Methyl Methacrylate Homopolymerization and Copolymerization with Styrene by Rare Earth Catalyst in Ionic Liquids

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Methyl methacrylate homopolymerization and copolymerization with styrene catalyzed by rare earth coordination catalysts were carried out in ionic liquids for the first time. It was found that the polymerization rate of MMA and molecular weight of PMMA were higher in ionic liquids than in toluene or in bulk under the same conditions. Both random and block copolymers of MMA with St could be prepared in ionic liquids. The copolymers were characterized by GPC, NMR, and IR measurements. Ionic liquids can be recycled and reused.

Ionic liquids (ILs), which are known as green and designable solvents due to their being environment benign, nonvolatile, reusable, and compatible with many organic and catalytic reactions, have attracted considerable attention as alternative solvents for a wide range of applications such as media of chemical reactions, polymerization and extraction procedures.[1–3] More recently, the use of ILs as polymerization medium has also attracted much interest.[4] Not only the conventional radical polymerization, but also the controlled radical polymerization have been carried out in ILs.[5] Carmichael et al.[5a] have reported that the polymerization rate of methyl methacrylate (MMA) mediated by CuBr/alkylpyridylmethanimine was enhanced and the required polymerization temperature was lower in 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]) than those in bulk or other organic solvents. So far, much work has been done on radical polymerization in ILs. To our knowledge, there have very few reports on the coordination polymerization in ILs.[1a,6]

Rare earth coordination catalysts, as a new kind of Ziegler–Natta type catalysts, have been exploited for the polymerizations of many monomers: butadiene, epoxides, styrene (St), methacrylates, etc.[7–9] Nevertheless, all these polymerizations were carried out in conventional organic solvents. In this work, we have explored the polymerizations of MMA by binary rare earth coordination catalyst, neodymium versatate (NdV_3)/Al(*i*-Bu)$_3$, in ILs, and have found that the polymerization rate of MMA enhanced and the molecular weight of PMMA were higher in ILs than in toluene or in bulk.

Versatic acid 10(*tert*-decanoic acid) is a kind of carboxylic acid with long side chains, which is easily available to prepare and widely used in the field of pesticide, medicine extraction and catalyst.[10] Neodymium versatate was synthesized according to our published method.[11]

Methylimidazo-Room temperature ionic liquids, 1-ethyl-3-methylimidazolium ([emim]) and 1-butyl-3-methylimidazolium ([bmim]) combined with BF_4^- or PF_6^-, were prepared according to the Ref. 12. The water in ILs obtained was removed by rotary evaporator in vacuum at 80 °C. All the polymerizations were performed in 20 mL ampoule under dry nitrogen. During the polymerization, the polymers were precipitated in ILs. The reaction was terminated by methanol with 5% hydrochloric acid, and then the polymers were washed by methanol and filtered. In order to recycle the ILs, the filtrate was passed through a neutral aluminum oxide column, and the methanol was evaporated in reduced pressure. The recovered ILs then was dried at 80 °C in vacuum to be reused. The copolymer was extracted with acetonitrile and cyclohexane in a Soxhlet for 48 h, to eliminate the homopolymer PMMA or PSt, respectively. Number average molecular weight and molecular weight distribution were determined by GPC (Waters 515 with Columns Styragel® HT3, HT4, and HT5) using THF as eluant. The results were calibrated by standard polystyrene. Table 1 shows the polymerization results.

It can be seen from Table 1 that the polymerization of MMA by NdV_3/Al(*i*-Bu)$_3$ in ILs proceeded quite well. Much higher yield and molecular weight of PMMA could be obtained in ILs than those in toluene or in bulk under the same conditions, which illustrates that the polymerization rate of MMA by NdV_3/Al(*i*-Bu)$_3$ was enhanced in ILs. The mechanism of MMA polymerization by similar rare earth catalysts Nd(P_{204})$_3$/Al(*i*-Bu)$_3$ was coordination radical process.[13] Maybe, the polymerization of MMA by NdV_3/Al(*i*-Bu)$_3$ proceeded via the same mechanism. It has been reported high molecular weight products and fast reaction rates could be obtained in the ILs than in other organic solvents or in bulk, which was explained by influences of ILs' relatively high viscosity on chain-termination processes. Moreover, precipitation of the polymeric radicals as the polymerization proceeds leads to "diffusion controlled termination" during the polymerization process.[14] The data in Table 1 also show that [emim][BF_4] gives the highest values among the four kinds of ILs used and it can be reused.

Moreover, copolymerizations of MMA with St by ternary catalytic system, NdV_3/Al(*i*-Bu)$_3$/CCl_4, were also conducted in ILs, Table 2 shows the results of copolymerization in

Table 1. MMA polymerization in ILs and toluene[a]

No.	Solvent	Yield/%	$M_n/10^3$	M_w/M_n
1	[emim][BF_4]	64.9	197.3	2.2
2	[bmim][BF_4]	48.0	191.1	2.0
3	[emim][PF_6]	40.7	120.1	1.9
4	[bmim][PF_6]	47.8	102.3	1.8
5[b]	[emim][BF_4]	57.6	189.2	2.3
6	Toluene	7.2	57.5	1.5
7[c]	—	4.2	5.3	1.4

[a]Reaction conditions: $[NdV_3] = 0.013\,mol{\cdot}L^{-1}$, $[MMA] = 3.8\,mol{\cdot}L^{-1}$, $[Al(i\text{-}Bu)_3]/[NdV_3] = 27$ (molar ratio), polymerization temperature: 60 °C, polymerization time: 6 h. [b]In recycled [emim][BF_4]. [c]Polymerization in bulk.

Table 2. Copolymerization of MMA and St in ILs[a]

No.	First-stage polymerization		Second-stage polymerization		Yield	M_n	M_w/M_n
	Monomer	Time/h	Monomer	Time/h	/%	/10^3	
8[b]	St	24	—	—	79.3	68.3	1.7
9	St	20	MMA	6	68.2	148.2	3.0
10	MMA	6	St	20	79.5	218.1	3.2
11	MMA + St[c]	24	—	—	88.6	135.1	3.0

[a]Reaction conditions: $[NdV_3] = 0.013\,mol{\cdot}L^{-1}$, $[MMA] = [St] = 1.9\,mol{\cdot}L^{-1}$, $[Al(i\text{-}Bu)_3]/[NdV_3] = 27$ (molar ratio), $[CCl_4]/[NdV_3] = 7$ (molar ratio); polymerization temperature: 60 °C. [b]Homopolymerization of St. [c]MMA and St were added simultaneously.

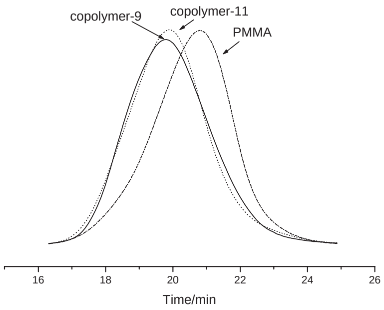

Figure 1. GPC curves of PMMA and copolymers.

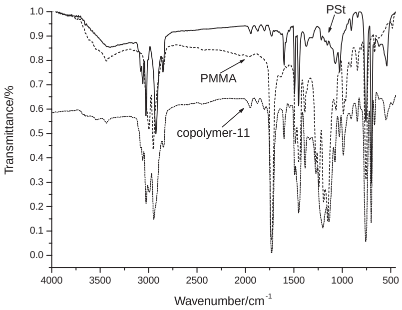

Figure 2. IR of PMMA, PSt, and copolymer.

$[emim][BF_4]$. It can be seen that both block copolymer and random copolymer of MMA with St can be prepared just by different feed sequences.

Figure 1 shows the GPC curves of PMMA and copolymer. In Table 2 and the GPC profile, there is an obvious increase in the molecular weight, which confirms the formation of diblock structural copolymer (PMMA–b–PSt). In addition, the unimodal GPC profile shows that there is no homopolymer in copolymer prepared. When MMA and St were fed simultaneously, the GPC curve also shows a unimodal peak (PMMA–co–PSt), which illustrates that there is only one active center in the polymerization process. As a result, random copolymer of MMA and St can also be prepared in $[emim][BF_4]$.

The IR spectra of PMMA, PSt, and copolymer are shown in Figure 2. By comparison of the IR spectra, there are absorption peaks of phenyl ($1600\,cm^{-1}$) and carbonyl ($1730\,cm^{-1}$) groups in the copolymer. This demonstrates that there are PMMA and PSt chains in the copolymer.

In conclusion, rare earth coordination catalyst was employed in the homopolymerization and copolymerization of MMA with styrene in ionic liquids for the first time. PMMA with a yield of 64.9% and molecular weight of 19.7×10^4 can be prepared in $[emim][BF_4]$ at 60 °C, $[emim][BF_4]$ can be recycled and reused. The yield and molecular weight of PMMA was much higher in ILs than in toluene or in bulk. Moreover, the random and block copolymers of MMA with St by ternary catalytic system were obtained in $[emim][BF_4]$. The copolymers were characterized by GPC, NMR, and IR measurements.

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References

1 a) P. Kubisa, *Prog. Polym. Sci.* **2004**, *29*, 3. b) T. Welton, *Chem. Rev.* **1999**, *99*, 2071.

2 a) Z. B. Zhou, H. Matsumoto, K. Tatsumi, *Chem. Lett.* **2004**, *33*, 1636. b) J. S. Yadav, B. V. S. Reddy, M. Srinivas, *Chem. Lett.* **2003**, *32*, 1060.

3 S. Csihony, C. Fischmeister, C. Bruneau, I. T. Horvath, P. H. Dixneuf, *New J. Chem.* **2002**, *26*, 1667.

4 a) H. Ma, X. Wan, X. Chen, Q. Zhou, *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 143. b) C. Hardacre, J. D. Holbrey, S. P. Katdare, K. R. Seddon, *Green Chem.* **2002**, *4*, 143. c) S. Perrier, T. P. Davis, A. J. Carmichael, D. M. Haddleton, *Chem. Commun.* **2002**, 2226.

5 a) J. Carmichael, D. M. Haddleton, S. A. F. Bon, K. R. Seddon, *Chem. Commun.* **2000**, 237. b) H. Y. Ma, X. H. Wang, X. F. Chen, Q. F. Zhou, *Polymer* **2003**, *44*, 5311.

6 D. C. Zhao, H. T. Xu, P. Xu, F. Q. Liu, G. Gao, *Prog. Chem.* **2005**, *17*, 700.

7 B. T. Huang, Z. Q. Shen, in *Progress in Coordination Polymerization of Olefin and Diene*, ed. by B. T. Huang, Z. Q. Shen, Science Press, Beijing, **1998**, Chap. 9, p. 227.

8 L. M. Jiang, Z. Q. Shen, Y. F. Zhang, F. R. Zhang, *J. Polym. Sci., Part A: Polym. Chem.* **1996**, *34*, 3519.

9 Z. Q. Shen, J. Ouyang, F. S. Wang, Z. Y. Hu, F. S. Yu, B. G. Qian, *J. Polym. Sci., Part A: Polym. Chem.* **1980**, *18*, 3345.

10 a) H. Y. Lee, S. G. Kim, J. K. Oh, *Hydrometallurgy* **2004**, *73*, 91. b) R. P. Quirk, A. M. Kells, K. Yunlu, *Polymer* **2000**, *41*, 5903.

11 Z. Q. Shen, W. Q. Chen, H. R. Zhao, F. S. Wang, in *Collection of Synthetic Rubber Catalyzed by Rare Earth Catalysts*, ed. by Changchun Institute of Applied Chemistry, Science Press, Beijing, **1980**, p. 381.

12 Y. L. Yang, X. H. Wang, Y. Kou, *Chin. J. Catal.* **2004**, *25*, 60.

13 Y. F. Zhang, Q. Su, Z. Q. Shen, *Acta Polym. Sin.* **1994**, 653.

14 K. Hong, H. Zhang, J. W. Mays, A. E. Visser, C. S. Brazel, J. D. Holbrey, W. M. Reichert, R. D. Rogers, *Chem. Commun.* **2002**, 1368.