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Synthesis and characterization of polystyrene-*b*-tetraaniline stars from polystyrene stars with surface reactive groups prepared via ATRP

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Abstract

Functionalized star polymers with tetraaniline on their surface have been successfully prepared by substitution reaction of *N*-succinimidyl-terminated star polymers with tetraaniline. A novel functional initiator bearing *N*-succinimidyl group was used in atom transfer radical polymerization (ATRP) of styrene, and polystyrenes (PSts) having *N*-succinimidyl groups with narrow molecular weight distribution were obtained. The star polymers with reactive *N*-succinimidyl groups on their surface were synthesized by ATRP of divinylbenzene (DVB). The *N*-succinimidyl-terminated PSt, polymer stars with surface *N*-succinimidyl groups and the PSt-*b*-tetraaniline stars were characterized by ^{1}H NMR spectroscopy, FT-IR and gel permeation chromatography.

Keywords: Tetraaniline; Substitution reaction; Functional star polymer

1. Introduction

Star polymers have attracted much attention due to their unique properties [1,2]. The synthesis of star polymers from vinyl monomers using living anionic polymerization [3,4], cationic polymerization [5,6], and controlled radical polymerization (CRP) [7,8] has been extensively studied. A wide range of monomers can be used in CRP for the synthesis of polymers with well-defined structures and complex architectures [9–18]. Star polymers have been prepared by various controlled radical polymerization approaches, including nitroxide-mediated stable free radical polymerization (SFRP) [19], atom transfer radical polymerization (ATRP) [20–25], and, more recently, reversible addition-fragmentation transfer (RAFT) polymerization [26]. There are two general synthetic approaches of star-shaped polymers via living radical polymerizations: (1) polymerization using a multifunctional initiator, namely the ‘‘core-first’’ method, and (2) coupling reactions of living polymers (arm) with a cross-linking reagent, namely the ‘‘arm-first’’ method. Among the CRPs, the metal-mediated living radical polymerization of appropriate cross-linking agents was an efficient method for the synthesis of such star polymers [27]. With the ‘‘arm-first’’ method by ATRP, various kinds of star polymers have been synthesized. Extending the ‘‘arm-first’’ method via ATRP to synthesize star polymers with surface reactive groups should be an interesting project because this approach provides a route to modify surface properties of the star polymers and to prepare new star polymers. The *N*-succinimidyl (NSI) ester group was selected as the reactive group in this study because it is very much reactive to the hydrolysis and substitution reactions by amino group [28,29]. Poly(*N*-acryloxysuccinimide) (PNAS) reacted with ethylenediamine to afford cross-linked polyacrylamides [30]. Thus we synthesized a new kind of ATRP initiator bearing NSI group, the star PSts with reactive NSI on their surface were obtained by ATRP of DVB using NSI-terminated PSt as macroinitiator. Further substitution reaction of NSI groups with functional reagents or polymers will yield various functional stars. With this objective in mind, we report here a novel approach to synthesize functionalized star PSts with

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tetraaniline segments on their surface, and their physical property was studied.

2. Experimental

2.1. Materials

N-Hydroxysuccinimide (Fluka, >97%), 2-bromoisobutyric acid (Aldrich, >98%) and dicyclohexylcarbodiimide (DCC) (Shanghai First Reagent Co., >98%) were used as received without further purification. St (Shanghai Chemical Reagent Co., >99%) was distilled under reduced pressure to remove the inhibitor. Divinylbenzene (50 wt% DVB mixture of isomers, Shanghai Chemical Reagent Co.) was dried over CaH_2 and distilled under reduced pressure prior to use. Tetrahydrofuran (THF) was refluxed for 24 h over sodium and distilled prior to use. *N*,*N*-Dimethylformamide (DMF) was dried over anhydrous $MgSO_4$, and then distilled under vacuum. The tetraaniline capped with amine was prepared in 90% yield from 4-aminodiphenylamine by oxidative coupling with ammonium persulfate in an acetone/HCl solution, and following reduction with phenylhydrazine [31]. All other reagents were of analytical grade and used as received.

2.2. Synthesis of ATRP initiator, N-(2-bromo-2-methylpropionyloxy)succinimide

2-Bromoisobutyric acid (1.67 g, 0.01 mol) and *N*-hydroxysuccinimide (1.38 g, 0.012 mol) were dissolved in 25 mL of anhydrous CH_2Cl_2. Dicyclohexylcarbodiimide (DCC) (2.06 g, 0.01 mol) was added into the solution. The reaction mixture was stirred at room temperature for 24 h. A white byproduct was separated by filtration. The filtrate was washed with distilled water three times for removal of the unreacted *N*-hydroxysuccinimide, and then dried over anhydrous sodium sulfate for 12 h. After removal of the solvent under reduced pressure, the residue was crystallized from hexanes, and then the pure ATRP initiator was obtained in 90% yield. ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 2.06 (s, 6H, $Br{-}C(CH_3)_2{-}CO{-}$), 2.80 (s, 4H, $-OCCH_2{-}CH_2{-}CO-$).

2.3. ATRP of St with N-(2-bromo-2-methylpropionyloxy)-succinimide as initiator

The synthesis of linear PSt polymers capped with NSI group is as follows. The ATRP initiator, *N*-(2-bromo-2-methylpropionyloxy)succinimide (0.132 g, 0.50 mmol), CuBr (0.072 g, 0.50 mmol), bipyridine (bpy, 0.234 g, 1.50 mmol), St (10.4 g, 0.1 mol), and THF (7.5 g) were successively added into a glass tube. The mixture in the tube was degassed by three freeze–vacuum–thaw cycles. The tube was sealed under vacuum, and then was immersed into an oil bath thermostated at 110 °C. After the reaction was carried out for 12 h, the tube was rapidly cooled to room temperature by ice water. The polymer solution in THF was passed through a short column of neutral alumina to remove the metal salt. By the addition of the polymer solution into an excess of methanol, the linear polymer capped with NSI group was precipitated, and then collected by filtration. The product was dried in vacuum oven at 40 °C for 24 h.

2.4. Preparation of star polymer with DVB as cross-linking agent

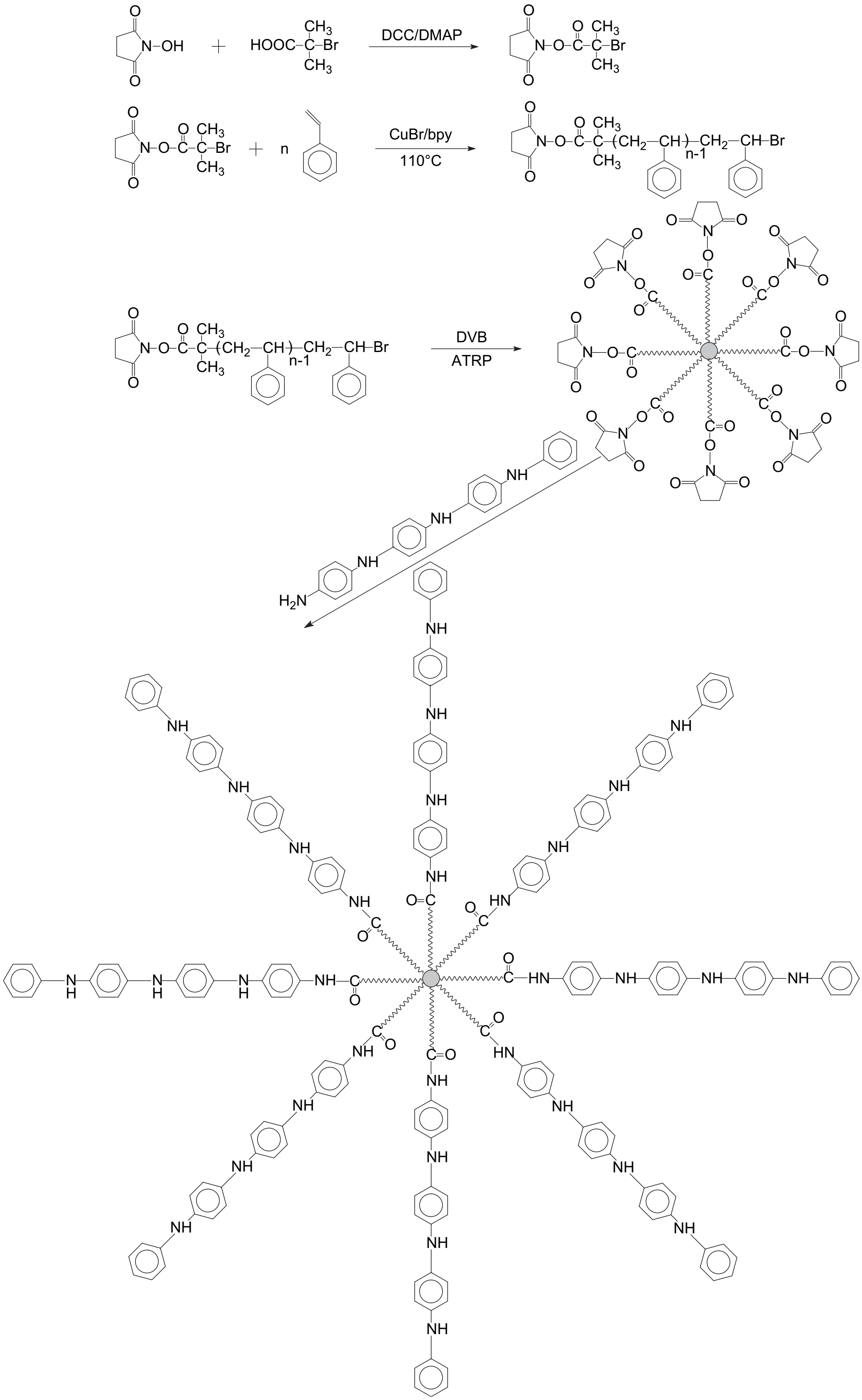
Various molar ratios of DVB, linear PSt initiator (NSI–PSt–Br), CuBr and bpy were used in the polymerization for determining optimum preparation conditions of star polymers. The reaction solutions were degassed by three freeze–evacuate–thaw cycles; the tube was sealed under vacuum, and then it was immersed in an oil bath at 110 °C. After prescribed time, the polymerization was stopped by placing the tube in an ice water bath. Then the tube was opened. The polymer solution in THF was passed through a short column of neutral alumina to remove the metal salt. By addition of the polymer solution into an excess of methanol, the star PSt with NSI groups on its surface was precipitated, and then collected by filtration. The product obtained was dried in vacuum oven at 40 °C for 24 h.

2.5. Modification of star PSt by substitution reaction with NH_2-capped tetraaniline

The NSI ester groups on the surface of star PSts are easily substituted by amine-capped tetraaniline. A typical procedure is as follows. Tetraaniline (300 mg) was added into a solution of 200 mg of star PSt (sample, SPS-5 in Table 2) in 10 mL distilled DMF under a N_2 atmosphere. After the reaction was performed at 50 °C for 48 h, the modified star polymer capped with tetraaniline groups was precipitated by pouring the polymer solution in DMF into methanol seven times, and the excess NH_2-capped tetraaniline was removed. The functionalized polymer obtained was dried in a vacuum oven at 40 °C for 24 h.

2.6. Measurements and instruments

^{1}H NMR (300 MHz) spectra were recorded on a Bruker 300 nuclear magnetic resonance (NMR) instrument, using $CDCl_3$ as a solvent and tetramethylsilane (TMS) as an internal reference. The molecular weight, M_n (GPC) and molecular weight distribution (MWD) were determined at 30 °C on a Waters 515 gel permeation chromatograph (GPC) equipped with microstyragel columns, 10^3, 10^4, and 10^5 Å. Narrow polystyrene standards were used in the calibration of molecular weight and molecular weight distribution, and THF was used as an eluent at a flow rate of 1 mL/min. Infrared spectra were recorded on a Bruker VECTOR-22 IR spectrometer. Cyclic voltammetry (CV) measurement was carried out on an automated LK98B Π electrochemical measurement system in a standard three-electrode cell: modified functional star PSt film coated on the surface of a platinum (Pt) wire (ca. 5 mm length and 0.5 mm diameter), which was used as working electrode, a platinum wire counter electrode and a saturated calomel reference electrode (SCE). All potentials obtained were



Scheme 1. Synthetic procedure of polystyrene-*b*-tetraaniline stars.

referred to the SCE. Prior to each experiment, the Pt wire was carefully rinsed with distilled water, and then immersed in concentrated HNO_3 for 5 min before it was finally dried using clean laboratory tissues.

3. Results and discussion

3.1. Synthesis of star PSt with reactive groups, N-succinimidyl groups on the surface

Polymer stars with tightly cross-linked cores were prepared by "arm-first" method via ATRP (Scheme 1). Obviously, the first step is the preparation of linear NSI–PSt–Br. As the arm of star polymers, it was achieved by ATRP of St using *N*-(2-bromo-2-methylpropionyloxy)succinimide as initiator. The preparation conditions and results are listed in Table 1. The molecular weight of the PSt increased with evolution of the polymerization, and the narrowed PSt ($M_w/M_n = 1.03 \sim 1.09$) was obtained. For confirmation of the polymer structure, ^{1}H NMR spectra were measured and a typical spectrum is shown in Fig. 1. Except for characteristic signals of PSt, we can also find signal "e" at $\delta = 4.50$ ppm ascribed to the methine proton next to the terminal bromine group and signal "a" at 2.80 ppm corresponding to methylene protons in the NSI group. The integration ratio of signal "a" to "e" is 4:1, which equals to the proton ratio of CH_2CH_2 and CHBr in these two groups. From the integral values of aromatic (I_d) at $\delta = 6.3 \sim 7.32$ ppm and methylene protons in the NSI group (I_a), the number-average molecular weight, $M_{n,PSt}$(NMR) can be calculated according to Eq. (1):

$$M_{n,PSt}(\mathrm{NMR}) = (4I_d/5I_a) \times 104 + 264 \quad (1)$$

here 104 and 264 are the molecular weights of St and ATRP initiator, respectively. The results are listed in Table 1, and the values of $M_{n,PSt}$ (NMR) agree with $M_{n,PSt}$ (th). We can see that the GPC curves of these polymers are single and symmetrical (Fig. 2). All these facts indicate the formation of NSI–terminated PSt–Br with narrow molecular weight distribution.

Table 1
Results and conditions of ATRP of St using *N*-(2-bromo-2-methylpropionyloxy)succinimide as initiator and CuBr/bpy as catalyst and ligand[a]

No.	Sample	Time (h)	Conv.[b] (%)	M_n (g/mol)			M_w/M_n[c]
				GPC[c]	NMR[d]	th[e]	
1	PSt-1	3	15	3400	3540	3380	1.09
2	PSt-2	6	27	6180	6470	5880	1.04
3	PSt-3	9	38	8050	8620	7930	1.03
4	PSt-4	12	46	10,940	11,030	9830	1.05
5	PSt-5	15	51	11,360	12,010	10,870	1.04

[a] The polymerization was carried out at 110 °C, $[St]_0/[initiator]_0/[CuBr]_0/[bpy]_0 = 200:1:1:3$ (molar ratio), St: 0.1 mol; THF: 7.5 g.
[b] Conv. (conversion) was measured by gravimetric method.
[c] Measured by GPC.
[d] Calculated by Eq. (1).
[e] Theoretical number-average molecular weight, M_n(th) was calculated according to $M_n(\mathrm{th}) = \{(\mathrm{Conv} \times [St]_0 \times 104)/[\mathrm{initiator}]_0\} + 264$, where $[St]_0$ and $[\mathrm{initiator}]_0$ are initial moles of St and ATRP initiator, respectively, 104 and 264 are molecular weights of St and ATRP initiator, respectively.

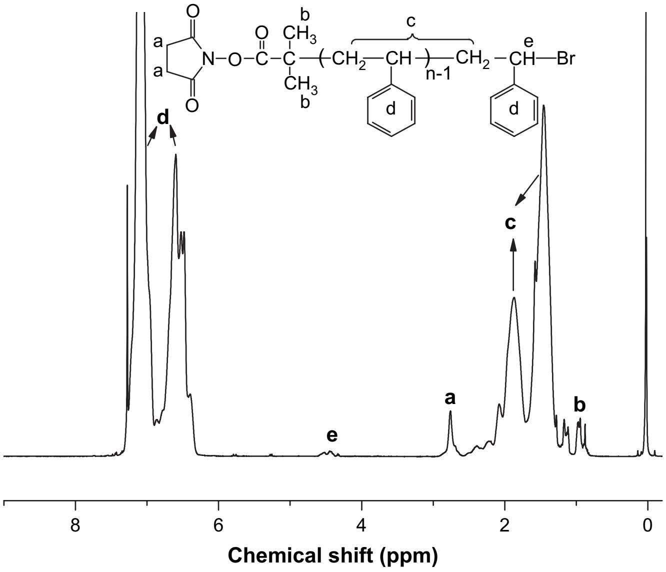


Fig. 1. ^{1}H NMR spectrum of linear NSI–PSt–Br (no. 3 in Table 1).

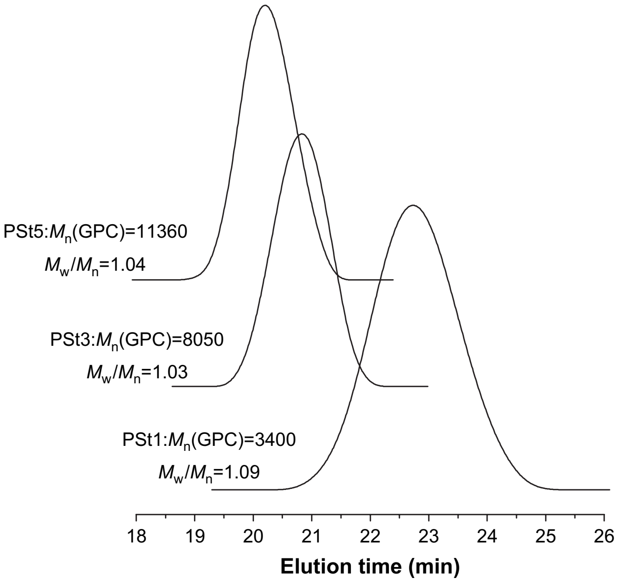


Fig. 2. GPC curves of linear PSt prepared at different polymerization times: 3 h (PSt-1), 9 h (PSt-3), and 15 h (PSt-5) with *N*-(2-bromo-2-methylpropionyloxy)succinimide as initiator. For polymerization conditions, see Table 1.

In the synthesis of star polymers using the "arm-first" approach via ATRP, various star polymers with different arms have been reported [32–35]. Two main factors influence the synthesis of the star polymer: one is the ratio of DVB to linear macroinitiator and the other is ATRP polymerization time. In order to study the effect of polymerization time on polymerization, the ratio of DVB to linear macroinitiator, PSt-3 (no. 3 in Table 1) was set to be 15, a series of experiments were carried out for various reaction times. The results are summarized in Table 2, and their corresponding GPC curves are shown in Fig. 3. The GPC curves of those polymers obtained at and

Table 2
Preparation of star polymers by ATRP of DVB[a]

No.	Sample	Time (h)	Yield[b] (%)	M_n, GPC[c] (g/mol)	M_w, GPC[c] (g/mol)	MWD[c]
6	SPS-1	8	91	28,060	41,530	1.48
7	SPS-2	15	92	35,130	49,880	1.42
8	SPS-3	20	94	44,830	61,860	1.38
9	SPS-4	25	93	58,650	77,420	1.32
10	SPS-5	30	94	71,310	115,520	1.62

[a] The polymerizations were carried out at 110 °C, the molar feed ratio of DVB to PSt-3: 15. PSt-3: 0.5 g; THF: 1.5 mL; CuBr: 9 mg; bpy: 27 mg.

[b] Calculated by gravimetric method.

[c] Measured by GPC method.

before 25 h displayed two peaks. One at lower molecular weight position, whose molecular weight is slightly higher than that of macroinitiator PSt-3, might be linear polymers. Other at higher molecular weight position should be PSt stars. With the increase of polymerization time the amount of linear PSt in polymerization system decreased, and most linear PSt chains were transferred to form star polymer at 25 h of polymerization. However, when the reaction time increased from 25 h to 30 h, the linear PSt did not disappear completely, and two peaks appeared at high molecular weight position (SPS-5 in Fig. 3). The highest molecular weight stars in the curve SPS-5 of Fig. 3 are ascribed to the star–star coupling reactions during the polymerization. The formation of PSt star was also confirmed by their ^{1}H NMR spectrum as shown in Fig. 4A. In comparison with ^{1}H NMR spectrum of its precursor, PSt-3 (no. 3 in Table 1) in Fig. 1, we could not observe the proton signal at $\delta = 4.50$ ppm ascribed to methine proton adjacent to the terminal Br group. This indicates the formation of the star-shaped polymers with PSt arms and cross-linked DVB core because the CHBr groups in the tightly cross-linked cores cannot be detected. But the signals of methylene protons in NSI groups at $\delta = 2.80$ ppm are clearly seen in Fig. 4A. This is understandable because the reactive NSI groups are on the surface of the PSt stars theoretically. Based on the integration ratio of aromatic protons' signals "d" to a corresponding to methylene protons of the NSI group in Fig. 4A, the M_ns of every PSt arm of the stars were estimated. For the sample SPS-5 in Table 2, the value is around 8510 g/mol, which agrees with M_n (8356 g/mol) of its linear precursor, NSI–PSt–Br (note: the value is equal to that of M_n (8620) of PSt-3 minus molecular weight (264) of ATRP initiator). Therefore, PSt stars with reactive NSI groups on their surface have been successfully prepared.

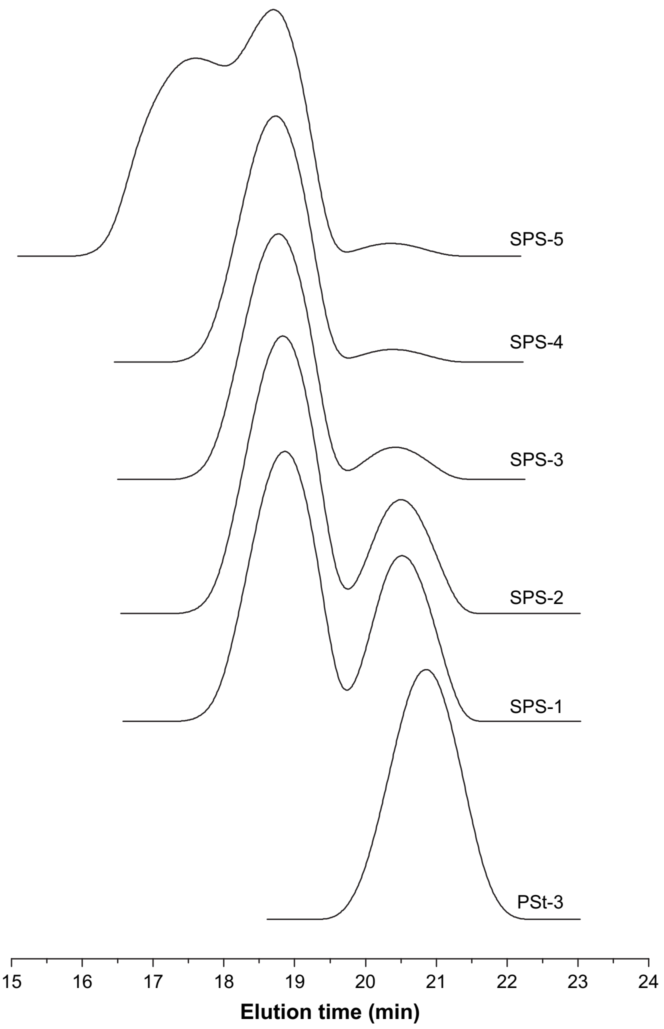


Fig. 3. GPC traces of PSt stars obtained from the ATRP of DVB at different polymerization times: 0 h (PSt-3), 8 h (SPS-1), 15 h (SPS-2), 20 h (SPS-3), 25 h (SPS-4), and 30 h (SPS-5). The molar ratio of DVB/macro transfer agent in feed: 15; CuBr: 9 mg; bpy: 27 mg.

3.2. *Modification of star PSt by substitution reaction with amine-capped tetraaniline*

As we know, the NSI ester group can be hydrolyzed or substituted by amino group very easily [28,29,36,37]. Theoretically, the reactive NSI ester groups on the surface of PSt stars could be transformed into other types of functional groups. Polyaniline is a well-known conductive polymer. Copolymerizations of linear aniline oligomers with common monomers have been studied for the synthesis of soluble conductive polymers [38]. For example, tetraaniline acrylamide or trianiline acrylamide copolymerized with common monomers yield conductive polymers [39]. Based on our knowledge, study on the synthesis of star block copolymers having linear aniline oligomers blocks has not been reported. Thus we tried to synthesize PSt-*b*-tetraaniline stars by substitution reaction of NSI ester groups on the surface of stars with linear tetraaniline. For estimating the substitution efficiency, ^{1}H NMR spectra of the reaction products were measured. Fig. 4B represents a typical ^{1}H NMR spectrum of diblock PSt-*b*-tetraaniline stars (TASPS-5) prepared from SPS-5 because it contained more surface reactive groups. In comparison with ^{1}H NMR spectrum of its precursor, SPS-5 in Fig. 4A, the signal "a" at 2.80 ppm ascribed to methylene protons in the NSI group is absent completely in Fig. 4B, indicating that *N*-succinimidyl ester groups on the surface of star PSt were transformed to tetraaniline functional groups. But to our regret, due to overlapping of the tetraaniline protons' signals with those of the star PSt chains, the characteristic signals of tetraaniline cannot

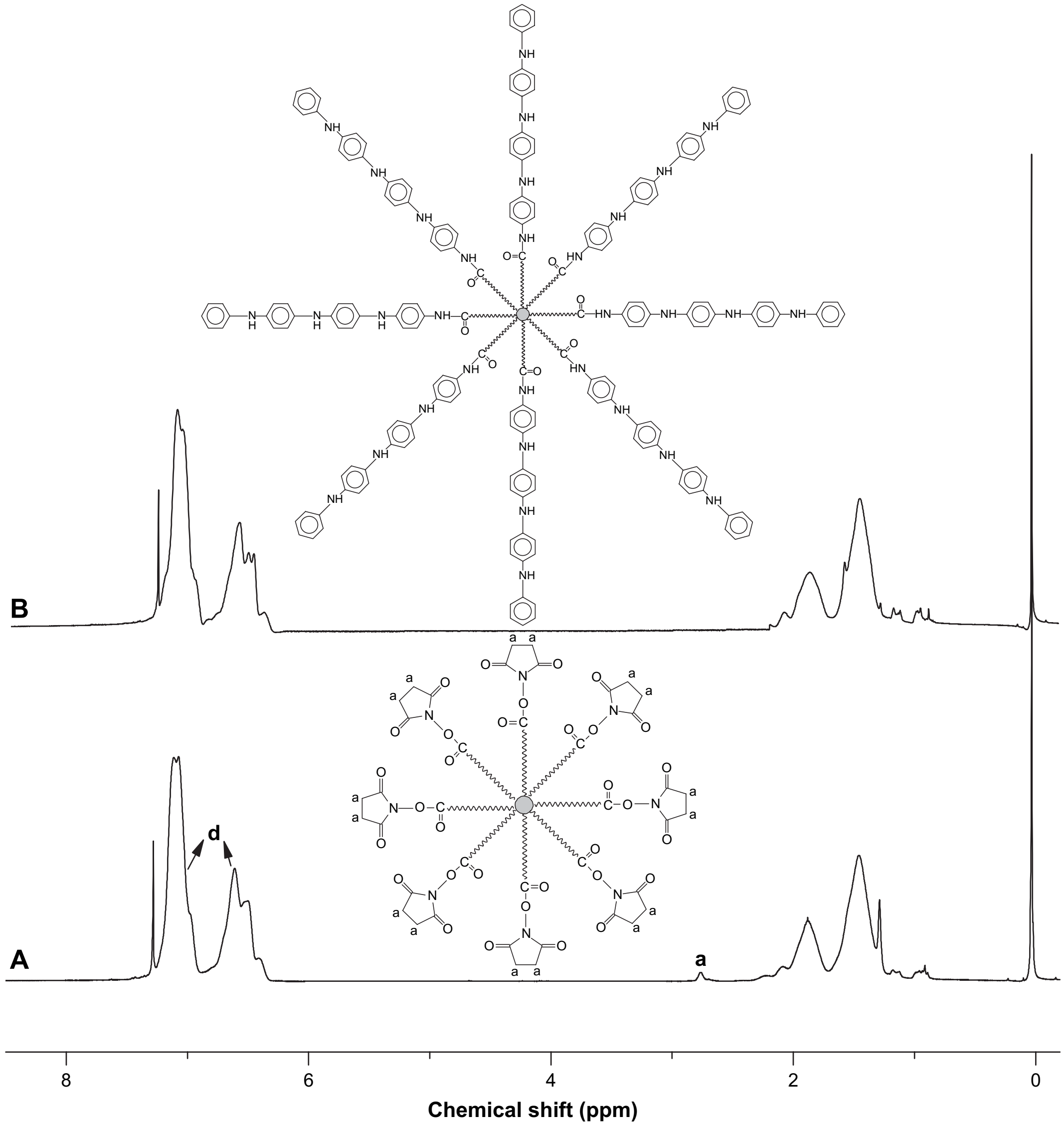


Fig. 4. ^{1}H NMR spectra of (A) star polymer SPS-5 (no. 10 in Table 2); (B) star functional polymer TASPS-5 (the precursor is the SPS-5).

be observed in Fig. 4B. For further verification, FT-IR measurement was performed. The FT-IR spectra of star PSt, SPS-5 and its modified product by tetraaniline are shown in Fig. 5A and B, respectively. By comparing the two figures, we can find that the characteristic ester carbonyl stretching band at $\nu = 1730\ \mathrm{cm}^{-1}$ in Fig. 5A disappeared completely in Fig. 5B, and a new characteristic peak at $\nu = 1665\ \mathrm{cm}^{-1}$ ascribed to the amides carbonyl group appears clearly in Fig. 5B. All these facts indicate the high transformation efficiency of NSI ester groups on the surface of PSt stars to amine-capped tetraaniline.

The electrochemical characterization of TASPS-5 film was carried out at room temperature in a standard three-electrode cell. The second cycle was recorded. Its cyclic voltammogram in Fig. 6 shows two oxidative waves at 0.42 and 0.64 V, similar to the polyaniline. We considered that the first wave corresponds to the transition of leucoemeraldine to emeraldine state and the second wave corresponds to the transition of

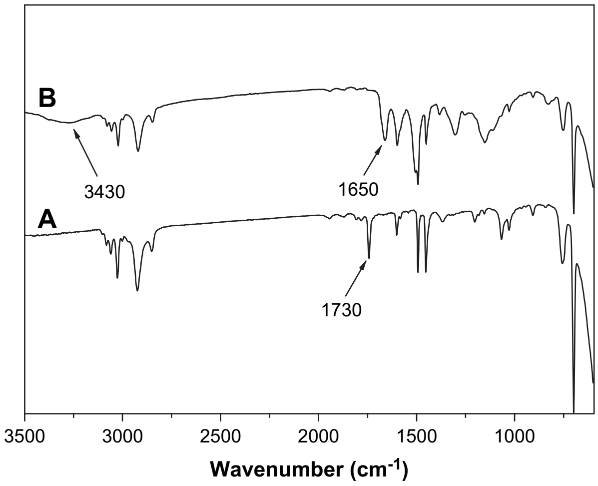


Fig. 5. FT-IR spectra of (A) star polymer SPS-5 (no. 10 in Table 2); (B) star functional polymer TASPS-5 (the precursor is the SPS-5).

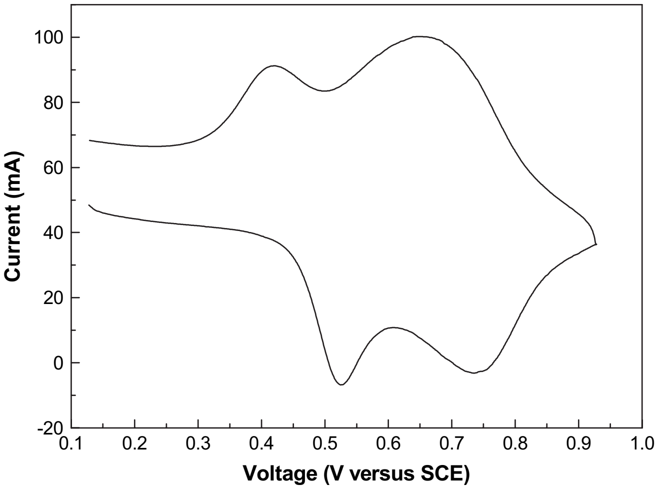


Fig. 6. Cyclic voltammogram of functional star PSt in aqueous H_2SO_4 (0.1 mol/L) with a scan rate of 50 mV/s.

emeraldine to pernigraniline state. The result further indicates the formation of PSt stars with tetraaniline on their surface.

4. Conclusions

PSt stars with very much reactive *N*-succinimidyl ester groups on their surface have been successfully synthesized by atom transfer radical polymerization of DVB using NSI–PSt–Br as macroinitiator. The NSI ester group is easily substituted by amine compounds. Thus the block copolymers, PSt-*b*-tetraaniline stars, were prepared by substitution reaction of NSI groups on the surface of PSt stars with linear amine-capped tetraaniline. The substitution reaction efficiency of surface NSI groups is high, and the density of tetraaniline on the surface of PSt stars is determined by the density of NSI groups on the surface. The PSt-*b*-tetraaniline stars displayed two redox peaks at 0.42 and 0.64 V. The advantage of this method is that the density of functional groups on the surface of stars can be controlled by adjusting the feed ratio of DVB to the macroinitiator and polymerization time. The star polymers with high density of functional groups can be obtained simply by the modification of *N*-succinimidyl groups with functional reagent bearing amine group. This novel strategy should be highly useful to synthesize various functional stars.

Acknowledgments

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