

Poly(aniline-co-*m*-aminobenzoic acid) deposited on poly(vinyl alcohol): Synthesis and characterization

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Abstract. In this work, we have deposited poly(aniline-co-*m*-aminobenzoic acid) on poly(vinyl alcohol) (PVA) by *in situ* polymerization. The polymerization was effected within maleic acid (MA) cross-linked PVA hydrogel. The copolymer was obtained by oxidative polymerization of aniline hydrochloride and *m*-aminobenzoic acid using ammonium persulfate as an oxidant. Instead of conventional solution polymerization, here synthesis was carried out on APS soaked MA cross-linked PVA (MA–PVA) film where the polymer was *in situ* deposited in its conducting form. The composite film was characterized by Fourier transform infra red (FT–IR) and ultraviolet visible (UV–VIS) spectroscopy and electrical measurements. Surface morphology of the composite films was studied by field emission scanning electron microscopy (FESEM). The variation of conductivity of the films was studied.

Keywords. Polyaniline; *m*-aminobenzoic acid; copolymer; self doping.

1. Introduction

The presence of carboxylic acid groups as ring substituents along the polyaniline (PANI) chain results in self doping of PANI and influence properties such as solubility, pH dependent redox activity, conductivity, thermal stability, etc. Polyanilines with carboxylic acid substituents are typically synthesized by chemical and electrochemical polymerization of the monomer in the form of homomer or comonomer with aniline (Freund and Deore 2007). Copolymers of aniline and aminobenzoic acids have been synthesized by chemical (Yan *et al* 1996) and electrochemical routes (Karyakin *et al* 1994; Thiemann and Brett 2001). Chan *et al* (1992) first prepared the homopolymer of anthranilic acid by chemical polymerization in order to improve the solubility of PANI, to study the self-doping mechanism and to evaluate thermal properties. Nguyen and Diaz (1995) prepared poly(aniline-co-*o*-anthranilic acid) copolymers following a similar procedure to that of Chan *et al* (1992) with some differences in monomer, oxidant and acid concentrations. The differences were a monomer oxidant ratio of 1.5 instead of 1.0, 1.2 M HCl instead of 1.0 M and extensive washing of the product instead of washing with a small amount of HCl. Copolymers prepared with these differences were reported to be soluble in aqueous alkaline as well as in organic solvents. Salavagione *et al* (2004) prepared copolymers by changing the position of carboxylic acid substituent on the aniline ring. Chemically polymerized poly(aniline-co-2-aminobenzoic acid) and poly(aniline-co-3-aminobenzoic acid) showed a difference in their properties such as specific charge and fluorescence behaviour, due

to the different reactivities of 2- and 3-aminobenzoic acid during copolymerization. Chemical homopolymerization of poly(*o*-aminobenzoic acid) in a HCl/H₂O/ammonium persulfate (APS) solution at 40 °C has been reported by Wang *et al* (1995). Yamamoto and Taneichi (2000) chemically synthesized the self-doped oligo(2,3-dicarboxyaniline), which exhibits redox activity up to pH 6. The synthesis of poly(4-aminobenzoic acid) catalyzed by horseradish peroxidase in the presence of hydrogen peroxide has been carried out by Alva *et al* (1996). Rao and Sathyanarayana (2002) chemically synthesized copolymers of 2- and 3-aminobenzoic acid with aniline using an inverse emulsion method in the presence of an organic oxidant, benzoyl peroxide. Although the polymers of anthranilic acid, 3- and 4-aminobenzoic acids are effectively nonconducting (Chan *et al* 1992), but the copolymers of aniline and *o*-anthranilic acid are conducting. These polymers of substituted aniline monomer retain the electrochemical and electrochromic properties but have much lower electrical conductivities (10^{-3} – 10^{-7} Scm⁻¹) than the parent PANI (Nguyen and Diaz 1995). The extent of solubility of the copolymers increases with increasing anthranilic acid content. Polyanilines with carboxyl group are also expected to be soluble in an aqueous alkaline solutions. The copolymers of aniline and *o*-anthranilic acid are reported to be soluble in *N*-methyl-2-pyrrolidone and dimethyl sulfoxide when they are in the base form, but not mentioned their solubility in aqueous solution (Chan *et al* 1992).

In this work, the *in situ* synthesis of poly(aniline-co-*m*-aminobenzoic acid) is reported. The polymerization was effected within maleic acid (MA) cross-linked poly(vinyl alcohol) (PVA) hydrogel. The copolymer was obtained by oxidative polymerization of aniline hydrochloride (AnHCl)

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and *m*-aminobenzoic acid (*m*-ABA) using ammonium persulfate (APS) as an oxidant. Instead of conventional solution polymerization, here synthesis was carried out on APS soaked MA cross-linked PVA (MA-PVA) film, where the polymer was *in situ* deposited in its conducting form. The composite of the copolymer with MA-PVA was obtained in the conducting form as a film, which did not require further processing. The composite film was characterized by Fourier transform infrared (FT-IR) and ultraviolet visible (UV-Vis) spectroscopy and electrical measurements. Surface morphology of the composite films was studied by field emission scanning electron microscopy (FESEM). The variation of conductivity of the films with AnHCl/*m*-ABA mole ratio was studied.

2. Experimental

2.1 Materials

Poly(vinyl alcohol) of molecular weight 57000–66000 was purchased from Alfa Aesar, USA. Aniline hydrochloride and maleic anhydride were purchased from LOBA Chemie, India. *m*-aminobenzoic acid was obtained from Spectrochem, India. Ammonium persulfate, hydrochloric acid and sulfuric acid were purchased from E. Merck, India. All the aqueous solutions were prepared in deionized water (18.2 M Ω).

2.2 Synthesis of poly(aniline-co-*m*-aminobenzoic acid) deposited on PVA

The composite of poly (aniline-co-*m*-aminobenzoic acid) with MA-PVA was synthesized by keeping the APS/AnHCl mole ratio as 0.233 and the AnHCl/*m*-ABA mole ratio was varied. Physical parameters for synthesis of the copolymer are presented in table 1. In a typical synthesis, PVA was initially cross-linked with MA. For cross-linking, an aqueous solution of PVA was prepared by dissolving 5 g of PVA in 50 ml of water. 2.25 g of maleic anhydride dissolved in 5 ml of water was added to it followed by the addition of 2 drops of concentrated sulfuric acid. The resultant solution was stirred for 1 h followed by film casting on a flat petri dish. The film was formed through slow evaporation of water by keeping the petri dish with PVA solution containing MA in a covered glass chamber at an ambient temperature. The

evaporated water was expelled from the chamber by maintaining a flow of dust free air for 3 days. Then the air dried film was cured in a vacuum oven (500 mm of Hg) at 60 °C for 2 h to obtain a MA cross-linked PVA (MA-PVA) film through formation of inter-molecular ester bond. The composite film was prepared by soaking of APS in a swollen film of cross-linked PVA, i.e. MA-PVA followed by immersion of the APS soaked MA-PVA in the solution of AnHCl and *m*-ABA of specific concentrations. In an actual preparation, the MA-PVA film was first kept immersed in water for 24 h to remove uncross-linked PVA and MA. The film was then dried by keeping in a covered glass chamber at an ambient temperature for 24 h. A saturated solution of APS was separately prepared by dissolving 8 g APS in 10 ml water. Next, the dry MA-PVA film was immersed in APS solution for a maximum time of 6 h during which the films swelled. The swollen film was then immersed in a solution of 8 g AnHCl and 4 g *m*-ABA in 20 ml of 1 M HCl. The swollen film started darkening immediately after immersion due to the formation of copolymer poly(aniline-co-*m*-aminobenzoic acid). The APS soaked MA-PVA film was kept in the monomer solution for overnight to ensure complete polymerization. The brown-coloured composite film, thus obtained, was washed with distilled water and 1 M HCl to remove the soluble components, followed by washing with deionized water and acetone. The film was dried by keeping in a covered glass chamber at an ambient temperature for 24 h and then heated in a vacuum oven at 60 °C for 2 h. The percentage of the copolymer formed in the composite was calculated by the difference in mass of the cross-linked PVA film before and after copolymerization.

3. Characterization

3.1 FT-IR spectroscopy

ATR-FT-IR spectra were recorded in Thermo Nicolet NEXUS 870 FT-IR spectrophotometer.

3.2 UV-Vis spectroscopy

UV-Vis spectra of the copolymer films were recorded by solid sample holder in a Perkin Elmer Lambda 750 spectrophotometer.

Table 1. Physical parameters and conditions of MA-PVA and PANI-MA-PVA film preparation.

Sample	MA-PVA film		AnHCl/ <i>m</i> -ABA mole ratio	Poly(aniline-co- <i>m</i> -ABA)		Poly(aniline-co- <i>m</i> -ABA) in composite (%)
	Weight (mg)	Thickness (mm)		Weight (mg)	Thickness (mm)	
a	18.46	0.10	0.014	18.85	0.11	2.12
b	19.08	0.10	0.030	20.27	0.12	6.23
c	24.25	0.10	0.090	25.87	0.11	6.66
d	19.48	0.11	0.193	22.32	0.12	14.56
e	24.04	0.12	0.115	27.92	0.14	16.16

3.3 Surface morphology

Surface morphology of the composite films was analysed by FESEM. FESEM measurements were performed in Carl Zeiss Supra 40 scanning electron microscope.

3.4 Electrical conductivity

Conductivity of the composite film samples were measured by four-probe technique using Keithley 2400 Source Meter and Keithley 2000 Digital Multimeter. Four electrical contacts on the film were made using silver paste.

4. Results and discussion

4.1 FT-IR analysis

Figure 1 shows FT-IR spectrum of composite film of the copolymer. FT-IR analysis shows characteristic bands of MA-PVA, PANI and *m*-ABA. The sharp band at 3292 cm^{-1} appears due to overlapping of N-H and O-H stretching vibrations (Dupare *et al* 2008). The band at 2935 cm^{-1} is assigned as an alkyl C-H stretching vibration (Mansur *et al* 2008). The sharp band at 1705 cm^{-1} appears due to C=O stretching of carboxylic acid and aminobenzoic acid. The absorption band at 1639 cm^{-1} arises due to overlapping of C-O stretching of acetate group (Mansur *et al* 2008) and C-C ring stretching of benzenoid ring. A band is observed at 1408 cm^{-1} due to overlapping of CH₂ bending deformation, C-O stretching and O-H in plane bending coupled vibrations (Williams and Fleming 2004; Mohan 2007), and C-N stretching of quinoid ring. The C-C ring stretching of benzenoid ring is red shifted and C-N stretching of quinoid ring is blue-shifted. This occurs possibly because of

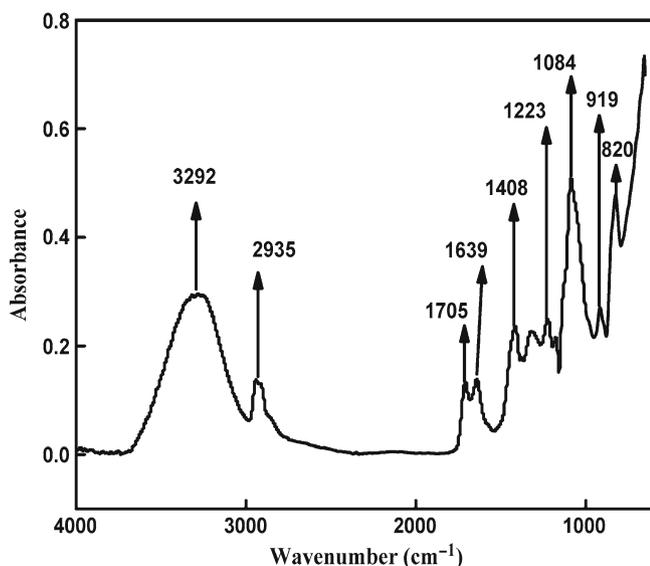


Figure 1. FT-IR spectrum of copolymer film deposited on PVA.

specific alignment in one direction leading to the formation of nanofibrous structure (Bhadra and Sarkar 2007). The band at 1223 cm^{-1} arises due to overlapping of C-O-C stretching of ester and C-N stretching of benzenoid ring (Mohan 2007). The band at 1084 cm^{-1} is assigned to aliphatic C-H in plane bending (Mohan 2007). The bands at 919 and 820 cm^{-1} correspond to aromatic C-H in plane bending and C-H out of plane bending for 1,4-disubstituted benzene ring, respectively (Mohan 2007).

4.2 UV-Vis spectroscopy

Figure 2 shows UV-Vis spectra of the copolymer with varying AnHCl/*m*-ABA mole ratio. The copolymer has shown fairly strong absorptions at 320, 423 and 800 nm. The former peak is ascribed to the π - π^* transition of the benzene rings (Dupare *et al* 2008). The remaining peaks at 411 and 810 nm have been assigned as due to the polaron transitions (Hino *et al* 2006). From the UV-Vis spectrum, it is observed that with decrease in the AnHCl/*m*-ABA mole ratio or in other words, with increasing amount of *m*-ABA in the copolymer films, intensity of the polaron band decreases. Due to the steric effect of -COOH group along the PANI backbone, there is a loss of coplanarity of the π system obstructing charge delocalization along the chains, as a result, formation of the polaron band within the forbidden gap is increased. Hence, the intensity of the polaron band decreases. This also confirms formation of the copolymer (Rao and Sathyanarayana 2002).

4.3 Surface morphology

Surface morphology of the copolymer film deposited on PVA is shown in figure 3. It shows nanofibrous structure which

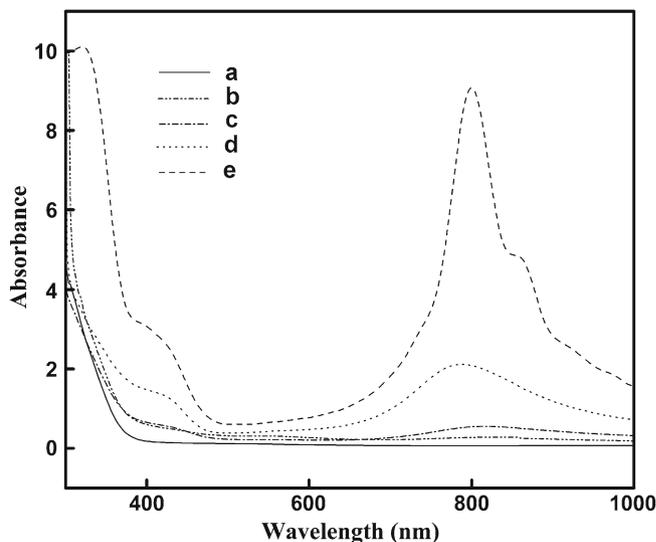


Figure 2. UV-Vis spectra of copolymer with varying AnHCl/*m*-ABA mole ratio.

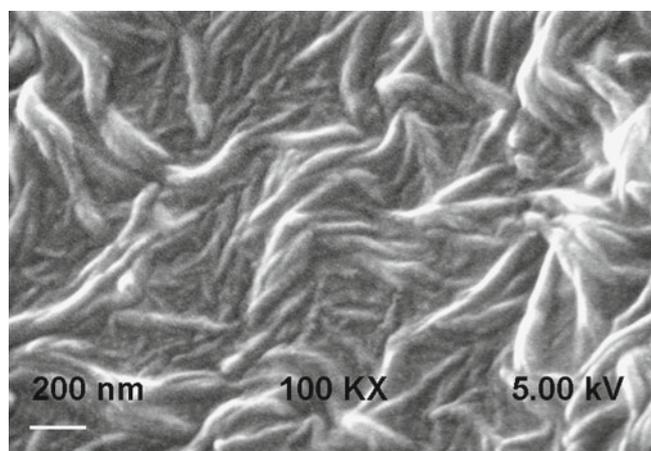


Figure 3. FESEM of copolymer film deposited on PVA.

Table 2. Variation of electrical conductivity of copolymer film with AnHCl/*m*-ABA mole ratio.

AnHCl/ <i>m</i> -ABA mole ratio	Electrical conductivity (Scm ⁻¹)
1.06	1.83×10^{-7}
1.60	1.35×10^{-7}
2.47	1.58×10^{-6}
4.23	2.31×10^{-5}
9.52	3.62×10^{-4}

is obtained due to *in situ* polymerization of the copolymer on swollen PVA gel. The cross-linked PVA film shows clusters of PVA nanostructures as reported in our previous publication (Adhikari and Banerji 2009). When these APS soaked PVA films are immersed in the monomer solution, deposition of PANI occurs with the formation of a nanofibrous structure. Zhang and Wan (2002) obtained nanorods with average diameter of 70–80 nm from nanostructured PANI- β -naphthalene sulfonic acid blend in PVA matrix.

4.4 Electrical conductivity

Electrical conductivity was measured by four-probe method (Stejskal and Gilbert 2002). The conductivity of the copolymers given in table 2 varies over a wide range from 1.83×10^{-7} to 3.62×10^{-4} Scm⁻¹ depending on the AnHCl/*m*-ABA mole ratio. The value of electrical conductivity is found to be very poor compared to the reported copolymer materials. The poor conductivity may be due to the presence of PVA-MA part which is non-conducting. Also, the average thickness of copolymer on PVA-MA hydrogel surface is 0.014–0.115 mm, which may lead to unstable contact between four probes. It is observed that with increasing AnHCl/*m*-ABA mole ratio, conductivity of the copolymer film increases. In other words, with increasing percentage of *m*-ABA in the copolymer, conductivity decreases.

The strong intramolecular interaction between carboxylic acid groups and polaronic nitrogen atoms or hydrogen bonding can give rise to favourable five or six membered chelates, in which the movement of electrons is more localized. Therefore, self doping by carboxylate group is much less effective than external doping by HCl. The steric effect of the carboxylate group due to intermolecular interaction between the carboxylic acid group and hydrogen on the adjacent phenyl is likely to force the aromatic rings out of the plane relative to each other lowering the degree of conjugation. The torsional angle between the aromatic rings may increase in order to relieve steric strain. Evidence for restrictions to π conjugation has been obtained from UV-Vis spectroscopy. This, therefore, implies that some of the nitrogen atoms have been self doped to maintain charge neutrality and self doping by the carboxylate group seems to be very much less effective than the corresponding doping by HCl. The conductivity was found to be dependent on the type of proton involved. Nguyen and Diaz (1995) also observed a decrease in conductivity from 5.2 for polyaniline salt to 10^{-8} Scm⁻¹ for poly(*o*-aminobenzoic acid) as the amount of aminobenzoic acid increased in the copolymer. The decrease in conductivity is attributed to the decrease in the number of charge carriers and conjugation length.

5. Conclusions

In this work, synthesis of poly(aniline-co-*m*-aminobenzoic acid) deposited on PVA is reported. The composites were synthesized varying the amount of *m*-ABA in the composites. The polymer was obtained as a film, hence, by overcoming the problem of insolubility of the doped form of the polymer in common organic solvents. The structures were confirmed by FT-IR spectroscopy. The copolymer formation was confirmed by UV-Vis spectroscopy and electrical measurements. The surface morphology showed a nanofibrous structure. The conductivity of the copolymer films decreased with increasing percentage of *m*-ABA in the composites.

References

- Adhikari S and Banerji P 2009 *Synth. Met.* **159** 2519
- Alva K S, Marx K A, Kumar J and Tripathy S K 1996 *Macromol. Rapid Commun.* **17** 859
- Bhadra J and Sarkar D 2007 *Mater. Lett.* **63** 69
- Chan H S, Ng S C, Sim W S, Tan K L and Tan B T G 1992 *Macromolecules* **25** 6029
- Dupare D B, Ghosh P, Datta K, Aswar A S and Shirsat M D 2008 *Sensors Transducers* **93** 103
- Freund M S and Deore B 2007 *Self-doped conducting polymers* (England: John Wiley & Sons) pp. 123–129
- Hino T, Namiki T and Kuramoto N 2006 *Synth. Met.* **156** 1327
- Karyakin A A, Strakhova A K and Yatsimirsky A K 1994 *J. Electroanal. Chem.* **371** 259

- Mansur H S, Sadahira C M, Souza A N and Mansur A A P 2008 *Mater. Sci. Eng.* **C28** 539
- Mohan J 2007 *Organic spectroscopy principles and applications* (India: Narosa Publishing House) pp. 78–95
- Nguyen M T and Diaz A F 1995 *Macromolecules* **28** 3411
- Rao P S and Sathyanarayana D N 2002 *Polymer* **43** 5051
- Salavagione H J, Acevedo D F, Miras M C, Motheo A J and Barbero C A 2004 *J. Polym. Sci.: Polym. Chem.* **42** 5587
- Stejskal J and Gilbert R G 2002 *Pure Appl. Chem.* **74** 857
- Thiemann C and Brett C M A 2001 *Synth. Met.* **123** 1
- Wang X H, Li J, Wang L X, Jing X B and Wang F S 1995 *Synth. Met.* **69** 147
- Williams D H and Fleming I 2004 *Spectroscopic methods in organic chemistry* (India: Tata McGraw-Hill Publishing Company Limited) Ch. 2, pp. 34–57
- Yamamoto K and Taneichi D 2000 *Macromol. Chem. Phys.* **201** 6
- Yan H, Wang H J, Adisasmito S and Toshima N 1996 *B. Chem. Soc. Jpn* **69** 2395
- Zhang Z and Wan M 2002 *Synth. Met.* **128** 83