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Polymer 46 (2005) 2802–2810

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Preparation of star polymers based on polystyrene or poly(styrene-*b*-*N*-isopropyl acrylamide) and divinylbenzene via reversible addition-fragmentation chain transfer polymerization

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Received 10 November 2004; received in revised form 11 January 2005; accepted 14 January 2005

Abstract

Star polymers based on styrene/divinyl benzene (St/DVB) and PSt-*b*-poly(*N*-isopropyl acrylamide) (NIPAAM)/DVB have been successively prepared by 'arm-first' method via reversible addition-fragmentation chain transfer (RAFT) polymerization. The linear macro RAFT agent PSt-SC(S)Ph was prepared by RAFT polymerization of St using benzyl dithiobenzoate and AIBN as RAFT agent and initiator. Successive RAFT polymerization of NIPAAM with PSt-SC(S)Ph as macro RAFT agent to afford diblock copolymer, PSt-b-PNIPAAM-SC(S)Ph. The coupling reactions of PSt-SC(S)Ph or PSt-b-PNIPAAM-SC(S)Ph in the presence of DVB produced the star copolymers, $C(PSt)_n$ or $C(PSt\text{-}b\text{-}PNIPAAM)_n$. The molar ratio of DVB/PSt-SC(S)Ph and polymerization time influenced the yields, molecular weight and distribution of the star-shaped polymers, which was characterized by ^{1}H NMR and IR spectra, GPC measurements as well as DLS.

Keywords: Star-shaped polymers; RAFT polymerization; Cross-linked polymerization

1. Introduction

Star-shaped polymers, which is composed of multiple polymer chains emanating from junction points, have received significant attention over the past decade because of their unique three-dimensional shape and highly branched structure [1]. They have possible processing advantages due to their compact structure in comparison with linear analogues. Well-defined star polymers are generally prepared by various polymerization methods including anionic [2,3], cationic [4], ring-opening metathesis [5], group-transfer polymerization [6], transition-metal catalysis [7], nitroxide-mediated free-radical polymerization (NMRP) [8,9], atom transfer radical polymerization (ATRP) [10–12] and reversible addition-fragmentation transfer (RAFT) polymerization [13,14] and the combination of controlled radical polymerization with ring-opening polymerization [15,16]. There are three general synthetic approaches: (1) living polymerization with multifunctional initiators; (2) coupling reactions of linear living chains with a multifunctional coupling agent; (3) linking reactions of linear living chains with divinyl compounds (linking agents). The first is often ascribed as the 'core-first' approach and the major limitation is the limited access to suitable star cores with sufficient functionalities to give polymer stars with larger arm numbers. While the third described as the 'arm-first' approach can provide larger number of arms than the 'core-first' approach. This technique employs the coupling of performed macroinitiators in the presence of divinyl compounds. A few of divinyl coupling reagents are initially added to the macroinitiator chain ends to form short block copolymers, and then they react each other to form tightly cross-liked cores, leading to the formation of star polymers.

NMRP [9,17,18], ATRP [10,11,19] and RAFT process [13] have been reported to be used in the preparation of star polymers. Davis T. P. and his coworkers reported the preparation of microgel polystyrene (PSt) using the RAFT polymerization of divinyl benzene (DVB) with 1-phenylethyl dithiobenzoate terminated PSt as macro RAFT agent [13]. They found that there was still a significant amount of linear polymers presented in the polymerization system

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doi:10.1016/j.polymer.2005.01.071

even after 48 h polymerization; no explanation for this phenomenon was described. Based on our knowledge, there is no report on the preparation of star polymers with thermally sensitive poly(*N*-isopropyl) acrylamide (PNIPAAM) as inner layer and PSt as outer layer. Since RAFT polymerization is more versatile to monomers in comparison with other controlled radical polymerization. In this paper, we report the synthesis of star polymers based on PSt and DVB or PSt-*b*-PNIPAAM and DVB using the 'arm-first' technique via RAFT polymerization. The star polymers were separated from linear polymers contaminant in the final product, the diameter of the single molecular sphere in tetrahydrofuran was measured.

2. Experimental

2.1. Materials

Tetrahydrofuran (THF) was refluxed over sodium for 24 h, and then distilled prior to use. St (Shanghai Chemical Reagent Co, 99%) and divinylbenzene (50 wt% DVB mixture of isomers, Shanghai Chemical Reagent Co.) were dried over CaH_2 and distilled under reduced pressure prior to use. *N*-isopropyl acrylamide (NIPAAM, Kohjin Chemical Co. Ltd) was recrystallized from a mixture of cyclohexane and benzene (65/35, v/v), and then dried in a vacuum oven. Azobisisobutylnitrile (AIBN) was purified by recrystallization from ethanol. Benzyl dithiobenzoate (BDTB) was prepared according to the published procedure [20]. All other reagents were of analytical grade and used as received.

2.2. Preparation of linear PSt macro transfer agent

Polymerization was carried out in sealed tubes. A general synthetic procedure is as follows. St (20 g, 0.19 mol), BDTB (0.488 g, 2 mmol) and AIBN (0.033 g, 0.2 mmol) were added into a 50 mL glass tube. After the mixture was degassed by three freeze-evacuate-thaw cycles, the tube was sealed under vacuum, and then immersed in an oil bath thermostated at 110 °C for 8 h. The polymerization was stopped by placing the tube in an ice water bath. Then the tube was opened, and the polymer was precipitated by pouring a polymer solution in THF into an excess of methanol while stirring, the precipitates were collected by filtration, and then dried in a vacuum oven at room temperature overnight. The PSt-SC(S)Ph with $M_{n,\mathrm{GPC}}=3300$, $M_w/M_n=1.17$ was obtained in 33% yield.

2.3. Preparation of linear block P(St-b-NIPAAM) macro transfer agent

Into a 10 mL glass tube, the macro transfer agent PSt with $M_{n,\mathrm{GPC}}=1300$ (0.278 g, 0.0485 mmol), NIPAAM (0.5 g, 4.42 mmol) and THF (4 mL) were added. The tube was sealed under vacuum after three freeze-evacuate-thaw cycles, and then placed in an oil bath thermostated at 90°C for 8 h. The final polymer was obtained by pouring the reaction mixture into excess petroleum ether (30–60 °C) while stirring, and the polymer collected by filtration was dried in a vacuum oven at room temperature overnight. The PSt-*b*-PNIPAAM with $M_{n,\mathrm{GPC}}=9600$, $M_w/M_n=1.34$ was obtained in 38% yield.

2.4. Preparation of star polymers

DVB and RAFT agent, PSt-SC(S)Ph with various ratios was used in the RAFT polymerization for determining optimum preparation conditions of star polymers. Six solutions with various molar ratios of DVB: PSt-SC(S)Ph with $M_{n,\mathrm{GPC}}=3300$ (5:1, 10:1, 15:1, 20:1, 35:1, 40:1, related to 0.6 g of PSt-SC(S)Ph) were prepared in THF (1.2 g) for each sample, and into each solution, AIBN (3.0 mg) was added as the initiator. Those solutions were degassed by three freeze-evacuate-thaw cycles; the tube was sealed under vacuum, and then immersed in an oil bath thermostated at 110 °C for 12 h. The polymerization was stopped by placing the tube in an ice water bath. Then the tube was opened, and the polymer was precipitated by pouring the polymer solution in THF into excess methanol while stirring, the precipitate collected by filtration was dried in a vacuum oven at room temperature overnight.

To determine the optimum polymerization time, PSt-SC(S)Ph ($M_{n,\mathrm{GPC}}=3300$, 1.8 g), DVB (2.7 g) and AIBN (9.0 mg) were dissolved in 3.6 g THF, the solution was equally divided into six polymerization ampoules, and then all the polymerizations were carried out with the same procedure described above except that the polymerizations stopped at intervals of the prescribed polymerization time.

2.5. Separation of star polymers from linear polymer contaminant by GPC

Separation of star polymers from linear polymer contaminant was carried on preparative gel permeation chromatography (GPC) with polymer standards service columns (19×300 mm) (guard, 10^4, 10^3) coupled with a Waters 2414 refractive index detector and a Waters 1515 HPLC pump at room temperature. THF was used as eluent at a flow rate of 6 mL/min. Narrow polystyrene standards were used in the calibration of molecular weights. Each injection volume of the star polymers solution in THF is 2 mL, and then each component was collected based on the GPC curve appeared.

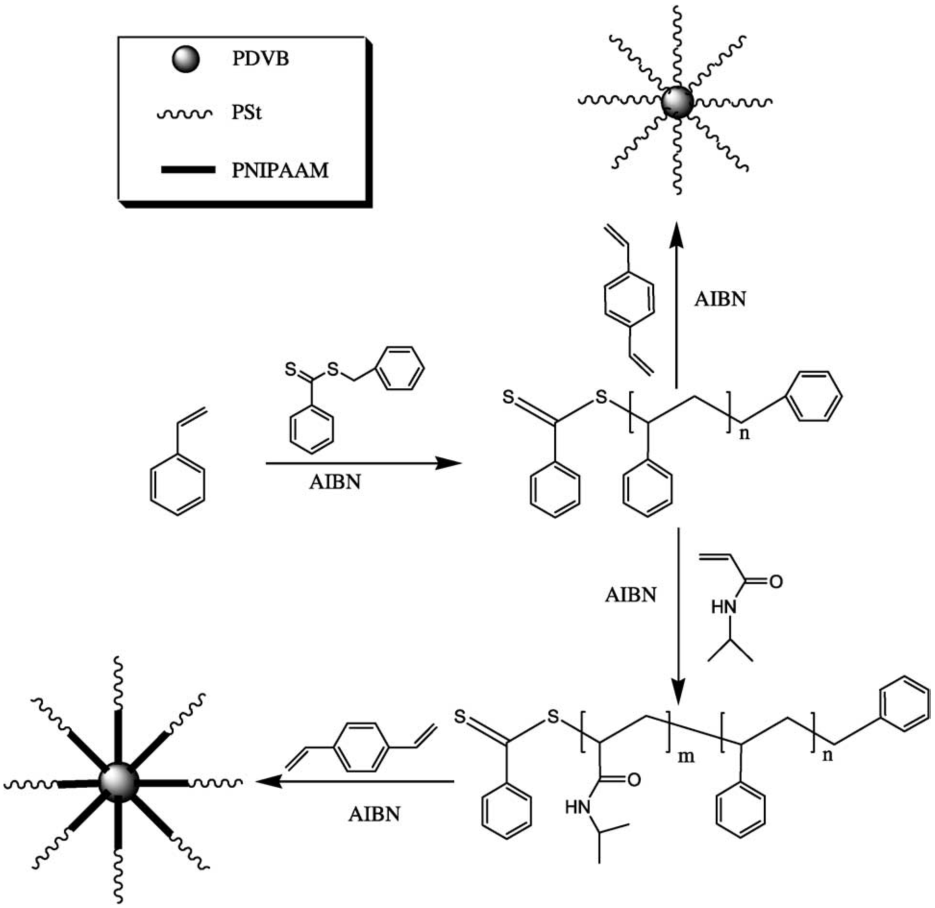
2.6. Measurements and instruments

^1H NMR spectra were measured on a Bruker DMX-400 nuclear magnetic resonance instrument with $CDCl_3$ as solvent, tetramethylsilane (TMS) as internal reference. The molecular weight and polydispersity index were determined on a Waters 150C gel permeation chromatograph (GPC) equipped with ultrastyragel columns (500, 10^3, 10^4 Å) at 30 °C using monodisperse polystyrene as calibration standard. DLS was carried out at 25 °C using a modified commercial light-scattering spectrometer (ALV/SP-125) equipped with an ALV-5000 digital time correlator and a solid-state laser (ADLAS DPY 425 II, output power ca. 400 mW at $\lambda = 532$ nm). In DLS, the Laplace inversion (the CONTIN procedure) of each measured intensity–intensity time correlation function $G^{(2)}(q,t)$ in the self-beating mode can be related to a line-width distribution $G(\Gamma)$. For a diffusive relaxation, Γ is related to the translation diffusion coefficient D by $(\Gamma/q^2)_{c\to 0,\, q\to 0} \to D$, so that $G(\Gamma)$ can be converted into a transitional diffusion coefficient distribution $G(D)$ or a hydrodynamic radius distribution $P(R_h)$ via the Stokes–Einstein equation, $R_h = (k_B T/6\pi\eta)D^{-1}$, where k_B, T, and η are the Boltzmann constant, the absolute temperature, and the solvent viscosity, respectively. The cumulant analysis of $G^{(2)}(t)$ of a narrowly distributed sample can result in an accurate average line-width ($<\Gamma>$); and the relative distribution width ($\mu_2/<\Gamma>^2$) was used as a polydispersity index (PDI) to indicate the degree of the dispersion of the polymer micelles or particles.

3. Results and discussion

3.1. Synthesis of macro RAFT agents

Polymer stars with tightly cross-linked cores or microgels were prepared according to Scheme 1. Obviously, the first step in all cases is the preparations of dithiobenzoate (DTB)-terminated PSt. It was achieved by RAFT polymerization of St using BDTB and AIBN as RAFT agent and initiator, respectively. The preparation conditions and results are listed in Table 1. Generally, RAFT polymerization of St is of living nature [21]. However, the PDI of PSt2 in Table 1 is higher ($M_w/M_n = 1.52$), this result may be reasonable because equal propagation probability was not reached at lower molecular weight ($M_n = 1300$) and only several RAFT reactions were taken place. When comparing GPC curve in Fig. 1B of PSt2 with that in Fig. 1A of PSt1, we will find that with the increase of molecular weight, the PDI of the PSt-SC(S)Ph obtained became narrow (PSt1, $M_n = 3300$, PDI = 1.17). In order to ensure one DTB group in each PSt chain, also for GPC measurements of star polymers obtained at various conversions, the PSt2 with $M_n = 1300$ was used in the preparation of polymer stars.



Scheme 1.

Table 1
The preparation conditions and results of PSt-SC(S)Ph and PSt-*b*-PNIPAAM-SC(S)Ph

No	Sample	T (°C)	Time (h)	Conversion (%)^a	$M_{n,\mathrm{NMR}}$ (g mol^{-1})	$M_{n,\mathrm{GPC}}$ (g mol^{-1})	M_w/M_n
1^b	PSt1	110	8	33	3600^c	3300	1.17
2^d	PSt2	110	6	26	1700^c	1300	1.52
3^e	PSN	80	12	46	5800^f	5400	1.33

[a] Conversions were calculated based on the gravimetric method.

[b] Feed ratio: St/BDTB/AIBN = 950:10:1 (molar ratio).

[c] $M_{n,\mathrm{PSt}}$ (NMR) was calculated according to $M_{n,\mathrm{PSt}}\,(\mathrm{NMR})=(2I_{7.32\text{–}6.30}/5I_{7.85})\times 104+258$, where $I_{7.32\text{–}6.30}$ and $I_{7.85}$ are integral values of the signals at $\delta=7.32$–6.30 and 7.85 ppm, 104 and 258 are molecular weights of St and BDTB.

[d] Feed ratio: St/BDTB/AIBN = 475:10:1 (molar ratio).

[e] Feed ratio: NIPAAM/PSt2/AIBN = 1000:10:2 (molar ratio); NIPAAM = 1 g; THF: 4 mL.

[f] $M_{n,\mathrm{PSt\text{-}PNIPAAM}}$ (NMR) of PSt-*b*-PNIPAAM was calculated according to $M_{n,\mathrm{PSt\text{-}PNIPAAM}}\,(\mathrm{NMR})=(5I_{4.04}/I_{7.32\text{–}6.30})\times DP_{\mathrm{St2}}\times 113+M_{\mathrm{PSt2}}$, where $I_{4.04}$ is integral value of the signal at $\delta=4.04$ ppm corresponding to methine next to nitrogen in NIPAAM unit, DP_{PSt} and M_{PSt2} are the degree of polymerization and the molecular weight of PSt, respectively, 113 is the molecular weight of NIPAAM unit.

From its ^{1}H NMR spectrum in Fig. 2A, we can see the signals at $\delta=7.85$ and 4.82 ascribed to aromatic protons of DTB group and methine proton next to terminal sulfur, respectively except characteristic signals of PSt. Assume each PSt chain has one DTB group, the $M_{n,\mathrm{PSt}}$ (NMR) can be calculated based on the integration ratio of signals at $\delta=$ 6.30–7.32 and 7.85 ppm. The calculated results are listed in Table 1. The agreement of $M_{n,\mathrm{PSt}}$ (NMR) with $M_{n,\mathrm{PSt}}$ (GPC) indicates almost no lost of DTB during the RAFT polymerization.

For the preparation of star polymers with PNIPAAM as inner layer and PSt as outer layer, the block copolymer, PSt-*b*-PNIPAAM-SC(S)Ph was prepared by RAFT block copolymerization of NIPAAM using PSt-SC(S)Ph (PSt2, $M_n=1300$) as macro RAFT agent and AIBN as initiator. The polymerization conditions and results are summarized in Table 1. The GPC curve of the block copolymer obtained in Fig. 1C shows lower PDI ($M_w/M_n=1.33$) than its precursor, PSt2 ($M_w/M_n=1.52$), probably due to the 'living' nature of RAFT polymerization of NIPAAM. For verifying the formation of diblock copolymer, PSt-*b*-PNIPAAM, its ^{1}H NMR spectrum was measured and is shown in Fig. 2B. Except characteristic signals of PSt, the signal at $\delta=$ 4.04 ppm corresponding to methine proton in isopropyl group of NIPAAM unit demonstrates the formation of diblock copolymer, PSt-*b*-PNIPAAM. The terminal DTB group at the end of block copolymer chain can be verified by the signals at $\delta=7.85$ and 5.33 ppm ascribed to aromatic protons of DTB group and methine proton of terminal NIPAAM unit next to sulfur of DTB group, respectively.

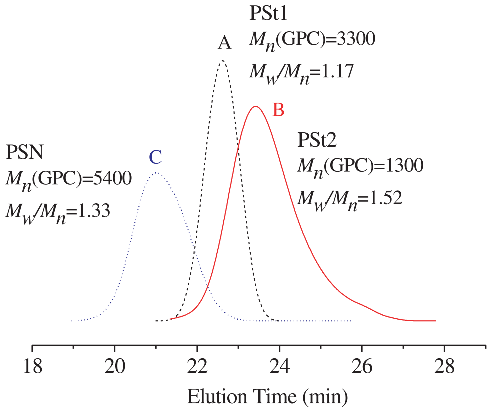


Fig. 1. GPC curves of (A) PSt1 in Table 1; (B) PSt2 in Table 1 and (C) PSt-*b*-PNIPAAM (PSN in Table 1).

3.2. Star polymers with PSt arms

3.2.1. Effect of DVB to macro RAFT agent ratio

For studying the effect of molar ratio of DVB to macro RAFT agent on the formation of star PSt with high cross-linked PDVB as core, the RAFT polymerization of DVB using PSt-SC(S)Ph as macro RAFT agent were investigated. The polymerization conditions and results are summarized in Table 2. In general, higher molar ratio of DVB to PSt-SC(S)Ph produces longer chain length of PDVB segment, resulted in larger cross-linked cores with more PSt arms. Thus the molecular weight of polymer stars increased with the increasing molar ratio of DVB to PSt (see Table 2). Too high this ratio will lead to the solution polymerization of DVB, forming a cross-linked polymer. This phenomenon

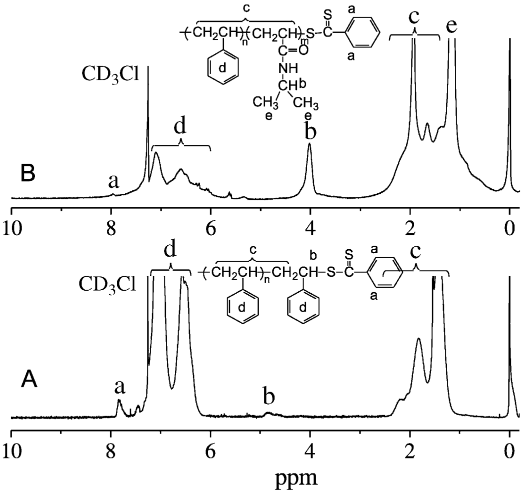


Fig. 2. ^{1}H NMR spectra of the polymers: (A) PSt2 in Table 1; (B) PSt-*b*-NIPAAM (PSN in Table 1).

Table 2
Formation of star polymers from RAFT polymerization at different weight ratio of DVB to BDTB

No	Sample	DVB/PSt molar ratio	Time (h)	$M_{n,\mathrm{GPC}}$[a] g mol^{-1}	$M_{\mathrm{w,GPC}}$[a] g mol^{-1}	MWD[a]
4	SPS-1	5	12	4800	6900	1.44
5	SPS-2	10	12	6400	10,100	1.58
6	SPS-3	15	12	8600	13,800	1.61
7	SPS-4	20	12	13,300	54,700	2.79
8	SPS-5	35	1	6100	9300	1.52
9	SPS-6	35	3	7300	11,700	1.60
10	SPS-7	35	5.5	7200	11,000	1.53
11	SPS-8	35	9	7800	12,600	1.62
12	SPS-9	35	12	19,600	61,700	4.64
13	SPS-10	35	46	20,600	60,300	2.93
14[b]	SPS-11	40	12	–	–	–

The polymerizations were carried out at 110 °C in the presence of AIBN as initiator (AIBN/PSt1 = 1:10, molar ratio), PSt1: 0.6 g, THF: 2 mL.
[a] Measured by GPC method.
[b] Cross-linking reactions occurred during the polymerization.

was observed, the whole system was cross-linked at molar ratio of DVB/PSt-SC(S)Ph = 40 (see Table 2). The ratio 35 of DVB to PSt was found to be optimal because the larger molecular weight of PSt stars was obtained. Low ratios of DVB to PSt produced polymer stars with smaller molecular weight. The effects of DVB to PSt-SC(S)Ph ratio on the formation of polymer stars can be further examined by their GPC curves. Fig. 3 shows the GPC curves of the star polymers obtained, respectively from the polymerization at the ratios of DVB to PSt = 5, 10, 15, 20 and 35. We can clearly see the two peaks, the first ranges from 24 to 21.5 min elution time, and the second ranges from 21.5 to 18.5 min in the GPC curves of SPS-1, SPS-2, SPS-3, SPS-4 and SPS-9 in Fig. 3. With the increase of DVB to PSt-SC(S)Ph ratio, the first peaks stay almost at the same elution time, and their relative integration values decrease gradually, thus the first peak must be ascribed to the linear macro RAFT agent, PSt-SC(S)Ph. However, the second peak, which corresponds to lower molecular weight polymer stars, moves to high molecular weight position continuously, and

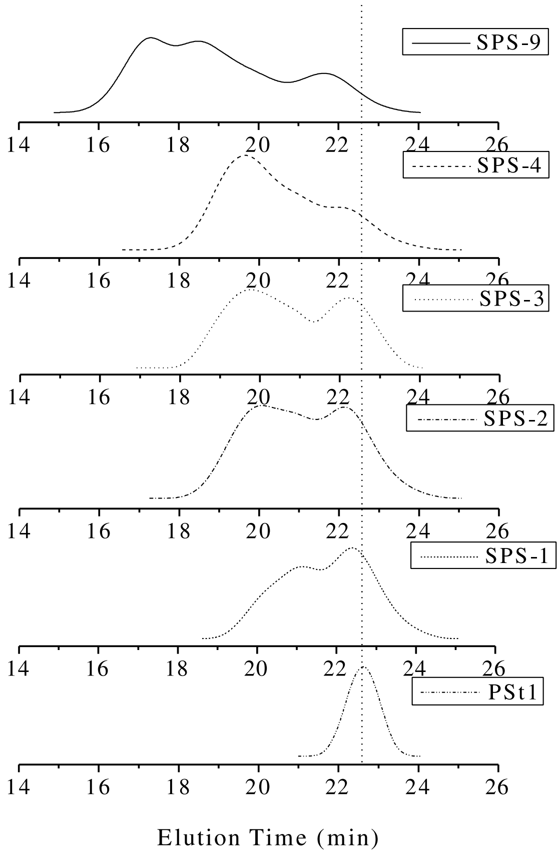


Fig. 3. GPC traces of PSt stars obtained from the polymerization of DVB with the DVB/macro transfer agent ratio = 5 (SPS-1); 10 (SPS-2); 15 (SPS-3); 20 (SPS-4); 35 (SPS-9) for 12 h.

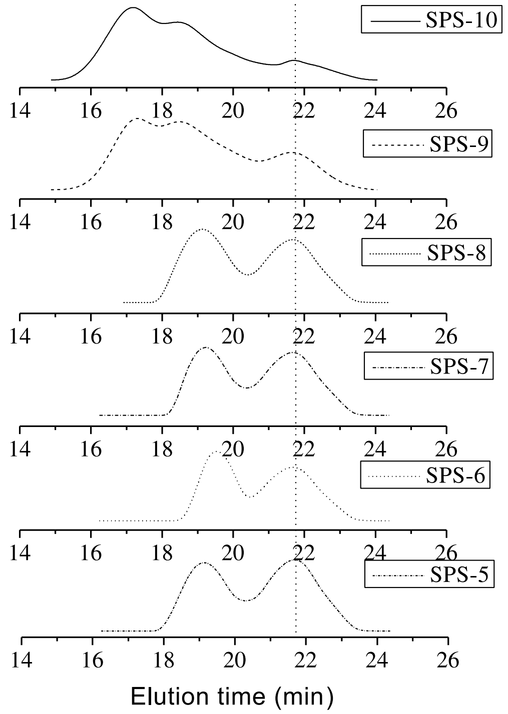


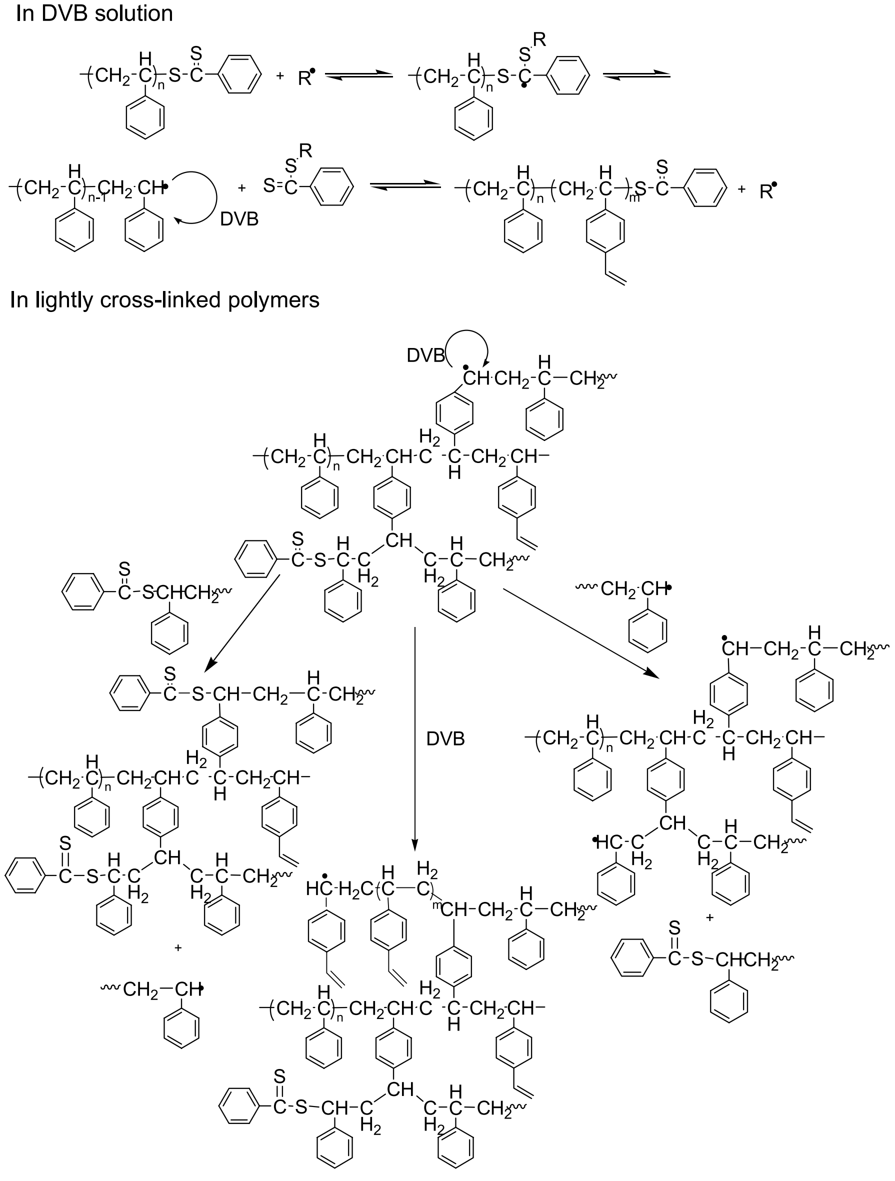
Fig. 4. GPC traces of PSt stars obtained from polymerization of DVB for various times: 1 h (SPS-5), 3 h (SPS-6), 5.5 h (SPS-7), 9 h (SPS-8), 12 h (SPS-9), 46 h (SPS-10). Polymerization conditions: DVB/PSt1 = 35:1 (molar ratio); temperature: 110 °C; AIBN: 9 mg; PSt1:1.8 g.

their relative peak areas increase (Fig. 3). When DVB/PSt ratio rises to 35, the third peak corresponding to polymer stars with higher molecular weight appears (SPS-9 in Fig. 3), and it may be resulted from the star–star coupling reactions [11].

3.2.2. *Effect of polymerization time*

Using a weight ratio of DVB/PSt = 35/1, the RAFT polymerization of DVB with PSt-SC(S)Ph as RAFT agent and AIBN as initiator was studied, GPC was used to follow the polymerization, and the results are shown in Fig. 4. In the first 9 h polymerization, all GPC curves in Fig. 4 display two peaks. One at longer elution time corresponds to macro RAFT agent, PSt-SC(S)Ph. The curve areas decrease slowly with evolution of the polymerization. However, those peaks at shorter elution times are ascribed to star polymers, their areas increase with proceeding of the polymerizations. These suggest that in the first 9 h reaction, the polymerization system contains linear macro RAFT agent, PSt-SC(S)Ph and lower molecular weight PSt stars. The linear PSt chain radicals continued to react with DVB molecules in solution and also to react with the dangling vinyl groups in the DVB block of other polymer chains (Scheme 2). As a result, the increase of molecular weight of the polymer stars formed is not so obvious.

From the curve of SPS-8 GPC in Fig. 4, at 9 h polymerization, there was still 50.3 wt% of linear PSt-SC(S)Ph left, even at 46 h polymerization, 10.4 wt% of the macro RAFT agent was still remained (SPS-10, in Fig. 4). This phenomenon is different from the preparation of star polymers by ATRP [10] or nitroxide-mediated radical polymerization [18]. In the later two cases, the



Scheme 2.

macroinitiators were consumed faster. This difference must be related to their polymerization mechanisms. For RAFT polymerization, the propagation reaction of any polymer chain radical with DTB group via RAFT process will produce one propagating radical and one DTB-terminated polymer chain. As shown in Scheme 2, in DVB solution, there are linear polymer chain radicals and polymer chains with DTB group. The linear chain radicals can attack DTB group to form radicals in lightly cross-linked polymers and to release linear polymer capped with DTB group into DVB solution; and linear polymers with DTB group is attacked by chain radicals in cross-linked polymers to form the cross-linked polymers with dangling DTB group, and the linear chain radical was released into DVB solution. Thus, it is reasonable that the linear polymers are consumed slowly. For the preparation of star polymers using ATRP or NMRP method, as shown in Scheme 3, the linear chain radicals produced in DVB solution can propagate to form cross-linked polymers and/or block copolymers, PSt-b-PDVB, they also can initiate polymerization of the vinyl groups in the lightly cross-linked polymers. Therefore, the macroinitiators, PSt-Br consumed relatively fast.

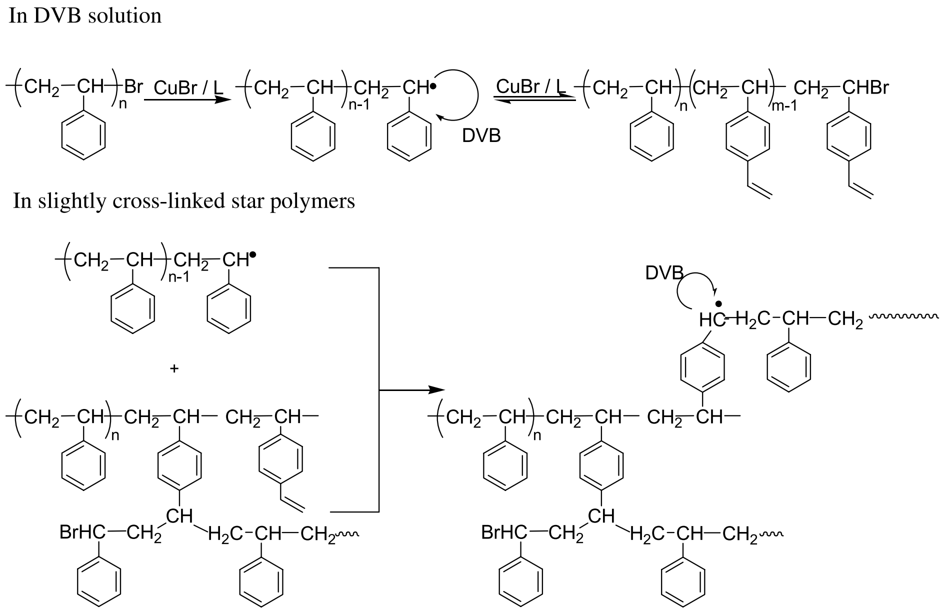
After 12 h polymerization, the most of DVB was consumed, the polymerization of DVB and/or residual vinyl groups occurred mainly in the star polymers because most of DTB groups were transferred into the star-shaped polymers. At the same time, the reactions between polymer stars were taken place, leading to the appearance of third peak in SPS-9 and SPS-10 in Fig. 4. Even for 46 h polymerization, the linear RAFT agent is still obvious due to the RAFT mechanism.

3.3. Star polymers with block arms

Star polymers with block copolymer chains, P(St-*b*-NIPAAM) were synthesized by RAFT polymerization of DVB for 72 h using the molar ratio of DVB/P(St-*b*-NIPAAM) = 35/1. Fig. 5 demonstrates the GPC traces of PSt-SC(S)Ph, PSt-*b*-PNIPAAM, star copolymer C(PSt-*b*-PNIPAAM)$_n$ and narrow star copolymer obtained from preparative GPC separation, and obviously, the molecular weights increase from PSt to PSt-*b*-PNIPAAM, and to C(PSt-*b*-PNIPAAM)$_n$. GPC traces in Fig. 5C is similar to that of the star polymers obtained from PSt-SC(S)Ph and DVB shown in Fig. 4. The increase of the third peak and decrease of the second peak demonstrate that most of the lower molecular weight star polymers reacted with each other to form larger molecular weight star polymers. However, linear polymer chains with DTB groups still exist. This must be related to RAFT mechanism as we discussed.

After separation of star copolymers C(PSt-*b*-PNIPAAM)$_n$, the narrower star-shaped copolymer was obtained as shown in Fig. 5D. When this sample was dissolved in THF to form transparent solution, the hydrodynamic radius (R_h) and size distribution were measured by DLS, and the results shown in Fig. 6 demonstrate that the particles with $R_h = 18$ nm and the relatively narrow polydispersity index ($\mu_2/\Gamma^2 = 0.18$) were formed.

In order to confirm further the formation of star polymers with tightly cross-linked core, ^{1}H NMR spectrum of the star polymer obtained from preparative GPC separation of the star copolymers C(PSt-*b*-PNIPAAM)$_n$ is shown in Fig. 7A.



Scheme 3.

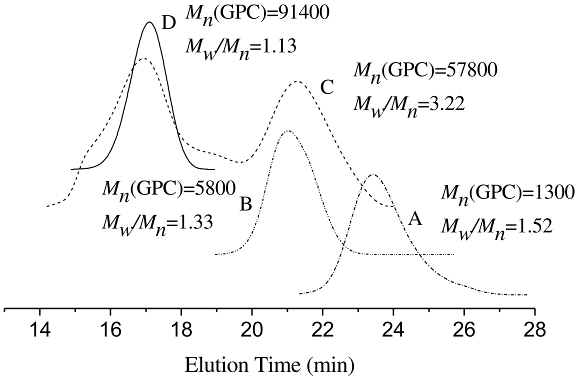


Fig. 5. GPC traces of A: PSt2; B: PSt-*b*-PNIPAAM; C: star block copolymer, C(St-*b*-NIPAAM)$_n$ and D: star copolymer obtained from the preparative GPC separation.

In comparison with ^{1}H NMR spectrum of its precursor in Fig. 1B, we could not find those proton signals (7.95 ppm) ascribed to the terminal DTB group and those unreacted vinyl proton signals in DVB units in Fig. 7A. However, from its IR spectrum in Fig. 7B, we can observe the out of plane bending vibration bands of C–H in carbon–carbon double bond of DVB unit in center of stars at $\nu = 907$ and $992\ \mathrm{cm}^{-1}$, and the stretching vibration band of C=S at $\nu = 1064\ \mathrm{cm}^{-1}$. This indicates that the star polymers have tightly cross-linked core, thus we call the products obtained in this study as star polymers.

4. Conclusions

Star PSt, C(PSt)$_n$ and star PSt-*b*-PNIPAAM, C(PSt-*b*-PNIPAAM)$_n$ have been successfully prepared by the RAFT polymerization of divinylbenzene using PSt-SC(S)Ph or PSt-*b*-PNIPAAM-SC(S)Ph as macro RAFT agent. With the increase of DVB/PSt-SC(S)Ph ratio, linear polymers decrease and star polymers formed increase. At the molar ratio of DVB/PSt-SC(S)Ph = 35, the high molecular weight star PSt was produced due to the reactions between the lower molecular weight star polymers. When the GPC was used to follow the RAFT polymerization, the results show that in comparison with ATRP and NMRP used in preparation of polymer stars by the arm first method, the linear polymers decrease slowly, around 10 wt% of linear polymers are still remained even after 48 h polymerization due to that any propagation reaction in the star polymers will release one linear chain radical or one linear chain capped with DTB group into DVB solution. When the most of DVB was consumed, such as after 12 h polymerization, the star polymers will reacted each other to form higher molecular weight star polymers. The RAFT polymerization is not good approach for the preparation of star polymers in comparison with ATRP or NMRP because higher content of linear polymers still exist even after long polymerization time. The star PSt-b-PNIPAAM with PNIPAAM inner layer and PSt outer layer were formed for 72 h polymerization in THF solution, the average R_h is 18 nm, the relatively polydispersity index is $\mu_2/\Gamma^2 = 0.18$.

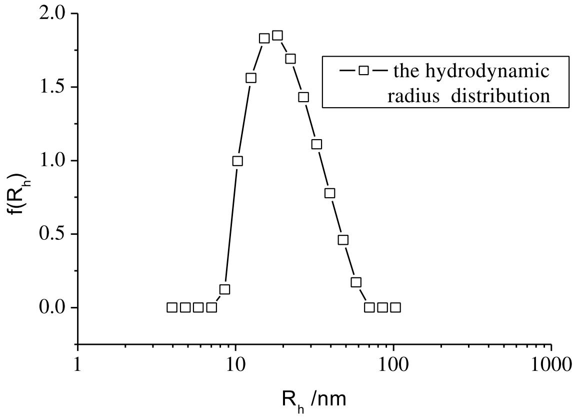


Fig. 6. Distribution of R_h of the star copolymers, C(St2-*b*-NIPAAM)$_n$ obtained from the preparative GPC separation in THF analyzed by DLS.

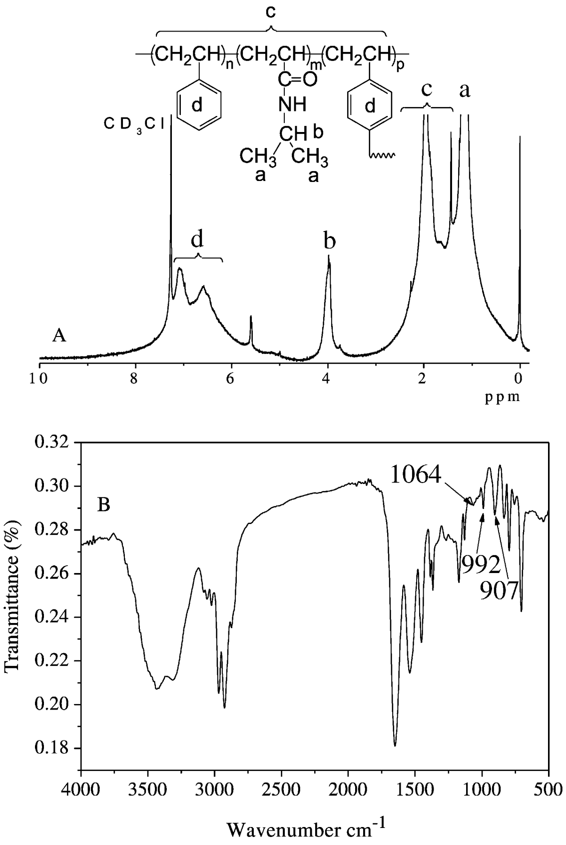


Fig. 7. ^{1}H NMR (A) and IR (B) spectra of PSt-*b*-PNIPAAM star polymers obtained from preparative GPC separation.

Acknowledgements

The author is thankful for the support of the National Nature Science Foundation of China (Grant 20374048).

References

[1] Mishra MK. Macromolecular engineering: recent advances. New York: Plenum Press; 1995.

[2] Tselikas Y, Hadjichristidis N, Lescanec RL, Honeker CC, Wohlgemuth M, Thomas EL. Macromolecules 1996;29:3390–6.

[3] Hsieh HL, Quirk RP. Anionic polymerization: principles and practical applications. New York: Marcel Dekker; 1996.

[4] Kanaoka S, Sawamoto M, Higashimura T. Macromolecules 1991;24:5741–5.

[5] Bazan GC, Schrock RR. Macromolecules 1991;24:817–23.

[6] Webster OW. Makromolekulare Chemie-Macromolecular Symposia 1990;33:133–43.

[7] Kadokawa J, Kobayashi S. Macromol Symp 1995;95:121–36.

[8] Pasquale AJ, Long TE. J Polym Sci, Part A: Polym Chem 2001;39:216–23.

[9] Tsoukatos T, Pispas S, Hadjichristidis N. J Polym Sci, Part A: Polym Chem 2001;39:320–5.

[10] Xia JH, Zhang X, Matyjaszewski K. Macromolecules 1999;32:4482–4.

[11] Zhang X, Xia JH, Matyjaszewski K. Macromolecules 2000;33:2340–5.

[12] Wang XZ, Zhang HL, Zhong GQ, Wang XY. Polymer 2004;45:3637–42.

[13] Lord HT, Quinn JF, Angus SD, Whittaker MR, Stenzel MH, Davis TP. J Mater Chem 2003;13:2819–24.

[14] Chong YK, Le TPT, Moad G, Rizzardo E, Thang SH. Macromolecules 1999;32:2071–4.

[15] Tao L, Luan B, Pan CY. Polymer 2003;44:1013–20.

[16] Guo YM, Pan CY. Polymer. Polymer 2001;42:2863–9.

[17] Bosman AW, Heumann A, Klaerner G, Benoit D, Frechet JMJ, Hawker CJ. J Am Chem Soc 2001;123:6461–2.

[18] Abrol S, Caulfield MJ, Qiao GG, Solomon DH. Polymer 2001;42:5987–91.

[19] Baek KY, Kamigaito M, Sawamoto M. Macromolecules 2001;34:215–21.

[20] Wu DC, Zou YF, Pan CY. Chin J Polym Sci 2002;20:525–30.

[21] Goto A, Sato K, Tsujii Y, Fukuda T, Moad G, Rizzardo E, et al. Macromolecules 2001;34:402–8.