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Synthesis of bis(2,2′:6′,2″-terpyridine)-terminated telechelic polymers by RAFT polymerization and ruthenium–polymer complexation thereof

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Abstract

Well-defined polystyrenes and poly(*n*-butyl acrylate)s of the two ends being functionalized with terpyridine groups were synthesized via addition-fragmentation chain transfer (RAFT) polymerization using a symmetric bisterpyridine-functionalized trithiocarbonate as a chain transfer agent (CTA). Kinetic studies on RAFT mediated thermal polymerization of styrene indicated the controlled polymerization. Corresponding triblock copolymers of styrene and *n*-butyl acrylate were obtained by utilizing the bisterpyridine-functionalized homopolymers as the macro-CTAs. Supramolecular metallo-polystyrenes with different repeat blocks were prepared by the chelating interaction between the terpyridine ends and Ru(II) ions. The formation of the metallo-polymers was proven by UV–vis spectra and dynamic light scattering (DLS).

Keywords: Reversible addition-fragmentation chain transfer (RAFT) polymerization; Supramolecular metallo-polymers; Telechelic polymers

1. Introduction

Transition metal containing polymers based on terpyridine, bipyridine and other *N*,*N*-chelating analogue complexes have attracted a great attention because these materials combine the distinct photophysical, electrochemical, and magnetic properties of metal complexes and the easy fabrication of organic thermoplastic polymers [1,2]. Furthermore, the metal ions link the ligand functionalized polymers to generate the so-called metallo-supramolecular architecture [1–9]. In recent years, various methods for preparation of these metallo-polymers have been investigated, which may be divided into two types. One is to introduce the metal ions during polymerization via metal containing monomers or initiators [3]. As an example, star poly(methyl methacrylate) with a ruthenium (Ru)/tris(bipyridine) core was prepared via $NiBr_2(PR_3)_2$ catalyzed atom transfer radical polymerization (ATRP) [3a]. The other option uses the polymers that bear functional groups to bind the metal ions. This is a widely used

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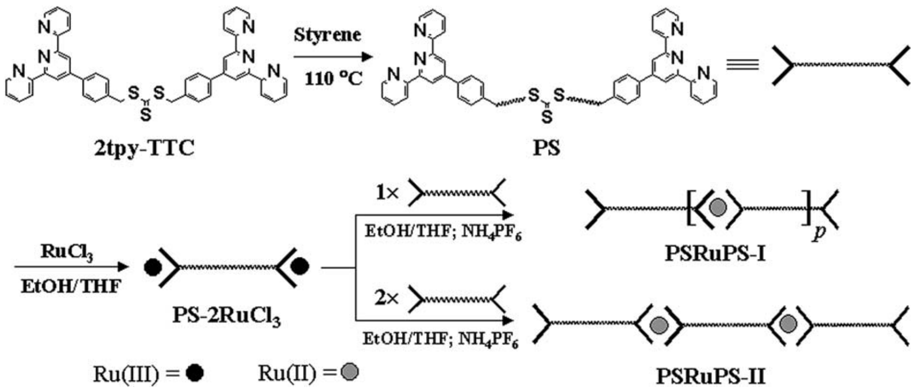

Scheme 1. The synthesis route of bisterpyridine functionalized polystyrene and metallo-supramolecular polystyrenes based on complexation of bisterpyridine functionalized polystyrenes and Ru ions.

method which becomes more attractive in terms of development of the metallo-supramolecular polymer chemistry [1,4,6,7]. For instance, Fraser's group has synthesized a series of monobipyridine-functionalized macroligands by ATRP and ring-opening polymerization (ROP) [5]. Schubert's group has reported a number of terpyridine-functionalized homopolymers or copolymers through traditional radical polymerization, nitroxide-mediated polymerization (NMP), ROP and post-modification of a polymer with terpyridine derivatives [6]. Zhou and Harruna have reported some bipyridine or terpyridine functionalized polymers via reversible addition-fragmentation chain transfer (RAFT) mediated polymerization [7]. The metallo-supramolecular polymers were further produced by the complexation between these functionalized polymers and those transition metal ions.

In particular, bisterpyridine and other bis-*N*,*N*-chelating analogue functionalized telechelic polymers (α,ω-bisfunctionalized polymers) are attracting significant interest because their chelation with metal ions is a facile way to generate the metallo-supramolecular polymers and metallo-multiblock copolymers [8]. However, these polymers were prepared by post-modification the two ends of a polymer with terpyridine derivatives [9]. Such approach is only applicable to limited polymers and the removal of those unfunctionalized polymers could be difficult. To the best of our knowledge, there is no report of α,ω-bisterpyridine functionalized vinyl-polymers prepared by in situ controlled radical polymerization. As a type of controlled radical polymerization, RAFT polymerization is readily applied to prepare well-defined polymers with predetermined molecular weight and narrow polydispersity [10]. Trithiocarbonates with two leaving groups are effective RAFT agents to propagate in two directions and generate well-defined α,ω-telechelic polymers [11]. Therefore, RAFT polymerization with the trithiocarbonates as chain transfer agents (CTA) is an excellent method for preparing telechelic polymers [12].

Herein, a bisterpyridine-functionalized RAFT agent, bis(4′-(*p*-methylenephenyl)-2,2′:6′,2″-terpyridine) trithiocarbonate (2tpy-TTC), was synthesized, which was used in the RAFT polymerization of styrene and acrylate. Well-defined polymers were synthesized and α,ω-bisterpyridine groups were introduced in situ during the polymerization. Furthermore, polystyrene (PS) with two ends being functionalized by terpyridine groups were applied to prepare metallo-multiblock polymers by the connection of terpyridine-ruthenium(II)-terpyridine (tpy-Ru-tpy) complexes. Supramolecular metallo-polystyrenes with different length were obtained. The outline of synthesis was shown in Scheme 1.

2. Experimental

2.1. Materials

Styrene and *n*-butyl acrylate (*n*BA) were stirred over CaH_2 overnight and distilled under reduced pressure. 2,2′-Azobisisobutyronitrile (AIBN) was recrystallized from ethanol. Toluene was stirred over CaH_2 overnight and distilled. 4′-(4-Bromomethylphenyl)-2,2′:6′,2″-terpyridine was prepared according to the literature [13]. Anionic exchange resin 201 × 4 was purchased from Weisi Chemical Reagent Co. Other reagents were used as received.

2.2. Measurement

Gel permeation chromatography (GPC) was performed by a set of a Waters 515 HPLC pump, a Waters 2414 refractive index detector, and a combination of Styragel® HT-2, HT-3 and HT-4, effective molar mass range is 100–10,000, 500–30,000 and 5000–600,000, respectively. THF was used as eluent at a flow rate of 1.0 mL/min at 35 °C. Polystyrene standards were used for the calibration. ^{1}H NMR spectra were recorded on a Varian 400 MHz spectrometer in $CDCl_3$ at room temperature. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry was performed on a Bruker Biflex III spectrometer equipped with a 337 nm nitrogen laser. Both matrix 4-hydroxy-α-cyanocinnamic acid (CCA) and sample were dissolved in 1:1 (v/v) acetonitrile:water with 1% trifluoroacetic acid. And 0.5 μL of this mixture solution was placed on a metal sample plate and air-dried at ambient temperature. Mass spectra were acquired in positive linear mode. External mass calibration was performed using a standard peptide mixture. The spectra were obtained by setting the laser power close to the threshold of ionization and generally 100 pulses were acquired and averaged. Elemental analyses were performed on Flash EA1112 elemental analysis instrument. UV–visible absorption spectra were recorded on a CARY 50 Conc UV–visible spectrum instrument. A slightly modified commercial laser light scattering (LLS) spectrometer (ALV/DLS/SLS-5022F) equipped with a multi-τ digital time correlator (ALV5000) and a cylindrical 22 mW UNIPHASE He–Ne laser ($\lambda_0 = 632$ nm) was used.

2.3. Synthesis of 2tpy-TTC

Following a general method of preparing trithiocarbonates [14]. Anionic exchange resin (9 g, exchange capacity is 30 mmol/g) was stirred with 4 × 100 mL of 1 mol/L NaOH aq. solution and washed with 4 × 100 mL of water. The resin was added to carbon disulfide (50 mL) and stirred at room temperature for about 5 min. The color of the resin changed from light yellow to deep red. Then 4′-(4-bromomethylphenyl)-2,2′:6′,2″-terpyridine (1 g, 2.5 mmol) was added, and the reaction mixture was stirred under reflux for 6 h. After cooled to room temperature, the mixture was filtered and the resin was washed with a large amount of carbon disulfide. The solutions were combined and the solvent was removed by rotary evaporation. The crude product was recrystallized in carbon disulfide twice. Yield: 0.64 g (68%). ^{1}H NMR ($CDCl_3$) (Fig. 1) δ (ppm): 8.72 (8H, s), 8.65–8.68 (4H, d), 7.85–7.89 (8H, m), 7.48–7.51 (4H, d), 7.33–7.36 (4H, t), 4.71 (4H, s). ^{13}C NMR ($CDCl_3$) (Fig. 2) δ (ppm): 222.2 (–S(*C*S)S–), 157.7, 157.5, 151.1, 150.7, 138.4, 125.3, 122.8, 120.3 (tpy*C*), 139.5, 137.5, 131.4, 129.2 (Ph*C*), 42.7 (Ph*C*H_2). MALDI-TOF MS: calcd for $C_{45}H_{32}N_6S_3$ $m/z = 752.2$, found 753.3 ($M + H^+$). Elemental analysis: calcd for $C_{45}H_{32}N_6S_3$: C 71.78%, H 4.28%, N 11.16%, found C 71.37%, H 4.32%, N 11.07%. Melting point: 264–266 °C.

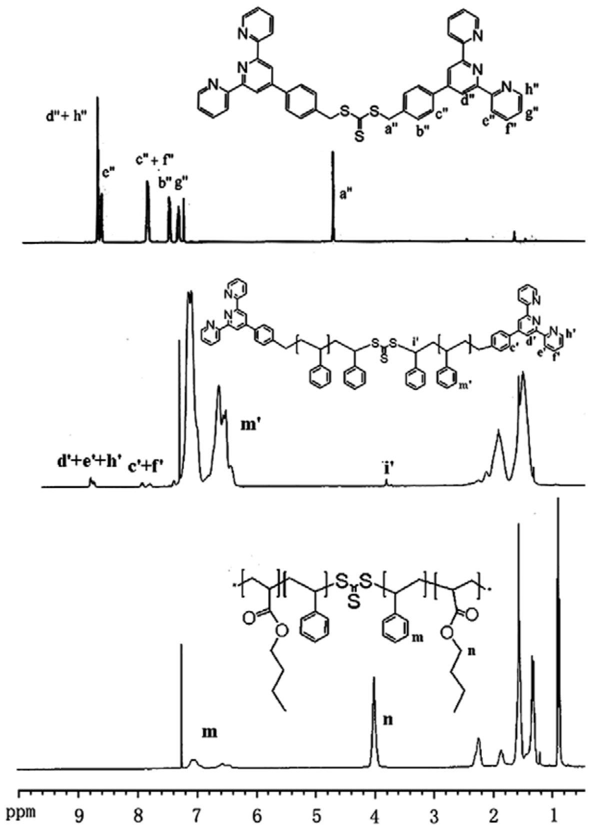

Fig. 1. The ^{1}H NMR spectra of the RAFT agent 2tpy-TTC, bis-terpyridine functionalized polystyrene PS1 and triblock copolymer PS1-*b*-P*n*BA-*b*-PS1.

2.4. RAFT polymerization of styrene – a general procedure

2tpy-TTC (51.7 mg, 0.0688 mmol) and styrene (4.29 g, 0.0413 mol) were introduced into a 10 mL glass tube. After three times of freeze–pump–thaw, the tube was placed in an oil bath at 110 °C with

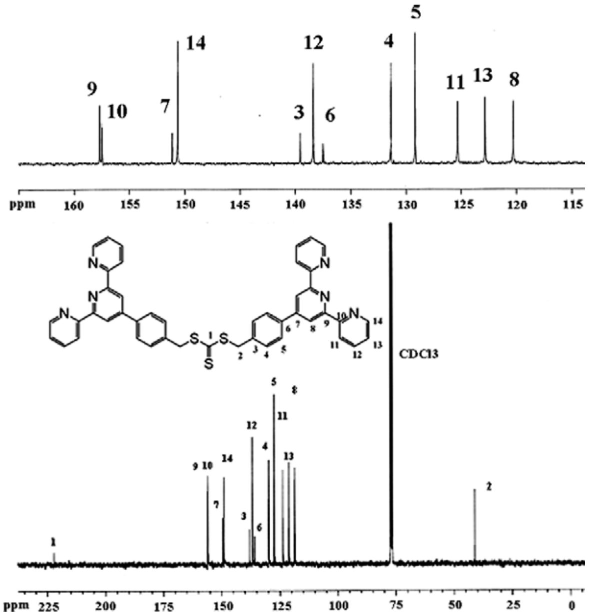

Fig. 2. The ^{13}C NMR spectrum of the RAFT agent 2tpy-TTC (below) and an enlarged region (upper).

stirring for 7 h. The product was dissolved in THF and precipitated in methanol twice and then dried under vacuum at 40 °C. Yield: 1.31 g.

2.5. Synthesis of PS1-b-PnBA-b-PS1

PS1 (0.37 g, 0.01 mmol) and AIBN (1.6 mg, 0.01 mmol) were dissolved in a mixture of toluene (2.56 mL) and *n*BA (2.59 g, 0.0202 mol). Then the solution was transferred into a 10 mL glass tube. After three times of freeze–pump–thaw, the tube was placed in an oil bath at 60 °C with stirring for 9.5 h. The product was dissolved in THF and precipitated in methanol/water (7/3) twice and then dried under vacuum at 40 °C. Yield: 2.90 g.

2.6. RAFT polymerization of n-butyl acrylate – a general procedure

2tpy-TTC (20.2 mg, 0.0269 mmol), AIBN (1.6 mg, 0.01 mmol) and *n*BA (0.93 g, 7.3 mmol) were introduced into a 10 mL glass tube. After three times of freeze–pump–thaw, the tube was placed in an oil bath at 60 °C with stirring for 16 h. The product was dissolved in THF and precipitated in methanol/water twice and then dried under vacuum at 40 °C. Yield: 0.82 g.

2.7. Synthesis of PnBA2-b-PS-b-PnBA2

P*n*BA2 (0.30 g, 0.024 mmol) was dissolved in styrene (1.30 g, 0.0125 mol). Then the solution was introduced into a 10 mL glass tube. After three times of freeze–pump–thaw, the tube was placed in an oil bath at 110 °C with stirring for 4.5 h. The product was dissolved in THF and precipitated in methanol/water (7/3) twice and then dried under vacuum at 40 °C. Yield: 0.63 g.

2.8. Preparation of PS3–2RuCl$_3$

PS3 (200.2 mg, 0.0082 mmol) and $RuCl_3 \cdot xH_2O$ (46.7 mg, 0.16 mmol) were introduced into a 50 mL two-neck-flask with 10 mL ethanol and 20 mL THF. The mixture was deoxygenated by bubbling with argon for 30 min and then heated at 85 °C under argon for 24 h. The solution was concentrated and the polymer was precipitated from methanol. Then the crude product was filtered and washed with water and diethyl ether. Finally the Ru(III) terpyridine–polystyrene monocomplex, PS3–2RuCl$_3$, was dried at room temperature under reduced pressure.

2.9. Preparation of PSRuPS-I and PSRuPS-II

PS3–2RuCl$_3$ (50.5 mg, 0.002 mmol) and PS3 (50.7 mg, 0.002 mmol for PSRuPS-I and 105.6 mg, 0.004 mmol for PSRuPS-II) were charged into a 50 mL two-neck-flask with 10 mL ethanol and 20 mL THF. The mixture was deoxygenated by bubbling with argon for 30 min and then heated at 85 °C under argon for 24 h. After *N*-ethylmorpholine (0.15 mL) was added, the mixture was heated at 85 °C for another 24 h. The solution was cooled to room temperature and stirred overnight after NH_4PF_6 (20 mg) was added. All solvents were removed. The product was washed with methanol, water and diethyl ether. Then the solid was dissolved in THF and filtered. After THF was removed, the metallo-supramolecular polystyrenes, PSRuPS-I and PSRuPS-II, were dried at room temperature under reduced pressure.

3. Results and discussion

3.1. Synthesis of bisterpyridine-functionalized CTA

Symmetric trithiocarbonates, RS–C(=S)–SR, can be easily prepared from corresponding halide, RX, but only those having good leaving groups, R, can be used as the RAFT agents [14,15]. When R is benzyl, the corresponding trithiocarbonate is a good CTA for RAFT polymerization of styrene and acrylate [16]. The bisterpyridine-functionalized RAFT agent, 2tpy-TTC, was synthesized from 4′-(4-bromomethylphenyl)-2,2′:6′,2″-terpyridine, in which R is a analogue of benzyl. The observed mass of 2tpy-TTC ($M + H^+ = 753.3$) and elemental analysis result (C 71.37%, H 4.32%, N 11.07%) agreed well with the calculated values ($C_{45}H_{32}N_6S_3$ $m/z = 752.2$, C 71.78%, H 4.28%, N 11.16%). ^{1}H NMR spectra (Fig. 1), ^{13}C NMR spectra (Fig. 2) and melting point also elucidated the structure and purity of 2tpy-TTC. The peak at 222.2 ppm in Fig. 2 was assigned to the C=S group, indicating the formation of the trithiocarbonate.

3.2. Synthesis of bisterpyridine-functionalized telechelic polymers

In order to check the performance of 2tpy-TTC as a RAFT agent, styrene (S) was polymerized by thermal initiation at 110 °C (Scheme 1) and *n*BA was polymerized using 2,2′-azobisisobutyronitrile (AIBN) as an initiator at 60 °C in the presence of 2tpy-TTC, respectively. As shown in Fig. 3a, the semilogarithmic plot of $\ln([M]_0/[M])$ vs reaction time of the RAFT mediated thermal polymerization of S at 110 °C was linear in the region studied (at least up to 54.2% conversion), indicating that the concentration of radical remained constant. It is noteworthy that no inhibition period, which is common for many RAFT mediated polymerizations, was found [10]. However, this phenomena has been observed in some trithiocarbonate mediated polymerizations [12b,12d,16]. It has been found that some factors, like higher temperature, the structure of leaving group of RAFT agent and the feeding ratio, can eliminate the inhibition period [17,18]. The present polymerization was carried out at 110 °C, therefore, no inhibition period is reasonable since the fragmentation of CTA is facilitated at higher temperature. Further more, the trithiocarbonate used in this work might fragmentate faster in initialization period than the macro-RAFT agent does during propagation. As a result, the radical concentration during the initialization period is higher than that during propagation [18]. Another possibility is that the trithiocarbonate decomposes into small thiocompound during higher temperature which retards the followed propagation. As indicated in Fig. 3b, number average molecular weights given by GPC ($M_{n,GPC}$) and by ^{1}H NMR ($M_{n,NMR}$) of the polymers increased linearly as the conversion increased. The above results indicate that the RAFT polymerization of styrene with 2tpy-TTC as a CTA corresponds a controlled polymerization. Some novel telechelic polystyrenes functionalized with the bisterpyridine have been prepared as listed in Table 1.

The terpyridine end group in PS1 can be found at 8.65–8.74 and 7.78–7.94 ppm by comparing the ^{1}H NMR spectra of 2tpy-TTC and PS1 (Fig. 1). Small peak at ca. 3.8 ppm is attributed to the C*H* of the styrene unit adjacent to the trithiocarbonate unit in the PS1. The molecular weight of the PS evaluated by comparing the integrated area of aromatic protons of PS at 6.39–7.26 ppm with that of the terpyridine end at 8.65–8.74 ppm agrees well with that given by GPC using polystyrene as standards, demonstrating the existence of two terpyridines in each polymer chain. But it needs to mention that a small amount of polymer chains might have only one or no terpyridine end group, as expected from RAFT polymerization mechanism, though it is not obviously in this work [7b,11]. To further confirm the telechelic PS had a trithiocarbonate group located in

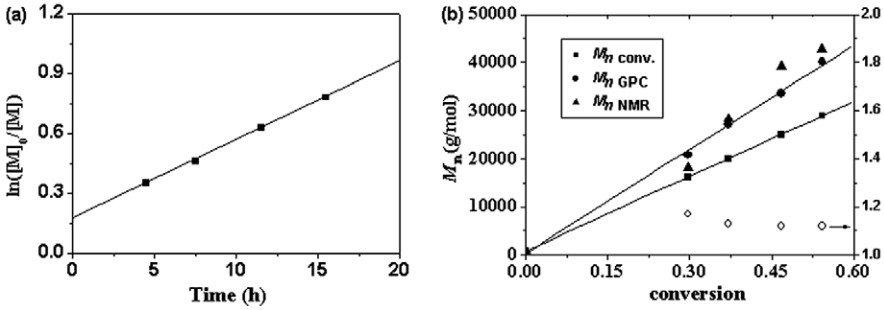

Fig. 3. (a) Dependence of $\ln([M]_0/[M])$ on time and (b) evolution of the molar weights and M_w/M_n with monomer conversion for thermal polymerization of styrene at 110 °C in bulk by bispyridine trithiocarbonate (2tpy-TTC) as a RAFT agent, [S]/[2tpy-TTC] = 500/1.

Table 1
Experimental conditions and characterization for preparing bisterpyridine functionalized homopolymer and triblock copolymer via raft polymerization

Sample	Monomer/CTA/AIBN[a]	CTA	Time (h)	Conv. (%)[b]	M_n[c] (Conv.)	M_n[d] (NMR)	M_n (GPC)	M_w/M_n (GPC)
PS1	500/1/0	2tpy-TTC	11.5	46.8	24,200	39,100	33,600	1.12
PS2	900/1/0	2tpy-TTC	11.0	32.5	31,400	44,500	46,700	1.14
PS3	600/1/0	2tpy-TTC	7.0	29.1	18,900	25,800	25,100	1.16
PS1-*b*-P*n*BA-*b*-PS1	2000/1/1	PS1	9.5	97.7	274,300	309,600	146,700	1.14
P*n*BA1	270/1/0.37	2tpy-TTC	16.0	85.0	30,100	31,500	23,800[e]	1.28
P*n*BA2	150/1/0.25	2tpy-TTC	9.0	60.2	12,300	16,500	13,400[e]	1.34
P*n*BA2-*b*-PS-*b*-P*n*BA2	520/1/0	P*n*BA2	4.5	25.4	29,200	38,400	36,700	1.19

[a] Polymerization of styrene was carried out at 110 °C in bulk, and polymerization of *n*-butyl acrylate was carried at 60 °C in toluene.

[b] Evaluated by $(W_{\text{product}} - W_{\text{CTA}})/W_{\text{monomer}} \times 100\%$, W_{product}, W_{CTA} and W_{monomer} are weight of product, CTA and monomer.

[c] Calculated by $([\text{monomer}]/[\text{CTA}]) \times \text{Conv.} \times M_{\text{monomer}} + M_{\text{CTA}}$, M_{monomer} and M_{CTA} are molecular weight of monomer and CTA.

[d] Evaluated by ^{1}H NMR spectrum: for polystyrene series, $[(A_{6.39-7.26}/5)/(A_{8.65-8.74}/12)] \times 104 + 752$; for P*n*BA series, $[(A_{3.9}/2)/(A_{8.6-8.8}/12)] \times 128 + 752$, $A_{6.39-7.26}$, $A_{8.65-8.74}$, $A_{3.9}$ and $A_{8.6-8.8}$ are integral areas at the region indicated; for triblock copolymers, comparison of the integrated area of peaks at 6.39–7.26 ppm with that at 3.9 ppm was made by using the molecular weight of corresponding macro-CTA. Attribution of proton resonances can be found in Fig. 1.

[e] With a tail.

its center, chain cleavage was made by aminolysis with ethylenediamine in THF at room temperature. The GPC traces of PS2 before and after dealt with ethylenediamine are shown in Fig. 4. The molecular weight of the cleaved PS is half that of PS2 and the polydispersity is narrow. This result clearly reveals that each polymer consists of two PS segments of equal length.

Further more, well-defined P*n*BA functionalized by bisterpyridine has also been synthesized. As shown in Table 1, the molecular weight of P*n*BA calculated by comparing the integrated area of the peaks at 3.9 ppm in ^{1}H NMR spectrum with that at 8.6–8.8 ppm, considering each polymer chain had two terpyridine groups, is consistent with that given by the monomer conversion.

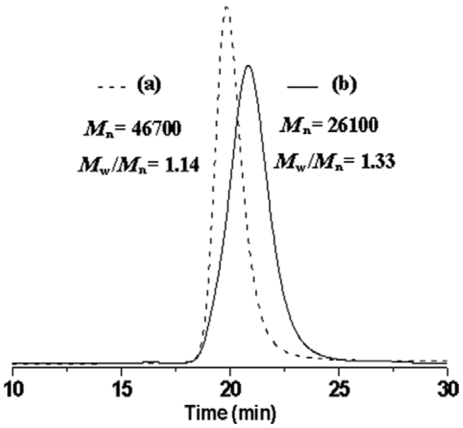

Fig. 4. GPC curves of (a) bisterpyridine functionalized polystyrene PS2 in Table 1 and (b) PS2 treated with ethylenediamine in THF at room temperature.

In order to further clarify the living character of the polymerization, the polystyrene (PS1, listed in Table 1) was used as a macro-CTA for the chain extension with a different monomer, *n*BA. The second monomer would insert into the middle of the macro-CTA, PS1, and PS1-*b*-P*n*BA-*b*-PS1 triblock copolymers could be synthesized. As shown in Fig. 5a, the GPC curve shifted obviously toward shorter elution time and a single narrow peak, signed to the triblock copolymer, was obtained. Combined with the ^{1}H NMR spectra of PS1 and PS1-*b*-P*n*BA-*b*-PS1 in Fig. 1, the formation of block copolymer has been confirmed. On the other hand, well-defined P*n*BA2-*b*-PS-*b*-P*n*BA2 triblock copolymer has been synthesized with P*n*BA2 as a macro-CTA in RAFT polymerization of styrene at 110 °C in bulk (Table 1). The GPC curves shown in Fig. 5b also demonstrate the efficiency of the P*n*BA2 as the macro-CTA of radical polymerization of styrene.

3.3. Preparation of tpy-Ru(II)-tpy complex-connected supramolecular multi-segment PSs

Well-defined PS, P*n*BA and corresponding triblock copolymers with two terpyridine functionalities were successfully prepared. As a ligand that can complex with a series of metal ions such as Fe(II), Ni(II), Co(II), Ru(II), Ru(III), etc., terpyridine–metal complexation has been applied widely in metallo-supramolecular chemistry [6a,8,19]. Ru(III) only forms stable complex with mono-terpyridine unit, Ru(III)-tpy, while Ru(II) tends to form the biscomplex, tpy-Ru(II)-tpy, steadily. Therefore, tpy-Ru(II)-tpy complex-connected multi-segment

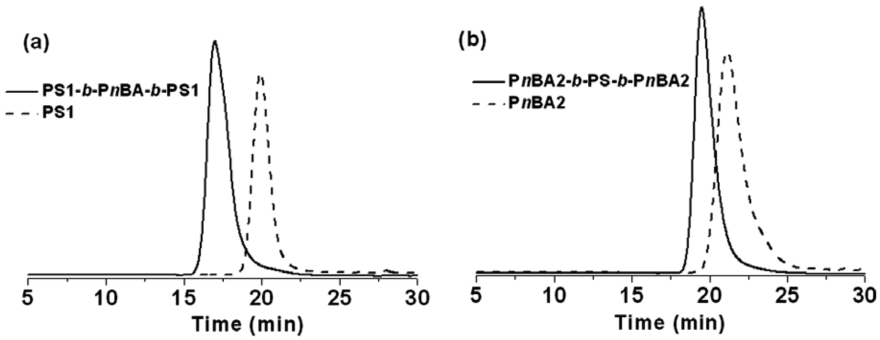

Fig. 5. GPC curves of bisterpyridine functionalized (a) polystyrene PS1 and triblock copolymer PS1-*b*-P*n*BA-*b*-PS1 and (b) poly(*n*-butyl acrylat) P*n*BA2 and triblock copolymer P*n*BA2-*b*-PS-*b*-P*n*BA2 in Table 1.

polymers could be prepared in two steps as shown in Scheme 1.

At first, the bisterpyridine-terminated polystyrene, PS3, was treated with an excess of $RuCl_3 \cdot xH_2O$ at reflux in ethanol/THF to give a monocomplex, PS3–$2RuCl_3$. Then the ethanol/THF (1:2, volume ratio) solutions of PS3–$2RuCl_3$ and PS3 (molar ratio 1:1 or 1:2) were heated at 85 °C under argon atmosphere. Utilizing ethanol as a reducing agent and *N*-ethylmorpholine as a catalyst, consequently, the supramolecular polymers linked by tpy-Ru(II)-tpy complexes could be obtained. In theory, PSRuPS-I (molar ratio: PS3–$2RuCl_3$/PS3 = 1/1) should be a multi-segment polystyrene by a process which is similar to a polycondensation reaction, while PSRuPS-II (molar feed ratio: PS3–$2RuCl_3$/PS3 = 1/2) should be a tri-segment polystyrene. After exchanging the counterions by introducing an excess of NH_4PF_6, the supramolecular PS ruthenium complexes were purified by precipitation in methanol and washed with water and diethyl ether.

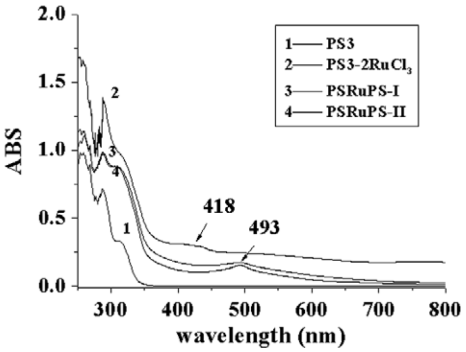

Fig. 6. UV–vis spectra (THF) of terpyridine-functionalized polystyrene, PS3, PS–2Ru(III) complex, PS3–$2RuCl_3$, multi-segment polystyrenes connected with tpy-Ru(II)-tpy complex, PSRuPS-I and PSRuPS-II.

UV–vis spectra of the bisterpyridine-functionalized polystyrene (PS3), the PS–2Ru(III) complex (PS3–$2RuCl_3$) and the multi-segment PS connected with tpy-Ru(II)-tpy complex (PSRuPS-I and PSRuPS-II) were made. As shown in Fig. 6, an absorption at about 493 nm, considered as the typical metal–ligand charge-transfer bond of the tpy-Ru(II)-tpy complex, was found in the curves of PSRuPS-I and PSRuPS-II. In addition, a peak at about 310 nm, attributed to π–π* transitions of the terpyridine ligand, was observed in every curves [20]. The characteristic peak at 418 nm, pointed to the Ru(III)-tpy complex, disappeared after formation of PSRuPS-I and PSRuPS-II, demonstrating the reduction of Ru(III) ions and formation of tpy-Ru(II)-tpy complexation. It is noteworthy that the absorption intensity of PSRuPS-I at 493 nm is different from that of PSRuPS-II when absorption intensity of two suprapolymers at 310 nm is kept the same. This result reveals that PSRuPS-I and PSRuPS-II have different concentrations of tpy-Ru(II)-tpy units while those of terpyridine groups are same. Therefore, multi-segment PSs connected by tpy-Ru(II)-tpy complex were prepared successfully.

To further confirm the formation of the complexation, the size evolution of the polystyrene chelating with Ru ions was studied with dynamic laser scattering (DLS). The values of the hydrodynamic radius (R_h) were calculated from the decay times using the Stokes–Einstein equation. The CONTIN analysis [21] of the DLS correlation functions for PS3, PS3–$2RuCl_3$, PSRuPS-I and PSRuPS-II toluene solutions are shown in Fig. 7. The R_h data of the metal-free polystyrene, PS3, was only ca. 3.2 nm, however, the PS–2Ru(III) complex, PS3–$2RuCl_3$, changed to 41 nm. This change is still unclear, it might result from micellization of PS3–$2RuCl_3$ in toluene owing to its amphiphilic nature. Meanwhile, PSRuPS-II

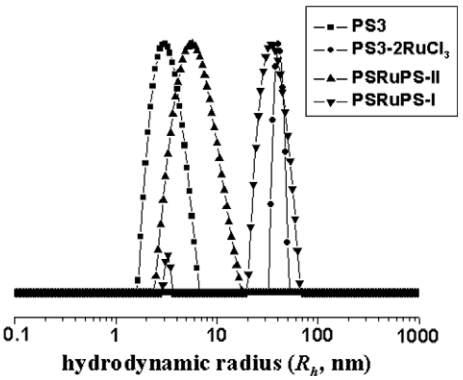

Fig. 7. CONTIN analysis from the DLS correlation functions of toluene solutions of the samples used in Fig. 2. Solution of PS3 was 10 mg/mL and others were 2 mg/mL.

had a R_{h} at about 6.0 nm while PSRuPS-I gave a broad peak at about 35.8 nm. The fact that the R_{h}s of PSRuPS-I and PSRuPS-II are different from that of PS3 strongly supports the formation of the supramolecular polymers. Thus supramolecular metallo-polystyrenes with different length can be prepared with different feed ratio of the PS–2Ru(III) complex and the bisterpyridine-functionalized telechelic PS. Other kinds of $(\mathrm{AB})_n$ type multiblock metallo-polymers can also be synthesized by using different bisterpyridine-functionalized telechelic polymers, such as bisterpyridine-functionalized telechelic P*n*BA homopolymer or P*n*BA-*b*-PS-*b*-P*n*BA triblock copolymer. More detailed research on the structures and properties of these novel metellopolymers is under going.

4. Conclusions

In conclusion, a symmetric bisterpyridine-functionalized trithiocarbonate has been synthesized and used in RAFT polymerization of styrene and *n*BA. Kinetic studies on RAFT thermal polymerization of styrene display a controlled radical polymerization. As a result, well-defined homopolymers and triblock copolymers of their two ends being functionalized with terpyridine groups are synthesized. Furthermore, supramolecular metallo-polystyrenes are prepared by the chelating between the terpyridine units and Ru(II) ions. Since versatile vinylmonomers are available for controlled radical polymerization and the vinylpolymers are very important materials, the polymers functionalized with bisterpyridines as their end groups in this presentation have a great potential for developing metallo-supramolecular chemistry and related materials.

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