

# Electrically Conductive Semi-IPNs Based on Polyaniline and Crosslinked Polyvinylacetate

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**ABSTRACT:** Electrically conductive semi-IPNs based on polyaniline and crosslinked polyvinylacetate were prepared. Polyaniline successfully percolated through the crosslinked PVAc networks and the resulting semi-IPNs show a continuous network morphology. The conductivity of the semi-IPN increases with increasing content of polyaniline and increasing acidity used during the polymerization of the polyaniline. The conductivity of the semi-IPN is 0.13 S/cm, with the highest polyaniline content of 19.3 wt %. The depression of polyaniline with temperature change is smallest followed by the depression of semi-IPN of the polyaniline/crosslinked polyvinylacetate, which is considerably smaller than the depression of crosslinked polyvinylacetate. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 2287–2293, 2002

**Key words:** conducting polymers; crosslinking; interpenetrating networks; gel permeation chromatography

## INTRODUCTION

As an electrically conductive polymer, polyaniline (PANI) has attracted considerable interest for several decades. Tremendous research has been done to improve the conductivity and processability of PANI by forming interpenetrating polymer networks (IPNs), copolymers, composites, and blends.<sup>1–8</sup> This report concerns the synthesis and characterization of PANI/crosslinked polyvinylacetate (PVAc) semi-IPNs. PVAc was chosen specifically because its solubility parameter is close in value to that of aniline (Hildebrand parameter  $\delta$  of aniline is 21.1 MPa<sup>1/2</sup>, and  $\delta$  of PVAc is 20 MPa<sup>1/2</sup>).<sup>9</sup> The linear chain of PANI is expected to

be able to weave itself into the spaces between the crosslinked chains of PVAc. The effects of the PANI content and the acidity used during the polymerization on the room-temperature dc conductivities of the resulting PANI/crosslinked PVAc semi-IPNs are reported. The effect of the acidity used during the polymerization on the molecular weight of PANI is also reported.

## EXPERIMENTAL

### Materials

The raw materials employed and their abbreviations are listed in Table I. Vinyl acetate was distilled under nitrogen flow. Aniline, ethylene glycol dimethacrylate (EGDMA), and toluene were vacuum distilled under nitrogen flow. Ammonium persulfate, hydrochloric acid, and benzoyl peroxide (BPO) were used without further purification. All solvents were stored over 4-Å molecular sieves.

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**Table I** Materials Employed and Their Abbreviations

Abbreviation	Name and Description	Source
Vinyl acetate	Vinyl acetate (99+%)	Aldrich Chemical
EGDMA	Ethylene glycol dimethacrylate (98%)	Aldrich Chemical
Toluene	Solvent grade	Aldrich Chemical
BPO	Benzoyl peroxide (97%)	Aldrich Chemical
Aniline	Aniline (99%)	Aldrich Chemical
Ammonium persulfate	ACS reagent grade (99.99+%)	Aldrich Chemical
Hydrochloric acid	ACS reagent grade (37%)	Pharmco Products
NMP	<i>N</i> -Methyl-2-pyrrolidinone (99+%)	Aldrich Chemical

## Sample Preparation

### Preparation of Crosslinked PVAc

Purified vinyl acetate was added to a mixture of toluene, BPO initiator (2.0 wt %), and EGDMA crosslinking agent. The mixture was stirred at room temperature for 1 h, then stirred at 50°C for 30 min under nitrogen flow. The mixture was sealed and placed in an oven at 60°C for 1 day and then cured in a vacuum oven at 75°C for 2 days to remove the solvent. The product was a white, translucent solid. The molecular weight between crosslinks ( $\bar{M}_c$ ) of the crosslinked PVAc was 5000, as calculated from the stoichiometry. Linear PVAc was prepared by the same procedure shown above without adding the crosslinking agent.

### Preparation of PANI/Crosslinked PVAc Semi-IPN

The crosslinked PVAc was cut into small pieces ( $9.6 \times 8.5 \times 1.8$  mm), which were then immersed in aniline in a water bath at 50°C for about 4 h until the pieces completely absorbed all the aniline. The pieces of crosslinked PVAc swelled and became transparent when they absorbed the aniline. The aniline/crosslinked PVAc was removed and put into hydrochloric acid solutions of various concentrations (1–5M), and an aqueous solution of ammonium persulfate was added to the stirred solution at a molar ratio of 1 : 2 oxidant to aniline. The solution was stirred for 2 h at 0°C and then allowed to warm up to 23°C for 12 h. The PANI/crosslinked PVAc semi-IPN was removed from the solution and washed with ultrapure water several times, and was then dried at 80°C for 2 days. Different samples were prepared, given that the acidity used during polymerization varied from 1 to 5M.

## Characterization

### Phase Morphological Characteristics

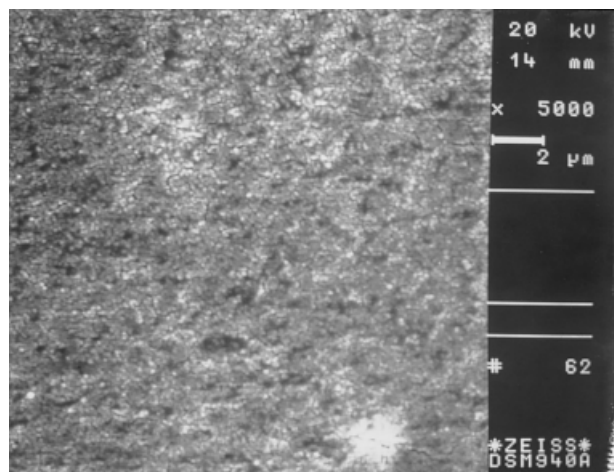
The phase morphological characteristics of the samples were studied by scanning electron microscopy (SEM). The specimens were mounted on stubs with silver paint. All the specimens for SEM were coated with platinum in a Hummer V sputter coater (SCD004; Balzers, Basel, Switzerland). They were then observed with a digital scanning microscope (DSM 940; Zeiss, Oberkochen, Germany) operating at a voltage of 20 kV. The electron images were recorded directly from the cathode ray tube on Polaroid 55 film.

### Molecular Weight

The molecular weights of PANI in PANI/crosslinked PVAc semi-IPNs were obtained by Viscotek GPC (gel permeation chromatography) with laser light scattering and T60A dual detector (Viscotek, Houston, TX) with a mobile phase of tetrahydrofuran (THF) using *N*-methyl-2-pyrrolidinone (NMP) as the solvent. The samples were filtered through a 0.2- $\mu$ m polytetrafluoroethylene filter before running through GPC. The molecular weight of linear PVAc was obtained by using THF as the solvent. Standard polystyrene was used to calibrate the dual detector before each run.

### Dc Conductivity

To measure the dc conductivity of the semi-IPN samples we prepared pellets (thickness: 1.7 to 2.3 mm), which were pressed at about 500 lb/cm<sup>2</sup>. The pellets were cut into cuboid pieces. The two opposite sides of the pellet were painted with silver paint (purchased from E. F. Fullam, Latham, NY). Silver paint was applied to minimize contact



**Figure 1** SEM micrograph of crosslinked PVAc ( $\times 5000$ ).

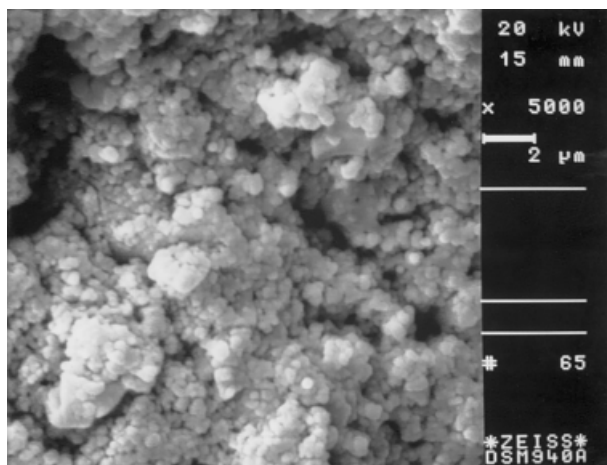
resistance between the sample and the test leads. Two pieces of copper wire were attached to each of the painted sides. The paint was dried at room temperature for 2 h. A fluke 70 series II multimeter (John Fluke Mfg. Co., Inc., Everett, WA) was used to test the resistance between the two sides by touching only the two pieces of wire for each sample. The time lag between each measurement and the next one on the same sample was 5 min. The room-temperature dc conductivity of pure PANI ( $[H^+] = 1M$ ) is 1.20 S/cm, as measured by a four-point probe technique.<sup>2</sup>

#### Thermal Mechanical Properties

Thermal mechanical properties of the samples were measured by Perkin–Elmer TMA-7 thermal mechanical analyzer (Perkin Elmer Cetus Instruments, Norwalk, CT). The samples were cut into small pieces ( $2 \times 5 \times 1.8$  mm) and then placed underneath the probe. A constant pressure of 110 mN was applied to the samples by the probe and the temperature was gradually increased to 420°C. The probe position was plotted versus temperature for semi-IPN, PANI, and crosslinked PVAc.

## RESULTS AND DISCUSSION

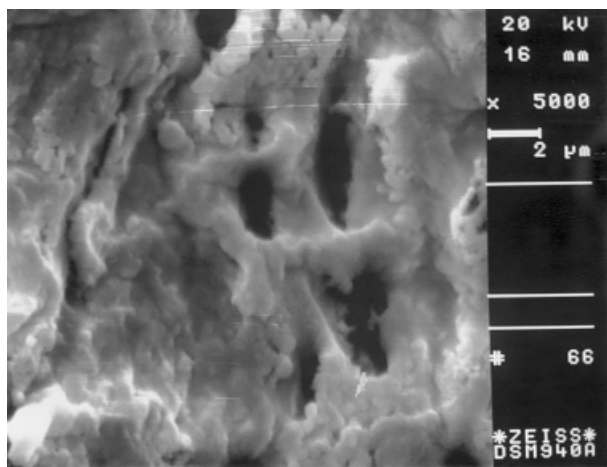
SEM micrographs of crosslinked PVAc, pure PANI, and PANI/crosslinked PVAc semi-IPN are shown in Figures 1 to 3. Compared with Figures 1 and 2, Figure 3 shows that the PANI component percolated into the crosslinked PVAc matrix and



**Figure 2** SEM micrograph of PANI ( $\times 5000$ ).

formed a continuous network morphology. This continuous network structure provides the composites electrically conducting paths. The PANI/crosslinked PVAc semi-IPNs are uniformly black-blue, which is the color of the PANI component.

The molecular weights of linear PVAc and PANI in the semi-IPNs at different acidities used during polymerization are listed in Table II. The number-average molecular weights ( $M_n$ ) of PANI in semi-IPNs increased linearly with increasing acidity used during the PANI polymerization. Given doped PANI's limited solubility in NMP, the samples were filtered through a 0.2- $\mu$ m filter to obtain the PANI/NMP solutions that were actually tested by GPC. Therefore the molecular



**Figure 3** SEM micrograph of PANI/crosslinked PVAc semi-IPN ( $\times 5000$ ). PANI : crosslinked PVAc = 1 : 4.26 (w/w).

**Table II** Molecular Weights of Linear PVAc and PANI in the Semi-IPNs

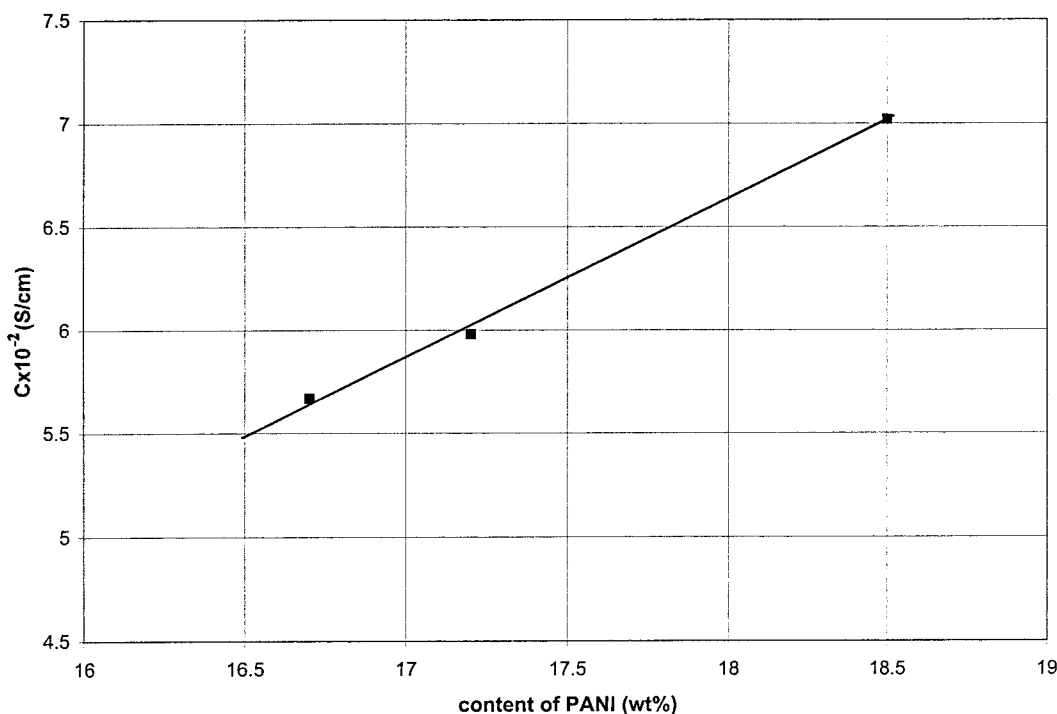
Material	$M_n$ ( $\times 10^5$ )	$M_w$ ( $\times 10^5$ )	$M_z$ ( $\times 10^5$ )
Linear PVAc	1.31	1.51	1.7
PANI in semi-IPNs (at different $[H^+]$ used during polymerization)			
$[H^+] = 1M$	2.27	2.28	2.28
$[H^+] = 2M$	3.09	3.30	3.55
$[H^+] = 3M$	4.00	4.10	4.21
$[H^+] = 4M$	4.76	4.81	4.86
$[H^+] = 5M$	5.64	5.67	5.70

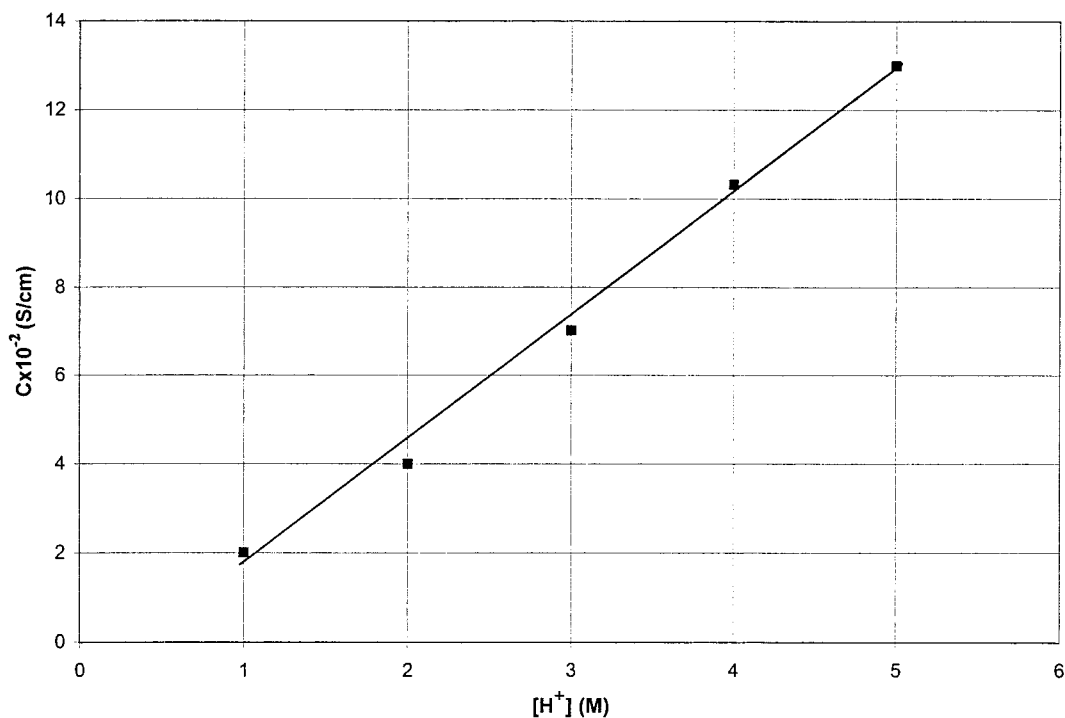
weight obtained by GPC represents just a fraction of the doped PANI either in pure form or as a component of semi-IPN.

The room-temperature dc conductivities of PANI/crosslinked PVAc semi-IPNs with different weight ratios of PANI content were measured at room temperature and the results are shown in Figure 4. The conductivity of the semi-IPN samples increased with the increasing weight content of PANI in the semi-IPNs in a linear fashion. This is because the PANI component can make more of

a continuous conducting network in the crosslinked PVAc matrix with more PANI. The dc conductivities of PANI/crosslinked PVAc semi-IPNs at different acidities used during polymerization are shown in Figure 5. The conductivity of the semi-IPNs increased linearly with increasing acidity used during polymerization. There are three reasons for this trend. First, the yield of PANI in the emeraldine form is expected to increase with greater acidity during the polymerization<sup>3</sup> (The three possible forms of PANI, emeraldine, pernigraniline, and leucoemeraldine, are shown in Fig. 6.) Second, the number of (proton) doped units of PANI is expected to increase with increased acidity of polymerization; and third, the molecular weight increases.

The TMA studies of crosslinked PVAc, pure PANI, and PANI/crosslinked PVAc semi-IPN are shown in Figure 7. From this figure, we see that the depression of PANI with temperature change is smallest, followed by the depression of semi-IPN of the PANI/crosslinked PVAc, which is considerably smaller than the depression of crosslinked PVAc. The PANI/PVAc semi-IPNs, as expected, showed moderate thermal mechanical strength that was between those of the pure PVAc and PANI at temperatures below 75°C. PANIs

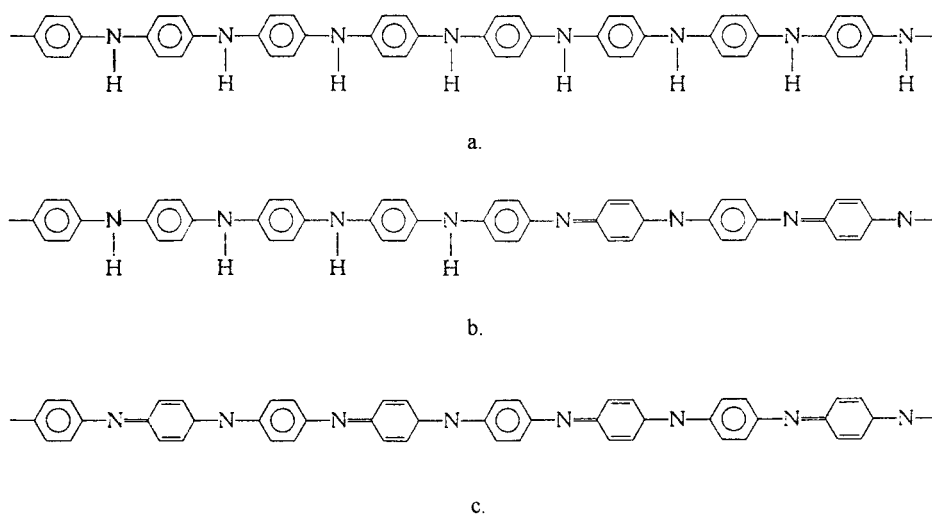
**Figure 4** Dc conductivities of semi-IPNs  $C$  versus weight content of PANI (wt %).



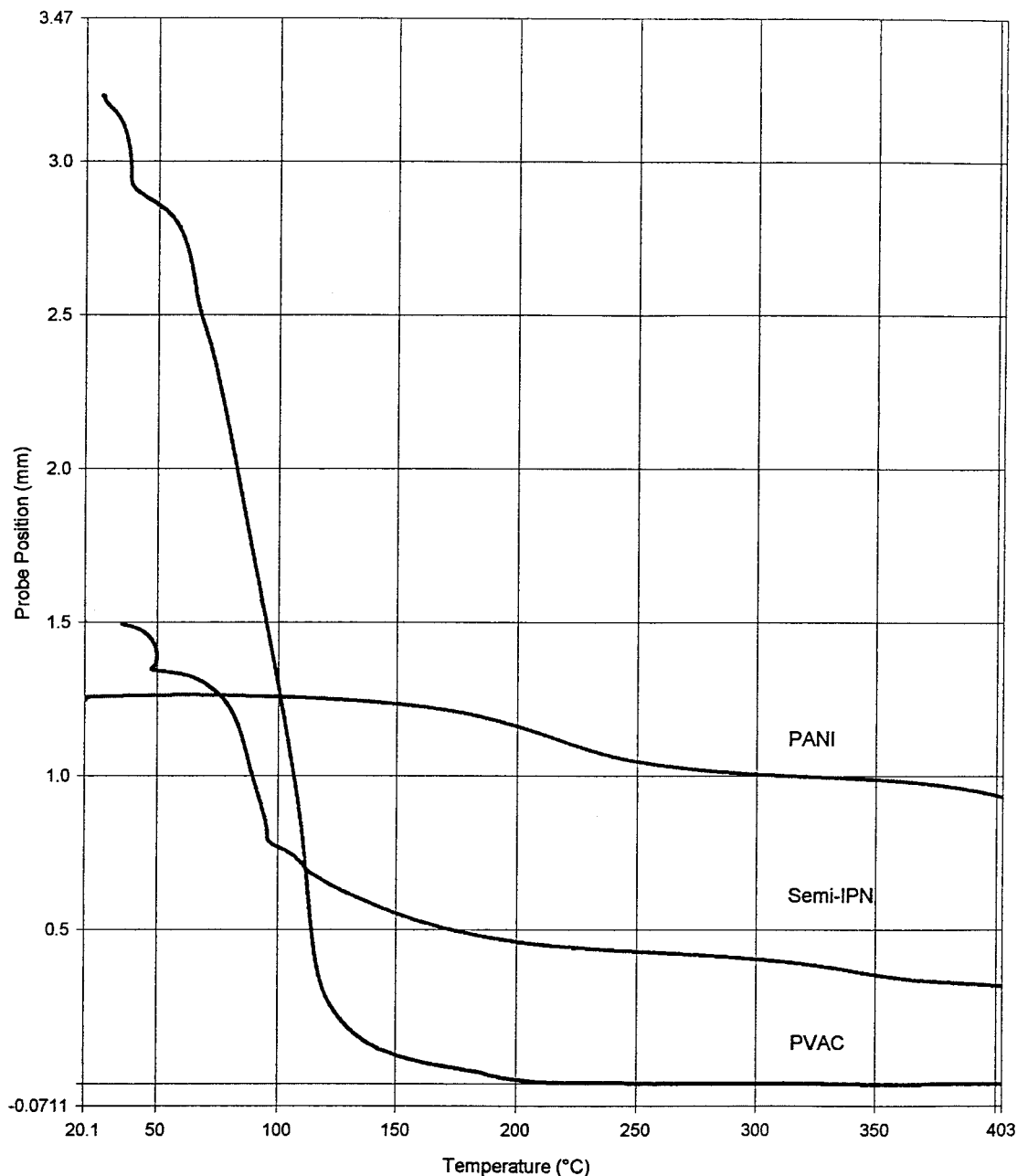
**Figure 5** Dc conductivities of semi-IPNs  $C$  versus acidity  $[H^+]$ , used during polymerization (samples prepared at  $[H^+] = 1M$ , PANI content = 19.0 wt %;  $[H^+] = 2M$ , PANI content = 15.4 wt %;  $[H^+] = 3M$ , PANI content = 18.5 wt %;  $[H^+] = 4M$ , PANI content = 18.6 wt %;  $[H^+] = 5M$ , PANI content = 19.3 wt %).

have very poor processability as industrial materials because they are usually in hard solid form and have very limited solubility in several uncommon solvents.<sup>10</sup> By forming semi-IPNs with an-

other polymer that has better processability, like PVAc, the industrial application of PANI could be extended; or, in other words, the processability of PANI was improved.



**Figure 6** The three different states of PANI: (a) leucoemeraldine; (b) emeraldine; (c) pernigraniline.



**Figure 7** Thermal mechanical analysis of crosslinked PVAc, pure PANI, and semi-IPN, probe position versus temperature.

## CONCLUSIONS

Conducting semi-IPNs based on PANI and crosslinked PVAc have been synthesized. The semi-IPNs have retained a high dc conductivity and improved the processability of PANI by forming interpenetrating polymer networks. The thermal mechanical strength of the semi-IPN is be-

tween that of crosslinked PVAc and PANI. The molecular weight of PANI and conductivity of the semi-IPNs increased with increasing acidity used during polymerization.

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