Research Article

Renewable co-polymers derived from castor oil and limonene*

Maulidan Firdaus[1], Michael A. R. Meier[1], Ursula Biermann[2] and Jürgen O. Metzger[2,3]

[1] Institute of Organic Chemistry, Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany
[2] Institute of Chemistry, University of Oldenburg, Oldenburg, Germany
[3] abiosus e.V., University of Oldenburg, Oldenburg, Germany

Biobased monomers derived from castor oil as well as from limonene suitable for thiol–ene copolymerization were synthesized. Di-10-undecenylether **2** was obtained via GaBr$_3$-catalyzed reduction of 10-undecenyl 10-undecenoate **1**. Diene ether **2** and (R)-limonene **5** were reacted in two steps using radical thiol–ene addition reactions to dithiol ether **4** and dithiol **7**, respectively. Diene ether **2** and dithiols **4** and **7** were copolymerized using thermal initiation with AIBN and photochemically initiated thiol–ene reaction, respectively. DSC characterization revealed that these monomers can be used to synthesize polyether polysulfides with good and adjustable thermal properties. Moreover, the synthesized polymers **P1** and **P2** have successfully been transformed into polyether polysulfones **P3** and **P4** by oxidation with H$_2$O$_2$. An increase of the melting transition of 40–50°C was observed after oxidation.

Keywords: Methyl 10-undecenoate / Polyether polysulfides / Polyether polysulfones / Renewable / Thiol–ene copolymerization

1 Introduction

Oils and fats of vegetable and animal origin are historically and currently the most important renewable feedstock of the chemical industry [1, 2]. Most of the native oils contain unsaturated fatty acids, such as oleic acid, which is a *cis*-configured alkene and thus allows, in principle, the application of the well-known reactions of petrochemical alkenes. Castor oil contains up to 90% of ricinoleic acid containing in addition to the C-9 double bond a hydroxyl group at C-12. This enables very interesting applications as renewable feedstock for the chemical industry [3]. The most important oleochemical reaction performed with ricinoleic acid is the thermal cleavage to 10-undecenoic acid, which is a platform chemical that can be used to synthesize a large variety of renewable monomers and polymers [3]. Terpenes represent another large and most diverse class of renewables and are a versatile chemical feedstock [4]. Limonene can be obtained as a byproduct of the citrus industry. The world production of the (R)-isomer amounts to over 70 000 tonnes per year [5].

The thiol–ene reaction has recently been applied by the Meier group to oleochemicals for the synthesis of plant oil derived monomers and polymers [6] as well as for the synthesis of terpene-based renewable monomers and polymers, e.g., polyamides and polyurethanes [7, 8]. Most interestingly, polyesters from terpene and castor oil based monomers with number-average molecular weights of up to 25 kDa have been reported [7]. Moreover, renewable polyethylene mimics derived from castor oil containing ether and sulfide groups in the linear polymer chain have been described [9]. We have been interested to use oleochemical as well as terpene based thiols and long chain oleochemical diene ethers for the synthesis of new renewable polymers containing alternating ether and sulfide functionalities via the thiol–ene reaction. Additionally, we thought to oxidize the sulfide functionality to obtain polymers with alternating ether and sulfone groups in the polymer chain.

2 Materials and methods

2.1 Materials

Methyl 10-undecenoate, 10-undecenol, tetramethyldisiloxane (TMDS), GaBr$_3$ (all Aldrich), (R)-(+)-limonene **5** (Sigma,

Correspondence: Prof. Michael A. R. Meier, Karlsruhe Institute of Technology (KIT), Institute of Organic Chemistry, Fritz-Haber-Weg 6, 76131 Karlsruhe, Germany
E-mail: m.a.r.meier@kit.edu
Web: www.meier-michael.com
Fax: +49-(0)721-60846801

97%), 2,2-dimethoxy-2-phenylacetophenone (DMPA, Aldrich, 99%), Na$_2$SO$_4$ anhydrous (Acros Organics, 99%), 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD, Aldrich, 98%), silica gel 60 (0.035–0.070 mm, Aldrich), thioacetic acid (Aldrich, 96%), and hydrogen peroxide solution (Sigma, 35 wt%), were used as received. 2,2′-Azobis(2-methylpropionitrile) (AIBN, Aldrich, 98%) was recrystallized from methanol. All solvents (technical grade) were used without further purification.

2.2 General methods and instrumentation

Thin layer chromatography (TLC) was performed on silica gel TLC-cards (layer thickness 0.20 mm, Fluka). Permanganate reagent was used as developing solution. ^{1}H NMR and ^{13}C NMR spectra were recorded in CDCl$_3$ on Bruker AVANCE DPX spectrometers operating at 300 or 600 MHz. Chemical shifts (δ) are reported in parts per million relative to the internal standard tetramethylsilane (TMS, $\delta = 0.00$ ppm). Fast-Atom-Bombardment (FAB)-mass spectra were measured with a MAT95 of the company *Finnigan*. High resolution mass spectra (HRMS) with electron impact ionization (EI) were recorded on a GC-TOF. Gel permeation chromatography (GPC) system LC-20 A from Shimadzu equipped with a SIL-20A auto sampler, PLgel 5 mm MIXED-D column (Polymer Laboratories, 300 mm × 7.5 mm, 100, 1000, and 10 000 Å) and a RID-10A refractive index detector in THF (flow rate 1 mL/min) at 50°C. All determinations of molar mass were performed relative to PMMA standards (Polymer Standards Service, M_p 1100–981 000 Da). Infrared spectroscopy (IR) was recorded on a FT-IR Bruker alpha. Differential scanning calorimetry (DSC) experiments were carried out with a DSC821e (Mettler Toledo) calorimeter, under nitrogen atmosphere, at a heating rate of 10°C/min up to a temperature of 250°C, and using a sample mass in the range 4–6 mg. The glass transition temperature, T_g, is reported as the midpoint of the heat capacity change. The melting temperature, T_m, is recorded as the minimum (endothermic transitions are represented downwards) of the endothermic melting peak.

2.3 Synthesis of the monomers

2.3.1 10-Undecenyl 10-undecenoate 1

10-Undecenyl 10-undecenoate **1** was synthesized by transesterification of methyl 10-undecenoate (20 g, 0.1 mol) and 10-undecenol (17.16 g, 0.11 mol) catalyzed by sodium methoxide (1 mmol) at 60°C for 4 h. After work-up as usual "Kugelrohr" distillation (130°C, 3×10^{-3} mbar) yielded 28.3 g (79%) product **1** which was identified by ^{1}H and ^{13}C NMR spectroscopy [10].

2.3.2 Di-10-undecenyl ether 2

A mixture of 10-undecenyl 10-undecenoate **1** (0.674 g, 2.0 mmol) and GaBr$_3$ (8.2 mg, 0.0265 mmol, 1.32%) was

degassed in a 2-necked round bottom flask and then flushed with nitrogen (2 freeze–thaw cycles). After dropwise addition of TMDS (0.39 mL, 2.2 mmol) an exothermic reaction started. The sample was cooled for 10 min. in a water bath and was then stirred at room temperature. The reaction was followed by gas chromatography or TLC. After 2 h, the ester was completely transformed. Ether **2** was separated by "Kugelrohr" distillation (135°C, 2×10^{-3} mbar) yielding 0.51 g (70%) and was identified by ^{1}H and ^{13}C NMR spectroscopy [9, 11].

2.3.3 Synthesis of di(11-thiol undecyl)ether 4

The synthesis of dithiol **4** was performed in a carousel reaction station™ RR98072 (Radleys Discovery Technologies, UK). A mixture of diene **2** (1.00 g, 3.1 mmol) and thioacetic acid (2.50 equiv.) was added to the carousel tube and stirred magnetically at room temperature. Samples were taken periodically for conversion analysis using ^{1}H NMR. After 1 h, the reaction to give **3** was complete, and the excess of thioacetic acid was removed under reduced pressure. **3** was then used for the next reaction step without further purification.

Dithioacetic ester **3** (1.5 g, 3 mmol), methanol (20.0 equiv.), and TBD catalyst (0.10 equiv.) were added to the carousel tube. The reaction mixture was then refluxed under argon atmosphere and the reaction progress was monitored via ^{1}H NMR. After 3 h the reaction was complete. The formed methyl acetate and the excess of methanol were removed under reduced pressure. Product **4** was recrystallized from methanol and was obtained as a white solid. Yield 1.1 g (93%).

^{1}H NMR (300 MHz, CDCl$_3$, δ in ppm): δ 3.38 (t, $J = 6.7$ Hz, 4H, –OCH$_2$–CH$_2$–), 2.52 (dd, $J = 14.7$, 7.5 Hz, 4H, –CH$_2$–CH$_2$SH), 1.67–1.48 (m, 8H, –OCH$_2$–CH$_2$–, –CH$_2$–CH$_2$SH), 1.43–1.16 (m, aliphatic, –SH, 30H).

^{13}C NMR (75 MHz, CDCl$_3$, δ in ppm): δ 71.07 (–OCH$_2$–), 34.17–26.31 (aliphatic), 24.78 (–CH$_2$SH).

FAB-MS of C$_{22}$H$_{46}$OS$_2$ (M+H$^+$ = 391.3).

HRMS (FAB) of C$_{22}$H$_{46}$OS$_2$ [M+H$^+$] calc. 391.3063, found 391.3064.

2.3.4 5-((R)-1′-Mercaptopropan-2′-yl)-2-methylcyclohexanethiol 7

(R)-Limonene (1 g, 7.3 mmol) was reacted with thioacetic acid (2.50 equiv.) for 16 h to give dithioacetic ester **6** as described for dithiol **4**. Dithioacetic ester **6** (1.5 g, 5.2 mmol) was transesterified with methanol catalyzed by TBD in 16 h of reaction time as described above. Purification of product **7** was carried out using column chromatography on silica gel (hexane–ethyl acetate 19:1) to yield 1 g (90%) of **7** as colorless liquid. **7** was identified by FAB-MS, ^{1}H (Fig. 1) and ^{13}C NMR spectroscopy [12].
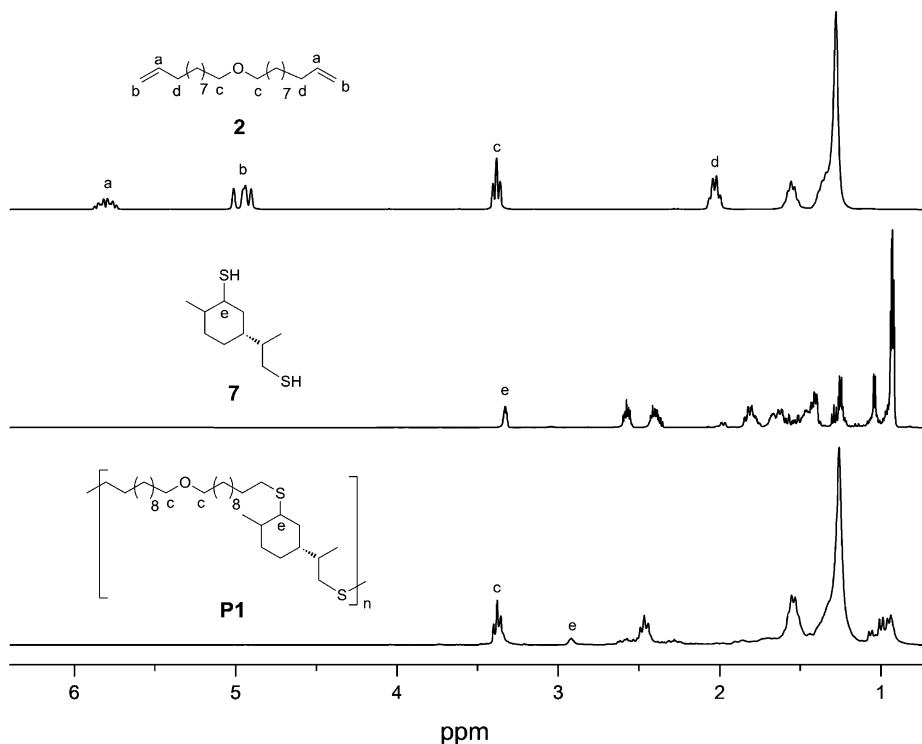
Figure 1. ^{1}H NMR spectra of **2** (top), **7** (middle), and **P1** (bottom).

2.4 Synthesis of polymers

2.4.1 Photo initiated copolymerization of diene ether 2 and dithiol 7

A mixture of diene ether **2** (0.200 g, 0.62 mmol), dithiol **7** (0.127 g, 0.62 mmol), and DMPA (7.94 mg, 0.031 mmol) was added into a reaction vessel. The mixture was stirred and exposed to a hand-held UV-lamp (2×4 W, $\lambda = 365$ nm) until the sample became very viscous and could not be stirred. Polymer **P1** was purified by precipitation from a concentrated THF solution of the reaction products into cold methanol. Yield (0.255 g, 78%).

2.4.2 Thermally initiated copolymerization of diene ether 2 and dithiol 4

The polymerization reactions were performed in a carousel reaction station™ RR98072 (Radleys Discovery Technologies, UK). Diene ether **2** (0.200 g, 0.62 mmol), dithiol **4** (0.242 g, 0.62 mmol), and AIBN (2.5 mg, 0,015 mmol) were introduced into a carousel tube and degassed via three times 200 mbar vacuum and subsequent purging with Argon. The reaction mixture was stirred magnetically at 80°C until the sample solidified. The resulting polymer was crushed into fine powder and stirred in THF for 16 h. The product was then filtered, washed three times with THF, and subsequently dried to obtain the polymer **P2**. Yield (0.367 g, 83%).

2.4.3 General procedure for oxidation to polysulfone

Polysulfide **P1** and **P2** (0.15 g) was dissolved and suspended, respectively, in THF (3.00 mL). Subsequently 35% hydrogen peroxide solution (5.00 equiv. to sulfur atom) was added to the reaction flask. The reaction mixture was stirred at 65°C for 24 h. The formed polymers **P3** and **P4**, respectively, were purified by precipitation in a methanol–water (70:30) mixture.

### 2.4.4 Characterization of the polymers by NMR and GPC

P1 could be dissolved in CDCl$_3$ for NMR and in THF for GPC. **P2**–**4** were not soluble at room temperature in most common NMR solvents such as CDCl$_3$, DMSO-d_6, methanol-d_4, THF-d_8, acetone-d_6, and not in THF or 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) for GPC.

3 Results and discussion

3.1 Syntheses of monomers

We started our investigation by synthesizing diene ether **2** from ester **1** and dithiol monomers **4** and **7** from diene ether **2** and limonene **5**, respectively (Scheme 1).

The synthesis of diene ether **2** has been described in the literature using Williamson ether synthesis [9] and a modified
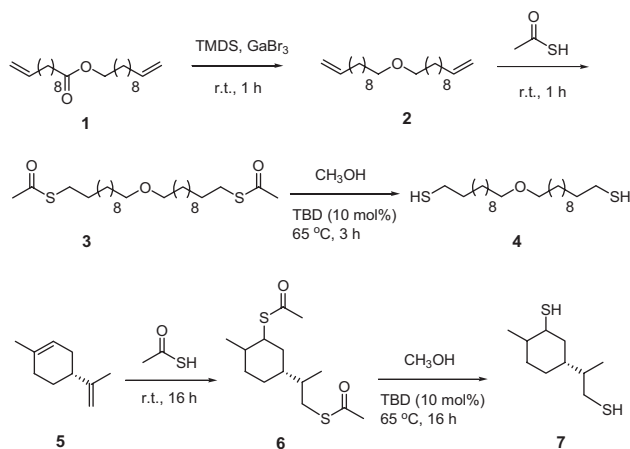
Scheme 1. Synthesis of dithiols **4** and **7**.

Williamson procedure [11]. These protocols exhibit long reaction times and are not at all sustainable due to the use of halogenated compounds and/or the production of large amount of waste. We applied a new procedure developed for the reduction of esters to ethers using tetramethyldisiloxane (TMDS) as reducing agent and GaBr$_3$ as catalyst without any solvent added [13]. Ester **1** was reacted with 1.1 equiv. of TMDS and 0.01 equiv. of GaBr$_3$ and was completely converted after 2 h of reaction time. Diene ether **2** was easily isolated by simple distillation of the reaction solution in 70% yield.

The addition of thioacetic acid to diene ether **2** was performed at room temperature under solvent-free conditions without any initiator. A white solid of dithioester **3** was formed after 1 h reaction time indicating the completion of the reaction, which was also confirmed by ^{1}H NMR spectroscopy. The resulting dithioester **3** was then transesterified with methanol and TBD as catalyst to obtain

dithiol **4** after 3 h reaction time. The transesterification was performed under argon atmosphere to avoid the formation of disulfides. The product was purified by recrystallization from methanol to afford dithiol **4** as a white solid in 93% yield.

Dithiol **7** is a commercially available product. Interestingly, Yan et al. [14] used it quite recently for the synthesis of thiourethane thermoset coatings. The synthesis of **7** from **5** was already reported by Marvel and Olson [15]. We prepared **7** using the slightly modified protocol of Marvel and Olson by thiol–ene addition of thioacetic acid to **5** followed by TBD catalyzed transesterification of the resulting thioester **6**. Initially, basic hydrolysis of **6** using a sodium hydroxide solution or acid catalyzed saponification was performed in order to cleave the dithioester as reported by Marvel and Olson [15]. However, these procedures required long reaction times of 48 h and thus further attempts were carried out in order to find a suitable method to significantly decrease the reaction time. As an alternative, cyclic guanidine base catalyst 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) in methanol was examined. Thus, complete conversion was reached after 16 h. The excess of methanol and the formed methyl acetate could be easily removed under reduced pressure. After purification by column chromatography **7** was obtained as a colorless liquid in high yield (90%).

The complete transformation of the dienes to dithiols was evidenced by ^{1}H NMR analyses. No double bond signals could be found and a new signal at 2.52 ppm (H^c) corresponding to a methyne proton next to the SH group appeared (Fig. 1). Both dithiols **4** and **7** are renewable and suitable substrates for thiol–ene polymerization with an appropriate diene.

3.2 Polymerization

Having different monomers in hand, we started to study their behavior in thiol–ene co-polymerizations (Scheme 2).
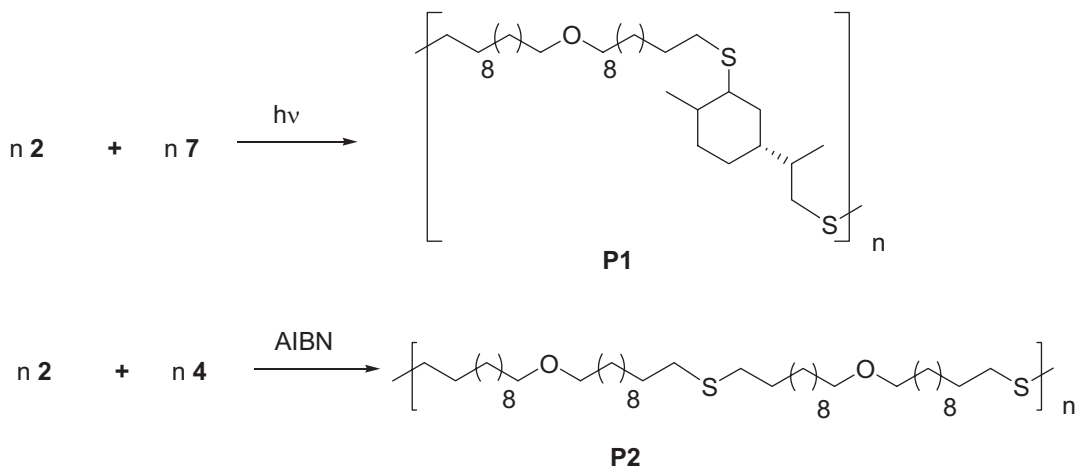
Scheme 2. Thiol–ene copolymerization of diene ether **2** and dithiols **7** and **4**, respectively, to give polymers **P1** and **P2**.

Table 1. Analytical data of the synthesized polymers

Polymer	Monomer	M_n (kDa)[a]	PDI[a]	T_m (°C)[b]	T_g (°C)[b]
P1	2 and 7	31.8	2.20	24.1	–
P2	2 and 4	–[c]	–[c]	84.7	–
P3	–	–[c]	–[c]	65.2	–
P4	–	–[c]	–[c]	130.8	–

[a]GPC data and polydispersity index (PDI) of precipitated polymers.
[b]DSC data second heating scan recorded at 10°C/min.
[c]Insoluble in THF and HFIP.

Initially, diene ether **2** was polymerized in bulk with dithiol **7** employing DMPA (5 mol%) as radical photoinitiator under UV irradiation. The polymerization was completed after 4 h and GPC analysis of the resulting polymer showed high molecular weight ($M_n = 31.8$ kDa) of **P1** (Table 1). ^{1}H NMR analysis verified the expected structure of the polymer. As an example, ^{1}H NMR spectra of **2**, **7**, and **P1** (Fig. 1), showed almost complete disappearance of the double bond signals at 5.80 and 4.95 ppm (H[a] and H[b]).

In the case of the thiol–ene polymerization of **2** and **4** solubility problems did not allow us to perform a photo-polymerization under the established condition. Thus, thermal polymerization using AIBN (2.5 mol%) was performed under the same condition as previously reported [16] to give polymer **P2**. Unfortunately, the resulting product is insoluble in common GPC or NMR solvents and molecular weight determination was thus not possible.

The synthesized polyether polysulfides **P1** and **P2** were modified into polyether polysulfones by oxidation with hydrogen peroxide [17]. The oxidations were performed using 35% hydrogen peroxide solution (5 equiv. to sulfur atom) in THF at 65°C for 24 h. Unfortunately, the synthesized polyether polysulfones **P3** and **P4** are not soluble in THF and it was not possible to determine their molecular weights by GPC. FT-IR analyses of the synthesized polymers revealed the successful oxidations. As a representative example (Fig. 2), the FT-IR spectra of polyether polysulfide **P1** and thereof derived oxidized polymer **P3**, showed the appearance of two strong and sharp characteristic absorption peaks for sulfones at 1285 and 1102 cm^{-1}. It is worth to mention that all of the synthesized monomers are renewable. Therefore, also the polyether polysulfides **P1** and **P2** and their oxidized products **P3** and **P4** are 100% renewable.

3.3 Thermal characterizations

To study the thermal properties of the synthesized polymers **P1–P4**, DSC analysis was performed. Table 1 summarizes the thermal properties of the prepared polymers and Fig. 3 shows DSC thermograms of the polymers. Based on the DSC
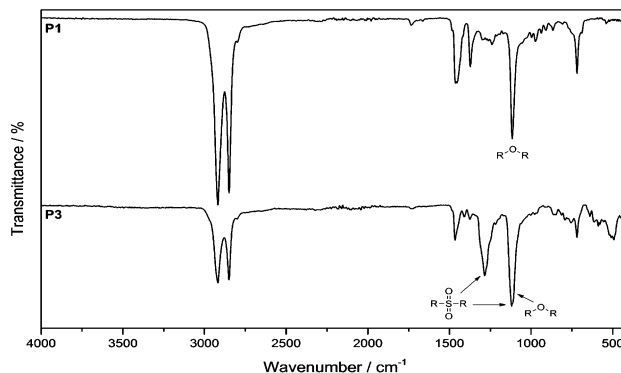
Figure 2. FT-IR spectra of **P1** (top) and **P3** (bottom).
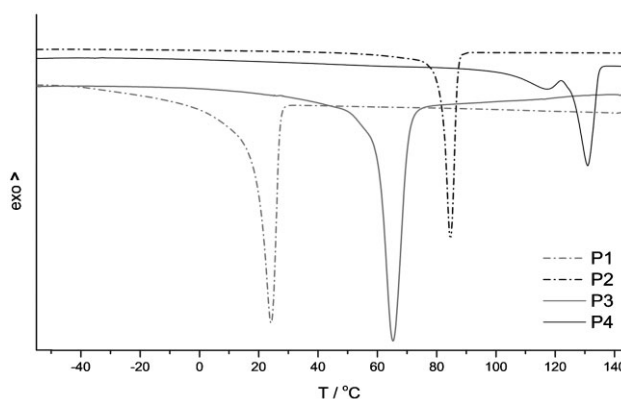
Figure 3. DSC traces of the synthesized polymers **P1–P4**.

result, **P1** ($T_m = 24.1$°C) exhibits a melting transition lower than **P2** ($T_m = 84.7$°C). **P1** contains a diastereomeric mixture of bulky cycloaliphatic units linked with long chain flexible aliphatic segments. The aliphatic chains are able to crystallize, but the cycloaliphatic units prevent this crystallization to a certain extent resulting in a lower melting transition for **P1** compared to **P2**. Interestingly, enormous changes in thermal properties are observed if the polysulfides are oxidized into polysulfones [17]. For example, an increase of 40 K in melting transition was observed going from **P1** to **P3**. An even more pronounced increase of about 50 K was observed for the oxidation of **P2** to **P4**, making **P4** an interesting plant oil derived material with high melting point. A reason for the observed increases might be the polarity of the introduced sulfone moieties that introduce intermolecular dipole–dipole interactions to the polymer chains. Remarkably, the polysulfide obtained by thiol–ene polymerization of 10-undecenylthiol exhibits a similar melting transition of about 85°C compared to polyetherpolysulfide **P2**, whereas the respective polysulfone having the double number of sulfone groups shows a significantly higher melting transition of >150°C [17] than our polyetherpolysulfone **P4**.

4 Conclusions

Long chain ω,ω'-diene ether **2** was synthesized by catalytic reduction of 10-undecenyl 10-undecenoate **1,** derived from renewable castor oil, has been shown to be a suitable substrate for the synthesis of dithiol ether **4**. via thiol–ene reaction and for the thiol–ene copolymerization with **4** as well as with dithiol **7** derived from renewable limonene to give high molecular polyether polysulfides. The polyether polysulfides could easily be oxidized to polyether polysulfones having increased melting transitions of about 50 K. ω,ω'-Unsaturated fatty acid esters of various chain length can be readily synthesized from plant oils. Thus, thiol–ene reaction opens the window for the synthesis of a great variety of polyether polysulfides and polyether polysulfones being interesting mimics of polyethylene.

References

[1] Biermann, U., Friedt, W., Lang, S., Lühs, W. et al., New syntheses with oils and fats as renewable feedstock for the chemical industry. *Angew. Chem. Int. Ed.* 2000, *39*, 2206–2224.

[2] Biermann, U., Bornscheuer, U., Meier, M. A. R., Metzger, J. O., Schäfer, H. J., New developments for the chemical utilization of oils and fats as renewable raw materials. *Angew. Chem. Int. Ed.* 2011, *50*, 3854–3871.

[3] Mutlu, H., Meier, M. A. R., Castor oil as a renewable resource for the chemical industry. *Eur. J. Lipid Sci. Technol.* 2010, *112*, 10–30.

[4] Schwab, W., Fuchs, C., Huang, F.-C., Transformation of terpenes into fine chemicals. *Eur. J. Lipid Sci. Technol.* 2013, *115*, 3–8.

[5] Kerton, F. M., in: Clark, J. H., Kraus, G. A. (Eds.), *Alternative Solvents for Green Chemistry*, RSC Green Chemistry, Cambridge, UK 2009, p. 109.

[6] Türünc, O., Meier, M. A. R., The thiol–ene (click) reaction for the synthesis of plant oil derived polymers. *Eur. J. Lipid Sci. Technol.* 2013, *115*, 41–454.

[7] Firdaus, M., Montero de Espinosa, L., Meier, M. A. R., Terpene-based renewable monomers and polymers via thiol-ene additions. *Macromolecules* 2011, *44*, 7253–7262.

[8] Firdaus, M., Meier, M. A. R., Renewable polyamides and polyurethanes derived from limonene. *Green Chem.* 2013, *15*, 370.

[9] Rybak, A., Meier, M. A. R., Acyclic diene metathesis with a monomer from renewable resources: Control of molecular weight and one-step preparation of block copolymers. *ChemSusChem* 2008, *1*, 542–547.

[10] Türünc, O., Montero de Espinosa, L., Meier, M. A. R., Renewable polyethylene mimics derived from castor oil. *Macromol. Rapid Commun.* 2011, *32*, 1357–1361.

[11] Dutta, S., Perring, M., Arafat, S., Barrett, S. et al., Cross metathesis on olefin-terminated monolayers on Si(111) using the Grubbs' catalyst. *Langmuir* 2006, *22*, 2146–2155.

[12] Firdaus, M., Terpenes as renewable resources for organic and macromolecular chemistry, Ph.D. thesis, KIT Karlsruhe, 2013, p. 166.

[13] Metzger, J. O., Biermann, U., Knott, W., Henning, F., Amajjahe, S., Verfahren zur Reduktion von Carbonsäureestern oder –lactonen zu den entsprechenden Ethern, PCT Int. Appl. 2013, WO 2013010747 A1 20130124.

[14] Yan, J., Ariyasivam, S., Weerasinghe, D., He, J. et al., Thiourethane thermoset coatings from bio-based thiols. *Polym. Int.* 2012, *61*, 602–608.

[15] Marvel, C. S., Olson, L. E., Polyalkylene sulfides. XIII. Polymers from 4-vinyl-1-cyclohexene and *d*-limonene. *J. Polym. Sci.* 1957, *26*, 23–28.

[16] Firdaus, M., Meier, M. A. R., Renewable co-polymers derived from vanillin and fatty acid derivatives. *Eur. Polym. J.* 1920, *49*, 156–166.

[17] van den Berg, O., Dispinar, T., Hommez, B., Du Prez, F. E., Renewable sulfur-containing thermoplastics *via* AB-type thiol-ene polyaddition. *Eur. Polym. J.* 2013, *49*, 804–812.

[18] Griesbaum, K., Problems and possibilities of the free-radical addition of thiols to unsaturated compounds. *Angew. Chem. Int. Ed.* 1970, *9*, 273–287.