Ring-Opening Polymerization of the Trimethylcaprolactone Isomers and Investigations of Their Polymerizability

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ABSTRACT: 3,5,5′-Trimethylcaprolactone and 3,3′,5-trimethylcaprolactone are characterized with various spectroscopic methods. Their ability of ring-opening is correlated with semiempirical calculations and is compared to unsubstituted lactones of different ring sizes. The results of the computations are verified by measurements of reaction kinetics of the polymerizations.

Introduction

The ring-opening polymerization (ROP) of ϵ-caprolactone has been widely studied in recent years. There are a lot of publications describing miscellaneous methods with different initiators of the ROP of ϵ-caprolactone. The reaction can be lipase-catalyzed,[1−3] metal-catalyzed,[4−14] and anionically[15,16] or cationically[17] initiated.

In contrast to it, trimethylcaprolactone isomers, 3,5,5′-trimethylcaprolactone (TMCL-1) and 3,3′,5-trimethylcaprolactone (TMCL-2), are two lactones which are not sufficiently investigated.[18] Isophorones can be synthesized through an alkaline catalyzed condensation of three molecules of acetone. Through hydrogenation of the isophorones and subsequent Baeyer−Villiger−oxidation trimethylcaprolactone isomers TMCL-1 and TMCL-2 are obtained. This isomer mixture is composed of two enantiomer pairs (R, S). Scheme 1 shows the reaction scheme of the synthesis route of trimethylcaprolactone and its polyester from acetone.

Whereas the trimethylcaprolactones come from the "C_3-chemistry", ϵ-caprolactone originates from the "C_6-chemistry". The trimethylcaprolactone isomers are a colorless liquid with a low viscosity and a boiling temperature of 92 °C (0.8 mbar). Up to now, their abilities of polymerizations are not researched in detail. Thus, the aim of this work is to analyze the exact composition of the trimethylcaprolactone isomers from various spectroscopy methods to prove their polymerizability and to compare it to unsubstituted lactones of different ring sizes.

Experimental Section

Materials. Trimethylcaprolactone was obtained from Evonik Industries AG (Degussa), dried over calcium hydride (CaH_2), vacuum-distilled, and stored under an argon atmosphere and over 4 Å molecular sieves. ϵ-Caprolactone was purchased from Aldrich, dried over calcium hydride, distilled under reduced pressure, and stored over 4 Å molecular sieves and under an argon atmosphere. Tin(II) 2-ethylhexanoate ($Sn(Oct)_2$) was purchased from Aldrich and used without further purification. Titanium(IV) *n*-butoxide ($Ti(O\text{-}nBu)_4$) (Aldrich, 97%) was used without further purification.

Characterizations. The ^{1}H NMR spectra were registered from solutions in deuterated chloroform as solvent on a Bruker DRX 500 operating at 500 MHz. The δ-scale was calibrated to TMS. The ^{13}C NMR spectra were registered from solutions in deuterated chloroform as solvent on a Bruker DRX 500 operating at 125 MHz.

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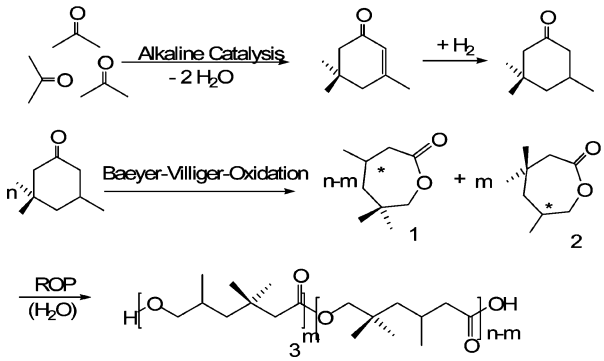
Scheme 1. Reaction Scheme of the Synthesis of Trimethylcaprolactone and Its Polyester



The δ-scale was calibrated to TMS. Gas chromatography was performed on a Thermo Finnigan Trace DSQ. HPLC measurements were performed on a Fa. Biotek Kontron Instruments system 525 with a 540 diode array detector and a Fa. Techsphere ODS-2-5μ column (125 mm length, 4.6 mm inside diameter). A solution of acetonitrile/ethanol/water (80:5:15 v/v/v) is used as eluent with a volume flow rate of 1.0 mL/min. The analysis was carried out with the software Kroma Systems 2000. TMCL concentrations were determined by peak area comparison to a standard RI response curve of known monomer concentrations. The evolution of degree of conversion vs time of ϵ-caprolactone polymerization was evaluated from the quantitative analysis ^{1}H NMR of aliquots extracted from reactive medium at different times and immersed immediately in a cold solution ($CDCl_3$). It was calculated from the ratio of number of moles of monomer that reacted to initial number of moles of monomer molecules for polymerization.

Polymerization. A representative experimental procedure was as follows: to a 25 mL two-neck, round-bottom flask equipped with septum and reflux condenser was added 10 g of TMCL (64.1 mmol). The reaction vessel was placed into a silicon oil bath and heated to 130 °C under stirring. $Sn(Oct)_2$ (2 mol %) was then added into the reaction vessel. Aliquots were taken after various time intervals as described.

Results and Discussion

The trimethylcaprolactone isomers show different signals at retention times of 5.46 and 5.56 min in the gas chromatograms. From the integration of the peak areas, a ratio of 70:30 of the composition of the constitution isomers TMCL-1 and TMCL-2 is calculated. In order to assign the signals to the isomers, ^{13}C and ^{1}H NMR spectra are taken from that mixture. Figure 1 shows the ^{13}C NMR spectrum. Because of the different position

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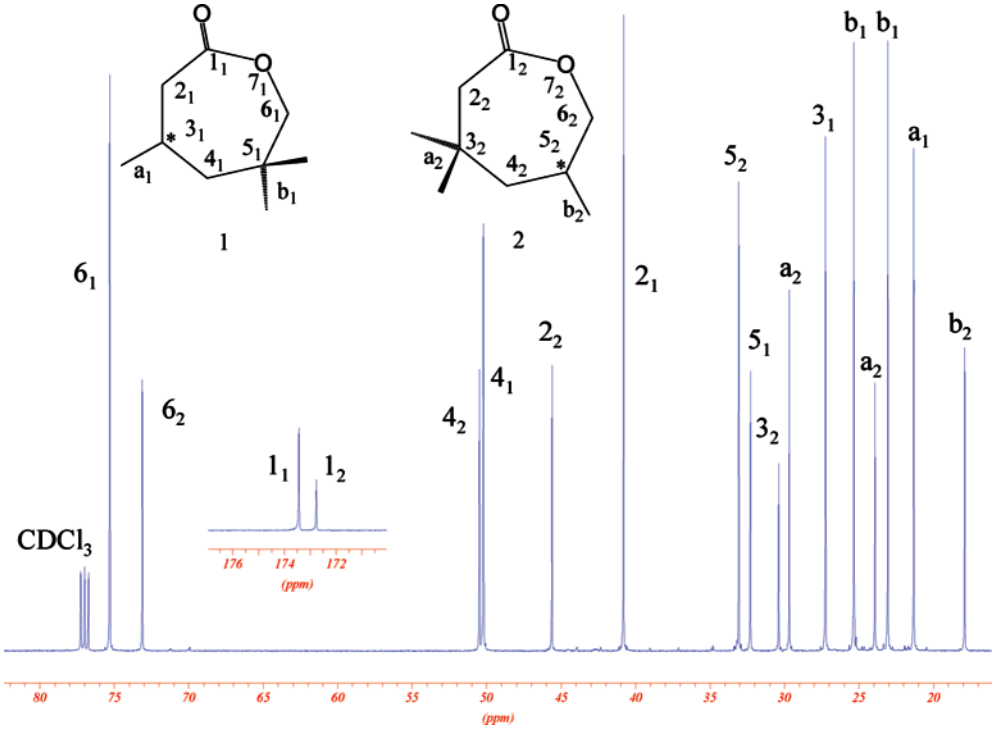


Figure 1. ^{13}C NMR spectroscopy of the trimethylcaprolactone mixtures TMCL-1 and TMCL-2 in $CDCl_3$.

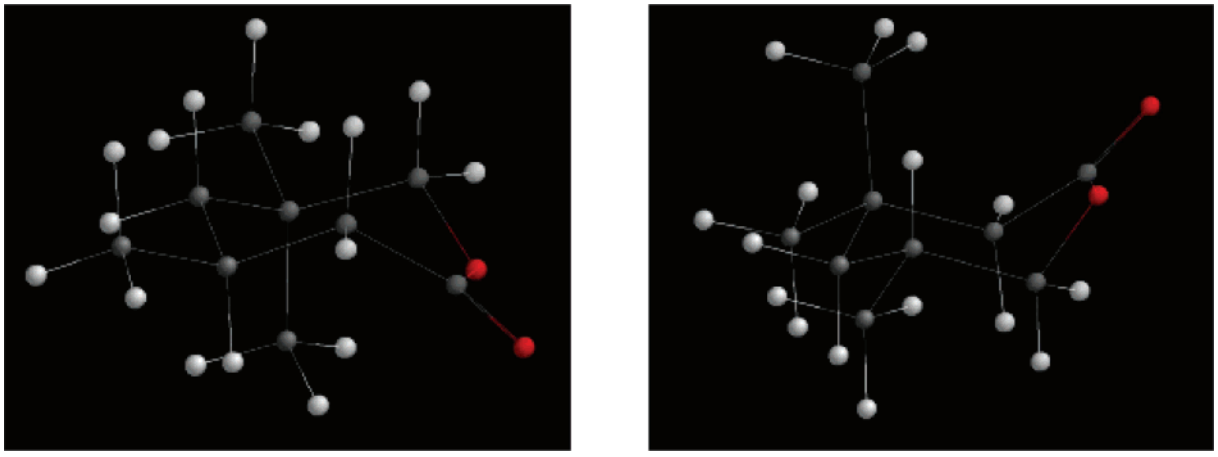


Figure 2. TMCL-1 (left) and TMCL-2 (right) in chair form.

of the methyl groups in TMCL-1 and TMCL-2, the C atoms should give different signals. Indeed, each peak can be assigned to a particular C atom. For example, the carbonyl C atoms of both isomers show signals at 173.4 ppm (TMCL-1) and 172.8 ppm (TMCL-2). The peaks at 75.3 and 73.1 ppm can be easily assigned to 6_1- and 6_2-C atoms. Through the average of the peak areas of each isomer in the ^1H NMR spectrum an exact ratio of 66:34 of the composition of the isomers can be obtained.

Through this analysis it becomes clear that TMCL-1 is available in excess in the isomer mixture. Thus, the two different signals in the gas chromatography can be assigned to the accordant isomers.

As mentioned above, the trimethylcaprolactone isomers show differences in gas chromatography and ^{13}C NMR spectroscopy. The two constitution isomers only differ in the position of the methyl groups. Accordingly, they should only have slight differences in their reactivities concerning to a polymerization. Additionally, their reactivities compared to other lactones are of particular interest. To answer these questions, semiempirical computations of diverse lactones were carried out on an AM1 level.

In accordance with Abraham and co-workers,[21] the computations of the trimethylcaprolactone isomers show that the rings are in chair form, the geometry with the lower energy (Figure 2).

Computation of the reaction enthalpy $\Delta(\Delta H_f)$, where ΔH_f is the heat of formation, for the simple ring-opening of the lactones with methanol to achieve the formation of the corresponding hydroxymethyl esters revealed that β-propiolactone has the highest reactivity and the lowest reaction enthalpy concerning a polymerization. The high ring stress of the four-membered ring is the reason for this behavior.

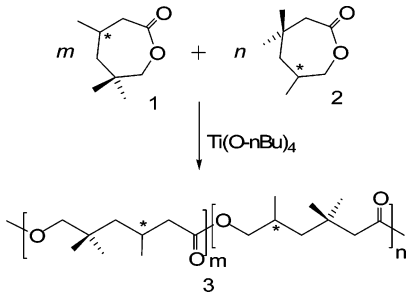
Corresponding to the decreasing ring stress, the reaction enthalpy increases from a four-membered ring (−399 kJ/mol) to a seven-membered ring (−264 kJ/mol). This is an increasing of 135 kJ/mol (34%). In the case of the trimethylcaprolactone isomers TMCL-1 is slightly energetically favored, although the

Table 1. Computation of ΔH_f (Heat of Formation) of Various Lactones and the Corresponding Methyl Esters and the Reaction Enthalpy $\Delta(\Delta H_f)$ of the Ring-Opening of the Lactones with Methanol

	C−O[a] [Å]	ΔH_f [kJ/mol]	$\Delta(\Delta H_f)$ [kJ/mol]
β-propiolactone	1.40	−227	
methyl ester	1.38	−625	−399
δ-valerolactone	1.37	−411	
methyl ester	1.38	−681	−270
ϵ-caprolactone	1.37	−436	
methyl ester	1.38	−700	−264
TMCL-1	1.37	−481	
methyl ester	1.38	−712	−231
TMCL-2	1.37	−482	
methyl ester	1.38	−709	−227

[a] Bond length of the single bond.

Scheme 2. Reaction Scheme of the Polymerization Reaction of Trimethylcaprolactone with Titanium(IV) *n*-Butoxide as Initiator



difference between the reaction enthalpies is only 4 kJ/mol (Table 1).

The bond length of the single bond between the carbonyl C atom and O atom can be an indicator of ring stress and reactivity because the catalyst attacks the lactone at this position. The data (Table 1) show that the C−O bond lengths do not differ very much so that further conclusions cannot be made.

In accordance with various investigations,[2,19,20] the data show that methyl-substituted lactones have a reduced polymerizability compared to unsubstituted ones.

These theoretical evaluations can be proved by measurements of the consumption of the trimethylcaprolactone isomers with gas chromatography during a polymerization reaction. The reaction scheme is shown in Scheme 2.

Figure 3 shows the changing of composition of the trimethylcaprolactone isomers during a polymerization. The concentration of TMCL-1 in the reaction solution rapidly decreases whereas TMCL-2 concentrates. This means that the TMCL-1 has a higher reactivity in the polymerization reaction compared to TMCL-2; it can be superiorly built in the polymer than TMCL-2. After 25 min, the ratio of the isomer composition changes from 69:31 to 55:45. This observation is in accordance with the theoretical calculations (Table 1).

In order to compare the polymerizability of TMCL with unsubstituted lactones, the kinetics of the polymerizations is analyzed via HPLC-measurements. Because the polymerization of ϵ-caprolactone is well studied, its polymerization is used as a standard reaction for comparisons. In Figures 4 and 5 the polymerizations of ϵ-caprolactone and TMCL with two different initiators $Sn(Oct)_2$ and $Ti(O\text{-}nBu)_4$ are compared.

As expected, the polymerizability of ϵ-caprolactone is higher in both cases than that of TMCL. This fact is also in agreement with the predication made above (Table 1). In the case of polymerization with $Sn(Oct)_2$ (Figure 4) the ROP of the ϵ-caprolactone only needs 1 h to reach a conversion of 94%, whereas the ROP of the trimethylcaprolactone isomers needs

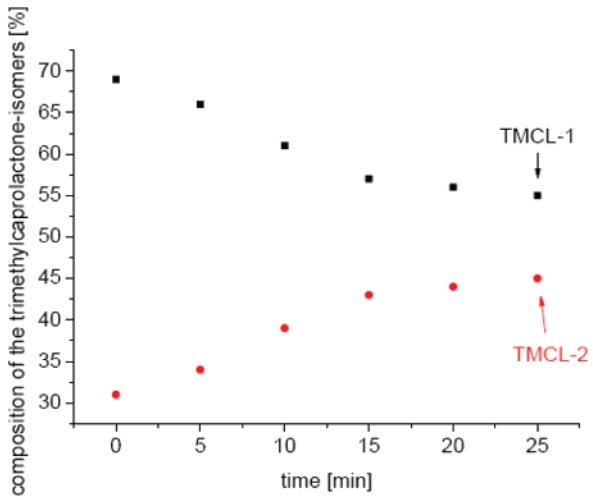


Figure 3. Composition of the trimethylcaprolactone isomers against time during a polymerization reaction with titanium(IV) *n*-butoxide as initiator in oil bath at 130 °C.

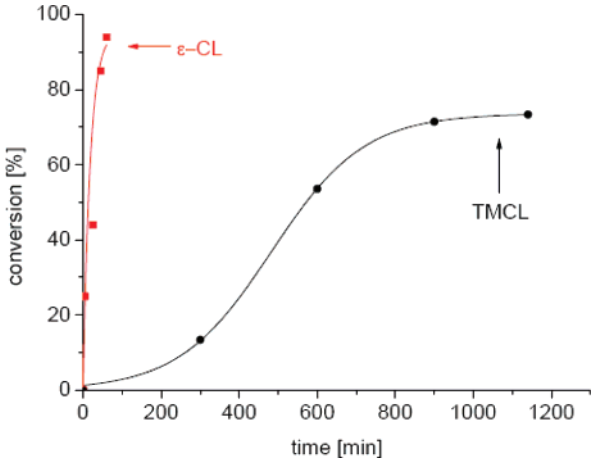


Figure 4. Time−conversion curves of polymerizations of ϵ-CL and TMCL with $Sn(Oct)_2$ (2 mol %) in bulk at 130 °C.

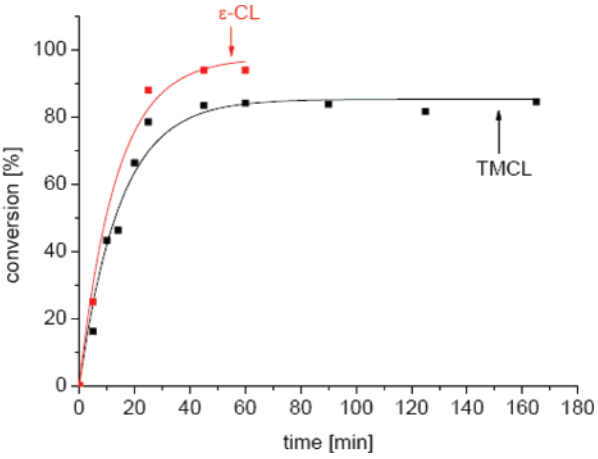


Figure 5. Time−conversion curves of polymerizations of ϵ-CL and TMCL with $Ti(O\text{-}nBu)_4$ (0.25 mol %) in bulk at 130 °C.

19 h to get a conversion of 73%. The new and surprising cognition is that the polymerizability of TMCL could be increased dramatically by using titanium(IV) *n*-butoxide instead of tin(II) 2-ethylhexanoate. In contrast, the kinetics of the polymerization reactions of ϵ-caprolactone with both catalysts shows only low differences (Figures 4 and 5). Until a conversion of 50% the polymerization time reduces from 11 h to 15 min,

and the absolut conversion increases to 84%. A lipase-catalyzed ROP of TMCL was not successful. The isomer mixture could not be polymerized.

Conclusion

In this work 3,5,5′-trimethylcaprolactone and 3,3′,5-trimethylcaprolactone were fully characterized by gas chromatography and ^{13}C NMR at first time. Concerning the reactivity of them and compared to unsubstituted lactones, it could be shown by computations and experiments that in fact both isomers have a minor polymerizability. In addition, the polymerizability of the trimethylcaprolactone isomers could be increased by using titanium(IV) *n*-butoxide instead of tin(II) 2-ethylhexanoate as initiator. Furthermore, the different reactivities of TMCL-1 and TMCL-2 that were predicted by the computations could be proved by measurements of concentrations of the trimethylcaprolactone isomers during a polymerization with titanium(IV) *n*-butoxide as initiator.

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References and Notes

(1) Kobayashi, S.; Uyama, H. *Adv. Biochem. Eng./Biotechnol.* **2001**, *71*, 241.
(2) Matsumura, S.; Kobayashi, S.; Ritter, H.; Kaplan, D. *Adv. Polym. Sci.* **2006**, *194*, 95.
(3) Gross, R. A.; Kaplan, D.; Swift, G. *ACS Symp. Ser.* **1998**, 648.
(4) Kowalski, A.; Duda, A.; Penczek, S. *Macromolecules* **2000**, *33*, 689−695.
(5) Kowalski, A.; Libiszowski, J.; Biela, T.; Cypryk, M.; Duda, A.; Penczek, S. *Macromolecules* **2005**, *38*, 8170−8176.
(6) Kowalski, A.; Duda, A.; Penczek, S. *Macromol. Rapid Commun.* **1998**, *19*, 567−572.
(7) Kricheldorf, H. R.; Bornhorst, K.; Hachmann-Thiessen, H. *Macromolecules* **2005**, *38*, 5017−5024.
(8) Storey, R. F.; Sherman, J. W. *Macromolecules* **2002**, *35*, 1504−1512.
(9) Libiszowski, J.; Kowalski, A.; Duda, A.; Penczek, S. *Macromol. Chem. Phys.* **2002**, *203*, 1694−1701.
(10) Ouhadi, T.; Stevens, C.; Teyssié, P. *Makromol. Chem. Suppl.* **1975**, *1*, 191−201.
(11) Liu, Y. C.; Ko, B. T.; Lin, C. C. *Macromolecules* **2001**, *34*, 6196−6201.
(12) Chen, H. L.; Ko, B. T.; Huang, B. H.; Lin, C. C. *Organometallics* **2001**, *23*, 5076−5083.
(13) Cayuela, J.; Bounor-Legaré, V.; Cassagnau, P.; Michel, A. *Macromolecules* **2006**, *39*, 1338−1346.
(14) Kricheldorf, H. R.; Berl, M.; Scharnagl, N. *Macromolecules* **1988**, *21*, 286−293.
(15) Cherdron, H.; Ohse, H.; Korte, F. *Makromol. Chem.* **1962**, *56*, 179.
(16) Hofman, A.; Slomkowski, S.; Penczek, S. *Makromol. Chem.* **1984**, *185*, 91−101.
(17) Baśko, M.; Kubisa, P. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 7071−7081.
(18) Fujiwa, T.; Takemoto, S.; Watanabe, M. Japanese Patent 04089822 A, Daicel Chem Ind LTD, Japan, 1992.
(19) Jung, M. E.; Marquez, R. *Tetrahedron Lett.* **1997**, *38*, 6521−6524.
(20) Keese, R.; Meyer, M. *Tetrahedron* **1993**, *49*, 2055−2064.
(21) Abraham, R. J.; Ghersi, A.; Petrillo, G.; Sancassan, F. *J. Chem. Soc., Perkin Trans.* **1997**, *2*, 1279−1286.

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