Renewable sulfur-containing thermoplastics via AB-type thiol-ene polyaddition

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Abstract

Polythioethers with molar masses up to 40 kDa were prepared by UV- or thermal initiated thiol-ene polyaddition polymerization of an aliphatic α-olefinic ω-thiol, an AB-type monomer derived from 10-undecenoic acid, which is a bio-sourced building block obtained from castor oil. The low polarity of the starting compound and the stability of the thioether functions formed during polymerization allowed for the synthesis of polymers with similar structures to existing bulk and engineering plastics such as polyethylene. The presence of the thioether functions offered the opportunity to oxidize these polyethylene analogues by hydrogen peroxide into sulfone linkages, resulting in polysulfones, which are valuable as engineering plastic in several application fields. Thermal analysis demonstrated the increased thermal stability and melting temperature (175°C) of these polysulfones.

Keywords: thiol-ene, polythioether, polysulfone, 10-undecenoic acid, castor oil.

1. Introduction

In the past decade the interest in environmental friendly, CO_2-neutral replacements of petroleum-based chemical products by renewable natural analogues has grown tremendously. Especially plant oils and fatty acids derived from these oils have received attention as useful raw materials to be used as a renewable feedstock for the chemical industry. Traditional uses of plant oils include, among others, the use as raw materials for the production of detergents, coatings, lubricants, and plasticizers [1-4].

Until now the multifunctionality of plant oil fatty acids and their glycerol esters have been mainly exploited for the preparation of multifunctional monomers. This multifunctionality is quite useful to form cross-linked coatings and resins. Although some bio-derived cross-linked materials are intrinsically biodegradable, a bio-derived thermoplastic can have many advantages over its cross-linked counterpart with regard to reusability or recyclability. Different approaches have been followed to obtain linear plant oil-derived polymers. One of the first commercially available examples of such a polymer was Nylon 11, which was commercialized as Rilsan® in the early 1950's. Nylon 11 is a polyamide derived from 11-aminoundecanoic acid, which can be prepared from castor oil, and finds applications as material for electrical cables, in automotive applications, and for pneumatic and hydraulic hoses [5]. Castor oil is also used as an important source of sebacic acid (decanedioic acid), a building block for polyesters, alkyd resins and polyamides (e.g. Nylon 6,10). A similar diacid, azaleic acid (nonanedioic acid), is prepared on large scale (Cognis) by ozonolysis of oleic acid and is used as a building block for polyesters, alkyd resins and polyamides (e.g. Nylon 6,9). An excellent review on this topic was published by Mutlu *et al.*[6].

Thiol-ene addition reactions on plant oils and unsaturated fatty acids have been often reported. For example, Bantchev *et al.* reported the use of alkylthiols to modify different plant oils in order to lower their cloud point [7]. Bromberg *et al.* used thiol-ene chemistry on oleic acid to prepare ligands for silver and cobalt nanoparticles [8]. Moreover, a castor oil derivative, 10-undecenoic acid, was widely used to prepare bio-based building blocks via thiol-ene reactions. [9-12]More recently, Türünç and co-workers reported the use of functional monothiols and dithiols for the functionalization of castor oil-derived 10-undecenoic acid [13]. It was proposed to use the synthesized materials as building blocks in the synthesis of novel polymeric structures. In another publication from the same research group, polycondensation monomers (esters and alcohols) were synthesized from terpenes using thiol-ene chemistry [14]. Such materials could find interesting new applications as alternatives for petroleum-based polymers. The large number of other publications on thiol-ene chemistry, not involving fatty acids or plant oils, mainly involve modification and functionalization of existing (polymer) structures and the design of new molecular architectures. In patent literature, thiol-ene polymerization of multifunctional thiols with multifunctional enes and ynes is described for the preparation of materials with different types of functionality. For example, Bowman *et al.* describe the polymerization of several multifunctional unsaturated urethanes, allylethers, acrylates and methacrylates with thiols, yielding cross linked end products exhibiting shape memory properties [15], which are claimed for medical applications. In other examples, similar thiol-ene chemistry is described for dental application [16-18], the preparation of low gas permeability membranes [19], sealants [20], stamps for lithography [21], degradable polymeric structures for biomedical application [22], liquid crystalline compositions for optical applications [23], and polymer electrolytes for e.g. batteries [24]. All these examples have cross linking as part of the process and none of these papers mention the preparation of a thermoplastic material. However, recently Türünç *et al.*

reported the condensation of bifunctional thiols with bifunctional enes to prepare polyethylene mimicking polymers [25]. The molar masses of the reported AA/BB-type polymers were relatively limited.

In this paper, a method will be described to prepare thermoplastic polymeric materials by thiol-ene based polyaddition polymerization of a completely bio-sourced monomer, containing both the thiol and ene functionality in one single molecule. The concept of using an α-olefinic ω-thiol as a monomer has the advantage, like any other A-B monomer used in polymer synthesis, of having intrinsic stoichiometry. This is in contrast to the polymerization of two bifunctional monomers where absolute precision of the reactant's molar ratios is required, in order to obtain polymers of sufficient molecular weight.

The chemical structure of the resulting polymer, including thioether-linkages formed during polymerization, allows for the synthesis of a wide spectrum of polymers with structures that are similar to existing bulk and engineering plastics. For example, high density polyethylene (HDPE) analogues can be prepared by polyaddition polymerization of a linear, fully aliphatic α-olefinic ω-thiol. Moreover, post polymerization oxidation is finally used to convert the thioether-linkages into sulfoxide and sulfone linkages, materials that could be valuable as surface modifiers for coatings, films and bulk plastics in order to improve paintability, adhesion or pigment wetting.

2. Experimental Section

2. 1. Materials

10-Undecenoic acid, lithium aluminum hydride (95 % pellets), thioacetic acid (96 %), propylamine (98 %), 2,2-dimethoxy-2-phenylacetophenone (DMPA) (99 %) are purchased from Sigma-Aldrich. 1,1'-Azobis(cyclohexane-1-carbonitrile) (V-40) was obtained from Wako Chemicals. Methanesulfonyl chloride (95.5 %), potassium tert-butoxide (98 %) and hydrogen

peroxide solution (35 w %) were purchased from Acros Organics. The other solvents were all HPLC grade and obtained from Aldrich.

2. 2. Instrumentation

Nuclear magnetic resonance spectra were recorded on a Bruker Avance 300, a Bruker DRX 500 or a Bruker Avance II 700 spectrometer at room temperature. *Size-exclusion chromatography* was performed on a Waters instrument fitted with a Styragel HR column (IR+UV detection) using chloroform as eluent with a flow rate fixed at 1 mL min^{-1} (with polystyrene standards). *Preparative size-exclusion chromatography* was performed on a Shimadzu instrument consisting of a Shimadzu LC-2OAT pump, a Shimadzu SIL-IOAF autosampler, a RID-IOA Differential Refractive Index Detector, a FRC-1OA Fraction Collector and a CBM-2OA PC Interface/System Controller. The system was fitted with a Shodex KF-2004 preparative column using chloroform as eluent, with a flow rate fixed at 2.5 mL min^{-1}. *Raman spectra* were collected using a Bruker FRA 106 FT-Raman spectrometer. IR spectra were collected using a Perkin-Elmer Spectrum1000 FTIR infrared spectrometer with a diamond ATR probe. *Thermogravimetric analyses* were performed with a Mettler Toledo TGA/SDTA851e instrument under air atmosphere at a heating rate of 5°C min^{-1} from 25°C to 800°C. *Differential scanning calorimetry (DSC) analyses* were performed with a DSC Perkin Elmer 7 under air atmosphere at a heating rate of 2°C min^{-1}. *Tensile testing* was performed on a Tinus-Olsen H10KT tensile tester equipped with a 100 N load cell, using flat dog bone type specimen with an effective gage length of 13 mm, a width of 2 mm, and a thickness of 1 mm. The tensile tests were run at a speed of 1 mm/min. Test specimens were prepared by compression molding of thin sheets at 200°C. After cooling, samples were cut from sheets using a Ray-Ran dog bone cutter.

2. 3. Transformation of biosourced 10-undecenoic acid into a multifunctional biobased monomer (**4**)

2. 3. 1. Synthesis of undec-10-en-1-ol (**1**)

10-Undecenoic acid (100 g, 0.54 mol) was dissolved in dry THF (1250 mL) under nitrogen in an oven-dried round bottom flask and the solution was cooled to 0°C in an ice-bath. Lithium aluminum hydride (31 g, 0.81 mol) was then added in small quantities under vigorous stirring. Afterwards, the grey suspension was stirred for 5 hours until the completion of the reaction was detected via TLC (100 % $CHCl_3$). The suspension was then transferred into a separatory funnel and added dropwise to vigorously stirred, ice-cold, diluted hydrochloric acid (15 % v:v, 800 ml). The solution was then extracted with diethylether (4×200 mL). The combined organic layer was successively washed with brine (400 mL), a saturated sodium bicarbonate solution (400 mL) and again with brine (400 mL). The organic layer was then dried with anhydrous magnesium sulfate before the solvent was removed on a rotary evaporator. Undec-10-en-1-ol was obtained with 97 % yield as colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) 5.8 (m, 1H, CH_2=C*H*-), 5-4.9 (m, 2H, C*H*$_2$=CH-), 3.64 (t, 2H, -C*H*$_2$-OH), 2.05 (q, 2H, CH_2=CHC*H*$_2$-), 1.56 (p, 2H, -CH_2C*H*$_2$$CH_2$OH), 1.4-1.28 (m, 12H, backbone C*H*$_2$s). ^{13}C NMR (300 MHz, $CDCl_3$, ppm) 139.2 (CH_2=CH-), 114.09 (CH_2=CH-), 63.00 ($CH_2CH_2CH_2O$-), 33.79 (CH_2=CHCH_2-), 32.77 (-$CH_2CH_2CH_2O$-), 29.54 (CH_2=CH$CH_2CH_2CH_2CH_2CH_2$-), 29.40 (CH_2=CH$CH_2CH_2CH_2CH_2CH_2$-), 28.91 (-$CH_2CH_2CH_2CH_2O$-), 25.73 (-$CH_2CH_2CH_2O$-).

2. 3. 2. Synthesis of undec-10-enyl methanesulfonate (**2**)

Prior to reaction, the glassware was dried in an oven at 80°C and cooled to room temperature under nitrogen atmosphere. Compound **1** (80 g, 0.47 mol) was dissolved in dry dichloromethane and the reaction flask was immersed into an ice-bath at 0°C. After the addition of dry triethylamine (72 mL, 0.52 mol), methanesulfonyl chloride (mesyl chloride) (37 mL, 0.48 mol)

was added dropwise. The reaction mixture was then stirred overnight at room temperature. The precipitated salt filtered out and the solution was washed with a saturated sodium bicarbonate solution (3×200 mL). The dichloromethane phase was then dried over magnesium sulfate and evaporated to dryness. The light yellow product was obtained with 88 % yield. ^{1}H NMR (300 MHz, $CDCl_3$, ppm) 5.8 (m, 1H, CH_2=C*H*-), 5.01-4.91 (m, 2H, C*H*$_2$=CH-), 4.22 (t, 2H, -CH_2C*H*$_2$O-), 3.0 (s, 3H, -OSO_2C*H*$_3$) 2.03 (q, 2H, CH_2=CHC*H*$_2$-), 1.75 (p, 2H, -CH_2C*H*$_2$$CH_2$O-), 1.4-1.28 (m, 12H, backbone C*H*$_2$). ^{13}C NMR (300 MHz, $CDCl_3$, ppm) 138.3 (CH_2=C H-), 114.16 (CH_2=CH-), 70.17 (CH_2CH_2CH_2O-), 37.38 (-OSO_2CH_3), 33.78 (CH_2=CHCH_2-), 29.33 (CH_2=CHCH_2CH_2CH_2CH_2CH_2-), 29.12 (CH_2=CHCH_2C$H_2CH_2CH_2$CH_2-), 29.05(-C$H_2CH_2CH_2CH_2$O-), 28.88 (-CH_2CH_2CH_2O-), 25.41 (-C$H_2CH_2CH_2$O-).

2. 3. 3. Synthesis of S-undec-10-enyl ethanethionate (**3**)

Potassium tert-butoxide (91 g, 0.81 mol) was suspended in DMF (500 mL). Once most of the potassium tert-butoxide was dissolved, the reaction flask was cooled to 0°C in an ice-bath. After slow addition of thioacetic acid (58 mL, 0.81 mol), the reaction mixture was brought to room temperature. Subsequently, compound **2** (100 g, 0.403 mol), which was dissolved in DMF (100 mL), was added all at once under vigorous stirring. An orange gel was formed within minutes due to the formation of potassium mesylate. After 3 hours, water (1.5 L) was added to liquefy the solidified reaction mixture and the aqueous dispersion was extracted with diethyl ether (4×300 mL). The combined organic extract was then washed with brine (3×200 mL) and dried on magnesium sulfate before the solvent was removed on a rotary evaporator. A clear, orange liquid product was obtained with 79 % yield. ^{1}H NMR (300 MHz, $CDCl_3$, ppm) 5.8 (m, 1H, CH_2=C*H*-), 5.01-4.91 (m, 2H, C*H*$_2$=CH-), 2.86 (t, 2H, -CH_2C*H*$_2$S-), 2.32 (s, 3H, -COC*H*$_3$) 2.04 (q, 2H, CH_2=CHC*H*$_2$-), 1.55 (p, 2H, -CH_2C*H*$_2$$CH_2$S-), 1.4-1.28 (m, 12H, backbone C*H*$_2$). ^{13}C DEPT 45 NMR (300 MHz, $CDCl_3$, ppm) 139.2 (CH_2=C H-), 114.11 (CH_2=CH-), 33.79 (CH_2=CHCH_2-),

31.23 (-$CH_2\underline{C}H_2S$-), 30.64 (-$CO\underline{C}H_3$), 29.40 (CH_2=$CHCH_2CH_2\underline{C}H_2\underline{C}H_2CH_2$-), 29.16 ($CH_2$=$CHCH_2\underline{C}H_2CH_2CH_2\underline{C}H_2$-), 29.09 (-$\underline{C}H_2CH_2CH_2CH_2S$-), 28.91(-$\underline{C}H_2CH_2CH_2S$-), 28.80 (-$\underline{C}H_2CH_2S$-).

2. 3. 4. Synthesis of undec-10-ene-1-thiol (**4**)

S-undec-10-enyl ethanethionate (**3**) (100 g, 0.44 mol) was brought under argon and propylamine (55 mL, 0.66 mol) was added under stirring at room temperature. After 1 hour, 10 % hydrochloric acid (180 mL) was added to quench the reaction. Subsequently, the mixture was extracted with diethylether (2×300 mL). The combined organic layer was then washed with brine (4×200 mL) and dried on magnesium sulfate. The crude thiol was purified by vacuum distillation at 0.1 mbar. The fraction boiling between 80-85°C was collected. ^{1}H NMR (300 MHz, $CDCl_3$, ppm) 5.8 (m, 1H, CH_2=C$\underline{H}$-), 5.01-4.91 (m, 2H, C$\underline{H_2}$=CH-), 2.52 (q, 2H, -$CH_2C\underline{H_2}SH$), 2.04 (q, 2H, CH_2=$CHC\underline{H_2}$-), 1.64-1.54 (m, 3H, -$CH_2C\underline{H_2}S\underline{H}$), 1.41-1.28 (m, 12H, backbone C$\underline{H_2}$). ^{13}C NMR (300 MHz, $CDCl_3$, ppm) 139.2 (CH_2=$\underline{C}$H-), 114.12 ($\underline{C}H_2$=CH-), 33.80 (CH_2=$CH\underline{C}H_2$-, -$\underline{C}H_2CH_2SH$), 29.41 (CH_2=$CHCH_2CH_2\underline{C}H_2\underline{C}H_2CH_2$-), 29.05 ($CH_2$=$CHCH_2\underline{C}H_2CH_2CH_2\underline{C}H_2$-), 28.91(-$\underline{C}H_2CH_2CH_2SH$), 28.36 (-$\underline{C}H_2CH_2CH_2SH$), 24.66 (-$\underline{C}H_2SH$).

2. 4. Synthesis of polythioethers

2. 4. 1. Photopolymerization

The solution of monomer **4** (5 g, 0.027 mol) and DMPA (16 mg- 0.062 mmol for **P1**, 50 mg- 0.19 mmol for **P2**) was purged with argon for 5 min in a closed vial. Subsequently, the solution was transferred into a two layered glass mold through the intermediate silicon layer of 2 mm. The closed system were then placed on a hot plate at 75°C in an UV oven in which the UV light (365 nm, ~ 2 W cm^{-2}) was exposed from the top for 40 min.

2. 4. 2. Thermal polymerization

The mixture of monomer **4** (5 g, 0.027 mol) and V-40 (0.18 g, 0.75 mol) was purged with argon for 5 min and the closed polymerization tube was immersed into an oil bath at 95°C for the specified time interval.

2. 5. Oxidation to polysulfone

Polythioether P2 (0.5 g) was dissolved in chloroform (50 mL) at 64°C. Subsequently glacial acetic acid (2.5 mL) and 35 % hydrogen peroxide solution (0.5 mL) were added to the reaction flask. After two hours of reaction under reflux, the formed polymer was precipitated in a methanol-water (60:40) mixture. The precipitated polymer was then washed successively with sodium bicarbonate (100 mL), water (100 mL), and methanol (100 mL) prior to drying in a vacuum oven at room temperature.

3. Results and discussion

3. 1. Synthesis of monomer for thiol-ene polyaddition

The starting compound was synthesized from commercially available 10-undecenoic acid in a four-step procedure (Fig. 1). First, the carboxylic acid functionality of 10-undecenoic acid was reduced to the corresponding primary alcohol with lithium aluminium hydride. Next, the alcohol functionality was reacted with mesylchloride in the presence of triethylamine. Subsequently, the obtained mesylate functionality was converted to the corresponding acetyl protected thiol by a mild treatment of the mesylate at room temperature with *in situ* generated potassium thioacetate. A peculiar observation after the addition of mesylchloride was that the reaction mixture turned into a stiff gel after 5 minutes of reaction, probably due to the formation of a potassium mesylate organogel. Addition of water at the end of the reaction dissolved the gel without further complications. In the last step, the thioacetate was deprotected by aminolysis using propylamine

to yield the unsaturated thiol-ene polyaddition monomer, which was further purified by vacuum distillation in a 73% overall yield based on 10-undecenoic acid. At -20°C, the α-olefinic ω-thiol is stable and no oligomers were observed after several months. However, storage of the purified product at room temperature should be avoided as a precipitation of crystalline oligomeric polythioethers occurs due to self-initiation. The successful isolation of an α-olefinic ω-thiol and especially its long-term stability is surprising, since there are several reports of self-initiated thiol-ene reactions, where no initiator is needed for the (poly)addition to proceed [26, 27].

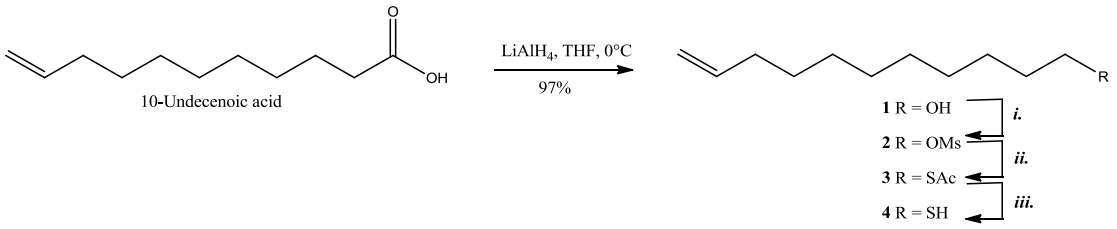


Fig. 1. Synthetic route for the preparation of the monomer for thiol-ene polyaddition (**4**). **i.** CH_3SO_2Cl, NEt_3, CH_2Cl_2 88 %, **ii.** KOtBu, CH_3COSH, 79 % **iii.** propylamine, 85 %.

3. 2. Thiol-ene polyaddition polymerization

In order to evaluate the compound **4** as a monomer for thiol-ene polyaddition, the pure material was polymerized in bulk by two different radical initiation systems. The first system involved a photopolymerization process using 2,2-dimethoxy-2-phenylacetophenone (DMPA) as initiator. The polymerization mixture consisting of the monomer and the initiator was purged with argon and polymerized between two glass layers with UV light (365 nm, 12 mW cm^{-2}). During polymerization, the glass plate was placed horizontally under a UV-source on a hot plate at 75 °C, which is required to prevent crystallization of oligomers and premature arrest of molecular weight build-up. The second system employed 1,1'-azobis(cyclohexane-1-carbonitrile) (V-40) as a radical initiator in a thermally initiated polymerization process. In this case, argon flushed bulk

monomer was polymerized in an oil bath at 95°C, considering the high decomposition temperature of V-40 ($t_{1/2(10h)}$=88°C).

Table 1: Polymerization conditions and molecular weight characteristics (relative to polystyrene standards) of polythioethers prepared by photochemical and thermal initiation.

Polymer	Initiation	Temperature (°C)	Time (min)	M_n (kDa)	PDI
P1	UV-DMPA (0.22 mol %)	75	40	16.2	13
P2	UV-DMPA (0.75 mol %)	75	40	40.2	30
P3	Thermal- V40 (3.7 w %)	95	60	15.0	2
P4	Thermal- V40 (3.7 w %)	95	300	31.5	8

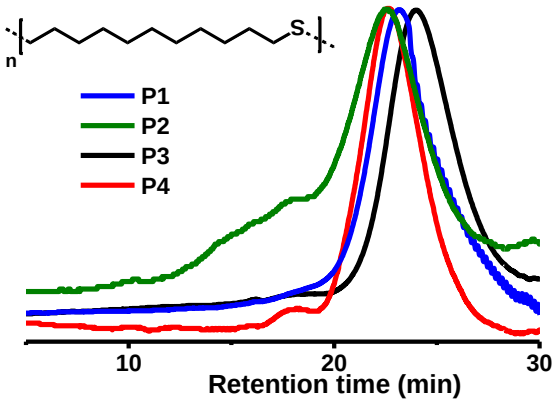


Fig. 2. Chloroform SEC traces of polythioethers prepared under different conditions.

In the photopolymerization process, it was possible to reach high molecular weights up to 40 kDa in 40 min (Table 1, P1-P2), with the molecular weight being dependent on the initiator concentration. However, high molecular weight shoulders and therefore large PDI values were observed for both low (16 kDa) and high molecular weight (40 kDa) polymers, being more pronounced in the latter (Fig. 2, P1-P2). In the thermal polymerization process, a relatively longer

polymerization time was necessary to obtain high molecular weight polymers. For example, a number average molecular weight of 31 kDa was reached in 5 hours (Table 1, P4). High molecular weight shoulders were also observed in this thermally initiated system while not in the other thermally initiated P3, leading us to consider the probability of a broadening of the molecular weight distribution by disulfide coupling of polymer chains. However, it was not possible to determine the exact polymer structure from NMR data as a result of the high molecular weights, resulting in line broadening and significant overlap of relevant NMR signals. Therefore, polythioether P2 was separated into three fractions by preparative SEC and each fraction was separately characterized by SEC and NMR spectroscopy. Table 2 shows the molecular weight characteristics of the fractionated polythioether P2.

Table 2: Molecular weight and weight distribution of the fractionated polythioether (P2) obtained from SEC (chloroform).

Fraction	M_n (kDa)	PDI
1^{st} (High M_n)	102	2.09
2^{nd} (Mid M_n)	37.8	1.24
3^{rd} (Low M_n)	16.8	1.50

A detailed NMR-study on the polythioether fractions indeed showed the formation of disulfide containing products in all fractions (triplet at 2.61 ppm). In addition, an overlapping quartet was observed at 2.65 ppm. In order to obtain sufficient resolution for the identification of this quartet, a 700 MHz ^{1}H-NMR COSY spectrum of the 2^{nd} fraction was recorded (Fig. 3).

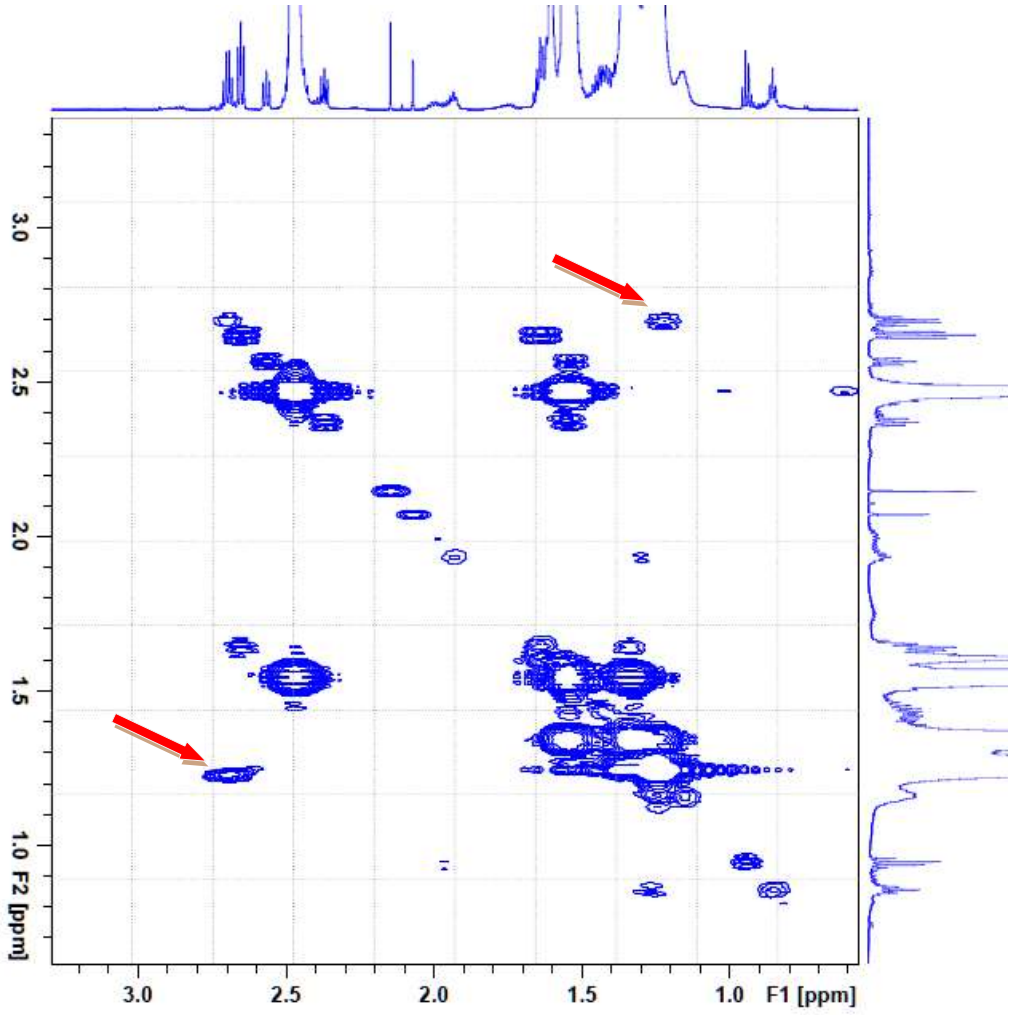
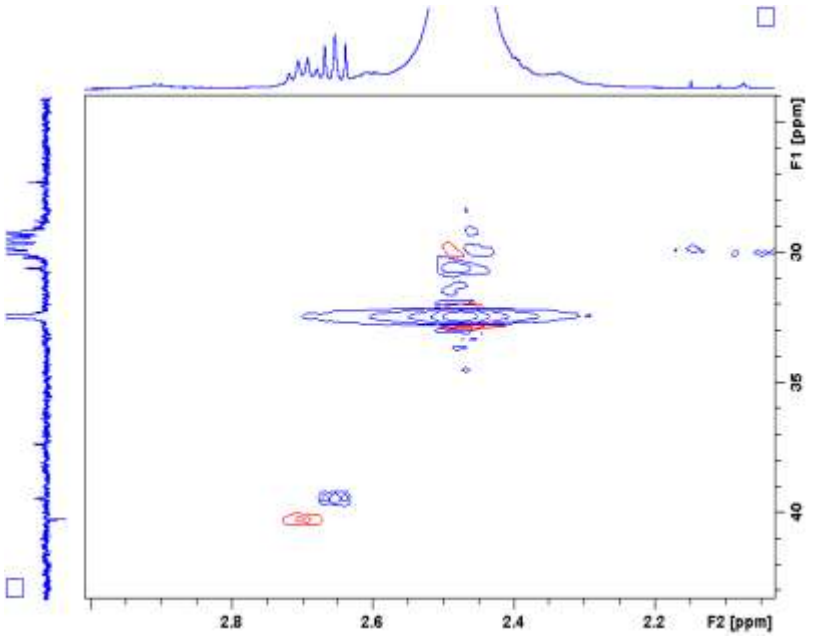
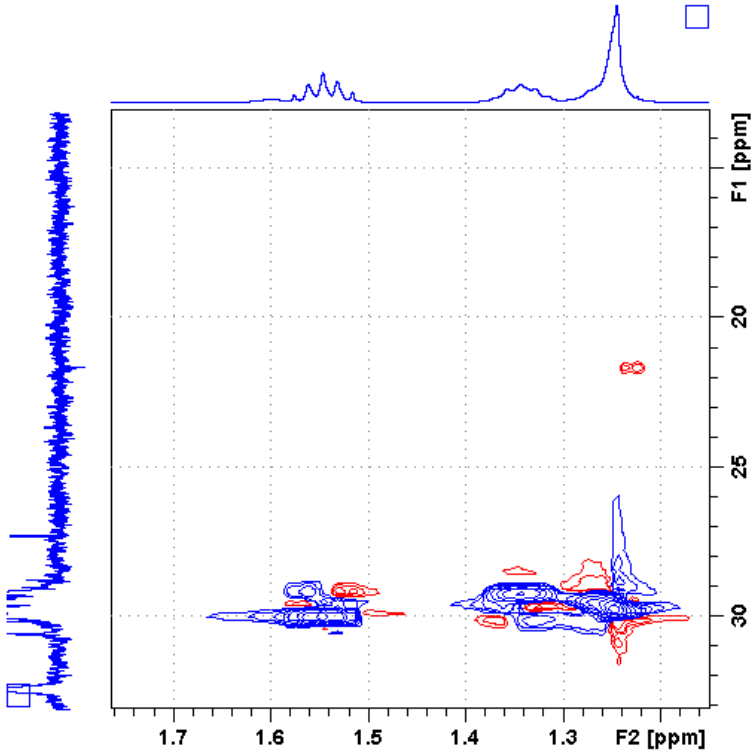


Fig. 3. 700 MHz COSY spectrum of fractionated polythioether P2 (2nd fraction) in $CDCl_3$.

The spectrum reveals a coupling with aliphatic signals at 1.22 ppm (red arrows) and no coupling with the neighboring disulfide peak. From an overnight 500 MHz HSQC measurement, a coupling between the unidentified quartet, and the signal from a tertiary C-H carbon atom at 40 ppm (Fig. 4A) is clearly visible. In addition to this tertiary carbon atom, one single low-intensity methyl signal is observed at 21.3 ppm (Fig. 4B). This methyl signal couples with a large overlapping alkyl-signal at 1.25 ppm.



A



B

Fig. 4. 500 MHz HSQC spectrum of fractioned polythioether P2 (2^{nd} fraction) in $CDCl_3$, showing the regions of the thioether linked structures (A) and the alkyl moieties (B).

From the COSY spectrum, a clear coupling between the alkyl-signal at 1.25 ppm and the unidentified quartet at 2.65 ppm is seen as well, which indicates that the unidentified signal originates from the protons of the β-thiol-ene addition product (Fig. 5). The content of 300 MHz ^{1}H-NMR analyses of the 1st and the 3rd fraction confirmed that the amount of β-thiol-ene addition product and the disulfide content does not vary significantly with molecular weight (~3% β-thiol-ene addition product and ~1.5% disulfide for all fractions).

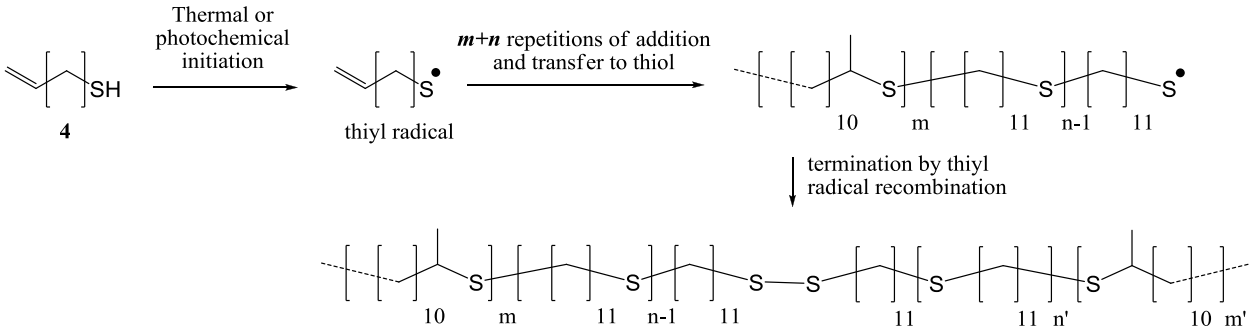


Fig. 5. Polymerization pathway of **4** with the chemical structure of the polythioethers P1-P4 with n,n'<<m,m'

It is well-known that the propagation step of the thiol-ene radical addition follows a cyclic mechanism where, after initiation, a thiyl-radical adds to a terminal double bond, forming a beta-thioether carbon-centered radical [28]. Transfer to thiol leads to the regeneration of a thiyl-radical, closing the cycle. Both steps in this propagation mechanism are, provided the thiol and ene are present in high and equal concentration, pseudo first-order. The thiyl-radical recombination reaction, on the other hand, is a second order reaction, which means that the formation of disulfides is favored over propagation for high radical concentrations. Photochemical initiation using DMPA, a type 1 photo initiator that creates a single reactive

radical for every efficient fission, generates high local radical concentrations and therefore leads to an increased formation of disulfides. When sufficiently high intensity UV-sources are used (in our case 2 W cm^{-2}), the whole process of polymerization is finished in a matter of minutes.[29] Thermal initiation, on the other hand, generates radicals that are equally distributed in the polymerizing liquid, which inevitably leads to lower local concentration of radicals, compared to photochemical initiation, even when both the thermal and photochemical initiators show equal half-lives under the applied reaction conditions. This was confirmed by a 500 MHz ^{1}H-NMR analysis of P3, showing an overall disulfide content of 0.68%, which is significantly less than half of the disulfide content compared to the photo-polymerized polymer P2.

3. 3. Oxidation to polysulfone

Polythioethers were modified by oxidation with hydrogen peroxide, a known process to oxidize the sulfur atom successively to sulfoxide and sulfones. This oxidation process was performed in chloroform at 65°C in the presence of glacial acetic acid and a 35 % hydrogen peroxide solution. In the process, 2 eq. excess of hydrogen peroxide compared to the sulfur function in the polymer chain was used and the oxidation was followed by FT-IR and FT-RAMAN. In the first half of the reaction, sulfur groups were converted to the sulfoxide form, as confirmed by FT-IR (1022 cm^{-1}; sulfoxide specific IR absorption) and FT-RAMAN (1025 cm^{-1}; sulfoxide specific Raman-line) (Fig. 6-red lines). Moreover, some of the sulfoxide moieties were already oxidized to form sulfone groups. As the oxidation continues, sulfoxide groups were further oxidized to sulfone (1125 cm^{-1}; sulfone specific Raman-line and 1132cm^{-1} and 1257 cm^{-1}; sulfone specific IR absorptions), thereby forming a polysulfone polymer (Fig. 6-blue lines).

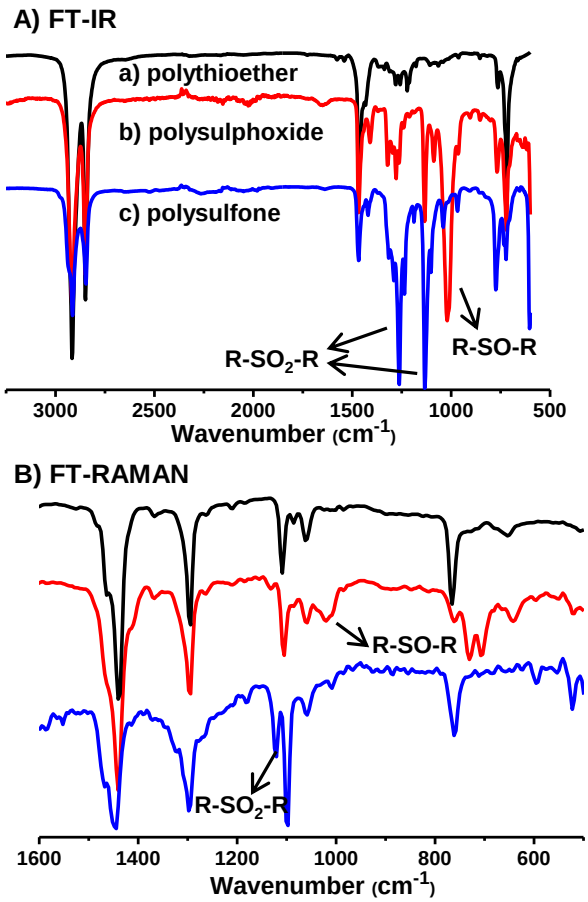


Fig. 6. A) FT-IR and B) FT-RAMAN spectra of the polythioether P2 and the oxidized forms. Black lines express the polythioether before oxidation. Red and blue lines show the spectra for intermediate polysulfoxide and the finally formed polysulfone, respectively.

3. 4. Characterization of the polymers

The synthesized polythioethers have a melting point around 90°C, which was recorded via differential scanning calorimetry (DSC) analysis (Fig. 7). Moreover, thermogravimetric analysis (TGA) shows that the synthesized polythioethers are stable until at least a temperature of 280°C under air atmosphere (Fig. 8). This large gap between melting and decomposition point gives an important value to these materials in terms of processability. The synthesized polymers not only show a high thermal stability but also exhibit a good chemical stability. They are insoluble in

common solvents such as acetone, THF, and ethyl acetate while they are soluble in chloroform and aromatic solvents like toluene and xylene at temperatures above 65°C. Oxidation of the thio-ether to sulfone (C-SO_2-C) functions, resulted in a significant increase of the melting temperature of the oxidized polymer to 175°C, shown as multiple melting peaks in a DSC analysis (Fig. 7).

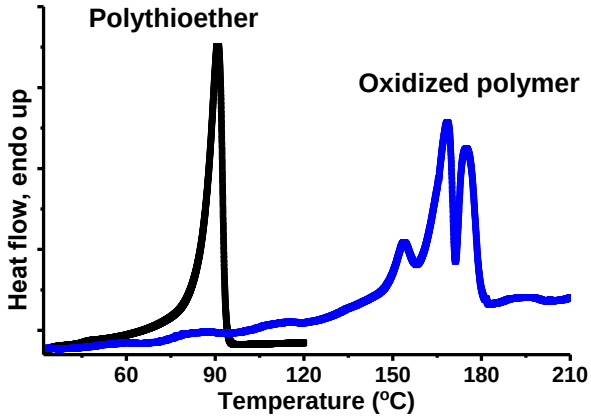


Fig. 7. DSC traces of polythioether (P2-black curve) and oxidized polymer (polysulfone, blue curve).

Such behavior is known to be indicative for the recrystallization of different crystal forms in polar polymeric materials, such as for example nylon-6.6 [30]. Also, the oxidation process further increased the thermal stability of the thermoplastic materials. Indeed, TGA-analysis of the polysulfone shows no significant weight loss up to 350°C (Fig. 8). As expected, the oxidation process further had a significant effect on the solubility of the polymer. The synthesized polysulfones did not show a significant solubility in any common solvent, including polar solvents such as DMF, DMSO and DMA, while remaining processable at elevated temperature (200°C). In comparison to the parent polythioether, the E-modulus of the polysulfone increased almost 1.5 times (Fig. 9). Other properties, such as crystallization temperature (T_c), heats of

melting and crystallization (ΔH_m and ΔH_c), which were significantly changed for the polysulfone, are mentioned in Table 3.

Table 3: Physical and thermal properties of polythioether (P2) and its oxidized product (polysulfone)

	T_m (°C)	T_c (°C)	ΔH_m (J/g)	ΔH_c (J/g)	E-modulus (MPa)	Elongation at break (%)	5% Weight loss (°C)
Polythioether	90	67	63	67	307	35	308
Polysulfone	175	158	86	84	470	25	358

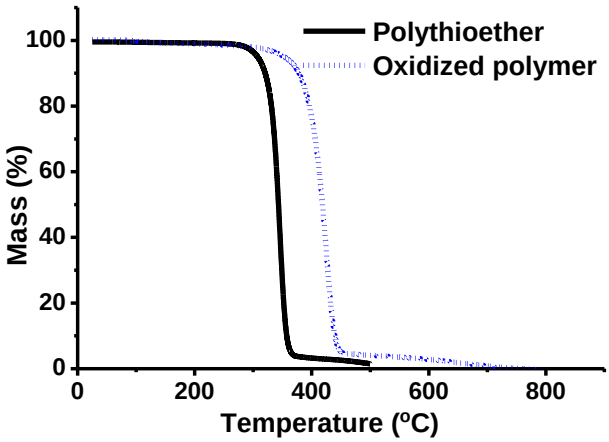


Fig. 8. TGA traces of polythioether (P2-black curve) and oxidized polymer (blue curve).

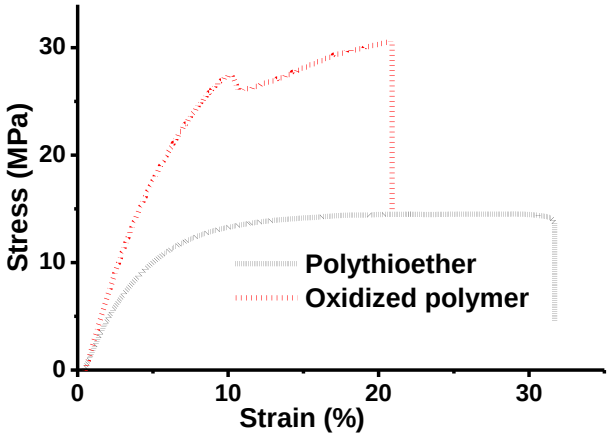


Fig. 9. Tensile testing curves of polythioether (P2-black curve) and oxidized polymer (red curve).

4. Conclusion

In summary, polyethylene-like polythioethers with variable molecular weight were successfully prepared by both thermal and photochemical thiol-ene polyaddition of 10-undecene thiol, a monomer that was synthesized with a yield over 70% from 10-undecenoic acid, a fully renewable material obtained from castor oil. Photochemical thiol-ene polyaddition yielded high molecular weight polymers (M_n up to 40 kDa) with high polydispersities. On the other hand, the use of azo-initiators resulted in the formation of polymers with lower polydispersities and M_n above 30 kDa. The disulfide concentrations in the photochemically initiated polymer samples were found to be approximately twice as high, compared to the thermally initiated ones. Fractionation of the photochemically initiated polymer P2 resulted in three fractions of equal disulfide content, which proves that the broader molecular weight distribution in this photochemically initiated polymer is not directly correlated to the amount of disulfide. Apart from disulfide formation, other radical-radical recombination products, which could prove the presence of branches, were not detected.

The physical properties of the prepared polymer resemble those of low density polyethylene (LDPE), with an E-modulus of about 300 MPa and a melting temperature of 90°C. Oxidation of the polythioether with hydrogen peroxide resulted in an intermediate sulfoxide functionalized polymer, which was still soluble in common polar solvents. Further oxidation yielded a sulfone functionalized polymer that was no longer soluble in any solvent tested. The E-modulus of the polymer increased almost 1.5 times upon oxidation. The melting temperature increased to 175°C, accompanied with the occurrence of multiple melting peaks. The onset of thermal decomposition was found to be around 350°C.

The polythioethers synthesized in this work are currently evaluated as surface modifiers for polyolefines, where the presence of a thioether moiety, after each eleventh carbon atom of the polymer chain, allows for facile superficial oxidation of the polymer, leading to a modified polymer surface energy with improved adhesion characteristics for e.g. gluing, painting and printing.

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Graphical abstract