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Di-, Tri- and Tetrafunctional Poly(ϵ-caprolactone)s by $Bi(OAc)_3$-Catalyzed Ring-Opening Polymerizations of ϵ-Caprolactone

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ABSTRACT: ϵ-Caprolactone was polymerized in bulk at 150 °C with either tetra(ethylene glycol) (TEG), 1,1,1-tris(hydroxymethyl)propane, or Pentaerythritol as initiator and bismuth(III) acetate $Bi(OAc)_3$ as catalyst. The reaction times needed for nearly quantitative conversion were determined. The polylactones isolated after precipitation were characterized by ^1H NMR spectroscopy and MALDI−TOF mass spectroscopy. Quantitative incorporation of the initiators were confirmed, so that polylactones having two, three, or four OH end groups were obtained. A coordination−insertion mechanism explaining these results is discussed. When used as catalyst for ring-opening polymerizations of lactones and lactides bismuth(III) carboxylates have three important advantages, particularly low toxicity, low transesterification activity ("backbiting degradation"), and no racemization when L-lactide is polymerized at temperatures up to 180 °C.

Introduction

Most biodegradable polymers which are currently under investigation or which are commercialy available are based on ring-opening polymerization of lactones, cyclic diesters (e.g., lactides) or cyclic carbonates. The most widely used group of initiators or catalysts for both academic research and technical syntheses are tin(II) and tin(IV) alkoxides or salts. The reactivity and preparative usefulness of these tin initiators/catalysts can be varied over a broad range. However, all these tin compounds have a high cytotoxicity in common. Therefore, selected tin compounds are widely applied as antifouling agents in paints, in textiles, or in food. For instance, tin(II) 2-ethylhexanoate ($SnOct_2$) has been admitted by the American FDA as stabilizing food additive, and this is one of the reasons why $SnOct_2$ was and is frequently used as initiator for syntheses and technical production of polylactides.[1]

The cytotoxicity of tin compounds has prompted several research groups to look for less toxic initiators/catalysts such as magnesium,[2−4] calcium,[5−7] and zinc[8−17] compounds. However, only two papers[5,18] report on a few experiments with a bismuth-based initiator, namely bismuth(III) 2-ethylhexanoate ($BiOct_3$). L-Lactide was polymerized in bulk at 120, 150, or 180 °C, and little or no racemization was found, while more basic metal salts such as those of Mg, Ca, or Zn cause partial racemization at such high temperatures (temperatures around 180 °C are needed for the technical polymerization of poly(L-lactide)). Bismuth(III) carboxylates or "subcarboxylates" (i.e., mixed oxides/carboxylates) are known for their low toxicity. For instance, ointments used for wound dressing (mainly in the case of burn wounds) may contain large amounts of Bi salts (European trademarks Dermatol, Xeroform, and Noviform). Furthermore, tablets designed against gastrointestinal complaints may contain bismuth subsalicylates.[19] Moreover, Bi salts were found to be less toxic than many other heavy metal salts (including Zn!) against kidney tubuli,[20] which are particular sensitive to poisoning by heavy metals. For all these reasons Bi salts are certainly worth to be studied in more detail as initiator/catalysts for ring-opening polymerizations of lactones and lactides. In this context the present work presents a first study based on ϵ-caprolactone as monomer.

Table 1. Tetra(ethylene glycol)/$Bi(OAc)_3$-Initiated Polymerizations of ϵ-CL in Bulk at 150 °C/4 h with Variation of the $Bi(OAc)_3$ Concentration (ϵ-Cl/TEG = 40/1)

expt no.	monomer[a]/ init.	yield (%)	η_{inh} [b] (dL/g)	apparent DP[c]	av segment length[c]
1	400	84	0.172	41	20
2	400	87	0.176	42	21
3	700	86	0.172	39	20
4	700	87	0.175	40	20
5	1000	85	0.176	42	21
6	1000	86	0.180	42	21

[a] Initial molar ϵ-CL/$Bi(OAc)_3$ ratio. [b] Measured at 20 °C with c = 2 g/L in CH_2Cl_2. [c] From ^1H NMR end group analyses (TEG signals *x* and *y* in Figure 4).

Experimental Section

Materials. Bismuth(III) acetate $Bi(OAc)_3$ (purity: 99.99%) was purchased from Aldrich Co. (Milwaukee, WI) and used as received. ϵ-Caprolactone was also purchased from Aldrich Co. and distilled over freshly powdered calcium hydride. Tetra(ethylene glycol), TEG (Aldrich Co.), was azeotropically dried with toluene and distilled in a vacuum of 10^{-3} mbar. 1,1,1-Tris(hydroxymethyl)propane and Pentaerythritol (Aldrich Co.) were dried over P_4O_{10} in vacuo.

Polymerizations. ϵ-Caprolactone (80 mmol) and dry TEG (2 mmol) were weighed into a 50 mL Erlenmeyer flask having silanized glass walls. The reaction vessel was closed with a glass stopper and immersed into an oil bath preheated to 150 °C. After homogenization (up to 1 h in the case of Pentaerythritol) $Bi(OAc)_3$ (0.08 mmol) was added under an atmosphere of dry nitrogen. Three times small samples were removed to check the conversion by ^1H NMR spectroscopy. After 98−99% conversion, the cold reaction product was dissolved in dichloromethane (40 mL) and precipitated into cold (+5 °C) diethyl ether. The product was dried overnight (16 h) in a vacuum (ca. 20 mbar). This procedure corresponds to experiments nos. 5 + 6, Table 1. All other polymerizations were conducted analogously. For all polymerizations listed in Tables 2−4 the ϵ-CL/$Bi(OAc)_3$ ratio was fixed at 1000:1.

The solutions in dichloromethane showed a faint turbidity which was difficult to remove regardless if filtration or

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Table 2. Tetra(ethylene glycol)/Bi(OAc)$_3$-Initiated Polymerizations of ϵ-CL in Bulk at 150 °C with Variation of the Co-Initiator Tetra(ethylene glycol) Concentration

expt no.	mon.^{a}/ co-init.	time (h)	yield (%)	η_{inh}^{b} (dL/g)	apparent $\overline{DP}$^{c}	av segment length^c
1	20	4	81	0.120	26	13
2	20	8	80	0.130	26	13
3	20	16	76	0.135	27	13
4	40	4	85	0.175	42	21
5	40	8	86	0.180	42	21
6	80	5	88	0.275^d	74	37
7	80	8	92	0.280	75	38
8	80	24	90	0.290	78	39
9	150	8	91	0.395^e	140	70
10	150	24	94	0.4005	145	73
11	150	36	93	0.4065	147	75

[a] Initial molar ϵ-CL/tetra(ethylene glycol) ratio. [b] Measured at 20 °C with $c = 2$ g/L in CH_2Cl_2. [c] From ^1H NMR end group analyses (TEG signal). [d] M_n(calcd): 9350 Da. SEC: $M_n = 10\,000$ Da; $M_w = 15\,000$ Da. [e] M_n(calcd): 17 400 Da. SEC: $M_n = 15\,000$ Da; $M_w = 23\,000$ Da.

Table 3. 1,1,1-Tris(hydroxymethyl)Propane/ Bi(OAc)$_3$-Initiated Polymerizations of ϵ-CL in Bulk at 150 °C with Variation of the Monomer/Co-Initiator Ratio

expt no.	monomer^a/ co-init.	time (h)	yield (%)	η_{inh}^{b} (dL/g)	ϵ-CL/co-init/^{c} ratio after isolation	av segment length^c
1	30	5	80	0.140	32	11
2	30	16	82	0.145	35	12
3	60	5	89	0.220	61	20
4	60	16	86	0.230	62	20
5	120	5	91	0.350^d	116	39
6	120	16	93	0.355	122	41

[a] Initial monomer/co-initiator ratio. [b] Measured at 20 °C with $c = 2$ g/L in CH_2Cl_2. [c] From ^1H NMR end group analyses based on the CH_3 signal of the co-initiator. [d] M_n(calcd): 13 850 Da. SEC: $M_n = 15\,000$ Da. $M_w = 22\,000$ Da.

Table 4. Pentaerythritol/Bi(OAc)$_3$-Initiated Polymerizations of ϵ-CL in Bulk at 150 °C with Variation of the Monomer/Co-Initiator Ratio

polym no.	monomer^a/ co-init.	time (h)	yield (%)	η_{inh}^{b} (dL/g)	ϵ-CL/co-init.^{c} ratio after isolation	av segment length^c
1	40	5	85	0.150	50	13
2	40	16	87	0.165	55	14
3	80	5	87	0.225	90	23
4	80	16	90	0.240	95	24
5	160	5	90	0.375^d	170	47
6	160	16	91	0.380	180	46

[a] Initial monomer/co-initiator (co-init.) ratio. [b] Measured at 20 °C with $c = 2$ g/L in CH_2Cl_2. [c] From ^1H NMR end group analyses based on the CH_2OH signal of the co-initiator. [d] M_n(calcd): 18 300 Da. SEC: $M_n = 16\,500$ Da; $M_w = 22\,000$ Da.

centrifugation was used. Furthermore, a turbidity remained, when the Bi(OAc)$_3$ was heated in ϵ-CL to 150 °C. However, when the crude ϵ-CL was used (as received) both melt and CH_2Cl_2 solutions were clear and the reaction product was almost identical with that prepared from dry and distilled ϵ-CL.

Measurements. The inherent viscosities were measured in dichloromethane with an automated Ubbelohde viscometer thermostated at 20 °C.

The 400 MHz ^1H NMR spectra were recorded on a Bruker Avance 400 FT NMR spectrometer in 5 mm o.d. sample tubes using $CDCl_3$ + TMS as solvent and shift reference.

The MALDI−TOF mass spectra were measured with a Bruker Biflex III mass spectrometer equipped with a nitrogen laser ($\lambda = 337$ nm). All spectra were recorded in the reflection mode using an acceleration voltage of 20 kV. The irradiation targets were prepared from chloroform solutions (containing approximately 10 vol % of hexafluoro-2-propanol) with dithranol as matrix and potassium trifluoroacetate as dopant. The SEC measurements were performed on a homemade SEC apparatus at 23 °C in tetrahydrofuran. A combination of three PSS−SDV mixed-bed columns was used along with UV and refractive-index detectors. Commercial polystyrene standards in combination with the universal calibration method (using the Mark−Houwink equations, (1) and (2)) served for calibration.

$$[\eta] = 1.25 \times 10^{-4} M^{0.717} \tag{1}$$

$$[\eta] = 1.40 \times 10^{-4} M^{0.766} \tag{2}$$

Results and Discussion

Tetra(ethylene glycol) as Co-Initiator. It is well-known from ring-opening polymerizations of lactones and lactides initiated by $SnOct_2$ that an alcohol added as co-initiator accelerates the polymerization and allows for a control of the number-average molecular weight via the monomer/initiator ratio (M/I). The alcohol forms a dead end group via an ester end group according to a coordination−insertion mechanism which has recently been elucidated.[21,22] Assuming that bismuth(III) carboxylates initiate in principle the same polymerization mechanism (see discussion below), a di- or multifunctional alcohol was used as co-initiator in all experiments of the present work. Since $BiOct_3$ had proven in previous experiments[5] to allow for polymerizations of L-lactide in bulk without racemization $BiOct_3$ was also foreseen to serve as initiator of ϵ-caprolactone in the present work. However, the commercial $BiOct_3$ was found to be a black oil which was difficult to purify. In our hands $BiOct_3$ did not crystallize, and it decomposed upon attempted distillation over a short-path apparatus in a vacuum of 10^{-3} mbar. Therefore, the white crystalline and relatively pure commercial Bi(OAc)$_3$ was used in all experiments of the present work.

In preliminary experiments not discussed here in detail, a standard reaction temperature was selected allowing for relatively fast polymerizations with high monomer/initiator ratios (M/I = 1000/1 or 5000/1)). As consequence of this screening a temperature of 150 °C was selected for all experiments of this work. With tetra(ethylene glycol) as co-initiator two series of polymerizations were conducted (at 150 °C in bulk) to elucidate the influence of the ϵ-CL/Bi(OAc)$_3$ ratio on both polymerization rate and degree of polymerization. As illustrated in Figure 1, time−conversion curves were recorded with M/I ratios of 1000 and 5000. Even with the high M/I ratio of 5000, a nearly complete conversion was achieved in an acceptable time (8 h). However, in small scale experiments an accurate weighing of a hydrolytically sensitive initiator for a M/I ratio of 5000 is difficult, and thus, all experiments of this work were performed with M/I ratios ≤ 1000.

The polymerizations listed in Table 1 were designed to elucidate the influence of Bi(OAc)$_3$ on the $\overline{DP}$. The ϵ-CL/co-initiator ratio was kept constant at 40/1. Since in the ^1H NMR spectra the signals of the TEG units are well separated from those of the ϵ-caprolactone units (Figure 2), the ^1H NMR spectra allowed for an easy determination of the $\overline{DP}$'s of the isolated polylactones. The results listed in Table 1 clearly prove that the M/co-initiator ratio and not the M/I ratio is decisive for the $\overline{DP}$. This conclusion is confirmed by the results of the polymerizations compiled in Table 2. These polymeriza-

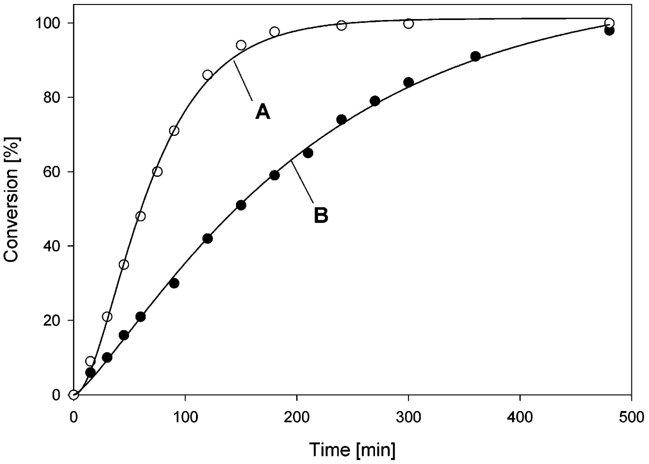
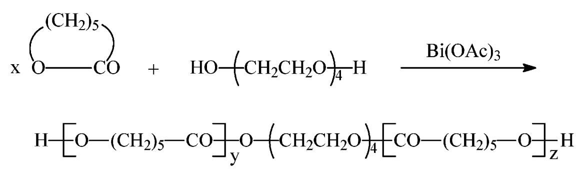


Figure 1. Time−conversion curve of a tetra(ethylene glycol) co-initiated polymerization of ϵ-CL (at 150 °C in bulk) performed with a monomer/$Bi(OAc)_3$ ratio of 1000/1 (A) and with a ϵ-CL/$Bi(OAc)_3$ ratio of 5000/1 (B).

tions were performed in such a way that the M/I ratio was kept constant and the M/co-initiator ratio was varied. Furthermore, the time was varied to achieve complete conversion. At least for the longest reaction time, an acceptable agreement between $\overline{\mathrm{DP}}$ and M/co-initiator ratio was found. The relatively high $\overline{\mathrm{DP}}$'s found for the M/co-initiator ratio of 20 resulted from fractionation upon precipitation into diethyl ether.

The structure of the isolated polylactones or, in other words, the covalent incorporation of the co-initiators into the polyester backbones was evidenced by ^1H and ^{13}C NMR spectroscopy. The methylene signals of the $-CH_2-CH_2-OH$ groups experience a characteristic downfield shift in the ^1H NMR spectra after reaction (i.e., acylation) of the OH groups by ϵ-CL (signals "f" and "g" in Figure 2). The corresponding CH_2 carbons experience an upfield shift after acylation of the OH groups by ϵ-CL as examplarily illustrated by the signals "f" and "g" in the ^{13}C NMR spectrum of Figure 3.

The MALDI−TOF mass spectra proved that the vast majority of the isolated polylactone chains possess the structure of formula **1** (see Figures 4 and 5). In the mass range below 2000 Da, weak signals of cyclic poly(ϵ-CL) were detectable, indicating that "backbiting" degradation had occurred, although to a very low extent. Furthermore, a very small fraction of linear chains having one acetate end group (e.g., structure **2**) was found. The acetate end groups obviously originate from (trans)esterification with the acetate groups of $Bi(OAc)_3$. Therefore, their concentration is necessarily low, because the molar ratio of ϵ-CL/$Bi(OAc)_3$ was 1000/1 in all experiments of this work. Moreover, a few chains having structure **3** were detected indicating a co-initiation with traces of water, despite drying of the ϵ-CL with calcium hydride. Considering the low concentration of the CO_2H and acetate end groups and considering the relatively low molar mass of these byproducts and the low intensity of their signals, the weight fractions of these byproducts seem to be below 1%. When short and long reaction times were compared, the content of cyclic oligolactones increased with longer times.



1

$$H{-}[O{-}(CH_2)_5{-}CO]_y{-}O{-}(CH_2CH_2O)_4{-}[CO{-}(CH_2)_5{-}O]_z{-}COCH_3$$

2

$$H{-}[O{-}(CH_2)_5{-}CO]_x{-}OH$$

3

Tri- and Tetrafunctional Polylactones. The successful synthesis of telechelic poly(ϵ-CL) having two OH-end groups (structure **1**) prompted us to use a trifunc-

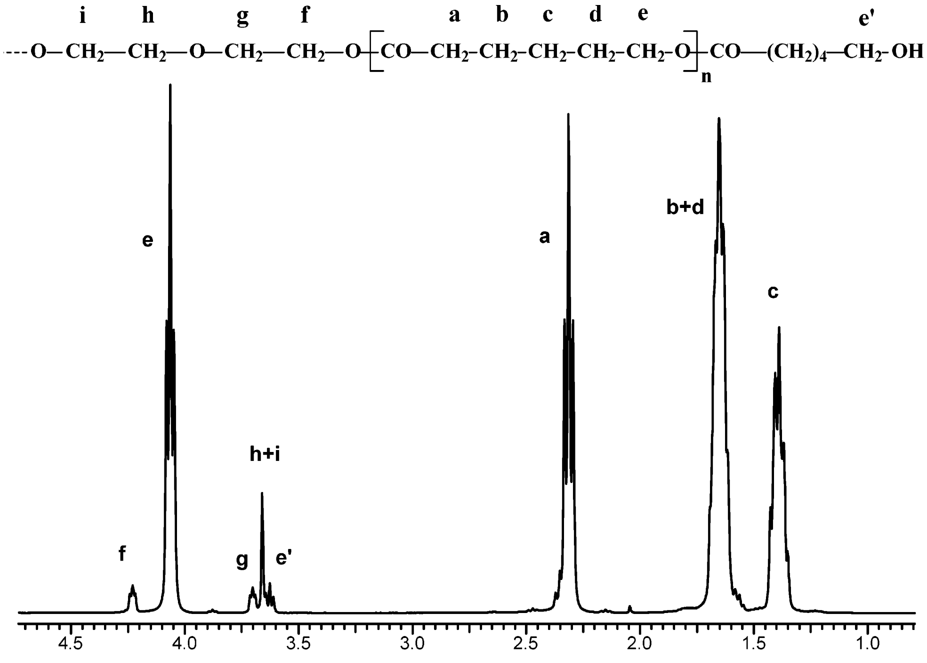


Figure 2. 400 MHz ^1H NMR spectrum of a poly(ϵ-CL) co-initiated with tetra(ethylene glycol) at a molar ratio of 20:1 (no. 1, Table 1).

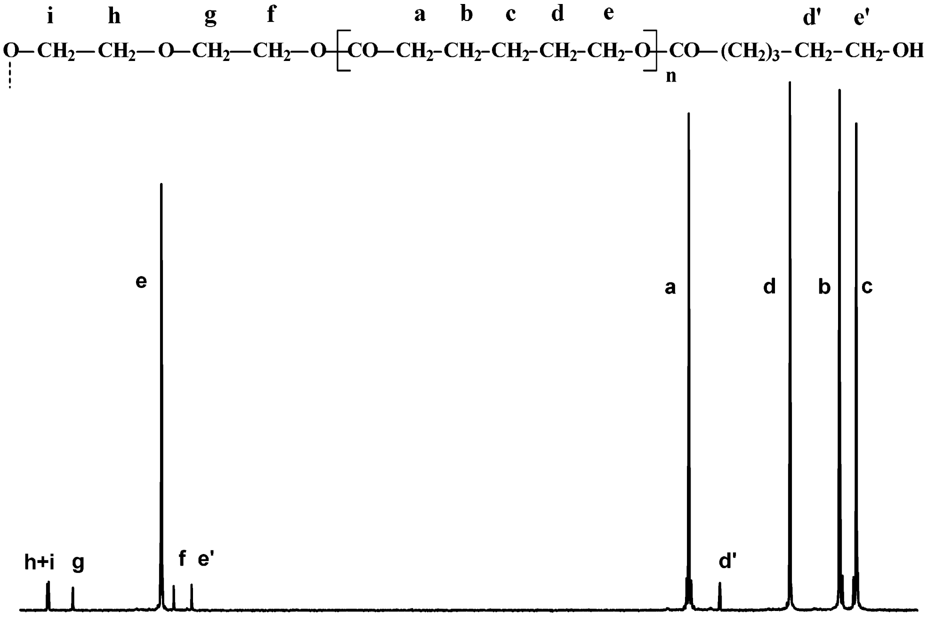


Figure 3. 100.4 MHz ^{13}C NMR spectrum of a poly(ε-CL) co-initiated with tetra(ethylene glycol) at a molar ratio of 20:1 (no. 1, Table 1). The OH groups exhibit a signal at 173.5 ppm.

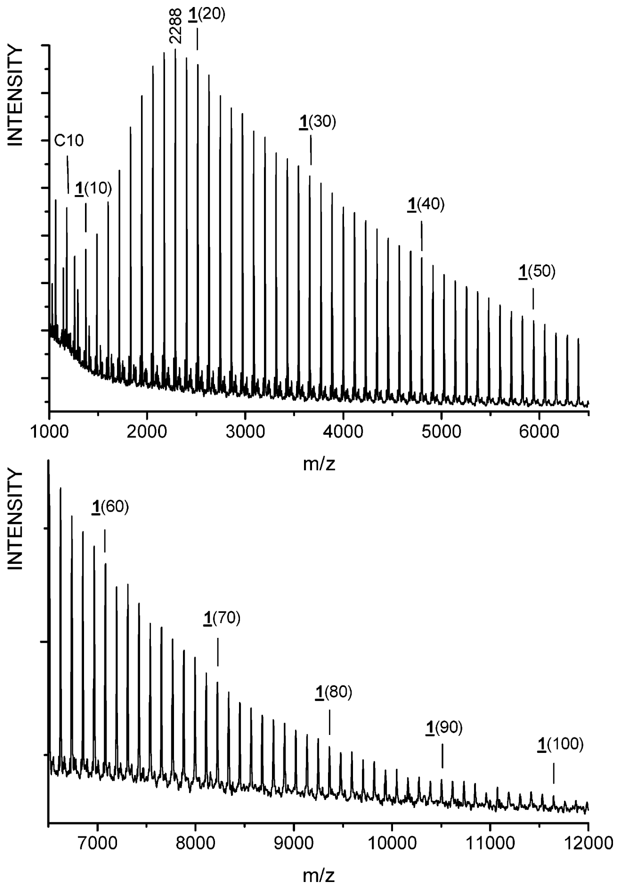


Figure 4. MALDI−TOF mass spectrum of a poly(ε-CL) co-initiated with tetra(ethylene glycol) at an ε-CL/co-initiator ratio of 40/1 (no. 4, Table 2). The numbers in brackets indicate the $\overline{DP}$.

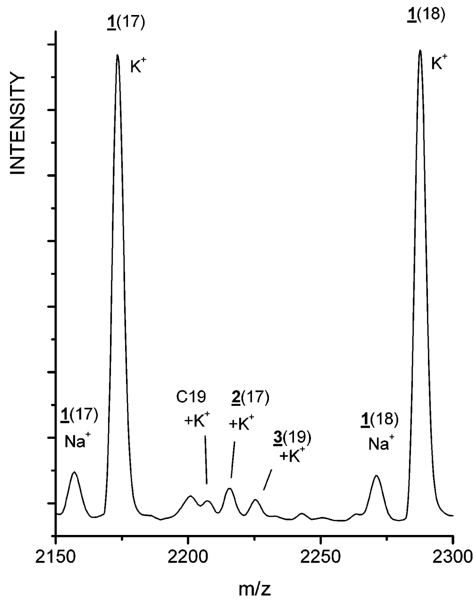
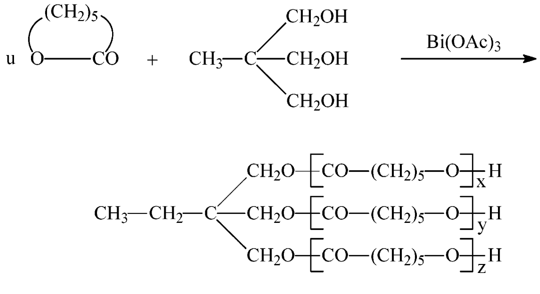


Figure 5. MALDI−TOF mass spectrum (segment) of a poly(ε-CL) co-initiated with tetra(ethylene glycol) at an ε-CL/co-initiator ratio of 40/1 (no. 4, Table 2). The numbers in brackets indicate the $\overline{DP}$. C19 means cyclic nonadecanomer.

tional co-initiator. For this purpose the commercial 1,1,1-tris(hydroxymethyl)propane was selected. The monomer/co-initiator ratio was varied from 30 to 60 and 120, so that poly(ε-CL) arms with average $\overline{DP}$'s of 10, 20, or 40 were obtained (Table 3). Furthermore, two reaction times were applied to ensure complete conversion of the ε-CL. The incorporation of the co-initiator and the average length of the individual poly(ε-CL) chains were determined from 400 MHz ^{1}H NMR spectra. These spectroscopic results and the viscosity data



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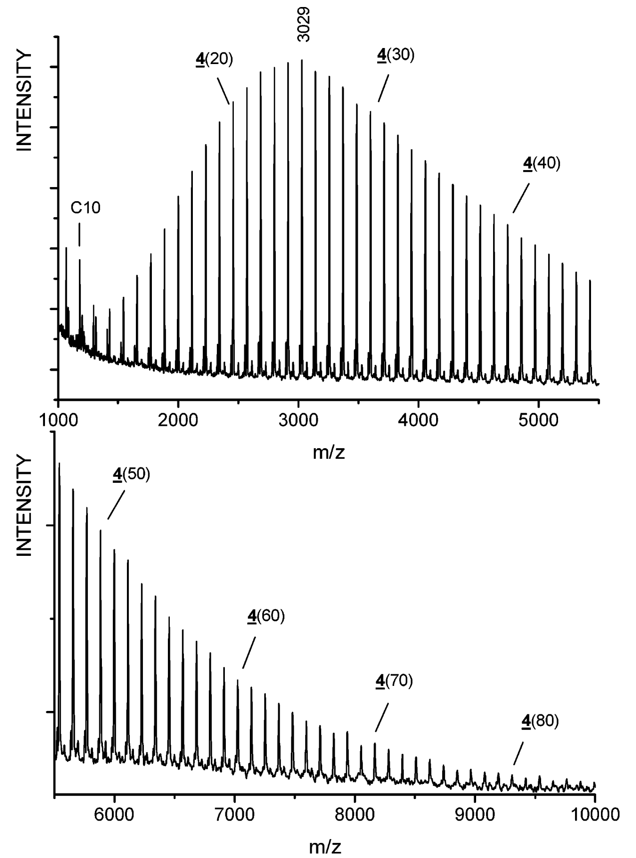
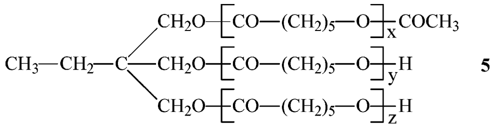


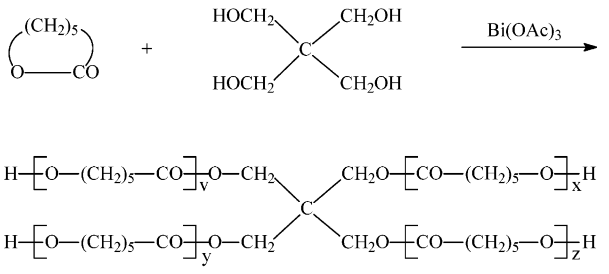
Figure 6. MALDI−TOF mass spectrum of a poly(ϵ-CL) co-initiated with 1,1,1-tris(hydroxymethyl)ethane (no. 1, Table 3). The numbers in brackets indicate the $\overline{DP}$.

proved that the polymerization took the expected course, and trifunctional polylactones of structure **4** were obtained. The MALDI−TOF mass spectra confirmed this conclusion (Figure 6). The mass spectra also revealed that a small fraction (presumably <1 wt %) of cyclic oligolactones was formed. Furthermore, a small fraction of trifunctional polylactones having one acetate group (structure **5**) was detected. Since the acetate groups resulted from side reactions of Bi(OAc)$_3$ the weight fraction of poly(ϵ-CL) with structure **5** is necessarily < 1%.



$$CH_3{-}CH_2{-}C\begin{cases}CH_2O{-}[CO{-}(CH_2)_5{-}O]_x{-}COCH_3\\ CH_2O{-}[CO{-}(CH_2)_5{-}O]_y{-}H\\ CH_2O{-}[CO{-}(CH_2)_5{-}O]_z{-}H\end{cases}$$

5



$$\underset{O{-}CO}{(CH_2)_5} + C(CH_2OH)_4 \xrightarrow{Bi(OAc)_3}$$

$$C\begin{cases}CH_2{-}O{-}[CO{-}(CH_2)_5{-}O]_v{-}H\\ CH_2{-}O{-}[CO{-}(CH_2)_5{-}O]_y{-}H\\ CH_2O{-}[CO{-}(CH_2)_5{-}O]_x{-}H\\ CH_2O{-}[CO{-}(CH_2)_5{-}O]_z{-}H\end{cases}$$

6

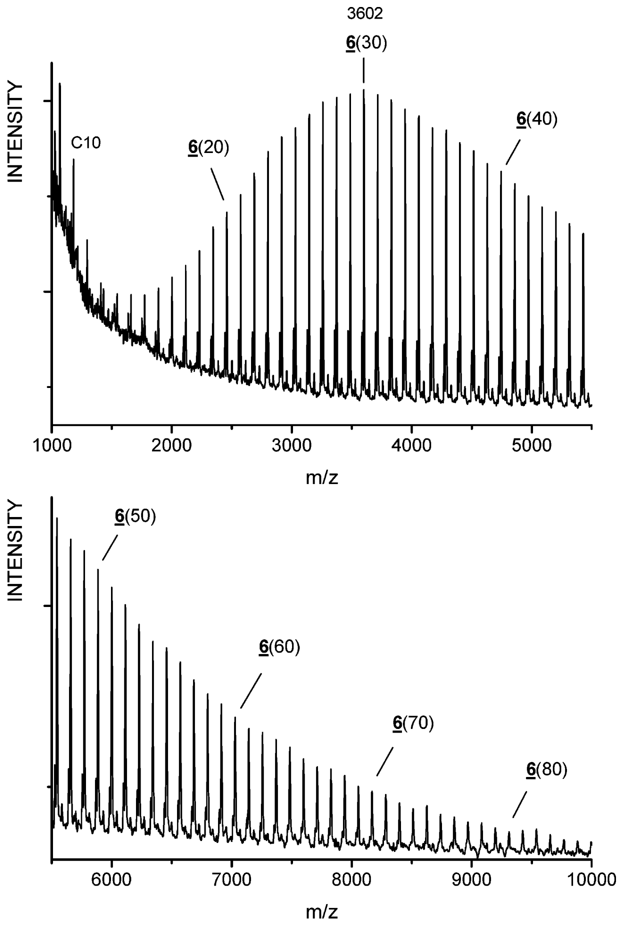
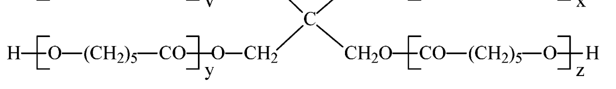


Figure 7. MALDI−TOF mass spectrum of a poly(ϵ-CL) co-initiated with Pentaerythritol (no. 1, Table 4). The numbers in brackets indicate the $\overline{DP}$.

For the preparation of tetrafunctional polylactones Pentaerythritol was used as co-initiator. Monomer/co-initiator ratios of 40, 80, and 160 were used to obtain “star arms” with average $\overline{DP}$’s around 10, 20, and 40 repeating units (Table 4). Again the time was varied to achieve a maximum conversion of ϵ-CL, and quite analogous to the results obtained from 1,1,1-tris(hydroxymethyl)propane (Table 3) a slight increase of $\overline{DP}$ and viscosity was found for the longer reaction time. The relatively high $\overline{DP}$’s of the polylactones prepared with M/co-initiator ratios of 40 and 80 result from fractionation upon precipitation into cold diethyl ether. The MALDI−TOF mass spectra confirmed the expected structure (**6**) and revealed the formation of small amounts of cyclic oligolactones (Figure 7). Furthermore, a small percentage of polylactones having one acetate end group (structure **7**) was detectable. In other words, all aspects of the polymerizations co-initiated with Pentaerythritol were in good agreement with those obtained from the other co-initiators.

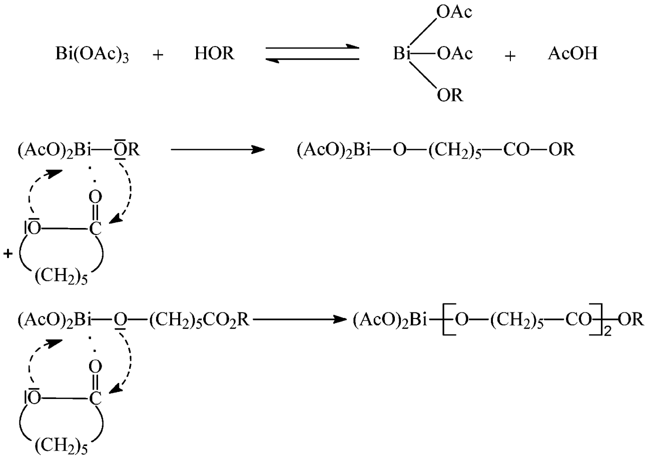


$$C\begin{cases}CH_2{-}O{-}[CO{-}(CH_2)_5{-}O]_v{-}H\\ CH_2{-}O{-}[CO{-}(CH_2)_5{-}O]_y{-}H\\ CH_2O{-}[CO{-}(CH_2)_5{-}O]_x{-}COCH_3\\ CH_2O{-}[CO{-}(CH_2)_5{-}O]_z{-}H\end{cases}$$

7

Finally, it should be mentioned that a few polylactones were subjected to SEC measurements. The resulting number-average (M_n) and weight-average molecular weight (M_w) were added as footnotes to Tables 2−4. It is known from publications of four research groups[23−26] that direct calibration of elution curves with polystyrene overestimates the real molecular weights

Scheme 1



of poly(ϵ-CL) by 50−100% (depending on whether low or high molar masses are measured). Therefore, the universal calibration method was applied using the Mark−Houwink equations (1) (for polystyrene) and (2)[27] (for poly(ϵ-CL). The M_n values obtained in this way are in acceptable agreement with the M_ns calculated from the feed ratios and 100% conversion. The conversions were in fact slightly lower, but the precipitation of the polylactones removed a small fraction of oligomers thereby increasing the M_ns of the isolated polylactones. Although the MALDI−TOF MS suggest at first glance broad molecular weight distributions, relatively low polydispersities (1.4−1.5) were found for all four samples.

Conclusion

The experiments presented in this work demonstrate that $Bi(OAc)_3$ is an useful initiator for ring-opening polymerizations of ϵ-CL in combination with various co-initiators. The covalent incorporation of alcohols added as co-initiators allows for the preparation of di-, tri- and tetrafunctional polylactones. The average chain (segment) lengths can easily be controlled by the ϵ-CL/co-initiator ratio. All the results together suggest that the polymerization mechanism obeys Scheme 1, which was recently elaborated for $SnOct_2$-initiated polymerizations of lactide and lactones. The successful polymerizations presented here and in another manuscript together with the extraordinarily low toxicity indicate that $Bi(OAc)_3$ or other Bi salts are extraordinarily interesting and useful initiators for syntheses of biodegradable polyesters designed to serve for pharmaceutical or medical applications.

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