



A COMPARATIVE STUDY ON SYNTHESIS, CHARACTERIZATION AND DC ELECTRICAL CONDUCTIVITY OF POLYANILINE AND COPOLYMER OF POLYANILINE WITH *o*-NITROANILINE AND *p*-NITROANILINE

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Abstract: Recently, polyaniline based materials become very promising in various technological applications. Also, the synthesis of pure substituted polyaniline, for example, *o*-nitroaniline and *p*-nitroaniline is challenging as well as hard to find in the literature. Here, we prepared pristine polyaniline and its copolymers with *o*-nitroaniline and *p*-nitroaniline by *in-situ* oxidative method in the presence of different molar ratio of aniline to the *o*-nitroaniline and *p*-nitroaniline. The as-formed materials were successfully characterized by Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and x-ray diffraction (XRD) techniques. The DC electrical conductivity of all the samples was investigated by four-in-line probe technique. The results showed that the polyaniline was major contributor in the electrical conductivity.

Keywords: Polyaniline, Electrical Conductivity, *o*-nitroaniline, *p*-nitroaniline, Stability

1. INTRODUCTION

Nowadays, conducting polymers hold a special and an important position in the field of material science. Previously, Polymers were believed to be electrical insulators and so were their applications as well. But, this perception was challenged with the discovery of electrically conducting polymers during 1970s by MacDiarmid, A.G. Heeger and Hideki Shirakawa. These electrically conducting polymers were called as “synthetic metals” [1-3].

The conducting polymers are perceived as macromolecules which possess the fully conjugated system of alternate single and double bond sequence along the backbone and can acquire a positive or a negative charge by oxidation or reduction process. The presence of extended conjugation in these polymers (conducting polymers) makes them highly susceptible to any chemical/electrochemical, oxidation/reduction processes [3-5]. Therefore, the properties (electrical and optical properties) of these polymers could be precisely tailored by cautiously controlling the oxidation and reduction processes. In most of the cases, the electrical/optical properties exhibited by conducting polymers are reversible in nature. So it is quite possible to systematically regulate these properties with a higher accuracy while switching from a highly electrically conducting state through semiconducting to an electrically insulating state. The two most important requirements for any

material to conduct electricity are (i) presence of charge carriers and (ii) their mobility within the material [6-8]. The electrical conductivity can be given as:

$$\sigma = ne\mu \quad (1)$$

Where: σ = electrical conductivity, n = number of charge carriers, e = electronic charge and μ = mobility of charge carriers.

The polymers with conjugated backbone possess the ability to sustain the charge carriers and to make them mobile along the backbone of conjugated polymer. Therefore, the conducting polymers on oxidation and reduction conduct electricity due to presence of charge carrier on their backbone generated due to their oxidation or reduction. For example, polyacetylene, polythiophene, polypyrrole, poly-phenylene and polyaniline etc. Among the many members of the conducting polymers, polyaniline has attracted special attention due to its easy synthesis, reversible redox chemistry, stability, economical preparation etc. It can be produced as bulk powder, cast films or fibers. It is due to its large availability, low- cost, large- scale production, makes it an ideal candidate for various applications [6-9].

The most commonly used synthesis procedure of polyaniline involves oxidative polymerization of monomer, herein, the polymerization of monomer and doping of the formed polymer occurs concurrently, and may be obtained either by electrochemical method or chemical oxidation method. It is general observation that higher yield is obtained during chemical oxidation methods as compared to that of electrochemical method. Synthesis of polyaniline by chemical oxidative route involves the use of protic acid like HCl, H₂SO₄ in the presence of oxidant (typically, ammonium or potassium peroxydisulfate) in water as reaction medium. The oxidant withdraws a proton from monomer (aniline) molecule, without developing any strong interaction (coordination bond) with the substrate molecule or intermediate species or with the final product. The concentration of oxidant lays important role the process of polymerization as the initial high concentration of a strong oxidant {(NH₄)₂S₂O₈}, during the polymerization reaction favours the fast oxidation of polyaniline and its existence in the oxidized form [1,5,7].

Besides, chemical oxidation polymerization, conducting polymers may also be synthesized via electrochemical polymerization method. During the electrochemical polymerization process, polymerization of a suitable monomer takes place in suitable electrolytic medium. In this method, doped flexible freestanding films of conducting polymers are produced on the surface of the electrode by oxidative coupling. It is in analogy to the electrochemical deposition of metal on a suitable surface. Electrochemically polymerized aniline produces a clean and highly ordered thin film of polyaniline. In this study, we have prepared the pristine polyaniline along with a series of copolymers of aniline:*o*-nitroaniline and aniline:*p*-nitroaniline by oxidative polymerization in 1M HCl solution medium using potassium persulphate as an oxidants [5,6,9].

2. EXPERIMENTAL

2.1 Materials:

Aniline (Merck, India), potassium persulfate (Fisher scientific), hydrochloric acid (Merck, India), *m*-nitro aniline, *p*-nitro aniline, ethanol were used as received. The water used in these experiments was double distilled.

2.2 Preparation of Polyaniline, copolymer of aniline:*o*-nitroaniline and aniline:*p*-nitroaniline

Polyaniline, copolymers of aniline:*o*-nitroaniline and aniline:*p*-nitroaniline) were synthesized by oxidative polymerization in 1M HCl solution medium using potassium persulphate as an oxidants. A series of five samples of aniline:*o*-nitro aniline (**Table 1**) and aniline:*p*-nitro aniline (**Table 2**) have been prepared by varying amount and concentration of monomers.

Nitroaniline with oxidant gave no reaction, so we proceed to prepare co-polymer of (aniline:*o*-nitroaniline) and (aniline:*p*-nitroaniline).

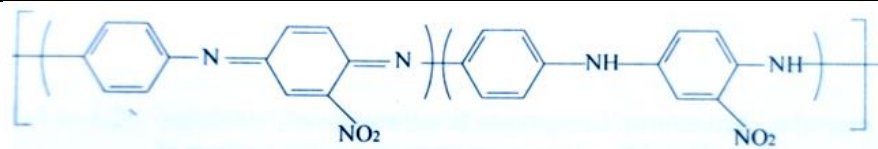


Figure 1. Expected structure of copolymer poly(aniline:*o*-nitroaniline)

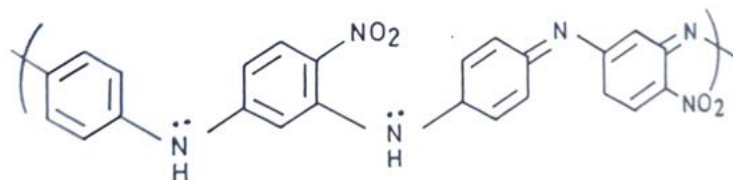


Figure 2. Expected structure of copolymer poly(aniline:*p*-nitroaniline)

Table 1: Details of preparation of co-polymer of aniline and *o*-nitroaniline.

Sample ID	Vol. of aniline (1 M) in mL	Vol. of <i>o</i> -nitro aniline (0.2 M) in mL	K ₂ S ₂ O ₇	Reaction
O-1	0	100	2.7	No
O-2	1	100	2.7	No
O-3	5	100	2.7	No
O-4	10	100	2.7	Yes
O-5	15	100	2.7	Yes
O-6	60	100	2.7	Yes

Table 2: Details of preparation of co-polymer of aniline and *p*-nitroaniline.

Sample ID	Conc. of aniline (100 mL)	Conc. of <i>p</i> -nitro aniline (100 mL)	K ₂ S ₂ O ₇	Aniline: <i>p</i> -nitroaniline	Reaction
P-1	-	0.2M	6.75gm	0 : 1	No
P-2	0.2M	0	6.75gm	1 : 0	Yes
P-3	0.2M	0.05M	6.75gm	4 : 1	Yes
P-4	0.2M	0.1M	6.75gm	2 : 1	Yes
P-5	0.2M	0.15M	6.75gm	4 : 3	Yes
P-6	0.2M	0.2M	6.75gm	1 : 1	Yes

3. CHARACTERIZATION

The prepared samples were characterized by advance analytical techniques, such as FTIR spectra were obtained by using Perkin-Elmer 1725 instrument, SEM micrographs were obtained by JOEL JSM-6480LV and XRD analysis were performed by Bruker D8 Advance, X-ray diffractometer. DC Electrical conductivity was measured using a four in line DC electrical conductivity meter equipped with a temperature controller (PID-200, Scientific Equipments, Roorkee, India).

4. RESULTS AND DISCUSSION

4.1 Fourier Transform Infrared (FTIR) Spectroscopy

FTIR spectra of as synthesized pure polyaniline, copolymer poly(aniline:*o*-nitroaniline) and poly(aniline:*p*-nitroaniline) are presented in Figure 3. The characteristic bands at ~1596 cm⁻¹ & ~1504 cm⁻¹ corresponding to C=C stretching vibration of quinoid and benzenoid rings respectively are present in both the copolymers [6, 7]. The relative intensity of the quinoid band to benzenoid band in the spectra of the samples is the measure of the degree of the oxidation of the polymer chain. There is also a possibility of overlap of bands due to the asymmetric N=O stretch in the region. The peak observed at the ~1305 cm⁻¹ is ascribed to asymmetric N=O stretching vibrations due to NO₂ group. The band at ~1300 cm⁻¹ and ~1245 cm⁻¹ is ascribed to C-N stretching vibration, C-H bending also occurs in this region. The bands due to the C-H out of plane bending modes (1000-1100 cm⁻¹) are also seen in the spectra. The band corresponding to the out of plane bending vibration of C-H bond of *p*-substituted benzene ring can be seen at ~830 cm⁻¹. The sharp band observed at ~1130 cm⁻¹ is due to charge defects. The broad band observed in the region 3300-3400 cm⁻¹ is ascribed to N-H stretching vibrations in polyaniline and copolymers [10,11,12].

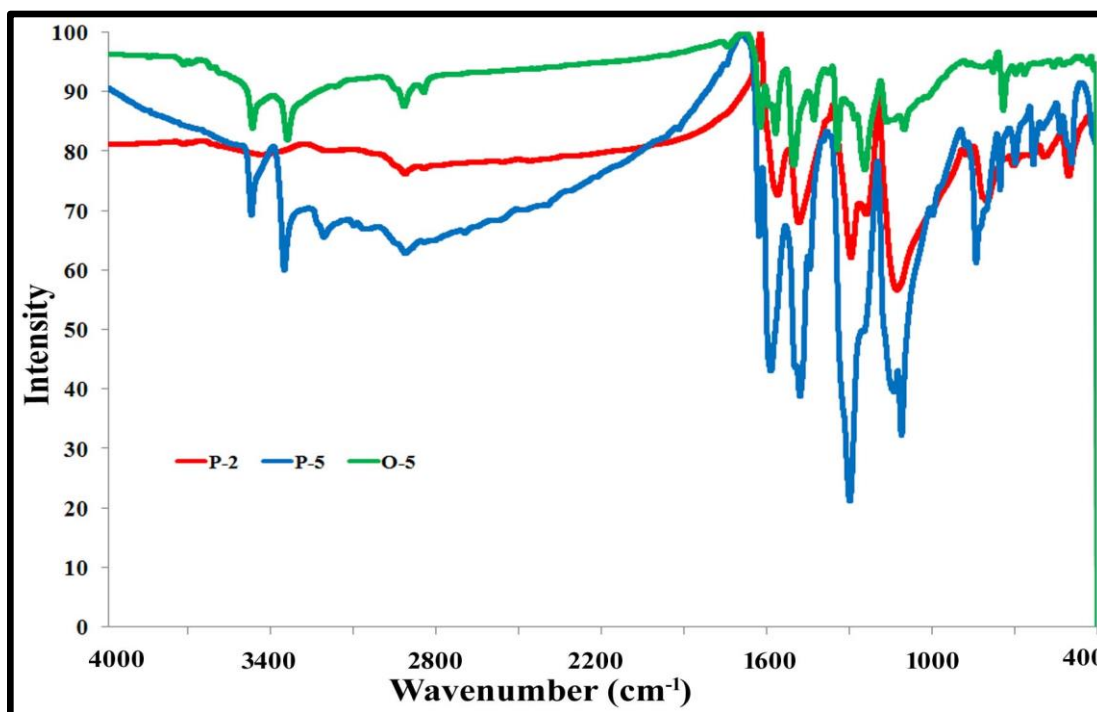


Figure 3. FTIR spectra of samples P-2, P-5 and O-5.

4.2 Scanning Electron Microscopy (SEM)

SEM micrographs of HCl doped polyaniline, poly(aniline:*o*-nitroaniline) (O5) and poly(aniline:*p*-nitroaniline) (P5) is presented in Figure 4. It can be seen from the micrographs that the particles size of the said polymers is close to nanometer range. The particles HCl doped polyaniline are uniformly distributed and flaky in nature (Figure 4a). The SEM micrographs of poly(aniline:*o*-nitroaniline) (O5) (Figure 4b) shows flakes of polymer particles and is also clear from the micrograph that the thickness is in the range of 100 nm while the SEM micrograph (Figure 4c) of poly(aniline:*p*-nitroaniline) (P5) shows particles of uniform size and round in shape and little or no sign of flakes.

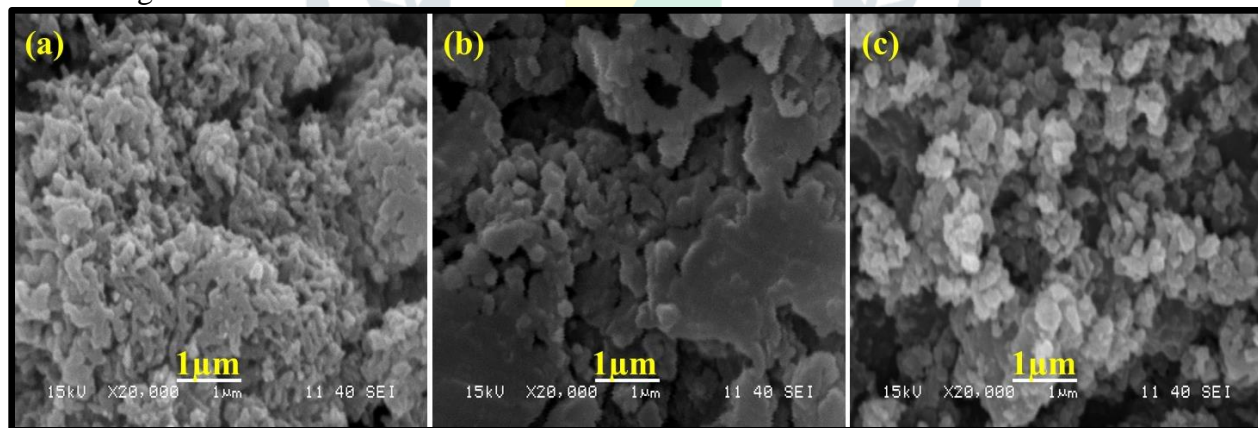


Figure 4. SEM micrographs of: (a) HCl doped polyaniline, (b) poly(aniline:*o*-nitroaniline) (O5) and (c) poly(aniline:*p*-nitroaniline) (P5).

4.3 X-ray Diffraction (XRD) Study

The XRD diffraction patterns of polyaniline, copolymers poly(aniline:*o*-nitroaniline) and poly(aniline:*p*-nitroaniline) are presented in Figure 5. It is clear from the Figure 5 that the sharp peaks of doped polyaniline at $2\theta = 14.8^\circ$, 23° and 27° are present. However, in copolymer (aniline:*o*-nitroaniline) these peaks are less prominent and in (aniline:*p*-nitroaniline) copolymer these peaks have diminished to negligible level. Therefore, it may be inferred from the diffraction patterns of the samples that with the formation of copolymers, the crystallinity of the polyaniline was compromised. This also affected its electrical conductivity as have been discussed above that polyaniline exhibited higher electrical conductivity compared to that of copolymers [10-14].

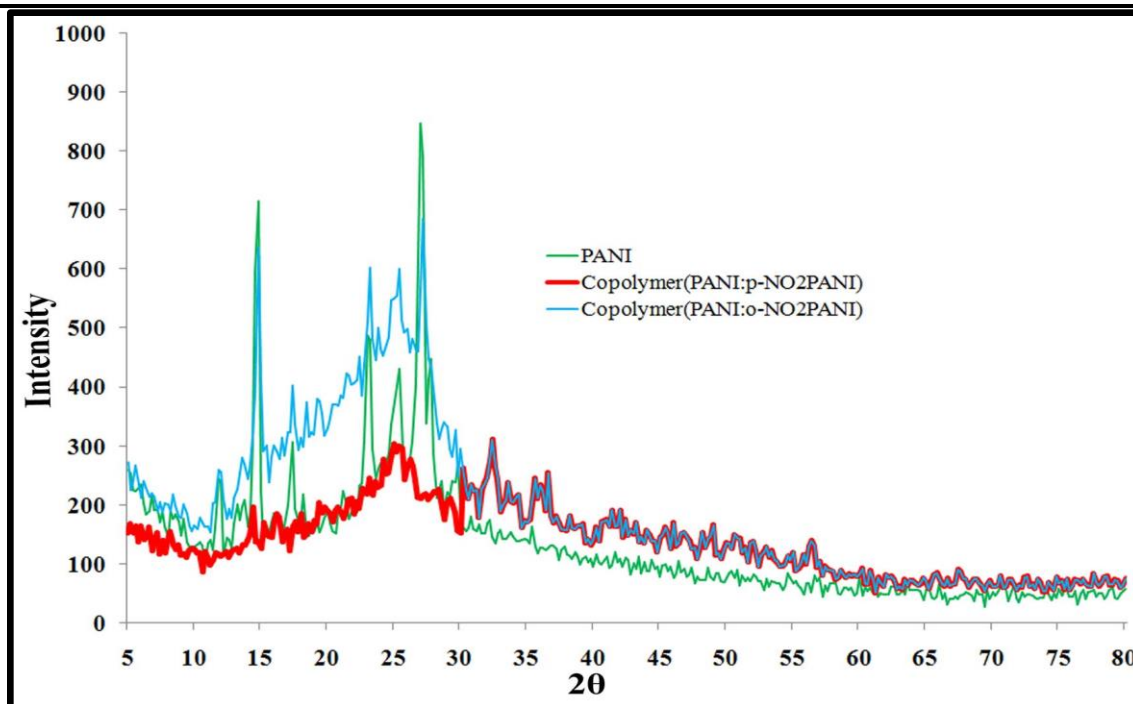


Figure 5. XRD spectra of polyaniline, poly(aniline:*o*-nitroaniline) (O-5) and poly(aniline:*p*-nitroaniline) (P-5).

4.4 Electrical Conductivity Study

DC electrical conductivity of the HCl doped polyaniline, poly(aniline:*o*-nitroaniline), poly(aniline:*p*-nitroaniline) is given in Figure 6. The electrical conductivity of the above samples were measured with increasing temperature (40°C-110°C) using four in line probe conductivity meter. The electrical conductivity was calculated by using following formula:

$$\sigma = \frac{2S}{W} \ln 2 / (V/I) (2\pi S) \quad (2)$$

Where, I, V, W and S are the current (A), voltage (V), thickness of the film (cm) and probe spacing (cm) respectively.

The DC electrical conductivity of the above samples was measured from 40°C-110°C and was found to be in the semiconducting region. All the samples followed the Arrhenius relation for temperature dependence of electrical conductivity as may be seen in Figure 6. It may also be seen Figure 6 that the conductivity of the copolymer is lower than that of pure polyaniline. Therefore, it may be suggested that the polyaniline is the main contributor to the electrical conductivity. It is worth important to mention that the only polyaniline exhibited stable behaviour at maximum temperature of study. In case of poly(aniline:*p*-nitroaniline) the electrical conductivity was found to deviate from the semiconducting characteristic while in case of poly(aniline:*o*-nitroaniline) copolymers the samples start to deviate from 70 °C onwards and no data could be obtained [.

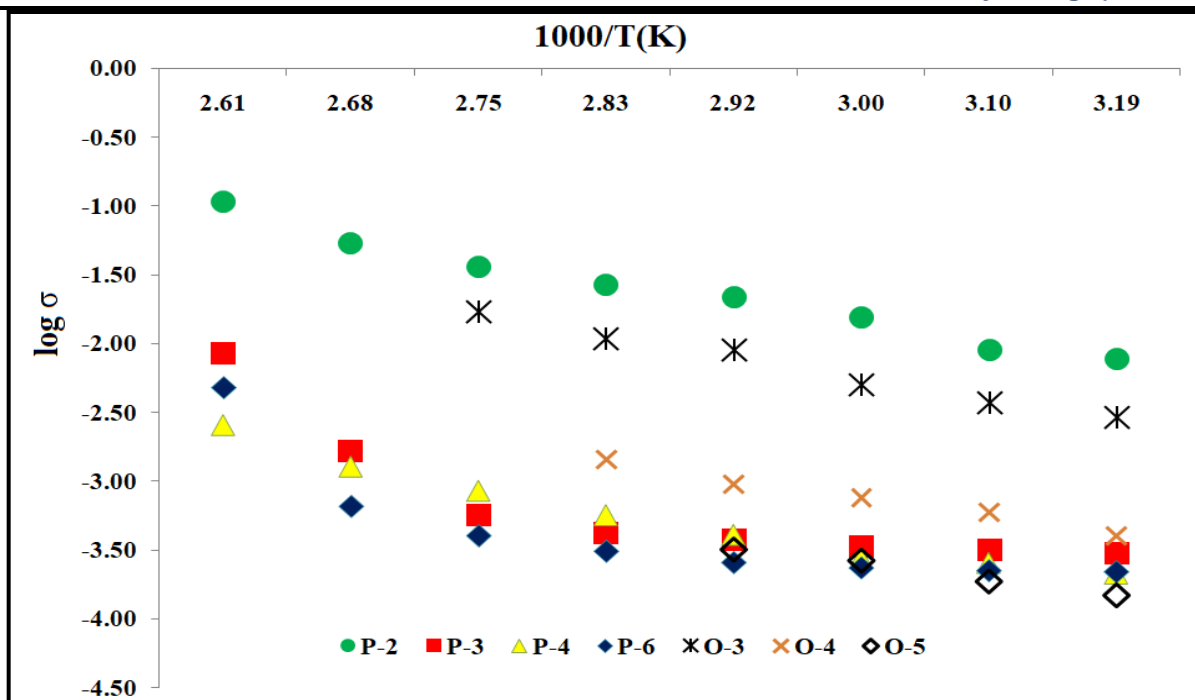


Figure 6. Arrhenius plot of polyaniline (P2), co-polymers poly(aniline:*o*-nitroaniline) (O3, O4, O5), co-polymers poly(aniline:*p*-nitroaniline) (P3, P4 and P6).

5. CONCLUSIONS

The synthesis of pure substituted polyaniline is difficult and hard to find in literature. Herein, we have successfully prepared a series of copolymer of aniline and substituted aniline (*o*-nitroaniline and *p*-nitroaniline) by varying their volume and molar ratio. The successful formation of products was confirmed by various techniques such as FTIR, SEM and XRD. The DC electrical conductivity of all the prepared samples were evaluated by four-in-line probe method. The conductivity of all the samples were found to be in the semiconducting region. The copolymers exhibit not only lower electrical conductivity compared to the pure polyaniline but also lesser stability of electrical conductivity. The SEM study suggested the uniformity in particles size and distribution and the shape varied from round to flakes. The XRD data suggest presence of crystalline and amorphous region in all the samples.

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