Producing Bimodal Molecular Weight Distribution Polymers Through Facile One-Pot/One-Step RAFT Polymerization

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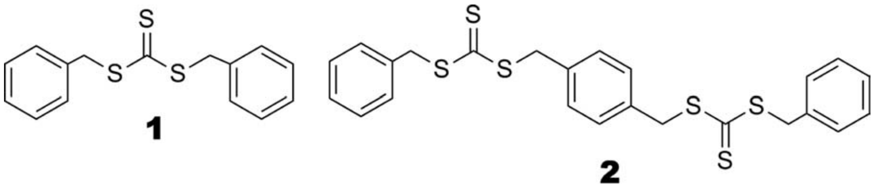
ABSTRACT: Well-defined bimodal molecular weight distribution (MWD) polystyrene and polystyrene-*b*-poly(acrylonitrile) were successfully synthesized using a pair of mono/difunctional trithiocarbonate RAFT agents **1** and **2** via one-pot RAFT polymerization. The kinetics of RAFT polymerization for styrene in bulk with a molar ratio of $[\mathrm{St}]_0$:$[\mathrm{AIBN}]_0$:$[\mathbf{1}]_0$:$[\mathbf{2}]_0 = 1200{:}1{:}2.5{:}2.5$ was studied at 75°C. The results indicated that the system showed excellent controllability and "living" characteristics to both higher and lower molecular weight fractions, providing an efficient and facile way to producing bimodal MWD (co)polymers with both controlled molecular weight (MW) and MWD in molecular level, and the plausible mechanism was discussed in this work. © 2012 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 000: 000–000, 2012

KEYWORDS: bimodal polymer; kinetics (polym.); trithiocarbonate; living radical polymerization; one-pot/one-step method; reversible addition-fragmentation chain transfer (RAFT)

INTRODUCTION The molecular weight (MW) and molecular weight distribution (MWD) of polymers have the key influence over their properties, such as physical properties, mechanical properties, and processing performance. Polymer resins with higher molecular weight (HMW) have higher strength but are difficult to process. On the contrary, lower molecular weight (LMW) polymer resins are endued with good toughness and rheological properties but lower rigidity. For some special end-use, mechanical properties and good processability are both needed. In order to synchronously possess these characteristics, bimodal MWD polymers, which contain both HMW and LMW fraction polymers, effectively balance the processing performance (LMW component) and mechanical performance (HMW component) of materials under extreme conditions.[1,2]

A traditional way to produce bimodal MWD polymer resins is physical blending, namely blending of different polymer resins during the final processing stage. However, in this case, the final performance of the polymer materials might be affected by the much less efficient mixing of the polymer chains. Therefore, there are incentives to produce polymer materials with bimodal MWD polymers at the reaction stage, which provides a common principle: mixing of different polymer materials at the molecular level.[3] Till now, a large number of techniques (e.g., two-step reaction,[4,5] using chain transfer agent[6,7] or cross-linking agent,[8,9] employing mixed catalysts[10]) have been made available for the production of bimodal MWD polymer resins.[3] More recently, an alternative strategy that combines conversional and living radical polymerization (LRP)[11–20] can also be used to produce bimodal MWD polymers.[3,21] For example, Lenzi et al.[3] produced bimodal MWD polymer resins of polystyrene and poly(butyl acrylate) using nitroxide-mediated polymerization combined with conventional free radical polymerization. Wan et al.[21] reported formation of bimodal MWD poly(methyl methacrylate) using controlled radical polymerization catalyzed by CuCl/bis(2-dimethyl-aminoethyl) ether (BDE) complex in aqueous medium. It must be emphasized, however, that all these strategies mentioned earlier have failed to synthesize bimodal MWD polymers with both controlled MW and MWD at the same time, which has been a great challenging topic until now.

Reversible addition-fragmentation chain transfer (RAFT) polymerization, one of the most efficient techniques of LRP, has been widely used for a variety of monomers, providing an efficient way to synthesize well-defined unimodal MWD polymers with designed structures and good controlled MW and narrow MWD.[22–29] However, whether it is possible to synthesize bimodal MWD polymers via the RAFT process remains to be answered. Barner-Kowollik and coworkers simulated a RAFT process where poly-RAFT species and a small molecule RAFT agent could grow simultaneously in the same polymerization system.[30] Very recently, we have reported a novel strategy for the facile synthesis of well-defined bimodal



SCHEME 1 Structures of trithiocarbonates **1** and **2**.

MWD (co)polymers via one-pot RAFT polymerization using a pair of mono- and difunctional dithiocarbamate RAFT agents.[31] Inspired by these results, in this work, we extend this strategy to another type of RAFT agents, a pair of mono- and difunctional trithiocarbonates to synthesize bimodal MWD (co)polymers. Here, monofunctional dibenzyl trithiocarbonates (**1**) and difunctional dibenzyl trithiocarbonates (**2**) (the structures are shown in Scheme 1) were simultaneously added to the RAFT polymerization of the styrene system, and well-defined bimodal MWD polymers with both controlled MW and MWD were obtained successfully.

EXPERIMENTAL

Materials

Unless otherwise specified, all chemicals were purchased from Shanghai Chemical Reagents Co. (Shanghai, China). The monomers, acrylonitrile (AN, +99%), and styrene (St, +99%) were passed through a neutral alumina column and stored at −18°C; 2,2′-Azobisisobutyronitrile (AIBN, chemically pure) was purified by crystallization from chloroform/methanol. α, α′-dibromo-*p*-xylene (+98%) was purchased from TCI and used as received. Benzyl mercaptan (+96%) was purchased from Aldrich and used without further purification. Benzyl bromide (+98%), triethylamine (Et_3N, +99%), carbon disulfide (CS_2, +99%), anisole (+99%), *N, N*-dimethylformamide (DMF, +99%), tetrahydrofuran (THF, +99%), and all other chemicals were used as received unless mentioned.

Synthesis of Dibenzyl Trithiocarbonate (1)

It was prepared according to literature.[32] ^1H NMR (399.97 MHz, $CDCl_3$, δ): 7.41–7.24 (m, 10 H, Ar H); 4.64 (s, 4 H, $ArCH_2$).

Synthesis of Carbonotrithioic Acid, S, S′-[1,4-Phenylenebis(methylene)] S, S′-Dibenzyl Ester (2)

Benzyl mercaptan (2.00 g, 14.70 mmol) was added to a stirred suspension of K_3PO_4 (3.44 g, 16.18 mmol) in acetone (50 mL) followed by stirring for 10 min. CS_2 (3.36 g, 44.12 mmol) was then added and the solution turned bright yellow. After stirring for 10 min, α, α′-dibromo-*p*-xylene (1.94 g, 7.35 mmol) acetone solution was added, and an instant precipitation of KBr and **2** was observed. After stirring for 15 min, the suspension was filtered and the cake was washed with deionized water and acetone several times. Then, a yellow solid was obtained. ^1H NMR (399.97 MHz, $CDCl_3$, δ): 7.42–7.16 (m, 14H, Ar H); 4.63–4.57 (d, 8H, $ArCH_2$); ^{13}C NMR (100.57 MHz, $CDCl_3$, δ): 217.4 (C=S), 129.6 (Ar C), 129.5 (Ar C), 124.4 (Ar C), 124.1 (Ar C), 123.5 (Ar C), 122.6 (Ar C), 36.4 (C—S), 35.8 (C—S).

General Procedure for RAFT Polymerization of St

A typical bulk RAFT polymerization with a molar ratio of $[St]_0:[AIBN]_0:[\mathbf{1}]_0:[\mathbf{2}]_0 = 1200:1:2.5:2.5$ was as follows: A mixture was obtained by adding AIBN (1.19 mg, 0.0073 mmol), **1** (5.26 mg, 0.019 mmol), **2** (9.10 mg, 0.019 mmol), St (1.0 mL, 8.70 mmol) to a dried ampoule with a stir bar. The ampoule was thoroughly bubbled with argon for 20 min to eliminate the dissolved oxygen in the solution. Then the ampoule was flame-sealed and transferred into an oil bath held by a thermostat at 75°C to polymerize under stirring. After the desired polymerization time, the ampoule was cooled by immersing it into iced water. Afterwards, it was opened and the contents were dissolved in THF (~2 mL); the polymerization product of St was dissolved in DMF (~2 mL) and precipitated into a large amount of methanol (~200 mL). The polymer obtained by filtration was dried under vacuum until constant weight at 35°C. The conversion of the monomer was determined gravimetrically.

Typical Procedures for Chain-Extension Reaction and Block Copolymerization Using PS as Macro-RAFT Agent

The PS sample ($M_{n,\ GPC} = 9640/28{,}180$ g mol^{-1}, $M_w/M_n = 1.19/1.12$) obtained with the molar ratio of $[St]_0:[AIBN]_0:[\mathbf{1}]_0:[\mathbf{2}]_0 = 1200:1:2.5:2.5$ was used as the macro-RAFT agent, St, or acrylonitrile (AN) as the monomer and AIBN as the initiator with a molar ratio of $[monomer]_0:[AIBN]_0:[macro\text{-}RAFT\ agent]_0 = 1200:1:2.5$. The polymerization procedure is as follows: PS (174.7 mg, 0.019 mmol) was dissolved in 1.0 mL of anisole or DMF, and then the predetermined quantities of AIBN (1.19 mg, 0.0073 mmol) and the monomer St (1 mL, 8.70 mmol) or AN (1 mL, 15.2 mmol) were added. The rest of the procedure was the same as that described previously.

Aminolysis of Polymer

A solution of PS (0.2 g, $M_{n,\ GPC} = 14{,}980$ g/mol, $M_w/M_n = 1.53$) and 1 mL of hexylamine in THF (2 mL) was stirred at ambient temperature for 24 h under a nitrogen atmosphere. Then the mixture was dropped into a large amount of methanol, and a white solid was precipitated. The solid was washed with water to neutral and re-dissolved in 2 mL of THF, followed by a period of 5 h at 50°C with stirring in the presence of acetic acid (1 mL) and zinc powder (0.5 g). A white solid was obtained after precipitation from methanol, washing with water to neutral, and drying in a vacuum.[33] White powder: yield 0.12 g; $M_{n,gpc} = 13{,}060/5260$ g/mol; $M_w/M_n = 1.09/1.12$.

TABLE 1 RAFT Polymerization of St with Different Amounts of Trithiocarbonates **1** and **2**[a]

Entry	**1/2**	Time (h)	Con. (%)	$M_{n,\ th}$[b] (g/mol)	$M_{n,\ GPC}$ (g/mol)	M_w/M_n
1	2.0/2.0	23	69.4	14,730/29,370	9,910/28,680	1.20/1.08
2	2.5/2.5	23	66.2	11,310/22,540	12,850/35,420	1.19/1.08
3	3.0/3.0	23	57.1	10,140/20,200	8,680/24,740	1.17/1.10

[a] $[St]_0$:$[AIBN]_0$:$[\mathbf{1}]_0$:$[\mathbf{2}]_0$ = 1200/1/*x*/*x* (*x* = 2.0, 2.5, 3.0); temperature = 75°C, in bulk.

[b] $M_{n,\ th}$ (lower MW fraction) = $\{[St]_0/([\mathbf{1}]_0 + 2 \times [\mathbf{2}]_0)\} \times M_{w,\ St} \times$ conversion % + $M_{w,\mathbf{1}}$, $M_{n,th}$ (higher MW fraction) = $2 \times \{[St]_0/([\mathbf{1}]_0 + 2 \times [\mathbf{2}]_0)\} \times M_{w,\ St} \times$ conversion % + $M_{w,\mathbf{2}}$.

Characterization

The number-average molecular weight ($M_{n,\ GPC}$) and molecular weight distribution (M_w/M_n) of the polymers were determined using a Waters 1515 gel permeation chromatograph (GPC) equipped with a refractive index detector (Waters 2414), using HR1, HR2, and HR4 (7.8 × 300 mm^2, 5-mm beads' size) columns with measurable molecular weights in the range of $10^2 - 5 \times 10^5$ g mol^{-1}. THF was used as an eluent at a flow rate of 1.0 mLmin^{-1} operated at 30°C. The GPC samples were injected using a Waters 1515 plus autosampler and calibrated with polystyrene standards from Waters. For PAN, DMF + 0.05 mol/L LiBr was used as an eluent at a flow rate of 0.8 mLmin^{-1} operated at 30°C. The GPC samples were injected using a Waters 1515 plus autosampler and calibrated with polystyrene standards from Waters. ^{1}H and ^{13}C NMR spectra were recorded on an Unity Inova 400 spectrometer (399.97 MHz for ^{1}H, 100.57 MHz for ^{13}C). All spectra were obtained in $CDCl_3$ or $(CD_3)_2SO$ at ambient temperature. Chemical shifts are given in ppm and are referenced to $SiMe_4$ (δ 0.00; ^{1}H, ^{13}C).

RESULTS AND DISCUSSION

Polymerization of St

In this work, we successfully obtained bimodal polymers where both higher and lower molecular weight chains possessed narrow MWDs with AIBN as the initiator; simultaneously we added **1** and **2**—two kinds of CTAs—to the polymerization system in bulk at 75°C. The experimental results shown in Table 1 demonstrate the effect of concentration of trithiocarbonates **1** and **2** on the polymerization of styrene. It is obvious that in the three cases, bimodal MWD polystyrene (PS) with narrow MWDs (M_w/M_n = 1.08–1.20) can be obtained with molecular weights close to their corresponding theoretical values, indicating that it is an effective and facile strategy to produce bimodal MWD polymers. In addition, from Table 1, the polymerization was better controlled with the molar ratio of $[St]_0$:$[AIBN]_0$:$[\mathbf{1}]_0$:$[\mathbf{2}]_0$ = 1200:1:2.5:2.5, and so this feed ratio was intensively investigated in this work.

In order to further investigate the polymerization behavior, the kinetics of RAFT polymerization of St was studied in detail. Figure 1(a) shows the kinetic plots of polymerization of St in bulk initiated by AIBN in the presence of RAFT agents with a ratio of $[St]_0$:$[AIBN]_0$:$[\mathbf{1}]_0$:$[\mathbf{2}]_0$ = 1200:1:2.5:2.5 at 75°C. The linearity of the plot indicates that the polymerization was approximately first-order with respect to the monomer concentration and that the number of active species remained constant during the polymerization process. Evolution of M_n with conversion was found to be linear as shown in Figure 1(b). At the same time, experimental M_w/M_n, values were narrow, indicating a well-controlled polymerization process. All the evidences demonstrated the features of "living"/controlled radical polymerization of this polymerization system.

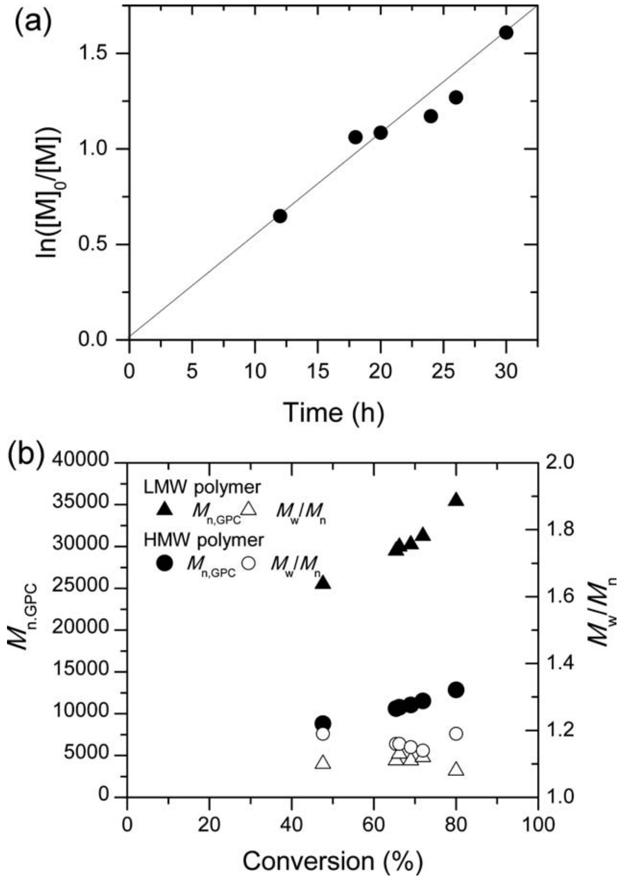


FIGURE 1 ln($[M]_0$/[M]) as a function of time (a) and average-number molecular weight ($M_{n,\ GPC}$) and molecular weight distribution (M_w/M_n) versus conversion (b) for the bulk RAFT polymerization of St. Polymerization conditions: $[St]_0$:$[AIBN]_0$:$[\mathbf{1}]_0$:$[\mathbf{2}]_0$ = 1200:1:2.5:2.5, V_{St} = 1 mL, temperature = 75°C.

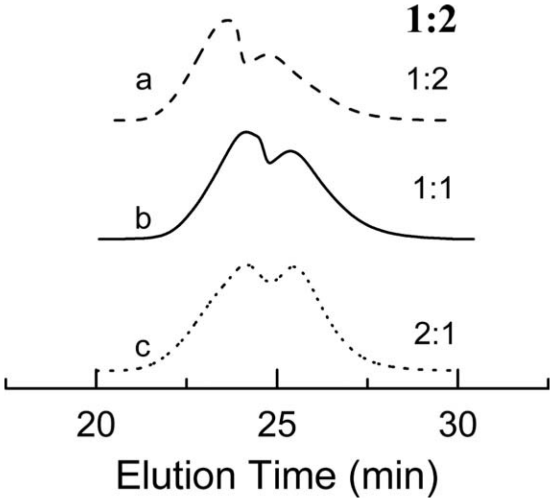


FIGURE 2 GPC curves of obtained polystyrenes using different molar ratios of **1**/**2**. (a) $[St]_0$:$[AIBN]_0$:$[\mathbf{1}]_0$:$[\mathbf{2}]_0$ = 1200:1.66:2.5:5; (b) $[St]_0$:$[AIBN]_0$:$[\mathbf{1}]_0$:$[\mathbf{2}]_0$ = 1200:1:2.5:2.5; (c) $[St]_0$:$[AIBN]_0$:$[\mathbf{1}]_0$:$[\mathbf{2}]_0$ = 1200:1.33:5:2.5; V_{St} = 1 mL, in bulk, temperature = 75°C.

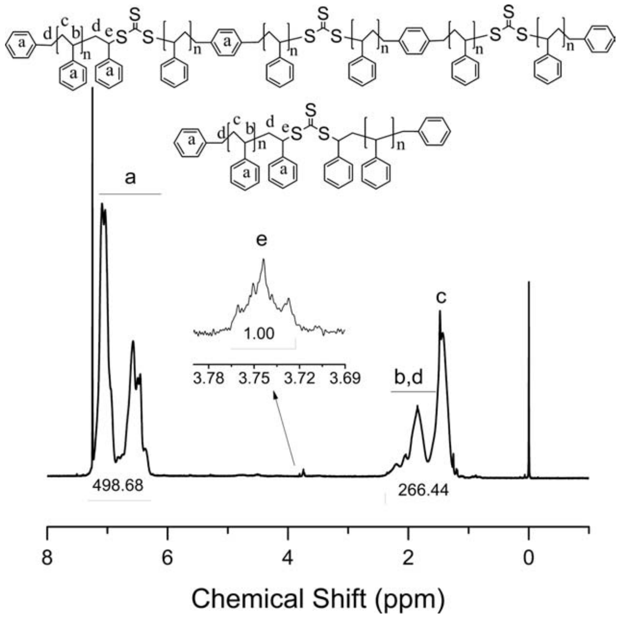


FIGURE 3 ^{1}H NMR spectrum of PS ($M_{n,\ GPC}$ = 9640/28,180 g mol^{-1}, M_w/M_n = 1.19/1.12) with $CDCl_3$ as a solvent and TMS as a internal standard. Polymerization conditions: $[St]_0$:$[AIBN]_0$:$[\mathbf{1}]_0$:$[\mathbf{2}]_0$ = 1200:1:2.5:2.5, V_{St} = 1.0 mL, in bulk, temperature = 75°C.

Figure 2 shows the GPC curves of the obtained polystyrenes via RAFT polymerization with different molar ratios of **1/2** (1:2, 1:1, and 2:1, respectively) using St as the monomer and AIBN as the initiator at 75°C. From Figure 2, it can be seen that two peaks (representing higher molecular weight and lower molecular weight polymer chains, respectively) were discernable and that the corresponding peak areas shifted with the molar ratios, indicating that the proportion of lower and higher molecular weight polymer chains can be adjusted by the feed ratio of RAFT agents **1** and **2**. After further changing of the molar ratio of **1** and **2** (Table 2), lower and higher molecular weight exhibited the same multiple relationship, while the peak coverage areas changed from 0.0% to 74.5% for the lower molecular weight fraction. In addition, it can be seen that the experimental mass concentrations were close to their corresponding theoretical values from 4.8% to 83.3%. Thus, the proportion of lower and higher molecular weight polymer chains could be easily adjusted by changing the feed molar ratio of **1** and **2**.

Analyses of (Co)polymer Structures and Chain-Extension or Block Copolymerization

To investigate the "living" features of RAFT polymerization for the synthesis of bimodal MWD polymers, the obtained PS ($M_{n,\ GPC}$ = 9640/28,180 g mol^{-1}, M_w/M_n = 1.19/1.12) was analyzed by ^{1}H NMR spectroscopy. The chemical shifts at 6.10–7.46 ppm (***a*** in Fig. 3) corresponded to the aromatic protons of the RAFT agent moieties and PS chains. The chemical shifts at 1.63–2.39 ppm (***b*** and ***d*** in Fig. 3) are assigned to the methylene protons of the RAFT agent moieties and methyne protons in the PS main chains. The

TABLE 2 Effect of Feed Molar Ratio of Trithiocarbonates **1** and **2** on RAFT Polymerization of St[a]

Entry	R[b]	Time (h)	Con. (%)	$M_{n,\ th}$ (g/mol)	$M_{n,\ GPC}$ (g/mol)	M_w/M_n	m_{th}[c] (%)	m_{GPC}[d] (%)
1[e]	1/1	23	66.2	11,310/22,540	12,850/35,420	1.19/1.08	33.3	40.9
2[f]	1/2	23	55.1	11,290/22,500	16,600/36,190	1.19/1.06	20	29.3
3[g]	1/4	23	74.4	8,540/17,010	12,910/25,110	1.17/1.05	11.1	19.2
4[h]	1/10	23	69.8	8,580/17,090	16,900	1.55	4.8	0.0
5[i]	2/1	23	51.5	13,130/26,200	11,930/31,970	1.10/1.17	50	47.0
6[j]	4/1	23	58.4	10,010/19,950	9,580/31,610	1.21/1.17	66.7	60.4
7[k]	10/1	23	50.9	10,860/21,650	8,420/22,890	1.24/1.18	83.3	74.5

[a] Polymerization temperature = 75°C, in bulk.

[b] $R = [\mathbf{1}]_0/[\mathbf{2}]_0$.

[c] m_{th} (%) = $R/(R + 2) \times 100\%$, theoretical mass concentration (%) of PS with lower molecular weight calculated by the feed molar ratio R.

[d] m_{GPC} (%) = $A_{LMW}/(A_{HMW} + A_{LMW}) \times 100\%$, mass concentration (%) of PS with lower molecular weight calculated by the corresponding peak area (A) measured by GPC.

[e–k] $[St]_0$:$[AIBN]_0$:$[\mathbf{1}]_0$:$[\mathbf{2}]_0$ = 1200:1:2.5:2.5, 2400:1.66:2.5:5, 2400:2.99:2.5:1, 2400:2.86:1.0:10, 2400:1.33:5:2.5, 2400:2.00:10:2.5, and 2400:1.74:10:1, respectively.

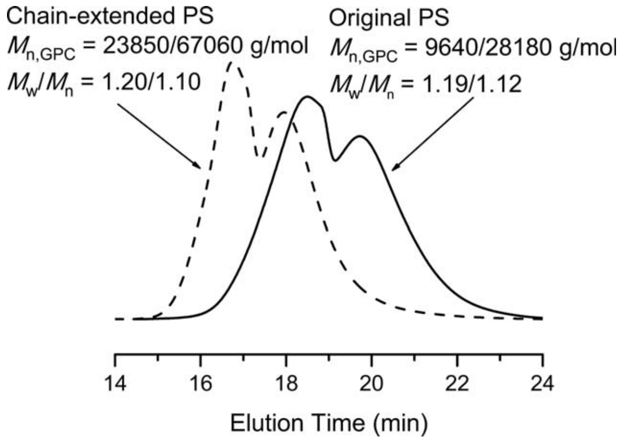


FIGURE 4 GPC curves of before and after chain extension using PS prepared by RAFT polymerization. Original PS: $[St]_0$:$[AIBN]_0$:$[\mathbf{1}]_0$:$[\mathbf{2}]_0$ = 1200:1:2.5:2.5, V_{St} = 1 mL, in bulk, temperature = 75°C, time = 18 h, conversion = 62.0%. Chain extended PS: $[St]_0$:$[AIBN]_0$:$[PS]_0$ = 1200:1:2.5, V_{St} = 1 mL, $V_{anisole}$ = 1 mL, temperature = 75°C, time = 24 h.

chemical shifts at 0.92–1.63 ppm (***c*** in Fig. 3) are assigned to the methylene protons in the PS main chains. The chemical shifts at 3.74 ppm (***e*** in Fig. 3) are attributed to the methyne protons in the chain of PS because of the influence of S atom, which indicates that the trithiocarbonate moieties were successfully maintained in the polymer chains. Therefore, the obtained PS can be used as macro-RAFT agents to conduct chain-extension reaction and block copolymerization. The PS ($M_{n,\ GPC}$ = 9640/28,180 g mol^{-1}, M_w/M_n = 1.19/1.12) obtained in the presence of thermal free radical initiators (AIBN) was used as the macro-RAFT agents, St and acrylonitrile (AN) as the monomers, AIBN as the initiator, with a molar ratio of $[monomer]_0$:$[AIBN]_0$:$[macro\text{-}RAFT\ agent]_0$ = 1200:1:2.5. There was a peak shift from the macro-RAFT agents to the chain-extended PS with $M_{n,\ GPC}$ = 23,850/67,060 g/mol and M_w/M_n = 1.20/1.10 (Fig. 4). As shown in Figure 5, bimodal block copolymer PS-*b*-PAN was also obtained successfully. This block copolymer ($M_{n,\ GPC}$ = 20,620/61,070 g mol^{-1}, M_w/M_n = 1.20/1.07) was analyzed by ^1H NMR spectroscopy. The chemical shifts at 6.10–7.46 ppm (***a*** in Fig. 6) corresponded to the aromatic protons of the RAFT agent moieties and PS main chains. The chemical shifts at 1.63–1.93 ppm (***b*** in Fig. 6) were assigned to the methyne protons in the PS main chains. The chemical shifts at 0.92–1.63 ppm (***c*** in Fig. 6) were assigned to the methylene protons in the PS main chains. The chemical shifts at 3.00–3.26 ppm (***d*** in Fig. 6) were assigned to the methyne protons in the PAN chains. The chemical shifts at 1.93–2.26 ppm (***e*** in Fig. 6) were assigned to the methylene protons in the PAN chains. The chemical shift at 3.38 ppm (***f*** in Fig. 6) is attributed to the methyne protons in the chain of PAN because of the influence of S atom, which indicates that after block copolymerization the trithiocarbonate moieties were still maintained in the polymer chains. The successful chain extension reaction and block copolymerization further verified the "living" features of RAFT polymerization of St.

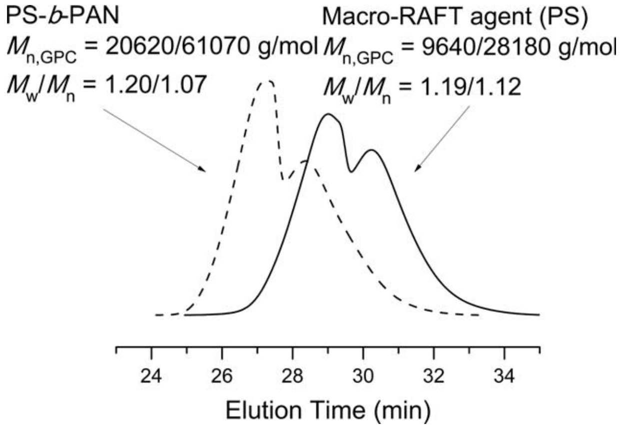


FIGURE 5 GPC curves before and after block copolymerization with bimodal PS as macro-RAFT agent. Polymerization conditions: $[AN]_0$:$[AIBN]_0$:$[PS]_0$ = 1200:1:2.5, V_{AN} = 1.0 mL, V_{DMF} = 1.0 mL, temperature = 75°C, time = 24 h.

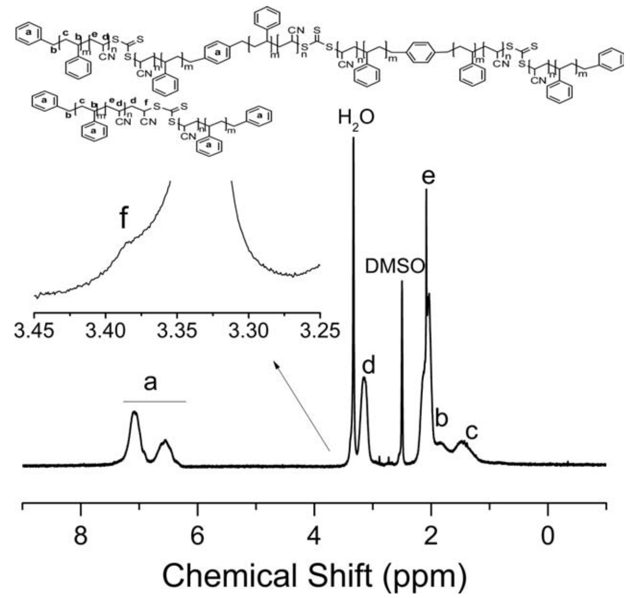
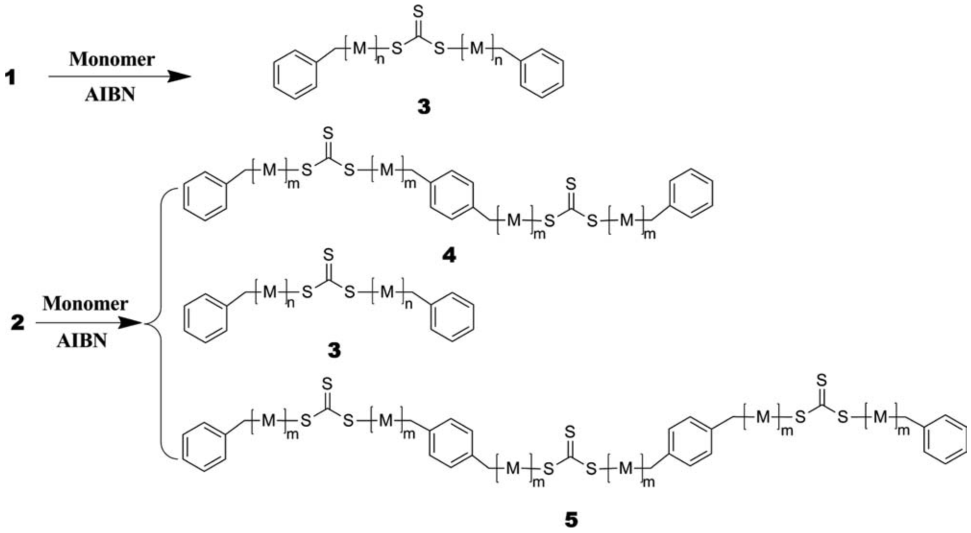


FIGURE 6 ^1H NMR spectrum of PS-*b*-PAN ($M_{n,\ GPC}$ = 20,620/61,070 g mol^{-1}, M_w/M_n = 1.20/1.07) with $(CD_3)_2SO$ as a solvent and TMS as an internal standard. Polymerization conditions: $[AN]_0$:$[AIBN]_0$:$[PS]_0$ = 1200:1:2.5, V_{AN} = 1.0 mL, V_{DMF} = 1.0 mL, temperature = 75°C.

Plausible Polymerization Mechanism for the Bimodal MWD Polymers

As simulated by Barner-Kowollik[30] and reported by our previous work,[31] the propagating radicals with different chain length could grow simultaneously in a same RAFT process. In this work, two RAFT agents, one monofunctional dibenzyl trithiocarbonate **1** and another difunctional trithiocarbonate **2** were simultaneously added into the RAFT polymerization system. According to the RAFT mechanism using trithiocarbonates as the RAFT agents,[34] monofunctional dibenzyl



SCHEME 2 Plausible polymer structures with different trithiocarbonates **1** and **2**.

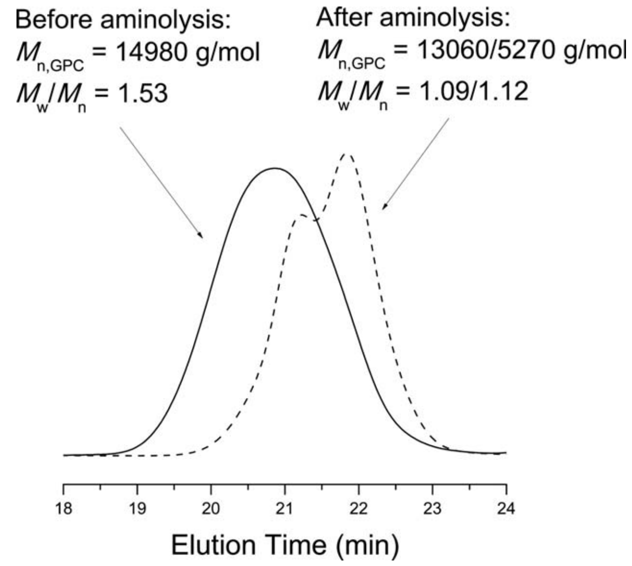
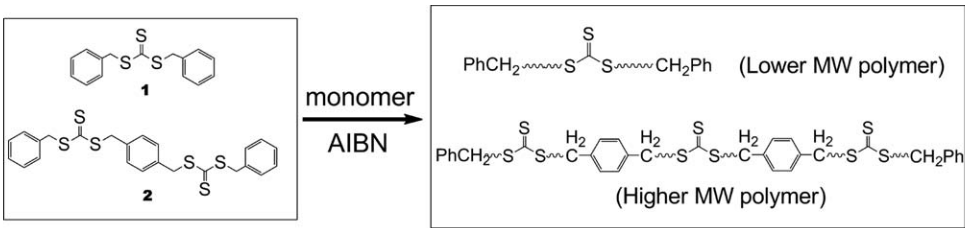


FIGURE 7 GPC curves of before and after aminolysis of the polymer (PS). Polymerization condition: $[\mathrm{St}]_0/[\mathrm{AIBN}]_0/[2]_0$ = 600:0.67:2.5, temperature = 75°C.

trithiocarbonate **1** should give rise to polymer with structure **3**; Similarly, difunctional trithiocarbonate **2** should grow in four directions, yielding polymers with structure **4**, as shown in Scheme 2. However, in this work, the molecular weights of HMW chains was almost three times (not twice) those of LMW chains in most cases, which indicated that the mechanism is more complicated than the hypothesis as reported by our previous work, where a pair of mono- and difunctional dithiocarbamate RAFT agents was used.[31] To further investigate the possible mechanism, the polymerization of St was conducted using difunctional trithiocarbonate **2** as the RAFT agent solely at 75°C. As shown in Figure 7, it was found that a bimodal MWD polymer with $M_{\mathrm{n,\ GPC}} = 13{,}060/5260$ g/mol and $M_{\mathrm{w}}/M_{\mathrm{n}} = 1.09/1.12$ was obtained after aminolysis of the obtained PS ($M_{\mathrm{n,\ GPC}} = 14{,}980$ g/mol, $M_{\mathrm{w}}/M_{\mathrm{n}} = 1.53$, polymerization condition: $[\mathrm{St}]_0/[\mathrm{AIBN}]_0/[\mathbf{2}]_0 = 600{:}0.67{:}2.5$, polymerization time = 15 h), which indicated that there exist several kinds of moieties of PS chains with different molecular weights from polymers with structures **3**, **4**, and **5**, as shown in Scheme 2. This is attributed to the fact that the polymers obtained from the difunctional RAFT agent having symmetrical trithiocarbonate should contain not only polymer **4** but also shorter polymer **3** and longer polymers (i.e., structure **5**) because scrambling of the growing chain would occur during polymerization. On the other hand, from the experimental results mentioned earlier, simultaneously adding RAFT agents **1** and **2** to the polymerization system can actually result in bimodal MWD polymers with HMW chains being almost three times those of LMW chains and low molecular weight distributions; therefore, it is possible that polymers **3** and **5** are main product in this case, as shown in Scheme 3.



SCHEME 3 Schematic diagram illustrating the process for preparing bimodal MWD polymers.

CONCLUSIONS

Bimodal MWD polymers were successfully synthesized using a pair of mono/difunctional trithiocarbonate RAFT agents **1** and **2** via one-pot RAFT polymerization. The system showed excellent controllability and "living" characteristics to both higher and lower molecular weight fractions, providing an efficient and facile way to producing bimodal MWD polymers with both controlled MW and MWD in the molecular level.

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