Doped Polyaniline in Brønsted Acid Ionic Liquid 1-Butyl-3-methylimidazolium *bis*[trifluoromethyl(sulfonyl)]imide/*Bis*[trifluoromethyl(sulfonyl)]imide

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ABSTRACT: We report the preparation and characterization of doped polyaniline (PANI) in an ionic liquid 1-butyl-3-methylimidazolium *bis*[trifluoromethyl(sulfonyl)]imide (BMImTFSI) medium. Aniline monomer was chemically polymerized via oxidation with $KMnO_4$ in an ionic liquid BMImTFSI solution containing a monoprotic Brønsted acid *bis*[trifluoromethyl(sulfonyl)]imide (HTFSI). HTFSI is the source of proton that doped PANI. The identity of PANI as the reaction product was confirmed with both ultraviolet–visible and Fourier transform infrared spectra. Unlike syntheses in aqueous media, the doped PANI did not readily precipitate from the ionic liquid; a transparent and stable green solution-like liquid dispersion was obtained (dispersion is used to refer the product hereafter). PANI precipitated when dedoped with organic bases such as triethylamine. The PANI precipitate can be redoped by HCl and the so-doped PANI has conductivity of about 2.0×10^{-2} S/cm. The liquid dispersion of doped PANI in the ionic liquid can be diluted by many organic solvents or other ionic liquids to diluted "solutions." © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

Synthetic conducting polymers such as polyaniline (PANI), polythiophene, and their derivatives have been the target of scientific research for decades. In addition to their conducting properties, materials such as PANI are often coveted for their competitive cost of use. However, a major obstacle in the application of PANI is its lack of solubility in common organic solvents. When synthesized chemically in an aqueous environment, PANI readily precipitates. This property of PANI restricts the processing and application of PANI. Developing a method for preparing soluble PANI, dispersible PANI, or PANI nanoparticles or nanofibers can solve the problems of PANI processing.[1–5] Within the last decade, methods have been developed to obtain PANI nanofibers or nanoparticles that are dispersible in aqueous media by a series of polymerization methods. In most cases, either micelle/H_2O or organic/aqueous interfacial polymerizations were utilized.[6–13] For example, a stable PANI dispersion in aqueous acidic solution has been prepared with a micelle-aided polymerization method.[10]

Ionic liquids (ILs) have also been the object of growing interest within the scientific community, owing to their remarkable properties such as negligible vapor pressure, low melting point, nonflammability, ability to solvate many organic and inorganic chemicals, high viscosity when compared to common organic solvents, and high ionic conductivity. These properties make ILs a suitable medium for chemical reactions, as well as for numerous other applications. In addition, ILs are considered "green solvents" because of their nonvolatility. ILs are potential candidates to replace the organic solvents that are being used in chemical and biochemical industries, making these industries more environmental friendly.[14–20]

PANI and other conductive polymers have been electrochemically prepared and characterized in ILs.[21–29] Snook reported a comparative study of electrochemical polymerization of aniline in IL 1-butyl-1-methylpyrrolidinium TFSI (C_4mpyrTFSI) and ethylammonium nitrate (EAN).[29] In an acidic EAN IL solution, the polymerization of aniline and electrochemical properties of PANI on Pt electrode resembled those of PANI prepared in an acidic aqueous solution. In the nonacidic C_4mpyrTFSI IL solution, the polymerization was rather slow and inefficient. Fuchigami reported that PANI was prepared from aniline monomer dissolved in an $EMICF_3SO_3$/$1.0M$ CF_3SO_3H solution.[30] Li and
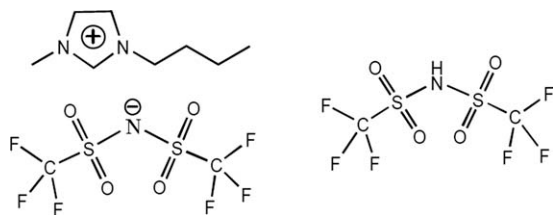
Figure 1. Structure of BMImTFSI (left) and HTFSI (right).

Xu reported the use of 1-ethylimidazolium trifluoroacetate as an electrolyte to deposit PANI on Pt electrode.[26,27] Kan reported the synthesis of PANI on Pt electrode in 1-ethyl-methylimidazolium ethyl sulfate.[31] PANI nanotubes were synthesized on indium tin oxide (ITO) electrodes in BMImPF$_6$ containing 1.0M CH$_3$COOH.[32] PANI can also be deposited on Pt, Au, or ITO electrodes by scanning the positional between −0.35 and 1.9 V vs. Ag wire in an aniline solution in pure 1-butyl-2,3-dimethylimidazolium bis[trifluoromethyl(sulfonyl)]imide.[33] In these electrochemical depositions of PANI in ILs, an organic acid was usually employed as the required proton source. The polymerization produced a solid thin film of doped PANI on the surface of electrodes.

In this study, the IL 1-butyl-3-methyl-imidazolium bis[trifluoromethyl(sulfonyl)]imide BMImTFSI was used as a solvent of aniline monomer and a monoprotic Brønsted acid HTFSI. Protons were produced by the ionization of HTFSI, which doped the PANI. Their structures are shown in Figure 1. Doped PANI in the IL BMImTFSI was obtained by chemical oxidation of aniline monomer with KMnO$_4$. The oxidizing reagent KMnO$_4$ has been used in aqueous solutions or at an organic/aqueous interface to polymerize aniline and produce MnO$_2$ as well.[34–36] In these systems, KMnO$_4$ can react with aniline and produce PANI precipitate or PANI/MnO$_2$ composite. In IL, the so-produced dispersion was solution-like. The highly concentrated PANI dispersion was very stable over 6 months. The dark green dispersion can be diluted by organic solvents such as acetone or ethanol without any precipitation after dilution. In addition to yielding a stable doped PANI solution-like dispersion, the IL medium was found to be suitable for the high-throughput chemical oxidation preparation of PANI.

EXPERIMENTAL METHODS

BMImTFSI was purchased from EMD Chemicals Inc. (Gibbstown, NJ) and used after dried in vacuum oven at 60°C overnight. HTFSI and KMnO$_4$ were purchased from Sigma-Aldrich Inc. (St. Louis, MO) and used as received. Aniline was also purchased from Aldrich; it was used after fresh distillation under vacuum. KMnO$_4$ solution in BMImTFSI/HTFSI was added dropwise into an aniline solution in BMImTFSI/HTFSI when temperature was controlled at 4°C in ice bath. The solution started to become green after about 30 minutes and became very dark green eventually. The solution was continuously stirred for several hours.

Concentrations of two typical polymerizations at the high-aniline concentration end are listed in Table I. In both cases, the ratio of the amount of the aniline monomer to the amount of

Table I. Concentrations of the Chemicals of Polymerization Reactions

Trial	1	2
BMImTFSI volume for aniline	5 mL	5 mL
[HTFSI] in BMImTFSI	0.5M	1.5M
[Aniline]	0.133M	0.5M
No. of mole of aniline	6.65×10^{-4} mol	2.5×10^{-3} mol
BMImTFSI volume for KMnO$_4$	4 mL	4 mL
[KMnO$_4$]	0.133M	0.5M
No. of mole of KMnO$_4$	5.32×10^{-4} mol	2.0×10^{-3} mol
Aniline/KMnO$_4$ ratio	1.25	1.25

oxidant was 5 : 4. Details of the experimental procedures are shown in Figure 2.

Ultraviolet–visible (UV–Vis) spectra were measured with a HP 1100 UV–Vis Spectrometer at room temperature with pure BMImTFSI as background. Fourier transform infrared (FTIR) spectra were measured with a Varian FTS 7000 FTIR Spectrometer with KBr pellet. Conductivity was obtained by a 4-point probe measurement with an even space of 0.635 mm between each two neighbor probes. A Keithley 224 current source and an HP 34401A multimeter were used.

RESULTS AND DISCUSSION

When started adding KMnO$_4$ solution into the aniline solution, emerald green color showed up after about 30 min. The solution was transparent at beginning; it turned to be very dark green eventually after all the KMnO$_4$ solution was added. During the process of the reaction, the solution was set in a 4°C ice bath; no significant temperature change or gas product was observed. This is different from the aniline polymerization in aqueous systems, in which temperature raised quickly in the initiation stage of polymerization. In IL BMImTFSI/HTFSI, the aniline monomer concentration can be as high as 0.5M, which yields a high-throughput synthesis of aniline. The polymerization of aniline requires strong acidity in the reaction mixture. In the IL solutions, HTFSI was added as an acid and proton source. HTFSI has been demonstrated to be a strong acid in aqueous solutions or IL solutions for PANI protonation. pH measurements indicated that the HTFSI behaved like an ideal strong monoprotic Brønsted acid in aqueous solutions. The HTFSI concentration can be raised to about 2.5M. When the HTFSI concentration is higher than 2.5M, KMnO$_4$ was no longer stable and not suitable for use as the oxidant of aniline polymerization.
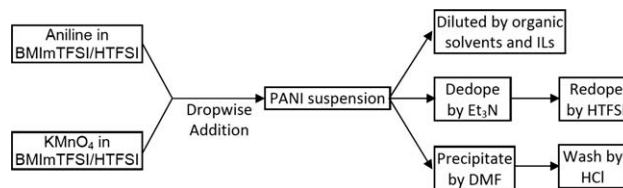

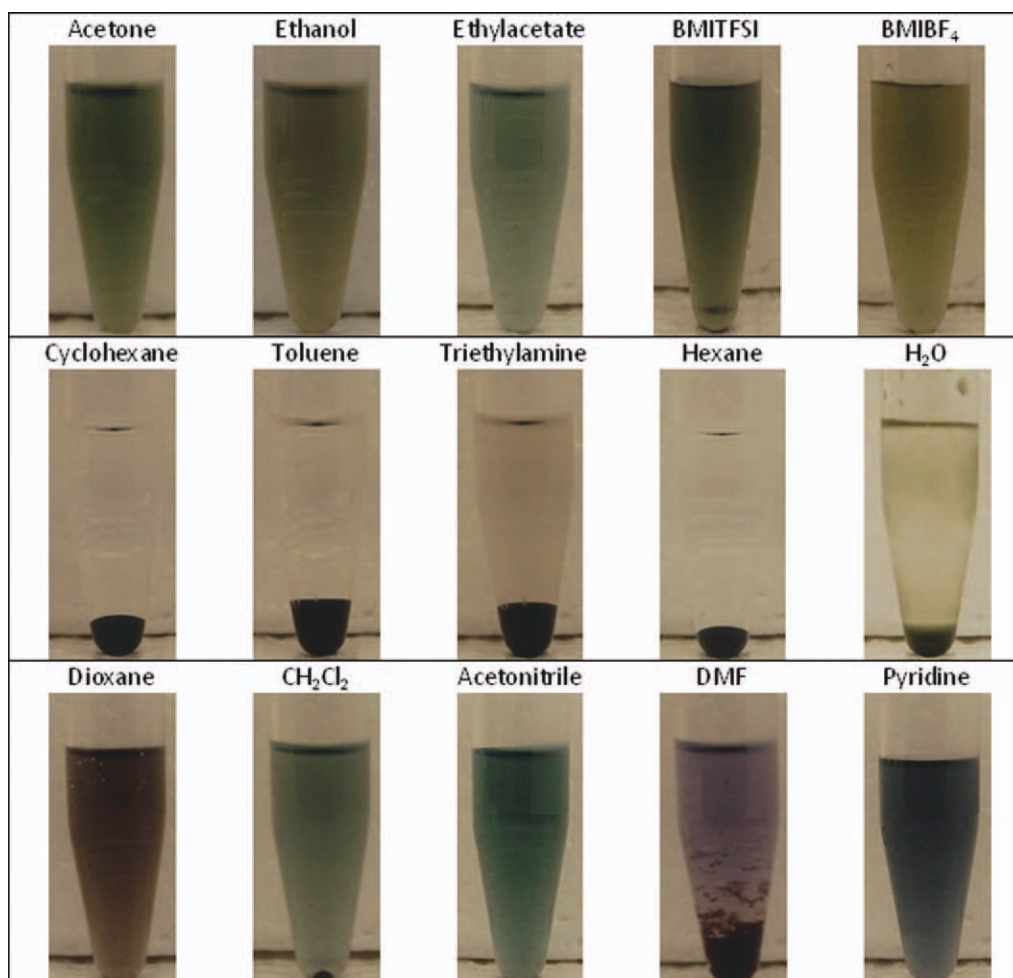**Figure 2.** Experimental produces of PANI preparation.

Figure 3. PANI dispersion in BMImTFSI diluted with different solvents. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

After polymerization, a homogeneous dark green liquid was obtained. Although it is usually hard to distinguish, a thermodynamic real polymer solution and colloidal polymer dispersion, the so-produced liquids have several solution-like properties. The PANI dispersion in BMImTFSI was very stable. No precipitate was observed when the solution was stored in air for several months or centrifuged for 30 min at 13,000 rpm. When the solution was pressed through an Acrodisk PSF PTFE 0.2-μm syringe filter, no solid was collected on the filter membrane.

In aqueous solutions, aniline can be polymerized with the existence of excess Brønsted acids and equivalent $(NH_4)_2S_2O_8$ in the solution.[2,3] Protonated anilinium $(C_6H_6NH_3^+)$ is oxidized to be a radical cation in the initiation step; a dimer is then formed. In the propagation step, the dimers bond to an additional radical cation to form a trimer and so on. The polymerization product yields pernigraniline (oxidized state of PANI). The pernigraniline is reduced to the emeraldine salt as aniline monomer is oxidized to the radical cation. The polymer (emeraldine salt) backbone is positively charged. Counter anions associate with the polymer backbone by ionic bonds. The emeraldine salt is not soluble in water and, therefore, precipitates from the water solution. Aniline is soluble in IL BMImTFSI, whereas HTFSI is a Brønsted acid that can dissociate to produce H^+ and $TFSI^-$ anion. Protons are required for the polymerization of aniline. Therefore, in BMImTFSI aniline can be protonated to be anilinium $(Ph-NH_3^+)$. The initiation and propagation steps may resemble the mechanisms in aqueous solutions. $Ph-NH_3^+$ may first be oxidized to be a radical cation $(Ph-NH_3^{+\bullet})$ by $KMnO_4$. This radical cation may connect with its resonance structure $(\bullet Ph-NH_3^+)$ to make a dimer. When oligomer or polymer forms, the positively charged polymer backbone bonds with negatively charged counter ions. In aqueous solution, the polymer cannot be solvated by water and dissolved in water. In the IL solution, the polymer backbone bonds to the counter ion $(TFSI^-)$ and may then be solvated by the $BMIm^+$ cation. As the bulk IL contains solely these two ions, the solvated emeraldine salt may be stable in the IL solution. Hence, no precipitate was obtained. Details of the polymerization mechanism and the solution thermodynamics have not been fully explored at this point.

The PANI/BMImTFSI dispersion can be diluted by many organic solvents or ILs. After dilution, homogeneous and
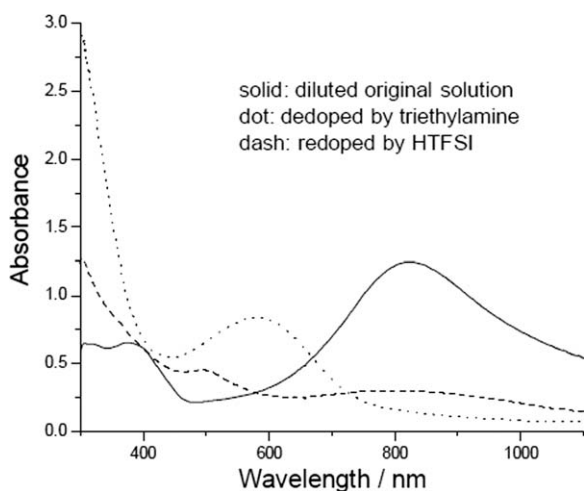
Figure 4. UV–Vis spectra of PAn/IL dispersions. Solid: reaction mixture diluted by BMImTFSI; Dot: Dedoped by triethylamine; Dash: Redoped by HTFSI.

transparent solution-like dispersions were obtained as shown in Figure 3. When the PANI/IL dispersion was diluted by acetone, ethanol, ethyl acetate, BMImTFSI, or BMImBF$_4$, transparent green solution-like dispersion was obtained. These dispersions were also stable. No precipitate was observed after several months or centrifuging at 13,000 rpm for 30 min. After dilution, the colors of the solution-like dispersions were slightly different. For example, the ethyl acetate solution was bluish compared to PANI solutions diluted with other solvents. BMImTFSI is immiscible with several nonpolar organic solvents and water. When the PANI/IL dispersion was added into these solvents, two phases existed. In hexane, cyclohexane, and toluene, neither the solvent nor the IL phases exhibited visible change. When the PANI/IL dispersion was added into water, some precipitate formed at the interface. BMImTFSI is soluble in triethylamine as opposed to miscible with it. After the PANI/IL dispersion was added into triethylamine, the PANI/IL dispersion converted to blue immediately and a precipitate formed over time. The precipitate was separated by centrifugation at 2800 rpm and thoroughly washed by HCl solution, NaOH solution, water, and acetone by turn. A black powder was obtained and the yield (from aniline monomer) was 25% or above. Dioxane, dichloromethane, acetonitrile, dimethylformamide (DMF), and pyridine were each separately used to dilute the PANI/IL dispersion. The color of the solution changed significantly from green to brown after dilution with dioxane, bluish after dilutions with dichloromethane and acetonitrile, and blue after dilutions with DMF and pyridine. In DMF, PANI precipitated immediately.

Afterward, a portion of the original PANI/IL dispersion was further diluted by BMImTFSI to yield a transparent green solution. The UV–Vis spectrum of the PANI solution was measured and is shown in Figure 4. Absorption bands at about 400 and 820 nm are typical characteristic peaks of doped PANI. When the organic base triethylamine was added into the solution, the PANI was dedoped and the color of the solution changed to blue first and brown later. Initially, no precipitate could be observed; however, brown precipitate settled to the bottom after

extended time. The brown color may also come from Mn^{2+} salts, which were the reduction product of MnO$_4^-$. This precipitate was partially soluble in 1.0M HCl, which also supports the presence of Mn^{2+} salts. The reduction products of MnO$_4^-$ have not yet been further investigated. The brown solution can be converted back to green by adding excess HTFSI to neutralize the extra triethylamine and redope the PANI. These color changes of solution indicate the dedoping and redoping of PANI, which can be confirmed by UV–Vis spectra of the solution. Figure 4 shows the doped PANI-BMImTFSI, as well as both the dedoped version achieved after further treatment with triethylamine and the redoped version achieved after additional treatment with HTFSI. Like typical PANI samples, the diluted PANI solution showed a distinct decrease in intensity at 800 nm after treatment with triethylamine, followed by a recovery of some absorbance at 800 nm when redoped by further treatment with HTFSI.

PANI was precipitated from the IL dispersion by adding triethylamine and separated by centrifuging at 13,000 rpm for 5 min. Then, it was washed in sequence with acetone and 1.0M HCl to produce doped PANI powder. The doped PANI was treated with 1.0M NH$_4$OH to obtain dedoped PANI. The sample was finally dried in vacuum oven overnight at 50°C. FTIR of the dedoped PANI powder is shown in Figure 5 and presents typical peaks of PANI. The peaks at about 1591 and 1503 cm^{-1} were characteristic of benzoid structure and quinoid (Q) structures, respectively. The peak at about 1310 cm^{-1} was caused by the stretching of C—N bonds; the peak at about 1167 cm^{-1} was assigned to the Q=N=Q bending; and the peak at about 833 cm^{-1} was characteristic of *para*-substituted benzoid structures.

Finally, the so-produced PANI was doped with 5% HCl and then washed by acetone. The doped PANI was pressed to make a pellet with a diameter of 7.0 mm and a thickness of 0.25 mm. The conductivity was measured to be 2.0 ± 0.6 × 10^{-2} S/cm (n = 16) at room temperature. The conductivity value further confirmed that conductive doped PANI has been prepared in IL solution of HTFSI in BMImTFSI.
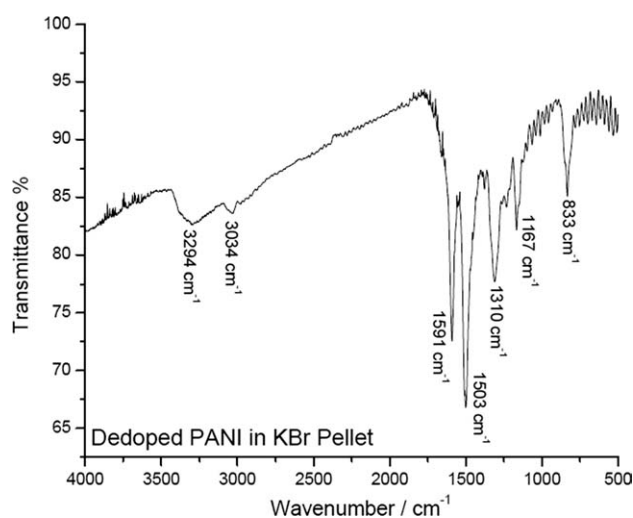

Figure 5. FTIR spectrum of dedoped PAn taken in KBr pellet.

CONCLUSIONS

It has been shown that it is possible to synthesize doped emeraldine PANI in an IL with a chemical oxidant. The identity of the product was verified with both UV–Vis and infrared spectroscopy. Furthermore, it can be concluded the PANI product does not readily precipitate, but rather forms a stable and dilutable solution-like dispersion in the IL. The emeraldine salt can be dedoped and redoped by organic Brønsted base and acid, respectively. Aniline was polymerized with concentrations as high as 0.5M in IL, providing a high-throughput polymerization method.

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