α-Cyanobenzyl Dithioester Reversible Addition–Fragmentation Chain-Transfer Agents for Controlled Radical Polymerizations

CHUNZHAO LI, BRIAN C. BENICEWICZ

NYS Center for Polymer Synthesis, Department of Chemistry and Chemical Biology, Rensselaer Polytechnic Institute, Troy, New York, 12180

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ABSTRACT: A series of new reversible addition–fragmentation chain transfer (RAFT) agents with cyanobenzyl R groups were synthesized. In comparison with other dithioester RAFT agents, these new RAFT agents were odorless or low-odor, and this made them much easier to handle. The kinetics of methyl methacrylate radical polymerizations mediated by these RAFT agents were investigated. The polymerizations proceeded in a controlled way, the first-order kinetics evolved in a linear fashion with time, the molecular weights increased linearly with the conversions, and the polydispersities were very narrow (~1.1). A poly[(methyl methacrylate)-*block*-polystyrene] block copolymer was prepared (number-average molecular weight = 42,600, polydispersity index = 1.21) from a poly(methyl methacrylate) macro-RAFT agent. These new RAFT agents also showed excellent control over the radical polymerization of styrenics and acrylates.
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Keywords: block copolymers; controlled radical polymerization; living radical polymerization; reversible addition fragmentation chain transfer (RAFT)

INTRODUCTION

Over the past several years, controlled radical polymerization (CRP) techniques have received a great deal of attention from academia and industry because of their ability to synthesize well-defined polymers with predetermined molecular weights and low polydispersities. Stable free-radical polymerization (SFRP),[1–4] atom transfer radical polymerization (ATRP) or metal-mediated polymerization,[5,6] macromolecular design via the interchange of xanthates (MADIX),[7] and reversible addition–fragmentation chain transfer (RAFT) polymerization have been explored as CRP techniques with various levels of success. Monomer candidates for SFRP are mostly confined to styrenics and alkyl acrylates and operate at higher temperatures than normally used for radical polymerizations. The ATRP method is compatible with a larger variety of monomers, but residual metal ions remain in the final polymer and need to be removed for many practical applications. MADIX polymerizations provide predictable molecular weights for some monomers but often produce a broader polydispersity than other CRP techniques. More recently, RAFT procedures have produced narrow-polydispersity (co)polymers with predictable molecular weights and different architectures and use special chain-transfer agents (CTAs) to control the polymerization.[8–16] This CRP method is compatible with

Correspondence to: B. C. Benicewicz (E-mail: benice@rpi.edu)

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monomers such as styrene, methacrylates, acrylates, acrylamides, and vinyl acetate and also uses polymerization conditions similar to those of conventional radical polymerization with the simple addition of a RAFT agent. However, the most common RAFT agents are dithioesters, which are generally oily and foul-smelling compounds. This requires careful handling in a laboratory environment and may be an obstacle for large-scale commercial applications.[17] In this article, we report the synthesis of a series of dithioester RAFT agents containing α-cyanobenzyl R groups and their excellent control over the radical polymerization of a variety of monomers, including methyl methacrylate (MMA).

EXPERIMENTAL

Materials

Unless otherwise specified, all chemicals were purchased from Acros and were used as received. Phenyl magnesium bromide, naphthyl magnesium bromide, *p*-anisyl magnesium bromide, 4-flurophenyl magnesium bromide, 4-biphenylmagnesium bromide, and 4-tolylmagnesium bromide were purchased from Aldrich. Tetrahydrofuran (THF) and benzene were dried over CaH_2 overnight and distilled before use. Styrene, *n*-butyl acrylate, *t*-butyl acrylate, 4-acetoxystyrene, and MMA were passed through a basic alumina column to remove the inhibitor before use.

Measurements

NMR spectra were recorded on a Varian 500 spectrometer with $CDCl_3$ as the solvent. FTIR spectra were measured with a BioRad Excalibur FTS3000. Elemental analyses were conducted by Midwest Microlab (Indianapolis, IN). The molecular weights and molecular weight distributions were determined with a Waters gel permeation chromatography (GPC) system equipped with a 515 high-performance liquid chromatography (HPLC) pump, a 2410 refractive-index detector, and three Styragel columns (HR1, HR3, and HR4 with effective molecular weight ranges of 100–5000, 500–30,000, and 5000–5,000,000, respectively) with THF as the eluent at 30 °C and at a flow rate of 1.0 mL/min. The GPC system was calibrated with polystyrene (PSt) and poly(methyl methacrylate) (PMMA) standards from Polymer Labs.

Synthesis of α-Cyanobenzyl Dithiobenzoate (1)

To a 100-mL, round-bottom flask was added 5 mL of phenyl magnesium bromide (3 M solution in ethyl ether), which was diluted to 20 mL with anhydrous THF. Carbon disulfide (1.2 g) was added dropwise to this mixture, and the mixture was stirred for 0.5 h at room temperature. To the dark red solution was added dropwise 3 g of α-bromobenzene acetonitrile, and the mixture was stirred for another 3 h. Water was added to the mixture, and the organic product was extracted with diethyl ether (3 $\times$ 50 mL), dried with magnesium sulfate overnight, and filtered. After the removal of the solvent and column chromatography (3:1 mixture of hexane and ethyl ether), pure **1** was obtained as a red, odorless solid (76% yield).

mp: 41 °C (capillary uncorrected). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 6.02 (s, 1H), 7.19–7.50 (m, 8H), 7.96 (d, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 43.22, 116.99, 127.35, 128.40, 128.97, 129.71, 129.93, 130.73, 133.75, 143.40, 222.69. ELEM. ANAL. Calcd.: C, 66.90%; H, 4.09%; S, 23.78%; N, 5.02%. Found: C, 67.12%; H, 4.15%; S, 23.68%; N, 5.18%. IR (NaCl disc): 2243 (CN), 1047 (C═S).

Synthesis of α-Cyanobenzyl Dithionaphthalate (2)

To a 100-mL, round-bottom flask was added 20 mL of 2-naphthylmagnesium bromide (0.5 M solution in THF). Carbon disulfide (0.76 g) was added dropwise to this mixture, and the mixture was stirred for 0.5 h at room temperature. To the dark red solution was added dropwise 2 g of α-bromobenzene acetonitrile, and the mixture was stirred for another 2 h. Water was added to the mixture, and the organic product was extracted with diethyl ether (3 $\times$ 50 mL), dried with magnesium sulfate overnight, and filtered. After the removal of the solvent and column chromatography (10:3 mixture of hexane and ethyl ether), pure **2** was obtained as an orange, odorless solid (63% yield).

mp: 85 °C (capillary uncorrected). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 6.12 (s, 1H), 7.4–7.6 (m, 7H), 7.8–7.9 (m, 2H), 7.94 (d, 1H), 8.08 (d, 1H), 8.5 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 43.24, 117.11, 124.61, 127.52, 127.59, 128.08, 128.46, 128.82, 129.10, 129.74, 129.95, 130.12, 130.81, 132.53, 135.96, 140.58, 222.01. ELEM. ANAL. Calcd.: C, 71.47%; H, 4.07%; S, 20.06%; N, 4.39%. Found: C, 71.66%; H, 4.13%; S, 20.27%; N, 4.36%. IR (NaCl disc): 2245 (CN), 1052 (C═S).

Synthesis of α-Cyanobenzyl 4-Methoxydithiobenzoate (3)

To a 100-mL, round-bottom flask was added 20 mL of *p*-anisyl magnesium bromide (0.49 M solution in ethyl ether). Carbon disulfide (0.76 g) was added dropwise to this mixture, and the mixture was stirred for 0.5 h at room temperature. To the dark red solution was added dropwise 2 g of α-bromobenzene acetonitrile, and the mixture was stirred for another 2 h. Water was added to the mixture, and the organic product was extracted with diethyl ether (3 × 50 mL), dried with magnesium sulfate overnight, and filtered. After the removal of the solvent and column chromatography (5:1 mixture of hexane and ethyl ether), pure **3** was obtained as an orange solid with a slightly agreeable odor (73% yield).

mp: 73 °C (capillary uncorrected). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 3.87 (s, 3H), 6.14 (s, 1H), 6.88 (d, 2H), 7.41–7.58 (m, 5H), 8.06 (d, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 42.90, 55.91, 114.13, 117.32, 128.39, 129.70, 129.74, 129.80, 131.08, 136.52, 164.79, 219.73. ELEM. ANAL. Calcd.: C, 64.20%; H, 4.32%; S, 21.40%; N, 4.68%. Found: C, 64.21%; H, 4.46%; S, 21.29%; N, 4.65%. IR (NaCl disc): 2244 (CN), 1051 (C═S).

Synthesis of α-Cyanobenzyl 4-Fluorodithiobenzoate (4)

To a 100-mL, round-bottom flask was added 10 mL of 4-fluorophenyl magnesium bromide (1.0 M solution in ethyl ether), which was diluted to 20 mL with anhydrous THF. Carbon disulfide (0.76 g) was added dropwise to this mixture, and the mixture was stirred for 0.5 h at room temperature. To the dark red solution was added 2 g of α-bromobenzene acetonitrile dropwise, and the mixture was stirred for another 2 h. Water was added to the mixture, and the organic product was extracted with diethyl ether (3 × 50 mL), dried with magnesium sulfate overnight, and filtered. After the removal of the solvent and column chromatography (10:3 mixture of hexane and ethyl ether), pure **4** was obtained as a red, odorless oil (62% yield).

^{1}H NMR ($CDCl_3$, δ): 6.01 (s, 1H), 7.07 (t, 2H), 7.35–7.55 (m, 5H), 8.03 (q, 2H). ^{13}C NMR ($CDCl_3$, δ): 43.22, 115.81, 115.99, 116.70, 128.21, 129.54, 129.56, 129.63, 129.80, 130.34, 139.48, 220.19. ELEM. ANAL. Calcd.: C, 66.90%; H, 4.09%; S, 23.78%; N, 5.02%. Found: C, 67.12%; H, 4.15%; S, 23.68%; N, 5.18%. IR (NaCl disc): 2244 (CN), 1052 (C═S).

Synthesis of α-Cyanobenzyl 4-Phenyldithiobenzoate (5)

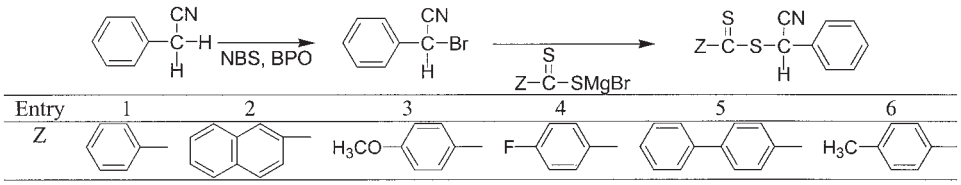
To a 100-mL, round-bottom flask was added 20 mL of 4-biphenylmagnesium bromide (0.5 M solution in ethyl ether). Carbon disulfide (0.76 g) was added dropwise to this mixture, and the mixture was stirred for 0.5 h at room temperature. To the dark red solution was added dropwise 2 g of α-bromobenzene acetonitrile, and the mixture was stirred for another 2 h. Water was added to the mixture, and the organic product was extracted with diethyl ether (3 × 50 mL), dried with magnesium sulfate overnight, and filtered. After the removal of the solvent and column chromatography (5:2 mixture of hexane and ethyl ether), pure **5** was obtained as a red, odorless solid (67% yield).

mp: 127 °C (capillary uncorrected). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 6.09 (s, 1H), 7.40–7.65 (m, 13H), 8.08 (d, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 42.94, 116.87, 127.21, 127.30, 127.79, 128.24, 128.55, 129.09, 129.52, 129.73, 130.62, 139.48, 141.85, 146.39, 221.28. ELEM. ANAL. Calcd.: C, 73.04%; H, 4.35%; S, 18.55%; N, 4.06%. Found: C, 72.91%; H, 4.43%; S, 18.21%; N, 3.96%. IR (NaCl disc): 2241 (CN), 1048 (C═S).

Synthesis of α-Cyanobenzyl 4-Methyldithiobenzoate (6)

To a 100-mL, round-bottom flask was added 10 mL of 4-tolylmagnesium bromide (1.0 M solution in ethyl ether), which was diluted to 20 mL with anhydrous THF. Carbon disulfide (0.76 g) was added dropwise to this mixture, and the mixture was stirred for 0.5 h at room temperature. To the dark red solution was added dropwise 2 g of α-bromobenzene acetonitrile, and the mixture was stirred for another 2 h. Water was added to the mixture, and the organic product was extracted with diethyl ether (3 × 50 mL), dried with magnesium sulfate overnight, and filtered. After the removal of the solvent and column chromatography (5:2 mixture of hexane and ethyl ether), pure **6** was obtained as a red, odorless solid (48% yield).

mp: 90 °C (capillary uncorrected). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 2.38 (s, 3H), 6.08 (s, 1H), 7.20 (d, 2H), 7.40–7.45 (m, 3H), 7.55 (d, 2H), 7.91 (d, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 21.66, 42.82, 116.95, 127.25, 128.20, 129.44, 129.48, 129.66, 130.72, 140.78, 144.89, 221.72. ELEM. ANAL. Calcd.: C, 67.84%; H, 4.59%; S, 22.61%; N,



Scheme 1. General procedure for RAFT agent synthesis.

4.95%. Found: C, 68.12%; H, 4.69%; S, 22.42%; N, 4.93%. IR (NaCl disc): 2245 (CN), 1056 (C═S).

General Procedure of RAFT Polymerization

Aliquots of RAFT agents, monomer, solvent, and azobisisobutyronitrile (AIBN) were added to a Schlenk tube. The tube was subjected to three cycles of freezing, pumping, and thawing to remove oxygen. The tubes were then placed in an oil bath of a preset temperature for various intervals. The polymerization was stopped by the quenching of the tubes in ice water, and the polymerization mixture was poured into a aluminum boat to evaporate the solvent in a fume hood. The aluminum boat was then transferred to a vacuum oven to remove traces of the solvent and monomer at 30 °C overnight to determine the monomer conversions. A portion of the polymer was dissolved in HPLC-grade THF for GPC analysis.

Polymerization Followed by *In Situ* ^{1}H NMR Analysis

Aliquots of MMA, AIBN, CTA, and benzene-d_6 were charged into a Young's tap NMR tube. The solution was degassed by three freeze–pump–thaw cycles and sealed *in vacuo*. The NMR tube was placed in a preheated NMR sample cavity at 60 °C. The sample was allowed to equilibrate for 5 min before the spectra were recorded. The spectra were recorded every 2 min for about 12 h. For quantitative analysis, the pulse angle was set to 30 °, and the relaxation delay time was set to 27 s, to ensure complete relaxation of the nuclei between the individual pulses.

RESULTS AND DISCUSSION

The synthesis of the new RAFT agents is shown in Scheme 1. α-Bromobenzene acetonitrile was obtained through the bromination of benzene acetonitrile with *N*-bromosuccinimide and benzoyl peroxide.[18] Alkylation of different dithiocarboxylic salts, prepared by the reaction of carbon disulfide with the aryl magnesium bromides, with α-bromobenzene acetonitrile yielded the RAFT agents in moderate yields (48–76%). All compounds except **4** were isolated as low-melting crystalline solids.

Surprisingly, none of the compounds in Scheme 1 displayed the strong, unpleasant odors associated with previously used dithioesters.[19,20] Initially, it was thought that the low odor was due to the low vapor pressure of solids in comparison with that of liquids. However, subsequent tests confirmed that the melted dithioesters produced little or no odor. This may be related to the unique R group structure[21] or be a result of the low level of impurities responsible for the odors reported previously.

Polymerization studies were conducted to test the effectiveness of the CTAs at exerting control over radical polymerizations. Table 1 shows the results for the free-radical polymerizations of several different monomers mediated by CTA **1**. The very low polydispersity of PSt prepared at low monomer conversions (entries 1 and 2) indicated that this CTA had a high chain-transfer constant for styrene polymerization. The thermally initiated bulk polymerization of styrene (entry 3) proceeded to higher conversions and molecular weights, with excellent agreement between the predicted and measured molecular weights and narrow polydispersity. For the polymerization of *n*-butyl acrylate (entries 4–6), a low-polydispersity polymer was produced at various [AIBN]/[CTA] ratios (0.17–0.22). The apparent difference between the predicted and measured molecular weights (for both *n*-butyl acrylate and *t*-butyl acrylate) was likely due to the use of PMMA standards for GPC calibration. Entries 7–10 demonstrated that low-polydispersity polymers

Table 1. Results of RAFT Polymerizations with CTA 1[a]

Monomer (M)	Solvent	CTA (M × 10^2)	[AIBN]/[CTA]	Time (h)	Conversion (%)[b]	M_n Theoretical[c]	M_n GPC[d]	PDI
St (6.9)	Benzene	2.0	0.045	9	13	4,448	3,600	1.03
St (6.9)	Benzene	2.0	0.045	29	22	7,585	7,800	1.03
St (8.6)	Bulk	1.6	0	29	67	37,453	38,100	1.12
*n*BA (5.4)	Benzene	2.0	0.17	29	35	12,171	16,600	1.09
*n*BA (5.4)	Benzene	2.0	0.19	29	47	16,206	23,200	1.08
*n*BA (5.4)	Benzene	2.0	0.22	29	49	16,826	20,900	1.07
*t*BA (5.6)	Benzene	1.9	0.14	29	38	14,476	21,700	1.08
*t*BA (5.6)	Benzene	1.9	0.17	29	48	18,285	26,100	1.10
*t*BA (5.6)	Benzene	1.9	0.17	50	63	24,000	34,300	1.13
*t*BA (5.6)	Benzene	1.9	0.19	29	55	20,952	32,600	1.11
AcSt (6.5)	Bulk	1.9	0	7	28	14,414	15,900	1.09
AcSt (6.5)	Bulk	1.9	0	16	36	18,661	22,000	1.10
AcSt (6.5)	Bulk	1.9	0	24	47	24,453	27,400	1.11
MMA (4.8)	Benzene	0.96	0.5	5	90	45,000	46,100	1.28

[a] Polymerizations were conducted at 80 °C, except for the bulk polymerizations of AcSt and St, which were conducted at 100 °C. St = styrene; *n*BA = *n*-butylacrylate; *t*BA = *t*-butylacrylate; AcSt = 4-acetoxystyrene.
[b] Determined gravimetrically.
[c] Calculated with the following formula: M_n = [Monomer]/[CTA] × $M_{monomer}$ × Conversion (%).
[d] Determined by GPC with THF as an eluent and PMMA or PS standards.

were also produced from the bulkier *t*-butyl acrylate ester. The RAFT agent was compatible with functionalized monomers such as 4-acetoxystyrene, as indicated by entries 11–13. PMMA with a predictable molecular weight and a narrow polydispersity was prepared (entry 14) in a high yield with **1**. Other CTAs incorporating the cyanobenzyl group also exhibited excellent control over the polymerizations of different monomers, as listed in Table 2.

The propagating radicals in the polymerization of styrene and acrylates are generally less sterically hindered than those of methacrylates and allow a wider choice of RAFT agents. The free-radical polymerization of MMA is characterized by bulky propagating radicals and modest polymerization rates. RAFT agents with bulky tertiary R groups are believed to be necessary to efficiently control the radical polymerization of MMA.[10,22–25] Thus, only a very lim-

Table 2. Polymerization Results for Polymers Prepared in the Presence of Various CTAs[a]

Monomer (M)/CTA	Solvent	CTA (M × 10^2)	[AIBN]/[CTA]	Time (h)	Conversion (%)	M_n Theoretical	M_n GPC	PDI	Temperature (°C)
MMA (6.0)/2	Benzene	1.2	0.5	23	58	29,000	24,500	1.04	60
MMA (6.7)/3	Benzene	1.34	0.5	13	44	33,377	31,600	1.05	60
St (8.6)/2	Bulk	2.6	0	48	60	20,658	21,600	1.08	100
St (8.6)/3	Bulk	2.6	0	48	63	21,723	25,500	1.07	100
St (8.6)/4	Bulk	2.6	0	48	61	21,002	21,400	1.07	100
St (8.6)/5	Bulk	2.6	0	48	57	20,084	20,700	1.06	100
*n*BA (5.4)/2	Benzene	2.0	0.14	29	42	14,155	21,700	1.06	80
*n*BA (5.4)/3	Benzene	2.0	0.14	29	65	21,906	29,200	1.06	80
*n*BA (5.4)/4	Benzene	2.0	0.14	29	45	15,166	24,000	1.07	80
*n*BA (5.4)/5	Benzene	2.0	0.14	29	32	10,784	14,000	1.04	80

[a] All polymerization mixtures were degassed by three freeze–pump–thaw cycles in Schlenk tubes and then placed in a preset oil bath for the stated time. The CTA numbers are from Scheme 1.

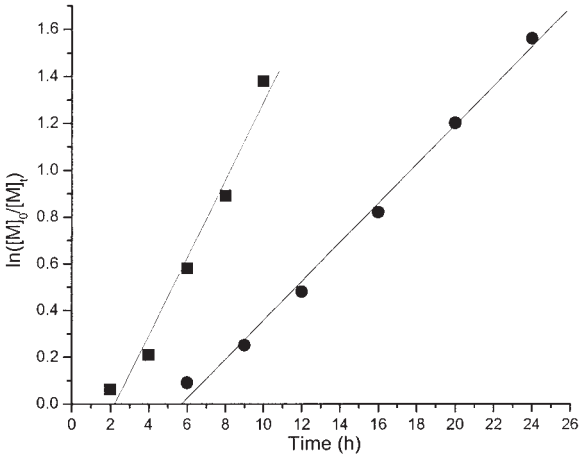


Figure 1. Pseudo-first-order rate plot for the polymerization of MMA (5.58 M in benzene), with AIBN as the initiator (0.0052 M), mediated with CTA **1** (0.011 M): (●) 60 and (■) 70 °C.

ited number of RAFT agents with bulky R groups (cumyl and cyanoisopropyl) have shown excellent control over the polymerization of MMA.

Kinetic data for the polymerization of MMA at 60 and 70 °C are shown in Figure 1. The plots of $\ln([M]_0/[M]_t)$ versus time (where $[M]_0$ is the initial monomer concentration and $[M]_t$ is the monomer concentration at time t) are linear within the investigated conversion ranges, and this implies a constant radical concentration. An induction period was observed at both temperatures. The cause for this inhibition may be associated with the slow reinitiation of the leaving R group of the initial RAFT agent or with the slow fragmentation of the initial intermediate macro-RAFT radical.[26–29] An investigation of these two effects is discussed later. As shown in Figure 2, CTA **1** was a very efficient CTA for the controlled polymerization of MMA. The number-average molecular weight (M_n) increased linearly with the monomer conversion, the measured molecular weight determined by GPC (calibrated with PMMA standards) agreed closely with the theoretical molecular weight, and the molecular weight distribution was narrow (<1.2) throughout the polymerization. This result indicated a very high chain-transfer constant for CTA **1**, which was largely consumed during the early stages of the polymerization (<20%), and it was comparable to those of cyano isopropyl dithiobenzoate and cumyl dithiobenzoate. It was thus concluded that the cyano and phenyl group substitutions on the homolytic leaving group provided both the radical stabilization and steric hindrance necessary for efficient homolytic cleavage and monomer initiation, obviating the need for a tertiary R group. During the submission of this article, Perrier et al.[30] reported that *S*-methoxycarbonylphenylmethyl dithiobenzoate, which also contained a secondary R group, showed good control over MMA radical polymerization [polydispersity index (PDI) < 1.3].

The kinetics of MMA polymerizations mediated by RAFT agents with cyanobenzyl R groups and different Z groups were then investigated to differentiate the aforementioned inhibition effects. Figure 3 shows the *in situ* ^{1}H NMR kinetics of MMA polymerization mediated by CTAs **1**, **3**, and **5**. Because of the electronic effects of the phenyl group substituents, the 4-methoxy phenyl Z group of CTA **3** and the biphenyl Z group of CTA **5** provided better stabilization effects for the macro-RAFT radical than the simple phenyl Z group of CTA **1**. The macro-RAFT radical derived from CTA **3** and CTA **5** would, therefore, have a slower fragmentation rate than CTA **1**. If the inhibition period had been dominated by the slow fragmentation of the initial intermediate macro-RAFT radical, a longer inhibition period would have been expected for the polymerization mediated by CTA **3** and CTA **5** in comparison with that of CTA **1**. However, an inhibition period of a similar length, around 2 h, was observed for all three polymerizations. This result indicated that the

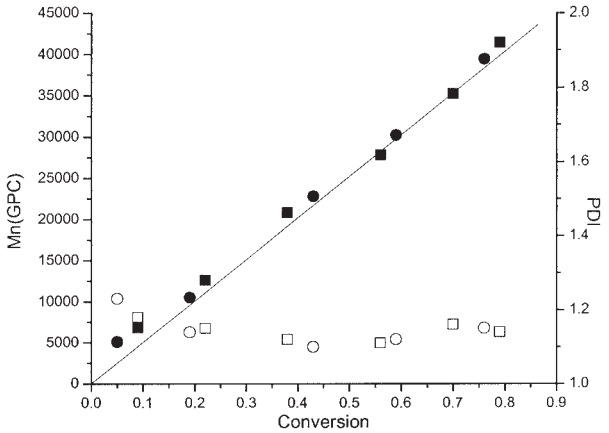


Figure 2. Dependence of the molecular weight and polydispersity on the conversion for MMA polymerization in the presence of CTA **1**: (●,○) 60 and (■,□) 70 °C.

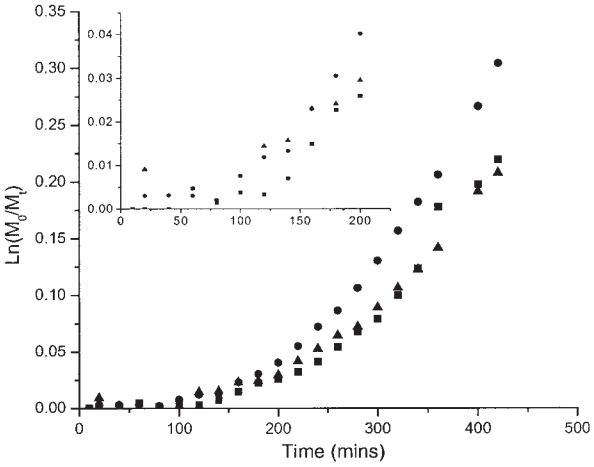


Figure 3. Pseudo first-order rate plot for the polymerization of MMA (5.58 M), with AIBN as the initiator (0.005 M), mediated with (●) CTA **1**, (▲) CTA **3**, and (■) CTA **5** and observed via online ^{1}H NMR spectroscopy at 60 °C in benzene-d_6 for a CTA concentration of 0.11 M.

similar inhibition periods observed for all three polymerizations were more likely governed by the slow reinitiation of the same cyanobenzyl R group of the CTAs than the slower fragmentation of the initial intermediate macro-RAFT radical. After the inhibition period, the rate of polymerization mediated by CTA **1** was apparently faster than that of CTA **3** and CTA **5**, and this could have been due to the stability difference of the macro-RAFT radical discussed previously. Similar results were reported by Quinn et al.[31] and Coote.[32]

The incorporation of the CTA into the polymer was confirmed by ^{1}H NMR spectroscopy. The ^{1}H NMR spectrum of PMMA (molecular weight = 11,700, polydispersity = 1.17) synthesized by RAFT polymerization in the presence of **1** is shown in Figure 4. The signals for the protons of the aromatic rings on the chain ends (a + b) could be clearly observed. The absence of a signal at 6.02 ppm and the appearance of a signal at 4.3 ppm were consistent with the cyanobenzyl group attached to the methylene terminus of the PMMA chain.

Another important feature of CRP is the ability to form block copolymers. Thus, a polymer chain with a dithioester end group can be considered a macro-CTA capable of reactivation to form block copolymers upon the addition of a second monomer. A PMMA homopolymer was prepared (M_n = 10,200, PDI = 1.14) with **1**, isolated, and then reinitiated in the presence of styrene to produce a block copolymer, PMMA-*block*-PSt. The styrene conversion was 65% after 30 h at 100 °C. The complete shift of the GPC trace (Fig. 5) and the low polydispersity (PDI = 1.21) of the final block copolymer indicated a very high reinitiation efficiency of the macro-CTA.

CONCLUSIONS

A series of new CTAs incorporating α-cyanobenzyl R groups were synthesized. These CTAs were prepared with a simple two-step procedure and, in most cases, were isolated as low-melting solids. The new RAFT agents were very effective for the controlled polymerization of styrenics, acrylates, and MMA, producing polymers with predictable molecular weights and narrow polydispersities at moderate-to-high conversions. Block copolymers were also prepared from PMMA macro-RAFT agents. The GPC results indicated a high reinitiation efficiency of the macro-RAFT agents and demonstrated that narrow-polydispersity block copolymers could be obtained.

The support of Eastman Kodak Co. and the Nanoscale Science and Engineering Initiative of the National Science Foundation (DMR-0117792) is gratefully appreci-

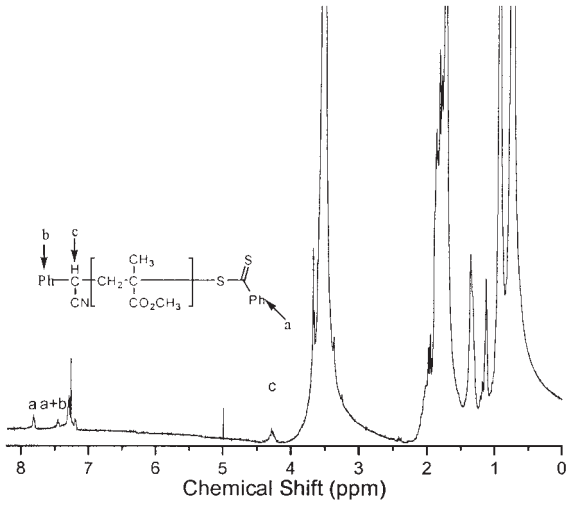


Figure 4. Structure and ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of PMMA prepared in the presence of CTA **1**.

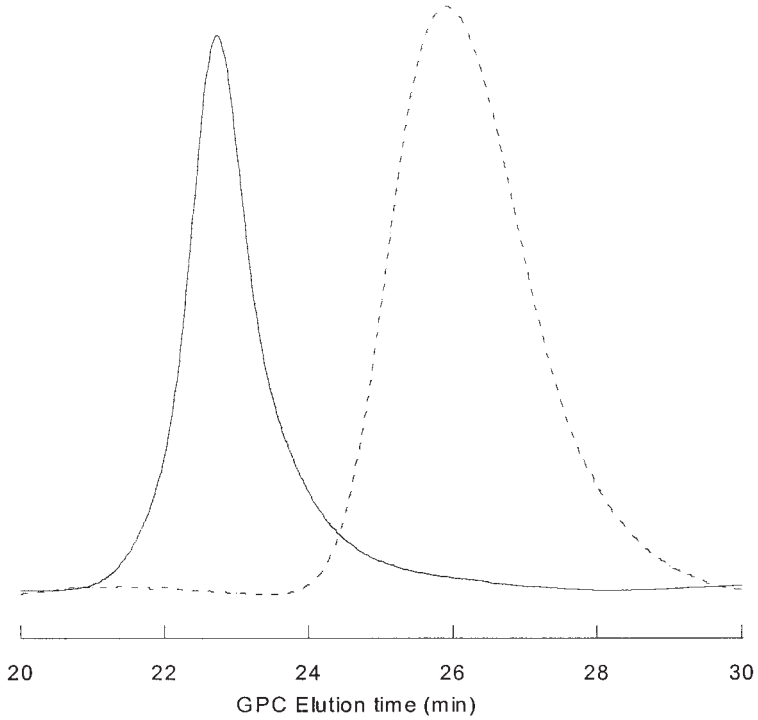


Figure 5. GPC traces for (—) PMMA-*block*-PSt (M_n = 42,600, PDI = 1.21) and (- - -) PMMA (M_n = 10,200, PDI = 1.14).

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