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Upon scope and limitations of sulfenyl bromides for the post-modification of polyolefins

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To my parents

and grandparents

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Abstract

Since the implementation of the concept named “click”-chemistry from *Sharpless* 2001, great efforts have been made to find those reactions whose outstanding qualities include simplicity in preparation combined with high yields and a broad application area. Thiol-ene chemistry satisfies all expectations and gains more and more interest from both academic research as well as industry due to its easy accessibility for material sciences and applications. In this context a new approach in dependence on the generation of a reactive thiol species by the cleavage of a disulfide according to the well-known *Zincke* reaction was realized. To gain a better insight in the conversion behavior, the obtained highly reactive thiol moiety was reacted with a couple of unsaturated low molecular model substances. The main focus was laid on the conversion of this *in-situ* generated sulfenyl halide for the post modification of several different sterically hindered vinyl containing precursor polymers prepared via ROMP (Ring Opening Metathesis Polymerization) and ADMET (Acyclic Diene Metathesis). Detailed investigations to determine the degree of succeeded modification were performed by means of NMR spectroscopy, GPC-, IR-absorption-, Elemental- as well as STA-analysis and are presented within this work.

Kurzfassung

Seit der Einführung des bekannten Konzeptes der “Klick”-Chemie von *Sharpless* 2001 wurden große Anstrengungen unternommen um derartige Reaktionen zu finden und zu implementieren. Deren überragende Eigenschaften vereinen eine einfache Handhabung in der Herstellung, kombiniert mit hohen Ausbeuten sowie eines weiten Einsatzbereiches. Thiol-En-Klickchemie erfüllt all diese Erwartungen, und erlangt immer mehr Aufmerksamkeit nicht nur seitens akademischer Forschung sondern auch vielmehr von industrieller Seite um sich diesen einfachen Zugang zu Materialwissenschaften sowie deren weitere Anwendungen lukrativ zu Nutze zu machen. In diesem Zusammenhang wurde ein neuartiger Zugang zur Bildung einer sehr reaktiven Thiol-spezies durch die Spaltung eines Disulfids nach der bekannten *Zincke* Reaktion durchgeführt. Um den Einsatzbereich solcher Sulfenyl Halogene abzuschätzen, wurden diese mit einer Hand voll ungesättigter niedermolekularer Modelsubstanzen umgesetzt. Das Hauptaugenmerk richtete sich jedoch auf eine weitere Umsetzung dieser *in-situ* hergestellten Sulfenyl Halogene mit verschiedenen Vinyl beinhaltenden Polymeren die mittels ROMP (Ring Öffnende Metathese Polymerisation) und ADMET (Azyklische Dien Metathese) hergestellt wurden. Die Untersuchungen zur Bestimmung des Funktionalisierungsgrads unter Verwendung von NMR Spektroskopie, Gel Permeations Chromatographie, Infrarot Spektroskopie, Elementaranalyse sowie einer simultanen thermischen Analyse werden innerhalb dieser Arbeit vorgestellt.

Contents

1. Introduction and Motivation

1.1. In-situ generation of “clickable” thiols for α,β functionalization of polyolefins

Over the past decade of investigations on “click” chemistry a wide range of reactions have been discovered and proven to be powerful additions to the chemist`s toolbox applying in chemistry, materials and biology.[1] As excellent example of such chemistry, thiol-ene-chemistry has gained tremendous attention due to the widespread field of applications, the ease of technical effort and the matrix of combinable systems.[2] The very often obtained insufficient results by using conventional polymer modification techniques accompanied by the formation of by-products and longsome purification procedures as well as reaction times can be summarized as the central issues.[3] Additionally steric hindrance in combination with different electronic properties of the reacting ene pointed out some limitations of this easy accessible way for functionalization.[4] Furthermore the still unsolved problem of the free thiol-species concerning oxidizing environments leading to the corresponding disulfide species is an important factor for the trouble free use of this versatile tool.[5] For that reason, further works have been aimed at the *in-situ* reaction to form thiobromides by the reactive cleavage of the disulfide bond according to the well-known *Zincke* reaction.[6] A subsequent addition of this species to olefinic double bonds highlights a broad conversion spectrum of possible reactants.[7]

[1] Kolb H. C.; Fin, M. G.; Sharpless K. B. *Angew. Chem., Int. Ed.* **2001**, 40, 2004-2021
[2] Justynska J.; Hordyjewicz Z; Schlaad H. *Polymer* **2005**, 46, 12064
[3] Hole C. E.; Lee T. Y.; Roper T.; J. *Polym. Sci.* **2004**, 42, 5301-5338
[4] Roper T. M.; Lee T. Y., Guymon C. A.; Hoyle C. E. *Macromolecules* **2005**, 38, 10109-10116
[5] Espeel, P.; Goethals F.; Du Prez F. E. *J. Am. Chem. Soc.* **2011**, 133, 1678
[6] Zincke T. *Chem. Ber.* ***1911****, 44, 769*
[7] Kühle E. Synthesis **1971**, 11, 563-86

1.2. Scope of this work

The objective of this work focused on the *in-situ* preparation and characterization of possible sulfenyl bromides for a subsequent electrophilic addition to vinyl containing polymers. Within this study, dibutyl disulfide was used as a model molecule and converted with a range of unsaturated polymers differing in their steric demand to define limitations of this highly reactive thiobromide species towards the degree of succeeded modification.

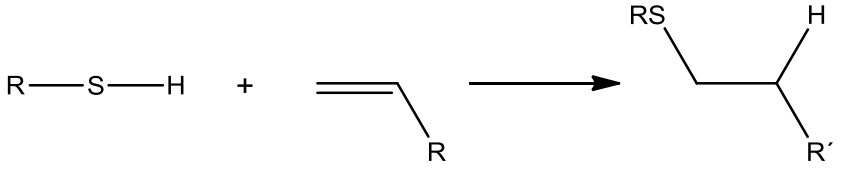
Different analysis methods such as ^{1}H and ^{13}C NMR spectroscopy, gel permeation chromatography (GPC), infrared absorption (FT-IR), elemental analysis as well as the thermal decomposition by the use of simultaneous thermal analysis (STA) should give an insight about qualitative and quantitative proceeded functionalization compared to the defined precursor polymers.

2. General Background

2.1. Thiol-ene "Click"-chemistry

Within the recent years many organic reactions found entrance to the concept labeled as "click" chemistry. From investigations on low molecular weight substances an extension to the macro- and supramolecular chemistry enabled the synthesis of several types of innovative polymeric architectures.[8] Originally introduced by Sharpless in 2001 a couple of similar chemical transformations relating to a set of specific criteria were centralized. The main requirements include quantitative yields from readily available starting materials in a broad range of solvents or in bulk. Under smooth reaction conditions a straightforward procedure should yield in high region-specific and orthogonal product without the use of chromatographic methods for purification. Also the absence of aggressive by-products should be achieved.[1] The radically induced Thiol-ene-reaction possesses in most instances these characteristics. A very broad application area ranging from material- and molecule-synthesis to the selective functionalization of biological compounds as well polymer synthesis and their modification makes it a very versatile method not only in chemist`s toolbox.[32] Nevertheless thiol-ene chemistry suffers from its limitations which should be contoured towards the kinetics of the reaction mechanism and accessibility of different types of olefins.[32] Additionally the number of commercial available thiols as starting material is rather limited. A poor shelf live by reason of oxidation reactions combined with an unpleasant smell confirms advantages of an *in-situ* generation of thiols and convert them in a one-pot process.[5]

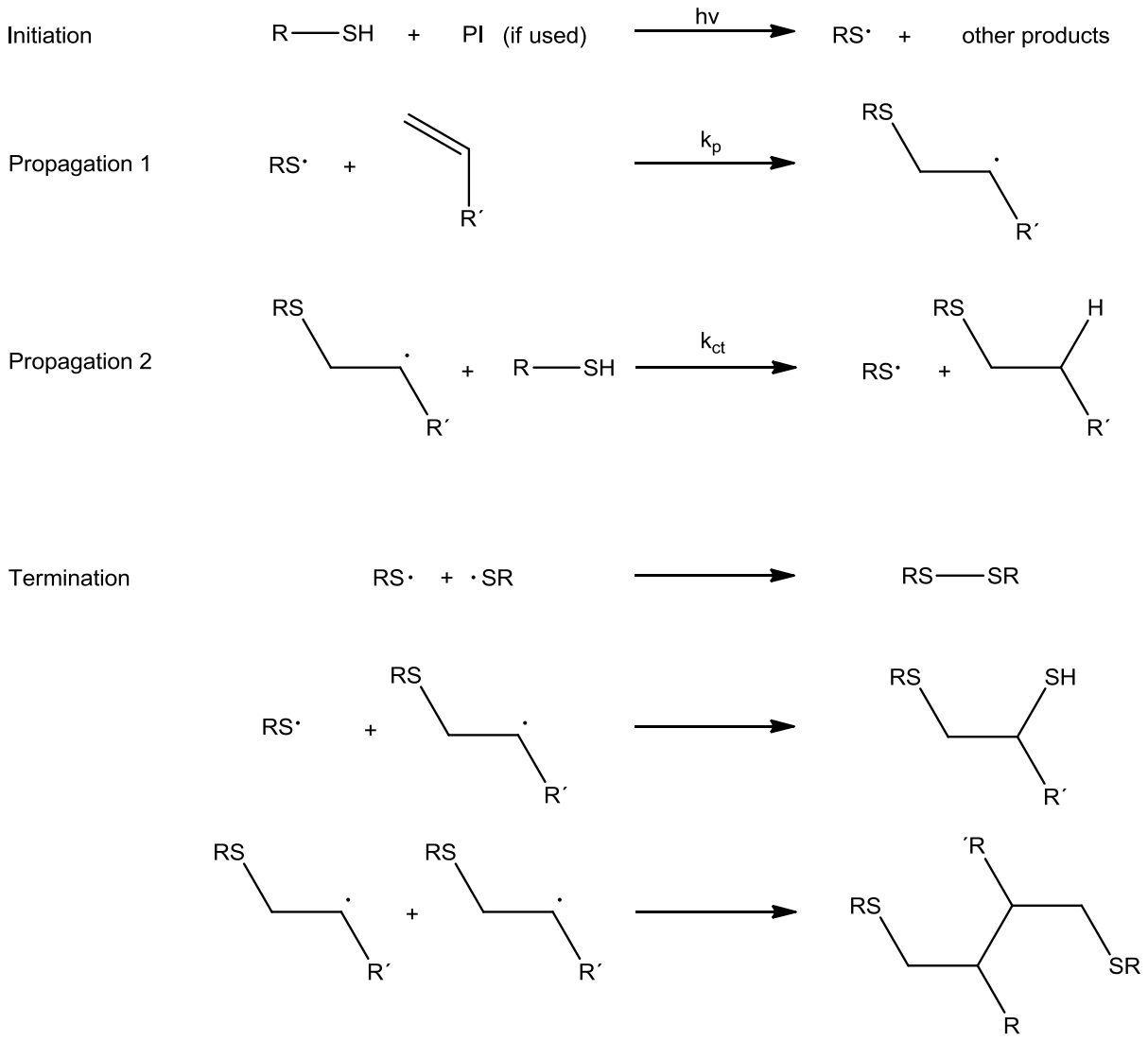
2.1.1. Kinetics of Thiol-ene polymerization



Scheme 1: Free radical chain mechanism of Thiol-ene polymerization

[8] Golas P.; Matyjaszewski K.; *Chem. Soc. Rev.* **2010**, 39, 1338-1354

Investigations of the influence according to the thiol as well as the ene structure on the overall rate of the addition process pointed out two basic rules of the chain reaction. A direct relation of the electron density on the ene is primary to consider. Electron-rich enes are converted quicker than electron poor enes with the expectation of highly conjugated double bonds in a copolymerization due to the stabilization of the carbon-centered allylic radical after the addition of thiyl radical to the C=C double bond.[9]



Scheme 2: General Thiol-ene photopolymerization process

[9] Morgan C. R.; Magnotta F.; Ketley A. D. *J Polym Sci Polym Chem* **1977**, 15, 627

One outstanding feature of thiol-ene photopolymerization is that almost any ene can be used which is shown below. The exact order may differ marginally depending on experimental conditions.

Norbornene > Vinyl ether > Propenyl > Alkene ~

Vinyl ester > *N*-Vinyl amides > Allyl ether ~

Allyltriazine > *N*-Vinylamides > Allylether ~

Allyltriazine ~ Allylisocyanurate > Acrylate >

Unsaturated ester > N-substituted maleimide >

Acrylonitrile ~ Methacrylate > Styrene

>Conjugated dienes

With exception of the norbornene and the three last mentioned entries the reactivity decreases with a decreasing electron density of the C=C double bond. This is related to the different velocities of the hydrogen abstraction, which occurs subsequent to the addition of the thiyl radical across the double bond. In the case of norbornene the significant relief of the ring strain results in an acceleration, whereas methacrylate, styrene and conjugated dienes are very stable and produce radicals.[3]

However, due to the circumstances that the electronic properties might lead in certain cases to the stabilization of radicals, which possibly may be in connection with a termination reaction arouses suspicion of insufficient modification behavior or product formation.

Additionally the influence of the extent of substitution on the olefin shows a decrease of reactivity towards a thiol-ene free radical chain reaction. For that reason it is nearby that highly substituted alkenes are less reactive than single substituted ones. Furthermore the position of the double bond position can have an effect on the conversion rate as shown three hexenes in a copolymerization with a monofunctional thiol.

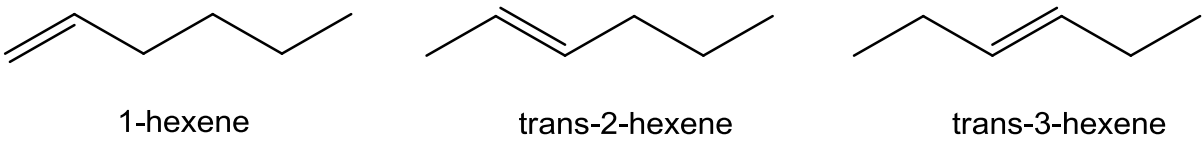
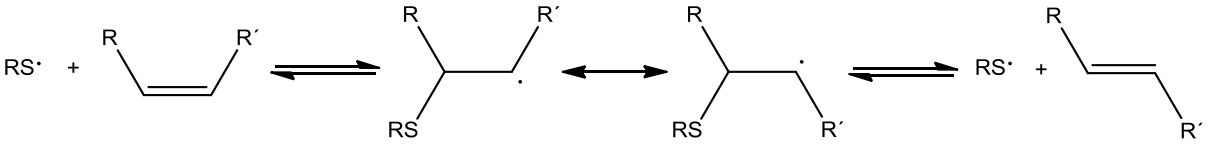


Figure 1: Structures of hexenes

1-hexene was 8 times more reactive than *trans*-2-hexene and 18 times more reactive *trans*-3-hexene in a 1:1 molar mixture. The reversible equilibrium in the two step propagation steric hindrance is a major factor. The addition of the thiyl radical to *cis*-ene bonds is reversible leading to the less active trans structure. Although the *trans*-ene structure reacts with thiyl radical efficiently the reaction is reversible and not as fast as with terminal enes.[10]



Scheme 3: Reversible addition of the thiyl radical to the disubstituted ene

A similar tendency towards the degree of functionalization in dependence of substitiution could be obtained by investigations regarding macromolecules within our workgroup. Therefore different types of polymers were converted with cysteamine either via UV-initiated coupling nor thermally induced.

Table 1: Conversion [%] determined using NMR-data in combination with EA for different polymers with cysteamine via Thiol-ene reaction[11,12]

Polymer	thermic	photolytic
1,2-PBD	n.d.	30-35 %
1,4-PBD	< 10 %	n.d.
1,2-PI	20-25 %	10-15 %
SBR	< 10 %	< 10 %
NR	5 %	5 %

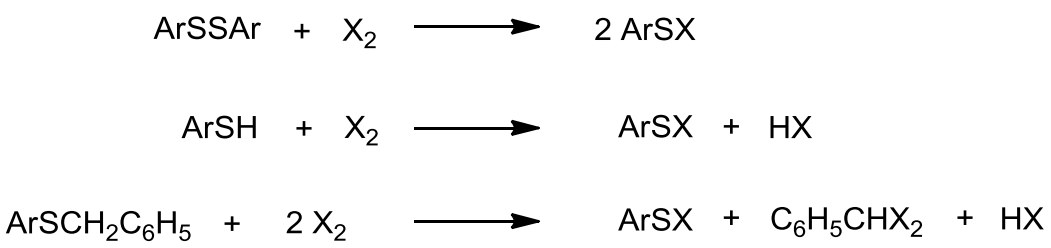
[10] Roper T. M.; Hoyle C. E.; Guymon A. C. *Polym Prepr (Am Chem Soc Div Polym Chem)* **2003**, 44, 11
[11] Dunst A.; Kienberger J.; Slugovc C. Biocidic Postmodification of Common Elastomers. **2011**,n14. Österreichische Chemietage
[12] Kienberger J.; Kreuzwieser E.; Noormofidi N.; Slugovc C. *Macromol Symp.* accepted

2.2. Sulfenyl halides

Generally they are used as precursors of derivatives of sulfenic acids.[13] Completely characterized sulfenyl halides can be found in literature in relatively small numbers and the major part consists of aromatic sulfenyl chlorides and bromides whereas a few aliphatic and even much less sulfenyl iodides can be found.[14] Many of these sulfenyl halides were only obtained in solution und further used for synthetic purposes, for example trimethylmethanesulfenyl halides.[15] Fist preparations of these substances can be attributed to *Zincke* who designated them as "arylsulfur halides" and can be found in many writings.

2.2.1. Preparation of sulfenyl halides "in the early years"

There are three essential similar methods by the use of chlorine and bromine on aryl disulfides, thiophenols or aryl benzyl sulfides for the synthesis of aromatic sulfenyl chlorides and bromides described by *Zincke* in his early studies of sulfenyl halides.

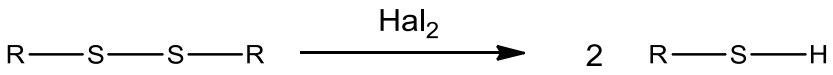


Scheme 4: Preparation of sulfenyl halides according to Zincke

These methods were used alternatively to synthesize the same sulfenyl halide by Zincke.[6]

[13] Connor R.; Gillman H. *Organic Chemistry* **1943**, 2nd edition, Vol. I, 920-3
[14] Rheinboldt H.; Motzkus E. *Chem. Ber.* **1939**, 72, 657
[15] Rheinboldt H.; Mott F. *Chem. Ber.* **1939**, 72, 668

2.2.2. Sulfenyl halides from disulfides



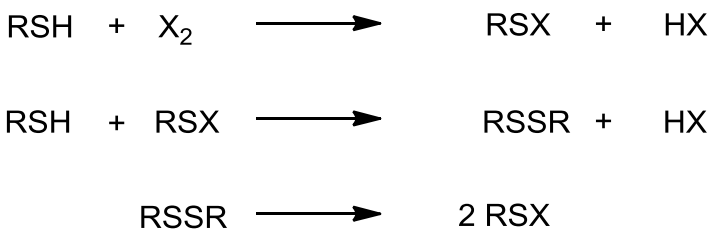
Scheme 5: Sulfenyl halides via halogination of disulfides

For the halogenation relative low temperatures, anhydrous conditions and solvents such as carbon tetrachloride, chloroform, ethylene chloride or benzene as well as other hydrocarbon solvents were used for the dissolubility of both reactants.[6] Restrictions could be found towards the formation of the sulfenyl halide according to the molar proportion of halogen. A decrease could be detected from chlorine to iodine. Nevertheless tetrahalogen derivates may occur as a result of excess of halogen, resulting in thiolsulfonic esters due to hydrolysis. Hydroxylic solvents or moisture from air result in the formation of sulfonyl halides after the sulfenyl halide stage.[16] The effect of preferred halogenation of the aromatic ring or aliphatic chain in contrast to the cleavage of disulfide linkage may also cause difficulties in the synthesis. A reduced tendency for substitution in the presence of nitrogen groups especially for the easy preparation in good yields of *o*-nitrobenzenesulfenyl chloride is reported. Compounds like benzenesulfenyl or naphtalenesulfenyl halides suffer from substitution in the aromatic system and need therefore special attention concerning definite reaction conditions as already mentioned as well as the exclusion of light and dilution of solvents.[17] For active hydrogen containing groups a reaction with the generated sulfenyl halide is promised. For example amino groups of aminoaryl disulfides are first acetylated followed by a subsequent scission of the disulfide to yield acetoamido aromatic sulfenyl halides.[18] The formation of amine hydrobromide during the cleavage may also be a possible occurring case.[16]

[16] Fries K.; Schürmann G. *Chem. Ber.* **1919**, 52, 2182
[17] Lechner H.; Wittwer M. *Chem. Ber.* **1922**, 55, 1474
[18] Child R.; Smiles S. *J. Chem. Soc.* **1926**, 2696

2.2.3. Sulfenyl halides from thiophenols

Another suitable method for the preparation of aromatic sulfenyl chlorides and bromides from thiophenols includes as a side reaction the formation of the disulfide followed by the further reaction of the halogen with the disulfide leading to the product.[19]



Scheme 6: Sulfenyl halides via halogination of thiophenols

Required conditions are basically the same as in the preparation from disulfides. In case of nitro-substituted benzenesulfenyl halides an excess of halogen does not interfere the desired formation sulfenyl halide in good yields according to the mentioned equations. For the preparation of benzenesulfenyl chloride the disulfide stage should be possibly avoided. Under effectual vigorous conditions to cleave the disulfide linkage also the aromatic ring is chlorinated simultaneously. By reducing the thiophenol concentration and the following addition to a solution of chlorine in an inert solvent this problem can be avoided. Therefore this preparation method offers essentially the same limitations but may be more advantageous for the synthesis of benzenesulfenyl chloride.[20]

[19] Zincke T.; Krüger O. *Chem. Ber.* **1912**, 45, 3468
[20] Lecher H.; Holschneider F.; Köberle K.; Speer W.; Stocklin P. *Chem. Ber.* **1925**, 58, 409

2.2.4. Sulfenyl halides from sulfides

Scheme 7: Sulfenyl halides via halogination of sulfides

The reaction of an aryl benzyl sulfide with chlorine is the original method employed by *Zincke* for the synthesis of aromatic sulfenyl chlorides. The method was only used for the synthesis of aromatic sulfenyl chlorides and no reasonable advantages to the other methods were obtainable. Even mentioned conditions for the cleavage of the carbon sulfur bond are practically similar. Noteworthy is the reaction of a methyl aryl sulfide with chlorine leading to give $ArSCCl_3$ due to the low electronegativity of the benzyl radical.[6]

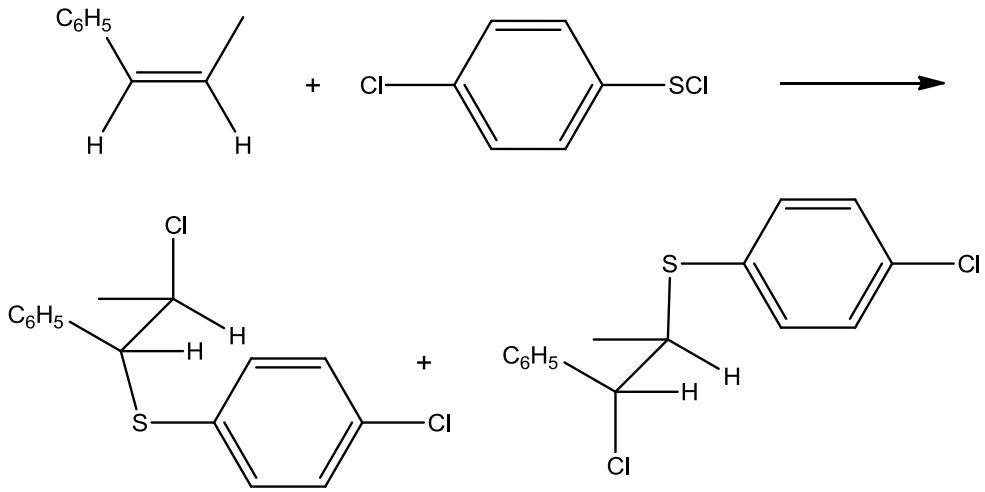
Other methods for the preparation of sulfenyl halides from sulfenic and sulfinic[16] acids, sulfinic esters or sulfinic anhydrides should at least be mentioned to cope up to the circuitousness of this topic.[21]

2.2.5. Addition Reactions to olefines

The simply adding of sulfenyl halides to carbon multiple bonds was often applied for characterization or for “trapping” them.[22] Addition reactions of simple olefins like ethylene and cyclohexene were known for a long time but not investigated with modern physical methods. From that moment the expectation of isomeric products could be clarified. Without irritation and radical initiators the reactions follows an ionic addition to the C=C double bond based on the attack of an electrophilic sulfenium ion. Accordingly three principles are applicable.

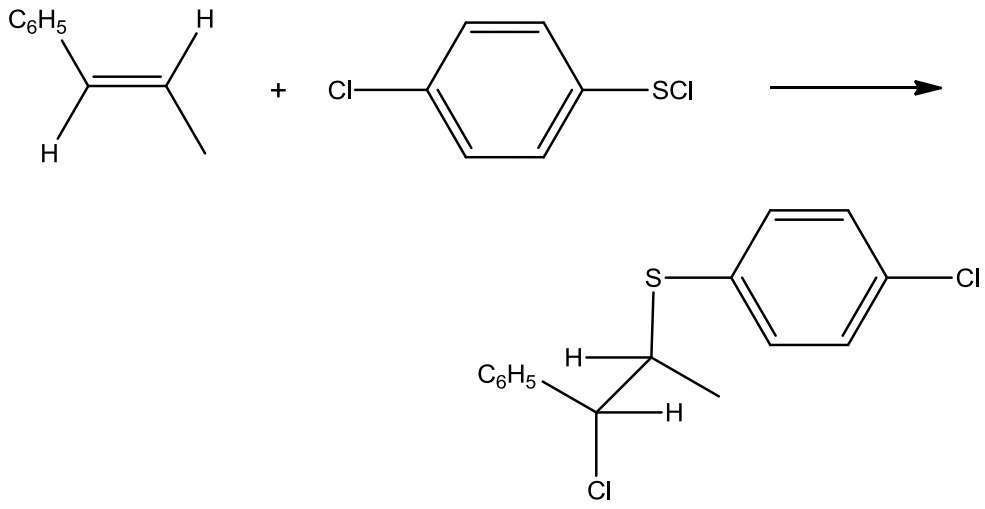
[21] Kharach N.; Potempa S. J.; Wehrmeister H. L. *Chem. Rev.* **1946**, 39, 269-332
[22] Böhme H.; Müller O.; *Chem. Ber.* **1965**, 98, 1455

(1) Stereospecific addition yields exclusively to *trans*-adducts[23,24] in an isomer mixture,



Scheme 8: Addition of 4-chloro-benzenesulfenyl chloride to *cis*-1-phenylpropene

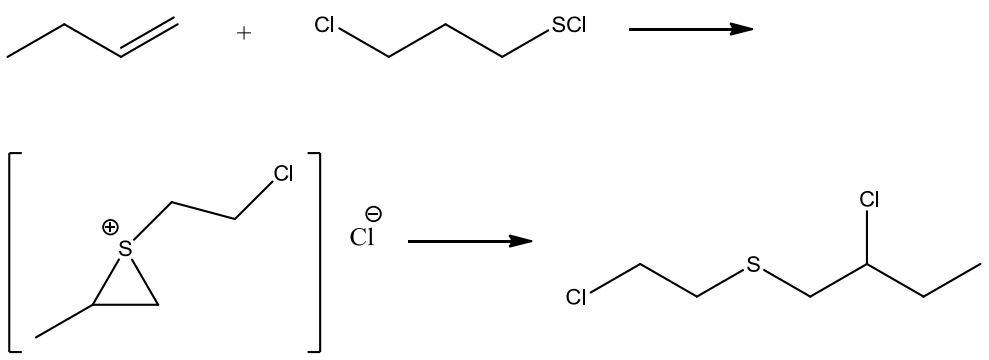
whereas the addition of an isomer is leading to the uniform adduct.[25]



Scheme 9: Addition of 4-chloro-benzenesulfenyl chloride to isomeric *trans*-1-phenylpropene

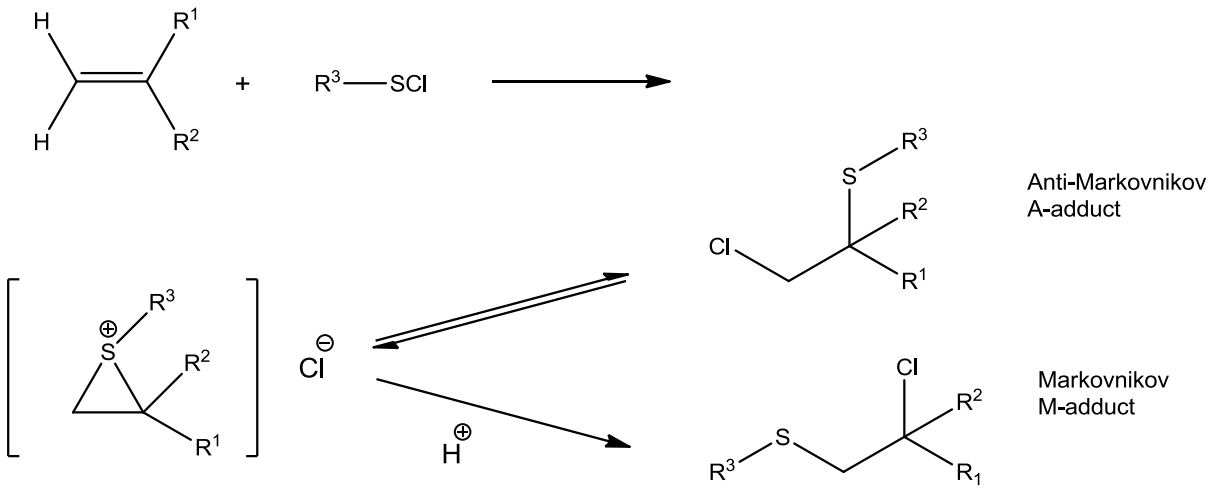
[23] Kharasch N.; Havlik A. J. *J. Am. Chem. Soc.* **1953**, 75, 3734
[24] Müller W. H.; Butler P. E. *J. Am. Chem. Soc.* **1968**, 90, 2075
[25] Schmidt G. H.; Csizmadia V. M. *Chem. & Ind.* **1968**, 1811

(2) Proceeding addition via an episulfonium intermediate.[26]



Scheme 10: Addition of 2-chloroethansulfenyl chloride to propene[27]

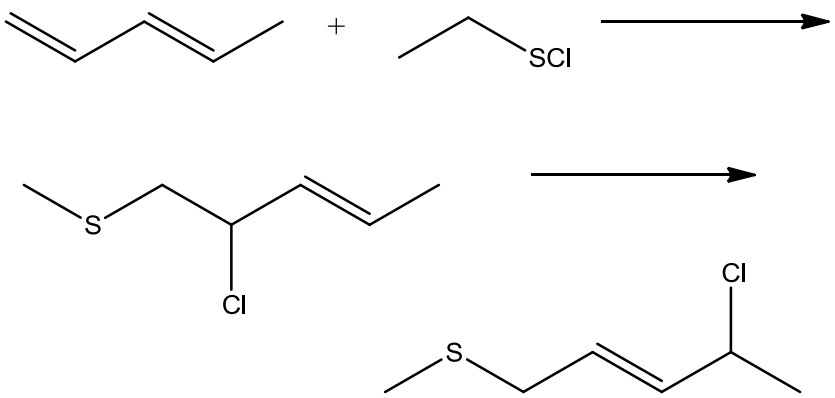
Investigations on more complicated olefins revealed the occurrence of Markovnikov and anti-Markovnikov isomers. Reacting terminal olefins with vinyl chloride methane- and benzenesulfenyl chloride yields preferentially to A-adducts. This isomeric proportion increases with an increase of alkyl residues of the used olefin due to a steric effect.[28] Thermodynamically stable M-isomers are observed by acid catalysis through a rearrangement of the A-adducts. Aryl substituted olefins, for example styrene preferentially yields only M-isomers due to an electronic effect.[24]



Scheme 11: Markovnikov and anti-Markovnikov isomers after sulfenyl halide addition

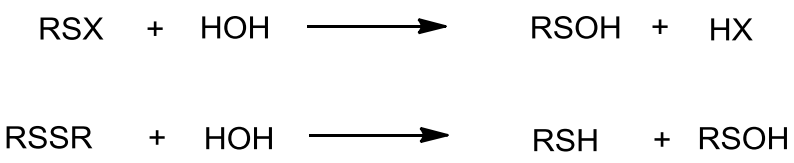
[26] Müller W. H. *Angew. Chem.* **1969**, 81, 475
[27] Fuson R. C.; Price C. C.; Burness D. M. *J. Org. Chem.* **1946**, 11, 475
[28] Müller W. H.; Butler P. E.; *J. Amer. Chem. Soc.* **1966**, 88, 2866

(3) The addition of sulfenyl chlorides to 1,3-dienes yields M-1,2-adducts. They partially isomerize to 1,4-adduct on standing.[29]



Scheme 12: Addition of methanesulfenyl chloride to 1,3-pentadiene

Additionally should be mentioned that dehydrohalogenation and oxidation reactions as subsequent reactions after or during the addition of the sulfenyl chloride are present in many cases. Therefore the reaction is accompanied directly with the evolution of hydrogen chloride.[30] For that reason the absence of water or the use of protic solvents in general is essential to avoid further unpleasant hydrolytic side reactions in our case of functionalization.



Scheme 13: Possible hydrolytic side reactions

Further reactions could yield in a broad variety of by-products of disulfides, sulfinic acids, sulfenic anhydrites as well as thiosulfonic esters.[31]

[29] Müller W. H.; Butler P. E. *Chem. Commun.* **1966**, 646
[30] Kharasch N.; Duesel H. H. *J. Org. Chem.* **1959,** 24, 1806
[31] Autenreith W.; Hefner H. *Chem. Ber.* **1925**, 58,2153

3. Results and Discussion

Thiol-Ene “Click” Chemistry offers versatile and easy possibilities for the modification of vinyl containing substances as well as polymers.[32] The amount of commercially available thiols is to a certain extent limited. Additionally a poor oxidation stability due to the free thiol functionalities might lead to insufficient results.[33]

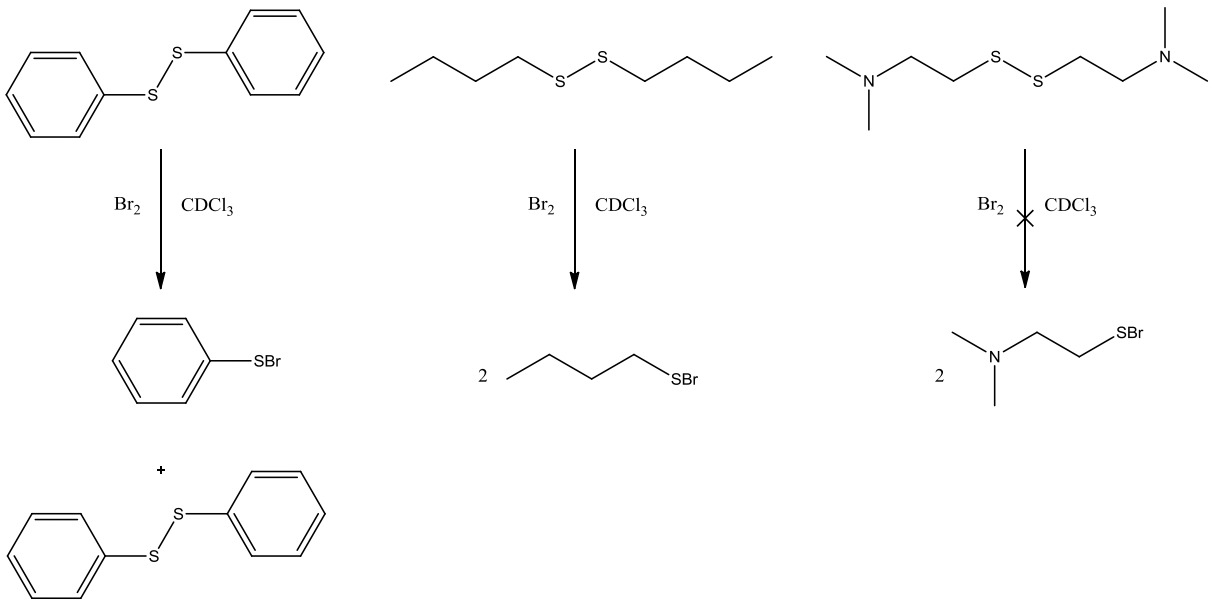
Therefore the approach of this work focused on the *in situ* generation of a sulfenyl bromide adduct under ambient conditions via the cleavage of disulfides. This straightforward and rapid procedure was used to determine the conversion to the desired product of a set of low-molecular weight model components with different steric and electronic character in reference to the containing double bond system. Resulting in the development of an appropriate succeeded implementation of a thio-ether-linkage, this one-pot setup was subsequently proceeded on several well defined synthetic as well as industrial produced polymers.

In the following chapter an overview of the achieved observations towards the conversion behavior will be presented. In this context, preparation procedures, ^{1}H, ^{13}C NMR, GPC, FT-IR, elemental analysis as well as the thermal decomposition by the use of simultaneous thermal analysis (STA) will be discussed.

[32] Bowman C. N.; Hoyle C. E. Angew. Chemie. **2010**, 122, 1584-1617.
[33] Espeel E.; Goethals F.; Du Prez F. E. J. Am. Chem. Soc. **2011**, 133, 1678-1681.

3.1. Investigations on several potential Disulfides

Initial investigations focused on the choice of appropriate disulfides for the cleavage according to *Zincke*[6] with elemental bromine. Therefore three potential disulfides were shortlisted including 1,2-dibutyldisulfane, 1,2-diphenyldisulfane as well as the tertiary amine 2,2'-disulfanediylbis(N,N-dimethylethanamine). Screening of these types occurred by the addition of 1.5 eq. bromine under ambient conditions to the respective disulfide dissolved in 0.75 mL deuterochloroform in a NMR-tube.



Scheme 14: Results towards *Zincke Disulfide Cleavage*

In case of 2,2'-disulfanediylbis(N,N-dimethylethanamine), directly after the addition of bromine a red precipitate was observable optically. That indicates a possible quaternization of the amine leading to the bad solubility in organic solvents. Despite intensive efforts a desired product could not be clearly identified using ^{1}H-NMR spectroscopy. Therefore a further treatment in combination with dissolved polymers seemed difficult in preparation and was not followed up so far, although the use of quaternary ammonium salts would also be of interest due to their antimicrobial activity for a further modification of surfaces.[34]

[34] Kenawy E.; Worley S. D.; Broughton R. Am. Biomacromolecules **2007**, Vol. 8, No. 5, 1360-1384

From 1,2-diphenyldisulfane under ambient conditions a conversion of approximately 45% to phenyl hypobromothioite could obtained. As for this insufficient conversion no further investigations were performed.

Whereas 1,2-dibutyldisulfane revealed a quantitative conversion to butyl hypobromothioite for which reason this disulfide was the first choice for all following research.

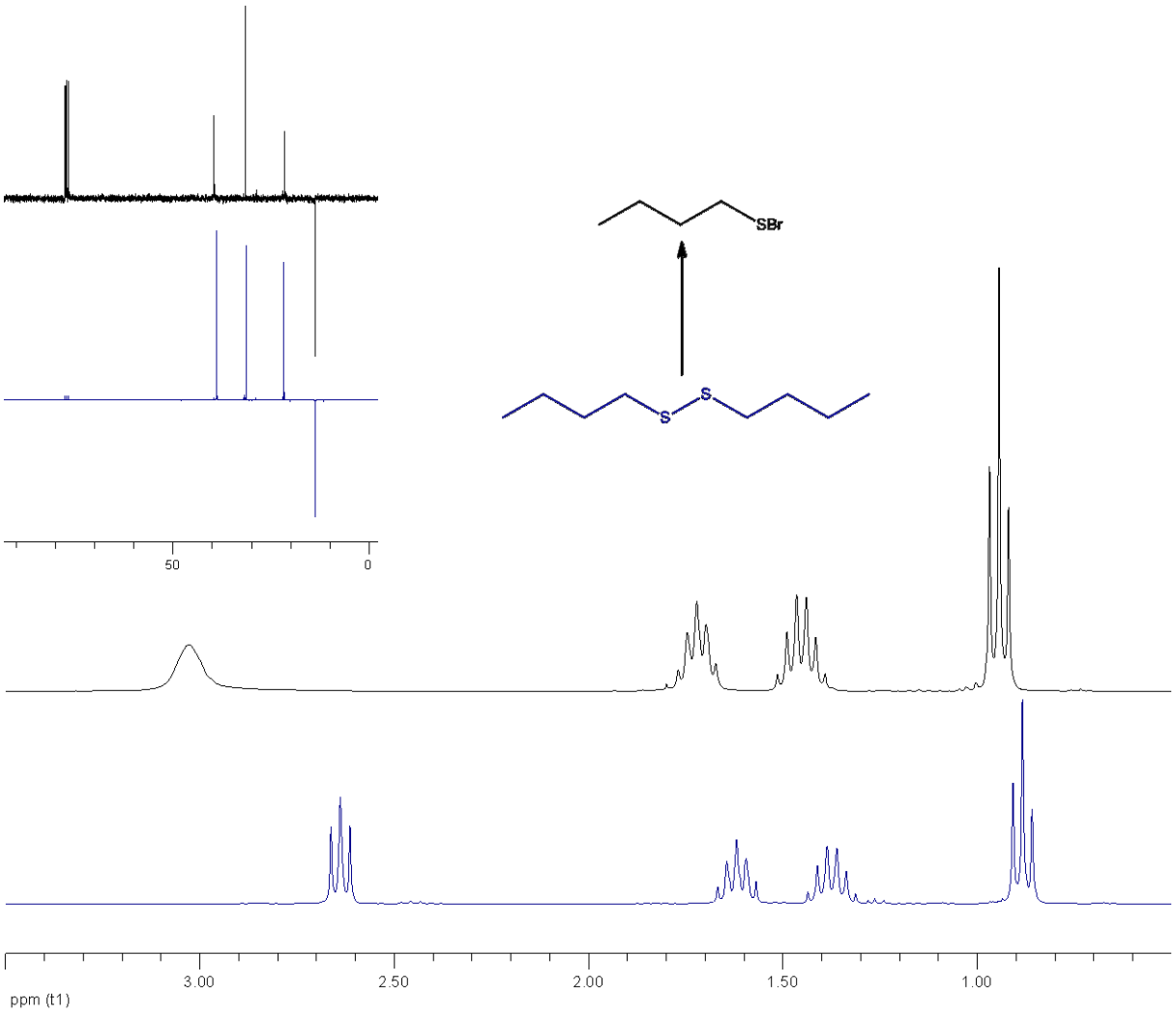


Figure 2: ^{1}H and ^{13}C-APT-NMR of the conversion from 1,2-dibutyldisulfane to butyl hypobromothioite

Regarding the ^{1}H-NMR spectra of 1,2-dibutyldisulfane all appearing peaks shifted to downfield region after total conversion, through a strong electron withdrawing effect. The characteristic peak regarding the protons of the methylene group next to the sulfenyl bromide appears either as broad singlet or as defined triplet in the region from 3.03 - 3.05 ppm, independent from the degree of conversion. This significant difference of the peak shapes

could be traced back to possible exchange equilibrium reactions or solubility differences. A detailed listing of all signals can be found in the experimental part of this work.

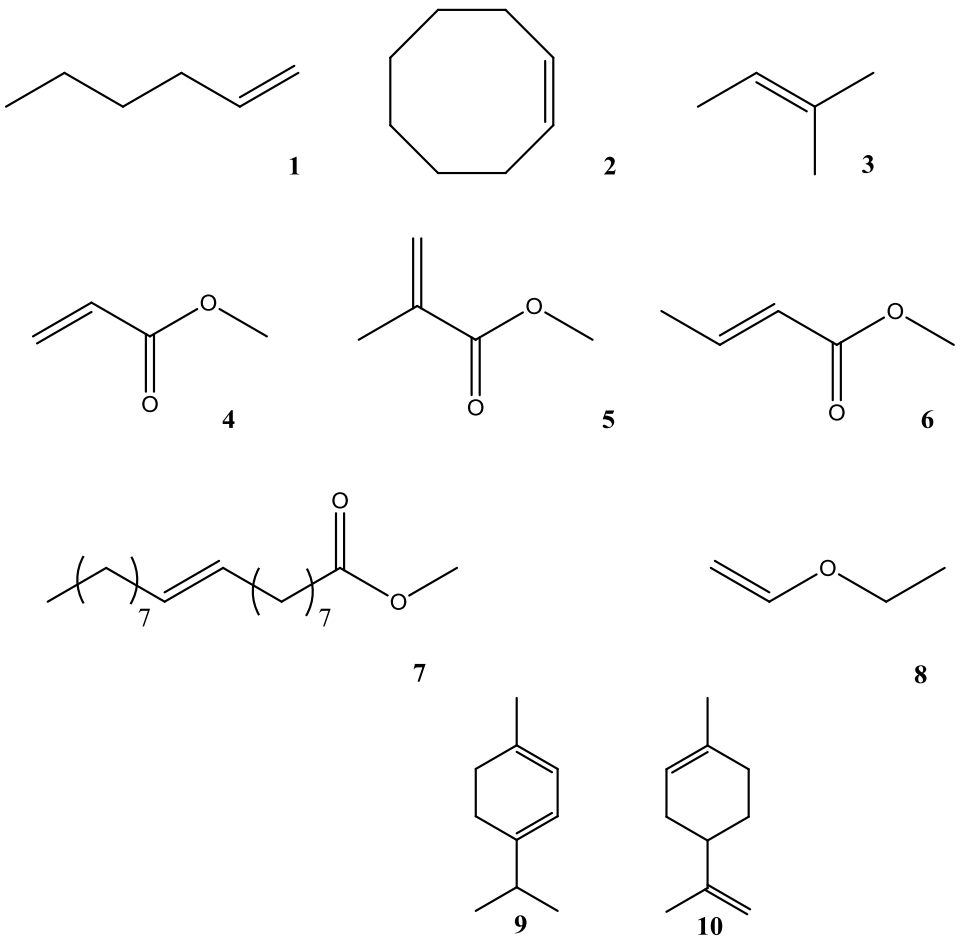
The ^{13}C-APT-NMR spectra resemble each other regarding their shifts. Again the most significant shift appears from 38.8 to 39.6 which can be assigned to the carbon next to the sulfenyl bromide.

For consecutive reactions the content of bromine is from substantial interest to minimize bromination as side reaction. In this context the bromine was reduced stepwise in 0.2 eq. proportions until a ratio of 1 eq. bromine in respect to the disulfide was reached. Also in that case only the described cleaved species could be obtained although the reproducibility was low.

To gain a better insight into the rate of the reaction kinetic measurements were performed. They illustrated that the reaction is totally finished within 2 minutes, even before the measurement cycle started, and no significant change (< 3%) could be monitored within 2 following hours.

3.2. Conversion behavior of low molecular model substances

Within this chapter the reactivity of the selected sulfenyl bromide in addition reactions to several types of olefins is compared. The main focus was set on the addition direction as well as effects due to electronic properties among differently substituted olefins. Moreover different proportions of disulfide to olefinic double bonds as well as bromine to disulfide were chosen to specify the ratio of bromination and the desired product formation. Also an approach in combination with dienes to gain insight in the selectivity of multiple bonds was tried to realize.



Scheme 15: Overview of investigated olefins

A quantification of proceeded reactions was done via the decrease of containing double bonds against an inert reference peak by the use of ^{1}H-spectroscopy. Furthermore significant peaks for the addition of the sulfenyl bromide as well as the brominated species were correlated via integration to observe the ratio of the achieved product mixture. For a better classification and determination, all substances were brominated separately in a reference experiment before.

Table 2: Ratios of reactant

	dibu : Olefine	Bromine : dibu
Experiment *1*	0.5 eq.	1.5 eq.
Experiment *2*	0.5 eq.	2.0 eq.
Experiment *3*	1.0 eq.	1.5 eq.
Experiment *4*	1.0 eq.	2.0 eq.

For nearly all selected low molecular model substances a product formation could be clearly detected with exception of **8** ethoxyethene. All substances were measured without a further purification step. The intrinsic complexity of **10** (*R*)-(+)-Limonen made it hardly possible to obtain a meaningful conclusion in that case. Noteworthy is that **9** α-Terpinene undergoes a favored aromatization under used conditions. This reaction occurs to a certain extend autocatalytic and was in that case accelerated.[35]

[35] Bueno A. C.; Brandao B. N. S.; Gusevskaya E. V. Applied Catalysis A: General **2008**, 351, 226–230

3.2.1. Conversion of (1) hex-1-ene

In the case of **1** hex-1-ene a total reduction of all double bonds was obtained for bromination as well as for the conversion with the sulfenyl bromide. The addition to double bonds followed to Markovnikov´s rule for the major product (66-87%). Minor amounts of 1,2-dibromohexane and the anti-Markovnikov product can be detected in the region from 3.25 to 3.89 ppm.

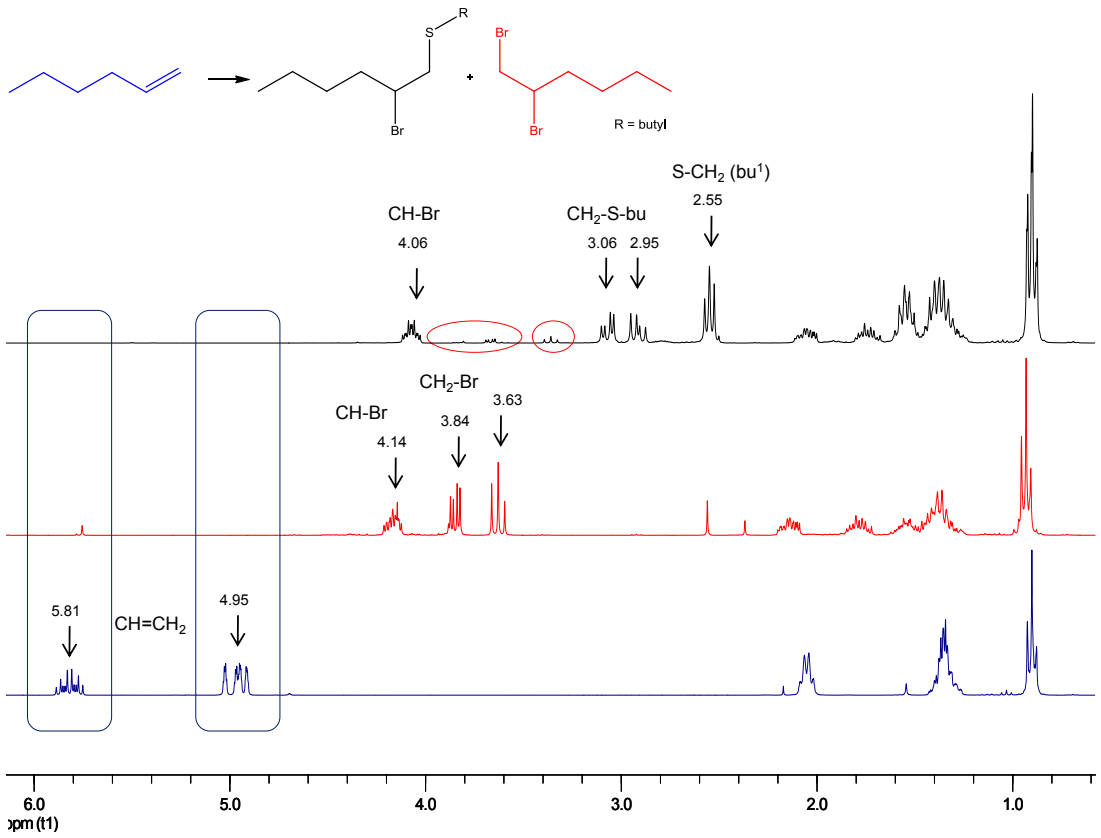


Figure 3: Comparison of ^{1}H-NMR spectra of the converson of hex-1-ene in Experiment 1

For Experiment *1* to *3* a product formation from 85 to 87% could be obtained. Only for Experiment *4* a decrease to 66% was observed. Experiment *2* and *3* show the same result whereas in Experiment *4* a significant trend to bromination is noticeable.

Table 3: Conversion [%] of hex-1-ene to (2-bromohexyl)(butyl)sulfane compared to 1,2-dibromohexane at different ratios of reagent

Experiment *1*	Experiment *2*
87 %	**85 %**
Experiment *3*	Experiment *4*
85 %	**66 %**

3.2.2. Conversion of (2) (Z)-cyclooctene

For the disubstituted cyclic olefin **2** (Z)-cyclooctene no remaining double bonds can be found in bromination reaction and conversion with the sulfenyl bromide species. Within the four performed experiments product yields from 66 up to 87% were possible. For the brominated side product a characteristic peak appears at 4.55 ppm. In the region from 5.25 to 5.52 ppm several peaks could be found but not identified. Their intensity increased from Experiment *1* to *4*.

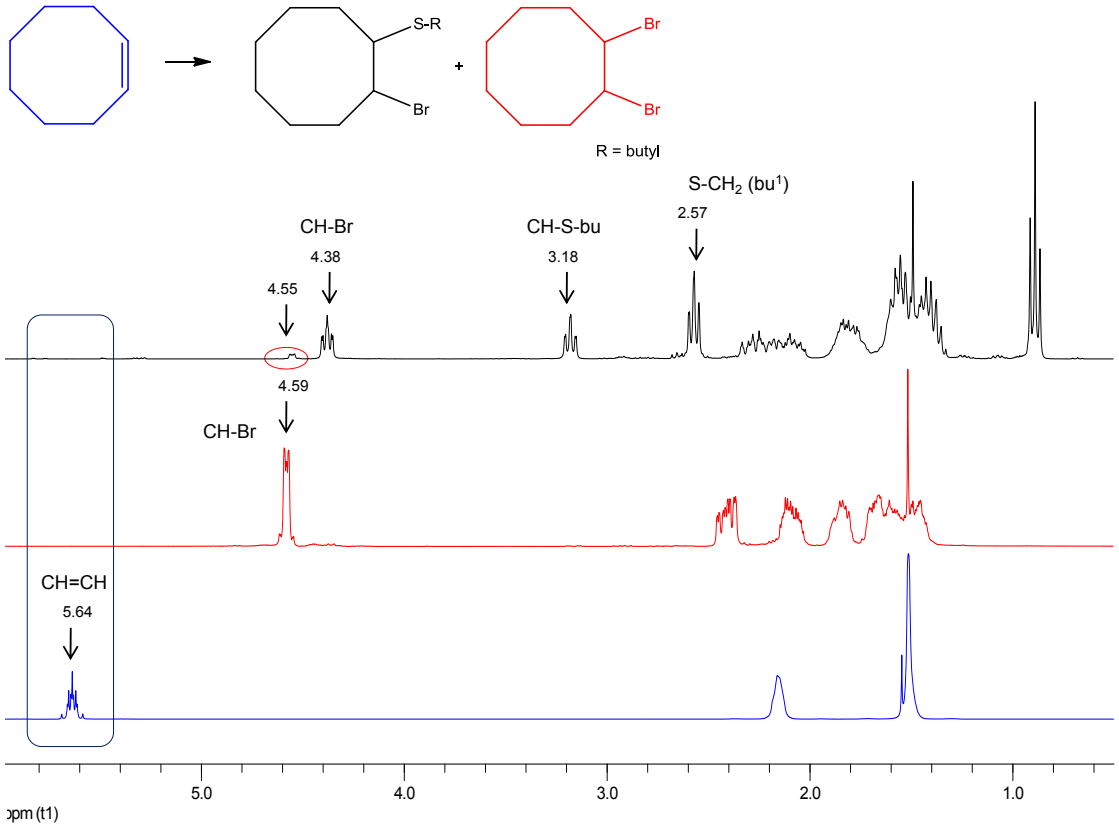


Figure 4: Comparison of ^{1}H-NMR spectra of the converson of (Z)-cyclooctene in Experiment 1

By the increase of bromine a decrease of product formation could be obtained in Experiment *2* and *4*. Rather good conversions of 95 and 88% can be found in Experiment *1* and *2*.

Table 4: Conversion [%] of (Z)-cyclooctene to (2-bromocyclooctyl)(butyl)sulfane compared to 1,2-dibromocyclooctane at different ratios of reactant

Experiment *1*	Experiment *2*
95 %	**82 %**
Experiment *3*	Experiment *4*
88 %	**62 %**

3.2.3. Conversion of (3) 2-methylbut-2-ene

For **3** 2-methylbut-2-ene a complete conversion of the educt could be observed. A broad range of product yield within all performed experiments of <5 up to 95% was found. The demanding trisubstituted olefin preferentially yields according to an anti-Markovnikov addition. The brominated side product could be assigned to an appearing signal at 4.42 ppm. A relative low content (1 - 2%) of the Markovnikov product has probably lead to a shift of 4.30 ppm in Experiment *1*.

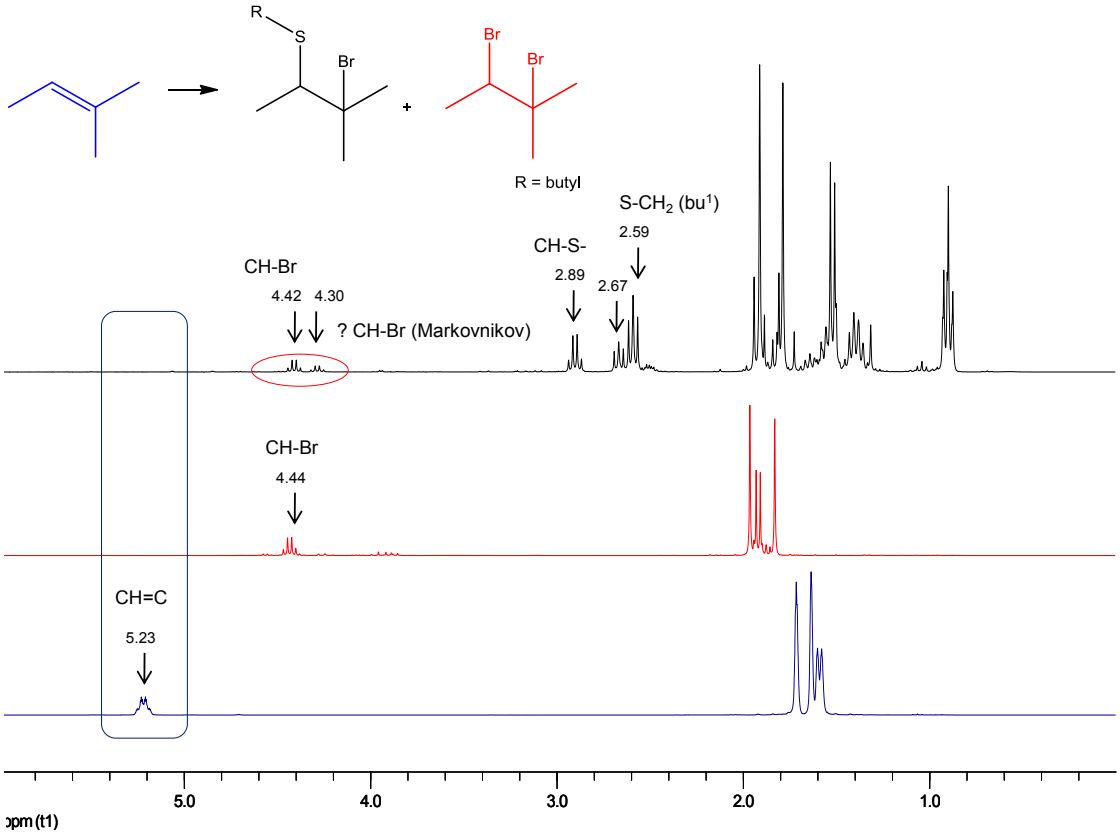


Figure 5: Comparison of ^{1}H-NMR spectra of the converson of 2-methylbut-2-ene in Experiment 1

A similar tendency of predominant bromination with an increasing bromine concentration within all performed Experiments *2* to *4* could be detected. The only expectation occurred in Experiment *1* yielding 95% of the major product.

Table 5: Conversion [%] of 2-methylbut-2-ene to (3-bromo-3-methylbutan-2-yl)(butyl)sulfane compared to 2,3-dibromo-2-methylbutane at different ratios of reactant

Experiment *1*	Experiment *2*
95 %	**20 %**
Experiment *3*	Experiment *4*
30 %	**< 5 %**

3.2.4. Conversion of (4) methyl acrylate

In the case of **4** methyl acrylate a complete conversion could not be detected neither for bromination nor for sulfenyl bromide addition in Experiment *1*. Two unidentified signals appeared at 3.18 and 2.62 ppm which could be possible be traced back to the disulfide educt as well as not reacted sulfenyl bromide. In comparison of brominated product with the resulting Markovnikov one, quite good degrees of functionalisation could be obtained, and ranging from 90 up to 96%. Nevertheless the existence of not yet identified side reactions should be mentioned.

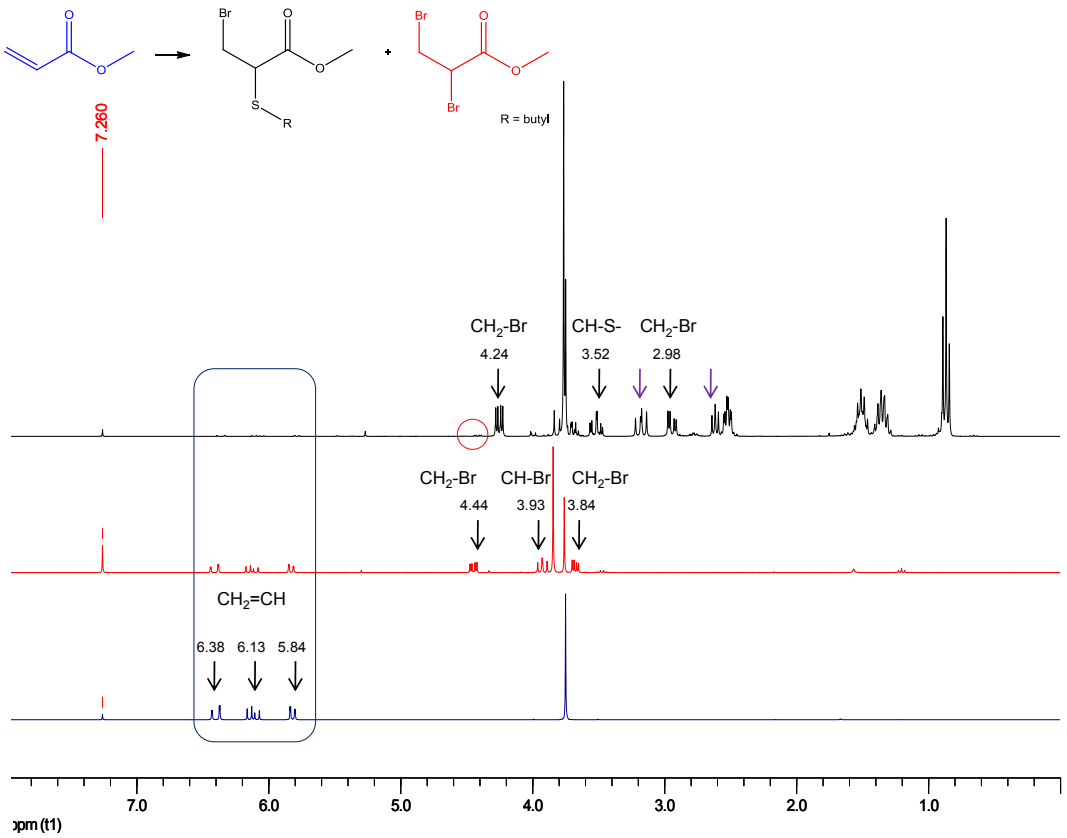


Figure 6: Comparison of ^{1}H-NMR spectra of the conversion of methyl acrylate in Experiment 1

According to the tendency of incomplete bromination in the reference Experiment (62%), in Experiment *1* to *4* quite high ratios of product formation could be observed. The occurrence of the not definitely clear side reactions is not considered in this ratio, but should be again mentioned.

Table 6: Conversion [%] of 2 of methyl acrylate to methyl 3-bromo-2-(butylthio)propanoate compared to methyl 2,3-dibromopropanoat at different ratios of reactant

Experiment *1*	Experiment *2*
96 %	**91 %**
Experiment *3*	Experiment *4*
96 %	**90 %**

3.2.5. Conversion of (5) methyl methacrylatet

The bromination of **5** methyl methacrylatet resulted in a quantitative conversion, whereas in Experiment *1* a minimal amount of educt (5%) could be detected. In all further Experiments from *2* to *4* no remaining double bonds could be found. A high degree of product formation consists of Markovnikov (1) as well as anti-Markovnikov (2) addition in the product mixture.

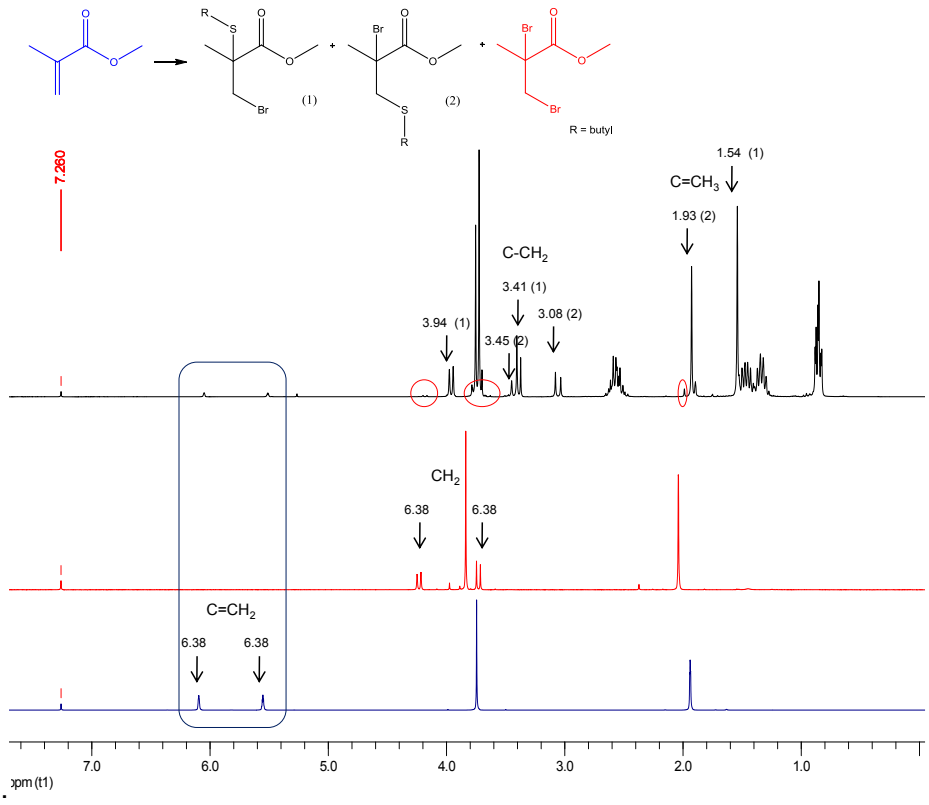


Figure 7: Comparison of ^{1}H-NMR spectra of the converson of methyl methacrylatet in Experiment 1

Table 7: Conversion [%] of methyl methacrylatet to 2-bromo-3-(butylthio)-2-methylpropanoate and methyl 3-bromo-2-(butylthio)-2-methylpropanoate compared to methyl 2,3-dibromopropanoat at different ratios of reactant

Experiment *1*	Experiment *2*
97 % 57% (1) + 40% (2)	**87 %** 42% (1) + 45% (2)
Experiment *3*	Experiment *4*
85 % 33% (1) + 52% (2)	**n.d.**

3.2.6. Conversion of (6) (E)-methyl but-2-enoate

For **6** (E)-methyl but-2-enoate a complete bromination was not detected. In Experiment *1* approximately 18% educt remained, but no brominated by product could be monitored. Only in that case the addition in direction (1) with 74% as well as direction (2) with 26% could be detected. Experiment *2* yielded to >95% in a product formation according to (1). Experiment *3* revealed a quantitative conversion to (1).

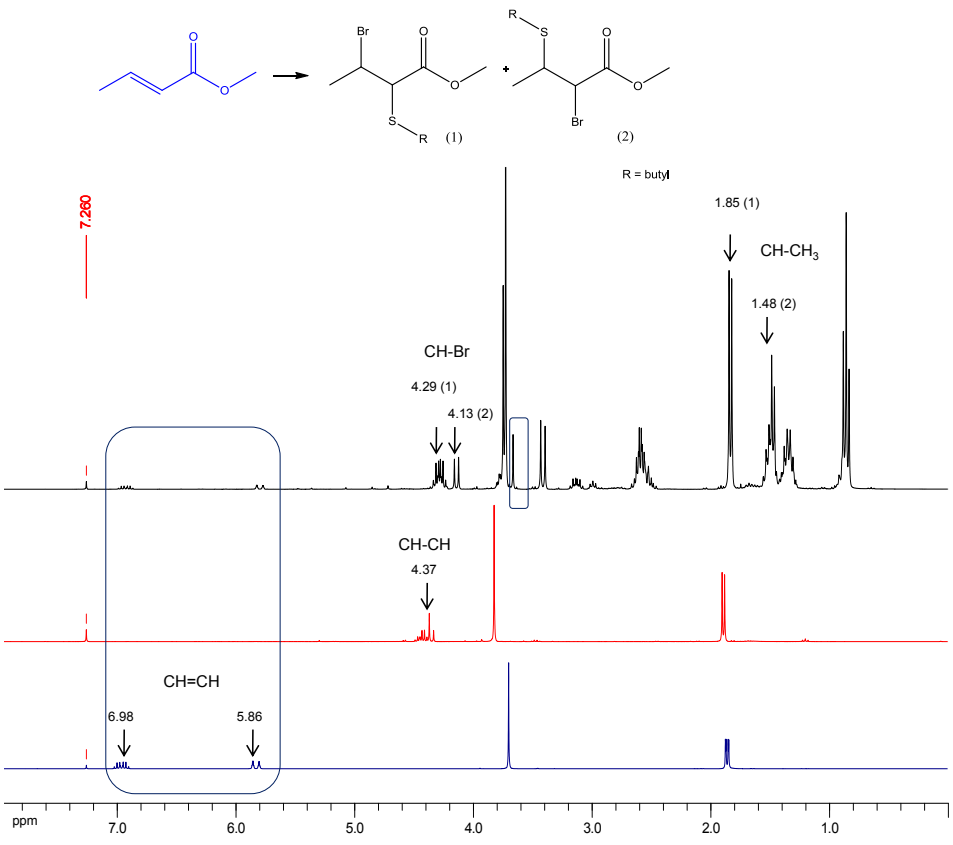


Figure 8: Comparison of ^{1}H-NMR spectra of the converson of (E)-methyl but-2-enoate in Experiment 1

Table 8: Conversion [%] of (E)-methyl but-2-enoate to methyl 2-bromo-3-(butylthio)butanoate and methyl 3-bromo-2-(butylthio)butanoate compared to methyl 2,3-dibromobutanoate at different ratios of reactant

Experiment *1*	Experiment *2*
100 % 75% (1) + 25% (2)	**100 %** 95% (1) + 5% (2)
Experiment *3*	Experiment *4*
100 % 100% (1) + 0% (2)	**n.d.**

3.2.7. Conversion of (7) methyl oleate

A quantitative conversion for **7** methyl oleate could be reported in case of bromination as well as for the sulfenyl bromide. The formation of the desired product could be identified. However a comparison to the brominated species could not be realized because of overlaying corresponding peaks.

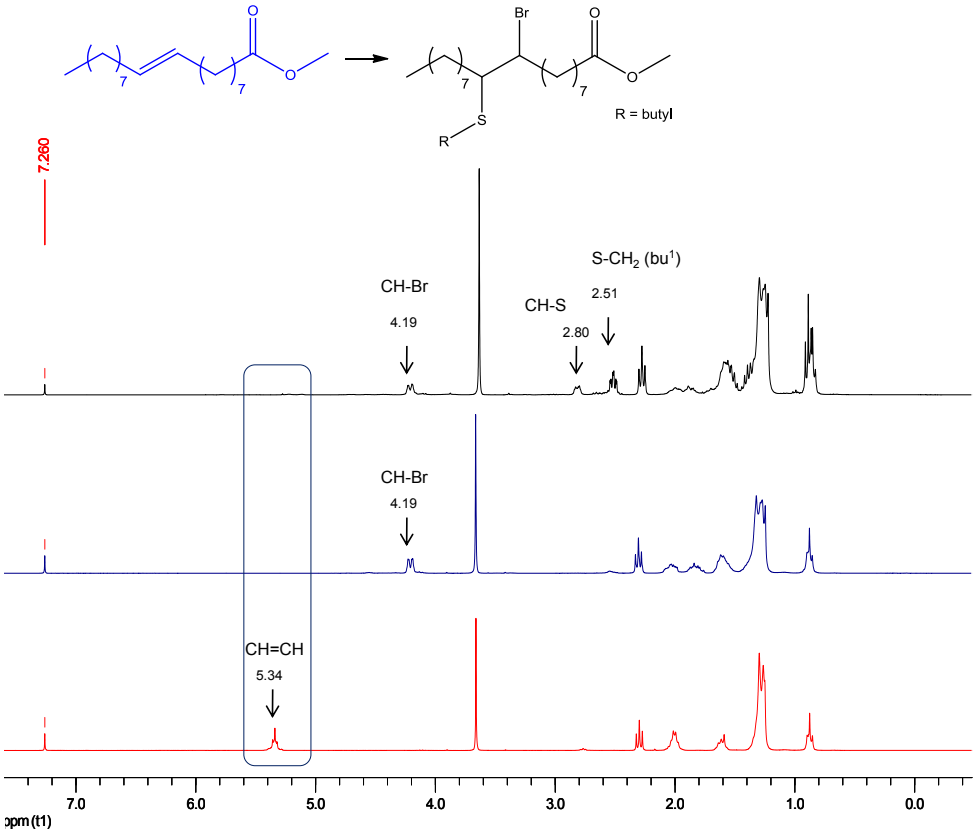
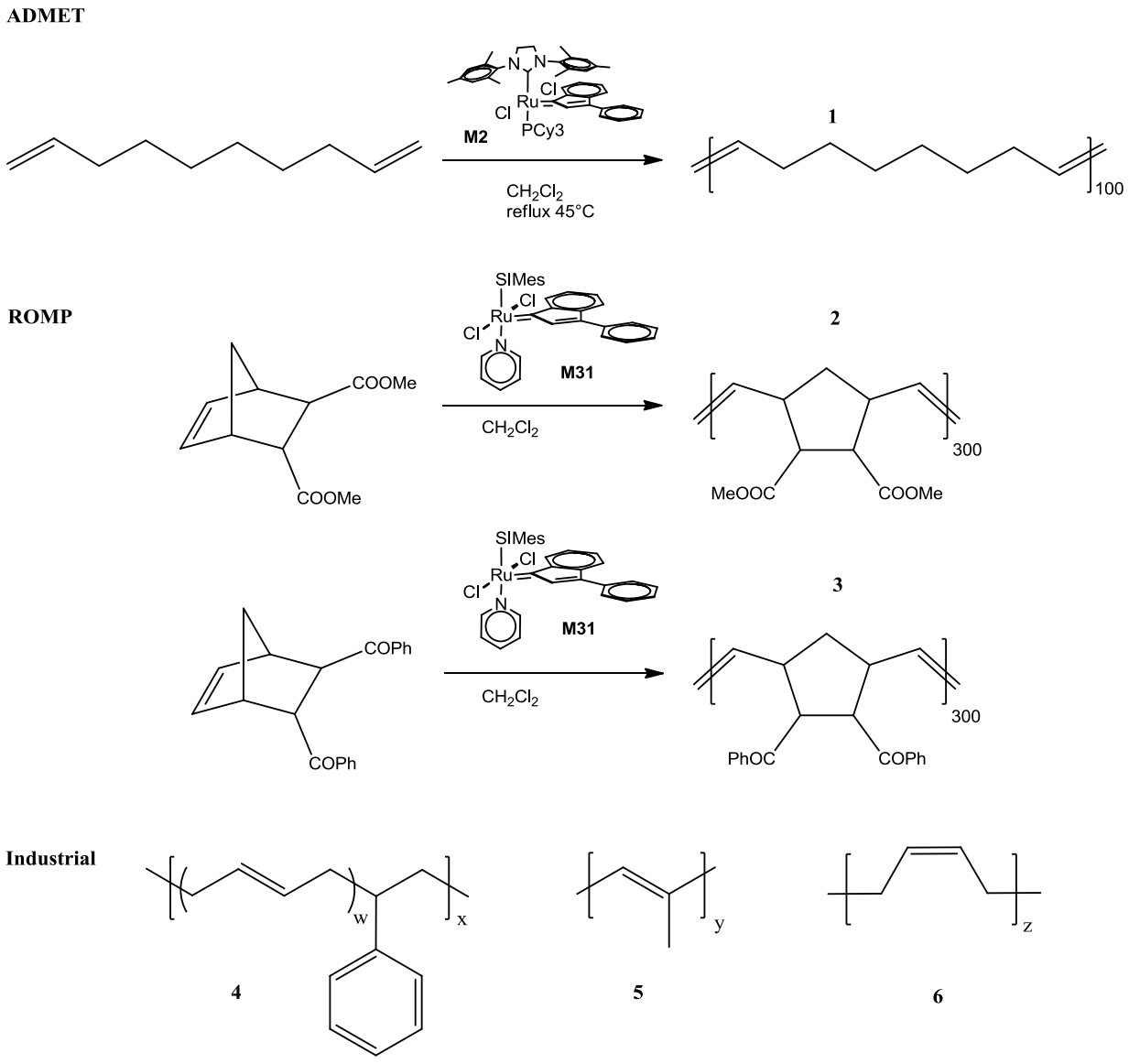


Figure 9: Comparison of ^{1}H-NMR spectra of the converson of methyl oleate in Experiment 1

Best ratio in respective to the product formation can be obtained in Experiment *1* for all investigated olefins. Experiment *2* and *3* show a quite similar scale of conversion, with exception of **3** 2-methylbut-2-ene. Within this series all terminal olefins yielded a Markovnikov addition. The trisubstituted compound resulted in anti-Markovnikov addition probably of steric reasons. Further increase of reagent showed a significant decrease in the desired product formation in that case. For acrylate compounds a mixture of Markovnikov and anti-Markovnikov products can be expected. Due to the implementation of the oxygen functionality possible side reactions should be considered.

3.3. Postmodification of Polymers

A set of polymers was prepared using acyclic diene metathesis polymerization (ADMET) and ring opening metathesis polymerization (ROMP) for the modification of containing double bonds with a sulfenyl bromide. Additionally this approach was realized on several technical manufactured polymers.

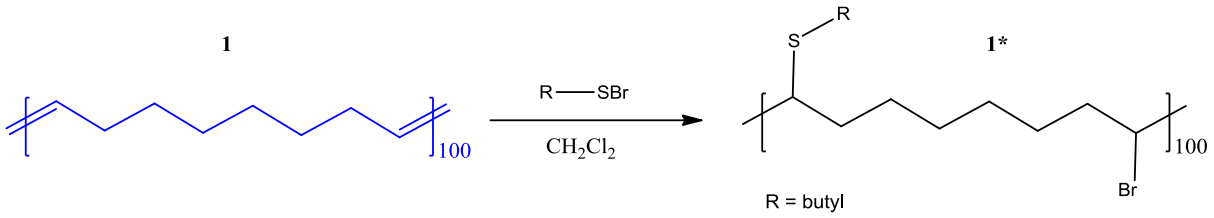


Scheme 16: Overview of the preparation of Polymer 1, 2, 3 and technical manufactured polymers 4, 5, 6

3.3.1. Preparation of Polymer precursors and post-modification

The polymer precursors were polymerized with the second generation Grubbs initiator **M2** in the case of **1** poly(DD) and the third generation Grubbs initiator **M31** for **2** poly(ME) and **3** poly(PK) under inert atmosphere of argon using standard Schlenk techniques. Further purification was done by dropwise addition of the solution into cold methanol for several times.

For post-modification all polymers were dissolved in an appropriate amount of dichloromethane. The separately *in situ* generated sulfenyl bromide was added and the reaction was allowed to proceed for two hours. Unless other noted a ratio of 1 eq. 1,2-dibutyldisulfane according to olefinic bonds as well as 1 eq. bromine according to 1,2-dibutyldisulfane was used. The polymers were purified by repeated precipitation, in order to seperate residual reactant. For **1*** poly(DD)mod. cold n-pentane whereas for all further modified polymers cold methanol was used.



Scheme 17: General procedure for post-modification using the example of poly(DD)

Difficulties in the modification due to high molecular weight of **4*** SBR (styrene butadiene rubber) and **5*** NR (natural rubber) for the modification made it hardly possible to perform an appropriate characterization. During the addition of reactant the polymers precipitated, became insoluble and consequently inaccessible for purification via precipitation. Also continuous extraction in methanol for even more than 24 hours did not succeed. For that reason no further investigations were performed.

Polymers **1**, **2, 3** were prepared analogously and also modification to **1***, **2***, **3***, **6*** was done in the same manner. Ratios of monomer to intiator and gel permeation chromatography (GPC) results of the polymer precursors as well as the modified polymers are summarized in Table 9.

Table 9: Ratios of monomer to initiator for polymers 1-3 as well as Gel permeationchromatography (GPC) results of polymer precursors and yields 1-4 and modified polymers 1*-4*

Polymer	MM:I	Mn [g/mol-1]	PDI	Mn [g/mol-1]*	PDI *	Yield* [%]
1	100:1	35300	1.90	40300	2.18	84
2	300:1	58300	1.14	83100	1.14	75
3	300:1	68300	1.15	87900	1.34	82
6	-	105300	3.49	201300	3.28	62

For all GPC profiles a unimodal molecular weight distribution could be detected. Also a detectable shift of the maximum value toward higher molecular weights indicated an occurred modification. Further specific information could not be obtained.

3.3.2. Polymer-characterization using ^{1}H-NMR and ^{13}C-NMR

For **1*** poly(DD)mod a quantitative conversion of the double bonds can be found through the vanishing signal of the CH=CH peak at 5.34 ppm. More evidence by appearing peaks at 4.14 ppm of CHBr and 2.71 ppm of CHS can be detected in ^{1}H-NMR spectrum.

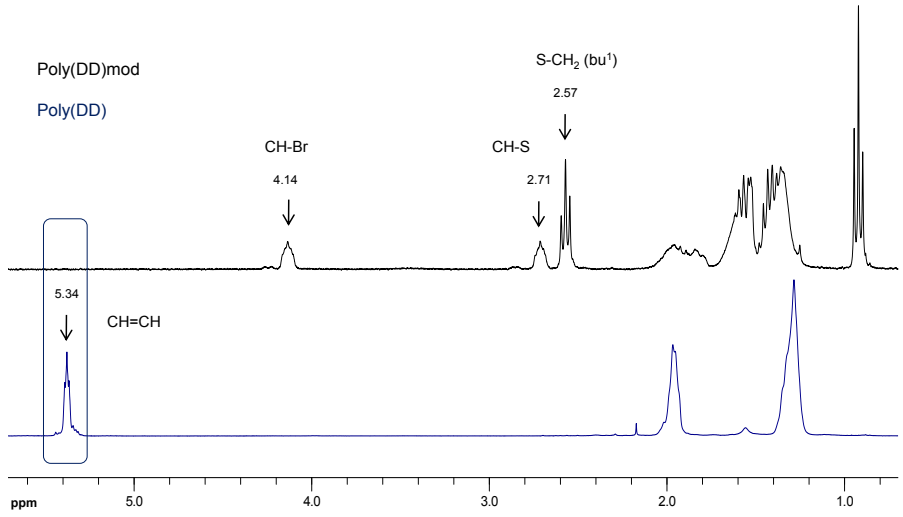


Figure 10: ^{1}H-NMR spectra of poly(DD) and poly(DD)mod.

The conversion could also be confirmed by ^{13}C-NMR, where a disappearance of the signal at 130.3 ppm according to the double bonds was monitored. Further the appearance of signals at 13.9, 22.2, and 32.2 ppm representative for the butyl chain can be found as well as signals at 63.4 ppm of CHBr and 53.2 ppm of CHS.

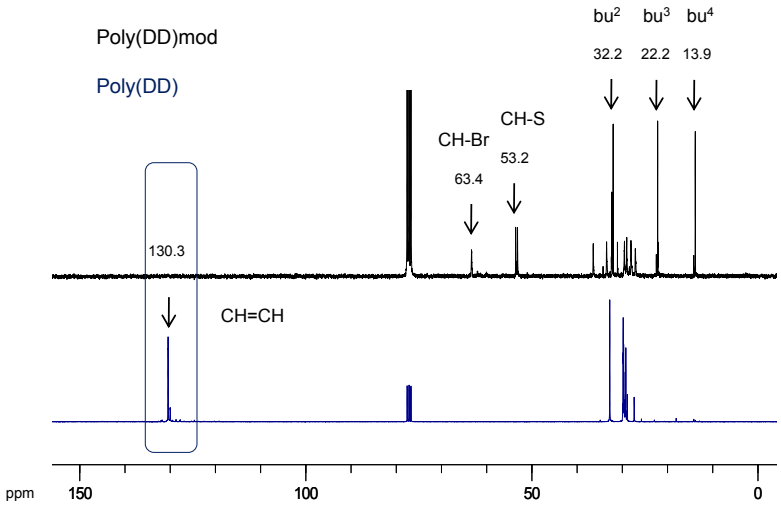


Figure 11: ^{13}C-NMR spectra of poly(DD) and poly(DD)mod.

Regarding the ^{1}H-NMR spectrum of **2*** poly(ME)mod only broad signals are obtained. An appearing signal at the range from 5.01 - 5.66 ppm could be evidence for remaining double bonds which can be found in the precursor polymer at the same region. On the other hand a signal ranging from 3.89 - 4.95 ppm could be assigned to the proton attached to the same carbon were the bromine or the sulfur is bond. To substantiate the suspicion of a succeeded modification the appearance of a broad singlet signal at 0.91 ppm corresponding to CH_3 of the butyl chain could be detected. A correlating number of protons in respect to the inert reference peak of the methyl ester at the rage 3.57 - 3.89 ppm confirm modification at least to a certain extend. Under these conditions quantification via integration of mentioned signals would suggest a conversion of approximately 85%.

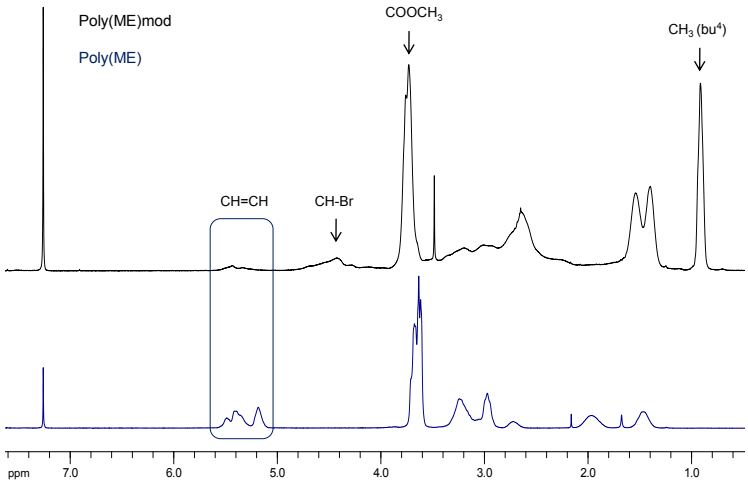


Figure 12: ^{1}H-NMR spectra of poly(ME) and poly(ME)mod

In contrast to a suspected incomplete conversion of the double bonds, in the ^{13}C-APT-NMR spectrum a disappearance of resonances from 129.5 - 133.6 ppm corresponding to the double bonds was observed. Analogously appearing sharp signals at 32.1, 22.2 and 13.9 correlated to the butyl chain were present. All other signals seemed to be broadened. The resonance referred to the methylene group next to the thioether linkage in the butyl chain should be included in the range of 32 - 33 ppm as consequence of the vicinity to the macromolecular backbone.

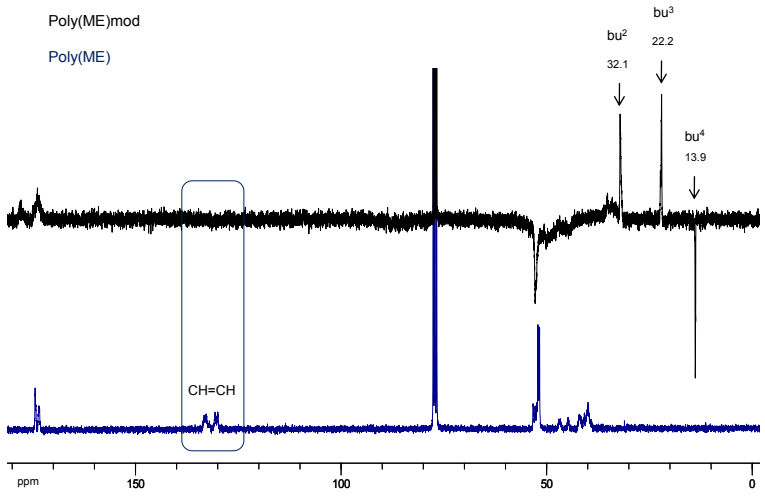


Figure 13: ^{13}C-APT-NMR spectra of poly(ME) and poly(ME)mod

In the case of **3*** poly(PK)mod a significant broadening of all peaks occurred what complicated an accurate attribution in the obtained ^{1}H-NMR spectrum. The only evidence for a possible successful modification could be the appearance of a broad signal at the range of 0.77 to 1.04 ppm correlated to the 3 protons of the methyl group at the end of the butyl chain. Again broad signal at the double bond region between 5.06 - 5.60 ppm of the polymer precursor can be found but must not be definitely traced back to a vinyl content as already ascertained for poly(ME)mod.

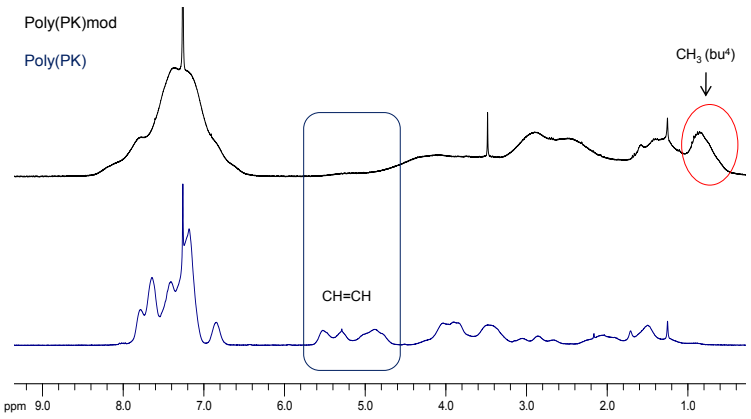


Figure 14: ^{1}H-NMR spectra of poly(PK) and poly(PK)mod

Due to the bad solubility of **3*** poly(PK)mod the quality of the observed ^{13}C-NMR is limited for a secured conclusion in the region of possible remaining double bonds at 130.4 ppm. Evidence for modification to a certain extend could be again promising sharp peaks at 32.2, 22.2 and 13.8 according to the butyl chain.

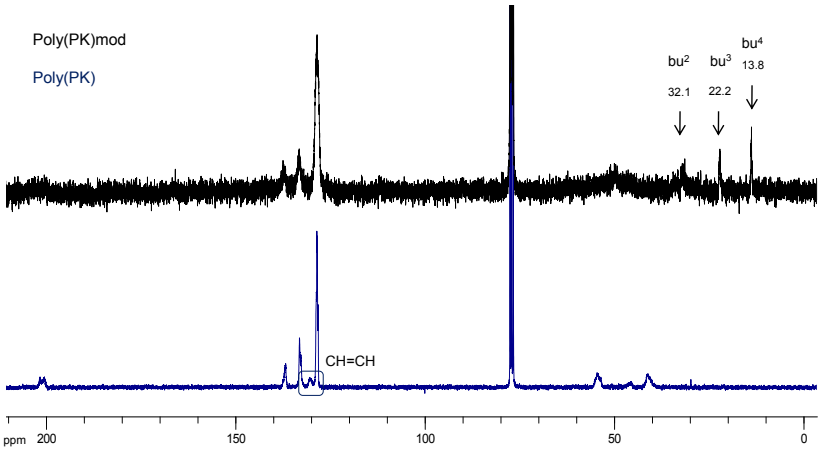


Figure 15: ^{13}C-NMR spectra of poly(PK) and poly(PK)mod

For the modification of **6*** polybutadiene a conversion of 10% can be detected using NMR-data. Appearing significant peaks can be found analogous to **1*** poly(DD)mod at 4.22 ppm for CH-Br, 2.89 ppm according to CH-S and 2.53 ppm assigned to S-CH_2 (bu^1).

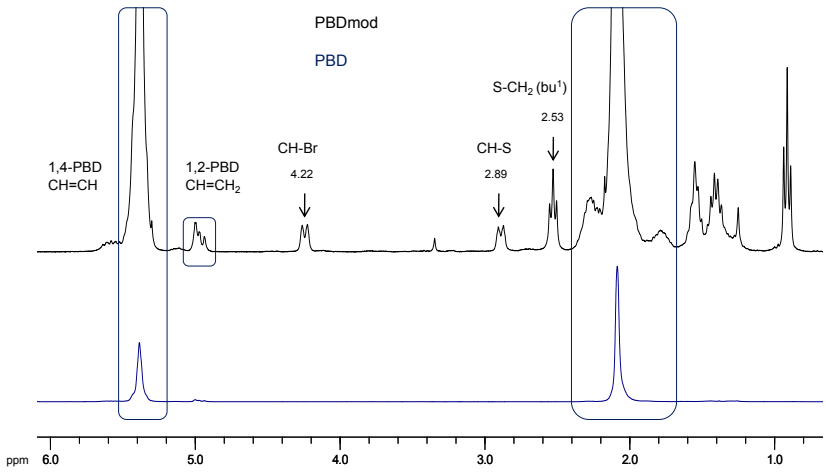


Figure 16: ^{1}H-NMR spectra of PBD and PBDmod

With regard to the ^{13}C-APT-NMR spectrum a conversion can be detected again by the appearing resonances at 13.8, 22.1 and 32.2 ppm corresponding to the butyl chain.

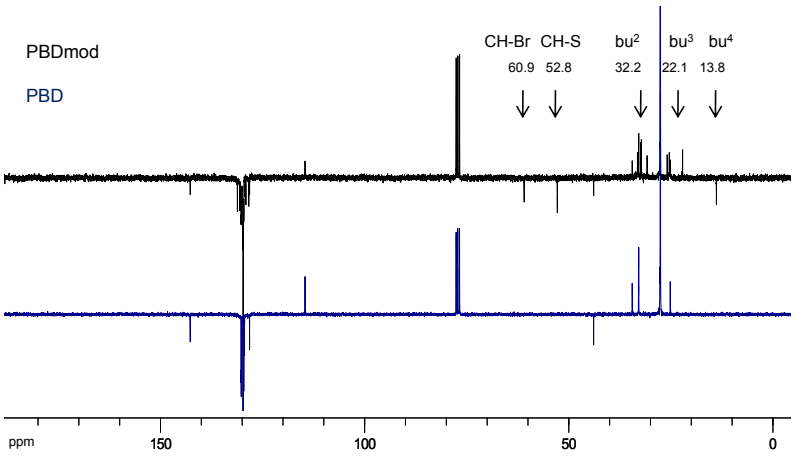


Figure 17: ^{13}C-APT-NMR spectra of PBD and PBDmod

3.3.3. Infrared absorption analysis

For further characterization of the polymers FT-IR analysis was used. Characteristic absorption bands of cis and trans double bonds, respectively, in vinylcyclopentane units due to ring-opening polymerization were monitored according to **2*** poly(ME)mod and **3*** poly(PK)mod. In case of **1*** poly(DD)mod containing trans double bonds show a strong and sharp absorption band at 959 cm^{-1}. For the mainly **6** 1,4-PBD an adsorption at 733 cm^{-1} could be assigned to the cis double bonds. Attention was also turned to new appearing bands at the region from 655-695 cm^{-1} representative for S-C vibration as well as on a range from 485-650 cm^{-1} according to C-Br stretching vibration.

Table 10: Monitored characteristic IR-vibrations due to functionalisation

Vibration	wavenumber [cm-1]
$C=C_{trans}$ def.	960-970
$C=C_{cis}$ def.	~730
C-S-C str.	655-695
C-Br str.	485-650

The FT-IR analysis for **1*** polyDDmod implied a significant decrease of the strong and sharp band at 959 cm^{-1} assigned to trans double bonds with a high degree of functionalization compared to **1** polyDD. The appearing absorption at 575 cm^{-1} indicated the stretching vibration of C-Br. About an appearing signal of the S-C stretching vibration only a guess of the as weak or medium predicted absorption can be done in the characteristic region, as a weak appearing shoulder at 699 cm^{-1}.

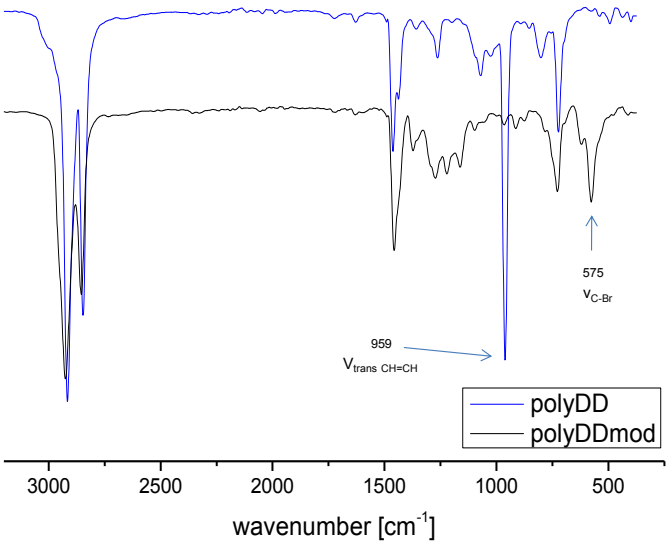


Figure 18: IR-measurements of 1 and 1*

In the compared IR-spectra of **2** polyME and **2*** polyMEmod the alkene C-H stretching vibrations above 3000 cm^{-1} showed a clear decrease in intensity. The visible shoulder at 970 cm^{-1} according to trans double bonds acted regressive after conversion. Predicted cis double bonds at approximately 730 ppm also followed this characteristic. Weak bands at 662, 613 or 550 cm^{-1} may be connection with vibrations due to C-Br or C-S and seem lowered through the high absorption coefficient of the carbonyl group (1725 cm^{-1}). A further interesting feature of the obtained spectrum concerning **2*** polyMEmod is the split of the carbonyl group band to 1775 cm^{-1}. The frequency of the carbonyl stretching vibration is depend on the structural environment of the C=O group. Increasing the double bond character of the carbonyl group via an attached electron accepting atom or group directly to the carbonyl group, the greater is the frequency. A possible addition of bromine could not be excluded.[36]

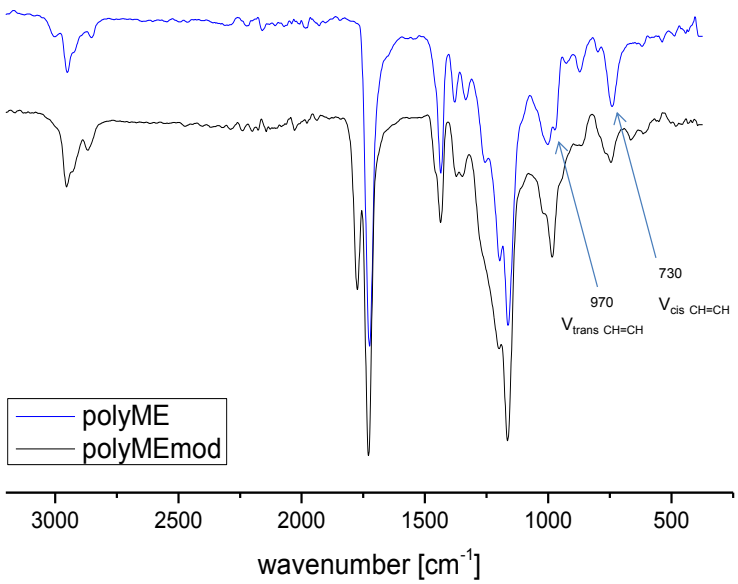


Figure 19: IR-measurements of 2 and 2*

[36] *Infrared Characteristic Group Frequencies, 2nd ed.*, George Socrates, Wiley 1994

In the case of **3*** polyPKmod the IR-spectrum revealed nearly the same characteristic absorption band as **3** polyPK. In the range from 2865 to 3060 cm^{-1} no significant intensity changes can be detected and the band shape also appeared almost identically. The disappearance of the band shoulder at 970 cm^{-1} indicated at least a possible conversion of cis vinylene units. For trans double bonds at the region of 730 cm^{-1} no well founded change can be detected. New appearing at 1330 and 780 cm^{-1} should be mentioned as well as a change in intensities of appearing peaks after conversion. According to this received information from the obtained spectrum after conversion a functionalization can be supposed, as well as a possible co-occurrence of side reactions on the aromatic part of the polymer or on the carbonyl group.

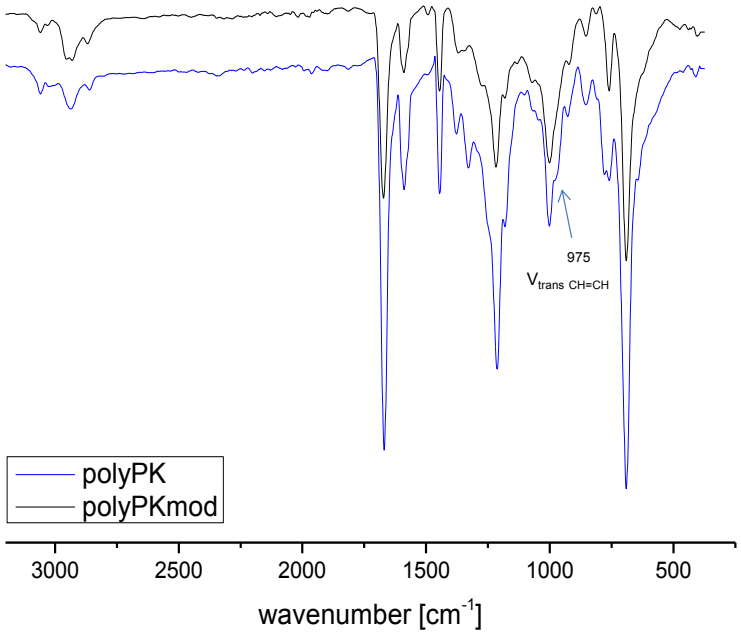


Figure 20: IR-measurements of 3 and 3*

Compared IR-spectra of **4** PBD and **4*** PBDmod indicated a succeeded modification by the decrease of adsorption bands representative for cis (730 cm^{-1}) and trans (970 cm^{-1}) double bonds. Further qualitative evidence can be found in the changing ratio of appearing bands at 2850 and 3005 cm^{-1} according to trans and cis absorptions. The characteristic absorption at 580 cm^{-1} has been assigned to C-Br stretching vibration.

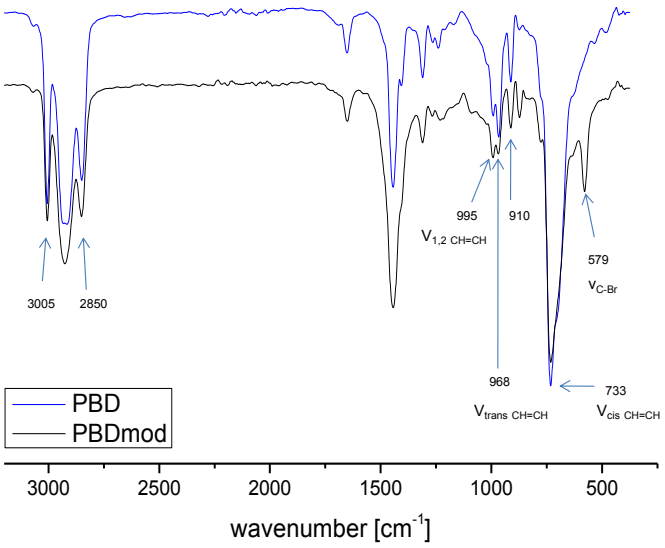


Figure 21: IR-measurements of 4 and 4*

3.3.4. Elemental and simultaneous thermogravimetric analysis

To gain a better insight about the sulfur content in the modified polymers and to quantify the degree of functionalization elemental analysis was performed. Calculated values were determined for a single monomer unit and presuming therefore a total conversion if not mentioned otherwise. Thus bromine and oxygen was not detected, stated values were calculated from the difference to the sum of all other elements to 100%. Due to this fact, the obtained results cannot be regarded as absolute values but rather a rough estimate because of possible oxidation processes or dibromination of double bonds which could not be considered. Via simultaneous thermogravimetric analysis a possible correlation to the elemental analysis was tried to achieve for bromine and sulfur contents.

Corresponding to the predicted values for $C_{12}H_{23}BrS$, the obtained results in the case of **1*** polyDDmod indicated a high degree of functionalization, which could be expected more than 95% at least. Carbon showed the highest difference with a threefold value referred to a tolerance limit of maximal 0.3 respectively.

Table 11: Elemental analysis results [w-%] for 1* polyDDmod

polyDDmod	%C	%S	%H	%N	%O	%Br	%total	%Δ
1.	52.71	11.20	8.07	0.16	-	n.d.		
2.	52.36	10.33	7.42	0.13	-	n.d.		
Avg.	52.54	10.76	7.74	0.14	-	n.d.	71.18	28.82
Calcd.	51.61	11.48	8.30	0	-	28.61	100	28.61
Diff.	+0.93	-0.72	-0.56	+0.14				+0.21

For **1** polyDD a continuous flat mass loss from 95°C to 400°C of 12% can be detected. This could be possibly attributed to oligomer species. Starting at 400°C a strong mass loss of 80% can be found till total degradation at 526 °C. The modified **1*** polyDDmod showed a lowered thermal stability with a strong mass loss from 95°C to 230°C of 40.5%. A smoother change of 14% from 230°C to the degradation characteristic at 400°C according to **1** polyDD can be monitored (43%). Assuming that at the point of 400°C a total loss of bromine and sulfur connected to the butyl chain already occurred and therefore the exclusive degradation of unfunctionalized polymer could be predominant, a mass according the approximately double of unfunctionalized monomer unit could be calculated.

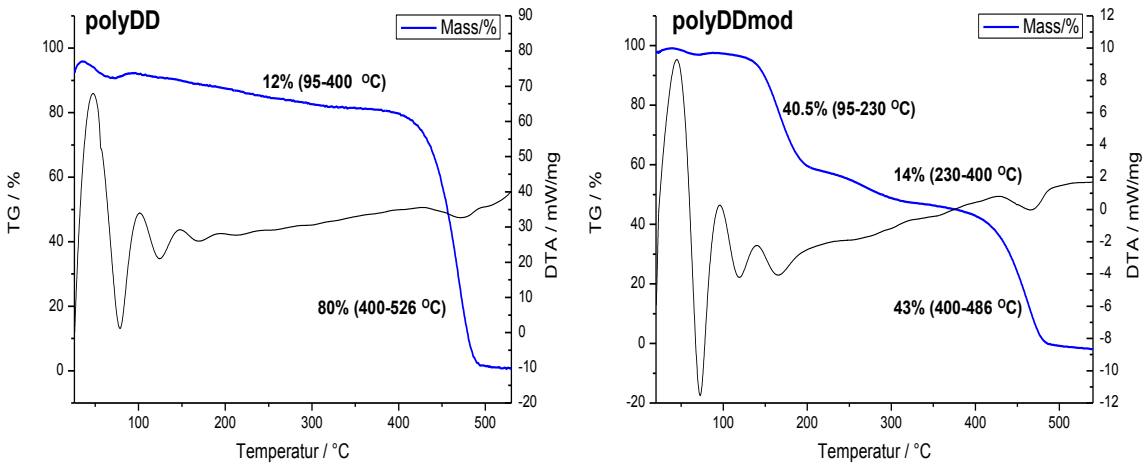


Figure 22: STA-analysis for 1 polyDD and 1* polyDDmod

Elemental analysis results for **2*** polyMEmod showed quite high differences to the predicted values for $C_{15}H_{23}BrO_4S$ within the requested acceptance and should be considered with reservation. A corresponding value for sulfur could indicate a high degree of functionalization above 90%. In particular an increased carbon value was not explainable so far.

Table 12: Elemental analysis results [w-%] for 2* polyMEmod

polyMEmod	%C	%S	%H	%O	%Br	%total	%Δ
1.	53.66	8.18	6.38	-	n.d.		
2.	53.57	8.32	6.57	-	n.d.		
Avg.	53.61	8.25	6.47	-	n.d.	68.33	31.67
Calcd.	47.50	8.45	6.11	16.87	21.07	100	37.94[3]
Diff.	+6.11	-0.2	+0.36				-6.27

In the case **2** polyME a significant change of mass occurs at 400°C. No total decomposition can be found at 540°C with 20% of remaining substance. For **2*** polyMEmod a mass loss of 9.5% can be detected at the first appearing step from 130 to 200°C lowering the thermal stability of the modified polymer compared to the precursor. Furthermore a change of 21.5% at to 358°C can be found in a second step. The decomposition characteristic of **2** polyMe seems to be lowered or occurring simultaneously to other processes. For an analog calculation as mentioned before at a temperature of 358°C and 400°C no corresponding mass could be obtained implying simultaneous processes.

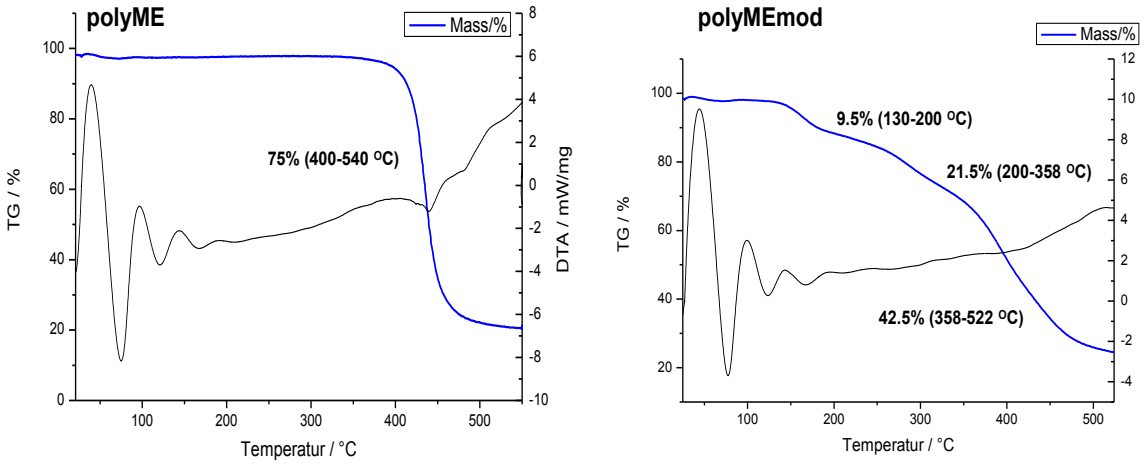


Figure 23: STA-analysis for 2 polyMe and 2* polyMEmod

Due to the strong difference of the received values compared to the calculations of $C_{25}H_{27}BrO_2S$ a possible functionalization of approximately 50% could be at least estimated according to the contained sulfur content.

Table 13: Elemental analysis results [w-%] for 3* polyPKmod

polyPKmod	%C	%S	%H	%O	%Br	%total	%Δ
1.	67.42	3.47	5.30	-	n.d.		
2.	67.21	3.55	5.16	-	n.d.		
Avg.	67.31	3.51	5.23	-	n.d.	76,05	23.95
Calcd.	63.69	6.80	5.77	6.79	16.95	100	23.74
Diff.	+3.62	-3.29	-0.54				+0.21

The precursor polymer **3** polyPK revealed a strong mass loss with significant change at 350°C. At 540°C still 20.5% remaining substance can be found. In comparison with **3*** polyPKmod two prominent steps of mass loss appeared in combination with a lowered thermal stability. The first one can be detected from 130 to 350°C with a decrease of 27.5%. From 350 to 548°C further 30% mass loss can be found which seemed to include two processes compared to the achieved characteristic of **3** polyPK. At 548°C still 37.5% substance remained. No clear trend of the decomposition towards functionalization could be achieved.

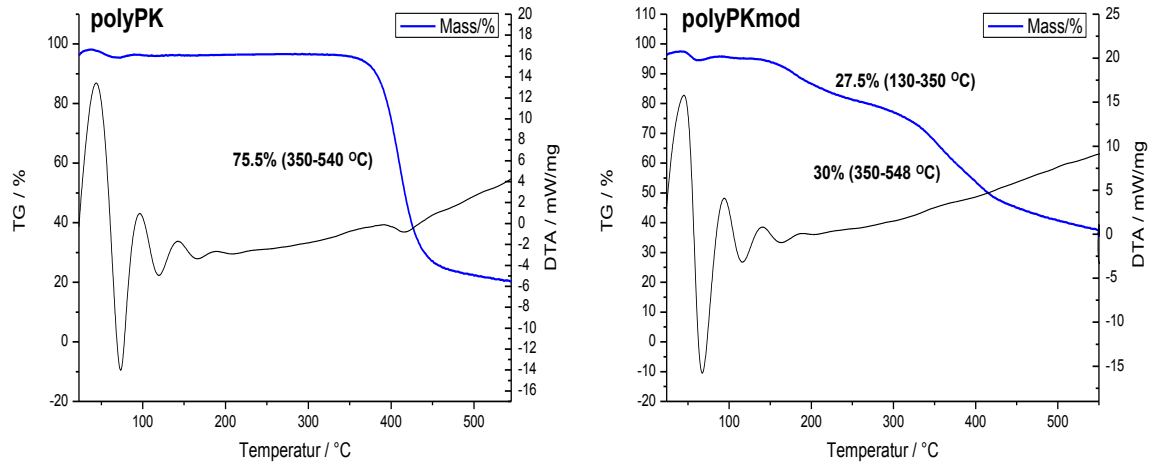


Figure 24: STA-analysis for 3 polyPK and 3* polyPKmod

The elemental analysis was calculated for $C_{46}H_{75}BrS$ which equates to a chain of ten monomer units whereas one of them is functionalized. For the received values a functionalization of at least 5-9% could be estimated corresponding to quantification via ^{1}H-spectroscopy.

Table 14: Elemental analysis results [w-%] for 4* polyPBDmod

PBDmod	%C	%S	%H	%O	%Br	%total	%Δ
1.	76.44	4.55	10.67	-	n.d.		
2.	76.05	4.21	10.51	-	n.d.		
Avg.	76.25	4.38	10.59	-	n.d.	91.22	8.78
Calcd.	74.66	4.33	10.21	-	10.80	100	10.80
Diff. [%]	+1.59	+0.05	+0.38				-2.02

The significant change in mass for **4** PBD can be detected at 350°C. At 496°C the whole polymer is lost. For the modified **4*** PBDmod another step ranging from 150 to 226°C with a resulting mass loss of 9% can be found, followed by a flat path till 350°C showing a decrease of 6% mass loss. Major mass loss according to the precursor characteristic of 81% occurred from that point with a complete decomposition at 493°C.

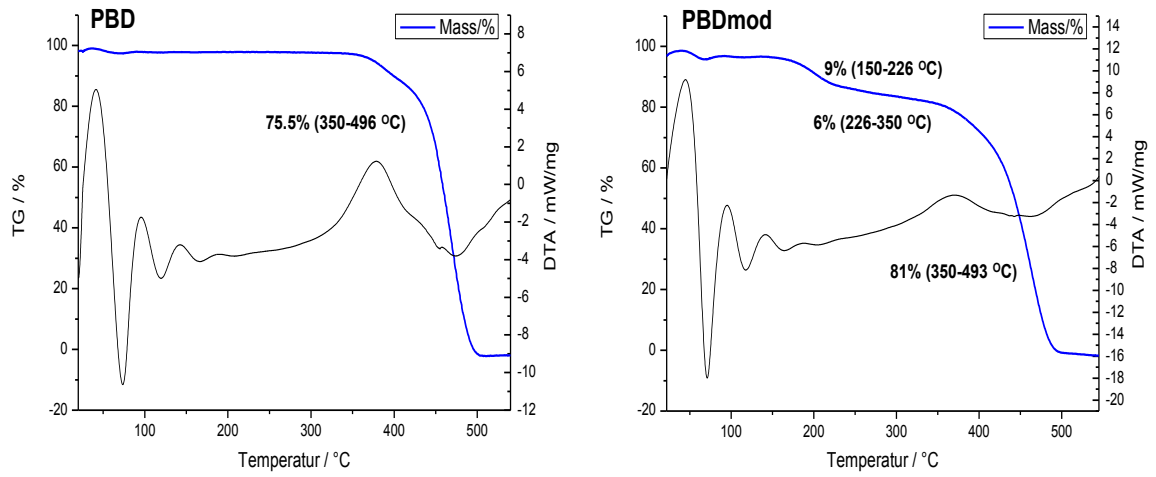


Figure 25: STA-analysis for 6 PBD and 6* PBDmod

4. Conclusion and Outlook

This work discloses alkyl hypobromothioites for the electrophilic postfunctionalization of double bond bearing polymers. Through the reaction of disulfides with elemental bromine a highly reactive thiobromide species could be obtained. The characterization of the modified polymers by means of NMR spectroscopy methods and elementary analysis revealed a complete addition of the disclosed reagent to sterically less hindered double bonds of a polymer. Through the increase of steric hindrance a decrease in conversion is observable. In the future this promising approach might be extended to functionalized disulfides with the aim to selectively and quantitatively introduce functional groups into polymer side chains.

5. Experimental Part

5.1. Instruments and Materials

All chemicals were purchased from commercial sources (Sigma Aldrich, Fluka and ABCR) and used without further purifications. **M2** and **M31** were obtained from Umicore AG & Co. KG. Solvents were used clean and dry according to standard procedures unless mentioned otherwise.[37] For reactions under inert atmosphere argon was used.

For Thin layer chromatography TLC sheets from Merck (silica gel 60 F_{254} on aluminium) were used. Visualization via UV light irradiation (254 and 365 nm) and dipping into an aqueous solution of $KMnO_4$ (0.5%) was performed.

NMR spectra (^{1}H, ^{13}C) were recorded on a Bruker Avance III 300 MHz spectrometer. Deuterated solvents were obtained from Cambridge Isotope Laboratories and referencing was done according to literature.[38] For different peak shapes were indicated using the following abbreviations: s (singlet), d (doublet), dd (doublet of doublets), t (triplet), q (quadruplet), m (multiplet), br (broad), bs (broad singlet).

Molecular weight data and polydispersity indices (PDI) were obtained from gel permeation chromatography using THF as eluent. Calibration was done with polystyrene standards from Polymer Standard Service. The following arrangement was used: Merck Hitachi L6000 pump (delivery volume 1 mL/min), separation columns of Polymer Standard Service (5 µm grade size), refractive index detector from Wyatt Technology.

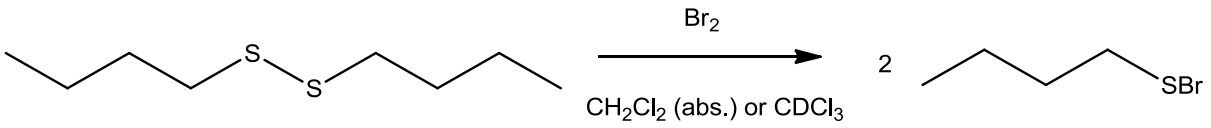
IR spectra were obtained with a Bruker ALPHA FT-IR Spectrometer in ATR mode. The intensities according to different wavenumbers (cm^{-1}) are characterized as s (strong), m (medium) and w (weak).

Simultaneous Thermal Analysis (STA) to determine decomposition temperatures of the polymers were obtained with a 449C Jupiter (Netzsch). A heating rate of 10°C/min from 25 to 500°C and a Helium gas stream of 50 mL/min were used.

Elemental analysis was done through thermal combustion on a Vario EL III for CHNS-analysis or by Mikroanalytisches Laboratorium, Universität Wien.

[37] Perrin D.D.; Armarego, W. L. F. *Purification of Laboratory Chemicals, 3rd edn.,* Pergamon, NewYork, **1988.**
[38] Gottlieb H.E.; Kotylar A.; Nudelman A. *J.Org.Chem.* **1997**, *62,* 7512.

5.2. Zincke Dissulfide Cleavage



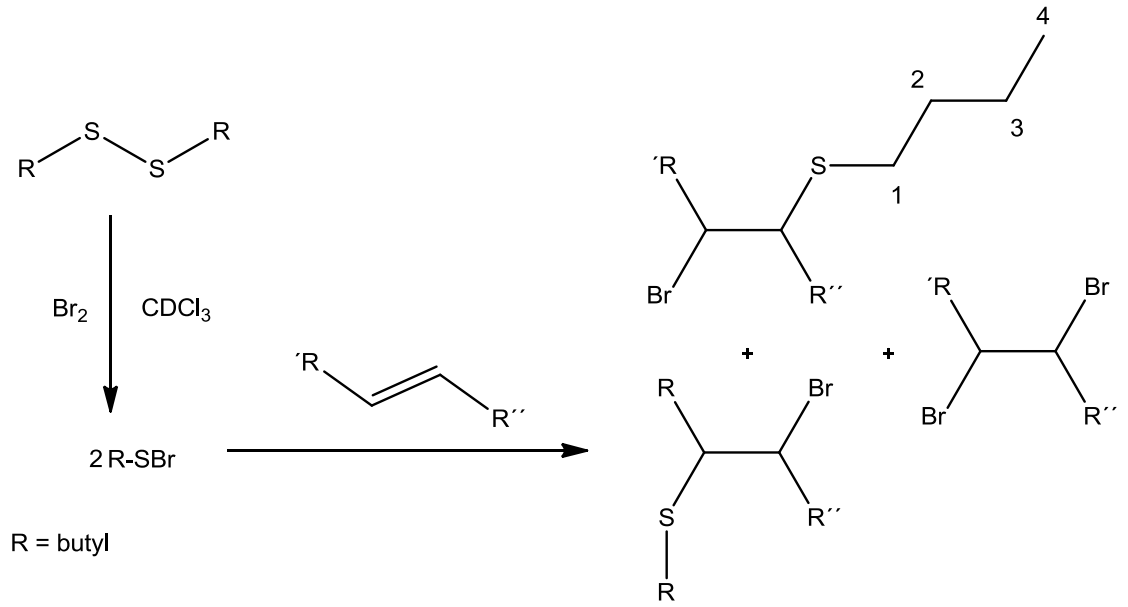
Scheme 18: Preparation of butyl hypobromothioite

To 1,2-dibutyldisulfane stirred in dichloromethane (abs.) or deuterochloroform at ambient conditions bromine was added. The reaction was carried out in glass vials. Progress of the reaction was monitored via NMR.

^{1}H-NMR (δ, 20°C, $CDCl_3$, 300 MHz): 3.41 (t or br, 2H, -CH_2SBr), 1.72 (m, 2H, -C*H*$_2$-CH_2-SBr), 1.46 (m, 2H, CH_3-C*H*$_2$-), 0.94 (t, 3H, -C*H*$_3$)

^{13}C-NMR (δ, 20°C, $CDCl_3$, 75 MHz): 39.6 (1C, -*C*H_2-S), 31.5 (1C, -*C*H_2-CH_2-S), 21.5 (1C, CH_3-*C*H_2-), 13.7 (1C, -*C*H_3)

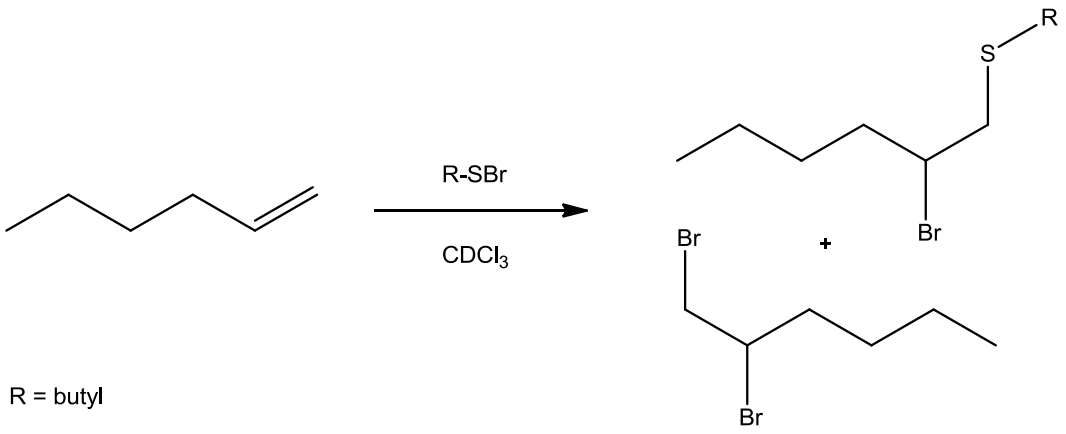
5.3. Conversion of selected model substances



Scheme 19: General procedure for the preparation of low molecular model-substances

To 1,2-dibutyldisulfane in 0.75 mL $CDCl_3$ stirred in a 3 mL vial, bromine was added at ambient conditions. Progress of the reaction was monitored via NMR. After the in situ formation of butyl hypobromothioite, the olefin was added to the reaction mixture. This was done for seven different types of olefin at different proportions of olefine to 1,2-dibutyldisulfane as well as 1,2-dibutyldisulfane to bromine which are summarized in the following Tables 15-22. Without further purification and a reaction time of two hours, the conversion in respect to the functionalized product and the brominated byproduct was determined by integration of the corresponding ^{1}H-NMR spectra. In the same manner bromination of the olefins was performed.

5.3.1. Conversion of hex-1-ene



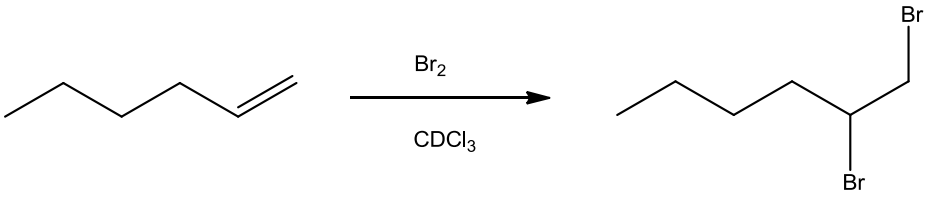
Scheme 20: Preparation to determine conversion of hex-1-ene to (2-bromohexyl)(butyl)sulfane and 1,2-dibromohexane

Table 15: Composition of the reagent according to hex-1-ene

Olefine	1,2-dibutyldisulfane	bromine	bromine
		1.5 eq (Br_2:dibu)	2 eq (Br_2:dibu)
74.6 µL, 1 eq, 0.59 mmol	113.9 µL, 1 eq, 0.59 mmol	45.8 µL, 1.5 eq, 0.88 mmol	61 µL, 2 eq, 1.2 mmol
74.6 µL, 1 eq, 0.59 mmol	56.9 µL, 0.5 eq, 0.29 mmol	22.9 µL, 1.5 eq, 0.44 mmol	30.5 µL, 2 eq, 0.58 mmol

^{1}H-NMR (δ, 20°C, $CDCl_3$, 300 MHz): 4.06 (m, 1H, C*H*-Br), 3.06 (2d, 1H, Br-CH-CH_2-S-), 2.95 (2d, 1H, Br-CH-CH_2-S-), 2.55 (t, 2H, bu^1), 2.06 (m, 2H, Br-CH-CH_2), 1.80 (m, 2H, bu^2), 1.55 (m, 2H, bu^3), 1.36 (m 4H, CH_3-CH_2-CH_2-), 0.90 (t, 6H, CH_3, bu^4)

5.3.2. Bromination of hex-1-ene

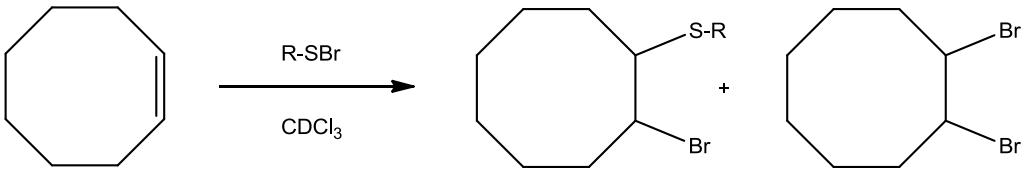


Scheme 21: Preparation to determine conversion of hex-1-ene to 1,2-dibromohexane

To hex-1-ene (74.62 µL, 1eq, 5.9 mmol) bromine (61 µL, 2eq, 11.8 mmol) was added. The formation of 1,2-dibromohexane was detected via NMR.

^{1}H-NMR (δ, 20°C, $CDCl_3$, 300 MHz): 4.14 (m, 1H, C*H*-Br), 3.84 (2d, 1H, CH_2-Br), 3.63 (t, 1H, CH_2-Br), 2.15 (m, 1H, Br-CH-CH_2), 1.80 (m, 1H, Br-CH-CH_2), 1.30-1.20 (m, 4H, CH_2CH_2CH_3), 0.93 (t, 3H, CH_3)

5.3.3. Conversion of (Z)-cyclooctene



R = butyl

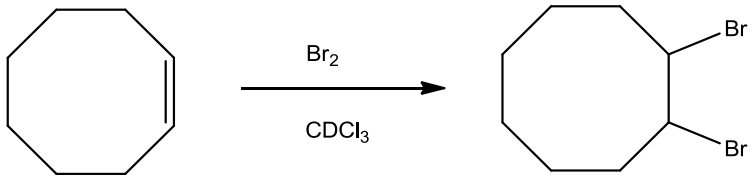
Scheme 22: Preparation to determine conversion of (Z)-cyclooctene to (2-bromocyclooctyl)(butyl)sulfane and 1,2-dibromocyclooctane

Table 16: Composition of the reagent according to (Z)-cyclooctene

Olefine	1,2-dibutyldisulfane	bromine	bromine
		1.5 eq (Br_2:dibu)	2 eq (Br_2:dibu)
58.9 µL, 1 eq, 0.45 mmol	87 µL, 1 eq, 0.45 mmol	34.9 µL, 1.5 eq, 0.68 mmol	46.6 µL, 2 eq, 0.9 mmol
58.9 µL, 1 eq, 0.45 mmol	43.5 µL, 0.5 eq, 0.22 mmol	17.5 µL, 1.5 eq, 0.33 mmol	23.3 µL, 2 eq, 0.44 mmol

^{1}H-NMR (δ, 20°C, $CDCl_3$, 300 MHz): 4.38 (m, 1H, C*H*-Br), 3.18 (dt, 1H, C*H*-S-), 2.57 (t, 2H, bu^1), 2.36-1.28 (m, 16H, (CH_2)$_6$, bu^2, bu^3), 0.89 (t, 3H, bu^4)

5.3.4. Bromination of (Z)-cyclooctene

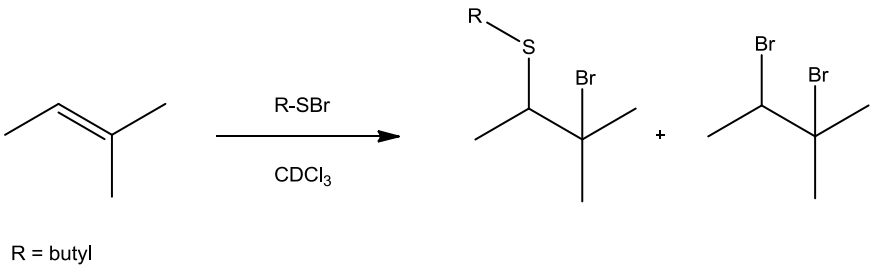


Scheme 23: Preparation to determine conversion of (Z)-cyclooctene to 1,2-dibromocyclooctane

To (Z)-cyclooctene (58.96 µL, 1eq, 0.45 mmol) bromine (46.6 µL, 2eq, 0.9 mmol) was added. The formation of 1,2-dibromocyclooctane was detected via NMR.

^{1}H-NMR (δ, 20°C, $CDCl_3$, 300 MHz): 4.59 (m, 2H, C*H*-Br), 2.40 (m, 2H, CH_2-CH-CH-CH_2), 2.12 (m, 2H, CH_2-CH-CH-CH_2), 1.83 (m, 2H, -CH-CH$_2$-CH_2), 1.74-1.36 (m, 6H, CH-CH$_2$-CH_2-CH_2CH_2-CH_2-)

5.3.5. Conversion of 2-methylbut-2-ene



R = butyl

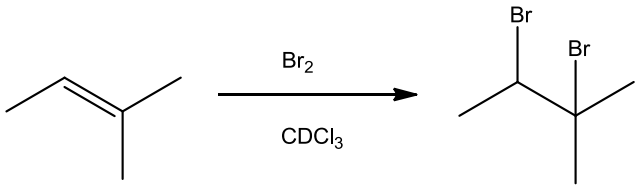
Scheme 24: Preparation to determine conversion of 2-methylbut-2-ene to (3-bromo-3-methylbutan-2-yl)(butyl)sulfane and 2,3-dibromo-2-methylbutane

Table 17: Composition of the reagent according to 2-methylbut-2-ene

Olefine	1,2-dibutyldisulfane	bromine	bromine
		1.5 eq (Br_2:dibu)	2 eq (Br_2:dibu)
75.7 µL, 1 eq, 0.71 mmol	136.7 µL, 1 eq, 0.71 mmol	54.9 µL, 1.5 eq, 1.07 mmol	73.3 µL, 2 eq, 1.42 mmol
75.7 µL, 1 eq, 0.71 mmol	68.4 µL, 0.5 eq, 0.36 mmol	27.5 µL, 1.5 eq, 0.53 mmol	36.6 µL, 2 eq, 0.72 mmol

^{1}H-NMR (δ, 20°C, $CDCl_3$, 300 MHz): 2.89 (q, 1H, C*H*-S-), 2.59 (t, 2H, bu^1), 1.91 (s, 3H, -C-C*H*$_3$), 1.78 (s, 3H, -C-C*H*$_3$), 1.56 (m, 2H, bu^2), 1.53 (d, 3H, -S-CH-C*H*$_3$), 1.41 (m, 2H, bu^3), 0.90 (t, 3H, bu^4)

5.3.6. Bromination of 2-methylbut-2-ene

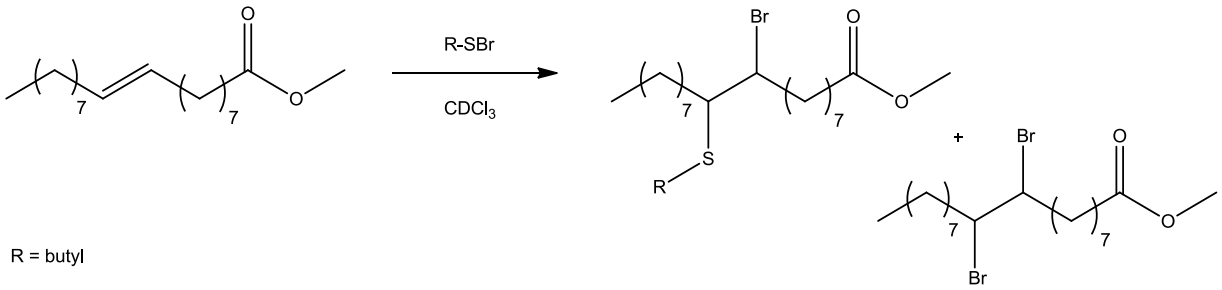


Scheme 25: Preparation to determine conversion of 2-methylbut-2-ene to 2,3-dibromo-2-methylbutane

To 2-methylbut-2-ene (75.7 µL, 1eq, 0.71 mmol) bromine (73 µL, 2eq, 1.4 mmol) was added. The formation of 2,3-dibromo-2-methylbutane was detected via NMR.

^{1}H-NMR (δ, 20°C, $CDCl_3$, 300 MHz): 4.44 (q, 1H, C*H*-Br), 1.97 (s, 3H, C-C*H*$_3$), 1.93 (d, 3H, CH-C*H*$_3$), 1.83 (s, 3H, C-C*H*$_3$)

5.3.7. Conversion of methyl oleate



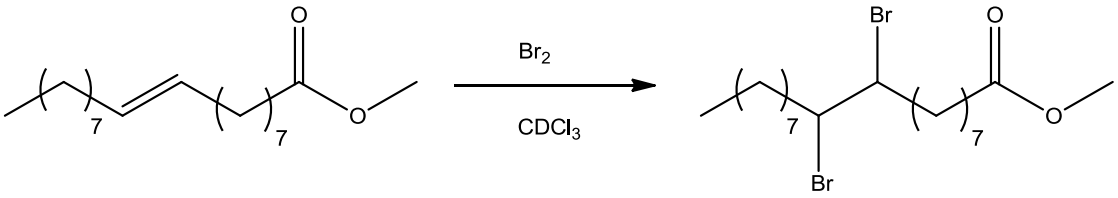
Scheme 26: Preparation to determine conversion of methyl oleate to methyl 9-bromo-10-(butylthio)octadecanoate and methyl 9,10-dibromooctadecanoate

Table 18: Composition of the reagent according to methyl oleate

Olefine	1,2-dibutyldisulfane	bromine	bromine
		1.5 eq (Br_2:dibu)	2 eq (Br_2:dibu)
57.1 µL, 1 eq, 0.17 mmol	32.3 µL, 1 eq, 0.17 mmol	13 µL, 1.5 eq, 0.26 mmol	17 µL, 2 eq, 0.34 mmol
57.1 µL, 1 eq, 0.17 mmol	16.2 µL, 0.5 eq, 0.08 mmol	65 µL, 1.5 eq, 0.12 mmol	8.7 µL, 2 eq, 0.16 mmol

^{1}H-NMR (δ, 20°C, $CDCl_3$, 300 MHz): 4.20 (m, 1H, C*H*-Br), 3.63 (s, 3H, -O-CH_3), 2.80 (m, 1H, C*H*-S-), 2.51 (dt, 2H, bu[1]), 2.28 (t, 2H, -CO-CH_2), 2.09-1.78 (m, 2H, Br-CH-CH_2), 1.56 (m, 6H, -S-CH-CH_2, Br-CH-CH_2, bu[2]), 1.30 (m, 22H, bu[3], $(CH_2)_{10}$, 0.89 (m, 6H, -CH_3, bu[4])

5.3.8. Bromination of methyl oleate

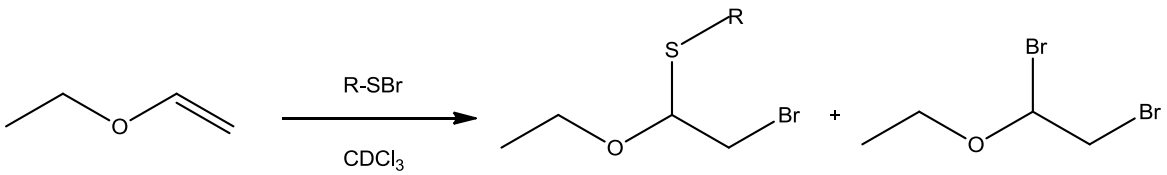


Scheme 27: Preparation to determine conversion of methyl oleate to methyl 9,10-dibromooctadecanoate

To methyl oleate (57.1 µL, 1eq, 0.17 mmol) bromine (17.3 µL, 2eq, 0.34 mmol) was added. The formation of methyl 9-bromo-10-(butylthio)octadecanoate was detected via NMR.

^{1}H-NMR (δ, 20°C, $CDCl_3$, 300 MHz): 4.19 (m, 2H, -C*H*-Br), 3.66 (s, 3H, -O-CH_3), 2.30 (t, 2H, -CO-CH_2), 2.03 (m, 2H, -CH_2-CH-Br), 1.84 (m, 2H, -CH_2-CH-Br), 1.62 (m, 4H, -CO-CH_2-CH_2, -CH_2-), 1.32 (m,18H, (CH_2)$_4$,(CH_2)$_5$), 0.88 (m, 3H, -CH_2-CH_3)

5.3.9. Conversion of ethoxyethene



Scheme 28: Preparation to determine conversion of ethoxyethene to (2-bromo-1-ethoxyethyl)(butyl)sulfane and ,2-dibromo-1-ethoxyethane

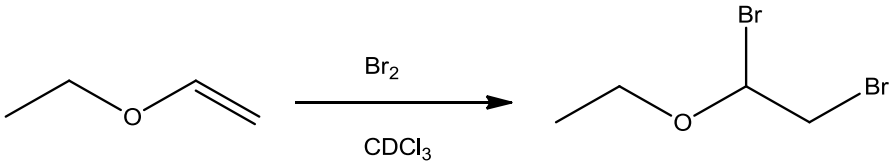
Table 19: Composition of the reagent according to ethoxyethene

Olefine	1,2-dibutyldisulfane	bromine	bromine
		1.5 eq (Br_2:dibu)	2 eq (Br_2:dibu)
66.4 µL, 1 eq, 0.69 mmol	132.9 µL, 1 eq, 0.69 mmol	53.4 µL, 1.5 eq, 1.04 mmol	71.3 µL, 2 eq, 1.38 mmol
66.4 µL, 1 eq, 0.69 mmol	66.5 µL, 0.5 eq, 0.35 mmol	26.7 µL, 1.5 eq, 0.53 mmol	35.6 µL, 2 eq, 0.7 mmol

^{1}H-NMR (δ, 20°C, $CDCl_3$, 300 MHz):

No corresponding peaks for the disired productformation could be achieved.

5.3.10. Bromination of ethoxyethene

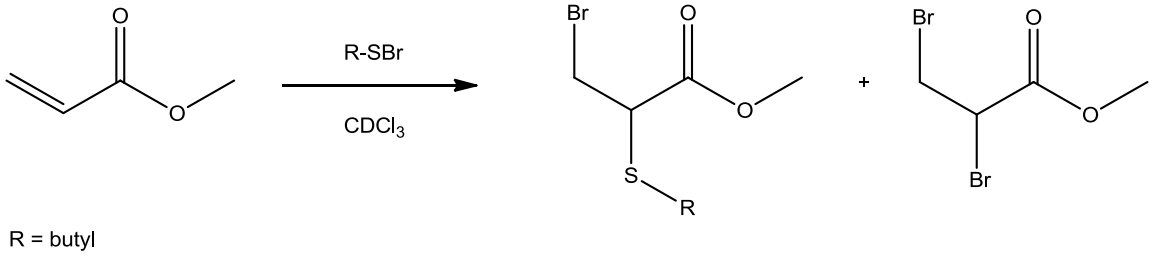


Scheme 29: Preoaration to determine conversion of ethoxyethene to 1,2-dibromo-1-ethoxyethane

To ethoxyethene (66.4 µL, 1eq, 0.69 mmol) bromine (71 µL, 2eq, 1.4 mmol) was added. The formation of methyl 9,10-dibromooctadecanoate was detected via NMR.

^{1}H-NMR (δ, 20°C, $CDCl_3$, 300 MHz): 5.99 (dd, 1H, C*H*-Br), 3.94 (m, 3H, O-CH_2, -CH_2-Br), 3.64 (m, 1H, -CH_2-Br), 1.31 (t, 3H, -CH_3)

5.3.11. Conversion of methyl acrylate



R = butyl

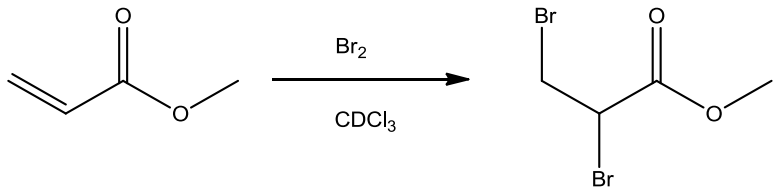
Scheme 30: Preparation to determine conversion of methyl acrylate to methyl 3-bromo-2-(butylthio)propanoate and methyl 2,3-dibromopropanoate

Table 20: Composition of the reagent according to methyl acrylate

Olefine	1,2-dibutyldisulfane	bromine	bromine
		1.5 eq (Br_2:dibu)	2 eq (Br_2:dibu)
52.6 µL, 1eq, 0.58 mmol	111.3 µL, 1 eq, 0.58 mmol	44.8 µL, 1.5 eq, 0.87 mmol	59.7 µL, 2 eq, 1.16 mmol
52.6 µL, 1eq, 0.58 mmol	55.7 µL, 0.5 eq, 0.29 mmol	22.4 µL, 1.5 eq, 0.44 mmol	29.8 µL, 2 eq, 0.58 mmol

^{1}H-NMR (δ, 20°C, $CDCl_3$, 300 MHz): 4.24 (2d, 1H, C*H*$_2$-Br), 3.77 (s, 3H, O-C*H*$_3$), 3.52 (dt, 1H, C*H*-S-), 2.98 (2d, 1H, C*H*$_2$-Br), 2.52 (dt, 2H, bu^1), 1.51 (m, 2H, bu^2), 1.36 (m, 2H, bu^3), 0.87 (t, 3H, bu^4)

5.3.12. Bromination of methyl acrylate

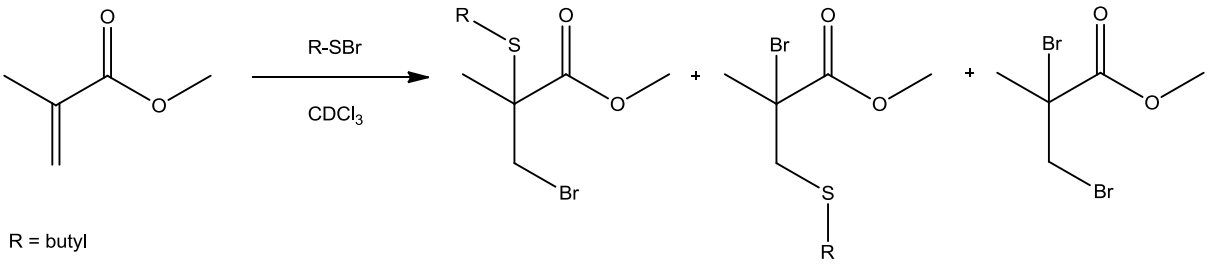


Scheme 31: Preparation to determine conversion of methyl acrylate to methyl 2,3-dibromopropanoat

To methyl acrylate (52.6 µL, 1eq, 0.58 mmol) bromine (24 µL, 2eq, 1.2 mmol) was added. The formation of methyl 2,3-dibromopropanoate was detected via NMR.

^{1}H-NMR (δ, 20°C, $CDCl_3$, 300 MHz): 4.44 (2d, 1H, -C*H*$_2$-Br), 3.93 (t, 1H, -C*H*-Br), 3.84 (s, 3H, O-C*H*$_3$), 3.69 (2d, 1H, -C*H*$_2$-Br)

5.3.13. Conversion of methyl methacrylate



Scheme 32: Preparation to determine conversion of methyl methacrylate to methyl methacrylatetomethyl 2-bromo-3-(butylthio)-2-methylpropanoate, methyl 3-bromo-2-(butylthio)-2-methylpropanoate and methyl 2,3-dibromo-2-methylpropanoate

Table 21: Composition of the reagent according to methyl methacrylate

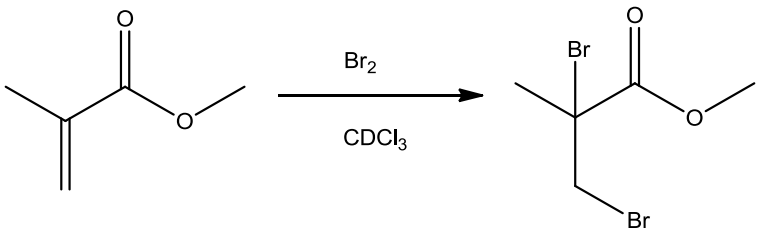
Olefine	1,2-dibutyldisulfane	bromine	bromine
		1.5 eq (Br_2:dibu)	2 eq (Br_2:dibu)
54.8 µL, 1 eq, 0.49 mmol	95.7 µL, 1 eq, 0.49 mmol	38.5 µL, 1.5 eq, 0.74 mmol	51.3 µL, 2 eq, 0.98 mmol
54.8 µL, 1 eq, 0.49 mmol	47.9 µL, 0.5 eq, 0.25 mmol	19.2 µL, 1.5 eq, 0.38 mmol	25.7 µL, 2 eq, 0.5 mmol

^{1}H-NMR (δ, 20°C, $CDCl_3$, 300 MHz):

methyl 2-bromo-3-(butylthio)-2-methylpropanoate: 3.94 (d, 1H, C-CH_2), 3.72 (s, 3H, O-CH_3), 3.41 (d, 1H, C-CH_2), 2.57 (m, 2H, bu^1), 1.54 (s, 3H, C-CH_3), 1.48 (m, 2H, bu^2), 1.35 (m, 2H, bu^3), 0.85 (t, 3H, bu^4)

methyl 3-bromo-2-(butylthio)-2-methylpropanoate: 3.75 (s, 3H, O-CH_3), 3.45 (d, 1H, C-CH_2), 3.08 (d, 1H, C-CH_2), 2.57 (m, 2H, bu^1), 1.93 (s, 3H, C-CH_3), 1.48 (m, 2H, bu^2), 1.35 (m, 2H, bu^3), 0.85 (t, 3H, bu^4)

5.3.14. Bromination of methyl methacrylate

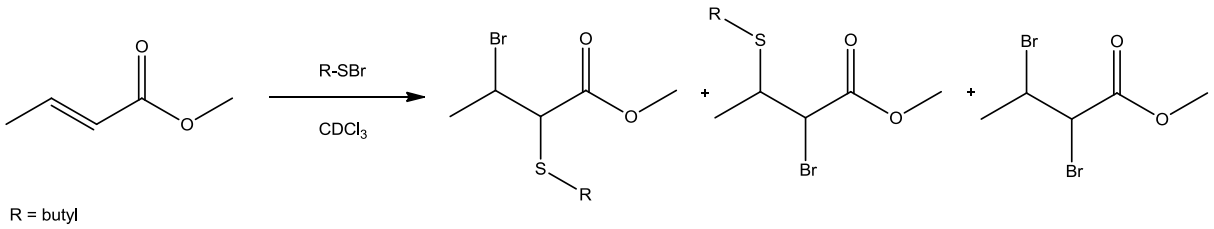


Scheme 33: Preparation to determine conversion of methyl methacrylate to methyl 2,3-dibromo-2-methylpropanoate

To methyl methacrylate (54.8 µL, 1eq, 0.49 mmol) bromine (51 µL, 2eq, 0.98 mmol) was added. The formation of methyl 2,3-dibromo-2-methylpropanoate was detected via NMR.

^{1}H-NMR (δ, 20°C, $CDCl_3$, 300 MHz): 4.22 (d, 1H, CH_2Br), 3.84 (s, 3H, O-CH_3), 3.75 (d, 1H, CH_2-Br), 2.04 (s, C-CH_3)

5.3.15. Conversion of (E)-methyl but-2-enoate



Scheme 34: Preparation to determine conversion of (E)-methyl but-2-enoate to methyl 3-bromo-2-(butylthio)butanoate, methyl 2-bromo-3-(butylthio)butanoate and methyl 2,3-dibromobutanoate

Table 22: Composition of the reagent according to (E)-methyl but-2-enoate

Olefine	1,2-dibutyldisulfane	bromine	bromine
		1.5 eq (Br_2:dibu)	2 eq (Br_2:dibu)
52.9 µL, 1 eq, 0.49 mmol	95.7 µL, 1 eq, 0.49 mmol	38.5 µL, 1.5 eq, 0.74 mmol	51.3 µL, 2 eq, 0.98 mmol
52.9 µL, 1 eq, 0.49 mmol	47.9 µL, 0.5 eq, 0.25 mmol	19.2 µL, 1.5 eq, 0.38 mmol	25.7 µL, 2 eq, 0.5 mmol

^{1}H-NMR (δ, 20°C, $CDCl_3$, 300 MHz):

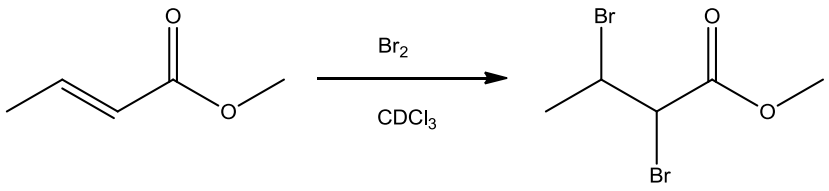
methyl 3-bromo-2-(butylthio)butanoate:

4.29 (m, 1H, C*H*-Br), 3.73 (s, 3H, O-CH_3), 3.43 (d, 1H, C*H*-S), 2.60 (m, 2H, bu^1), 1.85 (d, 3H, CH-CH_3), 1.49 (m, 2H, bu^2), 1.36 (m, 2H, bu^3), 0.86 (t, 3H, bu^4)

methyl 2-bromo-3-(butylthio)butanoate:

4.13 (d, 1H, C*H*-Br), 3.75 (s, 3H, O-CH_3), 3.14 (m, 1H, C*H*-S), 2.60 (m, 2H, bu^1), 1.50 (m, 2H, bu^2), 1.48 (d, 3H, S-CH-CH_3), 1.36 (m, 2H, bu^3), 0.86 (t, 3H, bu^4)

5.3.16. Bromination of (E)-methyl but-2-enoate



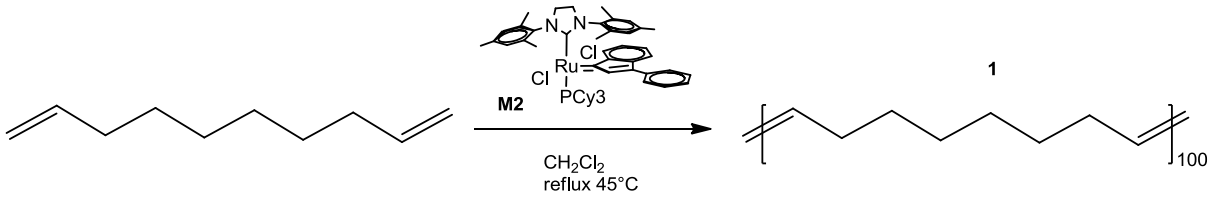
Scheme 35: Preparation to determine conversion of (E)-methyl but-2-enoate to methyl 2,3-dibromobutanoate

To (E)-methyl but-2-enoate (52.9 µL, 1eq, 0.49 mmol) bromine (51 µL, 2eq, 0.98 mmol) was added. The formation of methyl 2,3-dibromobutanoate was detected via NMR.

^{1}H-NMR (δ, 20°C, $CDCl_3$, 300 MHz):4.37 (m, 2H, Br-C*H*-C*H*-Br), 3.83 (s, 3H, O-CH_3), 1.91 (d, 3H, CH-CH_3)

5.4. Synthesis of Polymerprecursors

5.4.1. Synthesis of poly(DD)



Scheme 36: Preparation of poly(DD)

Deca-1,9-diene (0.72 g, 5.22 mmol, 1eq.) was added to 5.2 mL dry, degassed CH_2Cl_2 in a Schlenk flask and stirred under nitrogen atmosphere at 45 °C. After the addition of the initiator **M2** (49.5mg, 0,052mmol, 1mol%) the reaction mixture boiled under reflux for 12 hrs. The reaction was followed by TLC using Cy/EtOAc, 3:1 (v:v) and $KMnO_4$ solution for staining. The conversion was not complete, when the reaction was quenched with 200 mL of ethyl vinylether and stirred for 15 min. The polymer was precipitated by the dropwise addition of the solution into methanol and dried in vacuo.

Yield: 384 mg (53 %) of a brown, sticky polymer **1**

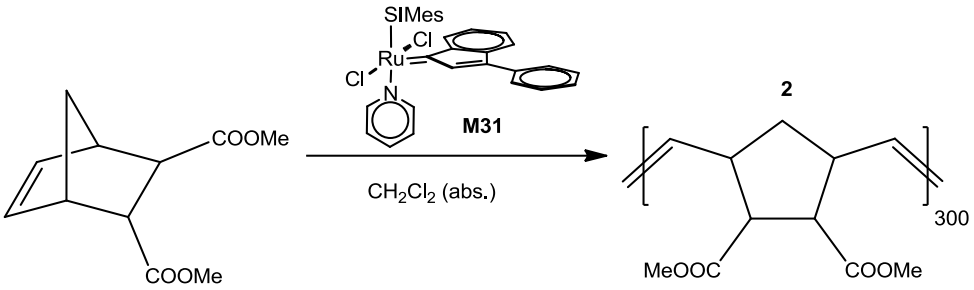
^{1}H-NMR (δ, 20°C, $CDCl_3$, 300 MHz): 5.38 (t, 2H, -C*H*=C*H*-), 1.97 (br, 4H, -HC=CH-CH_2-), 1.28 (br, 8H, -HC=CH-CH$_2$-(CH_2)$_4$-)

^{13}C-NMR (δ, 20°C, $CDCl_3$, 75 MHz): 130.3 (2C, -*C*H=*C*H-), 29.6, 29.5 (2C,-CH=CH-*C*H$_2$-), 29.2, 29.1 (2C, -CH=CH-CH$_2$-*C*H$_2$-), 28.7 (2C,-CH=CH-(CH$_2$)$_2$-*C*H$_2$-)

FT-IR (cm^{-1}): 2917 (s), 2845 (s), 1466 (m), 1262 (w), 1073 (w), 959 (s, $\nu_{trans\ C=C}$), 801 (w), 723 (w)

GPC Results: M_n [g/mol]: 35300; M_w [g/mol]: 67200; PDI: 1.90

5.4.2. Synthesis of poly(ME)



Scheme 37: Preparation of poly(ME)

In a Schlenk flask the monomer (500 mg, 2.4 mmol, 300 eq.) was dissolved in 24 mL degassed, dry CH_2Cl_2 under nitrogen atmosphere. Then the initiator **M31** (6 mg, 0.008 mmol, 1eq.) was added in the appropriate amount of degassed, dry CH_2Cl_2. The reaction was followed by TLC using Cy/EtOAc, 3:1 (v:v) and $KMnO_4$ solution for staining. After complete conversion the reaction was quenched with 200 mL ethyl vinylether and stirred for 15 min. The polymer was precipitated by the dropwise addition of the solution into methanol and dried in vacuo.

Yield: 405 mg (81 %) of a white, solid polymer **2**

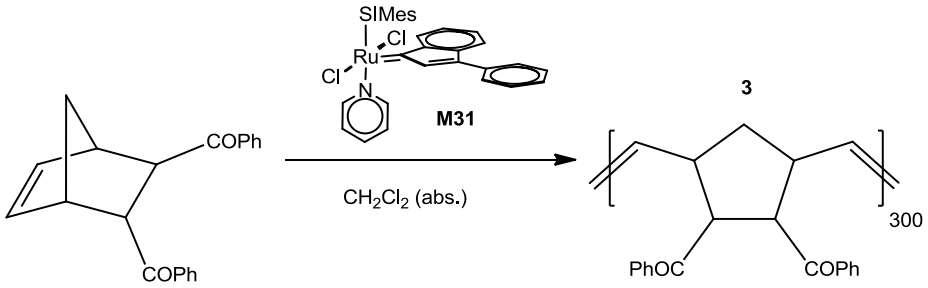
^{1}H-NMR (δ, 20°C, $CDCl_3$, 300 MHz): 5.6-5.06 (br, 2H, -C*H*=C*H*-), 3.99-3.47 (br, 6H, -COO-CH_3), 3.45-2.53 (br, 4H, MeOOC-C*H*-C*H*-), 1.73-2.13 (br, 1H, -HC=CH-CH-CH_2), 1.23-1.62 (br, 1H, -HC=CH-CH-CH_2)

^{13}C-NMR (δ, 20°C, $CDCl_3$, 75 MHz): 174.5, 173.4 (2C, *C*=O), 133.6-129.5 (2C, -H*C*=*C*H-), 53.1-51.5 (2C, -O-*C*H_3), 46.6, 44.6, 41.8, 40.6, 39.7 (5C, cp)

FT-IR (cm^{-1}): 3001, 2956, 2854 (w), 1725 (s, $\nu_{C=O}$), 1436 (m), 1381,1335 (w), 1164 (s), 971 (m, $\nu_{trans\ C=C}$), 872 (w), 740 (w, $\nu_{cis\ C=C}$)

GPC Results: M_n [g/mol]: 58300; M_w [g/mol]: 66400: PDI: 1.14

5.4.3. Synthesis of poly(PK)



Scheme 38: Preparation of poly(PK)

In a Schlenk flask the monomer (500 mg, 1.6 mmol, 300 eq.) was dissolved in 17 mL degassed, dry CH_2Cl_2 under nitrogen atmosphere. Then the initiator **M31** (4.13 mg, 0.006 mmol, 1eq.) was added in the appropriate amount of degassed, dry CH_2Cl_2. The reaction was followed by TLC using Cy/EtOAc, 3:1 (v:v) and $KMnO_4$ solution for staining. After complete conversion the reaction was quenched with 200 mL ethyl vinylether and stirred for 15 min. The polymer was precipitated by the dropwise addition of the solution into methanol and dried in vacuo.

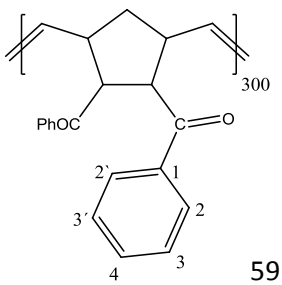
Yield: 220 mg (44 %) of a white, solid polymer **3**

^{1}H-NMR (δ, 20°C, $CDCl_3$, 300 MHz): 8.14-6.66 (br, 10H, ph), 5.73-4.46 (br, 2H, -CH=C*H*-), 4.45-2.46 (br, 4H, Ph-C-C*H*-C*H*-), 2.44-0.64, (br, 2H, -CH=CH-CH-CH_2)

^{13}C-NMR (δ, 20°C, $CDCl_3$, 75 MHz): 201.5, 200.4 (2C, -C=O), 136.9 (2C, ph^1), 133.2 (2C, ph^4), 130.4 (2C, -CH=CH-), 128.5-128.1 (8C Ph$^{2,2',3,3'}$), 54.4-41.1 (5C, cp)

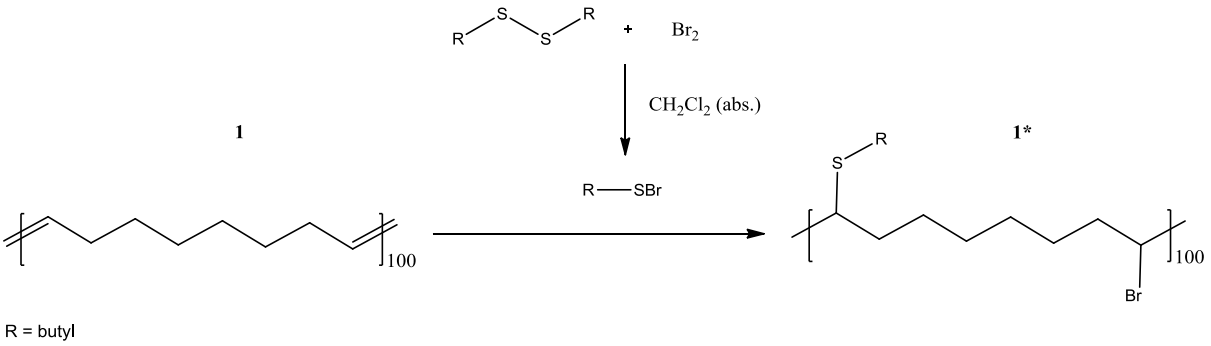
FT-IR (cm^{-1}): 3058-2860 (w, $\nu_{CH=CH}$), 1670 (s, $\nu_{C=O}$), 1592 (m), 1578 (m), 1443 (m),1379 (w), 1330 (w), 1214 (s), 1181 (m), 1004 (m), 976 (m, $\nu_{trans\ C=C}$), 926 (w), 848 (w), 784 (w), 687 (s, $\nu_{cis\ C=C}$)

GPC Results: M_n [g/mol]: 68300; M_w [g/mol]: 78700, PDI: 1.15



5.5. Modification of Polymers

5.5.1. Modification of poly(DD)



Scheme 39: Preparation of poly(DD)mod

To 1,2-dibutyldisulfane (69.4 µL, 0.36 mmol, 1 eq.) in 1mL CH_2Cl_2 (abs.) stirred in a 5 mL vial, bromine (18.6 µL, 0.36 mmol, 1 eq) was added slowly at ambient conditions. Progress of the reaction was monitored via NMR. After the in situ formation of butyl hypobromothioite the mixture was added to polymer **1** (50 mg, 0.36 mmol 1 eq.) dissolved in 1 mL CH_2Cl_2 (abs.) dropwise. After a reaction time of 2 hrs the polymer was precipitated by dropwise addition of the solution into *n*-pentane for three times, and the organic solvent was removed in vacuo.

Yield: 42 mg (84 %) of a brown, sticky polymer **1***

^{1}H-NMR (δ, 20°C, $CDCl_3$, 300 MHz): 4.14 (br, 1H -C*H*-Br), 2.71 (br, 1H bu-S-C*H*-), 2.57 (t, 2H bu^1) , 2.19-1.75 (br, 4H -*CH*$_2$-CHBr-, bu^2, 1.76-1.49 (m, 4H, bu-S-CH-*CH*$_2$-, bu^3), 1.52-1.18 (m, 8H, -CH-CH$_2$-(C*H*$_2$)$_4$-CH$_2$-CH-), 0.92 (t 3H bu^4)

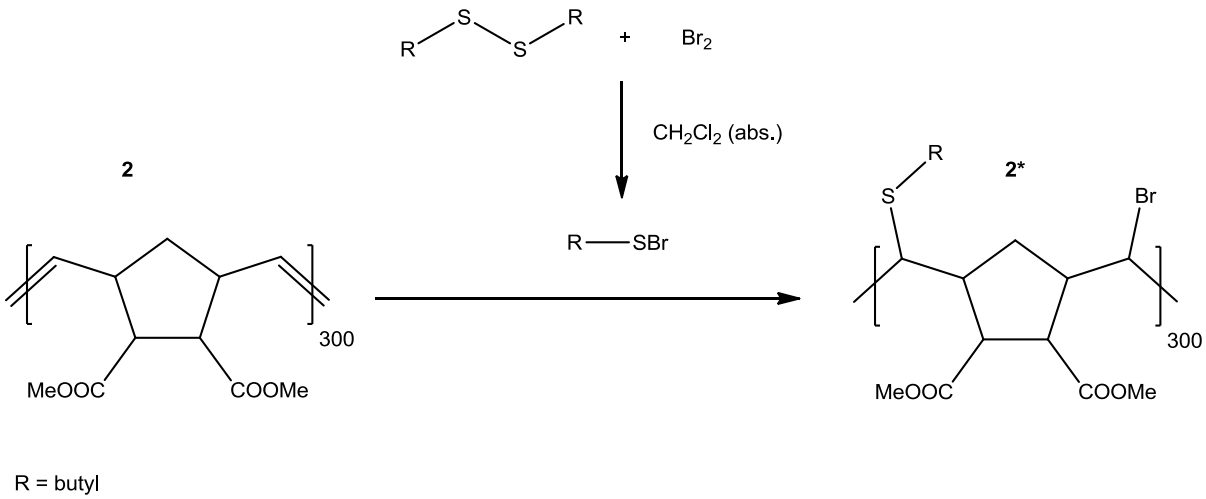
^{13}C-NMR (δ, 20°C, $CDCl_3$, 75 MHz): 63.4 (1C, *C*H-Br), 53.2 (1C, *C*H-S-), 36.4 (1C, *C*H$_2$-CH-Br), 33.5 (1C, CH$_2$-CH-S), 32.3 (1C, bu^1), 32.2 (1C, bu^2), 27.1-29.5 (4C, (CH$_2$)$_4$, 22.2 (1C, bu^3), 13.9 (1C, bu^4)

FT-IR (cm^{-1}): 2926 (s), 2850 (s), 1456 (m), 1379 (w), 1269 (w), 1218 (w), 1158 (w), 725 (m), 575 m, $\nu_{C\text{-}Br}$)

ELEM. ANAL. : Calcd. for $C_{12}H_{25}BrS$ (molecular weight = 281,30) C, 51.24%; H, 8.96%; S, 11.40% Br, 28.41% ; Found: C, 52.54%; H, 7.74%; S, 10.76%; N, 0.14%

GPC Results: M_n [g/mol]: 40300; M_w [g/mol]: 87800; PDI: 2.18

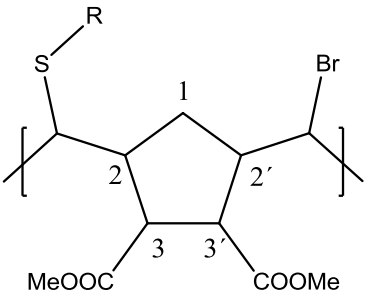
5.5.2. Modification of poly(ME)



Scheme 40: Preparation of poly(ME)mod

To 1,2-dibutyldisulfane (189 µL, 0.98mmol, 1 eq.) in 1mL CH_2Cl_2(abs.) stirred in a 5 mL vial, bromine (55.7 µL, 0.98mmol, 1 eq.) was added slowly at ambient conditions. Progress of the reaction was monitored via NMR. After the in situ formation of butyl hypobromothioite the mixture was added to polymer **2** (207.5 mg, 0.98 mmol 1 eq.) dissolved in 1 mL CH_2Cl_2 (abs.) dropwise. After a reaction time of 2 hrs the polymer was precipitated by addition of the solution into methanol for three times. The organic solvent was removed in vacuo.

Yield: 156 mg (75%) of a white polymer **2***



^{1}H-NMR (δ, 20°C, $CDCl_3$, 300 MHz): 3.57-4.95 (br, 2H, C*H*-Br, C*H*-S-), 3.57-3.89 (bs, 6H, O-CH_3), 1.82-3.57 (br, 6H, $cp^{2,2'}$, $cp^{3,3'}$, bu^1), 1.04-1.82 (br, 6H, bu^2, bu^3, cp^1), 0.77-1.04 (br, 3H, bu^4)

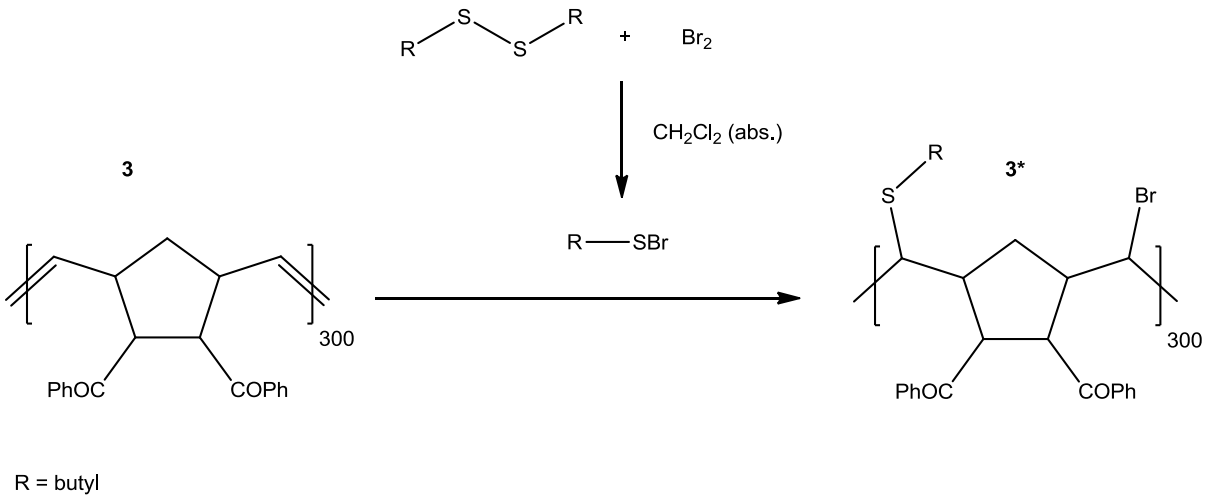
^{13}C-NMR (δ, 20°C, $CDCl_3$, 75 MHz): 174, 177.5 (2C, C=O), 52.8 (2C, O-CH_3), 51-43.2 (5C, cp), 35.1 (1C, bu^1), 31.9 (1C, bu^2), 21.9 (1C, bu^3), 13.9 (1C, bu^4)

FT-IR (cm^{-1}): 2956, 2865 (w), 1777 (m), 1728 (s), 1438 (w), 1369, 1347 (w), 1165 (s), 984 (m), 868 (w), 745 (w)

ELEM. ANAL. : Calcd. for $C_{15}H_{25}BrO_4S$ (molecular weight = 381.33) C, 47.25%; H, 6.61%; S, 8.41% Br, 20.95%; O, 16.78% ; Found: C, 53.61%; H, 6.47%; S, 8.25%

GPC Results: M_n [g/mol]: 83100; M_w [g/mol]: 94500; PDI: 1.14

5.5.3. Modification of poly(PK)



R = butyl

Scheme 41: Preparation of poly(PK)mod

To 1,2-dibutyldisulfane (181.4 µL, 0.94 mmol, 1 eq.) in 1mL CH_2Cl_2(abs.) stirred in a 5 mL vial, bromine (48.5 µL, 0.94 mmol, 1 eq) was added slowly at ambient conditions. Progress of the reaction was monitored via NMR. After the in situ formation of butyl hypobromothioite the mixture was added to polymer **3** (285 mg, 0.94 mmol 1 eq.) dissolved in 1 mL CH_2Cl_2 (abs.) dropwise. After a reaction time of 2 hrs the polymer was precipitated by addition of the solution into methanol for three times. The organic solvent was removed in vacuo.

Yield: 234 mg (82%) of a slightly brown polymer **3***

^{1}H-NMR (δ, 20°C, $CDCl_3$, 300 MHz): 6.32-8.44 (br, 10H, ph^{4-7}), 3.58-5.64 (br, 3H, $cp^{3,3'}$, -C*H*-Br), 1.15-3.58 (br, 11H, $cp^{1,1'}$, $cp^{2,2'}$, bu^{1}, bu^{2}, bu^{3}) , 0.1-1.15 (br, 3H, bu^{4})

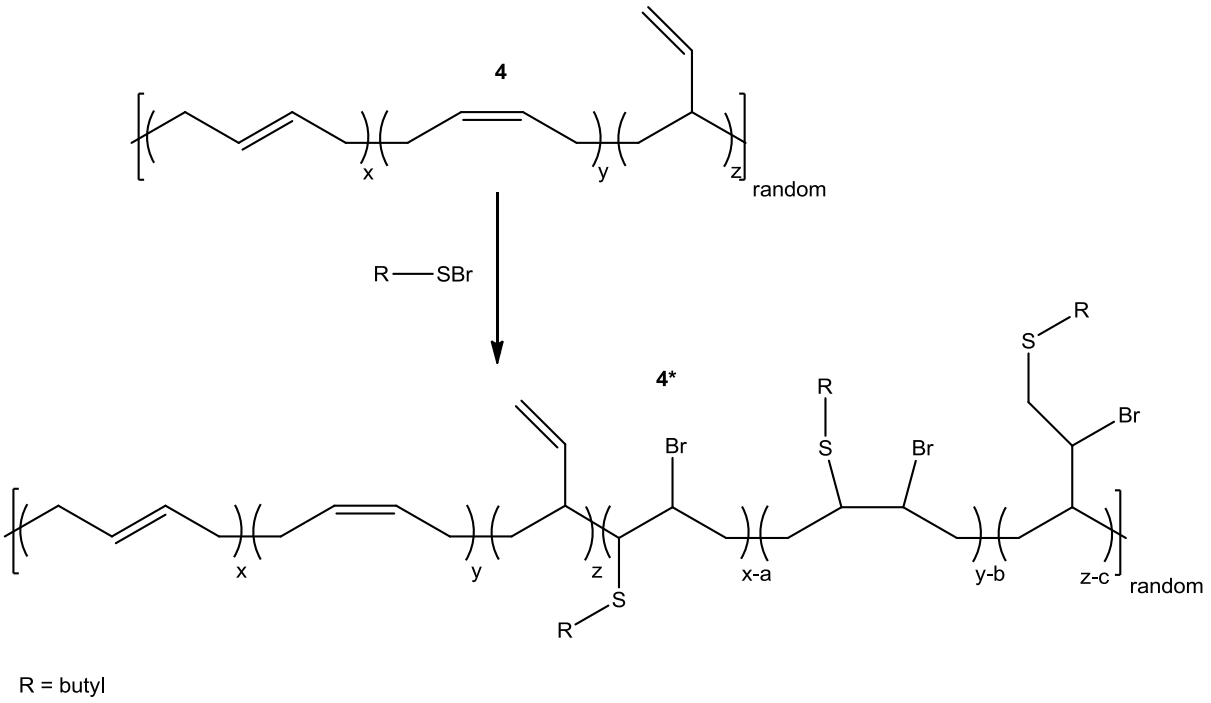
^{13}C-NMR (δ, 20°C, $CDCl_3$, 75 MHz): 202 (2C, C=O), 137.5 (2C, ph^{1}), 133.3 (2C, ph^{4}), 128.3 (8C, $ph^{2,2',3,3'}$), 44.7- 57 (5C, cp), 32.1-32.5 (2C, $bu^{1,2}$), 22.2 (1C, bu^{3}), 13.9 (1C, bu^{4})

FT-IR (cm^{-1}): 3058-2860 (w), 1673 (s), 1596 (m), 1578 (m), 1447 (m), 1375 (w), 1338 (w), 1221 (s), 1181 (m), 1004 (s), 927 (w), 848 (w), 759 (w), 689 (s)

ELEM. ANAL. : Calcd. for $C_{25}H_{29}BrO_2S$ (molecular weight = 473.47) C, 63.42%; H, 6.17%; S, 6.77% Br, 16.88%; O, 6.76% ; Found: C, 67.31%; H, 5.23%; S, 3.51%

GPC Results: M_n [g/mol]: 87900; M_w [g/mol]: 118050; PDI: 1.3

5.5.4. Modification of polybutadien



Scheme 42: Preparation of PBDmod

To 1,2-dibutyldisulfane (1.043 mL, 5.4 mmol, 1 eq.) in 2 mL CH_2Cl_2(abs.) stirred in a 5 mL vial, bromine (278.8 µL, 5.4mmol, 1 eq.) was added slowly at ambient conditions. Progress of the reaction was monitored via NMR. After the in situ formation of butyl hypobromothioite the mixture was added to polymer **4** (293 mg, 5.4 mmol 1 eq.) dissolved in 35 mL CH_2Cl_2(abs.)

dropwise. After a reaction time of 24 hrs the polymer was precipitated by addition of the solution into methanol for three times. A further purification was done via extraction in methanol for 24 hrs, and again precipitation in methanol. The organic solvent was removed in vacuo.

Yield: 150 mg (62%) of a slightly yellow polymer **4***

^{1}H-NMR (δ, 20°C, $CDCl_3$, 300 MHz): 5.38 (br, 2H, -C*H*=C*H*- $^{1,4\text{-PBD}}$), 4.2 (br, 1H, -C*H*-Br), 2.90 (br, 1H, -C*H*-S-), 2.50 (t, 2H, bu^{1}), 1.25-1.67 (br, 8H, bu^{2} , bu^{3} , Br-CH-C*H*$_2$-, -S-CH-C*H*$_2$), 2.10 (4H, CH_2 $^{1,4\text{-PBD}}$) 0.91 (t, 3H, bu^{4})

^{13}C-NMR (δ, 20°C, $CDCl_3$, 75 MHz): 142.7 (1C, -*C*H=CH $^{1,2\text{-PBD}}$), 131.1, (2C, -*C*H=*C*H- $^{1,4\text{-PBD}}$), 130.6, 130.2, 129.7, 129.6, 129.4, 129.1, 128.4, 128.2, (2C, -*C*H=*C*H- $^{1,4\text{-PBD}}$), 114.6, (1C, -CH=*C*H- $^{1,2\text{-PBD}}$), 60.9 (1C, *C*H-S-), 52.8 (1C, -*C*H-Br), 43.9 (1C, -*C*H-CH=CH_2 $^{1,2\text{-PBD}}$), 34.5 (1C, -CH=CH$^{(1,4\text{-PBD})}$ -CH_2-*C*H$_2^{(1,2\text{-PBD})}$), 32.9 (1C, C$^{(1,4\text{-PBD})}$-*C*$^{(1,2\text{-PBD})}$, 33.2, 32.3, 32.2, 30.8 (1C, bu^{1}) or (1C, bu^{2}) or C$^{(1,4\text{-PBD})}$ -C$^{(1,2\text{-PBD})}$ or C$^{(1,4\text{-PBDmod})}$ -C$^{(1,4\text{-PBD})}$ or C$^{(1,4\text{-PBDmod})}$ -C$^{(1,2\text{-PBD})}$, 27.6 (2C, HC=C-*C*H$_2$-*C*H$_2$-CH=CH $^{(1,4\text{-PBD})}$), 25.9, 25.4, 25.1 (1C, -CH=CH$^{(1,4\text{-PBD})}$ –*C*H$_2^{(1,2\text{-PBD})}$-), 22.1 (1C, bu^{3}), 13.8 (1C, bu^{4})

FT-IR (cm^{-1}): 3006 (s, $\nu_{cis\ C=C}$), 2926 (s, ν_{CH2}), 2848 (s, $\nu_{trans\ C=C}$), 1653 (w), 1447 (s), 1304 (w), 995 (m, $\nu_{1,2\text{-PBD}\ C=C}$), 965 (m, $\nu_{trans\ C=C}$), 910 (m, $\nu_{1,2\text{-PBD}\ C=C}$), 871 (m), 733 (s, $\nu_{cis\ C=C}$), 579 (m, $\nu_{C\text{-}Br}$)

ELEM. ANAL. : Calcd. for $C_8H_{15}BrS$ (molecular weight = 223.17) C, 43.05%; H, 6.77%; S,14.37% Br, 35.80%; Found: C, 76.25%; H, 10.59%; S, 4.38%

GPC Results: M_n [g/mol]: 201300; M_w [g/mol]: 660100; PDI: 3.28

6. Appendix

6.1. List of Abbreviations

ADMET	Acyclic Diene Metathesis
bu	butyl
DD	decadiene
DIBU	Dibutyldisulfide
EA	Elemental analysis
eq	Equivalent
FT-IR	Fourier Transform Infra Red
GPC	Gel Permeation Chromatography
M:I	Monomer:Initiator
ME	Methyl Ester
Mn	Number Average Molecular Weight
mod	modified
MW	Molecular Weight
NMR	Nulear Magnetic Resonance
NR	Natura Rubber
PBD	PolyButaDiene
PDI	Poly Dispersity Index
Ph	Phenyl
PK	Phenyl Ketone
ROMP	Ring Opening Metathesis Polymerization
SBR	Styrene Butadiene Rubber
STA	Simultaneous Thermal Analysis
TLC	Thin Layer Chromatography

6.2. List of Figures

6.3. List of Schemes

6.4. List of Tables