

Reverse Atom Transfer Radical Polymerization of MMA via Immobilized Catalysts in Imidazolium Ionic Liquids

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ABSTRACT: Reverse atom transfer radical polymerization (RATRP) of methyl methacrylate (MMA) employing immobilized catalyst was approached at 50 and 60°C in [C₈mim]PF₆, and compared with the polymerization of MMA DMF as solvent. Other ionic liquids, [C₆mim]BF₄, [C₈mim]BF₄, and [C₁₂mim]BF₄, were used as solvents to perform the RATRP of MMA. By comparison, we found that the [C₈mim]PF₆ was the best solvent in this immobilized catalyst system and the polymerization was best con-

trolled. In addition, the immobilized catalyst spherules can easily separate from the reaction mixture, which avoids the prevalent problem of the catalyst residual in RATRP and also gives us a possibility to recycle the catalyst system. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 3915–3919, 2007

Key words: reverse ATRP; immobilized catalyst; imidazolium ionic liquids

INTRODUCTION

It is well known that the advent of atom transfer radical polymerization (ATRP) has provided promising methods in the fields of synthesis polymers with predictable molecular weight, narrow polydispersity, and well-defined architecture.^{1–3} In both ATRP and reverse ATRP (RATRP), a transition metal complex is used to catalyze the redox process, which is responsible for the generation and concentration mediation of the propagating species.^{4–10} Thus the catalysts and the solution added in reaction are of great importance. A problem for both ATRP and RATRP is the low catalyst efficiency and the high catalyst concentration required. In addition, removal of catalyst from the resultant polymer to avoid contamination is unavoidable but intractable though many efforts have been done to resolve this problem.^{11–13} In addition, most (R)ATRP was performed commonly at a relatively high temperature, which is prone to generate side reaction.

Room temperature ionic liquids (RTILs) are molten organic salts at or near room temperature. It is

expected that the nonvolatile, nonflammable, and recyclable ionic liquids are environmental friendly media for green physical and chemical processes, such as separations, extractions, and chemical reactions.^{14–16} Recently, the application of ionic liquids as benign solvents in radical polymerization have been utilized^{17–19} since Carmichael et al.²⁰ first reported the use of 1-butyl-3-methylimidazolium hexafluorophosphate ([C₄mim]PF₆) as solvent in the copper (I)-mediated ATRP of methyl methacrylate (MMA). The polymerization was relatively fast and had a narrow polydispersity. And the ionic liquids containing catalysts were easily separated from the resultant polymer and unreacted monomer.

In this article, we first successfully used the immobilized catalyst to carried out the RATRP of MMA in [C₈mim]PF₆. We synthesized the nitrogen-based ligand anchored onto the crosslinked polystyrene and the polymer-supported ligand chelating with CuCl₂ formed the immobilized catalyst system of RATRP. So some disadvantages in conventional ATRP such as the separation of catalyst and toxicity of initiator can be avoided in some degree. The RATRP of MMA was carried out in different ionic liquids and in DMF, respectively. It was found that [C₈mim]PF₆ is an ideal solvent for RATRP of MMA in this polymerization system and the polymerization temperature could decrease to 50°C. In addition, the obtained PMMA and the immobilized catalyst could be easily separated from ionic liquid and recycled. Furthermore, the ionic liquid also could be reused as reaction solvent after simple purification without affecting the living nature of polymerization.

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EXPERIMENTAL

Materials

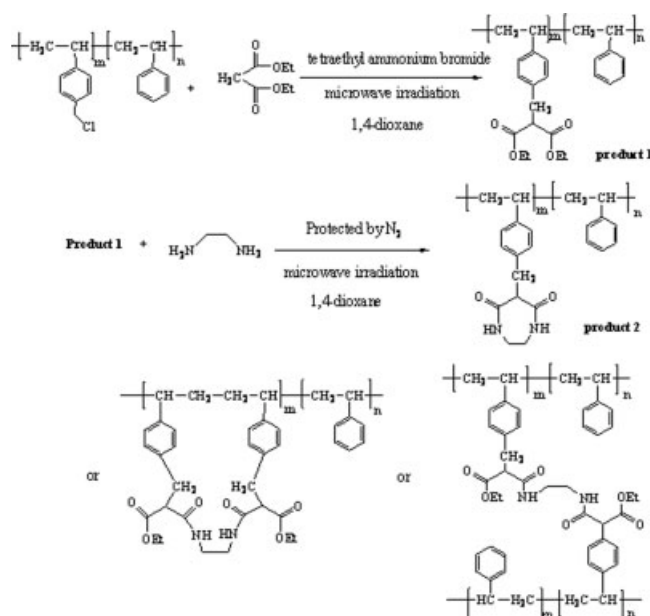
Chloromethylized crosslinked polystyrene (Chlorine content: 18% crosslinked degree: 3.5%, beads diameter 1 mm) was purchased from Naikai university in Tianjin, China. Diethylmalonate (AR), *N,N*-dimethyl formamide (DMF, AR), tetrahydrofuran (THF, AR), ethane-1,2-diamine (AR), and methyl methacrylate (MMA, AR) were all purchased from Shanghai Chemical Reagent, Shanghai and distilled under reduced pressure before use. CuCl_2 (AR) and 2,2-azobisisobutyronitrile (AIBN, AR) were recrystallized and dried at room temperature under vacuum. The ionic liquids were prepared according to previously literatures methods.^{21,22} Other solvents and reagents were used without further purification except as noted.

Instruments for characterization

FTIR spectra were recorded on Nicolet Magna 550 FTIR spectrometer with KBr discs. XPS spectra were performed on Perkin-Elmer PHI5000C X-rays energy spectrometer. ^1H NMR was performed on an INOVA 400 MHz spectrometer in CDCl_3 . ^{13}C NMR of the immobilized catalyst was measured on Varian Infinity Plus 300 MHz Solid State NMR using CP plus function. The number-average molecular weights (M_n) and molecular polydispersity (PDI) of PMMA samples were determined by Waters 1515 gel permeation chromatograph (GPC) conducted in tetrahydrofuran (THF) solution at 298 K with polystyrene as standard.

Synthesis of polymer-supported catalyst

In a three-necked flask, 20 g of washed crosslinked chloromethylated polystyrene was swelled in 1,4-dioxane (250 mL). Diethylmalonate (60 g), aqueous solution of potassium hydroxide (250 mL, 4.29 mol/L), and tetraethyl ammonium bromide (8 g) were added in turn. The three-necked flask was heated by a self-improved microwave oven at 90°C. After a certain period of time, the product was filtrated from the solvent, washed with acetone, and dried under infrared light. A yield of 43% was obtained by analysis of the element chlorine in Product 1. Then in a three-necked flask, Product 1 was swelled in 1,4-dioxane for 3 h. Ethane-1,2-diamine was added and the flask was heated by microwave in reflux under nitrogen atmosphere for a certain time and the polymer-supported catalyst was obtained after Product 2 linked with CuCl_2 . The detailed synthetic procedure was shown in Scheme 1.



Scheme 1 Synthesis route of polymer-supported ligand.

Polymerization

To a dry glass tube, Product 2– CuCl_2 [0.2 g, MMA (1 g, 10 mmol), AIBN (0.016 g, 0.1 mmol), and ionic liquid (1 g)] were added in. The mixture was degassed by three freeze-pump-thaw cycles and sealed under N_2 . The tube was placed in an oil bath at 50°C maintained by a thermostat. After a required time the flask was put into an ice bath to stop the reaction. The reaction mixture was dropped into 200 mL of methanol. After filtration, washed with methanol, and dried under infrared light, PMMA was obtained. The conversion of monomer was determined gravimetrically after the polymer was dried under infrared light for 24 h.

The polymerization of MMA was also performed by using DMF (2 mL) as solvent in the similar way at 80°C. The polymer was obtained by the same process.

RESULTS AND DISCUSSION

Characterization of polymer supported catalyst

New crosslinked catalyst with azocrown ether functional side chain was characterized by FTIR spectra and the solid-state ^{13}C NMR. The FTIR spectra of Product 1 exhibits the characteristic absorption band of $-\text{C}=\text{O}$ in carboxy at 1747.6 cm^{-1} . The stretching vibration absorption of $-\text{C}=\text{O}$ at 1651 cm^{-1} and $-\text{N}-\text{H}$ at 3318 cm^{-1} in acylamino group also appeared in the FTIR spectra of Product 2. Furthermore, the solid-state ^{13}C NMR confirmed the structure of the polymer-supported ligand. As shown in Figure 1, the band at 34–39.6 ppm was ascribed to the absorption of methylene and methenyl in main chain of polystyrene. And the band at 126.7–

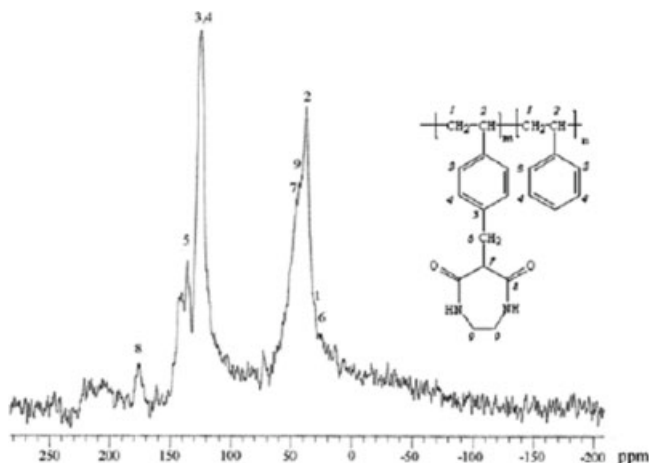


Figure 1 The solid-state ^{13}C NMR (300 MHz) spectra of Product 2.

137.4 ppm is the absorption of benzene ring in polystyrene. After annelation, the absorption band of the quaternary ^{13}C in diethyl malonate at 52.4 ppm and two peaks of ^{13}C in $-\text{C}=\text{O}$ at about 173 ppm were appeared in Product 2. We can conclude that the annelation has performed successfully and the annulus can be formed in three different situations (Scheme 1). Each of them is effective to catalyze ATRP as solid catalyst.

The XPS spectra showed the binding energy of Product 2, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, and Product 2-Cu (II) in Table I, from which we can see that the binding energy of $\text{Cu}2\text{p}_{3/2}$, $\text{Cu}2\text{p}_{1/2}$ in $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ are 934.2, 954.6 eV, respectively. After coordination, the 2p electron's binding energy values of Cu (II) $\text{Cu}2\text{p}_{3/2}$, $\text{Cu}2\text{p}_{1/2}$ were lower than those before coordination by 3.4 and 2.8 eV, respectively. These significant shifts were due to the coordination between Cu (II) and N atoms.

End group analysis of obtained PMMA

The ^1H NMR spectrum of obtained PMMA synthesized in $[\text{C}_8\text{mim}]\text{PF}_6$ was shown in Figure 2. The signals at 0.83–1.21 ppm, 1.43–2.132 ppm, and 3.41–3.78 ppm were attributed to protons of α -methyl groups (peak a), methylene groups (peak b), and methoxy groups (peak c), respectively. The absorption at 1.21 ppm (peak a_1), 2.132 ppm (peak b_1), and 3.78 ppm

TABLE I
Electron Binding Energy (eV) of XPS of Product 2 and Product 2-CuCl₂

Sample	$\text{Cl}_{2\text{p}}$	$\text{N}_{1\text{s}}$	$\text{Cu}_{2\text{p}}^{2+}$		
			Master peak	Shoulder peak	
			$2\text{p}_{3/2}$	$2\text{p}_{1/2}$	
Product 2		401.2			
$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	199.2		935.2	954.9	945.1
Product 2-CuCl ₂	198.1	403.25	931.8	952.1	Weak

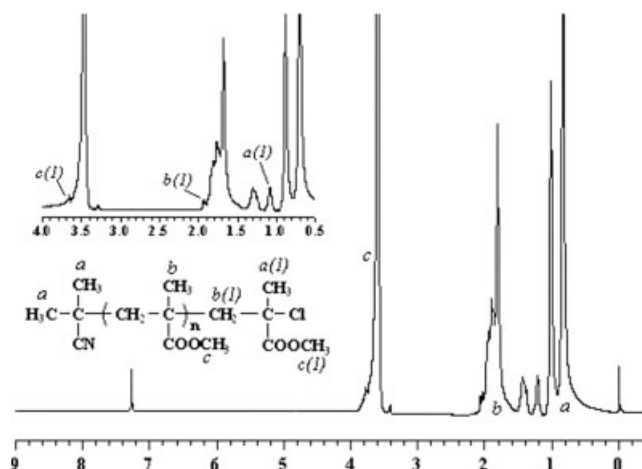


Figure 2 The ^1H NMR spectrum of PMMA initiated with $[\text{MMA}]/[\text{AIBN}]/[\text{Product 2-CuCl}_2] = 100 : 1 : 1$ $[\text{MMA}]/\{[\text{C}_8\text{mim}]\text{PF}_6\} = 1 : 1$ (M : M), temperature = 50°C.

(peak c_1) proved the presence of end group: $-\text{CH}_2\text{CCl}(\text{CH}_3)(\text{COOCH}_3)$. It showed that the polymerization was performed by RATRP.

RATRP of MMA in $[\text{C}_8\text{mim}]\text{PF}_6$ and DMF

It was the heterogeneous polymerization in this initiating system containing AIBN/Product 2-CuCl₂/ $[\text{C}_8\text{mim}]\text{PF}_6$ due to the good solubility of other ingredients in ionic liquid. When MMA was polymerized in bulk using $[\text{C}_8\text{mim}]\text{PF}_6$ as solvent at 50°C, the RATRP of MMA was proceeded in a well-controlled manner and the monomer conversion reached 75% and the kinetic plot was linear as shown in Figure 3. As expected, the crosslinked catalyst spherule is well-preserved in $[\text{C}_8\text{mim}]\text{PF}_6$ while other reaction mixture were all homogenous.

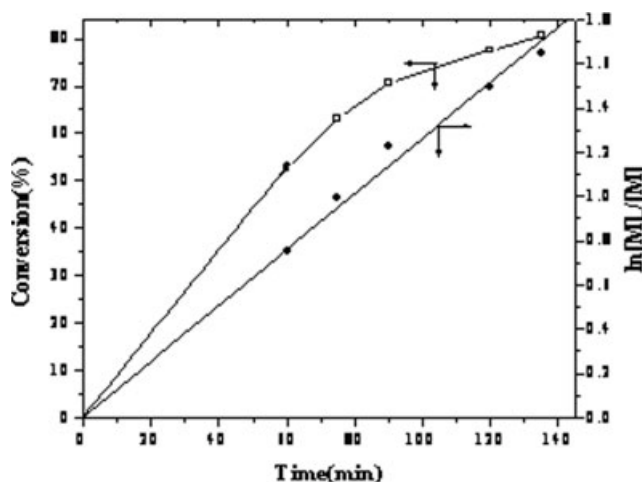


Figure 3 The kinetic plots of MMA polymerization using immobilized catalyst system in ionic liquid composed of AIBN and Product-CuCl₂. Polymerization condition: $[\text{MMA}]/[\text{AIBN}]/[\text{Product 2-CuCl}_2] = 100 : 1 : 1$ $[\text{MMA}]/\{[\text{C}_8\text{mim}]\text{PF}_6\} = 1 : 1$ (M/M), temperature = 50°C.

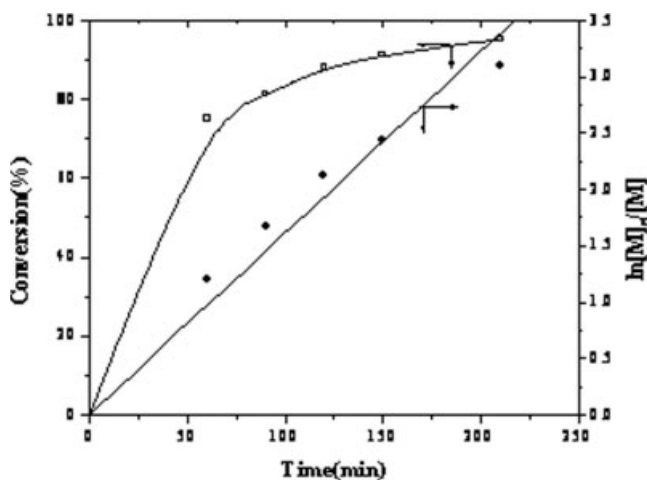


Figure 4 The kinetic plots of MMA polymerization using immobilized catalyst system in DMF composed of AIBN and Product 2-CuCl₂. Polymerization condition: [MMA]/[AIBN]/[Product 2-CuCl₂] = 100 : 1 : 1 [MMA]/[DMF] = 1 : 2 (V/V), temperature = 80°C.

The polymerization was performed in comparison with using ordinary solvent. Figure 4 showed the kinetic plot of RATRP of MMA in DMF solution at 80°C. The monomer conversion was approximate to that of the polymerization performed in ionic liquid at 50°C in the same period of time. When the conversion of MMA exceeded 60%, the polymerization became ill-controlled, which may be caused by the poor solubility of the immobilized catalyst and the growth of viscosity in the mixture of DMF solution. But in [C₈mim]PF₆, the rate constant of the polymerization at 50°C ($k_p^{app} = 26.8 \times 10^{-5} \text{ s}^{-1}$) was close to that in DMF at 80°C ($k_p^{app} = 21.1 \times 10^{-5} \text{ s}^{-1}$), although the reaction temperature was lower by 30°C.

As shown in Figures 5 and 6, the molecular weight of polymer increased with conversion and the polydispersity versus conversion remain lower in ionic liquid than that in DMF. The imidazolium ionic liquid was good solvent for the inorganic salts, Therefore, the good 'living' characteristics of RATRP of MMA might be attributed to good solubility of CuCl₂ chelated with Product 2 and the well-distributed immobilized catalyst in the reaction mixture, which remained liquid in the ionic liquid solvent. So the molecular weight of GPC was close to the calculated value in ionic liquid. While in DMF solution, the molecular weight increased with the monomer conversion, but the polydispersity was relatively high (1.76–1.84) because of deactivation rate of growing MMA chains was not fast contrast with the PMMA propagating.

RATRP of MMA using different ionic liquids

The RATRP of MMA in the immobilized catalyst was also carried out in other ionic liquids, [C₆mim]BF₄,

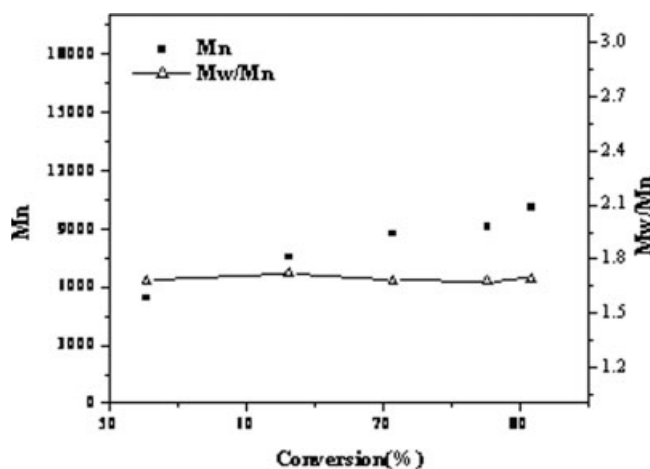


Figure 5 The dependence of molecular weight, M_n , and molecular weight distribution, M_w/M_n , upon monomer conversion for the RATRP of MMA using immobilized catalyst composed of AIBN and Product 2-CuCl₂. Polymerization condition: [MMA]/[AIBN]/[Product 2-CuCl₂] = 100 : 1 : 1 [MMA]/[C₈mim]PF₆] = 1 : 1 (M : M), temperature = 50°C.

[C₈mim]BF₄, and [C₁₂mim]BF₄, respectively. The solubility of PMMA in ionic liquids was [C₈mim]PF₆ > [C₁₂mim]BF₄ > [C₈mim]BF₄ > [C₆mim]BF₄, which got close touch with the result of polymerization. The reaction mixture kept heterogeneous and remained liquid all the reaction time in [C₈mim]PF₆ and [C₁₂mim]BF₄, while the reaction mixture in [C₆mim]BF₄ and [C₈mim]BF₄ turned viscous after 1 h.

The results of RATRP of MMA in the ionic liquids were shown in Table II. The $M_{n,GPC}$ of the obtained polymer in all the different ionic liquid is higher than its $M_{n,th}$. It maybe caused by the cage effect of

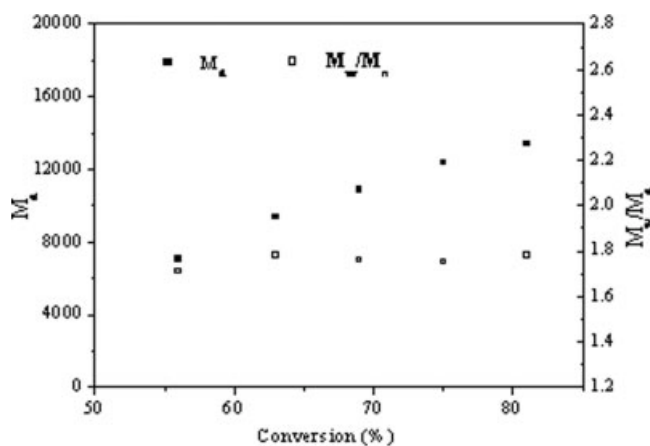


Figure 6 The dependence of molecular weight, M_n , and molecular weight distribution, M_w/M_n , upon monomer conversion for the RATRP of MMA using immobilized catalyst composed of AIBN and Product 2-CuCl₂. Polymerization condition: [MMA]/[AIBN]/[Product 2-CuCl₂] = 100 : 1 : 1 [MMA]/[DMF] = 1 : 2 (V/V), temperature = 80°C.

TABLE II
Reverse ATRP of MMA Using Different Ionic Liquids
in Presence of Immobilized Catalyst

Solvent ^a	Temperature (°C)	Time (h)	Conversion (%)	$M_{n,th}^b$	$M_{n,GPC}$	Polydispersity
[C ₆ mim]BF ₄	60	1.5	57	2,850	14,079	1.72
[C ₈ mim]BF ₄	60	1.5	68	3,400	12,311	1.65
[C ₁₂ mim]BF ₄	60	1.5	74	3,700	10,890	1.55
[C ₈ mim]PF ₆	60	1.5	75	3,750	8,560	1.50

^a Polymerization condition: MMA (1 g); ionic liquid (1 g); [MMA]/[AIBN]/[Product 2-CuCl₂] = 100 : 1 : 1.

^b $M_{n,th} = 100 \times ([MMA]/2[AIBN]) \times \text{Conversion}$.

high viscous ionic liquid, which led to more coupling reaction of primary radicals and the relatively lower solubility of PMMA in ionic liquid than that in conventional organic solvent like anisole and DMF. The high molecular weight of PMMA was reasonably attributed to prolonged life of the propagation radicals. The molecular weight distribution of the RATRP is relatively high (>1.50) for the immobilized catalyst in this initiator system. But better the solvating power of ionic liquid is, better the polymerization could be controlled. In [C₈mim]PF₆, the conversion and the initiating efficiency of the RATRP is the highest and the polydispersity is the lowest, which is touched to 1.50.

CONCLUSIONS

A RATRP of MMA using immobilized catalyst in ionic liquids was carried out successfully at relatively low temperature. The results show that [C₈mim]PF₆ is the best solvent in which the polymerization was well-controlled and the reaction temperature of RATRP in ionic liquid was reduced to 50°C. The immobilized catalyst and the obtained polymer can easily separate from the reaction mixture. And the immobilized catalyst and ionic liquid can both recycled in further polymerization.

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