

Free-Radical Solution Copolymerization of the Ionic Liquid Monomer 1-Vinyl-3-Ethylimidazolium Bromide with Acrylonitrile

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ABSTRACT: Ionic liquid monomer 1-vinyl-3-ethylimidazolium bromide ($\text{ViEtIM}^+\text{Br}^-$) was first used to copolymerize with acrylonitrile (AN) successfully under various conditions. This was achieved with azobisisobutyronitrile as the initiator and dimethyl sulfoxide as the solvent. The kinetics of this copolymerization were studied. The values of the monomer apparent reactivity ratios were calculated by the Kelen-Tüdös method. The apparent reactivity ratios of $\text{ViEtIM}^+\text{Br}^-$ ($r_{\text{ViEtIM}^+\text{Br}^-}$) and AN (r_{AN}) were similar at polymerization conversions of less than 10% ($r_{\text{AN}} = 0.954$,

$r_{\text{ViEtIM}^+\text{Br}^-} = 0.976$). The copolymers were obtained with high molecular weights and high hydrophilicities. The copolymers were characterized by $^1\text{H-NMR}$, differential scanning calorimetry, and thermogravimetric analysis. These copolymers may be potentially useful in the preparation of precursor fibers and carbon fibers. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 3337–3340, 2009

Key words: kinetics (polym.); radical polymerization; hydrophilic polymers; high performance polymers

INTRODUCTION

Carbon fibers are well known for their high tensile strength, high modulus, and lightweight. Polyacrylonitriles (PANs) are the most successful and promising precursors for making high-performance carbon fibers. Copolymer's composition can greatly influence the performance of precursors and carbon fibers,^{1,2} and many comonomers have been reported in the literature.^{3–10} Hydrophilic comonomers can promote the diffusion between water and a solvent and effectively improve the mechanical properties of precursors and the resulting carbon fibers.^{11–15} Thus, we tried to find a new comonomer with excellent hydrophilicity, such as a polymerizable ionic liquid.

Ionic liquids can be used as solvents for the polymerization processes.¹⁶ In recent years, the polymerization of acrylonitrile (AN) in ionic liquids has been studied carefully.^{17,18} Some ionic liquids with vinyl groups can also be polymerized to obtain various polymers, such as gel-type polymer beads and organic hydrogels.^{19–25} However, most of the studies focused on their homopolymerization. The use of polymeriz-

able ionic liquids as comonomers to copolymerize with AN to prepare hydrophilic copolymers, which may potentially be used to prepare precursor fibers and carbon fibers, have not been investigated so far. There have been no reports on the monomer apparent reactivity ratios for the copolymerization of ionic liquid monomers with AN.

In this article, we report first the preparation of the copolymers of the polymerizable ionic liquid 1-vinyl-3-ethylimidazolium bromide ($\text{ViEtIM}^+\text{Br}^-$) with AN. We investigated the synthesis and thermal characterization of copolymers of $\text{ViEtIM}^+\text{Br}^-$ with AN and the reactivity ratios in the copolymerization.

EXPERIMENTAL

Materials

AN (supplied as analytical reagent grade by Shanghai Chemical Reagents Co., Shanghai, China) was purified before use by distillation to remove the inhibitor. The comonomer $\text{ViEtIM}^+\text{Br}^-$ was prepared by the reaction of 1-vinyl imidazole with ethyl bromide.^{26,27} Azobisisobutyronitrile (AIBN) was used as the initiator and was recrystallized from acetone before use. Dimethyl sulfoxide (DMSO) was purified by distillation *in vacuo* before it was used as the polymerization medium.

Copolymerization

Poly(acrylonitrile-1-vinyl-3-ethylimidazolium bromide) was synthesized by radical polymerization in a

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TABLE I
Parameters for the Free-Radical Solution Copolymerization of ViEtIM⁺Br⁻ and AN at 60°C

Sample	Feed (wt %)		x (mol/mol)	Conversion (wt %)	Time (min)	Copolymer composition (wt %)		y (mol/mol)
	AN	ViEtIM ⁺ Br ⁻				AN	ViEtIM ⁺ Br ⁻	
P1	100	0	—	1.69	14	100	0	—
P2	98	2	1370	3.29	20	97.82	2.18	1280
P3	95	5	72.5	3.72	20	93.88	6.12	59.2
P4	90	10	34.5	3.86	22	88.73	11.2	30.3
P5	80	20	15.3	4.20	22	78.52	21.5	14.0
P6	60	40	5.74	4.40	29	64.35	35.7	6.91
P7	20	80	0.960	5.17	27	27.32	72.7	1.44

250-mL, three-necked, round-bottom flask equipped with a mechanical stirrer, a nitrogen inlet, and a condenser (also used as a nitrogen outlet). In a typical experiment, the required amounts of AN, ViEtIM⁺Br⁻, AIBN, and DMSO were added to the reactor, which was previously purged with ultrapure nitrogen gas. The reaction temperature was controlled by a thermostat-controlled water bath. After 24 h of polymerization, the resultant mixture was poured slowly into a large amount of ethanol for precipitation, and the precipitate was washed with ethanol several times, dried at 60°C *in vacuo*, and then weighed and characterized.

For the kinetic study of the aforementioned copolymerization, a typical polymerization procedure was as follows. A Schlenk polymerization tube filled with AN, ViEtIM⁺Br⁻, AIBN, and DMSO was degassed by five freeze–pump–thaw cycles, charged with nitrogen, and sealed. The polymerization tubes were heated at 60°C in a thermostated water bath. After a predetermined time, the mixture was poured slowly into an excess of ethanol to precipitate the copolymer. The resultant copolymer was filtered and dried at 50°C *in vacuo*.

Characterization

The monomer conversions were determined gravimetrically.

Thermal analysis of the copolymers was carried out in a PerkinElmer (Waltham, MA) Pyris 1 DSC differential scanning calorimeter at a heating rate 10°C/min and over the temperature range 50–340°C.

Thermogravimetric analysis (TGA) experiments were performed with a PerkinElmer Pyris 1 TGA with a scan rate of 10°C/min up to 800°C under a nitrogen atmosphere.

¹H-NMR of poly(acrylonitrile-1-vinyl-3-ethylimidazolium bromide) was measured on a Bruker 300-MHz spectrometer (Bruker Company, USA) with DMSO-*d*₆ as a solvent, by which the composition of the obtained copolymers was calculated.

The monomer reactivity ratios for the copolymerization of AN and ViEtIM⁺Br⁻ (r_{AN} and $r_{ViEtIM+Br-}$, respectively) were determined from the monomer feed ratios and the copolymer composition by the Kelen–Tüdös (KT)²⁸ method from eq. (1):

$$\tau = \frac{x(y-1)}{ay+x^2}, \quad \xi = \frac{x^2}{ay+x^2} \quad (1)$$

where x is the ratio of the molar fractions of AN and ViEtIM⁺Br⁻ in the monomer feed, y is the ratio of the molar fractions of AN and ViEtIM⁺Br⁻ in the copolymer, and a is an equation parameter. The equation parameter can be calculated according to eq. (2):

$$a = \frac{x_{\min} x_{\max}}{\sqrt{y_{\min} y_{\max}}} \quad (2)$$

where x_{\min} and x_{\max} are the minimal and maximal molar fractions, respectively, in the monomer feed and y_{\min} and y_{\max} are the minimal and maximal molar fractions, respectively, in the copolymer.

The plot of τ versus ξ is a straight line. Extrapolation of the line to $\xi = 1$ gives r_{AN} , and extrapolation to $\xi = 0$ gives $r_{ViEtIM+Br-}/a$.

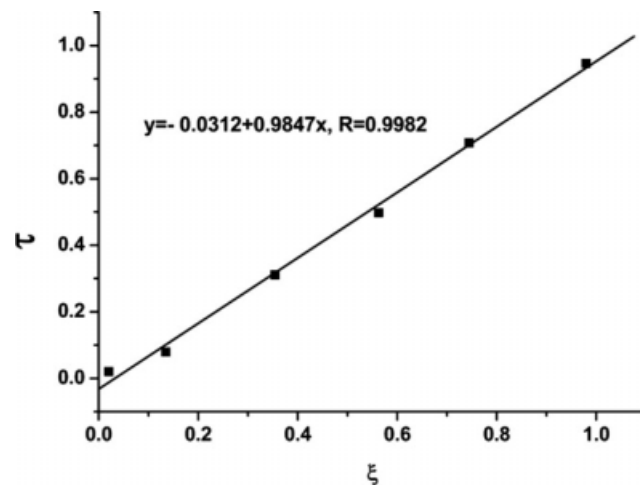
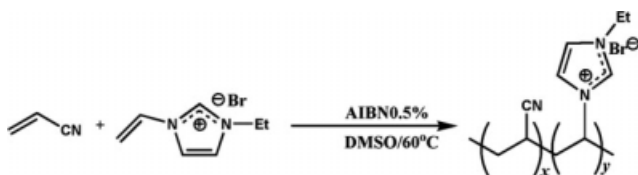


Figure 1 KT plots for the copolymer of ViEtIM⁺Br⁻ and AN system.

Scheme 1 Copolymerization of AN with ViEtIM⁺Br⁻.

RESULTS AND DISCUSSION

Monomer reactivity ratios for the copolymerization of AN with ViEtIM⁺Br⁻

The free-radical solution copolymerization technique was used to synthesize the AN/ViEtIM⁺Br⁻ copolymer. Table I shows some important parameters and the polymerization conditions of the copolymer. The KT method gave monomer apparent r_{AN} and $r_{ViEtIM+Br-}$ values of 0.954 and 0.976, respectively (Fig. 1). The result shows that $r_{ViEtIM+Br-}$ was very close to r_{AN} and $r_{AN} \times r_{ViEtIM+Br-}$ was close to 1, which could have resulted in a copolymer with a well-proportioned molecular chain, and this kind of copolymer is an ideal precursor for carbon fibers.

From the copolymer yield and time of copolymerization shown in Table I, the apparent polymerization rate (R_p) could be calculated.²⁹ The R_p values ($10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$) are given as follows: 2.26, 3.09, 3.54, 3.37, 3.59, 3.48, and 3.60 in turn from P1 to P7. On the addition of a small amount of ViEtIM⁺Br⁻, there was an increase in R_p . However, the value of R_p remained the same when more and more ViEtIM⁺Br⁻ was added to the feed. The result shows that a small amount of ViEtIM⁺Br⁻ promoted the polymerization of AN greatly.

Conversion of the copolymerization and intrinsic viscosity ($[\eta]$) of the copolymers

As shown in Scheme 1, AN and ViEtIM⁺Br⁻ were copolymerized with AIBN as the initiator and DMSO as the solvent.

TABLE II
Effect of ViEtIM⁺Br⁻ on the Conversion and $[\eta]$ Values of the Copolymers

Sample	Feed (wt %)		Conversion (wt %)	$[\eta]$ (dL/g)
	AN	ViEtIM ⁺ Br ⁻		
P8	100	0	91.5	1.43
P9	98	2	94.1	1.57
P10	95	5	99.5	2.33
P11	90	10	95.3	3.25
P12	80	20	94.5	4.97
P13	60	40	95.2	6.09

AIBN concentration = 0.5%; monomer concentration = 20%; reaction time = 24 h; solvent = DMSO; temperature = 60°C.

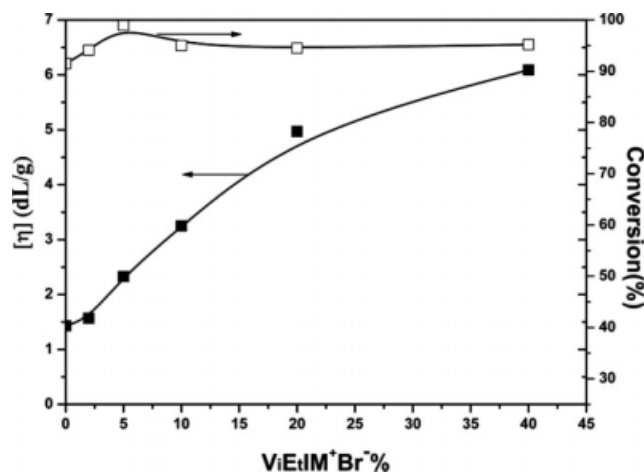


Figure 2 Plots of the (■) copolymer $[\eta]$ values and (□) monomer conversions versus the feed molar fraction of ViEtIM⁺Br⁻ (AIBN concentration = 0.5%, monomer concentration = 20%, reaction time = 24 h, solvent = DMSO, temperature = 60°C).

Table II shows the effects of the composition of monomers on the conversion of copolymerization and $[\eta]$. As shown in Figure 2, the copolymers obtained higher conversions than homopolyacrylonitrile (homoPAN), and copoly(ViEtIM⁺Br⁻-AN) (5 : 95) achieved the highest conversion (99.5%). As the concentration of ViEtIM⁺Br⁻ was increased in the feed, $[\eta]$ of the copolymers increased accordingly.

Differential scanning calorimetry (DSC) thermograms

To study the effect of ViEtIM⁺Br⁻ on the thermal properties of the copolymers, the DSC curves of the P(AN/ViEtIM⁺Br⁻) copolymers with various ViEtIM⁺Br⁻ concentrations were recorded under a

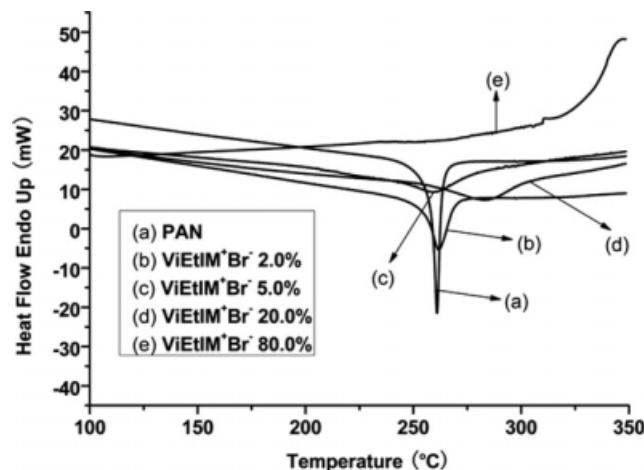


Figure 3 DSC thermograms of copolymers with various compositions of ViEtIM⁺Br⁻ (at 10°C/min under a nitrogen atmosphere).

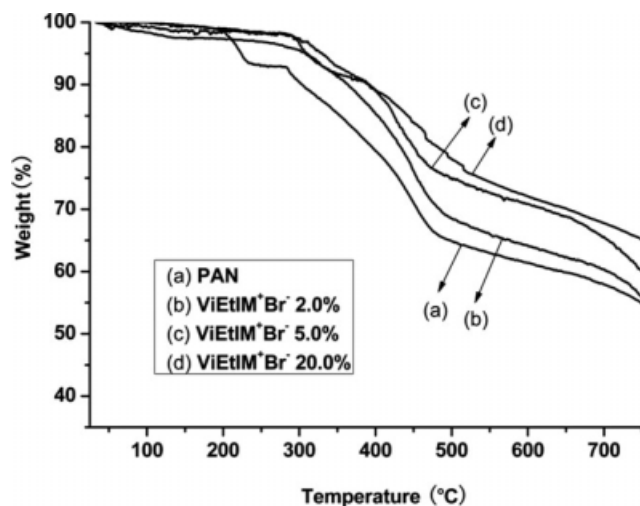


Figure 4 Typical TGA curves of copolymers with various compositions of ViEtIM⁺Br⁻ (at 10°C/min under a nitrogen atmosphere).

nitrogen atmosphere and are shown in Figure 3. It was obvious that the DSC curves of the AN/ViEtIM⁺Br⁻ copolymers were quite different from that of the homoPAN [Fig. 3(a)]: the homoPAN [Fig. 3(a)] showed a sharp and narrow exothermic peak with the lowest temperature, which was attributed to the free-radical cyclization reaction of nitrile groups in the PAN. However, the shape and width of the DSC exothermic peak of the copolymers showed great changes: the exothermic peak temperature of the copolymers increased with the ViEtIM⁺Br⁻ concentration, and the exothermic peaks of copolymers became wider and wider until no peak was observed. This phenomenon indicated that ViEtIM⁺Br⁻ could alleviate the exothermic process of the copolymers, whereas a large amount of ViEtIM⁺Br⁻ may have partially impeded the cyclization because of the breakage of continuous nitrile groups in the copolymers.

Thermal stability

The thermal stability of the homoPAN and the copolymers with various compositions of ViEtIM⁺Br⁻ was identified by TGA under a nitrogen atmosphere, with heating from 30 to 750°C at 10°C/min. Figure 4 presents typical TGA thermograms of the homoPAN and the copolymer. No weight loss in the temperature region of 30–230°C was observed for any sample. Figure 4 shows the tendency of the initial decomposition temperature to increase along with the ViEtIM⁺Br⁻ concentration. The char yields of the copolymers increased with increasing ViEtIM⁺Br⁻ content. This behavior is advantageous for the preparation of carbon fibers.

CONCLUSIONS

Copolymers of AN and ViEtIM⁺Br⁻ were synthesized for the first time by radical solution copolymerization. Kinetic studies of the copolymers showed that the monomer apparent r_{AN} and $r_{ViEtIM+Br-}$ values were very close, which may have resulted in a well-proportioned chain copolymer. ViEtIM⁺Br⁻ promoted the polymerization of AN, alleviated the exothermic process of the copolymers, and improved their thermal stability and char yields. The copolymers were characterized by ¹H-NMR, DSC, and TGA. The results suggest that ViEtIM⁺Br⁻ may be a promising comonomer for the preparation of AN precursors and carbon fibers.

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