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# Synthesis and self-assembly behaviors of three-armed amphiphilic block copolymers via RAFT polymerization

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## A B S T R A C T

The novel trifunctional reversible addition–fragmentation chain transfer (RAFT) agent, tris(1-phenylethyl) 1,3,5-triazine-2,4,6-triyl trithiocarbonate (TTA), was synthesized and used to prepare the three-armed polystyrene ($PS_3$) via RAFT polymerization of styrene (St) in bulk with thermal initiation. The polymerization kinetic plot was first order and the molecular weights of polymers increased with the monomer conversions with narrow molecular weight distributions ($M_w/M_n \leq 1.23$). The number of arms of the star PS was analyzed by gel permeation chromatography (GPC), ultraviolet visible (UV–vis) and fluorescence spectra. Furthermore, poly(styrene-*b*-*N*-isopropylacrylamide)$_3$ (PS-*b*-PNIPAAM)$_3$, the three-armed amphiphilic thermosensitive block copolymer, with controlled molecular weight and well-defined structure was also successfully prepared via RAFT chain extension method using the three-armed PS obtained as the macro-RAFT agent and *N*-isopropylacrylamide as the second monomer. The copolymers obtained were characterized by GPC and $^1$H nuclear magnetic resonance (NMR) spectra. The self-assembly behaviors of the three-armed amphiphilic block copolymers (PS-*b*-PNIPAAM)$_3$ in mixed solution (DMF/$CH_3OH$) were also investigated by high performance particle sizer (HPPS) and transmission electron microscopy (TEM). Interestingly, the lower critical solution temperature (LCST) of aqueous solutions of the three-armed amphiphilic block copolymers (PS-*b*-PNIPAAM)$_3$ decreased with the increase of relative length of PS in the block copolymers.

## 1. Introduction

Star polymers have being gained great attention over the past decades due to their unique three-dimensional shape and properties. According to linear polymers, star polymers manifest many advantages because of their compact structures, such as lower solution and melt viscosities than linear polymers at the same molecular weights. However, the preparative methods for well-defined star polymers have not grown easier until 'living'/controlled free radical polymerization (LFRP) methods were developed, such as atom transfer radical polymerization (ATRP) [1,2], nitroxide-mediated polymerization (NMP) [3], and reversible addition–fragmentation chain transfer (RAFT) polymerization [4–8]. Up to now, star polymers can be prepared by two main methods, i.e. "core-first" and "arm-first". The core-first technique means to synthesize multifunctional initiator primarily, while the arm-first technique tends to prepare the arms primarily and subsequently react with appropriate terminators or coupling agents to form the star polymers. Generally, the resulting star polymers have a statistical distribution of the number of arms by the "arm-first" technique [9]. On the other hand, the derivatives of 1,3,5-triazine have wide application in the biological area due to the structural similarity of the 1,3,5-triazine ring to purine and pyrimidine [10,11].

Amphiphilic copolymers, especially, core–shell particles with hydrophobic cores and thermosensitive shells have being attracted many interests because of a wide range of potential applications in biology, colloidal science, drug and gene delivery [12–15]. Poly(*N*-isopropylacrylamide) (PNIPAAM) is one of the well-known thermosensitive polymers due to its relatively low critical solution temperature (LCST) [16] and sharp reversible phase transition in aqueous solution [17,18]. Recently, linear amphiphilic block copolymers with PNIPAAM as hydrophilic block have already been widely studied in recent years, such as PNIPAAM-*b*-PS [19–21], PNIPAAM-*b*-PS-*b*-PNIPAAM [22], poly(benzyl ethyl-*b*-*N*-isopropylacrylamide) (PBE-*b*-PNIPAAM) [23], poly(lactide-*b*-*N*-isopropylacrylamide-*b*-lactide) (PLA-*b*-PNIPAAM-*b*-PLA) [24], poly(ethyleneglycol-*b*-*N*-isopropylacrylamide-*b*-styrene) (PEG-*b*-PNIPAAM-*b*-PS) [25], poly(methyl methacrylate-*b*-*N*-isopropylacrylamide) (PMMA-*b*-PNIPAAM) [26]. These block copolymers above mentioned can self-assemble into micelles in water, which have the potential to be used as nano-reactors, drug delivery and site-specific gene vehicles. Recently, star poly(*N*-isopropylacrylamide)

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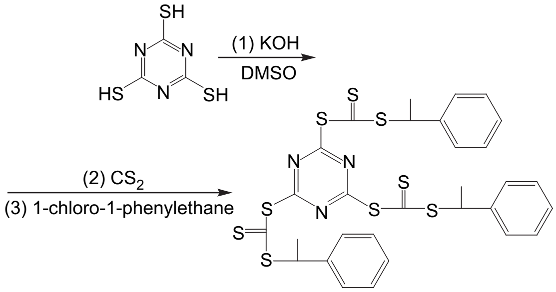
has also been successfully prepared by Whittaker et al. via RAFT polymerization [18]. The results shown that the star architecture has great effect on the LCST of PNIPAAM. However, based on our knowledge, there are few investigations on the star amphiphilic block copolymer with PNIPAAM as hydrophilic block [27]. Cao et al. reported the synthesis of three-armed star diblock copolymer, poly(2-hydroxyethyl methacrylate-*b*-*N*-isopropylacrylamide) (PHEMA-*b*-PNIPAAM), via two-step ATRP method at room temperature [28]. Star polymers based on PNIPAAM-*b*-PS with PNIPAAM as inner layer and PS as outer layer have also been successfully prepared via RAFT polymerization by Zheng and Pan [29]. However, according to their reported results, RAFT polymerization method is not a good approach to synthesize the star polymers by the "arm-first" method. One of the prime reasons is that the linear polymers still remain in the star polymer system.

Interestingly, the lower critical solution temperature (LCST) of PNIPAAM could be modified by free radical copolymerization to change the hydrophilic-to-hydrophobic balance [30,31]. However, conventional radical polymerization is hard to synthesize well-defined polymers with controlled molecular weights and molecular weight distributions. RAFT polymerization can be performed under mild experimental conditions and is able to control over the macromolecular structure, molecular weight distribution, and composition of the polymer. In this work, we synthesized novel trifunctional RAFT agent, tris(1-phenylethyl) 1,3,5-triazine-2,4,6-triyl trithiocarbonate (TTA) by the so-called Z-group approaches (Scheme 1) [32], (Scheme 1), and used it to synthesize three-armed amphiphilic block copolymers $(PS\text{-}b\text{-}PNIPAAM)_3$ with controlled molecular weights and well-defined structures via RAFT technique. Moreover, the self-assembly behaviors of three-armed amphiphilic block copolymers $(PS\text{-}b\text{-}PNIPAAM)_3$ were also reported.

## 2. Experimental sections

### 2.1. Materials

Styrene (St) (chemically pure, Shanghai Chemical Reagent Co. Ltd) was purified by extracting with 5% sodium hydroxide aqueous solution, followed by washing with water and dried with anhydrous sodium sulfate overnight, finally distillated under vacuum before use. *N*-isopropylacrylamide (NIPAAM, 97%; Kohjin Co) was purified by recrystallization from a toluene/hexane mixture. Trithiocyanuric acid (99%; Aldrich Chemical Co), 1-chloro-1-phenylethane (98%; Alfa Chemical Co), and Tetrahydrofuran (THF) (analytical reagent, Shanghai Chemical Reagent Co. Ltd) were used as-received. Carbon sulfide (analytical reagent, Shanghai Chemical Reagent Co. Ltd) and dimethyl sulphoxide (DMSO) (analytical reagent, Shanghai Chemical Reagent Co. Ltd) were dried by 4 Å molecular sieve. *N*, *N*-dimethyl formamide (DMF) and methanol (analytical reagent, Shanghai Chemical Reagent Co. Ltd) were distillated under vacuum. Hexane and petroleum ether (all commercially available) were used as-received.



**Scheme 1.** Synthesis route of tris(1-phenylethyl) 1,3,5-triazine-2,4,6-triyl trithiocarbonate (TTA).

### 2.2. Synthesis of tris(1-phenylethyl) 1,3,5-triazine-2,4,6-triyl trithiocarbonate

Tris(1-phenylethyl) 1,3,5-triazine-2,4,6-triyl trithiocarbonate (TTA) (Scheme 1) was synthesized based on the similar method reported by Davis et al. [33]. Trithiocyanuric acid (1.77 g, 0.01 mol) was added to a suspension of KOH (0.56 g, 0.01 mol) in DMSO (25 mL) under magnetic stirring. The solution was stirred for 8 h at room temperature and then carbon disulfide (2.28 g, 0.03 mol) was added dropwise. The solution was kept at room temperature for 8 h, and then 1-chloro-1-phenylethane (4.20 g, 0.03 mol) was added. The mixture was stirred for 24 h at room temperature. The resultant reaction mixture was poured into large amount of deionized water (300 mL), then was extracted by ethyl acetate (50 mL × 3). The solution was dried with $Na_2SO_4$, and the products were purified by means of column chromatography on silica oxide, with mixed petroleum ether and ethyl acetate (50:1, v/v) as the eluent. The TTA was obtained as a yellow liquid (Yield: 72%), HPLC (Waters 515) showed that the purity was above 98%. $^1H$ NMR ($CDCl_3$, $\delta$): 5.34 (m, 3H), 1.78 (d, 9H); $^{13}C$ NMR ($CDCl_3$, $\delta$): 221.6, 141.4, 141.3, 129.0, 128.1, 128.0, 50.3, 21.7. Elemental analysis calculated (%): C 50.17, H 3.79, N 5.85, S 40.19; found (%): C 50.54, H 3.31, N 5.65, S 40.50.

### 2.3. Preparation of three-armed polystyrene

The general preparative procedures of three-armed polystyrene are as follows: St (2 mL, 17.6 mmol) and TTA (21 mg, $29.3 \times 10^{-3}$ mmol) were added to one dry glass ampoule. After the reaction mixture was bubbled with argon for approximately 20 min to eliminate the oxygen, the ampoule was sealed under an argon atmosphere and placed in an oil bath at 115 °C. At timed intervals, the ampoule was immersed into ice water to stop polymerization, then opened and diluted with about 5 mL THF, and precipitated into about 250 mL methanol. The polymers obtained by filtration were then dried under vacuum at 50 °C for 24 h. The conversion of the monomer was determined by gravimetry.

### 2.4. Preparation of three-armed (PS-b-PNIPAAM)$_3$

Three-armed $PS_3$ synthesized via RAFT method was used as macro-RAFT agent to prepare three-armed amphiphilic block copolymer, $(PS\text{-}b\text{-}PNIPAAM)_3$, with NIPAAM as the second monomer by chain extension reaction. The reaction mixture containing NIPAAM (0.5 g, 4.4 mmol), THF (1 mL), macro-RAFT agent ($M_{n(GPC)} = 15{,}900$ g/mol, 0.175 g, 0.011 mmol) and AIBN (0.362 mg, 0.0022 mmol) in one ampoule was purged with argon for approximately 20 min to eliminate oxygen. The ampoule was then sealed and placed in an oil bath at 70 °C for a desired time. The other procedures were similar to those mentioned above.

### 2.5. Cleavage of three-armed PS$_3$ and (PS-b-PNIPAAM)$_3$

Three-armed $PS_3$ (1 g, $M_{n(GPC)} = 43{,}400$ g/mol, $M_w/M_n = 1.14$) and 2 mL of ethylamine were added into THF (8 mL) and the mixture was stirred with reflux under an argon atmosphere. After stirring for about 24 h, reducing agents, Zn (1 g) and acetic acid (2 mL) were added to the reaction mixture. Then the mixture was stirred with reflux for about another 24 h. The white solid was obtained after precipitation in a large amount of methanol, washed with deionized water to neutral and then dried under vacuum at 50 °C for 24 h. The cleavage of $(PS\text{-}b\text{-}PNIPAAM)_3$ was carried out with the similar procedures mentioned above.

### 2.6. Preparation of the micelle solutions

Three-armed amphiphilic block copolymer, (PS-*b*-PNIPAAM)$_3$ (5 mg), was first dissolved in dry DMF (1 mL) at room temperature to obtain a 5 mg/mL polymer solution. Then the polymer solution was added into 5 mL methanol at a rate of one drop every 10 s by a microsyringe under vigorous stirring. The micelle solution was used for the *Z*-average size analysis by high performance particle sizer (HPPS) and observation by TEM. The aqueous solutions of the three-armed amphiphilic block copolymers (PS-*b*-PNIPAAM)$_3$ used to test the LCST of amphiphilic block copolymers were prepared by the dialysis method from micelle solution which was in the mixed solvent of water and DMF (v:v = 5:1).

### 2.7. Characterization

$^1$H nuclear magnetic resonance (NMR) spectra were recorded on Inova 400-MHz nuclear magnetic resonance instrument with chloroform (CDCl$_3$) as the solvent and tetramethylsilane (TMS) as the internal standard. Ultraviolet visible (UV–vis) absorption spectra of the polymers in THF solutions were performed on a Shimadzu (Kyoto, Japan) UV-240 recording spectrophotometer at ambient temperature. The fluorescence emission spectra of the polymers were obtained on an Ediburger FLS920 fluorescence spectrophotometer at room temperature. Optical transmittance of aqueous solutions of star amphiphilic block copolymer at various temperatures was measured at 370 nm with Shimadzu UV-3150 spectrophotometer with a circular water jacket, and the heating rate was 0.1–0.3 °C/min. The *Z*-average size and the polydispersity index (PDI) of the self-assembled micelles of three-armed (PS-*b*-PNIPAAM)$_3$ copolymers were measured on a Malvern HPP 5001 high performance particle sizer (HPPS) at 25 °C. Transmission electron microscopy (TEM) was recorded on a Tecnai G$^2$-20 TEM at a 200 kV accelerating voltage. The samples were prepared by mounting a drop of the micelle solution (0.05 mL) on a copper EM grid covered with a thin film of formvar. The elemental analyses for C, H, and N were tested by a LECO-CHNS microanalyzer. The purity of product was determined by HPLC (mode 515 high-performance liquid chromatograph, Waters) with a mixed solvent of methanol and water as eluent at the ratio of 80:20 (v/v) at 30 °C. The molecular weights and molecular weight distributions of the polymers were determined with a Waters 1515 gel permeation chromatography (GPC) equipped with refractive index detector, using HR1, HR3, and HR4 columns with molecular weight range 100–500,000 calibrated with PS standard samples. THF was used as the eluent at a flow rate of 1.0 mL min$^{-1}$ operated at 30 °C.

## 3. Results and discussion

### 3.1. RAFT polymerization of styrene

To prepare three-armed polystyrene, a novel trifunctional RAFT agent, tris(1-phenylethyl) 1,3,5-triazine-2,4,6-triyl trithiocarbonate (TTA) (Scheme 1) was synthesized and used to mediate styrene polymerization. The polymerization results are shown in Figs. 1 and 2, respectively. As shown in Fig. 1, the kinetic plot was approximately linear without induction period, which indicated that the radical concentration almost kept constant during the polymerization process. Meanwhile, as shown in Fig. 2, the molecular weights ($M_{n(GPC)}$s) of polystyrene measured by GPC increased linearly with the monomer conversion. However, the molecular weight was close to the theory value ($M_{n(th)}$) at relatively low monomer conversion (conversion (%) < 40%), and was always little smaller than that for theory at relatively high monomer conversion (conversion (%) > 40%). The theory value of molecular weight was calculated as following: $M_{n(th)} = ([M]_0/[TTA]_0) \times M_M \times \text{Conversion} + M_{TTA}$, where $[M]_0$ and $[TTA]_0$ are initial concentrations of St and TTA, respectively. $M_M$ and $M_{TTA}$ are the molecular weights of St and TTA, respectively. Due to the lower hydrodynamic volumes of star-branched polymers relative to linear analogues with same molecular weight, the $M_{n(GPC)}$s from GPC were usually underestimated with the linear polystyrene standards, which could result in the lower molecular weight obtained by GPC than the theoretical one. We did the similar experiments and characterization again, the results obtained were analogical. The effect of hydrodynamic volumes on the molecular weight may be unconspicuous at relatively low monomer conversions and becomes apparent at relatively high monomer conversions. Vana and Boschmann [34] also reported the similar results when they synthesized the six-arm star polymers of methyl acrylate (MA), butyl acrylate (BA), and dodecyl acrylate (DA) via RAFT method. They found that such deviation, however, can only be observed at above 50% of monomer conversions. Furthermore, as presented in Fig. 2, the molecular weight distribution was also relatively narrow ($M_w/M_n \le 1.23$), and there are no apparent relationships of $M_w/M_n$ with monomer conversion. Fig. 3 shows the gel permeation chromatography (GPC) trace of polystyrene at different polymerization

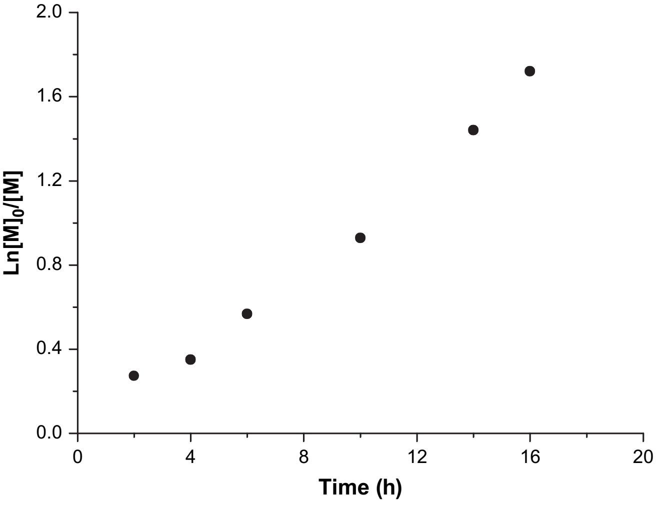


**Fig. 1.** Kinetic plot of the RAFT polymerization of styrene in bulk with thermal initiation. Conditions: $[St]_0/[TTA]_0 = 600:1$, 115 °C.

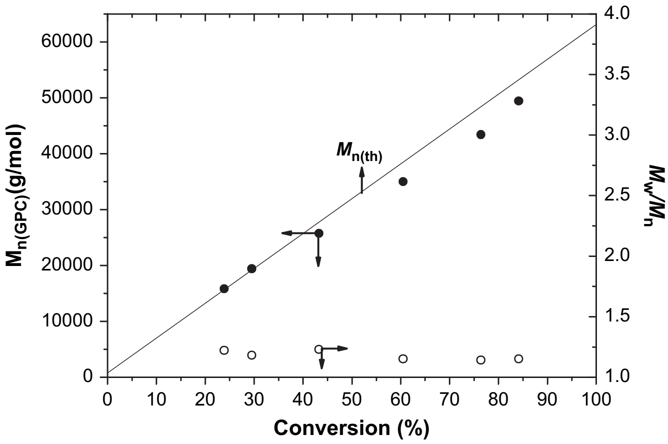


**Fig. 2.** The dependence of the molecular weights and molecular weight distributions on the monomer conversions for the RAFT polymerization of styrene. Polymerization conditions are the same as in Fig. 1.

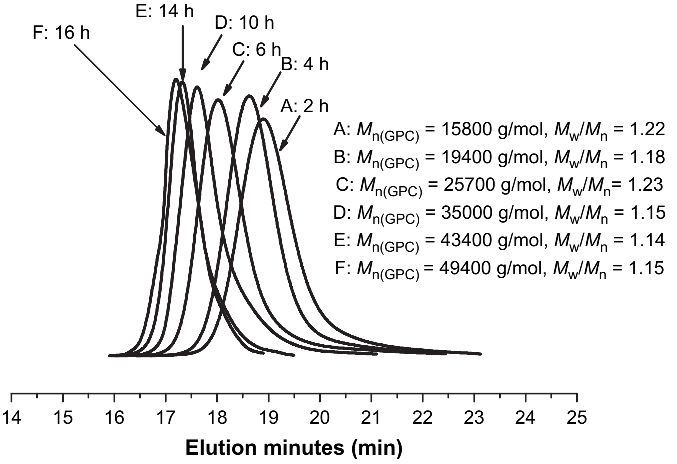


**Fig. 3.** GPC trace of $PS_3$ prepared by RAFT polymerization with TTA as the RAFT agent.

time. It can be seen from Fig. 3 that the GPC curves exhibited a decrease in retention time (higher molecular mass) with the polymerization time. All the results above demonstrated that the polymerization of styrene mediated by TTA was well controlled and TTA was an effective RAFT agent.

### 3.2. *Aminolysis of star polystyrene and star amphiphilic block copolymer*

As well known, the thiocarbonylthio group can be easily broken by aminolysis method [35–37] In order to confirm the arm number of PS obtained, we carried out the aminolysis experiment in the presence of ethylamine and the results are presented in Fig. 4. From Fig. 4, we can see that the molecular weight of the PS changed from 43,400 g/mol (before aminolysis) to 16,400 g/mol (after aminolysis), molecular weight distributions of the PS changed from 1.14 (before aminolysis) to 1.39 (after aminolysis). The product of molecular weight of linear polymer and the number of arms (three) of star polymer was in good agreement with the predicted molecular weight ($M_{n(th)}$) of star polymers ($M_{n(th)} = 48,400$ g/mol). The degree of aminolysis was also monitored by ultraviolet absorption and fluorescence spectra as shown in Figs. 5 and 6. From Fig. 5, we can see that the characteristic absorption intensity of trithiocarbonates at about 310 nm decreased with the aminolysis time, and disappeared after 48 h. Furthermore, the fluorescence emission at around 380 nm, 425 nm and 450 nm also disappeared after 48 h as presented in Fig. 6. These data above demonstrated that the three-armed PS was successfully prepared via RAFT polymerization of styrene. Furthermore, we also did the aminolysis experiment of $(PS\text{-}b\text{-}PNIPAAM)_3$ and measured the molecular weights of cleaved $(PS\text{-}b\text{-}PNIPAAM)_3$. The result is shown in Fig. 4. However, the results showed that the molecular weight of linear polymer PS-*b*-PNIPAAM ($M_{n(GPC)} = 9800$ g/mol, $M_w/M_n = 1.24$) was not the 1/3 molecular weight of $(PS\text{-}b\text{-}PNIPAAM)_3$ ($M_{n(GPC)} = 36,800$ g/mol, $M_w/M_n = 1.19$), that may be ascribed to the PS standard samples used.

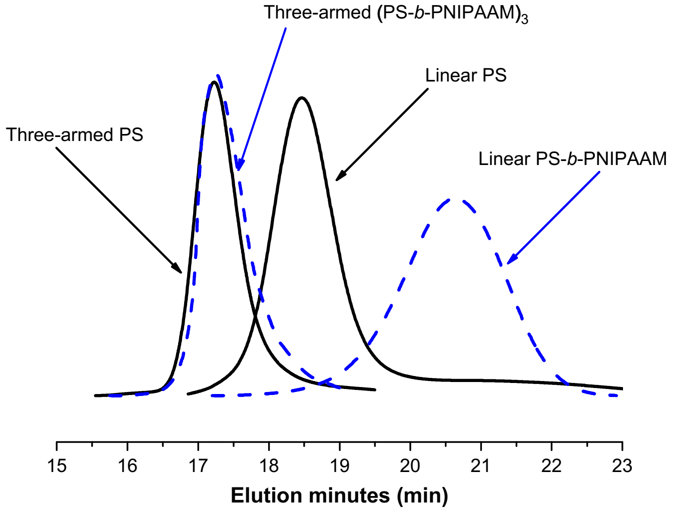


**Fig. 4.** GPC traces of PS and amphiphilic block copolymer PS-*b*-PNIPAAM before and after aminolysis. Three-armed $PS_3$: $M_{n(GPC)} = 43,400$ g/mol, $M_w/M_n = 1.14$; linear PS: $M_{n(GPC)} = 16,400$ g/mol, $M_w/M_n = 1.39$; three-armed $(PS\text{-}b\text{-}PNIPAAM)_3$ ($M_{n(GPC)} = 36,800$ g/mol, $M_w/M_n = 1.19$); linear PS-*b*-PNIPAAM: $M_{n(GPC)} = 9800$ g/mol, $M_w/M_n = 1.24$.

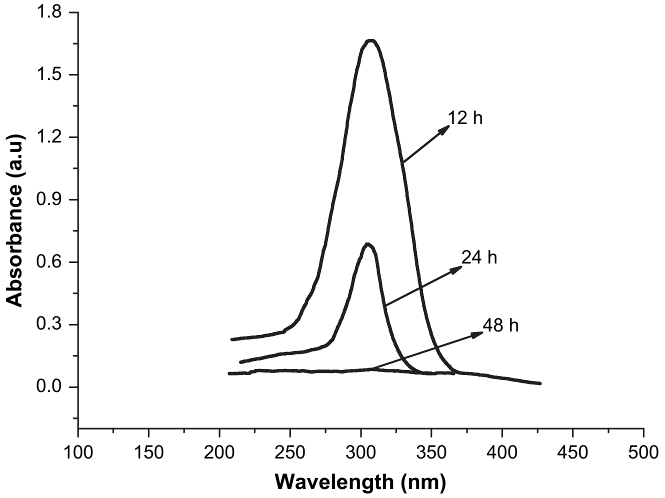


**Fig. 5.** Ultraviolet absorption spectra of PS at different aminolysis time. The concentration of polymer solution was $5.0 \times 10^{-5}$ M in THF.

### 3.3. *Preparation of three-armed amphiphilic block copolymer*

The three-armed amphiphilic copolymer, $(PS\text{-}b\text{-}NIPAAM)_3$, was prepared using $PS_3$ obtained as macro-RAFT agent and

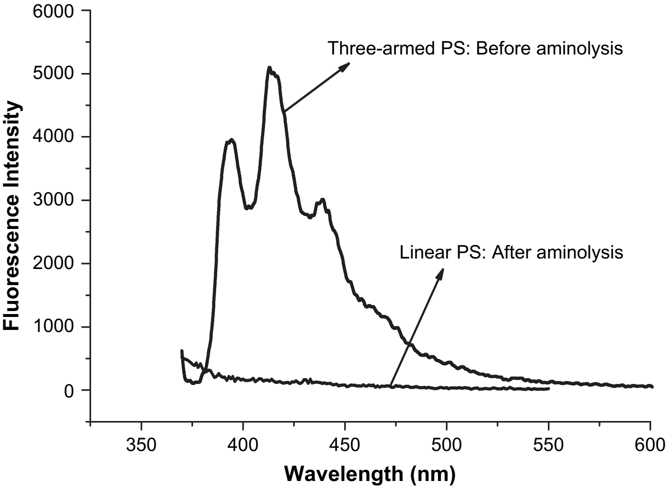


**Fig. 6.** Fluorescence spectra of three-armed $PS_3$ ($M_{n(GPC)} = 43,400$ g/mol, $M_w/M_n = 1.14$) and linear PS ($M_{n(GPC)} = 16,400$ g/mol, $M_w/M_n = 1.39$) in DMF at room temperature. Concentrations of polymer solutions were all $5.0 \times 10^{-5}$ M, $\lambda_{ex} = 370$ nm.

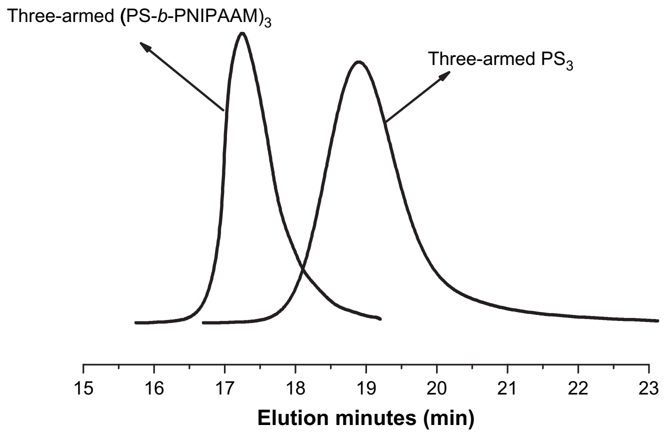


**Fig. 7.** GPC curves of three-armed polymers (A) macro-RAFT agent, $PS_3$ ($M_{n(GPC)} = 15{,}800$ g/mol, $M_w/M_n = 1.22$); (B) polymer obtained after chain extension using $PS_3$ as macro-RAFT agent $(PS\text{-}b\text{-}PNIPAAM)_3$, ($M_{n(GPC)} = 36{,}800$ g/mol, $M_w/M_n = 1.19$).

**Table 1**
Characterizations of micelle solutions of three-armed amphiphilic $(PS\text{-}b\text{-}PNIPAAM)_3$ copolymers with different molecular weights in the mixed solvents of methanol and DMF by HPPS

| Block polymer | $S/D$[a] | PS $M_{n(GPC)}$ | PNIPAAM $M_{n(NMR)}$ | $M_w/M_n$ | $Z$-size[b] (nm) | PDI[b] | PS[c] (mol%) |
|---|---|---|---|---|---|---|---|
| A | 186/233 | 19,400 | 26,300 | 1.18 | 23 | 0.07 | 44.39 |
| B | 186/372 | 19,400 | 42,000 | 1.16 | 33 | 0.08 | 33.33 |
| C | 240/354 | 25,700 | 40,000 | 1.18 | 47 | 0.12 | 40.40 |
| D | 240/320 | 25,700 | 36,100 | 1.19 | 40 | 0.11 | 42.85 |

[a] $S$ means the degree of polymerization of PS, and $D$ means the degree of polymerization of PNIPAAM.

[b] The $Z$-average size and the polydispersity index of the micelles in the mixed solvents of methanol and DMF.

[c] PS (mol%) means the mol content of PS.($S/(S+D)$).

*N*-isopropylacrylamide as the second monomer via chain extension experiments. The GPC curves presented in Fig. 7 show a decrease in retention time for the chain-extended polymer, which indicated that NIPAAM was successfully inserted into the polymer chain. The amphiphilic copolymer prepared was also characterized by $^1$H NMR spectra as shown in Fig. 8. In Fig. 8(B), the signals at 4.64–4.68 ppm (a) are assigned to methyne proton in St unit close to terminal sulfur. Furthermore, the relative compositions of the PS to PNIPAAM segments in the three-armed block amphiphilic copolymers were derived from $^1$H NMR spectra, that is, the integration of the aromatic proton in St units (a in Fig. 8(A), $\delta = 6.36$–$7.37$ ppm) to the methyne proton in isopropyl group of NIPAAM unit (b in (A), $\delta = 4.04$ ppm). The signals at $\delta = 1.10$–$2.14$ ppm ascribed to main chain methine proton and methylene proton of PS and PNIPAAM. From Figs. 7 and 8, the molecular weight of $PS_3$ measured by GPC ($M_{n(GPC)} = 15{,}800$ g/mol) was close to those measured by NMR ($M_{n(NMR)} = 15{,}200$ g/mol), which were both consistent with the theoretical value ($M_{n(th)} = 15{,}600$ g/mol). Table 1 lists the observed molecular weights on the basis of $^1$H NMR ($M_{n(NMR)}$) and GPC ($M_{n(GPC)}$). All results above demonstrated that the three-armed copolymers $(PS\text{-}b\text{-}PNIPAAM)_3$ with different ratios of PS and PNIPAAM were successfully prepared via chain extension experiment.

### *3.4. Optical transmittance*

PNIPAAM is one of the most studied thermosensitive polymer because of its reversible thermal phase separation above a critical temperature due to lower critical solution temperature (LCST) at about 32 °C. The LCST of PNIPAAM can be changed by copolymerization with hydrophobic or hydrophilic monomer. Copolymerization of NIPAAM with a hydrophilic monomer can increase the LCST of PNIPAAM [38–41], while copolymerization with a hydrophobic monomer tends to have the opposite effect [42,43]. In this work, we also studied the LCST of aqueous solutions of the obtained three-armed amphiphilic block copolymers $(PS\text{-}b\text{-}PNIPAAM)_3$ prepared by the dialysis method as presented in Fig. 9. From Fig. 9, we can see that the LCST of $(PS\text{-}b\text{-}PNIPAAM)_3$ shifted to relatively lower temperature (LCST < 32 °C) when styrene, one hydrophobic

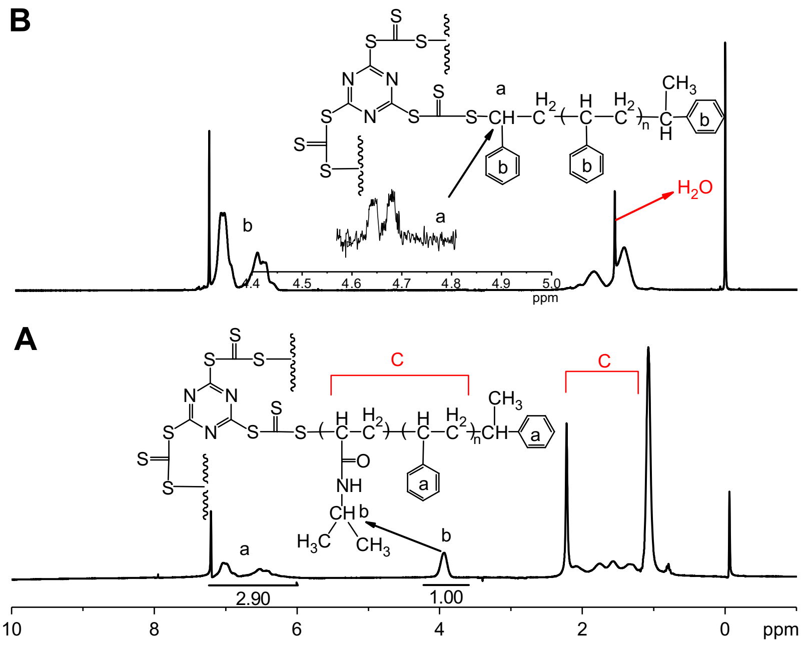


**Fig. 8.** $^1$H NMR spectra of three-armed $PS_3$ and $(PS\text{-}b\text{-}PNIPAAM)_3$ (PS: $M_{n(GPC)} = 15{,}800$ g/mol, $M_w/M_n = 1.22$. $(PS\text{-}b\text{-}PNIPAAM)_3$: $M_{n(NMR)} = 45{,}400$ g/mol, $M_w/M_n = 1.19$).

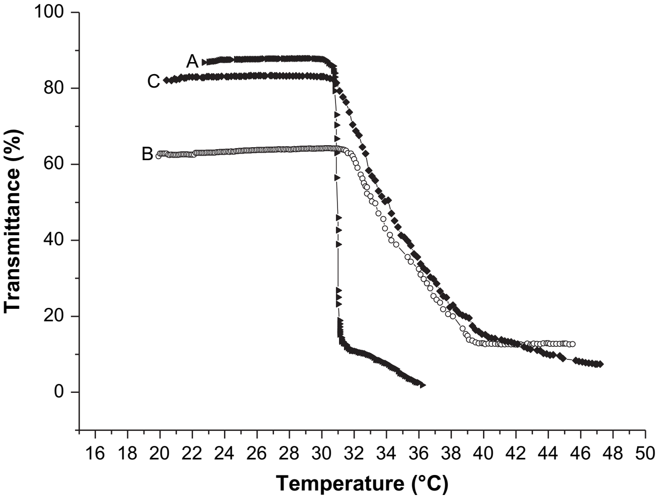


**Fig. 9.** Transmittance *vs* temperature plots for (PS-*b*-PNIPAAM)$_3$ aqueous solution with different molecular weights, [copolymer] = 1 mg/mL ((A) $M_{n(NMR)} = 45{,}700$ g/mol, $M_w/M_n = 1.39$; (B) $M_{n(NMR)} = 61{,}400$ g/mol, $M_w/M_n = 1.16$; (C) $M_{n(NMR)} = 65{,}700$ g/mol, $M_w/M_n = 1.18$).

monomer, was used as copolymerized monomer. Furthermore, the results also demonstrated that the LCST of amphiphilic block copolymers apparently decreased in the order of B > C > A, when the relative mol content of PS in copolymer (in Table 1) increased in the order of B < C < A, which was similar to the results reported by Rimmer group [33,44].

### 3.5. Self-assembly behaviors of three-armed amphiphilic block copolymer

As well known, the aggregated morphology of the self-assembly formed by the amphiphilic copolymers is affected by many factors, such as the chemical structure of copolymers, the block sequence, the relative lengths of the hydrophobic and hydrophilic blocks, and the nature of solvents [45,46]. In order to investigate the effect of the relative lengths of the hydrophobic and hydrophilic blocks on the morphologies of micelles, we observed the morphologies of micelles with different ratios of hydrophobic and hydrophilic blocks in the mixed solvent of methanol and DMF (v:v = 5:1) by TEM at room temperature. In all cases, the spherical micelles composed of a hydrophobic core (PS) and a hydrophilic shell (PNIPAAM) were prepared as shown in Fig. 10. In the mixed solvent of methanol and DMF, the hydrophobic segment PS was prone to pack together and reduce the touch area with the methanol, and the hydrophilic segment PNIPAAM tried to spread well as soon as possible in the methanol. So the self-assembled spherical micelles probably contained a hydrophobic PS as core and a hydrophilic PNIPAAM as corona. Interestingly, the size of micelle became larger with the increase of the relative lengths of the hydrophilic blocks (PNIPAAM). The *Z*-average size changed from 23 nm to 33 nm and from 40 nm to 47 nm, when the PS molar contents decreased from

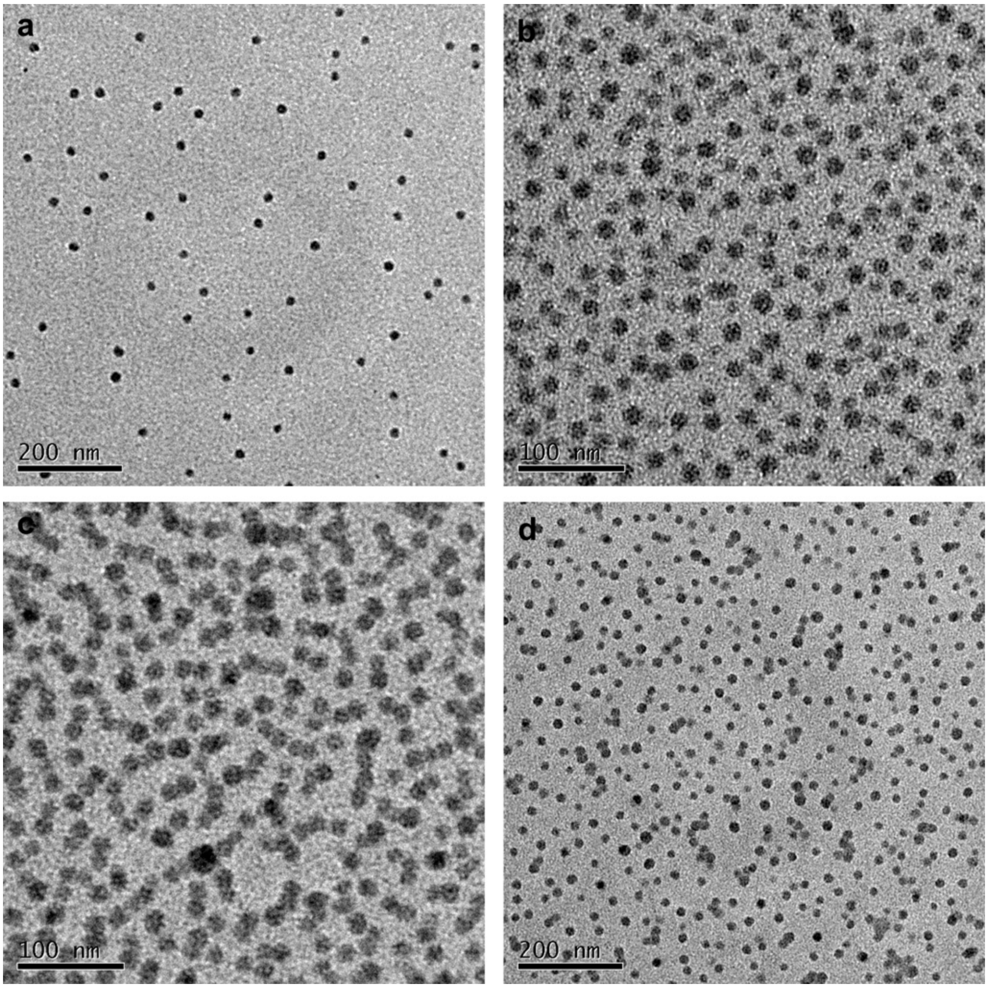


**Fig. 10.** TEM images of three-armed (PS-*b*-PNIPAAM)$_3$ formed on copper netting by casting the micelle solution at room temperature, with different molecular weights.

44.39% to 33.33% and from 42.85% to 40.40%, respectively, as shown in Table 1. Moreover, the polydispersity index (PDI) of the micelles increased with the increase of mol content of PNIPAAM chains. The results matched the results observed by TEM well.

## 4. Conclusions

The three-armed PS and amphiphilic copolymers (PS-*b*-PNIPAAM)$_3$ were successfully prepared by the core-first technique via RAFT polymerization with a novel trifunctional RAFT agent (TTA). The number of arms of star PS obtained via RAFT polymerization of St was proved by aminolysis method and further confirmed by UV–vis absorption and fluorescence spectra. The *Z*-average size of the nanosized micelles self-assembled from the amphiphilic block copolymers, (PS-*b*-PNIPAAM)$_3$, increased with the increase of the mol content of PNIPAAM of the copolymer, which was approved by HPPS and TEM. In addition, the LCST of the aqueous solution of the amphiphilic block copolymer also decreased with the increase of the relative mol content of PS in copolymer, and was also lower than that of NIPAAM homopolymer.

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