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Synthesis of (ABCB)$_n$ type ternary amphiphilic multiblock copolymer via poly(ethylene oxide) macro-chain transfer agent

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Abstract

A novel (ABCB)$_n$ type ternary amphiphilic multiblock copolymer was synthesized by stepwise insertion of monomers into the trithiocarbonate-embedded poly(ethylene oxide) (PEO) macro-chain transfer agent (PEO-CTA)$_n$. (PEO-CTA)$_n$ was synthesized first by coupling of α,ω-dihydroxyl PEO with dicarboxylic trithiocarbonate, then styrene (St) and *t*-butyl acrylate (^{t}BA) were inserted into the (PEO-CTA)$_n$ successively to yield (PEO-*b*-PS)$_n$ and (PEO-*b*-PS-*b*-P^{t}BA-*b*-PS)$_n$, respectively. After hydrolysis of the (PEO-*b*-PS-*b*-P^{t}BA-*b*-PS)$_n$, the final product (PEO-*b*-PS-*b*-PAA-*b*-PS)$_n$ was obtained.

Keywords: Multiblock copolymer; Controlled radical polymerization; Poly(ethylene oxide) (PEO)

1. Introduction

Synthesis of structure-tailored copolymers is always pursued by polymer chemists for their synthetic challenges and their interesting physical properties in bulk and in solution [1,2]. Among them, linear multiblock copolymers, especially triblock copolymers have attracted considerable attention due to their synthetic convenience. By means of the sequential polymerization of three different monomers, linear triblock copolymer can be easily synthesized via conventional controlled radical polymerization or living anionic polymerization. For example, poly(*t*-butyl acrylate)-*b*-polystyrene-*b*-poly(4-vinylpyridine) and polystyrene-*b*-poly(2-vinyl pyridine)-*b*-poly(*t*-butyl methacrylate) can be prepared by living anionic polymerization [3,4], and polystyrene-*b*-polyacrylate-*b*-polyvinylpyridine can be prepared by atom transfer radical polymerization (ATRP) [5–7] or reversible addition–fragmentation chain transfer (RAFT) polymerization [8,9].

When the hydrophilic, pH-responsive or thermo-responsive blocks, especially the PEO block, are introduced in ABC type copolymers, abundant self-assembled aggregates with environmental multiple responsive could be observed in selective solvents [10,11], and the primary applications in metal nanoparticle fabrication [12–14] and pH-responsive particulate emulsifiers are exploited [15,16]. Moreover, latest researches indicate that multiblock copolymers such as [poly(L-lactic acid)-*b*-poly(ε-caprolactone)]$_n$ and [poly(ethylene oxide)-*b*-poly(methylphenylsilane)]$_n$ have shown some special crystallized and self-assembled behavior, respectively [17,18], and some of them such as [poly(L-lysine)-*b*-poly(ethylene oxide)]$_n$ are used as a non-viral gene carrier [19]. However, the construction of linear amphiphilic multiblock copolymers containing hydrophilic PEO segment is mostly confined to coupling reaction of different α,ω-bifunctional prepolymers. Generally, prepolymers with functional end groups are synthesized first and then coupled with another α,ω-bifunctional prepolymers [18–20]. Later, the multifunctional chain transfer agent (CTA) [21,22] and poly(alkoxyamine) [23,24] are synthesized and successfully used to prepare the binary multiblock copolymers as [poly(*n*-butyl acrylate)-*b*-poly(isooctyl

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acrylate)]$_n$ and [poly(styrene)-*b*-poly(*p-tert*-butoxystyrene)]$_n$ via control/"living" radical polymerization. The synthesis of amphiphilic multiblock copolymers as (PEO-*b*-PS-*b*-P^{t}BA-*b*-PS)$_n$ and further product (PEO-*b*-PS-*b*-PAA-*b*-PS)$_n$, however, are still scarcely reported up to now. This kind of copolymer may show some special self-assembly morphologies which can also be used as templates for the preparation of metal nanoparticles due to the presence of PAA blocks [25,26].

Herein, we describe a universal method to synthesize the linear (ABCB)$_n$ type amphiphilic ternary multiblock copolymer (PEO-*b*-PS-*b*-PAA-*b*-PS)$_n$ by using trithiocarbonate-embedded PEO as macro-chain transfer agent.

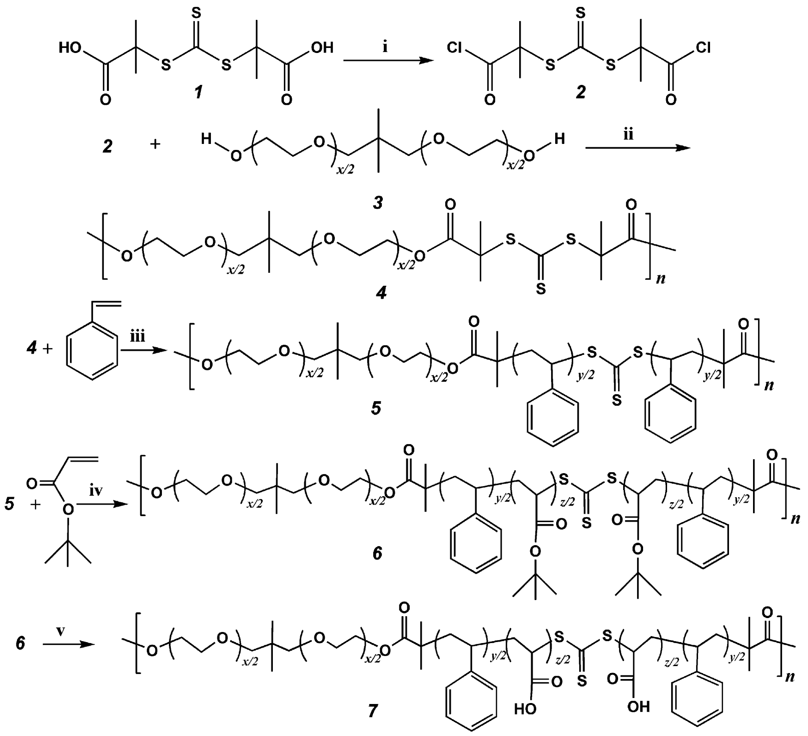
2. Experimental part

2.1. Materials

Pyridine and dioxane are distilled in the presence of sodium and dichloromethane is dried with CaH_2 and distilled before use. AIBN is recrystallized from the ethanol twice. Styrene (St) and *t*-butyl acrylate (^{t}BA) are dried with CaH_2 and distilled under reduced pressure before use. 2,2-Dimethyl-1,3-propanediol (99%), diphenylmethane (99%), thionyl chloride ($SOCl_2$) and other common agents and solvents are purchased from Sinopharm Chemical Reagent Co., Ltd (SRC) and purified by standard procedure. Trifluoroacetic acid (99%) (SRC) was used as received. CTA *S*,*S*′-bis(α,α′-dimethyl-α″-acetic acid)-trithiocarbonate (BDATC) **1** (see Scheme 1) is synthesized according to the previous report [27]. IR (KBr): 1700 (s, C=O), 1062 (s, C=S), 804 cm^{-1} (s, C–S). ^{1}H NMR (DMSO-d_6): $\delta = 1.59$ (s, 12H, $-(S-(CH_3)_2C-COOH)_2$), 12.92 (s, 2H ($-COOH)_2$). $C_9H_{14}O_4S_3$ (228.01): Calcd. C, 38.28; H, 5.00; S, 34.06. Found C, 38.17; H, 4.92; S, 34.21. α,ω-Dihydroxyl poly(ethylene oxide) **3** (see Scheme 1) is synthesized by using 2,2-dimethyl-1,3-propanediol and diphenylmethyl potassium in THF as co-initiator according to the Gnanou's method [28]. ^{1}H NMR ($CDCl_3$): $\delta = 3.2$ (s, 6H, $(CH_3)_2C(CH_2)_2O-$), 3.6 (b, 4H, $(CH_2CH_2O)_n$, PEO backbone), 0.88 (m, 4H, $(CH_3)_2C(CH_2)_2O-$), the number average molecular weight M_n of the obtained α,ω-dihydroxyl PEO is 2.3×10^3 and the polydispersity index M_w/M_n is 1.12.

2.2. Measurements

The number average molecular weight M_n and polydispersity index M_w/M_n are measured by gel permeation chromatography (GPC). For the α,ω-dihydroxyl PEO precursor and PEO macro-CTA, GPC is performed in 0.1 M $NaNO_3$ aqueous solution at 40 °C with an elution rate of 0.5 mL/min on an Agilent 1100 with a G1310A pump, a G1362A refractive index detector, and a G1315A diode-array detector. PEO standard samples are used for calibration. GPC traces of the binary and ternary multiblock copolymers are performed in tetrahydrofuran (THF) at 35 °C with an elution rate of 1.0 mL/min on an Agilent1100 with a G1310A pump, a G1362A refractive index detector, and a G1314A variable wavelength detector. Polystyrene standard samples are used for calibration. ^{1}H NMR spectra are obtained by a DMX 500 MHz spectrometer



Scheme 1. Schematic synthesis route of ternary multiblock copolymer (i) $SOCl_2$, 60 °C, 1 h; (ii) pyridine, 0 °C, 24 h; (iii) dioxane, AIBN (10 mol% eq. vs the trithiocarbonate groups in **4**); (iv) dioxane, AIBN (10 mol% eq. vs the trithiocarbonate groups in **5**); (v) CH_2Cl_2, triflouroacetic acid (5 eq. vs the ^{t}BA units in **6**) 25 °C, 24 h.

with tetramethylsilane (TMS) as the internal standard and $CDCl_3$ as the solvent except in some specified cases. Infrared spectra (IR) are recorded on Magna 550 FT-IR instrument (KBr pellets). The Ultra Filtration Membrane Separator is purchased from Shanghai Institute of Applied Physics, Chinese Academy of Science, the cut-off molecular weight of used poly(ether sulfone) film: $M_{\mathrm{w\ cut\ off}} = 20,000$ (calibrated by globin).

2.3. Synthesis and purification of trithiocarbonate-embedded PEO macro-CTA [(PEO-CTA)$_n$]

In a round-bottom flask, 7.2 g (3.1×10^{-3} mol) **3** (see Scheme 1) is dissolved in 100 mL toluene, after azeotropic distillation to remove the water, the 60 mL dry pyridine is added to dissolve the PEO and the flask is sealed with septum, and the solution is cooled in ice-water bath. To another one-neck flask, 1.0 g (3.5×10^{-3} mol) **1** (see Scheme 1) and 50 mL $SOCl_2$ are introduced. After stirring at 60 °C for 1 h, the excessive $SOCl_2$ is distilled, the remains are dissolved in 20 mL dry CH_2Cl_2 and added dropwise to the PEO solution with vigorous stirring. After continuously stirring for 24 h at 0 °C, the product is filtered to remove the pyridine chloride and precipitated twice in excess diethyl ether, the filtered solid is dried in vacuo. The purification of the obtained product is performed by dissolution of the product in water and then separating by ultra filtration membrane separator. The separated aqueous solution is extracted by chloroform thrice and the organic phase is collected and dried over anhydrous $MgSO_4$. Then the filtrate is concentrated to about 10 m Land precipitated in about 50 mL diethyl ether, the solid filtered is dried in vacuo for 24 h to give 1.9 g purified product. ^{1}H NMR ($CDCl_3$): $\delta = 3.2$ (s, 6H, $(CH_3)_2C(CH_2)_2O$–), 3.6 (b, 4H, $(CH_2CH_2O)_n$, PEO backbone), 0.88 (s, 4H, $(CH_3)_2C(CH_2)_2O$–), 1.66 (s, 12H, –S–$(CH_3)_2C$–COO–).

2.4. Synthesis of multiblock copolymer (PEO-b-PS)$_n$

Typically, styrene (1 mL, 8.75×10^{-3} mol), macroinitiator (PEO-CTA)$_n$ (150 mg, 1.06×10^{-5} mol, containing 6.89×10^{-5} mol trithiocarbonate groups), AIBN solution (2.2 mL, 0.5 mg/mL in dioxane, 6.90×10^{-6} mol, 10 mol% eq. vs the trithiocarbonate groups of (PEO-CTA)$_n$) are added to an ampoule successively, followed by three freeze–pump–thaw cycles. The reaction is conducted at 80 °C for 6 h and then ampoule is quenched in liquid nitrogen, the contents are precipitated twice in petroleum ether, separated by centrifugation, and dried in vacuo at 40 °C for 24 h to give 0.45 g of the white powder (yield 86%).

2.5. Synthesis of multiblock copolymer (PEO-b-PS-b-PAA-b-PS)$_n$

Typically, ^{t}BA (0.4 mL, 2.73×10^{-3} mol), (PEO-*b*-PS)$_n$ (135 mg, 4.22×10^{-6} mol, containing 2.74×10^{-5} mol trithiocarbonate groups), AIBN solution (0.9 mL, 0.5 mg/mL in dioxane, 2.74×10^{-6} mol, 10 mol% eq. vs the trithiocarbonate groups of (PEO-*b*-PS)$_n$) are added to an ampoule successively. Then the ampoule is vacuumed by three freeze–pump–thaw cycles under liquid nitrogen temperature. The polymerization is carried out at 80 °C for 10 h and then the ampoule is quenched in liquid nitrogen, the contents are precipitated twice in heptane and centrifugated, then the remains are dried under vacuum at 40 °C for 24 h and 0.41 g of the rubbery solid is formed. The further hydrolysis was carried out in a 5 mL flask, (PEO-*b*-PS-*b*-P^{t}BA)$_n$ (112 mg) was dissolved in 2 mL CH_2Cl_2, and trifluoroacetic acid (0.34 g, 3.0×10^{-3} mol, 5 eq. vs the ^{t}BA units) was added. The mixture was stirred at room temperature for 24 h. Subsequently, solvent and CF_3COOH were removed by rotating evaporation, the remains were dissolved in 0.5 mL THF, precipitated twice in petroleum ether and centrifugated, the solid was dried in vacuo at 40 °C for 24 h to give the white powdery (PEO-*b*-PS-*b*-PAA)$_n$ (65 mg, yield 83%).

3. Results and discussion

3.1. Synthesis of trithiocarbonate-embedded PEO macro-CTA [(PEO-CTA)$_n$]

In early reports, PEO is often chosen as one of the blocks in triblock copolymer due to its recognized biocompatibility and solubility in both aqueous and organic media [29,30]. The macro-CTA based PEO with monofunctional end group and bis-functional end groups are synthesized and used to control the polymerization of different monomers to yield linear triblock copolymers [31,32]. In this presentation, the dicarboxyl trithiocarbonate *S*,*S*′-bis(α,α′-dimethyl-α″-acetic acid)-trithiocarbonate (BDATC) **1** was converted to BDATC-acetyl chloride **2** (see Scheme 1) first, then the α,ω-dihydroxyl PEO **3** is reacted with **2**, the obtained trithiocarbonate-embedded multifunctional PEO macro-CTA **4** is used to synthesize the amphiphilic binary multiblock copolymer (PEO-*b*-PS)$_n$ **5**, and further to mediate the polymerization of third monomer ^{t}BA to obtain the ternary multiblock copolymer (PEO-*b*-PS-*b*-P^{t}BA-*b*-PS)$_n$ **6**. The whole procedure is outlined in Scheme 1. The molecular weight and chemical composition are listed in Table 1.

Fig. 1A shows the GPC trace of the α,ω-dihydroxyl PEO precursor **3** used in this work, its M_n (GPC)$_3$ is 2300 g/mol and M_w/M_n is 1.12. After coupling with **2** and separation to remove the byproduct of lower molecular weight formed by the partial acidolysis of PEO, the PEO macro-CTA **4** (named as (PEO-CTA)$_n$) is obtained as Fig. 1B shows. Its M_n (GPC)$_4$ is 14,200 g/mol and M_w/M_n is 1.60 (Table 1). Thus the average block number of PEO can be calculated by comparing the molecular weight of (PEO-CTA)$_n$ with that of α,ω-dihydroxyl PEO precursor, it is 6.2.

Typical ^{1}H NMR spectra of the macro-CTA (PEO-CTA)$_n$ and binary multiblock copolymer (PEO-*b*-PS)$_n$ are given in Fig. 2A and B, respectively. It was observed that all the data of the characteristic peaks as the signals at 3.6 ppm for the PEO units, at 0.88 and 3.20 ppm for the methyl and methylene groups respectively in the middle of the PEO chains, at

Table 1
GPC and ^{1}H NMR data of the ternary amphiphilic multiblock copolymer and its precursors

Sample		Time[a] (h)	Conv[b] (%)	GPC		^{1}H NMR[c]			
				M_n (g/mol)	M_w/M_n	M_n (g/mol)	wt% PEO	wt% PS	wt% TB[d]
3	PEO			2300	1.12				
4	(PEO-CTA)$_n$			14,200	1.60				
5	(PEO-*b*-PS)$_n$	6	21	19,000	1.43	32,000	44.4	55.6	
6	(PEO-*b*-PS-*b*-P^{t}BA-*b*-PS)$_n$	10	76	43,000	1.45	96,000	14.8	18.5	66.7
7	(PEO-*b*-PS-*b*-PAA-*b*-PS)$_n$					71,000	20.0	25.1	54.9

[a] Polymerization time of St and ^{t}BA.

[b] The conversion was calculated based on the gravimetrical method.

[c] Calculated based on Eqs. (1)–(3).

$$\overline{M}_n(\mathrm{NMR})_5 = (4I_{6.22-7.22}/5I_{3.65}) \times (104/44) \times \overline{M}_n(\mathrm{GPC})_4 + \overline{M}_n(\mathrm{GPC})_4 \tag{1}$$

$$\overline{M}_n(\mathrm{NMR})_6 = (4I_{2.22}/I_{3.65}) \times (128/44) \times \overline{M}_n(\mathrm{GPC})_4 + \overline{M}_n(\mathrm{NMR})_5 \tag{2}$$

$$\overline{M}_n(\mathrm{NMR})_7 = \left[4(I_{1.20-2.40} - 3I_{6.20-7.20}/5)/3I_{3.65}\right] \times (72/44) \times \overline{M}_n(\mathrm{GPC})_4 + \overline{M}_n(\mathrm{NMR})_5 \tag{3}$$

Here $I_{3.65}$ is the integral value of peak at 3.65 ppm. $I_{6.22-7.22}$, $I_{2.22}$ and $I_{1.20-2.40}$ are the integral values of peaks at 6.22–7.22, 2.22, and 1.20–2.40 ppm in Figs. 2B, 4A and B, respectively. $\overline{M}_n(\mathrm{GPC})_4$ is the molecular weights of (PEO-CTA)$_n$. While 44, 104, 128 and 72 are the molecular weights of EO, St, ^{t}BA and AA monomers, respectively.

[d] The third block is P^{t}BA or PAA.

1.66 ppm for methyl group of BDTAC and the triplet at 4.25 for the protons of methylene of PEO adjacent to the oxygen atom of the ester bond demonstrated the successful coupling of PEO with BDTAC. Indeed, in its IR spectrum as shown in Fig. 3A, the appearance of typical C=O, C=S and −C−O−C− stretching bands at 1731, 1046 and 1100 cm^{-1}, respectively, also implies the formation of macro-CTA agent. Additionally, the number of trithiocarbonates (N_T) in macro-CTA could be calculated by the comparison of the peak integral area of methyl groups at 0.88 ppm ($I_{0.88}$) located in the middle of PEO with that of methyl groups at 1.66 ppm ($I_{1.66}$) for the methyl group of BDATC as Eq. (4) showed; it was about 6.5 for (PEO-CTA)$_n$.

$$N_T = \frac{6.2I_{1.66}}{I_{0.88}} \tag{4}$$

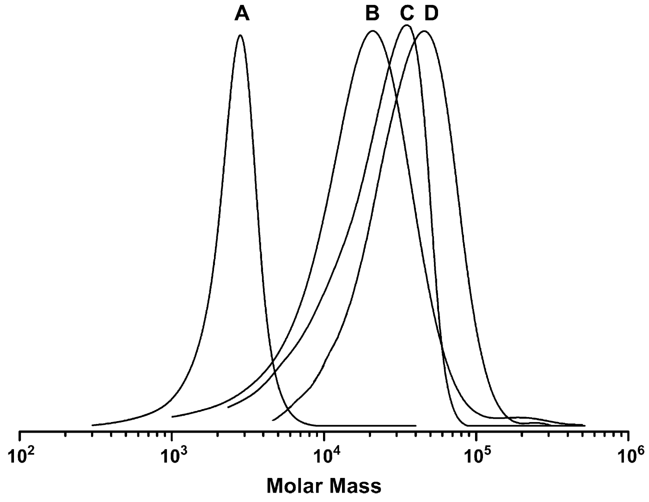


Fig. 1. GPC traces of (A) linear α,ω-dihydroxyl PEO, (B) macro-CTA (PEO-CTA)$_n$, (C) binary amphiphilic multiblock copolymer (PEO-*b*-PS)$_n$ and (D) ternary amphiphilic multiblock copolymer (PEO-*b*-PS-*b*-P^{t}BA-*b*-PS)$_n$.

Actually, as Fig. 1 shows that the polydispersity index of (PEO-CTA)$_n$ is wide (M_w/M_n 1.60), the number of trithiocarbonates in (PEO-CTA)$_n$ is in the range of 3–25, and 6.5 is only an average number of trithiocarbonates derived from the number average molecular weight of (PEO-CTA)$_n$.

3.2. Synthesis of binary multiblock copolymer (PEO-b-PS)$_n$

The macro-CTA (PEO-CTA)$_n$ is used to mediate the polymerization of styrene to yield the (PEO-*b*-PS)$_n$ **5** as Fig. 1C shows, its M_n (GPC)$_5$ equals to 19,000 g/mol and M_w/M_n is 1.43 (Table 1). The low polydispersity index relative to the macro-CTA and the unimodal GPC traces indicate that the

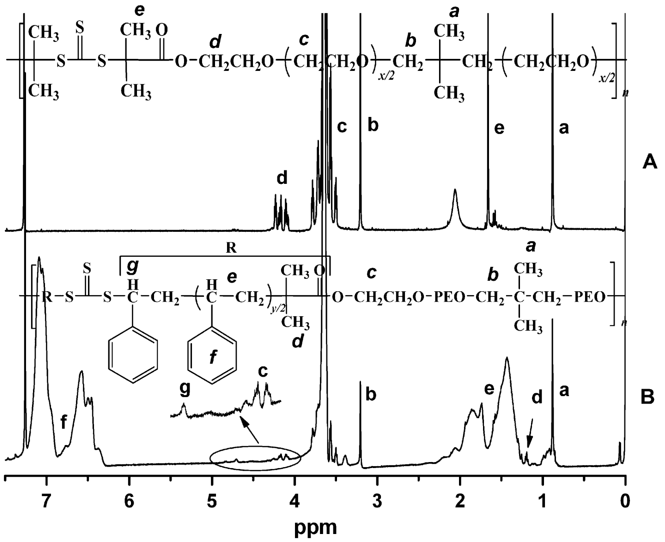


Fig. 2. ^{1}H NMR spectra of (A) macro-CTA (PEO-CTA)$_n$ and (B) binary amphiphilic multiblock copolymer (PEO-*b*-PS)$_n$.

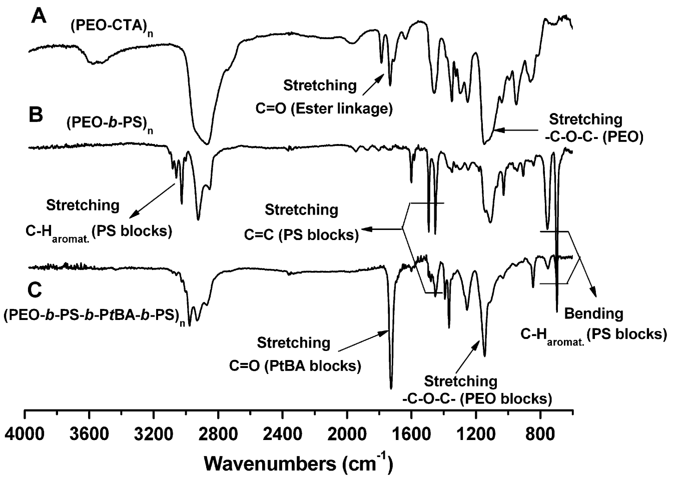


Fig. 3. FT-IR spectra of (A) macro-CTA (PEO-CTA)$_n$, (B) binary amphiphilic multiblock copolymer (PEO-*b*-PS)$_n$ and (C) ternary amphiphilic multiblock copolymer (PEO-*b*-PS-*b*-P^{t}BA-*b*-PS)$_n$.

polymerization of St mediated by the macro-CTA is under control. It was observed that an obvious tailing with low molecular weight was detected from Fig. 1C, it may be caused by the coupling of some propagating chain radicals with AIBN end groups each other to form some dead polymer. In Fig. 2B, a new peak at 4.50–4.70 ppm corresponding to the methine protons in the St unit adjacent to trithiocarbonate groups appeared besides the characteristic signals at 1.27–2.25 and 6.27–7.22 ppm. It is found that the distinct peak of methyl protons of BDATC shifts from 1.66 ppm for (PEO-CTA)$_n$ to 1.25 ppm for (PEO-*b*-PS)$_n$ because of the change of carbon–sulfur bond to carbon–carbon bond of the tertiary carbon. The initiating efficiency of trithiocarbonates in (PEO-CTA)$_n$ (E_{T1}) can be calculated by comparison of integral values of signal at 4.50–4.70 ppm ($I_{4.50-4.70}$) with the signal at 4.25 ppm ($I_{4.25}$) ascribed to the methylene protons of PEO adjacent to the oxygen atom of ester linkages in Fig. 2B (Eq. (5)), the value

$$E_{\mathrm{T1}} = \frac{2I_{4.50-4.70}}{I_{4.25}} \tag{5}$$

was about 90%. Thus it was confirmed that most trithiocarbonates in macro-CTA participated in the RAFT polymerization of St.

The IR spectrum of (PEO-*b*-PS)$_n$ is shown in Fig. 3B, the characteristic bands of PS blocks (C=C$_{\mathrm{aromat}}$ stretching at 1450–1600 cm^{-1}, C–H$_{\mathrm{aromat}}$ stretching at 3020–3080 cm^{-1}, C–H$_{\mathrm{aromat}}$ bending at 690–754 cm^{-1}) indicate the successful polymerization of St monomer.

3.3. Synthesis of ternary multiblock copolymer (PEO-b-PS-b-PAA-b-PS)$_n$

The (PEO-*b*-PS-*b*-P^{t}BA-*b*-PS)$_n$ **6** is prepared by using (PEO-*b*-PS)$_n$ as RAFT agent to mediate the polymerization of ^{t}BA. It should be noted that the trithiocarbonate selected in this work is symmetrical, when the third monomer ^{t}BA is polymerized, the resulted P^{t}BA block is inserted into the PS block, and (PEO-*b*-PS)$_n$ is changed to (PEO-*b*-PS-*b*-P^{t}BA-*b*-PS)$_n$ (Scheme 1). Fig. 1D shows the GPC curve of the copolymer **6**, the molecular weight M_{n} (GPC)$_6$ is 43,000 g/mol and the polydispersity is about 1.45, the latter does not change much when compared to the value of (PEO-*b*-PS)$_n$ (PDI: 1.43), which means that the polymerization of the third monomer ^{t}BA is still under control. Fig. 4A is the ^{1}H NMR spectra of the ternary multiblock copolymer **6**, the new peak at 2.22 ppm corresponding to the methine proton on the main chain of ^{t}BA units appears besides the characteristic signals of EO at 3.65 ppm and St units at 6.22–7.22 ppm. Additionally, in Fig. 4A, beside the appearance of methylene protons (**c**) of PEO adjacent to the oxygen atom of ester linkages at 4.25 ppm, signal at 4.60–4.70 ppm ascribed to the methine protons (**h**) of ^{t}BA units adjacent to trithiocarbonate groups could be also be observed. Based on the comparison of the

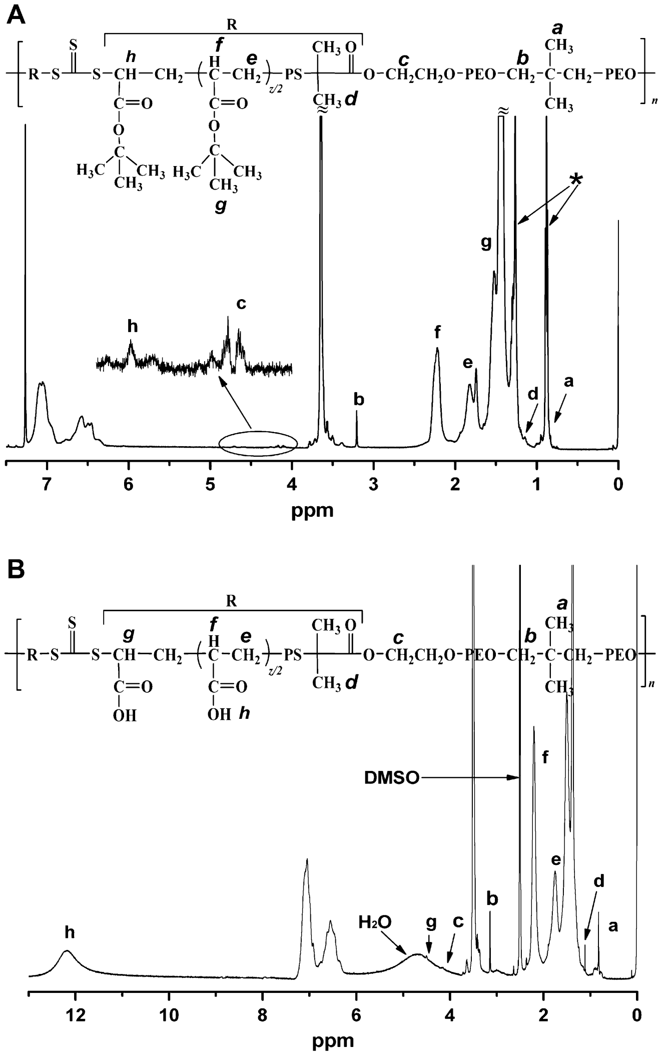


Fig. 4. ^{1}H NMR spectra of ternary amphiphilic multiblock copolymer (A) (PEO-*b*-PS-*b*-P^{t}BA-*b*-PS)$_n$ (the signals indicated as "*" at 0.9 and 1.29 ppm were assigned to the remnant heptane) and (B) (PEO-*b*-PS-*b*-PAA-*b*-PS)$_n$ (DMSO-d_6 as solvent).

integral values of signal **h** ($I_{4.60-4.70}$) with that of **c** ($I_{4.25}$), the initiating efficient (E_{T2}) of trithiocarbonates in (PEO-*b*-PS)$_n$ can also be calculated by Eq. (6):

$$E_{T2} = \frac{2I_{4.60-4.70}}{I_{4.25}} \tag{6}$$

the value of E_{T2} was about 72%, which was lower than that of the (PEO-CTA)$_n$ because of the space hindrance in the case of (PEO-*b*-PS)$_n$. The IR spectrum of (PEO-*b*-PS-*b*-P^{t}BA-*b*-PS)$_n$ is shown in Fig. 3C, except the typical absorption peaks of PS blocks (C=C$_{\text{aromat}}$ stretching at 1450–1600 cm^{-1}, C–H$_{\text{aromat}}$ stretching at 3020–3080 cm^{-1}, C–H$_{\text{aromat}}$ bending at 690–754 cm^{-1}) and PEO blocks (stretching band at 1100 cm^{-1}), a strong peak at 1727 cm^{-1} for P^{t}BA block (C=O stretching band) is observed. It is confirmed that the chemical components of desired ternary multiblock copolymer are synthesized successfully. After hydrolysis of P^{t}BA blocks of (PEO-*b*-PS-*b*-P^{t}BA-*b*-PS)$_n$, the amphiphilic multiblock copolymer (PEO-*b*-PS-*b*-PAA-*b*-PS)$_n$ was obtained. Fig. 4B shows the ^{1}H NMR spectrum of **7** (DMSO-d_6 as solvent), the appearance of a new broad peak at 12.23 ppm belonging to the protons of carboxyl groups and the decrease of the peak strength at 1.44 ppm overlapped with methylene protons of St units assigned to the methyl protons of ^{t}BA units confirmed the successful hydrolysis of the ester groups of ^{t}BA units. Meanwhile, the weight percentage (wt%) of every blocks in (PEO-*b*-PS-*b*-PAA-*b*-PS)$_n$ and its precursors can be calculated from ^{1}H NMR spectra and the results are listed in Table 1. In the final product, 20 wt% PEO blocks, 25.1 wt% PS blocks and 54.9 wt% PAA blocks were achieved.

4. Conclusion

In conclusion, a novel strategy for synthesis of (ABCB)$_n$ ternary amphiphilic multiblock copolymer is described. Trithiocarbonate-embedded PEO macro-CTA is synthesized first via coupling reaction procedure and is employed to control the polymerization of St and ^{t}BA successively. The resulting ternary amphiphilic multiblock copolymer (PEO-*b*-PS-*b*-PAA-*b*-PS)$_n$ and its corresponding precursors is well characterized by the IR, GPC and ^{1}H NMR. The unimodal GPC traces and narrow polydispersity indicated that the synthesis of this type of copolymer is under controlled.

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