Synthesis of Amphiphilic Miktoarm ABC Star Copolymers by RAFT Mechanism Using Maleic Anhydride as Linking Agent

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ABSTRACT: The preparation and characterization of amphiphilic ABC miktoarm star copolymers based on polystyrene, and poly(ethylene oxide), poly(methyl acrylate) or poly(*N*-isopropylacrylamide) blocks are described in this paper. First, macrotransfer agent polySt-MAh-S-C(S)Ph with maleic anhydride and a dithio group at one end of polymer chain was synthesized by the reaction of a dithio group at the end of the polystyrene with maleic anhydride (MAh) in tetrahydrofuran solution. The second, reversible addition−fragmentation chain transfer polymerization of methyl acrylate or *N*-isopropylacrylamide was carried out in the prescence of polySt-MAh-S-C(S)Ph and benzoyl peroxide. Finally, the anhydride group at the joint of two blocks was reacted with terminal hydroxyl group of poly(ethylene glycol methyl ether). The obtained ABC star copolymers were characterized by ^{1}H NMR spectroscopy and gel permeation chromatography.

Introduction

With progress in polymerization techniques, more triblock ABC copolymers have been synthesized and studied extensively during the last 2 decades.[1−8] 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.

Star polymers with different structural arms have been designated as miktoarm star polymers. They reveal interesting properties in solid state as well as in solution due to their unique architectures.[9−21] In comparison with linear ABC triblock copolymers, the synthesis of miktoarm ABC star polymers is one of the more challenging projects available. Three different procedures have been used to synthesize ABC star copolymers until now. The first, a multifunctional chlorosilane reacts subsequently with the active chain ends of different living polymers.[22,23] Substitution of the last chlorine atom by a difunctional diphenyl alkyl anion is necessary to incorporate a strongly segregating poly(methyl methacrylate) (polyMMA) as a polymer arm. Another approach is based on a macromonomer technique. A nonhomopolymerizable macromonomer bearing a 1,4-bis(1-phenylethenyl)benzene (DDPE) or a 1,1-diphenylethylene (DPE) group at one chain end is incorporated at the junction of two polymer blocks.[13,24−27] Different ABC star copolymers can be prepared by varying the monomers and the synthesis of various macromonomers. The third method is the so-called "bifunctional macroinitiator". The macroinitiator has two different functional groups which are able to initiate independently two different kinds of polymerizations.[28−31] The combinations of classical anionic and ring-opening polymerization using the hydroxyl function[28,29] and anionic and photoinduced charge-transfer polymerization[30] were used for the synthesis of ABC star copolymers. In our work, we synthesized poly(tetrahydrofuran) (THF)/poly(1,3-dioxepane) (DOP)/poly(styrene) (St) ABC star copolymers by combination of cationic ring-opening polymerization (CROP) and atom transfer radical polymerization (ATRP).[31] In this paper, we present the synthesis of amphiphilic ABC star copolymers with polySt or poly(methyl acrylate) (MA) as the hydrophobic segment and poly(ethylene oxide) (EO) or poly(*N*-isopropylacrylamide) (NIPAM) as the hydrophilic segment.

As described above, the macroinitiator method synthesizing ABC star copolymers was based on nonhomopolymerizable monomer or linking agents (DDPE, DPE) in the anionic polymerization. As we know, maleic anhydride is a nonhomopolymerizable monomer in the radical polymerization. Kallitsis reported the synthesis of polySt with terminal anhydride and bromine by ATRP. The functionality of polymers was determined through their reaction with poly(ethylene glycol methyl ether) (PEGM), and the effectiveness of terminal functionality was certified. However, the transfer efficiency of the bromine used for further initiation of ATRP was not detected, due to the interaction between maleic anhydride and the catalysts of ATRP.[32] We tried to use the same method to prepare polySt with terminal anhydride and bromine; then, it was used as the macroinitiator in the ATRP of the second monomer. Unfortunately, no good result was obtained due to the loss of some bromines in the reaction of polySt-Br with maleic anhydride. Recently, a new living radical polymerization via the reversible addition−fragmentation chain transfer process (RAFT) offers exceptional versatility of monomers in providing polymers with controlled molecular weight and narrow polydispersity.[33−35] The chain extension test showed that the polymer contained 6% or less of potentially inactive species (without dithio moieties at the chain end).[36] Here, we present the synthesis of ABC star polymers using RAFT technique and maleic anhydride as a nonhomopolymerizable linking agent (Scheme 1). The polySt with a terminal dithio group was reacted with excess maleic anhydride, forming polySt with terminal anhydride and dithio groups. By further polymerization of a second monomer via

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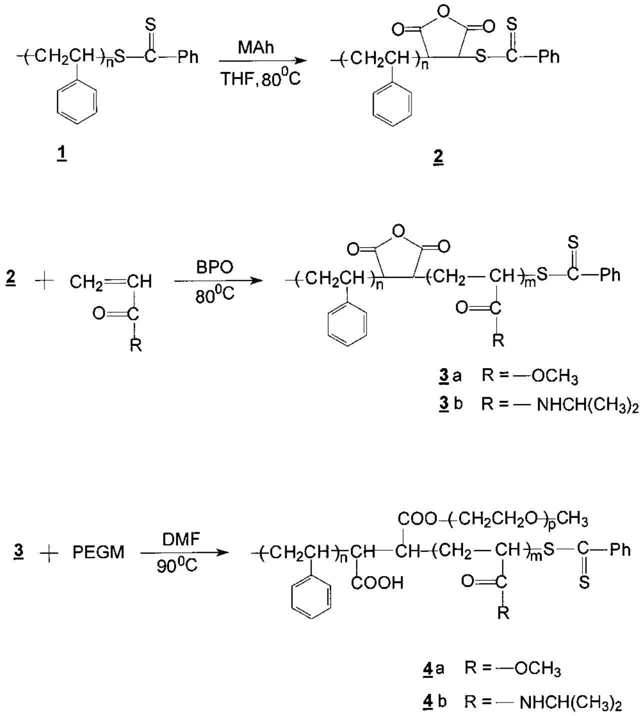
Scheme 1



RAFT process and reaction of the anhydride group at the junction of two polymer blocks with PEGM, ABC star polymers were prepared. This method not only can prepare new class star copolymers but also can provide a new easy route to prepare polymers with a terminal anhydride group.

Experimental Section

Materials. Poly(ethylene glycol methyl ether) (PEGM) was purchased from Fluka Co. All the other reagents (analytical grade) were purchased from Shanghai Chemical Reagents Co. THF and benzene were distilled from a purple sodium ketyl solution. Dimethylforamide (DMF) was distilled from CaH_2 under reduced pressure. St and MA were washed with an aqueous solution of sodium hydroxide (5 wt %) three times and then with water until neutralization. After being dried with anhydrous magnesium sulfate, monomers were distilled at reduced pressure. *N*-Isopropylacrylamide (NIPAM) was recrystallized from benzene and *n*-hexane. Maleic anhydride (MAh) was recrystallized from anhydrous chloroform free of ethanol. Benzoyl peroxide (BPO) was refined by pouring concentrated purchased BPO solution in chloroform into methanol, followed by filtration and drying in a vacuum at room temperature. Polystyrenes terminated with dithiobenzoate (**1**) were prepared by the RAFT mechanism according to ref 36. ^{1}H NMR (500 MHz, $CDCl_3$), δ (TMS, ppm): 7.85 [ortho *Ph*C(S)S], 7.32−6.30 (aromatic protons), 4.84 [C*H*SC(S)], 2.12−1.29 (CH_2C*H*), 1.03 (PhC−CH_3). Other reagents were used as received without further purification.

Synthesis of PolySt (2) (No. 4, Table 1). PolySt (**1b** in Table 1, 4 g, 0.93 mmol), MAh (2 g, 20 mmol), and THF (4 mL) were added into a 10-mL glass tube, followed by a freeze−vacuum−thaw cycle three times. The tube was sealed under vacuum and immersed in an oil bath thermostated at 80 °C. After reaction for 6 h, the tube was cooled to room temperature, the polymer with the terminal MAh group was precipitated by pouring the polymer solution in THF into petroleum ether (bp 30−60 °C) three times, and the excess MAh was removed. The polymer obtained was dried in a vacuum at 35 °C for 24 h. yield = 82.5%, M_n(NMR) = 4900; MWD = 1.04. ^{1}H NMR (500 MHz, $CDCl_3$), δ (TMS, ppm): 7.85 [ortho *Ph*C(S)S], 7.32−6.30 (aromatic protons), 4.40 [C*H*SC(S)], 2.12−1.29 (CH_2C*H*), 1.03 (PhC−CH_3). IR (KBr, cm^{-1}): ν = 1867, 1787 (−CO−O−CO−).

Synthesis of AB Diblock Copolymer (No. 6, Table 2). PolySt (**2b** in Table 1, 1 g, 0.22 mmol), MA (4 g, 46 mmol), BPO (5 mg, 0.022 mmol), and THF (4 mL) were added into a 10 mL glass tube. After three freeze−vacuum−thaw cycles, the tube was sealed under vacuum and then immersed in an oil bath thermostated at 80 °C. After polymerization for 6 h, the tube was rapidly cooled to room temperature, and the AB diblock copolymer was precipitated by pouring the polymer solution in THF into petroleum ether (bp 30−60 °C). After dried in a vacuum at 40 °C for 24 h, the block copolymer (2.2 g) was obtained. M_n(NMR) = 11 500; MWD = 1.15. ^{1}H NMR (500 MHz, $CDCl_3$), δ (TMS, ppm): 7.32−6.30 (aromatic protons), 3.66 (OCH_3), 2.32 (CH$_2$C*H*COO), 2.12−1.29 (CH_2C*H*, CH_2CHCOO).

Synthesis of Miktoarm ABC Triblock Copolymer. Before esterification, the trace water in the polymers was removed by azeotropic distillation with anhydrous benzene.

PolySt-*b*-MA-*b*-EO (No. 8, Table 3). Poly(St-*b*-MA) (0.8 g, no. 6, Table 2), PEGM (1 g, M_n = 5000), and DMF (10 mL) were added into a 25 mL one-neck round flask equipped with a magnetic bar under nitrogen. After being flushed with nitrogen for 3 min, the flask was sealed, and the reaction was carried out at 90 °C for 48 h. When the reaction mixture was cooled to room temperature, the polymer solution was poured into distilled water (100 mL), and the mixture was extracted with chloroform (2 × 50 mL). The extracts were combined and washed with distilled water three times to remove the unreacted PEGM. After the mixture was dried over anhydrous sodium sulfate, most of the chloroform was evaporated off, and the ABC miktoarm copolymer was precipitated into excess petroleum ether and then collected by filtration. After being dried in a vacuum at 40 °C for 24 h, the copolymer was obtained in 86% yield. M_n(NMR) = 17 600; MWD = 1.18. ^{1}H NMR (500 MHz, $CDCl_3$), δ (TMS, ppm): 7.32−6.30 (aromatic protons), 3.66 (COOCH_3, OCH_2CH_2), 3.39 (terminal, OCH_3), 2.32 (CH$_2$C*H*COO), 2.12−1.29 (CH_2C*H*, CH_2CHCOO).

PolySt-*b*-NIPAM-*b*-EO was synthesized similar to the procedure described above. M_n(NMR) = 15 300; MWD = 1.12. ^{1}H NMR (500 MHz, $CDCl_3$), δ (TMS, ppm): 7.32−6.30 (aromatic protons), 4.04 [NHC*H*(CH$_3$)$_2$], 3.64 (OCH_2CH_2), 3.39 (terminal, OCH_3), 2.32 (CH$_2$C*H*COO), 2.12−1.29 (CH_2C*H*, CH_2-CHCOO), 1.20 [NHCH(CH_3)$_2$].

Characterization ^{1}H NMR spectra were determined on a Bruker DMX-500 nuclear magnetic resonance instrument with $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal standard. FTIR spectra were recorded on a Vector-22 FTIR instrument. The measurement of molecular weights and molecular weight distribution of the polymers were carried out on a Waters 150C gel permeation chromatograph (GPC) equipped with microstyragel columns (500, 10^3, and 10^4 Å) and RI detector. Polystyrene was used as a calibration standard. THF was used as the eluent at a flow rate of 1.0 mL/min.

Results and Discussion

Synthesis and Characterization of PolySt with Terminal Maleic Anhydride and Dithiobenzoate (2). Kallitsis reported that the MAh-terminated polySt was obtained by the ATRP of polySt-Br and MAh.[32] In our experiments, although polySt terminated with MAh was obtained, most of the terminal bromine was lost, so the polymer cannot be used as a macroinitiator in ATRP of the second monomer. Therefore, we adopted the RAFT method, the polySt terminated with dithiobenzoate (polySt-S-C(S)Ph) was synthesized according to the procedure published,[36] and the results are listed in Table 1. The synthesized polySt-S-C(S)Ph was reacted with MAh in THF solution at 80 °C. To ensure complete reaction of the polySt-S-C(S)Ph with MAh, an excess amount of MAh was added. Under heating, the dithiobenzoate group was transferred to the vinyl group of

Table 1. GPC and ^{1}H NMR Results of PolySt Terminated with Dithiobenzoate (1) and MAh Dithiobenzoate (2)[a]

no.	sample	T (°C)	time (h)	convn or yield(%)[b]	M_n(NMR)[c]	M_n(GPC)	F (%)[d]	M_w/M_n
1	**1a**	80	7	15	3100	2900	94	1.08
2	**2a**	80	6	67	3600	3400	94	1.07
3	**1b**	80	12	21	4500	4300	96	1.03
4	**2b**	80	6	82	4900	4700	96	1.04

[a] PolySt-S-C(S)Ph (**1**) was prepared according to ref 36. Feed ratio: St/1-phenylethyl dithiobenzoate/BPO = 2000:10:1 (molar ratio). PolySt-MAh-S-C(S)Ph (**2**) was prepared through polySt-S-C(S)Ph (**1**) reacting with MAh in a sealed tube. Feed ratio: MAh/**1** = 20:1 (molar ratio); the concentration of MAh in THF was 5 M. [b] Conversion and yield was calculated based on the gravimetric method. [c] M_n(NMR) was calculated according to eqs 1 and 2. [d] Functionality = M_n(GPC)/M_n(NMR).

Table 2. Molecular Weight Data for AB Diblock Copolymer[a]

no.	polySt-MAh, **2**[b]	monomer B	time (h)	convn (%)[c]	M_n(th)[d]	M_n(NMR)[e]	M_n(GPC)	MWD
5	**2a**	MA	10	53	12 700	13 200	11 700	1.27
6	**2b**	MA	6	36	11 100	11 500	11 000	1.15
7	**2b**	NIPAM	6	20	9400	9400	8500	1.10

[a] The polymerizations were carried out at 80 °C in the presence of BPO (molar ratio: BPO/**2** = 1/10), and MA (or NIPAM)/**2a** (or **2b**) = 200:1 (molar ratio), solvent: THF. [b] PolySt macrotransfer agents are the same as those listed in Table 1. [c] Conversion was calculated based on the gravimetric method. [d] $M_n(\text{th}) = [\text{monomer}]/[\mathbf{2}] \times M_m + M_{n(\mathbf{2})}$, where M_m and $M_{n(\mathbf{2})}$ are the molecular weight of monomer and polySt (**2**) (based on NMR), respectively. [e] M_n(NMR) of the copolymer was calculated according to eqs 3 and 4.

Table 3. Data of ABC Miktoarm Star Copolymers Synthesized by Esterification of Diblock Copolymers with PEGM[a]

		PEO segment					
no.	AB copolymer[b]	M_n(act)[c]	M_n(app)[d]	yield (%)	efficiency[e]	M_n(GPC)	MWD
8	PSt-*b*-MA	6400	6100	86	0.95	15 400	1.18
9	PSt-*b*-NIPAM	6500	5900	90	0.91	9800	1.12

[a] The esterification was carried out in DMF solution at 90 °C for 48 h (copolymer/PEGM = 1:3, molar ratio). [b] PSt-*b*-MA (no. 6 in Table 2) and PSt-*b*-NIPAM (no. 7 in Table 2) were used. [c] Calculated according to eqs 5 and 6. [d] Calculated according to eqs 7 and 8. [e] Efficiency = M_n(app)/M_n(act).

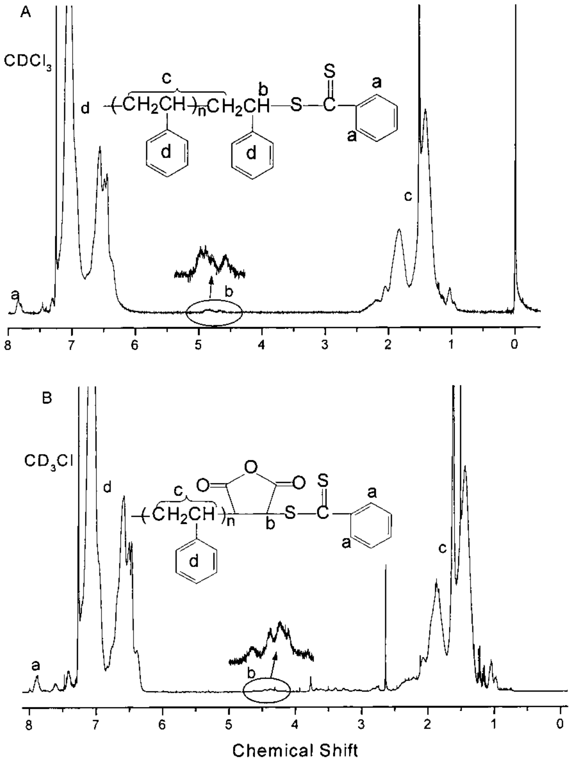


Figure 1. ^{1}H NMR spectra of polystyrene (A, no. 3 in Table 1) and anhydride capped polystyrene (B, no. 4 in Table 1).

MAh. The typical ^{1}H NMR spectrum of polymer **1** and **2** (nos. 3 and 4 in Table 1) are shown in Figure 1. The peaks at 7.32−6.30 and 2.12−1.29 ppm are the characteristic signals of polySt segments. In Figure 1A of polySt **1b**, peaks a and b at 7.85 and 4.84 ppm correspond to the signals of the two aromatic protons ortho to the dithio group and the end-standing methine proton next to the dithio group. Figure 1B shows the ^{1}H NMR spectrum of polySt **2b** prepared by the reaction of **1b** with MAh; the signal b at 4.84 ppm in Figure 1A is absent, and a new peak b at 4.40 ppm appears, which is ascribed to the methine proton of anhydride next to dithio groups. The integration ratio of a:b is 2.1:1.0, indicating the transfer of dithio group to the MAh unit. For further verification, IR spectroscopy was performed. The FTIR spectra of the polySt before and after reaction with MAh are shown in Figure 2, parts A and B. When the characteristic overtone absorptions of the benzene ring in the range of 1700−1900 cm^{-1} in Figure 2A are compared, a new absorption band at 1787 cm^{-1} is found, and the absorption band at 1867 cm^{-1} is remarkably strengthened. The two bands are the characteristic carbonyl stretching bands of the anhydride, confirming the existence of an anhydride group at the polymer chain end.

Assuming all the polySts were terminated by dithiobenzoates, the M_n(NMR) of **1** and **2** can be calculated according to the following two equations, eqs 1 and 2:

$$M_n(\text{NMR}) = (2I_{7.32-6.30}/5I_{7.85}) \times 104 + 258 \quad (1)$$

$$M_n(\text{NMR}) = (I_{7.32-6.30}/5I_{4.40}) \times 104 + 258 + 98 \quad (2)$$

Here $I_{7.32-6.30}$, $I_{7.85}$, and $I_{4.40}$ are the integral values of peaks at 7.32−6.30, 7.85, and 4.40 ppm, 258 and 98 are the molecular weights of 1-phenylethyldithiobenzoate and MAh, respectively. Although M_n(GPC) cannot be used as the absolute molecular weight standard of polySt samples, we can roughly estimate the relative amounts of dithiobenzoate in the MAh units by comparison of M_n(NMR) with M_n(GPC). If too many terminal dithiobenzoate groups were lost, M_n(NMR) would be much greater than M_n(GPC). According to the results in Table 1, the functionality is around 95% based on

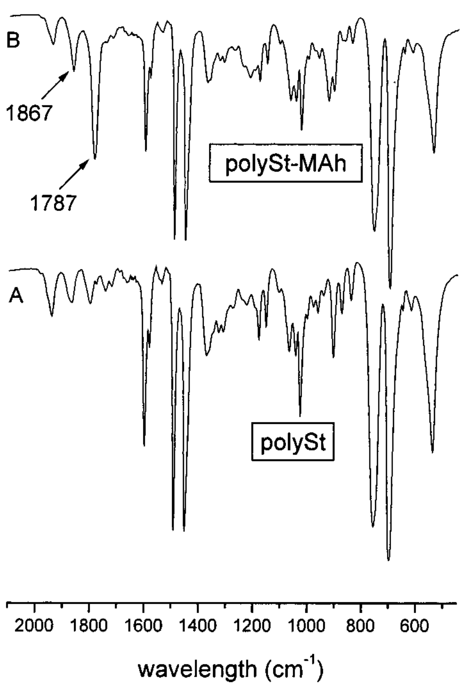


Figure 2. FTIR spectra of polystyrene (A, no. 3 in Table 1) and anhydride capped polystyrene (B, no. 4 in Table 1).

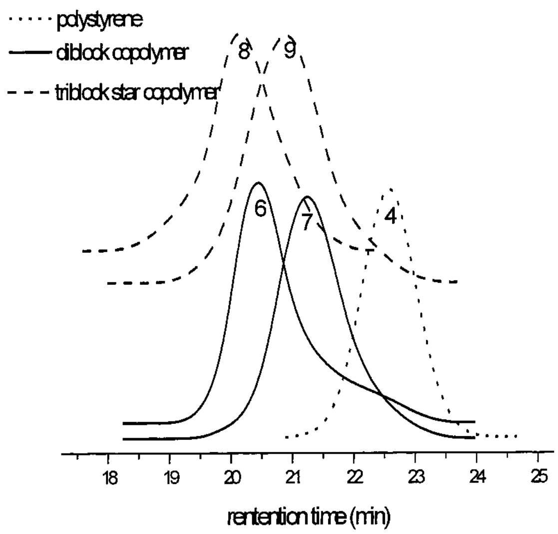


Figure 3. GPC traces of polystyrene (no. 4, MWD = 1.04), its diblock copolymer (no. 6, MWD = 1.15; no. 7, MWD = 1.10), and their miktoarm star copolymers (no. 8, MWD = 1.18; no. 9, MWD = 1.12) (the numbers in the figure are the sample numbers in Tables 1−3).

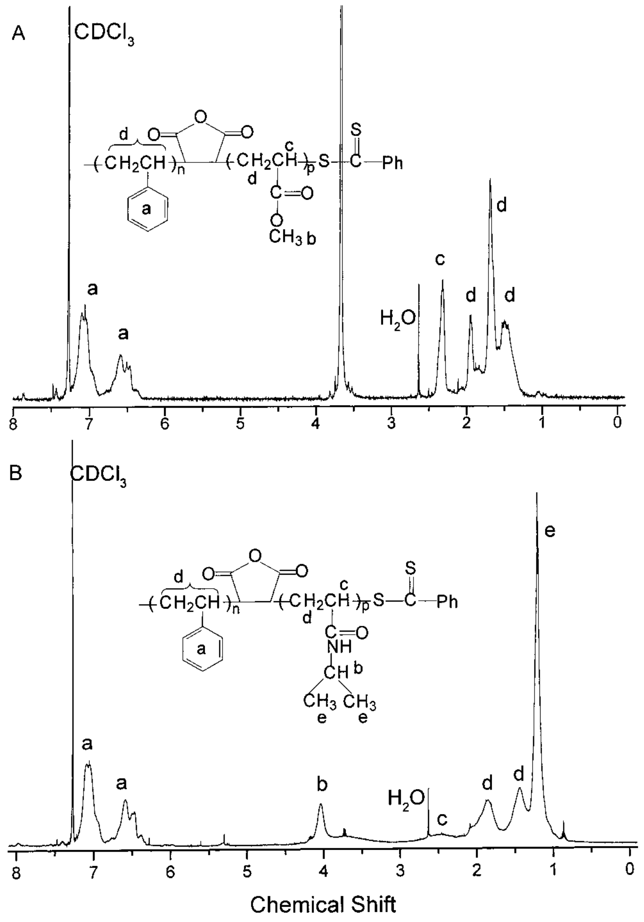


Figure 4. ^{1}H NMR spectra of diblock copolymers: (A) polySt-*b*-MA (no. 6 in Table 2); (B) polySt-*b*-NIPAM (no. 7 in Table 2).

the ratio of M_n(GPC) to M_n(NMR). The increase of M_n(NMR) and M_n(GPC) of polySts (**2**) is more than the molecular weight of MAh; this may be ascribed to a small amount of polySt with low molecular weight being removed after precipitation in petroleum ether. Of course, it is not excluded that a few of the RAFT groups were lost during the thermal transfer reaction, resulting in an increase of M_n(NMR), and the MAh at the terminal of polySts (**2**) may influence the veracity of molecular weights measured by GPC. However, it can be concluded that the dithio group for the next RAFT process is almost remained at the chain end, and MAh was successfully transferred to the end of the polySt chain by thermal fragmentation transfer mechanism (the point was also supported by esterification with PEGM; see the following section).

Synthesis of AB Diblock Copolyemr by RAFT (3). To avoid the loss of terminal dithiobenzoate during the esterification reaction with PEGM, RAFT polymerization of the second monomer was carried out first. The polymers were obtained by precipitation in nonprotonic solvents, such as petroleum ether, to avoid opening of the anhydride ring. The conditions and the results of AB diblock copolymers obtained are listed in Table 2. Besides MA, the polymerization of NIPAM was also carried out. All copolymers were characterized by ^{1}H NMR spectroscopy and GPC. Typical GPC traces (nos. 6, and 7 in Table 2) are shown in Figure 3. A little tail exists at the low molecular weight position, which can be attributed to the dead chain of macrotransfer agent and slight homopolymerization of MA. However, the polydispersities are narrow (1.27−1.10). The typical ^{1}H NMR spectra of poly(St-*b*-MA) and poly(St-*b*-NIPAM) are shown in Figure 4. In Figure 4A, the peaks at 7.32−6.30 ppm are assigned to the aromatic protons of St segment, peaks at 2.32 and 3.66 ppm are ascribed to the methine and ester methyl protons of MA segment, and the signals of methylene protons of MA segment are overlapped by the signal of aliphatic protons of the St segment at 2.12−1.29 ppm. In Figure 4B, besides the characteristic peaks of the St segment, peaks at 4.04, 2.32, and 1.20 ppm correspond to the signals of methine protons of the isopropyl group, the main chain methine proton of polyNIPAM, and six protons of two methyl groups in the NIPAM unit, respectively. The other two protons in the main chain of the NIPAM segment are overlapped at 2.12−1.29 ppm. All the facts confirm the formation of AB diblock copolymer.

Assuming that all macrotransfer agents were transferred to diblock polymer chain and no homopolymerization takes place, the $M_n(\mathrm{NMR})_{\mathrm{St}-b-\mathrm{MA}}$ and $M_n(\mathrm{NMR})_{\mathrm{St}-b-\mathrm{NIPAM}}$ of polySt-*b*-MA and polySt-*b*-NIPAM can be calculated according to eqs 3 and 4, and the results are listed in Table 2.

$$M_n(\mathrm{NMR})_{\mathrm{St}-b-\mathrm{MA}} = (5I_{3.66}/3I_{7.32-6.30}) \times \mathrm{DP}_{\mathrm{St}} \times 86 + M_{\mathrm{pSt}} \quad (3)$$

$$M_n(\mathrm{NMR})_{\mathrm{St}-b-\mathrm{NIPAM}} = (5I_{4.04}/I_{7.32-6.30}) \times \mathrm{DP}_{\mathrm{St}} \times 113 + M_{\mathrm{pSt}} \quad (4)$$

Here $I_{3.66}$, $I_{4.04}$, and $I_{7.32-6.30}$ are the integral values of peaks at 3.66, 4.04, and 7.32−6.30 ppm, $\mathrm{DP}_{\mathrm{St}}$ and M_{pSt} are the degree of polymerization and molecular weight of polySt (**2**) based on ^{1}H NMR data, and 86 and 113 are the molecular weights of MA and NIPAM monomers. The M_n(NMR) is slightly higher than M_n(th), resulting from the impure macrotransfer agent. Because of different hydrodynamic volume of block copolymers from polystrene standards, the M_n(GPC) is less than that M_n(NMR) and M_n(th), which also can be seen in Table 3.

Synthesis of ABC Star Copolymers by Esterification with PEGM (4). The esterification of AB diblock copolymer with PEGM was carried out according to a procedure similar to the Kallitsis method.[32] The reaction continued for 48 h in order to obtain a good esterification yield. After the reaction mixture was washed several times with water, the triblock copolymers were obtained by precipitation in petroleum ether. The ^{1}H NMR spectra of poly(St-*b*-MA-*b*-EO) and poly(St-*b*-NIPAM-*b*-EO) and their GPC traces are shown respectively in Figures 5 and 3, while the related data are listed in Table 3. The molecular weight distributions are narrow (1.18−1.12, see Table 3). Comparison with the GPC traces of diblock copolymers shown in Figure 3, ABC miktoarm star polymers show only one peak, which means that no evident diblock copolymers exist. In addition, the tails as shown in the GPC traces of diblock copolymers are absent, indicating that a small amount of homopolymerization products was removed after precipitation and washing. From the ^{1}H NMR spectra in Figure 5, we also can conclude that the miktoarm ABC triblock copolymers were formed. In addition to the characteristic peaks of diblock copolymers, a new peak at 3.64 ppm appeared in Figure 5B, which is ascribed to the methylene protons of PEO segment. However, for polySt-*b*-MA-*b*-EO in Figure 5A, this signal at 3.64 ppm is overlapped by the signal of the ester methyl group of the MA segment. Compared with the spectrum of polySt-*b*-MA in Figure 4A, the intensity of the peak at 3.66 ppm in Figure 5A is markedly strengthened. The peak at 3.39 ppm appears in both parts A and B of Figure 5, which is ascribed to the signal of the terminal methyl group of PEO. The facts described above suggest that the reaction of the anhydride at the joint of diblock copolymer with the terminal hydroxyl group of PEO occurred, and the amphiphilic copolymers were synthesized.

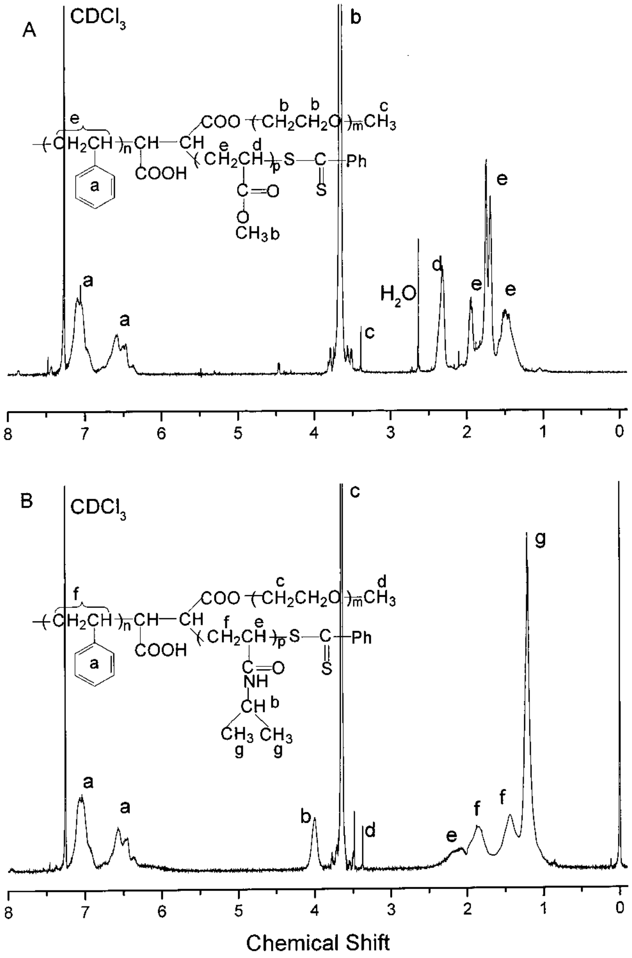


Figure 5. ^{1}H NMR spectra of triblock copolymers: (A) polySt-*b*-MA-EO (no. 7 in Table 3); (B) polySt-*b*-NIPAM-*b*-EO (no. 9 in Table 3).

On the basis of ^{1}H NMR data, the esterification efficiency can be calculated. The PEGM purchased was labeled as $M_n = 5000$, the molecular weight calculated according to our ^{1}H NMR data was around 6500. The actual molecular weights of the PEO segments in poly(St-*b*-MA-*b*-EO) and poly(St-*b*-NIPAM-*b*-EO), $M_{n(\mathrm{act})\mathrm{PEO},(\mathrm{St}-b-\mathrm{MA}-b-\mathrm{EO})}$ and $M_{n(\mathrm{act})\mathrm{PEO},(\mathrm{St}-b-\mathrm{NIPAM}-b-\mathrm{EO})}$, can be calculated by using the signal of the terminal methyl group as a reference according to eqs 5 and 6:

$$M_{n(\mathrm{act})\mathrm{PEO},(\mathrm{St}-b-\mathrm{MA}-b-\mathrm{EO})} = 3(I_{3.66} - 3I_{2.32})/4I_{3.39} \times 44 + 15 \quad (5)$$

$$M_{n(\mathrm{act})\mathrm{PEO},(\mathrm{St}-b-\mathrm{NIPAM}-b-\mathrm{EO})} = 3I_{3.64}/4\, I_{3.39} \times 44 + 15 \quad (6)$$

Here $I_{3.66}$, $I_{3.64}$, $I_{3.39}$, and $I_{2.32}$ the integral values of corresponding peaks at 3.66, 3.64, 3.39, and 2.32 ppm, respectively; 44 and 15 are the molecular weights of ethylene oxide and the methyl group. The results calculated are listed in Table 3, and the molecular weight of PEO segment is around 6500. However, due to the efficiency of esterification, some of the diblock copolymers did not react with PEGM. When the molecular weight of the polySt segment was used as reference in the calculation of the PEGM molecular weight, the apparent molecular weight of PEO should be less than its actual value. Assuming the molecular weight of St segment remains unchanged during polymerization and reaction, the apparent molecular weight of PEO segment can be calculated according to eqs 7 and 8:

$$M_{\mathrm{n(app)PEO,(St-MA-EO)}} = [5(I_{3.66} - 3I_{2.32})/4I_{7.32-6.30}] \times \mathrm{DP}_{\mathrm{St}} \times 44 + 15 \quad (7)$$

$$M_{\mathrm{n(app)PEO,(St-NIPAM-EO)}} = [5I_{3.64}/4I_{7.32-6.30}] \times \mathrm{DP}_{\mathrm{St}} \times 44 + 15 \quad (8)$$

Here $I_{3.66}$, $I_{3.64}$, $I_{7.32-6.30}$, and $I_{2.32}$ are the integral values of the peaks at 3.66, 3.64, 7.32−6.30, and 2.32 ppm, respectively; $\mathrm{DP}_{\mathrm{St}}$ are the number-average DP of St segment based on NMR data (no. 4 in Table 1). The efficiency of esterification can be estimated by the ratio of apparent and actual molecular weights. They are bigger than 90% (see Table 3), illustrating not only that the esterifications were almost completed but also that the MAh was successfully transferred to the end of the polySt chain.

Conclusions

A new synthetic route for preparation of ABC miktoarm star copolymers by the combination of the RAFT mechanism and the esterification reaction has been developed. PolySt was successfully capped by anhydride containing dithio transfer group in the reaction of polySt-S-C(S)Ph with MAh due to that MAh is nonhomopolymerizable, which provides a new easy way to prepare the polymers with terminal MAh-S-C(S)Ph. On the basis of NMR and GPC results, the terminal functionalities of MAh-S-C(S)Ph are around 95%. After the polymerization of MA or NIPAM via the RAFT process, diblock copolymers were obtained. Miktoarm triblock copolymers were finally prepared by the reaction of the anhydride group with the hydroxyl group of PEGM. The efficiencies of esterification are greater than 90%. The molecular weight distributions of ABC star copolymers are narrow (1.18−1.12).

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References and Notes

(1) Bates, F. S.; Fredrickson, G. H. *Phys. Today* **1999**, *52*, 32.
(2) Riess, G.; Schlienger, M.; Marti, S. *J. Macromol. Sci., Polym. Phys. Ed.* **1980**, *17*, 355.
(3) Kudose, I.; Kotaka, T. *Macromolecules* **1984**, *17*, 2325.
(4) Matsushite, Y.; Choshi, H.; Fujimoto, T.; Nagasawa, M. *Macromolecules* **1980**, *13*, 1053.
(5) Shibayama, M.; Hasegawa, H.; Hashimoto, T.; Kawai, H. *Macromolecules* **1982**, *15*, 274.
(6) Mogi, Y.; Nomura, M.; Kotsuji, H.; Ohnishi, K.; Matsushita, Y.; Noda, I. *Macromolecules* **1994**, *27*, 6755.
(7) Gido, S. P.; Schwark, D. W.; Thomas, E. L.; Gonclaves, M. C. *Macromolecules* **1993**, *26*, 2636.
(8) Goldacker, T.; Abetz, V.; Stadler, R.; Erukhimovich, I. Y.; Leibler, L. *Nature (London)* **1999**, *398*, 137.
(9) Pitsikalis, M.; Pispas, S.; Mays, J. W.; Hadjichritidis, N. *Adv. Polym. Sci.* **1998**, *135*, 1.
(10) Hadjichritidis, N.; Pispas, S.; Pitsikalis, M.; Vlahos, C.; Iatrou, H. *Adv. Polym. Sci.* **199**, *142*, 71.
(11) Hadjichritidis, N. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 857.
(12) Zioga, A.; Sioula, S.; Hadjichristidis, N. *Macromol. Symp.* **2000**, *157*, 239.
(13) Hückstädt, H.; Göpfert, A.; Abetz, V. *Macromol. Chem. Phys.* **2000**, *201*, 296.
(14) Beyer, F. L.; Gido, S. P.; Velis, G.; Hadjichristidis, N. *Macromolecules* **1999**, *32*, 6604.
(15) Sioula, S.; Hadjichristidis, N.; Thomas, E. L. *Macromolecules* **1998**, *31*, 5272.
(16) Sioula, S.; Hadjichristidis, N.; Thomas, E. L. *Macromolecules* **1998**, *31*, 8429.
(17) Okamoto, S.; Hasegawa, H.; Hashimoto, T.; Fujimoto, T.; Zhang, H.; Kazama, T.; Takano, A.; Isono, Y. *Polymer* **1997**, *38*, 5275.
(18) Pispas, S.; Hadjichristidis, N.; Potemkin, I.; Khokhlov, A. *Macromolecules* **2000**, *33*, 1741.
(19) Pispas, S.; Avgeropoulos, A.; Hadjichristidis, N.; Roovers, J. *J. Polym. Sci., Part B: Polym. Phys.* **1999**, *37*, 1329.
(20) Vlahos, C.; Hadjichristidis, N. *Macromolecules* **1998**, *31*, 6691.
(21) Lambert, O.; Jada, A.; Dumas, P. *Colloids Surf., A* **1998**, *136*, 263.
(22) Iatrou, H.; Hadjichristidis, N. *Macromolecules* **1992**, *25*, 4649.
(23) Sioula, S.; Tselikas, Y.; Hadjichristidis, N. *Macromolecules* **1997**, *30*, 1518.
(24) Fujimoto, T.; Zhang, H.; Kazama, T.; Isono, Y.; Hasegawa, H.; Hashimoto, T. *Polymer* **1992**, *33*, 2208.
(25) Hückstädt, H.; Abetz, V.; Stadler, R. *Macromol. Rapid Commun.* **1996**, *17*, 599.
(26) Quirk, R. P.; Yoo, T.; Lee, B. *J. Macromol. Sci. Pure Appl. Chem.* **1994**, *A31*, 911.
(27) Quirk, R. P.; Kim, Y. J. *Polym. Prepr.* **1996**, *37* (2), 643.
(28) Lambert, O.; Dumas, P.; Hurtrez, G.; Riess, G. *Macromol. Rapid Commun.* **1997**, *18*, 343.
(29) Lambert, O.; Reutenauer, S.; Hurtrez, G.; Riess, G.; Dumas, P. *Polym. Bull. (Berlin)* **1998**, *40*, 143.
(30) Lu, Z.; Chen, S.; Huang, J. *Macromol. Rapid Commun.* **1999**, *20*, 394.
(31) Feng, X. S.; Pan, C. Y. *Macromolecules* **2002**, *35*, 2084.
(32) Koulouri, E. G.; Kallistis, J. K. *Macromolecules* **1999**, *32*, 6242.
(33) Le, T. P.; Moad, G.; Rizzardo, E.; Thang, S. H. *PCT Int. Appl. WO* 9801478, *A1* 980115.
(34) Chiefari, J.; Chong, Y. K.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1998**, *31*, 5559.
(35) Chong, Y. K.; Le, T. P.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1999**, *32*, 2071.
(36) Goto, A.; Sato, K.; Tsujii, y.; Fukuda, T.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **2001**, *34*, 402.

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