

On the mechanism of radiation-induced polymerization of vinyl monomers in ionic liquid

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Received 17 June 2004; accepted 14 July 2004

Abstract

An attempt was made to investigate the mechanism controlling the radiation-induced polymerization of vinyl monomers in room temperature ionic liquids. For that purpose, copolymerization of styrene (St) and methyl methacrylate (MMA) was initiated by ^{60}Co gamma radiation in a moisture-stable ionic liquid, [choline chloride][ZnCl₂], and its mixture with THF (4:1 v/v). By analyzing the product composition with FTIR for a series of poly(St-co-MMA) samples, it was found that the mole fraction of St in the copolymer is linearly proportional to the mole fraction of St in the feed. Therefore, radiation polymerization in ionic liquid and its mixture with organic solvent is suggested to be a radical propagating process.

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Keywords: Ionic liquid; Radiation polymerization; Mechanism

1. Introduction

Room temperature ionic liquids (RTILs) have many advantages, such as non-volatility, high polarity, etc. (Welton, 1999). Most of them have good miscibility with other organic solvents or monomers. Since ionic liquids can be recycled easily, they are recognized as green solvents and have attracted increasing interest in recent years. Plenty of researches (Kubisa, 2004; Kunlun Hong et al., 2002) about ionic liquids have been carried out for chemical reactions and it has been found that high polarity of ionic liquids can prolong radical life and improve reaction conversion. In radiation chemistry

field, however, only few groups paid attention to the potential application of ionic liquids and little is known about the radiation chemistry or physics of ionic liquids. Allen et al. (2002) have studied radiochemical stability of ionic liquids under gamma and beta irradiation, they found that ionic liquids were relatively radiation resistant and there was certainly no major decomposition of the organic component. Yang and Dionysiou (2004) have studied the photolytic degradation of chlorophenol and its derivatives in [bmim⁺][PF₆⁻] and [emim⁺][beti⁻] ionic liquids upon UV irradiation. With the expansion of research on ionic liquids, there may be increasing applications and requirements in radiation chemistry as well.

It was found very recently that high-energy ionizing radiation leads to the formation of solvated electrons (Wishart and Neta, 2003) and radical ions in ionic

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liquids (Marcinek et al., 2001; Behar et al., 2001). These transient species can be utilized to initiate polymerization, since radiation has been applied extensively in initiating polymerization reactions in conventional solvents. In our preliminary study, we found that gamma radiation induces polymerization of different monomers and the molecular weight can be tuned by the addition of organic solvent. These results will be the subject of a forthcoming publication. In this article, we report the study of the mechanism for radiation polymerization of vinyl monomers in ionic liquids, which may be important for understanding the difference or similarity between radiation polymerization in ionic liquids and in conventional solvents.

2. Experimental section

In the experiment we used a moisture-stable ionic liquid composed of choline chloride and zinc chloride (molar ratio 1:2; m.p. 23–25 °C). It is a colorless and viscous liquid, prepared according to the literature method (Abbott et al., 2001). Samples were prepared by adding 5 vol% distilled monomer (styrene (St) and/or methyl methacrylate (MMA)) into the ionic liquid or a mixture of the ionic liquid and THF, followed by bubbling N₂ gas to remove the air. Samples sealed in glass tubes were exposed to γ radiation in the Cobalt-60 source at Shanghai Institute of Applied Physics. Irradiation was continued to a dose of 5 kGy (dose rate: 5.3 Gy/min) at room temperature. After irradiation, the sample was slowly dropped into a 10-fold excess amount of cooled methanol. Precipitated polymer was separated by filtration and dried at 60 °C overnight under vacuum.

Polymer film was prepared by casting 1 wt% PSt, PMMA, their copolymer or blend of THF solution on glass plate. The film composition was characterized by FTIR on Nicolet infrared spectrophotometer (Avater-360).

3. Results and discussion

Several active species (ion, radical, solvated electron, etc.) can be formed when the monomer solution of ionic liquid is subjected to ionizing irradiation; in principle, all these species are possible to initiate the polymerization. However, polymerization route is restricted by many factors. In this work, we adopted the copolymerization method to estimate the polymerization mechanism in ionic liquids under radiation. Its principle is that MMA and St initiated by different species have obviously different polymerization rates, so we can judge the polymerization mechanism by comparing the molar

ratio of St/MMA in the monomer feed and in the product.

Prior to the analysis of product composition in poly(St-co-MMA), a standard curve is required for correlating the absorption intensity at a selected wavelength with PSt or PMMA fraction. Fig. 1 shows FTIR spectra of pure PSt and PMMA. Strong absorption peaks are respectively observed at 1725 cm⁻¹ (C=O vibration) for PMMA and at 702 cm⁻¹ (C–H vibration on the phenyl group) for PSt. It is also seen that the absorption overlap for PSt and PMMA at these two wavenumbers is negligible. Since absorption intensity is proportional to mole fraction for each component, we have

$$\log(a_{\text{peak1}}/a_{\text{peak2}}) \propto \log(c_1/c_2),$$

where a_{peak1} , a_{peak2} , c_1 , and c_2 are peak area (absorption intensity) and mole fraction of PSt and PMMA, respectively.

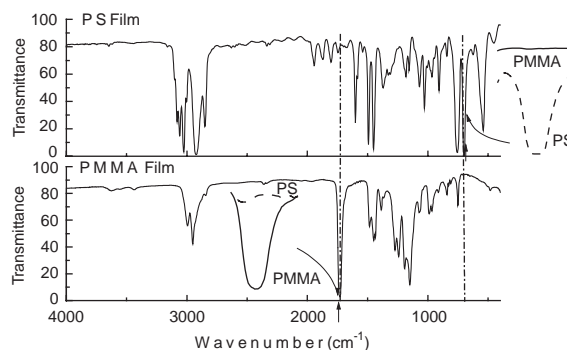


Fig. 1. FTIR spectra of PSt and PMMA.

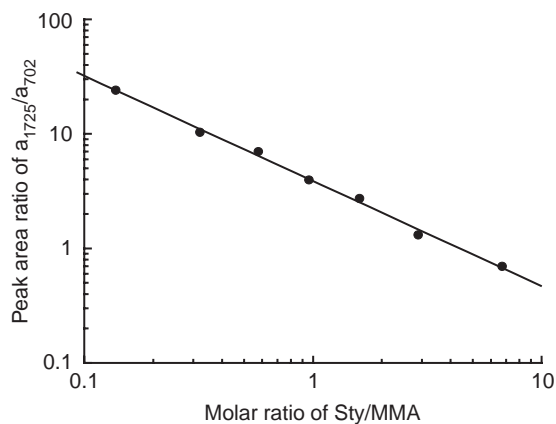


Fig. 2. Plot of the peak area ratio versus the mole concentration of St/MMA for standard PSt and PMMA blends.

Table 1

 a_{1725}/a_{702} and mole fraction of St for poly(St-co-MMA) samples prepared under different conditions^a

Sample	M_{St} in the feed	Pure IL			Solvent (IL/THF(v/v) = 4:1)				
		a_{1725}	a_{702}	a_{1725}/a_{702}	M_{Sty}	a_{1725}	a_{702}	a_{1725}/a_{702}	M_{Sty}
SM15	0.16	45.92	2.59	17.72	0.15	41.24	2.57	16.04	0.17
SM24	0.32	22.61	3.55	6.36	0.37	31.85	4.84	6.58	0.36
SM33	0.48	46.49	9.42	4.93	0.43	7.90	1.73	4.56	0.46
SM42	0.65	5.95	2.75	2.16	0.64	6.87	3.33	2.06	0.65
SM51	0.82	4.64	4.50	1.03	0.80	1.96	1.80	1.08	0.79

^a M_{St} : mole fraction of styrene; M_{Sty} : mole fraction of styryl in copolymer.

A straight line is expected by plotting a_{1725}/a_{702} versus molar ratio of St/MMA in the PSt/PMMA polymer blend. As shown in Fig. 2, a curve with good linearity is achieved. This enables us to obtain the exact molar ratio of St/MMA in the copolymer by the same method and the error is less than 5%.

Since the ratio of a_{1725}/a_{702} for poly(St-co-MMA) samples can be obtained from FTIR spectra, molar ratio of St/MMA in copolymers prepared in the ionic liquid was determined on the basis of the standard line. Five copolymer samples were prepared by irradiation with changing the volume ratio of St/MMA in the feed from 1/5 to 5/1 and the molar ratio of St/MMA in copolymers was measured. Mole fraction of St in the monomer feed and mole fraction of St in the polymer were calculated and listed in Table 1, together with other relevant data. To make clear the effect of the ionic liquid, pure ionic liquid and a mixture of the ionic liquid and THF (volume ratio 4/1) were used as the polymerization media.

A plot of mole fraction of St in the copolymer as a function of mole fraction of St in the feed is illustrated in Fig. 3. It is shown that, for both the ionic liquid and the mixture of ionic liquid and THF, mole fraction of St in product is linear to that in the monomer feed. This means that the polymerization rate is the same for St and MMA. The addition of THF into the ionic liquid has no effect on the polymerization mechanism, but it may cause the change in molecular weight and molecular weight distribution. We consider that radicals, not anions or cations, are dominantly responsible for initiating polymerization under radiation. It is suggested that radiation polymerization in ionic liquids has the same mechanism as in conventional organic solvents at room temperature. The speculated initiation mechanism in the ionic liquid under radiation is shown in Fig. 4.

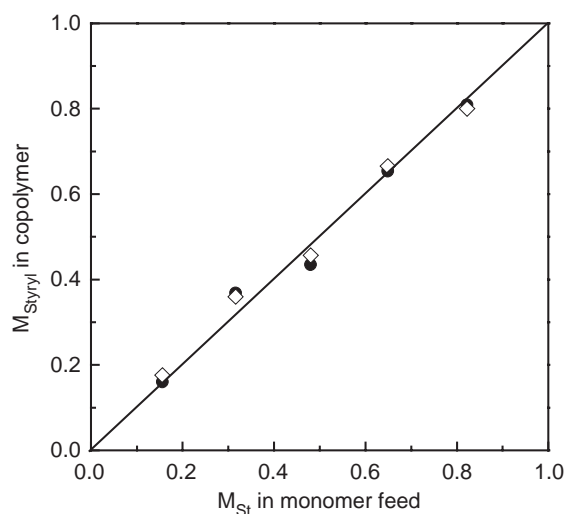


Fig. 3. Plotting of mole fraction of St in the copolymer versus mole fraction of St in the monomer feed. \diamond , Ionic Liquids; \bullet , Mixed solvent (IL:THF (v:v) = 4:1).

4. Conclusion

Copolymerization of St and MMA was initiated by γ radiation in the ionic liquid [choline chloride][ZnCl₂] and its mixture with THF. By the FTIR analysis, it was found that the mole fraction of St in the copolymer is linearly proportional to the mole fraction of St in the feed. We conclude that radiation polymerization in ionic liquids can be described by the radical polymerization mechanism, similarly to the polymerization in organic solvents at room temperature. This finding may be helpful for better understanding of polymerization behavior in other ionic liquids under radiation.

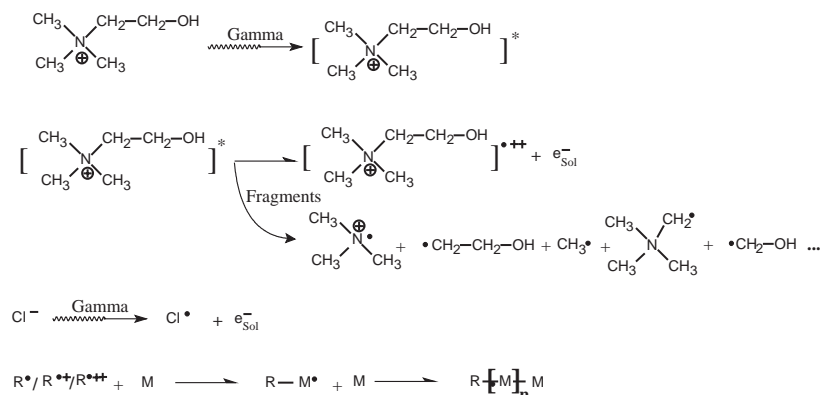


Fig 4. Proposed mechanism of the initiation process induced by ^{60}Co gamma radiation.

However, it remains a subject to know the structures of radicals generated from radiolysis of ionic liquids.

Acknowledgements

This work was financially supported by the ‘‘Hundred talents’’ project of the Chinese Academy of Science.

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