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ORIGINAL PAPER

ABA_2-type triblock copolymer composed of PCL and PSt: synthesis and characterization

Bao Zhang · Yapeng Li · Wei Wang · Jingyuan Wang · Xuesi Chen

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Abstract ABA_2-type (Y-shaped) triblock copolymer made from poly(ε-caprolactone) (PCL) and polystyrene were synthesized by the combination of enzymatic ring-opening polymerization (eROP) and atom transfer radical polymerization (ATRP). First, CCl_3-terminated PCL were synthesized by eROP of ε-caprolactone in the presence of initiator 2,2,2-trichloroethanol and biocatalyst Novozyme 435, followed by the esterification of the resulting PCL with 2,2-dichloro acetyl chloride to obtain trifunctional macroinitiator. The well-defined Y-shaped block copolymer was then synthesized by ATRP of styrene. The systems display characteristics of a living radical polymerization as indicated by linear first-order kinetics, linearly increasing molecular weight with conversion, and low polydispersities. The macromolecular structures and composition were characterized by HNMR, GPC, and FTIR. The thermal properties were characterized by differential scanning calorimetry.

Keywords Atom transfer radical polymerization (ATRP) · Enzyme · Ring-opening polymerization · Y-shape

B. Zhang · Y. Li (✉) · J. Wang
Alan G. MacDiarmid Institute, Jilin University, Changchun 130023, People's Republic of China
e-mail: liyapeng@jlu.edu.cn

B. Zhang · Y. Li · W. Wang · X. Chen (✉)
State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, People's Republic of China
e-mail: xschen@ciac.jl.cn

Introduction

Nonlinear block copolymers have attracted the interest of polymer scientists because of their unique rheological and mechanical properties and a significantly high degree of functionality as compared to their linear analogs with a similar molar mass [1–3]. A typical example of a nonlinear block copolymer is the Y-shaped block copolymer, which is the regular graft copolymer with perfectly and regularly spaced grafting points, and the grafts have the same size. The synthesis of Y-shaped copolymers is largely described in the literature, generally by the combination of different polymerization techniques [4, 5]. Especially, the combination of the ATRP and other methods has been used widely because ATRP is one of the most used techniques for synthesizing polymers with well-defined structures because it does not require stringent reaction conditions and have a high level of control over chain length and distributions [6–9].

Enzymes, harvested from living organisms, are finding increasing use as catalysts for polymer synthesis in vitro. The "green" biocatalyst enzyme has many special properties such as its nontoxicity, recyclability (enatio-, regio-, and chemo-), selectivity, biocompatibility, and ability to operate under mild conditions, are active in bulk reaction, organic media and at various interfaces [10, 11]. Moreover, features of enzymes can carry out novel polymerization reaction to prepare useful polymers which are often difficult synthesized by conventional polymerization [12]. However, enzymatic polymerization methods are difficult to synthesize functional polymers containing special groups due to the fact that a tedious synthesis process of functional monomers is necessary. Thus, the full exploitation of biocatalysis in polymer synthesis will require the development of mutually compatible chemo and biocatalytic methods.

Recently, research has been reported on the combination of biocatalytic polymerization and ATRP to synthesize block copolymers. For instance, Heise et al. [13] reported the first example of the chemoenzymatic synthesis of AB-type diblock copolymer PCL-*b*-PSt by combining eROP of CL and ATRP of St. The groups also made use of this method to synthesize the triblock copolymer PSt-*b*-PCL-*b*-PSt [14], functional amphiphilic epoxy-based diblock copolymer polyc-aprolactone-*block*-poly(glycidyl methacrylate) [15], and symmetric quintuplet pentablock copolymers PSt-*b*-PCL-*b*-PEO-*b*-PCL-*b*-PSt [16]. More recently, the group has made great progress in the synthesis of nonlinear block copolymers with this method, including AB_2-shape and B_2AB_2-shape block copolymers [17–19]. However, this chemoenzymatic method has not been employed in the synthesis of ABA_2 (Y-shaped) triblock copolymers, which has been one of the challenges in polymer science.

In this article, the authors investigate the chemoenzymatic synthesis of ABA_2-type triblock copolymer. The goal of this study was to provide a novel route to synthesize nonlinear multiblock copolymer. To the best of the knowledge, this was the first report to synthesize ABA_2-type block copolymer by the combination of eROP and ATRP. The method is general and can be extended to produce a large variety of nonlinear block copolymers. In future study, the plan is to extend the

synthetic methods to prepare well-defined functional block copolymers and study their application in biological and drug delivery.

Experiment section

Materials

Novozyme 435 (activity approximately 7000 PLU/g) was provided by Novozymes (Denmark). ε-CL were obtained from Aldrich Chemical Co. and distilled over calcium hydride (CaH_2) under vacuum before use. CuCl (Beijing Chemical Co.) was purified by precipitation from acetic acid to remove Cu^{2+}, filtrated and washed with ethanol and then dried. 2,2′-Bipyridine (Beijing Chemical Co.) was used without further purification. Styrene (Beijing Chemical Co.) was distilled over CaH_2 under reduced pressure prior to use. Toluene (Tianjin Chemical Co.) and dichloromethane (Tianjin Chemical Co.) were dried with CaH_2 and distilled. Triethylamine (Beijing Chemical Co.) was refluxed for 12 h in the presence of CaH_2 and distilled under vacuum. 2.2.2-trichloroethanol and 2,2-dichloro acetyl chloride (DCAC, 99%) were purchased from Aldrich Chemical Co. without further purification. All the reagents used in this study were of analytic grade.

Analytical methods

The monomer conversion was determined gravimetrically. ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker ARX-500 NMR spectrometer with $CDCl_3$ as solvent at 500 and 125 MHz, respectively. Chemical shifts (ppm) were reported downfield from 0.00 ppm with trimethylsilane (TMS) as internal standard. The molecular weights and molecular weight distributions were measured on a Waters 410 Gel permeation chromatography (GPC) apparatus equipped with a 10-μm Styragel HT6E column (300 mm × 7.8 mm) with linear polystyrene standards (range of molecular weight: 4,000–300,000). Tetrahydrofuran (THF) was used as the eluent at a flow rate of 1 mL/min. The infrared spectra (IR) of polymers were recorded on a NICOLET Impact 410 at room temperature. Dried samples (20 mg) were mixed with 100 mg of dry KBr and pressed into disk (100 kg cm^{-2}). Differential scanning calorimetry (DSC) was carried out on a DSC-7 (Perkin-Elmer) to study the thermal properties of the polymers at a heating and cooling rate of 10 °C/min under a nitrogen flow of 200 mL/min. A polymer (about 3.0 mg) was loaded in a cell, and the heat exchange was recorded during the heating and cooling cycles.

TCE-initiated eROP of ε-CL

The eROP was carried out according to the report described previously [20]. Novozyme-435 (0.216 g) was introduced into oven-dried reaction vial under an argon atmosphere. Toluene (4.3 mL), monomer ε-CL (2 mL, 1.89×10^{-2} mol) and initiator TCE (0.14 mL, 6.34×10^{-4} mol) were transferred into the reaction vial via gastight syringe. The vial was then placed into an oil bath (70 °C) under stirring

for 4 h. The product was purified and dried. The yield was 95%. $M_{n,NMR} = 3200$, $M_{n,GPC} = 11600$, $M_w/M_n = 1.27$. ^{1}H NMR ($CDCl_3$, δ): 4.75 (*t*, CCl_3–CH_2–O–), 4.1 (m, CH_2O in PCL), 3.65 (*t*, terminal CH_2O in PCL), 2.30 (m, $COCH_2$ in PCL), 1.6 (m, CH_2 in PCL), 1.4 (m, CH_2 in PCL).

Preparation of macroinitiator

Chlorine-terminated PCL (0.96 g, 3×10^{-4} mol) was dissolved in 10 mL of dry dichloromethane and then cooled in an ice bath (0 °C). To this solution was added 1 mL (7.2×10^{-3} mol) of triethylamine. After 5 min of stirring, 10 mL of a dichloromethane containing DCAC (0.6 mL, 6.2×10^{-3} mol) was added dropwise to the solution over a period of 1 h. The reaction was carried out at 0 °C for 2 h and then at room temperature for 22 h. The solution was filtrated to remove the quaternary ammonium halide $(CH_3CH_2)_3NH^+Cl^-$. The filtrate was concentrated and then precipitated in methanol. The yield is 85%. $M_{n,GPC} = 11700$, $M_w/M_n = 1.21$. ^{1}H NMR ($CDCl_3$, δ): 5.95 (s, Cl_2HCCO), 4.75 (*t*, CCl_3–CH_2–O–), 4.1 (m, CH_2O in PCL), 2.30 (m, $COCH_2$ in PCL), 1.6 (m, CH_2 in PCL), 1.4 (m, CH_2 in PCL).

Synthesis of Y-shaped triblock copolymers

The ATRP of styrene was carried out according to the report described previously [20]. CuCl (0.03 g, 3×10^{-4} mol), bpy (0.14 g, 9×10^{-4} mol), and macroinitiator (0.2 g, 6×10^{-5} mol) were added into a flask. Pre-degassed solvent toluene (7.2 mL) and monomer styrene (7.2 g, 7.2×10^{-2} mol) by argon were introduced into the flask via an Ar-washed syringe. Subsequently, the reaction flask was immersed in a constant temperature (120 °C) oil bath for the given time. Aliquots (about 0.6 mL of the reaction mixture) were removed from the reaction mixture at selected time intervals to monitor the reaction progress. The GPC data are listed in Table 1. ^{1}H NMR ($CDCl_3$, δ): 6.3–7.0 (m, aromatic protons), 4.1 (m, CH_2O in PCL), 2.30 (m, $COCH_2$ in PCL), 1.6 (m, CH_2 in PCL), 1.4 (m, CH_2 in PCL).

Hydrolysis of the block copolymer PSt-*b*-PCL-*b*-$(PSt)_2$

The triblock copolymer was hydrolyzed by dissolving the block copolymer in a 10 mL mixture of 1,4-dioxane/hydrochloric acid (37%; 20:1 v/v). The mixture was then stirred for 48 h at 85 °C. After hydrolysis, the solvents were removed under vacuum, and the crude product was precipitated in cold methanol.

Result and discussion

TCE-initiated eROP of ε–CL

The eROP of ε-CL was performed according to the report described previously [20]. The control of the PCL structure strongly depends on the frequency of the side

Table 1 Results of PCL, Macroinitiator and block copolymers

PCL	$[M]_0/[I]_0$	Carboxyl terminal[a] chains (mol %)	Monomer[b] conversion	$M^{c}_{n,th}$ (g/mol)	$M^{a}_{n.NMR}$ (g/mol)	EI[d]	$M^{e}_{n,GPC}$ (g/mol)	M_w/M^{e}_n
1	30/1	<2%	90%	3200	11400	28%	11600	1.27
Macroinitiator		The degree of end functionalization (mol%)			$M^{e}_{n,GPC}$ (g/mol)			M_w/M^{e}_n
2		>98%			124000			1.29

Copolymer	$[M]_0/[I]_0$	Time (min)	Monomer[b] conversion (%)	$M_{n,th}$ [c] (g/mol)	$M^{a}_{n,NMR}$ (g/mol)	$M^{e}_{n,GPC}$ (g/mol)	M_w/M^{e}_n
1	1200/1	120	10.0	23000	22200	15989	1.39
2	1200/1	210	20.0	34000	33000	18840	1.36
3	1200/1	330	26.0	40600	38700	20825	1.38
4	1200/1	480	31.0	46100	49100	22400	1.39
5	1200/1	660	42.3	58200	59300	24900	1.42
6	1200/1	900	56.8	73600	76200	30000	1.44

[a] Determined by ^{1}H NMR analysis

[b] The conversion was determined gravimetrically

[c] The theoretical molecular weights ($M_{n,th}$) calculated from the ratio of the monomer to the initiator $[M]_0/[I]_0$ and the monomer conversion. $M_{n,th} = ([M]_0/[I]_0) \times M_{monomer} \times \text{concentration}\% + M_{n(macro)initiator}$ (1)

[d] EI represents the efficiency of initiator, $EI = M_{n,th}/M_{n,NMR}$

[e] Determined by GPC measurements

reactions caused by the water reactivity. Because water is used as an acyl acceptor, and it not only induces nucleophilic attack but also causes hydrolysis. Both reactions will broaden the molecular weight distribution and alter the composition of groups at the PCL chain ends. So the water concentration in the reaction medium has to be reduced as much as possible in order to obtain a high yield of initiator-functionalized PCL.

The ^{1}H NMR spectrum of the TCE-initiated PCL 1 (Table 1) was shown in Fig. 1a. The multiplet signals, centered at 1.4, 1.6, 2.3, and 4.1 ppm, are assigned to the PCL main chain protons. The triplet signal *a* at 3.65 ppm corresponds to the methylene protons attached to the terminal hydroxyl group. It is significant that the characteristic signal *g* of the initiator segment (CCl_3–CH_2–O–) at the end of the PCL chains can be observed clearly at 4.75 ppm. Moreover, the ratio of integrated areas of peaks *a* and *g* is 1.12:1.00, which clarifies introduction of the initiator TCE at the polymer terminal and a lower amount of carboxylic acid end groups in the polymer (10.7%) at comparable monomer conversion (95%).

Trifunctional initiator was synthesized by the esterification of TCE-terminated polyester with DCAC (Scheme 1). In order to avoid the cleavage of the polymer chains, the reaction was carried out at 0 °C in dried CH_2Cl_2 in the presence of TEA. The catalyst TEA can absorb HCl from the solution to generate a precipitate of quaternary ammonium halide $(CH_3CH_2)_3NH^+Cl^-$, which benefited the

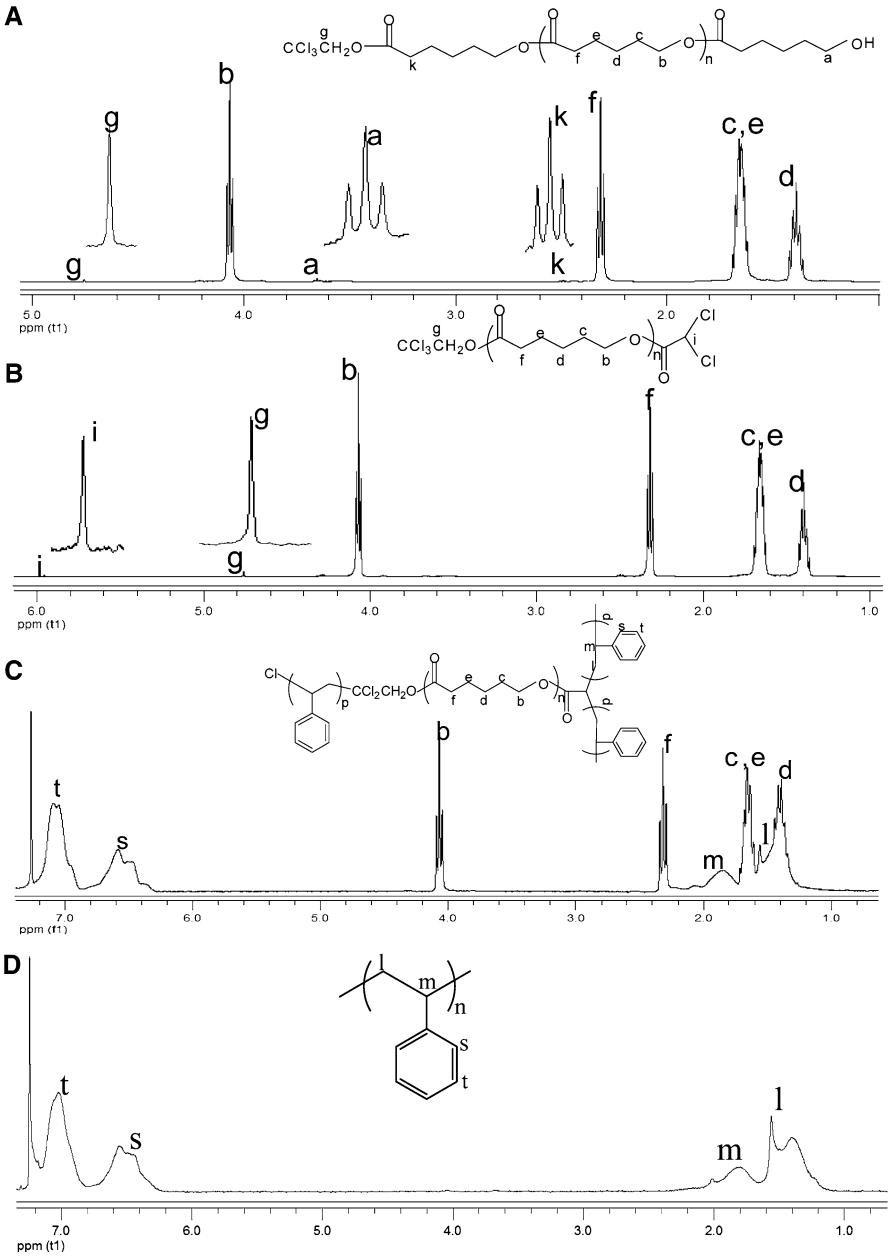
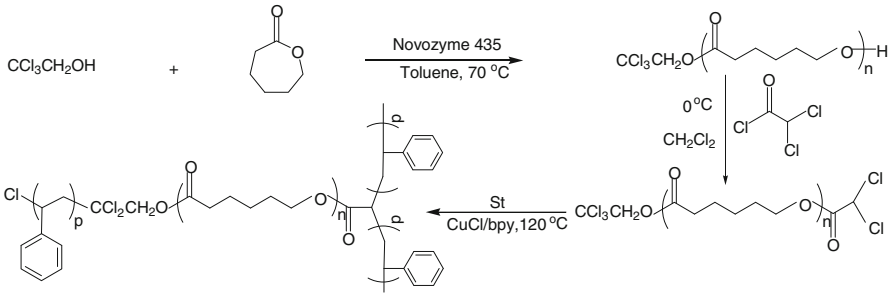


Fig. 1 ^{1}H-NMR spectrum of PCL-CCl_3 1 (**a**), macroinitiator 2 (**b**), and Y-shaped block copolymer PSt-*b*-PCL-*b*-$(PSt)_2$ (**c**), and the product PSt obtained after hydrolysis (**d**)

esterification. The chemical structure of the macroinitiator was further characterized by ^{1}H NMR (Fig. 1b). A new signal **h** at 5.95 ppm was assigned to the >CH– protons close to the active chloride. The existence of the signal **i** revealed that the



Scheme 1 Synthesis of the Y-shape block copolymer

esterification didn't interfere with the terminal TCE group. The results proved that the DCAC groups were attached to the PCL chain ends.

Halogenated alkanes, such as R–CCl_3/R–CBr_3 derivatives, have been employed successfully as initiating species in the ATRP of styrene and (meth)acrylates [21–23]. No evidence suggesting double or triple initiation at the CCl_3 terminus was observed in previous studies of –CCl_3 macroinitiator, it is implicitly accepted that the terminal groups are single initiator units, as proved by unimodal and symmetrical GPC traces of the resulting block copolymers [22]. Thus, the group carried out the ATRP of St from the –CCl_3 terminated PCL using CuCl/bpy as the catalyst system and toluene as the solvent, respectively, at 120 °C according to Scheme 1.

The ATRP of St from the trifunctional initiator was carried out in toluene at 120 °C using CuCl/bpy as the catalyst system. The basic elementary reactions in atom transfer radical polymerization (ATRP) are initiation, activation, deactivation, propagation, chain termination, and transfer to small molecule. At high temperatures (110 °C and higher), styrene thermal initiation may also become significant [24]. However, the effect of thermal initiation can generally be neglected in the presence of high-initiator concentrations. Pascual et al. [25] concluded that thermal initiation of styrene at 130 °C was negligible in the presence of 0.02 mol/L of initiator (1-phenylethyl chloride). In the system, to confirm that the polymerization of styrene was a living process, its reaction kinetics was investigated in detail. Figure 2 plots the time dependence of $\ln([M]_0/[M]_t)$. The linear relationship indicates that the polymerization is first order with respect to monomer concentration, and that the number of active species remains constant throughout the reaction. The GPC-determined number average molecular weight (M_n), GPC-light scattering determined number average molecular weight ($M_{n,\mathrm{ls}}$), theoretical molecular weight ($M_{n,\mathrm{th}}$), and polydispersity index (M_w/M_n) versus monomer conversion are depicted in Fig. 3. M_n increases linearly with conversion while the polydispersity index varies only a few degrees and relatively low (<1.50). $M_{n,\mathrm{ls}}$ and $M_{n,\mathrm{NMR}}$ values were in good correspondence with $M_{n,\mathrm{th}}$ values. The molecular weights increased from a starting value, which corresponded to the initial molecular weight of the trifunctional macroinitiator. The linear relationship implies that the trifunctional initiator does indeed initiate the controlled radical polymerization of St.

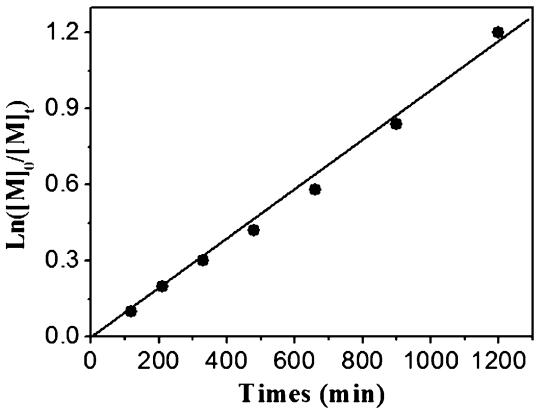


Fig. 2 $\ln([M]_0/[M]_t)$ versus time for ATRP of St initiated by PCL macroinitiator. $[M]_0$ and $[M]_t$ represent the initial monomer concentration and the monomer concentration after time t, respectively

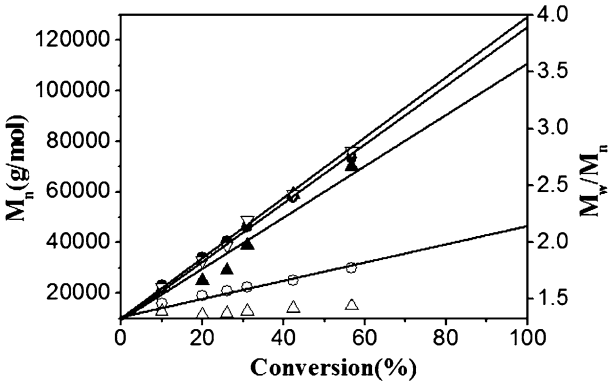


Fig. 3 Dependence of $M_{n,NMR}$ (*open inverted triangle*), $M_{n,th}$ (*filled circle*), $M_{n,ls}$ (*filled triangle*), M_n (*open circle*), and polydispersity index (*open square*) on monomer conversion for ATRP of St initiated by PCL macroinitiator

The kinetic behavior of ATRP proves that polymerization of St is a 'living'/controlled radical process and the thermal initiation can be neglected.

The ^{1}H-NMR spectrum of the Y-shaped block copolymer was shown in Fig. 1c. It is seen that besides the dominant PCL signals, the occurrence of the signals at 6.3–7.3 ppm corresponding to aromatic protons *s* and *t* of the PSt block shows that new well-defined PSt segments are connected with PCL.

The reaction process was monitored by GPC analysis (Fig. 4). The peaks are monomodal, yet have some tailing to lower molecular weights, as is often observed in polymers made by ATRP because of radical–radical termination. The GPC curves shifted left with the monomer conversion, indicating a gradual increase in the molecular weight.

Figure 5 shows the FTIR spectra of the CCl_3–PCL 1, macroinitiator 2, and Y-shaped block copolymer 3. For CCl_3–PCL 1 (Fig. 5a), the characteristic absorption bands appeared in the wavenumber region of 1732 cm^{-1} assigned to the ester carbonyl group of the PCL main chains. In the IR spectra (Fig. 5b), the

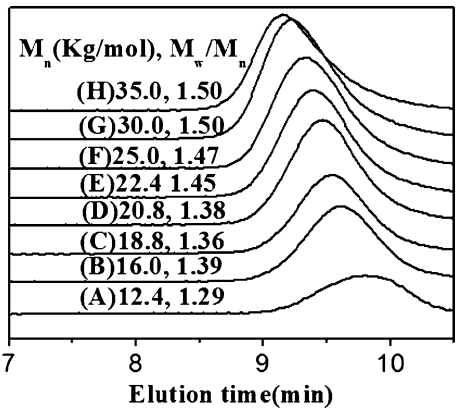


Fig. 4 GPC traces of *a* CCl_3-PCL, *b* macroinitiator, and *c–g* PSt-*b*-PCL-*b*-$(PSt)_2$ Y-shaped triblock copolymer at different conversions: *c* 10%, *d* 20%, *e* 26%, *f* 31%, *g* 42.3%, *h* 56.8%. M_n and polydispersities were determined by GPC calibrated with PSt

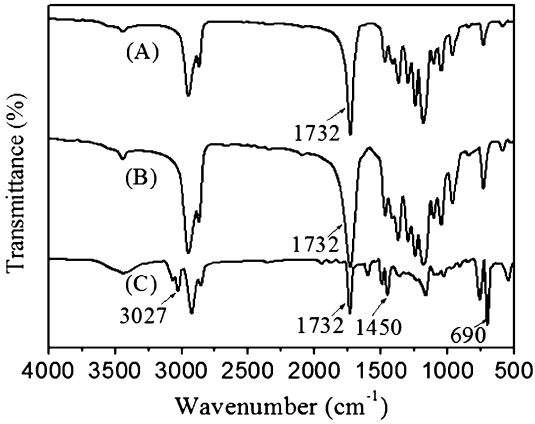


Fig. 5 IR spectra of *a* PCL-CCl_3, *b* macroinitiator, and *c* Y-shaped triblock copolymer PSt-*b*-PCL-*b*-$(PSt)_2$ 3

absorption peak did not show obvious change due to the consistence of the water. After ATRP of St from macroinitiator (Fig. 5c), the main absorption of PCL peaks still remained in the spectrum of block copolymer. Also, the new peaks at the wavenumbers of about 3027, 1450, and 690 cm^{-1} were ascribed to the ring vibration of the aromatic group of PSt. The variance of the IR spectroscopic results confirmed the formation of the PSt block.

In order to demonstrate further the structure of the Y-shaped triblock copolymer, the PSt-*b*-PCL-*b*-$(PSt)_2$ product **5** was dissolved in 1,4-dioxane and hydrolyzed with aqueous hydrochloric acid solution to remove the polyester block. The elimination of PCL from the block copolymer via hydrolysis was confirmed by ^{1}H NMR and GPC analysis. The ^{1}H NMR peaks at 1.40, 1.65, 2.30, and 4.05 ppm assigned to the PCL block (Fig. 1a) were absent in the spectrum of the hydrolyzed product (Fig. 1d). The GPC traces before and after hydrolysis are presented in Fig. 6. It was observed that hydrolysis led to a significant shift of the peak to lower M_n with a low polydispersity. More importantly, there is only one peak in GPC curves, which indicated that the initiation groups of initiator have similar initiation efficiency for

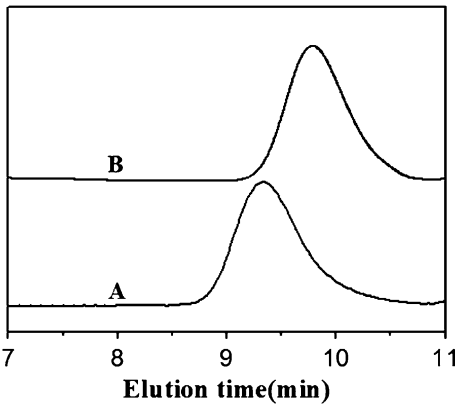


Fig. 6 GPC traces of (*a*) copolymers **5** (2.5×10^4 g/mol, 1.42) and (*b*) its subsequent hydrolysate PSt (1.3×10^4 g/mol, 1.36)

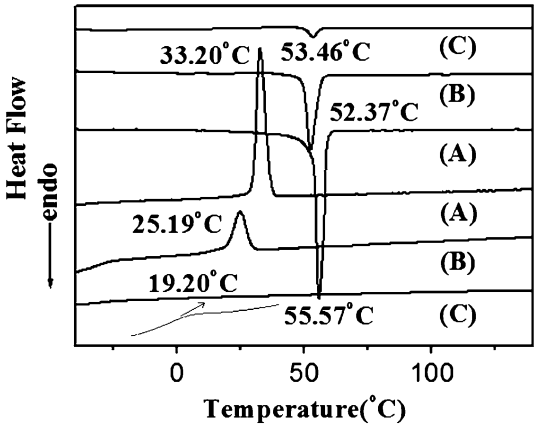


Fig. 7 DSC curves of the second heating and subsequent cooling for (*a*) PCL-CCl_3, and Y-shaped block copolymers PSt-*b*-PCL-*b*-$(PSt)_2$ (*b*) **1**, *c* **3**

the PSt. It also explained that why the polymerization is first-order with respect to monomer concentration.

DSC analysis was performed in a range from −50 to 160 °C. To minimize the effect of recrystallization from the solution, two thermal scans were collected for each sample. The evaluation of thermal properties was performed on the second thermal scan. The crystallinity of the block copolymer is attributed to the PCL block. PCL homopolymer shows a single melting peak $T_m = 55.57$ °C and a single crystallization peak $T_c = 33.20$ °C, respectively. However, PSt is an amorphous material, which does not shows any crystallization temperature. Figure 7 shows the DSC thermograms for the PCL homopolymer and for the block copolymer. The introduction of PSt segments changed T_c gradually from 33.20 to 19.20 °C. The melting enthalpy (ΔH_m) reflects the amount of crystallinity developed in each sample. The results were shown in Table 2. The melting temperature (T_m) of the PCL block in copolymer decreased in comparison with that of PCL; however, the melting temperature varied only a few degrees, from 55.57 to 53.46 °C.

Table 2 DSC results for PCL and copolymers PSt-*b*-PCL-*b*-$(PSt)_2$

Sample	T_c (°C)	T_m (°C)	(ΔH_m) (J g^{-1})	X_c (%)[a]
PCL	33.20	55.57	66.35	49.00
Copolymer 1	25.19	52.37	31.49	23.00
Copolymer 3	19.20	53.46	0.98	0.73

[a] $X_c = (\Delta H_m/\Delta H_m^*) \times 100\%$

Conclusion

Well-defined Y-shaped triblock copolymer PSt-*b*-PCL-*b*-$(PSt)_2$ has been successfully synthesized. The synthetic approach combines eROP of ε-CL and ATRP of styrene. The trifunctional macroinitiator $(Cl)_2$-PCL-CCl_3 effectively initiated ATRP of St with CuCl/bpy as the catalyst system. The kinetics analysis of the block copolymerization indicated a living/controlled process. Fine-tuning of the molecular parameters, that is, composition and low polydispersity, is effective with such a procedure. The structures and composition of the block copolymer have been well-characterized by means of NMR, IR, and GPC measurements. In addition, the analysis of the hydrolysate from the copolymer proved further the presence of a block copolymer structure. The thermal properties of the copolymer were investigated by DSC. The advantage of this strategy is that it can be easily extended to other monomers, which makes it very useful in preparation of nonlinear block copolymers difficult to get by other methods.

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