Synthesis of Poly(methyl methacrylate) Via Reverse Atom Transfer Radical Polymerization Catalyzed by FeCl₃/lactic Acid

Wenying Zhou, Hou Chen, Ying Liang, Mengmeng Yu, Lichun Chen

School of Chemistry and Materials Science, Ludong University, Yantai 264025, China

ABSTRACT: Reverse atom transfer radical polymerization (RATRP) of methyl methacrylate (MMA) with azobisisobutyronitrile (AIBN)/FeCl₃/lactic acid as initiating system was successfully carried out in *N,N*-dimethylformamide (DMF) for the first time. Kinetics as well as molecular weight distribution data indicated towards the controlled nature of polymerization. The polymerization not only showed the best control of molecular weight and its distribution but also provided a rather rapid reaction rate with the molar ratio of [MMA]:[AIBN]:[FeCl₃]:[lactic acid] = 300 : 1 : 1 : 2. The polymerization rate increased with increasing the polymerization temperature. The apparent activation energy was calculated to be 47.90 kJ/mol. The rate of polymerization in DMF was faster than that in acetonitrile, cyclohexanone, toluene, and xylene. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 1593–1597, 2009

Key words: synthesis; reverse atom transfer radical polymerization; living polymerization; methyl methacrylate; lactic acid

INTRODUCTION

Well-defined polymers with controlled architecture, molecular weight, and narrow polydispersity can be achieved by living radical polymerization process in which there is neither chain transfer nor chain termination. Atom transfer radical polymerization (ATRP) is one of the most widely used methods in the controlled radical polymerization, it involves a fast dynamic equilibrium between dormant species and active radical species to provide control.[1–4] Methyl methacrylate (MMA) is a common and important monomer. ATRP of MMA has been studied systemically.[3,5–19] However, ATRP has two major drawbacks: the halide species RX are toxic and not easily handled or obtained, and the catalysts M_t^n/L_x are easily oxidized by air.[20] To overcome these drawbacks, the RATRP was promoted by Matyjaszewski and his coworkers[21,22] and Teyssié and coworkers.[20] In this process, a conventional radical initiator and a higher oxidation state transition-metal species $M_t^{n+1}X/L_x$ were used instead of halide species RX and a lower oxidation state M_t^nX/L_x, respectively.

Recent studies have been aimed at developing new ligands and new metals that influence the activity and selectivity of the catalyst.[23–27] The ligands used in the RATRP are usually bipy or its derivatives and triphenylphosphine (PPh₃). Teyssié et al.[20] reported reverse ATRP of MMA in bulk and in toluene with PPh₃ as ligand. However, PPh₃ is harmful to human beings. It is necessary to find novel ligands with low toxicity. Organic acids were generally believed to deactivate the metal organic catalyst, resulting in poor control of the polymerization. However, organic acids, which are inexpensive and nontoxic, complex more easily with iron and may therefore act as ligands. Various organic acids such as pyromellitic acid,[23] iminodiacetic acid,[28] and isophthalic acid[25,29] have been successfully employed as new ligands in the iron-mediated RATRP of vinyl monomers such as acrylonitrile (AN) and MMA. Lactic acid, an important organic acid with wide application in many fields, is no toxicity. Xiong et al.[27] have successfully carried out a living/controlled radical polymerization of MMA by using SmCl₃/lactic acid as catalytic system.

In this study, a new catalytic system based on iron complexes with lactic acid was used for the first time to prepare poly(methyl methacrylate) (PMMA) in *N,N*-dimethylformamide (DMF) via RATRP. This article described the living polymerization of MMA in DMF with a conventional radical initiator, AIBN, and FeCl₃/lactic acid as a catalyst. The effects of the molar ratio of metal to ligand, temperature and different solvent on the polymerization were

investigated. The rate of polymerization in DMF was faster than that in acetonitrile, cyclohexanone, toluene, and xylene.

EXPERIMENTAL

Materials

MMA (A.R. grade, Tianjin Ruijinte Chemical Co., Tianjin, China) was dried over CaH_2 and distilled under reduced pressure before polymerization. AIBN (A.R. grade, Tianjin Fuchen Chemical Reagents Factory, Tianjin, China) was recrystallized from ethanol and dried in a desiccator. DMF (A.R. grade, Tianjin Ruijinte Chemical Co., Tianjin, China) was distilled at reduced pressure and stored over Type 4-Å molecular sieves before use. Anhydrous ferric chloride ($FeCl_3$, A.R. grade, Shanghai Jinghua Technology Institute, Shanghai, China), lactic acid (A.R. grade, Tianjin Ruijinte Chemical Co., Tianjin, China), and all the other reagents used were A.R. grade and used without further purification.

Polymerization

The general procedure of the polymerization was as follows. A dry glass tube with a magnetic stirring bar was filled with $FeCl_3$, lactic acid, AIBN, DMF, and MMA. Then it was vibrated until the mixture became a homogeneous solution. It was degassed in vacuum and charged with N_2 (three times) and was sealed under N_2. Then the tube was immersed in an oil bath held at the desired temperature by a thermostat. After a definite time, the tube was placed in an ice bath to stop the reaction. Afterward, the tube was opened, and the product was dissolved in tetrahydrofuran (THF). The resultant mixture was then pored into a large amount of methanol for precipitation, washed with methanol several times. The polymer was dried in vacuum drying oven at 50°C for 24 h.

Characterization

The conversion of the monomer was determined gravimetrically. The number average molecular weight ($M_{n,GPC}$) and polydispersity index (PDI) of MMA polymers were measured by gel permeation chromatography (GPC). GPC was performed with a Waters model 1515 solvent delivery system at a flow rate of 1.0 mL/min through a combination of Waters HT3, HT4, and HT5 styragel columns. PMMA standards were used to calibrate the columns. The analysis was performed at 35°C with purified high performance liquid chromatography grade-DMF as an eluant. A Waters model 2414 differential refractometer was used as the detector.
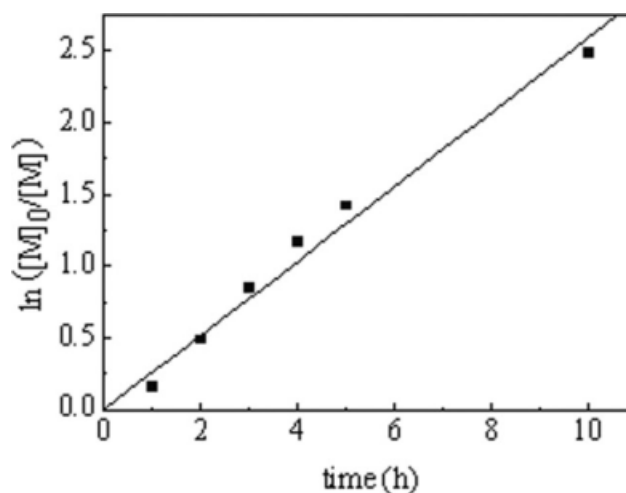
Figure 1 Time dependence of $\ln([M]_0/[M])$ at 80°C where $[M]_0$ and $[M]$ denote the MMA concentration at time 0 and t, respectively ($V_{MMA}:V_{DMF} = 1 : 1$, [MMA]:[AIBN]: [FeCl_3]:[lactic acid] = 300 : 1 : 1 : 2, V_{MMA} = 25 mL, [MMA] = 4.71 mol/L, [AIBN] = 0.0157 mol/L, [FeCl_3] = 0.0157 mol/L, [lactic acid] = 0.0314 mol/L).

RESULTS AND DISCUSSION

Polymerization of MMA with the AIBN/FeCl_3/lactic acid initiating system

RATRP of MMA in DMF was carried out with AIBN/$FeCl_3$/lactic acid initiating system at 80°C ([MMA]/[AIBN]/[FeCl_3]/[lactic acid] = 300 : 1 : 1 : 2). After heating, a change of color from deep orange to light yellow was observed, as described by Teyssié and coworkers.[20] This corresponded to the decomposition of AIBN and the establishment of the equilibrium between Fe^{3+} and Fe^{2+}. Figure 1 showed a kinetic plot of $\ln([M]_0/[M])$ versus time. The linearity of the plot indicated that the polymerization was approximately first-order with respect to the monomer concentration. The slope of the kinetic plots indicated that the concentration of propagating radicals remained constant during the polymerization process.

The radical polymerization rate can be expressed in the following equation:

$$-d[M]/dt = k_p[P\cdot][M] \qquad (1)$$

by integration of eq. (1), the kinetic equation was obtained as:

$$\ln([M]_0/[M]) = k_p^{app}t \qquad (2)$$

From eq. (2), the apparent rate constant (k_P^{app}) was obtained from the plot of $\ln([M]_0/[M])$ versus time, the k_p^{app} was 3.88×10^{-5} s^{-1}.

Figure 2 showed the dependence of the molecular weight and the PDI of obtained PMMA versus monomer conversion. The molecular weight
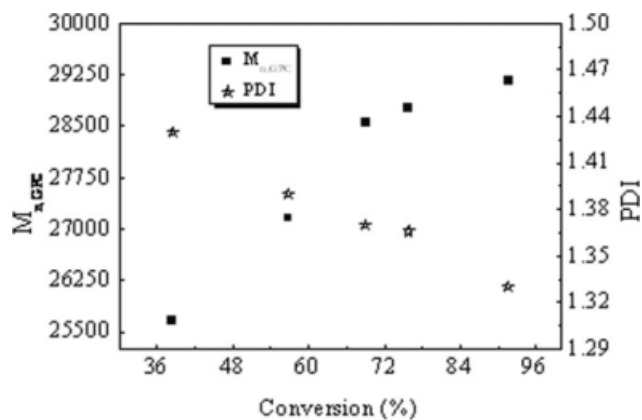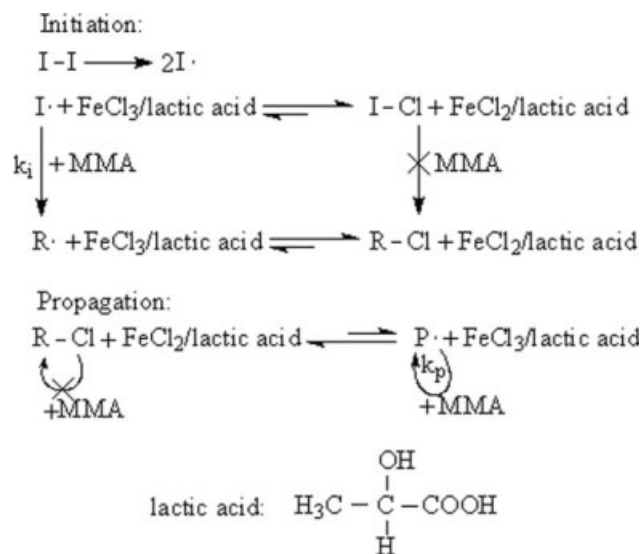
Figure 2 Dependence of $M_{n,GPC}$ and PDI on the monomer conversion for the RATRP of PMMA ($V_{MMA}:V_{DMF} = 1 : 1$, [MMA]:[AIBN]:[FeCl$_3$]:[lactic acid] = 300 : 1 : 1 : 2, $V_{MMA} = 25$ mL, [MMA] = 4.71 mol/L, [AIBN] = 0.0157 mol/L, [FeCl$_3$] = 0.0157 mol/L, [lactic acid] = 0.0314 mol/L, T = 80°C).

Scheme 1 Polymerization mechanism of RATRP of MMA including the ligand structure, k_i = initiation constant, k_p = propagation constant.

increased almost linearly with monomer conversion when it was below 69%. The linear line of the molecular weight versus monomer conversion indicated the absence or an insignificant amount of transfer reaction. However, the molecular weight began to deviate when the monomer conversion was over 69%. This indicated that some chain transfer or termination occurred when marked autoacceleration behaved. The PDI of the resulting polymer decreased from 1.43 to 1.33 in the course of conversion from 38.41% to 91.59%.

A polymerization mechanism was proposed to be as depicted in Scheme 1. The initiation step was the hemolytic decomposition of one AIBN (I-I) into two primary radicals (I·). Then the primary radicals could react with the monomer to create propagating/growing chains or directly react with FeCl$_3$/lactic acid complex by abstracting the chlorine atom to generate an organic chloride and a lower oxidation state metal complex FeCl$_2$/lactic acid. Finally, the polymer propagated via a conventional ATRP process.

Effect of FeCl$_3$/lactic acid catalytic system on RATRP of MMA

The molar ratio of [FeCl$_3$]/[lactic acid] played an important role in the polymerization rate, the molecular weight, and the PDI. A series of experiments of RATRP of MMA in DMF were carried out at various molar ratios of [FeCl$_3$]/[lactic acid] at 80°C. The results have been compiled in Table I. Table I showed that as more FeCl$_3$/lactic acid was added (entries 2, 5, 6), slower polymerization rates and narrower PDI were observed. The concentration of FeCl$_3$/lactic acid affected the concentration of the radicals as well as the rate of the initiating radicals and the propagating radicals to the dormant species. Indeed, if there was not enough FeCl$_3$/lactic acid, the radicals formed would not be stabilized and the termination reaction occurred; if there was too much of FeCl$_3$/lactic acid, the rate of the polymerization would probably be very slow because of its inhibiting effect. That suggested the concentration of FeCl$_3$/lactic acid had a favorable influence on the

TABLE I
Data for the RATRP of MMA Initiated by AIBN/FeCl$_3$/lactic Acid

Entry	[AIBN]:[FeCl$_3$]:[lactic acid]	[FeCl$_3$] (mol/L)	[lactic acid] (mol/L)	Conversion (%)	$M_{n,GPC}$	PDI	$k_p^{app} \times 10^5$ (s^{-1})
1	1 : 1 : 1	0.0157	0.0157	75.22	28,606	1.41	3.88
2	1 : 1 : 2	0.0157	0.0314	91.59	29,155	1.33	6.89
3	1 : 1 : 4	0.0157	0.0628	79.59	27,910	1.34	4.41
4	1 : 1 : 6	0.0157	0.0942	76.96	27,408	1.38	4.08
5	1 : 2 : 4	0.0314	0.0628	70.24	22,420	1.24	3.37
6	1 : 3 : 6	0.0471	0.0942	20.14	12,564	1.10	0.63

$V_{MMA}:V_{DMF} = 1 : 1$, [MMA]:[AIBN] = 300 : 1, $V_{MMA} = 25$ mL, [MMA] = 4.71 mol/L, [AIBN] = 0.0157 mol/L, T = 80°C, $t = 10$ h.

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TABLE II
Data of the Polymerization of MMA at Various Concentrations of AIBN

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Entry	[MMA]:[AIBN]	[AIBN] (mol/L)	[FeCl$_3$] (mol/L)	[lactic acid] (mol/L)	Conversion (%)	$M_{n,GPC}$	PDI	$k_p^{app} \times 10^5$ (s^{-1})
1	300 : 1	0.0157	0.0157	0.0314	91.59	29,155	1.33	6.89
2	400 : 1	0.0118	0.0118	0.0236	82.28	44,910	1.41	4.81
3	500 : 1	0.0106	0.0106	0.0212	83.03	37,149	1.36	4.93
4	600 : 1	0.0079	0.0079	0.0158	73.49	43,326	1.44	3.69
5	800 : 1	0.0059	0.0059	0.0118	74.98	55,172	1.44	3.85

$V_{MMA}:V_{DMF} = 1 : 1$, [AIBN]:[FeCl$_3$]:[lactic acid] $= 1 : 1 : 2$, $V_{MMA} = 25$ mL, [MMA] $= 4.71$ mol/L, $T = 80°C$, $t = 10$ h.

activation as well as equilibrium of RATRP. Lower or higher concentrations of lactic acid resulted in a low reaction rate (Entries 1, 2, 3, 4). Entries 2, 3, 4 showed that a further increase in the amount of lactic acid decreased the reaction rate, while PDI remained narrow. This illustrated that a large amount of lactic acid poisoned the metal catalyst, and it had a role in producing a more significant side reaction, such as a reaction with active species, or catalyzing the elimination of the initiator. In summary, FeCl$_3$/lactic acid with the molar ratio of 1 : 2 not only gave the good control of the molecular weight and its distribution but also provided rather rapid polymerization rate.

Effect of initiator concentration on RATRP of MMA

The polymerization of MMA with various initiator concentrations was investigated. The data were demonstrated in Table II. When [MMA]:[AIBN] = 300 : 1, the PMMA sample with $M_{n,GPC} = 29,155$, and PDI = 1.33 (entry 1) was obtained, this system showed good control for the polymerization of MMA. Table II showed that the conversion and the value of k_p^{app} decreased with the initiator concentration, and the PDI remained narrow (<1.45). The polymerization rate increased with an increase of initiator concentration, which was a result of more radicals being generated by the decomposition of initiator.

Effect of the polymerization temperature on RATRP of MMA

The effect of the polymerization temperature on RATRP of MMA was investigated over a temperature range of 70–90°C. The apparent rate constant and the rate of polymerization increased with increasing temperature, because of the increase in both the rate constant for radical propagation and the atom transfer equilibrium constant.[2] The polymerization could be better control at higher temperature, but chain transfer and other side reactions become more prominent at elevated temperatures.[30] The optimum polymerization temperature of MMA

using AIBN/FeCl$_3$/lactic acid as initiating system was 80°C.

The Arrhenius plot obtained from the experimental results was showed in Figure 3. The apparent activation energy was calculated to be 47.90 kJ/mol. Using $\Delta H_{prop} = 22.19$ kJ/mol and the following equation:[31]

$$\Delta H_{eq}^0 = \Delta H_{app} - \Delta H_{prop} \qquad (3)$$

where ΔH_{eq}^0 is the enthalpy of the equilibrium, ΔH_{app} is the apparent enthalpy of activation, and ΔH_{prop} is the activation enthalpy of propagation. Δ_{eq}^0 was calculated to be 25.71 kJ/mol for RATRP of MMA catalyzed by FeCl$_3$/lactic acid.

Effect of solvent on RATRP of MMA

To study the effect of solvents on RATRP of MMA, DMF, acetonitrile, cyclohexanone, toluene, and xylene were used as solvents. The results of these experiments were shown in Table III. The dielectric constants of the solvents are in the following order: ε_{DMF} (37.6, 20°C), $\varepsilon_{acetonitrile}$ (37.5, 20°C), $\varepsilon_{cyclohexanone}$ (18.2, 20°C), $\varepsilon_{toluene}$ (2.335, 20°C), and ε_{xylene} (2.4, 20°C). The polymerization was quite sensitive to the
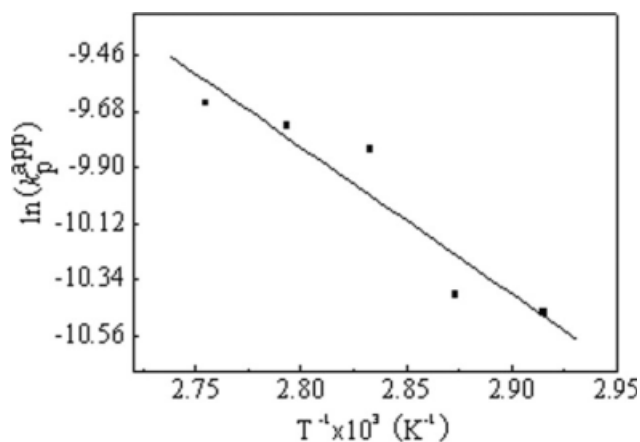

Figure 3 Effect of temperature on k_p^{app} ($V_{MMA}:V_{DMF} = 1 : 1$, [MMA]:[AIBN]:[FeCl$_3$]:[lactic acid] $= 300 : 1 : 1 : 2$, $V_{MMA} = 25$ mL, [MMA] $= 4.71$ mol/L, [AIBN] $= 0.0157$ mol/L, [FeCl$_3$] $= 0.0157$ mol/L, [lactic acid] $= 0.0314$ mol/L, $t = 10$ h).

Entry	Solvent	Conversion (%)	$M_{n,\text{GPC}}$	PDI	$k_p^{\text{app}} \times 10^5$ (s^{-1})
1	DMF	91.59	29,155	1.33	6.89
2	Acetonitrile	70.20	25,962	1.34	3.36
3	Cyclohexanone	45.33	23,765	1.35	1.68
4	Toluene	70.19	67,630	1.65	3.36
5	Xylene	41.49	44,236	1.72	1.49

V_{MMA}:V_{DMF} = 1 : 1, [MMA]:[AIBN]:[FeCl$_3$]:[lactic acid] = 300 : 1 : 1 : 2, V_{MMA} = 25 mL, [MMA] = 4.71 mol/L, [AIBN] = 0.0157 mol/L, [FeCl$_3$] = 0.0157 mol/L, [lactic acid] = 0.0314 mol/L, T = 80°C, t = 10 h

polarity of the solvent which could affect the metal complex structure. In a polar solvent, such as DMF, acetonitrile, Cl$^-$Fe^{2+}(lactic acid)$_2$Cl$^-$ may exist, but in a less polar solvent, (lactic acid)FeCl$_3$Fe(lactic acid) could exist.[32] The polarity of the solvent can also affect the rate of polymerization. A polar solvent can increase the solubility of the catalyst in MMA. A more polar solvent, such as DMF, provides a homogeneous catalytic system during the entire polymerization period, which was well controlled. This leads to a rapid establishment of equilibrium between Fe(II) and Fe(III). As shown in Table III, the rate of polymerization in DMF was faster than that of in others. In this study, there was no induction period in the polymerization, which was quite different from Teyssié and coworkers[20] reported. It could be explained that FeCl$_3$/lactic acid had good solubility in DMF and the concentration of the catalyst was larger than that in others. From Table III, we could also see the PDI in polar solvents was narrower than that in others. Thus, solvent polarity played an important role in controlling the polymerization reaction.

CONCLUSIONS

Well-defined PMMA was synthesized using a new initiating system consisting of AIBN, FeCl$_3$, and lactic acid. The rate of polymerization followed the first order with respect to the monomer. When the molar ratio of FeCl$_3$ to lactic acid was 0.5, the polymerization was best controlled. Increasing the dosage of catalyst would decrease the rate of polymerization and enhanced the degree of controlled polymerization. The rate of polymerization increased with increasing polymerization temperature, and the apparent activation energy was calculated to be 47.90 kJ/mol. The rate of polymerization in DMF was faster than that in acetonitrile, cyclohexanone, toluene, and xylene.

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