Post Modification of Liquid Polybutadienes and Their Rheological Properties

Dissertation

with the aim of achieving the doctoral degree at the Faculty of Mathematics, Informatics and Natural Sciences

submitted to the

Department of Chemistry

University of Hamburg

by

Hannes Jürgens

Hamburg 2018

Date of oral defense: 22.02.2019

Approval for printing: 22.02.2019

The experimental work described in this thesis has been carried out between May 2012 and July 2016 at the Institute of Technical and Macromolecular Chemistry, University of Hamburg in the research group of Professor Dr. Gerrit A. Luinstra

The following evaluators recommend the admission of the dissertation:

1. Evaluator: Professor Dr. Gerrit A. Luinstra
2. Evaluator: Professor Dr. Hans-Ulrich Moritz

Table of Contents

List of Abbreviations

$|\eta^*|$	Complex Oscillatory Viscosity
ABR	Aminated Butadiene Rubber
aq.	Aqueous
bp	Boiling Point
BR	Butadiene Rubber
c	Concentration
cat.	Catalyst
CR	Chloroprene Rubber
DSC	Dynamic Scanning Calorimetry
E_A	Activation Energy
EBR	Epoxidated Butadiene Rubber
EP-value	Epoxidation Value (Titration)
EPDM	Ethylene Propylene Diene Rubber
eq.	Equivalents
E-SBR	Emulsion Styrene Butadiene Rubber
f	Epoxidation Ratio
FA	Formic Acid
g	Structural Factor
G’	Oscillatory Shear Storage Modulus

G’’	Oscillatory Shear Loss Modulus
GPC	Gel Permeation Chromatography
HP	Hydrogen Peroxide
I-Gated	Inverse Gated Decoupling Experiment
IIR	Isobutylene Isoprene Rubber
IR	Isoprene Rubber
k	reaction rate constant
LiBr	Lithium Bromide
M	Molecular Weight
m	Mass
MALDI-Tof	Matrix Assisted Laser Desorption Ionisation – Time of Flight
M_n	Number Average Molecular Weight
M_w	Mass Average Molecular Weight
NBR	Acrylonitrile Butadiene Rubber
NMR	Nuclear Magnetic Resonance
PBu	Polybutadiene
PFA	Performic Acid
ppm	Parts per Million
PTFE	Polytetrafluorethylene (Teflon®)
R	Universal Gas Constant
SBR	Styrene-Butadiene-Rubber
SBC	Styrenic Block Copolymer Thermoplastic Elastomer

SEC	Size Exclusion Chromatography
S_N2	Bimolecular Nucleophilic Substitution
S-SBR	Solution Styrene Butadiene Rubber
T	Temperature
T_0	Reference Temperature
T_g	Glass Transition Temperature
T_m	Melting Point
THF	Tetrahydrofurane
t_{KOH}	Titer
TTS	Time Temperature Superposition
V	Volume
w	Weight Fraction
X	Conversion
α_T	Shift Factor
δ	Chemical Shift
η_0	Zero Shear Viscosity
ξ	Fiction Factor
φ	Volume Fraction
ω	Angular Frequency

1 Abstract

Polymers carrying functional groups for specific applications are accessible through two different routes. The polymerization of monomers showing the desired functionality or the post modification with the functional groups of existing polymers.[1] The former route requires a polymerization environment that is tolerating the functional group. The process often has limited versatility, because a monomer specific process is used. Post modification on the other hand poses additional process steps increasing the production costs, especially if expensive catalysts have to be used. In this thesis a versatile post modification process is shown with easy accessible catalytic systems for the functionalization of polybutadienes. The modification was done using low vinyl polybutadienes of molecular weights between 1500 and 26000 g/mol.

A two-phase semi batch epoxidation process using *in-situ* formed performic acid gave access to a versatile intermediate which could be further functionalized. Continuous addition of aqueous hydrogen peroxide to a toluene solution of polybutadiene, catalyzed by formic acid gave a controllable, safe and scalable reaction. The reaction progress could be monitored by ^{1}H-NMR spectroscopy or titration. The kinetics of the reaction were investigated and the formation of performic acid was identified as rate determining step. The activation energy using an Arrhenius-plot was determined and its value of 29 kJ/mol is in the range of those, shown in the literature.[2,3]

The glass transition temperature of the epoxidated polybutadienes rose with increasing epoxide content following the fox-equation. The bulk viscosity increased about one order of magnitude by epoxidation of about 50%.

The versatile epoxidized polybutadienes described above were characterized by oscillatory rheology. The change in viscosity by introduction of epoxide groups makes it necessary to predict the product properties for optimal process design. Using the model introduced here the final viscosity can be calculated based on conversion, molecular weight of polybutadiene, concentration in toluene and reaction temperature.

The epoxide groups on the polymer backbone can be opened by nucleophiles of which amines were investigated as an example in this thesis. A one step process with high conversion using *n*-butylamine catalyzed by lithium bromide was developed. The kinetics of the reaction were looked at and a cyclization side reaction competing with the addition of *n*-butylamine was identified.

The introduction of polar amine groups further increased the glass transition temperature to about -20 °C at 30% amine content relative to initial double bond concentration. Signs of conformational changes in the polymer chain could be observed using SEC measurements.

The secondary amine groups in aminated polybutadienes were methylated using iodomethane and potassium carbonate to introduce ammonium ions. The reaction proceeded at room temperature with an excess of iodomethane. The resulting polymer was a hard and brittle material with a glass transition temperature of about 45 °C at 30% ammonium ion content relative to initial double bond concentration. The solubility in polar solvents like methanol increased significantly.

2 Zusammenfassung

Polymere mit funktionellen Gruppen sind auf zwei verschiedenen Wegen zugänglich. Funktionelle monomere können polymerisiert werden oder existierende Polymere können in einer Post-Modifikation nachträglich funktionalisiert werden.[1] Die erste Route erfordert eine Polymerisationsumgebung, welche die funktionelle Gruppe toleriert. Dieser Prozess ist oft nur bedingt flexibel, da ein monomerspezifischer Prozess verwendet wird. Post-Modifikation hat andererseits den Nachteil, dass zusätzliche Prozessschritte erforderlich werden, was die Produktionskosten erhöht. Das gilt insbesondere, wenn teure Katalysatorsysteme verwendet werden. In dieser Arbeit wird ein variabler Prozess gezeigt, der die Post-Modifikation von Polybutadienen unter Verwendung von leicht zugänglichen Katalysatorsystemen ermöglicht. Die Modifikationen wurden durchgeführt an Polybutadienen mit niedrigem Vinylgehalt der Molmassen 1500 bis 26000 g/mol.

Ein zweiphasiger Semi-Batch-Prozess unter Verwendung von *in-situ* hergestellter Perameisensäure machte ein variables Intermediat zugänglich, welches weiter funktionalisiert werden konnte. Wässriges Wasserstoffperoxid wurde kontinuierlich zu einer toluolischen Polybutadienlösung gegeben, welche Ameisensäure als Katalysator enthielt. Dadurch wurde ein kontrollierbarer, sicherer und skalierbarer Prozess geschaffen. Der Reaktionsfortschritt konnte per ^{1}H-NMR und per Titration verfolgt werden. Die Kinetik der Reaktion wurde untersucht und die Bildung der Perameisensäure als geschwindigkeitsbestimmender Schritt identifiziert. Die Aktivierungsenergie wurde mit Hilfe einer Arrheniusauftragung bestimmt. Der ermittelte Wert der Aktivierungsenergie von 29 kJ/mol liegt im Bereich der literaturbekannten Werte.[2,3]

Die Glassübergangstemperatur der epoxidierten Polybutadiene erhöhte sich mit steigendem Epoxidgehalt und der Verlauf folgte der Fox-Gleichung. Die Viskosität erhöhte sich um etwa eine Größenordnung bei einem Epoxidgehalt von 50%.

Die oben beschriebenen epoxidierten Polybutadiene wurden mit Hilfe von Oszillationsmessungen rheologisch untersucht. Die Viskositätsänderung durch die Einführung von Epoxidgruppen macht eine Abschätzung der Produkteigenschaften unabdingbar für eine industrielle Prozessentwicklung. Das Modell, welches hier vorgestellt wird, erlaubt es, die Viskosität des Produktes zu berechnen bei Kenntnis des Umsatzes, des

Molekulargewichtes des eingesetzten Polybutadiens, dessen Konzentration in Toluol und der Reaktionstemperatur.

Die Epoxidgruppen an dem Polymerbackbone können durch Nukleophile geöffnet werden. In dieser Arbeit wurde die Reaktion mit Aminen als Beispiel gängiger Nukleophile genauer untersucht. Ein einstufiger Prozess wird vorgestellt, welcher einen hohen Umsatz unter Verwendung von *n*-Butylamin und Lithiumbromid als Katalysator verspricht. Die Kinetik der Reaktion wurde betrachtet und eine Cyclisierung als Nebenreaktion identifiziert, welche mit der *n*-Butylaminaddition konkurriert.

Die Einführung polarer Amingruppen erhöhte die Glassübergangstemperatur weiter auf etwa -20 °C bei 30% Amingehalt bezogen auf die Konzentration an Doppelbindungen des Ausgangspolybutadiens. Außerdem konnten Hinweise auf eine Konformationsänderung durch GPC-Messungen beobachtet werden.

Die sekundären Amine der funktionalisierten Polybutadiene wurden methyliert unter Verwendung von Iodmethan und Kaliumcarbonat. Mit einem Überschuss an Iodmethan lief die Reaktion bei Raumtemperatur bis zu quartären Ammoniumionen ab. Das so erhaltene Polymer war ein hartes sprödes Material mit einer Glassübergangstemperatur von etwa 45 °C bei einem Gehalt an quartären Ammoniumionen von 30% bezogen auf die Doppelbindungskonzentration der eingesetzten Polybutadiene. Die Löslichkeit in polaren Lösungsmitteln wie Methanol stieg signifikant.

3 Introduction and Background

3.1 Synthetic Rubber

Rubber is a material used in many industries like automotive, tires, medical applications and everyday life. Apart from natural rubber, synthetic rubbers are a growing field with increasing production capacities worldwide. Butadiene Rubber (BR) and butadiene containing copolymers like styrene-butadiene-rubber (SBR) made over 75% of the global rubber production capacity in 2015.[4]

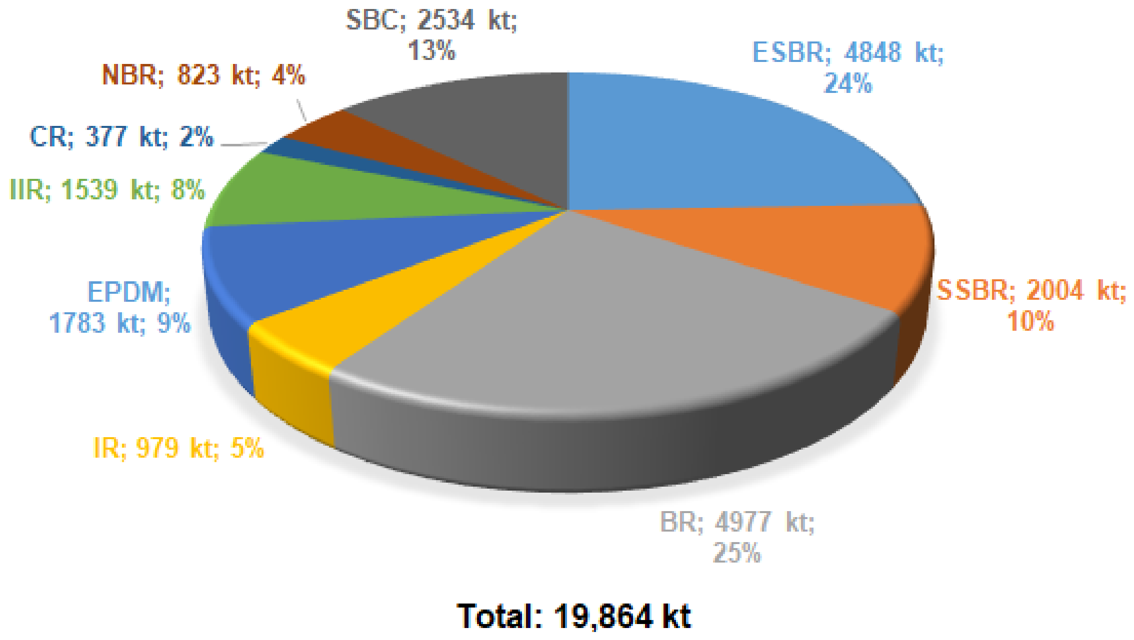


Figure 1. Global synthetic rubber production capacity 2015[4]

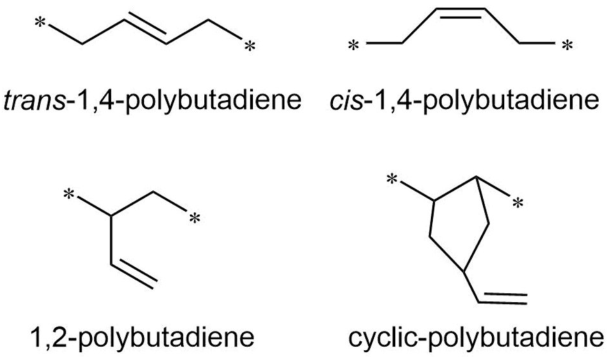
Even though SBR still is the most important synthetic rubber, BR production capacity was the fastest growing in recent years. Production capacity for BR was increased by roughly 2000 kt (66%) between 2010 and 2015. This was mostly attributed to increasing demand for high performance tires due to European tire labeling. That makes BR or Polybutadiene an essential synthetic rubber nowadays with the biggest application in tire industries e.g. for low rolling resistance.[5]

3.2 Polybutadiene

3.2.1 Introduction

The alkali metal catalyzed polymerization of butadiene was first described in the year 1910.[6–8] It was commercialized with the brand name BUNA in the 1920ies.[9] Stereoregular polybutadienes (PBu) were introduced after the advances of Ziegler-Nata-Catalysts in the 1950ies.[10] The most important polymerization method today is the Ziegler-Natta-process in solution. The largest quantities of polybutadiene today are used in tire industry.[5]

The properties of polybutadiene depend on the polymer microstructure. The butadiene can be inserted in 1,4 or 1,2 (≡ 3,4) addition. The 1,4 isomers can be present in *cis* or *trans* form. Additionally, a cyclic group can be formed out of two butadiene units carrying a terminal double bond (Figure 2):



trans-1,4-polybutadiene *cis*-1,4-polybutadiene

1,2-polybutadiene cyclic-polybutadiene

Figure 2. Polybutadiene isomers

Industrial scale polymerization of butadiene follows one of three different processes. Anionic polymerization, radical polymerization or coordinative insertion polymerization.[11] The microstructure of the polybutadiene depends on the method used.

Table 1. Microstructure and glass transition temperatures of polybutadienes[5]

Catalyst	*cis*-1,4-content	*trans*-1,4-content	1,2-content	T_g [°C]
Nd – BR	97%	2%	1%	-109
Co – BR	95%	3%	2%	-107
Ni – BR	96%	2%	2%	-107
Ti – BR	92%	4%	4%	-105

Li – BR	medium	medium	10-50%	-93[1]
E - BR	<20%	~70%	<20%	-78[1]

3.2.2 Anionic Polymerization of Polybutadiene

Anionic polymerization of elastomers was the first synthetic route in elastomer synthesis. It was described 1910 by different authors using sodium metal.[7,12,6] This process was later responsible for the trade name BUNA® which is still used by Arlanxeo and Trinseo today. The process was too expensive, which was why it wasn't successful commercially. That was achieved in the 1950ies with the introduction of homogenous catalysis using butyl lithium and sodium naphthalene (Figure 3).[5]

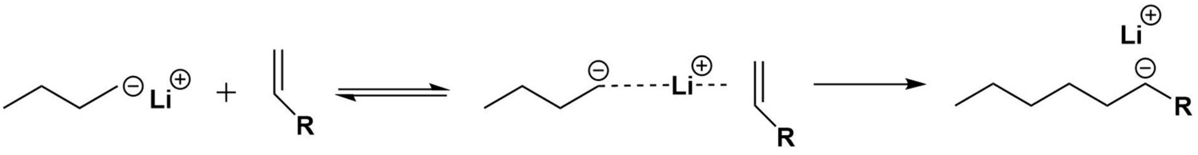


Figure 3. Anionic initiation of unsaturated carbohydrates

The anionic polymerization is initiated by lithium alkyls and is generating polybutadienes with medium *cis*-content and 10-50% vinyl content (depending on solvent polarity). The higher the solvents polarity, the higher the vinyl content. That is because polar solvents dissociate carbanion and metal ion and inhibit the formation of metal ion monomer aggregates. An ethyl-lithium initiated anionic polymerization of butadiene gives about 7% 1,2-vinyl content in hexane and about 91% in THF.[5]

---

[1] Varies with microstructure

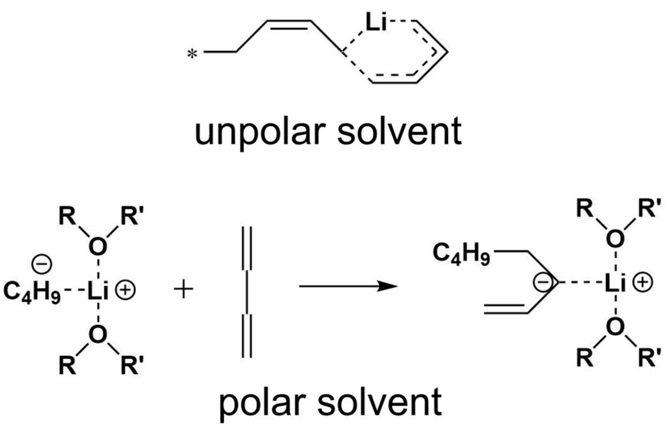


Figure 4. Solvent influence on polybutadiene microstructure

3.2.3 Radical Polymerization of Polybutadiene

Radical polymerization is conducted in aqueous emulsion polymerization at low temperatures (T = 5 °C). Redox systems like hydroperoxide or iron (II) complexes are used as initiators. The resulting micro structure is a low *cis*-content and low vinyl-content (both <20%). The industrial significance of radical polymerized polybutadiene is limited.[5]

3.2.4 Coordinative Polymerization of Polybutadiene

Coordinative polymerization of butadiene gives access to stereoregular polybutadienes. The microstructure consists usually of *cis* contents above 90% and differs with the catalyst system used. The commercially available Ziegler-Natta-polybutadienes are synthesized using titanium, cobalt, nickel or neodymium based catalysts.[5]

The Mechanism mostly accepted today was postulated by COSSÉE and ARLMAN.[13–17] The metal complex gets activated e.g. by triethylaluminium in a first step including the migration of the vacant reactive site. An olefin can then be inserted into the growing polymer chain via a four-center transition state (Figure 5).

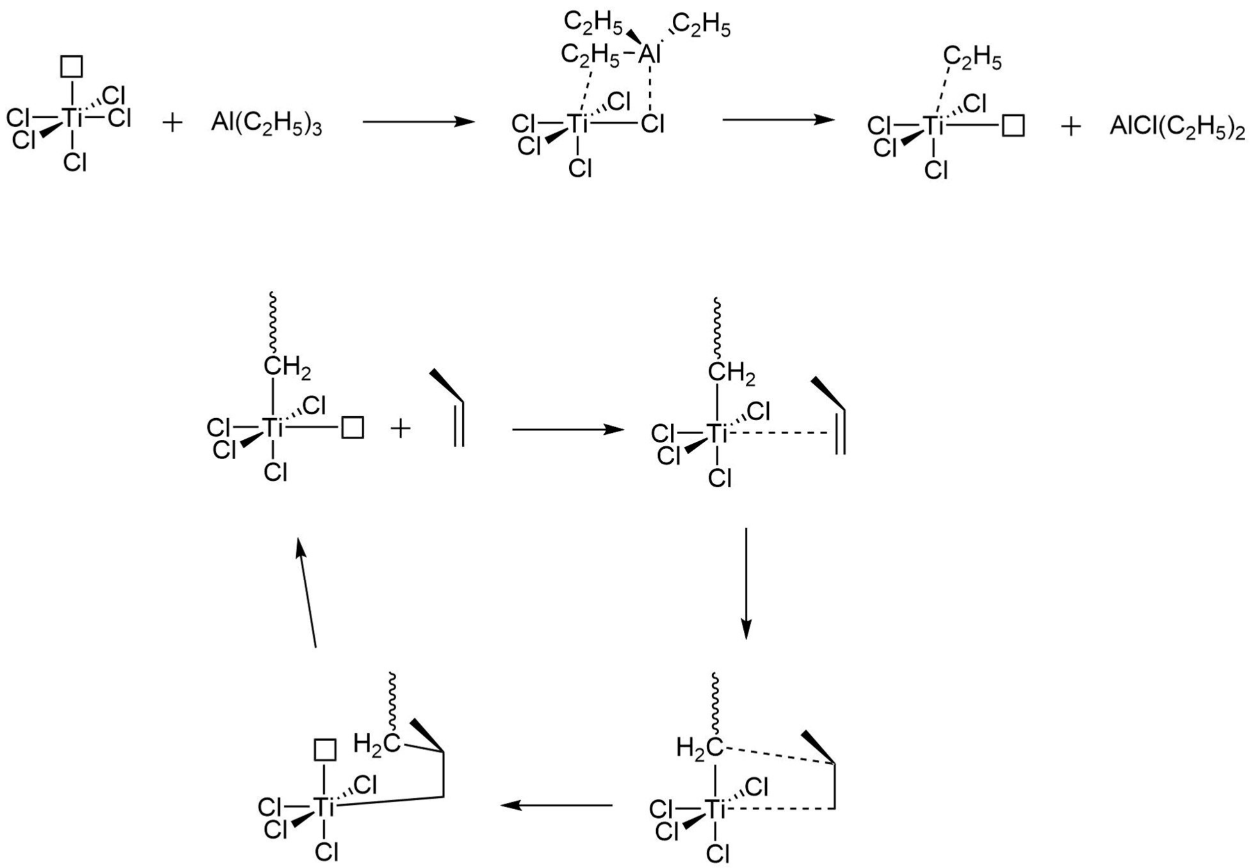


Figure 5. Mechanism of propene polymerization by Ziegler-Natta-Catalyst postulated by Cossee and Arlman

1,3-Butadiene gets inserted almost exclusively in cis-1,4 position because of a lower energy transition state of the *cis*-1,4-insertion (Figure 6).[18]

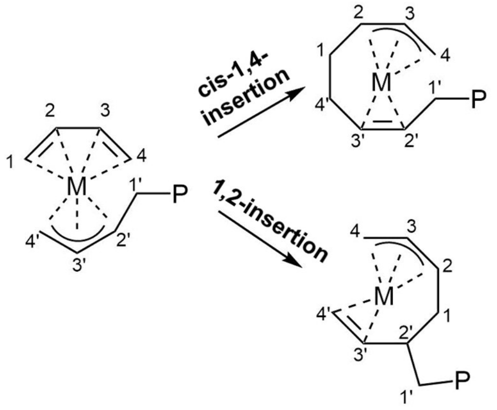


Figure 6. 1,3-Butadiene insertion by Ziegler-Natta Catalysts

The Polymerization of Butadiene with Ziegler-Natta Catalysts is done in solution with monomer concentrations of 10-15% to avoid high viscosities. The Ziegler-Natta catalyzed polymerization is the commercially most important process today for polybutadiene.[5]

High-*cis*-polybutadienes can crystallize and usually have melting points below room temperature. Polybutadienes made by radical or anionic polymerization are amorphous. Melting points and crystallization half-life at -20 °C highly correlate with cis-1,4-content and are listed in Table 2.[5]

Table 2. Melting points and crystallization half-life of different types of polybutadiene

Type	*cis*-1,4-content	T_m [°C]	crystallization half-life at -20 °C [min]
Nd-BR	97	-7	7
Co-BR	95	-11	40
Ni-BR	96	-10	25
Ti-BR	92	-23	360
Li-BR	38	amorph	-
E-BR	14	amorph	-

3.2.5 Liquid Polybutadiene

The viscosity of polymers is, apart from other factors like microstructure, dependent on their molecular weight. Since this dependency is continuous there is no sharp differentiation between a solid and liquid possible. Polybutadienes here are considered liquid at molecular weights below 50000 g/mol (for low vinyl content), since their flowability at room temperature then is easily visible to the naked eye. Since the term liquid polybutadiene is vague the grades used in this thesis are named low molecular weight polybutadienes, which all have a molecular weight below 50000 g/mol.

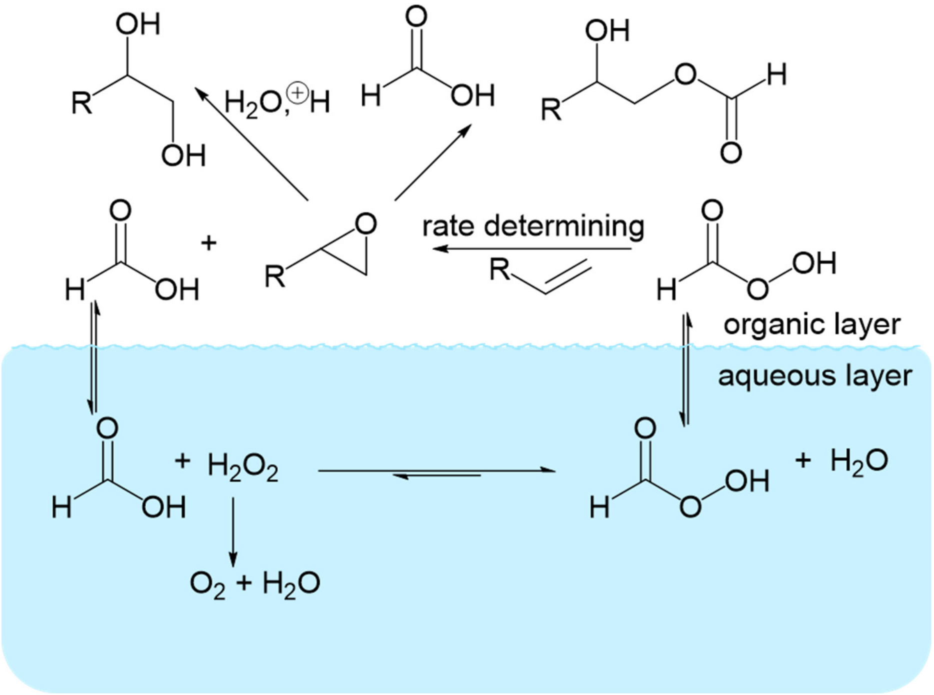
The synthesis of liquid polybutadienes mainly follows two methods: 1) a “telomerisation” system where e.g. toluene not only acts as a solvent but also as a transmetallating and chain transfer agent or 2) “living polymerization”. Anionic polymerization is used for both routes with n-butyl lithium as iniator. In route 1) in addition to the initiator, a promoter is used and the active chain end can be transferred to toluene to form benzyl lithium, which itself can initiate new chains. This CH exchange reaction is responsible for the benzyl end group of the vast majority of polymer chains made by this process. Lithene *ultra*® PM4 is made via route 1, e.g. Lithene *ultra*® N4 5000 is made via route 2.[19]

Low molecular weight polybutadiene (PBu) is a relatively cheap and readily available material. It represents a technically useful class of polymers with a variety of applications. It is equally applied as (reactive) plasticizer[20,21], binder for varnish colors[22], adhesive[23] and stabilizer[24].

3.2.6 Post Modification of Polybutadiene

Functionalized rubber is of high interest for some years now e.g. to improve the SBR filler interaction in tire rubber compounds.[25] The range of applications for low molecular polybutadienes can further be increased e.g. by introduction of epoxide groups on the polymer backbone.[26–32] Epoxidation changes the polarity of the material and transforms it into a reactive compatibilizer.[33–35] Epoxidized PBu could also function as a base polymer for reactive functionalization processes, and as access to functionalized polyolefins, i.e. after hydrogenation.[36,37] Epoxidation of PBu may be achieved by a variety of routes[36]; the epoxidation with carboxylic peracids is one of the most convenient processes concerning the availability of chemicals and experimental effort[38,39]. Latter may be provided as a presynthesized peracid[39–45] or by an *in-situ* formation from a carboxylic acid and hydrogen peroxide.[38,46,47,2,48–51,3] The *in-situ* procedure has the advantage of using smaller (final) amounts of acid and has better economics. A lower acid concentration has a positive effect on the rate of side reactions.[39,50] Formic acid as carboxylic acid has additional advantages as it combines the function of carboxylic acid for providing performic acid with toluene solubility with a pKs value that is low enough to catalyze the reaction. It is also used in this study.

The biphasic system of Scheme 1, comprising an organic phase holding the PBu and an aqueous phase with performic acid, is useful for preparing partly epoxidized PBu. The major part of the performic acid is formed in water by an (acid catalyzed) esterification of formic acid with hydrogen peroxide. It subsequently transfers into the toluene phase, where the double bonds in PBu are epoxized and formic acid is regenerated. Formic acid is thus an effective catalyst for the net oxidation of PBu with hydrogen peroxide.



Scheme 1. Biphasic epoxidation of polybutadiene by *in-situ* formed performic acid

Several side reactions may occur, in particular ring opening of the formed epoxide groups by reaction with formic acid. Formation of hydroxyl-formyl functionalized polybutadiene is favored at higher formic acid concentration and at elevated temperatures[50]. Hydroxyl groups on epoxidized PBu may crosslink the polymer by reaction with further epoxy entities. Low concentrations of formic acid are therefore favored. Hydrogen peroxide may also be decomposed in a redox disproportionation reaction, a reaction that is also faster at higher concentrations of hydrogen peroxide. It is most commonly added to the reactor in one batch because of the ease of handling.[38,2,52] The downside of the procedure next to the lower efficiency (oxygen formation) is the lower safety in comparison to a semi-batch procedure, the smaller control over the extent of epoxidation and the risk of epoxide ring opening reactions especially at elevated temperatures. Therefore, a robust procedure has been developed allowing to adjust the epoxide content to a desired level, and to provide kg scale of material. The protocol uses the principle depicted in Scheme 1 with low formic acid concentrations and the semi-batch operation in hydrogen peroxide.

These epoxidized polybutadienes represent a reactive intermediate for further functionalization reactions. The functionalization also opens new application possibilities such as electrolytes[53] or gas separation[54]. The addition of amines is therefore an interesting field of research in which many possible reaction pathways are reported[36].

A simple and straightforward method to add amines to the polymers backbone is the nucleophilic ring opening of epoxides[36]. Epoxide groups in the polybutadiene backbone, however, show a markedly low reactivity towards nucleophiles such as amines, compared to asymmetrically substituted epoxides[55]. Various catalysts were proposed over time for the ring opening of small molecular epoxides. Metal halides[56–58], metal triflates[59–62], solid phase fixed catalysts[63] and metal free catalysts[64,65] were studied for their activity in epoxide ring opening. Most of these studies however used asymmetric epoxides or cyclohexene oxide, which show a considerably higher reactivity towards the ring opening compared to epoxides on the polybutadiene backbone.

Very few studies cover the ring opening of epoxidized polybutadienes with amines and those published show low conversions of epoxide groups in the backbone.[36] In this study lithium bromide was used in a solvent free process for the nucleophilic ring opening of epoxides in low molecular weight polybutadiene with amines. A simple synthetic pathway is presented to quantitatively open the epoxide groups in the backbone of polybutadiene. Aditionally the kinetics of the ring opening, side reactions and changes in properties of the functionalized polybutadienes were studied.

Amines can be alkylated with alkylating agents like iodomethane or dimethyl sulfate in the presence of a base.[66–69] The methylation, if allowed, is proceeding until ammonium ion formation. Amines are very reactive towards alkylation because of their high nucleophilicity. The Alkylation with iodomethane usually is proceeding at room temperature without any additional catalysts. The quaternization of polybutadienes was reported before using modified initiators in anionic polymerization[70] or post modification reactions[71]. These examples include either intervention in the polymerization process or precious metal catalysts. A straight forward reaction scheme is presented here to introduce ammonium ions into the polybutadiene backbone using simple reaction steps without precious metal catalysts.

Ammonium ion carrying polymers can be used as ion exchanger[72] or antistatics[73].

3.3 Rheology and Viscoelasticity

Rheology is the science of flow and deformation. The correlation between the deformation ε of an ideal spring induced by a force F can be described by Hooke's law:

$$F = E * \varepsilon$$

E in this case is a material constant describing its elasticity. This can be transferred to the uniaxial deformation of an ideal solid where the force is replaced by the stress (force per area).[74]

In ideal fluids a correlation can be drawn between stress and deformation with time. In shear deformation these values are shear stress σ and shear rate $\dot{\gamma}$:

$$\sigma = \eta * \dot{\gamma}$$

The constant of proportionality is the viscosity η, which is independent on the shear rate.

Real materials are neither ideal solids nor ideal fluids which makes the dynamic viscosity η dependent on the shear rate $\dot{\gamma}$. The observed behavior can be e.g. shear thinning or shear thickening. Shear thinning is observed with most polymer melts, where entanglements are influencing the behavior at higher shear rates. They show newtonian behavior at low shear rates, at higher shear rates the loosening of entanglements predominates, and the viscosity decreases. The opposite behavior (shear thickening) can be observed e.g. due to the formation of strain induced crystallization (Figure 7).

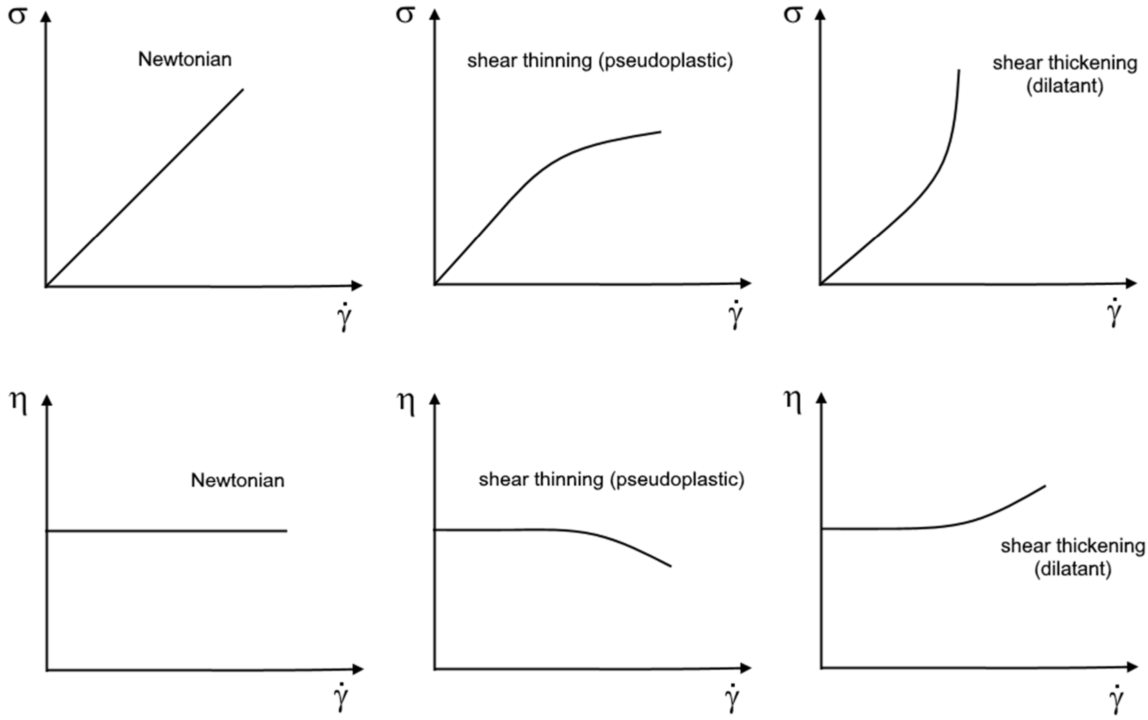


Figure 7. Newtonian, shear thinning (pseudo plastic) and shear thickening (dilatant) behavior

The range of shear rates in everyday life applications is very broad. Typical shear rates of some applications are depicted in Figure 8.[75]

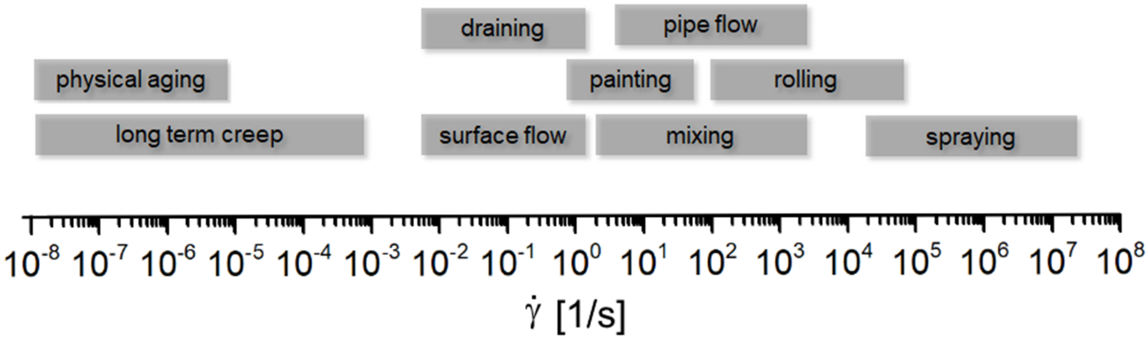


Figure 8. Shear rate and some applications

3.3.1 Cox-Merz Relation

Usual plate-plate rheometers cover a shear rate range of 10^{-2} to 10^{2} s^{-1}. Capillary viscometers cover shear rate ranges between 10^{-1} s^{-1} and 10^{4} s^{-1}. Combined both methods can cover a broad range of shear rate but requires extensive analytical effort and material.[1] An easy empirical method was introduced 1958 by W. P. COX AND E. H. MERZ.[76] They postulated the dynamic viscosity $\eta(\dot{\gamma})$ at a constant shear rate equals the absolute complex viscosity $|\eta^{*}(\omega)|$ at constant angular frequency ω if $\dot{\gamma} = \omega$. With this relation a broad range of shear rate can be covered by simple oscillatory shear experiments. This relation is valid for most unfilled polymer solution and melts and it makes the oscillatory shear experiment a powerful tool in analyzing polymer melts.[77]

3.3.2 Small Amplitude Oscillatory Shear (SAOS)

In oscillatory shear experiments the deformation is not continuously increasing but is applied sinusoidal. This sinusoidal deformation γ generates a stress response σ which is also sinusoidal as long as the amplitude does not exceed the linear viscoelastic region of the material.

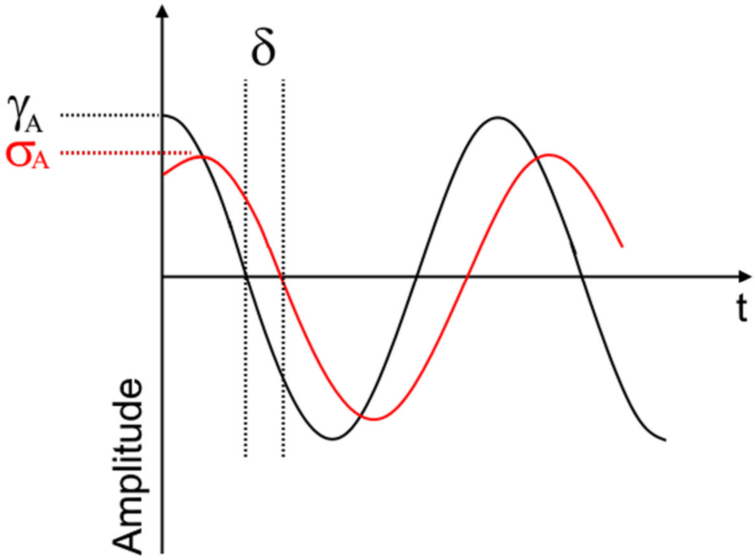


Figure 9. Applied amplitude and stress response in an oscillatory shear experiment

In ideal solids the response comes without delay and the phase angle δ is 0 °. Ideal fluids respond with a phase angle of 90 °. Viscoelastic materials like polymer melts have phase angles somewhere in between. This complex stress response G^{*} can be divided into elastic and viscous contribution to the stress response and are represented by the storage modulus G’ and the loss modulus G’’ which are defined as follows:

$$G' = \frac{\sigma_A}{\gamma_A} * cos\delta$$

$$G'' = \frac{\sigma_A}{\gamma_A} * sin\delta$$

$$G^* = G' + i * G''$$

The absolute complex viscosity can be determined from the absolute complex stress response and the angular frequency

$$|\eta^*| = \frac{|G^*|}{\omega}$$

The range of frequency in rheometers is limited to around 10^{-3} to 10^3 rad/s.[75] It is also very time consuming to measure at low frequencies. With time-temperature superposition the range of frequency can be expanded.

3.3.3 Time Temperature Superposition

The time temperature superposition (TTS) usually is applied to non-crosslinked, unfilled materials. Additionally, the following requirements for the investigated materials need to be met for the applied temperature range:[77]

- The investigated materials mustn’t follow erratic change in structural character
- The material mustn’t undergo strain crystallization
- The glass transition temperature of the material should be significantly below the temperature of measurement

The principle of TTS states a comparable influence on rheological properties for the time frame of shear stress and the temperature. A decrease in temperature has a similar influence on shear moduli like the increase in frequency. Several measurements in a certain range of frequency at different temperatures can therefore be shifted to a master curve with an expanded range of frequency. Frequency sweeps measured at higher temperatures compared to the reference temperature are shifted to lower frequencies and vice versa (Figure 10).

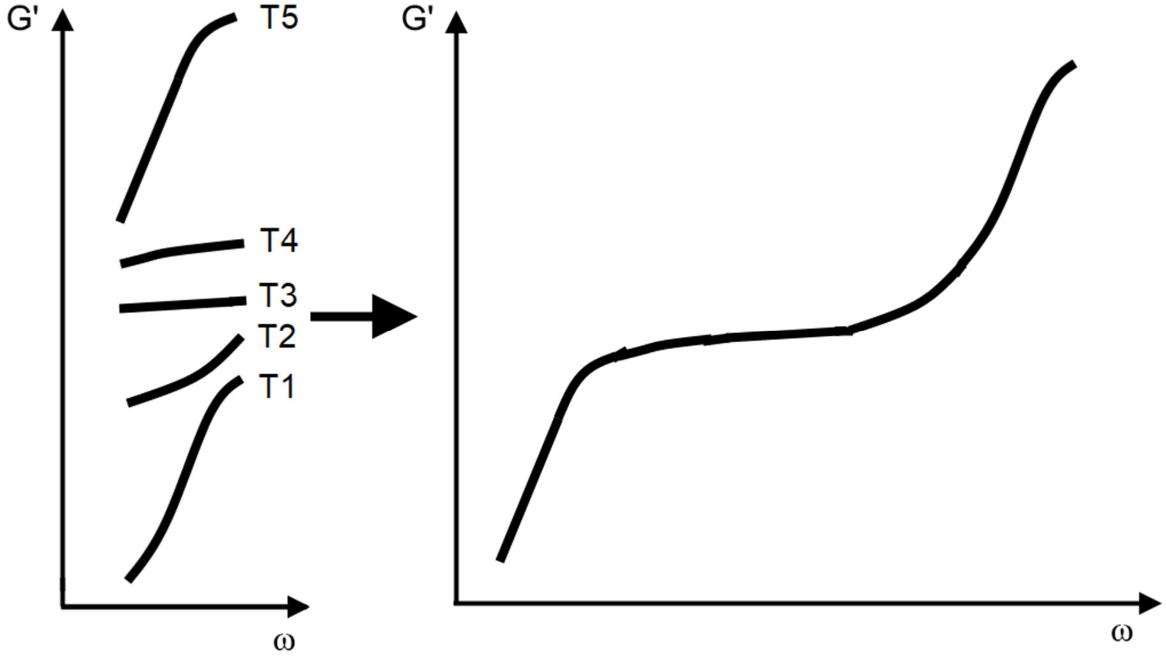


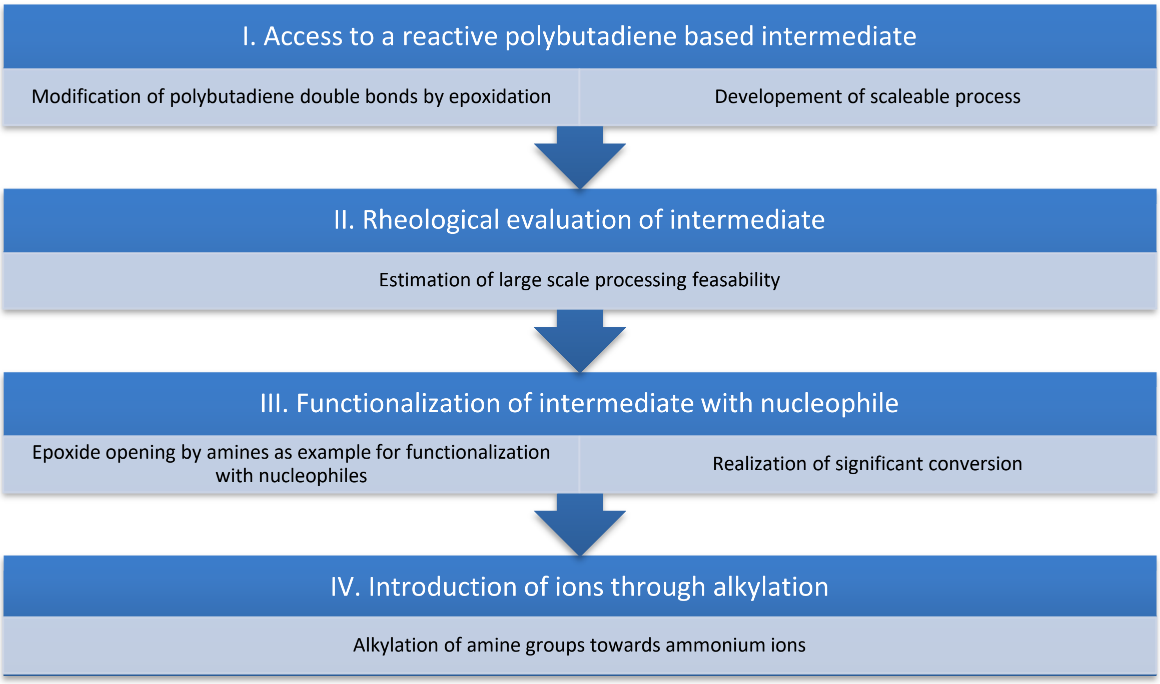
Figure 10. Schematic shifting of temperature sweep measurements to a master curve

4 Motivation

The aim of this work is the development of a reaction process for post modification of polybutadienes. The idea is to use the cheap and readily available polybutadiene and introduce polar groups to the polymer backbone to widen the range of application.

The identified pathway includes the epoxidation of double bonds to get a reactive intermediate. This intermediate can be further functionalized with various nucleophiles of which amines as an example are considered in detail. Additionally, the amine groups are alkylated towards ammonium ions to widen the range of possible applications even further. Since the functionalization is expected to have an influence on the polybutadiene properties, the rheological behavior is also of interest, and has been studied too.

Low molecular weight polybutadienes are used as model materials for better processing and analytical evaluation.



5 Results and Discussion

5.1 Scalable Semi-Batch Process for Epoxidation of Polybutadienes

Various commercially available polybutadienes with relatively low molecular weights were used in this study. They have a similar microstructure with a vinyl content below 20% and almost no cyclic groups (Table 3; Figure 11). They appear as low to medium viscous oils. The PBus were dissolved in toluene to a weight percentage of 10-15%, being in the range of concentration in a typical PBu production facility.[5] The resulting viscosity of the solutions guarantees a sufficient fast mass transport between the phases (vide infra). The phase relationships of the liquid-liquid system were kept in the range of 5-35 for V_{org}/V_{aq}.

Table 3. Low molecular weight polybutadienes

PBu	molecular mass (M_n) [g/mol]	1,4-DB [%]	1,2-DB [%]	cyclic-DB [%]	*cis:trans* ratio[2]
Lithene PM4	1500	80	19	<1	40:60
Lithene N4-5000	5000	88	12	0	40:60
LBR-307	8000	86	14	0	40:60
LBR-305	26000	91	9	0	40:60

The progress of the epoxidation was analyzed offline from samples taken during the reaction. Proton NMR spectroscopy is useful to analyze the mixture with respect to conversion of the double bonds. The ^{1}H-NMR was used as the main method to determine the degree of functionalization because of its quick and easy operability and its congruence with results from elemental analyses (vide infra). A typical spectrum with the assignments is shown in Figure 11. The stacked spectra of the samples show the course of an epoxidation with samples taken hourly from the reaction mixture.

---

[2] Due to overlapping peaks, the ratios are just approximate values

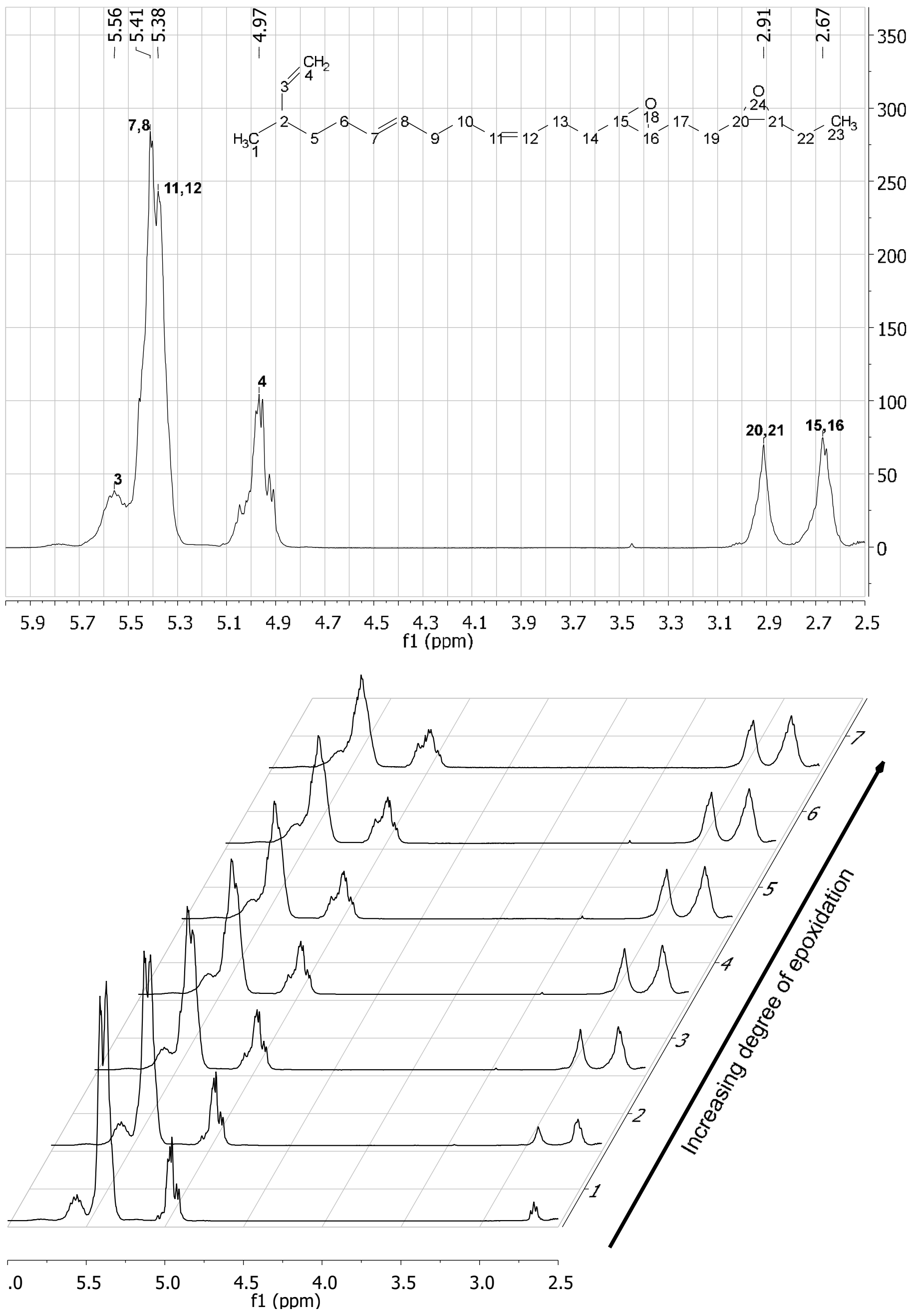


Figure 11. ^{1}H-NMR spectrum of epoxidized polybutadiene (Lithene PM4)

The epoxide content of the polymer was also determined by titration method of JUNG and KLEEBERG[78] (Figure 12). The titration measurements are only until 15% of conversion in good accordance with the ^{1}H-NMR based data.

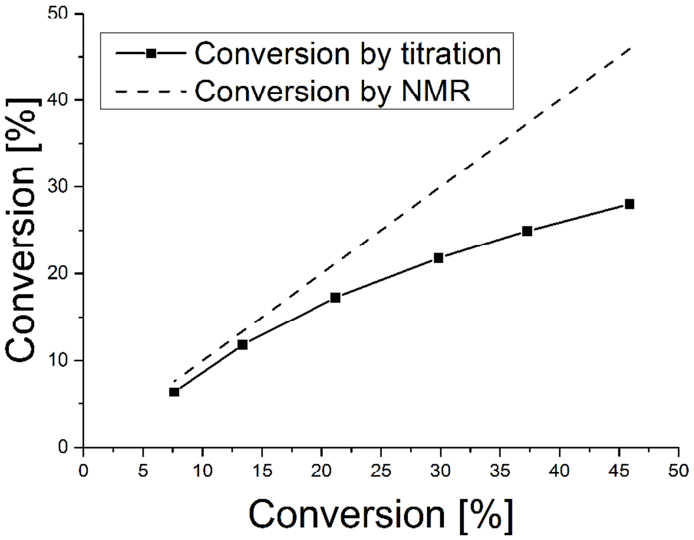


Figure 12. Titration of epoxidized polybutadiene (Lithene PM4) samples with different degrees of conversion

MALDI-Tof spectra show the expected mass separation of 54 (butadiene; Figure 13) and 70 (butadiene oxide; Figure 14) between the individual signals. The molecular weight of Lithene PM4 calculated from the distribution in the MALDI-Tof spectrum is 1458 g/mol, close to the producers provided value of 1500 g/mol. The spectrum of an epoxidized sample (43.4% by NMR) has many more signals and the intensity of the individual masses is much lower as expected from a random epoxidation of the double bonds. The differences of 16 Da in mass corresponding to the consecutive addition of oxygen atoms between signals are nevertheless recognizable and the signals can be assigned to chains with different degrees of epoxidation around 40% to 50%. Signals of higher mass seem of lower intensity, possibly because of instability of the ionized species.[79]

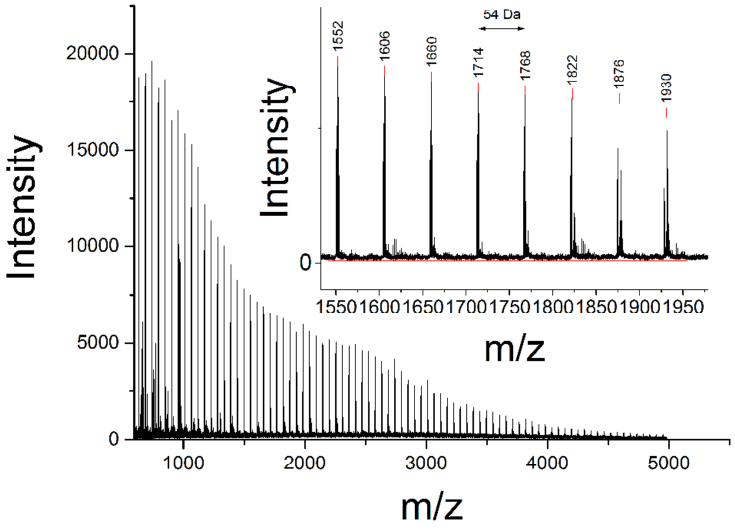


Figure 13. MALDI-TOF Analysis of Lithene PM4

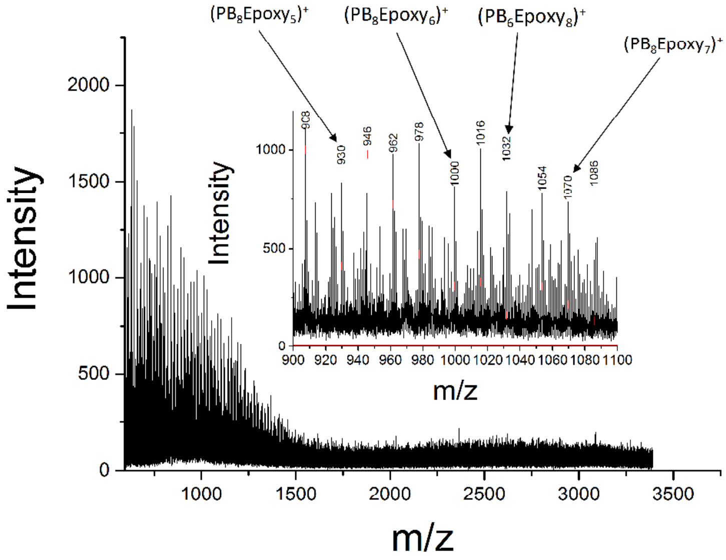


Figure 14. MALDI-TOF analysis of an epoxidized polybutadiene sample

The kinetics of the epoxidation of unsaturated rubbers with peracids has been reported upon for batch reactions.[80–82,3,83] The formation of performic acid is much slower than the epoxidation of the double bonds, and thus the concentration of formic acid (FA) and hence performic acid (PFA) will have a quasi steady state. The phase exchange process of performic acid is presumed fast under the conditions. Reactions at various stirrer frequencies above 300 rpm indeed showed no difference in conversion of the double bonds. It is thus not necessary to consider the rate of phase transfer. The actual concentration of FA in the aqueous phase however is of high relevance, and the distribution of FA over the organic and aqueous phase is complex and needs consideration[84–86] The major reactions are (I) the general, acid catalyzed, formation of PFA from FA and hydrogen peroxide (HP) in the aqueous phase (and probably partially in the organic phase), (II) the hydrolysis of PFA to FA and HP, and (III) the epoxidation of olefins by PFA (Scheme 2).[87]

$$FA + H_2O_2 \rightarrow PFA + H_2O \qquad -\frac{d[FA]}{dt} = k_1 * [FA] * [H^+] * [H_2O_2]$$

$$PFA + H_2O \rightarrow FA + H_2O_2 \qquad -\frac{d[PFA]}{dt} = k_{-1}[PFA]$$

$$PFA + olefin \rightarrow epoxide + FA \qquad \frac{d[epoxide]}{dt} = k_2[olefin][PFA]$$

$$FA_{tol} \leftrightarrow FA_{aq} \quad K\ as\ function\ of\ [H_2O_2], conversion,$$

$$3PFA \rightarrow 2FA + H_2O + CO_2 + O_2 \qquad -\frac{d[PFA]}{dt} = k_d[PFA]$$

Scheme 2. Reactions in the system and their rate laws

The initial rates of epoxidation at high olefin concentration may scale linearly with the rate of PFA formation. The overall epoxidation is thus initially determined by the rate law of $\frac{d[epoxide]}{dt} = k_{obs} * [FA_{aq}] * [H^+] * [H_2O_2]$; the concentration of PFA can be considered constant because of the assumed large differences in the rates of formation and consumption by hydrolysis and epoxidation. Overall a complex system arises, and it occurred non-trivial to simulate the process. In general, it seems necessary in simulations to consider many reactions of the system, also for a course description. The relevant concentration of FA_{aq} and consequently the pH-value is a function of the phase equilibrium constant and the volume of the organic and aqueous phase. The phase equilibrium constant may change with conversion (Scheme 2). In addition, HP is partly soluble in toluene, and may form PFA also in the organic phase. The decomposition of PFA proceeds along several pathways to several products, including water, carbon dioxide and oxygen and cannot apriori be neglected (Scheme 2).[87] The decomposition leads to a decrease in acid concentration and comprises a loss of oxidizing equivalents. Both effects may be relevant to the rate of reaction and conversion, and become more apparent at higher reaction temperatures, longer reaction times and higher conversion, in particular at high acid and hydrogen peroxide concentrations. Also dependencies of the epoxidation rate on olefin conversion have been observed.[3]

5.1.1 Epoxidation with Hydrogen Peroxide Feed

The semi-batch epoxidation of PBu was investigated with a feed of hydrogen peroxide, maintaining the initial amount of FA. The concentration of FA is therefore consequently decreasing with reaction time. This is advantageous for preventing side reactions, in particular for precluding the addition of FA to the epoxidized double bonds, which is also an acid catalyzed reaction. Thus, the acid concentration is decreasing by conversion and by dilution as the concentration of the epoxide entities increases. It would consequently allow a higher initial amount of FA at the start of the PBu functionalization and thus to have higher initial rates. The conversion of double bonds during an epoxidation reaction in semi-batch mode with respect to hydrogen peroxide shows an about linear dependency with time up to a conversion of 15% of the double bonds under the conditions used by DILCHER[88] (Figure 15; Table 4). Performing the reaction in semi-batch mode thus gives a high predictability up to that level of epoxidation. FA related ring opening reactions leading to hydroxyl carbonyl entities could not be detected. The initial rate increases linearly with the HP feeding rate to a rate of 7.23 mL/h. Higher H_2O_2 (30% in H_2O) feeding rates lead to a less than linear increase. This indicates that the conversion of HP is slower than the feeding rate or a saturation in PFA sets in. The initial about linear rate of epoxidation continuously decreases at conversions above 10-15 mol% (Figure 16), in particular noticeable for higher feeding rates. Course simulations show that this is majorly explainable by the decrease in $[FA_{aq}]$ and concomitantly the $[H^+]$, as has been observed by different HP concentrations in batch reactions.[3] The concentration of HP increases steadily as the rate of conversion to epoxides is lower than the feeding rate.

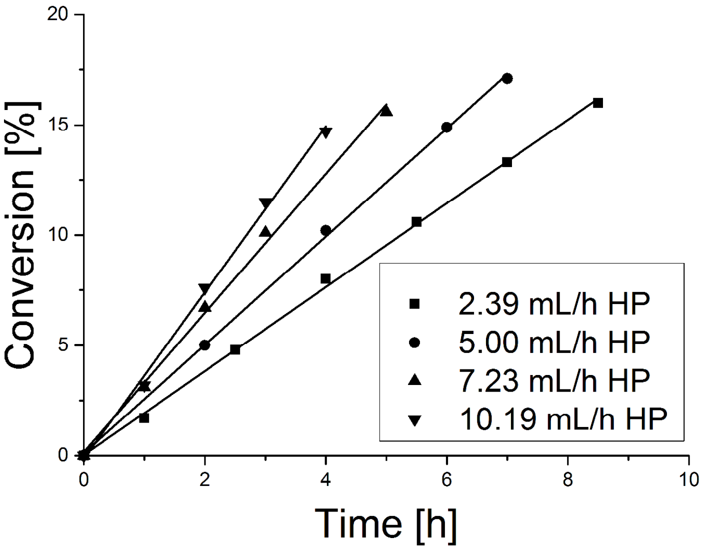


Figure 15. Double bond conversion and reaction rates in a semi-batch process (56.6 g Lithene PM4) with various feeds of hydrogen peroxide at 65 °C with 2.03 mL FA in 369 mL toluene (Table 6)[88]

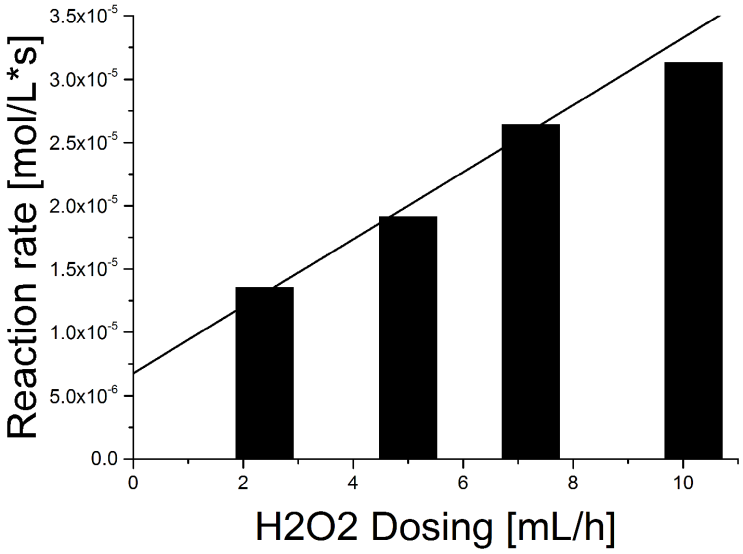


Table 4. Conversion and reaction rates of semi-batch-epoxidations – conditions: 2.03 mL FA, 369 mL toluene at 65 °C[88]

#	time [h]	final conversion [%]	H_2O_2 feeding rate [ml/h]	reaction rate [mol/L*s]
1	4	14.7	10.19	$3.13 \cdot 10^{-5}$
2	5	15.6	7.23	$2.64 \cdot 10^{-5}$
3	7	17.1	5.00	$1.91 \cdot 10^{-5}$
4	8.5	16.0	2.39	$1.35 \cdot 10^{-5}$

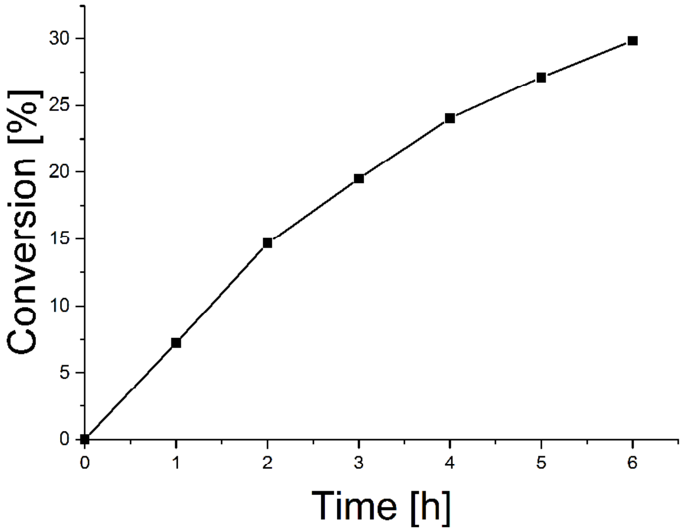


Figure 16. Double bond conversion of a typical epoxidation of 35.6 g Lithene PM4 in a semi-batch process - conditions: 10 mL/h HP at 64 °C, 3 mL FA and 255 mL toluene

The initial rates were consequently determined in dependence of the FA amounts at a feeding rate of 0.0981 mol/h HP (Figure 17, Table 5). The rate again shows an initial linear course followed by a continuously decrease in rate. The initial rates scale in a complex manner with the amount of FA as expected for the system of reactions in Scheme 2.

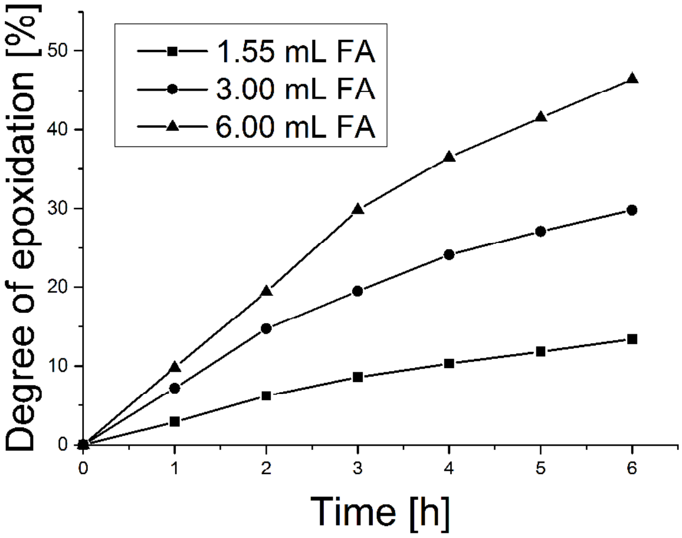


Figure 17: Double bond conversion for different amounts of formic acid and 14 wt% of Lithene PM4 in toluene with 10 mL/h HP at 65 °C (Table 6 entry 33-50)

Table 5. Conversion and reaction rates of epoxidation as a function of the FA concentration.

#	FA [mol/L]	Conversion (6 h) [%]	initial reaction rate [mol/L*s]
1	0.11	13.4	$3.25 \cdot 10^{-5}$
2	0.22	29.8	$5.35 \cdot 10^{-5}$
3	0.44	46.4	$6.46 \cdot 10^{-5}$

Table 6: Semi-batch epoxidations of Lithene PM4 in a 1 L steel and glass and 10 L steel reactor at 65 °C

#	PBu [g]	toluene [mL]	FA [mL]	feeding rate H_2O_2 [mL/h]	time [h]	conversion [%]
15	56.6	369	2.03	2.39	1	1.7
16	56.6	369	2.03	2.39	2.5	4.8
17	56.6	369	2.03	2.39	4	8.0
18	56.6	369	2.03	2.39	5.5	10.6
19	56.6	369	2.03	2.39	7	13.3
20	56.6	369	2.03	2.39	8.5	16.0
21	56.6	369	2.03	5.00	2	5.0
22	56.6	369	2.03	5.00	4	10.2
23	56.6	369	2.03	5.00	6	14.9
24	56.6	369	2.03	5.00	7	17.1
25	56.6	369	2.03	7.23	1	3.1
26	56.6	369	2.03	7.23	2	6.7
27	56.6	369	2.03	7.23	3	10.1
28	56.6	369	2.03	7.23	5	15.6
29	56.6	369	2.03	10.19	1	3.2
30	56.6	369	2.03	10.19	2	7.6
31	56.6	369	2.03	10.19	3	11.5
32	56.6	369	2.03	10.19	4	14.7
33	35.6	255	3.00	10.0	1	7.2
34	35.6	255	3.00	10.0	2	14.7
35	35.6	255	3.00	10.0	3	19.5
36	35.6	255	3.00	10.0	4	24.1
37	35.6	255	3.00	10.0	5	27.1

#	PBu [g]	toluene [mL]	FA [mL]	feeding rate H_2O_2 [mL/h]	time [h]	conversion [%]
38	35.6	255	3.00	10.0	6	29.8
39	37.1	263	1.55	10.0	1	2.9
40	37.1	263	1.55	10.0	2	6.2
41	37.1	263	1.55	10.0	3	8.6
42	37.1	263	1.55	10.0	4	10.3
43	37.1	263	1.55	10.0	5	11.8
44	37.1	263	1.55	10.0	6	13.4
45	35.5	255	6.00	10.0	1	9.8
46	35.5	255	6.00	10.0	2	19.4
47	35.5	255	6.00	10.0	3	29.8
48	35.5	255	6.00	10.0	4	36.5
49	35.5	255	6.00	10.0	5	41.4
50	35.5	255	6.00	10.0	6	46.4
51	679	4480	48.8	50.0	1.67	3.2
52	679	4480	48.8	50.0	3	6.2
53	679	4480	48.8	50.0	4.5	9.2
54	679	4480	48.8	50.0	6	12.1
55	679	4480	48.8	50.0	7.5	15.0
56	679	4480	48.8	60.0	1.5	3.8
57	679	4480	48.8	60.0	3	8.3
58	679	4480	48.8	60.0	4.5	11.8
59	679	4480	48.8	60.0	6	15.0
60	679	4480	48.8	60.0	7.5	18.1

The temperature dependence of the rate of epoxidation of Lithene PM4 was determined between 54 and 80 °C at higher temperatures than reported upon in the literature [2,44,50,3,83] The initial concentration of FA was 0.27 mol/L and the rate of feeding HP was 18 mol%/h in relation to 1,4-double bonds. The conversion of PBu after 6 h increases with temperatures up to 75°C (Figure 18). The observed rate constants as function of the temperature are indicating an overall activation energy for the process of about 29 kJ/mol. The somewhat lower activation energy compared to published numbers might be attributed to the lower molecular weight of the polybutadienes used in this study.[3],[3] Higher temperatures lead to a lower conversion. Evidence for epoxide opening reactions could not be found in any of the ^{1}H-NMR spectra of the samples. It has been reported that the decomposition rate of PFA has a stronger temperature dependence than the *in-situ* formation of the same[89]. Thus the decrease in the degree of epoxidation could be related to the increasing rate of decomposition of PFA or H_2O_2, due to a resulting decrease of PFA and FA concentration in the system (Scheme 2).[87] The progress of conversion was monitored at four of the eight reactions (Figure 18) of which the maximum rate constants are listed in Table 7.

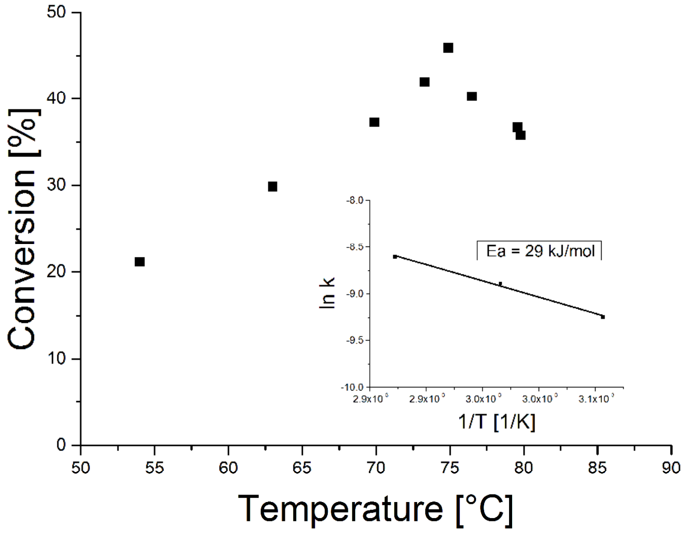


Figure 18. Temperature dependency of epoxidation degree with Arrhenius-plot – conditions: 16 wt% Lithene PM4 in toluene and 1.5 wt% FA, 18 mol% HP in relation to 1,4-double bonds per hour (Table 8)

Table 7. Rate constants and conversions of epoxidations at various temperatures

temperature [°C]	final conversion [%]	rate constant k [L/mol*s]
54	21.2	$9.67\cdot10^{-5}$
64	29.8	$1.38\cdot10^{-4}$
75	45.9	$1.83\cdot10^{-4}$
80	36.7	$1.54\cdot10^{-4}$

Table 8. Semi-batch epoxidations of Lithene PM4 in a 1 L glass reactor at different temperatures

#	PBu [g]	Temperature [°C]	toluene [mL]	FA [mL]	feeding rate H_2O_2 [mL/h]	time [h]	conversion [%]
61	35.4	54	256	3	10	1	3.7
62	35.4	54	256	3	10	2	8.8
63	35.4	54	256	3	10	3	12.4
64	35.4	54	256	3	10	4	15.8
65	35.4	54	256	3	10	5	18.3
66	35.4	54	256	3	10	6	21.2
67	35.6	64	255	3	10	1	7.2
68	35.6	64	255	3	10	2	14.7
69	35.6	64	255	3	10	3	19.5
70	35.6	64	255	3	10	4	24.1
71	35.6	64	255	3	10	5	27.1
72	35.6	64	255	3	10	6	29.8
73	64.6	70	475	6	18	6	37.3
74	65.2	73	474	6	18	6	42.0
75	61.6	75	450	5.5	17	1	11.4
76	61.6	75	450	5.5	17	2	21.9
77	61.6	75	450	5.5	17	3	30.1
78	61.6	75	450	5.5	17	4	37.3
79	61.6	75	450	5.5	17	5	42.1
80	61.6	75	450	5.5	17	6	45.9
81	64.8	77	495	6	18	6	40.3
82	65.3	80	477	6	18	1	7.1
83	65.3	80	477	6	18	2	18.5
84	65.3	80	477	6	18	3	25.5
85	65.3	80	477	6	18	4	30.6
86	65.3	80	477	6	18	5	34.0
87	65.3	80	477	6	18	6	36.7
88	64.1	80	484	6	18	6	35.8

5.1.2 Larger Scale Reactions

The reaction conditions of the semi-batch operation in form of polybutadiene concentration, formic acid concentration and the relative feeding rate of hydrogen peroxide were transferred to larger scale. A temperature of 65 °C was chosen for the scale up reactions, somewhat below the maximum rate at 75 °C where the decomposition of PFA becomes noticeable. It was found, that reactions in a 10 L reactor are very comparable to those in a 1 L steel reactor (Figure 19).[88] Again, a linear increase of double bond conversion was found with time and feeding rate. The observed rate constants are basically the same even though a higher concentration in FA is needed. The process is thus easily scaled up.

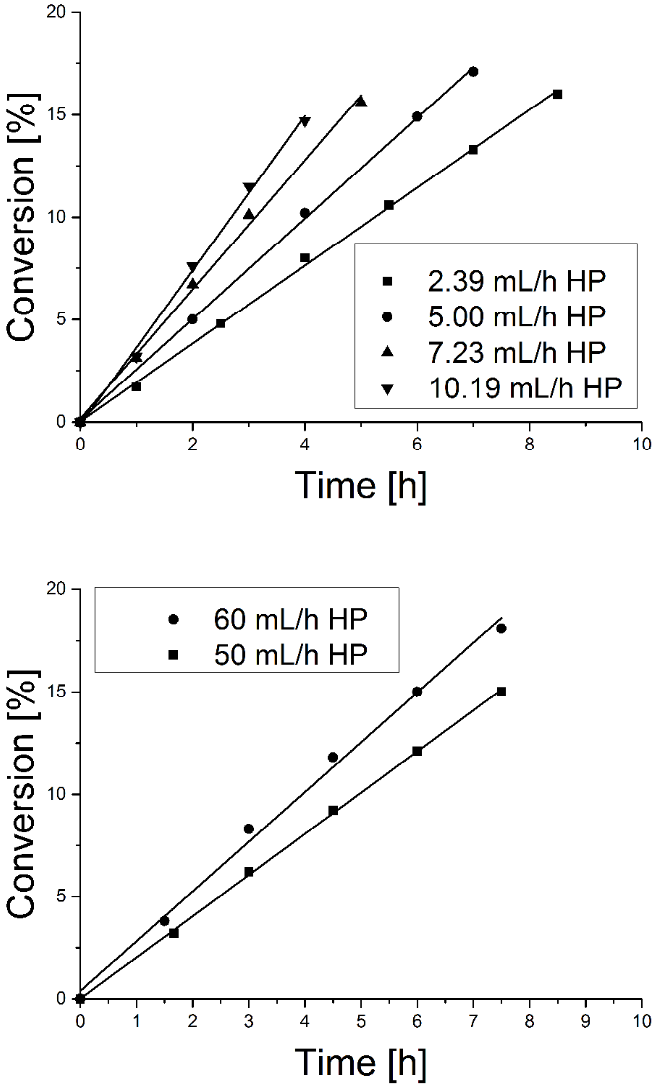


Figure 19. Double bond conversion of 56.6 g and 679 g Lithene PM4 in a 1 L (top) and 10 L (bottom) steel reactor respectively with various dosing rates - conditions: 65 °C and 2.03 mL and 48.8 mL in 369 mL and 4482 mL toluene respectively[88]

5.1.3 Higher molecular weight polybutadienes

The process described was also applied to the other polybutadiene samples (Table 3). The differences in microstructure and molecular mass of the PBus of this study are of minor importance for the rate of conversion in the range considered here (Figure 20; Table 9). The higher viscosity of the toluene solution of PBu with a higher molecular mass is not influencing the reaction rate. The formation of PFA remains the rate determining step of the reactions in **Scheme 2**.[87] Likewise, the cis/trans ratio of the 1,4-double bonds is not substantially changed by the epoxidation. Former studies revealed a rate of epoxidation descending in the order *cis*-1,4 > *trans*-1,4 > *vinyl*-1,2.[2] Indeed the cis-1,4 entities are somewhat faster epoxidized than trans-1,4 units (Table 10). None of the polybutadienes in this work showed an epoxidation of vinyl groups within the degrees of epoxidation reached. The vinyl double bond content of maximum 19% might be too low to detect epoxidation, which will be negligibly.

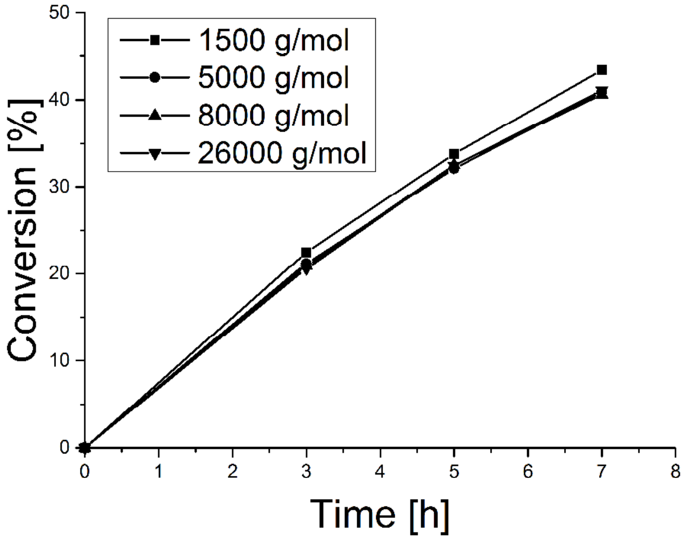


Figure 20. Double bond conversion of different polybutadienes in a 10 L steel reactor - conditions: 75 °C, 18 wt% PBu in toluene and 1.5 wt% FA, 0.3 mol% HP in relation to double bonds per hour (Table 11)

Table 9. Reaction rates of different molecular weight polybutadienes.

molecular mass [g/mol]	conversion (7h) [%]	initial reaction rate [L/mol*s]
1500	43.4	$4.73 \cdot 10^{-5}$
5000	40.9	$4.79 \cdot 10^{-5}$
8000	40.6	$4.77 \cdot 10^{-5}$
26000	41.1	$4.75 \cdot 10^{-5}$

Table 10. Cis:trans selectivity of 1,4-epoxidation

PBu	degree of epoxidation [%]	*cis*:*trans* ratio
Lithene PM4	22.5	48:52
Lithene PM4	33.8	48:52
Lithene PM4	43.4	47:53
Lithene N4-5000	21.2	51:49
Lithene N4-5000	32.1	50:50
Lithene N4-5000	40.9	49:51
LBR-307	20.9	50:50
LBR-307	32.5	49:51
LBR-307	40.6	48:52
LBR-305	20.6	51:49
LBR-305	32.4	50:50
LBR-305	41.1	49:51

Table 11. Semi-batch epoxidations of different polybutadienes in a 10 L steel reactor at 75 °C

#	PBu	PBu [g]	toluene [mL]	FA [mL]	feeding rate H_2O_2 [mL/h]	time [h]	conversion [%]
89	PM4	1002	6514	82	200	3	22.5
90	PM4	1002	6514	82	200	5	33.8
91	PM4	1002	6514	82	200	7	43.4
92	N4	1000	6514	82	200	3	21.2
93	N4	1000	6514	82	200	5	32.1
94	N4	1000	6514	82	200	7	40.9
95	LBR-307	700	4561	58.2	140	3	20.9
96	LBR-307	700	4561	58.2	140	5	32.5
97	LBR-307	700	4561	58.2	140	7	40.6
98	LBR-305	700	4562	57.4	140	3	20.6
99	LBR-305	700	4562	57.4	140	5	32.4
100	LBR-305	700	4562	57.4	140	7	41.1

5.1.4 Material Properties

The introduction of epoxide groups increases the rigidity and polarity of the polymer, and therefore is increasing the glass transition temperature (Figure 21).[3] The glass transition temperatures of the various PBus are about the same, and this holds also for the epoxidized derivatives as along as the degree of epoxidation is comparable (Table 12).[3,90] The minor differences are related to differences in the microstructure, i.e. the content of 1,2-vinyl entities (Table 3). The increase of the glass transition temperature (T_g) follows a general Fox equation (eq. 1, Figure 21). An increase in T_g of 0.83-0.93 K per mol% of epoxide groups is found, in accordance with prior results[3].

$$\frac{1}{T_g} = \frac{w_{epoxides}}{T_{g,100\%}} + \frac{w_{polybutadiene}}{T_{g,0\%}} \tag{1}$$

$w_{epoxides}$ and $w_{polybutadiene}$ define the ratio of weight of epoxidized and non-epoxidized butadiene building blocks, $T_{g,100\%}$ and $T_{g,0\%}$ represent the T_g of PBu with all double bonds oxidized and non-epoxidized PBu respectively.

Table 12. Glass transition temperatures of investigated polybutadienes

PBu	molecular mass (M_n) [g/mol]	glass transition (T_g) [K]
Lithene PM4	1500	181.9
Lithene N4-5000	5000	181.3
LBR-307	8000	180.6
LBR-305	26000	178.7

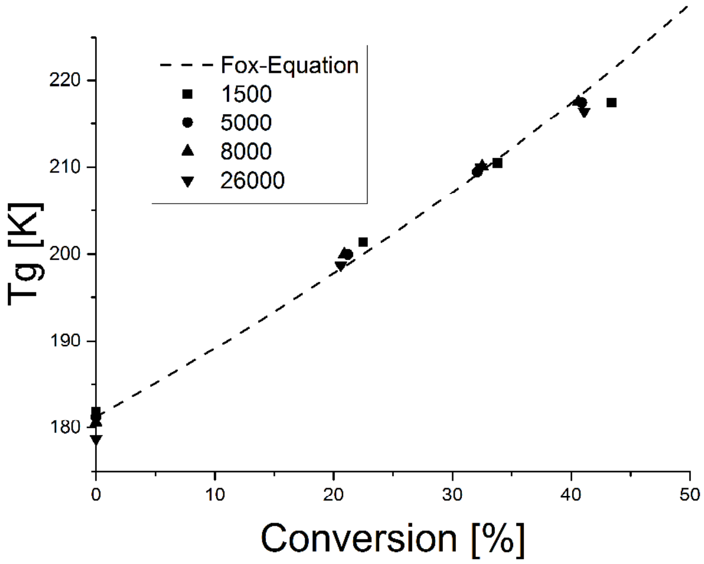


Figure 21. Increase in T_g with degree of epoxidation following the fox-equation

Table 13. Increase of T_g per percentage point of epoxidation

molecular weight (M_n) [g/mol]	increase in T_g per mol% of double bond epoxidation [K]
1500	0.83
5000	0.88
8000	0.91
26000	0.93

The bulk viscosity of the polybutadienes increases about one order of magnitude by epoxidizing to about 50 mol% (Figure 22; Table 15).[16] This is again related to change in chain stiffness and the concomitant increase in glass temperature.[91]

Table 14. Melt viscosities of polybutadiene of this study at 25°C.

PBu	molecular weight (M_n) [g/mol]	viscosity [Pa*s]
Lithene PM4	1500	0.7-0.95 [3]
Lithene N4-5000	5000	3-5 [3]
LBR-307	8000	1.5 [4]
LBR-305	26000	40 [4]

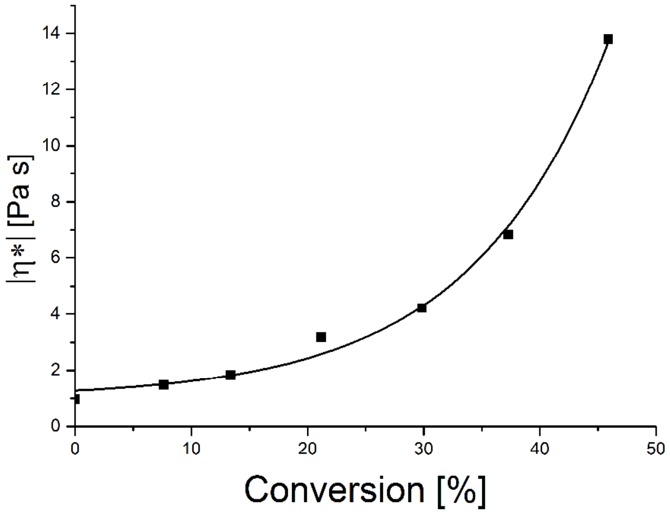


Figure 22. Viscosity [η*] at 1.6 Hz with increasing degree of epoxidation of Lithene PM4 at room temperature.

Table 15. Complex oscillatory viscosity of PBu with various degrees of epoxidation

conversion [%]	complex oscillatory viscosity [Pa*s]
0	0.96
7.6	1.48
13.4	1.83
21.2	3.18
29.8	4.23
37.3	6.83
45.9	13.79

---

[3] Melt viscosity at 25 °C

[4] Melt viscosity at 38 °C

5.1.5 Summary

The epoxidation of low molecular weight polybutadienes using a semi-batch process was reported in this work. The temperature of 75 °C is particular useful for the reaction. Formation of performic acid is rate determining at this temperature, and the decomposition rate is low and the ring opening reaction of the product is negligible. The process was successfully scaled up to a reaction volume of 10 L obtaining 1 kg of product material. The reaction of various molecular weights between 1500 and 26000 g/mol showed a universal applicability of the process in this range. The increase in glass transition temperature follows the Fox equation and the viscosity increases roughly by one order of magnitude to about 50% of epoxidation.

5.2 Rheological Properties of Epoxidized Liquid Rubber in Bulk and Solution

It is essential for material processing to know about the material properties. The knowledge of the viscosity of a material can be vital for processing steps such as mixing or pumping. Therefore the prediction of the viscosity in synthetic steps is of high interest due to the layout of equipment. In this work a model for the prediction of the complex oscillatory viscosity (η^*) of low molecular weight polybutadienes is developed. This model allows the prediction of complex oscillatory viscosity as a function of molecular weight, epoxidation ratio, concentration in toluene and temperature.

Experimental data[92,93] support the approach to factorize the viscosity into a temperature- and concentration-dependent friction factor $\zeta(T,\Phi)$ and a molecular weight- and concentration-dependent structural (topology) factor $g(M,\Phi)$. The viscosity can therefore be expressed as:

$$\boldsymbol{\eta_0 = \zeta(T,\phi) \cdot g(M,\phi)} \qquad (2)$$

The viscosity was determined using rheology with oscillatory shear. A typical measurement is depicted in Figure 23a. The measurement shows Maxwell type behavior as expected for a viscoelastic fluid. The viscosity is independent of the applied frequency (Figure 23), showing that the PBus can be considered newtonian liquids.

The frequency region relevant for extrusion, mixing or pipe flow is $10-10^4$ [rad $\cdot$ s^{-1}] [77].

The viscosity of the investigated polybutadienes in this region is $1-430$ Pa $\cdot$ s (Figure 23b).

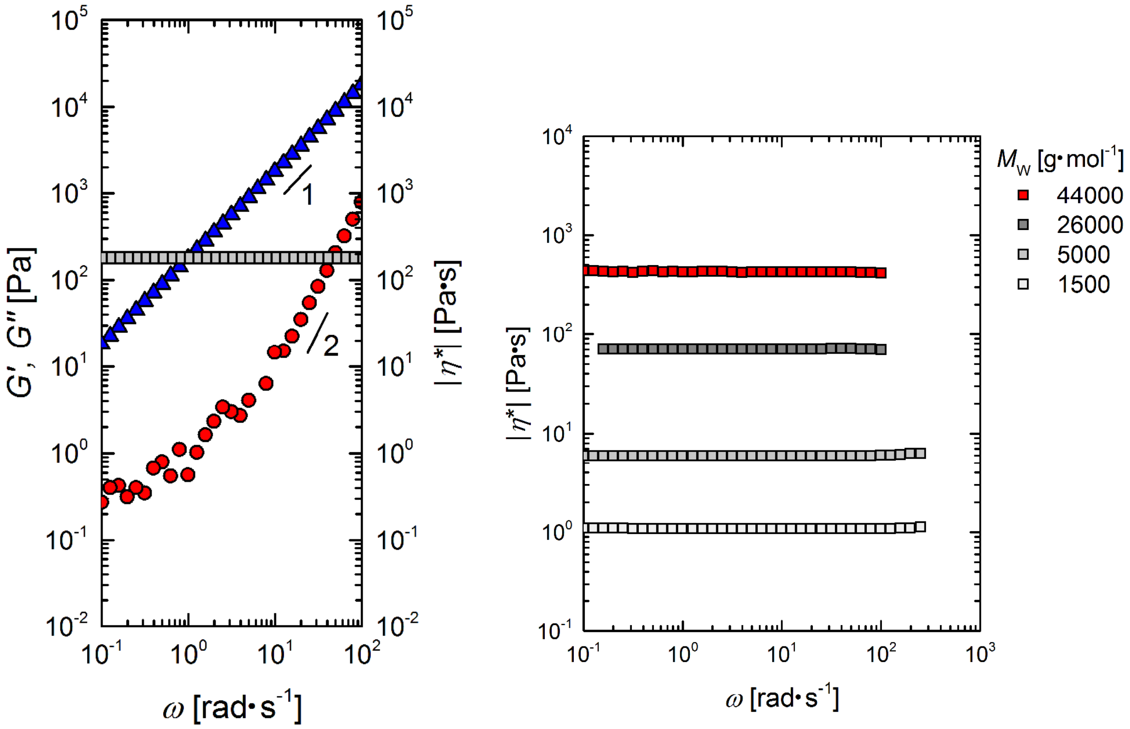


Figure 23. a) Oscillatory shear experiment of LBR-300 (Mw = 44000) at 45 °C, b) Complex viscosities of polybutadienes with different molecular masses

5.2.1 Molecular Weight Dependance

The viscosity in the region depicted in Figure 23 is independent of frequency and therefore equates the zero-shear-viscosity (η_0) which is proportional to the weight average molecular mass (Figure 24) in the usual power law of

$$\boldsymbol{\eta_0 \propto M_W^1} \tag{3}$$

below and

$$\boldsymbol{\eta_0 \propto M_W^{3.4}} \tag{4}$$

above the entanglement molecular mass.

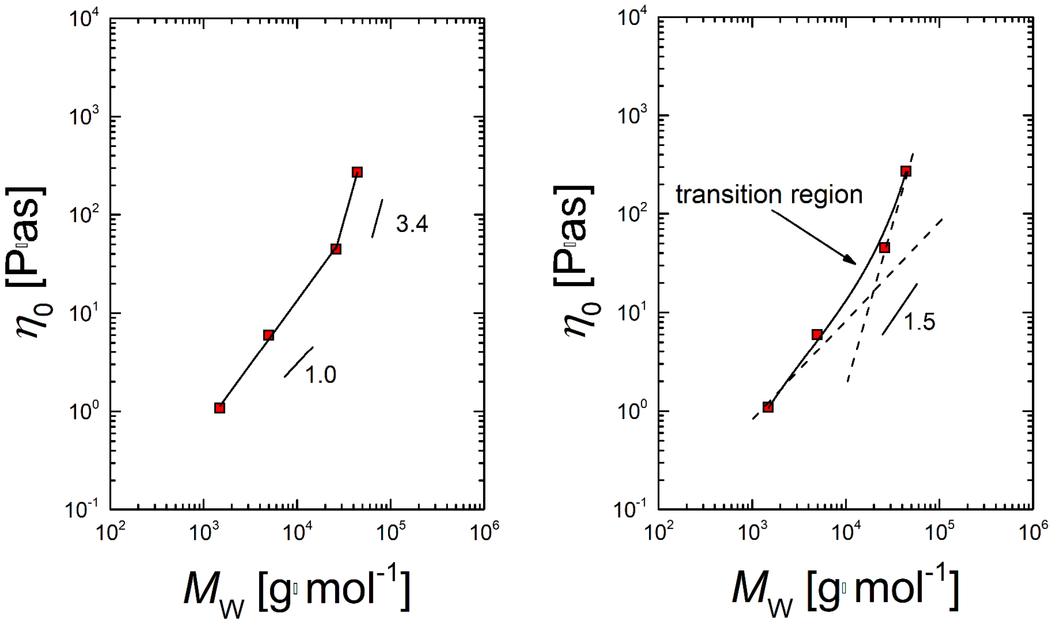


Figure 24. Zero-shear-viscosity in relation to molecular weight in bulk at room temperature

The expected slope of viscosity versus molecular mass is 1.0 below the entanglement molecular mass and 3.4 above it. RENDELL and NGAI found the critical molecular mass at 6400 g/mol for their system[94] and indeed the slope in Figure 24 is slightly higher than 1.0 even for the part of lower molecular weight. However, since the molecular masses investigated are still very low and the influence of entanglements is expected to be low in this case, an average slope of 1.5 was chosen for the following discussion. This would adequately describe the transition region.

5.2.2 Concentration Dependance

The polybutadiene samples were measured in bulk as well as volume fractions of 0.75 and 0.5 in toluene which is a common solvent for polybutadiene synthesis.[5] The slope of the viscosity vs. molecular weight plot is independent of the volume fraction in toluene but is shifted towards lower viscosities at lower concentrations as expected for these molecular masses. At higher molecular masses the slope would also be expected to be concentration dependent[95]. The viscosity shift covers roughly one magnitude per 0.25 of toluene volume fraction (Figure 25a).

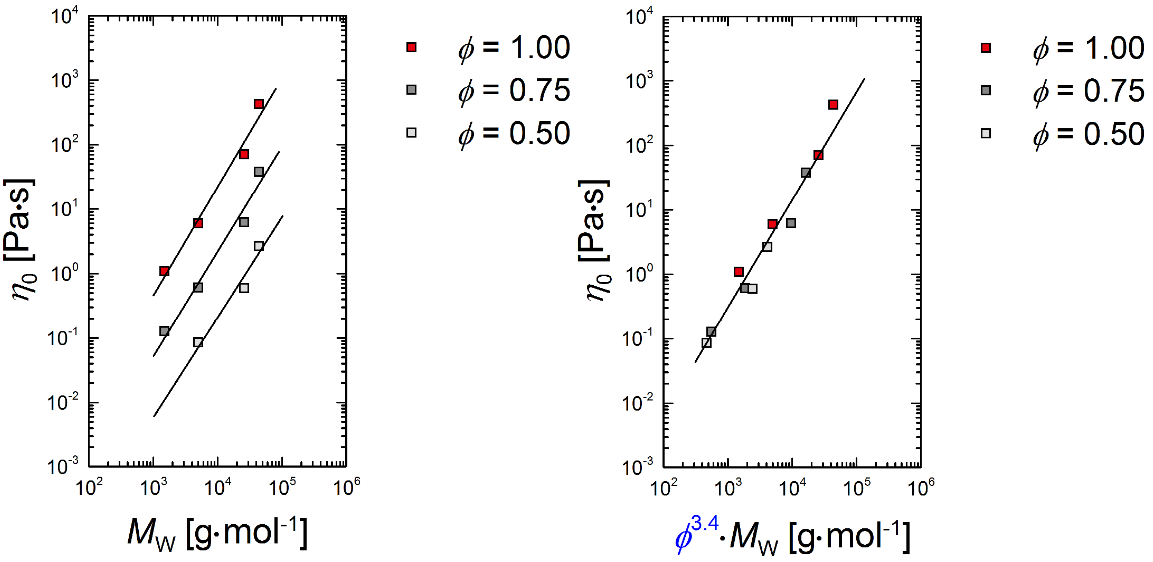


Figure 25. a) Viscosity developement with molecular weight at different volume fractions in toluene b) Mastercurve of the shifted viscosities

If a shift factor of $\phi^{3.4}$ is considered, these three slopes can be transformed on to a master curve (Figure 25b). The proportionality of the zero shear viscosity could ergo be described as follows:

$$\eta_0 \propto \phi^{3.4} \cdot M_W^{1.5} \tag{5}$$

Knowing the concentration (volume fraction, Φ) and molecular weight of a polybutadiene sample, it is possible to predict the viscosity of the solution of unfunctionalized polybutadiene in this molecular weight region with this master curve.

5.2.3 Functionality dependence

The epoxidation ratio needs also be considered if the polybutadienes are functionalized. The epoxidation ratio is influencing the viscosity of the polybutadienes due to changes in chain stiffness and polarity (s. 5.1.4). The degrees of freedom are reduced with an epoxide group compared to the double bond. Additionally, the more polar epoxide groups are increasing the chain-chain interaction parameter.[96] The viscosity is therefore gradually increasing during epoxidation reactions. To take these changes into account a shift factor for the changes in viscosity due to the epoxidation ratio (f) was introduced:

$$\eta_0 \propto (1 + f)^{3.4} \cdot M_W^{1.5} \tag{6}$$

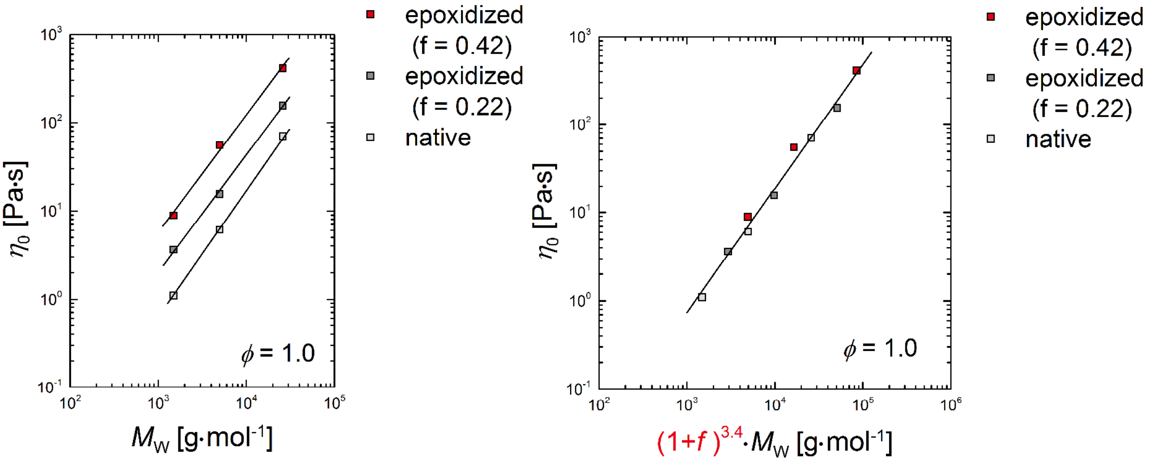


Figure 26. a) Viscosity developement with molecular weight at different epoxidation ratios b) Mastercurve of the shifted viscosities

The slope again is the same for all functionalization ratios but the curves are shifted with $(1+f)^{3.4}$.

5.2.4 Interim Conclusion

The dependence of the viscosity on molecular weight, concentration and epoxide ratio can be merged into one equation:

$$\boldsymbol{\eta_0 \propto (1+f)^{3.4} \cdot \phi^{3.4} \cdot M_W^{1.5}} \tag{7}$$

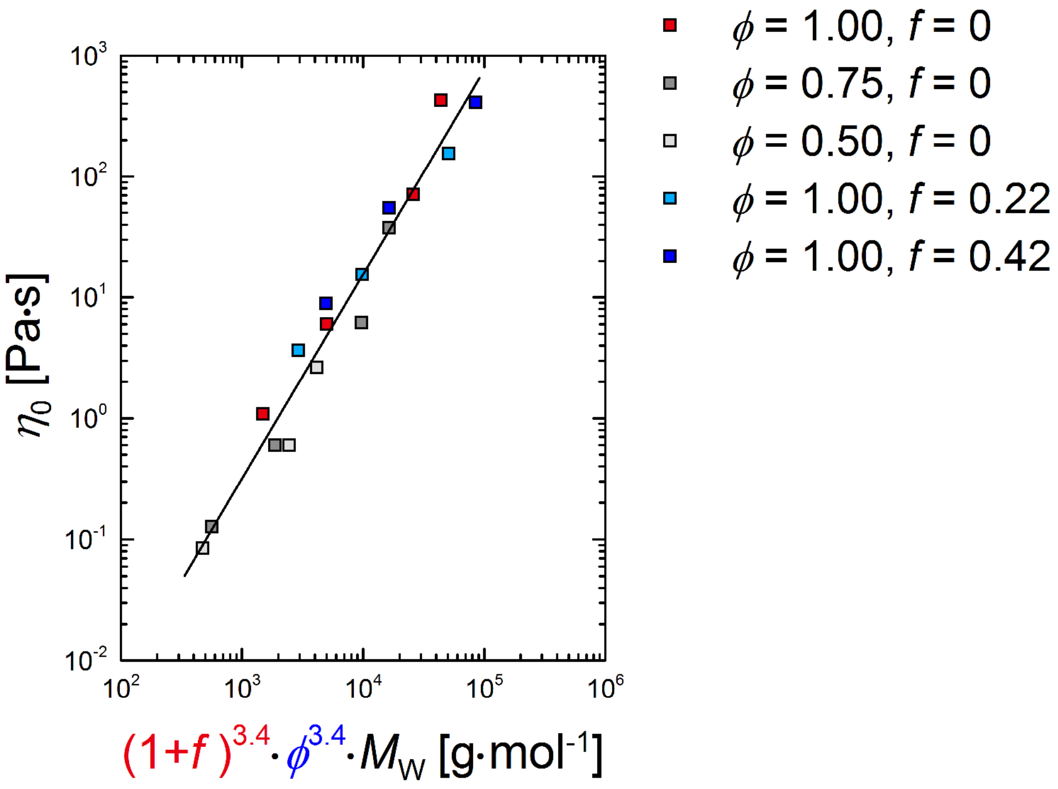


Figure 27. Mastercurve considering degree of epoxidation, concentration and molecular weight

The influence on viscosity by the epoxidation ratio is based on the changes in structure whilst the influence by the concentration in toluene is based on the solution states of polymer solutions.

The viscosity can therefore be shifted onto a master curve taking the epoxidation ratio and concentration into account. Furthermore, the viscosity during epoxidation is now predictable with the knowledge of concentration and expected epoxidation ratio.

Additionally, the temperature dependence is needed for the prediction of viscosities at reaction temperatures other than room temperature.

5.2.5 Temperature Dependence

The glass transition temperatures for the polybutadiene samples in this work are below 0 °C and therefore low enough for the ARRHENIUS law to be applicable.

The temperature dependence of the zero shear viscosity shows a similar progress for all samples (Figure 28).

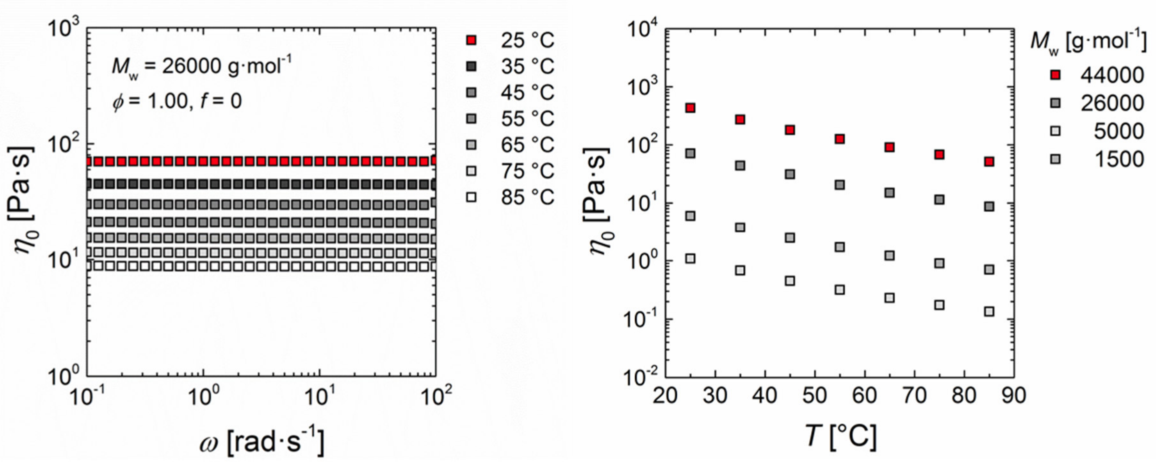


Figure 28. a) Temperature dependence of viscosity at 26000 g/mol, b) Temperature dependence of viscosity at different molecular weights

Following the ARRHENIUS law, a shift factor (a_T) for the temperature dependence can be introduced:

$$a_T = \exp\left\{\frac{E_a}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right\} \text{ with } a_T = \frac{\eta_0(T)}{\eta_0(T_0)} \tag{8}$$

The reference temperature T_0 was set to 25 °C and the resulting ARRHENIUS plot shows no dependence of the flow activation energy (E_a) on molecular weight of the polybutadienes (Figure 29).

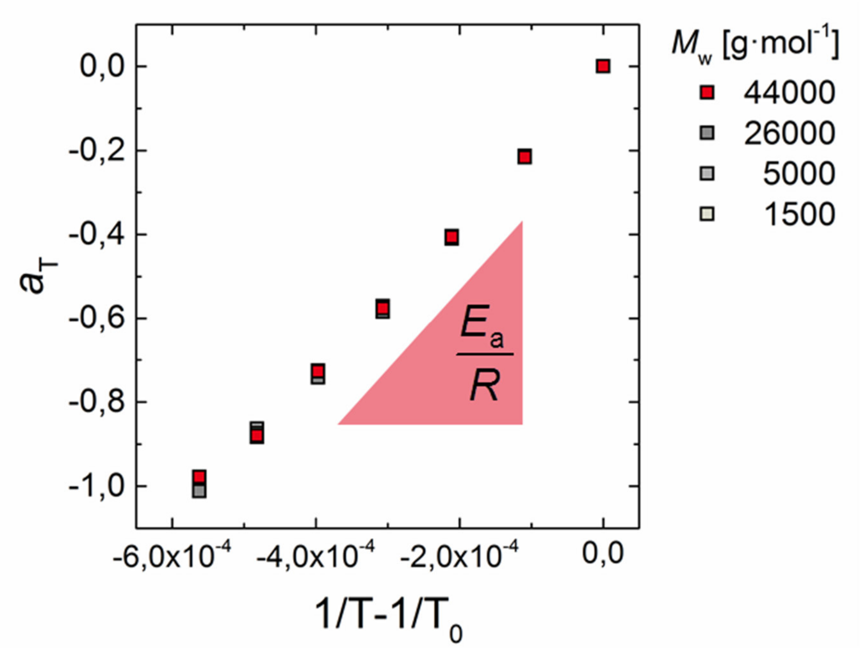


Figure 29. ARRHENIUS plot of the tested polybutadiene samples

However, the epoxidation ratio has an influence on the flow activation energy (Figure 30).

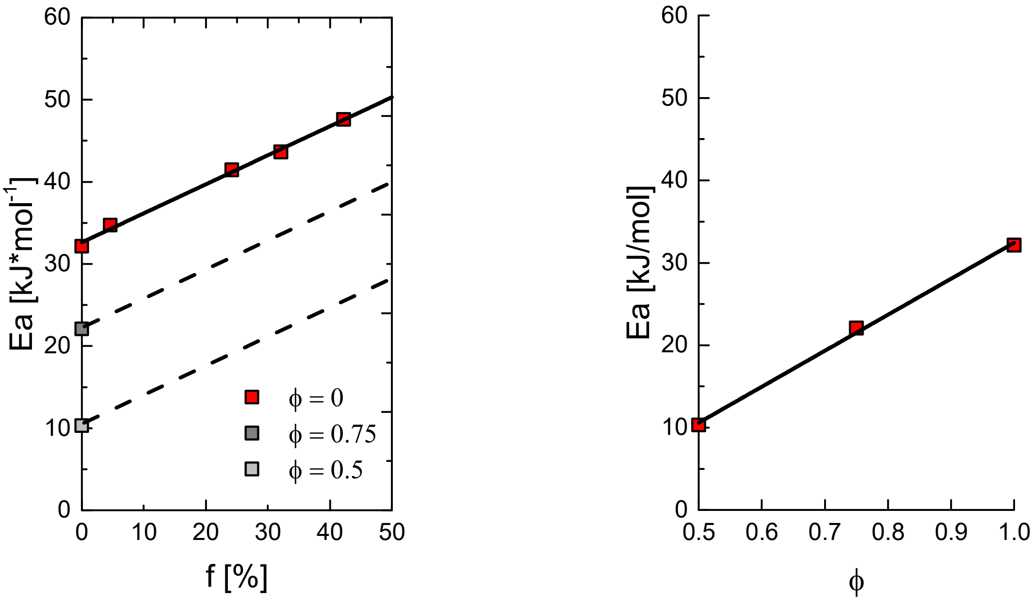


Figure 30. Functionalization dependence of the flow activation energy

These dependencies were expected since the flow activation energy is a function of chain rigidity and degree of freedom and the epoxide groups increase the chain stiffness. The flow activation energy also is concentration dependent, which leads to the following relation:

$$\boldsymbol{E_A = 32.15 - (1 - \phi) \cdot 43.00 + 36.81 \cdot f} \qquad (9)$$

Uniting all influencing parameters into one equation, it is now possible to predict the viscosity of a polybutadiene system with the knowledge of epoxidation ratio, concentration, molecular weight and temperature of the system:

$$\boldsymbol{\eta_0 \propto \frac{(1+f)^{3.4} \cdot \phi^{3.4} \cdot M_W^{1.5}}{exp\left\{\frac{E_A}{R}\left(\frac{1}{298} - \frac{1}{T}\right)\right\}}} \qquad (10)$$

The flow activation energy (E_a) is a function of the concentration (Φ) as well as the epoxidation ratio (f).

5.2.6 Conclusion

The present model can be used to predict the viscosity evolution during epoxidation reactions of low molecular weight polybutadienes. This equation enables the operator to design the optimal reactor system for the processing of the reaction mixture during epoxidation of polybutadienes. The dependencies of the zero shear viscosity on the epoxidation ratio as well as the concentration are to the power of 3.4 whilst the molecular weight dependence is to the power of 1.5 most likely due to the lack of entanglements at lower molecular weights.

The temperature has its influence through the ARRHENIUS law and the flow activation energy. This relation is shown in the overall equation for the prediction of the shear viscosity of low molecular weight polybutadienes

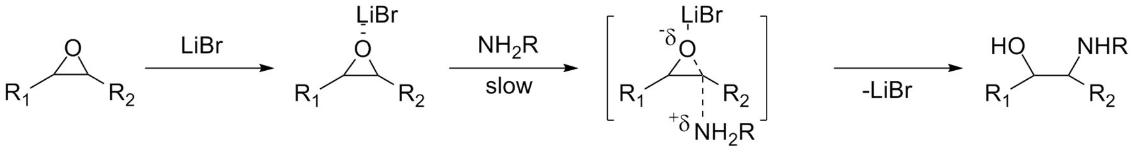
$$\boldsymbol{\eta_0 \propto \frac{(1+f)^{3.4} \cdot \phi^{3.4} \cdot M_W^{1.5}}{exp\left\{\frac{32.15-(1-\phi)\cdot 43.00+36.81\cdot f}{R}\left(\frac{1}{298}-\frac{1}{T}\right)\right\}}} \tag{11}$$

5.3 Aminolysis of Epoxidized Polybutadienes Catalyzed by Lithium Bromide

The synthesized epoxidated polybutadienes were opened by nucleophilic addition of amines. Butyl amine was chosen for the addition because of its ability to dissolve polybutadiene, good NMR signature and relatively high nucleophilicity. Lithium bromide was chosen as Lewis acid catalyst because it is inexpensive, nontoxic, oxophilic and has good availability. The reactivity of different epoxide isomers in this system was first evaluated with a model system.

5.3.1 Reaction Mechanism

Lithium bromide is an inexpensive, easy to handle, non-toxic Lewis acid. The additionally high affinity of lithium to oxygen makes lithium bromide an excellent choice catalyst for the aminolysis of epoxides.[56]



Scheme 3. Lithium bromide catalyzed aminolysis

Lithium bromide coordinates with the oxygen atom of the epoxide group forming a donor-acceptor complex. This complex is more susceptible to nucleophilic attack because of the carbon oxygen bond weakening. The rate determining step most likely is the attachment of the amine.[97]

5.3.2 Analysis of a Model System

The aminolysis was initially carried out using a set of simple epoxides to better understand the relative reactivities of asymmetric and symmetric *cis* and *trans* epoxides. The reaction was carried out using 1.0 mL (11.2 mmol) of butylene oxide mixture, 1.0 eq. of *n*-butylamine in relation to epoxide groups and 10 mol% of lithium bromide in relation to epoxide groups as catalyst.

The mix of epoxides consisted of 1,2-butylene oxide, *cis*-2,3-butylene oxide and *trans*-2,3-butylene oxide with a ratio of 1:3:6. The ^{1}H-NMR spectrum shows the good distinguishable signals of the different epoxides (Figure 31).

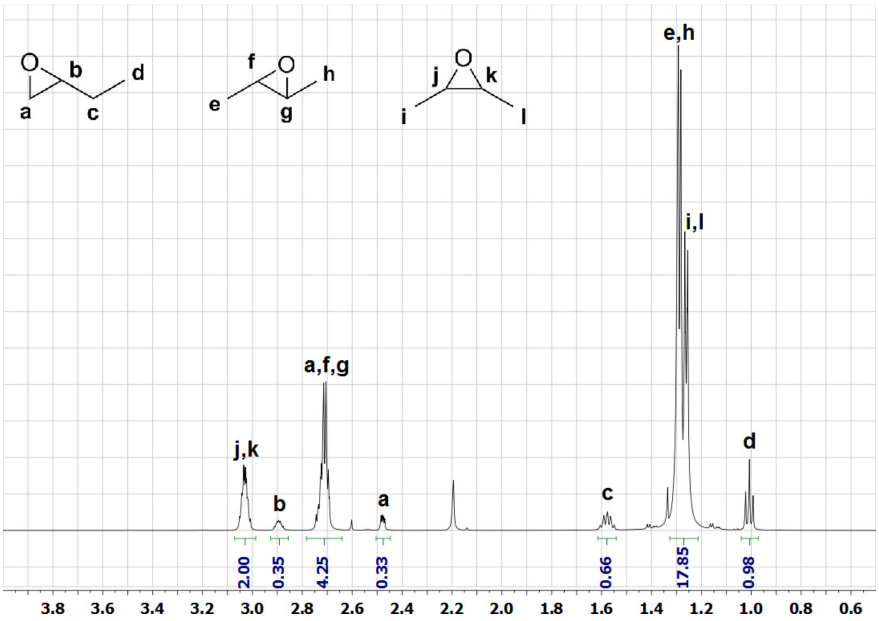


Figure 31. ^{1}H-NMR spectrum of the mix of different butylene oxides

Adding butylamine as well as LiBr to the mixture at room temperature and recording another ^{1}H-NMR spectrum after 30 min, already shows an ongoing reaction of butylamine with the asymmetric 1,2-butylene oxide (Figure 32).

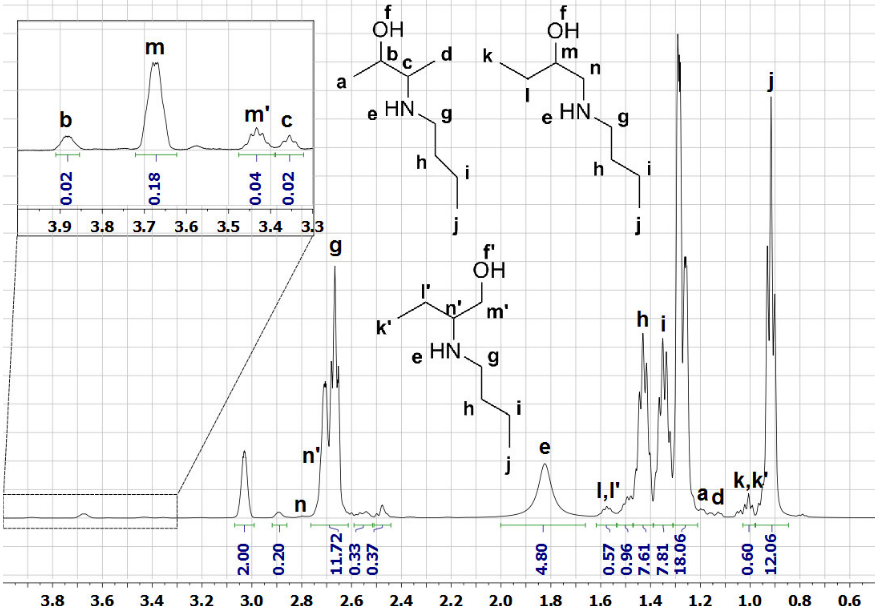


Figure 32. ^{1}H-NMR spectrum of the butylene oxide mixture with butyl amine added at room temperature

The spectrum shows a conversion of approximately 50% of the 1,2-butylene oxide whereas the 2,3-butylene oxides show conversions below 1%. Additionally roughly 90% of the 1,2-butylene oxide opening leaves the amine substituent at the less hindered 1 position.

After 150 h at room temperature another spectrum shows a complete conversion of the 1,2-butylene oxide as well as roughly 70% and 35% conversion of the *cis*- and *trans*-butylene oxide respectively. Taking the different concentrations into account, the reaction rates can be sorted to the following order: 1,2-butylene oxide >> *cis*-2,3-butylene oxide > *trans*-2,3-butylene oxide.

The results can only partly be transferred to the epoxidized polybutadiene, since the differences in structure of the polymer chain also influence the reactivity of the different isomers.[98]

The reactivity of epoxide groups on the polybutadiene backbone was therefore low for the reaction conditions of the model system to be applied here. The butyl amine was used in high excess (usually around 5-10 eq in relation to double bonds). Additionally, temperatures of 90-150 °C were applied. A glass autoclave was used for these reactions.

5.3.3 Progression of Aminolysis with Butyl Amine

Several reactions with different reaction times were conducted to follow the course of the reaction, given by the difficulties of sample taking in the high pressure process. The aminolysis was conducted at 90 and 150 °C with different concentrations of catalyst and with various polybutadienes epoxidized to a different extent.

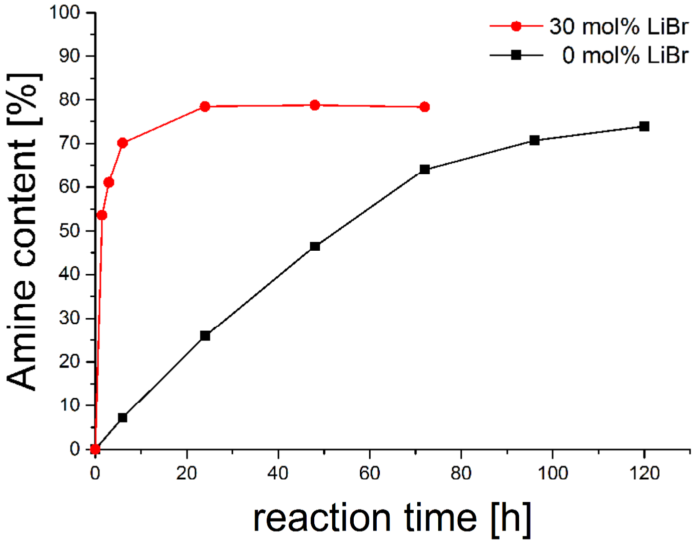


Figure 33. Yield-time curves of Lithene PM4 (with 30% epoxide functionalization) amination with butyl amine at 150 °C

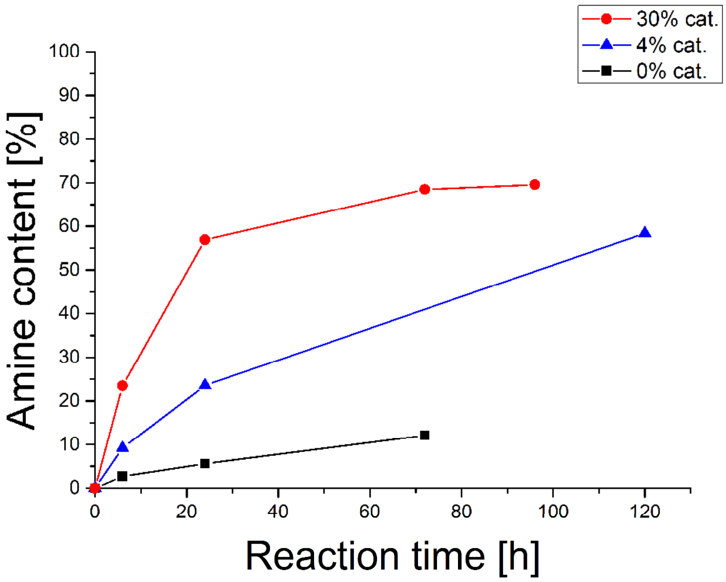


Figure 34. Yield-time curves of Lithene PM4 (with 42% epoxide functionalization) amination with butyl amine at 90 °C

Table 16. Conversion of epoxide groups measured by different methods (30% epoxidized BR, 150 °C)

c(LiBr) [mol%]	reaction time [h]	conversion		
		^{1}H-NMR	Elemental analysis	^{13}C-NMR IG
-	6	7.1%	7%	
-	24	26.0%	23%	
-	48	46.6%	40%	47.8%
-	72	64.0%	54%	
-	96	70.7%	63%	
-	120	74.0%	67%	
30	1.5	53.7%		
30	3	61.1%		
30	6	70.1%	65%	
30	24	78.5%	75%	
30	48	78.8%	73%	
30	72	78.5%	75%	

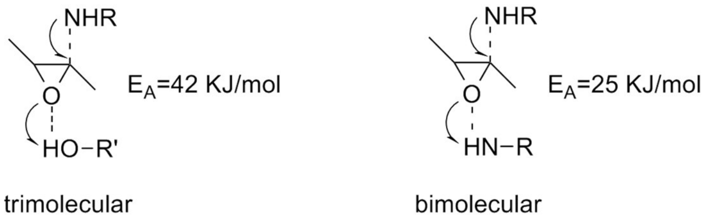
Table 17. Conversion of epoxide groups (42% epoxidized BR, 90 °C)

catalyst [mol%]	reaction time [h]	conversion (^{1}H-NMR)
-	6	2.7%
-	24	5.6%
-	72	12.1%
4	6	9.2%
4	24	23.6%
4	120	58.4%
30	6	23.5%
30	24	56.9%
30	72	68.5%
30	96	69.6%

The results of ^{1}H-NMR spectroscopy and elemental analysis are in good accordance. The lower conversions calculated by elemental analysis are most likely because of the hygroscopic nature of the aminated rubbers. A small water content increases the oxygen content and therefore falsifies the calculated conversion.

The kinetics of aminolysis has been thoroughly discussed in the literature.[99,100] The system is expected to undergo an S_N2 like mechanism. However, a reaction order of two is only observed under conditions with very low concentrations of hydroxyl-containing entities. Usually the observed reaction order is between one and two with respect to the amine resulting of two competing mechanisms:[99]

- The reaction is first order with respect to the amine if hydroxyl-containing impurities are present because of their promotion of the nucleophilic attack (trimolecular mechanism, Scheme 4a).
- The amine proton is acting as an electrophile promoting the attack on the epoxide group in addition from its role as a nucleophile if no hydroxyl-containing impurities are present (bimolecular mechanism, Scheme 4b).



Scheme 4. a) Trimolecular mechanism with hydroxyl impurities present, b) bimolecular mechanism without hydroxyl impurities present.[99]

The reaction order is also temperature dependent, as the activation energies of the above mechanisms are different (depicted activation energies are for the aminolysis of phenylglycidyl ether). Higher temperatures are therefore reducing the reaction order with respect to the amine.[99,100] At temperatures used in this work the reaction order in respect to the amine should be one. In this work the amine is used in high excess and its concentration is therefore considered constant during the reaction. The reaction should ergo follow a pseudo zero order kinetics with respect to the amine and only be limited by the epoxide concentration.

The lithium cation is expected to have a higher affinity to the epoxide oxygen relative to the amine or hydroxide impurities. Therefore the catalyzed reaction pathway should have a lower activation energy leading to a second order reaction, or with an excess of amine, a pseudo first order reaction.

The order of the aminolysis is affected by a competing cyclization reaction (see 5.3.4). The ratio of cyclization is expected to increase with the progress of the reaction since one of the neighboring epoxide groups needs to be opened prior to a possible cyclization.

The overall order of the reaction is therefore expected to be of pseudo first order at low conversions changing to a more complex mixed order at higher conversions when the effect of cyclization increases. That is why an evaluation of the rate constants was only carried out at the start of the reaction until roughly 40% conversion.

Table 18. Initial rate constants of the aminolysis with butyl amine

cat. [%]	Temp. [°C]	k [1/s]
0	90	4.7E-7[5]
4	90	3.0E-6[5]
30	90	9.2E-6[5]
0	150	3.6E-6[6]
30	150	1.4E-4[6]

Lithium bromide strongly increases the reaction rate. At 150 °C the reaction with 30 mol% lithium bromide is almost 40 times faster than without it. At 90 °C 30 mol% of lithium bromide still inceases the rate constant by a factor of 20.

5.3.4 Intramolecular Cyclization

The yield-time curves of the epoxide opening with butyl amine are heading towards a maximum below full conversion. ^{13}C-NMR I-Gated measurements however show no remaining epoxide groups. Therefore, a side reaction will have occured in which the epoxide groups are opened without additional consumption of butyl amine.

GELLING and others discovered an internal cyclization of highly epoxidated natural rubber during epoxide opening with hydroxyl functionalities.[101–103] In this cyclization a hydroxyl

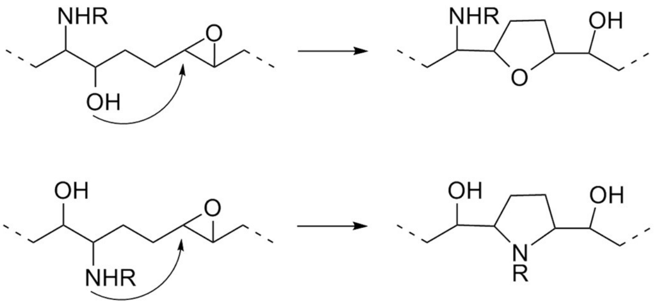
---

[5] 42% epoxidized polybutadiene

[6] 30% epoxidized polybutadiene

functionality, deriving from epoxide opening, attacks a neighboring epoxide entity forming a five-membered cyclic ether.

Transferring this reactivity to the present system, two cyclization reactions seem plausible (Scheme 5).



Scheme 5. Internal rearrangement of epoxide groups

Which cyclization reaction is occurring depends on the position the amine has added to in the previous epoxide opening and therefore which nucleophilic group is adjacent to the neighboring epoxide. Since no real differences between the epoxides carbon atoms exist, a statistical distribution seems likely. Looking into the ^{13}C-NMR I-Gated spectra the signals between 69 and 72 ppm are attributed to the oxygen neighboring carbon atoms of the THF ring[104,105] whereas the nitrogen neighboring carbons would be expected somewhat further upfield where at 62 ppm a corresponding peak is observed (Figure 35). The ^{1}H-NMR spectrum doesn't give much information on account of overlapping signals, but resonances could be found at the expected positions (Figure 36). The expected statistical cyclization is backed up from the observation of the integrals of the ^{13}C-NMR reverse I-Gated spectrum.

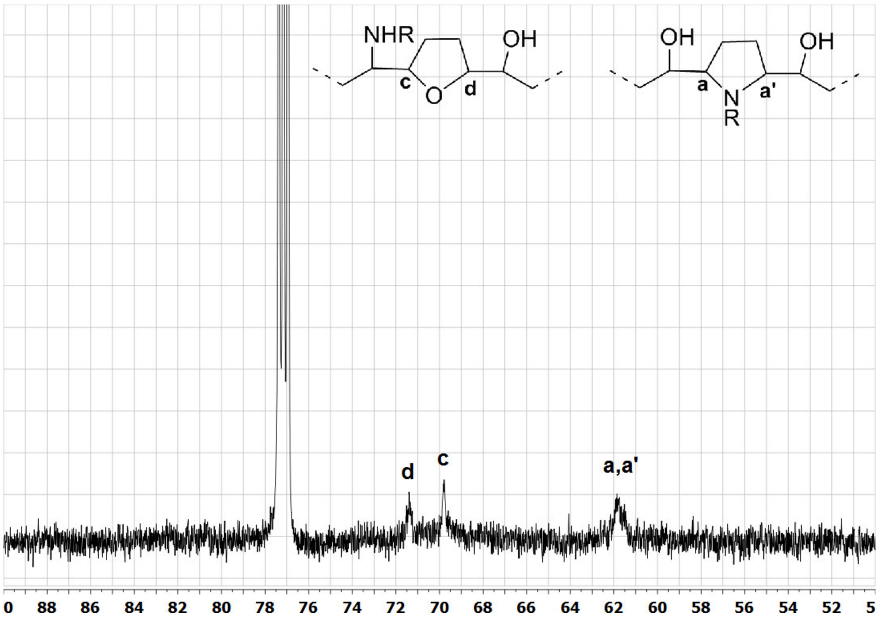


Figure 35. ^{13}**C I-Gated NMR spectrum of aminated polybutadiene rubber**

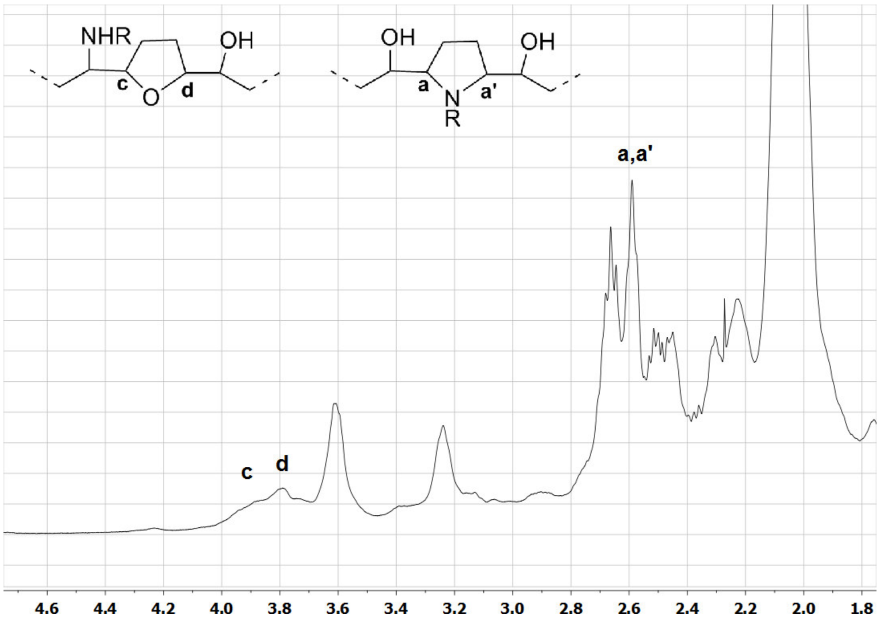


Figure 36. ^{1}**H-NMR spectrum of aminated polybutadiene rubber (detail)**

Since the epoxidation of polybutadiene under the used conditions is statistically, the probability of neighboring epoxide groups, allowing such cyclization, increases with increasing epoxidation ratio. A higher relative butyl amine functionalization could indeed be observed with lower epoxidated polybutadienes (Figure 37).

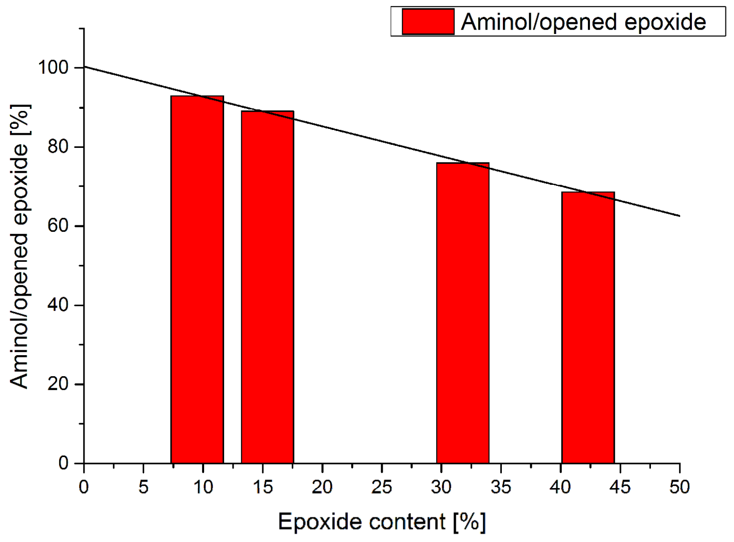


Figure 37. Degree of aminolysis by amine content with Lithene PM4 with different degrees of epoxidation

In conclusion the remaining epoxide groups not getting opened by the primary butyl amine are most likely undergo an internal cyclization where either the secondary amine or the hydroxyl entity attached to the polymer chain is attacking a neighboring epoxide group.

The linear fit of Figure 37 crosses the Y-axis at 100% as expected since without epoxide groups no neighboring epoxides for cyclization exist. At 100% epoxidation there should be a 100% chance of two epoxide groups to have a neighboring epoxide group, which would lead to 100% heterocycles. This would only be true for 100% 1,4-polybutadiene without any branching or 1,2-vinyl groups. The theoretical heterocyclic content of 75% at 100% epoxidation therefore seems a reasonable number.

The ratio of cyclization is not temperature dependent at temperatures above 90 °C. The aminolysis with a 42% epoxidized sample at 90 °C and 150 °C gave the same maximum amine introduction of 70%. This fact leads to the conclusion that the activation energy of the cyclization reaction is lower than the activation energy of the aminolysis with butylamine. A reason for the lower activation energy could lie in the favorable five membered transition state of the intramolecular cyclization.

The concentration of lithium bromide also doesn’t influence the maximum amine introduction. Reactions with the same epoxidized polybutadiene but different LiBr concentrations gave the same maximum conversion but different reaction rates. This also was expected because the lithium cation is expected to attach to the oxygen atom weakening the oxygen carbon bond and making it more vulnerable for nucleophilic attacks independent of the type of attacking nucleophile. Hence the ratio of cyclization is only affected by the concentration of neighboring epoxide groups.

5.3.5 Higher Molecular Mass Epoxidized Polybutadienes

In the same process polybutadienes with a similar configuration but higher molecular mass were aminated under the same conditions. The polybutadienes all had a similar epoxidation grade (about 40%) and were treated with 13 eq of butyl amine and 30 mol% of lithium bromide at 150 °C for 24 h. The conversion of aminolysis show basically no differences (Table 19).

Table 19. Aminolysis of epoxidized polybutadienes of different molecular masses

Initial molecular mass (M_n) [g/mol]	Epoxide ratio [%]	Conversion [%]
1500	41.1	68.6
8000	39.0	73.5
26000	40.5	73.2

The somewhat higher conversion with the polybutadiene of 8000 and 26000 g/mol might result from differences in the molecular configuration (see Table 20). The lower content of 1,2-double bonds would lower the probability of two neighboring epoxide groups, which leads to a lower probability of cyclization (see 5.3.4) and ergo a higher possible amine concentration.

5.3.6 Material Properties

The introduction of amine groups increases the polarity of the polymer increasing chain-chain interactions and therefore increases the glass transition temperature (Figure 38). The fitting curve represents the results of the Fox equation, only in accordance with the experimental results, if a lower glass transition temperature for the epoxidized polybutadiene starting material is used. A change in polymer-chain-conformation with introduction of amine groups might be a reason for this deviation.

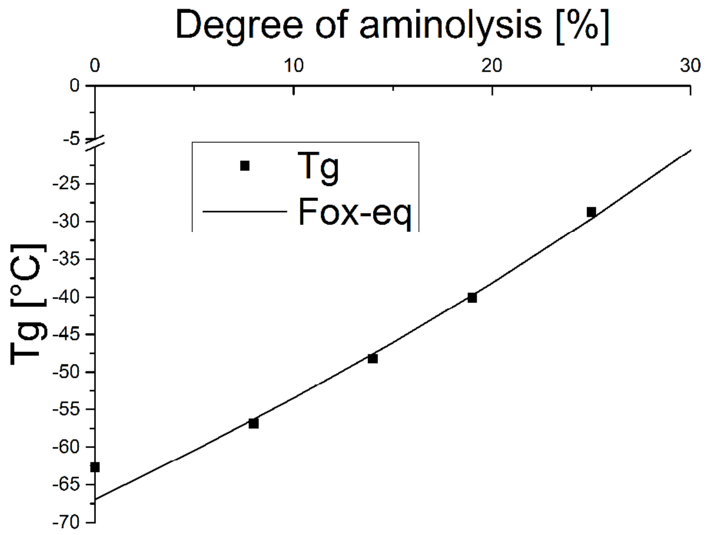


Figure 38. Glass transition temperatures of Lithene PM4 with different degrees of aminolysis

The molecular masses by GPC seem to decrease with increasing amine content (Figure 39). The GPC elugrams were recorded against a polystyrene standard in THF. With ongoing reaction the aminated rubber becomes more and more dissimilar to polystyrene and probably shows different coil expansion behavior. The seeming decrease in molecular mass (M_n) to almost 200 g/mol would equal 1-4 repeating units in a chain. This drastic decrease in chain length wouldn't go unnoticed in ^{1}H-NMR or DSC measurements which look very similar independent of the degree of aminolysis.

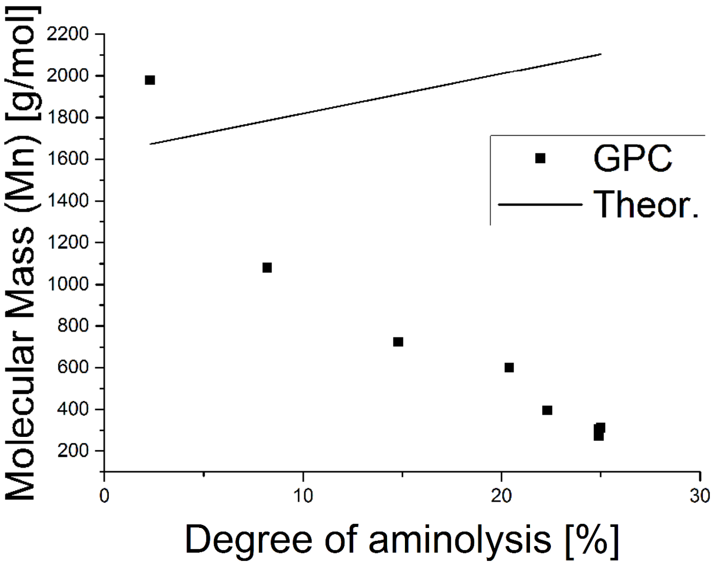


Figure 39. Molecular masses (M_n) by GPC (■) and theoretical progression of the molecular mass (–)

The molecular mass was also measured by vapor pressure osmometry in THF against a standard of benzil (210.23 g/mol). For verification a sample of Lithene PM4 was also measured. The expected molecular masses were 1500 g/mol (Lithene PM4) and 2300 g/mol (aminated BR). The values measured by vapor pressure osmometry were 1670±115 g/mol (Lithene PM4) and 1985±77 g/mol (aminated BR).

MALDI-Tof spectra of the aminated BR show relatively low intensity, which makes it difficult to calculate a molecular weight distribution. The flight pattern of the chains might represent a false molecular weight distribution due to different stabilities of the chains. The high molecular weight signals are difficult to separate from the noise. The best results were achieved with Dithranol as matrix and sodium trifluoroacetate as added salt (Figure 40). Nevertheless, the spectrum shows molecular masses and a distribution of the same in the expected range. The signals at 685 and 2441 m/z respectively belong to the matrix.

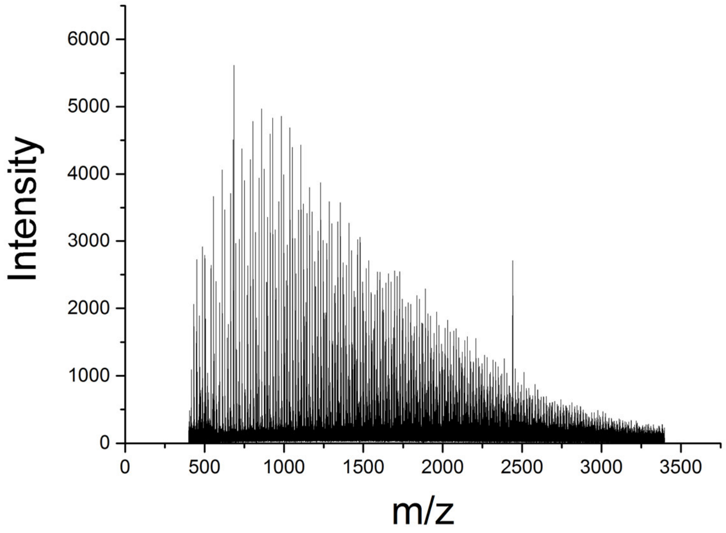


Figure 40: MALDI-Tof spectrum of aminated BR

5.3.7 Summary

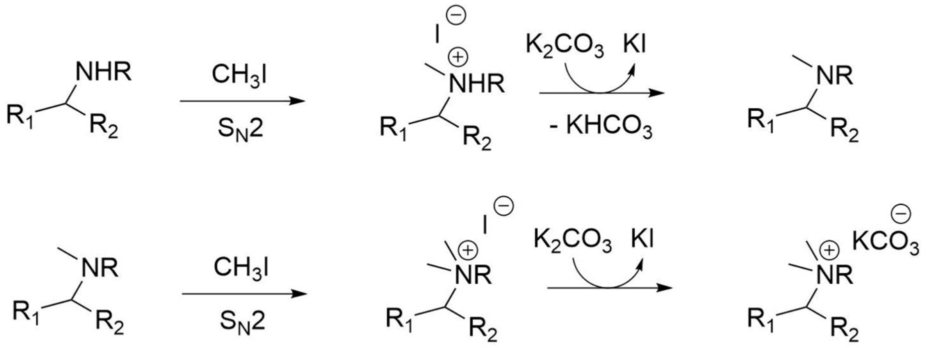
The aminolysis of epoxidated low molecular weight polybutadienes using a lithium bromide catalyst was reported in this work. A solvent free process with elevated temperatures was used to achieve high yields at moderate reaction times. The maximum yield depends on the epoxidation ratio of the starting material, due to an intramolecular cyclization reaction. The process was successfully applied to molecular masses of epoxidized polybutadiene of up to 26000 g/mol. The change in polarity and rigidity of the chains reduces the hydrodynamic volume as well as increases the glass transition temperature of the aminated products.

5.4 Quaternization of aminated polybutadienes

The aminated polybutadienes were treated with methyl iodide to quaternize the amine functions, creating quaternary ammonium ions. Methyl iodide has a sterically low hinderance, and iodide is a good leaving group making methyl iodide an excellent methylating agent.[106] Potassium carbonate was chosen as base, which can promote the quaternization of amines at room temperature.[69]

5.4.1 Reaction Mechanism

The amine is attaching to the electrophilic carbon of iodomethane by nucleophilic attack. The reaction is following S_N2 mechanism because of the high nucleophilicity of secondary amines. In a second step potassium carbonate is binding the amine proton forming potassium bicarbonate and potassium iodide. The tertiary amine is usually further methylated to the quaternary ammonium ion with monopotassium carbonate as counterion.[69,107]



Scheme 6. Methylation of secondary amines by iodomethane and potassium carbonate

The aminated polybutadienes also contain hydroxyl functionalities which can be methylated too. Theoretically the nucleophilicity of alcohols is much lower compared to that of secondary amines and should therefore react much slower with iodomethane. Nevertheless, a set of simple aminoalcohols was treated with iodomethane and potassium carbonate to get a feeling of reactivity under given reaction conditions.

5.4.2 Analysis of a Model System

Two different aminoalcohols were used for this test reaction. 2-(Dimethylamino) ethanol and 2-amino-2-methylpropan-1-ol were treated with one and three equivalents of iodomethane respectively in the presence of one and three equivalents potassium carbonate for 24 h at room temperature in THF. The reaction was quenched with aqueous ammonia solution after 24 h. 2-(Dimethylamino) ethanol was completely quaternized which was accompanied by a downfield shift of the methyl signals. No sign of alcohol methylation and therefore ether formation was visible (Figure 41).

2-Amino-2-methylpropan-1-ol was quaternized to 75% under the described conditions. The remaining 25% stopped at tertiary amine. Evaporation of iodomethane (bp.: 42 °C[108]) might be a reason for the incomplete quaternization. No sign of ether formation was visible (Figure 42).

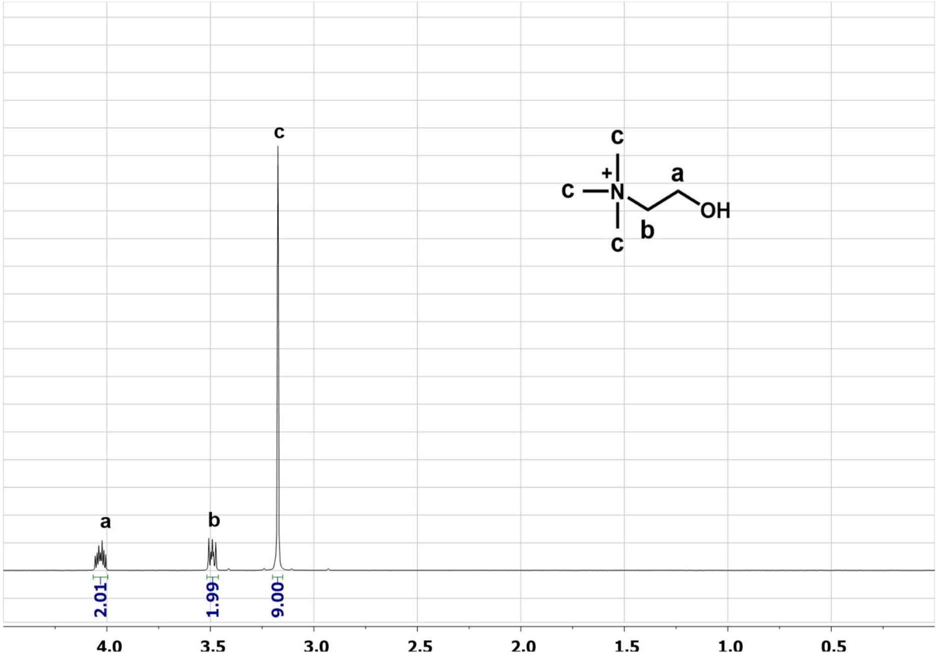


Figure 41. ^{1}H-NMR spectrum of quaternized 2-(dimethylamino) ethanol

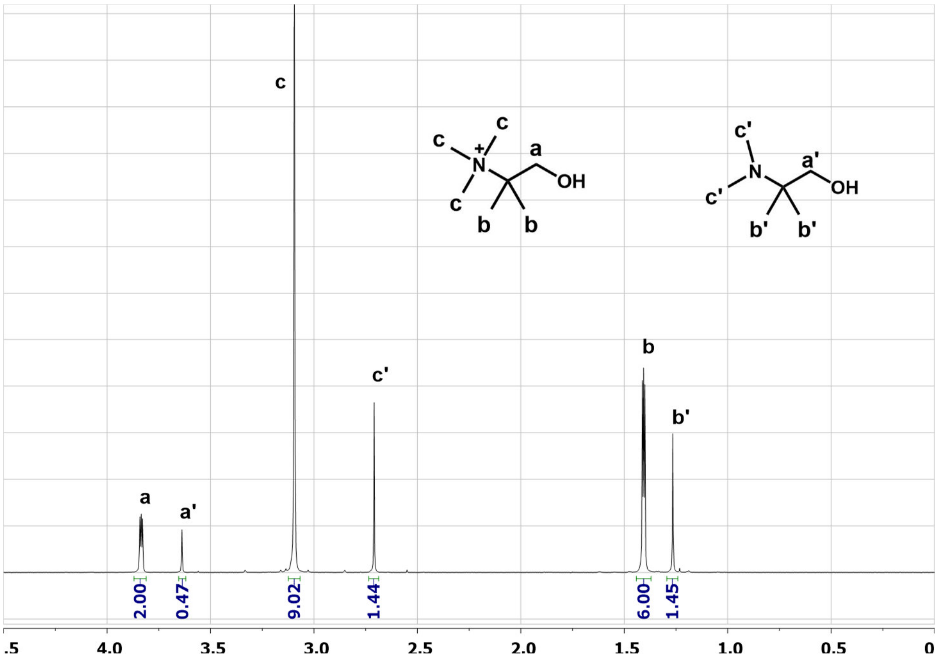


Figure 42. ^{1}H-NMR spectrum of quaternized 2-amino-2-methylpropan-1-ol

Even the sterically more hindered 2-amino-2-methylpropan-1-ol was readily quaternized under given conditions. The reaction rate was probably lower compared to that of 2-(Dimethylamino) ethanol, but the alkylation was still highly selective towards amine methylation and no primary or secondary amine was left unreacted.

These reaction conditions were transferred to the quaternization of aminated polybutadienes.

5.4.3 Progression of Quaternization with Iodomethane

The quaternization of 2-amino-2-methylpropan-1-ol showed an insufficient conversion to ammonium ions with three equivalents of iodomethane. The methylation of aminated polybutadienes carrying secondary amines would need at least two equivalents of iodomethane to give the quaternary ammonium ion. An excess of iodomethane (5-10 eq relating to the concentration of amine groups) was used for the quaternization of aminated polybutadienes to avoid insufficient methylation like seen with 2-amino-2-methylpropan-1-ol. Iodomethane was divided into two halves, to compensate for the probable evaporation of iodomethane over the course of the reaction. The first half was added at the start of the reaction, the other half after a certain time of reaction.

The aminated polybutadiene was dissolved in THF and potassium carbonate was dispersed in the solution under stirring. Iodomethane was added to start the reaction. Samples were taken during the reaction. After 24 to 72 h the dispersion was treated with aqueous ammonia solution to quench the reaction. The reaction mixture was precipitated in cold water and dried under reduced pressure. The resulting quaternized polybutadiene was analyzed by NMR-spectroscopy.

The NMR signals of the ammonium ion's N-methyl groups are interfering with the polybutadiene signals. The methyl group of the n-butyl rest attached to the nitrogen atom has a distinctive shift in ^{1}H-NMR spectrums and can be used for the monitoring of conversion from amine to ammonium ion groups (Figure 43). Lorentzian function was used for peak fitting due to overlapping signals. Elemental analysis is supporting the NMR results.

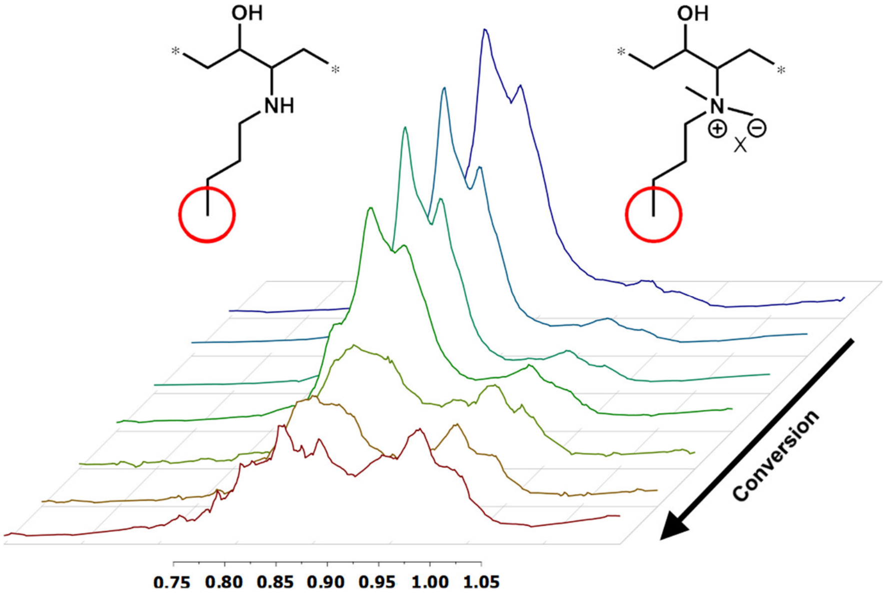


Figure 43. Signal changes over the course of the reaction

A typical progression of quaternization at room temperature in THF over time is shown in Figure 44. 5 eq iodomethane relating to the concentration of amine groups were added. 3 eq at the beginning of the reaction and 2 eq after 5 h. Additionally 2 eq potassium carbonate were added at the beginning.

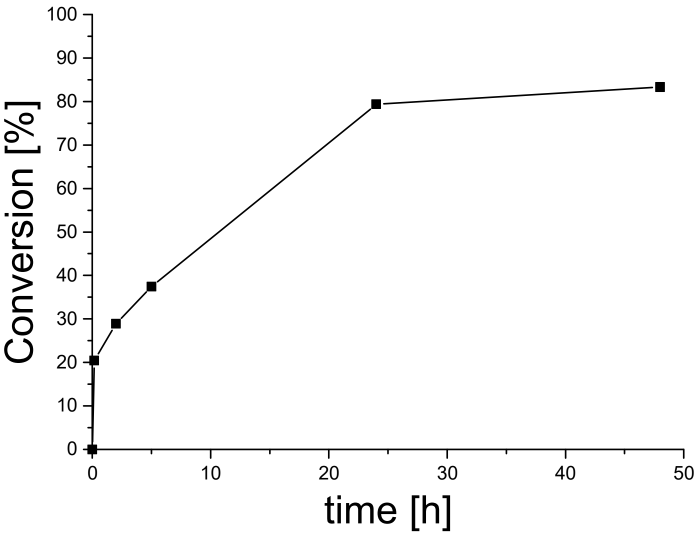


Figure 44. Conversion of quaternization reaction

The reaction rate is very high at the beginning of reaction and slowing down significantly with more ammonium ions forming. A reduced solubility with increasing polarity of the polybutadiene could be the reason. A sterically more hindered center of reaction with proceeding methylation might be another reason. The introduction of iodomethane after 5 h seemed to boost the reaction and preventing further deceleration. At high conversions a distinction of peaks in ^{1}H-NMR spectra is challenging which results in increasing error in conversion determination. The cyclic tertiary amine groups are most probably slower in quaternization reaction compared to the secondary amine groups.

5.4.4 Material properties

The resulting quaternized polybutadiene at room temperature is no longer a liquid rubbery material, but hard and brittle. The polymer structure is resembling polyquaterniums, cationic polyelectrolytes e.g. used in personal care industry as antistatics and film former.[73] The cationic charges along the chain are expected to repel themselves and lead to a more expended rod-like structure compared to the random-coil structure in nonionic polybutadiene.[109] These conformational changes have a significant impact on the polymer bulk properties like melt viscosity. The increasing polarity seems also to increase chain-chain interaction and chain stiffness which results in the increasing glass transition temperature. The glass transition temperature is increasing to 45 °C (DSC). The significant increase in polarity is the reason for increasing solubility in more polar solvents. The product is soluble in methanol.

Based on conversion of aminolysis and quaternization 20% of initial double bonds are transferred to an ammonium entity if 30% epoxidated polybutadiene is used. For 42% epoxidated polybutadiene 25% of initial double bonds are holding an ammonium entity after quaternization. For Lithium PM4 that would be five to seven ammonium ion entities per chain, or one ammonium ion every 16-22 carbon atoms in average.

6 Summary

Low molecular weight polybutadienes of molecular weights between 1500 and 26000 g/mol (M_n) were used in this thesis as base materials. The microstructure of these polybutadienes showed mainly 1,4 double bonds (80-90%). The polybutadienes were epoxidized using *in-situ* formed performic acid in a two-phase system. The polybutadienes were dissolved in toluene and formic acid was added to the solution at elevated temperatures. Hydrogen peroxide then was added continuously to the stirred solution. This semi batch process was scaled up to 10 L and the product properties could be controlled by the chosen reaction parameters. The degree of epoxidation could be regulated by the chosen temperature, hydrogen peroxide feed-rate and reaction duration. 1,4 Double bonds showed higher reactivity towards epoxidation than vinyl pendant groups. The epoxide groups therefore were almost exclusively introduced on the polymer backbone. The viscosity and glass transition temperature of the polybutadienes were increased by epoxidation on account of increasing polarity and stiffness of the chains.

An empirical model was developed to predict the increase of viscosity by epoxidation. The influence of molecular weight, concentration in toluene, degree of epoxidation and temperature were investigated by rheological oscillatory shear experiments. Minor influences of chain entanglements with the higher molecular weight polybutadiene samples were found. A correction factor was implemented to account for this effect. The viscosity as function of the molecular weight of the polybutadienes scales with concentration and degree of epoxidation. The viscosity molecular weight curves were shifted towards higher viscosities with higher epoxidation ratio or higher concentration. Shift factors were found to meet these influencing parameters. An ARRHENIUS plot of the zero-shear viscosity at different temperatures revealed no influence of molecular weight on the flow activation energy of the polybutadienes. A formula for the prediction of zero shear viscosity of epoxidized low molecular weight polybutadienes could be developed by combining the shift factors for molecular weight, concentration, degree of epoxidation and temperature.

The epoxidized polybutadienes were subjected to nucleophilic ring opening by amines. The epoxide groups located on the polymer backbone showed relatively low reactivity towards ring opening conditions. Elevated pressures and temperatures as well as Lewis acid catalysis were necessary for quantitative conversions. The reactions were performed in bulk with the amine as solvent in high excess and lithium bromide as catalyst. Lithium bromide was chosen as catalyst because of its low cost and easy removal from the amine modified polybutadiene product. However, even with catalyst concentrations of 30 mol% quantitative conversion was achieved only after 24 hours. Apart from this low reactivity there was a mismatch between epoxide group conversion and aminol formation, hinting towards occurring side reactions. An intramolecular ring opening of neighboring epoxide groups was identified as a possible mechanism. The probability of existing neighboring epoxide groups increases with increasing degree of epoxidation due to the statistical nature of the epoxidation reaction. A lower maximum degree of amine modification is therefore achieved with higher degree of epoxidated polybutadienes.

The amine groups in the aminated polybutadiene were alkylated using iodomethane and potassium carbonate at room temperature. The secondary amine groups were N-permethylated to get access to quaternary ammonium ions on the polybutadiene backbone. The introduction of ionic groups to the polymer chain had a significant impact on bulk properties such as glass transition temperature, which rose above room temperature making this polyelectrolyte a hard and brittle material. Additionally, solubility in polar solvents like methanol was increased.

7 Experimental Part

7.1 Materials

Toluene (technical grade) was obtained from VMP Chemiekontor. hydrogen peroxide (30 wt% aq.) was purchased from VWR Chemicals or Grüssing GmbH Analytika. formic acid (analytical grade, 99%) was purchased from Grüssing GmbH Analytika, n-butylamin (99%) was purchased from ABCR GmbH, lithium bromide (>=99%) was purchased from Sigma-Aldrich, Chloroform-d was purchased from Deutero GmbH. All chemicals were used without prior purification unless otherwise specified. Four different types of low molecular weight polybutadienes were used in this study. Lithene *ultra*© PM4 (M_n = 1500 g/mol) and Lithene *ultra*© N4-5000 (M_n = 5000 g/mol) were kindly provided by Synthomer plc. LBR-307 (M_n = 8000 g/mol) and LBR-305 (M_n = 26000 g/mol) were kindly provided by Kuraray Europe GmbH. Polybutadienes were used as received.

Table 20: Polybutadienes used in this work with molecular configuration

PBu	molecular mass (M_n) [g/mol]	1,4-DB [%]	1,2-DB [%]	cyclic-DB [%]	*cis:trans* ratio[7]
Lithene PM4	1500	80	19	<1	40:60
Lithene N4-5000	5000	88	12	0	40:60
LBR-307	8000	86	14	0	40:60
LBR-305	26000	91	9	0	40:60

7.2 Nuclear Magnetic Resonance (NMR)

NMR spectra were recorded at room temperature with a Bruker AVANCE 400 MHz or a Bruker Fourier 300 MHz spectrometer. Chloroform-d was used as solvent.

7.3 Matrix Assisted Laser Desorption (Time of Flight) Mass Spectrometry (MALDI)

MALDI spectra were recorded on a Bruker UltrafleXtreme Smartbeam II Laser

---

[7] Due to overlapping peaks, the ratios are just approximate values

7.4 Rheometry

Rheometry measurements were done on an ARES G2 Rheometer from TA instruments with a 60 mm 2° steel cone geometry and peltier plate. The software TRIOS v4.2.1.36612 was used for measurements and data evaluation.

7.5 Differential Scanning Calorimetry (DSC)

A Mettler Toledo DSC 1 or DSC 821 instrument calibrated with indium was used for thermal analysis. The weight of samples sealed in an aluminium pan was about 10-15 mg.

First, the samples were cooled from room temperature to -20 °C at -20 K/min, held for 2 min. In a second step, the samples were heated from -20 °C to 60 °C at 10 K/min and held for 2 min to erase the thermal history. After a second cooling from 60 °C to -120 °C at -20 K/min and second holding for 2 min, the samples were heated from -120 °C to 60 °C at 10 K/min to record heating curves of each sample.

7.6 Gel Permeation Chromatography (GPC)

GPC elugrams were measured on a set up using a precolumn MZ Gel SDplus, 5 µm, 100 Å from MZ-Analysentechnik, two 5µm Polypore columns from Polymer Laboratories (now Agilent), an HPLC Pump Intelligent Pump AI12 from Flom, a degasser PLDG 802 from Polymer Laboratories (now: Agilent), a RI Detector RI 101 from Shodex. The interface hs 2600 and software NTeQGPC V 6.4 version V 1.0.25 used were from hs GmbH.

7.7 Titration of Epoxidized Polybutadienes

Titration of epoxidized polybutadienes for determination of epoxide content was done using the automatic titration system Titroline alpha plus from SI Analytics. A pH-electrode N4680 eth was used. The end-point determination was done potentiometric with the software TitriSoft 4.3.

7.8 Epoxidation of Polybutadienes

7.8.1 Reaction Setup

The epoxidation of low molecular weight polybutadienes was performed in various reaction vessels of glass (250 mL) or steel (1 and 10 L). The double walled cylindrical 250 mL glass reactor (Büchi AG) was equipped with an anchor stirrer, a thermostat and a syringe pump. The double walled cylindrical 1 L and double walled conical 10 L steel reactor (Juchheim Laborgeräte GmbH) were equipped with an anchor stirrer, a thermostat and a double piston pump (Pharmacia LKB P-500) for uninterrupted feeding of hydrogen peroxide. The conversion showed a dependence on the reactor material: The first couple of reactions in steel reactors showed lower conversions, i.e. before the surface was deactivated. This may be related to metallic ions accelerating the decomposition of hydrogen peroxide.[110] After each experiment the vessel was extracted three times with toluene for 30 min at the reaction temperature.

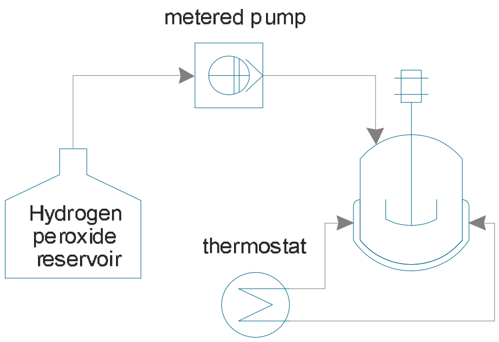


Figure 45. Reaction set-up of the semi-batch process

7.8.2 General Procedure of Epoxidation with *in-situ* Formed Performic Acid

PBu was dissolved in toluene to a concentration of 10-15 wt%. The solution was transferred to the reactor and heated to reaction temperature. Formic acid (FA) was added. Hydrogen peroxide (30 wt%) was subsequently added to the stirred mixture, either in one batch or in semi-batch mode. After the reaction, the organic phase of the final reaction mixture was phase separated from the aqueous phase, and subsequently washed twice with a saturated $NaHCO_3$-solution and with a saturated NaCl-solution to remove residual peroxide and acid. The organic phase was then dried over Na_2SO_4 and the toluene was removed under reduced pressure at 60 °C. The epoxidized polybutadienes were obtained in yields between 90 and 98% based on the applied PBu.

7.8.3 Degree of Epoxidation

The degree of epoxidation was conveniently determined from the ^{1}H-NMR spectra in $CDCl_3$. The degree of epoxidation was calculated using equation 12. The integrals refer to the signals indicated by the chemical shift δ in ppm.

$$X\,[\%] = \frac{\int(\delta = 2.7 + 2.9\,ppm)}{\int(\delta = 2.7 + 2.9\,ppm) + \int(\delta = 5.0\,ppm) + \int(\delta = 5.4 + 5.6\,ppm)} \cdot 100\% \quad (12)$$

The signals of the 1,2- and 1,4-double bonds ($\delta = 5.0 - 5.6\ ppm$) broaden as a result of the epoxidation, the integrals however can be obtained without additional effort. Additionally, elemental analysis was performed to determine the degree of double bond epoxidation. The results of elemental analysis are in accordance with the ^{1}H-NMR results (Table 21).

Table 21. Comparison of results of conversion by ^{1}H-NMR and elemental analysis.

conversion by ^{1}H-NMR [%]	conversion by elemental analysis [%]
10	12
21	21
30	32
37	37
39	38
42	42

The progress of the reaction was monitored from samples taken from the reacting mixture. The stirring was stopped, a sample of about 2 mL was taken from the reaction mixture with a pipette and transferred to a glass vial. It was treated two times with 1 mL of $NaHCO_3$ solution and once with 1 mL of NaCl solution. The organic phase was transferred to another glass vial and the toluene removed under reduced pressure.

7.8.4 Titration of Epoxide Groups

The titration was based on the method of JUNG and KLEEBERG.[78] The epoxidized PBu sample was put into a 50 mL Erlenmeyer flask. The sample mass added was calculated by ^{1}H-NMR results, that 1.5 mmol epoxide groups were present in the sample. 5 mL butanone was added and slewed until the PBu sample was dissolved. 10 mL of a solution (8 mL concentrated hydrochloric acid in 300 mL butanone) was added and the closed flask stored for 30 min. 5 mL of demineralized water was added prior to titration to dissolve potassium chloride formed during reaction. The titration was conducted using 0.1 M ethanol solution of potassium hydroxide.

A blank value was determined once every day of measurement. The titer potassium hydroxide solution was determined using 200 to 300 mg potassium hydrogen phthalate in boiled demineralized water.

The EP-value was calculated using the following equation:

$$\boldsymbol{EP = \frac{(V_{blank} - V_{sample}) \cdot c(KOH) \cdot t_{KOH}}{m_{sample} \cdot 10}} \qquad (13)$$

V_{blank} and V_{sample} are the volumes of potassium hydroxide solution used until titration end point of the blank value and the sample titration respectively. c(KOH) describes the concentration of potassium hydroxide solution and t_{KOH} the titer of the same. The samples mass is given by m_{sample}. The EP-value describes the molar amount of epoxide per 100 g of epoxidized PBu, which can be calculated into a relative epoxidation ratio with the knowledge of the polymers molecular mass.

7.9 Rheological Characterization of Epoxidized Polybutadienes

7.9.1 Materials

Toluene was destilled and stored over molecular sieves (4 Å) prior to use.

7.10 Oscillatory Rheology measurements

A strain sweep measurement from 0.1% to 1% or 10% was done for every sample type to determine the linear viscoelastic range of the material under the given conditions. The strain for the frequency measurements was then set to a value well in the linear region of the complex oscillatory viscosity.

For the toluene diluted samples a solvent trap cap was used to prevent solvent evaporation during the measurement.

The time-temperature-superposition (TTS) mastercurves were calculated using the TRIOS software and with the measurement at 25 °C as reference curve.

7.11 Aminolysis of Epoxidized Polybutadienes

7.11.1 Process

The ring opening of epoxidized 1,4-polybutadiene is much slower compared to epoxidized 1,2-polybutadiene (vide supra). High temperatures are therefore needed, which exceed the boiling point of n-butylamine (b.p.: 78 °C). These reactions are thus conducted in glass autoclave vessels sealed by a PTFE cap and PTFE sealing tape (35 mL, max. 10 bar) at temperatures above boiling point. The vessels were heated in a glass beaker filled with sunflower oil. A Heidolph MR 3002 control heating plate was used as heating device.

1 or 2 g of the epoxidized polybutadiene was dissolved under stirring in 20 mL of butyl amine, lithium bromide was added, the vessel was sealed tight and heated to the reaction temperature.

After the reaction time the vessel was allowed to cool, the excess amine was evaporated under reduced pressure and the resulting high viscous product was precipitated out of THF in water to remove residual free n-butylamine. The product was received as a highly viscous, slightly yellow liquid.

7.11.2 Degree of Aminolysis

The decrease of epoxy content and increase of amine functionalization was monitored by ^{1}H-NMR and ^{13}C-NMR I-Gated measurements. In ^{1}H-NMR spectroscopy, the signals at 2.7 ppm and 2.9 ppm are attributed to the *trans and cis* epoxy groups respectively. In ^{13}C-NMR I-Gated measurements the signals at 56.7 ppm and 58.3 ppm are attributed to the *cis* and *trans* epoxy groups respectively (Figure 46). The analysis of the amine conversion is illustrated exemplarily for the aminolysis with n-butylamine, where the signal of the terminal methyl group is shown at 0.92 ppm in ^{1}H-NMR measurements. The signals of the remaining methylene groups coincide with the signals of the polybutadiene chain. In ^{13}C-NMR I-Gated measurements the signal at 14.0 ppm is attributed to the terminal methyl group of butylamine and the signal at 20.5 ppm to the adjacent methylene group (Figure 46).

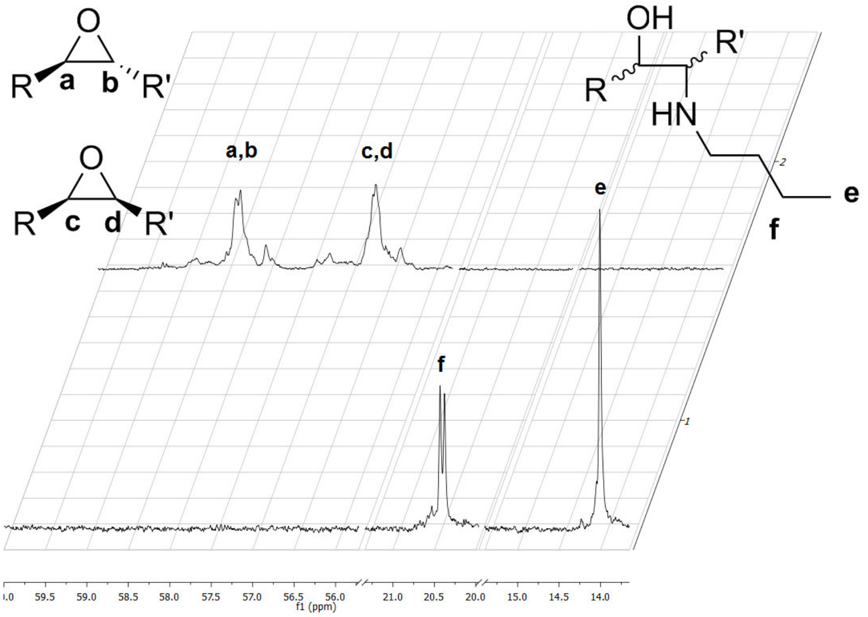


Figure 46: ^{13}C-NMR I-Gated spectra of the epoxidized sample (a) and the aminated sample (b).

The integrals of the peaks in ^{13}C-NMR I-Gated spectra are only reliable with long relaxation times. Because of the resulting very long measuring times the degree of aminolysis was determined by ^{1}H-NMR spectra and elemental analysis measurements. However qualitative results were drawn from the ^{13}C-NMR I-Gated spectra. A ^{13}C-NMR I-Gated measurement with a relaxation time of 80 s showed good accordance with the results of ^{1}H-NMR and elemental analysis (Table 16).

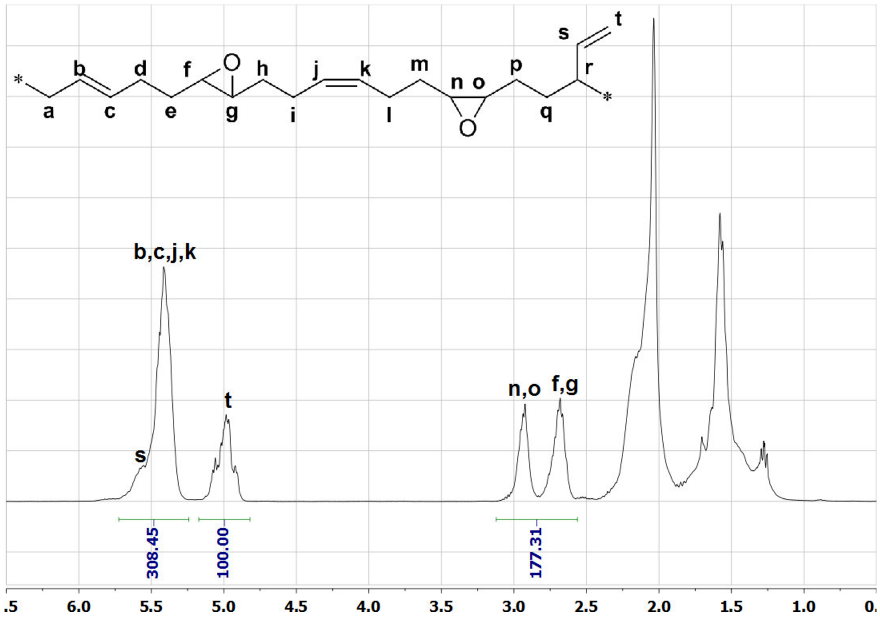


Figure 47: ^{1}H-NMR spectrum of the epoxidized sample

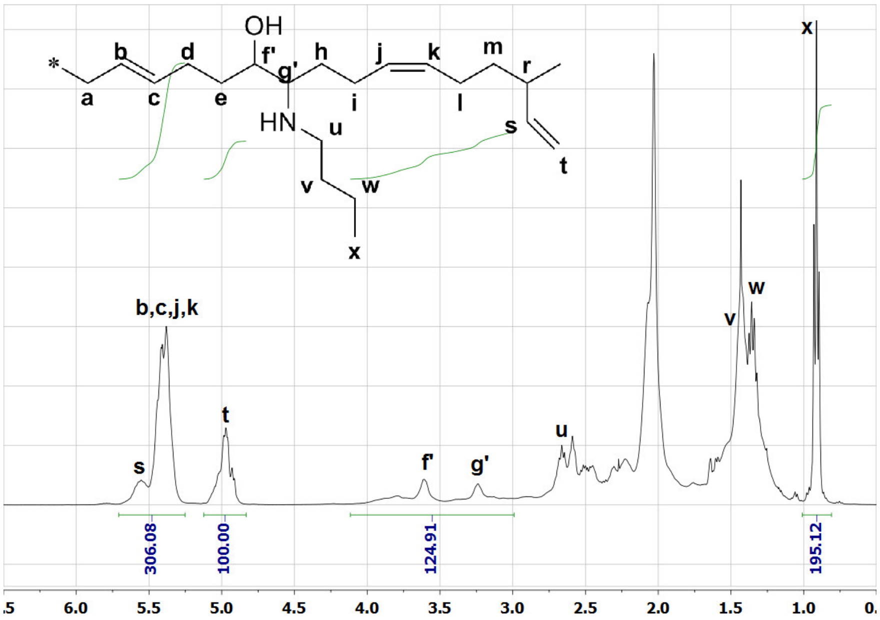


Figure 48: ^{1}H-NMR spectrum of the aminated sample

The Degree of aminolysis relative to the initial double bonds was therefore determined using ^{1}H-NMR (equation 14).

The Integrals were normalized to the integral of the t signal, which is visible without overlapping in epoxidated polybutadiene as well as in aminated polybutadiene and doesn't change during aminolysis reaction.

The integrals of n, o, f and g in the spectrum of the epoxidated polybutadiene precurser (EBR) were divided by two, since two protons represent one epoxide group. The integral of x in the spectrum of the aminated polybutadiene product (ABR) was divided by three, since three protons represent one amine group. The integrals of b, c, j, k, t in the spectra of epoxidized as well as aminated polybutadiene were divided by two, since two protons represent one double bond. The corrected integrals were used in equation (14.

$$\Sigma \int n, o, f, g, t, s, b, c, j, k = EBR, \Sigma \int x, t, s, b, c, j, k = ABR$$

$$X\% = \frac{\int x}{\int x + (EBR - ABR) + \int t + \int b, c, j, k} * 100 \qquad (14)$$

The difference of EBR and ABR equals the integrals of epoxide groups not opened by n-butylamine, representing either unopened epoxide groups or epoxide groups opened by a neighboring aminol group forming a cyclic ether or cyclic amine (see chapter 5.3.4). The formation of cycles does open an epoxide group without the addition of *n*-butylamine.

7.12 Quaternization of aminated polybutadienes

7.12.1 Process

In a glass flask equipped with a magnetic stirrer 1-10 g aminated polybutadiene were dissolved in THF (10-15 times by weight) under stirring at room temperature. 2-3 eq potassium carbonate, relative to the concentration of amine groups, were added under stirring. The first half of 5-10 eq iodomethane, relative to the concentration of amine groups, were added to the resulting suspension to start the reaction. The flask was sealed, to avoid evaporation of iodomethane. During the reaction a fine colorless precipitation was visible, which was distinguishable from the coarse potassium carbonate and most likely was potassium iodide. After a certain time (usually 24 h) the second half of iodomethane was added.

After 72 h the reaction was quenched by adding 50 mL of aqueous ammonia (30%). The resulting mixture was precipitated in cold water, filtered, washed with water and dried under reduced pressure. The product was received as a hard, slightly brown foam.

7.12.2 Degree of Quaternization

The degree of quaternization was monitored using ^{1}H-NMR spectroscopy. The triplet at 0.92 ppm, attributed to the methyl group of bound *n*-butylamine, shifts downfield with the introduction of quaternary ammonium ions (Figure 49). The remaining methylene groups of bound *n*-butylamine shift as well but coincide with the rubber signals of polybutadiene. The shifted triplet has still some overlapping with the triplet of non-ionized amines methyl group, which is why a lorentzian fit was used to distinguish both peaks (Figure 50).

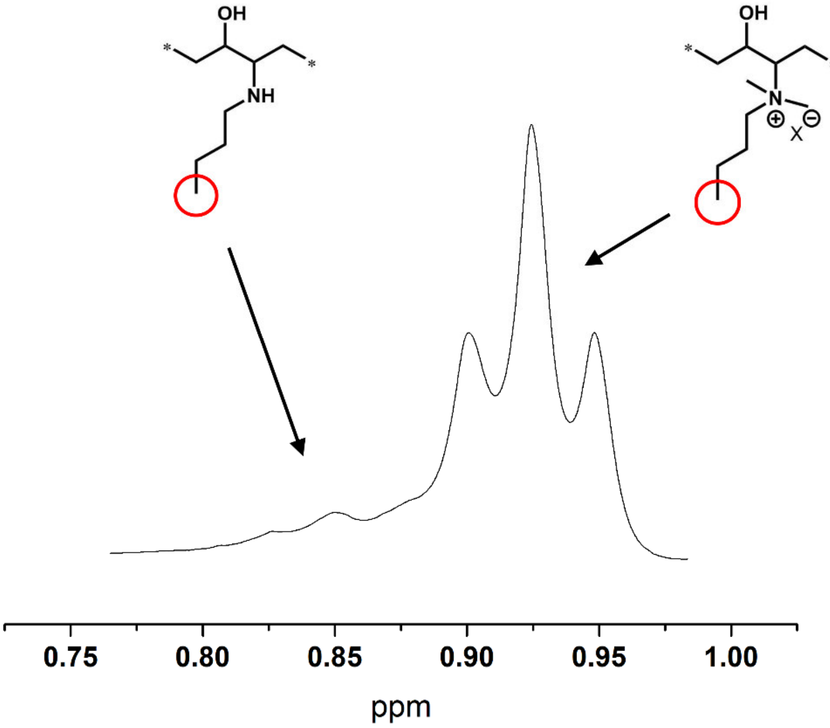


Figure 49. Assignement of the two overlapping triplets

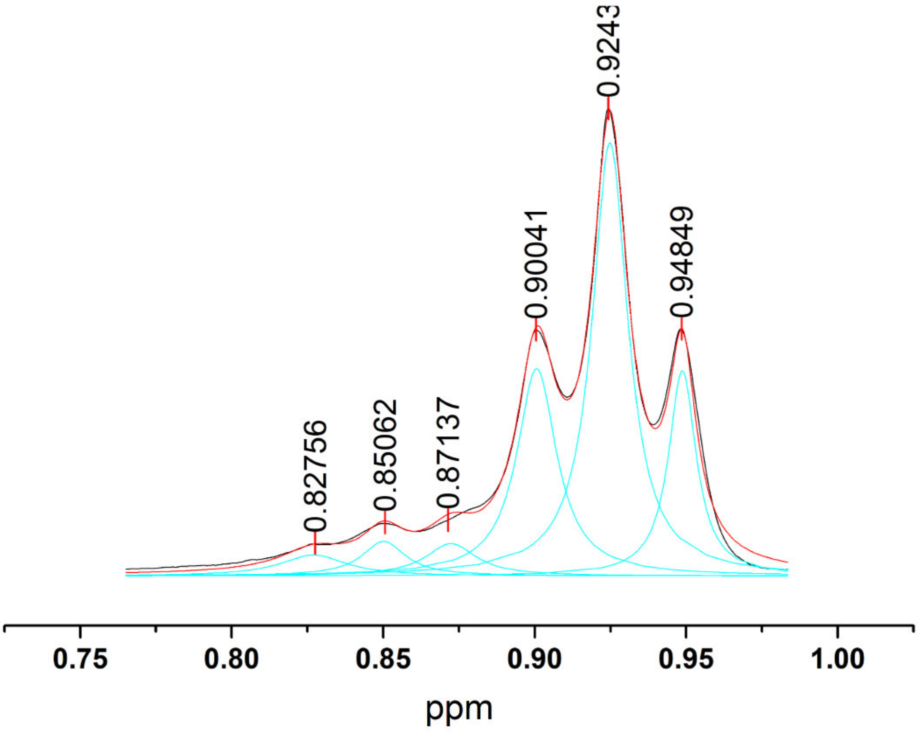


Figure 50. Lorentzian fit (red line) of the two overlapping triplets

The conversion was calculated using equation (15):

$$\mathrm{X\%} = \frac{\int 0.90, 0.92, 0.95\ ppm}{\int 0.90, 0.92, 0.95\ ppm + \int 0.83, 0.85, 0.87\ ppm} * 100 \tag{15}$$

8 Safety Data

Table 22. Hazard statements according to GHS[108]

Substance	GHS pictograms	Hazard Sentences	Precaution Sentences
1,2-Epoxybutane	 **Danger**	H225, H302+H312+H332, H315, H319, H335, H351, H412	P21, P261, P273, P280, P305+P351+P338, P308+P313, P403+P235
2-(Dimethylamino)-ethanol	 **Danger**	H226, H331, H312, H302, H314, H335	P210, P280, P303+P361+P353, P305+P351+P338, P312, P405
2,3-Epoxybutan	 **Danger**	H225, H315, H319, H335	P210, P261, P305+P351+P338
2-Amino-2-methylpropan-1-ol	 **Danger**	H315, H318, H412	P273, P280, P305+P351+P338
Aqueous ammonia (30%)	 **Danger**	H290, H314, H335, H400	P260, P273, P280, P301+P330+P331, P303+P361+P353, P305+P351+P338
Butanone	 **Danger**	H225, H319, H336	P210, P305+P351+P338, P403+P233
Chloroform-d	 **Danger**	H302, H331, H315, H319, H351, H361d, H372	P201, P260, P264, P280, P304+P340+P311, P403+P233
Benzil	 **Caution**	H315, H319	P302+P352, P305+P351+P338

Substance	GHS pictograms	Hazard Sentences	Precaution Sentences
Dimethylsulfate	 **Danger**	H301, H314, H317, H330, H341, H350	P201, P280, P301+P330+P331, P302+P352, P304+P340, P305+P351+P338, P308+P310
Formic acid	 **Danger**	H226, H302, H314, H331	P210, P280, P303+P361+P353, P304+P340+P310, P305+P351+P338, P403+P233
Hydrochloric acid aq. (36%)	 **Danger**	H290, H314, H335	P260, P280, P303+P361+P353, P304+P340+P310, P305+P351+P338
Hydrogen peroxide aq. (30%)	 **Danger**	H318, H412	P280, P305+P351+P338+P310
Iodomethane	 **Danger**	H301+H331, H312, H315, H319, H335, H351, H410	P273, P302+P352, P304+P340, P305+P351+P338, P308+P310
LBR-305	No hazardous substance		
LBR-307	No hazardous substance		
Lithene ultra® N4-5000	No hazardous substance		
Lithene ultra® PM4	No hazardous substance		
Lithium bromide	 **Caution**	H302, H315, H317, H319	P280, P305+P351+P338

Substance	GHS pictograms	Hazard Sentences	Precaution Sentences
Methanol	 **Danger**	H225, H331, H311, H301, H370	P210, P233, P280, P302+P352, P304+P340, P308+P310, P403+P235
n-Butylamine	 **Danger**	H225, H302, H311+H331, H314	P210, P233, P240, P280, P301+P330+P331, P302+P352, P305+P351+P338, P308+P310, P403+P235
Potassium carbonate	 **Caution**	H315, H319, H335	P302+P352, P305+P351+P338
Potassium hydrogen phthalate	No hazardous substance		
Potassium hydroxide 0.1 N in ethanol	 **Danger**	H225, H315, H319	P210, P240, P302+P352, P305+P351+P338, P403+P233
Sodium bicarbonate	No hazardous substance		
Sodium chloride	No hazardous substance		
Tetrahydrofurane	 **Danger**	H225, H302, H319, H335, H351	P210, P280, P301+P312+P330, P305+P351+P338, P370+P378, P403+P235
Toluene	 **Danger**	H225, H304, H315, H336, H361d, H373	P210, P240, P301+P310+P330, P302+P352, P314, P403+P233

CMR substances used are listed in Table 23.

Table 23. CMR substances used.[111]

CAS-No.	Name	Procedure	Quantity	Catagory
77-78-1	Dimethylsulfate	Quarternization	~200 mL	Carc. 1B
106-88-7	1,2-Epoxybutane	Aminolysis	~14 mL	Carc. 1B
67-66-3	Trichloromethane-d	NMR-Measurements	~200 mL	Carc. 1B

9 Bibliography

[1] H.-G. Elias in *Makromoleküle* (Ed.: H.-G. Elias), **1999**.

[2] D. Zuchowska, *Polymer* **1980**, *21*, 514–520.

[3] M. M. Jacobi, C. K. Santin, M. E. Viganico, R. H. Schuster, *Kautschuk Gummi Kunststoffe* **2004**, *3/2004*, 82–89.

[4] R. J. Salinas, R. B. Petrovic, *Synthetic Rubber Overview*, Goa, India, **2016**.

[5] F. Röthemeyer, F. Sommer (Eds.) *Kautschuk-Technologie. Werkstoffe - Verarbeitung - Produkte*, Hanser, München [u.a.], **2006**.

[6] S. V. Lebedev, *Zh. Russ. Fiz.Khim. Ova. Chast.* **1910**, *42*, 949.

[7] C. Harries, *Justus Liebigs Ann. Chem.* **1911**, *383*, 157–227.

[8] F. E. Mathews, E. H. Strange, GB 24,790, **1910**.

[9] I.G. Farbenfabriken, FR 668113, **1928**.

[10] Phillips Petroleum Comp., GB 848065, **1956**.

[11] M. D. Lechner, K. Gehrke, E. Nordmeier, *Makromolekulare Chemie. Ein Lehrbuch für Chemiker, Physiker, Materialwissenschaftler und Verfahrenstechniker*, Birkhäuser, Basel, **2010**.

[12] F. E. Matthews, E. H. Strange, GB24.700, **1910**.

[13] P. Cossee, *Tetrahedron Letters* **1960**, *1*, 12–16.

[14] P. Cossee, *Journal of Catalysis* **1964**, *3*, 80–88.

[15] P. Cossee, *Recl. Trav. Chim. Pays-Bas* **1966**, *85*, 1151–1160.

[16] E. Arlman, *Journal of Catalysis* **1964**, *3*, 89–98.

[17] E. Arlman, *Journal of Catalysis* **1964**, *3*, 99–104.

[18] C. Costabile, G. Milano, L. Cavallo, G. Guerra, *Macromolecules* **2001**, *34*, 7952–7960.

[19] *Pigment & Resin Technology* **1977**, *6*, 11–15.

[20] E. Piorkowska, A. S. Argon, R. E. Cohen, *Polymer* **1993**, *34*, 4435–4444.

[21] H. R. Brown, A. S. Argon, R. E. Cohen, O. S. Gebizlioglu, E. J. Kramer, *Macromolecules* **1989**, *22*, 1002–1004.

[22] H. Fischer, B. Wegemund, W. Gress, M. Gorzinksi, DE3442200 A1, **1984**.

[23] S. Ichimura, Y. Tsuzuki, K. Hino, US5965255, **1997**.

[24] A. Konietzny, H.-D. Zagefka, K. Rombusch, H.-J. Bax, DE3233949 A1, **1982**.

[25] D. C. Edwards, K. Sato, *Rubber Chemistry and Technology* **1980**, *53*, 66–79.

[26] Y. Arai, US4594388, **1984**.

[27] J. Y. Choi, J. K. Lee, Y. You, W. H. Park, *Fibers Polym* **2003**, *4*, 195–198.

[28] G. Heublein, B. Heublein, P. Hortschansky, H. Meissner, H. Schutz, *Journal of Macromolecular Science: Part A - Chemistry* **1988**, *25*, 183–200.

[29] J. W. Holubka, US4486571, **1983**.

[30] M. Soga, Y. Takase, M. Ishikawa, M. Nakazawa, M. Nakayama, US4074034, **1975**.

[31] Y. Tsuchiya, K. Ito, K. Hagihara, H. Sakamoto, Y. Otsuki, US4730010, **1986**.

[32] H. Yasuno, T. Yoshinaga, T. Nakano, US4250007, **1979**.

[33] A. N. Bibi, D. A. Boscott, T. Butt, R. S. Lehrle, *European Polymer Journal* **1988**, *24*, 1127–1131.

[34] P. Bussi, H. Ishida, *J. Polym. Sci. B Polym. Phys.* **1994**, *32*, 647–657.

[35] A. G. Margaritis, N. K. Kalfoglou, *European Polymer Journal* **1988**, *24*, 1043–1047.

[36] J.-P. Dilcher, H. Jürgens, G. A. Luinstra in *Advances in Polymer Science*, *Vol. 269* (Ed.: P. Theato), Springer International Publishing, Cham (Switzerland), **2015**.

[37] Q. Zhou, S. Jie, B.-G. Li, *Polymer* **2015**, *67*, 208–215.

[38] F. P. Greenspan, R. E. Light, US2829135, **1955**.

[39] C. Wheelock, *Ind. Eng. Chem.* **1958**, *50*, 299–304.

[40] W. Kirchhof, W. Stumpf, B. Schleimer, US3253000, **1962**.

[41] H. S. Makowski, M. Lynn, D. H. Rotenberg, *Journal of Macromolecular Science: Part A - Chemistry* **1970**, *4*, 1563–1597.

[42] T. Hirai, Y. Hatano, S. Nonogaki, *J. Electrochem. Soc.* **1971**, *118*, 669.

[43] El Fayoumi, Ali A. Z., *Journal of Thermal Analysis* **1982**, *23*, 135–141.

[44] W.-K. Huang, G.-H. Hsiue, W.-H. Hou, *J. Polym. Sci. A Polym. Chem.* **1988**, *26*, 1867–1883.

[45] R. Siegmeier, A. Grund, G. Prescher, U. Brandt, 4851556, **1988**.

[46] O. Hayashi, K. Kimura, Y. Ooi, H. Ueno, *Kobunshi Ronbunshu* **1980**, *37*, 327–334.

[47] O. Hayashi, T. Takahashi, H. Kurihara, H. Ueno, *Kobunshi Ronbunshu* **1980**, *37*, 195–198.

[48] K. Maenz, H. Schütz, D. Stadermann, *European Polymer Journal* **1993**, *29*, 855–861.

[49] S. Roy, Namboodri, C. S. S., B. R. Maiti, B. R. Gupta, *Polym. Eng. Sci.* **1993**, *33*, 92–96.

[50] Y. Kurusu, Y. Masuyama, M. Miyamoto, *Polym J* **1994**, *26*, 1163–1169.

[51] M. M. Jacobi, C. P. Neto, C. G. Schneider, Rocha, T. L. A. C., R. H. Schuster, *Kautschuk Gummi Kunststoffe* **2002**, *11/2002*, 590–595.

[52] K. Maenz, M. Möllhoff, D. Stadermann, *Acta Polym.* **1996**, *47*, 208–213.

[53] A. Iraqi, S. Seth, C. A. Vincent, D. J. Cole-Hamilton, M. D. Watkinson, I. M. Graham, D. Jeffrey, *J. Mater. Chem.* **1992**, *2*, 1057.

[54] M. P. Achalpurkar, U. K. Kharul, H. R. Lohokare, P. B. Karadkar, *Sep. Purif. Technol.* **2007**, *57*, 304–313.

[55] D. Zuchowska, *Makromol. Chem. Rapid Commun.* **1981**, *2*, 135–138.

[56] A. K. Chakraborti, S. Rudrawar, A. Kondaskar, *European Journal of Organic Chemistry* **2004**, *2004*, 3597–3600.

[57] T. Ollevier, G. Lavie-Compin, *Tetrahedron Letters* **2002**, *43*, 7891–7893.

[58] A. Solladié-Cavallo, P. Lupattelli, C. Bonini, *The Journal of organic chemistry* **2005**, *70*, 1605–1611.

[59] A. T. Placzek, J. L. Donelson, R. Trivedi, R. A. Gibbs, S. K. De, *Tetrahedron Letters* **2005**, *46*, 9029–9034.

[60] M. Fujiwara, M. Imada, A. Baba, H. Matsuda, *Tetrahedron Letters* **1989**, *30*, 739–742.

[61] M. Meguro, N. Asao, Y. Yamamoto, *J. Chem. Soc., Perkin Trans. 1* **1994**, 2597.

[62] J. Augé, F. Leroy, *Tetrahedron Lett* **1996**, *37*, 7715–7716.

[63] G. R. Krishnan, K. Sreekumar, *Polymer* **2008**, *49*, 5233–5240.

[64] C. M. Kleiner, P. R. Schreiner, *Chem. Commun.* **2006**, 4315.

[65] M. Vijender, P. Kishore, P. Narender, B. Satyanarayana, *Journal of Molecular Catalysis A: Chemical* **2007**, *266*, 290–293.

[66] H. Chen, H. Zhang, D. Thor, R. Rahimian, X. Guo, *Eur. J. Med. Chem.* **2012**, *52*, 159–172.

[67] V. M. Dem’yanovich, I. N. Shishkina, A. A. Kuznetsova, K. A. Potekhin, A. V. Chesnova, *Russ. J. Org. Chem. (Russian Journal of Organic Chemistry)* **2006**, *42*, 986–989.

[68] C. Zhang, H. Ito, Y. Maeda, N. Shirai, S.-i. Ikeda, Y. Sato, *J. Org. Chem.* **1999**, *64*, 581–586.

[69] T. Hunt, H. C. Atherton-Watson, S. P. Collingwood, K. J. Coote, S. Czarnecki, H. Danahay, C. Howsham, P. Hunt, D. Paisley, A. Young, *Bioorganic & Medicinal Chemistry Letters* **2012**, *22*, 2877–2879.

[70] C. Roberts, W. E. Lindsell, I. Soutar, *Brit. Poly. J.* **1990**, *23*, 55–62.

[71] J. Hazziza–Laskar, N. Nurdin, G. Helary, G. Sauvet, *J. Appl. Polym. Sci.* **1993**, *50*, 651–662.

[72] K. Dorfner, *Ion Exchangers*, De Gruyter, **2011**.

[73] R. Schueller, P. Romanowski, *Conditioning Agents for Hair and Skin*, Taylor & Francis, **1999**.

[74] N. Phan-Thien, *Understanding Viscoelasticity. An Introduction to Rheology*, Springer, Berlin, Heidelberg, **2013**.

[75] TA instruments -, "Understanding Rheology of Thermoplastic Polymers".

[76] W. P. Cox, E. H. Merz, *J. Polym. Sci.* **1958**, *28*, 619–622.

[77] T. Mezger, *Das Rheologie-Handbuch. Für Anwender von Rotations- und Oszillations-Rheometern*, Vincentz Network, Hannover, **2012**.

[78] G. Jung, W. Kleeberg, *Kunststoffe* **1961**, *51*, 714–715.

[79] B. Kona, M. St. Weidner, J. F. Friedrich, *International Journal of Polymer Analysis and Characterization* **2005**, *10*, 85–108.

[80] N. V. Bac, L. Terlemezyan, M. Mihailov, *J. Appl. Polym. Sci.* **1991**, *42*, 2965–2973.

[81] S. Gnecco, A. Pooley, M. Krause, *Polymer Bulletin* **1996**, *37*, 609–615.

[82] S.-M. Wang, R. C.-C. Tsiang, *J. Polym. Sci. A Polym. Chem.* **1996**, *34*, 1483–1491.

[83] M. I. Abdullin, A. A. Basyrov, O. S. Kukovinets, A. B. Glazyrin, G. I. Khamidullina, *Polym. Sci. Ser. B* **2013**, *55*, 349–354.

[84] N. E. Gordon, *Dissertation*, Johns Hopkins University, Baltimore, Maryland, **1917**.

[85] Kolossowsky, Megenine, *Bull. Soc. Chim. Fr.* **1932**, *51*, 1000–1004.

[86] Atherton Seidell, *Solubilities of Organic Compounds. A compilation of Quantitative Solubility Data from the Periodical Literature*, D. Van Nostrand Company, Inc., New York, **1941**.

[87] X. SUN, X. ZHAO, W. DU, D. LIU, *Chinese Journal of Chemical Engineering* **2011**, *19*, 964–971.

[88] J. P. Dilcher, *Dissertation*, Universität Hamburg, Hamburg, **Unveröffentlicht**.

[89] P. D. Filippis, M. Scarsella, N. Verdone, *Ind. Eng. Chem. Res.* **2009**, *48*, 1372–1375.

[90] J. K. Jackson, M. E. de Rosa, H. H. Winter, *Macromolecules* **1994**, *27*, 2426–2431.

[91] M. Ballauff, *Angewandte Chemie* **1989**, *101*, 261–276.

[92] G. C. Berry, T. G. Fox, *Adv. Polymer Sci.* **1968**, *5*, 261–357.

[93] B. L. Hager, G. C. Berry, *J. Polym. Sci. Polym. Phys. Ed.* **1982**, *20*, 911–928.

[94] R. W. Rendell, K. L. Ngai, G. B. McKenna, *Macromolecules* **1987**, *20*, 2250–2256.

[95] Y. Takahashi, Y. Isono, I. Noda, M. Nagasawa, *Macromolecules* **1985**, *18*, 1002–1008.

[96] De Risi, F. R., L. D'Ilario, A. Martinelli, *J. Polym. Sci. A Polym. Chem.* **2004**, *42*, 3082–3090.

[97] I. T. Smith, *Polymer* **1961**, *2*, 95–108.

[98] Y. Kurusu, *Polym. Adv. Technol.* **1996**, *7*, 67–72.

[99] B. A. Rozenberg in *Advances in Polymer Science*, *Vol. 75* (Eds.: K. Dušek, J. P. Bell), Springer-Verlag, Berlin, New York, **1986**.

[100] P. K. Sundaram, M. M. Sharma, *Bull. Chem. Soc. Jpn.* **1969**, *42*, 3141–3147.

[101] I. R. Gelling, *Rubber Chemistry and Technology* **1985**, *58*, 86–96.

[102] I. R. Gelling, *Prog. Rubb. & Plast Tech.* **1991**, *7*, 271–297.

[103] A. Challioui, D. Derouet, A. Oulmidi, J. C. Brosse, *Polym. Int.* **2004**, *53*, 1052–1059.

[104] S. Roth, S. Göhler, H. Cheng, C. B. W. Stark, *Eur. J. Org. Chem.* **2005**, *2005*, 4109–4118.

[105] S. Göhler, S. Roth, H. Cheng, H. Göksel, A. Rupp, L. Haustedt, C. Stark, *Synthesis* **2007**, *2007*, 2751–2754.

[106] G. A. Sulikowski, M. M. Sulikowski, M. H. Haukaas, B. Moon, *Iodomethane*, **2005**, American Cancer Society, zu finden unter https://onlinelibrary.wiley.com/doi/full/10.1002/047084289X.ri029m.pub2.

[107] H. Z. Sommer, L. L. Jackson, *J. Org. Chem.* **1970**, *35*, 1558–1562.

[108] IFA, "GESTIS-Stoffdatenbank", zu finden unter http://gestis.itrust.de/nxt/gateway.dll?f=templates&fn=default.htm&vid=gestisdeu:sdbdeu.

[109] J. E. Mark, *J. Am. Chem. Soc.* **1966**, *88*, 4354–4359.

[110] C. Walling, A. Goosen, *J. Am. Chem. Soc.* **1973**, *95*, 2987–2991.

[111] Deutsche Gesetzliche Unfallversicherung, "Liste der krebserzeugenden, keimzellmutagenen und reproduktionstoxischen Stoffe (KMR-Stoffe)", zu finden unter https://publikationen.dguv.de/dguv/pdf/10002/kmr_oktober_2018.pdf, **2018**.

10 Acknowledgements

In this chapter I like to thank a number of people who have accompanied and supported me during my PhD. This part is written in German.

Zunächst möchte ich mich bei Herrn Professor Dr. Gerrit A. Luinstra bedanken für die Aufnahme in seinen Arbeitskreis, die fachliche Betreuung und die Ermöglichung der Promotion trotz meiner kreativen Schaffenspause nach der Diplomarbeit.

Herrn Professor Dr. Hans-Ulrich Moritz möchte ich für die Übernahme des Zweitgutachtens, sowie informative und unterhaltsame Vorlesungen danken.

Kathrin Rehmke und Stefan Bleck danke ich für die Messung der zahlreichen GPC und DSC Proben. Jens Pagel möchte ich für die kompetente und unkomplizierte Hilfe bei Reaktorbau und anderen technischen Problemen danken. Holger Stockhusen danke ich für die Hilfe bei Problemstellungen mit der Elektrik. Kathleen Pruntsch danke ich für die reibungslose Abwicklung von Bestellungen und Laborbedarfsanforderungen, sowie ihr fröhlich direktes Auftreten.

Dem gesamten AK Luinstra danke ich für die entspannte, lockere Atmosphäre, die Hilfe bei fachlichen und organisatorischen Problemen, sowie die zahllosen Grillabende, Bierrunden, Exkursionen, private Feiern, AK Fahrten und sportlichen Kampfhandlungen digitaler und analoger Natur. Meinen Labormitbewohnern Claudi, Franzi, Daniel, Helena und Karen danke ich für die kurzweilige und motivierende Arbeitsatmosphäre, sowie Gesprächen innerhalb und abseits der Chemie. Daniel danke ich außerdem für die abwechslungsreiche Musikauswahl, die geduldige theoretische und praktische Unterstützung (vor allem in der Rheologie) und den hohen Entertainment Wert besonders nach ein paar Bierchen.

Herausheben möchte ich außerdem Jan für die Unterstützung bei Epoxidierung, Titration, etc. und für die Fussballdiskussionen und Lars für Filmabende und Rain in Africa.

Ich danke meinen Praktikanten und Bachelorstudenten für die Unterstützung bei der Synthesearbeit und besonders Stefanie Schmidt, Fabian Wenzel und Fabian Ratzke für ihren engagierten Einsatz.

André, Dirk, Martin, Marcel und Matthias, danke ich für die Standhaftigkeit unter digitalem Artilleriefeuer und Beschuss, die Stammtischrunden, Operation „Mustache“, Junggesellenabschiede, Hochzeiten, Feiern, und und und.

Außerhalb der Uni möchte ich besonders Benni danken für seine vielen Jahre als Freund, Kumpel und WG-Mitbewohner. Zusammen mit Jan und Tim gab es so schön viel Ablenkung vom manchmal stressigen Uni-Alltag beim ein oder anderen Bier - egal wo (hauptsache warm und Musik). Danke euch Jungs!

Meinen Schwiegereltern Elke und Karl-Heinz möchte ich danken für ihre Unterstützung auf ganz vielen Ebenen und die sehr herzliche Aufnahme in die Familie.

Meinen Eltern gilt ganz besonderer Dank für ihre Unterstützung, ihren Stolz und ihre Geduld. Vielen Dank dafür, dass ich immer auf euch zählen kann!

Meinen Schwestern Lene und Inga danke ich für lustige, gemütliche und spannende Tage, Abende und Gespräche.

Mein Größter Dank gilt meiner Frau Ulrike, mit der ich nun schon über 13 Jahre mein Leben teilen darf und seit über zwei Jahren eine wundervolle Tochter, sowie seit kurzem einen aufgeweckten, kleinen Sohn habe. Ich danke Dir, dass Du mich motivierst, mir den Rücken stärkst, mich ausgleichst, mich manchmal wieder auf den Weg bringst, Dich nicht verbiegst, Dir treu bleibst und Dir nicht für Blödeleien zu schade bist!

11 Declaration of 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. I hereby declare that I have not previously applied or pursued for a doctorate (Ph.D. studies).