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Thermal Decomposition of Dithioesters and Its Effect on RAFT Polymerization

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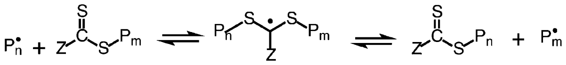
ABSTRACT: Thermal decomposition of dithioesters, e.g., cumyl dithiobenzoate (CDB), poly(methyl methacrylate) (PMMA) end-capped with dithioester, and 2-(ethoxycarbonyl)prop-2-yl dithiobenzoate (EPDB), and the consequent effect on reversible addition−fragmentation chain transfer polymerization were investigated. The former two dithioesters underwent thermal decomposition at 120 °C. The thermal decomposition yielded unsaturated compound and dithiobenzoic acid, leading to some loss of living character of the polymerization, such as retarded reaction rate and broadened molecular weight distribution. Nevertheless, thermal decomposition of EPDB, a model compound for PMMA dithioester, does not yield unsaturated product despite the resemblance of the chemical structures. Thermogravimetric analysis shows that PMMA dithioesters are more thermally unstable than the other two.

Introduction

Since the first report by the CSIRO group,[1] controlled/“living” radical polymerization based on the reversible addition−fragmentation chain transfer (RAFT) process has received much attention and become one of the most versatile methodologies to prepare well-defined polymers from a variety of monomers.[2] The RAFT polymerization achieves “living” growth of molecular weight starting from the initial chain transfer agent, dithioesters or trithiocarbonates (eq 1),[1] which is activated by radicals generated from a traditional radical initiator such as 2,2′-azobis(isobutyronitrile) (AIBN). Since the feed amount of initiator is a small fraction of that of thiocarbonylthio compound, the majority of the resulting polymer chains are derived from the latter,[1,3−6] which usually gives the products a pink or yellow color.

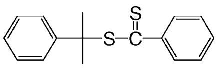


(1)

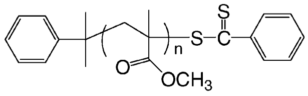
The fidelity of thiocarbonylthio group to chain ends is not only an illustration of living feature of the RAFT polymerization but also important to the chain end functionalization.[6−8] The most widely performed functionalization reaction is the transformation of thiocarbonylthio group into thiol group[5,9−15] which can successively recouple to form disulfide bond[16] or couple with Au to fabricate polymer grafted gold surface.[15]

In other cases, it would be desirable to remove the thiocarbonylthio terminus and produce colorless products. This can be accomplished by themolysis,[7,17] UV irradiation,[18,19] or postpolymerization reaction with a radical initiator.[20,21] For instance, Moad,[7] Davis,[17] and co-workers achieved quantitative thermolysis at 210−250 °C of terminal trithiocarbonate groups in polystyrene and poly(*n*-butyl acrylate) prepared by RAFT polymerization. They also predicted that the same reaction exists for other forms of RAFT agent, such as dithioesters and xanthates.[17]

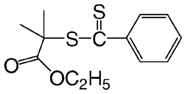
In our previous work, we found that cumyl dithiobenzoate (CDB), a widely used RAFT agent, underwent remarkable thermal decomposition at 90−120 °C,[22] which is much lower than that working for thermolysis. Since the reaction yields dithiobenzoic acid and related derivatives, it can affect the polymerization rate, molecular weight, and molecular weight distribution of the resulting polymers, especially when the living chains in the RAFT polymerization, i.e., the polymeric dithioesters, undergo similar side reactions at the same temperature. This paper reports the thermal decomposition of thiocarbonylthio end group of PMMA prepared by RAFT polymerization and its effect on the polymerization kinetics. Similar effects of CDB and another model compound, 2-(ethoxycarbonyl)prop-2-yl dithiobenzoate (EPDB), were also discussed.



CDB



PMMA dithioester



EPDB

Experimental Section

Materials. Methyl methacrylate (MMA, Shanghai 4th Factory of Chemicals, 98%) and styrene (Yonghua Special Chemicals, 99%) were passed through Al_2O_3 and silica gel columns, respectively, distilled at reduced pressure and stored under argon. Benzene (Shanghai 4th Factory of Chemicals, 99.5%) and tetrahydrofuran (THF, Shanghai Feida, 99.5%) were refluxed over sodium and distilled. *tert*-Butylbenzene (Wulian Chemicals, 99%) was dried over $CaCl_2$ and distilled before use. Carbon disulfide (CS_2, Shanghai 4th Factory of Chemicals, 99%) was purified by vigorously shaking with $KMnO_4$ (0.4 wt % based on CS_2) followed by filtration and distillation to collect a colorless fraction. Bromobenzene (Wulian Chemicals, 99.5%) was dried over $CaCl_2$ and distilled before use. Ethyl α-bromoisobutyrate (Aldrich, 98%) was used as received.

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2,2′-Azobis(isobutyronitrile) (AIBN, Shanghai 4th Factory of Chemicals, 99%) was recrystallized from methanol. Dicumyl peroxide (DCPO, Chemical Reagent Co. Ltd. of China National Pharmaceutical Group, 99%) was dried in a vacuum at room temperature for 24 h.

Measurement. Gel permeation chromatography (GPC) was performed on a Agilent-1100 series GPC system equipped with a PL GEL linear column (5 μm, pore size: 500 Å) and two PL GEL mixed columns (the molecular weight limits ranging from 200 to 3×10^6 g mol^{-1}) and a HP1100 RI detector HP1100 VWD detector, using THF as eluent at a flow rate of 1 mL/min at 35 °C. The system was calibrated by narrow poly(methyl methacrylate) standards (MW range: $700-3 \times 10^4$ Da) and narrow polystyrene standards (MW range: $200-3 \times 10^6$ Da). Number-average molecular weight, M_n, and polydispersity index, M_w/M_n, were obtained using HP ChemStation for LC-3D (Rev. A. 06. 04) software. Conversions of MMA were determined by the ratio of height of the UV signal. Thermogravimetric analysis (TGA) was performed on a NETZSCH TG209 instrument under a nitrogen atmosphere (20 mL/min). The temperature was raised from 20 to 550 °C at a rate of 20 K/min. ^{1}H NMR measurements were carried out on a Bruker (500 MHz) NMR instrument using $CDCl_3$ as solvent and tetramethylsilane as reference. The ultraviolet absorption of CDB and dithiobenzoate-mediated poly(methyl methacrylate) solution in THF was recorded by a Perkin-Elmer Lambda35 UV−vis spectroscope at 25 ± 0.1 °C with wavelength from 190 to 650 nm. High-performance liquid chromatography (HPLC) was performed on an instrument composed of a Waters 515 pump, a C-18 column (SymmetryShield RP-18, 5.0 μm, 4.6×250 mm), and a UV detector with the wavelength settled at 254 nm. Acetonitrile/water (85/15, v/v) was used as eluent (1.0 mL/min) at 40 °C. Fourier transform infrared spectroscopy (FT-IR) was performed on a Magna-550 instrument (potassium bromide pellet). Mass spectroscopy (MS) was performed on a Finnigan Voyager instrument in electrospray ionization mode (70 eV). Elemental analysis was carried on a Heraeus 1106 instrument.

Synthesis of Cumyl Dithiobenzoate (CDB). CDB was synthesized according to the literature procedure.[23] To obtain product of high purity, recrystallization was performed twice from petroleum ether. Purple-red crystals: yield 19% (based on dithiobenzoic acid); purity 99.1% by HPLC. FT-IR: υ/cm^{-1} = 1224 and 1046 (vs $C{=}S$). UV−vis max (CCl_4): 303 and 531 nm. ^{1}H NMR: δ (ppm) = 2.0 (s, 6H, C**H**$_3$), 7.21 (t, 1H, Ar**H**), 7.30 (m, 4H, Ar**H**), 7.43 (t, 1H, Ar**H**), 7.54 (d, 2H, Ar**H**), 7.84 (d, 2H, Ar**H**). MS: m/e = 272. Calcd for $C_{16}H_{16}S_2$: C, 70.49; H, 5.88; S, 23.63%. Found: C, 70.83; H, 6.00; S, 23.39%.

Synthesis of 2-(Ethoxycarbonyl)prop-2-yl Dithiobenzoate (EPDB). EPDB was synthesized using a modified Grignard process according to the literature.[23] The Grignard reagent, phenylmagnesium bromide, was prepared from bromobenzene (6.28 g, 0.04 mol) and magnesium powder (1 g) in dry THF (30 mL). The solution was warmed to 50 °C, and CS_2 (3.05 g, 0.04 mol) was added over 15 min while maintaining the reaction temperature at 50 °C. Ethyl α-bromoisobutyrate (7.00 g, 0.036 mol) was added to the resultant dark brown solution. The reaction temperature was raised to 80 °C and maintained for 60 h. Then, ice water (50 mL) was added, and the organic layer was extracted with diethyl ether (3 × 50 mL). The combined organic extracts were washed with water and dried over anhydrous magnesium sulfate. After the solvent was evaporated, the crude product was purified by silica gel column chromatography, using *n*-hexane/diethyl ether (9:1) as eluent. Red oil: 1.48 g, yield 10.8%, purity 96% by HPLC. ^{1}H NMR: δ (ppm) = 1.24 (t, 3H, CH$_2$C**H**$_3$), 1.76 (s, 6H, 2×C**H**$_3$), 4.17 (q, 2H, OC**H**$_2$CH$_3$), 7.35 (dd, 2H, *meta* Ar**H**), 7.52 (dd, 1H, *para* Ar**H**), 7.95 (d, 2H, *ortho* Ar**H**).

Synthesis of Poly(methyl methacrylate) with Dithiobenzoate Terminus. MMA (6.20 g, 0.06 mol), CDB (0.57 g, 2.1 mmol), and AIBN (0.16 g, 0.97 mmol) were dissolved in benzene (16 mL) in a 50 mL flask, and the solution was degassed with three cycles of freezing−pump−thawing. The reaction mixture was heated under argon at 60 °C for 8 h before quenched into liquid nitrogen to stop the polymerization. The resulting PMMA was obtained as a pink powder by dissolving in THF and precipitating from 20-fold petroleum ether for three times. The product was analyzed by GPC, ^{1}H NMR, TGA, and UV−vis spectroscopy. Number-average molecular weight, M_n = 3600 Da; polydispersity index, M_w/M_n = 1.08. The product was denoted hereafter as PMMA3600.

RAFT Polymerizations of Styrene Mediated by CDB and Preheated CDB. Two parallel styrene polymerizations were carried out in the presence of as-prepared CDB and preheated CDB, respectively, under otherwise identical conditions. Styrene (10.4 g, 0.10 mol), AIBN (0.03 g, 0.16 mmol), and CDB (0.14 g, 0.50 mmol) were dissolved in *tert*-butylbenzene (10 mL) in a 50 mL flask, and the solution was degassed with three cycles of freezing−pump−thawing. The reaction mixture was warmed at 60 °C. Samples were taken from the flask at predetermined periods and analyzed by GPC calibrated with polystyrene standards and TGA.

For the system using preheated CDB, a solution of CDB (0.14 g, 0.50 mmol) in *tert*-butylbenzene (10 mL) was heated at 120 °C for 9 h. Then the same amount of styrene and AIBN as above was mixed directly with the heating mixture before the starting of the polymerization.

Chain Extension of PMMA3600. Two parallel MMA polymerizations were carried out using above-synthesized PMMA3600 (M_n = 3600 Da, M_w/M_n = 1.08) and the preheated PMMA3600 as the RAFT agents under otherwise identical conditions. A solution of MMA (2.74 g, 0.027 mol), AIBN (0.011 g, 0.069 mmol), and PMMA3600 (0.50 g, 0.14 mmol) in *tert*-butylbenzene (7 mL) was degassed with three cycles of freezing−pump−thawing. The solution was warmed at 60 °C. Samples were taken at predetermined periods and analyzed by GPC calibrated with PMMA standards.

For the system using preheated PMMA3600, a solution of PMMA3600 (0.50 g, 0.14 mmol) in *tert*-butylbenzene (7 mL) was heated at 120 °C for 10 h. Then the same amount of MMA and AIBN as above was mixed directly with the heating mixture before the starting of the polymerization.

MMA Polymerization Using DCPO as Initiator and CDB as the CTA at 120 °C. A solution of MMA (3.0 g, 0.03 mol), DCPO (0.014 g, 0.052 mmol), and CDB (0.045 g, 0.17 mmol) in *tert*-butylbenzene (4 mL) was degassed with three cycles of freezing−pump−thawing. The reaction mixture was heated at 120 °C. Samples were taken at predetermined periods and analyzed by GPC calibrated with PMMA standards.

Results and Discussion

1. Effect of Thermal Decomposition of CDB on Kinetics of RAFT Polymerization. We have previously studied the thermal decomposition of CDB and its effect on the kinetics of the RAFT polymerization of styrene.[22] There was only a slight difference in polymerization rate between two parallel polymerizations at 120 °C, i.e., that mediated by pure CDB and preheated CDB.[22] However, further study indicates that the preheated CDB caused remarkable retardation when the polymerizations were conducted at 60 °C (see next).

Two parallel polymerizations of styrene were carried out at 60 °C, with one regulated by freshly prepared CDB (as the reference) and the other by preheated CDB under otherwise identical reaction conditions. Figure 1 shows the GPC plots for these systems. While both displayed shifts to larger molecular weight during polymerization, the system with preheated CDB resulted in notably broader distribution than the reference, indicating some loss of living character due to the preheating reaction of CDB.

Figure 2 shows the dependence of measured number-average molecular weight, M_n, and polydispersity index, M_w/M_n, on monomer conversion for the two polymerization systems. The reference system yielded low-polydispersity products with M_n predictable by the calculation based on the molar ratio of consumed monomer and the feed CDB. The system with

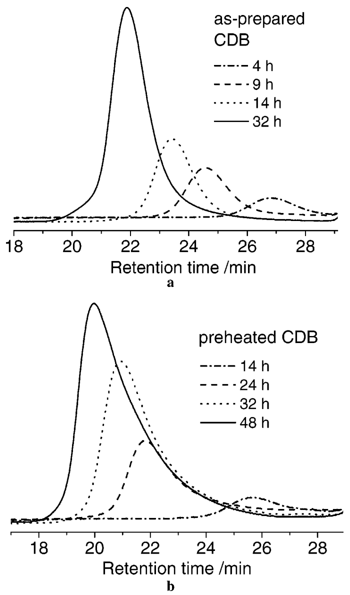


Figure 1. Gel permeation chromatograms of the samples at different reaction periods during the polymerization mediated by as-prepared (a) and preheated (b) cumyl dithiobenzoate (CDB). Preheating conditions: 120 °C for 9 h. Polymerization conditions: 60 °C, 10 mL of *tert*-butylbenzene, 0.10 mol of styrene, 0.16 mmol of 2,2′-azobis(isobutyronitrile), 0.50 mmol of CDB.

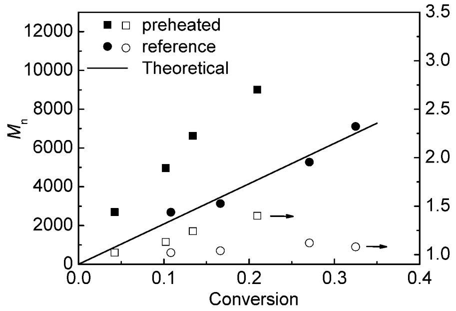


Figure 2. Dependence of M_n and M_w/M_n of the preheated (■, □) and reference (●, ○) polymerization systems of cumyl dithiobenzoate (CDB) on styrene conversion. The line is the theoretical result based on the equation $M_{n,THEO} = M_{styrene} \times$ conversion × ([styrene]$_0$/[CDB]$_0$) + M_{CDB}. The preheating and polymerization conditions are identical with those in Figure 1.

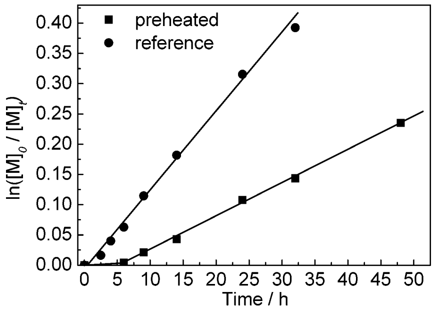


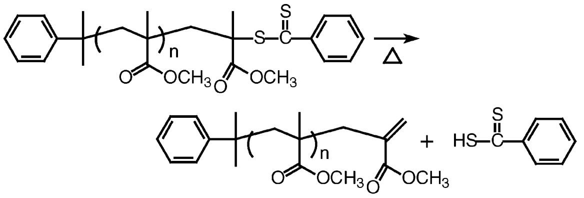
Figure 3. Kinetic plots for the preheated (■) and reference (●) polymerization systems of cumyl dithiobenzoate. The preheating and polymerization conditions are identical with those in Figure 1.

preheated CDB, however, resulted in higher M_n and larger polydispersity indices. From the kinetic plots in Figure 3, it is clear that the polymerization was retarded in the system mediated by preheated CDB, with both longer induction period up to 5 h and smaller slope of the kinetic line.

Our previous results showed that the thermal decomposition of CDB yields α-methylstyrene and dithiobenzoic acid, with the latter being very difficult to isolate and tends to form numerous peaks in HPLC analysis.[22] The resulted dithiobenzoic acid and its derivatives are responsible for the retarded polymerization rate and broader molecular weight distribution for the system mediated by the preheated CDB. Because of the loss of RAFT agent, the molecular weight of the resulting polymer is larger than prediction. Therefore, although the thermal decomposition has little effect on the polymerization at high temperature, it indeed has a strong effect at 60 °C, a typical temperature at which the RAFT polymerization is carried out.

2. Thermal Decomposition of PMMA with Thiocarbonylthio Terminus and Its Effect on RAFT Polymerization. PMMA with thiocarbonylthio terminus was synthesized by CDB-mediated RAFT polymerization of MMA at 60 °C. The resulting pink product had M_n of 3600 Da and M_w/M_n of 1.08 by GPC analysis and was denoted PMMA3600 hereafter. The purified PMMA3600 was heated at 120 °C for a period of up to 30 h, during which the pink color changed to yellow steadily. Figure 4 shows photographs of the reaction solutions and the powder precipitated from petroleum ether before (a) and after (b) heating. White powder was obtained after heating, indicative of the removal of the thiocarbonylthio terminus.

Figure 5 shows the ^{1}H NMR spectra of PMMA3600 before and after heating. The signal intensity at 7.9 ppm for *ortho* protons of thiocarbonylthio group was remarkably reduced after 10 h of heating, accompanied by the appearance of unsaturated terminus as indicated by olefinic protons at chemical shifts of 5.5 and 6.2 ppm. After 30 h of heating, the signal at 7.9 ppm disappeared. This indicates that PMMA3600 underwent thermal decomposition in analogy to CDB as well as trithiocarbonate moieties,[7,17] resulting in unsaturated terminus and dithiobenzoic acid:



(2)

The detachment of thiocarbonylthio group was also evidenced by GPC results shown in Figure 6 using different detectors. While the chromatograms obtained with RI detector displayed little change in molecular weight of PMMA3600 before and after heating, a UV detector at 300 nm (the absorption maximum of dithiobenzoate) detected great reduction of the chromophores at the chain end. On the meantime, chromophores of small molecular weight formed as indicated by the strong absorption at longer retention time of 29.4 min.

The fraction of the residual thiocarbonylthio end group can be calculated from the ratio of signal integrations at $\delta = 7.9$ ppm (2H$_c$) and 7.2 ppm (*para* H of cumyl) in line A Figure 5 as well as the peak areas in GPC−UV chromatograms. These values are 2% and 5%, respectively. Therefore, at this condition more than 95% of the initial thiocarbonylthio species decomposed after 10 h of heating at 120 °C. Nevertheless, the intensity of the resulting olefinic proton is far weaker than anticipated, implying that there may be other pathway(s) to consume thiocarbonylthio species in addition to that in eq 2. A similar phenomenon was also observed in the thermal decomposition of CDB.[22]

The two kinds of PMMA3600, as-prepared and preheated, were then used to mediate RAFT polymerization of MMA to perform chain extension at 60 °C. Figure 7 shows GPC profiles monitoring the processes of chain extension reactions. With the

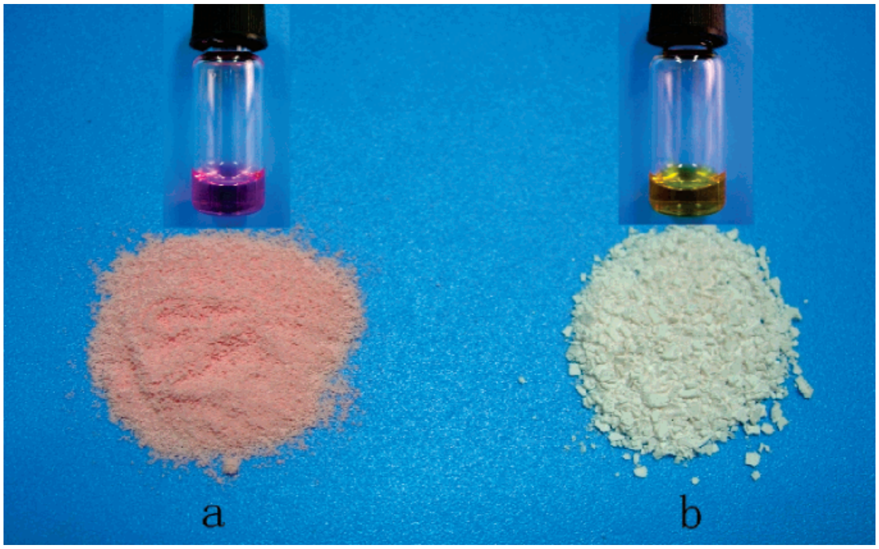


Figure 4. Photographs of poly(methyl methacrylate) (PMMA3600, M_n = 3600 Da) in *tert*-butylbenzene solution and precipitated powder before (a) and after (b) heating for 30 h at 120 °C. PMMA3600 was synthesized by cumyl dithiobenzoate-mediated reversible addition−fragmentation chain transfer polymerization at 60 °C.

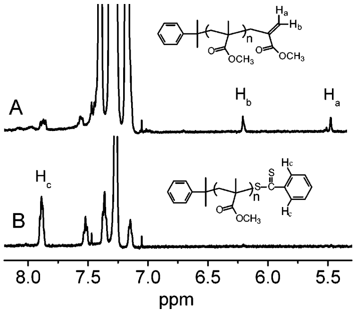


Figure 5. Partial ^{1}H NMR spectra of the preheated product of poly(methyl methacrylate) (PMMA3600, M_n = 3600 Da) (A) and the as-prepared PMMA3600 (B). PMMA3600 was synthesized by cumyl dithiobenzoate-mediated reversible addition−fragmentation chain transfer polymerization at 60 °C.

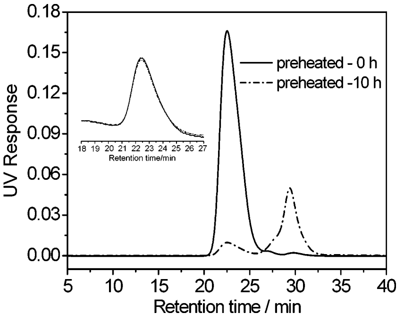


Figure 6. Gel permeation chromatograms of poly(methyl methacrylate) (PMMA3600, M_n = 3600 Da) solution in *tert*-butylbenzene before (solid line) and after heating (dashed line) at 120 °C for 10 h, measured by UV detector at the wavelength of 300 nm and RI detector (the inset). PMMA3600 was synthesized by cumyl dithiobenzoate-mediated reversible addition−fragmentation chain transfer polymerization at 60 °C.

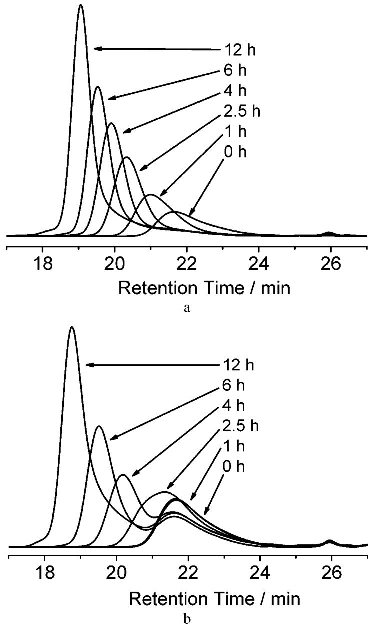


Figure 7. Gel permeation chromatograms of the samples at different reaction periods during the polymerizations mediated by as-prepared (a) and preheated (b) poly(methyl methacrylate) (PMMA3600, M_n = 3600 Da). Preheating conditions: 120 °C for 10 h. Polymerization conditions: 60 °C, 7 mL of *tert*-butylbenzene, 0.027 mol of methyl methacrylate, 0.069 mmol of 2,2′-azobis(isobutyronitrile), 0.14 mmol of PMMA3600. PMMA3600 was synthesized by cumyl dithiobenzoate-mediated reversible addition−fragmentation chain transfer polymerization at 60 °C.

as-prepared PMMA3600, the chain extension polymerization ran steadily with high efficiency as indicated by the narrow peak and negligible residue of the starting material. The system using preheated PMMA3600, however, resulted in broader distribution and low efficiency of reinitiation with a large part of unreacted precursor. The kinetic plots in Figure 8 demonstrate that this system exhibited retarded polymerization rate with an induction period of 1 h.

Since the GPC profiles show bimodal distribution, we plot M_p, the molecular weight at peak, of the resulting polymers, instead of M_n, against monomer conversion in Figure 9. The reference system shows linear plot of $M_p \sim$ conversion and a decreasing M_w/M_n during the whole reaction process, whereas the preheated PMMA3600 resulted in two stages of molecular weight growth. Within the early period, the molecular weight remained almost unchanged while the monomer conversion increased notably. This may be due to formation of short living chains by the reaction of propagating radicals with the resulting dithiobenzoic acid and its derivatives. After this period, the molecular weight increased obviously faster than that of the reference system. The polydispersity index increased during the whole process of polymerization, approaching 2.0 (bimodal) at monomer conversion of 56%.

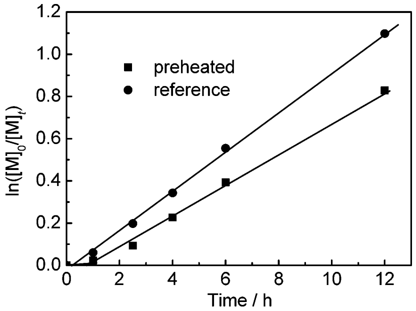


Figure 8. Kinetic plots for the preheated (■) and reference (●) polymerization systems of poly(methyl methacrylate) (PMMA3600, M_n = 3600 Da). The preheating and polymerization conditions are identical with those in Figure 7. PMMA3600 was synthesized by cumyl dithiobenzoate-mediated reversible addition−fragmentation chain transfer polymerization at 60 °C.

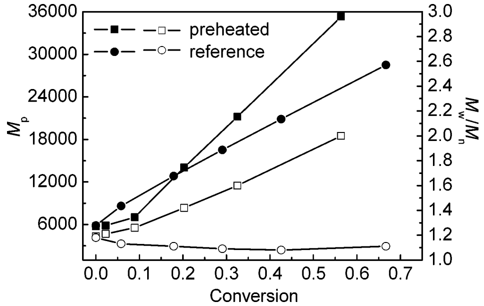
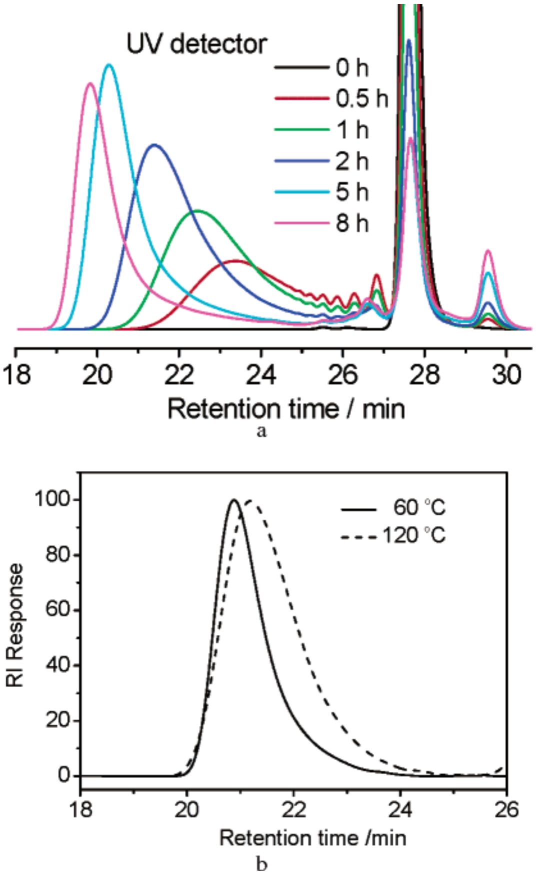


Figure 9. Evolution of M_p and M_w/M_n with methyl methacrylate conversion of the preheated (■, □) and reference (●, ○) polymerization systems of poly(methyl methacrylate) (PMMA3600, M_n = 3600 Da). The preheating and polymerization conditions are identical with those in Figure 7. PMMA3600 was synthesized by cumyl dithiobenzoate-mediated reversible addition−fragmentation chain transfer polymerization at 60 °C.

3. RAFT Polymerization of MMA at 120 °C. The thermal unstability of PMMA prepared by the RAFT polymerization reminded us of investigating RAFT polymerization of MMA at high temperatures such as 120 °C. Since AIBN would be immediately consumed at this temperature,[24] we used dicumyl peroxide (DCPO) as the radical initiator which afforded a steady radical source through relatively slow homolysis. Parts a and b of Figure 10 are GPC results recorded by UV and RI detectors, respectively, monitoring the polymerization process. For comparison, GPC trace of MMA polymerization at 60 °C was also presented in Figure 10b. The steady growth of the molecular weight demonstrated living feature of the polymerization. However, a new peak appeared with increasing intensity at retention time of 29.7 min, which may be assigned to the product of thermal decomposition of thiocarbonylthio compound(s), most probably dithiobenzoic acid and its derivatives, since the signal was detected at the wavelength of 300 nm. The tailing effect, together with remaining peak of CDB at 27.8 min, suggests a slow RAFT process to the initial and the polymeric dithioesters. Figure 10b shows that the GPC profile of the system polymerized at 120 °C was clearly broader than that at 60 °C, which is correlated to the thermal decomposition of living chains.



a

b

Figure 10. Gel permeation chromatograms using UV (a) and RI (b) detectors for cumyl dithiobenzoate (CDB)-mediated RAFT polymerization of methyl methacrylate (MMA) initiated by dicumyl peroxide (DCPO) at 120 °C. Polymerization conditions: MMA, 0.03 mol; DCPO, 0.05 mmol; and CDB, 0.17 mmol in 4 mL of *tert*-butylbenzene. The system at 60 °C: MMA, 0.02 mol; 2,2′-azobis(isobutyronitrile), 0.03 mmol; and CDB, 0.11 mmol in 3.5 mL of benzene for 9 h.

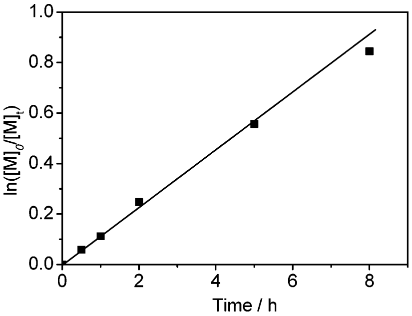


Figure 11. Kinetic plot for the dicumyl peroxide initiated polymerization of methyl methacrylate at 120 °C. Polymerization conditions are identical with those in Figure 10.

Figure 11 shows the linear kinetics of the RAFT polymerization of MMA mediated by CDB and initiated by DCPO at 120 °C. The constant polymerization rate implies a constant concentration of propagating radicals, which is a consequence of dynamic balance between continuous initiation and irreversible termination. Figure 12 plots the molecular weights and polydispersity indices against monomer conversion. The molecular weight of the resulting polymer is larger than theoretical anticipation (line in Figure 12). The measured polydispersity indices are about 1.3, larger than those usually obtained, 1.2 or less. These characters can be attributed to thermal decomposition of living chains which resulted in more chain-breaking events during the polymerization.

4. Thermal Stability of the Model Compound, EPDB. To better understand the mechanism of the thermal decomposition of thiocarbonylthio terminus, we synthesized a dithioester, EPDB, as a model compound of PMMA3600. The obtained EPDB was heated at 120 °C in degassed benzene solution in a sealed ample. The NMR spectrum of the heating mixture showed no signal in the region of 5−6.5 ppm, indicating the absence of unsaturated terminus. Surprisingly, a small amount of polymer-like substance was formed during the heating proce-

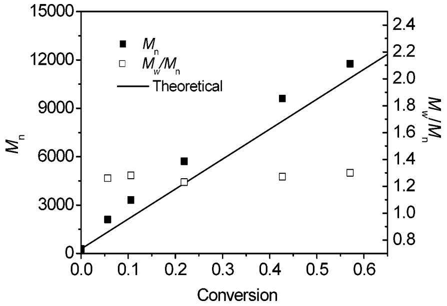


Figure 12. Evolution of M_n and M_w/M_n with methyl methacrylate conversion during the dicumyl peroxide-initiated polymerization at 120 °C. Polymerization conditions are identical with those in Figure 10.

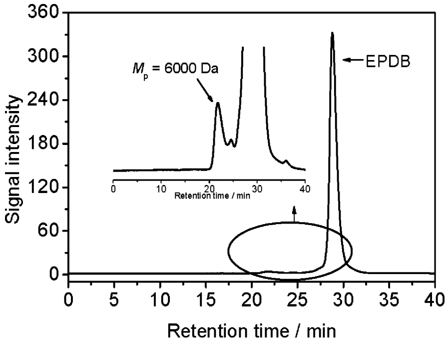


Figure 13. Gel permeation chromatogram of model compound 2-(ethoxycarbonyl)prop-2-yl dithiobenzoate solution in benzene after heating at 120 °C for 5 h. Concentration: 0.01 g/mL. Working wavelength of the UV detector is 300 nm.

dure. The substance is insoluble in methanol or acetonitrile/water (85/15, v/v) but soluble in THF. Figure 13 is the GPC trace of the heating mixture, showing a fraction with $M_p = 6000$ Da. We did not isolate and characterize the fraction due to the tiny amount of it, and it is difficult to give explanation to its formation mechanism currently. These results show that, although EPDB resembles very much the structure of PMMA3600, it exhibits different behavior on heating at 120 °C.

The thermal stabilities of CDB, EPDB, and PMMA3600 before and after defunctionalization by heating at 120 °C for 30 h were determined by thermogravimetric analysis (TGA) under nitrogen, and the results are shown in Figure 14. PMMA3600 has the lowest onset temperature of decomposition at 65 °C as compared to its analogue after defunctionalization and to the other two dithioesters. It is also noted that there are more than one stages of weight loss during the analysis, indicating complex mechanism of thermal decomposition. The onset temperature is similar to that of poly(*n*-butyl acrylate) reported by Davis and co-workers[17] and lower than that of PMMA reported by Lima[25] and Advincula[8] due to the differences in molecular weights.

One of the referees suggests to investigate the rate of decomposition to show how it will affect the real polymerization. Thus, two parallel experiments were performed at 120 °C, with different initial concentrations of PMMA3600 ($[\text{PMMA3600}]_0 = 0.021$ and 0.005 M). The reactions were monitored by means of GPC−UV, and the residual thiocarbonylthio moieties were obtained by peak height of UV absorption. Figure 15 shows that the decomposition rate is dependent on $[\text{PMMA3600}]_0$. For the higher $[\text{PMMA3600}]_0$, the residual thiocarbonylthio moiety is ∼54% after 10 h of reaction, while lower $[\text{PMMA3600}]_0$ resulted in faster decomposition, i.e., 16% residual within the same period. The dependence of decomposition rate on $[\text{PMMA3600}]_0$ indicates that the thermal decomposition could be a complex reaction.

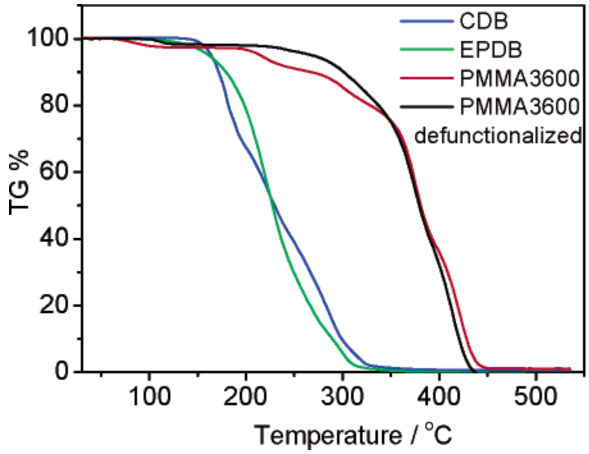


Figure 14. Thermogravimetric analysis curves for the thermal decomposition of cumyl dithiobenzoate (blue), 2-(ethoxycarbonyl)prop-2-yl dithiobenzoate (green), poly(methyl methacrylate) with thiocarbonylthio terminus (PMMA3600, M_n = 3600 Da) (red), and PMMA3600 after defunctionalized (black) by heating at 120 °C for 30 h. The temperature was raised at a rate of 20 K/min. PMMA3600 was synthesized by cumyl dithiobenzoate-mediated reversible addition−fragmentation chain transfer polymerization at 60 °C.

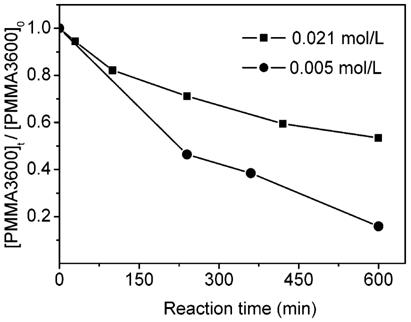


Figure 15. Residual poly(methyl methacrylate) (PMMA3600, M_n = 3600 Da) in percentage as a function of heating time. Conditions: 0.500 g of PMMA3600 in 7 mL of *tert*-butylbenzene (0.021 M) and 0.025 g of PMMA3600 in 1.5 mL of *tert*-butylbenzene (0.005 M), 120 °C. PMMA3600 was synthesized by cumyl dithiobenzoate-mediated reversible addition−fragmentation chain transfer polymerization at 60 °C.

The thermal decomposition should take place throughout the RAFT polymerization of MMA at 120 °C, leading to broadened molecular weight distribution (Figures 10 and 12) as compared to the polymerization at 60 °C. However, in real polymerization, it is possible that the thio-containing products of the thermal decomposition react with monomer and/or radicals to form species that can modulate the radical polymerization; thus, the polymerization is not totally “dead” despite many “chain breaking” events due to thermal decomposition.

It is also difficult to evaluate the effect of thermal decomposition on reaction rate of a real polymerization because we cannot find a reference system of MMA RAFT polymerization free of thermal decomposition. Nevertheless, the retardation effect was observed for MMA polymerization using preheated PMMA3600 as RAFT agent.

Summary

Thermal decomposition of thiocarbonylthio group and its effect on the kinetics of RAFT polymerization were investigated. This work reveals that the thermal decomposition of thiocarbonylthio group is quite often encountered for different kinds of dithioesters. While the decomposition can be employed to remove thiocarbonylthio terminus of RAFT polymers, it can also retard the polymerization rate, yielding polymer products with larger molecular weight and broader molecular weight distribution of the resulting polymers. The temperature of thermal decomposition (120 °C) in this work is much lower than that working for thermolysis (210−250 °C) reported in the literature.[17] TGA results show the onset temperature of PMMA3600 is about 65 °C. Thus, in RAFT polymerization of MMA at higher temperature, the effect of thermal decomposition of living chains should not be ignored, although it is negligible in the styrene system.[26]

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References and Notes

(1) Chiefari, J.; Chong, Y. K.; Ercole, F.; Krstina, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, G.; Moad, C. L.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1998**, *31*, 5559−5562.

(2) Here are some examples: (a) Chong, Y. K.; Le, T. P.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1999**, *32*, 2071−2074. (b) Favier, A.; Charreyre, M.-T.; Chaumont, P.; Pichot, C. *Macromolecules* **2002**, *35*, 8271−8280. (c) Loiseau, J.; Doërr, N.; Suau, J. M.; Egraz, J. B.; Llauro, M. F.; Ladavière, C.; Claverie, J. *Macromolecules* **2003**, *36*, 3066−3077. (d) Tang, C.; Matyjaszewski, K.; Kowalewski, T. *Macromolecules* **2003**, *36*, 8587−8589. (e) Vosloo, J. J.; Tonge, M. P.; Fellows, C. M.; D'Agosto, F.; Sanderson, R. D.; Gilbert, R. G. *Macromolecules* **2004**, *37*, 2371−2382. (f) Duréault, A.; Taton, D.; Destarac, M.; Leising, F.; Gnanou, Y. *Macromolecules* **2004**, *37*, 5513−5519. (g) You, Y.; Hong, C.; Wang, W.; Wang, P.; Lu, W.; Pan, C. *Macromolecules* **2004**, *37*, 7140−7145. (h) Albertin, L.; Stenzel, M.; Barner-Kowollik, C.; Foster, L. J. R.; Davis, T. P. *Macromolecules* **2004**, *37*, 7530−7537. (i) Schilli, C. M.; Zhang, M.; Rizzardo, E.; Thang, S. H.; Chong, B. Y. K.; Edwards, K.; Karlsson, G.; Müller, A. H. E. *Macromolecules* **2004**, *37*, 7861−7866. (j) Bussels, R.; Bergman-Gottgens, C.; Meuldijk, J.; Konig, C. *Macromolecules* **2004**, *37*, 9299−9301. (k) Liu, B.; Kazlauciunas, A.; Guthrie, J. T.; Perrier, S. *Macromolecules* **2005**, *38*, 2131−2136. (l) Stenzel-Rosenbaum, M.; Davis, T. P.; Chen, V.; Fane, A. G. *J. Polym. Sci.*, *Part A*: *Polym. Chem.* **2001**, *39*, 2777−2783. (m) for a review on architecture design: Moad, G.; Mayadunne, R. T. A.; Rizzardo, E.; Skidmore, M.; Thang, S. H. *Macromol. Symp.* **2003**, *192*, 1−12. (n) For a review on aqueous phase RAFT polymerization: McCormick, C. L.; Lowe, A. B. *Acc. Chem. Res.* **2004**, *37*, 312−325.

(3) Ganachaud, F.; Monteiro, M. J.; Gilbert, R. G.; Dourges, M.-A.; Thang, S. H.; Rizzardo, E. *Macromolecules* **2000**, *33*, 6738−6745.

(4) Vana, P.; Albertin, L.; Barner, L.; Davis, T. P.; Barner-Kowollik, C. *J. Polym. Sci.*, *Part A*: *Polym. Chem.* **2002**, *40*, 4032−4037.

(5) Favier, A.; Ladaviere, C.; Charreyre, M.-T.; Pichot, C. *Macromolecules* **2004**, *37*, 2026−2034.

(6) D'Agosto, F.; Hughes, R.; Charreyre, M.-T.; Pichot, C.; Gilbert, R. G. *Macromolecules* **2003**, *36*, 621−629.

(7) Moad, G.; Chong, Y. K.; Postma, A.; Rizzardo, E.; Thang, S. H. *Polymer* **2005**, *46*, 8458−8468.

(8) Patton, D. L.; Mullings, M.; Fulghum, T.; Advincula, R. C. *Macromolecules* **2005**, *38*, 8597−8602.

(9) Mayadunne, R. T. A.; Rizzardo, E.; Chiefari, J.; Krstina, J.; Moad, G.; Postma, A.; Thang, S. H. *Macromolecules* **2000**, *33*, 243−245.

(10) Wang, Z.; He, J.; Tao, Y.; Yang, L.; Jiang, H.; Yang, Y. *Macromolecules* **2003**, *36*, 7446−7452.

(11) Lowe, A. B.; Sumerlin, B. S.; Donovan, M. S.; McCormick, C. L. *J. Am. Chem. Soc.* **2002**, *124*, 11562−11563.

(12) Thomas, D. B.; Convertine, A. J.; Hester, R. D.; Lowe, A. B.; McCormick, C. L. *Macromolecules* **2004**, *37*, 1735−1741.

(13) Schilli, C.; Lanzendörfer, M. G.; Müller, A. H. E. *Macromolecules* **2002**, *35*, 6819−6827.

(14) Mayadunne, R. T. A.; Jeffery, J.; Moad, G.; Rizzardo, E. *Macromolecules* **2003**, *36*, 1505−1513.

(15) Sumerlin, B. S.; Lowe, A. B.; Stroud, P. A.; Zhang, P.; Urban, M. W.; McCormick, C. L. *Langmuir* **2003**, *19*, 5559−5562.

(16) Tsarevsky, N. V.; Matyjaszewski, K. *Macromolecules* **2002**, *35*, 9009−9014.

(17) Postma, A.; Davis, T. P.; Moad, G.; O'Shea, M. S. *Macromolecules* **2005**, *38*, 5371−5374.

(18) Quinn, J. F.; Barner, L.; Barner-Kowollik, C.; Rizzardo, E.; Davis, T. P. *Macromolecules* **2002**, *35*, 7620−7627.

(19) de Brouwer, H.; Schellekens, M. A. J.; Klumperman, B.; Monteiro, M. J.; German, A. L. *J. Polym. Sci.*, *Part A*: *Polym. Chem.* **2000**, *38*, 3596−3603.

(20) Perrier, S.; Takolpuckdee, P.; Mars, C. A. *Macromolecules* **2005**, *38*, 2033−2036.

(21) Chen, M.; Ghiggino, K. P.; White, J.; Thang, S. H.; Wilson, G. J. *J. Org. Chem.* **2005**, *70*, 1844−1852.

(22) Liu, Y.; He, J.; Xu, J.; Fan, D.; Tang, W.; Yang, Y. *Macromolecules* **2005**, *38*, 10332−10335.

(23) Le, T. P.; Moad, G.; Rizzardo, E.; Thang, S. H. PCT Int. Appl. WO 9801478 A1 980115; *Chem. Abstr*. **1998**, *128*, 115390.

(24) Brandrup, J.; Immergut, E. H. In *Polymer Handbook*, 2nd ed.; Wiley-Interscience: New York 1975; p II-4.

(25) Lima, V.; Jiang, X. L.; Brokken-zijp, J.; Schoenmakers, P. J.; Klumperman, B.; Linde, R. V. D. *J. Polym. Sci.*, *Part A*: *Polym. Chem.* **2005**, *43*, 959−973.

(26) Arita, T.; Buback, M.; Vana, P. *Macromolecules* **2005**, *38*, 7935−7943.

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