Effect of the Medium on the Stereostructure of Poly(methyl methacrylate) Synthesized in Ionic Liquids

Da Li, Yumei Zhang, Huaping Wang, Jianzhong Tang, Biao Wang

State Key Laboratory for Modification of Fiber Materials, Donghua University, Shanghai, 200051, People's Republic of China

ABSTRACT: Poly(methyl methacrylate) (PMMA) was synthesized in different ionic liquids (IL) by free radical polymerization. The average molecular weight and polydispersity of the PMMA were measured by gel permeation chromatography. It is found that ILs have effect not only on the molecular weights but also on the stereostructure of PMMA. From the FTIR and NMR analysis, it was confirmed that the chemical structure of PMMA synthesized in ILs was similar to the one obtained in conventional solvents while the stereostructure was influenced by the different IL used. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 2199–2202, 2006

Key words: radical polymerization; ionic liquids; methyl methacrylate; gel permeation chromatography (GPC); NMR

INTRODUCTION

Ionic liquids (ILs), as well as water and supercritical fluids, have been known as prospective environmental friendly media for green physical and chemical processes.[1] ILs are composed of organic cations and inorganic anions. They are nonvolatile, highly polar solvents that dissolve several organic, inorganic, and metalo-organic compounds.[2] Therefore, ILs have been widely applied in electrochemical processes, separations, extractions, chemical and biochemical reactions, and functional materials.[3–5]

ILs have been explored as reaction media in various organic transformations. In addition, the unique properties exhibited by ILs can lead to significant improvements in the rate, yield, and selectivity of reactions.[6] The use of ILs as a polymerization medium has also recently attracted considerable interest. In 1984, Pickup and his coworkers first described the polymerization of pyrrole in *N*-alkylpyridinium chloroaluminate.[7] From 1990s, many polymerizations, including free radical, living/controlled free radical (ATRP and RAFT), electrochemical, condensation, ring-opening metathesis, block, and statistical polymerization have been carried out in various ILs with the development of air and water-stable ILs.[8–10] Interestingly, in spite of high polarity of ILs that would rather make them potentially attractive solvents for ionic polymerization, the research on radical polymerizations has still attracted great interests for the researchers.[2] Mays and his coworkers[11–14] conducted free radical polymerization of MMA and St in several ILs and found that the polymer formed in ILs had molecular weights up to 10 times higher than samples synthesized in benzene. It has been found using pulse laser polymerization technique[15] that the rate constant of methyl methacrylate propagation increases considerably when polymerization is carried out in IL ([BMIM][PF$_6$]). Furthermore, Benton and coworkers[16–18] used [BMIM]PF$_6$ as solvents in the free radical solution polymerization of poly (methyl methacrylate) (PMMA). They also found that the degree of polymerization was five times higher in [BMIM]PF$_6$ than in benzene, while the rate of reaction was approximately four times faster in [BMIM]PF$_6$. However, we found that the IL used can not only lead to rapid reaction rates and high molecular weights for polymerization but also have effect on the stereostructure of the polymer synthesized, as well.[19] In this article, we reported the free radical polymerization of MMA in different solvents. The influence of ILs on the steric regularity of PMMA will be discussed in detail.

EXPERIMENTAL

Materials

MMA (CP, 99%) was distilled to remove inhibitors and stored in calibrated ampules. ILs, including 1-butyl-3-methylimidazolium chloride ([BMIM]Cl), 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIM]BF$_4$),

TABLE I
Polymerization Data for Methyl Methacrylate in Different Solvents

Samples	Solvent	MMA (wt %)	Temperature (°C)	AIBN (wt %)	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$
PMMA1	Acetontrile	25	65	1	5335	9877	1.855
PMMA2	[BMIM]Cl	25	65	1	27,699	31,218	1.127
PMMA3	[EMIM]BF$_4$	25	65	1	32,197	37,497	1.165
PMMA4	[BMIM]BF$_4$	25	65	1	41,278	48,562	1.176

and 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM]BF$_4$), were synthesized in our laboratory and purified according to the literature.[3] AIBN (AR, 97%) was recrystallized from methanol and dried under vacuum. Acetonitrile and methanol (AR, > 99.5%) were used as received.

Free radical polymerization

Solutions of monomers (25 wt %) in ILs and acetonitrile were polymerized with AIBN (1 wt %, based on the monomer) as initiator under nitrogen at 65°C for 3 h. The raw product was purified by washing with methanol to remove residual IL and monomer, filtered, and dried under high vacuum to constant weight.
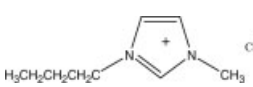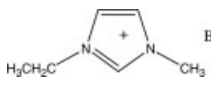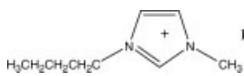
Instrumentation

Molecular weights and polydispersity, $\overline{M}_w/\overline{M}_n$, were determined with a Waters gel permeation chromatograph (GPC, model 1500) with Ultrastyragel columns (7.8 × 300 mm^2) of 10^4, 10^5, and 10^6 Å porosities, using THF as the eluent. The experiments were carried out at 50°C, with an injection volume of 200 μL and a pumping rate of 1 mL/min.

FTIR curves were obtained using Nicolet NEXUS-670 spectrometer with the distinguishing rate of 0.09 cm^{-1}. The polymer was blended with KBr to prepare the samples.

NMR spectra of the polymer were recorded on a Bruker ARX-400 spectrometer at room temperature. The sample concentration was about 5 wt % in CDCl$_3$.

RESULTS AND DISCUSSION

Molecular weight and molecular weight distribution

Polymerization of MMA was carried out in ILs using AIBN as initiator. To compare the results, parallel experiment was done in acetonitrile under the same conditions. The polymerization data were shown in Table I.

GPC analysis shows considerable differences in molecular weight and polydispersities for PMMA synthesized in different solvents. In all cases, the molecular weights of PMMA polymerized in ILs were much higher than that in acetonitrile (3–5 times higher). However, the polydispersities ($\overline{M}_w/\overline{M}_n$) of PMMA in ILs were lower than those in acetonitrile. The results were accordant with Strehmel's report.[9] It is also clear that the structure of IL had little effect on the polydispersities while it influenced the molecular weight dramatically.

The higher viscosity of ILs when compared with acetonitrile presumably is regarded as one reason for this phenomenon (shown in Table II). Because of the high viscosity polymerization medium, both chain terminations and/or chain transfers were diminished in viscous system. In the case of ILs having the same cation ([BMIM]BF$_4$, [EMIM]BF$_4$), the viscosity of ILs increases with the chain length of the alkyl group substituted at the nitrogen atom of the imidazolium ring. Meanwhile, the longer chain of the substituted alkyl group increases the solubility of PMMA in ILs, which makes the viscosity of the polymerization system grow much higher. Although the mechanism of

TABLE II
Structure and Viscosity of the Solvents

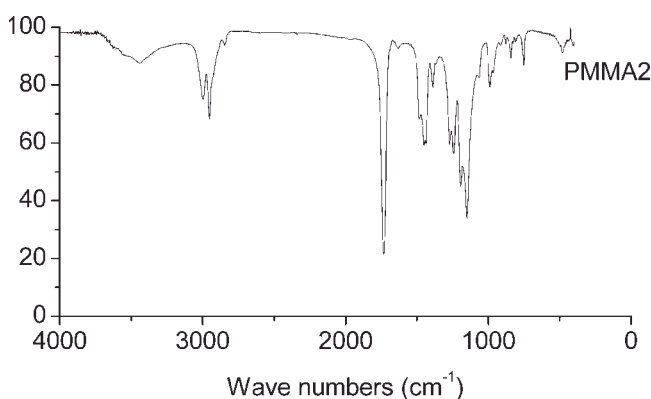| Solvent	Structure	Viscosity (cP)
Acetontrile	CH$_3$CN	0.35 (293 K)
[BMIM]Cl		1100 (298 K)
[EMIM]BF$_4$		43 (298 K)
[BMIM]BF$_4$		233 (303 K)

Figure 1 FTIR spectra of the PMMA2 sample.

TABLE III
Chemical Shifting of PMMA Synthesized in Different Solvents

Chemical shifting (ppm)	$-CH_3$	$-\overset{\mid}{\underset{\mid}{C}}-$	$-O-CH_3$	$-CH_2-$	$\overset{\mid}{C}=0$
PMMA1	16.54	44.59	51.80	54.66	177.79
PMMA2	16.51	44.58	51.82	54.45	177.80
PMMA3	16.56	44.60	51.81	54.45	177.80
PMMA4	16.54	44.59	51.80	54.45	177.83

TABLE IV
Proportion of Two Absorptions (A_{751}/A_{1388}) Data

Sample	A_{751}/A_{1388}
PMMA1	1.296
PMMA2	0.973
PMMA3	1.196
PMMA4	1.138

TABLE V
Diads and Triads Content of PMMA Calculated Based on ^{13}C NMR Peak of Quaternary Carbon Atom

Samples	ρ	m	r	rr	mr	mm
PMMA1	1.000	0.221	0.779	0.607	0.344	0.049
PMMA2	0.898	0.228	0.772	0.576	0.392	0.032
PMMA3	0.969	0.219	0.781	0.604	0.353	0.043
PMMA4	1.001	0.223	0.777	0.604	0.346	0.050

the polymerization in ILs was not completely understood at the present time, according to the "diffusion-controlled termination" mechanism proposed by Zhang and coworkers,[14] both of these effects could contribute to the observed relative increase in molecular weight. However, in the case of the ILs having the same anion ([BMIM]BF$_4$, [BMIM]Cl), the molecular weight of PMMA2 is lower although the viscosity of [BMIM]Cl is much higher than that of [BMIM]BF$_4$.

In addition to the viscosity effects, the ionic structure of ILs would lead to special interaction between ILs and macromolecules, which will influence the steric regularity of the macromolecular chain. So the structure of PMMA polymerized in different solvent will be discussed in the following section.

Chemical structure of PMMA

The chemical structure of PMMA synthesized in ILs was analyzed by FTIR and NMR. Figure 1 illustrates the FTIR spectra for PMMA, which can be identified
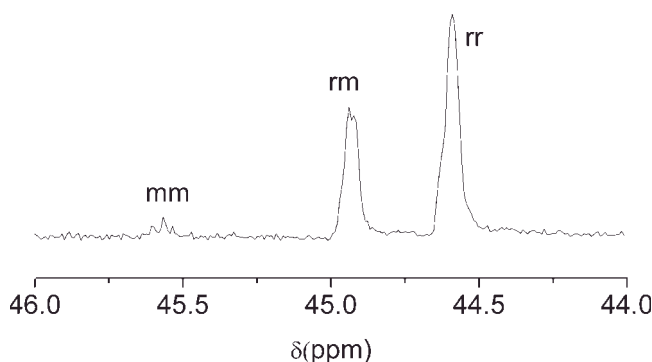
from the main absorption peaks as follows: The absorption peak of C=O stretch is at 1727 cm^{-1} and the absorption peak of C—O stretch at 1140–1170 cm^{-1}. There is no absorption peak of C=C stretch from MMA. It confirms that the chemical structure of PMMA synthesized in ILs is same as that in acetonitrile.

The ^{13}C NMR spectra show the characteristic peaks of CH$_3$, $-\overset{\mid}{\underset{\mid}{C}}-$, —O—CH$_3$, —CH$_2$—, and C=O at about 16.5, 44.6, 51.8, 54.5, and 177.8 ppm respectively, as shown in Table III. It clearly demonstrates that ILs had no obvious effect on the chemical shifts of carbon atom in PMMA.

Stereoregularity analysis

The stereoregularity of PMMA synthesized in ILs and acetonitrile were analyzed by FTIR and NMR.

According to the triads distribution, the stereoregularity of PMMA can be grouped into isotactic (mm), syndiotactic (rr), and atactic (mr) structure. In the FTIR spectrum of PMMA, three absorption peaks at 751, 910, and 1063 cm^{-1} are attributed to the syndiotactic structure and the absorption peak at 757 cm^{-1} is characteristic of the isotactic structure. From Figure 1, it can be seen that the absorption peak at 757 cm^{-1} is very weak, which indicates that there is little isotactic structure in PMMA even synthesized in ILs. The polymerization mechanism is similar to that obtained in common solvents. As it is known, the steric hindrance of the substituted group
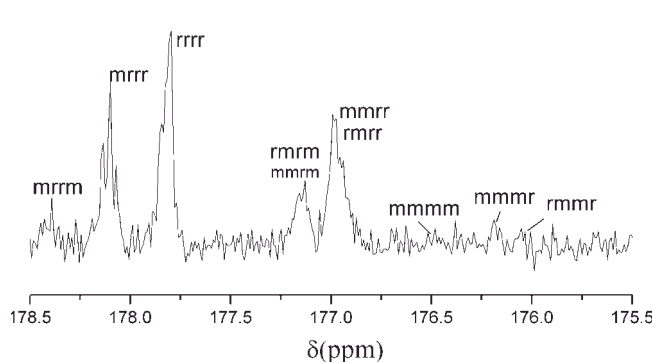

Figure 2 Chemical shift of quaternary carbon atom and the corresponding stereo structure.

Figure 3 Chemical shift of tetrad carbon atom and the corresponding stereo structure of PMMA.

TABLE VI
Experimental and Calculated Pentads Content of PMMA

	PMMA1		PMMA2		PMMA3		PMMA4	
	E	FM	E	FM	E	FM	E	FM
mmmm	0.006	0.001	0.001	0.001	0.001	0.008	0.009	0.002
mmmr	0.024	0.011	0.013	0.014	0.069	0.035	0.029	0.014
rmmr	0.009	0.027	0.029	0.046	0.009	0.043	0.039	0.031
mmrm	0.002	0.016	0.080	0.081	0.071	0.030	0.071	0.027
rmrm	0.105	0.080	0.002	0.068	0.105	0.063	0.105	0.119
mmrr	0.006	0.049	0.273	0.057	0.180	0.087	0.074	0.057
rmrr	0.287	0.236	0.001	0.210	0.003	0.180	0.146	0.249
mrrm	0.041	0.037	0.027	0.036	0.032	0.037	0.047	0.053
rrrm	0.207	0.224	0.209	0.223	0.220	0.215	0.157	0.225
rrrr	0.321	0.321	0.368	0.346	0.310	0.303	0.323	0.338
Deviation σ	/	0.029	/	0.008	/	0.027	/	0.033

E, experimental data; FM, first order Markov model.

$—COOCH_3$ on PMMA chain make the C—C in the end of growing chain rotate, which is helpful to form syndiotactic and atactic structures. The syndiotactic content of PMMA can be calculated by the absorptions peak ratio of A_{751}/A_{1388}. From Table IV, it is shown that the high viscosity and polarity of ILs can partially influence the stereo structure of PMMA, which leads to less formation of syndiotactic structure.

In the ^{13}C NMR spectrum of PMMA (shown in Fig. 2), the peak of quaternary carbon atom splits into three peaks at 44.6, 44.9, and 45.5 ppm corresponding to syndiotactic (rr), atactic (mr), and isotactic (mm) structure, respectively. The triad content of the stereoregularity can be calculated from Figure 2 and we obtained the continuous ratio ($\rho = 2(m)(r)/(mr)$) of the syndiotactic (r) diad and atactic (m) diad further (shown in Table V). The isotactic (mm) peak is also very weak, which is coordinated with the FTIR results. At the same time, the syndiotactic content of PMMA2 polymerized in [BMIM]Cl is low and the continuous ratio deviated from 1. It is suggested that the polymerization kinetics of PMMA2 in [BMIM]Cl is not accordant with Bernouli model.

The stereoregularity of PMMA can be analyzed further from the pentads distribution of tetrad carbon atom in ^{13}C NMR spectrum. The splitting peak of the tetrad carbon atom is much more complicated (shown in Fig. 3). There are eight stereo sequences corresponding to the isotactic (mmmm), syndiotactic (rrrr), and atactic structure. It also reveals that the atactic structure (mmmm) is not significant. Further calculation data based on the pentad sequences and statistic models is shown in Table VI. It indicates that the experimental pentad concentrations of PMMA2, polymerized in [BMIM]Cl, is more close to the calculated value by first order Markov model. It further confirmed that the high viscosity and interaction between [BMIM]Cl and the radical chain have effect on the stereo structure of PMMA, so the poly-merization kinetics of MMA in [BMIM]Cl well coordinated with first order Markov model. The terminal effect is more dramatic in [BMIM]Cl.

CONCLUSIONS

This research clearly shows that ILs are feasible replacement solvents for free radical polymerization of PMMA. The molecular weights of PMMA polymerized in ILs were 3–5 times higher than that in acetonitrile, with lower polydispersities. The syndiotactic content of PMMA polymerized in [BMIM]Cl is low and the stereo sequence well coordinated with first order Markov model, which indicated that there is an end group effect in the polymerization in [BMIM]Cl.

References

1. Seddon, K. R. J Chem Technol Biotechnol 1997, 68, 351.
2. Kubisa, P. Prog Polym Sci 2004, 29, 3.
3. Friberg, S. E.; Yin, Q.; Pavel, F. J Dispersion Sci Technol 2000, 21, 185.
4. Suarez, P. A. Z.; Selbach, V. M.; Dullius, J. E. L. Electrochim Acta 1997, 42, 2533.
5. Sedden, K. P.; Cooper, A. I.; Scott, K.; Winterton, N. Macromolecules 2003, 36, 4549.
6. Welton, T. Chem Rev 1999, 99, 2071.
7. Oudard, J. F.; Allendoerfer, R. D.; Osteryoung, R. A. J Electroanal Chem 1988, 241, 231.
8. Biedron, T.; Kubisa, P. J Polym Sci Part A: Polym Chem 2002, 40, 2799.
9. Strehmel, V.; Kraudelt, H.; Wetzel, H. Polym Prepr 2004, 45, 323.
10. Gao, H.; Jiang, T.; Han, B. Polymer 2004, 45, 3017.
11. Harrison, S.; Mackenzie, S. R.; Haddleton, D. M. Macromolecules 2003, 36, 5072.
12. Zhang, H.; Hong, K.; Mays, J. W. Macromolecules 2002, 35, 5735.
13. Zhang, H.; Hong, K.; Mays, J. W. Chem Commun 2003, 1356.
14. Zhang, H.; Hong, K.; Mays, J. W. Polym Prepr 2004, 45, 331.
15. Zhang, H.; Hong, K.; Mays, J. W. Polym Prepr 2004, 45, 313.
16. Scott, M. P.; Brazel, C. S.; Benton, M. G. Chem Commun 2002, 1370.
17. Benton, M. G.; Brazel, C. S. Polym Int 2004, 53, 1113.
18. Benton, M. G.; Brazel, C. S. Polym Prepr 2002, 43, 881.
19. Cheng, L.; Zhang, Y. M.; Zhao, T. T. Macromol Symp 2004, 216, 9.