

# Influence of the Chemical Structure of Dithiocarbamates with Different R Groups on the Reversible Addition-Fragmentation Chain Transfer Polymerization

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**ABSTRACT:** Four dithiocarbamates, carbazole-9-carbodi-thioic acid benzyl ester (R1), carbazole-9-carbodithioic acid naphthalen-1-ylmethyl ester (R2), 2-(carbazole-9-carbothioyl-sulfanyl)-2-methyl-propionic acid ethyl ester (R3), and (carbazole-9-carbothioylsulfanyl)-phenyl-acetic acid methyl ester (R4), were synthesized and used to the reversible addition-fragmentation chain transfer (RAFT) polymerizations of styrene (St), methyl methacrylate (MMA), and methyl acrylate (MA), respectively. The influence of chemical structure of dithiocarbamates with different R groups on the RAFT polymerizations was investigated. The results showed that the four RAFT agents were effective RAFT agents for the polymerizations of styrene or MA, and that the polymerizations were well-controlled with the characteristics of controlled/

“living” polymerization. The polymerization rate of styrene with thermal initiation was markedly influenced by the chemical structures of the group R in dithiocarbamates, and decreased in the order of R3 > R2 > R4 > R1. For the polymerization of MA, the efficiency of RAFT agents was in the following order: R2–R3 > R1 > R4. However, they were not efficient enough to control the polymerization of MMA. The obtained polystyrene (PSt) with carbazole group labeled strongly absorbed UV light at 294 nm and emitted fluorescent light in *N,N*-dimethyl formamide (DMF). © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 982–988, 2007

**Key words:** fluorescence; polystyrene; radical polymerization; structure

## INTRODUCTION

Dithio derives  $[Z-C(=S)-SR]$  have been known for a long time and their preparation and reactivity have been widely investigated.<sup>1</sup> In recent years, these compounds attracted the attention of polymer chemist for their abilities to control free radical polymerization, especially the reversible addition-fragmentation chain transfer (RAFT) polymerization of such monomers as styrene, acrylates, and methacrylates.<sup>2–8</sup> RAFT process is a polymerization in the presence of RAFT

agent, which is reacted by a series of reversible addition-fragmentation steps.<sup>2,3,9–15</sup> General structures of RAFT agents are dithioester,<sup>2,3</sup> xanthate,<sup>14–16</sup> trithio-carbonate,<sup>17,18</sup> and dithiocarbamate.<sup>19–22</sup> Rizzado and other researchers have reported that the RAFT polymerization under a particular set of reaction conditions depended on the nature of the Z and R groups of RAFT agents.<sup>23–26</sup> With appropriate choice of the RAFT agent and reaction conditions, RAFT polymerization can be successfully used to produce polymer with narrow molecular weight distribution and pre-determined molecular weight. Considerable efforts have been expended to synthesize RAFT agents with different Z group or different R group by various synthetic techniques.<sup>10,27–30</sup> Among these synthetic methods, we notice that the dithiocarbamates can be synthesized by a convenient way showed in Scheme 1. Our group recently reported the influence of the chemical structure of dithiocarbamates with different *N*-groups (Z group) on the RAFT polymerization of styrene.<sup>26</sup> In this work, the influence of R group on the effectiveness of dithiocarbamates (Z group = carbazole group) as RAFT agents is studied in detail. Fluorescence of dithiocarbamates and obtained well-controlled carbazole group labeled polymer has also been investigated.

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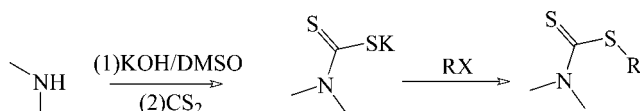
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**Scheme 1** Synthesis route of dithiocarbamate.

## EXPERIMENTAL

### Materials

All chemicals (analytical grade) used in this study were purchased from Shanghai Chemical Reagents (China) and J and K-Acros. Monomers were washed with an aqueous solution of sodium hydroxide (5 wt %) thrice, and then with deionized water until neutralization. After being dried with anhydrous magnesium sulfate, these monomers were distilled under reduced pressure and kept in a refrigerator under 4°C. Other materials were used without further purification. Dithiocarbamates (Scheme 2) were prepared by the following procedure. A suspension of KOH (0.56 g, 0.01 mol) in DMSO (50 mL) was prepared, and carbazole (1.67 g, 0.01 mol) was added under vigorous stirring. The solution was stirred for 1 h at room temperature and then CS<sub>2</sub> (0.76 g, 0.01 mol) was added dropwise. The resultant reddish solution was stirred for 2 h at room temperature, and then halogenated hydrocarbon (RX) was added. After the mixture was stirred for a night, the mixture was precipitated in large amount of water, and a yellow solid was obtained. After being recrystallized twice from alcohol, yellow crystal was obtained and characterized by nuclear magnetic resonance (<sup>1</sup>H-NMR), elementary analysis (EA), and high-performance efficiency liquid chromatography (HPLC). The results were listed below:

#### Carbazole-9-carbodithioic acid benzyl ester (R1)

Yield 20%, <sup>1</sup>H-NMR. δ: 4.73 (s, 2H), 7.23–7.48 (m, 7H), 8.00 (d, 2H, *J* = 7.6 Hz), 8.09 (d, 2H, *J* = 8.0 Hz), 8.66 (d, 2H, *J* = 6.8 Hz). EA. C<sub>20</sub>H<sub>15</sub>NS<sub>2</sub>, calculated: C 72.03 H 4.53N 4.20, found: C 71.77 H 4.55N 4.48. The purity was above 99% by HPLC.

#### Carbazole-9-carbodithioic acid naphthalen-1-ylmethyl ester (R2)

Yield 40%, <sup>1</sup>H-NMR. δ: 5.18 (s, 2H), 7.31–8.46 (m, 15H). EA. C<sub>14</sub>H<sub>27</sub>NS<sub>2</sub>, calculated: C 75.16 H 4.47N 3.65, found: C 74.54 H 4.57N 2.98. The purity was 98% by HPLC.

#### 2-(Carbazole-9-carbothioylsulfanyl)-2-methyl-propionic acid ethyl ester (R3)

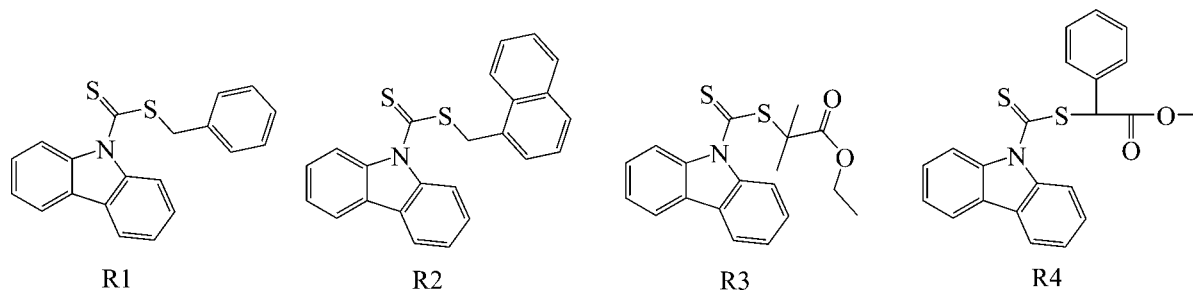
Yield 43%, <sup>1</sup>H-NMR. δ: 1.32 (m, 3H), 1.88 (s, 6H), 4.27 (m, 2H), 7.33–7.47 (m, 4H), 8.00 (d, 2H, *J* = 7.2 Hz), 8.34 (d, 2H, *J* = 8.4 Hz). EA. C<sub>19</sub>H<sub>19</sub>NO<sub>2</sub>S<sub>2</sub>, calculated: C 63.83 H 5.36N 3.92, found: C 63.64 H 5.33N 3.74. The purity was above 99% by HPLC.

#### (Carbazole-9-carbothioylsulfanyl)-phenyl-acetic acid methyl ester (R4)

Yield 31%, <sup>1</sup>H-NMR. δ: 3.83 (s, 3H), 5.85 (s, 1H), 6.85–8.51 (m, 13H). EA. C<sub>22</sub>H<sub>17</sub>NO<sub>2</sub>S<sub>2</sub>, calculated: C 67.49 H 4.38N 3.58, found: C 67.17 H 4.33N 3.61. The purity was above 98% by HPLC.

### Polymerizations

The following are the typical procedure of polymerization. A stock solution of 8 mL (69.5 mmol) of styrene and 115.7 mg (0.348 mmol) R1 (for MA and MMA, proper dose of AIBN was added) was prepared, and then aliquots of 1 mL were placed in ampules. The content was purged with argon for ~ 10 min to eliminate the dissolved oxygen. Then, the ampules were flame-sealed. The polymerization reaction was performed at the appropriate temperature. After the desired reaction time, each ampule was quenched in ice water and opened. The reaction mixture was diluted with a little of THF (about 2 mL), and precipitated in large amount of methanol (about 300 mL, for MA using ligroin). The polymer was obtained by filtering and dried at room temperature under vacuum to constant weight. Conversion was determined gravimetrically.



**Scheme 2** Chemical structure of dithiocarbamates.

**TABLE I**  
**Polymerization of MMA Using Dithiocarbamates**  
**as RAFT Agent at 60°C<sup>a</sup>**

Dithiocarbamate	Conversion (%)	$M_{n,th}^b$	$M_n$	$M_w/M_n$
R1	15.4	5,100	16,900	2.04
R2	29.1	9,700	37,600	1.70
R3	24.2	8,100	36,200	1.60
R4	53.1	18,100	23,700	1.54

<sup>a</sup>  $[MMA]_0/[AIBN]_0/[RAFT\ agent]_0=1,000 : 1 : 3$ , the polymerization time is 3 h.

<sup>b</sup> The theoretic molecular weight calculated according the follow equation:  $M_{n,th} = [monomer]_0 \times M_{w,monomer} \times conversion/[RAFT\ agent]_0$  ( $M_{w,RAFTagent}$  was ignored).

### Characterization

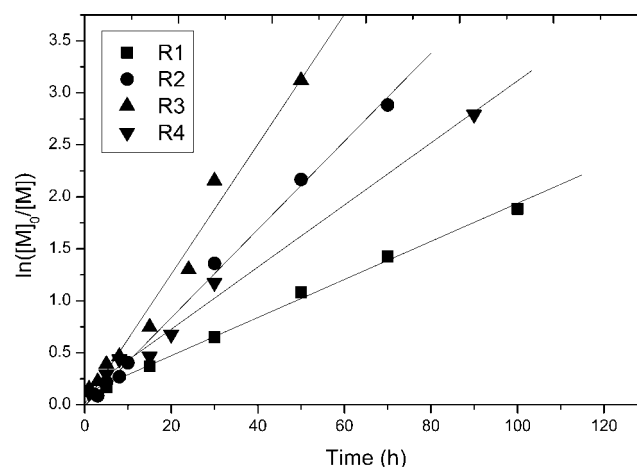
The molecular weights ( $M_n$ ) and molecular weight distribution ( $M_w/M_n$ ) of polymers were determined with a Waters 1515 gel permeation chromatographer (GPC) equipped with refractive index detector, using HR 1, HR 3, and HR 4 column. Calibration was performed with PSt or poly(methyl methacrylate) (molecular weight range 100–500,000) as standard samples. Tetrahydrofuran was used as the eluent at a flow rate of 1.0 mL min<sup>-1</sup> operated at 30°C. <sup>1</sup>H-NMR spectra of the polymers were recorded on an INOVA400 nuclear magnetic resonance (NMR) instrument using CDCl<sub>3</sub> as a solvent and tetramethylsilane (TMS) as the internal standard. Elemental analyses (EA) of C, H, and N were measured by the EA1110 CHND-S. The purity of dithiocarbamates was by Waters 515 HPLC: the mixture of methanol and water ( $V_{methanol}:V_{water} = 80:20$ ) was used as the eluent at a flow rate of 0.8 mL min<sup>-1</sup> operated at 30°C using C18 column and using Waters 996 as detector. The fluorescence intensity was measured by FLS920.

## RESULTS AND DISCUSSION

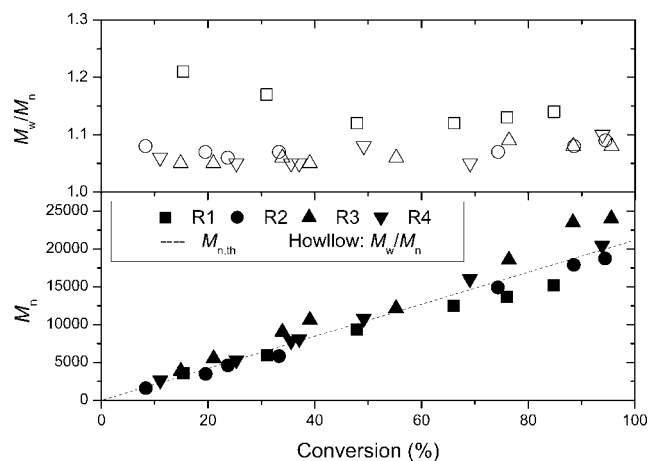
Accepted opinion about R group is that the R group should be a good leaving group when compared with the growing polymeric chain and a good reinitiating species toward the monomer. Chong et al.<sup>24</sup> showed the effect of the substituents R group of dithiobenzoate RAFT agents  $[S=C(Ph)S-R]$  on the outcome of MMA polymerizations at 60°C, the efficiency of dithiobenzoate RAFT agent depends strongly on R group in the following order:  $-C(alkyl)_2CN > -C(Me)_2Ar > -C(Me)_2C(O)O(alkyl) > -C(Me)_2C(O)NH(alkyl) > -C(Me)_2CH_2C(Me)_3 > -C(Me)HPh > -C(Me)_3 > -CH_2Ph$ , and only the compounds with R =  $-C(Me)_2Ph$  and  $-C(Me)_2CN$  has been successful in RAFT polymerization of MMA.<sup>24</sup> Recently, Perrier et al. synthesized a RAFT agent with R =  $-CH(C_6H_5)CO_2Me$  and this RAFT agent also offered very good

control over the polymerization of MMA.<sup>31</sup> However, from our experimental results (some typical data are listed in Table I), we found that the four RAFT agents, R1, R2, R3, and R4, were not efficient enough to control the polymerization of MMA. This may be because of the stability of the expelled radical and steric bulk of R group.<sup>24,27,31</sup>

For the polymerizations of styrene or MA, R1, R2, R3, and R4 were effective RAFT agents, and the polymerizations were well-controlled. Figure 1 shows the plots of  $\ln([M]_0/[M])$  versus polymerization time for the bulk polymerizations of styrene with thermal initiation using R1, R2, R3, and R4 as RAFT agents, respectively. In the studied range of conversions, the plots are approximately linear without obvious inhibition/induction period at the beginning of the polymerization in all cases, which indicates that the propagating radical concentrations are constant during the polymerization. The polymerization rate of styrene with thermal initiation is markedly influenced by the chemical structure of the group R in dithiocarbamates, and it decreases in the order of R3 > R2 > R4 > R1. Figure 2 shows the evolutions of the molecular weights ( $M_n$ ) and molecular weight distribution ( $M_w/M_n$ ) with styrene conversion in the polymerization of styrene under thermal initiation using dithiocarbamates as RAFT agents. The results of Figure 2 show that the molecular weight increases linearly with styrene conversion and is very close to the calculated value in all cases. The  $M_w/M_n$  of PSt obtained are very narrow (usually lower than 1.10). Comparing the results of R1 and R2, we found that naphthalen-1-ylmethyl (in R2) was a better R group than benzyl (in R1) for the RAFT polymerizations of styrene with thermal initiation under same conditions, although they had similar chemical structure. This may be



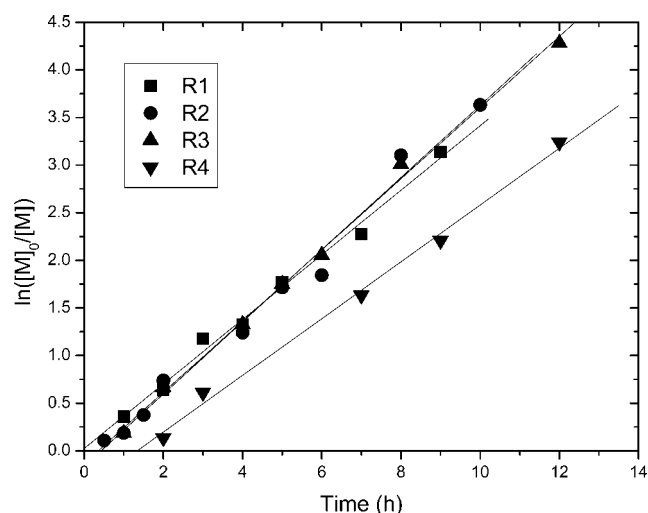
**Figure 1** Plots of  $\ln([M]_0/[M])$  versus time for the polymerizations of styrene with thermal initiation using R1, R2, R3, and R4 as RAFT agents at 100°C,  $[St]_0/[RAFT\ agent]_0 = 200 : 1$ .



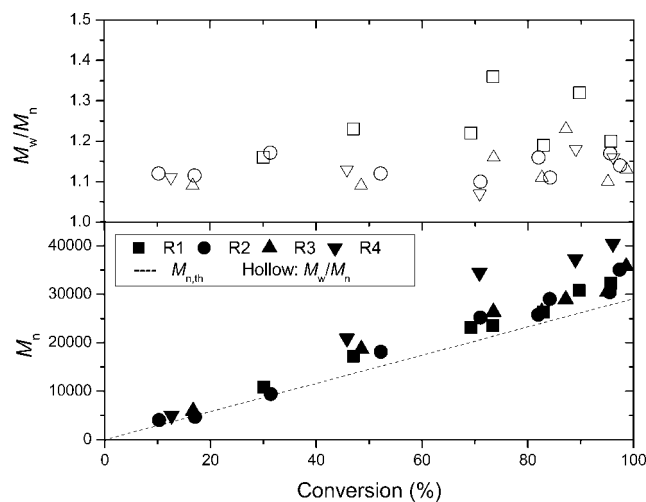
**Figure 2** Evolutions of the molecular weight ( $M_n$ ) and molecular weight distribution ( $M_w/M_n$ ) with styrene conversion. The conditions are same as in Figure 1.

because naphthalen-1-ylmethyl had a bigger conjugated structure than benzyl, which resulted in the expelled radical of naphthalen-1-ylmethyl being more stable than that of benzyl.

Figure 3 shows the first-order plots for the polymerizations of MA with AIBN as an initiator at 60°C using R1, R2, R3, and R4 as RAFT agents ( $[MA]_0/[AIBN]_0/[RAFT\ agent]_0 = 1000:1:3$ ), respectively. The rates of polymerizations in the cases of R1, R2, and R3 as RAFT agents are almost same and the polymerizations have no obvious inhibition period. However, the polymerization in the case of R4 has an inhibition period about 75 min. This may be because of the stability and steric bulk of  $-\text{CH}(\text{C}_6\text{H}_5)\text{CO}_2\text{Me}$  group in



**Figure 3** Plots of  $\ln([M]_0/[M])$  versus time for the polymerizations of methyl acrylate (MA) using R1, R2, R3, and R4 as RAFT agents at 60°C,  $[MA]_0/[AIBN]_0/[RAFT\ agent]_0 = 1000 : 1 : 3$ .



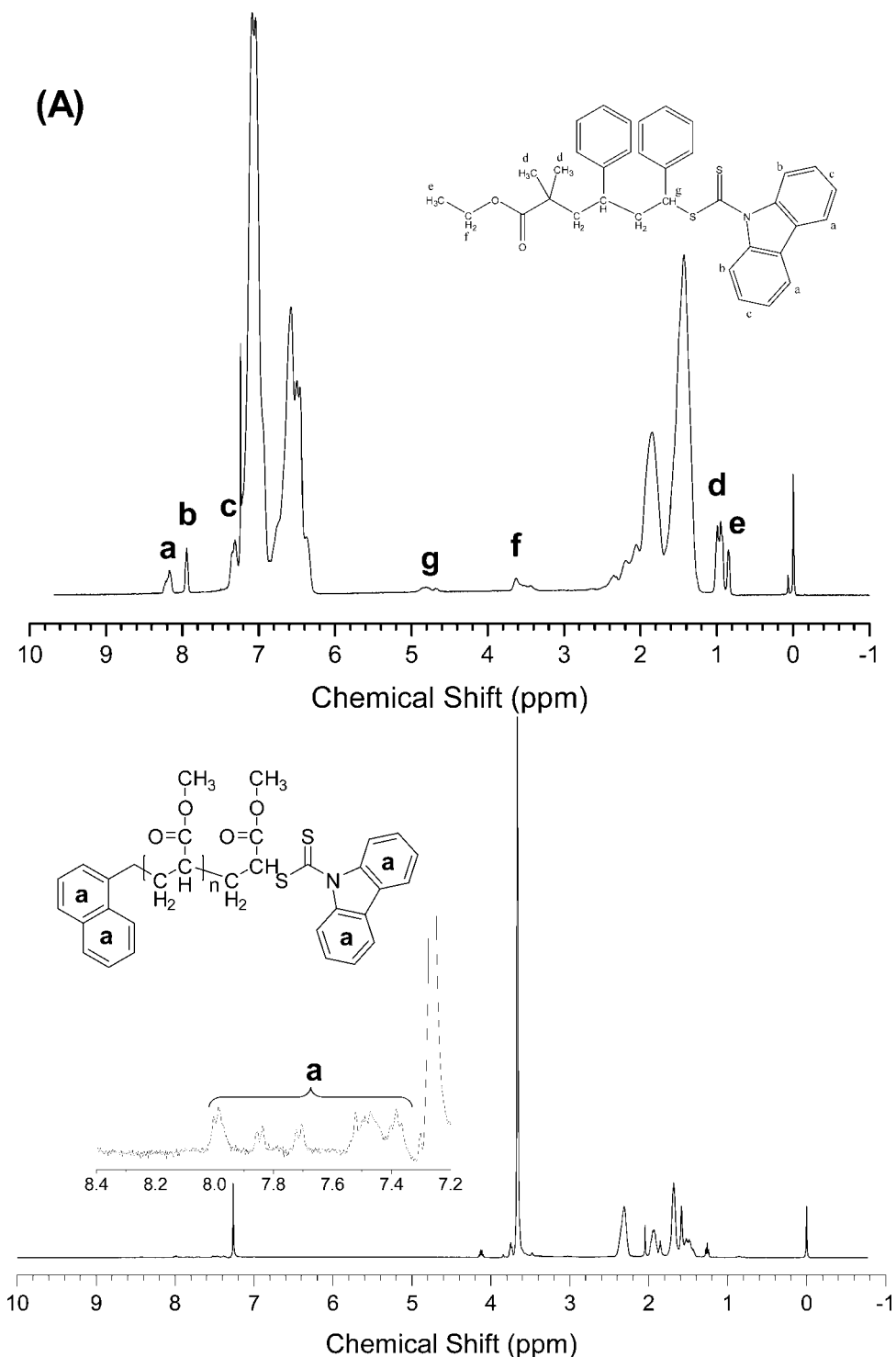
**Figure 4** Evolutions of the molecular weight ( $M_n$ ) and molecular weight distribution ( $M_w/M_n$ ) with methyl acrylate (MA) conversion. The conditions are same as in Figure 3.

R4. As shown in Figure 4, the molecular weights increase linearly with MA conversion in all cases. The molecular weights are very close to the calculated values in the cases of R1, R2, and R3, whereas higher than the calculated values in the case of R4, especially at higher conversion. The molecular weight distributions are relatively narrow (most of  $M_w/M_n < 1.3$ ) in all cases.

The structures of polymers obtained were characterized by  $^1\text{H-NMR}$ . Two typical  $^1\text{H-NMR}$  spectra of PSt and PMA are shown in Figure 5. Figure 5(A) shows the characteristic signals of R3 moieties at  $\delta = 7.52\text{--}8.87$  (a, b, c),  $3.40\text{--}3.63$  (f), and  $0.85\text{--}0.99$  (d, e) in PSt obtained by using R3 as RAFT agent, and Figure 5(B) shows the characteristic signals of R2 moieties at  $\delta = 7.33\text{--}8.18$  (carbazole unit and naphthyl) in PMA by using R2 as RAFT agent. To satisfy the RAFT mechanism of these polymerizations, block reaction with the second monomer was performed. The results were listed in Table II.

A typical GPC plot (Fig. 6) explicitly illustrates the changes in  $M_n$  and  $M_w/M_n$  before (a) and after (b) chain extension reaction. There is an apparent peak shift when compared with the original polymer and block copolymer and no obvious change in molecular weight distributions ( $M_w/M_n$  from 1.15 to 1.17), which indicate that the original polymer is active. All these results show that these dithiocarbamates are effective control agents for the RAFT polymerization of styrene and MA and the end of polymers obtained is labeled with carbazole group.

The carbazole unit and naphthyl group in dithiocarbamates are rigid conjugated molecule, and from RAFT mechanism, it will exist at the end of obtained polymer. Therefore, the polymer obtained will have fluorescence. Figure 7 shows the excitation spectra of



**Figure 5** Typical  $^1\text{H-NMR}$  spectra of obtained polymer. (A) PSt using R3 as RAFT agent,  $M_n = 3900$ ,  $M_w/M_n = 1.05$ ; (B) PMA using R2 as RAFT agent,  $M_n = 18,100$ ,  $M_w/M_n = 1.12$ .

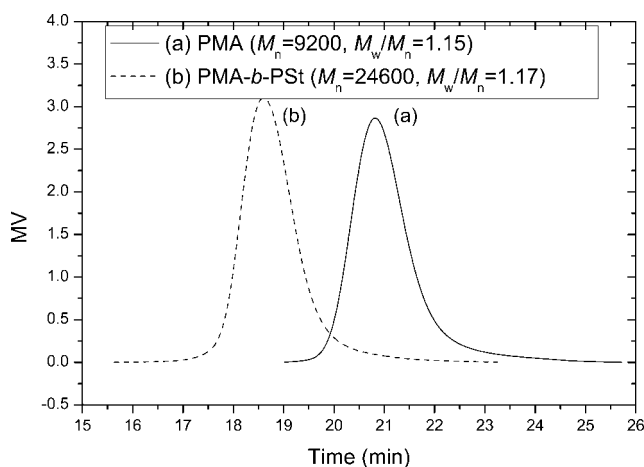
R1, R2, R3, and R4 in dimethyl formamide (DMF) at room temperature. All these dithiocarbamates absorb light strongly at 294 nm. The fluorescence intensity of PSt obtained excited at 294 nm is higher than that of dithiocarbamate at the same chromophore concentra-

tion in all cases (Fig. 8). It may be attributed to the stronger molecular movement of RAFT agent than its polymer, and thus partly self-quenched the fluorescence intensity. The emission spectra of PSt using R1, R3, and R4 as RAFT agents are similar, and the maxi-

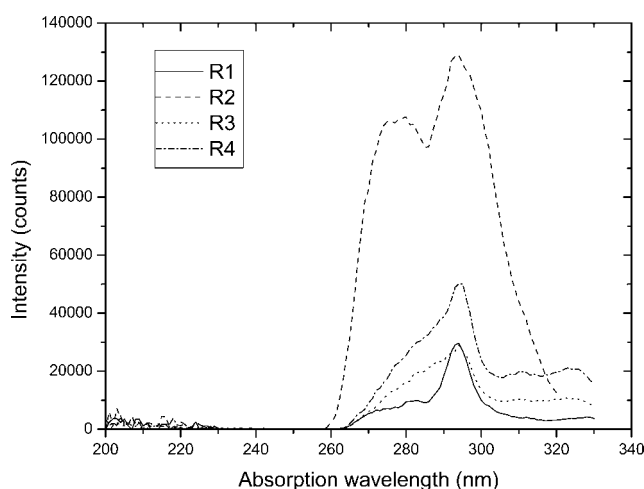
**TABLE II**  
Block Reaction Data Using PMA as Macro-RAFT Agent

	Initial polymer (PMA)		Block copolymer (PMA- <i>b</i> -PSt) <sup>a</sup>			
	$M_n$	$M_w/M_n$	Conversion (%)	$M_{n,th}$	$M_{n,GPC}$	$M_w/M_n$
R1	9,200	1.15	45.1	23,300	24,600	1.17
R2	9,500	1.17	51.5	25,600	27,000	1.15
R3	5,900	1.09	78.0	30,300	32,900	1.14
R4	5,000	1.11	50.9	20,900	22,200	1.32

<sup>a</sup>  $[St]_0/[PMA]_0 = 300 : 1$ , at 100°C, 5 h.

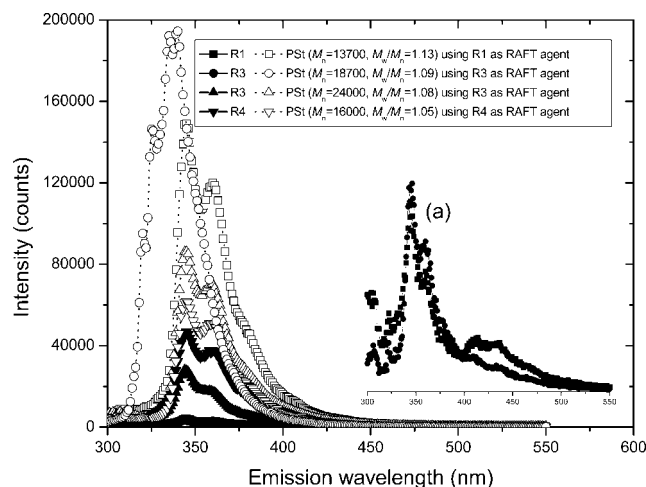


**Figure 6** GPC traces of polymer before (a) and after (b) chain extension reaction.



**Figure 7** Absorption spectra of RAFT agent measured at the concentration of  $1 \times 10^{-4}$  carbazole unit  $\text{mol L}^{-1}$  in DMF at room temperature.

lum emissions are around 345 nm. For PSt obtained using R2 as RAFT agent, the emission spectra shows multiplet due to the presence of both carbazole group and naphthyl group.



**Figure 8** Fluorescence spectra of dithiocarbamate and PSt in DMF at room temperature. The concentration of dithiocarbamate moieties was  $1 \times 10^{-4} \text{ mol L}^{-1}$ ; the excitation wavelength was 294 nm; (a) magnified figure of R1 and R2.

## CONCLUSIONS

The results showed that the R1, R2, R3, and R4 were effective RAFT agents for the controlled/"living" polymerizations of styrene and MA under conventional polymerization condition, and the polymerizations were well-controlled with the characteristics of controlled/"living" polymerization. The polymerization rate of styrene with thermal initiation decreased in the following order: R3 > R2 > R4 > R1. The naphthalen-1-ylmethyl was a better R group than benzyl in the RAFT polymerizations of styrene. For MA, the polymerization in the case of R4 had an obvious inhibition period and the efficiency of RAFT agents was in the following order: R2–R3 > R1 > R4. These dithiocarbamates mentioned earlier were not efficient enough to control the polymerizations of MMA. The obtained well-controlled carbazole or naphthyl group end-labeled PS had strong fluorescence absorption.

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