High Molar Mass Poly(ε-caprolactone) by Means of Diphenyl Bismuth Ethoxide, a Highly Reactive Single Site Initiator

Hans R. Kricheldorf,*,[†] Gesa Behnken,[†] Gert Schwarz,[†] and Juergen Kopf[‡]

Institut für Technische and Makromolekulare Chemie, Bundesstrasse 45, 20146 Hamburg, Germany,
Institut für Anorganische Chemie, Martin-Luther-King Platz 6, 20146 Hamburg, Germany

Received August 9, 2007; In Final Form March 7, 2008;
Revised Manuscript Received February 22, 2008

ABSTRACT: Diphenylbismuth ethoxide, Ph_2BiOEt, initiates the ring-opening polymerization of ε-caprolactone via a coordination-insertion mechanism. The matrix assisted laser induced desorption and ionization-time-of-flight (MALDI−TOF) mass spectra proved the formation of one ethyl ester and one CH_2OH endgroup. The reactivity of this initiator is high enough to allow even for polymerizations at 20 °C. At 120 °C the reactivity of Ph_2BiOEt is lower than that of tin(II) 2-ethylhexanoate ($SnOct_2$) + ethanol, whereas below 90 °C, the reactivity of Ph_2BiOEt is higher. Small amounts of cyclic oligoesters are even formed at 20 °C. At 120 °C the number average molecular weights (M_ns) parallel the monomer-initiator ratios, and M_ns up to 115 000 Da were obtained. The time−conversion curves and the crystal structure indicate association of Ph_2BiOEt via O → Bi donor–acceptor interactions.

Introduction

For both academic research and technical production of biodegradable polyesters tin compounds and, in particular, tin(II) 2-ethylhexanoate ($SnOct_2$) play a predominant role as initiators or catalysts. Yet, tin compounds are cytotoxic, which means they are toxic to almost all animals, microbes, and fungi. Therefore, it is predictable that on the long-term tin compounds need to be replaced by less toxic initiators/catalysts. A first step in this direction is the banning of tributyl tin derivatives from marine paints since 2003, where they were long used as efficient antifouling agents.

In the field of biodegradable polyesters, several research groups have began to evaluate the usefulness of magnesium,[1–5] calcium,[6–8] zinc,[9–17] and iron salts[18–22] or complexes as nontoxic initiators or catalysts. Calcium and magnesium salts or complexes may possess an extremely low toxicity and high reactivity, but they are so basic that they racemize L-lactide at the temperatures needed for technical polymerizations.[1,6] Particularly reactive calcium and magnesium compounds such as Bu_2Mg racemize L-lactide even at 20–25 °C.[5] Zinc salts and compounds are far less toxic than tin derivatives, but are also less reactive, and most zinc salts also racemize L-lactide at temperatures >100 °C.[6] None the less, initiators or catalysts based on zinc seem to be the best compromise. Recently, zirconium acetyl acetonate and alkoxides were also considered,[23–26] because zirconium compounds seem to be less toxic than tin compounds. Yet, zirconium is more toxic than zinc and is not significantly more reactive as initiator.

About 5 years ago, the first author of this work launched a research program concerning the usefulness of bismuth compounds as initiators or catalysts in the field of biodegradable and biocompatible polymers.[27–35] Bismuth oxides and carboxylates (e.g., "subcitrate" or "subsalicylate") have a tradition of more than 100 years as an internal drug against gastrointestinal complaints (including stomach ulcer).[36,37] Furthermore, they have a long tradition as external drugs, namely as compounds of ointments designed for skin care and treatment of burn wounds (Xeroform, Noviform, and Dermatol in Europe, for example). Furthermore, it was recently found[38] that bismuth nitrate is less toxic for kidney tubuli than other heavy metals including zinc ions. Hence, bismuth may be the least toxic heavy metal and from this point of view an interesting candidate for substitution of tin, lead, or mercury salts in various reactions. Several publications recently demonstrated that bismuth salts catalyze homopolymerizations of ε-caprolactone and L-lactide and copolymerizations of these monomers with each other or with glycolide and trimethylene carbonate. A variety of telechelic polymers and other architectures were prepared. However, it is difficult to prepare high molar mass polyesters having number average molecular weights (M_ns) > 40 000 Da. The purpose of this study is to present the first results obtained with a single-site Bi-initiator having a bismuth alkoxide group. Since metal alkoxides are usually the most reactive type of initiators, it was intended to elucidate, if Ph_2BiOEt allows for the preparation of high molar mass polylactones together with a control of M_n via the monomer−initiator (M/I) ratio. Furthermore, its reactivity as initiator should be compared with that of $SnOct_2$.

Experimental Section

Materials. ε-Caprolactone (εCL, purity 99%) was purchased from ACROS Organics (Geel, Belgium) and distilled in vacuo over powdered calcium hydride (called "dry"). Alternatively, it was distilled over P_4O_{10} in vacuo (with a loss around 50%) after distillation over freshly powdered CaH_2 (called "ultra dry"). Tetra(ethylene glycol), TEG (purity 99.5%), purchased from ACROS was azeotropically dried with toluene and distilled in a vacuum of 10^{-2} mbar. Tin(II) 2-ethylhexanoate ($SnOct_2$, purity 95%) was purchased from Aldrich Co. (Milwaukee, WI) and purified as described previously.[39] Bismuth(III) *n*-hexanoate was prepared from bismuth(III) acetate as described previously.[35] Phenyl magnesium chloride (2.0 M in tetrahydrofuran), bismuth trichloride (purity >98%), and bismuth tribromide (purity >98%) were all purchased from Aldrich Co. and used as received. Toluene, diethyl ether, and tetrahydrofuran (THF) were refluxed and distilled over sodium wire. Dichloromethane were distilled over P_4O_{10}. Diphenyl bismuth ethoxide (Ph_2BiOEt) was prepared according to a published procedure,[40] but potassium *tert*-butoxide (purity >95%) was used instead of sodium methoxide (mp 143–146 °C dec, in agreement with the litaterature data).

---

* Corresponding author.

[†] Institut für Technische and Makromolekulare Chemie.

[‡] Institut für Anorganische Chemie.

10.1021/ma071797i CCC: $40.75

Table 1. Ph_2BiOEt-Initiated Polymerizations of ε-Caprolactone in Bulk at 120 °C

expt. no.	M/I	time (h)	yield (%)	η_{inh}[c] (dL/g)	M_n (calcd)[d]	M_n[e] (PS calibr)	M_n[f] (corr)	polydispersity
1[a]	50/1	0.5	66	0.26	6000	10500	7000	1.70
2	100/1	0.5	82	0.40	11500	20000	13500	1.73
3	150/1	0.5	86	0.47	17000	23500	16500	2.00
4	200/1	6.0	81	0.55	22000	23500	18500	1.87
5	300/1	6.5	80	0.75	34000	41500	30000	1.82
6A	400/1	8.0	82	0.68	45000	50500	35500	1.75
6B[a]	400/1[a]	5.0	93	1.00	45000	61000	44000	2.21
7A	600/1	24.0	86	1.01	68000	52000	36500	2.15
7B[a,b]	600/1[a]	2.0	92	1.33	68000	97000	68000	2.29
8A	1000/1	2.4	91	1.12	110000	85000	50000	1.89
8B[a]	1000/1[a]	17.0	93	1.62	110000	120000	85000	1.95
9[a,b]	1000/1	2.0	87	1.87	110000	160000	110000	1.95

[a] Ultra dry εCL was used. [b] Conducted under argon. [c] Inherent viscosities at 20 °C with $c = 2$ g/L in CH_2Cl_2. [d] Number average molecular weight calculated from M/I with 98% conversion [e] Size-exclusion chromatography calibrated with polystyrene. [f] Size-exclusion chromatography values corrected with a factor of 0.68.

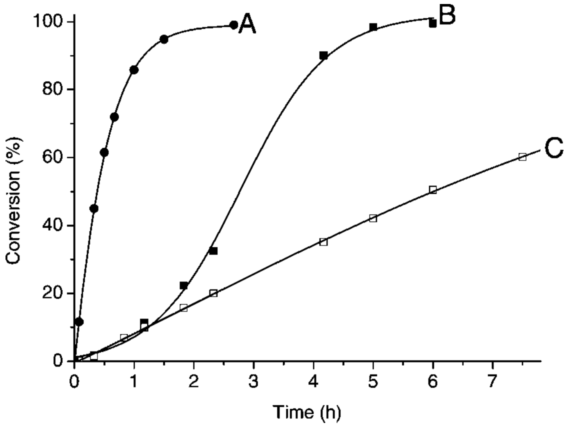


Figure 1. Time−conversion curves obtained from polymerizations of εCL in bulk at 120 °C with (A) $SnOct_2$ + ethanol as initiator, (B) with Ph_2BiOEt, and (C) with $BiHex_3$ + ethanol (M/I = 200 in all three cases).

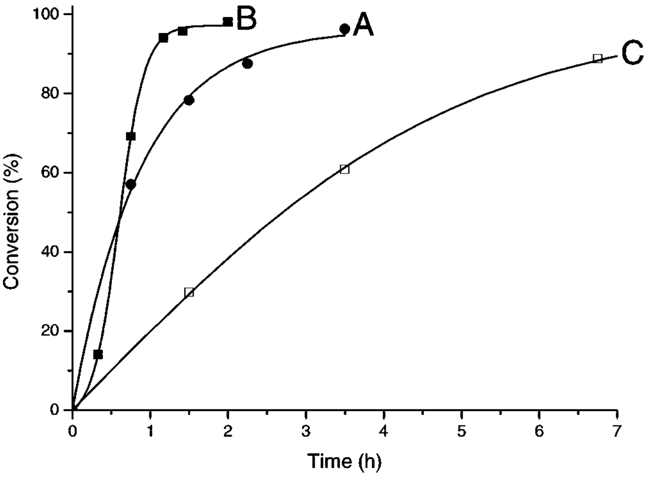


Figure 2. Time−conversion curves obtained from polymerizations of εCL in bulk at 90 °C with (A) $SnOct_2$ + ethanol, (B) with Ph_2BiOEt, and (C) with $BiHex_3$ + ethanol (M/I = 50 in all three cases).

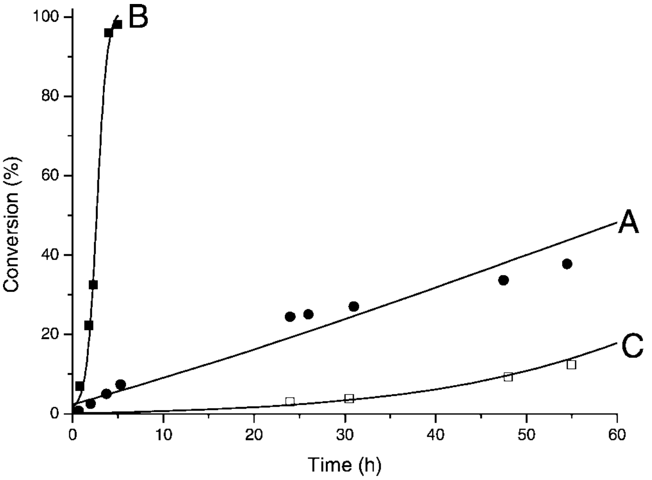
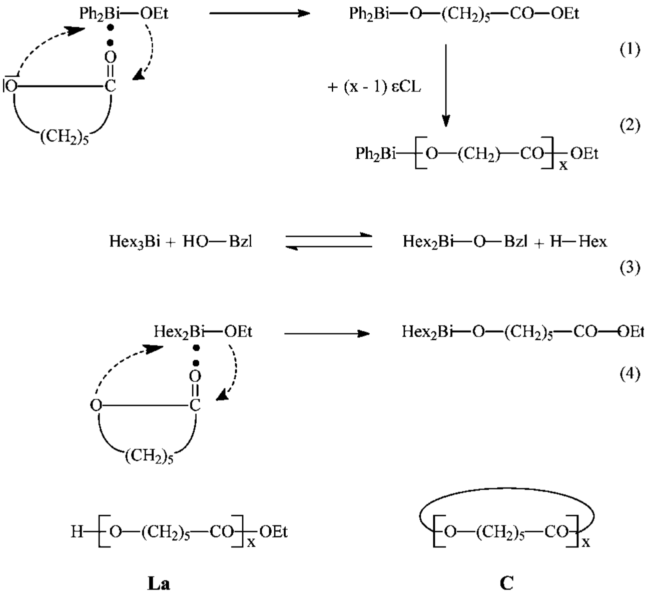


Figure 3. Time−conversion curves obtained from polymerizations of εCL in bulk at 60 °C with (A) $SnOct_2$ + ethanol, (B) with Ph_2BiOEt, and (C) with Ph_2BiOEt and $BiHex_3$ + ethanol (M/I = 50/1 in all three cases).

Scheme 1



$$[\eta] = 1.395 \cdot 10^{-4} \times M_w^{0.786} \quad \text{(ref. 39)} \qquad (5)$$

Polymerizations. *(A) With Dry ε-Caprolactone (No. 2, Table 1).* ε-Caprolactone (50 mmol) and Ph_2BiOEt (0.5 mmol) were weighed under nitrogen into a 25 mL Erlenmeyer flask having silanized glass walls. The reaction vessel was closed with glass-stopper and steel spring and immersed into an oil bath preheated to 120 °C. After 0.5 h at 120 °C and cooling the polylactone was dissolved in dichloromethane and precipitated into cold diethyl ether.

(B) With Ultradry ε-Caprolactone (No. 8, II, Table 1). Ultradry ε-caprolactone (100 mmol) and Ph_2BiOEt (0.1 mmol) were weighed under pure argon into a 50 mL Erlenmeyer flask having silanized glass walls. Polymerization and workup procedure were the same as described above.

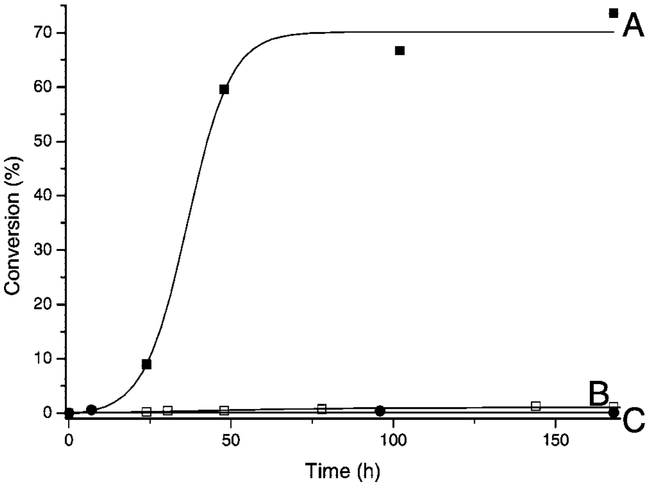


Figure 4. Time−conversion curves obtained from Ph_2BiOEt-initiated polymerizations of εCL (M/I = 50/1) in concentrated solutions of (A) THF, (B) toluene, and (C) dichloromethane.

Measurements. The inherent viscosities were measured in CH_2Cl_2 with an automated Ubbelohde viscometer thermostated at 20 °C. The size exclusion chromatography (SEC) measurements were conducted with an apparatus of Polymer Laboratories equipped with a RI-detector "Shodex RI detector". Three identical PC mixed-bed columns (PL mixed C, 5 μ) were used and chloroform served as eluent at a flow rate of 1 mL/min. Commercial polystyrene standards served for calibration. The 400 MHz ^1H NMR spectra were recorded on a Bruker Avance 400 FT spectrometer in 5 mm o.d. sample tubes. $CHCl_3$ containing tetramethyl silane served as solvent. The MALDI−TOF mass spectra were measured with a Bruker Biflex III mass spectrometer equipped with a nitrogen laser (λ = 337 nm). All spectra were recorded in the reflection mode with an acceleration voltage of 20 kV. The irradiation targets were prepared from chloroform solutions (1 mL) with the following quantities: polylactone, 10 mg (or less); dithranol, 25 mg; and potassium trifluoroacetate, 3 mg.

X-Ray Crystal-Structure Determination of Ph_2BiOEt. Transparent colorless needles (0.50 × 0.22 × 0.17 mm) from EtOH, $(C_{14}H_{15}BiO)_n$, M_r 408.24: orthorhombic, space group $P2_12_12_1$, $Z = 4$, $a = 8.3836(4)$ Å, $b = 10.4446(5)$ Å, $c = 14.9207(7)$ Å; $V = 1306.51(11)$ Å^3, $D_x = 2.076$ g/cm^{-3}.

CCDC-654355 contains the supporting crystallographic data. This data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

Results and Discussion

Reactivity Studies. In addition to the preparative aspects it was of great interest to elucidate, how the reactivity of Ph_2BiOEt correlates with the reactivities of other established initiators. For this purpose, polymerizations of εCL were conducted in bulk at 120 °C (Ph_2BiOEt decomposes at higher temperatures) and the conversions were determined from time-to-time by means of ^1H NMR spectroscopy. For this evaluation the CO-CH_2 signal of εCL at 2.6 ppm and the CO-CH_2 signal of poly(εCL) at 2.3 ppm were used. Since Bi(III) n-hexanoate in equimolar combination with an alcohol was preferentially used in previous studies of Bi-initiated ROPs,[30,33,35] $BiHex_3$ + ethanol served as second standard. The time conversion curves obtained from these three initiators are displayed in Figure 1. As expected Ph_2BiOEt is more reactive than $BiHex_3$ + ethanol (by a factor of 2:1 at 50% conversion).

This expectation was based on the following facts. First, it is well-known from several metals that their alkoxides are more

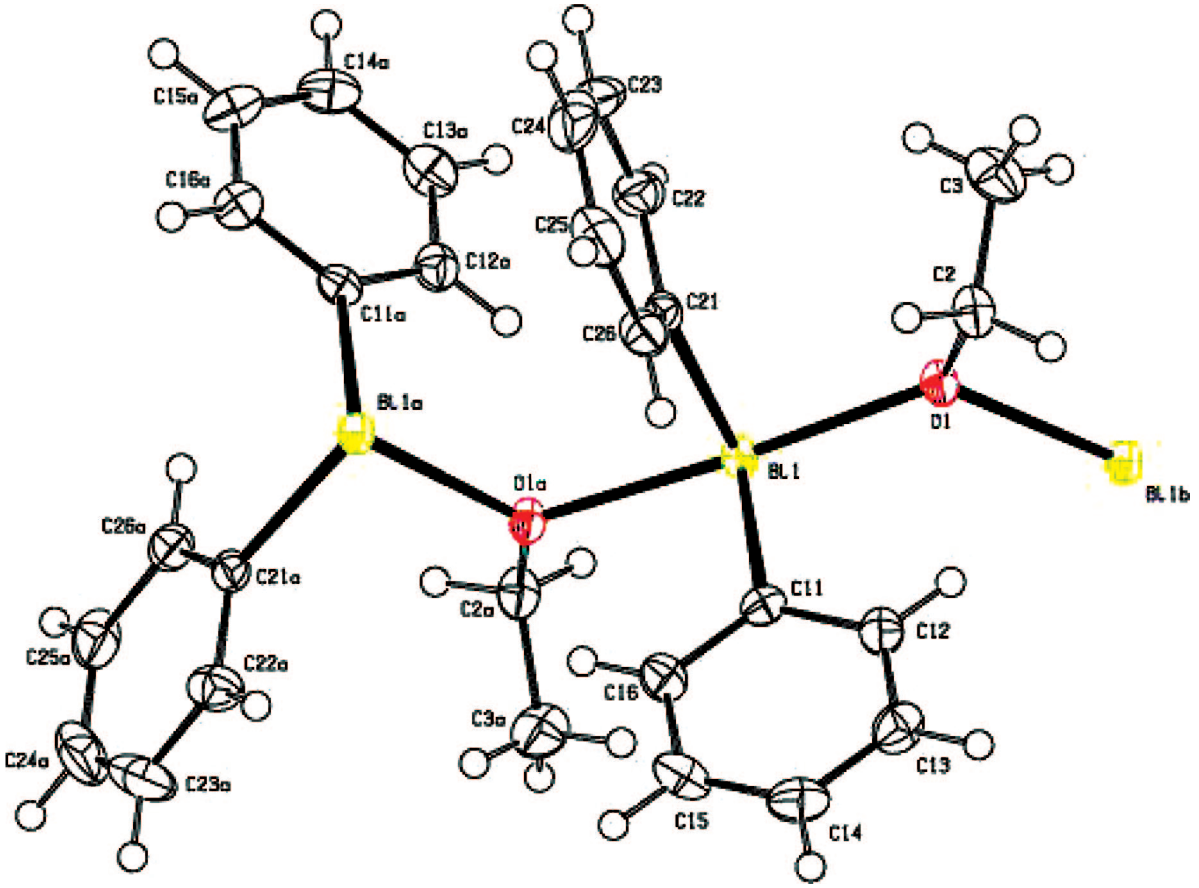


Figure 5. Refined crystallographic structure of Ph_2BiOEt. Thermal ellipsoids at 50% probability level.

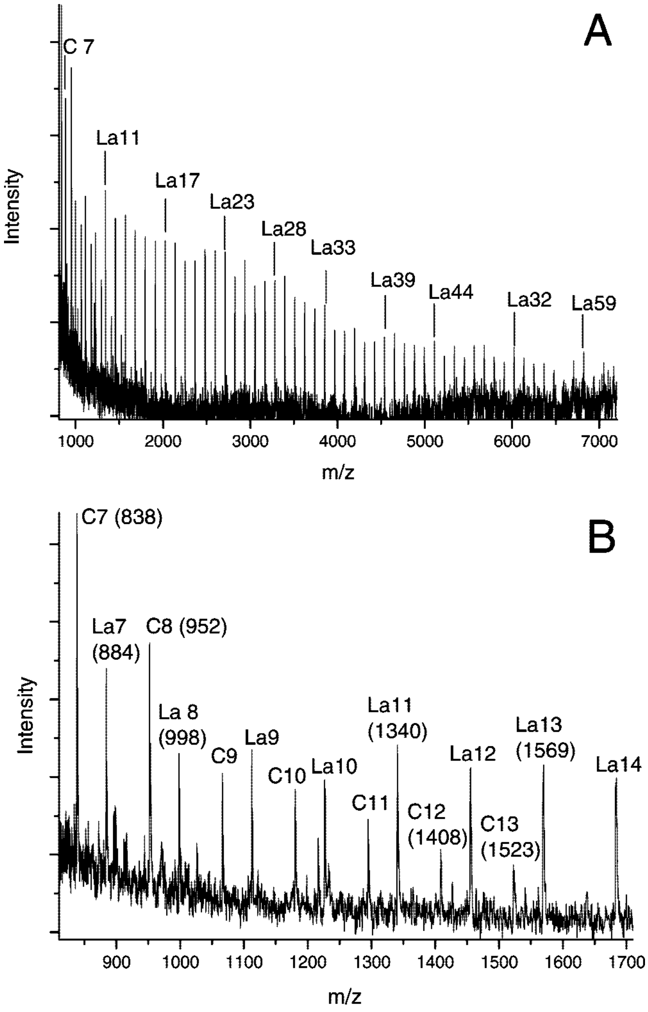


Figure 6. MALDI−TOF mass spectrum of a poly(εCL) initiated with Ph_2BiOEt at 60 °C in THF.

reactive as initiators than their carboxylates or halides. Detailed studies of reactivities and reaction mechanisms were recently published[39,41,42] for various tin(III) and tin(IV) alkoxides and carboxylates. The coordination insertion mechanism outlined for Ph_2BiOEt in eqs 1 and 2 was confirmed for all tin alkoxides. In the case of carboxylates, addition of an alcohol accelerated the polymerization and yields ester endgroups. These observations and model reactions confirmed that a (partial) exchange of carboxylate against alkoxide groups precedes the propagation step as formulated for $BiHex_3$ in eqs 3 and 4. All experimental observations made for Bi-salt-initiated polymerizations agree with these reaction mechanisms, and the MALDI−TOF mass spectra discussed below provide additional evidence. Figure 1 also demonstrates that Ph_2BiOEt is less reactive than $SnOct_2$ + ethanol (by a factor of 7 at 50% conversion). The observation that $BiHex_3$ + alcohol is a less reactive initiator system than $SnOct_2$ + alcohol was already reported in previous publications.[29,30] The results presented in Figure 1 suggest at first glance that Ph_2BiOEt brings little progress in direction of a higher reactivity.

The reactivity of Ph_2BiOEt was further studied by reducing the M/I ratio to 50/1 to accelerate the conversion, and the temperature was lowered in steps of 20 °C. The conversion was complete in a few hours even at 60 °C. Surprisingly, a nearly complete polymerization was also achieved at 40 °C, although partial crystallization of poly(εCL) affected the course of this polymerization. These results prompted us to compare the reactivity of Ph_2BiOEt with those of $BiHex_3$ + ethanol and $SnOct_2$ + ethanol at 90 and 60 °C. As illustrated by Figure 2, the Ph_2BiOEt-initiated polymerization is as rapid as the $SnOct_2$ + ethanol-initiated one and faster at higher conversions, when compared at 90 °C. At 60 °C the difference in the reactivities of $SnOct_2$ + ethanol and $BiHex_3$ + ethanol did again not significantly change. Yet, Ph_2BiOEt proved to be approximately 25 times more efficient as initiator than $SnOct_2$ + ethanol (Figure 3). This result demonstrates for the first time that a bismuth-based initiator may be more reactive than the combination of $SnOct_2$ with a primary alcohol. To the best of our knowledge a similar comparison of a metal alkoxide with $SnOct_2$ and ethanol was not published yet, and we cannot forward a satisfactory explanation of the experimental data at this time.

Finally, three Ph_2BiOEt-initiated polymerizations were performed at 20 °C. These polymerizations were conducted in concentrated solutions to avoid problems with rapidly crystallizing oligo(εCL)s and to find out, if the nature of the solvent has a significant influence on the rate of polymerization. The results presented in Figure 4 demonstrate that Ph_2BiOEt initiates the ROP of εCL even at 20 °C, but the solvent plays a key role for the success of the polymerization. The polymerization should be particularly slow in THF, because this solvent can better coordinate with the Bi atom than toluene or dichloromethane, and the coordination with Bi should hinder the access of εCL. However, the opposite trend was found. In this connection, the time conversion curves of Ph_2BiOEt presented in Figures 1−3 show a sigmoidal shape. This means that in the beginning of the polymerization an activation process takes place. This observation and the positive influence of THF may speculatively be interpreted by assuming an association between two (or more) Ph_2BiOEt molecules which is broken up by THF or εCL and its growing chain thereby activating the initiator. This hypothesis is supported by the following observations. First, the hitherto unknown crystal structure was determined, and its schematic illustration in Figure 5 demonstrates that the O-atom forms a bridge between two Bi atoms. Second, it is well documented in numerous publications that tin alkoxides associate via donor–acceptor interactions.[43]

Finally, the MALDI−TOF mass spectra should be discussed. Regardless of the polymerization temperature the mass spectra display the same pattern exemplarily illustrated in Figure 6. The only class of linear chains are polylactones having ethyl ester and one CH_2OH endgroup in perfect agreement with the coordination-insertion mechanism outlined in Scheme 1. Furthermore, a small percentage of cyclic oligoesters was found. The oligomers (regardless if cyclic or not) are not detectable as a separate maximum in the SEC elution curves and represent a weight fraction $\leq 1\%$. The formation of cyclic oligoesters by back-biting was observed for metal-alkoxide initiated polymerizations of lactones (and lactide) at temperatures ≥ 100 °C. Yet, surprising is the finding that cyclic oligolactones were found in

Table 2. $Bi(OAc)_3$-Initiated,[a] TEG-Coinitiated[b] Polymerizations of εCL in Bulk

expt no.	temp (°C)	time (h)	yield[c] (%)	η_{inh}[d] (dL/g)	M_n (corr)[c,e]	polydispersity[c,e]
1	120	13	87.0	1.15	48000	2.2
2	120	40	87.5	0.96	42000	2.2
3	150	3	86.0	0.88	35000	2.1
4	150	7	86.5	0.85	33000	2.1

[a] εCL/$Bi(OAc)_3$ feed ratio: 1000/1. [b] εCL/TEG feed ratio: 1000/1. [c] Determined after precipitation into diethyl ether. [d] Inherent viscosity measured at 20 °C with $c = 2$ g/L in CH_2Cl_2. [e] Size-exclusion chromatography measurements calibrated with polystyrene and multiplied with the correction factor 0.68.

this study even at a reaction temperature as low as 20 °C, although only traces of cycles were detectable at this temperature.

Preparative Aspects. The influence of the M/I ratio on M_n was studied by two series of polymerizations conducted at 120 °C in bulk. This relatively high temperature was selected, because the conversion per time decreases with higher M/I ratios. At first, εCL distilled over powdered calcium hydride served as monomer and the experiments nos. 1–5 and 6A, 7A, and 8A in Table 1 were performed with εCL of this quality (dry εCL). The inherent viscosities increased with higher M/I ratios, but the measured M_ns (corrected values) deviated from the calculated M_ns at M/I ratios above 300/1 with a tendency toward lower molar masses. The calculated values were obtained by multiplication of the M/I ratio with a conversion of 98% (as indicated by ^{1}H NMR spectroscopy). The corrected M_n values resulted from multiplication of the experimental data obtained by calibration with polystyrene with the factor 0.68. This factor (±0.02) came into play for the following reasons. First, Schindler et al.[44] reported a Mark–Houwink−Sakurada equation (eq 5), which as demonstrated previously[45] suggests such a correction factor for M_n values above 10 000 Da. Second, ^{1}H NMR endgroup analyses of copolyesters of εCL confirmed this factor.[31] Third, several research groups[46–49] have demonstrated by means of various analytical methods that the direct calibration with polystyrene overestimates the real molar masses of poly(εCL) and other aliphatic polyesters by 50–80%. The relatively low yields listed in Table 1 resulted from incomplete precipitation into diethyl ether.

From previous polymerizations of εCL, it was learned[50] that this monomer when distilled once or twice over calcium hydride may still contain traces of water. To find out if these traces of water are responsible for the lower M_n values obtained with M/I ratios ≥400, four more polymerizations were conducted with a so-called ultradry εCL. This εCL was first distilled over CaH_2 and immediately afterward over P_4O_{10} (with a loss of 45–50%). Furthermore, these polymerizations were performed under an atmosphere of dry argon (footnotes [a] and [d] in Table 1). Under these optimized conditions, M_n values were obtained which were in satisfactory agreement with the calculated ones. These results prove that the Ph_2BiOEt-initiated polymerizations allow a control of the molar masses via the M/I ratio at least up to 115 000 Da. Another useful piece of information concerns the polydispersities which increase with longer reaction times.

In our first studies of bicatalyzed polymerizations of εCL or L-lactide Bi(III)acetate or *n*-hexanoate were used in combination with diols, triols, or tetraols to prepare telechelic and star-shaped polymers. In these experiments M_ns up to 23 000 Da were realized, but no attempt was made to test the upper limit of the polymerization process. With the results of Ph_2BiOEt in hand four more experiments were performed in this work using Bi(III)acetate in a 1:1 combination with ethanol as initiator. For comparison with Ph_2BiOEt, the M/I ratio was fixed at 1000/1, the temperature at 120 °C (nos. 1 + 2, Table 2) and ultradry εCL was used. Because of the lower reactivity of Bi(III)acetate two more polymerizations were conducted at 150 °C (nos. 3 + 4, Table 2). Regardless of the reaction conditions, viscosity and SEC measurements proved that the highest M_n values did not exceed 50% of the best result obtained from Ph_2BiOEt. Together with the rather low reactivity of $BiHex_3$ illustrated in Figures 1−3, these results indicate that the simple Bi(III)carboxylates are not suited to prepare high molecular weights poly εCL (but they have the advantage of an extraordinarily low toxicity).

Conclusions

Diphenylbismuth ethoxide was the first single-site bismuth initiator used for the ring-opening polymerization of a lactone. As expected, it proved to be considerably more reactive than bismuth(III) *n*-hexanoate and enabled polymerizations of εCL even at 40 °C. At temperatures ≤90 °C it was more reactive than the $SnOct_2$/ethanol initiator combination. Furthermore, it allowed for a control of the molecular weight of poly(εCL) via the M/I ratio up to molecular weights above 10^5 Da. These results indicate that bisaryl bismuth alkoxides are an interesting class of initiators for lactones (and possibly for other cyclic esters) and certainly deserve further studies.

References and Notes

(1) Dunsing, R.; Kricheldorf, H. R. *Polym. Bull. (Berlin)* **1985**, *14*, 491–495.
(2) Kricheldorf, H. R.; Berl, M.; Scharnagl, N. *Macromolecules* **1988**, *21*, 286–293.
(3) Wurm, B.; Keal, I. H.; Hocker, H.; Sylvester, G.; Leitz, E.; Olt, K. U. *Makromol. Chem. Rapid Commun.* **1992**, *13*, 9–14.
(4) Kricheldorf, H. R.; Lossin, M. *J. Macromol.Sci.*−*Pure Appl. Chem.* **1997**, *34*, 179–189.
(5) Kricheldorf, H. R.; Lee, S.-R. *Polymer* **1995**, *36*, 2995–3003.
(6) Kricheldorf, H. R.; Serra, A. *Polym. Bull. (Berlin)* **1985**, *14*, 497–502.
(7) Zhong, Z.; Ankone, M.; Dijkstra, P. J.; Birg, C.; Westerhausen, M.; Feijen, J. *Polym. Bull. (Berlin)* **2001**, *46*, 51–57.
(8) Zhong, Z.; Dijkstra, P. J.; Birg, C.; Westerhausen, M.; Feijen, J. *Macromolecules* **2001**, *34*, 3863–3868.
(9) Kleine, J.; Kleine, H. *Makromol. Chem.* **1959**, *30*, 23–38.
(10) Dittrich, W.; Schulz, R. *Angew. Makromol. Chem.* **1971**, *15*, 109–126.
(11) Chabot, F.; Vert, M.; St; Chapelle, S.; Granger, P. *Polymer* **1983**, *24*, 53–59.
(12) Schwach, G.; Coudane, J.; Engel, R.; Vert, M. *Polym. Bull. (Berlin)* **1994**, *32*, 617–623.
(13) Bero, M.; Kasperczyk, J.; Jedlinski, Z. *J. Makromol. Chem.* **1990**, *191*, 2287–2296.
(14) Nijenhuis, H.; Grijpma, D. A.; Pennings, A. J. *Macromolecules* **1992**, *25*, 6419–6424.
(15) Kricheldorf, H. R.; Damrau, D. O. *Macromol. Chem. Phys.* **1997**, *198*, 1753–1766.
(16) Kricheldorf, H. R.; Damrau, D. O. *Macromol. Chem. Phys.* **1998**, *199*, 1089–1097.
(17) Kricheldorf, H. R.; Damrau, D. O. *Macromol. Chem. Phys.* **1998**, *199*, 1747–1752.
(18) Kricheldorf, H. R.; Boettcher, C. *Macromol. Chem. Phys.* **1993**, *194*, 463–473.
(19) Kricheldorf, H. R.; Damrau, D. O. *Macromol. Chem. Phys.* **1997**, *198*, 1767–1774.
(20) Stolt, M.; Hiltunen, K.; Sodergard, A. *Biomacromolecules* **2001**, *2*, 1243–1248.
(21) O'Keefe, B. J.; Monnier, S. M.; Hillmyer, M. A.; Tolman, W. B. *J. Am. Chem. Soc.* **2001**, *123*, 339–340.
(22) O'Keefe, B. J.; Breyfogl, L. E.; Hillmyer, M. A.; Tolman, W. B. *J. Am. Chem. Soc.* **2002**, *124*, 4384–4393.
(23) Kricheldorf, H. R.; Berl, M.; Scharnagl, N. *Macromolecules* **1988**, *21*, 286–293.
(24) Miola-Delaite, Ch.; Hamaide, T.; Spitz, R. *Macromol. Chem. Phys.* **1999**, *200*, 1771–1778.
(25) Kasperczyk, J. *Macromol. Chem. Phys.* **1999**, *200*, 903–910.
(26) Dobrzynski, P. *J. Polym. Sci. Part A: Polym. Chem.* **2002**, *40*, 1379–1394.
(27) Kricheldorf, H. R.; Boettcher, C. *J. Macromol. Sci.*−*Pure Appl. Chem.* **1993**, *A30*, 441–448.
(28) Kricheldorf, H. R.; Hachmann-Thiessen, H.; Schwarz, G. *Biomacromolecules* **2004**, *5*, 492–496.
(29) Kricheldorf, H. R.; Hachmann-Thiessen, H.; Schwarz, G. *Macromolecules* **2004**, *37*, 6340–6345.
(30) Kricheldorf, H. R.; Hachmann-Thiessen, H. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 3667–3674.
(31) Kricheldorf, H. R.; Rost, S. *Biomacromolecules* **2005**, *6*, 1345–1352.
(32) Kricheldorf, H. R.; Rost, S. *Macromolecules* **2005**, *38*, 8220–8226.
(33) Kricheldorf, H. R.; Bornhorst, K.; Hachmann-Thiessen, H. *Macromolecules* **2005**, *38*, 5017–5024.
(34) Kricheldorf, H. R.; Behnken, G.; Schwarz, G. *Polymer* **2005**, *46*, 11219–11224.
(35) Kricheldorf, H. R.; Behnken, G. *J. Macromol. Sci.*−*Pure Appl. Chem.* **2007**, *44*, 795–800.
(36) Guo, Z.; Sadler, P. J. *Angew. Chem.* **1999**, *111*, 1610–1629. Guo, Z.; Sadler, P. J. *Angew. Chem. Int. Ed. (Engl.)* **1999**, *38*, 1512–1531.
(37) Briand, G. C.; Burford, N. *Chem. Rev.* **1999**, *99*, 2601–2657.
(38) Rodilla, V.; Miles, A. T.; Jenner, W.; Harksworth, G. M. *Chem. Biol. Interact.* **1998**, *115*, 71–83.

(39) Kricheldorf, H. R.; Kreiser-Saunders, I.; Stricker, A. *Macromolecules* **2000**, *33*, 702–709.

(40) Wieber, M.; Baudis, U. *Z. Anorg. Allg. Chem.* **1978**, *439*, 139–144.

(41) Kowalski, A.; Duda, A.; Penczek, S. *Macromolecules* **2000**, *33*, 7359–7370.

(42) Kowalski, A.; Libiszowski, J.; Duda, A.; Penczek, S. *Macromolecules* **2000**, *33*, 1964–1971.

(43) Davies, A. G. *Organotin Chemistry*; VCH Publishers: Weinheim, Germany, 1997; Chapter *12*, p 169.

(44) Schindler, A.; Hibionada, Y. M.; Pitt, C. G. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, 319–326.

(45) Kricheldorf, H. R.; Eggerstedt, S. *Macromol. Chem. Phys.* **1998**, *199*, 283–290.

(46) Hiltunen, K.; Härkönen, M.; Seppala, J.; Vaänen, T. *Macromolecules* **1996**, *29*, 8677–8682.

(47) Pasch, H.; Rode, K. *J. Chromatogr. A* **1995**, *699*, 21–29.

(48) Kowalski, A.; Libiszowski, J.; Duda, A.; Penczek, S. *Macromolecules* **2000**, *33*, 1964–1971.

(49) Save, M.; Schappacher, M.; Soum, A. *Macromol. Chem. Phys.* **2002**, *203*, 889–899.

(50) Kricheldorf, H. R. Unpublished results (analyzed groups identified by ^{1}H NMR spectroscopy and MALDI−TOF mass spectrometry).

MA071797I