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# Synthesis of comb-shaped copolymers by combination of reversible addition–fragmentation chain transfer polymerization and cationic ring-opening polymerization

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**Abstract**

Comb-shaped graft copolymers with poly(methyl acrylate) as a handle were synthesized by reversible addition–fragmentation chain transfer (RAFT) polymerization and ring-opening polymerization (ROP) techniques in three steps. First, copolymers of poly(styrene-co-chloromethyl styrene), poly(St-*co*-CMS), were prepared by RAFT copolymerization of St and CMS using 1-(ethoxycarbonyl)prop-1-yl dithiobenzoate (EPDTB) as RAFT agent. Second, the polymerization of MA using poly(St-*co*-CMS)-SC(S)Ph as macromolecular chain transfer agent produced block copolymer poly(St-*co*-CMS)-*b*-PMA. Third, cationic ring-opening polymerization of THF was performed using poly(St-*co*-CMS)-*b*-PMA/$AgClO_4$ as initiating system to produce comb-shaped copolymers. The structures of the poly(St-*co*-CMS), poly(St-*co*-CMS)-*b*-PMA and final comb-shaped copolymers were characterized by $^1H$ NMR spectroscopy and gel permeation chromatography (GPC).

*Keywords:* RAFT; Ring-opening polymerization; Comb-shape copolymer

## 1. Introduction

From all of the possible architectures or topologies for the organic/inorganic hybrid polymers, graft copolymers exhibit good phase separation and are used for a variety of applications, such as impact-resistant plastics, thermoplastic elastomers, compatibilizers and polymeric emulsifiers [1–8]. Comb-shaped copolymers are special graft copolymers in which many branches are connected to a polymer chain, and they have attracted much attention in both polymer chemistry and physics [4–12]. Comb-shaped copolymers can be prepared by three general methods: grafting-onto, grafting-from, and macromonomers polymerization [13]. Grafting-onto method was the earliest method to graft polymer chains onto the main chain, however, it is very difficult to remove the unreacted side polymer chains. Although the macromonomer method is an attractive method for the synthesis of well-defined comb-shaped copolymers, and a variety of comb-shaped grafted copolymers with randomly distributed branches on their backbones have been prepared by the homopolymerization of macromonomers with anionic, cationic, group-transfer polymerization, and atom transfer radical polymerization, it is still very difficult to remove the unreacted macromonomers [14–17]. Therefore, synthesis of comb-shaped copolymers is still some difficult and more attractive subject. Having studied the syntheses of comb-shaped copolymers, and the interesting properties of comb-shaped copolymers with a handle, we report the synthesis of comb-shaped copolymers by combination of RAFT and ROP method, which provides an easy method to prepare comb-shaped copolymers. The advantage of this method over 'graft onto' and 'macromomonomer polymerization' methods is that the graft chains grow from the main chain and there is no request to remove the ungrafted polymer chains from the resultant products.

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## 2. Materials

Silver perchlorate was prepared in this laboratory and dried at 110 °C for 24 h before it was used. Tetrahydrofuran (THF) was refluxed over sodium for 24 h and distilled before it was used. Methyl acrylate (MA), styrene (St) and chloromethyl styrene (CMS) were dried over $CaH_2$, distilled under reduced pressure, and stored under $N_2$ at $-10$ °C. All other reagents were purchased from Shanghai Chemical Reagent Co., and used as received without further purification.

### *2.1. Synthesis of 1-(ethoxycarbonyl)prop-1-yl dithiobenzoate (EPDTB)*

Magnesium (2.0 g, 0.083 mol) and dry THF (80 mL) were added to a 250 mL, three-necked flask, and bromobenzene (15.7 g, 0.1 mol) was added dropwise over 0.5 h. The reaction was carried out at 40 °C until the magnesium completely disappeared. Then, carbon disulfide (7.62 g, 0.1 mol) was dropped over 20 min. After the reaction had proceeded for 4 h at 40 °C, ethyl α-bromobutyrate (17.5 g, 0.09 mol) was added. The reaction mixture was heated to 80 °C and maintained at this temperature for 80 h. After the addition of 100 mL of ice water to the reaction mixture, the water phase was extracted with carbon disulfide ($3\times50$ mL). The organic extracts were combined and washed with water and were dried over anhydrous magnesium sulfate. After the solvent was removed with a rotating evaporator, the product obtained was purified through silica column chromatography, with hexane/diethyl ether (9/1 v/v) as an eluent. After the solvent was removed under reduced pressure, EPDTB was obtained as red oil (9.31 g, yield 43.5%).

$^1H$ NMR (δ, ppm): 0.91 (t, 3H $CHCH_2CH_3$), 1.25 (t, 3H $OCH_2CH_3$), 1.56 (m, 2H $CHCH_2CH_3$), 4.18 (q, 2H $OCH_2CH_3$), 4.76 (t, 1H $S—CHCH_2CH_3$), 7.25 (1H p-Ar*H*), 7.35 (dd, 2H m-Ar*H*), 7.95 (d, 2H o-Ar*H*).

### *2.2. Copolymerization of St and CMS*

The general procedure for the copolymerization of St and CMS was as follows. To a glass polymerization tube, St, CMS, EPDTB, AIBN and THF were added according to a predetermined ratio. The mixture was degassed with three freeze–vacuum–thaw cycles. The tube was sealed under a high vacuum and then subjected to 110 °C oil bath. After a prescribed time, the tube was opened, and the copolymers of poly(St-*co*-CMS) were obtained by pouring the reaction mixture into methanol with stirring at room temperature twice, and it was dried in vacuum oven at 40 °C overnight.

### *2.3. Block copolymerization of MA with poly(St-co-CMS) as RAFT agent*

The polymerization was performed similarly to the copolymerization of St and CMS. A typical process was as follows. MA, poly(St-*co*-CMS), and THF were added to a 10-mL glass tube according to a predetermined ratio. Then, the tube was degassed with three freeze–pump–thaw cycles and sealed in vacuum. The sealed tube was subjected to 90 °C oil bath for prescribed time, then the tube was opened, and the final copolymers were obtained by the addition of the polymer solution in THF to a 10-fold excess of methanol; it was then isolated by filtration and dried in vacuum oven at 40 °C overnight.

### *2.4. Preparation of comb-shaped copolymer*

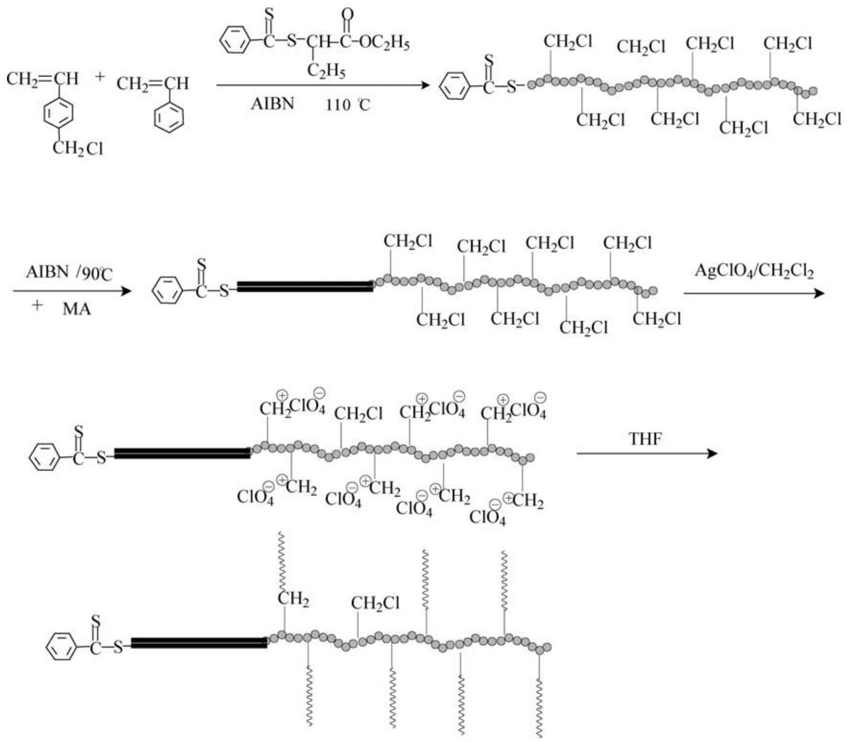
A typical procedure was as follows. A 100-mL, two-necked flask with a magnetic bar was alternately evacuated and purged with pure nitrogen three times. Into the flask, 1.158 g (5.58 mmol) of silver perchlorate was transferred into the flask at $-70$ °C under a nitrogen atmosphere. Then 5.0 g poly(St-*co*-CMS)-*b*-PMA in 10 mL of dichloromethane were added with stirring. After stirring for 2 h at $-78$ °C, 60 mL (0.738 mol) of THF was added. Then, the reaction was carried out for a prescribed time, and the sample was withdrawn from the system so that the conversion and molecular weight could be measured. The polymerization was stopped by the addition of excess water to the reaction mixture. The polymerization solution was filtered for the removal of AgCl, and product was purified by the addition of a polymer solution to methanol at $-30$ °C. The final product was precipitated, collected by filtration, and dried at 40 °C in vacuum oven.

### *2.5. Characterization*

$^1H$ NMR spectra of the polymers were recorded on a Bruker DMX-500 NMR spectrometer with $CDCl_3$ as a solvent and with TMS as an internal reference. The molecular weights and molecular weight distributions were determined on a Waters 150C gel permeation chromatograph equipped with Ultrastyragel columns (500, $10^3$, and $10^4$ Å) with monodispersed polystyrene as a calibration standard. THF was used as an eluent at a flow rate of 1.0 mL/min.

## 3. Results and discussions

The outline for the synthesis of comb-shape copolymers is shown in Scheme 1. First, RAFT copolymerization of St and CMS using 1-(ethoxycarbonyl)prop-1-yl dithiobenzoate (EPDTB) as RAFT agent produced copolymers **1** (poly(St-*co*-CMS)) with side chloride functionalities. Second, block copolymerization of MA using poly(St-*co*-CMS) as macromolecular RAFT agent afforded poly(St-*co*-CMS)-*b*-PMA diblock copolymer. The third, using poly(St-*co*-CMS)-*b*-PMA diblock copolymer as ring-opening polymerization centers of THF afforded comb copolymers with PMA as handle.



Scheme 1.

### 3.1. Copolymerization of St and CMS

The RAFT polymerizations of various monomers are controlled based on the previous researches [18–22]. The copolymerization of St and CMS with different added ratios were performed in THF using 1-(ethoxycarbonyl)prop-1-yl dithiobenzoate (EPDTB) as chain transfer agent at the temperature of 110 °C. All the copolymers of poly(St-*co*-CMS) obtained were of red color. The copolymerization conditions and the results are listed in Table 1. In the experiments, we used GPC and NMR to trace the copolymerization of St and CMS, the GPC results showed that the copolymers obtained have very narrow molecular weight distribution, and the GPC curves are symmetric as shown in Fig. 1(A). The structures of the copolymers obtained are analyzed by $^1$H NMR method; the typical $^1$H NMR spectra are shown in Fig. 2. The peaks at $\delta = 1.4$ and 1.8 ppm are ascribed to the methylene protons and methine proton of the main chain, respectively, the peaks at $\delta = 6.5$ and 7.0 ppm are ascribed the protons of benzene ring and the peak at $\delta = 4.5$ ppm is ascribed to the methylene protons of benzyl chloride groups connected with benzene ring of CMS. From the integral value ratio of $I_{4.5}$ to $I_{6.5}$, we can calculate the composition ratio of CMS units and St units in the

Table 1
The conditions and results of RAFT polymerization of CMS and MA

| No | Polymer composition[a] | Polym. time (h) | Conv. (%) | Composition in polymer (mol%) | | | $M_n$ (NMR)[b,c] | $M_n$(GPC) | $M_n$(th) | $M_w/M_n$ |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | CMS | St | MA | | | | |
| 1 | $\mathrm{PCMS}_0$ | 20 | 32 | 100 | 0 | | 4079 | 3071 | 3148 | 1.05 |
| 2 | $\mathrm{PCMS}_2$ | 30 | 45 | 33 | 67 | | 4568 | 3785 | 4318 | 1.04 |
| 3 | $\mathrm{PCMS}_5$ | 48 | 60 | 17 | 83 | | 5786 | 4943 | 5668 | 1.07 |
| 4 | $\mathrm{PCMS}_0$-*b*-PMA | 11 | 43 | 21 | 0 | 79 | 10,472 | 9657 | 8563 | 1.18 |
| 5 | $\mathrm{PCMS}_2$-*b*-PMA | 11 | 50 | 10 | 21 | 69 | 11,268 | 9975 | 12,954 | 1.21 |
| 6 | $\mathrm{PCMS}_5$-*b*-PMA | 18 | 68 | 5 | 24 | 71 | 18,908 | 15,263 | 20,178 | 1.25 |

Polymerization conditions: Monomer:EPDTB = 9000 (g/mol). PCMSn:MA = 1:4 (g/g).

[a] PCMSn mean the copolymers with added monomer ratio of CMS/St = 1/n.

[b] For $M_n$(NMR) of PCMSn, $M_{n\ \mathrm{PCMSn}}(\mathrm{NMR}) = (2I_{1-2.3})/(3I_{8.0})\times 104\times(\mathrm{St})\% + (2I_{1-2.3})/(3I_{8.0})\times 152.5\times(\mathrm{CMS})\% + 268$.

[c] For $M_n$(NMR) of poly(St-*co*-CMS)-*b*-PMA, $M_{n\ \mathrm{PCMSn}\text{-}b\text{-}\mathrm{PMA}}(\mathrm{NMR}) = M_{n\ \mathrm{PCMSn}}(\mathrm{NMR}) + (2I_{3.7})/(3I_{8.0})\times 86$.

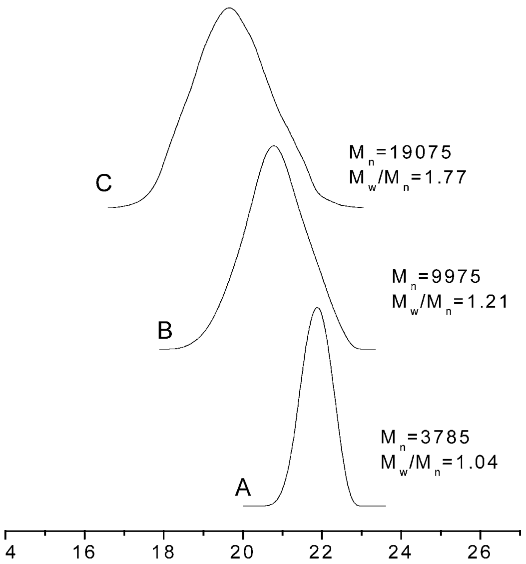


Fig. 1. GPC curves of polymer samples (A) poly(St-*co*-CSM) with $M_n$ = 3785, $M_w/M_n$ = 1.04, (B) poly(St-*co*-CSM)-*b*-PMA with $M_n$ = 9975, $M_w/M_n$ = 1.21 and (C) (PCMS$_2$-*g*-PTHF)-*b*-PMA with $M_n$ = 19075, $M_w/M_n$ = 1.77.

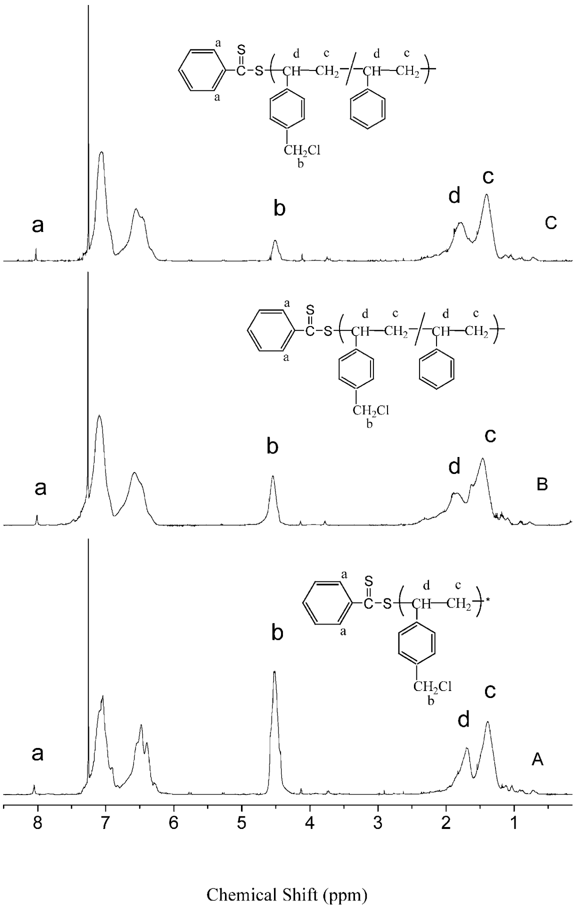


Fig. 2. $^1$H NMR spectra of poly(St-*co*-CMS) (A) No1, $M_n$ = 3071, $M_w/M_n$ = 1.05, (B) No2, $M_n$ = 3785, $M_w/M_n$ = 1.04 and (C) No3, $M_n$ = 4943, $M_w/M_n$ = 1.07.

copolymers obtained. The calculation results are listed in Table 1. In this table, it is clear that the composition of the copolymers obtained is almost the same with that of monomer ratio added. On the other hand, we calculated the composition of the copolymers obtained at different stage from $^1$H NMR spectra, and the results showed that the composition of the copolymers obtained at different stage almost remained the same. All these facts indicate that the number of CMS units in the copolymers obtained can be controlled by the monomer ratio added and the CMS units are almost homogeneously distributed the main chain of poly(St-*co*-CMS). The small peaks at $\delta = 8.0$, 4.1, 3.7,1.2 ppm, originating from RAFT agent—EPDTB, also appeared in the copolymers obtained, which indicating that the copolymers of poly(St-*co*-CMS) can be used as macromolecular chain transfer in RAFT block copolymerization. Fig. 3(A) shows the relationship of monomer conversion and $\ln([M]_0/[M]_t)$ with the polymerization time, it is clear that $\ln([M]_0/[M]_t)$ linearly increases with polymerization time. The plot of $M_n$ and $M_w/M_n$ vs monomer conversion is shown in Fig. 3(B), it is clear that the molecular weight is developed linearly with comonomer conversion and the molecular weight distribution is very narrow. On the other hand, the $^1$H NMR number average molecular weights ($M_n$(NMR)) are close to the theoretical molecular weight ($M_n$(th)) as shown in

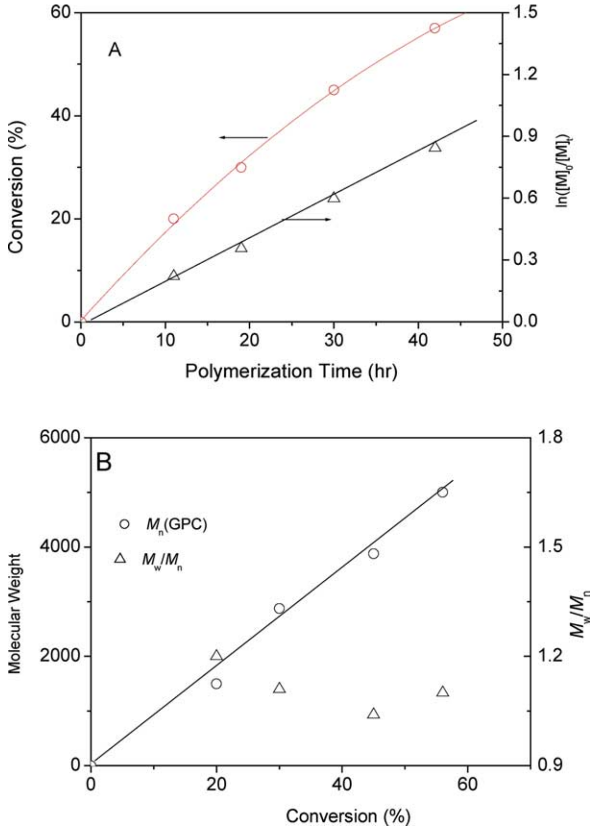


Fig. 3. The relationship of conversion and $\ln([M]_0/[M]_t)$ with polymerization time (A) and the relationship of $M_n$(GPC) and $M_w/M_n$ with comonomer conversion (the molar ratio of St and CMS monomer added is 76:34) (B).

Table 1. All these facts verify that this polymerization is living free radical polymerization.

### *3.2. Block copolymerization of MA with poly(St-co-CMS) as RAFT agent*

It has been reported that block copolymers with well defined structure and controlled molecular weight can be prepared by RAFT polymerization using macromolecular RAFT agent [23,24]. The diblock copolymers of poly(St-*co*-CMS)-*b*-PMA was prepared by RAFT polymerization of MA using poly(St-*co*-CMS) as macromolecular chain transfer agent. The block copolymerization conditions and the results are listed in Table 1. The GPC curve of poly(St-*co*-CMS)-*b*-PMA is symmetric as shown in Fig. 1, after the block copolymerization, the GPC curve was completely shifted toward high molecular weight position. All the copolymers obtained have narrow molecular weight distributions. The typical $^1$H NMR spectrum of poly(St-*co*-CMS)-*b*-PMA is shown in Fig. 5(B). It is clear that the characteristics peak of PMA at $\delta = 3.7$ ppm appeared in this spectrum besides the appearance of characteristics peaks of poly(St-*co*-CMS). From the molar integral value ratio of peaks at $\delta = 3.7$, 4.5 and 6.5 ppm, we can calculate the composition of the block copolymers obtained and NMR molecular weight, $M_n$(NMR). The calculating results are listed in Table 1. On the other hand, the molecular weight of block copolymers obtained increases linearly with monomer conversion and the molecular weight distribution is narrow during the block copolymerization (as shown in Fig. 4), and the $^1$H NMR number average molecular weights ($M_n$(NMR)) are close to the theoretical molecular weight ($M_n$(th)) as shown in Table 1. All these facts show that the chain length of PMA can be controlled.

### *3.3. Preparation of comb-shape copolymer*

As shown in Scheme 1, benzyl chloride in block copolymer of poly(St-*co*-CMS)-*b*-PMA can react with $AgClO_4$ to form benzyl cations on the side of the block copolymer of poly(St-*co*-CMS)-*b*-PMA, these benzyl cations can be used as initiating center of ring-opening polymerization of THF. It was reported that in the ring-opening polymerization of THF using PSt-Br/$AgClO_4$ as initiator, there were some β-H eliminations occurred, which resulted some dead PSt chains [25,26]. However, these β-H eliminations can be decreased greatly by decrease of the ring-opening polymerization temperature to −78 °C. In our experiments, the formation of benzyl cations was carried out at −78 °C, and we found that there was almost no H elimination occurred. We use the GPC to trace the polymerization of THF, the GPC results of the produced comb-shaped copolymers are listed in Table 2 and Fig. 1(C). From Table 2, it is clear that the comb-shaped copolymers have higher molecular weights than those of block copolymer used as initiating centers. The structure of the comb-shaped copolymer was analyzed by $^1$H NMR. A typical $^1$H NMR of comb-shaped copolymers is shown in Fig. 5(C). Besides that characteristic peaks of poly(St-*co*-CMS) and PMA remained in Fig. 5(C), a peak at $\delta = 3.4$ ppm ascribed to the ether methylene protons of PTHF also appeared, which indicates that PTHF chains were grafted from the main chain. In Fig. 5(C), we can found that

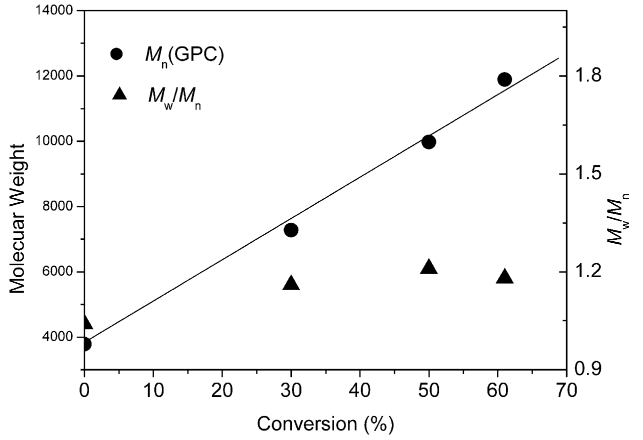


Fig. 4. The relationships of $M_n$(GPC) and $M_w/M_n$ with monomer conversion.

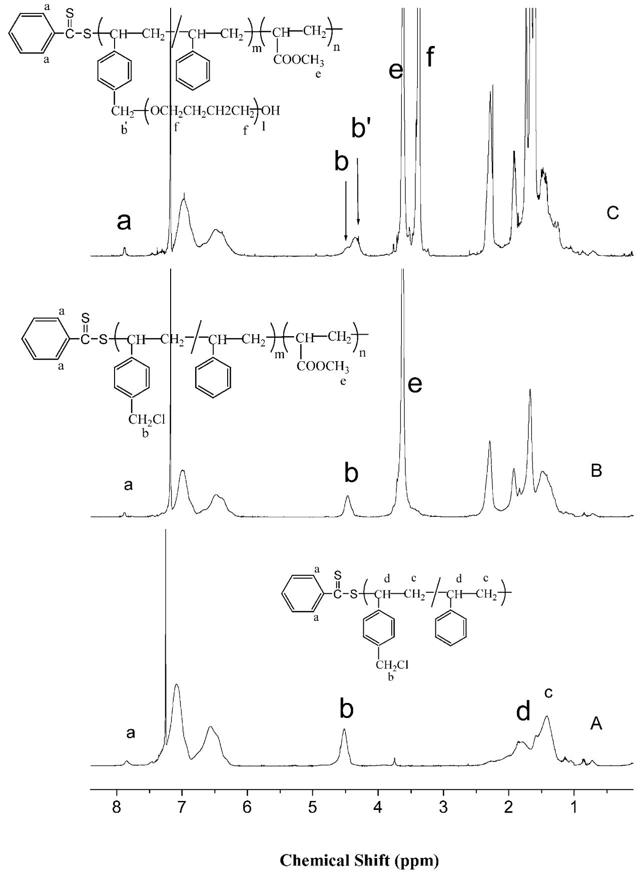


Fig. 5. $^1$H NMR spectra of polymers (A) poly(St-*co*-CMS) with $M_n = 3785$, $M_w/M_n = 1.04$, (B) poly(St-*co*-CMS)-*b*-PMA with $M_n = 9975$, $M_w/M_n = 1.21$ and (C) ($PCMS_2$-*g*-PTHF)-*b*-PMA with $M_n = 19075$, $M_w/M_n = 1.77$.

Table 2
The conditions and results of ROP of THF

| No. | Polymer composition | Time (h) | Conv. (%) | Composition in polymer (mol%) | | | | $M_n$(GPC) | $M_w/M_n$ |
|---|---|---|---|---|---|---|---|---|---|
| | | | | CMS | St | MA | THF | | |
| 7 | (PCMS$_0$-*g*-PTHF)-*b*-PMA | 3 | 7 | 3 | | 13 | 84 | 48,031 | 1.86 |
| 8 | (PCMS$_2$-*g*-PTHF)-*b*-PMA | 4 | 6 | 5 | 9 | 31 | 55 | 19,075 | 1.77 |
| 9 | (PCMS$_5$-*g*-PTHF)-*b*-PMA | 5 | 5 | 3 | 16 | 47 | 34 | 21,431 | 1.71 |

most of the peak at $\delta=4.5$ ppm ascribed to methylene protons of benzyl chloride moved to $\delta=4.4$ ppm, which resulted from that the benzyl cation initiated ring-opening polymerization of THF, and the benzyl chloride became benzyl oxide. However, in Fig. 5(C), we can found that not all the peak at $\delta=4.5$ ppm moved to $\delta=4.4$ ppm, there is about 5% remained at $\delta=4.5$ ppm (not move to $\delta=4.4$ ppm), which is resulted from that 5% benzyl chlorides have not participated in the ring-opening polymerization of THF. If we increase the reaction time of benzyl chloride and $AgClO_4$, the ratio of $I_{4.5}/I_{4.4}$ will decrease, this phenomenon is similar to previous findings.

In summary we use the RAFT copolymerization of St and CMS to produce copolymer of poly(St-*co*-CMS), in which the composition of St and CMS units in the copolymers obtained can be controlled by the ratio of St monomer with CMS monomer, CMS units are homogenously distributed in the main chain. The copolymers poly(St-*co*-CMS) have controlled molecular weights and narrow molecular weight distributions. Block copolymer of poly(St-*co*-CMS)-*b*-PMA with well defined structure and narrow molecular weight distribution was prepared by RAFT polymerization of MA with poly(St-*co*-CMS)-SC(S)Ph as macromolecular chain transfer agent. The comb-shaped copolymer with well-defined structure can be prepared by the ring-opening polymerization of THF using poly(St-*co*-CMS)-*b*-PMA/$AgClO_4$ as initiating system.

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