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Iron(II) Chloride Complex for Living Radical Polymerization of Methyl Methacrylate[1]

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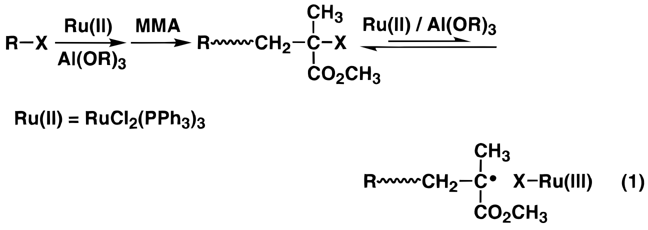
ABSTRACT: Iron(II) bis(triphenylphosphine)dichloride [$FeCl_2(PPh_3)_2$] induced living radical polymerization of methyl methacrylate (MMA) in conjunction with organic halides as initiators [R−X: CCl_4, $CHCl_2COPh$, $(CH_3)_2CBrCO_2C_2H_5$, and $CH_3CBr(CO_2C_2H_5)_2$] in the absence or presence of $Al(O^iPr)_3$ in toluene at 80 °C. The added aluminum compounds were not needed for the Fe(II)-mediated living polymerization unlike the $RuCl_2(PPh_3)_3$-based counterpart. With $CH_3CBr(CO_2C_2H_5)_2$ as initiator, the number-average molecular weights of polymers increased in direct proportion to monomer conversion, and the MWDs were narrow throughout the reactions ($\bar{M}_w/\bar{M}_n = 1.1-1.3$). The polymers possessed one initiator moiety at the α-end per one polymer chain. The tacticity was similar to that prepared by AIBN. These results indicate that the Fe(II) complex is effective in the homolytic and reversible cleavage of the carbon−halogen terminal originating from the halide initiators into a transient radical growing species to induce living MMA polymerization.

Introduction

Transition-metal complexes have been employed widely in organic synthesis as well as polymerizations for precise control of the reactions. Noting their versatility, we have recently found that a ruthenium complex, $RuCl_2(PPh_3)_3$ (Ph = C_6H_5), induces living radical polymerization of methyl methacrylate (MMA) to produce polymers with controlled molecular weights and narrow molecular weight distributions (MWDs), when coupled with organohalogen (R−X) and aluminum compounds; a typical combination is $RuCl_2(PPh_3)_3/CCl_4/Al(O^iPr)_3$.[2−6] The living polymerization apparently proceeds via a radical pathway, where the ruthenium complex activates or cleaves, reversibly and homolytically, the carbon−halogen bond of R−X or at the polymer terminal derived therefrom and thus generates a carbon radical species that subsequently adds to the monomer (eq 1). During this process, the ruthenium center undergoes the reversible one-electron redox reaction from Ru(II) to Ru(III) or vice versa. It is therefore suggested that similar living radical polymerizations would be possible with the use of such transition metal complexes that induce analogous reversible and homolytic cleavage of C−X bonds via a single redox reaction.



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Although this type of metal-catalyzed radical addition reactions has widely been used for the carbon−carbon bond-forming processes for the synthesis of small organic molecules,[7] few have been employed for living or controlled radical polymerizations. For example, however, in addition to our ruthenium system,[2−6] copper(I) halides (CuX; X = Cl, Br)[8−12] and nickel(II) bromides[13,14] with appropriate ligands have proven effective in similar living radical polymerizations. Such transition-metal catalyzed living radical polymerizations, as well as those with nitroxyl and related stable radical species, have thus become attractive, because they have opened a way to precisely control radical polymerization, which has hitherto been considered fundamentally difficult to regulate.[15]

This study was directed toward living radical polymerization of MMA based on an iron complex, in which the central metal belongs to the group 8 element as with ruthenium (eq 2). While the possible oxidation states of iron varies from −II to +IV, metal iron [Fe(0)][16] and some Fe(II) complexes[17] have been known to promote redox-type radical addition reactions via the activation

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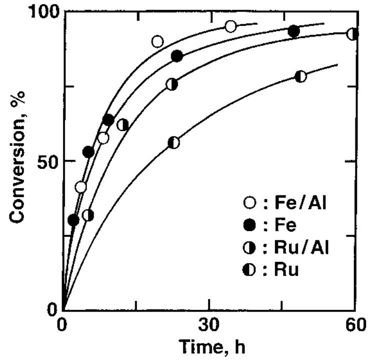
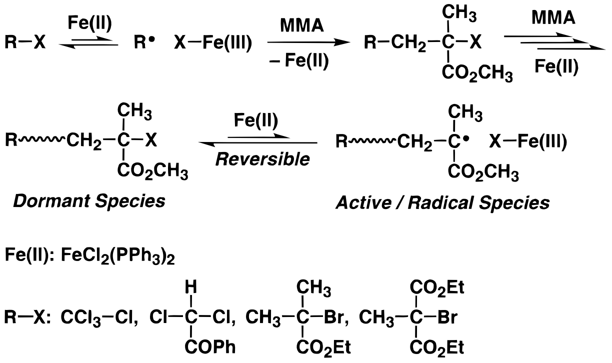


Figure 1. Polymerization of MMA with $CCl_4/MCl_2(PPh_3)_n$ in the absence or presence of $Al(O^iPr)_3$ in toluene at 80 °C: $[M]_0$ = 2.0 M; $[CCl_4]_0$ = 20 mM; $[MCl_2(PPh_3)_n]_0$ = 10 mM; $[Al(O^iPr)_3]_0$ = 40 mM. Key: (○) $FeCl_2(PPh_3)_2/Al(O^iPr)_3$; (●) $FeCl_2(PPh_3)_2$; (◑) $RuCl_2(PPh_3)_3/Al(O^iPr)_3$; (◐) $RuCl_2(PPh_3)_3$.

of carbon−halogen bonds. We employed iron(II) bis(triphenylphosphine) dichloride, $[FeCl_2(PPh_3)_2]$, which carries the same ligand as does $RuCl_2(PPh_3)_3$, in conjunction with organic halides such as CCl_4, $CHCl_2COPh$, $(CH_3)_2CBrCO_2Et$, and $CH_3CBr(CO_2Et)_2$ as initiators. Herein we report that the Fe(II) complex induces living radical polymerization of MMA without use of the aluminum compounds that are necessary for the Ru(II)-based counterparts previously described.[2,3]



(2)

Results and Discussion

(a) Polymerization of MMA with $FeCl_2(PPh_3)_2$. Coupled with CCl_4 as initiator, $FeCl_2(PPh_3)_2$ was first employed for the polymerization of MMA in toluene at 80 °C. As shown in Figure 1, the $CCl_4/FeCl_2(PPh_3)_2$ system induced smooth polymerization proceeding much faster than that with $CCl_4/RuCl_2(PPh_3)_3$. The additional use of $Al(O^iPr)_3$ accelerated the polymerization as with the Ru(II)-based system. Thus, the Fe(II) complex/CCl_4 pair induced smooth polymerization of MMA both in the absence and presence of the aluminum compound.

The polymers obtained with $CCl_4/FeCl_2(PPh_3)_2$ had unimodal and narrow MWDs ($\bar{M}_w/\bar{M}_n \sim 1.4$) where molecular weights increased with conversion (Figure 2). On the other hand, the presence of $Al(O^iPr)_3$ broadened polymer MWDs ($\bar{M}_w/\bar{M}_n \sim 3$), and the molecular weights decreased with conversion, in sharp contrast to the polymerizations with the Ru(II) complex, where the MWDs become narrower by the addition of the aluminum alkoxide. These results indicate that the Fe(II)-based system also induces controlled polymerization of MMA and that added aluminum compounds are not needed for it.

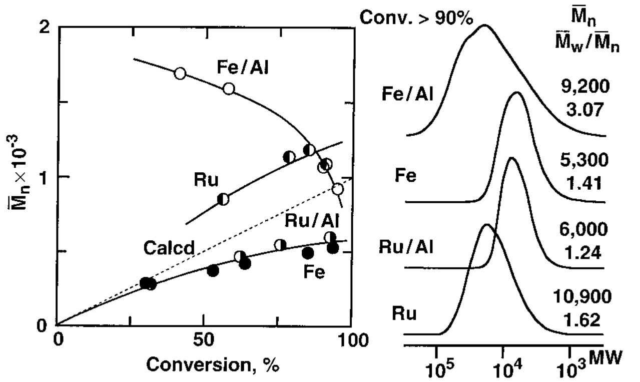


Figure 2. $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and MWD chromatogram curves of poly(MMA) obtained with $CCl_4/MCl_2(PPh_3)_n$ in the absence or presence of $Al(O^iPr)_3$ in toluene at 80 °C: $[M]_0$ = 2.0 M; $[CCl_4]_0$ = 20 mM; $[MCl_2(PPh_3)_n]_0$ = 10 mM; $[Al(O^iPr)_3]_0$ = 40 mM. Key: (○) $FeCl_2(PPh_3)_2/Al(O^iPr)_3$; (●) $FeCl_2(PPh_3)_2$; (◑) $RuCl_2(PPh_3)_3/Al(O^iPr)_3$; (◐) $RuCl_2(PPh_3)_3$.

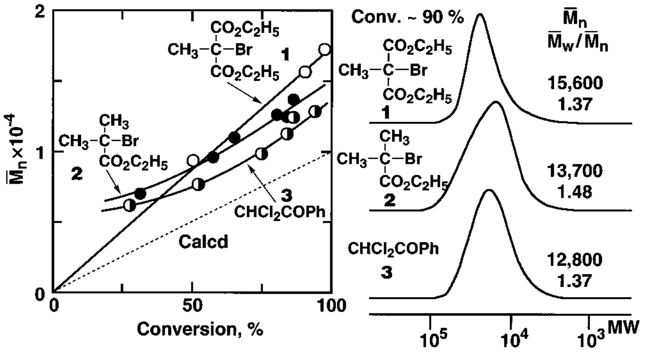


Figure 3. $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and MWD chromatogram curves of poly(MMA) obtained with $R{-}X/FeCl_2(PPh_3)_2$ in toluene at 80 °C: $[M]_0$ = 2.0 M; $[R{-}X]_0$ = 20 mM; $[FeCl_2(PPh_3)_2]_0$ = 10 mM. R−X: (○) $CH_3CBr(CO_2Et)_2$; (●) $(CH_3)_2CBrCO_2Et_2$; (◑) $CHCl_2COPh$.

In place of CCl_4, a series of organic halides [$CHCl_2COPh$, $(CH_3)_2CBrCO_2Et$, and $CH_3CBr(CO_2Et)_2$] were also employed with $FeCl_2(PPh_3)_2$ but without an added aluminum compound; these initiators were selected among those that possess a carbon−halogen bond similar to that at the polymer terminal. All these halides led to quantitative polymerization of MMA in toluene at 80 °C. As shown in Figure 3, the MWDs of the polymers were unimodal and relatively narrow ($\bar{M}_w/\bar{M}_n$ = 1.3−1.5). The number-average molecular weights $\bar{M}_n$ increased with monomer conversion, and specifically with the malonate-type initiator, the $\bar{M}_n$ increased in direct proportion to monomer conversion (open circles).

The polymerization with $CH_3CBr(CO_2Et)_2/FeCl_2(PPh_3)_2$ was then examined in detail. Figure 4 shows the $\bar{M}_n$ and MWD curves of the polymers obtained at varying concentrations of $CH_3CBr(CO_2Et)_2$. Regardless of this variable the MWDs were narrow. Although the $\bar{M}_n$ increased in direct proportion to monomer conversion and depended on the bromide concentration, it was consistently higher than the calculated value, assuming that one molecule of $CH_3CBr(CO_2Et)_2$ generates one living polymer chain. It turned out, however, the observed polymer molecular weights agree well with the values, assuming that the active (living) center concentration ([P*]) is equal to the difference between those of the bromide initiator and $FeCl_2(PPh_3)_2$; namely [P*] = $[CH_3CBr(CO_2Et)_2]_0 - [FeCl_2(PPh_3)_2]_0$ = 10 and 30 mM for $CH_3CBr(CO_2Et)_2/FeCl_2(PPh_3)_2$ = 20/10 mM (open circles) and 40/10 mM (filled circles), respectively. This means that part of $CH_3CBr(CO_2Et)_2$ does not serve as initiator and that the concentration of the “unused” bromide is equal to that of $FeCl_2(PPh_3)_2$ (10 mM).

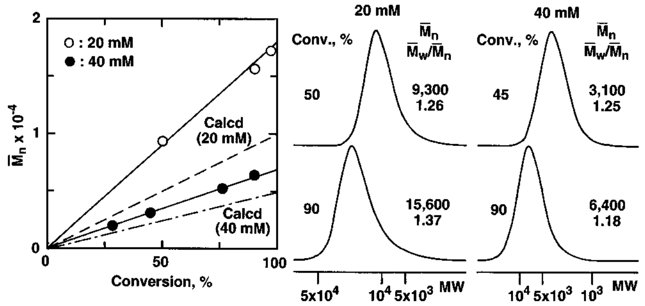


Figure 4. $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and MWD chromatogram curves of poly(MMA) obtained with $CH_3CBr(CO_2Et)_2$/ $FeCl_2(PPh_3)_2$ in toluene at 80 °C at varying concentrations of $CH_3CBr(CO_2Et)_2$: $[M]_0 = 2.0$ M; $[CH_3CBr(CO_2Et)_2]_0 = 20$ (○) and 40 (●) mM; $[FeCl_2(PPh_3)_2]_0 = 10$ mM. The dashed and dashed–dotted lines indicate the calculated $\bar{M}_n$ assuming the formation of one living polymer per with use of $CH_3CBr(CO_2Et)_2$ at 20 and 40 mM, respectively.

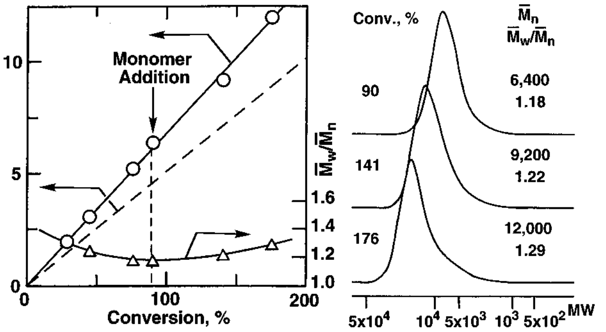


Figure 5. $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and MWD chromatogram curves of poly(MMA) obtained in monomer-addition experiments with $CH_3CBr(CO_2Et)_2/FeCl_2(PPh_3)_2$ in toluene at 80 °C: $[M]_0 = [M]_{add} = 2.0$ M; $[CH_3CBr(CO_2Et)_2]_0 = 20$ mM; $[FeCl_2(PPh_3)_2]_0 = 10$ mM.

Presumably, that portion of the initiator was consumed by a reaction with $FeCl_2(PPh_3)_2$ to generate a new iron complex, as further indicated by the fact that the yellow solution of $FeCl_2(PPh_3)_2$ changed purple on addition of $CH_3CBr(CO_2Et)_2$. ^{1}H, ^{13}C, and ^{31}P NMR analysis of a mixture of $CH_3CBr(CO_2Et)_2$ and $FeCl_2(PPh_3)_2$ (20/20 mM; in toluene-d_8 at 80 °C) also suggests some interaction between them. The isolation of the possible new complex is now under way.

To investigate the living nature of the polymerizations, a fresh feed of MMA was added to the reaction mixture when its initial charge had almost been consumed. The added monomer was smoothly polymerized, and the $\bar{M}_n$ of the resulting polymers further increased in direct proportion to conversion (Figure 5). The MWDs were narrow even after the monomer addition. These results indicate that the $CH_3CBr(CO_2Et)_2$/ $FeCl_2(PPh_3)_2$ initiating system induces living polymerization of MMA without any other additives.

A radical pathway was suggested for the Fe(II)-mediated polymerizations by the fact that the polymers obtained with $CCl_4/FeCl_2(PPh_3)_2$ and $CH_3CBr(CO_2Et)_2$/ $FeCl_2(PPh_3)_2$ were more or less syndiotactic (*rr*:*rm*:*mm* = 58:37:5 and 59:37:4, respectively), similar to poly(MMA) (e.g. *rr*:*rm*:*mm* = 58:38:4) radically prepared by AIBN in toluene at 80 °C.

(b) End-Group Analysis. The terminal groups of the polymers obtained with $CH_3CBr(CO_2Et)_2/FeCl_2(PPh_3)_2$ were then analyzed by ^{1}H NMR spectroscopy. As seen in Figure 6, the spectrum showed signals characteristic of the methylene protons (*b*) of the ester ethyl group at the α-end, along with the large absorptions of the main-chain poly(MMA) units (e.g., *f* for the ester methyl). In addition, the small signal (*g*) near *f* was attributed to the ester methyl protons adjacent to the bromine atom at the ω-end. The number-average degrees of polymerization ($\overline{DP}_n$), obtained from the peak intensity ratios *f*/*b* and *f*/*g*, were 35 [$\overline{DP}_n$(NMR, α-end)] and 41 [$\overline{DP}_n$(NMR, ω-end)], respectively. These were in close agreement with that by size exclusion chromatography [$\overline{DP}_n$(SEC) = 38] calibrated against standard poly(MMA) samples. The number-average end functionalities $\bar{F}_n$ of the α-end and ω-end, obtained as $\overline{DP}_n$(SEC)/$\overline{DP}_n$(NMR), were 1.09 and 0.93, respectively. Thus, the living polymerization proceeded via the activation of the C−Br bond originating from $CH_3CBr(CO_2Et)_2$ by the Fe(II) complex (eq 2).

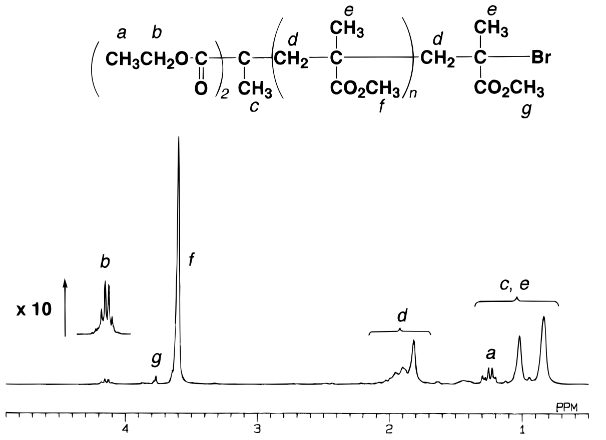


Figure 6. ^{1}H NMR spectrum of poly(MMA) obtained with $CH_3CBr(CO_2Et)_2/FeCl_2(PPh_3)_2$ in toluene at 80 °C. $\overline{DP}_n$(NMR, α-end) = 35; $\overline{DP}_n$(NMR, ω-end) = 41; $\overline{DP}_n$(SEC) = 38; $\bar{M}_w/\bar{M}_n$(SEC) = 1.19.

To conclude, living radical polymerization of MMA is possible with an Fe(II) complex coupled with organic halides like $CH_3CBr(CO_2Et)_2$. Similar to that with Ru(II), the polymerization seems to proceed via the homolytic and reversible activation of carbon−halogen bonds at the polymer terminal by the redox reaction between Fe(II) and Fe(III). This also suggests the generality of transition-metal-catalyzed living radical polymerizations. In contrast to the Ru(II)-based system, however, the Fe(II) counterpart does not need added aluminum compounds for smooth living polymerizations. Other features of the Fe(II)-based systems are faster polymerizations and lower cost of the complex, particularly in comparison with $RuCl_2(PPh_3)_3$. However, initiator components should be more carefully selected for better controlled polymerizations. Efforts for improvement of the Fe(II)-based living radical polymerizations are now being made in our laboratory.

Experimental Section

(a) Preparation of $FeCl_2(PPh_3)_2$.[18] $FeCl_2(PPh_3)_2$ was prepared by stirring a mixture of anhydrous $FeCl_2$ (1.36 g, 10.7 mmol) and PPh_3 (10.5 g, 40.0 mmol) in reflux benzene (60 mL) under dry nitrogen for 4 h.[19] The reaction mixture was filtered while hot and allowed to stand for 1 day at room temperature. The precipitated colorless crystal was washed with benzene and dried under reduced pressure (5 mmHg) at 70 °C for 6 h. Anal. Calcd for $C_{36}H_{30}P_2Cl_2Fe$: C, 66.4, H, 4.7, Cl, 10.9. Found: C, 66.3, H, 4.5, Cl, 10.9.

(b) Living Polymerization. The polymerization was carried out under dry nitrogen in baked glass tubes equipped with a three-way stopcock or in baked and sealed glass tubes.[2,3] All reagents were used after ordinary purifications, and the toluene solvent was bubbled with dry nitrogen for more than 15 min immediately before use. A typical example with $CH_3CBr(CO_2Et)_2$ is given below. The polymerization was initiated by adding, via dry syringes, a solution of $FeCl_2(PPh_3)_2$ (1.5 mL) in toluene into a mixture (1.0 mL) of MMA (0.535 mL), *n*-octane (0.361 mL), and $CH_3CBr(CO_2Et)_2$ (0.019 mL) in toluene at 25 °C; thus the total volume of the reaction mixture was 2.5 mL. Immediately after mixing, the mixture was placed in an oil bath kept at 80 °C. In predetermined intervals, the polymerization was terminated by cooling the reaction mixtures to −78 °C. Monomer conversion was determined from the concentration of residual monomer measured by gas chromatography with *n*-octane as an internal standard. The quenched reaction solutions were diluted with toluene (ca. 20 mL) and rigorously shaken with an absorbent [KYOWAAD-2000G-7 ($Mg_{0.7}Al_{0.3}O_{1.15}$); Kyowa Chemical Industry] (ca. 5 g) to remove the metal-containing residues. After the absorbent was separated by filtration (Whatman 113V), the filtrate was washed with water, and evaporated to dryness to give the products, which were subsequently vacuum dried overnight.

(c) Polymer Characterization. The $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and MWD chromatographs of the polymers were determined by size-exclusion chromatography in chloroform with a calibration based on 11 poly(MMA) standard samples (Polymer Laboratories; $\bar{M}_n = 630-220\,000$; $\bar{M}_w/\bar{M}_n = 1.06-1.22$).

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References and Notes

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