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Zero-valent Iron/RAFT Agent-Mediated Polymerization of Methyl Methacrylate at Ambient Temperature

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ABSTRACT: In this work, zero-valent iron powder (Fe(0)) was used to catalyze the polymerization of methyl methacrylate (MMA) in the presence of a reversible addition−fragmentation chain transfer (RAFT) agent, 2-cyanoprop-2-yl 1-dithionaphthalate (CPDN) without any ligand at ambient temperature. The polymerization behavior complied with the features of typical “living”/controlled radical polymerizations. The number-average molecular weights of poly(methyl methacrylate) increased linearly with monomer conversion, while maintaining narrow molecular weight distributions ($M_w/M_n < 1.50$). Even at low concentration of Fe(0), such as at $[\mathrm{MMA}]_0$:$[\mathrm{CPDN}]_0$:$[\mathrm{Fe(0)}]_0 = 200{:}1{:}0.2$, the polymerization was also controllable; however, it presented a depressed polymerization rate and a prolonged induction period (about 12 h). The polymerization rate also decreased with increasing of CPDN concentration. From experimental results, it was deduced that the initiating species were derived from the cooperative reaction of Fe(0) and CPDN, in which CPDN acted as a pseudohalide alkyl initiator. The control process was supposed to proceed via a synactic mechanism. One mechanism was the synergic mediation by Fe(0) and CPDN, in which Fe(III) formed in situ acted as an deactivator, however, this deactivation was supposed to be ineffective. The other was the RAFT mechanism with CPDN as the RAFT agent, which may dominate the whole control.

Introduction

During the past decades, “living”/controlled radical polymerization (LRP) has attracted more and more attentions for its powerful capability of designing and fabricating well-defined macromolecules.[1−10] Among those well-developed LRP methods, metal-catalyzed living radical polymerizations pioneered by Sawamoto, Matyjaszewski and Percec et al. have been widely employed for precise polymer synthesis.[4,5,7] Another milestone in LRP evolution is the ingenious invention and development of the reversible addition−fragmentation chain transfer (RAFT) by Rizzardo et al.[9,10] for its large scope of available monomers and good controllability. From the viewpoints of practical and industrial applications, the acceptable LRP should be eco-friendly,[5,6] economical and effective. Actually, the searching for a versatile LRP technique has never stopped since the first advent of LRP. Recently, the optimization of the current LRP methods, such as the concurrent mechanism of two LRP techniques has been explored,[11−17] in which a typical RAFT agent was used as two roles, a pseudoalkyl halide initiator and a chain transfer agent.

Iron is a preferential metal catalyst that has been widely used in LRP area for its particularly attractive merits, such as biocompatibility, easy separation and low cost.[6,18−22] Percec[23] and Noh[24] demonstrated that the alkyl halide could act as the initiator for the polymerization of vinyl chloride or methyl methacrylate (MMA) by the activation of zero-valent iron (Fe(0)). The initiating species was produced from alkyl halide by the catalysis of Fe(0). However, no control over the polymerizations was found. These uncontrolled polymerizations may be due to the improper equilibrium constant between Fe(II) and Fe(III). The initiation and control process are claimed in Scheme 1.[23] Inspired by the concurrent LRP mechanisms and the Fe(0)−halide alkyl activated polymerization, in this work, we investigated the polymerization of MMA with Fe(0) and RAFT agent as the mediators. The RAFT agent was 2-cyanoprop-2-yl 1-dithionaphthalate (CPDN), which had been confirmed as an efficient RAFT agent for the RAFT polymerization of alkyl (meth)acrylate,[25,26] as well as an effective initiator/mediator for ATRP.[11]

Scheme 1. Polymerization Mechanism of Halide Alkyl/Fe(0) System[23]

$$\mathrm{Fe(0)} + 2\mathrm{R{-}X} \longrightarrow 2\mathrm{R}\bullet + \mathrm{FeX_2}$$

$$\mathrm{R{-}X} + \mathrm{FeX_2} \longrightarrow \mathrm{R}\bullet + \mathrm{FeX_3}$$

$$\mathrm{Pn}\bullet + \mathrm{FeX_3} \longrightarrow \mathrm{Pn{-}X} + \mathrm{FeX_2}$$

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. *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. 2-Cyanoprop-2-yl 1-dithionaphthalate (CPDN) was synthesized according to the method reported elsewhere,[23] achieving a purity greater than 96% (Waters 515 HPLC; ^{1}H NMR ($\mathrm{CDCl_3}$): 1.95 (s, 6H), 7.42 (m, 2H), 7.51 (m, 2H), 7.85 (m, 2H), and 8.10 (m, 1H)). Cumyl dithionaphthalenoate (CDN) (96%, Waters 515 HPLC; ^{1}H NMR

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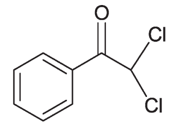
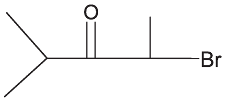
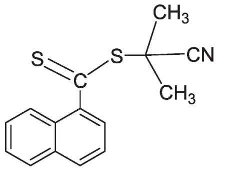
($CDCl_3$): 1.76 (s, 6H), 7.10−8.10 (m, 12H)) was prepared using a procedure similar to the one for CDB described elsewhere.[25] Zero-valent iron powder (Fe(0), < 200 mesh, 99+%, metals basis, Alfa Aesar), ethyl 2-bromoisobutyrate (EBiB) (98%), 2,2-dichloroacetophenone (DCAP) (97%, Alfa Aesar Co.), dimethyl 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.



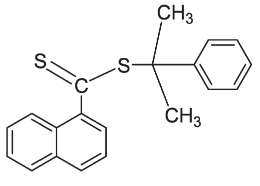
DCAP



EBiB



CPDN



CDN

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 to 5×10^5 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. 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. 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. Samples were prepared by dissolving the polymer in tetrahydrofuran (THF) at a concentration of 5 mg/mL. Matrices, including dithranol, 3-β-indoleacrylic acid and 2,5-dihydroxybenzoic acid (sDHB) were dissloved in THF at a concentration of 10 mg/mL. Silver trifluoroacetate (AgTFA) was dissloved in THF at a concentration of 1 mg/mL. Solutions of sample, matrix, and AgTFA were mixed in a volume ratio 1:1:1. This mixture solution (0.5 μL) was placed on a metal sample plate. The sample was air-dried at ambient temperature before insertion into the ion source chamber.

Typical Procedures for the Polymerization of MMA in the Presence of Fe(0) and CPDN. The monomer (MMA, 1.00 mL, 9.42 mmol), solvent (DMSO, 1.00 mL), initiator (CPDN, 0.0127 g, 0.0471 mmol), and catalyst (Fe(0), 1.32 mg, 0.0235 mmol) were added to a 5.0 mL ampule in the following order: Fe(0), monomer, solvent, and initiator. Then, the ampule was immediately frozen in liquid nitrogen, and the valve connecting to pump was opened and pumped to 0.01 MPa. The ampule was then warmed to room temperature. Afterward, the valve was closed and the ampule was frozen again. Three freeze−pump−thaw cycles were used to deoxygenate the solution. The ampule was then flame-sealed and placed in a stirred oil bath equipped with a thermostat at 25 ± 0.1 °C. After 8 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 iron 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 10.8% 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 ($M_{n,GPC} = 9.37 \times 10^3$ g/mol, $M_w/M_n = 1.24$).

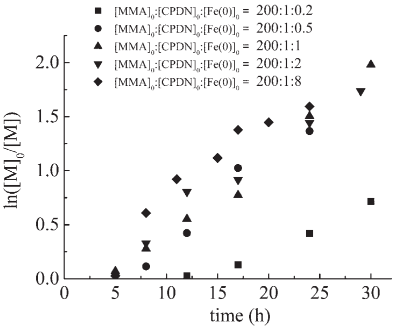


Figure 1. Kinetic investigation ($\ln([M]_0/[M])$ versus time) of CPDN/Fe(0) mediated polymerization of methyl methacrylate (MMA) with dimethyl sulfoxide (DMSO) as solvent at various concentrations of Fe(0). $[MMA]_0 = 4.71$ mol/L, MMA/DMSO = 1/1 (v/v), temperature = 25 °C. $[M]_0$ and $[M]$ refer to the initial concentration and instant concentration of MMA, respectively. CPDN = 2-cyanoprop-2-yl 1-dithionaphthalate.

Typical Procedures for Chain Extension of PMMA using PMMA as Precursor. The PMMA sample ($M_{n,GPC} = 1.76 \times 10^4$ g/mol, $M_w/M_n = 1.15$) obtained by CPDN/Fe(0) was used as the macro-mediator for the chain extension reaction. PMMA (0.365 g, 0.0206 mmol) was dissolved in 1.10 mL of fresh MMA and 1.00 mL of DMSO. This solution was added by catalyst (Fe(0), 1.15×10^{-3} g, 0.0206 mmol). The solution was deoxygenated by three standard freeze−pump−thaw cycles. The ampule was then flame-sealed and placed in a stirred oil bath equipped with a thermostat at 25 ± 0.1 °C. After 25 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 21.6% by gravimetrical calculation. The M_n and M_w/M_n values were determined by GPC with PMMA standards ($M_{n,GPC} = 2.56 \times 10^4$ g/mol, $M_w/M_n = 1.12$).

Results and Discussion

The polymerization of MMA with DMSO as solvent was executed at 25 °C in the presence of Fe(0) and CPDN. Fe(0) powder with a particle size of about 200 mesh was used as the primary activating species. The $[MMA]_0$ and molar ratio of $[MMA]_0/[CPDN]_0$ were kept at 4.71 mol/L and 200/1, respectively. Various concentrations of the initial Fe(0) on the polymerization were probed. The behaviors of the polymerization, including polymerization rates and living characteristics, were mainly focused on. Figure 1 summarizes the polymerization data for Fe(0)-catalyzed MMA together with CPDN in DMSO. As shown in Figure 1, the polymerization proceeded smoothly. When the ratio of $[MMA]_0/[CPDN]_0/[Fe(0)]_0$ was 200/1/1, the monomer conversion reached to about 87% within 30 h. Changing the Fe(0) concentration, with the ratios of $[MMA]_0/[CPDN]_0/[Fe(0)]_0$ = 200/1/0.5, 200/1/2, 200/1/4 and 200/1/8, the polymerization rates altered slightly. An induction period with about 5 h uniformly occurred in all cases. When lower concentration of Fe(0) ($[MMA]_0/[CPDN]_0/[Fe(0)]_0$ = 200/1/0.2) was used, the induction period was prolonged to 12 h with the remarkably reduced polymerization rate. This result indicated that Fe(0) assuredly worked as a catalyst in the polymerization system. Figure 2

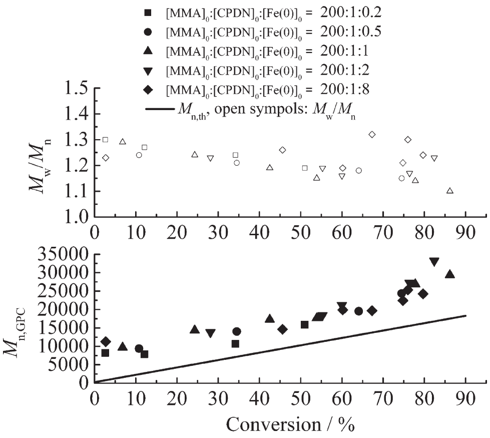


Figure 2. Number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) of poly(methyl methacrylate) (PMMA) from CPDN/Fe(0) mediated polymerization versus the conversion of MMA at various concentrations of Fe(0). Reaction conditions are the same as in Figure 1. Theoretical molecular 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.

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 Fe(0) concentrations. As shown in Figure 2, the molecular weights of PMMA increased linearly with monomer conversion and the molecular weight distributions remained narrow in most cases ($M_w/M_n < 1.50$). The $M_{n,GPC}$ of PMMA was a little higher than the theoretical molecular weights ($M_{n,th}$, = ([MMA]$_0$/[CPDN]$_0$) × M_{MMA} × conversion + M_{CPDN}, where M_{MMA} and M_{CPDN} represent the molecular weights of MMA and CPDN, respectively), indicating that CPDN was not consumed completely as deactivator in the polymerization process. The GPC traces of PMMA showed monomodal profiles with different ratios of [MMA]$_0$/[CPDN]$_0$/[Fe(0)]$_0$ (Figure S1 in Supporting Information). All of this evidence demonstrated that the polymerization was controlled in the presence of Fe(0) and CPDN.

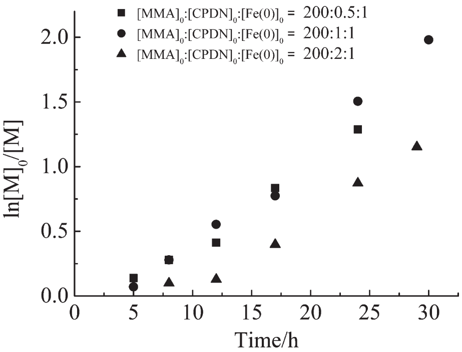


Figure 3. Kinetic investigation (ln([M]$_0$/[M]) versus time) of CPDN/Fe(0) mediated polymerization of methyl methacrylate (MMA) with dimethyl sulfoxide (DMSO) as solvent at various concentrations of CPDN. [MMA]$_0$ = 4.71 mol/L, MMA/DMSO = 1/1 (v/v), temperature = 25 °C. [M]$_0$ and [M] refer to the initial concentration of MMA and instant concentration of MMA, respectively. CPDN = 2-cyanoprop-2-yl 1-dithionaphthalate.

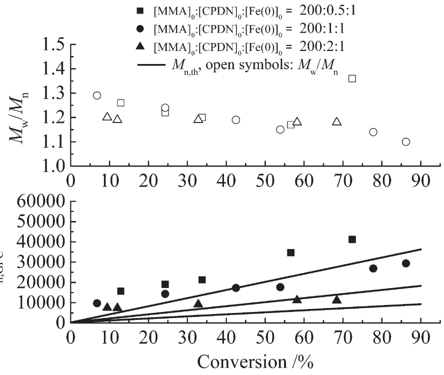


Figure 4. Number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) of poly(methyl methacrylate) (PMMA) from CPDN/Fe(0) mediated polymerization versus the conversion of MMA at various concentrations of CPDN. Reaction conditions are the same as in Figure 3. Theoretical molecular 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 initiator, respectively.

The effects of the concentration of CPDN on polymerization were also investigated for a deep understanding of the process. The molar ratios of [MMA]$_0$/[CPDN]$_0$/[Fe(0)]$_0$ were 200/0.5/1, 200/1/1 and 200/2/1, respectively, with the constant concentration of Fe(0). The results of [MMA]$_0$/[CPDN]$_0$/[Fe(0)]$_0$ = 200/1/1 were presented again here for a comparison purpose. It was found from Figure 3, that there was no obvious difference of the polymerization rates between the [MMA]$_0$/[CPDN]$_0$/[Fe(0)]$_0$ = 200/1/1 and [MMA]$_0$/[CPDN]$_0$/[Fe(0)]$_0$ = 200/0.5/1. While, when [MMA]$_0$/[CPDN]$_0$/[Fe(0)]$_0$ was 200/2/1, the polymerization rated was slightly lowered, which was similar to that of RAFT polymerization.[10] In a typical RAFT polymerization, it has been reported that the polymerization rate of MMA is sometimes retarded when the RAFT agent concentration was elevated to a higher degree.[10] $M_{n,GPC}$ and M_w/M_n as functions of the monomer conversion at various concentrations of CPDN were also explored, as shown in Figure 4. The $M_{n,GPC}$ of the polymers obtained increased linearly with the monomer conversion up to high conversions (> 90.0%) with relatively low M_w/M_ns (< 1.35) in almost all cases. Similarly, the $M_{n,GPC}$ also deviated positively from the $M_{n,th}$. The GPC elution traces showed typical monomodal distributions in all the cases (Figure S1 in the Supporting Information). All these evidence showed that the polymerization proceeded in a "living"/controlled process in the concurrence of CPDN and Fe(0). When the polymerization was conducted by the addition of a radical trapper, 2,2,6,6-tetramethylpiperidine-1-oxyl, no polymerization was observed after 72 h. This result validated that the polymerization proceeded via a radical process. In addition, control experiments at 25 °C with MMA and CPDN ([MMA]$_0$/[CPDN]$_0$ = 200:1) in the absence of Fe(0) was performed. No polymer yielded after 144 h, suggesting that the combination of MMA and CPDN could not yield the initiator species at 25 °C, and the initiator species were produced from the cooperative reactions of CPDN and Fe(0).

The chain end of the PMMA sample prepared in the presence of CPDN and Fe(0) was analyzed by ^{1}H NMR spectroscopy (Figure 5). The PMMA sample ($M_{n,GPC} = 9.37 \times 10^3$ g/mol, $M_w/M_n = 1.24$) was obtained at 10.8% conversion from the polymerization with 200:1:0.5 of [MMA]$_0$/[CPDN]$_0$/[Fe(0)]$_0$ (Figure 1). The signals at $\delta = 7.4-8.1$ ppm (7H, integral value = $I_{8.1} = 0.46$) were corresponded to the aromatic protons of the naphthalene units in CPDN,[25] which revealed that the dithiocarbonate 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 = $I_{3.60} = 18.34$). 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:

$$M_{n,\mathrm{NMR}}\ (\mathrm{g/mol}) = (I_{3.60}/3) \times 100.1/(I_{8.1}/7) + 271.5 \qquad (1)$$

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 9.58 × 10^3 g/mol, which was close to the GPC value (9.37 × 10^3 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 (^{1}H NMR) were ascribed to syndiotactic (rr), atactic (mr), and isotactic (mm) methyl groups, respectively. The tacticity of PMMA obtained in the presence of CPDN and Fe(0) was calculated with 5.3% mm, 27.7% mr and 67.0% rr triads, which agreed with the tacticity distribution for common radical polymerization of MMA, confirming further that the polymerization was via a radical-mediated mechanism.

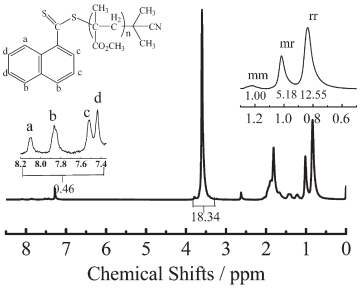


Figure 5. ^{1}H NMR spectrum of poly(methyl methacrylate) (PMMA, $M_{n,GPC}$ = 9.37 × 10^3 g/mol, M_w/M_n = 1.24) obtained from the Fe(0)/CPDN mediated polymerization. CDCl$_3$ was used as the solvent and tetramethylsilane (TMS) as the internal standard. CPDN and CDCl$_3$ refer to the respective 2-cyanoprop-2-yl 1-dithionaphthalate and deuteronchloroform. $M_{n,GPC}$ and M_w/M_n refer to the number-average molecular weight and molecular weight distribution by GPC, respectively.

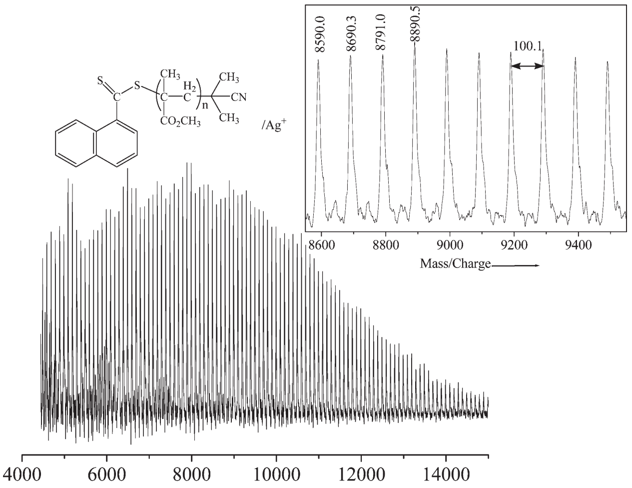


Figure 6. Matrix-assisted laser desorption/ionization time-of-flight (MALDI–TOF) mass spectrometry of poly(methyl methacrylate) (PMMA, $M_{n,GPC}$ = 1.16 × 10^4 g/mol, M_w/M_n = 1.18) obtained from the CPDN and Fe(0) mediated polymerization. CPDN refers to 2-cyanoprop-2-yl 1-dithionaphthalate. $M_{n,GPC}$ and M_w/M_n refer to the number-average molecular weight and molecular weight distribution by GPC, respectively.

To further investigate the chain end functionality of PMMA, the CPDN moieties on the polymers were characterized by MALDI–TOF mass spectrometry. 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 spectrum (with the subtraction of m/z value of silver cation (Ag$^+$, 107.87 g/mol) are in good agreement with the theoretical values in eq 2:

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

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 molecular weight measured by MALDI–TOF was about 8.92 × 10^3 g/mol (M_w/M_n = 1.06).

The living nature of the polymer was further confirmed by chain extension reaction upon the addition of fresh MMA monomer. Two PMMA samples ($M_{n,GPC}$ = 1.76 × 10^4 g/mol, M_w/M_n = 1.15 and $M_{n,GPC}$ = 1.40 × 10^4 g/mol, M_w/M_n = 1.21) obtained were used as the macroinitiators/mediators. The chain extensions were successful at ambient temperature using Fe(0) as a catalyst, and the PMMAs with much higher molecular weights of $M_{n,GPC}$ = 2.56 × 10^4 g/mol (M_w/M_n = 1.12) and $M_{n,GPC}$ = 2.77 × 10^4 g/mol (M_w/M_n = 1.10), were obtained as shown in Figure 7, parts a and b, respectively. It was clear from this result that most of the end groups of the polymers were active for participation in chain extension reaction, and the dithiocarbonate end groups could be reactivated as the macroinitiator/mediator under the catalysis of Fe(0).

For a comprehensive understanding of the polymerization mediated by CPDN and Fe(0), many other control experiments were conducted. These results are summarized in Table 1. It can be found that no polymer was obtained in the absence of Fe(0) (item 1), or CPDN (item 2), or both (item 3). It proved that it was the cooperative reaction of Fe(0) and CPDN which induced the initiating species. Items 4–7 were the results from the polymerizations with CPDN replaced by two common alkyl halides,

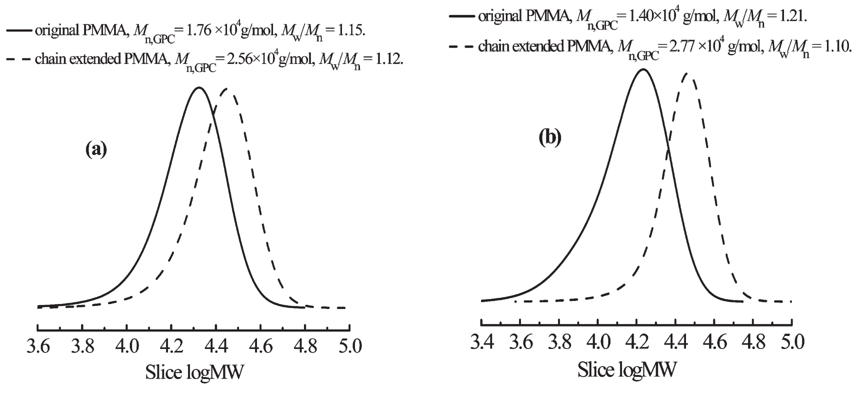


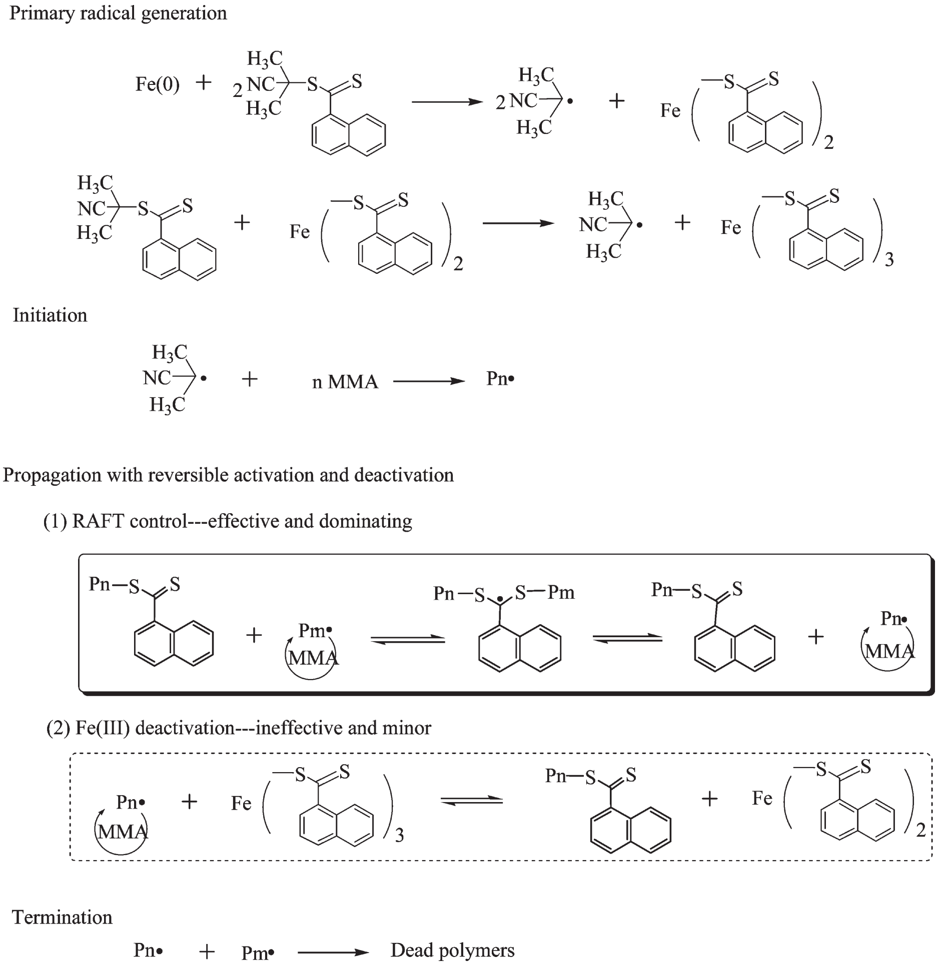
Figure 7. GPC curves before and after chain extension in DMSO with poly(methyl methacrylate) (PMMA) as the macroinitiator/mediators at 25 °C: (a) [MMA]$_0$/[PMMA]$_0$/[Fe(0)] = 500/1/1, [MMA]$_0$ = 4.94 mol/L, MMA = 1.10 mL, DMSO = 1.00 mL, 25 h, 21.6% conversion; (b) [MMA]$_0$/[PMMA]$_0$/[Fe(0)]$_0$ = 500/1/1, [MMA]$_0$ = 4.70 mol/L, MMA = 0.76 mL, DMSO = 1.00 mL, 32 h, 26.1% conversion. MMA = methyl methacrylate, 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.

Table 1. Polymerizations of MMA under Various Conditions[a]

item	contents	time (h)	convn (%)	$M_{n,GPC}$ (g/mol)	M_w/M_n	$M_{n,th}$ (g/mol)
1	MMA/CPDN	0				
2	MMA/Fe(0)/DMSO	51	trace			
3	MMA/DMSO	48	0			
4	MMA/DCAP/Fe(0)/DMSO	4	6.5	dual-modal		
5	MMA/DCAP/Fe(0)/DMSO	23	23.3	high		
6	MMA/EBiB/Fe(0)/DMSO	4	14.8	2.20×10^5	2.25	3.15×10^3
7	MMA/EBiB/Fe(0)/DMSO	6	26.0	1.61×10^5	2.27	5.40×10^3
8	MMA/CPDN/Fe(0)/DMF	17	41.5	1.56×10^4	1.22	8.58×10^3
9	MMA/CPDN/Fe(0)/DMF	24	62.0	2.36×10^4	1.19	1.26×10^3
10	MMA/CPDN/Fe(0)/toluene	72	0			
11	MMA/CDN/Fe(0)/DMSO	17	42.1	1.91×10^4	1.24	8.75×10^3
12	MMA/CDN/Fe(0)/DMSO	24	65.9	2.38×10^4	1.26	1.35×10^4

[a] Temperature = 25 °C. 1: MMA = 1.0 mL, DMSO = 1.0 mL. 2 and 3: MMA = 1.0 mL, DMSO = 1.0 mL; $[MMA]_0/[Fe(0)]_0$ = 200/1. 4 and 5: $[MMA]_0/[DCAP]_0/[Fe(0)]_0$ = 200/1/1, MMA = 1.0 mL, DMSO = 1.0 mL. 6 and 7: $[MMA]_0/[EBiB]_0/[Fe(0)]_0$ = 200/1/1, MMA = 1.0 mL, DMSO = 1.0 mL. 8 and 9: $[MMA]_0/[EBiB]_0/[Fe(0)]_0$ = 200/1/1, MMA = 1.0 mL, DMF = 1.0 mL. 10: $[MMA]_0/[CPDN]_0/[Fe(0)]_0$ = 200/1/1, MMA = 1.0 mL, toluene = 1.0 mL. 11 and 12: $[MMA]_0/[CDN]_0/[Fe(0)]_0$ = 200/1/1, MMA = 1.0 mL, DMSO = 1.0 mL. MMA, methyl methacrylate; DCAP, 2,2-dichloroacetophenone; EBiB, ethyl 2-bromoisobutyrate; CPDN, 2-cyanoprop-2-yl 1-dithionaphthalate; CDN, cumyl dithionaphthalenoate; 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.

Scheme 2. Proposed Synactic Mechanism of the Polymerization of MMA Mediated by Fe(0)/CPDN



respectively, 2,2-dichloroacetophenone (DCAP) and ethyl 2-bromoisobutyrate (EBiB). It can be seen that the polymerizations can also produce considerable PMMA in a short time; however, the polymerizations were out of control with uncontrollable molecular weights and broad molecular weight distributions (items 4−7). The results confirmed that the polymerization was mainly regulated by CPDN. During the generation of initiating species, the Fe(0) was converted to its higher-valent status, Fe(II) and Fe(III) species.[23,24] In ATRP system, the Fe(III) compounds were usually used as the deactivators. Thus, in this work, the deactivation of propagating radicals by Fe(III) cannot be ruled out, despite of its low efficiency.[23,24] When DMSO was replaced by DMF as solvent, the polymerizations were successful with good control over molecular weights, similar to that in DMSO (items 8 and 9). Whereas, when toluene was used as the solvent, the polymerization yielded no polymer in 72 h (item 10).

The other typical RAFT agent, cumyl dithionaphthalenoate (CDN), was used instead of CPDN. Similar results were observed as that CPDN-mediated polymerization (items 11 and 12). On the basis of these discussions, we proposed a tentative mechanism as depicted in Scheme 2. However, the exact mechanism is not so clear at this stage, which is needed an in-depth study in the future. Whereas, this work provided an effective and convenient LRP method of MMA at 25 °C, which should be highly potential in the design and fabrication of well-defined polymers.

Conclusions

In this work, we used a typical RAFT agent as an initiator/mediator in the polymerization of MMA by the catalysis of Fe(0) without any ligand at 25 °C. The polymerization proceeded successfully, and the polymerization profiles complied with that of the "living"/controlled radical polymerization. A hypothetical mechanism was proposed based on the results, and the clarification of the mechanism is ongoing in our lab. Despite of the indistinct mechanism at this stage, this work provided an effective and facile LRP method for the polymerization of MMA at 25 °C, and would be an interesting invention in the area of LRP.

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Supporting Information Available: Figure showing GPC traces of the polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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