

SYNTHESIS AND CHARACTERIZATION OF FOUR-ARMED BLOCK POLY(STYRENE-*b-p*-NITROPHENYL METHACRYLATE) PREPARED BY THE ATRP METHOD*

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Abstract A novel tetrafunctional initiator, $C[CH_2O(CH_2)_3OOCCH(Br)CH_3]_4$ (1), was synthesized through the reaction of tetraol with α -bromopropionyl chloride, and then was used as initiator of atom transfer radical polymerization (ATRP) in the preparation of 4-armed polystyrene (PSt) with narrow polydispersity. The structure, molecular weight and molecular weight distribution (MWD) of each arm were studied by ^1H -NMR and GPC data of hydrolyzed products of the 4-armed PSt. The ATRP of St using $1/CuBr/bpy$ as initiator system is of “living” character based on the following evidence: narrow MWD, constant concentration of chain radical during the polymerization, control of molecular weight by the molar ratio of monomer consumed to 1. The 4-armed poly(St-*b-p*-nitrophenyl methacrylate) [poly(St-*b*-NPMA)] was prepared by the ATRP of NPMA using 4-armed PSt with terminal bromine as the initiator, and characterized by FT-IR, ^1H -NMR spectra and GPC curves. The micelles with PSt as core, and PNPMA as shell were formed by dropping DMSO into a solution of 4-armed poly(St-*b*-NPMA) in DMF, as proved by laser light scatter (LLS) method.

Keywords Tetrafunctional initiator, Atom transfer radical polymerization, 4-Armed polystyrene, 4-Armed poly(styrene-*b-p*-nitrophenyl methacrylate), Unimolecular micelles

INTRODUCTION

Unimolecular micelles have great potential applications in controlling the release of drugs^[1], because of their concentration independence. The micelles formed by a linear amphiphilic diblock polymer are concentration dependent. The thermodynamic equilibrium between surfactants and micelles may cause serious toxicity problems due to potentially large fluctuation in drug concentrations^[2]. Most of the unimolecular micelles studied were prepared from dendritic polymers^[1, 3–6]. Due to the difficulty of preparing dendritic polymers, we explore the possibility that star block copolymers form unimolecular micelles in water or organic solvents depending on the properties of two polymer segments. Generally, the synthesis of well-defined star polymers is difficult and there are two methods to obtain them. One is by linking a given number of linear chains to a central core (“arm-first” method)^[7]; the second is by growing branches from an active core (“core-first” method)^[8, 9]. For the core-first method, the only examples that have been proven to afford well-defined star polymers are those developed for use in carbon-cationic polymerization^[8, 9]. In contrast, only a very few papers on use of multi-anionic initiators have been published^[10]; this might be due to the poor solubility in the latter cases. The recent development of the controlled/“living” radical polymerization has opened up a new and potentially wide road to prepare well-defined macromolecules.

For example, Matyjaszewski has coined the term of atom transfer radical polymerization (ATRP) for his system constituted of alkyl halide, transitional metal halide and bipyridyl (bpy)^[11–13]. The ATRP has been used in macromolecular engineering to synthesize star-shape polymers, e.g. the preparation of hexa-armed stars using

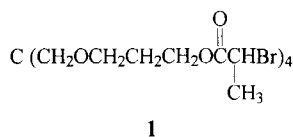
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hexakis(bromomethyl)benzene as the initiator^[14], and synthesis of a tri-armed poly(methyl methacrylate) (PMMA)^[15]. But the characterization of the star polymers has not been described in detail. Yves Gnanou reported the ATRP of styrene (St) by using octafunctional initiator. The well-defined stars could be prepared by maintaining the monomer conversion below 15%–20%, beyond which, a significant intermolecular termination occurs^[16].

In designing a research program on the synthesis, characterizations and applications of star polyether or polyester polyols, several well-defined multi-functional initiators were prepared, and the well-defined star polymers were obtained by living cationic polymerization^[17]. By the reaction of tetraol compound with α -bromopropionyl chloride, compound **1** was easily synthesized. With a 4-armed block copolymer having a hydrophobic polymer, PSt, as the core, and hydrophilic polymer as shell, the unimolecular micelles should be formed in aqueous solution. Thus ATRP of St was carried out in the presence of compound **1**/CuBr/bpy, then 4-armed star block copolymer was synthesized by the ATRP of *p*-nitrophenyl methacrylate (NPMA) with 4-PSt-Br/CuBr/bpy as the initiator system. PNPMA can dissolve in dimethyl sulfoxide (DMSO), but PSt does not dissolve in this solvent; thus, the micelles could be observed in DMSO. In addition, PNPMA can undergo hydrolysis or other reactions easily, a series of functional polymers in the shell can be formed. Here we report the synthesis and characterization of 4-armed star poly(St-*b*-NPMA), and the formation of unimolecular micelles in DMF-DMSO.



EXPERIMENTAL

Materials

St (Shanghai Chemical Reagent Plant) was distilled over CaH₂ before use. Bpy (Shanghai Chemical Reagent No. 1 Plant) was used as received. CuBr (98%, Shanghai Chemical Reagent Plant) was purified in acetic acid, washed with methanol and dried under vacuum (100 °C/27 Pa) to afford a white powder. The compound C[CH₂O(CH₂)₃-OH]₄ was prepared by the reaction of acrylonitrile with pentaerythritol. It was then hydrolyzed in concentrated HCl, and reduced by LiAlH₄^[18]. α -Bromopropionyl chloride was prepared by the reaction of α -bromopropionic acid with sulfinyl chloride. NPMA was synthesized^[19, 20] and purified by recrystallization from petroleum ether, and the melting point of which is 94–95 °C. All other reagents were purified by standard procedures.

Synthesis of **1**

Into a 50 mL round-bottom three-necked flask equipped with a magnetic stirrer, 1.5 g (4.08 mmol) C[CH₂O-(CH₂)₃-OH]₄ and 10 mL dry CH₂Cl₂ were added. After the mixture was cooled to 0 °C, 19 g (0.11 mol) α -bromopropionyl chloride in 10 mL dry CH₂Cl₂ was added dropwise within 0.5 h. Then the reaction mixture was stirred at room temperature for 24 h, the HCl evolved was removed by water pump. The volatile compounds were removed at 110 °C/27 Pa. The residue was a colorless viscous liquid in quantitative yield.

¹H-NMR(CDCl₃, δ): 1.83 (d, 12H, 4-CH₃), 1.91 (m, 8H, 4-CH₂-CH₂-CH₂-), 3.36 (s, 8H, 4-CH₂-O-), 3.47 (t, 8H, 4-O-CH₂-), 4.26 (t, 8H, 4-CH₂-OCO-), 4.36 (q, 4H, 4-(Br)CH-).

ATRP of St

The procedure of ATRP was similar to that reported in our previous work^[21]. Into a series of 50 mL dry glass tubes with magnetic stirrer, CuBr (0.0717 g), bpy (0.2343 g), St (10.4 g, 0.1 mol/L), and a solution of initiator (0.113 g) in 10 mL chlorobenzene were added. The tubes were closed with three-way stopcocks. After three freeze-pump-thaw cycles were performed, the tubes were sealed under vacuum, and then placed in an oil bath thermostated at 110 °C. At a prescribed time interval, one tube in succession was taken out, and cooled in ice water to stop the polymerization. Afterwards, the tube was opened. Several drops of the polymerization solution

were put into a NMR measuring tube with CDCl_3 as the solvent, then the NMR spectrum was measured. Based on the change of the integral value of the peak of vinyl hydrogen, the conversion was calculated. The rest of the contents was passed through a short neutral alumina column to remove the metal salts, the polymer obtained was precipitated from an excess of methanol, filtered, and dried at 40°C in a vacuum oven for 24 h.

Preparation of Poly(St-*b-p*-NPMA)

In a 30 mL glass tube, star PSt with terminal bromine group (1.0 g, 0.025 mmol), CuBr (0.0166 g), bpy (0.056 g) and NPMA (3.5 g, 0.017 mol) were added. After three freeze-pump-thaw cycles, the tubes were sealed under vacuum, and then placed in a 110°C oil bath for 24 h. The polymerization was stopped by cooling the tube in ice-water and the tube was opened. A procedure similar to that of preparing star PSt was carried out. About 20 mg of the reaction mixture was dissolved in *d*-DMSO to measure the ^1H -NMR spectrum. Based on the change of integral value of the peak of vinyl protons, the conversion was calculated. The rest of the contents was dissolved in THF, and then the polymerization solution was passed through a short neutral alumina column. The polymer was precipitated from an excess of methanol at -10°C , filtered and dried at 40°C in a vacuum oven for 24 h. The M_n and M_w/M_n were measured by GPC and found to be 0.9×10^5 and 1.28, respectively. The number average molecular weight from NMR data M_n (NMR) was 1.6×10^5 .

Hydrolysis of the Star PSt

The star polymer (0.5 g) was added to 40 mL THF in a 150 mL round-bottomed flask equipped with a refluxing condenser, then 10 mL aqueous KOH solution (40% *W/V*) and 10 mL triethylamine were added. The reaction was carried out at 80°C for 72 h while stirring, then the volatile compounds were removed under reduced pressure. Concentrated HCl solution (30 mL, 37%) was added, the mixture was stirred at room temperature for 1 h, then distilled under vacuum. The residue was dissolved in 100 mL CH_2Cl_2 , washed with water until $\text{pH} = 7$. The product was finally precipitated in methanol at -10°C , the hydrolyzed product was collected by filtering, and dried in vacuum oven.

Characterizations

NMR spectra were measured on a Bruker DMX500 NMR spectrometer with CDCl_3 or *d*-DMSO as solvent, tetramethylsilane as internal reference. M_n , M_w and M_w/M_n of the star PSt and its hydrolyzed products were obtained by a Waters 150C GPC instrument equipped with microstyragel columns (50 nm, 100 nm and 10^4 nm) at 25°C ; THF was used as solvent at a flow rate of 1.0 mL/min. Monodisperse polystyrene standards were used in calibration. The measurements of IR spectra were performed on a Bruker vector-22 spectrometer. Polymer particles were characterized on a LLS detector (ALV/SP-125) equipped with an ALV-5000 digital time correlator and solid-state laser (ADLAS DPY 425II, output power ca. 400 mW at $\lambda = 253$ nm).

RESULTS AND DISCUSSION

ATRP of St

The compound **1** was prepared by the reaction of $\text{C}[\text{CH}_2\text{O}(\text{CH}_2)_3\text{OH}]_4$ with α -bromopropionyl chloride. Its structure was confirmed by its proton NMR spectrum shown in Fig. 1. From the fact that the integral value of the peak at $\delta = 3.36$ is twice that at $\delta = 4.36$, it could be concluded that almost complete esterification of tetraol occurred (see Fig. 1).

The star PSt was synthesized by using **1** as initiator of ATRP for synthesizing star PSt. The experimental conditions and results are listed in Table 1. Assuming that each star PSt macromolecule contains one molecule of **1**, the theoretical number molecular weight, $M_n(\text{theor.})$ was estimated from the conversion (conv.) and feed ratio (see Eq. 1).

$$M_n(\text{theor.}) = \text{Conv.} \times (M_{\text{st}}/M_{\text{B}}) \times 104 + 907.6 \quad (1)$$

where M_{st} and M_{B} are respectively the initial moles of St and compound **1**; 104 and 907.6 are the molecular weight of St and **1** respectively. The structures of the polymers were analyzed by ^1H -NMR spectroscopy (see Fig. 1b). The peak at $\delta = 4.36$ corresponding to methine proton next to bromine and carbonyl group in the

initiator has completely disappeared in Fig. 1(b), and the peak of methyl protons in the initiator at $\delta = 1.83$ in Fig. 1(a) is shifted to a new position at $\delta = 0.84$ in Fig. 1(b). These facts reveal that all bromines of each initiator molecule took part in the initiation reaction and tetra-armed PSt was formed. The signals at $\delta = 3.22$ and 3.85 in Fig. 1(b) correspond two methylene groups: one next to ether oxygen and another next to ester oxygen in initiator respectively. A signal at $\delta = 4.42$ is indicative of methine proton adjacent to bromine at the end of the PSt segment. Based on the integral values of the peak at $\delta = 3.22$ ($I_{3.2}$) and the peaks at $\delta = 6.57$ and 7.09 ($I_{7.0}$) representing the aromatic protons in PSt unit, the $M_n(\text{NMR})$ was calculated according to Eq. (2).

$$M_n(\text{NMR}) = (16I_{7.0}/5I_{3.2}) \times 104 + 907.6 \quad (2)$$

The results listed in Table 1 show that $M_n(\text{NMR})$ agrees well with $M_n(\text{theor.})$.

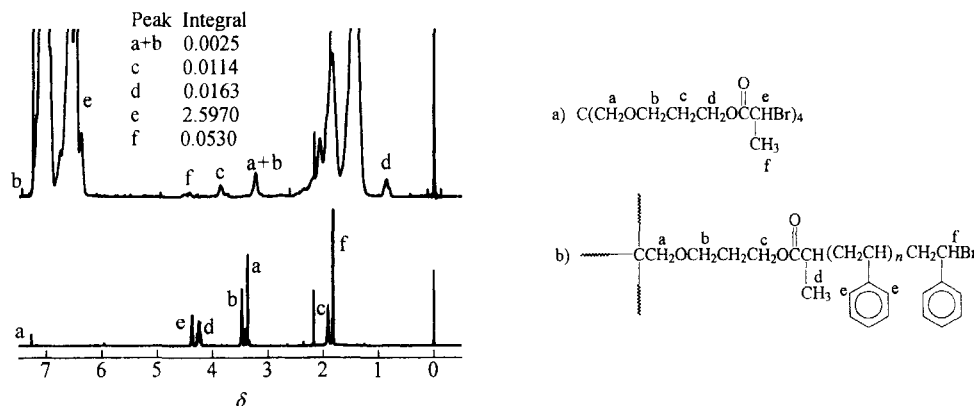


Fig. 1 ¹H-NMR spectra of tetrafunctional initiator (a) and four-armed polystyrene (b) in CDCl₃

Table 1. Conditions and results of ATRP of St using tetrabromide/CuBr/bpy as initiation system and hydrolysis of tetra-armed polystyrene^a

Polymer no.	Time (h)	Conv. (%)	$M_n (\times 10^3)$			M_w/M_n^e	N_B^f
			Theor. ^c	NMR ^d	GPC ^e		
1	3	13	11.3	10.7	6.77	1.31	
1-h ^b				2.57	2.73	1.21	3.6
2	9	30	24.9	24.6	12.9	1.22	
2-h ^b				6.07	6.14	1.18	3.9
3	15	43	35.4	41.1	20.8	1.21	
3-h ^b				9.37	9.48	1.17	4.2

^a Polymerization conditions: [St] = 100 mmol/L; 1/CuBr/bpy = 1:4:12 (molar ratio); [1] = 0.125 mmol/L; $T = 110^\circ\text{C}$

^b PSt was obtained by hydrolysis of the corresponding tetra-armed PSt.

^c $M_n(\text{theor.})$ was calculated according to Eq. (1).

^d $M_n(\text{NMR})$ was calculated based on proton NMR data.

^e Measured on Waters-150C GPC instrument

^f N_B (branch number) = $[M_n(\text{NMR}) - 907.6]/M_n(\text{GPC})$

Characterization of "Living" Polymerization

When **1** is used as the initiator, more than one radical in one molecule may exist at the same time, and the termination of two radicals to form cyclics might occur; thus it is necessary to study the "living" characters. As we know, we can use experimental evidence to evaluate a living polymerization^[22]. Such evidence comes from first-order kinetics, linear evolution of molecular weight with conversion, and narrow polydispersity index. The conversions of St at a prescribed time interval were measured; plotting $\ln[M]_0/[M]_t$ against polymerization time afforded a straight line as shown in Fig. 2(a). It infers that the concentration of chain radical kept constant during the polymerization.

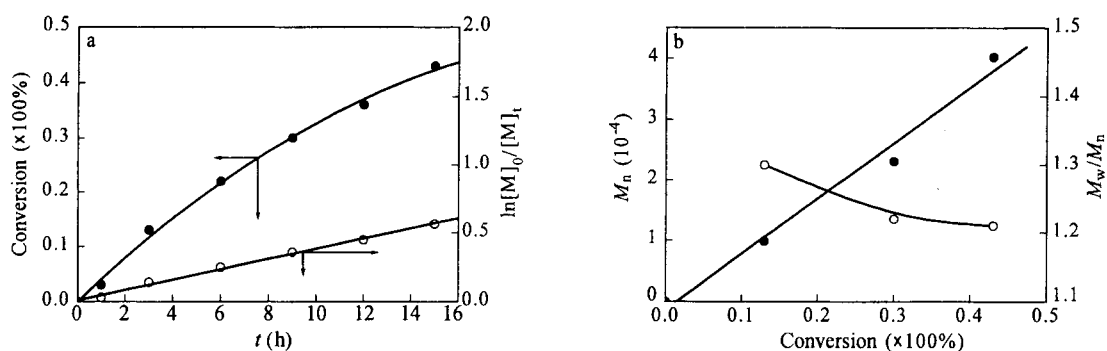


Fig. 2 Dependence of $\ln[M]_0/[M]$ and conversion on polymerization time (a) and M_n (NMR), M_w/M_n via conversion (b) for the ATRP of St

Conditions: $[St]_0 = 4.5 \text{ mol/L}$; $1/\text{CuBr}/\text{bpy} = 1:4:12$ (molar ratio); $[1] = 0.0056 \text{ mol/L}$; Solvent: chlorobenzene

The plot of M_n versus conversion is given in Fig. 2(b) and a linear molecular weight-conversion profile was observed. Figure 3 shows GPC curves of the star polymers obtained by the ATRP of St at various reaction times. ATRP of St shows the same phenomena as generally observed in ATRP, such as the increase of conversion, the narrowing of MWD. All the facts verify that the ATRP of St using compound **1**/CuBr/bpy as initiation system is of “living” nature.

It was reported that when polybromide was used as the initiator of ATRP, and the conversion was kept at higher than 20%, intermolecular termination easily occurred. The GPC curve would show a shoulder at high molecular weight^[16]. Only a single symmetric curve in Fig. 3 proves that intermolecular termination might be neglected. Probably, the solution polymerization reduced the concentration of propagating radicals, resulting in neglectable termination.

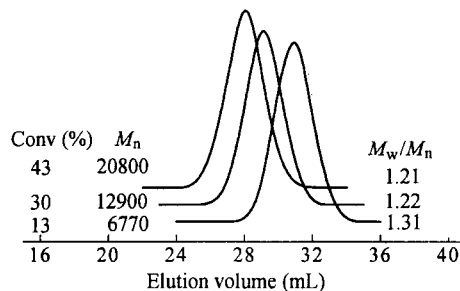


Fig. 3 GPC curves of the star polymer obtained by the ATRP of styrene at various times
Conditions: $[St]_0 = 4.5 \text{ mol/L}$; $1/\text{CuBr}/\text{bpy} = 1:4:12$ (molar ratio); $[1] = 0.0056 \text{ mol/L}$;
Solvent: chlorobenzene

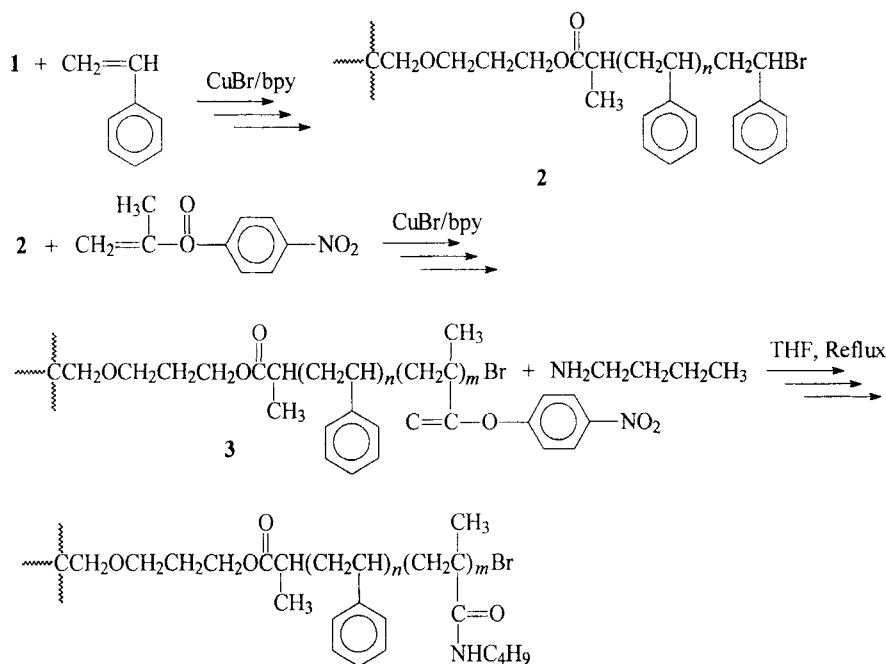
In order to study whether each initiator site in the same molecule of **1** can initiate monomer almost at the same time, and whether each site has the same possibility to propagate, the hydrolysis of the star PSt was carried out in an aqueous solution of KOH, then ^1H -NMR spectra and GPC curves of the hydrolyzed product were measured. The M_n of the hydrolyzed PSt is almost one fourth of the corresponding star PSt, and M_w/M_n values varying from 1.17 to 1.21 (see Table 1). From these facts, it can be concluded that the hydrolyzed PSt belongs to one arm of the star PSt, and each initiating site in one initiator molecule has almost the same possibility to participate in initiation and propagation reactions.

Synthesis of Star-Block Copolymer

In order to prepare a well-defined block copolymer, each macroinitiator, $\text{S}(\text{PSt-Br})_4$ should have 4 terminal bromines. Based on the ratio (1:4) of the integral value of the peak at $\delta = 4.42$ to that at 3.22 in the ^1H -NMR

spectrum of the star PSt-Br, we can find that almost no bromine was lost during the polymerization. Therefore, ATRP of NPMA was carried out at 110°C using star PSt-Br as the initiator, CuBr and bpy as the catalyst and the ligand, respectively. It was reported in our previous paper^[20] that NPMA could not undergo homopolymerization with ATRP initiation, but the block copolymerization of NPMA using PSt-Br/CuBr/bpy as initiation system was well-controlled. Therefore, it might be possible to produce the star block copolymer, S(PSt-*b*-PNPMA)₄ by the ATRP process.

A typical IR spectrum of poly(St-*b*-NPMA) is shown in Fig. 4, the peaks at 1755.3, 1525 and 1349.3 cm⁻¹ are attributed to the carbonyl group of ester and NO₂ group, respectively. The peaks at 746.2 and 697.9 cm⁻¹ are characteristic bands of PSt. Thus the NPMA was initiated by macroinitiator (PSt-Br), and star block copolymer was formed. Because the S(PSt-*b*-PNPMA)₄ obtained could not dissolve in common deuterium solvents in our laboratory, the star block copolymer was treated with butylamine to afford a new star block copolymer 4 (see Scheme 1). The ¹H-NMR spectrum of 4 in CDCl₃ is shown in Fig. 5. By comparing this spectrum with the ¹H-NMR spectrum of star PSt shown in Fig. 1(b), it was found that besides the characteristic signals of PSt and polymethacrylate, the new peaks at δ = 0.91, 3.21 and 3.57 corresponding to methyl protons in butyl and propionyl group and methylene protons next to nitrogen of C₄H₉NH-, respectively, appeared in Fig. 5. A small peak at δ = 8.15 belongs to aromatic protons at the *ortho* position to the nitro group, indicating that the substitution reaction of *p*-nitrophenyl group of NPMA by butyl amine was not completed. GPC curves of 4-armed poly(St-*b*-NPMA) and its original 4-armed PSt are shown in Fig. 6. In comparison with the star PSt, the molecular weight of the star block copolymer is increased, and the *M_w*/*M_n* value increases from 1.21 to 1.28, probably due to the loss of a very small amount of bromine groups at the end of the polymer chain during the propagation.



Scheme 1

Formation and Characterization of Unimolecular System

PSt and PNPMA have different polarity, the former could be dissolved in dimethyl formamide (DMF), but is insoluble in dimethyl sulfoxide (DMSO) which is a good solvent of PNPMA. Therefore, as DMSO was added to the solution of the star-block polymer in DMF, PSt chains in the center of 4-armed poly(St-*b*-NPMA)₄

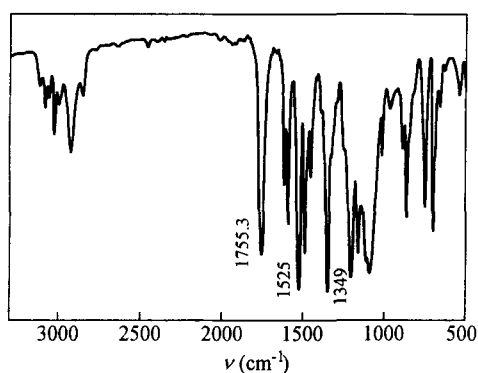


Fig. 4 The FT-IR spectrum of tetra-armed poly(St-*b*-NPMA)

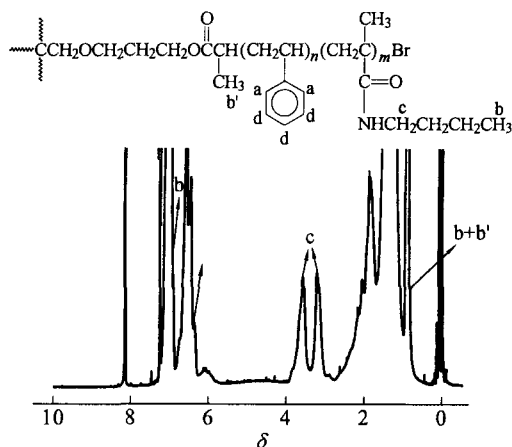


Fig. 5 ^1H -NMR spectra of four-armed poly(St-*b*-BAMA) in CDCl_3

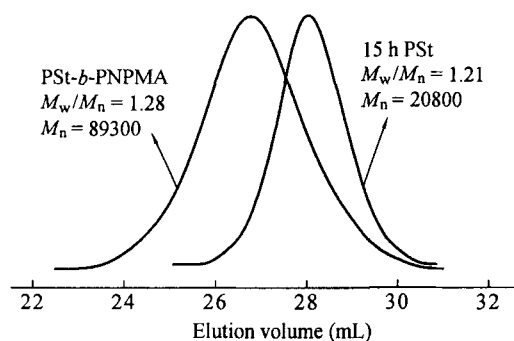


Fig. 6 GPC curves of star block copolymer and its initiator (PSt)

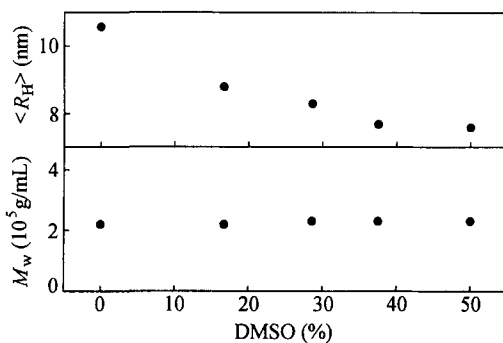


Fig. 7 Dependence of $\langle R_H \rangle$ and M_w of tetra-armed poly(St-*b*-NPMA) on DMSO content in DMF-DMSO mixture, at 25°C , $\theta = 60^\circ$

aggregated and contracted to form a core, while PNPMa chains which are soluble in the solvents formed a shell. Thus unimolecular micelles with PSt as core and PNPMA as shell were formed. In order to confirm this assumption, hydrodynamic radius (R_H) and M_w of S(St-*b*-NPMA) $_4$ were measured at different volume ratios of DMF to DMSO by a LLS instrument. The results obtained are shown in Fig. 7. The star-block copolymer in DMF has the largest R_H (see Fig. 7), because DMF is a good solvent for both PSt and PNPMA. As the amount of DMSO in the mixed solvents increases from 0% to 16.7%, R_H decreases slightly, which is a result of aggregation and contraction of PSt segments in the center of the star block copolymer. The change of R_H value is very small between 16.7%–50.0% of DMSO content (see Fig. 7), indicating that further big contraction of PSt segments does not occur. At the same time, M_w kept at almost the same value as the amount of DMSO increases, because the solubility of the solvents changed gradually and slightly, but all the change happened in one molecule, that is, the micelles are composed of one molecule of 4-armed poly(St-*b*-NPMA) $_4$. Based on the conversion of NPMA, and molar ratio of NPMA ($[\text{NPMA}]_0$) to 4-armed PSt-Br ($[\text{PSt-Br}]_0$), the $M_n(\text{theor.})$ could be calculated according to Eq. (3).

$$M_n(\text{theor.}) = \text{Conv.} \times ([\text{NPMA}]_0/[\text{PSt-Br}]_0) \times 207 + M_n(\text{PSt}) \quad (3)$$

where, $M_n(\text{PSt})$ is the number-average molecular weight of the 4-armed PSt on the basis of NMR data, 207 is the molecular weight of NPMA. The $M_w(\text{theor.})$ was calculated from the value of M_w/M_n , and is 2.1×10^5 g/mol, which is consistent with $M_w = 2.2 \times 10^5$ obtained from the LLS. It can be concluded that each micelle formed in DMF-DMSO consisted of only one macromolecule of 4-armed block copolymer, that is, unimolecular micelles were formed.

CONCLUSIONS

Tetra-armed macroinitiator PSt can be prepared by ATRP of St at lower conversion. The "living" ATRP of St is verified by the following evidence: first-order kinetics, a linear molecular weight-conversion profile and narrow molecular weight distribution ($M_w/M_n = 1.21$). No bromine at the end of polymer was lost during polymerization up to 45% of monomer conversion. The tetra-armed poly(St-*b*-NPMA) was prepared by ATRP of NPMA in bulk at 110°C using a PSt-Br/CuBr/bpy initiation system. Because PSt is soluble in DMF and insoluble in DMSO, the micelles with PSt as core and PNPMA as shell could be formed in the DMF-DMSO mixed solvents. DMSO content in DMSO-DMF does not affect the M_w , and good agreement between $M_w(\text{theor.})$ and M_w obtained from LLS method support the conclusion that unimolecular micelles are formed.

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