J MATER SCI 41 (2006) 1983–1990

Synthesis and characterization of poly (aniline-co-o-anisidine-co-o-toluidine) thin films in inorganic and organic supporting electrolytes

D. D. BOROLE, U. R. KAPADI, P. P. MAHULIKAR, D. G. HUNDIWALE
School of Chemical Sciences, North Maharashtra University, Jalgaon 425001, M.S., India
E-mail: ddborole@indiatimes.com

The influence of inorganic and organic supporting electrolytes on electrochemical, optical and conducting properties of poly(aniline-co-o-anisidine-co-o-toluidine), a terpolymer thin films have been investigated. Homo and terpolymer thin films were synthesized electrochemically, under cyclic voltammetric conditions in aqueous solutions of inorganic acids, viz. H_2SO_4, HCl, HNO_3, H_3PO_4 and $HClO_4$ and organic acids, viz. benzoic acid, cinnamic acid, oxalic acid, malonic acid, succinic acid and adipic acid at room temperature. The films were characterized by cyclic voltammetry, UV-Visible spectroscopy and conductivity measurements using four probe technique. It was observed that the current densities are strongly influenced by the size and the nature of the anion present in the electrolyte. The optical absorption spectra indicated that the conducting emeraldine salt (ES) phase formed in all the inorganic electrolytes used, whereas it formed only in oxalic acid amongst the organic acids supporting electrolytes. The conductivity of thin films was found to be greatly affected by the nature and size of the anion present in the electrolyte. In case of terpolymer (PA-co-POA-co-POT), the conductivity lies in between the conductivity of the homopolymers PA, POA and POT, irrespective of the supporting electrolyte used. Differential scanning colorimeter (DSC) study also proved the formation of terpolymer.

1. Introduction

Polymers that exhibit high electrical conductivity have now been successfully synthesized and the past two decades have witnessed unabated interest in the synthesis and characterization of such conducting polymers due to the potential technological applications of these materials [1–4]. Amongst all reported conducting polymers, polyaniline receives greater attention as conducting organic material due to good environmental stability [5, 6] and moderately high conductivity upon doping with simple bronsted acids [7]. Polyaniline is recognized to be an air-stable organic conducting polymer with interesting electrochemical properties which make it suitable for a number of practical applications, such as in biosensors [8, 9], light weight batteries [10], electrochromic display devices [11], microelectronic devices [12], actuators [13] and electochromic material [14].

Conducting polymers can be prepared by chemical or electrochemical polymerization. Although the chemical method offers mass production at a reasonable cost, the electrochemical method involves the direct formation of conducting polymer thin films with better control of thickness and morphology, which are suitable for application in electronic devices. The most widely used laboratory techniques for the preparation of conducting polymer thin films are potentiostatic (constant potential), galvanostatic (constant current) and potentiodynamics (cyclic voltammetry) [15] modes. Although it is established that the conducting properties of the polymer films greatly depend on the mode of synthesis and also on the number of parameters such as type of counter-ion, the type of electrolyte and their concentration, synthesis temperature, electrochemical voltage, pH of the electrolyte, etc. [16–18], research on the preparation and characterization of the conducting polymers is still continuing. Thus, in order to improve conducting properties of polymer films suitable for a desired application, it is necessary to critically control and optimize the various synthesis parameters.

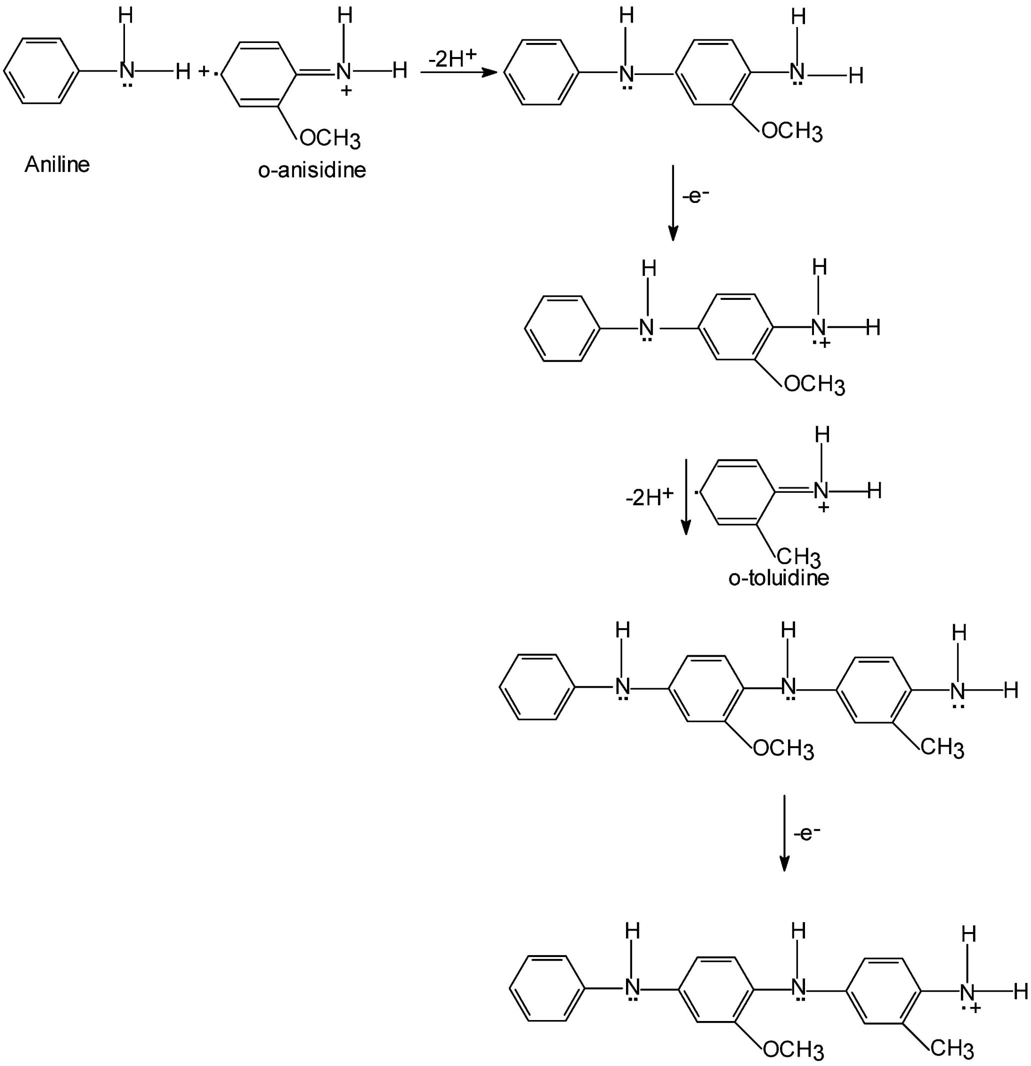
Electrochemical synthesis of copolymer and terpolymer is a convenient method to prepare new conducting material with desired properties different from individual homopolymers. Synthesis of polyaniline and its

0022-2461 © *2006 Springer Science + Business Media, Inc.*
DOI: 10.1007/s10853-006-1863-0

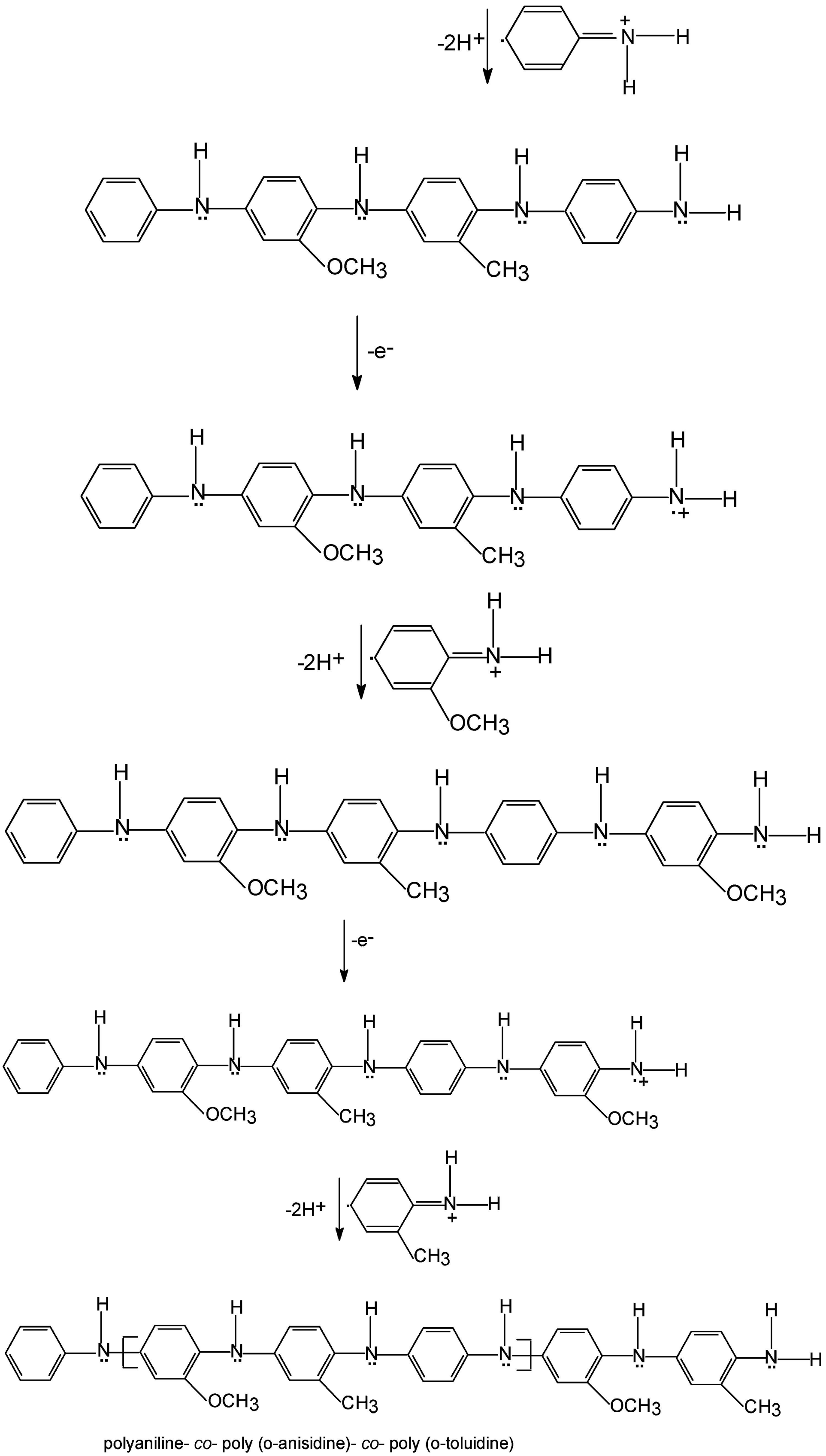
derivative thin films with excellent electrical properties, coupled with good environmental stability, boosted the research to tailor physical and chemical properties of different conducting polymers suitable for a particular applications [19, 20].

Earlier reports on electrochemically generated conducting copolymers have been related to pyrrole derivatives [21] as well as pyrrole and thiophenes [22]. With regards to polyaniline based copolymers, a pioneering work has been done by Wei and co-workers [23, 24]. They have shown that aniline could be copolymerized with o-toluidine such that conductivity could be controlled in a broad range. Dao *et al*. [25] have reported electrosynthesis of copolymer of aniline and N-butylaniline with good conductivity and solubility in common organic solvents. A successful coploymerization of aniline with Nmethylaniline [26], 3-aminophenyl-boricacid [27] and o-aminobenzonitrile [28] have also been reported. The optical and electrical properties of soluble terpolymers of pyrrole, thiophene and 3-decylthiophene have also been studied [29]. These reports reveal that the electrochemical synthesis of copolymers is a convenient method to prepare new conducting materials with desired properties, somewhat different form individual homo polymers. When polymer is produced by the anodic oxidation of monomer, the doping ions (anions) are incorporated into the polymer in order to influence overall properties of conducting polymers.

In continuation of our work on conducting homopolymers and copolymers [30–39], our efforts have been focussed at the systematic investigation on the influence of various supporting electrolytes, both inorganic and organic, on the electrochemical synthesis of terpolymer, poly(aniline-co-o-anisidine-co-o-toluidine) (PA-co-POA-co-POT) films, characterization of films by cyclic voltammetry, UV-Visible spectroscopy, conductivity measurements, differential scanning colorimeter (DSC) and thermogravimetric analysis (TGA). On the basis of early reports on copolymerization [40], the mechanism for terpolymerization of (PA-co-POA-co-POT) has been suggested as shown in Scheme I.



Scheme 1 Terpolymerization of aniline, o-anisidine and o-toluidine.



polyaniline- *co*- poly (o-anisidine)- *co*- poly (o-toluidine)

Scheme 1 Continued.

2. Experimental

The monomers aniline, o-anisidine, o-toluidine were distilled twice before used. Various inorganic acids, viz. H_2SO_4, HCl, HNO_3, H_3PO_4 and $HClO_4$ and organic acids, viz. benzoic acid, cinnamic acid, oxalic acid, malonic acid, succinic acid and adipic acid were used as supporting electrolytes in the present study. The thin films of polyaniline (PA), poly(o-anisidine) (POA), poly(o-toluidine) (POT) and a terpolymer (PA-co-POA-co-POT) were synthesized electrochemically on platinum substrates under cyclic voltammetric conditions in a simple one 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 monomers and 1 M supporting electrolyte by applying sequential linear potential scan rate of 50 mV/s between −0.1–0.8 V versus Ag/AgCl electrode. The cyclic voltammetric conditions were maintained using Potentio-Galvano Stat-30 (Metrohm autolab electrochemical instrument with 663 VA stand). The homopolymer and terpolymer films were deposited with 20 cycles for the polymerization in all supporting electrolytes and their voltammograms were recorded on P.C. After deposition, the films were rinsed with the corresponding 0.2 M supporting electrolytes. Throughout the studies, anaerobic conditions were maintained with nitrogen gas atmosphere.

The optical absorption study of all synthesized films was carried out using UV-Vsible spectrophotometer (Simadzu, UV-1601). The UV-Visible spectra were obtained *ex situ* in DMSO. All the spectra were recorded in the wavelength range 300–1100 nm. The conductivity was measured on platinum electrode, 4 mm in diameter and about 1 μm thick. The thickness of polymer thin films was measured using a digital micrometer. The thickness of polymer thin films was measured using a digital micrometer. After synthesis, films were washed thoroughly using 0.2 M respective supporting electrolyte solution and then was immersed in 0.2 M respective supporting electrolyte solution for 24 h. Finally the film was dried at 50°C for 2 h. The dried film was used for the determination of conductivity at constant current 10 mA. The electrical conductivity of the films was measured using four probe technique. Differential scanning colorimetric (DSC) studies were carried out on DuPont 2100 colorimeter with a standard heating rate 20°C/min in a nitrogen atmosphere. Temperature range of 25 to 200°C was selected for each scan. Thermogravimetric analysis (TGA) (TGA, Mettler Toledo 851^e) was studied in a nitrogen atmosphere with a temperature range 40 to 700°C with a heating rate 20°C/min in a nitrogen atmosphere.

3. Results and discussion

3.1. Cyclic voltammetric study

Figs 1a–f show the cyclic voltammograms (CVs) recorded during the synthesis of PA-co-POA-co-POT films in aqueous solutions of five inorganic acids as

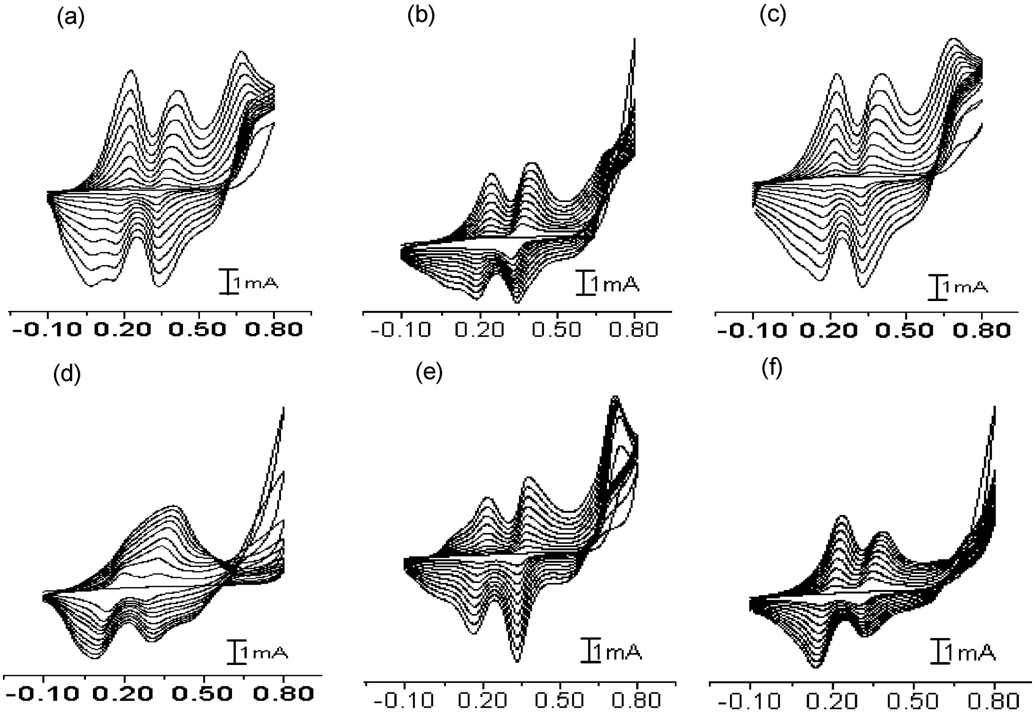


Figure 1 Cyclic voltammograms recorded during the synthesis of PA-co-POA-co-POT films in aqueous solution of (a) H_2SO_4, (b) HCl, (c) HNO_3, (d) H_3PO_4, (e) $HClO_4$, (f) Oxalic acid.

supporting electrolytes, Viz. H_2SO_4, HCl, HNO_3, H_3PO_4 and $HClO_4$ and organic acid (oxalic acid) at room temperature. Other organic acids, viz. benzoic acid, cinnamic acid, malonic acid, succinic acid and adipic acid did not show response in the formation of conducting polymer films. The overall observations and results based on CVs are concluded as follows.

1. In case of inorganic acid supporting electrolytes, averagely three peaks (A, B & C) are observed in repetitive cycling, while in case of organic acid (oxalic acid) generally two peaks are observed and other organic acids do not reflect any peak, indicating their inability to form conducting ES phase of polymers. The redox potentials and current densities corresponding to these peaks for different supporting electrolytes are summarized in Tables I and II.
2. The CV curves grow with the number of cycles for all supporting electrolytes, indicating 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.
3. The highest current densities corresponding to the anodic peaks are observed for the terpolymerization in H_2SO_4 followed by HCl, HNO_3, H_3PO_4 and $HClO_4$ and then oxalic acid. The current densities, in general, are lower for individual polymerization (Table I) than terpolymerization (Table II) in these electrolytes in the given order. Current densities of copolymers are observed to be higher than those of the individual homopolymers. This could be the additive effect of concentration of each monomer. When the concentration of the monomer in the copolymerization bath increases, the polymeric forms of copolymer dominate on the electrode surface [41].
4. The redox peaks observed for the polymerization of aniline are three in H_2SO_4, HCl, HNO_3 and H_3PO_4 and two in oxalic acid, however, three in $HClO_4$. The redox peaks are observed for aniline HCl are similar to that reported by Wei *et al.* [42]. The redox peaks for the polymerization of o-toluidine are three in H_2SO_4, HCl and $HClO_4$ and two in HNO_3, while only one in H_3PO_4 and oxalic acid. The redox peaks of o-toluidine carried out in H_2SO_4 are similar as reported by Wei *et al.* [43]. In case of o-anisidine polymerization, three peak observed in H_2SO_4, HCl, HNO_3 and $HClO_4$ and two in H_3PO_4 and oxalic acid. The CV result of poly o-anisidine is in well agreement with the result of Lacroix *et al.* [44]. Similarly, in case of terpolymerization of aniline-co-o-anisidine-co-otoluidine, three peaks are observed in H_2SO_4, HCl, HNO_3 and $HClO_4$ and two in oxalic acid while only one in H_3PO_4. It reveals that the increase in the number of redox peaks, in general, are strongly dependent on the nature and size of the anion present in the electrolyte. Redox potential values of terpolymeris slightly higher to that of POA homopolymer.

TABLE II Redox potentials and current densities at the redox peaks of PA-*co*-POA-*co*-POT film in various supporting electrolytes

		Redox potential (mV) PA-*co*-POA-*co*-POT			Current density (mA/cm^2) PA-*co*-POA-*co*-POT		
Sr. no	Supporting electrolyte	A	B	C	A	B	C
1	H_2SO_4	225	413	667	7.57	6.30	8.66
2	HCl	239	401	715	4.14	4.08	5.54
3	HNO_3	225	401	674	3.33	3.91	4.59
4	H_3PO_4	379	–	–	3.97	–	–
5	$HClO_4$	217	376	708	1.91	2.61	5.25
6	Oxalic acid	232	391	–	4.03	3.19	–

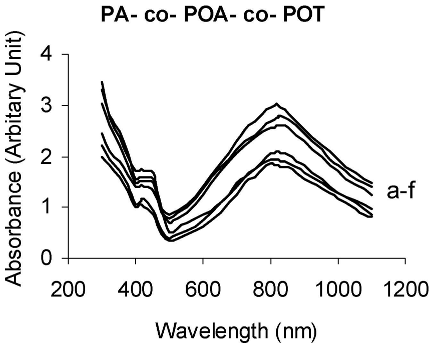


Figure 2 Optical absorption spectra of PA-co-POA-co-POT films synthesized electrochemically under cyclic voltammetric conditions in aqueous solutions of (**a**) H_2SO_4 (**b**) HCl (**c**) HNO_3 (**d**) H_3PO_4 (**e**) $HClO_4$ (**f**) Oxalic acid.

5. Higher current densities are found in inorganic supporting electrolytes than in organic ones. In the case of organic acids as supporting electrolyte, only oxalic acid

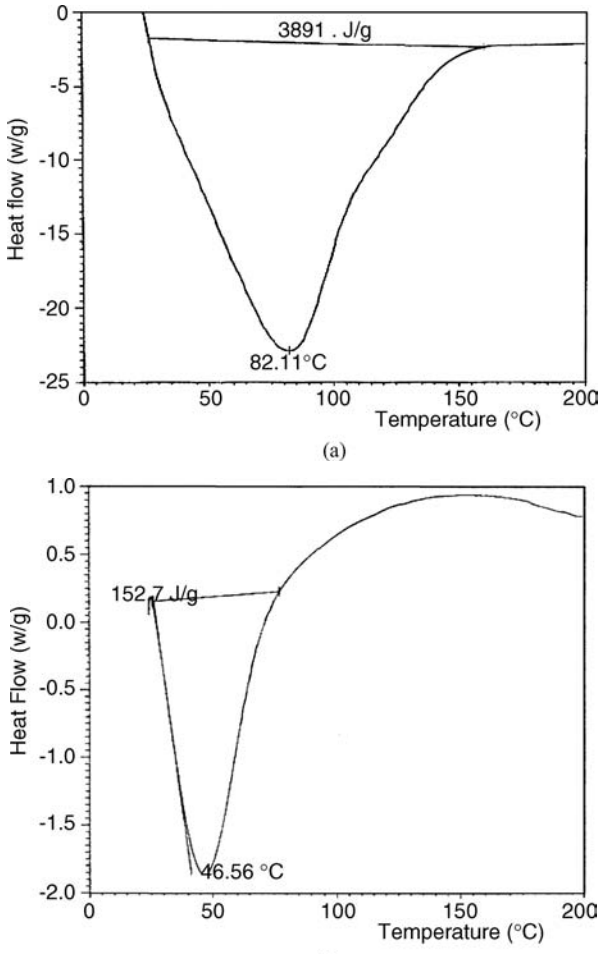
TABLE I Redox potentials and current densities at the redox peaks of PA, POA, POT films in various supporting electrolytes

		Redox potential (mV)									Current density (mA/cm^2)								
		PA			POA			POT			PA			POA			POT		
Sr. 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	188	462	–	215	381	762	235	418	650	6.24	1.34	–	3.55	5.78	7.98	4.04	3.23	4.30
2	HCl	178	534	–	220	415	654	257	427	632	5.31	1.96	–	4.01	4.10	4.02	3.27	3.91	4.19
3	HNO_3	191	487	–	230	435	713	274	637	–	4.79	1.09	–	2.75	3.55	3.67	2.33	3.44	–
4	H_3PO_4	359	543	–	361	591	–	383	–	–	3.72	2.96	–	3.09	1.24	–	1.88		–
5	$HClO_4$	161	481	757	225	403	747	276	481	598	2.66	1.50	4.65	1.48	2.29	5.61	1.04	1.87	1.71
6	Oxalic Acid	173	479	–	225	379	–	496	–	–	2.55	1.99	–	2.40	3.24	–	1.94	–	–

TABLE III Influence of inorganic and organic supporting electrolytes on electrical conductivity and UV-Visible spectra (peak and shoulder) for PA, POA, POT, PA-*co*-POA-*co*-POT films

Sr. no	Supporting electrolyte	Electrical Conductivity (S/cm)$\times 10^{-2}$				UV-Visible Spectroscopy (nm)							
		PA	POA	POT	PA-*co*-POA-*co*-POT	PA		POA		POT		PA-*co*-POA-*co*-POT	
						Peak	Shoulder	Peak	Shoulder	Peak	Shoulder	Peak	Shoulder
1	H_2SO_4	9.72	2.75	5.63	5.91	810	416	826	426	802	410	816	420
2	HCl	9.14	2.34	5.27	5.37	820	425	835	440	810	420	830	425
3	HNO_3	8.63	1.29	4.14	4.24	815	420	830	435	805	415	825	420
4	H_3PO_4	8.44	1.21	3.93	4.07	815	425	830	440	805	420	825	420
5	$HClO_4$	8.22	1.11	3.72	3.91	805	410	820	420	800	405	810	425
6	Oxalic acid	7.19	0.84	3.25	3.62	800	410	810	415	790	405	800	410

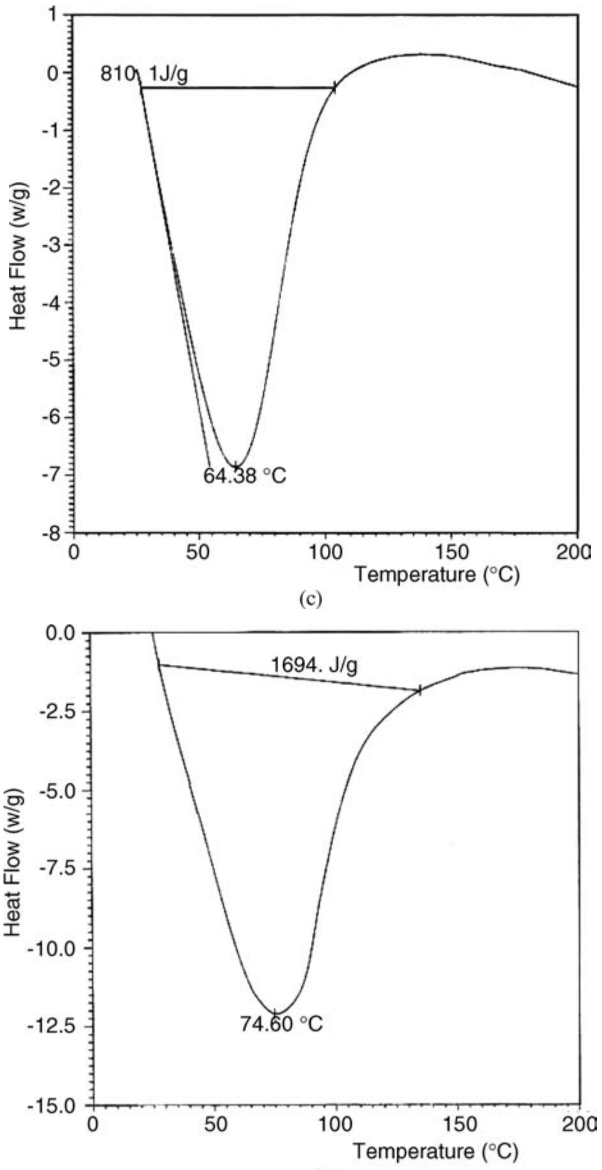
favored the formation of ES phase, however, other organic acids reflected negative results because of either insolubility of these acids in the aqueous medium or formation of lecuoemraldine phase (pale brown colored films). For these acids, CVs are not observed but only a straight line is seen.



(a)

(b)

Figure 3 (a) DSC thermogram of PA (b) DSC thermogram of POA (c) DSC thermogram of POT (d) DSC thermogram of PA-co-POA-co-POT.



(c)

(d)

Figure 3 Continued.

Thus the CVs clearly revealed the formation of electroactive polymer films in all the case of various monomers ratio of o-anisidine and o-toluidine. 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 [45]. The peak B in the cyclic voltammograms is due to adsorption of quinone/hydroquinone, generated during the growth of polymer film which is strongly adsorbed in the polymer matrix [46]. 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 individual homopolymers POA and POT, clearly supports the formation of a copolymer.

3.2. UV-visible spectroscopy

The optical absorption spectra of PA-co-POA-co-POT films in presence of various supporting electrolyte are shown in Fig. 2 and corresponding values are summarized in Table III. The UV-Visible spectra are 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 800–830 nm with a shoulder at 410–425 nm corresponding to the ES phase of PA-co-POA-co-POT polymer.

3.3. Conductivity measurements

The highest electrical conductivity is observed for homo polymer PA followed by POT and POA. However, the electrical conductivity of terpolymer PA-co-POA-co-POT is in between PA and POA, but close to POT. Since the terpolymer films show the values of conductivity much closer to the average value of the three individual monomers, it implies that each monomer has contributed to form terpolymer. The influence of various supporting electrolytes on the electrical conductivity of these films is given in Table III. Additionally it is found that conductivity strongly depends on the anion present and follows the order $HSO_4^- > Cl^- > NO_3^- > PO_4^- > ClO_4^- > COO^-$. This dependence might be related to the adsorption phenomena of electrolyte species, which is in accordance with the optical spectroscopy results.

3.4. Differential scanning colorimeter (DSC)

The thermal properties of PA, POA and POT homopolymers and PA-co-POA-co-POT terpolymer prepared in H_2SO_4 as electrolyte were studied on DSC. The nature of graph of temperature (°C) versus heat flow (W/g) has been shown in Fig. 3a–d. The peak for PA, POA, POT and PA-co-POA-co-POT are observed at 82.11°C, 46.56°C, 64.38°C and 74.60°C, respectively. Since a single peak is obtained for terpolymer on DSC thermograms it confirms the formation of terpolymer and not the layers of individual homopolymer.

3.5. Thermo gravimetric analysis (TGA)

The thermal stability of PA, POA, POT and PA-*co*-POA-co-POT films prepared in a solution containing 0.1 M monomer(s) and 1M H_2SO_4 as electrolyte were measured by TGA. The graph of temperature (°) versus weight (%C) is shown in Fig. 4. The thermal stability for PA, POA, POT and PA-co-POA-co-POT are observed upto 407.41, 287.85, 320.81 and 333.49°C respectively. This study shows the stability of PA-co-POA-co-POT lies in between PA, POA and POT.

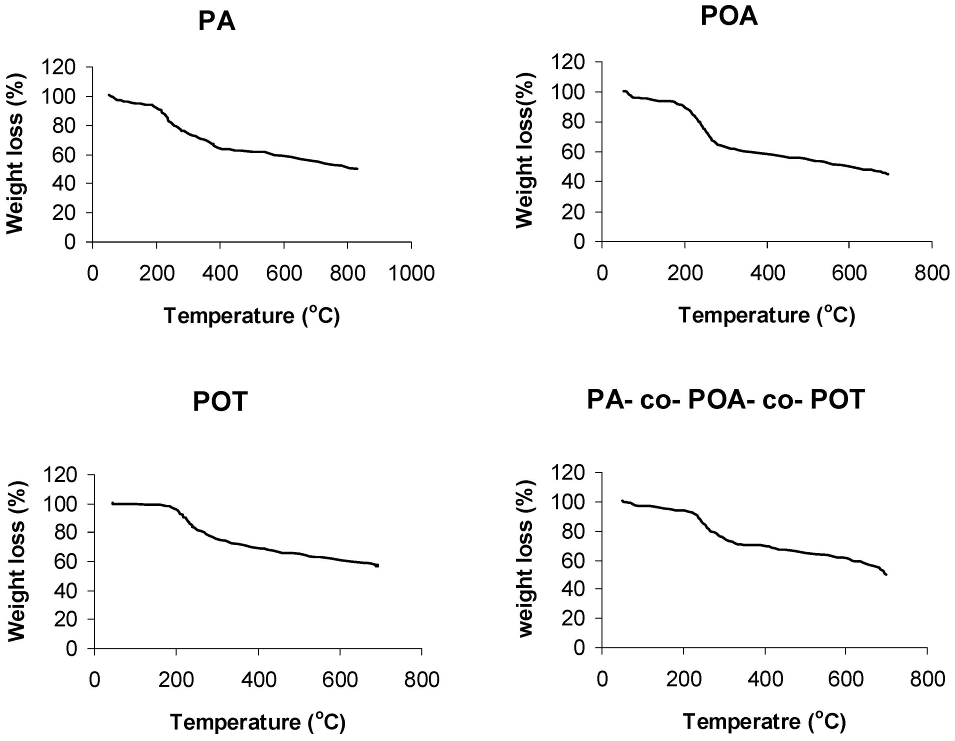


Figure 4 TGA of PA, POA, POT and PA-co-POA-co-POT.

4. Conclusion

Following conclusions have been drawn from the present study.

1. The cyclic voltammetric investigation clearly indicate the formation of electroactive PA*co*-POA-*co*-POT films in all inorganic supporting electrolytes, viz. H_2SO_4, HCl, HNO_3, H_3PO_4 and $HClO_4$ and only in oxalic acid as organic supporting electrolyte.
2. It is observed that the anodic current densities of polymerization, in general, are strongly influenced by the anion present in the electrolyte.
3. The optical absorption spectroscopy results reveal the formation of conducting ES phase of PA-*co*-POA-*co*-POT irrespective of the electrolyte used. However, the optical absorption varies with the electrolyte species.
4. The electrical conductivity depends on monomers and also on the electrolyte species. However, the electrical conductivity of terpolymer is an average of conductivites of the three individual homopolymers.
5. The inorganic supporting electrolytes are found to be more suitable than organic ones as they favor the formation of good conducting ES phase of polymers due to their easy solubility and mobility in the aqueous medium.
6. The values of conductivity, UV-visible absorption, DSC and CVs confirm the formation of terpolymer PA-*co*-POA-*co*-POT.

References

1. T. A. SKOTHEIM, "Handbook of Conducting Polymers" (Marcel Dekker: New York, 1986).
2. S. N. BHADANI, M. K. GUPTA and S. K. SEN GUPTA, *J. Polym. Mater.* **9** (1992) 147.
3. L. ALCACER, "Conducting Polymers—Spectral Application Riedel" (Dordrecht, Holland, 1987).
4. W. R. SALANEEK, D. T. CLARK and E. J. SAMUELSEN, "Science and Applications of Conducting Polymers" (Adam Hilger: Bristol, 1991).
5. J. C. LACROIX and A. F. DIAZ, *J. Electrochem. Soc.* **135** (1988) 1457.
6. J. L. CAMALET, J. C. LACROIX, S. ACIYACH, K. CHANECHING and P. C. LACAZE, *Synth. Met.* **93** (1998) 133.
7. C. H. YANG and T. C. WEN, *J. Appl. Electrochem.* **24** (1994) 166.
8. D. C. LIAO, K. H. HSICH, Y. C. CHERN and K. S. HO, *Synth. Met.* **87** (1997) 61.
9. S. ROTH and W. GRAUPNER, *ibid.* **57** (1993) 3623.
10. P. N. BARTLETT and P. R. BIRKIN, *Anal. Chem.* **65** (1993) 1118.
11. M. A. DEPAOLI, G. GASALBOREMICELI, E. M. GIROTTO, W. A. GAZZOTI and A. G. MCDIARMID, *Electrochim. Acta.* **44** (1999) 2983.
12. D. M. DELCCUM, M. M. J. SIMENON, A. R. BROWN and R. E. F. EINERCHAND, *Synth. Met.* **87** (1997) 53.
13. K. KANCTO, M. KANECO, Y. MIN and A. G. MACDIARMID, *ibid.* **71** (1995) 2211.
14. S. A. CHEN and C. J. CHAO, *ibid.* **79** (1996) 93.
15. D. E. STILLWELL and S. M. PARK, *J. Electrochem. Soc.* **135** (1988) 2254.
16. J. LEI, Z. CAI and R. C. MARTIN, *Synth. Met.* **46** (1992) 53.
17. E. L. KUPILA and J. KANKARE, *ibid.* **55** (1993) 1402.
18. R. STANKOVIE, O. PAVLOVIC, M. VOJNOVIC and S. JOVANOVIC, *Eur. Polym. J.* **30** (1994) 385.
19. L. H. C. MATTOSO, S. K. MANOHAR, A. G. MACDIARMID and A. J. EPSTEIN, *J. Polym. Sci. Part A Polym. Chem.* **33** (1995) 1227.
20. R. STANKOVIE, O. PAVLOVIC, M. VOJNOVIC and S. JOVANOVIC, *Eur. Polym. J.* **30** (1994) 385.
21. C. P. ANDRIEUX and P. AUDEBERT, *J. Electroanal. Chem.* **285** (1990) 163.
22. E. M. PETERS and J. D. VAN DYKE, *J. Polym. Sci., Polym. Chem. Ed.* **29** (1991) 1379.
23. Y. WEI, W. W. FOCKE, G. E. WNEK, A. RAY and A. G. MACDIARMID, *J. Phys. Chem.* **93** (1989) 495.
24. Y. WEI, R. HARIHARAN and S. A. PATEL, *Macromolecles* **23** (1990) 764.
25. J. Y. BERGERON and L. H. DAO, *Polym. Commun.* **32** (1991) 403.
26. J. J. LANGER, *Synth. Met.* **35** (1990) 301.
27. T. L. PORTER, G. CAPLE and C. Y. LEE, *ibid.* **46** (1992) 105.
28. M. SATO, S. YAMANAKA, J. NAKAYA and K. HYODO, *Electrochimica Acta* **39** (1994) 2159.
29. W. CZERWINSKI, G. WRZESZCZ, K. KANIA, J. F. RABEK and L. A. LINDEN, *J. Mater. Sci.* **35** (2000) 2305.
30. D. D. BOROLE, U. R. KAPADI, P. P. KUMBHAR and D. G. HUNDIWALE, *Mater. Lett.* **56** (2002) 685.
31. *Idem., ibid.* **57** (2002) 844.
32. *Idem., Poly. Plastic Tech. Engng.* **42** (2003) 415.
33. D. D. BOROLE, U. R. KAPADI, P. P. MAHULIKAR and D. G. HUNDIWALE, *Mater. Lett.* **57** (2003) 3629.
34. *Idem., J. Appl. Poly. Sci.* **90** (2003) 2634.
35. *Idem., Poly. Plastic Tech. Engng.* **43** (2004) 41.
36. D. D. BOROLE, U. R. KAPADI, P. P. KUMBHAR and D. G. HUNDIWALE, *ibid.* **43** (2004) 81.
37. D. D. BOROLE, U. R. KAPADI, P. P. MAHULIKAR and D. G. HUNDIWALE, *Design. Monom. Poly.* **7** (2004) 45.
38. *Idem., ibid.* **7** (2004) 337.
39. *Idem., Poly. Plastic Tech. Engng.* **43** (2004) 1443.
40. K. DHANALAKSHMI and R. SARASWATHI, *J. Mat. Sci.* **36** (2001) 4114.
41. J. WIDERA, B. PALYS, J. BUKOWSAKA and K. JACKOWSAKA, *Synth. Met.* **94** (1998) 265.
42. Y. WEI, Y. SUN and X. TANG, *J. Phys. Chem.* **93** (1989) 4878.
43. Y. WEI, W. W. FOCKE, G. F. WNEK, A. RAY and A. G. MACDIARMID, *ibid.* **93** (1989) 495.
44. J. C. LACROIX, P. GARCIA, J. P. AUDIERE, R. CLEMENT and O. KAHN, *Synth. Met.* **44** (1991) 117.
45. W. S. HUANG, B. D. HUMPHREY and A. G. MACDIARMID, *J. Chem. Soc. Faraday Trans.* **82** (1986) 2385.
46. S. K. DHAWAN and D. C. TRIVEDI, *J. Appl. Electrochem.* **22** (1992) 563.

Received 27 December 2004
and accepted 4 May 2005