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The Conductivity of poly(o-anisidine), poly(o-toluidine) and their Copolymer with Various Inorganic Dopants in the Presence of Electrolyte

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An attempt has been made to prepare poly(o-anisidine) (POA), poly(o-toluidine) (POT) and copolymer poly(o-anisidine)-co-poly(o-toluidine) (POA-co-POT) thin films doped by several inorganic salts (sulphates and chlorides) with varying size of cations using aqueous solution of H_2SO_4 as electrolyte. The effect of dopant in the presence of electrolyte is rarely studied in the field of conducting polymers. Various inorganic salts as dopants, namely, K_2SO_4 , Na_2SO_4 , Li_2SO_4 , $MgSO_4$, KCl , $NaCl$, $LiCl$, and $MgCl_2$ are used at room temperature. The films were electro-polymerized in solution containing 0.1 M monomer(s), 1 M H_2SO_4 as electrolyte and 1 M inorganic salt, by applying sequential linear potential scan rate 50 mV/s between -0.2 to 1.0 V versus Ag/AgCl electrode. The electro-synthesized films were characterized by cyclic voltammetry, UV-visible spectroscopy, and conductivity measurements. It was observed that the UV-visible peaks usually appearing at about 802–826 nm with a shoulder at 410–426 nm shows a shift in presence of doping salt for emeraldine salt (ES) phase of POA, POT, POA-co-POT. In overall study, a significant increase in conductivity is observed for all mentioned dopants and among these K_2SO_4 is found to be the best in sulphate category and KCl in chloride category. The formation of copolymer has been confirmed by differential scanning calorimetry.

Keywords: conducting polymers, electrochemical polymerization, copolymer, dopants, inorganic salts

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INTRODUCTION

The electrochemical oxidation of aniline in aqueous sulphuric acid solution can be traced back over 100 years; its final product obtained at a platinum anode is a dark precipitate [1–2]. In recent years the electrochemical synthesis of conducting polymer thin films has become an attractive interdisciplinary research field because of the potential technological applications of these materials [3–5]. Synthesis of polyaniline and its derivatives thin films with excellent electrical, optical, and electrochemical properties coupled with good environmental stability boosted the research to tailor the physical and chemical properties of different conducting polymer films suitable for a particular application [6–9]. The overall properties of the conducting polymers are greatly affected by the neutral salts used as dopant [10–11], in addition to other factors, such as electrolyte, synthesis temperature, deposition time, pH, and so on. When the polymer is produced by the anodic oxidation of monomer, the doping ions (anions) are incorporated into the polymer and their nature is known to influence the properties of conducting polymers. The redox processes were shown to depend on the pH value and on the type of ion in the supporting electrolyte solution [7,12–13]. Polyaniline derivatives, poly(*o*-toluidine) and poly(*o*-anisidine) were demonstrated to exhibit electrochemical properties similar to polyaniline. Earlier reports on electrochemically generated copolymers of the conducting type have appeared for pyrrole derivatives, for instance, copolymerization of pyrrole and substituted pyrrole [14] as well as pyrrole and thiophene [15]. With regards to a polyaniline type copolymer, pioneering work has been done by Wei and co-workers [16–17]. They have shown that aniline copolymerized with toluidine gives rise to a copolymer film, whose conductivity could be controlled over a broad range. Dao et al. [18] reported copolymerization of aniline with *N*-butylaniline. The resulting copolymer film showed both good conductivity and solubility in common organic solvents. Lately, copolymerization of aniline with *N*-methylaniline [19] and that with 3-aminophenyl-boric acid [20] have also been reported. Masaaki Sato et al. [21] also studied electrochemical copolymerization of aniline with *o*-aminobenzonitrile. These reports suggest that the copolymerization provides a convenient synthetic method to prepare new conducting materials with desired properties. When the polymer is produced by the anodic oxidation of monomer, the doping ions (anions) are incorporated into the polymer and their nature is known to influence the properties of conducting polymers.

In continuation of the present authors' work on conducting homopolymers and copolymers [22–26], for this study they we have chosen a number of inorganic salts and the effect of dopant anion with increasing size of the cation on both electrical conductivity and optical absorption in electrochemical synthesis of poly (*o*-anisidine) (POA), poly (*o*-toluidine) (POT), and their copolymer (POA-co-POT) in aqueous medium using H_2SO_4 as electrolyte. Two categories of inorganic salts, sulphates and chlorides, were selected for the study so that the effect of the cation present in the salt could be studied. Furthermore, an influence of added salts on pH of solution containing H_2SO_4 electrolyte is also noted to correlate with the electrochemical properties of polymers.

EXPERIMENTAL

The monomers *o*-anisidine and *o*-toluidine were double distilled before use. The eight inorganic salts K_2SO_4 , Na_2SO_4 , Li_2SO_4 , MgSO_4 , KCl , NaCl , LiCl , and MgCl_2 were used as doping agents in the present study. The thin films of POA, POT, and POA-co-POT were synthesized electrochemically on platinum substrates under cyclic voltammetric conditions in a single compartment glass cell. A three electrode geometry was employed during the electrochemical polymerization using platinum substrate as working electrode (1.5 cm^2), carbon as counter electrode, and Ag/AgCl as 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 solution containing 0.1 M monomer(s), 1 M H_2SO_4 as electrolyte, and 1 M inorganic salt by applying sequential linear potential scan rate 50 mV/s between -0.2 to 1.0 V versus the Ag/AgCl electrode. The cyclic voltammetric conditions were maintained using Potentiostat-30 (Metrohm Autolab Electrochemical Instrument with 663 VA Stand). The POA, POT, and POA-co-POT films were deposited with 20 cycles for the polymerization in all dopants and their voltammograms were recorded on a computer. After deposition, the films were washed with 0.2 M H_2SO_4 solution. Throughout the studies, anaerobic conditions were maintained with nitrogen gas atmosphere.

The optical absorption studies of all synthesized films were carried out using UV-visible spectrophotometer (Shimadzu, UV-1601). All the spectra were recorded in the wavelength range 300–1100 nm. The electrical conductivity of the films was measured using conventional four probe technique. The pH of the solution was measured by using Equip-tronics pH meter (EQ-614).

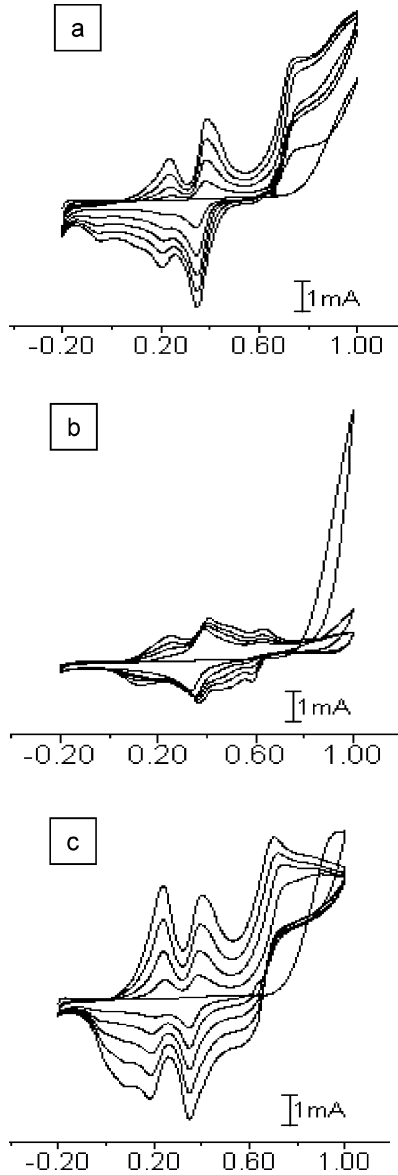


FIGURE 1 Cyclic voltammograms recorded during the synthesis of (a) POA, (b) POT, (c) POA-POT films in aqueous solution of H_2SO_4 as electrolyte without dopants.

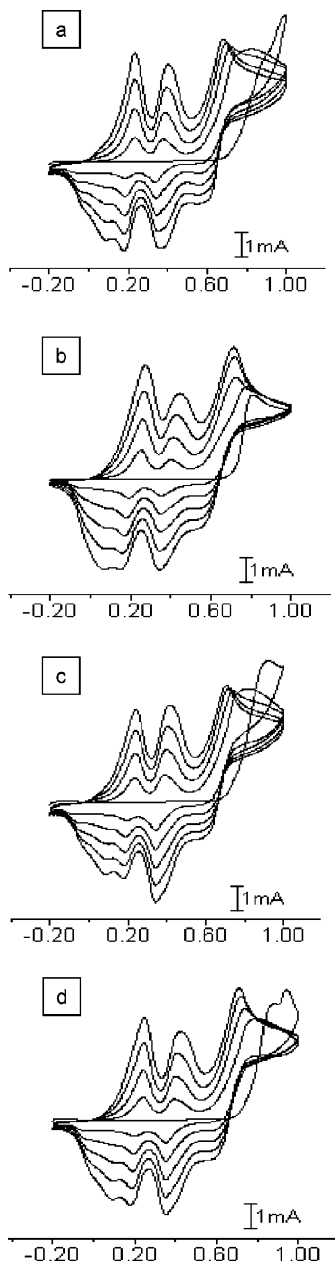


FIGURE 2 a) Cyclic voltammograms recorded during the synthesis of POA films in aqueous solution of H_2SO_4 as electrolyte in presence of doping agent as (a) K_2SO_4 , (b) Na_2SO_4 , (c) Li_2SO_4 , (d) MgSO_4 ; b) Cyclic voltammograms recorded during the synthesis of POA films in aqueous solution of H_2SO_4 as electrolyte in presence of doping agent as (e) KCl , (f) NaCl , (g) LiCl , (h) MgCl_2 .

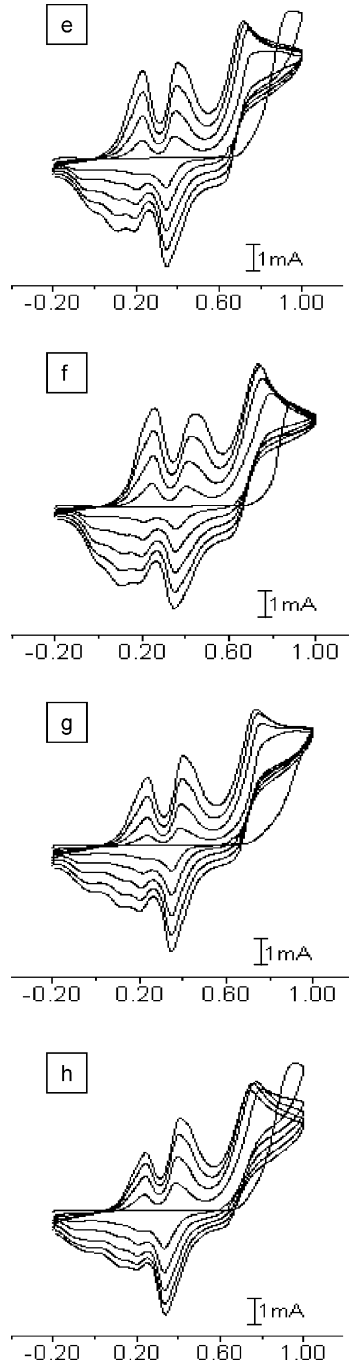


FIGURE 2 (Continued)

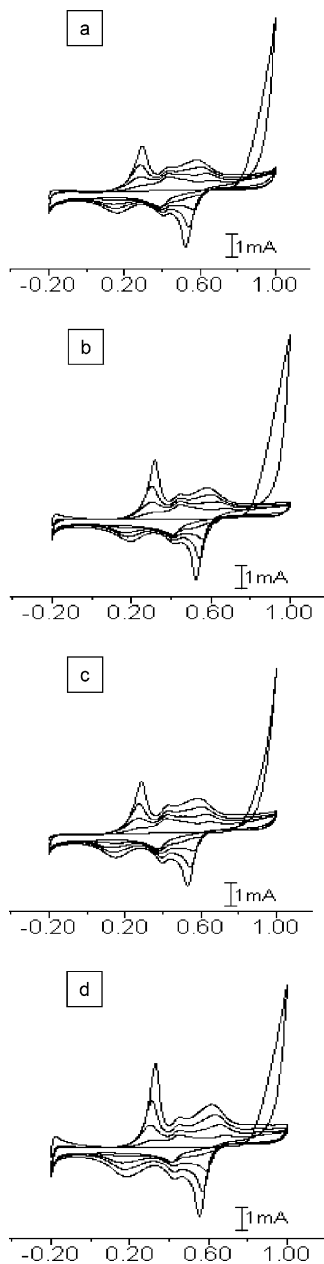


FIGURE 3 a) Cyclic voltammograms recorded during the synthesis of POT films in aqueous solution of H_2SO_4 as electrolyte in presence of doping agents (a) K_2SO_4 , (b) Na_2SO_4 , (c) Li_2SO_4 , (d) MgSO_4 ; b) Cyclic voltammograms recorded during the synthesis of POT films in aqueous solution of H_2SO_4 as electrolyte in presence of doping agents (e) KCl , (f) NaCl , (g) LiCl , (h) MgCl_2 .

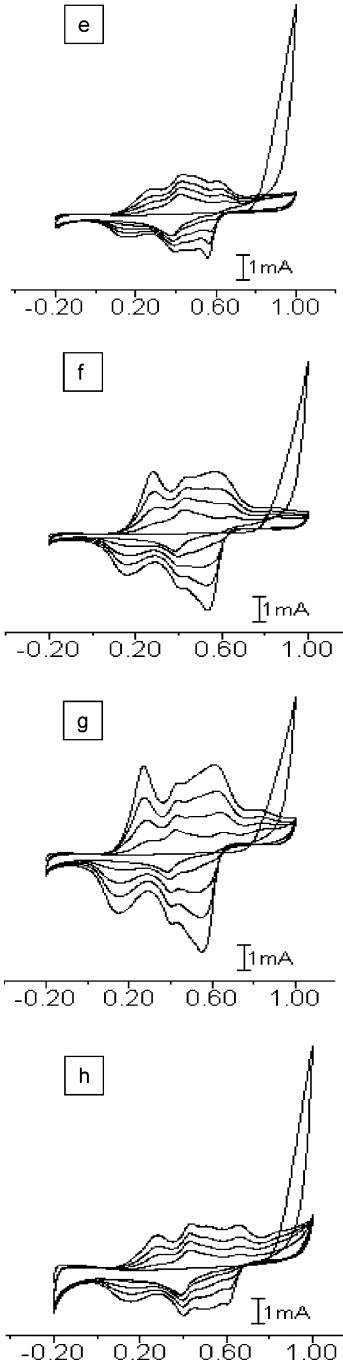


FIGURE 3 (Continued)

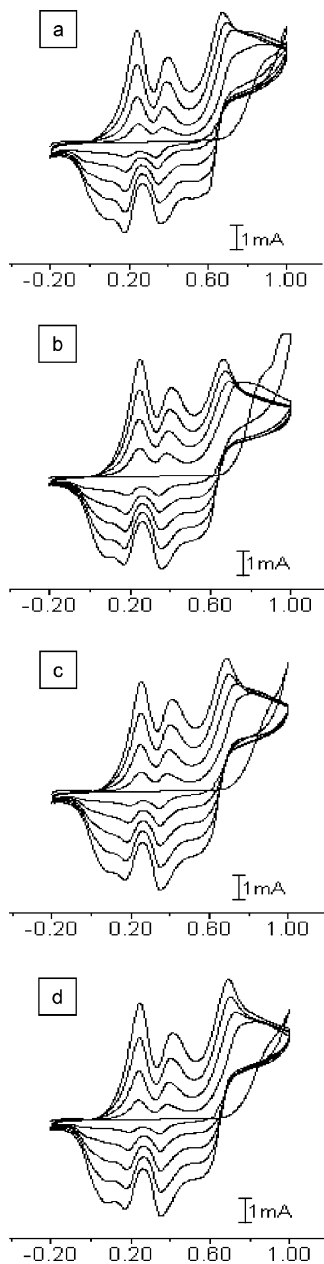


FIGURE 4 a) Cyclic voltammograms recorded during the synthesis of POA-POT films in aqueous solution of H_2SO_4 as electrolyte in presence of doping agent as (a) K_2SO_4 , (b) Na_2SO_4 , (c) Li_2SO_4 , (d) MgSO_4 ; b) Cyclic voltammograms recorded during the synthesis of POA-POT films in aqueous solution of H_2SO_4 as electrolyte in presence of doping agent as (e) KCl , (f) NaCl , (g) LiCl , (h) MgCl_2 .

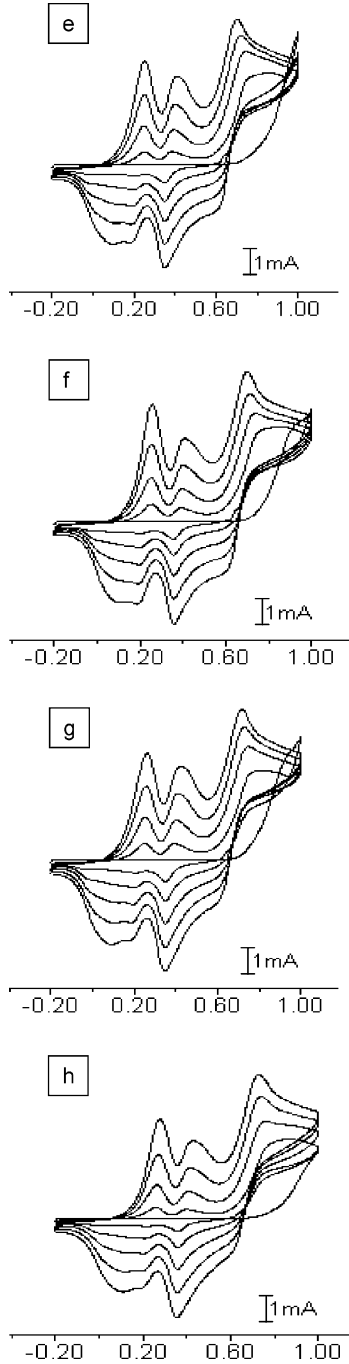


FIGURE 4 (Continued)

TABLE 1 Redox Potentials and Current Densities at the Redox Peaks of POA, POT, POA-co-POT Films in Electrolyte and with Added Salts

Electrolyte + Salt	Redox potential (mV)									Current density (mA/cm ²)								
	POA			POT			POA-co-POT			POA			POT			POA-co-POT		
	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C
H ₂ SO ₄	230	388	—	239	413	635	235	398	698	215	4.52	—	1.76	2.95	2.25	3.78	3.42	5.13
H ₂ SO ₄ + K ₂ SO ₄	232	403	679	288	430	606	235	396	672	4.96	4.25	5.41	3.04	3.97	3.26	5.91	4.42	6.37
H ₂ SO ₄ + Na ₂ SO ₄	271	444	713	276	442	569	247	410	664	4.73	3.59	5.54	3.12	2.99	3.20	5.54	4.17	5.89
H ₂ SO ₄ + Li ₂ SO ₄	237	410	703	266	426	623	250	408	684	4.53	4.76	5.65	2.36	2.62	2.29	5.16	4.42	6.17
H ₂ SO ₄ + MgSO ₄	244	418	708	274	430	664	254	442	679	4.28	3.72	5.39	2.03	2.69	2.66	5.13	3.82	5.69
H ₂ SO ₄ + KCl	230	401	711	296	430	591	247	412	698	4.70	5.01	6.52	2.86	1.61	1.95	4.91	4.07	6.25
H ₂ SO ₄ + NaCl	252	440	733	318	442	588	252	405	696	4.28	4.11	6.51	2.79	1.19	1.51	4.69	3.39	6.06
H ₂ SO ₄ + LiCl	235	404	730	286	425	589	259	420	713	3.59	4.63	7.03	2.19	1.22	1.46	4.29	3.81	6.03
H ₂ SO ₄ + MgCl ₂	239	410	740	330	449	625	274	427	720	3.42	5.19	6.79	2.91	1.04	1.43	4.26	3.32	6.02

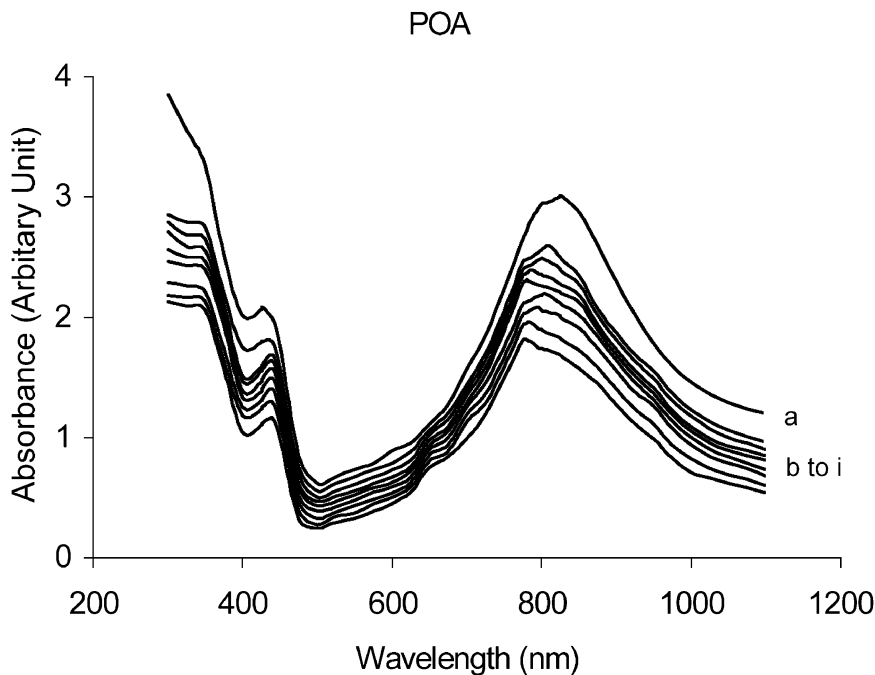


FIGURE 5 Optical absorption spectra of POA films synthesized electrochemically under cyclic voltammetric conditions in aqueous solutions of (a) H_2SO_4 and in presence of salts, (b) K_2SO_4 , (c) Na_2SO_4 , (d) Li_2SO_4 , (e) MgSO_4 , (f) KCl , (g) NaCl , (h) LiCl , (i) MgCl_2 .

RESULTS AND DISCUSSION

Effect of Salts on Cyclic Voltammograms

Figures 1–4 show the cyclic voltammograms (CVs) recorded during the synthesis of POA, POT, and POA-co-POT films in aqueous solutions of H_2SO_4 as electrolyte and in presence of the salts K_2SO_4 , Na_2SO_4 , Li_2SO_4 , MgSO_4 , KCl , NaCl , LiCl , and MgCl_2 at room temperature, respectively. The overall observations based on CVs are summarized as follows:

1. The electrochemical polymerization characteristics of these monomers in aqueous solution of H_2SO_4 as electrolyte in presence of salts on the platinum electrode is almost the same during the first positive cycle. At higher potentials ($>0.6\text{ V}$) little oxidation takes place and therefore high anodic current flows.

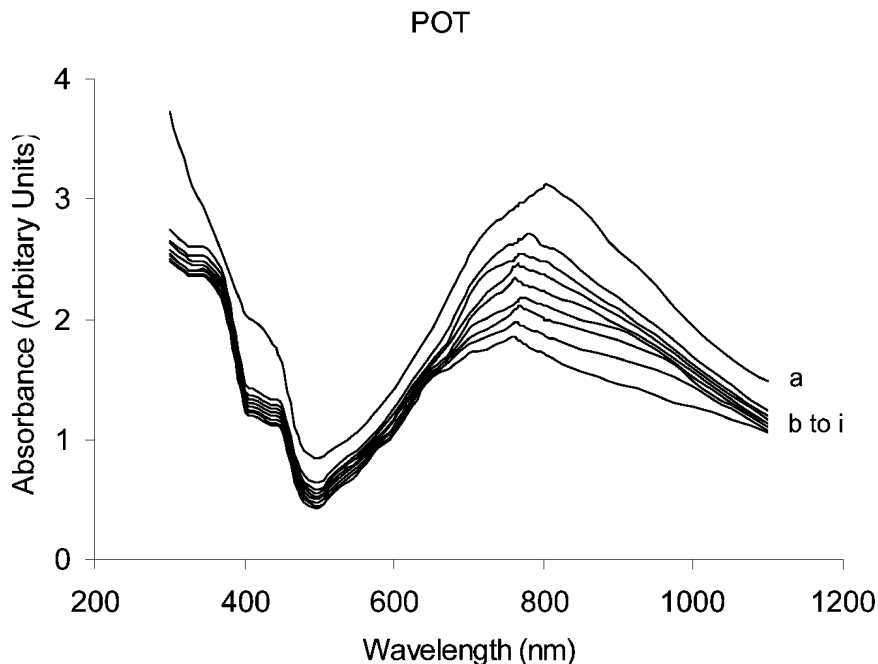


FIGURE 6 Optical absorption spectra of POT films synthesized electrochemically under cyclic voltammetric conditions in aqueous solutions of (a) H_2SO_4 and in presence of salts, (b) K_2SO_4 , (c) Na_2SO_4 , (d) Li_2SO_4 , (e) MgSO_4 , (f) KCl , (g) NaCl , (h) LiCl , (i) MgCl_2 .

2. In POA, POT, and POA-co-POT films, in presence of salts three peaks are observed in repetitive cycling. The redox potentials and current densities corresponding to these peaks for different salts are summarized in Table 1.
3. The current of redox peaks gradually increase with the number of cycles indicating the growth of conducting polymer film in each cycle.
4. The highest current densities corresponding to the anodic peaks are observed for the polymerization in presence of salts K_2SO_4 followed by Na_2SO_4 , Li_2SO_4 , MgSO_4 , KCl , NaCl , LiCl and MgCl_2 [27].

Thus the CVs clearly reveal the formation of electroactive polymer films in all supporting electrolytes. The anodic peak A and/or C are assigned to the oxidation of polymer deposited on the electrode surface, which corresponds to the conversion of amine units into radical cations [28]. The peak B in the cyclic voltammograms is due to

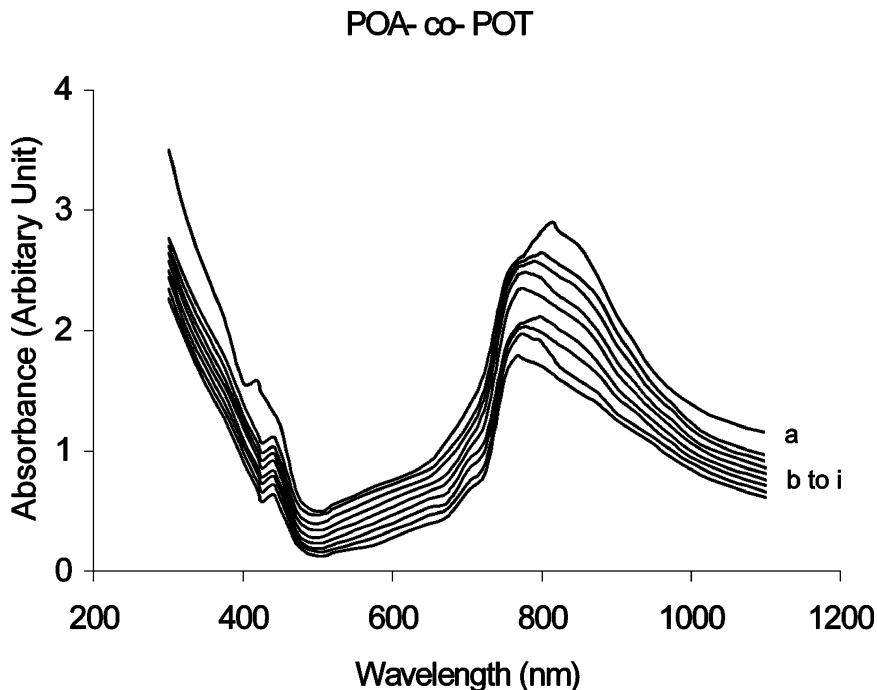


FIGURE 7 Optical absorption spectra of POA-POT films synthesized electrochemically under cyclic voltammetric conditions in aqueous solutions of (a) H_2SO_4 and in presence of salts, (b) K_2SO_4 , (c) Na_2SO_4 , (d) Li_2SO_4 , (e) MgSO_4 , (f) KCl , (g) NaCl , (h) LiCl , (i) MgCl_2 .

adsorption of quinone/hydroquinone, generated during the growth of polymer film, which is strongly adsorbed in the polymer matrix [29]. The appearance and intensity of peak B is highly dependent on the electrolytic medium. The CV of copolymer POA-co-POT is different (A, B, or C peaks) than that of the individual homopolymers POA and POT and clearly supports the formation of a copolymer (Table 1).

Effect of pH on UV-Visible Spectra

The pH values of 1 M H_2SO_4 and its mixture with salts are listed in Table 2. Similarly, in Table 3, pH values of solution containing monomer(s) along with electrolyte and salts is reported. The addition of salts has resulted in a decrease in pH values of acid solution (Table 2) showing an increase in the degree of protonation of monomers. However, the overall pH values for electrochemical solution containing

TABLE 4 Influence of Electrolyte and Added Salts on Electrical Conductivity and UV-Visible Spectra (Peak and Shoulder) for POA, POT, POA-co-POT Films

Electrolyte + Salt	Conductivity (S/cm)			UV-visible spectroscopy (nm)					
	POA	POT	POA-co-POT	POA		POT		POA-co-POT	
				Peak	Shoulder	Peak	Shoulder	Peak	Shoulder
H ₂ SO ₄	0.0275	0.0563	0.0375	826	426	802	410	815	418
H ₂ SO ₄ + K ₂ SO ₄	0.778	1.669	1.089	810	440	780	435	800	440
H ₂ SO ₄ + Na ₂ SO ₄	0.773	1.653	1.082	800	440	771	435	791	440
H ₂ SO ₄ + Li ₂ SO ₄	0.761	1.619	1.055	787	440	765	435	778	440
H ₂ SO ₄ + MgSO ₄	0.754	1.606	1.049	780	440	761	435	770	440
H ₂ SO ₄ + KCl	0.747	1.589	1.039	804	440	774	435	797	440
H ₂ SO ₄ + NaCl	0.743	1.570	1.027	795	440	767	435	786	440
H ₂ SO ₄ + LiCl	0.735	1.540	1.016	783	440	764	435	774	440
H ₂ SO ₄ + MgCl ₂	0.729	1.536	1.009	778	440	760	435	767	440

monomers (Table 3) are higher than those of electrolyte and salt mixtures (Table 2). It is found that in the presence of salts a shift in the absorption peak of UV-visible spectra (Figures 5, 6, 7 for POA, POT, and POA-co-POT respectively) is observed (Table 4). Peaks appearing at about 802–826 nm shifted toward lower wavelength (between 760–810 nm) whereas the shoulder appearing at about 410–426 nm shifted to higher wavelength (between 435–440 nm). Thus, widening the gap between the absorption peaks, which is caused by an increase in anion concentration.

Conductivity of POA, POT, and POA-co-POT Films

The conductivity of POA, POT, and POA-co-POT films prepared in a solution containing 0.1 M monomer(s) and 1 M H₂SO₄, are 0.0275, 0.0563, and 0.0375 S/cm respectively. However, the conductivity of these films prepared in a solution containing 0.1 M monomer(s), 1 M H₂SO₄ and 1 M K₂SO₄ is observed to be 0.778, 1.669, and 1.089 S/cm, respectively. Thus, there is 27–30 fold increase in the conductivity of POA, POT, and POA-co-POT and it is found that the larger the size of the cation the higher the conductivity. The effect is similar in both categories of salts, that is, sulphates or chlorides and the salt having potassium cation, having large size, shows maximum positive doping effect. However, among sulphate and chloride anions, the effect of sulphate anion (large size) is maximum as far as conductivity concerned.

Effect of pH on Electrical Conductivity

A large increase in pH from solution containing H₂SO₄ electrolyte alone, compared with the solution of added salts, resulted in a large increase in conductivity of polymer thin films.

CONCLUSIONS

The following conclusions have been drawn from the present study.

1. The cyclic voltammetric investigation clearly indicates the formation of electroactive POA, POT, and POA-co-POT films in H₂SO₄ as electrolyte and in presence of inorganic salts as dopants.
2. It is observed that the anodic current densities of polymerization of POA, POT, and POA-co-POT films are influenced by the presence of salt in the bath.

3. The optical absorption spectroscopy studies reveal the formation of conducting emeraldine salt (ES) phase of POA, POT, and POA-co-POT films in H_2SO_4 as electrolyte and in presence of salts as dopants. Due to the presence of salts, a widening of the gap between the two peaks in absorption spectra is observed.
4. The electrical conductivity also depends on the salt present in the bath and the conductivity of these films is increased by 27–30 times higher in presence of salts. Further, the conductivity is found to depend on the size of the cation present in the dopant.
5. K_2SO_4 as dopant shows the highest conducting phase due to the combination of largest size of the cation (K^+) and largest size of the anion (SO_4^{2-}). The highest conducting properties obtained in the case of sulphates could be due to the common ion effect (from electrolyte and the salt).

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