

# Melt/Solution Processable Polyaniline with Functionalized Phosphate Ester Dopants and Its Thermoplastic Blends

RAJI K. PAUL, C. K. S. PILLAI

Regional Research Laboratory (CSIR), Thiruvananthapuram – 695 019, India

Received 10 November 1999; accepted 2 May 2000

**ABSTRACT:** Polyaniline (PANI) was doped with five novel dopants, 3-pentadecylphenylphosphoric acid (PDPPA), pentadecylphenyl(bis)phosphoric acid [PDP(bis)PA], monocardanylphosphoric acid (MCPA), dicardanylphosphoric acid (DCPA), and phosphorylated cashew nut shell liquid prepolymer (PCNSL) and the doping behavior was studied. All dopants were synthesized from inexpensive naturally existing monomers [obtained from cashew nut shell liquid (CNSL)] having a long hydrophobic hydrocarbon side chain in the *meta* position of the aromatic ring. These dopants can act as plasticizing *cum* protonating agents for PANI so that free-standing films of PANI could be prepared by both thermal processing and solution processing techniques. Protonation was performed either by mechanical mixing of emeraldine base and the dopant or by an *in situ* doping emulsion polymerization route using xylene or chloroform as the solvent. Further, conductive flexible blends of the protonated PANI with poly(vinyl chloride) (PVC) were also prepared and studied for their conductivity and related properties. The PANI–PDPPA complex obtained by the *in situ* doping emulsion polymerization route exhibited an exceptionally high degree of crystalline order and orientation. A maximum conductivity value of  $1.8 \text{ S cm}^{-1}$  was obtained for a PANI–PDPPA film hot-pressed at  $120^\circ\text{C}$ . On the other hand, dopants based on cardanol having an unsaturated side chain gave only lower values. This was understood to be due the capability of the saturated analog to contribute to the ordered arrangement of PANI, thus improving the crystallinity. The conductivity values further decreased when bulky/oligomeric dopants such as PCNSL were used. The thermoplastic blends with PVC exhibited an exceptionally low-level percolation threshold because of the plasticizing nature of the dopants. The doped polymers and blends were characterized by FTIR and UV-visible spectroscopic methods, four-probe conductivity measurements, XRD, SEM, TGA, and DSC. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 1354–1367, 2001

**Key words:** polyaniline; doping studies; phosphate ester dopants; melt/solution processability; thermoplastic blends

## INTRODUCTION

Since the discovery of conducting polyacetylene films in 1977,<sup>1</sup> there has been substantial interest in scientific and engineering communities in

understanding intrinsically conductive polymers (ICPs) and finding applications for their unique properties.<sup>2</sup> The most common ICPs of current interest are polyaniline, polypyrrole, polythiophene, polyacetylene, poly(*p*-phenylene), and poly(*p*-phenylene sulfide). Since the backbone of these polymers contains conjugated double bonds, they exhibit extraordinary electronic properties such as a low ionization potential

---

Correspondence to: C. K. S. Pillai.

*Journal of Applied Polymer Science*, Vol. 80, 1354–1367 (2001)  
© 2001 John Wiley & Sons, Inc.

and a high electron affinity and, as a result, can be easily reduced or oxidized. These polymers undergo "doping" upon exposure to a protonic acid and become electrically conductive.<sup>3</sup> Unfortunately, these polymers are highly intractable and infusible because of their highly aromatic nature, interchain hydrogen bondings, and charge delocalization effects. So, one of the main present research areas, of both scientific and industrial importance, has been to develop electrically conductive polymers which are fusible or soluble in common solvents. Over the last decade, significant progress has been made in the processing of ICPs into coatings and films.

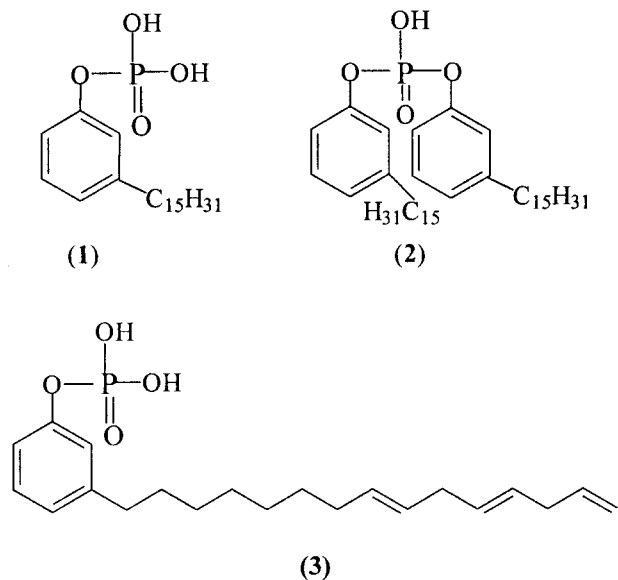
Polyaniline (PANI), the most promising conductive polymer, has been the subject of intense investigations during the last two decades because of its straightforward polymerization and desirable electrical, electrochemical, and optical properties coupled with excellent environmental stability.<sup>4-6</sup> Being inexpensive and relatively simple to synthesize, it has immense industrial potential for a number of applications such as in static films for transparent packaging of electronic components, electromagnetic shielding, rechargeable batteries, light-emitting diodes, nonlinear optical devices, sensors for medicine and pharmaceuticals, and membranes for the separation of gas mixtures.<sup>7-9</sup>

However, PANI is highly intractable because of its aromatic nature, interchain hydrogen bonding, and charge delocalization effects.<sup>10</sup> Among the methods to improve the melt and solution processability of PANI, covalent substitution such as ring substitution<sup>11-13</sup> and *N*-alkylation<sup>14-16</sup> and protonation with functionalized protonic acids such as dodecylbenzene sulfonic acid,<sup>17,18</sup> camphor sulfonic acid,<sup>19</sup> phosphoric acid esters,<sup>20-24</sup> or phosphonic acids<sup>25</sup> merit mention. The use of specific functionalized protonic acid dopants render the high solubility of PANI into particular common solvents<sup>19</sup> and allow the preparation of solution-cast<sup>26</sup> or melt-processable blends with a low percolation limit.<sup>27,28</sup> But according Laaska et al.,<sup>29</sup> the selection of an appropriate solvent is of crucial importance for electrical conductivity of solution-cast PANI films. For example, PANI protonated with camphor sulfonic acid, in selected solvents, such as *m*-cresol, induce extended coil conformation of PANI chains which facilitate polaron delocalization and crystallization of the polymer upon casting.<sup>29</sup> From the in-

dustrial point of view, the fabrication of a thermally processable conducting polymer would be preferable because it is easier and much cheaper. Thermally processable PANI has recently been fabricated using aliphatic and aromatic diesters of phosphoric acid as protonating agents,<sup>20-24,29</sup> where the two hydrophobic groups introduced to PANI with each dopant ion lead to its plastification. In a previous communication,<sup>30</sup> we showed that protonation of PANI with a dopant, 3-pentadecylphenylphosphoric acid, induces melt and solution processability to PANI.

To improve the mechanical properties of PANI, one of the methods still in the development stage is the blending of it with conventional polymers because there is an increasing demand for polymeric materials that can be processed using conventional melt-processing techniques, whose electrical conductivity can be tailored for a given application and that have attractive mechanical and other properties<sup>31</sup> of the two components, that is, high electrical conductivities of PANI together with the physical and mechanical properties of the matrix polymer. The applications include electrostatic dissipation (ESD), static discharge, and electromagnetic interference shielding (EMI). The required conductivity levels are approximately  $10^{-5}$  to  $10^{-9}$  S cm<sup>-1</sup> for ESD and greater than 1 S cm<sup>-1</sup> for EMI. Several conductive composites of PANI with vinyl polymers such as polystyrene,<sup>32</sup> poly(alkyl methacrylates),<sup>33-36</sup> poly(vinyl chloride) (PVC),<sup>20,21,37-40</sup> and poly(ethylene-co-vinyl acetate)<sup>41</sup> were reported in the literature. There exists a great demand for flexible, conductive plastic films fabricated on the basis of plasticized PVC.

This article presents the results of studies on the doping behavior of a series of phosphoric acid derivatives of 3-pentadecylphenol (hydrogenated cardanol) and 3-pentadecadienylphenol (cardanol) such as 3-pentadecylphenylphosphoric acid (PDPPA) (**1**), 3-pentadecylphenyl(bis)phosphoric acid [PDP(bis)PA] (**2**), monocardanylphosphoric acid (MCPA) (**3**), dicardanylphosphoric acid (DCPA), and phosphorylated cashewnut shell liquid prepolymer (PCNSL) on PANI. Further, conductive flexible blends of the protonated PANI with PVC were also prepared and studied for their conductivity and related properties. The conductive blends exhibited a comparatively low percolation threshold and a high transparency:



## EXPERIMENTAL

### Preparation of Poly(emeraldine base)

PANI was synthesized chemically according to the method of MacDiarmid et al.<sup>42</sup> The neutral base form of PANI was obtained by dedoping the PANI-salt in a 3 wt % ammonia solution for 3 h, then washing with acetone and drying in a vacuum for 8 h at 60°C.

### Synthesis of PDPPA

PDPPA was synthesized by the reaction of 1 mol of 3-pentadecyl phenol (hydrogenated cardanol) and 1 mol of POCl<sub>3</sub> in the presence of AlCl<sub>3</sub>.<sup>43</sup> The product, phosphorodichloridate, obtained was then hydrolyzed with diluted HCl and then purified by column chromatography over silica gel (100–200 mesh). The phosphorous content analysis is in agreement with the proposed structure.

### Synthesis of MCPA

MCPA was synthesized by a similar procedure as that of PDPPA.

### Synthesis of PDP(bis)PA

PDP(bis)PA was synthesized by the reaction of 2 mol of 3-pentadecyl phenol and 1 mol of POCl<sub>3</sub> in the presence of AlCl<sub>3</sub>. The product obtained was then hydrolyzed with diluted HCl and then purified by column chromatography over silica gel (100–200 mesh). The phosphorous content anal-

ysis indicates the presence of 15–20% of the monoester.

### Synthesis of DCPA

DCPA was synthesized by a similar procedure as that of PDP(bis)PA.

### Synthesis of PCNSL

PCNSL was synthesized by phosphorylating preheated CNSL with *o*-phosphoric acid at 175 ± 5°C for 4 h according to a patented process.<sup>44</sup>

### Preparation of PANI-Dopant Complex

#### Emulsion Polymerization

Doping of PANI was carried out by the *in situ* doping emulsion polymerization of aniline in the presence of the dopant PDPPA (1:1 molar ratio of aniline and the dopant) or PDP(bis)PA (1:0.75 molar ratio of aniline and the dopant) in xylene as the solvent according to the procedure of Osterholm et al.<sup>18</sup> Polymerization was initiated by the addition of ammonium peroxy disulfate, (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, in distilled water which was added over a period of 30 min to avoid heating of the reaction mixture. The emulsion was then kept under stirring for 24 h and the polymerization was terminated by pouring the resulting highly viscous emulsion into 750 mL of acetone, causing the doped PANI complex to precipitate. The dark green powder was then recovered, filtered, and extensively washed with acetone and distilled water in order to remove the unreacted dopant and trace amounts of inorganic by-products present. Finally, the powder was dried in a vacuum oven for 48 h at 55°C. Polymerization was carried out at room temperature in order to avoid the precipitation of anilinium phosphate. The aniline-to-oxidant molar ratio was 1:1. The aniline monomer concentration was 0.05 mol/L.

The polymers obtained by this emulsion polymerization method are hereinafter referred to as PANI-PDPPA 1 and PANI-PDP(bis)PA 1. The protonated complexes obtained were converted to the emeraldine base form by treatment with a 3 wt % ammonia solution for 3 h, then washed with acetone and dried in a vacuum for 8 h at 60°C.

#### Mechanical Mixing

Emeraldine base (synthesized by the aqueous polymerization method) of an inherent viscosity 1.2 dL g<sup>-1</sup> (measured at room temperature in concen-

trated sulfuric acid) was mixed with the dopant PDPPA, PDP(bis)PA, MCPA, DCPA, or PCNSL in a molar ratio of 0.5 dopant to the polymer repeat unit PhN, using an agate mortar and pestle at room temperature to obtain PANI–PDPPA **2**, PANI–PDP(bis)PA **2**, PANI–MCPA **2**, PANI–DCPA **2**, or PANI–PCNSL **2**, respectively. Different molar ratios of the PANI–dopant combination were prepared to determine the plastification threshold.

### Characterization Methods

The inherent viscosities of PANI and PANI–dopant systems were determined in 0.1% w/w solutions in concentrated H<sub>2</sub>SO<sub>4</sub> using an Ubbelohde viscometer at 25°C. The phosphorus content was determined by the stannous chloride method.<sup>45</sup> FTIR spectra were recorded on a Nicolet IMPACT 400 D spectrophotometer. The UV-visible spectrum was taken in a Shimadzu UV-2100 spectrophotometer. Conductivity was measured on pressed pellets by the four-probe method. The XRD pattern was recorded on a Rigaku Geiger–Flex D/MAX series using CuK $\alpha$  radiation. SEM was recorded using a JEOL JSM-35 scanning microscope. TG thermograms were recorded on a DuPont thermogravimetric analyzer 951 attached to a thermal analyst 200. DSC thermograms were taken on a differential scanning calorimeter 2010 attached to a thermal analyst 2100.

## RESULTS AND DISCUSSION

### General Observations

As reported in the case of the PANI–dodecyl benzene sulfonic acid system,<sup>18</sup> PDPPA and PDP(bis)PA were also found to act as emulsifying *cum* protonating agents for PANI. The hydrophobic–hydrophilic nature of these dopants permits it to act as an emulsifying *cum* protonating agent. The *in situ* doping emulsion-polymerized PANI–PDPPA **1** and PANI–PDP(bis)PA **1** typically had the composition PANI(PDPPA)<sub>0.2</sub> and PANI(PDP(bis)PA)<sub>0.19</sub>, respectively, as determined from the observed weight differences between the as-polymerized complex and the corresponding reduced emeraldine base and also by the phosphorous content estimation. [It should be noted here that because of the extremely bulky nature of PDP(bis)PA, and also due to the precipitation of ani-

linium phosphate, we are took a 1:0.75 molar ratio of aniline and PDP(bis)PA for the emulsion polymerization.] This indicates that some deprotonation occurred during the washing procedure of the PANI–ester complex. PANI is almost fully protonated at this level for PANI–PDPPA **1** as PDPPA has two hydrogens for protonation, but the protonation level is comparatively less for PANI–PDP(bis)PA **1**. Protonation of PANI with PDPPA and PDP(bis)PA results in a heavily plasticized mixture which can be thermally processed to give free-standing films.

### Solubility Studies

A number of interesting observations were made on doping PANI with PDPPA and PDP(bis)PA: As reported in the cases of doping PANI with functionalized dopants, the protonated PANI becomes soluble in nonpolar or weakly polar organic solvents such as xylene, chloroform, and tetrahydrofuran (THF). Thin films of the doped polymer could be easily prepared by the solution-casting method from these solvents. It should be pointed out here that the solubility theory of Heeger and others<sup>16–19,26,27</sup> was criticized by Wessling<sup>46,47</sup> in that conductive polymers cannot form true solutions. In the case of the PANI–PDPPA **2** system, we got transparent and clear solutions, the formation of which is aided by the surfactant-type counterions of the bulky phosphoric acid moieties located at the particle surface with their unpolar tail directed to the outside, inducing PANI to behave as a random coil, enabling solubility. Table I indicates the solubility of PANI–PDPPA **2** (1:0.5 molar ratio) and PANI–PDP(bis)PA **2** (1:0.5 molar ratio) in some of the organic solvents and the conductivity of the films cast from the corresponding solutions. The solubility of the complex in nonpolar or weakly polar organic solvents can be explained on the basis of the solvation effects of the long hydrophobic alkyl side chain of the dopant. There is no considerable change for the solubility of each system from different solvents.

### Viscosity Studies

The inherent viscosity of emeraldine base synthesized by aqueous polymerization was found to be 1.2 dL g<sup>-1</sup>, whereas those obtained for PANI–PDPPA **1** and PANI–PDP(bis)PA **1** were 0.85 and 0.88 dL g<sup>-1</sup>, respectively, and for the corresponding PANI bases, 1.25 and 1.31 dL g<sup>-1</sup>, respectively. Aqueous polymerization of aniline is gen-

**Table I** Percentage of Solubility of PANI-PDPPA **2** and PANI-PDP(bis)PA **2** in Some of the Organic Solvents and the Conductivity of the Films Cast from the Corresponding Solutions

Polymer	Solvent	% Solubility	Conductivity (S cm <sup>-1</sup> )
PANI(PDPPA) <sub>0.5</sub>	Chloroform	2-3	0.39
	Xylene	2-3	0.82
	Tetrahydrofuran	2	0.19
	<i>m</i> -Cresol	2	1.25
PANI(PDP(bis)PA) <sub>0.5</sub>	Chloroform	6-7	0.021
	Xylene	6-7	0.055
	Tetrahydrofuran	6	0.08
	<i>m</i> -Cresol	5	0.13

erally carried out at 0°C to obtain the maximum molecular weight.<sup>42</sup> But the complexes PANI-PDPPA **1** and PANI-PDP(bis)PA **1** synthesized by the *in situ* doping emulsion polymerization route could not be carried out at 0°C because anilinium phosphate precipitates at this temperature. So, polymerization was carried out at ambient temperature and this could be the reason why the higher viscosity expected of an emulsion polymerization was not obtained. But the inherent viscosity values of the PANI base synthesized by the emulsion polymerization method significantly exceeded the viscosities normally observed for the PANI base polymerized in aqueous solutions. The value is slightly increased for PANI-PDP(bis)PA **1** because of the bulky nature of the dopant, where the use of bulky PDP(bis)PA as a counterion increases the chain separation between adjacent PANI chains and, consequently, decreases the interchain interactions. An increased solubility of the growing chains in the emulsion is thus to be expected, leading to the observed increase in viscosity.<sup>18</sup>

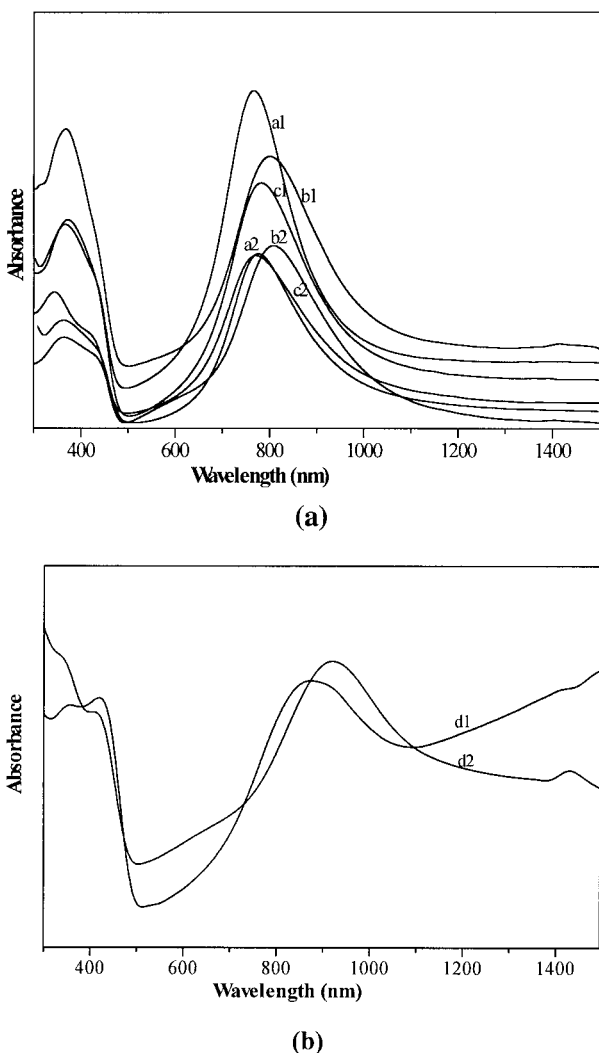
In the case of the systems PANI-PDPPA **2** and the PANI-PDP(bis)PA **2**, the plasticized PANI exhibits rheological parameters characteristic of a Bingham-type liquid with the apparent viscosity decreasing with increase of the ester content. The plastification threshold was found to occur at ester/PANI molar ratios of 0.3 and 0.15 for PANI-PDPPA **2** and the PANI-PDP(bis)PA **2**, respectively. It was, however, noted that the emulsion-polymerized PANI-PDPPA **1** is not thermally processable because the molar ratio of aniline and PDPPA is 1:0.2. But PANI-PDP(bis)PA **1** is thermally processable, even though the film obtained by the hot-pressing method is very brittle.

### Spectroscopic Investigations

The FTIR spectra taken for PANI-PDPPA and PANI-PDP(bis)PA complexes have features characteristic of the protonated state. The band at 1160 cm<sup>-1</sup>, assigned to Q=N-B, B-NH-B, or the C-H bending coupled to the carbon backbone of emeraldine base, shifts to 1128 cm<sup>-1</sup> for PANI-PDPPA **1** and to 1135 cm<sup>-1</sup> for PANI-PDP(bis)PA **1** on protonation. Upon protonation, a very broad absorption appears at 3450 cm<sup>-1</sup> (O-H stretch) and the 3285 cm<sup>-1</sup> band (N-H stretch) of poly(emeraldine base) shifts downward to 3230 cm<sup>-1</sup>.

Similarly, the bands corresponding to the quinoid (N=Q=N), 1593 cm<sup>-1</sup>, and benzenoid (N-B-N), 1506 cm<sup>-1</sup>, ring-stretching modes of polyemeraldine base are shifted toward lower frequencies, namely, 1566 and 1480 cm<sup>-1</sup>, respectively, for PANI-PDPPA and to 1573 and 1490 cm<sup>-1</sup>, respectively, for PANI-PDP(bis)PA. This 1590/1490-cm<sup>-1</sup> band intensity ratio is comparatively smaller for the PANI-PDP(bis)PA and it shows that the degree of protonation is comparatively less for the diester protonated PANI because of the bulky nature of the dopant, which hinders its easy diffusion into the polymer backbone. Also, for the protonated samples, new absorptions appear at about 880 and 810 cm<sup>-1</sup>. The P=O stretching mode occurring at 1248 cm<sup>-1</sup> is superimposed on the B-B-B stretching of PANI occurring at 1238 cm<sup>-1</sup>. Also, the features characteristic of the dopant were also present.

Figure 1(a) shows the UV-visible spectrum of PANI-PDPPA and the PANI-PDP(bis)PA complexes in the solvents THF, chloroform, and xylene. Figure 1(b) shows the UV-visible spectrum of PANI-PDPPA and the PANI-PDP(bis)PA complexes in *m*-cresol. The spectrum gives strong ev-



**Figure 1** (a) UV-vis spectra of PANI-PDPPA in (a1) xylene, (b1) THF, and (c1) chloroform and PANI-PDP(bis)PA in (a2) xylene, (b2) THF, and (c1) chloroform. (b) UV-vis spectra of (d1) PANI-PDPPA in *m*-cresol and (d2) PANI-PDP(bis)PA in *m*-cresol.

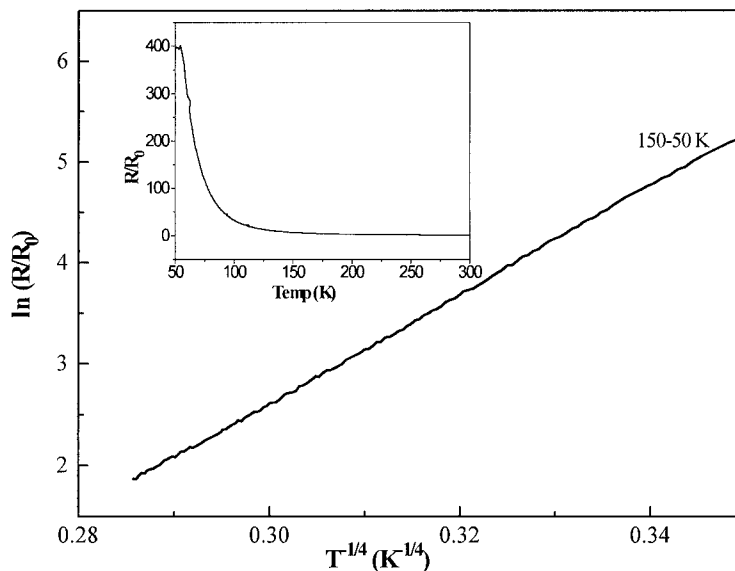
idence for the protonation of PANI as seen from the bands at about 444 and 801 nm in these solvents, where the spectrum is almost the same for both PANI-PDPPA and PANI-PDP(bis)PA. For PANI-PDPPA in *m*-cresol, a sharp polaronic peak at about 444 nm and a broad band extending beyond 1500 nm occurs. But the peaks characteristic of a localized polaron at about 900 nm were present. The thin film of PANI-PDPPA cast from *m*-cresol exhibited a conductivity of  $2.1 \text{ S cm}^{-1}$ . But the UV-visible spectrum of PANI-PDP(bis)PA in *m*-cresol exhibited spectral features resembling those characteristic of a localized polaron at about 900 nm and a less intense

broad band extending beyond 1500 nm. The film of PANI-PDP(bis)PA cast from *m*-cresol exhibited a conductivity value of  $8.2 \times 10^{-2} \text{ S cm}^{-1}$  and this indicates that PDPPA in *m*-cresol succeeded in partially changing the conformation of the PANI chains to the extended coil confirmation, but PDP(bis)PA showed a weak effect because of its extremely high bulky nature even though PDP(bis)PA succeeded to make PANI highly soluble in almost all the weakly polar or nonpolar solvents. The IR and UV-visible spectra of the other PANI-dopant complexes also showed similar behavior.

### Conductivity Studies

The conductivity values were measured on pressed pellets for the powder samples by the four-probe method. PANI-PDPPA **1** gave a higher conductivity value of  $6.1 \times 10^{-1} \text{ S cm}^{-1}$  compared to PANI-PDP(bis)PA **1** ( $5.1 \times 10^{-2} \text{ S cm}^{-1}$ ) and these values are higher than are those of the mechanically mixed samples PANI-PDPPA **2** of a 1:0.5 molar ratio ( $2.41 \times 10^{-1} \text{ S cm}^{-1}$ ) and PANI-PDP(bis)PA **2** of a 1:0.5 molar ratio ( $2.1 \times 10^{-2}$ ). [Detailed studies were conducted only on the PANI-PDPPA and PANI-PDP(bis)PA systems.] The higher conductivity value of the emulsion-polymerized samples compared to that of the mechanically mixed samples may be due to the more homogeneous protonation of PANI achieved by the emulsion technique. Table I indicates the solubility of PANI-PDPPA **2** (1:0.5 molar ratio) and PANI-PDP(bis)PA **2** (1:0.5 molar ratio) in some of the organic solvents and the conductivity of the films cast from the corresponding solutions. (The solubilities of the other PANI-dopant complexes did not differ much and, hence, are not shown here.) The conductivity value is comparatively lower for the solution-cast films of PANI-PDP(bis)PA **2** because of the bulky nature of the dopant, which hinders its easy diffusion into the polymer backbone. For each dopant system, there is no considerable change for the conductivity of films cast from different solvents, except for PANI-PDPPA in *m*-cresol, where the conductivity value is  $2.1 \text{ S cm}^{-1}$  (increase of one order of magnitude), indicating the secondary doping effect.

Figure 2 represents a plot of the  $\ln$  of the normalized resistance versus  $T^{-1/4}$  for PANI-PDPPA **2** (1:0.5), which shows that the  $\ln$  of the normalized resistance is proportional to  $T^{-1/4}$  in the temperature range 150–50 K, which is indicative of three-dimensional variable range hopping conduction. Normalized resistance on pressed pel-



**Figure 2** Plot of  $\ln$  resistance versus  $T^{-1/4}$  of PANI-PDPPA **2**. The normalized resistance-temperature plot is shown in the inset.

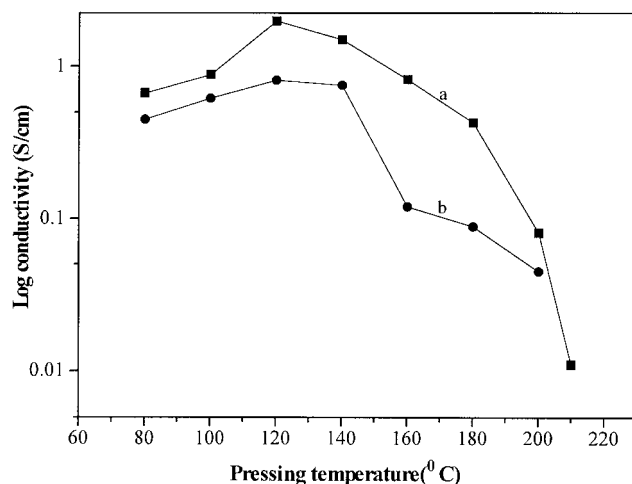
lets, measured in the temperature range 300–50 K, is shown in the inset of Figure 2. The data are analyzed in the Mott's variable range hopping conduction in three dimensions in the temperature range 150–50 K.

Doping of PANI with the dopants PDPPA, PDP(bis)PA, MCPA, DCPA, and PCNSL results in a heavily plasticized mixture so that free-standing flexible films could be prepared by the hot-pressing method. Figure 3(a) represents the conductivity against the temperature of pressing for PANI-PDPPA **2** (1:0.3 molar ratio) and PANI-PDP(bis)PA **2** (1:0.3 molar ratio). A maximum conductivity value of  $1.8 \text{ S cm}^{-1}$  was obtained for the PANI-PDPPA **2** film pressed at  $120^\circ\text{C}$ , and for the PANI-PDP(bis)PA **2** film at  $120^\circ\text{C}$ , the conductivity value is  $6.1 \times 10^{-1} \text{ S cm}^{-1}$ . Both polymers are thermally stable to  $200^\circ\text{C}$  for preparing highly conducting films by melt processing. The comparatively low value of conductivity for these phosphate ester systems in comparison to other PANI-phosphate ester<sup>20–25</sup> systems may be due to the bulky nature of the dopant species which hinders its easy diffusion into the polymer backbone,<sup>48</sup> and in the PANI-PDPPA system, due to the divalent nature of the phosphate ions, there is also a possibility of crosslinking between the chains or intrachain sharing of the same dopant species which results in a hindrance to electron transport.<sup>48</sup> Figure 3(b) represents the conductivity against the temperature of pressing for PANI-MCPA (1:0.3 molar ratio) and PANI-DCPA (1:0.3

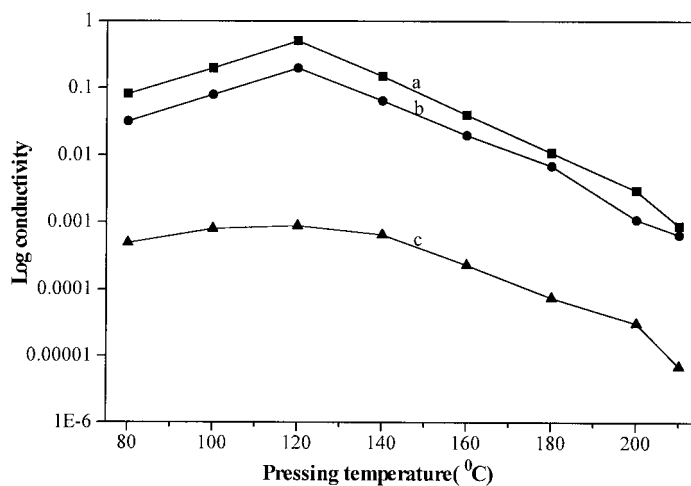
molar ratio). But the conductivity values are less for PANI-MCPA, PANI-DCPA, and PANI-PCNSL when compared to PANI-PDPPA and PANI-PDP(bis)PA because the crystallinity of protonated PANI is less when doped with the dopants synthesized from unsaturated cardanol than from the dopants synthesized from hydrogenated cardanol.

### Morphology and Crystallinity

This difference in the behavior between the mechanically mixed sample and the emulsion-polymerized sample could also be observed in the cases of morphology and crystallinity as well. The PANI-PDPPA **1** synthesized by the emulsion polymerization route showed an exceptionally high degree of crystalline order and orientation. The X-ray analysis shown in Figure 4 suggests that PANI-PDPPA **1** is highly crystalline compared to PANI-PDP(bis)PA **1**. An ordered structure occurs in the case of PANI-PDPPA **1**, but PANI-PDP(bis)PA **1** is less crystalline in nature because of the extremely bulky nature of the dopant which hinders its easy diffusion into the polymer backbone. The emulsion-polymerized PANI-PDPPA is highly crystalline in nature and this can be understood on the basis of a more homogeneous protonation of PANI by the emulsion polymerization route. The crystalline structure of PDPPA was retained in the case of the mechanically mixed PANI-PDPPA samples, whereas the peaks



(a)



(b)

**Figure 3** (a) Conductivity versus pressing temperature for films of (a) PANI-PDPPA **2** (1: 0.3 molar ratio) and (b) PANI-PDP(bis)PA **2** (1: 0.3 molar ratio). (b) Conductivity versus pressing temperature for (a) PANI-MCPA **2**, (b) PANI-DCPA **2**, and (c) PANI-PCNSL **2**.

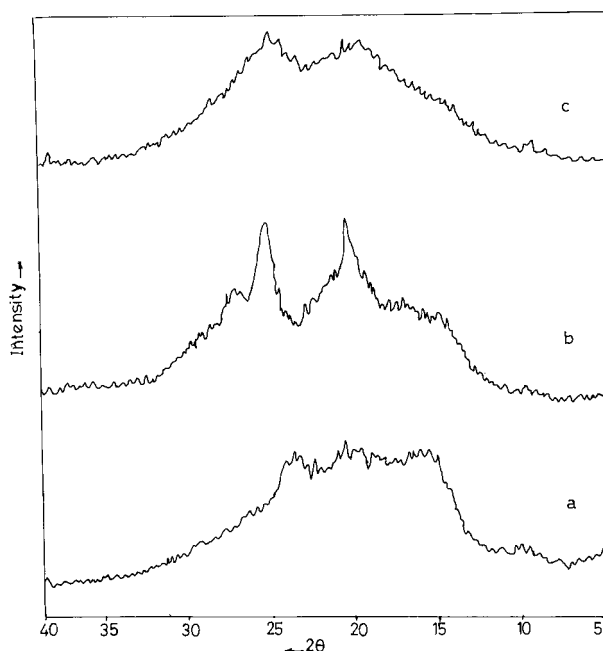
due to PDPPA were not observed in the case of the emulsion-polymerized samples. The X-ray diffraction of PANI-MCPA **2**, PANI-DCPA **2**, and PANI-PCNSL **2** showed that they are less crystalline in nature than is the PANI-PDPPA **2** complex. The presence of the unsaturated side chain might possibly be the reason for the low crystallinity of the dopants. The bulky and oligomeric nature of PCNSL might further decrease the crystallinity and conductivity.

Scanning electron micrographs of PANI-PDPPA **2** and PANI-PDP(bis)PA **2** above the plastication threshold and PANI-PDPPA film at 120°C are shown in Figure 5. Also, it indicates

that the nonplasticized samples consist of loosely packed distinguishable grains. Above the plastication threshold, the PANI grains are smooth, swollen, and continuous in nature which upon hot pressing gives free-standing films. Laaska et al.<sup>22</sup> also reported similar results with PANI-phosphate diester systems. The morphology of the other PANI-dopant complexes were similar in nature.

It is also interesting here to note that PANI-PDPPA **II** (1:1 molar ratio) prepared by the mechanical-mixing method when sheared on a glass plate exhibited birefringence when observed under a polarized light microscope. It is possible





**Figure 4** XRD patterns of (a) emeraldine base, (b) PANI-PDPPA **1**, and (c) PANIPDP(bis)PA **1**.

that cooperation of the stiff polymer chain and the flexible side chains of the dopant which acts as the bound solvent can induce liquid crystallinity.<sup>49</sup>

### Thermal Studies

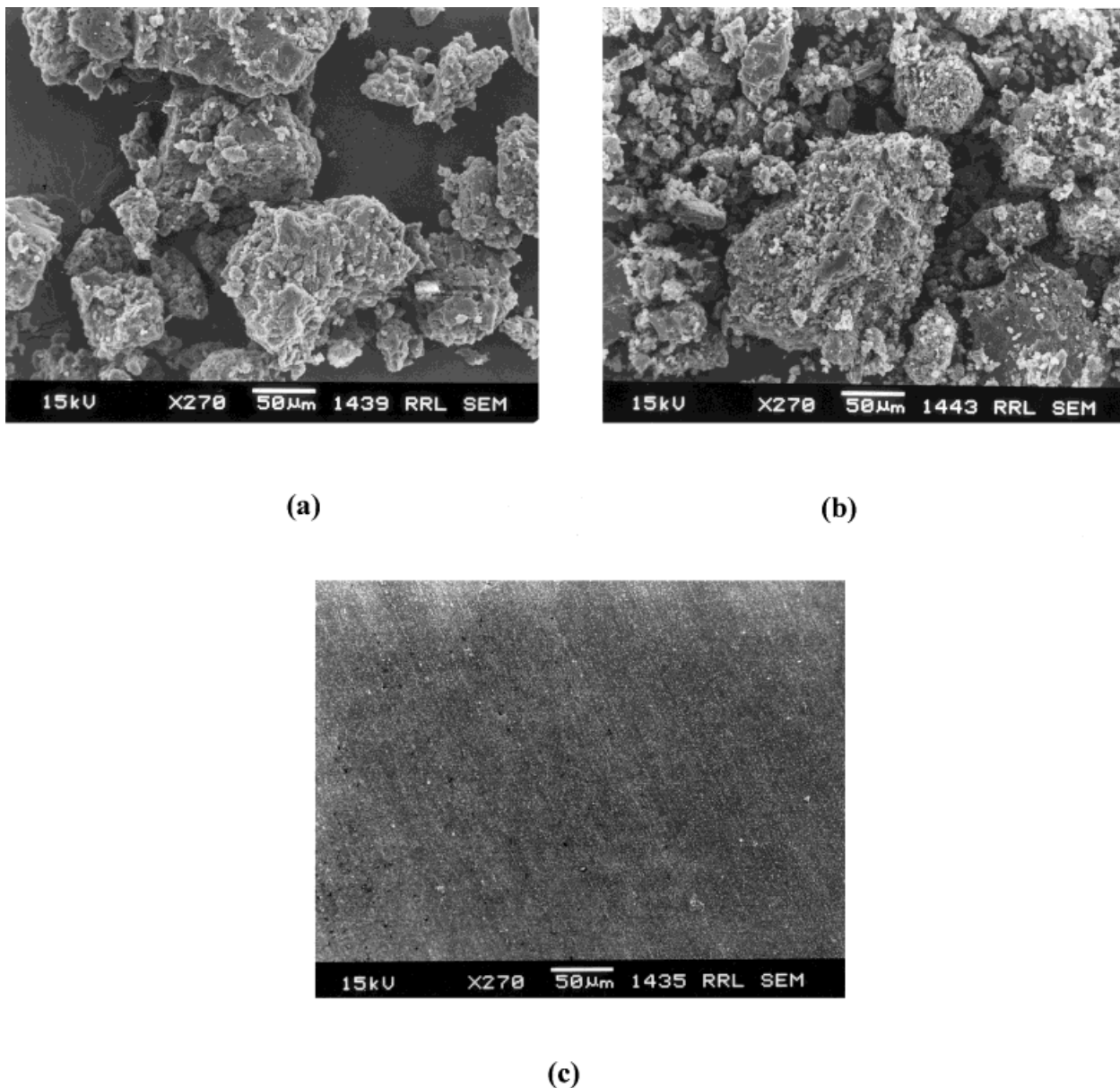
The emulsion-polymerized PANI-dopant complexes and the mechanically mixed samples differ very much in their thermal stabilities. Figure 6(a) represents the TG thermograms of PANI base, PANI-PDPPA **1**, PANI-PDP(bis)PA **1**, PANI-PDPPA **2**, PANI-PDP(bis)PA **2**, pure PDPPA, and pure PDP(bis)PA heated at 20°C/min in a nitrogen atmosphere. In the case of pure PDPPA, a small weight loss of 5% occurs between 80 and 150°C due to the loss of water molecules from the phosphate ester because phosphate esters are known to form strong intramolecular hydrogen bonds. The decomposition of PDPPA starts at about 250°C. The three PANI thermograms also exhibited a small weight loss (2–5%) below 150°C, due to the loss of water and low molecular weight oligomers. In the case of PANI-PDPPA **1**, the decomposition starts at 280°C. But in the case of PANI-PDPPA **2**, there is a two-stage decomposition starting at 240 and 350°C. The first decomposition is due to the loss of an excess of PDPPA and the second one is due to the loss of bound

PDPPA. It should be noted that the emulsion-polymerized PANI-PDPPA complex is more thermally stable than is the other reported for protonated PANIs. As there is no excess of the dopant in the emulsion-polymerized PANI-PDPPA, a single-stage decomposition was observed. Figure 6(b) represents the TG thermogram of PANI-PCNSL (1:0.3 molar ratio) compared with that of PANI base and PANI-PDPPA **2**. The thermal stability is exceptionally higher for this protonated PANI system than that of other mineral acid and functionalized acid-doped PANI. This could possibly be due to the oligomeric nature of the dopant and higher P content of the dopant, PCNSL.

In Figure 7, DSC thermograms of (a) PANI base, (b) PANI-PDPPA **1** by the emulsion polymerization route, (c) mechanically mixed PANI-PDPPA **2**, and (d) pure PDPPA in the atmosphere of nitrogen heated at 20°C/min to 500 °C are shown. The DSC curve of the pure PDPPA shows one endotherm at 70°C (due to the melting of PDPPA) and another endotherm at 120°C (due to the loss of water molecules corresponding to the small weight loss observed in the TGA. Phosphate esters can undergo dehydration at higher temperatures with the loss of water molecules). The thermograms of PANI and doped PANIs show an endotherm between 20 and 170°C corresponding to the small weight loss in TGA which is explained as due to the loss of water and oligomers. In the case of PANI-PDPPA **1**, an endotherm below 120°C is observed and this is due to the loss of water molecules. The endotherm at about 300°C is due to the loss of bound dopant. The mechanically mixed sample (PANI-PDPPA **2**) exhibits endotherms at 70 and 120°C, a broad exothermic peak which starts around 140°C and reaches a maximum around 170°C, and a double peak endotherm at about 260°C. The endothermic peaks occurring at 70°C correspond to the melting of the excess of the dopant. This double-peak endotherm is in agreement with the TGA results and it is not observed in the case of PANI-PDPPA **1** where there is no excess of the dopant. The reactions are irreversible, since in the second run, peaks are not observed.

### Blends of Plasticized PANI with PVC

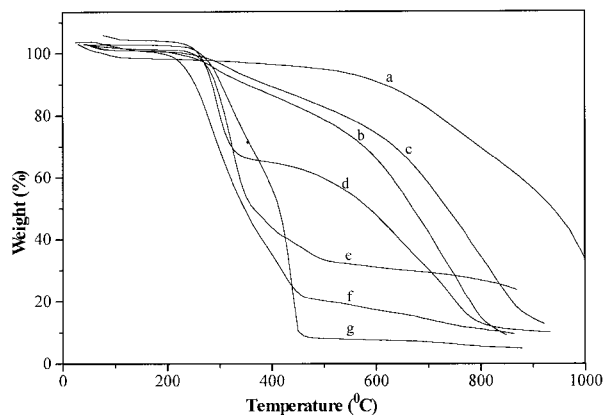
Highly conducting composites of PANI and PVC were prepared by mechanical mixing at room temperature for an extended period of time to achieve optimum homogeneity. Various PANI-(PDPPA)<sub>0.5</sub>/PVC ratios were used. Then, thin



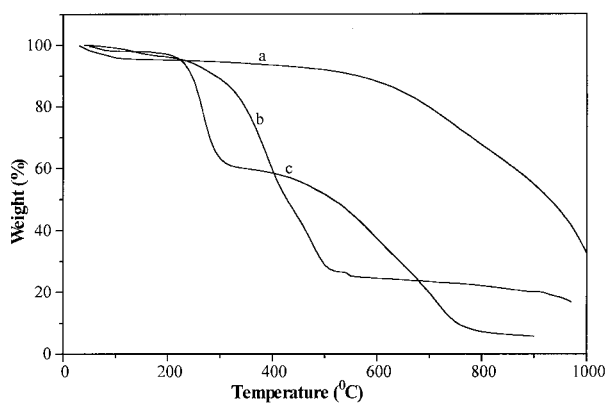
**Figure 5** SEM photographs of (a) PANI-PDPPA **2**, (b) PANI-PDP(bis)PA **2**, and (c) PANI(PDPPA)<sub>0.3</sub> film at 120°C.

films of an approximate thickness of about 0.2 mm were prepared by the hot-pressing method at 160°C for 20 min (only PDPPA was studied here as this dopant gave the maximum conductivity values). This method results in good mixing of plasticized PANI and PVC because the plastification of PANI strongly facilitates the mixing of the components of the blend, and as a result, a lower percolation threshold of 5 wt % of PANI is obtained for the polyblend of PANI-PDPPA-PVC, that is, the dispersion of PANI grains in the PVC matrix was considerably enhanced by the pres-

ence of the plasticizers, which apparently loosened the PANI grain-grain adhesion forces. The SEM indicates a good mixing of PANI and PVC. It is to be explained as being due to the flexible side chains which plasticize the PANI. Actually, the incorporation of flexible side chains to the rigid-rod backbone remarkably improves the solubility and lowers the melting or softening points for the stiff polymers.<sup>50</sup> In the case of these blends, the long side chains of the dopants could even induce molecular miscibility of the two rigid polymers. The flexible side chains acting like “bound sol-



(a)



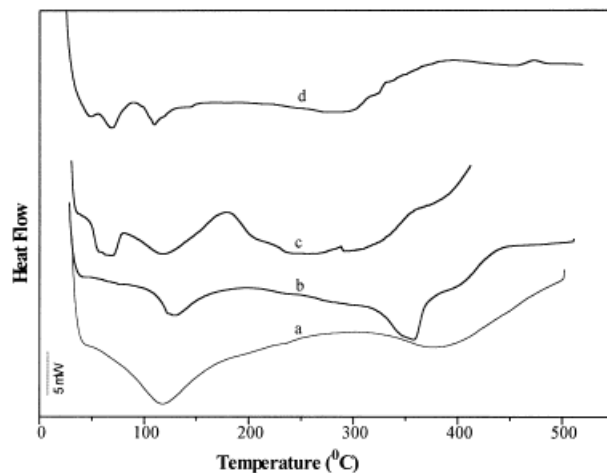
(b)

**Figure 6** (a) TG thermograms of (a) PANI base, (b) PANI-PDPPA **1**, (c) PANI-PDP(bis)PA **1**, (d) PANI-PDPPA **2**, (e) PANI-PDP(bis)PA **2**, (f) pure PDPPA, and (g) pure PDP(bis)PA heated at 20°C/min in a nitrogen atmosphere. (b) TG thermograms of (a) PANI base, (b) PANI-PCNSL, and (d) PANI-PDPPA **2**.

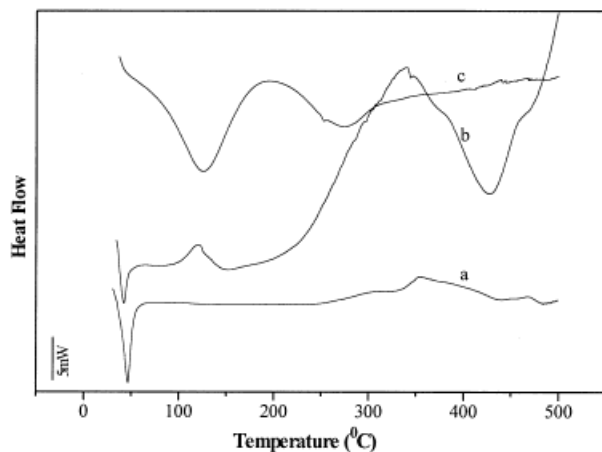
vent" induce the miscibility of rigid backbones in common solvents and also induce the distortion of aromatic rings in the backbone with an increase in the flexibility.<sup>50</sup>

The blending was performed also by a solution-mixing method where a 2 wt % solution of PANI(PDPPA)<sub>0.5</sub> was mixed with a 10 wt % solution of PVC in THF to obtain various PANI(PDPPA)<sub>0.5</sub>/PVC ratios. Thin films of approximate 0.2- $\mu$ m thickness were prepared by solution-casting techniques. Earlier patents on the preparation of melt-processable conducting thermoplastic blends used the dry mixing of a functionalized dopant protonated an electrically conducting PANI complex with the thermoplastic polymer, and a process of heat treatment of the blends before the processing to reduce the percolation threshold

was practiced.<sup>51-54</sup> Shacklette et al.<sup>55</sup> also reported the melt-mixing of protonated PANI and a thermoplastic polymer in a Brabender mixer in the presence of a plasticizer to make conducting polymer blends with a low percolation threshold. In the present case, a multifunctional dopant having the properties of plasticization, solubilization, and protonation was used to facilitate the loosening of the grain-grain adhesion forces and, hence, blends with a very low percolation threshold were obtained. Figure 8 indicates the log conductivity versus the content of PANI in both the mechanically mixed one and in the solution-mixed one. The percolation threshold occurs at about a 5 wt % of PANI content. A conductivity

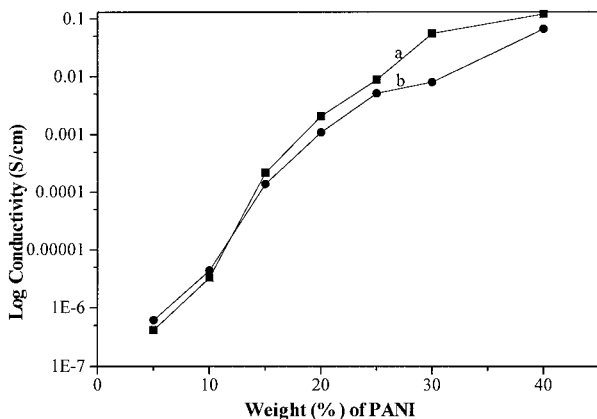


(a)



(b)

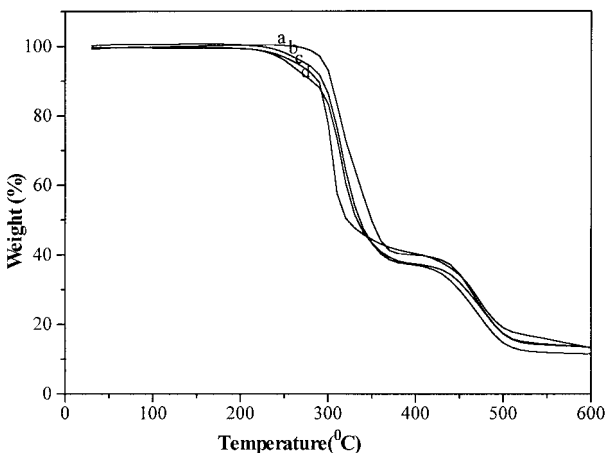
**Figure 7** (a) DSC thermograms of (a) PANI base, (b) PANI-PDPPA **1**, (c) PANI-PDPPA **2**, and (d) pure PDPPA. (b) DSC thermograms of (a) pure PDP(bis)PA, (b) PANI-PDP(bis)PA **2**, and (c) PANI-PDP(bis)PA **1**.



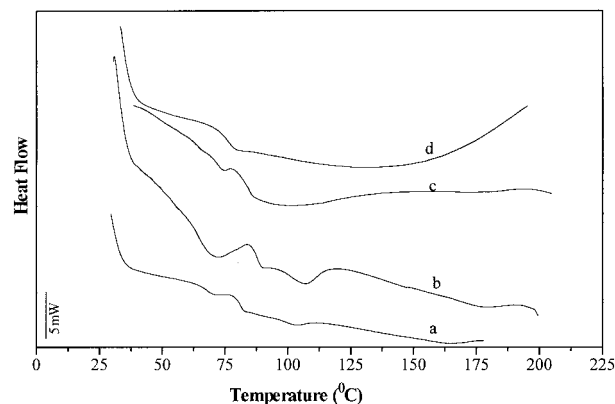
**Figure 8** Log conductivity versus PANI content for PANI-PDPPA-PVC polyblend films prepared (a) by melt-processing method and (b) by solution-mixing method.

value of  $2.5 \times 10^{-2} \text{ S cm}^{-1}$  occurs for a melt-processable film having a 30 wt % PANI content, whereas for the solution-mixed film with a 30 wt % PANI content, the conductivity value is  $3.8 \times 10^{-3} \text{ S cm}^{-1}$ . This indicates that the melt-processing method is more favorable in the case of blends of this plasticized PANI.

Figure 9 represents the TGA thermograms for PANI-PDPPA-PVC blends of different compositions. The composites are thermally stable to 250°C. Figure 10 represents the DSC thermograms of PANI-PDPPA-PVC blends. The miscibility of polymer blends is commonly ascertained through  $T_g$  measurements. The  $T_g$  increases with increasing PANI content in the blend and this



**Figure 9** TG thermograms of (a) PVC itself and PANI-PDPPA-PVC polyblend films with (b) 10 wt % of PANI, (c) 20 wt % of PANI, and (d) 30 wt % of PANI.



**Figure 10** DSC thermograms of (a) PVC itself and PANI-PDPPA-PVC polyblend with (b) 10 wt %, (c) 20 wt %, and (d) 30 wt % of PANI.

increase with the PANI content is taken to indicate the miscibility as reported by Ong et al.<sup>56</sup> Therefore, the DSC of different compositions of PANI is taken to indicate the miscibility.

## CONCLUSIONS

The dopants, PDPPA, PDP(bis)PA, MCPA, DCPA, and PCNSL, derived from an inexpensive naturally existing biomonomer, CNSL, are found to act as very good plasticizing *cum* protonating agents for PANI. Among these dopants, PDPPA, having a long saturated hydrocarbon side chain, was found to give a maximum conductivity of  $1.8 \text{ S cm}^{-1}$ . On the other hand, dopants based on cardanol having an unsaturated side chain gave only lower values. This was understood to be due to the capability of the saturated analog to contribute to the ordered arrangement of PANI, thus improving the crystallinity. It is also interesting to note that the conductivity values decreased when bulky/oligomeric dopants such as PCNSL were used. The blend of protonated PANI doped with PDPPA and PVC exhibited a low percolation threshold. Because of the high surface-to-volume ratio, these blends can be suggested for potential applications.

The authors would like to thank Prof. S. Hedge, Indian Institute of Science, Bangalore, for providing the facilities for the low-temperature conductivity measurements. Thanks are also due to Dr. Peter Koshy, RRL, for the SEM measurements and to Dr. Vijay Nair, Director, RRL, for encouragement and support.

## REFERENCES

- Chiang, C. K.; Fincher, C. R.; Park, Y. W.; Heeger, A. J.; Shirakawa, H.; Louis, E. J.; Gau, S. C.; MacDiarmid, A. G. *Phys Rev Lett* 1977, 39, 1098.
- Handbook of Conducting Polymers, Skotheim, T. A., Ed.; Marcel Dekker: New York, 1989; Vols. 1 and 11.
- Traore, M. K.; Stevenson, W. T. K.; Mc Cormic, B. J.; Dorey, R. C.; et al. *Synth Met* 1991, 40, 137.
- MacDiarmid, A. G.; Epstein, A. J. In *Science and Applications of Conducting Polymers*; Salaneck, W. R.; Clarkand, D. T.; Samuelson, E. J., Eds.; IOP: Bristol, 1991; p 117.
- Conjugated Polymer; Bredas, J. L.; Silbey, R., Eds.; Kh Academic: Dordrecht, 1991.
- Chiang, J.-C.; MacDiarmid, A. G. *Synth Met* 1986, 13, 193.
- Epstein, J.; Wand, Z. H.; Li, E. M.; MacDiramid A. G. *Phys Rev Lett* 1991, 66, 1745.
- Frommer, J. E.; Chance, R. R. In *Encyclopedia of Polymer Science and Engineering*; Mark, H. F., Ed.; Wiley: New York, 1988; Vol. 5.
- Angelopoulos, M. In *the Handbook of Conductive Polymers*, 2<sup>nd</sup> ed.; Skotheim, T.; Elsenbaumer, R.; Reynolds, Eds.; Marcel Dekker: New York, 1997.
- Vikki, T.; Pietila, L. O.; Osterholm, H.; Ahjopalo, L.; Takala, A.; Toivo, A.; Levon, K.; Passiniemi, P.; Ikkala, O. *Macromolecules* 1996, 29, 2945.
- MacDiarmid, A. G.; Epstein, A. J. *Faraday Discuss Chem Soc* 1989, 88, 317.
- D'Aprano, G.; Leclerc, M.; Zotty, G.; Schiavon, G. *Chem Mater* 1995, 7, 33.
- Wei, Y.; Focke, W. N.; Wnek, G. E.; Ray, A.; MacDiarmid, A. G. *J Phys Chem* 1989, 93, 495.
- Zheng, W.-Y.; Levon, K.; Laakso, J.; Osterholm, J.-E. *Macromolecules* 1994, 27, 7754.
- Oka, O. *Jpn Kokai Tokkyo Koho JP 95 239 207 [93 239 208]* (CIC08G73/00.17, Sept. 1993); *JP Appl* 91/19 356 509, July, 1991; *Chem Abstr* 120-135499m.
- Ma Coy, H.; Lorkovic, I. M.; Writon, M. S. *J Am Chem Soc* 1995, 117, 33.
- Cao, Y.; Smith, P.; Heeger, A. J. *Synth Met* 1992, 48, 91.
- Osterholm, J. E.; Cao, Y.; Klavetter, F.; Smith, P. *Synth Met* 1993, 55-57, 1034.
- Cao, Y.; Smith, P. *Polymer* 1993, 34, 3139.
- Laaska, J.; Pron, A.; Zagorska, M.; Lapkowski, S.; Lefrant, S. *Synth Met* 1995, 69, 113.
- Pron, A.; Laska, J.; Osterholm, J. E.; Smith, P. *Polymer* 1993, 34, 4235.
- Laaska, J.; Pron, A.; Lefrant, S. *J Polym Sci Part A Polym Chem* 1995, 33, 1437.
- Kulszewicz-Bajer, I. *Macromolecules* 1995, 28, 610.
- Kulszewicz-Bajer, I.; Sobczak, J.; Hasik, M.; Pretula, J. *Polymer* 1996, 37, 25.
- Chan, H. S. O.; Ng, S. C.; Ho, P. K. H. *Macromolecules* 1994, 27, 2159.
- Yang, Y. Cao, Y. Smith, P. Heeger, A. J. *Synth Met* 1993, 53, 293.
- Cao, Y.; Smith, P.; Heeger, A. J. *PCT Patent Application WO 22/22 911*, 1992.
- Ikkala, O. T.; Laakso, J.; Vakiparta, K.; Virtanen, E.; Ruohonen, H.; Jarvinen, H.; Taka, T.; Passiniemi, P.; Osterholm, J. E.; Cao, Y.; Andreatta, A.; Smith, P.; Heeger, A. J. *Synth Met* 1995, 69, 97.
- Pron, A.; Luzny, W.; Laaska, J. *Synth Met* 1996, 80, 191.
- Paul, R. K.; Vijayanathan, V.; Pillai, C. K. S. *Synth Met* 1999, 104, 189.
- Ikkala, O. T.; Laakso, J.; Vakiparta, K.; Virtanen, E.; Ruohonen, H.; Jarvinen, H.; Taka, T.; Passiniemi, P.; Osterholm, J. E. *Synth Met* 1995, 69, 97.
- Ruckenstein, A. E.; Yang, S. *Synth Met* 1993, 53, 283.
- Yang, Y.; Cao, Y.; Smith, P.; Heeger, A. J. *Synth Met* 1993, 53, 293.
- Subramaniam, K.; Kaiser, A. B.; Gilberd, P. W.; Liu, C. J.; Weissling, B. *Solid State Commun* 1992, 97, 235.
- Terlemezyan, L.; Mihailov, M.; Ihanov, B. *Polym J* 1995, 27, 867.
- Yang, S.; Ruckenstein, E. *Synth Met* 1993, 59, 1.
- Banerjee, P.; Mandal, B. M. *Synth Met* 1995, 74, 257.
- Subramaniam, K.; Kaiser, A. B.; Gilberd, P. W.; Liu, C. J.; Weissling, B. *J Polym Sci Polym Phys Ed* 1993, 31, 25.
- Conn, C.; Booth, N.; Unsworth, J. *Adv Mater* 1995, 7, 790.
- Roichman, Y.; Silverstein, M. S.; Siegmann, A.; Narkis, M. *J Macromol Sci Phys B* 1999, 38, 145.
- Zheng, W.; Levon, K.; Taka, T.; Laakso, J.; Osterholm, J. E. *J Polym Sci Polym Phys Ed* 1995, 33(12), 89.
- Asturias, G. E.; MacDiarmid, A. G.; McCall, R. P.; Epstein, A. J. *Synth Met* 1989, 29, E157.
- Antony, R.; Pillai, C. K. S. *J Appl Polym Sci* 1993, 49, 2129.
- Pillai, K. S.; Sudha, J. D.; Prasad, V. S.; Menon, A. R. R.; Damodaran, A. D.; Alwan, S.; Lakshmidasan, S. K.; Govindaraman, K. N. *Indian Patent* 176 069, 1988.
- Greenberg, R.; Trussel, R. R.; Clesceri, L. S. *Standard Methods for the Examination of Water and Wastewater*, 16<sup>th</sup> ed.; 1985; p 437.
- Wessling, B. In *Handbook of Nanostructured Materials and Nanotechnology*; Nalwa, E., Ed.; Academic: New York, 1999; Vol. 5, pp 501-575.
- Wessling, B. In *Handbook of Conductive Polymers*; Nalwa, E., Ed.; Wiley: New York, 1997.
- Singh, R.; Arora, V.; Tandon, R. P.; Chandra, S.; Kumar, N.; Mansingh, A. *Polymer* 1997, 38, 4897.

49. Levon, K.; Mark, H. F. *Polym Prepr* 1996, 37, 60.
50. Ballauff, M. *J Polym Sci Part B Polym Phys* 1987, 25, 739.
51. Karhu, E.; Karna, T.; Laakso, J.; Suominen, M.; Jussila, M.; Kirmanen, P. WO Patent 9 528 716, 1995.
52. Jarvinen, H.; Karna, T.; Laakso, J.; Levon, K.; Ruohonen, H.; Savolainen, E. EP Patent 668 594, 1995; JP Patent 07 258 409, 1995.
53. Karna, T.; Laakso, J.; Savolainen, E.; Levon, K. U.S. Patent 5 928 565, 1999.
54. Karhu, E.; Karna, T.; Laakso, J.; Suominen, M. FI Patent 101 075, 1998.
55. Wan, C.; Lucy, P.; Shacklette, L. W.; Han, C. C. U.S. Patent 5 908 898, 1999; WO Patent 9 941 756, 1999.
56. Ong, C. H.; Goh, S. H.; Chan, H. S. O. *Polymer* 1997, 38, 1065.