

# Didecyl Ester of 4-Sulfophthalic Acid as a Plast Dopant and Emulsifier in the Chemical Polymerization of Aniline into Polyaniline Salt

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**ABSTRACT:** Polyaniline salt was synthesized through the chemical oxidation of aniline with sodium persulfate as the oxidant and didecyl ester of 4-sulfophthalic acid via three different polymerization pathways (aqueous, emulsion, and interfacial). In these polymerization processes, the ester acted as a novel plast dopant and as an emulsifier. The yield, conductivity, and number of ester units present in the polyaniline salts were determined. A polyaniline salt prepared by emulsion polymerization was soluble in chloroform and showed excellent solution-processing properties. Polyaniline samples prepared by aque-

ous or interfacial polymerization were not soluble in chloroform. A soluble polyaniline salt was successfully synthesized through the washing of an organic layer containing the polyaniline salt with water in emulsion polymerization. X-ray diffraction spectra of polyaniline salts prepared by the three different methods showed an ordered, layer-type supramolecular structure. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 2704–2711, 2010

**Key words:** conducting polymers; emulsion polymerization; morphology; X-ray

## INTRODUCTION

Polyaniline (PANI) is the most important of all conducting polymers because of its straightforward polymerization (via electrochemical and chemical processes), chemical stability, relatively high conductivity, redox properties, lower cost, and potential applications in various fields.<sup>1–7</sup> Gospodinova and Terlemezyan<sup>1</sup> regarded both the electrochemical and chemical polymerization of aniline and the subsequent transformations of PANI as typical redox processes in which the direction and establishment of equilibrium are dependent on the oxidation potentials, the concentrations of the reactants, and the pH of the medium. Pron and Rannou<sup>3</sup> critically discussed the synthetic routes to the principal conjugated polymers with a special emphasis on dopant engineering, that is, on the design of dopants that not only increase the electronic conductivity of the

polymer but also induce desired properties in the doped polymer system (e.g., improved processability, special catalytic properties, or special optical or spectroscopic properties). Selected examples of technological applications of doped conjugated polymers (e.g., conductive plastics, optical pH sensors, heterogeneous catalysts, and gas-separation membranes) were presented. Zhang and Wang<sup>4</sup> examined various synthesis approaches to one-dimensional, nanostructured PANI via template synthesis and nontemplate synthesis in a review. One-dimensional, nanostructured PANI has a large surface area, high conductivity, controllable chemical/physical properties, and good environmental stability; this makes the nanomaterial a promising candidate for applications ranging from sensors to energy storage to flash welding to digital nonvolatile memory. Bhadra et al.<sup>5</sup> reported different methods used for the synthesis of PANI along with a number of special methods used to obtain nanostructured PANI. A detailed discussion of the mechanism of electrical conduction in PANI and the factors influencing the conductivity of PANI was also included. Possible applications of PANI were discussed as well. The synthesis, processing, properties, and applications of PANI nanofibers and metal composites in the areas of flash welding, monolithic actuators, ultrafast nonvolatile memory devices, sensors, and chemical catalysis were discussed by Kaner et al.<sup>6</sup> Applications of conducting polymers such as polypyrrole and PANI in

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drug delivery systems, biosensors, and the preparation of artificial muscles (e.g., robots and artificial limbs) were discussed by Entezami and Massoumi<sup>7</sup> in a review.

Chemical polymerization is a more feasible route for producing large-scale PANI for industrial use in comparison with electrochemical polymerization. For chemical polymerization, different techniques, such as aqueous polymerization,<sup>8</sup> dispersion polymerization,<sup>9,10</sup> emulsion polymerization,<sup>11</sup> interfacial polymerization,<sup>12,13</sup> hard and soft templates,<sup>14</sup> and seeding,<sup>15</sup> have been reported. Various acids such as mineral acids,<sup>8</sup> organic acids,<sup>8</sup> and plast dopant acids<sup>16</sup> with emulsifying properties (e.g., dodecylbenzenesulfonic acid,<sup>17–19</sup> camphorsulfonic acid,<sup>20,21</sup> and dinonylnaphthalenesulfonic acid<sup>22</sup>) have been used in PANI synthesis as protonating agents.

The properties of PANI mainly depend on the process of polymerization, solvents, dopants, and reaction conditions. In chemical synthesis, emulsion and interfacial polymerization techniques have attracted more attention because of their simplicity, processability, purity, nanomaterial preparation, and so forth. We very recently wrote a review of the emulsion polymerization of aniline.<sup>11</sup> We recently synthesized a PANI salt containing maleic acid and didecyl ester of 4-sulphthalic acid via an inverted emulsion polymerization pathway.<sup>23</sup>

Generally, a PANI salt is not soluble in common organic solvents. During emulsion or interfacial polymerization, a PANI salt in carrier organic solvents can be isolated; it contains oligomers and other byproducts. The subsequently isolated pure PANI salt in a powder form is not generally soluble in organic solvents. To obtain a pure solution of a processable PANI salt, it is important to synthesize a PANI salt that is soluble in a powder form. In this work, aniline was oxidized by sodium persulfate in the presence of a sulphthalic ester into a PANI salt; it acted as a novel dopant containing plasticizing groups and as a surfactant. The PANI salt in a powder form prepared by this method was soluble in a solvent.

## EXPERIMENTAL

### Materials and equipment

Aniline (Rankem, New Delhi, India) was distilled before use. 4-Sulphthalic acid (Aldrich, St. Louis), 1-decanol, and sodium persulfate (S.D. Fine Chemicals, Mumbai, India) were used as received. Solvents were distilled before use.

To take advantage of the solubility of the prepared polymer, we used both solution and solid-state characterization methods. Ultraviolet–visible (UV–vis) spectra of PANI salt solutions in chloroform (CHCl<sub>3</sub>)

and dimethylformamide (DMF) and spectra of PANI base solutions in DMF were recorded with a Lab-omed (Culver City, CA) Spectro UV–vis double-beam PC spectrometer. Fourier transform infrared (FTIR) spectra of the PANI salts and base were registered on a Nicolet (Minnesota) Nexus 670 gas chromatography/FTIR spectrometer with the pressed KBr pellet technique. The steady shear and dynamic viscosity measurements were performed with an Anton Paar (Graz, Austria) Physica MCR51 rheometer with cup and bob geometry. The rheological behavior of PANI salt solutions was studied at the ambient temperature. The measurements were carried out with a 1–3% PANI salt solution in CHCl<sub>3</sub>; the samples were monitored at shear rates ranging from 1 to 10 s<sup>-1</sup>. X-ray diffraction (XRD) profiles for PANI salt powders were obtained on a Siemens D-500 X-ray diffractometer (Karlsruhe, Germany) with Cu K $\alpha$  radiation (land continuous) at a scan speed of 0.045°/min. For the determination of the conductivity, powders of PANI salts were pressed into disks (13 mm in diameter and ca. 1.5 mm thick) under a pressure of 400 MPa. The resistance was measured in a four-probe configuration with a Keithley (Cleveland, Ohio) 2010 digital multimeter.

### General procedure for the synthesis of didecyl ester of 4-sulphthalic acid (DDESPA)

DDESPA was synthesized by a reported procedure.<sup>24</sup> In a typical experiment, 9.0 g of 4-sulphthalic acid in the form of a 50 wt % solution in water (18.3 mmol) along with a slight excess of 1-decanol (6.7 g, 41.7 mmol) was placed in a double-necked, round-bottom flask fitted with a Dean–Stark apparatus. The esterification reaction was carried out at 110°C for 4 h with constant bubbling of nitrogen gas to remove water formed as a side product in the reaction. HCl (100 mL, 1M) was added to the reaction mixture, and the organic phase was extracted with ether. The ether solution was dried with anhydrous sodium sulfate and filtered, and the ether solvent was evaporated through a rotary evaporator to get the product.

### General procedure for the synthesis of PANI salts by an interfacial polymerization pathway (I-1)

Distilled aniline (1 mL, 0.11 mol) was dissolved in 30 mL of distilled water. The plast dopant (2.9 g, 0.05 mol, aniline/dopant = 2.2), dissolved in CHCl<sub>3</sub> (35 mL), was added to the aforementioned solution slowly without the solution being disturbed. Sodium persulfate (2.88 g, 0.11 mol) was dissolved in 45 mL of distilled water and added slowly over 15–20 min to the mixture without the interface being disturbed. The reaction mixture was allowed to stand at the

**TABLE I**  
Yield, Conductivity, Solubility, and XRD Data for PANI Salts Synthesized by Different Polymerization Pathways

Sample <sup>a</sup>	Aniline/Dopant <sup>b</sup>	Yield (%) <sup>c</sup>	Conductivity (S/cm)	Soluble in CHCl <sub>3</sub>	XRD	
					Peak at 2θ (°)	d-spacing (Å)
E-1	1.76	54.1	0.15	Yes	6.0, 9.0, 14.6, 20.4, 25.4, 27.0	14.7, 9.8, 6.0, 4.3, 3.5, 3.2
E-2	2.2	59.7	0.25	Yes	14.6, 20.0, 25.2, 27.2	6.0, 4.4, 3.5, 3.2
E-3	3.04	58.3	0.03	Yes	20.0, 25.0, 26.6	4.4, 3.5, 3.3
I-1	2.2	44.6	0.02	No	5.8, 20.0, 25.0	15.2, 4.4, 3.5
A-1	2.2	45.6	0.1	No	15.0, 20.0, 25.0, 26.8	5.9, 4.3, 3.5, 3.3

<sup>a</sup> The letters E, I, and A refer to samples prepared via emulsion, interfacial, and aqueous polymerization routes.

<sup>b</sup> Concentration ratio of aniline to the dopant with a fixed aniline concentration of 0.11M.

<sup>c</sup> Calculated according to the formula in Scheme 1.

ambient temperature for 24 h without disturbance. PANI was formed at the interface and diffused into the organic phase. The organic layer was separated from the aqueous layer with a separating funnel and was washed three times with 100 mL of distilled water. The organic phase was poured into 200 mL of acetone. The solid mass was filtered and washed with distilled water and then acetone. The solid product was dried in an oven at 50°C until a constant mass was obtained.

#### General procedure for the synthesis of PANI salts by an emulsion polymerization pathway (E-2)

Distilled aniline (1 mL, 0.11 mol) was dissolved in 30 mL of distilled water. The plast dopant (2.9 g, 0.05 mol, aniline/dopant = 2.2), dissolved in CHCl<sub>3</sub> (35 mL), was added to the aforementioned solution, and it was stirred at a constant speed for 10 min at the ambient temperature. Sodium persulfate (2.88 g, 0.11 mol), dissolved in 45 mL of distilled water, was added slowly over 15–20 min to the aforementioned solution with constant stirring for 6 h at the ambient temperature. The green polymer product was obtained in an organic layer. Isolation of the PANI salt was carried out with the same procedure mentioned for the interfacial method. PANI salts were also prepared with this procedure by adjustments in the aniline/dopant ratio to 1.76 (E-1; see Table I) and 3.04 (E-3; see Table I).

#### General procedure for the synthesis of PANI salts by an aqueous polymerization pathway (A-1)

In this process, aniline (1 mL, 0.11 mol) was dissolved in 30 mL of distilled water. The plast dopant (2.9 g, 0.05 mol, aniline/dopant = 2.2), mixed in 35 mL of distilled water, was added to the aforementioned solution, and it was stirred for 10 min at the ambient temperature. Sodium persulfate (2.88 g, 0.11 mol) in 45 mL of distilled water was added to

the reaction mixture over 15–20 min. The reaction mixture was stirred for 6 h at a constant speed at the ambient temperature. The reaction mixture was poured into 200 mL of acetone. The reaction mixture was filtered and washed with distilled water and then acetone. The solid product was dried in an oven at 50°C until a constant mass was obtained.

#### General procedure for the synthesis of PANI bases by a dedoping process

PANI salt E-2, synthesized by the emulsion polymerization pathway, was dedoped with an aqueous sodium hydroxide solution. The PANI salt (1.0 g) was stirred in 100 mL of a 1N sodium hydroxide solution for 12 h at the ambient temperature. The solution was filtered and washed with a sodium hydroxide solution, then distilled water, and finally acetone. The powder was dried at 60°C for 12 h.

## RESULTS AND DISCUSSION

#### General structure of PANI

The base form of PANI can in principle be described with the general formula in Figure 1(a). In the generalized base form,  $1 - y$  measures the function of oxidized units. At  $1 - y = 0$ , the polymer has no such oxidized groups and is commonly known as a leucoemeraldine base. The fully oxidized form ( $1 - y = 1$ ) is called a pernigraniline base. The half-oxidized polymer, in which the numbers of reduced units and oxidized units are equal ( $1 - y = 0.5$ ), is of special importance and is termed the emeraldine oxidation state or emeraldine base. The corresponding emeraldine salt can be represented with the formula shown in Figure 1(b).

#### Yield, conductivity, solubility, and morphology of the PANI salt

A PANI salt containing the plast dopant DDESPA was synthesized by oxidization of aniline with

sodium persulfate in the presence of DDESPA via three different polymerization pathways (emulsion, interfacial, and aqueous polymerization; Scheme 1). In this polymerization process, the ester (DDESPA) acted as a dopant and an emulsifier. The number

of ester units per aniline unit ( $n$ ) present in the PANI salt was determined from the amount of the PANI base, which was obtained from the amount of the PANI salt used in the dedoping process:

$$\text{Weight loss} = \frac{\text{Weight of polyaniline salt} - \text{Weight of polyaniline base}}{\text{Weight of polyaniline salt}} \times 100$$

$$n = \frac{\text{Weight loss} \times \text{Molecular weight of aniline}}{(100 - \text{Weight loss}) \times \text{Molecular weight of DDESPA}}$$

The numbers of ester units per four units of aniline in PANI salts prepared by emulsion, aqueous, and interfacial polymerization pathways were found to be 0.4, 0.36, and 0.16, respectively. The

yield of the PANI salt was calculated according to the structure in Scheme 1. The theoretical yield of 100% from the structure was determined as follows:

Theoretical yield

$$= \frac{\text{Molecular weight of 4 repeating aniline units in polyaniline} + (n \times \text{Molecular weight of DDESPA})}{4 \times \text{Molecular weight of aniline}}$$

Through the substitution of the molecular weight, the value of the theoretical yield became

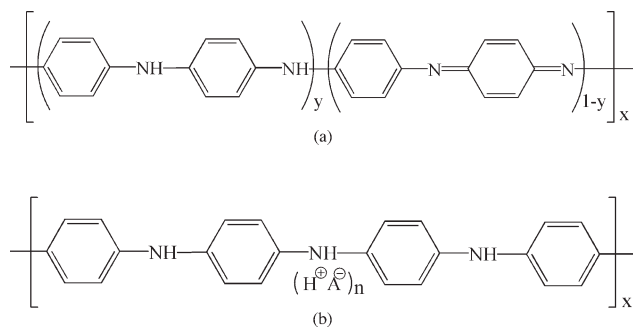
$$\text{Theoretical yield} = \frac{362 + (n \times 526)}{372.5}$$

$$\text{Experimental yield (\%)} = \frac{\text{Experimental yield (g)}}{\text{Theoretical yield}} \times 100$$

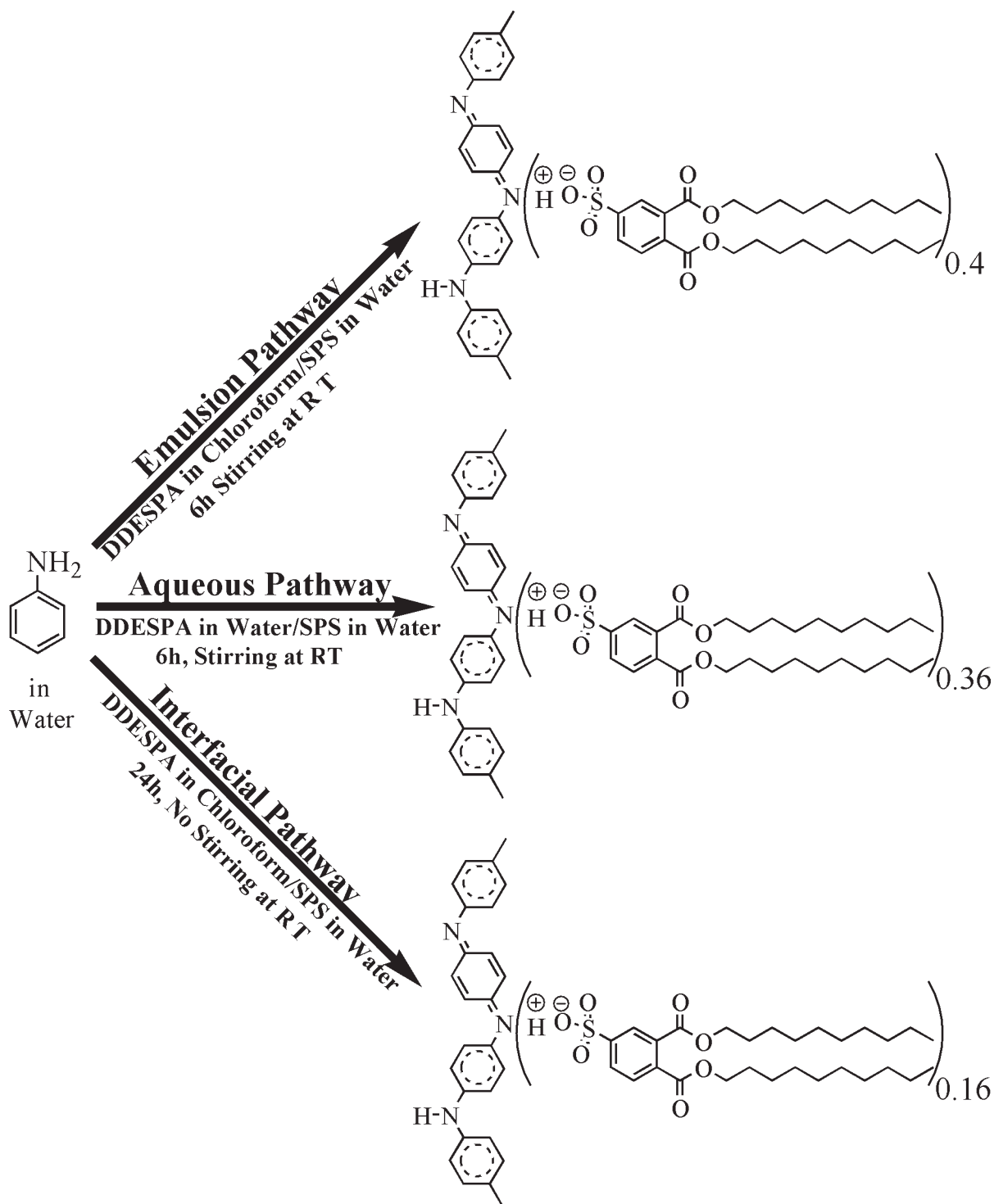
The yield and conductivity of the PANI salts are reported in Table I. The yield and conductivity of the PANI salt prepared by emulsion polymerization increased, attained maxima, and then decreased with increases in the aniline/dopant ratio. A higher yield was obtained for the PANI salt prepared by the emulsion pathway (59.7%) versus those prepared by the interfacial (44.6%) and aqueous pathways

(45.6%). The conductivity of the PANI salts prepared by emulsion polymerization (0.25 S/cm) and aqueous polymerization (0.1 S/cm) was found to be higher than that of the PANI salt prepared by the interfacial polymerization pathway (0.02 S/cm). In the case of interfacial polymerization, the polymerization proceeded under static conditions at the interface between water and  $\text{CHCl}_3$ ; the sulfonic terminals in the micelles may have had less opportunity to interact with imines. However, in the case of the emulsion and aqueous polymerization pathways, stirring may have made interactions with imines easy, and this resulted in higher doping levels and conductivity (Table I). Zhang et al.<sup>25</sup> reported a low doping percentage possibly due to extensive phase segregation of the bulk emeraldine oxidation state into extended runs of fully reduced leucoemeraldine segments and fully oxidized pernigraniline segments. The PANI salt prepared by the emulsion pathway was soluble in  $\text{CHCl}_3$ , whereas the salts prepared by the interfacial and aqueous pathways were insoluble. Even though the PANI salt prepared by the emulsion pathway was soluble in  $\text{CHCl}_3$ , it did not yield a good film for measuring the conductivity in the film form.

In emulsion polymerization, at the end of the reaction, the organic layer was separated from the aqueous layer, and washing the organic layer containing PANI salt three times with distilled water led to a soluble PANI salt; without washing, this led to an insoluble PANI powder. The solubility of the PANI salt may have been due to the large amount of long



**Figure 1** General formulas for (a) the PANI base and (b) the PANI salt.

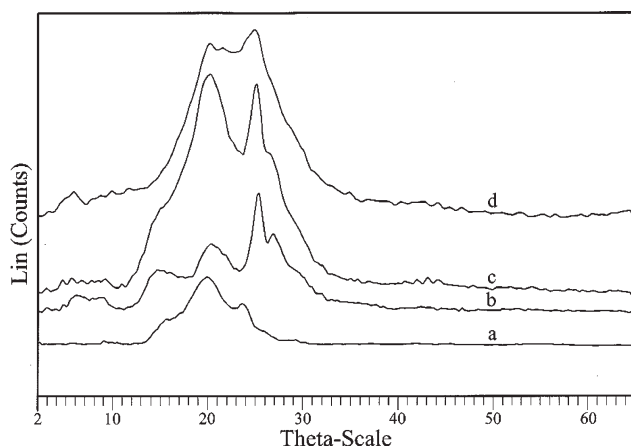


**Scheme 1** General synthesis of PANI salts by emulsion, aqueous, and interfacial polymerization pathways (RT = room temperature; SPS = sodium persulfate).

and nonpolar chain dopant present in the PANI chain, which provided space for the PANI backbone, allowed the penetration of solvent molecules inside the chain, and induced the solubility of the polymer in a polar solvent; washing with water led to the removal of unwanted side products.

#### XRD profile of PANI

Typical powder XRD profiles registered for the PANI salts prepared by three different pathways and for the PANI base are shown in Figure 2. The XRD pattern of PANI salt E-1, which was synthesized by



**Figure 2** XRD powder profiles for (a) the PANI base, (b) PANI salt E-1, (c) PANI salt A-1, and (d) PANI salt I-1.

the emulsion polymerization pathway and was used as a representative system, showed peaks at  $2\theta$  values of 6, 9, 14.6, 20.4, 25.4, and  $27^\circ$  with corresponding  $d$ -spacing values of 14.7, 9.8, 6.0, 4.3, 3.5, and 3.2 Å, respectively [Fig. 2(b)]. The peaks at  $2\theta$  values of 14.6, 20.4, 25.4, and  $27^\circ$  were similar to the crystalline structure of the PANI salt reported in the literature.<sup>26,27</sup> Bragg peaks centered at  $2\theta = 25.4^\circ$  and  $2\theta = 20.4^\circ$  ( $d$ -spacings of 3.5 and 4.3 Å) corresponded to the  $\pi$ -stacking distance of the PANI chains and the average separation distance between the alkyl substituents of the DDESPA dopant. Reflections centered at  $2\theta$  values of 6, 9, and  $14.6^\circ$  were accompanied by a second-order counterpart at  $20.4^\circ$  and can be considered direct confirmation of the layered structure of the doped polymer with the coherence length in the direction perpendicular to the PANI chain direction. A similar XRD pattern was observed for the PANI salts prepared by aqueous [Fig. 2(c)] and interfacial polymerization pathways [Fig. 2(d)]. The XRD pattern of the PANI base [Fig. 2(a)] was very similar to the X-ray pattern of the PANI base reported by MacDiarmid et al.<sup>26</sup>

### IR spectra of PANI

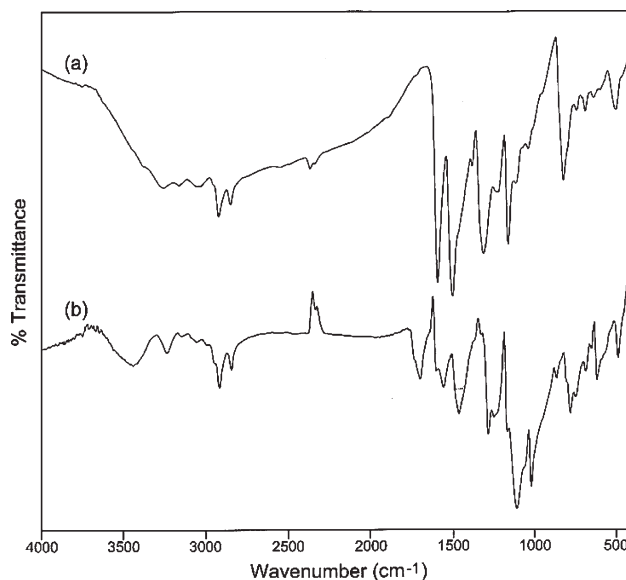
The incorporation of DDESPA into the PANI matrix was confirmed by IR spectroscopy. IR spectra of PANI salt E-2 and its corresponding base are shown in Figure 3. The spectrum of the PANI base [Fig. 3(a)] showed major characteristic vibrational bands of PANI at 3425 (N–H stretching), 2925 and 2850 (C–H stretching), 1585 (N=Q=N, quinonoid ring), 1495 (N=B=N, benzenoid ring), 1385 (C–N stretching of QBQ), 1310 (C–N stretching of QBC, QBB, BBQ), 1230 (C–N stretching of BBB aromatic), 1160 (N=Q=N), 1140 (electronic band or vibrational band of nitrogen quinone), and  $820\text{ cm}^{-1}$  (1,4-disub-

stituted benzene). These values were similar to those of a previously reported IR spectrum of PANI.<sup>28,29</sup> The IR spectrum of the PANI salt [Fig. 3(b)] was similar to that of the PANI base, except that a peak at  $3245\text{ cm}^{-1}$  due to  $\text{NH}_2^+$ , which indicated the formation of the salt, and peaks due to the dopant group, that is, strong peaks at 2925 and 2850 (C–H stretching), 1705 (C=O stretching), and  $1025\text{ cm}^{-1}$  (O=S=O group), were observed.

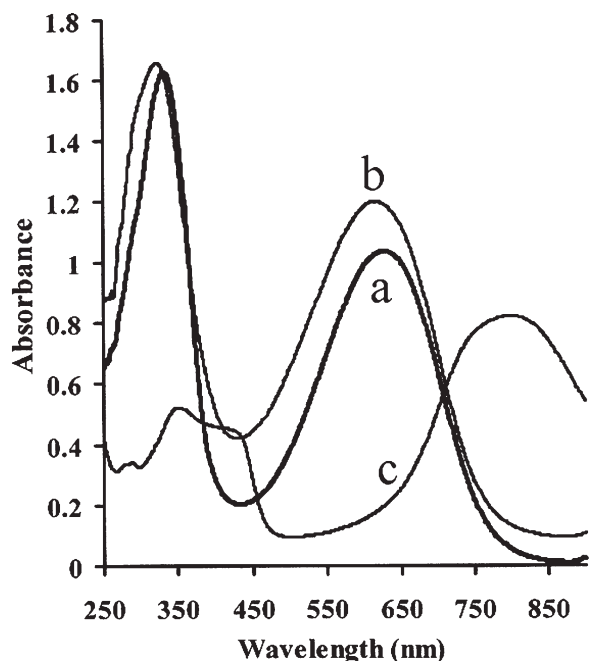
### Electronic absorption spectra of PANI

UV–vis spectroscopy is a very sensitive tool for studying electronic structure changes in conducting polymers. Literature reports of the absorption spectrum of PANI bases<sup>30,31</sup> generally show two distinct absorption bands located between 315 and 345 nm and 590 and 650 nm; they depend on the preparation and/or processing of PANI. The band around 315–345 nm may be assigned to the  $\pi$ - $\pi^*$  transition, and the band around 590–650 nm may be assigned to the excitation of the amine segment of the polymer chain. However, the electronic absorption of the PANI salt showed three absorption bands at 325–360, 400–430, and 780–825 nm.<sup>29,30,32</sup> An intense peak at 350 nm was assigned to the  $\pi$ - $\pi^*$  transition, whereas the shoulder at 420 nm was typical of the polaron-to- $\pi^*$  transition generally observed for emeraldine salts. The third absorption band at 870 nm originated from the  $\pi$ -to-polaron transition.

In this work, the electronic absorption spectrum of the PANI base in DMF [Fig. 4(b)] showed two peaks at 335 and 630 nm, which indicated the presence of the base. The electronic absorption spectrum of PANI salt E-2 in  $\text{CHCl}_3$  showed three peaks at 350,



**Figure 3** FTIR spectra of (a) the PANI base and (b) PANI salt E-2.

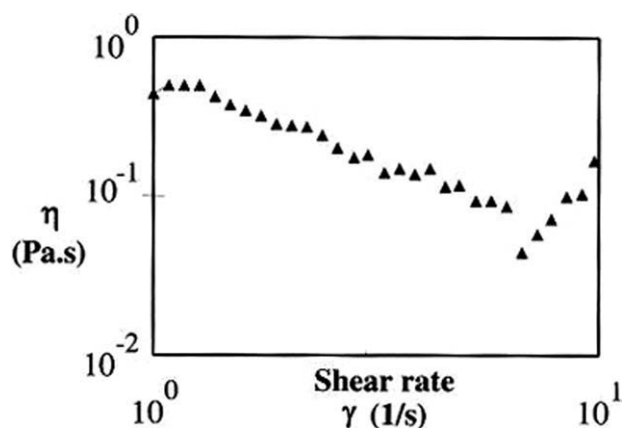


**Figure 4** UV-vis solution spectra of (a) PANI salt E-2 in DMF, (b) PANI base E-2 in DMF, and (c) PANI salt E-2 in  $\text{CHCl}_3$ .

430, and 800 nm [Fig. 4(c)], which indicated the presence of the salt. This result indicated that the PANI salt was soluble in  $\text{CHCl}_3$ . However, the PANI salt was slightly soluble in DMF, which appeared blue, and the corresponding electronic absorption spectrum showed two peaks at 325 and 615 nm [Fig. 4(a)], which indicated the presence of the PANI base. This result indicated that the PANI salt was not soluble in DMF and that a small amount of the PANI base, present in the PANI salt, was soluble in DMF.

### Rheological properties of PANI

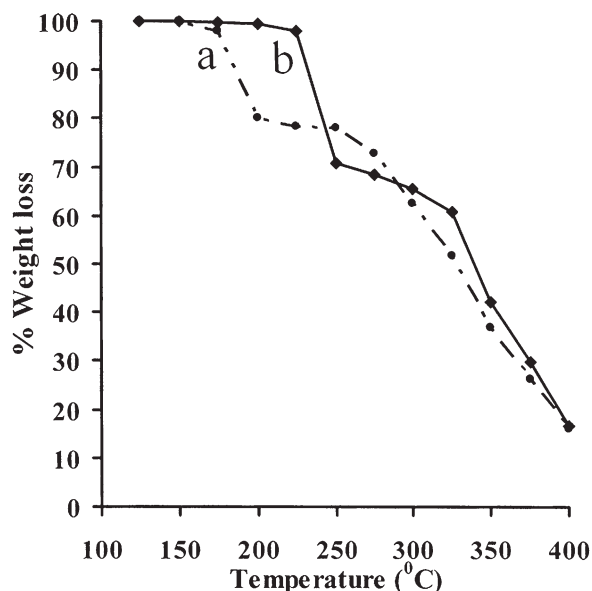
The rheological properties of PANI salt E-2 are especially important because one of its potential applications is solution blending with conventional polymers and other admixtures modifying the properties of the blends. The rheological behaviors of the polymer solutions at three different concentrations (1–3 wt % in  $\text{CHCl}_3$ ) were found to be similar. A representative example is shown in Figure 5, in which the shear viscosity is plotted against the shear rate. All the studied solutions displayed non-Newtonian behavior, which was manifested by continuous shear thinning with the shear rate increasing up to  $6.7 \text{ s}^{-1}$ . At higher rates, shear thickening was observed. Several contributions may have accounted for these non-Newtonian characteristics (i.e., viscosity changes with the shear rate), including molecular entanglement and shear-induced formation of multiple aggregates of PANI chains.



**Figure 5** Shear viscosity ( $\eta$ ) versus the shear rate ( $\gamma$ ) for a 2% solution of an emulsion-polymerized PANI (E-2) at the ambient temperature.

### Macroscale thermal studies of PANI

To accurately determine the stability of the PANI salt and its base, the thermal behavior of a polymer sample was examined by the subjection of the sample on a macroscale (1 g) to temperatures up to  $400^\circ\text{C}$  in steps of  $25^\circ\text{C}$ . The PANI salt and base contained moisture; to remove the moisture, first we heated the sample to  $125^\circ\text{C}$  and kept them at this temperature for 30 min. We took out the sample, cooled it to room temperature, and determined its weight. We kept the sample at  $150^\circ\text{C}$  for 10 min and then took out the sample, cooled it to room temperature, and weighed it. This procedure was repeated up to  $400^\circ\text{C}$  in steps of  $25^\circ\text{C}$ . The weight-loss behavior of the PANI salt and its base are shown in Figure 6. The results showed that the PANI base was



**Figure 6** Macroscale thermogravimetric analysis of (a) PANI salt E-2 and (b) its base.

stable up to 225°C, which was higher than that of the PANI salt (175°C).

### CONCLUSIONS

We developed a cheaper and direct one-step emulsion polymerization pathway for preparing a PANI salt containing a plast dopant with an ordered, layer-type supramolecular structure with a reasonable yield (59.7%), conductivity (0.25 S/cm), and stability (up to 175°C). A PANI salt powder prepared by the emulsion polymerization pathway showed excellent solution-processing properties. A PANI salt containing a plast dopant may be useful for making, by a simple solution-processing technique, conducting PANI blend films with a low percolation threshold due to the plast dopant group (the plasticizer present on the PANI salt, which has a plasticizing effect during the manufacturing of polymer blend films).

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