

# Synthesis, Characterization, and Comparison of Self-Doped, Doped, and Undoped Forms of Polyaniline, Poly(*o*-anisidine), and Poly[aniline-*co*-(*o*-anisidine)]

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**ABSTRACT:** Polyaniline (PANI), poly(*o*-anisidine), and poly[aniline-*co*-(*o*-anisidine)] were synthesized by chemical oxidative polymerization with ammonium persulfate as an oxidizing reagent in an HCl medium. The viscosities, electrical conductivity, and crystallinity of the resulting polymers (self-doped forms) were compared with those of the doped and undoped forms. The self-doped, doped, and undoped forms of these polymers were characterized with infrared spectroscopy, ultraviolet–visible spectroscopy, and a four-point-probe conductivity method. X-ray diffraction characterization revealed the crystalline nature of the polymers. The observed decrease in the conductivity of the copolymer and poly(*o*-anisidine) with respect to PANI was attributed to the incorporation of the methoxy moieties into the PANI chain. The homopolymers attained conductivity in the range of  $3.97 \times 10^{-3}$  to 7.8 S/cm after doping with HCl. The conductivity of the undoped forms of the poly[aniline-*co*-(*o*-anisidine)] and poly(*o*-anisidine) was observed to be

lower than  $10^{-5}$  J/S cm<sup>-1</sup>. The conductivity of the studied polymer forms decreased by the doping process in the following order: self-doped → doped → undoped. The conductivity of the studied polymers decreased by the monomer species in the following order: PANI → poly[aniline-*co*-(*o*-anisidine)] → poly(*o*-anisidine). All the polymer samples were largely amorphous, but with the attachment of the pendant groups of anisidine to the polymer system, the crystallinity region increased. The undoped form of poly[aniline-*co*-(*o*-anisidine)] had good solubility in common organic solvents, whereas doped poly[aniline-*co*-(*o*-anisidine)] was moderately crystalline and exhibited higher conductivity than the anisidine homopolymer. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 2182–2192, 2006

**Key words:** conducting polymers; infrared spectroscopy; solution properties; UV-vis spectroscopy; X-ray

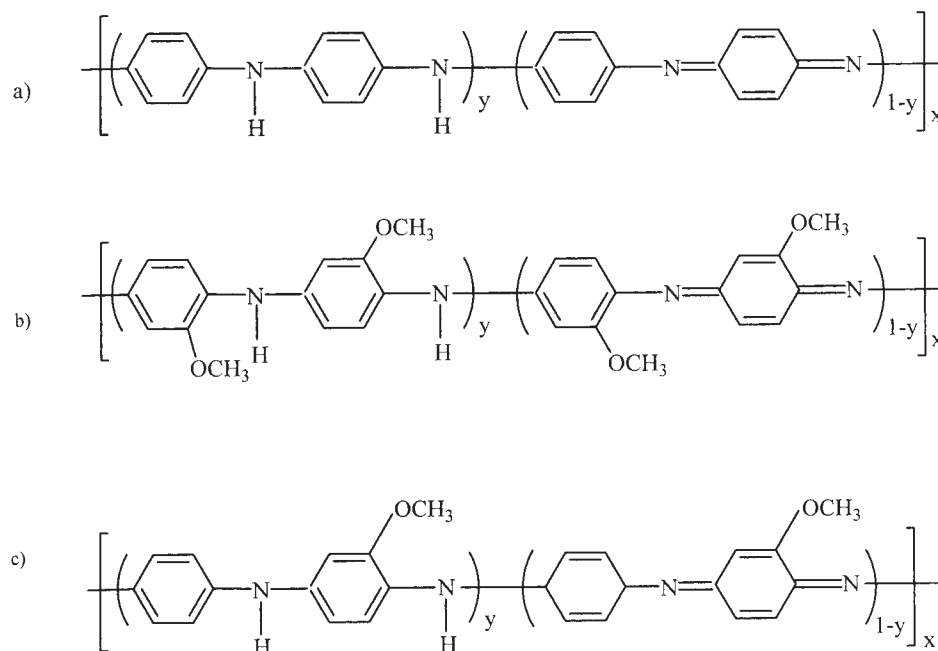
## INTRODUCTION

The discovery of intrinsically conductive polymers (ICPs), such as polypyrrole, polyacetylene, polythiophene, and polyaniline (PANI), is unique in that it has provided possible substitutes for metallic conductors and semiconductors. Efforts to produce tailor-made polymers with respect to the electrical, mechanical, optical, and thermal properties have been pursued by several research groups.<sup>1</sup> ICPs have been intensively studied in the last years because of their potential applications in several electronic, electrochromic, and photoelectrochemical devices,<sup>2–4</sup> rechargeable batteries,<sup>2,5,6</sup> smart windows,<sup>6</sup> sensors,<sup>7</sup> light-emitting diodes<sup>8,9</sup> and nonlinear optical devices.<sup>10</sup> Furthermore, PANI, poly(*o*-anisidine), and poly[aniline-*co*-(*o*-ansi-

dine)] have been extensively studied for devices operated by solar energy because of their photoelectrochemical properties,<sup>11</sup> for the protection of corrosion and memory storage in computers because of their electrochromic properties,<sup>12</sup> for the coating of floppy disks with low surface resistance,<sup>13</sup> for sensors in bioelectrochemical devices,<sup>14</sup> and so forth.

These materials exhibit high conductivities, and some of them exhibit good environmental stability. However, their practical use has been hampered by the fact that many of these conjugated polymers are insoluble and infusible because of the delocalized  $\pi$  bonds along their macromolecular chains. One way of eliminating this disadvantage is to produce composites and copolymer in which the conductive polymer constitutes the conductive component and the insulating polymer component contributes to the flexibility.<sup>15</sup> PANI is commonly called the most stable material within the class of conducting polymers.<sup>16–19</sup> However, the commercial exploitation of most of the applications based on PANI is closely linked to the ease

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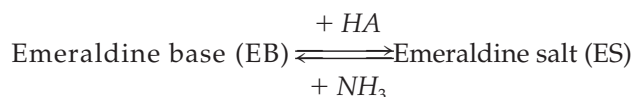


**Scheme 1** Schematic representation of (a) PANI, (b) poly(*o*-anisidine), and (c) poly[aniline-*co*-(*o*-anisidine)].

of its processability. This processability can be enhanced either by a substitution into the aromatic nucleus or by copolymerization in such a way that there is variation in the torsion angle between the adjacent phenyl rings of the polymer. Comprehensive efforts have been made toward the copolymerization of aniline monomers by some workers to improve the processability of the polymer.<sup>20,21</sup> Pandey et al.<sup>22</sup> synthesized poly[aniline-*co*-(*o*-anisidine)] and compared the physicochemical properties (electrical conductivity, glass-transition temperature, composition temperature, and solubility) of this polymer with those of PANI and poly(*o*-anisidine).<sup>22</sup> The copolymerization of the PANI system gives rise to a lower electrochromic response with enhanced electrochemical stability.<sup>23</sup> Recently, the solubility of poly(*o*-anisidine) and its *K* and *a* constants of the Mark–Houwink equation were investigated.<sup>24</sup>

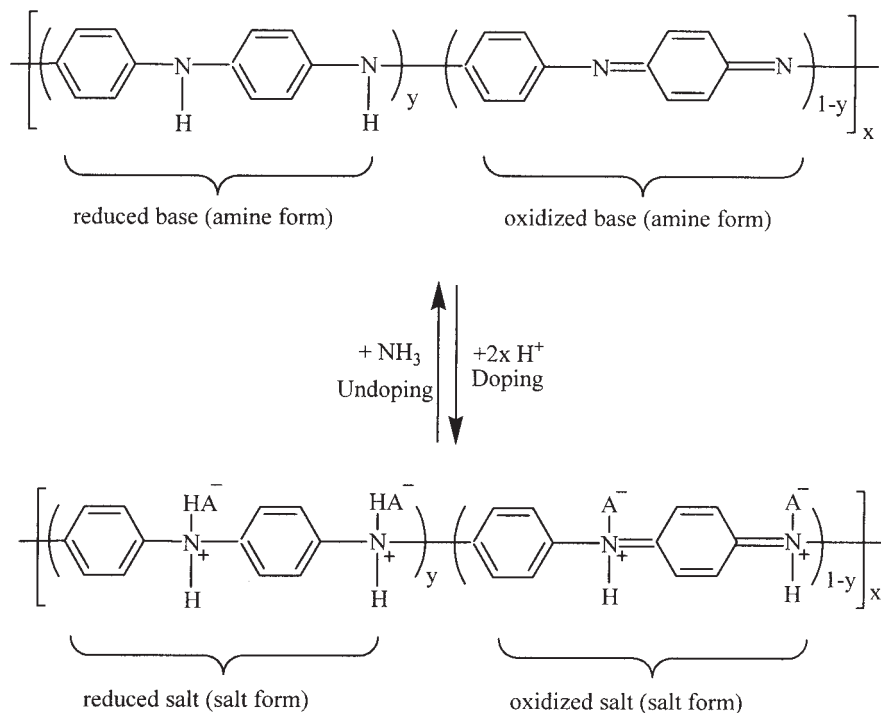
Keeping this in mind, we have synthesized PANI, poly(*o*-anisidine), and poly[aniline-*co*-(*o*-anisidine)]. The synthesized homopolymers and copolymers of aniline and anisidine in their self-doped, doped, and undoped forms and their physical (yield, color, and solubility) and chemical properties were investigated with Fourier transform infrared (FTIR), ultraviolet–visible (UV–vis), X-ray diffraction (XRD), and electrical conductivity and viscosity measurements. Synthesized PANI, poly(*o*-anisidine), and poly[aniline-*co*-(*o*-anisidine)] conductive polymer structures are shown in Scheme 1.<sup>17</sup> PANI has different forms that may be interconverted by an acid–base treatment or oxidation–reduction process. Scheme 2 shows a schematic

representation of the doping and undoping process of synthesized PANI in this study. As can be seen easily in Scheme 2, the interconversion of the emeraldine base (EB; undoped agent) to the emeraldine salt (ES; doped agent),  $A^-$ , is a dopant anion. The emeraldine state is the half-oxidized state of PANI. If  $0 \leq y \leq 1$ , EB can be doped:



Solid doped forms of PANI, poly(*o*-anisidine), and poly[aniline-*co*-(*o*-anisidine)] in the oxidation state are in the bipolaron (dianion), predominantly polaron (radical anion), or soliton pair forms<sup>25,26</sup> (Scheme 3). The delocalization of bipolarons and conversion to polarons will be dependent on the sequencing of the oxidized and reduced groups.

It has been postulated that an electron added to polyacetylene by doping goes not into the conduction band but into an intermediate electronic state within the band gap. The product of the reduction is a radical anion, with the intergap energy states occupied by the two electrons from one  $\pi$  bond and the electron added by reduction. This state is known as a polaron. The addition of a second electron to the same site yields a dianion, which is called a bipolaron. The bipolaron contains no unpaired electrons, but its energy levels in the band gap allow facile jumps of electrons into the conduction band. Conduction pathways are thus generated without the presence of semipermanent free-



Scheme 2 Doping and undoping process of PANI.

electron states. A soliton is a structure that provides an alternative mechanism of conduction via defects, and it is located at defect sites of unpaired electrons.<sup>26</sup>

PANI initially has a low doping degree because of polaron formation in an oxidized form. During polymerization steps, the doping degree of the polymer is enhanced, with bipolaron formation. The presence of polarons and bipolarons requires a counteranion (or dopant) for charge compensation.

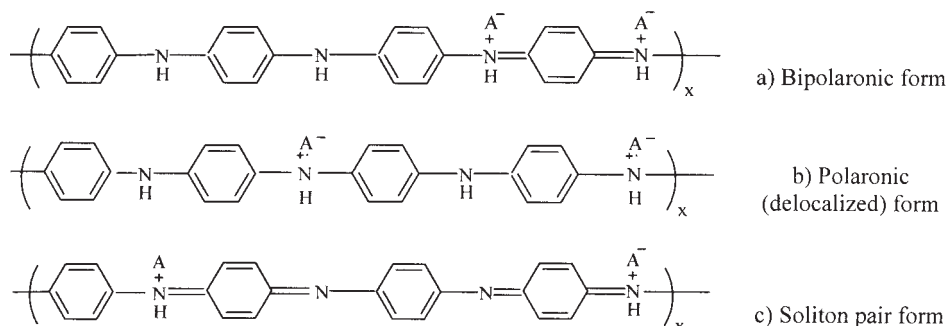
## EXPERIMENTAL

### Synthesis of self-doped polyaniline, poly(*o*-anisidine), and poly[aniline-*co*-(*o*-anisidine)]

All reagents were supplied by Merck (extrapure) and were used without further purification. Self-doped

polymers were synthesized by the chemical oxidative polymerization of aniline and *o*-anisidine in aqueous acidic media (HCl) with ammonium peroxydisulfate [(NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> or APS] as an oxidizing agent according to the procedure described by MacDiarmid and Epstein<sup>27</sup> and modified by Pron et al.<sup>28</sup> for PANI. It has been reported<sup>17</sup> that APS is most extensively used and the yield, elemental composition, conductivity, and degree of oxidation of the resulting polymer are essentially independent of the value of the initial aniline/APS molar ratio, *r*, when *r* ≤ 1.15.<sup>29</sup> The normalized *o*-anisidine/oxidizing agent ratio, *k*, was calculated according to the following formula:<sup>28</sup>

$$k = \frac{2.5}{n_e} \frac{n_{\text{monomer}}}{n_{\text{oxidant}}} = 2.5 \frac{r}{n_e}$$



Scheme 3 Reduction (doping) of PANI to form a polaron, a bipolaron, and a soliton pair.

where  $n_{\text{monomer}}$  is the number of moles of monomer,  $n_{\text{oxidant}}$  is the number of the oxidizing agent (APS), and  $n_e$  is the number of electrons required to reduce one molecule of the oxidizing agent.

PANI ( $k = 1.25, r = 1$ ) was synthesized with 9.13 mL of aniline (density ( $\rho$ ) = 1.02 g/cm<sup>3</sup>) and was dissolved in 100 mL of 1.5M HCl, and the mixture was cooled below  $-5^\circ\text{C}$  with an ice bath. A precooled solution of 22.8 g (0.1 mol) of APS in 100 mL of 1.5M HCl was added dropwise under vigorous stirring for 80 min. Then, the reaction mixture was left in the bath under stirring for 4 h. The precipitated polymer was filtered and washed with 1.5M HCl, and the sample was dried at room temperature until a constant mass was reached.

Poly(*o*-anisidine) ( $k = 1.25, r = 1$ ) was synthesized with 11.3 mL of *o*-anisidine ( $\rho = 1.09$  g/cm<sup>3</sup>), which was dissolved in 100 mL of 1.5M HCl and 22.8 g (0.1 mol) of APS in 100 mL of 1.5M HCl, according to the procedure described previously.

The preparation procedure of the aniline/*o*-anisidine (50/50) copolymer was as follows. Poly[aniline-*co*-(*o*-anisidine)] ( $k = 1.25, r = 1$ ) was synthesized by the dissolution of 9.13 mL of aniline and 11.3 mL of *o*-anisidine in 100 mL of 1.5M HCl separately and then 45.6 g of APS in 100 mL of 1.5M HCl, and the aforementioned procedure was followed.

The self-doped term is described with a procedure involving polymerization in the presence of an acid (with HCl). That is, the polymer that was obtained in the presence of an acid in the system during polymerization was partially doped. Therefore, the predoping process was done automatically. The second doping process was external doping.

#### Doping of the synthesized polymers (formation of ES)

The polymer (1 g,  $\sim 0.01$  mol of repeated units) was powdered and placed in a round-bottom flask. A certain amount of HCl (4–5 mol of the doping agent/mol of the repeat unit) was dissolved in 100 mL of distilled water. The solution was added to the polymer, and the mixture was slowly stirred for 24 h at room temperature. It was then filtered and left to dry at room temperature and was stored in a desiccator.

#### Undoping of the synthesized polymers (formation of EB)

A sample of the doped polymer was converted to the base form by a treatment with an aqueous NH<sub>4</sub>OH solution (10%,  $\sim 8M$ ) for 4 h at room temperature. Then, the mixture was filtered, dried at room temperature, and stored in desiccators.

#### Characterization of the solubility of PANIs

The solubility of the polymers was evaluated with the following method. A powder polymer sample (20 mg) was added to 10 mL of a solvent [dimethyl sulfoxide (DMSO) and *N*-methyl-2-pyrrolidone] and dispersed thoroughly. After the mixture was swayed continuously for 24 h at room temperature, the solubility of the polymers was characterized.

#### Measurements of the intrinsic viscosity ( $[\eta]$ ) values

The self-doped, doped, and undoped polymer samples were dissolved in DMSO. The dynamic viscosity measurements were performed at  $25^\circ\text{C}$  with an Ubbelohde type capillary viscometer. The temperature of the thermostat was controlled within a range of  $\pm 0.1^\circ\text{C}$ , and the flow times were measured with a digital accuracy of  $\pm 0.1$  s. The dynamic viscosities were always measured 20 h after the preparation of the solutions. The concentration ( $c$ ) dependence of the viscosity results of the dilute polymer solutions ( $c = 0.03$ – $0.06$  g/dL) was followed.  $[\eta]$  was calculated according to the Solomon–Ciuta equation:<sup>30</sup>

$$[\eta] = 2(\eta_{\text{sp}} - \ln \eta_{\text{rel}})^{1/2} / c$$

where  $\eta_{\text{sp}}$  is the specific viscosity and  $\eta_{\text{rel}}$  is the relative viscosity.

#### Electrical conductivity measurements

For the electrical conductivity measurements, pellets of PANI, poly(*o*-anisidine), and poly[aniline-*co*-(*o*-anisidine)] were prepared. The pellets were squeezed between four stainless steel electrodes with a 1-cm<sup>2</sup> area and were tightly mounted on a copper sample holder. An HP 740B standard voltage source was used to apply between  $5 \times 10^{-5}$  and 0.294 V to the electrodes, and the current was measured with a Keithley 6512 electrometer. The electrical conductivities [ $\sigma$  (S/cm)] of PANI, poly(*o*-anisidine), and poly[aniline-*co*-(*o*-anisidine)] were recorded at room temperature:

$$\sigma = \frac{\ln 2}{\pi \ell} \frac{I}{V}$$

where  $I$  is the current (A),  $V$  is the voltage (V), and  $\ell$  is the thickness of the pellet (cm).

#### UV–vis spectroscopy studies

The optical absorption spectra in the UV–vis range (270–700 nm) were studied with a Shimadzu 100 double-beam UV–vis spectrophotometer (Hitachi, Osaka, Japan).

TABLE I  
Some Physical Properties of Polyaniline, Poly(*o*-anisidine), and Poly[aniline-*co*-(*o*-anisidine)]

Copolymer poly(anisidine) poly(aniline)	% yield	[ $\eta$ ] (dL/g) <sup>a</sup>	Powder color <sup>b</sup>	Solubility <sup>c</sup> and solution color <sup>b</sup>	
				in NMP	in DMSO
Self-doped	32.6	—	dg	Slightly soluble, lg	Slightly soluble, lg
Doped	3.23	—	bb	Slightly soluble, lg	Slightly soluble, lg
Undoped	10.7	0.184	lc	Partially soluble, db	Partially soluble, db
Self-doped	27.5	0.359	dg	Partially soluble, lb	Soluble, db
Doped	2.58	0.399	bb	Partially soluble, bb	Partially soluble, bg
Undoped	8.51	0.343	lc	Soluble, db	Soluble, db
Self-doped	7.96	0.234	dg	Partially soluble, dg	Partially soluble, dg
Doped	2.03	0.421	bb	Partially soluble, dg	Partially soluble, dg
Undoped	6.70	0.353	lc	Soluble, db	Soluble, db

<sup>a</sup> Intrinsic viscosity in DMSO at 25 °C.

<sup>b</sup> Powder and solution color: bb, brownish black; bg, bluish green; db, dark blue; dg, dark green; lb, light blue; lc, lustrous copper; lg, light green.

<sup>c</sup> sol > 0.2 g/100 mL  $\Rightarrow$  soluble, 0.1–0.2 g/100 mL  $\Rightarrow$  partially soluble, >0.1 g/100 mL  $\Rightarrow$  slightly soluble.

### FTIR spectroscopy studies

FTIR spectra of thin coatings of PANI, poly(*o*-anisidine), and poly[aniline-*co*-(*o*-anisidine)] on KBr pellets were recorded with a Nicolet 510 spectrometer (Madison, WI) in the 4000–400-cm<sup>-1</sup> range, in which 30 scans were taken at a 4-cm<sup>-1</sup> resolution.

### XRD studies

The powder diffraction patterns of the synthesized samples were recorded with a Philips manual spectrogoniometer (The Netherlands) with Cu K $\alpha$  radiation [wavelength ( $\lambda$ ) = 1.54184 Å] over the range of 5°  $\leq$  2 $\theta$   $\leq$  50° (where  $\theta$  is one-half the angle of deviation of the diffracted rays from the incident X-rays). The degree of crystallinity ( $X_c$ ) of the new products was determined with the area ratio method:

$$X_c = \frac{\int_0^\infty s^2 I_c(s) ds}{\int_0^\infty s^2 I(s) ds}$$

where  $s$  is the magnitude of the reciprocal-lattice vector and is given by  $s = (2 \sin \theta) / \lambda \theta$ ,  $I(s)$  is the intensity of X-ray scattering coherent from a specimen (both crystalline and amorphous), and  $I_c(s)$  is the intensity of X-ray scattering coherent from the crystalline region. With this method, the areas of the amorphous and crystalline parts of the patterns were calculated.

## RESULTS AND DISCUSSION

### Polymerization and physical properties

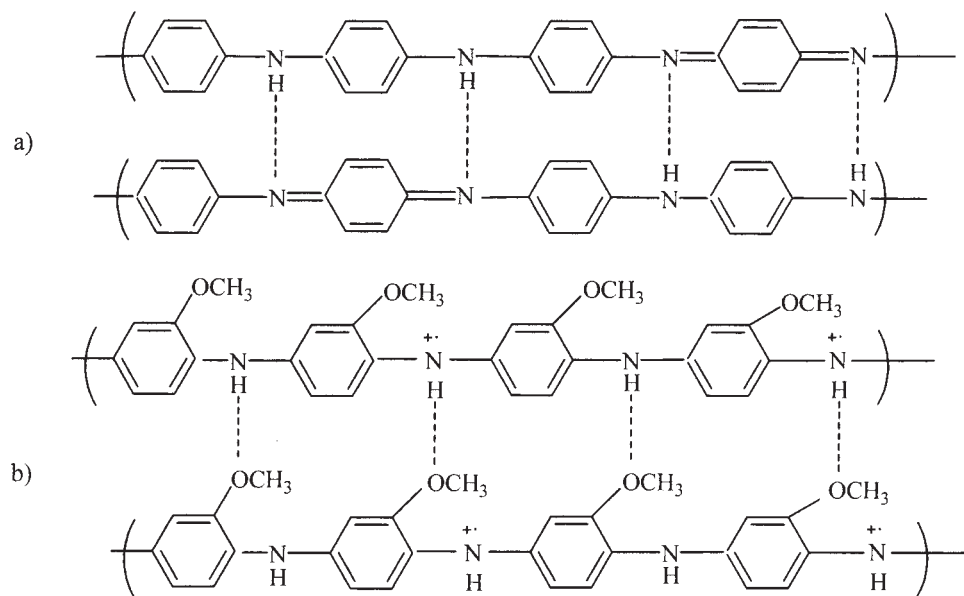
The nature of the medium, concentration of the oxidant, duration of the reaction, temperature of the medium, and dropping time of the oxidant were the same in all

the polymerization processes. The properties of the prepared conductive polymers were enormously influenced by the self-doped, undoped, and doped forms.

Table I summarizes the polymerization yields, color solubility, and [ $\eta$ ] values of PANI, poly(*o*-anisidine), and poly[aniline-*co*-(*o*-anisidine)] in their doped, self-doped, and undoped forms.

### Yield

The polymerization yield of the self-doped homopolymers was the higher than that of the copolymer. The doped forms of PANI, poly(*o*-anisidine), and poly[aniline-*co*-(*o*-anisidine)] had lower yields, whereas the self-doped and undoped forms gave higher yields. In a comparison of the self-doped form of PANI with poly(*o*-anisidine), the polymerization yield was higher for the former than the latter. This can be explained by the bulky side group at the ortho position. The —OCH<sub>3</sub> groups gave chain mobility to the homopolymer and reduced its yield. Regular —NH groups of PANI increased the yield of the polymer. Similar results were observed for meta-substituted aniline.<sup>31</sup> This may be attributed to the bulky side group at the position, which hindered polymerization at the 4-position, leading to more twisted polymer chains of low molecular weights, which had been washed off by ethanol. This is supported by the results of Leclerc et al.,<sup>31</sup> who compared the polymerization yields of a pair of ortho- and meta-substituted isomers. The polymerization yields of this series of copolymer was rather low with respect to the homopolymers. In poly[aniline-*co*-(*o*-anisidine)], the presence of —OCH<sub>3</sub> and —NH groups on the side chains of the copolymer may have facilitated intermolecular bonding between the monomers, which may have further impeded polymerization. The yield of self-doped forms was



**Scheme 4** Intermolecular hydrogen bonds: (a) PANI (undoped form) and (b) poly(*o*-anisidine) (doped form).

higher than that of doped and undoped forms. Reduced and oxidized base forms of the self-doped structure for all polymer samples provided the right convenience for polymerization. In the doped form, the doping process forced the polymerization to regularity, so the yields of the polymers were lower than those of the self-doped forms. Similarly to the self-doped form, the undoped form of the polymer facilitated polymerization and increased the yield.

### Color

All self-doped powder forms of PANI, poly(*o*-anisidine), and poly[aniline-*co*-(*o*-anisidine)] were dark green; the doped forms were brownish-black, and the undoped forms were reflective, lustrous, and copper. Dark blue was characteristic of EB formed by the deprotonation of nitrogen atoms from ES with an alkali solution. Because of a solvatochromic effect, a light blue solution of poly(*o*-anisidine) in NMP became dark blue in DMSO.

### Solubility

In this study, PANI, poly(*o*-anisidine), and poly[aniline-*co*-(*o*-anisidine)] were classified as soluble, partially soluble, and slightly soluble in polar solvents with a hydrogen-bonding nature, such as NMP and DMSO. As can be seen in Table I, the solubility of the polymers was strongly influenced by the doping form. In comparison with the self-doped and doped polymers, all the undoped polymers had much better sol-

ubility in DMSO and NMP because of the disordering of the polymer chain regularity.

PANI, poly(*o*-anisidine), and poly[aniline-*co*-(*o*-anisidine)], especially in the doped states, are considered intractable materials. The doped forms of PANI, poly(*o*-anisidine), and poly[aniline-*co*-(*o*-anisidine)] are not soluble in common organic solvents because of their chain stiffness.<sup>32</sup> The doped forms of PANI, poly(*o*-anisidine), and poly[aniline-*co*-(*o*-anisidine)] are insoluble; protonation together with the accompanying chloride dopant anion will occur at the imine ( $\text{—N=}$ ) sites to produce bipolarons. Their delocalization and conversion to polarons will be dependent on the sequencing of the oxidized and reduced groups.

The absence of solubility in the doped forms of the polymer samples could be considered evidence of hydrogen-bonding formation within the  $\text{—OCH}_3$  groups of the anisidine and  $\text{—NH}$  groups of the aniline. Two possibilities should be taken into account. First, hydrogen bonds can form between amine and imine groups in undoped EB macromolecules [Scheme 4(a)].<sup>33</sup> Second, a hydrogen bond is particularly pronounced in the doped form because the hydrogen atoms attached to the protonated amine or imine nitrogen atoms are made more electropositive [Scheme 4(b)].

Protonation of EB hydrogen bonding is less possible because no imine groups are present in the completely protonated backbone. The conformation of the polymer changes during protonation (from expanded-coil conformation to compact-coil conformation). These changes can be due to an acid excess in the EB solutions and an increase in the ionic strength of the solu-

tions. PANI exhibits a slightly soluble character in the doped form. This can be explained by the steric hindrance of ES of PANI. Self-doped and undoped forms of aniline are much better than the doped form.

Poly(*o*-anisidine) is soluble in common solvents because of its  $-\text{OCH}_3$  groups. When the amount of anisidine in the polymer structure was increased, the solubility of the polymer and copolymer also increased.

The solubility of poly(*o*-anisidine) and poly[aniline-*co*-(*o*-anisidine)] increases with increasing side-chain groups. This gives a chance to diffuse the solvent molecules into the polymer chains and enhances polymer-solvent interactions. Therefore, poly(*o*-anisidine) was more soluble than PANI in NMP. It was estimated that the solubility of the obtained forms of PANI, poly(*o*-anisidine), and poly[aniline-*co*-(*o*-anisidine)] decreased in the following order of doping processes: undoped  $\rightarrow$  self-doped  $\rightarrow$  doped. According to the monomer species, the synthesized polymers showed decreasing solubility in the following order: poly(*o*-anisidine)  $\rightarrow$  poly[aniline-*co*-(*o*-anisidine)]  $\rightarrow$  PANI.

The solubility of the copolymer was strongly influenced by the aniline/anisidine molar ratio. The incorporation of the anisidine unit into the PANI backbone possibly decreased the structural regularity and rigidity of the chains of PANI. In addition, improved solubility with the addition of an anisidine unit into poly(*o*-anisidine) was evidence that the polymerization product was indeed a copolymer containing aniline and anisidine units rather than a simple mixture of two homopolymers.

### Viscosity

Polymer aggregation of the dilute EB form of PANI solutions in polar organic solvents, such as NMP and DMSO, prevented the accurate determination of  $[\eta]$ . Aggregation prevented a full understanding of the colligative and hydrodynamic properties of the polymer.<sup>34</sup>

The  $[\eta]$  values of the polymers decreased with increasing undoped character. The lowest  $[\eta]$  value provided better solubility than the undoped polymers.

The enhancement of  $[\eta]$  may be responsible for the enhancement of the molecular weight of the copolymers and of the rigidity of the copolymer chains. Almost no report on  $[\eta]$  of PANI can be found because PANI is insoluble in most organic solvents. Therefore, it was impossible for us to compare the  $[\eta]$  values of poly[aniline-*co*-(*o*-anisidine)] with PANI. It could be concluded that  $[\eta]$  of the copolymer of aniline with *o*-anisidine was significantly influenced by the monomer ratio. The  $[\eta]$  values of the copolymers decreased with increasing feed aniline content.

**TABLE II**  
Some Characteristic Spectral Bands of PANI,  
Poly(*o*-anisidine), and Poly[aniline-*co*-(*o*-anisidine)]

H bonding	PANI 3050–3255	Poly( <i>o</i> -anisidine) 3278–2930	Poly[aniline- <i>co</i> -( <i>o</i> -anisidine)] 3255–3050
$\nu_{\text{N-H}}$	3201–3263	3502–3587	3787–3818
$\nu_{\text{C-N}}$	1103–1123	1157–1178	1110–1111
$\nu_{\text{C=N}}$	1558	1592–1597	—
$\nu_{\text{C=H}}$	779–787	—	—
$\nu_{\text{N=N}}$	—	1465–1592	—
$\nu_{\text{C-N=}}$	—	1166	—
$\nu_{\text{C-O-C}}$	—	987–1018	—
$\nu_{\text{NH}^+}$	—	—	2415–3726

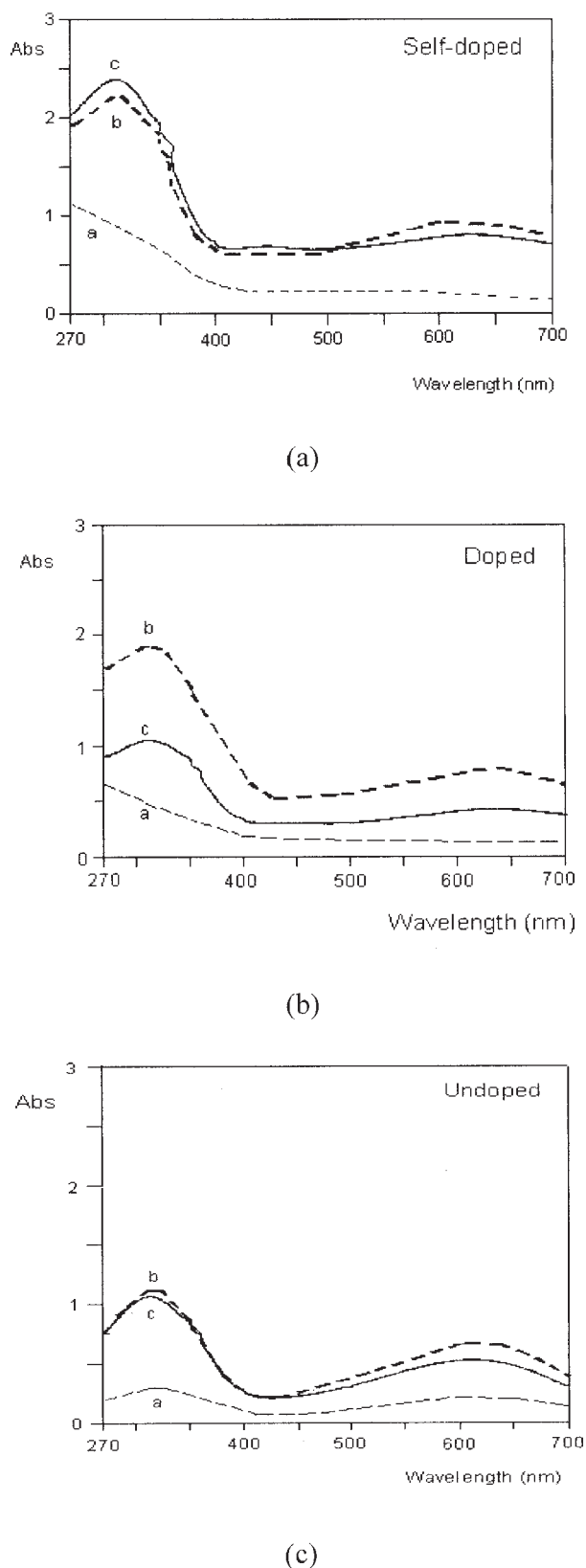
### FTIR spectroscopy studies

Table II represents the FTIR bands observed for PANI, poly(*o*-anisidine), and poly[aniline-*co*-(*o*-anisidine)]. The results given in Table II demonstrate some distinctions of poly(*o*-anisidine) from PANI. For example, the bands at 980–1018 and 1190  $\text{cm}^{-1}$  represent the signal from the methoxy of anisidine. The peak at 1592  $\text{cm}^{-1}$  is due to the  $-\text{C}=\text{C}-$  double band of quinoid rings (signal from undoped forms), whereas the peak at 1466–1490  $\text{cm}^{-1}$  arises because of the vibration of the  $-\text{C}=\text{C}-$  double band associated with the benzenoid ring.

Furthermore, the broad bands obtained at 2900–3310  $\text{cm}^{-1}$  lead to the formation of the hydrogen bond (in the undoped forms of the polymers). This is confirmed by the FTIR measurements summarized in Table II. Besides, the increment of the band intensity at 780  $\text{cm}^{-1}$  and the splitting of the band at 1500  $\text{cm}^{-1}$  are attributed to the combination of  $-\text{C}=\text{N}$  and  $-\text{C}-\text{N}$  bonds in the quinoid and benzenoid sequences in the undoped form.

At 671 and 486  $\text{cm}^{-1}$ , the bands belong to ES. Concomitantly, new bands formed at 586 and 509  $\text{cm}^{-1}$  are the characteristics of EB, and this is the evidence for the occurrence of deprotonation.

It is clear from Table II that the copolymer exhibited two additional peaks at 1265 and 1002  $\text{cm}^{-1}$  in the FTIR spectra of all the self-doped, doped, and undoped forms of PANI, poly(*o*-anisidine), and poly[aniline-*co*-(*o*-anisidine)]. This fact suggests that the synthesized polymer was a copolymer and not a mixture of homopolymers. In the FTIR spectra of the copolymer, there appeared absorption bands at 1249 and 1265  $\text{cm}^{-1}$ , indicating the existence of a methoxy group on a benzene ring. The relative intensity of 1600–1500  $\text{cm}^{-1}$  is between those of poly(*o*-anisidine) and PANI, and so the coexistence of anisidine and aniline units in the copolymer was further confirmed.



**Figure 1** Absorption spectra of doped, self-doped, and undoped forms of polymer solutions in DMSO: (a) poly[aniline-*co*-(*o*-anisidine)], (b) poly(*o*-anisidine), and (c) PANI.

### UV-vis spectroscopy studies

UV-vis spectra of the polymer samples were recorded at room temperature and are shown in Figure 1. The UV-vis spectra of PANI, poly(*o*-anisidine), and poly[aniline-*co*-(*o*-anisidine)] in DMSO show an absorption band at 310 nm, a small shoulder between 330 and 360 nm, and another weak broad peak around 600 nm.

This first one corresponds to the  $\pi \rightarrow \pi^*$  transition and  $n \rightarrow \pi^*$ . The second shoulder peak can be ascribed the polaron band,<sup>16</sup> which is still evident because of the incomplete undoping, and it increased in the self-doped PANI, poly(*o*-anisidine), and poly[aniline-*co*-(*o*-anisidine)]. The third one at 600 nm can be attributed to the exciton transition, which was rather weak in these polymers. After doping with HCl, the  $\pi \rightarrow \pi^*$  transition band shifted to a higher energy form and a shorter wavelength of 390 nm, whereas the 600-nm band increased slightly. The  $\lambda_{\max}$  values of the polymers were located at 300 nm and were close to each other.

The continuous variation of the wavelength and intensity of the UV-vis bands may have resulted from the copolymerization effect of anisidine and aniline. In other words, the polymer formed by the oxidative polymerization of anisidine with aniline was the copolymer of two monomers rather than a mixture of two homopolymers.

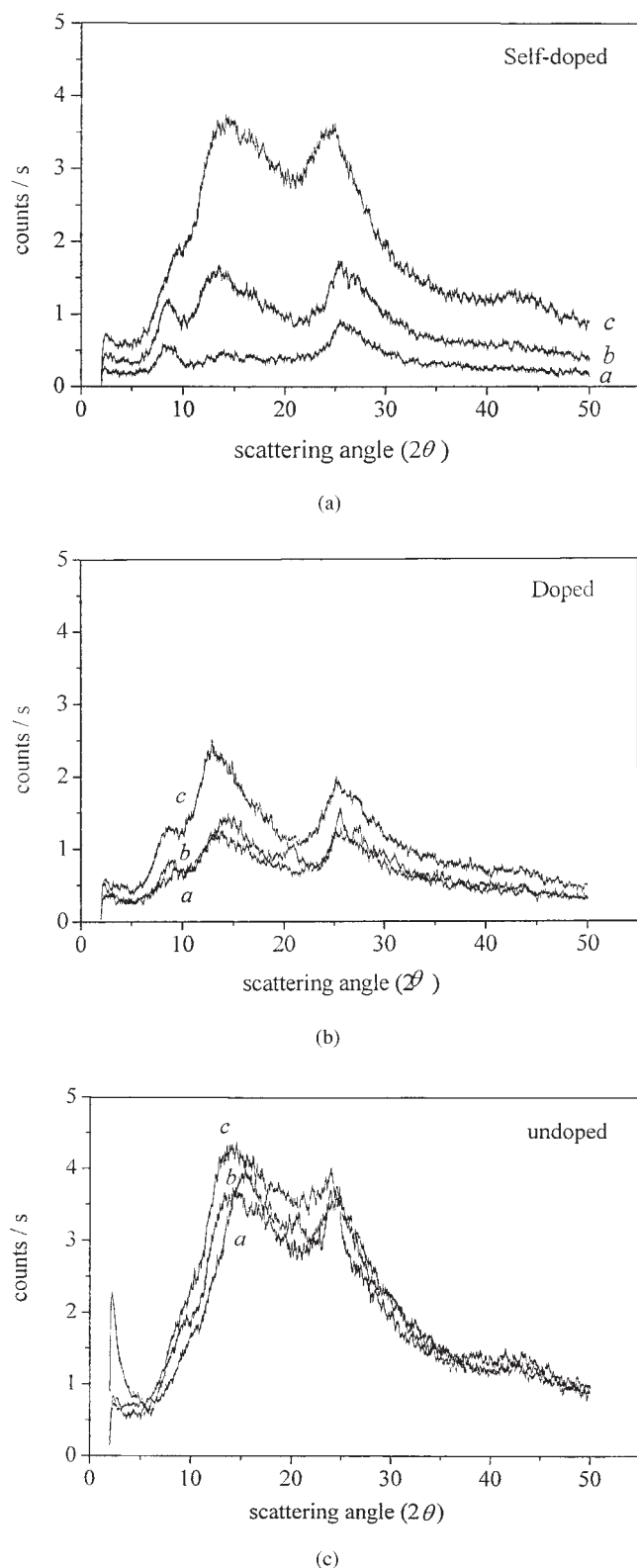
A hydrogen bond could form between amine and imine groups in the undoped EB macromolecules. Therefore, the undoped form solutions demonstrated a hyperchromic effect. Upon the protonation of EB, hydrogen bonding was less possible because no imine groups were present in the full protonated backbone.

### XRD studies

XRD of the self-doped, doped, and undoped homopolymers and copolymer in powder forms revealed that the crystallinity of the doped and self-doped polymers<sup>31</sup> was enhanced with respect to the undoped polymers (Fig. 2). These features were also confirmed by the conductivity behavior of the polymers.

As can be seen in Figure 2, the PANI, poly(*o*-anisidine), and poly[aniline-*co*-(*o*-anisidine)] samples had different XRD patterns. The ratio of the crystalline component to the amorphous one changed because of the different  $X_c$  values. The doped homopolymer of the aniline powder showed a crystalline structure. Indeed, some investigations by Lux<sup>35</sup> have supported a correlation between the crystalline arrangements in powders of aniline oligomers and polymers.  $X_c$  of self-doped poly[aniline-*co*-(*o*-anisidine)] was higher than that of the homopolymers. In addition, pure





**Figure 2** XRD pattern of the doped, self-doped, and undoped polymer powders: (a) poly[aniline-co-(*o*-anisidine)], (b) poly(*o*-anisidine), and (c) PANI.

**TABLE III**  
 $X_c$  of PANI, Poly(*o*-anisidine), and Poly[aniline-co-(*o*-anisidine)]

Polymer sample	$X_c$ (%)		
	Self-doped	Doped	Undoped
PANI	19	22	14
Poly( <i>o</i> -anisidine)	19	17	13
Poly[aniline-co-( <i>o</i> -anisidine)]	24	20	8

doped PANI powder exhibited an  $X_c$  value corresponding to that of other doped polymers.

The  $X_c$  values of the self-doped, doped, and undoped polymers are given in Table III. The crystallinity was greatly enhanced by intra- and intermolecular intersections that were explained by hydrogen bonding.<sup>36</sup> It is possible that increasing the polarity could help hydrogen-bond formation because of the —OCH<sub>3</sub> and NH groups of the aniline and *o*-anisidine monomers. Therefore, high crystallinity was obtained for the self-doped copolymer. The higher crystallinity of the self-doped forms could be explained by the salt effect of ES. The actual crystallinity was slightly higher than that generated by ES because of the additional ions provided by the salt. The doping process also gave higher  $X_c$  values to all the homopolymer and copolymer samples.<sup>37</sup>

### Electrical conductivity

The electrical conductivity properties are tabulated in Table III. As indicated in Table III, in the doped form, all the polymer powders were highly conductive, whereas the undoped state of the polymers had a low conductivity level:

Emeraldine base (insulator)  $\rightleftharpoons$

Emeraldine salt (conductor)

ES is a stable, delocalized polysemiquinone radical cation with a half-filled polaron conduction band and is accompanied by an increase in the conductivity. The electrical conductivity depends mainly on the number and mobility of the charge carriers and can be correlated with the chemical composition and morphology; the type, the extent of the crystallinity, and the tacticity each play a role in evaluating the electrical properties of polymers.<sup>37</sup>

The electrical conductivity of PANI was higher than that of the other polymers in their self-doped and doped forms. Poly(*o*-anisidine) had lower electrical conductivity in its self-doped, doped, and undoped forms with respect to PANI.

The preparation of the copolymer with PANI enhanced the electrical conductivity of the copolymer.<sup>16</sup>

**TABLE IV**  
**Electrical Conductivity ( $\sigma$ ) at Room Temperature**  
**of PANI, Poly(*o*-anisidine), and**  
**Poly[aniline-*co*-(*o*-anisidine)]**

Polymer sample	$\sigma$ (S/cm)		
	Self-doped	Doped	Undoped
PANI	4.13	7.80	$4.38 \times 10^{-5}$
Poly( <i>o</i> -anisidine)	$1.54 \times 10^{-3}$	$3.97 \times 10^{-3}$	$<10^{-5}$
Poly[aniline- <i>co</i> -( <i>o</i> -anisidine)]	0.103	0.148	$<10^{-5}$

The undoped polymers had conductivity lower than  $10^{-5}$  S/cm. However, they were conducting after doping. The long side chain exerted a strong steric effect on the doping process, making it more difficult for HCl to protonate the nitrogen group. The copolymers had higher conductivity than the corresponding poly(*o*-anisidine). The conductivity decreased with an increase in the side group of anisidine. This could have resulted from the decreasing doping level from PANI to poly(*o*-anisidine). Furthermore, it may be that with the bonding of the side group, the distance between the two main chains increased, and this made interchain polaron or bipolaron doping more difficult.

As for the corresponding copolymer besides PANI, the same trend was observed. However, the conductivity of each doped homopolymer was slightly higher than that of the undoped homopolymers.

All the undoped polymer forms had lower crystallinity and lower electrical conductivity. The relationship of the crystallinity and electrical conductivity of the self-doped, doped, and undoped polymers can be seen in Tables III and IV. The electrical conductivity behavior of the polymers was strongly affected by the crystalline nature of the polymer samples. The apparent conductivity of the doped copolymer was reduced to 0.148 S/cm in comparison with that of PANI. The importance of crystallinity as a factor in promoting high conductivity is well exemplified by the fact that the replacement of HCl anions in the doped polymer with chloride ions by simple exchange in aqueous HCl resulted in a considerable retention of crystallinity.

## CONCLUSIONS

A series of self-doped, doped, and undoped forms of PANI, poly(*o*-anisidine), and poly[aniline-*co*-(*o*-anisidine)] were synthesized. The crystallinity, solubility, and electrochromic properties of PANI, poly(*o*-anisidine), and poly[aniline-*co*-(*o*-anisidine)] in these forms were characterized with methods such as FTIR, UV-

vis, XRD, and viscosity and electrical conductivity measurements.

The presence of the  $-\text{OCH}_3$  group facilitated the torsional angle between aniline and *o*-anisidine rings and resulted in better electrochromic properties than those of PANI. With a substituted  $-\text{OCH}_3$  group, the solubility of poly(*o*-anisidine) was increased in common organic solvents. Nevertheless, its conductivity decreased with an increase in the side group. The solubility of PANI in the doped form was less. The conductivity of the undoped forms of poly[aniline-*co*-(*o*-anisidine)] and poly(*o*-anisidine) dropped to zero. The self-doped and doped forms of poly[aniline-*co*-(*o*-anisidine)] appeared to be less conductive but had improved optical properties with respect to PANI. The undoped copolymer showed good solubility in common organic solvents if the doped copolymer was moderately crystalline and semiconducting according to self-monomers.

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