

Electrical Conductivity and Dielectric Properties of Self Doped Copolymer: Poly (aniline-co-N-methylaniline)

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ABSTRACT: Aniline has been copolymerized in the presence of substituted aniline as comonomer to prepared conducting copolymer of poly(aniline-co-N-methylaniline) type via the chemical oxidation polymerization route. The conductivity of copolymer is slightly less than pure polyaniline but processability has been improved significantly. Conduction mechanism has been found to be 3D-VRH in case of pure HCl-doped polyaniline and 1D-VRH for copolymer. The room temperature conductivities of doped polyaniline and poly(aniline-co-N-methylaniline) are found to be 6.550×10^{-2} and 3.885×10^{-5} S Cm^{-1} respectively. The increase in activation energy of copolymer is noticed that it would be a conducting material. The temperature dependence of dielectric constant and conductivity suggests that copolymer is 1D-disordered state composed of 3D-metallic crystalline region and 1D-localized amorphous region.

KEYWORDS: Polyaniline, Poly(N-methylaniline), Copolymer, Conductivity, Dielectric properties.

I. INTRODUCTION

Conducting polymers such as polyacetylene, polypyrrole etc., have been subjects numerous investigations in the past two decades. These materials have properties that make them suitable for several applications in sensor, biosensor, rechargeable batteries, molecular electronic devices, corrosion inhibitors electromagnetic shielding materials etc. In general, conducting polymers are a special class of organic polymers that have alternate single-double bond conjugation and can conduct electricity. Among all the conducting polymers polyaniline (PANI) demonstrates outstanding properties due to its environmental stability, redox reversibility, high electrical conductivity and ease of synthesis which drives it towards potential electrical device applications[1-5]. PANI can be doped to highly conducting stable by protonic acids or by electrochemical oxidation show moderate conductivity upon doping with protonic acids and have excellent stability under ambient conditions. The main issue with polyaniline is processing difficulties due to its infusibility and relative insolubility in common organic solvents. It can be made processable/soluble either by polymerizing functionalized anilines[6,7] or by copolymerizing aniline with substituted monomers[8-11]. Electronic properties of these synthetic metals can be tailored by carrying out the polymerization under the controlled conditions and in the presence of specific dopants.

In the present study, the copolymerization of aniline in presence of N-methylaniline as comonomer to prepare conducting copolymer of poly(aniline-co-N-methylaniline) type via the chemical oxidative polymerization route has been reported. The copolymer was characterized by the various techniques like UV-Visible spectroscopy and FTIR and their electronic conductivity has been measured by two- probe technique, where resistivity and conductivity varies with temperature.

II. MATERIALS AND METHODS

Materials: Aniline, N-methylaniline were purified by distillation. Ammonium peroxodisulphate and all other solvents were used as purchased.

Synthesis of Polymers and Copolymer: The doped polyaniline, substituted polyaniline and their processable copolymer was chemically prepared by free radical oxidative polymerization route. The concentration of both of aniline and substituted aniline was 0.1M and that of HCl was 1.0 M for the copolymer, aniline and substituted aniline were

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mixed in the mole ratio 60 : 40 polymerization was initiated by the drop wise addition of ammonium peroxodisulphate 0.1M (NH₄)₂S₂O₈ in 100 ml H₂O). The polymerization was carried out at a temperature of 0-4⁰C and over a period of 4-6 hrs. Then the doped polymer powder was obtained by the process of precipitation, filtration, rinsing and drying, successively. The above synthesized powder was treated with 0.1M aqueous ammonia and stirred for 2 hours to obtain their base (undoped) forms.

Measurements: FTIR spectra were recorded on Shimadzu FTIR-8101A spectrophotometer. UV-Visible spectra were recorded on Shimadzu UV-1601. Temperature dependent DC conductivity measurements were carried out with the samples in the temperature range from 30 to 140⁰C. The resistance was measured on DC resistance bridge LCR meter 923. The conductivity value was calculated from the measured resistance and sample dimensions.

III. RESULTS & DISCUSSION

Polymerization mechanism: The Polymerization of aniline and copolymer proceeds via a typical free radical oxidative polymerization route. The main steps are involved in the process are :

Initiation: Initiation was effected by (NH₄)₂S₂O₈ (APS), which generates the free radicals. These under the proper pH conditions react with aniline monomer to form radical cations. However, the radical cations are resonance stabilized and can be represented by various canonical forms[12].

Propagation: Propagation step involves the addition of radical cations to oligomeric species to form polymeric chains. Each radical cation has two active sites that may be attributed to the increased electron density at ortho and para positions of benzene ring. However, coupling of radicals depends upon several factors including reaction medium, temperature, pH and presence of bulky substituents. Therefore, due to the steric hindrance offered by the - NH₂ group, ortho coupling has almost been excluded leading to the formation of para product. However some ortho coupling[13] also occurs leading to the formation of corrupted polymer. Chain growth continued till it is arrested either by chain transfer or by coupling of radicals. Low temperature favours the formation of long chains (high molecular weights) due to the retardation of the rate of termination and chain transfer reactions.

Termination: Termination occurs due to the exclusion of radicals either due to coupling or by disproportionation reaction.

The copolymerization is a powerful method to improve processability of conducting polymers. In general solubility of substituted polyanilines in organic solvents is significantly higher than pure polyaniline. However, their thermal stability and electronic conductivities are substantially lower than doped polyaniline. In order to maintain balance between conductivity, stability and processability copolymerization has been done. However, the relative proportions of aniline and substituted aniline in the copolymers determine exact properties.

FTIR Spectra: The FTIR spectra of copolymer was obtained. The vibrational peak at 1587 cm⁻¹ assigned to the stretch of the quinoid ring and a peak at 1485 cm⁻¹ assigned to the stretch of the benzenoid ring. The stretching peak of N-H appeared in the range 3500-3100 cm⁻¹. In the spectra of the salt form copolymer, absorption peak at 1260 cm⁻¹ and 1490 cm⁻¹, indicates the existence of the methyl group on the benzene ring.

UV- Visible absorption spectra: The absorption band of copolymer was recorded in NMP DMF and DMSO solvents. There are two peaks in the UV -Visible range one around 310 nm is due to π-π* transition (band gap) and is directly related to the extent of conjugation. The other peak 610 nm is due to the molecular excitation associated with the quinone-diimine structure[14], i.e transition between HOMO orbitals of benzenoid rings and LUMO orbitals of the quinoid rings. The UV- visible data reveals that π-π* band in copolymer shifts to the lower wavelength (hypsochromic shift) which can be attributed to the addition of more side groups which alters the torsional angle and leads to the lower conjugation lengths. The degree of hypsochromic shift is directly related to the size of the substituent.

Conductivity: The temperature dependence of electrical conductivity of copolymer was estimated in the range of applicability of Arrhenius type equation

$$\sigma_{(T)} = \sigma_0 [\exp^{-E_a/2kT}] \quad (1)$$

and the measured values were plotted semilogarithmically as a function of reciprocal of temperature (Fig.1). The conductivity increases exponentially with temperature. Also tried to fit the appropriate model for the variation of conductivity of material with temperature. For the above model considered that sample follows the VRH model. In the VRH regime, temperature dependence of conductivity (σ) follows the generalized relation.

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$$\sigma = \sigma_0 [\exp^{-(T_0/T)^{1/r}}] \quad (2)$$

Where T_0 is the Mott characteristics temperature and is a measure of the hopping barrier. The σ_0 is the conductivity at infinite temperature. Their values are determined by density of states, localization length and average hopping distance. The value of r is related to the dimensionality (d) of the system as $r=(d+1)$. For the one, two and three-dimensional systems, d is equal to the 1, 2 and 3 respectively and corresponding values of r are 2, 3 and 4 respectively.

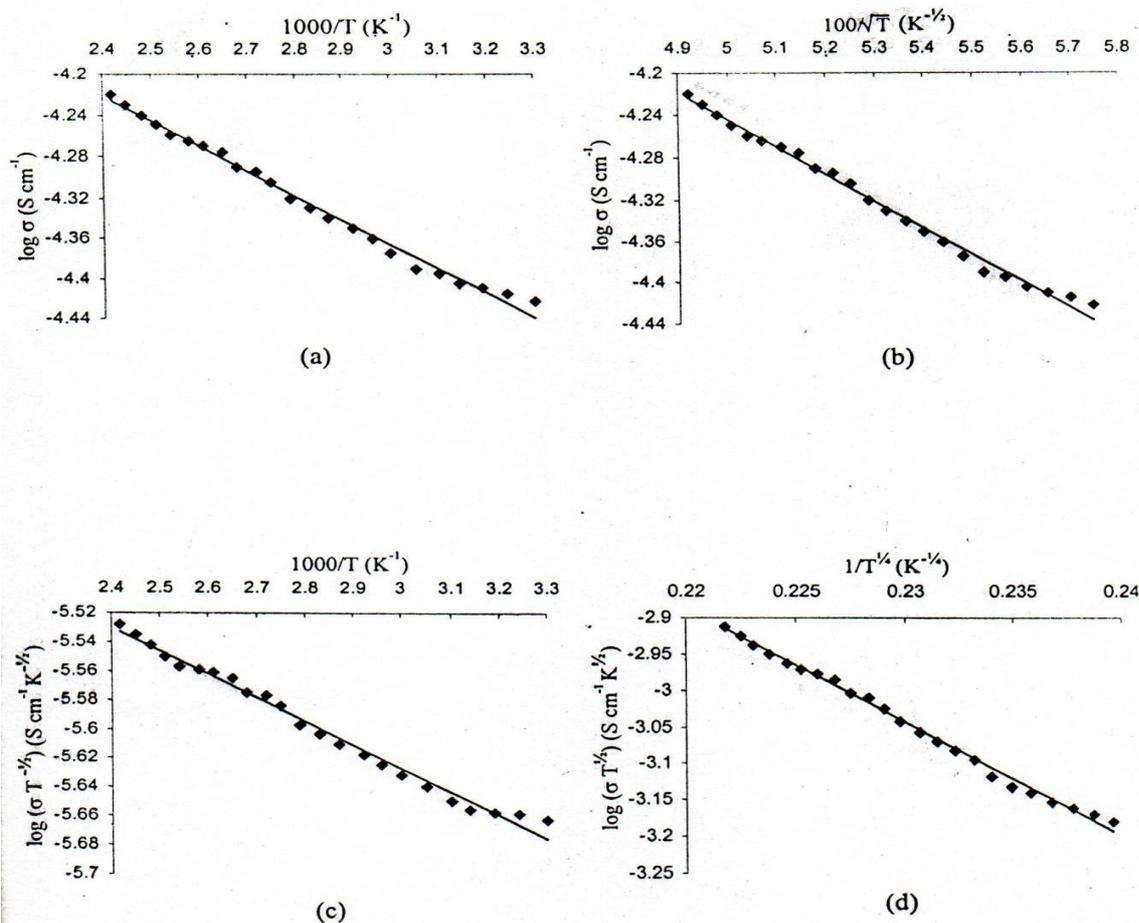


Fig.1 Electrical conductivity plots of poly(aniline-co-N-methylaniline)

(a) Band Theory (b) Tunneling Conduction
(c) Grain Boundary (d) Hopping Mechanism

The temperature dependence of electrical conductivity (Fig.1 (b)) for copolymer, which suggests that the charge conduction is 1D-VRH between nearest neighbouring chains[15]. In case of HCl doped polyaniline Cl^{-1} ions are small and the interchain separation is small, resulting in appreciable coupling interaction between the chains. Thus, charge carriers could easily hop from one chain to other to give of 3D-VRH conduction[16]. However in the case of copolymer although the charge carriers hop between granular particles as 3D-VRH but interchain hopping has been strongly inhibited leading to 1D-VRH.

The temperature dependence of electrical conductivity indicates that the observed semiconducting nature is due to only small fraction of delocalized carriers. Using equation (1) activation energies are determined for samples (Table1). These

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activation energy values suggested that the hopping conduction is the prominent conducting mechanism in these types of systems. Hopping mechanism requires low activation energy with higher dielectric permittivity. Due to this E_a , electrical conductivity is expected to be weakly temperature dependent around 300 K [17]. The conductivity of copolymer increased with increase in temperature. The conductivity and activation energy of PANI, PNMANI and PANI-co-PNMANI are reported in Table 1.

Table1: Conductivity and Activation energy of PANI, PNMANI and PANI-co-PNMANI

Polymer/Copolymer	Conductivity($S\ cm^{-1}$, 303K)	Activation Energy (E_a , eV)
PANI	6.550×10^{-2}	0.047
PNMANI	1.340×10^{-5}	0.202
PANI-co-PNMANI	3.885×10^{-5}	0.072

Conductivity data clearly shows that the copolymer is less conducting relative to the polyaniline. The conductivity decreases both due to decrease in conjugation length as well as less doping level achieved.

Dielectric Behaviour: The dielectric constant and dielectric loss of PANI, PNMANI and PANI-co-PNMANI are reported in Table 2.

Table2: Dielectric constant and dielectric loss of PANI, PNMANI and PANI-co-PNMANI at 303 K

Polymer/Copolymer	Dielectric Constant	Dielectric Loss
PANI	6.40×10^3	4.80×10^{-2}
PNMANI	3.30×10^2	2.40×10^{-1}
PANI-co-PNMANI	4.90×10^2	3.10×10^{-1}

From table2 it is observed that the dielectric constant and dielectric loss values of PANI are greater than those of PNMANI and PANI-co-PNMANI. The lower values of dielectric constant and dielectric loss of PNMANI and PANI-co-PNMANI may be due to bulkiness of substituents present on the chain also in copolymer. The dielectric constant and dielectric loss decrease with increase in the content of substituted aniline monomer, also found to be depends on the nature and size of the substituent.

Further the dielectric constant and dielectric loss both increase with temperature as shown in Fig.2.

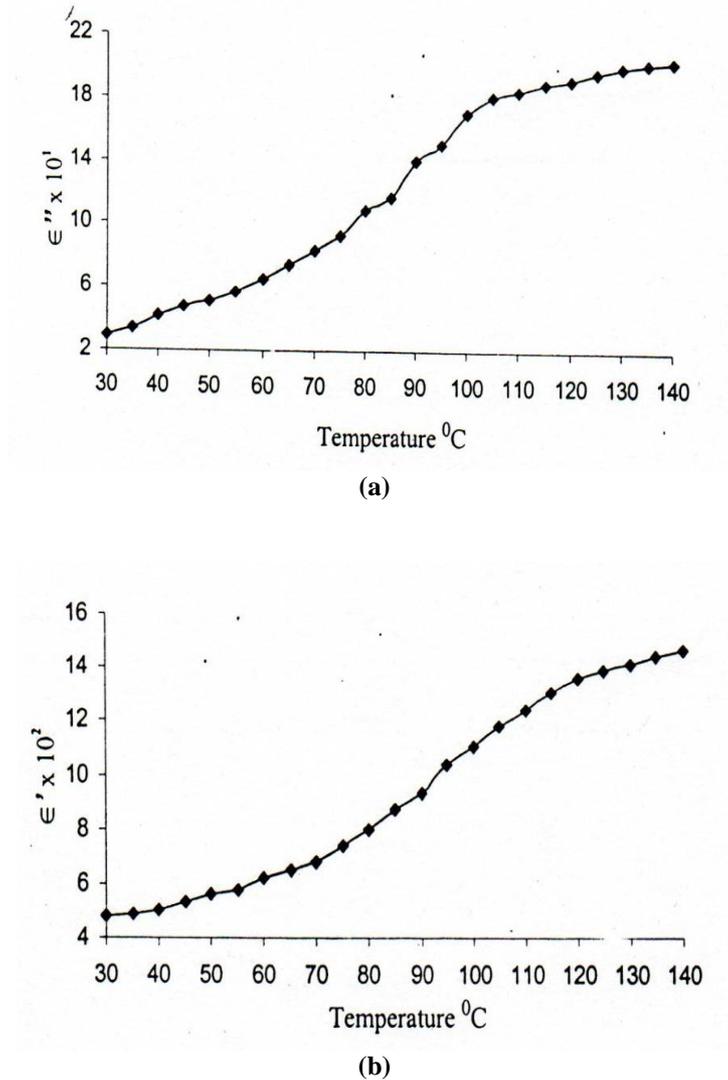


Fig.2 Temperature dependence of dielectric constant and dielectric loss of poly(aniline-co-N-methylaniline) (a) Dielectric constant (b) Dielectric loss

The dielectric constant is a measure of the capacitance of the sample and is due to the capacitive coupling of conducting islands separated by insulating barriers. So on heating, barrier between the conducting grains continue to widen (localization of electrons increases) or develop a larger barrier potential. This increase in localization will increase the dielectric constant.

IV. CONCLUSIONS

Conducting copolymer of poly(aniline-co-N-methylaniline) type have been prepared. The electrical conductivity of copolymer increases with decreasing reaction temperature and is optimum at stoichiometric ratio of oxidant, dopant and monomer. The temperature dependence of dielectric constant and conductivity suggests that homopolymer and

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copolymer are 1D-disordered state composed of 3D-metallic crystalline region and 1D-localized amorphous regions. Conductivity plots suggest that 3D-VRH is proper model for HCl-doped polyaniline whereas for copolymer 1D-VRH seems to be apt choice. Activation energy being an empirical parameter is employed to characterize the exponential temperature dependence of the change in the conductivity. The increase in activation energy of copolymer is noticed that it would be a conducting material.

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