

# $^{60}\text{Co}$ $\gamma$ -Initiated polymerization of vinyl monomers in room temperature ionic liquid/THF mixed solutions

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## Abstract

Radiation induced polymerization of styrene (St), methyl methacrylate (MMA) and *n*-butyl methacrylate (BMA) is carried out in a room temperature ionic liquid (RTIL),  $[\text{Me}_3\text{NC}_2\text{H}_4\text{OH}]^+ [\text{ZnCl}_3]^-$ , and in its mixed solutions with THF. The presence of ionic liquid (IL) leads to a significant increase in monomer conversion and polymer's molecular weight. Molecular weight distribution (MWD) of resulting polymer varies with the IL fraction in the RTIL/THF solutions and is also dependent on the monomer used. For polystyrene (PSt) and poly(*n*-butyl methacrylate) (PBMA), multi-modal broad MWD is observed at IL > 50 v% while single-modal narrow MWD is observed at IL < 40 v%. For poly(methyl methacrylate) (PMMA), however, nearly a single-modal MWD is observed at THF > 20 v%. The measured miscibility of polymer with RTIL is in the order: PMMA > PBMA > PSt. Here we propose that the difference in MWD is due to the inhomogeneous nature of the ionic liquid in micro-region and the immiscibility of polymer with medium.

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**Keywords:** Room temperature ionic liquid (RTIL); Radiation; Polymerization

## 1. Introduction

Room temperature ionic liquids (RTILs) have many advantages [1–3] over conventional organic solvents and have attracted ever-increasing interest in recent years. The advantages often cited are non-volatility, high polarity, ease of recycling, etc. Owing to their unique properties, application of ionic liquids as reaction media for polymerization may offer some other advantages. In fact, many types of polymerization have been studied using ionic liquids as media in common reaction routes including living/controlling radical polymerization (ATRP, RAFT, NMP) [4–12], ionic and coordination polymerization [13–15], polycondensation and polyaddition [16], electrochemical polymerization [17–19], etc. In above-mentioned polymerization processes, a significantly enhanced polymerization rate was usually observed. Compared to conventional solvents, the high polarity and viscosity of ionic liquids greatly increase the propagation rate constant ( $k_p$ )

and decrease the termination rate constant ( $k_t$ ) in radical polymerization [20,21]; consequently, higher molecular weight and monomer conversion are achieved in ionic liquids.

The possibility of applying ionic liquids to processes in the nuclear industry has also been the subject of further investigation. It has been demonstrated that RTILs can be used for the extraction of metal species from aqueous media [22,23], opening a way for the potential use of ionic liquid for reprocessing spent nuclear fuel in the PUREX process. In a preliminary investigation [24], the stability of 1,3-dialkylimidazolium based ionic liquid under gamma and beta radiation was found to be close to that of benzene. Similar to the radiolysis of water and organic solvents, radiolysis of ionic liquids also generates solvated electrons, ionic radicals or transient ions [25–27], which may be utilized to initiate polymerization. RTILs may play an important role in controlling the polymerization rate and polymer properties in radiation polymerization since the radical concentration is constant during the course of irradiation [28].

As to our knowledge, however, there are still few reports on the radiation polymerization in RTILs although radiation polymerization in a number of solvents has been reported in

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the literature [29–31]. Since radiation polymerization proceeds without heating, the intrinsic property of ionic liquids may be reflected from the molecular weight ( $M_w$ ) and MWD of polymers. In a previous communication [32], polymerization of MMA in RTIL/DMF and RTIL/EtOH mixed solvents was reported. It was revealed that the so-obtained PMMA has a multi-modal MWD at higher ionic liquid fractions. In this paper, radiation-induced polymerization of three monomers (St, MMA, BMA) was investigated in detail in the RTIL/THF (tetrahydrofuran) mixed solutions. The RTIL/THF solution is chosen due to its good solvency of many polymers.

## 2. Experimental section

### 2.1. Materials

A quaternary ammonium based ionic liquid,  $[\text{Me}_3\text{NC}_2\text{-H}_4\text{OH}]^+[\text{ZnCl}_3]^-$ , is prepared according to the method described in the literature [33]. The used molar ratio of choline chloride to  $\text{ZnCl}_2$  is 1:2, making the freezing point of ionic liquid close to room temperature (23–25 °C). All chemicals used are of analytical grade and were purchased from Acros Corporation. As described previously, this ionic liquid is relatively stable under gamma radiation up to a dose of 100 kGy.

### 2.2. Polymerization in RTIL/THF mixed solvent

In all cases, 5.0 v% newly distilled monomer was added into the RTIL or the RTIL/THF mixture. After bubbling  $\text{N}_2$  gas to remove the air, samples (5.0 mL) sealed in glass ampoules were subjected at room temperature to gamma rays from the  $^{60}\text{Co}$  source in Shanghai Institute of Applied Physics. The resulting polymer was separated by pouring the irradiated sample into an excess amount of cooled methanol (over 15–20 fold); the solid product was collected by centrifugation and followed by drying at 60 °C for 24 h under vacuum. The conversion was calculated by the gravimetric method.

### 2.3. Methods

Gel permeation chromatography (GPC) is used to analyze the molecular weight and MWD; eight standard polystyrene samples with narrow polydispersity were used for the calibration. GPC measurements were carried out in THF (flow rate: 1.0 ml/min) at 35 °C, using a Waters pump and a differential refractive index detector.

Fluorescence spectra were recorded on Hitachi-FL4500 fluorospectrometer at 25 °C, all instrumental parameters keep constantly during experimental process. Viscosities were measured on Ares Rheometer with a rolling cylinder at 25 °C.

## 3. Results and discussion

### 3.1. Polymerization of vinyl monomer

Behar et al. [19] subjected  $[\text{C}_4\text{mim}]^+[\text{PF}_6]^-$  and  $[\text{C}_4\text{mim}]^+[\text{BF}_4]^-$  ionic liquids to pulsed electron beam and showed the spectroscopic evidence of the formation of transient  $[\text{C}_4\text{mim}]^\cdot$  and  $[\text{C}_4\text{mim}]^{\cdot 2+}$  radicals. Marcinek et al. [20] also observed the generation of radical ions by radiation in some other ionic liquids. In the RTIL used in this study, radical ions of choline chloride and Cl atoms may be formed by gamma radiation. These transient species as well as those from the THF radiolysis are believed to initiate the polymerization [28].

Fig. 1 shows the GPC traces of polystyrene obtained in the RTIL/THF mixed solutions. As can be clearly seen, PSt from the pure ionic liquid has a multi-modal broad MWD. Molecular weight of the main peak is over  $3 \times 10^6$  while that of the smallest peak is less than  $3 \times 10^4$ . With adding THF into the ionic liquid, the number of peaks decreases and the relative peak area and  $M_w$  of each component change continuously with the RTIL/THF ratio. Nearly a single-modal MWD is observed at RTIL/THF volume ratio of 40/60 and the corresponding  $M_w$  is about  $1.2 \times 10^5$ . When polymerized at IL 20 v% or in pure THF, PSt has definitely a single-modal narrow MWD and its  $M_w$  is much less. The  $M_w$  observed in pure THF is less than  $3 \times 10^4$ , smaller than that of the main component in the pure ionic liquid by two orders of magnitude.

To further clarify the effects of ionic liquid on the  $M_w$  and MWD, polymerization of MMA and BMA was carried out under identical conditions. As the polarity of MMA and BMA is higher than that of St and there is also a difference in polarity between MMA and BMA, one may expect a difference in MWD pattern. As shown in Fig. 2, the

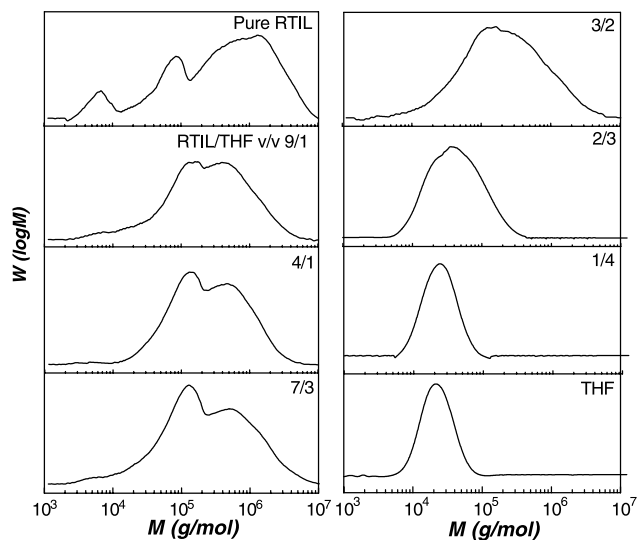


Fig. 1. GPC curves for polystyrene obtained by radiation in different solvents at the dose of 5 kGy (dose rate: 5.3 Gy/min).

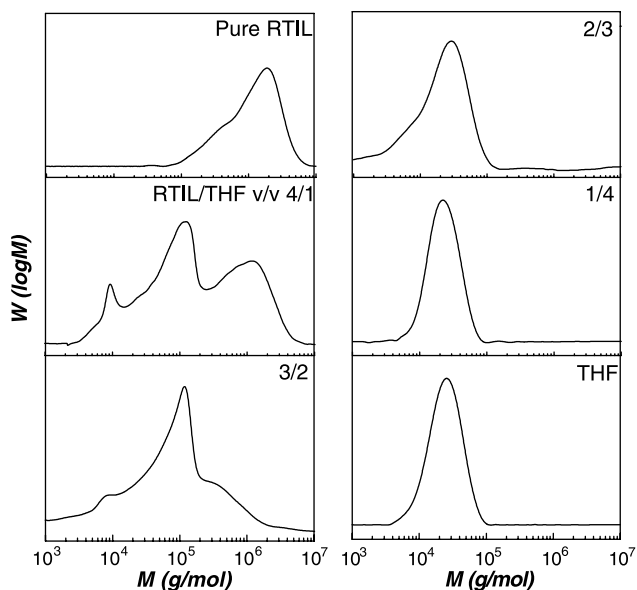


Fig. 2. GPC curves for poly-(butyl  $\alpha$ -methacrylate) obtained by radiation in different solvents at the dose of 5 kGy (dose rate: 5.3 Gy/min).

tendency of the change of MWD for PBMA with the RTIL/THF ratio is similar to that for PSt, despite of a difference to some extent. Multi-modal broad MWD is also observed for PBMA obtained from the pure ionic liquid and the RTIL/THF mixture at IL > 60 v%, while single-modal MWD is observed at IL < 50 v%. Molecular weight of the main GPC peak also increases with increasing the IL fraction and it is slightly smaller than that of PSt under similar conditions.

Fig. 3 shows the GPC traces of PMMA obtained in RTIL/THF solutions. Of particular interest is the observation of nearly single-modal MWD at THF > 20 v%. Although minor components with lower molecular weights can be also identified, their contribution is minor as compared to the main peak. The clear difference in MWD between PMMA and PBMA may be ascribed to the differences in

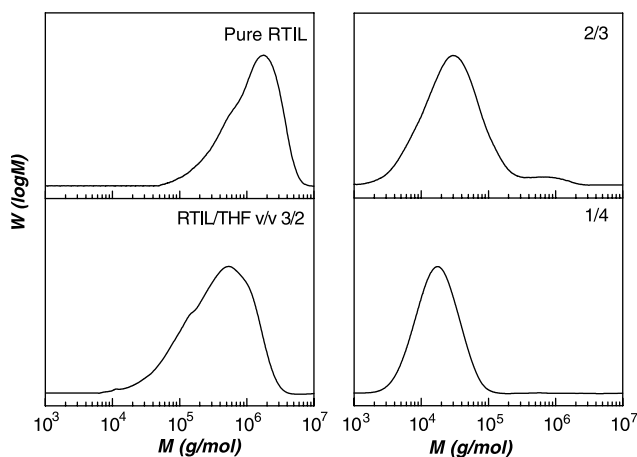


Fig. 3. GPC curves for poly-(methyl methacrylate) obtained by radiation in different solvents at the dose of 5 kGy (dose rate: 5.3 Gy/min).

monomer polarity and interactions among the monomer, the ionic liquid and the resulting polymer.

For St, BMA and MMA, radiation polymerization in pure THF leads to the formation of low-molecular-weight polymers. Their molecular weights are almost identical, about  $2\text{--}3 \times 10^4$ . Such low  $M_w$  is probably due to the efficient chain transfer from the polymer to the solvent. Molecular weight of polymer increases with increasing of the RTIL/THF ratio and it can be higher than that in neat THF by two orders of magnitude.

It is also worthy noting that the monomer conversion in neat THF is very low, being less than 10%. However, the conversion is higher than 70% at RTIL > 50 v% under otherwise identical conditions. Fig. 4 shows the effect of IL on the conversion of St in RTIL/THF mixture at the doses of 2 and 5 kGy. A significant increase in conversion (from < 10 to > 70%) is found with increasing IL fraction from 20 to 60 v%. At IL > 60 v%, the conversion at a fixed dose remains almost unvaried. The conversion of St is also dependent on the radiation dose; lower dose leads to lower conversion. However, it should be noted that the conversion is higher than 40% even at a relative lower dose (2 kGy).

### 3.2. Dose dependence of $M_w$ and MWD

Since the conversion is dose dependent, the possibility of the change in  $M_w$  and MWD with radiation dose is further studied. Fig. 5 shows the GPC traces of PBMA obtained from RTIL/THF at 2 kGy. By comparing with that at 5 kGy (Fig. 2), it is found that the MWD is independent of the dose but dependent on the RTIL/THF ratio. However, molecular weight decreases slightly and the fraction of lower  $M_w$  component increases at lower dose.  $M_w$  and MWD of PSt obtained from a series of RTIL/THF solutions at 10 and 5 kGy were also compared and the same phenomena were observed.

Dose dependence of  $M_w$  and MWD of PSt was

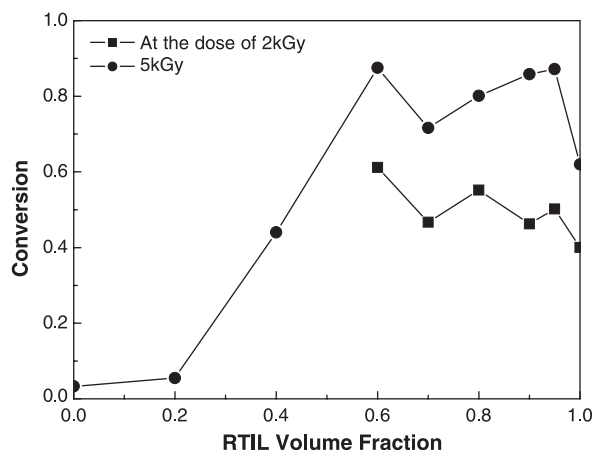


Fig. 4. Conversion of PSt in RTIL/THF mixed solvent at the different doses. (■) At the dose of 2 kGy (dose rate: 2.1 Gy/min); (●) at the dose of 5 kGy (dose rate: 5.3 Gy/min).

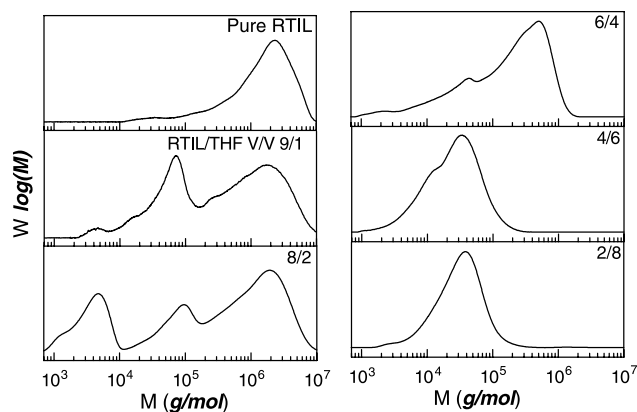


Fig. 5. GPC curves for poly-(butyl methacrylate) obtained by radiation in different solvents at the dose of 2 kGy (dose rate: 5.3 Gy/min).

investigated in the range of 5–21 kGy with RTIL/THF volume ratio fixed at 1:1. As shown in Fig. 6, there is no significant change in  $M_w$  and MWD in the applied dose range, but a dose dependence of  $M_w$  is observed. Arrow (a) shows the augment of high-molecular-weight component as radiation dose increases from 5 to 13 kGy, while arrow (b) shows the bulge of peak on the side of lower  $M_w$ . The appearance of lower  $M_w$  component is explained by the degradation of PSt at higher dose. Since high conversion (> 50%) can be achieved at IL > 40 v% at 5 kGy, the continued radiation upon polymer component can lead to the scission of polymer chain. The product analysis in the same dose range revealed an increase in St conversion from 5 to 13 kGy, but a slight decrease at > 15 kGy. This also proves that the resulting polymer undergoes partial degradation at higher dose.

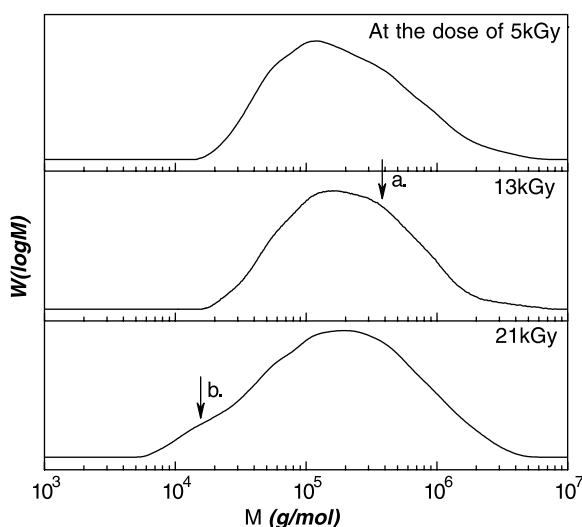


Fig. 6. GPC curves for polystyrene obtained by radiation in the mixed solvent (RTIL/THF v/v 1/1) at different doses with the same dose rate (5.3 Gy/min).

### 3.3. Miscibility of polymer and RTIL

We suggest that the MWD pattern of polymer is probably related to the miscibility of polymer and the solvent. To explore the miscibility of polymerized product and solvent, an experiment was carried out to detect the mixed state of the resulting polymer and the RTIL/THF system by observing the color change after being steadily placed at room temperature for one week.

The results are shown in Table 1. It is demonstrated that the miscibility of polymer with RTIL/THF solvent is in the order: PMMA > PBMA > PSt. This is consistent with the difference in MWD observed for the same polymer at various RTIL/THF ratios.

### 3.4. Fluorescence characters of mixed solvent system

Fluorescent probes are sensitive to the variation of environment and fluorescent probing is widely used in the study of heterogeneous media, e.g. micro-emulsion. Here steady state fluorescence spectra were recorded with varying the RTIL/THF ratio in an attempt to probe the nature of RTIL/THF solvent. It is found that with the addition of THF, peak position of the fluorescence emitted from the ionic liquid remains unaffected while the peak intensity changes. By normalizing the fluorescence intensity with the molar concentration of ionic liquid, a plot of fluorescence intensity as a function of molar ratio of THF/RTIL is shown in Fig. 7(a). It clearly shows that the fluorescence intensity always increases with increasing the THF/RTIL ratio. Two transition points are observed at THF/RTIL molar ratios of 3.0–3.5 and 5.0–5.3, corresponding to RTIL of 47–43 and 35–34 v%. The first point indicates a change from inhomogeneous phase to homogeneous phase, but complex zinc chloride clusters remain in the liquid. The second point may indicate the formation of a well-miscibilized phase. For confirmation, we further investigated the change of solvent property by using Coumarin-314 as an external fluorescent probe. Coumarin-314 solution is excited at 320 nm to avoid the emission from the ionic liquid. As shown in Fig. 7(b), peak intensity of the

Table 1  
Diaphaneity of the RTIL/THF/polymer systems placed at room temperature for 1 week

RTIL/THF/ Monomer (V/ V/V) <sup>a</sup>	Polymer <sup>b</sup>		
	PSt	PBMA	PMMA
100/0/5	O	O	O
90/10/5	O	O	T
80/20/5	O	O	T
60/40/5	O	O	T
50/50/5	O	T	T
40/60/5	T	T	T

<sup>a</sup> Radiation dose: 5 kGy; dose rate: 5.3 Gy/min.

<sup>b</sup> T, transparent; O, opaque.

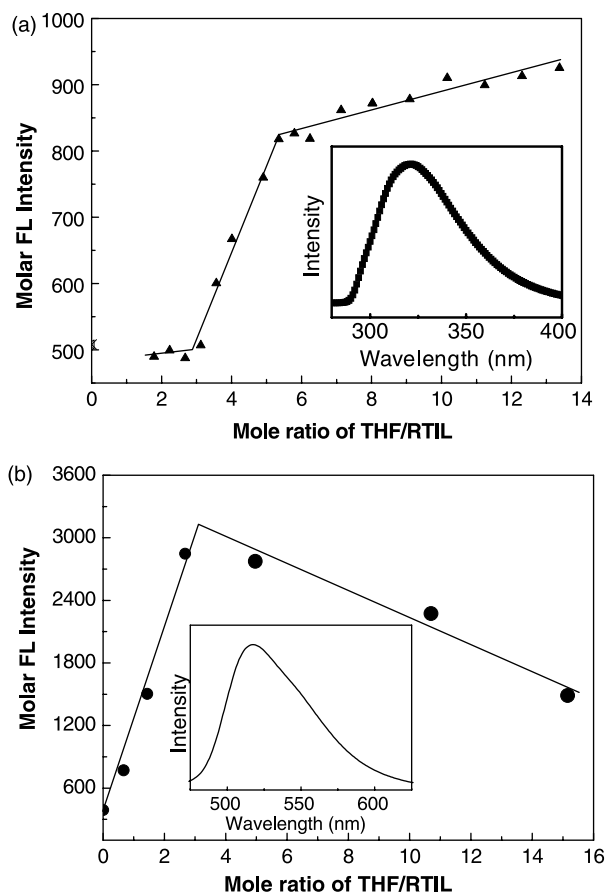


Fig. 7. Normalized fluorescence intensity as a function of THF/IL ratio, detected using RTIL (a) and Coumarin-314 (b) as fluorescent probes. Inset: (a) The emission spectra of RTIL excited at 270 nm (b) the emission spectra of C-314 excited at 320 nm (fluorescence intensity (FL) is normalized by the molar concentration of RTIL, which comprises of choline chloride and ZnCl<sub>2</sub> (mole ratio: 1:2)).

fluorescence increases with THF/RTIL molar ratio at the beginning and then dramatically decreases as the ratio is further increased. Maximum fluorescence intensity is observed at the THF/RTIL molar ratio of 3.0–3.3, corresponding to RTIL at 47–43%, in good accordance with the observation using the ionic liquid as the probe.

These results prove a phase transformation in the RTIL/THF mixture at IL ca. 50 v%. In fact, the rheological measurement (Fig. 8) also indicates a transition at the same IL fraction. Therefore, the solution at IL < 50 v% can be considered to be nearly homogeneous. When a monomer is added, the phase structure of RTIL/THF solution may also change. However, the RTIL/THF/monomer system was not studied by the fluorescence probing method due to technical problems, e.g. efficient quenching of fluorescence by styrene.

### 3.5. Explanation of the increasing conversion and $M_w$ in RTIL

The role of RTIL is considered to enhance the conversion

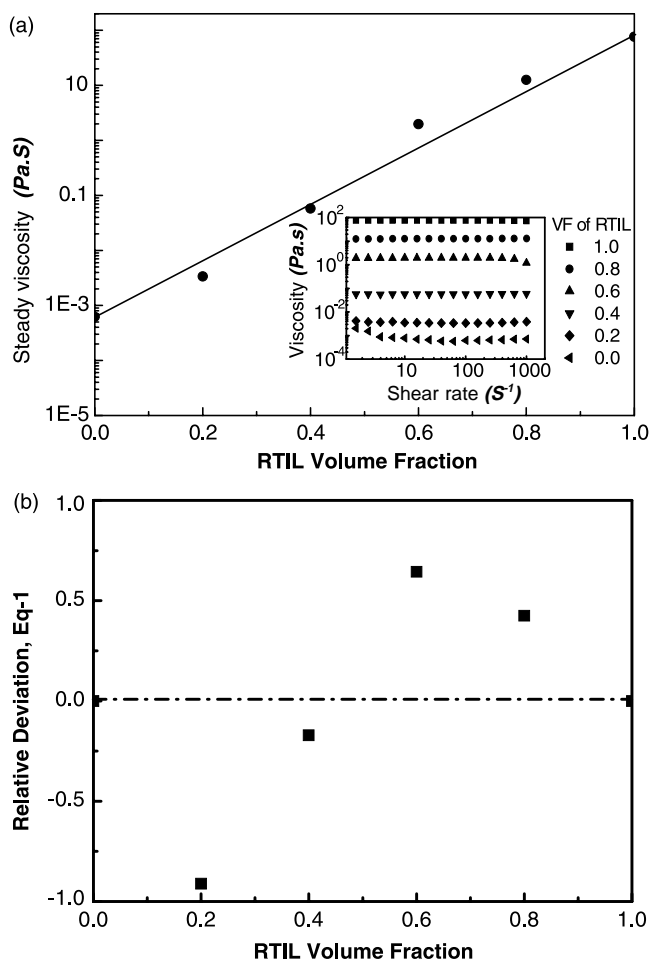


Fig. 8. Steady viscosity of RTIL/THF mixed solvent at 298.15 K (a) and the relative deviation ( $(\eta_m - \eta_p)/\eta_p$  to Eq. (1) (b) as a function of RTIL volume fraction. Inset: Viscosity as a function of shear rate for the mixed solvent at 298.15 K (VF means volume fraction).

rate and tune the molecular weight for polymerization in THF. These phenomena are likely due to the high polarity and viscosity of the reaction media [20,21]. Fig. 8(a) shows that the steady viscosity of the mixed solvent at 25 °C increases dramatically with the increase of RTIL fraction. The viscosity of RTIL is higher than that of neat THF by four orders of magnitude. The real line in Fig. 8(a) shows the calculated viscosity of the mixed system according to the following equation:

$$\ln(\eta_{\text{Mix}}) = \phi_1 \ln(\eta_1) + \phi_2 \ln(\eta_2) \quad (1)$$

$\Phi$ ,  $\eta$ : volume fraction and viscosity of each component.

It is shown that the measured viscosity ( $\eta_m$ ) deviates from the predicted addition ( $\eta_p$ ). The measured value is lower than the prediction at IL < 45–50 v% but higher than the prediction at IL > 50 v%. To more clearly demonstrate this difference, a plot of the relative difference in viscosity,  $(\eta_m - \eta_p)/\eta_p$ , as a function of RTIL fraction is shown in Fig. 8(b).

The effects of ionic liquid on free radical polymerization have been previously observed [6]. More recently, a study



by Harrison et al. [21] of pulsed laser induced polymerization of MMA in the ionic liquid  $[\text{bmim}]^+[\text{PF}_6]^-$  revealed that the presence of ionic liquid causes a significant increase in the rate of propagation and an order of magnitude decrease in the rate of termination. The authors propose that the increased propagation rate is due to the increased polarity of the ionic liquid solution, while the decreased termination rate is due to the increased viscosity of the reaction medium. The termination rate ( $k_t$ ) decreased quickly when the viscosity of system increased, for the increasing viscosity leads to the reduction of molecular diffusion coefficients [34] and probability of the radical's collision. This is applicable to the explanation of the fast overall conversion and high molecular weight observed in our system.

### 3.6. Explanation of the multi-modal MWD in RTIL

Although the high  $M_w$  can be explained by the high polarity and viscosity of the ionic liquid, it is not answered why multi-modal MWD is observed for radiation polymerization in the RTIL/THF system. Multi-modal MWD seems to be one of the features of the polymers prepared in RTILs. In pulsed laser induced polymerization of MMA in an ionic liquid at 25 °C, overtone peaks in addition to the main peak were also observed in GPC traces [35]. The overtone peaks were explained that the polymer chains surviving one or more pulses to be terminated by the second or subsequent pulses. However, in our case, a continuous and regular flux of radicals are produced by gamma radiation, multi-modal MWD is difficult to be explained by the assumption that some polymer chain radicals survive longer time.

Maybe there are two reasons for the observation of multi-modal MWD. One is the immiscibility of polymer in the media [36]. The media's high viscosity can lead to a broad and complex MWD and the immiscibility of product in reaction media results in an ill-controlled polymerization. The other possible explanation is the presence of micro-phases in the ionic liquid or in the RTIL/THF 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. The micro-phase area may act as micro-reaction cases. Polymer with lower  $M_w$  is produced in the area containing more THF, whereas higher  $M_w$  component is produced in the areas containing more RTIL. As gamma ray 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. In fact, many studies [37] on the phase-equilibrium in ionic liquids and solvent/ionic liquid binary mixture revealed that ionic liquids form complex phase structure and the phase structure varies with the change of volume ratio. The binary mixture may be composed of dispersed aggregates behaving like a mixture of two phases that interpenetrate themselves [38]. The

solvation dynamics studied [39] by time dependent fluorescence spectroscopy in  $[\text{bmim}][\text{BF}_4]$  also indicated the biphasic nature of the ionic liquid. Our previous work also implies that inhomogeneous phases may exist in the RTIL/DMF and RTIL/EtOH mixed solvents [32]. Similar to that, the fluorescence variation of RTIL/THF mixed solvent shows that the system is inhomogeneous when the volume fraction of RTIL is higher than 43–47%.

We tend to consider that the above two reasons are both responsible for the multi-modal MWD of polymer observed in RTIL/THF. However, it is necessary to stress that the inhomogeneity of RTIL/THF system and the immiscibility of polymer with RTIL varies significantly with the IL fraction.

## 4. Conclusion

It has been shown that radiation-initiated polymerization of St, BMA, and MMA in the RTIL/THF mixed solutions exhibits many unique features as compared to that in THF, in terms of higher conversion, higher  $M_w$  and multi-modal MWD. For PSt and PBMA, single-modal MWD are observed at IL < 40 v% and multi-modal MWD at IL > 50 v%. In contrast, PMMA has a nearly single-modal MWD at THF > 20 v%. The miscibility of these polymers with RTIL detected by storage stability is in the order: PMMA > PBMA > PSt. Multi-modal MWD is explained by the possibility of radiation induced in situ polymerization of monomer present in micro-regions of the RTIL/THF solution and the immiscibility of resulted polymer.

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