Synthesis of Modified Polycaprolactams Obtained from Renewable Resources

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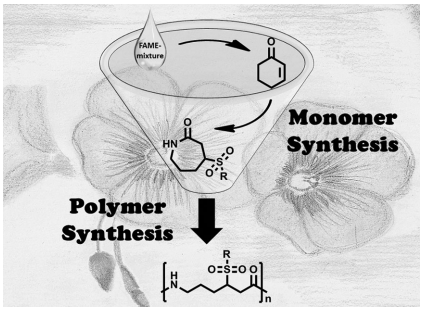
Modified caprolactam monomers, derived from renewable resources, are prepared to obtain novel polyamides with tunable properties. Starting from 2-cyclohex-1-enone, a thia-Michael addition is used as key step to synthesize modified monomer precursors. The monomer synthesis is optimized in order to achieve high yields utilizing environmentally benign synthesis procedures. The modified caprolactam monomers are obtained with high regioselectivity via the Beckmann rearrangement of the prepared cyclohexanone oximes. Using tin(II)2-ethylhexanoat ($Sn(Oct)_2$) as catalyst, it is possible to obtain the modified polycaprolactams in good yields. It is noteworthy that for the synthesis of the regioselective caprolactam monomers, the use of toxic reagents is avoided and the generation of waste is minimized in order to meet the requirements for environmentally benign synthesis procedures.



1. Introduction

The contamination of the oceans and the land with plastic waste and the depletion of fossil resources are issues seriously affecting our environment. Today, it is it is difficult to imagine live without plastics, evidenced by the steady increase of the global production of plastics.[1] Therefore, it is very important to develop and establish sustainable alternatives, where renewable resources as starting materials show great promise for the synthesis of these plastics.

Polyamides represent an important class of engineering plastics, because polyamides usually exhibit a high impact and tensile strength, show good electrical insulation, heat resistance, chemical resistance and abrasion resistance. Therefore, polyamides are extensively used in the automotive industry, electrical industry as well as the textile industry.[2] The annual global production of all polyamides is about 4×10^6 tons, whereby 95% of the produced polyamides are PA 6.6 and 6.[3] Polyamides are mainly obtained by polycondensation of dicarboxylic acids and diamines from AA- and BB-type or AB-type monomers. For instance, the well-known PA 6.6 is prepared by polycondensation of adipic acid and 1,6-hexamethylene diamine, a process that was developed in 1936 by DuPont and brought to market as Nylon.[4] Another method to synthesize polyamides is the ring-opening polymerization of lactams. In 1937, IG Farben developed a process to prepare polycaprolactam, known as Perlon, which was obtained by ring-opening polymerization of ε-caprolactam.[5,6]

Renewable polyamides, often called bio-polyamides, have been commercially available since the first half of the last century. Bio-polyamides are completely or partially bio-based, depending on whether the dicarboxylic acid, the diamine, or both are produced from renewable raw materials.[7,8] An economically important dicarboxylic acid for the production of bio-polyamides is sebacic acid obtained by reaction of ricinoleic acid with sodium or potassium hydroxide at 250 °C.[9] Ricinoleic acid, the major fatty acid of castor oil, is obtained by hydrolysis.[10] With this monomer, partially bio-based polyamides, such as PA 4.10 or PA 6.10 are available. The partially bio-based

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PA 4.10, PA 5.10, and PA 6.10 are commercially available.[11] Fully renewable and also commercially available polyamides are PA 10.10 and PA 11. PA 10.10 is obtained by polycondensation of sebacic acid and 1,10-diaminodecane, which are castor oil based platform chemicals. PA 11, on the other hand, has been on the market for more than 60 years and can also be derived from castor oil. After esterification of the castor oil derived ricinoleic acid, the respective methyl ester enables the synthesis of methyl 11-undecenoate by pyrolysis at 500 °C. Subsequent hydrolysis and bromination of the double bond, followed by a nucleophilic substitution with ammonia yields 11-aminoundecanoic acid, an AB-type monomer for the synthesis of PA 11.[12–14]

In all of these aforementioned examples, the respective polyamides were obtained by polycondensation. However, ε-caprolactam, a suitable monomer for a ring-opening polymerization, can also be obtained from renewable raw materials. Heeres and co-workers reported that 5-hydroxymethylfurfural, which can be obtained from renewable raw materials such as D-fructose, can be converted in just three steps to ε-caprolactone, which can in turn be converted to ε-caprolactam using ammonia.[15] The described examples only give a brief overview of renewable polyamides. Ongoing research further addresses the synthesis conditions, industrial development and application, highlighting the importance of polyamides and renewable analogues.[16–22]

In order to create novel polyamides with new properties for varying applications, polyamides can be modified in different ways before or after polymerization. In the literature, prominent examples exist describing a modification after the polymerization at the nitrogen atom.[23–26] In this case, the amide groups are activated using formaldehyde for further functionalization. Modifying the nitrogen atom may lead to a reduction of the melting point due to reduced hydrogen bonding. Burillo and co-workers described another modification method using acrylic acid and 4-vinyl pyridine in γ-ray grafting onto nylon films.[27] Furthermore, Wang and Lin described the reinforcement of nylon using various aromatic polyamides to obtain copolyamides with higher melting points, higher glass transition temperatures as well as better thermal stability compared to unmodified nylon.[28] Different aromatic copolyamides were obtained using a nylon prepolymer, an aromatic prepolymer and a coupling agent.

In this work, modified polyamides were prepared to receive a novel class of polycaprolactams from renewable resources with varying properties using a new way of modification. In contrast to the abovementioned examples, the modification was achieved prior to polymerization. Due to their importance and the demand of monomers based on renewable resources, we searched for an environmentally benign synthesis pathway to synthesize these modified caprolactam monomers from renewable resources with tunable properties.

2. Experimental Section

2.1. Materials

Hydroxylamine hydrochloride (97%, Aldrich), sodium bicarbonate (>99%, Fisher Scientific), sodium chloride (>99.5%, Aldrich), sodium sulfate (99%, Acros Organics), hydroxylamine solution (50 wt% in H_2O, Aldrich), sulfuric acid (96%, Acros Organics), ammonia (>99%, Aldrich), cyclohex-2-enone (≥98%, Aldrich), cyclohexanethiol (97%, Aldrich), 1-butanethiol (99%, Aldrich), 1-octanethiol (≥98.5%, Aldrich), triethylamine (99%, Acros), sodium hydroxide (98%, Aldrich), sodium tungstate dehydrate (>99%, Aldrich), Aliquat 336 (Aldrich), hydrogen peroxide solution (35 vol%, Aldrich), tin(II) 2-ethylhexanoate ($Sn(Oct)_2$) (≈95%, Aldrich), octylamine (99%, Aldrich), silica gel 60 (0.035–0.070, Aldrich), hexafluoroisopropanol (HFIP) (>99.9%, ChemPur), chloroform-*d* ($CDCl_3$, 99.8 at% D, Armar Chemicals), dimethyl sulfoxide-d_6 (DMSO-d_6, 99.8 at% D, euriso-top) were used as received. All organic solvents were of technical grade.

2.2. Methods

Thin-layer chromatography (TLC) identification of reactants and products was performed on silica-gel-coated aluminum foil (silica gel 60, F 254 with fluorescence indicator) from Aldrich. Compounds were visualized by Seebach reagent (mixture of phosphomolybdic acid, cerium (IV) sulfate, water and sulfuric acid).

NMR spectra were recorded on a Bruker AVANCE DPX spectrometer (measuring frequency: ^{1}H-NMR = 300 MHz, ^{13}C-NMR = 75 MHz) or a Bruker AMX R 500 spectrometer (measuring frequency: ^{1}H-NMR = 500 MHz, ^{13}C-NMR = 126 MHz) spectrometer. NMR spectra were obtained in $CDCl_3$ or DMSO-d_6. All ^{1}H-NMR spectra are reported in ppm relative to the solvent signal for $CDCl_3$ at 7.26 ppm and DMSO-d_6 at 2.50 ppm, ^{13}C-NMR spectra are reported relative to the solvent signal for $CDCl_3$ at 77.16 ppm and DMSO-d_6 at 39.52 ppm. Assignments of the signals were supported by measurements applying distortionless enhancement by correlation spectroscopy (COSY) techniques. ^{1}H-NMR spectra of polymers are reported in DMSO-d_6 and HFIP due to the poor solubility of synthesized polymers.

Polymer molecular weights were determined using a Tosoh EcoSEC HLC-8320 SEC system with HFIP as solvent, containing 0.1 wt% potassium trifluoroacetate. The solvent flow was 0.40 mL × min^{-1} at 30 °C. The analysis was performed on a 3-column system: PSS PFG Micro precolumn (3.0 × 0.46 cm, 10 000 Å), PSS PFG Micro (25.0 × 0.46 cm, 1000 Å) and PSS PFG Micro (25.0 × 0.46 cm, 100 Å). The system was calibrated using linear poly(methyl methacrylate) standards (Polymer Standard Service, M_p 102–981 000 Da).

FAB (fast atom bombardment) mass spectra were recorded on a MAT95 (Finnigan).

Infrared (IR) spectra were recorded on a Bruker alpha-p instrument applying KBr- as well as ATR-technology.

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The thermal properties of the prepared polymers were studied via DSC with a Mettler Toledo DSC star system, operating under nitrogen atmosphere and using about 5 mg of the respective polymer for the analysis. The glass transition temperature (T_g) was recorded on the second heating scan by using the following method: heating from –70 to 250 °C at 20 °C min^{-1}, cooling from 250 to –70 °C at 20 °C min^{-1}, and heating from –70 to 250 °C at 10 °C min^{-1}.

2.3. Synthesis Procedure

2.3.1. Monomer synthesis: Thia-Michael addition

General Procedure: Cyclohex-2-enone **1** (3.00 g, 31.2 mmol), the respective thiols **2a–c** (37.4 mmol) and triethylamine (10 mol%) were mixed and heated to 50 °C for 4 h. 50.0 mL ethyl acetate was added to quench the reaction. The organic layer was washed with 1 M NaOH solution (100 mL), water (3 × 50 mL) and the combined organic layers were dried over sodium sulfate. After evaporation of the solvent, the pure product was obtained as colorless oil in quantitative yields.

*3-(n-Butylthio)cyclohexanone (**3a**)*: Following the aforementioned general procedure, the reaction of cyclohex-2-enone **1** (3.00 g, 3.03 mL, 31.2 mmol), 1-butanethiol **2a** (3.37 g, 4.01 mL, 37.4 mmol), and triethylamine (0.38 g, 0.52 mL, 10 mol%) yielded **3a** as colorless oil in quantitatively. TLC (*n*-hexane/ethyl acetate 7:1) R_f = 0.41; ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 3.06–2.99 (m, 1 H, –S–C*H*–), 2.68 (dd, J_{HH} = 14.4, 4.3 Hz, 1 H, –S–CH–CH_2–), 2.52 (td, J_{HH} = 7.4 , 1.4 Hz, 3 H, 1 × –S–CH–CH_2–CO–, 2 × –CO–CH_2–CH$_2$–), 2.39–2.30 (m, 2 H, –CH_{2cy}–), 2.16–2.10 (m, 2 H, –CH_{2cy}–), 1.68 (t, J_{HH} = 8.0 Hz, 2 H, –S–CH_2–), 1.53 (quint, J_{HH} = 7.3 Hz, 2 H, –S–CH$_2$–CH_2–), 1.38 (sext, J_{HH} = 7.3 Hz, 2 H, CH$_3$–CH_2–), 0.89 (td, J_{HH} = 7.3, 1.6 Hz, 3 H, –CH_3) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 208.8 (–C=O), 48.1 (–S–CH–CH_2–CO–), 42.6 (–S–C*H*–), 40.8 (–CO–CH_2–CH$_2$–), 31.6 (–CH_{2cy}–), 31.5 (–S–CH_2–), 30.1 (–S–CH$_2$–CH_2–), 24.1 (–CH_{2cy}–), 21.9 (CH$_3$–CH_2–), 13.5 (–CH_3–) ppm; FAB of $C_{10}H_{18}OS$ ([M+H]$^+$ = 187.1, M–S–$C_4H_9^+$ = 97.1); HRMS (FAB) of $C_{10}H_{18}OS$ [M+H]$^+$ calc. 187.1078, found 187.1071; IR (KBr) ν = 2929.2, 2869.2, 1709.0, 1445.6, 1419.5, 1377.8, 1341.1, 1312.7, 1274.9, 1219.0, 1173.8, 1093.5, 1052.7, 1030.9, 971.9, 908.8, 877.4, 746.5, 510.0 cm^{-1}.

*3-(n-Octylthio)cyclohexanone (**3b**)*: Following the aforementioned procedure, the reaction of cyclohex-2-enone **1** (3.00 g, 3.03 mL, 31.2 mmol), 1-octanethiol **2b** (5.47 g, 6.47 mL, 37.4 mmol), and triethylamine (0.38 g, 0.52 mL, 10 mol%) yielded **3b** oil in quantitatively. TLC (*n*-hexane/ethyl acetate 7:1) R_f = 0.56; ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 3.06–2.97 (m, 1 H, –S–C*H*–), 2.67 (dd, J_{HH} = 14.0, 4.1 Hz, 1 H, –S–CH–CH_2–CO–), 2.51 (td, J_{HH} = 7.4, 1.4 Hz, 3 H, 1 × –S–CH–CH_2–CO–, 2 × –CO–CH_2–CH$_2$–), 2.38–2.28 (m, 2 H, –CH_{2cy}–), 2.16–2.08 (m, 2 H, –CH_{2cy}–), 1.77–1.64 (m, 2 H, –S–CH_2–), 1.60–1.49 (m, 2 H, –S–CH$_2$–CH_2–), 1.32–1.24 (m, 10 H, 5 × (–CH_2–)), 0.85 (td, J_{HH} = 6.5, 1.6 Hz, 3 H, –CH_3) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 208.8 (–C=O), 48.2 (–S–CH–CH_2–CO–), 42.7 (–S–C*H*–), 40.9 (–CO–CH_2–CH$_2$–), 31.7 (–CH_{2cy}–), 31.6 (–S–CH_2–), 30.5 (–S–CH$_2$–CH_2–), 29.6 (–CH_{2cy}–), 29.1 (2 C, –CH_2–), 28.9 (–CH_2–), 24.1 (–CH_2–), 21.9 (CH$_3$–CH_2–), 13.5 (–CH_3–) ppm; FAB of $C_{14}H_{26}OS$ ([M+H]$^+$ = 243.2, M–S–$C_8H_{17}^+$ = 97.2); HRMS (FAB) of $C_{14}H_{26}OS$ [M+H]$^+$ calc. 243.1777, found 243.1778; IR (KBr) ν = 3323.3, 2922.1, 2852.0, 1712.2, 1446.5, 1376.6, 1341.0, 1312.6, 1276.9, 1219.2, 1172.8, 1093.8, 1053.0, 1030.5, 972.0, 908.1, 877.5, 721.6, 509.3, 430.2 cm^{-1}.

*3-(Cyclohexylthio)cyclohexanone (**3c**)*: Following the aforementioned procedure, the reaction of cyclohex-2-enone **1** (3.00 g, 3.03 mL, 31.2 mmol), cyclohexanethiol **2c** (4.37 g, 5.17 mL, 37.4 mmol), and triethylamine (0.38 g, 0.52 mL, 10 mol%) yielded **3c** as colorless oil in quantitatively. TLC (*n*-hexane/ethyl acetate 7:1) R_f = 0.51; ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 3.07–3.01 (m, 1 H, –CO–CH$_2$–C*H*–S–), 2.71–2.55 (m, 2 H, 1 × –S–C*H*–, 1 × –CO–CH_2–), 2.30–2.22 (m, 3 H, 1 × –CO–CH_2–CH, 2 × –CO–CH_2–CH$_2$–), 2.04–2.00 (m, 2 H, –CH_2–), 1.92–1.82 (m, 2 H, –CH_2–), 1.57–1.52 (m, 4 H, 2 × (–CH_2–)), 1.30–1.08 (m, 6 H, 3 × (–CH_2–)) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 208.6 (–C=O), 48.5 (–CO–CH_2–CH–S–), 42.0 (–S–C*H*–), 40.8 (–CO–CH$_2$–C*H*–), 40.6 (–CO–CH_2–CH$_2$–), 33.7 (–CH_2–), 33.6 (–CH_2–), 31.8 (–CH_2–), 25.7 (2 H, 2 × –CH_2–), 25.4 (–CH_2–), 24.0 (–CH_2–) ppm; FAB of $C_{12}H_{21}OS$ ([M+H]$^+$ = 213.3, M–S–$C_6H_{11}^+$ = 97.2); HRMS (FAB) of $C_{12}H_{21}OS$ [M+H]$^+$ calc. 213.1308, found 213.1306; IR (KBr) ν = 2924.3, 2849.6, 1708.2, 1445.6, 1418.8, 1339.9, 1312.3, 1263.3, 1219.4, 1172.0, 1094.3, 1051.7, 1029.9, 998.1, 971.3, 908.3, 885.1, 818.2, 743.7, 627.3, 508.1 cm^{-1}.

2.3.2. Monomer Synthesis: Sulfur Oxidations

General Procedure: The thia-Michael products **3a–c** (32.2 mmol), Na_2WO_4*2H_2O (1.61 mmol), Aliquat 336 (1.61 mmol), ethyl acetate (15 mL), cyclohexane (7.50 mL), and water (3.00 mL) were mixed in an argon purged flask and cooled to 0 °C with an ice bath. Afterward, 225 mmol hydrogen peroxide solution (35 vol%) was added within 1 h. After further stirring for 4 h at room temperature, the reaction mixture was quenched with ethyl acetate (30 mL) and water (30 mL). The organic layer was separated and the aqueous phase was extracted with ethyl acetate (3 × 50 mL). The recombined organic layers were washed with brine, dried over sodium sulfate and filtered through silica gel. After evaporation of the solvent, the pure products were obtained in yields of 92%–93%.

*3-(Butylsulfonyl)cyclohexanone (**4a**)*: Following the aforementioned procedure, the reaction of 3-(*n*-butylthio)cyclohexanone **3a** (6.00 g, 32.2 mmol), Na_2WO_4*2H_2O (0.53 g, 1.61 mmol), Aliquat 336 (0.65 g, 1.61 mmol), and hydrogen peroxide solution (35 vol%, 25.6 g, 23.1 mL, 225 mmol) yielded **4a** as a colorless solid in a yield of 93%. TLC (*n*-hexane/ethyl acetate 1:1) R_f = 0.46; ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 3.33–3.08 (m, 1 H, –S–C*H*–), 2.97–2.92 (m, 2 H, –S–CH–CH_2–CO–), 2.72–2.63 (m, 1 H, 1 × –CO–CH_2–CH$_2$–), 2.44–2.18 (m, 3 H, 1 × –CO–CH_2–CH$_2$–, 2 × –CH_{2cy}–), 2.01–1.72 (m, 4 H, 2 × –CH_{2cy}–, 2 × –S–CH_2–), 1.62–1.44 (m, 4 H, 2 × –S–CH$_2$–CH_2–, 2 × CH$_3$–CH_2–), 0.96 (t, J_{HH} = 7.3 Hz, 3 H, –CH_3) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 206.6 (–C=O), 59.2 (–S–CH–CH_2–CO–), 50.0 (–S–C*H*–), 40.4 (–CO–CH_2–CH$_2$–), 39.9 (–CH_{2cy}–), 23.45 (–S–CH_2–), 23.3 (–S–CH$_2$–CH_2–), 23.0 (–CH_{2cy}–), 21.7 (CH$_3$–CH_2–), 13.4 (–CH_3–) ppm; FAB of $C_{10}H_{18}O_3S$ ([M+H]$^+$ = 219.1, M–O$_2$–$C_4H_9^+$ = 129.1, M-SO$_2$-$C_4H_9^+$ = 97.1); HRMS (FAB) of $C_{10}H_{18}O_3S$ [M+H]$^+$ calc. 219.1055, found 219.1054; IR (KBr) ν = 3375.7, 2958.0, 2872.4, 1713.1, 1450.7, 1409.6, 1350.3, 1294.6, 1263.8, 1198.8, 1125.0, 964.9, 919.0, 728.5, 701.9, 592.2, 522.5 cm^{-1}.

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*3-(Octylsulfonyl)cyclohexanone (**4b**)*: Following the aforementioned procedure, the reaction of 3-(*n*-octylthio)cyclohexanone **3b** (7.80 g, 32.2 mmol), $Na_2WO_4{}^*2H_2O$ (0.53 g, 1.61 mmol), Aliquat 336 (0.65 g, 1.61 mmol), and hydrogen peroxide solution (35 vol%, 25.6 g, 23.1 mL, 225 mmol) yielded **4b** as colorless oil in a yield of 92%. TLC (*n*-hexane/ethyl acetate 1:1) R_f = 0.49; ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 3.33–3.02 (m, 1 H, –S–C*H*–), 2.91 (t, J_{HH} = 8.0 Hz, 2 H, –S–CH–CH_2–CO–), 2.74–2.58 (m, 1 H, 1 × –CO–CH_2–CH$_2$–), 2.48–2.04 (m, 3 H, 1 × –CO–CH_2–CH$_2$–, 2 × –CH_{2cy}–), 1.92–1.66 (m, 4 H, 2 × –CH_{2cy}–, 2 × –S–CH_2–), 1.62–1.39 (m, 4 H, 2 × –S–CH$_2$–CH_2–, 2 × –CH_2–), 1.24–1.19 (m, 8 H, 4 × (–CH_2–)), 0.84 (t, J_{HH} = 6.5 Hz, 3 H, –CH_3) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 206.7 (–C=O), 60.4 (–*S*–CH–*C*H$_2$–CO–), 59.2 (–*S*-*C*H–), 50.2 (–CO–*C*H$_2$–CH$_2$–), 40.3 (–*C*H$_{2cy}$–), 31.5 (–S–*C*H$_2$–), 28.9 (–S–CH$_2$–*C*H$_2$–), 28.8 (–*C*H$_{2cy}$–), 28.4 (–*C*H$_2$–), 23.3 (–*C*H$_2$–), 23.0 (–*C*H$_2$–), 22.4 (–*C*H$_2$–), 21.3 (CH$_3$–*C*H$_2$–), 13.9 (–*C*H$_3$–) ppm; FAB of $C_{14}H_{26}O_3S$ ([M+H]$^+$ = 275.2, M–$C_3H_7{}^+$ = 232.1, M–SO_2–$C_8H_{17}{}^+$ = 97.2); HRMS (FAB) of $C_{14}H_{26}O_3S$ [M+H]$^+$ calc. 275.1675, found 275.1677; IR (KBr) ν = 2920.6, 2850.9, 1710.6, 1454.0, 1423.3, 1313.8, 1289.3, 1258.7, 1238.7, 1207.3, 1125.7, 1097.3, 1061.8, 1034.1, 973.0, 911.1, 884.0, 864.6, 765.0, 641.0, 593.0, 525.1, 511.7, 487.3, 401.4 cm^{-1}.

*3-(Cyclohexylsulfonyl)cyclohexanone (**4c**);* Following the aforementioned procedure, the reaction of 3-(cyclohexylthio)cyclohexanone **3c** (6.84 g, 32.2 mmol), $Na_2WO_4{}^*2H_2O$ (0.53 g, 1.61 mmol), Aliquat 336 (0.65 g, 1.61 mmol), and hydrogen peroxide solution (35 vol%, 25.6 g, 23.1 mL, 225 mmol) yielded **4c** as colorless oil in a yield of 92%. TLC (*n*-hexane/ethyl acetate 1:1) R_f = 0.24; ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 3.43–3.08 (m, 1 H, –CO–CH$_2$–C*H*–S–), 2.88 (tt, J_{HH} = 12.0, 3.4 Hz, 1 H, –S–C*H*–), 2.47–2.31 (m, 2 H, –CO–CH_2–CH), 2.25–2.19 (m, 2 H, –CO–CH_2–CH$_2$–), 2.06–2.02 (m, 2 H, –CH_2–), 1.91–1.86 (m, 3 H, 2 × –CH_2–, 1 × –CH_2–), 1.73–1.65 (m, 2 H, 1 × –CH_2-, 1 × –CH_2–), 1.58–1.44 (m, 3 H, 1 × –CH_2–, 2 × –CH_2–), 1.31–1.15 (m, 4 H, 2 × (–CH_2–)) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 206.8 (–C=O), 58.0 (–CO–*C*H$_2$–CH–S–), 55.8 (–S–*C*H–), 40.3 (–CO–CH$_2$–*C*H–), 39.7 (–CO–*C*H$_2$–CH$_2$–), 24.9 (–CH_2–), 24.8 (2 × –CH_2–), 24.7 (–CH_2–), 24.0 (2 H, –CH_2–), 23.3 (–CH_2–), 22.7 (–CH_2–) ppm; FAB of $C_{12}H_{21}O_3S$ ([M+H]$^+$ = 245.1, M–$C_6H_{11}{}^+$ = 161.1, M–SO_2–$C_6H_{11}{}^+$ = 97.2); HRMS (FAB) of $C_{12}H_{21}O_3S$ [M+H]$^+$ calc. 245.1206, found 245.1205; IR (KBr) ν = 2933.3, 2855.9, 1713.0, 1450.1, 1419.9, 1295.1, 1257.7, 1241.2, 1226.4, 1122.7, 1038.6, 997.9, 971.5, 912.7, 884.1, 851.1, 818.1, 753.9, 634.6, 603.7, 534.2, 513.2, 453.9, 401.9 cm^{-1}.

2.3.3. Monomer Synthesis: Oxime Formation

General Procedure: **4a–c** (18.4 mmol) were dissolved in a solvent mixture of THF/EtOH/H_2O in a ratio of 2:4:1 (1.00 mL THF per mmol **4a–c**). Afterward, hydroxylamine hydrochloride (27.6 mmol) and sodium bicarbonate (27.6 mmol) were added and the reaction mixture was stirred overnight at room temperature. The aqueous phase was extracted with ethyl acetate (3 × 50 mL). The combined organic layers were washed with brine and dried over sodium sulfate. After evaporation of the solvent, the pure product was obtained in quantitative yields.

Alternative Procedure: **4a–c** (11.0 mmol) were added to 5.00 g of a hydroxylamine solution (50 wt% in H_2O) in 12 mL H_2O, respectively. Afterward, the reaction mixture was stirred for 1 h at 100 °C. The aqueous layer was extracted with ethyl acetate (3 × 50 mL). The combined organic layers were washed with water (3 × 50 mL) and dried over sodium sulfate. After evaporation of the solvent, the pure product was obtained in good yields.

*3-(Butylsulfonyl)cyclohexanone oxime (**5a**)*: Following the general procedure, the reaction of 3-(butylsulfonyl)cyclohexanone **4a** (4.02 g, 18.4 mmol), hydroxylamine hydrochloride (1.93 g, 27.6 mmol), and sodium bicarbonate (2.33 g, 27.6 mmol) yielded **5a** as colorless oil in quantitatively. TLC (*n*-hexane/ethyl acetate 1:1) R_f = 0.39; ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 3.73–3.29 (dd, J_{HH} = 119.1, 14.6 Hz, 1 H, –S–C*H*–), 3.09–2.87 (m, 3 H, 2 × –S–CH–CH_2–CO–, 1 × –CO–CH_2–CH$_2$–), 2.50–2.03 (m, 4 H, 1 × –CO–CH_2–CH$_2$–, 2 × –CH_{2cy}–, 1 × –CH_{2cy}–), 1.86–1.68 (m, 4 H, 1 × –CH_{2cy}–, 2 × –S–CH_2–; 1 × –S–CH$_2$–CH_2–), 1.54–1.39 (m, 3 H, 1 × –S–CH$_2$–CH_2–, 2 × CH$_3$–CH_2–), 0.93 (td, J_{HH} = 7.3, 1.7 Hz, 3 H, –CH_3) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 156.8 (–C=N–), 59.2 (–S–CH–*C*H$_2$–CO–), 49.9 (–S–*C*H–), 30.7 (–CO–*C*H$_2$–CH$_2$–), 30.6 (–*C*H$_{2cy}$–), 24.3 (–S–C*H*$_2$–), 23.7 (–S–CH$_2$–*C*H$_2$–), 23.2 (–*C*H$_{2cy}$–), 21.8 (CH$_3$–*C*H$_2$–), 13.5 (–*C*H$_3$–) ppm; FAB of $C_{10}H_{19}NO_3S$ ([M+H]$^+$ = 234.1, M-SO_2-$C_4H_9{}^+$ = 112.1); HRMS (FAB) of $C_{10}H_{19}NO_3S$ [M+H]$^+$ calc. 233.1086, found 233.1085; IR (KBr) ν = 3292.3, 2957.3, 2871.9, 1711.8, 1450.1, 1288.1, 1264.7, 1124.3, 1036.2, 943.7, 914.9, 848.9, 728.6, 644.5, 593.3, 515.5 cm^{-1}.

*3-(Octylsulfonyl)cyclohexanone oxime (**5b**)*: Following the general procedure, the reaction of 3-(octylsulfonyl)cyclohexanone **4b** (5.05 g, 18.4 mmol), hydroxylamine hydrochloride (1.93 g, 27.6 mmol), and sodium bicarbonate (2.33 g, 27.6 mmol) yielded **5b** as colorless solid in quantitatively. TLC (*n*-hexane/ethyl acetate 1:1) R_f = 0.71; ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 3.73–3.28 (dd, J_{HH} = 118.0, 14.2 Hz, 1 H, –S–C*H*–), 3.07–2.89 (m, 3 H, 2 × –S–CH–CH_2–CO–, 1 × –CO–CH_2–CH$_2$–), 2.44–2.02 (m, 4 H, 1 × –CO–CH_2–CH$_2$–, 2 × –CH_{2cy}–, 1 × –CH_{2cy}–), 1.86–1.69 (m, 4 H, 1 × –CH_{2cy}–, 2 × –S–CH_2–; 1 × –S–CH$_2$–CH_2–), 1.53–1.19 (m, 11 H, 1 × –S–CH$_2$–CH_2–, 2 × CH$_3$–CH_2–, 4 × (–CH_2–)), 0.84 (t, J_{HH} = 6.5 Hz, 3 H, –CH_3) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 156.5 (–C=O), 59.5 (–S–CH–*C*H$_2$–CO–), 50.1 (–S–*C*H–), 31.5 (–CO–*C*H$_2$–CH$_2$–), 30.7 (–*C*H$_{2cy}$–), 30.5 (–S–C*H*$_2$–), 28.9 (–S–CH$_2$–*C*H$_2$–), 28.8 (–*C*H$_{2cy}$–), 28.4 (–*C*H$_2$–), 23.9 (–*C*H$_2$–), 23.4 (–*C*H$_2$–), 22.4 (–*C*H$_2$–), 21.2 (CH$_3$–*C*H$_2$–), 13.9 (–*C*H$_3$–) ppm; FAB of $C_{14}H_{27}NO_3S$ ([M+H]$^+$ = 290.2, M–SO_2–$C_8H_{17}{}^+$ = 112.1); HRMS (FAB) of $C_{14}H_{27}NO_3S$ [M+H]$^+$ calc. 290.1784, found 290.1783; IR (KBr) ν = 2920.7, 2854.2, 1709.2, 1466.9, 1425.2, 1313.0, 1265.2, 1251.8, 1125.8, 1095.2, 1043.4, 973.4, 948.2, 920.4, 878.6, 848.3, 755.5, 725.9, 672.2, 651.8, 602.6, 557.3, 510.1, 450.0 cm^{-1}.

*3-(Cyclohexylsulfonyl)cyclohexanone oxime (**5c**)*: Following the general procedure, the reaction of 3-(cyclohexylsulfonyl)-cyclohexanone **4c** (4.50 g, 18.4 mmol), hydroxylamine hydrochloride (1.93 g, 27.6 mmol), and sodium bicarbonate (2.33 g, 27.6 mmol) yielded **5c** as colorless oil in quantitative yield. TLC (*n*-hexane/ethyl acetate 1:1) R_f = 0.47; ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 3.68–3.29 (dd, J_{HH} = 105.2, 14.7 Hz, 1 H, –CO–CH$_2$–C*H*–S–), 3.18–2.89 (m, 2 H, 1 × –S–C*H*–, 1 × –CO–CH_2–CH), 2.47–2.38 (m, 1 H, 1 × –CO–CH_2–CH), 2.18–2.03 (m, 4 H, 2 × –CO–CH_2–CH$_2$–, 2 × –CH_2), 1.91–1.40 (m, 8 H, 4 × (–CH_2–)), 1.33–1.13 (m, 4 H, 2 × (–CH_2–)) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 156.7 (–C=O), 58.0 (–CO–*C*H$_2$–CH–S–), 56.1 (–S–*C*H–), 30.8 (–CO–CH$_2$–*C*H–), 30.5 (–CO–*C*H$_2$–CH$_2$–), 24.9 (–CH_2–), 24.7 (–CH_2–), 24.4 (–CH_2–), 24.2 (2 H, –CH_2–), 23.7 (–CH_2–), 23.2 (–CH_2–), 22.9 (–CH_2–) ppm;

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FAB of $C_{12}H_{21}NO_3S$ ($[M+H]^+$ = 260.1, M–SO_2–$C_6H_{11}^+$ = 112.1, M–SO_2—C_6H_{11}—OH^+ = 95.1); HRMS (FAB) of $C_{12}H_{21}NO_3S$ $[M+H]^+$ calc. 260.1315, found 260.1314; IR (KBr) ν = 3417.6, 2935.7, 2853.8, 1728.8, 1445.8, 1294.0, 1253.1, 1235.0, 1211.2, 1189.1, 1119.3, 1077.1, 978.9, 943.4, 915.5, 897.3, 884.8, 849.0, 820.6, 787.7, 768.8, 646.5, 604.6, 569.7, 533.6, 497.0, 473.8, 452.6 cm^{-1}.

2.3.4. Monomer Synthesis: Beckmann Rearrangement

General Procedure: Concentrated sulfuric acid (13.8 mmol) and oximes **5a–c** (6.91 mmol) were mixed at 0–20 °C. This mixture was added dropwise to concentrated sulfuric acid (10.4 mmol) at 130 °C and the reaction mixture was then stirred for 45 min at this temperature. After cooling to room temperature, the reaction mixture was cooled to 0 °C by an ice bath and neutralized with concentrated ammonia carefully, not exceeding 20 °C. The aqueous phase was extracted with ethyl acetate (3 × 50 mL). The recombined organic layers were washed with water (3 × 50 mL) and dried over sodium sulfate. After evaporation of the solvent, the pure product was obtained in yields of 60%–72%.

*6-(Butylsulfonyl)azepin-2-one (**6a**)*: Following the aforementioned procedure, the reaction of 3-(butylsulfonyl)cyclohexanone oxime **5a** (1.61 g, 6.91 mmol) and concentrated sulfuric acid (1.35 g, 0.73 mL, 13.8 mmol; 1.02 g, 0.55 mL, 10.4 mmol) yielded **6a** as yellowish oil in a yield of 60%. TLC (*n*-hexane/ethyl acetate 1:1) R_f = 0.41; ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.06 (brs, 1 H, –NH–), 3.29–3.27 (m, 2 H, –NH–CH_2–), 3.08–3.02 (m, 2 H, 1 × –S–C*H*–, 1 × –S–CH_2–), 3.01–2.92 (m, 1 H, 1 × –S–CH_2–), 2.89–2.79 (m, 2 H, –CO–CH_2–), 2.49–2.25 (m, 1 H, 1 × –NH–CH_2–CH_2–CH_2–), 2.13–2.06 (m, 1 H, 1 × NH–CH_2–CH_2–), 1.97–1.86 (m, 1 H, 1 × –NH–CH_2–CH_2–CH_2–), 1.83 (quint, J_{HH} = 7.6 Hz 2 H, –S–CH_2–CH_2–), 1.65–1.57 (m, 1 H, 1 × –NH–CH_2–CH_2-), 1.48 (sext, J_{HH} = 7.5 Hz, 2 H, CH_3–CH_2), 0.93 (td, J_{HH} = 7.6, 1.8 Hz, 3 H, –CH_3) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 173.8 (–C=O), 56.4 (–S–CH–CH_2–CO–), 49.7 (–S–C*H*–), 41.9 (–NH–CH_2–), 35.9 (–CH_{2cy}–), 28.0 (–S–CH_2–), 27.9 (–S–CH_2–CH_2–), 23.5 (–CH_{2cy}–), 21.8 (CH_3–CH_2–), 13.5 (–CH_3–) ppm; FAB of $C_{10}H_{19}NO_3S$ ($[M+H]^+$ = 234.1, M-SO_2-$C_4H_9^+$ = 112.1); HRMS (FAB) of $C_{10}H_{19}NO_3S$ $[M+H]^+$ calc. 234.1086, found 234.1085; IR (KBr) ν = 3340.8, 2932.4, 2872.0, 1655.8, 1459.1, 1367.2, 1343.1, 1271.2, 1125.9, 1024.0, 955.8, 916.1, 770.7, 728.5, 582.6, 518.6 cm^{-1}.

*6-(Octylsulfonyl)azepin-2-one (**6b**)*: Following the aforementioned procedure, the reaction of 3-(octylsulfonyl)cyclohexanone oxime **5b** (2.00 g, 6.91 mmol) and concentrated sulfuric acid (1.35 g, 0.73 mL, 13.8 mmol; 1.02 g, 0.55 mL, 10.4 mmol) yielded **6b** as yellowish oil in a yield of 60 %. TLC (*n*-hexane/ethyl acetate 1:1) R_f = 0.61 (*n*-Hexan/EE 1:1); ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 6.21 (brs, 1 H, –NH–), 3.34–3.23 (m, 2 H, –NH–CH_2–), 3.22–3.11 (m, 3 H, 1 × –S–C*H*–, 2 × –S–CH_2–), 2.87–2.77 (m, 2 H, –CO–CH_2–), 2.59–2.47 (m, 1 H, 1 × –NH–CH_2–CH_2–CH_2–), 2.17–2.10 (m, 1 H, 1 × NH–CH_2–CH_2–), 1.97–1.80 (m, 3 H, 1 × –NH–CH_2–CH_2–CH_2–, 2 × –S–CH_2–CH_2–), 1.74–1.55 (m, 1 H, 1 × –NH–CH_2–CH_2–), 1.48–1.42 (m, 2 H, –CH_2–), 1.37–1.21 (m, 8 H, 4 × (–CH_2)), 0.88 (t, J_{HH} = 7.6, Hz, 3 H, –CH_3) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 173.6 (–C=O), 56.4 (–S–CH–CH_2–CO–), 50.0 (–S–C*H*–), 41.9 (–CO–CH_2–CH_2–), 35.9 (–CH_{2cy}–), 31.6 (–S–CH_2–), 28.9 (–S–CH_2–CH_2–), 28.8 (–CH_{2cy}–), 28.5 (–CH_2–), 27.8 (–CH_2–), 22.5 (–CH_2–), 21.4 (–CH_2–), 21.3 (CH_3–CH_2–), 14.0 (–CH_3–) ppm; FAB of $C_{14}H_{27}NO_3S$ ($[M+H]^+$ = 290.2, M–SO_2–$C_8H_{17}^+$ = 112.1); HRMS (FAB) of $C_{14}H_{27}NO_3S$ $[M+H]^+$ calc. 290.1784, found 290.1787; IR (KBr) ν = 3209.7, 3079.6, 2921.9, 2852.0, 1655.1, 1486.0, 1454.0, 1427.3, 1414.7, 1365.8, 1313.0, 1281.3, 1169.3, 1128.6, 1032.7, 971.4, 866.1, 853.0, 806.2, 765.2, 721.9, 660.7, 626.0, 606.9, 588.5, 507.3, 448.7, 408.8 cm^{-1}.

*6-(Cyclohexylsulfonyl)azepin-2-one (**6c**)*: Following the aforementioned procedure, the reaction of 3-(cyclohexylsulfonyl)-cyclohexanone oxime **5c** (1.79 g, 6.91 mmol) and concentrated sulfuric acid (1.35 g, 0.73 mL, 13.8 mmol; 1.02 g, 0.55 mL, 10.4 mmol) yielded **6c** as yellowish oil in a yield of 72%. TLC (*n*-hexane/ethyl acetate 1:1) R_f = 0.42; ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 6.93 (brs, 1 H, –NH–), 3.31–3.17 (m, 2 H, –NH–CH_2–), 3.16–2.97 (m, 2 H, 1 × –S–C*H*–, 1 × –CO–CH_2–CH), 2.84–2.68 (m, 2 H, –CO–CH_2–), 2.61–2.38 (m, 2 H, 2 × –NH–CH_2–CH_2–CH_2–), 2.18–2.02 (m, 2 H, 1 × NH–CH_2–CH_2–, 2 × –CH_2–), 1.95–1.82 (m, 3 H, 2 × –CH_2–, 1 × –CH_2–), 1.77–1.69 (m, 1 H, 1 × –CH_2), 1.62–1.46 (m, 3 H, 1 × NH–CH_2–CH_2–, 2 × –CH_2–), 1.39–1.14 (m, 3 H, 2 × –CH_2–, 1 × –CH_2– ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 173.9 (–C=O), 57.8 (–CO–CH_2–CH–S–), 52.8 (–S–C*H*–), 41.9 (–CO–CH_2–C*H*–), 35.7 (–CO–CH_2–CH_2–), 27.9 (–CH_2–), 27.6 (–CH_2–), 25.3 (–CH_2–), 25.2 (2 H, –CH_2–), 24.9 (–CH_2–), 24.8 (–CH_2–), 24.0 (–CH_2–) ppm; FAB of $C_{12}H_{22}NO_3S$ ($[M+H]^+$ = 260.1, M–SO_2–$C_6H_{11}^+$ = 112.1, M–SO_2–C_6H_{11}–OH^+ = 95.1); HRMS (FAB) of $C_{12}H_{21}NO_3S$ $[M+H]^+$ calc. 260.1315, found 260.1317; IR (KBr) ν = 3336.8, 2931.0, 2857.1, 1647.2, 1478.2, 1449.6, 1343.1, 1291.0, 1266.3, 1123.4, 1023.4, 895.6, 849.9, 818.2, 617.3, 535.2, 500.1 cm^{-1}.

2.3.5. Polymer Synthesis

General Procedure: The respective monomers **6a–c** (0.30 g) were heated to 150 °C and degassed for at least 15 min using argon. Afterward, octylamine and tin(II)octanoate were added. After predefined reaction times (6–36 h) at 150 °C, the reaction mixture was cooled to room temperature, diluted with THF and precipitated in ice-cold methanol. In order to measure the NMR-spectra, each homopolymer was dissolved in DMSO-d_6 including a few drops of HFIP (hexafluoroisopropanol).

*Homopolyamide Derived from Monomer **6a** (**P1**)*: ^{1}H-NMR (DMSO-d_6, 500 MHz): δ = 3.69–3.57 (m, –S–CH_2–, –NH–CH_2–), 3.29–3.23 (m, –NH–CH_2–), 2.79–2.71 (m, –S–C*H*–), 2.69–2.61 (m, –CO–CH_2–), 2.16–2.10 (m, –S–CH–CH_2–), 2.03–1.97 (m, –S–CH_2–CH_2–), 1.93–1.70 (m, –CO–CH_2–CH_2–), 1.56–1.52 (m, CH_3–CH_2–), 1.10–1.30 (m, CH_3) ppm; DSC T_m = 193 °C.

*Homopolyamide Derived from Monomer **6b** (**P4**)*: ^{1}H-NMR (DMSO-d_6, 500 MHz): δ = 3.86–3.77 (m, –S–CH_2–, –NH–CH_2–), 3.48–3.41 (m, –NH–CH_2–), 2.36–2.28 (m, –S–C*H*–), 2.25–2.16 (m, –CO–CH_2–), 2.03–1.91 (m, –S–CH–CH_2–, -S–CH_2–CH_2–), 1.85–1.59 (m, –CO–CH_2–CH_2–), 1.57–1.43 (m, 5 × –CH_2–), 1.25–1.04 (m, CH_3) ppm; DSC T_m = 170 °C, T_g = 46 °C.

*Homopolyamide Derived from Monomer **6c** (**P5**)*: ^{1}H-NMR (DMSO-d_6, 500 MHz): δ = 3.75–3.51 (m, –S–CH_{cy}–, –NH–CH_2–), 3.29–3.17 (m, –NH–CH_2–, –S–C*H*–), 2.74–2.61 (m, –CO–CH_2–), 2.44–2.29 (m, –S–CH–CH_{2cy}–), 2.16–1.95 (–S–CH–CH_{2cy}–), 1.79–1.74 (m, –S–CH–CH_2–), 1.59–1.47 (m, –CO–CH_2–CH_2–), 1.33–1.22 (m, 3 × –CH_{2cy}-) ppm; DSC T_m = 191 °C, T_g = 52 °C.

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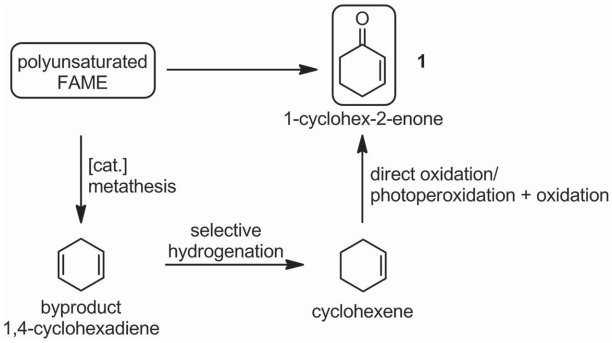

Figure 1. Formation of 1,4-cyclohexadiene as byproduct of the intermolecular self-metathesis of linolenic acid derivatives and the following synthesis of 1-cyclohex-2-enone 1.

3. Results and Discussion

3.1. Monomer Synthesis

One aim of this work was the synthesis of modified caprolactam monomers from renewable resources. Applying olefin metathesis, it is possible to obtain AA-type diester monomers from unsaturated fatty acid methyl esters.[29] By using a mixture of polyunsaturated fatty acid methyl esters, the metathesis equilibrium can be shifted to full conversion[30] due to the formation of volatile compounds that can be removed during the reaction by distillation. One of these byproducts is 1,4-cyclohexadiene, obtained by intermolecular ring closing metathesis of linolenic acid methyl ester (Figure 1). The group of Mathers described a direct synthesis of renewable 1,4-cyclohexadiene from plant oils via metathesis.[31] This solvent free method needed no plant oil purification, less catalyst and only a distillation as purification step, which made this synthesis very easy and environmentally friendly. Furthermore, Cole-Hamilton and co-workers described the metathesis of cardanol with ethylene, wherein 1,4-cyclohexadiene was also formed as a byproduct.[32] This synthetic method also offers a green alternative to conventionally produced 1,4-cyclohexadiene.

In this work, we used 1-cyclohex-2-enone **1** as key substrate to prepare modified caprolactams. 1-Cyclohex-2-enone **1** can be obtained in a three-step synthesis procedure from 1,4-cyclohexadiene as illustrated in Figure 1. First, 1,4-cyclohexadiene is converted to cyclohexene by a catalytic two-phase hydrogenation system.[33] Very interestingly, the used catalyst can be reused up to 15 times without any loss of activity or selectivity. In the next two reaction steps, cyclohexene is first oxidized to hexane-3-hydroperoxide and subsequently converted to 1-cyclohex-2-enone **1**, the starting material in this work.[34] Another very interesting possibility to obtain 1-cyclohex-2-enone **1** is the direct oxidation of 1,4-cyclohexadiene in a single reaction step.[35]

To synthesize the modified caprolactam monomers, different thiols were used to prepare modified cyclohexanones **3a–c** via thia-Michael addition (see Figure 2 for complete synthesis procedure). The thia-Michael addition was highly suitable to modify 1-cyclohex-2-enone **1**, as already described recently.[36] With a slight excess of the thiols **2a–c** (1.20 equivalents), the products could be obtained at a temperature of 50 °C in quantitative yields under solvent-free conditions using triethylamine as catalyst.

In order to reduce the elimination tendency of the modified cyclohexanones **3a–c** at the elevated temperatures of the following Beckmann rearrangement, the sulfides were oxidized to the corresponding sulfones. To

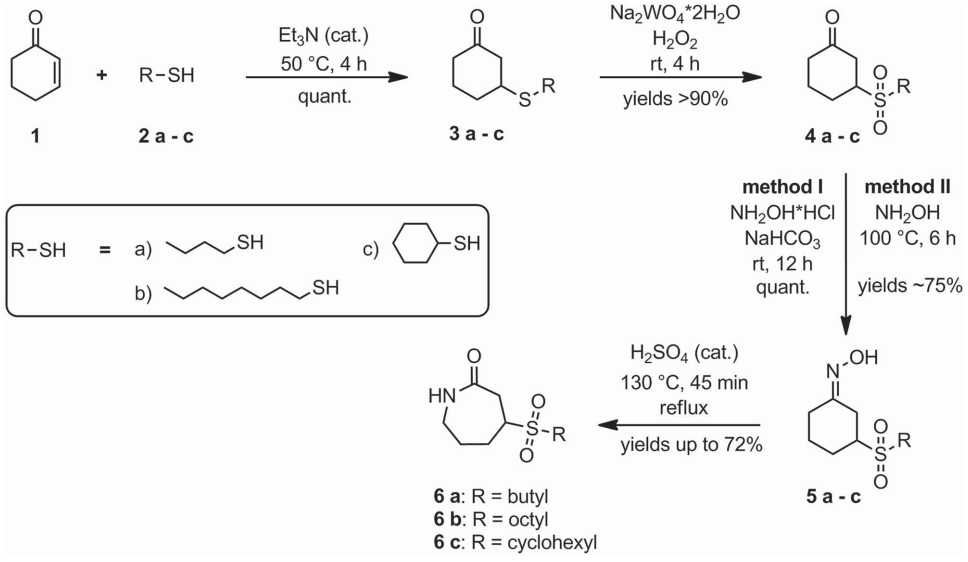

Figure 2. Synthesis of the modified caprolactam monomers **6a–c** starting from 1-cyclohex-2-enone 1.

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perform such an oxidation, usually *m*CPBA (*meta*-chloroperbenzoic acid), oxone or hydrogen peroxide are used. In this study, a different oxidation method was used to avoid the undesired formation of the respective lactone, a common reaction for oxidations of cyclohexenones using *m*CPBA also known as Baeyer–Villiger oxidation. Thus, a method of Jegelka and Plietker was used instead, employing hydrogen peroxide and a metal catalyst as oxidizing agent.[37] High yields and a very good selectivity toward the sulfonyl cyclohexanones was obtained for oxidations using sodium tungstate ($Na_2WO_4{}^*2H_2O$) as catalyst and Aliquat 336, also known as Stark catalyst, which was applied as phase transfer catalyst.

For the preparation of the oximes **4a–c**, two different methods were tested. In method I, hydroxylammonium chloride and sodium bicarbonate were used. This reaction exhibited a high E-factor[38] (= mass of waste/mass of product) of 54. The formation of the salt and the use of organic solvents as reaction media and for the work up were considered for the calculation of the E-factor. The advantage of this method is the low energy consumption, since the reaction can be carried out at room temperature. However, the disadvantage of this reaction is the formation of a salt by reaction of the hydroxylamine salt with sodium hydrogen carbonate. The recovery or disposal of this salt would be inefficient and expensive due to the accumulation of large amounts of nonrecyclable waste.

Therefore, another method was explored, wherein an aqueous hydroxylamine solution was used. The product was obtained in yields of around 75% and the reaction was performed under reflux at a temperature of 100 °C. In this way, the reaction time could be reduced to 1 h. Despite the higher energy demand, method II is favored due to the significantly lower waste production if compared to method I. The E-factor of this reaction was calculated to four and was therefore significantly lower, and thus represented a much more environmental-friendly alternative to method I.

Subsequently, the prepared oximes **5a–c** were converted to the lactams **6a–c** via a Beckmann rearrangement. With sulfuric acid as catalyst, yields of up to 72% were attained (Figure 2).

Due to the presence of the sulfone group, two different regioisomers (**6a** and **6a′**) can possibly be formed by the Beckmann rearrangement. The exact structure of the caprolactams obtained by Beckmann rearrangement was elucidated by ^{1}H-COSY-NMR analysis (Figure 3). The coupling of the aliphatic protons a–d with each other and the respective neighboring protons is obvious. The two protons h couple with g and themselves, because the proton i of the NH-group is not observed in the NMR. The proton e of the CH group coupled (except with itself) only with the neighboring protons j and f. All cross-signals and proton couplings observed in the ^{1}H-COSY-NMR analysis revealed that the Beckmann rearrangement selectively provided only one regioisomer. The reason for this possibly is a destabilization of the transition state by the electron-withdrawing sulfonyl-groups.

This four-step synthesis presents several advantages. Indeed, the high yields, easy implementations, simple purification steps, and mild conditions make this approach highly attractive and environmentally friendly. Moreover, the solvent-free thia-Michael addition with its 100% atom-efficiency enables to produce differently substituted molecules, thus offering versatile application possibilities and tuning of the resulting monomers and polymers. Overall, the presented synthetic strategy is simple, efficient, versatile and highly sustainable.

3.2. Homopolymer Synthesis

Subsequently, the ring-opening polymerization of modified caprolactam monomers **6a–c** was investigated. In the literature, different instructions of the ring-opening polymerization of cyclic esters with guanidine organocatalysts were reported.[39–41] In our work, first polymerisation tests on the modified caprolactams were carried out with such catalysts. But neither TBD (1,5,7-triazabicyclo[4.4.0]dec-5-ene) nor DBU (1,8-diazabicyclo[5.4.0]undec-7-en) led to the desired ring opening polymerization, although these catalysts are also known to catalyze transamidations.[42] Since these organocatalysts did not lead to the desired results, two other commonly used catalysts were employed for the polymerization. Using titanium isopropoxide resulted only in low molecular weight oligomers, whereas tin(II)octanoate performed better and was thus selected for further studies. The best polymerization results were obtained at 150 °C under solvent-free conditions using tin(II)octanoate as catalyst and octylamine as initiator. The monomers **6a–c** were polymerized with a $[M]_0$:$[I]_0$-ratio of 100:1 and the polymerization was stopped after 24 h (Figure 4). The homopolymers **P1**, **P2**, and **P3** were precipitated in methanol and characterized by size-exclusion chromatography (SEC).

In order to investigate the polymerization parameters and to follow the evolution of the molecular weight, the polymerization of polymer **P1** was stopped at different times and the dependence of molecular weight and dispersity on the monomer to initiator ($[M]_0$:$[I]_0$) ratio was investigated. Polyamides with moderate molecular weights and narrow dispersities were obtained after 24 h, suggesting a controlled polymerization mechanism. In theory, higher concentrations of the initiator lead to higher reaction rates and shorter chain lengths. This could also be confirmed here by the polymerization tests, but the kinetics were not further studied, since the aim of this report was the establishment of a route to renewable polycaprolactams with tunable side-groups.

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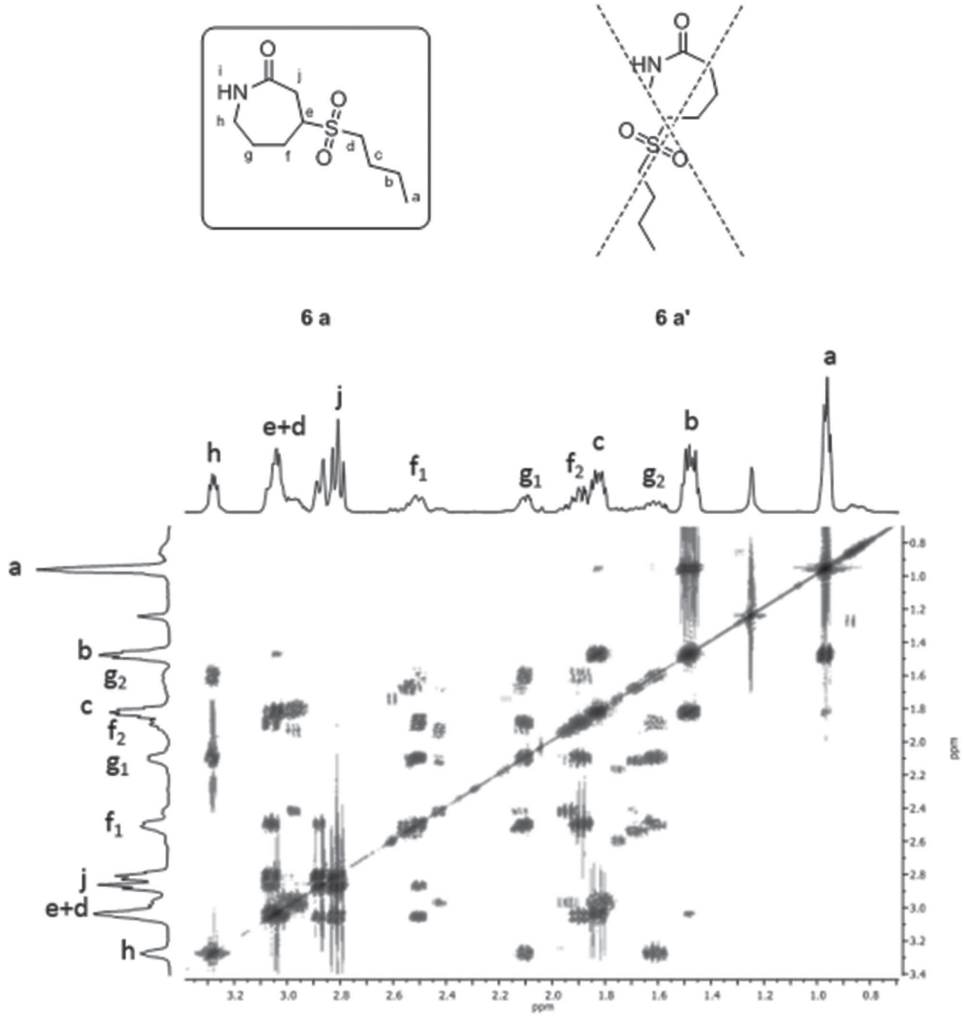

Figure 3. COSY-NMR spectrum of modified caprolactam **6a**.

The obtained molecular weights of the different polymers are in the range of 4.5 to 8.5 kDa with a low dispersity of 1.20–1.40 (Table 1). It is noteworthy that the molecular weights achieved in the industry for conventional polycaprolactam range between 5 and 15 kDa.[3] In this regard, the molecular weights obtained in the polymerizations of the modified caprolactams **P1– P3** are similar to those of industrially produced ε-caprolactam.

In HFIP (hexafluoroisopropanol), a standard solvent for polyamides, the polymers were partially, but not always completely soluble. SEC measurements were performed in HFIP, but the obtained molecular weight values are underrepresented, since the highest molecular weight macromolecules were not dissolved and were therefore filtered during the preparation of SEC samples before the measurement. The dissolved amount of the modified polymers was approximately 70% to 80% for all samples. Moreover, the modified polycaprolactams were not soluble in any conventional organic deuterated solvents [deuterated THF (tetrahydrofuran), deuterated methanol or hot deuterated DMSO (dimethyl sulfoxide)], even by heating or after several hours in ultrasonic bath, so no ^{1}H-NMR spectrum could be measured. A further possibility to dissolve polyamides was described in the literature.[43,44] For this, the

Table 1. Results of the SEC and DSC analysis of the homopolymers **P1**, **P4**, and **P5**.

Polymer	M_n [g mol^{-1}]	M_w [g mol^{-1}]	$Đ$ M_w/M_n	T_m [°C]	T_g [°C]
P1 (*n*-butyl)	4500	6200	1.35	170	–
P2 (*n*-octyl)	8500	11 800	1.40	193	46
P3 (cyclohexyl)	6800	8300	1.20	191	52

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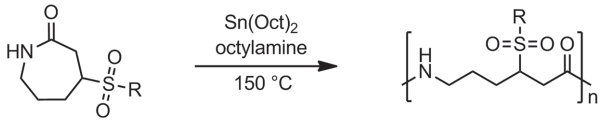

6 a: R = *n*-butyl
6 b: R = *n*-octyl
6 c: R = cyclohexyl

P 1: R = *n*-butyl
P 2: R = *n*-octyl
P 3: R = cyclohexyl

Figure 4. Homopolymerization of caprolactam monomers **6a–c** to polyamides **P1**, **P2**, and **P3**.

deuterated solvents should be mixed with small amounts of dichloromethane and TFAA (trifluoroacetic anhydride). The dichloromethane should slightly dissolve the polyamide, so that TFAA can react with the amide group, to obtain soluble *N*-trifluoroacetylated derivatives. However, also using these conditions, the modified polycaprolactams could not be adequately dissolved. Since the polymers were partially soluble in HFIP, a few drops of HFIP were added to a deuterated solvent. After a few days in this solution, the respective polymer was completely dissolved. The proton signal of HFIP in the ^{1}H-NMR spectrum did not influence the analysis, since it does not superimpose the signals of the polymers. All peaks were present in the expected integrals (see the Experimental Section) and the spectrum contained no unexpected signals.

The thermal behavior of polymers **P1**, **P2**, and **P3** was investigated by differential scanning calorimetry (DSC). Polymer **P2** and **P3** displayed a similar glass transition temperature (T_g) of 46 and 52 °C, respectively. The reason for the lower T_g of **P2** is the bulky sulfonyl group, which decreases the van der Waals interactions and the hydrogen bonding between the polymer chains. Moreover, due to a high amide-group frequency, all homopolymers showed high melting points (T_m) of up to 193 °C. However, compared to nylon 6 (T_m = 220 °C), the melting points of the modified polycaprolactams are lower since the long and flexible side chains act as a plasticizer that hampers chain–chain interactions. Polymer **P2**, with an octyl side chain moiety, exhibited the highest T_m, whereas polymer **P1**, having a butyl group, had the lowest T_m. Large side groups, such as in polymer **P2**, reduce the chain mobility and increase the melting point. The butyl group of polymer **P1**, even though not bulky, acted as a short chain branching of the main chain and lowered T_m. The most important factor affecting T_g and T_m is the hydrogen bonding of the amide groups, which is disturbed by bulky or dangling side chain moieties. However, it has to be mentioned that also the molecular weight often has a significant effect on T_m.

4. Conclusions

In this work, the efficient synthesis of modified polycaprolactams from 2-cyclohexen-1-one **1** was demonstrated. The modification was achieved by thia-Michael addition. This reaction provides very high yields and by using different thiols **2a–c**, different modified cyclohexanones **3a–c** were obtained. In order to prevent the cleavage of the thioether during the Beckmann rearrangement, the sulfur was first oxidized with a catalytic procedure using hydrogen peroxide as oxidizing reagent. Herein, the products **4a–c** were obtained in high yields without extensive purification. The synthesis of the oximes **5a–c** was accomplished via two synthetic procedures, which were compared to each other to establish an environmentally friendly and sustainable synthesis protocol. Via Beckmann rearrangement of the prepared oximes, the desired modified caprolactams **6a–c** were obtained in a very high regioselectivity. Different polymers (**P1–P3**) were obtained by ring-opening polymerization using tin(II)octanoate as catalyst. Depending on the attached side chain moiety, the modified polycaprolactames exhibited different melting points. The larger the side group, the higher was the melting point. In conclusion, a sustainable and straightforward synthesis procedure of renewable modified monomers suitable for ring opening polymerization was established leading to polyamides with interesting properties and materials that are potential substitutes to fossil based polyamides. Due to this very simple and effective method, a new material class could be developed, which is very considerable due to the high importance of polycaprolactams as plastics.

After having established this new route to renewable polycaprolactams, it would be interesting to further improve the monomer synthesis in the future by using even more benign methods. For instance, the Beckmann rearrangement could be started from ketones in a one-pot synthesis under solvent free conditions,[45] or sulfamic acid could be applied as a recyclable catalyst in the Beckmann rearrangement to avoid waste production.[46] Moreover, the use of ionic liquids instead of other organic solvents could be interesting in this regard.[47,48] Furthermore, by varying the used thiol, it should be possible to tune the polymer properties for certain applications; for instance, more bulky side chains could be introduced to obtain amorphous (transparent) polyamides.

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