



Radiation induced polymerization of MMA in imidazolium ionic liquids and their mixed solutions with organic solvents

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ABSTRACT

Considerably higher molecular weight (M_w) and multi-modal molecular weight distribution (MWD) of poly(methyl methacrylate) (PMMA) were observed in neat ionic liquids ([bmim][PF₆] and [bmim][BF₄]), as well as their mixed solutions with organic solvents, probably due to the high viscosity and inhomogeneity of ionic liquids. FTIR spectra for PMMA showed that a slight amount of ionic liquid remained in the resulting polymer, and DSC measurement indicated the increase of glass transition point of PMMA with increasing of ionic liquid fraction in mixed solutions.

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1. Introduction

Room temperature ionic liquids (RTILs) have attracted growing interest in the application as reaction media for polymerization. A lot of work on free radical polymerization has been carried out using ionic liquids as media in common reaction routes. In these polymerization processes, it is realized that the presence of ionic liquid results in a considerably higher molecular weight and an enhanced polymerization rate (Kubisa, 2004; Hong et al., 2002). Recently, it was observed that the stereostructure of poly(methyl methacrylate) (PMMA) was also influenced by the imidazolium based ionic liquids ([bmim]Cl and [bmim][BF₄]) (Li et al., 2006). An atom-transfer radical polymerization of MMA in several ionic liquids demonstrated that the initiator efficiency decreased as higher quantities of IL were used (Sarbu and Matyjaszewski, 2001). In addition, polymer gels by in situ radical polymerization of MMA in an ionic liquid ([emim][TFSI] or [bmim][PF₆]) were investigated, and it was found that the addition of ionic liquid induces a decrease of glass transition point and an increase of ionic conductivity of the gels (Susan et al., 2005; Jiang et al., 2006).

In comparison, there are still few reports on radiation polymerization in RTILs, although irradiation is an easy method to initiate polymerization of vinyl monomer. Generation of radicals and solvated electrons induced by radiation in ionic liquids has been observed experimentally, these transient species can be utilized to initiate polymerization, in a manner similar to the radiation polymerization in water and conventional organic solvents. Pulsed laser induced polymerization of MMA in ionic

liquid [bmim][PF₆] was reported by Harrison et al. (2003). Microwave-assisted homogeneous free radical polymerization of MMA in water-soluble ionic liquids ([bmim][BF₄] and [bmim][OTf]) revealed a more efficient heating profile of the reaction mixtures (Guerrero-Sanchez et al., 2007). Radiation polymerization of vinyl monomers in a quaternary ammonium based ionic liquid ([Me₃NC₂H₄OH][ZnCl₃]) has been reported in our previous work. Compared to the high moisture sensitivity and incommodity of very high viscosity of quaternary ammonium based ionic liquids, imidazolium based ionic liquids with good stability to water and air may be more suitable in polymerization. In this work, radiation polymerization of MMA was carried out in two typical imidazolium based ionic liquids, hydrophobic [bmim][PF₆] and hydrophilic [bmim][BF₄], as well as in RTIL/organic (DMF or THF) mixed solutions. High monomer conversion, high molecular weight and multi-modal molecular weight distribution (MWD) are observed in the presence of ionic liquid, especially in neat ionic liquids. FTIR spectra and DSC curves showed that the presence of ionic liquid affects the structure and enhances the glass transition point of resulting PMMA.

2. Experimental section

2.1. Materials

All reagents were of the commercially available highest purity. [bmim][BF₄] and [bmim][PF₆] were purchased from Hangzhou Chemer Chemistry Company (purity ~99%). RTILs were kept in vacuum at 100 °C overnight to remove volatile impurities such as water and volatile organic substances remained in ionic liquids

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before use. MMA, DMF and THF were distilled under reduced pressure to remove impurities prior to the use.

2.2. Polymerization and analysis

In all cases, 5.0 vol% newly distilled MMA was added into the ionic liquid or the RTIL/organic solution. After bubbling N_2 gas to remove the air, samples (about 4.0 mL) sealed in glass ampoules were subjected to ^{60}Co rays from the cobalt-60 source in Shanghai Institute of Applied Physics, exposed to a total dose of 5 kGy at a dose rate of 5.3 Gy/min. The resulting polymers were separated by dropping slowly the irradiated samples into an excess amount of cooled methanol and drying the precipitated product at 60 °C for 24 h under vacuum.

Gel permeation chromatography (GPC) is used to analyze the molecular weight and MWD; eight standard polystyrene samples were used for the calibration. GPC measurements were carried out using THF (flow rate: 1.0 mL/min) at 35 °C, using a Waters pump and a differential refractive index detector. Viscosity was measured on Ares rheometer with a rolling cylinder at room temperature (298.15 K) at shear rate of $15.8 s^{-1}$. Glass transition point was determined by differential scanning calorimetry (DSC-822e, Mettler-Toledo Corporation). The samples were scanned from -50 to 200 °C at a programmed rate of 10 °C/min, using indium to calibrate the temperature and heat flow of the DSC device. Polymer samples were characterized by FTIR on Nicolet infrared spectrophotometer (Avatar-360).

3. Results and discussion

3.1. Polymerization of MMA in [bmim][PF₆]/organic mixed solutions

Fig. 1 shows the GPC traces of PMMA obtained from radiation polymerization in [bmim][PF₆]/DMF and [bmim][PF₆]/THF mixed

solutions. It is seen that the MWD changes from narrow single-mode in pure DMF and THF to broad multi-mode in the mixed solutions. However, a clear difference in the MWD pattern is observed between [bmim][PF₆]/DMF and [bmim][PF₆]/THF. For the [bmim][PF₆]/DMF system, the addition of ionic liquid leads to a multi-modal MWD of PMMA at RTIL 40–80 vol%, indicating a remarkable effect of the ionic liquid on molecular weight and MWD. For the [bmim][PF₆]/THF system, a single-modal MWD is observed up to RTIL 40 vol% and the MWD curve of PMMA at RTIL 60–80 vol% is composed of two broad overlapping peaks. Peak position and relative peak intensity changed continuously but not significantly with an increase of the [bmim][PF₆] fraction. In pure [bmim][PF₆], multi-modal MWD becomes more complicated and the M_w corresponding to the main peak of GPC is very high.

Weight-average molecular weights of all the fitted (Gaussian distribution) components are illustrated in Table 1. The M_w of PMMA obtained in pure DMF and THF is about $1-2 \times 10^4$. However, the M_w of main component increases substantially to 1.07×10^6 (a 50-fold increase) in neat [bmim][PF₆]. Moreover, at RTIL 60–80 vol%, the M_w of the main peak in [bmim][PF₆]/DMF system is $\sim 2 \times 10^5$, but the M_w in [bmim][PF₆]/THF is $\sim 4 \times 10^4$. The M_w of PMMA increases much less with an increase of the [bmim][PF₆] content in RTIL/organic mixed system. This comparison reveals that the choice of organic solvent also considerably affects the M_w and MWD of PMMA. Similar but less significant effects of RTIL on chemically induced radical polymerization have also been observed. Hong et al. (2002) found that the PMMA and polystyrene samples formed in [bmim][PF₆] had molecular weights up to 10 times higher than PMMA formed in benzene. Furthermore, Benton and Brazel (2004) found polymerization degree of PMMA was five times higher in [bmim][PF₆] than in benzene, while the rate of reaction was approximately four times faster in [bmim][PF₆].

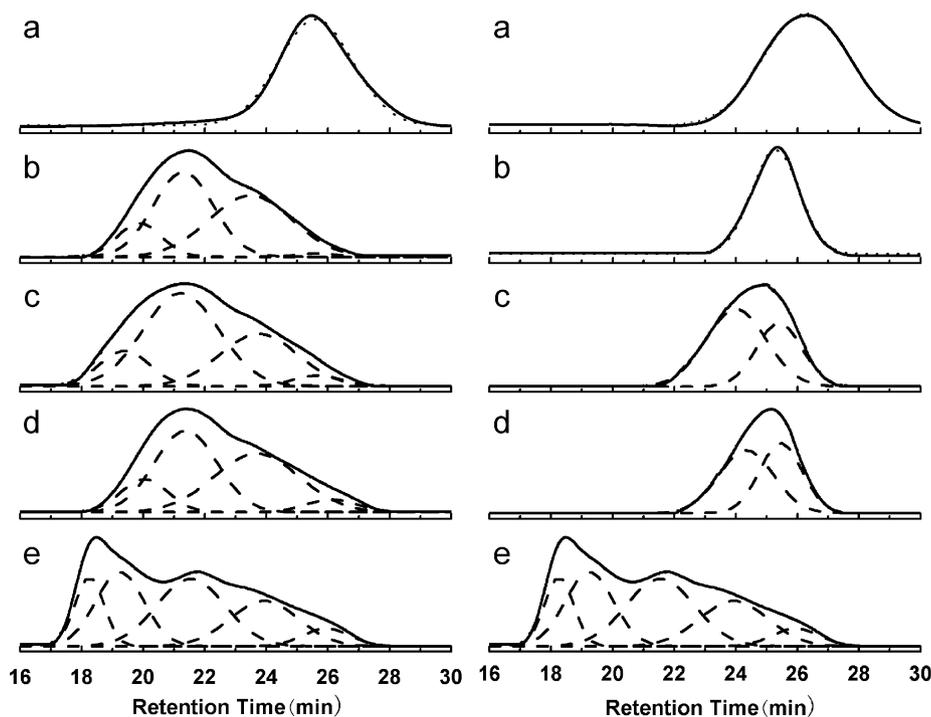


Fig. 1. GPC traces of PMMA obtained by radiation polymerization in [bmim][PF₆]/DMF (left) and [bmim][PF₆]/THF (right) mixed solutions at a dose of 5 kGy (dose rate: 5.3 Gy/min). [bmim][PF₆]/Organic (v/v): (a) pure DMF (or THF), (b) 2/3, (c) 3/2, (d) 4/1 and (e) pure IL.

Table 1
Calculated M_w and relative peak area for each Gaussian distribution component of PMMA in [bmim][PF₆]/DMF and [bmim][PF₆]/THF mixed solutions shown in Fig. 1

IL/DMF (or THF) v/v	PMMA in [bmim][PF ₆]/DMF			PMMA in [bmim][PF ₆]/THF		
	Retention time (min)	Relative peak area	M_w	Retention time (min)	Relative peak area	M_w
Pure IL	18.3	43	1.80×10^5	18.3	43	1.80×10^5
	19.2	78	1.07×10^6	19.2	78	1.07×10^6
	21.5	100	6.27×10^5	21.5	100	6.27×10^5
	23.9	68	4.97×10^4	23.9	68	4.97×10^4
	25.9	18	1.68×10^4	25.9	18	1.68×10^4
4/1	20.0	31	4.07×10^5	24.3	100	4.00×10^4
	21.4	100	1.97×10^5	25.5	31	2.18×10^4
	23.7	98	5.67×10^4			
	26.1	13	1.52×10^4			
3/2	19.4	25	5.79×10^5	24.0	100	4.78×10^4
	21.2	100	2.14×10^5	25.5	61	2.18×10^4
	23.8	58	5.47×10^4			
	25.7	7	1.94×10^4			
2/3	19.9	29	4.45×10^5	25.3	100	2.38×10^4
	21.3	99	2.06×10^5			
	23.5	100	6.32×10^4			
	25.6	3	1.97×10^4			
Pure DMF (or THF)	25.4	100	2.26×10^4	26.3		1.38×10^4

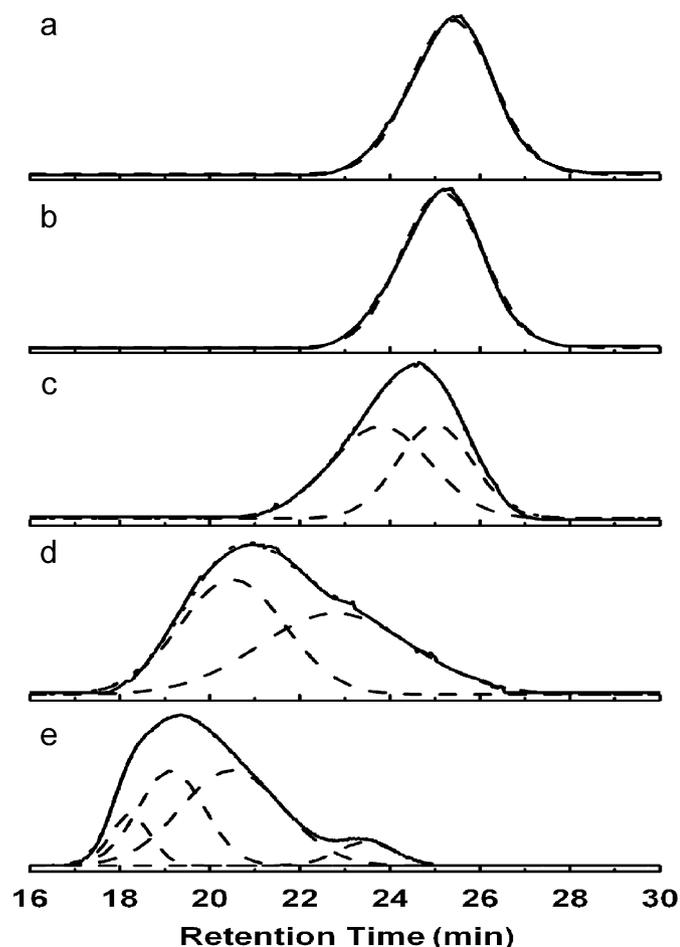


Fig. 2. GPC traces of PMMA obtained by radiation polymerization in [bmim][BF₄]/THF mixed solutions at a dose of 5 kGy (dose rate: 5.3 Gy/min). [bmim][BF₄]/THF (v/v): (a) 1/4, (b) 2/3, (c) 3/2, (d) 4/1 and (e) pure IL.

Table 2
Calculated M_w and relative peak area for each Gaussian distribution component of polymers in [bmim][BF₄]/THF mixed solutions shown in Fig. 2

IL/THF v/v	PMMA in [bmim][BF ₄]/THF		
	Retention time (min)	Relative peak area	M_w
Pure IL	18.2	21	6.61×10^5
	19.1	65	1.08×10^6
	20.5	100	3.19×10^5
	23.5	14	6.39×10^4
4/1	20.5	98	3.17×10^5
	22.8	100	9.22×10^4
3/2	23.8	100	5.36×10^4
	25.0	77	2.79×10^4
2/3	25.2	100	2.55×10^4
1/4	25.4	100	2.27×10^4

3.2. Polymerization of MMA in [bmim][BF₄]/THF mixed solutions

Radiation polymerization of MMA was further carried out in mixed solutions of [bmim][BF₄]/THF. This enables one to understand the difference in polymerization between two ionic liquids. As shown in Fig. 2, with the addition of [bmim][BF₄], the MWD of PMMA changes from single-modal to multi-modal distribution, and M_w of PMMA increases with the increase of [bmim][BF₄] content. At [bmim][BF₄] 20–40 vol%, the MWD of PMMA shows narrow single-modal distribution, and the M_w is only about $\sim 2 \times 10^4$; at [bmim][BF₄] 60–80 vol%, the MWD of PMMA presents overlapping double-peaks distribution, and the M_w increases from 5×10^4 to 3×10^5 ; in the neat [bmim][BF₄], the MWD of PMMA indicates obvious multi-modal distribution, and M_w of the main peak is over 1×10^6 while that of the smallest peak is less than 7×10^4 (Table 2). This is consistent with our previous observation

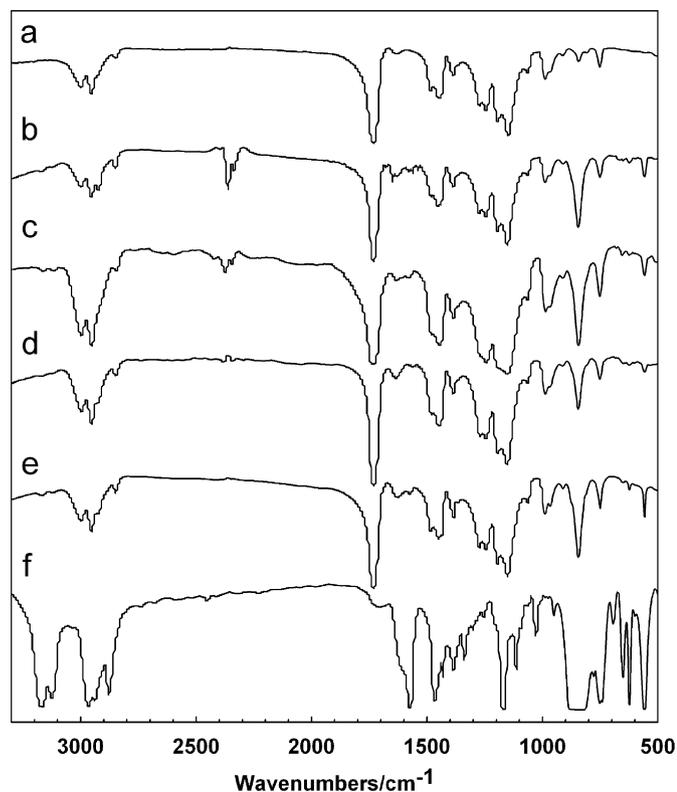


Fig. 3. FTIR spectra of neat [bmim][PF₆] and PMMA polymerized in [bmim][PF₆]/DMF mixed solutions. PMMA in [bmim][PF₆]/DMF (v/v):(a) pure DMF, (b) 2/3, (c) 3/2, (d) 4/1, (e) pure IL and (f) neat [bmim][PF₆].

on PMMA polymerized in [Me₃NC₂H₄OH]⁺[ZnCl₃]⁻/THF mixed solutions (Liu et al., 2005).

By comparing the radiation polymerization of MMA in three different ionic liquids under identical conditions, it is found in all cases that the addition of ionic liquid results in an increase of M_w of PMMA and a multi-modal MWD, and the maximal M_w is about 1×10^6 in neat ionic liquids in spite of their viscosity difference. However, the degree of change of M_w and MWD with ionic liquid fraction in RTIL/THF system is dependent on the ionic liquid used. This difference may be due to the property difference of three ionic liquids, such as viscosity, micro-phase structure, and miscibility with monomer and organic solvent.

3.3. FTIR spectra and DSC curves of PMMA obtained in [bmim][PF₆]/DMF mixed solutions

Fig. 3 shows FTIR spectra of PMMA polymerized in [bmim][PF₆]/DMF mixed solutions. Compared to PMMA obtained in pure DMF, PMMA polymerized in RTIL/DMF mixed solutions still represents the characteristic absorption vibrations at 2953, 1440 and 1244 cm^{-1} (asymmetric stretching, bending and symmetrical bending vibration of CH₃), 1485–1365 cm^{-1} (deformed vibration of C–H), 1485, 1193, 966 and 844 cm^{-1} (scissoring, twisting, wagging and rocking modes of CH₂), 1733 cm^{-1} (stretching vibration of C=O), 1272 and 1149 cm^{-1} (symmetrical and nonsymmetrical stretching vibration of C–O–C), 989 cm^{-1} (stretching vibration of CH₃–O). It is interesting that a new absorption peak is observed at 558 cm^{-1} , and absorption intensities of peaks at 845 and 752 cm^{-1} obviously increase for PMMA in polymerized in RTIL/DMF mixed solution. The higher peak intensity at 845 cm^{-1} and the appearance of peak at 558 cm^{-1} for PMMA obtained in RTIL/DMF mixed solutions are due to the P–F bond in PF₆⁻ anion. The higher absorption peak at 752 cm^{-1} is due to the C–H vibration for cyclic bmim⁺ cation.

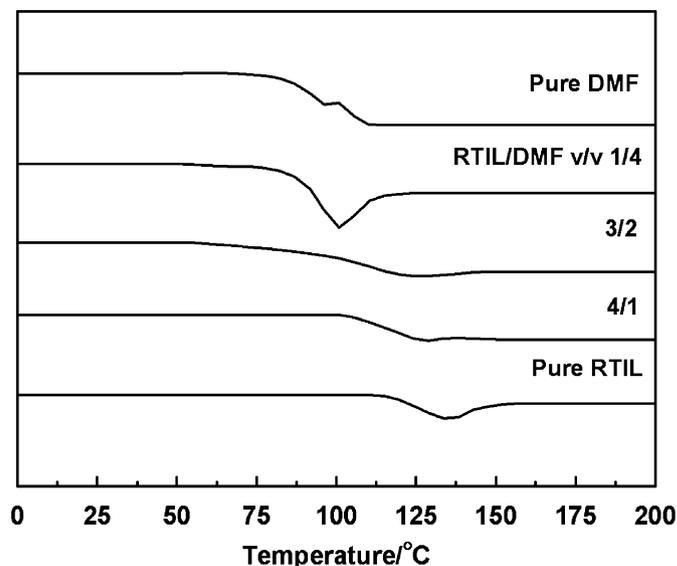


Fig. 4. DSC curves for PMMA obtained in [bmim][PF₆]/DMF mixed solutions.

Although the PMMA samples were washed by an excess amount of cooled methanol for three times, FTIR spectra indicated the presence of [bmim][PF₆] in the polymer.

Fig. 4 shows the glass transition point (T_g) of PMMA obtained in [bmim][PF₆]/DMF mixed solutions. The addition of [bmim][PF₆] results in an increase of T_g for PMMA, increasing from 103 °C in pure DMF to 134 °C in neat [bmim][PF₆]. The increase of T_g may be explained by the significantly higher molecular weight of PMMA obtained in [bmim][PF₆], weakening the segmental motion of polymer chains. The result is different from the observation of T_g of PMMA/[bmim][PF₆] binary mixture. Jiang et al. (2006) observed a decrease of T_g of PMMA/[bmim][PF₆] mixture with an increase of the mass fraction of [bmim][PF₆], in agreement with the observation by Scott et al. (2003) using [bmim][PF₆] as a plasticizer for PMMA.

3.4. Interpretation of higher M_w and multi-modal MWD in RTIL

The role of RTILs in radiation polymerization is considered to enhance the conversion rate, increase the molecular weight, and tune the MWD of polymer from single mode to multi-mode. Similar but less significant effects of RTILs on chemically induced radical polymerization have also been observed. These phenomena are likely due to the high polarity, high viscosity and inhomogeneity of the reaction media.

We measured the viscosity of [bmim][PF₆]/DMF mixed solutions with varying the RTIL content at room temperature using an Ares rheometer. As shown in Fig. 5, the viscosity of DMF is 1.31 mPa.s at room temperature, while the viscosity of neat [bmim][PF₆] is 278.4 mPa.s. The viscosity of neat [bmim][PF₆] is higher than that of pure DMF by two orders of magnitude. In [bmim][PF₆]/DMF mixed solutions, the solution viscosity increases much less with the continuous addition of [bmim][PF₆]. The viscosity is 5.09 mPa.s at RTIL 50 vol% and increases to 57.68 mPa.s at RTIL 80 vol%. The increase trend of viscosity is consistent with that of M_w of PMMA in [bmim][PF₆]/DMF mixed solutions, implying that the M_w greatly lies on the viscosity of RTIL/organic solutions. The study of pulsed laser induced polymerization of MMA in [bmim][PF₆] previously also indicated that high polarity and viscosity of ionic liquid led to higher molecular weight and monomer conversion, by increasing the propagation rate constant and decreasing the termination rate constant

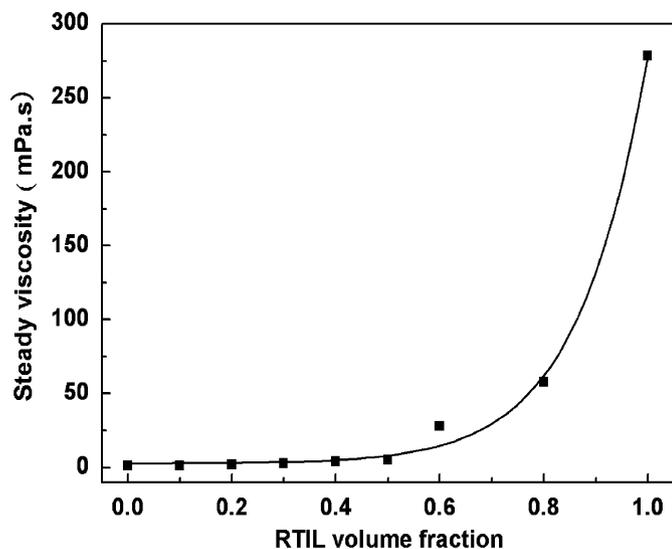


Fig. 5. Steady viscosity of [bmim][PF₆]/DMF mixed solvent vs. [bmim][PF₆] volume fraction at 298.15 K at a shear rate of 15.8 s⁻¹.

(Harrison et al., 2003). In addition, inhomogeneity of reaction media may be the major factor responsible for broad multi-modal MWD observed in radiation polymerization in RTILs. In fact, many studies on phase-equilibrium of ionic liquids and solvent/ionic liquid binary solution have revealed that ionic liquids form complex phase structure and the phase structure varies with the change of volume ratio to ionic liquids. The binary mixture may be composed of dispersed aggregates behaving like a mixture of two phases that interpenetrate themselves. The solvation dynamics studied by time dependent fluorescence spectroscopy indicated the biphasic nature of [bmim][BF₄] (Karmakar and Samanta, 2002) and [bmim][PF₆] (Ingram et al., 2003). Our previous work also found the addition of ionic liquid [Me₃NC₂H₄OH][ZnCl₃] to DMF or THF causes complex changes in phase equilibrium, which is in accordance with the observation of multi-modal MWD of polymers. The presence of microphases in the ionic liquid or in the RTIL/organic system at room temperature, radiation-induced in situ polymerization in different micro-regions leads to the formation of components with different molecular weight and MWD. As radiation can initiate polymerization uniformly in the medium, the reactions in different micro-phase area lead to the multi-modal M_w distribution of resulting polymer.

4. Conclusion

Very high molecular weight and complex multi-modal molecular weight distribution of PMMA were observed for radiation

polymerization in neat ionic liquids [bmim][PF₆] and [bmim][BF₄]. For polymerization in RTIL/organic mixed solutions, M_w of PMMA increases, but not significantly with the increase of RTIL fraction in the RTIL/organic solutions. Higher M_w and broad multi-modal MWD are explained by the high viscosity and inhomogeneity of ionic liquids, respectively. FTIR spectra for PMMA showed the presence of ionic liquid in the resulting polymer, even after repeatedly washing. The glass transition point of PMMA increased with the increase of ionic liquid fraction in the mixed solutions.

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