

Synthesis and characterization of poly(*o*-methoxy aniline) and its copolymer for electrochromic device energy applications

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Poly(*o*-methoxy aromatic amine) and its copolymer PTSA-doped poly(3-ABSA-co-OMAA) were synthesized by both chemical oxidation as well as electrochemical method in the presence of external dopant *p*-toluenesulfonic acid (PTSA). The synthesis of the homopolymer and copolymer poly(3-ABSA-co-OMAA) was confirmed by FT-IR spectroscopy. The growth of the electrochemically synthesized samples has been investigated by cyclic voltammogram and chronoamperometry studies for their applications to the electrochromic devices. Both the samples show switching behaviour. The electrochromic switching stability of both devices has been calculated from switching times between their oxidized and reduced states. It has been observed that ECDs based on *o*-methoxy aromatic amines are promising candidates for electrochromic devices.

Keywords: *o*-methoxy aniline, Electrochromic devices, Chronoamperometry

1 Introduction

Polymer equipment has gained great research interests due to their exclusive characteristics which have created possible applications like corrosion protection, rechargeable batteries, antistatic materials, catalysis, textile industry, electrochromic materials and some other applications. Several conducting polymers, e.g. polythiophene, polypyrrol and polyaniline display interesting photoelectronic properties. Graeff *et al.*¹ produced field effect transistors (FET) from simply processable thin films of poly(*o*-methoxyaniline). For electrochromic devices applications, poly(aromatic amine) (PAA) was found to be suitable material however, Paoli and co-worker have shown that poly(*o*-methoxyaniline) (POMA) is a promising candidate for the application in electrochromic devices^{2,3}. The purpose of the use of copolymers is to improve the optical, mechanical, and electrochemical properties with respect to those of the close relative conducting polymeric materials. Different copolymers, poly(pyrrole-thiophene), poly(pyrrole-*N*-methyl pyrrole), copoly(3-thiophenes), poly(aniline-co-ortho-ethoxyaniline), poly(aniline-ortho-anisidine), etc. have been prepared either by chemical or electrochemical polymerization techniques⁴⁻¹⁰. An electrochromic material is one where a reversible colour change takes place upon

oxidation (loss of electrons) or reduction^{11,12} (gain of electrons). In other words, the presentation of the device is governed by how in minimum time maximum oxidation or reduction potential is achieved. Commercial applications of electrochromic materials in the devices include electrochromic strips as battery state-of-charge indicators, anti-glare car rear-view mirrors and electrochromic sunglasses^{13,14,17}.

The poly(*o*-methoxyaniline) POMA and its copolymer poly(OMA-co-ABSA) were synthesized by electrochemical and chemical oxidation polymerization method, have been reported in the present paper. The chemical oxidation of poly(OMA-co-ABSA) with *m*-aminobenzenesulfonic acid was carried out in the presence of external dopant *p*-toluenesulfonic acid. The synthesis of the POMA and copolymer poly(OMA-co-ABSA) was confirmed by FT-IR, UV-Vis, spectroscopy. The electrochemically synthesized polymer and copolymer have been characterized by analyzing the growth of the copolymers by cyclic voltammogram and chronoamperometry studies for their applications to the electrochromic devices. The electrochromic properties of the polymer films have been investigated. The chronoamperometry results of POMA show the switching behaviour. The

electrochromic switching stability of the devices has been estimated from switching times between their oxidized and reduced states and indicate that ECDs based on *o*-methoxy aniline are promising candidates for electrochromic devices.

2 Experimental Details

2.1 Electrochemical polymerization

The 3-aminobenzenesulfonic acid and *o*-methoxyaniline were used as monomers. The *p*-toluenesulfonic acid (PTSA) was used as a synthesizing medium. Aqueous solutions were prepared from the double distilled water having a specific resistivity of 1.0 M Ω -cm.

The copolymerization of 3-aminobenzenesulfonic acid with 0.1 M *o*-methoxyaniline in 0.2 M *p*-toluenesulphonic acid (PTSA) was carried out at 1V by electrochemical polymerization technique. Electropolymerization, cyclic voltametry and chronoamperometry investigations were carried out using Autolab30, Potentiostat/Galvanostat, Netherlands. Silver chloride was used as a reference electrode, the working and the counter electrodes were platinum foils. Cyclic potential sweep technique was used and the potentials were swept continuously in the range of -0.2 V to + 0.80 V at various scan rates of 5, 10, 20, 50 and 100 mV/s. Peak potential values of the corresponding copolymers were recorded in PTSA.

2.2 Chemical polymerization

In the case of POMA 3-aminobenzene sulfonic acid with *o*-ethoxyaniline was taken in ratio of 2:1. In case of poly(3-ABSA-co-OMA), the molar ratio of 3-ABSA and (*o*-methoxyaniline) was 1:1. The copolymer was synthesized with PTSA. The concentration of PTSA was 0.2 M. Polymerization was initiated by the drop wise addition of ammonium persulphate solution (0.1 M, (NH₄)₂S₂O₈ in distilled water). The polymerization was carried out at a temperature of 0°C for a period of 6 h. The synthesized POMA and poly(3-ABSA-co-OMA) were isolated from reaction mixture by filtration and washed with distilled water to remove oxidant and oligomers. Copolymers were collected by filtration followed by drying under vacuum oven at 50°C. The surface morphology of the prepared films was investigated by scanning electron microscope model (ZeissEVOMA-10). The SEM samples have been prepared by dispersing the powder in iso-propanol using sonification and placing small drops of the

suspension on silicon wafers. The FT-IR of both samples were recorded on (nicolet 5700 FTIR) in KBr pellets in the range 400-4000 cm⁻¹. The UV-Vis spectra were recorded in DMSO solution.

3 Results and Discussion

The FTIR spectra of polymer (POMA) and copolymer poly(3-ABSA-co-OMA) are shown in Fig. 1. The IR spectra of POMA display intense bands at 1574 and 1505 cm⁻¹, which are assigned to the ring stretching vibrations of the quinoid and benzenoid ring, respectively. In case of poly(3-ABSA-co-OMA) copolymer, these bands are shifted to higher wave numbers, 1621 and 1506 cm⁻¹, respectively. The other bands which were present on POMA was observed at around 1036, 1114 and 1236 cm⁻¹. These bands can be assigned to the symmetrical stretching of -SO₃ group, asymmetrical stretching of -SO₃ group and C-N stretching of aromatic amine, respectively. Also, for the case of poly(3-ABSA-co-OMA) these bands are shifted at higher wave numbers, 1036, 1125, and 1240 cm⁻¹, respectively. A band at 985 cm⁻¹ is assigned to the ring-breathing mode of the quinoid group, which becomes active on rotation. The NH₂ wagging of the protonated group is found at 693 cm⁻¹. For poly(3-ABSA-co-OMA), these bands are shifted at the wave numbers 1002 and 688 cm⁻¹, respectively¹⁵.

Figure 2 shows the SEM image of the prepared poly(OMA). The particle size estimated from Scanning Electron Micrography (SEM) is around 200 nm. Figure 3 shows the Uv-vis spectra of POMA and poly(3-ABSA-co-OMA) taken in DMSO solutions. Two major bands located at 280 and 630 nm with a mark shoulder at ~332 nm have been observed².

The polymer films were grown electrochemically (Fig. 4) on the platinum electrode (working) in an

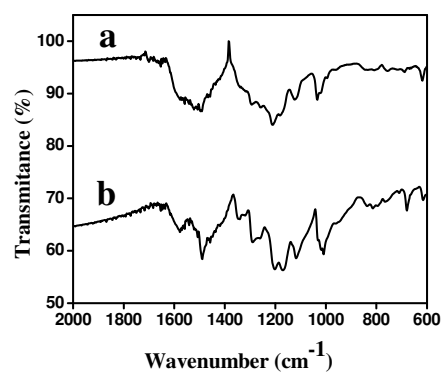


Fig. 1 — FT-IR spectra of (a) self-doped poly(3-ABSA-co-OMA) (b) PTSA-doped poly(3-ABSA-co-OMA)

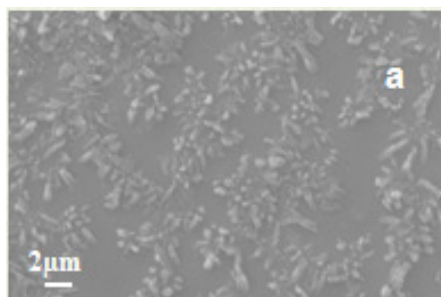


Fig. 2 — SEM image of poly(3-ABSA-co-OEA)

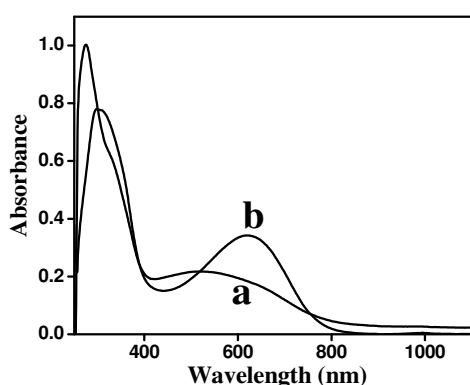


Fig. 3 — UV-vis of self-doped (a) poly(3-ABSA-co-OEA) (b) and PTSA-doped poly(3-ABSA-co-OEA)

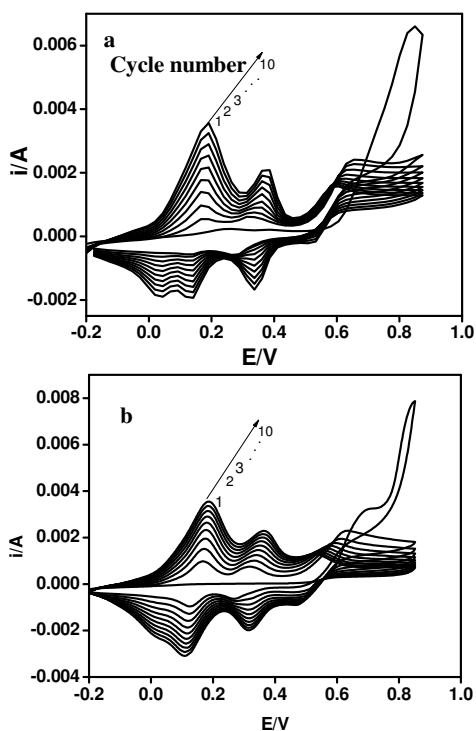


Fig. 4 — Electrochemical growth in PTSA medium (a) poly(OMA) (b) poly(3-ABSA-co-OEA)

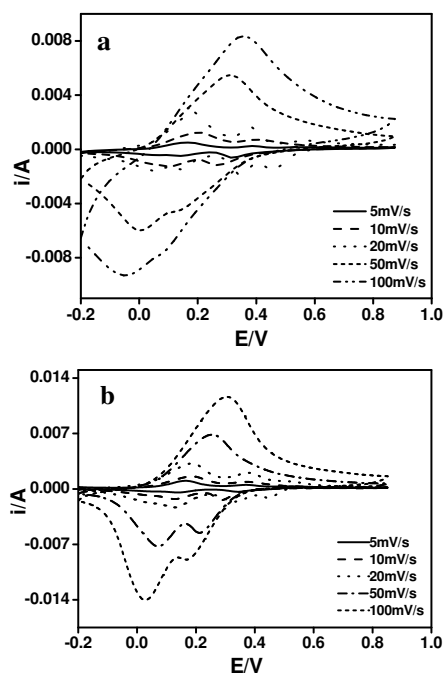


Fig. 5 — Cyclic voltammetric of (a) poly(OMA) (b) poly(3-ABSA-co-OEA)

aqueous PTSA medium at room temperature using cyclic potential sweep techniques. Peak potential values of the corresponding polymer and the copolymer were recorded in p-toluenesulfonic acid medium. In electrochemical copolymerization growth of POMA in Fig. 4(a), and the electrochemical polymerization growth of poly(3-ABSA-co-OEA) in Fig. 4(b) the current values of each oxidation and reduction peaks are greater than that of a previous cycle which indicate the built up of an electroactive polymeric material on the platinum electrode. Cyclic voltammetry is a highly successful method that qualitatively reveals the reversibility of electron transfer during electrochemical polymerization and also examines the electrical activity of copolymer films by monitoring the oxidation and reduction in the form of a current-potential diagram (cyclic voltammogram, CV). To investigate the electrochemical polymerization behaviour of the POMA and the effect on the copolymerization process¹⁶, the CV for POMA and poly(3-ABSA-co-OEA) films were obtained by potential sweeping in a blank 0.2 M PTSA medium. Figure 5(a) shows the first peak value of at (0.263) V for POMA and Fig. 5(b) shows two main redox couples at +0.258 (peak I) and +0.377V (peak II) for poly(3-ABSA-co-OEA) at scan rate 20 mV/s. The electrochemical activities of POMA and its

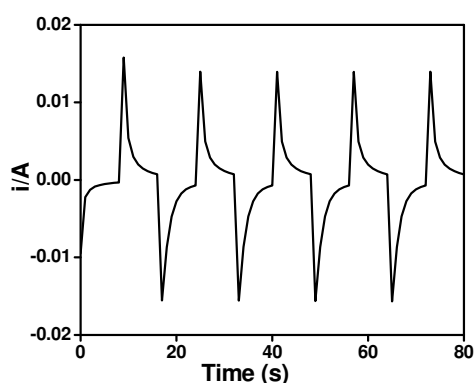


Fig. 6 — Chronoamperometry of poly(OMA)

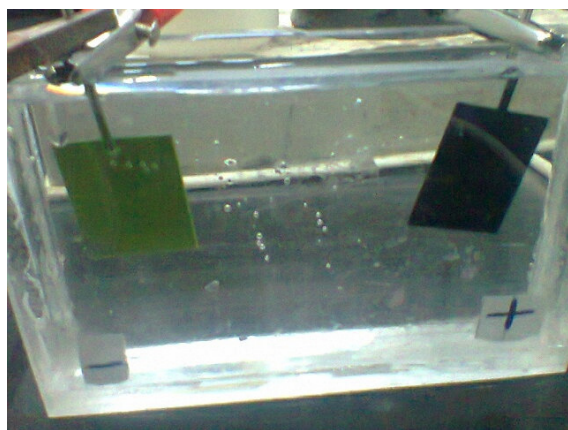


Fig. 7 — Electrochromic devices of poly(OMA)

copolymers describe the configuration of radical cations near peak I, which are consequently oxidized in the imines near peak II. The first peak is assigned to the transformations of leucoemeraldine to emeraldine salt and the second peak is assigned to the transition from emeraldine salt to the pernigraniline state. Figure 6 shows the chronoamperometry results of POMA, where in the response time observed ongoing from oxidized state to reduce state is found to be 6 s and shows quite reversible behaviour on cycling from anodic potential to reduction potential.

The rate of coloration is influenced by the ease of oxidation to its maximum state. The electrochromic devices (ECDs) were constructed as shown in Fig. 7.

4 Conclusions

The particle size estimated from Scanning Electron Microscope (SEM) is around 200 nm. The electrochromic switching stability of the devices was estimated from switching times between their oxidized and reduced states, and indicate that ECDs based on, *o*-methoxy aniline are promising candidates for electrochromic devices.

References

- 1 Graeff C F O, Onmori R K, Guimar F E G & Faria R M, *Synthetic Metal*, 105 (1999) 151.
- 2 Saharan R, Kaur A & Dhawan S K, *J Appl Electrochem*, 42 (2012) 225.
- 3 Gazotti W A, Jannini M J D M, Cordoba de Torresi S I & De Paoli M A, *J Electroanalytical Chem*, 193 (1997) 440.
- 4 Kraljic Rokovic M & Duic L, *Electrochimica Acta*, 51 (2006) 6045.
- 5 Kanazawa K K, Diaz A F, Diaz M F, Krounbi M T & Street G B, *Synthetic Metal*, 4 (1981) 119.
- 6 Esenbaumer R L, Jen K Y & Oboodi R, *Synthetic Metal*, 15 (1986) 169.
- 7 Mattoso L H C, Paterno L G, Campana S P & Oliveira O N J *Synthetic Metal* 84 (1997) 123.
- 8 Choi H J, Kim J W & To K, *Polymer* 40 (1999) 2163.
- 9 Kuwabata S, Ito S & Yoneyama H, *J Electrochemical Society*, 135 (1988) 1691.
- 10 Ram M K, Paddeu S, Carrara S, Maccioni E & Nicolini C, *Langmuir*, 13 (1997) 2760.
- 11 Paddeu S, Ram M K, Carrara S & Nicolini C, *Nanotechnology*, 9 (1998) 228.
- 12 Bamfield P, *Royal Society of Chem*, Cambridge, (2001).
- 13 Mortimer R J, Dyer A L & Reynolds J R, *Displays*, 2 (2006) 27.
- 14 Rosseinsky D R & Mortimer R J, *Advance Mater*, 13 (2001) 783.
- 15 Dhawan S K & Trived D C, *J Appl Polymer Sci*, 56 (1995) 815.
- 16 Bhandari H, Sathiyaranayan S, Choudhary V & Dhawan S K, *J Appl Polymer Sci*, 111 (2009) 2328.
- 17 Zhang L, Lang Q & Shi Z, *American J Analytical Chem*, 1 (2010) 102.