Polymerization of Aniline by Copper-Catalyzed Air Oxidation

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ABSTRACT: A novel method for preparing organosoluble and conducting polyaniline (PANI) is presented. It is demonstrated that Cu(II) is an excellent catalyst for the polymerization of aniline by air oxygen in aqueous emulsions. Reactions carried out at 0 °C or at room temperature yield PANIs of reasonably high molecular weights (number-average molecular weight = 23,000–114,000 Da) in an emeraldine base form that are soluble in many organic solvents, such as tetrahydrofuran, dimethylformamide, *N*-methylpyrrolidinone, chloroform, and acetone. Spectroscopic investigations (ultraviolet, Fourier transform infrared, and ^{1}H NMR) have shown that PANI obtained by this procedure has the same structure as those prepared by the conventional persulfate oxidation method. The resulting PANIs show reasonable electronic conductivities (0.067–0.320 S cm^{-1}) upon doping with *p*-toluenesulfonic acid or dodecyl benzene sulfonic acid.

Keywords: air oxidation; catalysts; conducting polymers; conjugated polymers; copper catalysts; oxidative polymerization; soluble polyaniline

INTRODUCTION

Polyaniline (PANI) is known as the most important inherently conducting polymer. Its excellent stability to air oxidation,[1] tunable electrochromic behavior,[2] controllable electrical conductivity,[3] and simplicity of preparation from cheap materials make it superior to other conducting polymers. Because of these peculiarities, PANI has found a wide range of applications in preparing light-weight batteries,[4] electrochromic devices,[5] sensors,[6] and electroluminescent devices.[7]

One important drawback of PANI obtained by the oxidation of anilinium salts in aqueous solutions is its insolubility in common organic solvents. Only 1% solubility has been observed in *N*-methylpyrrolidinone (NMP), which also acts as a plasticizer.[8] A great deal of work has been devoted to preparing organosoluble PANI. The incorporation of alkyl substituents has been demonstrated to increase solubility, but the electrical conductivity is reduced.[9] The polymerization in an NMP solution of LiCl (1.0 M) has been claimed to enhance both the solubility and conductivity.[10] The oxidation of aniline in aqueous solutions of poly(4-styrene sulfonic acid)[11] or poly(acrylic acid)[12] has been reported to give self-doped and soluble PANIs.

Chloroform-soluble PANI has been obtained by the oxidation of an aniline/dodecyl benzene sulfonic acid (DBSA) mixture in an aqueous suspension of chloroform.[13] Also, the polymerization of dibutyl naphthalene sulfonic acid salt of aniline in the presence of acetone has been reported to give PANIs that are highly soluble in many organic solvents such as toluene, tetrahydrofuran, and chloroform.[14]

Recently, we have described the oxidation of anilinium chloride in an ionic liquid, 2-hydroxyethyl ammonium formate, which yielded highly conducting (37.0 S cm^{-1}) and organosoluble PANI.[15] The solubility of PANI is an important

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parameter for its processing. The solubility of PANI obtained by the persulfate method has not been well understood yet. According to Genies and Tsintavis,[16] a side coupling reaction via the ortho position resulting in crosslinking might be responsible for its insolubility.

$FeCl_3$ and MnO_2 are common oxidants used extensively in the polymerization of aniline salts in acidic media. Kanatzidis et al.[17] reported the *in situ* oxidative polymerization of aniline by a $V_2O_5{\cdot}nH_2O$ xerogel yielding conducting PANI with an intercalative lamellar structure. The enzyme-catalyzed polymerization of aniline with H_2O_2 in micelles[18] or in the presence of polymer templates[19] has been employed successfully to obtain conducting PANIs.

Here we report a novel method in which air oxygen is used as an oxidant for the polymerization of aniline in the presence of $Cu(NO_3)_2$ as a catalyst. To the best of our knowledge, no report has been published on the use of air in such process. As shown in this article, the catalytic process has been studied under various conditions, and the PANIs obtained were characterized with spectral measurements.

EXPERIMENTAL

Materials

Aniline (E. Merck) was redistilled before use. DBSA (Henkel), *p*-toluenesulfonic acid (PTSA; Fluka), NMP (Fluka), and all the other chemicals were analytical-grade commercial products. They were used as purchased.

Polymerization of Aniline by Air Oxygen

A typical procedure was as follows. A 100-mL-volume, two-necked flask was mounted in an ice bath and equipped with an air inlet and a condenser. Ten milliliters (0.11 m) of redistilled aniline and 20 mL of chloroform were added to the flask. The air delivery tube was dipped into the mixture cautiously. A solution of 0.25 g (1.0 m) of $Cu(NO_3)_2$ in 40 mL of distilled water was added to the solution in the flask under continuous stirring. The mixture darkened immediately. During stirring, air was passed through the mixture for 6 h at this temperature by means of an air pump (ca. 1 L min^{-1}). Chloroform residues were removed *in vacuo*. A dark product was digested in 50 mL of a 1 M HCl solution, filtered, and washed several times with distilled water (5 × 100 mL). The crude product was dissolved in 60 mL of NMP and reprecipitated in 200 mL of a 1 M HCl solution to remove copper residues. The product was dried *in vacuo* at 40 °C for 16 h. The yield was 7.4 g (75.6%).

To obtain PANI in a free base form, this product was dissolved again in NMP (50 mL) and precipitated in 250 mL of a 1 M NaOH solution. Then, it was filtered, washed with water (5 × 100 mL), and dried as described previously. This procedure was repeated at room temperature. The same reactions were also performed without $CHCl_3$ at 0 °C and at room temperature to investigate the influences of the solvent and temperature.

Reduction with Hydrazine

For the NMR measurements, the neutral products [emeraldine bases (EBs)] were reduced to leucoemeraldine bases (LBs) by hydrazine. A typical procedure was as follows. A 1-g sample was dissolved in 15 mL of NMP. To this solution, 5 mL of hydrazinium hydroxide (85%) was added dropwise during stirring. The mixture was stirred overnight at room temperature. The product was collected by suction, washed with distilled water (3 × 50 mL), and dried *in vacuo* at 40 °C. The products were sensitive to air oxygen. They were stored in tightly closed bottles under a nitrogen atmosphere.

Ultraviolet–Visible (UV–vis) Spectra

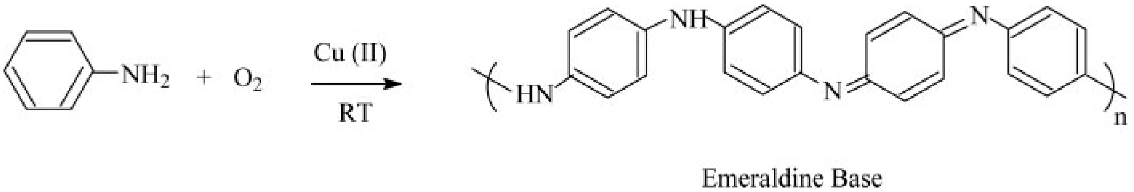
UV–vis spectra of PANIs were recorded with a Chebios Optimum-One UV–vis spectrophotometer in NMP as the solvent.

Gel Permeation Chromatography (GPC)

GPC traces were taken with an Agillant 1100 series apparatus consisting of a pump, a refractive-index detector, and Waters Styragel columns (HR 4, HR 3, and HR 2). Tetrahydrofuran was used as the eluent, and the flow rate was 0.3 mL/min.

Fourier Transform Infrared (FTIR) Spectra

FTIR spectra were recorded on a PerkinElmer FTIR Spectrum One B spectrometer.



Scheme 1. Polymerization of aniline by catalytic air oxidation.

^{1}H NMR Spectra

These were obtained from dimethyl sulfoxide-d_6 (DMSO-d_6) solutions of the polymers in free base forms by a Bruker Ac (250-MHz) spectrometer.

Conductivity Measurements

The electronic conductivity (σ) of the polymers was measured with the four-probe method with pellets on a Keithley 617 electrometer connected to a four-probe head with gold tips and calculated from the following equation:

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

where V is the potential (V), I is the current (A), and d_n is the thickness (cm).

Doped samples were prepared as follows. Solutions of 1.82 g (2×10^{-2} mol of repeat units) of PANI samples in 25 mL of NMP were mixed with 2×10^{-2} mol of PTSA or DBSA as the dopant.

The mixtures were precipitated in 200 mL of water, filtered, and dried *in vacuo* at 40 °C for 72 h. For conductivity measurements, the samples (doped or undoped) were ground into fine powders in a mortar. The disk pellets with a diameter of 1 cm were prepared by being pressed under 10^4 kg cm^{-2} and dried again for 24 before the measurements. The thickness was 0.2 ± 0.01 mm.

Cyclic Voltammograms

Experiments were carried out with an Autolab PGSTAT 30 (Eco Chemie) potentiostat. A classical three-electrode cell was used for the measurements. A standard calomel electrode (SCE) was the reference, and a silver wire with a geometric area of 1.5 cm^2 was used as the counter electrode. The working electrode was platinum. PANI films were cast from NMP solutions onto Pt electrode. Cycles were obtained in a 0.1 M HCl solution.

RESULTS AND DISCUSSION

Synthesis

Cu(II) is easily reduced by aniline to Cu(I) in weakly basic or neutral aqueous mixtures. The reaction can be followed visually by the disappearance of the characteristic blue color of the Cu(II) solution. However, no reaction takes place in an acidic medium. The reaction with anilinium chloride in water is very slow and does not yield any isolable product even after 48 h of reaction at room temperature. The Cu(I) formed by the reaction with free aniline can be reoxidized by air oxygen in a weakly basic medium. Such reoxidation makes possible the polymerization of aniline by air oxygen in the presence Cu(II) salts as a catalyst (Scheme 1). Although aniline itself is a weak base (pK_a 4.6), the basicity of the aqueous aniline emulsion (pH 9.3) is appropriate to realize the reaction in the presence of Cu(II) salts (1/20 mol) as a catalyst.

The limited solubility of Cu(I) salts in water or in other solvents can be considered to be a problem during the polymerization. However, the Cu(I) salt remains soluble in the reaction medium because of its complexation with aniline. The polymerization is performed by the bubbling of air through the aqueous aniline emulsions in the presence of $Cu(NO_3)_2$ (ca. 1–2 mol %). Apparently, the reaction occurs at the interphase of the aniline droplets by dissolved oxygen. The yields attained within 6 h are generally low (66–74%), presumably because of the partial loss of aniline by air flow during the reaction (Table 1).

One important aspect of this method is the solubility of the resulting PANI. If the side reaction via ortho coupling is considered to be responsible for the insolubility, as suggested by Genies and Tsintavis,[16] the solubility of PANI in this case might be due to suppressed oxidative coupling via the ortho position under the weakly basic conditions studied. Because the coupling via the ortho position is avoided in this way, a linear and soluble polymer forms by favored coupling via the para position of the aniline monomer.

Table 1. Molecular Weights and Conductivities of PANIs Prepared by Catalytic Air Oxidation

				Molecular Weight		Conductivity (S cm^{-1})	
Entry	Temperature	Solvent	Yield (%)[a]	M_n[b]	PDI[c]	PTSA	DBSA
1	Room temperature	—	65.9	23,300	4.46	0.095	0.287
2	Room temperature	$CHCl_3$	69.7	114,900	2.67	0.067	0.290
3	0 °C	—	74.0	17,600	4.61	0.072	0.320
4	0 °C	$CHCl_3$	75.6	86,900	3.17	0.200	0.295

[a] Isolated yield within 6 h.
[b] Number-average molecular weight determined by GPC with polystyrene standards.
[c] Polydispersity index.

The molecular weights of the products obtained within 6 h were reasonably high. The highest molecular weight (number-average molecular weight = 114,900) was attained in an aqueous emulsion with $CHCl_3$ at room temperature. The molecular weights of the polymers obtained at 0 °C were lower than those of the products prepared at room temperature. Interestingly, all the polymers showed a broad molecular weight distribution (weight-average molecular weight/number-average molecular weight). One possibility might be a higher complex forming tendency for copper ions with the aniline monomer than for those with the PANI chains in the medium. All the polymers in the free base forms showed the same patterns in their UV–vis and IR spectra.

Because LB (fully reduced form of EB) is quantitatively oxidized to EB by Cu(II),[20] the polymers obtained by catalytic oxidation must be in the EB form.

UV

Indeed, the UV–vis spectrum (Fig. 1) of the air oxidation product (entry 1) indicates the EB structure. Thus, two bands exhibiting absorption maxima at 350 and 365 nm and a broad shoulder around 530 nm can be assigned to the EB form of PANI, and this is in accordance with the results reported by Yamamoto et al.[20] The two bands are associated with π–π^* transitions of benzenoid and semiquinoid rings, respectively.[21] The shoulder at 530 nm indicates pure quinoid segments in the structure.

Doping with PTSA or DBSA results in a significant blueshift of the second band to 420 nm. Similarly, the maximum of the shoulder shifts to 620 nm upon doping.

The intensity of the second band is higher than that of the first band for undoped EB. This can be ascribed to the presence of a slightly excess semiquinoid portion in the polymer structure.

Moreover, PANIs prepared by the persulfate method generally present a very broad absorption band, a so-called polaron band above 800 nm. The nature of this band and its relation to the conductivity are not well understood yet.[18] It is known that the intensity of this band is proportional to the acid strength of the dopant and increases at the expense of the band strength at 420 nm. The absence of this band at longer wavelengths, in our case, supports the assumption of the excess semiquinoid portion.

IR

To make a more precise assignment, a PANI sample was also prepared in an HCl solution by the conventional persulfate method. The FTIR spectrum of this product [Fig. 2(a)] was compared

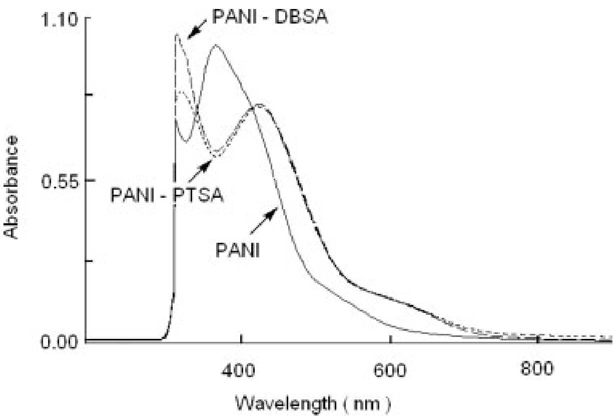


Figure 1. UV–vis absorption spectra of the free base form of PANI (entry 1) in the absence and presence of dopants DBSA and PTSA (in NMP as the solvent).

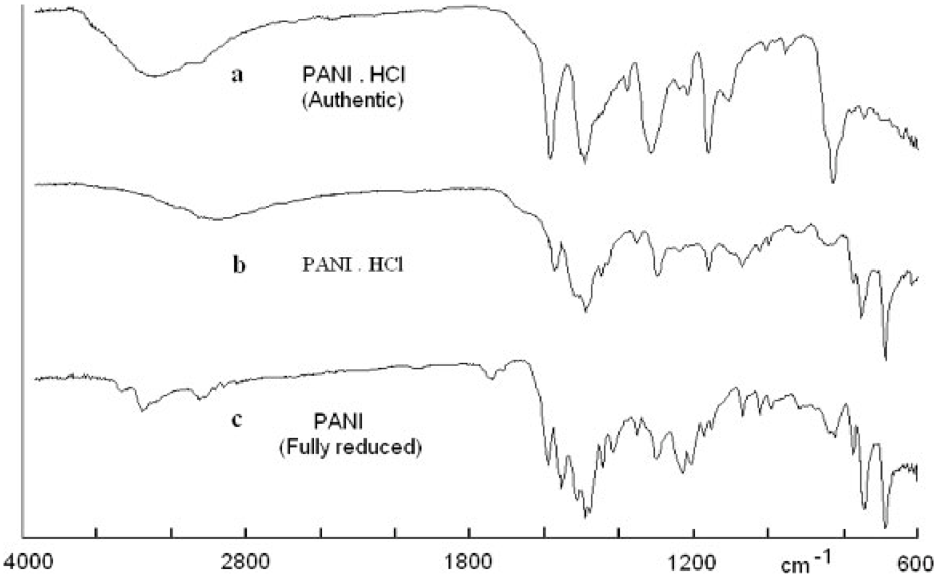


Figure 2. FTIR spectra of the polymers: (a) PANI obtained by the persulfate oxidation method (emeraldine green), (b) HCl-doped PANI (entry 1) prepared by air oxidation, and (c) its fully reduced form (LB).

with that [Fig. 2(b)] obtained in this work. Characteristic peaks in both spectra appear at the same positions, indicating that the product obtained is PANI in the EB form.

The resemblance of the two spectra reveals, in principle, that the two structures are the same. A marked difference is the relatively weak intensity of the N—H plane bending vibration band at 1595 cm^{-1} in comparison with the skeletal benzene ring vibration band at 1508 cm^{-1} [Fig. 2(b)]. Another characteristic peak around 1300 cm^{-1} is associated with the C—N stretching vibration. This peak appears at the same position in the UV–vis spectrum of the authentic PANI sample [Fig. 2(a)].

There is a controversy about the peak at 1595 cm^{-1}. This peak has been assigned mostly to the quinoid ring vibration.[22] However, it must include

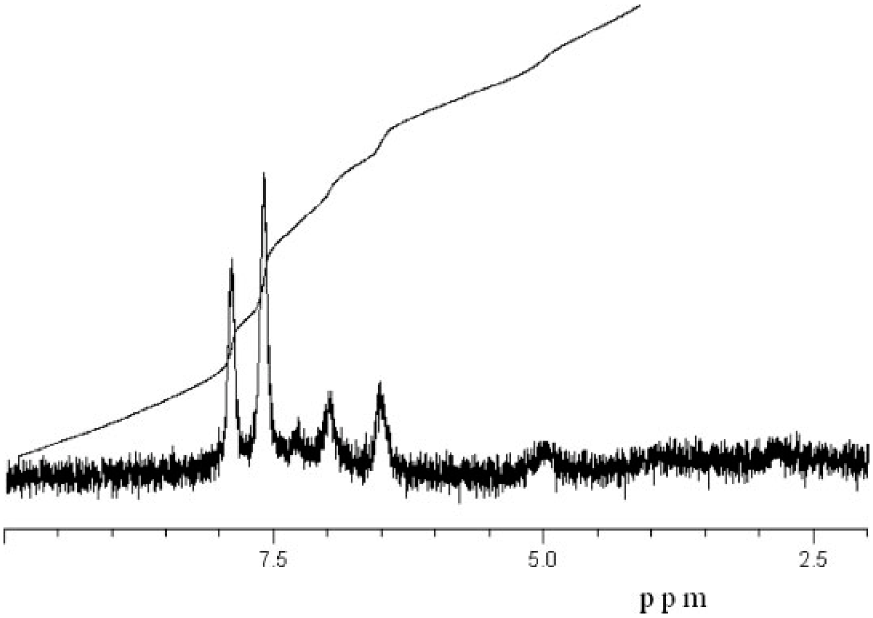


Figure 3. ^{1}H NMR spectrum of fully reduced PANI [obtained by the reduction of the sample (entry 1) with hydrazine] in DMSO-d_6.

also the N—H plane bending vibration. Indeed, the FTIR spectrum of the fully reduced form [Fig. 2(c)] of the polymer sample (entry 1) clearly indicates more intense N—H bending peaks in this region, in addition to a characteristic stretching vibration band at 3350 cm^{-1}. This implies that a less intense peak around 1590 cm^{-1} [in Fig. 2(b)] must not be ascribed only to the quinoid ring vibration. In another words, the weakness of this band in Figure 2(b) is not a contradiction to the assumption of a less semiquinoid portion.

^{1}H NMR

The products in the free base and doped forms showed typical ^{1}H NMR spectra of authentic PANI sample prepared by $(NH_4)_2S_2O_8$ in water. For a better understanding, the free base of the sample (entry 1) was reduced to the LB form by hydrazine in NMP.

Its ^{1}H NMR spectrum in Figure 3 shows proton signals of the phenyl ring in the 6.5–8 ppm range. The broad signal at 5.0 ppm can be assigned to the N—H proton. The integral ratio of the two group protons approximates the expected value, 1/4 for the LB form of the polymer. This fully reduced form is air-sensitive. The sensitivity can be followed visually by the color change of its dilute hydrochloride solution in NMP from blue to dark-green upon air exposure for 5–10 min.

Redox Behavior

Cyclic voltammograms were obtained from thin-film samples cast from an NMP solution onto a Pt electrode. Figure 4 shows a typical cyclic voltammogram of PANI prepared at room temperature in an aqueous emulsion. The voltammogram obtained at a 10 mV/s scanning rate (after 20-fold cycling in the −0.2 to 1.2 V range) shows two peaks at 260 and 520 mV (vs SCE) in the forward scan (in a 0.1 M HCl solution). The reverse peaks can be observed at −20 and 230 mV, respectively. Corresponding midpoint potentials of 120 and 375 mV can be attributed to the imine-to-cation-radical and emeraldine-to-pernigraniline transitions, respectively.

Because the peak potential of the first transition is scanning-rate-dependent,[23] the cyclic voltammogram recorded cannot be used in making a direct structure assignment. However, the cyclic voltammogram represents at least reversible redox behavior for these products as in the case of PANI prepared by well-known methods.

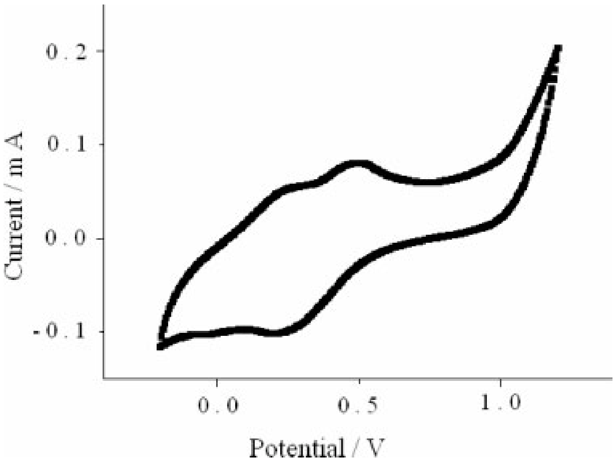


Figure 4. Cyclic voltammogram of a PANI film (entry 1; cast from NMP onto a Pt electrode) in an aqueous solution of 0.1 M HCl (scan rate = 10 mV s^{-1}). The potential was recorded versus a Ag/Ag^+ reference electrode (SCE).

Conductivity

The direct-current conductivities of the polymer samples were measured over compressed disks (0.2 mm thick). The free base form of the polymers (EB form) did not show any conductivity. Moderate conductivities were obtained via doping with PTSA and DBSA (Table 1). A number of factors affect the conductivity of PANI. The polymerization procedure, nature, and ratio of the dopant and doping process are known to influence the conductivity. Direct mixing with camphorsulfonic acid in a 0.6:1 molar ratio in *m*-cresol and evaporation of the solvent have been reported to yield the highest conductivity.[24]

In this work, we followed an alternative pathway for doping. For this purpose, equimolar quantities of the dopants were mixed with PANI in NMP, and they were precipitated in water. We expected to obtain the proper dopant–PANI combinations in this way. The measurements by the four-probe method showed that DBSA is a better dopant and gives substantially higher conductivities (0.287–0.320 S cm^{-1}) in comparison with PTSA (Table 1). This might be due to the plasticizing effect of the former. We have not dealt with the optimization of the doping compositions any further to attain better conductivities.

CONCLUSIONS

The Cu(II)-catalyzed air oxidation of aniline in aqueous emulsions yields soluble and high-molecular-weight PANIs in the EB form. These polymers are soluble in many organic solvents and have the same structure as those of PANIs obtained by common persulfate oxidation methods, as indicated by FTIR and NMR.

Because the air oxygen involved is a cheap reagent, the presented procedure seems to be attractive for the mass production of soluble/processable PANIs of high molecular weights.

Moreover, preliminary experiments have shown that this catalytic process works also without water and gives aniline solutions of PANI by partial polymerization. The resulting solutions form excellent films on flat surfaces by air exposure because of the continued polymerization of the residual aniline. This will be examined in the next studies.

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