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Synthesis and characterization of dendritic–linear–dendritic triblock copolymers based on poly(amidoamine) and polystyrene

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ABSTRACT

Dendritic–linear–dendritic triblock copolymers composed of linear polystyrene (PSt) and poly(amidoamine) dendrons have been successfully synthesized. Two bromines-terminated PSt with $M_n = 13{,}000$ was prepared by atom transfer radical polymerization (ATRP) using α,α′-dibromo-*p*-xylene as initiator. Then the terminal bromines at both ends of PSt chains were replaced by one imine group of piperazine (PZ), and further Michael addition reaction of terminal PZ with excess 1,3,5-triacryloylhexahydro-1,3,5-triazine (TT) produced the first generation (G_1) of the triblock copolymer. Continuous growth of dendrons from G1.5 to G4 at the both ends of PSt chains was carried out by the iterative Michael addition reactions with excess PZ and following TT. The ABA triblock copolymers composed of the G_1–G_4 dendrons and the linear PSt were obtained. Structures of the triblock polymers were characterized by GPC and ^{1}H NMR spectra. Thermal phase transitions of the polymers were studied by DSC measurements, and all of the copolymers displayed a glass transition temperature.

1. Introduction

Dendritic–linear–dendritic triblock copolymers have attracted much attention of polymer scientists because of their unique structures and extensive applications such as in catalysis and drug delivery [1–3]. Their properties, such as solution properties [4] and crystallization [5] have been studied. Based on the dendritic-*b*-linear-*b*-dendritic copolymers reported, three synthetic strategies can be classified. (1) Coupling method, such as coupling reaction of a living anionic polystyrene chain with reactive dendrimers [6]. This method requires strict reaction conditions and only limited monomers are suitable for anionic polymerization. (2) Macro reagent method, macro reagents, in which two dendritic chains are connected by a small molecular initiator or chain transfer reagent, were used in the controlled radical polymerizations or ring-opening metathesis polymerizations, forming triblock copolymers [7–9]. (3) Divergent method, the dendritic blocks at the both ends of linear chains are prepared by divergent method, and after every divergent reaction the purification of the resultant product is necessary because excess divergent reagents are used generally [10–13]. Among the three synthetic strategies, the third method is extensively applied due to its universality although troublesome purification has to be adopted during the synthesis. The linear block mostly used in the synthetic strategy is poly(ethylene oxide) (PEO), and the dendrimers are poly(carbosilane) [10], poly(benzyl ester) [11], poly(aliphatic ester) [12–14], poly(triazine) [15,16] and poly(amidoamine) (PAMAM) prepared from methyl acrylate and ethylene diamine [1]. The triblock copolymer composed of linear poly(propylene oxide) and dendritic PAMAMs was also reported; the aqueous solution properties of this amphiphilic block copolymer demonstrated that it is a promising candidate for drug delivery and can form micelles by self-assembling [2].

Relatively few studies have been reported for this type of triblock copolymers with a hydrophobic linear block and pH-sensitive hydrophilic dendritic blocks. Based on our knowledge, synthesis of triblock copolymers consisted of linear vinyl polymer and dendritic PAMAM has not been reported. PAMAM is a well-known biocompatible polymer, and has broad applications in various areas, such as drug carrier [17], catalysts [18] and fabrication of nanoparticles [19,20]. Here we report one synthetic strategy to the dendritic–linear–dendritic triblock copolymer via iterative Michael addition reaction of piperazine and 1,3,5-triacryloylhexahydro-1,3,5-triazine on the both ends of the linear PSt.

2. Experimental

2.1. Materials

Styrene (St, Shanghai Chemical Reagent Co. 99%) was washed with an aqueous solution of sodium hydroxide (5 wt%) three times

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and then washed with distilled water until neutralization. After dried with anhydrous calcium chloride, St was distilled under reduced pressure. CuBr was synthesized by the reduction of $CuBr_2$ with Na_2SO_3. α,α′-Dibromo-*p*-xylene (Fluka, 98+%), 2,2′-bipyridyl (bpy, Fluka, 99+%), 1,3,5-triacryloylhexahydro-1,3,5-triazine (TT, Aldrich, 98+%) and piperazine (PZ, Aldrich, 99+%) were used as-received. Other regents were of analytical grade purchased from Shanghai Chemical Reagent Co. and used as-received.

2.2. Characterization

^{1}H NMR (300 MHz) was recorded on a Bruker DRX-300 nuclear magnetic resonance (NMR) instrument at room temperature, tetramethylsilane and $CDCl_3$ were used as internal standard and solvent. The molecular weight, M_n (GPC) and molecular weight distribution (M_w/M_n) were determined at 30 °C on a Waters 150C gel permeation chromatography (GPC) equipped with microstyragel columns (10^3, 10^4 and 10^5 Å) and a Waters 2414 refractive index detector, THF was used as eluent at a flow rate of 1 mL/min. Narrow polystyrene standards were used in the calibration of molecular weight and molecular weight distribution. DSC measurements were carried out on a Mettler Toledo DSC 822E under nitrogen at a heating rate of 20 °C/min from −40 to 150 °C.

2.3. ATRP of St using α,α′-dibromo-p-xylene as initiator

α,α′-Dibromo-*p*-xylene (0.264 g, 1 mmol), CuBr (0.289 g, 2 mmol), bpy (0.936 g, 6 mmol) and St (21 g, 0.2 mol) were successively added into a 50 mL glass tube, and then the polymerization system was degassed by three freeze–vacuum–thaw cycles. The tube was sealed under vacuum, and then immersed into an oil bath at 110 °C. After polymerization was carried out for 5 h, the tube was rapidly cooled to room temperature. The polymer solution was diluted with THF, and then was passed through a short column of neutral alumina for the removal of metal salt. After twice precipitation in methanol, the precipitate was collected by filtration and then dried in a vacuum oven at 30 °C overnight. The polymer Br–PSt–Br (12 g) with $M_{n,NMR} = 13{,}000$, $M_w/M_n = 1.11$ was obtained in 57% yield. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ (ppm): 1.43 ($-CH_2-$CH– of PSt backbone); 1.84 ($-CH_2-CH-$ of PSt backbone); 4.52 (–C*H*–Br); 6.57–7.08 (aromatic H).

2.4. Capped reaction with piperazine

Br–PSt–Br ($M_{n,NMR} = 13{,}000$, 3 g, 0.23 mmol) and excess of PZ (0.97 g, 11 mmol) were dissolved in 50 mL DMF. After the mixture was reacted at 80 °C for 48 h, the polymer was precipitated in excess of methanol; the precipitate was filtered and then dried in a vacuum oven at 30 °C overnight. The product, PZ–PSt–PZ ($M_{n,NMR} = 13{,}000$, $M_w/M_n = 1.10$) was obtained in 95% yield. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ (ppm): 1.43 ($-CH_2-$CH– of PSt backbone); 1.84 ($-CH_2-CH-$ of PSt backbone); 2.15–2.40 ($-N-CH_2-$ of piperazine ring); 2.70–2.87 ($HN-CH_2-$ of piperazine ring); 3.73 (–C*H*–N– at the end of PSt); 6.57–7.08 (aromatic H).

2.5. Synthesis of G1 dendrons

PZ–PSt–PZ with NH end groups ($M_{n,NMR} = 13{,}000$, 2.8 g, 0.21 mmol) was dissolved in 20 mL $CHCl_3$, and slowly dropped into 20 mL TT solution in $CHCl_3$ (2 g, 8 mmol) with stirring at 50 °C. Then the reaction was carried out for 48 h at 50 °C. Excess of TT was removed by dialysis against methanol. After methanol was removed through rotatory evaporation, the polymer was dissolved in $CHCl_3$, and precipitated in petroleum ether. The product was obtained in 96% yield after dried in a vacuum oven at 30 °C overnight. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ (ppm): 1.43 ($-CH_2-$CH– of PSt backbone); 1.84 ($-CH_2-CH-$ of PSt backbone); 2.15–2.40 ($-N-CH_2-$ of PZ ring close to PSt); 2.50–2.74 ($-N-CH_2-$ of PZ ring close to TT, $-N-CH_2-CH_2-C{=}O$); 3.73 (–C*H*–N– at the end of PSt); 5.30 ($-CH_2-$ of TT ring close to PSt); 5.37 ($-CH_2-$ of TT ring close to terminal vinyl group); 5.83 ($-CH{=}CH_2$); 6.36 ($-CH{=}CH_2$); 6.57–7.08 (aromatic H).

2.6. Synthesis of G1.5 dendrons

PSt with G1 dendrons ($M_{n,NMR} = 13{,}500$, 2.9 g, 0.21 mmol) was dissolved in 20 mL $CHCl_3$, and then dropped slowly into 20 mL $CHCl_3$ solution of PZ (3 g, 35 mmol) while stirring at 50 °C. Then the reaction was carried out at 50 °C for 48 h. Excess of PZ was removed by dialysis against methanol. After methanol was removed through rotatory evaporation, the polymer was dissolved in $CHCl_3$, and then precipitated in petroleum ether. The product was obtained in 93% yield after dried in a vacuum oven at 30 °C overnight. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ (ppm): 1.43 ($-CH_2-$CH– of PSt backbone); 1.84 ($-CH_2-CH-$ of PSt backbone); 2.15–2.50 ($-N-CH_2-$ of piperazine ring, $-N-CH_2-CH_2-C{=}O$); 2.50–2.75 ($HN-CH_2-$ of piperazine ring, $-N-CH_2-CH_2-C{=}O$); 3.73 (–C*H*–N– at the end of PSt); 5.23 ($-CH_2-$ of TT ring); 6.57–7.08 (aromatic H).

2.7. Synthesis of G2–G4 dendrons at the both ends of PSt chain

G2–G4-terminated PSts were prepared with the same procedure of preparing G1–PSt–G1. Their feed molar ratios are as follows: PSt with G1.5 dendrons ($M_{n,NMR} = 13{,}800$, 2.6 g, 0.19 mmol), TT (1.5 g, 6 mmol) and 40 mL $CHCl_3$ for preparation of G2–PSt–G2; PSt with G2.5 dendrons ($M_{n,NMR} = 15{,}500$, 2.4 g, 0.15 mmol), TT (4 g, 16 mmol) and 40 mL $CHCl_3$ for G3–PSt–G3; PSt with G3.5 dendrons ($M_{n,NMR} = 18{,}900$, 1 g, 0.05 mmol), TT (2.2 g, 9 mmol) and 40 mL $CHCl_3$ for G4–PSt–G4.

Their ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ (ppm): for G2–PSt–G2, 1.43 ($-CH_2-$CH– of PSt backbone); 1.84 ($-CH_2-CH-$ of PSt backbone); 2.17–3.00 ($-CH_2-$ of PZ ring, $-N-CH_2-CH_2-C{=}O$); 3.73 (–C*H*–N– at the end of PSt); 5.30 ($-CH_2-$ of TT ring close to PSt); 5.37 ($-CH_2-$ of TT ring close to double bonds of chain ends); 5.83 ($-CH{=}CH_2$); 6.36 ($-CH{=}CH_2$); 6.57–7.08 (aromatic H); for G3–PSt–G3, 1.43 ($-CH_2-$CH– of PSt backbone); 1.84 ($-CH_2-CH-$ of PSt backbone); 2.17–2.88 ($-CH_2-$ of PZ ring, $-N-CH_2-CH_2-C{=}O$); 3.73 (–C*H*–N– at the end of PSt); 5.27 ($-CH_2-$ of TT ring close to PSt); 5.36 ($-CH_2-$ of TT ring close to double bonds of chain ends); 5.83 ($-CH{=}CH_2$); 6.36 ($-CH{=}CH_2$); 6.57–7.08 (aromatic H); for G4–PSt–G4, 1.43 ($-CH_2-$CH– of PSt backbone); 1.84 ($-CH_2-CH-$ of PSt backbone); 2.16–3.08 ($-CH_2-$ of PZ ring, $-N-CH_2-CH_2-C{=}O$); 3.73 (–C*H*–N– at the end of PSt); 5.26 ($-CH_2-$ of TT ring close to PSt); 5.35 ($-CH_2-$ of TT ring close to double bonds of chain ends); 5.84 ($-CH{=}CH_2$); 6.39 ($-CH{=}CH_2$); 6.57–7.08 (aromatic H).

2.8. Synthesis of G2.5, G3.5 dendrons at the both ends of PSt

G2.5–PSt–G2.5 and G3.5–PSt–G3.5 were prepared with the same procedure of preparing G1.5-PSt-G1.5. Their feed ratios are as follows: for preparation of G2.5–PSt–G2.5, G2–PSt–G2 ($M_{n,NMR} = 14{,}800$, 2.8 g, 0.18 mmol) and PZ (2 g, 23 mmol); for G3.5–PSt–G3.5, G3–PSt–G3 ($M_{n,NMR} = 17{,}500$, 2.2 g, 0.12 mmol), and PZ (3 g, 35 mmol). Their ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ (ppm): 1.43 ($-CH_2-$CH– of PSt backbone); 1.84 ($-CH_2-CH-$ of PSt backbone); 2.16–2.80 ($-CH_2-$ of PZ ring, $-N-CH_2-CH_2-C{=}O$); 3.73 (–C*H*–N– at the end of PSt); 5.27 ($-CH_2-$ of TT ring); 6.57–7.08 (aromatic H); 1.43 ($-CH_2-$CH– of PSt backbone); 1.84 ($-CH_2-CH-$ of PSt backbone); 2.17–2.85 ($-CH_2-$ of piperazine ring, $-N-CH_2-CH_2-C{=}O$); 3.73 (–C*H*–N– at the end of PSt); 5.28 ($-CH_2-$ of TT ring); 6.57–7.08 (aromatic H).

2.9. Synthesis of hyperbranched poly(amidoamine)

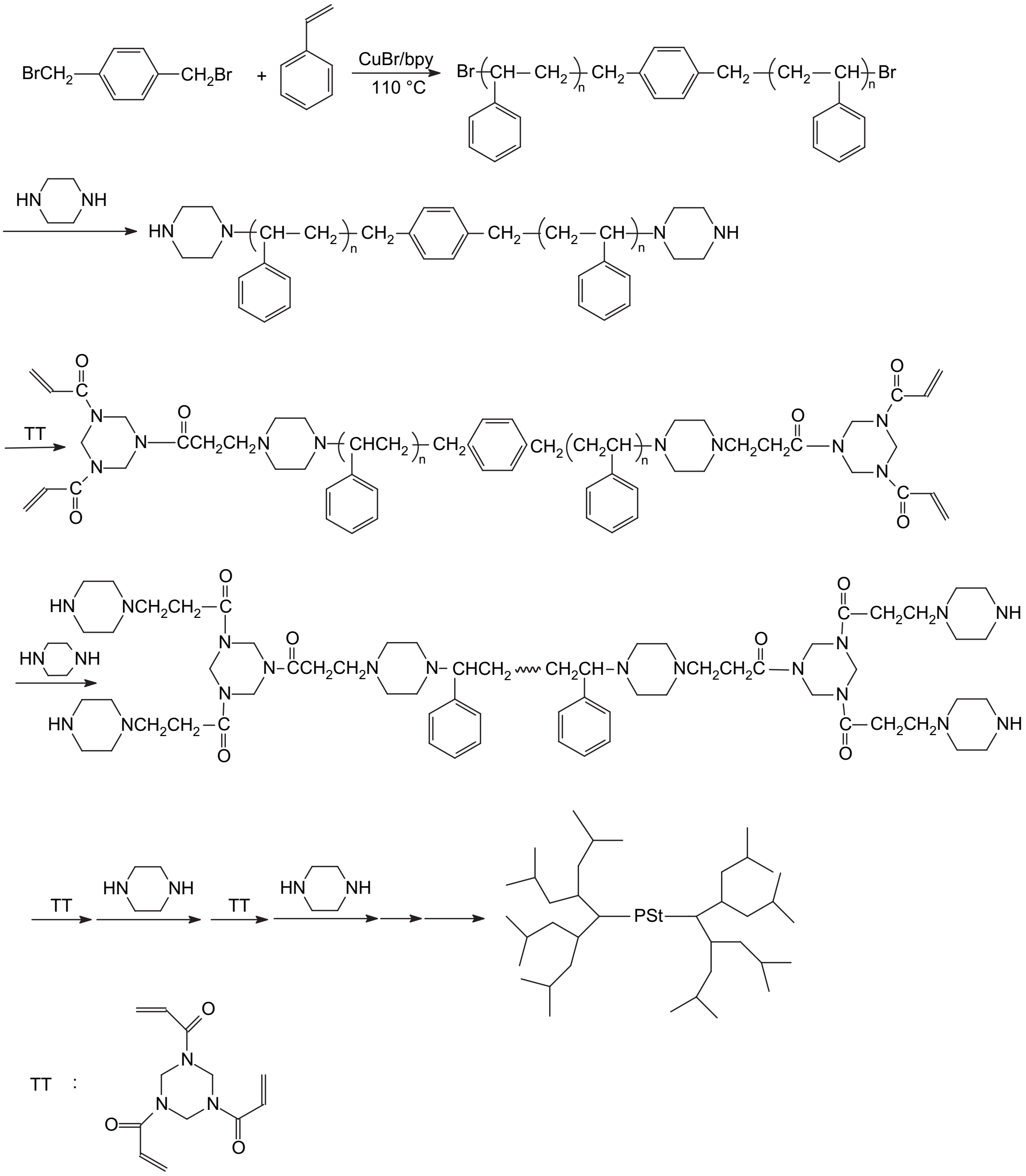
TT (0.498 g, 2 mmol) and PZ (0.172 g, 2 mmol) were dissolved in 7 mL $CHCl_3$, and the reaction was carried out for 24 h at 40 °C. The product was precipitated twice in petroleum ether, and then dried in a vacuum oven at 30 °C overnight. The polymer with $M_{n,NMR} = 6000$ was obtained in 75% yield.

^1H NMR (300 MHz, $CDCl_3$, TMS) δ (ppm): 2.20–2.90 ($-CH_2-$ of PZ ring, $-N-CH_2-CH_2-C{=}O$); 5.20–5.40 ($-CH_2-$ of TT ring); 5.82–5.85 ($-CH{=}CH_2$); 6.35–6.40 and 6.72–6.80 ($-CH{=}CH_2$).

3. Results and discussion

3.1. Synthesis and characterization of PAMAM–PSt–PAMAM triblock copolymers

Dendritic PAMAM–linear PSt–dendritic PAMAM triblock copolymers (PAMAM–PSt–PAMAM) were synthesized according to Scheme 1. The first step is the preparation of the linear PSt with two terminal bromines (Br–PSt–Br) through atom transfer radical polymerization (ATRP) of St. The second step is the synthesis of dendritic PAMAM via Michael addition reactions, and for successful preparation the reactants must be selected properly. We did the reaction on excess ethylene diamine (EDA) with Br–PSt–Br for synthesis of $(H_2NCH_2CH_2NH)_2PSt$. Subsequently the resulting polymer reacted with excess TT at 50 °C for 48 h, complete reaction of the secondary amines with TT was not obtained. The ^1H NMR spectra of the product showed coexistance of the secondary amines and acryl groups, and GPC curves demonstrated shoulder peaks at twice and four times molecular weight of the main peak. Probably the secondary amine (formed) has low reactivity [21,22], its complete transformation to TT groups is difficult. The coupling reactions between the secondary amines remained and acryl groups in two different chains during purification process led to the formation of high molecular weight polymers. In order to get complete reaction efficiency, the monomer PZ with high reactivity [23] was selected to react with TT. After Br–PSt–Br reacted with excess PZ, the dendritic chain growth on the linear PSt chains occurred via iterative



Scheme 1. Synthesis of triblock copolymers of dendritic PAMAM and linear PSt.

Table 1
Characterization of the dendritic–linear–dendritic triblock copolymers with different generation dendrons

Sample	Conversion[a] (%)	$M_{n,GPC}$[c]	$M_{n,NMR}$[d]	M_w/M_n[c]	T_g[e] (°C)
Br–PSt–Br	57[b]	13,000	13,000	1.09	92.7
PZ–PSt–PZ	~100	13,000	13,000	1.09	97.0
G1	99	13,800	13,500	1.11	87.4
G2	~100	15,500	14,800	1.19	92.4
G2.5	~100	13,100	15,500	1.20	98.3
G3	98	17,000	17,500	1.18	83.4
G3.5	~100	15,000	18,900	1.19	97.1
G4	95	18,600	22,700	1.16	81.1

[a] The conversions of the terminal functional groups were calculated based on ^{1}H NMR spectra.
[b] Conversion of St was calculated gravimetrically.
[c] Obtained from GPC measurements.
[d] Calculated based on the integration ratios of signals at $\delta = 6.57$–7.08 (I_{Ar}) to the signals at $\delta = 4.52$ ppm (I_c, methine proton next to bromines) for $M_{n,NMR}$ of Br–PSt–Br; $\delta = 3.73$ ppm ($I_{c'}$, methine proton next to PZ) for PZ–PSt–PZ and $\delta = 5.37$, 5.29 (methylene groups in triazine ring) or at 5.83 ppm (I_{vinyl}, vinyl groups in TT) for G*n* ($n = 1$–4).
[e] Obtained from DSC measurements.

Michael addition reactions of TT and PZ. For complete conversion of terminal imine (or acryl) groups to acryl (or imine) groups, excess of TT (or PZ) was added. After every step reaction, the unreacted PZ or TT was removed by dialysis against methanol and then precipitation in petroleum ether. The reaction conditions and results are listed in Table 1. The GPC traces and ^{1}H NMR spectra of all the products are shown in Figs. 1–6.

Fig. 1 shows GPC traces of the linear PSt and the triblock copolymers with G1–G4 dendrons and linear PSt block. GPC curve of the triblock copolymer with G4 dendrons has slight tail at the lower molecular weight position, and other curves show unimodal and symmetrical peaks and narrow molecular weight distributions. It indicates that the Michael addition reaction in every step had high reaction efficiency because not so efficient reaction will lead to the block copolymers having double bonds and imine groups, their further Michael addition reaction will result in the resultant polymers with unsymmetrical, even multi-peaks GPC traces.

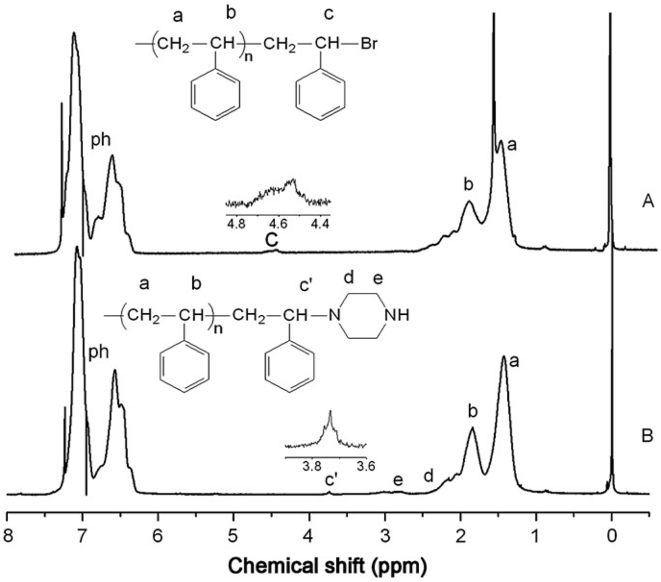


Fig. 2. ^{1}H NMR spectra of linear PSt prepared by ATRP (A) and PSt with two terminal piperazine groups (B).

To make sure structure of the polymers obtained, ^{1}H NMR spectra of all the products were measured. Fig. 2A and B are the ^{1}H NMR spectra of linear PSt prepared by ATRP using α,α′-dibromo-*p*-xylene as initiator and its reaction product with PZ, respectively. The characteristic signals of PSt at $\delta = 6.4$–7.4 (phenyl protons) and 1.33–2.7 ppm (methine and methylene protons in the backbone) are observed, and a signal at $\delta = 4.5$ ppm (c) corresponds to the methine proton next to terminal bromine in Fig. 2A. The number-average molecular weight, M_n(NMR) (13,000) of PSt can be calculated based on the integration ratio of the signal c to the signals at $\delta = 6.4$–7.4 ppm, which is consistent with that obtained from GPC (M_n(GPC) = 13,000). The signal at $\delta = 4.5$ ppm is absent, and new signals of the methine proton at $\delta = 3.7$ ppm (c′), methylene protons in PZ ring at $\delta = 2.1$–2.2 (d) and $\delta = 2.8$–3.0 ppm (e) appeared in the ^{1}H NMR spectra of PZ–PSt–PZ obtained by the reaction of Br–PSt–Br with PZ in Fig. 2B. The conversion of terminal bromine

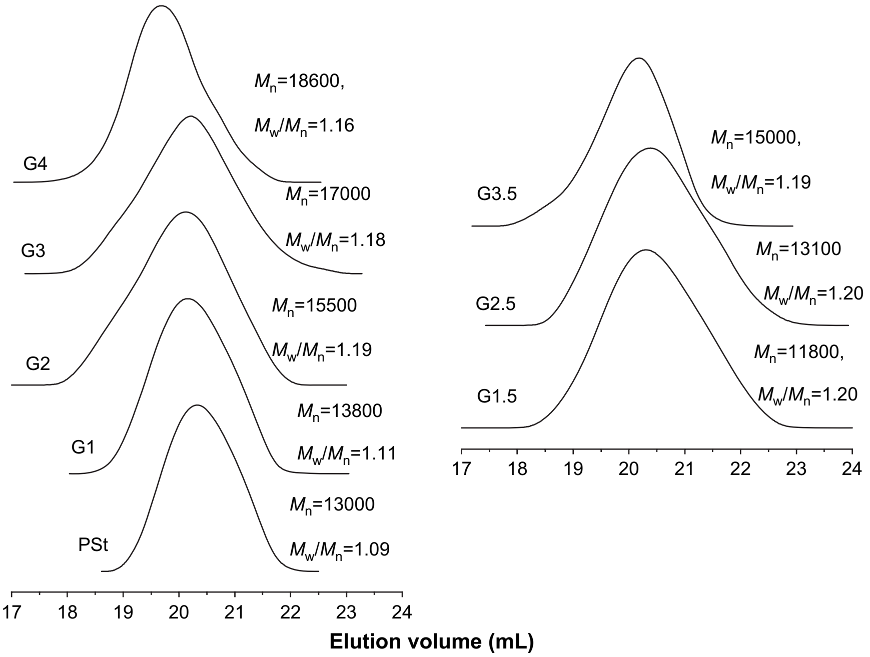


Fig. 1. GPC curves of linear PSt and triblock copolymers with different generation dendritic poly(amidoamine)s.

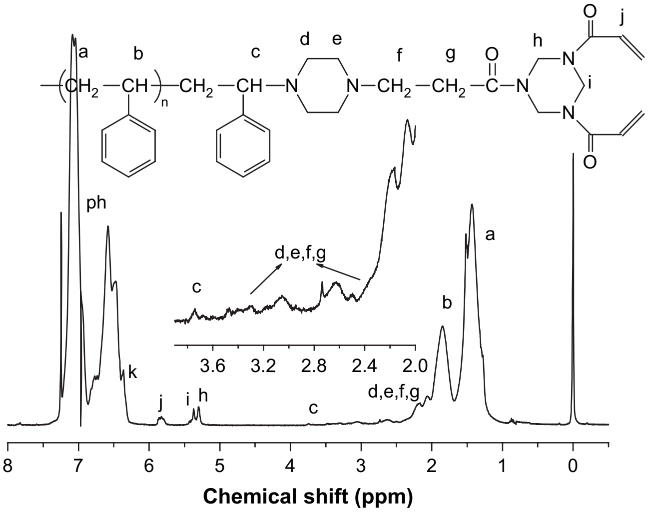


Fig. 3. ^{1}H NMR spectrum of triblock copolymer, G1–PSt–G1.

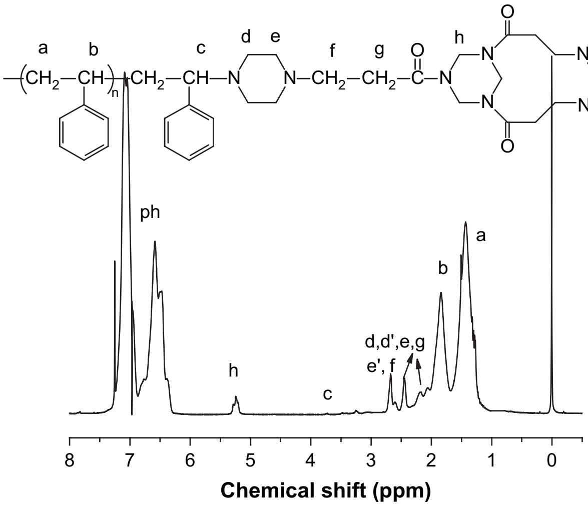


Fig. 4. ^{1}H NMR spectrum of triblock copolymer, G1.5–PSt–G1.5.

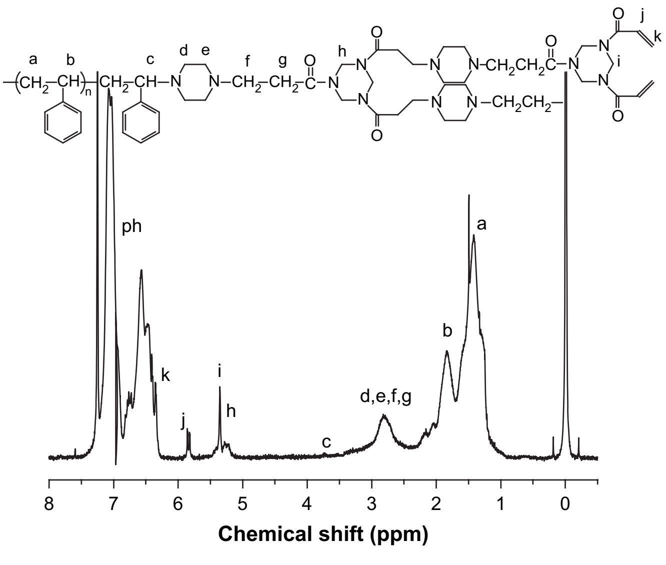


Fig. 5. ^{1}H NMR spectrum of triblock copolymer, G2–PSt–G2.

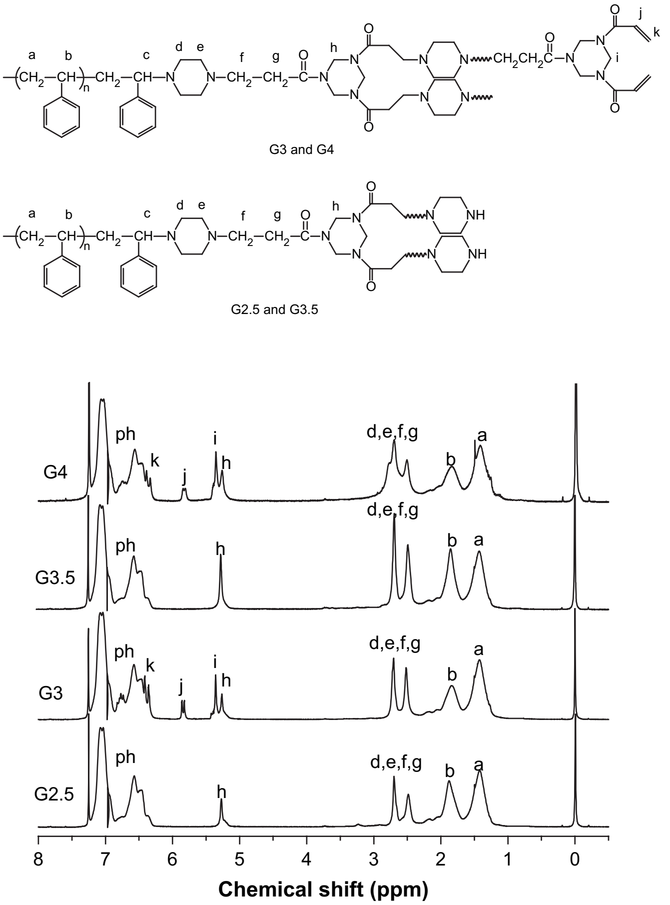


Fig. 6. ^{1}H NMR spectra of triblock copolymers, G2.5–PSt–G2.5, G3–PSt–G3, G3.5–PSt–G3.5 and G4–PSt–G4.

groups was estimated based on the integration ratio of signal c′ and signals ph, and it was almost 100%.

The first generation (G1) in triblock copolymers was achieved by Michael addition reaction of terminal PZ with excess divergent reagent, TT. In order to avoid coupling reaction of two polymer chains, and ensure complete transformation of terminal bromines, PZ–PSt–PZ solution was slowly dropped into excess TT solution (20 times of TT than PZ groups). Because emulsion occurred during the precipitation in methanol, and complete removal of TT was not achieved by precipitation in petroleum ether due to its poor solubility, dialysis method was used to remove TT and then precipitation in petroleum ether was carried out. ^{1}H NMR spectrum of the product is shown in Fig. 3. In comparison with Fig. 2B, new signals corresponding to double bond protons of acryl groups and methylene protons in triazine ring appeared at $\delta = 5.83$ (j), 6.36 (k), 5.30 (h) and 5.37 ppm (i), respectively. Among these signals, k signal overlaps with the signals of phenyl protons. So we can calculate conversion of the imine groups based on the integration ratio of signal j or signals h + i to signal c. The result obtained was around 99%, indicating that the Michael addition reaction was almost completed.

The 1.5-generation PAMAMs in the triblock copolymer were achieved by Michael addition reaction of terminal acryl groups with excess PZ. After purification, its ^{1}H NMR spectrum is shown in Fig. 4. Evidences for the complete reaction are that the signals of vinyl protons at $\delta = 5.83$ and 6.36 ppm disappeared completely, and the signals i and h of methylene protons in 1,3,5-triazine ring became a multi-signal at $\delta = 5.24$ ppm (h). In addition, two stronger signals at $\delta = 2.44$ ppm (d, d′, e, g) and 2.66 ppm (e′ and f) could be observed, and conversion of acryl groups at the ends of polymer chains was calculated based on the integration ratio of the signal at $\delta = 2.66$ ppm and the signals of phenyl protons (ph), about 100% conversion was obtained.

With the same procedure described above, and the triblock copolymer with G2 dendrons and linear PSt (G2–PSt–G2) was synthesized successively by the reaction of terminal PZ units with excess TT. This can be confirmed by its ^{1}H NMR spectrum in Fig. 5. These signals of vinyl protons in TT at $\delta = 5.83$ and 6.36 ppm (j and k) appeared again, and a broad signal at $\delta = 2.83$ ppm, which corresponds to methylene protons on PZ ring (d and e) and on propionyl groups (f and g), was observed. Based on the integration ratio of the signal at $\delta = 5.83$ ppm and phenyl proton signals, almost 100% conversion of terminal imine groups was estimated.

The triblock copolymers, G2.5–PSt–G2.5, G3–PSt–G3, G3.5–PSt–G3.5 and G4–PSt–G4 were prepared successfully by iterative Michael addition reaction. Their structures were verified by the corresponding ^{1}H NMR spectra in Fig. 6. The triblock copolymers G3–PSt–G3 and G4–PSt–G4 have the similar proton signals, but their intensities are different. We can see the signals of vinyl protons (j and k) at $\delta = 5.83$ and 6.36 ppm, methylene proton signals of 1,3,5-triazine ring (i and h) at $\delta = 5.37$ and 5.29 ppm, and methylene proton signals in PZ ring (d and e) and propionyl groups (f and g) at 2.36–2.86 ppm in addition to the characteristic signals of PSt in Fig. 6G3 and G4. Conversions of the terminal PZ groups into acryl groups were estimated based on the integration ratios of vinyl proton signal j and phenyl proton signals ph, and they are 98 and 95%, respectively. The ^{1}H NMR spectral difference of G2.5–PSt–G2.5 and G3.5–PSt–G3.5 with G3–PSt–G3 and G4–PSt–G4 is complete disappearance of vinyl proton signals j and k, the combination of two signals i and h to one signal h in Fig. 6G2.5 and G3.5.

3.2. *Thermal phase transition of PAMAM–PSt–PAMAM triblock copolymer*

The thermal behaviors of hyperbranched PAMAM and PAMAM dendrimers have been studied [24–26]. The hyperbranched or dendritic PAMAM prepared from ethylene diamine and methyl acrylate had low glass transition temperature ($T_g < 20$ °C) [24,26], and the PAMAMs with ring structure in their backbone had high T_g due to the rigidity of the polymer chains. For example, the hyperbranched PAMAMs prepared from TT and *n*-butyl amine had higher T_g (about 50–60 °C) [27]. To estimate the T_g of the hyperbranched PAMAM made from two cyclic compounds, the hyperbranched PAMAM with $M_n = 6000$ g/mol, which is similar to the molecular weight of G4 dendron, was prepared via Michael addition polymerization of TT and PZ, its T_g measured by DSC was 86.2 °C. Considering influence of DB on T_g, the T_g of G4 dendron should be slightly lower than or close to 86.2 °C. Obviously, T_gs of the PAMAM dendrimers and linear PSt ($T_g = 92.7$ °C for Br–PSt–Br) are very close. Clearly observing the two T_gs of PSt and PAMAM on the DSC curves of the triblock copolymers might be difficult.

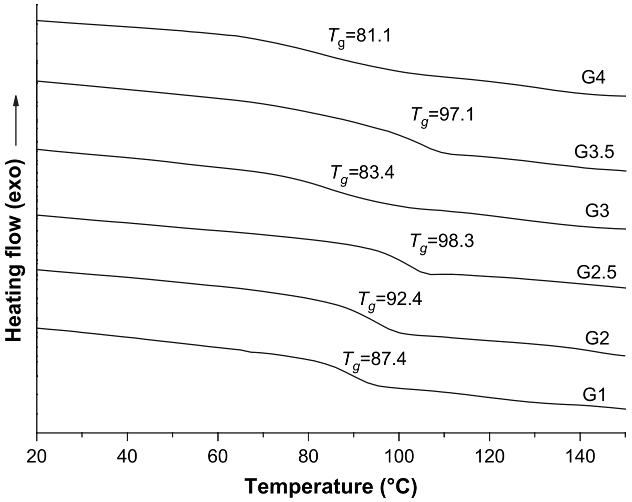


Fig. 7. DSC curves of triblock copolymers, G1–PSt–G1, G2–PSt–G2, G2.5–PSt–G2.5, G3–PSt–G3, G3.5–PSt–G3.5 and G4–PSt–G4.

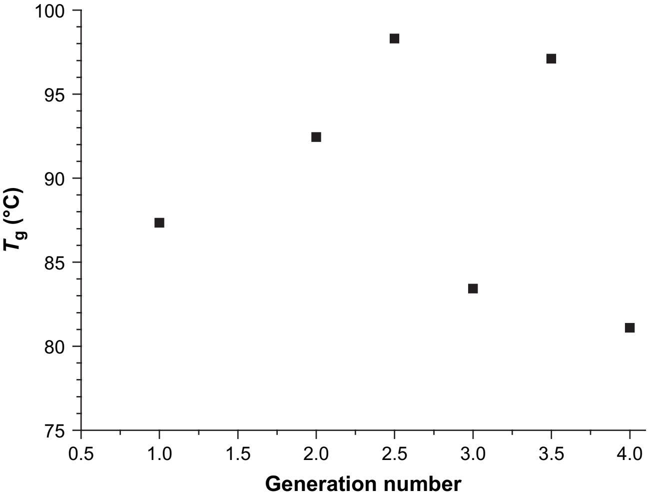


Fig. 8. Relationship of glass transition temperatures with generation number of PAMAM–PSt–PAMAM triblock copolymers.

The DSC curves of the triblock copolymers with different generation PAMAM dendrons are shown in Fig. 7, and the results are listed in Table 1. All the copolymers have only one T_g, and the relationship of T_g with generation number is shown in Fig. 8. The molecular weights of the dendrons had obvious influence on the T_g; generally, the T_g tends to increase with the molecular weight increase of dendrons. However, Fig. 8 shows T_gs of G3 and G4 are lower than that of that of G2.5 and G3.5. Possibly the surface groups of the dendrimers have big influence on T_g. The T_gs (98.3 and 97.1 °C) of the G2.5–PSt–G2.5 and G3.5–PSt–G3.5 with surface PZ groups are over 15 °C higher than that (83.4 and 81.1 °C) of the G3–PSt–G3 and G4–PSt–G4 with surface TT groups. Possibly the dendrons in the former case act as crosslinker due to their strong interaction via hydrogen bonding, so their T_gs are close to the T_g (97 °C) of PZ-terminated PSt (Table 1). In addition, The T_g ranges (76.3–102.8 and 76.8–105.7 °C) of the triblock copolymers containing G3 and G4 dendrons, which seem to overlap two T_g ranges of the linear PSt and the PAMAM dendrons, are quite broader than that (95.4–107 and 95.9–110 °C) of those polymers containing G2.5 and G3.5, which may be the T_g of PSt. For the triblock copolymers containing G0.5–G2, the effect of the terminal groups on T_gs is not so big in comparison with the triblock copolymers containing G2.5–G4 dendrons, but can be observed clearly probably due to less terminal groups on their chains. The T_g ranges for G1–PSt–G1 (83.2–95.1 °C) and G2–PSt–G2 (89.2–100.7 °C) are relatively narrow in comparison with T_g ranges of G3–PSt–G3 and G4–PSt–G4, probably low molecular weight G1 and G2 dendrons have no glass transition.

4. Conclusions

The dumbbell shaped triblock copolymers composed of two PAMAM dendrons and a linear PSt have been synthesized successfully by iterative Michael addition reactions of TT and PZ at both ends of linear PSt chains. When the polymers with terminal PZ or

TT units reacted with excess TT or PZ, complete transformation of the terminal functional groups is obtained, which was confirmed by GPC and ^{1}H NMR spectra. The DSC curves of all the triblock copolymers obtained have one glass transition, and the triblock copolymers with terminal PZ groups have higher T_gs and narrower T_g ranges than the copolymers with terminal TT groups do. With the transformation of terminal TT groups to PZ groups, the T_g variation of the copolymers containing G0.5–G2 was not so big as that of the copolymers containing G2.5–G4.

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