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High-Throughput Synthesis of Oligo(ε-caprolactone) / Oligotetrahydrofuran Based Polyurethanes

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ABSTRACT

Robot assisted synthesis as part of high-throughput (HT) technology can assist in the creation of polymer libraries, e.g. polymers with a variety of molecular weights, by automatizing similar reactions. Especially for multiblock copolymers like polyurethanes (PUs) synthesized from telechels via polyaddition reaction, the adjustment of equivalent molar amounts of reactants requires a comprehensive investigation of end group functionality.

In this work, PUs based on oligo(ε-caprolactone) (OCL) / oligotetrahydrofuran (OTHF) as model components were designed utilizing HT synthesis enabling the quantitative determination of the optimized ratio between reactive end-groups via fully automated syntheses without major characterization effort of end group functionality. The semi-crystalline oligomeric telechelics were connected with a diisocyanate and OCL with a molecular weight of 2, 4, or 8 kg$\cdot$mol^{-1} was integrated. Here, optimized molecular weights between 90 ± 10 kg$\cdot$mol^{-1} (in case of OCL 8 kg$\cdot$mol^{-1}) and 260 ± 30 kg$\cdot$mol^{-1} (in case of OCL 2 kg$\cdot$mol^{-1}) were obtained with an isocyanate content of 120 mol%, whereby 100 mol% of isocyanate groups resulted only in molecular weights between 60 ± 6 kg$\cdot$mol^{-1} (OCL 8 kg$\cdot$mol^{-1}) and 80 ± 10 kg$\cdot$mol^{-1} (OCL 2 kg$\cdot$mol^{-1}). In addition to the optimized ratio between isocyanate and hydroxy end groups, quantitative influences of the OCL chain length and overall molecular weights of PUs on thermal and mechanical properties were detected. The melting temperatures (T_ms) of OCL and OTHF domains were well separated for PUs of low molecular weight, the temperature interval between the T_ms decreased when the molecular weight of the PUs was increased, and were even overlapping towards one broad T_m, when OCL 2 kg$\cdot$mol^{-1} was incorporated. The storage modulus E' was highly dependent on OCL chain length exhibiting an increase with increasing molecular weight of OCL from 220 MPa to 440 MPa at 0 °C and decreased with increasing chain length of PUs. The elongation at break (ε_b) was analyzed below and above T_m of OTHF resulting in $\varepsilon_b = 780\text{-}870\%$ at 0 °C and $\varepsilon_b = 510\text{-}830\%$ at 30 °C for PUs of high molecular weight. Accordingly, stretchability of PUs was almost independent of the state of OTHF (semi crystalline or amorphous) but correlated with the OCL precursor chain length (increasing ε_b with increasing chain length) and overall molecular weight of PUs (PUs at higher molecular weight exhibited higher ε_b). Hence, the analysis of these quantitative influences between

macromolecular structure of multiblock copolymers and the resulting properties (well separated T_ms versus overlapping melting transition, improvement of stretchability) would enable the design of new tailored PUs.

INTRODUCTION

High-throughput (HT) synthesis can assist in the determination of optimized reaction conditions and parameters by fully automated syntheses [1-4]. The influence of different encapsulation parameters (surfactant type, concentration, and core to shell ratio) on the microcapsule formation and morphology of melamine-formaldehyde microcapsules obtained by *in situ* polymerization could be explored by means of robot assisted synthesis [5]. Furthermore, the limitation of conversion of n-butyl methacrylate by nitroxide-mediated miniemulsion polymerization could be addressed using a robotic platform by changing the radical source, nitroxide scavenger, or pH value [6]. Robot assisted synthesis helped also in the optimization of aluminosilicate zeolite synthesis. Here, significantly higher degrees of crystallinity and larger sizes of crystals were realized when compared to zeolites prepared by the classical synthesis [7].

Based on this broad application spectrum of the HT technology, it was explored whether a robot assisted synthesis can be used to address also other challenges of chemical synthesis. The polyaddition reaction is such an example. Polymers of high molecular weights can only be obtained by polyaddition when equivalent amounts of reactants have been adjusted. The determination of an exact number of reactive end groups especially when oligomeric precursors are used, requires an considerable analytical effort as they produce a tremendous size distribution [8, 9]. However, polymers of high molecular weights by a polyaddition reaction can also be obtained without an exact investigation of end group functionality by robot assisted synthesis. Here, HT technology substitutes the characterization effort by numerous fully automated syntheses.

In this work, polyurethane (PU) model compounds based on OCL and OTHF were synthesized via polyaddition reaction following a HT synthesis approach. The model PUs were synthesized from hydroxy telechelic oligo(ε-caprolactone) (OCL-diOH) of different molecular weights (2, 4, and 8 kg·mol^{-1}) and oligotetrahydrofuran (OTHF-OH, 2.9 kg·mol^{-1}) coupled with trimethylhexamethylene diisocyanate (TMDI). By variation of the isocyanate content, the optimized ratio between TMDI and oligomeric precursors can be determined. Furthermore, a variety of multiblock copolymer PUs can be obtained and the influences of chain length of the OCL precursor and overall molecular weight on thermal and thermomechanical properties of the resulting PUs will be investigated.

EXPERIMENTAL PART

Materials

An isomeric mixture of 2,2,4- and 2,4,4-trimethylhexamethylene diisocyanate (TMDI) was obtained from Sigma-Aldrich (Steinheim, Germany) and distilled prior use. OCL-diols (2, 4, and 8 kg·mol^{-1}) were obtained from Solvay Caprolactones (Warrington, UK) and OTHF-diOH (2.9 kg·mol^{-1}) was purchased from Polysciences (Eppelheim, Germany).

All other solvents (Merck, Darmstadt, Germany) and chemicals (Sigma-Aldrich, Steinheim, Germany) were of commercial grade and were used as received unless noted otherwise.

Methods and Instruments

PUs synthesis was performed in vortexed reactor arrays (16 reactors per array) employing the automated parallel synthesizer platform Accelerator SLTII/106 (Chemspeed Technologies, Augst, Switzerland). The double-jacket reactors had a round-bottom cylindrical shape, an inner diameter of about 16 mm and an effective volume of 7.5 mL, whereby the temperature was adjusted by an external circulation thermostat. The

volumetric transfers were performed with a 4-needle head (septum piercing needles), connected to syringe pumps (2x1 mL, 1x10 mL, 1x25 mL).

Molecular weights of starting materials and products were determined with a high-throughput gel permeation chromatography (HT-GPC) system Tosoh EcoSEC HLC-8320 GPC including a refractive index detector (Tosoh Bioscience, Stuttgart, Germany) combined with a PSS Universal Data Center (PSS, Mainz, Germany), a viscometer ETA2010 (PSS), an EcoSEC UV detector 8320 (Tosoh Bioscience), and a light scattering detector SLD7100 (PSS) and two HT-GPC columns type PSS SDV analytical linear M 5 µm (PSS, Mainz, Germany) connected in series. Tetrahydrofuran (THF) was used as eluent (35 °C, flow rate 1.0 mL·min^{-1}) with 0.05 weight content 3,5-di-*tert*-butyl-4-hydroxytoluene (BHT) as internal standard, and polystyrene standards (PSS, Mainz, Germany) were used for standard calibration to determine the weight-average of the molecular weight.

^{1}H-NMR spectra were recorded at 25 °C in DMSO-d6 with a Bruker Avance 500 spectrometer (500 MHz, Bruker, Karlsruhe, Germany) with a relaxation time of 2 seconds.

Differential scanning calorimetry (DSC) experiments were performed on a Netzsch DSC 204 Phoenix (Netzsch, Selb, Germany) in the temperature range between 0 °C and 100 °C with heating and cooling rates of 10 K·min^{-1} in sealed aluminium pans. Thermal properties were determined from the second heating run.

Thermomechanical tensile tests were performed on a tensile tester (Zwick Z1.0, Ulm, Germany) equipped with a thermo chamber and a temperature controller (Eurotherm Regler, Limburg, Germany). Tensile tests to determine the elongation at break (ε_b) were performed at 0 °C and 30 °C on standard test specimens (ISO 527-2/1BB) of polymer films prepared by solvent casting. In each experiment the strain rate was 5 mm·min^{-1}.

Dynamic mechanical thermal analysis (DMTA) was performed on a Gabo Eplexor 25 N (Gabo, Ahlden, Germany) using standard test specimen (ISO 527-2/1BB) punched from the polymer network films. All experiments were performed in temperature sweep mode with a constant heating rate of 2 K·min^{-1} and a frequency of 1 Hz. The polymer films were investigated in a temperature interval from –100 to 100°C.

Polyurethane Synthesis

Prior performing the robot assisted synthesis the reactors were dried at 180 °C for 24 h. The solutions of OCL-diOH and OTHF-diOH (molar ratio between OCL-diOH and OTHF-diOH 1:1) in dimethyl carbonate (resulting concentration 0.17 g·mL^{-1}) were transferred using a 10 mL syringe of the 4-needle head unit with a pipetting speed of 4 mL·min^{-1}. The TMDI (1.7 mmol·mL^{-1}) and the catalyst solution with dibutyltin dilaurat (0.1 weight content with respect to oligomer) were transferred with a 1 mL syringe (pipetting speed of 0.5 mL·min^{-1}) to the reactors, which were heated to 80 °C and vortexed with 700 rpm for 24 h. Afterwards the reaction products were dried, dissolved in dichloromethane, precipitated from cold hexane, filtered off, washed with cold hexane, and dried under vacuum until constant weights were achieved.

RESULTS AND DISCUSSION

Synthesis of Polyurethanes

Polyurethanes based on OCL and OTHF were synthesized by HT synthesis using a robot assisted synthesizer platform (Figure 1). The oligomers were transferred via volumetric transfer to the reactor blocks to which the diisocyanate (between 60 mol% and 140 mol% isocyanate in relation to hydroxy end groups) as coupling agent and dibutyltin dilaurate as catalyst were added. The polyaddition reaction was performed in dimethyl carbonate at 80 °C for 24 h under nitrogen atmosphere.
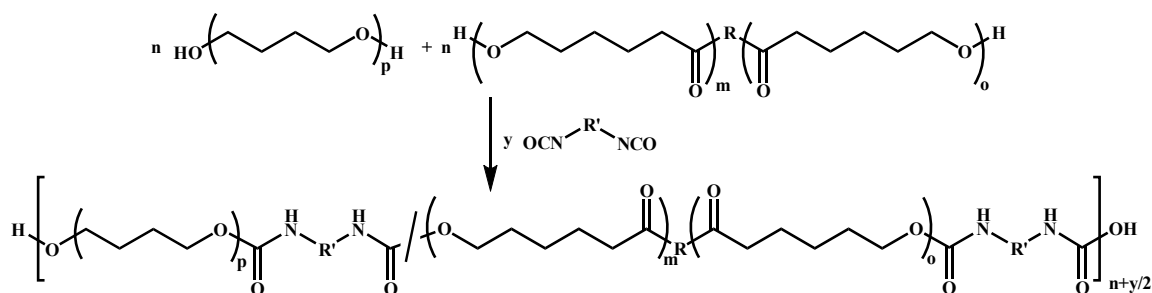
Figure 1. Synthesis of polyurethanes based on OCL and OTHF via polyaddition reaction with diisocyanates.

The resulting molecular weights of PUs were analyzed by HT-GPC measurements (standard calibration). The weight averages of molecular weights (M_w) were determined for comparison the efficiency of the PUs synthesis (Figure 2). The successful polyaddition reaction via urethane synthesis was reflected by the increase in overall molecular weight for all chain lengths of the OCL precursors. In case of OCL of 2 kg·mol^{-1}, the highest molecular weight was achieved when a diisocyanate content of 122.5 mol% was used resulting in $M_w = 260 \pm 30$ kg·mol^{-1}. This deviation of the molar ratio between reactive groups was attributed on the one hand to the unknown exact number of reactive end groups of the oligomeric precursors used and on the other hand to the reactivity of diisocyanate in addition to water in the reactors and solvents [10]. Here, water would reduce the number of diisocyanate groups, which are needed for the polyaddition reaction to generate PUs. Furthermore, allophanate branching's could be created, which would also increase the optimum of the diisocyanate content [11]. An optimum of TMDI was also observed for PUs based on the OCL of 4 kg·mol^{-1}. Here, $M_w = 100 \pm 10$ kg·mol^{-1} was achieved with 120 mol% of isocyanate groups and $M_w = 90 \pm 10$ kg·mol^{-1} was obtained with OCL 8 kg·mol^{-1} as precursor when 120 mol% of reactive groups from TMDI were used. Furthermore, it was observed that the chain length of the OCL precursors affected the maximum molecular weights of PUs. When M_w decreased the chain length of the prepolymer was increased. This observation was attributed to the lowered mobility of the polymer chain segments [12] with increasing chain length of OCL as well as to the lower number of terminal groups and by this a higher influence of side reactions like reaction with hydroxy groups of the glassware.
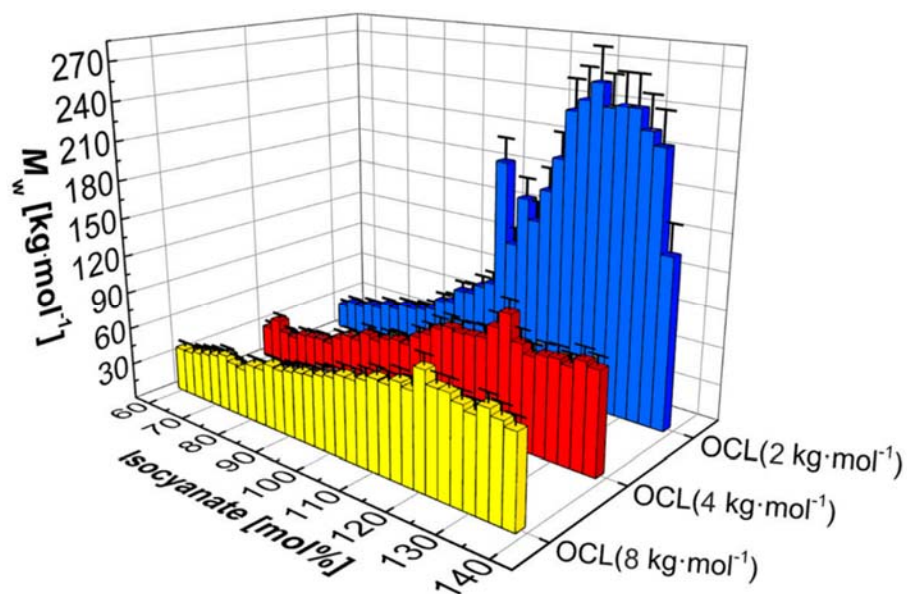

Figure 2. Weight average molecular weight as function of the chain length of the OCL precursor and molar ratio of isocyanate groups. Error bars indicate the error of GPC measurements (±10%).

Thermal and Thermomechanical Properties of Polyurethanes

The thermal properties of PUs were analyzed by means of DSC measurements in order to investigate the influence of the PU composition, chain length of the OCL precursor, and overall molecular weight of multiblock copolymers on the melting transition temperature (T_ms). The T_ms of the second heating run are compiled in Table 1.

The first $T_{m,1}$ was attributed to the melting transition of OTHF segments in PUs and ranged between 18 °C and 25 °C. The second melting transition of the integrated OCL denominated as $T_{m,2}$ was affected by the integrated OCL chain length, by the overall molecular weight of PUs, and by the composition of PUs (content of created urethane bonds). This finding agreed well with literature [11, 13, 14]. PUs based on OCL 2 kg·mol^{-1} provided $T_{m,2}$ between 41 °C and 35 °C, OCL 4 kg·mol^{-1} provided $T_{m,2}$ about 48 °C, and for PUs with OCL 8 kg·mol^{-1} a melting transition about 54 °C was obtained [15]. Furthermore, the melting peaks of OTHF and OCL were slightly reduced when PUs of higher M_w were investigated, which might be attributed to the raised number of urethane bonds integrated in the multiblock copolymers and potential entanglements limiting the OTHF and OCL crystallization. The urethane bonds would create strong hydrogen bonds, which can interfere with the crystallization process of semi-crystalline oligomers and would therefore reduce T_m [16, 17]. Furthermore, it was observed that the molecular weight significantly influenced the thermal properties of PUs with OCL 2 kg·mol^{-1}. While PUs with $M_w \leq 80$ kg·mol^{-1} exhibited two separated melting transitions, overlapping signals for T_m were detected for PUs of $M_w > 100$ kg·mol^{-1}. Here, a lower ratio between urethane bonds to CL repeating units is obtained for PUs based on OCL 2 kg·mol^{-1} (in contrast to other PUs with OCL 4 or 8 kg·mol^{-1}). Therefore, the interaction with hydrogen bonds is more pronounced resulting in a higher influence on crystallization processes. Furthermore, only a slight interspace of 16 °C is present between $T_{m,1}$ and $T_{m,2}$ for these type of PUs with low molecular weight, whereby the baseline separation of melting transitions can easily be abrogated by an increasing content of urethane bonds.

Table 1. Characterization of polyurethanes named OCL(x)OTHF$_y$ (x: chain length of utilized OCL in kg·mol^{-1}, y: M_w of PU) with determination of melting temperature (T_ms), storage modulus (E') and elongation at break (ε_b).

Sample-ID	$T_{m,1}$ [°C]	$T_{m,2}$ [°C]	E' at 0 °C [MPa]	E' at 30 °C [MPa]	ε_b at 0 °C [%]	ε_b at 30 °C [%]
OCL(2)OTHF$_{40}$	25 ± 1	41 ± 1	220 ± 20	70 ± 20	10 ± 5	10 ± 5
OCL(2)OTHF$_{80}$	25 ± 2	35 ± 1	170 ± 20	50 ± 10	280 ± 10	110 ± 10
OCL(2)OTHF$_{200}$	23* ± 2		100 ± 10	30 ± 10	350 ± 20	350 ± 20
OCL(2)OTHF$_{260}$	23* ± 2		80 ± 10	20 ± 10	780 ± 20	510 ± 20
OCL(4)OTHF$_{40}$	21 ± 1	49 ± 2	260 ± 20	90 ± 10	10 ± 5	20 ± 10
OCL(4)OTHF$_{70}$	19 ± 2	49 ± 1	200 ± 10	70 ± 10	70 ± 20	70 ± 20
OCL(4)OTHF$_{80}$	18 ± 1	48 ± 2	210 ± 10	60 ± 10	280 ± 40	100 ± 20
OCL(4)OTHF$_{100}$	18 ± 3	48 ± 2	180 ± 10	60 ± 10	830 ± 90	640 ± 40
OCL(8)OTHF$_{60}$	22 ± 1	55 ± 1	440 ± 30	220 ± 20	20 ± 10	10 ± 5
OCL(8)OTHF$_{70}$	21 ± 2	54 ± 2	340 ± 20	180 ± 10	130 ± 20	80 ± 20
OCL(8)OTHF$_{80}$	21 ± 2	54 ± 2	380 ± 30	200 ± 10	580 ± 40	520 ± 30
OCL(8)OTHF$_{90}$	21 ± 3	54 ± 1	370 ± 30	190 ± 10	870 ± 70	830 ± 20

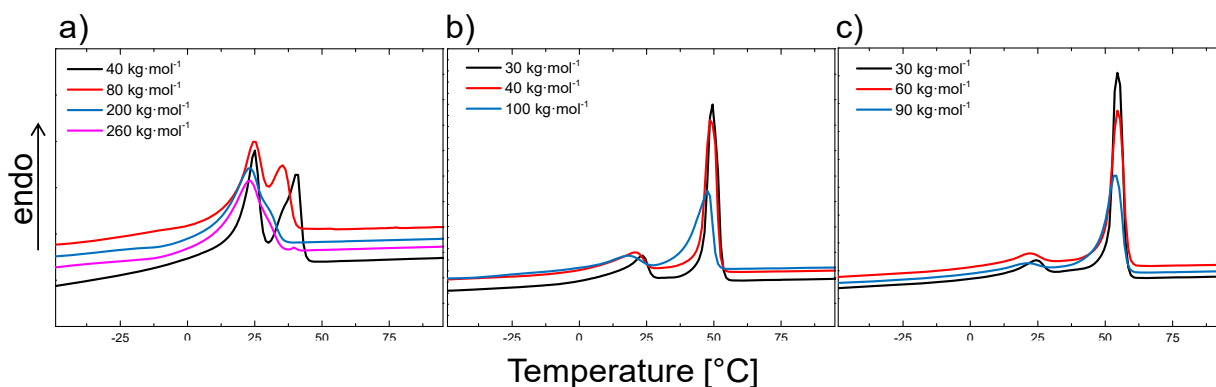* overlapping melting transition towards one broad peak

Figure 3. Thermal Properties of PUs based on OTHF and OCL with chain lengths of a) 2 kg·mol^{-1}, b) 4 kg·mol^{-1}, and c) 8 kg·mol^{-1}.

In order to analyze the mechanical properties as a function of temperature, which are important values for the processing of PUs, the storage moduli (E') were investigated by DMTA measurements and are listed in Table 1. Below the melting transition of OTHF and OCL, E' decreased with increasing M_w of PUs from 220 MPa to 80 MPa when OCL 2 kg·mol^{-1} was used for multiblock copolymer synthesis. This change in mechanical behavior was attributed to the hindered crystallization when M_w of PUs is increased, which would raise the number of urethane bonds. Here, hydrogen bonds created by urethane units act as weaker interactions between polymer chains in contrast to crystalline domains. Hence, the stiffness of PUs decreases with a decreasing amount of crystalline fraction. When PUs were synthesized by means of OCL with a higher chain length, E' was increased and was obtained between 260 MPa and 180 MPa for PUs based on OCL 4 kg·mol^{-1} and E' from 440 MPa to 370 MPa was achieved when OCL 8 kg·mol^{-1} was used. This increase in E' was also attributed to the crystallization behavior of the oligomeric precursors resulting in an increased stiffness of the material with increasing crystallinity (lower content of urethane bonds). In addition, while the molar ratio between OCL and OTHF precursors is constant for the three different series of PUs, the weight content of the integrated oligoester increases with increasing chain length of OCL. For this reason, PUs based on OCL 8 kg·mol^{-1} possess a higher amount of crystalline domains within OCL segments compared to PUs with OCL 2 kg·mol^{-1}. Accordingly, the chain length of OCL precursors, which controls the degree of crystallinity, presents a key parameter to adjust mechanical properties. This finding, where the mechanical properties of multiblock copolymers is directed by the molecular weight of precursors, agrees well with reported PUs based on OCL and oligo(L-lactide acid) [18].

The mechanical properties of PUs were controlled by their thermal transitions. At 30 °C E' was drastically reduced for all multiblock copolymers, which was attributed to the transition from the semi-crystalline to the amorphous state of OTHF and therefore to a reduction of crystalline domains within PUs.

The elongation at break (ε_b) determined by tensile tensile tests is affected by intermolecular interactions and was therefore controlled by the M_w of PUs, OCL chain length, as well as by the temperature. Here, ε_b increased when the overall molecular weight of multiblock copolymers increased. An ε_b between 780% and 870% was obtained for high molecular weight PUs at 0 °C. Polymer chains in an amorphous state would be deformed preferentially when an external force is applied [19, 20]. Here, chain segments in their random coil formation will be stretched according to the deformation direction. In case of crystalline domains (acting as physical crosslinks), the chain mobility is reduced and an exceeding force would result into sliding or ripping of these crystalline fractions. Hence, an increasing amorphous character (as result of an increasing urethane content) would increase the elongation at break as detected for PUs of increasing M_w. When the temperature was increased to 30 °C, ε_b was slightly reduced to a maximum between 510% and 830%. Furthermore, ε_b increased when the chain length of OCL precursors was increased. This phenomenon might be attributed to the ratio

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between crystalline and amorphous fractions within OCL domains. While a higher number of crystalline domains (physical netpoints) can be obtained when OCL 8 kg·mol^{-1} is used (in comparison to OCL 2 and 4 kg·mol^{-1}), also an enlargement of the chain length within an amorphous region cannot be excluded. As result, a higher ratio between amorphous to crystalline fraction for PUs based on 8 kg·mol^{-1} can be obtained, whereby also the elongation until break of the material would be increased.

CONCLUSION

Multiblock copolymer based PUs with OTHF and OCL as oligomeric precursors were created by polyaddition reaction using a robotic synthesizer platform and TMDI as linker. The utilization of this HT technology enabled the synthesis of PUs with high molecular weights without an exact investigation of end group functionality of oligomeric precursors and the influence of the OCL chain length (2, 4, or 8 kg·mol^{-1}) on different material properties was analyzed. For the three PU series an optimum ratio between hydroxy and isocyanate groups between 120 mol% and 122.5 mol% was obtained, which was attributed to potential side reactions of diisocyanate groups with traces of water. The resulting melting transitions of synthesized PUs were well separated for PUs with low M_w, and a reduced separation was detected when the overall molecular weight of the multiblock copolymers was increased. In case of PUs based on OCL 2 kg·mol^{-1} even an overlapping towards one broad T_m was obtained. Furthermore, thermomechanical properties could be adjusted by the chain length of OCL and M_w of PUs. In this way this work provides a target-oriented modulation of melting transitions of PUs towards specific applications by using oligomeric semi-crystalline precursors.

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