Synthesis of Poly(ε-caprolactone)-*block*-Poly(*n*-butyl acrylate) by the Combination of Ring-Opening Polymerization and Atom Transfer Radical Polymerization with $Ti[OCH_2CCl_3]_4$ as a Difunctional Initiator. II. Synthesis and Characterization of Poly(ε-caprolactone)-*block*-Poly(*n*-butyl acrylate) Copolymers

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ABSTRACT: The kinetics and controllability of the $Ti[OCH_2CCl_3]_4$-initiated atom transfer radical polymerization (ATRP) of *n*-butyl acrylate were investigated. Then, with $Ti[OCH_2CCl_3]_4$ as the initiator, poly(ε-caprolactone)-*block*-poly(*n*-butyl acrylate) (PCL-*b*-PBA) copolymers were synthesized by the combination of the ring-opening polymerization (ROP) of ε-caprolactone and ATRP of *n*-butyl acrylate. With different sequential combinations of ROP and ATRP, three routes were used to synthesize PCL-*b*-PBA copolymers. The composition characterization results demonstrated that the first-ROP-then-ATRP route was most efficient; it was followed by the *in situ* ATRP and ROP route and then the first-ATRP-then-ROP route. Furthermore, with a Haake Rheomix reactor (Thermo Electron Corp., Karlsruhe, Germany), the PCL-*b*-PBA copolymers were *in situ* synthesized in a poly(methyl methacrylate) matrix. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 115: 1958–1966, 2010

Key words: atom transfer radical polymerization (ATRP); diblock copolymers; metal-organic catalysts/organometallic; ring-opening polymerization

INTRODUCTION

Poly(ε-caprolactone) (PCL) is one of the most widely studied aliphatic polyesters for all kinds of purposes, such as pharmacological, biomedical, agricultural, and environmental applications.[1–5] By the careful selection of the initiator systems, PCLs functionalized with different end groups, such as halogen groups,[6,7] double-bond groups,[8–10] hydroxyl groups,[11,12] and silane groups,[13–15] have been obtained, and these groups provide a wide range of possibilities for the synthesis of PCL-based copolymers with advanced structures such as block,[16–18] star-shaped,[19,20] comblike,[21] brushlike,[22] and crosslinked network structures.[23,24] Meanwhile, atom transfer radical polymerization (ATRP) has been proved to be efficient for synthesizing polymers with desirable macromolecular architectures.[25–28] Therefore, it is very interesting to combine ring-opening polymerization (ROP) and ATRP to synthesize PCL-containing copolymers with controlled segment chain lengths, compositions, and polymer chain architectures.[29–32]

This work is part of a study of the design and synthesis of well-defined PCL-containing copolymers. Copolymers with crosslinked structures and controlled chain lengths of PCL by ROP and classical radical polymerization have been synthesized.[33] The synthesis of well-defined block copolymers is of great interest in investigations of ameliorating the defects of individual components and improving the properties of matrix polymers. In this article, we present the kinetics and controllability of the $Ti[OCH_2CCl_3]_4$-initiated ATRP of *n*-butyl acrylate

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(BA), the synthesis and characterization of poly(ε-caprolactone)-*block*-poly(*n*-butyl acrylate) (PCL-*b*-PBA) copolymers synthesized by the combination of ROP of ε-caprolactone (CL) and ATRP of BA, and the synthesis and characterization of *in situ* synthesized PCL-*b*-PBA copolymers in a poly(methyl methacrylate) (PMMA) matrix.

EXPERIMENTAL

Materials

$Ti[OCH_2CCl_3]_4$ was synthesized according to a procedure described in a previous study;[34] *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (PMDETA; Aldrich, Lyon, France; 99%), and copper(I) chloride (Cu^ICl; Aldrich; ≥99%) were used as received. CL (Solvay Co., Warrington, United Kingdom; 99%) and BA (Aldrich; 98%) were distilled over calcium hydride (CaH_2). PMMA (Brazil Resarbras Co., Bahia, Brazil; extrusion-grade) was dried in a vacuum oven at 80°C for 8 h before the experiment.

$Ti[OCH_2CCl_3]_4$-initiated ATRP of BA

$Ti[OCH_2CCl_3]_4$ was halogenated with —CCl_3, which can be used as an initiator in ATRP. Although there are three chlorine atoms in each arm of the initiator, it is suggested in the literature that only one chlorine atom is viable for initiation.[35–37] ATRP of BA was carried out as follows. $Ti[OCH_2CCl_3]_4$ (6.26×10^{-2} g, 9.75×10^{-5} mol) and BA (5 g, 3.9×10^{-2} mol) were charged into a dry Schlenk flask (25 mL) equipped with a magnetic stirring bar and sealed with a rubber septum at room temperature. After $Ti[OCH_2CCl_3]_4$ was dissolved, Cu^ICl (3.86×10^{-2} g, 3.90×10^{-4} mol) was charged, and it was followed by PMDETA (6.76×10^{-2} g, 3.90×10^{-4} mol). Then, the mixture was degassed by three freeze–pump–thaw cycles and back-filled with nitrogen. The Schlenk flask was immersed into an oil bath thermostated at 110°C. At timed intervals, samples were taken with a syringe. To use size exclusion chromatography (SEC) to study the polymerization kinetics, the collected samples were diluted with tetrahydrofuran (THF; 0.01 g/mL) and then filtered on a filter plate (0.45-μm pore size) to remove the catalysts. For the other experiments, only the degree of polymerization [DPn(set)] and the polymerization temperature were changed. For the entire ATRP process, DPn(set) was set according to the following equation:

$$\mathrm{DPn(set)} = \frac{1}{4} \times \frac{m_{BA}/M_{BA}}{m_{Ti}/M_{Ti}} \quad (1)$$

where m_{BA} and M_{BA} are the mass and molecular weight of BA, respectively, and m_{Ti} and M_{Ti} are the mass and molecular weight of $Ti[OCH_2CCl_3]_4$, respectively.

Synthesis of the PCL-*b*-PBA copolymers

PCL and poly(*n*-butyl acrylate) (PBA), synthesized with $Ti[OCH_2CCl_3]_4$, contained both —OCH_2CCl_3 groups and Ti—O bonds, which made PCL and PBA the macroinitiators in ATRP and ROP, respectively. With $Ti[OCH_2CCl_3]_4$, a PCL-*b*-PBA copolymer was synthesized by the combination of ROP of CL and ATRP of BA. Because of the different requirements of the production techniques, such as reactive extrusion and bulk polymerization in a reactor, and the expected morphology of the final materials, different sequential combinations of ROP and ATRP were investigated, as shown in Scheme 1.

In the PCL-*b*-PBA copolymers, the polymerization degree of the individual PCL and PBA segments was set according to the following equation:

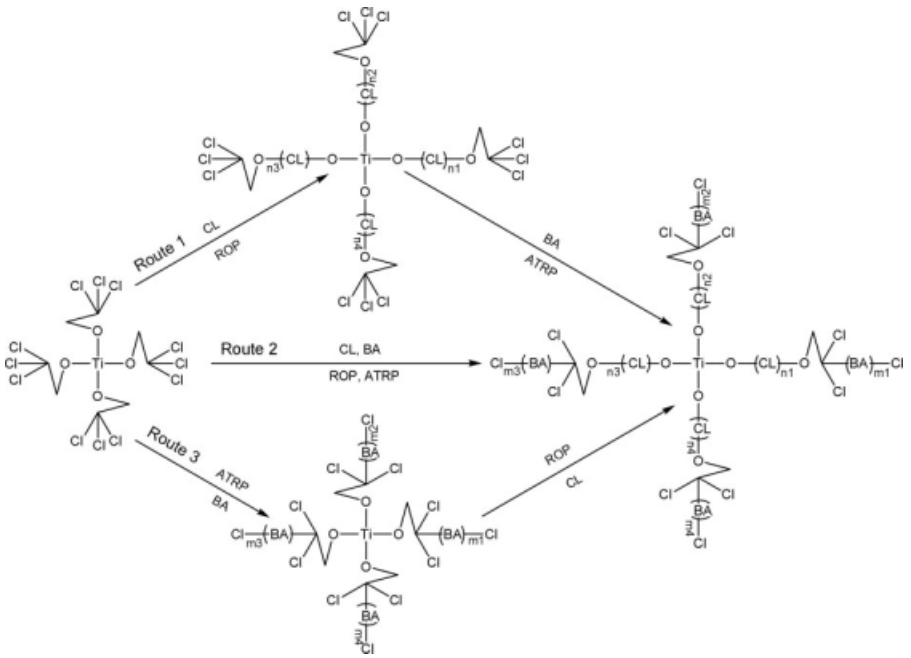
$$\mathrm{DPn(set, PCL)} = \frac{M_0^{CL}}{4 \times I_0} \quad (2)$$

$$\mathrm{DPn(set, PBA)} = \frac{M_0^{BA}}{4 \times I_0} \quad (3)$$

where I_0 is the initial concentration of $Ti[OCH_2CCl_3]_4$ and M_0^{CL} and M_0^{BA} are the initial concentrations of CL and BA, respectively. In the following experiments, the ratio of PCL to PBA was set as 1/1 mol/mol for all the copolymers; therefore, the PCL and PBA segments in each copolymer had the same set polymerization degree.

First-ROP-then-ATRP

The first-ROP-then-ATRP route can be described as follows. CL (4.45 g, 3.90×10^{-2} mol) and $Ti[OCH_2CCl_3]_4$ (0.25 g, 3.90×10^{-4} mol) were charged into a dry Schlenk flask equipped with a magnetic stirring bar and sealed with a rubber septum at room temperature. After the initiator had dissolved, the flask was immersed into an oil bath thermostated at 80°C for 12 h. Then, the flask was cooled to room temperature, and BA (5.00 g, 3.90×10^{-2} mol) was charged. After the PCL macroinitiator had dissolved, Cu^ICl (0.15 g, 1.56×10^{-3} mol) and PMDETA (0.41 g, 2.34×10^{-3} mol) were charged. The resulting solution was degassed by three freeze–pump–thaw cycles and back-filled with nitrogen. Then, the flask was immersed into an oil bath held at 80°C for 12 h. For the other experiments, only the $CL/Ti[OCH_2CCl_3]_4/BA/Cu^ICl/PMDETA$ ratio was changed according to the set polymerization degree of the PCL or PBA segment.



Scheme 1 Synthesis of the PCL-*b*-PBA copolymers: (1) first-ROP-then-ATRP route, (2) simultaneous ATRP and ROP route, and (3) first-ATRP-then-ROP route.

In situ ATRP and ROP

The *in situ* ATRP and ROP route can be described as follows. CL (4.45 g, 3.90×10^{-2} mol), $Ti[OCH_2CCl_3]_4$ (0.25 g, 3.90×10^{-4} mol), and BA (5.00 g, 3.90×10^{-2} mol) were charged into a dry Schlenk flask (25 mL) equipped with a magnetic stirring bar and sealed with a rubber septum at room temperature. After the initiator had dissolved, Cu^ICl (0.15 g, 1.56×10^{-3} mol) was added, and it was followed by PMDETA (0.41 g, 2.34×10^{-3} mol). The mixture was degassed by three freeze–pump–thaw cycles and back-filled with nitrogen. Then, the flask was immersed into an oil bath thermostated at 80°C for 12 h. For the other experiments, only the CL/$Ti[OCH_2CCl_3]_4$/BA/Cu^ICl/PMDETA ratio was changed according to the set polymerization degree of the PCL or PBA segment.

First-ATRP-then-ROP

The first-ATRP-then-ROP route can be detailed by the following experiment. $Ti[OCH_2CCl_3]_4$ (0.25 g, 3.90×10^{-4} mol) and BA (5.00 g, 3.90×10^{-2} mol) were charged into a dry Schlenk flask (25 mL) equipped with a magnetic stirring bar and sealed with a rubber septum at room temperature. After $Ti[OCH_2CCl_3]_4$ had dissolved, Cu^ICl (0.15 g, 1.56×10^{-3} mol) was charged, and it was followed by PMDETA (0.41 g, 2.34×10^{-3} mol). The mixture was degassed by three freeze–pump–thaw cycles and back-filled with nitrogen. Then, the Schlenk flask was immersed into an oil bath thermostated at 80°C. ATRP of BA was stopped after 12 h by the flask being opened and the catalyst being exposed to air. When the flask was cooled to room temperature, CL (4.45 g, 3.90×10^{-2} mol) was injected with a syringe. After the PBA macroinitiator had dissolved in CL, the flask was immersed into an oil bath thermostated at 80°C for 6 h. For the other experiments, only the CL/$Ti[OCH_2CCl_3]_4$/BA/Cu^ICl/PMDETA ratio was changed according to the set polymerization degree of the PCL or PBA segment.

In situ synthesized PCL-*b*-PBA copolymer in a PMMA matrix

The *in situ* synthesized PCL-*b*-PBA copolymer [1/1 mol/mol, DPn(set, PCL) = 50] in a PMMA matrix was prepared with a Haake PolyLab mixer (Thermo Electron Corp., Karlsruhe, Germany) equipped with a Rheomix 600p rotor; the rotation speed was 30 rpm, and the chamber temperature was 180°C. In the experiment, 40 g of PMMA was charged into the Rheomix at the very beginning; after 15 min, 5.4 g of PBA [DPn(set, PBA) = 50; synthesized with $Ti(OCH_2CCl_3)_4$] was charged into the Rheomix; and then, after another 15 min, 4.6 g of CL was injected into the Rheomix chamber. After 10 min, the Rheomix internal mixer was stopped, and the sample was collected. In the other experiment, only the polymerization time of CL was prolonged to 15 min. The samples collected from the Rheomix were characterized by nuclear magnetic resonance (NMR) without any further treatment to evaluate the conversion of CL.

Characterization

^{1}H-NMR spectra were recorded in deuterated chloroform ($CDCl_3$) on a Bruker (Courtaboeuf, France) Avance 250 instrument working at 250 MHz and 25°C. Chemical shifts of protons (δ) were recorded with reference to internal tetramethylsilane. The samples used in ^{1}H-NMR were the copolymers directly collected from the experiment without any further treatment.

The number-average molecular weight (M_n), the weight-average molecular weight (M_w), and the molecular weight polydispersity index (PDI = M_w/M_n) were determined by SEC. The detectors employed to measure the absolute molecular weights were a triple-detector system with a Waters (Guyancourt, France) 2414 refractive-index detector, a Wyatt Technology (Toulouse, France) ViscoStar viscometer detector, and a Wyatt Technology miniDAWN Treos multi-angle laser light scattering detector with a light wavelength of 690 nm. Four columns were used (Shodex KF-G, Shodex KF-801, Shodex KF-803, and Shodex KF-805, Munich, Germany). The PCL-*b*-PBA copolymers were hydrolyzed before the test. The eluent was THF, and the flow rate was 1 mL/min. The absolute molecular weights were determined with Astra software from Wyatt Technology. The refractive-index increment (dn/dc) values used for the PBA and PCL-*b*-PBA copolymers were 0.055 and 0.075 mL/g, respectively, in THF at 25°C. A BA solution was injected to obtain the dn/dc value, which was 0.009 mL/g for BA in THF at 25°C.

RESULTS AND DISCUSSION

Kinetics of the Ti[OCH_2CCl_3]$_4$-initiated ATRP of BA

In our experiments, SEC was applied to determine the conversion of the BA monomer in ATRP; therefore, the samples used in SEC were not hydrolyzed because if water had been used to hydrolyze the PBA samples, the residual BA monomer could not have been determined. Figure 1 shows the SEC elution curves of different ATRP samples.

Typically, for Cu(I)-mediated ATRP, the polymerization proceeds by first-order kinetics with respect to the monomer concentration, initiator concentration, and Cu(I) concentration and by negative first-order kinetics with respect to the Cu(II) concentration; therefore, a plot of $-\ln(1-\alpha)$ (where α is the conversion) versus time should yield a linear relationship. Figure 2 presents plots of the conversion versus time and plots of $-\ln(1-\alpha)$ versus time. The relation between $-\ln(1-\alpha)$ and time is not completely linear, and an upward curvature can be observed; this indicates that the initiation is slow in comparison with the initiation in ideal ATRP.

Figure 3 shows M_n and PDI as functions of the monomer conversion in the ATRP experiment. The theoretical molecular weight [M(theoretical)] of linear PBA at different monomer conversions was calculated according to eq. (4):

$$M\,(\text{theoretical}) = M(\text{BA}) \times \text{DPn(set)} \times \alpha + M(-\text{OCH}_2\text{CCl}_3) \quad (4)$$

where M(BA) and M(—OCH_2CCl_3) are the molecular weights of the BA and —$OCH_2CCl_3]_4$ groups, respectively.

As mentioned previously, the ATRP samples used for SEC were not completely hydrolyzed, so the SEC-determined molecular weight of PBA was not the mass of linear PBA. Figure 3 shows that under the conditions in our study, the molecular weight of PBA was approximately linear with respect to the monomer conversion within a range up to 80%. At the same time, PDI decreased with the monomer conversion increasing. This observation indicates that to some extent, controllability can be achieved in the Ti[OCH_2CCl_3]$_4$-initiated ATRP of BA.

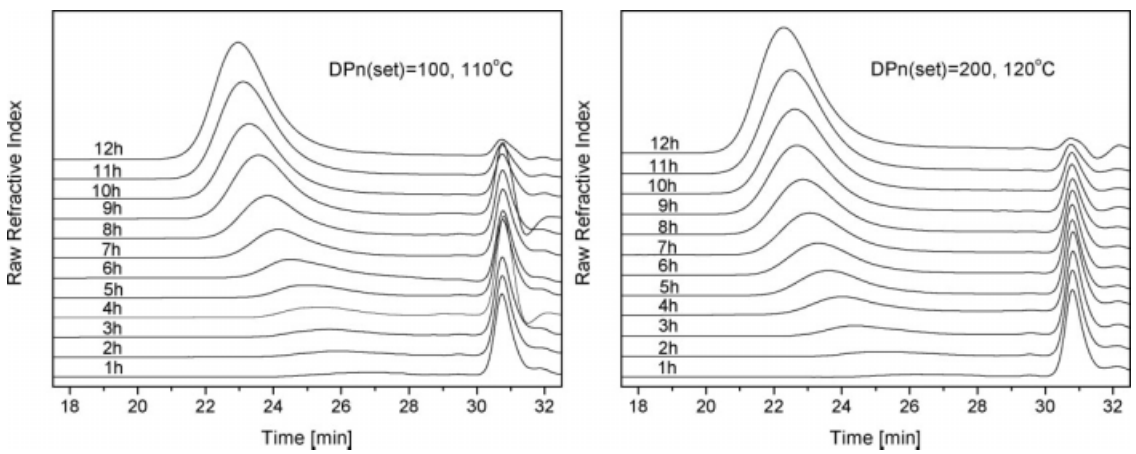


Figure 1 SEC traces of ATRP samples collected at different times during ATRP.

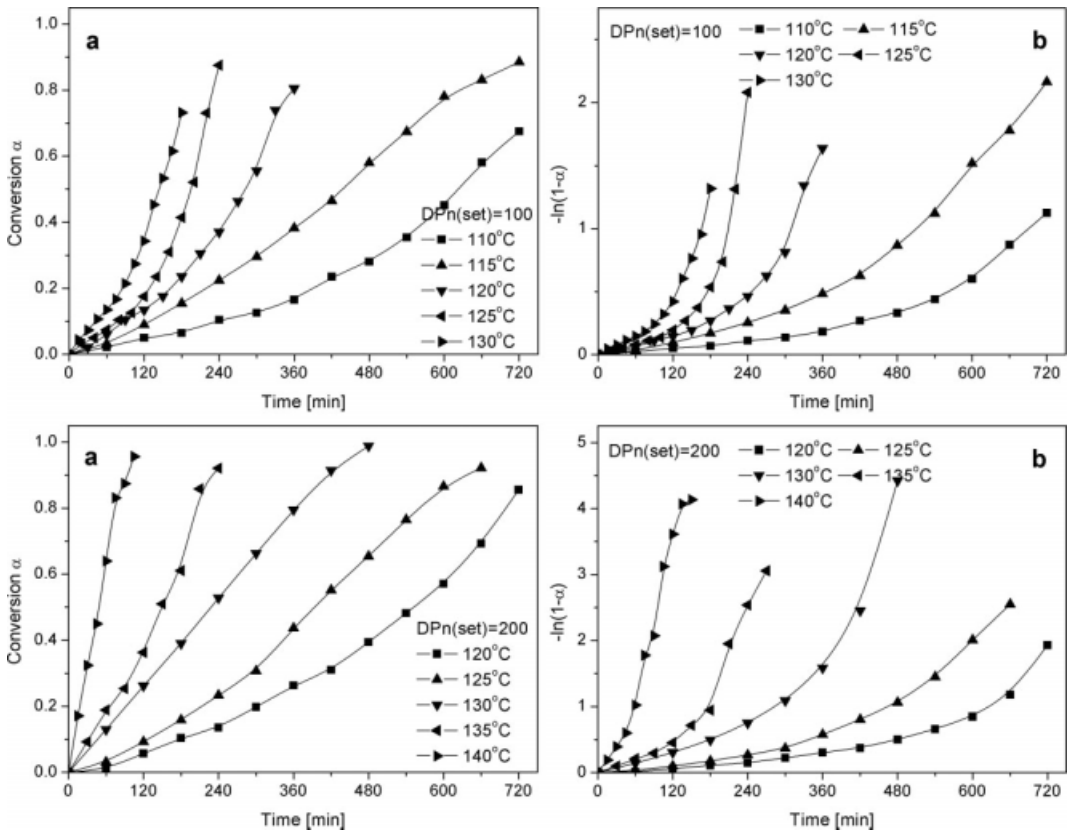


Figure 2 (a) Conversion as a function of the polymerization time and (b) $-\ln(1 - \alpha)$ as a function of the polymerization time.

^{1}H-NMR-evaluated composition of the PCL-*b*-PBA copolymers

To evaluate the efficiency of the three different PCL-*b*-PBA copolymer synthesis routes, the compositions of PCL-*b*-PBA copolymers synthesized by the different routes were characterized with ^{1}H-NMR. The chemical shifts of different protons in $Ti[OCH_2CCl_3]_4$, CL, PCL, BA, and PBA are summarized in Table I.

The ^{1}H-NMR spectra of PCL-*b*-PBA copolymers with different molecular weights are shown in Figure 4. In Figure 4, the signals for the protons of CH_2=CH in the BA monomer totally disappear from the spectrum of the PCL-*b*-PBA copolymer; this observation demonstrates that the conversion of BA was complete, and in the following calculation, it was taken to be 100%. With the protons in the repeating units of PCL and PBA, the molar fraction of the PCL and PBA segments in the PCL-*b*-PBA copolymers could be determined according to eq. (5):

$$\frac{\text{PCL}}{\text{PBA}} = \frac{\left[I_{(\text{a}+\alpha+\text{C})} - 2 \times I_{(F)}/3\right]/2}{I_{(F)}/3} \tag{5}$$

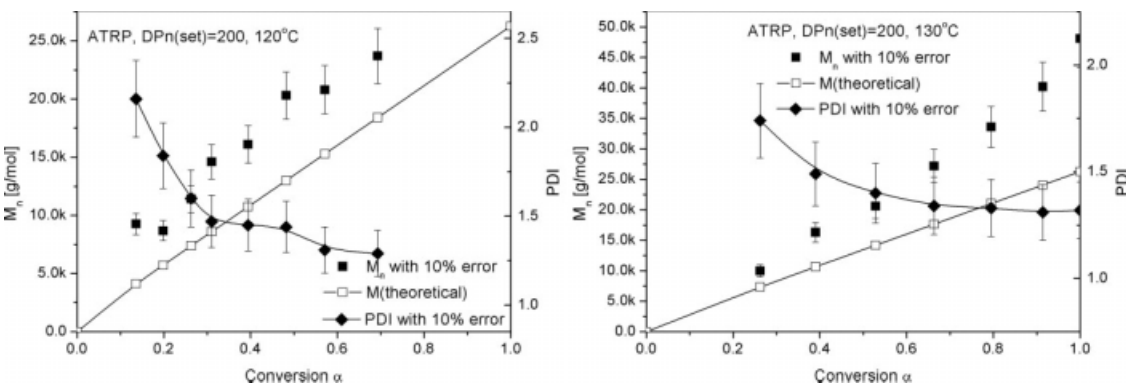
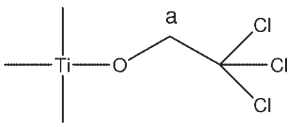
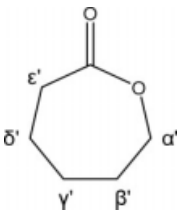
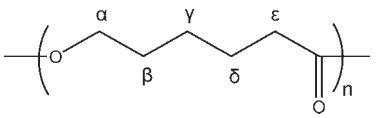
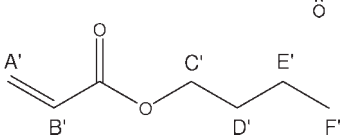
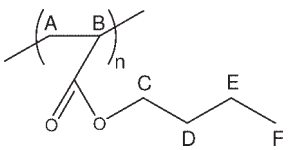


Figure 3 M_n and PDI as functions of the monomer conversion in ATRP.

TABLE I
Chemical Shifts of Different Protons in $Ti[OCH_2CCl_3]_4$, CL, PCL, BA, and PBA

Sample	δ (ppm)					
	a 4.2–5.5					
	α′ 4.2–4.3	β′ + γ′ + δ′ 1.65–1.95	ε′ 2.5–2.7			
	α 4.2–4.3	β + γ + δ 1.25–1.75	ε 2.2–2.4			
	A′ 5.75–5.85 6.35–6.45	B′ 6.05–6.2	C′ 4.1–4.2	D′ 1.6–1.7	E′ 1.3–1.5	F′ 0.9–1.0
	A + B + D + E 1.3–2.5	C 3.9–4.15	F 0.9–1.0			

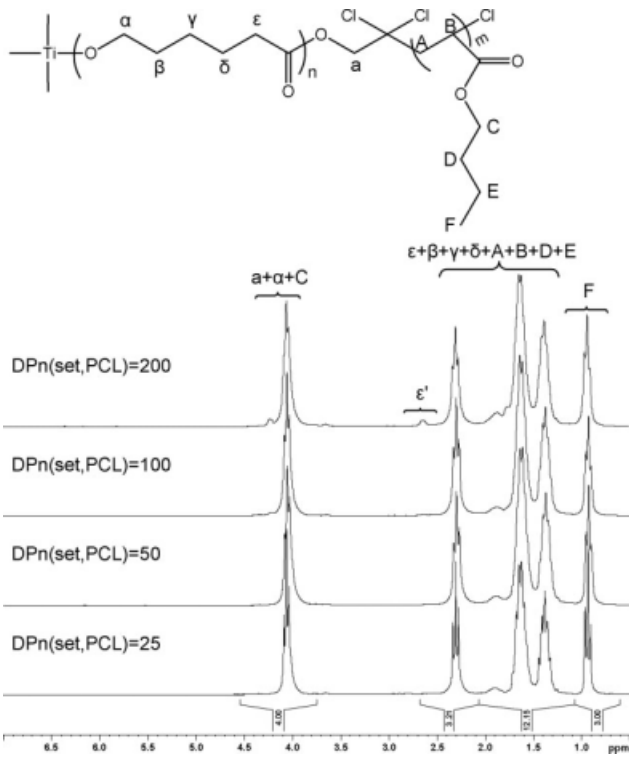


Figure 4 ^{1}H-NMR spectra of the PCL-*b*-PBA copolymers synthesized via the first-ROP-then-ATRP route.

where $I_{(a+\alpha+C)}$ and $I_{(F)}$ are the integrals of peaks a+α+C and F in Figure 4, respectively. In addition, peak a of $-CH_2CCl_3$ is very small, so the integral of peak a is negligible in comparison with peak α+C.

Figures 5 and 6 show the ^{1}H-NMR spectra of the PCL-*b*-PBA copolymers synthesized by the *in situ* ATRP and ROP route and the first-ATRP-then-ROP route, respectively.

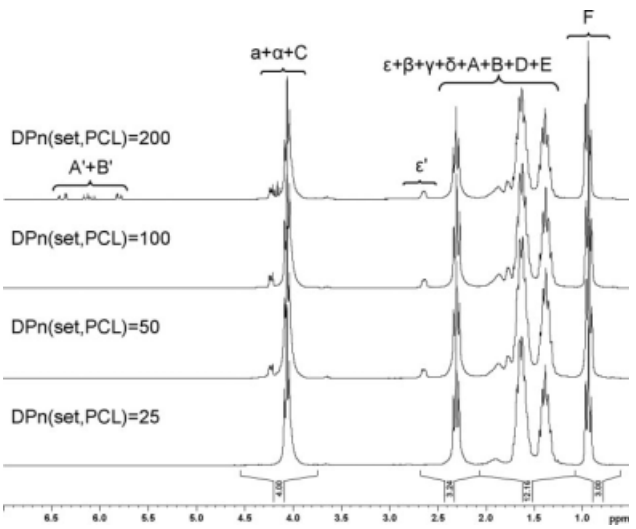


Figure 5 ^{1}H-NMR spectra of the PCL-*b*-PBA copolymers synthesized via simultaneous ATRP and ROP.

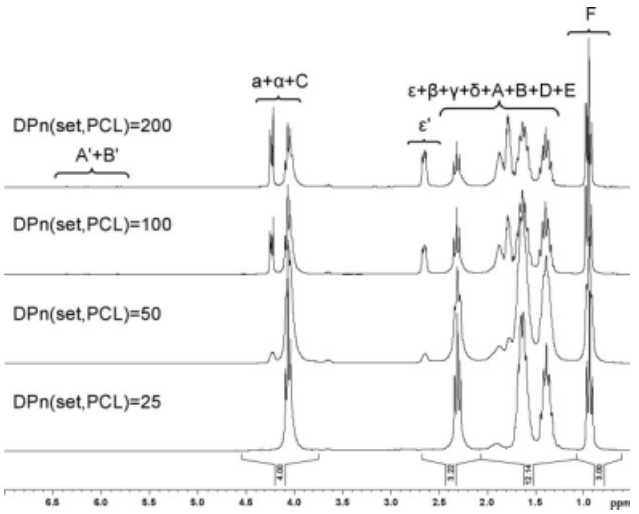


Figure 6 ^{1}H-NMR spectra of PCL-*b*-PBA copolymers synthesized via the first-ATRP-then-ROP route.

The molar fractions of the PCL and PBA segments determined by ^{1}H-NMR for those PCL-*b*-PBA copolymers are summarized in Table II.

The results in Table II demonstrate that the molar fraction of the PCL segment with respect to the PBA segment in the synthesized PCL-*b*-PBA copolymers decreased from 0.95 to 0.91 and from 0.95 to 0.90 when the polymerization degree of the PCL segment increased from 25 to 200 for the first-ROP-then-ATRP route and the *in situ* ATRP and ROP route, respectively; this is close to 1/1 mol/mol, the feeding ratio of the CL and BA monomers. However, the molar fraction of the PCL segment with respect to the PBA segment in the synthesized PCL-*b*-PBA copolymers decreased from 0.95 to 0.24 when the polymerization degree of the PCL segment increased from 25 to 200 for the first-ATRP-then-ROP route because when $Ti[OCH_2CCl_3]_4$-synthesized PBA was used as the macroinitiator for ROP of CL, the steric hindrance increased with the chain length of PBA increasing; this resulted in the reduction of the CL conversion and also the incorporation of the PCL segment into the copolymer.

SEC-evaluated molecular weight of the PCL-*b*-PBA copolymers synthesized via the first-ROP-then-ATRP route

Figure 7 shows the SEC traces of the PCL-*b*-PBA copolymers synthesized via the first-ROP-then-ATRP route. For each PCL-*b*-PBA copolymer, the SEC trace showed only one peak, and the peak shifted to a shorter elution time with the molecular weight increasing. In comparison with the SEC elution curve of the PCL macroinitiator [DPn(set) = 50], the peak of the PCL-*b*-PBA copolymer [DPn(set, PCL) = 50] shifted to a shorter elution time.

The SEC determined molecular weight are summarized in Table III, and M(theoretical) was calculated with eq. (6):

$$M(\text{theo}) = \text{DPn}(\text{set}, \text{PCL}) \times M(\text{CL}) + \text{DPn}(\text{set}, \text{PBA}) \times M(\text{BA}) + M(-\text{OCH}_2\text{CCl}_3) \quad (6)$$

where DPn(set, PCL) and DPn(set, PBA) are the polymerization degrees of PCL and PBA, respectively, and M(CL) is the molecular weight of CL.

The results in Table III demonstrate that there was a difference of around 10% between the theoretical and SEC-determined molecular weights. When SEC is used, the obtained molecular mass depends on the hydrodynamic volume, which is different between the copolymer and the homopolymer blend. Also, the composition distribution of the copolymer is not homogeneous, as in a random copolymer, and the refractive indices of the two components are not equal. Under these conditions, the results showed a disparity between the theoretical and SEC-determined molecular weights. Furthermore, the results demonstrated that with a PCL macroinitiator, at a high monomer conversion, the ATRP-synthesized PCL-*b*-PBA copolymer had a higher PDI than the copolymer from perfectly controlled ATRP.

In situ synthesized PCL-*b*-PBA copolymer in a PMMA matrix

As proven previously, three different routes can be applied to synthesize PCL-*b*-PBA copolymers

TABLE II
Conversions of CL and Molar Fractions of PCL and PBA Segments in PCL-*b*-PBA Copolymers Synthesized via Different Routes

	First-ROP-then-ATRP		*In situ* ATRP and ROP		First-ATRP-then-ROP	
DPn(set, PCL)	CL/BA (mol)	Conversion of CL (wt %)	CL/BA (mol)	Conversion of CL (wt %)	CL/BA (mol)	Conversion of CL (wt %)
25	0.95/1	98	0.95/1	98	0.95/1	98
50	0.95/1	98	0.94/1	93	0.94/1	93
100	0.93/1	97	0.90/1	91	0.62/1	67
200	0.91/1	94	0.90/1	90	0.24/1	30

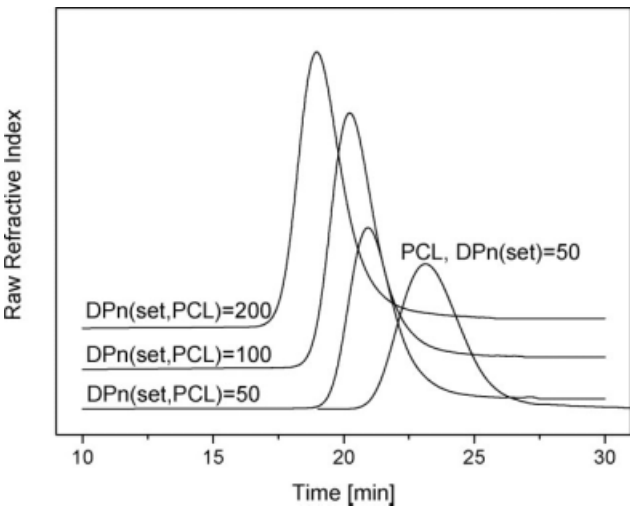


Figure 7 SEC traces of different PCL-*b*-PBA copolymers synthesized via the first-ROP-then-ATRP route (hydrolyzed).

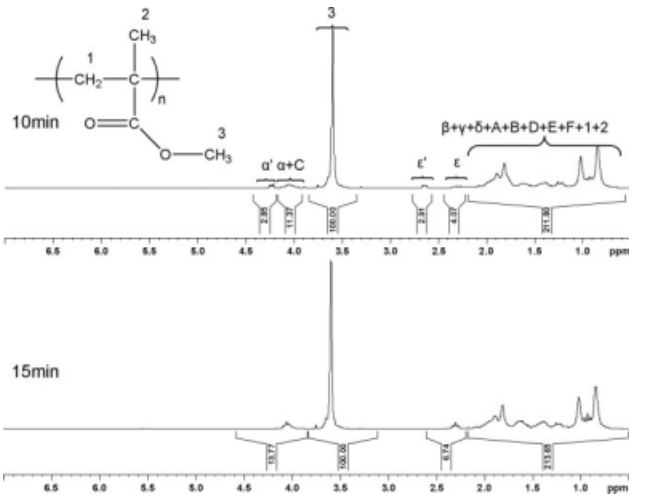


Figure 8 ^{1}H-NMR spectra of the *in situ* synthesized PCL-*b*-PBA copolymer in a PMMA matrix.

through the combination of ROP of CL and ATRP of BA. However, because the reaction time is very short in the extruder, whereas ATRP requires a long time to achieve a high monomer conversion, we applied route 3 to synthesize PCL-*b*-PBA copolymers in the extruder: with $Ti[OCH_2CCl_3]_4$-synthesized PBA as the macroinitiator, ROP of CL can achieve a high monomer conversion in a comparatively short period of time.

^{1}H-NMR spectra of the *in situ* synthesized PCL-*b*-PBA copolymer (1/1 mol/mol, 20 wt %) in a PMMA matrix are shown in Figure 8. For the sample collected at 10 min, the CL monomer was found, and the conversion of CL, calculated according to eq. (7), was 60 wt %. However, for the sample collected at 15 min, no CL monomer was found. In our previous experiment, we found that the residence time of reactive extrusion under the conditions of the synthesis of *in situ* crosslinked PCL/PBA networks (by ROP and classical radical polymerization) in a PMMA matrix was about 5 min, but the mixing in the twin-screw extruder was much better than that in the Haake Rheomix; therefore, further experiments should be performed to explore the possibility of the *in situ* synthesis of PCL-*b*-PBA copolymers in a thermoplastic matrix such as PMMA:

$$C = \left(1 - \frac{I_{(\alpha')}}{\left(I_{(\alpha')} + I_{(\alpha+C)}\right)/2}\right) \times 100\% \qquad (7)$$

where C is the conversion of CL and $I_{(\alpha')}$ and $I_{(\alpha+C)}$ are the integrals of peak α' and peak α+C, respectively.

CONCLUSIONS

The kinetic evaluation has demonstrated that in the $Ti[OCH_2CCl_3]_4$-initiated ATRP of BA, the initiation is slow in comparison with the initiation in ideal ATRP. However, the SEC-determined molecular weight and PDI of PBA indicate that to some extent, controllability can be achieved in the $Ti[OCH_2CCl_3]_4$-initiated ATRP of BA. Then, with $Ti[OCH_2CCl_3]_4$ as a difunctional initiator, ROP of CL and ATRP of BA were combined to synthesize PCL-*b*-PBA copolymers. With different sequential combinations of ROP and ATRP, three routes for synthesizing PCL-*b*-PBA copolymers—first-ROP-then-ATRP, *in situ* ROP and ATRP, and first-ATRP-then-ROP—were examined. A comparison of the PCL-*b*-PBA copolymers obtained with these three routes has demonstrated that the first-ROP-then-ATRP route is the most efficient, and it is followed by the *in situ* ATRP and ROP route and

TABLE III
SEC-Determined Molecular Weights of PCL-*b*-PBA Copolymers Synthesized by the First-ROP-Then-ATRP Route (Hydrolyzed Samples)

DPn(set, PCL)	Theoretical M_n (g/mol)	M_w (g/mol)	M_n (g/mol)	M_w/M_n
50	12,300	15,000	11,000	1.36
100	24,400	28,000	21,000	1.34
200	48,600	63,000	52,000	1.21

the first-ATRP-then-ROP route. For the synthesis of PCL-*b*-PBA copolymers, the route selection will depend on the production method; for example, with reactive extrusion, a PBA macroinitiator should be adopted because the reaction time is very short, whereas the *in situ* ATRP and ROP route might be used if the reaction will be carried out in a batch reactor. In addition, with PBA synthesized by $Ti[OCH_2CCl_3]_4$-initiated ATRP as the macroinitiator for ROP of CL, a PCL-*b*-PBA copolymer with a polymerization degree of 50 for PCL and PBA segments was *in situ* synthesized in a PMMA matrix in a Haake Rheomix. Furthermore, a crosslinked nodule based on this PCL-*b*-PBA copolymer with a controlled chain length was obtained by the addition of a small portion of the divinyl monomer when the polymerization ended.

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