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Synthetic Metals 155 (2005) 105–109

SYNTHETIC METALS

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Preparation of organo-soluble polyanilines in ionic liquid

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Received 12 July 2004; received in revised form 20 December 2004; accepted 17 June 2005

Abstract

A method for preparation of organo-soluble polyaniline (PANI) is described. Oxidative coupling polymerization of anilium chloride with ammonium persulfate in a new ionic liquid, 2-hydroxyethyl ammonium formate (HAF), gives organo-soluble polyaniline with appreciable molecular weights ($M_w = 86{,}400$). Interestingly polyaniline (PANI) prepared by this method is highly soluble in many organic solvents such as acetone, tetrahydrofurane, dioxane, dimethyformamide and *N*-methyl, 2-pyrrolidinone. Thin films of PANI prepared at 0 °C (by solvent casting) show reasonable conductivities (up to $37.0\,\mathrm{S\,cm^{-1}}$) when doped with *p*-toluene sulfonic acid.

Keywords: Organo-soluble polyaniline; Ionic liquid; Ammonium persulfate; Oxidative polymerization

1. Introduction

Among conducting polymers, PANI has received greater attention due to its advantages over other conducting polymers. Simplicity of its preparation from cheap materials, superior stability to air oxidation, controllable electrical conductivity by doping and de-doping [1], reversible electrochromism [2] make it very useful in preparing light-weight batteries [3], electrochromic devices [4], sensors [5] and electro-luminescent devices [6].

Ammonium persulfate (APS) has been demonstrated to be the best oxidizing agent in mass production of PANI. Molar ratios of APS must be 1.20–1.25 to avoid over oxidation [7]. Gradual addition of APS below 20 °C has been reported to give highly conducting PANI's when doped with *p*-toluene sulfonic acid (PTSA), camphor sulfonic acid [8] and dodecyl benzene sulfonic acid [9].

Despite great potential use of PANI it's processing has remained a difficult problem due to its insolubility in common organic solvents. About 1% of solubility is observed in *N*-methyl, 2-pyrrolidone (NMP) which also acts as plasticizer [10]. Polymerization in 1.0 M solution of LiCl in NMP has been claimed to enhance both solubility and conductivity [11]. Incorporation of alkyl substituents increases solubility, however, electrical conductivity reduces [12].

Preparation of PANI in aqueous solution of poly(4-styrene sulfonic acid) [13], polyacrylic acid [14] or dodecyl benzene sulfonic acid [15] has been reported to give self-doped soluble PANI.

Preparation of soluble PANI has been subjected in many articles. Oxidation of aniline in concentrated H_2SO_4 has been reported to give PANI soluble in H_2SO_4, CF_3SO_3H and CH_3SO_3H [16].

However, resulting product of this procedure must be mostly sulfonated rather than naked PANI. Polymerization of aniline–dodecylbenzene sulfonic acid salt in aqueous suspension of chloroform has been reported to yield doped PANI, which is soluble in chloroform [17]. Also polymerization of dibutyl naphthalene sulfonic acid salt of aniline in the presence of acetone has been reported to give polyanilines, which are highly soluble in many organic solvents such as toluene, THF and chloroform [18]. PANI with high solubility in toluene and other simple organic solvents has been commercialized under trade name of "PANDA^{TM}" from Omercon Chemie in Germany and from Monsanto Co. in USA.

There appear quite a few articles describing preparative methods of soluble PANI. Main principle of those studies is oxidation

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doi:10.1016/j.synthmet.2005.06.010

of aniline in a solution of organic sulfonic acid providing solubility in organic solvents.

Herein, we describe an alternative pathway for preparation organo-soluble PANI. In the method described anilinium hydrochloride is oxidized by ammonium persulfate in a new ionic liquid. During researches in our laboratory, we have noticed that formic acid salt of 2-hydroxyethyl amine (ethanol amine) is an ionic liquid having a freezing point of −82 °C. It has been observed that this ionic liquid is able to dissolve many inorganic salts and PANI. This phenomenon envisaged us to prepare PANI in this liquid.

In this study, solubility of the PANI obtained in the ionic liquid has been investigated and its structure has been discussed based on ^{1}H-NMR, FT-IR, UV–vis spectra, conductivity and GPC measurements.

2. Experimental

The chemicals used were all of reagent grade. Aniline was distilled before use.

2.1. UV–vis spectra

UV–vis spectra of PANI in 1,4-dioxane was recorded using A Schimadzu 160A UV–vis spectrophotometer.

2.2. FT-IR spectra

FT-IR spectra were taken by a Mattson 1000 FT-IR Spectrometer.

2.3. Conductivity measurements

Electronic conductivities of the polymers were measured using by four-probe method, using pellets on a Keithley 617 electrometer connected to a four-probe head with gold tips and calculated from the following equation:

$$\sigma = V^{-1} I \left(\ln \frac{2}{\pi d_n} \right)$$

where V is the potential in volts, I is the current in amperes and d_n is the thickness in cm.

2.4. ^{1}H-NMR spectra

These were obtained from DMSO-d$_6$ solutions by a Bruker Ac (250 MHz) spectrometer.

2.5. Elementary analysis

Elementary analysis were performed by a CHNS-932 LECO model instruments.

2.6. Gel permeation chromatography (GPC)

GPC traces were taken by using an Agillant 1100 series consisting of a pump, a RI detector and Waters styrogel (HR 4, HR 3 and HR 2) columns. Tetrahydrofuran was used as the eluent, and the flow rate was 0.3 mL/min.

2.7. Cyclic voltamograms (CV)

CV of PANI.HCl films casted from dioxane solution onto Pt electrode were recorded using POS Wenking 73 Model potentiostat connected to a Kipp and Zonen X-Y recorder.

2.8. Preparation of the ionic liquid

The ionic liquid (2-hydroxyethyl ammonium formate) has been prepared and characterized as described before [19].

2.9. Polymerization of anilinium hydrochloride in ionic liquid

Soluble polyaniline has been synthesized by the chemical oxidation of anilinium hydrochloride with ammonium persulfate as oxidant. 1.3 g (0.01 mol) anilinium hydrochloride was dissolved in 35 g of the ionic liquid. To this solution, there was added ammonium persulfate (2.85 g, 0.0125 mol) in small portions while stirring. The reaction was continued for 3 days at room temperature. After this time, viscous reaction mixture was poured into 200 mL of aqueous NaOH solution (0.1 M). The polymer precipitated was filtered and washed excess of water to remove soluble fractions. The filtered cake was then dried under vacuum for 24 h (yield 0.7 g (75.3%)).

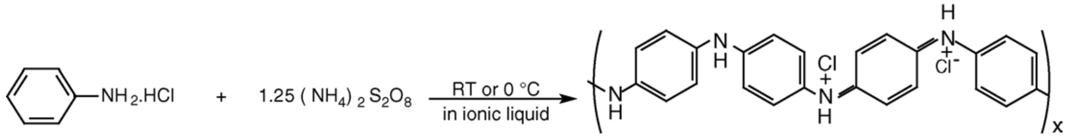
The product was not pure enough. It was purified by dissolving in 20 mL acetone and precipitate in 30 mL of diethyl ether. This was repeated once again. A darker product was isolated by suction and dried under vacuum. The filtrate after removal of solvent mixture gave brownish water insoluble product (about 0.15 g). This product is soluble in ether and contains benzoquinone as confirmed qualitatively by its characteristic odor.

2.10. Reduction with hydrazine

The product described above (Emeraldine base) was reduced to leucoemeraldine base form as follows. One gram of the above product was dispersed in 20 mL of hydrazinium hydroxide solution (20%) and stirred for 4 h at room temperature. The product was collected by suction, washed with distilled water (3 × 50 mL) and dried under vacuum at room temperature. Elementary analysis of product found in % (calculated for C_6H_5N) C: 74.33 (79.12); H: 5.40(5.49); N 14.00 (15.38). These results are not well matched with the theoretical composition. However it seems likely that elementary analysis is not reliable due to incomplete char formation, which is common for many polymeric materials.

3. Results and discussion

In this study, we report a new method for preparing organo-soluble PANI in a new ionic liquid, 2-hydroxyethyl ammonium



Scheme 1.

formate (HAF). Oxidation of anilinium chloride with ammonium persulfate (APS) (in 1.25:1.0 molar ratios) in the ionic liquid yields organo-soluble PANI (Scheme 1).

The ionic liquid is able to dissolve many inorganic salts including APS, anilinium chloride and PANI prepared in water. Reaction of ANI.HCl in ionic liquid with 1.25 equivalents of APS proceeds with simultaneous pitch darkening of the mixture.

Interestingly polyanilines prepared in the ionic liquid are all soluble in organic solvents, such as NMP, DMSO, THF, ethanol, methanol, acetone and 1,4-dioxane. Water, diethyl ether and *n*-heptane are non-solvents. Neutral PANI obtained by the conventional method in aqueous solution is slightly soluble (1.0 g $\mathrm{dL^{-1}}$) in NMP. Whereas, solubilities of the products prepared in the ionic liquid are about 25 g/100 mL in the same solvent and solubilities of the neutral (Emeraldine base) or HCl forms of PANI do not vary so much.

Gel permeation chromatography (GPC) traces of 3 days-product indicate a molecular weight of $M_\mathrm{w} = 86{,}400$.

This result reveals that high-molecular weights of polyanilines can be obtained in the ionic liquid.

The product (obtained by room temperature reaction in 3 days) which was reduced with 20 mL of hydrazine solution (20%) displays two groups of signals in the ^{1}H-NMR spectra (Fig. 1). The down field signals centered at 7.2 ppm are due to four aromatic protons of the pure reduced form (leucoemeraldine base). Integral ratio of the NH proton signal appeared at 3.55 ppm to those of aromatic protons is $0.9/4.7 \approx 1/5$.

Whereas non-reduced form of the product (Emeraldine base) gave a ^{1}H-NMR spectra with slight shift of the peak positions (i.e. NH protons appear at 3.7 ppm and aromatic protons centered at 7.3 ppm). Integral ratio of protons is $1.1/9.1 = 1/8.3$ which approximates to the expected value (1/8) for the semi oxidized form.

No precipitation is observed throughout the reactions. The reaction is somewhat slow in the ionic liquid, in comparison to the reactions in aqueous solutions. For 3 days of reaction at room temperature, viscosity of the polymer is slightly higher (0.24 dL $\mathrm{g^{-1}}$) than that of PANI (0.19 dL $\mathrm{g^{-1}}$) obtained in aqueous solution for 24 h. Extended reaction times yield higher viscosities (Table 1).

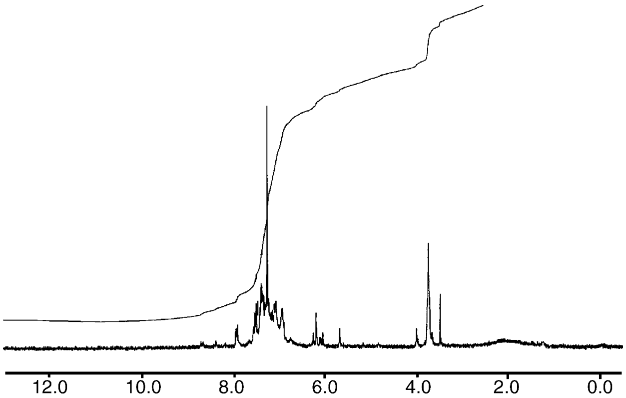


Fig. 1. ^{1}H-NMR spectra of PANI (prepared at 0 °C in the ionic liquid).

Solubility of the polyanilines can be ascribed to non-branching of the products formed in the ionic liquid. The mechanism of this action is yet unclear. But apparently, such an action of the ionic liquid is to suppress coupling via ortho position of aniline and prevents branching by phenazine ring formation [20]. Most probably effect of the ionic liquid is to generate some kind of steric repulsion by Coulombic forces, which avoid the ortho-coupling.

UV–vis spectrum of the product prepared in the ionic liquid shows typical spectra of PAN1 obtained by common methods (Fig. 2). Two absorption bands, one with maximum at 330 nm and another at 430 nm are associated with π–π* transitions of benzenoid and semiquinoid rings respectively [21]. Blue shift of the second band by doping with *p*-toluene sulfonic acid is observed as usual. Another shoulder around 620 nm can be ascribed to the π–π* transition for quinoid moiety.

FT-IR spectra (Fig. 3) of the neutral polymers show characteristic patterns of PANI. Only difference is that, quinoid ring

Table 1
Physical characteristics of PANI prepared in ionic liquid by reaction of anilinium chloride with ammonium persulfate

Concentration ANI.HCl	Reaction temperature (°C)	[OX]/[M][a]	Reaction time (h)	Viscosity (η_inh)[b]	Solubility (g/100 mL)	Conductivity (S $\mathrm{cm^{-1}}$)	
						Undoped	Doped
0.1 M (in water)	25	1.0	24	0.19	1.0	1×10^{-3}	8.6 H_2SO_4 (pellet)
0.1 M	25	1.0	72	0.24	24.9	1.2×10^{-4}	0.2 MSA (film)[c]
0.1 M	25	1.25	288	0.7	24.0	1×10^{-4}	1.2 PTSA (film)
0.1 M	0	1.25	24	0.08	24.6	3×10^{-3}	37.0 PTSA (film)

[a] Molar ratio of oxidant ($(NH_4)_2S_2O_8$) to the monomer (ANI.HCl).

[b] Inherent viscosity at 30 ± 1 °C (1.0 g/dL in *N*-methyl, 2-pyrrolidinone).

[c] In case of *m*-cresol doping, conductivity is 4.4×10^{-2} S $\mathrm{cm^{-1}}$; MSA, methanesulfonic acid.

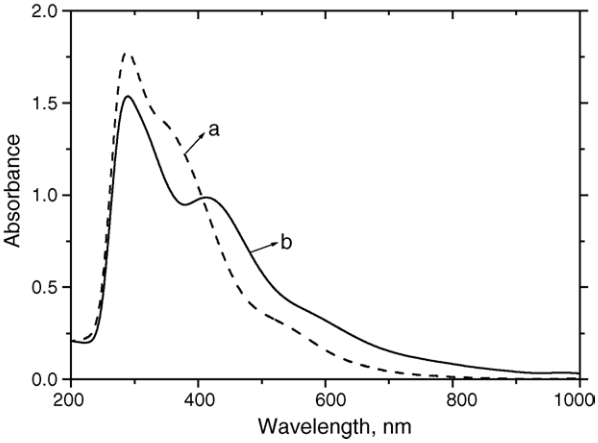


Fig. 2. UV–vis spectra of PANI in dioxane (obtained in ionic liquid by APS in 24 h) (a) Emeraldine base (EB) form and (b) its protonated form with PTSA.

vibration band at 1593 cm^{-1} is weaker in comparison to those of benzenoid ring vibration at 1508 cm^{-1}. In the case of PANI prepared in water, these two peaks have almost equal intensities. This reveals that, the quinoid portion of the polymer must be around 40–50%, as suggested by Asturias et al. [22].

Solubility of those polyanilines allows preparing thin films by solvent casting method. Mechanical strengths of the films are enough to peeling out from ITO glasses. The electronic conductivities of polymer films were measured using the four-probe method on a Keithley 617 electrometer connected to a four-probe head with gold tips.

Electrical conductivities of the products obtained by room temperature-reactions are of order of 1 S cm^{-1} in doped forms. These values are even lower than those of PANI (8.6 S cm^{-1}) obtained by ordinary methods. Nevertheless highly conducting PANI was obtained by the reaction carried out at 0 °C. Indeed conductivity of the film of zero-temperature product (for 24 h) rises up to 37.0 S cm^{-1} by doping with PTSA. This result is consistent with those reported by Nicolau and co-workers [23] in 1998. According to their report excellent conductivities can be attained by the reactions at sub-zero temperatures.

Cyclic voltamograms of PANI.HCl film (Fig. 4) casted from dioxane solution on Pt electrode (after 60-fold cycling from −0.2 to 1.1 V) shows two main peaks at 435 and 515 mV versus SCE in forward scan (in the presence of 0.5 M PTSA) and corresponding reverse peaks are observed at 215 and 425 mV versus SCE, respectively. Corresponding midpoint potentials of the two-redox transitions are 325 and 470 mV. These transitions might be attributed to imine to cation radical and Emeraldine to pernigraniline transitions. The middle peak resulting from cross-linking via phenazine ring formation [20] is not observed around 420 mV. Absence of this peak can be considered to justify solubility of PANI obtained in ionic liquid. In order to prove absence of this peak, we have also attempted to electropolymerize anilinium chloride in ionic liquid. However any polymer film did not form on electrode surface. This might be owing to high solubility of PANI in ionic liquid.

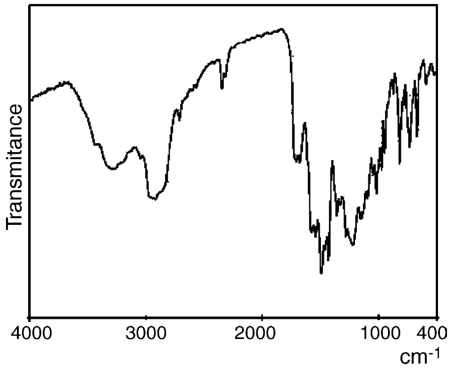


Fig. 3. FT-IR spectra of PANI (prepared at 0 °C in the ionic liquid).

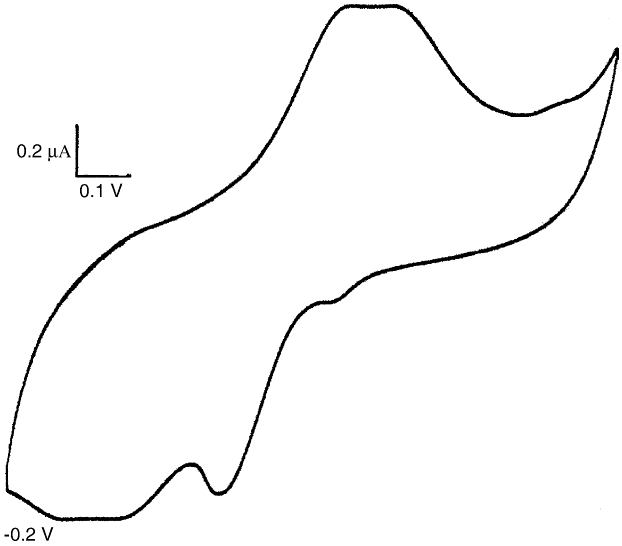


Fig. 4. Cyclic voltamogram of PANI film (casted from dioxane on Pt electrode) in aqueous solution of 0.5 M PTSA. Scan rate = 100 mV s^{-1} (formal potentials of the first and second peaks are 0.320 and 0.465 V vs. SCE, respectively).

“The shape of CV differs from those of PANI prepared by electropolymerization method yielding well-resolved oxidation peaks. Such a difference observed by some authors [24] and broadening of the peaks observed from the samples obtained by chemical oxidation has been ascribed to thickness of the solvent cast films [25].”

In conclusion, new ionic liquid, 2-hydroxyethyl ammonium formate is a versatile solvent as reaction medium in preparing organo-soluble polyanilines with reasonable molecular weights. Thin polyaniline films can be prepared by casting from organic solutions. Lower reaction temperatures seem to be essential for high electrical conductivities. Reaction in the ionic liquid at 0 °C results in highly conducting PANI with a conductivity of 37.0 S cm^{-1}, when doped with PTSA.

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