Synthesis and Characterization of Conductive Nanoblends Based on Poly(aniline-*co*-3-aminobenzoic acid) in the Presence of Poly(styrene-*alt*-maleic acid)

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ABSTRACT: In this article, we describe electrically conductive nanoblends containing poly(aniline-*co*-3-aminobenzoic acid) (PANABA), poly(styrene-*alt*-maleic acid) (PSMAC), and polystyrene. PANABA copolymers on a nanoscale were prepared under ultrasonic irradiation by the oxidative copolymerization of aniline and 3-aminobenzoic acid at different molar ratios. PSMAC was also prepared in our laboratory. The obtained conductive nanoblends formed films with good homogeneity and flexibility. The conductivity of the obtained nanoblends was measured with a four-probe method. The maximum electrical conductivity obtained was 0.60 S/cm. The characterization of the obtained copolymers and nanoblends was carried out by Fourier transform infrared spectroscopy, ultraviolet–visible spectroscopy, and X-ray diffraction. Scanning electron microscopic images were taken from the obtained nanoblends. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 122: 97–104, 2011

Key words: blends; conducting polymers; copolymerization

INTRODUCTION

During the past 2 decades, electrically conducting conjugated polymers, such as polyaniline (PANI), have received considerable attention because of their remarkable electronic, magnetic, and optical properties. However, the applications of such polymers still remain limited because of two possible reasons:[1–3]

1. Most of the conducting polymers show a weak resistance; this leads to limitations in the field of applications requiring good durability.
2. One of the main difficulties in the control of the structure–properties relationship is the insolubility of most of these polymers so that they cannot be characterized in solution.

To solve the processability of PANI, several methods have been developed. For instance, PANI processability and thermal stability can be improved by redoping with functionalized organic acids. Although soluble PANI with bulky dopants, such as dodecylbenzene sulfonic acid and camphor sulfonic acid, have been developed, their commercialization has also been considered to be inadequate because of the toxicity of the solvent used and the difficulty of their preparation.[4–6] Structural modification by ring substitution is another method used to improve PANI solubility and processability. Structural modification by ring substitution can be done by the modification of the polymer backbone by synthetic reactions on the whole polymer and copolymerization. Because copolymerization leads to materials with intermediate properties between two polymer systems and creates soluble systems, it has received extensive interest because of its high potential for modifying the physical properties of conducting polymers. The copolymerization of aniline (ANI) and 3-aminobenzoic acid (AC) with generated processable conductive copolymers with various molar ratios has resulted in different optical and electrical properties.[7,8]

Another approach for enhancing the processability of PANI is a nanocomposite or nanoblend method that uses various polymeric materials.[9–11] It is well known that the electrical properties of nanocomposites depend on the concentration, size, and shape of the conductive particles. Furthermore, the intermixing of two phases will also play a major role in the control of the physical properties. Two types of PANI nanocomposites are available according to the polymerization of PANI, such as postpolymerization and *in situ* polymerization. The postpolymerization method implies that chemically synthesized PANI is dispersed in a polymer matrix under either a solution state or a molten state of the matrix.

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Nonetheless, because the doped PANI salt is very hydrophilic with a high surface energy, it is hard to directly disperse the PANI in a polymer matrix, such as polystyrene (PS) and poly(methyl methacrylate).[12–14] In this study, to solve PANI processability, the copolymerization of ANI with AC was carried out in the presence of ultrasonic irradiation to prepare poly(aniline-co-3-aminobenzoic acid) (PANABA) on a nanoscale. Then, the prepared nanocopolymer was used for the preparation of a nanoblend.

EXPERIMENTAL

Materials

ANI (Merck, Germany) was doubly distilled in the presence of zinc dust to eliminate oxidation impurities. AC, styrene, maleic anhydride, a concentrated solution of hydrochloric acid (HCl), ammonium peroxydisulfate [$(NH4)_2S_2O_8$], tetrahydrofuran (THF), sodium hydroxide (NaOH), and benzoyl peroxide were purchased from Merck and were used without further purification. Commercial-grade PS was donated by Tabriz Petrochemical Co (Tabriz-Iran). All solvents (Merck) were used as received without further purification. Aqueous solutions were prepared with twice-distilled water.

Spectroscopy

Fourier transform infrared (FTIR) spectra were recorded on a Thermo Nicolet (Nexus 670) spectrometer, and transmission spectra were obtained by the formation of thin transparent KBr pellets. Ultraviolet–visible absorption spectra were recorded on a T-80 ultraviolet–visible spectrophotometer (PG Instruments, Ltd. UK) with a solution of the blend in dimethyl sulfoxide (DMSO). The conductivity measurements were performed by a standard four-probe technique. The samples were flexible films that we obtained by pressing the powder at a pressure of 15 MPa. The particle size and morphology of the particles were examined via scanning electron microscopy (SEM) (Burker, Germany).

The molecular weights of the resulting polymers were obtained with a Agilent 1100 (USA) gel permeation chromatography analysis instrument with PS calibration standards with THF as the mobile phase at a flow rate of 1.0 mL/min at room temperature.

Preparation of PANABA

In a 250-mL Erlenmeyer flask, 0.01 mol of ANI and AC monomer were mixed with an HCl solution (140 mL) with stirring at room temperature until the solid monomer was dissolved completely. The molar ratios of ANI to AC in the mixed monomers were

1 : 1, 1 : 2, 2 : 1, and 3 : 1. Polymerization was initiated by the addition of the ammonium persulfate in the HCl solution (1 mol/L). This addition was carried out over a period of 1 h under ultrasonic irradiation at below 5°C. The reaction mixture was maintained at below 5°C and was irradiated for 6 h more. At the end of the polymerization time, the precipitated copolymer was filtered and washed with the HCl solution (1 mol/L) three to four times, and then, it was washed by water and methanol, respectively, until the filtrate became colorless. The black powder was dried in a vacuum oven at 60°C for 24 h. The products were labeled as ANI-co-AC (1 : 1), ANI-co-AC (2 : 1), and ANI-co-AC (3 : 1).

Preparation of poly(styrene-*alt*-maleic acid) (PSMAC)

First, poly(styrene-*alt*-maleic anhydride) (PSMA) was prepared through the thermally initiated free-radical polymerization of styrene and maleic anhydride according to a literature method.[15] Briefly, equimolar amounts (0.005 mol) of styrene (0.573 mL) and maleic anhydride (0.49 g) were combined in a 100-mL, round-bottom flask with benzoyl peroxide and dried THF. The mixture was degassed by nitrogen to remove oxygen from the reaction vessel before polymerization. Polymerizations were carried out overnight at 80°C with stirring under a nitrogen atmosphere. The polymerization product was diluted in THF and then added dropwise to a 100-fold excess (v/v) of cold diethyl ether to precipitate the pure PSMA polymer. Then, it was filtered and dried *in vacuo* at room temperature. In the second stage, PSMA copolymer (1 g) was subject to base-catalyzed hydrolysis. Briefly, 1 g of the PSMA was added to 20 mL of a 2N NaOH solution and stirred for 5 h at room temperature. The copolymer was recovered from the NaOH solution by acid precipitation with 1N HCl. It was washed with distilled water several times and dried *in vacuo* for 24 h at 60°C.

Preparation of the PANABA/PSMAC/PS conducting nanoblends

PSMAC (1.5 g) was added to 20 mL of THF at room temperature and stirred until complete dissolution. Afterward, 2 g of the PANABA nanoparticles doped with HCl was added to the aforementioned solution and stirred to form a homogeneous dispersion. The dispersion obtained was then mixed with a 20-mL solution of PS (2.5 wt %); this was prepared by the dissolution of the PS beads in THF with a magnetic stirring bar. Then, the mixture was stirred for an additional 2 h. Finally, a homogeneous coating solution was obtained. Additional coating formulations with different amounts of PANABA nanoparticles and different ratios of PSMAC to PS were prepared. The
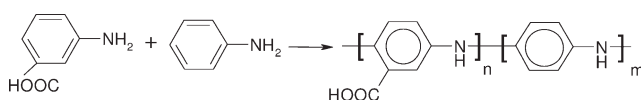
TABLE I
Conductivity Results of PANABA Copolymers

Run	Ratio of monomers in the feed (Ani : acid)	Conductivity (S/cm)
1	1 : 1	1.7
2	1 : 2	0.04
3	2 : 1	2.39
4	3 : 1	4.3

coating solutions were cast onto glass plates to obtain smooth films and dried at room temperature for 48 h.

RESULTS AND DISCUSSION

The copolymers of ANI with AC were synthesized according to the following general reaction:

The copolymers were synthesized by a different feeding ratio of the aforementioned monomers, and the conductivity of the copolymers in doped form in HCl were measured and are listed in Table I. The results of Table I show that the copolymers with carboxylic acids pendant groups in the PANI backbone had decreased conductivity in comparison with the PANI homopolymer. The copolymer with a 3 : 1 molar ratio of ANI to AC in the feed of the polymerization had the highest conductivity in the synthesized copolymer series. Although the conductivity of the obtained copolymer with a 1 : 1 molar ratio was good, it decreased with increasing AC in the feed of the copolymerization so that it showed no recordable conductivity in the case of the copolymers with 1 : 3 and 1 : 4 molar ratios of ANI to AC. When the molar ratio of the aforementioned monomers in the feed of the copolymerization was higher than 2, the obtained copolymers were soluble in 12% NH_4OH. This was attributed to the higher content of carboxylic groups in the copolymer.

Acidic groups, such as the carboxyl and sulfonic groups on the aromatic ring, could react with the C=N— group to form polarons in PANI. The self-doped effect, which was different from the external doped effect of the protonic acid, provided higher electrochemical activities and electrical conductivities because self-protonation was independent of external protonation in a broad pH range, and the conductivity did not dramatically decrease with increasing pH.[16,17]

Figure 1 shows the SEM micrographs of typical PANABA–HCl nanoparticles, in which the particles possessed an almost uniform distribution of size with spherical shapes. The diameter of the observed particles in the SEM images changed approximately from 100 to 200 nm. The maximum conductivity of the PANABA nanoparticles in doped form in HCl was obtained as 4.3 S/cm for the copolymer with a 3 : 1 molar ratio of ANI to AC in the feed of the copolymerization.

Figure 2 shows the FTIR spectra of ANI and AC copolymer particles synthesized with different molar ratios of ANI to AC. The most important absorption band was 1716 cm^{-1}, for carbonyl groups of carboxylic acids. The absorptions at 1576 and 1478 cm^{-1} corresponded to the stretching vibrations of the quinoid and benzenoid rings, and the peaks at 1146 and 1301 cm^{-1} were due to C—N and C=N stretching modes.[18] In addition, the peak at 802 cm^{-1} was for aromatic C—H stretching vibrations. We, thereby, confirmed the existence of carboxylic groups in this copolymer. All FTIR spectra of the copolymers with different molar ratios of monomers were similar; only when AC increased in the copolymer structure was the increase of carbonyl group intensity clearly seen in the FTIR spectra. These results are shown in Figure 2(A–D).
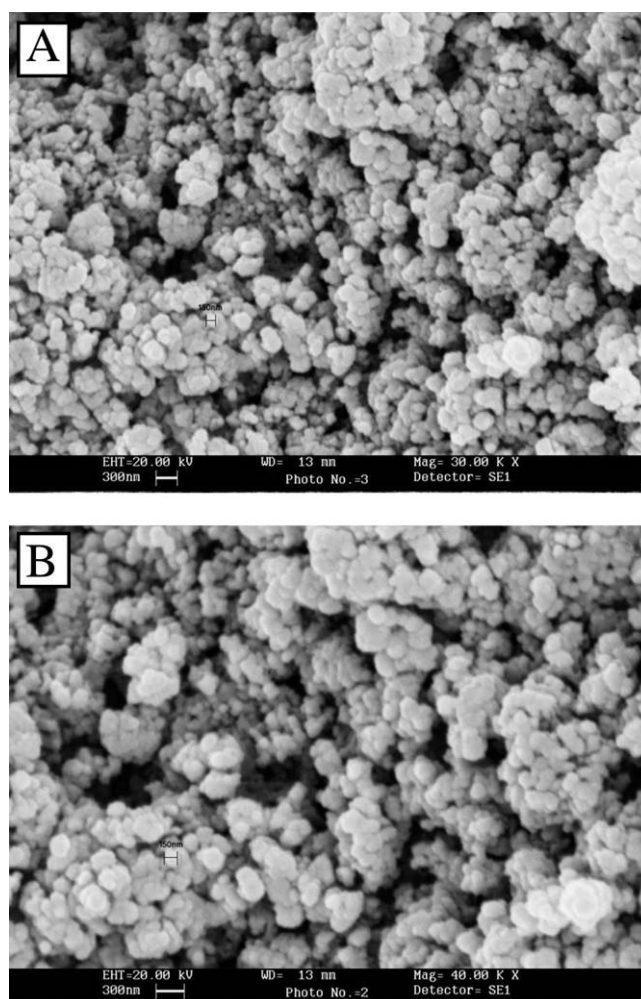

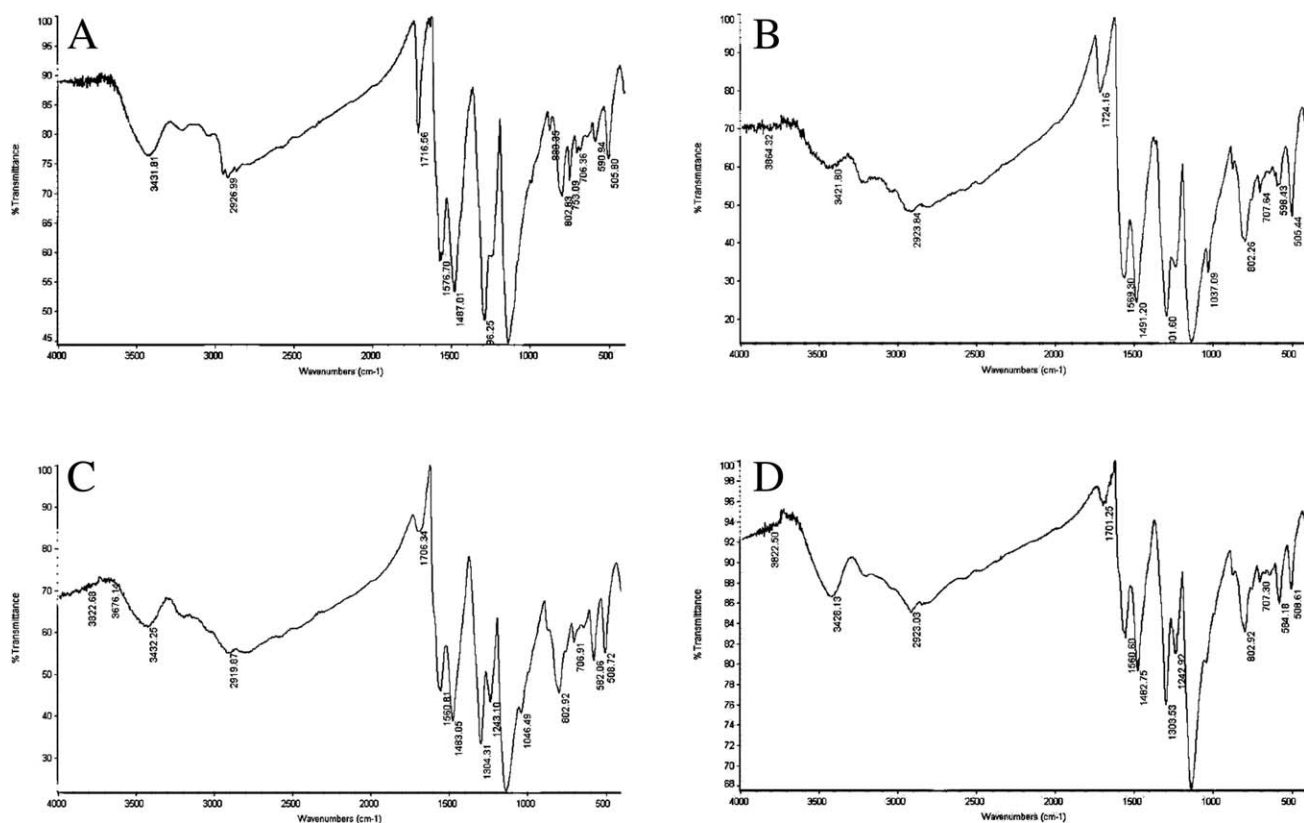**Figure 1** SEM images of PANABA at different magnifications: (A) 30,000 and (B) 40,000×.

Figure 2   FTIR spectrum of PANABA: (A) 1 : 1, (B) 1 : 2, (C) 2 : 1, and (D) 3 : 1.
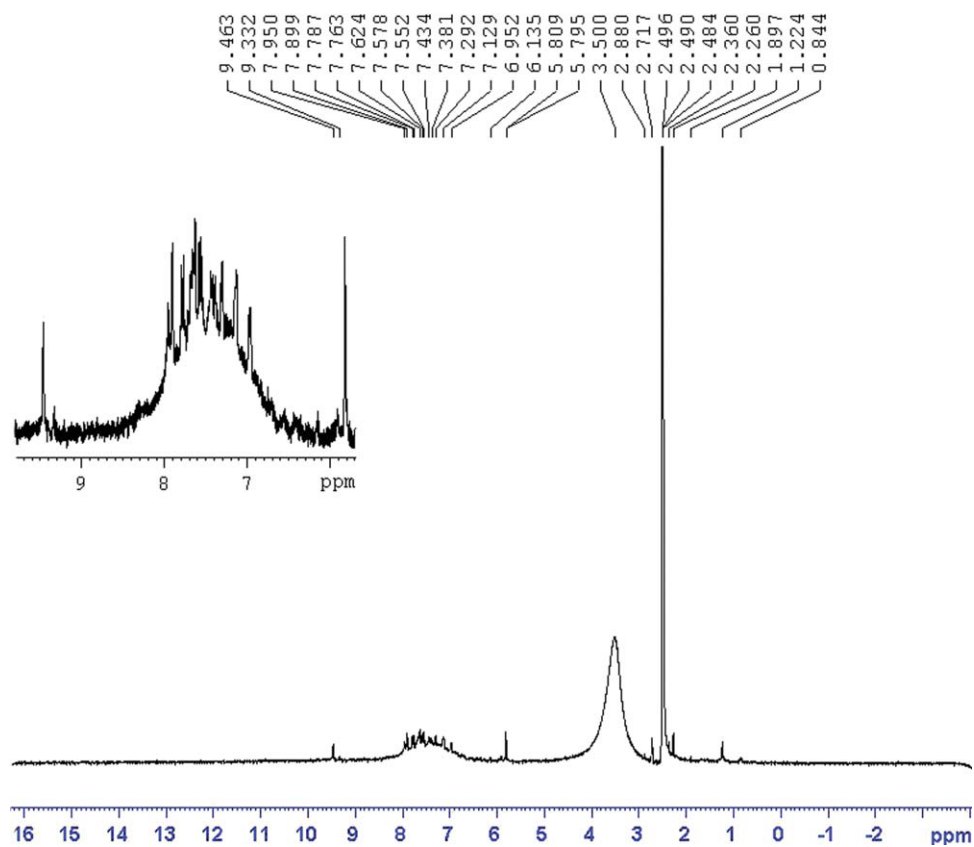

Figure 3   ^{1}H-NMR spectrum of PANABA in hexadeuterated DMSO. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
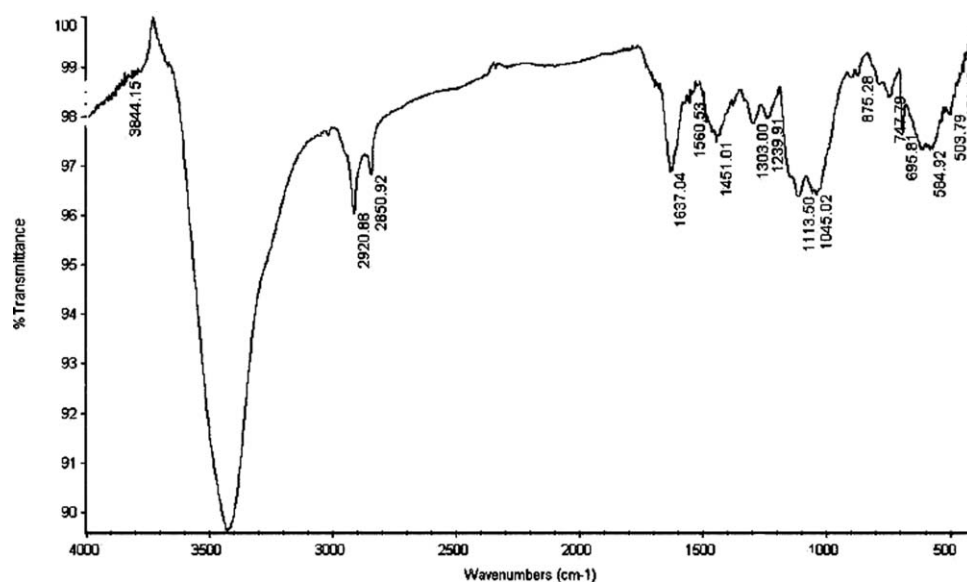
Figure 4 FTIR spectra of the PANABA/PSMAC/PS nanoblend.

Figure 3 shows the ^{1}H-NMR spectrum of PANABA in hexadeuterated DMSO at a molar ratio of 1 : 2 (ANI/AC). The proton signal ascribable to —COOH could not be found because COOH groups existed in the deprotonated form because of a self-doping effect. The peaks at $\delta = 6$–8 ppm were attributed to the protons of benzene rings in the benzenoid and quinoid forms, and the broad peak at about 4 ppm was attributed to N—H groups in the polymer backbone.

The free-radical polymerization of PSMA was facile, and the copolymer was readily recovered. Styrene and maleic anhydride are known to produce alternating copolymers, and the molecular weight of the copolymers could be controlled by variation of the molar ratio of the free-radical initiator to the volume of added solvent.[15] The molecular weight and polydispersity of the obtained PSMA was determined by gel permeation chromatography, and a weight-average molecular weight of 13,845 with a polydispersity of 3.02 was obtained. The PSMA copolymer was subjected to base-catalyzed hydrolysis to complete the hydrolysis of the maleic anhydride repeated groups in the backbone of the copolymer. Hydrolysis of the maleic anhydrides in the copolymer produced carboxylic acid repeated groups in the copolymer backbone. The FTIR spectrum of the PSMA copolymer (not shown) displayed characteristic anhydride peaks at 1778 and 1857 cm^{-1}, whereas in the FTIR spectrum of PSMAC, the anhydride peaks disappeared, and instead, the carbonyl peak of carboxylic acid was displayed at 1710 cm^{-1}, and the broad band of hydroxyl groups of carboxylic acid at 3429 cm^{-1} was also displayed.

The preparation of conducting nanocomposites based on nanoparticles of PANABA–HCl was investigated in this study by a dispersion mixing method
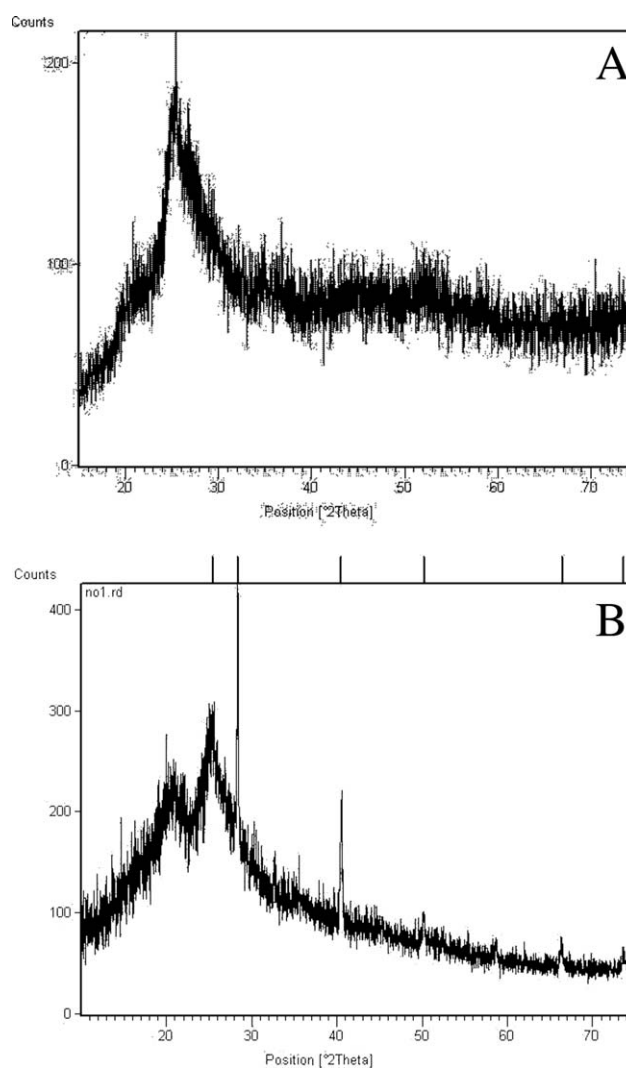

Figure 5 XRD pattern of (A) PANABA and (B) the PANABA/PSMAC/PS nanoblend.

TABLE II
Mean Diameters of PANABA Obtained from the Scherer Equation at Different Positions

Peak	Position peak (2θ)	Height	fwhm (2π)	Diameter (nm)
1	20.92	114.60	0.20012	40.52
2	25.96	339.82	0.25843	31.57
3	33.34	143.20	0.2972	28.05

followed by the evaporation of the solvent.[19] Figure 4 shows a typical FTIR spectrum of the PANABA/PSMAC/PS nanocomposite. The FTIR spectrum of the nanocomposites showed the characteristic absorption peaks of PANABA at 1560 and 1451 cm^{-1}; these were assigned to the nonsymmetric benzene ring stretching mode (ring stretching in the quinoid unit and ring stretching in the benzenoid unit, respectively). The peaks at approximately 1239 and 1303 cm^{-1} should have been due to the aromatic amine nitrogen (C—N stretching vibrations) for doped PANI associated with the oxidation or protonation states.[19] The peak at 1637 cm^{-1} were attributed to the carbonyl groups of PSMAC in the nanocomposite structure; the peak was shifted considerably with respect to the expected free carbonyl group absorption around 1700 cm^{-1} because of interactions with PANI macromolecules via intermolecular H bonding.[20]

It is very important to study the crystal structure of conductive polymers because a highly ordered chain structure of a conductive polymer will endow a high electrical conductivity. Pouget, Jozefowica, Epstein, Tang, and MacDiarmid (1991) investigated the crystal structure of PANI prepared through conventional polymerization in detail, suggesting a pseudo-orthorhombic crystal form.[21] In this study, we examined the crystal structure of the PANABA component in the PANABA/PSMAC/PS nanoblend.

The X-ray diffraction (XRD) patterns of the PANABA/PSMAC/PS nanoblend and PANABA–HCl are shown in Figure 5(A,B). Pure PANABA showed a typical noncrystalline pattern, whereas for the PANABA/PSMAC/PS nanoblend, the XRD pattern showed a nearly semicrystalline structure. In the

XRD pattern of the PANABA/PSMAC/PS nanoblend, the diffraction peaks at $2\theta = 25.33$, 28.38, 40.52, 50.18, 66.34, and 73.60° corresponded to PANABA. The peaks centered at $2\theta = 25.33$ and 28.38° were ascribed to the periodicity parallel and perpendicular to the PANABA chains. From the XRD pattern of the PANABA/PSMAC/PS nanoblend, PANABA had a highly ordered crystal structure, which was expected to exhibit a high electrical conductivity.

Comparison of the XRD pattern of the nanoblend with the XRD pattern of PANABA showed that the crystalline structure of the nanoblend was improved. The mean particle size (D) was calculated with the Scherer equation:[22]

$$D = \frac{9\lambda}{\beta \cos \theta} \tag{1}$$

where λ is the wavelength of the X-ray source (Cu Kα = 1.54056 Å) and β is the full width at half-maximum (fwhm) of the XRD peak at the diffraction angle (θ). Tables II and III show the mean diameter of PANABA and the PANABA nanocomposite particles at various angles. This data showed that the PANABA nanoparticles existed in the nanoblend structure.

The compositions of the nanoblends and the results of the conductivity measurements are listed in Table IV. All of the prepared nanoblends showed conductivity, and among them, the obtained maximum conductivity was 0.6 S/cm. As shown in Table IV, the conductivity of the obtained nanoblends increased with increasing PANABA content in the nanoblend structure. Also, the content of PSMAC in the structure of the nanoblend had a determinative effect on the conductivity of the obtained nanoblends because the PSMAC copolymer could act as an external dopant for PANABA. Therefore, when the amount of PSMAC in the nanoblend structure was increased, the conductivity increased.

The ionic interaction between the PSMAC copolymer and PANABA caused good dispersion of PANABA in the matrix of PSMAC. On the other hand, the PSMAC copolymer in the nanoblend structure

TABLE III
Mean Diameters of PANABA Obtained from the Scherer Equation at Different Positions in Nanocomposites

Peak	Position peak (2θ)	Height	fwhm (2π)	Diameter (nm)
1	25.33	173.29	0.4446	19.63
2	28.38	503.59	0.0984	86.62
3	40.52	234.98	0.1968	47.79
4	50.18	59.28	0.2362	37.45
5	66.34	53.59	0.3149	33
6	73.60	15.38	0.5760	17.32

TABLE IV
Conductivity of the Obtained Nanocomposites

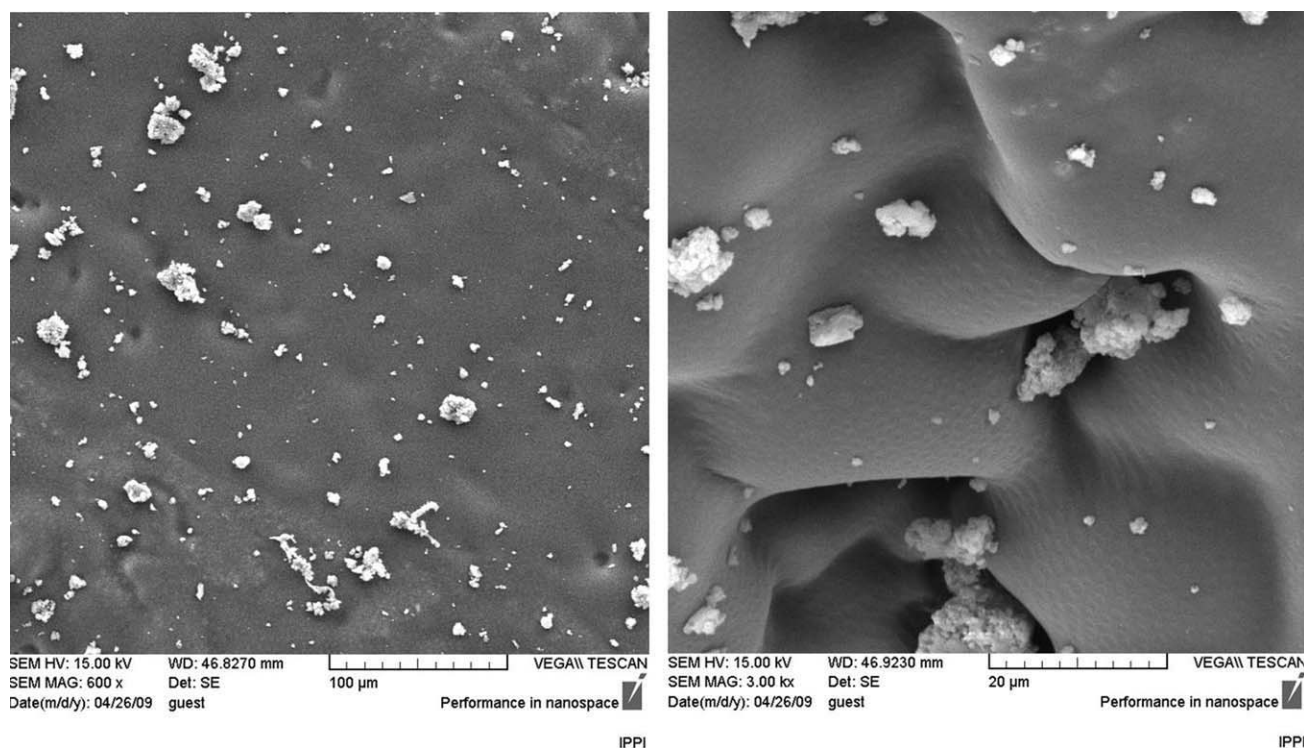| Nanocomposite film	PANABA/HCl (g)	PS (g)	PSMAC (g)	Conductivity (S/Cm)
1	0.5	0.5	0.5	0.10
2	0.75	0.5	0.5	0.25
3	1	0.5	0.5	0.32
4	1	0.25	0.75	0.49
5	1.25	0.25	0.75	0.6
6	1	—	0.75	0.78

Figure 6 SEM images of the PANABA/PSMAC/PS nanoblends at different magnifications.

caused of better compatibility with PS, so the homogeneous nanoblends were obtained with good mechanical properties and flexibility with only a mixing procedure and without any external dispersant added.

The microstructural characterization of the PANABA/PSMAC/PS nanoblends was carried out by means of SEM. As shown in Figure 6, the micrographs revealed a quite homogeneous morphological appearance. Evidently, the homogeneous formation of the nanoblends of PANABA in the PSMAC and PS occurred, and the presence of polymeric agglomerates was not observed in the obtained nanoblend structures.

Films of the PANABA/PSMAC/PS nanoblends were obtained by evaporation of the organic solvent from a homogeneous coating solution on the surface of a glass plate. Digital photographs of the obtained films were taken and are depicted in Figure 7. The photographs show smooth films with a homogeneous structure.
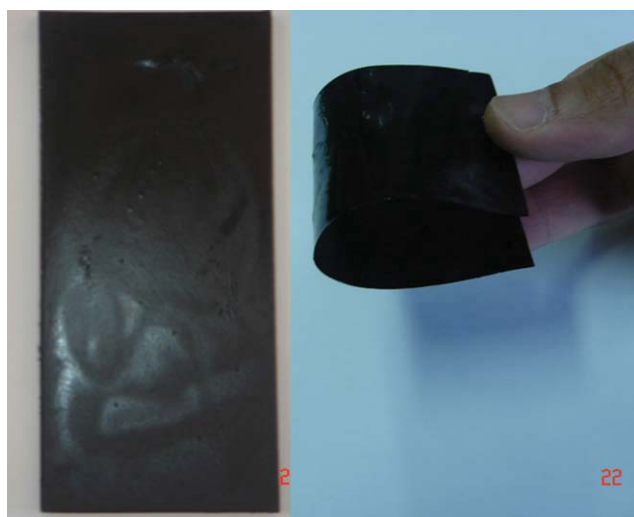

Figure 7 Digital micrographs of the PANABA/PSMAC/PS nanoblend films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

CONCLUSIONS

PANABA nanoparticles were prepared by the oxidative copolymerization of ANI and AC in the presence of ultrasonic irradiation with different molar ratios of the two monomers. PANAB/PSMAC/PS nanoblends were prepared with a solution blending method with various ratios of the components. With only a mixing procedure and without any dispersant added, the PANABA nanoparticles were dispersed well in the matrix polymer, as indicated by SEM images. We obtained nanoblends with good homogeneity and conductivity. Also, the obtained nanoblends formed films with good homogeneity and flexibility. The results of the experiments showed that the conductivity of the nanoblend increased with increasing PANABA and PSMAC content in a nanoblends structure.

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