Direct Observation of the RAFT Polymerization Process by Chromatography

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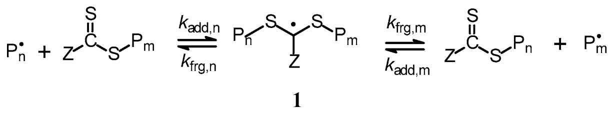
Introduction

Controlled/"living" radical polymerization based on the RAFT (reversible addition−fragmentation chain transfer) process (Scheme 1) is a versatile tool to synthesize polymers with well-defined structures.[1−17] It is well-established that the living nature originates from the reversible exchange between different propagating radicals ($P_m^\bullet$ and $P_n^\bullet$) through an intermediate radical (**1**) process,[1] as evidenced by ESR spectroscopy.[18−21] However, the study of the mechanism and kinetics of the RAFT polymerization is still an ongoing issue. This is, on one hand, due to the debating interpretations on the retardation/inhibition kinetics of the RAFT polymerization.[22] The inhibition is a consequence of radical loss in the pre-equilibrium in which the initiator-derived and oligomeric radicals react with the starting RAFT agent, while the retardation is caused by the radical loss in the main equilibrium in which polymeric radicals react with polymeric RAFT agent. The fundamental cause for the radical loss is thought to be the stability of the intermediate radical due to the fact that the RAFT polymerization using less stabilized dithioester exhibit a lower retardation effect.[23] However, there are different opinions on how the stabilized intermediate leads to radical loss. The CAMD group[24,25] proposed a slow fragmentation model in which the intermediate radical itself plays a role of radical storage, leading to non-stationary decreasing concentration of the propagating radicals, whereas Monteiro[26] and Fukuda[20,27] proposed that the cross-termination between propagating radical and the intermediate radical is responsible for the radical loss, leading to low stationary concentration of the propagating radicals. The former is supported by the ab initio quantum calculation[27,28] on the bond energy of small molecular dithioesters while the latter is supported by the isolation and characterization of the three-arm star species formed in a model reaction of small molecular radicals and dithioesters.[20,27] The slow fragmentation model was later modified, in order to fit to the ESR-measured low intermediate concentration,[20,21] by the incorporation of reversible cross-termination between propagating and the intermediate radicals or reversible self-termination of the intermediates.[23,24,29−35] In addition, it was observed that the rate coefficients of addition and fragmentation strongly depend on chemical nature[36,37] and chain length of the radical's chain-length dependence.[32,38−40] This indicates that the RAFT polymerization can be properly described by a composite of slow fragmentation model and cross-termination model using varying coefficients for the pre-equilibrium and main equilibrium.[22] This agrees with the conclusion by earlier computer simulation work.[41]

Scheme 1



On the other hand, the mechanistic study is complicated by the fact that a different pair of monomer/RAFT agent leads to specific polymerization behavior in spite of the general regulation by the reaction in Scheme 1. For the most widely used monomers, styrene and methyl methacrylate (MMA), the former polymerized at a retarded rate[20,24−27,40,42,43] while the latter exhibited an inhibition period when the polymerization was mediated by cumyl dithiobenzoate (CDB).[36,37,44] The intermediate radical was detected by ESR for styrene polymerization but not for the methacrylate system.[18] When cumyl phenyldithioacetate was used as RAFT agent, styrene polymerization yielded narrow unimodal disperse product with linear dependence of molecular weight on monomer conversion, while the MMA system exhibited a hybrid of conventional chain transfer and living behavior, yielding bimodal distributed product at the early stage of polymerization.[23] On-line NMR spectrometry revealed that styrene polymerization mediated by cyanoisopropyl dithiobenzoate[45b] or cumyl dithiobenzoate[45c] showed an initialization period in which the chain propagation took place in a selective way. These differences between styrene and MMA systems were ascribed to different chain transfer abilities of thiocarbonylthio moieties at PMMA and PS chain ends.[40,43] The difference in chain transfer ability also results in sequence selectivity in the preparation of block copolymer, PMMA-*b*-PS, in which PMMA should be synthesized as the first block since it is a better leaving group.[40,43] In addition, styrene can polymerize to very high molecular weight and narrow distribution at high temperature[46] or high pressure[47] while the living chains of PMMA tends to decompose when the temperature is high.[48]

In an attempt to purify PMMA product produced by CDB-mediated RAFT polymerization, we use column chromatography and find remarkable residual CDB in samples of medium and even high (75%) monomer conversions (TOC graphic). This is quite unexpected, since in a good living polymerization the initiator (in the present case the RAFT agent) should be converted to living chains completely at the early stage. The incomplete conversion of the RAFT agent has already been noted by Benaglia and co-workers[36] and Rizzardo and co-workers[37] from the fact that the molecular weights in the early stage were remarkably larger than theoretical values. Nevertheless, direct measurement of the residual RAFT agent, especially up to high monomer conversion, has never been reported. In this paper, we present our study on quantitative correlation between molecular weight and the residual RAFT agent as well as the influence of reaction conditions on the consumption rate of the RAFT agent.

Experiments

Materials. 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. 2,2′-Azobis(isobutyronitrile) (AIBN, Shanghai 4th Factory of Chemicals, 99%)

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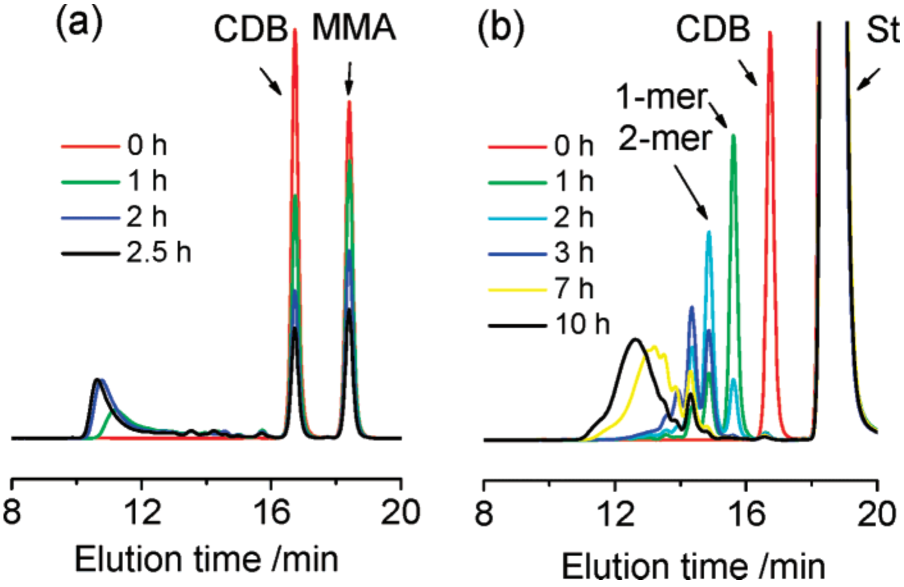


Figure 1. GPC diagrams for bulk polymerizations of MMA and St initiated with AIBN and mediated with CDB at 60 °C. (a) MMA: 9.36 M, AIBN: 0.09 M, CDB: 0.19 M. (b) St: 8.74 M, AIBN: 0.09 M, CDB: 0.17 M.

was recrystallized from methanol. Cumyl dithiobenzoate (CDB) was synthesized according to the literature procedure[49] and recrystallized twice from petroleum ether. Purple 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, CH_3), 7.21 (t, 1H, ArH), 7.30 (m, 4H, ArH), 7.43 (t, 1H, ArH), 7.54 (d, 2H, ArH), 7.84 (d, 2H, ArH). 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%.

Measurement. Gel permeation chromatography (GPC) was performed on a Waters 410 system equipped with two TSK-GEL H-type columns (particle size: 5.0 μm, MW range: 0−1000 and 0−2 × 10^4 g/mol), a Waters 410 RI detector, and a Waters 486 UV detector (254 nm), using THF as the eluent at a flow rate of 1 mL/min at 40 °C. The columns were calibrated by narrow PMMA (MW range: 700−3 × 10^4 g/mol) and narrow polystyrene (MW range: 200−3 × 10^6 g/mol) standards. The ultraviolet absorption of cumyl dithiobenzoate 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 (Symmetry Shield RP-18, 5.0 μm, 4.6 × 250 mm), and a UV detector with the wavelength set 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). Elemental analysis was determined by oxygen flask combustion. NMR measurement was carried out on a Bruker DMX500 instrument, using $CDCl_3$ as solvent and tetramethylsilane (TMS) as the reference.

Synthesis of PS with Dithiobenzoate Terminus. Styrene (15.00 g, 0.14 mol), CDB (0.26 g, 9.60 × 10^{-4} mol), and AIBN (0.08 g, 4.80 × 10^{-4} mol) were dissolved in benzene (6 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 25 h before quenched into liquid nitrogen to stop the polymerization. The resulting PS was obtained as a pink powder after three times of dissolving in THF and precipitating from methanol. The product was analyzed by GPC. Number-average molecular weight: M_n = 4400 g/mol; polydispersity index (PDI): M_w/M_n = 1.15.

Synthesis of PMMA with Dithiobenzoate Terminus. MMA (6.20 g, 0.06 mol), CDB (0.57 g, 2.10 × 10^{-3} mol), and AIBN (0.16 g, 9.70 × 10^{-4} mol) 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 9 h before quenched into liquid nitrogen to stop the polymerization. The resulting PMMA was obtained as a pink powder after three times of dissolving in THF and precipitating from petroleum ether. The product was analyzed by GPC. Number-average molecular weight: M_n = 4000 g/mol, PDI = 1.15.

RAFT Polymerization of MMA or St Mediated by CDB. A typical procedure is as follows: MMA (7.30 g, 7.30 × 10^{-2} mol) or St (7.60 g, 7.30 × 10^{-2} mol), AIBN (0.12 g, 7.30 × 10^{-4} mol), and CDB (0.40 g, 1.46 × 10^{-3} mol) were transferred to a 25 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 out from the flask at predetermined periods and analyzed by GPC calibrated with PMMA/PSt standards. $M_{n,PMMA}$ = 5200 g/mol (2.5 h), PDI = 1.24; $M_{n,PS}$ = 2300 g/mol (32 h), PDI = 1.25.

RAFT Polymerization of MMA or St Mediated by Both CDB and PMMA or PS with Dithiobenzoate Terminus. A typical procedure is as follows: MMA (4.20 g, 0.04 mol), styrene (4.37 g, 0.04 mol), PMMA with dithiobenzoate terminus (0.84 g, 2.10 × 10^{-4} mol)/PS with dithiobenzoate terminus (0.90 g, 2.10 × 10^{-4} mol), AIBN (0.03 g, 2.10 × 10^{-4} mol), and CDB (0.06 g, 2.10 × 10^{-4} mol) were dissolved in benzene (14 mL) in a 25 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 out from the flask at predetermined periods and analyzed by GPC. $M_{n,PS}$ = 6100 g/mol (30 h), PDI = 1.27 (bimodal distribution); $M_{n,PMMA}$ = 10 800 g/mol (30 h), PDI = 1.24.

Results and Discussion

The polymerizations of styrene and MMA are carried out in bulk and in solution at 60 °C, using AIBN as the initiator and freshly purified CDB as the RAFT agent, respectively. The purity of CDB is 99.1% determined by HPLC. Monteiro reported that CDB of >99% purity determined by elementary analysis caused shorter inhibition period and less retardation than that of 97%.[50] One should keep in mind that the remaining 0.9% impurity in the present work would also cause inhibition and/or retardation, although possibly not to a remarkable extent. The samples for GPC measurement are precisely weighted and dissolved in THF for quantitative evaluation.

Figure 1 shows the GPC monitoring of RAFT polymerizations of styrene and MMA at feed ratio of AIBN/CDB/monomer = 1/2/100. The two columns used in the measurement are able to resolve small molecular weight species and oligomers. Thus,

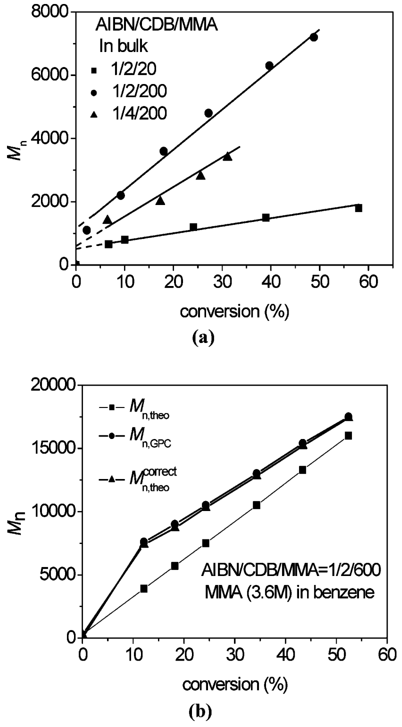


Figure 2. Increase of molecular weight with monomer conversion for MMA polymerization at 60 °C initiated with AIBN in the presence of CDB. (a) (■) MMA: 9.36 M, AIBN: 0.47 M, CDB: 0.94 M (●) MMA: 9.36 M, AIBN: 0.05 M, CDB: 0.09 M (▲) MMA: 9.36 M, AIBN: 0.05 M, CDB: 0.19 M. The lines are drawn only for guiding the eyes. (b) MMA (3.67 M) in benzene. $M_{n,theo}$ (■) calculated from eq 1, $M_{n,GPC}$ (●) obtained by GPC, and $M_{n,theo}^{correct}$ (▲) calculated from eq 2.

the polymer, monomer, and CDB are clearly resolved to a baseline level. The contents of various species are then quantified using calibration curves of the corresponding pure compounds (monomer and CDB). Comparison of parts a and b of Figure 1 shows clearly the difference between styrene and MMA polymerizations under identical reaction conditions. In the former system, CDB is consumed up rapidly within 1 h, yielding 1-mer product that reached maximum content at the same time. Then the content of 1-mer decreases while the 2-mer appears and subsequently increases with reaction time. The reaction profile agrees very well with that of the initialization period as reported by Klumperman and co-workers,[45] in which high selectivity of the reaction was ascribed to biased fragmentation toward cumyl radical. On the other hand, the selectivity in MMA polymerization is not significant. The content of CDB decreases to ~59% of the feed within the same period, while the chain propagates rapidly to high molecular weight. The species of 1-, 2-, and 3-mers are only slightly visible, and their contents change little with reaction time. At 2.5 h the reaction mixture is nearly solidified. In addition, it seems that only a fraction of the species increases in molecular weight with reaction time, with remarkable tailing effect on GPC traces. This skewed increase in molecular weight was also observed in cumyl phenyldithioacetate-mediated polymerization of MMA and was correlated to hybrid of conventional chain transfer and living character.[23] Thus, in MMA polymerization, a chain propagates a number of steps (adding to a number of monomer units) within each period when the chain is activated by fragmentation. This fast chain propagation leads to uncontrolled molecular weight and broadened molecular weight distribution.

Figure 2 shows that, for MMA polymerization, the growth of molecular weight vs monomer conversion does not start from zero at zero conversion as indicated by the linear extrapolations. This is a result of the uncontrolled polymerization as well as incomplete conversion of CDB during this period. The phenomenon appeared in a number of previous studies[36,37,40,43,51,52] and was used by Rizzardo and co-workers to estimate the residual CTA[36,37] by comparison of the measured molecular weight and the theoretical ones, $M_{n,theo}$

$$M_{n,theo} = \frac{[MMA]_0 \times \text{conversion}}{[CDB]_0} \times MW_{MMA} + MW_{CDB} \tag{1}$$

in which the subscript 0 denotes molar concentrations at time zero. MW_{MMA} and MW_{CDB} are molecular weights of MMA and CDB, respectively. In the present work, the molecular weight and the residual amount of CDB are virtually measured in the same sample, facilitating a correction for $M_{n,theo}$ by taking into account the residual RAFT agent, $[CDB]_t$, at time t

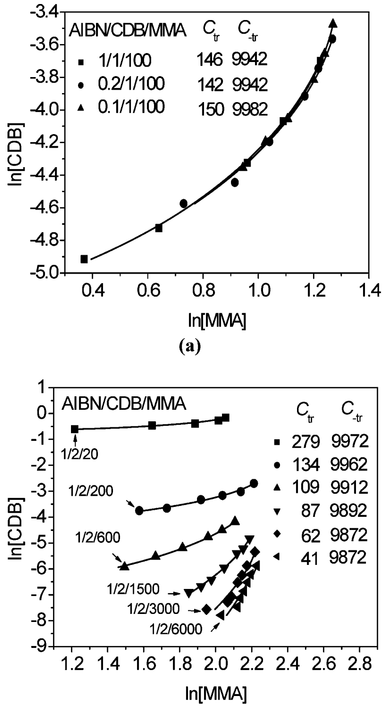
$$M_{n,theo}^{correct} = \frac{[MMA]_0 \times \text{conversion}}{[CDB]_0 - [CDB]_t} \times MW_{MMA} + MW_{CDB} \tag{2}$$

Figure 2b shows, for a MMA polymerization, the theoretical molecular weights agree very well with the measured values after correction by eq 2. It is also noteworthy that the discrepancy between the measured and the theoretical (without correction) molecular weights become smaller at higher monomer conversion due to the increasing consumption of the RAFT agent.

It is interesting to find that the relative consumption rate of CDB and MMA depends strongly on the feed ratio of these two species but is independent of the feed amount of radical initiator, as shown in Figure 3. Smaller amount of monomer leads to more unconverted CDB. For the system of AIBN/CDB/MMA = 1/2/20, the conversion of CDB never exceeds 50% even when the system became solid at 2.5 h. Whereas, in a system with larger amount of monomer, such as 1/2/1500, nearly complete consumption of CDB is observed within 3 h, which is consistent with the results of CSIRO group.[37a] These kinetic results indicate that, in the RAFT polymerization of MMA with larger target molecular weight, it is easy to observe an agreement between the theoretical and practical molecular weights, even with a very small amount of AIBN (i.e., tenth of $[CDB]_0$). However, in the system with smaller target molecular weight, the measured molecular weight is remarkably larger than the theoretical one.

The slow consumption of CDB also indicates that, in MMA RAFT polymerizations with relative high amount of CDB, the pre-equilibrium and the main equilibrium do not necessarily occur one after another. Instead, the pre-equilibrium exists throughout the reaction process. These equilibria have different addition and fragmentation rate coefficients and thus different equilibrium constants.[22] The leaving groups also show different addition rates to monomer.[22] The kinetics of this situation should be described by a composite of simultaneous RAFT processes of pre-equilibrium and main equilibrium; that is to say, the retardation effect caused by CDB itself would exceed the initial pre-equilibrium period.

The CAMD group proposed a method[39] for evaluation of k_{add} from the degree of polymerization at zero monomer conversion, DP_n^{inst}, which in the present work can be derived from the intercept of molecular weight axis in Figure 2a. However, the method is valid for thiocarbonylthio compound with leaving group identical to the propagating radical, which is not the case



(a)

(b)

Figure 3. Double-logarithmic plots of transfer agent concentration vs monomer concentration during polymerizations of MMA at 60 °C, initiated by AIBN and mediated by CDB, with various feed ratio of CDB/MMA. (a) (□) MMA: 3.67 M, AIBN: 0.04 M, CDB: 0.04 M (○) MMA: 3.67 M, AIBN: 7.0 mM, CDB: 0.04 M (△) MMA: 3.67 M, AIBN: 4.0 mM, CDB: 0.04 M. Lines are numerical fitting results by eq 4 with $C_{tr} = 146$, 142, and 150 and $C_{-tr} = 9942$, 9942, and 9982, respectively. (b) (■) MMA: 9.36 M, AIBN: 0.47 M, CDB: 0.94 M (●) MMA: 9.36 M, AIBN: 0.05 M, CDB: 0.09 M (▲) MMA: 9.36 M, AIBN: 16.0 mM, CDB: 31.0 mM (▼) MMA: 9.36 M, AIBN: 6.3 mM, CDB: 13.0 mM (♦) MMA: 9.36 M, AIBN: 3.1 mM, CDB: 6.2 mM (tilted ▲) MMA: 9.36 M, AIBN: 1.6 mM, CDB: 3.1 mM. Lines are numerical fitting results by eq 4 with $C_{tr} = 279$, 134, 109, 87, 62, and 41 and $C_{-tr} = 9972$, 9962, 9912, 9892, 9872, and 9872, respectively.

in the present work. In addition, the leaving group and the propagating radical add to monomer at different rate, causing more uncertainty for the evaluation.

The CSIRO group[37] estimated the chain transfer constant, C_{tr}, from the relative consumption rate of monomer and dithioester (small molecular or polymeric) according to the following equation:

$$C_{tr} = \frac{k_{tr}}{k_p} = \frac{d(\ln[\mathrm{CTA}]_t)}{d(\ln[\mathrm{M}]_t)} \tag{3}$$

Equation 3 is a simplified form of eq 4, derived by the same authors[37]

$$\frac{d[\mathrm{CTA}]}{d[\mathrm{M}]} = C_{tr}\frac{[\mathrm{CTA}]}{[\mathrm{M}] + C_{tr}[\mathrm{CTA}] + C_{-tr}[\mathrm{PCTA}]} \tag{4}$$

in which C_{-tr} describes the chain transfer reactivity of the expelled radical and PCTA represents the resulting dithioester in the chain transfer reaction. When the feed quantity of dithioester and the reverse reaction rate are small (such as in the initial stage of the RAFT polymerization), items of C_{tr}[CTA] and C_{-tr}[PCTA] are negligible, and therefore eq 4 can be regressed to eq 3. Indeed, Fukuda and co-workers[40,43] measured the consumption rates of both monomer and a polymeric dithioester, PSt−SCSCH$_3$, by a time-resolved GPC protocol developed in their group. They found that both the monomer and the dithioester consume linearly with reaction time, *t*. Thus, C_{tr} can be calculated from the integrated form of the kinetic equation:

$$C_{tr} = \ln\left(\frac{[\mathrm{CTA}]_0}{[\mathrm{CTA}]_t}\right)/\ln\left(\frac{[\mathrm{M}]_0}{[\mathrm{M}]_t}\right) \tag{5}$$

Nevertheless, for the system in which C_{tr}[CTA] and C_{-tr}[PCTA] cannot be neglected, the consumption rate may be deviated from linear kinetics. Thus, eq 4 was solved numerically by the CSIRO group to fit MMA polymerization kinetics mediated by CDB at 60 °C, yielding $C_{tr} = 56$ and $C_{-tr} = 2400$.[37]

We performed a series of kinetic experiments using the chromatography approach and subsequently solved eq 4 numerically to fit the measured data. Figure 3 shows that the calculated results, using independent pairs of input C_{tr} and C_{-tr}, agree quite well with the experiments of various feed ratios. The relative rate deviates from a straight line, illustrating the effectiveness of eq 4. From the calculation, C_{-tr} is evaluated as ∼9900, and C_{tr} varies in the range of 40−280. While the latter is comparable to those obtained by Rizzardo[37] and Fukuda,[40,43] the former is notably larger, although still in the same order, than that reported in ref 37.

There are three points that should be emphasized. First, the numerical results can only be viewed as model-dependent apparent values because the derivation of eq 4 is based on assumptions such as the stationary concentration of the initial leaving radical. Without this assumption the differential kinetic equations cannot be solved. Within this very period, however, the concentration of the leaving radical should exhibit a nonsteady state due to the slow consumption of CDB. Second, the numerical fitting results give varying C_{tr} values decreasing monotonically with the decrease of CDB/MMA feed ratio (see the number in Figure 3). This is quite unusual because C_{tr} represents an intrinsic property for a given set of CTA and monomer. The variation of C_{tr} is not likely due to the impurity in CDB because increase of AIBN does not change the kinetics for the same feed ratio of CDB to monomer (Figure 3a). The dependence suggests a more complicated kinetic process of the RAFT polymerization. We hereby tentatively ascribe the phenomenon to the possible interference of the thermal decomposition of CDB.[53] Thermal decomposition not only consumes additional CDB but also produces dithiobenzoic acid that inhibits or retards the polymerization rate of MMA.[53] These effects will alter the measured kinetics as shown in Figure 3. Third, we note that the simulated sensitivity of kinetics to the input parameters, C_{tr} and C_{-tr}, falls into two regions (Figure 4). With lower input values, for instance less than 1/5 of the best-fitted values, the results deviate obviously from the experimental data. In the range from half to 100-fold, or even higher, of those best-fitted values, the calculated results are insensitive to the input parameters, and all these input values lead to good fit to the experimental results. Thus, it would be more proper for the numerically solved C_{tr} and C_{-tr} being regarded as lower limits than as absolute values.

In order for better understanding of the origin of the slow CDB consumption, the chain transfer ability of CDB is compared with two kinds of polymeric RAFT agents (MacroCTAs), PMMA−SCSPh and PS−SCSPh, using polymerizations in the simultaneous presence of MacroCTAs and CDB. The polymerizations of MMA and styrene exhibit again interesting different behaviors (Figure 5). In the former, both CDB and PMMA−SCSPh consume gradually, indicating comparable

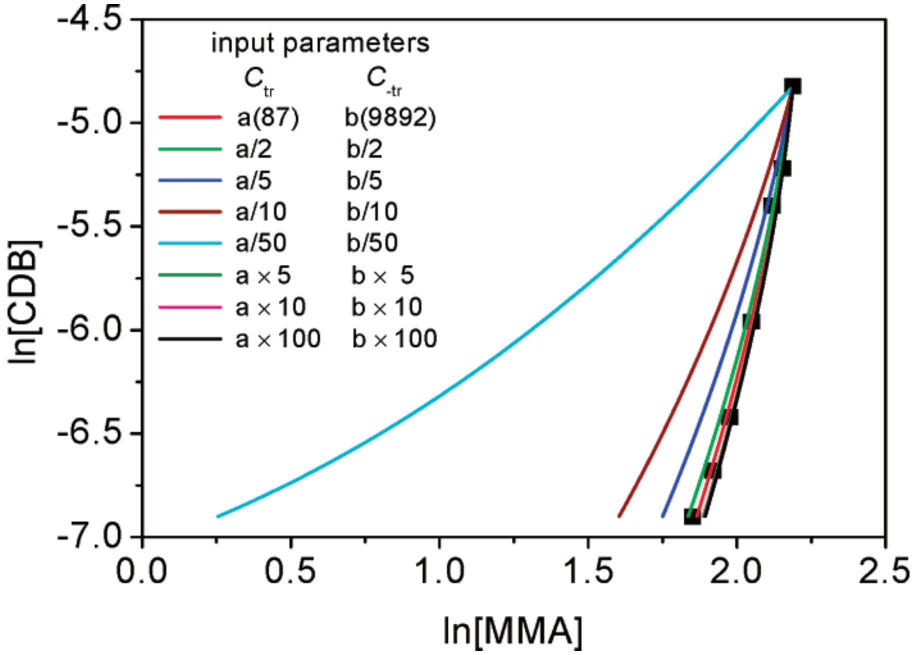


Figure 4. Sensitivity of the numerical results on input parameters and the fitting to the experimental results. Experiment: (■) MMA: 9.36 M, AIBN: 6.3 mM, CDB: 13.0 mM. The lines are numerical results with different input pairs of C_{tr} and C_{-tr} in the range of (a/50, b/50) to (a × 100, b × 100). The red line with $a = 87$ and $b = 9892$ is the best fitting to the experiment.

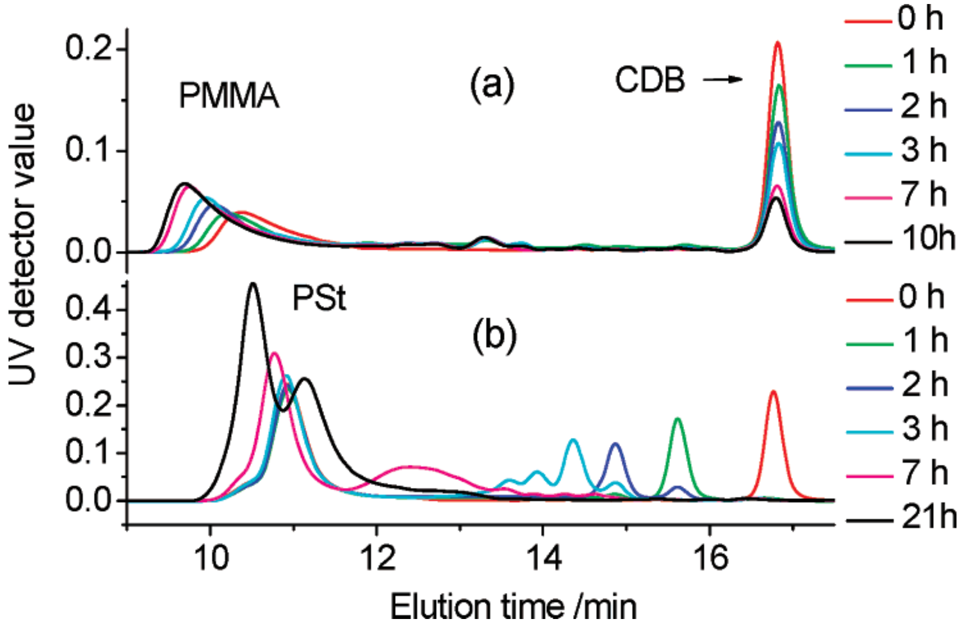


Figure 5. GPC diagrams of polymerizations of MMA and St at 60 °C in benzene initiated with AIBN in the presence of (a) CDB/PS−SCSPh and (b) CDB/PMMA−SCSPh. Feeds: (a) MMA: 2.27 M, AIBN: 0.01 M, CDB: 0.01 M, PMMA−SCSPh: 0.01 M. (b) St: 2.23 M, AIBN: 0.01 M, CDB: 0.01 M, PS−SCSPh: 0.01 M.

chain transfer abilities between them. After 10 h of polymerization, there is still ∼30% remaining CDB. The GPC profile of the final product is unimodal but tails at the low molecular weight. In the latter, CDB consumes up in the very initial period, while no change of PS−SCSPh is observed (The peaks of PS−SCSPh at 0, 1, 2, and 3 h overlap.) Thus, the initialization period as proposed by Klumperman exists, in which only the low molecular weight species grow stepwise, i.e., from 1-mer to 2-mer, and so on, with high selectivity. After 3 h, most of the low molecular weight species become 3-mer. From this point, these two kinds of CTAs grow simultaneously to a final product with a bimodal distribution of the GPC profile.

To summarize, this is the first report on direct observation of the RAFT polymerization process by chromatography, starting from small molecular materials. The results clearly show that styrene and MMA polymerize in different ways in the presence of CDB. The former exhibits the “initialization” kinetics[23,45] in which the chain propagation occurred in a selective way, while the latter exhibits hybrid behavior of conventional and controlled chain transfer,[23] in which CDB is consumed slowly. The remaining CDB not only is responsible for the discrepancy between measured and theoretical molecular weights but also should cause complicated kinetics in which the pre-equilibrium and main equilibrium coexist throughout the polymerization process. The chain transfer constant of CDB, C_{tr}, is estimated to be in a range of 40−280 by numerical fitting. The value of C_{tr}, although agreeing with those obtained by the CSIRO group[37] and Fukuda group,[40,43] shows unexpectedly a dependence on the ratio of CDB to MMA. The dependence is presumably ascribed to the interference of thermal decomposition of dithioester on the kinetic measurement. Finally, chromatography monitoring of the RAFT polymerization in the presence of both CDB and polymeric dithioesters allows direct comparison on their chain transfer abilities, which decrease in the order of CDB ≈ PMMA−SCSPh > PS−SCSPh. The chromatography approach can serve as a useful tool in the kinetic and mechanistic study of the RAFT polymerization.

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Supporting Information Available: GPC and ^{1}H NMR data of 1-mer and mixture of 1- and 2-mers. This material is available free of charge via the Internet at http://pubs.acs.org.

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