Biodegradable Multiblock Copolyesters Prepared from ϵ-Caprolactone, L-Lactide, and Trimethylene Carbonate by Means of Bismuth Hexanoate

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ABSTRACT: Telechelic random copolymers were prepared by copolymerization of ϵ-caprolactone (ϵCL) and trimethylene carbonate (TMC) in bulk using bismuth(III) hexanoate, $Bi(OHex)_3$, as initiator. These copolymers were characterized by ^1H and ^{13}C NMR spectroscopy. A−B−A triblock copolymers were synthesized by chain extension of these random copolymers with L-lactide, whereby the chain length of the amorphous central blocks and of the crystalline poly(L-lactide) blocks were varied. Finally, the triblock copolymers were transformed into multiblock copolymers by chain extension with 1,6-hexamethylene-diisocyanate. All three synthetic steps were performed in a "one-pot-procedure". The resulting multiblock copolymers were characterized by ^1H NMR spectroscopy, SEC measurements, DSC measurements, and stress−strain measurements. Typical mechanical properties of thermoplastic elastomers were detected.

Introduction

The purpose of the present work was synthesis (and characterization) of biodegradable multiblock copolymers by in situ coupling of A−B−A triblock copolymers. The central B-blocks should be prepared by copolymerization of ϵCL and TMC so that noncrystalline soft segments with low glass-transition temperatures were obtained. Chain extension with L-lactide should yield crystalline A-blocks. Biodegradable A−B−A triblock copolymers containing crystalline poly(L-lactide) or poly(ϵCL) blocks were described by numerous research groups. However, in almost all cases the soft segment was a polyether, a polysiloxane or a polyalkene, and therefore, the problem of transesterification between soft and hard block did not exist. Furthermore, a coupling of A−B−A triblocks to multiblock copolymers was only reported in very few publications. [1−5]

A−B−A triblock copolymers composed of a central poly TMC block and poly L-lactide or polylactone B-blocks were prepared by Kricheldorf and Stricker[6] by means of cyclic tin alkoxide initiators. The molecular weights of these triblock copolymers were too low to impart elastic properties and chain extension was necessary to achieve elasticity. However, biodegradable block copolymers showing elastic properties were prepared by several research groups.[1−5,7−15] Multiblock copolymers prepared by chain extension of TMC/LLA A−B−A triblock copolymers were recently studied by Pospiech et al.[8] No elastic properties were found when the B-blocks consisted of neat poly TMC. Obviously, the poly TMC blocks partially crystallized under the influence of mechanical stress. However, when the B-blocks were prepared by copolymerization of ϵCL and TMC (feed ratio 1:3), multiblock copolymers with interesting mechanical properties were obtained. Random copolymers of ϵCL and TMC were prepared by two more research groups,[16−18] but not in connection with the synthesis of thermoplastic elastomers. Therefore, the present work was aimed at synthesizing multiblock copolymers consisting of crystalline poly(L-lactide) A-blocks in combination with random 1:1 copolymers of ϵCL and TMC as noncrystallizable B-blocks.

For this purpose, bismuth hexanoate was selected as catalyst because bismuth oxides and carboxylates are known for their extraordinarily low toxicity.[19] They are components of several ointments designed for skin care and wound treatment, and bismuth subsalicylate has been known as a gastrointestinal drug for almost 100 years.[20] Furthermore, bismuth carboxylates were recently found to be good catalysts for homopolymerization of ϵCL[21] and LLA[22] and for the copolymerization of ϵCL and glycolide.[23] For all these reasons, it seemed to be worthwhile to study the usefulness of $BiHex_3$ as a catalyst for the preparation of the desired multiblock copolymers. In this work it should be elucidated if bismuth(III) *n*-hexanoate ($BiHex_3$) is suited for the following:

(1) the preparation of these random ϵCL/TMC copolymers;

(2) the preparation of A−B−A triblock copolymers from LLA without significant transesterification between A and B blocks;

(3) catalyzing the chain extension of the triblock copolymers by means of 1,6-hexamethylene diisocyanate (HMDI).

Experimental Section

Materials. ϵ-Caprolactone (ϵCL) was purchased from Aldrich Co. (Milwaukee, WI) and distilled (in vacuo) over freshly powdered calcium hydride. Trimethylene carbonate, TMC, and L-lactide were kindly supplied from Boehringer KG (Ingelheim/Rhein, Germany). They were recrystallized from dry ethyl acetate and ligroin and stored in a desiccator over P_4O_{10}. Bismuth(III) acetate was also purchased from Aldrich Co. and transformed into the hexanoate as described previously. 1,6-Hexamethylene diisocyanate was purchased from ACROS Organics (Geel, Belgium) and distilled in vacuo prior to use. Tetra(ethylene glycol), TEG, was also purchased from ACROS. It was azeotropically dried with toluene and distilled in vacuo. Diethyl ether was refluxed and distilled over sodium wire. Chloroform was distilled over P_4O_{10}.

Copolymerization of ϵCL and TMC (Table 1). ϵCL (10 mmol), TMC (10 mmol), and dry TEG (0.5 mmol) were weighed into a 50 mL Erlenmeyer flask having silanized glass walls. The reaction vessel was closed with a glass stopper and a steel spring and immersed into an oil bath preheated to 120°C. When a homogeneous melt was formed 0.02 mL of a 0.5 M

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Table 1. Copolymerizations of ϵCL and TMC Initiated by TEG/BiHex$_3$[a]

polym	temp (°C)	time (h)	ϵCL/TMC/TEG found[b]	alt. dyads[b] (^{1}H NMR)	$\bar{L}_{\mathrm{CL}}$[b,c] (^{1}H NMR)	alt. dyads[b] (^{13}C NMR)	$\bar{L}_{\mathrm{CL}}$[c] (^{13}C NMR)	T_g[d] (°C)
1	100	24	19:18:1	47	2.15	47	2.15	−50
2	120	24	19:19:1	50	2.00	49	2.05	−50
3	100	48	20:19:1	46	2.16	45	2.23	−53
4	120	48	20:17:1	45	2.24	44	2.30	−57

[a] ϵCL/TMC/TEG = 20/20/1; ϵCL/TMC/BiHex$_3$ = 2000/1. [b] From ^{1}H NMR spectra of the isolated copolymers. [c] Calculated via eq 1. [d] DSC measurements with a heating rate of 20°C/min.

solution of Bi(OHex)$_3$ in chlorobenzene was injected by means of a syringe (M/I = 2000/1). The reaction mixture was then thermostated at 100 or at 120 °C (see Table 1). The crude products were characterized by ^{1}H NMR spectroscopy and complete conversion of both monomers was found after 24 h.

In parallel experiments, dry chlorobenzene (20 mL) was added to the monomer mixture prior to the injection of the catalyst. In these cases, the conversion of TMC was not complete after 24 h.

In all these experiments the reaction mixture was prepared in an atmosphere of dry nitrogen.

A—B—A Triblock Copolymers. ϵCL (10 mmol), TMC (10 mmol), and TEG (0.5 mmol) were weighed into a 50 mL Erlenmeyer flask with silanized glass walls. After homogenization at 120 °C, 0.02 mL of a 0.5 M solution of Bi(OHex)$_3$ in chlorobenzene was injected. The reaction mixture was thermostated at 120 °C for 24 h and cooled to 20−30 °C. L-Lactide (50 mmol) and dry chlorobenzene (30 mL) were added, and the reaction vessel was again immersed into an oil bath heated to 120 °C. Occasional shaking helped to homogenize the reaction mixture within 10 min. After 24 h at 120 °C ^{1}H NMR spectroscopy proved that almost complete conversion of the l-lactide took place. After cooling, the reaction mixture was diluted with dichloromethane (20−30 mL) and precipitated into cold diethyl ether. The isolated copolyester was dried at 20 °C in vacuo.

Multiblock Copolyesters. A hot solution of a A−B−A triblock copolyester in chlorobenzene was prepared as described above. The temperature was adjusted to 100 °C and a 1 M solution of HMDI in chlorobenzene (0.5 mL) was injected. After 2 h at 100 °C, the reaction mixture was cooled to 25−30 °C and diluted with CH$_2$Cl$_2$ (25−35 mL). The solution was precipitated into cold diethyl ether and the isolated polymer was dried at 40 °C in vacuo.

Measurements. The inherent viscosities were measured in CH$_2$Cl$_2$ by means of an automated Ubbelohde viscometer thermostated at 20 °C. The ^{1}H NMR and ^{13}C NMR spectra were recorded with a Bruker Avance 400 FT NMR spectrometer in 5 mm o.d. sample tubes. CDCl$_3$ served as solvent and TMS as shift reference. The SEC measurements were performed on a homemade SEC apparatus at 23 °C with tetrahydrofuran as eluent. A combination of three PSS−SDV mixed-bed columns was used along with UV and RI detectors. The elution curves were calibrated with polystyrene and with the Mark−Houwink eq 1 reported for poly(ϵ-caprolactone) in ref 24 (see Table 3).

$$[\eta] = 1.395 \times 10^{-4} M_{\mathrm{w}}^{\;0.786} \tag{1}$$

The stress−strain measurements were performed with films hotpressed on a Metrowatt RO-8 press. The polymers were molten 20 °C above the melting temperature and kept for 2 min under a pressure of 1 kN/mm^2. Afterward, the films were annealed 20 °C below T_m for 24 h. For the measurements SA3 specimens according to DIN 53544 were cut from the films. A Zwick 210 apparatus was used and the measurements were started at a stress of 1 N with a speed of 10 mm/min.

The DSC measurements were performed on a Mettler Toledo 821 in aluminum pans under nitrogen with a heating rate of 20 °C/min.

Table 2. Syntheses of A−B−A Triblock Copolymers and Related Multiblock Copolymers

polym	ϵCL/TMC/TEG[a] (feed ratio)	LLA/TEG[a] (feed ratio)	molar excess of HMDI[b]	yield (%)	η_{inh}[c] (dL/g)
1	10/10/1	50		91	0.180
2	10/10/1	50	2	96	0.650
3	10/10/1	50	6	93	0.765
4	10/10/1	50	10	94	1.300
5	10/10/1	100		89	0.255
6	10/10/1	100	2	92	0.940
7	10/10/1	100	10	96	1.740
8	20/20/1	50		82	0.205
9	20/20/1	50	2	87	0.730
10	20/20/1	50	10	85	1.510
11	20/20/1	100		92	0.260
12	20/20/1	100	2	95	0.800
13	20/20/1	100	10	95	1.970

[a] Temperature: 120 °C. Time: 24 h. [b] Temperature: 100 °C. Time: 2 h (relative to TEG). [c] Measured at 20 °C with c = 2 g/L in CH$_2$Cl$_2$.

Results and Discussion

Syntheses of the Soft Segments. The preparation of the multiblock copolymers studied in this work required three steps, which should be performed in a “one-pot procedure”. To have a full understanding and full control of the chemical structure, the first two steps were studied separately. The first step consisted of copolymerizations of ϵCL with TMC at a feed ratio 1:1. All copolymerizations were conducted in bulk with TEG as co-initiator. The temperature was varied from 100 to 120 °C and the time from 24 to 48 h (Table 1). The molar composition of the isolated copolymers was determined by ^{1}H NMR spectroscopy. Regardless of the temperature, the composition agreed with the feed ratio when the time was limited to 24 h. After 48 h, a partial loss of TMC units was detectable. The composition determined after 24 h also allowed for a calculation of the number-average molecular weight (M_n) of the SS which corresponded to 4300 Da.

From the dyad splitting of the ^{1}H NMR O−CH$_2$ signals (illustrated in Figure 1) the percentage of alternating dyads was determined and the average lengths of the ϵCL blocks ($\bar{L}_{\mathrm{CL}}$) was calculated according to eq 2.

$$\bar{L}_{\mathrm{CL}} = \frac{I_{\mathrm{CL-CL}}}{I_{\mathrm{CL-TMC}}} + 1 \tag{2}$$

where $I_{\mathrm{CL-CL}}$ = signal intensity of the CL−CL-dyad (e.g., signal g in Figure 1 and signal a in Figure 2) and $I_{\mathrm{CL-TMC}}$ = Signal intensity of the CL−TMC-dyad (e.g., signal j in Figure 1 and b in Figure 2).

Both values agreed with a nearly random sequence. This interpretation was confirmed by the ^{13}C NMR spectra which displayed a dyad splitting of the CO-signals (Figure 2). Finally, the DSC measurements should be mentioned. These measurements yielded glass-transitions (T_g) around −50 °C as expected for copolymers of ϵCL and TMC. Since the T_g of poly(ϵCL) is lower than that of poly TMC, it was a satisfactory

Table 3. SEC Measurements of Triblock Copolymers and of Selected Multiblock Copolymers

polym	M_n[a] (Da)	M_w[a] (Da)	M_w/M_n[a]	M_n[b] (Da)	M_w[b] (Da)	M_w/M_n[b]	M_n (^{1}H NMR)
1	13 000	15 000	1.19	9000	11 000	1.18	9800
4	35 000	66 000	1.87	25 000	45 000	1.80	
5	21 000	26 000	1.24	15 000	18 000	1.23	15 800
7	160 000	330 000	2.06	108 000	216 000	1.99	
8	13 000	16 000	1.23	10 000	12 000	1.22	11 000
10	120 000	240 000	2.00	84 000	160 000	1.90	
11	22 000	27 000	1.24	15 000	19 000	1.22	18 000
13	167 000	336 000	2.02	119 000	222 000	1.88	

[a] Calibration with commercial polystyrene standards. [b] Calibration with the M.-H.- eq 1 reported for poly(εCL) in ref 24.

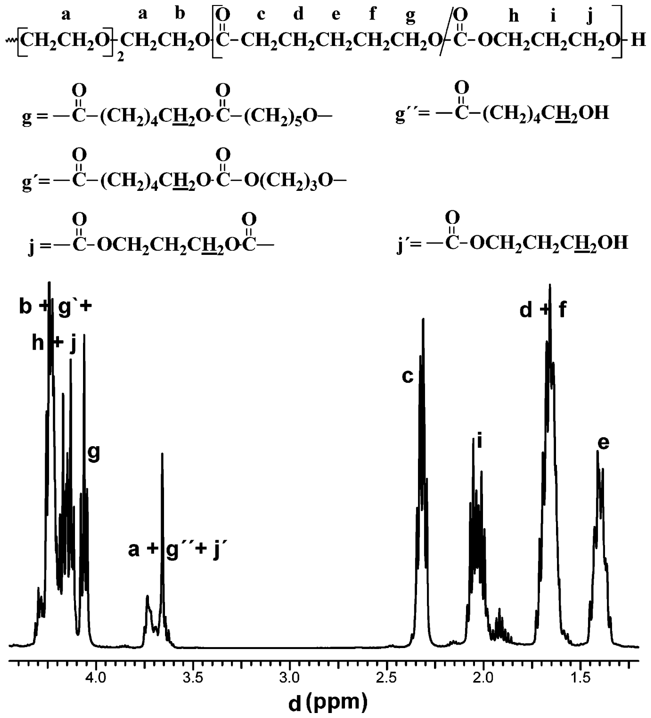


Figure 1. 400 MHz ^{1}H NMR spectrum of a telechelic εCL-TMC copolymer initiated with TEG: **2**, Table 1.

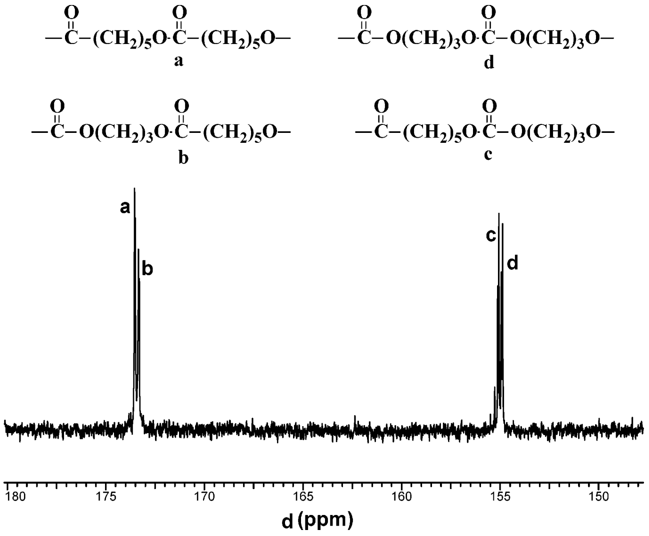


Figure 2. 100.4 MHz ^{13}C NMR spectrum of a telechelic εCL-TMC copolymer initiated with TEG: **2**, Table 1.

Table 4. NMR-spectroscopic Characterization of the Triblock- and Multiblock Copolymers

polym	εCL/TMC/LLA/TEG (found)[a]	alt dyad (^{1}H NMR)	$\bar{L}_{CL}$[b] (^{1}H NMR)	alt dyad (^{12}C NMR)	$\bar{L}_{CL}$[b] (^{13}C NMR)
1	10/10/48/1	52	1.93	50	2.00
2	10/10/46/1	53	1.89	48	2.10
3	10/10/49/1	54	1.85	n.d.	n.d.
4	10/10/49/1	53	1.90	51	1.97
5	10/10/93/1	53	1.88	50	2.01
6	10/10/97/1	53	1.90	n.d.	n.d.
7	10/10/98/1	51	1.97	n.d.	n.d.
8	20/20/45/1	51	1.95	50	1.98
9	20/20/46/1	49	2.05	48	2.09
10	20/20/48/1	51	1.95	54	1.83
11	20/20/93/1	49	2.05	50	1.99
12	20/20/95/1	49	2.03	52	1.92
13	20/20/97/1	49	2.05	54	1.83

[a] Molar composition as determined by ^{1}H NMR spectroscopy. [b] Calculated according to eq 2.

Table 5. DSC Measurements: First Heating with a Rate of 20 °C/min

polym	T_g of soft segm (°C)	T_g of poly LLA blocks (°C)	T_m of poly LLA blocks (°C)
1	−21	20	148
2	n.d.	24	143
3	n.d.	25	143
4	−39	29	142
5	n.d.	37	159
6	n.d.	37	153
7	−41	38	152
8	−35	5	131
9	−38	2	138
10	n.d.	−10	133
11	−46	20	155
12	n.d.	17	138
13	n.d.	30	150

result to see that the sample with the highest εCL/TMC ratio (**4**, Table 1) had the lowest T_g.

A−B−A Triblock Copolymers. The preparation of the A−B−A triblock copolymers was performed in such a way that L-lactide (LLA) was added to the virgin melt of the εCL/TMC copolymer, when the copolymerization was complete. The ring-opening polymerization of LLA initiated by both ends of the soft segment was continued without addition of a new catalyst. The completion of the LLA polymerization was monitored by ^{1}H NMR spectroscopy. The triblock copolymers were then isolated by precipitation into cold dry diethyl ether. Four different triblock copolymers were prepared, because two soft segments having a M_n around 2200 Da and a M_n around 4300 Da were combined with two different polylactide blocks. These polylactide blocks had either an average length of 50 lactyl (O−CHMe−CO) units on both sides or an average length of 100 lactyl units. The yields and inherent viscosities of these four triblock copolymers were listed under **1**, **5**, **8**, and **11** in Table 2. Their properties were listed under the same numbers in Tables 3−5.

The inherent viscosities qualitatively reflect the variation of the lengths of both soft segments and poly LLA blocks (Table 2). Furthermore, SEC measurements were conducted, and their results are summarized in Table

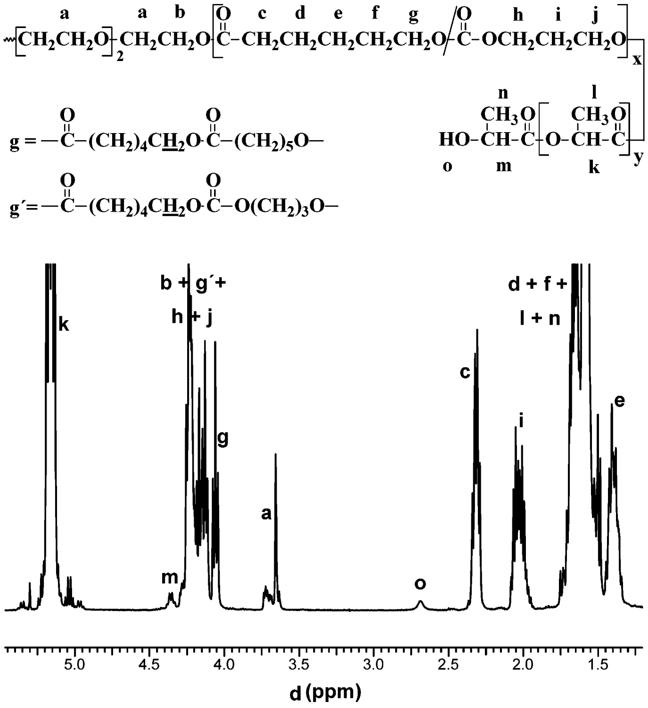


Figure 3. 400 MHz ^{1}H NMR spectrum of an A–B–A triblock copolymer: **8**, Table 2.

3 (**1**, **5**, **8**, **11**). Calibration of the elution curves with commercial polystyrene standards (as usual) yielded the data presented in columns 2–4. However, it is known from the work of several research groups[24–29] that calibration with polystyrene overestimates the real molar masses of aliphatic polyesters by 50–80%. Therefore, the mass data obtained in this way either need correction by multiplication with a factor of 0.56–0.68[25–29] or the elution curves of poly(ϵCL) are calibrated with the Mark–Houwink eq 1 elaborated by Schindler et al.[24] In the present work, the second method was applied and the molar masses and polydispersities obtained in this way were listed in columns 6–7 of Table 3. Furthermore, M_ns were calculated from the molar composition determined by ^{1}H NMR spectroscopy (second column of Table 4). A comparison with M_n data obtained via the Mark–Houwink equation revealed a satisfactory agreement.

The ^{1}H NMR and the ^{13}C NMR spectroscopy were also used to characterize the sequences of the triblock copolymers (see Table 4 and Figures 3 and 4). The percentage of alternating dyads and the average lengths of ϵCL blocks were determined by both NMR methods and acceptable agreement was achieved. All NMR data clearly proved the formation of random sequences in perfect agreement with the model copolymers presented in Table 1. Another important result of the NMR spectroscopic characterization was the absence of significant transesterification between LLA units and soft segment as demonstrated by the ^{13}C NMR spectrum of Figure 4. The CO signals of the central B-block agree with those of the neat ϵCL/TMS copolymer in Figure 2. The sharp CO-signal labeled x represents the polylactide blocks. However, a tiny signal emanating from the foot of this strong signal (on the downfield side) perhaps indicates a low extent of transesterification.

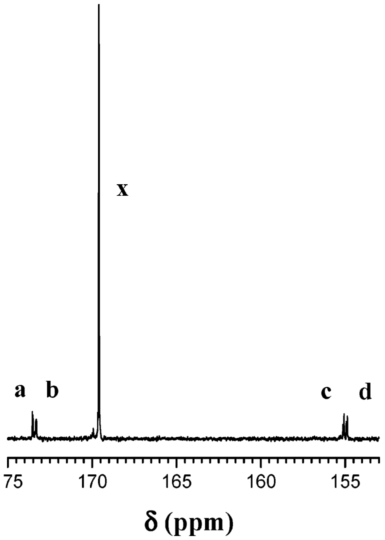


Figure 4. 100.4 MHz ^{13}C NMR spectrum of the A–B–A triblock copolymer: **8**, Table 2. Signal x represents the CO-groups of the polylactides blocks. The signal assignments of the middle (B) block correspond to those of Figure 2.

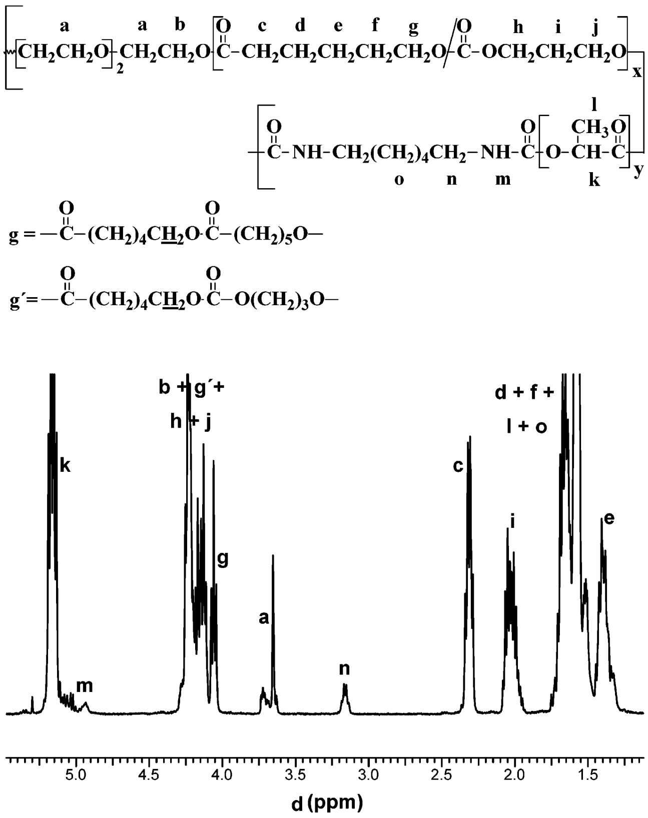


Figure 5. 400 MHz ^{1}H NMR spectrum of a multiblock copolymer: **10**, Table 2.

The absence of significant transesterification was confirmed by the DSC measurements compiled in Table 5. Strong melting endotherms of the polylactide blocks were found for all four triblock copolymers (Figure 6). As expected, the melting temperatures (T_ms) of the L-lactide blocks were higher, when the blocks were longer (**5** + **11** relative to **1** + **8**). Particularly interesting is the observation of two T_gs in the heating curves of the triblock copolymers **1** and **8**. This finding proves the existence of two amorphous phases as it may be expected for a perfect block structure. In contrast, considerable transesterification will reduce or eliminate the crystallinity and generate one single amorphous phase. In summary, the preparation of A–B–A triblock co-

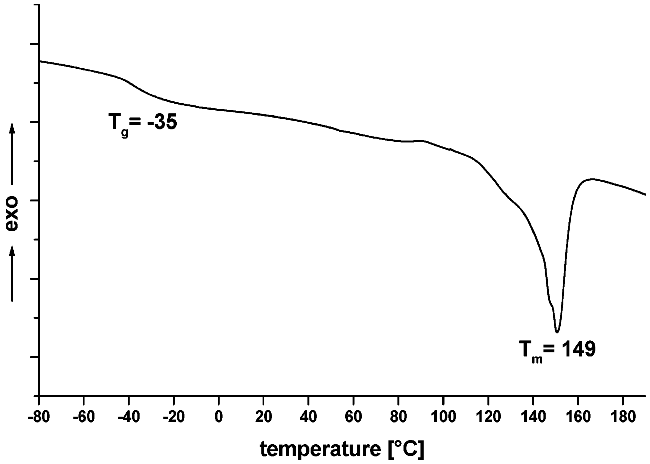


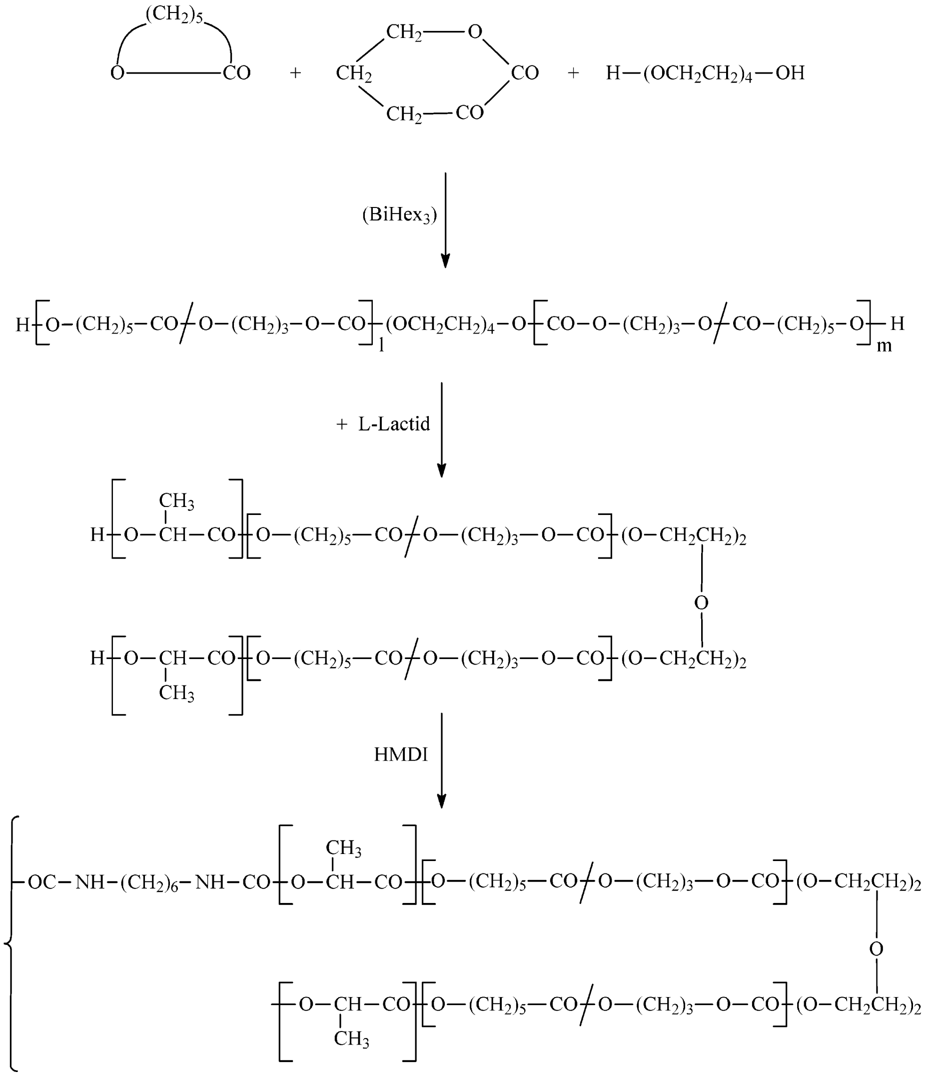
Figure 6. DSC heating curve of an A−B−A triblock copolymer: **8**, Table 2.

polymers by in situ chain extension with LLA was successful.

Multiblock Copolymers. The multiblock copolymers were prepared in situ from the A−B−A triblock copolymers by addition of HMDI in an equimolar amount relative to the co-initiator TEG. This chain extension with HMDI was conducted in concentrated chlorobenzene solution at 100 °C. The viscosity data listed in Table 2 and the molecular weights compiled in Table 3 proved that the chain extension was successful. The ^{1}H NMR spectrum presented in Figure 5 indicates the incorporation of 1,6-diaminohexane units, and thus, confirms the chain extension by HMDI. However, it was also found that an increasing excess of HMDI significantly enhanced the molecular weights (e.g., **1**−**4**, Table 2). The most likely explanation of this finding is based on the assumption that a small fraction of the isocyanate groups react with free or with bismuth-activated urethane groups (Scheme 2). The formation of allophanate groups means that branching and an efficient growth of the molecular weight takes place. The formation of allophanate groups at elevated temperatures is known since the pioneering work of Bayer on isocyanate-based polyaddition reactions. We have recently demonstrated[30] that the tin-catalyzed polyaddition of TEG onto HMDI for a complete conversion of the OH-groups is due to the competing formation of allophanate groups. The catalytic role of $BiHex_3$ in this chain extension is outlined in Scheme 2 as a hypothesis paralleling the mechanism formulated by Davies[31] for the S_n carboxylate-catalyzed addition of alcohols onto isocyanates.

Multiblock copolyesters built up by an alternating sequence of crystalline (and rapidly crystallizing) blocks and mobile blocks (T_gs < 0 °C) were synthesized from a

Scheme 1. Synthesis of Multiblock Copolymers



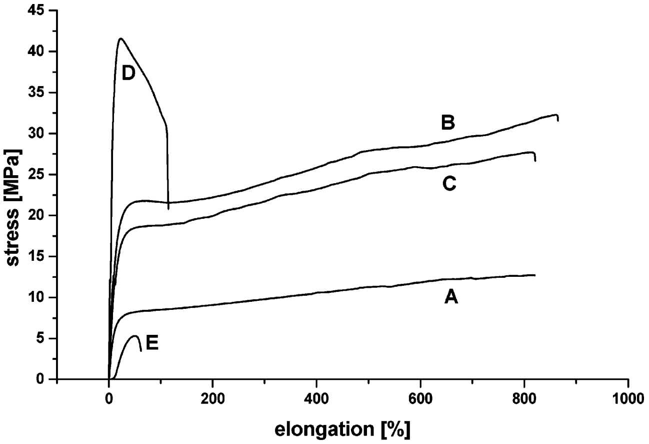
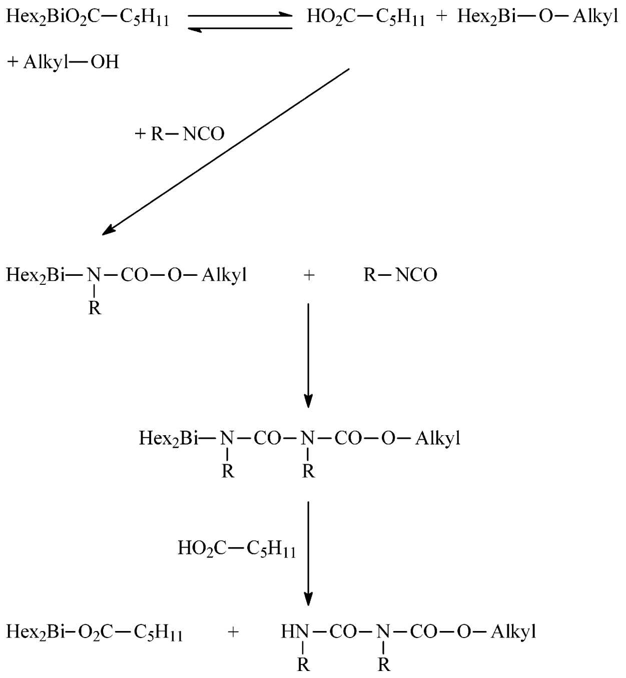


Figure 7. Stress-strain measurements of multiblock copolymers: (A) **10**, Table 2; (B) **13**, Table 2; (C) **4**, Table 2; (D) **7**, Table 2; (E) analogous to **10**, Table 2 containing a GL/ϵCL soft segment (14/26) prepared with BiSS−Cat.

Scheme 2. Hypothetical Mechanism of the BiHex$_3$-Catalyzed Formation of Urethane and Allophanate Groups



broad variety of monomers, because they combine the useful properties of "vulcanized" elastomers with those of an engineering plastic processable from the melt. Several such thermoplastic elastomers (TPEs) were commercialized over the past 2 decades,[32] but none of them falls into the group of biodegradable materials. From part of the multiblock copolymers prepared in this work, mechanical properties characteristic for TPEs were expected. To obtain first-hand information, if this expectation was justified, the multiblock copolymers were subjected to simple stress−strain measurements. The results were presented in the form of curves A−D in Figure 7. As expected, the lowest initial stress together with the highest elongation was found for the combination of a long soft-segment with short poly(L-lactide) blocks (curve A). A considerably higher initial stress with a similar elongation at break were found for combinations of short soft-segments with short poly(L-lactide) blocks (curve C) or for long soft-segments combined with long hard-segments (curve B). A short soft-segment in combination with long hard-segments gave a high initial stress but a negligible elongation at break. In summary, these measurements demonstrate that the multiblock copolyesters of this work may possess mechanical properties which can rival with those of commercial TPEs, when the block lengths were accordingly optimized.

Finally, curve E needs to be mentioned. This curve was recorded from a multiblock copolymer consisting of poly(L-lactide) blocks (chain extended with HMDI) in combination with a soft-segment consisting of a random copolymer of ϵCL and glycolide.[33] In other words, the structure of this copolyester paralleled that of the copolyester **10**, Table 2, of this work. The poor mechanical properties (curve E) demonstrate that the good mechanical properties found for some multiblock copolymers of this work are not trivial and cannot be achieved by any kind of biodegradable multiblock copolymer.

Conclusions

The syntheses of biodegradable A−B−A triblock copolymers and multiblock copolymers described above allow the following conclusions. BiHex$_3$ proved to be an efficient catalyst for three different reactions. First, it initiated (or catalyzed) the random copolymerization of ϵCL or TMC, so that upon co-initiation with a diol, OH-terminated telechelic copolymers were obtained. Second, it initiated (or catalyzed) the extension of these preformed main co-initiators by ring-opening polymerization of L-lactide without significant transesterification reactions.[3] Third, it catalyzed the chain extension of the triblock copolymers by 1,6-hexamethylene diisocyanate. Because of these multiple catalytic activities, BiHex$_3$ allowed for the preparation of multiblock copolyesters in a "one-pot procedure". These multiblock copolyesters are interesting, because their mechanical properties may resemble those of commercial thermoplastic elastomers, provided the structure (mainly the block lengths) is accordingly optimized. Furthermore, BiHex$_3$ is particularly useful and attractive as catalyst/initiator because it is far less toxic than the most widely used tin catalysts/initiators and less toxic than almost all other heavy metals.

References and Notes

(1) Kricheldorf, H. R.; Langanke, D. *Macromol. Chem. Phys.* **1999**, *200*, 1183.
(2) Kricheldorf, H. R. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 4723.
(3) Kricheldorf, H. R.; Rost, S. *Macromol. Chem. Phys.* **2004**, *205*, 1031.
(4) Kim, J.-H.; Lee, J. H. *Macromol. Res.* **2002**, *10*, 54.
(5) Pospiech, D.; Komber, H.; Jehnichen, D.; Häussler, L.; Eckstein, K.; Scheibner, H.; Janke, A.; Kricheldorf, H. R.; Petermann, O. *Biomacromolecules* **2005**, *6*, 439.
(6) Kricheldorf, H. R.; Stricker, A. *Macromol. Chem. Phys.* **1999**, *200*, 1726.
(7) Bachari, A.; Belorgey, G.; Helary, G.; Sauvet, G. *Macromol. Chem. Phys.* **1995**, *196*, 411.
(8) Stridsberg, K.; Albertsson, A.-C. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 1774.
(9) Edlund, V.; Albertsson, A.-C. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 1074.
(10) Frick, E. M.; Zalusky, A. S.; Hillmyer, M. A. *Biomacromolecules* **2003**, *4*, 216.
(11) Song, M.; Zhu, J.; Zang, B.; Hao, G.; Zhou, Q.; Zhang, Y.; Zhao, F.; Zhao, Y.; Yang, Si; Zhou, Y. *Lizi Jiaohuan Yu Xifu* **1998**, *14*, 289.
(12) Kim, J.-H.; Lee, J. A. *Polym. J.* **2002**, *34*, 203.
(13) Frick, E. M.; Zalusky, A. S.; Hillmayer, M. A. *Biomacromolecules* **2003**, *4*, 216.

(14) Zhang, Z.; Grijpma, D. W.; Feijen, J. *Macromol. Chem. Phys.* **2004**, *205*, 867.

(15) Timbert, L.; Renard, E.; Langlois, V.; Guerin, O. *Macromol. Biosci.* **2004**, *4*, 1014.

(16) Pego, A. P.; Poot, A. A.; Grijpma, D. W.; Feijen, J. *J. Biomater. Sci.* **2001**, *12*, 35.

(17) Matsuda, T.; Mizutani, M.; Arnold, S. C. *Macromolecules* **2000**, *33*, 795.

(18) Mizutani, M.; Arnold, S. C.; Matsuda, T. *Biomacromolecules* **2002**, *3*, 668.

(19) Rodilla, V.; Miles, A. T.; Jenner, W.; Harcksworth, G. M. *Chem. Biol. Interact.* **1998**, *10*, 220.

(20) Called Pepto-Bismol in the USA.

(21) Kricheldorf, H. R.; Hachmann-Thiessen, H. *Macromolecules* **2004**, *37*, 6340.

(22) Kricheldorf, H. R.; Hachmann-Thiessen, H.; Schwarz, G. *Biomacromolecules* **2004**, *8*, 492.

(23) Kricheldorf, H. R.; Hachmann-Thiessen, H. *Biomacromolecules* **2005**, in press.

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

(25) McLain, S. J.; Drysdale, N. E. *Prepr. Pap. (Am. Chem. Soc., Div. Polym. Chem.)* **1992**, *33* (1), 174.

(26) Pasch, H.; Rode, K. *J. Chromatogr.* **1995**, *A699*, 24.

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

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

(29) Save, M.; Schappacher, M.; Soum, A. *Macromol. Chem. Phys.* **2002**, *203*, 884.

(30) Kricheldorf, H. R.; Schwarz, G. *Macromol. Rapid Commun.* **2003**, *24*, 359.

(31) Davies, A. G. *Organotin Chemistry*; VCH PublishersL Weinheim, Germany, and New York, 1997; Chapter 12, p 172.

(32) Holden, G., Kricheldorf, H. R., Quirk, R., Eds. *Handbook of Thermoplastic Elastomers*, 3rd ed.; Hanser Publ.: München, Germany, and Cincinatti, OH, 2004.

(33) Kricheldorf, H. R.; Rost, S. *Polymer* **2005**, in press.

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