

# Synthesis of heteroarm star-shaped (polystyrene)<sub>n</sub>–[poly(ethyl acrylate)]<sub>m</sub> via atom transfer radical polymerization

Ying Wu, Yan Shi, Zhifeng Fu \*

Key Laboratory for Controlled Chemical Reactions of Education Ministry, Department of Polymer Engineering,  
Beijing University of Chemical Technology, Beijing 100029, China

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## Abstract

Heteroarm star-shaped polymer, (polystyrene)<sub>n</sub>–[poly(ethyl acrylate)]<sub>m</sub> [(PS)<sub>n</sub>–(PEA)<sub>m</sub>], was synthesized in three steps. In the first step, star-shaped polystyrene, (PS)<sub>n</sub>, was synthesized by the arm-first method via atom transfer radical polymerization (ATRP) using a preformed PS macroinitiator, which was obtained by ATRP of styrene with ethyl 2-bromoisobutyrate as the initiator, in the presence of divinyl benzene (DVB). In the microgel core of (PS)<sub>n</sub>, there were not only a number of active initiating sites for ATRP, but also some unreacted vinyl groups. Then, in the second step, the residual vinyl groups were converted to 1-bromoethylbenzene groups by hydrobromination. In the last step, heteroarm star-shaped polymer, (PS)<sub>n</sub>–(PEA)<sub>m</sub>, where the arm number of PEA was greater than that of PS, was prepared by ATRP of ethyl acrylate using the hydrobrominated (PS)<sub>n</sub> as the macroinitiator from 1-bromoethylbenzene initiating sites, obtained by both the addition of linear PS macroinitiators to vinyl groups of DVB and the hydrobromination of residual vinyl groups.

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**Keywords:** Atom transfer radical polymerization (ATRP); Heteroarm star-shaped polymer; Divinyl benzene (DVB)

## 1. Introduction

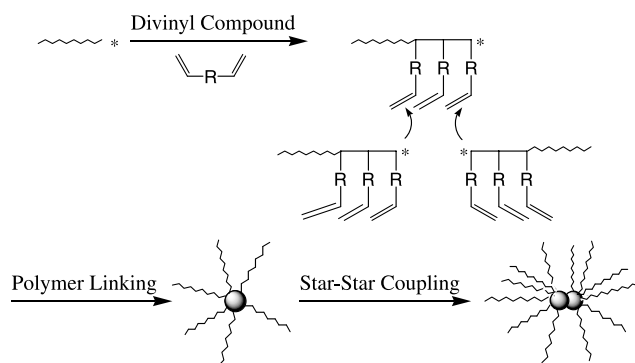
Star-shaped polymers, consisting of a core and a number of arms radiating from the core, have attracted more and more attention because of their highly branched structures and unique rheological properties [1,2].

Previously, star polymers with controlled structures have been synthesized by three methods based on living ionic polymerization: (1) living polymerization with a multifunctional initiator [3–5]; (2) coupling reaction of linear living polymers with a multifunctional coupling agent [6–9]; (3) linking reaction of linear living polymers with a divinyl compound [10–13]. However, the rigorous reaction conditions for living ionic polymerization and their incompatibility with functional monomers have limited the application of these living ionic polymerization methods. In contrast, recent reports have demonstrated the potential of living free radical polymerization for the preparation of star polymers because of its mild reaction conditions and extensively available

monomers. Indeed, reversible addition-fragmentation chain transfer polymerization (RAFT) [14–16], nitroxide-mediated stable free radical polymerization (SFRP) [17,18], atom transfer radical polymerization (ATRP) [19–27] using a multifunctional initiator have been reported for the synthesis of well-defined star polymers with a precise arm number. The linking reaction of linear living polymers obtained by living free radical polymerization with a divinyl compound was also used to prepare star polymers characterized by a crosslinked gel core and a random distribution of the number of arms per polymer molecule [28–39]. The mechanism of divinyl compound method is shown in Scheme 1. Firstly, a few units of divinyl reagents add to the reactive macroinitiators (arms) to form short block copolymers with hanging vinyl groups. Then, the reactive macroinitiator chain ends react with the hanging vinyl groups to form a microgel core or add to a sterically accessible star core. Finally, core–core coupling reaction can occur to form a higher-order star polymer.

The star polymer thus obtained still carries a number of active sites within its microgel core, which is theoretically equal to the number of incorporated arms of the star polymer. These ‘core’ active sites can initiate the living polymerization of another monomer to grow new arms from the core, yielding a ‘heteroarm’ star polymer, A<sub>n</sub>B<sub>n</sub> [40]. Using this method, heteroarm star polymers, A<sub>n</sub>B<sub>n</sub>, have been synthesized not only

\* Corresponding author. Tel.: +86 106 443 5758; fax: +86 106 441 3808.  
E-mail address: [fuzf@mail.buct.edu.cn](mailto:fuzf@mail.buct.edu.cn) (Z. Fu).



Scheme 1.

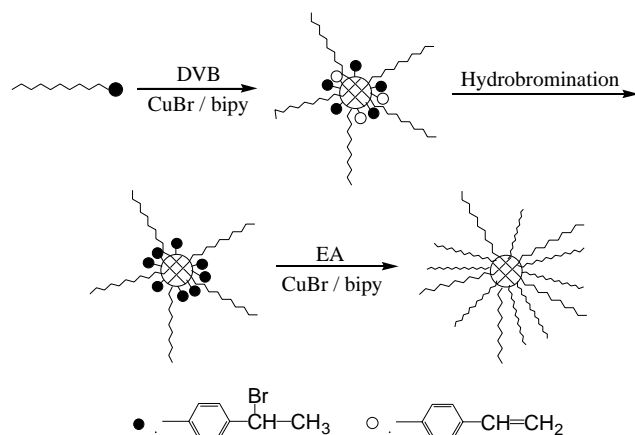
by anionic [41–46] and cationic polymerization [47–49], but also by living free radical polymerization [50–52].

Recently, Taromi and co-workers [53] reported that star polymers obtained from living anionic polystyrene chains and a small amount of divinyl benzene (DVB) would have many unreacted vinyl groups in the gel core, and that these vinyl groups could be attacked by carbonions of another kind of polymer chain, forming heteroarm star polymers,  $A_nB_m$ . In our work, star polystyrene,  $(PS)_n$ , was first synthesized by the arm-first method via ATRP using a preformed PS macroinitiator in the presence of divinyl benzene. Then, the residual vinyl groups in the gel core were converted to 1-bromoethylbenzene groups by hydrobromination. Lastly, heteroarm star polymer,  $(polystyrene)_n-[poly(ethyl\ acrylate)]_m$  [ $(PS)_n-(PEA)_m$ ], where the arm number of PEA was greater than that of PS, was prepared by ATRP of ethyl acrylate from 1-bromoethylbenzene initiating sites, obtained by both the addition of linear PS macroinitiators to vinyl groups of DVB and by hydrobromination of residual vinyl groups (Scheme 2).

## 2. Experimental

### 2.1. Materials

Styrene (>99%), ethyl acrylate (>99%) and DVB (>45%) were all from Beijing Chemical Reagent Co. and dried over  $CaH_2$  (Aldrich, 90–95%) overnight, and then distilled



Scheme 2.

under reduced pressure. CuBr (Shanghai Reagent Co.) was purified by stirring in glacial acetic acid, washed with ethanol and then dried in a vacuum oven at 70 °C. 2,2'-Bipyridine (bipy) (Beijing Shiyong Chemical Plant) were recrystallized from *n*-hexane. Ethyl 2-bromoisobutyrate (Aldrich) and all other reagents were used as received without any further purification.

### 2.2. Synthesis of linear PS arm

A Schlenk flask with a magnetic stirrer and a rubber septum was charged with CuBr (6 mmol), bipy (12 mmol), styrene (150 g) and ethyl 2-bromoisobutyrate (30 mmol) which were deoxygenated by bubbling argon for 30 min before addition into the flask. The flask was degassed by three freeze–pump–thaw cycles and subsequently purged under argon atmosphere, and then immersed in an oil bath thermostated at 110 °C. After polymerization for 2 h under magnetic stirring, the crude product was dissolved in THF, passed through a short column of alumina to remove the catalyst, precipitated in methanol and dried under vacuum at room temperature until a constant weight was obtained.

### 2.3. Synthesis of star PS homopolymer, $(PS)_n$

A typical preparation of star PS homopolymer using ATRP was as follows: a Schlenk flask with a magnetic stirrer and a rubber septum was charged with CuBr (1.148 g, 8 mmol), bipy (3.744 g, 24 mmol), PS arm obtained above (16.8 g, 8 mmol), toluene (114 mL) and DVB (18.48 g) which were

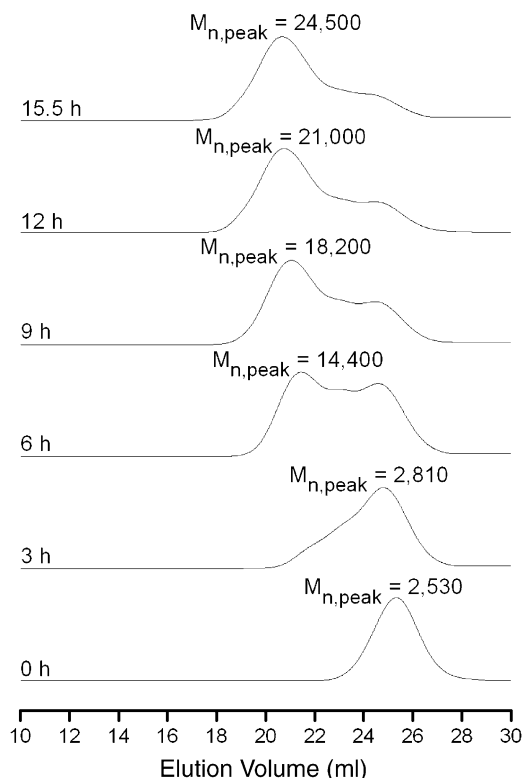


Fig. 1. GPC curves of star PS homopolymers formed at various reaction times.

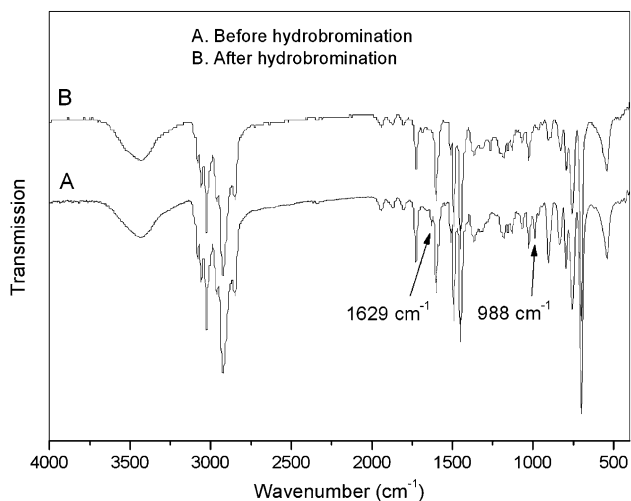


Fig. 2. FT-IR spectra of star PS homopolymers before (A) and after (B) hydrobromination.

deoxygenated by bubbling argon for 30 min before addition into the flask. The flask was degassed by three freeze–pump–thaw cycles and subsequently purged under argon atmosphere, and then immersed in an oil bath thermostated at 110 °C. At predetermined time, aliquots of reaction mixture were withdrawn with argon-filled gas-tight syringe to measure number-average molecular weights and molecular weight distributions. The final crude product was passed through a short column of alumina to remove catalyst, precipitated in methanol and dried under vacuum at room temperature.

#### 2.4. Hydrobromination of residual vinyl groups in microgel core of star PS homopolymer

The pure star PS homopolymers (8 g) after fractionation of the crude star PS obtained above was dissolved in 200 mL of dried toluene in a 500 mL two-neck roundbottomed flask. Dry hydrogen bromide (HBr) was slowly passed through the solution for 8 h at room temperature. The flow rate of HBr was

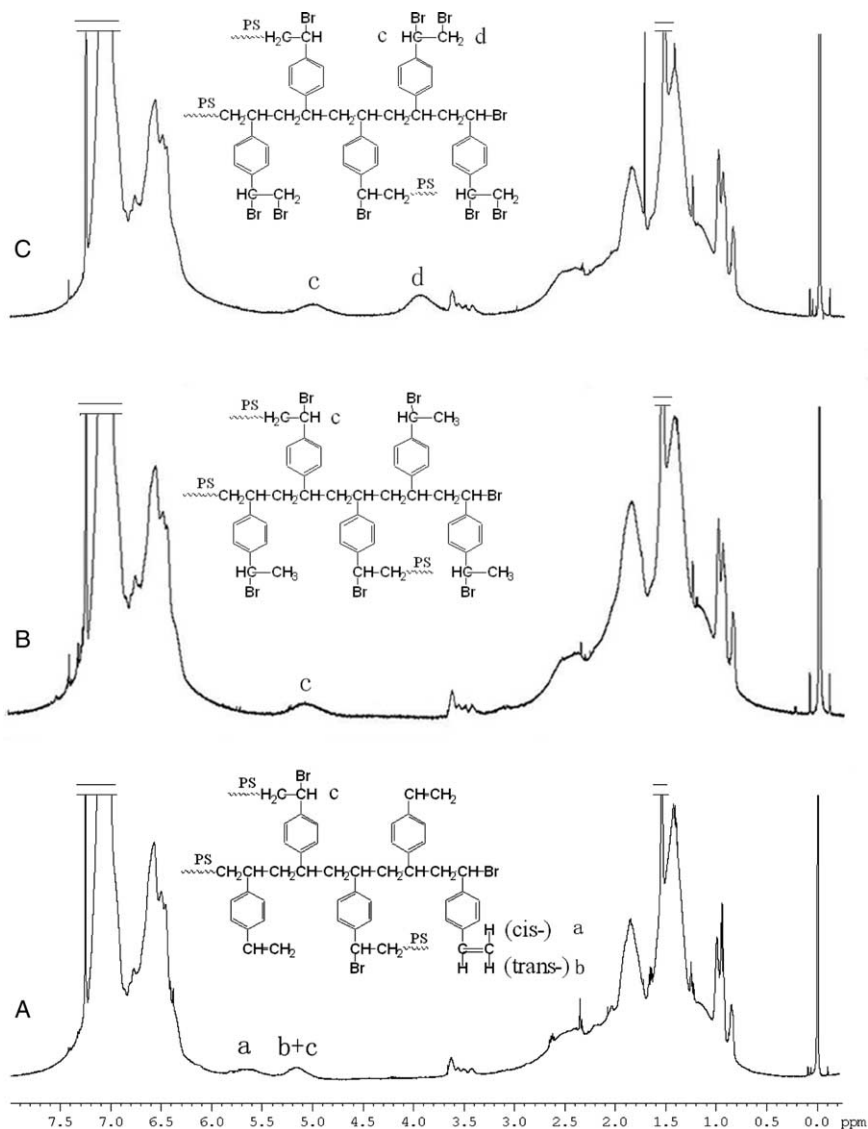


Fig. 3.  $^1\text{H}$  NMR spectra of star PS homopolymers before (A) and after (B) hydrobromination, and after bromination with  $\text{Br}_2$  (C).

controlled such that almost all HBr introduced dissolved in the solution at early stage. The HBr was generated through slow addition of hydrobromic acid into  $P_2O_5$ .

### 2.5. Synthesis of heteroarm star polymer, $(PS)_n-(PEA)_m$

Heteroarm star polymer,  $(PS)_n-(PEA)_m$ , was synthesized by the similar procedure as above. In a typical experiment, hydrobrominated star PS (1.152 g), CuBr (0.1507 g, 1.05 mmol), CuBr<sub>2</sub> (0.0469 g, 0.21 mmol), bipy (0.5897 g, 3.78 mmol), EA (23.87 g) and toluene (47 mL) were added to a Schlenk flask with a magnetic stirrer and a rubber septum. The flask was degassed by three freeze–pump–thaw cycles and subsequently purged under argon atmosphere, and then immersed in an oil bath thermostated at 90 °C. At pre-determined time, about 2 mL of reaction mixture were withdrawn with argon-filled gas-tight syringe to measure monomer conversion, number-average molecular weight and molecular weight distribution.

### 2.6. Characterization

The number-average molecular weights and molecular weight distributions were determined by gel permeation chromatography (GPC) equipped with Waters microstiyragel columns (HR1, HT3, and HT4) and Waters 515 high performance liquid chromatograph (HPLC) with a Water 2410 refractive index detector and GPC software. Measurements were conducted in distilled tetrahydrofuran (THF) (30 °C) at a flow rate of 1 mL/min. Linear PS standards were applied as the calibration. <sup>1</sup>H NMR spectra were recorded on a Bruker AV600-MHz spectrometer with CDCl<sub>3</sub> as solvent at room temperature. Fourier transform infrared spectroscopic analyses were performed on a Nicolet 210 spectrometer.

### 3. Results and discussion

The PS macroinitiator used in this study was obtained by the polymerization of styrene using ethyl 2-bromoisobutyrate as the initiator and cuprous bromide complexed by bipy as the

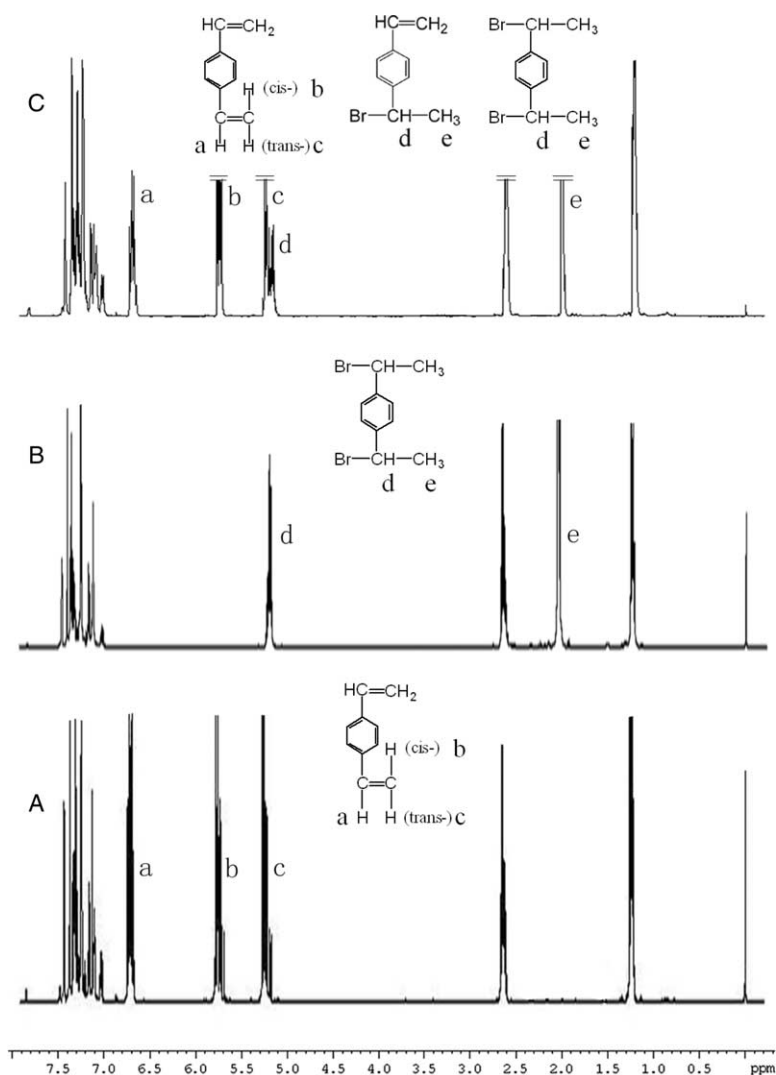


Fig. 4. <sup>1</sup>H NMR spectra of crude DVB (A), the completely hydrobrominated (B) and partially hydrobrominated (C) products of DVB.

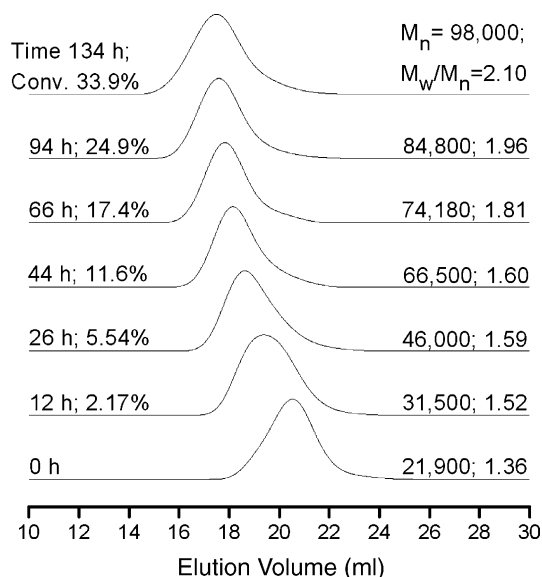


Fig. 5. GPC curves of  $(PS)_n-(PEA)_m$  heteroarm star polymers at various times.

catalyst in bulk at 110 °C. The isolated PS macroinitiator had the predicted molecular weight and low polydispersity ( $M_n = 2100$  by GPC,  $M_w/M_n = 1.25$ ). The terminal structure of PS macroinitiator was analyzed by  $^1H$  NMR spectroscopy. The results showed that every PS chain had an active bromine atom at the  $\omega$ -end.

Matyjaszewski and his co-workers [37] compared divinyl benzene (DVB), 1,4-butanediol diacrylate (BDA) and ethylene glycol dimethacrylate (EGDMA) in the synthesis of star PS via ATRP and found that DVB led to soluble star polymer without gelation, while insoluble polymer was obtained with BDA or EGDMA. Therefore, DVB was used as the coupling reagent for the star PS formation.

Fig. 1 shows a series of GPC curves of the products at various reaction times. After 3 h, there was some broadening in the molecular weight distribution with a slight increase of the peak molecular weight corresponding to the PS macroinitiator, indicating the formation of styrene–DVB block copolymers or the addition of more than one unit of the latter to the PS macroinitiator. The DVB units in the block copolymer then started to react with each other, forming star polymers. The product obtained after 6 h showed a new peak in the higher molecular weight region, indicating the formation of star polymers by the expected polymer linking reaction. As the linking reaction proceeded, the fraction of the styrene–DVB block copolymers decreased gradually, and the molecular weight of the higher fraction increased. After 15.5 h, the star polymers became the majority with a rather small amount of unlinked block copolymers. Because longer reaction time would result in coupling reaction between star polymers as reported by Matyjaszewski et al. [37] and Sawamoto et al. [31], the reaction was stopped at this time.

In order to obtain pure star PS homopolymers without residual styrene–DVB block copolymers, the crude product was fractionated. Fractionation was done on a 1% solution of the crude product in THF with the slow addition of methanol as

a nonsolvent. GPC curve of fractionated star PS homopolymer showed that the fractionation process was successful. Its apparent number-average molecular weight of star PS homopolymer, calibrated by linear PS standards, was 21,600 and  $M_w/M_n$  was 1.37.

Similar with the star polymers obtained by DVB method via ionic polymerization, there should be a number of active bromine atoms for ATRP on the core of the star PS homopolymers, which is equal to the number of incorporated PS arms. At the same time, there should be some unreacted double bonds on the core. Fig. 2(A) shows the IR spectrum of fractionated star PS homopolymer. The absorption of double bonds of the hanging styrene units on the core can be clearly seen at 1629 and 988  $cm^{-1}$ .

The  $^1H$  NMR spectrum of fractionated star PS homopolymer is shown in Fig. 3(A). According to the results obtained by Faust et al. [54] and Matyjaszewski et al. [38], the broad peaks at about 5.2 and 5.7 ppm should correspond to the protons of hanging vinyl on DVB units. However, the signal corresponding to the methine protons adjacent to the bromine atoms could not be found, which was usually thought to be at about 4.4 ppm. Obviously, the microgel core of DVB was not highly crosslinked, at least in our experiment conditions, because the  $^1H$  NMR signals of the hanging vinyl protons on DVB units were relatively strong. Therefore, the  $^1H$  NMR signal of the methine protons should be visible as that of the methene protons of the initiator moiety (still present at 3.6 ppm).

Fig. 2(B) shows the IR spectrum of star PS after hydrobromination. It can be seen that the characteristic absorption of hanging double bonds at 1629 and 988  $cm^{-1}$  disappears, which indicates that the hydrobromination reaction of the double bonds with HBr proceeded completely and there was no residual unreacted double bond on the microgel cores. However, in the  $^1H$  NMR spectrum of star PS after hydrobromination (Fig. 3(B)),

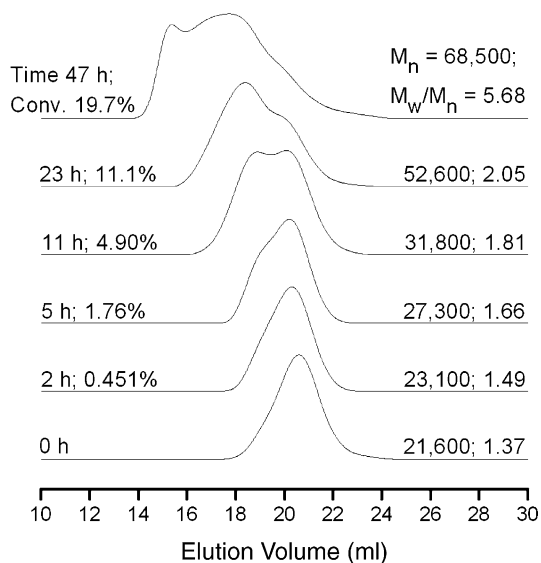
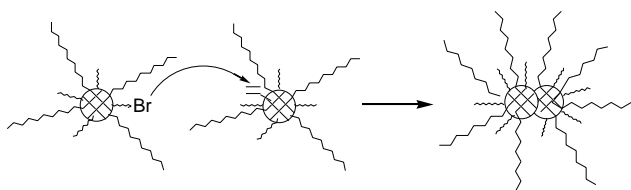


Fig. 6. GPC curves of  $(PS)_n-(PEA)_n$  heteroarm star polymers at various times. Reaction conditions: PS star macroinitiator  $[(star-Br)]_0 = [CuBr]_0 = 0.2[CuBr_2]_0 = 3.6[bipy]_0 = 200[EA]$  in toluene at 110 °C.



Scheme 3.

although the broad peak at about 5.7 ppm disappeared completely, the peak at about 5.1 ppm still existed. Therefore, we think that the peak at about 5.1 ppm may correspond to the methine protons adjacent to the bromine atoms.

To prove this, the double bonds were added directly with  $\text{Br}_2$ . It should be emphasized that the addition reaction of double bonds by  $\text{Br}_2$  is much easier than that by  $\text{HBr}$ , and this reaction is often used to determine the concentration of double bonds quantitatively. The  $^1\text{H}$  NMR spectrum of star PS after bromination with  $\text{Br}_2$  is shown in Fig. 3(C). It can be seen that the broad peak at about 5.7 ppm corresponding to the protons of hanging vinyl on DVB units disappears, and a new peak appears at about 3.9 ppm corresponding to the methene protons adjacent to another kind of bromine atoms. Obviously, the broad peak near 5.1 ppm should be ascribed to methine protons adjacent to bromine atoms in the microgel core.

Fig. 4(A)–(C) show the  $^1\text{H}$  NMR spectra of crude DVB, the completely hydrobrominated and partially hydrobrominated products of DVB, respectively. It can be seen that the resonance corresponding to the methine protons (5.17 ppm) adjacent to bromine atoms is indeed very near that corresponding to vinyl protons (5.20, 5.75, 6.70 ppm). This indicates that the signal at about 5.1 ppm in Fig. 3(B) should be ascribed to the methine protons obtained by both the addition of linear PS arms to vinyl groups of DVB and the hydrobromination of residual vinyl groups in the gel core.

Matyjaszewski et al. [50] prepared heteroarm star polymer,  $[\text{poly}(\textit{tert}\text{-butyl acrylate})]_n\text{-}[\text{poly}(n\text{-butyl acrylate})]_m$ , using arm-first method by growth from the DVB microgel core via ATRP, and Chen et al. [51,52] reported the syntheses of

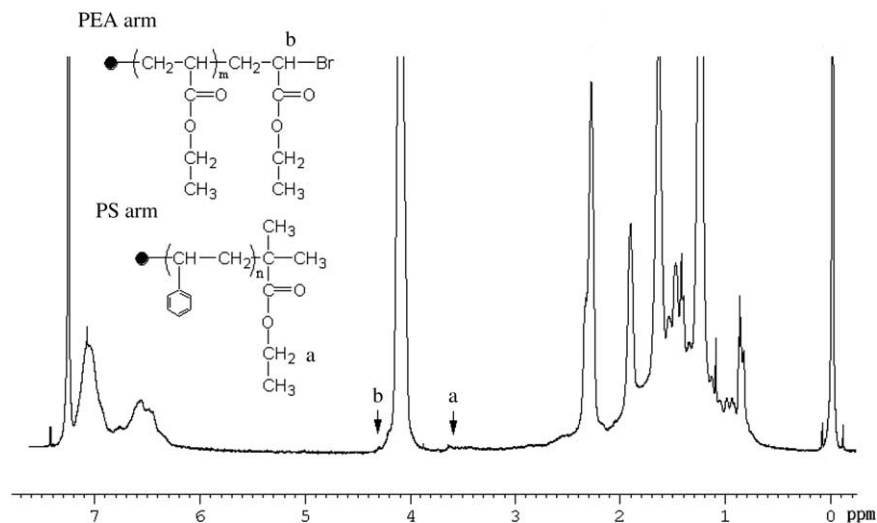
$(\text{PCL})_n\text{-}(\text{PS})_n$  and  $(\text{PEO})_n\text{-}(\text{PS})_n$  heteroarm star polymers through similar method. In their heteroarm star polymers, the number of two different polymer arms was same. Whereas in this paper, after hydrobromination of the residual vinyl groups in the gel core of star polystyrene, the number of initiating sites in the gel core increased. Then, by using hydrobrominated star PS homopolymer as the macroinitiator for ATRP of EA, heteroarm star polymers with more PEA arms than that of PS would be obtained.

Fig. 5 shows the GPC curves of the growing polymers by grafting PEA from the core of PS star at various reaction times. The molecular weight increased remarkably without a significant increase in molecular weight distribution.

In the research of Chen et al. [51,52], the monomer conversion did not exceed 10%, otherwise star–star coupling would occur and insoluble gel would be produced. However, in our reaction conditions, EA conversion could reach at least 33.9% without star–star coupling.

In order to elucidate why there was such a large difference between our results and Chen's, we ran another experiment. In this case, star PS homopolymer before hydrobromination treatment was used as the macroinitiator for ATRP of EA. The GPC curves of obtained products at different reaction times are shown in Fig. 6. Although the molecular weight increased remarkably, broad molecular weight distributions appeared even at lower EA conversion. After 5 h (EA conversion was only 1.76%), a higher molecular weight shoulder corresponding star–star coupling began to be generated. Longer reaction time resulted in an increasing amount of star–star coupling. These results show that the star–star coupling was generated not only through bimolecular termination reaction between PEA propagating radicals but also through addition reaction of PEA propagating radicals to vinyl groups in the gel core (Scheme 3). It is because all the residual vinyl groups in the gel core were exhausted by hydrobromination in our experiment that the star–star coupling was suppressed greatly.

Fig. 7 shows the  $^1\text{H}$  NMR spectrum of  $(\text{PS})_n\text{-}(\text{PEA})_m$  heteroarm star polymer. The characteristic signal at about

Fig. 7.  $^1\text{H}$  NMR spectrum of  $(\text{PS})_n\text{-}(\text{PEA})_m$  heteroarm star polymer.

5.1 ppm corresponding to the methine protons of the benzyl group adjacent to bromine atoms disappeared, whereas a new peak at 4.25 ppm corresponding to the methine protons of the end EA unit adjacent to bromine atoms appeared, indicating a high initiation efficiency of the 1-bromoethylbenzene groups in the gel core.

#### 4. Conclusion

In conclusion, star polystyrene, (PS)<sub>n</sub>, could be synthesized by the arm-first method via ATRP using a preformed PS macroinitiator in the presence of DVB. In the microgel core of (PS)<sub>n</sub>, there were not only a number of active initiating sites for ATRP, but also some unreacted vinyl groups. Heteroarm star polymers, (PS)<sub>n</sub>–(PEA)<sub>m</sub>, could be obtained by ATRP of EA with (PS)<sub>n</sub> as the macroinitiator. However, EA conversion had to be very low, otherwise serious star–star coupling reaction would take place because of the addition reaction of PEA propagating radicals to the residual vinyl groups in the gel core. After the residual vinyl groups were converted to 1-bromoethylbenzene groups by hydrobromination, heteroarm star-shaped polymers [(PS)<sub>n</sub>–(PEA)<sub>m</sub>] with relatively narrow molecular weight distributions, where the arm number of PEA was greater than that of PS, could be synthesized successfully with higher EA conversion (at least 33.9%) by ATRP of EA using the hydrobrominated (PS)<sub>n</sub> as the macroinitiator.

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