

Synthesis and Characterization of Poly(2-ethylaniline)–Poly(styrenesulfonic Acid) and Poly(*o*-phenetidine)–Poly(styrenesulfonic Acid) Complexes

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ABSTRACT: This research focuses on the synthesis of ethyl and ethoxy substituted polyaniline with poly(styrenesulfonic acid) comprising a poly(*o*-phenetidine)–poly(styrenesulfonic acid) [P(O-P)-PSSA] and poly(2-ethylaniline)–poly(styrenesulfonic acid) [P(2-E)-PSSA]. The complexes P(O-P)-PSSA and P(2-E)-PSSA were prepared by chemical polymerization of monomer (*o*-phenetidine, 2-ethylaniline) with PSSA using an oxidant of ammonium persulfate in 1M HCl solution; polyaniline (PANI), poly(2-ethylaniline) (P2E), poly(*o*-phenetidine) (POP), and polyaniline-poly(styrenesulfonic acid) (PANI-PSSA) also were prepared by chemical polymerization to be the reference samples. The products were characterized by IR, VIS, EPR, water solubility, elemental analysis, conductivity, SEM, and TEM. IR spectral studies shown that the structure of P(2-E)-PSSA and P(O-P)-PSSA complexes is similar to that of polyaniline. EPR and visible spectra indicate the formation of polarons. The mor-

phology of the blend was investigated by measured SEM and TEM, indicating the conducting component and electrically conductive property of the polymer complexes. The pH value for deprotonation [pH \geq 9.5 for P(2-E)-PSSA and pH \geq 8.0 for P(O-P)-PSSA] are higher than that of corresponding HCl salts, indicating an intimate interaction between polymer chains. Elemental analysis results show that P(O-P)-PSSA has a nitrogen-to-sulfur ratio of \sim 52%, larger than that for P(2-E)-PSSA, \sim 41%. The conductivity of the complexes is around 10^{-2} S/cm, and the solubility of P(2-E)-PSSA and P(O-P)-PSSA in water is 2.9 and 1.9 g/L, respectively. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 1198–1205, 2005

Key words: substituted; polyaniline; ethyl; ethoxy; complexes; polymers

INTRODUCTION

Polyaniline finds application in a variety of devices such as secondary batteries and electrochromic devices^{1–4} The low cost of the precursor, aniline, the ease of preparation and doping, and the stability of doped polyanilines in air make polyaniline a conducting polymer of great potential. However, the stiffness of the polymer backbone makes it insoluble in most solvents, especially in the conductive form. Polyaniline synthesized with small inorganic counter ions is an intractable solid. It is insoluble in aqueous and organic solvents and decomposes before reaching the melting point. This can pose a serious hindrance for processing in large-scale industrial production. Improvements in the solubility of polyaniline in common organic solvents were reported in recent years.⁵ A water-soluble complex of polyaniline with poly(styrenesulfonic acid)⁶ shows solubility in water and a high

optical contrast between the reduced and the oxidized forms. They are also more stable toward thermal treatment and have good adhesion properties. These characteristics make them suitable for use in such applications as electrochromic devices. Moreover, an improvement in the solubility properties opens up opportunities for solution processing and blending, thus leading to materials with high electrical conductivity and mechanical strength.^{7,8} The adhesive properties and chemical inertness of poly(styrenesulfonic acid) will make polyaniline blends suitable for conductive coatings.

In this paper, we report the synthesis of substituted polyaniline with polyelectrolyte by chemical polymerization of *o*-phenetidine or 2-ethylaniline with poly(styrenesulfonic acid) (PSSA) using an oxidant of ammonium persulfate. The water solubility characteristics of the products are correlated with their structural features.

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EXPERIMENTAL

Synthesis

The preparation was carried out in 1M HCl solution. First, substituted polyaniline hydrochloride salt:

TABLE I
Preparation Condition of the Substituted Polyaniline Complexes and Their Conductivity

Sample	Concentration(M)			Conductivity (S/cm)
	B	PSSA	APS	
POP	0.003	—	0.003	—
P2E	0.003	—	0.003	—
PANI	0.003	—	0.003	—
P(O-P)-PSSA	0.003	0.003	0.0015	3.8×10^{-2}
P(2-E)-PSSA	0.003	0.003	0.0015	2.4×10^{-2}
PANI-PSSA	0.003	0.003	0.0015	4.7×10^{-2}

Note. B, aniline, *o*-phenetidine, 2-ethylaniline; APS, ammonium persulfate; PSSA, 30% (styrenesulfonic acid) in water.

polyaniline (PANI), poly(2-ethylaniline) (P2E), and poly(*o*-phenetidine) (POP) were prepared, following the procedure employed by MacDiarmid and colleagues.^{9,10} The substituted polyaniline polyelectrolyte complexes of the P2E and POP with PSSA (MW = 70,000, PolyScience) were carried out as follows: ammonium persulfate (Merck) solution was added drop by drop into an aqueous solution containing the monomer (*o*-phenetidine, 2-ethylaniline, or aniline) with PSSA at 25 °C. After all the ammonium persulfate was added the reaction mixture was left for 24 h; the mixture was purified by filtration and then by dialysis (Cellu. Sep. T1 46 mm, pore size 10 Å, MW < 3500) with 0.5M PAA solution (25% polyacrylic acid solution; 8000–12,000 cp; MW = 90,000; Showa Chemicals, Inc.) to remove inorganic ions, monomer, oligomeric polyaniline, and HCl; finally, the samples were dried at 70 °C until a constant mass was reached; the concentration of the reaction ratio is given in Table I.

Characterization

Spectral

FTIR spectra of the complexes were recorded on a Jasco 410 FTIR spectrophotometer by the KBr pellet method; UV-vis spectral data were obtained with a UV-vis spectrophotometer (Jasco 7850); EPR spectra were recorded at 298 and 77 K in air and argon using a EMX-10 (Bruker) EPR spectrometer operating in the X band and equipped with a liquid nitrogen cooled temperature controller.

Solubility

Solubility measurements were carried out by dissolving ethyl and ethoxy substituted polyaniline complexes [P(2-E)-PSSA, P(O-P)-PSSA] in water, suction-filtering the solution through a 0.2- μ m filter membrane, extracting 100 mL of the solutions with a syringe, and drying at 60 °C to a constant weight.

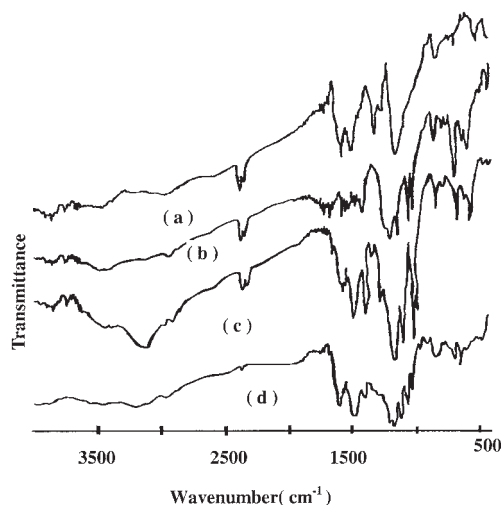


Figure 1 IR spectra of polyaniline complexes (a) PANI, (b) PANI-PSSA, (c) P(O-P)-PSSA, and (d) P(2-E)-PSSA.

Elemental analysis

Elemental analysis was done using a Heraeus CHNOS Rapid F002 Elemental Analyzer (Gemmary) on 5- to 10-mg samples.

Conductivity measurement

The four-probe method was used for the measurement of the conductivity of the sample films; we used a

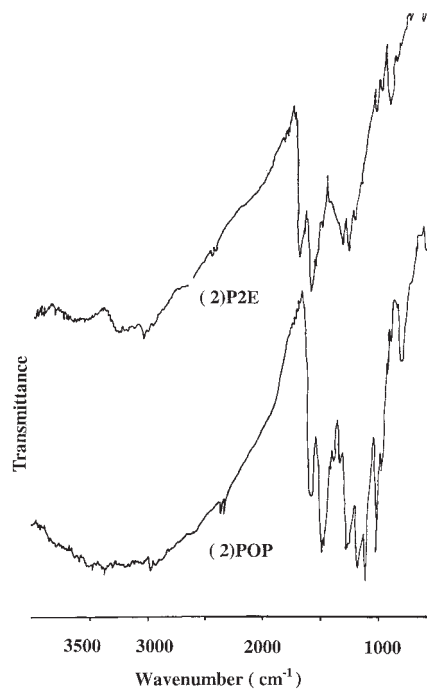


Figure 2 IR spectra of polyaniline salts (1) P2E and (2) POP. Wavelength (nm).

TABLE II
The Maximum UV-Vis Absorption Peaks of the Substituted Polyaniline Complexes

Sample	λ max (nm)		
	Acid form	form	Base form
PANI-PSSA	820	420	553
P(2-E)-PSSA	820	420	580
P(O-P)-PSSA	780	440	620

Keithley Model 238 programmable current source and voltmeter, and error was less than 2%.

Morphology measurement

Transmission electron imaging (TEM) was performed on a JEM-2000 FXII microscope, operated at 160 kV. Scanning electron micrography (SEM) was performed on a Hitachi S-3500 microscope to study the morphology of the conductive fibers at an accelerating voltage of 20 kV and the samples were gold-sputtered prior to observation.

RESULTS AND DISCUSSION

Synthesis

The effect of the molar ratios of the polyacid and oxidizing agent on the monomer by chemical polymerization and conductivity of the substituted polyaniline salts and their poly(styrenesulfonic acid) complexes, P(O-P)-PSSA and P(2-E)-PSSA, are presented in Table I. The chemical polymerization of *o*-phenetidine and 2-ethylaniline with PSSA at a lower temperature (3 °C) minimizes the formation of by-products, which improves the complexes properties; the P(2-E)-

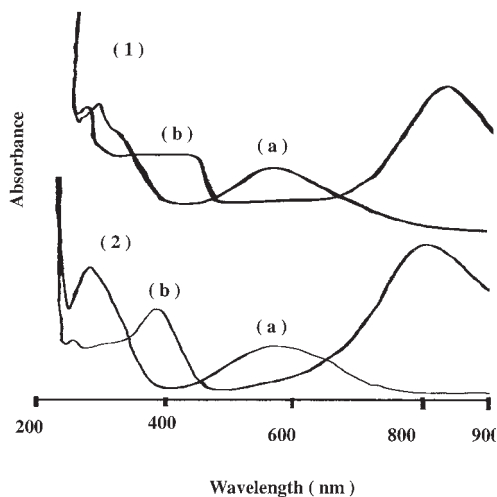


Figure 3 UV-vis spectra of polyaniline complexes (1) P(O-P)-PSSA, (2) P(2-E)-PSSA; (a) acid form and (b) base form.

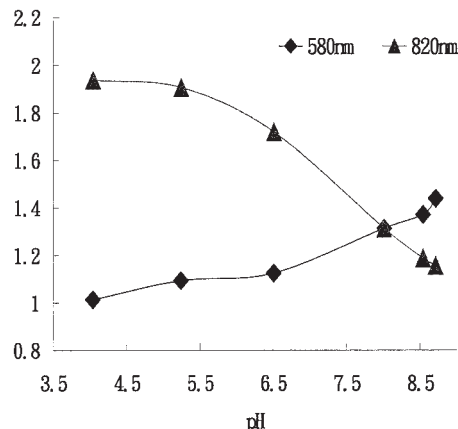


Figure 4 Deprotonation of P(O-P)-PSSA complexes by adding 0.1M NH_3 (aq).

PSSA complexes were easy to synthesis at 25 °C. However, when the ratio of APS to monomer was high, the film cast was fragile; the best synthesis condition for conductivity formation was a PSSA to monomer ratio of 1 and an oxidizing reagent to monomer ratio of 0.5.

Characterization

IR spectra

The infrared spectra of the substituted polyaniline-polyelectrolyte complexes, P(O-P)-PSSA and P(2-E)-PSSA, and their salts are shown in Figures 1 and 2, prepared from *o*-phenetidine and 2-ethylaniline with poly(styrenesulfonic acid) in 1M HCl, respectively; they are very nearly the same, which in turn closely matches the infrared spectrum of the polyaniline base prepared from polyaniline hydrochloride. The IR absorption bands are at $\sim 1600 \text{ cm}^{-1}$ (C = C stretching in the quinoid unit), $\sim 1500 \text{ cm}^{-1}$ (C = C stretching in the benzenoid unit), 1200, 1040, and 1020 cm^{-1} ($-\text{SO}_3\text{H}$), 1100 cm^{-1} (aromatic C-O stretching), and

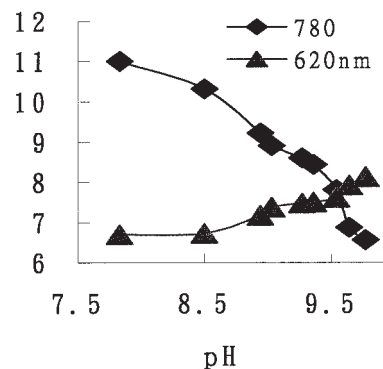


Figure 5 Deprotonation of P(2-E)-PSSA complexes by adding 0.1M NH_3 (aq).

TABLE III
Elemental Analysis of the Substituted Polyaniline Salts and Complexes

Sample	C:	H:	N:	S	Experimental	Theoretical
POP	1	1.13	0.12	0	C ₃₂ H _{36.7} N _{3.8} O _{8.2}	C ₃₂ H ₄₀ N ₄ O ₄
P2E	1	1.06	0.13	0	C ₃₂ H _{33.4} N _{3.2}	C ₃₂ H ₄₀ N ₄
PANI	1	1.08	0.16	0	C ₂₄ H ₂₆ N _{3.7}	C ₂₄ H ₂₀ N ₄
P(O-P)PSSA	N:S:C:H=1:1.93:29.18:45.24				N ₃₆ S ₆₉ C ₁₀₅₁ H ₁₆₂₉ O _{641.7}	N ₃₆ S ₆₉ C ₈₄₃ H ₇₇₆ O ₂₄₄
P(2-E)-PSSA	N:S:C:H=1:2.43:21.55:31.33				N ₂₄ S ₅₈ C ₅₁₇ H ₇₅₂ O _{246.5}	N ₂₄ S ₅₈ C ₆₅₈ H ₅₉₀ O ₁₇₅
PANI-PSSA	N:S:C:H=1:2.65:35.96:50.68				N ₁₆ S ₄₂ C ₅₇₅ H ₈₁₁ O ₆₃	N ₁₆ S ₄₂ C ₄₃₅ H ₃₃₅ O ₁₂₇

930–800 and 770–750 cm⁻¹ (1, 2, 4-trisubstituted phenyl ring).

UV-vis spectra

The UV-vis absorption peaks of substituted polyaniline polyelectrolyte complexes, P(O-P)-PSSA and P(2-E)-PSSA, in water are presented in Table II and Figure 3. The products show absorption peaks at ~420 and ~800 nm in the visible region and an absorption peak at 580–630 nm appeared; the spectral changes indicate the formation of the base form. However, the absorption peak of P(O-P)-PSSA and P(2-E)-PSSA shifts to ~580 nm, indicating a higher oxidation state than in emeraldine salts. Solutions of P(O-P)-PSSA and P(2-E)-PSSA complexes can be chemically doped by acid (1M HCl); and undoped by base [0.1M NH₃ (aq)] to go through the normal sequence of reversible color changes from green to blue. The spectra of P(O-P)-PSSA and P(2-E)-PSSA complexes in aqueous solution show that the doped and undoped forms have the same spectra as the ordinary PANI¹²; this indicates that the substituted polyaniline-poly(styrenesulfonic acid) complexes P(O-P)-PSSA and P(2-E)-PSSA have the same electronic structures as the PANI-PSSA complexes.¹³

Deprotonation

The UV-vis absorption spectra were recorded as the titration of P(O-P)-PSSA and P(2-E)-PSSA with 0.1M NH₃ (aq) progressed; the clear, dark-green solution can change color according to the acid-base reactions; the λ_{max} were ~580 and ~820 nm for P(2-E)-PSSA and ~620 and ~780 nm for P(O-P)-PSSA. The absorbance changed very little during the initial stage of titration

when free HCl or excess sulfonic acid group in the solution was being neutralized; as more base was added, the color changed to blue at pH ~8.0 for P(O-P)-PSSA (Fig. 4) and ~9.5 for P(2-E)-PSSA (Fig. 5). The initial deprotonation was monitored at a wavelength of ~580 nm for P(2-E)-PSSA and ~620 nm for P(O-P)-PSSA; the pH value for deprotonation is higher than that of the HCl salts of substituted polyaniline. The results indicate intimate interactions between the two polymer chains. As more reductant was added to the solution, the absorbance at ~620 nm for P(O-P)-PSSA and ~580 nm for P(2-E)-PSSA increased, and the ~800-nm band leveled off, which indicated that the complexes were close to their fully reduced leuco forms.

The stability of the P(O-P)-PSSA and P(2-E)-PSSA complexes seems to be established by the attractive forces between the secondary amine of substituted polyaniline and the sulfonic acid group of poly(styrenesulfonic acid) within the complexes; complexes P(O-P)-PSSA and P(2-E)-PSSA are soluble in water and are easily dispersed into various coating systems. Direct interaction with reducing agents (1M HCl) should be avoided to minimize loss in conductivity of the P(O-P)-PSSA and P(2-E)-PSSA complexes. Deprotonation of the polyaniline could occur with an organic base such as amine (0.1M NH₃ aqueous).

The P(O-P)-PSSA and P(2-E)-PSSA complexes do not get easily dedoped by either heating¹⁴ or water extraction. A unique feature of polyanilines in the emeraldine oxidation state is that they can be reversibly converted between conductive and insulating forms by an acid/base reaction; emeraldine base is a weak organic base (pK_a ~ 5), which when treated with an acid (1M HCl) of

TABLE IV
Elemental Analyses (N:S Ratio) of the Substituted Polyaniline Complexes and Solubility (in DI Water)

Sample	N:S	(N/S) %	g/L
P(O-P)-PSSA	1:1.93	52	1.9000
P(2-E)-PSSA	1:2.43	41	2.9000
PANI-PSSA	1:2.65	38	3.1000

TABLE V
The Sample of P(O-P)-PSSA and P(2-E)-PSSA; Complexes Insoluble In Organic Solvent Used

Solvent	P(2-E)-PSSA	P(O-P)-PSSA
Tetrahydrofuran	—	—
Acetonitrile	—	—
Isopropanol	—	—
Methanol	—	—

Note.—, Precipitate.

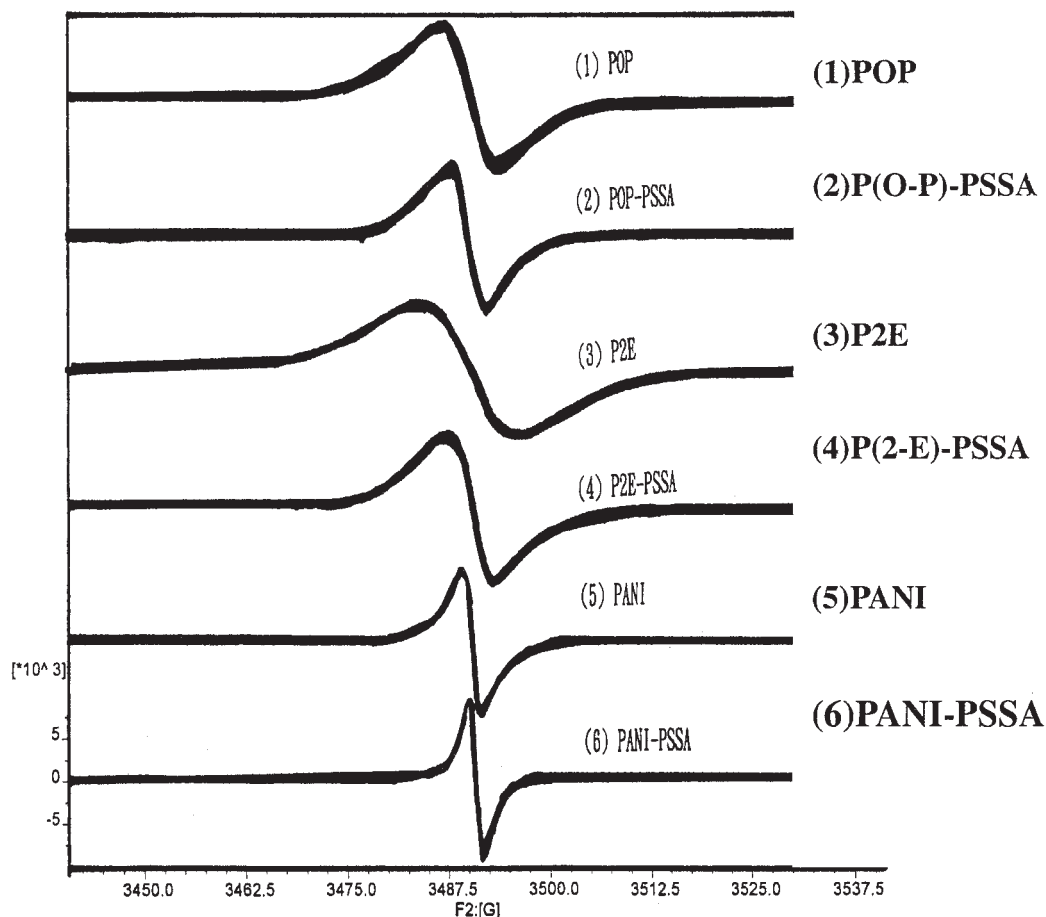


Figure 6 EPR spectra polyaniline complexes of (1) POP, (2) P(O-P)-PSSA, (3) P2E, (4) P(2-E)-PSSA, (5) PANI, and (6) PANI-PSSA.

lower P_{ka} will react to become the conductive salt form; in the reverse procedure, the conductive form can be converted back to the insulating form by exposure to an organic base [0.1M NH_3 (aq)].

Elemental analysis

The results of elemental analysis and solubility studies on the unsubstituted and substituted polyaniline complexes are showed in Tables III and IV, respectively. The elemental analysis indicates that the products have specific chemical compositions and are consistent with the formation of P(2-E)-PSSA and P(O-P)-PSSA molecular complexes; the effect of the sulfonic acid group on the polyaniline backbone, aimed at delineating the significant changes in polyaniline upon going from external protonic doping to internal doping, shows the formation of self-doped conducting polymers P(O-P)-PSSA and P(2-E)-PSSA complexes; those polymer complexes have a wide range of solubility, which improves the processability of the polymer. Elemental analysis (Table III) shows that the values of N/S for the complexes are 52% for P(O-P)-PSSA and 41% for P(2-E)-PSSA. Comparative studies of polyaniline salt and its polyelectrolyte

complexes show similarities due to the same backbone structure and differences of the $-\text{SO}_3\text{H}$ group on the polyelectrolyte template, the role the $-\text{SO}_3\text{H}$ (and $-\text{SO}_3^-$) groups play in affecting the solubility, the doping mechanism, and the charge transport in the polyaniline system; the N/S ratio of the P(2-E)-PSSA complexes is nearly 41% and it is a double-strand complex, which means that it is a double-strand structure. The main chains are emeraldine salts (i.e., N), which interact with the poly(styrenesulfonic acid) (i.e., S) chain by lone-pair induced interaction, while the other 1.43 poly(styrenesulfonic acid) chain containing sulfonic acid ($-\text{SO}_3\text{H}$) functional groups is left free, with no interaction with emeraldine salts; the latter free groups can increase the solubility in water (2.9 g/L). The N/S ratio of the P(O-P)-PSSA complexes is nearly 52% (larger than that of the PANI-PSSA complexes); it is also a double-strand complex, which means that emeraldine salts have one lone-pair induced interaction with the poly(styrenesulfonic acid) chain and have the other 0.93 poly(styrenesulfonic acid) chain containing sulfonic acid ($-\text{SO}_3\text{H}$) functional groups left free, increasing the solubility in water (1.9 g/L).

TABLE VI
EPR Results of Substituted Polyaniline
Complexes under Air

	298 K		77 K	
	ΔH_{pp} (Gauss)	g value	ΔH_{pp} (Gauss)	g value
POP	7.161	2.00304	9.577	2.00317
P(O-P)-PSSA	5.258	2.00302	6.177	2.00315
P2E	12.227	2.00319	14.089	2.00312
P(2-E)-PSSA	6.091	2.00298	8.469	2.00292
PANI	2.270	2.00299	1.942	2.00298
PANI-PSSA	1.626	2.00296	1.537	2.00300

Solubility

The solubility results of P(2-E)-PSSA and P(O-P)-PSSA complexes in water are shown in Table IV; the solubility is 2.9 g/L for P(2-E)-PSSA and 1.9 g/L for P(O-P)-PSSA. The complexes P(O-P)-PSSA and P(2-E)-PSSA are insoluble in organic solvent used, including tetrahydrofuran, acetonitrile, 2-isopropanol, and methanol (Table V); they are water solubility polymers.

EPR spectra

EPR spectra of substituted polyaniline-HCl salts and their complexes show a single Lorentzian-shape signal (Fig. 6) without any hyperfine splitting in air and argon (Table VI and Table VII); the g values of all the substituted polyaniline hydrochloride salts and their complexes lie around 2.00,290–2.00,321, which is almost the free electron g value, suggesting that polyaniline exists primarily as the polysemiquinone radical cation. The g value and line width are temperature-dependent; this g value, typical of π radicals in conjugated carbon systems, is consistent with the unpaired delocalized spin, primarily on the phenyl ring.

EPR is a powerful tool for probing spin localization and dimensionality through the measurement of spin concentration, g value, line width, and line shape; the EPR line-width is determined by the relaxation time

TABLE VII
EPR Results of Substituted Polyaniline
Complexes under Argon

	298 K		77 K	
	ΔH_{pp} (Gauss)	g value	ΔH_{pp} (Gauss)	g value
POP	4.665	2.00300	5.835	2.00305
P(O-P)-PSSA	4.454	2.00301	5.909	2.00321
P2E	7.183	2.00300	10.344	2.00298
P(2-E)-PSSA	5.448	2.00298	7.830	2.00299
PANI	0.965	2.00300	1.437	2.00294
PANI-PSSA	1.356	2.00290	1.483	2.00294

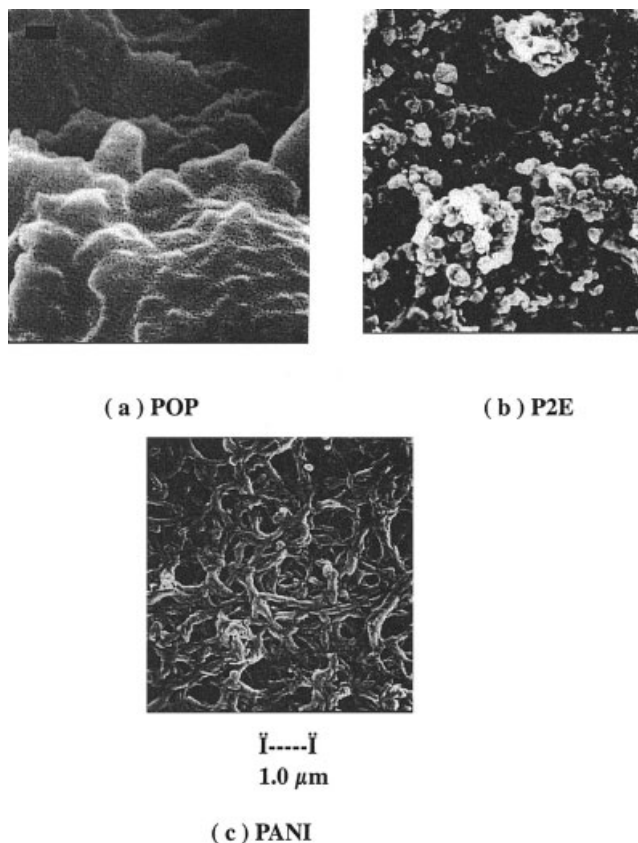


Figure 7 SEM micrographs of polyaniline complexes. (a) Poly(*o*-phenetidine) [POP], (b) poly(2-ethylaniline) [P2E], and (c) polyaniline [PANI] (20 kV; $\times 30,000$).

(T_2). Several relaxation processes can cause the shortening of T_2 , hence the broadening of an EPR line, one of them being the spin-lattice relaxation characterized by a time constant (T_1)^{15,16}. The narrower line width in polyaniline complexes [P(O-P)-PSSA and P(2-E)-PSSA] compared to their salts (POP and P2E) can be attributed to the lower degree of structural disorder and the oxygen absorption on the polymer molecular complexes.^{17,18} The substituted polyanilines have a steric effect by the alkyl group ($-C_2H_5$ or $-OC_2H_5$) and the $-SO_3H$ group on the polyelectrolyte template which higher density¹⁹ in their molecules complexes to form a different crystal structure. The EPR spectra also give evidence for the existence of highly mobile radical cations or polarons in P(O-P)-PSSA and P(2-E)-PSSA complexes. The temperature-dependent transport property suggests that all polyaniline complexes show a single fine signal without any hyperfine splitting structure.

Conductivity

The conductivity of the complexes PANI-PSSA (4.7×10^{-2} S/cm), P(2-E)-PSSA (2.4×10^{-2} S/cm), and P(O-P)-PSSA (3.8×10^{-2} S/cm) were $\sim 10^{-2}$ S/cm; as

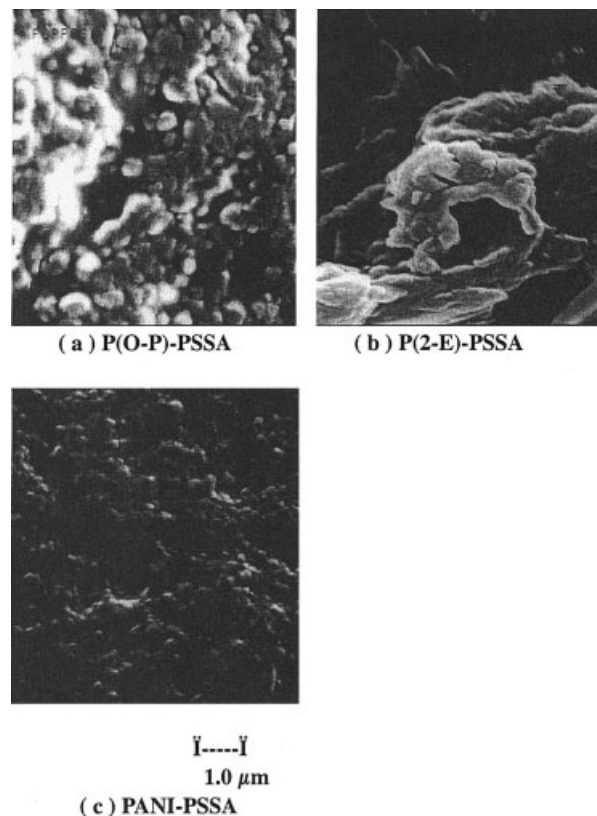


Figure 8 SEM micrographs of polyaniline complexes: (a) P(O-P)-PSSA, (b) P(2-E)-PSSA, and (c) PANI-PSSA (20 kV; $\times 30,000$).

well, the EPR data give evidence for the existence of highly mobile radical cations or polarons in the substituted polyaniline salts and their complexes, to be localized since the samples are heavily doped and less disordered.

Morphology

The SEM micrographs of the poly(*o*-phenetidine), poly(2-ethylaniline), and polyaniline are shown in Figure 7. The surface morphology of poly(*o*-phenetidine) is a particulate structure of the film with porous feature, poly(2-ethylaniline) is a globular structure, and polyaniline is a network structure. The micrographs of the P(O-P)-PSSA, P(2-E)-PSSA, and PANI-PSSA are shown in Figure 8. The surface morphology of the P(O-P)-PSSA is a globular structure, P(2-E)-PSSA has a roll-like and irregular structure, and PANI-PSSA is a particles structure.

The TEM micrographs of the P(2-E)-PSSA complexes are shown in Figure 9 and correspond to different magnifications; the poly(2-ethylaniline) particulates would have been circular [Fig. 9(a)] and should have been distributed in the poly(styrenesulfonic acid) polyelectrolyte [Fig. 9(b)]; particulates connected together [Fig. 9(c)], and particulates that form a channel

[Fig. 9(d)], useful in electron transfer. Figure 10 shows the TEM micrographs of the P(O-P)-PSSA complexes (a-d) with different magnifications. The shape of the poly(*o*-phenetidine) is particulate-type morphology. This indicates [Fig. 10(d)] that the intramolecular interaction between poly(*o*-phenetidine) and poly(styrenesulfonic acid) crosslink²⁰ is introduced into the P(O-P)-PSSA complexes; the crosslink characteristics of each poly(*o*-phenetidine) were connected by particulates arrangement, crosslink subsequent to form a channel, useful for the electron transfer.

CONCLUSIONS

We have prepared new substituted polyaniline-polyelectrolyte complexes, P(O-P)-PSSA and P(2-E)-PSSA. IR spectra absorption bands are at $\sim 1600\text{ cm}^{-1}$ (C = C stretching in the quinoid unit), $\sim 1500\text{ cm}^{-1}$ (C = C stretching in the benzenoid unit), 1200, 1040, and 1020 cm^{-1} ($-\text{SO}_3\text{H}$), 1100 cm^{-1} (aromatic C-O stretching), and $930\text{--}800$ and $770\text{--}750\text{ cm}^{-1}$ (1,2,4-trisubstituted phenyl ring). This shows that P(2-E)-PSSA and P(O-P)-PSSA complexes have structures similar to those of the unsubstituted polyanilines. After deprotonation with base [P(O-P)-PSSA (pH [mteq] 8.0); P(2-E)-PSSA (pH [mteq] 9.5)], a peak at $\sim 580\text{ nm}$ appears. The pH value for deprotonation is higher than that of HCl salt

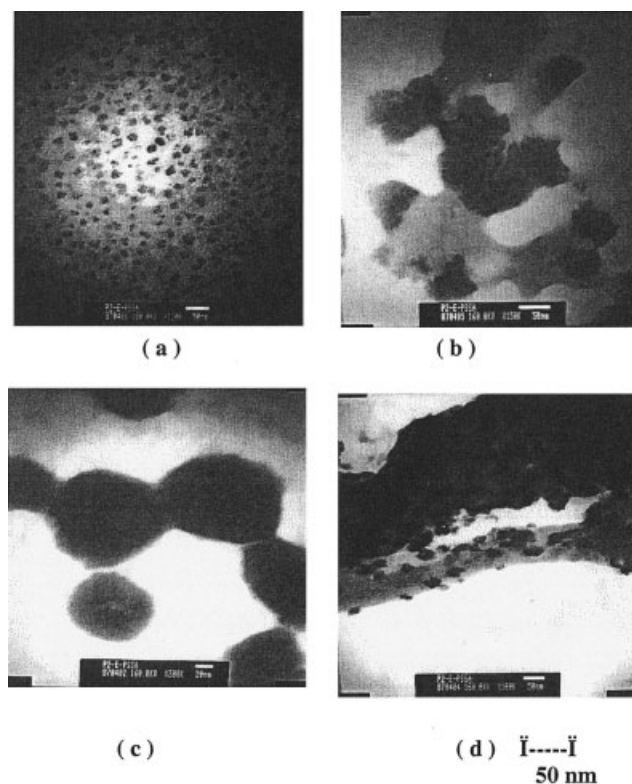


Figure 9 TEM micrographs of P(2-E)-PSSA complexes [160 kV; (a) $\times 120,000$; (b) $\times 150,000$; (c) $\times 200,000$; (d) $\times 100,000$].

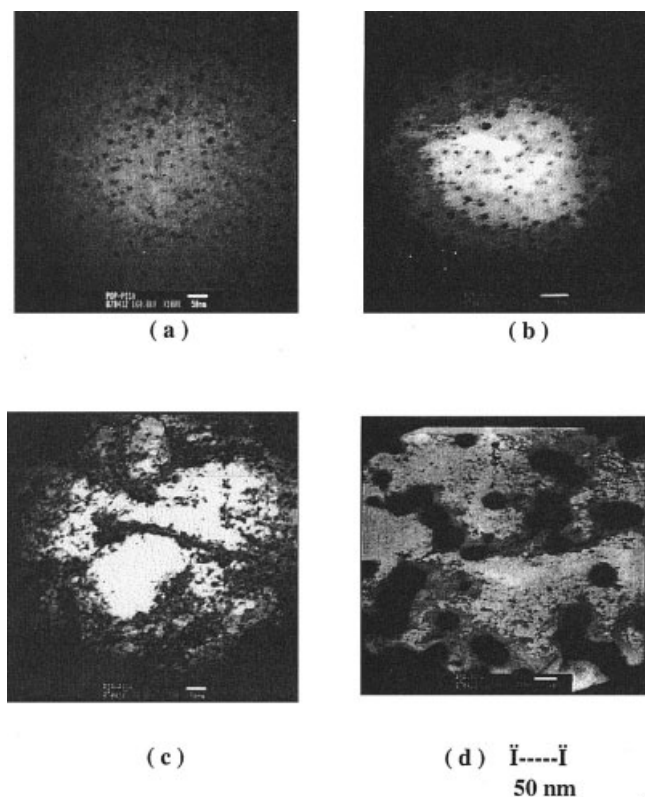


Figure 10 TEM micrographs of P(O-P)-PSSA complexes [160 kV; (a) $\times 120,000$; (b) $\times 150,000$; (c) $\times 200,000$; (d) $\times 100,000$].

of polyaniline. These results indicate an intimate interaction between the two polymer chains. Products with good water solubility [2.9 g/L for P(2-E)-PSSA and 1.9 g/L for P(O-P)-PSSA] have been obtained. EPR and VIS spectra indicate the formation of polarons. Elemental analysis shows that P(O-P)-PSSA has a high nitrogen-to-sulfur ratio of 52%, larger than that for P(2-E)-PSSA(41%). the conductivity of substituted polyaniline-polyelectrolyte complexes P(O-P)-PSSA and P(2-E)-PSSA is around 10^{-2} S/cm. Low conductivity is due to localization, heavy doping, and high disorder.

Temperature-dependent transport properties suggest that all polyaniline complexes have a single fine signal without any hyperfine splitting structure; the g value of all the salts and complexes is between 2.00,290 and 2.00,321, which is almost the free-electron g value. The narrower line widths of P(O-P)-PSSA and P(2-E)-PSSA complexes can be attributed to the lower degree of structural disorder; the steric effect of the substituents, decreasing degree of delocalization of the radical cation, the side group ethyl- or ethoxy-group, which appears to reduce the conductivity, and the presence of excessive $-\text{SO}_3^-$, which leads primarily

to the formation of bipolarons and thus to a high conductivity.

The SEM micrographs show that the surface morphology of the P(O-P)-PSSA is a globular structure, and P(2-E)-PSSA has a roll-like irregular structure. Those P(O-P)-PSSA and P(2-E)-PSSA complexes, measured by TEM, shown as the particulates of poly(*o*-phenetidine) and poly(2-ethylaniline) in complexes, respectively; which crosslink subsequent to form a channel, useful for the electron transfer.

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References

- Ryu, K. S.; Kim, K. M.; Kang, S. G.; Lee, G. J.; Joo, J.; Chang, S. H. *Synth Met* 2000, 110, 213.
- Somani, P.; Mandale, A. R.; Radhakrishnan, S. *Acta Mater* 2000, 48, 2859.
- Michalak, F.; Aldebert, P. *Solid State Ionics* 1996, 85, 265.
- Tsutsumi, H. *Synth Met* 1995, 69, 143.
- Chen, S. A.; Lee, H. T. *Macromolecules* 1995, 28, 2858.
- Sun, L. F.; Liu, H. B.; Clark, R.; Yang, S. C. *Synth Met* 1997, 84, 67.
- Yang, C. Y.; Reghu, M.; Heeger, A. J.; Cao, Y. *Synth Met* 1996, 79, 27.
- Tomozawa, H.; Saida, Y.; Ikenoue, Y.; Murai, F.; Suzuki, Y.; Tawa, T.; Ohta, Y. *J Photopolym Sci Technol* 1996, 9, 707.
- MacDiarmid, A. G.; Chang, J. C.; Richter, A. F.; Somasiri, N. L. D.; Epstein, A. J. In *Conducting Polymers*; Alcaer, L., Ed.; Dordrecht: The Netherlands, 1987; p 105.
- Wang, Z. H.; Li, C.; Scherr, E. M.; MacDiarmid, A. G.; Epstein, A. J. *Phys Rev Lett* 1991, 66, 1745.
- Palaniappan, S.; Narayana, B. H. *J Polym Sci A Polym Chem* 1994, 32, 2431.
- McManus, P. M.; Cushman, R. J.; Yang, S. C. *J Phys Chem* 1987, 91, 744.
- Cushman, R. J.; McManus, P. M.; Yang, S. C. *J Electroanal Chem* 1986, 291, 235.
- Sun, L. F.; Yang, S. C.; Liu, T. M. *Abs Paper Am Chem Soc* 1992, 204, 137.
- Weil, J. A.; Botton, J. R.; Wertz, J. E. *Electron Spin Resonance: Elementary Theory and Practical Applications*; Wiley-Interscience: New York, 1994.
- Drago, R. S. *Physical Method in Chemistry*; Saunders: New York, 1977.
- Nechtschein, M.; Genoud, F. *Solid State Commun* 1994, 91, 471.
- Aasmundtveit, K.; Genoud, F.; Houze, E.; Nechtschein, M. *Synth Met* 1995, 69, 193.
- Lee, W.; Du, G.; Long, S. M.; Epstein, A. J.; Shimizu, S.; Saitoh, T.; Uzawa, M. *Synth Met* 1997, 84, 807.
- Zhang, Q.; Jin, H.; Wang, X.; Jing, X. *Synth Met* 2001, 123, 481.