''Living''/Controlled Polymerization of Methyl Acrylate Mediated by Dithiocarbamates under γ-Ray Irradiation

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ABSTRACT: γ-Ray initiated reversible addition–fragmentation chain transfer (RAFT) polymerizations of methyl acrylate (MA) were investigated in bulk using five different dithiocarbamate structures, 2-phenyl-benzoimidazole-1-carbodithioic acid benzyl ester (**1b**), 2-methyl-benzoimidazole-1-carbodithioic acid benzyl ester (**1c**), 2-pheny-indole-1-cardithioic acid benzyl ester (**1d**), 2-(carbazole-9-carbothioylsulfanyl)-2-methyl-propionic acid ester (**1e**), and carbazole-9-carbodithioic acid naphthalene-1-ylmethyl ester (**1f**), as RAFT agents. The experiment results showed that MA polymerized in a controlled way under a low irradiation dose rate, i.e., first-order kinetic plots, the experimental molecular weights increased linearly with monomer conversions. The polydispersity indices of polymers generally remained at a relatively low value (lower than 1.4). The effect of irradiation dose on the polymerization results was investigated. The obtained polymers were characterized with ^{1}H NMR and GPC. Chain-extension reaction was also successfully carried out using the obtained polymer as the macro-RAFT agent and styrene as the second monomer. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 1769–1775, 2007

Key words: dithiocarbamate; RAFT polymerization; γ-ray irradiation

INTRODUCTION

Reversible addition–fragmentation chain transfer (RAFT) polymerization as one of the most robust living radical polymerization techniques was paid more and more attention by researchers these years for its powerful versatility.[1–4] The RAFT process undergoes a series of reversible addition-fragmentation steps in the presence of a RAFT agent [Z—C(=)S—SR], in which *Z* group strongly influences the stability of the thio-carbonyl-thio radical intermediate. Therefore, strong stabilizing groups will favor the formation of the intermediate, and hence enhance the reactivity of the C=S bond toward radical addition. Numerous groups have investigated the effect of the *Z* group structure on the polymerization of a variety of monomers.[5–9] In the case of *N*,*N*-dialkyl dithiocarbamate (**1a**, Scheme 1), the nonbonded electron pair on N is delocalized with the C=S double bond. This lowers the reactivity of the C=S toward radical addition, and thereby the rate of addition of the propagating radical on the sulfur atom decreases, which leads to poor control over the molecular weight of the growing polymeric chains.[5,6,10] Although the nitrogen proton is involved in an aromatic structure or conjugated with electron-withdrawing group, it will increase the reactivity of the C=S bond and the overall rate of chain transfer. For instance, dithiocarbamates derived from pyrrole and imidazole are effective RAFT agents for the polymerization of styrene or methacrylates.[5,9]

Since Pan and coworkers conducted ^{60}Co γ-radiation polymerization in the presence of dibenzyl trithiocarbonate,[11] a new method of ''living''/controlled polymerization without using any thermal or photoinitiator was developed.[10,12–19] According to the results reported by Davis and coworkers,[16–19] the γ-ray irradiation living free radical polymerization mediated by RAFT agents would undergo a RAFT mechanism, which is shown in Scheme 1.

First, Pan and coworkers reported the γ-ray irradiation initiated RAFT polymerization in the presence of benzyl 9H-carbazole-9-carbodithioate.[14] Recently, they investigated the effects of different dithiocarbamates on the polymerizations of methyl acrylate

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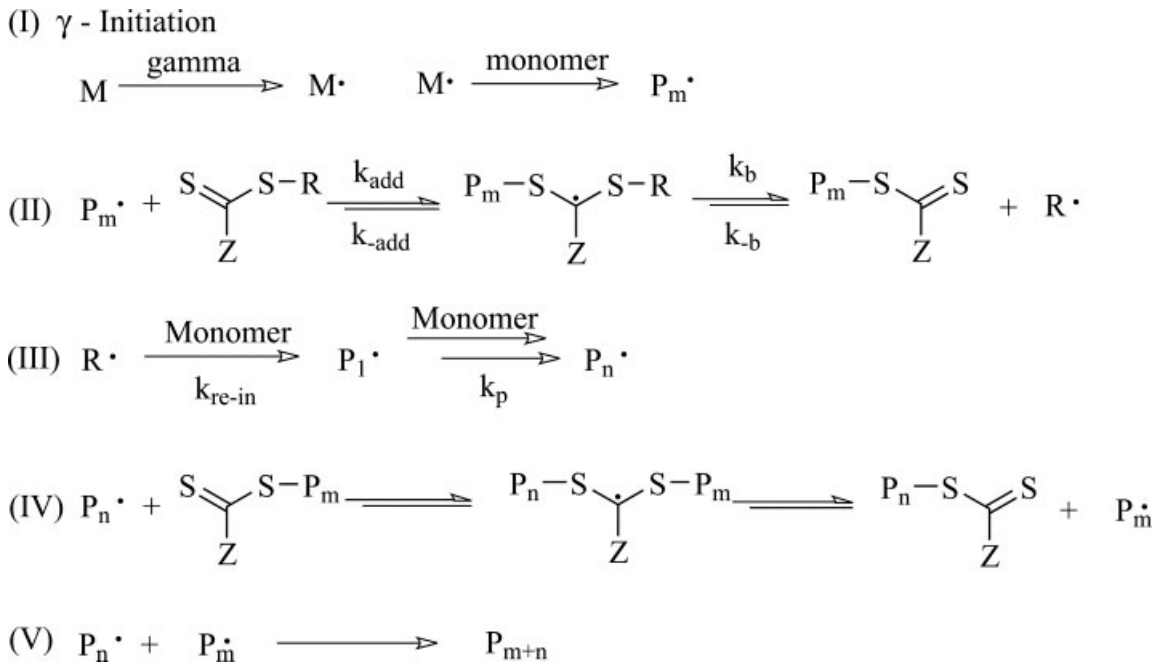


Scheme 1 Possible mechanism for γ-ray irradiation initiated RAFT polymerization.

under γ-ray irradiation.[10] The results indicated that the polymerization rate was influenced by the conjugation structure of the N-group of the dithiocarbamate, and the aromatic polycyclic structure of the N-group led to slow polymerization. In this work, five different dithiocarbamates (the structures are shown in Scheme 2) were selected for RAFT polymerization initiated by γ-ray irradiation. The effectiveness of the dithiocarbamates for the ''living''/controlled free-radical polymerization of MA was investigated.

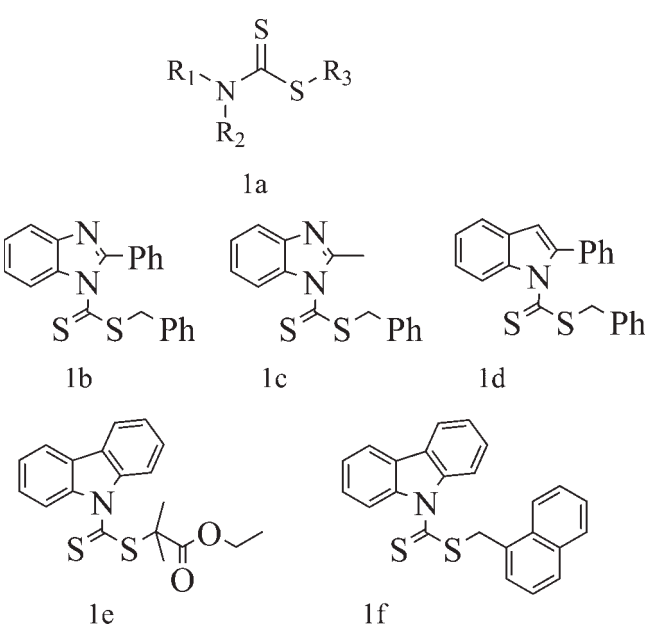
EXPERIMENTAL

Materials

All chemicals (analytical-grade) used in this work were purchased from Shanghai Chemical Reagents (China) and J and K-Acros. Methyl acrylate (MA) and styrene were washed first with 5% NaOH solution thrice, and then with deionized water until neutralization, dried overnight with anhydrous $MgSO_4$, and finally distilled twice under reduced pressure prior to use. Other materials were used without further purification.

Synthesis of dithiocarbamates

The dithiocarbamates **1b**, **1c**, and **1d** were synthesized according to the literature.[20–22] The synthesis procedure of **1e** and **1f** were described as follows. A suspension of NaOH (0.4 g, 0.01 mol) in dimethyl sulfoxide (50 mL) was prepared at room temperature. Carbazole (1.67 g, 0.01 mol) was added under vigorous stir. The reaction mixture was stirred for 1 h. Then, CS_2 (0.76 g, 0.01 mol) was added dropwise. The resultant reddish-orange solution was stirred for another 2 h at room temperature, and then ethyl 2-bromoisobutyrate (1.95 g, 0.01 mol) was added. Meanwhile for the synthesis of **1f**, 1-chloromethyl-naphthalene (1.76 g, 0.01 mol) was added. After stirred overnight, the mixture was poured into large amount of icy water with vigorous stir and extracted with diethyl ether (40 × 3 mL). The com-



Scheme 2 Chemical structures of the dithiocarbamates.

bined extracts were washed with deionized water, then dried over anhydrous $MgSO_4$, and evaporated under vacuum to afford crude products. After recrystallized from alcohol twice, the pure products were obtained as yellow crystallines (**1e**) or yellow brown crystalline (**1f**). The received dithiocarbamates were characterized by ^1H NMR, elemental analysis, and high-efficiency liquid chromatography (HPLC). The results were shown as follows:

2-Phenyl-benzoimidazole-1-carbodithioic acid benzyl ester (**1b**)

Yellow crystalline. The purity was 98% by HPLC. ELEM. ANAL. Calcd. For $C_{21}H_{16}N_2S_2$: C, 69.97%; H, 4.47%; N, 7.77%. Found: C, 69.73%; H, 4.72%; N, 7.52%. ^1H NMR (δ): 4.54 (s, 2H), 7.22–7.47 (m, 10H), 7.72–7.84 (m, 4H).

2-Methyl-benzoimidazole-1-carbodithioic acid benzyl ester (**1c**)

Orange oil. The purity was above 99% by HPLC. ELEM. ANAL. Calcd. For $C_{16}H_{14}N_2S_2$: C, 64.39%; H, 4.73%; N, 9.39%. Found: C, 63.56%; H, 4.83%; N, 9.00%.

2-Pheny-indole-1-cardithioic acid benzyl ester (**1d**)

Orange crystalline. The purity was above 99% by HPLC. ^1H NMR (δ): 4.58 (s, 2H), 7.37–7.55 (m, 13H), 8.22–8.24 (m, 1H), 8.42 (s, 1H).

2-(Carbazole-9-carbothioylsulfanyl)-2-methyl-propionic acid ester (**1e**)

Yellow crystalline. The purity was greater than 99% by HPLC. ELEM. ANAL. Calcd. For $C_{19}H_{19}NO_2S_2$: C, 63.83%; H, 5.36%; N, 3.92%. Found: C, 63.37%; H, 5.58%; N, 3.88%. ^1H NMR (δ): 1.32 (m, 3H), 1.88 (s, 6H), 4.27 (m, 2H), 7.33–7.47 (m, 4H), 8.00 (d, 2H, $J = 7.2$ Hz), 8.34 (d, 2H, $J = 8.4$ Hz).

Carbazole-9-carbodithioic acid naphthalene-1-ylmethyl ester (**1f**)

Yellow brown crystalline. The purity was greater than 98% by HPLC. ELEM. ANAL. Calcd. For $C_{14}H_{27}NS_2$: C, 75.16%; H, 4.47%; N, 3.65%. Found: C, 74.54%; H, 4.57%; N, 2.98%. ^1H NMR (δ): 5.18 (s, 2H), 7.31–8.46 (m, 15H).

Polymerizations

γ-Ray irradiation RAFT polymerization of MA

The general procedure was as follows. Solution of **1b** (10.5 mg) in MA (5 g) with predetermined concentration ($[\mathbf{1b}]_0 : [MA]_0 = 2000 : 1$) was prepared. One milliliters of above-mentioned solution was poured into a 2-mL ampoule and deoxygenated by purging with argon for 15 min, and then the ampoule was flame-sealed. Afterward, the ampoules were placed in an insulated room with a ^{60}Co source at dose rates of 0.6 and 1.8 kGy h^{-1}, respectively. The ampoules were taken out after predetermined time period and opened. The content was diluted with a little THF (2 mL) and then precipitated in the large amount of petroleum ether (300 mL). The polymer was separated by filtration and dried in a vacuum oven at 40°C for 24 h. The conversion was determined gravimetrically.

Chain extension using PMA as macro-RAFT agent

PMA, obtained by γ-ray irradiation initiated reversible addition–fragmentation chain transfer (RAFT) polymerization, and styrene with predetermined concentration ($[PMA]_0 : [St]_0 = 1 : 1500$) were added into a 5-mL ampoule. The ampoule was purged with argon for 15 min, and then was flame-sealed, and placed in an oil bath at 100°C for 6 h. The other procedures were the same as described earlier.

Characterization

The molecular weights and polydispersities of the polymers were measured on a Waters 1515 gel-permeation chromatograph (GPC) equipped with refractive index detector using HR 1, HR 3, and HR 4 column with molecular weight range 100–500,000 calibrated with poly(methyl methacrylate) standard samples. The eluent was tetrahydrofuran (THF) with a flow rate of 1.0 mL min^{-1}. The column temperature was set at 30°C. ^1H NMR spectra were recorded in $CDCl_3$ on an INOVA 400MHz spectrometer at an ambient temperature. Tetramethylsilane was used as an internal standard. Elemental analyses of C, H, and N were measured with an EA1110 CHND-S. The purity of the dithiocarbamates was determined with a Waters 515 HPLC apparatus: a mixture of methanol and water (methanol : water = 80 : 20, v/v) was used as the eluent at a flow rate of 0.8 mL min^{-1} at 30°C with a C18 column and with a Waters 996 detector.

RESULTS AND DISCUSSION

Living radical polymerizations of MA using dithiocarbamates as RAFT agents

Dithiocarbamates **1b**, **1c**, and **1d** have been previously reported to be efficient RAFT agents for the polymerizations of styrene initiated thermally.[23,24] In this work, the polymerizations of MA were performed at an ambient temperature with γ-ray irradi-

TABLE I
RAFT Polymerization Results of MA Under γ-Ray Irradiation Using the Different RAFT Agents

Entry	RAFT agent	Dose rate (kGy/h)	Time (h)	Conversion (%)	$M_{n,GPC}$ (g mol^{-1})	$M_{n,th}$ (g mol^{-1})	PDI
1	**1b**	0.6	2	21.4	39,000	37,100	1.10
2	**1b**	1.8	3	56.3	110,400	97,300	1.25
3	**1c**	0.6	2	1.9	4,900	3,600	1.39
4	**1c**	1.8	5	31.2	68,400	53,900	1.23
5	**1d**	0.6	3	21.0	41,500	36,500	1.22
6	**1d**	1.8	2	32.3	65,700	55,800	1.18
8	**1e**	0.6	3	30.1	68,100	52,100	1.10
7	**1e**	1.8	1	20.8	46,000	36,100	1.10
9	**1f**	0.6	1	2.4	4,700	4,500	1.30
10	**1f**	0.6	5	46.2	88,200	79,900	1.21
11	**1f**	1.8	3	39.1	80,100	67,700	1.18
12	**1f**	1.8	5	60.1	107,100	103,700	1.30

$[MA]_0 : [RAFT\ agent]_0 = 2000 : 1$.

ation using the dithiocarbamates **1b**, **1c**, **1d**, **1e**, and **1f**, respectively, as the RAFT agents.

The results of polymerizations are listed in Table I. From Table I, it can be seen that the five RAFT agents were all effective for controlling the polymerizations of MA, which resulted in PMA with controlled molecular weight and low polydispersity. The theoretical molecular weights ($M_{n,th}$) were calculated according to eq. (1):

$$M_{n,th} = ([MA]_0/[RAFT\ agent]_0) \times MW_{MA} \times conversion + MW_{RAFT\ agent} \quad (1)$$

where $[MA]_0$ and $[RAFT\ agent]_0$ are the initial concentrations of MA and RAFT agent, respectively. The MW_{MA} and $MW_{RAFT\ agent}$ are the molecular weights of MA and RAFT agent, respectively.

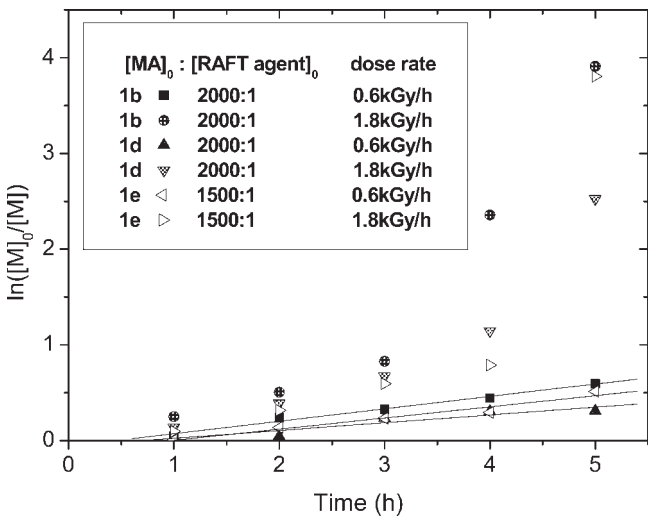


Figure 1 Kinetic plots for γ-irradiation initiated RAFT polymerization of MA mediated by dithiocarbamates (**1b**, **1d**, and **1e**).

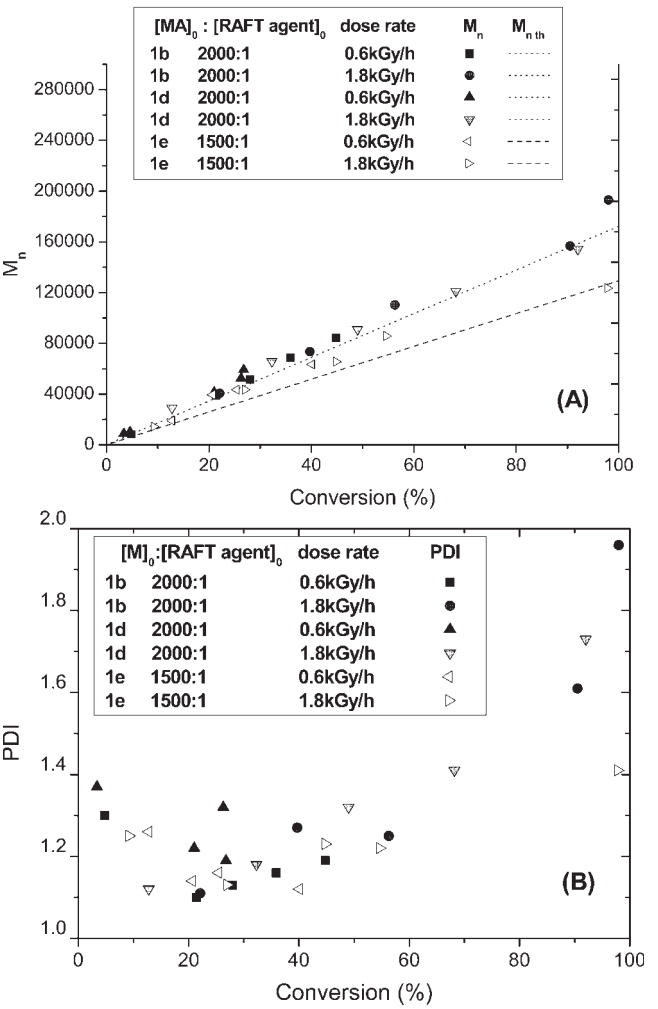


Figure 2 Dependence of M_n (A) and polydispersity index (PDI) (B), on conversion for γ-irradiation initiated RAFT polymerization of MA using dithiocarbamates (**1b**, **1d**, and **1e**) as RAFT agents.

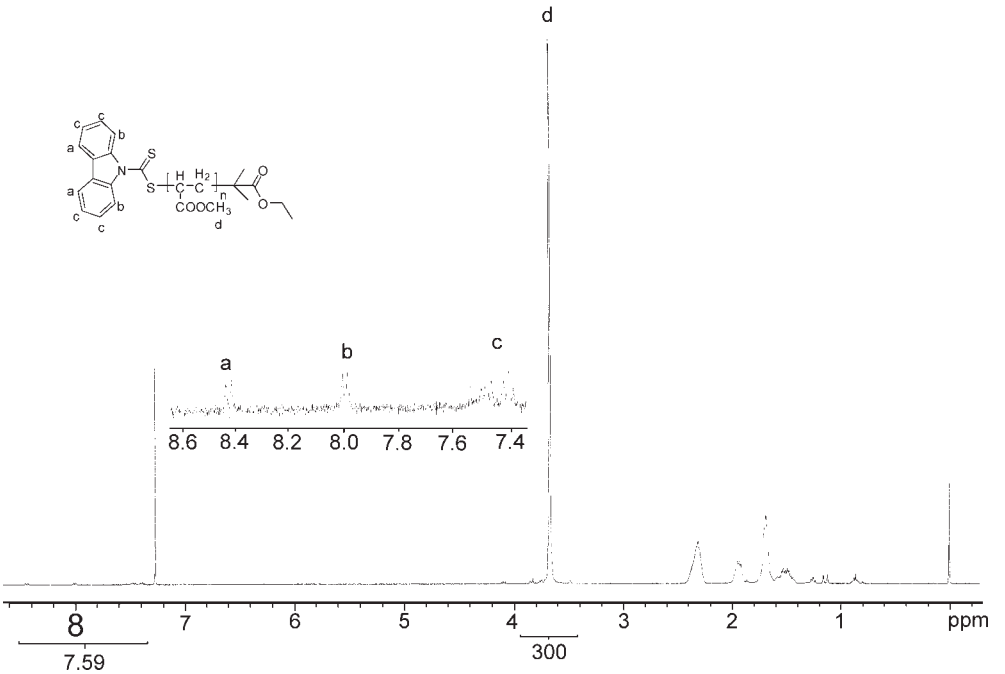


Figure 3 ^{1}H NMR of PMA (M_n = 10,500 g mol^{-1}, PDI = 1.18) polymer using $CDCl_3$ as solvent and tetramethylsilane (TMS) as the internal standard.

To further investigate the polymerization behavior, three dithiocarbamates **1b**, **1d**, and **1e**, respectively, were used to mediate the polymerizations of MA under two different dose rates (0.6 and 1.8 kGy/h). The polymerization kinetics are shown in Figure 1. A linear relationship between $\ln([M]_0/[M])$ and polymerization time indicated that the number of radicals remained constant during the polymerization under dose rate of 0.6 kGy/h. However under the dose rate of 1.8 kGy/h, the radical concentration induced by the irradiation were higher than that under the dose rate of 0.6 kGy/h, which resulted in the polymerization rate significantly accelerated. The results also showed that the polymerization rate abruptly enhanced as the polymerization time prolonged beyond 4 h. This result might indicate that the uncontrollable polymerization became obvious as the free radical continuously generated under the irradiation.

It can be seen that there was an inhibition period at the beginning of the polymerization. Inhibition phenomenon was often observed during a RAFT polymerization process, which may be contributed to slow fragmentation of intermediated radical **2** (Scheme 1), as evidenced by experimental data[25] and *ab initio* calculations.[26] McCormick and coworkers[27] and some other groups[28,29] offered an alternative explanation of inhibition, which is the slow reinitiation of the initial RAFT agent leaving group (R, Scheme 1). As shown in Figure 1, **1d** had a longer inhibition period than that of **1b**. Furthermore, after the inhibition period, the polymerization rate of **1d** was slower than that of **1b**. Since the R groups of both RAFT agents **1b** and **1d** are identical, we consider the reason for the inhibition is more likely to be the slow fragmentation mechanism. The intermediate radicals formed in the case of **1d** would be more stable than those in the case of **1b**. It can be approved that the polymerization rate was markedly influenced by the conjugation structure of the N-group of the dithiocarbamate.

Figure 2 shows the evolution of molecular weight and polydispersity index with the monomer conversion in the polymerizations of MA with **1b**, **1d**, and **1e**. It can be seen that the molecular weights increased linearly with the conversion. The experimental molecular weights were close to the theoretical molecular weights in the cases of **1b** and **1d,** however, in the case of **1e**, the experimental molecular weights were higher than the corresponding theoretical values. The probable reason was that the RAFT agent was slowly consumed at an ambient temperature, while the theoretical molecular weight was calculated based on complete consumption of the RAFT agent during this period.[30]

The polydispersity indices of the polymers in most cases were kept to be lower than 1.4. However, when the monomer conversion was up to over 90%, the polydispersity indices trended higher. These results confirmed the conclusion that the increase of irradiation dose rate could accelerate the rate of the RAFT polymerization of MA, but the side reactions also increased. Therefore, it is important to choose appropriate irradiation dose rate and reaction time during γ-ray initiated RAFT polymerization.

End group analysis

Figure 3 shows a typical ^{1}H NMR spectrum of PMA prepared by using **1e** as the RAFT agent ($[MA]_0$: $[\mathbf{1e}]_0$ = 1000 : 1) under ^{60}Co γ-irradiation with the conversion of 11.9%, molecular weight of 10,500 g mol^{-1}, and PDI = 1.18. The appearance of signals at δ = 7.3–8.5 ppm indicate the existence of carbazyl groups in the polymer chain. The signal at δ = 3.67 ppm corresponds to the methyl protons in the MA units. Assuming that each macromolecule contains a moiety of the RAFT agent, $M_{n,\mathrm{NMR}}$ (9400 g mol^{-1}) can be calculated based on Eq. (2):

$$M_{n,\mathrm{NMR}} = ((I_{3.67}/3)/(I_{7.3-8.5}/8)) \times 86 + 357 \quad (2)$$

where $I_{3.67}$ is the integral values of the peaks at δ = 3.67 ppm. $I_{7.3-8.5}$ is the integral values of the peaks at δ = 7.3–8.5 ppm, corresponding to the carbazole group at the end of the polymer. The molecular weights of MA and **1e** are 86 and 357, respectively.

Furthermore, the chain extension with styrene using the PMA prepared by using **1e** as a RAFT agent with the molecular weight of 14,400 g mol^{-1} and PDI = 1.25 as the macro-RAFT agent had been carried out. The ratio of styrene and PMA was $[St]_0$: $[PMA]_0$ = 1500 : 1. The polymerization was carried out with thermal initiation at 100°C for 6 h. The resulted GPC traces of PMA and the corresponding block polymers, PMA-*b*-PS, were shown in Figure 4. There was an obvious peak shift from the macro-RAFT agent (M_n = 14,400 g mol^{-1}, PDI = 1.25) to the PMA-*b*-PS block copolymer (M_n = 41,800 g mol^{-1}) with a narrower polydispersity index (PDI = 1.14). The peak of PMA macro-RAFT agent was disappeared thoroughly, which demonstrated that the macro-RAFT agent had completely converted to a PMA-*b*-PS copolymer.

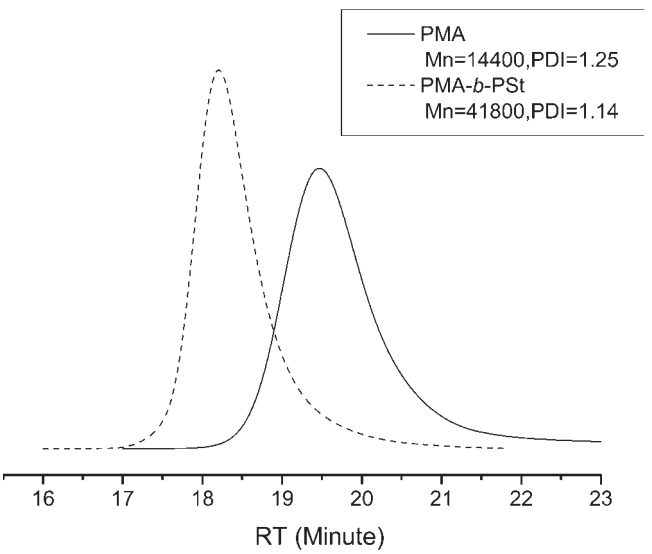


Figure 4 GPC traces of PMA before and after chain-extension reaction using thermal initiated RAFT polymerization. Conditions: temperature = 100 °C; $[St]_0$: $[PMA]_0$ = 1500 : 1; time = 6 h; conversion = 25.5%.

The agreement among $M_{n,\mathrm{NMR}}$ (9400 g mol^{-1}), $M_{n\mathrm{GPC}}$ (10,500 g mol^{-1}), and $M_{n,\mathrm{th}}$ (10,600 g mol^{-1}) as well as the successful chain extension further confirmed the ''living''/controlled character of the polymerization of MA in the presence of **1e** initiated by γ-irradiation. All evidences mentioned earlier supported that the polymerizations of MA initiated by γ-ray in the presence of dithiocarbamates with conjugation structure on N-group were well controlled and the polymerization was via a RAFT mechanism.

CONCLUSIONS

The γ-ray initiated polymerizations of MA showed living characteristics in the presence of RAFT agents **1b**, **1c**, **1d**, **1e**, and **1f** with the conjugation structure of N-group. The PMAs with controlled molecular weights and low polydispersity indices could be prepared at proper selection of conditions in this manner. Polymerization rate increased along with the irradiation dose rate and was influenced by the structure of N-group. ^{1}H NMR characterization of obtained PMA showed that the moiety of RAFT agent remained at the end of the polymer chain. GPC results indicated that the polymer could be used as a marco-RAFT agent to conduct chain extension reaction with second monomer to prepare the block copolymers with narrow polydispersity.

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