

SYNTHESIS OF HETEROARM STAR-SHAPED POLYMER BY THE USE OF POLYFUNCTIONAL CHAIN-TRANSFER AGENT *via* CONVENTIONAL FREE RADICAL POLYMERIZATION

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Abstract Heteroarm star-shaped polymers were synthesized by conventional free radical polymerization in two steps by the use of polyfunctional chain transfer agent. In the first step, free radical polymerization of methyl methacrylate was carried out in the presence of a polyfunctional chain transfer agent, pentaerythritol tetrakis(3-mercaptopropionate). At appropriate monomer conversions, two-arm PMMA having two residual thiol groups at the chain center or three-arm PMMA having one residual thiol group at the core were obtained. In the second step, free radical polymerization of styrene was carried out using PMMAs obtained above as macro-chain transfer agent. When styrene conversion was lower than 30%, heteroarm star-shaped polymers, (PMMA)₂(PS)₂ and (PMMA)₃(PS), were obtained successfully.

Keywords: Heteroarm star-shaped polymer; Conventional free radical polymerization; Polyfunctional chain-transfer agent.

INTRODUCTION

In recent years, much attention has been paid to heteroarm star-shaped polymers because of their unique properties both in solid state and in solution^[1]. They are generally prepared by the following methods. The first method is through the use of anionic polymerization technique where the living chain ends are consecutively grafted onto a multifunctional chlorosilane^[2–5]. The second approach utilizes the addition of anionically or cationically derived living polymers to a small amount of a difunctional monomer, such as divinylbenzene. This leads to the formation of a star molecule with additional sites in the polymerizable core. Subsequent addition of another monomer yields the heteroarm star-shaped polymers^[6–8]. This approach has been extended to controlled radical polymerization techniques^[9–11]. The third method is based on macromonomer technique^[12–16]. In this method, a nonhomopolymerizable macromonomer bearing a 1,4-bis(1-phenylethenyl)benzene or a 1,1-diphenylethylene group at one chain end is incorporated at the junction of two polymer blocks. The last technique is by the use of heterofunctional initiators by combining stable free radical polymerization (SFRP), atom transfer radical polymerization (ATRP), reversible addition-fragmentation transfer (RAFT) polymerization and ring open polymerization (ROP)^[17–30]. Our group ever synthesized heteroarm star-shaped polymers using the second and the last methods by ATRP or by combination of ATRP and SFRP^[31, 32]. All of the above methods are based on various living polymerizations, which need to be carried out under rigorous conditions or in the presence of catalyst or expensive agents.

The use of polyfunctional chain transfer agents (P-CTA) in free radical polymerization is a simple method to synthesize polymers with star-branched structures. Tobita *et al.*^[33–35] predicted the molecular weight distribution in free radical polymerization that involves P-CTA. For solution polymerization of styrene whose bimolecular termination is by combination, a complex branched structure was generated^[36]. Yuan *et al.*^[37–39] also

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investigated theoretically and experimentally free radical polymerization in the presence of P-CTA, in which star polymers formed exclusively in the absence of combination termination.

Based on the results of Yuan's study, in this paper, we tried to prepare heteroarm star-shaped polymers using conventional free radical polymerization in the presence of P-CTA.

EXPERIMENTAL

Materials

Styrene (polymerization grade, Yanshan Petrochemical Co.) and methyl methacrylate (MMA) (> 99%, Beijing Chemical Reagent Company) were dried over anhydrous MgSO_4 , then distilled under reduced pressure, and stored at -15°C in a freezer. 2,2'-Azobis(isobutyronitrile) (AIBN, 98%, Fluka) was recrystallized from ethanol. Pentaerythritol tetrakis(3-mercaptopropionate) (PETMP) (> 97%, Fluka), petroleum ether (bp: $30\text{--}60^\circ\text{C}$, Beijing Chemical Reagent Company) and all other reagents were used as received without further purification.

Solution Polymerization of MMA in the Presence of PETMP

In a typical example, MMA (20 g, 200 mmol), AIBN (0.1264 g, 0.7698 mmol), PETMP (1.486 g, 3.045 mmol) and benzene (40 g) were added to a 100 mL dried round-bottomed flask equipped with a magnetic stirrer. After the flask was sealed with a rubber septum, it was degassed by three freeze-pump-thaw cycles and subsequently purged under argon atmosphere, and then immersed in an oil bath thermostated at 70°C . At definite time intervals, portions of the sample were withdrawn from the flask using argon-filled gas-tight syringes to determine molecular weights and monomer conversions. PMMA was obtained by precipitation in a large amount of cold petroleum ether, dried under vacuum and stored at -15°C until further use.

Synthesis of Heteroarm Star-Shaped Polymers

In a typical example, styrene (3.0 g, 28.8 mmol), AIBN (0.0224 g, 0.136 mmol), PMMA obtained above ($M_{n,\text{GPC}} = 5240$, $M_w/M_n = 1.38$, 1.640 g, 0.313 mmol) and benzene (10.24 g) were added to a 100 mL dried round-bottomed flask equipped with a magnetic stirrer. After the flask was sealed with a rubber septum, it was degassed by three freeze-pump-thaw cycles and subsequently purged under argon atmosphere, and then immersed in an oil bath thermostated at 70°C . At definite time intervals, portions of the sample were withdrawn from the flask using argon-filled gas-tight syringes to determine molecular weights and monomer conversions. The heteroarm star-shaped polymer was obtained by precipitation in a large amount of cold methanol and dried under vacuum.

Characterization

Monomer conversion was obtained gravimetrically. The apparent number-average molecular weights and molecular weight distributions were determined by using a Tosoh HPLC 8220 chromatograph (column, TSK-Gel Super HZM-M $\times$ 2) with THF (40°C) as the eluent. Polystyrene standards were used to generate the calibration curve. $^1\text{H-NMR}$ spectra were recorded on a Bruker AV 600-MHz spectrometer with CDCl_3 as solvent at room temperature.

RESULTS AND DISCUSSION

Free Radical Polymerization of MMA with PETMP as P-CTA

For conventional free radical polymerization system, material balances for the different reaction species by definition can be written as:

$$\frac{-d[\text{M}]}{dt} = k_p[\text{M}][\text{M}\cdot] \quad (1)$$

$$\frac{-d[\text{CTA}]}{dt} = k_{tr}[\text{CTA}][\text{M}\cdot] \quad (2)$$

Where, $\frac{d[M]}{dt}$, $\frac{d[CTA]}{dt}$, k_p , k_{tr} , $[M]$, $[CTA]$ and $[M\cdot]$ are monomer consumption rate, chain transfer agent consumption rate, chain propagation rate constant, chain transfer rate constant, monomer concentration, chain transfer agent concentration and the radical concentration in the polymerization system, respectively.

Dividing Eq. (1) by Eq. (2) and integrating, it gives:

$$C_{tr} \frac{d[M]}{[M]} = \frac{d[CTA]}{[CTA]} \quad (3)$$

$$C_{tr} \int_{M_0}^M \frac{d[M]}{[M]} dt = \int_{CTA_0}^{CTA} \frac{d[CTA]}{[CTA]} dt \quad (4)$$

$$C_{tr} \ln(1 - F_M) = \ln(1 - F_{CTA}) \quad (5)$$

Where $C_{tr} = k_{tr}/k_p$, F_M and F_{CTA} are monomer conversion and chain transfer agent conversion, respectively.

Generally speaking, nucleophilic radical can abstract a hydrogen atom from a thiol molecular much easier than electrophilic radical. So the chain transfer constant (C_{tr}) of a thiol for styrene is much larger than that of the similar thiol for MMA. For example, C_{tr} of 1-dodecanethiol and 3-mercapo propionic acid for styrene at 70°C are 19 and 9.4 respectively, while those for MMA at the same temperature are 0.55 and 0.38^[40]. By using Eq. (5), it is possible to calculate the relationship between the monomer conversion and chain transfer agent conversion. Assuming that C_{tr} of PETMP for MMA is 0.8, when MMA conversion is 31.0%, 57.9% and 82.3%, there is still 75%, 50% and 25% thiol groups of PETMP existing, respectively. That is to say, when MMA conversion is about 30%, on average, one-arm PMMA or PMMA with three thiol groups will be generated. When MMA conversion is about 50%, on average, two-arm PMMA or PMMA with two thiol groups will be generated. When MMA conversion is about 80%, on average, three-arm PMMA or PMMA with one thiol group will be generated. If C_{tr} of PETMP for MMA is assumed to be 0.6, 75%, 50% and 25% residual thiol groups of PETMP correspond to 38.1%, 68.5% and 99.9% MMA conversions, respectively.

Radical polymerization of MMA in benzene was carried out at 70°C in the presence of PETMP with the molar ratio of PETMP to AIBN to be 3.95:1. Figure 1 shows the GPC curves of PMMAs obtained at different monomer conversions for two experiments with molar ratio of MMA to PETMP to be 45:1 and 66:1, respectively. It can be seen that, the GPC curves of PMMAs were unimodal throughout the polymerization process, and shifted to higher molecular weight direction with the increase of monomer conversion. The polydispersity indexes obtained at higher monomer conversions were relatively low.

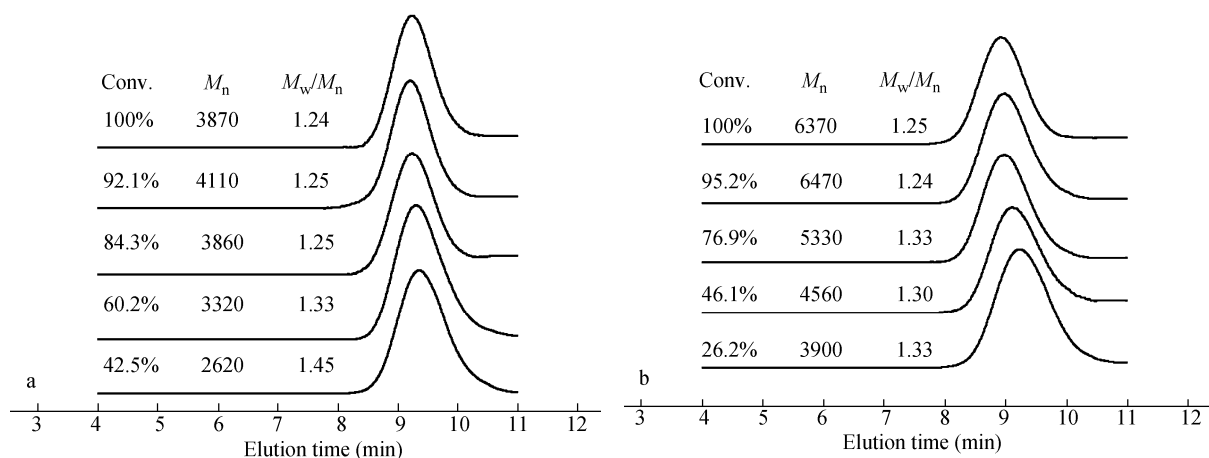


Fig. 1 GPC curves of PMMAs obtained at different monomer conversions in benzene at 70°C
Reaction conditions: $[MMA] = 3 \text{ mol/L}$; a) $[MMA]:[PETMP]:[AIBN] = 180:3.95:1$; b) $[MMA]:[PETMP]:[AIBN] = 260:3.95:1$

The ^1H -NMR spectra of PMMAs obtained with PETMP as P-CTA at different monomer conversions are shown in Figs. 2(B), 2(C) and 2(D). For comparison, ^1H -NMR spectrum of PETMP is given in Fig. 2(A). Figure 2(A) shows the presence of two methylene group protons of $-\text{CH}_2-\text{O}-\text{CO}-$ (a) at $\delta = 4.17$, two methylene group protons of $-\text{CH}_2-\text{O}-\text{CO}-\text{CH}_2-$ (b) at $\delta = 2.65$ – 2.69 and two methylene protons of $-\text{CH}_2-\text{SH}$ (c) at $\delta = 2.74$ – 2.78 . The ^1H -NMR spectra of PMMAs obtained with PETMP as P-CTA at different monomer conversions were similar. The characteristic signals ($-\text{CH}_3$, $\delta = 0.8$ – 1.1 ; $-\text{OCH}_3$, $\delta = 3.5$ – 3.6) for PMMA were observed. However, along with the increase of MMA conversion, the chemical shift at $\delta = 2.74$ – 2.78 due to the protons adjacent to the thiol group ($-\text{CH}_2-\text{SH}$) (c) gradually disappeared. At the same time, a new signal at $\delta = 2.55$ – 2.68 due to newly formed $-\text{CH}_2-\text{S}-\text{CH}_2-$ appeared. Furthermore, with the increase of MMA conversion, the relative strength of the signal at $\delta = 2.55$ – 2.68 became stronger gradually.

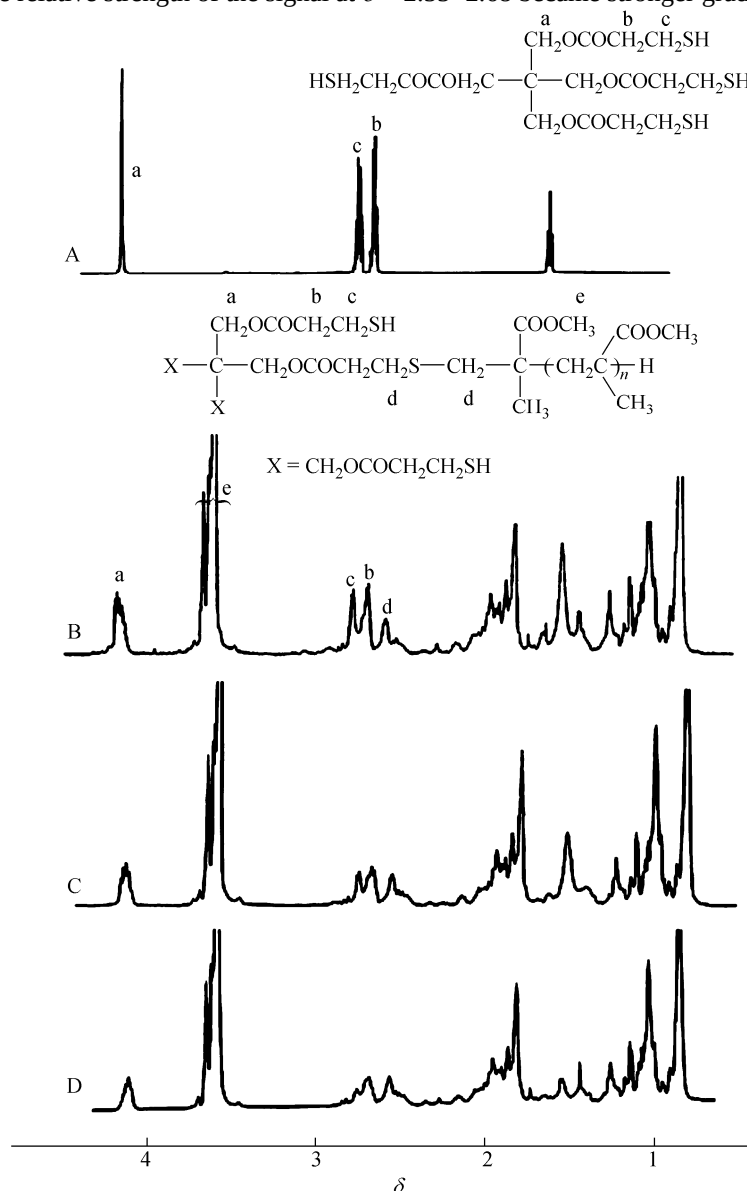


Fig. 2 ^1H -NMR spectra of PETMP and PMMAs obtained with PETMP as chain transfer agent at different monomer conversions
 A) PETMP; B) PMMA obtained at 42.5% conversion; C) PMMA obtained at 60.2% conversion; D) PMMA obtained at about 100% conversion

For pure PETMP, the ratio of $I_b + I_c$ to I_a is 2.0. When four-arm PMMA is obtained by complete chain transfer reaction of all the thiol groups of PETMP to MMA, the theoretical ratio of $I_b + I_c + I_d$ to I_a should be 3.0. The ratio of $I_b + I_c + I_d$ to I_a should be 2.0–3.0 when PMMA is obtained by chain transfer reaction of part thiol groups of PETMP to MMA. Therefore, the actual average number of arms (N) for star-shaped PMMAs obtained by chain transfer reaction of the thiol groups of PETMP to MMA can be calculated using the following equation:

$$N = \frac{8(I_b + I_c + I_d - 2I_a)}{2I_a} \quad (6)$$

The number-average molecular weights of star-shaped polymer PMMAs can be calculated using the following equation:

$$M_{n,NMR} = \frac{8I_e}{3I_a} \times M_{n,MMA} + M_I \quad (7)$$

Where, I_a , $(I_b + I_c + I_d)$, and I_e are the integral values of peaks at $\delta = 4.17$ – 4.11 , $\delta = 2.56$ – 2.75 , and $\delta = 3.5$ – 3.6 , respectively. $M_{n,MMA}$ and M_I are the molecular weights of MMA and PETMP, respectively. X is the number-average molecular weight of each arm. The calculated results for PMMAs obtained at different monomer conversions are listed in Table 1.

Table 1. The molecular weights and the number of arms for star-shaped PMMAs obtained at different monomer conversions

Conversion (%)	$M_{n,GPC}$	$M_{n,NMR}$	N	$X = \frac{M_{n,NMR} - M_I}{N}$
42.5	2620	2500	1.6	1260
60.2	3320	3250	2.4	1150
100	3870	4040	4.0	890

The $M_{n,NMR}$ values calculated from the $^1\text{H-NMR}$ spectra were in good agreement with those determined by GPC calibrated by standard PS samples, especially at lower monomer conversions. The difference between the average lengths of each arm obtained at different conversion was relatively small, which indicates that chain transfer rate constant of PETMP was close to chain propagation rate constant of MMA. That is to say, C_{tr} of PETMP for MMA was close to 1.0. From Table 1 it can also be seen that the average arm length decreased slightly with the increase of monomer conversion, indicating that chain transfer rate constant of PETMP was a little lower than chain propagation rate constant of MMA. This confirmed that the above assumption, C_{tr} of PETMP for MMA was between 0.6 and 0.8, was reasonable.

The $^1\text{H-NMR}$ spectrum of PMMA obtained with PETMP as P-CTA at 42.5% monomer conversion was shown in Fig. 2(B). The ratio of $I_b + I_c + I_d$ to I_a was 2.4. According to Eq. (6), the average number of arms was calculated to be 1.6. In other words, the average residual thiol groups were 2.4.

Similarly, when monomer conversion increased to 60.2%, the ratio of $I_b + I_c + I_d$ to I_a became 2.6 (Fig. 2C). The average number of arms was calculated to be 2.4, and the average residual thiol groups were 1.6.

When monomer conversion was about 100%, the ratio of $I_b + I_c + I_d$ to I_a became 3.2 (Fig. 2D), the average number of arms was calculated to be about 4.0. All these results indicated that the discussion above was reasonable and the chain transfer constant of PETMP actually was indeed between 0.6 and 0.8.

Free Radical Polymerization of Styrene with PMMAs Obtained at Different Monomer Conversions as Macro-Chain Transfer Agents

As discussed above, PMMAs obtained at different monomer conversions still had residual thiol groups. Therefore, we used them as macro-chain transfer agents for free radical polymerization of styrene in order to prepare heteroarm star-shaped polymers. It should be pointed that thiol-terminated PMMAs may be unstable

under oxygen atmosphere^[41], so they were stored at -15°C under argon atmosphere until further use.

In this section, two PMMAs with different molecular weights were used in the free radical polymerization of styrene. Their molecular characteristics determined by GPC and $^1\text{H-NMR}$ were listed in Table 2.

Table 2. Molecular characteristics of PMMA macro-chain transfer agents

	Conversion (%)	$M_{n,\text{GPC}}$	M_w/M_n	$M_{n,\text{NMR}}$	N
MTa	73.5	5240	1.38	5140	3.0
MTb	50.9	4460	1.36	4360	2.1

Reaction condition: $[\text{MMA}] = 3 \text{ mol/L}$; $[\text{MMA}]:[\text{PETMP}]:[\text{AIBN}] = 260:3.95:1$

Free Radical Polymerization of Styrene with MTa as Macro-Chain Transfer Agent

On average, MTa had three PMMA arms and one unreacted thiol group. If styrene is polymerized with MTa as macro-chain transfer agent, $(\text{PMMA})_3(\text{PS})$ would be obtained.

The free radical polymerization of styrene was carried out at 70°C in benzene with AIBN as initiator and MTa as macro-chain transfer agent. The GPC traces of macro-chain transfer agent and the products obtained at different monomer conversions are shown in Fig. 3. It can be seen that as monomer conversion increased, GPC curves were unimodal and molecular weight shifted to higher molecular weight direction without visible trace of the PMMA macro-chain-transfer agent. Moreover, no high molecular weight shoulder was observed, indicating the successful formation of heteroarm star-shaped polymer $(\text{PMMA})_3(\text{PS})$. In addition, no polystyrene homopolymer was detected by GPC. This may be due to that the chain-transfer constant of MTa for styrene was large enough and only a little amount of PSt homopolymer was produced. However, the chain transfer constant of a thiol for styrene is much larger than that of the similar thiol for MMA. Assuming that C_{tr} of residual thiol group in PMMA for styrene is 10, according to Eq. (5), it can be calculated for styrene polymerization system that there is only 0.03% thiol group existing when monomer conversion reaches 30%. Polystyrene homopolymer may occur beyond 30% conversion because thiol group in MTa was almost consumed completely. Therefore, styrene conversion was controlled at about 30%.

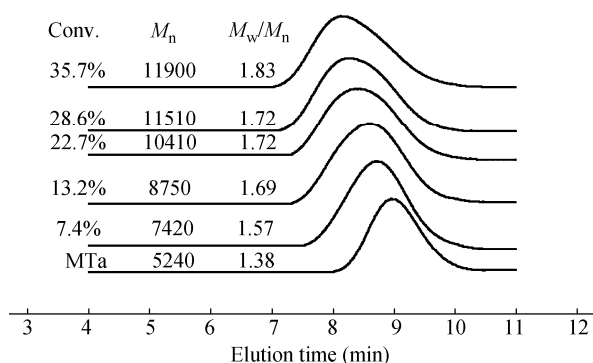


Fig. 3 GPC traces of macro-chain transfer agent and the products obtained at different monomer conversions in benzene at 70°C

Reaction condition: $[\text{St}] = 2.2 \text{ mol/L}$; $[\text{St}]:[\text{MTa}]:[\text{AIBN}] = 247:2.3:1$

Figure 4 shows that $^1\text{H-NMR}$ spectra of macro-transfer agent MTa and one of the heteroarm star-shaped polymers. Compared with the $^1\text{H-NMR}$ spectrum of MTa, the chemical shift at $\delta = 2.74$ due to the protons adjacent to the thiol group ($-\text{CH}_2-\text{SH}$) almost disappeared completely in the $^1\text{H-NMR}$ spectrum of heteroarm star-shaped polymer. At the same time, the relative strength of the peaks at $\delta = 2.55-2.68$ due to protons of $-\text{CH}_2-\text{S}-\text{CH}_2-$ became stronger, and the characteristic signals of styrene repeating unit appeared at $\delta = 6.4-7.2$. These results support that heteroarm star-shaped polymer $(\text{PMMA})_3(\text{PS})$ was successfully synthesized.

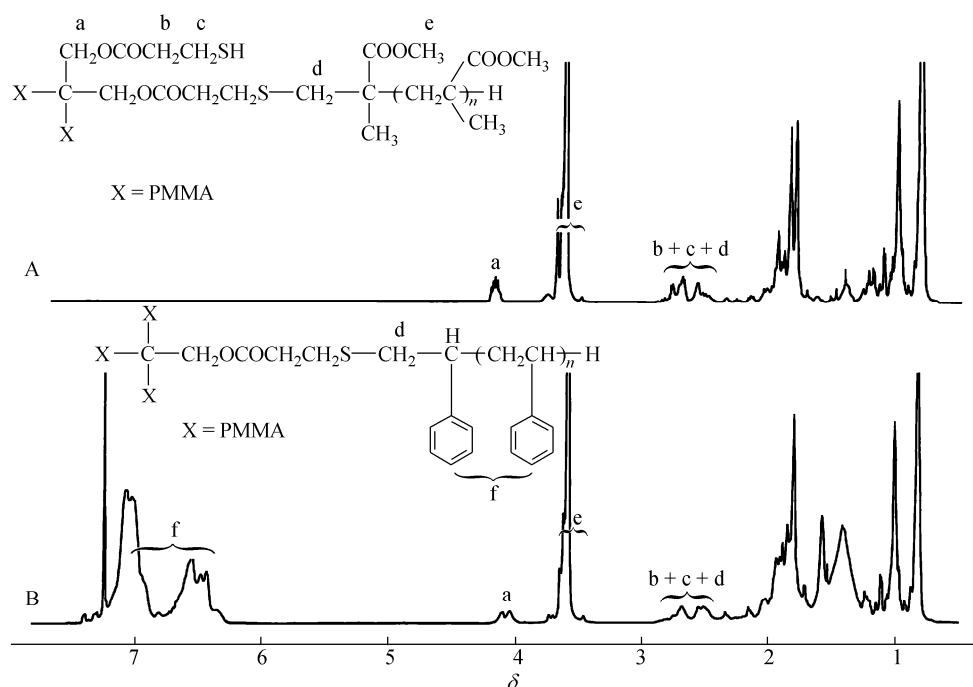


Fig. 4 ^1H -NMR spectra of macro-transfer agent MTa (A) and one of heteroarm star-shaped polymers (B) obtained at 13.2% styrene conversion

The length of polystyrene arm could be calculated according to the peak intensity ratio of I_f/I_a using Eq. (8).

$$M_{\text{NMR,St}} = \frac{8I_f}{5I_a} \times M_{\text{n,St}} \quad (8)$$

Where, I_a , I_f and $M_{\text{n,St}}$ are the integral values of peaks at $\delta = 4.04$ and $\delta = 6.4\text{--}7.2$ and the molecular weight of styrene, respectively.

The molecular weight of the heteroarm star-shaped polymer could be calculated according to Eq. (9).

$$M_{\text{n,NMR}} = \frac{8I_e}{3I_a} \times M_{\text{n,MMA}} + M_I + \frac{8I_f}{5I_a} \times M_{\text{n,St}} \quad (9)$$

Where, I_e is the integral value of peak at $\delta = 3.5\text{--}3.6$. $M_{\text{n,MMA}}$ and M_I are the molecular weight of MMA and PETMP, respectively.

The heteroarm star-shaped polymer shown in Fig. 4(B) was obtained at 13.18% styrene conversion. The molecular weights of polystyrene arm and heteroarm star-shaped polymer calculated using Eqs. (8) and (9) were 4100 and 9200, respectively. The latter value was slightly larger than that obtained by GPC ($M_{\text{n,GPC}} = 8750$) calibrated by linear standard PS samples.

Free Radical Polymerization of Styrene with MTb as Macro-Chain transfer Agent

On average, MTb had two PMMA arms and two unreacted thiol group. If styrene is polymerized with MTb as macro-chain transfer agent, $(\text{PMMA})_2(\text{PS})_2$ would be obtained.

The free radical polymerization of styrene was carried out at 70°C in benzene with AIBN as initiator and MTb as macro-chain transfer agent. The GPC traces of macro-chain transfer agent and the products obtained at different monomer conversions are shown in Fig. 5. It can be seen that the molecular weight shifted to higher molecular weight direction with the increase of monomer conversion. GPC curves were unimodal when styrene conversion was below 27.5%. However, higher molecular weight shoulder was observed when styrene conversion was above 33.2%. This may be due to that thiol group in MTb was consumed completely at higher styrene conversion as discussed above.

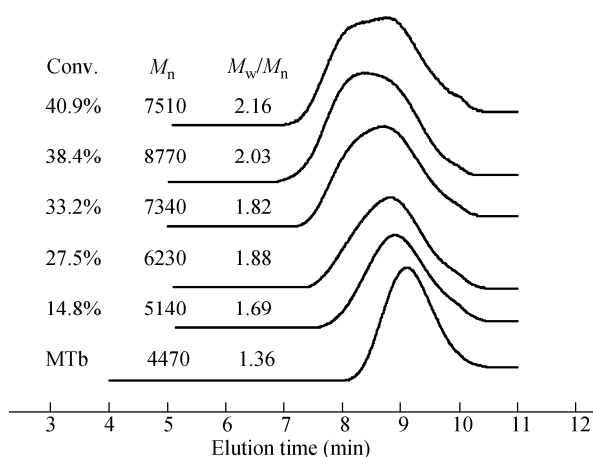


Fig. 5 GPC traces of macro-chain transfer agent and the products obtained at different monomer conversions in benzene at 70°C

Reaction conditions: $[St] = 2.2 \text{ mol/L}$; $[St]:[MTb]:[AIBN] = 247:2.3:1$

Figure 6 shows that $^1\text{H-NMR}$ spectra of MTb and heteroarm star-shaped polymer obtained at 27.5% styrene conversion. Compared with the $^1\text{H-NMR}$ spectrum of MTb, the chemical shift at $\delta = 2.75$ due to the protons adjacent to the thiol group ($-\text{CH}_2-\text{SH}$) almost disappeared completely in the $^1\text{H-NMR}$ spectrum of heteroarm star-shaped polymer. At the same time, the relative strength of the peaks at $\delta = 2.55\text{--}2.68$ due to protons of $-\text{CH}_2-\text{S}-\text{CH}_2-$ became stronger, indicating the successful formation of heteroarm star-shaped polymer. According to Eqs. (8) and (9), it can be calculated that the molecular weight of each polystyrene arm was 1250 and that of this heteroarm star-shaped polymer was 6850, which was slightly larger than that determined by GPC ($M_{n,\text{GPC}} = 6230$) calibrated by linear standard PS samples.

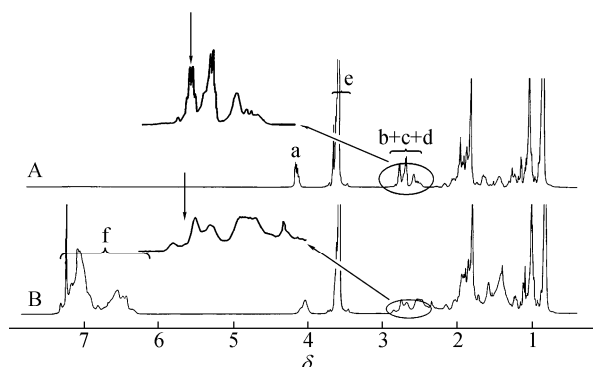


Fig. 6 $^1\text{H-NMR}$ spectra of MTb (A) and heteroarm star polymer (B) obtained at 27.50% styrene conversion

CONCLUSIONS

In the free radical polymerization of MMA with PETMP as P-CTA, two-arm (linear), three-arm and four-arm star-shaped PMMAs were obtained at different monomer conversions. Two-arm and three-arm PMMAs still had two and one thiol groups, respectively. They were further used as macro-chain transfer agent for free radical polymerization of styrene, giving heteroarm star-shaped polymers, $(\text{PMMA})_3(\text{PS})$ and $(\text{PMMA})_2(\text{PS})_2$, at styrene conversion lower than 30%.

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