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Synthesis of azobenzene-centered (co)polymers via reversible addition-fragmentation chain transfer (RAFT) polymerization

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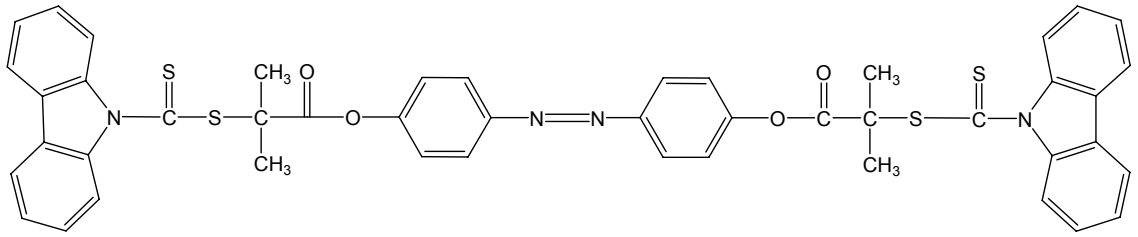
Abstract: An azobenzene-based dithiocarbamate, 4,4'-bis[2-(carbazole-N-dithio formatyl)-2-methyl-propionatyl]-azobenzene (CDMPA), was synthesized and used as the chain transfer agent (CTA) for reversible addition-fragmentation chain transfer (RAFT) polymerization of styrene in anisole solution. Well-defined azobenzene-centered and carbazole-ended polystyrene (PS) with well-controlled molecular weight (M_n) and narrow molecular weight distributions (M_w/M_n) was obtained. The good agreement between the theoretical molecular weight ($M_{n,th}$) and the 1H NMR determined molecular weight ($M_{n,NMR}$) indicated that most of the polymer chains contained an azo-functional center-group end-capped with the carbazole moieties, which were derived from the RAFT agent. The obtained polystyrene (PS) showed a strong ultraviolet absorption in tetrahydrofuran (THF) and emitted fluorescence after excited by UV-irradiation in N,N'-dimethyl formamide (DMF) solutions. The PS was used as the macro-RAFT agent to carry out the polymerization of methyl acrylate (MA) and N-isopropylacrylamide (NIPAAM). Triblock copolymers (PMA-b-PS-b-PMA), and pentablock copolymers (PNIPAAM-b-PMA-b-PS-b-PMA-b-PNIPAAM) were obtained, respectively. These copolymers were characterized by gel permeation chromatography (GPC), FT-IR spectroscopy and NMR spectroscopy.

Introduction

The "living"/controlled radical polymerization (LRP) [1-7] has become a powerful tool in the preparation of well-defined polymers, which mainly include nitroxide-mediated polymerization (NMP) [8], atom transfer radical polymerization (ATRP) [9-11] and reversible addition-fragmentation chain transfer (RAFT) [1, 2, 12-15] polymerization. Among these LRP methods, RAFT polymerization is a much better way to synthesize polymers with a wide range of monomers, versatile polymerization conditions, and well-designed architectures. The successful operation of RAFT polymerization depends on the use of a highly efficient RAFT agent, such as dithioester [1], xanthate [16], trithiocarbonate [17, 18], and dithiocarbamate [19], etc. RAFT polymerization can be applied to the polymerization of (methyl) acrylate monomers with different functional ester group to prepare functional polymers [20], and was also demonstrated as an efficient technique to prepare block copolymers under controlled manner. In addition, if a functional compound is used as the chain transfer agent (CTA) for RAFT polymerization, the fragment of RAFT agent will remain at the end of polymeric chain. As the result, polymers with terminal functionality can be prepared, which provides another way to prepare functional polymers [21, 22].

Following this way, a large number of block copolymers have been synthesized via RAFT process by employing mono- or bis-functional RAFT agent. The use of a bis-functional RAFT agent as a triblock precursor means that tri-block copolymers can be accomplished in two polymerization steps, and three polymerization steps for penta-block copolymers. Meanwhile, the blocks with same length and composition are symmetrically distributed at the two directions of polymer chains [12, 23]. Earlier efforts on the synthesis of triblock copolymers using bis-RAFT agent [24-28] have been reported.

In this work, a novel dithiocarbamate, 4,4'-bis[2-(carbazole-*N*-dithioformatyl) -2-methyl-propionatyl]-azobenzene (CDMPA), was synthesized and used as a bis-functional RAFT agent for the thermally initiated RAFT polymerization of styrene to examine the effectiveness for the controlled polymerization of styrene. The polymerization finally yielded the polystyrene (PS) with predetermined molecular weights and narrow molecular weight distributions. The obtained PS chains contained an azo-functional center-group and were end-capped with the carbazole moieties. The carbazole group is a well known fluorescence functional group [29] and the azo-benzene group shows cis- to trans- transformation under UV-irradiation [30, 31]. Thus, with the terminal carbazole group, it provides the possibility to monitor the cis- to trans- transformation of azo-group through fluorescence. Furthermore, the PS was then used as a macro-RAFT agent to synthesize tri-block copolymer (PMA-*b*-PS-*b*-PMA), and penta-block copolymer (PNIPAAM-*b*-PMA-*b*-PS-*b*-PMA-*b*-PNIPAAM). The structure of CDMPA is shown in Scheme 1.



Scheme 1. Chemical structure of the RAFT agent 4,4'-bis[2-(carbazole-*N*-dithioformatyl)-2-methyl-propionatyl]-azobenzene (CDMPA).

Results and discussion

Living polymerization of styrene with CDMPA as the RAFT agent

The RAFT polymerization of styrene was carried out with thermal initiation using CDMPA as the RAFT agent in anisole solution (50% v/v) at 110 ^{o}C. The plots of $\ln([M]_0/[M])$ (where $[M]_0$ is the initial monomer concentration and [M] is the monomer concentration, respectively) and conversion versus polymerization time are shown in Fig. 1. The linear relationships between $\ln([M]_0/[M])$ and polymerization time indicated that the polymerizations were first-order reactions with respect to the monomer concentration. The concentration of propagating radicals remained almost constant during the polymerization process. There was no visible inhibition period during the polymerizations. The number-average molecular weights (M_ns) and molecular weight distributions (M_w/M_n) are shown in Fig. 2 along with monomer conversion. The molecular weights measured by GPC ($M_{n,GPC}$) increased linearly with the monomer conversion and was very close to the theoretical molecular weight ($M_{n,th}$, $M_{n,th}$ = $[\text{styrene}]_0/[\text{CDMPA}]_0$ × Conversion × M_{styrene} + M_{CDMPA}). However, because of the

irreversible chain termination and other side reactions [12], the molecular weights increased a little and the M_w/M_n value became a little broader at high conversions. Thus, all results demonstrated that the CDMPA was an effective RAFT agent for the polymerization of styrene.

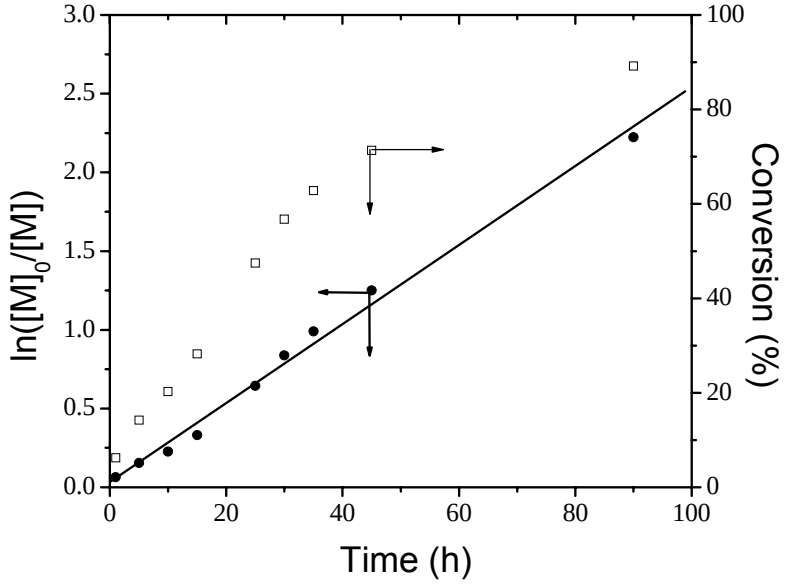


Fig. 1. Kinetic plots for the polymerizations of styrene with thermal initiation using CDMPA as the RAFT agent in anisole solution (50% v/v) at 110 °C, $[Styrene]_0$: $[CDMPA]_0$ = 300 : 1, $[Styrene]_0$ = 21.7 mmol, $[CDMPA]_0$ = 72.5 μmol.

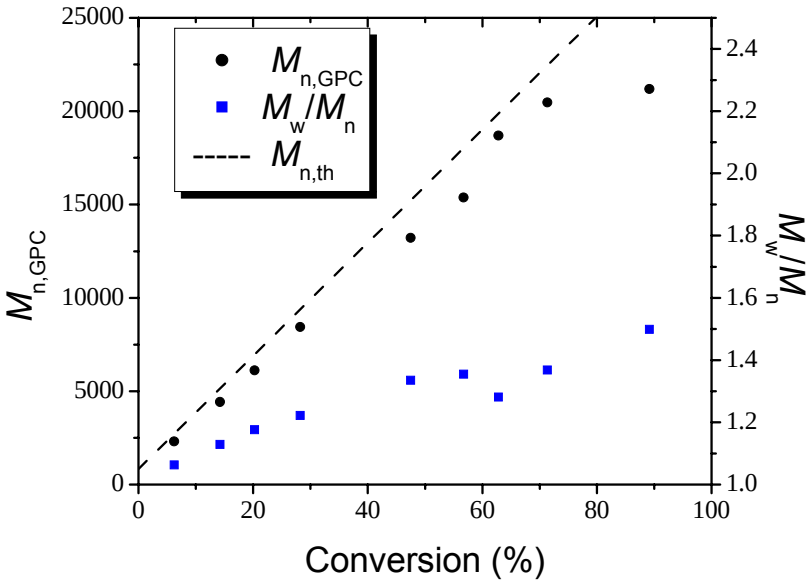


Fig. 2. Evolution of $M_{n,GPC}$ and M_w/M_n with the conversion for the polymerizations of St with CDMPA as the RAFT agent, the conditions are same as those in Fig. 1.

End-group analysis and chain-extension reaction

To confirm the existence of the carbazole and azo-benzene moieties derived from CDMPA in the polymer chain, the obtained PS was analyzed by ^{1}H NMR. The resultant ^{1}H NMR spectrum of PS is shown in Fig. 3. The resonances of chemical shift δ = 8.17, 7.81 and 7.35 ppm can be assigned to the aromatic protons at carbazole functional group (labeled as a, b, and c), which were derived from the RAFT agent CDMPA. The signals of δ = 7.95 ppm can be assigned to aromatic protons of the phenyl group from the azo-functional group (labeled as f). The signals at δ = 0.82-1.22 ppm can be assigned to the methyl protons of the R group of CDMPA (labeled as e). The signals at δ = 1.22-2.10 ppm and at δ = 4.57-4.94 ppm represented methylene and methenyl protons from styrene. The appearance of carbazole and azobenzene proton signals in ^{1}H NMR of obtained PS means these groups, which were derived from RAFT agent, has remained in the polymer chain after polymerization. Furthermore, the integral value of resonances labeled as f can be used to calculate the molecular weight ($M_{n,NMR}$) of obtained PS with the assumption that each PS chain was centered by an azo-benzene group derived from the RAFT agent. The equation is showed follows [28]:

$$M_{n,NMR} = \left(\frac{I_{1.22-2.10}}{3} \Big/ \frac{I_{7.95}}{4} + \frac{I_{4.57-4.94}}{2} \Big/ \frac{I_{7.95}}{4} \right) \times MW_{styrene} + MW_{CMAMP}$$

Where, $I_{1.22\text{-}2.10}$ is the integral of the signals at 1.22-2.10 ppm; $I_{4.57\text{-}4.94}$ is the integral of the signals at 4.57-4.94 ppm; $I_{7.95}$ is the integral of the signals at 7.95 ppm. The result of the molecular weight calculated from the ^{1}H NMR spectroscopy ($M_{n,NMR}$) was 3300 g/mol, which is very close to the theoretical molecular weight, 3400 g/mol. The good agreement between $M_{n,th}$ and $M_{n,NMR}$ showed that most of the PS chain containing the azo-benzene functional group at the chain center, were derived from CDMPA.

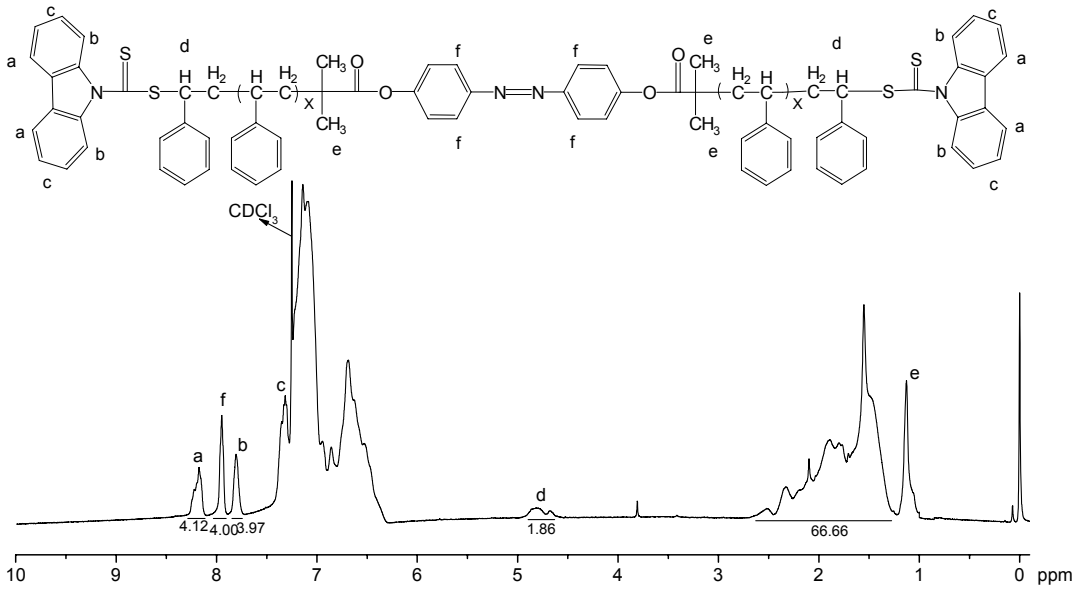


Fig. 3. Structure and ^{1}H NMR spectrum of PS obtained from the RAFT polymerization using CDMPA as the RAFT agent. $M_{n.GPC}$ = 3000 g/mol and M_w/M_n = 1.06.

The PS end-capped with the CDMPA moiety was used as a macro-RAFT agent to carry out the chain-extension reaction. A typical chain-extension reaction was carried out by the addition of fresh styrene monomer with $[Styrene]_0 : [PS]_0 = 300 : 1$ at 110 °C for 12 h, and resulted in a 33.7% conversion. The GPC traces of the original and the extended polymer are shown in Fig. 4. There was an obvious peak shift from the macro-RAFT agent to the product with the molecular weight increasing from 4600 to 18100 g/mol. The peak of the original polymer disappeared in the GPC trace of chain-extended polymer, which indicated the occurrence of chain extension reaction. However, the molecular weight distribution of the chain-extended product was broader (1.32) than that of the original polymer (1.15), which might be caused by dead polymer chains existing in the original polymer [32, 33]. This evidence showed that the RAFT polymerization of styrene with CDMPA as the RAFT agent was well controlled and consistent with the RAFT mechanism.

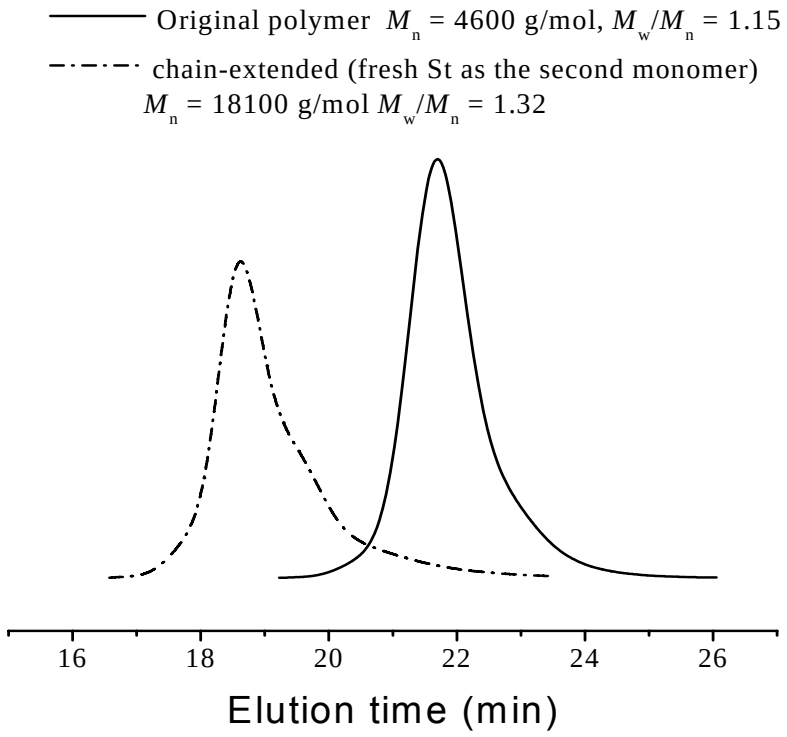


Fig. 4. GPC traces of the original polymer and the chain extended polymer.

Spectroscopic analysis of the azobenzene and carbazole functionalized polymers

There are azo-benzene and carbazole moieties in the RAFT agent (CDMPA) structure. According to the RAFT polymerization mechanism, the obtained polymer chains will contain an azo-functional center-group and is end-capped with the carbazole moieties when using CDMPA as the RAFT agent. The evidences showed in the NMR and chain-extension also demonstrated the same results. The measurement of UV spectroscopy of carbazole, the azobenzene-based RAFT agent and the corresponding polymers in THF were carried out. Fig. 5 shows the UV spectra of carbazole, CDMPA and the corresponding PS. The first peak appeared in the wavelength region (ca. 240-250 nm) corresponded to the absorption of the biphenyl

moiety [34], both CDMPA and the corresponding polymers appeared at the characteristic intense π–π^* transition of azobenzene at round 320 nm, corresponding to the absorption by the azobenzene moiety [31, 35]. Furthermore, as shown in Fig. 5, the absorption intensity of CDMPA and the corresponding polymer displayed no significant difference in the same concentrations. On the other hand, the molecular weight also had no apparent effect on the UV absorption intensity. These results further indicated that almost each polymer chain centered with azobenzene moiety was derived from the R group of CDMPA.

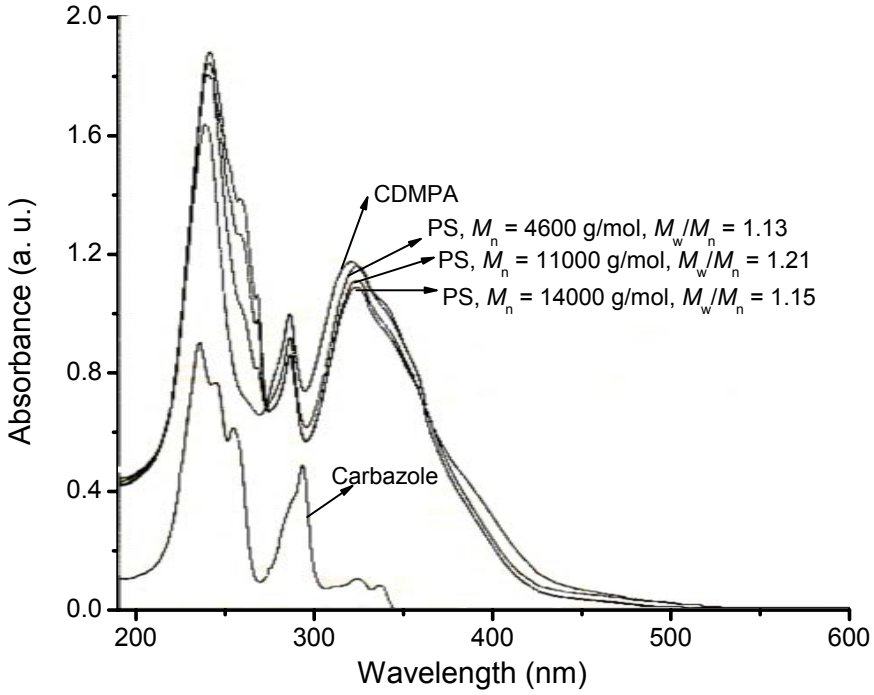


Fig. 5. UV–vis spectra of azo-functionalized CDMPA and PS in THF solution. The solution concentration was 3×10^{-5} mol·L^{-1} (azobenzene unit).

In addition, carbazole is one of typical groups which shows strong fluorescence. The carbazole structure has been selected as the Z group in CDMPA. The final polymers would be end-capped with the moiety of RAFT agent, which was confirmed in the ^{1}H NMR spectrum of PS (Fig. 3). Fig. 6 shows the fluorescence emission spectra of CDMPA and PS-attached carbazole unit dissolved in DMF at room temperature with excitation wavelength λ_{ex} = 293 nm. The result showed that the RAFT agent end-labeled with carbazole moiety exhibited strong fluorescence emission in a short wavelength region, and the fluorescence maximum wavelengths were 365 nm. While, it could also be found that the RAFT agent exhibited apparently higher fluorescence emission under the same concentration according to the obtained PS. This may be due to the structural self-enhancement effect and formation of intermolecular or intramolecular exciplex between electron-deficient chromophore (e.g. the azobenzene group) and electron-donating carbazole group [36-40] in the CDMPA. This self-enhancement intermolecular effect would be reduced to a low level or even disappear in the obtained polymer due to the insertion of polystyrene chain between the azobenzene and carbazole group [41]. A long soft polystyrene chain increases the

proximity chance of azobenzene and carbazole group which resulted in an enhancement in the fluorescence of large molecular weight polymer, as shown in Fig. 6.

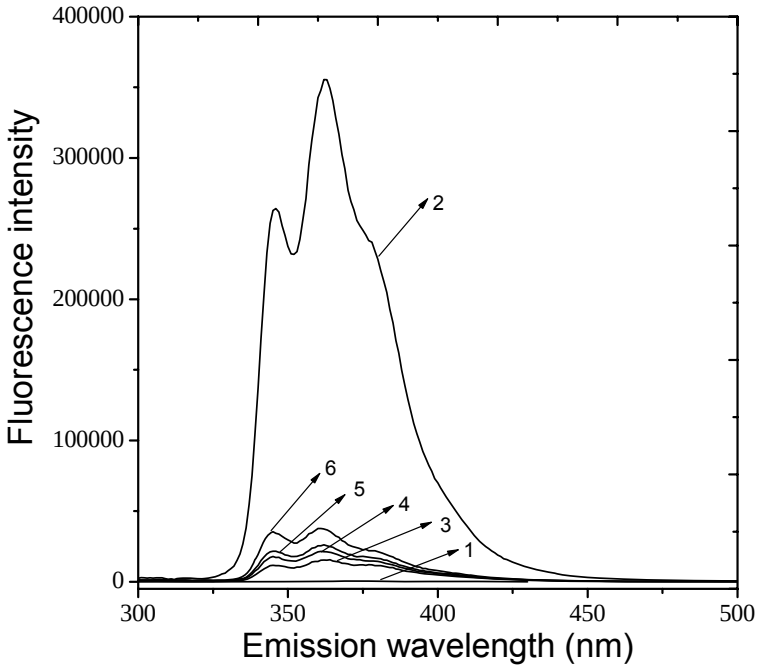


Fig. 6. Fluorescence spectra of CDMPA and PS in DMF at room temperature. The concentration was 1×10^{-4} mol·L^{-1} (carbazole unit); the excitation wavelength was 293 nm. (1) DMF solvent; (2) CDMPA; (3) PS: $M_{n,GPC}$ = 2400 g/mol, M_w/M_n = 1.05; (4) PS: $M_{n,GPC}$ = 5600 g/mol, M_w/M_n = 1.10; (5) PS: $M_{n,GPC}$ = 8100 g/mol, M_w/M_n = 1.11; (6) PS : $M_{n,GPC}$ = 9300 g/mol, M_w/M_n = 1.27.

Synthesis of the multiblock copolymers

With the well-controlled RAFT polymerization technique, using a bis-functional RAFT agent as precursor, the triblock and pentablock copolymers, both arms with same length and composition, can be obtained in two polymerization steps and three polymerization steps, respectively. The obtained PS was then used as a macro-RAFT agent to synthesize tri-block copolymer (PMA-*b*-PS-*b*-PMA), with methyl acrylate (MA) as the second comonomer, and penta-block copolymer (PNIPAAM-*b*-PMA-*b*-PS-*b*-PMA-*b*-PNIPAAM), with MA and *N*-isopropylacrylamide (NIPAAM) as the second and third comonomers, respectively. The GPC traces of PS, PMA-*b*-PS-*b*-PMA, and PNIPAAM-*b*-PMA-*b*-PS-*b*-PMA-*b*-PNIPAAM are shown in Fig. 7. There was an obvious peak shift from the macro-RAFT agent to the chain-extended block copolymer, the molecular weight increased from 2900 g/mol to 8000 g/mol and the peak of the original polymer disappeared, which indicated that the polymer chains were almost living. The M_w/M_n values of the copolymers were low (M_w/M_n = 1.14–1.17). Furthermore, in order to verify the living nature of the obtained polymer and the successful synthesis of the block polymers.

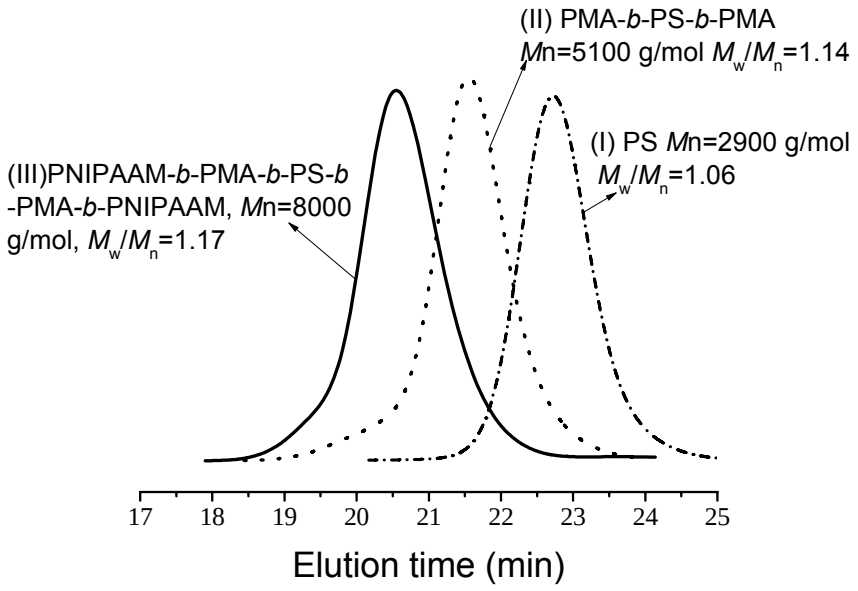


Fig. 7. GPC traces of multiblock polymers: (I) $[Styrene]_0$: $[CDMPA]_0$ = 300 : 1, temperature 110 °C, time = 5 h, and anisole as solvent; (II) $[MA]_0$: $[PS]_0$: $[AIBN]_0$ = 200 : 1 : 3, time = 5 h, temperature = 70 °C, and THF as solvent; (III) $[NIPAAM]_0$: $[PMA\text{-}b\text{-}PS\text{-}b\text{-}PMA]_0$: $[AIBN]_0$ = 200 : 1 : 3, time = 5 h, temperature = 70 °C, and THF as the solvent.

Tab. 1. Conversion, molecular weight, and polydispersity data for the PS and the PMA-b-PS-b-PMA as the macro-CTAs.

Entry	Polymer	CTA	Monomer	Initiator	Time (h)	$M_{n.th}$ (g/mol)	$M_{n.GPC}$ (g/mol)	M_w/M_n	Conversion (%)
S1[a]	PS	CDMPA	styrene	thermal	15	2600	2700	1.06	16.25
T1[b]	PMA-b-PS-b-PMA	S1	MA	AIBN	4	3400	3700	1.11	10.62
T2[b]					6	4850	5000	1.18	25.72
T3[c]					8	5900	5800	1.17	35.65
T4[b]					10	6800	6500	1.17	43.69
T5[b]					12	7350	7600	1.29	56.29
P1[d]	PNIPAAM-b-PMA-b-PS-b-PMA-b-PNIPAAM	T3	NIPAAM	AIBN	6	7150	7300	1.39	24.02
P2[d]					12	7700	10100	1.31	42.56

[a] S1 prepared by heating 26.11 mmol St in 2 mL anisole solution at 110 °C for 15 h, $[S]_0$: $[CDMPA]_0$=100 : 1;

[b] T1-T2 and T4-T5 prepared by heating 2.22 mmol MA, 7.22×10-3 mmol AIBN and 21.66×10-3 mmol S1(as the macro-RAFT agent) in 1 mL THF at 70 oC;

[c] T3 prepared by heating 5.55 mmol MA, 18.05×10-3 mmol AIBN and 54.15×10-3 mmol S1(as the macro-RAFT agent) in 1 mL THF at 70 oC;

[d] P1, P2 prepared by heating 1.29 mmol NIPAAM, 4.26 ×10-3 mmol AIBN and 12.79×10-3 mmol T3 (as the macro-RAFT agent) in 1 mL THF at 70 oC.

Conversion, molecular weight, and polydispersity data for the PS and the PMA-b-PS-b-PMA as the macro-CTAs are shown in Table 1.

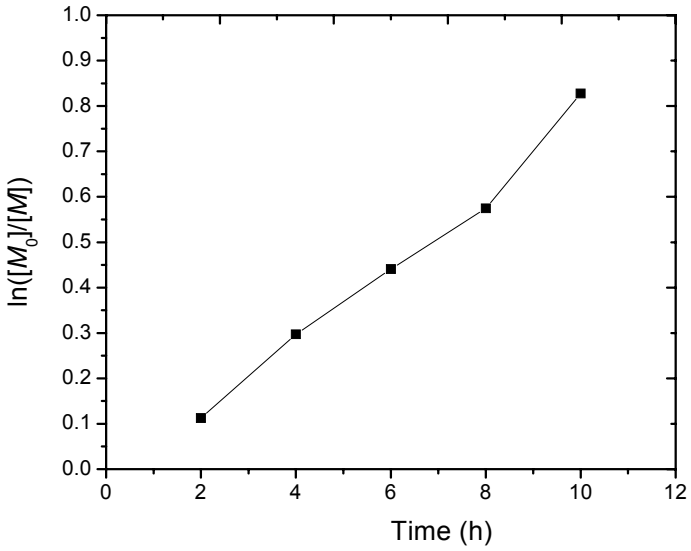


Fig. 8. Plots of ln([M_0]/[M]) versus time for triblock copolymers synthesized with S1 PS, $M_{n.GPC}$ = 2700 g/mol, M_w/M_n = 1.06) as the macro-RAFT agent.

Evidence of the controlled nature of the block copolymerization can be observed in the kinetic plot for the polymerization of MA with polystyrene (S1) as the macro-CTA (Fig. 8). A first-order relationship was maintained to approximately a 60% conversion. These results can be shown that the polymer chains were almost living and the block polymers were successfully synthesized.

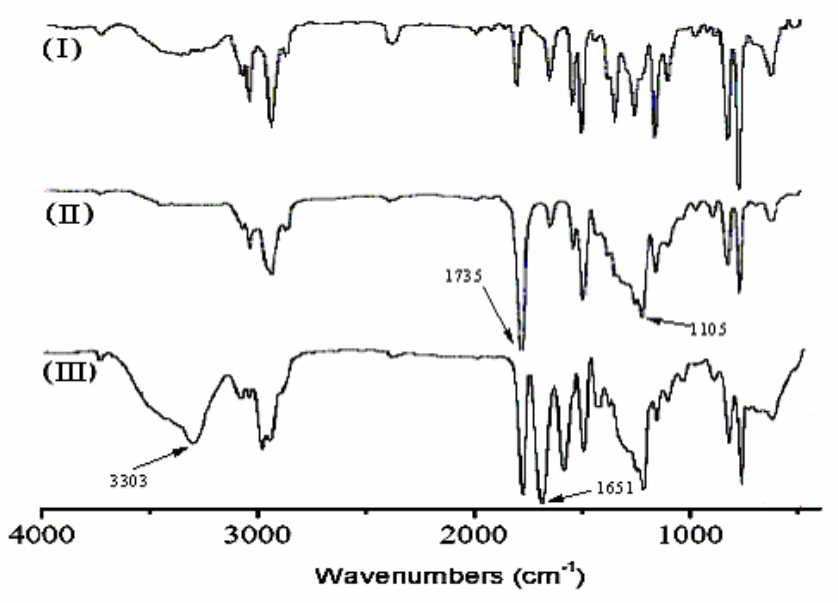


Fig. 9. The FT-IR spectra of multiblock copolymers: (I) PS ($M_{n.GPC}$ = 3000 g/mol, M_w/M_n = 1.06); (II) PMA-*b*-PS-*b*-PMA ($M_{n.GPC}$ = 5100 g/mol, M_w/M_n = 1.14); (III) PNIPAAM-*b*-PMA-*b*-PS-*b*-PMA-*b*-PNIPAAM ($M_{n.GPC}$ = 8000 g/mol, M_w/M_n = 1.17).

Fig. 9 shows the FT-IR spectra of (I) PS, (II) PMA-*b*-PS-*b*-PMA, and (III) PNIPAAM-*b*-PMA-*b*-PS-*b*- PMA-*b*-PNIPAAM. The absorption bands at 1105, 1200 and 1260 cm^{-1} (characteristic of C-O stretching vibration of MA) showed in FT-IR spectra of (II) and (III) were consistent with the presence of PMA block in the pentablock copolymer. Similarly, the characteristic absorption bands at 1651 cm^{-1} (C=O stretching vibration of *N*-isopropylacrylamide) and 3303 cm^{-1} (N-H stretching vibration of NIPAAM) showed in FT-IR spectra of (III) were consistent with the PNIPAAM block in the pentablock polymer. The ^{1}H NMR spectra of PMA-*b*-PS-*b*-PMA and PNIPAAM-*b*-PMA-*b*-PS-*b*- PMA-*b*-PNIPAAM are presented in Fig. 10.

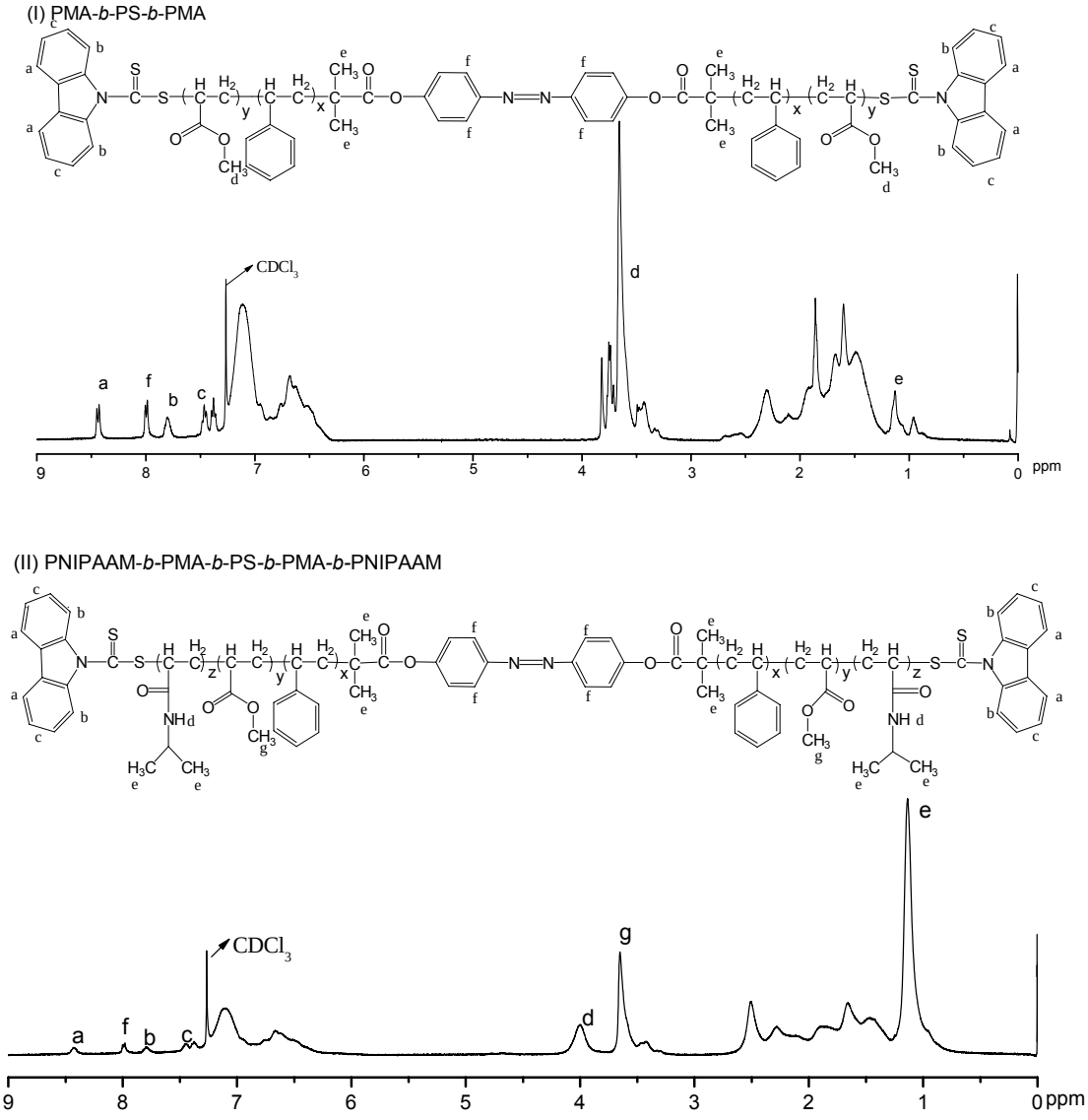


Fig. 10. The ^{1}H NMR spectra of multiblock copolymers: (I) PMA-*b*-PS-*b*-PMA $M_{n.GPC}$ = 5100 g/mol, M_w/M_n = 1.14; (II) PNIPAAM-*b*-PMA-*b*-PS-*b*-PMA-*b*- PNIPAAM, $M_{n.GPC}$ = 8000 g/mol, M_w/M_n = 1.17.

The chemical shifts at δ = 8.17, 7.95, 7.81 and 7.35 ppm in Fig. 3 and Fig. 10 can be assigned to the aromatic protons of CDMPA in the polymers. In Fig. 10 (I) the chemical shifts from 3.38-3.64 ppm corresponded to the protons of methoxyl group

(-OCH_3) in the PMA block. The chemical shifts at 4.00 ppm in Fig. 10 (II) corresponded to the protons of amino group (-NH) in the PNIPAAM block. All the characteristic FT-IR absorption bands and chemical shifts in the ^{1}H NMR spectra indicated that the PMA-*b*-PS-*b*-PMA and PNIPAAM-*b*-PMA-*b*-PS-*b*-PMA-*b*-PNIPAAM were obtained, and the CDMPA showed well controlled ability in the RAFT polymerization of multiblock copolymers.

Conclusions

The novel dithiocarbamate was first synthesized and successfully used as a bis-functional RAFT agent in the RAFT polymerization of styrene to prepare the triblock copolymers (PMA-*b*-PS-*b*-PMA), and pentablock copolymers (PNIPAAM-*b*-PMA-*b*-PS-*b*-PMA-*b*-PNIPAAM) with well-controlled molecular weight and narrow molecular weight distribution. The ^{1}H NMR spectrum confirmed the obtained polymers were centered by azobenzene functional group, which was derived from CDMPA. The obtained PS showed carbazole fluorescence and azobenzene ultraviolet absorption. These results further confirmed that presence of moieties of CDMPA in the center and the ends of chains.

Experimental

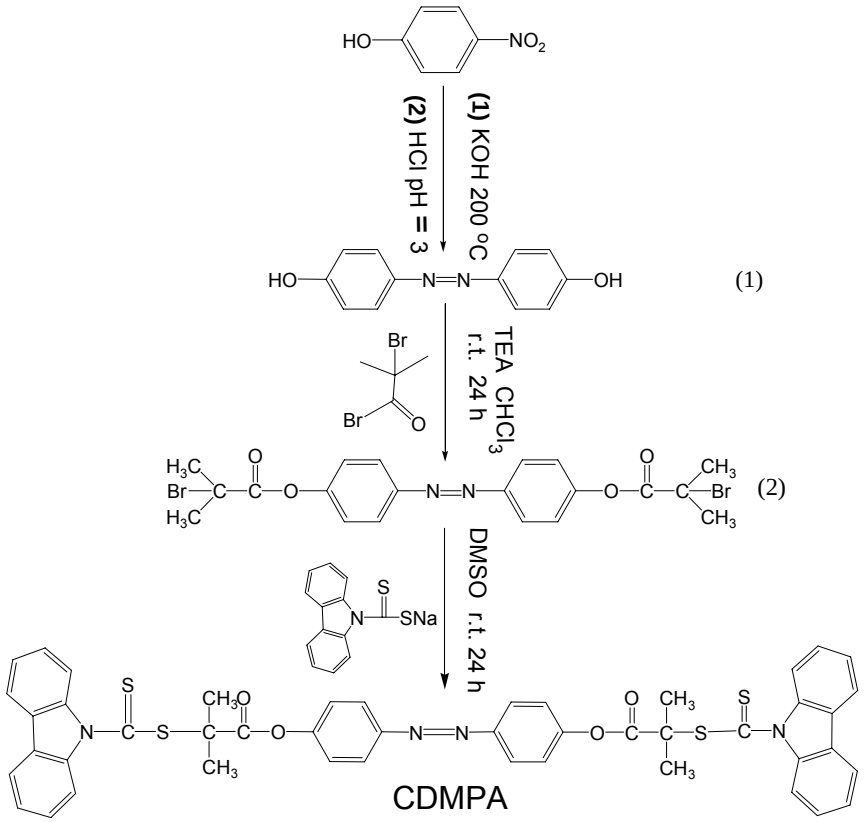
Materials

2-Bromo-isobutyryl bromide (98%) was purchased from Aldrich. *N*-isopropylacrylamide (NIPAAM) (97%) was purchased from Kohjin (Japan). All other chemicals were obtained from Shanghai Chemical Reagent Co., Ltd, China. NIPAAM was recrystallized from a mixed solvent of 50% (v/v) toluene and n-hexane. The monomers, styrene (St) and methyl acrylate (MA), were washed with an aqueous solution of sodium hydroxide (5 wt%) and then with deionized water, dried with anhydrous magnesium sulfate overnight, finally distilled over calcium hydride under vacuum. Dimethyl sulfoxide (DMSO) was dried with activated molecular sieve (4Å). *N,N'*-dimethyl formamide (DMF) used in fluorescence measurements was distilled under vacuum before use. All other reagents were analytical grade and used as received.

Synthesis of CDMPA

The synthetic routes of CDMPA are presented in Scheme 2.

4,4'-Dihydroxyazobenzene (1): Compound (**1**) was prepared by a modified procedure of the literature [42]: a mixture of potassium hydroxide (50 g, 760 mmol), *p*-nitrophenol (10 g, 72 mmol), and water (10 mL) was heated to 120 °C and left to stand for 1 h. When the temperature was slowly elevated to 195-200 °C, the reaction vigorously started to give brown viscous liquid with a large number of bubbles developing. After the reaction was completed, the products were dissolved in water. A dark-red solution was acidified to pH 3 with concentrated hydrochloride and then was extracted with ether. Combined ether extracts were dried by anhydrous magnesium sulfate overnight. Then, the ether was removed under reduced pressure. Residue was recrystallized from 50% (v/v) ethanol aqueous solution to give yellow crystal of compound (**1**) 3.30 g. Yield: 43%. Elem. Anal. Calcd.: C, 67.28%; H, 4.71%; N, 13.08%, Found: C, 66.66%; H, 4.99%; N, 12.33%. ^{1}H NMR (DMSO-*d6*): 10.10 (s, 2H); 7.71 (d, 4H); 6.90 (d, 4H).



Scheme 2. Synthetic routes of 4,4'-bis[2-(carbazole-*N*-dithioformatyl)-2-methyl-propionatyl] -azobenzene (CDMPA).

4,4'-bis [2-bromo-2-methyl-propionatyl]-azobenzene (2): Triethylamine (15.3 g, 152 mmol) was added to a solution of compound (**1**) (16.3 g, 76 mmol) in chloroform ($CHCl_3$) (130 mL). The solution was stirred in an ice bath, and 2-bromo-isobutyryl bromide (37.4 mL, 69.9 g, 304 mmol) in $CHCl_3$ (20 mL) was added dropwise over a period of 1 h under argon. The mixture was then stirred at room temperature overnight. The solution was washed with deionized water three times, and dried with anhydrous magnesium sulfate overnight. Then, the solvent was removed under reduced pressure. The obtained crude product was purified by recrystallization three times from acetone, and a pale yellow solid was obtained (24.50 g). Yield: 63%. Elem. Anal. Calcd.: C, 46.90%; H, 3.94%; N, 5.47%, Found: C, 46.62%; H, 3.97%; N, 5.38%. ^{1}H NMR ($CDCl_3$): 2.10 (s, 12H); 7.30 (d, 4H); 7.99 (d, 4H).

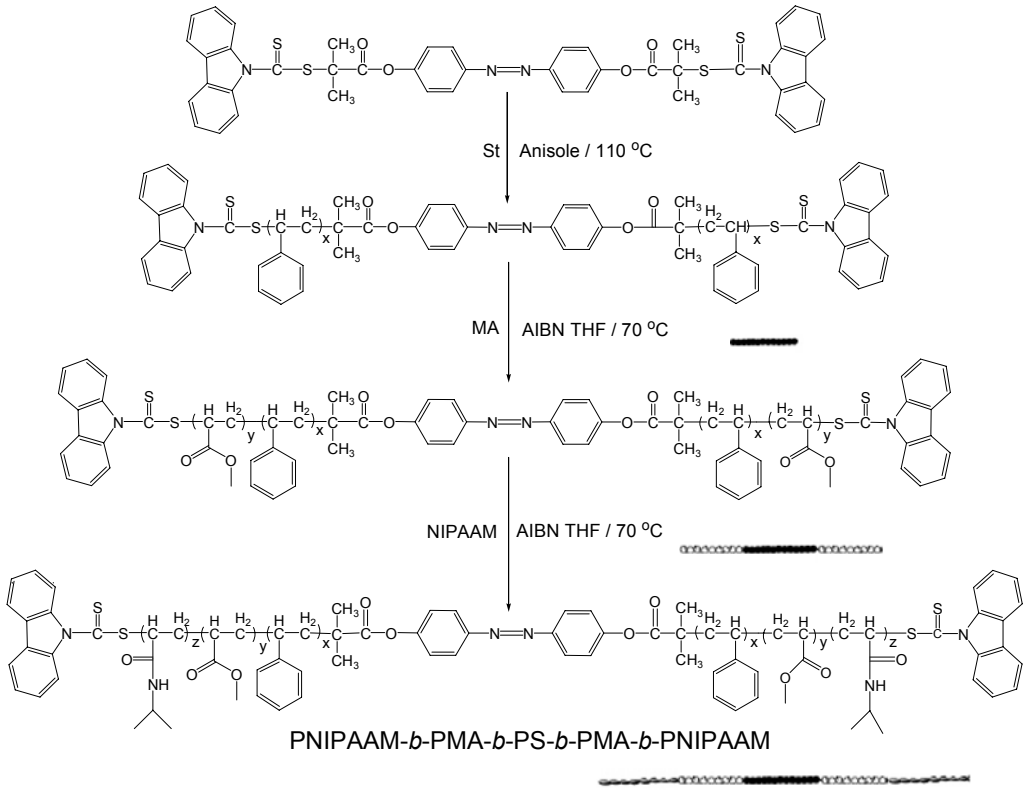
CDMPA: Sodium hydride (60% in mineral oil, 1.4 g, 35 mmol) was added to a solution of carbazole (5.0 g, 30 mmol) in DMSO (15 mL) at room temperature under argon. After stirring for 0.5 h, carbon disulfide (1.8 mL, 30 mmol) was added at 0 ^{o}C. The reaction mixture was stirred for 0.5 h at room temperature. Then the compound (**2**) (8.71 g, 17 mmol) was added into the reaction mixture. The resultant mixture was stirred overnight and then precipitated in large amount of water. A yellow solid was collected by filtration. After being recrystallized twice from $CHCl_3$, the CDMPA was obtained as a yellow powder (9.85 g). Yield: 63%. IR (KBr): υ = 3063.9, 2979.0, 2932.7, 1751.9, 1643.9, 1589.9, 1489.5, 1443.2, 1389.2, 1296.6, 1196.2, 1142.2, 1111.4, 1041.9, 918.4, 879.8, 740.9, 717.7 cm^{-1}. Elem. Anal. Calcd.: C, 65.99%; H, 4.33%; N, 6.69%, Found: C, 64.30%; H, 4.44%; N, 6.96%. ^{1}H NMR ($CDCl_3$): 2.05 (s, 12H), 7.34-7.53 (m, 12H); 7.96 (m, 8H); 8.44 (d, 4H).

RAFT polymerization of styrene using CDMPA as the RAFT agent

The typical procedures were as follows: a solution of styrene (2.5 mL, 21.7 mmol), CDMPA (0.0606 g, 0.72 mmol) and anisole (2.5 mL) were placed in a polymerization ampoule (5 mL). The content was purged with argon to eliminate oxygen for approximately 10 min. Then the ampoule was flame sealed. The polymerization reaction was performed at 110 ^{o}C. After predetermined time, the ampoule was immersed into cold water and opened. The reaction mixture was diluted with 3 mL of THF and precipitated into 250 mL of methanol. The polymer was filtered and dried at room temperature in vacuum until a constant weight. The conversion of the polymer was determined gravimetrically.

RAFT polymerization of MA using PS as the macro-RAFT agent

The synthetic routes are presented in Scheme 3. The procedures used for the block copolymerization of MA were similar to those used for the RAFT polymerization of styrene. The reaction mixture, containing 0.15g (5.1 μmol, $M_{n.GPC}$ = 3000 g/mol and M_w/M_n = 1.06) of PS, 0.31 mL (3.5 mmol) of MA, 0.0028 g (17.0 μmol) of AIBN, and 1.0 mL of THF, was introduced into a 2 mL ampoule. The homogeneous solution was purged with argon to eliminate oxygen for approximately 10 min. Then, the ampoule was flame sealed and placed in an oil bath thermostated at 70 ^{o}C. The other procedures were the same as the synthesis of PS.



Scheme 3. Synthetic routes of pentablock copolymer PNIPAAM-*b*-PMA-*b*-PS-*b*-PMA-*b*-PNIPAAM.

RAFT polymerization of NIPAAM using PMA-b-PS-b-PMA as the macro-RAFT agent

The procedures used for the block copolymerization of NIPAAM were similar to those used for the RAFT polymerization of styrene. 0.089 g (0.8 mmol) of NIPAAM, 0.0537

g (10 μmol, $M_{n.GPC}$ = 5100 g/mol and M_w/M_n = 1.14) of PMA-*b*-PS-*b*-PMA, 0.6 mg (3.7 μmol) of AIBN, and 1 mL of THF were added to a 2 mL ampoule. The content was purged with argon to eliminate oxygen for approximately 10 min. Then, the ampoule was flame sealed and placed in an oil bath thermostated at 70 ^{o}C. The other procedures were same as that in the synthesis of PS.

Characterization

Elemental analysis of C, H, and N were measured with an EA1110 CHNO-S instrument. The molecular weight (M_n) and molecular weight distributions (M_w/M_n) of the polymers was determined with a Waters 1515 gel permeation chromatographer (GPC) equipped with a refractive-index detector, with HR 1, HR 3, and HR 4 columns (molecular weight 100-500,000) calibrated with PS standard samples. THF was used as the eluent at a flow rate of 1.0 mL·min^{-1} at 30 ^{o}C. ^{1}H NMR spectra of the polymers were recorded on an Inova 400-MHz NMR instrument with $CDCl_3$ or DMSO-d_6 as the solvent and tetramethylsilane (TMS) as the internal standard. The UV–vis absorption spectra of the polymers and RAFT agent in THF solution were determined on a Shimadzu RF540 spectrophotometer. The fluorescence spectra of the polymers and RAFT agent were obtained on a PerkinElmer LS-50B fluorescence spectrophotometer with DMF as solvent. FT-IR spectra were recorded on a Perkin-Elmer 2000 FT-IR spectrometer.

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