Narrow Disperse Polymers Using Amine Functionalized Dithiobenzoate RAFT Agent and Easy Removal of Thiocarbonyl End Group from the Resultant Polymers

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ABSTRACT: A novel amine functionalized RAFT agent, 2-cyanoprop-2-yl(4-*N,N*-dimethylaminophenyl) dithiobenzoate has been synthesized and used to control the polymerization of vinyl monomers. This dithiobenzoate RAFT agent, although air sensitive, controlled the polymerization of MMA and St very well in an inert atmosphere and the polymerization results obtained were marginally better than using the most popular 2-cyanoprop-2-yl dithiobenzoate RAFT agent. The living nature of these polymerizations was confirmed by kinetics study and chain extension reactions to yield narrow disperse di-block copolymers. Most importantly, use of this novel RAFT agent simplified the removal procedure of the color causing end thiocarbonyl group from the RAFT derived polymers and thereby leading to polymers with improved appearance. The removal of end group from the polymer was confirmed by ^{1}H NMR and UV-vis spectroscopic techniques. © 2011 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 49: 1494–1502, 2011

KEYWORDS: dithiobenzoate; end group removal; kinetics (polym.); living radical polymerization; reversible addition fragmentation chain transfer (RAFT)

INTRODUCTION In the past few decades significant developments in controlled or living radical polymerization (CRP/LRP) techniques have allowed increased control over the polymerization processes and polymerized products. Reversible addition fragmentation chain transfer (RAFT) mediated polymerization is believed to be one of the most versatile CRP methods in the view of the variety of monomers used, tolerance towards different functional groups and simplicity of the polymerization procedure.[1] RAFT mediated polymerization works by simple addition of RAFT agents, usually thiocarbonylthio compounds (S=C(Z)-SR), to a free radical polymerization system. Dithioesters are one of the most popular RAFT agents among all and are explicitly useful for controlling polymerization of more activated vinyl monomers like methyl methacrylate (MMA), styrene (St) etc.[1,2] However dithioester RAFT agents are colored and the polymers synthesized using these RAFT agents are also colored due to the presence of RAFT agent derived thiocarbonylthio (S=C—S—) group attached to the end of the polymer chains. This chain end thiocarbonylthio group could be interesting to synthesize different end functional polymers as reported in the literature.[3] However, there is still concern over this color causing thiocarbonylthio (S=C—S—) end group of RAFT derived polymers especially when the polymer is to be applied for certain color related applications directly after synthesis and may lead to toxicity (although depend on the type of dithiocarbonyl end group and cells used for the study[4]) and odor associated with the final polymers produced.[1a,c,d,5] There are indeed a number of different approaches used to remove the thiocarbonylthio end groups include hydrolysis,[6] aminolysis,[7] thermolysis,[8] reduction,[9] and radical induced process[5,10] etc. However, most of these processes require an additional reagent to react with the thiocarbonylthio end group. In addition, such reagents are used in large excess in order to ensure complete removal of the end groups. Hence, the discovery of a RAFT agent, which controls the polymerizations well and at the same time simplifies the removal procedure of end thiocarbonyl group from the resultant polymer in the post polymerization process, preferably without any additional use of reagents or in a simple and mild condition will be of great importance for the RAFT process.

Herein, we report the synthesis of novel 2-cyanoprop-2-yl(4-*N,N*-dimethylaminophenyl) dithiobenzoate (CPDADB) RAFT agent and its use for the homopolymerization and copolymerization of MMA and styrene (St). This amine functionalized dithiobenzoate RAFT agent controls the polymerization of MMA and St in an excellent manner and simplifies the removal procedure of color causing thiocarbonyl end group from the resulting polymers to produce polymers with improved appearance.

Additional Supporting Information may be found in the online version of this article. Correspondence to: S. Jana (E-mail: satyasankar_jana@ices.a-star.edu.sg) or C. L. L. Chai (E-mail: christina_chai@ices.a-star.edu.sg)

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EXPERIMENTAL

Materials and Characterizations

Methyl methacrylate (MMA, 99%), styrene (St, 99+%), carbon disulfide (99.9%), and 4-bromo-*N,N*-dimethylaniline (97%) were obtained from Aldrich, magnesium chips (99+%), phenylacetyl chloride (98%), and 4-methylstyrene (98%) were obtained from Alfa Aesar, potassium hexacyanoferrate (III) ($K_3Fe(CN)_6$, 99%) was obtained from Merck and 2,2′-Azobisisobutyronitrile (AIBN) was obtained from Hallo-Chem Pharm. The monomers MMA and St were purified by passing through neutral alumina column and stored in freezer before polymerizations. AIBN was purified by recrystallization from absolute alcohol.

^1H and ^{13}C NMR spectra were recorded on a 400 MHz Bruker UltraShield AVANCE 400SB spectrometer. Residual solvent peaks were used as internal standard. UV-vis spectra were recorded on SHIMAZDU UV-2550 spectrophotometer. Elemental microanalysis was performed using Eurovector E300 elemental analyzer. High resolution mass spectra were recorded on Agilent 6210 TOF/LCMS. The THF run SEC system was equipped with Waters 515 HPLC pump, 717plus autosampler, and 2414 refractive-index detector. The following Styragel GPC columns were arranged in series: guard, HR5E (×2, 4.6 mm ID × 300 mm), HR1 and HR0.5. The eluant flow rate was 0.3 mL/min and the columns were maintained at 40 °C.

Synthesis of 2-Cyanoprop-2-yl(4-*N,N*-dimethylaminophenyl)dithiobenzoate (CPDADB)

4-Bromo-*N,N*-dimethylaniline (2.0 g, 9.995 mmol) was slowly added to a dispersion of Mg chips (0.267 g, 11 mmol) in dry THF (40 mL) under N_2 atmosphere. The mixture was then heated to 40 °C for 1.5 h. The light blue color of 4-bromo-*N,N*-dimethylaniline solution dissipated slowly and a colorless solution was obtained. Carbon disulfide (3.131 g, 41.1 mmol) was added dropwise to the solution above at room temperature. The reaction mixture was raised to 40 °C and allowed to react for 1 h. The resultant red solution was poured into an acidified ice/water mixture (300 mL) and the yellow precipitate of corresponding dithiobenzoic acid formed was extracted with DCM (250 mL). The DCM phase was concentrated to 150 mL and the product from DCM phase was extracted with 2N NaOH solution (2 × 150 mL) as its sodium salt. This sodium salt was converted to corresponding disulfide by the addition of aqueous solution (50 mL) of $K_3Fe(CN)_6$ (3.29 g, 9.995 mmol). The precipitate formed was filtered, washed with water, and then dried in a vacuum oven at 40 °C for 18 h to yield bis(4-*N,N*′-dimethylthiobenzoyl) disulfide as a brick red solid (1.65 g). A part of this compound (1.0 g, 2.547 mmol) was mixed with excess AIBN (0.627 g, 3.82 mmol) in ethyl acetate (50 mL) and the resultant heterogeneous mixture was heated under N_2 at 90 °C for 18 h to produce homogeneous solution. The solution was filtered and the filtrate was dried in vacuo to yield an orange solid. The product was purified by column chromatography using 30% ethyl acetate in hexane under nitrogen to yield a bright orange solid. The product was stored in glove box before use. Yield 65%. ^1H NMR (400 MHz, $CDCl_3$, δ, ppm): 1.94 (s, 6H, 2 × $C{-}CH_3$), 3.07 (s, 6H, 2 × $N{-}CH_3$), 6.57 (d, 2H, C_6H_4), 8.03 (d, 2H, C_6H_4). ^{13}C NMR (400 MHz, $CDCl_3$, δ, ppm): 27.0, 40.1, 41.1, 110.5, 121.0, 129.1, 133.1, 154.1, 217.2. HRMS (*m/z*): 287.06470 $[M + Na]^+$; Calcd. $C_{13}H_{16}N_2S_2$: 287.06471. Calcd. $C_{13}H_{16}N_2S_2$: C, 59.35; H, 6.10; N, 10.59; S, 24.25%; Found C, 59.68; H, 6.09; N, 10.83; S, 23.21%.

Typical RAFT Polymerization of MMA Using CPDADB (P3)

AIBN (4.4 mg, 2.67×10^{-5} mol) and CPDADB (14.1 mg, 5.342×10^{-5} mol) were weighed into a 25 mL Schlenk tube inside a glove box. Nitrogen purged MMA (2 mL, 18.69 mmol) and dry toluene (0.7 mL) were then added to the Schlenk tube and immediately frozen on a liquid N_2 bath. The solution was degassed with three freeze-pump-thaw cycles using N_2 and warmed to room temperature and then heated at 60 °C for the required time. The stoichiometries of reagents are MMA:CPDADB:AIBN = 350:1:0.5. Samples from the reaction mixture were collected for NMR and GPC analysis, when required. Polymer samples were analyzed by GPC as collected from the reaction mixture. Finally, polymerization was stopped by cooling the content to room temperature and exposing in air. Bright yellow powdery polymer sample was collected on precipitation from excess hexane, which was dried in a vacuum oven.

Typical RAFT Polymerization of St Using CPDADB (P7)

A mixture of styrene (3 mL, 26.2×10^{-3} mol), AIBN (2.46 mg, 1.495×10^{-5} mol), CPDADB (19.78 mg, 7.48×10^{-5} mol) and anisole (5 drops) were taken into a 25 mL Schlenk tube. The solution was degassed with three freeze-pump-thaw cycles using N_2 and then heated to 80 °C for the required time. The stoichiometries of the reagents are St:CPDADB:AIBN = 350:1:0.2. Samples from the reaction mixture were collected for NMR and GPC analysis, when required. Polymer samples were analyzed by GPC as collected from the reaction mixture. Polymerization was stopped by cooling the content to room temperature and exposing in air and finally polymer was precipitated out from excess methanol to produce bright yellow powder.

Synthesis of Poly(methyl methacrylate)-*block*-poly(styrene) (PMMA-*b*-PS) Copolymer by Chain Extension Reaction

At first MMA was polymerized similar to the process mentioned above for **P3**. After 7 h, the polymerization reaction was stopped and the excess MMA was removed by high vacuum to yield a yellow-orange colored solid polymer (conversion 46.8%; obtained $M_{n,GPC}$ 21,900, PDI 1.1). Next, the resultant polymer was dissolved thoroughly in St (3 mL, 0.026 mol) with the addition of AIBN (1.5 mg) and anisole (5 drops), degassed with three freeze-pump-thaw cycles using N_2 and then heated at 80 °C for 20 h to yield poly(methyl methacrylate)-*block*-poly(styrene) (PMMA-*b*-PS) copolymer (St conversion 50.9%; obtained $M_{n,GPC}$ 58800; PDI 1.22). Polymer samples were analyzed by GPC as collected directly from the reaction mixture.

Synthesis of Poly(styrene)-*block*-poly(4-methylstyrene) (PS-*b*-P4MS) Copolymer by Chain Extension Reaction

At first St (2 mL, 17.45 × 10^{-3} mol) was polymerized for 46 h at 80 °C in presence of AIBN (1.63 mg, 9.932 × 10^{-6} mol), CPDADB (13.18 mg, 4.98 × 10^{-5} mol) and anisole (5 drops) (St: CPDADB:AIBN = 350:1:0.2). Excess St was removed by high vacuum to yield a yellow-orange colored solid polymer (conversion 72.7%; calculated $M_{\mathrm{n,Theor}}$ 26760; obtained $M_{\mathrm{n,GPC}}$ 25,900 and PDI 1.07). Next, the resultant polymer was dissolved thoroughly in 4-methylstyrene (4MSt, 3 mL) with the addition of AIBN (1.5 mg) and anisole (5 drops), degassed and then heated at 80 °C for 30 h under N_2 to yield a poly(styrene)-*block*-poly(4-methylstyrene) (PS-*b*-P4MS) copolymer. 4MSt conversion 49%, obtained $M_{\mathrm{n,GPC}}$ 55,700; PDI 1.12.

Typical Thiocarbonyl End Group Removal from CPDADB Derived PS in THF

First, PS was synthesized as the process for **P7** (St:CPDADB:AIBN = 350:1:0.2, at 80 °C, 46 h). The final product was then mixed with about 20 mL THF. (a) A portion (5 mL) of the polymer solution was used to precipitate out PS from methanol. The bright yellow powder solid was characterized by ^{1}H NMR spectroscopy and GPC (colored PS, $M_{\mathrm{n,GPC}}$ 24,700 and PDI 1.04). (b) Rest of the polymer solution was purged compressed air for 5–10 min and then kept at room temperature in a closed bottle until it became colorless after 2 months. White fine powder PS was obtained on precipitation from methanol. The white PS sample was dried in vacuum oven at 60 °C overnight and characterized by ^{1}H NMR spectroscopy and GPC (white PS, $M_{\mathrm{n,GPC}}$ 23,900 and PDI 1.08).

Another batch of PS was synthesized by the above procedure (St:CPDADB:AIBN = 350:1:0.2, 80 °C, 47 h) and the final product was similarly mixed with about 20 mL THF (produce yellow polymer solution). A portion of the solution (~10 mL) was used to precipitate out polymer from excess methanol. The bright yellow solid was dried in vacuum oven at 60 °C overnight and characterized by ^{1}H NMR spectroscopy and GPC (colored PS, $M_{\mathrm{n,GPC}}$ 24,900 and PDI 1.08). The remaining 10 mL solution was purged with compressed air for 5–10 min and then heated at 60 °C for 2 days. A colorless solution was obtained which when precipitated from excess methanol produced completely white polymer product. The white polymer was dried in a vacuum oven at 60 °C overnight and characterized by ^{1}H NMR spectroscopy and GPC (white PS, $M_{\mathrm{n,GPC}}$ 24,100 and PDI 1.07). Similarly a colorless polymer solution (and white powder) was also obtained when the THF solution (5 mL) of bright yellow PS (200 mg) was heated at 60 °C for 2 days.

Typical Thiocarbonyl End Group Removal from CPDADB Derived Low Molecular Weight PMMA in THF Using Con. HCl Followed by Functionalization

A small portion (200 mg) of CPDADB derived bright yellow colored PMMA (**P4** in Table 1, $M_{\mathrm{n,GPC}}$ 11,200 and PDI 1.18) was dissolved in 5 mL THF. Concentrated HCl (5 drops) was added and stirred for 5 min at room temperature. The mixture was then heated to 60 °C for 1 h to yield a colorless solution. White polymer was precipitated out from cold methanol and dried in a vacuum oven at 60 °C for 18 h and characterized by ^{1}H NMR spectroscopy and GPC (white PMMA, $M_{\mathrm{n,GPC}}$ 12,200 and PDI 1.17).

The resultant white PMMA (100 mg) was dissolved in dry $CHCl_3$ (2 mL) and purged with N_2. Triethylamine (2 drops) and phenylacetyl chloride (2 drops, ~15 mg, excess) were added by syringe and the stirring was continued for 24 h. Polymer was precipitated out from excess methanol and collected after centrifugation. The polymer was washed

TABLE 1 RAFT Polymerization Results of MMA and St

Entry	Monomer	RAFT Agent (RA)	Monomer: RA[a]:AIBN	Time (h)	Conversion[b] (%)	$M_{\mathrm{n,Theor}}$	$M_{\mathrm{n,GPC}}$[c]	PDI[c]
P1	MMA	None	350:0:0.5	4	24	NA	226,000	2.32
P2	MMA	CPDB	350:1:0.5	2	9.8	3,750	5,000	1.33
				20	92.8	32,740	25,900	1.20
P3	MMA	CPDADB	350:1:0.5	2	12.5	4,650	5,400	1.31
				20	96.2	33,990	26,700	1.15
P4	MMA	CPDDDB	100:1:0.5	20	99.5	10,230	11,200	1.18
P5	St	None	350:0:0.2	6	39.5	NA	97,900	1.97
P6	St	CPDB	350:1:0.2	23	46	16,990	17,500	1.10
P7	St	CPDADB	350:1:0.2	2	15.3	5,850	5,900	1.07
				23	54.8	20,230	19,300	1.09
				47	72.6	26,740	24,900	1.08
P8	St	CPDADB	1000:1:0.2	48	70.2	70,580	67,800	1.15
P9	St	CPDADB	100:1:0.2	30	76.4	8,220	8,200	1.06

MMA was polymerized in toluene solution (with ~74 volume % MMA) at 60 °C and St was polymerized in bulk at 80 °C.

[a] RA is RAFT agent used.

[b] Determined by ^{1}H NMR spectroscopy.

[c] In THF using PS calibration.

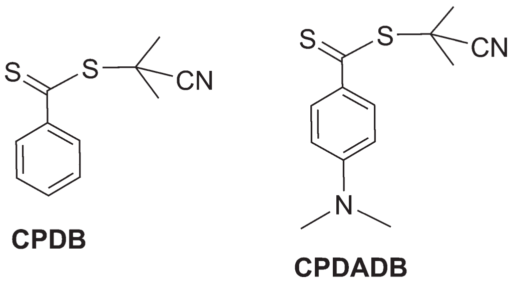


FIGURE 1 Dithiobenzoate RAFT agents used in this study.

thoroughly for 5 times with excess MeOH before drying in a vacuum oven at 60 °C overnight to produce white powder (functionalized white PMMA, $M_{\mathrm{n,GPC}}$ 12,600 and PDI 1.16).

RESULTS AND DISCUSSION

Synthesis of RAFT Agents

2-Cyanoprop-2-yl dithiobenzoate (CPDB) was synthesized using a similar procedure reported in the literature[11] while the novel 2-cyanoprop-2-yl(4-*N,N*-dimethylaminophenyl) dithiobenzoate (CPDADB) (Fig. 1) was synthesized, following a modified method because of the different solubility behavior of the intermediates and air sensitivity of the final product. These RAFT agents were purified by column chromatography and characterized by ^{1}H (Fig. 2) and ^{13}C NMR spectroscopic techniques, high resolution mass spectroscopy, elemental microanalysis, and UV-vis spectroscopy. CPDB was used as a reference RAFT agent for the polymerization studies. Noteworthy is the observation that CPDADB is sensitive to air and was therefore synthesized and purified under nitrogen atmosphere and finally stored in a glove box before using in polymerization reactions. On exposure to air CPDADB degrades 10 and 55% in 24 h when stored in solid state and solution state (15 mg/mL in $CDCl_3$) respectively proved by ^{1}H NMR spectroscopy. However, we are unable to identify the degradation products and the mechanism by LC-MS or GC-MS studies.

CPDB has only one absorption maximum in its UV-vis spectrum in between 250–600 nm, that is, at ~303 nm but CPDADB has two absorption maxima at ~333 nm and ~423 nm possibly due to the extended conjugation by *para-N,N*-dimethylamino group through the phenylene unit of CPDADB. The conjugation of *para-N,N*-dimethylamino group in CPDADB was also further supported by the fact that the C=S resonance of CPDADB appears at highfield (217 ppm) in ^{13}C NMR spectrum in compare to the same one in CPDB (223 ppm). The absorption maximum of CPDADB at ~423 nm was the most intense one and therefore was more appropriate to monitor the presence or absence of end thiocarbonyl group in the CPDADB derived polymers.

RAFT Mediated Synthesis of Homopolymers and Copolymers

The novel amine functionalized dithioester RAFT agent, CPDADB, was independently used for the polymerization of MMA and St. The polymerization of MMA in toluene using this RAFT agent in the presence of AIBN as initiator was well controlled. The polymerization using CPDADB followed first order kinetics [Fig. 3(A)] and showed a linear increase in molecular weight with monomer conversion [Figs. 3(B,C)]. The polydispersity index (PDI, M_w/M_n) of the poly(methyl methacrylate) (PMMA; **P3** in Table 1) obtained was very low in compare to the polymerization without using the RAFT agent (**P1** in Table 1) and slightly lower in compare to using CPDB (**P2** in Table 1). The experimental molecular weight from GPC ($M_{\mathrm{n,GPC}}$) for these polymerizations matched quite

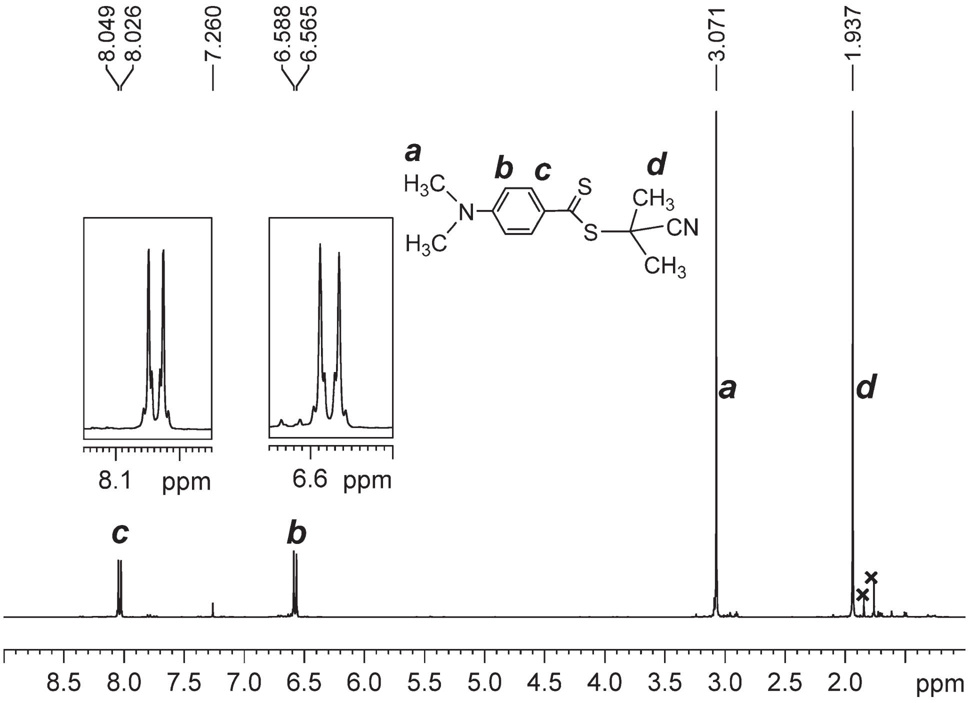


FIGURE 2 ^{1}H NMR spectrum of 2-cyanoprop-2-yl(4-*N,N*-dimethylaminophenyl) dithiobenzoate (CPDADB).

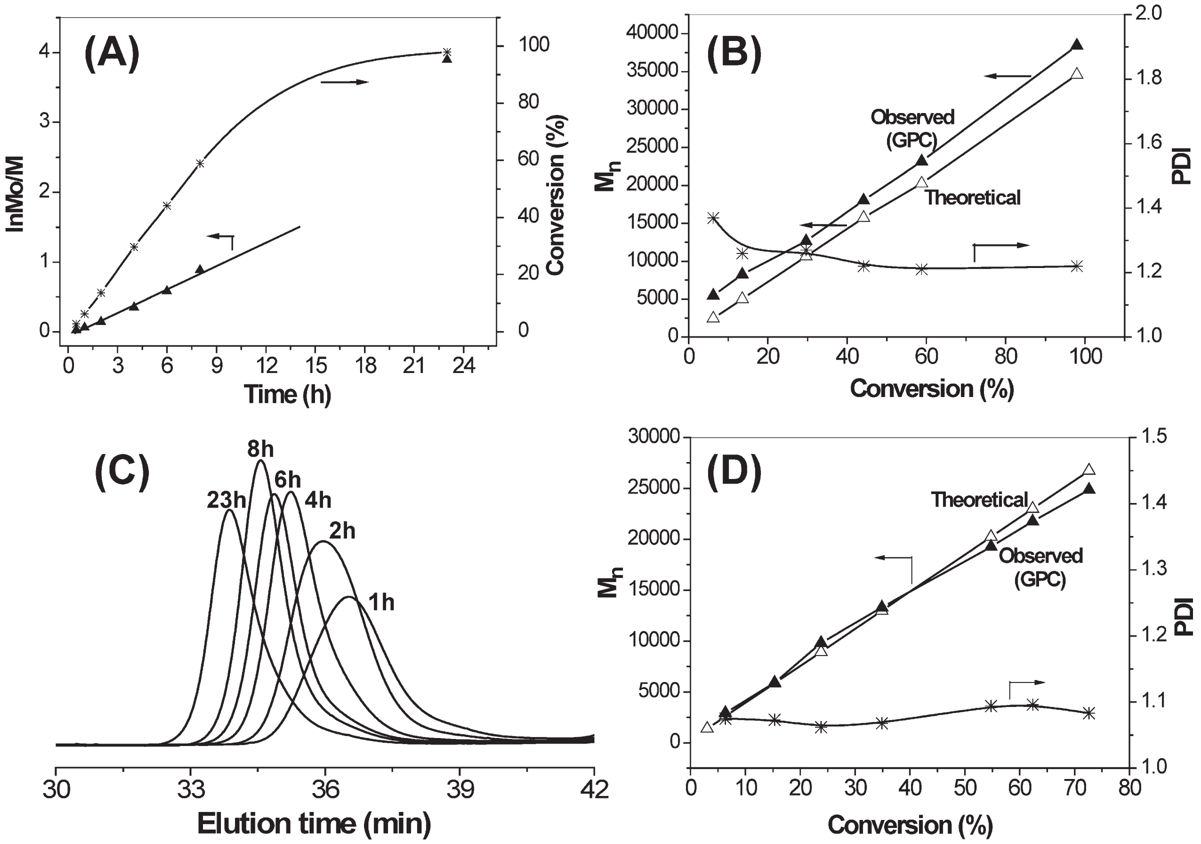


FIGURE 3 (A) Kinetic plots, (B) evolution of M_n and PDI with monomer conversion and (C) GPC traces of MMA polymerization using CPDADB; (D) evolution of M_n and PDI in St polymerization using CPDADB.

well with the theoretical values ($M_{n,Theor}$) at different monomer to initiator ratios [**P3** and **P4** in Table 1 and Fig. 3(B)].

Interestingly, a better controlled polymerization was observed for the bulk polymerization of St at 80 °C using CPDADB to yield poly(styrene) (PS) with very low PDI [**P7** in Table 1 and Fig. 3(D)]. The $M_{n,GPC}$ of the polymers was very close to the theoretical values ($M_{n,Theor}$) and the PDI values of these polymers were marginally lower relative to the polymers obtained using CPDB under similar conditions. Indeed, we have also synthesized relatively high and low molecular weight PS of very low PDI separately using different monomer to CPDADB ratios (**P8** and **P9** in Table 1). In general, less retardation was observed for the CPDADB mediated polymerizations of both MMA and St in comparison to CPDB mediated ones. For example, the monomer conversions at 2 h in St polymerizations using CPDB and CPDADB (**P6** and **P7** in Table 1) were 10.3% and 15.3%, respectively where as monomer conversion at the same time without using any RAFT agent was 15.8% (**P5** in Table 1). This was most probably due to the better re-initiation for the CPDADB mediated polymerizations because of the π–conjugations of *para*-aminophenyl group, which slightly destabilizes the intermediate polymer-RAFT agent adduct radicals in the equilibrium steps of the polymerization reaction.

Furthermore, the living nature of the polymerization of MMA and St using CPDADB was confirmed by the synthesis of di-block copolymers by chain extension reactions (Fig. 4). At first, narrow disperse PMMA ($M_{n,GPC}$ 21,900 and PDI 1.1) and PS ($M_{n,GPC}$ 25,900 and PDI 1.04) were synthesized separately using CPDADB. The PMMA chain was then extended with the polymerization of St to yield a narrow disperse di-block copolymer poly(methyl methacrylate)-*block*-poly(styrene) (PMMA-*b*-PS; $M_{n,GPC}$ 58,800 and PDI 1.22). The chain extension reaction of PS (M_n 25,900 and PDI 1.04) in 4-methylstyrene (4MS) yielded poly(styrene)-*block*-poly(4-methylstyrene) (PS-*b*-P4MS; $M_{n,GPC}$ 55,700 and PDI 1.12) (Scheme 1). In all chain extension reactions pure di-block copolymers were obtained as indicated by the monomodal GPC chromatograms (Fig. 4) of polymers. Chain extension reaction of PMMA ($M_{n,GPC}$ 20,700 and PDI 1.13) by its own monomer was also successful (resultant PMMA: $M_{n,GPC}$ 62,900 and PDI 1.24) as indicated by the monomodal GPC chromatograms of respective polymers.

End Group Analysis RAFT Derived Polymers and End Group Removal Procedures

Like other dithioester derived polymers, polymers synthesized using CPDADB RAFT agent (both before and after precipitation from nonsolvent) were bright yellow in color [Fig. 5(A)] due to the presence of (4-*N,N*-dimethylaminophenyl) dithiobenzoate end group. The presence of this end group in polymer **P7** (Table 1) (after reprecipitation from methanol) was further confirmed by the appearance of proton

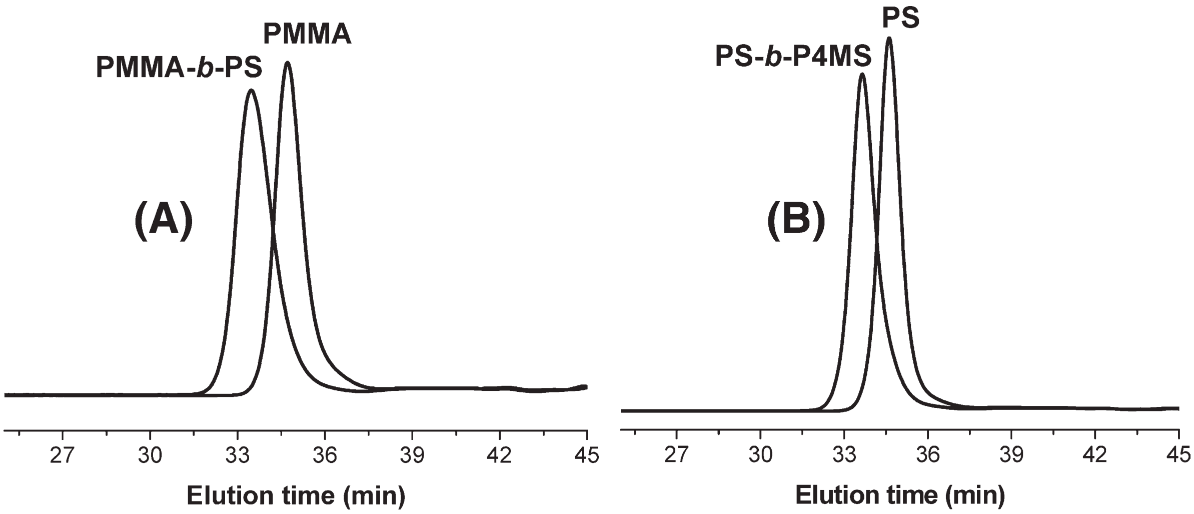
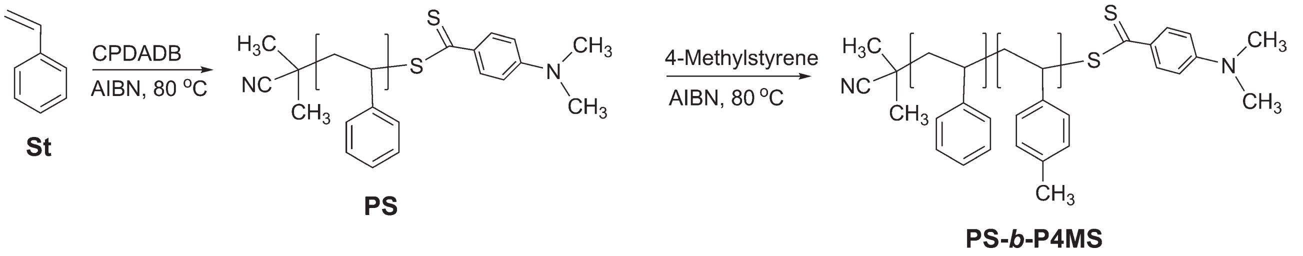


FIGURE 4 GPC traces of (A) PMMA and PMMA-*b*-PS copolymer and (B) PS and PS-*b*-P4MS copolymer synthesized by respective chain extension reactions.

resonances of *N,N*-dimethylamine (—N(CH_3)$_2$, 6H) functional group and phenylene group (—C_6H_4—, 2H, *ortho* to thiocarbonylthio group) at 3.03 and 8.02 ppm, respectively with ~3:1 ratio in ^{1}H NMR spectrum [Fig. 5(A)]. The resonances of other two protons of phenylene group (*meta* to thiocarbonylthio group) overlapped with the region of the phenyl resonances of styrene repeat units. The UV-vis spectrum of the same sample in THF also revealed the characteristic absorption maxima at ~339 nm and ~417 nm corresponding to the (4-*N,N*-dimethylaminophenyl) dithiobenzoate end group [Fig. 6(B)] similar to the maxima for CPDADB RAFT agent. The absorption maximum at ~417 nm was the most intense one and therefore used to monitor the presence or absence of end thiocarbonyl group in the CPDADB derived polymers. The absorption maximum ~260 nm is apparently due to the presence of styrene repeat units of the polymer.[5a] Similar characteristic NMR spectra and UV-vis absorption maxima were observed for all CPDADB derived PMMA and PS samples.

It was previously mentioned that CPDADB was sensitive to air. Therefore, it was expected that this air sensitivity of (4-*N,N*-dimethylaminophenyl) dithiobenzoate end group can be exploited to produce polymers with easily removable end functional groups. Gratifyingly, when the THF solution of a yellow colored PS sample, **P7** was purged with compressed air for 5–10 min, a colorless polymer solution (and white powder when precipitated from methanol) was obtained after 2 months of storage at room temperature with very little change of its $M_{n,GPC}$ and PDI (yellow PS, $M_{n,GPC}$ 24,700 and PDI 1.06; white PS obtained after treatment, $M_{n,GPC}$ 23,900 and PDI 1.08). Similar colorless polymer solution (and as white polymer when precipitated from methanol) was obtained [Fig. 5(B)] only after 2 days when the THF solution of a yellow PS sample, **P7** was heated at 60 °C and again without any major change in molecular weight characteristics (yellow PS, $M_{n,GPC}$ 24,900, PDI 1.08 and white PS, M_n 24,100, PDI 1.07; see Figure S2 in Supporting Information). The UV-vis spectrum of the precipitated white PS sample produced by the heating process mentioned above also confirmed the disappearance of absorption maxima at ~339 nm and ~417 nm corresponding to the (4-*N,N*-dimethylaminophenyl) dithiobenzoate end group (Fig. 6). However, similar attempts of heating **P7** in other solvents, for example, dichloroethane, toluene, and DMF failed to produce colorless solutions. These above observations made us assume that the discoloration may be due to the THF-generated peroxide-induced oxidation of dithioester (S=C—S—) end group to yield sulfine (O=C—S—) end group similar to the observations reported by Vana et al.[10a] However, surprisingly, ^{1}H NMR study of the resultant white PS, **P7**, obtained from the



SCHEME 1 Synthesis of di-block copolymer by chain extension reaction.

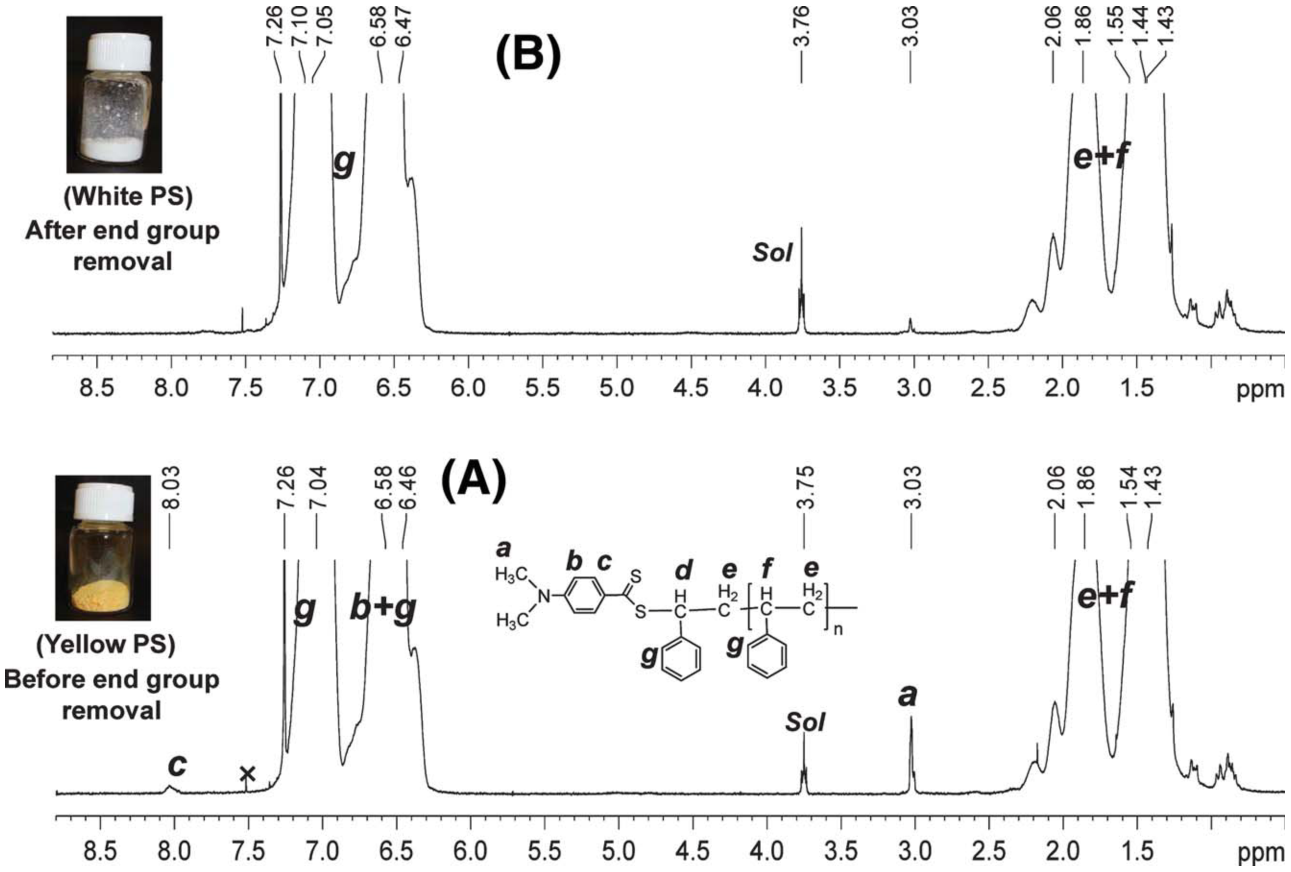


FIGURE 5 Photograph and ^{1}H NMR spectra of PS samples (after precipitation from methanol) (A) **P7** (yellow) and (B) **P7** after the removal of thiocarbonyl end group (white) obtained by heating the THF solution at 60°C for 2 days (sol = solvent). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

above heat treatment confirmed the absence of proton resonances of *N,N*-dimethylamine ($-N(CH_3)_2$, 6H) functional group and phenylene group ($-C_6H_4-$, 2H, *ortho* to thiocarbonylthio group) at 3.03 ppm and 8.02 ppm, respectively [Fig. 5(B)], which would not happen in the case of sulfine formation through the oxidation of dithioester group. Therefore the discoloration of PS, **P7** in THF solution was due to the removal of (4-*N,N*-dimethylaminophenyl) attached thiocarbonyl end group and the most plausible explanation for the observations is the hydrolysis of dithioester end group.

For relatively low molecular weight PS and PMMA (**P9** and **P4** respectively in Table 1) only 50–60% end thiocarbonyl group was removed when the THF solutions of individual polymer were separately heated at 60 °C for 3 days, as confirmed by ^{1}H NMR spectroscopy. However, the addition of a few drops of concentrated hydrochloric acid to the same PS solution (**P9** in Table 1) speeded up the thiocarbonyl end group removal, which was almost completed in 1 day at 60 °C to produce colorless polymer solution (and white polymer when precipitated from methanol) with very slight increase of its original $M_{n,GPC}$ and PDI (**P9**: yellow PS before end group removal, $M_{n,GPC}$ 8200 and PDI 1.06; white PS after end group removal, $M_{n,GPC}$ 8300 and PDI 1.1). The closer look on the GPC chromatogram reveled the appearance of high molecular weight shoulder corresponding to the double ($M_{n,GPC}$ 17,000) of the original molecular weight of the polymer (see Supporting Information Figure S3). ^{1}H NMR

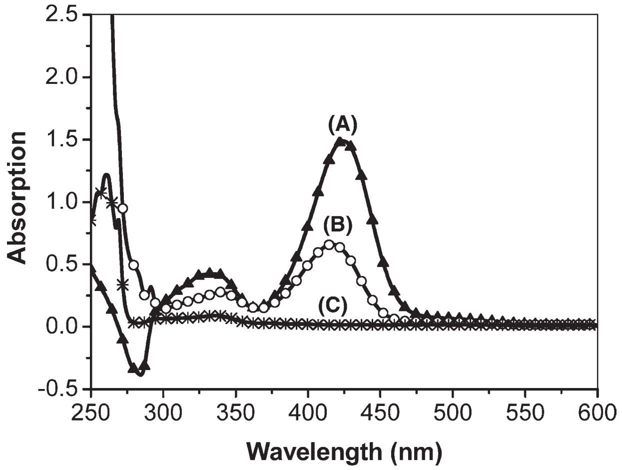


FIGURE 6 UV-vis spectra of THF solution of (A) CPDADB (0.0125 mg/mL); precipitated PS samples (0.5 mg/mL) (B) **P7** (yellow) and (C) **P7** after the removal of thiocarbonyl end group (white) obtained by heating the THF solution at 60°C for 2 days.

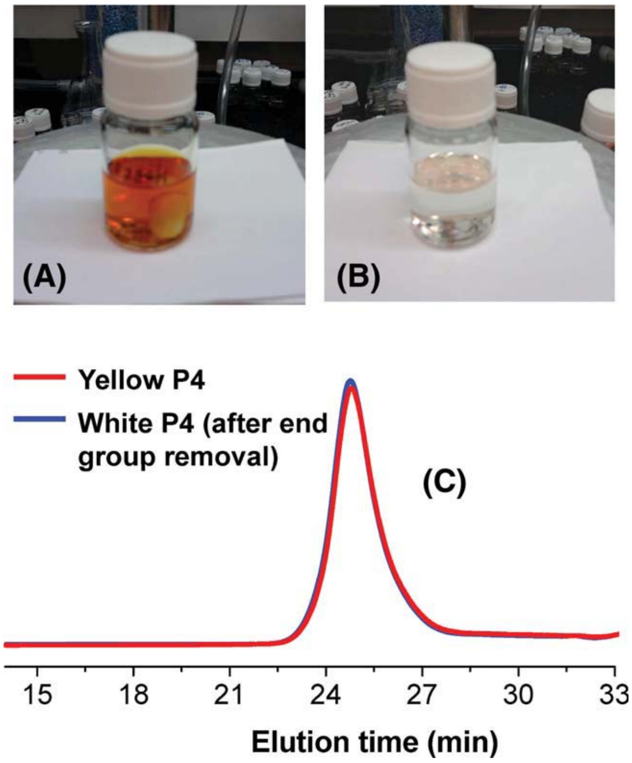


FIGURE 7 Photograph of relatively low molecular weight PMMA: (A) THF solution of yellow **P4**, (B) the same solution after heating at 60°C for 1 h in presence of five drops of conc. HCl and (C) overlay GPC chromatograms of yellow **P4** before end group removal (red line) and white PMMA after end group removal (blue line) obtained by the HCl treatment.

spectrum of the resultant polymer indicated that more than 90% of (4-*N,N*-dimethylaminophenyl) attached thiocarbonyl end group was removed in this process (see Figure S4 in Supporting Information). The UV-vis spectra of white PS obtained after acid treatment showed complete disappearance of absorption maximum at ~417 nm corresponding to thiocarbonylthio end group. All these observations made us believe that the this end group removal procedure of PS (**P9**) would have happened by the acid promoted hydrolysis of dithioesters group to yield thiol end functional group (Scheme S1 in Supporting Information) partly which may be subsequently oxidized or hydrolyzed.

A similar acid treatment of low molecular weight yellow PMMA (**P4**) in THF at 60 °C produced colorless solution (and white powder when precipitated from hexane or cold methanol) (Fig. 7) only just after 1 h with slight increase in its $M_{\mathrm{n,GPC}}$ and PDI (yellow **P4**, before end group removal, $M_{\mathrm{n,GPC}}$ 11,200 and PDI 1.18; white **P4**, after end group removal, $M_{\mathrm{n,GPC}}$ 12,200 and PDI 1.17). Unlike for PS (**P9**) mentioned above, in this case high molecular weight shoulders due to subsequent oxidation of thiol end group formed were not obtained [Fig. 7(C)]. The absence of (4-*N,N*-dimethylaminophenyl) attached thiocarbonyl end group was also observed in the ^{1}H NMR spectrum of the white PMMA obtained (Figure S5 in Supporting Information). The UV-vis spectra of white PMMA showed complete disappearance of absorption maximum at ~417 nm corresponding to thiocarbonylthio end group. Previously Xu et al.[12] have proposed the formation of thiolactone end group for the aminolysis product of RAFT derived PMMA. However in our case, the end group remains as thiol as indicated by the subsequent reaction with phenylacetyl chloride (Scheme S2 and Figure S5 in Supporting Information).

Our efforts to establish the exact nature of end group by MALDI-TOF analysis of these polymers were inconclusive most likely due to the transient nature of the end group of the polymers.

CONCLUSIONS

In conclusion, we have synthesized a novel amine functionalized dithiobenzoate RAFT agent to be used for the RAFT polymerization of vinyl monomers. This dithiobenzoate RAFT agent controlled the polymerization of MMA and St in excellent manner and the polymerization results obtained were marginally better than using the most popular 2-cyanoprop-2-yl dithiobenzoate RAFT agent. The living nature of the polymerizations was confirmed by kinetic study and the synthesis of di-block copolymers by chain extension reactions. Most importantly, we have demonstrated that the air sensitivity of this RAFT agent can be exploited to produce polymers with easily removable color causing RAFT agent derived thiocarbonyl end functionality. The thiocarbonyl end functional group of the poly(styrene) and poly(methyl methacrylate) synthesized using the amine functionalized RAFT agent was easily removed either simply by heating the THF solution of the polymer or by the addition of few drops concentrated hydrochloric acid. The removal of end group from the polymer was confirmed by ^{1}H NMR and UV-vis spectroscopic techniques.

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