

# Synthesis of Amphiphilic Heteroarm Star-Shaped Polymer via Free Radical Polymerization Using Polyfunctional Chain Transfer Agent and Its Self-Assembly Behavior

Meng-Qing Lv, Yan Shi, Wan-Tai Yang, Zhi-Feng Fu

Department of Materials Science and Engineering, State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, China

Correspondence to: Y. Shi (E-mail: shiyan@mail.buct.edu.cn)

**ABSTRACT:** Amphiphilic heteroarm star-shaped polymers have important theoretical and practical significance. In this work, amphiphilic heteroarm star-shaped polymer was synthesized by the use of polyfunctional chain transfer agent via sequential free radical polymerization in two steps. First, conventional free radical polymerization of methyl methacrylate (MMA) initiated by 2,2'-azobis(isobutyronitrile) (AIBN) was carried out in the presence of polyfunctional chain transfer agent, pentaerythritol-tertrakis (3-mercaptopropionate) (PETMP). At appropriate monomer conversion, about two-arm s-PMMA having two residual thiol groups at the chain center was obtained. Second, the s-PMMA obtained above was used as macro-chain-transfer agent for free radical polymerization of acrylic acid (AA). The heteroarm star-shaped polymer with the hydrophobic PMMA segment and the hydrophilic PAA segment was obtained. The successful synthesis of heteroarm star-shaped polymers, (PMMA)<sub>2</sub>(AA)<sub>2</sub>, was confirmed by <sup>1</sup>H-NMR and its self-assembly behavior in different solvents. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

**KEYWORDS:** heteroarm star-shaped polymer; conventional free radical polymerization; polyfunctional chain-transfer agent; self-assembly

Received 22 February 2011; accepted 7 June 2012; published online

DOI: 10.1002/app.38173

## INTRODUCTION

In recent years, the development of the polymerization technology has provided various methods to synthesize nonlinear structure polymers, such as, star-shaped polymer, star-shaped block or heteroarm copolymers, graft polymers, dendritic or ultra-branched polymers. Among these nonlinear structure polymers, heteroarm star-shaped polymers with linear chains having different chemical composition connected to the identical central core have important theoretical and practical significance.<sup>1</sup>

Heteroarm star-shaped polymers 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.<sup>2–5</sup> 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.<sup>6–8</sup> This approach has been extended to controlled radical polymerization techniques.<sup>9–11</sup> The third method is based on macromonomer

technique.<sup>12–16</sup> 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 fourth 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, ring open polymerization (ROP) or other living/controlled polymerization methods.<sup>17–30</sup> Our group ever synthesized heteroarm star-shaped polymers using the second and the four methods by ATRP or by combination of ATRP and SFRP.<sup>31,32</sup> Recently, hydrogen-bonding has proved to be one of the most prominent supramolecular motifs and has been utilized for the generation of a wide variety of supramolecular copolymers, such as block copolymers, star copolymers, and so on. Bernard and coworkers synthesized miktoarm stars copolymers by assembling reversible addition-fragmentation chain transfer (RAFT) polymerized chains bearing hydrogen-bonding heterocomplementary associating units.<sup>33</sup> Barner reported the synthesis of star and miktoarm star block (co)polymers via hydrogen-binding self-assembly of ATRP generated polymer segments with hamilton wedge and cyanuric acid terminal

groups.<sup>34</sup> The very last developments in the synthesis of a variety of star polymers via efficient polymer-polymer modular ligation reactions were reviewed by Tunca and coworkers recently.<sup>35</sup> Especially, the combination of modular ligation strategies with different living radical polymerization techniques affords the synthesis of increasingly complex macromolecular structures including star copolymers. All of the above methods are based on various living polymerizations, which need to be carried out under relative 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.<sup>36–38</sup> predicted the molecular weight distribution in free radical polymerization that involves P-CTA, e.g., tris(mercaptoglycolate) or pentaerythritol-tetrakis(3-mercaptopropionate) (PETMP). For solution polymerization of styrene whose bimolecular termination was by combination, a complex branched structure was generated.<sup>39</sup> Yuan et al.<sup>40,41</sup> also investigated theoretically and experimentally free radical polymerization of MMA in the presence of PETMP, in which star polymers formed exclusively in the absence of combination termination. Loubat and Boutevin<sup>42</sup> investigated the transfer constants of acrylic acid (AA) for PETMP in different solvents and discovered ideal telomerization ( $C_T = 1$ ) of AA in water/THF (70/20, v/v) solvent. On the basis of the above research, our group synthesized heteroarm star-shaped PMMA/PS copolymer using conventional free radical polymerization in the presence of P-CTA<sup>43</sup>. In this paper, we reported the synthesis of amphiphilic heteroarm star-shaped PMMA/PAA copolymers. First, two-arm s-PMMA having two residual thiol groups at the chain center was obtained by conventional free radical polymerization of MMA in the presence of PETMP. Second, heteroarm amphiphilic star-shaped PMMA/PAA copolymer was prepared through AA polymerization with s-PMMA with residual thiol as macro-transfer-agent. To the best of our knowledge, it is the first time that heteroarm star-shaped PMMA/PAA copolymer was prepared through conventional radical polymerization.

## EXPERIMENTAL

### Materials

Acrylic acid (AA) (polymerization grade, Beijing Chemical Reagent Company) and methyl methacrylate (MMA) (polymerization grade, Beijing Chemical Reagent Company) were dried over anhydrous  $MgSO_4$ , then distilled under reduced pressure, and stored at  $-15^\circ C$  in a freezer. 2,2'-Azobis(isobutyronitrile) (AIBN, 98%, Fluka) was recrystallized from ethanol. Pentaerythritol tetrakis(3-mercaptopropionate) (PETMP) (>97%, Fluka) and all other reagents were used as received without further purification.

### Solution Polymerization of MMA in the Presence of PETMP

In a typical example, the mole feed ratio of MMA : PETMP : AIBN was 70 : 1 : 0.3, the concentration of MMA was 3 mol/L, and benzene was used as solvent. All the reagents 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  $70^\circ C$ . 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  $-15^\circ C$  until further use.

### Synthesis of Heteroarm Star-Shaped Polymers

In a typical example, AA (4.0 g), AIBN (0.012 g) and PMMA obtained above ( $M_n, GPC = 3300$ ,  $M_w/M_n = 1.47$ , 0.66 g) and solvent (20 mL) 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  $60^\circ C$ . 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.

### Self-Assembly of Amphiphilic Heteroarm Star-Shaped Polymers

PMMA-PAA weighed about 25 mg was dissolved in 5 mL of tetrahydrofuran (THF), and then the solution was added dropwise to 0.1 N KOH aqueous solution (10 mL) with vigorous stirring. A blue tint or milky dispersion appeared, indicating the formation of aggregates. The solution was stirred for several hours for the evaporation of THF.

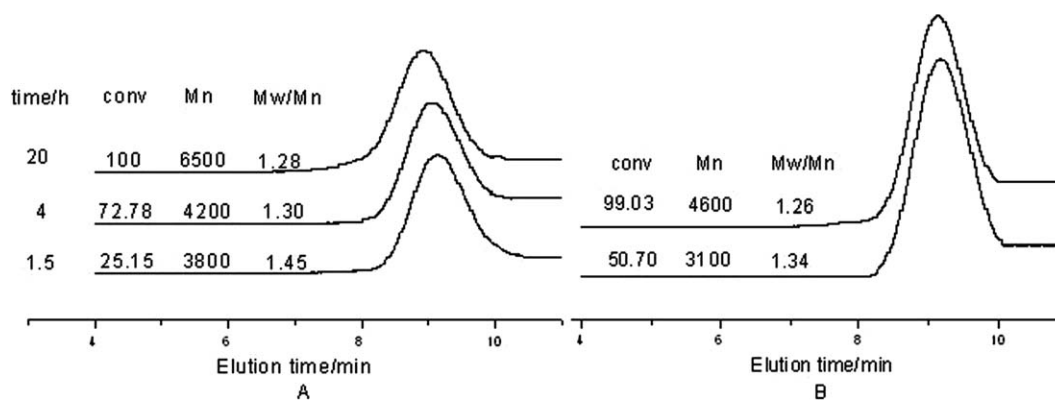
### Characterization

Monomer conversion was obtained gravimetrically. The apparent number-average molecular weights and molecular weight distributions were determined by Tosoh HPLC-8320 chromatograph (column, TSK-Gel SuperMultipore HZ-M2) with THF ( $40^\circ C$ ) as the eluent at a flow rate of 0.35 mL/min. Polystyrene standards were used to generate the calibration curve.  $^1H$ -NMR spectra were recorded on a Bruker AV 600-MHz spectrometer with  $CDCl_3$  (for PMMA) or  $CD_3OD$  (for PAA and amphiphilic heteroarm star-shaped polymer) as solvent at room temperature. The self-assembly solutions of amphiphilic polymers were filtered through 0.45  $\mu m$  filters before analysis. Transmission electron microscopy (TEM) was carried out on a Hitachi H-800 microscope operated at an acceleration voltage of 200 kV. Samples were prepared by dropping a droplet of latex (formed by self-assembly of amphiphilic polymers in KOH aqueous solution) on a copper TEM grid, which was coated with thin films of Formvar and carbon successively, and the solvent was let to evaporate under ambient atmosphere for 1 h. Dynamic light scattering (DLS, Brookhaven 200-SM) (wavelength 532 nm, testing temperature  $25^\circ C$ ) were used to characterize the size and size distribution of the aggregates of the amphiphilic heteroarm star-shaped polymer.

## RESULTS AND DISCUSSION

### Free Radical Polymerization of MMA in the Presence of PETMP

Radical polymerization of MMA in benzene was carried out at  $70^\circ C$  in the presence of PETMP with the molar ratio of PETMP to AIBN to be 1 : 0.3. Figure 1(A, B) shows the GPC curves of PMMAs obtained at different monomer conversions for two experiments with molar ratio of MMA to PETMP to be 70 : 1



**Figure 1.** GPC curves of PMMAs obtained at different monomer conversions in benzene at 70°C. Reaction conditions: [MMA] = 3 mol/L; (A) [MMA] : [PETMP] : [AIBN] = 70 : 1 : 0.3; (B) [MMA] : [PETMP] : [AIBN] = 50 : 1 : 0.3.

and 50 : 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 lower. In Figure 1(B), because the amount of the chain transfer agent increased, compared with Figure 1(A), the molecular weight reduced under similar monomer conversion.

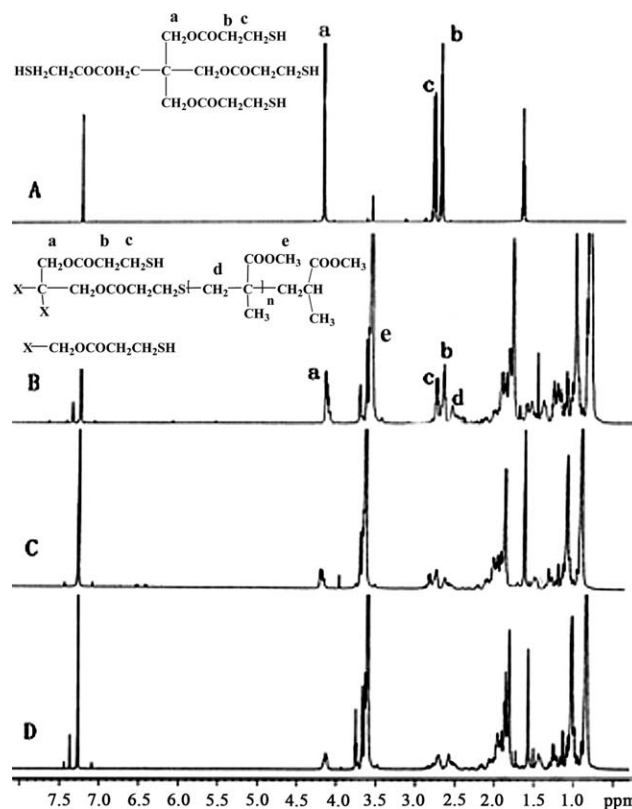
The  $^1\text{H-NMR}$  spectra of PMMAs obtained with the ratio of MMA to PETMP to be 70/1 at different monomer conversions are shown in Figure 2(B–D). For comparison,  $^1\text{H-NMR}$  spectrum of PETMP is also given in Figure 2(A). Figure 2(A) shows the presence of two methylene group protons of  $-\text{CH}_2-\text{O}-\text{CO}-$  (a) at 4.14–4.18 ppm, two methylene group protons of  $-\text{CH}_2-\text{O}-\text{CO}-\text{CH}_2-$  (b) at 2.66–2.69 ppm and two methylene protons of  $-\text{CH}_2-\text{SH}$  (c) at 2.75–2.79 ppm. The  $^1\text{H-NMR}$  spectra of PMMAs obtained with PETMP as P-CTA at different monomer conversions were similar. The characteristic signals ( $-\text{CH}_3$ , 0.8–1.1 ppm;  $-\text{CH}_2$ , 1.1–1.5 ppm;  $-\text{OCH}_3$ , 3.6 ppm) for MMA units were clearly observed. Along with the increase of MMA conversion, the signal at 2.75–2.79 ppm 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 2.42–2.65 ppm due to newly formed  $-\text{CH}_2-\text{S}-\text{CH}_2-$  (d) appeared. Furthermore, with the increase of MMA conversion, the relative strength of the signal at 2.42–2.65 ppm became stronger gradually.

For pure PETMP, the ratio of  $(I_b + I_c)$  to  $I_a$  was about 2.0 as is shown in Figure 2A. (that is,  $I_d$  was 0 when the monomer conversion of MMA was 0). When four-arm PMMA was formed by complete chain transfer reaction of all four thiol groups in PETMP to PMMA, the theoretical ratio of  $(I_b + I_c + I_d)$  to  $I_a$  was 3.0. The real ratios of  $(I_b + I_c + I_d)$  to  $I_a$  of PMMA formed when the thiol groups in PETMP were completely converted into polymer was about 3.0 [Figure 2(D)]. And the ratios of  $(I_b + I_c + I_d)$  to  $I_a$  of PMMAs at different monomer conversions [Figure 2(B–D)] were in the range of 2.0–3.0 and were proportional to the monomer conversions. Therefore, the actual average number of arms ( $N$ ) for star-shaped PMMAs obtained by chain transfer reaction of the thiol groups in PETMP to MMA can be calculated using the following equation:

$$N = \frac{8(I_b + I_c + I_d - 2I_a)}{2I_a} \quad (1)$$

where,  $I_a$ ,  $(I_b + I_c + I_d)$ , and  $I_e$  are the integral values of peaks at 4.14–4.18 ppm, 2.42–2.79 ppm, and 3.6 ppm, respectively. The number-average molecular weights of star-shaped polymer PMMAs can be calculated using the following equation:

$$M_{n,\text{NMR}} = \frac{8I_e}{3I_a} \times M_{n,\text{MMA}} + M_I \quad (2)$$



**Figure 2.**  $^1\text{H-NMR}$  spectra of PETMP and PMMAs obtained with the ratio of MMA to PETMP to be 70/1. (A) PETMP; (B) PMMAs obtained at 37.75% conversion; (C) PMMAs obtained at 54.96% conversion; (D) PMMAs obtained at about 100% conversion.

**Table I.** The Molecular Weights and the Number of Arms for Star-Shaped PMMAs Obtained at Different Monomer Conversions in Benzene at 70°C

Conversion (%)	$M_n$ , GPC	$M_n$ , NMR	$N$	$X^* = \frac{M_{n,NMR} - M_I}{N}$
37.75	3300	2890	1.60	1500
54.96	3900	4370	2.79	1390
100	6500	5900	4.00	1350

$X$  is the number-average molecular weight of each PMMA arm.  
Reaction conditions: [MMA] = 3 mol/L; [MMA] : [PETMP] : [AIBN] = 70 : 1 : 0.3.

where  $M_{n, MMA}$  and  $M_I$  are the molecular weights of MMA and PETMP, respectively. The calculated results for PMMAs obtained at different monomer conversions are listed in Table I. In the  $^1\text{H-NMR}$  spectrum of PMMA at 37.75% monomer conversion [Figure 2(B)], the ratio of  $(I_b + I_c + I_d)$  to  $I_a$  was 2.4. According to eq. (1), 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 54.96%, the ratio of  $(I_b + I_c + I_d)$  to  $I_a$  became 2.7 [Figure 2(C)]. The average number of arms was calculated to be 2.8, and the average residual thiol groups were 1.2.

The differences between the average lengths of each arm obtained at different monomer conversion in Table I 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 and the polymerization proceeded according to ideal telomerization fashion. Therefore, PMMA having certain residual thiol groups could be prepared at appropriate monomer conversions and PMMA chain without P-CTA could be neglected.<sup>44,45</sup>

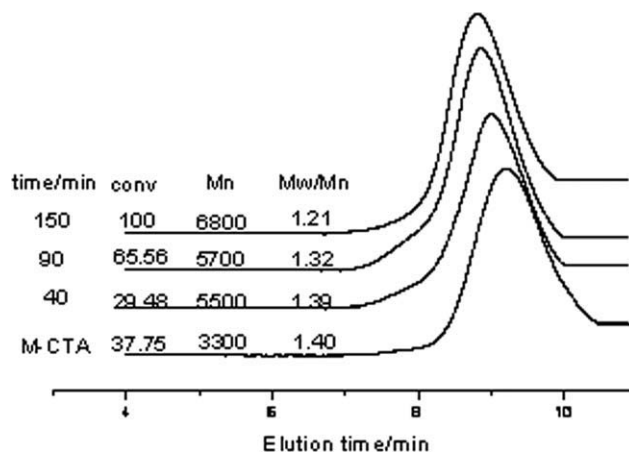
#### Free Radical Polymerization of AA with PMMA as Macro-Chain Transfer Agents (M-CTA)

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 acrylic acid in order to prepare heteroarm star-shaped polymers. In this section, PMMA with 2.4 residual thiol groups was used as Macro-Chain Transfer Agents in the free radical polymerization of acrylic acid. Its number average molecular weight determined by GPC was 3300.

On average, M-CTA had 1.6 PMMA arms and 2.4 unreacted thiol group. If acrylic acid is polymerized with M-CTA,  $(\text{PMMA})_{1.6}(\text{PAA})_{2.4}$  copolymer could be obtained.

#### Free Radical Polymerization of AA with THF as Solvent

The free radical polymerization of AA was carried out at 60°C in the presence of M-CTA with AIBN as initiator and THF as solvent. The polymerization system was transparent throughout the polymerization process, even when the conversion of AA was over 90%, indicating that the chain transfer reaction of the thiol groups on M-CTA took place, generating heteroarm star-shaped polymers (not PAA homopolymer, because high molecular weight of PAA formed without chain transfer agents would precipitate in THF).<sup>44,46</sup> The GPC traces of the products obtained at different monomer conversions are shown

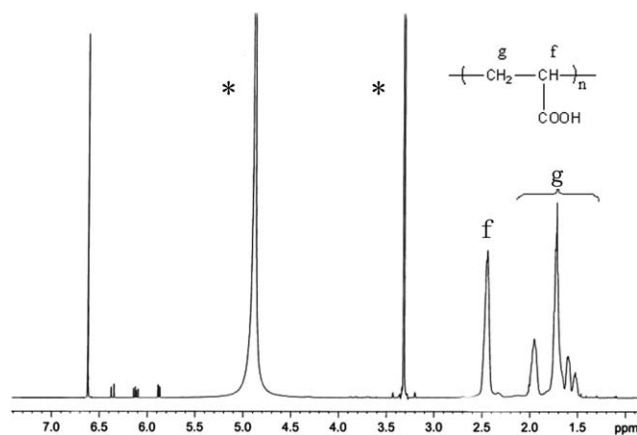


**Figure 3.** GPC curves of products obtained at different monomer conversions in THF at 60°C. Reaction conditions: [AA] = 2.4 mol/L;  $m(\text{S-PMMA}) = 0.66$  g (0.2 mmol),  $m(\text{AA}) = 4$  g  $m(\text{AIBN}) = 0.01\text{--}0.015$  g.

in Figure 3. It can be seen that the GPC curves were unimodal throughout the polymerization process and that the molecular weight shifted to higher molecular weight direction with the increase of monomer conversion. This showed that along with the conversion increased, the polymerization of AA chain segments indeed took place on M-CTA.

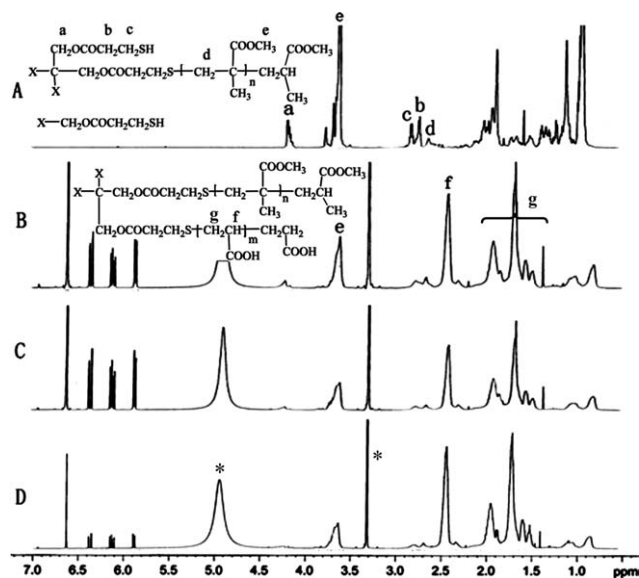
To calculate the molecular weights and numbers of the arms of heteroarm star-shaped polymers, the  $^1\text{H-NMR}$  spectra of pure PAA is shown in Figure 4. It was clear that two methylene group protons of  $-\text{CH}_2-\text{CH}-$  (g) at 1.52–1.86 ppm and the methine group proton of  $-\text{CH}_2-\text{CH}-$  (f) at 2.36–2.46 ppm appeared. In addition, the ratio of  $I_m$  to  $I_n$  was 2.0.

Figure 5(A–D) shows  $^1\text{H-NMR}$  spectra (in  $\text{CD}_3\text{OD}$ ) of M-CTA and heteroarm star-shaped polymers obtained at 26.45%, 56.62%, and 96.0% AA conversion. D-substituted dioxane should be chosen as the cosolvent of PMMA and PAA for accurate calculation of the copolymer composition, but no deuterated drugs was available. We found that the methanol solution of PMMA with 3300 molecular weight was transparent (perhaps due to branched architecture and low molecular weight of



**Figure 4.**  $^1\text{H-NMR}$  spectra of pure PAA ( $\text{CD}_3\text{OD}$  as solvent). \*Attributed to  $\text{CH}_3\text{OH}$  and  $\text{H}_2\text{O}$  in  $\text{CD}_3\text{OD}$ .



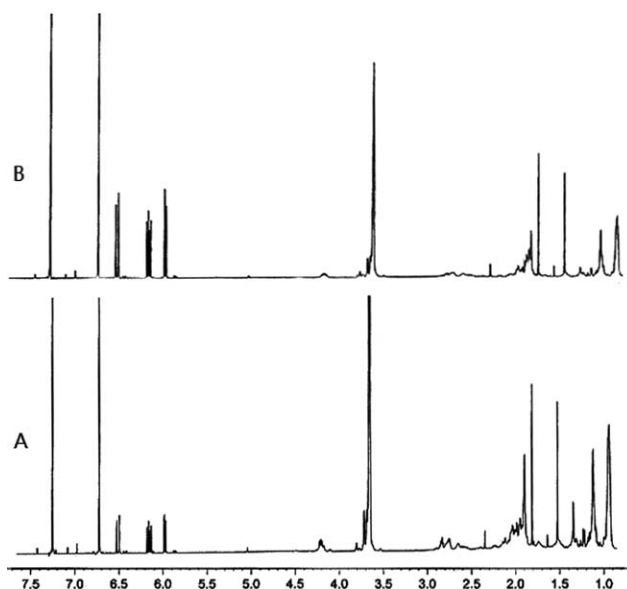


**Figure 5.**  $^1\text{H}$ -NMR spectra of M-CTA and heteroarm star-shaped polymers obtained at different AA conversions in  $\text{CD}_3\text{OD}$ : (A) M-CTA; (B) 29.48% AA conversion; (C) 65.56% AA conversion; (D) 96.0% AA conversion. \*Attributed to  $\text{CH}_3\text{OH}$  and  $\text{H}_2\text{O}$  in  $\text{CD}_3\text{OD}$ .

PMMA, therefore, the PMMA sample in this article were precipitated in petroleum ether (see Experiment section) because they can not be precipitated in methanol and seemed to be dissolved gradually.) The situation of copolymer was the same. Consequently,  $\text{CD}_3\text{OD}$  was used as the solvent for NMR determination.

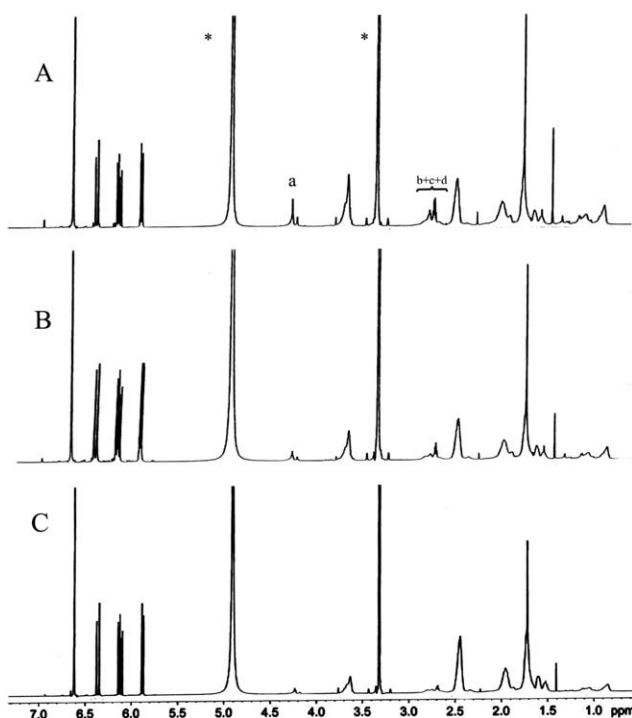
In Figure 5(B, C), in addition to the characteristic signals ( $-\text{CH}_3$ , 0.8–1.1 ppm;  $-\text{OCH}_3$ , 3.5–3.6 ppm) of MMA units, the methine group proton of  $-\text{CH}_2-\text{CH}-$  (f) of AA units was present at 2.36–2.48 ppm, which confirmed the incorporation of PAA in heteroarm star-shaped polymers. Along with the increase of AA conversion, the chemical shift at 2.76–2.78 ppm due to the protons adjacent to the thiol group ( $-\text{CH}_2-\text{SH}$ ) (c) gradually decreased. At the same time, the signal at 2.45–2.70 ppm due to newly formed  $-\text{CH}_2-\text{S}-\text{CH}_2-$  (d) increased. In Figure 5(A), the ratio of  $(I_b + I_c + I_d) / I_a$  was 2.40. The ratio changed to 2.72 in Figure 5(B), 2.96 in Figure 5(C), 3.20 in Figure 5(D). According to eq. (1), it can be calculated that when monomer conversion reached 26.45%, the total number of residual thiol groups was 1.12, meaning that heteroarm star-shaped polymer with average 1.60 PMMA arms and average 1.28 PAA arms was synthesized. When monomer conversion reached 56.62%, the total number of residual thiol groups was 0.16, meaning that heteroarm star-shaped polymers with average 1.60 PMMA arms and average 2.24 PAA arms was synthesized. When monomer conversion reached 96.0%, the total number of chain transfer reaction of the thiol groups was 0, meaning that heteroarm star-shaped polymers with average 1.60 PMMA arms and average 2.40 PAA arms was synthesized.

Certainly, there may be some linear PAA homopolymer in the final product. We have tried to separate the homopolymer from the final products by select several solvent/nonsolvent for PMMA and PAA respectively, but no homopolymer could be



**Figure 6.**  $^1\text{H}$  NMR spectra of heteroarm star-shaped polymers obtained at different monomer conversions in  $\text{CDCl}_3$ : (A) 26.45% AA conversion; (B) 56.62% AA conversion.

collected. For example,  $\text{CDCl}_3$  was solvent for PMMA and nonsolvent for PAA, the final products dissolved in  $\text{CDCl}_3$  completely and formed visually transparent solution. The situation in toluene was also the same. Therefore, the amount of PAA homopolymer may be very small. Methanol was solvent for PAA and nonsolvent for PMMA, but the final products



**Figure 7.**  $^1\text{H}$ -NMR spectra of heteroarm star-shaped polymers obtained at 5.65%, 13.05%, and 82.5% AA conversion. \*Attributed to  $\text{CH}_3\text{OH}$  and  $\text{H}_2\text{O}$  in  $\text{CD}_3\text{OD}$ .



**Figure 8.** Images of A, B, and C in 1% KOH aqueous solution.

dissolved in methanol completely and formed transparent solution. And the final products self-assembled into emulsion in water. No precipitation was observed. So the amount of PMMA homopolymer is neglected. Yuan et al.,<sup>40,41</sup> investigated theoretically and experimentally free radical polymerization of MMA in the presence of PETMP, in which star polymers formed exclusively in the absence of combination termination. Consequently, the results of the heteroarm copolymers of PMMA/PAA calculated above were relatively reasonable.

The ratios of  $I_g$  to  $I_f$  were 0.56, 0.51, and 0.32 in Figure 5(B–D) respectively, and the molar ratios of MMA units to AA units were 0.19, 0.17, and 0.11 by  $^1\text{H-NMR}$  spectra accordingly. The molar ratios of MMA units to AA units calculated according to batch feeding and AA conversion were 0.45, 0.21, and 0.11, respectively. Obviously, when AA conversion was low, the ratio of MMA units to AA units from NMR was much lower than that from monomer conversion and the experimental recipe. When AA conversion was high, they were very close. This maybe because the weak self-assembly behavior of PMMA/PAA heteroarm star-shaped polymer in methanol with PMMA as core, although the methanol solution of the PMMA/PAA copolymers was visibly transparent.

The  $^1\text{H-NMR}$  spectra of heteroarm star-shaped polymers obtained at 26.45% and 56.62% AA conversion with  $\text{CDCl}_3$  as solvent were shown in Figure 6(A, B). In  $\text{CDCl}_3$ , the solution

was also visibly transparent. This further confirmed that PAA formed during the polymerization was nearly all connected to the core of PMMA macro-chain transfer agents because  $\text{CDCl}_3$  was nonsolvent for PAA. It was obvious from Figure 6 that the characteristic absorption peak due to PAA in Figure 5 disappeared and that due to hydrophobic PMMA segment was very clear. This also indirectly indicated that amphiphilic heteroarm star-shaped polymers self-assembled in  $\text{CDCl}_3$  with PAA as the core of micelle.

#### Free Radical Polymerization of Acrylic acid with THF/Water as Solvent

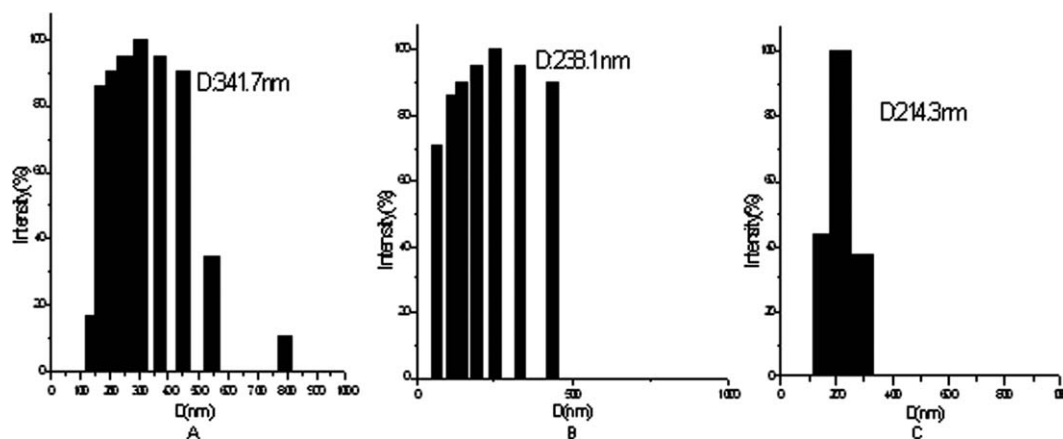
The free radical polymerization of AA was also carried out in THF/water mixture ( $v/v = 3/1$ ). First, M-CTA was dissolved in THF and then THF/water was added dropwise into the solution to adjust the ratio of THF to water.

Figure 7 shows  $^1\text{H-NMR}$  spectra of the heteroarm star-shaped polymers obtained at 5.65% (A), 13.05% (B) and 82.50% (C) conversion. The ratios of  $(I_b + I_c + I_d)$  to  $I_a$  were 2.44, 2.70, and 3.05 respectively. The total numbers of residual thiol groups were 2.24, 1.20, and 0, respectively. Compared this heteroarm star-shaped sample prepared in THF/water to the samples prepared in THF, chain transfer ability of M-CTA to AA in THF/water was little higher than that in THF.

According to eq. (1), when the AA conversion was 13.05%, heteroarm star-shaped polymer with average 1.60 PMMA arms and average 1.10 PAA arms was obtained. The molar ratio of MMA units to AA units was 0.22 : 1 from  $^1\text{H-NMR}$ , which was much smaller than 0.9 : 1 calculated according to the feeding ration and AA conversion. This further confirmed that PMMA/PAA formed micelle by self-assembly in methanol with PMMA as the core.

#### Self-Assembly Behavior of the Amphiphilic Heteroarm Star-Shaped Polymer

With regard to the self-assembly behavior of amphiphilic heteroarm star-shaped polymers, it depended on the nature and the molecular weights of polymer arms. In 1% KOH aqueous solution, hydrophilic PAA chains could be dissolved, while hydrophobic PMMA chains could not. If PAA chains were long enough, the amphiphilic polymers could self-assemble into



**Figure 9.** DLS columnar section of A, B, and C by self-assembly in 1% KOH aqueous solution. AA conversion: (A) 26.45%, (B) 56.62%, (C) 96.0%.

micelle, with insoluble PMMA chains as core and soluble PAA chains as shell. In contrast, in chloroform or toluene solution, hydrophobic PMMA chains could be dissolved, while hydrophilic PAA chains could not. If PMMA chains were long enough, the amphiphilic polymers could self-assemble into micelle with insoluble PAA chains as nuclear, soluble PMMA chains as shell.

Figure 8 shows images of sample A, B and C prepared in THF [AA conversion: 26.45%(A), 56.62%(B), 96.0%(C)] in 1% KOH aqueous solution with 2.5 mg/mL concentration. The self-assembly solution was milky, semitransparent milky, and pale blue, respectively, indicating the size of the micelles of the product decreased with the increase of AA conversion.

Figure 9 shows DLS columnar section of A, B, and C in 1% KOH aqueous solution. It can be seen that with the increase of AA conversion, the number average diameter ( $D$ ) decreased from 341.7 nm for 26.45% conversion to 214.3 nm for 96.0% conversion.

Figure 10 shows TEM image of Sample A in 1% KOH aqueous solution. It can be seen that the micelle was all spheres and the number average diameter was about 200 nm, which was smaller than that from DLS. The TEM image is included here for the sole purpose of showing the spherical morphology of the micelles, as opposed to the variety of shapes the block copolymer aggregates could assume.

Table II shows the number average diameter of Samples A, B, by self-assembly in different solvent. The self-assembly solution was colorless and transparent in chloroform. PAA could not dissolve in chloroform, so the transparent solution further indicated that PAA was indeed bonded on PMMA through the chain transfer reaction. In addition, the number average diameter of the self-assembly solution increased with the increase of the AA conversion.

The self-assembly solution in toluene was also colorless and transparent. PAA could not dissolve in toluene either, so the transparent solution indicated that PAA was bonded on the PMMA macromolecule through chain transfer reaction.

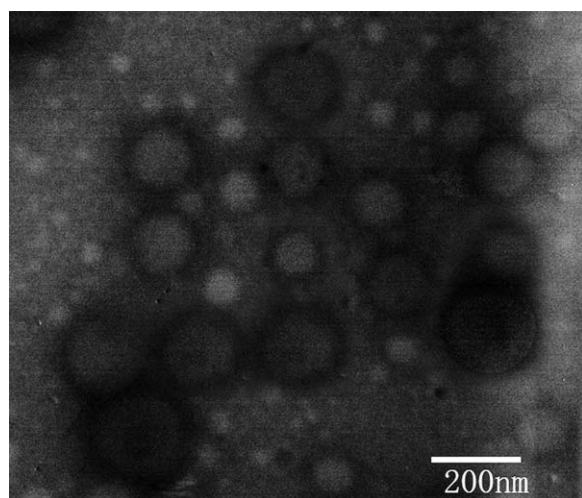


Figure 10. TEM image of sample A in 1% KOH aqueous solution.

Table II. The Number Average Diameter (nm) of Sample A, B by Self-Assembly in Different Solvent (Sample A, B (25 mg) Were Prepared in THF (5 mL) as solvent, MMA conversion: 37.75%(A) (B), AA conversion: 26.45%(A), 56.62%(B))

	A	B
Chloroform	50.3	67.6
Toluene	49.6	54.1

The particle sizes were 50–70 nm in organic solvent, which were obviously smaller than those in 1% KOH aqueous solution. This was because hydrophilic PAA segments formed sodium salt in KOH solution, and shell macromolecule stretched fully enough and formed the hydration layer.

## CONCLUSIONS

In the free radical polymerization of MMA with PETMP as P-CTA, about two-arm (linear) star-shaped PMMAs could be obtained at appropriate monomer conversions. Two-arm PMMAs still had two residual thiol groups. They were further used as macro-chain transfer agent in free radical polymerization of AA, giving heteroarm star-shaped polymers, (PMMA)<sub>2</sub>(PAA)<sub>2</sub>. The self-assembly behavior of the amphiphilic heteroarm star-shaped polymer in 1% KOH, chloroform and toluene were investigated. The self-assembly micellar grain-size decreased gradually with the increase of monomer conversion.

## REFERENCES

- Hadjichristidis, N.; Iatrou, H.; Pitsikalis, M.; Pispas, S.; Avgeropoulos, A. *Prog. Polym. Sci.* **2005**, *30*, 725.
- Tsoukatos, T.; Hadjichristidis, N. *J. Polym. Sci. Part A* **2002**, *40*, 2575.
- Iatrou, H.; Hadjichristidis, N. *Macromolecules* **2000**, *33*, 6993.
- Wang, X. S.; Mitchell, A. W.; Ian, M. *Macromol. Rapid Commun.* **2003**, *24*, 403.
- Mavroudis, A.; Hadjichristidis, N. *Macromolecules* **2006**, *39*, 535.
- Storey, R. F.; Shoemaker, K. A. *J. Polym. Sci. Part A* **1998**, *36*, 471.
- Kanaoka, S.; Fujita, Y.; Higashimura, T. *Macromol. Rapid Commun.* **2000**, *21*, 218.
- Fazeli, N.; Taromi, F. A. *J. Polym. Sci. Part A* **2003**, *41*, 135.
- Du, J. Z.; Chen, Y. M. *J. Polym. Sci. Part A* **2004**, *42*, 2263.
- Du, J. Z.; Chen, Y. M. *Macromolecules* **2004**, *37*, 3588.
- Gao, H. F.; Tsarevsk, V.; Matyjaszewsk, K. *Macromol. Rapid Commun.* **2003**, *24*, 979.
- Bae, Y. C.; Faust, R. *Macromolecules* **1998**, *31*, 2480.
- Hayashi, M.; Kojima, K.; Hirao, A. *Macromolecules* **1999**, *32*, 2425.
- Hirao, A.; Tokuda, Y.; Morifuji, K.; Hayashi, M. *Macromol. Chem. Phys.* **2001**, *202*, 1606.
- Hirao, A.; Hayashi, M.; Matsuo, A. *Polymer* **2002**, *43*, 7125.

16. Reutenauer, S.; Hurtrez, G.; Philippe, D. *Macromolecules* **2001**, *34*, 755.
17. Heise, A.; Trollsås, M.; Magbitang, T.; Hedrick, J. L.; Frank, C. R.; Miller, R. D. *Macromolecules* **2001**, *34*, 2798.
18. Miura, Y.; Sakai, Y.; Yamaoka, K. *Macromol. Chem. Phys.* **2005**, *206*, 504.
19. He, T.; Li, D.; Sheng, X.; Zhao, B. *Macromolecules* **2004**, *37*, 3128.
20. Deng, G. H.; Zhang, L. W.; Liu, C. D.; He, L. H.; Chen, Y. M. *Eur. Polym. J.* **2005**, *41*, 1177.
21. Celik, C.; Hizal, G.; Tunca, U. *J. Polym. Sci Part A* **2003**, *41*, 2542.
22. Durmaz, H.; Karatas, F.; Tunca, U.; Hizal, G. *J. Polym. Sci Part A* **2006**, *44*, 499.
23. Tunca, U.; Ozyurek, Z.; Erdogan, T.; Hizal, G. *J. Polym. Sci Part A* **2004**, *42*, 4228.
24. Angot, S.; Tato, D.; Gnanou, Y. *Macromolecules* **2000**, *33*, 5418.
25. Francis, R.; Lepoittevin, B.; Taton, D.; Gnanou, Y. *Macromolecules* **2002**, *35*, 9001.
26. Guo, Y. M.; Pan, C. Y. *Polymer* **2001**, *42*, 2863.
27. Guo, Y. M.; Pan, C. Y.; Wang, J. *J. Polym. Sci Part A* **2001**, *39*, 2134.
28. Feng, X. S.; Pan, C. Y. *Macromolecules* **2002**, *35*, 2084.
29. Li, Y. G.; Wang, Y. M.; Pan, C. Y. *J. Polym. Sci Part A* **2003**, *41*, 1243.
30. Chenm, J.; Zhang, H.; Liu, M.; Wang, Y. *Acta Polym Sinica (in Chinese)* **2006**, *2*, 314.
31. Shi, Y.; Fu, Z. F.; Li, B. Y.; Zhang, L. Q.; Cai, X. P.; Zhang, D. S. *Eur. Polym. J.* **2007**, *43*, 2612.
32. Wu, Y.; Shi, Y.; Fu, Z. F. *Polymer* **2005**, *46*, 12722.
33. Chen, S.; Bertrand, A.; Chang, X. J.; Alcouffe, P.; Bernard, J. *Macromolecules* **2010**, *43*, 5981.
34. Altintas, O.; Tunca U.; Barner-Kowollik, C. *Polym. Chem.* **2011**, *2*, 1146
35. Altintas, O.; Vogt, A. P.; Barner-Kowollik, C.; Tunca, U. *Polym. Chem.* **2012**, *3*, 34.
36. Tobita, H. *Macromolecules* **1996**, *29*, 693.
37. Tobita, H.; Hayashi, M. *Macromol. Theory Simul.* **2001**, *10*, 573.
38. Tobita, H. *Macromol. Theory Simul.* **2001**, *10*, 581.
39. Tobita, H.; Mima, T.; Okada, A.; Mori, J.; Tanabe, T. *J. Polym. Sci. Part B* **1999**, *37*, 1267.
40. Yuan, C. M.; Silvestro, G. D.; Farina, M. *Macromol. Theory Simul.* **1994**, *3*, 193.
41. Yuan, C. M.; Farina, M. *Macromol. Theory Simul.* **1994**, *3*, 203.
42. Loubat, C.; Boutevin, B. *Polym. Int.* **2001**, *50*, 375.
43. Luo, Z. H.; Fu, Z. F.; Shi, Y. *Chinese J. Polym. Sci.* **2008**, *26*, 1.
44. Boutevin, B. *J. Polym. Sci Part A* **2000**, *38*, 3235.
45. Yuan, C. M.; Silvestro, G. D. *Macromol. Chem. Phys.* **1995**, *196*, 2905.
46. Lan, D.; Chen, D.; Fu, Z. F.; Shi, Y. *Polym. Bull.* **2011**, *66*, 175.