

## Chemical Oxidative Polymerization of Aniline with *o*-Ethyl Aniline: Their Molecular Structure, Morphology and Conducting Properties

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A new series of novel poly (aniline-co-*o*-ethyl aniline) copolymer has been synthesized by the chemical oxidative polymerization method in the presence of hydrochloric acid and ammonium persulphate as oxidant. The copolymer is found to be soluble in polar solvents like NMP, DMSO and THF. The copolymer was characterized by various analytical methods such as UV-visible spectroscopy, FTIR spectroscopy, X-ray diffraction and scanning electron microscopy. The electrical conductivity of the copolymer was also studied. UV-visible spectra shows two characteristic peaks of  $\pi$  to  $\pi^*$  transition and  $n$  to  $\pi^*$  transition. The FTIR spectrum shows the characteristic peaks confirming the copolymer. X-ray diffraction pattern shows the characteristic broad peak confirming the amorphous nature of the copolymer. SEM image shows the agglomerated spherical shape of the copolymer particles. The conductivity values are found to be  $1.143 \times 10^{-3}$  S/cm. This new copolymer will find significant applications in the field of organic semiconductor.

**Keywords:** Conducting polymer, Poly (aniline-co-*o*-ethyl aniline) copolymer, Electrical conductivity, Surface morphology.

### INTRODUCTION

Advancements in the organic semiconductor field prompt the researcher to fabricate flexible and low-cost devices with superior properties. The field of conducting polymers has been well established and conducting polymers hold an important position in the field of materials science. They have gained much attention due to its unique structure, morphology, optical and electrical properties. In order to be more useful in the field of organic electronics, a material must possess excellent electronic and mechanical properties and it should be a melt processable with high environmental stability. Among the conjugated polymers, polyaniline plays a vital role due to its desirable electrical, optical, electrochemical properties and excellent environmental stability<sup>1-5</sup>. There are several short-comings when polyaniline is synthesized by the traditional methods including usage of strong acids, high amount of oxidants and poor solubility in common organic solvents. The poor solubility of polyaniline in common organic solvents is due to polymer chain stiffness, inter-chain interactions and cross linking and it limits the application perspectives. In order to overcome this obstacle, functional group substituents have been introduced on the nitrogen atom<sup>6-8</sup> or on *ortho*, *meta* and *para* position of the polymeric chain to inhibit inter-chain interactions and degree of cross linking, resulting in short chain polymers that can increase solubility more easily in organic solvents<sup>9,10</sup>.

In order to increase the solubility, researchers also used functionalized acids such as DBSA, CSA and other acids<sup>11-14</sup>. Recently, polyaniline has been synthesized by emulsion polymerization, reversed emulsion polymerization, ionization radiation and micellar surfactants<sup>15-18</sup>.

One of the effective approaches to increase the solubility of the polymer is the copolymerization of aniline with other substituted aniline derivatives<sup>19</sup>. The copolymers are advantageous over homopolymers because of solubility and with remarkable electrical conductivity by adjusting the monomer and the comonomer concentration in the feed. The combination of different monomeric units with different ratios in the identical structure provides a fine modulation of the properties of the materials<sup>20</sup>. Aniline has been copolymerized with *o*-toluidine to increase the processability and it can be used as an antistatic spray coating on an insulating surface to dissipate the electrostatic charge<sup>21</sup>. Huang *et al.*<sup>22</sup> reported that the copolymer showed lower decomposition temperature, but larger char yield at 900 °C and higher activation energy of decomposition in nitrogen than air. Copolymers of aniline and *o*-anisidine showed a good electrochromic effect than polyaniline for practical applications<sup>23</sup>. Aniline has been copolymerized with *o*-chloroaniline by the pulse potentiostatic method and its various parameters were studied<sup>24</sup>. Our research group reported the studies of poly(aniline-co-*m*-aminoacetophenone) copolymer synthesis in a controlled dimension

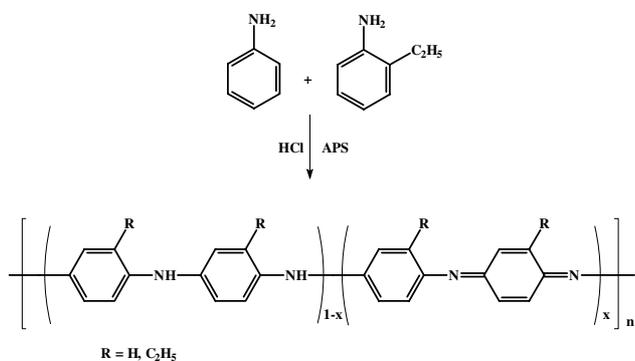
and aniline has also been copolymerized with 4-fluoroaniline and found to be more soluble than polyaniline with remarkable conductivity<sup>25,26</sup>.

In this work we provide a detail report on the synthesis of poly(aniline-co-*o*-ethyl aniline) copolymer poly(An-co-*o*-EAn), its UV absorption, morphology and electrical properties were investigated.

## EXPERIMENTAL

Aniline (Ranken India) was purified by vacuum distillation method. *o*-Ethyl aniline was purchased from Hi media (India). Ammonium peroxydisulfate and HCl were purchased from E-Merck (India). The solvents NMP, DMSO and DMF were purchased from Hi Media and used as such. Double distilled water was used for the synthesis.

**Synthesis of copolymer:** The synthesis procedure for poly(aniline-co-*o*-ethyl aniline) copolymer as follows. 0.05 M (0.466 g) aniline and 0.05 M (0.6509 g) of *o*-ethyl aniline monomers were dissolved in 100 mL of 1 M hydrochloric acid solution. 0.1 M (2.28 g) of ammonium persulfate solution was added drop wise to the monomer mixture. The temperature of the mixture was maintained between 0 and 5 °C. A green coloured precipitate was obtained and it was filtered with Whatman filter paper. The precipitate was washed with acetone and distilled water till the filtrate was colourless and dried in vacuum oven at 40 °C for 6 h. The obtained copolymer was 3:3 equal ratios of aniline and *o*-ethyl aniline respectively. A similar procedure has been carried out to prepare 3:2 and 3:1 ratio also (**Scheme-I**).



**Scheme-I:** Poly(An-co-*o*-EAn)

The UV-visible spectra were recorded using ELICO SL-218 double beam spectrophotometer. FT-IR transmittance spectrum is recorded using SHIMADZU 8400S in the region of 4000-400  $\text{cm}^{-1}$  using KBr pellets. The surface morphology of the copolymer was analyzed by scanning electron microscopy (HR-SEM) HITACHI-SU 6600L instrument operating at 20 kV. X-ray diffraction pattern of the sample was recorded by Philips X'pert Pro X-ray diffractometer with Nickel filtered  $\text{CuK}\alpha$  radiation ( $\lambda = 1.5402 \text{ \AA}$ ) operating at 40 kV. The analysis was performed in the diffraction angle  $2\theta$  from 10 to 80° at a rate of 10°/min. The samples were pelletized to a diameter of 13 mm using a vacuum press at 12 MPa. The electrical conductivity of the pelletized samples was measured using digital Keithley 6517B electrometer at room temperature.

## RESULTS AND DISCUSSION

**Solubility:** Solubility test is the most important parameter that determines the application of the copolymer. The copolymer was dissolved in various polar solvents such as NMP, DMSO, DMF and THF. The copolymer material is found to be readily soluble in all the polar solvents. The increase in the solubility of the copolymer is due to the plasticizing nature of the solvent that decreases the stiffness of the copolymer and inhibits the inter-chain interactions and decreases the degree of cross linking of the polymer chain<sup>27</sup>.

**UV-visible spectra:** Fig. 1 shows the absorption spectra of poly(aniline-co-*o*-ethyl aniline) copolymer. The absorption spectra were recorded by dissolving the copolymer in dimethyl sulfoxide solvent. The absorption peaks at 327, 322 and 326 nm are attributed to  $\pi$ - $\pi^*$  transition that takes place within benzenoid segment for 3:1, 3:2 and 3:3 ratio of aniline and *o*-ethyl aniline respectively. The peak values at 622 and 617 nm correspond to excitonic transition between highest occupied molecular orbital of the benzenoid ring and the lowest unoccupied molecular orbital in the quinoid ring. The hypsochromic shift is observed for equal monomer ratio (3:3 ratio) and it may be attributed to the reflection of the difference in the extension of  $\pi$  conjugation<sup>28</sup>. There is a new peak at 448 nm which may correspond to the polaron to  $\pi^*$  transition formation in the copolymer which is responsible for the electrical conductivity of the copolymer. There is a small shoulder peak around 850 nm attributing the bipolaron peak in the higher wavelength region.

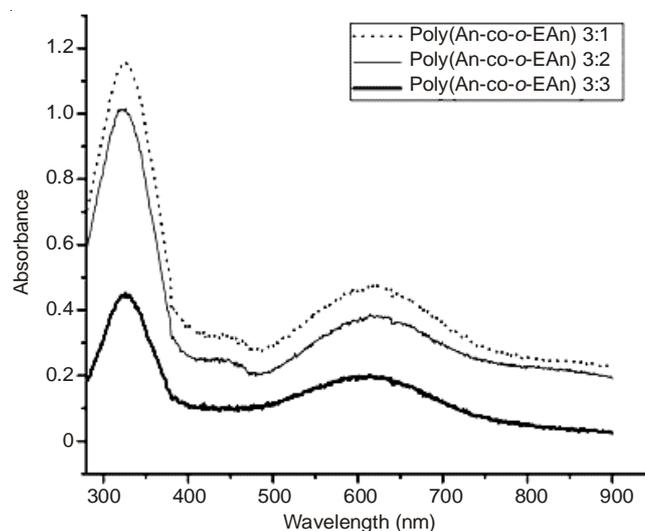
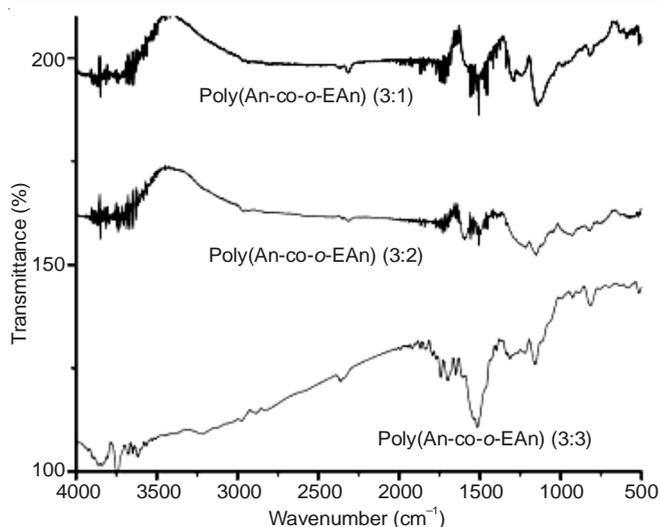


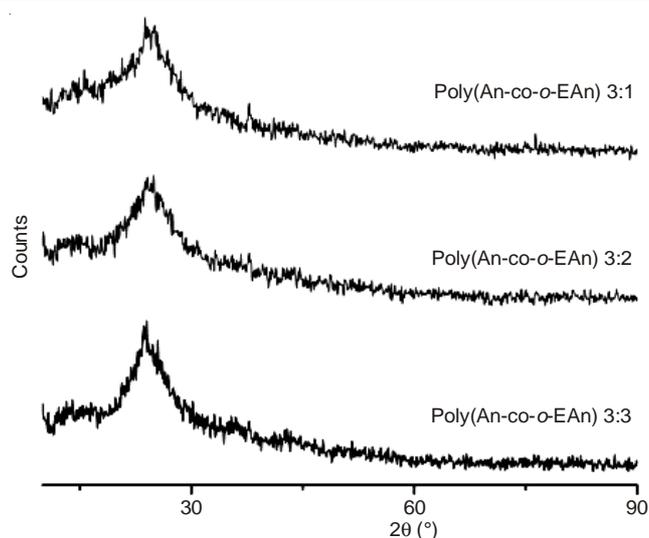
Fig. 1. UV-visible absorption spectra of poly(An-co-*o*-EAn)

**FTIR spectra:** Fig. 2 shows the FT-IR spectra of the copolymers. The characteristic bands appear at 2926, 1604, 1512, 1296, 1157, 817  $\text{cm}^{-1}$ . The peak at 2926  $\text{cm}^{-1}$  confirms the presence of  $\text{CH}_2$  stretching in ethyl group. The intensity of the absorption peak increases as the concentration of ethyl aniline increases in the feed ratio. The peak at 1604  $\text{cm}^{-1}$  corresponds to the  $\text{C}=\text{C}$  in quinoid rings and 1512  $\text{cm}^{-1}$  corresponds to  $\text{C}=\text{C}$  stretching in the benzenoid ring of the copolymer. The characteristic peak at 1157  $\text{cm}^{-1}$  is due to the charge delocalization in the copolymer backbone<sup>29</sup>. The peak

Fig. 2. FT-IR spectra of poly(An-co-*o*-EAn)

at  $817\text{ cm}^{-1}$  attributes C-H out of plane bending and head-to-tail coupling in the phenyl ring of the copolymer (Table-1). The short intensity peak at  $1840\text{ cm}^{-1}$  indicates the ethyl group is attached to *ortho* position.

**X-ray diffraction:** Fig. 3 shows the X-ray diffraction pattern of poly(aniline-co-*o*-ethyl aniline) copolymer. It shows a broad peak at  $24^\circ$  due to the presence of benzenoid and quinoid rings of the copolymer<sup>30</sup>. This amorphous nature of the copolymer is due to the irregular arrangement of the polymer chain. As the comonomer concentration increases, the peak is turning narrow implying that the copolymer gets crystallized. In the amorphous polymer having a regular arrangement of its polymer chains, the intermolecular force of attraction may be increased further and the presence of bulky side group or complex nature that makes molecules less amorphous. In this case, however, it can be partially crystalline and partially amorphous. When

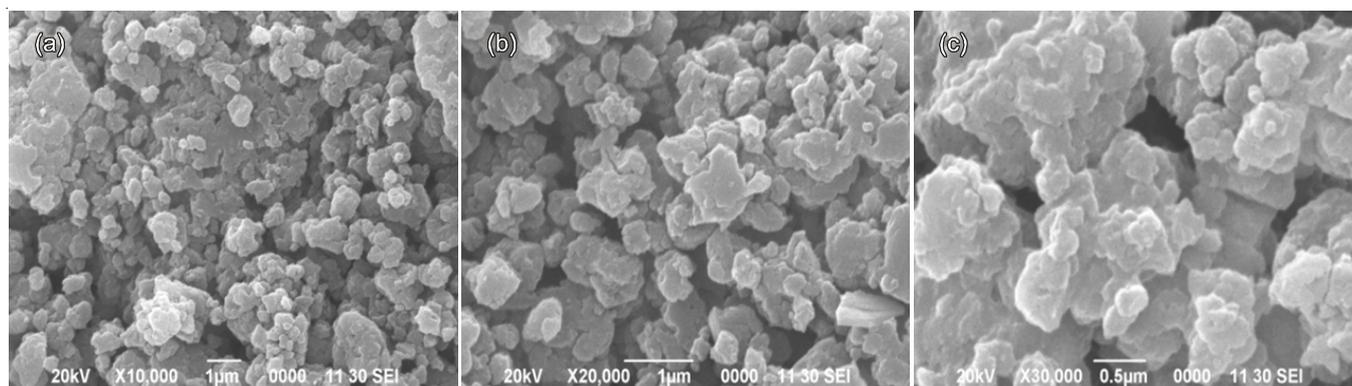
Fig. 3. XRD pattern of poly(An-co-*o*-EAn)

the comonomer concentration increases, it increases the crystalline domain, flexibility and plasticizing nature.

**Surface morphology:** Fig. 4 shows the scanning electron microscope image of poly(An-co-*o*-EAn) copolymer. Here the polymers are agglomerated to form a granular and fragment like structure and the size of granules are found to be 200 nm to 300 nm. The formation of granules is due to the high concentration of nucleates. A nucleate with phenazine unit and high oxidation potential under acidic condition results in the formation of supramolecular structures. These nucleates randomly agglomerate in the continuous phase, which is known as stacking. The aggregation of nucleates starts the growth of granule by propagation of polymer chains and coiling of the polymer chain takes place continuously to form small spherical granulated structures. These spherical granules overlapped in a narrow fashion to give nano pillar like morphology with

TABLE-1  
FTIR SPECTRA ( $\text{cm}^{-1}$ ) OF POLY(An-co-*o*-EAn)

Band assignments	Poly(An-co- <i>o</i> -EAn): 3:1	Poly(An-co- <i>o</i> -EAn): 3:2	Poly(An-co- <i>o</i> -EAn): 3:3
CH <sub>2</sub> stretching vibration	2926	2962	2977
Quinoid unit	1556	1591	1604
Benzenoid unit	1506	1504	1512
C-N stretching vibration of polar on units	1287	1337	1311
Charge delocalization in the copolymer	1138	1151	1157
Para coupled phenyl ring	821	823	817

Fig. 4a-c. SEM images of poly(An-co-*o*-EAn) 3:3

inter-particular porous spacing between them<sup>31</sup>. The hydrophobic nucleates adsorb the copolymer granules as droplets and generate new granules at the surface of the former and it results in highly organized granular clusters or networks of fine globular particles that are aligned radially.

**Conductivity:** The electrical conductivity of the copolymer was measured at room temperature and the values are tabulated in the Table-2. The conductivity of the copolymer is found to be  $1.143 \times 10^{-3}$  S/cm. The conductivity in the copolymer is due to delocalization of the charge transfer between the polaron units and the  $\pi$  conjugated electrons in the polymer chain. These polarons are formed by charge injecting on the polymer chain. Polaron formation produces new localized electronic states in the forbidden energy gap. Further addition of the comonomer concentration, the conductivity decreases to  $6.39 \times 10^{-5}$  S/cm<sup>32</sup> and this may be due to increase in ethyl group may decrease the delocalization of electrons in the polymer chain and ethyl group may hinder the charge transfer process.

TABLE-2  
CONDUCTIVITY VALUES OF POLY(An-co-*o*-EAn)

Polymer	Conductivity (S/cm)
Polyaniline	$1.98 \times 10^{-2}$
Poly(An-co- <i>o</i> -EAn) 3:1	$1.143 \times 10^{-3}$
Poly(An-co- <i>o</i> -EAn) 3:2	$4.79 \times 10^{-5}$
Poly(An-co- <i>o</i> -EAn) 3:3	$6.39 \times 10^{-5}$

## Conclusion

Poly(aniline-co-*o*-ethyl aniline) copolymer has been successfully synthesized through chemical oxidative polymerization. The copolymer shows better solubility than polyaniline in common organic solvents. FT-IR results confirm the formation of copolymer. UV spectrum shows a blue shift in the absorption peak indicating difference in the extension of  $\pi$  conjugation. X-ray diffraction patterns show the amorphous nature of the copolymer. Scanning electron microscope shows granular and layered morphology that are aligned radially. The electrical conductivity of the copolymer shows remarkable values with high solubility.

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