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Emulsion Polymerization Process for Organically Soluble and Electrically Conducting Polyaniline

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ABSTRACT: An emulsion process has been developed for the direct synthesis of the emeraldine salt of polyaniline (PANI) that is soluble in organic solvents. The process entails formation of emulsion particles with a mean hydrodynamic diameter of 150 nm and consisting of a water-soluble organic solvent (e.g., 2-butoxyethanol), a water-insoluble organic acid (e.g., dinonylnaphthalenesulfonic acid), aniline, and water. Aniline is protonated by the organic acid to form a salt which partitions into the organic phase. As oxidant (ammonium peroxydisulfate) is added to the reaction mixture, PANI intermediates are formed in the organic phase. As the reaction proceeds, the emulsion flocculates, forming a two-phase system. The reaction features an induction period followed by an exothermic polymerization, at which time soluble PANI forms in the organic phase. The reaction progress is conveniently monitored by temperature, pH, and open circuit potential. When dinonylnaphthalenesulfonic acid (DNNSA) is employed as the organic acid, the resulting product is highly soluble in organic solvents such as xylene and toluene (not a dispersion), has high molecular weight ($M_w > 22\,000$), and forms moderately conductive (10^{-5} S/cm) films. We have also found that the conductivity of PANI−DNNSA films may be enhanced (up to 5 orders of magnitude) by treating the films with surfactants such as benzyltriethylammonium chloride (BTEAC) or low-molecular-weight alcohols and ketones such as methanol and acetone. Electron microscopy shows that the conductivity enhancement phenomenon observed upon treatment with surfactants is due to self-assembly of PANI−DNNSA molecules into an interconnected network morphology. In the case of alcohol or ketone treatment the film conductivity is enhanced due to extraction of excess dopant, densification of the polymer, and a concomitant increase in crystallinity.

Introduction

Polyaniline (PANI), an inherently conducting polymer (ICP), has attracted considerable attention because of its ease of preparation and environmental stability. PANI is unique among ICPs in that its conductivity can be reversibly controlled either electrochemically (by oxidation/reduction) or chemically (by protonation/deprotonation). Applications of PANI include electrostatic dissipation, anticorrosion coatings, actives delivery, batteries, and solar control.

Synthesis of polyaniline is commonly performed by chemical oxidative polymerization in an aqueous solution (see, e.g., Cao et al.[1]). The method involves combining water, aniline, a protonic acid, and an oxidizing agent and allowing the mixture to react while maintaining the reaction mixture at a constant low temperature (normally about 5 °C). After a period of several hours, the conducting emeraldine salt of polyaniline precipitates. Material synthesized by this approach is predominately amorphous, intractable, and insoluble in most organic solvents.[2]

Recently several investigators have developed methods to improve the processibility of polyaniline by a postprocessing step which involves (1) neutralization of the emeraldine salt to form emeraldine base and (2) reprotonating the emeraldine base with a second protonic acid. Tzou and Gregory[3] used this approach and reported that polyaniline salts containing carboxyl and amino substituents were soluble in NMP and DMSO. Cao et al.[4,5] reported on the use of this method to prepare polyaniline salts of a number of protonic acids including DBSA (4-dodecylbenzenesulfonic acid) and DNNSA (dinonylnaphthalenesulfonic acid). The polyaniline salts produced were reported to be soluble in nonpolar solvents, however, the maximal solubility was low (e.g., the maximum solubility of the DBSA salt in xylene was found to be less than 0.5% w/w[5]). Shacklette et al.[6] have developed a surface−core doping process in which polyaniline is predominately doped with one acid at the core of a particle (e.g., *p*-toluenesulfonic acid, PTSA) and a second dopant predominantly at the surface (e.g., DBSA). The surface dopant is chosen to achieve increased compatibility between the polyaniline particles and a second polymer matrix (e.g., Nylon).

Emulsion polymerization processes for preparing polyaniline salts have been reported.[5,7−10] In these disclosures, aniline, a protonic acid, and an oxidant are combined with a mixture of water, and a nonpolar or weakly polar liquid, for example, xylene, chloroform, or toluene, all of which are sparingly soluble or insoluble in water. To form an emulsion in the above systems, protonic acids were employed that have substantial emulsifying properties in weakly polar liquids, for example, dodecylbenzene sulfonic acid. In addition, the products of the above reactions were not isolable directly, since the polyaniline salt remained entrained in the emulsion at the completion of the reaction along with the byproducts of the reaction. In most cases, the product was isolated by breaking the emulsion (adding acetone, for example) and collecting the precipitated polyaniline salt, filtering, and washing.

This paper describes a new emulsion polymerization process for polyaniline which yields a truly soluble, conducting emeraldine salt directly without the need for a postdoping process step. The reaction is unique, since the emulsion flocculates during the course of reaction to form a two-phase system, the polyaniline remaining as a soluble component in the organic phase. Ammonium sulfate, a byproduct of the reaction, remains in the aqueous phase, which is readily removed from

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the organic layer. When DNNSA is employed as the dopant organic acid, the polyaniline produced has a high molecular weight (>22 000) and a moderate conductivity (10^{-5} S/cm) and exhibits high solubility in low-dielectric-constant solvents. The conductivity of thin films of the polymer was enhanced up to 5 orders of magnitude by treatment with quaternary ammonium salts or solvents such as methanol or acetone. TEM images show the self-assembly of PANI−DNNSA molecules into an interconnected network morphology during the polymer−quaternary salt interaction, which appears to explain the observed conductivity enhancement. In the case of methanol or acetone treatment, conductivity increases due to removal of excess dopant, densification of the polymer, and a resultant increase in crystallinity.

Experimental Section

Materials. DNNSA (dinonylnaphthalenesulfonic acid), DBSA (4-dodecylbenzenesulfonic acid), and DNNDSA (dinonylnaphthalenedisulfonic acid) were obtained from King Industries. Diphenyloxide disulfonates (DOWFAX 2AO, 2A1, 8339) were obtained from Dow Chemical Company. Versicon (PANI−PTSA/DBSA prepared by surface−core doping[6]) was obtained from Monsanto Company. Unless otherwise noted, all other chemicals were reagent grade and used as received.

Preparation of Polyaniline Dinonylnaphthalenesulfonic Acid Salt. One tenth of a mole of DNNSA (as a 50% w/w solution in 2-butoxyethanol) was mixed with 0.06 mol of aniline and 200 mL of water to form a milky white emulsion. The emulsion was chilled to 5 °C, mechanically stirred, and blanketed with nitrogen. Ammonium peroxydisulfate (0.074 mol in 40 mL of water) was added dropwise to the mixture over a period of approximately 1 h. During this period the emulsion changed color from white to amber. The reaction was allowed to proceed for 17 h, during which time the emulsion separated into a green 2-butoxyethanol phase and a colorless aqueous phase. The progress of the synthesis was monitored by pH, OCP (open circuit potential, mV), and temperature.

The organic phase was washed three times with 100-mL portions of water, leaving a dark green, highly concentrated polyaniline phase in 2-butoxyethanol. This concentrate was readily soluble in xylene, from which thin films were cast. Addition of acetone to a portion of the above concentrate resulted in the precipitation of the polyaniline salt as a green powder. After thorough washing of the powder with acetone and drying, elemental analysis indicated the expected stoichiometric ratio of sulfonic acid to aniline of 1:2.

Using the same process polyaniline DNNSA salts were prepared using acid/aniline molar ratios of 1:1, 1:2, and 1:5 while the peroxydisulfate/aniline mole ratio was kept constant at 1.23:1.

Attempts at synthesizing the polyaniline DNNSA salt employing either kerosene or xylene as the organic solvent yielded no product. UV/VIS/NIR measurements were made on a Cary 5E spectrophotometer.

Conductivity Measurements. A 0.15 mm thick wet coating of PANI−DNNSA concentrate (ca. 50% solids in xylene) was applied across a pattern of four gold contacts using a 0.006-in. draw down blade, 3.8-mm wide. The gold stripes sputtered onto a PET film were 6-mm wide by 50-mm long by 0.5-μm thick and spaced 6-mm apart. After it was dried overnight at 80 °C/75 mmHg, the sample was stored in a desiccator over P_2O_5. Resistance measurements between two adjacent gold contacts were taken using a Keithly Model 2001 Multimeter in the two-point resistant mode. The contact resistance was judged to be minor, since the resistance through the coating between adjacent gold bars was additive.

Molecular Weight Determinations. Molecular weight distribution averages were determined by size-exclusion chromatography (SEC). Chromatograms were obtained with two SEC systems: a model 150-CV SEC/viscometry (SEC/VISC) system (Waters Chromatography Inc.) and a multicomponent SEC system (Waters Chromatography Inc.) assembled from a model 590 pump, a model 712 autoinjector, a model 410 differential refractive index detector, and a model TCH column heater. Both SEC systems were operated at 45 °C and employed a bank of two styragel SEC columns (Waters Chromatography Inc.) with mean permeabilities 10^5 and 10^3 Å. UV-grade *N*-methylpyrolidone (Burdick & Jackson Co.) modified with 0.02 M NH_4HCO_2 (Fluka Chemical Co.) was used as the mobile phase and polymer solvent. A flow rate setting of 0.5 mL/min was employed. The actual flow rate was determined gravimetrically before the start of the analysis.

The preparation of polyaniline salt solutions in NMP/0.02 M NH_4HCO_2 deprotonated the polymer and produced the emeraldine base. The presence of the dinonylnaphthalenesulfonic acid dopant in the solutions necessitated a determination of emeraldine base concentration in order to obtain accurate SEC/VISC-based polymer molecular weights. This was accomplished by the measurement of the emeraldine base's visible absorbance at 636 nm and the use of a literature value[11] of 7.7×10^6 M^{-1} cm^{-1} for the polymer's molar absorptivity.

Calibration of the SEC was performed with a set of 12 nearly monodisperse polystyrene standards (Toya Soda Inc.) ranging in molecular weight from 1.1×10^6 to 2698. Intrinsic viscosities of the polystyrene calibrants were measured using the SEC/viscometric detector. These values provided the Mark−Houwink expression for polystyrene in NMP/0.02 M NH_4HCO_2 at 45 °C needed to calibrate the size-exclusion chromatograph according to universal calibration:

$$[\eta]\ (\mathrm{dL/g}) = (1.947 \times 10^{-4})M^{0.66}$$

A linear least-squares fitting was used to generate a universal calibration curve or a polystyrene-based molecular weight calibration curve.

Calculations of SEC/VISC-based molecular weight distribution employed previously described methodology.[12] Mark−Houwink constants for polyaniline were determined from the set molecular weight distribution averages and intrinsic viscosities calculated for individual data points of SEC/VISC chromatograms.

Data acquisition and reduction were provided by TRISEC software (Viscotek Corp.). Reported molecular weight distribution averages are means of two determinations.

Emulsion Particle Hydrodynamic Diameter Analysis. The hydrodynamic diameters of emulsion particles were determined by dynamic light scattering (DLS). The DLS instrumentation was a Brookhaven Instruments Co. (Holtsville, NY) system consisting of a model BI-200SM goniometer, a model EMI-9865 photomultiplier, and a model BI-9000AT digital correlator. Incident light was provided by a model 95-2 Ar ion laser

(Lexel Corp., Palo Alto, CA) operated at 514.5 nm. All measurements were made at 19.5 ± 1 °C. Prior to analysis, the emulsion was diluted 1:22500 with 0.2-μm-filtered deionized water. Residual dust and dirt in the diluted emulsion were removed by centrifugation for 10 min using a model 5414 microfuge (Brinkman Inst. Co., Westbury, NY).

Scattered light was collected at a fixed angle of 90°. The digital correlator was operated with 522 channels, initial and final delay times of 5 μs and 20 ms, respectively, ratio channel spacing, and a duration of 4 min. A photomultiplier aperture of 200 μm was used, and the incident laser intensity was adjusted to obtain a photon counting rate of 200 kcps. Only measurements in which measured and calculated baselines of the intensity autocorrelation function agreed to within 0.1% were used to calculate particle diameter. The calculation of particle diameter distribution and distribution averages was performed with the ISDA software package (Brookhaven Instruments Co., Holtsville, NY), which employed single-exponential fitting, cumulants analysis, and nonnegatively constrained least-squares particle diameter distribution analysis routines.[13]

Electron Microscopy. Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) techniques were used to extract information about the structure and morphology of the PANI−DNNSA films.

Electron beam transparent thin films were prepared by dipping a gold grid into a 5 w/w % PANI−DNNSA/xylene solution and slowly withdrawing the grid from the solution. Thin films of PANI−DNNSA were obtained by drying the grid in air for approximately 10 min before TEM observation. Thick films for SEM observation were prepared by spin coating the PANI-DNNSA solution onto optically flat Si wafers.

TEM experiments were carried out using a JEOL 2000FX instrument. A scientific-grade charge-coupled device (CCD camera) from Gatan Inc. was used to acquire low-dose digital TEM images. SEM experiments were performed in a field-emission scanning electron microscope (Hitachi S-4500). To reduce the effects of the electron beam on the polymer structure, a low-current and low-voltage (1-kV) incident beam was used to obtain SEM images.

HPLC Analysis. Aqueous phases from the polymerization reaction were analyzed by HPLC. The chromatograph (Spectra Physics) was equipped with a SP8800 ternary pump, a SP8775 autosampler, a SP8480 254-nm UV detector, and a SP4400 integrator. The separation of aniline and other low-molecular-weight species was achieved using an ALLTIMA C18 5-μm column (250 mm × 4.6 mm, Alltech). The solvent gradient was 10% acetonitrile/90% trimethylammonium acetate to 85/15 in 12 min. Anisole was used as an internal standard. Samples were prepared by adding 0.15 mL of standard solution (7976 ppm anisole in acetonitrile) to 0.85 mL of the aqueous sample and filtering through a Acrodisc LC13 filter (0.2 μm).

Filtration Tests. A nominally 60 wt % solution (2.12 g) of PANI−DNNSA (acid/aniline = 2:1) in 2-butoxyethanol was dissolved in 25 mL of xylene to give a concentration of 4.99 wt %. The entire 10 mL of the 4.99% solution was readily filtered through a 0.2-μm filter without clogging. The concentration of the filtrate was found to be 4.83%, a loss of 3.2%.

Solubility Measurements. The polyaniline salt was prepared as described above using a 1:2 mole ratio of aniline to DNNSA. A 10−100-mg sample of the PANI−DNNSA salt (60% w/w in 2-butoxyethanol) was mixed with a test solvent (0.5−1.5 g). Solubility was determined immediately after preparation.

Results and Discussion

Polymerization Mechanism. The mechanism of polyaniline formation has been the subject of many papers in the literature.[14−17] The generally accepted mechanism, based largely upon electrochemical evidence, begins with a slow oxidation of aniline by persulfate to form a radical cation $C_6H_5NH_2^{\bullet +}$, possibly followed by loss of a proton and a second electron to give a nitrenium cation, $C_6H_5NH^+$.[18] Because these species are short-lived and direct observation has been difficult, there has been considerable debate over which intermediate is present. The key step is the combination of two nitrenium cations[19] or two radical cations $C_6H_5NH_2^{\bullet +}$ [20] to give a dimer of aniline: the combination primarily occurs head-to-tail to give *N*-phenyl-1,4-phenylenediamine (NPPD) but also can occur head-to-head to give azobenzene or tail-to-tail to give benzidine. The benzidine path is suppressed above pH 4[21] or can be suppressed by fast electrochemical scan rates. Evidence for these coupling products has been observed in electrochemical oxidations of aniline at aniline concentrations well below that normally used in the chemical synthesis, normally about 0.2−0.3 M; NPPD is generally the dimer favored, depending on the aniline concentration.

Once the dimer is formed, it is rapidly oxidized to a quinone imine structure, since its oxidation potential is lower than that of aniline.[22] Another aniline unit can nucleophilicly attack the oxidized dimer to form a trimer, without the need to oxidize two aniline molecules, as was the case to form the dimer. With each aniline unit added, the oligomer is more easily oxidized and is more susceptible to nucleophilic attack by aniline; this oligomeric oxidized intermediate is pernigraniline.[23] Growth of the chain proceeds in a head-to-tail fashion.[24] Thus, once the concentration of this species is sufficiently high, it is capable of oxidation and reaction with the remaining aniline present, and the reaction rate autoaccelerates (it should be noted that each aniline-derived species is really in equilibrium with a protonated species, since the synthesis is conducted under strong acid conditions).

The kinetics of the polymerization may be described by the following equation:[25,26]

$$\text{rate} = -\mathrm{d}[\mathrm{AN}]/\mathrm{d}t = k_1[\mathrm{AN}][\mathrm{AP}] + k_2[\mathrm{AN}][\mathrm{P}]$$

where [AN] is the aniline concentration, [AP] is the ammonium persulfate concentration, [P] is the equivalent concentration of polymer, and k_1 and k_2 are rate constants. The value of k_2 is much higher than that for k_1, so that once the equivalent concentration of polymer becomes appreciable, the second term of the equation determines the rate. The k_1 term represents the induction period.

Once the polymer is formed and the aniline is depleted, nucleophilic attack on imine units of the oxidized polymer by water predominates, and the degradative hydrolysis reaction becomes important.[27,28] The products of the hydrolysis are quinone species and shorter polymer chains.

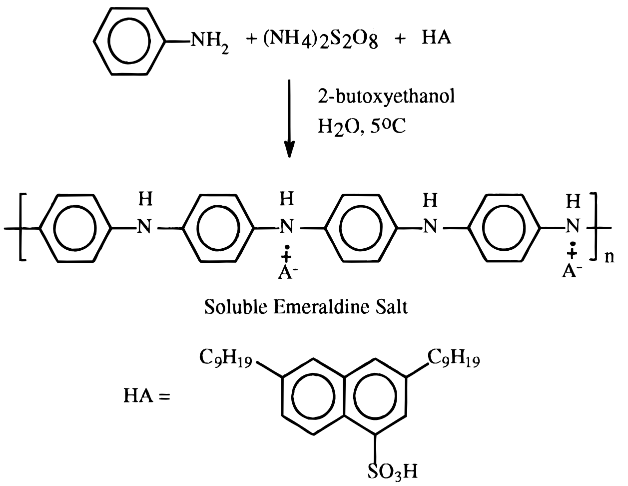

Figure 1. Emulsion polymerization scheme.

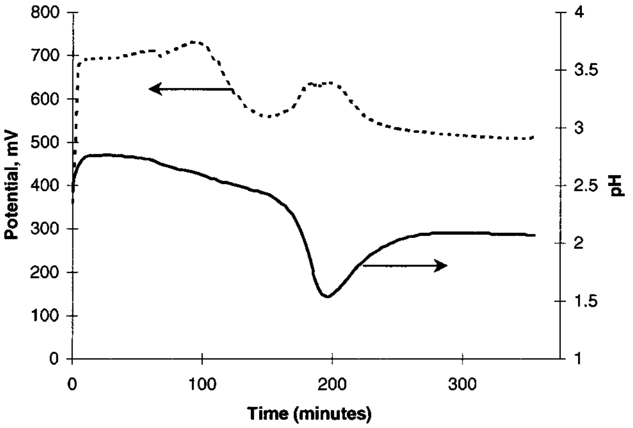

Figure 2. pH and open circuit potential (OCP) versus time profile of the PANI–DNNSA polymerization reaction.

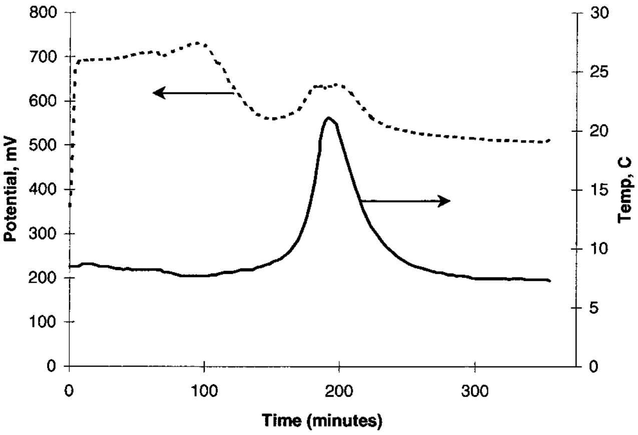

Figure 3. Temperature and open circuit potential (OCP) versus time profile of the PANI–DNNSA polymerization reaction.

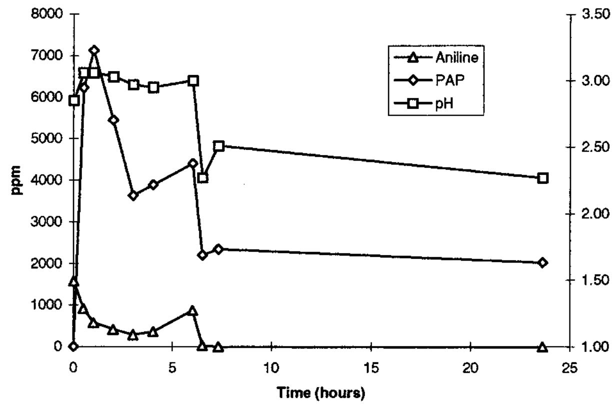

Figure 4. Quenched aqueous phase composition versus time profile of the PANI–DNNSA polymerization reaction.

Emulsion Process. The emulsion polymerization process, illustrated in Figure 1, utilizes a water-soluble organic solvent (2-butoxyethanol) that facilitates the polymerization of polyaniline salts of hydrophobic organic acids such as DNNSA.

The synthesis was monitored by pH, OCP,[29,30] and temperature, as well as color changes (see Figures 2 and 3).

Addition of ammonium persulfate oxidant to the aniline/DNNSA/2-butoxyethanol/water mixture causes the OCP to increase to about 700 mV (this potential is approximately that of the ammonium peroxydisulfate solution). Prior to addition of the oxidant, dynamic light scattering analysis of emulsion size indicated a mean hydrodynamic diameter of 150 nm for emulsion particles. As the reaction proceeds, the emulsion flocculates, forming a two-phase system. After approximately 100 min into the reaction, the mixture begins to turn green, and the OCP drops to about 550 mV, suggesting that the ammonium persulfate has been consumed and a new oxidizing species is formed. As discussed above, pernigraniline is believed to be an intermediate present at this point; however, sampling of the reaction mixture at this time showed very little polymer. The small amount of polymer found had a similar molecular weight distribution to that of the final product (coatings of this material exhibited very low conductivity). Sampling and warming to room temperature at this time resulted in precipitation of black solids from the colorless aqueous phase, indicating a decomposition of some intermediate species of limited stability (quinone imines, for example). As seen from Figure 2, the pH shows a steady decline during the first phase of the reaction due to sulfuric acid generation.

The induction period ends as the pH begins to drop rapidly, and the temperature rises 10–15 °C. At this point, the amount of polymer builds rapidly, and the product has much higher conductivity. After the exotherm, virtually no changes in temperature, pH, or millivolts are observed, and the reaction is considered complete. The aqueous phase, which contains ammonium sulfate and sulfuric acid reaction byproducts, is normally colorless or faint brown and shows no instability upon warming.

HPLC was used to characterize the chemical composition of the aqueous phase during the course of the reaction. Samples were "quenched" (i.e. reduced) with bisulfite immediately after removal from the reaction vessel to stop additional oxidation reactions. As shown in Figure 4, the aniline concentration dropped during the induction period and disappeared completely during the exotherm.

Also present were other UV-absorbing species including *p*-aminophenol, whose concentration rose during the induction period and dropped during the exotherm, as shown in Figure 4. *p*-Aminophenol results from reduction of quinone imine by bisulfite. Since quinoneimine is a product of the hydrolysis of pernigraniline, we believe the *p*-aminophenol concentration essentially tracks the formation of pernigraniline. NPPD, the head-to-tail dimer, was not detected above background (<5

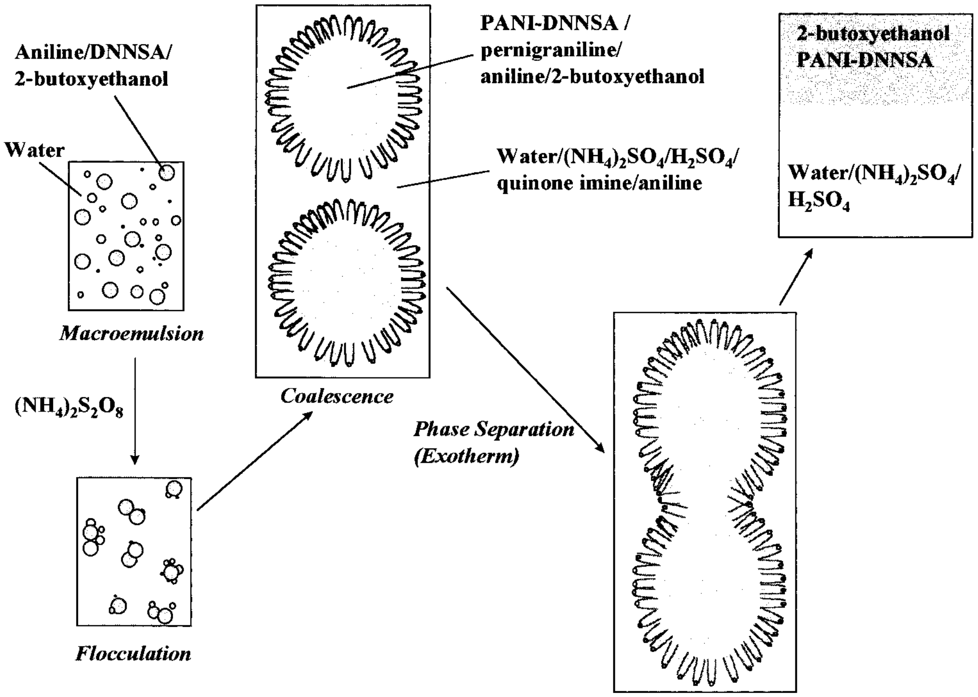

Figure 5. Pictorial representation of the PANI–DNNSA emulsion reaction sequence.

ppm), suggesting it is not an isolable intermediate. Other species such as benzidine were not identified by either GC-MS or LC-MS due to very low (<1 ppm) concentrations. The chromatogram of the aqueous phase components became much simpler after the exotherm, indicating any intermediates formed during the course of the reaction were consumed.

Syntheses using PTSA or DNNDSA as the organic acid formed precipitates in the 2-butoxyethanol system due to the high solubilities of the respective amine salts in water, which moved the polymerization reaction from the organic phase to the aqueous phase. In these two examples, as with conventional PANI syntheses, the mode of polymerization is heterogeneous. In the case of DBSA, the reaction medium remains an emulsion throughout the reaction due to the inherently strong emulsifying ability and water solubility of DBSA itself. To isolate the polymer, the emulsion was broken with acetone and a precipitate was isolated.

Our observations of the PANI–DNNSA synthesis are generally consistent with the mechanisms described in the literature. For example, a similar OCP versus time curve is observed, an induction period exists, and the polymerization becomes autocatalytic. However, there are important differences because of the presence of butylcellosolve (which is miscible in both aqueous and organic phases) and the dopant DNNSA, which is hydrophobic and insoluble in water.

A pictorial representation of the reaction sequence is presented in Figure 5.

At the onset of the reaction essentially all of the aniline is in the butylcellosolve phase as the DNNSA salt. At 1/22500 dilution of the standard emulsion, laser light scattering shows that the primary emulsion particle has a mean hydrodynamic diameter of 150 nm and ranges in diameter from about 115 to 210 nm. As ammonium persulfate is added to the emulsion, it flocculates and coalesces as the ion content of the aqueous phase increases. We conjecture that at this point pernigraniline begins to form in the 2-butoxyethanol phase, as indicated by the appearance of quinone imine in the aqueous phase.

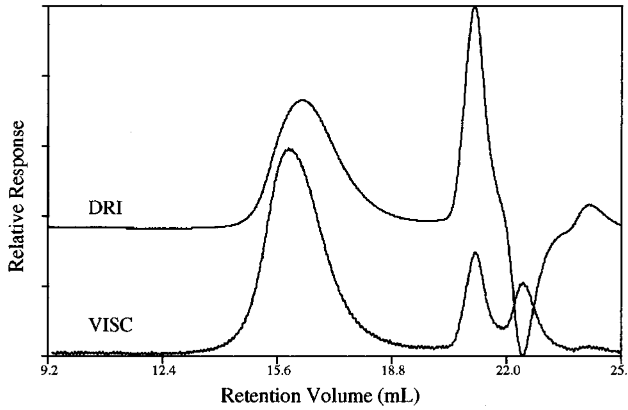

Figure 6. Size-exclusion chromatogram of PANI with viscometric (VISC) and differential refractive index (DRI) detection.

Table 1. Molecular Weights of Polyaniline Salts

polymer	mole ratio of DNNSA to aniline	M_w(SEC/viscosity)	M_w(polystyrene equivalent)
PANI–DNNSA	1.7	31 250	70 400
PANI–DNNSA	0.5	25 300	63 300
PANI–DNNSA	0.2	5 690	16 750
Versicon		19 600	55 800

The observation of a long induction period (hours compared to minutes when using water, hydrochloric acid, sulfuric acid, or PTSA) may be explained by the slow diffusion of peroxydisulfate into the organic phase.

Polymer Characterization. Molecular Weight. The SEC/VISC chromatograms for deprotonated polyaniline salts were typically unimodal, and nearly baseline resolution of the PANI and its sulfonic acid component was found, as shown in the representative data in Figure 6.

Table 1 lists the SEC/VISC molecular weights of several of the polyaniline salts synthesized as well as that of Versicon. The sulfonic acid components sepa-

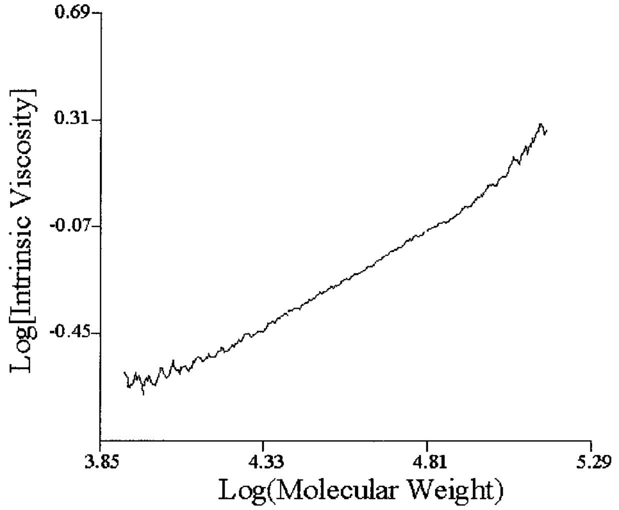

Figure 7. Mark−Houwink behavior for PANI (1.7:1 acid/aniline).

Table 2. Comparison of M−H Behavior for Polyanilines

polymer	mole ratio of DNNSA to aniline	α	log *K*
PANI−DNNSA	1.7	0.671	−3.146
PANI−DNNSA	0.5	0.667	−3.05
Versicon		0.667	−2.997
average		0.668	−3.059

rated from the polyaniline peak and were not included in the molecular weight calculations. In general the polyaniline salts tested produced broad size-exclusion chromatograms, with M_w/M_n (polydispersity) > 1.5. As shown in Figure 7, a Mark−Houwink (M−H) plot for PANI−DNNSA (1:2) is linear with $\alpha = 0.671$ and $\log K = -3.146$.

Table 2 compares the M−H behavior of the PANI−DNNSA polymers synthesized as well as that of Versicon. These values are in the range expected for typical linear random coil polymers.[31]

The accuracy of polystyrene-equivalent molecular weights for polyaniline was evaluated by comparing these values against those determined by SEC/viscometry. The latter approach has the important advantage of using universal calibration and measured intrinsic viscosities to correct the SEC calibration for the difference in polystyrene and polyaniline hydrodynamic volumes.

The comparison between polystyrene-equivalent and SEC/viscosity weight-averages molecular weights, summarized in Table 1, points out the overestimation of molecular weight resulting from polystyrene-equivalent calibration. These results are in agreement with previous conclusions based on the comparison of light scattering and SEC molecular weights,[32] which indicated that the polystyrene-equivalent SEC overestimates the true molecular weight by approximately a factor of 2.

Table 3 compares molecular weights of PANI-DNNSA prepared in various water-solvent systems. n-Octanol, chloroform and xylene-water systems do not yield product, apparently due to the very low persulfate concentration in the organic phase.

Solubility/Particle Size. Polymer solubility is generally favored when the free energy of mixing is negative:[33]

$$\Delta G = \Delta H - T\Delta S \tag{1}$$

Table 3. Polystyrene-Equivalent Molecular Weights of Polyanilines Prepared in Various Water−Solvent Systems (Mole Ratio DNNSA/AN = 1.7/1.0; Volume Ratio Solvent/Water = 1.0/1.0)

solvent	M_w	M_n
n-butanol	30 400	17 100
n-hexanol	82 200	57 400
n-octanol	NR[a]	NR
diethyl ether	39 300	25 800
chloroform	NR	NR
xylene	NR	NR

[a] NR = No reaction.

Table 4. Solubility of PANI−DNNSA (1.7:1 DNNSA/aniline Ratio)

solvent	initial solubility	dielectric constant	solubility parameter
hexane	S	1.9	14.9, p
cyclohexane	S	2.0	16.8, p
1,4-dioxane	S	2.2	20.5, m
xylene	S	2.4	18.0, p
trichloroethylene	S	3.4	18.8, p
chloroform	S	4.8	19.0, p
butylacetate	S	5.1	17.4, m
n-decyl alcohol	S[a]	7.9	
2-butoxyethanol	S[a]	9.4	
1-octanol	S[a]	10.3	21.1, s
m-cresol	S	12.4	20.9, s
4-methyl-2-pentanone	S	13.1	17.2, m
1-pentanol	S	15.1	
2-methoxyethanol	SS	17.2	
1-butanol	S[a]	17.8	23.3, s
methyl ethyl ketone	S	18.6	19.0, m
2-propanol	SS	20.1	23.5, s
acetone	I	21.0	20.3, m
N-methyl-2-pyrrolidinone	S	32.2	23.1, m
acetonitrile[b]	SS	36.6	24.3, p
N,*N*-dimethylformamide	S	38.2	24.8, m
dimethyl sulfoxide	SS	47.2	24.6, m
water	I	80.1	47.9, s
propylene carbonate	I		27.2, m
diethylene glycol	I		18.0, m
diethylene glycol monoethyl ether	SS		20.9, m
diethylene glycol monobutyl ether	S		19.4, m

[a] Polymer phase settled out within 24 h of preparation. [b] Solution turned brown.

The heat of mixing is approximated by

$$\Delta H = \nu_1 \nu_2 (\delta_1 - \delta_2)^2 \tag{2}$$

where ν is the volume fraction, δ is the solubility parameter (or Hildebrand parameter), and the subscripts 1 and 2 refer to the solvent and polymer, respectively. The solubility parameter is defined as the square root of the cohesive energy density, where the cohesive energy density is the energy of vaporization per unit volume:

$$\delta_i = (\Delta E^{v}{}_{i}/V_i)^{1/2} \tag{3}$$

The solubility parameter, δ_i, may be thought of as the attractive strength between molecules of the material. In general, for nonpolar systems, $(\delta_1 - \delta_2)$ must be small for components to be miscible. For polar systems, solvents are categorized by poor (p), medium (m), and strong (s) hydrogen bonding capacities.

Table 4 lists the solubility of the PANI-DNNSA salt (2:1 molar ratio of sulfonic acid to aniline) in a variety of solvents. The rating of solubility was designated as follows: S, solubility equal to or greater than 1 wt %;

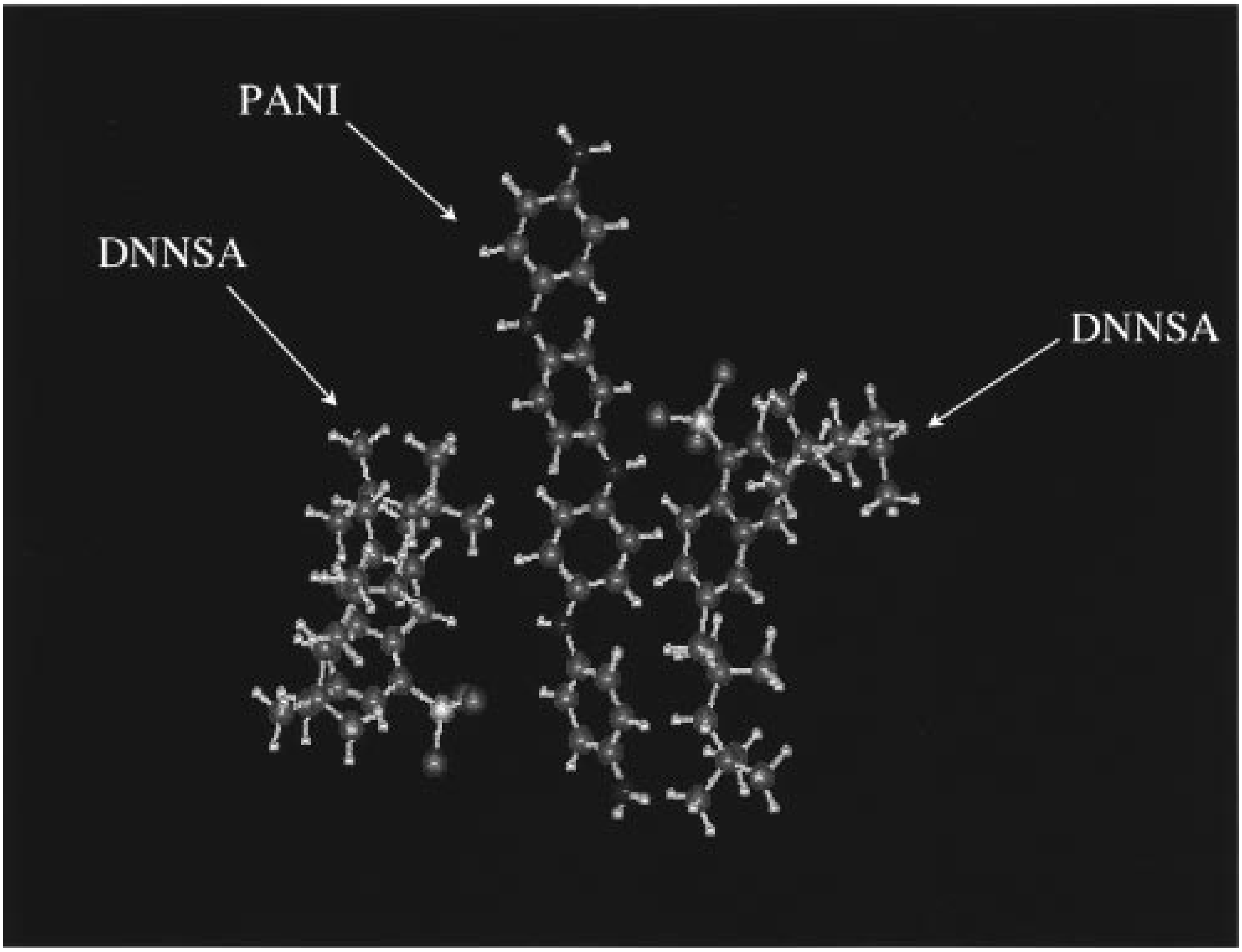

Figure 8. Molecular model of PANI–DNNSA.

SS, solubility less than 1 wt % and greater than about 0%; and I, insoluble (approximately 0% soluble). Also listed in Table 4 are solvent dielectric constants and Hildebrand solubility parameters.[34]

As seen in Table 4, good solvents for PANI–DNNSA include hexane, cyclohexane, xylene, dioxane, trichloroethylene, chloroform, butyl acetate, *m*-cresol, 4-methyl-2-pentanone, methyl ethyl ketone (MEK), *N*-methyl-2-pyrrolidinone (NMP), and *N*,*N*-dimethylformamide. It should be noted, however, that the solubilities of the acetone precipitated DNNSA salts were found to be very low in solvents that are excellent for the unprecipitated polymer (e.g., xylene and toluene). It thus appears that once the polymer chains entangle and/or crystallize, it is very difficult to resolubilize them.

The results show that PANI–DNNSA tends to exhibit exceptional solubility in all three H-bonding groups (p, m, and s) if δ is less than 25 $(\mathrm{MPa})^{1/2}$, indicating $\delta > 25$ $(\mathrm{MPa})^{1/2}$ for the PANI–DNNSA salt. For comparison, the δ values for poly(vinyl acetate), poly(ethylene terephthalate), Nylon-66, and polyacrylonitrile are 21.7, 21.9, 27.8, and 31.5,[35] respectively. PANI–DNNSA and polyacrylonitrile are both soluble in DMF which allows for solution spinning of PANI/polyacrylonitrile fibers.[36]

A molecular model of PANI–DNNSA (Figure 8) was constructed to give insight into where charges/dopant molecules are located and how they are distributed throughout the structure.[37]

For illustrative purposes, the system chosen has a 1:2 molar stoichiometry (DNNSA to aniline). All work was done using HYPERCHEM (release 3). The DNNSA anion was constructed with branching at C2 and C5.[38] The geometry of this structure was optimized with the MM+ force field using the block-diagonal Newton–Raphson minimization algorithm. A single-point semiempirical computation (CNDO) was performed in order to obtain the charges on (especially) the oxygen atoms.

The polyaniline radical cation backbone was created from four aniline moieties (total charge was +2). The separated polaron was energy-minimized/geometry-optimized through a semiempirical quantum mechanical AM1 calculation using a conjugate gradient minimizer. Finally, two DNNSA anions were sequentially introduced into the region of the aforementioned polaron. Geometry optimization proceeded using MM+ with the Polak-Ribiere conjugate gradient minimizer to produce the depiction.

The model clearly shows dinonylnaphthalene substituents play a major role in defining the solubility/conductivity for PANI and act much like branches extending from the PANI. These calculations serve as a prelude to future work involving density functional theory calculations which will probe the electronic (band) structure of the system.

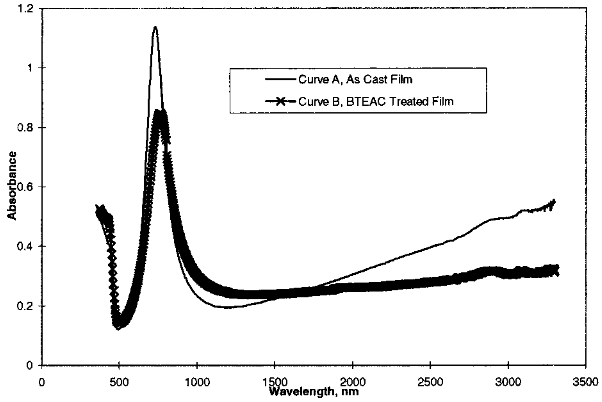

Figure 9. UV/VIS/NIR spectra of PANI–DNNSA films: curve A, "as cast" film; curve B, film treated with 0.5 M BTEAC.

Electrical Conductivity/Spectroscopy of PANI–DNNSA. Films of PANI–DNNSA approximately 0.15-mm thick cast from xylene solutions and dried at 70 °C at 10–20 mmHg for 7 h yielded conductivities ranging from 6.5×10^{-6} to 63×10^{-6} S/cm. The UV/VIS/NIR spectrum of a dried PANI–DNNSA film is shown in Figure 9, curve A.

A strong polaron absorption at 720 nm is observed with a "free carrier tail" commencing at approximately 1000 nm. Similar spectra have been observed for PANI-camphorsulfonic acid exposed to a secondary dopant (e.g. *m*-cresol) and have been explained by an "expanded coil model"[39,40] or, alternatively, a model based upon "solvent quality".[41] PANI–DNNSA exhibits a free carrier tail without addition of a secondary dopant, implying an inherently high degree of charge delocalization and an effective doping level for this polymer system.

After treatment of the PANI–DNNSA films in 0.05 M or 0.5 M benzyltrimethylammonium chloride (BTEAC) solutions at 22 or 58 °C, conductivities were found to increase by 3–4 orders of magnitude, as shown in Table 5. Figure 9, curve B shows a decrease in the polaron absorption band at 720 nm with a concomitant decrease or "flattening" of the free carrier tail absorption.

A pronounced humidity dependence of the BTEAC-treated film was noted. Thorough drying of the BTEAC-treated films caused the conductivity to decrease significantly (although final values were still 10× greater than that of the original untreated samples). In contrast to the methanol-treated films discussed below, the BTEAC-treated films remained flexible and soluble in xylene. No extraction of DNNSA into the BTEAC solutions was detected. As discussed below, we believe the BTEAC treatment results in morphological change from discontinuous (PANI–DNNSA) conducting domains to multiple connected pathways of PANI–DNNSA in an amorphous dopant (DNNSA/BTEAC) matrix. Other surfactants such as diphenyloxide disulfonates (DOWFAX 2AO, 2A1, 8339) as well as 3-cyclohexylamine-1-propanesulfonic acid (CAPS) gave similar conductivity enhancements (Table 5).

It was also discovered that treatment of PANI–DNNSA films with methanol or acetone caused a large increase in conductivity, up to 5 orders of magnitude. The effect was also observed with MEK, 2-propanol, and ethanol. No effects were noted with water or heptane treatment. The rate at which resistance dropped was very rapid, and substantial increases in conductivity were observed with as little as 5 s of contact with the solvent. During the treatment process, the coating underwent shrinkage and became insoluble in solvents such as dichloromethane and xylene (these solvents readily dissolve dried PANI–DNNSA coatings as well as the BTEAC treated coatings discussed above). The coatings were soluble in NMP, and no loss in molecular weight was noted. Quantitative extraction experiments in conjunction with HPLC showed that the treatment procedure extracts excess DNNSA from the films, leaving the stoichiometric equivalent of DNNSA behind (i.e., the mole ratio of DNNSA to aniline decreases from 1.6 to 0.5). As in the case of the BTEAC-treated film, the UV/VIS/NIR spectrum of the methanol-treated film exhibits a decrease in both the polaron absorption and the free carrier absorption (Figure 10).

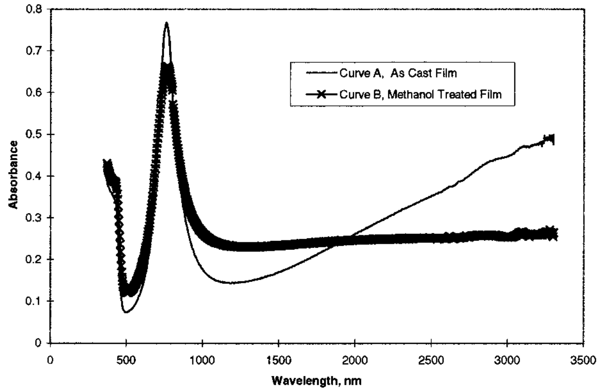

Figure 10. UV/VIS/NIR spectra of PANI–DNNSA films: curve A, "as cast" film; curve B, film treated with methanol.

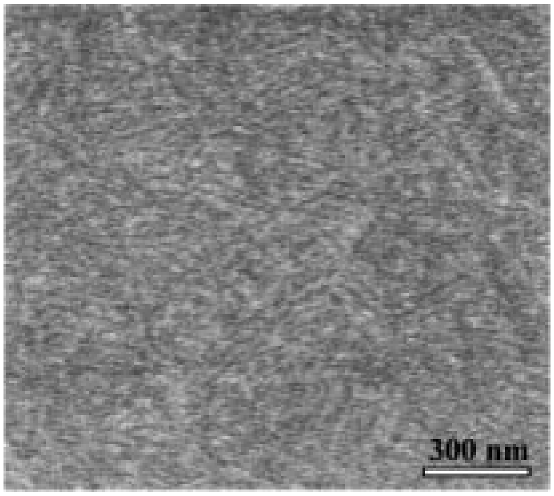

Figure 11. SEM image of the spin-coated PANI–DNNSA film revealing needle-like structures.

Preliminary XRD analysis shows an increase in crystallinity for both the methanol- and BTEAC-treated films.[42]

Microscopy. A 5% solution of PANI–DNNSA in xylene was found to be easily filterable through a 0.2-μm filter, indicating a particle size less than 0.2-μm. Figure 11 shows a typical high-magnification SEM image of a spin-coated film prepared from a PANI–DNNSA xylene solution. Small particles with sizes less than 0.2-μm and some needle-like structures were revealed.

The nanostructures of the PANI–DNNSA films were shown more clearly in TEM images. Figure 12 shows a typical bright-field TEM image of PANI-DNNSA films.

Table 5. Effect of Surfactant Treatment on PANI–DNNSA Conductivity

	0.05 M BTEAC, 22 °C (30 s)	0.05 M BTEAC, 58 °C (10 min)	0.5 M BTEAC, 22 °C (30 s)	0.5 M BTEAC, 58 °C (10 min)	17% 2A1, 58 °C (10 min)	5% 8339, 58 °C (10 min)	0.1 M CAPS, 58 °C (10 min)	16% 2AO, 58 °C (10 min)
conductivity before treatment ($\times 10^{-6}$ S/cm)	6.5	12.0	8.1	63.0	18.0	12.0	9.0	29.0
conductivity after treatment and drying at 22 °C ($\times 10^{-6}$ S/cm)	18 000	130 000	40 000	610 000	92 000	71 000	57 000	300 000
conductivity after treatment and drying at 70 °C under 10–50 mmHg vacuum ($\times 10^{-6}$ S/cm)	320	160	1400	2500	35 000	28 000	31 000	30 000
fold increase in conductivity	49	13	170	40	1900	2300	3400	1000

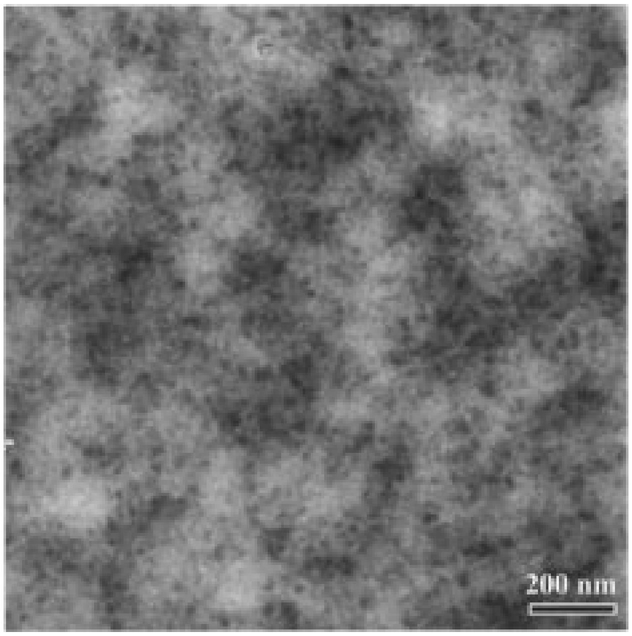

Figure 12. Bright-field TEM image of the PANI–DNNSA film (darker domains represent conducting PANI islands; bright regions represent the nonconducting dopant phase).

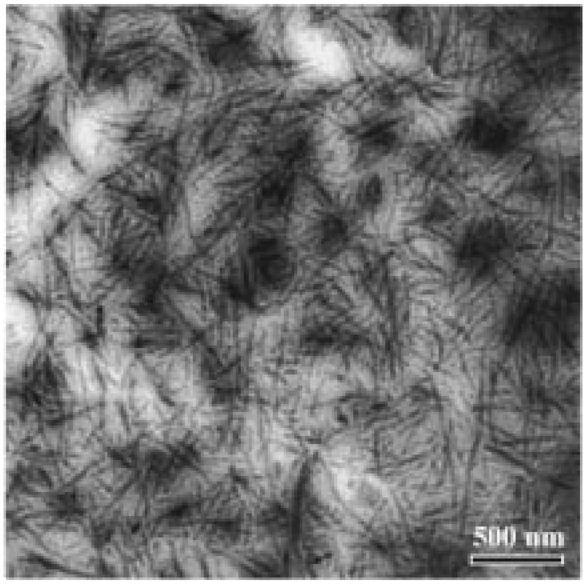

Figure 13. Bright-field TEM image of the PANI–DNNSA film prepared after sonicating a xylene/PANI-DNNSA solution for 5 min.

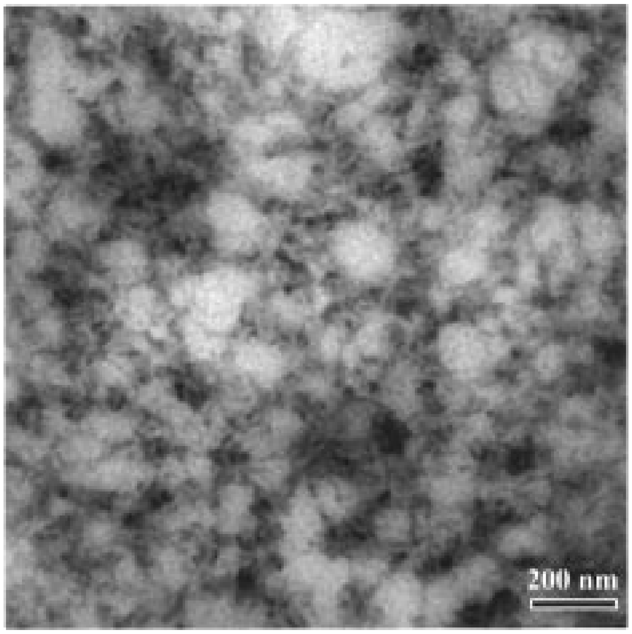

Figure 14. Bright-field TEM image of the PANI–DNNSA film treated for 2 min in 0.1 M BTEAC solution.

The darker spots or domains represent conducting PANI islands. The brighter regions represent the nonconducting dopant phase. Analysis of these TEM images suggested that small islands of conducting PANI were imbedded in a nonconducting, amorphous dopant matrix. Depending on the specific preparation conditions, these small islands may "aggregate" to form conducting domains or long fibrils of PANI. Figure 13 shows that fibrils of PANI up to 500 nm in length are formed after sonicating a xylene/PANI–DNNSA solution for 5 min prior to forming the film.

Figure 14 shows a typical bright-field TEM image of the PANI–DNNSA film after the film was soaked for 2 min in a 0.1 M aqueous solution of BTEAC.

Again, the darker and brighter regions represent conducting and nonconducting phases, respectively. The images clearly show that the morphology of the PANI–DNNSA films changed significantly after treatment in the quaternary ammonium ion solution. In the nontreated films small islands of conducting polymer are "embedded" in the nonconductive dopant matrix. Some of these islands aggregate to form conducting domains. For the BTEAC-treated PANI–DNNSA films, interconnected networks of polyaniline were observed. The solution treatment thus seems to facilitate self-assembly of the conducting islands to form multiple connected pathways and hence the significant increase in conductivity observed as shown in Table 5.

Summary

A new emulsion process has been discovered for the direct synthesis of the emeraldine salt of polyaniline (PANI) that is soluble in organic solvents. As the reaction proceeds, the reaction mixture changes from an emulsion to a two-phase system, the soluble PANI remaining in the organic phase. Thus, organically soluble polyaniline is formed directly. SEC/viscometry shows that the polymer behaves as a linear random coil. Thin films of the polymer are readily cast from xylene and have relatively low conductivities due to aggregation of conducting domains. Treatment of thin films of PANI−DNNSA with quaternary ammonium salt solutions changes the morphology to one of multiply connected conducting pathways and results in a 3−4 order of magnitude increase in conductivity. Treatment of the films with acetone or methanol also results in an increase in conductivity; however, the mechanism is through densification and crystallization of the film by removal of excess dopant.

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