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Chemoenzymatic synthesis of Y-shaped diblock copolymer

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Abstract Y-shaped diblock copolymer polycaprolactone-*block*-(polystyrene)$_2$ [PCL-*b*-(PSt)$_2$] was synthesized successfully by the combination of enzymatic ring-opening polymerization (eROP) and atom transfer radical polymerization (ATRP). CH_3O-terminated PCL was synthesized firstly by eROP of ε-caprolactone (ε-CL) in the presence of biocatalyst Novozyme 435 and initiator CH_3OH, subsequently the resulting PCL was converted to macroinitiator by the esterification of it with 2,2-dichloro acetyl chloride (DCAC). PCL-*b*-(PSt)$_2$ diblock copolymers were synthesized in an ATRP of the styrene with CuCl/2,2′-bipyridine as the catalyst system. The kinetic analysis of ATRP indicated a controlled/'living' radical polymerization. The structure and composition of obtained polymers were characterized with NMR, GPC and FTIR. The thermal behavior was characterized by differential scanning calorimetry (DSC).

Keywords Atom transfer radical polymerization (ATRP) · Enzymatic polymerization · Ring-opening polymerization · Y-shaped block copolymers

Introduction

Star-shaped polymers has been received great interest since Schaefgen and Flory first proposed this concept in 1948 [1] because of its unique properties such as impact-resistant plastics, different phase behavior, thermoplastic elastomers, variety of morphologies, polymeric emulsifiers, sol–gel states, and gas permeation

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membranes[2]. Y-shaped block copolymer is a type of star-shaped polymer, which is typically synthesized by living anionic polymerization, [3–5] cationic polymerization [6] and controlled/'living' radical polymerization[7]. Teyssié et al. [8] firstly reported the synthesis of Y-shaped block copolymers. PS-$(PEO)_2$ was obtained by end-capping a living polystyryl carbanion by a naphthalene derivative followed by polymerization of ethylene oxide using naphthalene sodium radical ion as the initiator. However, the synthesis of block copolymers is particularly suited to investigate the combination of fundamentally different synthetic techniques. Because various combinatorial approaches enables those polymers obtained from different types of polymerizations. The new polymers obtained can have variable compositions and architectures, thus they may have astonishing properties [9–11]. Many groups investigated the synthesis of Y-shaped block copolymers by the combination of different modes of polymerizations [12–16].

For instance, Hizal et al. [12] synthesized an ABC-type miktoarm star polymer using a core-out method via a combination of ROP, SFRP and ATRP. Gnanou et al. [13] prepared AA'_2-type asymmetric star and AB_2-type miktoarm star polymers by the combination of ATRP and chemical modification of the termini of ATRP-derived polymers. Armes et al. [14] synthesized two bifunctional ATRP macroinitiators via Michael addition, followed by the synthesis of Y-shaped block copolymers from these macroinitiators by polymerizing various hydrophilic methacrylic monomers via ATRP. Shortly after, a series of well-defined Y-shaped (AB_2-type) zwitterionic block copolymers were synthesized by Armes with the same method [15]. Dumas et al. [16] synthesized well-defined $(PCL)_2$-arm-PtBuMA and $(PCL)_2$-arm-PS star block copolymers from a heterotrifunctional initiator bearing two hydroxyl groups able to initiate ROP of ε-CL [with $AlEt_3$ or $Sn(Oct)_2$ as coinitiator] and a bromide function group able to initiate ATRP of tBuMA or styrene.

The enzymatic polymerization in vitro is evaluated as a new, environmental friendly methodology in polymer science. "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 [17, 18]. Moreover, enzymatic polymerization can prepare useful polymers which are often difficult to be synthesized by conventional polymerization. Consequently, the above merits of biocatalytic polymerizations motivated more researchers to study the chemoenzyme-catalyzed route to block copolymer synthesis.

Heise et al. [19–22] first made use of this strategy to carry out the consecutive/one-step cascade/simultaneous synthesis of the diblock copolymer from a dual-initiator, which contained a primary alcohol and single α-bromoester. Our group also demonstrated the feasibility of 2,2,2-trichloroethanol as another novel dual-initiator, [23, 24] which permits a sequential two-step synthesis combining eROP and ATRP. In addition, our group introduced another synthetic technique. It usually requires an intermediate transformation step to convert the end group of the PCL into an active initiating site for the polymerization of the second monomer [25–28]. It has also been employed successfully in the preparation of block copolymers, where the esterification of the end hydroxyl groups of preformed polyester PCL

from eROP of ε-CL with halogenated acyl halide proved to be an excellent method for producing macroinitiators suitable for the block-ATRP of styrene.

In this work, we reported the synthesis of Y-shaped block copolymer by the combination of eROP and ATRP. The kinetic analysis of ATRP indicated a controlled/'living' radical polymerization. The structure and composition of obtained polymers were characterized with NMR, GPC and FTIR. The thermal behavior was investigated by differential scanning calorimetry (DSC). We believe that Y-shaped block copolymers will exhibit peculiarity in morphology and have important applications in the fields such as controlled drug delivery, advanced materials.

Experimental

Materials

CH_3OH was refluxed for 6 h in the presence of magnesium which was activated by iodine and distilled**.** Novozyme-435 (activity approximately 7,000 PLU/g) was a gift from Novo Nordisk A/S and employed without further purification. 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. 2,2-dichloro acetyl chloride (DCAC, 99%) was purchased from Aldrich Chemical Co. Styrene (Beijing Chemical Co.) was distilled over CaH_2 under reduced pressure. 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. All the reagents used in this study were of analytic grade.

Synthesis of CH_3O-terminated polyester (CH_3O-PCL)

Novozyme-435 (0.216 g, 10% w/w of the monomer weight), dried in a desiccator with P_2O_5 as desiccant under vacuum (0.1 mmHg, 25 °C, 24 h), was transferred into an oven-dried 50 ml reaction vial under dry argon atmosphere, and the vial was immediately sealed with a rubber septum. The monomer ε-CL (2.156 g, 1.89×10^{-2} mol), solvent toluene (4.3 mL, twice v/w of the monomer weight), and initiator CH_3OH (0.025 mL, 6.3×10^{-4} mol) were transferred into the reaction vial via a gastight syringe under argon. The vial was then placed into a constant temperature (70 °C) oil bath with magnetic stirring for 4 h. The reaction was terminated by pouring excess cold chloroform into the reactants and the enzyme was removed via filtration. The filtrate was concentrated by rotary evaporation. The crude products was precipitated in methanol and dried in a vacuum oven. The yield is 90%. $M_{n.\mathrm{NMR}} = 5{,}500$, $M_{n,\mathrm{GPC}} = 10{,}200$, $M_w/M_n = 1.24$. ^{1}H-NMR ($CDCl_3$, δ): 4.1 (m, CH_2O in PCL), 3.65 (t, terminal CH_2O in PCL), 3.67 (s, CH_3O in methanol), 2.30 (m, $COCH_2$ in PCL), 1.6 (m, CH_2 in PCL), 1.4 (m, CH_2 in PCL).

Synthesis of macroinitiator [CH_3O-PCL$(Cl)_2$]

The resulting PCL (1 g, 1.8×10^{-4} mol) was dissolved in 5 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, 5 mL of a dichloromethane containing 0.6 ml of 2,2-DCAC (0.92 g, 6×10^{-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 80%. $M_{n,GPC} = 11{,}700$, $M_w/M_n = 1.21$. ^{1}H-NMR ($CDCl_3$, δ): 5.95 (s, Cl_2HCCO), 4.28 (t, terminal CH_2O in PCL), 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 diblock copolymers [PCL-*b*-$(PSt)_2$]

A dry flask equipped with a magnetic stirrer was charged with CuCl (0.018 g, 1.8×10^{-4} mol), bpy (0.084 g, 5.4×10^{-4} mol), and macroinitiator (0.2 g, 3.6×10^{-5} mol). The reaction vial was sealed and degassed three times by freeze-pump-thaw cycles. Solvent toluene (2 mL) and monomer styrene (2 g, 2×10^{-2} mol) degassed by inert dry argon were introduced into the flask via an Ar-washed syringe. After PCL macroinitiator was completely dissolved, the reaction flask was placed into a constant temperature (120 °C) oil bath with magnetic stirring for a predetermined time. Aliquots (about 0.8 mL of reaction mixture) were removed from the reaction mixture at selected time intervals to monitor the reaction progress. The reaction was rapidly terminated in an ice bath. The catalyst was removed by passage of the polymer solution through an aluminum oxide column. The crude polymer was precipitated in methanol, and then dried under vacuum overnight. 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), 0.90–2.18 (m, CH and CH_2 in PSt), 1.6 (m, CH_2 in PCL), 1.4 (m, CH_2 in PCL).

Characterization

The monomer conversion was determined gravimetrically. ^{1}H 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 × 7.8 mm) with linear polystyrene standards. 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

Table 1 Results for PCL, macroinitiator and block copolymers

PCL	$[M]_0/[I]_0$	Carboxyl terminal[a] chains (mol%)	Monomer[b] conversion	$M_{n,th}^{c}$ (g/mol)	$M_{n.nmr}^{d}$ (g/mol)	EI[d]	$M_{n,GPC}^{e}$ (g/mol)	M_w/M_n^{e}
1	30/1	<2%	90%	3,100	5,500	56%	1,0,200	1.24

Macroinitiator	The degree of end functionalization (mol%)	$M_{n,GPC}^{e}$ (g/mol)	M_w/M_n^{e}
2	>98%	11,700	1.21

Copolymer	$[M]_0/[I]_0$	Time (min)	Monomer[b] conversion (%)	$M_{n,th}^{c}$ (g/mol)	$M_{n.nmr}^{a}$ (g/mol)	$M_{n,GPC}^{e}$ (g/mol)	M_w/M_n^{e}
3	720/1	180	15.2	17,900	17,500	16,400	1.25
4	720/1	270	22.1	23,600	22,400	18,800	1.21
5	720/1	360	27.3	27,800	28,050	20,800	1.20
6	720/1	480	33.1	32,600	33,000	22,300	1.19
7	720/1	600	40.2	38,300	38,000	25,000	1.19
8	720/1	780	46.3	43,200	44,300	27,200	1.15
9	720/1	1,200	66.7	59,600	58,700	37,600	1.29

[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 $M_{n,th} = \left([M]_0/[I]_0\right) \times M_{monomer} \times \text{concentration}\% + M_n(\text{macro})\text{initiator}$

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

[e] Determined by GPC measurements

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.

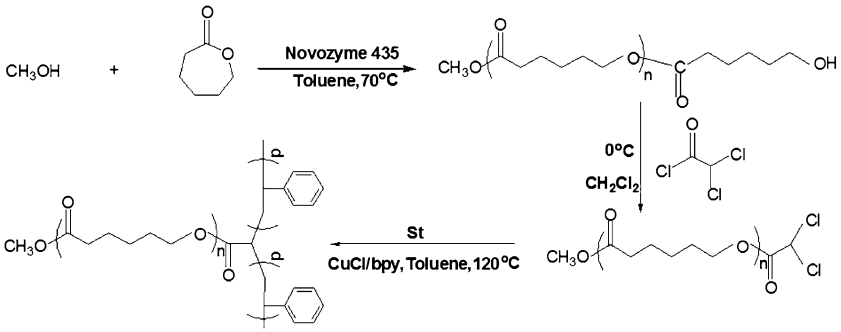
Results and discussions

Synthesis of CH_3O-terminated polyester

The methanol-initiated eROP of lactones was investigated in previous reports [29]. Lipase porcine pancreatic lipase (PPL) and lipase PS 30 (pseudomonas, Ceracia lipase) were used as biocatalysts; their poor catalytic activity enabled the preparation of low-molecular-weight oligomers with a rather long polymerization time (about several weeks). Therefore, our group has made use of the more active biocatalyst Novozyme 435 (lipase CALB immobilized on an acrylic resin) to carry out eROP of ε-CL at 70 °C in toluene (twice w/v of monomer) where methanol was used as the initiator. The general synthetic route used for the preparation of the Y-shaped block copolymers is shown in Scheme 1.

Control of the PCL structure (polydispersity, end-group structure, and molecular weight) strongly depends on the frequency of the side reactions caused by the water reactivity because of competitive initiation reactions between water and initiator CH_3OH. Water is used as an acyl acceptor, and it cannot only induce the nucleophilic initiation but also cause the hydrolysis. Both of the reactions will broaden the molecular weight distribution and result in the polyester chains terminated with a carboxylic acid groups other than the initiator segment. So it is crucial to dry the reaction components as much as possible to minimize the water initiation.

Figure 1a shows the ^{1}H-NMR spectrum of CH_3O-PCL **1**. The multiplet signals, centered at 1.4, 1.6, 2.3, and 4.1 ppm, represented the PCL main chain protons, the triplet signal **a** at 3.65 ppm corresponded to the methylene protons of the terminal hydroxyl groups. The characteristic signals **g** of the initiator segment (CH_3O–) at the end of the chain could be pointed out at 3.67 ppm, which clarified methanol initiated successfully eROP of ε-CL. Also, if a fraction of the PCL chains were



Scheme 1 Synthesis route of the Y-shape block copolymer

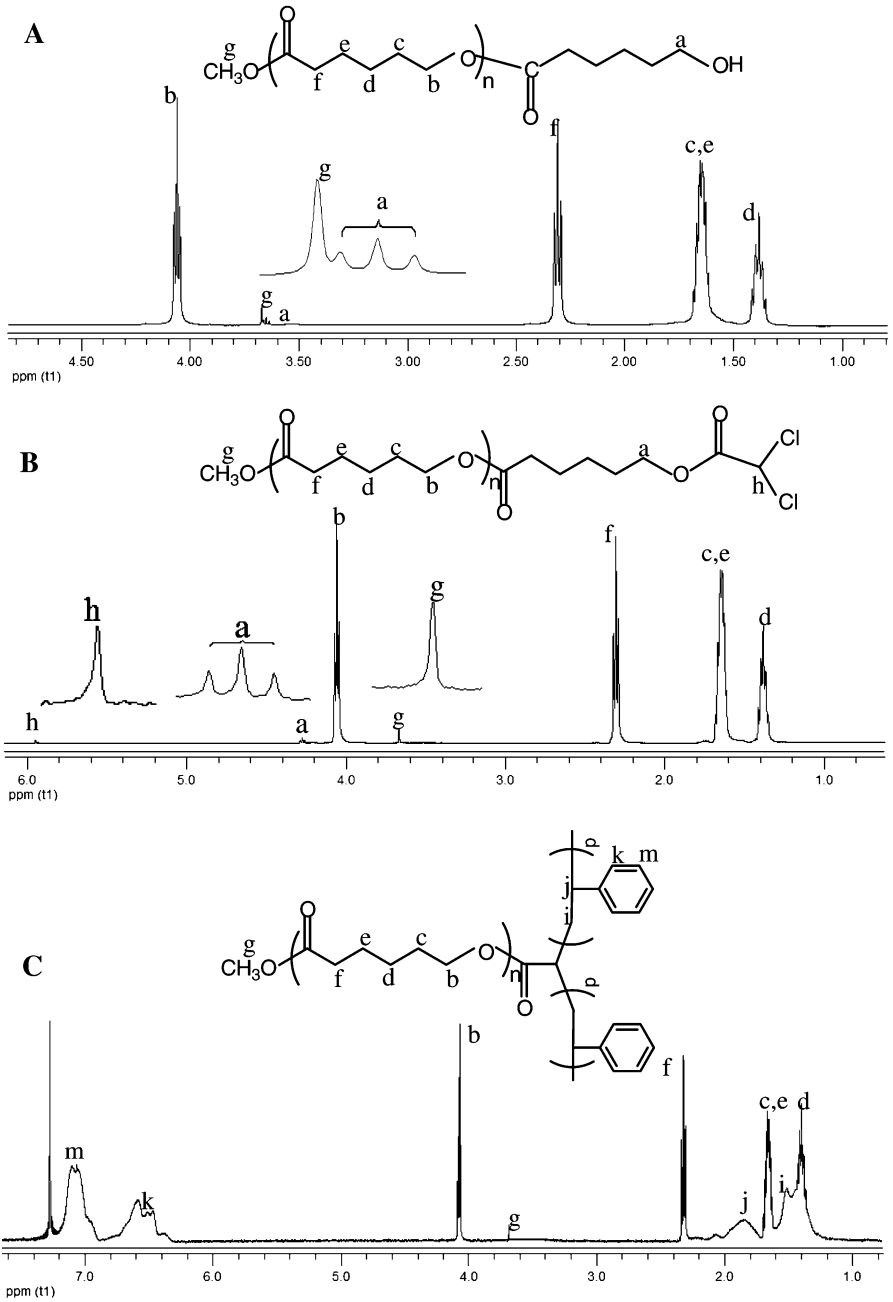


Fig. 1 ^{1}H-NMR spectrum of PCL 1 (**a**) macroinitiator 2 (**b**) and Y-shaped PCL-*b*-$(PSt)_2$ 3 (**c**) were recorded at room temperature in $CDCl_3$

initiated by water, it would result in terminal carboxyl acid groups, thus, the methylene protons linked to it should appear in the region of about 2.4 ppm. The absence of any resonance at 2.4 ppm in Fig. 1a suggested that the initiation of the PCL chains was carried out quantitatively by methanol, and the amount of water-initiated PCL could reduce to less than 2% (the limitation of detection by NMR analysis). Combining GPC analysis, it was clear that the $M_{n,\mathrm{th}}$ 1 (3,100 g/mol) was lower than those (10,200 g/mol) obtained by GPC. The discrepancy could mainly be resulted from the GPC technique underestimating M_n because of different hydrodynamic volumes of the PCL and the linear polystyrene standards. The $M_{n.\mathrm{nmr}}$ determined by ^{1}H-NMR was higher than the expected molecular weight ($M_{n.\mathrm{th}}$) of PCL **1** (Table 1), which was possibly caused by the low efficiency of initiation (about 56%) of the methanol due to the partial volatilization of the initiator at the initial stage of the reaction at 70 °C.

Synthesis of macroinitiator

The macroinitiator **2** was prepared by an esterification reaction between terminal OH group of the resulting PCL **1** and 2,2-DCAC. During the process, triethylamine was used as the catalyst and absorbed HCl from the solution to generate a precipitate of quaternary ammonium halide $(CH_3CH_2)_3NH^+Cl^-$, which benefited the esterification. The structure of macroinitiator is determined by ^{1}H-NMR. Due to the ester formation, the methylene protons **a** experienced a shift from 3.65 to 4.28 ppm. The new signal **h** at 5.95 ppm assigned to the >CH– protons close to the active chloride (Fig. 1b), which indicated that the 2,2-dichloro acetyl group was attached to the PCL chain end. The existence of the signal **g** revealed that the esterification didn't interfere with the terminal CH_3O– group. Based on the above result, it was obvious that the macroinitiator had been prepared. The peak area ratio of **a** and **g** is 1:1, which confirmed the complete substitution of the terminal hydroxyl groups. As shown in Table 1, it was noted that the polydispersity after the esterification reaction was lower than those of the starting PCL, whereas number average molecular weight (M_n) was slightly higher. This could be due to inevitable fractionation of macroinitiator during the course of precipitation after esterification.

Synthesis of Y-shaped block copolymer

The ATRP of St from macroinitiator **2** was carried out in toluene at 120 °C with CuCl/bpy as the catalyst system. GPC-determined M_n, theoretical molecular weight ($M_{n,\mathrm{th}}$), and polydispersity index (M_w/M_n) versus monomer conversion for ATRP are shown in Fig. 2. M_n increased linearly with conversion while the polydispersity index varied only a few degrees and was relatively low (<1.30). The $M_{n,\mathrm{th}}$ values were higher than the experimental ones (M_n), which resulted from the GPC technique underestimating M_n because of different hydrodynamic volumes of the copolymers and the linear polystyrene standards. Figure 3 shows the time dependence of $\ln([M]_0/[M]_t)$. The linear relationship indicated that the polymerization was first-order with respect to monomer concentration, and the number of active species remained constant throughout the course of reaction. The kinetic

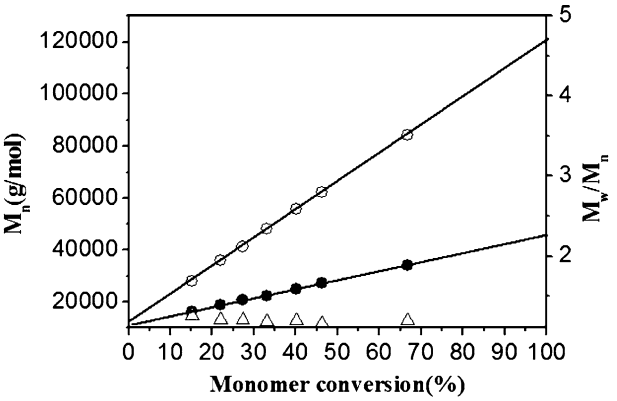


Fig. 2 Dependence of $M_{n,\mathrm{th}}$ (*open circle*), M_n (*filled circle*) and polydispersity index (*triangle*)on monomer conversion for ATRP of St initiated by PCL macroinitiator (I) [St]:[I]:[CuCl]:[bpy] = 720:1:5:15, reaction temperature: 120 °C. M_n and polydispersity were determined by GPC calibrated with polystyrene. The theoretical molecular weights ($M_{n,\mathrm{th}}$) were calculated from Eq. 1 (Table 1)

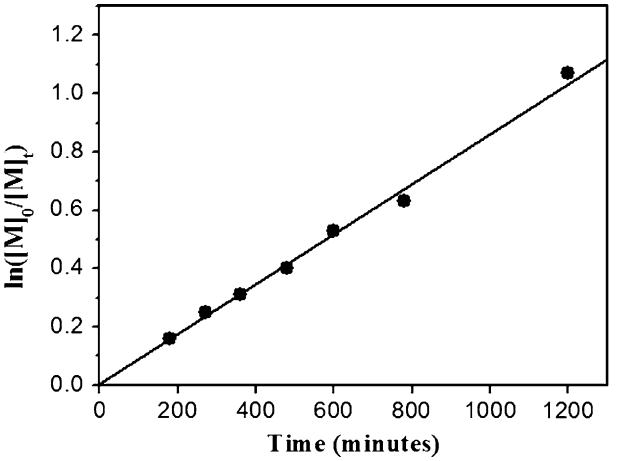


Fig. 3 $\ln([M]_0/[M]_t)$ versus time for ATRP of St initiated by PCL macroinitiator. $[M]_0$ and $[M]_t$ represent the initial monomer concentration and the monomer concentration after time t, respectively

behavior of ATRP proves that polymerization of St is a 'living'/controlled radical process.

From the ^{1}H-NMR spectra of the Y-shaped diblock copolymer **3** [PCL-*b*-$(PSt)_2$] (Fig. 1C), we could see that besides the dominant PCL signals b–f, the occurrence of the signals at 6.5–7.0 ppm were due to aromatic protons **D** and **E** of the PSt block. The GPC traces of the starting PCL **1**, macroinitiator **2** and the final block copolymer **3** were present in Fig. 4. It was clear that the ATRP of styrene using macroinitiator **2** resulted in an increase in molecular weight. The unimodal and symmetrical shape on the GPC plot of the block copolymer suggested the absence of a homopolymer composed of either styrene or ε-CL and the complete initiation of

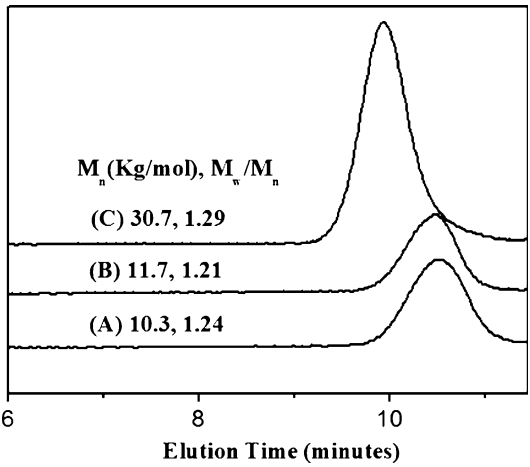


Fig. 4 GPC traces of PCL 1 (M_n = 10,200 g/mol, polydispersity = 1.24), macroinitiator 2 (11,700 g/mol, 1.21) and Y-shaped diblock copolymer (30,700 g/mol, 1.29). The molecular weight and polydispersity were determined by GPC calibrated with PSt

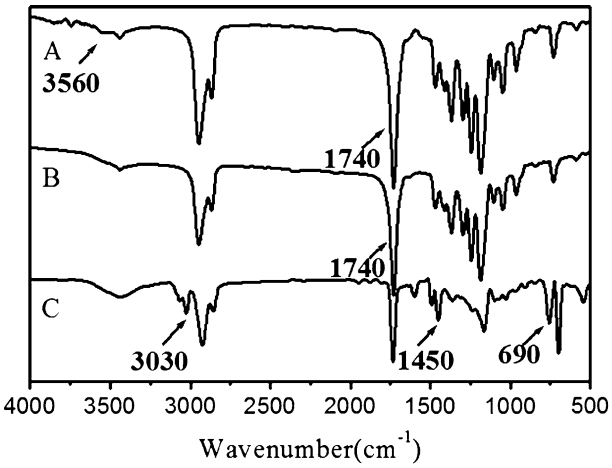


Fig. 5 IR spectra of PCL 1 *A* macroinitiator 2 *B* and Y-shaped block copolymer PCL-*b*-$(PSt)_2$ 3 *C*

the macroinitiator during the ATRP process. Combing the GPC analysis and ^{1}H-NMR results indicated the formation of the Y-shaped block copolymer [PCL-*b*-$(PSt)_2$].

Figure 5 shows the FTIR spectra of the obtained polymers. For PCL, the characteristic absorption bands appeared in the wave number region of 1,740 cm^{-1} assigned to the ester carbonyl group of the PCL main chains. Compared with PCL, PCL-*b*-$(PSt)_2$ copolymers showed the new peaks at the wave numbers of approximately 3,030, 1,450, and 690 cm^{-1}, which 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.

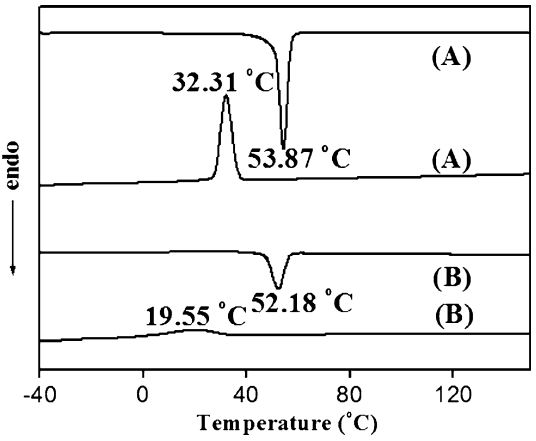


Fig. 6 DSC thermogram of the PCL homopolymer *A* and the block copolymer PCL-*b*-$(PSt)_2$ 3 *B*

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

Sample	T_c (°C)	T_m (°C)	(ΔH_m) (J g^{-1})	X_c (%)[a]
PCL 1	32.31	53.87	67.86	50.3
Copolymer 3	19.55	52.18	27.26	20.2

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

DSC was carried out to investigate the melting and crystallization behaviors of the Y-shaped block copolymers. DSC analysis was performed in a range from −50 to 160 °C at a rate of 10 °C/min under nitrogen. To minimize the effect of recrystallization from the solution, the evaluation of thermal properties was performed on the second thermal scan. Figure 6 shows a single melting peak and a single crystallization peak of PCL homopolymer (A) at $T_m = 53.87$ °C and $T_c = 32.31$ °C, respectively. Since PSt is an amorphous material (without any crystallinity), the crystallinity of the block copolymers were attributed to the PCL block. Obviously, the introduction of PSt segments changed T_c gradually from 32.31 to 19.55 °C. The melting enthalpy (ΔH_m) reflects the amount of crystallinity developed in each sample. The degree of crystallinity (X_c) was determined by the equation $X_c = (\Delta H_m/\Delta H_m^*) \times 100\%$, where ΔH_m is the heat of enthalpy of polymer and ΔH_m^* is the theoretical heat of enthalpy of PCL at 100% crystallinity (135 J g^{-1}). The X_c values in the polymers declined gradually from 50.3 to 20.2% with increasing PSt content. As shown in Table 2, the lower T_c and X_c values of copolymer could be attributed to the crystalline imperfections because the introduction of PSt segments rendered crystallization more difficult. The melting temperature (T_m) of the PCL block in copolymer decreased in comparison with that of PCL; however, T_m varied little, from 53.87 to 52.18 °C. The DSC results indicated the difference in the thermal properties between PCL and copolymers, which confirmed the formation of PSt blocks from PCL block.

Conclusions

The eROP and ATRP was combined to synthesize the Y-shaped block copolymer. The ATRP macroiniitiator effectively initiated ATRP of styrene with CuCl/2,2′-bipyridine as the catalyst system. Linear first-order kinetics, linearly increasing molecular weight with conversion, and low polydispersities (<1.29) were observed in this process. The structures and composition of the Y-shaped copolymer were well characterized by means of NMR, IR and GPC measurement. DSC analysis showed that the crystallinity of the copolymer decreased with the introduction of the PSt block. Chemoenzymatic synthesis of Y-shaped block copolymer is a novel technique, which not only allows the variation of the polymer composition by adjusting the ratios between the macroinitiator and monomer, but also can control the structure of polymer exactly. In addition, the research for the morphology of Y-shaped block copolymers is in progress.

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