

Investigations of Chemically Synthesized Poly(aniline-*co*-*o*-toluidine)s Doped with Dodecylbenzenesulfonic Acid

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ABSTRACT: *In situ* ultraviolet–visible (UV–vis) and Raman spectroelectrochemical investigations of chemically synthesized homopolymers and copolymers of aniline and *o*-toluidine are reported and discussed. The copolymers in their metallic state are soluble in volatile solvents such as chloroform and thus could be processed easily for electrochemical investigations. The oxidation wave in cyclic voltammograms corresponding to the emeraldine-to-*pernigraniline* transformation of poly(*o*-toluidine) (POT), unlike in polyaniline (PANI), does not show multiple peaks, and this indicates a relatively faster exchange of counterions. *In situ* UV–vis and Raman spectroscopy has revealed that

the electrode potential at which the transformation from the emeraldine state to the *pernigraniline* state occurs is influenced by the fraction of *o*-toluidine in the feed. The spectroelectrochemical behavior of copolymers containing higher feed fractions of aniline resembles that of PANI, whereas the spectroelectrochemical behavior of copolymers with a higher feed fraction of *o*-toluidine resembles that of POT. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 700–708, 2009

Key words: conducting polymers; copolymerization; electrochemistry

INTRODUCTION

The undiminished research interest in polyaniline (PANI) is due to its environmental stability, inexpensive synthesis costs, various possible technological applications, and wide range of conductivity (up to the order of 10^3 S/cm).^{1,2} It is well known that solubility and processability problems associated with PANI can be overcome by the copolymerization of aniline with toluidines.³ Meanwhile, research aimed at a more soluble form of the parent compound PANI has attracted greater interest in recent years.^{4–7} The enhanced solubility of PANI in these reports is due to the bulky organic acids used as dopants. We have reported an inverse emulsion protocol for the synthesis of PANI–dodecylbenzenesulfonic acid (DBSA), which is completely soluble in chloroform.⁸ DBSA, being a large molecule, facilitates the solubility of the resulting PANI. Electrochemical and spectroelectrochemical investigations of soluble PANI–DBSA have already been reported.^{8,9}

In parallel to the research on the solubility of the parent polymer PANI, copolymers of aniline and *o*-

toluidine, as mentioned previously, are also of potential research interest because the properties of the copolymers can be tuned. Poly(aniline-*co*-*o*-toluidine)s (PATs) synthesized both chemically with ammonium persulfate as an oxidizing agent^{3,10,11} and electrochemically^{12–14} have been reported. Their spectroscopic, electrochemical, and microscopic properties have been extensively investigated. Most of these studies have employed aqueous mineral acids as dopants, and thus the solubility of the reported copolymers is for the nonprotonated emeraldine base form of the copolymers. All these reported studies were successful either in retaining the electrical conductivity of PANI or in tuning the conductivity over a broad range. However, copolymers in their conducting emeraldine salt state exhibit partial solubility in high-boiling solvents such as dimethyl sulfoxide, dimethyl formamide, and *N*-methyl-2-pyrrolidone (NMP). They are only sparingly soluble in weakly polar solvents such as chloroform. Because of such solubility problems, there are few reports on the electrochemical properties of chemically synthesized PANI or its copolymers.^{10,15,16} The pioneering work on copolymers of aniline and *o*-toluidine was reported by Wei et al.;¹⁰ however, they stated that the electrochemical properties of the chemically synthesized copolymers are similar to the those of the electrochemically synthesized copolymers. Su et al.¹⁶ studied the cyclic voltammetry of chemically synthesized PAT camphorsulfonic acid salts. They followed an elaborate process for coating in which copolymers dissolved

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in nonvolatile solvents such as dimethyl sulfoxide, NMP, or *m*-cresol were drop-coated onto a platinum electrode.

DBSA, which is extensively used to protonate PANI (mainly to induce solubility), has not been used to protonate poly(*o*-toluidine) (POT). One of the main reasons is the steric hindrance arising from the methyl substituent near the nitrogen atom. However, in our previous report, we showed that DBSA can significantly dope the POT backbone by undergoing conformational rearrangements.¹⁷ An inverse emulsion procedure and benzoyl peroxide as an oxidant have been employed to synthesize soluble POT and PATs. The synthesis procedure and spectroscopic and microscopic investigations of the copolymers have been reported.¹⁷ In this report, spectroelectrochemical investigations of these chemically synthesized copolymers are discussed. An attempt is made to compare the electrochemical behaviors of the chemically and electrochemically synthesized copolymers.

EXPERIMENTAL

Chemicals

Aniline (VEB Laborchemie Apolda, Apolda, Germany; analytical-reagent grade) and *o*-toluidine (Merck, Darmstadt, Germany) were distilled under reduced pressure and stored under nitrogen. DBSA (70 wt % in 2-propanol; 70% solution; Aldrich, Taufkirchen, Germany), tetrabutylammoniumtetrafluoroborate (Aldrich), and fluoroboric acid (as a diethyl ether complex; purum; Fluka, Buchs, Switzerland) were used as received. Ultrapure water (Pro 90 C, Seralpur, Ransbach - Baumbach, Germany) was used. All other chemicals were analytical-grade reagents and were used as received. Indium-doped tin oxide (ITO) coated glass sheets (R (surface resistance) = 20 Ω/cm^2), used in the spectroelectrochemical studies, were supplied by Merck.

Synthesis of PATs

The copolymerization of aniline and *o*-toluidine was carried out in an inverse emulsion medium composed of toluene and 2-propanol (V/V 2 : 1) and water in the presence of DBSA with benzoyl peroxide as an oxidant. Details of the synthesis and purification procedure have been described elsewhere.¹⁷ We synthesized copolymers with molar aniline/*o*-toluidine compositions of 7 : 3, 5 : 5, and 3 : 7 by varying the molar feed ratios of the comonomers; these are labeled PAT-73, PAT-55, and PAT-37, respectively. The total concentrations of the monomers in the feed and the ratios of the monomer to the oxidant were kept constant. Homopolymers of aniline

(PANI) and *o*-toluidine (POT) were also synthesized in a similar fashion.

Characterization

For the *in situ* ultraviolet-visible (UV-vis) measurements, polymers dissolved in CHCl_3 were drop-coated onto clean ITO-coated glass sheets that were subsequently used as working electrodes. A quartz cell with a 1-cm path length fitted with a platinum wire as a counter electrode and a saturated calomel electrode (SCE) connected via a salt bridge as a reference electrode served as a three-electrode cell. *In situ* measurements were carried out with a Shimadzu UV-2101 PC-driven scanning spectrometer (resolution = 0.1 nm) under ambient conditions.

Cyclic voltammograms (CVs) were recorded under a nitrogen atmosphere in a three-electrode H cell using a custom-built potentiostat connected to a computer with an analog-digital/digital-analog (AD/DA) converter. CVs were recorded in three different 1N aqueous acids (sulfuric, perchloric, and hydrochloric acids). The homopolymer/copolymer, dissolved in chloroform and drop-coated onto a glassy carbon electrode (GCE; HTW, Thierhaupten, Germany), was used as a working electrode. A Pt sheet and an SCE were used as counter and reference electrodes, respectively.

In situ Raman spectra were measured on an ISA 64000 spectrometer (Instrument SA, Longjumeau, France) equipped with a liquid-nitrogen-cooled charged coupling device camera detector at a resolution of 2 cm^{-1} . Samples were illuminated with 514.5-nm laser light from a Coherent Innova (Santa Clara, CA) 70 argon-ion laser (laser light intensity P_0 is given in the figures). A special three-compartment cell containing an aqueous electrolyte solution of 1N H_2SO_4 (99.995%) was used, and the cell was purged with nitrogen for 6 min before the measurements. Homopolymers/copolymers dissolved in CHCl_3 were drop-coated onto a platinum disc electrode polished with $\gamma\text{-Al}_2\text{O}_3$ (0.05 μm) and subsequently used as a working electrode. A platinum sheet electrode and an SCE were used as counter and reference electrodes, respectively. The Raman spectra thus obtained were slightly smoothed and baseline-corrected for better visibility. All electrode potentials are given as E_{SCE} versus the saturated calomel electrode.

RESULTS AND DISCUSSION

Polymerization yield, solubility, elemental composition, *in situ* electrical conductivity, and structural characterizations of POT and its copolymers have already been reported.¹⁷ Use of the inverse emulsion polymerization route enables bulky DBSA to efficiently dope POT and copolymers by overcoming the steric hindrance exerted by the methyl group.

Copolymers of aniline and *o*-toluidine exhibit better solubility in chloroform and in a (V/V) 2 : 1 mixture of toluene and 2-propanol than POT; however, the solubility is lower than that of PANI. The difference in the solubility can be attributed to the difference in the bulk morphology of the polymers. A clear, bright green solution obtained after filtration can be drop-coated, spin-coated, or dip-coated onto various metallic and glass substrates. UV-vis spectroscopy, Fourier transform infrared spectroscopy, and cyclic voltammetry studies have confirmed the formation of real copolymers. The results of a comprehensive investigation using cyclic voltammetry, *in situ* UV-vis spectroscopy, and Raman spectroscopy are described next.

Cyclic voltammetry

CVs of POT drop-coated onto a GCE and recorded in three different aqueous mineral acids (1N) are shown in Figure 1(a). CVs with all three mineral acids show two redox processes corresponding to leucoemeraldine-to-emeraldine transformations and then pernigraniline transformations. It is clear from Figure 1(a) that the first oxidation wave of POT ($E_{ox,1}$), compared to that of PANI, has shifted to a more positive potential, whereas the second oxidation wave ($E_{ox,2}$) has shifted to less positive potentials. However, the magnitude of the cathodic shift in $E_{ox,2}$ is much smaller than that of the anodic shift in $E_{ox,1}$. The conductivity in the emeraldine oxidation state (the region between $E_{ox,1}$ and $E_{ox,2}$) is due to the presence of radical cations (polarons). The ease of formation of these radical cations and their stability determine the potential window in which this conductive form of the polymer is stable. The presence of methyl groups, despite their electron-donating tendency, strongly hinders the free rotation of the C—N—C chain of the polymeric backbone where the radicals are generated. Hence, the energy required to create the radicals is increased, and this is reflected by the anodic shift of $E_{ox,1}$. The steric interactions also make the radical cations unstable, and so their transformation to a higher oxidation state becomes easier, as indicated by the cathodic shift of $E_{ox,2}$. Similar trends were observed by Probst and Holze¹² for electrochemically synthesized POT in HClO₄. Hence, the electrochemical behavior of POT chemically synthesized with this protocol is similar to that of electrochemically synthesized POT. However, the lower magnitude of the cathodic shift observed for $E_{ox,2}$ may be due to the sterically favorable molecular conformation of the polymer synthesized with this protocol, which leads to the improved stability of the radical cations.

The oxidation potential of POT, particularly $E_{ox,2}$, is strongly influenced by the counterions present in

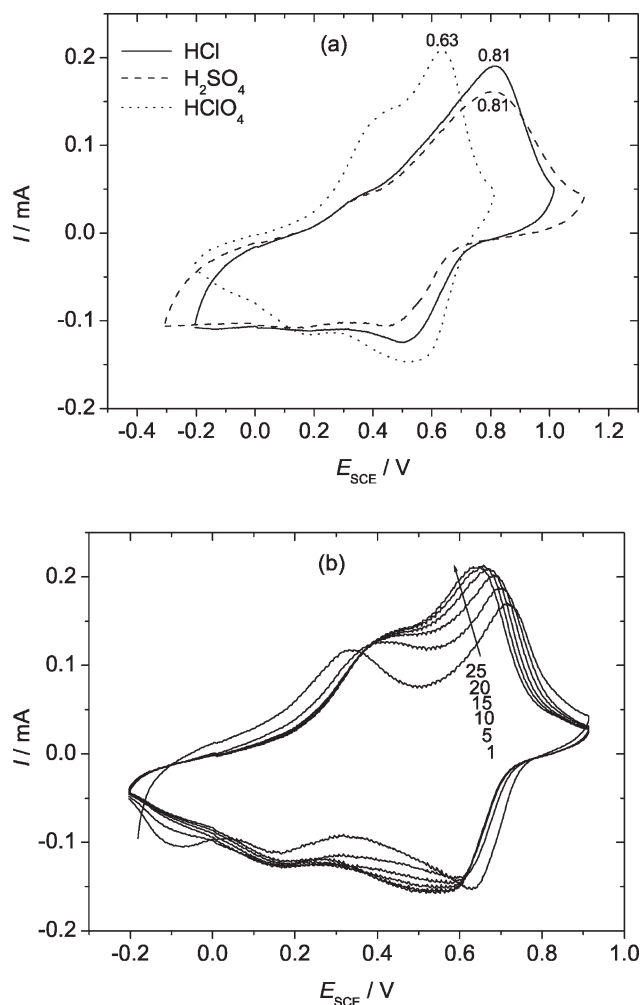


Figure 1 CVs of a POT drop-coated GCE recorded in (a) three different mineral acids (1N, 30th cycle) and (b) 1N HClO₄ with progressively increasing cycle numbers (scanning rate = 50 mV/s).

the electrolyte. In HCl and H₂SO₄, $E_{ox,2}$ appears at $E_{SCE} = 0.81$ V, whereas it appears at $E_{SCE} = 0.63$ V in HClO₄. During the first 20 cycles, $E_{ox,2}$ of POT in HClO₄ shifts to more negative potentials, and a gradual increase in the peak current can be observed [Fig. 1(b)]. In solutions of HCl and H₂SO₄, the cathodic shift is very small, and the peak current shows a gradual decrease. With a further increase in the number of cycles, more reproducible CVs are obtained. These observations suggest that in HClO₄, the radical cations formed above $E_{ox,1}$ are not stable, and this may be due to the conformational rearrangement taking place in this electrolyte. Interestingly, unlike PANI, no new oxidation wave appears during cycling, and this indicates faster exchange of the anions in the acid and the bulky dopant anions present in the polymer film.⁸

CVs recorded in 1N HClO₄ for homopolymers and copolymers with different molar fractions of the

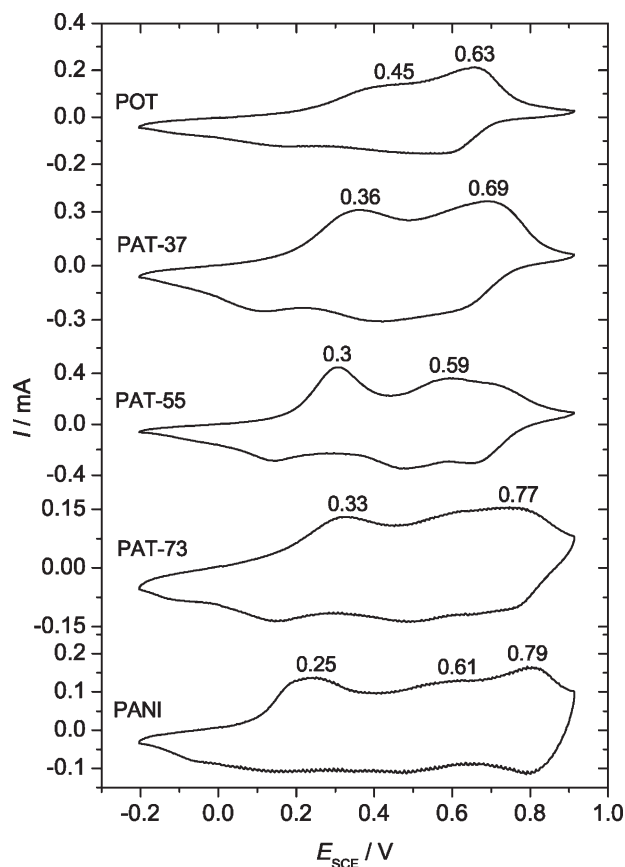


Figure 2 CVs of homopolymers and copolymers recorded in 1N HClO₄. Solutions of the polymers were drop-coated onto a working GCE (scanning rate = 50 mV/s, 30th cycle).

comonomers in the feed are shown in Figure 2, and their oxidation potentials are listed in Table I. The electrochemical responses of the copolymers are strongly influenced by the molar fraction of the comonomers in the feed. The value of $E_{ox,1}$ of the copolymers falls between the values of PANI and POT. When the feed concentration of *o*-toluidine is increased, $E_{ox,1}$ of the copolymer gradually shifts toward $E_{ox,1}$ of POT. Copolymers containing a higher molar fraction of aniline in the feed exhibit two oxidation waves in the region of $E_{SCE} = 0.6\text{--}0.8$ V

(Fig. 2), and this indicates their resemblance to PANI. Similarly, copolymers with a higher molar fraction of *o*-toluidine in the feed resemble POT. The potential window of POT ($E_{ox,2} - E_{ox,1}$; high conductivity range) is approximately 330 mV smaller than that of PANI (Table I). We have shown earlier that copolymerization improves the conductivity of POT.¹⁷ In addition, it also extends the applicable potential window (Table I). As mentioned in the previous paragraph for POT, CVs of the copolymers recorded in 1N HCl and H₂SO₄ do not show broad variations in the position of $E_{ox,2}$, thereby not showing any conformational rearrangement destabilizing the radical cations (Fig. 3). As in the case of PANI, the electrochemical responses of POT and PATs are not very good because of the poor wettability of the bulky counter ions. The presence of a single redox pair in the copolymers for each redox process suggests the formation of real copolymers and not of composites, which otherwise would have resulted in separate redox pairs for PANI and POT.^{10,16} This indicates that the expected copolymers are produced by this protocol using benzoyl peroxide as the oxidant and DBSA as the dopant.

Generally, the first oxidation peak in the CV of electrochemically synthesized PANI, POT, or copolymers is sharp, and its peak current is much higher than the second oxidation peak.^{12,10,18} However, homopolymers as well as copolymers synthesized by this protocol exhibit an opposite behavior; that is, the peak current of the second oxidation peak is much higher than that of the first one. In the case of PANI-DBSA, such a trend can be observed only in the first 10 cycles. During an electrochemical reduction, counterions are expelled from the polymer film, whereas their insertion takes place during oxidation. The emeraldine state is the inherent oxidation state of a chemically synthesized polymer, and it is further stabilized by a stable chain conformation. Because of the strong complexation of the polar head group of DBSA with the amine/imine moiety of the polymer backbone, the emeraldine-to-leuco-emeraldine transformation is much slower during potential cycling.⁹ *In situ* UV-vis spectroscopy

TABLE I
Molar Concentrations of the Monomers in the Feed and the Oxidation Potentials ($E_{ox,1}$ and $E_{ox,2}$) and the peak potential differences ΔE of the Homopolymers and Copolymers Obtained from Their CVs Recorded in HClO₄ at a Scanning Rate of 50 mV/s

Sample code	Monomer concentration		$E_{ox,1}$ (V)	$E_{ox,2}$ (V)	ΔE (mV)	
	Aniline (M)	<i>o</i> -Toluidine (M)				
PANI	0.01	0	0.25	0.61	0.79	540
PAT-73	0.007	0.003	0.33	0.63	0.77	440
PAT-55	0.005	0.005	0.30	0.59	0.69	390
PAT-37	0.003	0.007	0.36	—	0.69	300
POT	0	0.01	0.45	—	0.66	210

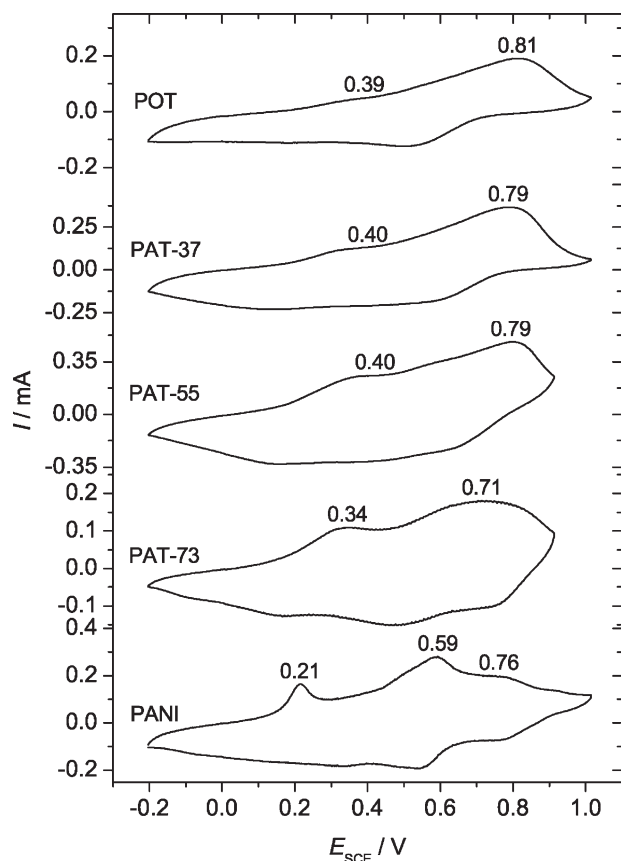


Figure 3 CVs of homopolymers and copolymers recorded in 1N HCl. Solutions of the polymers were drop-coated onto a working GCE (scanning rate = 50 mV/s, 30th cycle).

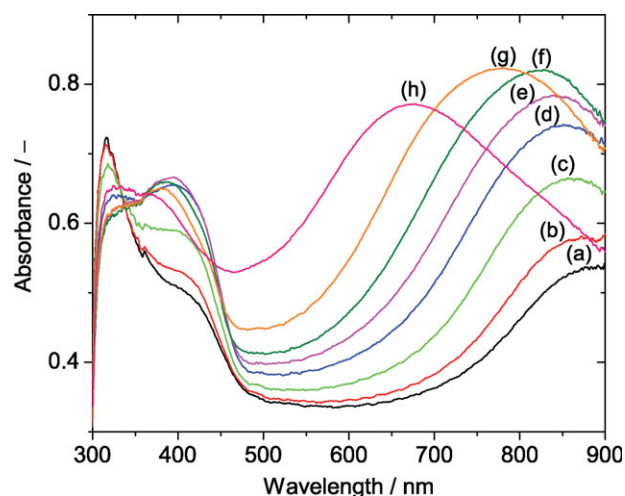


Figure 4 *In situ* UV-vis spectra of POT-coated ITO glass sheets recorded in 1N H₂SO₄ at successively shifting positive potentials. The E_{SCE} values were (a) -0.2, (b) 0.1, (c) 0.2, (d) 0.3, (e) 0.4, (f) 0.5, (g) 0.6, and (h) 0.7 V. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

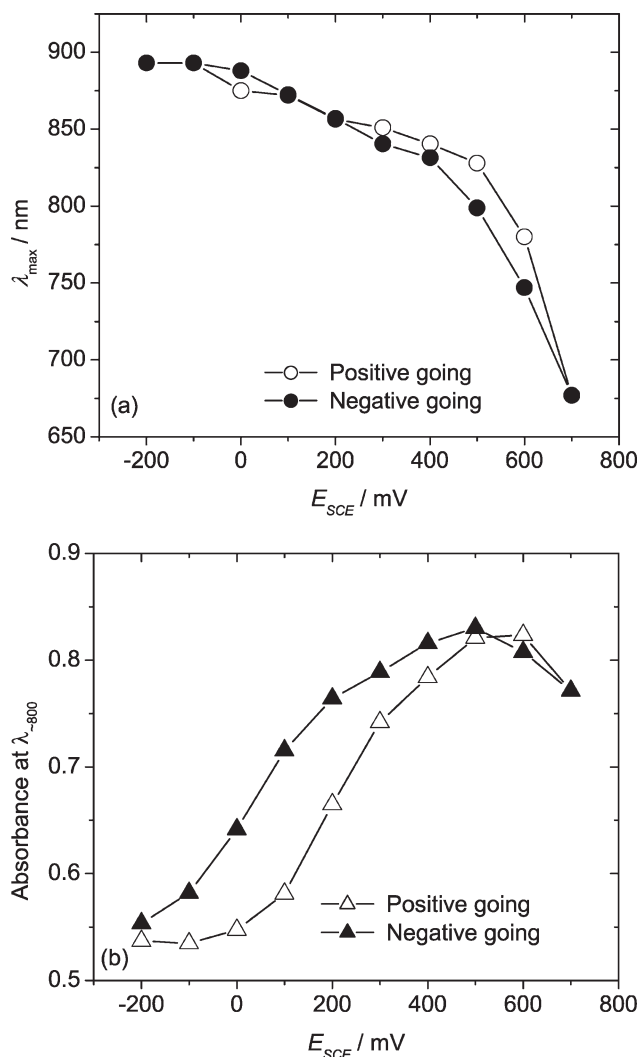


Figure 5 Plots of (a) absorption maximum (λ_{max}) and (b) absorbance at λ_{max} versus the applied potential for POT.

(discussed later) also reveals the presence of radical cations at the applied potential at which PANI and POT are in their completely reduced states. This leads to higher peak currents for the second oxidation potential. Su et al.¹⁶ observed a similar trend for POT and copolymers of aniline and toluidine synthesized with 2,3-dichloro-5,6-dicyanobenzoquinone as an oxidant and (+)-camphorsulfonic acid as a dopant but gave no explanation for the observed trend. Wei et al.¹⁰ reported that CVs of chemically prepared PATs (dissolved in NMP and drop-coated on the electrode surface) were identical to those of electrochemically synthesized ones; however, no detailed discussion on the CV profile was given.

In later sections of this article, results obtained with both Pt discs and ITO-coated glass plates as electrode surfaces are reported, and they are compared with results of CV studies carried out on GCEs. As these homopolymers or copolymers were synthesized chemically and drop-coated onto these

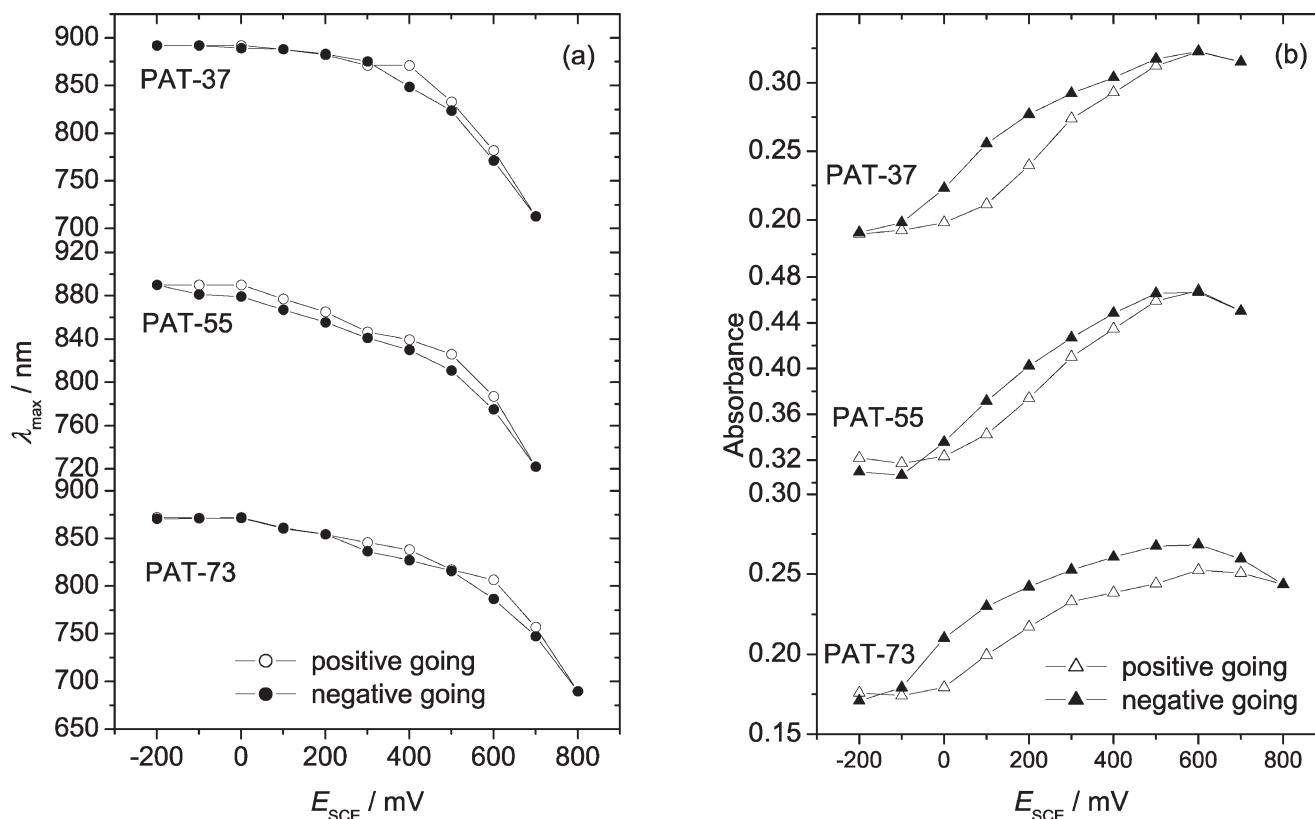


Figure 6 Plots of the (a) λ_{\max} and (b) absorbance of a low-energy polaron band as a function of the applied potential for copolymers containing different molar fractions of the comonomers in the feed.

various electrode surfaces, it is fair to assume that their electrochemical responses did not depend on the electrode material. This was further confirmed by the recording of CVs of homopolymers and copolymers on Pt-sheet and GC electrodes, on which similar CV profiles have been observed.

In situ UV-vis spectroscopy

Figure 4 shows *in situ* UV-vis spectra of POT recorded in 1N H_2SO_4 at different potentials successively shifted into the anodic direction. *In situ* UV-vis spectral responses of the POT film are similar to those of PANI, except for the fact that electrode potentials at which interconversions of the oxidation states take place have been shifted.⁸ The absorption band at $\lambda = 800$ nm, corresponding to the polaron transition, shows a blueshift as the applied potential (E_{SCE}) increases from -0.2 to 0.8 V. The emeraldine-to-pernigraniline transformation, evidenced by the steep blueshift of the low-energy polaron band ($\lambda \approx 800$ nm), can be observed at $E_{\text{SCE}} \geq 0.5$ V for POT ($E_{\text{SCE}} \geq 0.7$ V for PANI). Interestingly, the broad overlapping band at $\lambda \approx 385$ nm, observed in the solution-state spectrum of POT, splits into two bands during an ongoing potential sweep. The high-energy polaron band originating from the radical cations

exhibits maximum absorbance at $E_{\text{SCE}} = 0.2$ V for PANI, whereas its absorbance increases up to $E_{\text{SCE}} \sim 0.4$ V in the case of POT. This is in accordance with the first oxidation peak potential observed in the CV of POT (Fig. 1). Similar to those of PANI, the UV-vis responses of the POT film follows its CV profile.⁸ At $E_{\text{SCE}} < 0.2$ V, UV-vis responses, characteristic of leucoemeraldine, have been observed (Fig. 4). However, the band corresponding to radical cations is present even at $E_{\text{SCE}} = -0.2$ V, as in the case of PANI, indicating the presence of charged species in the reduced state. Similar results were reported by Yang et al.¹⁴ for electrochemically synthesized HCl-doped POT on ITO glass electrodes.

In situ spectroelectrochemical measurements were also carried out in the negative direction soon after the anodic sweep to check the electrochromic reversibility and electrochemical stability of the material. POT synthesized by this method shows good electrochromic reversibility in terms of band position (related to the average conjugations lengths), as reflected by the overlapping lines in Figure 5(a); however, hysteresis is shown in Figure 5(b). It was initially thought that instability of POT at the higher applied potential causes the hysteresis, but multiple-cycle cyclic voltammetry measurements in the range of $E_{\text{SCE}} = -0.2$ to 1 V have not supported this

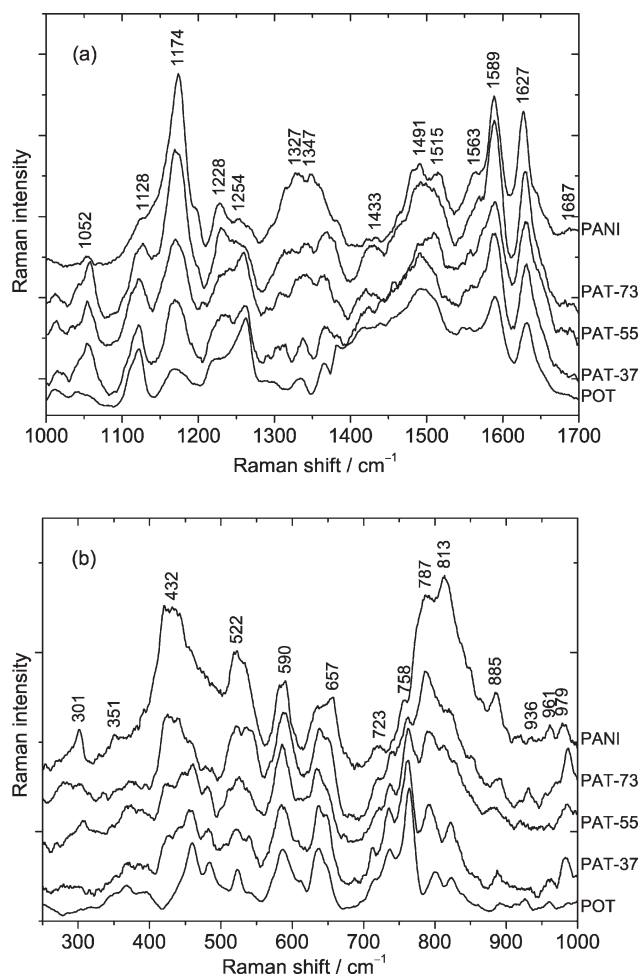


Figure 7 *In situ* Raman spectra of films of PANI, POT, and the copolymers with 7 : 3, 5 : 5, and 3 : 7 molar ratios of aniline to *o*-toluidine in the feed recorded in 1N H₂SO₄ ($E_{\text{SCE}} = 0.8$ V, $\lambda_0 = 514.5$ nm, $P_0 = 100$ mW at the sample). Parts a and b show two different Raman shift regions. The spectra are stacked for better visibility.

assumption because peak currents of $E_{\text{ox},2}$ do not decrease during the first 20 cycles. Furthermore, careful observation of Figure 5(b) shows the recovery of the absorbance at more negative potentials. Therefore, the hysteresis has been attributed to the slower reduction kinetics. This also explains the higher absorbance values during the cathodic sweep [Fig. 5(b)].

The general trend in the UV-vis spectral responses of films of copolymers in the applied range of electrode potentials is similar to that of POT. However, the electrode potential at which the emeraldine-to-pernigraniline transformation takes place depends on the fraction of *o*-toluidine in the copolymer. This transformation takes place at less positive potentials ($E_{\text{SCE}} = 0.4$ – 0.5 V) for the copolymers generated from a higher concentration of *o*-toluidine in the feed (≥ 0.005 M), but it occurs at $E_{\text{SCE}} \geq 0.6$ V for the copolymers with the lower feed concentration of *o*-toluidine (≤ 0.005 M). Likewise, E_{SCE} , at which the

highest concentration of the radical cations is observed ($A_{\sim 420 \text{ nm}}$, the absorbance A taken as a measure of concentration), also depends on the *o*-toluidine content of the copolymer. All these observations clearly indicate that the spectral responses of copolymers containing a higher molar fraction of aniline in the feed are similar to that of PANI, whereas copolymers containing a higher molar fraction of *o*-toluidine behave like POT. Like PANI and POT, the copolymers also exhibit good electrochromic reversibility [overlapping lines in Fig. 6(a)]. However, as described earlier, the electrochemical stability of the copolymer films in the applied potential range ($E_{\text{SCE}} = -0.2$ to 0.8 V) could not be evaluated because of the slower reduction kinetics [Fig. 6(b)].

Raman spectroscopy

The laser excitation ($\lambda_0 = 514.5$ nm) falls in the lower wavelength wing of the absorption band centered at 570–650 nm (the position depends on the applied potential), originating from the pernigraniline oxidation state of the polymer backbone, which exists at $E_{\text{SCE}} > 0.5$ V. Beyond this applied potential, the intensity of the Raman signals is considerably enhanced by preresonance enhancement.^{8,19} Hence, Raman spectra of homopolymers and copolymers recorded at a constant applied potential of $E_{\text{SCE}} = 0.8$ V (Fig. 7) are compared to study the influence of the *o*-toluidine fraction on the molecular structure. It is important to note that at this applied potential, the dominant oxidation state is pernigraniline, and so bands mainly due to quinoid rings are present in the Raman spectra. Major Raman bands and their assignments are summarized in Table II.

The Raman spectrum of POT exhibits all the bands that are observed in the spectrum of PANI with a small shift in their positions.⁸ *In situ* Raman spectra of PANI, POT, and copolymers with different molar fractions of the comonomers in the feed are displayed in Figure 7. The multiplicity of quinoid C–C stretching (1515 , 1563 , and 1589 cm⁻¹), which is sensitive to the applied potential, is visible in the Raman spectra of all the polymers and more clearly in the spectrum of PANI.²⁰ PANI exhibits a strong band at approximately 1345 cm⁻¹ due to the C–N stretching mode of the semiquinone radical cation, which splits into a new band at 1327 cm⁻¹ at higher applied potentials.²¹ Interestingly, this band further splits into three well-resolved bands in the case of POT (Fig. 7), with the third band appearing at approximately 1365 cm⁻¹. The multiplicity of the band due to the semiquinone radical in the Raman spectra of all the copolymers is similar to that of POT. The influence of the comonomer feed ratios on the structure of the polymer can be observed in the region of 1226 – 1260 cm⁻¹. The strong band at

TABLE II
Major Raman Bands and Their Assignments for the PANI, POT, and PAT Films Recorded in 1N H₂SO₄

Raman shift (cm ⁻¹)			State ^a	Band assignments ^{20,21}
PANI	POT	Copolymer		
1626–1630	1627–1632	1627–1632	B	C–C ring stretching
1585–1600	1589–1603	1590–1605	Q	C–C ring stretching
1506–1516	1490–1510	1510–1520	Q	C=N stretching
1480–1486	—	1490–1500	Q	C=N stretching
—	1365–1370	1360–1365	SQR	C–C stretching + C–H bending
1339–1349	1330–1335	1330–1350	SQR	C–N ⁺ stretching
1257–1266	1260–1270	1260–1265	B	C–N stretching
—	1250–1255	1250–1255	—	C–C twisting of methyl group
1228	1226	1226–1230	Q	C–N stretching
1190–1197	1200–1210	1190–1200	B	C–H in-plane bending
1171–1174	1160–1170	1165–1175	Q	C–H in-plane bending
—	1110–1125	1110–1125	—	C–C stretching of methyl group
1008–1015	1010–1015	1005–1020	—	May be DBSA
885	887–900	880–900	B	In-plane ring deformation
830–836	820–830	811–820	Q	In-plane ring deformation
800–815	800	775–800	Q	C–H out-of-plane bending
712–724	720–730	710–720	B	Out-of-plane ring deformation
685–698	—	—	SQR	Out-of-plane ring deformation
630	630–640	630–640	B	In-plane ring deformation

^a B = benzoid ring; Q = quinoid ring; SQR = semiquinone radical.

1228 cm⁻¹ in the Raman spectrum of PANI originates from the C–N stretching of quinoid rings and shows a gradual decrease in the intensity with an increase in the molar fraction of *o*-toluidine in the feed. The band at 1254 cm⁻¹ due to C–C twisting of the methyl group increases in intensity with an increase in the feed concentration of *o*-toluidine (Table II). Another characteristic band of POT appears at 1128 cm⁻¹ and is assigned to the C–C stretching of the methyl side group.²² The intensity of this band increases with an increase in the feed ratio of *o*-toluidine, and this confirms that more and more *o*-toluidine units have entered the polymer chain. A band at 813 cm⁻¹ in the spectrum of PANI, assigned to the out-of-plane C–H bending mode of quinoid rings, shows a gradual decrease in its intensity in the spectra of the copolymers. The bands in the region of 730–830 cm⁻¹ are well resolved for POT and the copolymers [Fig. 7(b)]. This better resolution is due to the more positive applied potential ($E_{SCE} = 0.8$ V). At this potential, the concentration of quinoid segments is higher for POT and the copolymers than for PANI. In both POT and the copolymers, the spectral behaviors of the bands at 1628, 1590, 1195, and 1173 cm⁻¹ are similar to those of PANI (Fig. 7), except for the fact that the appearance or bleaching of the bands takes place at lower potentials with an increase in the *o*-toluidine fraction in the copolymers.

In the case of POT, the intensity of the band at 1510 cm⁻¹, which is attributed to a C–N stretching vibration, exhibits a sharp increase when E_{SCE} is greater than 0.2 V. As reported by Goff and Ber-

nard,²⁰ this band is sensitive to the applied potential, and the transformation of any smaller segments of the polymer leads to an increase in the intensity of this band. In copolymers, this band appears at higher potentials and is strongly influenced by the molar fraction of the comonomers in the feed. For example, in the case of PAT-55, it appears at 1519 cm⁻¹ at $E_{SCE} > 0.5$ V and is redshifted to 1509 cm⁻¹ with a further increase in the applied potential (Fig. 8). The intensity of the band at 1114 cm⁻¹ due to the methyl group increases with an increase in the applied potential and is blueshifted to 1122 cm⁻¹. As discussed for UV-vis spectroscopy and cyclic

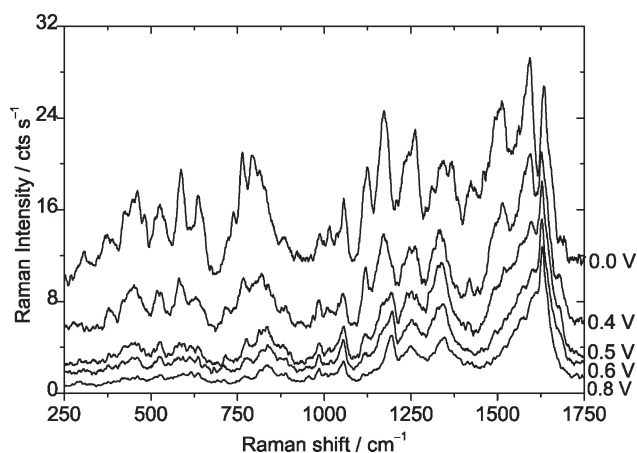


Figure 8 *In situ* Raman spectra of a PAT-55 drop-coated film in 1N H₂SO₄ recorded at various applied potentials progressively shifted in the positive direction ($\lambda_0 = 514.5$ nm, $P_0 = 100$ mW at the sample).

voltammetry, the application of an electrode potential to a chemically synthesized POT film induces a conformational change that is responsible for the blueshift of the band at 1114 cm^{-1} . A similar trend can be observed for the copolymers. The bands in the region of $1140\text{--}1350\text{ cm}^{-1}$ are well resolved at $E_{\text{SCE}} > 0.4\text{ V}$, and a new band appears at 1020 cm^{-1} . A further increase in the applied potential shifts this band to 1012 cm^{-1} .

CONCLUSIONS

The spectroelectrochemical characterization of PANI, POT, and their copolymers could be successfully carried out because of the improved solubility of the homopolymers and copolymers synthesized with an inverse emulsion route. *In situ* UV-vis responses of POT as well as the copolymers resemble those of PANI, except for the fact that the emeraldine-to-pernigraniline transformation occurs at a lower positive potential than that of PANI. In the applied potential range, POT and the copolymers exhibit good electrochromic reversibility. The electrochemical behavior of POT in aqueous acids does not exhibit a kinetic influence of anion exchange during cycling. The electrochemical response of copolymers containing higher concentrations of aniline is more similar to that of PANI, whereas the copolymers containing higher fractions of *o*-toluidine behave like POT. *In situ* Raman spectroscopy confirms that the amount of *o*-toluidine moieties incorporated into the

polymer backbone depends on the feed ratios of the comonomers.

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