

Synthesis of tadpole-shaped copolyesters based on living macrocyclic poly(ϵ -caprolactone)

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Abstract

Synthesis of an asymmetric tadpole-shaped aliphatic copolyester consisting of a poly(ϵ -caprolactone) ring and two poly(L-lactide) tails was reported for the first time. First, a high molecular weight cyclic PCL macroinitiator ($M_n = 31,000$) was prepared by intramolecular photocross-linking of "living" chains. Polymerization of L-lactide was resumed by the tin dialkoxide containing macrocycles, thus making the targeted tadpole-shaped copolyester available. A preliminary investigation of the crystallization of these copolyesters was carried out by differential scanning calorimetry and polarized optical microscopy.

Keywords: Tadpole-shaped copolyester; Ring-opening polymerization; Poly(ϵ -caprolactone)

1. Introduction

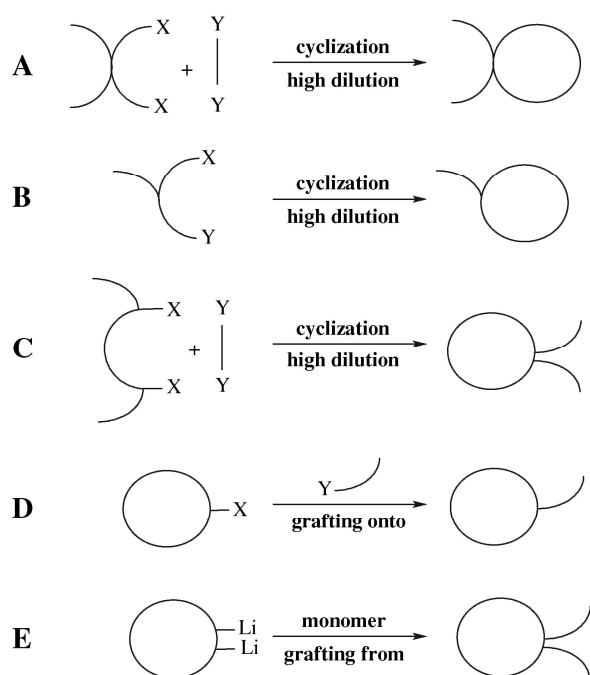
Because the macroscopic properties and potential applications of synthetic polymers directly depend on their molecular structure, the design of the molecular characteristics of the chains, including the architecture (e.g., mono-/pluri-macrocyclic, hyperbranched, star-shaped, comb-shaped and dendrimeric) is of prime importance [1-3].

At the time being, only a limited effort has been devoted to the synthesis of tadpole-shaped polymers, thus macrocycles substituted by either one [4-7] or two side chains [6,8-11]. Most of them are synthesized by cyclization of a linear precursor, according to two main strategies. A first approach relies on the direct cyclization of a duly substituted linear precursor (Scheme 1). For example, a difunctional coupling agent (Y—R—Y) can be reacted with, e.g., a four-arm A_2B_2 star-shaped polymer, whose arms A are end-capped by a group X reactive towards Y (Scheme 1, route A). In a synthesis reported by Ma, A was polybutadiene and B was polystyrene [8]. A one-arm tadpole-shaped copolymer was also prepared by cyclization of a linear precursor capped by a reactive group Y at one chain-end and bearing a mutually reactive group X along the chain (Scheme 1, route B). This strategy was implemented by Deffieux et al., who synthesized macrocyclic poly(chloroethyl vinyl ether) substituted by one polystyrene tail from linear poly(chloroethyl vinyl ether)-*b*-polystyrene copolymer [4]. Whenever two reactive groups X are located along a preformed polymer (Scheme 1, route C), a two-arm tadpole-shaped copolymer is formed by coupling with a difunctional compound Y—R—Y. For example, Tezuka et al. prepared a two-arm tadpole-shaped poly(THF) by this strategy based on electrostatic interactions followed by covalent fixation [6]. In a less direct two-step strategy, a macrocycle is preformed and substituted by a functional group X, followed by reaction with a linear chain end-capped by a complementary functional group Y (Scheme 1; route D). Itoh et al. reported the synthesis of tadpole-shaped polystyrene by grafting a carboxyl end-capped poly(styrene) onto one amine containing cyclic polystyrene [5]. An alternative relies on a "grafting from" technique rather than on the aforementioned "grafting onto" technique. Hemery et al. synthesized two-arm tadpole-shaped poly(isoprene) [9] by anionic polymerization of isoprene initiated by a dianionic macrocycle, that was prepared by cyclization of dianionic linear poly(isoprenyl Li) chains by 1,2-bis(isopropenyl-4-phenyl) ethane (Scheme 1; route E). The same strategy was extended to styrene [10]. Nevertheless, all these strategies require the cyclization of linear precursors under high dilution conditions in order to prevent polycondensation from competing cyclization.

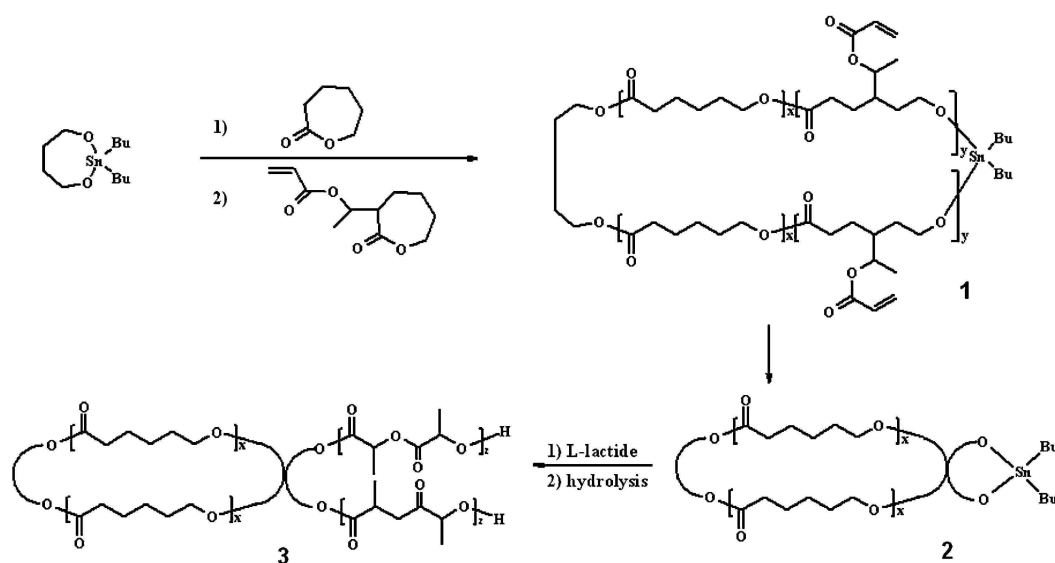
Although aliphatic polyesters have great potential in the biomedical field because of biocompatibility, biodegradability and good mechanical properties [1], no example of tadpole-shaped aliphatic polyesters is known, at least to the best of our knowledge. This work aims at reporting the controlled synthesis of semi-crystalline macrocyclic poly(ϵ -caprolactone) (PCL) with two semi-crystalline poly(L-lactide) tails (PLLA), thus combining permeability and high flexibility of PCL and rapid biodegradability and high tensile strength of

PLLA. The general strategy is illustrated in Scheme 2 [11]. Remarkably, no linear precursor is involved in any step of the synthesis. The ring-opening polymerization of ϵ CL is first initiated by 2,2-dibutyl-2-stanna-1,3-dioxepane (DSDOP) [12], followed by the sequential polymerization of approximately 15 units of α -(1-acryloxyethyl)- ϵ -caprolactone (α A ϵ CL). The macrocyclic poly(ϵ -caprolactone) chains are then stabilized by intramolecular photocross-linking in non-highly diluted solution (~ 0.5 wt%). Because the dibutyl tin dialkoxide is unaffected by the UV cross-linking, polymerization of L-lactide can be directly initiated, with the formation of two PLLA chains attached to the ring in the close vicinity to each other. In contrast to traditional procedures, this strategy is very well-suited to the synthesis of high molecular weight macrocycles because an increase in the chain length does not decrease the probability of intramolecular cyclization.

Scheme 1. Possible routes for the synthesis of tadpole-shaped polymers.



Scheme 2. Synthesis of tadpole-shaped copolyesters.



2. Experimental section

2.1. Materials

(1-Hydroxyethyl)- ϵ -caprolactone was synthesized according to Christoffers et al. [13]. ϵ -Caprolactone (ϵ CL) (Aldrich) was dried over calcium hydride at room temperature for 48 h and distilled under reduced pressure just before use. L lactide was purified by recrystallization (three times) from dry toluene and dried in vacuo at room temperature for 24 h. 2-Dibutyl-2-stanna-1,3-dioxepane (DSDOP) was synthesized as reported in the scientific literature [14]. Benzophenone (Aldrich) was purified by sublimation at 40 °C in vacuo and further dried by azeotropic distillation of toluene. Toluene (Aldrich, 99.5%) was dried over sodium benzophenone and distilled under nitrogen.

2.2. Preparation of *a*-(1-acryloyloxyethyl)- ϵ -caprolactone (*a*A ϵ CL)

A solution of acryloyl chloride (2.3 mL, 2.58 g, 28.5 mmol) in 20 mL of CH₂Cl₂ was added dropwise to a mixture of (1-hydroxyethyl)- ϵ -caprolactone (4.1 g, 25.9 mmol) and Et₃N (4.0 mL, 2.88 g, 28.5 mmol) in 40 mL of CH₂Cl₂ at 0 °C. Then, the temperature was slowly increased up to room temperature under stirring for 16 h. After filtration, the solution was washed with deionized water (1 x 50 mL), saturated aqueous NaHCO₃ (1 x 50 mL) and deionized water (1 x 50 mL). The organic phase was dried by anhydrous MgSO₄, filtered, and the solvent was eliminated under reduced pressure. *a*A ϵ CL was finally purified by elution through SiO₂ (EtOAc/Hexane, 2:3). The yield was 84% (4.63 g). IR: 1728 ($\nu_{C=O}$), 1637 ($\nu_{C=C}$), 1618 ($\nu_{C=C}$) cm⁻¹.

2.3. Synthesis of tadpole-shaped copolyester (Scheme 2)

In a typical experiment, 2.0 mL of ϵ -CL (18 mmol), 11.5 mL of dry toluene and 0.4 mL of a DSDOP solution [0.2 M in toluene] were sequentially added into a previously flamed glass reactor with a syringe through a rubber septum. After 2 h at 40 °C, 0.30 g of *a*A ϵ CL (1.4 mmol) in 2 mL of toluene was added to the reactor, and the reaction temperature was increased to 60 °C. After 2 h, 3 mL of the reaction mixture was picked out and hydrolyzed into the parent linear copolyester for characterization. The solution of the living cyclic precursor was cooled down to room temperature under nitrogen, added with a benzophenone solution (2.0 mg, 11.4 μ mol, in 0.5 mL toluene), and finally diluted with dry toluene until a polymer concentration of 0.5 wt%. This solution was UV irradiated (350-420 nm, 1000 W) at room temperature for 120 min. After part of the solvent was evaporated, half the solution was hydrolyzed by a few drops of acetic acid (1 M in toluene), the polymer was precipitated in cold heptane, recovered by filtration and dried in vacuo for characterization. The second part of the solution, i.e., the macroinitiator 2 (0.0325 mmol), was added with a solution of 0.6 g L-lactide (4.17 mmol) in dry toluene (5 mL) preheated at 60 °C. After stirring at 60 °C for 4 h, the polymerization mixture (concentration, 25 wt%) was added with acetic acid (1 M in toluene), precipitated in methanol, collected by filtration and dried in vacuo.

2.4. Characterization

Size exclusion chromatography (SEC) was performed in THF at a flow rate of 1.0 mL min⁻¹ at 40 °C with a Hewlett-Packard 1090 liquid chromatograph equipped with a Hewlett-Packard 1073A refractive index detector and styragel columns (HP PL gel 5 μ m; pore size of 10⁵, 10⁴, 10³, and 10² Å). Polystyrene (PS) standards were used for calibration and, for the sake of comparison with linear PCL, the experimental molecular weights were converted by the following equation: $M_n(\text{PCL}) = 0.259 \times M_n(\text{PS})^{1.073}$ [18]. ¹H NMR spectra were recorded in CDCl₃ with a Bruker AN 400 apparatus at 25 °C. Differential scanning calorimetry (DSC) was carried out with a TA 2010 DSC thermal analyzer calibrated with indium. Samples of 5-8 mg were encapsulated in aluminum pans, cooled down to -90 °C and heated up to 200 °C at a 10 °C/min rate. Polarized optical micrographs of thin polymer films (prepared by solvent casting) were observed with a ZEISS Axioplan microscope equipped with a hot stage and a digital camera (Ikegami). The samples were heated up to the melting temperature at a 10 °C/min rate, maintained at this temperature for 3 min and then cooled at 10 °C/min down to 120 °C for the linear PLLA to crystallize and then down to 40 °C for crystallization of cyclic PCL to be observed.

3. Results and discussion

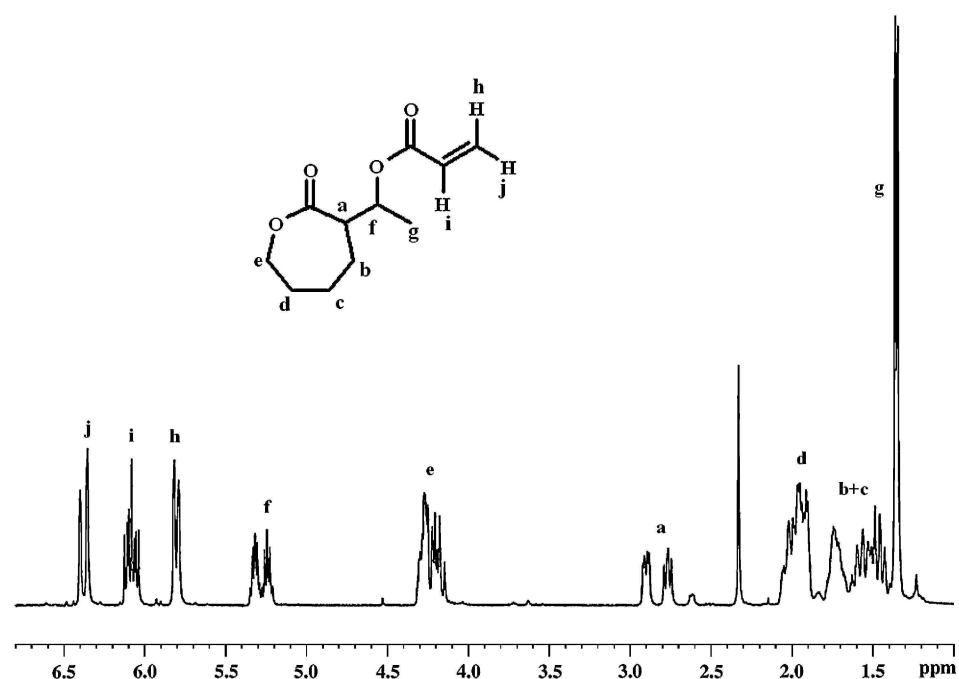
3.1. Synthesis of the cyclic PCL macroinitiator

The strategy shown in Scheme 2 relies on the synthesis of macrocyclic PCL by ring-opening polymerization of lactones (ϵ CL and *a*A ϵ CL) initiated by a cyclic tin(IV) dialkoxide. The accordingly preformed macrocyclic polyester is then stabilized by the intramolecular photocross-linking of the pendant unsaturations next to the

growing site. The detailed information can be found elsewhere [11] and in Supplementary data. Nevertheless, the synthesis of the monomer α -(1-acryloyloxyethyl)- ϵ -caprolactone (α A ϵ CL) which is at the origin of the intramolecular cross-linking step (Scheme 2), has not been reported so far. Briefly, (1-hydroxyethyl)- ϵ -caprolactone was synthesized from ϵ -caprolactone by Christoffers' procedure [13] (Scheme 3). The alcohol was then esterified by acryloyl chloride in the presence of triethylamine (Scheme 3). The lactone was purified by elution through silica and collected with a yield of 85%. This lactone is very sensitive to radical polymerization and must be stored in toluene at -20 °C. The ^1H NMR spectrum shows two diastereoisomers in a 63/37 molar ratio, as testified by two multiplets at 2.75 ppm and at 2.95 ppm, respectively, assigned to the $-\text{CH}-\text{CO}$ protons (Fig. 1). This assignment was confirmed by 2D COSY NMR (Fig. 2). The diastereoisomers were not separated and used as such in this work (Scheme 2).

The macrocyclic PCL used in this work contains 240 ϵ CL units and 8.8 unsaturations, that remained unmodified by the UV treatment (cfr infra) ($M_{n,\text{NMR}} = 27,500$; $M_{n,\text{SEC}} = 20,500$; $M_w/M_n = 1.4$) (Table 1). The thermal properties of the cyclic polyester and the linear counterpart were analyzed by differential scanning calorimetry (DSC) at a heating rate of 10 °C/min. T_g and T_m were recorded during the second heating run (Table 2). The degree of crystallinity $X_c = [\Delta H_m / \Delta H_{\text{PCL}}^0] \times 100$ was calculated from the experimental melting enthalpy with $\Delta H_{\text{PCL}}^0 = 136.4$ J/g for the 100% crystalline PCL [15]. Cyclization of PCL ($M_n = 27,500$) has only a minor effect on T_g , in contrast to the important impact on crystallization. Indeed, the melting temperature (T_m) decreased by 7 °C and the degree of crystallinity (X_c) by at least a factor of two (Table 2).

Fig. 1. ^1H NMR spectrum for α A ϵ CL.



Scheme 3. Synthesis of α A ϵ CL.

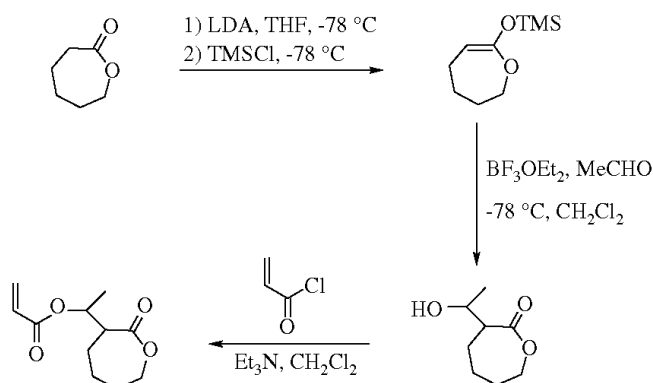


Fig. 2. 2D COSY spectrum for $\alpha A\epsilon CL$.

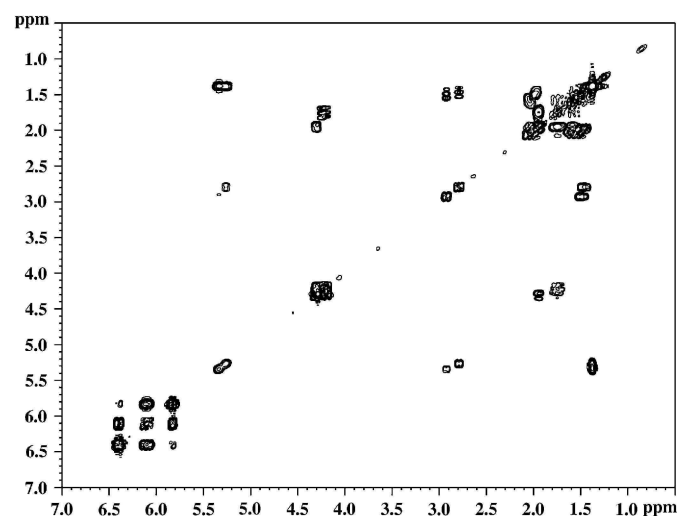


Table 1 : Molecular characteristic features of linear and cyclic polyesters, and tadpole-shaped and triblock copolyesters

Samples	$M_{n,th}$	$M_{n,NMR}$	$M_{n,SEC}$	M_w/M_n	F_{CL}^a
PCL _{linear}	25,600	27,500	24,000	1.40	1
PCL _{macrocyclic}	25,600	27,500	20,500	1.40	1
Tadpole-shaped	43,500	44,500	24,500	1.40	0.67
Triblock PLLA- <i>b</i> -PCL- <i>b</i> -PLLA	44,000	42,000	31,000	1.40	0.67
PLLA _{linear}	9000	8500	9000	1.04	0

$$F_{CL} = (DP_{\epsilon\text{-caprolactone}})/(DP_{\epsilon\text{-caprolactone}} + DP_{L\text{-lactide}}).$$

3.2. Synthesis of poly(ϵ -caprolactone) tadpole-shaped with two poly(L-lactide) tails

In order to synthesize a two-tail tadpole-shaped PCL/PLLA copolymer, the solution of the macroinitiator 2 was concentrated, followed by the addition of a L-lactide solution in dry toluene. The polymerization mixture (concentration: 25 wt%) was stirred at 60 °C for 4 h (optimized conditions). The 1H NMR spectrum for the tadpole-shaped copolymer (comparison of Fig. 3A with Fig. 1) clearly shows new peaks at 5.09-5.18 ppm typical of the protons f for the L-lactide units. A peak of low intensity at 4.3 ppm can be assigned to the —CHOH end-group of the PLLA chains, whereas the peak at 3.6 ppm for the PCL end-group (—CH₂OH) has completely disappeared, in agreement with the expected resumption of the L-lactide polymerization. The L-lactide conversion was 90% as calculated from the intensity of the signals at 5.09-5.18 ppm for L-lactide and at 2.25 ppm for ϵCL . The average polymerization degree was accordingly calculated for each tail ($DP_{L\text{-lactide}} = 59$, $M_{n,NMR} = 8500$). Moreover, the absence of transesterification reaction was confirmed by ^{13}C NMR spectrum (Fig. 3B). Indeed, the expanded carbonyl region shows two peaks at 173.5 ppm for cyclic PCL and at 169.5 ppm for the two PLLA tails. This observation of the PCL and PLLA homodiads without any additional signal is consistent with the coexistence of "pure" macrocyclic PCL and linear PLLA tails. It is also worth noting that the peak at 3.6 ppm assigned to the CH₂OH of the macroinitiator 2 disappeared completely upon the resumption of the lactide polymerization, consistent with a high initiation efficiency.

The SEC trace (Fig. 4) was shifted towards shorter elution times, while keeping the polydispersity index unchanged ($M_w/M_n=1.40$). The apparent molecular weight was actually increased ($M_{n,SEC} = 24,500$), compared to the macrocyclic precursor ($M_{n,SEC} = 20,500$, $M_w/M_n = 1.40$). It can, thus, be concluded that the polymerization resumption is effective and that tadpole-shaped poly(ϵ -caprolactone) with two PLLA tails of a tunable length can be readily prepared.

Table 2: Physical properties of linear and cyclic polyesters, and tadpole-shaped and triblock copolyesters

Samples	T_g^a [°C] (PCL)	T_g^a [°C] (PLLA)	X_c^b [%] (PCL)	T_m^a [°C] (PCL)	X_c^b [%] (PLLA)	T_m^a [°C] (PLLA)
PCL _{linear}	-59.5	-	49.0	51.0	-	-
PCL _{macrocyclic}	-57.0	-	21.5	44.0	-	-
Triblock PLLA- <i>b</i> -PCL- <i>b</i> -PLLA	-59.0	-	46.5	51.0	30.5	134.5
Tadpole-shaped	-56.5	-	18.5	39.0	9.5	132.5
PLLA _{linear}	-	34.0	-	-	11.5	148.0

^a T_g and T_m measured during the second heating run at a 10 °C/min rate.

^b $X_c = (\Delta H_m / \Delta H_{PCL}^0) \times 100$ for homo-PCL; $X_c^{PLLA} = [\Delta H_m / (W_{PLLA} \times \Delta H_{PLLA}^0)] \times 100$, $X_c^{PCL} = [\Delta H_m / (W_{PCL} \times \Delta H_{PCL}^0)] \times 100$ for the tadpole-shaped copolyester, where ΔH_m is the actual melting enthalpy, W_{PLLA} and W_{PCL} are the weight fractions of PLLA and PCL in the copolyester, respectively (NMR analysis). ΔH_{PCL}^0 (136.4 J g⁻¹) [15] and ΔH_{PLLA}^0 (93 J g⁻¹) [17] are the melting enthalpies for 100% crystalline PCL and PLLA, respectively.

Fig. 3. ¹H (A) and ¹³C (B) NMR spectra for a tadpole-shaped copolyester.

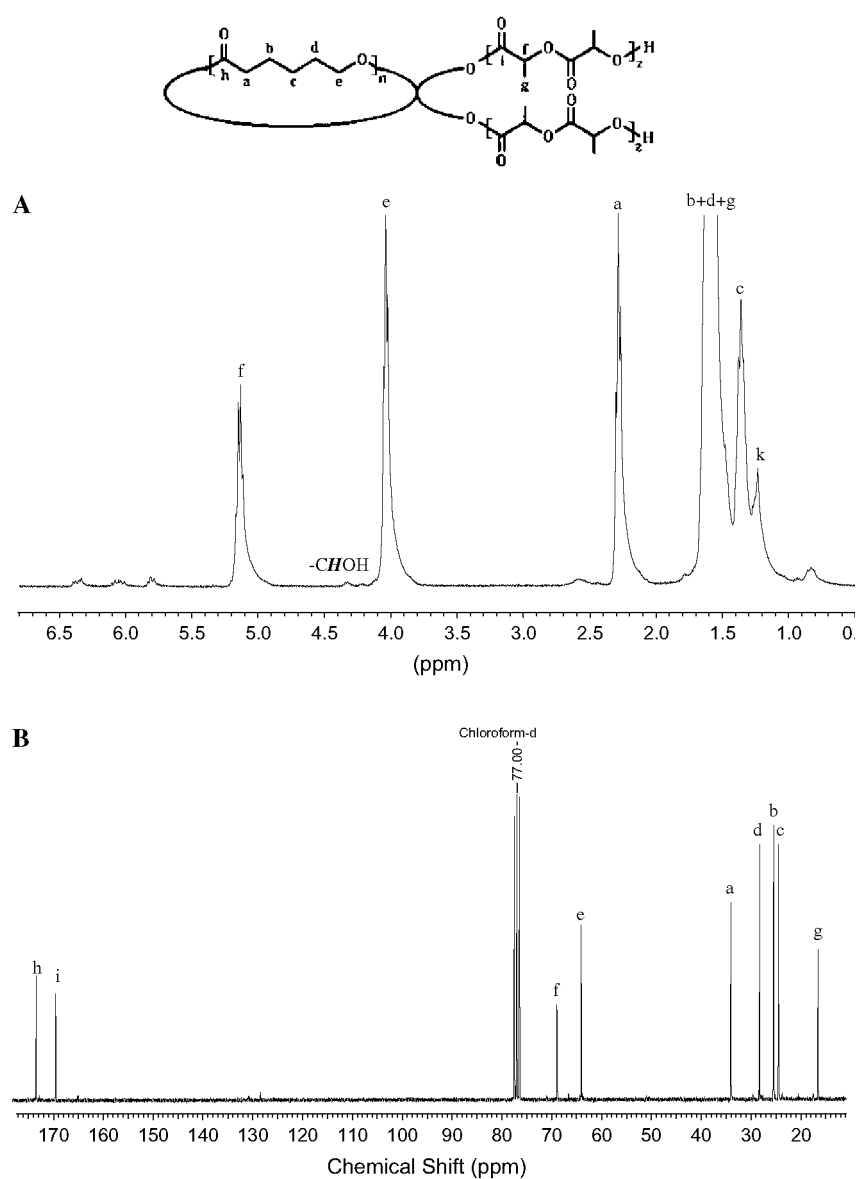


Fig. 4. SEC traces for cyclic polyester after UV treatment (a), and tadpole-shaped copolyester (b).

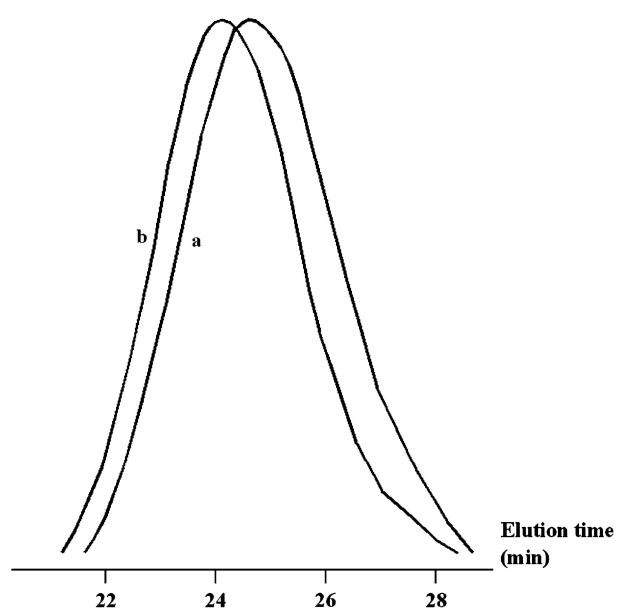
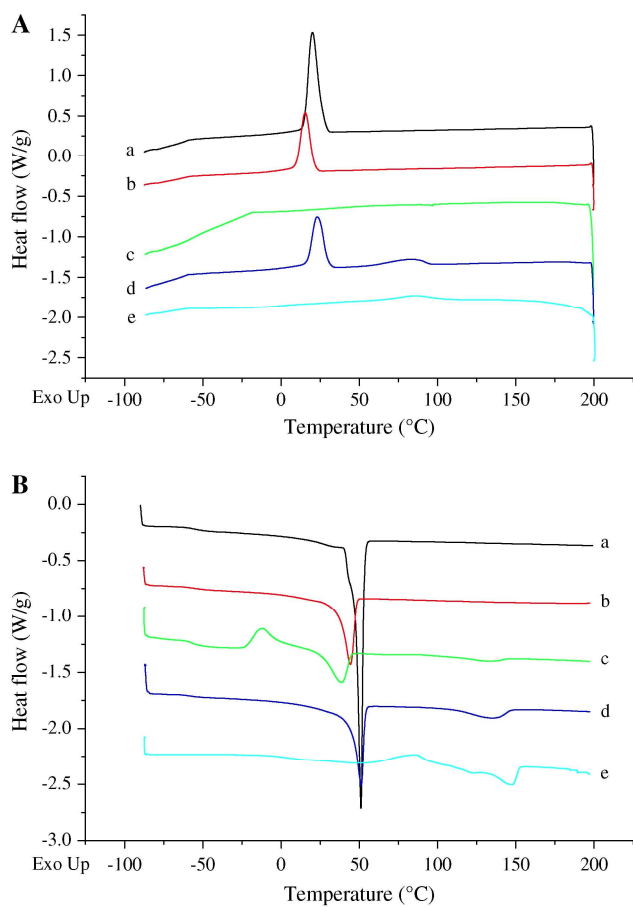


Fig. 5. DSC traces from the cooling (A) and second heating (B) runs for linear PCL (a), macrocyclic PCL (b), tadpole-shaped copolyester 3 (c), linear triblock (d), and linear homo-PLLA (e).



In order to confirm that tin alkoxides remain unmodified by the UV treatment, ϵ CL was polymerized by DSDOP and analyzed by SEC ($M_n = 27,500$; $M_w/M_n = 1.4$). The living chains were then UV irradiated under the conditions used for the intramolecular cross-linking of the α A ϵ CL containing macrocyclic PCL. Finally, a second feed of ϵ CL was added to the polymerization medium. M_n increased up to 41,000 in line with the theoretical value of 44,000, and the polydispersity remained unchanged ($M_w/M_n = 1.4$). Clearly, tin alkoxides tolerate UV irradiation.

For the sake of comparison, a linear poly(LLA-*b*- ϵ CL-*b*-LLA) triblock copolymer ($M_{n,NMR} = 42,000$; $M_w/M_n = 1.40$; $F_{\epsilon\text{-caprolactone}} = 0.67$) was synthesized by sequential ring-opening polymerization of ϵ CL and L-LA initiated by DSDOP, according to Kricheldorf's procedure (Table 1) [16]. Linear poly(L-lactide) ($M_{n,NMR} = 8500$; $M_w/M_n = 1.04$) was also prepared by ROP of L-lactide initiated by DSDOP.

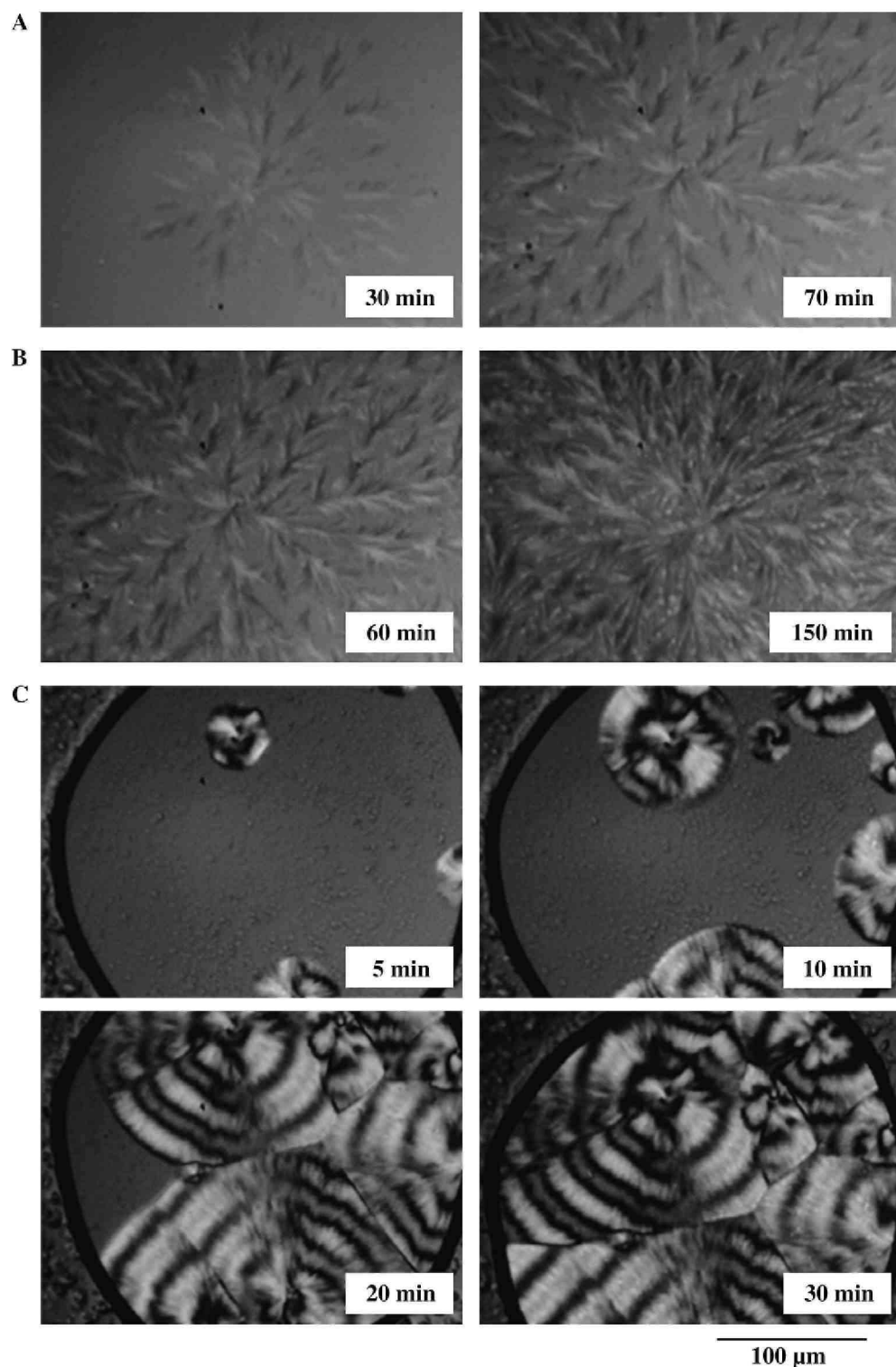
The thermal behavior of tadpole-shaped copolyester 3 (Scheme 2) was compared to cyclic PCL (precursor), linear PLLA and linear triblock P(LLA-*b*- ϵ CL-*b*-LLA) by differential scanning calorimetry (DSC) (Fig. 5). The polyesters were first heated above the melting temperatures (200 °C), and then cooled down to -90 °C at a rate of 10 °C/min. The cooling traces are shown in Fig. 5(A). A crystallization peak is observed for the macrocyclic PCL 2 at 15.0 °C, whereas only a very faint peak at 83 °C is observed for homo-PLLA of quite a comparable molecular weight ($M_n = 9000$). Two crystallization peaks are observed at 23 °C and 83 °C for the triblock copolymer. When the tadpole-shaped copolyester is concerned, no crystallization is detected anymore, consistent with a much slower crystallization for the macrocyclic PCL as a result of the grafting of two PLLA arms.

All the samples were then heated from -90 °C at 10 °C/min, and the DSC traces are shown in Fig. 5(B). Expectedly, a melting endotherm is clearly observed for the cyclic PCL (44 °C), whereas PLLA, which did not crystallize significantly during cooling, crystallizes at 85.0 °C followed by melting at 148 °C. A similar behavior is observed for the cyclic PCL in the tadpole-shaped copolyester. Indeed, the crystallization that did not occur during cooling, is observed during heating at -11.5 °C, followed by melting at 39 °C. The melting temperature of cyclic PCL is thus decreased by 5 °C as a result of the PLLA grafting. Although crystallization of PLLA could not be observed during both the cooling and the heating steps (possibly because of a too low content of PLLA in the copolyester), a small melting endotherm was observed at a much lower temperature (132.5 °C) compared to homo-PLLA (148 °C). In parallel to T_m , the crystallinity degree for cyclic PCL and PLLA is also decreased as a result of incorporation into the tadpole-shaped architecture (Table 1). It thus appears that the coexistence of two crystallizable constitutive components in the copolyester has a mutually detrimental impact on their crystallization. Finally, only T_g of the cyclic PCL could be observed by DSC, which remained unaffected by grafting of PLLA (Table 1).

In contrast to the tadpole-shaped copolyester, the crystallization of the triblock copolymer is observed during cooling from the melt and no longer during the next heating step. Moreover, the melting temperature of the PCL (51 °C) and PLLA (134.5 °C) blocks of the linear triblock copolymer is slightly higher and their degree of crystallinity is much higher compared to the tadpole-shaped copolyester (46.5% vs. 18.5% for PCL and 30.5% vs. 9.5% for PLLA) (Table 2). As a rule, the tadpole-shaped architecture has a direct impact on the crystallization of the constitutive components.

Although a detailed analysis of the crystallization of the tadpole-shaped copolyesters is beyond the scope of this paper, the isothermal crystallization of PLLA at 120 °C was observed by polarized optical micrography and compared to that of the tadpole-shaped copolyester first at 120 °C and then at 40 °C. The samples were previously heated at 180 °C for 3 min. At 120 °C, homo-PLLA crystallizes much faster than the PLLA tails in the copolyester, with the formation of banded spherulites that result from the periodic twisting of growing lamellae. Under the same conditions of temperature and time, the spherulitic growth of the low content of PLLA tails in the copolyester is quite a problem. Only dendritic-type crystallites are observed, which is a very preliminary step in the spherulite formation (Fig. 6A). These crystallites serve as templates for the cyclic PCL crystallization at 40 °C, as illustrated by Fig. 6B.

Fig. 6. Polarized optical micrographs for isothermally crystallized (A) tadpole-shaped copolyester, first at 120 °C and then at 40 °C (B), (C) homo-PLLA (at 120 °C).



4. Conclusion

Synthesis of asymmetric tadpole-shaped aliphatic copolyesters consisting of a PCL ring and two PLLA tails was reported for the first time. A cyclic PCL macroinitiator was prepared by sequential polymerization of ϵ CL and a few units of α A ϵ CL, followed by intramolecular photocross-linking. Resumption of the L-lactide polymerization gave rise to the targeted tadpole-shaped copolyester. In contrast to the classical methods of synthesis of macrocycles that rely on the cyclization of linear chains, cyclic precursors are prepared in this work by living

ring-opening polymerization initiated by a cyclic tin(IV) dialkoxide followed by covalent fixation by photocross-linking of pendant unsaturated units. This method is thus well-suited to the synthesis of predictable high molecular weight macrocycles [10]. In addition to the polymerization of ϵ -CL and α A ϵ CL, that one of L-lactide is living, which allows size and composition of the tadpole-shaped copolyesters to be extensively tuned.

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Appendix. Supplementary data

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.polymer.2006.10.008.

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