



Synthesis of Controllable Imidazole Based Partly Ionic-Liquid Polymers

ZHEN JIAO* and XINGLONG FANG

School of Chemistry and Chemical Engineering, Southeast University, Nanjing 211189, Jiangsu Province, P.R. China

*Corresponding author: Email: jiao.zh@gmail.com

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The ionic-liquid polymers, $p[\text{vbim}][\text{PF}_6]$, based on the conventional ionic liquid and the ones, $p[\text{vpNH}_2\text{im}][\text{PF}_6]$, based on the task-specific ionic liquid have been synthesized. The ionic-liquid-structure segment mole fraction of the polymers could be controlled by adjusting the reactants' mole fraction. The ionized segment fractions in $p[\text{vmim}]\text{PF}_6$ were 19.7, 38.5 and 85.0 % at the condition of the mole fractions of 1-bromobutane to imidazole unit in the reaction mixture were 0.2, 0.5 and 1.2, respectively. And the latter was 78.1 % at 3-bromopropylamine hydrobromide to imidazole unit in the reaction mixture was 1.2. Thermal analysis indicated that the polymers had good thermal stability and the grafted chain had little effects on the polymer's glass transition temperatures.

Key Words: Ionic-liquid polymer, Synthesis, Carbon dioxide.

INTRODUCTION

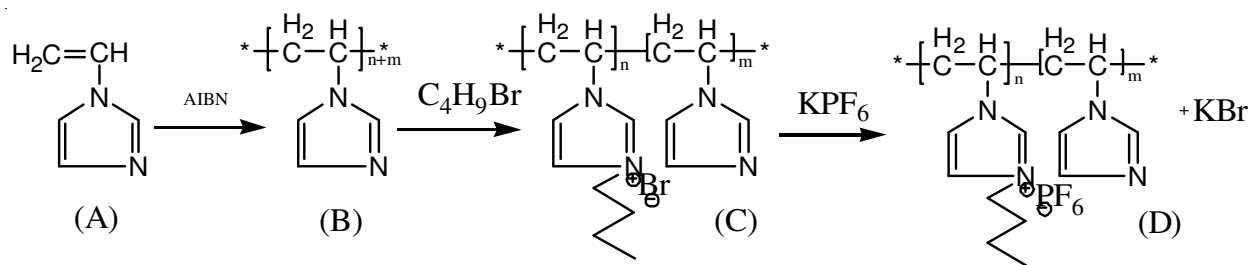
In the past few years, ionic liquids have been paid great attention because of their chemical stability, low flammability, negligible vapour pressure, low toxicity, high ionic conductivity and wide electrochemical windows, *etc.*^{1,2}. Many investigators focused on synthesizing a lot of ionic liquids to meet potential usages, such as batteries, capacitors, transistors and electro dialysis membranes. In some cases, the fluidness of ionic liquids sometimes may limit their applications. Therefore, some pioneers reported their efforts on introducing ionic liquids structure into polymers, in order to synthesize a new material, which is ionic-liquid polymers.

Watanabe *et al.*³ reported the ionic-liquid polymers of poly(1-butyl-vinylpyridinium halides) (chloride and bromide) as a new class of highly conductive polymer electrolytes. Marcilla *et al.*⁴ synthesized the polymers with polycations and the common anions as used in most ionic liquids, poly(1-vinyl-3-ethylimidazolium) or poly(1-vinyl-3-butylimidazolium) in order to investigate their solubilities in different solutions. Ohno's group⁵⁻⁹ extensively investigated ionic-liquid polymer electrolytes and made excellent achievements on improving the polymer's electrochemical performance. Shen's group¹⁰⁻¹² indicated that the poly(ionic liquid)s, especially ammonium-based ones, have much higher CO₂ sorption capacities than the room-temperature ionic liquids. After that, they investigated the permeability, diffusivity, solubility and selectivity of CO₂ relative to methane and nitrogen in polyethylene glycol-grafted polyionic membranes and found satisfactory results¹³. However,

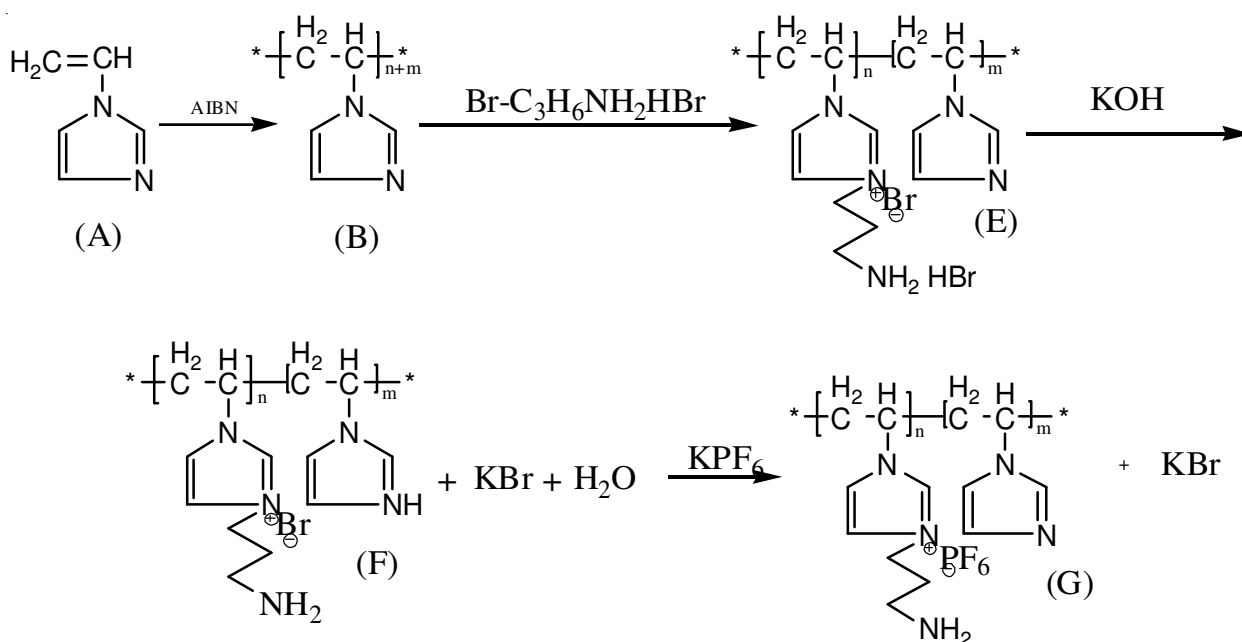
a lot of researches have proved that the task-specific ionic liquid with amino group would obtain much higher CO₂ absorption loading than normal ones¹⁴⁻¹⁶. Therefore, we believed that the ionic-liquid polymers with amino group would further improve their CO₂ sorption capacities. In this work, we polymerized 1-vinylimidazole to poly(1-vinylimidazole) followed by the reaction of alkyl bromine with the polymer to obtain ionic-liquid polymer. Instead of polymerizing the 1-vinylimidazole-based ionic liquid monomer, the advantage of this work was that the fraction of ionogenic segment could be easily controlled by reacting with different alkyl bromine at different mole ratios. These new partly ionic-liquid polymers may have potential applications in electrochemistry. According that ionic liquid with amino group could greatly increase the solubility of CO₂, we also synthesized another ionic-liquid polymer with amino group for the possible potential usage of CO₂ separation technology.

EXPERIMENTAL

Synthesis a typical ionic-liquid polymer: 1-Vinylimidazole(A) was polymerized using 2,2'-azobis(isobutyronitrile) (AIBN) (0.3 mol % to the 1-vinylimidazole) as a radical polymerization initiator in benzene at 70 °C for 5 h. The solvent was removed by rotary distillation and the pale-yellow solid product, poly(1-vinylimidazole) (B), was dried under vacuum at 70 °C for more than 24 h¹⁷. The obtained poly(1-vinylimidazole) was reacted with 1-bromobutane (the mole fraction of 1-bromobutane to 1-vinylimidazole monomer was 0.2, 0.5 and 1.2, respectively) in ethanol under refluxing condition for 24 h.



Routine-1: Synthesis of p[vbim]-p[vim]

Routine-2: Synthesis of p[vpNH₂im][PF₆]-p[vim]

The yellow, solid, ionic-liquid polymer, denoted as p[vbim][Br]-p[vim] (C), was obtained by evaporation the solvent and dried under vacuum at 80 °C for 24 h. The fraction of $n:(n + m)$ was determined by adding the different mole fraction of 1-bromobutane to imidazole unit. The p[vbim][Br]-p[vim] was dissolved in de-ionized water and followed by adding the same molar potassium hexafluorophosphate. After stirring several minutes, a solid product was generated and collected from the solution by filtration. The final product, p[vbim][PF₆]-p[vim] (D), was obtained the solid using deionized water for several times and drying under vacuum at 80 °C for 24 h.

Synthesis an amino group containing ionic-liquid polymer: Poly(1-vinylimidazole)(B) was synthesized by the same method described in route-1. The synthesized procedure was illustrated in route-2. The 3-bromopropylamine hydrobromide was prepared according to the reported of Sen¹⁸. Poly(1-vinylimidazole) (0.05 mol) and 3-bromopropylamine hydrobromide (0.05 mol) were dissolved in ethanol and reacted under refluxing. The solid reaction product, p[vpNH₂im]Br.HBr (E) was obtained after the solution turned to opacity. After filtration and being washed several times with ethanol, the solid was collected and dissolved using deionized water, followed by the addition of potassium hydroxide (0.06 mol) to release the amine from the protection by hydrobromic acid. Potassium hexafluorophosphate (0.05 mol) was dissolved

in the solution to give ionic exchange of Br⁻, generating a solid product p[vpNH₂im][PF₆]-p[vim] (G) (10.1 g). The final product was separated by filtration, followed by washing with deionized water and drying at 100 °C for 24 h.

RESULTS AND DISCUSSION

Typical ionic-liquid polymer: The elementary analysis results indicated that the ionized segment fractions in p[vbim][Br]-p[vim] were 0.197, 0.385, 0.850, respectively, at the condition of the mole fractions of 1-bromobutane to imidazole unit in the reaction mixture were 0.2, 0.5, 1.2, respectively. It revealed that the ionized segment fraction would be increased with the increasing mole fraction of 1-bromobutane in the reaction mixture. However, the conversion of 1-bromobutane would be decreased at the same condition. An important reason of the decreasing conversion was that the charges in the ionized segment might prevent the ionization of the other segments beside them. On the other hand, the steric effect of the alkyl on the ionized segment may also play another important role.

The FT-IR spectra of the three p[vbim][PF₆]-p[vim], were determined using the NICOLET Nexus 870 and shown in Fig. 1(a-c). Fig. 1 (d) was the FT-IR spectra of p[vpNH₂im][PF₆](G), being similar to that of p[vbim][PF₆]. The most apparent difference was the appearance of the peak at 1085 cm⁻¹, which was the characteristic peak of NH₂ group. Most peaks were similar besides the difference of relative intensity. Thermo-

gravimetric analysis was run on Perkin-Elmer Pyris 1 TGA, indicating that the polymer of 85 % ionized segment was stated to decompose at about 350 °C. This is in well accordance with Ohno's ionized polymers¹¹. Differential scanning calorimetric experiments were also performed on a PerkinElmer DTA7 and showed that the glass transition temperatures (T_g) of the ionized polymers having 0.197, 0.385, 0.850, mole fraction ionized segment were 161 °C, 163 °C, 158 °C, respectively. It indicated that the grafted chain (C_4H_9 group) had little effects on the polymer's glass transition temperatures.

Thermogravimetric analysis indicated that the product was stated to decompose at about 320 °C and differential scanning calorimetric experiments showed that the glass transition temperatures (T_g) was 197 °C.

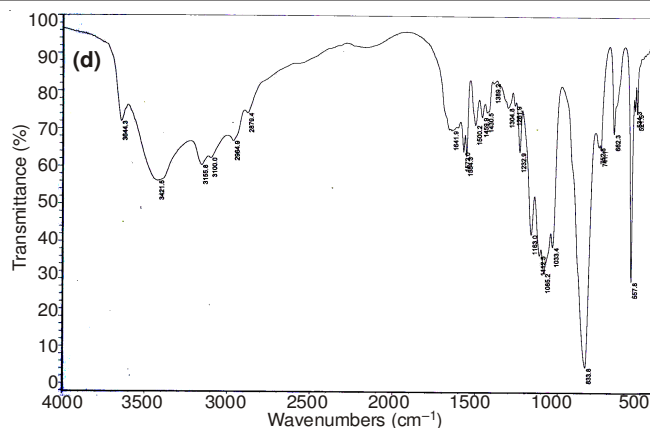
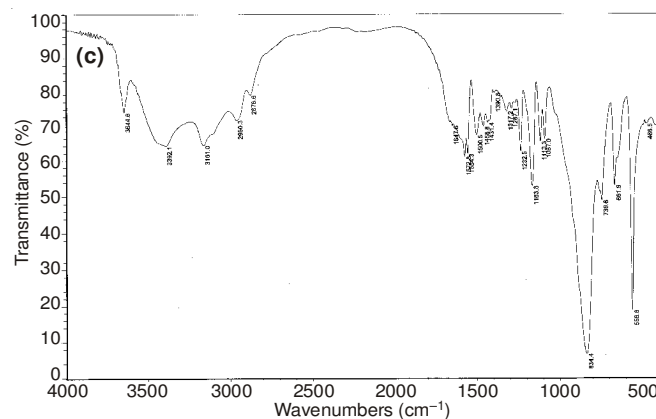
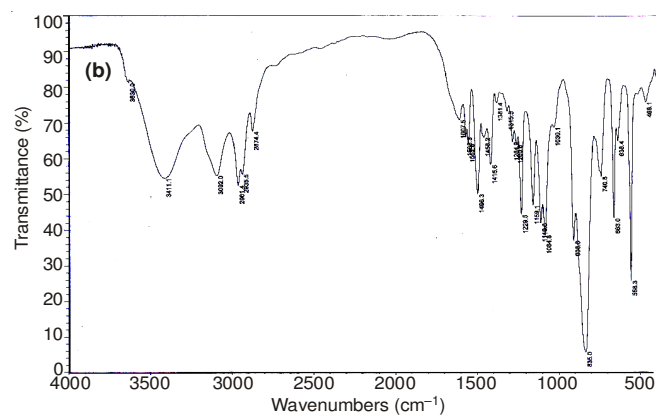
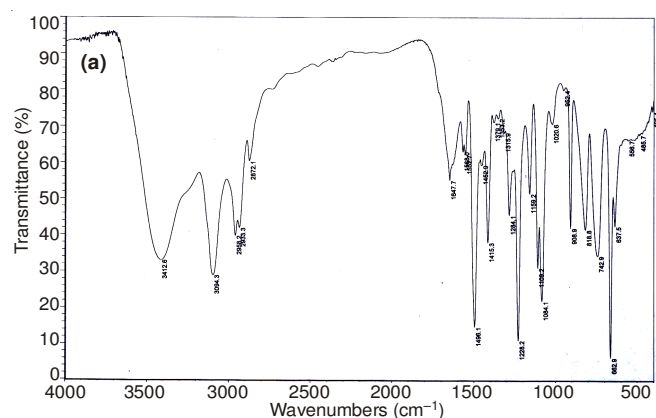


Fig. 1. FT-IR spectra of p[vybim][PF₆]s with 0.197 (a), 0.385 (b), 0.850 (c) and p[vpNH₂im][PF₆]d (d)

Amine group contained ionic-liquid polymer: The fraction of ionized segment of p[pv-pNH₂-im]PF₆(G) calculated by the elementary analysis result 0.781, which was closed to the yield of 1-bromobutane when reacting with poly(1-vinylimidazole)(in 1.2:1 mole ratio).

Conclusion

A typical ionic-liquid polymers, p[vybim][PF₆], which might be used for potential electrolytes has been synthesized. The synthesized polymer shows excellent thermal stability and the grafted alkyl chain had little effects on the polymer's glass transition temperatures. Furthermore, an amino group contained ionic-liquid polymer was also successfully synthesized. It might be used as a potential CO₂ absorbent.

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