Ring-Opening Homo- and Copolymerization of α-Methylene-ϵ-caprolactone

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ABSTRACT: The ring-opening polymerization of α-methylene-ϵ-caprolactone (α-MCL) is presented for the first time. Poly(α-MCL) was characterized by ^{1}H NMR, GPC, DSC, and MALDI-TOF. The ring-opening copolymerization of α-MCL with ϵ-caprolactone (ϵ-CL) yields to formation of radically cross-linkable poly(ϵ-CL)s with melting points in the range of 35−54 °C depending on the copolymer composition.

Introduction

Various exo-methylene O-heterocycles are known to undergo both free radical and ring-opening polymerization at appropriate conditions.[1a,b] Unfortunately, up to now, only a few examples of exo-methylene lactones have been described in the literature.

Akkapeddi et al. were the first who reported about the radical polymerization of α-methylene-γ-butyrolactone (α-MBL), which can be regarded as a cyclic analogue of methyl methacrylate.[2a,b] Systematic investigations about the radical homo- and copolymerization of α-MBL and its derivatives followed.[3a−f] Furthermore, it was found that the high ring stability of γ-butyrolactone, including that of α-MBL, usually prevents the normal ring-opening homopolymerization[4] under standard conditions mainly because of a positive change of polymerization enthalpy (ΔH_p^0).[5]

However, reports about the polymerization of higher α-methylenelactones are relatively rare. The main reason for that may be due to the fact that these unsaturated lactones are difficult to make because of their low ring stability under the conditions of α-substitution. As an exception, only the ring-opening polymerization of 2-methylene-4-oxa-12-dodecanolide leading to radical cross-linkable polyesters has been investigated up to now.[6] Surprisingly, regarding our knowledge, no information is available in the literature about the polymerization of α-MCL **4** although the corresponding unmodified ϵ-caprolactone (ϵ-CL)-itself is a well-known monomer for various polyester syntheses that has even found industrial application.[7] Additionally, poly(ϵ-caprolactone) dimethacrylates have been described to be suitable precursors to create shape memory materials after radically cross-linking.[8]

Thus, in this paper we wish to report for the first time about the ring-opening homopolymerization of α-MCL **4** and the corresponding copolymerization with ϵ-CL **1**, focusing also on the crystalline character of the samples. We finally describe our first experiments about the free radical copolymerization of methylene function of α-MCL **4** with styrene as comonomer.

Experimental Section

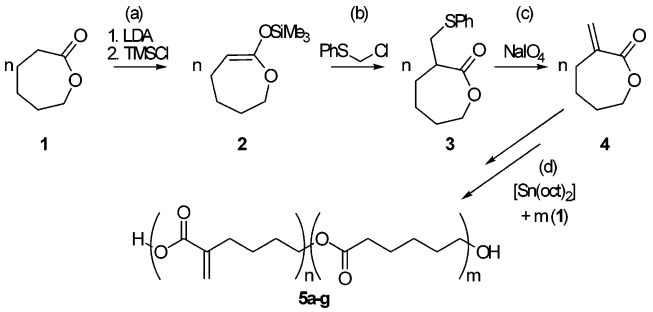
Materials and Characterization. Diisopropylamine (Merck), *n*-butyllithium (Acros), chlorotrimethylsilane (Acros), chloromethylphenyl sulfide (Aldrich), sodium (metha) periodate (Fluka), and tin(II) 2-ethylhexanoate (Aldrich) were used as received. ϵ-Caprolactone (Fluka) was distilled over calcium hydride and stored under a nitrogen atmosphere. The synthesized polymers were characterized by ^{1}H NMR spectroscopy using a Bruker Avance DRX 500 spectrometer at 500.13 MHz for hydrogen nuclei and 125.99 MHz for carbon nuclei, using $CDCl_3$ as solvent. The δ-scale was calibrated to TMS. Thermal properties were determined using a Mettler Toledo DSC822 controller apparatus in a temperature range between −10 and 100 °C at a heating rate of 10 °C/min. The melting point values are reported as the average of the peak maxima of the second and the third measurements. Gel permeation chromatography (GPC) was performed on a Waters system equipped with a set of three 300 × 8 mm^2 MZ Gel SDplus columns (with 10^4, 10^3, and 10^2 Å porosity) in THF relative to poly(styrene) standards. Matrix-assisted laser desorption−ionization time-of-flight spectrometry (MALDI-TOF) was performed on a Bruker Ultraflex TOF mass spectrometer using the linear mode and a 337 nm nitrogen laser. The samples were dissolved in chloroform and mixed with a dithranol solution. For optical polarization light microscopy

Table 1. Characterization of α-MCL Homo- and Copolymers

entry	[ϵ-CL]/[α-MCL]	M_n[a]/10^3 g mol^{-1}	PD[a]	T_m[b]/°C	yield/%
5a	0	1.3	1.7	28.6	84
5b	2.5	9.5	1.9	34.8	93
5c	5	13.4	1.8	43.6	80
5d	10	13.6	1.8	49.5	97
5e	20	11.3	1.8	51.2	93
5f	40	10.7	1.9	52.7	92
5g	60	11.6	1.8	53.6	89

[a] GPC with poly(styrene) calibration. [b] DSC.

Scheme 1. (a−c) Synthesis of α-MCL 4;[9] (d) Preparation of Homopolymer 5a and of Copolymers 5b−g



	5a	5b	5c	5d	5e	5f	5g
$\frac{m}{n}$	0	2.5	5	10	20	40	60

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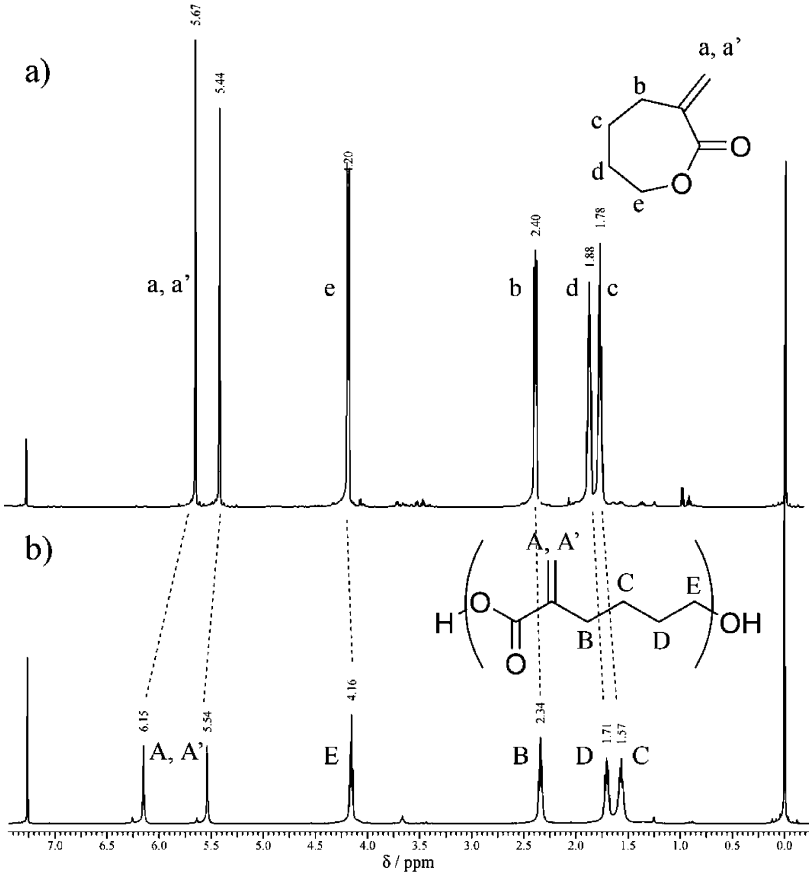


Figure 1. ^{1}H NMR spectra of (a) α-MCL **4** and (b) poly(α-MCL) **5a**.

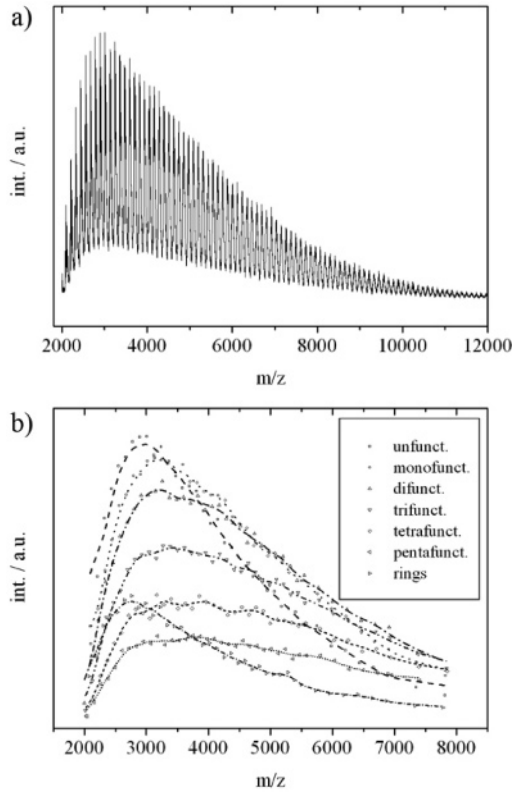


Figure 2. (a) MALDI-TOF mass spectrum (linear mode) of the reprecipitated poly(α-MCL-*co*-ϵ-CL) **5e**. (b) Mass fractions of poly-(α-MCL-*co*-ϵ-CL) **5e** with various proportions vinylidene groups as a function of molar mass (*m*/*z*).

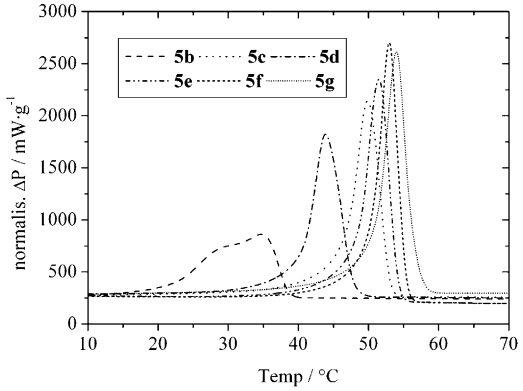


Figure 3. DSC scans of poly(α-MCL-*co*-ϵ-CL)s **5b**−**g** (second heating: −10 to 100 °C; 10 °C min^{-1}).

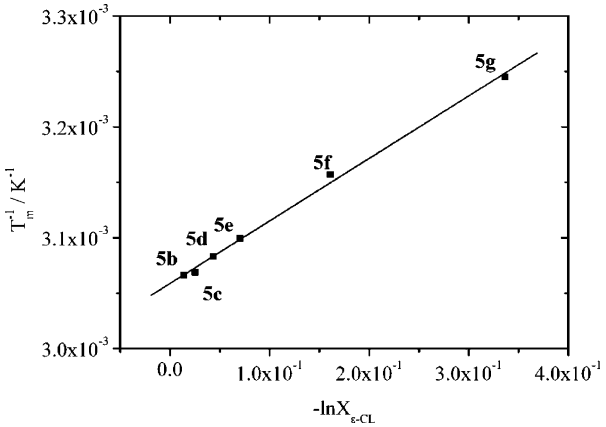


Figure 4. Dependence of the reciprocal melting points on the negative natural logarithmic mole fraction of ϵ-CL **1**.

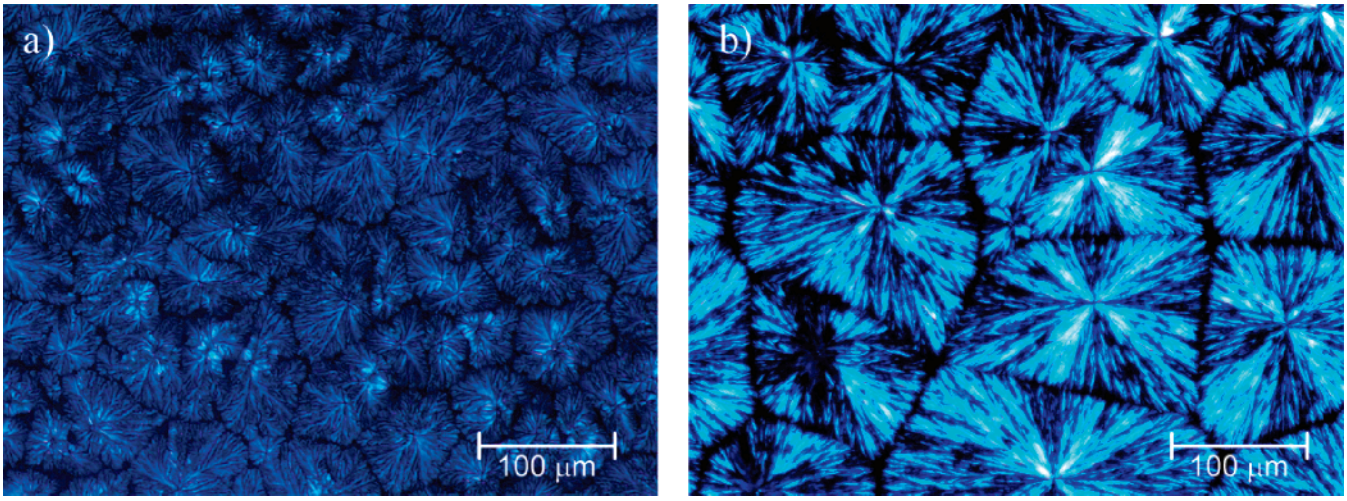


Figure 5. Spherolitic structures of (a) poly(α-MCL-*co*-ϵ-CL) **5b** and (b) poly(ϵ-CL).

we used an Olympus BH-2 microscope equipped with an Olympus DP12 microscope digital camera system. Polymer samples were crystallized from solution (10 mg in 2 mL of THF) on a microscopic slide.

Synthesis of α-Methylene-ϵ-caprolactone (α-MCL) 4. α-MCL **4** was prepared from ϵ-CL **1** according to the procedure of Takeda:[9] a colorless oil, $R_f = 0.34$ (hexane: AcOEt 2:1) (lit.[9] $R_f = 0.34$). ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.76-1.81$ (m, 2H, $-OCH_2C\mathbf{H}_2-$), 1.86−1.90 (m, 2H, $-OCH_2CH_2C\mathbf{H}_2-$), 2.40 (t, 2H, $^3J_{HH} = 5.8$ Hz, $-C(=O)C(=CH_2)-C\mathbf{H}_2-$), 4.20 (t, 2H, $^3J_{HH} = 4.9$ Hz, $-OC\mathbf{H}_2CH_2-$), 5.43 and 5.67 ppm (each s, 1H,C(=C$\mathbf{H}_2$)).

Synthesis of Poly(α-methylene-ϵ-caprolactone) 5a and Poly(α-methylene-ϵ-caprolactone-*co*-ϵ-caprolactone)s 5b−g. 0.50 g (4.0 mmol) of α-MCL was mixed with 2 mol % of the catalyst tin 2-ethylhexanoate in a 10 mL vial sealed with a septum (for copolymerization ϵ-CL was added according to Table 1). The mixture was heated to 130 °C for 3 h. After cooling to room temperature, the reaction mixture was diluted with 5 mL of chloroform and poured into 250 mL of a mixture of cold hexane/diethyl ether (1/1). The precipitated polymer was isolated by filtration and dried under vacuum. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.54-1.60$ (m, 2H, $-OCH_2C\mathbf{H}_2-$), 1.68−1.74 (m, 2H, $-OCH_2CH_2C\mathbf{H}_2-$), 2.34 (t, 2H, $^3J_{HH} = 7.4$ Hz, $-C(=O)C(=CH_2)-C\mathbf{H}_2-$), 4.16 (t, 2H, $^3J_{HH} = 6.6$ Hz, $-OC\mathbf{H}_2CH_2-$), 5.54 and 6.15 ppm (each s, 1H,C(=C$\mathbf{H}_2$)).

Synthesis of Poly(α-methylene-ϵ-caprolactone-*co*-styrene) 6. 0.50 g (4.8 mmol) of styrene was mixed with 0.30 g (2.4 mmol) of α-MCL and 0.023 g (0.144 mmol, 2 mol %) of 2,2′-azobis(isobutyronitrile) (AIBN). After the addition of 0.25 mL of DMF the mixture was purged with nitrogen for 10 min. The mixture was sealed with a septum and heated under stirring to 60 °C for 24 h. After cooling to room temperature, the reaction mixture was diluted with 5 mL of THF and poured into 250 mL of cold methanol. The precipitated polymer was isolated by filtration and dried under vacuum. Yield: 0.74 g (93%). ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.8-2.8$ (backbone and ring), 3.5−4.3 ($-OC\mathbf{H}_2-$), 6.4−7.4 ppm (phenyl). FT-IR: $\tilde{\nu} = 3082$ (w), 3059 (w), 3025 (w), 3000 (w), 2974 (w), 2853 (w), 1712 (s), 1601 (w), 1583 (w), 1493 (s), 1452 (w), 1391 (w), 1357 (w), 1282 (w), 1221 (w), 1162 (s), 1068 (s), 1029 (s), 966 (w), 909 (w), 846 (w), 812 (w), 757 (s), 699 cm^{-1} (ss). DSC: $T_g = 83$ °C. GPC: $M_n = 5040$ g mol^{-1}, PDI = 2.0.

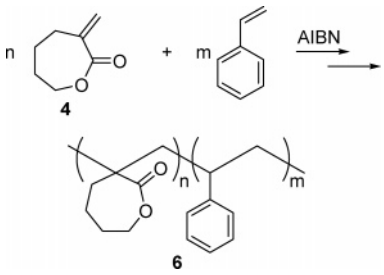
Results and Discussion

α-Methylen-ϵ-caprolatone (α-MCL) **4** was synthesized in three steps (Scheme 1). First, ϵ-caprolactone **1** was O-silylated, followed by a phenylthioalkylation and completed by the oxidative sulfur removal as described in the literature.[9] The ring-opening homo- and copolymerizations of α-MCL **4** were carried out by use of tin octoate as transesterification catalyst (Scheme 1). This metal catalyst is one of the most common catalysts for the successful polymerization of lactones and lactides. The obtained results of polymerization experiments are summarized in Table 1. The conversion of α-MCL **4** was estimated by ^{1}H NMR spectroscopy. For that, the relative ratio between the intensity of the hydrogen atoms of the double bond in the α-MCL **4** (singlet at 5.43 and 5.67 ppm) was compared to the hydrogen atoms of the methylene group of the polyesters **5a**−**g** (singlet at 5.64 and 6.15 ppm). These measurements indicate a complete conversion of α-MCL **4** after 3 h. However, the conversion of α-MCL 4 is slower compared to ϵ-CL **1**. Within the detection limit of ^{1}H NMR spectroscopy, the exo-vinylidene group remains intact. Thus, the ratio of the relative integrals of the hydrogen signals of the double bond and the integrated ϵ-hydrogen signals are nearly exactly 1:1:2, as expected. The molecular weight distributions were determined by GPC with poly(styrene) as standards. It was found that, under the applied conditions, the achieved number average of the molecular weights for the homopolymer **5a** is rather low with 1300 g mol^{-1}. To carry out ring-opening copolymerizations, we used mole fractions of α-MCL **4** in the mixture with ϵ-CL **1** from 0.016 up to 1.0 (Table 1). The achieved M_n values of the obtained copolymers **5b**−**g** are in the range of 10^3-10^4 g mol^{-1}.

To study the molecular composition of poly(α-MCL-*co*-ϵ-CL)s **5b**−**g** depending on the concentrations of the incorporated comonomers, we investigated the mass fractions of **5e** by use of MALDI-TOF. Therefore, the mass spectra were transformed into the molar mass distribution curves for various abundances of incorporations of α-MCL **4**. In Figure 2a, the MALDI-TOF mass spectrum (linear mode) of the reprecipitated poly(α-MCL-*co*-ϵ-CL) **5e** is shown as a typical example. Figure 2b shows the complete set of distribution curves obtained for the various abundances of incorporations of α-MCL **4**. The incorporation of α-MCL **4** extends from zero to five with decreasing frequency of each distribution. In addition to the linear chains, rings of unfunctionalized poy(ϵ-CL) can be identified.

According to DSC measurement, poly(α-MCL) **5a** has a melting point of 28.6 °C. The relatively low melt enthalpy of 220 ± 62 J/mol of poly(α-MCL) **5a** indicates a rather low tendency of crystallization. It was interesting to study the dependence of the melting points on the polymer composition. As a result from our DSC measurements, Figure 3 shows the second heating segment (−10 to 100 °C; 10 °C min^{-1}) of the obtained

Scheme 2. Free Radical Copolymerization of α-MCL (4) with Styrene



poly(α-MCL-*co*-ϵ-CL)s **5b**−**g**. It becomes clearly visible that an increasing amount of α-MCL **4** in the copolyester leads to a lowering of the melting point of the material. Regarding the literature, eq 1 describes the influence of noncrystallizable components on the melting point of a crystalline material. T_m means the melting point of the polymer, T_m^0 is the melting point for the homopolymer with an infinite molecular weight, and ΔH_m is the repeating unit molar heat of fusion.[10] According to our results, the substitution of activity (*a*) by the mole fraction ($X_{\epsilon-CL}$) is an ideal approximation (eq 2).

$$\frac{1}{T_m} - \frac{1}{T_m^0} = -\frac{R}{\Delta H_m}\ln(a) \quad (1)$$

$$\frac{1}{T_m} - \frac{1}{T_m^0} = -\frac{R}{\Delta H_m}\ln(X_{\epsilon-CL}) \quad (2)$$

As shown in Figure 4, the dependence of the reciprocal melting point on the mole fraction of ϵ-CL **1** was all linear with respect to negative natural logarithmic mole fraction of ϵ-CL **1**. Values for T_m^0 = 53.6 °C and ΔH_m = 14.8 kJ/mol were calculated from the straight line (*y*-axis intercept and slope, respectively) and are confirmed by values from literature[11] (T_m^0 = 55 °C and ΔH_m = 15.4 kJ/mol).

The crystallization behavior of poly(α-MCL-*co*-ϵ-CL)s (**5b**−**g**) was additionally investigated by optical polarization light microscopy. As shown in Figure 5, poly(α-MCL-*co*-ϵ-CL) (**5b**) shows only a weak formation of spherolites (Figure 5a) compared to the picture of pure poly(ϵ-CL) (Figure 5b).

Finally, to evaluate the free radical vinyl polymerization properties of α-MCL **4**, a mixture of styrene and α-MCL **4** (2:1) was kept in DMF at 60 °C in the presence of AIBN for 24 h to give the copolymer with number-average of molecular weights of 5000 g mol^{-1} nearly quantitatively (Scheme 2).

Conclusion

It can be confirmed from the above-described results that α-MCL **4** is a new type of ring-opening monomer characterized by the existence of two different polymerizable functions. Ring-opening copolymerizations of α-MCL **4** and ϵ-CL **1** yield novel radically cross-linkable unsaturated polyesters. The melting points are strongly dependent on the polymer composition according to general equations and are in the range of 36−54 °C.

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