

Measurement of the Electrochemical Response Time and Electron Paramagnetic Resonance Behavior of Poly(*o*-phenetidine)–Poly(styrene sulfonic acid) and Poly(2-ethylaniline)–Poly(styrene sulfonic acid) Complexes

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ABSTRACT: Two studies were mainly focused on the measurement of electrochemical response time and the electron paramagnetic resonance (EPR) of the substituted polyaniline (PANI) complexes poly(*o*-phenetidine) (POP)–poly(styrene sulfonic acid) (PSSA) and poly(2-ethylaniline) (P2E)–PSSA, which were prepared by the electrochemical polymerization of the monomer (*o*-phenetidine or 2-ethylaniline) with PSSA, with indium tin oxide (ITO) as a working electrode in a 1M HCl solution. Ultraviolet–visible spectra measurements showed evidence for the doped substituted PANI system to have a highly electrochemical response time recorded at a temperature of 298 K, and the results were further analyzed on the basis of the color–discolor model, which is typical of protonation systems. At the reaction time (3 s) and monomer concentration (0.6M) with PSSA (0.15 μ), the best electrochemical color/discolor time of the POP–PSSA complexes was 125/125 ms (thickness = 3.00 μ m), which was faster than that of the P2E–PSSA complexes. At the same thickness (10 μ m), the best electrochemical color/discolor time of the POP–PSSA complexes

was 500/250 ms, which was faster than the P2E–PSSA complexes (750/500 ms). With regard to film growth rate, the POP–PSSA complexes (1.0 μ m/s) were faster than the P2E–PSSA complexes (0.79 μ m/s); this was attributed to the substituted PANI having a steric effect and to good reactivity by the ethoxy group ($-\text{OC}_2\text{H}_5$) in the molecules. The EPR spectra of the two samples were recorded both at 298 and 77 K and were further analyzed on the basis of the polaron–bipolaron model. The narrower line width of the substituted PANI complexes arose due to polarons; that is, we propose that charge transport took place through both polarons and bipolarons. Compared to their salts, this could be attributed to the lower degree of structural disorder, the oxygen absorption on the molecules, and the steric effect by the side chain group. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 1211–1221, 2005

Key words: conjugated polymers; polyelectrolytes; ESR/EPR

INTRODUCTION

Intrinsically conductive polymers have been intensively investigated since 1976, with a focus on their potential technological applications, including electrochemical devices¹ and button batteries.² Polyaniline (PANI) is a smart optical and electronic material and is unique among conducting polymers in that its electrical properties and structural properties can be reversibly controlled both by changing the oxidation state of the polymer main chain and by protonation of the imine nitrogen atoms,^{3,4} that is, by proton doping and dedoping.⁵ PANI is a reversibly switchable material; with a color change from transparent to green, revers-

ibly color-switched for 2.5×10^5 cycles,⁶ and it is easily deposited on ITO. The adhesive properties and chemical inertness of poly(styrene sulfonic acid) (PSSA)⁷ should make a PANI blend suitable for conductive coating or electromagnetic interference shielding; the substituted PANI salts have good electrochromic properties,⁸ and PSSA can also be applied in electrochromic devices.⁹ Hydrochloric acid presents very attractive properties as an electrochromic material with a good transport rate not only for the positive charges as H^+ ions, lower molecular weight (molecular weight = 1), fast delivery, and lower formal potential but also for its excellent and ideal electrolytes. It is a good, strong electrolyte. Protonation-induced spin unpairing of PANI¹⁰ causes a rearrangement of the structure, so PANI is extremely paramagnetic.^{11,12} The electron paramagnetic resonance (EPR) signal can be analyzed as two different independent signals,¹³ one of which is Lorentzian in shape and the other one of which is Gaussian. In both of these studies, the EPR signal was a single fine line. The electrochemical doping of the

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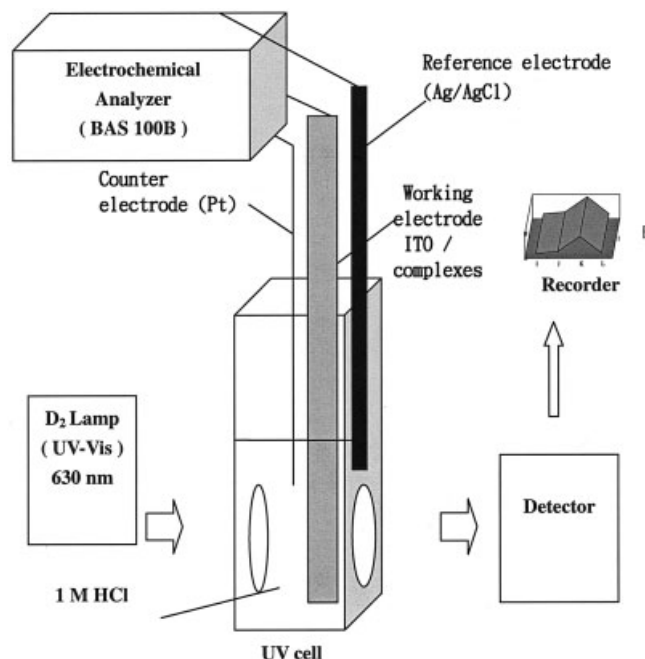


Figure 1 Electrochemical response time measurement apparatus.

PANI polymer with HCl gave rise to an equilibrium of polarons and bipolarons.¹⁴

In this study, an electrochromic window configuration based on the substituted PANI with PSSA was measured and compared their color/discolor time. Ultraviolet-visible (UV-vis) absorption spectra of the electrochromic device in a window containing poly(*o*-phenetidine) (POP)-PSSA or poly(2-ethylaniline) (P2E)-PSSA complexes, HCl and Pt, was used to investigate changes in absorption modulation. The electrochemical device became a glass/ITO/conducting polymer/HCl/Pt/glass. We also present in this article

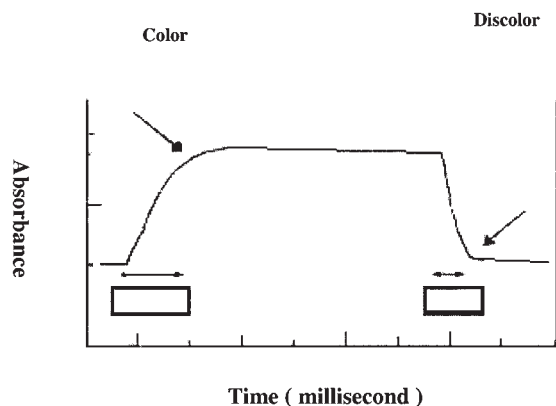


Figure 2 Electrochemical response time calculated from the absorption during color and discolor for the substituted PANI complexes.

TABLE I
Conductivity of the Substituted PANI Complexes

Sample	Conductivity (S/cm)
POP-PSSA	3.8×10^{-2}
P2E-PSSA	2.4×10^{-2}
PANI-PSSA	4.7×10^{-2}

temperature-dependent EPR studies on the substituted PANI polyelectrolyte complexes to gain an information base on any relation that may have existed between the spin and the charge-carrying species. A direct correlation between line width and charge transport is very important because it establishes the transport mechanism involving the conduction of polarons.

EXPERIMENTAL

Films

For all device configurations, the substituted PANI-PSSA complexes, POP-PSSA and P2E-PSSA, were electrochemically synthesized by cycling (50 mV/s) in the potential region -200 to 700 mV, with ITO ($1 \times 50 \times 10$ mm) as the working electrode, Ag/AgCl as the reference electrode, and platinum (Pt; $10 \times 50 \times 1$ mm) as the auxiliary electrode; the reaction solution was 7.5 mL of 0.2M monomer (2-ethylaniline or *o*-phenetidine) with 0.2M PSSA (7.5 mL). Reference samples, including PANI-PSSA and poly(*o*-ansidine) (POA)-PSSA, were also prepared, and optical characterization¹⁵ was carried out *in situ* with a UV-vis spectrophotometer in the UV-vis region.

EPR samples were also prepared by the electrochemical polymerization of P2E or POP with PSSA (PSSA molecular weight = 70,000) as previously reported.¹⁶ The substituted PANI salts, including POP, P2E, PANI, and PANI-PSSA, were the reference samples.

Characterization

Fourier transform infrared (FTIR) spectroscopy

FTIR spectra of the complexes were recorded on a Jasco 410 FTIR spectrophotometer (Japan) by the KBr pellet method.

Elemental analysis

Elemental analysis was done with a Heraeus CHNOS Rapid F002 elemental analyzer (Gemmary) with 5–10-mg samples.

TABLE II
Elemental Analysis of the Substituted PANI 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	
POP-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
P2E-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

Morphology measurements

Scanning electron microscopy (SEM) was performed on a Hitachi S-3500 microscope (Japan) to study the morphology of the conductive polymer complexes at an accelerating voltage of 20 kV, and the samples were gold-sputtered before observation.

Absorbance measurement

The electrochromic device cell ITO/POP-PSSA or the P2E-PSSA/HCl/Pt system showed the different materials and layers used. The substituted PANI complexes P2E-PSSA and POP-PSSA were measured and compared with respect to their color/discolor time. The reference samples, including PANI, P2E, POP, and PANI-PSSA complexes, were electrochemically polymerized.¹⁵ The absorption spectra of the films, deposited on glass, were recorded with a UV-vis spectrometer (Jasco model 7850) (Japan), with uncoated glass as a reference electrode (shown in Fig. 1). At a fixed wavelength of 630 nm, the relation between the film thickness, as determined by the reaction time, and monomer concentration was determined with an electrochemical analyzer (BAS 100) (BAS Instruments Ltd., West Lafayette, IN). Film thickness was calculated from nanospectrometry; we took the average of five measurements. Both safe voltage operation and the color were reversible when the color/discolor time was measured.

Calculation of color/discolor time

Electrochemical response times were calculated from the absorption during color and discolor for the sub-

TABLE III
Elemental Analyses (N/S Ratio) and Solubility of the Substituted PANI Complexes in Deionized Water

Sample	N/S (%)	Solubility (g/L)
POP-PSSA	52	1.9
P2E-PSSA	41	2.9
PANI-PSSA	38	3.1

stituted PANI complexes. Color time was calculated when the absorption color was at 50%. Discolor time was calculated when absorption discolor was at 50%, as shown as Figure 2. The color changes of PANI, POP, and P2E with and without PSSA by the electrochromic device in 1M HCl electrolyte were cycled at a 50 mV/s sweep rate, which cycled between -300 and 700 mV/s.

Conductivity measurements

Electrical conductivity (direct current) of the samples were measured at 298 K with the four-probe method on the polymer complex films. Under galvanostatic conditions with a Keithley model 238 (Keithley Instruments Inc., Cleveland, OH) programmable current source and a voltmeter.

EPR spectra

EPR spectra were obtained for the powder samples at different temperatures, both 298 and 77 K, in air and argon with an EMX-10 (Bruker, Gemmery) spectrom-

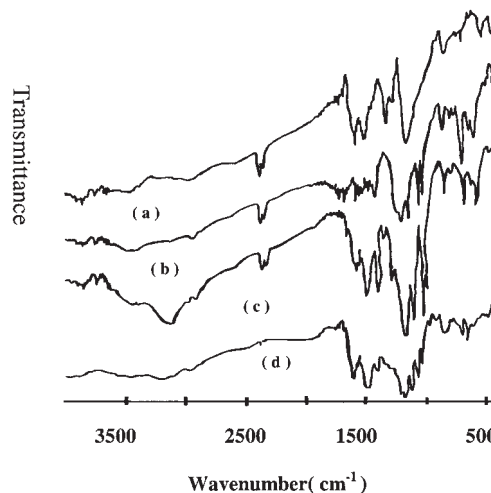


Figure 3 IR spectra of the PANI complexes: (a) PANI, (b) PANI-PSSA, (c) POP-PSSA, and (d) P2E-PSSA.

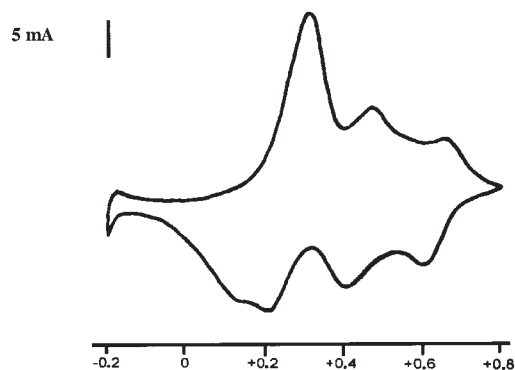


Figure 4 Cyclic voltammogram for the electrochemical synthesized thin POP film in 0.2M *o*-phenetidine. (scan rate: 50 mV/s)

eter operating in the X band and equipped with a liquid nitrogen cooled temperature controller.

RESULTS AND DISCUSSION

Characterization

Characteristics of the POP-PSSA and P2E-PSSA complexes, including conductivity and infrared spectra absorption, were used as reported earlier¹⁷ to characterize the polymer complexes; the conductivity and elemental analysis results are shown in Tables I-III. IR characteristic absorption peaks of the substituted PANI complexes are shown in Figure 3, those prepared from the monomer (2-etylaniline, or *o*-phenetidine) with PSSA, which in turn, closely matched the IR spectrum of the PANI base prepared from PANI hydrochloric. IR absorption bands of POP-PSSA and P2E-PSSA were at about 1600 cm^{-1} (C=C stretching in a quionoid unit); 1500 cm^{-1} (C=C stretching in a benzenoid unit); 1200, 1040, and 1020 cm^{-1} ($-\text{SO}_3\text{H}$);

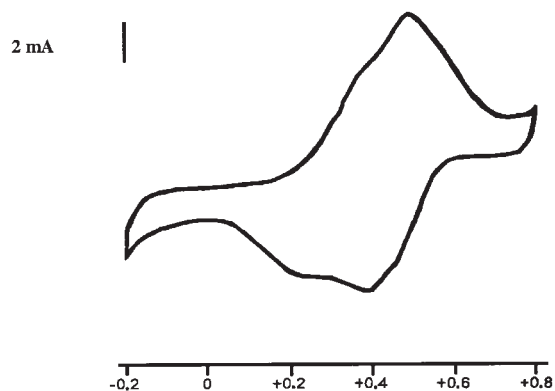


Figure 5 Cyclic voltammogram for the electrochemical synthesized thin P2E film in 0.2M 2-ethylaniline. (scan rate: 50 mV/s)

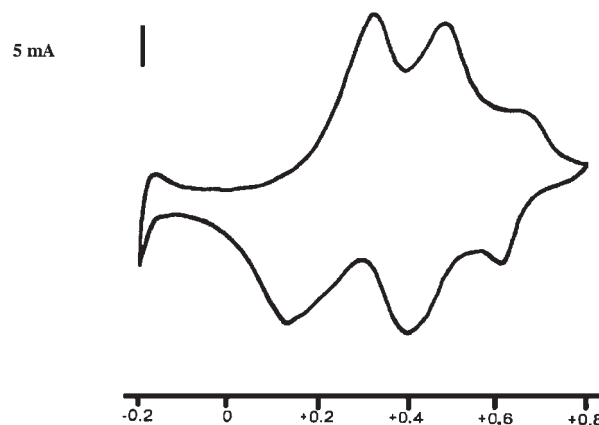


Figure 6 Cyclic voltammogram for the electrochemical synthesized thin POP-PSSA film in 0.2M *o*-phenetidine with 0.2M PSSA. (scan rate: 50 mV/s)

1100 cm^{-1} (aromatic C—O stretching); 930–800 and 770–750 cm^{-1} (1,2,4-trisubstituted phenyl ring), respectively.

Cyclic voltammograms (50 mV/s) of the POP and P2E on ITO in the potential region -200 to 700 mV are shown in Figures 4 and 5. Cyclic voltammograms (50 mV/s) of the POP-PSSA and P2E-PSSA on ITO in the potential region -200 to 800 mV, are shown in Figures 6 and 7. There were two oxidation state peaks showing PANI peak characteristics near 0.5 and 0.3 V, respectively. In the anodic sweep, three major redox couples were distinguishable: the first was formation of a radical cation peak (polaromeric emeraldine), the second was the formation of a benzoquinone peak, and the third was the formation of diradical dication,¹⁸ which commenced at approximately 600 mV and reached a maximum at 800 mV. In the cathodic sweep, they were three corresponding broad reduction peaks. A

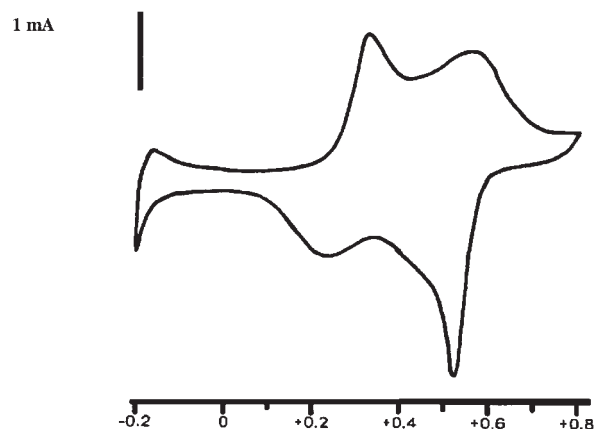
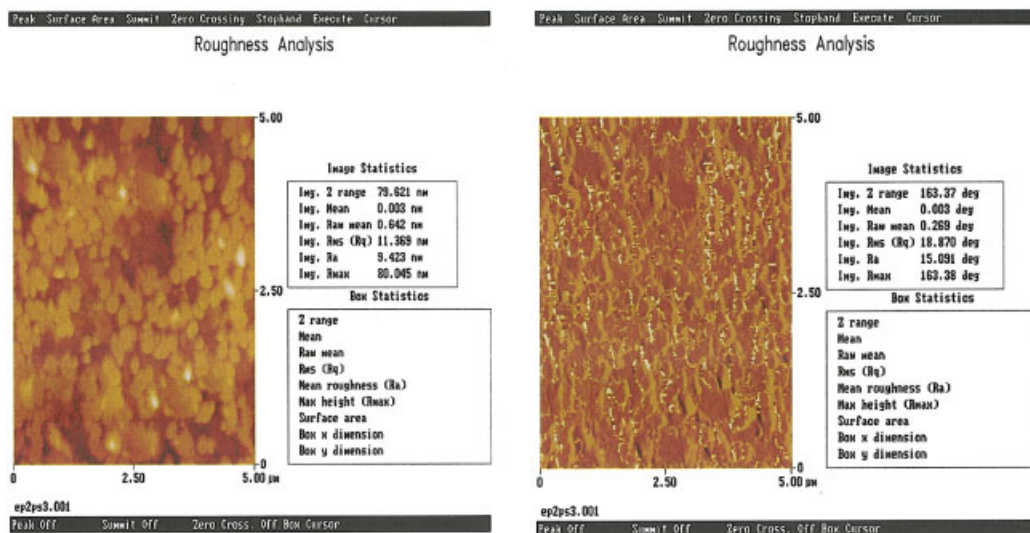
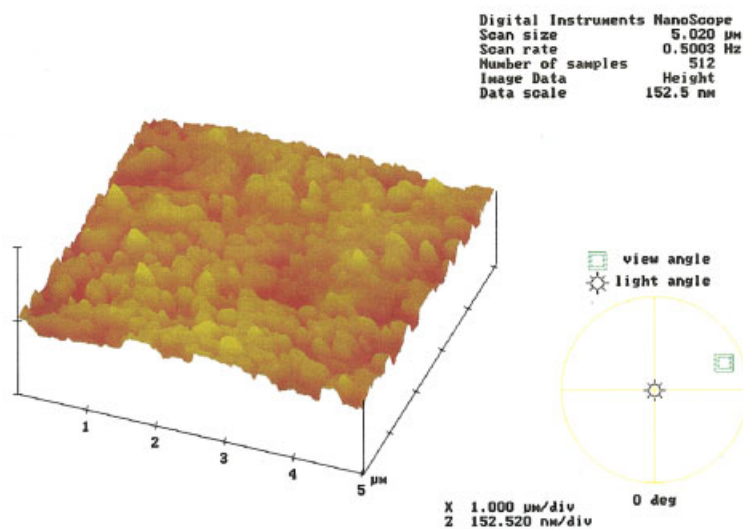


Figure 7 Cyclic voltammogram for the electrochemical synthesized thin P2E-PSSA film in 0.2M 2-ethylaniline with 0.2M PSSA. (scan rate: 50 mV/s)



(a) Tapping Mode

(b) Phase Detector



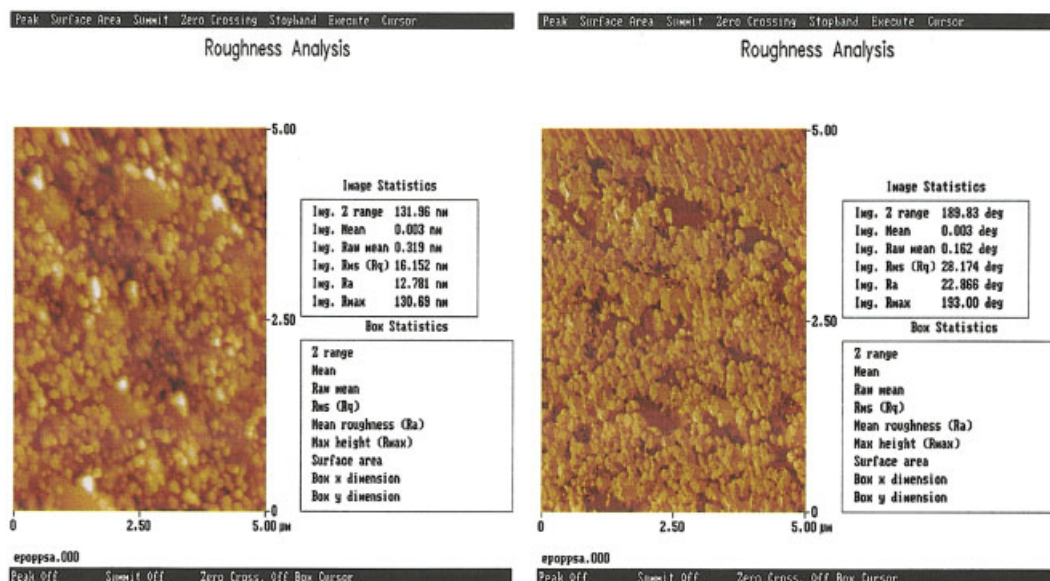
(c) three-dimensional image

Figure 8 AFM topography of the P2E–PSSA blend on ITO (substrate): (a) tapping mode without a phase detector, (b) tapping mode with a phase detector, and (c) a three-dimensional image.

comparison of the cyclic voltammograms of POP–PSSA and POP and P2E and P2E –PSSA showed that the two oxidation peaks of POP–PSSA and P2E–PSSA were much stronger and closer than those observed in P2E and POP, respectively, which suggested that PSSA had a template effect. That the two oxidation peaks of POP–PSSA were much closer than those observed in P2E–PSSA also suggested the

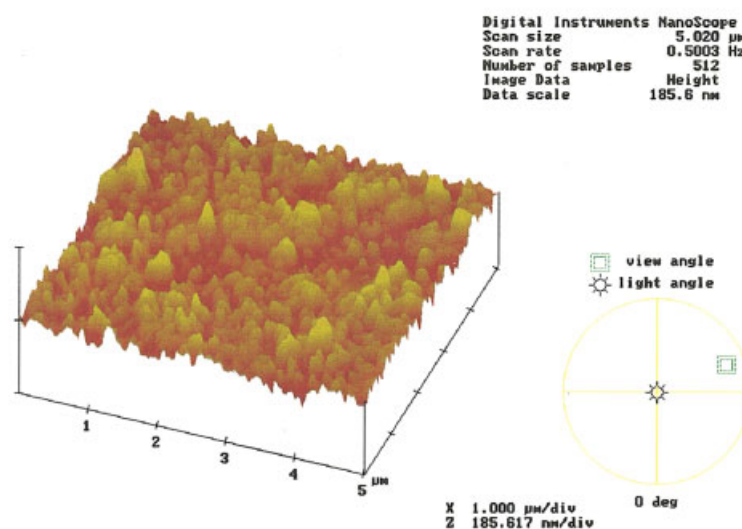
reactivity of the $\text{—OC}_2\text{H}_5$ side-group chains was larger than that of $\text{—C}_2\text{H}_5$.

Atomic force microscopy (AFM) and SEM results of the substituted PANI salts and their complexes formed by electrochemical polymerization on ITO are shown in Figures 8–11; the surface morphology of the substituted PANI complexes and their salts was a globular structure.



(a) Tapping Mode

(b) Phase Detector



(c) three-dimensional image

Figure 9 AFM topography of the POP-PSSA blend on ITO (substrate): (a) tapping mode without a phase detector, (b) tapping mode with a phase detector, and (c) a three-dimensional image.

Under the same film thickness

Best color/discolor times of P2E-PSSA and POP-PSSA

A film thickness of 10 μm was chosen and estimated from the charge crossing in the electrolytic cell. The average film growth rates of the POP-PSSA (Fig. 12) and P2E-PSSA (Fig. 13) complexes were

1.00 and 0.79 $\mu\text{m}/\text{s}$, respectively. The best color/discolor times of the POP-PSSA and P2E-PSSA complexes were 500/250 and 750/500 ms, respectively; the POP-PSSA complex film thicknesses were larger than those of the P2E-PSSA complexes; that is, the reactivity of *o*-phenetidine was larger than that of 2-ethylaniline.

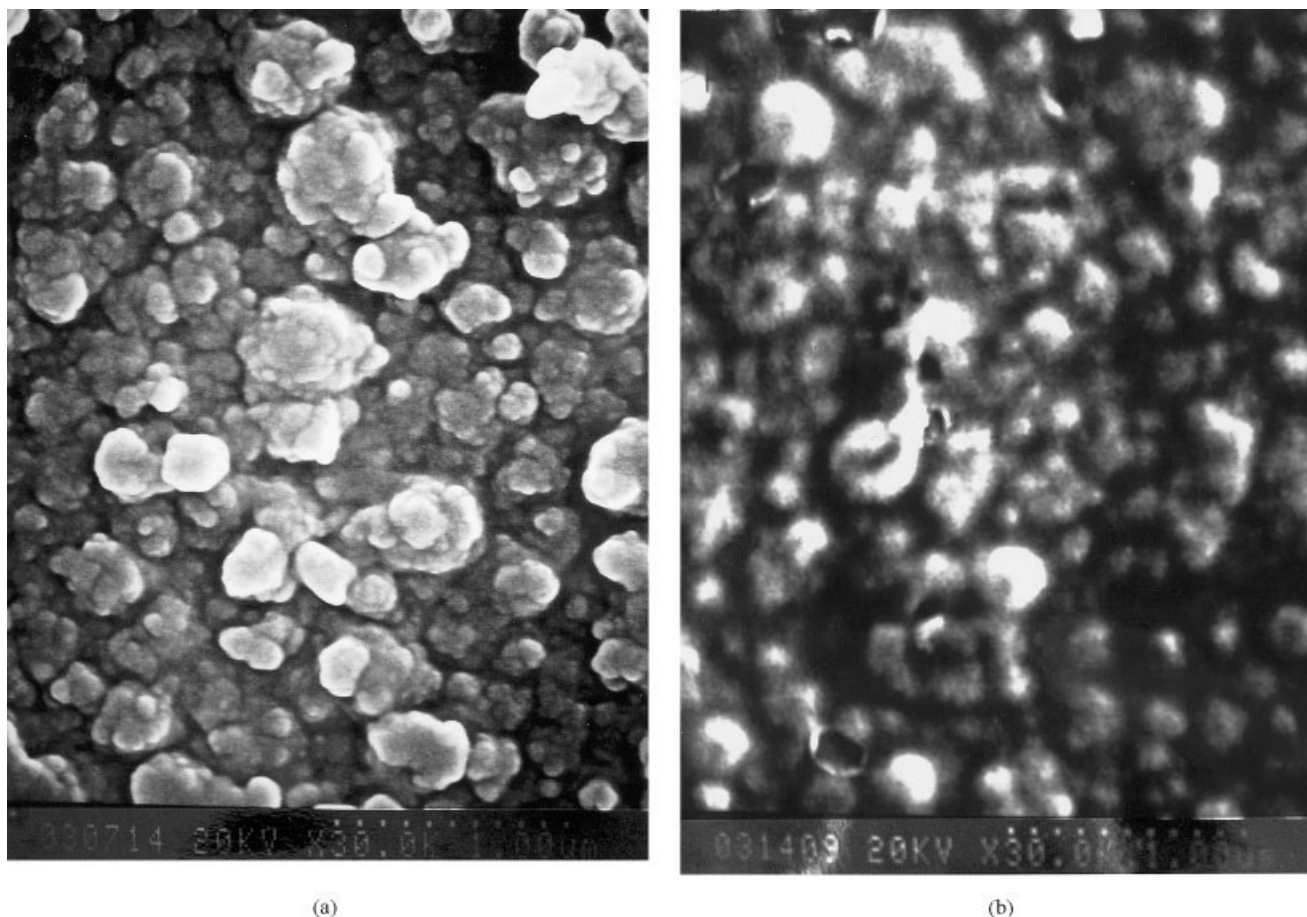


Figure 10 SEM micrographs of PANI complexes on ITO: (a) POP and (b) P2E (20 kV, 30,000 \times).

Under the same reaction time and same monomer concentration

Best color/discolor times of the POP-PSSA and P2E-PSSA complexes

The electrochemical polymerization film thicknesses of the POP-PSSA and P2E-PSSA complexes are shown in Table IV. Under the same reaction concentration and a reaction time of 3 s, the average color/discolor times of POP-PSSA was 175/150 ms; the best color/discolor time of POP-PSSA was 125/125 ms. POP-PSSA had a faster time than PANI-PSSA.

Under the same reaction concentration and a reaction time of 10 s, the average color/discolor times of POP-PSSA and P2E-PSSA were 322/288 and 719/563 ms, respectively. The best color/discolor times of POP-PSSA and P2E-PSSA were 250/200 and 625/500 ms, respectively, as shown in Table V. Under the same reaction concentration and a reaction time of 25 s, the average color/discolor time of POP-PSSA was 1005/808 ms; the best color/discolor time of POP-PSSA was 550/375 ms. For the electrochemical polymerization of POP-PSSA and P2E-PSSA on ITO, the film thickness

was higher and the color/discolor response time was longer. POP-PSSA also had a steric effect and induced this effect through the alkyl group ($-\text{OC}_2\text{H}_5$) and the $-\text{SO}_3\text{H}$ group on the polyelectrolyte, which allowed the color/discolor time to be shorter.

With the same film thickness, reaction time, and monomer concentration, the results in hydrochloric acid show that the substituted PANI had a steric effect on the alkyl group ($-\text{C}_2\text{H}_5$, $-\text{OC}_2\text{H}_5$), which formed a network structure with a porous surface, easy ion transfer and conductivity, and a short color/discolor time. For *o*-phenetidine, both monomer reactivity and the steric effect by the alkyl group allowed the substituted PANI to have much shorter chain and, thus, a shorter color/discolor time.

The side chain groups $-\text{OC}_2\text{H}_5$ and $-\text{C}_2\text{H}_5$ are electron-donating groups, with the $-\text{OC}_2\text{H}_5$ group having a steric effect and an inducing effect and the $-\text{C}_2\text{H}_5$ group only having a steric effect. Related to the electrochemical polymerization reactivity of the monomer (*o*-phenetidine, 2-ethylaniline, or aniline) with PSSA, the film growth rate of POP-PSSA was larger than P2E-PSSA, and the film

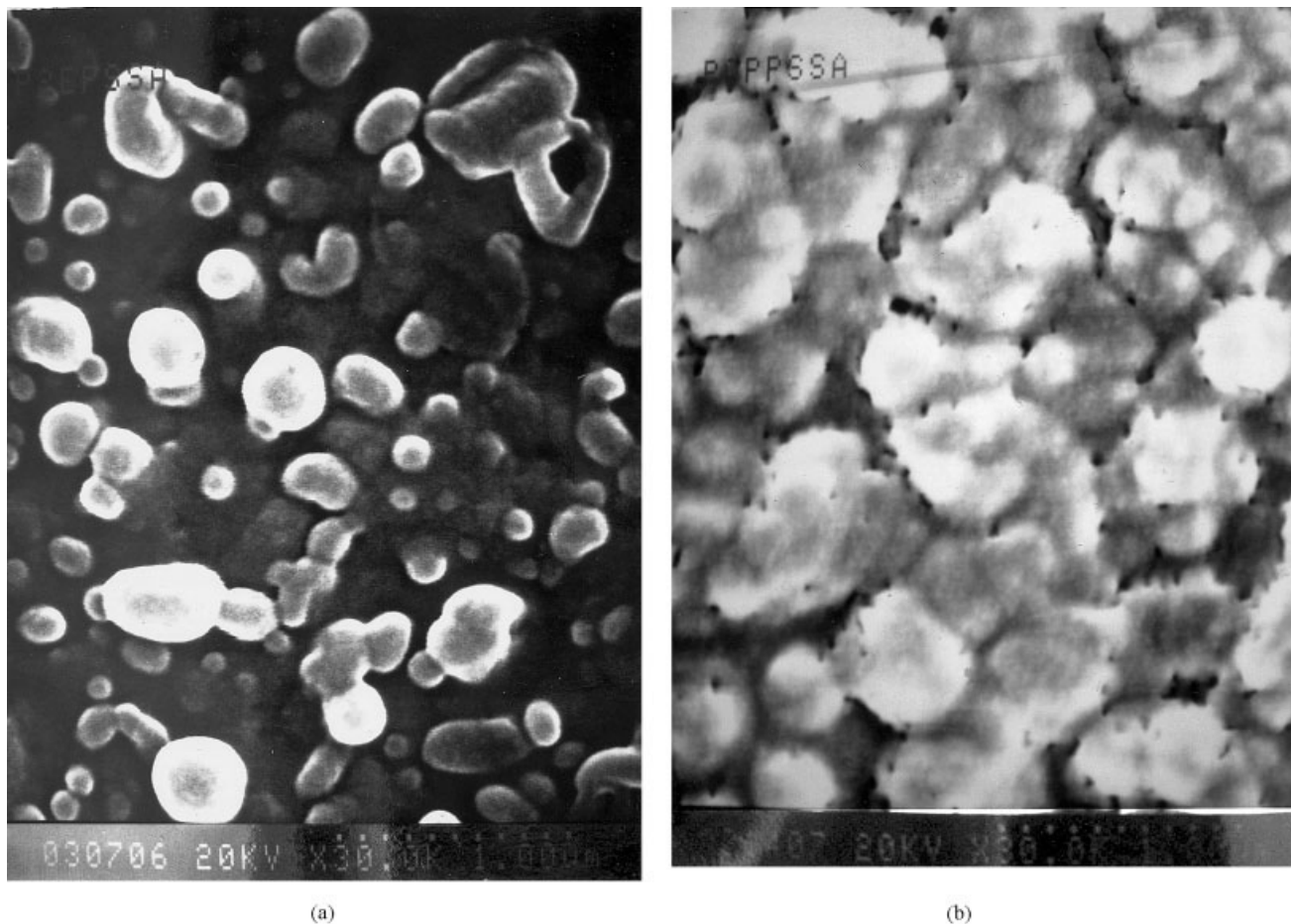


Figure 11 SEM micrographs of PANI complexes on ITO: (a) P2E-PSSA and (b) POP-PSSA (20 kV, 30,000 \times).

growth rate of PANI-PSSA was the lowest. During the electrochemical process, relative to the oxidation potential of PANI-PSSA, P2E-PSSA was lower, POP-PSSA was the lowest, and the oxidation reversibility of POP-PSSA was larger than that of P2E-PSSA.

Ambient-temperature conductivity

The EPR spectra of all of the substituted PANI salts and their complexes showed a single Lorentzian-shaped signal without any hyperfine splitting (Fig.

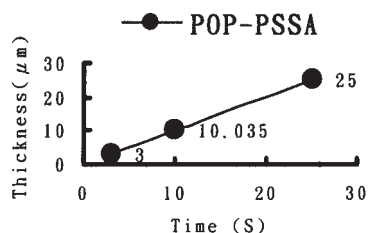


Figure 12 Film growth rates of the POP-PSSA complexes.

14). The electrical conductivities of P2E-PSSA (2.4×10^{-2} S/cm) and POP-PSSA (3.8×10^{-2} S/cm) were lower than that of PANI-PSSA (4.7×10^{-2} S/cm), which suggested that the side group ($-\text{C}_2\text{H}_5$ or $-\text{OC}_2\text{H}_5$) had a definite influence on the polymer chain.

Low-temperature EPR spectra

Temperature-dependent EPR studies were performed at 298 and 77 K; Tables VI and VII show the

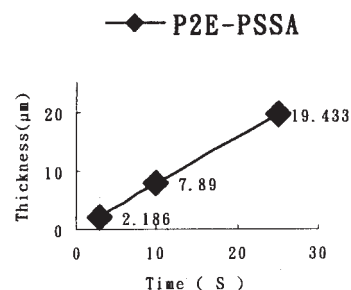


Figure 13 Film growth rates of the P2E-PSSA complexes.

TABLE IV
Film Thicknesses of POA-PSSA, POP-PSSA, P2E-PSSA,
and PANI-PSSA at Various Reaction Times

Sample	Reaction time (s)	Film thickness (μm) ^a	Average film growth rate ($\mu\text{m/s}$)
POA-PSSA	3	4.13	≥ 1.20
	10	12.31	
	25	>25	
	60	>25	
POP-PSSA	3	3	1.00
	10	10.04	
	25	25	
	60	>25	
P2E-PSSA	3	2.19	≥ 0.79
	10	7.89	
	25	19.43	
	60	25	
	120	>25	
PANI-PSSA	3	1.00	≤ 0.54
	10	5.39	
	25	11.09	
	60	11.53	
	120	>25	

^a Average of five measurements by a nanospectrometer.

results of the EPR spectra of all of substituted PANI HCl salts and substituted PANI-polyelectrolyte complexes in argon and air, respectively. The g values (g = the central point of wavecrest and wave-trough) were around 2.00290–2.00321, which were almost the free-electron g value, and this suggested that PANI existed primarily as a polysemiquinone radical cation.

The line widths of the substituted PANI complexes were rather small (1.626–5.448 G) compared to those of the substituted PANI salts (2.270–12.227 G), where the dominant broadening mechanism was hyperfine interaction with adjacent protons.

Factors influencing the EPR line width

The electrical conductivity (i.e., line width) of the substituted PANI HCl salts and their complexes decreased on exposure to oxygen and increased reversibly in argon. The narrower line widths of the substituted PANI complexes compared to those of the HCl salts was attributed to the lower degree of structural disorder. The conductivity of the substituted PANI-polyelectrolyte system was low due to localization because it was a heavily doped and highly disordered system. Electron localization in the P2E-PSSA and POP-PSSA was greater than PANI-PSSA; the electron-donating characteristic of the ethyl and ethoxy groups appeared to reduce conductivity.

Relationship of EPR to conductivity

The conductivity of P2E-PSSA and POP-PSSA were around 10^{-2} S/cm. EPR spectral data gave evidence

for the existence of highly mobile radical cations or polarons of the substituted PANI salts and their complexes, which was shown to be due to localization because they were heavily doped and highly disordered systems.

CONCLUSIONS

The results of electrochemical color/discolor time of the substituted PANI complexes are described as follows. First, with a reaction time of 3 s, when the monomer (aniline, *o*-phenetidine, or 2-ethylaniline) concentration was 0.6M and the PSSA concentration was 0.15M, the best color/discolor time (film thickness) of P2E-PSSA was 500/300 ms (2.19 μm); for POP-PSSA complexes, the best time was 125/125 ms (3.00 μm). The results were due to the fact that the substituted PANI had a steric effect caused by the alkyl group ($-\text{OC}_2\text{H}_5$), which allowed the color/discolor time of POP-PSSA to be faster than that of P2E-PSSA.

Second, with the same film thickness (10 μm) for electrochemical polymerization with a concentration of PSSA of 0.15M and monomer concentration of 0.6M (reaction time) [aniline (18.5 s), *o*-phenetidine (10 s), or 2-ethylaniline (12.7 s)], the best color/discolor time of PANI-PSSA was 1500/750 ms; the best time for POP-PSSA was 500/250 ms; and the best time for P2E-PSSA was 750/500 ms. The color/discolor time of POP-PSSA was faster than that of PANI-PSSA.

Third, the film growth rate of POP-PSSA (1.00 $\mu\text{m/s}$) was faster than those of P2E-PSSA (0.79 $\mu\text{m/s}$) and PANI-PSSA (0.54 $\mu\text{m/s}$). From the surface morphology, the porous density of the POP-PSSA was much higher than those of the P2E-PSSA and PANI-PSSA complexes, with very easy proton and ion transfer. The color/discolor time change was very large. In

TABLE V
Best Color and Discolor Times for POA-PSSA, POP-PSSA, and PANI-PSSA Complexes by Electrochemical Polymerization

Reaction time (s)	Sample	Substituted group	Color time (ms)	Discolor time (ms)	Film thickness (μm) ^a
3	POA-PSSA	$-\text{OCH}_3$	125	125	4.13
	POP-PSSA	$-\text{OC}_2\text{H}_5$	125	125	3.00
	P2E-PSSA	C_2H_5	500	300	2.19
10	POA-PSSA	$-\text{OCH}_3$	250	320	12.31
	POP-PSSA	$-\text{OC}_2\text{H}_5$	250	200	10.04
	P2E-PSSA	C_2H_5	625	500	7.89
25	POA-PSSA	$-\text{OCH}_3$	875	750	>>25
	POP-PSSA	$-\text{OC}_2\text{H}_5$	550	375	>25

^a Average of five measurements by a nanospectrometer.

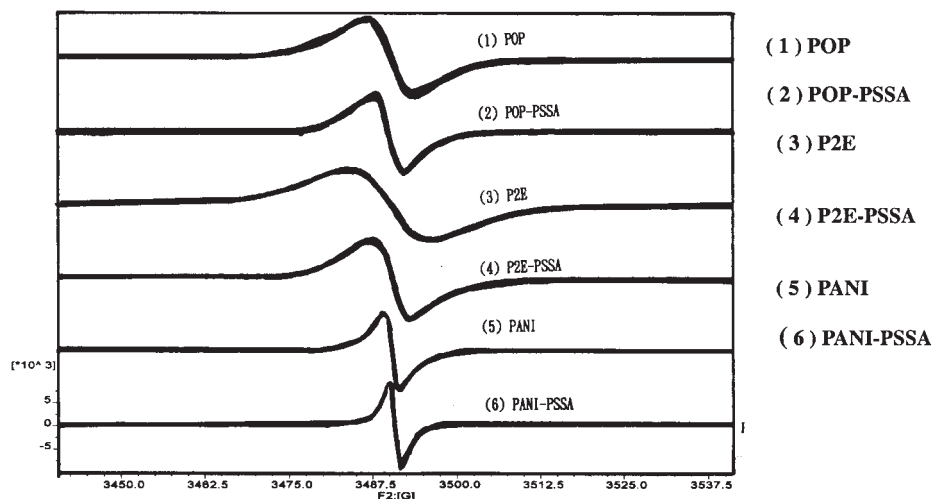


Figure 14 EPR spectra of all the six PANI complexes.

the PANI structure, for the steric effect of the substituted group, a bigger group ($-\text{OC}_2\text{H}_5$) with larger reactivity and more porosity was very useful for proton and ion transfer.

The substituted PANI complexes POP-PSSA and P2E-PSSA showed a single fine signal without any hyperfine splitting structure. The g values were around 2.00296–2.00321, which was almost the free-electron g value. The narrower line width in PANI complexes compared to HCl salts was attributed to a lower degree of structural disorder. The larger line width of the substituted PANI complexes was attributed to the steric effect of the substituents, which decreased the degree of delocalization of radical cations. The electron-donating characteristics of the ethyl group and ethoxy group appeared to reduce conductivity. The addition of side groups ($-\text{C}_2\text{H}_5$ or $-\text{OC}_2\text{H}_5$) and the presence of excessive $-\text{SO}_3^-$ led primarily to the formation of bipolarons and,

TABLE VI
EPR Results for Substituted PANI Complexes Under Argon

	298 K		77 K	
	ΔH_{pp} (Gauss)	g	ΔH_{pp} (Gauss)	g
POP	4.665	2.00300	5.835	2.00305
POP-PSSA	4.454	2.00301	5.909	2.00321
P2E	7.183	2.00300	10.344	2.00298
P2E-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

g = The central point of wavecrest and wavetrough; ΔH_{pp} = Linewidth between centerline of peaks (that is, perpendicular).

TABLE VII
EPR Results for Substituted PANI Complexes Under Air

	298 K		77 K	
	ΔH_{pp} (Gauss)	g	ΔH_{pp} (Gauss)	g
POP	7.161	2.00304	9.577	2.00317
POP-PSSA	5.258	2.00302	6.177	2.00315
P2E	12.227	2.00319	14.089	2.00312
P2E-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

ΔH_{pp} = Line width between center line of peaks.

thus, lower conductivity, due to localization because they were heavily doped and highly disordered systems. We concluded, therefore, that although the magnetic properties were due to polaron spins, both the paramagnetic polarons (radical cations) and the diamagnetic bipolarons (spinless; dications) were involved in charge transport.

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