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Atom Transfer Radical Polymerization of Methyl Methacrylate Catalyzed by Iron^{II} Chloride/Isophthalic Acid System

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ABSTRACT: Iron^{II} chloride coordinated by isophthalic acid was successfully used as the catalyst in ethyl 2-bromopropionate initiated atom transfer radical polymerization (ATRP) of methyl methacrylate (MMA). The polymerization was controlled up to a molecular weight of 50 000. *N*,*N*-Dimethylformamide was used to improve the solubility of the ligand. However, the amount of *N*,*N*-dimethylformamide has no significant effect on the living nature of the polymerization. Chain extension was performed to confirm the "living"/controlled nature of the polymerization system. The effect of various ratios of iron^{II} chloride to ligand on the polymerization was investigated, and the initiator efficiency reached 0.82 when the ratio of transition metal to ligand was equal to 0.5 in DMF. The ready availability and nontoxicity of isophthalic acid makes it very attractive as a new ligand in iron-mediated ATRP.

Introduction

Atom transfer radical polymerization (ATRP) is among the most promising approaches to controlled radical polymerization.[1] Recent studies have been aimed at developing new ligands and new metals that increase the activity and selectivity of the catalyst.[2,3] The catalyst consists of a transition metal and ligand.[4−7] The choice of ligand is one of the key factors influencing the reactivity of the catalyst. Previously, 2,2′-bipyridine (bpy)[8] was employed as the ligand in copper-mediated ATRP. Recently, the control of ATRP was further improved, and polymers with polydispersities as low as 1.05 were obtained by employing the more soluble 4,4′-di-5-nonyl-2,2′-bipyridine (dNbpy)[9] or 4,4′-diheptyl-2,2′-bipyridine (dHbpy).[10] Novel ligands such as alkylpyridylmethanimine,[11,12] phenanthroline derivatives,[13] unsubstituted terpyridine, and its derivatives[14] have also been used. The best results were reported with multidentate amine ligands,[15] such as multidentate aliphatic amines Me_6TREN [(tris(2−dimethylamino)-ethylamine), TMEDA (tetramethylethylenediamine), PMDETA (*N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine), and HMTETA (1,1,4,7,10,10-hexamethyltriethylenetetramine). Monodentate nitrogen ligands produce polymers with uncontrolled molecular weights and high polydispersities.[16,17] Sulfur, oxygen, or phosphorus ligands are reportedly less effective in ATRP catalyzed by copper.[18,19] Iron-mediated ATRP has been successfully implemented with precise end functionalities, predetermined molecular weights, and low polydispersities.[20,21] PPh_3,[21] dNbpy,[5] $P(^nBu)_3$,[5] and $N(^nBu)_3$[5] have been used as coordinating ligands in iron-mediated ATRP. Acids were generally believed to deactivate the metal organic catalyst, resulting in poor control of the polymerization.[22−24] However, acids, which are inexpensive and nontoxic, complex more easily with iron than copper and may therefore act as a ligand in iron-mediated ATRP. We[25] recently reported the atom transfer radical polymerization of styrene initiated by $FeCl_2$/succinic acid. The reaction was carried out at 40−100 °C in bulk, and the polydispersity index was relatively low ($M_w/M_n = 1.30$). This paper reports a new catalytic system based on iron complexes with isophthalic acid for controlled/"living" radical polymerization of MMA. The polymerization is controlled over a broad range of molecular weights and produces polymers with relatively low polydispersity and rapid kinetics. The influence of the ratio of metal to ligand and the concentration was also investigated.

Experimental Section

Materials. Methyl methacrylate (MMA, Shanghai Chemical Reagents Co., A.R. grade) was vacuum distilled from CaH_2 just before polymerization. $FeCl_2$ (Shanghai Chemical Reagents Co., 98%) was washed with acetone and dried under vacuum at 60 °C before use. Ethyl 2-bromopropionate (Aldrich, 99%) and isophthalic acid (Shanghai Chemical Reagents Co., A.R. grade) were used as received. *N*,*N*-Dimethylformamide (DMF, Shanghai Dongyi Chemical Reagents Co, 99.5%) was distilled at reduced pressure and stored over type 4 Å molecular sieves until use.

Characterization. The conversion of polymerization was determined gravimetrically. Molecular weight and molecular weight distribution were measured on a PE Series200 gel permeation chromatography (GPC) equipped with a mixed 5μ PS columns (range of pore sizes: 1×10^5, 1×10^4, and 1×10^3 Å) and a refractive index detector. All samples were run in THF at 25 °C with a flow rate of 1.0 mL/min; PMMA standards were used for calibration. The ^{1}H NMR spectrum was recorded on a Bruker AVANCE500 500 MHz NMR spectrometer at room temperature in $CDCl_3$. Ultraviolet−visible (UV/vis) spectroscopic measurements were performed on a PE Lambda 20 spectrophotometer in DMF.

General Procedure for Homogeneous Polymerization. In a typical example, ethyl 2-bromopropionate (17.4 mg, 9.40×10^{-3} mol/L), $FeCl_2$ (23.9 mg, 1.88×10^{-2} mol/L), isophthalic acid (62.5 mg, 3.76×10^{-2} mol/L), MMA (5 mL, 4.7 mol/L), and DMF (50% v/v) were added to a flask with a stirrer. Three cycles of rapid vacuum to nitrogen were applied in order to remove oxygen, and the flask was then degassed with nitrogen for 10 min. The mixture was stirred at room temperature until the catalyst was dissolved (half an hour). The flask was then immersed in an oil bath thermostat at 90 °C. After 10 h, the polymerization was stopped. The product was dissolved in THF. Finally, the resultant polymer was isolated by precipitation in methanol and dried under vacuum at 60 °C for 24 h. (The best way to isolate the polymer is to precipitate it in hexane since the low molecular weight PMMA may be soluble in methanol.) The monomer conversion reached about 89%,

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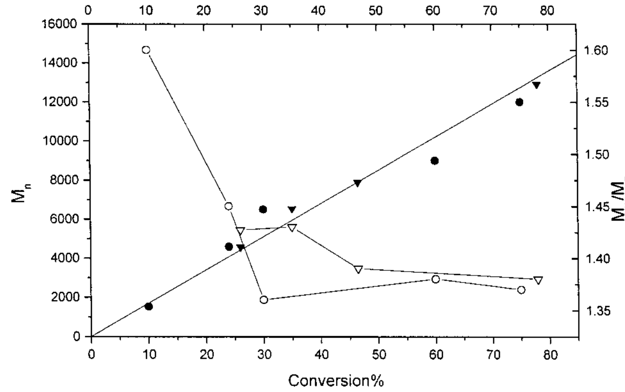


Figure 1. Evolution of molecular weight (▼, ●) and polydispersity (▽, ○) with conversion for ATRP of MMA catalyzed by $FeCl_2$/isophthalic acid. $[I]_0:[FeCl_2]_0:[ligand]_0:[M]_0 = 1:1:2:142$ at 80 °C in heterogeneous, $[I]_0 = 6.40 \times 10^{-2}$ mol/L, and $[M]_0 = 9.1$ mol/L in 3.23% DMF (v/v). ▼/▽ and ●/○ represent the results from two different experiments in the same conditions except the room temperatures ($T = 8$ and 20 °C, respectively). Symbols: [I] = [ethyl 2-bromopropionate], [M] = [MMA], [ligand] = [isophthalic acid].

and the number-average molecular weight and the polydispersity index were measured to be $M_n = 54\,100$ and $M_w/M_n = 1.39$.

General Procedure for Heterogeneous Polymerization. In a typical procedure, $FeCl_2$ (0.127 g, 6.45×10^{-2} mol/L), isophthalic acid (0.332 g, 1.29×10^{-1} mol/L), and DMF (3.23% v/v) were added to a flask with a stirrer. Three cycles of rapid vacuum to nitrogen were applied in order to remove oxygen, and the flask was then degassed with nitrogen for 10 min. After the mixture was stirred at room temperature for 1 h, MMA (15 mL, 9.1 mol/L) and ethyl 2-bromopropionate (0.183 g, 6.40×10^{-2} mol/L) were introduced via a syringe; the flask was immersed in an oil bath at 80 °C. After 5 h, the reactions were stopped. The content was dissolved in THF, followed by precipitation in methanol, and dried under vacuum at 60 °C for 24 h. The monomer conversion reached about 35%, and the number-average molecular weight and the polydispersity index were measured by GPC to be $M_n = 6540$ and $M_w/M_n = 1.43$. The molecular weight obtained by ^{1}H NMR was $M_{n(\mathrm{H\ NMR})} = 5880$.

Results and Discussion

ATRP of MMA Catalyzed by $FeCl_2$/Isophthalic Acid. ATRP of MMA with [ethyl 2-bromopropionate]$_0$:$[FeCl_2]_0$:[isophthalic acid]$_0$:$[MMA]_0 = 1:1:2:142$ at 80 °C in DMF (3.23% v/v) was fully controlled under heterogeneous conditions. During the reaction, the white color of the $FeCl_2$/isophthalic acid complex changed to yellowish-red as the reaction proceeded, which indicates that an Fe^{III} compound forms. The monomer conversion reached about 80% within 10 h.

The polymerization showed a linear increase in molecular weights with conversion and matched the theoretical values well (Figure 1). The polydispersity index (1.38) was relatively low throughout the polymerization process.

The linearity of the semilogarithmic plots of $\ln([M]_0/[M])$ versus time in Figure 2 indicates that the polymerization was first-order with respect to monomer and that the concentration of growing radicals remained constant. The induction period may be due to the slow formation of the catalytic center during the first stage at 80 °C.

PMMA prepared from ethyl 2-bromopropionate was characterized by ^{1}H NMR spectroscopy (Figure 3). A characteristic resonance originating from the α-halocarbonyl moieties is visible at both 4.1 and 3.8 ppm. The former signal is derived from the methylene protons of the ethyl ester group while the latter is derived from that of the methyl ester group adjacent to the terminal halogen. The protons of OCH_3 in the backbone are observed at 3.58 ppm. Furthermore, the molecular weight obtained by GPC equals 6540 and is close to that estimated from ^{1}H NMR (5880) using the intensity ratio of methoxy groups in the main chain to protons from residual initiator groups.

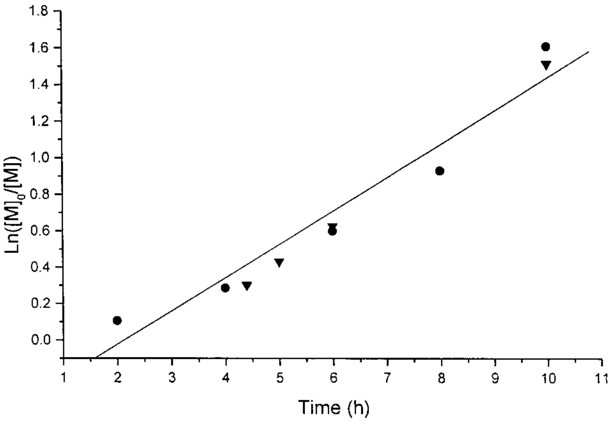


Figure 2. Time−$\ln([M]_0/[M])$ plots for MMA polymerization with $FeCl_2$/isophthalic acid as the catalyst at 80 °C. $[I]_0:[FeCl_2]_0:[ligand]_0:[M]_0 = 1:1:2:142$, using the same reaction conditions as in Figure 1.

Chain Extension of PMMA−X. An additional method toward verifying the functionality of a polymer prepared by ATRP is its use as a macroinitiator for the same or other monomers. A chain extension of MMA with PMMA ($M_{n(\mathrm{GPC})} = 12\,900$, $M_w/M_n = 1.40$) as the macroinitiator was performed. The polymerization was carried out using $FeCl_2$/isophthalic acid as the catalyst in 50% (v/v) DMF at 90 °C with $[MMA]_0 = 4.7$ mol/L and $[FeCl_2]_0 = [\text{isophthalic acid}]_0/2 = 0.02$ mol/L. A conversion of (65%) was achieved after polymerization for 12 h. The M_n of the chain-extended PMMA increased to 60 200; however, the polydispersity index (1.58) was a little higher than that of the macroinitiator ($M_w/M_n = 1.40$). A small part of the macroinitiator probably remains unreacted. Figure 4 shows the increase in the molecular weight. These results demonstrate the conclusion that the polymerization of MMA catalyzed by $FeCl_2$/isophthalic acid in the presence of DMF is controlled.

UV/vis Spectra Curves. To further characterize the elementary process leading to the formation of active species in DMF, the catalytic system was analyzed by UV−vis spectroscopy. As shown in Figure 5, the corresponding $FeCl_2$/isophthalic acid complex does not show any characteristic UV−vis adsorption between 260 and 600 nm. As the reaction proceeded, two absorption bands appeared in curves c to f of Figure 5; the main peak is centered at 360 nm, and the other one is located at 314 nm. The change in absorption spectra of the reaction system can be attributed to the formation of $FeCl_3$/isophthalic acid from $FeCl_2$/isophthalic acid through halogen transformation. At the end of the reaction, the bands at 360 and 314 nm are of very high intensity, and they correspond to a large amount of $FeCl_3$/isophthalic acid.

Effect of the Ratio of Metal to Ligand. Another series of experiments were carried out with different $[FeCl_2]_0/[ligand]_0$ ratios. The concentration of $FeCl_2$ was

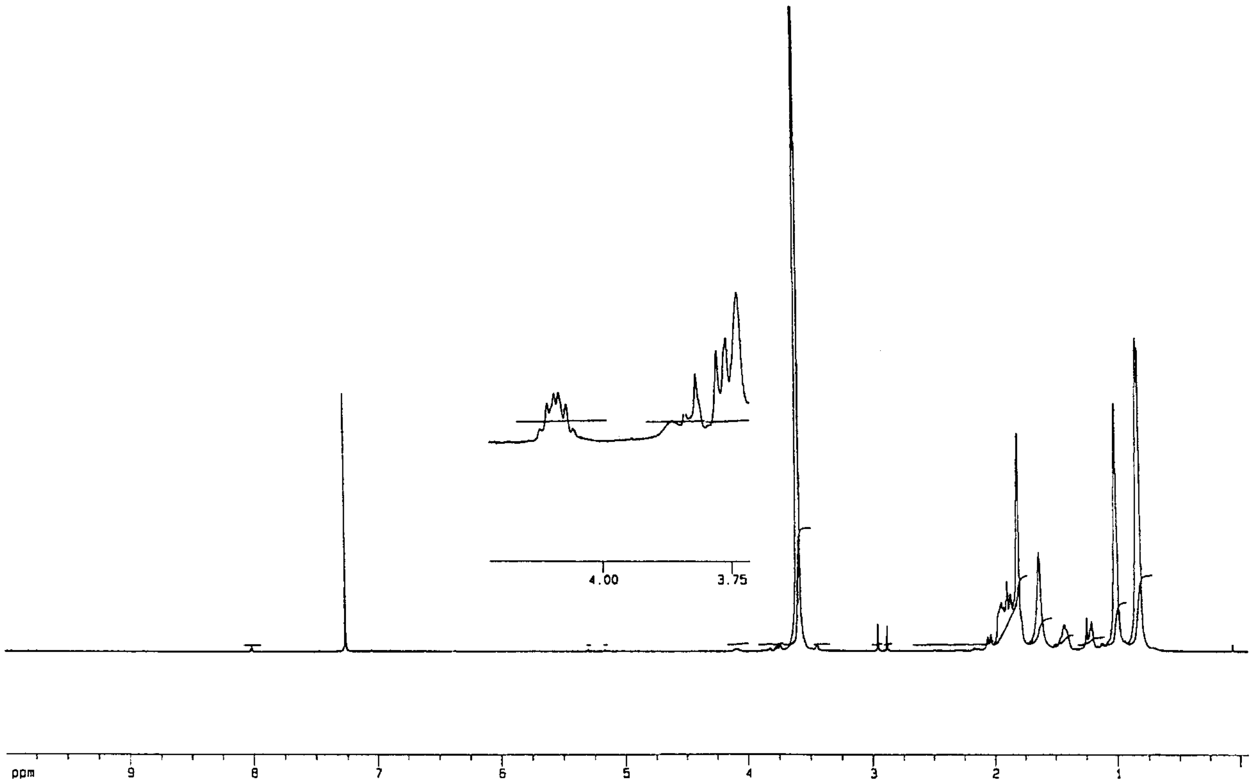


Figure 3. ^{1}H NMR spectrum of PMMA catalyzed by $FeCl_2$/isophthalic acid.

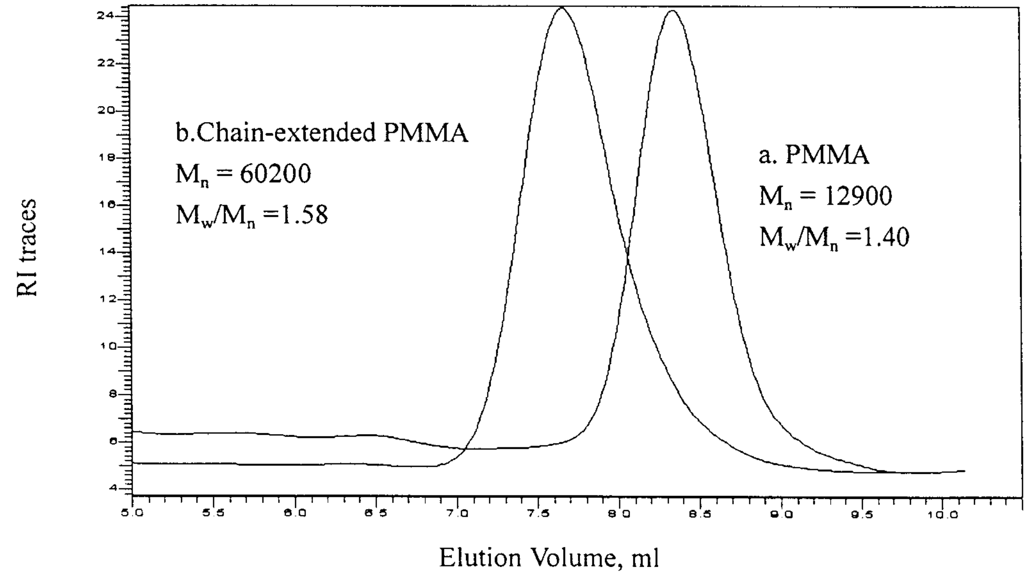


Figure 4. GPC curves of PMMA (a) before and (b) after chain extension.

kept constant at $[FeCl_2]_0 = 1.88 \times 10^{-2}$ mol/L. The polymerization was conducted with $FeCl_2$/isophthalic acid as the catalyst when $[MMA]_0 = 4.7$ mol/L and $[MMA]_0$:[ethyl 2-bromopropionate]$_0$ = 500:1 in 50% v/v DMF. The color of the homogeneous polymerization in DMF was red-yellow. The effects of metal-to-ligand ratios of 0.5, 1, and 2 are shown in Figure 6. The molecular weights of the resulting polymers measured by GPC increased linearly with conversion at all $[FeCl_2]_0$/[ligand]$_0$ ratios, and the polydispersity was as low as 1.5. The initiator efficiency, $f(M_n^{cal}/M_n^{sec})$, calculated by comparison of the GPC and calculated M_n values is 0.4, 0.6, or 0.82 corresponding to 2, 1, or 0.5 of $[FeCl_2]_0$ to [ligand]$_0$ ratio. This indicates there is some termination or side reaction at the beginning of the reaction because the radicals are not immediately deactivated if the [ligand]$_0$ to $[FeCl_2]_0$ ratio was lower than 2.

When the ratio of [ligand]$_0$ to $[FeCl_2]_0$ equals 2, the polymerization was controlled as shown in Figures 7 and 8. The molecular weights of the resulting polymer increased linearly with monomer conversion, and the initiator efficiency was improved to 0.82 (Figure 8). The plot of $\ln([M]_0/[M])$ versus time was linear throughout the polymerization. The corresponding value of the apparent rate constant calculated from the kinetic plot ($d \ln[M]/dt = k_p[P]$) in Figure 8 is 5.78×10^{-5} s^{-1}. In the present case, assuming a propagating rate constant of 1.616×10^3 M^{-1} s^{-1} for MMA at 90 °C,[26] the

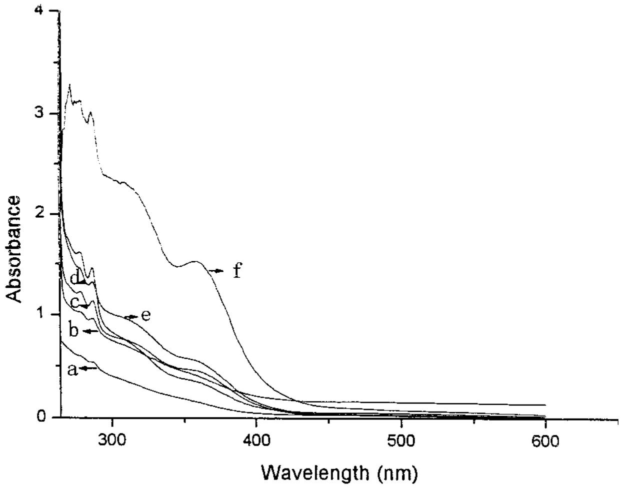


Figure 5. UV/vis spectra curves of $FeCl_2$/isophthalic acid during the polymerization of MMA in DMF. Reactions time: (a) 0, (b) 2, (c) 10, (d) 30, (e) 60, and (f) 300 min.

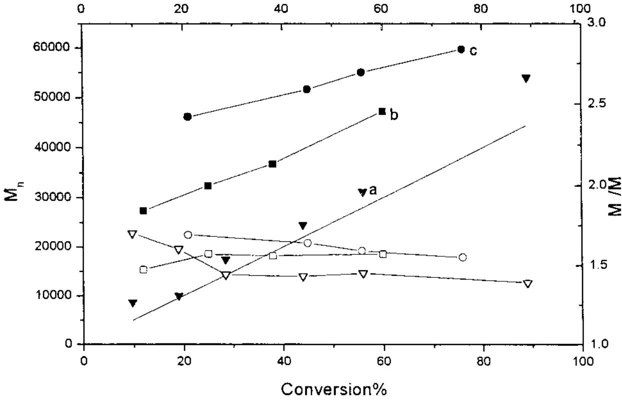


Figure 6. Evolution of measured molecular weight (●, ■, ▼) and polydispersity (○, □, ▽) with conversion for ATRP of MMA catalyzed by $FeCl_2$/isophthalic acid at various molar ratios of $[FeCl_2]_0/[\text{isophthalic acid}]_0$ in 50% DMF (v/v) at 90 °C, $M_{n(th)} = 50\ 000$, $[I]_0 = 9.40 \times 10^{-3}$ mol/L, $[M]_0 = 4.7$ mol/L, $[FeCl_2]_0 = 1.88 \times 10^{-2}$ mol/L. (a) $[FeCl_2]/[\text{ligand}] = 1/2$ (▼/▽); (b) $[FeCl_2]/[\text{ligand}] = 1/1$ (■/□); (c) $[FeCl_2]/[\text{ligand}] = 1/0.5$ (●/○).

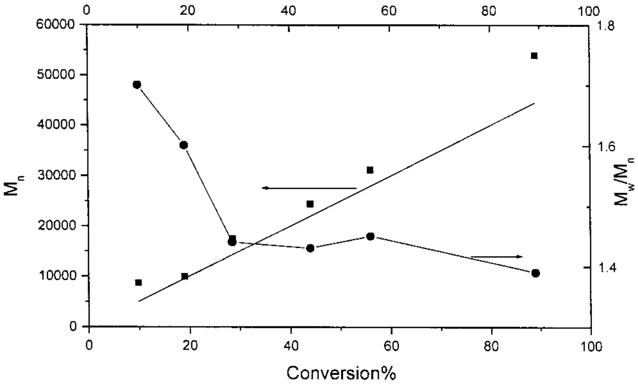


Figure 7. Evolution of measured molecular weight and polydispersity with conversion for ATRP of MMA catalyzed by $FeCl_2$/isophthalic acid. $[I]_0:[FeCl_2]_0:[\text{ligand}]_0:[M]_0 = 1:2:4:500$ in 50% DMF (v/v) at 90 °C, $M_{n(th)} = 50\ 000$.

concentration of active centers is about 3.58×10^{-8} M, which is sufficiently low to prevent a significant amount of chain termination.

Comparing the apparent rate constants derived from the kinetic plots in Figure 9, the reaction rate corresponding to the ratio of 0.5 is the highest one (Figure 10). Lower or higher concentrations of ligand will result in low reaction rate.

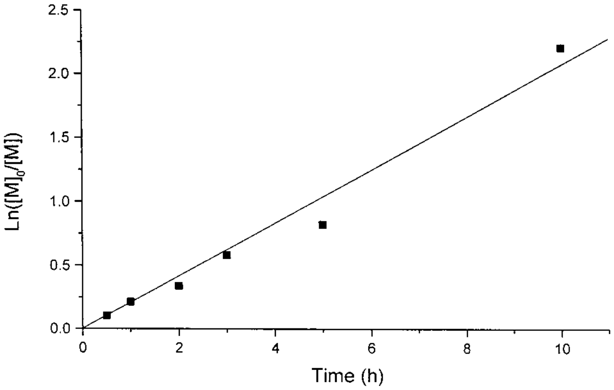


Figure 8. Time–$\ln([M]_0/[M])$ plots for MMA polymerization with $FeCl_2$/isophthalic acid as catalyst. $[I]_0:[\text{ligand}]_0:[FeCl_2]_0\ [M]_0 = 1:2:4:500$ in 50% DMF (v/v) at 90 °C, $M_{n(th)} = 50\ 000$.

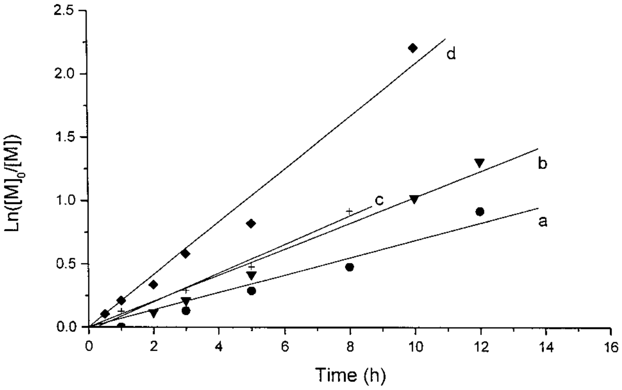


Figure 9. Time–$\ln([M]_0/[M])$ plots for MMA polymerization at various ratios of $FeCl_2$ to isophthalic acid. $[FeCl_2]_0 = 1.88 \times 10^{-2}$ mol/L, $[M]_0 = 4.7$ mol/L, $[I]_0 = 9.40 \times 10^{-3}$ mol/L. (a) $[FeCl_2]_0/[\text{ligand}]_0 = 1$; (b) $[FeCl_2]_0/[\text{ligand}]_0 = 0.125$; (c) $[FeCl_2]_0/[\text{ligand}]_0 = 0.25$; (d) $[FeCl_2]_0/[\text{ligand}]_0 = 0.5$.

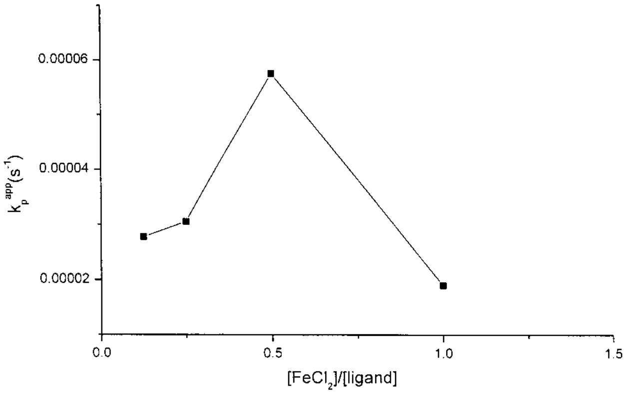


Figure 10. Dependence of apparent rates constant on the ratio of $FeCl_2$ to isophthalic acid. $[FeCl_2]_0 = 1.88 \times 10^{-2}$ mol/L, $[M]_0 = 4.7$ mol/L, $[I]_0 = 9.40 \times 10^{-3}$ mol/L.

In summary, an $[\text{isophthalic acid}]_0$ to $[FeCl_2]_0$ ratio of 2 not only gave the best control of molecular weight and its distribution but also provide rather rapid reaction rate in a controlled fashion.

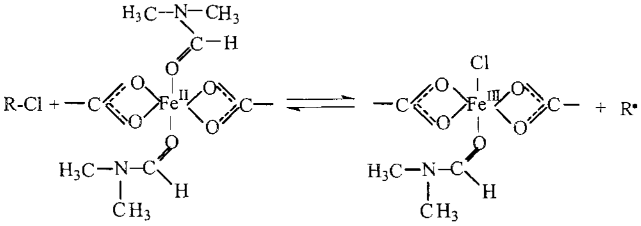
Effect of Solvent. Several experiments were conducted using various solvents in different amounts. The results of these experiments are shown in Table 1. The reaction is quite sensitive to the polarity of the solvent. A more polar solvent, such as DMF, provides a homogeneous catalyst system, which was well controlled. We

Table 1. Results of ATRP of MMA Catalyzed by $FeCl_2$/Isophthalic Acid in Different Solvents[a]

no.	solvent	T (°C)	time (h)	conv (%)	$M_{n(GPC)}$ $\times 10^{-3}$	M_w/M_n
1	bulk	90	24	0		
2[b]	4.5% DMF	80	5	35	6.1	1.43
3[b]	8.5% DMF	90	64	71	6.5	1.35
4[c]	48% DMF	90	4	70	9.4	1.35
5	anisole	90	20	1	*d*	
6	*o*-xylene	90	20	0		

[a] All reactions were run at [ethyl 2-bromopropionate]$_0$:[$FeCl_2$]$_0$:[isophthalic acid]$_0$:[MMA]$_0$ = 1:1:2:130, T = 90 °C. [b] In heterogeneous conditions. [c] In homogeneous conditions. [d] Oligomer.

Scheme 1



failed to carry out the polymerization of MMA in bulk and in nonpolar solvent xylene (entry 6, Table 1) and only got an oligomer in anisole (entry 5, Table 1). In the absence of DMF, the polymerizations were heterogeneous due to the limited solubility of the catalyst and the ligand in monomer. In this case, isophthalic acid cannot complex with $FeCl_2$ sufficiently and fails to catalyze the polymerization. The addition of a polar solvent should increase the solubility of the catalyst in MMA. When 4.5−10% DMF (v/v) was added (entries 2 and 3, Table 1), the reaction was heterogeneous; the reaction mixture was homogeneous if a relatively large amount of DMF (entry 4, Table 1) was added. The rate of the homogeneous polymerization in DMF was unexpectedly faster than the heterogeneous polymerization with a small amount of DMF, even though the ratio of initiator to monomer was significantly higher in the latter case. A similar result was reported by Matyjaszewski[27] in 1998 for copper-mediated ATRP. All of the reactions shown in Figure 6 proceeded in a controlled fashion. Excess solvent does not affect the living nature in ATRP of MMA catalyzed by $FeCl_2$/isophthalic acid.

The experimental data reported in this work are different from those reported by Vairon,[28] who used bpy, and Matyjaszewski,[29] who used monodentate amines as the ligands in copper-mediated systems. They concluded that excess DMF affects the living nature of ATRP. In our ATRP system, the quantity of DMF has no significant effect on the living nature if there is sufficient ligand to complex the transition metal. It may be explained by the different properties of the complexes. In this system, we assumed that the two oxygen atoms of each carboxylate group chelate the iron atom in the equatorial plane, and two atoms from DMF molecules coordinate the iron atom in the axial direction, forming a six-coordinative geometry (Scheme 1). The DMF molecules can easily exchange with other ligands such as chloride (Scheme 1). When there are halide species in the system, a reversible equilibrium between active species and dormant species can be established via the ATRP mechanism. If there is enough stronger ligand to complex with metal in this system, ligand exchange by DMF will be negligible. Alternatively, if there is not enough other of the stronger ligands, DMF molecules may reduce the activity of the catalyst. In this case, active species cannot become sufficient dormant through halogen transformation resulting in radical−radical termination. Therefore, the molecular weights are higher than the theoretical values at the beginning of the reaction as shown in Figure 6.

Table 2. Results of Polymerization of MMA in DMF without Ligand Initiated by $FeCl_2$/Ethyl 2-Bromopropionate

V_{DMF}/V_{MMA} (%)	time (h)	conv (%)	$M_{n(GPC)}$ $\times 10^{-4}$	$M_{n(th)}$ $\times 10^{-3}$	M_w/M_n
4.5	1.3	9	3.1	1.2	1.80
8.5	5	55	1.3	7.2	1.70
48	9.4	59	1.7	7.7	1.70

[a] All experiments were performed at [ethyl 2-bromopropionate]$_0$:[$FeCl_2$]$_0$:[MMA]$_0$ = 1:1:130, T = 90 °C.

Polymerization of MMA without Ligand in DMF. From the analysis of the results given above, we found that the polymerization of MMA catalyzed by [$FeCl_2$]$_0$/[ligand]$_0$ = 1 demonstrated some “living” characteristics. That is, the molecular weights increased with monomer conversion, and the kinetic plot was almost linear. Moreover, Figure 6 shows that the initiator efficiency decreases with increasing [$FeCl_2$]$_0$ to [ligand]$_0$ ratio. The initiator efficiency decreased from 0.82, 0.6, to 0.4 with increasing [$FeCl_2$]$_0$ to [ligand]$_0$ ratio from 0.5, 1, to 2. We assume that there is ligand exchange between iron species and DMF. Similar phenomena were reported by Pascual[28] and Matyjaszewski[29] for ATRP with copper complexes as the catalyst system. The effect of DMF on the ATRP of MMA was verified by the polymerization in absence of ligand. The results are summarized in Table 2.

These polymerizations were ill-controlled. The molecular weights of the resulting polymer are higher than predetermined, and the molecular weight distributions are broad. This implies that DMF itself is not an effective ligand in ATRP.

Conclusions

The new catalyst system, $FeCl_2$/isophthalic acid, was used in the ATRP of MMA. Well-defined PMMA was synthesized under heterogeneous conditions in the presence of a small amount of DMF (3.2% v/v) and under homogeneous conditions if DMF was used as the solvent. Chain extension was performed to further confirm the “living”/controlled nature of the new polymerization system. ^1H NMR was used to characterize the end group of the resulting polymer. End group analysis supports that the polymerization proceeds via reversible activation of the terminal C−X bond derived from the initiator, ethyl 2-bromopropionate. The concentration of DMF in the reaction system has no effect on the polymerization.

References and Notes

(1) Wang, J. S.; Matyjaszewski, K. *J. Am. Chem. Soc.* **1995**, *117*, 5614.
(2) Moineau, C.; Minet, M.; Teyssié, Ph.; Jérôme, R. *Macromolecules* **1999**, *32*, 8277.
(3) Matyjaszewski, K. *Chem. Eur. J.* **1999**, *5*, 3095.
(4) Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1995**, *28*, 1721.
(5) Matyjaszewski, K.; Wei, M. L.; Xia, J. H.; McDermott, N. T. *Macromolecules* **1997**, *30*, 8161.
(6) Granel, C.; Dubois, Ph.; Jérôme, R.; Teyssié, Ph. *Macromolecules* **1996**, *29*, 8576.

(7) Lecomte, P.; Drapier, I.; Dubois, Ph.; Jérôme, R.; Teyssié, Ph. *Macromolecules* **1997**, *30*, 7631.

(8) Wang, J. S.; Matyjaszewski, K. *Macromolecules* **1995**, *28*, 7901.

(9) Patten, T. E.; Xia, J.; Abernathy, T.; Matyjaszewski, K. *Science* **1996**, *272*, 866.

(10) Matyjaszewski, K.; Patten, T. E.; Xia, J. *J. Am. Chem. Soc.* **1997**, *119*, 674.

(11) Haddleton, D. M.; Jasieczek, C. B.; Hannon, M. J.; Shooter, A. J. *Macromolecules* **1998**, *31*, 5958.

(12) Haddleton, D. M.; Crossman, M. C.; Dana, B. H.; Duncalf, D. J.; Heming, A. M.; Kukulj, D.; Shooter, A. J. *Macromolecules* **1999**, *32*, 2110.

(13) Destarac, M.; Bessière, J. M.; Boutevin, B. *Macromol. Rapid Commun.* **1997**, *18*, 967.

(14) Kickelbick, G.; Matyjaszewski, K. *Macromol. Rapid Commun.* **1999**, *20*, 341.

(15) Xia, J.; Gaynor, S. G.; Matyjaszewski, K. *Macromolecules* **1997**, *30*, 7697.

(16) Bernhardt, P. V. *J. Am. Chem. Soc.* **1997**, *119*, 771.

(17) Coessens, V.; Matyjaszewski, K. *J. Macromol. Sci., Pure Appl. Chem.* **1999**, *A36*, 653.

(18) Xia, J.; Matyjaszewski, K. *Macromolecules* **1999**, *32*, 2434.

(19) Xia, J.; Zhang, X.; Matyjaszewski, K. *Polym. Prepr.* **1999**, *40*, 453.

(20) Xia, J.; Paik, H.; Matyjaszewski, K. *Macromolecules* **1999**, *32*, 8310.

(21) Ando, T.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1997**, *30*, 4507.

(22) Sawamoto, M.; Kamigaito, M. *Trends Polym. Sci.* **1996**, *4*, 371.

(23) Matyjaszewski, K.; Coessens, V.; Nakagawa, Y.; Xia, J.; Qiu, J.; Gaynor, S.; Coca, S.; Jasieczek, C. *ACS Symp. Ser.* **1998**, *704*, 16.

(24) Nishikawa, T.; Ando, T.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1997**, *30*, 2244.

(25) Zhu, S.; Yan, D.; Zhang, G.; Li, M. *Macromol. Chem. Phys.*, in press.

(26) Gilbert, R. G. *Pure Appl. Chem.* **1996**, *68*, 1491.

(27) Matyjaszewski, K.; Nakagawa, Y.; Jasieczek, C. B. *Macromolecules* **1998**, *31*, 1535.

(28) Pascual, S.; Coutin, B.; Tardi, M.; Polton, A.; Vairon, J.-P. *Macromolecules* **1999**, *32*, 1432.

(29) Ziegler, M. J.; Paik, H.; Davis, K. A.; Gaynor, S. G.; Matyjaszewski, K. *Polym. Prepr.* **1999**, *40*, 432.

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