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An all ATRP route to PMMA–PEO–PS and PMAA–PEO–PS miktoarm ABC star terpolymer

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ABSTRACT

An all Atom Transfer Radical Polymerization (ATRP) route to synthesize miktoarm ABC star terpolymer, μ-(poly(methyl methacrylate)–poly(ethylene oxide)–polystyrene) (μ-(PMMA–PEO–PS)), was demonstrated. Poly(methyl methacrylate) (PMMA) with a halide end group was first prepared by ATRP of MMA. It was then activated under ATRP conditions at 30 °C to add a styrenic-terminated PEO macromonomer, resulting in the formation of PMMA-*b*-PEO. Finally, the active halide at the junction point of the diblock copolymer was used to initiate the ATRP of St at higher temperature. By a similar approach, μ-(poly(phenyl methacrylate)–poly(ethylene oxide)–polystyrene) (μ-(PhMA–PEO–PS)) was synthesized, hydrolysis of which in basic medium gave μ-(PMAA–PEO–PS). The polymers were characterized by ^{1}H NMR spectroscopy and gel permeation chromatography.

1. Introduction

For the past decades, much interest has been directed to investigate the synthesis and properties of miktoarm star (μ-star) copolymers which consist of chemically different branches connected to a common junction. Among these μ-stars, ABC μ-star terpolymers are noticeable due to the distinct properties and challenges in synthesis compared to that of ABC linear block copolymers [1,2]. These ABC μ-stars were mostly prepared by anionic polymerization, such as coupling three different types of polymer chains to a linking agent; or using the 'capping agent' strategy based on 1,1-diphenylethylene (DPE) and its derivatives [3–10]. While these methods are very useful in preparation of well-defined ABC μ-star polymers, they show disadvantages of limited kinds of monomers and rigorous operations associated with anionic polymerization.

Combination of different living polymerization methods, especially with the controlled/living radical polymerization (CRP) [11–14], has expanded the availability of ABC μ-star polymers [15–17]. When these polymerization methods were coupled with the effective "click chemistry", more new ABC μ-star polymers have been prepared [18,19].

Here, we report a new method to synthesize ABC μ-star terpolymer consisting of poly(methyl methacrylate) (PMMA), poly(ethylene oxide) (PEO) and polystyrene (PS). To the best of our knowledge, this method was the first report to construct the stable joint core using ATRP only. The concept is similar to the DPE method in anionic polymerization and is based on control of the activation/deactivation process of ATRP for different initiating species at different temperatures. This method can be extended to other monomers, which makes it useful to prepare new ABC star terpolymers. As one example, μ-(PMAA–PEO–PS) was also prepared by this method. Considering the pH-responsive nature of PMAA block and its ability to form hydrogen bond with PEO, the property and self-assembly of μ-(PMAA–PEO–PS) in aqueous solution will be very interesting.

2. Experimental

2.1. Materials

4-Vinylbenzyl chloride (90%, Acros), poly(ethylene glycol) monomethyl ether (PEO2000, $M_n = 2000$, and PEO5000, $M_n = 5000$, Fluka), phenol (AR, Beijing Duxin Chemical Company), copper(I) bromide (CuBr, 99.999%, Aldrich), copper(II) bromide ($CuBr_2$, 99%, Aldrich), copper(II) chloride ($CuCl_2$, 99.99%, Aldrich), α-bromo isobutyryl bromide (98%, Aldrich), ethyl α-bromo isobutyrate (EBiB, 98%, Aldrich) and *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA, 99%, Aldrich) were used as received. *p*-Toluenesulfonyl chloride (*p*-TsCl, CP, Beijing Chemical Works) was recrystallized from petroleum ether and dried under vacuum. Copper(I) chloride (CuCl, 99.995%, Aldrich) was washed

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with acetic acid, ethanol and ethyl ether followed by drying under vacuum. Triethylamine (CP, Beijing Chemical Works) was dried with KOH and distilled before use. Methyl methacrylate (MMA) and styrene (St) were first washed with 2 mol/L NaOH solution, dried and distilled over CaH_2 under reduced pressure. Acetone was purified by refluxing with $KMnO_4$, dried with anhydrous K_2CO_3 and distilled. Chlorobenzene was washed with sulfuric acid, saturated $NaHCO_3$ and water, dried with P_2O_5 and distilled. Methacryloyl chloride and phenyl α-bromo isobutyrate (PhBiB) were prepared by literature methods [20,21].

2.2. Measurements

Molecular weight and molecular weight distribution were measured with a gel permeation chromatography (GPC) equipped with a 2410 refractive index detector, a Waters 515 HPLC pump, and three Waters Styragel Columns (1×10^4, 1×10^3 and 500 Å pore sizes). The columns were thermostated at 35 °C and tetrahydrofuran (THF) was used as an eluent at a flow rate of 1 mL/min. Against the calibration with standard monodisperse polystyrene, the obtained datum was processed on professional software (Millennium 32). NMR spectra were recorded in $CDCl_3$, acetone-d_6 or DMSO-d_6 on a Bruker ARX-400 spectrometer or a Varian Gemini 300 spectrometer, and tetramethylsilane (TMS) was used as the internal reference for chemical shifts. IR spectra were obtained using a Nicolet Magna-IR 750 Fourier Transform Infrared spectrometer. Matrix assisted laser desorption/ionization time-of-flight mass spectrometry (MALDIToF MS) was performed on a Bruker Biflex III spectrometer equipped with a 337 nm nitrogen laser. Matrix 2-indoleacrylic acid (IAA), cation source NaI and polymer sample was dissolved in acetone at a concentration of 10 mg/mL, 20 mg/mL and 4 mg/mL, respectively. The solution was mixed at a volume ratio of 20/1/1 and then one drop of this mixture solution was placed on a metal sample plate to dry at room temperature. Mass spectrum was acquired in positive linear mode at an acceleration voltage of 19 kV.

2.3. Synthesis of phenyl methacrylate (PhMA)

To the solution of phenol (60 g, 0.64 mol) and triethylamine (70 mL, 0.5 mol) in 150 mL of THF, methacryloyl chloride (46 mL, 0.48 mol) was added with a dropping funnel at 0 °C. The mixture was stirred at room temperature for 24 h. The triethylammonium chloride was filtered out and the solution was washed with 1 M NaOH, 1 M HCl solution and water, followed by drying with anhydrous $CaCl_2$. The product was obtained after vacuum distillation with a yield of 65%. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 7.40 (t, 2H), 7.26 (t, 1H), 7.14 (d, 2H), 6.35 (s, 1H), 5.75 (s, 1H), 2.06 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm): 165.96 (C-3), 150.96 (C-2), 135.91 (C-1), 129.44 (C-4), 127.27 (C-5), 125.77 (C-6), 121.63 (C-7), 18.31 ($-CH_3$).

2.4. Synthesis of styrenic-terminated PEO macromonomer (St-PEO2000 and St-PEO5000) [22]

Take the synthesis of St-PEO2000 as an example. PEO2000 (20 g, 10 mmol) was dissolved in THF (100 mL), and then NaH (50%, 1.2 g, 25 mmol) was added. The mixture was stirred at 40 °C for 4 h, 4-vinylbenzyl chloride (2 g, 12 mmol) was then added and the reaction was left overnight at 30 °C. The reaction mixture was neutralized with HCl, concentrated and the product was precipitated from ethyl ether for 3 times and dried under vacuum. 16.2 g of St-PEO2000 was obtained with a yield of 81%. ^{1}H NMR (400 MHz, $CDCl_3$, Fig. S1): δ (ppm): 3.38 (s, 3H), 3.66 (s, 180H), 4.55 (s, 2H), 5.23 (d, 1H), 5.74 (d, 1H), 6.70 (q, 1H), 7.34 (d, 2H), 7.38 (d, 2H). St-PEO5000 was synthesized from PEO5000 by a similar approach with a yield of 90%.

2.5. Synthesis of PMMA macroinitiators (PMMA–Br and PMMA–Cl) by ATRP

To a self-made long-necked tube equipped with a stirring bar, $CuBr_2$ (0.035 g, 0.16 mmol), PhBiB (0.389 g, 1.60 mmol), MMA (16 g, 0.16 mol), acetone (16 mL) and PMDETA (190 μL, 0.48 mmol) were charged. Three freeze–pump–thaw cycles were conducted after the $CuBr_2$ was dissolved in the mixture under stirring. The tube was backfilled with N_2, opened, and CuBr (0.046 g, 0.32 mmol) was added immediately. The tube was sealed under vacuum after another freeze–pump–thaw cycle. The polymerization was carried out at 60 °C for 5 h and terminated by quenching in liquid nitrogen. After removing the catalysts by passing through a short neutral Al_2O_3 column, the polymer solution was concentrated and precipitated in petroleum ether for three times, and one time in methanol to recover PMMA–Br with a yield of 31%. **M-1**: $M_{n,GPC} = 3800$, $M_w/M_n = 1.09$.

The macroinitiator PMMA–Cl was synthesized according to the above procedure with *p*-TsCl as the initiator, CuCl/$CuCl_2$ as the catalyst, at 60 °C for 5 h. The recipe for the polymerization was: *p*-TsCl (0.304 g, 1.60 mmol), MMA (16 g, 0.16 mol), PMDETA (192 μL, 0.88 mmol), $CuCl_2$ (0.010 g, 0.080 mmol), CuCl (0.079 g, 0.80 mmol), acetone (16 mL). The polymer was precipitated in methanol. **M-2**: yield = 52%, $M_{n,GPC} = 7200$, $M_w/M_n = 1.07$.

2.6. Synthesis of PMMA-b-PEO

The reaction tube was charged with PMMA macroinitiator (**M-1**, 1.5 g, 0.38 mmol), St-PEO2000 (1.1 g, 0.55 mmol), $CuBr_2$ (0.017 g, 0.076 mmol), PMDETA (0.23 mmol), acetone (25.2 mL) and CuBr (0.022 g, 0.15 mmol), and was sealed under vacuum following the operation as in the synthesis of **M-1**. The reaction was kept at 30 °C for 20 h. After removal of the catalyst, the solution was condensed and precipitated in cold methanol (−20 °C to 15 °C), polymer was recovered through centrifugation. The procedure was repeated for three times to remove the unreacted St-PEO2000 macromonomer completely as monitored by GPC and NMR spectroscopy. Unreacted **M-1** was removed by passing the polymer solution through a short silica column eluted with ethyl acetate and finally with methanol/acetone ($V/V = 2/1$). The eluent was condensed and precipitated in petroleum ether to get the purified diblock copolymer by filtration. **D-1**: yield = 30%, $M_{n,GPC} = 7100$, $M_w/M_n = 1.07$.

D-2 was synthesized and purified according to the same procedure as for **D-1** with **M-2** as the macroinitiator and PMDETA/CuBr/$CuBr_2$ as the catalyst. **D-2**: yield = 43%, $M_{n,GPC} = 10{,}900$, $M_w/M_n = 1.06$.

2.7. Synthesis of μ-(PMMA–PEO–PS)

With the same procedure aforementioned, **D-1** and **D-2** coupled with catalyst (CuBr for **D-1**, CuCl for **D-2**) and PMDETA were used to initiate the bulk ATRP of styrene at 90 °C (**D-1**) and in chlorobenzene at 110 °C (**D-2**), respectively. Product from **D-1** was precipitated in methanol to get the star terpolymer (**T-1**). For the product from **D-2**, fractionation was performed with THF and methanol as the solvent/non-solvent pair. The final product was dissolved in THF at a concentration of 10 mg/mL and methanol was added slowly under stirring until just appearance of precipitate, the precipitate (**T-2**) was separated by filtration and dried under vacuum. The yield of **T1** and **T2** were 10% and 22%, respectively.

2.8. Synthesis of μ-(PMAA–PEO–PS)

PhMA was first polymerized under similar ATRP conditions as for the preparation of **M-2** to get PPhMA-Cl. Then it was used as a macroinitiator to add one St-PEO5000 under atom transfer radical addition (ATRA) condition at 30 °C, the crude PPhMA-*b*-PEO was purified by silica column to remove the unreacted PPhMA-Cl (eluted with ethyl acetate), and then by alumina column to remove the excess St-PEO5000 (eluted with ethanol). In both cases, PPhMA-*b*-PEO was recovered with methanol/CH_2Cl_2 mixture ($V/V = 1/2$) as an eluent. Purified PPhMA-*b*-PEO was used to initiate the ATRP of St at 110 °C, μ-(PPMA–PEO–PS) thus obtained was purified by an alumina column using acetone/methanol ($V/V = 1/1$) to remove the unreacted diblock initiator. Finally, the purified μ-(PPMA–PEO–PS) (0.27 g) was hydrolyzed with tetrabutylammonium hydroxide (1.2 g) in 6 mL of dioxane at 60 °C for 3 days. The reaction solution was precipitated in acidic water for 3 times to give 0.19 g product with 95% yield.

3. Results and discussion

The ATRP system involves activation/deactivation processes during the propagation of active chains. In general, methacrylates can be polymerized at a wide range of temperature with suitable ligands, while styrene and its derivatives are usually polymerized at relative high temperatures (80–130 °C). This is due to the different activation ability of the dormant species from these two monomers. Haddleton et al. [23] utilized the difference in activation to end-cap a PMMA chain with a divinylbenzene group at room temperature. Our concept in this paper is based on the same idea, which is to control the activation/deactivation process of ATRP for different initiating species at different temperatures. As described in Scheme 1, an ATRP macroinitiator from methacrylate monomer was prepared first, then it was allowed to react with a styrenic macromonomer at room temperature to get the diblock copolymer with the dormant halogen in the junction point, and finally, at higher temperature, St was polymerized to get the ABC μ-star terpolymer. With this method, μ-(PMMA–PEO–PS) and μ-(PMAA–PEO–PS) were synthesized via three successive ATRP.

3.1. Synthesis of PMMA macroinitiators by ATRP

We prepared two PMMA macroinitiators bearing a bromine (**M-1**) or a chlorine (**M-2**) end group by the ATRP of MMA in acetone initiated with PhBiB and *p*-TsCl, respectively. High degree of chain end functionality and narrow polydispersity of PMMA are critical for the following addition reaction. Therefore, we added persistent radicals ($CuBr_2$ or $CuCl_2$), used small amount of catalyst and stopped the polymerization at relatively lower conversion (Table 1) [24].

PMMA–Br (**M-1** in Table 1) was characterized by GPC (Fig. 1), the GPC trace of **M-1** was monomodal with a very slight tailor to low molecular weight side due to the back strain effect of MMA ATRP [25]. Nevertheless, the polydispersity of **M-1** was <1.10. The ^{1}H NMR spectrum of **M-1** is shown in Fig. 2(a). Peaks at 7.0–7.5 ppm (a, b, c) assigned to the phenyl protons of PhBiB initiator were clearly seen. The multiple peaks appear at 2.7 ppm (d′) are assigned to the two methylene protons in the terminating MMA unit as reported by Sawamoto et al. [26]. Integration ratio of these two groups of peaks approaches 1/1, suggesting that PMMA chains were bromine-end-capped with a high functionality. In addition, based on the integration of peak at 3.6 ppm (ester methyl of MMA units) and peaks at 7.0–7.5 ppm (end phenyl group of PhBiB), the absolute M_n of **M-1** was calculated to be 4400. This value is higher than the theoretical value based on polymer yield ($M_n = 3300$), which is caused by precipitation in methanol, some lower molecular weight PMMA dissolved in methanol.

Table 1
Conditions to prepare μ-(PMMA–PEO–PS).[a]

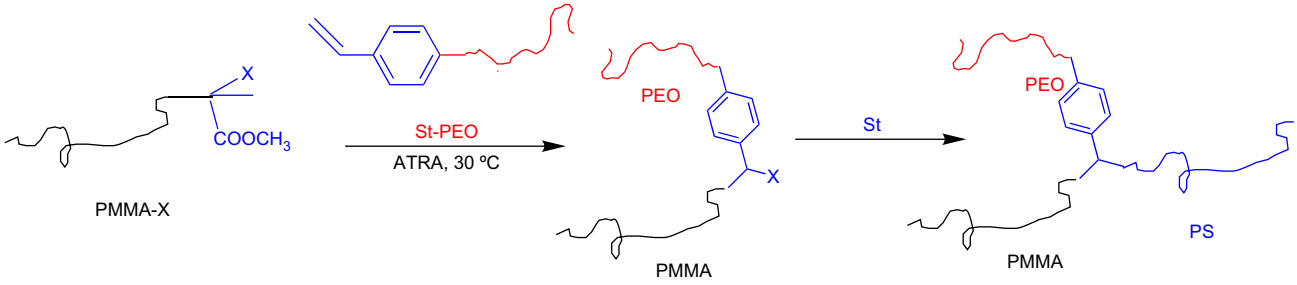
Entry	Initiator	[I]/[M][b]/[Cu(I)]/[Cu(II)][c]	Time (h)	*T* (°C)	Yield (%)	$M_{n,GPC}$ (M_w/M_n)	$M_{n,NMR}$
M-1	PhBiB	1/100/0.2/0.1	9	30	31	3800 (1.09)	4400
M-2	*p*-TsCl	1/100/0.5/0.05	5	60	52	7200 (1.07)	8300
D-1	**M-1**	1/1.5/0.4/0.2	20	30	30[d]	7100 (1.07)	7000
D-2	**M-2**	1/1.5/0.5/0.15	20	30	43[d]	10,900 (1.06)	11,400
T-1	**D-1**	1/500/2	3	90	10	46,800 (1.24)	44,600
T-2	**D-2**	1/500/2	4	110	22	37,400 (1.18)	37,700

[a] PMDETA as the ligand, equivalent to the sum of Cu(I) and Cu(II) in molar ratio.
[b] Acetone as the solvent: [MMA] = 4.8 M for **M-1** and **M-2**; [St-PEO2000] = 22 mM for **D-1** and **D-2**; bulk for **T-1** and 55 wt% St in chlorobenzene for **T-2**.
[c] CuCl/$CuCl_2$ for **M-2**; CuBr/$CuBr_2$ for **M-1**, **D-1** and **D-2**; CuBr for **T-1** and CuCl for **T-2**.
[d] Yield of the purified copolymer.

PMMA–Cl (**M-2**) with a higher molecular weight and a chlorine end group was also prepared with *p*-TsCl as the initiator [27], and characterized by GPC and ^{1}H NMR spectroscopy (Fig. 3 and Fig. 4(a)). PMMA with low polydispersity index and a symmetric GPC trace was obtained. From the integration of NMR peaks at 3.6 ppm and 7.7 ppm as denoted in Fig. 4(a), we calculated the M_n of **M-2**, which is 8300. This value is much larger than that estimated from polymer yield ($M_n = 5400$). We attributed this mainly to the low initiating efficiency of the *p*-TsCl/PMDETA system [28].

3.2. Synthesis of PMMA-b-PEO

It is reported that α-bromo isobutyrate can be activated with CuBr/PMDETA at room temperature [29] due to the weak C–Br bond associated with the formation of stable tertiary carbon radical. In contrast, α-alkyl benzyl bromide (similar to the bromine-end-capped PS chain in ATRP) is slowly activated at this temperature, with its k_a being 10 times smaller than that of α-bromo isobutyrate at 35 °C in CuBr/PMDETA system [30,31]. α-Alkyl benzyl chloride is even more difficult than α-alkyl benzyl bromide to be activated under the similar condition. On the other hand, the large k_{Dact} and small k_p of styrene will ensure that only one styrene



Scheme 1. Synthetic way for the μ-(PMMA–PEO–PS) via a three-step ATRP.

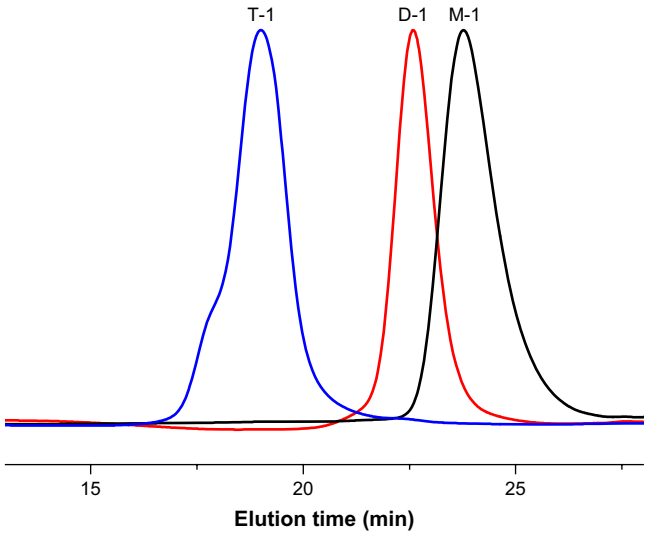


Fig. 1. GPC traces of **M-1** ($M_n = 3800$, $M_w/M_n = 1.09$), **D-1** ($M_n = 7100$, $M_w/M_n = 1.07$) and **T-1** ($M_n = 46{,}800$, $M_w/M_n = 1.24$).

monomer is added in several activation/deactivation cycles [32]. This is the basis for a controlled ATRA of PMMA–Br to styrene or a styrenic macromonomer. When a methacrylate type radical formed under ATRP conditions reacted with a styrene type monomer at room temperature, the cross-addition will occur to form an end polystyryl radical. This radical will quickly deactivate to form a stable dormant halide at room temperature before another monomer to be added. As a result, a stable monoadduct with a styrene unit end may be formed. Based on this fact, we carried out the ATRA of a styrenic PEO macromonomer to **M1** or **M2** at room temperature.

Firstly, **M-1** was activated with CuBr/$CuBr_2$/PMDETA at 30 °C to add an St-PEO2000. The conditions are shown in Table 1. To suppress side reactions, such as chain termination and multiple additions, the concentration of St-PEO2000 was much lower than a normal ATRP, and the molar ratio of **M-1** to St-PEO2000 was 1/1.5. In addition, $CuBr_2$ was added to shift the equilibrium to the dormant side. This resulted in a very slow addition and low conversion of **M-1** (about 50%) even after 30 h. The crude product was analyzed by GPC and NMR spectroscopy, a bimodal GPC was observed, with the existence of unreacted **M-1** and excess of St-PEO2000 at the lower molecular weight side (Fig. S2), but no high molecular weight species due to chain coupling or multiple additions existed. Therefore, purification is necessary. First, St-PEO2000 was removed by precipitation of the crude product in cold methanol. PEO can dissolve in cold methanol, while PMMA-*b*-PEO can disperse in methanol as a surfactant, especially when PMMA block is short. Three times reprecipitation was necessary to completely

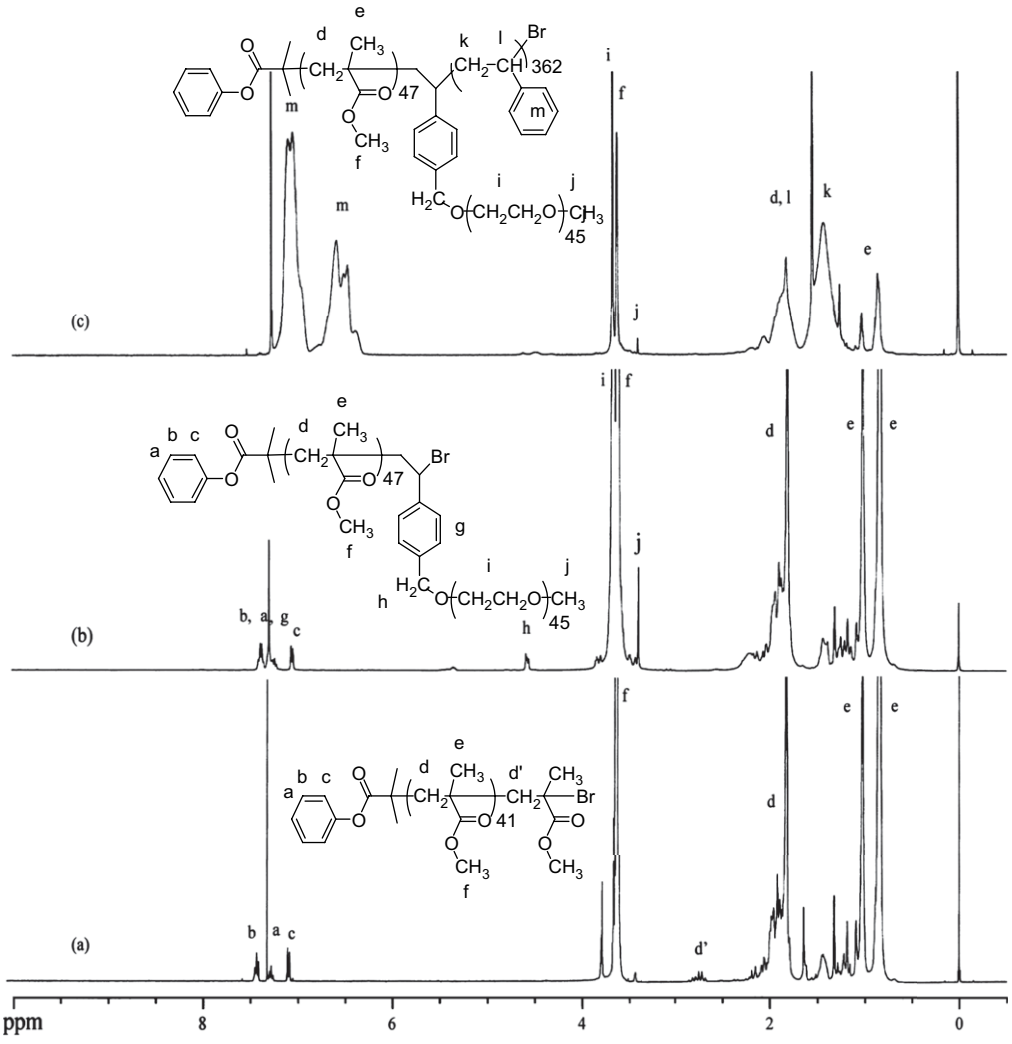


Fig. 2. ^{1}H NMR spectra of **M-1** (a), **D-1** (b) and **T-1** (c) in $CDCl_3$.

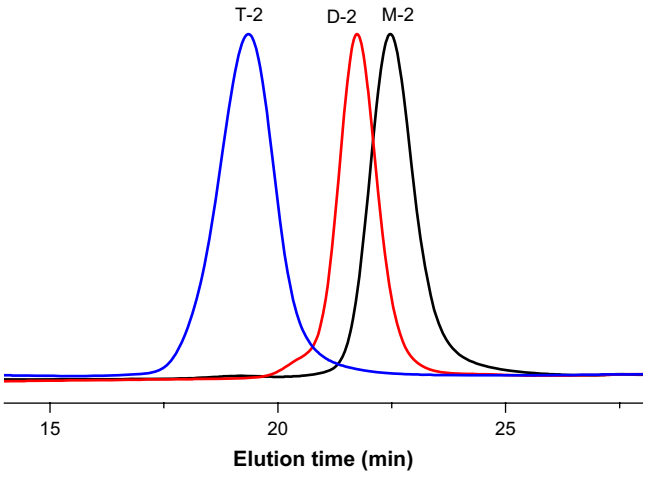


Fig. 3. GPC traces of **M-2** ($M_n = 7200$, $M_w/M_n = 1.07$), **D-2** ($M_n = 10{,}900$, $M_w/M_n = 1.06$) and **T-2** ($M_n = 37{,}400$, $M_w/M_n = 1.18$).

remove St-PEO2000 as monitored from GPC (retention time of St-EPO2000 at 25 min) and NMR spectroscopy (disappearance of the vinyl groups). It should be pointed out that the longer the PMMA block is, the higher is the yield of block copolymer due to the poorer solubility of the longer PMMA chain in methanol. Then, the unreacted **M-1** was removed with silica column chromatography, similar to the process in the literature [25a,33]. PMMA was first eluted with ethyl acetate, followed by changing the eluent to acetone/methanol mixture (*V*/*V*, 1/1) to recover PMMA-*b*-PEO. Complete removal of **M-1** and St-PEO2000 was confirmed from the GPC trace of purified **D-1** (Fig. 1), it clearly shows a shift towards higher molecular weight with very narrow molecular weight distribution of PMMA-*b*-PEO. We should say that these purification procedures lowered the final yield of **D-1** to 30%. ^{1}H NMR spectrum of the purified **D-1** is shown in Fig. 2(b), the multipeaks at 2.7 ppm disappeared as the chain end C–Br bond has changed to C–C bond after addition; and the integration ratio of peaks c, h and j is 2.10:2.18:3.00, suggesting that only one St-PEO2000 was added to the end of PMMA–Br. Based on the M_n of PEO, the M_n of PMMA block in PMMA-*b*-PEO copolymer is calculated to be 4900, a little higher than that of the original **M-1** (4400). This was caused by the purification process; block copolymers with shorter PMMA chains were removed. This can also account for the low final yield of **D-1**.

α-Chloro isobutyrate can also be easily activated at 30 °C, though the activation rate is lower than that of α-bromo isobutyrate. In the beginning, we used CuCl/$CuCl_2$/PMDETA to activate **M-2** for the addition of St-PEO2000. The conversion of **M-2** was close to 100%, but GPC trace of the reaction mixture revealed that no St-PEO 2000 left, and a shoulder peak at the high molecular side appeared (Fig. S3). This indicates that multiple additions of St-PEO2000 or radical coupling occurred due to the less efficiency of chloride in the deactivation step [27a,30b]. Therefore, we changed

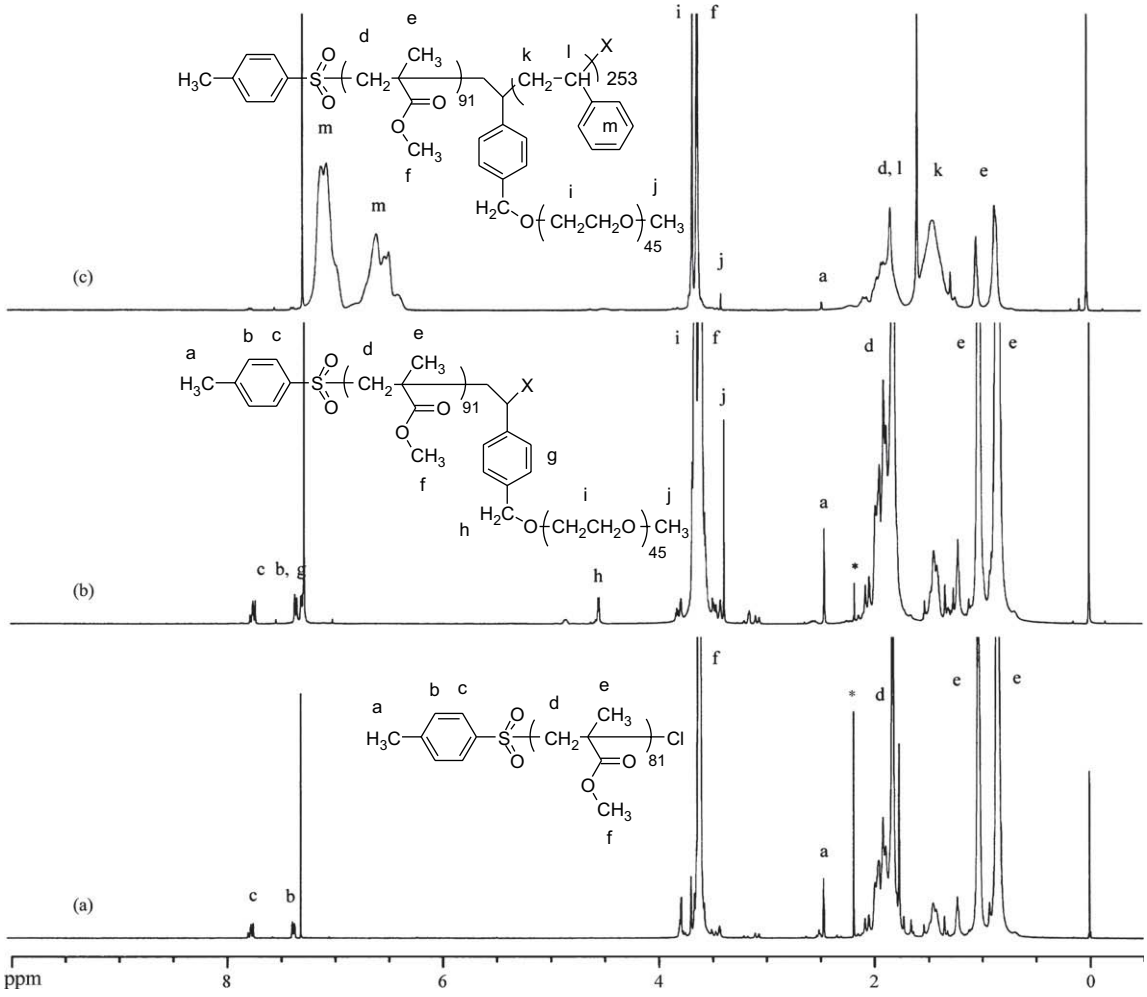


Fig. 4. ^{1}H NMR spectra of **M-2** (a), **D-2** (b) and **T-2** (c) in $CDCl_3$.

the catalyst system to CuBr/$CuBr_2$/PMDETA (Table 1). The reaction mixture was light blue and changed to light green gradually, indicating that the halogen exchange occurred via activation/deactivation cycles. The reaction was terminated at 20 h and the conversion of **M-2** reached 60% as estimated by ^{1}H NMR spectroscopy. Purification of **D-2** was much easier than **D-1** due to the longer PMMA chain, about 70% of the diblock copolymer formed was recovered after the same purification procedure as for **D-1**. The purified **D-2** displays a symmetric GPC trace and narrow molecular weight distribution (Fig. 3). From the ^{1}H NMR spectrum of the purified **D-2** (Fig. 4(b)), the integration ratio of peaks at 7.7 ppm, 2.4 ppm (tosyl end group) and peaks at 3.3 ppm, 4.5 ppm (methyl protons and benzyl protons of St-PEO2000) is 2.02:3.00:3.00:1.99, indicating that only one St-PEO2000 was added by a PMMA macroinitiator. The calculated M_n of **D-2** is 11,400, with the M_n of PMMA block being 9300. This value again is little bit higher than that of **M-2** (8300), which is also caused by precipitation process as in the case of **D-1**. To further confirm the structure integrity of **D-2**, we measured the MALDI-ToF MS of **D-2** (Fig. 5). The main peak is around 11,500, which is in good agreement with the M_n estimated by NMR spectrum. No contamination of **M-2**, St-PEO2000 and high molecular weight polymers from multiple additions or coupling termination can be seen.

In the process of ATRP, the deactivation of radicals with Cu(II)X_2 competes with the addition reaction of radicals to vinyl monomers. High reactivity of the PMMA radicals toward the styrenic macromonomer and fast deactivation of the Cu(II)X_2 benefit the monoadduct formation by addition reaction. In the **D-1** system, $CuBr_2$ deactivated the formed polystyryl radical rapidly so that one macromonomer was added via many activation/deactivation cycles. In the case of **D-2**, part of $CuCl_2$ or CuBrCl formed during halogen exchange, which decreased the deactivation rate, but increased the conversion of **M-2**. Based on these results, it is concluded that **D-2** coupled with CuBr/PMDETA was preferred in the addition reaction.

3.3. Synthesis of μ-(PMMA–PEO–PS)

With **D-1** and **D-2** as the macroinitiators, further ATRP of styrene was performed to construct the PS chain from the junction point of PMMA-*b*-PEO. Inefficient initiation existed in both polymerization systems as evidenced from the GPC traces of the crude product (Figs. S4 and S5). Initiation efficiency (IE) of **D-1** seems even poorer than that of **D-2**. The residual diblock copolymers were removed by precipitation for **T-1** (Fig. 1) and by fractionation for **T-2** (Fig. 3), respectively. The shoulder peak of **T-1** at higher molecular weight in Fig. 1 may be caused by coupling reaction of polystyryl radicals. We assumed that local steric hindrance around the dormant halogen account for the low initiating efficiency. The poor initiation of **D-1** was ascribed to loss of bromine during column fractionation, for the bromide moiety is more sensitive to nucleophilic substitution than chlorine [34]. Finally, the M_n of PS chain can be calculated from the ^{1}H NMR spectra (Fig. 2(c) and 4(c)) with the following equation: $M_{n,PS} = [(I_{6.3-7.3}/5)/(I_{3.65}/4)] \times 45 \times 104$ where $M_{n,PS}$, and 104 are molecular weight of PS chain and styrene, respectively, and 45 is DP of PEO2000 chain. $I_{6.3-7.3}$ and $I_{3.65}$ are the integration of the NMR peaks at 6.3–7.3 ppm (phenyl group) and 3.65 ppm ($-CH_2CH_2O-$). Final characterizations of **T-1** and **T-2** were summarized in Table 1.

The above results show that well-defined μ-(PMMA–PEO–PS) can be prepared by controlling three successive ATRP. It seems that the procedure with PMMA–Cl was better than PMMA–Br, with higher conversion of the ATRA and higher initiation efficiency for ATRP of styrene. Though the yield of the second step is not so high and the separation procedure of the polymer is time-consuming, this method is still useful to increase the availability of new ABC star terpolymers. For example, other polymethacrylates can be used instead of PMMA, PS can also be changed to other polymers, and both chain lengths can be tuned easily. In addition, the three arms are connected by stable covalent bond, which is not easily realized by CRP with multifunctional initiators.

Table 2
Conditions to prepare μ-(PhMA–PEO–PS).

Polymer	Feed ratio[a]	Time (h)	T (°C)	Yield (%)	$M_{n,GPC}$ (M_w/M_n)[b]	$M_{n,NMR}$
PPhMA–Cl	1/100/0.5/0.05[b]	2.5	60	64	12,200 (1.13)	11,500
PPhMA-*b*-PEO	1/2/0.9/0.2[c]	24	30	25	21,800 (1.08)	19,800
μ-(PPhMA–PEO–PS)	1/200/2/2[d]	3	110	40	34,200 (1.11)	32,000

[a] PMDETA as the ligand, equivalent to sum of Cu(I) and Cu(II) in molar ratio.
[b] *p*-TsCl/PhMA/CuCl/$CuCl_2$, acetone as solvent, [PhMA] = 3 mol/L.
[c] PPhMA-Cl/St-PEO5000/CuBr/$CuBr_2$, acetone as solvent, [St-PEO5000] = 0.027 mol/L.
[d] PPhMA-*b*-PEO/styrene/CuCl/$CuCl_2$, chlorobenzene as solvent, [St] = 4.4 mol/L.

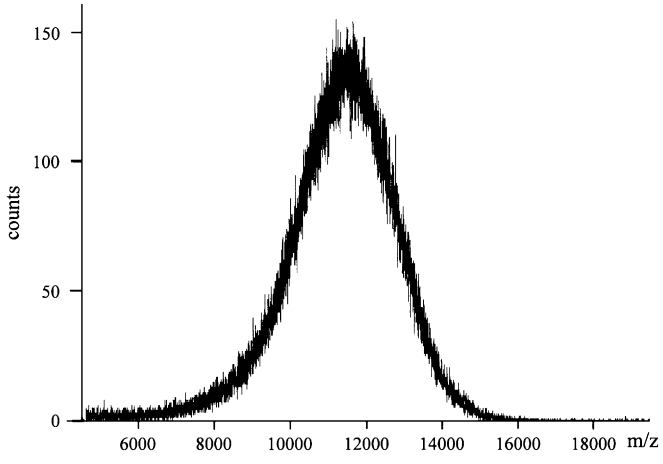


Fig. 5. MALDI-ToF MS of **D-2**.

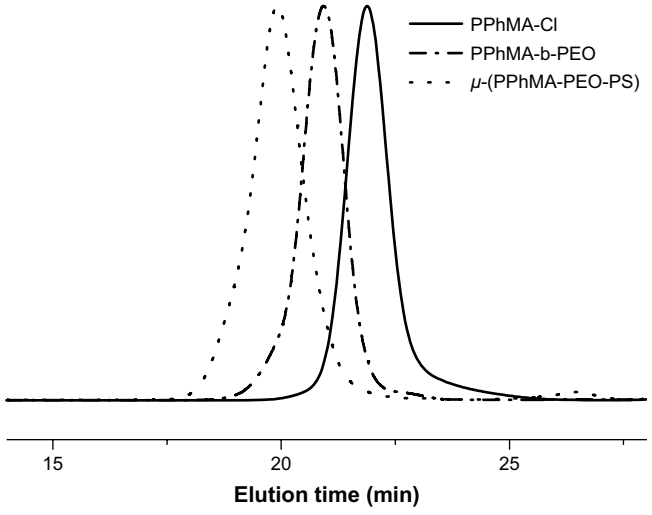


Fig. 6. GPC traces of PPhMA–Cl (M_n = 12,200, M_w/M_n = 1.13), PPhMA-*b*-PEO (M_n = 21,800, M_w/M_n = 1.08) and μ-(PPhMA–PEO–PS) (M_n = 34,200, M_w/M_n = 1.11).

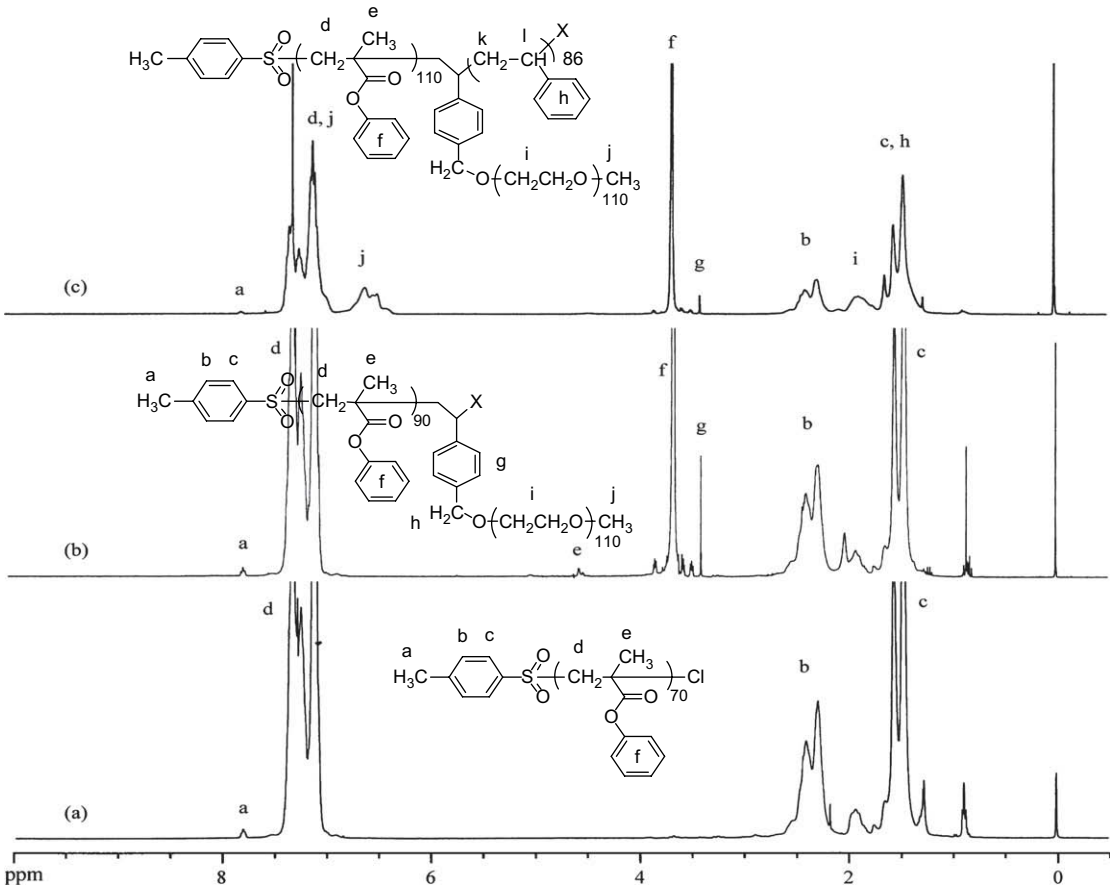


Fig. 7. ^{1}H NMR spectra of PPhMA–Cl (a), PPhMA-*b*-PEO (b) and μ-(PPhMA–PEO–PS) (c) in $CDCl_3$.

3.4. Synthesis of μ-(PMAA–PEO–PS)

To show the potential of the current strategy, we synthesized μ-(PMAA–PEO–PS) as another example. The conditions and characterization of polymers are listed in Table 2.

We first synthesized PPhMA–Cl as the precursor of PMAA by ATRP of PhMA, and then it was used to add an St-PEO5000 under ATRA conditions to form PPhMA-*b*-PEO. Unreacted PPhMA–Cl was removed by silica column eluted with ethyl acetate. But removal of St-PEO5000 cannot be done by precipitation in cold methanol, due to its poor solubility in cold methanol. It was therefore achieved by alumina column separation eluted with ethanol. The conversion of PPhMA–Cl was about 45%, but the yield of the purified diblock copolymer was 25%. This macroinitiator was used to the ATRP of St, resulting in the formation of μ-(PPhMA–PEO–PS). All the polymers were characterized by GPC and NMR spectroscopy (Figs. 6 and 7), they all show narrow molecular weight distribution and proposed structure.

Finally, the PPhMA block of the star polymer was hydrolyzed in homogenous solution. As can be seen in the ^{1}H NMR and IR

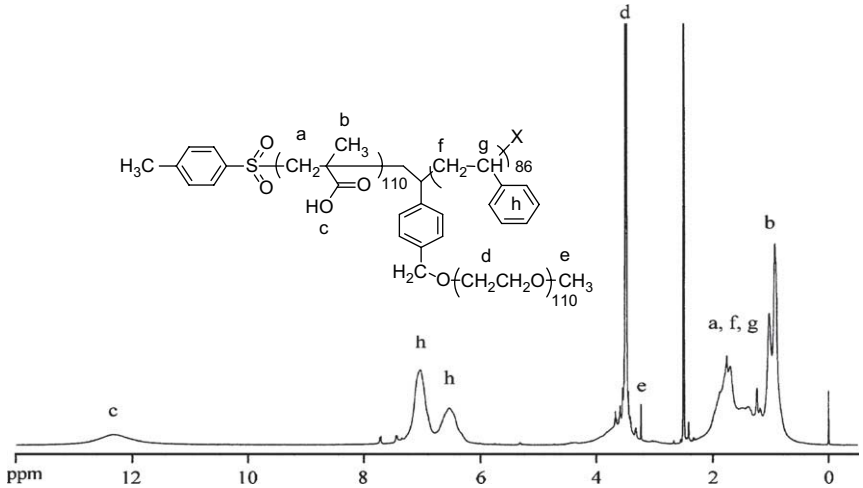


Fig. 8. ^{1}H NMR spectrum of μ-(PMAA–PEO–PS) in DMSO-d_6.

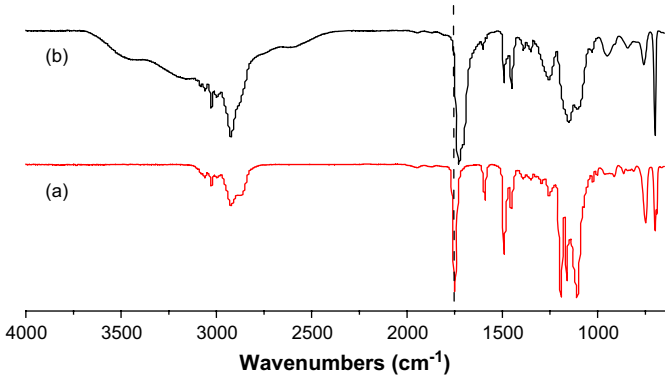


Fig. 9. IR spectra of μ-(PPhMA–PEO–PS) (a) and μ-(PMAA–PEO–PS) (b).

spectrum (Figs. 8 and 9), the phenyl esters have been completely converted to carboxylic acid groups, thus well-defined μ-(PMAA–PEO–PS) was obtained. Since the solubility of the PMAA block is pH-dependent and it can form complex with PEO though hydrogen bonding at lower pH, the solution property as well as the self-assembly of this amphiphilic star copolymer will be much interesting. We are currently investigating on this.

4. Conclusions

Synthesis of ABC μ-star terpolymers was demonstrated by a three-step ATRP. The method was based on the control of activation/deactivation process in ATRP, which was realized by selection of type of monomers, polymerization sequence and control of temperature. Two important issues must be taken into consideration when using this method to prepare ABC star polymers: one is that the sequence to introduce each of the three chains must be from A to C; and the other is the chemical nature of each chain, A is a polymethacrylate derivative, B is from a styrenic macromonomer and C can be from any monomer that can be polymerized under ATRP. The advantage of this strategy is that it can be easily extended to other monomers, which makes it very useful in preparation of ABC star terpolymers difficult to get by other methods. While we must say that the total yield of the current synthesis is not so high due to the less effective reaction of the second step and several fractionations, but we believe it can be improved by further optimizing reaction conditions (selection of other ligand, increase of macromonomer concentration).

Acknowledgements

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Appendix. Supporting information

The ^{1}H NMR spectrum of St-PEO2000 (Fig. S1), GPC traces of crude **D-1**, **D-2**, **T-1** and **T-2** (Figs. S2–5) are provided as supplementary material. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.polymer.2008.10.046.

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