Macromolecular Engineering of Lactones and Lactides. 24. Controlled Synthesis of (*R,S*)-β-Butyrolactone-*b*-ϵ-Caprolactone Block Copolymers by Anionic and Coordination Polymerization

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ABSTRACT: Block copolymers of (*R,S*)-β-butyrolactone and ϵ-caprolactone have been synthesized by combining the anionic polymerization of the first monomer with the coordinative ring-opening polymerization of the second one. The copolymerization yield is close to 100% and the final molecular weight of each sequence can be predicted from the initial monomer-to-initiator molar ratio. The molecular weight distribution of copolymers obtained is quite narrow ($M_w/M_n \leq 1.3$). According to NMR and DSC analysis, the polybutyrolactone block is atactic and totally amorphous, in contrast to the polycaprolactone block which is semicrystalline. A partial miscibility of the two blocks in the amorphous phase has however been detected. Thermal and enzymatic degradations of the block copolymers have been investigated. The enzymatic degradation rate promoted by the lipase form *Rhizopus arrhizus* strongly depends on the copolyester composition and increases with the β-butyrolactone content.

Introduction

The ring-opening polymerization (ROP) of β-butyrolactone (BL) has been the subject of numerous studies since the chemical structure of the related polyester is similar to natural poly(β-hydroxybutyrate) (PHB). However, in contrast to the completely stereoregular (*R*)-PHB produced by bacteria, the microstructure of poly(β-butyrolactone) (PBL) resulting from ROP of BL strongly depends on the nature of initiator used.[1−3] Actually the high crystallinity of isotactic (*R*)-PHB is a limitation for practical applications.[4] Different strategies have been investigated to improve the physical properties of PHB including blending with other polymers such as poly(ethylene oxide),[5] poly(vinyl alcohol),[6] poly(ϵ-caprolactone) (PCL),[7] and atactic PBL.[8] Many of these polymeric blends are miscible in the amorphous phase, whereas some others, such as the PHB/PCL blends, are phase separated in the amorphous region.[7] A compatibilization of these immiscible blends may be achieved by incorporation of diblock copolymers, e.g., β-butyrolactone-*b*-ϵ-caprolactone diblock copolymers (P(BL-*b*-CL)) in PHB/PCL blends. Recently Reeve *et al.*[9] have reported the synthesis of low molecular weight P[(*R*)-BL-*b*-CL] copolymers with quite broad molecular weight distribution (DP $\leq$ 50; MWD $\sim$ 1.5). Block copolymers between BL and CL have also been synthesized by Abe *et al.*[10] by ROP of (*R,S*)-BL followed by the subsequent polymerization of CL in the presence of $Zn(C_2H_5)_2/H_2O$ as the catalyst. The final MWD was again quite broad, ca. 1.5.

The anionic ROP of (*R,S*)-BL, which provides well-defined atactic PBL (a-PBL),[11,12] has been shown to proceed *via* carboxylate-active species, independently of the anionic initiator used.[1,13−15] In contrast, anionic ROP of ϵ-caprolactone occurs through alkoxide-active species. Moreover, it is well-known that some aluminum alkoxides, e.g., the commercially available Al(OiPr)$_3$, are very efficient initiators for the controlled ROP of unsubstituted β-, δ-, and ϵ- lactones.[16−18] A "coordination-insertion" mechanism and livingness of the polymerization have been ascertained by kinetics and structural investigations.[17,18] However, the ROP of BL initiated by Al(OiPr)$_3$ is extremely slow and leads to chains of a relatively low molecular weight (M_n < ca. 5000).[19]

This work aims at synthesizing well-defined P[BL-*b*-CL] diblock copolymers combining the living anionic polymerization of racemic BL and the living coordination−insertion polymerization of CL. The first step consists of the synthesis of hydroxyl-terminated atactic PBL by anionic polymerization initiated by the alkali-metal salt of a hydroxycarboxylic acid complexed with a crown ether. The hydroxyl end group of PBL would then be reacted with Et_3Al to form the Et_2AlO(PBL) macroinitiator for the CL polymerization.

Experimental Part

Materials. (*R,S*)-β-Butyrolactone (BL) (Aldrich) and ϵ-caprolactone (CL) (Janssen Chimica) were dried over calcium hydride at room temperature for 48 h and then distilled under reduced pressure. BL was additionally distilled over a Na/K alloy under reduced pressure just prior to use. Triethylaluminum (Fluka) was distilled and then dissolved in dry toluene. The solution concentration was determined by complexometric titration of aluminum with EDTA and by quantitative hydrolysis of an aliquot and measurement of the ethane evolved. 3-Hydroxybutanoic acid sodium salt (Aldrich) was dried under reduced pressure at 60 °C for 48 h, prior to use. 12-Hydroxydodecanoic acid potassium salt was prepared by reacting potassium hydride with an excess of 12-hydroxydodecanoic acid (Aldrich) in THF under dry nitrogen at 40 °C for 24 h. The salt was repeatedly washed with dry THF in order to remove the unreacted acid and then dried under reduced pressure at 60 °C for 48 h. 18-Crown-6 was purified and dried as detailed elsewhere.[20] Methyl iodide (Aldrich) was used as received, without any additional purification. Toluene and tetrahydrofuran (THF) were dried by refluxing over CaH_2 and Na/benzophenone complex, respectively. The lipase from *Rhizopus arrhizus* was purchased from Sigma and used as received. Its activity was determined by the supplier as 580 000 units/mg of protein using olive oil (30 min incubation).

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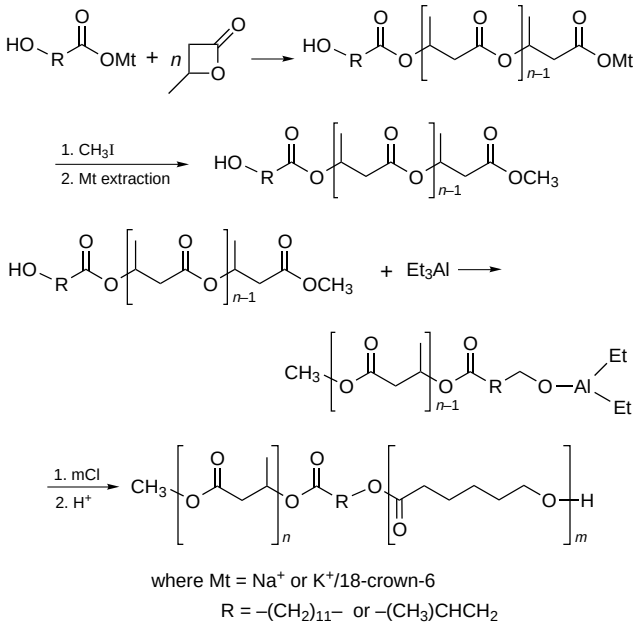
Measurements. FTIR spectra were recorded using a Perkin-Elmer FTIR 1600. ^{1}H and ^{13}C NMR spectra were recorded at 25 °C in $CDCl_3$ using a Bruker AM400 spectrometer. Gel permeation chromatography was performed at 40 °C, using a Hewlett Packard 1090 liquid chromatograph equipped with a Hewlett Packard 1037A refractive index detector and a set of columns of 10^5, 10^3, 500, and 100 Å pore sizes. Columns were calibrated with Polystyrene standards and eluted with THF at a flow rate of 1 mL/min. M_n of the PCL block of diblocks was inferred from M_n of the first PBL block as determined by GPC and the ^{1}H NMR analysis of the diblock composition (relative intensity ratio of the PBL methine group and the PCL methylene ester group). Differential scanning calorimetry (DSC) was performed with a DuPont DSC-910 instrument calibrated with indium. Samples were previously heated up to 80 °C and slowly cooled down to −150 °C. The melting enthalpies (ΔH_m) and melting temperatures (T_m) were then determined from the DSC endotherms recorded from −150 to +100 °C at a heating rate of 20 °C/min. TGA experiments were performed by using a DuPont TGA-51 thermogravimetric instrument. The temperature was increased from 20 to 400 °C at a heating rate of 10 °C/min. The degradation temperature was defined as the temperature at the maximum of the differential thermogravimetric curve. Mass spectra were recorded with a Finnigan MAT SSQ 700 spectrometer. Pyrolysis was carried out using a standard direct insertion probe for solid materials, heated from 50 to 400 °C at a 20 °C/min rate. The CI-MS spectra recorded with isobutane as the reactive gas showed two series of molecular ions: $m/z = 87 + n \times 86$ ($n = 0-7$) and $m/z = 115 + n \times 114$ ($n = 0-4$).

Enzymatic Degradation. Chloroform cast films of PCL homopolymer and block copolymers were degraded at 37 ± 0.1 °C in Tris-HCl buffer (pH = 7.4). Film samples (known amount, ca. 20 mg; diameter, 1.6 cm) were introduced into small bottles containing 2 mL of buffer and then added with 100 μL of solution of lipase from *R. arrhizus* (21.7 μg of enzyme). After well-defined immersion times, the samples were picked out, washed with distilled water, dried to constant weight, and weighed on an analytical electronic balance (Sartorius RC210D; reproducibility ±0.02 mg). The average of weight loss of three independent samples was taken as the weight loss value. The degradation rate was accordingly calculated. In a control experiment carried out in the absence of lipase, no weight loss was observed at 37 °C, pH = 7.4, during the time corresponding to enzymatic degradation experiments.

Polymerization of (*R,S*)-β-Butyrolactone (BL). BL was polymerized in bulk or in THF solution under stirring in a previously flamed and nitrogen-purged glass reactor. A premixture of monomer, 18-crown-6, and THF if required was added into the reactor with a stainless steel capillary through a rubber septum. The reactor already contained the required amount of initiator (3-hydroxybutanoic acid sodium salt (HBAN) or 12-hydroxydodecanoic acid potassium salt (HDDAK) previously weighed in a glovebox under a dry nitrogen atmosphere. The polymerization progress was measured by ^{1}H NMR spectroscopy. When polymerization was complete (6−36 h depending on the $[M]_0/[I]_0$ molar ratio), an excess of methyl iodide was added into the reactor in order to methylate the carboxylate salt/18-crown-6-active species.[21] Ten hours later, THF and unreacted MeI were distilled off, the polymer was redissolved in CH_2Cl_2, and the alkali-metal iodide/18-crown-6 complex was extracted (five times) with water. The polymer solution was then dried over magnesium sulfate, evaporated to dryness, and further dried under vacuum for 48 h. The expected structure of PBL was ascertained by ^{1}H NMR analysis. In addition to the signals characteristic of the PBL repeating units, at $\delta = 5.25$ (multiplet; C**H**(CH_3)), 1.25 (doublet; C**H**$_3$), and centered on 2.50 ppm (multiplet; C**H**$_2$), minor resonances typical of the expected end groups were observed at $\delta = 3.67$ (singlet; C**H**$_3$O), 3.63 (triplet; C**H**$_2$OH), and 2.25 ppm (triplet; C**H**$_2$C(O) from the initiator) in a 3:2:2 molar ratio when 12-hydroxydodecanoic acid potassium salt (HDDAK) was the initiator. Minor resonances at 4.20 (multiplet; (CH_3)C**H**OH) and 3.67 ppm (singlet; C**H**$_3$O) were reported in a 1:3 molar ratio when the BL polymerization was initiated by 3-hydroxybutanoic acid sodium salt (HBAN). No signal characteristic of the 18-crown-6 ether was detected.

Scheme 1



where Mt = Na^+ or K^+/18-crown-6

R = $-(CH_2)_{11}-$ or $-(CH_3)CHCH_2$

Block Copolymerization. The CL polymerization was initiated in toluene (1 mol/L) with the equimolar reaction product of $AlEt_3$ and the previously prepared hydroxy-terminated PBL. Into a previously flamed and nitrogen-purged glass reactor, a required amount of hydroxy-terminated a-PBL was dried by repeated azeotropic distillation of toluene and then added with the equimolar amount of Et_3Al, and the solution was maintained at 40 °C for 1 h. After cooling down to room temperature, CL was added and the reaction was quenched 16 h later with 0.1 N HCl (3-fold molar excess with respect to Et_3Al). The polymer solution was washed with water up to neutral pH and then with an EDTA solution in water for extracting Al traces and finally precipitated in methanol. After filtration, the polymer was dried under vacuum at room temperature for 48 h and weighed. The final block copolymer was characterized by GPC, NMR, FTIR, TGA, and DSC techniques.

Results and Discussion

Synthesis and Characterization. The alkali-metal salts of carboxylic acids are known to initiate the polymerization of β-lactones through the selective cleavage of the alkyl−oxygen bond of the monomer.[22] However, in the particular case of the anionic polymerization of β-butyrolactone, initiator has to be added with strong cation complexing agents, e.g., crown ethers,[12,23] in order to enhance the polymerization rate.

In order to prepare P(BL-*b*-CL) diblock copolymers, according to Scheme 1, (*R,S*)-β-butyrolactone (BL) was first polymerized with a hydroxy acid alkali-metal salt (either 3-hydroxybutanoic acid sodium salt (HBAN) or 12-hydroxydodecanoic acid potassium salt (HDDAK)), complexed with the 18-crown-6 ether. In accordance with the livingness of the ROP that was previously published,[13−15,23] whatever the initiator employed, the polymerization is quantitative at room temperature and leads to PBL (Scheme 1) of a narrow molecular weight distribution (1.05−1.15) and a molecular weight in good agreement with the expected value based on the initial monomer-to-initiator molar ratio. The sequential polymerization of CL requires one to convert the hydroxyl end groups of PBL into aluminum alkoxides by reaction with Et_3Al. In order to prevent any side reactions or complexation of the Al derivatives, the carboxylic end groups of PBL have previously been methylated and the

Table 1. Molecular Weight, MWD, Composition, and Thermal Properties of Poly(*β*-butyrolactone-*b*-ϵ-caprolactone) Copolymers[a]

no.	$M_{n,PBL}$[b]	composition BL:CL	$M_{n,PCL}$[c]	$M_{n,copo}$	MWD copo	T_m[d] (°C)	ΔH_m[d] (J/g)	T_g[d] (°C)
1	4500	36:65	11 5 00	16 500	1.25	59	55.0	−43
2	5500	15:85	40 000	45 500	1.30	59	56.8	−54
3	6000	36:64	14 500	21 000	1.30	59	54.2	−31
4	6000	31:69	18 500	25 000	1.25	58	54.5	−43
5	6000	24:76	33 000	39 000	1.30	58	58.4	−46
6	14000	40:60	28 000	42 500	1.30	54	51.2	−28
7	6000	100:0			1.05			−2
8[e]	4500	25:75	17 000	21 500	1.30	59	55.9	−47
9		0:100	20 000		1.20	60	66.2	−63
10[f]	6000	31:69	20 000			60	43.0	−2

[a] Polymerization was initiated by a Et_2AlO(PBL) macroinitiator in toluene for 16 h at 20 °C. PBL was initiated by the 12-hydroxydodecanoic acid potassium salt/18-crown-6 complex. [b] M_n of the first PBL block ($M_{n,NMR}$). [c] $M_{n,PCL}$ block determined by ^1H NMR (see the Experimental Part). [d] Heating rate: 20 °C/min. [e] PBL initiated with the 3-hydroxybutyric acid sodium salt/18-crown-6 complex; reaction temperature 50 °C; reaction time 10 h. [f] Data for the PBL/PCL blend.

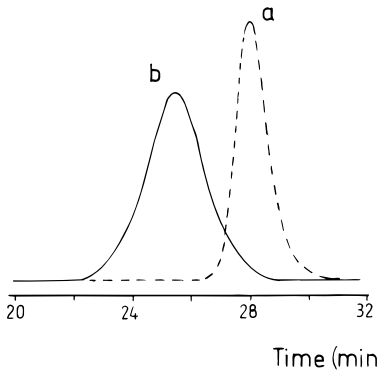


Figure 1. SEC traces of (a) the PBL macroinitiator (M_n = 6000) and (b) the P(a-BL-*b*-CL) diblock copolymer (M_n = 25 000) (entry 4, Table 1).

18-crown-6 ether completely extracted. The expected structure of PBL has then been ascertained by ^1H NMR analysis (see the Experimental Part), which confirmed the efficiency of the crown ether extraction and the nature of the end groups, i.e., a hydroxyl group and a carboxylic one that has been quantitatively methylated.

Carefully dried α-hydroxy-, *ω*-carboxylato-PBL was then reacted with an equimolar amount of triethylaluminum for 1 h at 40 °C. After cooling down to room temperature, the (CL) comonomer was added to the PBL macroinitiator, i.e., PBL end-capped with an aluminum alkoxide group. ROP of CL went close to completion after ca.16 h at 20 °C (entries 1−7, Table 1). The copolymerization product showed a molecular weight higher than that of the PBL macroinitiator and a monomodal molecular weight distribution, which are evidence for an effective block copolymerization reaction (Figure 1).

It is very informative to note that CL is not polymerized at all when the PBL macroinitiator results from a PBL chain initiated by HBAN and thus end-capped by a secondary aluminum alkoxide in the *β* position with respect to a carbonyl function. This experimental observation might be accounted for by an intramolecular coordination of the Al-active species onto the carbonyl function with formation of a six-membered ring (Chart 1). The same explanation might also hold when the BL homopolymerization is initiated by $Al(O^iPr)_3$ in toluene at 75 °C.[19] Indeed, the coordination−insertion polymerization is then unusually slow, which would reflect a loss of reactivity of the aluminum alkoxide species by

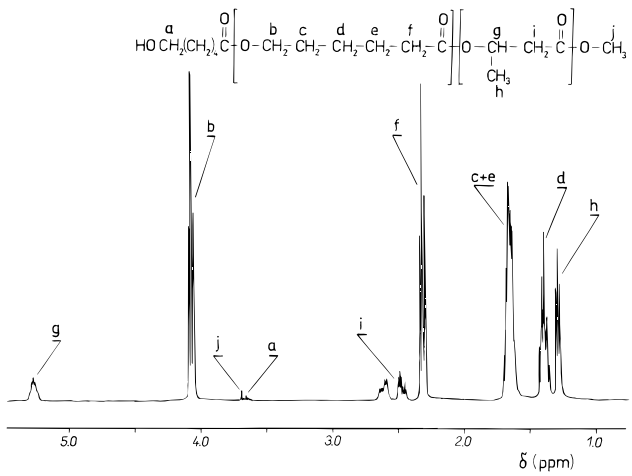
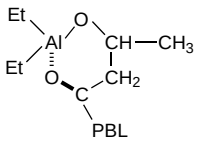


Figure 2. ^1H NMR spectrum of poly(a-BL-*b*-CL) (M_n = 21 500; BL/CL = 25/75) initiated by the (PBL)$OAlEt_2$ macromonomer prepared by ROP of BL with the 3-hydroxypropanoic acid sodium salt/18-crown-6 complex as the initiator (entry 8, Table 1).

Chart 1



internal coordination. Thus the same cause might have a slightly different effect depending on the monomer involved and the polymerization temperature used, since CL polymerization at 25 °C is completely inhibited, in contrast to BL which is polymerized very slowly at 75 °C in the same solvent.

Actually, the polymerization temperature has a more decisive effect than the monomer structure. Indeed, an increase in the copolymerization temperature from 25 to 50 °C is enough to trigger the initiation of the CL polymerization by the α-aluminum alkoxide PBL. After 10 h at 50 °C, the aluminum alkoxide propagating species are hydrolyzed and the copolymerization product is recovered with a quantitative yield (entry 8, Table 1).

The P(BL-*b*-CL) diblock copolymers have been characterized by ^1H NMR spectroscopy. In addition to the signals characteristic of the PCL (protons b−f) and PBL (protons g−i) sequences, two minor resonances at δ = 3.67 and 3.62 ppm of a 3:2 relative intensity have been assigned to the C**H**$_3$O− methyl ester and the −C**H**$_2$OH hydroxyl end groups, respectively (Figure 2, for a diblock copolymer, whose PBL block has been initiated by HBAN; entry 8, Table 1). It is also worth noting that the signal of the α-hydroxymethine end group of the PBL macroinitiator (δ = 4.20 ppm) has completely disappeared in favor of a C**H**−O−C(O) methine ester linkage (proton g in Figure 2) and a new C**H**$_2$OH α-hydroxymethyl end group (proton a at δ = 3.62 ppm).

The blocky structure of the P(BL-*b*-CL) copolymers has been confirmed by ^{13}C NMR spectroscopy (Figure 3). Both signals typical of the PBL (carbons 1−4) and of the PCL (carbons 5−10) sequences are detected. Interestingly enough, the resonance of the PBL carbonyl carbons is split into two signals assigned to *syndio* and *iso* diads with a 50:50 intensity ratio. The atactic microstructure of the PBL blocks is also confirmed by the resonance of the PBL methylene carbons (C^2) split into signals of the same relative intensity and characteristic of *heterosyndio* (H_s), *iso* (I), *syndio* (S), and

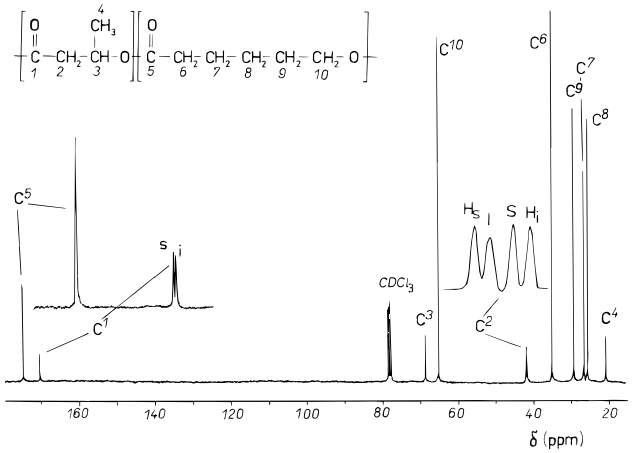


Figure 3. ^{13}C NMR spectrum of poly(a-BL-*b*-CL) (M_n = 25 000; BL/CL = 31/69) (entry 4, Table 1).

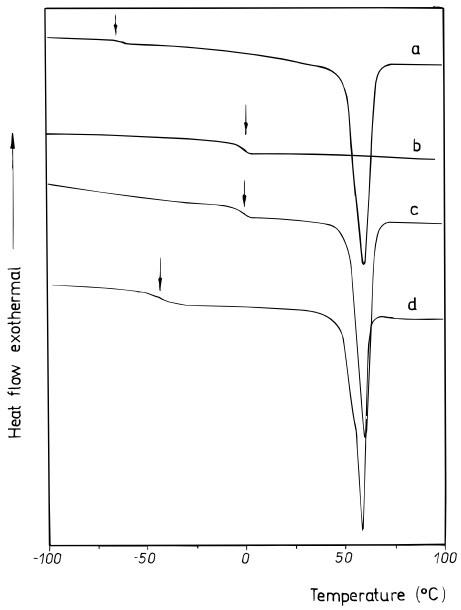


Figure 4. DSC traces of a P(a-BL-*b*-CL) diblock copolymer and the parent homopolymers: (a) PCL (M_n = 20 000); (b) PBL (M_n = 6000); (c) solvent-cast PBL/PCL blend (BL/CL molar ratio = 31/69, $M_{n,PBL}$ = 6000, $M_{n,PCL}$ = 20 000), and (d) P(BL-*b*-CL) diblock (BL/CL molar ratio = 31/69; M_n = 25 000; entry 4, Table 1). T_g's are shown by arrows.

heteroiso (H_i) triads. No intermediate resonance can be detected in between the two homo-PCL and PBL carbonyl signals; such intermediates would have been the result of some alternation of the BL and CL sequences[24] and therefore the signature for the occurrence of transesterification side reactions.

The experimental observations thus support the selective formation of P(a-BL-*b*-CL) diblock copolymers with a totally atactic PBL block (a-PBL) in agreement with Scheme 1.

Thermal Properties. Figure 4 shows a comparison of the typical DSC traces for a P(a-BL-*b*-CL) diblock copolyester (entry 4, Table 1), the parent homopolymers and a homopolymers blend (BL/CL molar ratio = 31/69), respectively. In contrast to the semicrystalline PCL homopolymer (T_m = 60 °C, T_g = −63 °C), the atactic PBL homopolymer is totally amorphous with a T_g at −2 °C. In addition to the melting endotherm of PCL, the PCL/PBL blend shows a T_g at −2 °C. Even though the T_g characteristic of PCL is not detected under the experimental conditions used, unchanged T_g for the PBL chains is a clear indication of the homopolymer's immiscibility. In contrast, the DSC trace of the block copolymer shows only one T_g but at an intermediate temperature compared to the homopolymer T_g's (Figure 4d). This intermediate T_g indicates that the chemical bonding between PCL and a-PBL in the diblock triggers at least a partial miscibility in the amorphous region. The thermal properties of the P(a-BL-*b*-CL) copolymers are listed in Table 1. The melting enthalpy depends on the block copolymer composition, and for samples containing a PBL block of the same length, the melting enthalpy increases with the PCL content (entries 3−5, Table 1).

TGA analysis of the block copolymer (sample 3, Table 1) shows a two-step thermal decomposition with a maximum at 296 and 358 °C, respectively. The parent homopolymers are typically decomposed at 294 and 380 °C for a-PBL (M_n = 6200) and for PCL (M_n = 20 000), respectively. Therefore, the two maxima observed on the TGA trace for the P(a-BL-*b*-CL) copolymers might be assigned to the decomposition of the PBL blocks at 296 °C and the PCL blocks at higher temperature, even though lower than the temperature at which homo-PCL decomposes. This assignment has been confirmed by direct pyrolysis mass spectrometry (DPMS)[25] with chemical ionization (CI) and isobutane as the reagent gas. The trace of the recorded ion current (RIC) for the thermal decomposition products of the same P(a-BL-*b*-CL) copolymer sample also shows two maxima at temperatures which are in good agreement with those ones recorded by TGA. CI-MS spectra of the pyrolysis products evolved at each decomposition stage clearly indicate that the thermal decomposition of the PBL blocks is first occurring. The molecular ions $m/z = 87 + n \times 86$ (n = 0−7), which are observed in the temperature range of the lower maximum, have been previously assigned to the ($M^+ + H$) ions of crotonic acid and linear oligomers containing crotonate and carboxylic acid end groups.[26−28] In the temperature range of the higher maximum CI-MS spectra show peaks at $m/z = 115 + n \times 114$ (n = 0−4) characteristic of the ($M^+ + H$) ions of cyclic caprolactone oligomers.[29] Thus, the thermal decomposition of the P(a-BL-*b*-CL) copolymers occurs according to two degradation mechanisms, i.e., the random scission of the PBL blocks with formation of unsaturated BL oligomers,[26−28] and scission of the PCL blocks with formation of cyclic oligomers. Formation of cyclic CL oligomers has previously been reported by Montaudo *et al.* for the thermal degradation of PCL homopolymer.[29]

Enzymatic Degradation. The enzymatic degradation of the PCL homopolymer and P(a-BL-*b*-CL) copolymer films has been investigated in the presence of lipase from *R. arrhizus* at pH = 7.4 (Tris-HCl buffer) at 37 °C. A systematic weight loss was observed for all investigated samples. The biodegradation rate has been determined from the linear time dependence of the sample weight loss as presented in Figure 5. It has been found that the biodegradation rate of block copolymer films containing 15 and 24 mol % of a-PBL was higher than that of the PCL homopolymer. It is worth pointing out that the copolymer containing 15 mol % of a-PBL degraded almost 3 times faster than the PCL homopolymer. The composition (as estimated by ^1H NMR) of the block copolymers degraded for 96 h perfectly agrees with the composition calculated from the weight loss, assuming that only PCL segments can be degraded under the above conditions. For a block copolymer initially containing 15 mol % of a-PBL, the content of PBL as determined by ^1H NMR after a 96 h enzymatic degradation was 17 mol % to be compared to 16.8 mol %

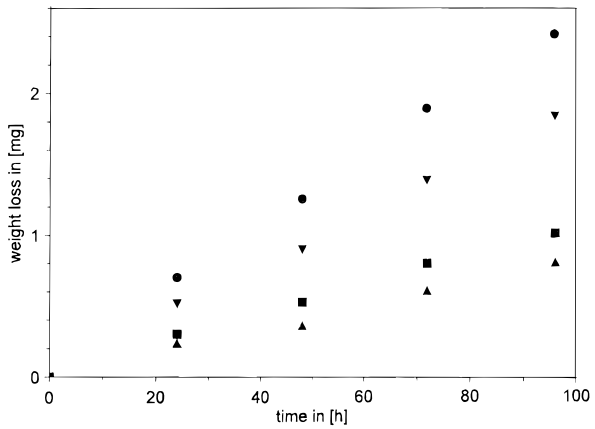


Figure 5. Biodegradation profiles of various composition P(a-BL-*b*-CL) and PCL films in an aqueous solution of lipase from *R. arrhizus* at 37 °C and pH = 7.4; (●) 15 mol % of a-PBL (rate of the enzymatic degradation, 6.2 μg/cm^2 h), (▼) 24 mol % of a-PBL (4.7 μg/cm^2 h), (■) PCL homopolymer (2.4 μg/cm^2 h), (▲) 40 mol % of a-PBL (1.9 μg/cm^2 h).

calculated from the weight loss. For a copolymer containing 24 mol % the respective values were 26 mol % (NMR) and 25.7 mol % (calculated). Actually, although microbial lipases are known to hydrolyze PCL,[24,30,31] the erosion of PBL by lipase has never been reported. In agreement, similar enzymatic degradation experiments have been performed on an atactic BL homopolymer (M_n = 18 000) and no weight loss has been measured.

The above results indicate that composition of the P(a-BL-*b*-CL) block copolymers has a significant effect on the rate of degradation by lipase from *R. arrhizus* and control of the atactic PBL content is an effective way to make available biodegradable materials with "tailored" enzymatic degradation properties. To the best of our knowledge, the lipase-catalyzed enzymatic degradation of atactic PBL/PCL block copolymer has not been reported until now. Nevertheless, a similar composition effect on the enzymatic degradation has been observed for random copolymers of stereoregular (*R*)-BL and CL in the presence of lipase from *Rhizopus delemar*.[24] The authors suggested that the rate of enzymatic degradation of such copolymers is regulated not only by the crystallinity of the polymer but also by the chemical structure of monomeric units and substrate specificity of a given enzyme. The present study indicates that in spite of the different nature of lipases (*R. arrhizus* versus *R. delemar*) and tacticity of PBL segments (atactic versus isotactic) the analogue biodegradation behavior of the caprolactone-based copolymers display a very similar biodegradation behavior.

In conclusion, combination of the anionic ROP of BL and the coordination−insertion ROP of CL is an easy and efficient route to the synthesis of well-defined diblock copolymers. No side reactions, e.g., *inter*- and *intra*molecular transesterification reactions, have been observed under the investigated conditions. Poly(β-butyrolactone-*b*-ϵ-caprolactone)s consist of totally amorphous PBL and partially crystalline PCL, that show at least a partial miscibility in the amorphous phases of the bulk material. The enzymatic degradation rate of the P(a-BL-*b*-CL) copolymers strongly depends on their composition, in such a way that copolymers containing low amounts of BL degrade much faster than PCL homopolymer and block copolymers rich in BL.

It is also worth pointing out that the strategy reported in this paper can be extended to the controlled synthesis of P(CL-*b*-BL-*b*-CL) triblock copolymers starting from a α,ω-hydroxy-PBL prepolymer. This hydroxy telechelic precursor can be prepared by initiating the anionic polymerization of BL by the hydroxy acid salt/18-crown-6 complex as discussed above and quenching the living chains with, e.g., 2-iodoethanol. The addition of 2 equiv of $AlEt_3$ to the α,ω-hydroxy-PBL prepolymer is straightforward to prepare a difunctional initiator for the CL polymerization.

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