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ORIGINAL PAPER

Synthesis of poly(acrylic acid)-*g*-polystyrene copolymer by successive ATRP

Dan Peng · Xiaohuan Zhang · Rongjun Zhang · Jinhui Li · Xiao Xiao

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Abstract A series of well-defined amphiphilic graft copolymers consisting of hydrophilic poly(acrylic acid) backbone and hydrophobic polystyrene side chains were synthesized by hydrolysis of poly(methyl acrylate)-*g*-polystyrene under basic condition. The backbone and the side chains were synthesized by atom transfer radical polymerization (ATRP), so the molecular weight could be tuned by the variation of the feed ratio or monomer conversion, and the molecular weight distributions of amphiphilic graft copolymers were kept low (PDI < 1.35). The products were characterized by FT-IR, ^{1}H NMR, ^{13}C NMR, and gel permeation chromatography (GPC). The study of self-assembly behavior can benefit the formation of the well-defined structures of the products.

Keywords Amphiphilic graft copolymer · Atom transfer radical polymerization · Poly(methyl acrylate) · Poly(acrylic acid) · Polystyrene

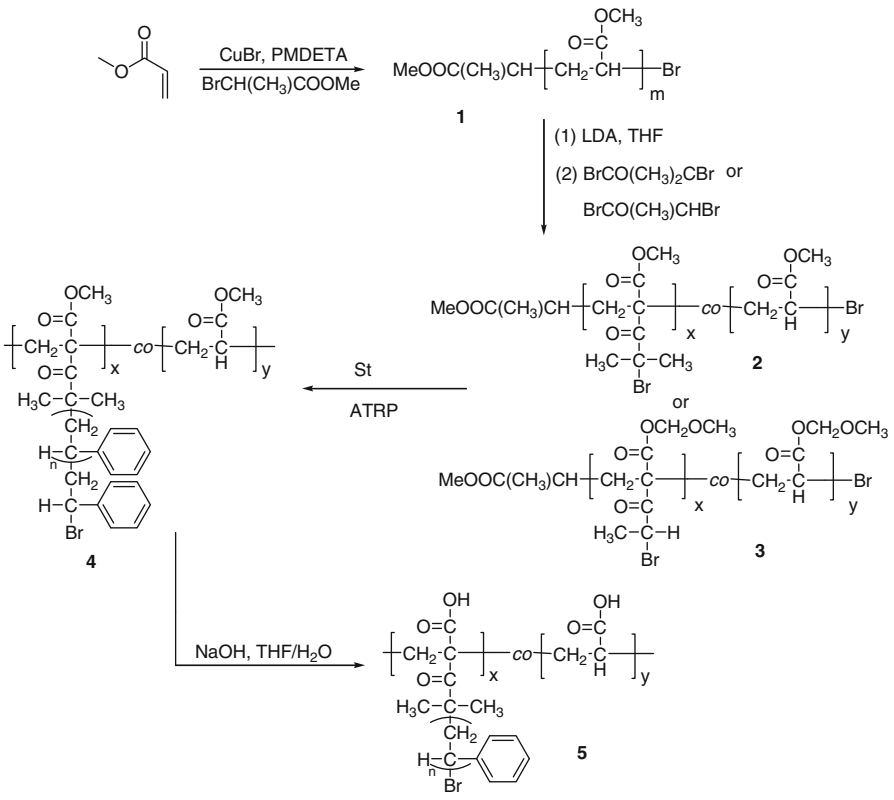
Introduction

Compared with linear block copolymers, amphiphilic graft copolymers exhibit different self-assembly behaviors because of its complicated and confined structures

D. Peng (✉) · R. Zhang · J. Li · X. Xiao
New Material Institute of Shandong Academy of Sciences, 19 Keyuan Road, Jinan, Shandong 250014, China
e-mail: lonarpeng@yahoo.com.cn

X. Zhang
Laboratory of Polymer Materials and Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Science, 354 Fenglin Road, Shanghai 200031, China

[1–3]. In the past years, the studies of the self-assembly of graft copolymers were restrained due to the difficulty in the synthesis of graft copolymers with controlled molecular weights and low polydispersities. With the development of living radical polymerization, especially the atom transfer radical polymerization (ATRP), more and more well-defined amphiphilic graft copolymers were synthesized [4–6], which promoted the studies of their self-assembly behaviors. In our previous reports [7], the amphiphilic graft copolymers bearing hydrophilic poly(acrylic acid) backbone and hydrophobic side chains were synthesized by the combination of ATRP and grafting-from technique. To build the poly(acrylic acid) backbone with controlled molecular weights and low polydispersities, methoxymethyl acrylate was selected as the monomer to synthesize the backbone due to its mild acidic hydrolysis conditions. However, highly toxic methoxymethyl chloride is employed in the synthesis of methoxymethyl acrylate. In this article, the use of methyl acrylate as the monomer to build the poly(acrylic acid) backbone is explored, since it is cheap and commercial (Scheme 1).



Scheme 1 Synthesis of amphiphilic graft copolymer PAA-*g*-PS

Experimental

Materials

Methyl acrylate (MA) and styrene (St) were washed with 5% aqueous NaOH solution to remove inhibitor, and then with water, dried over $MgSO_4$ and distilled twice over CaH_2 under reduced pressure. Copper(I) bromide (CuBr, Aldrich, 98%) was purified by stirring overnight over CH_3CO_2H at room temperature, followed by washing the solid with ethanol, diethyl ether, and acetone prior to drying at 40 °C under vacuum for 1 day. Diisopropylamine (Aldrich, 99.5%) was dried over KOH for several days followed by distilling from CaH_2 under N_2 atmosphere. Tetrahydrofuran (THF) was dried over CaH_2 for several days and distilled from sodium and benzophenone under N_2 atmosphere. *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (PMDETA, Aldrich, 99%), methyl 2-bromopropionate (2-MBP, Acros, 99%), *n*-butyl-lithium (*n*-BuLi, Aldrich, 1.6 M in hexane), and α-bromoisobutyryl bromide (TCI, 98%) were used as received.

Typical procedure of polymerization of MA by ATRP

CuBr (54.1 mg, 0.38 mmol) was first added to a 25-mL Schlenk flask (flame-dried under vacuum just before use) sealed with a rubber septum for degassing and kept under N_2 atmosphere. MA (2.0 mL, 22.1 mmol), PMDETA (0.08 mL, 0.38 mmol), and 2-MBP (0.05 mL, 0.45 mmol) were then introduced via a gas-tight syringe, and the mixture was degassed by three cycles of freeze–pump–thaw followed by immersing the flask into an oil bath thermostated at 50 °C for 4.5 h. The polymerization was terminated by putting the flask into liquid nitrogen. THF was added to dissolve the viscous crude product, and the solution was filtered through a short Al_2O_3 column to remove the copper catalyst. The resulting solution was concentrated and precipitated in hexane for thrice. The precipitation was dried under reduced pressure to obtain 1.54 g glassy solid of 81% yield. GPC: $M_n = 6.4 \times 10^3$ g/mol, $M_w/M_n = 1.08$. ^{1}H NMR ($CDCl_3$): δ (ppm): 1.15 (d, 3H, CH_3CH), 1.37–1.62, 1.80–2.06 (br, 2H, mesoCH_2–CH), 1.62–1.80 (br, 2H, racemoCH_2–CH), 2.16–2.47 (br, 1H, CH_2–C*H*), 3.67 (s, 3H, OCH_3), 4.25 (t, 1H, C*H*Br). ^{13}C NMR ($CDCl_3$): δ (ppm): 34.6 (–CH_2CH–), 41.0 (–CH_2*C*H–), 51.6 (–OCH_3), 173.9 (*C*OOCH_3). E.A.: Br% = 0.81%.

Synthesis of PMA-Br macroinitiator

Dried THF (20.0 mL) and diisopropylamine (3.0 mL, 20.0 mmol) were added to a sealed 250-mL three-necked flask. Then, the solution was cooled to −78 °C, and *n*-BuLi (1.6 M, 11.3 mL, 18.1 mmol) was added slowly. After 1 h, the mixture was treated with PMA ($M_n = 6.4 \times 10^3$, $M_w/M_n = 1.08$, 1.4660 g, 17.0 mmol CH_2CH repeat unit) in 80 mL of dried THF under −78 °C. The reaction lasted for 4.5 h. Next, α-bromoisobutyryl bromide (2.5 mL, 20.0 mmol) was introduced. After 5 h, the reaction was terminated by an aqueous solution of NH_4Cl. The organic phase

was washed with water and brine, and dried over $MgSO_4$ overnight. The solution was concentrated after filtration and precipitated into hexane for thrice. The product was dried under vacuum to give yellow powder (1.46 g). GPC: $M_n = 4.1 \times 10^3$ g/mol, $M_w/M_n = 1.21$. ^{1}H NMR ($CDCl_3$): δ(ppm): 1.15 (d, 3H, CH_3CH), 1.37–3.14 (m, CH_2CH), 1.98 (C(CH_3)$_2$Br), 3.67 (s, 3H, OCH_3). E.A.: Br% = 16.42%. If the reactant was α-bromopropionyl bromide, we can find an additional peak at $\delta = 4.46$ ppm (s, CH(CH$_3$)Br). ^{13}C NMR ($CDCl_3$): δ (ppm): 21.2 (CH(CH_3)Br), 28.0–38.2 (–CH_2CH–), 39.3, 40.9 (–CH$_2$$CH$–), 47.8 ($CH$(CH$_3$) Br), 52.0 (O$CH_3$), 171.1, 174.8 ($COOCH_3$), 207.2 ($C$=O). E.A.: Br% = 10.89%.

Synthesis of graft copolymer PMA-*g*-PS

A dried 25-mL Schlenk flask was charged with CuBr (30.9 mg, 0.22 mmol) and PMA-Br (100.5 mg, $M_n = 4.1 \times 10^3$ g/mol, $M_w/M_n = 1.21$, Br% = 16.42%). The flask was degassed and kept under N_2 atmosphere. PMDETA (0.04 mL, 0.19 mmol) and St (7.3 mL, 63.7 mmol) were introduced via a gas-tight syringe, and the mixture was degassed by three cycles of freeze–pump–thaw followed by immersing the flask into an oil bath thermostated at 80 °C for 4 h. The polymerization was terminated by putting the flask into liquid N_2. The reaction mixture was diluted by THF and filtered through a short Al_2O_3 column to remove the copper catalyst. After concentration, PMA-*g*-PS was obtained by precipitation in methanol and dried under vacuum (0.48 g, monomer conversion = 5.8%). GPC: $M_n = 4.2 \times 10^4$ g/mol, $M_w/M_n = 1.28$. ^{1}H NMR ($CDCl_3$): δ (ppm): 1.43 (br, 2H, –CH_2CH–), 1.84, 2.36 (br, 1H, –CH$_2$CH–), 3.66 (s, 3H, OCH_3), 4.35–4.61 (br, 1H, CHBr), 6.60, 7.09 (br, 5H, C$_6H_5$). FT-IR (film): ν (cm^{-1}): 3083, 3061, 3026, 2924, 2850, 1739, 1602, 1494, 1453, 1373, 1166, 1029, 907, 757, 698, 539.

Typical procedure of hydrolysis of PMA backbone

PMA-*g*-PS (0.2020 g, $M_n = 1.3 \times 10^4$, $M_w/M_n = 1.22$) was dissolved in 20 mL THF and treated with 25 mL aqueous solution of NaOH (1.3710 g) at 60 °C for 10 h. After reaction, the solution was neutralized to weak acidic by HCl (10 wt%). The organic phase was washed with water and brine, and dried over $MgSO_4$ overnight. After filtration of $MgSO_4$, the solution was concentrated and precipitated into hexane. The hydrolysis product was dried under vacuum (0.16 g). ^{1}H NMR ($CDCl_3$): δ (ppm) 1.48 (br, 2H, –CH_2CH–), 1.87, 2.23 (br, 1H, –CH$_2$CH–), 4.37–4.52 (br, 1H, CHBr), 6.62, 7.12 (br, 5H, C$_6H_5$). FT-IR (film): ν (cm^{-1}): 3391, 3061, 3026, 2924, 2850, 1730, 1602, 1494, 1453, 1058, 1029, 757, 698, 539.

Characterization

Relative molecular weights and molecular weight distributions were measured by gel permeation chromatography (GPC) system equipped with a Waters 1515 Isocratic HPLC pump, a Waters 2414 refractive index detector (RI), a Waters 2487 dual absorbance detector, and a set of Waters Styragel columns (HR3, HR4, and HR5, 7.8 × 300 mm). GPC measurements were carried out at 35 °C using THF as eluent with a 1.0 mL/min flow rate. The system was calibrated with polystyrene

standards. ^{1}H NMR and ^{13}C NMR analyses were performed on a Varian Mercury 300 spectrometer (300 MHz) in $CDCl_3$ and with TMS (^{1}H NMR) and $CDCl_3$ (^{13}C NMR) as internal standard. FT-IR spectra were recorded on a Nicolet AVATAR-360 FT-IR spectrophotometer with 4 cm^{-1} resolution. Bromine content was determined by titration with $Hg(NO_3)_2$.

Results and discussions

Synthesis of PMA backbone

In order to obtain well-defined PAA-*g*-PS copolymer, the ATRP technique was employed to synthesize the backbone and the side chains. Since the ATRP of acrylic acid is uncontrolled and the carboxylic acid has effect in the next procedures [8], methyl acrylate (MA) was chosen to synthesize the backbone by ATRP and transfer to acrylic acid by hydrolysis after the graft copolymer was built.

PMA with low molecular weight distribution (PDI < 1.10) was obtained by bulk polymerization at 50 °C with 2-MBP as initiator, using CuBr as catalyst and PMDETA as ligand [9]. The molecular weight of PMA could be tuned by regulating the feed ratio of monomer to initiator (Table 1).

^{1}H NMR spectrum of PMA is shown in Fig. 1. The peaks of the double-bond protons disappeared, and the poly(acrylate) backbone signals appeared at

Table 1 Polymerization of MA by ATRP

PMA	[MA]:[2-MBP]	T (°C)	t (h)	M_n^a (g/mol)	M_w/M_n^a	Yield (%)
1a	32:1	50	1	3,100	1.08	92
1b	49:1	50	3	6,400	1.08	81
1c	113:1	50	4.5	10,000	1.04	71

Feed ratio: [CuBr]:[PMDETA]:[2-MBP] = 1:1:1

[a] Measured by GPC

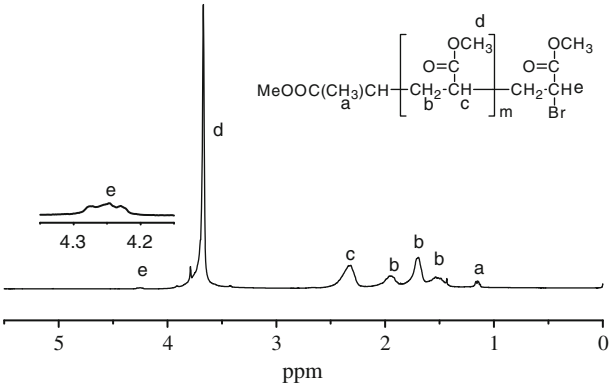


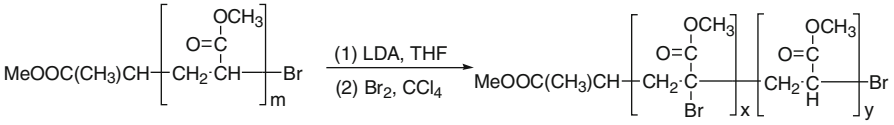
Fig. 1 ^{1}H NMR spectrum of PMA 1

$\delta = 1.37$–2.47 ppm, which meant the polymerization of MA. The mechanism of the polymerization was confirmed to be ATRP by the peak "a" at 1.15 ppm and the peak "e" at 4.25 ppm, which were attributed to three protons of CH_3CH of the initiation group at one end of the backbone and one proton of C*H*Br at the other end of the backbone [10], respectively.

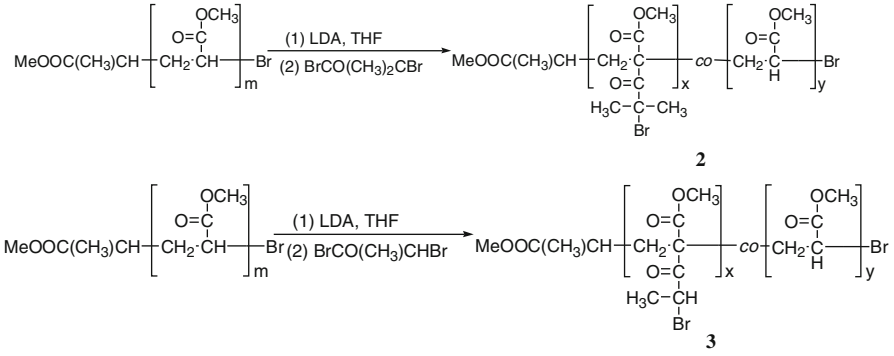
Synthesis of the PMA-Br macroinitiator

In previous literature, to prepare graft copolymers by ATRP, the ester groups on the backbone were converted to halogen-containing ATRP initiation groups [4–6]. However, this technique is unsuitable for our work, since the ester groups on the backbone should be retained so that they could be transformed into hydrophilic carboxylic groups via hydrolysis. Two methods were used to connect ATRP initiation groups to the α-carbon of the ester groups as shown in Scheme 2 [11] and Scheme 3 [12]. If the reactant was bromine water, a brown product was obtained and the structure could not be confirmed by ^{1}H NMR and ^{13}C NMR. The GPC curve of the brown product showed multimodal distribution, which meant the occurrence of side reactions due to the strong oxidation ability of bromine water. Therefore, α-bromoisobutyryl bromide and α-bromopropionyl bromide were chosen to prepare macroinitiator as shown in Scheme 3. By this approach, the ATRP initiation groups were successfully introduced into the backbone through stable C–C bonds instead of C–O bonds.

Figure 2a and b showed ^{1}H NMR spectra of macroinitiators 2 and 3 with different initiation groups. A new peak appeared at 4.46 ppm (peak g) in Fig. 2b



Scheme 2 Synthesis of macroinitiator by bromine water



Scheme 3 Synthesis of macroinitiator 2 and 3

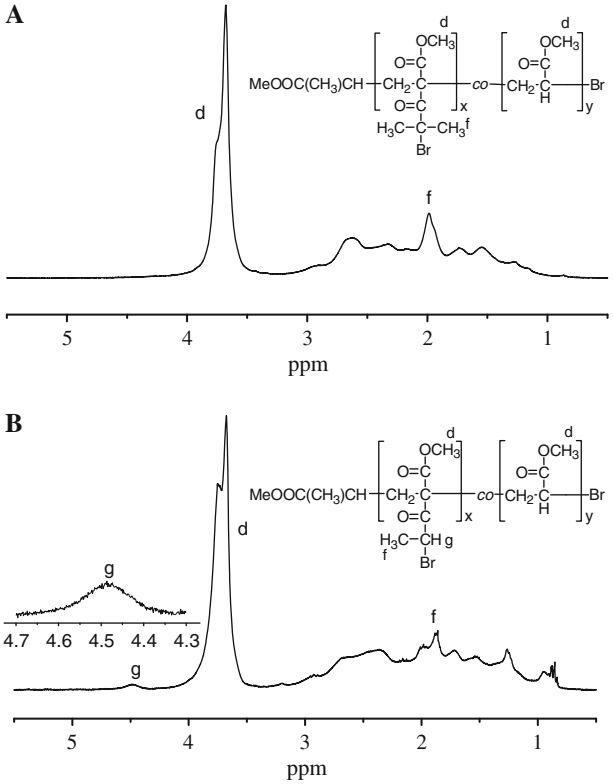


Fig. 2 ^{1}H NMR spectra of macroinitiator 2 (**a**) and macroinitiator 3 (**b**)

when the macroinitiator 3 was made from α-bromopropionyl bromide, but there is no peak at that position in ^{1}H NMR of macroinitiator 2 made from α-bromoisobutyryl bromide in Fig. 2a. Therefore, this peak can be assigned to the proton of –C*H*(CH_3)Br of the newly introduced ATRP initiation groups. Moreover, a new peak at 207.2 ppm, which belonged to the ketone carbon of –*C*O(CH_3)$_2$Br, was found in ^{13}C NMR spectrum of macroinitiators 2 and 3, and a new peak at 580 cm^{-1}, which belonged to the C–Br stretching vibration, was also found in FT-IR spectrum of macroinitiators 2 and 3 as compared with that of PMA.

The successful introduction of ATRP initiation groups into the PMA backbone was also confirmed by the increase in the bromine percentage of macroinitiator 2 (from 0.81 to 16.42% for 2b, listed in Table 2). From the results of Br% determined by titration with $Hg(NO_3)_2$, we can obtain the approximate graft efficiency: 1/5 for 2a, 1/4 for 2b and 1/6 for 2c, which means ATRP initiation groups were introduced to one-fifth, one quarter, or one-sixth of repeating units of PMA backbone.

Only a unimodal peak was found in the GPC curve of macroinitiator 2 and the molecular weight distribution remained narrow ($M_w/M_n \leq 1.23$). It should be noteworthy that M_n of macroinitiator 2, which was calibrated with linear polystyrene standards, was smaller than that of PMA 1 because of the branched ATRP initiation groups.

Table 2 Characterization of macroinitiator 2

Macroinitiator	M_n (g/mol)	M_w/M_n	Br (%)	Graft efficiency
2a[a]	2,400	1.23	14.67	1/5
2b[b]	4,100	1.21	16.42	1/4
2c[c]	7,500	1.23	11.39	1/6

[a] 2a was prepared from 1a

[b] 2b was prepared from 1b

[c] 2c was prepared from 1c

Graft copolymerization of St

PMA-*g*-PS graft copolymers were synthesized by the ATRP of St initiated by macroinitiator 2 at 80 °C, as listed in Table 3. The molecular weights increased with the extending of the polymerization time and unimodal peak was found in the GPC curve of graft copolymer (Fig. 4), which are characteristics of ATRP [13]. Compared the results of 4a–4d with 4e–4h in Table 3, we can find that the higher feed ratio of St to macroinitiator 2 gives the lower molecular weight distribution. It seems that a high feed ratio of monomer to initiator and a low conversion (<11%) of monomer were necessary to suppress intermolecular coupling reactions [4, 7].

Figure 3a showed ^{1}H NMR spectrum of PMA-*g*-PS. The corresponding peaks of both the PMA backbone and PS side chains can be found in the spectrum. A new peak assigned to the signal of proton of –C*H*(Ph)Br end group appeared at 4.46 ppm (peak j) in Fig. 3a, which also confirmed ATRP mechanism [10].

Hydrolysis of PMA backbone

Hydrolysis of PMA backbone with NaOH was carried out at 60 °C for 10 h. The ^{1}H NMR spectrum of the hydrolyzed product is shown in Fig. 3b. The

Table 3 Synthesis of graft copolymers initiated by macroinitiator 2b

Graft copolymer	[St]:[Br]:[CuBr]:[PMDETA]	t (h)	M_n (g/mol)	M_w/M_n	St (%)[a]
4a	200:1:1:1	0	4,100	1.21	0
4b	200:1:1:1	0.5	13,000	1.22	78
4c	200:1:1:1	1	19,000	1.30	83
4d	200:1:1:1	1.5	22,000	1.32	86
4e	300:1:1:1	1	21,000	1.23	86
4f	300:1:1:1	2	33,000	1.25	92
4g	300:1:1:1	3	39,000	1.27	94
4h	300:1:1:1	3.5	42,000	1.28	95

[a] Obtained by ^{1}H NMR

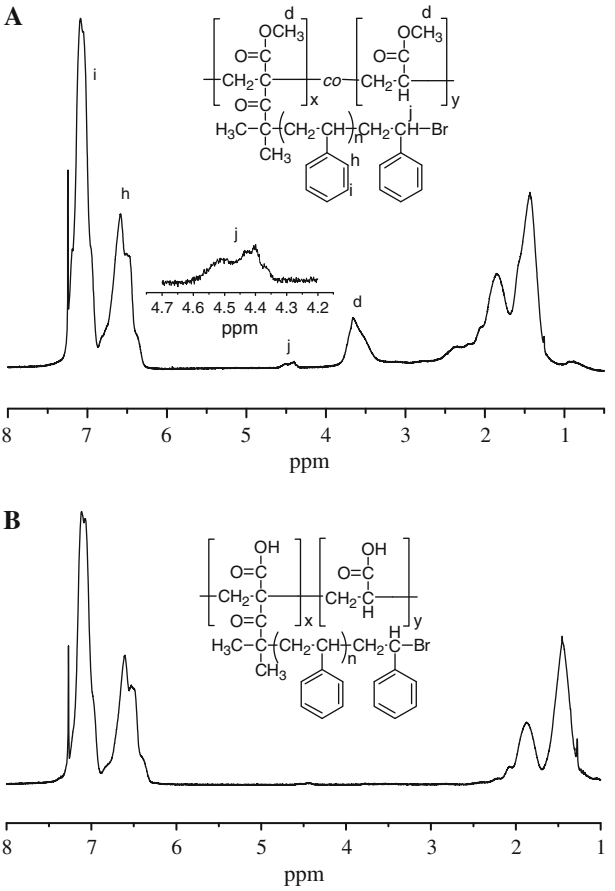


Fig. 3 ^{1}H NMR spectra of PMA-*g*-PS 4 (**a**) and PAA-*g*-PS 5 (**b**)

disappearance of the signals of the protons of methyl at 3.66 ppm assured the hydrolysis of PMA backbone. The signals of the corresponding protons of PS side chains still existed. The appearance of a broad peak of –COOH at 3391 cm^{-1} in the FT-IR spectrum indicated the formation of PAA backbone. Many experiments confirmed that more than 90% methyl group could be hydrolyzed under the used condition and the hydrolysis degree could be controlled by the reaction time.

In order to study the effect of hydrolysis condition on the structure of graft copolymer, PAA backbone was reprotected by CH_2N_2 to be transformed into poly(methyl acrylate) backbone for GPC measurement [14]. A unimodal GPC curve, whose shape and position were almost identical to those of the curve of PMA-g-PS 4 before hydrolysis, can be observed in Fig. 4. Therefore, the hydrolysis condition did not destroy the structure of the graft copolymer, and well-defined amphiphilic graft copolymer PAA-*g*-PS was synthesized.

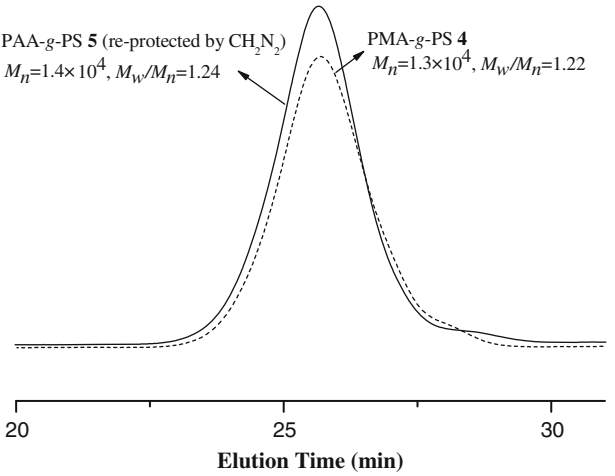


Fig. 4 GPC curves of PMA-*g*-PS 4 and re-protected PAA-*g*-PS 5

Conclusions

In this article, well-defined amphiphilic graft copolymers PAA-*g*-PS were synthesized by the hydrolysis of PMA-*g*-PS under basic condition. Since the PMA backbone and PS side chains were polymerized by ATRP, the molecular weights of both the backbone and side chains can be controlled by the feed ratio of monomer to initiator, and the molecular weight distributions of graft copolymers are kept low (PDI < 1.35). This technique provides a good way for the synthesis of amphiphilic graft copolymers since the side chains can be extended to other polymer blocks, such as Chloro-styrene and fluoro-styrene. Such kind of amphiphilic graft copolymers are very good templates for the study of self-assembly behaviors.

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