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ARTICLE

Single-Electron Transfer Living Radical Polymerization (SET−LRP) of Methyl Methacrylate (MMA) with a Typical RAFT Agent as an Initiator

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ABSTRACT: A typical reversible addition−fragmentation chain transfer (RAFT) agent, 2-cyanoprop-2-yl 1-dithionaphthalate (CPDN), was used as a single electron transfer-living radical polymerization (SET−LRP) initiator for methyl methacrylate (MMA) polymerization at 25 °C. At 1:1 molar ratio of $[CPDN]_0/[Cu(0)]_0$, the apparent rate constants of propagation (k_p^{app}) were 0.037, 0.049, and 0.072 h^{-1} for $[MMA]_0/[CPDN]_0$ of 225/0.2, 225/0.5, and 225/1, respectively. The number-average molecular weight of poly(methyl methacrylate) (PMMA) increased linearly with monomer conversion, and narrow molecular weight distributions ($M_w/M_n < 1.50$) were found at most cases. At high molar ratio of $[CPDN]_0$ to $[Cu(0)]_0$, such as 1:0.1 in this work, the polymerization was also controllable, whereas it a presented markedly depressed polymerization rate and an obvious induction period. ^{1}H NMR spectroscope and matrix assisted laser desorption/ionization time-of-flight mass spectrometry confirmed that PMMA chain was end-capped by CPDN species with high fidelity. The tacticity of PMMA from ^{1}H NMR calculation was about 3.15% isotactic (mm), 29.65% atactic (mr) and 67.20% syndiotactic (rr) triads, consistent with the tacticity distribution for traditional radical polymerizations. Chain extension reactions substantiated further that the obtained PMMA from CPDN mediated SET−LRP was living, and can be reactivated for chain extension reaction. This work demonstrates that a typical RAFT agent can act as a SET−LRP initiator as well as an atom transfer radical polymerization initiator. Furthermore, these results also suggested that the single electron transfer initiation-reversible addition−fragmentation chain transfer control (SET−RAFT) invented by Dhamodharan may not be RAFT at all, but rather SET−LRP initiated by a RAFT reagent, or a combination of SET−LRP and RAFT. Analogously, the exact polymerization process in this work may also proceed in two manners, a fully SET−LRP process and a combination of SET−LRP/RAFT process, which is needed to clarify in the future.

Introduction

The advent of controlled/"living" radical polymerization (CRP) over the past decade has enabled the synthesis of a wide range of macromolecules with well-defined architectures, compositions, and functionalities.[1−3] CRP combines the advantages of traditional free radical polymerization and living ionic polymerization.[4] To date, the most widely used CRPs include nitroxide-mediated radical polymerization (NMP),[5] atom transfer radical polymerization (ATRP),[1,6] and reversible addition−fragmentation chain transfer (RAFT).[7,8] The basic mechanism of CRP involves a dynamic equilibrium between dormant species and propagating radicals via a reversible activation−deactivation process. This equilibrium is governed by several parameters that are specific to the CRP method of interest. On the basis of this primary theory, some novel CRPs have been developed, such as iodine transfer polymerization,[9,10] Te, Sb, and bimediated radical polymerizations,[11,12] quinone transfer radical polymerization,[13] reversible chain transfer catalyzed polymerization,[14] and single electron-transfer living radical polymerization (SET−LRP).[15−31] Of particular interest, SET−LRP has shown distinct advantages over other CRPs since its emergence in 2006,[15] including low temperature (room temperature and below), small amount of catalyst, ultrafast polymerization, and high molecular weight polymers with low polydispersity. Low temperature needed in the initiation and polymerization process was considered as one the most outstanding attributes of SET−LRP. Recently, Dhamodharan intelligently conducted the polymerization of styrene by SET initiation, followed by RAFT control at ambient temperature.[28] Low-temperature characteristic of SET−LRP was ascribed to its specific mechanism, which was concluded to be an outer-sphere single electron transfer process.[15] In this process, Cu(0) donates an electron to P_n/P−X, resulting in a radical-anion $[P_n/P\text{-}X]^{\bullet-}$. The Cu(I) species is rapidly disproportionated into highly reactive atomic Cu(0)− and Cu(II)−X_2/L species. $P_n^{\bullet}/P^{\bullet}$ is then generated from the heterolytic cleavage of the radical-anion intermediate $[P_n/P-X]^{\bullet-}$.

Since the core mechanism of all CRPs is the same as previously described, the CRP process can be transferred from one to the other by some technical treatment, such as from RAFT to ATRP,[32] or conducted with both concurrently.[33,34] In this shift mechanism (RAFT to ATRP) or concurrent mechanism (RAFT and ATRP), the common RAFT agent also serves as the ATRP initiator in the presence of an ATRP catalyst. However, in both of these works,[32−34] the exact polymerization mechanism was not defined. This is a challenge since the polymerization profiles are similar and the same resultant polymer structure is obtained in both ATRP and RAFT. Since the structure of the SET−LRP initiator was similar to the ATRP initiator, the RAFT agent can be assumed to act as a SET−LRP initiator at ambient temperature.

In this work, the feasibility of a typical RAFT agent to act as a SET−LRP initiator was investigated at 25 °C. The low polymerization temperature (25 °C) reduces the possibility of thermal

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initiation or thermal polymerization in the time scale of interest. The results are solid evidence validating the possibility of a shift mechanism (RAFT to ATRP)[32] and a concurrent mechanism (RAFT and ATRP).[33,34] The behavior of the polymerization was explored in detail, including the polymerization kinetics and features of SET−LRP.

Experimental Section

Materials. Methyl methacrylate (MMA) (>99%) monomer was purchased from Shanghai Chemical Reagents Co. (Shanghai, China). The monomer was washed three times with an aqueous solution of sodium hydroxide (5 wt %), followed by washes with deionized water until the solution was neutralized. The resulting solution was then dried over anhydrous magnesium sulfate, distilled twice at reduced pressure, and stored at −18 °C. 2-Cyanoprop-2-yl 1-dithionaphthalate (CPDN) was synthesized according to the method reported elsewhere,[35] achieving a purity greater than 96% (Waters 515 HPLC; ^{1}H NMR ($CDCl_3$): 1.95 (s, 6H), 7.42 (m, 2H), 7.51 (m, 2H), 7.85 (m, 2H), and 8.10 (m, 1H)). *N*,*N*,*N*′,*N*″,*N*″-Pentamethyldiethylenetriamine (PMDETA) (98%, Jiangsu Liyang Jiangdian Chemical Factory, China) was dried with 4 Å molecular sieves and distilled under vacuum. Copper (75 μm powder, 99%, Aldrich), dimethyl sulfoxide (DMSO) (99.9%, Shanghai Chemical Reagents Co.) and *N,N*-dimethylformamide (DMF) (99.9%, Shanghai Chemical Reagents Co.) were used as received. All other chemicals were obtained from Shanghai Chemical Reagents Co. and used as received unless mentioned.

Characterization. The number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) of the resulting polymers were determined using a Waters 1515 gel permeation chromatograph (GPC) equipped with a refractive-index detector (Waters 2414), using HR 1 (pore size: 100 Å, 100−5000 Da), HR 2 (pore size: 500 Å, 500−20 000 Da) and HR 4 (pore size 10 000 Å, 50−100 000 Da) columns (7.8 × 300 mm, 5 μm beads size) with molecular weights ranging from $10^2 \sim 5 \times 10^5$ g/mol. Tetrahydrofuran (THF) was used as the eluent at a flow rate of 1.0 mL/min and 30 °C. GPC samples were injected using a Waters 717 plus autosampler and calibrated with poly(methyl methacrylate) standards purchased from Waters. Matrix assisted laser desorption/ionization time-of-flight (MALDI−TOF) mass spectrometry measurement was performed using a Bruker Autoflex III (MALDI−TOF) mass spectrometer equipped with a 337 nm nitrogen laser. Both matrix, 4-hydroxy-α-cyanocinnamic acid, and sample were dissolved in 1:1 (v/v) acetonitrile: water with 1% trifuoroacetic acid. This mixture solution (0.5 μL) was placed on a metal sample plate. The sample was air-dried at ambient temperature. The ^{1}H NMR spectrum of the precipitated polymer was recorded on an INOVA 400 MHz nuclear magnetic resonance instrument using $CDCl_3$ as the solvent and tetramethylsilane (TMS) as an internal standard.

Typical Procedures for SET−LRP with CPDN as the Initiator. The monomer (MMA, 2.0 mL, 18.8 mmol), solvent (DMSO, 1.0 mL), initiator (CPDN, 0.0228 g, 0.0835 mmol), catalyst (Cu(0), 5.30 mg, 0.0835 mmol), and ligand (PMDETA, 21.0 μL, 0.0835 mmol) were added to a 5.0 mL ampule in the following order: Cu(0), monomer, ligand, solvent, and initiator. The solution was deoxygenated by bubbling with argon for 20 min. The ampule was then flame-sealed and placed in a stirred oil bath equipped with a thermostat at 25 ± 0.1 °C. After 10 h, the ampule was cooled by immersion in ice water. Afterward, the ampule was opened, and the contents were dissolved in 5.0 mL of THF and passed through a small basic Al_2O_3 chromatographic column to remove any unreacted Cu(0) catalyst and Cu(II) compounds. The resulting solution was precipitated into 150 mL of cool methanol (0 °C) with stirring. The polymer was isolated by filtration and dried under vacuum until a constant weight was recorded at room temperature. The monomer conversion was 40.9% by gravimetrical calculation. Samples were dissolved in $CDCl_3$ for test by ^{1}H NMR spectroscopy. The M_n and M_w/M_n values were determined by GPC with PMMA standards ($M_{n,GPC}$ = 15 020 g/mol, M_w/M_n = 1.18).

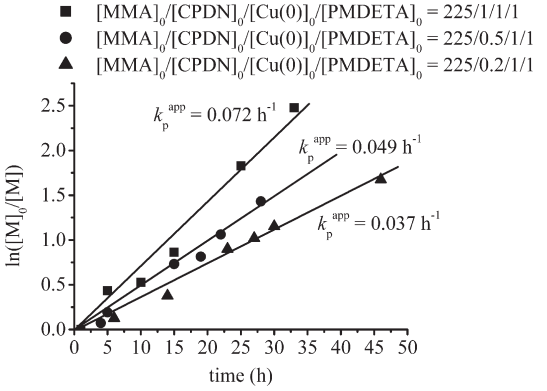

Figure 1. Kinetic investigation (ln([M]$_0$/[M]) versus time) of single-electron transfer living radical polymerization (SET−LRP) of methyl methacrylate (MMA) with dimethyl sulfoxide (DMSO) as solvent at various concentrations of CPDN. [MMA]$_0$ = 6.28 mol/L, MMA/DMSO = 2/1 (v/v), temperature = 25 °C. [M]$_0$ and [M] refer to the initial concentration of MMA and instant concentration of MMA, respectively. CPDN and k_p^{app} refer to 2-cyanoprop-2-yl 1-dithionaphthalate and apparent rate constant of propagation, respectively.

Typical Procedures for Chain Extension of PMMA using PMMA as Macroinitiator. The PMMA sample ($M_{n,GPC}$ = 1.77×10^4 g/mol, M_w/M_n = 1.26) obtained by SET−LRP was used as the macroinitiator for the chain extension reaction. PMMA (0.234 g, 0.0132 mmol) was dissolved in 0.7 mL of fresh MMA and 0.35 mL of DMSO. This solution was added by catalyst (Cu(0), 0.845 mg, 0.0132 mmol) and ligand (PMDETA, 3.32 μL, 0.0132 mmol). The solution was deoxygenated by bubbling with argon for 20 min. The ampule was then flame-sealed and placed in a stirred oil bath equipped with a thermostat at 25 ± 0.1 °C. After 17 h, the ampule was cooled by immersion in ice water. The rest of the procedure was identical to that described above with CPDN replaced by PMMA. The monomer conversion was 32.3% by gravimetrical calculation. The M_n and M_w/M_n values were determined by GPC with PMMA standards ($M_{n,GPC}$ = 3.91×10^4 g/mol, M_w/M_n = 1.37).

Results and Discussion

To investigate the feasibility of a typical RAFT agent to act as an initiator in SET−LRP, a Cu(0)/PMDETA-catalyzed polymerization of MMA was carried out at 25 °C in DMSO using CPDN as initiator. The reaction conditions were as follows: [MMA]$_0$/[CPDN]$_0$/[Cu(0)]$_0$/[PMDETA]$_0$ = 225:1(0.5, 0.2):1:1, [MMA]$_0$ = 6.28 mol/L. Cu(0) powder with a particle size of less than 75 μm was used as the primary activating species. The maintenance of the manners of SET−LRP, including polymerization kinetics and living characteristics, were mainly stressed. Figure 1 summarizes the kinetic data for the Cu(0)/PMDETA-catalyzed SET−LRP of MMA initiated with CPDN in DMSO. As shown in Figure 1, the polymerization proceeded smoothly. The time dependence of ln([M]$_0$/[M]) was linear for various concentrations of CPDN, which indicates a first-order propagation rate with respect to both propagating radicals and monomer concentrations and that the concentration of active species was constant during the polymerization. It should also be noted that the polymerization rate increased with CPDN concentration. The apparent rate constant of propagation (k_p^{app}) was 0.037, 0.049, and 0.072 h^{-1} for [MMA]$_0$/[CPDN]$_0$ molar ratios of 225/0.2, 225/0.5, and 225/1, respectively. In a typical RAFT polymerization, it has been reported that the polymerization rate of MMA is sometimes retarded by an increase in RAFT agent concentration,[36,37] although the causes for this retardation are still under

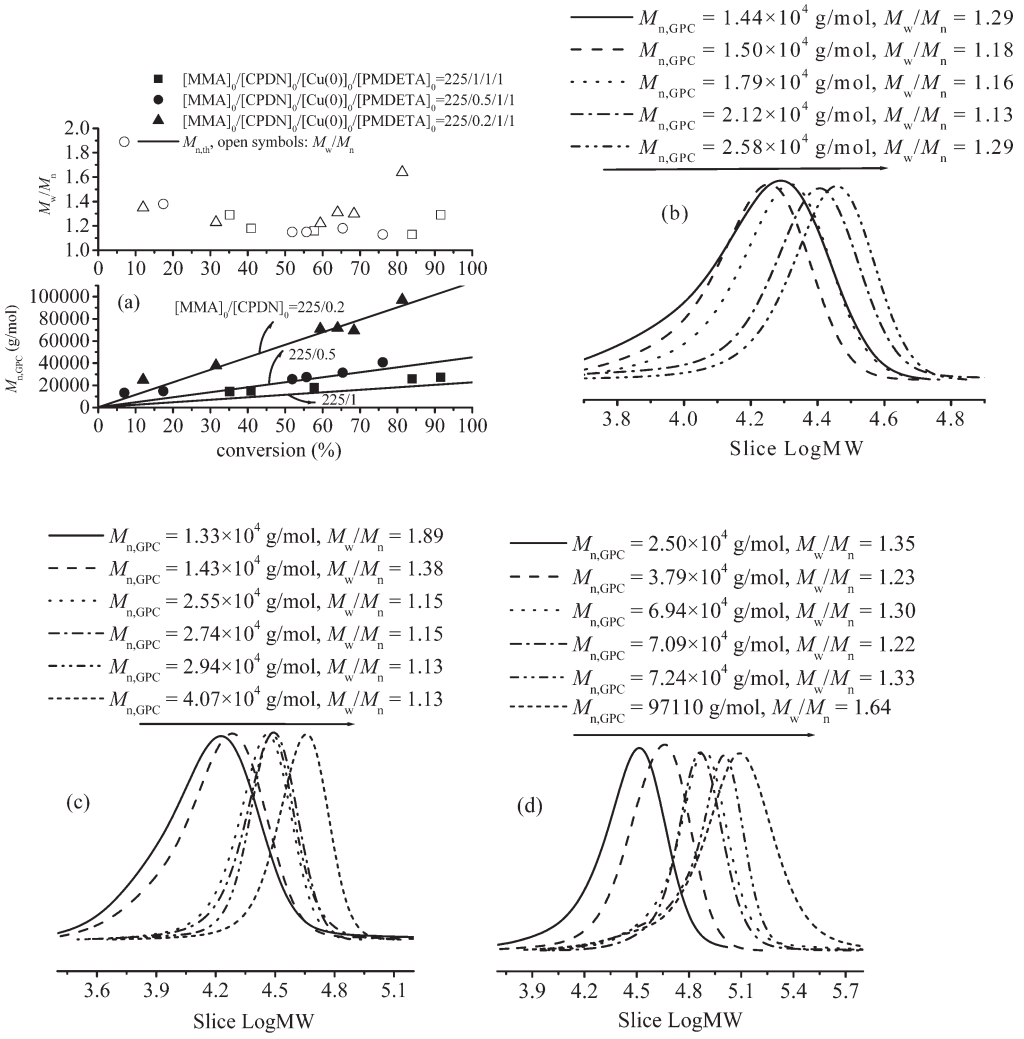

Figure 2. (a) Number average molecular weight (M_n) and molecular weight distribution (M_w/M_n) of poly(methyl methacrylate) (PMMA) from single-electron transfer living radical polymerization (SET−LRP) versus the conversion of MMA at various concentrations of CPDN. Reaction conditions are the same as in Figure 1. (b) $[MMA]_0/[CPDN]_0/[Cu(0)]_0/[PMDETA]_0 = 225/1/1/1$. (c) $[MMA]_0/[CPDN]_0/[Cu(0)]_0/[PMDETA]_0 = 225/0.5/1/1$. (d) $[MMA]_0/[CPDN]_0/[Cu(0)]_0/[PMDETA]_0 = 225/0.2/1/1$. MMA, CPDN, and PMDETA refer to the methyl methacrylate, 2-cyanoprop-2-yl 1-dithionaphthalate and *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine. Theoretical molecular weight ($M_{n,th}$) = ($[MMA]_0/[CPDN]_0$) × M_{MMA} × conversion + M_{CPDN}, where M_{MMA} and M_{CPDN} represent the molecular weights of MMA and CPDN, respectively.

investigation.[36−42] In the present polymerization, in which Cu(0) and PMDETA were added, the polymerization rate increased with CPDN concentration. In additional, control experiments at 25 °C with MMA and CPDN ($[MMA]_0/[CPDN]_0$ = 500:1) in the absence of Cu(0)/PMDETA, no polymer yielded after 162 h. This result validated that the combination of MMA and CPDN could not yield the initiator species at 25 °C, and the initiator species originated from the synergistic reactions of CPDN and Cu(0)/PMDETA. The above kinetic exploration demonstrated that the polymerization may proceed mainly via the SET−LRP mechanism. However, at this stage, we do not know the exact polymerization process. A fully SET−LRP or a combination of SET−LRP and RAFT may be ascribed to the polymerization process.

Figure 2 describes the number-average molecular weight ($M_{n,GPC}$) and molecular weight distribution (M_w/M_n) as functions of the monomer conversion at various CPDN concentrations. We found that the molecular weight of PMMA increased linearly with monomer conversion and the molecular weight distribution remained narrow in most cases (Figure 2a). Moreover, the $M_{n,GPC}$ of PMMA was close to the theoretical molecular weight ($M_{n,th}$, $M_{n,th}$ = ($[MMA]_0/[CPDN]_0$) × M_{MMA} × conversion + M_{CPDN}, where M_{MMA} and M_{CPDN} represent the molecular weight of MMA and CPDN, respectively) (Figure 2a). The GPC traces of PMMA showed monodistribution profiles at different molar ratios of $[MMA]_0/[CPDN]_0$ (Figure 2b−d). All of this evidence indicates

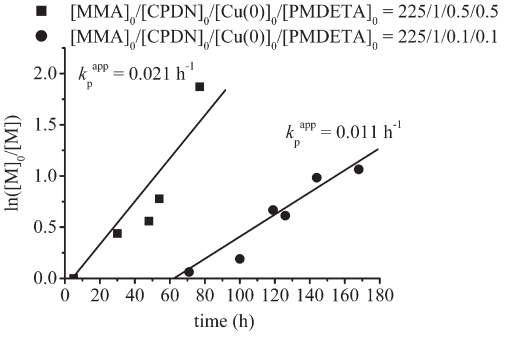

Figure 3. Kinetic investigation (ln($[M]_0/[M]$) versus time) of single-electron transfer living radical polymerization (SET−LRP) of methyl methacrylate (MMA) with dimethyl sulfoxide (DMSO) as solvent at various concentrations of Cu(0)/PMDETA. $[MMA]_0$ = 6.28 mol/L, MMA/DMSO = 2/1 (v/v), temperature = 25 °C. $[M]_0$ and [M] refer to the initial concentration of MMA and instant concentration of MMA, respectively. CPDN and PMDETA refer to 2-cyanoprop-2-yl 1-dithionaphthalate and *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine, respectively. k_p^{app} refers to the apparent rate constant of propagation.

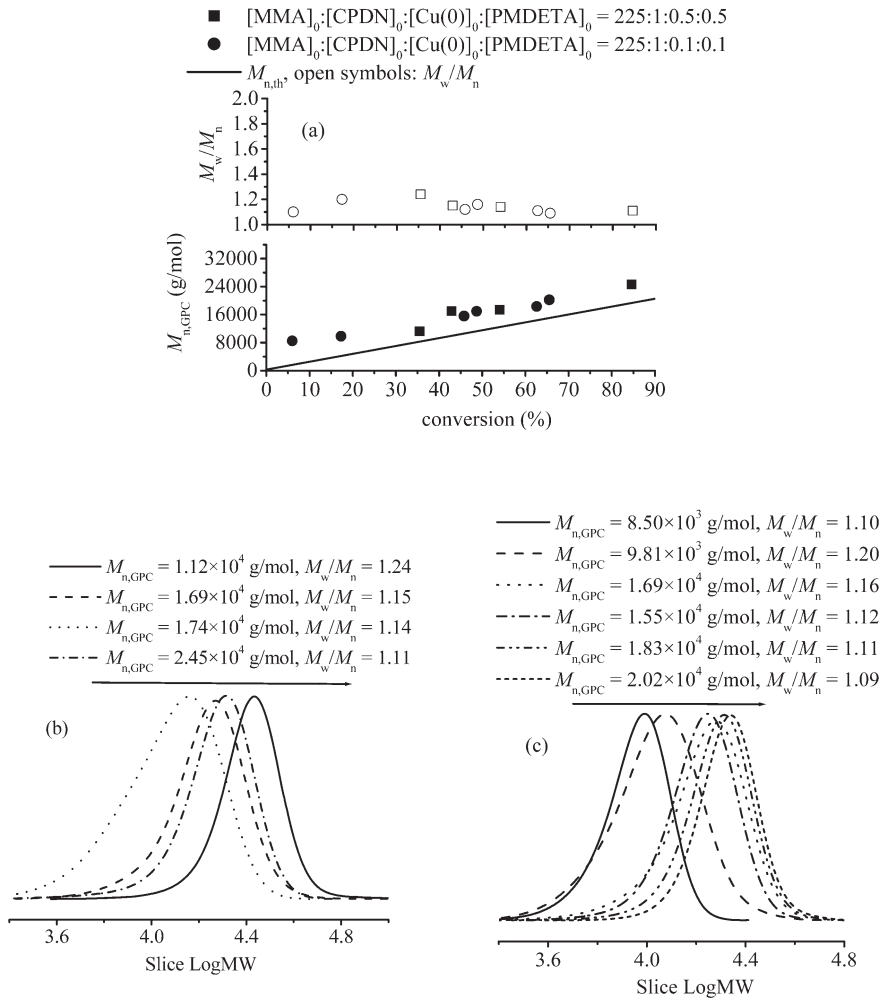

Figure 4. (a) Number average molecular weight (M_n) and molecular weight distribution (M_w/M_n) of poly(methyl methacrylate) (PMMA) from single-electron transfer living radical polymerization (SET−LRP) versus the conversion of MMA at various concentrations of Cu(0)/PMDETA. Reaction conditions are the same as in Figure 3. (b) GPC traces of $[MMA]_0/[CPDN]_0/[Cu(0)]_0/[PMDETA]_0 = 225/1/0.5/0.5$; (c) GPC traces of $[MMA]_0/[CPDN]_0/[Cu(0)]_0/[PMDETA]_0 = 225/1/0.1/0.1$. MMA, CPDN and PMDETA refer to the methyl methacrylate, 2-cyanoprop-2-yl 1-dithionaphthalate and *N*,N,*N*′,*N*″,*N*″-pentamethyl diethylenetriamine, respectively. Theoretical molecular weight ($M_{n,th}$) = ($[MMA]_0/[CPDN]_0$) × M_{MMA} × conversion + M_{CPDN}, where M_{MMA} and M_{CPDN} represent the molecular weights of MMA and CPDN, respectively.

that the polymerization was well-controlled. These results also suggested that the SET−RAFT developed by Dhamodharan et al.[28] may not be RAFT at all, but rather SET−LRP initiated by a RAFT reagent, or at a minimum a mixture of the two.

It has been reported that Cu(0) can play an important role on the SET−LRP profiles, including the polymerization rate and living behavior.[15,17,30,31] SET−LRP could be carried out at low concentrations of Cu(0) without loss of living features.[15,17] A low concentration of Cu(0) is preferred in SET−LRP since a small quantity of Cu species residue exists in the resultant polymer. The kinetic plots in Figure 3 show the effect of decreasing the concentration of Cu(0) at an equal ratio of $[Cu(0)]_0/[PMDETA]_0$, on the rate of polymerization. As the molar ratio of CPDN to Cu(0) was decreased from 1:1 (Figure 1) to 1:0.5 and 1:0.1 (Figure 3), obvious induction periods were observed. The length of the induction period increased with the decrease of Cu(0) concentration, with about 5 and 61 h in 1:0.5 and 1:0.1 of CPDN/Cu(0) molar ratio system, respectively. Simultaneously, k_p^{app} decreased from 0.072 h^{-1} (1:1 of $[CPDN]_0/[Cu(0)]_0$, Figure 1) to 0.021 h^{-1} (1:0.5 of $[CPDN]_0/[Cu(0)]_0$, Figure 3) and 0.011 h^{-1} (1:0.1 of $[CPDN]_0/[Cu(0)]_0$, Figure 3). The decrease of Cu(0) concentration lowered the activation rate of initiator to form polymer chains, resulting in the reduced polymerization rate.[15,17]

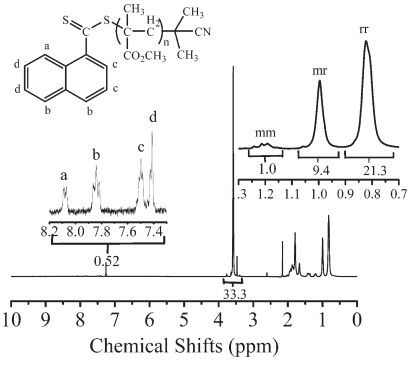

Figure 5. ^{1}H NMR spectrum of poly(methyl methacrylate) (PMMA, $M_{n,GPC} = 1.50 \times 10^4$ g/mol, $M_w/M_n = 1.18$) obtained from the CPDN and Cu(0)/PMDETA mediated SET−LRP. $CDCl_3$ was used as the solvent and tetramethylsilane (TMS) as the internal standard. CPDN, PMDETA and $CDCl_3$ refer to the respective 2-cyanoprop-2-yl 1-dithionaphthalate, *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine and deuterochloroform. $M_{n,GPC}$ and M_w/M_n refer to the number-average molecular weight and molecular weight distribution by GPC, respectively.

Living behavior of polymerization with decreased concentration of Cu(0) was explored as indicated in Figure 4. It can be found that at 1:0.5 and 1:0.1 molar ratios of CPDN to Cu(0), the

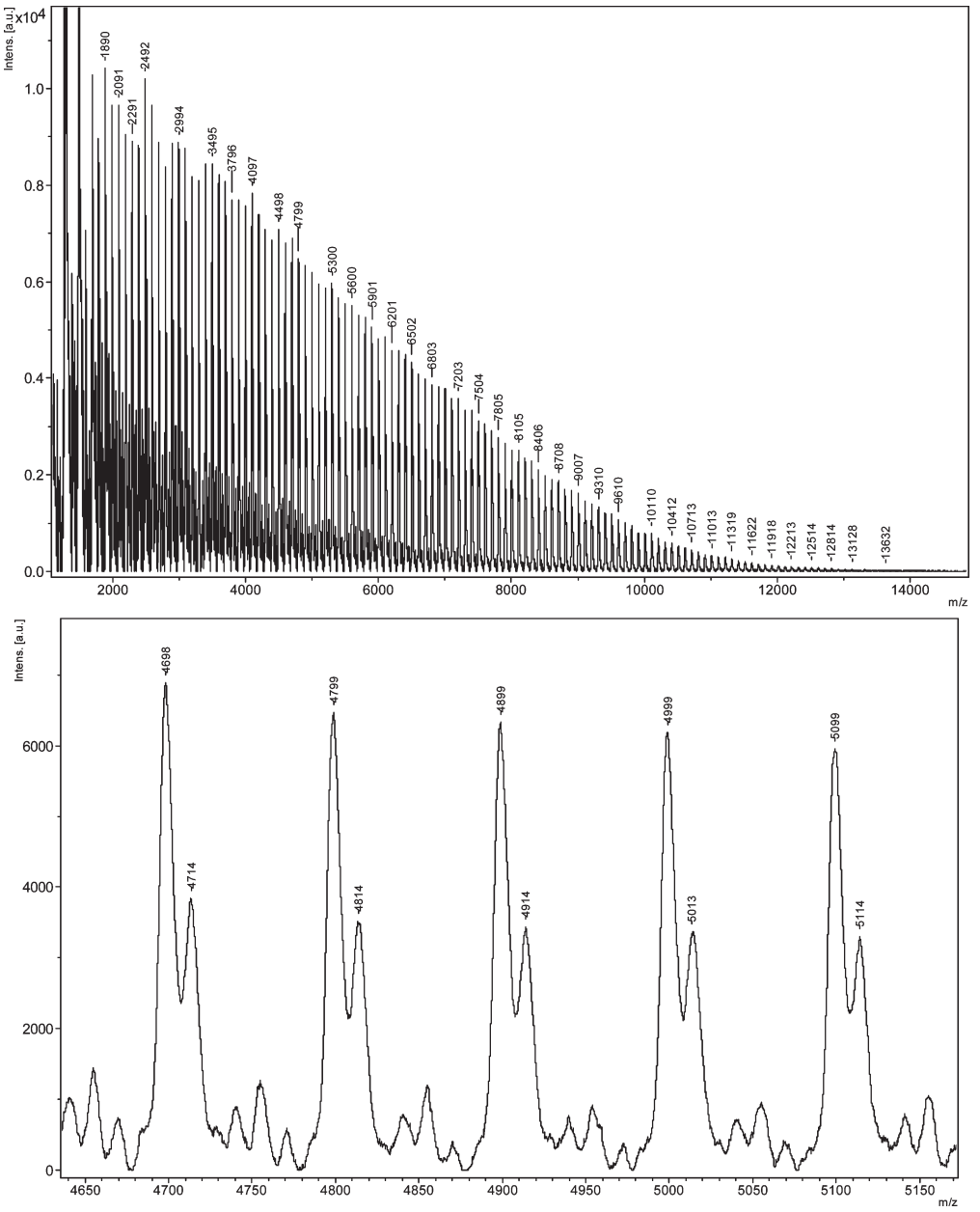

Figure 6. Matrix assisted laser desorption/ionization time-of-flight (MALDI−TOF) mass spectrometry of poly(methyl methacrylate) (PMMA, $M_{n,GPC} = 9.81 \times 10^3$ g/mol, $M_w/M_n = 1.20$) obtained from the CPDN and Cu(0)/PMDETA mediated SET−LRP. CPDN and SET−LRP refer to 2-cyanoprop-2-yl 1-dithionaphthalate and single-electron transfer living radical polymerization, respectively. $M_{n,GPC}$ and M_w/M_n refer to the number-average molecular weight and molecular weight distribution by GPC, respectively.

molecular weight of PMMA increased linearly with monomer conversion and the molecular weight distribution remained narrow. This result indicated that the polymerization was controllable at low concentration of Cu(0). The value of $M_{n,GPC}$ of PMMA was slightly higher with respect to the theoretical molecular weight ($M_{n,th}$, $M_{n,th} = ([MMA]_0/[CPDN]_0) \times M_{MMA} \times$ conversion + M_{CPDN}, where M_{MMA} and M_{CPDN} represent the molecular weight of MMA and CPDN, respectively) (Figure 4a). The deviation $M_{n,GPC}$ from $M_{n,th}$ indicated some loss of initiator efficiency. The initiator efficiency was calculated to be 88%, 86% and 78% for the MMA/CPDN/Cu(0)/PMDETA molar ratio of 225/1/1/1 (Figure 2a), 225/1/0.5/0.5 (Figure 4a) and 225/1/0.1/0.1(Figure 4a), respectively. These results indicated that initiator efficiency was moderately decreased with the decrease of Cu(0) concentration. It was complied with literature that in SET−LRP, low concentration of Cu(0) may induce low activation rate of the initiator as well as the dormant polymer chain, which may reflect in some loss of initiator efficiency as well as living features.[17] The GPC traces of PMMA showed monodistribution profiles at 1:0.5 (Figure 4b) and 1:0.1 (Figure 4c) molar ratios of CPDN to Cu(0). This evidence demonstrates that the polymerization can be also controlled with a low concentration of Cu(0).

The chain ends of the PMMA prepared in the presence of CPDN and Cu(0)/PMDETA were analyzed by ^{1}H NMR spectroscopy (Figure 5). The PMMA sample ($M_{n,GPC} = 1.50 \times 10^4$ g/mol, $M_w/M_n = 1.18$) was obtained at 40.9% conversion from the polymerization with 225:1:1:1 of $[MMA]_0/[CPDN]_0/[Cu(0)]_0/[PMDETA]_0$ (Figure 1). The observed signals at $\delta = 7.4-8.1$ ppm (7H, integral value = $I_{8.1} = 0.52$) corresponded to the aromatic protons of the naphthalene units in CPDN, revealing that the dithioester moieties of CPDN were attached to the polymer chain ends (ω chain end). The signals at $\delta = 3.40-3.81$ ppm in the ^{1}H NMR spectrum were assigned to the protons of methoxy in PMMA repeat units (3H, integral value = $I_{3.81} = 33.3$).

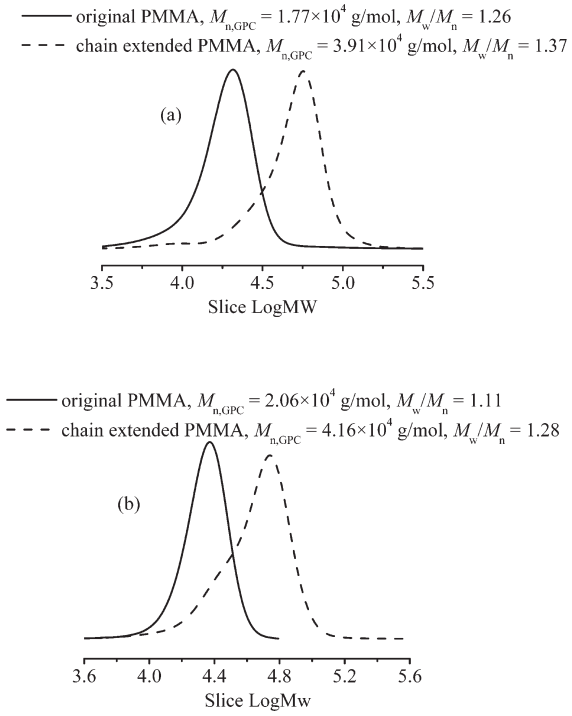

Figure 7. GPC curves before and after chain extension in DMSO with poly(methyl methacrylate) (PMMA) as the SET−LRP macroinitiators at 25 °C. (a) $[MMA]_0/[PMMA]_0/[Cu(0)]_0/[PMDETA]_0$ = 500/1/1/1, $[MMA]_0$ = 4.7 mol/L, 0.70 mL of MMA, MMA/DMSO = 1/1 (v/v), 17 h, 32.3% conversion; (b) $[MMA]_0/[PMMA]_0/[Cu(0)]_0/[PMDETA]_0$ = 500/1/1/1, $[MMA]_0$ = 4.7 mol/L, 1.0 mL of MMA, MMA/DMSO = 1/1 (v/v), 4 h, 27.6% conversion. SET−LRP: single-electron transfer living radical polymerization. MMA, PMDETA and DMSO refer to methyl methacrylate, *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine and dimethyl sulfoxide, respectively. $M_{n,GPC}$ and M_w/M_n refer to the number-average molecular weight and molecular weight distribution by GPC, respectively.

Assuming that each polymer chain was captured by a naphthyl moiety from CPDN, the molecular weight ($M_{n,\,NMR}$) of PMMA can be calculated from the integrals in ^{1}H NMR, according to eq 1

$$M_{n,\,NMR}\ (g/mol) = (I_{3.81}/3) \times 100.1/(I_{8.1}/7) + 271.5 \quad (1)$$

where 100.1 and 271.5 are the molecular weights of MMA and CPDN, respectively. The molecular weights of PMMA sample calculated from the ^{1}H NMR spectrum ($M_{n,NMR}$) was 1.52 × 10^4 g/mol, which was very close to the GPC value (1.50 × 10^4 g/mol), indicating that the PMMA was end-capped by CPDN species with high fidelity. The chemical shifts at about 0.82, 1.02, and 1.18 ppm can be ascribed to syndiotactic (rr, integral value = $I_{0.82}$ = 21.3), atactic (mr, integral value = $I_{1.02}$ = 9.4), and isotactic (mm, integral value = $I_{1.18}$ = 1.0) methyl groups, respectively. The tacticity of PMMA obtained with CPDN as SET−LRP initiator was calculated as 3.15% mm, 29.65% mr, and 67.20% rr triads, which is in good agreement with the tacticity distribution for traditional radical polymerizations.[43] This result indicates that the SET−LRP with CPDN as the initiator proceeded via a radical-mediated mechanism.

To further investigate the chain end functionality of PMMA, the dithiocarbonyl moieties on the polymers were characterized by MALDI−TOF mass spectrometry. Figure 6 shows the expanded MS spectrum of a PMMA sample obtained at 17.3% conversion from the polymerization with 1:0.1 molar ratio of CPDN to Cu (Figure 3). It can be found from Figure 6 that there was one main series of peaks whose interval was regular, ca. 100.1, the molar mass of MMA, and the experimental isotopic mass distribution values in main peak series of MALDI−TOF

Table 1. Effects of DMF as Solvent and Concentration of DMSO on CPDN Initiated SET−LRP[a]

entry	time (h)	conversion (%)	$M_{n,GPC}$ (g/mol)	M_w/M_n	$M_{n,th}$
1	19	47.1	1.56 × 10^4	1.18	1.08 × 10^4
2	48	87.9	2.36 × 10^4	1.15	2.00 × 10^4
3	19	49.5	2.41 × 10^4	1.11	2.25 × 10^4
4	19	55.7	2.75 × 10^4	1.15	2.53 × 10^4
5	19	67.8	2.97 × 10^4	1.14	3.08 × 10^4

[a] Entry 1, 2: $[MMA]_0/[CPDN]_0/[Cu(0)]_0/[PMDETA]_0$ = 225/1/1/1, MMA = 2.0 mL, DMF = 1.0 mL. Entry 3: $[MMA]_0/[CPDN]_0/[Cu(0)]_0/[PMDETA]_0$ = 225/0.5/1/1, MMA = 2.0 mL, DMSO = 0.5 mL, $[DMSO]_0$ = 2.81 mol/L. Entry 4: $[MMA]_0/[CPDN]_0/[Cu(0)]_0/[PMDETA]_0$ = 225/0.5/1/1, MMA = 2.0 mL, DMSO = 1.0 mL, $[DMSO]_0$ = 4.69 mol/L. Entry 5: $[MMA]_0/[CPDN]_0/[Cu(0)]_0/[PMDETA]_0$ = 225/0.5/1/1, MMA = 2.0 mL, DMSO = 3.0 mL, $[DMSO]_0$ = 8.45 mol/L. SET−LRP: single-electron transfer living radical polymerization. MMA, PMDETA, and CPDN refer to methyl methacrylate, *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine and 2-cyanoprop-2-yl 1-dithionaphthalate, respectively. DMF: *N*,*N*-dimethylformamide. DMSO: dimethyl sulfoxide. $M_{n,GPC}$ and M_w/M_n refer to the number-average molecular weight and molecular weight distribution by GPC, respectively. The polymerization temperature was 25 °C for all cases.

spectrum (with the subtraction of *m*/*z* value of soduim cation (Na^+)) are in good agreement with the theoretical values in eq 2:

$$M_{theo} = 68.05 + n \times 100.1 + 203.0 \quad (2)$$

M_{theo} refers to the theoretical mass value by eq 2. 68.05 and 203.0 refer to the molecular weights of 2-cyanoisopropyl and dithionaphthyl species of CPDN, respectively. Here, 100.1 and *n* are the average mass of MMA repeat unit and number of the MMA unit in the polymer chains. The lower intensity of peak series with about 16 lower mass can be assigned to the potassium cation (K^+) cationized chains. Other minor peak series in Figure 6 can be ascribed to the byproduct arising from the side reactions during RAFT polymerization,[44,45] fragmentation of polymer chain and dithioester moiety by MALDI-generated ions.[46−49] These results clearly showed that the CPDN moieties were attached at polymer chain ends. The molecular weight of PMMA by MALDI−TOF mass spectra, was 4.77 × 10^3 g/mol (M_w/M_n = 1.16), which was much smaller than the GPC value ($M_{n,GPC}$ = 9.81 × 10^3 g/mol, PDI = 1.20). The deviation was due to the mass discrimination during the MALDI−TOF measurement process.[50−53]

The living nature of the polymer was further confirmed by chain extension reaction upon the addition of fresh MMA monomer. Two PMMA samples ($M_{n,GPC}$ = 1.77 × 10^4 g/mol, M_w/M_n = 1.26 and $M_{n,GPC}$ = 2.06 × 10^4 g/mol, M_w/M_n = 1.11) obtained by SET−LRP were used as the macroinitiators. The chain extensions were successful at ambient temperature using Cu(0)/PMDETA as a catalyst, and much higher molecular weights of PMMA, $M_{n,GPC}$ = 3.91 × 10^4 g/mol with M_w/M_n = 1.37 and $M_{n,GPC}$ = 4.16 × 10^4 g/mol with M_w/M_n = 1.28, were obtained in Figure 7, parts a and b, respectively. It is clear from this result that most of the end groups are active for participation in chain extension reaction, and the dithioester end groups can be reactivated as the SET−LRP initiator.

The polymerization was also performed with *N*,*N*-dimethylformamide (DMF) as the solvent. The results are summarized in the first two entries of Table 1. It was ultimately observed that the SET−LRP with CPDN initiator was also successful in DMF. The conversion after 19 h was 47.1%, which is moderately slow in comparison to that with DMSO as the solvent (15 h, 57.8% conversion). DMF and DMSO are suitable solvents for SET−LRP; however, different solvents may produce different polymerization profiles.[15,29] Meanwhile, in SET−LRP, the k_p^{app} strongly depends on the concentration of DMSO used in the polymerization.[15] An increase in the solvent concentration led to faster polymerization, which is contrary to ATRP and is the

important evidence for differentiating the SET−LRP mechanism from that of ATRP. In this work, the effect of the concentration of DMSO on the polymerization was also investigated. The results are presented in entries 3−5 of Table 1, and it is observed that the polymerization rate increased with the DMSO concentration. After 19 h of polymerization time, the conversions were 49.5%, 55.7% and 67.8% for 2.81 mol/L, 4.69 mol/L, and 8.45 mol/L of DMSO, respectively. The polymerizations at different concentrations of DMSO showed well-controlled features. These results suggest that SET−LRP with CPDN initiator has similar characteristics as common SET−LRP.

Conclusion

In this work, we used a typical RAFT agent as an SET−LRP initiator at 25 °C. The polymerization proceeded successfully, and the polymerization profiles complied with that of the SET−LRP process. These interesting results demonstrate that a typical RAFT agent can serve as a SET−LRP initiator and an ATRP initiator. This work suggested that the SET−RAFT by Dhamodharan may not be RAFT at all, but rather SET−LRP initiated by a RAFT reagent, or at a minimum a mixture of the two. Analogously, in this work, the mechanism of controlled process is also amphibolous at this stage, a fully SET−LRP process or a combination of SET−LRP and RAFT process? More evidence is needed to clarify this. In conclusion, this work is an interesting invention in the fields of CRPs, and should be much beneficial for understanding of the inherent relations of various CRP methods.

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