

Flexible, Highly Transparent, and Conductive Polyaniline-Cellulose Acetate Composite Films

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ABSTRACT: Highly transparent and conductive polyaniline-cellulose acetate composite films were cast from *m*-cresol solutions of protonated polyaniline and cellulose acetate. The following polyaniline protonating agents were used: camphor sulfonic acid, phenylphosphonic acid, dibutyl phosphate, and dioctyl phosphate. The films were plasticized with a mixture of phthalic and phosphoric acid esters added to the solution used for the casting. The addition of plasticizers not only improved the flexibility of the composite films but also significantly lowered the percolation threshold, which is 0.05 wt % (expressed as emeraldine base) for phenylphosphonic acid protonated polyaniline in cellulose acetate matrix. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **63**: 971–977, 1997

INTRODUCTION

Preparation of “all polymeric” conductive composites, that is, composites in which the conductive and insulating components are of macromolecular nature, has drawn significant research interest in the last decade. Unfortunately the fabrication of such materials has been severely impeded for several years, mainly due to rather poor processability of the majority of conductive polymers. Therefore, special techniques, frequently very difficult to use on an industrial scale, had to be applied, for example, electrochemical polymerization, inside a porous matrix of an insulating polymer.¹

Polyaniline (PANI) seems to be one of the best candidates for the fabrication of polymer based conductive composites. It is environmentally stable in its conducting form, and recently significant progress was achieved in the preparation of pro-

cessable forms of PANI. Cao et al.^{2–4} showed that PANI protonated with camphor sulfonic acid (CSA) or dodecylbenzene sulfonic acid can be processed from solutions. Similarly, protonating agents like phosphoric acid diesters or phosphonic acids also induce solution processability of PANI. In addition some of them plasticize PANI which, in turn, greatly facilitates its thermal processing.^{5–8}

Several conductive composites of PANI with vinyl polymers such as polystyrene,⁹ poly(alkyl methacrylates),^{4,10–12} poly(vinyl chloride),^{5,7,13–15} and poly(ethylene-*co*-vinyl acetate)¹⁶ were reported in the literature. Similarly conductive composites of PANI with polyamides,^{17,18} polyurethanes,¹⁹ and thermoplastics²⁰ were fabricated. PANI based latex composites were also prepared.²¹

The percolation threshold in PANI based conducting composites is of crucial importance for at least two reasons: due to the rather high extinction coefficients of PANI for the blue and red light, highly transparent, green films can be fabricated only at extremely low contents of this polymer in the composite; mechanical properties characteris-

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tic of the host insulating polymer can be retained only for a small content of the conductive polymer in the composite.

These requirements can be fulfilled only if the conductive phase exhibits a special morphology of the self-assembled, interpenetrating polymer network type.²²

There exists a great demand for flexible, conductive plastic films. Such films have been fabricated on the basis of plasticized poly(vinyl chloride).^{7,15} Cellulose derivatives are another group of polymers that are used in the plasticized state. Thus, they are very good candidates for the fabrication of such films. In this article we report on the preparation of conductive, flexible composites of PANI and cellulose acetate (CA) that exhibit a low percolation threshold and high transparency.

EXPERIMENTAL

Reagents

The emeraldine base (EB) used in this research was prepared using the method described by MacDiarmid et al.²³ A low molecular weight fraction was extracted with acetonitrile and subsequently with tetrahydrofuran. The polymer exhibited number-average (M_n) and weight-average (M_w) molecular weights of 21,500 and 71,000 g/mol, respectively, and a PI of 3.3, as determined by GPC in 0.5% LiCl-NMP with respect to polystyrene standards. It had an inherent viscosity (η_{inh}) of 1.0 dl/g at 0.1% in 96% H₂SO₄. (+-)-10-CSA (98%), phenyl phosphonic acid (PPA, 98%), and aliphatic diesters of phosphoric acid [i.e., dibutyl and dioctyl phosphates (DBP, DOP, 97%) and diphenyl phosphate (DPP, 99%)] were purchased from Aldrich. Aromatic diesters of phosphoric acid such as di-*p*-cresyl phosphate and di-*m*-cresyl-phosphate (DpCP, DmCP) were synthesized using the method described in detail by Laska et al.⁸ CA (molecular weight ca. 50,000 g/mol) and its plasticizers [i.e., dimethyl phthalate (99%), diethyl phthalate (99%), and triphenyl phosphate (99%)] were also purchased from Aldrich. *m*-Cresol (>99%, Merck) was used as received.

Protonation of EB

As already stated, four groups of protonating agents were tested: sulfonic acids (CSA); phosphonic acids (PPA); aliphatic diesters of phos-

phoric acid (DBP and DOP); aromatic diesters of phosphoric acid (DPP, DpCP, and DmCP).

For the protonation reaction polyemeraldine base was mixed with the appropriate protonating agent in the molar ratio of [acid molecule] : [PANI mer] = 0.5. This mixture was then transferred to *m*-cresol to give a suspension of 0.5 wt % PANI content (with respect to the EB). The suspension was then vigorously stirred at room temperature, typically for 2–3 weeks, the time required to reach the maximum dissolution. After that time the suspension was centrifugated at 5000 rpm for 15 min. Two fractions of protonated PANI were separated upon centrifugation: the fraction that sedimented upon centrifugation and the one that remained in the *m*-cresol. In the following text the sedimented fraction will be called insoluble whereas that remaining in *m*-cresol will be named soluble.

For the preparation of composites with CA only the soluble fraction was used. The concentration of PANI in the soluble fraction was determined in the following way. First the suspension of protonated PANI was centrifuged. After centrifugation the soluble fraction was separated and stored for composite fabrication. The insoluble fraction was washed twice with *m*-cresol, then twice with acetone. Acetone was then removed by evaporation. In the next step PANI was deprotonated with an excess of 2 wt % ammonia aqueous solution. The sample was then washed twice with ammonia and 3 times with water. Finally the sample was dried until constant mass. Knowing the initial amount of PANI base taken for the protonation and the amount of PANI base determined from the insoluble protonated fraction, we calculated the concentration of PANI in the soluble fraction.

The concentration of PANI in the soluble fraction depended on the protonating agent used. In the case of CSA usually 75–85 wt % of initially used PANI could be solubilized. Protonation with aliphatic esters led to the solubilization of 55–70 wt % of initially used PANI. The lowest fraction of soluble PANI was found for PPA where the amount of soluble PANI never exceeded 20 wt % of the initial PANI content.

Fabrication of Conductive Composites with CA

Two types of composites were prepared: unplasticized and plasticized. In the preparation of unplasticized composites a 5 wt % solution of CA in *m*-cresol was mixed with appropriate amounts of an *m*-cresol soluble fraction of protonated PANI.

Then films were cast by slow evaporation of the solvent at temperatures of 50–60°C.

Plasticized composites were prepared by adding plasticizers to the *m*-cresol solution of CA. The following composition of the plasticized material was used (in weight parts): CA 100, dimethyl phthalate 25, diethyl phthalate 25, triphenyl phosphate 2. This composition is frequently used to produce plasticized CA. The plasticized composite films were prepared exactly in the same manner as the unplasticized ones.

Measurements

UV visible near IR (UV vis. NIR) absorption spectra of films and solutions were recorded using a Cary Varian 2400 spectrometer. To record spectra of solutions we used quartz infrasil cells of 1 mm optical path filled with 0.01 wt % PANI solution.

The composite morphology was observed in transmitted light using a Reichert–Jung metallographic Polyvar microscope.

The conductivity of the film was measured using the four probe method in van der Pauw geometry. Pressure contacts were applied.

RESULTS AND DISCUSSION

In a recent paper Xia et al.²⁴ discussed the relationship between the UV vis. NIR spectra of protonated PANI and the conformation of its chain. They pointed out that in particular solvent-protonating acid systems, like *m*-cresol-CSA, the emeraldine adopts an extended coil conformation that promotes the delocalization of polarons. This delocalization is, in turn, manifested in the UV vis. NIR spectra by an intense broad band extending far in the NIR.

In the solutions of protonated PANI studied in this research three types of spectra were distinguished. PANI protonated with CSA gave essentially identical spectra as those reported by Xia et al.,²⁴ showing a sharp polaronic peak at 444 nm (2.79 eV) and a strong broad band extending beyond 2100 nm [see Fig. 1(a)]. PANI protonated with PPA or aliphatic diesters of phosphoric acid also showed the sharp polaronic peak at 444 nm and the broad band extending beyond 2100 nm, but the peak characteristic of localized polarons at ca. 920 nm (1.35 eV) was still present. Additionally a hump toward 1660 nm (0.75 eV) could be seen. Both features evince some different level of polaron localization [see Fig. 1(b–d)]. PANI

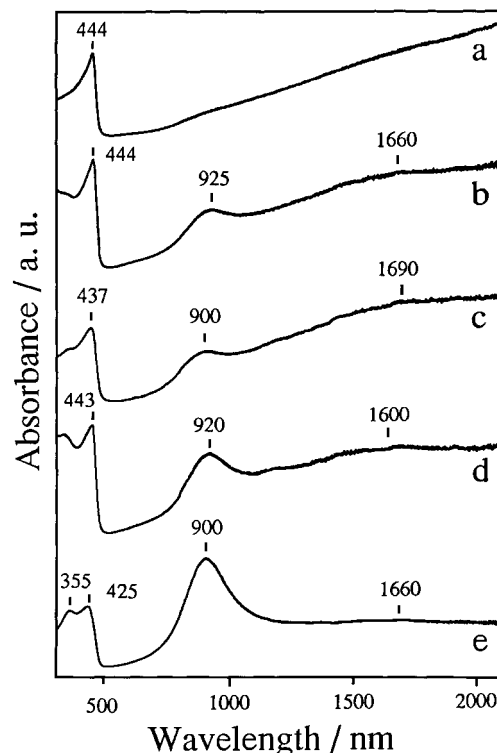


Figure 1 UV vis. NIR spectra of protonated emeraldine in *m*-cresol. Protonating acids: (a) CSA, (b) PPA, (c) DBP, (d) DOP, and (e) DmCP.

protonated with aromatic diesters of phosphoric acid exhibited spectral features resembling merely those characteristic of localized polarons, showing the characteristic strong peak at ca. 900 nm. However, a weak hump at ca. 1660 nm and a less intense broad band extending beyond 2100 nm were present [Fig. 1(e)].

The spectra show that phenylphosphonic acid and aliphatic diesters of phosphoric acid in *m*-cresol succeeded in partially changing the conformation of the PANI chain to the extended coil conformation, but aromatic esters showed only a weak effect.

It is known that PANI films cast from the solutions exhibiting spectral features of the third type exhibit lower conductivities as compared to films obtained from the other two types of solutions. Indeed these solutions were not suitable for the fabrication of conducting composites of PANI and CA because PANI tends to form aggregates upon film casting and high percolation thresholds were observed. Therefore, we selected only the two other groups of protonating agents, namely CSA, PPA, DBP, and DOP.

DBP protonated PANI and DOP protonated

PANI did not give good composites with unplasticized CA. Cast films consisted of three concentric zones with a distinctly different content of PANI in each zone. The inner zones were enriched in PANI whereas in the outer zone the content of PANI was much smaller. The composites showed poor mechanical strength along the borders of the zones.

Uniform looking composite films were obtained for CSA protonated PANI and unplasticized CA. The observed percolation threshold was, in this case, in the vicinity of 4 wt %. A characteristic image of CSA protonated PANI-CA composite film with 5.4% PANI content (i.e., above the percolation threshold) is presented in Figure 2(a). The film shows a characteristic randomly distributed and agglomerated PANI grain structure. The grains are revealed as green dots that show a black contrast on the photomicrographs. The grains of PANI swollen by *m*-cresol are quasi-spherical, 0.5–0.8 μm in diameter. A significant number of grain clusters can be seen, which of course leads to an increase in the value of the percolation threshold.

Figure 2(b,c) shows images of plasticized CSA protonated PANI-CA composite films having a PANI content above and near the optically determined percolation threshold. The dispersion of PANI grains in the CA matrix was considerably enhanced by the presence of the plasticizers, which apparently loosened the PANI grain–grain adhesion forces. However, the dispersion of PANI grains induced by the plasticizers was not total. Small clusters formed via aggregation of PANI grains were still observed, even at PANI contents below the percolation threshold. It is not known at the present time whether this grain structure was formed during the mixing of the two polymer solutions or during evaporation of *m*-cresol or if it was inherited from the PANI solution. However, it is worth noting that the solution of PANI in *m*-cresol, before centrifugation if observed in transmitted light across a capillary film between microscope glass lamellae, showed a similar structure of *m*-cresol swollen grains. The percolation threshold could not be determined exactly by optical microscopy because at the high magnification ($1000\times$) used the field thickness in focus was thin, enabling only an estimate of the in-plane 2-dimensional percolation threshold, which was higher than the actual 3-dimensional one. Three other types of composites that were studied gave similar microscopic pictures.

The addition of the plasticizing mixture sig-

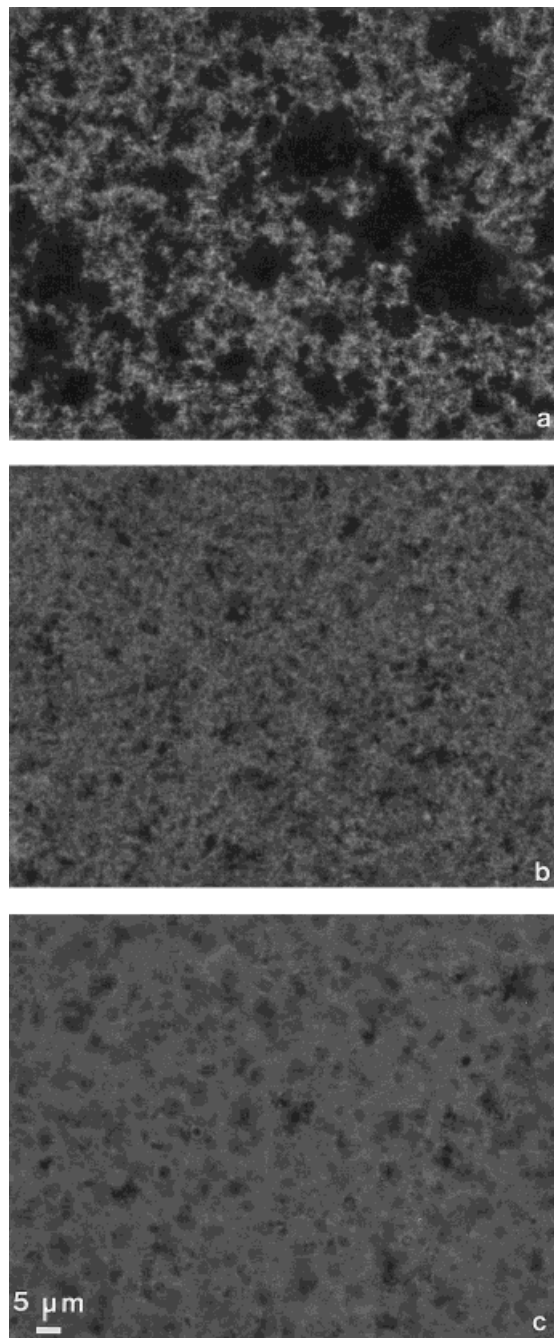


Figure 2 Photomicrographs of CSA protonated PANI-CA composite films: (a) 5.4 wt % PANI in unplasticized CA (above the percolation threshold), (b) 2.1 wt % PANI in plasticized CA (above the percolation threshold), and (c) 0.8 wt % PANI in plasticized CA (below the optically determined percolation threshold).

nificantly lowered the percolation threshold in CA based conductive composites. In Figure 3(a–d) the conductivity of the plasticized composite is plotted versus PANI content. For comparative

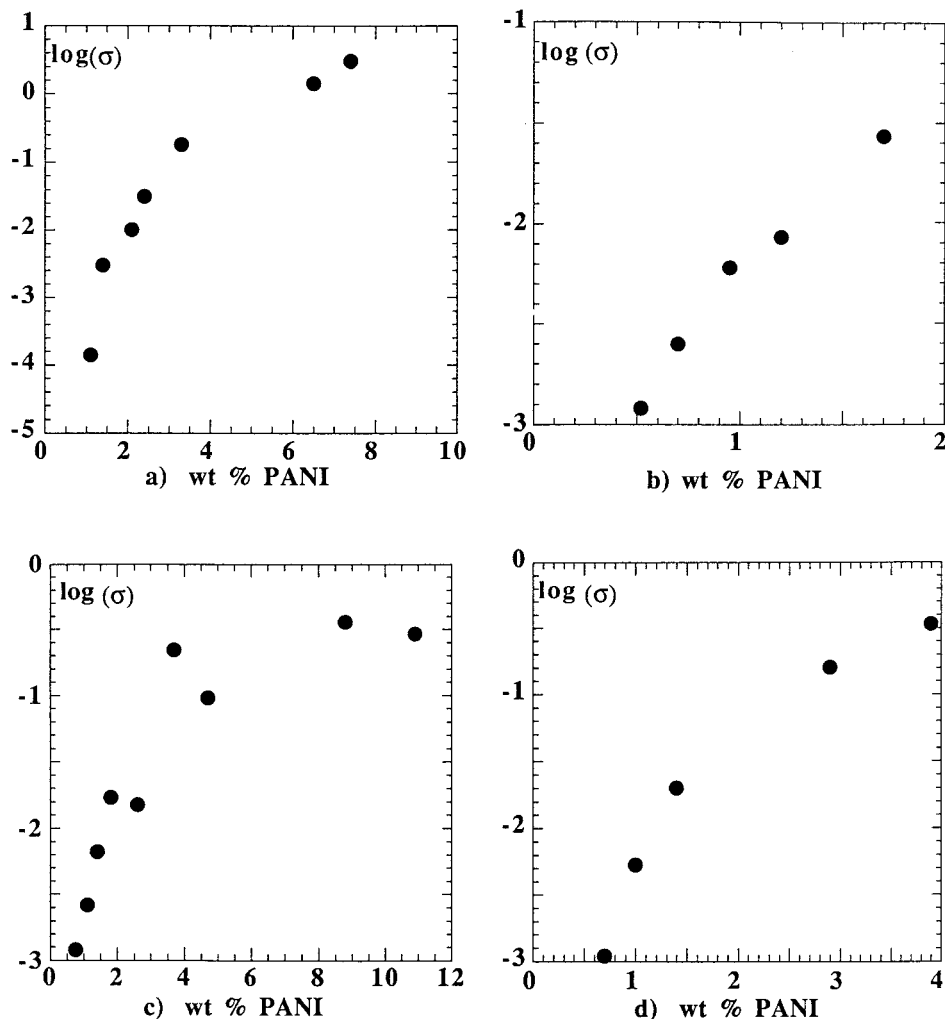


Figure 3 Conductivity in Siemens/centimeter (S/cm) vs. polyaniline content in PANI-plasticized CA composite films. PANI protonating acids: (a) CSA, (b) PPA, (c) DBP, and (d) DOP.

reasons we expressed the PANI content here and throughout as EB wt % because the molecular weights of the used protonating agents were different.

The data presented in Figure 3(a–d) can be fit to the scaling law of percolation theory,

$$\sigma(f) = c(f - f_p)^t, \quad (1)$$

where c is a constant, t is the critical exponent, f is the volume fraction of the conductive medium, and f_p is the volume fraction at the percolation threshold. In our study we expressed the percolation threshold in a mass fraction, which is proportional to the volume fraction.

The calculations give the highest percolation threshold, $f_p = 0.84$ wt %, for CSA protonated

PANI-CA composite. DBP protonated PANI-CA composite and DOP protonated PANI-CA composite showed similar percolation thresholds: 0.44 and 0.41 wt %, respectively. The fits to eq. (1) were very good, giving the correlation coefficients above 0.99 for CSA and DOP protonated PANI and 0.97 for DBP protonated PANI.

Plasticized DOP protonated PANI-CA composite films containing more than 5 wt % PANI were inhomogeneous as unplasticized DOP protonated PANI-CA films (*vide supra*). Thus, homogeneous films with PANI loads < 5 wt % could only be prepared.

PPA protonated PANI-CA composite is the most interesting case. The data presented in Figure 3(b) seem to indicate that an order of magnitude lower percolation threshold was obtained for

this composite because the sample having 0.5 wt % PANI still showed a conductivity of ca. 10^{-3} S/cm, that is, three orders of magnitude higher than that usually required for antistatic materials. The fit of the data from Figure 3(b) to eq. (1) led to an extremely low percolation threshold of ca. 0.05 wt %. The obtained value only exceeded the percolation thresholds slightly as reported by Banerjee and Mandal²⁵ for PANI nanoparticles in several vinyl type polymer matrices.

The very low percolation threshold observed in PANI-CA composites was the result of a preferential unidimensional aggregation of PANI grains. This unidimensional aggregation might be attributed to the anisotropic nature of (probably crystallized, spherulitic) the PANI grains that would be polarized. CSA protonated PANI suspension solutions in *m*-cresol showed an induced birefringence when submitted to high magnetic fields, implying a grain anisotropy (J. Torbet and Y. F. Nicolau, unpub. results, 1996). Thus, a unidimensional aggregation of grains induced by strong polarization forces prevailed on 3-dimensional aggregation induced by weak Van der Waals forces. Consequently, a very good dispersion of aggregated grains was a key factor in obtaining very low percolation threshold composites.

The composites having a low PANI content were highly transparent and pale green. Figure 4(a–c) shows the spectra of protonated PANI in the plasticized CA matrix. The spectra of PANI protonated with different acids in the plasticized CA matrix were similar to those of PANI in *m*-cresol. Only the polaronic peaks at ca. 440 nm were a little less intense, broader, and for PPA protonated PANI shifted to higher energies. Films of CSA protonated PANI (as EB) cast from *m*-cresol on quartz slides underwent similar changes: the sharp peak at 444 nm broadens and shifts to slightly higher energies (437 nm) indicating some electron and possibly conformation changes in the polymer upon drying [see Fig. 4(d)]. The minor changes observed in the spectra of protonated PANI in CA matrix with respect to the corresponding spectra of protonated PANI in *m*-cresol suggested that only a small fraction of *m*-cresol contained in the PANI grains was lost during casting and drying of the composite films. It is worth noting that PANI protonated with PPA, DBP, and DOP in CA film still exhibited the broad peak at ca. 850 nm that is characteristic of localized polarons in addition to the absorption band indicating polaron delocalization. As a result PANI protonated with this agent was

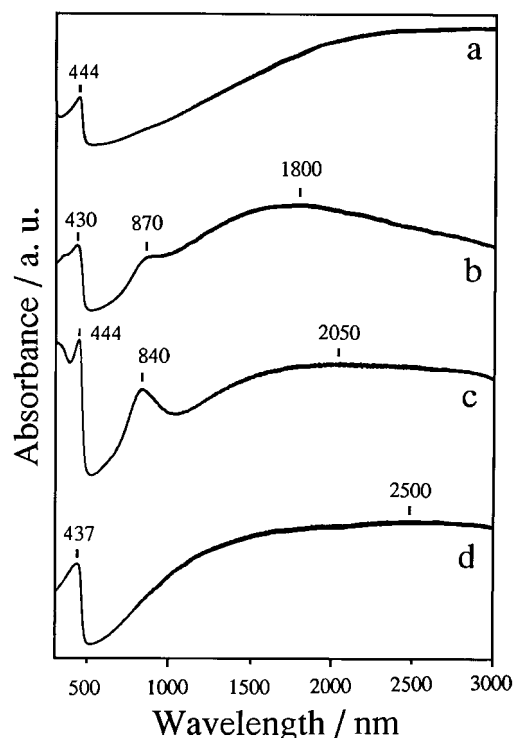


Figure 4 UV vis. NIR spectra of protonated PANI in the matrix of plasticized CA. Protonating acids: (a) CSA, (b) PPA, (c) DOP, and (d) spectrum of a thin film of CSA protonated PANI cast from *m*-cresol on a quartz slide.

slightly less conductive than CSA protonated PANI. However, despite lower conductivities of the electroactive phase in these composites, lower than for CSA protonated PANI-CA composite, percolation thresholds were obtained, owing probably to an enhanced dispersion of PANI grains induced by these dopants in the CA matrix.

Finally it should be stressed that all conductive films exhibited excellent flexibility of the plasticized CA.

CONCLUSIONS

To summarize, flexible, conductive, and highly transparent composite films can be obtained from plasticized CA and protonated PANI. Three groups of protonating agents lead to composites with low percolation threshold: sulfonic acids, phosphonic acids, and aliphatic diesters of phosphoric acid. For all these protonating agents significant delocalization of polarons is achieved as judged from UV vis. NIR spectra of PANI in *m*-cresol and in the solid composite films.

The addition of the plasticizing mixture not only induces flexibility of the film but also significantly lowers the percolation threshold in the composite. As seen by optical microscopy, the plasticizing mixture improves the dispersion of PANI grains in the matrix by loosening the grain-grain adhesion forces.

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