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Electrochemical synthesis and characterization of conducting copolymer: poly(o-anisidine-co-o-toluidine)

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Copolymerization of o-anisidine and o-toluidine was achieved electrochemically in aqueous solution containing H_2SO_4 as supporting electrolyte. The copolymer compositions can be altered by varying the monomer feed ratios during electrosynthesis. The films were electropolymerized in solution containing monomers in various ratio (0.025–0.1 M) and 1 M sulphuric acid as electrolyte by applying sequential linear potential scan rate 50 mV/s between −0.2 to 1.0 V. versus Ag/AgCl electrode. The copolymers were characterized by cyclic voltammetric, conductivity measurement, UV-Visible spectroscopy, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA).

1. Introduction

Polymers are generally used as insulators. However, the discovery that the organic polymers can also have conductivities comparable to metals and semiconductors has revolutionized this area of research especially in the electronics industry. The prospective utility of these conducting polymers or synthetic metals in electronic displays, telecommunication, electrochemical storage systems, biosensors and molecular electronics, etc., has further enhanced the interest in this important field [1–4]. Considerable research efforts are currently being devoted to electrochemical studies on conducting polymers [5]. Among conducting polymers, polyaniline and its derivatives have attracted much attention due to its ease of synthesis, good stability in the presence of oxygen/ water and an interesting electrochemical properties including unique conduction mechanism, their interesting electrical, optical and catalytical properties [6–10]. However their properties depend on the synthesis conditions such as type of supporting electrolyte, reagent concentration, applied potential, type of solvent and pH of polymerization bath [11–13].

With regard to polyaniline based copolymers, a pioneering work has been done by Wei and coworkers [14, 15] who showed that aniline could be copolymerized with o-toluidine to control conductivity in a broad range. Dao *et al.* [16] have reported electrosynthesis of copolymer of aniline and N-butylaniline with good conductivity and solubility in common organic solvents. A successful copolymerization of aniline with N-methylaniline [17], 3-aminophenyl-boronic acid [18] and o-aminobenzonitrile [19] have also been reported. Optical and electrical properties of soluble terpolymers of pyrrole, thiophene and 3-decylthiophene have also been studied [20]. All these reports reveal that the electrochemical synthesis of copolymers is a convenient method to prepare new conducting materials with desired properties different from individual homo polymers. When polymer is synthesized by anodic oxidation (of monomer), the anions of supporting electrolyte function as doping ions (anions) and in turn influence overall properties of conducting polymers.

In continuation of our work on conducting homopolymers and copolymers [21–25], poly(o-anisidine-*co*-o-toluidine) (POA-*co*-POT) films synthesized by changing the mole ratio of monomers and characterized by cyclic voltammetry, UV-Visible spectroscopy, conductivity measurements, differential scanning calorimetry (DSC) thermogravimetric analysis (TGA). A mechanism for homo and copolymerization of POA and POT has been suggested.

2. Experimental

The monomers, o-anisidine and o-toluidine were distilled twice before use. The thin films of poly(o-anisidine) (POA), poly(o-toluidine) (POT) and a copolymer (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 in which platinum substrate as working electrode (1.5 cm^2), carbon as counter electrode and Ag/AgCl as the 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 monomers (various mole ratio) and 1 M supporting electrolyte (Sulphuric acid) by applying sequential linear potential scan rate of 50 mV/s

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between −0.2 to 1.0 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 copolymer films were deposited with 20 cycles for the polymerization and their voltammograms were recorded on P.C. After deposition, the films were rinsed with the solution of 0.2 M supporting electrolyte. Throughout the studies, anaerobic conditions were maintained with nitrogen gas atmosphere.

The optical absorption study of all synthesized films was carried out using UV-Visible 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 a platinum electrode, 4 mm with diameter and thickness of 1 μm. The thickness of polymer thin films was measured using a digital micrometer. After the synthesis, films were washed thoroughly using 0.2 M solution of respective supporting electrolyte and then the films were immersed in the solution for 24 h. Finally the film were dried at 50°C for 2 h. The dried films were used for the determination of conductivity at constant current of magnitude10 mA. The electrical conductivity of the films was measured using four probe technique. Differential scanning calorimetry (DSC) studies were carried out on DuPont 2100 calorimeter with a standard heating rate of 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 volammetric study

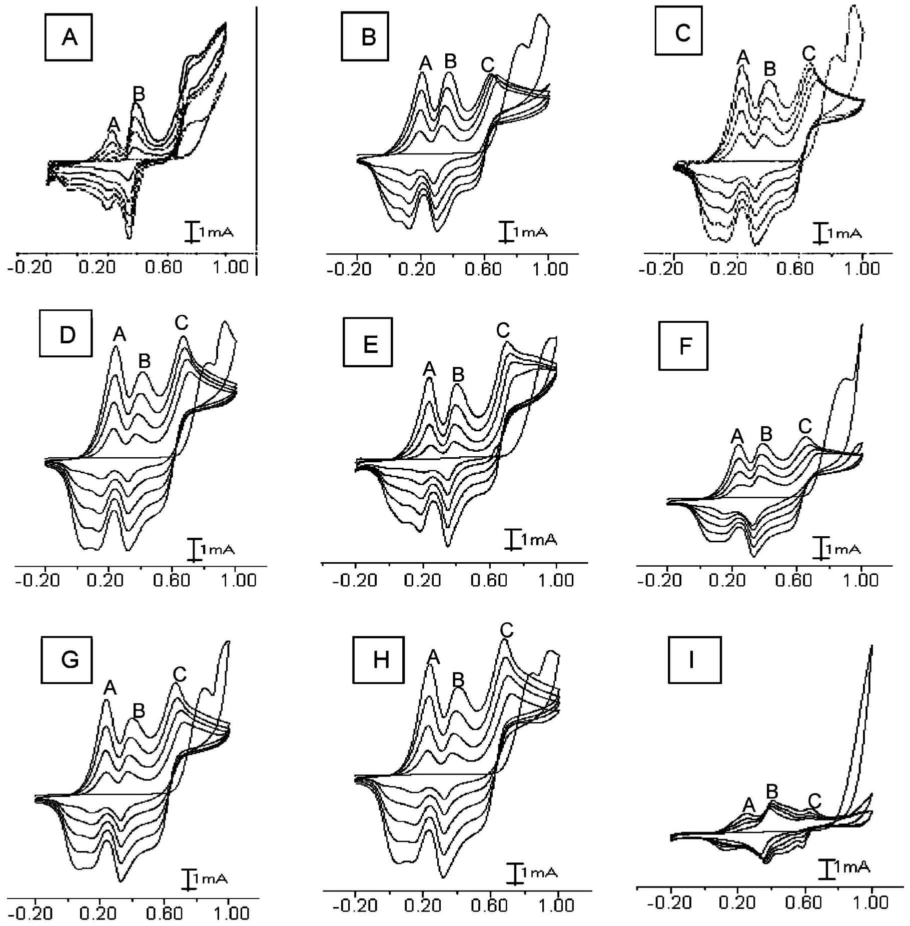
There are three ways to carry out electrochemical oxidative polymerization as: (i) to control the anodic current, (ii) to hold the applied potential at certain value and (iii) to scan the applied potential within a certain potential region. Only the third method, cyclic voltammetry, resulted in the formation of homo and copolymer better thin films of o-anisidine and o-toluidine

Figs 1 A–I show the cyclic voltammograms (CVs) recorded during the synthesis of POA, POT and POA-*co*-POT films in aqueous solutions using sulphuric acid as supporting electrolyte by changing the concentration of monomer at room temperature. The overall observations and results based on CVs are concluded as follows.

- Three peaks (A, B and C) are observed in repetitive cycling. The redox potentials and current densities corresponding to these peaks are summarized in Table I.
- The height of CV curves increase with the number of cycles for various monomer concentrations of o-anisidine and o-toluidine, indicating the formation of conducting polymer films in each case. It signifies that the oxidation potential depends on the concentration of monomer.
- The highest current densities corresponding to the anodic peaks are observed for the copolymerization of 0.1:0.1 M ratio of o-anisidine and o-toluidine in 1 M H_2SO_4. The current densities observed during cyclic voltammograms are summarized in Table I. Current densities of copolymers are observed to be higher than those of the individual homopolymers for peak A. 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 POA-*co*-POT dominate on the electrode surface [26].
- In the case of o-anisidine polymerization, two redox peaks are observed in H_2SO_4 as supporting electrolyte. The CV result of poly o-anisidine is in well agreement with the reported result of Lacroix [27]. The redox peaks for the polymerization of o-toluidine are three in H_2SO_4 as supporting electrolyte. The redox peaks of o-toluidine carried out in H_2SO_4 are similar as reported by Wei [28]. Similarly, for copolymer poly(o-anisidine-*co*-o-toluidine) prepared in various concentration of monomer, three peaks are observed. Redox potential values of copolymer POA-*co*-POT are different to that of POA and POT homopolymers [25].
- In the reverse scan, as the applied potential decreased from 1 to −0.2 V versus Ag/AgCl, the film became reduced, which was seen by an increase in the cathodic current.

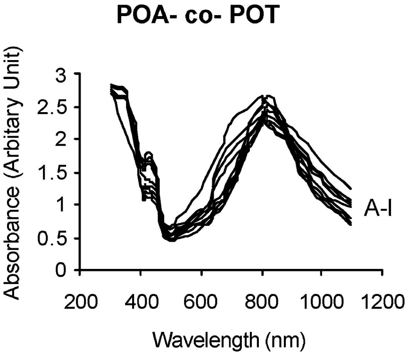
TABLE I Redox potentials and current densities at the redox peaks of POA-*co*-POT films prepared in various mole ratios using sulphuric acid as electrolyte

Concentration of monomer (M)		Redox potential (mV)			Current density (mA/cm^2)		
o-anisidine	o-toluidine	A	B	C	A	B	C
0.1	0	230	388	–	2.15	4.52	–
0.1	0.025	200	376	637	4.62	4.59	4.51
0.1	0.050	230	405	659	5.07	4.25	5.26
0.1	0.075	237	413	669	5.42	4.14	5.86
0.1	0.1	222	420	672	6.56	6.41	8.48
0.025	0.1	232	383	654	4.16	3.34	3.26
0.050	0.1	235	396	667	4.33	3.48	5.12
0.075	0.1	237	403	676	4.52	3.54	5.49
0	0.1	239	441	663	1.76	2.95	2.25



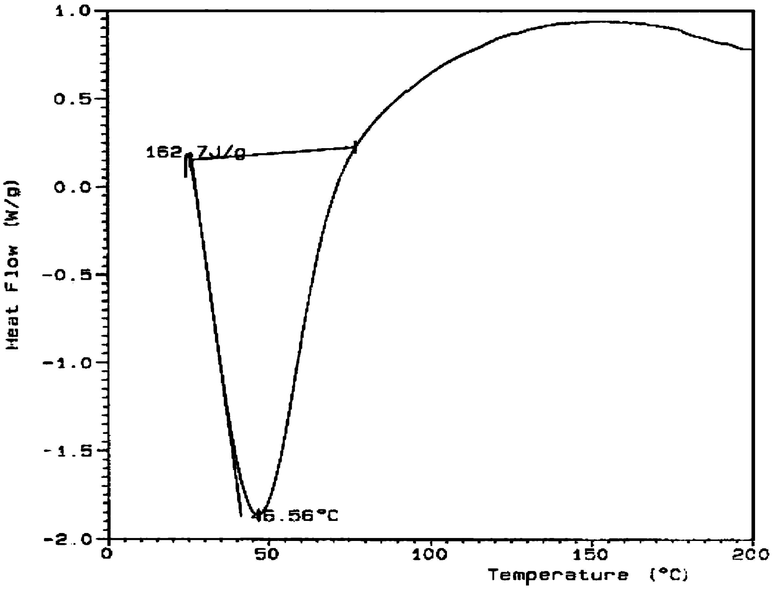
Type	A	B	C	D	E	F	G	H	I
Polymer	POA	POA-co-POT	POA-co-POT	POA-co-POT	POA-co-POT	POA-co-POT	POA-co-POT	POA-co-POT	POT
Concentration of monomer o-anisidine: o-toluidine	0.1:0	0.1: 0.025	0.1: 0.05	0.1: 0.075	0.1: 0.1	0.025: 0.1	0.05: 0.1	0.075: 0.1	0:0.1

Figure 1 Cyclic voltammograms recorded during the synthesis of POA, POT and POA-*co*-POT films in aqueous solution of H_2SO_4 as electrolyte.

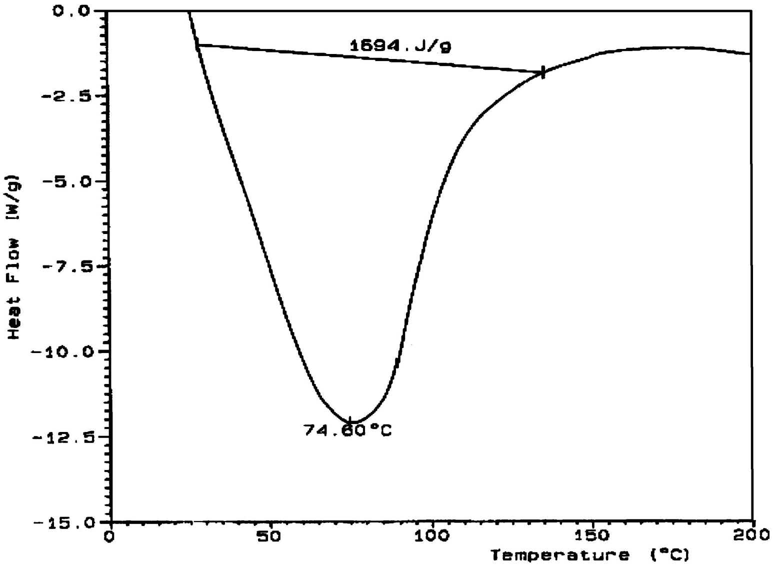


Type	A	B	C	D	E	F	G	H	I
Polymer	POA	POA-co-POT	POA-co-POT	POA-co-POT	POA-co-POT	POA-co-POT	POA-co-POT	POA-co-POT	POT
Concentration of monomer o-anisidine: o-toluidine	0.1: 0	0.1: 0.025	0.1: 0.05	0.1: 0.075	0.1: 0.1	0.025: 0.1	0.05: 0.1	0.075: 0.1	0:0.1

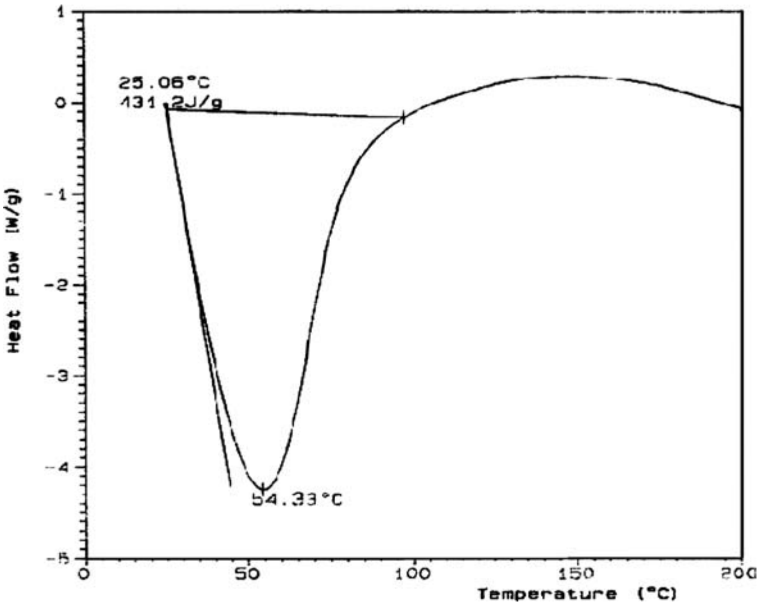
Figure 2 Optical absorption spectra of POA-*co*-POT films synthesized electrochemically under cyclic voltammetric conditions in aqueous solutions of 1 M H_2SO_4 as electrolyte taking respective monomers mole ratio.



(a)



(b)



(c)

Figure 3 (a) DSC thermogram of POA in H_2SO_4. (b) DSC thermogram of POT in H_2SO_4. (c) DSC thermogram of POA-*co*-POT in H_2SO_4.

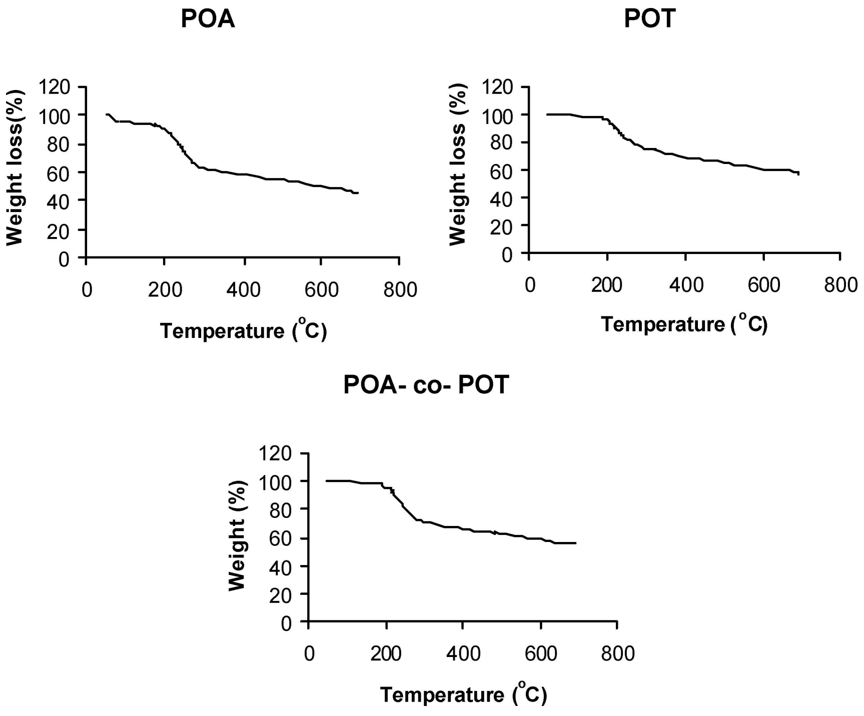


Figure 4 TGA of POA, POT and POA-*co*-POT in H_2SO_4.

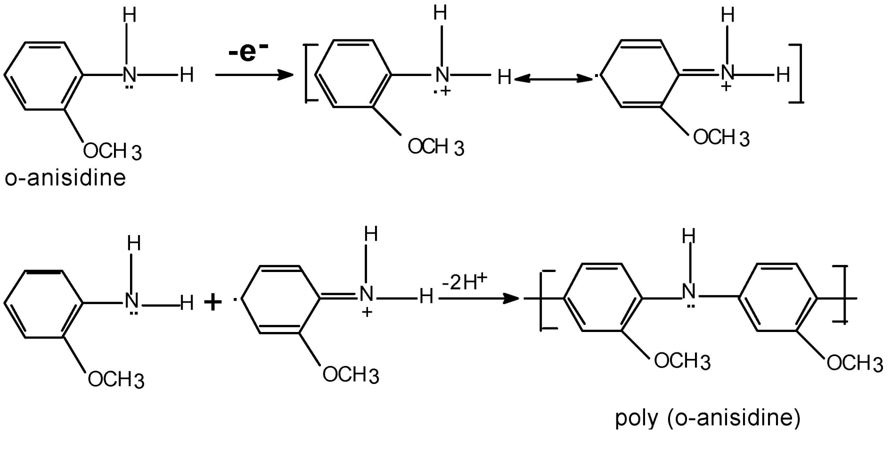
Thus the CVs clearly revealed the formation of electroactive polymer films in all the case of various monomers ratio of o-anisidine and o-toluidine. The anodic peak A and/or C are assigned to the oxidation of polymer deposited on the electrode surface, which corresponds to the conversion of amine units into radical cations [29]. 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 [30]. 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 spectra of the homo- and copolymers

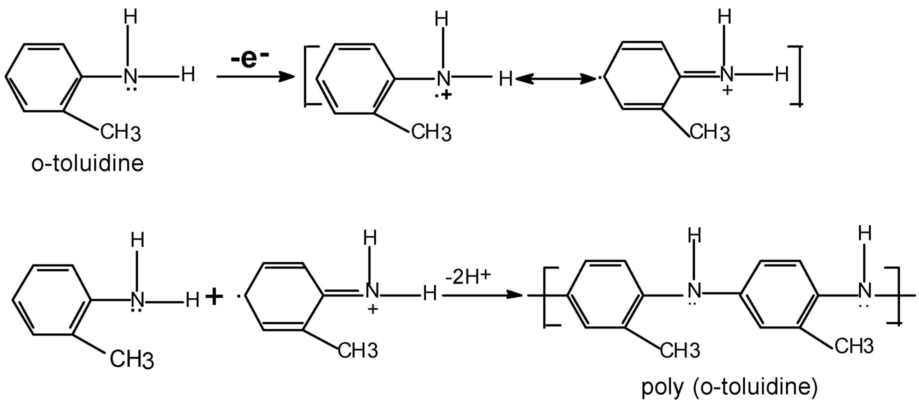
The peak values of optical absorption spectra of POA, POT and POA-*co*-POT films deposited in presence of sulphuric acid under identical experimental conditions are summarized in Table II and the nature is visualized in Fig. 2. The UV-visible spectra are obtained *ex situ* in DMSO and peaks appearing at about 802–826 nm with a shoulder at 410–426 nm are for emeraldine salt (ES) phase of POA, POT, and POA-*co*-POT in sulphuric acid as electrolyte. From Table II, we can see that an average absorption for the polymerized products obtained using both the monomers indicate the formation of copolymer (POA-*co*-POT) i.e. absorption peaks for (POA-*co*-POT) copolymer are different from individual polymers POA and POT.

3.3. Conductivity of the homo- and copolymers

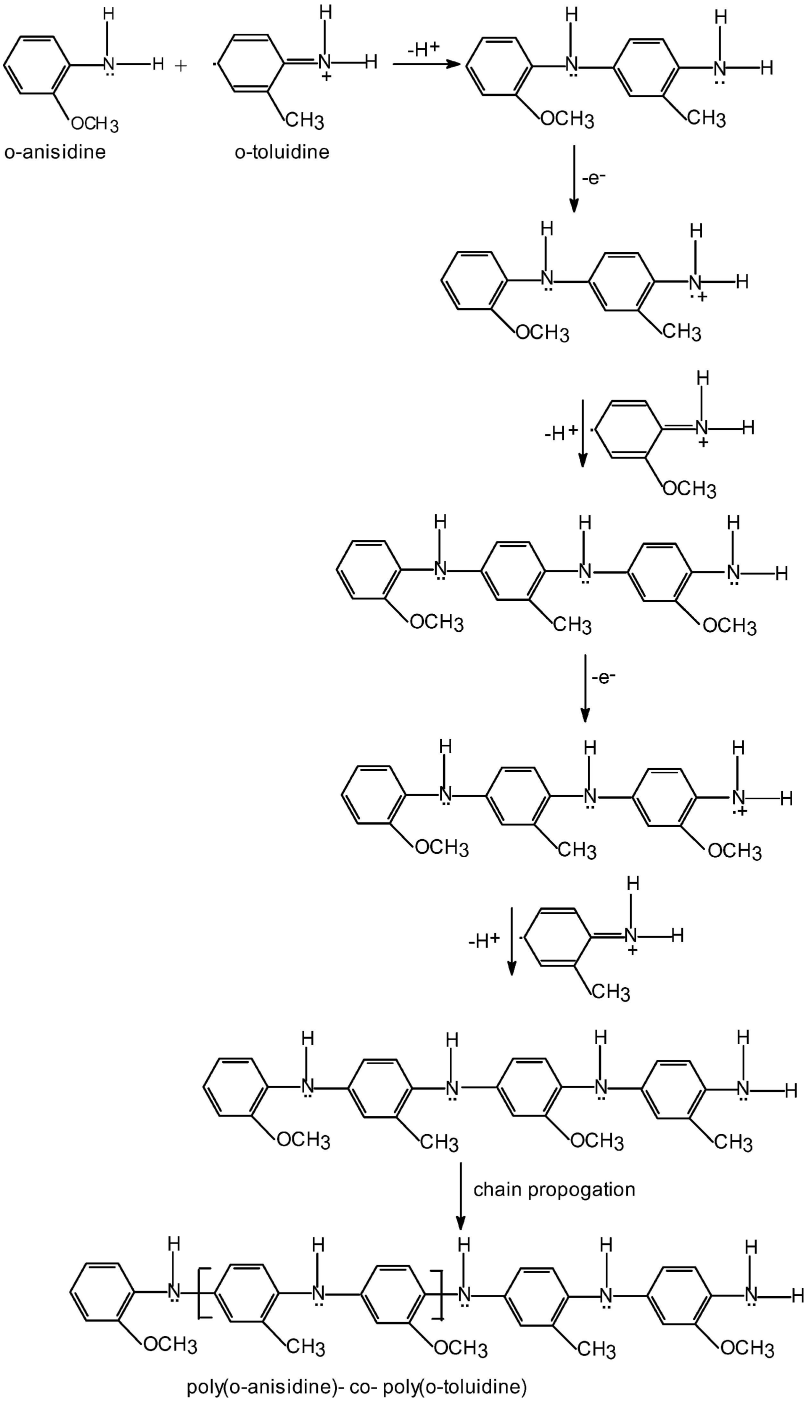
The conductivity of POA, POT and POA-*co*-POT films prepared in a solution containing 0.1 M monomer(s) and 1 M H_2SO_4, are 0.0275, 0.0563 and 0.0375 S/cm respectively. The conductivity of these films prepared



Scheme Ia Homopolymerization of poly(o-anisidine).



Scheme Ib Homopolymerization of poly(o-toluidine).



Scheme II Copolymerization of poly (o-anisidine)-co-poly(o-toluidine).

TABLE II Influence of mole ratios of monomer of POA-*co*-POT films on electrical conductivity and UV-visible spectra (peak and shoulder)

Concentration of monomer (M)		Conductivity (S/cm)	UV-visible spectroscopy (nm)	
o-anisidine	o-toluidine		Peak	Shoulder
0.1	0	0.0275	826	426
0.1	0.025	0.0297	825	426
0.1	0.050	0.0315	822	426
0.1	0.075	0.0343	819	424
0.1	0.1	0.0375	815	418
0.025	0.1	0.0410	811	416
0.050	0.1	0.0457	808	415
0.075	0.1	0.0512	806	415
0	0.1	0.0563	802	410

in a solution containing different ratio of monomer(s) in 1 M H_2SO_4 are as shown in Table II. The formation of copolymer (POA-*co*-POT) has also been confirmed by average values obtained for electrical conductivities of individual polymers POA and POT.

3.4. Differential scanning colorimetery (DSC)

The thermal properties of POA, POT and POA-*co*-POT films prepared in a solution containing 0.1 M monomer(s) and 1 M H_2SO_4 as electrolyte were measured by DSC. The graph of temperature (°C) versus heat flow (W/g) is shown in Figs 3 a–c. The peak values (melting) for POA, POT and POA-*co*-POT are observed at 46.56, 64.38 and 54.33°C respectively. It is clear from the DSC thermogram that the film of copolymer is formed by the polymerization of both monomers and not the layers of individual homopolymers. In case of formation of layers of homopolymers, it would have shown two different peaks for individual melting, which is not the case here, confirming the formation of copolymers.

3.5. Thermo gravimetric analysis (TGA)

The thermal stability of POA, POT and POA-*co*-POT films prepared in a solution containing 0.1 M monomer(s) and 1 M H_2SO_4 as electrolyte were measured by TGA. The graph of temperature (°C) versus weight (%) is shown in Fig. 4. The thermal stability for POA, POT and POA-*co*-POT are observed upto 287.85, 320.81 and 299.35°C respectively. This study shows the stability of POA-*co*-POT lies in between POA and POT.

3.6. Mechanism of homo and copolymerization

The initiation process of the electrochemical copolymerization was thought to be the formation and reactions of the cation radicals [31] and dimeric species [32]. The mechanism of the electrochemical polymerization of monomer is believed to proceed via a radical cation which reacts with a second radical cation to give a dimer. This reacts further with the radical cation of the monomer to build up the polymer chain. In case of copolymerization a chain might be built up by formation through conjugation of radicals of two different monomers followed by propagation. The possible reaction mechanisms [33] for homo and copolymerization have been given in Scheme I a and b and Scheme II respectively.

4. Conclusions

Following conclusions have been drawn from the present study.

1. The cyclic voltammetric investigation clearly indicated the formation of electroactive POA, POT and POA-*co*-POT films prepared using various monomers feed ratio in sulphuric acid as electrolyte.
2. It is observed that the anodic current densities of polymerization of POA, POT and POA-*co*-POT films are greatly influenced by the concentration of monomer in the bath.
3. The optical absorption spectroscopy results also show that UV-visible spectra for copolymer lies in between individual homopolymers. However the optical absorption varies with the changing the concentration of monomer.
4. In general, the electrical conductivity depends on monomers and its concentration.
5. The peaks for POA, POT and POA-*co*-POT copolymer prepared in H_2SO_4 as electrolyte are observed at 46.56, 64.38 and 54.33°C respectively. The formation of copolymer has been confirmed by DSC studies.
6. Thermo gravimetric analysis suggests that stability of copolymer lie in between their individual homopolymers.

References

1. K. G. NEOH, H. W. TEO, E. T. KANG and K. L. TAN, *Langmuir* **14** (1998) 2820.
2. H. OKAMOTO, M. OKAOMOTO and T. KOTAKA, *Polymer* **39** (1998) 4359.
3. M. RETHI, S. PONRATHNAM and C. R. RAJAN, *Macromol. Rapid Commun.* **19** (1998) 119.
4. T. P. MCANDREW, *Trends in Polym. Sci.* **5** (1997) 7.
5. D. E. STILWELL and S. M. PARK, *J. Electrochem. Soc.* **135** (1988) 2254.
6. D. KMAR, *Eur. Polym. J.* **35** (1999) 1919.
7. D. MACINNES and B. L. FUNT, *Synth. Met.* **25** (1988) 235.
8. M. LECLERC, J. GUAY and L. H. DAO, *Macromolecules* **22** (1989) 649.
9. Y. CAO and P. SMITH, *Polymer* **34** (1993) 3139.
10. F. LUX, *ibid.* **35** (1994) 2915.
11. J. LEI, Z. CAI and R. C. MARTIN, *Synth. Met.* **46** (1992) 53.
12. E. L. KUPILA and J. KANKARE, *ibid.* **55** (1993) 1402.
13. R. STANKOVIE, O. PAVLOVIC, M. VOJNOVIC and S. JOVANOVIC, *Eur. Polym. J.* **30** (1994) 385.
14. Y. WEI, W. W. FOCKE, G. E. WNEK, A. RAY and A. G. MACDIARMID, *J. Phys. Chem.* **93** (1989) 495.
15. Y. WEI, R. HARIHARAN and S. A. PATEL, *Macromolecles* **23** (1990) 764.
16. J. Y. BERGERON and L. H. DAO, *Polym. Commun.* **32** (1991) 403.
17. S. K. DHAWAN and D. C. TRIVEDI, *Synth. Met.* **60** (1993) 63.
18. J. J. LANGER, *ibid.* **35** (1990) 301.

19. T. L. PORTER, G. CAPLE and C. Y. LEE, *ibid.* **46** (1992) 105.
20. M. SATO, S. YAMANAKA, J. NAKAYA and K. HYODO, *Electrochimica Acta* **39** (1994) 2159.
21. D. D. BOROLE, U. R. KAPADI, P. P. KUMBHAR and D. G. HUNDIWALE, *Mater. Lett.* **56** (2002) 685.
22. *Idem.*, *ibid.* **57** (2002) 844.
23. *Idem.*, *Poly. Plastic Tech. Engg.* **42** (2003) 415.
24. D. D. BOROLE, U. R. KAPADI, P. P. MAHULIKAR and D. G. HUNDIWALE, *Mater. Lett.* **57** (2003) 3629.
25. *Idem.*, *J. App. Poly. Sci.* **90** (2003) 2634.
26. J. WIDERA, B. PALYS, J. BUKOWSAKA and K. JACKOWSAKA, *Synth. Met.* **94** (1998) 265.
27. J. C. LACROIX, P. GARCIA, J. P. AUDIERE R. CLEMENT, and O. KAHN, *Synth. Met.* **44** (1991) 117.
28. Y. WEI, W. W. FOCKE, G. F. WNEK, A. RAYAND and A. G. MACDIARMID, *J. Phys. Chem.* **93** (1989) 495.
29. W. S. HUANG, B. D. HUMPHREY and A. G. MACDIARMID, *J. Chem. Soc. Farad. Trans.* **82** (1986) 2385.
30. S. K. DHAWAN and D. C. TRIVEDI, *J. Appl. Electrochem.* **22** (1992) 563.
31. T. INOUE and T. YAMASE, *Bull. Chem. Soc. Jpn.* **56** (1983) 985.
32. Y. WEI, C. C. CHAN, J. TIAN, G. W. JANG and K. F. HSUEH, *Chem. Mater.* **3** (1991) 888.
33. K. DHANALAKSHMI and R. SARASWATHI, *J. Mat. Sci.* **36** (2001) 4114.

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