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Polymer 46 (2005) 3248–3256

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A-B-A-Triblock and multiblock copolyesters prepared from ε-caprolactone, glycolide and L-lactide by means of bismuth subsalicylate[☆]

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Received 5 November 2004; received in revised form 2 February 2005; accepted 3 February 2005
Available online 17 March 2005

Abstract

Bismuth (III) subsalicylate, a commercial drug, was used as catalyst for 1,4-butanediol-initiated copolymerizations of ε-caprolactone (εCL) and glycolide (GL). Telechelic copolyesters having two OH-endgroups and predominantly alternating sequences were obtained. These copolyesters are amorphous with glass transition temperatures (T_gs) below −30 °C. In a second series of polymerizations, in situ chain extension with L-lactide (LLA) was performed, whereby A-B-A triblock copolymers were obtained without significant transesterification between A- and B-blocks. Finally, these A-B-A triblock copolymers were transformed into multiblock copolymers by chain extension with 1,6-hexamethylene diisocyanate. The block copolymers were characterized by ^{1}H and ^{13}C NMR spectroscopy, by viscosity, SEC and DSC measurements.

Keywords: ε-Caprolactone; Glycolide; L-Lactide

1. Introduction

ε-Caprolactone (εCL), glycolide (GL) and L-lactide (LLA) are the most widely used monomers for syntheses of biodegradable polyesters [1–3]. However, the homopolyesters poly-GL and poly-LLA are too brittle for most applications. Thermoplastic elastomers (TPEs) are a group of materials which combines several useful properties due to the covalent connection of so-called soft (flexible) segments and hard (crystalline) segments [4–6]. Depending on length and structure of soft and hard segments, the mechanical properties of TPEs may vary over a broad range from slightly flexible engineering plastics to highly elastic gums. Therefore, it is desirable to synthesize biodegradable polymers with architectures imparting the typical properties of TPEs. Biodegradable A-B-A triblock copolymers or multiblock copolymers showing typical properties of TPEs were prepared by several research groups [7–15]. Most biodegradable TPEs contain poly(LLA)-blocks as hard segments and their syntheses involved initiators based on tin-compounds. However, almost all tin salts and covalent tin compounds are highly cytotoxic, and thus, undesirable for pharmaceutical or biomedical applications of the resulting biomaterials. In this context, the present work served the following purposes. Bismuth subsalicylate (BiSS) which has been used as drug against gastrointestinal problems for several decades [16], should be used as catalyst. Bismuth (III) salts are used for a variety of medical applications, and this fact together with toxicity studies [17] suggests that bismuth may be the least toxic heavy metal. Furthermore, it was found in recent studies that Bi (III) *n*-hexanoate possesses unusual properties when used as initiator for copolymerization of εCL and LLA [18]. Random sequences useful as soft segments were obtained under conditions yielding blocky sequences when tin (II) 2-ethylhexanoate was used as initiator. Therefore, it was the main purpose of this work to explore the preparation of

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[☆] Polylactones, Part 77.

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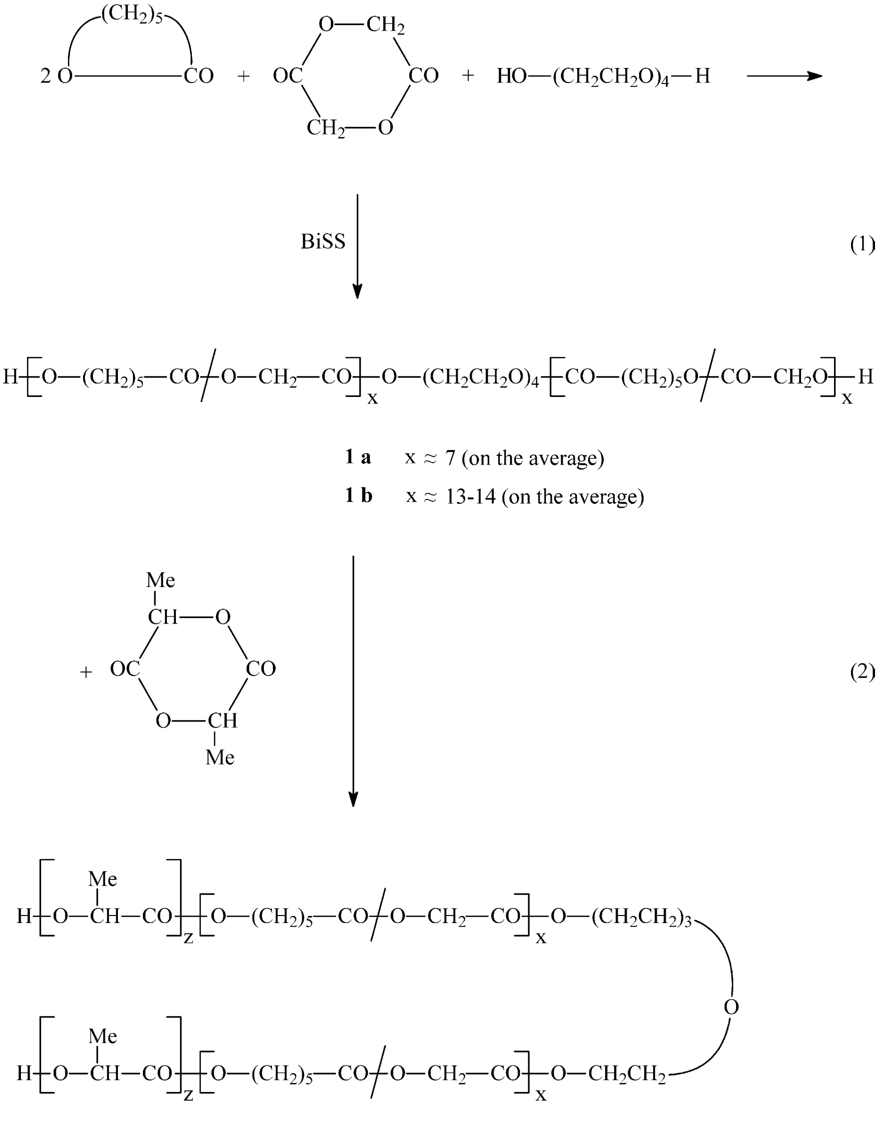
doi:10.1016/j.polymer.2005.02.004

amorphous soft segments via BiSS catalyzed copolymerization of εCL and GL (Eq. (1)). These soft segments (**1a** and **1b**) should serve as basis for the preparation of A-B-A triblock copolymers (Eq. (2), structure **3a**,**b** and **4a**,**b**) or multiblock copolymers (**5a**,**b** and **6a**,**b**) having the typical character of TPEs.



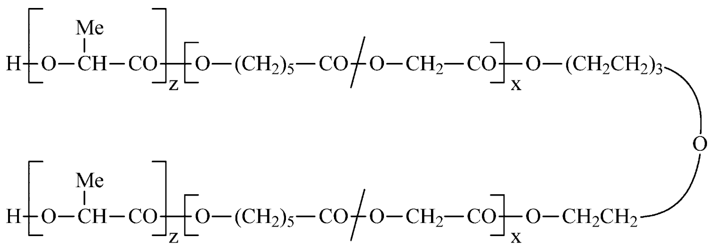
1 a x ≈ 7 (on the average)

1 b x ≈ 13-14 (on the average)

2 a : x ≈ 7, z ≈ 50 (on the average)

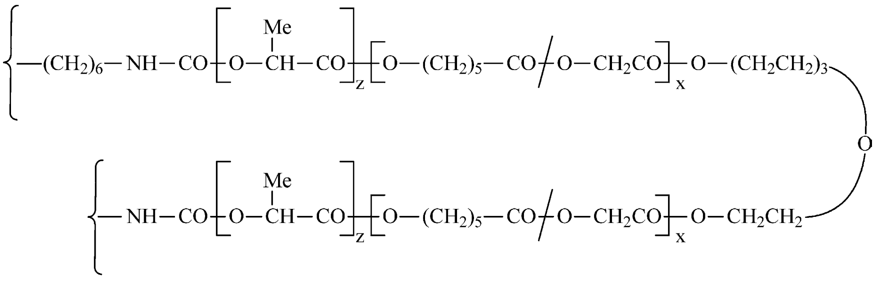
2 b : x ≈ 13-14, z ≈ 50 (on the average)

(1)



3 a : x ≈ 7, z ≈ 100 (on the average)

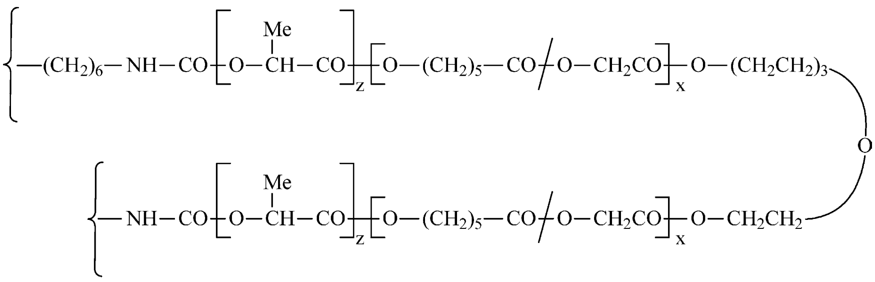
3 b : x ≈ 14, z ≈ 100 (on the average)



(2)

4 a : x ≈ 7, z ≈ 50

4 b : x ≈ 20, z ≈ 50



5 a : x ≈ 7, z ≈ 100 (on the average)

5 b : x ≈ 14, z ≈ 100 (on the average)

2. Experimental

2.1. Materials

Bismuth subsalicylate (BiSS) was purchased from Aldrich Co. (Milwaukee, WI, USA) and used as received. ε-Caprolactone (εCL) was also purchased from Aldrich Co. and distilled over freshly powdered calcium hydride in vacuo. Glycolide and L-lactide (S-grade) were kindly supplied by Boehringer KG (Ingelheim-Rhein, Germany). LLA was recrystallized from dry ethyl acetate and GL from dry dioxane. Tetraethyleneglycol (TEG) was azeotropically dried with toluene and distilled over a short path apparatus in vacuo.

2.2. Copolymerization of εCL and GL (No. 2, Table 1)

εCL (13 mmol), GL (7 mmol) and TEG (0.5 mmol) were weighed into a 50 mL Erlenmeyer flask having silanized glass walls and containing a magnetic bar. The closed reaction vessel was placed into an oil bath preheated to 140 °C. When a homogeneous solution was obtained, BiSS (0.04 mmol) was added under an atmosphere of dry nitrogen. The reaction mixture

Table 1
Compositions and properties of εCL/GL copolyesters prepared by initiation with TEG/BiSS at 140 °C in bulk (5 h)

Exp. no.	εCL/GL/TEG (feed)	εCL/GL/TEG (^{1}H NMR)	^{1}H NMR		^{13}C NMR		M_n Calcd.	M_n (^{1}H NMR)	PD[a] (SEC)[b]	T_g (°C)
			% Alt. dyad[c]	L_{CL}[d]	% Alt. dyad[b]	L_{CL}[d]				
1	13/7/1	13/6/1	62	1.62	60	1.68	2500	2400	1.55	−42
2	26/14/1	25/13/1	70	1.42	70	1.43	4800	4600	1.60	−37
3	50/26/1	50/25/1	71	1.40	73	1.38	8900	8800	1.63	−33

[a] Polydispersities based on polystyrene calibrated SEC measurements in chloroform.
[b] Alternating dyad (b in Fig. 2) relative to the sum of both dyads.
[c] Alternating dyad (c′ or g′ in Fig. 1) relative to the sum of both dyads.
[d] Calculated according to Eq. (3).

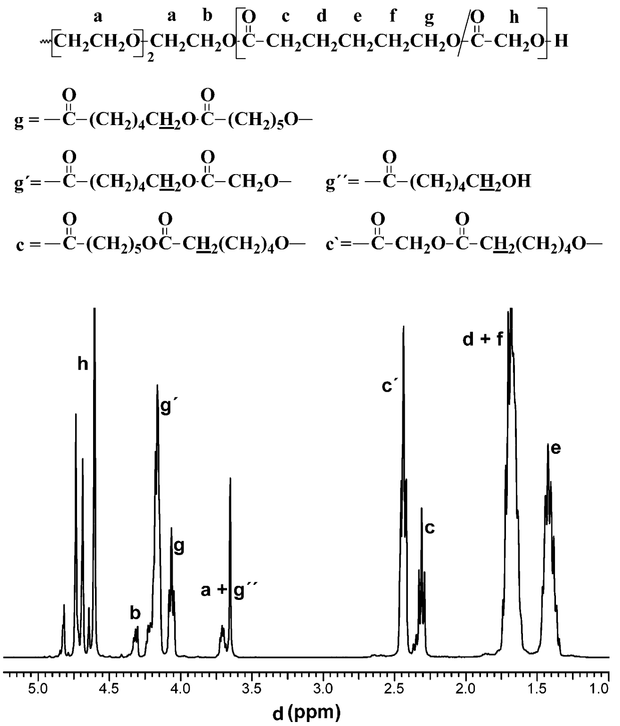


Fig. 1. 400 MHz ^{1}H NMR spectrum of the εCL/GL copolyester No. 1, Table 1.

was thermostated (initially with stirring) at 140 °C for 5 h. After cooling, the virgin reaction product was characterized (Table 1). Complete conversion of both monomers was confirmed by ^{1}H NMR spectroscopy. An analogous polymerization was conducted with 1 mmol of TEG (No.

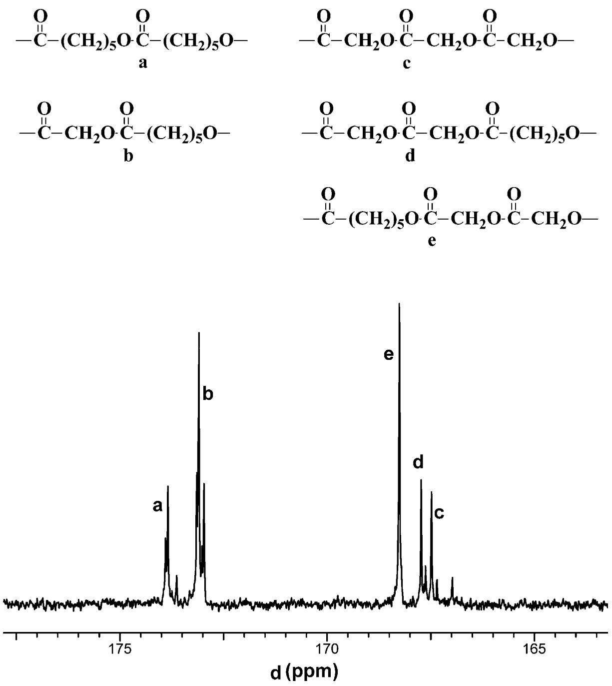


Fig. 2. 100.4 MHz ^{13}C NMR spectrum (CO-signals) of the εCL/GL copolyester No. 1, Table 1.

2, Table 1). A third copolymerization (No. 3) was performed with 25 mmol of εCL, 13 mmol of GL, 0.5 mmol of TEG and 0.076 mmol of BiSS (Eq. (3)).

2.3. A-B-A Triblock copolymers

εCL (13 mmol), GL (6 mmol), TEG (0.5 mmol) were polymerized with BiSS (0.04 mmol) as described above. After cooling, LLA (50 mmol) and chlorobenzene (30 mL) were added under an atmosphere of dry nitrogen. The reaction mixture was then thermostated at 120 °C and a homogeneous solution was obtained after 10 min of stirring. After 48 h, when the ^{1}H NMR spectrum indicated complete conversion of the LLA, the reaction mixture was cooled, diluted with dichloromethane (25 mL) and poured into dry diethyl ether. The precipitated polymer was isolated by filtration and dried by 40 °C in vacuo. An analogous polymerization was conducted with 1 mmol of TEG.

2.4. Multiblock copolymers

An A-B-A triblock copolymer was prepared as described above. The chlorobenzene solution obtained after 48 h at 120 °C was cooled to 100 °C and HMDI (0.55 mmol) was injected in the form of a 1 M solution in chlorobenzene. After 2 h at 100 °C, the reaction mixture was cooled, diluted with dichloromethane (35 mL) and poured into diethyl ether. The precipitated polymer was isolated by filtration and dried at 40 °C in vacuo.

2.5. Measurements

The inherent viscosities were measured with an automated Ubbelohde viscometer thermostated at 20 °C. The 400 MHz ^{1}H NMR spectra and the 100.4 MHz ^{13}C NMR spectra were recorded on a Bruker Avance 400 FT spectrometer in 5 mm o.d. sample tubes. $CDCl_3$ containing TMS served as solvent and internal shift reference.

Average block lengths (Table 3) were calculated from Eq. (3).

$$L_{\mathrm{CL}} = \frac{I_{\mathrm{CL-CL}}}{I_{\mathrm{CL-GL}}} + 1 \tag{3}$$

where $I_{\mathrm{CL-CL}}$, signal intensity of the CL–CL dyad; $I_{\mathrm{CL-CL}}$, signal intensity of the CL–GL dyad.

The SEC measurements were performed on a home-made SEC apparatus at 23 °C in tetrahydrofuran as eluent. A combination of three PSS-SDV mixed-bed columns were used along with UV and RI detectors. Commercial polystyrene standards served for calibration which overestimate the real molecular weights of aliphatic polyesters by 50–60% (see Table 4). The DSC measurements were conducted with a Mettler-Toledo Md 821 in aluminum pans with a heating rate of 20 °C/min.

3. Results and discussion

3.1. Syntheses of εCL/GL copolymers

The first step of the synthetic approach elaborated in this work consisted of studies of copolymerizations of εCL and GL. Since telechelic copolyesters having two OH-endgroups were needed for the preparation of A-B-A triblock copolymers, TEG was used as initiator. This diol was preferred to α,ω-alkane diols because its signals are easy to detect and to quantify in ^{1}H NMR spectra. In preliminary experiments not described here in detail, it was found that a reaction temperature around 140 °C is needed to achieve quantitative conversion of both monomers within a few hours. After 4–8 h (depending on the feed ratio), quantitative conversion of both monomers was observed, and under these conditions, three copolyesters of different length were prepared by variation of the monomer/initiator ratio (i.e. εCL + GL/TEG). For all three copolymerizations, the monomer/BiSS ratio was fixed at 500:1. All polymerizations were conducted in bulk and the virgin reaction products were characterized, so that it did not make sense to determine yields. Compositions and properties of these copolyesters were summarized in Table 1.

In agreement with an almost quantitative conversion of both monomers, the compositions of the copolyesters determined by ^{1}H NMR spectroscopy agreed with the feed ratios. Furthermore, the glass transition temperatures (T_gs) increased with the degree of polymerization (DP) which

Table 2
Yields and structures of the block copolyesters

Polymer no.	εCL/GL/TEG (feed)	L-lactide/TEG (feed)	Structure	Yield (%)	η_{inh}[a] (dL/g)
2a	14/7/1	50	Triblock	81	0.224
4a	14/7/1	50	Multiblock[b]	90	1.053
3a	14/7/1	100	Triblock	86	0.303
5a	14/7/1	100	Multiblock[b]	84	1.447
2b	27/14/1	50	Triblock	80	0.272
4b	28/14/1	50	Multiblock[b]	91	1.081
3b	28/14/1	100	Triblock	86	0.346
5b	28/14/1	100	Multiblock[b]	84	1.371

[a] Measured in CH_2Cl_2 (2 g/L) at 20 °C.

[b] Chain extension with HDMI (excess: 10 mol%).

Table 3
NMR spectroscopic characterization of all block copolyesters

Polymer no.	εCL/GL/L-lactide/ TEG (NMR)	L_{CL}[a] (^{1}H NMR)	L_{CL}[a] (^{13}C NMR)	% Alt. dyad (^{1}H NMR)	% Alt. dyad (^{13}C NMR)
2a	14/7/52/1	1.60	1.62	62	62
4a	14/7/49/1	1.58	1.59	63	63
3a	14/7/98/1	1.59	1.55	63	65
5a	14/7/95/1	1.57	1.58	64	63
2b	28/14/51/1	1.45	1.39	69	72
4b	27/13/49/1	1.45	1.39	69	74
3b	27/14/98/1	1.43	1.36	70	74
5b	27/14/99/1	1.43	1.43	70	70

[a] Calculated according to Eq. (3).

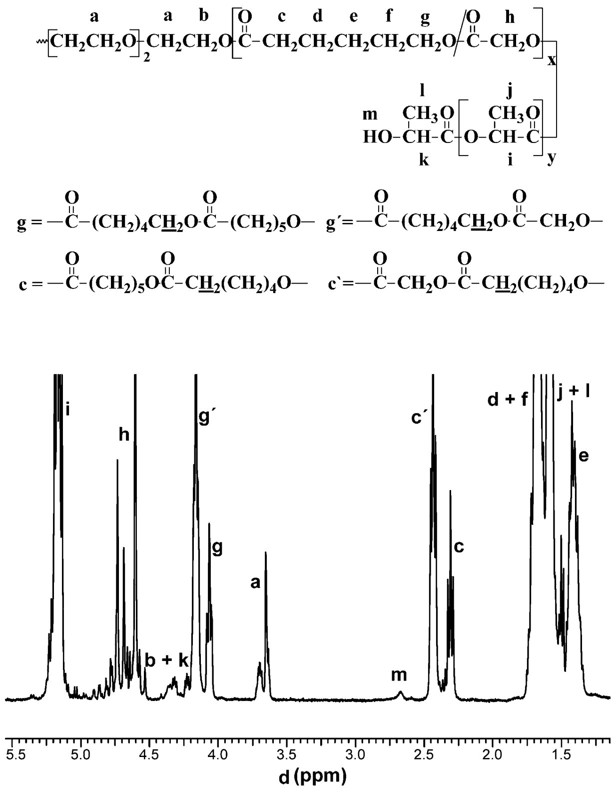


Fig. 3. 400 MHz ^{1}H NMR spectrum of the A-B-A-triblock copolymer No. **2b**, Table 2.

matches the εCL+GL/TEG ratio. The most interesting aspect concerns the sequence analyses performed by ^{1}H and ^{13}C NMR spectroscopy. As illustrated by the ^{1}H NMR spectrum of Fig. 1, the –O–CH$_2$– and –CO–CH$_2$ protons of the εCL unit display a dyad splitting, depending on whether a εCL unit is connected to another εCL unit or to a GL unit. From the signal intensities it can be calculated that the hetero dyads (crossover steps) are almost twice as frequent as the homo dyads. In other words, the sequences had a predominantly alternating character. The evaluation of the ^{13}C NMR CO-signals exemplarily illustrated in Fig. 2 confirmed this interpretation. At this point it should be mentioned that ^{13}C NMR sequence analyses of copolyesters and the signal assignments presented in this work were for the first time reported by Kricheldorf et al. [15,21]. The predominant formation of alternating sequences of εCL and GL units is quite unusual because GL is more reactive than εCL or other lactones and lactides, regardless if cationic, anionic or coordination-insertion initiators are used. Therefore, copolymerizations of GL normally yield blocky sequences due to a faster incorporation of GL into the growing chains. However, a predominance of alternating dyads was also observed for aluminium isopropoxide-initiated copolymerizations [19]. A mechanistic discussion of this aspect will be presented in another publication reporting on a detailed study of Bi^{3+}-initiated copolymerizations of εCL and GL [20]. For the present work it was an important result that the predominantly alternating

Table 4
Molar masses of all block copolyesters

Polymer no.	M_n[a] (^{1}H NMR)	M_n[b] (SEC corr.)	M_n[c] (SEC)	M_w[c] (SEC)	M_w/M_n[c] (SEC)
2a	6300	7300	11,000	18,000	1.67
4a	–	47,000	70,000	14,1000	2.00
3a	9600	12,000	18,000	27,000	1.54
5a	–	80,000	120,000	232,000	1.93
2b	8400	8000	12,000	22,000	1.74
4b	–	46,000	69,000	127,000	1.84
3b	11,700	12,000	18,000	31,000	1.76
5b	–	71,000	105,000	203,000	1.98

[a] Calculated from ^{1}H NMR spectra.
[b] SEC measurement corrected with factor 0.67.
[c] Polystyrene calibration.

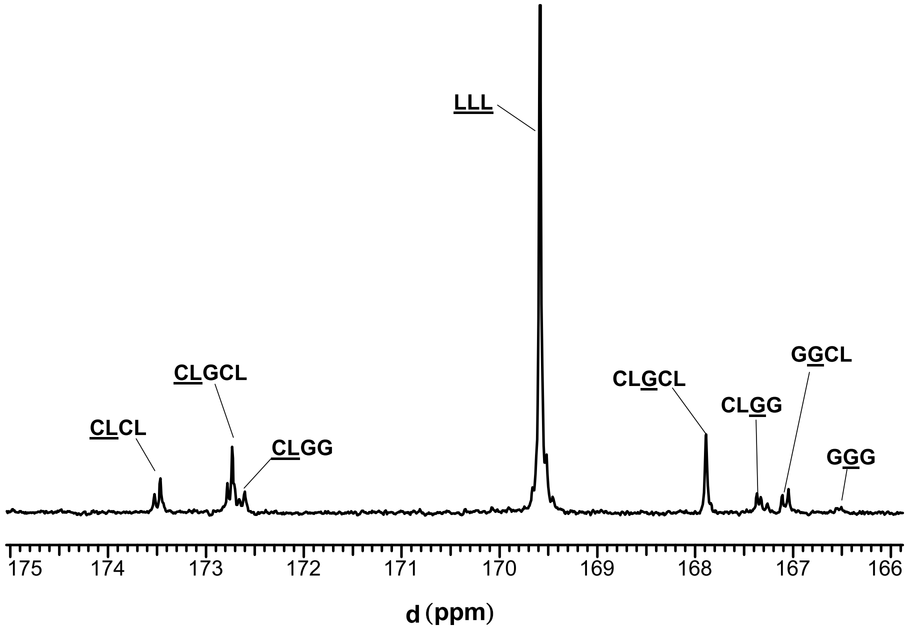


Fig. 4. 100.4 MHz ^{13}C NMR spectrum (CO-signals only) of the A-B-A triblock copolymer **2b**, Table 2.

copolyesters of εCL and GL were amorphous with T_g-values below −30 °C (Table 1) so that they were capable to play the role of soft segments in block-copolymers.

3.2. Syntheses of block copolymers

Four triblock copolyesters (**2a**, **2b**, **3a**, **3b**) were prepared by a two-step process in a ‘one-pot procedure’. The first step consisted in the TEG/BiSS-initiated copolymerization of εCL and GL discussed above. Two soft segments (SS) of different length were prepared, namely 27–28 repeat units (εCL + glycolyl (O–CH$_2$–CO–)) and 54–56 repeat units (εCL + glycolyl). When the ^{1}H NMR spectra indicated almost complete conversions of both lactones, L-lactide was added and the polymerization was continued at 120 °C until ^{1}H NMR spectra indicated almost complete conversion of this third comonomer. Typically 5 h were needed for the first step and 48 h for the polymerization of L-lactide. The resulting A-B-A triblock copolyesters were characterized after precipitation into diethyl ether. Four triblock copolymers were prepared, because both soft segment (SS) were combined either with PLA blocks having an average length of 50 lactyl (O–CHMe–CO) units (**2a** and **2b**) or with an average block length of 100 lactyl units (**3a** and **3b**). All triblock copolymers were isolated in yields between 80 and 86% (entries 1, 3, 5 and 7, Table 2).

Finally, four multiblock copolymers were prepared in such a way that the A-B-A triblock copolymers were subjected to chain extensions with 1,6-hexamethylene diisocyanate. This last reaction step was again performed in situ, so that the entire synthesis of a multiblock copolymer was based on a three-step process conducted in a ‘one-pot procedure’. After precipitation from diethyl ether, the multiblock copolymers **4a,b** and **5a,b** were isolated in yields between 84 and 91% (entries 2, 4, 6 and 8, Table 2).

3.3. Characterization of block copolymers

The properties of all triblock- and multiblock copolymers were summarized in Tables 2–5. Their chemical structure was characterized by ^{1}H and ^{13}C NMR spectroscopy. These

Table 5
DSC measurements of all block copolyesters (heating rate 20 °C/min)

Polymer no.	T_g of soft segment (°C)	T_g of polylactide blocks (°C)	T_m of polylactide blocks (°C)
2a	n.d.[a]	27	148
4a	n.d.[a]	32	142
3a	n.d.[a]	39	158
5a	n.d.[a]	45	152
2b	−19	13	140
4b	−10	15	134
3b	n.d.[a]	28	154
5b	n.d.[a]	34	149

[a] Not detectable.

measurements are exemplarily illustrated by the ^{1}H and ^{13}C NMR spectra of the A-B-A triblock copolymer **2b** in Figs. 3 and 4. The ^{1}H NMR spectra of the multiblock copolymers differ from those of the corresponding triblock copolymers only by the additional signals of the 1,6-diaminohexane unit. As illustrated in Fig. 5 for the multiblock copolymer **4b**, only the N–CH_2 protons are detectable as a separate signal (at 3.2 ppm). However, this signal suffices to check the quantitative incorporation of HMDI. The ^{13}C NMR spectra of triblock copolymers and of the corresponding multiblock copolymers were identical, because the signal-to-noise ratio did not suffice to detect the signals of the 1,6-diaminohexane units.

The molar compositions of all block copolymers was determined by ^{1}H NMR spectroscopy. The results listed in the second column of Table 3 were in good agreement with the feed ratios given in Table 2. The sequences of the central blocks (SS) were characterized by both ^{1}H and ^{13}C NMR spectroscopy. In terms of average block lengths and percentage of alternating dyads (Table 3). The results were in satisfactory agreement with the data presented for the neat copolylactones in Table 1. Again average block lengths below 2.0 and a predominance of alternating dyads were found.

The ^{1}H NMR spectra also allowed for the determination of the number average molecular weights (M_n) for this purpose the signal intensities of the εCL, GL and LA units were measured relative to the TEG signals. These M_n values (listed in Table 4) were compared to those obtained by SEC measurements. The SEC elution curves were calibrated as usual with commercial polystyrene standards. However, it is known from the work of four research groups [21–24] that calibration with polystyrene overestimates the real molecular weights of aliphatic polyesters in general and PεCL in particular, by approx. 50%. Therefore, the original SEC data were corrected by multiplication with the factor 0.67[24], and these corrected M_ns show a good agreement with the M_n values determined via NMR spectroscopy. The result is satisfactory in two directions. First, it proves that the correction factor is reasonable. Second, it indicates that our block copolyesters do not contain significant amounts of cyclic oligoesters, which have the consequence that end-group analyses overestimate the real M_ns.

Since the chain extension with 1,6-hexamethylene diisocyanate should obey a step growth kinetic, it is a reasonable consequence that the polydispersities of the multiblock copolymers are higher than those of the triblock copolymers and approach values around 2.0. The SEC measurements revealed two more positive results. First, the molecular weights of multiblock copolymers should be high enough to impart useful mechanical properties. Second, they indicate in all cases a chain extension by a factor around 6. When the inherent viscosities of the triblock- and multiblock copolymers are compared, the difference corresponds to a factor in the range of 4.0–4.5. Considering that flexible aliphatic chains typically have an exponent of 0.70–0.75 in their Mark-Houvink equations, the 'chain extension factors' found for the viscosities and for the molecular weights stand in reasonable correlation to each other.

The thermal properties of all block copolymers were characterized by DSC measurements and the following observations were made (Table 5). Surprisingly no glass transitions (T_gs) of the soft segments were found (with two exceptions (Fig. 6)), although the DSC measurements started at −80 °C. Obviously, the glass-transition is too broad to yield a detectable step in the DSC heating traces. In

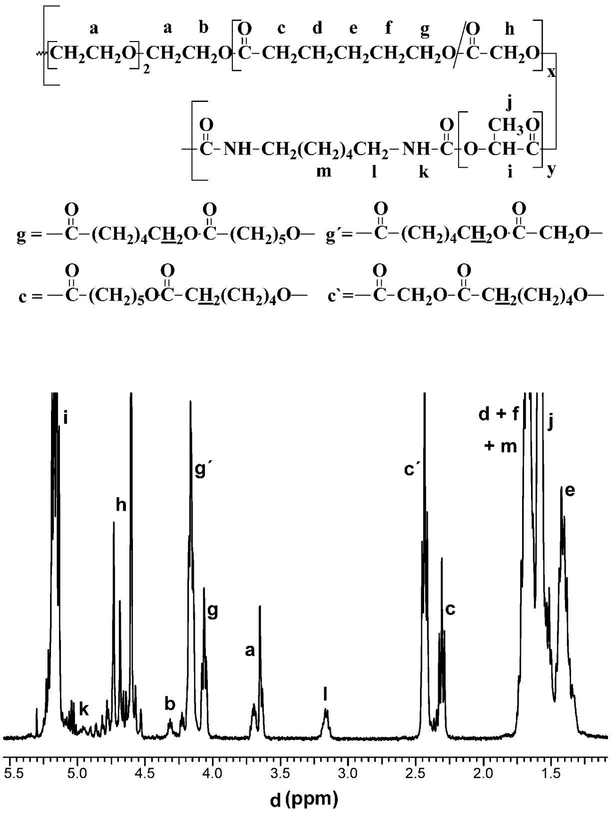


Fig. 5. 400 MHz ^{1}H NMR spectrum of the multiblock copolymer No. **4b**, Table 2.

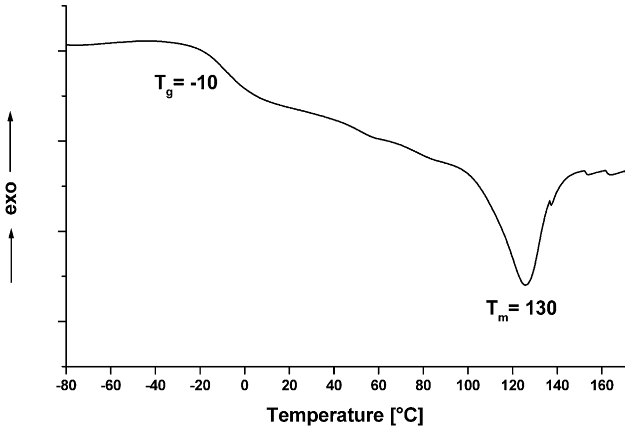


Fig. 6. DSC heating curve of the multiblock copolymer No. **4b**, Table 5.

contrast, the T_gs of the polylactide blocks were detectable in all heating curves, what demonstrates that our DSC measurements were sensitive enough to allow for the detection of glass transitions. The detection of T_gs of the PLA blocks also demonstrates that the amorphous phases of these blocks and of the soft segments were largely separated.

It is characteristic for all four pairs of block copolymers that the T_gs of the multiblocks were higher, as expected for polymers of higher molecular weight. The melting endotherms (T_ms) displayed an opposite trend, because those of the multiblock copolymers were lower. Obviously, the chain extension somehow reduces size or perfection of the crystallites. Nonetheless, the observation of strong melting endotherms for all block copolymers indicates that the polymerization of LLA was not significantly affected by transesterification with the εCL/GL segments. This conclusion is confirmed by the ^{13}C NMR spectra which exhibit one intensive CO-signal of the PLA blocks, again indicating the absence of transesterification. In other words, the terms 'triblock' and 'multiblock' are fully justified.

4. Conclusion

The results of this work evidence that the long known commercial drug BiSS is a useful initiator for syntheses of biodegradable block copolymers from lactones and cyclic diesters. The success of the syntheses reported in this work is based on four points. First, nearly quantitative conversions of all monomers were achieved within a reasonable time-temperature window. Second, the copolymerization of εCL and GL gave a sequence rich in alternating dyads, thus avoiding the formation of crystallizing blocks. Third, the chain extension with L-lactide proceeded without significant transesterification between both kinds of blocks. Fourth, BiSS catalyzed the chain extension with 1,6-hexamethylene diisocyanate (it was checked that this chain extension does not proceed in the absence of BiSS). Taking into account the extraordinarily low toxicity, BiSS is certainly a particularly attractive initiator and catalyst for syntheses of biodegradable materials. Further studies concerning the usefulness of the triblock and multiblock copolyesters of this work for drug-delivery systems or as thermoplastic elastomers are in progress.

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