	universal gas constant
λ_0	relaxation time of the slowest chain
ROMP	ring opening metathesis polymerization
ROP	ring opening polymerization
SBR	styrene-butadiene-rubber
$\dot{\gamma}$	shear rate
γ	shear strain
σ_{21}	shear stress

T	actual temperature (Arrhenius-fit)
T_H	temperature of hydrogenation
TfOH	trifluoromethanesulfonic acid
T_g	glass transition temperature
t_H	time of hydrogenation
T_m	melting temperature
T_0	reference temperature (Arrhenius-fit)
TOF	turnover frequency
th.OHV	theoretical OHv (hydroxide value (*OHv*))
TON	turnover number
TSH	*p*-toluenesulfonyl-hydrazide
TTS	time-temperature sweep
V_b	blind value KOH consumption
V_H	overall hydrogen consumption
η	dynamic shear viscosity
η_0	zero-shear viscosity
V_s	sample KOH consumption
X_EP	degree of epoxidation
X_H	degree of hydrogenation
X_OH	degree of epoxide opening
Y_EP	epoxide content

1. Zusammenfassung

Die Doppelbindungen in Polybutadien ermöglichen eine Vielzahl an Modifikationen und Funktionalisierungen in das Polymer einzuführen. Der Nachteil an dieser Eigenschaft, ist die hohe Anfälligkeit gegenüber Alterungsprozessen wie z.B. der photoinduzierten Vernetzung. Die Teilhydrogenierung bietet die Möglichkeit die Anfälligkeit gegenüber Alterungsprozessen zu reduzieren und gleichzeitig Einfluss auf die Materialeigenschaften zu nehmen. Verschiedene Typen an Polybutadienen mit unterschiedlicher Mikrostruktur wurden mit einem Titan basierenden Katalysatorsystem teilhydrogeniert. Die Selektivität der Hydrogenierung ist abhängig von der sterischen Zugänglichkeit der Gruppen und lässt sich wie folgt ordnen: 1,2-*cyclic* > 1,2-*vinyl* > 1,4-Doppenbindungen. Die weitere Analyse des Katalysators zeigte gewisse Konzentrationsabhängigkeiten. Hohe Katalysatorkonzentrationen zeigen eine höhere Tendenz zu Katalysatordeaktivierungen und reduzieren die turnover number und den Hydrogenierungsgrad. Niedrige Konzentrationen wiederum erhöhen die turnover number und erlauben die Hydrogenierung von 1,4-Doppelbindungen auf Kosten einer niedrigeren tunover frequency.

Die partiell hydrogenierten Polybutadiene wurden als Edukte für nachfolgende Modifizierungen verwendet. Die erste Modifizierung war das Einbringen von OH-Gruppen zur Herstellung einer Polyolkomponente für die Polyurethansynthese. Die Polyole wurden in einer Mehrstufensynthese aus zwei Polybutadienen mit unterschiedlicher Mikrostruktur und je drei verschiedenen Hydrogenierungsgraden hergestellt. Die gegossenen Polyurethane zeigten Unterschiede in der Phasenseparation basierend auf der Mikrostruktur und dem Hydrogenierungsgrad. PUs die auf den Polyolen mit einem niedrigeren Molekulargewicht und einem höheren Anteil an *vinyl*-Doppelbindungen basieren, zeigten mechanische Eigenschaften ähnlich dem von Thermoplasten. Die anderen Polyole zeigten das Verhalten von Elastomeren und Phasenseperation, welche vom Hydrogenierungsgrad abhängig war.

Die zweite Modifikation war die Bromierung gefolgt von einer Dehydrobromierung. Hierbei wurden mono- und didehydrobromierte Produkte in Abhängigkeit von der Reaktionstemperatur erhalten. Bei Raumtemperatur bildete sich das mono-Produkt. Der vollständige Umsatz zum *trans*-Produkt konnte mit *t*-BuOK und 18-Krone-6 erreicht werden. Das didehydrobromierte Produkt, welches bei höheren Temperaturen erhalten wurde, konnte als Polyallen identifiziert werden. Alle Produkte wurden rheologisch vermessen und die dynamische Viskosität mit dem CARREAU-YASUDA-Modell angenähert. Es konnte eine signifikante Scherverflüssigung bei hohen Scherraten für die bromierten Produkte beobachtet werden. Das Vinylbromid zeigte die insgesamt höchste Viskosität.

2. Abstract

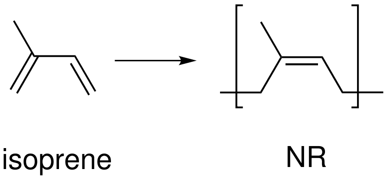
Double bonds in polybutadienes offer multiple possibilities for modification and the introduction of a variety of functional groups. The downside of this high reactivity is the associated potential for aging processes such as crosslinking. Partial hydrogenation is a useful tool to lower the thermo-oxidative sensitivity and also an opportunity to tune material properties. Several types of polybutadiene rubber with various microstructures and molecular weights were partial hydrogenated using a titanium-based catalytic system. The affinity of the different double bonds for hydrogenation was primarily dependent on the accessibility and follows the order 1,2-*cyclic* > 1,2-*vinyl* > 1,4-double bonds. Analysis of the catalyst action revealed some concentration dependencies: high catalyst concentrations suffer from catalyst deactivation and result in a lower turnover number and a lower degree of hydrogenation. Lower catalyst concentration increases the turnover number and allows for hydrogenation of 1,4-double bonds at the cost of a lower turnover frequency.

The partial hydrogenated polybutadienes were used as starting materials for subsequent modifications. The first modification was the introduction of alcohol groups in the polymer backbone; such derivatives were screened as polyol component in PU castings. The polyols were prepared in a multiple-step procedure using starting materials with three degrees of hydrogenation and two different microstructures. The casted PUs did show differences in phase separation based on the degree of hydrogenation and microstructure. The PUs based on polyols with the lower molecular weight and higher 1,2-double bond content yielded products with a thermoplastic-like mechanical behavior. The PU based on the other polyols did show elastomeric behavior and phase separation, which extent was dependent on the degree of hydrogenation.

The second modification of parent polybutadiene rubbers was bromination followed by dehydrobromination. Mono- or didehydrobrominated products were obtained in dependence on the reaction temperature. At room temperature a monobromo vinyl polymer was received. The preparation of all *trans*-vinyl bromide polybutadiene was successful using *t*-BuOK in combination with 18-crown-6 ether. A polyallene product was formed at higher temperatures as the product of the didehydrobromination. All compounds were characterized by rheometry; the frequency dependent viscosity could be fitted by the CARREAU-YASUDA-model. Significant shear thinning is observed for brominated polymers at high shear rates. The vinyl bromide polymer has the highest viscosity in the series.

3. Introduction

Polymers are a large class of synthetic molecules. They are found basically everywhere in our daily life. Common examples are polyolefins used for packaging, various biopolymers used for medical applications or rubbers which are primarily used in the mobility sector. Rubbers find their origin in natural rubber (NR).



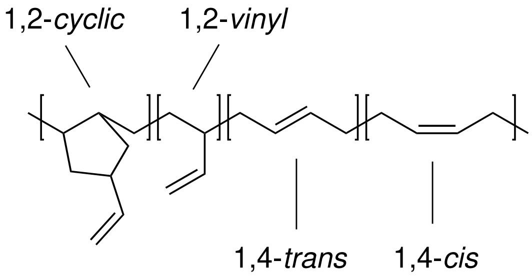
Scheme 3.1: Schematic polymerization of isoprene to natural rubber (NR).

NR is a high 1,4-*cis* polyisoprene (Scheme 3.1) and is prepared by drying the latex of the rubber tree hevea brasiliensis. Charles Goodyear discovered in 1839 that if rubber was heated with sulphur it became "stronger" and more elastic.[1] Since then a variety of different synthetically rubbers were developed. One of the most important synthetical rubbers is butadiene rubber (BR).

3.1. Polybutadiene rubber

Polybutadiene rubber is made of 1,3-butadiene. It can be polymerized by various types of catalysts. Depending on the catalyst and the reaction conditions BR can contain 4 different types of double bonds (Scheme 3.2).

These can be differentiated into 1,2- and 1,4-double bonds. 1,2-double bonds are vinylic double bonds. At low monomer concentrations 1,2-cyclic double



Scheme 3.2: Microstructure elements of butadiene rubber (BR).

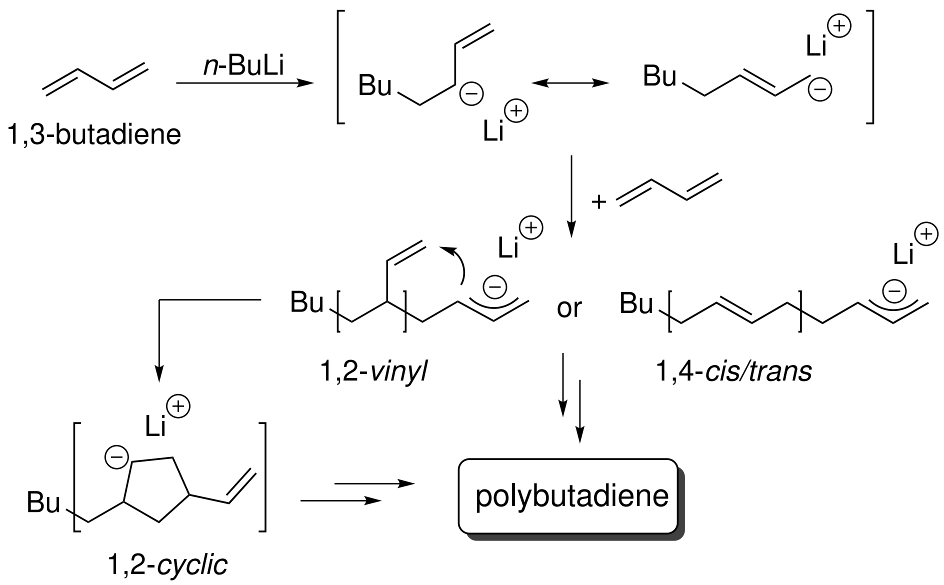
bonds are formed. They contain a cyclopentane ring formed from 2 butadiene molecules. 1,4-double bonds can have either *cis* or *trans* configuration. The most relevant microstructure is the 1,4-*cis* double bond. High *cis*-BR are amorphous elastomers with good mechanical properties predominantly used in the tire industry. About 66% of the polybutadienes sold in 2016 were high *cis*-BR. The other double bond types had a market share in 2016 of 19.7% for low *cis*, 13.5% for high *vinyl* and 0.8% for high *trans*.[2]

3.1.1. Preparation of polybutadienes

Polybutadienes are prepared by the polymerization of 1,3-butadiene. Usually the reaction either is an anionic polymerization or catalyzed by a transition metal catalyst. Cationic polymerizations have a minor role while radical polymerizations are used for co-polymers of butadiene such as styrene-butadiene-rubber (SBR) or acrylonitrile-butadiene-styrene (ABS).[3–6] About 80% of the prepared butadiene rubbers are used in tire manufacturing and about 10% are transformed in a polymer analogue reaction.[2]

The first synthetic rubber was prepared in solution over multiple days using pure sodium or sodium salt.[7,8] The prepared Buna (ger.: *Butadien-Natrium-Polymerisate*) had a high 1,2-content and weak elastomeric properties. The invention of the Ziegler-catalysts[9] gave new opportunities for the preparation of synthetic rubbers. Co and Nd based catalyst allow to prepare high *cis*-polybutadienes with *cis*-contents of >96% and good elastomeric performance.[3,5,6]

Low *cis*-polybutadienes with an average double bond content of 40% *cis*, 50% *trans* and 10% *vinyl* entities and can be prepared by applying *n*-butyl lithium (*n*-BuLi) as catalyst. Depending on the stabilization of the carbanion



Scheme 3.3: Polymerization of polybutadiene with *n*-butyl lithium (*n*-BuLi).

a 1,2- or 1,4-double bond is formed (Scheme 3.3). Lewis-bases influence the process and increase the *vinyl* content to 20% for Et_3N and 60% for THF.[5] At high conversions low monomer concentration leads to formation of 1,2-*cyclic* double bond. It is formed by the intramolecular attack of the carbanion on a *vinyl*-group. The formed cyclopentane ring is the new reactive center to which more monomers can be added.

3.1.2. Liquid butadiene rubber (LBR)

The molecular weight of polybutadiene rubber can be adjusted by the ratio of active polymerization sites to monomer concentration. High initiator concentrations give liquid polybutadiene rubber (LBR) with low molecular weights of Mn < 10.000 g/mol.[4,5] Examples are the Lithenes prepared by Synthomer (Table 3.1).

Low bulk and solution viscosities of LBR make them important in the field of microelectronics, coatings, and adhesives.[4] In rubbers they are used as curable additives for automotive related sealants or tires.[10,11] The presence of unsaturations facilitates subsequent chemical modifications as will be discussed in the next chapters.

Table 3.1.: Double bond composition and number average molecular weight (M_n) of the liquid polybutadiene rubber (LBR) Lithene ultra AL, PM4 and N4.

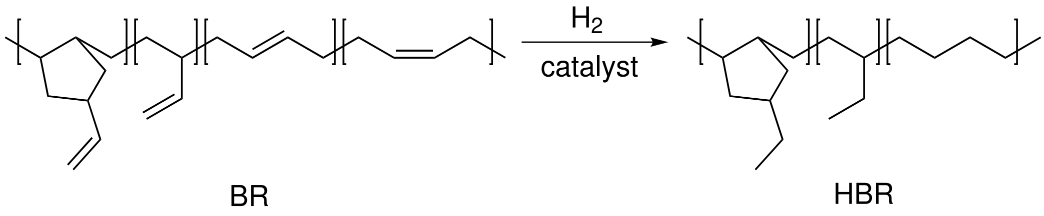
Polymer	Double Bond Content			M_n
	1,2-*cyclic*	1,2-*vinyl*	1,4-*cis*/*trans*	[g/mol]
Lithene ultra AL	30%	29%	41%	750
Lithene ultra PM4	4%	15%	81%	1500
Lithene ultra N4	2%	10%	88%	5000

[a] corrected value

3.2. Functionalization - Hydrogenation

The first modification studied in this work is hydrogenation. Hydrogenation describes the reduction of double bonds or other reactive groups. Alkenes are reduced to the corresponding alkanes e.g high *cis*-BR is reduced to a high-density-polyethylene-like product[12] (Scheme 3.4).

Usually polyethylene is prepared in a step-growth polymerization. The anionic polymerization of BR followed by full hydrogenation allows to prepare special polyethylene e.g. those with a very low polydispersity index (PDI).[13,14]



Scheme 3.4: Catalytic hydrogenation of butadiene rubber (BR) to hydrogenated polybutadiene rubber (HBR).

Depending on the catalyst, almost every double bond containing polymer can be hydrogenated. Advantages of hydrogenation are higher resistance to aging by an improved fluid resistance[15], higher stability against oxidative, thermal and UV degradation[15,16], an improved wear-resistance and better conservation of rubber elasticity after heating.[12,15] Vulcanized hydrogenated rubber possess higher tensile strength and lower glass transition temperature (T_g)[16] compared to the non-hydrogenated polymer.

One of the first reports on hydrogenated rubber was by H. Staudinger and J. Fritschi in 1922.[17,18] They reported the catalytic reaction of a NR by the use of platinum at 270 °C and hydrogen pressure of 93 bar. Full saturation was achieved in bulk after 10 h. They described the prepared hydrogenated rubber as a high molecular paraffin. In the following years a large variety of different catalytic and non-catalytic systems were developed. The most important systems are described in the following sections.

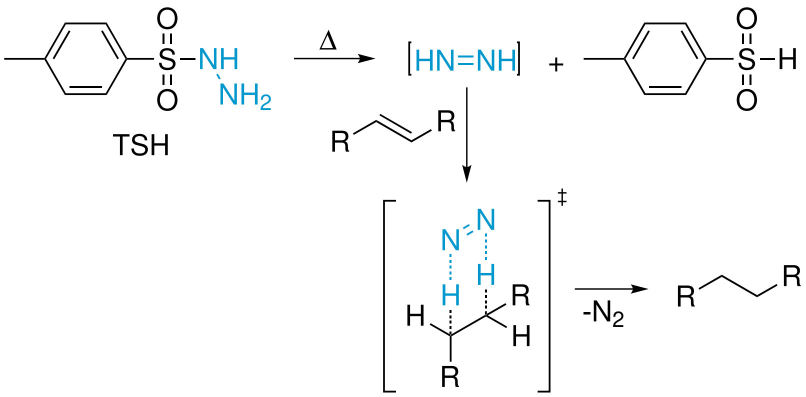
3.2.1. Hydrogenation by Palladium Based Catalysts

In organic chemistry, one common way for saturation of double bonds is the reduction by palladium. The heterogenic catalysts $Pd/CaCO_3$[19] and Pd/C[20] are able to reduce the double bonds in high *vinyl* or high *cis*-BR at different reaction conditions. While the degree of hydrogenation (X_H) of 85%[19] is quite satisfying the work-up is a tedious procedure. In contrast to a heterogenic catalyst, homogeneous catalysts can often remain in the product and may therefore be more desirable.

3.2.2. Hydrogenation by *in situ* formed Diimide

A homogenous but non-catalytic system is the hydrogenation by diimide. Diimide is a reactive molecule and is prepared in situ by decomposition of a precursor hydrazine[21] or thermal decomposition[22–26] of *p*-toluenesulfonylhydrazide (TSH) (Scheme 3.5).

Over the years several methods for the hydrogenation of BR by diimide were described. Harwood *et al.*[27] used a 5 fold excess of TSH to hydrogenate high *cis*-BR and NR at temperatures of 135-140 °C. After 8 h they observed quantitative conversion of BR and non-conversed TSH. Hahn *et al.*[28] reduced the amount of TSH to a 2 fold excess and could show quantitative conversion of high *cis*-BR after 4 h. Differences in reactivity regarding the type of the double bond were observed for high *trans*-BR. High *trans*-BR was hydrogenated at similar conditions with a conversion of 74% after 6 h.[29] This indicates a higher reactivity of the 1,4-*cis* compared to the 1,4-*trans* double bond in polybutadiene



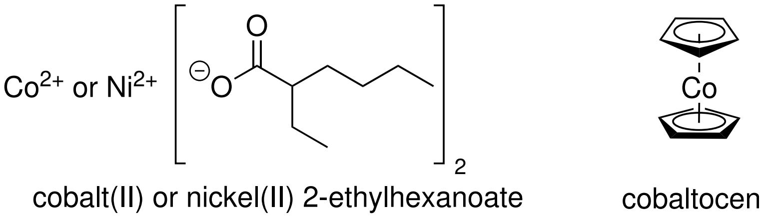
Scheme 3.5: Thermal decomposition of *p*-toluenesulfonyl-hydrazide (TSH) to form diimide (blue) and double bond hydrogenation.[21]

rubbers for the diimide hydrogenation.[28–30] For both reactions by-products from TSH were observed. Theses by-products seem to cause degradation of high molecular weight rubbers.[28,29] By-products, degradation and necessity of at least quantitative amounts of TSH make the hydrogenation by diimide generally unfavorable for hydrogenations.

3.2.3. Hydrogenation by Cobalt or Nickel Based Catalysts

Catalytic systems containing cobalt or nickel (Scheme 3.6) use Li-compounds or Et_3Al as co-catalyst. Depending on the co-catalyst the double bond selectivity is influenced.[31,32] For cobalt catalysts ligands such as 2-ethylhexanoate[31–33] or cyclopentadienyl[34] are used. Hydrogenation of BR with cobalt(II) 2-ethylhexanoate gives fully saturated products within 30 min at moderate conditions (50 °C, 3.4 bar). Reactivity of the double bonds can be ordered for Co catalysts as: 1,2-*vinyl* > *cis*-1,4 > *trans*-1,4.[12,32,34] This order can be explained by sterically hinderance of the different double bonds. The less hindered double bonds have a better access to the catalyst and therefore a higher reactivity.

Nickel catalysts can be heterogeneous[7,35–37] or homogenous[31,38–44]. Heterogeneous catalysts are compounds such as Raney-nickel[7] or elementary Ni adsorbed on aluminum[35] or silicon[37] oxides. They are used as catalysts at temperatures over 120 °C and hydrogen pressures up to 60 bar. The homogenous catalyst nickel(II) 2-ethylhexanoate can be used at milder conditions as described by Sabata *et al.*[41] They showed quantitative conversions at temperatures of 10 - 35 °C and hydrogen pressures of 0.72 - 1.78 bar. The used



Scheme 3.6: Catalysts containing Co and Ni with 2-ethylhexanoate and cyclopentadienyl ligands.

BR contained 60% 1,2-*vinyl*, 15% 1,4-*cis*, and 25% 1,4-*trans* double bonds. Similar to cobalt(II) 2-ethylhexanoate they found the highest reactivity towards the 1,2-double bonds, but the opposite reactivity for the 1,4-double bonds (*trans*-1,4 > *cis*-1,4).

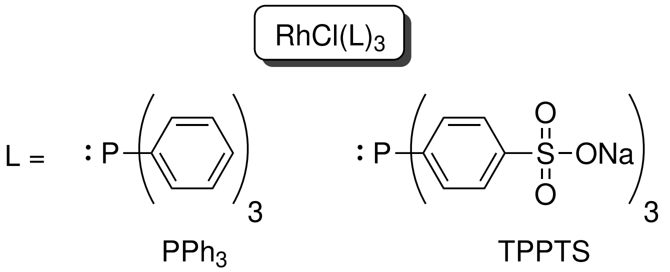
Cobalt and nickel catalysts show a high degree of hydrogenation at mild conditions. This makes them interesting catalysts for partial hydrogenation. Like Pd catalysts the heterogenic nature makes them less desirable for hydrogenation. In addition to this Co and Ni compounds are often toxic and sensitizing.

3.2.4. Hydrogenation by Rhodium Based Catalysts

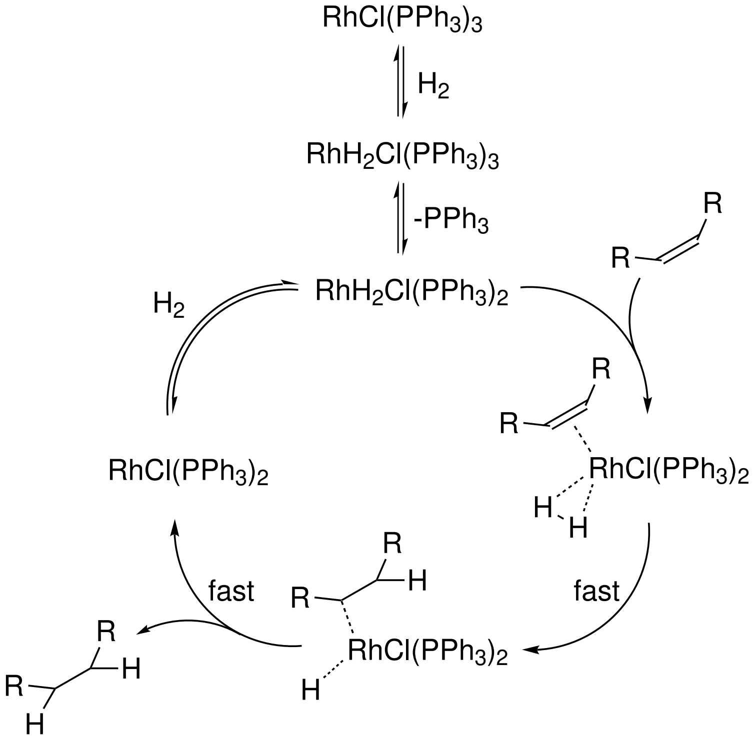
One of the most famous hydrogenation catalysts is the Wilkinson catalyst Tris-(triphenylphosphine)rhodium(I) chloride (Scheme 3.7). In 1966 Wilkinson[45] described the catalytic hydrogenation of different unsaturated molecules such as 1-hexene. Birch *et al.*[46] continued the hydrogenation of various compounds and described the reduction of different polybutadiene rubbers. This led to the invention of different analogous ruthenium-based hydrogenation catalysts used for rubber hydrogenation.[47]

When used in bulk tris(triphenylphosphine)rhodium(I) chloride was able to hydrogenate high *vinyl*-BR up to 94% at 60 °C over multiple days.[48] Reaction time can be decreased by addition of triphenylphosphine (PPh_3). PPh_3 allows better diffusion of the catalyst through the bulk. After 6 h at 145 °C a conversion of 98% can be achieved.[49] In solution at temperatures of 40 - 70 °C and hydrogen pressures below 1 bar quantitative hydrogenation was found within 10 h.[50] Like the Co and Ni catalysts, the reactivity towards 1,2-double bonds is higher than of to 1,4-double bonds.[50]

Rempel *et al.*[50–53] proposed a mechanism for the hydrogenation of the Wilkin-



Scheme 3.7: The Wilkinson catalyst Tris(triphenylphosphine)rhodium(I) chloride and the analogous catalyst with TPPTS (Tri-(natrium-meta-sulfonatophenyl)-phosphane) as ligand.



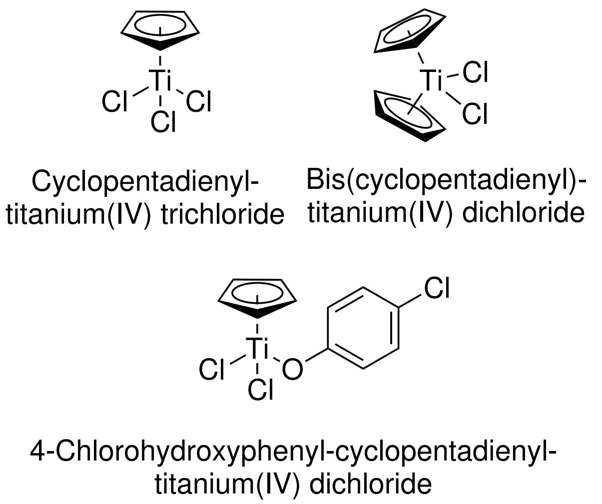
Scheme 3.8: Proposed mechanism for the Wilkinson catalyst RhCl(PPh3)3.[50–52]

son catalyst (Scheme 3.8). First a hydrogen molecule is added to the catalyst. Then a PPh_3-group leaves the catalyst to allow subsequent coordination of an olefin. When the olefin is coordinated, the hydrogenation starts. The hydrogenation is fast. The hydrogenated olefin leaves the complex and another hydrogen molecule can add. The initial addition can either be a hydrogen or an olefin.

These reactions are usually performed in non-polar organic solvents. Sulfonation of the ligand PPh_3 (Scheme 3.7) to increases the compatibility to polar solvents. In a mixture of toluene and the ionic liquid $BMI(BF_4)$ a BR containing 40% 1,2-*vinyl* groups was hydrogenated up to 94% within 4 h at 100 °C and 31 bar hydrogen pressure.[15] In a micellar system with dodecyltrimethylammonium chloride (DTAC) as detergent, water and n-hexane a high *vinyl* BR was hydrogenated up to 91% within 20 minutes at a temperature of 100 °C and 20 bar hydrogen pressure.[54] Unfortunately rhodium compounds are quite expensive and hydrogenation of large amounts of rubber will not be cost-effective.

3.2.5. Hydrogenation by Titanium Based catalysts

The report of a titanium-based Ziegler catalyst[9] for the ethene polymerization started the development of a large number of titanium catalyst for various applications.



Cyclopentadienyl-titanium(IV) trichloride

Bis(cyclopentadienyl)-titanium(IV) dichloride

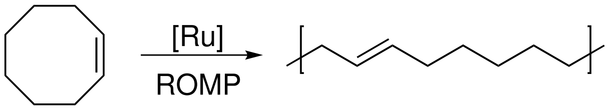
4-Chlorohydroxyphenyl-cyclopentadienyl-titanium(IV) dichloride

Scheme 3.9: Different hydrogenation catalyst based on titanium.

The catalysts are soluble in most organic solvents and are able to hydrogenate double bonds at moderate conditions. Sloan *et al.* described the overnight hydrogenation of small molecules such as *n*-octene with $TiCp_2Cl_2$ at r.t. and 4.4 bar of hydrogen pressure.[55] In the following decades multiple hydrogenation catalysts following the structure $TiCp_{(2-z)}X_2Y_z$ were developed.[56–65] These catalyst use alkyl lithium or Et_3Al as co-catalyst to increase the reactivity at a Al (or Li) : Ti ratio of 4.[58,66,67] The advantage of titanium as a catalyst is the non-toxicity, the easy handling and the broad availability.

3.2.6. Hydrogenation Analogous Polymers

The broad variety of different hydrogenation catalysts shows the importance of this type of modification. For almost every double bond containing polymer there is a suitable catalyst for hydrogenation. Partially hydrogenated polymers show a random structure regarding the repeating unit of the double bond.
In some cases a more ordered structure with defined repeating units is needed. Co-polymerization as well as metathesis of unsaturated compounds can give HBR analogous polymers. One example is the ring opening metathesis polymerization (ROMP) of cyclooctene (Scheme 3.10).[68]



Scheme 3.10: Preparation of Octenamer from cyclooctene in a ring opening metathesis polymerization (ROMP).

It contains 8 carbon atoms and a double bond an is analogous to high *trans*-polybutadiene rubber with a degree of hydrogenation of 50%.

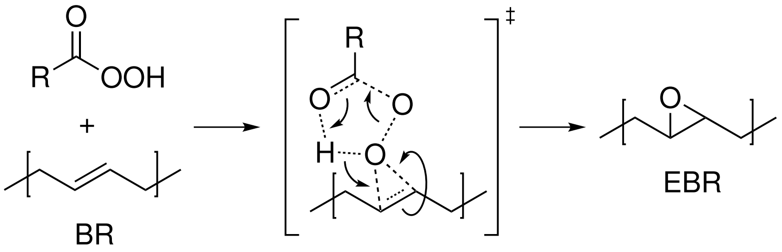
3.3. Functionalization - Polyols for Polyurethanes

Polyurethanes (PUs) are a versatile class of polymers with a modular-like structure. Their thermoplastic, elastomeric or thermoset behavior allow them to be used in a broad range of applications.[69] High tensile strength, tear strength and high abrasion resistance as well as resistance to degradation by oils, greases, and solvents make PUs interesting for various applications.[69–72] The usual preparation of PU includes a polyol, isocyanate, a short diol as chain extender and further additives. The PU is formed in a exothermic polyaddition reaction after combining all components.[73] The first commercially available PU was prepared from polyisocyanate and a polyester in 1943.[74] The PU shows phase separation that occurs during the polyreaction. The long chains of the polyols form an amorphous phase referred to as soft phase. Chain extender and isocyanate form a semi-crystalline hard phase and contain most of the PU-bonds. Polyester-polyols show hydrogen bonding between soft and hard phase and improve mechanical properties of the PU.

On account of the polar urethane and polyol groups many PUs are moisture permeable. For applications requiring low moisture permeability polybutadiene-based polyols may be used.[75,76] The use of polybutadiene in PUs is of further interest for their low glass transition temperature and electric insulation properties.[75–78] The majority of BR-based polyols are hydroxyl-terminated polybutadiene rubber (HTBR). Low polarity of HTBRs related to other polyols alters the phase separation and distribution in the PU. Hydrogen bonding can only occur in the hard phase due to lack of internal functional groups in HTBRs.[75] For good mechanical properties well dispersed and separated soft and hard phases are needed.[76,79] In order to achieve good separation in casted PU, compatibility of all components is crucial during mixing. If the components do not form one phase during mixing, large domains will be the result. Large domains reduce the mechanical properties of the PU. Compatibility of hydrophobic HTBR and hydrophilic isocyanate can be improved by adjusting the polarity of the polyol. As described by our group[78] capping polyols with polyester such as ϵ-caprolactone (ϵ-CL) can improve the compatibility.

3.3.1. Epoxidation of Polybutadienes

Polyols can be either prepared during the polymerization or in a post-modification. Hydroxyl groups can be introduced in BR by activating the double bonds. The reactivity of double bonds in polybutadienes compared to other functional groups such as carbonyls is quite low. They are activated by reactive molecules usually containing heteroatoms such as oxygen or sulphur.



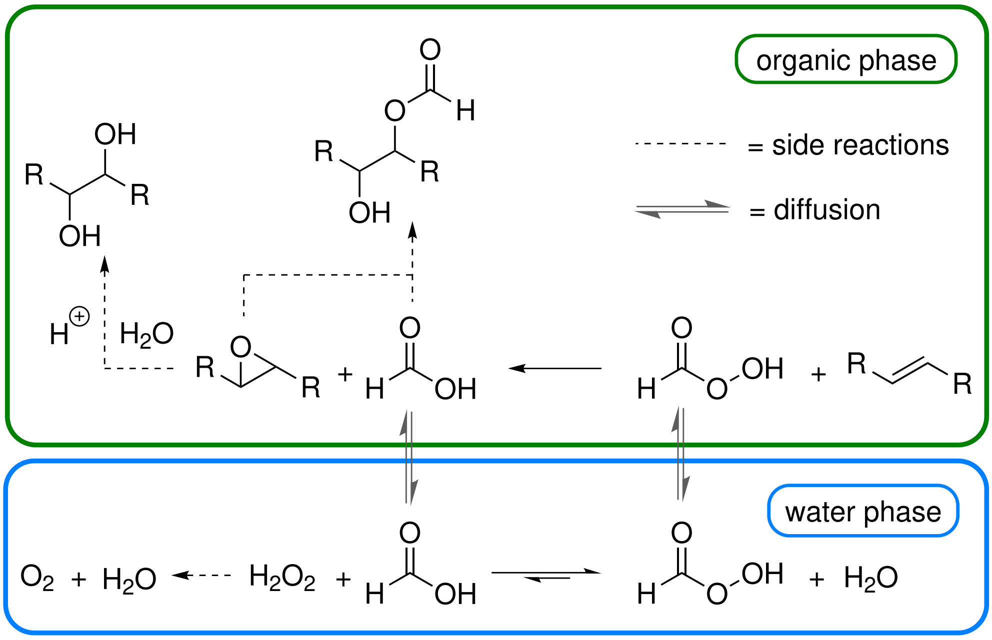
Scheme 3.11: Mechanism for epoxidation of a butadiene rubber by a peracid.[80,81]

In this work double bonds of BR were activated by epoxidation. In 1909 epoxidation was first described by Prileschajew.[82] Double bonds were epoxidized with various organic peroxides. In the following century numerous methods of epoxidation of diene polymers using different peroxides and peracids were described.[83]

The epoxide is formed by the reaction of the nucleophilic double bond and the electrophilic oxygen (Scheme 3.11).[80,81] In a concerted mechanism the oxygen is transferred to the double bond and the stereo information remains in the molecule.[84]

Reactivity of the double bonds towards epoxidation depends on the amount of substituents. 1,4-double bonds of BR have two carbon-carbon bonds and 1,2-*vinyl* bonds have one. +I-effect of carbons substituents increase the electron density in the double bond and therefore its nucleophilicity. As a result, 1,4-double bonds show a significantly higher reactivity towards epoxidation than 1,2-double bonds. The difference in reactivity can be so large, that no conversion of the 1,2-bonds is observed.[85–87]

At least stoichiometric amounts of peracids are needed for quantitative epoxidation. The cheapest and simplest peracids for epoxidation are aliphatic peracids. During the reaction high amounts of the corresponding acid is formed. The acidity of aliphatic acids and high temperatures lead to side reactions involving epoxide opening (see subsection 3.3.2).[88] These side reactions can be avoided by the aromatic peracids such as perbenzoic acid[89] and *meta*-chloroperoxybenzoic acid[90,91]. The corresponding acids have a lower acidity and are unable to open the formed epoxides.

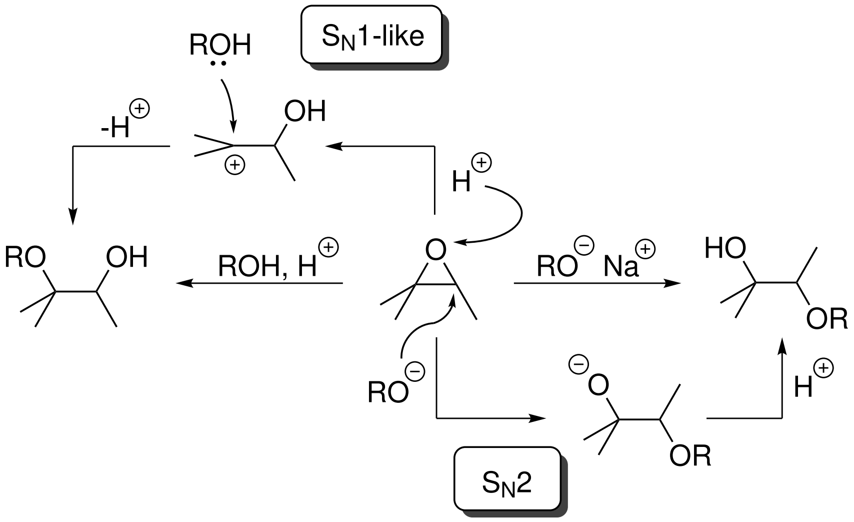


Scheme 3.12: Two phase catalytic system for epoxidation of butadiene rubber.

Unfortunately, these peracids are rather expensive and hardly used on an industrial scale. For a cost-effective epoxidation an *in situ* method is preferable. These *in situ* methods use oxidizing agents such as hydrogen peroxide and low amounts of acid. This reduces the possibility of side reactions and allows to use higher acidic aliphatic acids.[85,92–94] For the auto-catalytic formation of peracid a certain acidity is needed. Formic acid has the highest acidity of the aliphatic acids and is able to form performic acid without further additives.[94] The *in situ* method uses a two-phase system of an organic solvent containing the polymer and water containing the acid and hydrogen peroxide (Scheme 3.12). Once the peracid is formed it migrates into the organic phase and epoxidation takes place. Formation of peracid is an endothermic process and is usually assumed as the rate determining step.[95] The epoxidation itself is an exothermic reaction and therefor faster.[96] After epoxidation the acid migrates back to the water phase where it can be re-oxidized. Sometimes the migration can be so slow that it becomes rate determining. This can be avoided by the use of detergents, which lower the surface tension, increase the transition area and increase the diffusion rates.[94]

3.3.2. Mechanism of Epoxide Opening

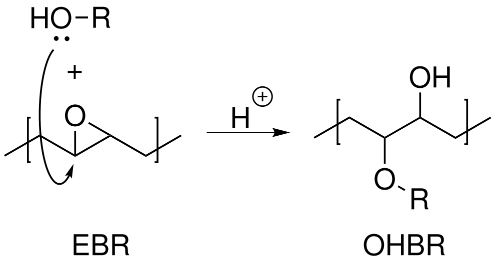
After epoxide activation a variety of nucleophiles can be used to open the epoxide. Usually alcohols or amines are used.[80,81] Amine-opening of partial epoxidized BR for example can be used to prepare stabilizer for plastics.[97] Although epoxides are quite reactive they require either acid catalysis or a powerful nucleophile to react fast.



Scheme 3.13: Regioselectivity of epoxide opening. Acidic conditions give a S_N1-like opening and basic condition an opening following the S_N2 path.

The regioselectivity of the epoxide opening is based on the degree of substitution (Scheme 3.13). The nucleophile is bound to be attached to the higher substituted side in acid catalyzed reactions. The acid first protonates the epoxide-oxygen and gives a carbo cation. Cation stabilization is larger at higher substituted carbons and allows the nucleophile to attack here. For good nucleophiles at basic condition a S_N2 pathway is taken. The nucleophile attacks predominantly on the less substituted carbon on account of steric hinderance.

For the partial epoxidized polybutadiene rubber this selectivity has a minor role as they mainly contain epoxides in the polymer backbone. These former 1,4-double bonds have the same substitution on both sides and therefor will not influence the regioselectivity. The opening with alcohols (Scheme 3.14) give polybutadiene-based polyols (OHBRs) suitable as OH-component for the Polyurethane (PU) preparation.



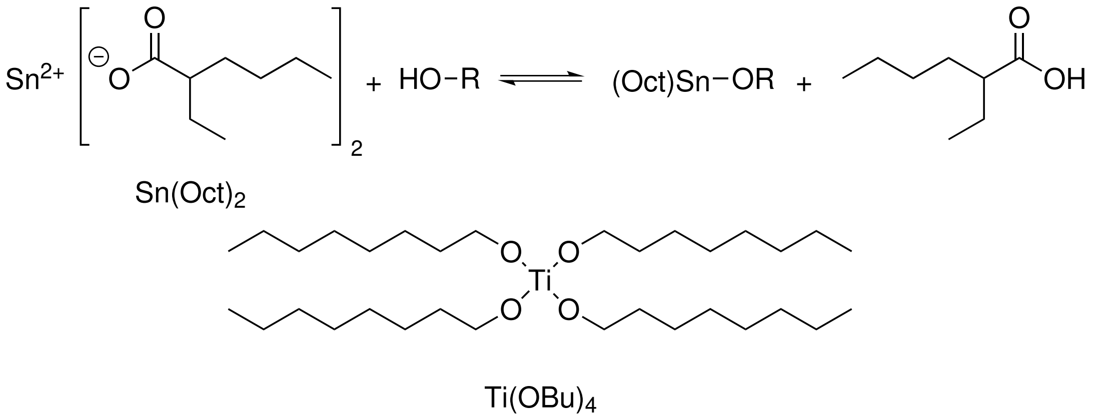
Scheme 3.14: Acidic epoxide opening of epoxidized polybutadiene rubber (EBR) with an alcohol as nucleophile.

However the polymeric structure of EBRs makes the opening challenging.[98] Strong bases such as KOH or *t*-BuOK are not able to open the epoxides. Strong acids such as sulphuric acid are able to open the epoxides at elevated temperatures and long reaction times. The products showed some color change, so degradation during the reaction is assumed.[99] The superacid trifluoromethanesulfonic acid (TfOH) is able to open polymeric epoxides within reasonable times at low temperatures.[98]

3.3.3. Polybutadiene-Polycaprolactone Copolymers

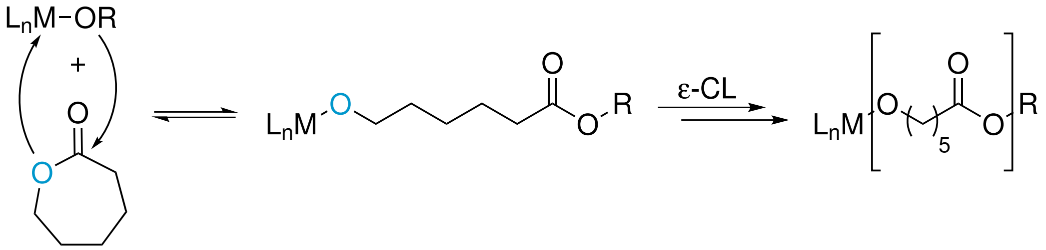
Polybutadiene-based polyols offer properties such as low moisture permeability in films and good insulation properties. However, they show low compatibility to polar polymers and isocyanates. Polycaprolactone (PCL) copolymers can improve the compatibility between the different polymers.[100]

Especially for the preparation of PU elastomers the capping with PCL with is crucial to achieve good material properties.[78]
Polycaprolactone is a aliphatic polyester with good material properties as well as good mixing properties with other polymers and it is biodegradable.[101] It has a low glass transition point of -70 to -60 °C depending on the crystallinity. Melting point of the crystalline phase is around 60 °C.[100]



Scheme 3.15: Different catalyst for ROP. $Sn(Oct)_2$ needs to be activated by a alcohol to give the reactive catalyst.

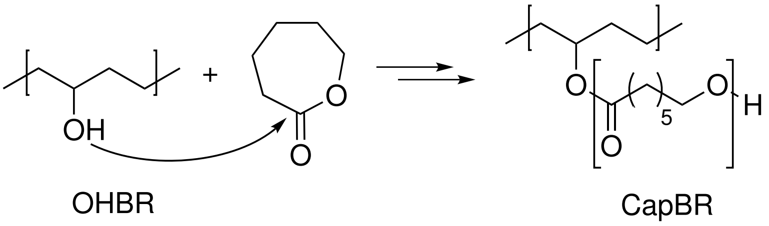
PCL is prepared from ϵ-caprolactone (ϵ-CL) either in an anionic, cationic or coordinative polymerization. The type of polymerization influences molecular weight as well as PDI.[101] The most commonly used polymerization is the coordinative polymerization with a Lewis-acidic metal catalysts. Those are predominantly titanium(IV) tetrabutanolate[102] ($Ti(OBu)_4$) and tin(II) 2-ethylhexanoate[103,104] ($Sn(Oct)_2$). The catalytic active species in the polymerization are alkoxides, so for Sn(Oct)2 alcohols have to be added (Scheme 3.15). ϵ-CL is polymerized along a migratory insertion pathway (Scheme 3.16). The alkoxide attacks the coordinated ϵ-CL at the carbonyl group and opens the lactone. The ester oxygen (blue) becomes attached to the catalytic center and further ϵ-CL molecules can be inserted.[103–105] Excess of alcohols used in the polymerization act as chain transfer agent. When the chain transfer reaction is faster than the propagation step, PCL with narrow molecular weight distributions can be prepared.[105] For low catalyst concentrations compared to the alcohol the degree of polymerization is defined by the relation of monomers



Scheme 3.16: Polymerization of ϵ-caprolactone (ϵ-CL).[103–105]

to alcohols (M/OH).

Most catalysts are able to also catalyze transesterification. This can either be an intra or inter molecular reaction. In the intra molecular reaction the active chain ends attack the polymeric chain and forms macro cycles in a so called backbiting reaction. These macro cycles broaden the molecular weight distribution. The inter molecular reaction forms longer polymer chains by forming ester bonds between two poly caprolactones. The tendency for transesterification increases in this order: Al < Zr < Ti < Sn.[102]

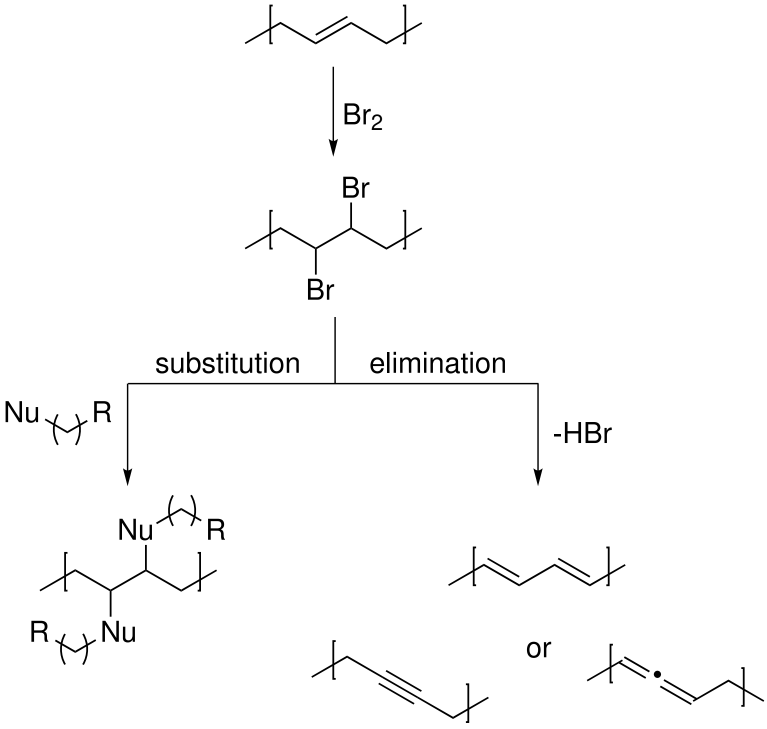


Scheme 3.17: Polyols can act as starting point for ROP and give polybutadiene-polycaprolactone copolymer (CapBR).

The coordinative polymerization can be used for the preparation of block copolymers (Scheme 3.17). They can be prepared in bulk and used the same insertion mechanism as the homo polymerization.[106] Capped polyols show good compatibility to isocyanates and can be used as polyol component in PU elastomer preparation.

3.4. Functionalization - Building Double Bonds

Bromination is a simple method to introduce functionalization in BR. The addition of bromine to a double bond is a well-know reaction in organic chemistry.[81,107–110]

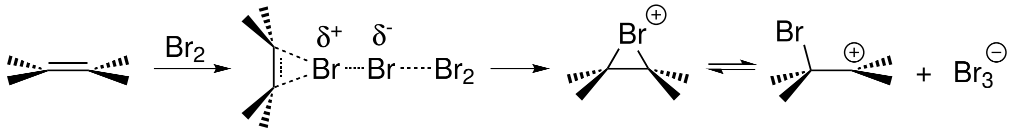


Scheme 3.18: Bromination of BR followed by substitution or elimination .

Once bromine is introduced in BR it can either be removed in a substitution or an elimination. Through substitution different nucleophiles can be attached to the BR. Elimination results in double bond containing compounds depending on substitution and reaction conditions (Scheme 3.18).

3.4.1. Bromination

Electrophilic bromination of double bonds is a common reaction in organic chemistry. It involves the formation of the bromonium ion proposed by Roberts and Kimball (Scheme 3.19).[111]

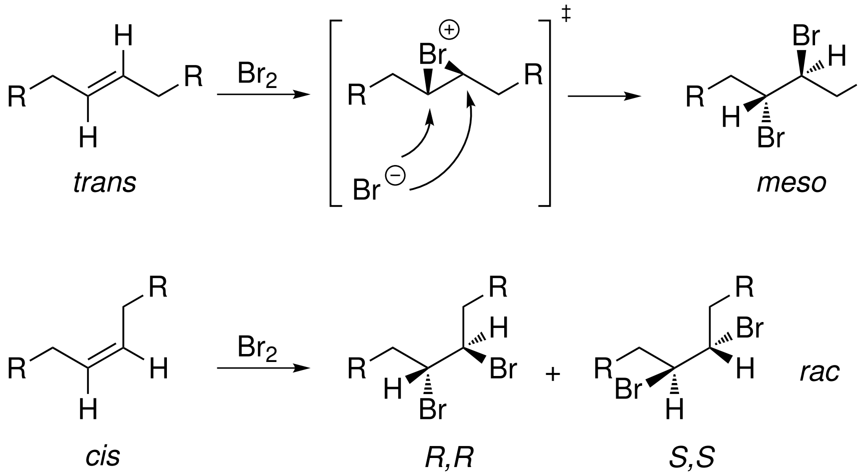


Scheme 3.19: Bromination can be stereospecific depending on the formation of a bromonium bridge.

The bromonium ion is formed by the heterolytic cleavage of a Br_2 molecule catalyzed by either another Br_2 or a solvent molecule. Catalyzing solvents are protic solvents such as methanol that are able to solvate the formed bromide. Driving force is either solvation or formation of the stable tribromide in halogenated or non-protic solvents.[108,112] Formation of the bromine bridge is dependent on the substituents of the former double bond. For substituents that are strongly electron donating and are able to stabilize a positive charge a β-bromocarbocation is formed.[80,108,111,112] When a β-bromocarbocation is formed, the bond is free to rotate and the products are non-stereospecific. For substituents containing no heteroatoms, such as polybutadiene rubber, the bromine bridge structure is expected.[112]
The nucleophile attack of bromide is an *anti*-addition and can occur at two different carbons (Scheme 3.20). In the case of a *trans* double bond the formed diastereomer is a *meso* compound. For a *cis* double bond a racemic mixture of the *R,R* and *S,S* diastereomers is formed.[80,81]

3.4.2. Stereo Selectivity of Dehydrobromination

Dehydrobromination is an elimination reaction involving a base and bromine as leaving group. Like every other elimination it is competing with the substitution depending on the nucleophilicity of the base. If the base is high

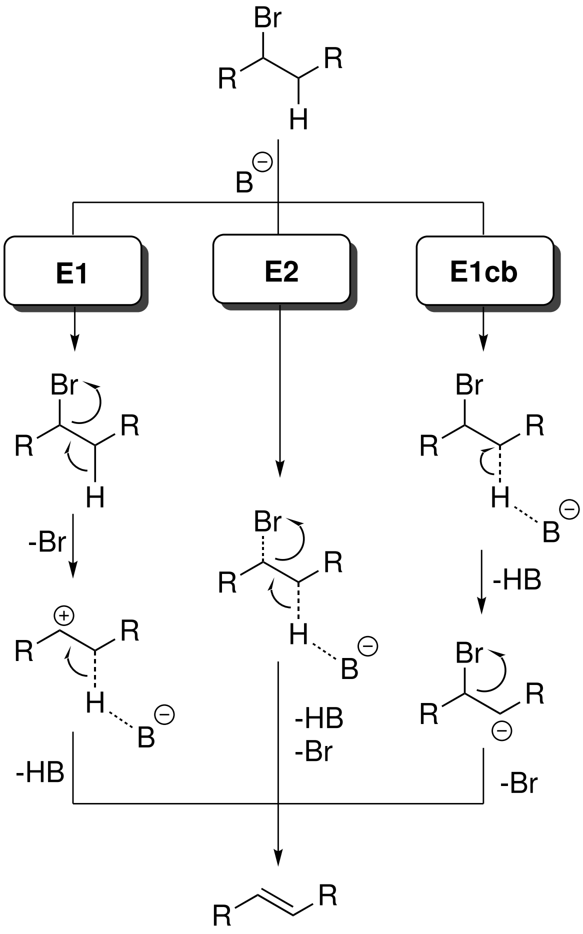


Scheme 3.20: Different double bond configurations give different brominated products. *Trans* double bonds give a *meso* compounds and *cis* double bonds give a racemic mixture of the *R,R* and *S,S* enantiomers.[81]

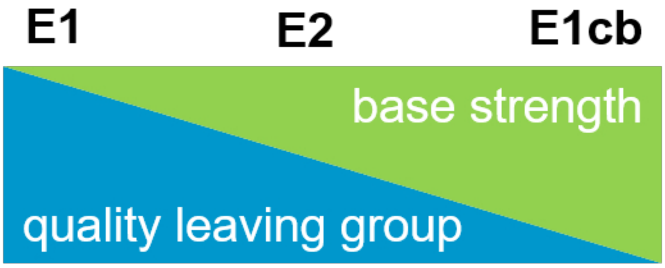
nucleophilic substitution will take place. Sterically hindered bases such as potassium *tert*-butoxide give the elimination product.

The elimination can proceed on three different reaction pathways namely E2, E1 and E1cb (Scheme 3.21). E2 elimination is a concerted reaction where the base removes the proton at the same time as the bromine is leaving the molecule. Proton and bromine are in *anti*-conformation and dictate configuration of the double bond.

E1 and E1cb eliminations involve formation of a carbocation or carbanion respectively. The C-C bond can rotate and the conformation is not fixed. Depending on the stability of the ions versus the rotational barrier either the kinetically or thermodynamically product is formed. When the ion is well-stabilized in the transition state the thermodynamically product is formed. This usually is the *trans*-product.



Scheme 3.21: Elimination pathways E1, E1cb or E2 for dehydrobromination.



Scheme 3.22: Dependence of base strength and leaving group quality on the elimination pathway.

Elimination depends on multiple factors such as ion stabilization or the solvent. But the two most important factors are the basicity of the used base and the "quality" of the leaving group. Quality of a leaving group is defined by its ability for ionization. Both factors give a good indication which type of elimination will happen. For example, a strong base will usually give E1cb mechanism and a good leaving group will result in E1 mechanism. E2 eliminations are a mixture of both extrema, a medium base and medium leaving group.[80,81]

4. Motivation

The reactive double bonds make polybutadiene rubber an interesting starting material for various applications. Various functional groups can be introduced in the polymer backbone by reaction with the double bonds. The high reactivity of the double bonds especially at elevated temperatures and UV radiation makes them vulnerable for ageing reactions such as UV induced crosslinking. A way to influence ageing resistance and other material properties is the partial hydrogenation of double bonds. Once a partial hydrogenation routine is established different partial hydrogenated and functionalized polymers such as functionalized polyethylene are possible.

The correlation between polymer properties and degree of hydrogenation of various functionalized polymers is the major scopes of this thesis.

5. Results and Discussion - Hydrogenation

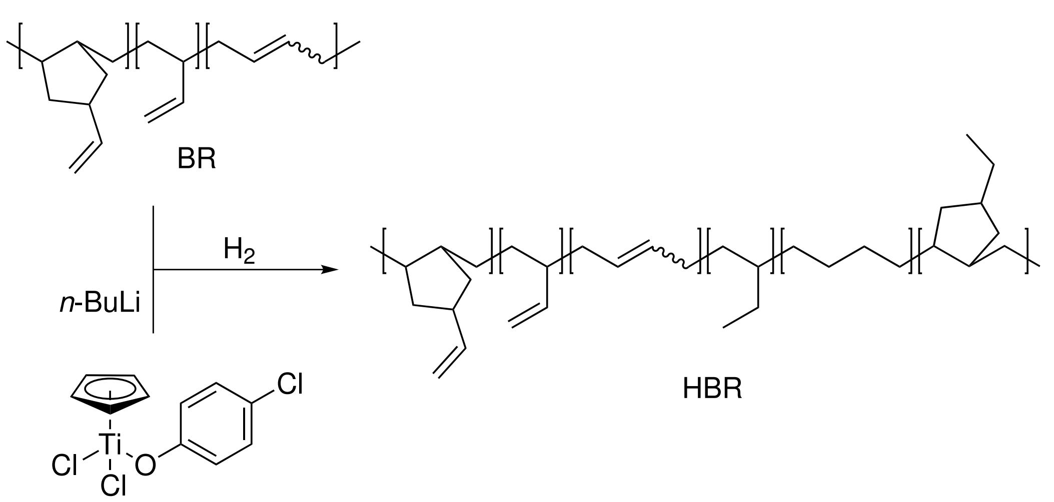
butadiene rubber consist of reactive double bonds. On the one hand reactivity of these double bonds makes BR vulnerable to aging and degradation, but on the other hand a variety of functional groups can be introduced onto the molecular backbone. In this chapter the partial hydrogenation of low molecular weight BR is discussed, regarding the double bond selectivity, concentration dependency, catalyst behavior and material properties of the products. The set-up of a hydrogenation system is also described.

5.1. Introduction of the used catalytic system and butadiene rubber

In the past century different hydrogenation methods for various applications have been developed (see section 3.2). Depending on experimental conditions as well as starting materials they show certain advantages and disadvantages. For the preparation of partial hydrogenated polybutadiene rubber (HBR) the catalytic system has to fulfill certain requirements. The degree of hydrogenation (X_H) has to be adjustable, reaction had to be at relatively mild conditions and should be scalable for possible industrial use.

The catalytic system that fulfills most of these requirements is the titanium-based catalyst 4 Chlorohydroxyphenyl-cyclopentadienyl-titanium(IV) dichloride (Scheme 5.1). It uses *n*-BuLi as co-catalyst at temperatures of 50 °C and 8 bar hydrogen pressure.

For evaluation of hydrogenation three different low molecular weight polybutadiene rubber were used. They offer differences in double bond composition, molecular weight, viscosity and glass transition temperature (Table 5.1). This



Scheme 5.1: Hydrogenation of butadiene rubber (BR) to hydrogenated polybutadiene rubber (HBR) with hydrogen, $TiCpCl_2$–*p*–($O–C_6H_4–Cl$) as catalyst and *n*-butyl lithium (*n*-BuLi) as co-catalysst.

allows to evaluate the influence of the double bond microstructure on hydrogenation as well as the influences of time of hydrogenation (t_H), catalyst concentration (c_{cat}) and concentration of polybutadiene rubber (c_{BR}).

Table 5.1.: Microstructure and molecular weight of the used Lithenes.

Butadiene Rubber	Double Bonds 1,2-*cyclic*	1,2-*vinyl*	1,4-*cis*/*trans*	M_n [g/mol][a]	η [Pa s]	T_g [°C]
vBR	30%	29%	41%	750	1.03	-60.1
ctBR	4%	15%	81%	1500	0.552	-93.0
ctBR-5k	2%	10%	88%	5000	2.84	-92.0

[a] corrected value

The products of the hydrogenation were also studied regarding changes in dynamic shear viscosity (η) and glass transition temperature (T_g).

5.2. Set-up of the hydrogenation reactor

The catalytic system used for the hydrogenation requires parameters such as hydrogen pressure and constant reaction temperature. To fulfill these requirements (Table 5.2) two similar hydrogenation reactors (R1 and R2) were used (Figure 5.1).

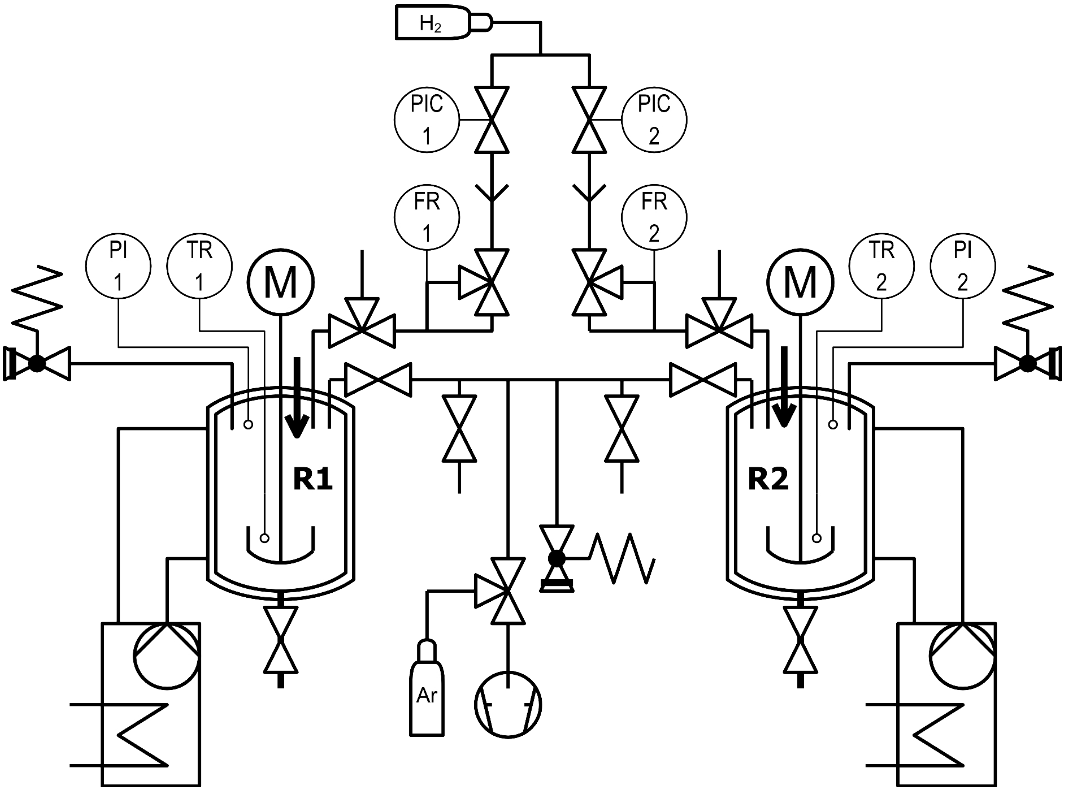


Figure 5.1.: Flow chart of the build hydrogenation reactors. It contains two independent reactors R1 and R2. The pressure inside of the reactors can be adjusted by the vales PIC 1 and 2 respectively. Hydrogen flow is recorded by two thermal mass flow controllers (FR1, FR2). Temperature (TR1, TR2) and pressure (PI1, PI2) is measured for each reactor. Temperature could be controlled independently by two thermostats. Each reactor could be evacuated and purged with Argon.

Both reactors could be used independently at hydrogen pressures p_{H} , temperatures T_{H} , hydrogen flow Q_{H} and stirring speeds. The reactors could be evacuated and filled with argon gas. The reactors were designed for pressures of -1 - 10 bar and temperatures of up to 120 °C. Reaction temperature and hydrogen flow were measured online. This allowed to keep track of degree of hydrogenation (X_H) and overall hydrogen consumption (V_{H}) as well as the catalyst action.

Table 5.2.: Required and actual value of hydrogenation reactor parameter.

Paramerters	Required Value[†]	Actual Value
p_{H} [bar gauge]	8	1 - 10
p_{heating} [bar]	$< 1 \cdot 10^{-3}$	$3 \cdot 10^{-4}$
Q_{H} [mL/min]	< 50	0.1 - 50
T_{H} [°C]	50	50 - 70
T_{heating} [°C]	> 100	max. 120

[†] according to Jamanek *et al.*[67]

5.3. Hydrogenation Activity of Different Double Bonds

Reactivity of a double bond is dependent on the substitution-pattern. In general substitution influences reactivity either by inductive effects or by steric hindrance. In case of hydrogenation the influence is primarily by steric hindrance, as the usual order regarding reactivity is 1,2-double bond > 1,4-double bond.

To investigate reactivity of the double bonds in the used BR, the hydrogenation was performed at constant temperature (T_{H}), hydrogen pressure (p_{H}) and concentration. Reaction temperature was at 50 °C and p_{H} at 8 bar. The catalyst concentration (c_{cat}) and concentration of polybutadiene rubber (c_{BR}) were constant at 1 mmol/L and 50 g/L respectively. Reaction time (t_{H}) was varied to 1, 3, 5 and 7 h.

The BR first studied was vBR (Figure 5.2). It has about 40% 1,4-double bonds and 60% 1,2-double bonds. As expected 1,2-double bonds show a higher reactivity towards hydrogenation than 1,4-double bonds. After 1 h of hydrogenation no change was observed with respect to the 1,4-double bond content, while the amount of 1,2-*vinyl* double bonds was reduced. The 1,2-*cyclic* double bonds – the most exposed double bonds – had the best accessibility for the catalyst. After 1 h one third were hydrogenated. Once the majority of 1,2-*cyclic* double bonds were hydrogenated their conversion rate declined as expected. Its higher reactivity was overturned by higher concentration of the other double bonds. With ongoing hydrogenation, 1,4-double bonds slowly

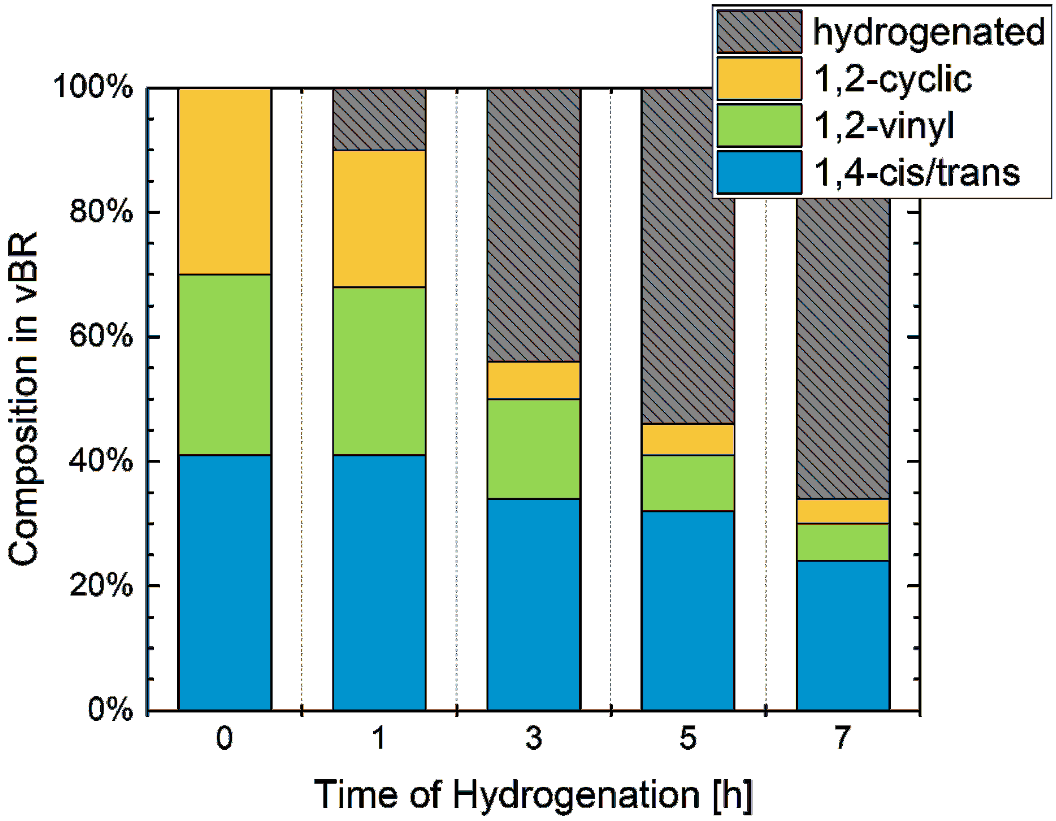


Figure 5.2.: Composition of partly hydrogenated vBR as function of time. $p_{\mathrm{H}} = 8$ bar, $t_{\mathrm{H}} = 50$ °C, $c_{\mathrm{cat}} = 1$ mmol/L, $c_{\mathrm{BR}} = 50$ g/L.

became hydrogenated. After 3 h about 10% were hydrogenated. Once the majority of the 1,2-double bonds were hydrogenated the conversion rate increased for 1,4-double bonds. After 7 h of hydrogenation overall degree of hydrogenation was $X_H = 66\%$. Double bonds left in vHBR were dominated by 1,4-double bonds with a content of $Y_{\mathrm{ct}} = 24\%$ (about 70% of the double bonds left).

The second evaluated rubber was ctBR (Figure 5.3).). It consisted of 81% 1,4-double bonds, 15% 1,2-*vinyl* and 4% 1,2-*cyclic* double bonds. In comparison to vBR the lower amount of 1,2-double bonds resulted in an earlier hydrogenation of the 1,4-double bonds and an overall lower X_H. During the first hours the hydrogenation of all double bonds was rather slow. High concentration of 1,4-double bonds competed with the better accessibility of 1,2-double bonds in terms of reactivity. Once the majority of the 1,2-double bonds were hydrogenated the hydrogenation rate increased. After 7 h of hydrogenation the overall degree of hydrogenation had increased to $X_H = 54\%$. The initial low

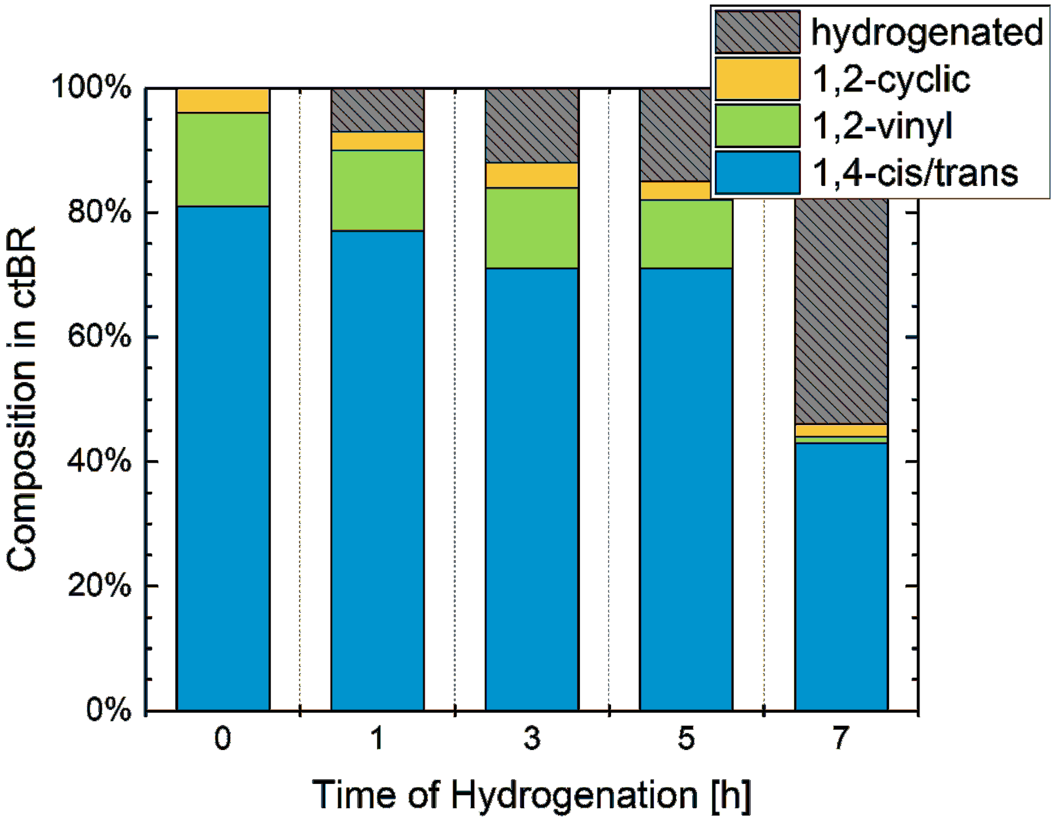


Figure 5.3.: Composition of partly hydrogenated ctBR as function of time. p_{H} = 8 bar, t_{H} = 50 °C, c_{cat} = 1 mmol/L, c_{BR} = 50 g/L.

amount of 1,2-double bonds allowed for almost quantitative conversion after 7 h. A 1,2-double bond content of about Y_{cy} = 2% (1,2-*cyclic*) and Y_{v} = 1% (1,2-*vinyl*) was left in the polymer.

The third evaluated BR was ctBR-5k (Figure 5.4). In comparison to ctBR it had a slightly higher 1,4-double bond content of 88% and a higher molecular weight of M_{n} = 5000 g/mol (ctBR: M_{n} = 1500 g/mol). Both factors were expected to lower the hydrogenation rate. A higher molecular weight reduces the mobility and lowers the accessibility of the double bonds inside the polymer coil. As presumed the hydrogenation rate was lower. After 1 h about 3% of the polymer was hydrogenated. With ongoing hydrogenation, the amount of the double bonds decreased in a constant manner. In contrast to ctBR the hydrogenation almost ceased completely once most of the 1,2-double bonds were hydrogenated. This might be related to the higher molecular weight of ctBR-5k. After 7 h, an overall degree of hydrogenation of X_H = 43% was reached.

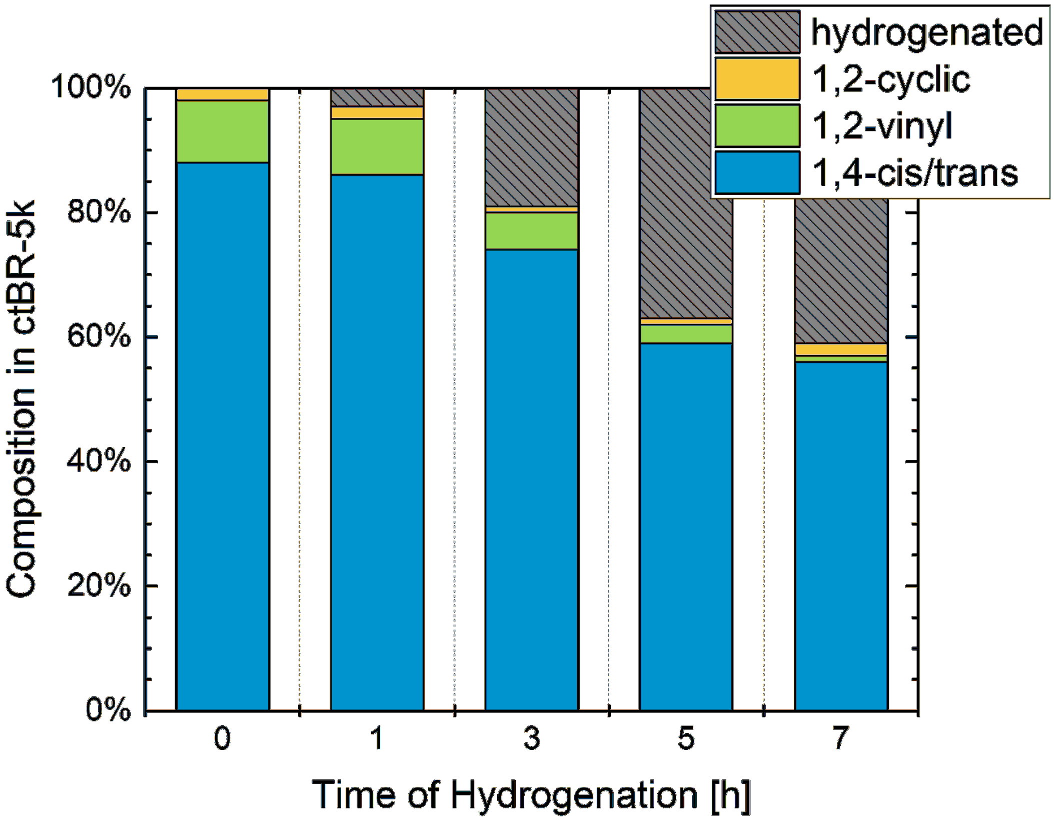


Figure 5.4.: Composition of partly hydrogenated ctBR-5k as function of time. $p_{\mathrm{H}} = 8$ bar, $t_{\mathrm{H}} = 50$ °C, $c_{\mathrm{cat}} = 1$ mmol/L, $c_{\mathrm{BR}} = 50$ g/L.

After analyzing the three BR with different double bond microstructure and molecular weight the assumed order of double bond reactivity can be confirmed. The better accessibility of the 1,2-*cyclic* double gave an advantage in terms of reactivity and results in the following order:

1,2-*cyclic* > 1,2-*vinyl* > 1,4-double bonds.

The effect of molecular weight on the hydrogenation rate can be assumed. The difference in 1,4-double bond content between ctBR and ctBR-5k cannot account for the difference in X_H of more than 10 percentage points. As previously stated, for higher molecular weights the double bonds inside of the polymer coil have a reduced reactivity. This reduces the overall hydrogenation rate.

5.4. Thermal Material Properties of Partial Hydrogenated BR

The material properties such as dynamic shear viscosity (η) and the glass transition temperature (T_g) are important values regarding processability and application of the polymer. Hydrogenation influences theses values as it turns the polybutadiene rubber into polyolefin-like polymers. To evaluate the influence of hydrogenation on these values each prepared HBR was analyzed by rheology and differential scanning calorimetry (DSC).

The viscosity of a polymer is influenced by its molecular weight and structural factors such as branching. Longer polymer chains have more interaction points with other polymers compared to shorter chains. The longer amount of interactions per chain increases the amount of energy needed for a chain to diffuse through a polymer melt. At a constant temperature this results in a lower diffusion rate, which corresponds to a higher dynamic viscosity.[113] In polybutadiene rubber polymer branching is referred to the 1,2-double bond content. When a polymer chain diffuses through a polymer melt it has to evade other chains by a conformation change. Relative to 1,4-double bonds, the rotational barrier of 1,2-double bonds is much higher.[114] So more energy is needed for a conformational change in a high 1,2-double bond BR. Again, the higher need of energy results in a higher dynamic viscosity.

Considering those factors, it was not surprising that ctBR had the lowest viscosity of the three BRs (Figure 5.5). Results for vBR and ctBR-5k show the different impacts of molecular weight and chain branching on the viscosity. The higher amount of 1,2-double bonds in vBR doubled the viscosity compared to ctBR. This is remarkable considering the molecular weight of ctBR is twice as high. Viscosity of ctBR-5k was about six times higher than of ctBR at almost similar double bond composition.

Hydrogenation of BRs had little impact on the dynamic viscosity of ctBR and ctBR-5k. With increasing X_H only a slight increase in η was visible. However, the viscosity of vBR already shows a jump in viscosity for small degrees of hydrogenation. A further increase of X_H only results in slight increases in η. This jump in viscosity might be caused by the increased rotational barrier of ethyl group compared to an ethylene group. But this would lead to a further

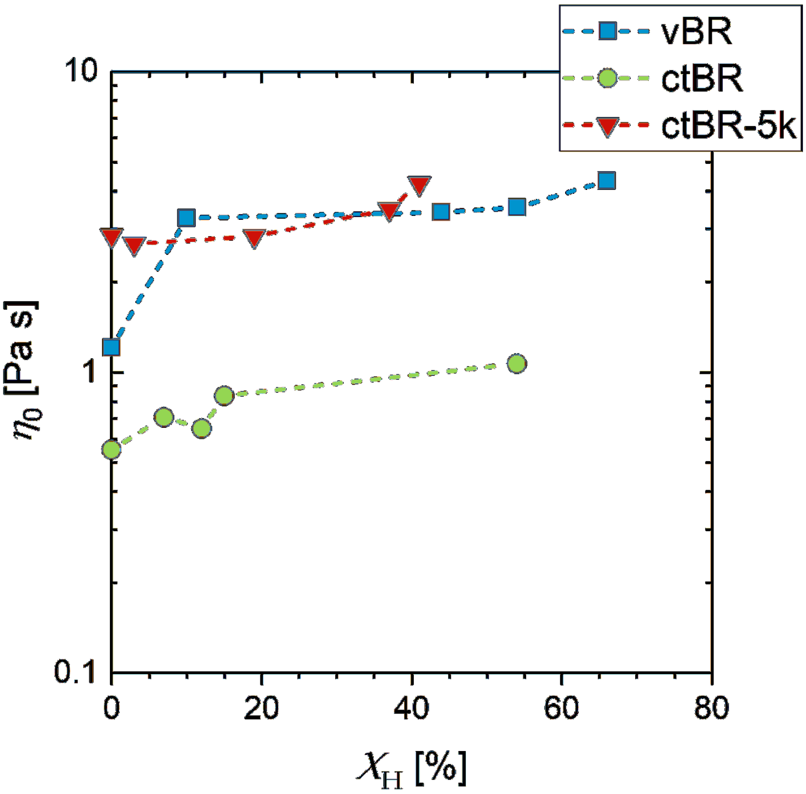


Figure 5.5.: Dynamic viscosity η of vBR, ctBR and ctBR-5k in relation to the degree of hydrogenation (X_H).

increase of viscosity for higher X_H. More likely the process of hydrogenation removed small molecules contained in vBR and therefor results in an increased viscosity.

Similar correlations can be made for glass transition temperature (T_g) (Figure 5.6). While the molecular mass has a minor influence, T_g is highly influenced by the amount of 1,2-double bonds.[115] The higher rotational barrier and lower chain flexibility increases the energy needed for the glass transition.[116] In case of the three BRs this resulted in a 30 °C higher T_g of vBR compared to ctBR and ctBR-5k. Concerning hydrogenation, no significant influence of X_H on T_g was visible. The jump in T_g is probably caused by the removal of small molecules during the hydrogenation process.

In conclusion the influence of the hydrogenation on dynamic viscosity and glass transition temperature was small. Larger effects can be achieved by altering the amount of 1,2-double bonds and the molecular weight.

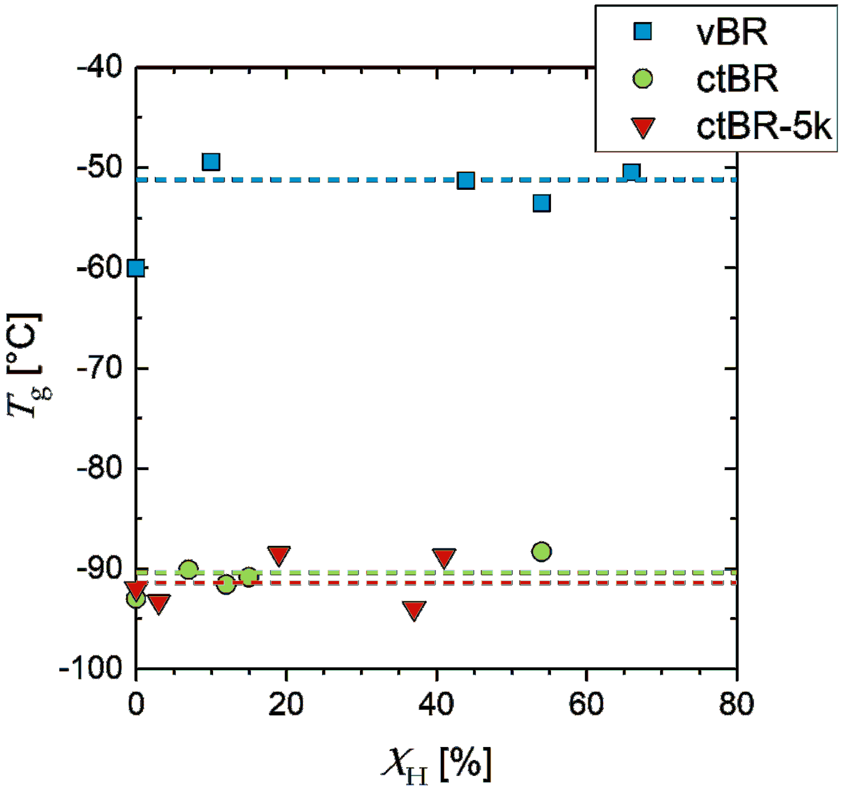


Figure 5.6.: Glass transition temperature (T_g) of vBR, ctBR and ctBR-5k in relation to the degree of hydrogenation (X_H).

5.5. Influence of Water Removal on the Catalytic System

The majority of the used catalysts for hydrogenation are hydrolysis-sensitive. In order to achieve high degrees of hydrogenation water free solvents are essential. In the previous described reactions, the used cyclohexane was distilled over sodium to remove water. However, this process is highly energy and time consuming. In order to simplify the drying process, an excess of *n*-BuLi was added to the dissolved BR prior to the catalyst addition. Excess of *n*-BuLi results in a decreased degree of hydrogenation at similar reaction conditions (Figure 5.7).

The reason for the decrease in degree of hydrogenation was not further analyzed as X_H was high enough for subsequent functionalization.

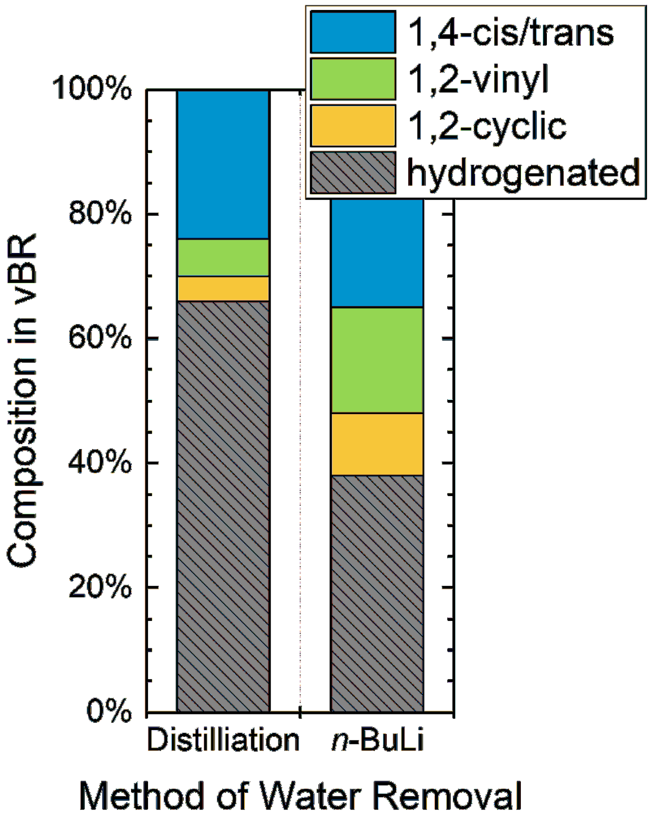


Figure 5.7.: Water removal and degree of hydrogenation (X_H) for vBR.

5.6. Influence of the Catalyst and BR Concentration on X_H

The influence of a concentration change on the degree of hydrogenation was evaluated by varying concentrations of vBR (c_{BR}) and the catalyst (c_{cat}). Various effects that lower the degree of hydrogenation can occur at increased concentrations, e.g. at high c_{cat} insoluble bis titanium hydride complexes can be formed from cyclopentadienyl titanium complexes in the presence of hydrogen.[117] These lower the concentration of the active catalyst and therefor would reduce X_H.

To evaluate the concentration dependencies, three different concentrations of vBR were used (Figure 5.8). In addition to the concentration of the previous experiments of 50 g/L two higher concentrations of 150 and 250 g/L were tested. For each c_{BR} three different catalyst concentrations were chosen. These were based on the catalyst to BR ratio of 0.01, 0.02 and 0.04 mmol/g. The catalyst concentrations were 0.5, 1 and 2 mmol/L for c_{BR} = 50 g/L, 1.5, 3 and 6 mmol/L for c_{BR} = 150 g/L and 2.5, 5 and 10 mmol/L for c_{BR} = 250 g/L.

The first obvious observation was the expected increase of X_H for higher catalyst concentrations for the same c_{BR}. However, the increase of X_H for the second c_{cat}c doubling was smaller than for the first one. This might indicate an increased deactivation of catalyst at higher catalyst concentrations. At higher concentrations an increased amount of free catalyst was present. This encourages formation of inactive bis-complex and reduces X_H at similar conditions.[118]

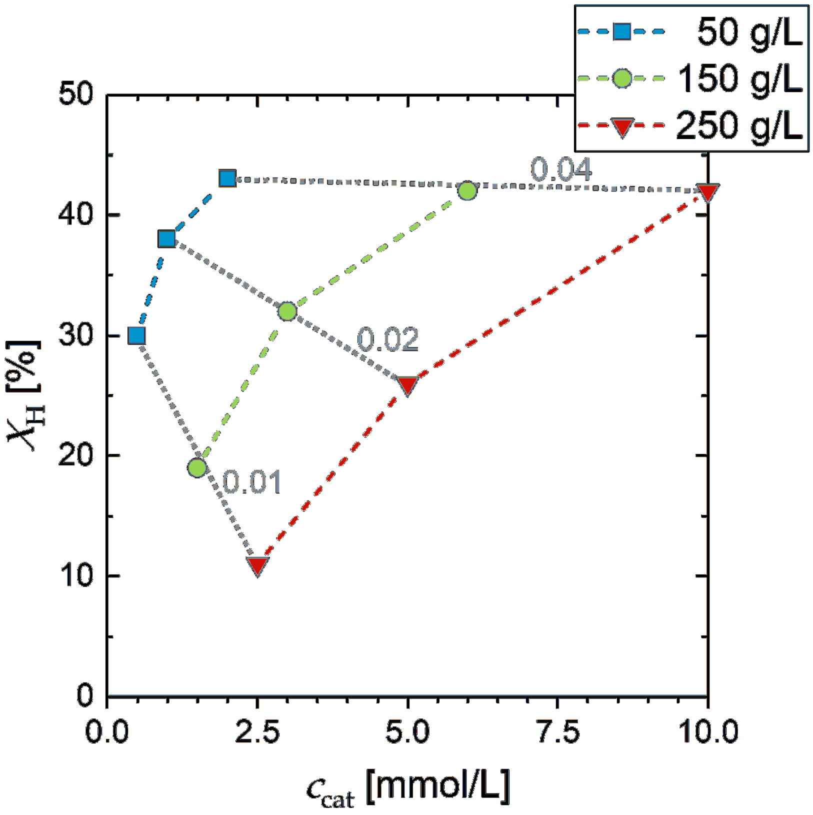


Figure 5.8.: Degree of hydrogenation with catalyst concentration (c_{cat}) and concentration of polybutadiene rubber (c_{BR}).

The increase of cBR at constant catalyst to vBR ratio revealed an influence of cBR on the turnover frequency (TOF). In a system where the turnover frequency and the resulting X_H were independent of cBR, the slope of the grey dotted line would be zero and the hydrogenation would only be dependent on the concentration of the active catalyst. At a small catalyst to vBR ratio, X_H is lowered for higher cBR. This means the TOF is lowered by the higher amount of double bonds available in the system. The effect decreases for higher catalyst to vBR ratios and almost becomes independent of c_{BR} for a ratio of 0.04 mmol/g. To further analyze the behavior of the catalyst, the products were analyzed by NMR regarding their double bond composition. Additionally, the hydrogen consumption (Q_{H}) was tracked online.

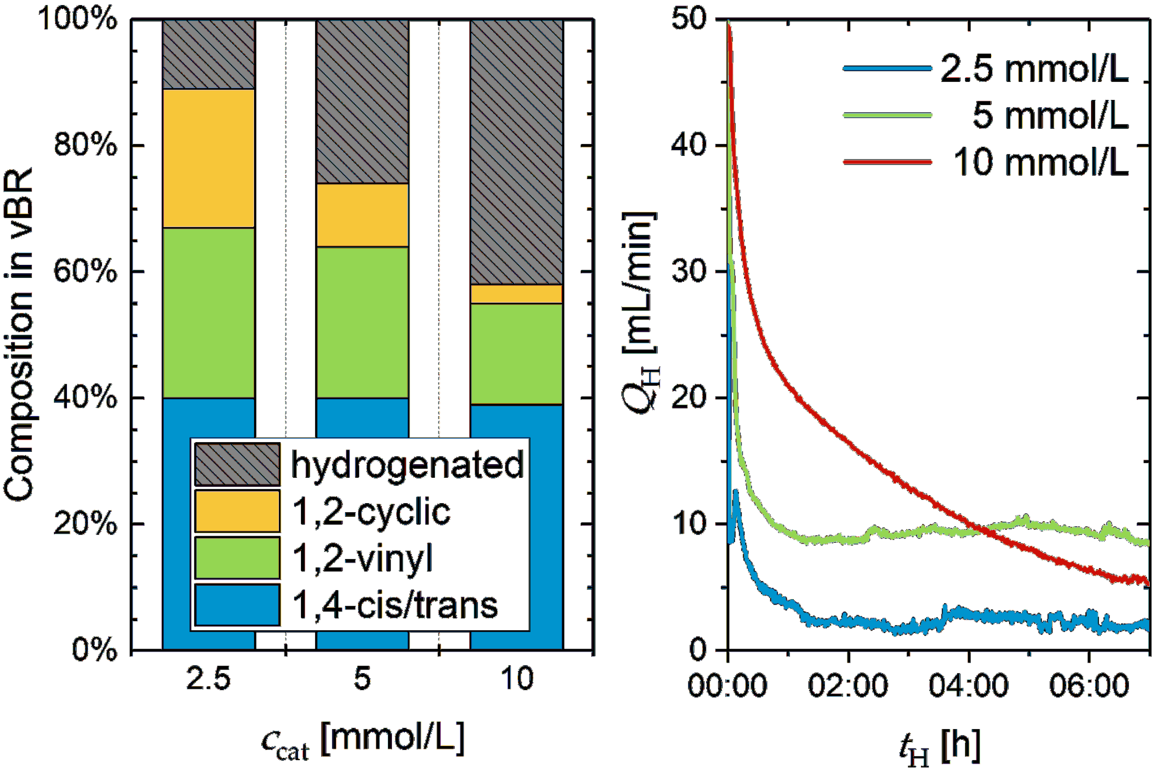


Figure 5.9.: Double bond composition and hydrogen consumption (Q_{H}) for different catalyst concentration (c_{cat}) at constant rubber concertation of c_{BR} = 250 g/L.

At a concertation of 250 g/L vBR the catalyst concentration was set from 2.5 mmol/L to 5 and 10 mmol/L (Figure 5.9). NMR analysis showed different conversions of 1,2-double bonds and almost no conversion of 1,4-double bonds. Like previous results 1,2-*cyclic* double bonds showed a higher reactivity than 1,2-*vinyl* double bonds. For an increase in catalyst concentration, a higher conversion of the 1,2-double bonds and no increased conversion of the 1,4-doube bonds was observed. At this cBR the catalyst predominantly hydrogenates the 1,2-double bonds, which have a lower steric hinderance. The MFC data shows a high hydrogen consumption at the beginning of hydrogenation. Within the first hour consumption dropped to a constant level for c_{cat} = 2.5 and 5 mmol/L. This level was higher for higher c_{cat} as more hydrogen could be conversed. For c_{cat} = 10 mmol/L a continuous decrease of Q_H after the initial drop was visible. This indicates a lower turnover number (TON) and supports the assumption of catalyst deactivation for high c_{cat}. This deactivation seems to be so significant that Q_H dropped below the value of c_{cat} = 5 mmol/L after about 4 h of hydrogenation.

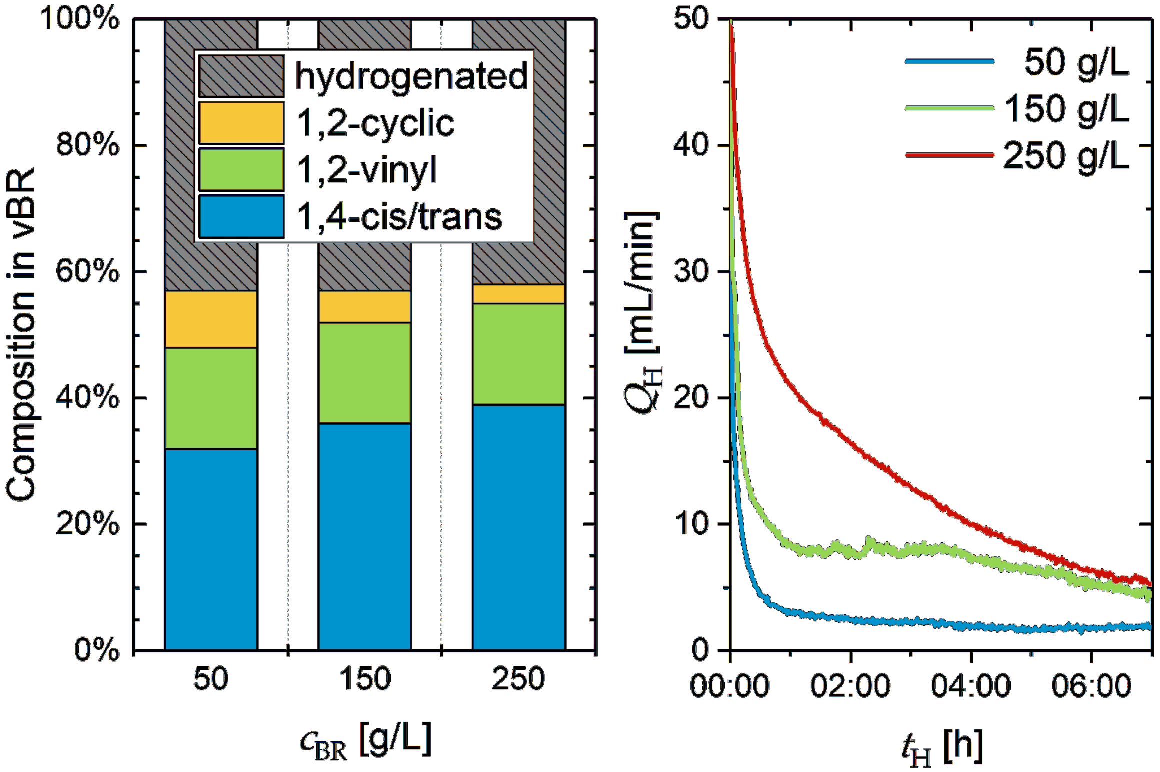


Figure 5.10.: Double bond composition and hydrogen consumption (Q_H) for different rubber concentration (c_{BR}) at constant catalyst to BR ratio of 0.04 mmol/g.

For a catalyst to BR ratio of 0.04 mmol/g c_{cat} was set at 2, 6 and 10 mmol/L for c_{BR} = 50, 150 and 250 g/L respectively (Figure 5.10). All three HBR showed a similar overall X_H but differed in their double bond composition. At the

highest vBR concentration almost no 1,4-double bond was hydrogenated. At lower vBR concentration a portion of the 1,4-double bonds was hydrogenated at the cost of a lower 1,2-double bond conversion. The overall hydrogen consumption was larger for higher cBR, as the catalyst concentrations were also higher at a constant catalyst to BR ratio. The initial drop in Q_H within the first hour was similar for all concentrations. The shape of the curves after this drop describe the differences in TON caused by catalyst deactivation. Lower cBR have a higher TON, as the change in hydrogen consumption is smaller. In combination with the double bond composition it can be assumed: The longer a catalyst is active, it becomes more likely for the catalyst to hydrogenate 1,4-double bonds. Since the 1,4-double bonds are less reactive the TOF is lowered. This results in similar values for X_H at the different concentrations.
In conclusion, the degree of hydrogenation is dependent on various variables. High catalyst concentrations increase the X_H but suffer from catalyst deactivation and a lower TON. High rubber concentrations at constant catalyst to BR ratio decrease TON and give HBR with higher amounts of hydrogenated 1,2-double bonds. Low rubber concentrations give HBR with higher amounts of hydrogenated 1,4-double bonds at the cost of lower amounts of hydrogenated 1,2-double bonds. This is caused by the lower TOF for 1,4-double bonds. At higher catalyst to BR ratio the loss in X_H for higher cBR at constant catalyst to BR ratio is reduced.

5.7. Correlation between NMR and MFC Results

The degree of hydrogenation is dependent on various factors such as double bond constitution and molecular weight. Since NMR analysis is an offline analysis, the degree of hydrogenation can only be determined after the workup of the HBR. For hydrogenation of new polymers this is a tedious procedure, as a new series of tests had to be run for each polymer. The degree of hydrogenation can be determined by MFC data. First the amount of double bonds n_DB was calculated (equation 5.1) from sample mass (m_s) and molecular weight of the repetition unit (M_rep = 54.09 g/mol).

$$n_\mathrm{DB} = \frac{m_\mathrm{s}}{M_\mathrm{rep}} \tag{5.1}$$

Afterwards, the amount of consumed hydrogen was calculated (equation 5.2). $V_{\mathrm{m}}(\mathrm{H}_2)$ is the molar volume of hydrogen (22.4 L/mol) and V_{H} the consumed hydrogen volume.

$$n_{\mathrm{H}} = \frac{V_{\mathrm{H}}}{V_{\mathrm{m}}\,(\mathrm{H}_2)} \tag{5.2}$$

Consumed hydrogen volume is the integral of the mass flow Q_{H} over the reaction time t_{H} (equation 5.3).

$$V_{\mathrm{H}} = \sum_{t_{\mathrm{H}}=1}^{t_{\mathrm{H}}} Q_{\mathrm{H}}\,(t_{\mathrm{H}}) \tag{5.3}$$

The quotient of the amount of consumed hydrogen and the amount of double bonds gives the degree of hydrogenation (equation 5.4).

$$X_{\mathrm{H}} = \frac{n_{\mathrm{H}}}{n_{\mathrm{DB}}} \tag{5.4}$$

To verify the coherence of X_H calculated by NMR and MFC the results of seven hydrogenations of ctBR were compared (Figure 5.11). The values calculated for X_H from MFC data are slightly higher but overall in good agreement with the NMR data. The calculated deviation (MFC/NMR) averages a value of 1.05. Higher values for the MFC data are probably caused by a minor hydrogen leakage and are negligible.

The good correlation between NMR and MFC results allows to use MFC for online measurement of X_H. MFC analysis was used to calculate X_H of prepared HBR for subsequent functionalizations.

5.8. Conclusion and Outlook

The partly hydrogenation of polybutadiene rubber with different double composition could be achieved by the catalytic system 4-Chlorohydroxyphenyl-cyclopentadienyl-titanium(IV) dichloride/*n*-BuLi. The activity of the double bonds is primarily dependent on the accessibility and follows the order 1,2-*cyclic* > 1,2-*vinyl* > 1,4-double bonds. In terms of achieving a high overall degree of hydrogenation, high amounts of 1,2-double bonds and water-free conditions are needed. High catalyst concentrations suffer from catalyst deac-

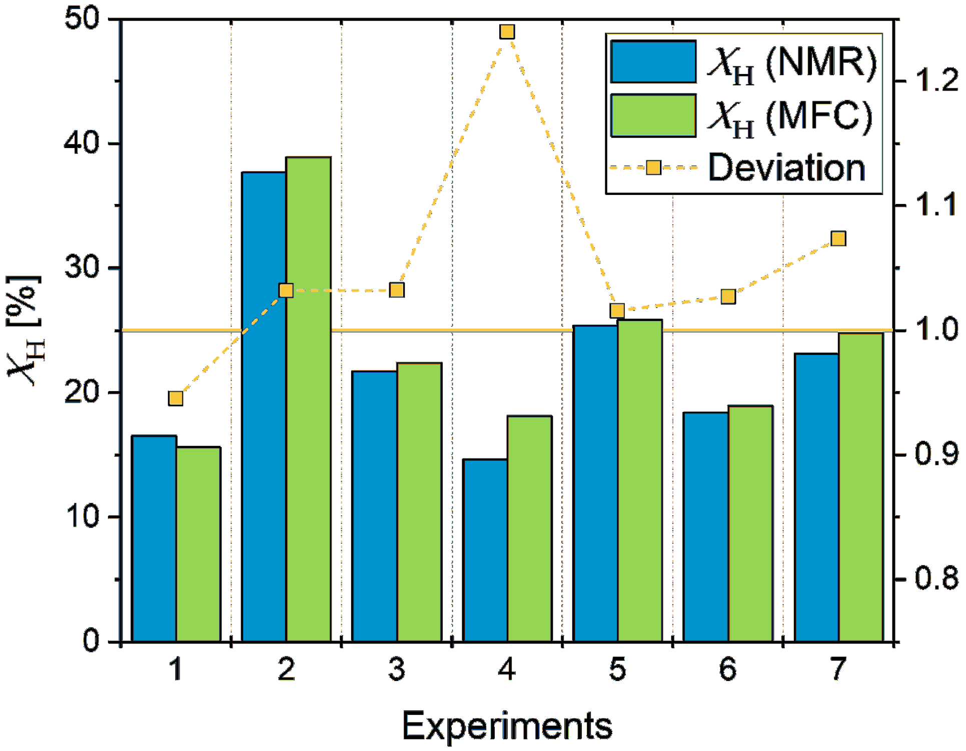


Figure 5.11.: NMR and MFC results for ctBR, and the average deviation as MFC/NMR

tivation and result in a lower turnover number (TON) and lower X_H. Lower catalyst concentration increases the TON and allows for hydrogenation of 1,4-double bonds at the cost of a lower turnover frequency (TOF). Glass transition temperature and dynamic viscosity are primarily influenced by the 1,2-double bond content and only by a low extend by hydrogenation. NMR and MFC results did show good agreement and allowed the MFC data to be used for online determination of X_H.

Since the scope of this work is primarily on the products of hydrogenation, more experiments are needed to fully understand and characterize this complex catalytic system.

6. Results and Discussion - Polyurethanes

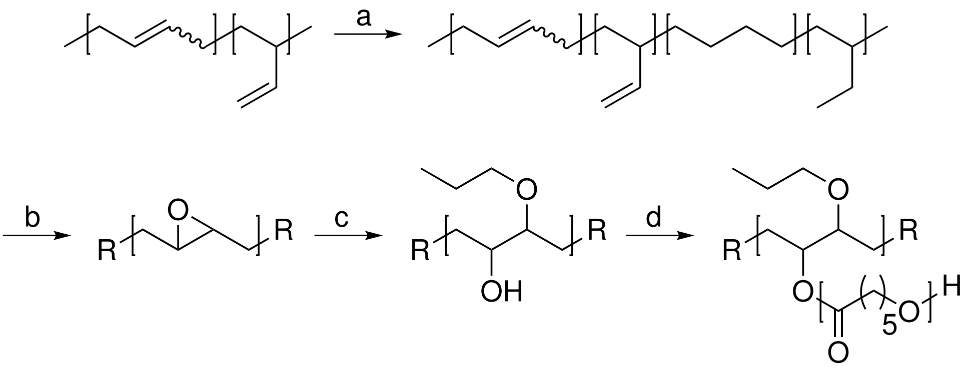
Polyurethanes (PU) may be prepared from a polyol, an isocyanate and further additives such as chain extender. The following sections describe the preparation and analysis of a polybutadiene rubber-based polyol followed by the examination of material properties of the casted PU elastomer.

6.1. Preparation of polyols

The catalytic system used for hydrogenation allows to hydrogenate polybutadiene rubbers at moderate temperatures and a reasonable time of hydrogenation. Unfortunately the Lewis acidity of the catalyst inhibits the hydrogenation of materials containing OH-groups. The OH-groups react with the catalyst to alkoxides and deactivate the catalyst. To prevent this hydroxyl groups were introduced after partial hydrogenation in a multiple step reaction procedure (Scheme 6.1).

Partial hydrogenated polybutadiene rubber (a) was activated by epoxidation (b). The epoxides were opened by acid catalysis (c) and the hydroxide groups were capped with ϵ-caprolactone (d). Starting material consisted of the already analyzed polybutadiene rubber vBR and ctBR. vBR has a 1,2-*vinyl* double bond content of 60% and an uncorrected molecular weight of M_n = 1500 g/mol. ctBR has a lower 1,2-*vinyl* double bond content of 20% and a higher molecular weight of M_n = 3000 g/mol.

Three HBR with different degrees of hydrogenation were prepared for each BR. X_H was determined through online mass flow analysis. The degree of hydrogenation was 0%, 20% and 40%. The HBR were named accordingly (vBR$_0$, vBR$_{20}$, vBR$_{40}$ and ctBR$_0$, ctBR$_{20}$, ctBR$_{40}$. These six prepared HBR were



Scheme 6.1: Preparation of secondary, ϵ-CL capped, polybutadiene-based polyols, in four steps: hydrogenation, epoxidation, epoxide opening and capping with polycaprolactone.

used as starting materials for the introduction of hydroxyl groups.

6.1.1. Results for HBR Epoxidation

Activation of the residual double bonds in the partial hydrogenated polybutadienes was achieved by epoxidation.

Epoxidation was performed in an easy to handle, two phase catalytic system.[83,85,87,88,93] The double bonds were epoxidized by peroxidic acid. Peroxidic acid was formed *in situ* by continuously added hydrogen peroxide. This reduced the amount of acid and that suppressed the occurrence of side reactions. Side reactions can occur at high acid concentrations and long reaction times.[83,93] If the hydrogen peroxide addition is kept at a constant rate, epoxidation becomes primarily dependent on epoxidation time.[119] Since different rubbers with different X_H and molecular weight were used, solubility becomes a factor. Higher molecular weight and higher degree of hydrogenation reduced the solubility in the toluene/water suspension. To achieve comparable functionalities (F_n) for all epoxidized polybutadiene rubber (EBR) epoxidation times were adjusted accordingly.

$$F_\mathrm{n} = \frac{EPv \cdot M_\mathrm{n}}{100} = \frac{OHv \cdot M_\mathrm{n}}{M_\mathrm{KOH} \cdot 100} \tag{6.1}$$

Functionality describes the amount of functional groups per polymer chain (equation 6.1) and was calculated from the epoxide value (EPv) or the hydroxide value (OHv) and the number average molecular weight (M_n).

Analysis of ^{1}H-NMR data gave the degree of epoxidation (X_{EP}) of the remaining double bonds (Table 6.1). The true epoxide content (Y_{EP}) per chain was calculated considering the degree of hydrogenation. The three prepared vEBR showed similar values and averaged around 30%. Only vEBR$_{40}$ showed a slightly higher value of Y_{EP} = 36.7%. ctEBRs had a molecular weight (M_{n}) almost twice as high as vEBR. Values of Y_{EP} had to be about half of Y_{EP} for vEBR to achieve similar functionality. The three prepared polymers had calculated values of about 15%.

In PU chemistry, the functionality of a polyol is usually determined volumetrically. Therefor epoxide values (*EPv*s) were determined for each EBR. vEBR$_0$and vEBR$_{20}$showed similar *EPv* and F_{n}. Although vEBR$_{40}$had the highest Y_{EP} a lower epoxide value was found. The lower value of *EPv* for high X_H indicates solubility issues either during the epoxidation or during the determination of *EPv*. *EPv* determination was repeated at lower concentrations but did not result in significant increase of *EPv*. Solvation dependency during epoxidation is assumed.

EPv for ctEBR were very similar and averaged about 0.16 mol/100 g. Similar to the results for vEBR a decreased *EPv* was observed for ctEBR with X_H = 40%. Higher molecular weight of ctEBR$_{40}$compensated lower *EPv* and give a similar functionality. Besides the significantly lower F_{n} of vEBR$_{40}$of 4.1 all other EBR had values around 5.5.

Table 6.1.: Results of epoxidation for vEPBx and ctEPBx with x = degree of hydrogenation. Degree of epoxidation (X_{EP}) was calculated from NMR, epoxide value (*EPv*) was determined by titration.

	X_{EP} [%]	Y_{EP} [%]	*EPv* [mol/100g]	M_{n} [kg/mol]	F_{n} [-]
vEBR$_0$	29.7	29.7	0.293	1.8	5.3
vEBR$_{20}$	39.5	31.6	0.283	1.9	5.5
vEBR$_{40}$	61.2	36.7	0.212	1.9	4.1
ctEBR$_0$	13.1	13.1	0.160	3.5	5.6
ctEBR$_{20}$	19.1	15.2	0.171	3.5	6.0
ctEBR$_{40}$	26.0	15.6	0.143	3.8	5.5

In conclusion, the goal to prepare EBRs with similar functionality was successful. Only for $vEBR_{40}$ a lower functionality was achieved.

6.1.2. Epoxide opening

Polyols (OHBR) were prepared from EBR by opening epoxides. They were opened in an acid catalyzed reaction in 1-propanol. The degree of epoxide opening (X_{OH}) (equation 6.2) was determined by volumetric determination of the hydroxide value (*OHv*). It was calculated from the quotient of *OHv* and theoretical OHv) (*th.OHV*) (equation 6.3).

$$\mathrm{X}_{\mathrm{OH}} = \frac{OHv}{th.OHv} \tag{6.2}$$

$$th.OHv = \frac{EPv \cdot M_{\mathrm{KOH}} \cdot 1000}{100 + EPv \cdot M_{\mathrm{1\text{-}PrOH}}} \tag{6.3}$$

Opening conditions were based on previous opening results of similar polyepoxides. Epoxide opening was expected to give polyols at almost quantitative conversion. Surprisingly results of epoxide opening (Table 6.2) did not show a quantitative conversion. Even an increase in reaction time was not able to significantly increase X_{OH}. Epoxide conversion was about 75% for vOHBRs and above 80% for ctOHBRs. Only $ctOHBR_0$ showed a satisfying *OHv*.

The non-quantitative conversion lowers the functionality of the prepared OHBR. Functionalities of OHBR show a similar trend compared to EBR. $vOHBR_0$ and $vOHBR_{20}$ have similar functionalities and $vOHBR_{40}$ has the lowest F_{n}. At this point the higher molecular weight of ctOHBRs seems to become an influence. ctOHBR with a higher X_H show lower values for *OHv* and F_{n}.

Table 6.2.: Results for the epoxide opening to give vOHPBx and ctOHPBx with x = degree of hydrogenation.

	th.OHV	*OHv*	X_{OH}	F_n
	[mg KOH/g]		[%]	[-]
vOHBR$_0$	140	104	74.6	3.9
vOHBR$_{20}$	136	103	75.9	4.1
vOHBR$_{40}$	106	82.3	78.0	3.2
ctOHBR$_0$	81.9	76.1	92.9	5.4
ctOHBR$_{20}$	87.0	72.3	83.1	4.9
ctOHBR$_{40}$	73.9	61.0	82.6	3.8

The reduced functionality of OHBR caused by the low conversion rated of the epoxide is still high enough to form PU elastomers. Elastomers can be prepared for functionalities above 2. This could be achieved for all OHBRs.

6.1.3. Results for OHBR ϵ-Caprolactone Capping

Polyols were capped by ϵ-caprolactone (ϵ-CL) to improve miscibility with isocyanates. The ϵ-CL cap improves the hydrophilicity of the polyols and therefor raises the compatibility to the isocyanate. Compatibility of polyol and isocyanate is crucial for a well dispersed PU elastomer and good elastomeric properties. All OHBRs were capped in a ring opening polymerization (ROP) catalyzed by $Ti(O{-}n{-}Bu)_4$.

NMR analysis of the prepared CapBR did show full conversion of the added ϵ-CL. Compared to the previous modifications capping had a significant influence on the molecular weight of the polyols. *OHv* (Table 6.3) were reduced as the molecular weight increased while the calculated functionality was maintained. Differences in acsohv were confirmed by molecular weight distribution (MWD) of the different CapBR (Figure 6.1). Higher *OHv* lead to a shift of the MWD to higher molecular weights. With the capping the last modification was complete, and the polyols were used for casting PU elastomers.

Table 6.3.: Results for the capping with ϵ-caprolactone for vCapPBx and ctCapPBx with x = degree of hydrogenation.

	OHv [mg KOH/g]	F_n [-]
vCapBR$_0$	70.4	3.6
vCapBR$_{20}$	70.0	3.7
vCapBR$_{40}$	65.0	2.9
ctCapBR$_0$	63.0	5.6
ctCapBR$_{20}$	60.2	5.1
ctCapBR$_{40}$	57.8	4.1

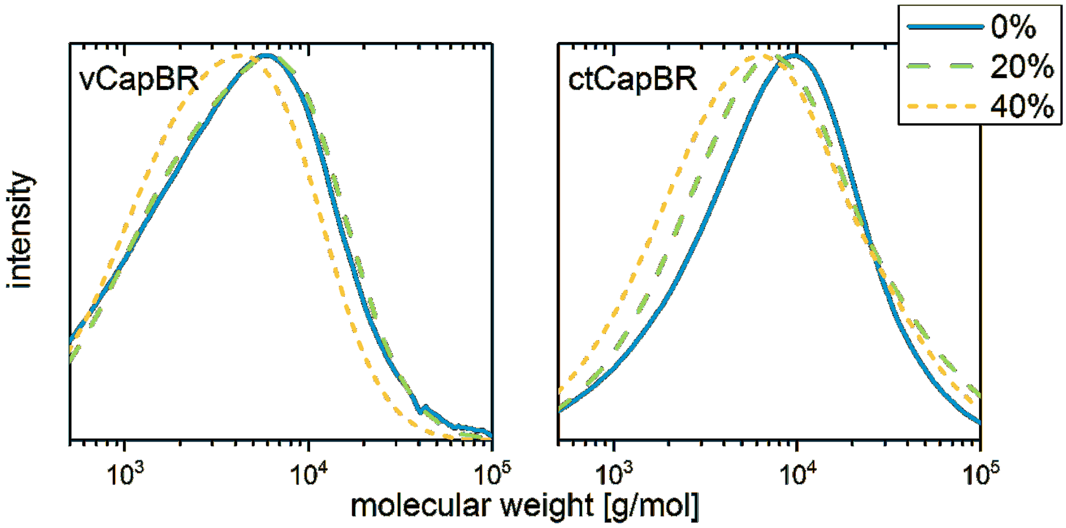


Figure 6.1.: Molecular weights distribution (MWD) for the polycaprolactone capped polyols vCapPB and ctCapPB with degrees of hydrogenation of 0% (blue), 20% (green) and 40% (orange).

6.1.4. Thermal properties of CapBRs

The diffent modifications during the preparation of polyols influenced the thermal behavior of the polymer. Thermal behavior was analyzed by determining dynamic shear viscosity (η), glass transition temperature (T_g) and melting temperature (T_m). Hydrogenation of vBR and ctBR had only little influence on viscosity and T_g and was discussed in a previous section (5.4).
Epoxidation of vEBR and ctEBR increased η (Figure 6.3) by an increased stiffness of the polymer chains. The higher rotational barrier reduces the ability of a polymer chain to flow through a polymer melt and increases the required energy. This effect is even higher for high 1,2-double bonds containing polymers

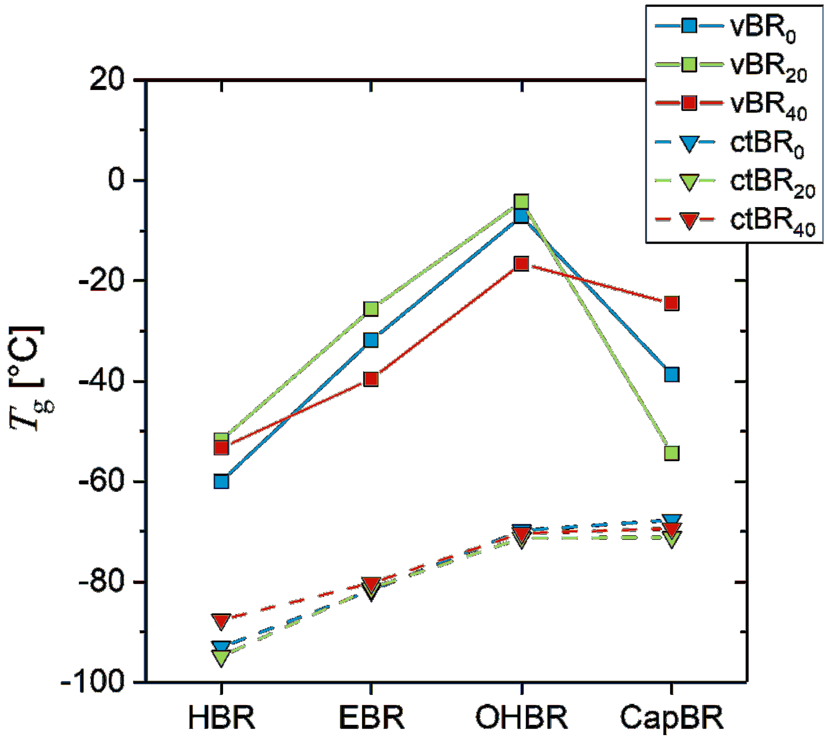


Figure 6.2.: Glass transition temperature (T_g) for different modifications (HBR: hydrogenated polybutadiene; EBR: epoxidized BR; OHBR: polyol; CapBR: polycaprolactone capped polyol) of partial hydrogenated vPBx and ctPBx with x = degree of hydrogenation.

such as vBR. This explains the steeper increase seen for vEBR. The increase in viscosity for higher degrees of hydrogenation can also be explained by an increase in chain stiffness.

Acidic opening of epoxides in 1-propanol creates hydroxyl groups and propyl ether in the polymer backbone. Hydroxyl groups were able to form hydrogen bonds. This further increased η for both vOHBR and ctOHBR. Similar functionality of ctOHBR resulted in similar viscosities. vOHBR showed a different behavior. vOHBR_0 and vOHBR_{20} had a similar functionality but showed different values for η. The degree of hydrogenation seems to have a significant impact on viscosity. The lower functionality of vOHBR_{40} reduces the viscosity. Preparation of block copolymers by capping OHBRs with ϵ-CL exceeded the previously discussed influences on η. The polar caprolactone increases the amount of hydrogen bonding and further increases the viscosity of ctCapBR. Similar behavior was observed for glass transition temperature. T_g was pri-

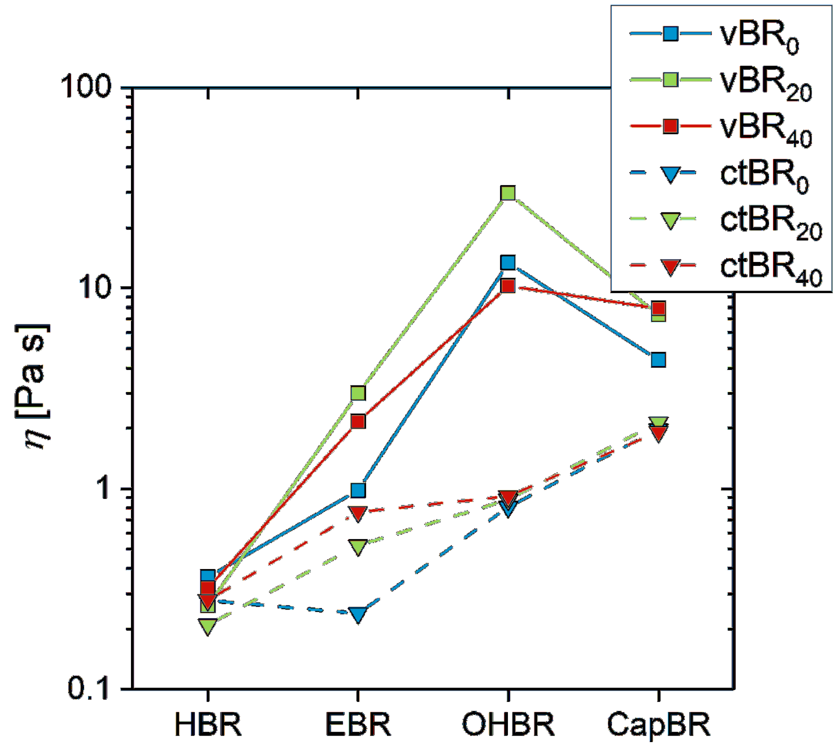


Figure 6.3.: Dynamic shear viscosity (η) for different modifications (HBR: hydrogenated polybutadiene; EBR: epoxidized BR; OHBR: polyol; CapBR: polycaprolactone capped polyol) of partial hydrogenated vPBx and ctPBx with x = degree of hydrogenation.

marily influenced by 1,2-double bond content and interaction with the modifications.

Thermal analysis by DSC showed no melting points (T_m) for HBR, EBR and OHBR. For CapBR different melting points and enthalpy of fusion (ΔH_m) were detected (Figure 6.4). Melting points were between 40 - 50 °C and enthalpy of fusion was between 10 - 30 J/g. Copolymers containing polycaprolactone (PCL) usually showed melting points of PCL in the observed range.[73,120,121] Higher melting temperatures usually are related to a higher lattice energy of higher ordered and larger crystals. Enthalpy of fusion is usually related to the crystallinity of a polymer and is higher for amounts of crystallites. Non-hydrogenated ctCapBR had the highest and vCapBR$_0$ the lowest values for T_m and ΔH_m of all six polyols. The hydrogenated polyols showed similar crystallinity depending on X_H but differences in T_m. Hydrogenated polyols with X_H = 40% showed a lowered crystallinity compared to polyols with

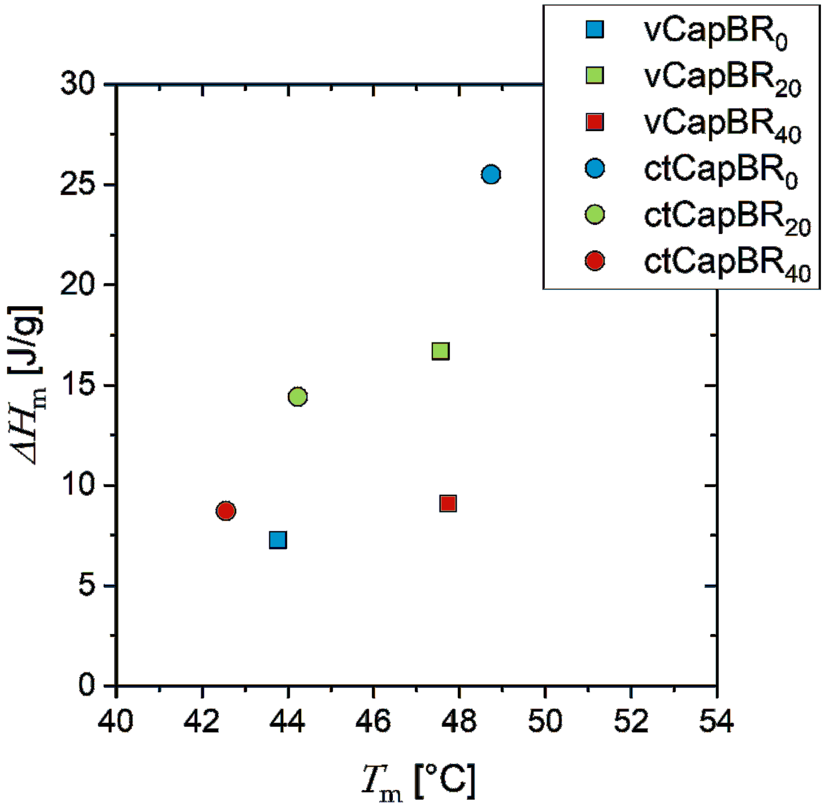


Figure 6.4.: Melting points (T_m) and enthalpy of fusion (ΔH_m).

$X_H = 20\%$.

In conclusion hydrogenation has a positive impact regarding the size and amount of the crystallites for vCapBR and a negative impact for ctCapBR.

6.1.5. Miscibility of Polyol and Isocyanate

Miscibility of CapBRs and isocyanate was tested by mixing both at room temperature (Figure 6.5). Compatible mixtures form one phase and appear transparent. Incompatibilities create phase separation and render the mixture non-transparent.

Mixtures for $X_H = 0\%$ and 20% were transparent and fully miscible for vCapBR and ctCapBR. Mixtures for $X_H = 40\%$ were transparent right after mixing but turned non-transparent after a short while. Heating them to 60 °C turned them transparent again.

All prepared polyols are fully miscible with the isocyanates at 60 °C.

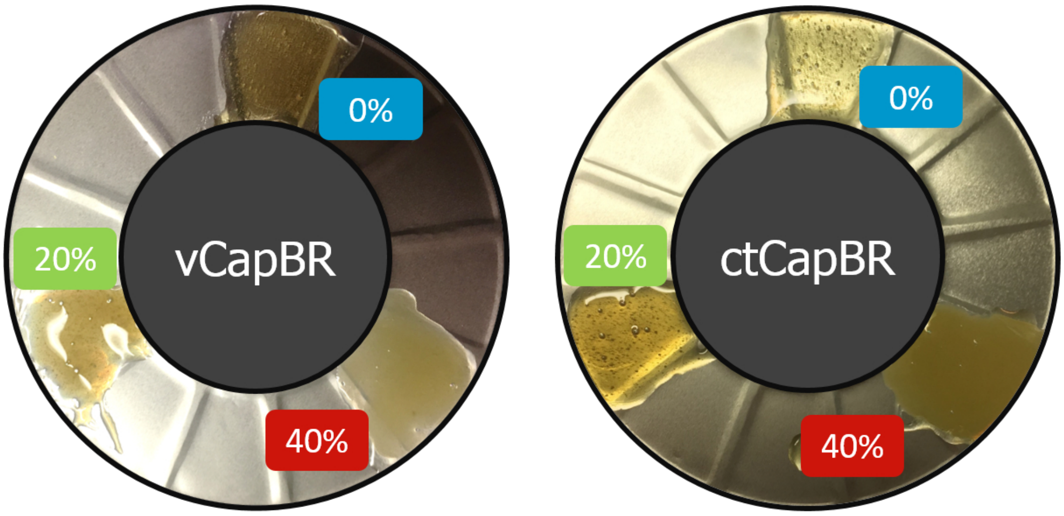


Figure 6.5.: Miscibility test of vCapBR and ctCapBR with isocyanate.

6.2. Polyurethanes

All six polyols were successfully prepared and analyzed. They were used to cast Polyurethane (PU) elastomer films by mixing them with isocyanate at a ratio of NCO/OH = 1.0. For all prepared films the opening time was approximately 3 minutes.

After deforming and curing, PU films were analyzed regarding the conversion of the isocyanates as well as thermal and mechanical properties. Isocyanate conversion was determined by the characteristic stretch band for isocyanates at 2250 cm – 1. IR spectra of all prepared PU films did not feature any stretch band in the isocyanate region. Full conversion of the isocyanates was therefore assumed.

6.2.1. Thermal analysis

Casted PU elastomers show melting points between 165 - 175 °C (Figure 6.6). These T_m were caused by a crystalline phase containing former isocyanate and chain extender. Melting points of polyols were not observed. ΔH_m was between 0.5 - 1.5 J/g which was low. Melting points of vPUs and ctPUs decreased for higher degree of hydrogenation while enthalpy of fusion increased. For vPU_0 no distinct melting point was observable. This implies fewer but higher ordered crystallin phases for lower degree of hydrogenation.

6.2.2. Analysis of the Phase Separation in PUs by AFM

PU consists of two major phases, the crystalline hard phase and amorphous soft phase. Sometimes meso phases are observed. Composition and ratio of these phases determine material properties to a certain extend. Phase separation of the prepared films was analyzed by atomic force microscopy (AFM) (Figure 6.7). Phases differ in their rigidity. The hard phase has a higher rigidity. Differences in rigidity were determined by phase contrast. Phases with higher rigidity show as brighter areas.

AFM image of vPU_0 showed diagonal lines caused by the cutting procedure and some dots scattered throughout the surface. It had few small bright areas, which could be interpreted as areas of higher rigidity. More likely, some of the

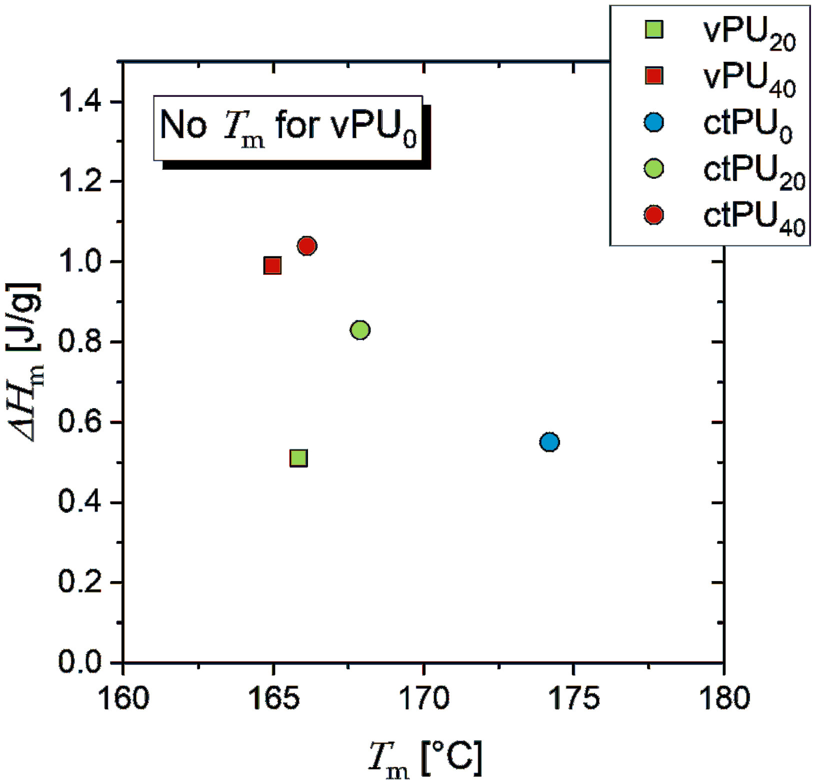


Figure 6.6.: Peaks of the melting points (T_m) and the corresponding enthalpy of fusion (ΔH_m) of casted PU.

dots were more prominent then others and therefor appeared in brighter color. These dots seemed to be some kind of structure which was different from the rest of the polymer. However, no distinct hard phases were visible and the polymer appeared one phasic with respect to rigidity. vPU_{20} had a rugged but homogeneous surface. Aside from some height differences no differences in color were visible. The PU appeared as one phase. The surface of vPU_{40} was a little different. It was also rugged but showed some inhomogeneities throughout the surface. It appeared that bright and dark areas were close together which can be intepretated as some kind of lamellar system. However it remained unclear if this was caused by a phase separation process or by the sample preparation.

Overall no typical phase separation was observed in the vPUs. One phase PUs are usually observed for polyols with hydrogen bonding acceptors.[121] The low molecular weight of the polyol backbone and the relatively large ϵ-CL cap increased the compatibility of the polyol to such an extent, that it formed

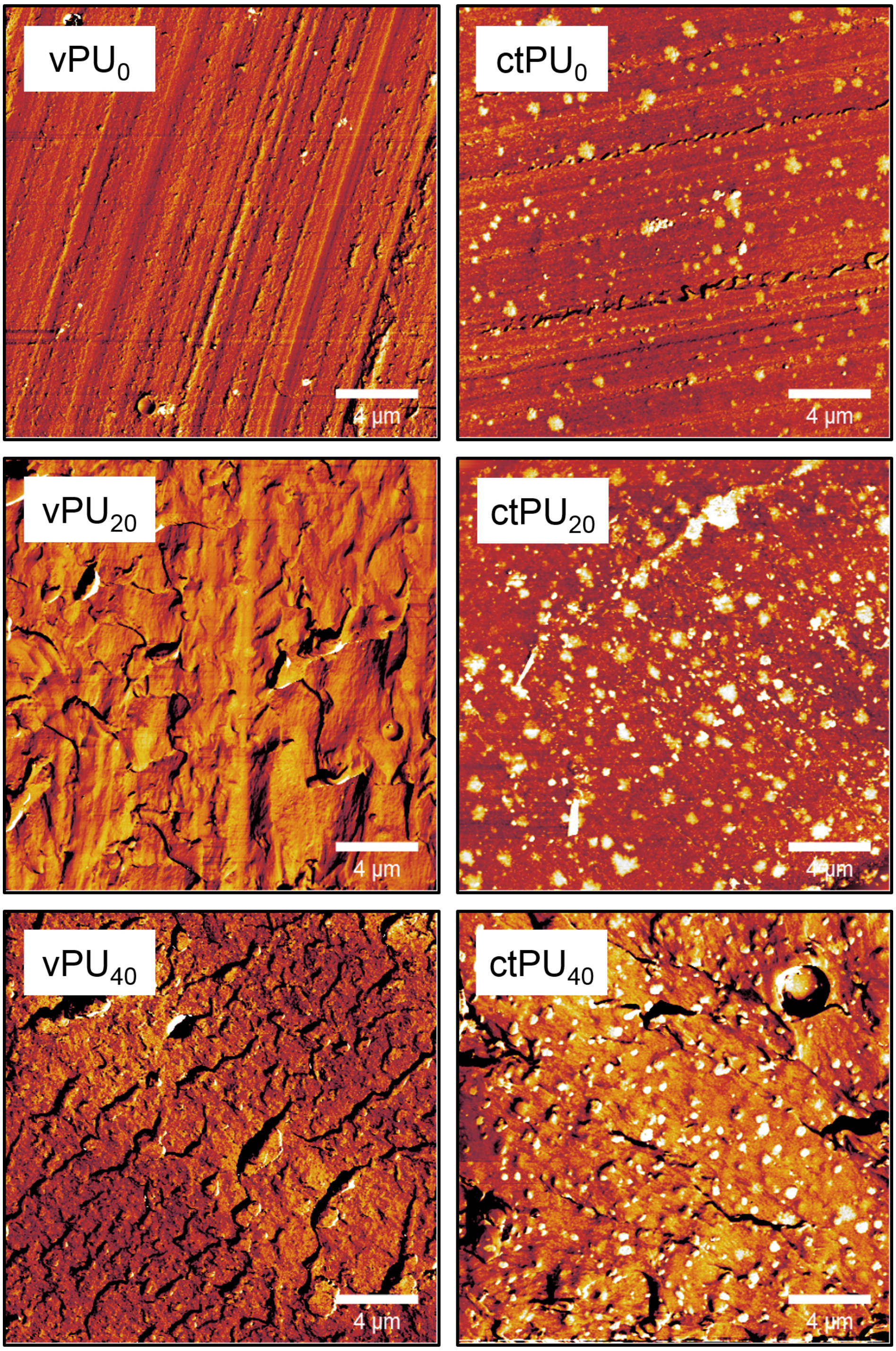


Figure 6.7.: Atomic force microscopy (AFM) images of the prepared PU films vPUx and ctPUx with x = degree of hydrogenation of the used polyol.

a stable homogeneous phase with isocyanate. The stability was enhanced by hydrogen bonding between the PCL cap of the polyol and the urethane group. Polyols in ctPUs had a higher molecular weight and PU elastomers showed typical phase separation in the AFM images. ctPU$_0$ hhad bright areas scattered around the surface. These areas were more rigid. Those hard phases contain the former isocyanate and chain extender. Phases had the typical fringed shape and diameters between 0.2 - 1 μm.The surface showed some artefacts caused by the cutting procedure. The AFM image of ctPU$_{20}$ showed a higher number of bright spots compared to ctPU$_0$. Hard phases were larger and only few small phases were visible. Diameter of these phases were between 1 μm and up to 1.5 μm on average. ctPU$_{40}$ showed uniform hard phases with an average diameter of about 0.5 μm. Compared to the other two ctPUs the hard phases appeared rounder. This is observed in the case of early phase separation between isocyanate, chain extender and polyol and reveals increased incompatibilities between the components. The reason for this incompatibility is assumed to be a reduced polarity of the polyol caused by higher degree of hydrogenation.

ctPUs showed phase separation to a more rigid hard phase and a less rigid soft phase. A degree of hydrogenation of X_H = 40% reduced polarity of the polyol to such an extent, that phase separation is too early to form the usual fringed shape.

In conclusion a degree of hydrogenation of X_H = 40% had a significant influence on the phase separation during elastomer casting. vPUs formed a more homogenous phase and ctPUs formed the typical phase separated hard and soft phases. The differences were primarily caused by differences in molecular weight and was in accordance with literature.[121]

6.2.3. Shore A Hardness of Casted PUs

Shore A hardness is highly influenced by the amount and morphology of the hard phase. In polybutadiene rubber-based PUs hydrogen bonding usually occurs between urethane groups and therefor in the hard phase. When the PU only consist of one phase hydrogen bonding can occur throughout the polymer. This increased the Shore A hardness (Figure 6.8). Difference in Shore A hardness between vPU and ctPU were caused by the differences in phase separation and higher amounts of hard domains in vPU.

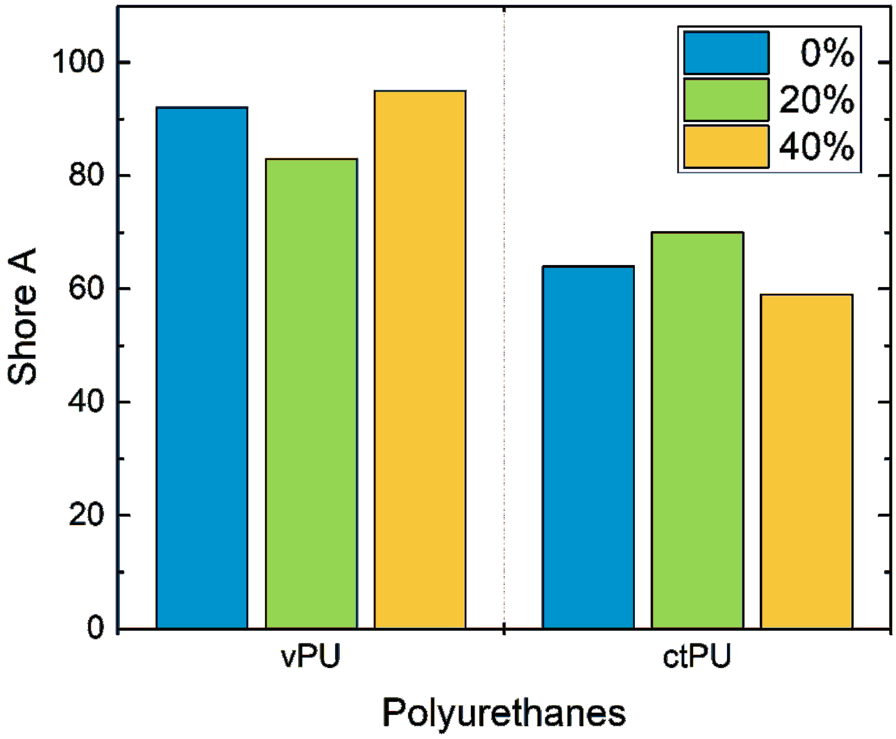


Figure 6.8.: Shore A hardness of vPUs and ctPUs with degrees of hydrogenation of 0% (blue), 20% (green) and 40% (orange).

6.2.4. Water Uptake of Casted PUs

Hydrophilicity of PU was determined by water uptake (Figure 6.9). Polybutadiene-based PUs usually show low amounts of water uptake on account of their low polarity. Capping with PCL increased polarity of the polyol and the resulting PU. The prepared PUs did show water uptakes between 0.5w% - 1.5w%. Differences can be explained by the functionality of the polyols. High functionality increased the amount of PCL in the PU.

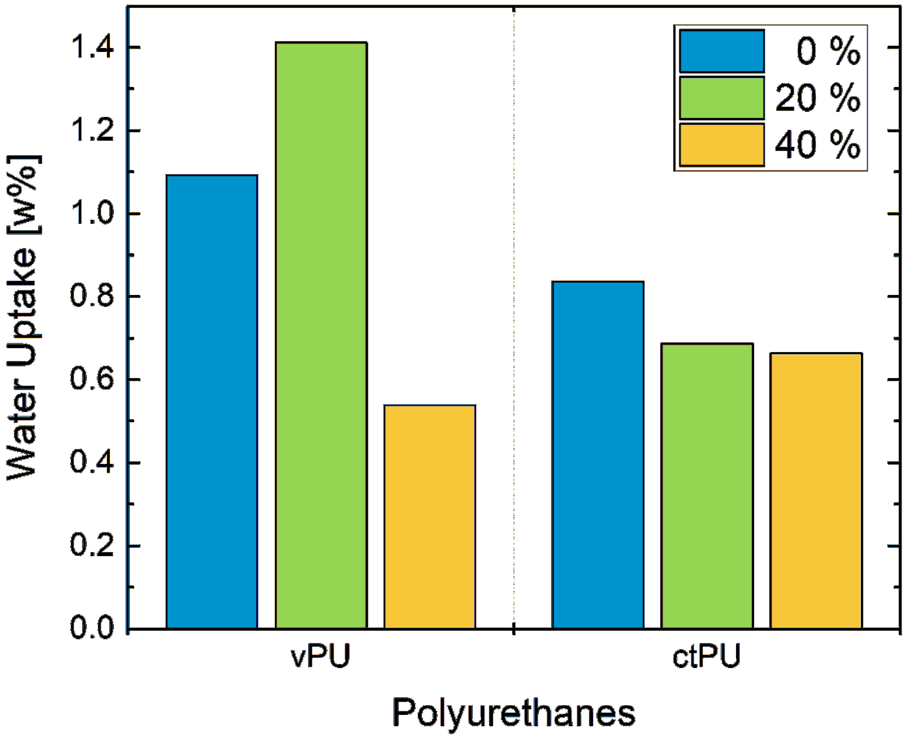


Figure 6.9.: Water swelling results for the polyurethane films vPU and ctPU with degrees of hydrogenation of 0% (blue), 20% (green) and 40% (orange). The water uptake is between 0.5 and 1.5w%.

6.2.5. Mechanical Properties of Casted PUs

Mechanical properties of a PU result from a combination of material characteristics such as the arrangement of the different phases and their intrinsic properties.[122] Relevant mechanical properties are for example Young's modulus, stress at break and elongation at break. These properties are usually determined by tensile testing (Figure 6.10). Typical values for PU elastomers are 5 - 20 MPa Young's modulus, 3 - 20 MPa stress at break and 100 - 900% elongation at break.[71,72,75] These values are typical for polyols containing primary OH-groups. The structure of the prepared polyols reduces the overall mechanical performance of the PUs. Chain ends containing no further hydroxyl-groups are not part of the network and cannot contribute to the mechanical properties of the polyurethanes.

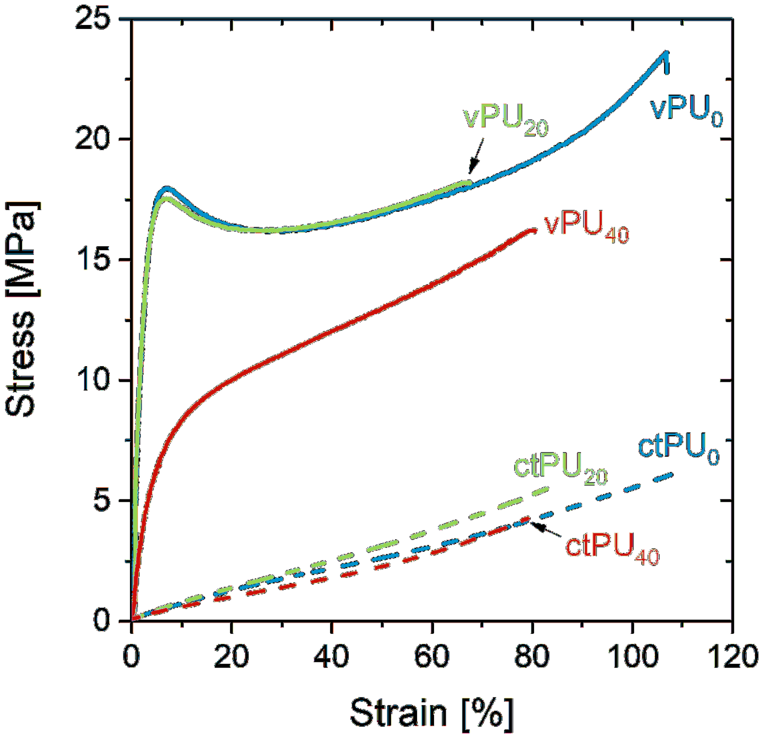


Figure 6.10.: Strain-stress curves for the prepared PU films vPUx and ctPUx with x = degree of hydrogenation of the used polyol.

Basically, two different shapes of stress-strain curves were received. ctPUs showed typical behavior of an elastomer with poor performance. Curves had an almost linear increase with small differences in slope and maximum elongation. vPUs showed the shape of thermoplastic polymer with an initial steep increase up to a yield point for vPU_0 and vPU_{20}. For vPU_{40} no yield point was observed. vPU_0 and vPU_{20} showed stress softening after yield point.

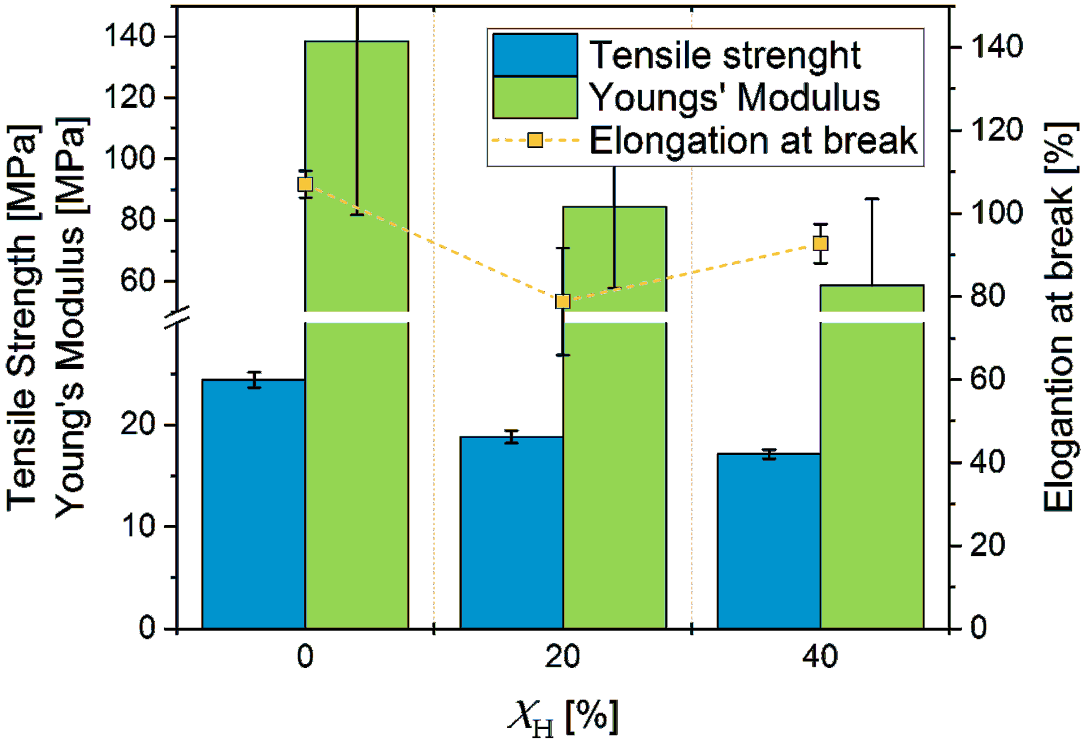


Figure 6.11.: Mechanical testing data for vPUs with degrees of hydrogenation of 0%, 20% and 40%.

vPUs showed relatively high values for Young's modulus of up to 138 MPa for vPU_0 (Figure 6.11). The modulus decreased for higher degree of hydrogenation to 59 MPa for vPU_{40}. A similar trend was observed for tensile strength at break. Elongation at break was slightly decreased for hydrogenated vPUs and had overall poor values compared to literature data.[71,72,75]

ctPUs showed values between 4 - 6 MPa for Young's modulus and tensile strength (Figure 6.12). No significant influence of degree of hydrogenation was observed. Elongation at break was at similar values as for vPUs below 100%.

Overall performance of prepared PUs is lower than the literature data. The

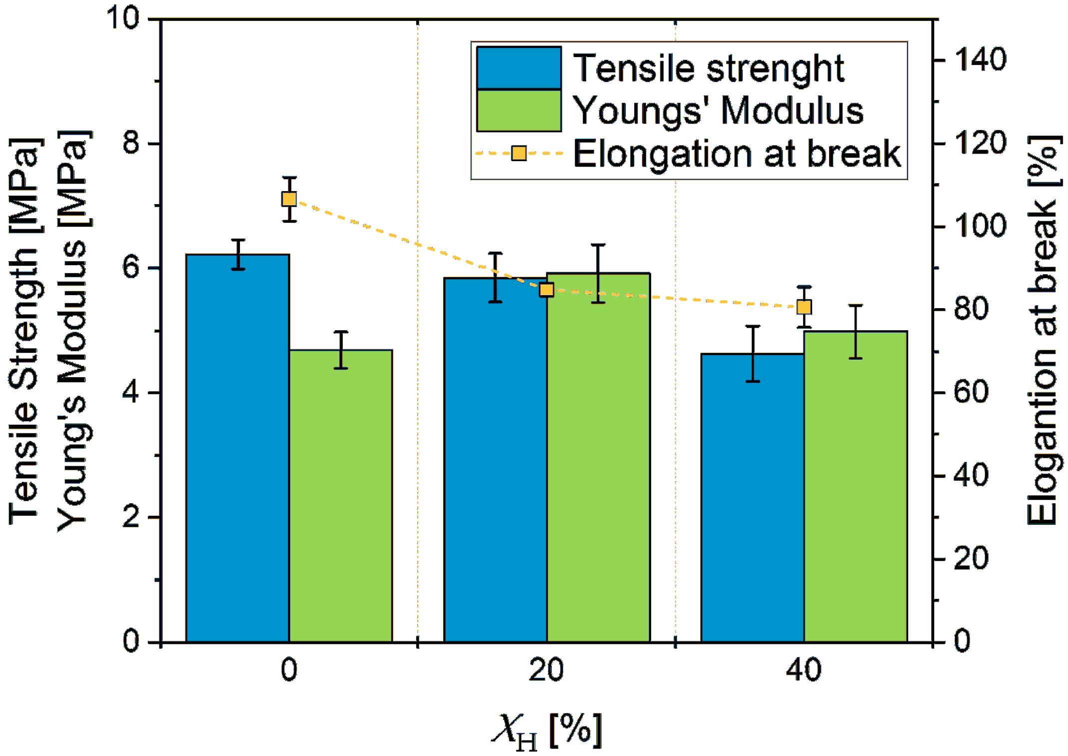


Figure 6.12.: Mechanical testing data for ctPUs with degrees of hydrogenation of 0%, 20% and 40%.

secondary structure of the polyols has a significant influence on the mechanical performance. The degree of hydrogenation had no significant influence on ctPUs and little influence on vPUs. Mechanical properties were primarily dominated by molecular weight and size of the PCL cap.

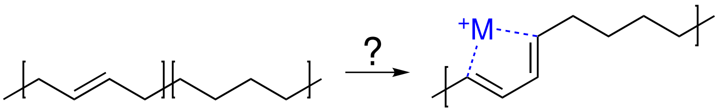
6.3. Conclusion and Outlook

The preparation of partly hydrogenated polyols was achieved in a four-step procedure with vBR and ctBR as starting materials. After hydrogenation, epoxides were introduced in the polymer backbone. After the acidic opening of the epoxides they were capped by ϵ-CL for an improved compatibility between polyol and isocyanate. The casted PU films were analyzed regarding their phase separation by AFM and their mechanical properties were determined by tensile testing. In the AFM images the vPUs appeared as one phase while ctPUs did show phase separation. The phase separation of ctPU was dependent on the degree of hydrogenation. Caused by the secondary nature of the hydroxy groups the PUs did show poor mechanical performance. However, the monophasic vPUs did show stress-strain-curves similar to a thermoplastic material. ctPUs curves had an elastomeric shape with elongation at break values around 100%.

Further evaluations can include variation of the hard segment content, cap-length or the degree of hydrogenation. For improved mechanical properties a catalytic system tolerating an OH-groups has to be used.

7. Results and Discussion - Bromination

Polybutadienes have a high content of double bonds, which makes them interesting for ion coordination. Such non-aqueous solvents are described for the solvation of different alkali metals. One example is the polybutadiene acrylonitrile copolymer (PBAN) that allows the coordination of Li^+ ions.[123]



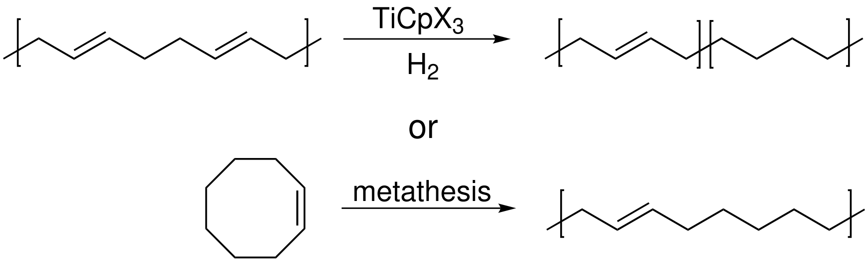
Scheme 7.1: Coordination of metal ions by a diene system prepared from HBR.

A higher number of coordinative groups usually improve the ability to coordinate ions. Bromination and dehydrobromination was used to modify double bonds of a partial hydrogenated polybutadiene. A dien structure would allow to coordinate different metal ions (Scheme 7.1). Partial hydrogenation allows to modify the number of coordinative sites in the polymer.

7.1. Starting Material for Bromination

Properties and reactivity of partially hydrogenated polybutadienes depend on different factors such as degree of hydrogenation, double bond composition and tacticity. HBR prepared by titanium catalyst are amorphous polymers with randomly distributed double bonds (Scheme 7.2).

A highly order structure regarding the hydrogenated/non-hydrogenated double bonds HBRs can be achieved by co-polymerization or metathesis. One ex-



Scheme 7.2: Preparation of different "partial hydrogenated" polybutadiene rubber.

ample is polyoctenamer prepared from cyclooctane in a ring opening metathesis. The structure is equals a hydrogenated polybutadiene rubber with every second double bond hydrogenated (X_H = 50%).

As a first iteration a high ordered polymer is desirable. A high ordered structure simplifies polymer analysis and helps to formulate structure property relationships. The used octenamer had a molecular weight of about M_n = 60.000 g/mol and a *cis*-content of about 20%.

7.2. Bromination of HBR

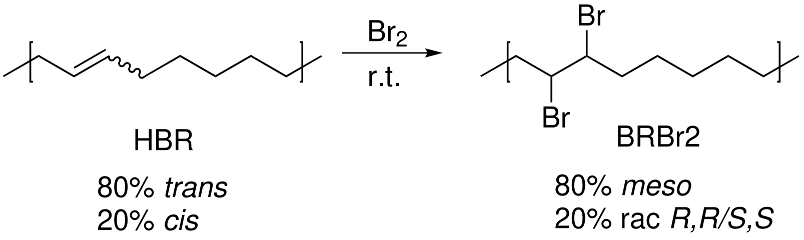
Bromination of double bonds is a well-known procedure in organic chemistry. It is performed with bromine in chloroalkanes such as dichloromethane (DCM). The reaction is exothermic and either needs low temperatures or enough solvent to take up the heat developed. Low reaction temperatures are usually not suitable for polymers due to solvation limitations. Therefor reactions were performed at room temperature. The first evaluated solvent was THF that ensures a full solvation of HBR. A conversion of up to 93% was reached after addition of 1 equivalent Br_2 (Table 7.1).

Table 7.1.: Experimental conditions of bromination and NMR integrals.

#	Br_2 [equiv]	solvent	integrals NMR HBR	BRBr2
1	1	THF	0.07	0.93
2	1	DCM	0.03	0.97
3	1.02	DCM	–	1

Conversion was lowered by side-products formed from reactions of THF with bromine. It was not easy to fully remove these side-products from the brominated product (BRBr2). This disqualified THF as solvent and removed the possibility for a one-pot approach including bromination and dehydrobromination.

Chloroalkanes are used for bromination because they are inert at given reaction conditions. Conversion was increased to 97% with DCM as solvent. Full conversion was achieved by increasing the amount of bromine to 1.05 equivalents. Non-conversed bromine was separated by precipitating the product in MeOH.

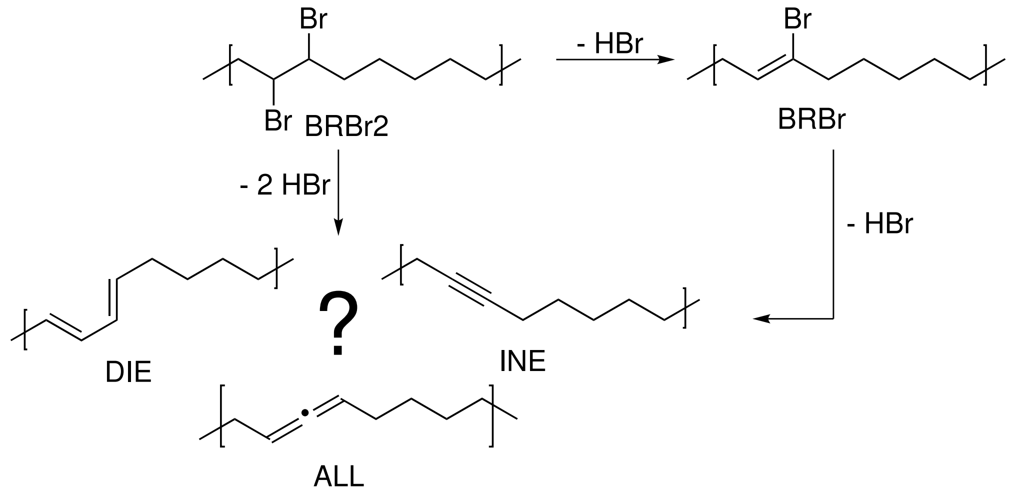


Scheme 7.3: Bromination of HBR.

The brominated product (BRBr2) consisted of about 80% *meso* and 20% *R,R* and *S,S* enantiomer (Scheme 7.3). The reaction followed an *anti*-addition pathway where the bromonium ion locked the conformation of the double bond (see subsection 3.4.1) and maintained the ratio in the diastereomers. Former trans-double bonds gave the *meso* product and former *cis*-double bonds the racemic *R,R*- and *S,S*-enantiomers.

7.3. Monodehydrobromination of BRBr2

Dehydrobromination of BRBr2 can lead to three obvious products (Scheme 7.4). This can either be a diene (DIE), an alkyne (INE) or an allene (ALL). During dehydrobromination the bromines were removed one by one. Depending on the product of the first dehydrobromination the products of the second dehydrobromination is predetermined.



Scheme 7.4: Dehydrobromination of BRBr2 can result in three different products. These are either the diene (DIE), the alkyne (INE) or the allene (ALL).

The diene is formed by elimination of both bromines with one of the allylic protons. If a vinylic proton is used for the first dehydrobromination the diene cannot be the product of the second dehydrobromination. Results will show the product of the first dehydrobromination was vinyl bromide. This implies the product of the second dehydrobromination is either the alkyne or the allene.

First suitable conditions for the first dehydrobromination had to be found. Dehydrobromination of BRBr2 had two limitations that had to be addressed. First the solvent had to be suitable for both base and the polymer. Second the basicity had to be high enough for deprotonation. Also, it had to be ensured that no solvent DCM was left in BRBr2, as chloroalkanes tend to form carbenes at basic conditions.

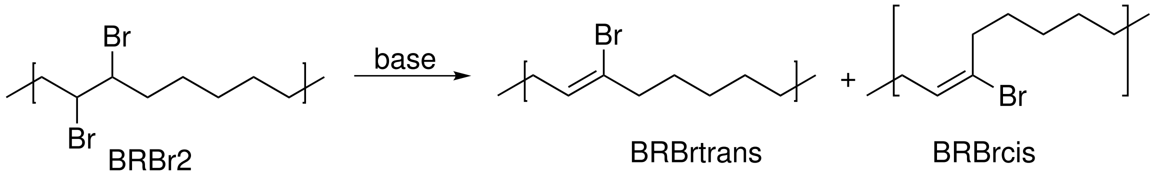
First evaluation with KOH as base and ethanol as solvent did not show any conversion after 18 h at reflux (Table 7.2). While KOH was fully soluble in ethanol, the solubility of BRBr2 was low. THF as solvent increased solubility of BRBr2 but reduced solubility of inorganic bases. Soluble bases were amines such as DABCO or Et_3N. Unfortunately, their base strength was too low for deprotonation even after 6 h of reflux. Potassium tert-butoxide had a higher base strength and a medium solubility in THF. At a 2.5-fold excess of *t*-BuOK per bromine the first dehydrobromination was complete within one minute at room temperature.

Product analysis revealed presences of two different entities. These were

Table 7.2.: Experimental conditions of mono-Dehydrobromination and NMR integrals.

#	base/solvent	base [equiv]	time	integrals NMR BRBr2	BRBrtrans	BRBrcis
1	KOH/EtOH	1	18 h	1	–	–
2	DABCO/THF	0.6	5 h	1	–	–
3	Et_3N/THF	1.25	6 h	1	–	–
4	*t*-BuOK/THF	1.25	1 min[a]	–	0.84	0.16
5		1.25[b]	1 min[a]	–	1	–

[a] r.t., [b] 0.025 equiv 18-crown-6



Scheme 7.5: First dehydrobromination forms *trans* and *cis* poly vinylbromide.

identified by NMR as *trans*- (BRBrtrans) and *cis*-product (BRBrcis) of the vinyl bromide (Scheme 7.5). A closer look at the stereo chemistry of the dehydrobromination showed the elimination was not following an E2 mechanism. A E2 mechanism would result in an inversion of the former double bonds configuration from *trans* to *cis* and vice versa. As the main product was BRBrtrans dehydrobromination must follow a E1cb mechanism. The α substituents have increased acidity in the order Br > Cl > F and favor deprotonation of the vinylic proton.[80] After deprotonation a stabilized carbanion was formed. The bond was free to rotate to the thermodynamically favored *trans*-configuration.

Adding a crown ether such as 18-crown-6 to the reaction mixture shifted the equilibrium to 100% *trans*-product. The ether further stabilized the transition state and allowed for full conversion to the thermodynamic product. Carbanion-stabilizing substituents control the regiochemistry of E1cb eliminations by favoring deprotonation at the most acidic carbon.[80]

7.4. Didehydrobromination of BRBr2

The second dehydrobromination was achieved at the same concentration of *t*-BuOK in THF (Table 7.3). After 16 h at room temperature about 6% of a product was received. The product was identified by 2D-NMR as poly allene (ALL).

Table 7.3.: Experimental conditions of di-Dehydrobromination and NMR integrals.

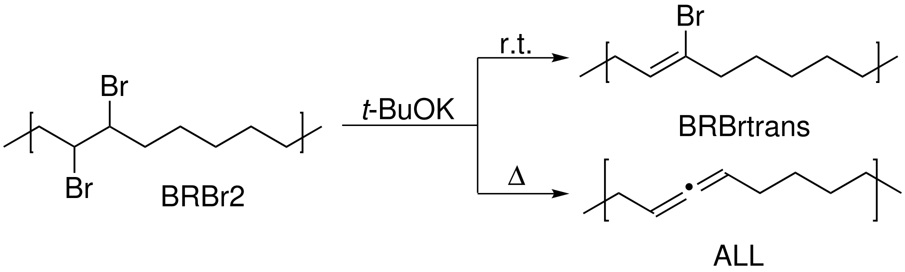
#	base/solvent	base [equiv]	time	integrals NMR BRBr	ALL
1	*t*-BuOK/THF	1.25	16 h[a]	0.94	0.06
2		1.25	4.5 h	0.63	0.37
3		1.25[b]	4 h	0.22	0.78
4		1.25[b]	8 h	0.19	0.81

[a]r.t., [b]0.025 equiv 18-crown-6

Yield of poly allene was increased to about 37% after 4.5 h by increasing the reaction temperature to reflux. The crown ether 18-crown-6 was able to increase the yield to 78% after 4 h at reflux. A further increase of reaction time increased degradation of the polymer and could only increase the yield to 81%. Higher base concentration and higher reaction time lead to degraded, insoluble polymers. Small soluble parts that could be extracted from the polymer contained 100% poly allene.

In conclusion, the mono- and di-dehydrobromianted product were prepared from BRBr2 by changing the reaction temperature. The product of the mono-dehydrobromination was poly vinyl bromide. The didehydrobromination gave poly allene (Scheme 7.6).

The different products were identified by NMR according to their characteristic shifts (Figure 7.1).



Scheme 7.6: Dehydrobromination is performed with *t*-BuOk as base. Dependening on the reaction temperature either poly vinylbromide or poly allene is formed.

7.5. Structure-Property Relationships by Rheology

Viscoelastic properties are a key factor regarding the processability and usage of a polymer. Modifications such as bromination have a significant impact on these properties. All prepared polymers were analyzed regarding their viscoelastic properties at different temperatures. Time-temperature sweeps (TTS) showed a decrease in the moduli for increased temperatures (Figure 7.2a). Shifting the TTS curves horizontally by the shift factor a_T (Figure 7.2b) allows to generate master curves for a specific reference temperature. For this work the reference temperature was set to 100 °C.

Influence of the modifications on the viscoelastic properties can be well observed from the master curves (Figure 7.3). The brominated polymer BRBr2 showed a significant increase regarding complex shear viscosity (η^*)storage modulus (G') and loss modulus (G''). Bromination of the polymer increased the chain rigidity. A more rigid polymer chain uses smaller volume and has more interaction points with other polymer chains. This increases the interactions between segments and higher moduli were observed. At the crossover point (*cp*) of G' and G'' the viscous parts start to dominate over the elastic parts (Table 7.4).

The shift factors (a_T) obtained from TTS allow the determination of the flow activation energy (E_a) by a Arrhenius approach (equation 7.1), with the R, the reference temperature (T_0) and the actual temperature (T).

$$ln(a_\mathrm{T}) = \frac{E_\mathrm{a}}{R} \cdot \left(\frac{1}{T} - \frac{1}{T_0}\right) \tag{7.1}$$

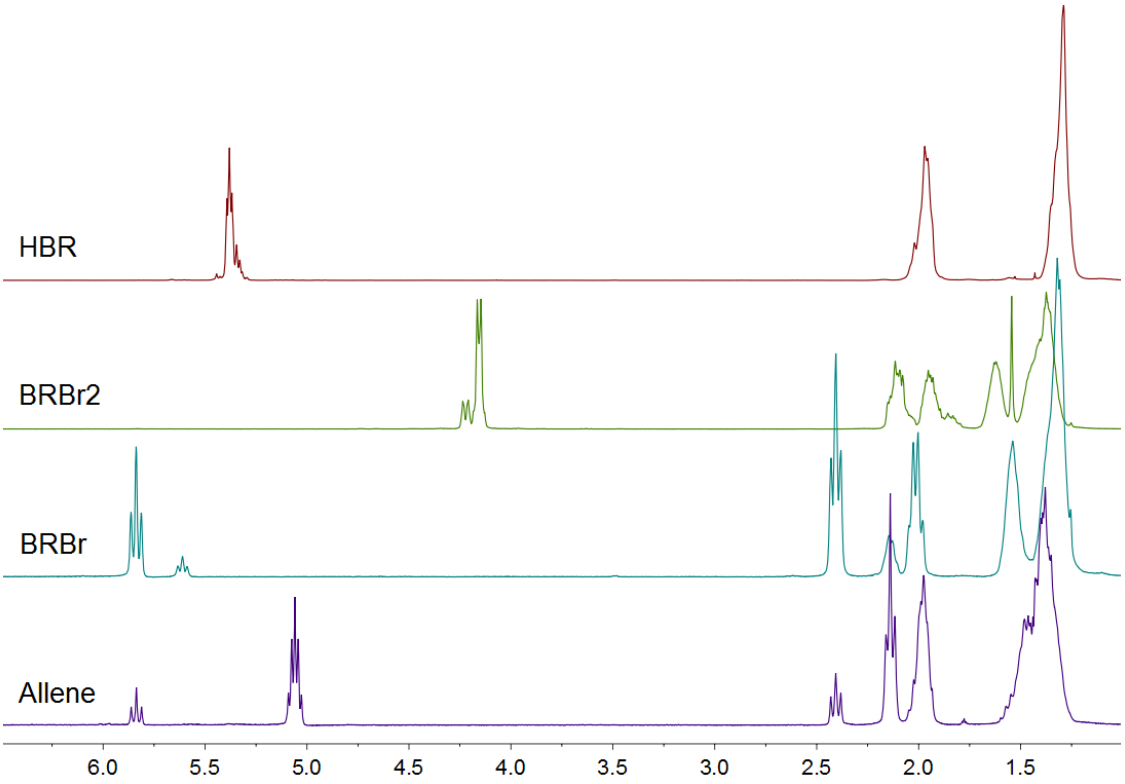


Figure 7.1.: ^{1}H-NMR spectra for the different products of the bromination.

This approach is valid for a temperature range of:

$$T > T_g + 100\ K$$

The glass transition temperature (T_g) of each prepared polymer was determined to verify if E_a can be determined for a TTS temperature range of 80 - 140 °C by the Arrhenius approach (Table 7.4).

Glass transition temperatures of polybutadienes and analogous polymers usually are in a range of -60 to -100 °C. As seen for the polyols (see subsection 6.1.4), modifications significantly increased T_g. The same was observed for the brominated product BRBr2 which had the highest glass transition temperature. Interestingly T_g of the poly vinyl bromide was similar to theT_g of HBR and poly allene. Prerequisite for the Arrhenius approach was fulfilled and a_T was determined following this approach.

The calculated flow activation energies are in line with the previous observations. BRBr2 had the highest E_a caused by high chain rigidity. Rigid chains have a lower degree of freedom and therefore more energy is needed. Compared to BRBr2 the degree of freedom was higher for BRBr and the poly allene.

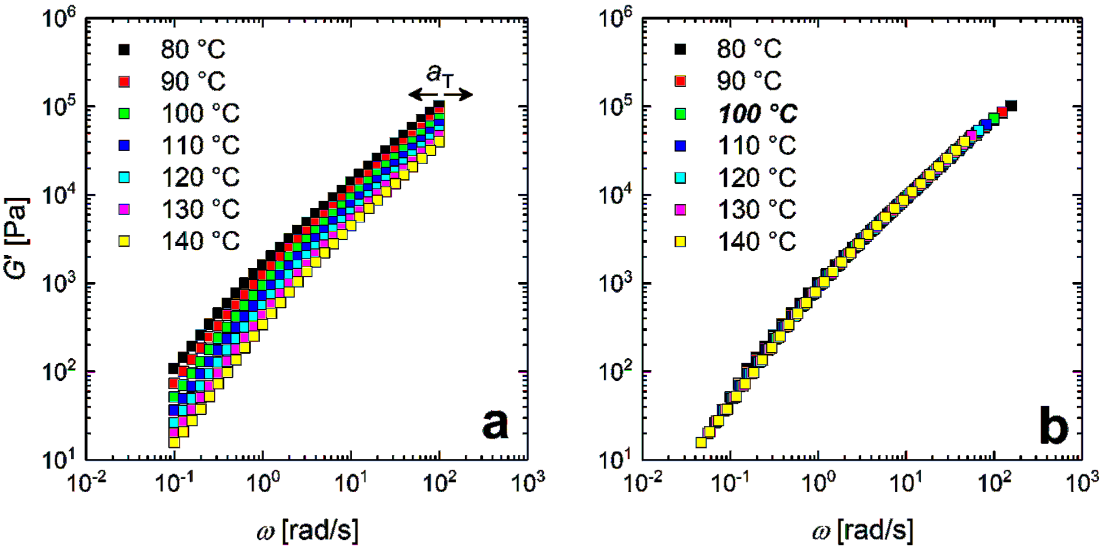


Figure 7.2.: TTS curves are shifted by the shift factor a_T to create a master curve at a specific temperature (100 °C).

As a result, E_a was about 25 kJ/mol lower for BRBr2. HBR had the lowest flow activation energy of about 27 kJ/mol.

The viscosity of a polymer describes the behavior of a polymer under stress. The shape of a viscosity curve for a pseudo plastic polymer can be described by Carreau-Yasuda-model[124] (equation 7.2).

$$\eta = \eta_0 \cdot [1 + (\lambda_0 \cdot \dot{\gamma})^b]^{n \cdot b^{-1}} \tag{7.2}$$

The dynamic shear viscosity (η) is dependent on the shear rate ($\dot{\gamma}$), the zero-shear viscosity (η_0), the relaxation time of the slowest chain λ_0 and the slope of the non-Newtonian region n. The parameter b describes the transition region between the zero-shear-rate and non-Newtonian region.

The η^* and angular frequency (ω) from the TTS analysis can be transformed to the dynamic shear viscosity (η) and shear rate ($\dot{\gamma}$) by the Cox-Merz-rule[125] (7.3).

$$|\eta^*|(\omega) \cong \eta(\dot{\gamma})_{\omega=\gamma} \tag{7.3}$$

The Carreau-Yasuda-model was fitted to the dynamic viscosity (Figure 7.4) with the parameters in Table 7.4. Besides the curve for BRBr2 all fits had an $R^2 > 0.998$.

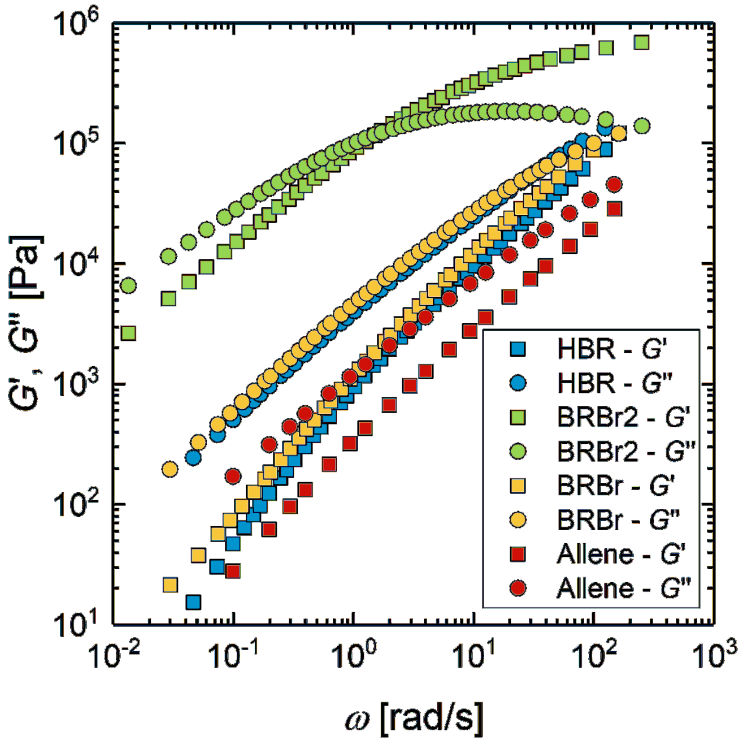


Figure 7.3.: Storage modulus (G') and loss modulus (G'') of the mastercurves for the starting material HBR and the bromination products BRBr2, BRBr and Allene.

Effects of chain rigidity could be observed for the zero-shear viscosity (η_0). η_0 of the more rigid BRBr2 was 3 decades higher. While differences in λ_0 for HBR, BRBr and ALL were fairly small, vinyl bromide had a slightly higher and ALL a slightly lower η_0 compared to the starting material HBR.

As mentioned before, when shear is applied and the polymer can give a viscous answer the chains get aligned and slide along each other. After removing the shear stress the polymer chains try to go back to the thermodynamically most stable form, which is the coil. The time needed for this relaxation is the relaxation time λ_0. It is influenced by the chain mobility and is higher for a less mobile more rigid polymer. As expected BRBr2 had the highest relaxation time. Surprisingly BRBr had a very low λ_0 which indicated a high chain mobility. The polymers without bromine showed similar relaxation times.

Non-Newtonian regions describe the polymer in the state of flowing. The observed shear-thinning was caused by the applied shear-rates above the critical shear-rate. The critical shear-rate $\dot{\gamma}_c$ is described as:

Table 7.4.: Rheological and thermal data for the starting material HBR and the bromination products BRBr2, BRBr and Allene.

polymer	T_g [°C]	E_a [kJ/mol]	cp [rad/s]	η_0 [kPa.s]	λ_0 [s]	$\dot{\gamma}_c$ [s^{-1}]	n [-]	b [-]
HBR	-74.76	26.69	–	5.62	0.780	1.28	-0.31	0.59
BRBr2	-13.10	63.08	1.59	1040	1.92	0.520	-0.82	0.32
BRBr	-61.74	38.35	162	7.63	0.0206	48.5	-0.74	0.35
ALL	-69.44	37.95	–	2.58	0.454	2.20	-0.40	0.31

Crossover point (cp), zero-shear viscosity (η_0), relaxation time of the slowest chain (λ_0), critical shear-rate ($\dot{\gamma}_c$), slope of the non-NEWTONIAN region (n), transition parameter (b).

$$\dot{\gamma}_c = [\lambda_0]^{-1} \tag{7.4}$$

Above $\dot{\gamma}_c$ the chains were not fully relaxed and less force is needed to align the chains. The slope n of the non-Newtonian region describes the shear thinning effect on the polymer. A lower value indicates higher orientation of the chains and less ability to return to the thermodynamic favored state. The order from a steep slope to a less steep slope was BRBr2 > BRBr > ALL > HBR. It follows the previously described chain stiffness of the polymers. For b similar values for the modified polymers of about 0.3 were observed. The starting material HBR has a higher value of 0.59. In conclusion the viscoelastic properties are dominated by bromination. Bromination increases rotational barrier and chain stiffness of a polymer. At low shearing rates this increases the viscosity. At high shear rates above $\dot{\gamma}_c$ significant shear thinning is observed for brominated polymers.

7.6. Conclusion and Outlook

Bromination and dehydrobromination was performed in a two-step procedure with an octenamer (HBR) as starting material. Bromination of HBR gave the di-brominated compound BRBr2. Depending on the reaction temperature either the mono- or didehydrobrominated product was achieved. At room temperature the mono-product was received. Addition of the crown

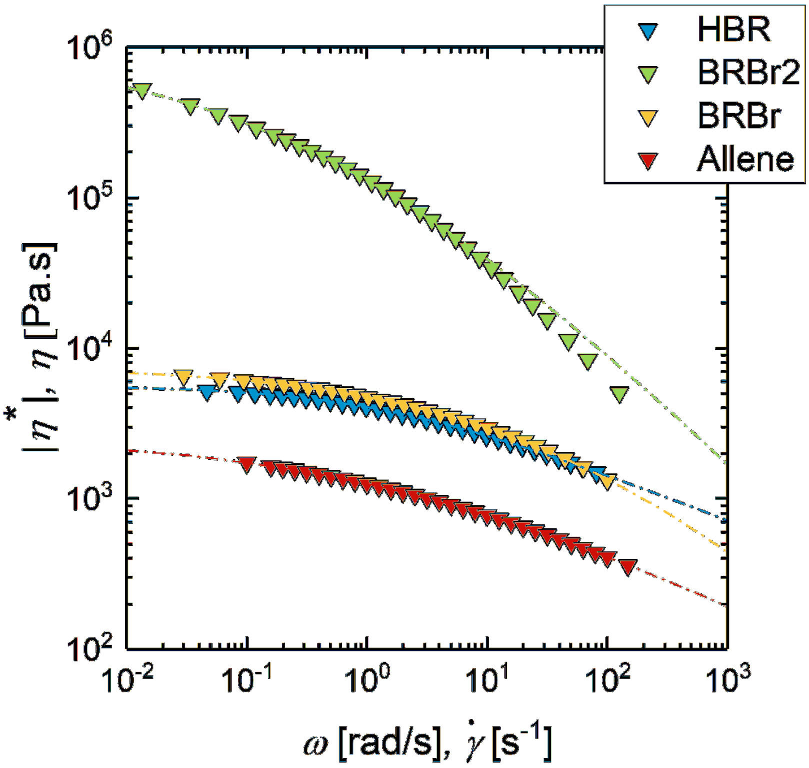


Figure 7.4.: Dynamic viscosity of the mastercurves for the starting material HBR and the bromination products BRBr2, BRBr and Allene. These are fitted by the CARREAU-YASUDA-model (dashed lines).

ether 18-crown-6 allowed the preparation of 100% *trans*-vinyl bromide. At reflux an allene was formed as the product of the didehydrobromination. All compounds were characterized by rheology regarding their viscoelastic properties and the viscosity curves were fitted by the CARREAU-YASUDA-model. The viscoelastic properties were dominated by bromination caused by a higher rotational barrier and chain stiffness. At low shearing rates this increases the viscosity. At high shear rates above $\dot{\gamma}_c$ significant shear thinning is observed for brominated polymers.

The polyvinyl bromide is a promising compound for further functionalization of the polymer backbone. The reaction steps allow for a variety of different polymers containing double bonds.

8. Experimental

8.1. Analytical methods and analyses

The following sections describe the different analytical methods and analyses used is this thesis.

8.1.1. Atomic Force Microscopy (AFM)

The atomic force microscopy (AFM) is a microscopy that allows to determine the topography as well as the local rigidity of a sample. It measures differences in the van der Waals interaction between the sample and the cantilever and has a resolution of about 1 Å.
Polymer samples for AFM measurements were cut from polymer films by a Leica Ultracut UCT with a glass knife. The samples had a diameter of 1 - 10 μm. Due to the amorphic structures the polymer films were cooled in a Cryo-system by RMC Boeckeler prior to cutting. AFM images (20 x 20 μm) were recorded in intermittent contact mode in air on a JPK Instruments NanoWizard 2 AFM. From the images a 10 x 10 μm was selected for a better visualization.

8.1.2. Differential Scanning Calorimetry (DSC)

The glass transition temperature (T_g) was determined by differential scanning calorimetry (DSC) with a DSC 821 (Mettler Toledo) calorimeter. DSC measures the differences in the amount of heat required to increase the temperature of a sample and a reference as a function of temperature. 5 - 15 mg samples in open aluminum pans were heated and cooled in two cycles. The lowest temperature was 120 °C for all sample. The highest temperature was 120 °C for hydrogenated and modified BR and 220 °C for the PU elastomers. First cycle rate was at 20 K/min, second cycle rate at 10 K/min. Second cycle data was used for evaluation. Glass transition temperature was determined as a middle point between the tangential baseline before and after transition.

8.1.3. Density determination

The density of the modified BR was measured gravimetrically at a given volume. The used pycnometer had a volume of 25 mL. The density was calculated from the weight difference of the water filled pycnometer with and without polymer at a constant temperature. The sample size was about 1 g.

8.1.4. Gel Permeation Chromatography (GPC)

Molecular weight distributions were determined by gel permeation chromatography (GPC). Polymer solutions are separated on a column by their hydrodynamic volume. Polymers with a lower hydrodynamic volume more often get stuck in in the column pores and therefor elute later. The samples were prepared in different solvent such as chloroform, THF and trichlorobenzen at a concentration of about 3 g/mL. They were calibrated with a polystyrene standard. Molecular weights (M_n , M_w) were calculated with Chromatographica. For the calculation masses only greater 500 Da were used due to methodical limitations.

Molecular weights are usually corrected to match the weights obtained from other analytics and to describe the real molecular weight. The correction factor of polybutadiene rubber is 0.6 for a polystyrene standard. The modifications described in this thesis tend to influnce the obtained molecular weight by GPC. Unless further noted no correction of the calculated molecular weights was applied.

8.1.5. Infrared Spectroscopy (IR)

Infrared spectra of polymer films were measured on a Smart iTR by Thermo Fisher Scientific at a resolution of 2 cm^{-1}. They were analyzed by OMNIC (Thermo Fisher Scientific).

8.1.6. Thermal Mass flow analysis

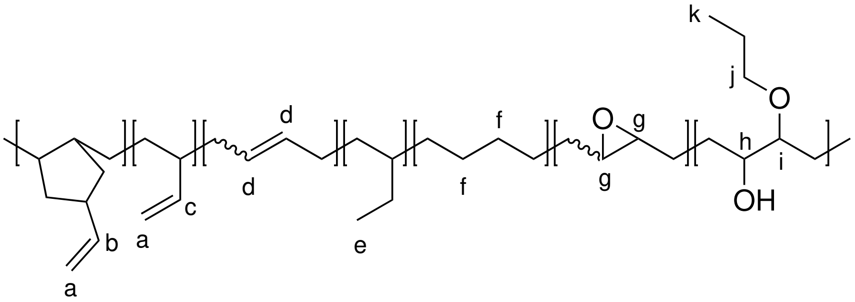
The consumption of hydrogen was monitored with a thermal mass flow controller by BROOKS INSTRUMENT and the software ProfiSignal by Delphin Technology.

8.1.7. Miscibility determination

The miscibility of the prepared polyols and isocyanates was determined by mixing both for several minutes at room temperature. When a homogeneous phase has formed both components are miscible. Heterogeneous mixtures were heated to 60 °C and checked again for heterogeneity.

8.1.8. Nuclear Magnetic Resonance (NMR)

For the identification of the prepared compounds ^{1}H and ^{13}C nuclear magnetic resonance (NMR) experiments were used. The ^{1}H-NMR spectra were recorded on a Bruker Fourier 300 MHz. For further identification the 2D experiments H,H-COSY, HSQC and HMBC were used. ^{13}C experiments were recorded as ATP experiments. 2D and ^{13}C experiments were recorded on a Bruker AVANCE 400 MHz spectrometer. NMR samples were prepared at a concentration of 5 - 20 mg/0.8 mL $CDCl_3$ or THF$-d_8$. Spectra were analyzed with MestReNova by Mestrelab Research S.L. and were referenced to the solvent peak.



Scheme 8.1: Corresponding NMR integrals for hydrogenation and polyol preparation. (see Figure 8.1)

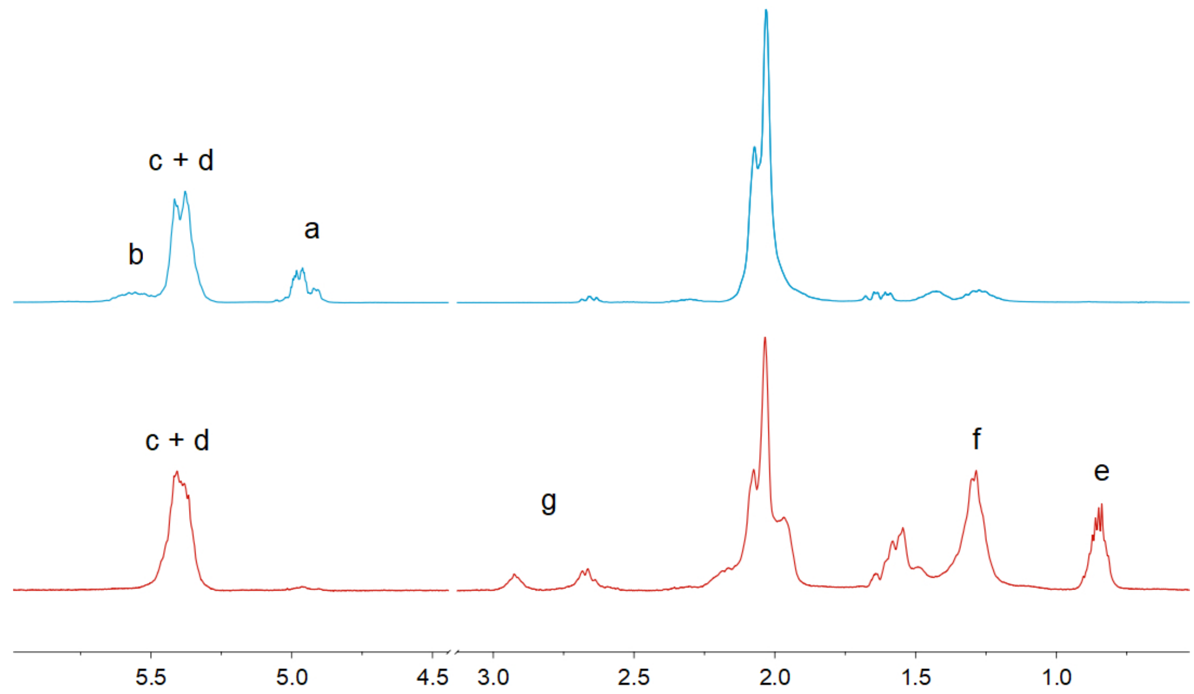


Figure 8.1.: Integrals for hydrogenation and epoxidation. (see Scheme 8.1)

Degree of hydrogenation

For the calculation of the degree of hydrogenation (X_H) two different methods were used. The low molecular weight polybutadienes suffer from peak overlapping between 1.5 - 0.7 ppm where the peaks e and f for the hydrogenated parts are located. To encounter this, the spectra were calibrated on a fixed amount of 1,4-dioxane. With this the spectra before and after hydrogenation can be compared. This allows the calculation of the conversion with respect to the current sample mass (m_s) and the mass of the non-hydrogenated sample (m_0). To encounter errors from 1,4-dioxane dosing double determinations were conducted.

Polybutadienes with 1,2-double bonds show peak overlapping. The calculated Integrals for the 1,2-*cyclic* (I_{cy}), 1,2-*vinyl* (I_v) and 1,4-*cis*/*trans* (I_{ct}) double bonds were calculated according to equations 8.1 to 8.3.

$$I_{cy} = 2 \cdot \int_b \tag{8.1}$$

$$I_v = \int_a - I_{cy} \tag{8.2}$$

$$I_{\mathrm{ct}} = \int_{\mathrm{c+d}} - 0.5 \cdot I_{\mathrm{v}} \tag{8.3}$$

The calculated Integrals I_{x} (x = cy, v or ct) are normed on two protons and are calculated from the integrals of the NMR peaks $\int_{\mathrm{a}}$, $\int_{\mathrm{b}}$, $\int_{\mathrm{c}}$ and $\int_{\mathrm{d}}$ (in accordance to Scheme 8.1 and Figure 8.1).

The double bond content $Y_{0,\mathrm{x}}$ for each individual double bond in the non-hydrogenated polybutadienes is calculated from the calculated Integrals $I_{0,\mathrm{x}}$ (equation 8.4).

$$Y_{0,\mathrm{x}} = \frac{I_{0,\mathrm{x}}}{\sum(I_{0,\mathrm{x}})} \cdot \frac{m_0}{m_{\mathrm{s}}} \tag{8.4}$$

The specific degree of hydrogenation X_{x} (equation 8.5) for each double bond x is calculated from the quotient of the calculated integrals I_{x} (hydrogenated) and $I_{0,\mathrm{x}}$ (non-hydrogenated).

$$X_{\mathrm{x}} = 1 - \frac{I_{\mathrm{x}}}{I_{0,\mathrm{x}}} \cdot \frac{m_0}{m_{\mathrm{s}}} \tag{8.5}$$

The double bond content Y_{x} for each double bond x in HBR can be calculated from the previous content $Y_{0,\mathrm{x}}$ and the specific degree of hydrogenation X_{x} (equation 8.6).

$$Y_{\mathrm{x}} = Y_{0,\mathrm{x}} \cdot (1 - X_{\mathrm{x}}) \tag{8.6}$$

The degree of hydrogenation X_{H} is calculated by the quotient of the sums of the calculated integrals I_x and $I_{0,x}$. It can also be calculated from the sum of the double bond contents Y_x (equation 8.7).

$$X_H = 1 - \frac{\sum(I_x)}{\sum(I_{0,x})} \cdot \frac{m_0}{m_s} = 1 - \sum(Y_x) \tag{8.7}$$

Polybutadiene rubber with higher molecular weights allow the calculation of the degree of hydrogenation from the calculated integral of the hydrogenated groups I_H (equation 8.9). The calculated integral of the hydrogenated groups I_H is calculated from the integrals $\int_e$ and $\int_f$ (see Scheme 71) according to equation 8.8.

$$I_H = \frac{2}{3}\int_e + 0.5\int_f \tag{8.8}$$

$$X_H = \frac{I_H}{I_{cy} + I_v + I_{ct} + I_H} \tag{8.9}$$

Degree of epoxidation

Degree of epoxidation X_{EP} is calculated from the quotient of the calculated integral I_{EP} and the sum of the calculated integrals for double bonds and epoxides (equation 8.11). The calculated integral I_{EP} equals the integral $\int_g$ of the epoxide group (equation 8.10).

$$I_{EP} = \int_g \tag{8.10}$$

$$X_{EP} = \frac{I_{EP}}{I_{cy} + I_v + I_{ct} + I_{EP}} \tag{8.11}$$

Epoxide content Y_{EP} is calculated from the degree of epoxidation X_{EP} and the degree of hydrogenation X_{H} (equation 8.12).

$$Y_{\mathrm{EP}} = X_{\mathrm{EP}} \cdot (1 - X_{\mathrm{H}}) \tag{8.12}$$

Determination of the ROP

The conversion of ϵ-CL to PCL was analyzed by the shift of the α and ϵ peaks of ϵ-CL.

Conversion of the bromination and dehydrobromination

The different products of bromination and dehydrobromination all show significant peaks in the ^{1}H-NMR (Scheme 8.2).

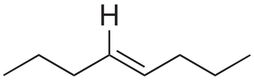
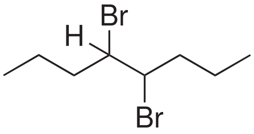
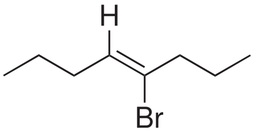
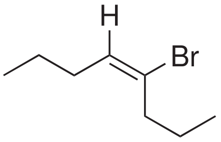
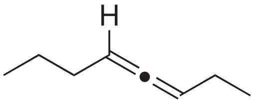
As all of these peaks have an integral of 1 they can all be used directly for conversion determination.

8.1.9. Rheology

Rheological analysis was used to determine the material properties of the different prepared polymers. For the determination of properties such as viscosity stress was applied to the polymer samples. In rheology stress is usually applied by rotation or oscillation. When a force F is applied to a surface A in the way shown in Figure 8.2 the result is the shear stress (σ_{21}) (equation 8.13).
The deformation of the material creates the offset ΔL. The height H of the sample is usually defined by the gap between the two plates of the geometry. Those combined give the shear strain (γ) (equation 8.14)

$$\sigma_{21} = \frac{F}{A} \tag{8.13}$$

$$\gamma = \frac{\delta L}{H} \tag{8.14}$$

name	functional group	chemical shift [ppm]
HBR		5.39
BRBr2		4.19
BRBrtrans		5.84
BRBrcis		5.61
ALL		5.06

Scheme 8.2: Characteristic peaks of the bromination and dehydrobromination prodducts.

For ideal elastic materials according to Hooke's law the quotient of γ and σ_{21} gives the shear modulus (G) (equation 8.15). The shear modulus describes the stiffness of a material as the quotient gets large for high γ and low σ_{21}.

$$G = \frac{\sigma_{21}}{\gamma} \tag{8.15}$$

Ideal viscous materials, also called Newtonian fluid, are described by the dynamic shear viscosity (η). The dynamic viscosity η is dependent on the shear rate ($\dot{\gamma}$) (equation 8.16), which is the change in shear strain over time.

$$\eta = \frac{\sigma_{21}}{\dot{\gamma}} \tag{8.16}$$

Most polymers are neither ideal elastic nor ideal viscous. When the strain deformation γ is applied the material response σ_{21} is phase shifted by the phase angle δ (Figure 8.3). The phase angle δ has a value between 0° (ideal

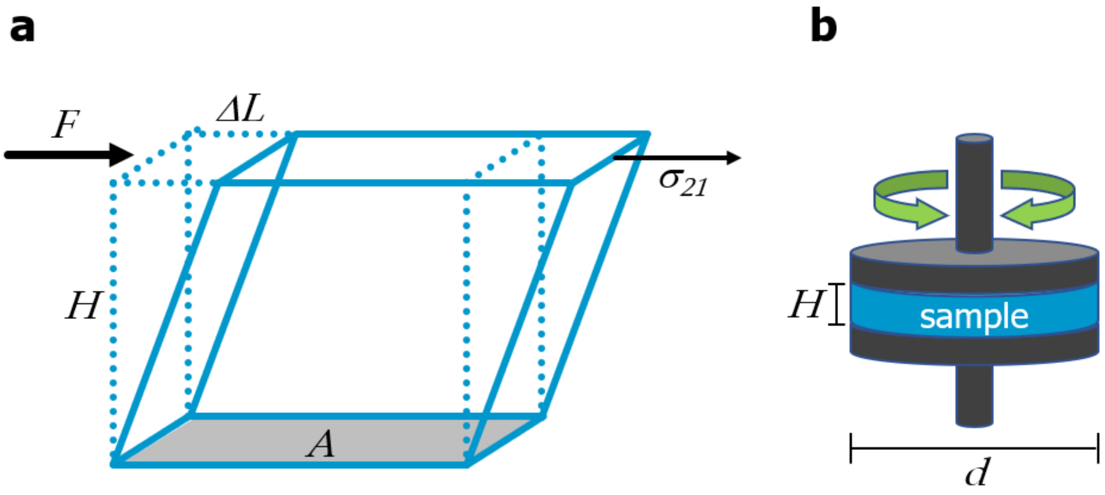


Figure 8.2.: a. Shear field in oscillation experiments. b. Setup of a plate-plate geometry.

elastic) and 90° (ideal viscous).

To describe the material properties of a visco-elastic material the complex modulus (G^*) was introduced (equation 8.17). It consists of an elastic and viscous part described by the storage modulus (G') and the loss modulus (G'') respectively.

$$G^* = G' + i \cdot G'' \tag{8.17}$$

With these moduli and the angular frequency (ω) the can be determined (equation 8.18).

$$|\eta^*| = \frac{\sqrt{G'^2 + G''^2}}{\omega} \tag{8.18}$$

For the determination of the dynamic viscosity of the partial hydrogenated low molecular weight HBR and the polyols a steel plate-plate geometry was used. The geometry had a diameter of $d = 40$ mm and the measurements were performed with a AR G2 by TA instrument at 40 °C and a gap size of $H = 1000$ μm. The angular frequency range was $\omega = 0.1$ to 100 Hz. The viscosity plot was fitted by a NEWTONIAN fit to give the dynamic viscosity.

The rheological analysis of the bromination/dehydrobromination was performed on a DHR-2 by TA instruments. The plate-plate geometry had a diameter of $d = 8$ mm and the gap size was $H = 1000$ μm. Time-temperature

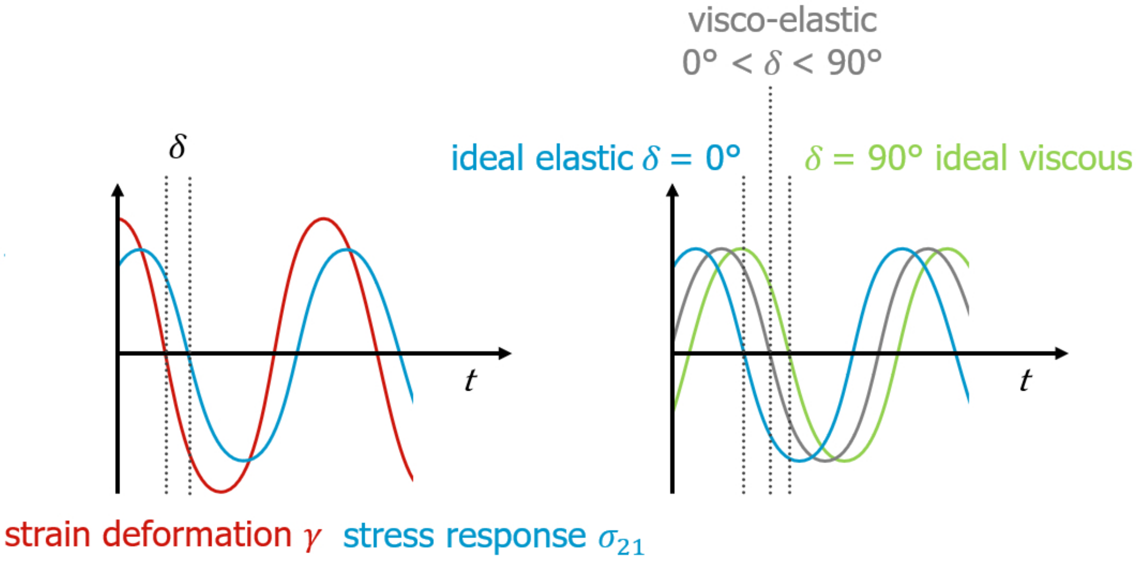


Figure 8.3.: The stress response σ_{21} is shifted by the phase angle δ to the strain deformation γ.

sweeps were recorded at temperatures between 80 - 140 °C. The data was analyzed with TRIOS and Origin.

8.1.10. Tensile testing

For tensile testing the PU samples were stored for one week at 19.1 °C and 39% humidity. Tensile bar samples S2 (DIN 53504) were punched out of polymer film and tested five times with Z1.0 by ZWICK ROELL.
Young's modulus was determined between 0.05% and 0.25% elongation for thermoplastic polymers and in the linear regime for elastomers.

8.1.11. Volumetric determinations

Different volumetric determinations were used for the epoxide value (EPv) , the hydroxide value (OHv) and water content.

Epoxide value

The epoxide value (EPv) was determined in an automated titration with KOH solution. The automated titration was performed by a Titroline alpha plus and the software TitriSoft by SI Analytics. The electrode was a ScienceLine

N 6480 eth by SI Analytics and the turning point was detected voltametric. *EPv* samples were dissolved in 5 mL 2-butanone and 10 mL of a 3% HCl solution in 2-butanone was added. Samples were stirred for at least 1 h. 5 mL was added and the solution was titrated with KOH in EtOH ($c_{\mathrm{KOH}} = 0.5M$) until the turning point was reached. For each titration a blind value KOH consumption (V_b) was determined. The blind value titration was treated like a sample titration but did not contain polymer. *EPv* was calculated from V_b, the sample KOH consumption (V_s) and the sample mass (m_s) (equation 8.19). The *EPv* has the unit mol epoxides/100 g polymer.

$$EPv = \frac{(V_\mathrm{b} - V_\mathrm{s}) \cdot c_{\mathrm{KOH}}}{10 \cdot m_\mathrm{s}} \tag{8.19}$$

Hydroxide value

The hydroxide value (*OHv*) was determined in an automated titration with KOH solution. The automated titration was performed by a Titroline alpha plus and the software TitriSoft by SI Analytics. The electrode was a ScienceLine N 6480 eth by SI Analytics and the turning point was detected voltammetric. *OHv* samples were dissolved in 15 mL catalyst solution containing 1% 4-DMAP in NMP. For acetylation 5 mL of a 10% acetic anhydride (AcAc) solution was added and stirred for at least 1.5 h. 5 mL H2O was added for hydrolysis of non-conversed AcAc. To improve solubility 10 mL 2-butanone was added and the solution was stirred for at least 1 h. After hydrolysis the solution was titrated with KOH in EtOH ($c_{\mathrm{KOH}} = 0.1$ M) until the turning point was reached. For each titration a blind value KOH consumption (V_b) was determined. The blind value titration was treated like a sample titration but did not contain polymer. *OHv* was calculated from V_b, the sample KOH consumption (V_s) and the sample mass (m_s) and the molecular weight of KOH ($M_{\mathrm{KOH}} = 56.1$ g/mol) (equation 8.20). The *OHv* has the unit mg KOH/g polymer.

$$EPv = \frac{(V_\mathrm{b} - V_\mathrm{s}) \cdot M_{\mathrm{KOH}} \cdot c_{\mathrm{KOH}}}{m_\mathrm{s}} \tag{8.20}$$

8.1.12. Water swelling

For water swelling 40x25 mm samples were cut and were immersed in water at 100 °C for 5 h. Degree of swelling was determined by the weight increase of the dry swollen sample.

8.2. Materials

All chemicals and solvents were commercially available and used as supplied unless otherwise noted. Purchased dry solvents were stored over molecular sieves.

8.2.1. Purification of chemicals and solvents

Polymers

Lithene AL, **Lithene PM4** and **Lithene N4-5000** were generously supplied by Synthomer. The molecular weight are M_n = 1.5 kg/mol, 3.0 kg/mol and 5.0 kg/mol respectively. The double bond content for AL is 30% 1,2-*cyclic*, 29% 1,2-*vinyl* and 41% 1,4-*cis/trans*. The double bond content for PM4 is 4% 1,2-*cyclic*, 15% 1,2-*vinyl* and 81% 1,4-*cis/trans*. The double bond content for AL is 2% 1,2-*cyclic*, 10% 1,2-*vinyl* and 88% 1,4-*cis/trans*.
VESTENAMER 8012 was generously supplied by Evonik. It was prepared in a ring opening metathesis from cyclooctene and equals a polybutadiene with a degree of hydrogenation = 50% with an alternating structure. It contains 80% *trans* and 20% *cis* double bonds. The molecular weight is M_n = 60 kg/mol (PDI = 2.52; THF).

Purification of solvents

Toluene was dried over potassium at reflux for several hours. Benzophenone was used as indicator.
Cyclohexane was dried over sodium at reflux for several hours. Benzophenone was used as indicator.
N-Methyl-2-pyrrolidone (NMP) was distilled at reduced pressure and 90 °C. The water containing first fraction was discarded.
NMR solvents were stored over 3 Å molecular sieve for water removal.

Purification of chemicals

ϵ-Caprolactone was distilled at reduced pressure and 150 °C. The water containing first fraction was discarded.

Cyclopentadiene was prepared by cracking the dimer dicyclopentadiene. It was heated to 150 °C and distilled by a column filled with iron fillings. The water containing first fraction was discarded. The prepared cyclopentadiene was used immediately to avoid dimerization.

8.2.2. Hydrogenation Reactor

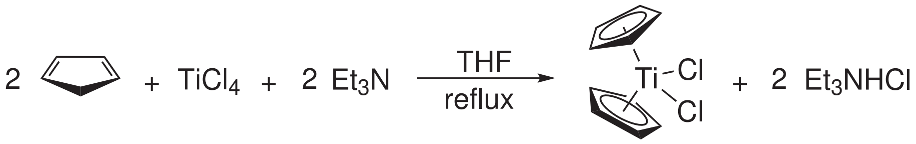
The 1 L hydrogenation-reactor including the top flange was made of stainless steel by BÜCHI and was heated by a LAUDA C6 CS thermostat. The top had six openings for temperature detection, analogue pressure detection, gas inlet, gas outlet, safety valve and material feed. Temperature was detected by a Typ K (NiCr - Ni) thermoelement by Rössel Messtechnik. The gas inlet flow was controlled and monitored by a thermal mass flow controller (MFC) SLA5850 by BROOKS INSTRUMENT. The reaction mixture was stirred with an anchor stirrer. All fittings were made by Swagelok. The safety valve SV 805-ES-7 made by WITT-Gasetechnik allows pressures up to 10 bar.

The data from the MFC and the temperature was processed in ProfiSignal by Delphin Technology. For continuous catalyst feed the syringe pump LSP02-1B by Baoding Longer Precision Pump was used. For a detailed construction overview see 5.2.

8.3. Experiments

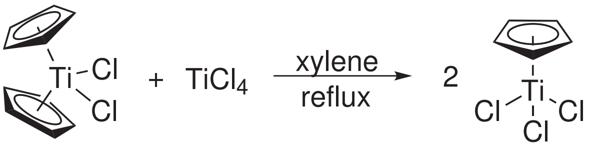
8.3.1. Hydrogenation catalyst

Synthesis of dichlorobis(cyclopentadienyl)titanium(IV)



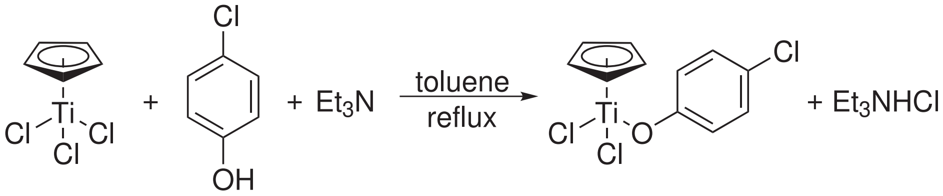
For the synthesis of dichlorobis(cyclopentadienyl)titanium(IV) 1 equivalent $TiCl_4$ was dissolved in dry THF (c = 1.2 mol/L) and heated to 80 °C. To this mixture a solution of 2 equivalents fresh distilled cyclopentadiene (CpH) and 2 equivalents dry Et_3N in dry THF (c = 4.8 mol/L; both CpH and Et3N) was added dropwise within 2 h. The mixture was allowed to stir for 3 h. After cooling to r.t. the precipitated Et_3NHCl was filtered and washed with THF. The solution was reduced to about 1 L, filtered and poured in PE to precipitate the crude product. This was repeated until a pure product was obtained. The pure product was dried under reduced pressure for a couple of days.

Synthesis of trichloro(cyclopentadienyl)titanium(IV)



For the synthesis of trichloro(cyclopentadienyl)titanium(IV) 1 equivalent of dry dichlorobis(cyclopentadienyl)titanium(IV) was dissolved in xylene (c = 0.16 mol/L). 1 equivalent $TiCl_4$ was added and the solution heated to reflux. After 7 h of stirring the solvent was removed at reduced pressure. The crude product was sublimed to give the pure product. The pure product was stored in argon atmosphere.

Synthesis of dichloro(4-chlorophenolato)cyclopentadienyltitanium(IV)



For the synthesis of dichloro(4-chlorophenolato)cyclopentadienyltitanium(IV) ($TiCpCl_2$–p–(O–C_6H_4Cl)) 1 equivalent of trichloro(cyclopentadienyl)titanium(IV) was dissolved in dry toluene (c = 0.05 mol/L) in argon atmosphere. 1.6 equivalents dry Et_3N was added and the mixture was heated to reflux. To the mixture a solution of 1 equivalent 4-chlorophenol in dry toluene (c = 0.05 mol/L) was added dropwise over 2 h. The mixture was allowed to stir for 1 h. The solvent was removed at reduced pressure to give the crude product. The crude product was dispersed in a small amount of dry toluene, filtered and washed multiple times in argon atmosphere. The product was dried at reduced pressure and stored in argon atmosphere.

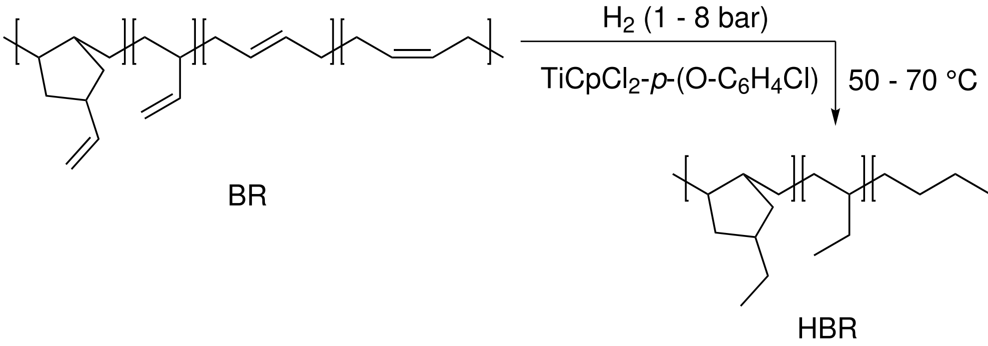
8.3.2. Hydrogenation

Catalyst activation

To a 0.2 M solution of the catalyst $TiCpCl_2$–p–(O–C_6H_4Cl) in dry toluene a 2.5 M solution of n-BuLi in n-hexane was added under argon atmosphere. The Li:Ti ratio was 4:1. The mixture was stirred for 15 minutes. The activated catalyst was transferred into the reactor under argon atmosphere.

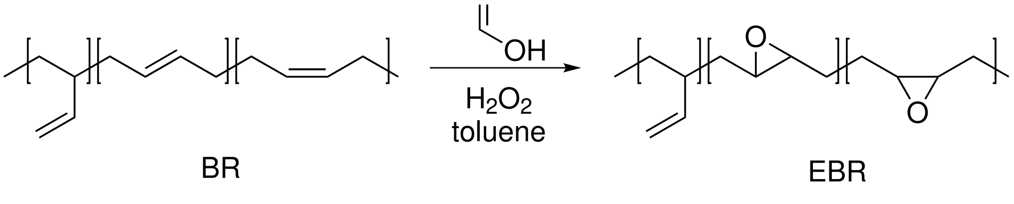
Hydrogenation procedure

For the preparation of partial hydrogenated polybutadiene rubber (HBR) the reactor was dried over night at < 1 mbar and 105 °C. The BR was degassed at 50



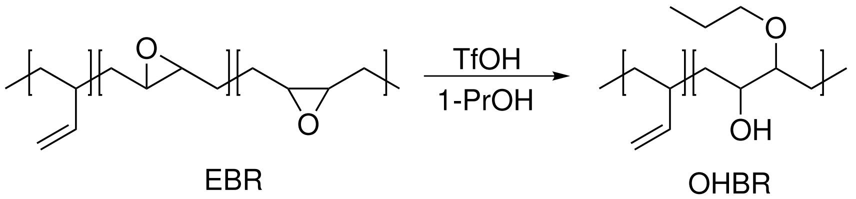
°C and dissolved in dry cyclohexane or dry toluene in argon atmosphere. The reactor was cooled to room temperature, filled with argon and the BR solution was added. The solution was saturated with hydrogen and the activated catalyst was added. The reactor was closed, the mixture stirred at 600 rpm, the hydrogen pressure raised to 8 bar and the temperature set to 50 - 70 °C. After reaching the temperature the reaction time was started. The reaction was stopped after either a certain time or when the desired degree of hydrogenation was reached. For quenching the hydrogen pressure was removed and the reaction mixture was poured into cold methanol with 1 mL of conc. HCl to deactivate the catalyst. The solvent was decanted, the HBR re-dissolved in some cyclohexane or toluene, filtered and dried under reduced pressure at 40 - 80 °C. Lömi anders

8.3.3. Epoxidation



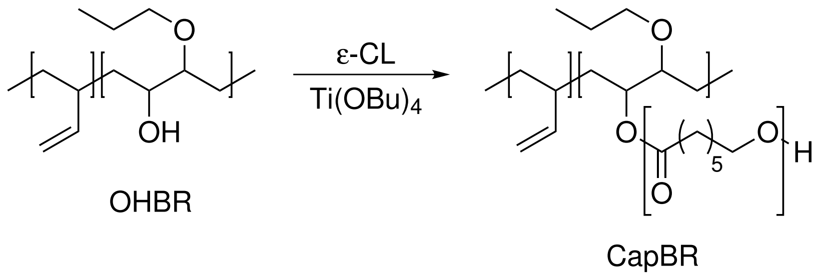
For the preparation of epoxidized polybutadiene rubber (EBR) the rubber was dissolved in toluene (15w%) and 1.65w% formic acid was added. The mixture was heated to 70 °C. Once the temperature was reached the reaction time started with the dosing of hydrogen peroxide. Hydrogen peroxide was dosed at a constant rate of 30 mL/h to form peroxoformic acid in situ. Once the desired degree of epoxidation was reached the reaction was quenched with saturated sodium bicarbonate solution. The organic phase was washed with brine and dried over sodium sulfate. The toluene was removed at reduced pressure at 40 - 80 °C.

8.3.4. Acidic epoxide opening



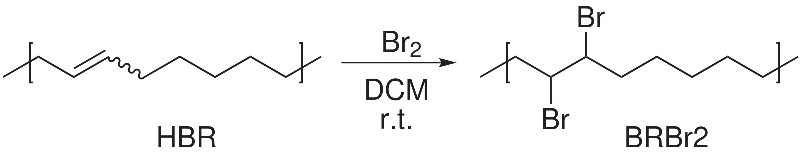
For the synthesis of polybutadiene-based polyol (OHBR) by opening the epoxide 20w% of EBR was dispersed in 1-propanol. To the dispersion 300 ppm trifluoromethanesulfonic acid (TfOH) was added and stirred at 80 °C for 3.5 h. The reaction was quenched with sodium bicarbonate, filtered and 1 propanole was removed at reduced pressure at 40 - 80 °C for several days.

8.3.5. ROP for PCL-BR block copolymers



ϵ-Caprolactone-butadiene rubber block copolymers were prepared by capping the OHPBs with ϵ-CL in a ring opening polymerization (ROP). The OHBR was poured in a glass reactor and 30w% ϵ-CL was added. The bulk was heated to 150 °C and stirred. 100 ppm of the ROP catalyst $Ti(OBu)_4$ was added and the mixture stirred for 6 h.

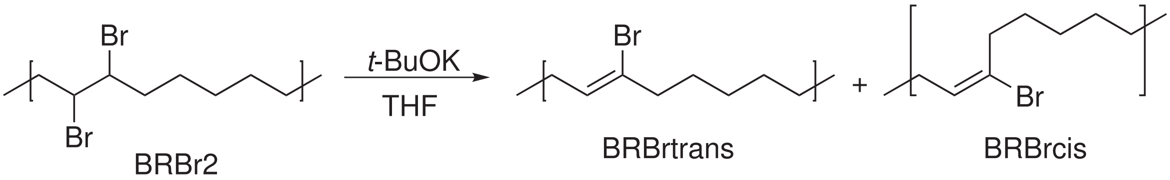
8.3.6. Bromination



For bromination HBR (Vestenamer, X_H = 50%) was dissolved in dichloromethane (c = 185 mmol DB/L) and 1.05 equivalents bromine (Br_2) was added. After stirring for 1 h the yellow solution was poured into MeOH to precipitate the colorless product. Product was dried over night at 40 °C and reduced pressure.

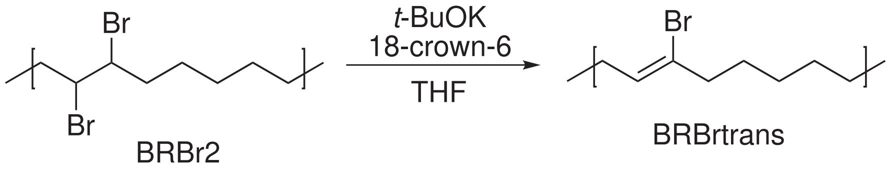
8.3.7. Dehydrobromination

Monodehydrobromination



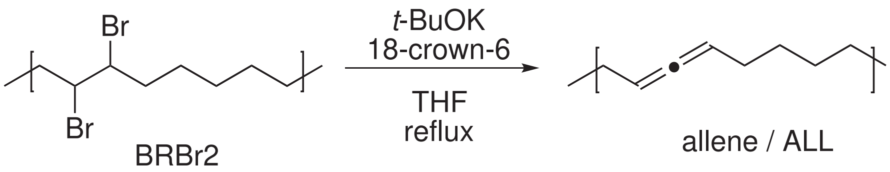
The brominated polymer (BRBr2) was dissolved in THF (c = 359 mmol Br/L). To perform the dehydrobromination 1.25 equivalents potassium tert-butanolate was added and the dispersion was stirred for 1 min at room temperature. The reaction mixture was poured in MeOH with 0.75 equivalents HCl to precipitate the product. To remove MeOH it was dried overnight at reduced pressure and 40 °C to give the orange product.

Monodehydrobromination - Pure *trans*-Product



The brominated polymer (BRBr2) was dissolved in THF (c = 359 mmol Br/L) and 0.025 equivalents 18-crone-6 was added. To perform the dehydrobromination 1.25 equivalents potassium tert-butanolate was added and the dispersion was stirred for 1 min at room temperature. The reaction mixture was poured in MeOH with 0.75 equivalents HCl to precipitate the product. To remove trapped MeOH it was dried overnight at reduced pressure and 40 °C to give the orange product.

Didehydrobromination



The brominated polymer (BRBr2) was dissolved in THF (c = 359 mmol Br/L) and 0.025 equivalents 18-crone-6 was added. To perform the dehydrobromination 1.25 equivalents potassium tert-butanolate was added and the dispersion was stirred for several hours at reflux. The reaction mixture was poured in MeOH with 0.75 equivalents HCl to precipitate the product. To remove trapped MeOH it was dried overnight at reduced pressure and 40 °C to give the brown product.

9. Literature

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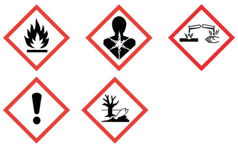
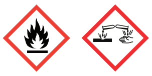
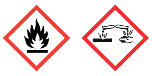
A. Savety data

List of hazardous substances[126]

Substance	Pictogram	Hazard statements	Precautionary statements
Acetone		H225, H319, H336, EUH066	P210, P261, P305 + P351 + P338
Anti-foaming agent	Substance not yet tested completely		
Argon		H280	P410 + P403
Benzene-d_6		H225, H304, H315, H319, H340, H350, H372, H412	P201, P210, P280, P308 + P313, P370 + P378, P403 + P235
Bromine		H314, H330, H400	P260, P273, P280, P284, P305 + P351 + P338, P310
n-Butyllithium 2.5N in *n*-hexane		H225, H250, H261, H304, H314, H336, H361f, H373, H411, EUH014	P210, P222, P231 + P232, P261, P273, P422
Chloroform-*d*		H302, H315, H319, H331, H351, H361d, H372	P260, P280, P301 + P312 + P330, P304 + P340 + P311, P305 + P351 + P338, P403 + P233

Substance	**Pictogram**	**Hazard statements**	**Precautionary statements**
Cyclohexane		H225, H304, H315, H336, H410	P210, P261, P273, P301 + P310, P331, P501
Cyclopentadienyl-titanium trichloride		H314, H330, H400	P280, P305 + P351 + P338, P310
Dichloro(4-chlorophenolato)-cyclopentadienyl-titanium(IV)	Substance not yet tested completely		
Dichlorobis(cyclo-pentadienyl)-titanium(IV)		H315, H335	P261
Dichloromethane		H315, H319, H335, H336, H351, H371	P260, P280, P305 + P351 + 338
Dicyclopentadiene		H226, H302, H315, H319, H330, H335, H411	P260, P273, P284, P305 + P351 + P338, P310
ϵ-Caprolactone		H319	P280, P305 + P351 + P338, P337 + P313
Ethanol		H225, H319	P210, P280, P305 + P351 + P338, P337 + P313, P403 + P235
Ethyl acetat		H225, H319, H336, EUH066	P210, P305 + P351 + P338, P370 + P378, P403 + P235

Substance	Pictogram	Hazard statements	Precautionary statements
Formic acid $>$ 90%		H226, H302, H314, H331, EUH071	P210, P280, P303 + P361 + P353, P304 + P340 + P310, P305 + P351 + P338, P403 + P233
Hydrochloric acid conc.		H290, H314, H335	P260, P280, P303 + P361 + P353, P304 + P340 + P310, P305 + P351 + P338
hydrogen		H220, H280	P210, P377, P381, P410 + P403
hydrogen peroxide 30%		H302, H412	P280, P301 + P312 + P330, P305 + P351 + P338 + P310
Lithene "ultra" AL	Not a hazardous substance $^{a)}$		
Lithene "ultra" N4-5000	Not a hazardous substance $^{a)}$		
Lithene "ultra" PM4	Not a hazardous substance $^{a)}$		
Methanol		H225, H301 + H311 + H331, H370	P210, P280, P302 + P352 + P312, P304 + P340 + P311, P370 + P378, P403 + P235
Nitrogen (liquid)[127]		H282	P336 + P315, P403
Nitrogen		H280	P410 + P403

Substance	**Pictogram**	**Hazard statements**	**Precautionary statements**
N-Methyl-2-pyrrolidone		H315, H319, H335, H336D	P201, P280, P305 + P351 + P338, P308 + P313
Potassium hydroxide 1N in ethanol		H225, H290, H314	P210, P240, P280, P301 + P330 + P331, P305 + P351 + P338, P308 + P310, P403 + P233
Potassium hydroxide		H290, H302, H314	P280, P301 + P312 + P330, P303 + P361 + P353, P304 + P340 + P310, P305 + P351 + P338
Potassium *tert*-butanolate		H228, H260, H314, EUH014	P210, P231 + P232, P280, P305 + P351 + P338, P370 + P378, P402 + P404
PU catalyst	Substance not yet tested completely		
Sodium bicarbonate	Not a hazardous substance *a)*		
Sodium chloride	Not a hazardous substance *a)*		
Sodium sulfate	Not a hazardous substance *a)*		
Sodium thiosulfate	Not a hazardous substance *a)*		

Substance	Pictogram	Hazard statements	Precautionary statements
Terahydrofuran		H225, H302, H319, H335, H351	P210, P280, P301 + P312 + P330, P305 + P351 + P338, P370 + P378, P403 + P235
Terahydrofuran-d_8		H225, H315, H319, H351	P210, P281, P305 + P351 + P338
Titanium tetrachloride		H314, H330, H370, H372, EUH014, EUH 071	P260, P280, P284, P305 + P351 + 338, P310
Titanium(IV) butoxide		H226, H315, H318, H335, H336	P210, P280, P304 + P340 + P312, P305 + P351 + P338 + P310, P403 + P235
Toluene		H225, H304, H315, H336, *H361d*, H373	P210, P260, P280, P301 + P310, P370 + P378, P403 + P235
Triethylamine		H225, H302, H311 + H331, H314, H335	P210, P280, P303 + P361 + P353, P304 + P340 + P310, P305 + P351 + P338, P403 + P233
Trifluoromethanesulfonic acid		H302 + H312, H314	P280, P305 + P351 + P338, P310
Vestenamer	Not a hazardous substance [a)]		

Substance	Pictogram	Hazard statements	Precautionary statements
Xylene		H226, H304, H312 + H332, H315, H319, H335, H412	P261, P273, P280, P301 + P310, P305 + P351 + P338, P331

a) Not a hazardous substance or mixture according to Regulation (EC) No. 1272/2008.

Used CMR-substances in category 1A or 1B (GHS)

Substance	CAS-number	Usage and quantity	C	M	R
N-Methyl-2-pyrrolidone	106-89-8	Solvent, 200 mL	1B	-	-

C: carcinogenic - M: mutagenic - R: toxic to reproduction

B. Acknowledgment

Tja, da sind wir nun. Eine Reise geht zu Ende. Oder beginnt sie erst?! Das wird wohl die Zukunft zeigen...

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C. Declaration on oath

I hereby declare on oath, that I have written the present dissertation by my own and have not used other than the acknowledged resources and aids. The submitted written version corresponds to the version on the electronic storage medium. I hereby declare that I have not previously applied or pursued for a doctorate (Ph.D. studies).

July 10, 2018 in Hamburg

Jim Christoph Uther