Synthesis and Characterization of Conducting Homopolymers and Copolymers of *o*-Anisidine and *o*-Toluidine in Inorganic and Organic Supporting Electrolytes

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ABSTRACT: The influence of inorganic and organic supporting electrolytes on the electrochemical, optical, and conducting properties of poly(*o*-anisidine), poly(*o*-toluidine), and poly(*o*-anisidine-*co*-*o*-toluidine) thin films was investigated. Homopolymer and copolymer thin films were synthesized electrochemically, under cyclic voltammetry conditions, in aqueous solutions of inorganic acids (H_2SO_4, HCl, HNO_3, H_3PO_4, and $HClO_4$) and organic acids (benzoic acid, cinnamic acid, oxalic acid, malonic acid, succinic acid, and adipic acid) at room temperature. The films were characterized by cyclic voltammetry, ultraviolet–visible spectroscopy, and conductivity measurements with a four-probe technique. The ultraviolet–visible spectra were obtained *ex situ* in dimethyl sulfoxide. The optical absorption spectra indicated that the formation of the conducting emeraldine salt (ES) phase took place in all the inorganic electrolytes used, whereas in organic acid supporting electrolytes, ES formed only with oxalic acid. Moreover, the current density and conductivity of the thin films was greatly affected by the nature and size of the anion present in the electrolyte. For the copolymer, the conductivity lay between the conductivity of the homopolymers, regardless of the supporting electrolyte used. The formation of the copolymer was also confirmed with differential scanning colorimetry. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 2634–2642, 2003

**Key words:** conducting polymers; electrochemistry; copolymerization

INTRODUCTION

Because of the numerous technological applications of conducting polymers as active electrode materials in energy storage,[1] optoelectronic devices,[2] and display devices,[3] as antistatic coatings,[4] and as chemically modified electrodes,[5] they have received a great deal of attention from chemists and physicists alike.

Polymers that exhibit high electrical conductivity have successfully been synthesized, and the past 2 decades have witnessed unabated interest in the synthesis and characterization of such conducting polymers because of the potential technological applications of these materials.[6–9] The most widely used laboratory techniques for the preparation of conducting polymer films are potentiostatic (constant potential), galvanostatic (constant current), and potentiodynamic (cyclic voltammetry) techniques.[10] Although it is established that the conducting properties of polymer films greatly depend on the mode of synthesis and on the number of parameters, such as the type of counterion, the type of solvent, their concentrations, the synthesis temperature, the electrochemical voltage, and the pH of the electrolyte,[11–13] research on the preparation and characterization of conducting polymers is continuing. Therefore, to improve the conducting properties of polymer films to make them suitable for particular applications, we must critically control and optimize the various synthesis parameters.

With respect to polyaniline-based copolymers, a pioneering work was carried out by Wei and coworkers.[14,15] They reported that aniline could be copolymerized with *o*-toluidine to give rise to a copolymer film, the conductivity of which could be controlled over a broad range. Bergeron and Dao[16] and Dhawan and Trivedi[17] studied the copolymerization of aniline with *N*-butylaniline and *o*-toluidine, respectively, and found that the resulting copolymer films had good conductivity and solubility in common organic solvents. Sato et al.[18] also studied the electrochemical copolymerization of aniline with *o*-aminobenzonitrile. Dhanalakshmi and Saraswathi[19] reported the electrochemical preparation, characterization, and mechanism of poly(pyrrole-*co*-indole). It has also been observed[20] that some copolymers have better solubility than their homopolymers in various organic solvents; this simplifies polymer processability and is advantageous for producing polymers and copolymers in bulk. The literature suggests that the copolymeriza-

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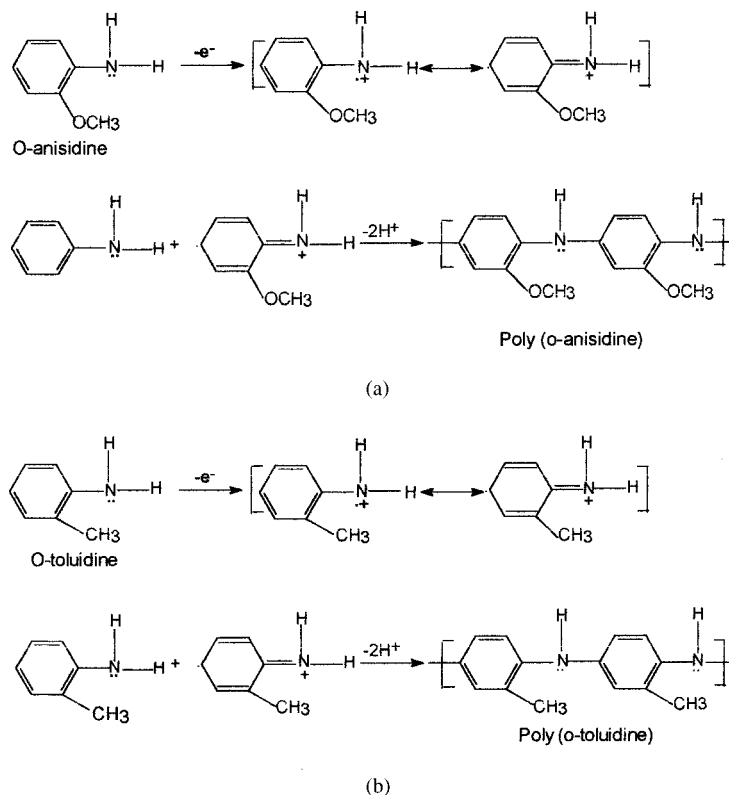
Scheme 1 Homopolymerizations of (a) *o*-anisidine and (b) *o*-toluidine.

tion could provide a convenient synthetic method and process for preparing new conducting materials with desired and improved properties for various applications.

Therefore, a systematic investigation of the influence of various supporting electrolytes, both inorganic and organic, on the electrochemical synthesis of poly(*o*-anisidine) (POA), poly(*o*-toluidine) (POT), and their copolymer poly(*o*-anisidine-*co*-*o*-toluidine) (POA-*co*-POT) films was carried out. These thin films were characterized by cyclic voltammetry, ultraviolet–visible (UV–vis) spectroscopy, conductivity measurements, and differential scanning colorimetry (DSC). The mechanism proposed for the homopolymerization and copolymerization of POA and POT is shown in Schemes 1 and 2.

EXPERIMENTAL

The monomers *o*-anisidine and *o*-toluidine were double-distilled before use. Five inorganic acids (H_2SO_4, HCl, HNO_3, H_3PO_4, and $HClO_4$) and six organic acids (benzoic acid, cinnamic acid, oxalic acid, malonic acid, succinic acid, and adipic acid) were used as supporting electrolytes. The thin films of POA, POT, and POA-*co*-POT were synthesized electrochemically on platinum substrates under cyclic voltammetry conditions in a simple one-compartment glass cell. A three-electrode geometry was employed during the electro-

chemical polymerization with a platinum substrate as a working electrode (1.5 cm²), carbon as a counter electrode, and Ag/AgCl as a reference electrode. The reference electrode was kept in close proximity to the working electrode to minimize the electrolytic ohmic drop. The films were electropolymerized in a solution containing 0.1*M* monomer(s) and 1*M* supporting electrolyte by the application of a sequential linear potential scanning rate of 50 mV/s between −0.1 and 0.8 V versus the Ag/AgCl electrode. The cyclic voltammetry conditions were maintained with a Potentio-Galvano Stat-30 (with a 663 VA stand; Metrohm Autolab). The POA, POT, and POA-*co*-POT films were deposited with 20 cycles for the polymerization in all the supporting electrolytes, and their voltammograms were recorded on a personal computer. After deposition, the films were rinsed with the corresponding supporting electrolytes. Throughout the study, anaerobic conditions were maintained with a nitrogen gas atmosphere.

The optical absorption study of all synthesized films was carried out with a UV–vis spectrophotometer (UV-1601, Simadzu). The UV–vis spectra were obtained *ex situ* by each film being dissolved separately in 5 mL of dimethyl sulfoxide (DMSO). The solvent did have an effect on the emeraldine salt (ES) phase of the film if the film was dissolved for more than 8 h. Hence, the ultraviolet spectra were recorded immediately after the dissolution in DMSO. All the spectra
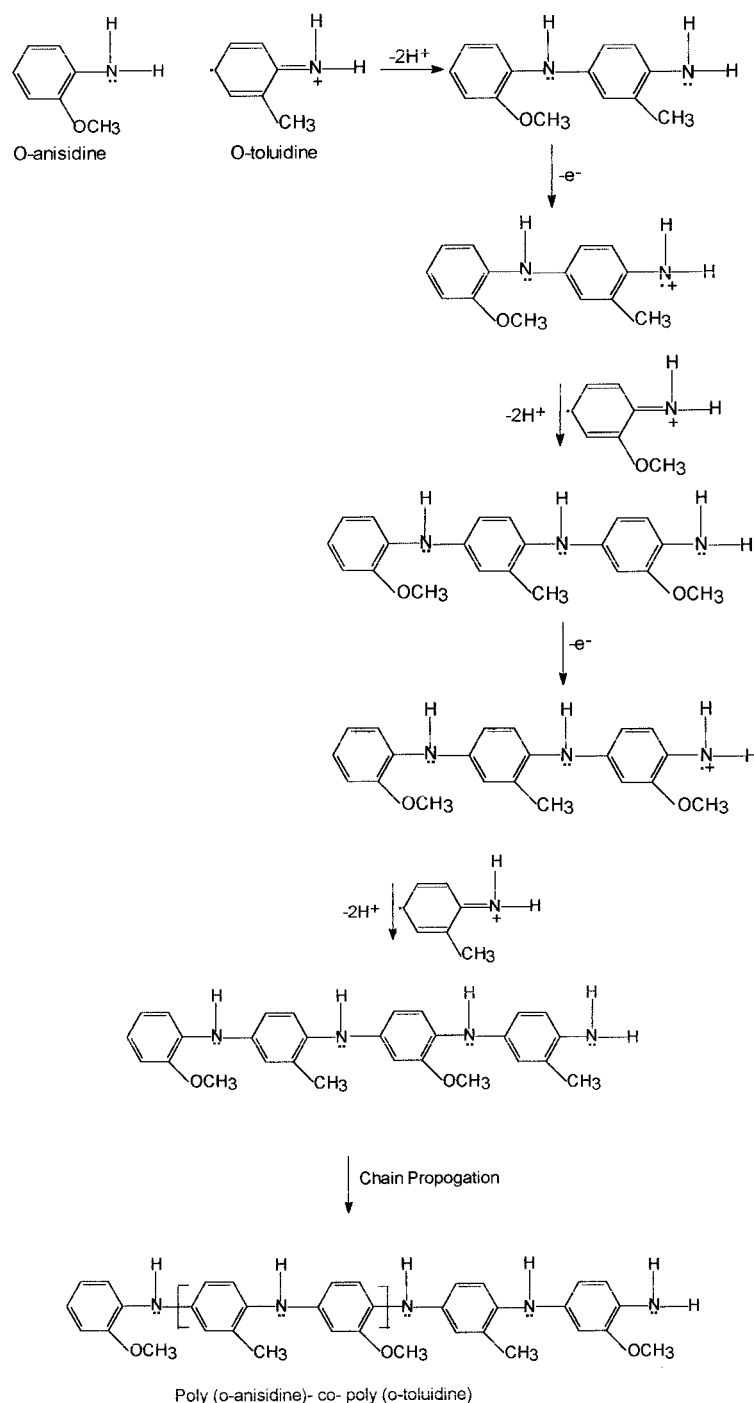
Scheme 2 Copolymerizations of (a) *o*-anisidine and (b) *o*-toluidine.

were recorded in the wavelength range of 300–1100 nm. The conductivity was measured with a four-probe technique on a platinum electrode 4 mm in diameter and about 1 μm thick. The thickness of the polymer thin films was measured with a digital micrometer. After the synthesis, the films were washed thoroughly with a 0.2M solution of the respective supporting electrolyte and then immersed in a 0.2M solution of the respective supporting electrolyte for 24 h. Finally, the films were dried at 50°C for 2 h. The dried films were

used for the determination of the conductivity at a constant current of 10 mA. The accuracy of this measurement was 0.0001 S/cm. The formation of the copolymer was studied by DSC (DuPont 2100) in a nitrogen atmosphere over a temperature range of 25–200°C.

RESULTS AND DISCUSSION

Figures 1–3 show the cyclic voltammograms (CVs) recorded during the synthesis of POA, POT, and POA-

co-POT films in aqueous solutions of five inorganic acids used as supporting electrolytes (H_2SO_4, HCl, HNO_3, H_3PO_4, and $HClO_4$) and an organic acid (oxalic acid) at room temperature. For the other organic acids (benzoic acid, cinnamic acid, malonic acid, succinic acid, and adipic acid), no response was observed in the formation of the conducting films, as shown by the CVs of these monomers. The overall observations and results based on the CVs are as follows:

1. The electrochemical polymerization characteristics of these monomers in different supporting electrolytes on the platinum electrode are almost the same during the first positive cycle. At higher potentials (>0.5 V), little oxidation takes place, and so a high anodic current flows.
2. In the case of inorganic acids used as supporting electrolytes, two to three peaks (A, B, and C) are observed in repetitive cycling, whereas for the organic acid oxalic acid, one or two peaks are observed, and the other organic acids do not reflect any peak; this indicates an inability to form a conducting ES phase. The redox potentials and current densities corresponding to these peaks for the different supporting electrolytes are summarized in Table I.
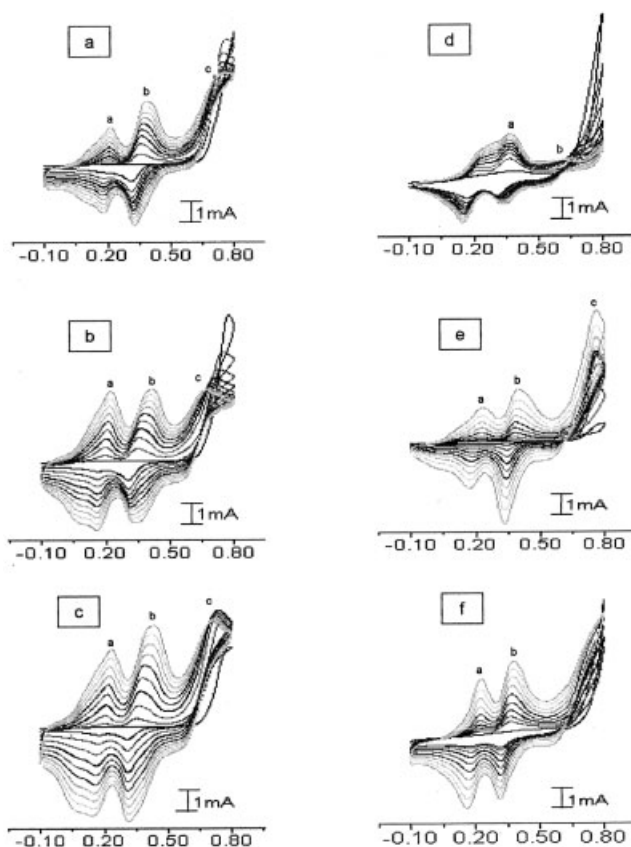

Figure 2 CVs recorded during the synthesis of POT films in aqueous solutions of (a) H_2SO_4, (b) HCl, (c) HNO_3, (d) H_3PO_4, (e) $HClO_4$, and (f) oxalic acid.
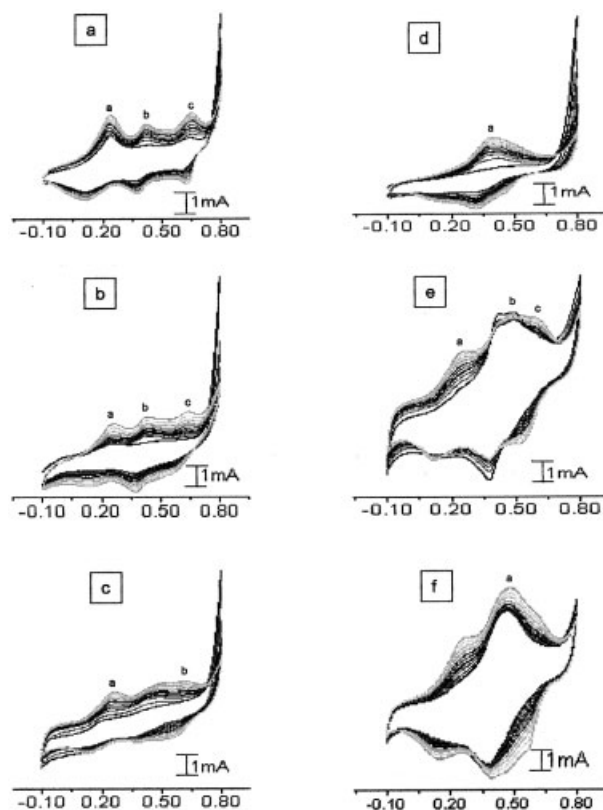
3. The CV curves grow with the number of cycles for all supporting electrolytes, and this indicates the formation of conducting polymer films in each case. It signifies that the oxidation potential of the monomers is dependent on the size and type of the anion present.
4. The polymerization of *o*-toluidine show three redox peaks in H_2SO_4, HCl, and $HClO_4$, two in HNO_3, and only one in H_3PO_4 and oxalic acid. Similar redox peaks of *o*-toluidine in H_2SO_4 were observed by Wei et al.[21] In the case of *o*-anisidine, polymerization in H_2SO_4, HCl, HNO_3, and $HClO_4$ shows three peaks, whereas in H_3PO_4 and oxalic acid, only two peaks are shown. The CV results for POA are in agreement with the results of Lacroix et al.[22] Similarly, in the case of the copolymerization of *o*-anisidine-*co*-*o*-toluidine, three peaks in H_2SO_4, HCl, HNO_3, and $HClO_4$, two peaks in oxalic acid, and only one peak in H_3PO_4 can be observed. The single peak obtained for POT and POA-*co*-POA in H_3PO_4 indicates that the dimer or cyclization products are not formed during polymerization.[23]
5. The highest current densities corresponding to the anodic peaks are observed for the polymerization in H_2SO_4, followed by HCl, HNO_3, H_3PO_4, and $HClO_4$ and then oxalic acid. The
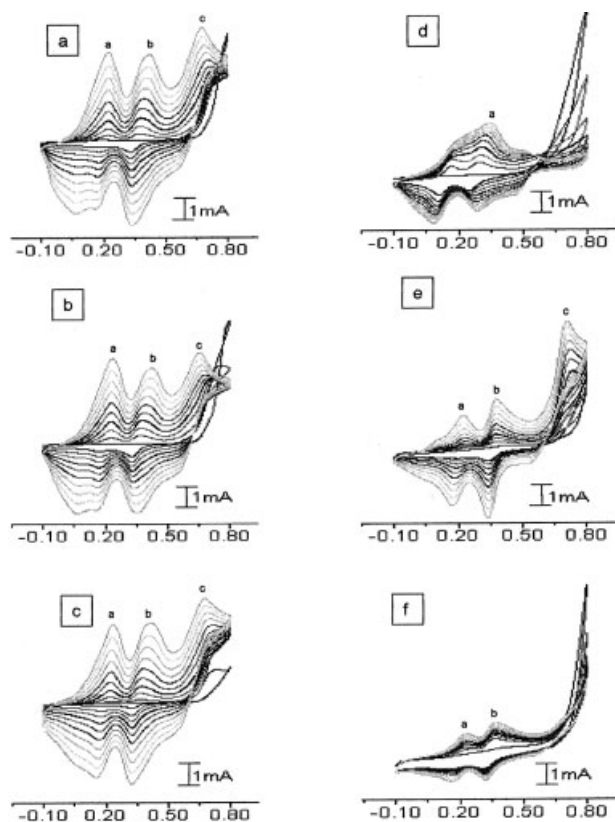

Figure 1 CVs recorded during the synthesis of POA films in aqueous solutions of (a) H_2SO_4, (b) HCl, (c) HNO_3, (s) H_3PO_4, (e) $HClO_4$, and (f) oxalic acid.

Figure 3 CVs recorded during the synthesis of POA-*co*-POT films in aqueous solutions of (a) H_2SO_4, (b) HCl, (c) HNO_3, (d) H_3PO_4, (e) $HClO_4$, and (f) oxalic acid.

current densities of the copolymer are higher than those of the individual homopolymers. This could be a combined effect of the concentrations of the monomers. When the concentration of the monomer in the copolymerization bath increases, the polymeric forms of POA-*co*-POT dominate on the electrode surface.[24]

6. An increase in the values of the redox peaks, in general, is strongly dependent on the nature and size of the anion present in the electrolyte. The redox potential values of the copolymer are

slightly higher or equal to those of POA homopolymer films.

7. Inorganic supporting electrolytes show higher current densities than organic ones. Of the organic acids used as supporting electrolytes, only oxalic acid favors the formation of an ES phase; however, benzoic acid, cinnamic acid, malonic acid, succinic acid, and adipic acid are not suitable because of either insolubility in the aqueous medium or the formation of a leucoemeraldine phase (pale brown films). In these cases, CVs are not observed, but only a straight line graph is seen.

Thus, the CVs clearly reveal the formation of electroactive polymer films in all inorganic supporting electrolytes and in only oxalic acid among organic supporting electrolytes. The anodic peaks A and C are assigned to the oxidation of polymers deposited on the electrode surfaces, corresponding to the conversion of amine units into radical cations.[25] Peak B in the CVs is due to the adsorption of quinone/hydroquinone generated during the growth of polymer films that is strongly adsorbed into the polymer matrix.[26] The appearance and intensity of peak B are highly dependent on the electrolytic medium. The CV of copolymer PA-*co*-POA is different from those of homopolymers PA and POA, clearly supporting the formation of a copolymer.

The initiation process of electrochemical copolymerization is thought to be the formation and reactions of the cation radicals[27] and dimeric species.[28] The mechanism of the electrochemical polymerization of the monomer is believed to proceed via a radical cation that reacts with a second radical cation to give a dimer (Scheme 1). This reacts further with the radical cation of the monomer to build up the polymer chain. For copolymerization, a chain might be built up by formation through the conjugation of radicals of two different monomers followed by propagation (Scheme 2).

TABLE I
Redox Potentials and Current Densities at the Redox Peaks of POA, POT,
and POA-*co*-POT Films in Various Supporting Electrolytes

		Redox potential (mV)									Current density (mA/cm^2)								
		POA			POT			POA-*co*-POT			POA			POT			POA-*co*-POT		
No.	Supporting electrolyte	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C
1	H_2SO_4	215	381	762	235	418	650	222	420	672	3.55	5.78	7.98	4.04	3.23	4.30	6.56	6.41	8.48
2	HCl	220	415	654	257	427	632	232	423	652	4.01	4.10	4.02	3.27	3.91	4.19	4.77	4.26	5.06
3	HNO_3	230	435	713	274	637	—	232	413	667	2.75	3.55	3.67	2.33	3.44	—	3.34	3.32	4.43
4	H_3PO_4	361	591	—	383	—	—	344	—	—	3.09	1.24	—	1.88		—	3.64	—	—
5	$HClO_4$	225	403	747	276	481	598	220	376	701	1.48	2.29	5.61	1.04	1.87	1.71	1.61	2.37	6.09
6	Oxalic acid	225	379	—	496	—	—	220	371	—	2.40	3.24	—	1.94	—	—	2.22	3.37	—

TABLE II
Influence of Inorganic and Organic Supporting Electrolytes on the Electrical Conductivity
and UV–vis Spectra (Peak and Shoulder) for POA, POA, and POA-*co*-POT Films

No.	Supporting electrolyte	Electrical conductivity (S/cm) × 10^{-2}			UV–visible spectroscopy (nm)					
		POA	POT	POA-*co*-POT	POA		POT		POA-*co*-POT	
					Peak	Shoulder	Peak	Shoulder	Peak	Shoulder
1	H_2SO_4	2.75	5.63	3.75	826	426	802	410	815	418
2	HCl	2.34	5.27	3.47	835	440	810	420	825	425
3	HNO_3	1.29	4.14	2.43	830	435	805	415	820	420
4	H_3PO_4	1.21	3.93	2.39	830	440	805	420	820	425
5	$HClO_4$	1.11	3.72	2.26	820	420	800	405	810	410
6	Oxalic acid	0.84	3.25	2.04	810	415	790	405	800	410

UV–vis spectroscopy

The peak values of the optical absorption spectra of POA, POT, and POA-*co*-POT films deposited with different supporting electrolytes under identical experimental conditions are summarized in Table II and are shown in Figures 4–6. The UV–vis spectra were obtained *ex situ* in DMSO. It is apparent that the optical absorption depends on the electrolyte species and decreases in the order $HSO_4^- > Cl^- > NO_3^- > PO_4^- > ClO_4^- > COO^-$. In each case, the spectrum indicates a major peak in the wavelength region of 790–835 nm with a shoulder at 405–440 nm corre-

sponding to the ES phases of POA, POT, and POA-*co*-POT polymer films. The peak values of the copolymer films lie between the values of the individual homopolymer films, supporting the formation of a copolymer. The observations of the UV–vis spectra of POA are the same as those reported by Patil et al.[29]

Conductivity measurements

The influence of different supporting electrolytes on the electrical conductivity is summarized in Table II. The conductivity strongly depends on the anion
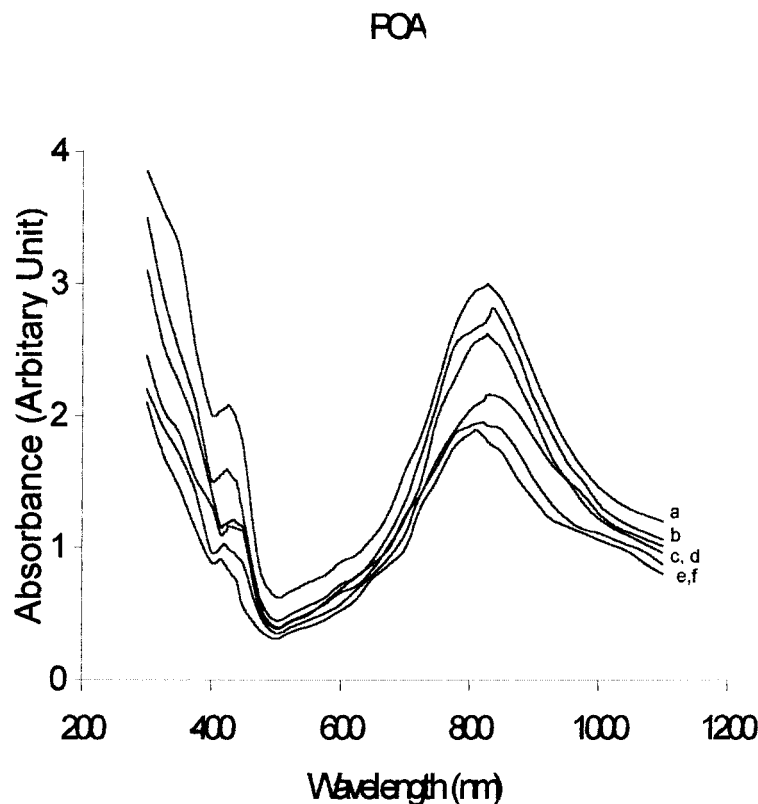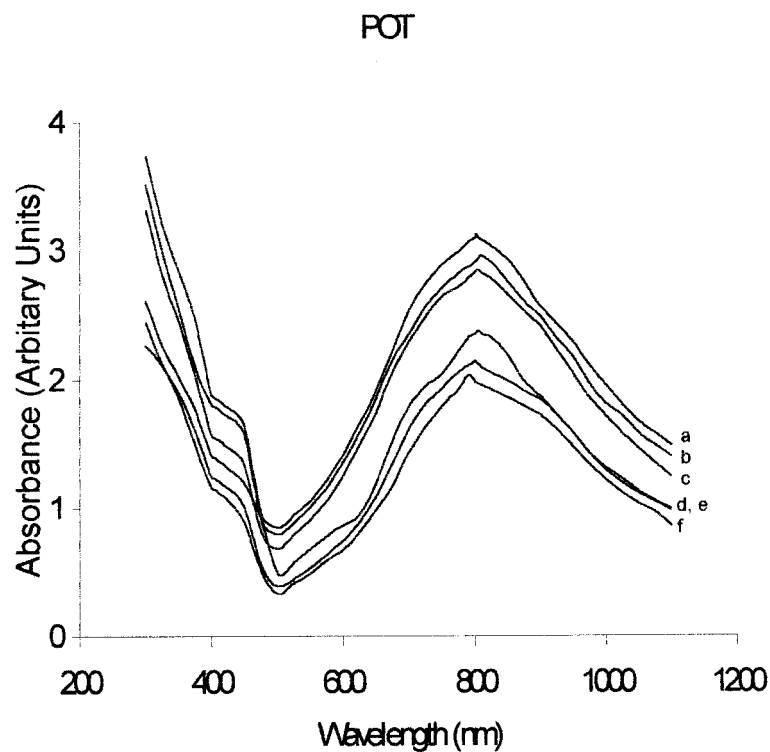
Figure 4 Optical absorption spectra of POA films synthesized electrochemically under CV conditions in aqueous solutions of (a) H_2SO_4, (b) HCl, (c) HNO_3, (d) H_3PO_4, (e) $HClO_4$, and (f) oxalic acid.
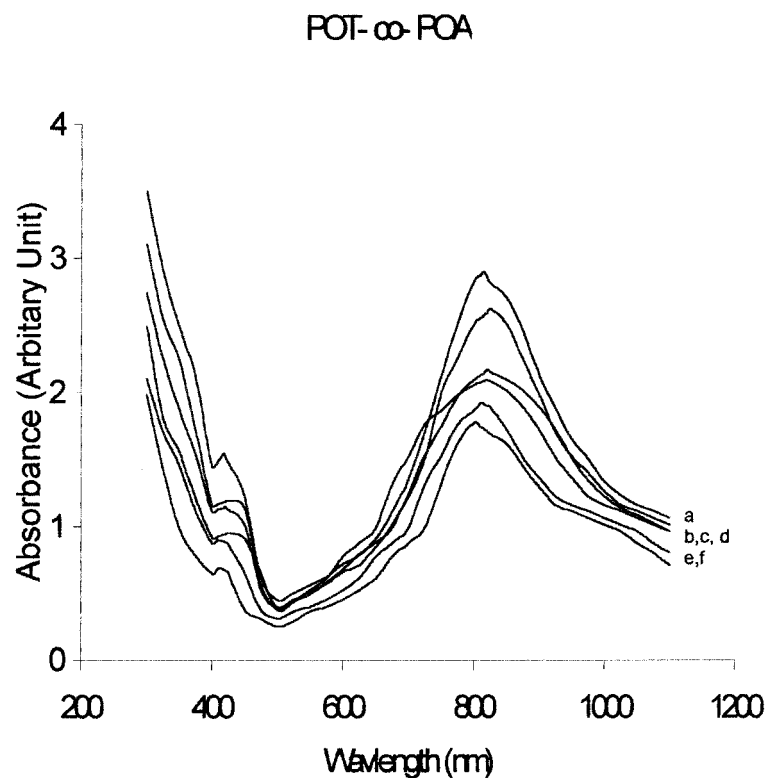
POT

Figure 5 Optical absorption spectra of POT films synthesized electrochemically under CV conditions in aqueous solutions of (a) H_2SO_4, (b) HCl, (c) HNO_3, (d) H_3PO_4, (e) $HClO_4$, and (f) oxalic acid.

POT-co-POA

Figure 6 Optical absorption spectra of POA-*co*-POT films synthesized electrochemically under CV conditions in aqueous solutions of (a) H_2SO_4, (b) HCl, (c) HNO_3, (d) H_3PO_4, (e) $HClO_4$, and (f) oxalic acid.
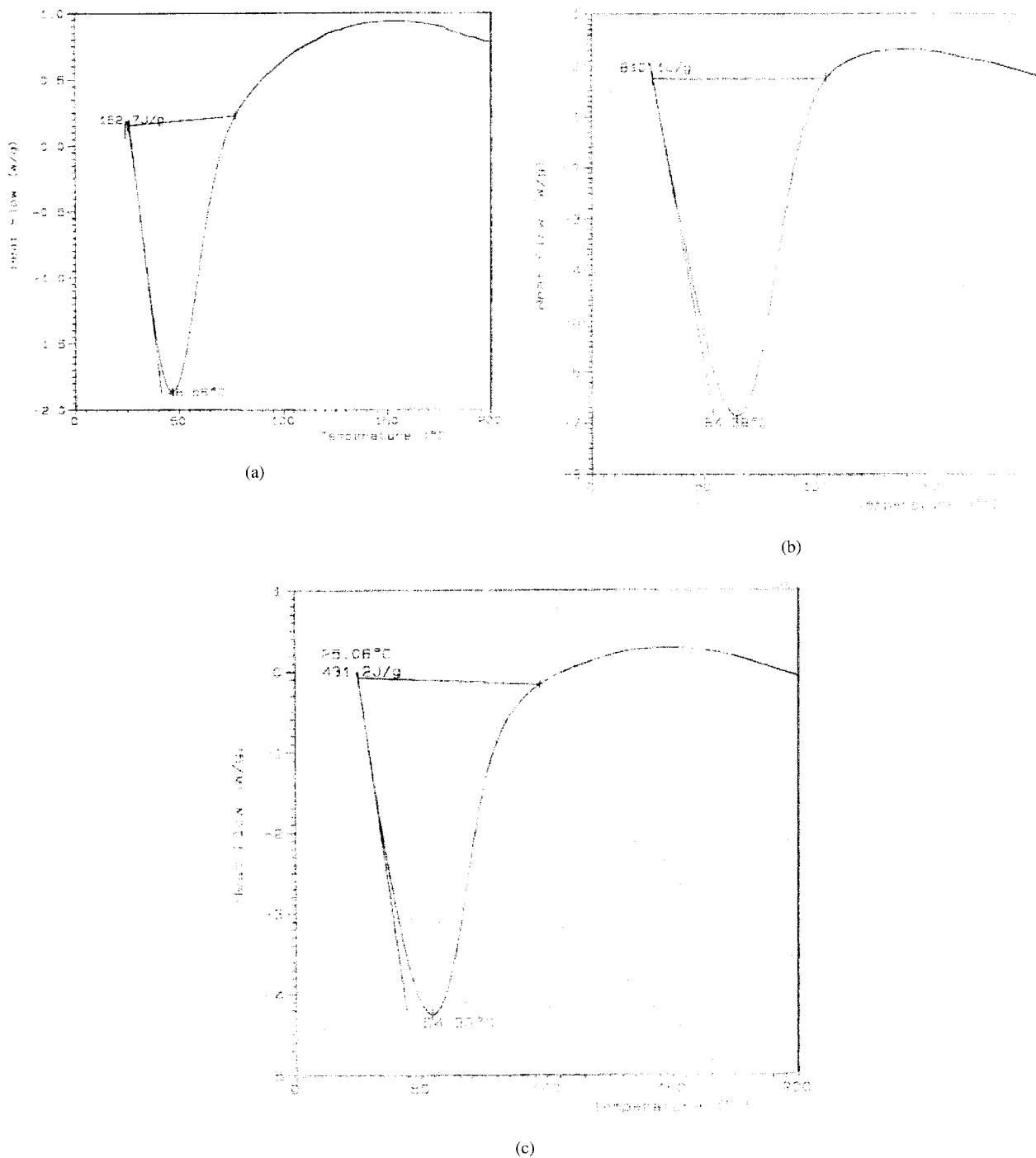
(a)

(b)

(c)

Figure 7 DSC thermograms of (a) POA, (b) POT, and (c) POA-*co*-POT.

present and follows the order $HSO_4^- > Cl^- > NO_3^- > PO_4^- > ClO_4^- > COO^-$; it may be related to the adsorption phenomena of electrolyte species. This agrees with the optical spectroscopy results. Moreover, the conductivity of the copolymer lies between the conductivities of the homopolymers, regardless of the supporting electrolytes used. The CVs and optical data clearly support the results of the electrical conductivity of these films.

DSC

The thermal properties of POA, POT, and POA-*co*-POT prepared in H_2SO_4 as an electrolyte were measured by DSC. A graph of the temperature versus the heat flow is shown in Figure 7. The peak values (melting) for POA, POT, and POA-*co*-POT can be observed at 46.56, 64.38, and 54.33°C, respectively. It is clear from the DSC thermogram that the film formed by the

mixture of the monomers is a copolymer and not layers of the homopolymers. For the formation of layers of the homopolymers, it would have shown two different peaks for individual melting; this is not the case here, and the formation of the copolymer is confirmed.

CONCLUSIONS

The following conclusions can be drawn from this study:

1. The CVs clearly indicate the formation of electroactive POA, POT, and POA-*co*-POT copolymer thin films in all inorganic supporting electrolytes but only in oxalic acid among the organic supporting electrolyte.
2. The anodic current densities of the polymerization of POA, POT, and POA-*co*-POT polymer films are strongly influenced by the anion present in the electrolyte. The current densities of the copolymer are higher than those of the individual homopolymers
3. The optical absorption spectroscopy results reveal the formation of conducting ES phases of POA, POT, and POA-*co*-POT films, regardless of the electrolyte used. However, the optical absorption varies with the electrolyte species.
4. The electrical conductivity depends on the monomers and the electrolyte species. For POA-*co*-POT, it lies between those of the POT and POA homopolymers.
5. The inorganic supporting electrolytes are more suitable than organic ones because they favor the formation of good conducting ES phases of the polymers on account of their easy solubility and mobility in the aqueous medium.
6. The peaks for the POA and POT homopolymers and POA-*co*-POT copolymer prepared in H_2SO_4 as an electrolyte can be observed at 46.56, 64.38, and 54.33°C, respectively. The formation of the copolymer has been confirmed by DSC studies.
7. The conductivity values, UV–vis absorption peaks, DSC peaks values, and CVs confirm the formation of the POA-*co*-POT copolymer.

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