Emulsion polymerization of aniline

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In this communication, we report that aniline can be conveniently polymerized directly into conducting material using an emulsion polymerization technique. The polymerization is carried out in non-polar or weakly polar solvents in the presence of a functionalized protonic acid that acts simultaneously as a surfactant (emulsifier) and as a protonating agent (dopant) for the resulting electrically conducting polyaniline. It was found that the present direct, one-step preparation of polyaniline–protonic acid complexes in organic solvents may lead to polyaniline with significantly higher molecular weight than that prepared in acidic aqueous solutions. In addition, the present polyaniline–functionalized acid complexes displayed higher solubilities in non-polar or weakly polar organic solvents than corresponding complexes obtained by mechanically mixing the emeraldine base form of polyaniline with the protonic acid. Films cast from concentrated solutions routinely exhibit conductivities in excess of $100\,\mathrm{S\,cm^{-1}}$. Additionally, it was found that, using the emulsion polymerization route, polyaniline–functionalized protonic acid complexes of fibrillar morphology can be produced, which have an exceptional degree of crystalline order and orientation.

(Keywords: emulsion polymerization; polyaniline; electrical conductivity)

Introduction

Polyaniline (PANI) has emerged as one of the more promising conducting polymers for commercial applications[1,2]. PANI is unique among conducting polymers in that its electrical properties can be reversibly controlled both by changing the oxidation state of the main chain and by protonation of the imine nitrogen atoms[3]. In addition to a wide range of desirable electrical, electrochemical and optical properties, PANI exhibits excellent environmental and thermal stability, particularly in the conducting emeraldine salt form.

PANI can be synthesized from the monomer aniline by both electrochemical[4,5] and chemical[6–9] oxidative polymerization. Considerable effort has been devoted to the development of relationships between the synthesis conditions and the properties of polyanilines obtained by electrochemical polymerization[5]. Chemical polymerization of aniline is, however, particularly important since this synthesis is the more feasible route for the production of polyaniline on a large scale.

Traditionally, aniline is chemically polymerized in an acidic aqueous medium to which an oxidant is added[6–9]. Generally, the polymer is obtained in irregular, powder form, often with low degrees of crystallinity and molecular orientation, which is associated with modest values of the electrical conductivity of the as-polymerized polymer. Moreover, the inherent viscosity of PANI, polymerized in aqueous systems, is difficult to control and is relatively low, usually between 0.2 and $1.2\,\mathrm{dl\,g^{-1}}$ as measured, for example, in concentrated sulfuric acid at room temperature in 0.1% w/w solution[10,11].

Here, we report a polymerization route to conducting PANI complexes in which aniline is polymerized in an emulsion of water and a non-polar or weakly polar organic solvent. This polymerization is carried out in the presence of a functionalized protonic acid, such as dodecylbenzenesulfonic acid (DBSA), which acts simultaneously as a surfactant (or emulsifier) and as a protonating agent for the resulting PANI. It is shown that, using emulsion polymerization, PANI–DBSA complexes can be produced with high molecular weight, high solubility and, under specific experimental conditions, with an interesting fibrillar morphology showing an exceptional degree of crystalline order and orientation.

Experimental

Synthesis. In a typical polymerization, a solution of 4.65 ml (0.05 mol) of aniline (Aldrich) and 24.48 g (0.075 mol) of DBSA (Tokyo Kasei) and xylene (Aldrich) was prepared in a 250 ml Erlenmeyer flask which was cooled in an ice bath. Polymerization was initiated by the addition of 4.68 g (0.02 mol) of ammonium peroxydisulfate, $(NH)_4S_2O_8$, (Fisher) in 20 ml distilled water; the latter solution was added over a period of 30 min, in order to avoid heating of the reaction mixture. The molar ratio of DBSA to aniline was 1.5; the molar ratio of oxidant to aniline was 0.4; the aniline monomer concentration was $0.2\,\mathrm{mol\,l^{-1}}$; and the total polymerization time was 24 h, unless indicated otherwise.

The polymerization was terminated by pouring the resulting highly viscous emulsion into 750 ml of acetone, causing the PANI–DBSA complex to precipitate. The dark green powder was recovered, filtered and washed three times with 150 ml acetone, three times with 150 ml distilled water and further three times with 150 ml acetone. Finally, the powder was dried in a vacuum desiccator for 48 h at room temperature.

Part of the PANI–DBSA complexes were converted to the emeraldine base form by treatment with 3% NH_4OH for 2 h.

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Characterization. The inherent viscosities of PANI–DBSA and the corresponding PANI base form were determined at 25°C in 0.1% w/w solutions in concentrated (97%) H_2SO_4 using an Ubbelohde viscometer.

The as-polymerized PANI–DBSA complex typically had the composition $PANI(DBSA)_{0.35}$ as determined from the observed weight differences between the as-polymerized complex and the corresponding reduced emeraldine base. Apparently some deprotonation occurred during the washing procedure of the PANI–DBSA complex, since it contained less DBSA than would be expected for a complex in which all the imine nitrogen sites were protonated, i.e. $PANI(DBSA)_{0.5}$.

Electrical conductivities of the as-polymerized polymers were measured on dried pressed pellets or films cast from xylene solutions, employing the usual four-probe method under laboratory conditions.

Transmission electron microscopy and electron diffraction studies were carried out using a Jeol 100 CX instrument.

Results and discussion

Influence of polymerization temperature. Table 1 summarizes the results of polymerizations carried out at 0 and 25°C in two different organic media, xylene and chloroform. The inherent viscosities of the as-polymerized PANI–DBSA complexes, as well as of the corresponding compensated emeraldine base samples, were found to increase with decreasing polymerization temperature, which is in accord with previously reported polymerizations of aniline in aqueous systems[9–11]. *Table 1* also reveals that, in contrast to the inherent viscosity, the polymerization yield and electrical conductivity of the resulting PANI–DBSA complexes were relatively insensitive to polymerization temperature.

The addition of aqueous solutions of the oxidant, $(NH_4)_2S_2O_8$, to the reaction mixture containing the aniline monomer is highly exothermic. Cooling of the polymerization reactor prior to oxidant addition is thus necessary to avoid local heating and possible crosslinking of the growing PANI chains. The latter phenomena would lead to premature precipitation of PANI from the reaction mixture, thereby limiting the achievable molecular weight. We found it to be advantageous to execute the polymerization at low temperatures, preferably between 0 and 5°C.

We observed that the inherent viscosities of emulsion-polymerized PANI–DBSA complexes, and of the corresponding compensated emaraldine base forms of PANI, exceeded the inherent viscosities commonly observed for polyanilines polymerized in acidic aqueous solutions. Typical inherent viscosities of emulsion-polymerized PANI ranged from 1.0 to 2.6 dl g^{-1}, which is in contrast to the values of 0.8–1.2 dl g^{-1} that are often reported for PANI polymerized in acidic aqueous solutions[10,11]. From the observed inherent viscosity data one can estimate that the molecular weight of emulsion-polymerized PANI is significantly higher than that of PANI polymerized in aqueous solutions; depending on the chain conformation, it is greater by a factor of 2 (in the rigid-chain limit) to a factor of 4 (flexible-chain limit)[9]. The observed increase in molecular weight can be rationalized by the fact that use of organic solvents, in combination with the functionalized protonic acid DBSA which effectively solubilizes the PANI[11], prevents the immediate precipitation of the growing PANI–DBSA chains from the reaction mixture.

Table 1 Effect of polymerization temperature

	Organic medium	Temperature (°C)	Conductivity, σ^a (S cm^{-1})	Viscosity, η_{inh} (dl g^{-1}) Salt	Base
1	Xylene	25	3.7	0.99	1.27
2	Xylene	0	1.0	1.21	1.70
3	Chloroform	25	0.8	1.26	1.67
4	Chloroform	0	0.5	1.92	2.61
5	Chloroform	25	0.2	1.28	1.69
6	Chloroform	0	2.4	1.60	2.42

Polymerization parameters: aniline concentration, 0.2 mol l^{-1}; molar ratio DBSA/aniline, 1.5; time, 24 h; molar ratio oxidant/aniline, 0.4 (1–4), 0.2 (5 and 6)

[a] Conductivity measured on pressed pellets of powder PANI complex

Influence of polymerization time. Table 2 reveals that the polymerization time did not significantly influence the properties of the PANI–DBSA produced. The reaction yield and the electrical conductivity of the as-synthesized PANI–DBSA were found to be essentially identical when derived from polymerizations that were carried out over periods ranging from 6 to 72 h. Surprisingly, it was observed that the inherent viscosity showed a slight increase at longer polymerization times. This finding is in contrast to observations made for PANI polymerized in acidic aqueous solutions[9], where reduced inherent viscosities were observed at polymerization times exceeding 4 h. It would appear likely, therefore, that the emulsion medium, in addition to solubilizing the growing PANI chains, effectively prevents hydrolysis of the polymer and reduction of the inherent viscosity.

Table 2 Effect of polymerization time

Time (h)	Conductivity, σ^a (S cm^{-1})	Viscosity, η_{inh} (dl g^{-1}) Salt	Base
6	2.2	0.86	1.22
24	3.7	0.99	1.27
48	4.4	1.00	1.39
72	1.3	1.00	1.39

Polymerization parameters: temperature, 25°C; aniline concentration, 0.2 mol l^{-1}; molar ratio oxidant/aniline, 0.4; molar ratio DBSA/aniline, 1.5; organic medium, xylene

[a] Conductivity measured on pressed pellets of powder PANI complex

Table 3 Effect of aniline monomer concentration

Aniline concentration (mol l^{-1})	Conductivity, σ^a (S cm^{-1})	Viscosity, η_{inh} (dl g^{-1}) Salt	Base
0.4	0.6	0.54	0.75
0.2	3.7	0.99	1.27
0.1	0.9	0.64	0.77
0.05	0.4	0.33	0.45

Polymerization parameters: temperature, 25°C; time, 24 h; molar ratio oxidant/aniline, 0.4; molar ratio DBSA/aniline, 1.5; organic medium, xylene

[a] Conductivity measured on pressed pellets of powder PANI complex

Effect of reactant concentrations. It was found that the inherent viscosity of PANI–DBSA, and of the corresponding compensated emeraldine base, was rather sensitive to the concentration of aniline monomer present in the emulsion. A maximum viscosity of the polymer was observed at an aniline concentration of around 0.2 mol l^{-1}, regardless of the organic liquid used. However, the monomer concentration did not significantly affect the reaction yield or the conductivity of the polymer at monomer concentrations between 0.05 and 0.4 mol l^{-1}. The effect of aniline monomer concentration on selected properties of PANI are summarized in *Table 3*.

The oxidant $(NH_4)_2S_2O_8$/aniline molar ratio had only a minor effect on the electrical conductivity of the PANI produced. However, the polymer yield and its viscosity were found to depend strongly on this ratio. The polymer yield increased almost linearly with increasing oxidant/aniline molar ratio (*Figure 1*). By contrast, a significant decrease in viscosity of polyaniline with increasing oxidant/aniline molar ratio was observed (*Figure 2*), especially above a ratio of about 0.4.

It was found that the molar ratio of DBSA/aniline was critical in order to produce high-quality materials. While the polymer yield was virtually unaffected by this reaction variable, both the viscosity and conductivity of PANI–DBSA reached their maximum values at a molar ratio of about 1.5, as shown in *Table 4*.

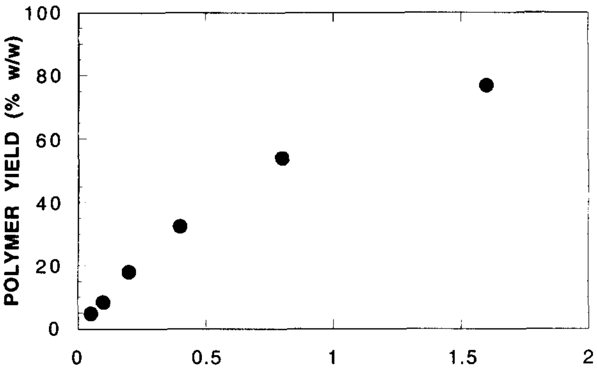

Figure 1 Polymer yield as a function of the oxidant/aniline molar ratio

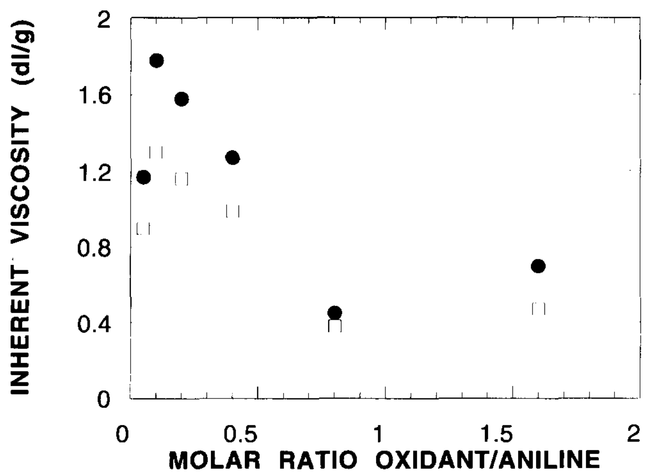

Figure 2 Inherent viscosity (0.1% w/w in 97% H_2SO_4) of PANI–DBSA (□) and PANI emeraldine base (●) as a function of oxidant/aniline molar ratio

Table 4 Effect of molar ratio DBSA/aniline

DBSA/aniline molar ratio	Conductivity, σ^a (S cm^{-1})	Viscosity, η_{inh} (dl g^{-1}) Salt	Base
4.0	0.4	0.38	0.61
3.0	0.2	0.21	0.39
2.0	0.2	0.24	0.45
1.5	3.7	0.99	1.27
1.2	0.7	0.48	0.68

Polymerization parameters: temperature, 25°C; time, 24 h; aniline concentration, 0.2 mol l^{-1}; molar ratio oxidant/aniline, 0.4; organic medium, xylene

[a] Conductivity measured on pressed pellets of powder PANI complex

High quality, high molecular weight PANI–DBSA complexes were thus produced, although in moderate yields, using an aniline concentration of 0.2 mol l^{-1}, an oxidant/aniline molar ratio of 0.4–0.6 and a DBSA/aniline molar ratio of 1.5.

In order to enhance the polymer yield, without an accompanying drastic decrease in PANI viscosity, polymerizations were carried out using oxidant/aniline ratios of 0.8–1.15. In these cases the oxidant was added very slowly and continuously to the reaction mixture throughout the polymerization. This method of oxidant addition ensured that the reaction mixture always contained active oxidant capable of polymerizing remaining aniline and, furthermore, minimized excessive heating of the reaction mixture. We found that PANI–DBSA complexes with viscosities >1.0 dl g^{-1} could be produced in yields in excess of 90% using this procedure of oxidant addition. The high solubility of the PANI–DBSA complexes formed, for example, in xylene (see below) demonstrated that essentially crosslink-free PANI was obtained, also at relatively high oxidant/aniline ratios.

Solubility. The present conducting PANI–DBSA complexes displayed remarkably high solubility in common, non-polar or weakly polar organic solvents, such as xylene and chloroform. Solutions containing up to 20% w/w were readily prepared from the complexes produced via the emulsion polymerization route, which was not possible with mechanically mixed emeraldine base–DBSA[12]. We attribute the improved solubility of the emulsion-polymerized complexes to a more homogeneous protonation of PANI by DBSA using the former method.

Conductivity. The electrical conductivities of the various PANI–DBSA complexes produced under different reaction conditions were measured on pressed pellets of the PANI–DBSA powders (see *Tables 1–4*) and occasionally on films cast from solution. The results collected in these tables show that, generally, conductivities of the pressed pellets were in the range 0.1–5 S cm^{-1}, i.e. values similar to those reported for PANI synthesized in acidic aqueous solutions and subsequently doped.

However, the conductivity of non-oriented, free-standing films, produced by casting from concentrated solutions of the conducting complex in xylene ($\sim$20%

w/w PANI–DBSA), routinely exhibited conductivities in excess of $100\,\mathrm{S\,cm^{-1}}$. By contrast, non-oriented films of PANI, derived from solutions of the emeraldine base form in *N*-methylpyrrolidone, followed by protonation by HCl, typically exhibit conductivities[13] in the range $1\text{–}10\,\mathrm{S\,cm^{-1}}$. The much higher conductivities observed for the present solution-cast films suggest that a high degree of self-ordering occurred during solvent evaporation and, perhaps, a more homogeneous protonation of the imine nitrogens of the emulsion-polymerized PANI–DBSA in comparison with that obtained in post-synthesis treatments.

Morphology. Generally, PANI, produced either electrochemically or by the traditional chemical oxidation of aniline in acidic aqueous solutions, is obtained in irregular, powder form with moderate degrees of crystallinity, and lacks macroscopic molecular orientation. The shape of chemically polymerized PANI particles is commonly difficult to control, and is most often globular rather than fibrillar. Formation of fibrillar morphologies of conductive polymers is highly desirable because, owing to a high length/diameter ratio (i.e. high aspect ratio), the percolation threshold for the onset of the electrical conductivity in blends with non-conducting polymers may be dramatically reduced[14].

Interestingly, we observed that emulsion polymerization of aniline provides a route to the direct, *in situ* formation of fibrillar particles of PANI–DBSA, not unlike those of polyacetylene polymerized in liquid crystalline solvents[15]. Fibril formation was observed in the xylene-rich part of the three-phase system xylene–DBSA–water, using the polymerization conditions described in the Experimental section.

Figures 3a and *b* show optical micrographs of PANI–DBSA particles under non-polarized and cross-polarized light, respectively. *Figure 4* shows a transmission electron micrograph of fibrillar as-synthesized PANI–

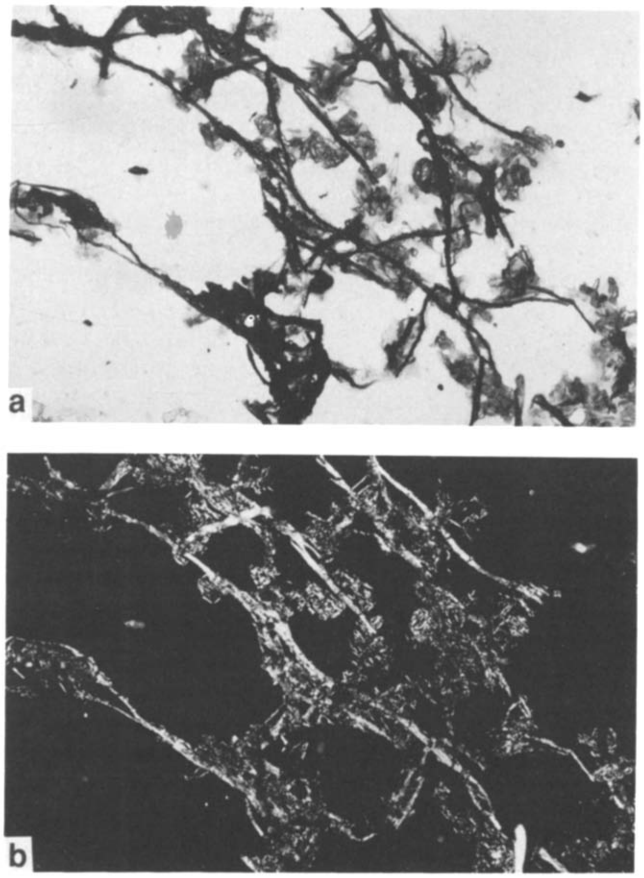

Figure 3 Optical micrographs of fibrillar PANI–DBSA particles under (a) non-polarized and (b) cross-polarized light. The average length and width of the fibrils are about 1 mm and 1 μm, respectively

Figure 4 Transmission electron micrograph of fibrillar PANI–DBSA particles. The average length and width of the fibrils are about 1 mm and 1 μm, respectively

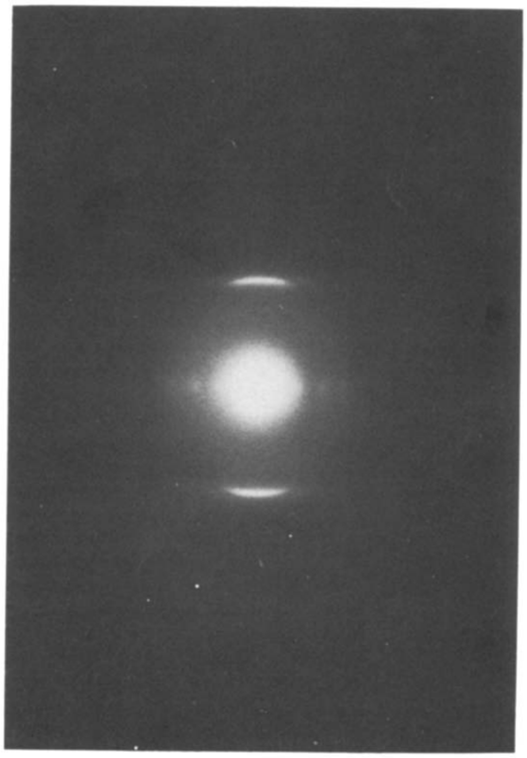

Figure 5 Electron diffraction pattern of fibrillar PANI–DBSA particles

DBSA particles that were dispersed in acetone and transferred onto carbon-coated grids. These PANI–DBSA fibrils are long and entangled with an average size of about 1 mm in length and 1 μm in width, giving an average aspect ratio of the fibrils in excess of 1000. The electron diffraction pattern of *Figure 5* reveals that the fibrillar PANI–DBSA particles were of an exceptional degree of crystalline order, and that the PANI chain molecules were oriented along the long axis of the fibrils. We speculate that polymerization of aniline in highly structured phases of the rich three-phase system xylene–water–DBSA favours, or in fact may be the origin of, the observed formation of fibrillar morphology of PANI–DBSA. A detailed study of the formation and structure of these fibrils is in progress and will be reported elsewhere.

Conclusions

We studied emulsion polymerization of aniline in non-polar or weakly polar solvents, in the presence of the sulfonic acid DBSA. Optimum synthesis conditions were established with respect to viscosity (molecular weight), electrical conductivity and polymer yield. It was found that the optimal polymerization temperature was 0–5°C, and that higher temperatures had a detrimental effect on the viscosity of the polymer. Of the polymerization variables studied, only the oxidant/aniline molar ratio was found to significantly affect the polymer yield. By contrast, it was found that most variables markedly affected the viscosity of the resulting PANI–DBSA complexes. The as-synthesized, electrically conducting PANI–DBSA complexes, as well as the corresponding compensated, non-conducting emeraldine base form of PANI, exhibited higher viscosities (molecular weights) than commonly observed for PANI made in acidic aqueous solutions. It is suggested that these higher molecular weights originated in the high solubility of the growing (DBSA-complexed) PANI chains in the emulsion medium, which prevented premature precipitation of PANI from the reaction mixture.

The as-synthesized PANI–DBSA complexes, which were soluble in non-polar and weakly polar solvents such as xylene, displayed an improved solubility in comparison with complexes produced by mechanically mixing the emeraldine base form of PANI with DBSA. This latter observation was attributed to a more homogeneous protonation in the emulsion-polymerized PANI complexes. Furthermore, we found that, under specific synthesis conditions, PANI–DBSA complexes of a unique fibrillar morphology could be produced. The aspect ratios of the fibrils were measured to be in excess of 1000, and the fibrillar particles showed an exceptional degree of crystalline order and orientation of the polyaniline chain molecules along the long axis of the fibrils.

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