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Block and star block copolymers by mechanism transformation. VIII Synthesis and characterization of triblock poly(LLA-*b*-St-*b*-MMA) by combination of ATRP and ROP

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Abstract

Block copolymers, poly(LLA-*b*-St)s and triblock copolymes, poly(LLA-*b*-St-*b*-MMA)s have been synthesized by the combination of the atom transfer radical polymerization (ATRP) with ring-opening polymerization (ROP) using bifunctional initiator β-hydroxylethyl α-bromoisobutyrate (HEBIB) without intermediate function transformation. The molecular weight (MW) and the molecular weight distribution (MWD) can be controlled. The structures of the copolymers were confirmed by ^{1}H NMR spectroscopy and GPC.

Keywords: Atom transfer radical polymerization; Block copolymer; Bifunctional initiator

1. Introduction

It is well-known that the segregation of different polymer blocks in the block copolymer will form ordered structures at the microscope [1–3]. Diblock copolymers consist of two chemically dissimilar polymer chains, and will be segregated, resulted in different morphologies depending on the chain length of two blocks.

In comparison with diblock copolymers, linear triblock ABC copolymers have more independent parameters on their phase behavior, such as two volume fractions, three segmental interaction parameters and three possible sequences of blocks, thus displaying a variety of different morphologies [4]. Therefore, more triblock ABC copolymers have been synthesized and studied extensively in the last two decades [5–15].

Traditionally, block copolymers are synthesized by the sequential living polymerizations of different monomers in the same polymerization system [16–19] or by coupling reaction of the preformed functional polymers [20]. To prepare well-defined triblock copolymers with narrow polydispersity index (PDI), living anionic polymerization is usually used [8,21–23], but the monomers used in the anionic polymerization are limited.

The recent development of 'living'/controlled radical polymerizations has opened a new route to synthesize polymers with well-defined structures [24–29]. Among them, atom transfer radical polymerization (ATRP) has been well-studied because it is not only fit for a variety of monomers [30–32], but also one of most effective methods to prepare precise block copolymers by the sequential polymerization of different monomers [33–36]. By combining ATRP with other 'living' polymerizations, such as anionic [37–39], cationic [40,41] and cationic ring-opening [42–45] polymerizations, many novel copolymers have been obtained.

Because the hydroxyl group is compatible with the ATRP of vinyl monomers, some initiators with terminal hydroxyl group were designed and used to prepare block copolymers without the intermediate transformation step. For example, Hawker and his co-workers prepared diblock and triblock copolymers using CBr_3CH_2OH as initiator and aluminum compound as catalyst [46–49]. Our research group synthesized diblock copolymer, poly(1,3-dioxepane-*b*-styrene) [P(DOP-*b*-St)] with β-hydroxylethyl α-bromobutyrate (HEBB) as initiator [50]. Heise's research group coupled enzymatic ring-opening polymerization (ROP)

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with ATRP to prepare the diblock copolymer poly(caprolactone-*b*-St) [51].

Here, we report the preparation of triblock copolymer, poly(L-lactide-*b*-St-*b*-methyl methacrylate) [P(LLA-*b*-St-*b*-MMA)] by combination of ATRP and ROP, the aim of the research is to study their self-assembly behavior. To our knowledge, it is the first time to synthesize a triblock copolymer with such structure. In this article, the hydroxyl-terminated diblock copolymer HOPSt-PMMA was prepared by the sequential polymerization in ATRP system, and then the diblock copolymer was used as macroinitiator to initiate the polymerization of LLA with the stannous 2-ethyl-hexanoate [$Sn(OCt)_2$] as catalyst.

2. Experimental section

2.1. Materials

Methyl methacrylate (MMA), and styrene (St) were stirred over CaH_2 overnight and distilled before use. CuBr and CuCl (Shanghai Chemical Reagent Plant, analytical grade, 98%) were purified by stirring in glacial acetic acid, washed with ethanol, and then dried in a vacuum oven at 70 °C. 2,2′-Bipyridine (bpy, Aldrich, 99%) was recrystallized from *n*-hexane. The LLA (Aldrich, 98%) was recrystallized from ethyl acetate two times, and then dried under vacuum (0.1 mmHg) at room temperature for 48 h. Stannous 2-ethyl-hexanoate ($Sn(OCt)_2$, Aldrich, 95%), 1,1,4,7,10,10-hexamethyltriethylenetetraamine (HMTETA) (Aldrich, 98%) and α-bromoisobutyric acid (Aldrich, 98%) were used as received. Other reagents were purified according to standard methods. The initiator, β-hydroxylethyl α-bromoisobutyrate (HEBIB) was synthesized according to our previous published method [50]. ^{1}H NMR (500 MHz, $CDCl_3$) δ (TMS, ppm):1.50 (s, 6H, $C(Br)(CH_3)_2$); 4.28 (t, 2H, $COOCH_2$); 3.85 (m, 2H, $-CH_2OH$); 2.59 (s, 1H, $-CH_2OH$).

2.2. Characterization

^{1}H NMR spectra were recorded on a Bruker DMX-500 NMR spectrometer; $CDCl_3$ as solvent and tetramethylsilane (TMS) as the internal standard. The molecular weight (MW) and molecular weight distribution (MWD) were determined on a Waters-150C gel permeation chromatograph equipped with microstyragel columns (500, 10^3 and 10^4 Å) at 30 °C with a flow rate of 1.0 ml/min. THF was used as solvent. Narrow polydispersity polystyrenes were used in the calculation of MW.

2.3. Bulk ATRP of St initiated by HEBIB/CuBr/bpy

Hydroxyl-terminated polystyrene, HOPStBr, was prepared by the bulk ATRP of St with HEBIBas initiator, and CuBr/bpy as catalyst/ligand. The typical procedure is as follows:

A glass tube with a magnetic stirrer was charged with HEBIB (105.5 mg, 0.5 mmol), CuBr (72 mg, 0.5 mmol) and bpy (234.3 mg, 1.5 mmol). Then 10.4 g of St (0.1 mole) was added, the system was degassed with three freeze–pump–thaw cycles. The polymerization tube was sealed under vacuum, and placed into an oil bath thermostated at 110 °C with stirring. After polymerization for a prescribed time, the mixture was cooled down to 0 °C, and the tube was opened. Conversion was determined by ^{1}H NMR and gravimetric methods; both gave the similar results. The mixture was diluted by THF and passed through a short column of neutral alumina to remove the metal salt. After precipitation by adding polymer solution in THF into methanol, the HOPStBr was collected by filtration and dried under vacuum at 40 °C overnight.

2.4. Preparation of block copolymer poly(LLA-b-St)

The diblock copolymer was synthesized using PSt capped with hydroxyl group, HOPStBr as macroinitiator, and $Sn(OCt)_2$ as catalyst, the typical polymerization procedure is as follows.

Into a 5 ml dry glass tube equipped with a magnetic stirrer, 0.5 g HOPStBr (0.05 mmol, sample 3 in Table 1), 0.65 g LLA (4.5 mmol) and 1 ml dry toluene were added, the tube was connected to a Schlenkline, then an exhausting-refilling process was operated three times. The tube was put into an oil bath at 115 °C with stirring for 10 min. $Sn(OCt)_2$ (6 mg) in 0.5 ml dry toluene was added into the mixture, and the exhausting-refilling process was carried out again to remove the toluene. The tube was put into an oil bath thermostated at 115 °C for 24 h, and then cooled down to room temperature rapidly. After precipitation by adding polymer solution in CH_2Cl_2 into methanol, the product was collected by filtration, and dried in a vacuum oven at 40 °C overnight. The monomer conversion was determined gravimetrically.

Table 1
Results and conditions of ATRP of St by HEBIB/CuBr/bpy

No.	Time (h)	Conversion[a] (%)	M_n			M_w/M_n[b]
			GPC[b]	NMR[c]	th[d]	
1	2	34	7500	7200	7300	1.15
2	2.5	42	8800	8000	8900	1.13
3	3.5	51	10,400	9700	10,800	1.14
4	5	64	12,600	12,800	13,500	1.19

The polymerization was carried out at 110 °C, $[St]_0/[HEBIB]_0/[CuBr]_0/[bpy]_0 = 200{:}1{:}1{:}3$ (molar ratio).

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

[b] Measured by GPC.

[c] Calculated by Eq. (1).

[d] The M_n(th) were calculated according to: $M_n(\text{th}) = ([M]_0/[I]_0) \times \text{conversion} \times 104 + 211$ where $[M]_0$ and $[I]_0$ are initial concentrations of St and HEBIB, 104 and 211 are the molar masses of St and HEBIB.

2.5. Preparation of block copolymer HOPSt-b-PMMA

A typical block copolymerization was as follows. Into a 10 ml glass tube equipped with a magnetic stirrer, HOPStBr (1 g, 0.125 mmol), CuCl (12.5 mg, 0.125 mmol), bpy (59 mg, 0.375 mmol) and 5 ml MMA solution in toluene (4 M) were added. The system was sealed under vacuum after three freeze–pump–thaw cycles, and put into an oil bath kept at 85 °C. After a prescribed time, the polymerization was quenched by putting the tube into an ice–water bath. Conversion was calculated by ^{1}H NMR and gravimetric methods. The mixture was dissolved in THF and passed through a short column of neutral alumina for removing the copper salt. After precipitation by adding polymer solution in THF into methanol, the HOPSt-*b*-PMMA was collected by filtration and dried in a vacuum oven at 40 °C overnight.

2.6. Ring-opening polymerization of LLA with HOPSt-b-PMMA as macroinitiator

The triblock copolymer poly(LLA-*b*-St-*b*-MMA) was prepared by ROP of LLA with HOPSt-*b*-PMMA as macroinitiator and Sn(Oct)$_2$ as catalyst. The copolymerization procedure is similar to the preparation of diblock copolymer, P(LLA-*b*-St).

3. Results and discussions

3.1. Bulk ATRP of St initiated by HEBIB/CuBr/bpy

The synthetic procedures of hydroxyl-terminated PSt, diblock copolymer, P(LLA-*b*-St) and triblock copolymer, P(LLA-*b*-St-*b*-MMA) are shown in Scheme 1.

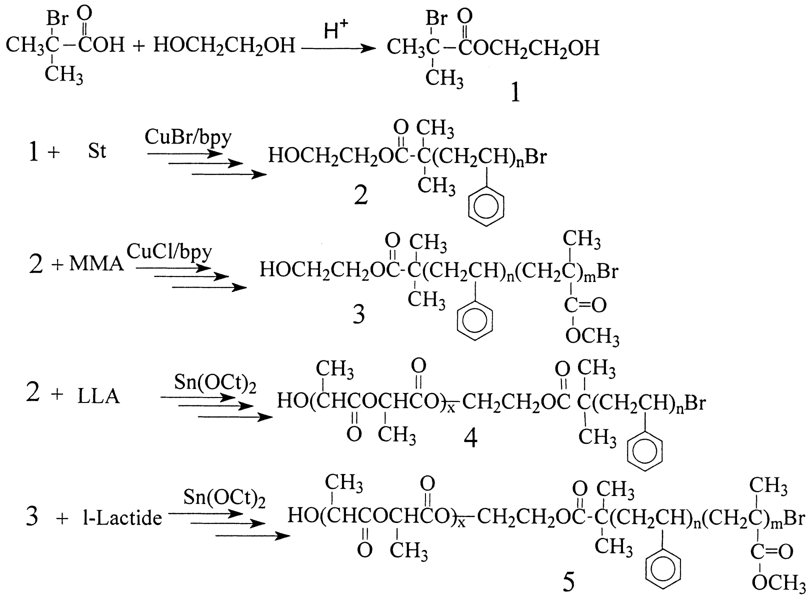
Our previous paper demonstrated that the ATRP of St using HEBB as initiator is of living nature [50]. When using HEBIB as initiator, the same result could be observed for ATRP of St, and the results of the bulk ATRP of St are listed in Table 1.

Linear relationship between ln $[M]_0/[M]$ and polymerization time as shown in Fig. 1(a) indicates that the chain radical concentration remains constant during the polymerization. The linear evolution of number average MW (M_n) with conversion is shown in Fig. 1(b), and the M_ns determined by GPC and NMR are in good agreement with theoretical value, indicating that the MW can be controlled by initial feed ratio and conversion. All the facts and symmetric GPC traces (Fig. 2), and the narrow PDI of the polymers obtained suggest the living nature for ATRP of St with HEBIB as initiator and CuBr/bpy as catalyst/ligand.

Fig. 3(a) is a typical ^{1}H NMR spectrum of HOPStBr prepared by the ATRP of St. The peak at 0.96 ppm (c) is assigned to the methyl protons from initiator, the peak at 4.4 ppm (e) corresponds to the methine proton next to the terminal bromine group. The protons of the methylene group connected to the oxygen of the ester group from the initiator appear at about 3.75 ppm (b), and the methylene protons next to the hydroxyl group appear at about 3.55 ppm (a). The integration ratio of the peaks at 0.96, 4.4, 3.75 and 3.55 ppm is almost 6:1:2:2, indicating that no change of the hydroxylethyl ester group occurred and the bromine was almost not lost during the polymerization. From the integral value of aromatic (I_{Ar}) and methyl protons ($I_{0.96}$), the MW can be calculated according to Eq. (1)

$$M_{\mathrm{n,PS}}(\mathrm{NMR}) = (6I_{\mathrm{Ar}}/5I_{0.96}) \times 104 + 211 \tag{1}$$

where 104 and 211 are the MWs of St and HEBIB, respectively. The results are listed in Table 1. The



Scheme 1.

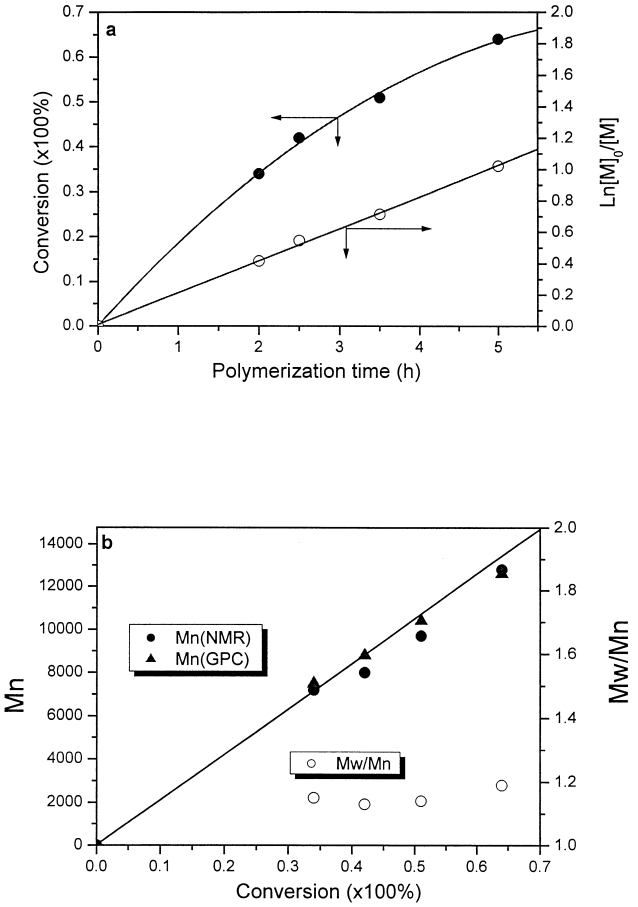


Fig. 1. The relationships of conversion and ln $[M]_0/[M]$ with polymerization time (a) and the effects of conversion of St on M_n and M_w/M_n (b) for the bulk ATRP of St with HEBIB/CuBr/bpy as initiation system. Polymerization conditions: see Table 1.

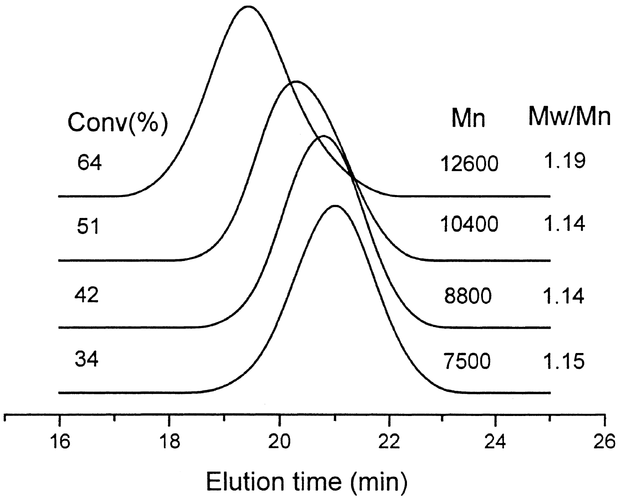


Fig. 2. GPC curves of PSt prepared at different conversions for ATRP of St with HEBIB/CuBr/bpy as initiation system. Polymerization conditions: see Table 1.

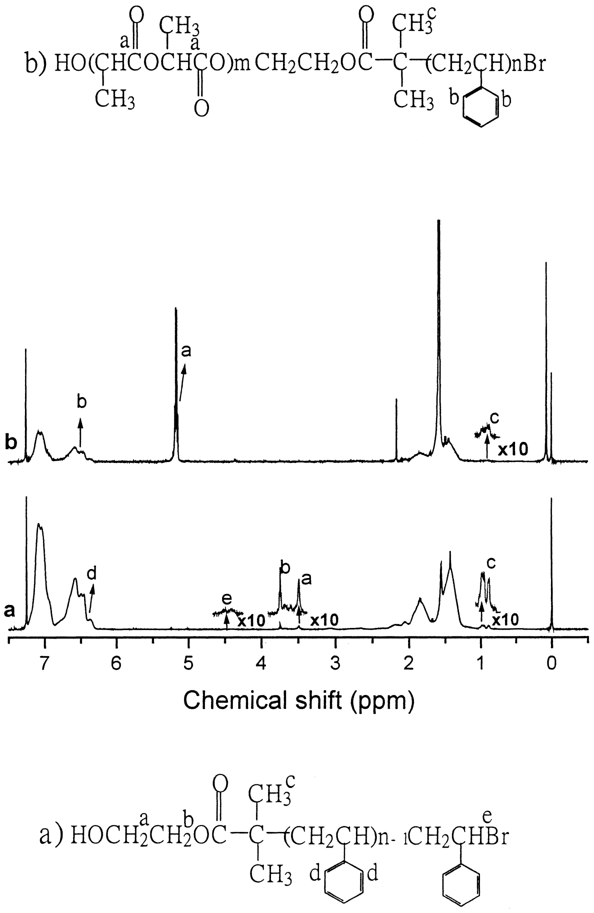


Fig. 3. ^{1}H NMR spectra of HOStBr (a) and PSt-*b*-P(LLA) (b).

agreement of M_n(NMR) with M_n(th) proves that all initiator molecules participated in the polymerization.

3.2. Ring-opening polymerization of LLA in the presence of HOPStBr

Diblock copolymers, P(LLA-*b*-St)s, were prepared by ROP of LLA at 115 °C with HOPStBr as macroinitiator and $Sn(OCt)_2$ as catalyst. The results are listed in Table 2. Almost complete conversion of LLA in 24 h (see Table 2) indicates the high reactivity of macroinitiator, HO-PSt-Br.

Fig. 4 shows the linear increase of M_n of the obtained copolymers with the molar ratio of monomer to initiator, the PDI remained narrow ($M_w/M_n < 1.2$). The M_n(NMR) of the copolymer agrees with the M_n(th) (see Table 2). These facts suggest that the M_n of the P(LLA) block in the copolymer can be precisely controlled by the molar ratio of monomer to initiator and the monomer conversion.

The formation of the block copolymer, P(LLA-*b*-St) was verified by its ^{1}H NMR spectrum shown in Fig. 3(b). In comparing with the ^{1}H NMR spectrum of HOPStBr in Fig. 3(a), a new peak appeared at 5.16 ppm (a) and another peak at 1.58 ppm in Fig. 3(b) belong to the methine proton between ester and carboxyl groups, and the methyl protons in the LLA unit, respectively. Assume that each

Table 2
Results and conditions of ROP of LLA with HOPSt-Br as macroinitiator[a]

No.	$[M]_0/[I]_0$ (molar ratio)	Conversion[b] (%)	M_n			M_w/M_n[c]
			GPC[c]	NMR[d]	th[e]	
1[a]	0	0	10,400	9700	10,800	1.14
2	20	98	12,852	12,600	12,500	1.08
3	60	97	15,900	17,900	18,100	1.03
4	90	98	17,200	22,100	22,400	1.19

[a] The copolymerization was carried out at 115 °C for 24 h. The HOPSt-Br (sample 3 in Table 1) was used as macroinitiator; $[Sn(OCt)_2]_0$:$[LLA]_0 = 1:300$ (molar ratio).

[b] Determined by gravimetry method.

[c] Measured by GPC and with narrow polydispersity polystyrene standards in the calibration of molecular weight.

[d] Calculated by Eq. (2).

[e] The M_n(th) were calculated according to: $M_n(\text{th}) = ([M]_0/[I]_0) \times \text{conversion} \times 144 + M_{n,PS}(\text{NMR})$, where $[M]_0$ and $[I]_0$ are the initial concentrations of LLA and HO-PSt-Br, 144 is the molecular weight of LLA. M_n(NMR) is the number-average molecular weight of HO-PSt-Br.

macromolecule contains one molecule of HOPStBr, the number-average MW of poly(LLA-*b*-St), $M_{n,PLAPS}$(NMR) can be calculated according to Eq. (2).

$$M_{n,PLAPS}(\text{NMR}) = [(I_{5.16}/2)/(I_{0.96}/6) \times 144 + M_{n,PS}(\text{NMR}) \qquad (2)$$

where $I_{5.16}$ and $I_{0.96}$ are the integral values of the peaks at 5.16 and 0.96 ppm, respectively, 144 and $M_{n,PS}$(NMR) are the MWs of LLA and the HOPStBr used. The values of $M_{n,PLAPS}$(NMR) are similar to that of $M_{n,PLAPS}$(th), indicating that the diblock copolymers, P(LLA-*b*-St)s, were essentially formed. This can be further confirmed by GPC traces of the block copolymers shown in Fig. 5. Symmetric curves appeared at higher MW position are the result that all macroinitiators, HOPStBr initiated the polymerization of LLA.

3.3. Preparation of HOPSt-b-PMMA

In our previous work, we found that the PSt-Br is not a good initiator for the ATRP of MMA, and the initiation is usually uncompleted. Probable reason is too fast propagation rate of MMA. To improve the initiating ability of PSt-Br, we compared the results of CuBr/HMTETA, CuCl/HMTETA and CuCl/bpy systems in the ATRP of MMA using HOPSt-Br as initiator, and the CuCl/bpy system produced better result, but there was still shoulder peak at the low MW position on their GPC curves, which is assigned to the precursor HOPSBr. Thus before it was used in the subsequent polymerization, the fractionation precipitation was carried out by adding diblock copolymer solution in THF into the mixture of cyclohexane/ethanol (2:1, v/v). Typical GPC traces of the macroinitiator, diblock copolymers before and after precipitation are shown in Fig. 6.

It can be clearly seen that a shoulder peak appeared in Fig. 6 for the diblock copolymer before precipitation, but disappeared after precipitation because cyclohexane is a good solvent for PSt. In order to estimate the composition of the diblock copolymers, the purified copolymers were characterized by ^{1}H NMR spectroscopy. A typical ^{1}H NMR spectrum of HOPSt-*b*-PMMA is shown in Fig. 7(b). In comparison with the ^{1}H NMR spectrum of HOPStBr in Fig. 7(a), besides the characteristic peaks of HOPStBr, the signal at 3.64 ppm (b) belongs to the ester methyl protons in

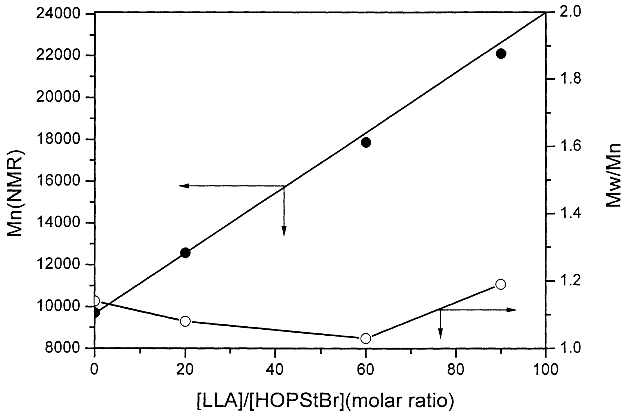


Fig. 4. The relationships of M_n of poly(LLA) segment in the copolymer and M_w/M_n with [LLA]/[HOPStBr] for the block copolymerization of LLA at 115 °C for 24 h using HOPStBr as macroinitiator and $Sn(OCt)_2$ as catalyst.

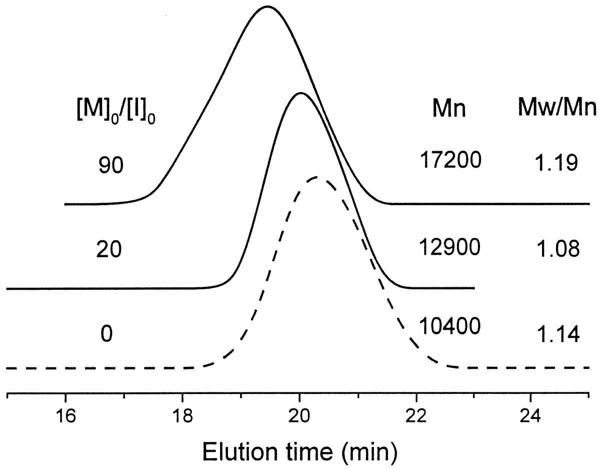


Fig. 5. GPC curves of diblock copolymers, poly(LLA-*b*-St) prepared by block copolymerization of LLA at 115 °C for 24 h using HOPStBr as macroinitiator (dot line) and $Sn(OCt)_2$ as catalyst.

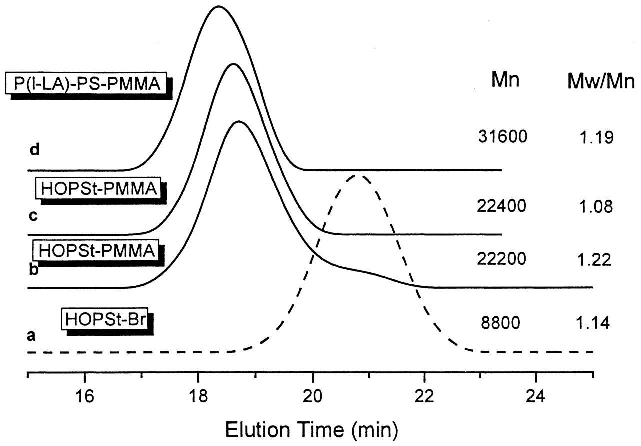


Fig. 6. GPC curves of (a) macroinitiator, HOPStBr (No. 2 in Table 1); (b) diblock copolymer, HOPStBr-*b*-PMMA before fractionation; (c) HOPStBr-*b*-PMMA after fractionation in cyclohexane/ethanol (2:1) (No. 2 in Table 3); (d) triblock copolymer, P(LLA)-*b*-PSt-*b*-PMMA (No. 2 in Table 4).

MMA unit. From the integration ratio value of aromatic (I_{Ar}) protons to ester methyl protons ($I_{3.64}$), the number of MMA units in the copolymer can be calculated; the results are listed in Table 3. Although the initiation system CuCl/HMTETA is more reactive than that of CuCl/bpy (No. 1 and 2 in Table 3), it remained more unreacted HOPStBr in the diblock copolymers. Thus we used CuCl/bpy as catalyst/ligand to prepare HOPSt-*b*-PMMA.

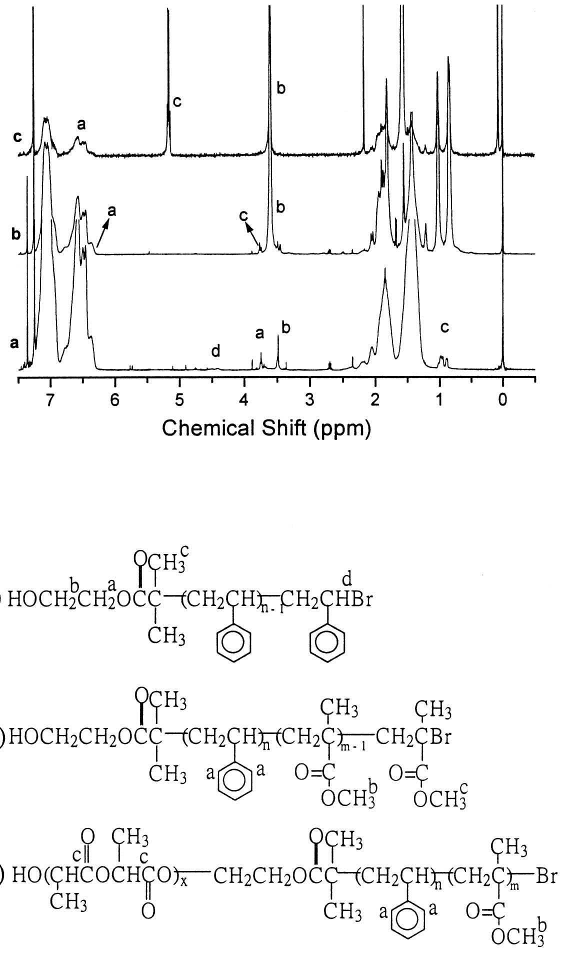


Fig. 7. ^{1}H NMR spectra of (a) macroinitiator, HOPSt-Br (No. 2 in Table 1); (b) diblock copolymer, HO-PSt-*b*-PMMA (No. 2 in Table 3); (c) triblock copolymer, P(LLA)-*b*-PSt-*b*-PMMA (No. 2 in Table 4).

Table 3
Conditions and results of copolymerization of MMA using HOPStBr as catalyst

No.	Time (min)	M_n		M_w/M_n[a]	DP of PSt/PMMA[b]
		GPC[a]	NMR[b]		
1[c]	20	24,300	19,300	1.15	67/121
2[d]	20	22,400	17,600	1.08	75/96
3[d]	30	28,400	19,800	1.10	75/118

The copolymerization was carried out at 85 °C. $[\mathrm{MMA}]_0 = 4$ M, Solvent: toluene, 5 ml.

[a] Measured by GPC calibrated with narrow molecular weight distribution polystyrene as calibration standard, all samples were measured after fractional purification.

[b] Calculated based on ^{1}H NMR data.

[c] CuCl/HMTETA = 1:1 (molar ratio) as catalyst/ligand, the HOPSt-Br (No. 1 in Table 1) as macroinitiator.

[d] CuCl/bpy = 1:3 (molar ratio) as catalyst/ligand, the HOPSt-Br (No. 2 in Table 1) as macroinitiator.

3.4. Synthesis of the triblock copolymer P(LLA-b-St-b-MMA)

The hydroxyl-terminated diblock copolymer, HOPSt-*b*-PMMA was used as macroinitiator for the block copolymerization of LLA with $\mathrm{Sn(OCt)_2}$ as catalyst. The results are listed in Table 4. The monomer conversions are very high (>95%) at different molar ratios of LLA to HOPSt-*b*-PMMA. The PDI kept narrow at different conversions ($M_w/M_n < 1.2$). The typical GPC traces of the triblock copolymers with the original diblock macroinitiator are shown in Fig. 6.

We can see clearly that the triblock copolymers is completely shifted to higher MW position in Fig. 6(d), indicating that all primary hydroxy group in HOPSt-*b*-PMMA took part in the initiation, and triblock copolymer P(LLA)-*b*-PSt-*b*-PMMA is really formed.

A typical ^{1}H NMR spectrum of the triblock copolymer is shown in Fig. 7(c). In addition to the characteristic peak of PSt and PMMA, a new signal appeared at 5.16 ppm (c), which is assigned to the methine proton between ester and carboxyl groups in the LLA unit, was observed. The $M_{n,\mathrm{PLA}}$(NMR) can be calculated based on the integration ratio of aromatic (I_{Ar}) and methine protons ($I_{5.16}$), and the results listed in Table 4 show that $M_{n,\mathrm{PLA}}$(NMR) agrees well with that of M_n(th), all these facts proved that triblock copolymer, P(LLA)-*b*-PSt-*b*-PMMA was eventually formed.

4. Conclusions

The hydroxyl terminated polymers, HOPStBr, and

Table 4
Synthesis and characterizations of triblock copolymers P(LLA)-*b*-PSt-*b*-PMMA

No.	$[M]_0/[I]_0$	Conversion[a]	M_n			M_w/M_n[b]	DP of L/S/M[c]
			GPC[b]	NMR[c]	th[d]		
1[e]	67	97	42,300	28,000	28,700	1.13	60/67/121
2[f]	61	98	31,600	26,100	26,200	1.19	59/75/96

The polymerization was carried out at 115 °C for 24 h with $Sn(OCt)_2$ as catalyst. $[Sn(OCt)_2]_0$: $[LLA]_0 = 1:300$ (molar ratio).

[a] Determined by gravimetry method.

[b] Measured by GPC and narrow molecular weight polystyrene standards were used in calculation.

[c] Calculated based on ^1H NMR data.

[d] Theoretical number-average molecular weight is calculated based on the equation: $M_n(\text{th}) = [M]_0/[I]_0 \times \text{conversion} \times 144 + M_{n,\ \text{PS-PMMA}}(\text{NMR})$, where $[M]_0$ and $[I]_0$ are initial concentrations of LLA and macroinitiator, 144 and $M_{n,\ \text{PS-PMMA}}(\text{NMR})$ are the molecular weight of LLA and macroinitiator HOPSt-*b*-PMMA.

[e] HOPSt-*b*-PMMA (No. 1 in Table 3) was used as macroinitiator.

[f] HOPSt-*b*-PMMA (No. 2 in Table 3) was used as macroinitiator.

diblock copolymers, HOPSt-*b*-PMMA, were prepared using bifunctional initiator HEBIB in ATRP system. Those copolymers were used as macroinitiators in the ROP of LLA with $Sn(OCt)_2$ as catalyst to prepare the diblock copolymer P(LLA-*b*-St) and triblock copolymer P(LLA-*b*-St-*b*-MMA). The monomer, LLA, can be polymerized with high conversions (>95%) and the PDI of the copolymers obtained kept narrow (<1.2). The MWs and the compositions of each block in the block copolymers can be controlled by the molar ratio of monomer to hydroxyl groups of the macroinitiators. The structures of the copolymers were determined by ^1H NMR and GPC. The study on the self-assembly with this triblock copolymer is in progress, the computer-simulation is still carried out at the same time.

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References

[1] Brinder K. Adv Polym Sci 1994;112:181.

[2] Thomas EL. Science 1999;286:1307.

[3] Gido SP. Nature 1999;398:107.

[4] Bates FS, Fredrickson G. Phys Today 1999;32:38.

[5] Hückstädt H, Goldacker T, Göpfert A, Abetz V. Macromolecules 2000;33:3757.

[6] Goldacker T, Abetz V. Macromolecules 1999;32:5165.

[7] Elbs H, Drummer C, Abertz V, Krausch G. Macromolecules 2002;35:5570.

[8] Kudose I, Kotaka T. Macromolecules 1984;17:2325.

[9] Stupp SI, LeBonheur V, Walker K, Li LS, Huggins KE, Keser M, Amstutz A. Science 1997;276:384.

[10] Phan S, Fredrickson GH. Macromolecules 1998;31:59.

[11] Avgeropoulos A, Paraskeva S, Hadjichristidis N, Thomas EL. Macromolecules 2002;35:4030.

[12] Pantazis D, Schulz DN, Hadjichristidis N. J Polym Sci, Part A: Polym Chem 2002;40:1476.

[13] Grubbs RB, Dean JM, Bates FS. Macromolecules 2001;34:8593.

[14] Tsarevsky NV, Sarbu T, Göbelt B, Matyjaszewski K. Macromolecules 2002;35:6142.

[15] Liu SY, Weaver JVM, Tang YQ, Billingham NC, Armes SP. Macromolecules 2002;35:6121.

[16] Kurcok P, Dubois Ph, Sikorska W, Jedlmski Z, Jérôme R. Macromolecules 1997;30:5591.

[17] He T, Zou YF, Pan CY. J Polym Sci, Part A: Polym Chem 2002;40:3367.

[18] Tian D, Dubois Ph, Jérôme R. Macromolecules 1997;30:1947.

[19] Yuan JY, Pan CY. Chin J Polym Sci 2002;20(2):171.

[20] Fradet A. In: Aggarwal SL, Russo S, editors. Comprehensive polymer science. London: Pergamon; 1996. p. 133. Second supp.

[21] Auschra C, Stadler R. Polym Bull 1993;30:257.

[22] Lescanec RL, Fetters FJ, Thomas EL. Macromolecules 1998;31:1680.

[23] Goldacker T, Abetz V, Stadler R, Erukhimorich I, Leibler L. Nature 1999;398:137.

[24] Georges MK, Veregin RPN, Kazmaier PM, Hamer GK. Trends Polym Sci 1994;2:66.

[25] Davis TP, Knkulj D, Haddleton DM, Malomey DR. Trends Polym Sci 1995;3:365.

[26] Patten TE, Xia J, Abernathy T, Matyjaszewski K. Science 1996;272:866.

[27] Hawker CJ. Trends Polym Sci 1996;4:183.

[28] Sawamoto M, Kamigaito M. Trends Polym Sci 1996;4:371.

[29] Chiefari J, Chong YK, Ercole F, Kristine J, Jeffery J, Le TPT, Mayadunne RTA, Meijs GF, Moad G, Rizzardo E, Thang SH. Macromolecules 1998;31:5559.

[30] Wang JS, Matyjaszewski K. J Am Chem Soc 1995;117:5614.

[31] Wang JS, Matyjaszewski K. Macromolecules 1995;28:7901.

[32] Patten TE, Matyjaszewski K. Adv Mater 1998;10:901.

[33] Granel C, Dubois Ph, Jérôme R, Teyssié Ph. Macromolecules 1996;29:8576.

[34] Kotani Y, Kamigaito M, Sawamoto M. Macromolecules 2000;33:2819.

[35] Matyjaszewski K, Shipp DA, McMurtry GP, Gaynor SG, Pakula T. J Polym Sci, Part A: Polym Chem 2000;38:2023.

[36] Sedjo RA, Mirous BK, Brittain WJ. Macromolecules 2000;33:1492.

[37] Acar MH, Matyjaszewski K. Macrolmol Chem Phys 1999;200:1094.

[38] Tong JD, Ni S, Winnik MA. Macromolecules 2000;33:1482.

[39] Angot S, Taton D, Gnanou Y. Macromolecules 2000;33:5418.

[40] Cheng X, Ivan B, Kaps J, Batsberg W. Macromol Rapid Commun 1998;19:585.

[41] Coca S, Matyjaszewski K. J Polym Sci, Part A: Polym Chem 1997;35:3595.

[42] Feng SX, Pan CY. Macromolecules 2002;35:2084.

[43] Xu YJ, Pan CY. Macromolecules 2000;33:4750.

[44] Xu YJ, Pan CY. J Polym Sci, Part A: Polym Chem 2000;38:337.

[45] Baskan Düz A, Yagei Y. Eur Polym J 1999;36:2031.

[46] Hawker CJ, Hedrick JL, Malmström EE, Trollsäs M, Mecerreyes D, Moineau G, Dubois Ph, Jérôme R. Macromolecules 1998;31:213.
[47] Mecerreyes D, Moineau G, Dubois Ph, Jérôme R, Hedrick JL, Hawker CJ, Malmström EE, Trollsäs M. Angew Chem Int Ed 1998;37:1274.
[48] Hedrick JL, Trollsäs M, Hawker CJ, Auhoff B, Claesson H, Heise A, Miller RD, Mecerreyes D, Jérôme R, Dubois Ph. Macromolecules 1998;31:8691.
[49] Zhang Q, Remsen EE, Wooley KL. J Am Chem Soc 2000;122:3642.
[50] Xu YJ, Pan CY, Tao L. J Polym Sci, Part A: Polym Chem 2000;38: 436.
[51] Meyer U, Anja RAP, Loontjens T, Heise A. Macromolecules 2002;35: 2873.