Thermal Decomposition of Cumyl Dithiobenzoate

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Introduction

There have been many studies on the mechanism of controlled/"living" radical polymerization regulated by the reversible addition−fragmentation chain transfer (RAFT) process.[1−10] These studies addressed three questions essential to the RAFT-based polymerization, i.e., the presence of the intermediate radical, the origin of the retarded polymerization rate, and the terminal structure of the dormant chains. The presence of the intermediate radical was observed by direct ESR (electron spin resonance) analysis,[3] although more radical species were detected and remained to be assigned.[4,5] The intermediate radical, with two arms of polymer chains, can undergo cross-termination with propagating radical as well as fragmentation at either of its two arms. In the elucidation of the observed retardation kinetics, Monteiro et al.[6,7] proposed that the cross-termination is the origin of the retardation, while Davis and co-workers[8,9] proposed a model of long-lived intermediate radical of which the fragmentation is slow. The cross-termination model, later modified by including a reversible termination between two intermediate radicals, was supported by the end-group analysis of dormant chains derived from ^{13}C-labled dithioester by Calitz et al.,[10] by the first isolation of a 3-arm product of the reaction of low molar mass analogy in Fukuda's group[11] and by the observation of 3- and 4-arm polymeric species in a cross-reaction between polymers synthesized by the RAFT process and ATRP (atom transfer radical polymerization).[12] The slow fragmentation model was supported by Coote's ab initio molecular orbital calculations[13] and the consistent experimental facts.[14] Klumperman studied[15] the process during the early stage of AIBN (2,2′-azoisobutyronitrile)-initiated styrene polymerization in the presence of cyanoisopropyl dithiobenzoate and found a high selectivity in radical addition, i.e., cyanoisopropyl radical adds to monomer much more faster than styryl radical. They proposed that if the reverse is true, the polymerization could be inhibited.[15] However, Charleux and co-workers[16] observed little radical selectivity but high concentration of the intermediate radicals in the early period of AIBN-initiated *n*-butyl acrylate polymerization in the presence of *tert*-butyl dithiobenzoate. Therefore, they attributed the inhibition to slow fragmentation and the retardation to cross-termination, respectively.[16] Most recently, Monteiro and co-workers[17] observed that the impurities in dithioesters, with varying amount depending on storage period, caused inhibition and retardation to the RAFT-based polymerization.

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The retaining of the thiocarbonylthio moieties as terminal groups of the resulting polymers was evidenced by NMR[1,2] and MALDI−TOF MS (matrix-assisted laser desorption ionization time-of-flight mass)[18−20] spectrometry. The latter demonstrated that, in addition to the dormant chains, there were chains derived from the fragmentation and the oxidation of the dormant chains. Thus, it was proposed that the dormant chains were susceptible to the conditions in MALDI−TOF spectrometer.[20]

In these studies, little attention was paid to the thermal stability of the starting dithioesters, which could have a detrimental effect on the subsequent polymerization. Although C−S bond undergoes both oxidation[20] in the presence of air and degradation under UV[6,21] and γ[22,23] irradiation, dithioesters were thought to be thermally stable because polymerization cannot be initiated just by heating in the absence of an initiator.[20] During the preparation of this paper, Davis and Moad report[24] their new results on the thermolysis of trithiocarbonate end groups of polymers synthesized by the RAFT polymerization.

We have carried out computer simulation[25,26] on the kinetics of the RAFT-based radical polymerization and synthesized polymers with controlled structures in the presence of thiocarbonylthio compound.[27,28] In an attempt to characterize cumyl dithiobenzoate (CDB), a reagent widely used in controlled polymerization of various monomers, we found unexpectedly that there are mainly two peaks in gas chromatography, while NMR of the same sample shows high purity. Therefore, we assume that CDB underwent thermal decomposition in GC (gas chromatography) column. This note presents the results of the study of thermal decomposition phenomenon of CDB.

Results and Discussion

CDB was synthesized according to the literature,[1] purified by flash chromatography followed by recrystallization and obtained as large purple crystals (Supporting Information). Figure 1 presents product characterization. While HPLC (high-pressure liquid chromatography) and NMR indicate that the purity is quite high, GC-MS (combination of gas chromatography and mass spectrum) shows completely no peak that displays a mass spectrum of CDB. Instead, there are mainly two peaks at retention time (RT) of 2.83 and 6.46 min, which can be assigned to α-methylstyrene and dithiobenzoic acid according to the MS spectra (Figure 1d,e). Figure 1 also shows four small peaks at RT = 2.38, 9.02, 10.22, and 13.73 min. A close analysis of the MS spectra (Supporting Information) reveals the presence of isopropylbenzene (2.38 min, $m/e = 120$) and cumyl thiobenzoate (10.22 min, $m/e = 256$), an oxidized product of cumyl dithiobenzoate. This observation is comparable with the results of MALDI−TOF MS,[20] in which proton-terminated and thioester-terminated chains were observed. However, it is difficult to identify the peaks at 9.02 and 13.73 min by merely the results of GC-MS.

In analyzing the above result of GC-MS, we assume that CDB is thermally unstable and undergoes degradation in the GC column. Therefore, we performed a test to heat CDB in a *tert*-butylbenzene solution at 120 °C. Figure 2 shows the HPLC profiles of the samples taken
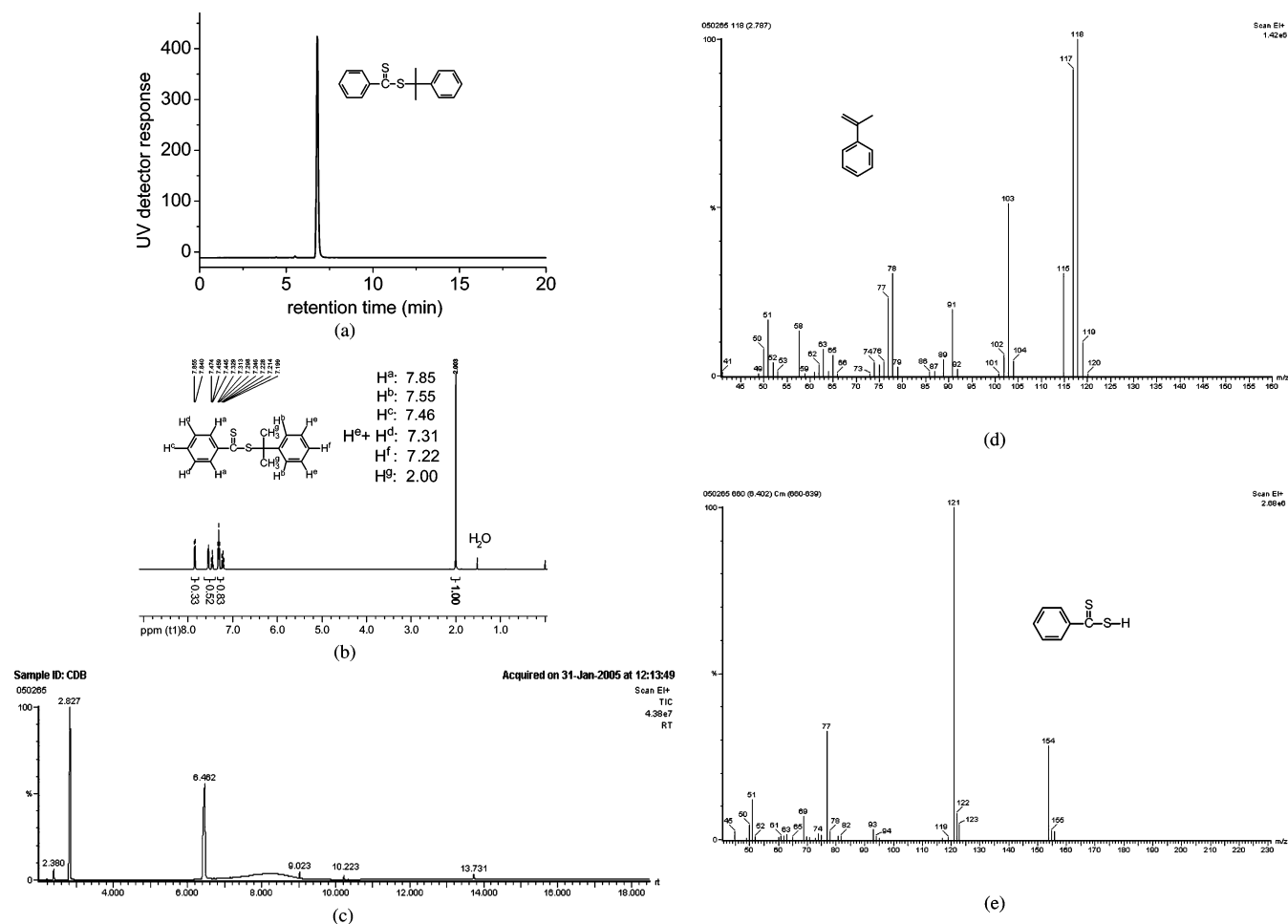
Figure 1. HPLC (high-pressure liquid chromatography) (a), NMR (b), GC-MS (combination of gas chromatography and mass spectroscopy) (c: GC; d and e: MS for peaks at RT = 2.83 and 6.46 min, respectively) of CDB (cumyl dithiobenzoate). Conditions: eluent for HPLC: actonitrile/water = 85/15 (v/v), 1.0 mL/min, 40 °C; eluent for GC: helium, 1.0 mL min^{-1}, from 100 to 300 °C, 20 K min^{-1}.
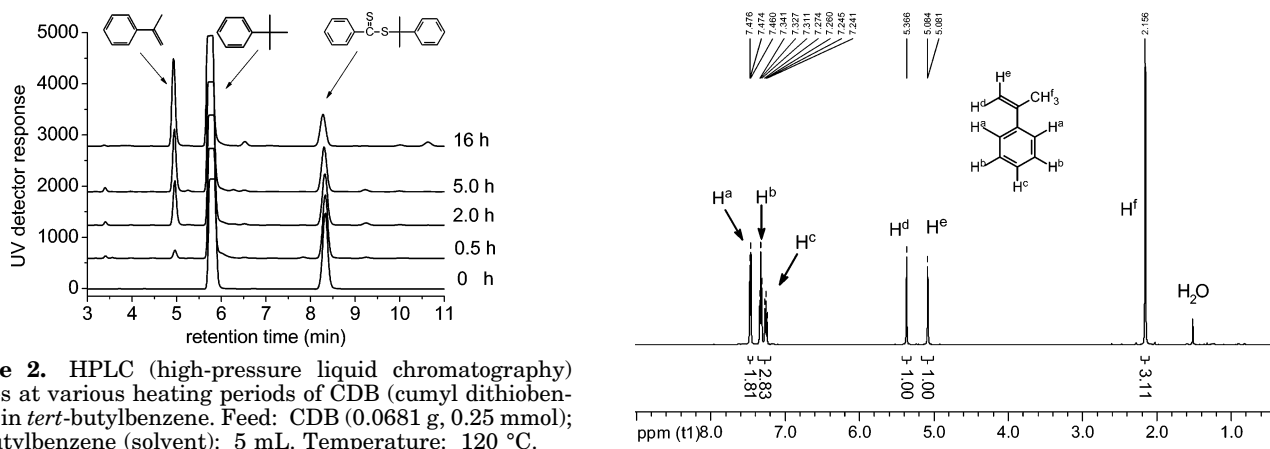

Figure 2. HPLC (high-pressure liquid chromatography) profiles at various heating periods of CDB (cumyl dithiobenzoate) in *tert*-butylbenzene. Feed: CDB (0.0681 g, 0.25 mmol); *tert*-butylbenzene (solvent): 5 mL. Temperature: 120 °C.

Figure 3. ^{1}H NMR spectrum of the isolated fraction (RT = 4.95 min in Figure 2) by a preparative HPLC (high-pressure liquid chromatography) column, confirming the structure of α-methylstyrene.

at different reaction periods. The three main peaks at RT = 4.95, 5.77, and 8.33 min were assigned to α-methylstyrene, *tert*-butylbenzene (solvent), and residual CDB, respectively, by correlation with authentic compounds. Obviously, the amount of α-methylstyrene increased while that of CDB decreased with reaction time.

To further confirm the presence of α-methylstyrene, the exact component at RT = 4.95 min was fractionated by injection 50 times (50 × 0.2 mL) through a preparative HPLC column. Figure 3 shows the NMR spectra of the isolated compound, confirming the structure of α-methylstyrene.

Surprisingly, we did not observe a peak in HPLC with reasonable intensity that corresponds to dithiobenzoic acid (DTBA). A hint for the acid formation can be drawn from the following experiment. After heating a 0.05 M solution of CDB at 120 °C for 16 h, an aqueous solution of NaOH (1.25 M) was added, and the aqueous phase immediately became red in color. The separated aqueous phase was mixed with diethyl ether, and the mixture

was acidified using aqueous HCl (1.4 M). Upon acidification, the organic phase immediately became red in color. The separated ether phase was washed three times with water and dried over CaCl$_2$. After distillation of the solvent, a red oil was obtained which was subject to HPLC, NMR, and EA (elementary analysis). HPLC showed numerous peaks, and NMR gave numerous signals (Supporting Information) that are difficult to interpret. EA (Supporting Information) gave weight percentage of C: 50.81, S: 40.31, and H: 6.29%, which are quite close to the calculated fraction of C: 54.45 and S: 41.17% of DTBA and comparable to those obtained by Monteiro[17] for synthesized DTBA. The measured percentage of hydrogen, 6.29%, is however much larger than the theoretical value, 3.92%. This could be correlated to side reactions during the extraction.

The appearance of a red color in the extracting phase in the above experiment was supposed to be due to the presence of dithiobenzoic acid. Although CDB itself can also undergo hydrolysis in a basic solution, this possibility was excluded by a blank experiment in which a solution of CDB (without heating) was mixed directly with an aqueous solution of NaOH. No red color was observed in the aqueous phase during the same operation period.

The difficulty in the analysis of the obtained red oil is due to the instability of DTBA. Indeed, it was reported[17] that even isolated DTBA showed numerous peaks in HPLC, possibly due to the very easy oxidation of the molecules. Although DTBA was utilized to achieve controlled/"living" radical polymerization, no detailed characterization result on the purified DTBA was presented.[29] We found that, in the preparation of DTBA by a Grignard reagent, the isolated product changed very easily from purple to yellow in color in storage overnight exposed to air. With the protection of argon, the purple color remained more stable for the same period. However, when the purple oil-like product was subject to HPLC, numerous peaks appeared in the chromatogram, indicating the product underwent degradation in the column.

The evolution of concentrations of α-methylstyrene and CDB along with time at varying temperatures is shown in Figure 4. The concentration of α-methylstyrene reaches a steady value after a period that depends on the reaction temperature. It is well-known that DTBA reacts readily with α-methylstyrene or styrene in the preparation of the corresponding dithioesters.[1] Thus, the steady concentration may be a consequence of dynamic balance between the decomposition and the addition reactions. Nevertheless, Figure 4a shows that the concentration of CDB decayed even after α-methylstyrene reached the steady concentration, indicating the presence of other consumption pathways of dithioester.

Despite this, the decomposition shows a first-order kinetics within the initial period (Figure 4b, inset), especially at temperatures lower than 120 °C. Therefore, we ignore the reverse reaction, which forms CDB, and the side reaction(s), which consumes CDB, and obtain the following kinetic equations:

$$\ln\left(\frac{[\text{CDB}]_t}{[\text{CDB}]_0}\right) = \ln\left(1 - \frac{[\text{MSt}]_t}{[\text{CDB}]_0}\right) = -k_{\text{dec}}t \quad (1)$$

in which k_{dec} is the rate constant of CDB decomposition. $[\text{CDB}]_0$ and $[\text{CDB}]_t$ are the feed concentration and the
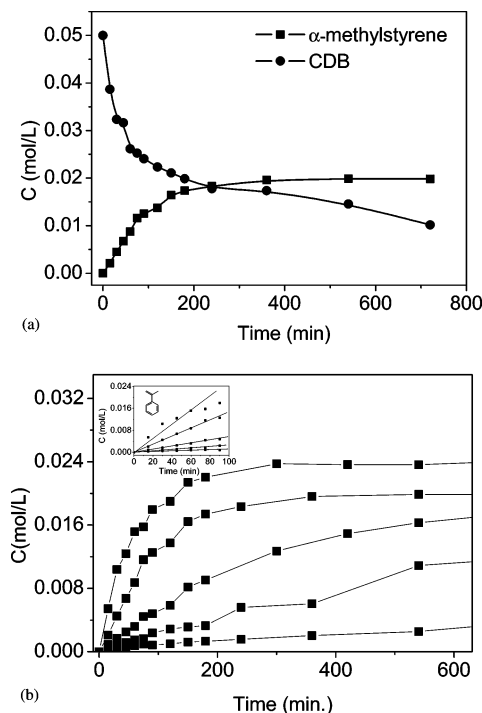

Figure 4. (a) Evolution of concentrations of CDB (cumyl dithiobenzoate) (●) and α-methylstyrene (■) along with time during heating CDB at 120 °C in *tert*-butylbenzene. The reaction condition is identical to that in Figure 2. (b) Dependence of α-methylstyrene concentrations on heating time at temperatures of 90, 100, 110, 120, and 130 °C (from bottom to top). The inset shows a first-order kinetics within the initial period.
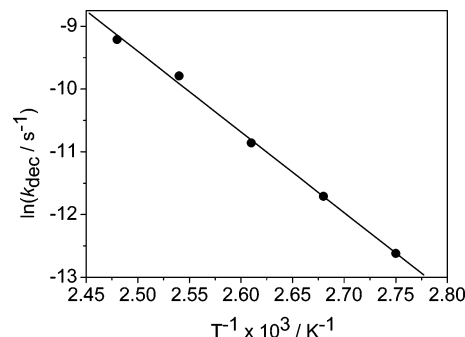

Figure 5. Arrhenius plot for k_d values of CDB (cumyl dithiobenzoate) decomposition in *tert*-butylbenzene. Data for the heating experiment of CDB, and the calculated Arrhenius equation, with $E_{\text{dec}} = 107$ kJ mol^{-1} and $A_{\text{dec}} = 7.74 \times 10^9$ s^{-1}.

instant concentration of CDB at time $t = t$, respectively. $[\text{MSt}]_t$ denotes the instant concentration of α-methylstyrene at time t.

Various k_{dec} were obtained for different temperatures. Figure 5 shows the Arrhenius plot that corresponds to the formula in eq 2:

$$k_{\text{dec}} = A_{\text{dec}}e^{-E_{\text{dec}}/RT}$$

$$\text{with } A_{\text{dec}} = 7.74 \times 10^9 \text{ s}^{-1} \text{ and } E_{\text{dec}} =$$

$$107 \text{ kJ mol}^{-1} \quad (2)$$

From eq 2, a decomposition rate constant of $k_{\text{dec}} = 4.64 \times 10^{-5}$ s^{-1} was estimated for CDB at 60 °C, a temperature at which the RAFT polymerizations are often performed.
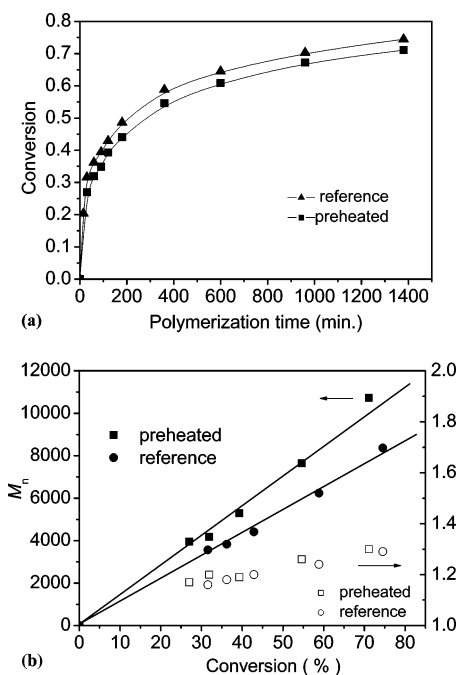
Figure 6. Polymerization kinetics (a) and the molecular weight (filled dots) and polydispersity (open dots) (b) for styrene RAFT polymerization mediated by cumyl dithiobenzoate (CDB) (circle) and preheated CDB (square). Conditions: styrene 10.4 g (0.1 mol), styrene/CDB/2,2′-azobis(isobutyronitrile) (AIBN) = 200/2/1 (molar ratio), in 20 mL of *tert*-butylbenzene. Temperature: 120 °C; preheating time: 9 h.

Conclusions

On the basis of the experimental facts in this work and that in the preparation of CDB, we proposed the reversible reaction mechanism in eq 3:
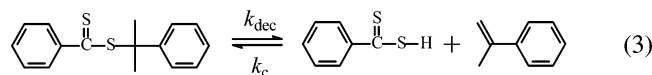
Higher temperature drives the reaction to the right-hand side, i.e., the decomposition of CDB. At lower temperature, the reverse is favored and was virtually employed in the synthesis of CDB by the reaction of α-methylstyrene and DTBA.[1]

Other dithioesters, such as 1-phenylethyl dithiobenzoate and its derivatives, show very slight decomposition, and benzyl dithiobenzoate does not decompose when heated at 120 °C (Supporting Information). Therefore, the thermal decomposition is quite specific for CDB. Nevertheless, the decomposition of CDB has only a minor effect on polymerization of styrene at 120 °C. Figure 6 compares two polymerization systems mediated by CDB and preheated (120 °C, 9 h) CDB, showing only a small difference between the polymerization rates, although the loss of CDB for the latter was indicated by the larger molecular weight on the same monomer conversion. The reason could be due to the inevitable styrene thermal initiation at 120 °C as well as the loss of DTBA by oxidation and addition reaction to styrene to form the corresponding dithioester, phenylethyl dithiobenzoate, which is quite stable and mediates the polymerization through the RAFT mechanism. It should be pointed out that the polymeric dithioesters, which are more stable than CDB, are formed after the initiation period, accounting for the fact that CDB-mediated RAFT polymerization of styrene works well at high temperatures.[30]

Supporting Information Available: Materials; measurements; experiments details; GC-MS, NMR, HPLC, and EA data. This material is available free of charge via the Internet at http://pubs.acs.org.

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