Study of dc Electrical Conductivity, Magnetic Susceptibility and Thermal Behavior of Pyrrole Aniline Copolymer

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Abstract: Chemical copolymerization of pyrrole and aniline has been carried out by taking the monomers in equimolar proportion. The structural analysis of the copolymer was done with the help of FTIR, WAXD and SEM techniques, the results confirm the formation of new material involving both pyrrole and aniline units. The dc electrical conductivity of the copolymer has been recorded up to 673k using two probe method. The log σ Vs 1/T plot shows the transition of the sample from metallic to semi conducting behavior and vice versa, at a particular temperature. The magnetic susceptibility was recorded at magnetic field of 0.1KG in the temperature range 313-507 K by using Guoy’s method. The Thermal behavior of the copolymer was studied using DTA-TGA revealing variation in the Tg of copolymer when compared to homopolymers.

Key Words: Copolymer, Electrical Conductivity, Susceptibility, Pyrrole.

1. Introduction
The search of improved materials for applications like rechargeable batteries, corrosion protection, and electrochromic display devices, sensors, electromagnetic radiation shielders and many more [1-3] has stimulated the studies of related homopolymers and copolymers. Copolymerization serves as a tool for the synthesis of polyfunctional macromolecules with specific composition, properties, and structure thereby offering a technique to polymerize those monomers that do not polymerize independently [4]. Hence this chemical heterogeneity achieved by simultaneous polymerization of two entirely different monomers in the same reaction mixture is of substantial importance regarding the influence of complexation on the chain formation and propagation. Thus in the present work copolymer of pyrrole and aniline have been copolymerized chemically. Its structural characterization was done by using FTIR, WAXD and SEM. The dc electrical conductivity was recorded at various temperatures using two probe method at a field of 27 V/cm and is reported here. Further the magnetic susceptibility of the copolymer has been recorded by using Guoy’s method. The thermal response of the sample was studied using DTA-TGA and the Tg values have been presented herewith.

2. Experimental
Aniline (SRL Mumbai) and Pyrrole (SRL Mumbai) were purified by distillation process before use. Also sulphuric acid (Qualigen, Mumbai) was used to generate acidic medium and anhydrous FeCl3 (SRL Mumbai) was used as an initiator for copolymerization. In the present work the copolymerization has been carried out chemically by taking the monomers in equimolar proportion. For this pyrrole and aniline (1 mole each) were mixed together and stirred for about 15 minutes. About 30ml of 0.5M H2So4 was added to the reaction mixture and the solution was stirred till it became clear. Finally 0.25M of anhydrous FeCl3 was added to this and the whole reaction mixture was stirred for about one hour, continuously at room temperature i.e. 30°C. The reaction mixture was then allowed to polymerize for a period of 24 hrs. The reaction mixture was then filtered and the precipitate was washed with distilled water and acetone alternately, to remove the impurities. The precipitate was then dried at room temperature and was further studied. The precipitate was then further dried and was further studied.
2.1 Infrared Spectroscopy: This copolymer was then subjected to Fourier Transform Infrared Spectroscopy (FTIR). The transmission spectrum was recorded in the wavenumber region 400-4000 cm⁻¹ by using a Schimadzu IR spectrometer (FTIR-8101A).

2.2 Wide Angle X-ray Diffraction: The X-Ray diffraction pattern of the prepared copolymer was recorded using PANAnalytical X-Ray B.V. model PW 1710 unit. The X-Ray beam was CuKa radiation from a sealed tube. The specimen sample in the form of powder was fixed on the rotating stage of the diffractometer and was then scanned in the reflection mode over a range of 2θ from 5° to 40°.

2.3 Scanning Electron Microscopy: The scanning electron microscopy was utilized for the morphological investigation of the prepared copolymer sample. The scanning was carried out with the help of Scanning Electron Microscope JEOL 6380 A for various magnifications.

2.4 Measurement of dc Electrical Conductivity: The dc electrical conductivity of the sample was measured using two probe method. The conductivity was recorded within the temperature range 313 K to 673 K at a field of 27 V/cm. All the measurements were done with the help of KEITHLY 6514 system ELECTROMETER. The heating rate was maintained constant throughout the measurement i.e. 5°C per minute.

2.5 Measurement of Magnetic Susceptibility: The magnetic susceptibility of the sample was measured with the help of Guoy’s Method. The measurement was done in the temperature range of 313-507K.

2.6 Thermal Analysis: The sample was further investigated for its thermal properties. The DTA-TGA spectrum was recorded by using THERMOGRAVIMETRIC/DIFFERENTIAL THERMAL ANALYZER (PERKIN ELMER DIAMOND TG/DTA) in the temperature range of 305 – 873K.

3. Results and Discussion

In order to ensure that during synthesis copolymer is formed and not mixtures of two homopolymers (polyaniline and polypyrrole) solubility test was carried out. Polyaniline and polypyrrole are both completely insoluble in DMF (Dimethyl Formamide) and DMSO (Dimethyl Sulphoxide); whereas the synthesized material is soluble to a good extent in both these solvents. Also the IR spectrum of the copolymer was compared with that of the physical mixtures of polypyrrole and polyaniline in 1:1 proportion (by weight). The bands obtained in both these cases are quite different from each other. Hence it can be said that copolymer has been formed.

The FTIR spectroscopy was used to identify the structure of synthesized copolymer. The IR spectra for copolymer has been shown in figure I. From figure it can be observed the charge delocalization peak appearing at 1114 cm⁻¹ in PANI [4-5] is shifted to 1118 cm⁻¹ in the copolymer. Also the N-H stretching peak appearing at 1706 cm⁻¹ in PANI is shifted to 1743 cm⁻¹ in copolymer. The C-N stretching band appearing at 1302 and 1385 cm⁻¹ in PANI [6-7] and 1250 and 1290 cm⁻¹ in PPy [8] have totally disappeared from the spectrum of copolymer. Likewise the benzenoid and quinoid peak appearing at 1493 cm⁻¹ and 1599 cm⁻¹ for PANI [5, 9] have been vanished from the copolymer spectrum. Similarly the band due to ring stretching vibrations of PPy unit appearing at 1451 cm⁻¹ has been disappeared from the copolymer spectrum. However altogether new bands have been observed in IR spectrum of copolymer at 462cm⁻¹, 1020cm⁻¹, 1411cm⁻¹, 1618cm⁻¹, 2804 cm⁻¹ and 2924 cm⁻¹. The subsequent shifts as well as appearance of new IR bands in the copolymer can be thought as a result of the hetero association between monomer units. Also due to subsequent attachment of new side groups, the nature of the bond/bond lengths as well as vibrational frequency associated with it are
altered. Hence disappearance or shifting of bands can be associated with the interaction between permanent and temporary charges, developed during the co polymerization leading to the polar effects.

Figure I: FTIR spectra of the copolymer. Figure II: SEM image of the copolymer. Figure III: log $\sigma$ Vs 1/T plot of the copolymer.

The X-ray diffraction peaks for PANI, Copolymer and PPy have been tabulated in table I. Further the diffraction peaks of copolymer do not match at all with those of the pure homopolymers indicating that there are structural changes taking place due to copolymerization process. Thus some new material is getting synthesized whose geometrical structure is entirely different from that of the homopolymers. The Scanning electron micrograph of copolymer is shown in figure II. When compared with the electron micrographs of parent polymers it has been noticed that the PANI exhibits lamellar structure whereas PPy shows globules [10]. However the copolymer shows agglomerated spheres of approximate 10-20 $\mu$m diameter which are dispersed in the matrix. It has been noticed copolymer feed affects the morphology of the copolymer. Also copolymer shows more irregular, disordered spherical agglomerates.

| PANI  | Copolymer | PPy  |
|-------|-----------|------|
| 9.5   | 10.2      | 23.6 |
| 14.7  | 22.5      | 25.8 |
| 20.4  | 24.2      |      |
| 25.1  | 27.4      |      |
|       | 32.8      | 35.7 |

Table I: X-ray diffraction peaks of PANI, copolymer and PPy.

The log $\sigma$ Vs 1/T plot for the copolymer is shown in figure III. It is observed that the sample shows a transition from semi conducting to metallic behavior at a certain temperature and vice versa above this transition temperature. The electrical conductivity of copolymer was found to be 1.70105 X 10^{-08} S/cm. As the primary copolymer chain comprises of monomer units of pyrrole and aniline; the charge carriers associated with these units can propagate only upto certain common sequences of either polymer. As soon as the hetero junction is achieved the energy of the charge carriers becomes insufficient for crossing the junction. Thus charge carriers get trapped or their motion is hindered due to the presence of second monomer unit. Hence the conjugation does not remain uniform over the entire polymer chain and overall reduction in the conductivity is observed. Further the steric effects arising due to the attachment of bulky substituents provide torsional twists in the copolymer backbone, reducing the co planarity and average electron delocalization length, and the conductivity [12-13]. Further the magnetic susceptibility measurements have been carried out to investigate the nature of charge carriers dominating the conduction process. The susceptibility versus temperature curve shows diamagnetic nature of the sample indicating spinless bipolarons as majority charge carriers.
4. Conclusion

Copolymer of pyrrole and aniline has been synthesized by using chemical oxidative copolymerization method in equimolar proportion at room temperature. The structural characterization of the prepared copolymer was carried out with the help of FTIR, WAXD and SEM techniques. The results show the formation of new material with modified bands, new IR bands and geometrical structure. The electron micrographs show agglomerated spheres distributed in the matrix. The dc electrical conductivity was found to be $1.70 \times 10^{-8} \text{S/cm}$ which has been reduced to greater extent when compared with that of the parent polymers. The magnetic susceptibility shows diamagnetic nature of the sample. The thermal property is improved as compared to parent polymers with two $T_g$ values.

5. References

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