Free-Radical Copolymerization Kinetics of Acrylonitrile and Methyl Acrylate in [BMIM]BF$_4$

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ABSTRACT: The copolymerization of acrylonitrile (AN) and methyl acrylate (MA) was carried out in ionic liquid [BMIM]BF$_4$ in the presence of azobisisobutyronitrile (AIBN) as an initiator to investigate the polymerization kinetic, including the copolymerization rate, reactivity ratios, and activation energy. The copolymerization rate equation was established according to the effect of initiator and monomer concentrations on the conversion. The copolymerization rate R_p can be noted as $R_p = KC_{AIBN}^{0.74}C_{MA}^{0.61}C_{AN}^{0.44}$, when the copolymerization was in the steady state.

The apparent activation energy is 87.94 kJ/mol, while the value of that in the conventional organic solvent (DMF) is $\sim$ 81 kJ/mol. The reactivity ratios of the investigate system are $r_{AN} = 0.36$ and $r_{MA} = 0.68$. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 4254–4257, 2006

Key words: copolymerization; kinetics; ionic liquid; polyacrylonitrile; yielding

INTRODUCTION

Ionic liquids (ILs) have attracted much attention in both academia and industry as nonvolatile, recyclable media for a wide range of chemical processes, including extraction, electrochemistry, and polymerization.[1] The free-radical polymerization in ILs has been reported by Zhang et al.[2–5] and Bonton and Brazel.[6,7] They investigated the strong solvent impact of ILs on the apparent reactivity ratios, reaction rates, and products. It was noted that, as reaction media, ILs could lead to significant improvements in rate and yield. The detail mechanisms have been reported by Haddleton and coworkers[8,9] and Huddleston et al.[10] It was suggested that the increase in the rate of the propagation process was due to the polar effect of the ILs solution. However, these dynamic researches were conducted in different monomers/IL systems and the results were system-dependent. The more systematic law is still unknown.

Polyacrylonitrile is traditionally made by solution polymerization in different organic or inorganic solvents. This process has its shortcoming: first, the polymerization must last for 20 h or much longer to achieve the high conversion. Second, the volatile solvents used were blamed for the increasing air pollution. In looking for a new solvent for AN polymerization, our group has successfully conducted the homopolymerization of acrylonitrile in ionic liquid.[11] In this article, we reported the free-radical copolymerization kinetics of MA and AN in [BMIM]BF$_4$. The impact of the various factors on the copolymerization process, including initiator concentration, monomer concentration, monomer ratio, and temperature will be discussed in detail. The copolymerization rate formula in the steady polymerization state was then established to give some guidance to the copolymerization controlling process.

EXPERIMENTAL

Materials

All materials were purchased from local companies in Shanghai. Methyl acrylate (MA) (99%) and acrylonitrile (AN) (99%) were distilled to remove inhibitors and stored in calibrated ampules. 1-Butyl-3-methylimidazolium tetrafluoroborate ([BMIM]BF$_4$) was synthesized, according to the method of Huddleston et al.[10] The thermal initiator, azobisisobutyronitrile (AIBN, 97%) was recrystallized from methanol and dried under vacuum.

Copolymerization

The rates of copolymeriztion was carried out using Pyrex glass dilatometers with calibrated and graduated capillary tubes with the capacity of 3–5 mL, and fitted with ground joint. The monomers (AN and MA) with

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TABLE I
Conditions for the Copolymerization of AN and MA in [BMIM]BF$_4$

Scheme	Temperature (K)	AN concentration (mol/L^{-1})	MA concentration (mol/L^{-1})	Initiator concentration (mol/L^{-1})
I	338	3.16	0.49	0.02
				0.03
				0.04
				0.05
II	338	3.16	0.49	0.04
			1.10	
			1.72	
			2.39	
III	338	1.76	0.49	0.04
		2.20		
		2.65		
		3.16		
IV	328	3.16	0.49	0.04
	333			
	338			
	343			
V	338	0	2.41	0.04
		1.19	1.71	
		2.00	1.23	
		2.82	0.74	
		3.23	0.50	
		3.65	0.25	

required amount of initiator, AIBN, were dissolved in [BMIM]BF$_4$, in advance. Monomer concentration was determined in mol L^{-1} (Table I). The reaction mixture was transferred to the dilatometer and placed in a water thermostat adjusted to the required temperature ($\pm 0.1°$C), and the conversion was controlled below 10%. At the end of the polymerization, the dilatometer was immersed in an ice-water-salt mixture to stop the radical polymerization reaction. The polymer solution was washed with water several times and dried in an air oven at 60°C, until constant weight and the monomer conversion was determined gravimetrically. The initial copolymerization rate (R_p) was determined from the slope of the graph of monomer conversion versus time.

Elemental analyses

Elemental analyses were done on a Vario el3 Elemental Analyzer to estimate the composition of the AN and MA copolymers.

RESULTS AND DISCUSSION

Establishment of the copolymerization rate equation

Generally, in free-radical polymerization, the concentration of initiator and monomer play the major role on the polymerization rate. When the polymer conversion was low (< 10%), there is an assumption that the polymerization is conducted in a steady state. And according to this assumption, the polymerization rate equation[12] is:

$$R_p = KC_{AIBN}{}^n C_{MA}{}^m C_{AN}{}^l \qquad (1)$$

where C_{AIBN}, C_{AN}, and C_{MA} denote the concentration of the AIBN, AN, and MA, respectively, n is the order of copolymerization rate to the initiator concentration, and m and l represent the orders of copolymerization rate to the MA and AN monomer concentration, respectively.

Relationship between initiator concentration and copolymerization rate in [BMIM]BF$_4$

The dependence of polymerization rate on the initiator concentration (C_{AIBN}) is illustrated in Figure 1. The polymerization reaction was performed under the conditions of scheme I (Table I). A straight line was obtained when log R_p was plotted versus log C_{AIBN}, which means log $R_p \propto \ln C_{AIBN}$. The slope of the line shows the reaction order n as 0.74.

However, in ideal polymerization process, where only dimolecular chain termination exists, the order of copolymerization rate to initiator concentration is 0.5, which indicated that monomolecular chain termination existed along with dimolecular chain termination. This may be due to the high viscosity of the [BMIM]BF$_4$, that is, 154 mPa s in the room temperature, much higher than that of the conventional organic solvent, such as DMF(56 mPa s),[13] which limits the diffu-
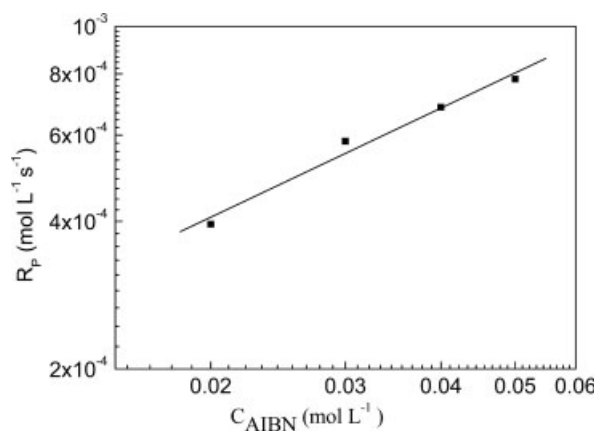
Figure 1 Relationship between polymerization rate and azobisisobutyronitrile concentration.

sion rates of large polymer chains within the solution. At the same time, the increasing conversion will also increase the cage reaction and lower the initiation efficiency. These all attributed to the existence of the monomolecular chain termination.

Relationship between monomer concentration and copolymerization rate in [BMIM]BF$_4$

According to the conditions of schemes II and III (Table I), we got the relationship between monomer concentration and reaction rate (Figs. 2 and 3), the log-log plots of which shows good linear relationship. Using the same method, the reaction order m and l are 0.61 and 0.44, which means $R_p, \propto C_{MA}^{0.61}$ $R_p \propto C_{AN}^{0.44}$.

Interestingly, the reaction order of two monomers has the relationship as follows: $(m + l) - 1$. It is thus considered that in the [BMIM]BF$_4$ ionic liquid system the relationship between copolymerization rate and monomer concentration is very close to the first-order reaction.
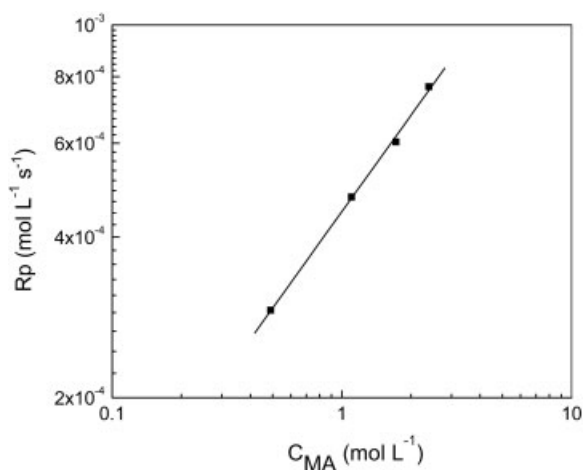

Figure 2 Relationship between polymerization rate and methyl acrylate concentration.
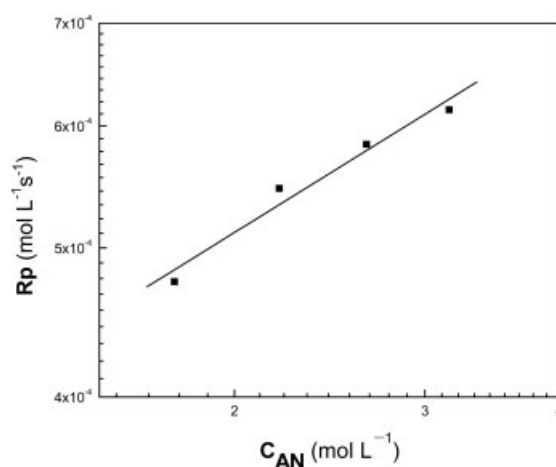

Figure 3 Relationship between polymerization rate and acrylonitrile concentration.

As detailed earlier, the copolymerization rate R_p can be noted as:

$$R_p = KC_{AIBN}^{0.74}C_{MA}^{0.61}C_{AN}^{0.44} \qquad (2)$$

Effect of temperature on the copolymerization in [BMIM]BF$_4$

The effect of temperature on the polymerization in [BMIM]BF$_4$ is represented in Figure 4. The polymerization reaction was performed under the conditions of scheme IV (Table I). The obtained R_p data were used to determine the effect of the ionic liquid on the Arrhenius parameters. The apparent activation energy, calculated from the Arrhenius plot, was 87.94 kJ/mol while the value of that in the conventional organic solvent, DMF, is $\sim$ 81 kJ/mol.

Reactivity ratio in [BMIM]BF$_4$

According to the conditions of scheme V (Table I), the copolymerization in [BMIM]BF$_4$ ionic liquid system
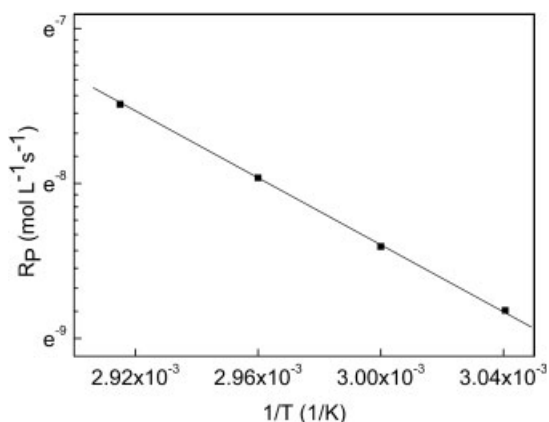

Figure 4 Relationship between polymerization rate and $1/T$.

was conducted and the copolymerization time was adjusted to keep the conversion below 6%. The composition of the AN and MA copolymers was estimated by the percentage nitrogen content of the copolymers. The values of reactivity ratios obtained from the Fineman–Ross[14] method are $r_{AN} = 0.36$ and $r_{MA} = 0.68$. These results are different from those typically obtained from copolymerizations in ordinary solvents or in bulk, in that $r_{AN} \gg r_{MA}$.[15,16] In general, monomer reactivity ratios are typically but not always independent of the reaction medium. The dipole monomers of the solvent, interactions between solvent and monomer (e.g., solvent-monomer complexes), viscosity and system heterogeneity are all found to have some effect on reactivity ratios. [BMIM]BF$_4$ is an ionic solvent of polarity and high viscosity. Although BF$_4^-$ is a poor hydrogen-bond acceptor, it has been proposed that [BMIM]BF$_4$ or its components could form complexes with the monomers and radical centers.[3] All of these factors could contribute to differences in the reactivity ratios as compared to those in organic solvents.

CONCLUSIONS

In conclusion, it is shown that [BMIM]BF$_4$ was a excellent reaction media for free-radical polymerization. The copolymerization rate R_p can be noted as $R_p = KC_{AIBN}^{0.74}C_{MA}^{0.61}C_{AN}^{0.44}$, when the copolymerization was in the steady state. During the polymerization process, monomolecular chain termination existed along with dimolecular chain termination in the AN-MA-ionic liquid system. The relationship between copolymerization rate and monomer concentration is very close to the first-order reaction. The apparent activation energy, calculated from R_p at different temperature, was 87.94 kJ/mol while the value of that in the conventional organic solvent (DMF) is ~ 81 kJ/mol. The reactivity ratios of the investigate system are $r_{AN} = 0.36$ and $r_{MA} = 0.68$.

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