

## Synthesis and Characterization of a Novel Ionic Liquid Polymer: Poly(1-(3-aminobenzyl)-3-methylimidazolium chloride)\*

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**Abstract** A new type of polymerizable ionic liquid (IL) 1-(3-aminobenzyl)-3-methylimidazolium chloride (AMIC) was synthesized to obtain a novel polymer salt poly(1-(3-aminobenzyl)-3-methylimidazolium chloride) (PAMIC). The AMIC was structurally characterized by mass spectrometry and Fourier transform infrared spectrometry (FTIR). The structure, morphology and properties of PAMIC were investigated by FTIR, ultraviolet visible absorption spectra (UV-Vis), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), conductivity measurement and thermogravimetric analysis (TGA). The PAMIC was spherulitic with an average diameter of about 50 nm and showed high conductivity and excellent thermal stability.

**Keywords:** Ionic liquid; 1-(3-Aminobenzyl)-3-methylimidazolium chloride; Polymerization; Poly(1-(3-aminobenzyl)-3-methylimidazolium chloride).

### INTRODUCTION

As is well-known, ionic liquids (ILs) are attracting considerable attention because of their intriguing characteristics such as low volatility, low flammability, high thermal stability, high ionic conductivity and ease of recyclability. Over the last two decades, ILs have been popularly used as green organic solvents over some traditional organic solvents<sup>[1–5]</sup> for extraction processes<sup>[6–9]</sup> and polymerization processes<sup>[10–12]</sup>. In recent years, many researchers have focused on functional polymers of polymerizable ILs<sup>[13, 14]</sup> because they exhibit excellent physical and chemical properties. Many polymer electrolytes have been synthesized by polymerization of IL-based monomers<sup>[15–19]</sup>, including the use of IL-based vinyl monomers<sup>[20, 21]</sup>, the use of polymeric ILs as a kind of host matrix for the preparation of proton-conducting anhydrous polymer electrolyte membranes<sup>[22]</sup>, and the use of 1-benzyl-3-methylimidazolium hexafluorophosphate ([bmim]PF<sub>6</sub>) monomer to prepare IL substituted polyphenylene<sup>[23]</sup>.

Polyaniline (PANI) is one of the most promising conducting polymers with many unique advantages such as its high electrical conductivity, good redox reversibility, as well as good stability in aqueous solutions and air<sup>[24–26]</sup>. Many studies on the combination of PANI and ILs were reported<sup>[27]</sup>. Our group has also successfully prepared PANI nanoparticles and films in several IL media<sup>[28, 29]</sup>. However, as were reported, ILs were just used as solvents or doping agents. In this work, we attempted to design and synthesize a new polymer of IL aniline by combining the advantages of PANI and the IL. 1-(3-Aminobenzyl)-3-methylimidazolium chloride (AMIC) and

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its polymer (PAMIC) were synthesized and characterized. PAMIC has good ionic conductivity and excellent thermal stability, probably being a promising supercapacitive material or electrolyte.

## EXPERIMENTAL

### Materials

3-nitrobenzyl chloride and *N*-methylimidazole were purchased from Sigma-Aldrich. *N*-methylimidazole was distilled under reduced pressure before use. Ammonium persulfate (APS), hydrochloric acid and other chemicals were analytical grade (Sinopharm Chemical Reagent Co., Ltd). All aqueous solutions were prepared with deionized water.

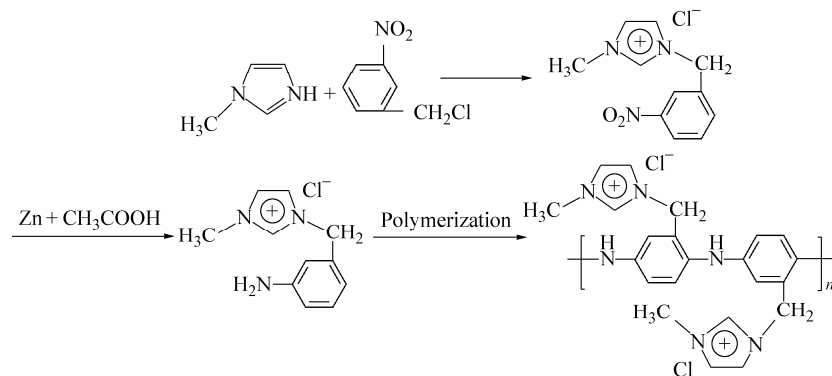
### Syntheses of AMIC and PAMIC

1-(3-Nitrobenzyl)-3-methylimidazolium chloride (NMIC) was prepared, which was then reduced to AMIC. Finally, PAMIC was synthesized by polymerization of AMIC, as described in Scheme 1.

3-Nitrobenzyl chloride (0.01 mol, 1.475 g), *N*-methylimidazole (0.01 mol, 0.81 mL) and absolute ethyl alcohol (30 mL) were introduced into a three-necked round bottom flask. After 3-nitrobenzyl chloride and *N*-methylimidazole completely dissolved in absolute ethyl alcohol, the reaction mixture was refluxed at 50 °C for 12 h under the high purity argon (99.99%) atmosphere. Then the reaction solution was evaporated under reduced pressure and the absolute ethyl alcohol was separated out. Thereafter, the mixture was washed with some distilled water and the precipitate was filtrated under reduced pressure at 80 °C. To remove residual *N*-methylimidazole, the crude product was washed with 1, 1, 1-trichloroethane. After being dried in vacuum at room temperature for 24 h, the ionic liquid NMIC was obtained as a slightly pale yellow solid.

After zinc powder and acetic acid at a molar ratio of 10:1 mixed in 20 mL distilled water under the high purity argon atmosphere, 0.005 mol NMIC was added, and then the mixture was refluxed at 80 °C for 4.5 h under magnetic stirring. After cooling down, a bit of sodium hydroxide solution was added, and then the precipitate was filtrated. The remaining solution was evaporated under reduced pressure with rotary evaporator, dried in vacuum at room temperature for 24 h. AMIC was obtained as a slightly pale yellow solid.

AMIC (0.005 mol) was dissolved in deionized water, and then 0.1 mol/L HCl (10 mL) was added. Thereafter 0.01 mol ammonium persulfate (APS) was added dropwise with constant magnetic stirring and the reaction mixture was kept for 12 h at room temperature. The precipitate was filtrated and washed with water, methanol and ethanol several times, respectively. Finally, the product was dried in vacuum at room temperature for 24 h and the polymer PAMIC was obtained as slightly rusty-brown powder.



**Scheme 1** Synthesis process of PAMIC

### Characterization Methods

The chemical structure of AMIC in methanol was characterized by a Waters ZQ4000 mass spectrometer. Fourier transform infrared spectra (FTIR) were recorded using a Perkin Elmer Fourier transform infrared spectrophotometer to identify the structures of AMIC and PAMIC. The morphology and chemical composition of PAMIC were examined by an S-4800 scanning electron microscope (SEM) and energy dispersive X-ray

spectroscopy (EDX). The ultraviolet visible absorption spectra (UV-Vis) was performed on a Lab Tech UV-240 spectrophotometer. The electrical conductivity ( $\sigma$ ) was measured by a DDS-307 electrical conductivity instrument. The thermo-gravimetric analysis (TGA) was carried out on a NETZSCH STA409PC TGA apparatus in a dynamic nitrogen atmosphere at a heating rate of 5 K/min.

## RESULTS AND DISCUSSION

### Structural Characterization of AMIC

Mass spectrometry was used to attest the structure of AMIC. As shown in Fig. 1, the most intense peak (relative abundance of 100) at  $m/z$  188 corresponding to the cation of AMIC was detected, supporting that the synthesized substance was AMIC.

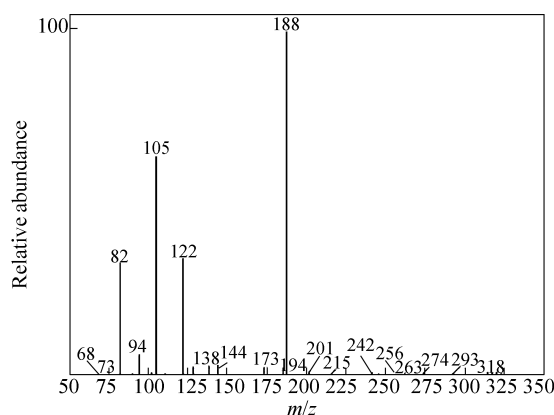


Fig. 1 Mass spectrum of AMIC

As shown in Fig. 2(a), the FTIR bands at 3293 and 3354  $\text{cm}^{-1}$  can be assigned to N—H stretching vibration mode of  $-\text{NH}_2$ . The peaks at 3006 and 1338  $\text{cm}^{-1}$  were related to C—H of the aromatic rings and C—N of imidazole ring, respectively. The spectra exhibited clearly the presence of methyl and methylene hydrogen stretching vibrations around 2937 and 2789  $\text{cm}^{-1}$ . Meanwhile the peaks at 1369 and 1429  $\text{cm}^{-1}$  corresponded to the bending modes of methyl and methylene hydrogens. The peaks at 1587 and 1485  $\text{cm}^{-1}$  can be attributed to the stretching mode of C=C of aromatic rings (imidazole ring and benzene ring). The absorption bands assignable to C—N of the benzene ring were observed at 1167 and 1047  $\text{cm}^{-1}$ . Therefore, it can be concluded from the IR spectra and mass spectra that the IL monomer AMIC was synthesized successfully according to the designed route.

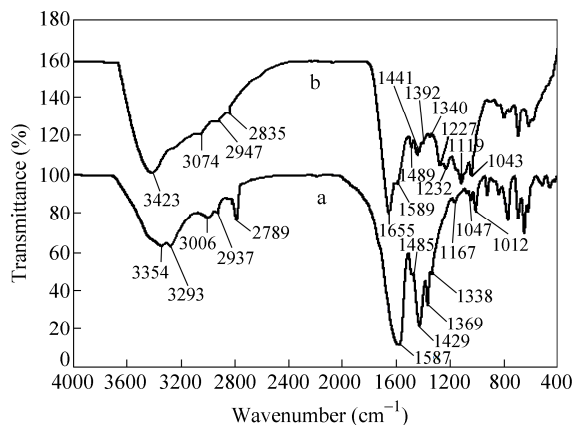


Fig. 2 FTIR spectra of (a) AMIC and (b) PAMIC

### Characterization and Properties of PAMIC

The UV-Vis absorption spectra of AMIC and PAMIC are shown in Fig. 3. Both the spectra of AMIC and PAMIC showed the characteristic absorption in the range of 300 to 350 nm which was assigned to  $\pi$ - $\pi^*$  transitions of aromatic rings<sup>[30]</sup>. Besides, Fig. 3(b) presents a new absorption peak at around 615 nm which was  $n$ - $\pi^*$  (quinoid) ring transitions in the PAMIC chain.

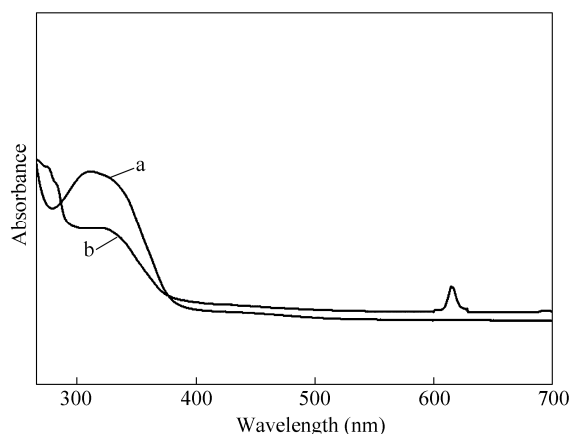


**Fig. 3** UV-Vis spectra of (a) AMIC and (b) PAMIC

The FTIR spectrum of PAMIC is shown in Fig. 2(b), it can be seen that some peaks have shifted and some new peaks appeared comparing with AMIC. For example, N—H stretching band has shifted at  $3423\text{ cm}^{-1}$  and became only one peak which was a characteristic of the emeraldine. The C=C stretching vibration of benzene ring and C—N stretching in the neighborhood of quinonoid ring have shifted from  $1587, 1485$  to  $1589, 1489\text{ cm}^{-1}$ , respectively. Besides, C—H stretching vibration and C—N stretching vibration of imidazole ring, methyl hydrogen bending and methylene bending vibration all have shifted to higher wave numbers. The new peak at  $1655\text{ cm}^{-1}$  was C=N stretching mode of the quinoid, which was typical for the PANI base. The new peak at  $1119\text{ cm}^{-1}$  can be assigned to the vibrational mode of the benzene quinoid structure ( $\text{N}=\text{Q}=\text{N}$ ,  $\text{Q}=\text{N}^+\text{H}=\text{B}$  and  $\text{B}-\text{N}^+\text{H}-\text{B}$ ), which indicated the presence of a positive charge on the chain.

Figure 4 presents SEM pictures of PAMIC particles with different magnifications. As shown in Fig. 4, the morphology of PAMIC particles was compact and regular with a growth of aggregates shaped as spheres. However, some congeries and interspaces were found, which caused by the volume steric effect of side chain, it may attribute to the low extent of reaction. Figure 4(b) shows that the average size of PAMIC particles was about 50 nm and the pore diameter was about 40–60 nm.

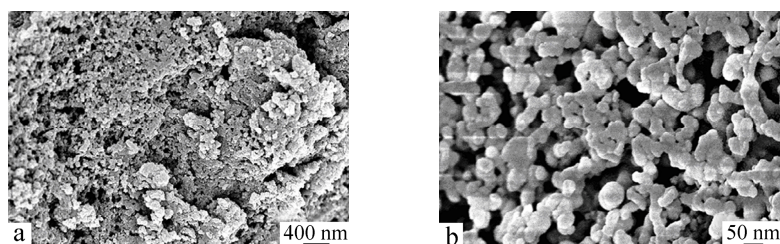


**Fig. 4** SEM micrographs of PAMIC

The composition of PAMIC was examined by EDX as shown in Fig. 5. The peaks of C and N originating from the cation of PAMIC can be found at 0.24 and 0.35 keV. The  $\text{Cl}^-$  of PAMIC was demonstrated by the Cl signals at 2.61 and 2.82 keV. The peaks of Cu, O and Au, which originated from the Cu support and sputtering gold of the polymer, were found. According to the results of EDX, PAMIC was synthesized successfully.

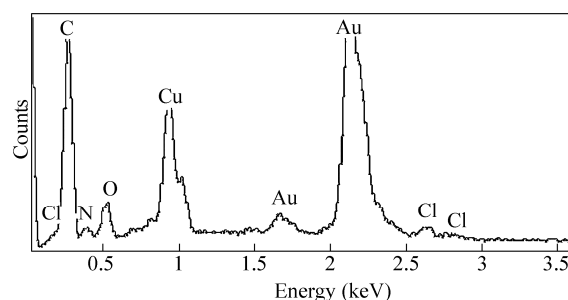


**Fig. 5** EDX spectrum of PAMIC

The conductivities of PAMIC and the commercial polyaniline were measured in dimethyl phosphate phenol. The conductivity of PAMIC at 20 °C was 23.7  $\mu\text{S}/\text{cm}$ , this value was much higher than that of the commercial polyaniline (14.5  $\mu\text{S}/\text{cm}$ ). The higher conductivity of PAMIC compared to the commercial polyaniline was probably based on the large pendant chains of PAMIC which lowered the symmetry of the molecule and then reduced the interaction between imidazolium cation and anion of PAMIC. This was also due to the more free ions that existed in the PAMIC solution in comparison with the polyaniline one, it facilitated the mobility of the free ions and polymer chains.

The TGA curve of PAMIC is presented in Fig. 6. There were three-step weight loss stages observed in the temperature range of 50–800 °C. The first step indicated 15% weight loss at temperature up to 105 °C, this may be attributed to the loss of unbound water and unbound HCl<sup>[31]</sup>. The second step of weight loss occurring from 210 to 335 °C may be due to the loss of bound water, free Cl<sup>−</sup> of the PAMIC and bound HCl acting as dopant, respectively. The third step occurring from 460 to 610 °C was ascribed to the degradation of the PAMIC backbone<sup>[32]</sup>. Results obtained above 610 °C were associated only with the polymer residues. Thermal degradation of the polymer chain occurred above 460 °C. The high degradation temperature may be due to the ionic groups stabilizing the polymer main chains. So it implied that the novel polymer possessed excellent thermal stability and was difficult to degrade under heat.

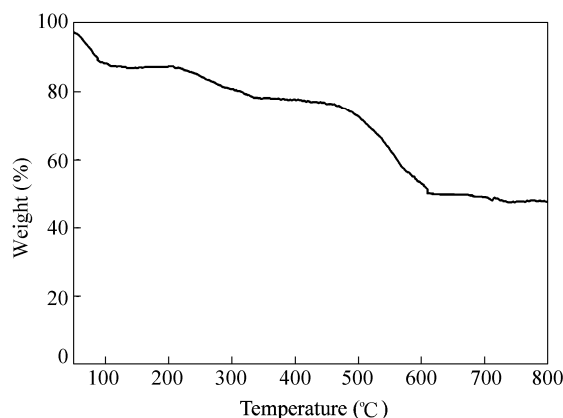


**Fig. 6** TGA curve of PAMIC

## CONCLUSIONS

In summary, we have synthesized the polymerizable aniline-group-containing IL AMIC to obtain a new conducting polymer PAMIC. Various instrumental analysis methods have been used to characterize PAMIC. The PAMIC particles are spherulitic with an average diameter of about 50 nm and show high ionic conductivity and good thermal stability. We believe that the new PAMIC material is useful for the supercapacitor and ion conductive matrix. Further work on the use of PAMIC in electrolytes and capacitors is being carried out.

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