

Temperature Dependence Electrical Conductivity and XRD Studies of Hydroquinone Modified Amberlite XAD-4 Resin

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Abstract—Commercial amberlite XAD-4 resin was modified with hydroquinone moiety through the azo spacer (–N=N–) technique and abbreviated as AXAD-N=N-HQ. It was characterized by elemental analysis, FT-IR spectra and XRD. The number average molecular weight was determined by non-aqueous conductometric titration. Electrical conducting behavior of resin found to be in the range 0.01×10^{-6} to 0.03×10^{-6} mho cm^{-1} for temperature range 300-598 K. The activation energy (E_a) of conduction was evaluated by Wilson's law and found to be $1.774 \text{ kJ mol}^{-1}$. The resin was found to exhibit semiconducting behavior. Percentage of crystallinity and crystalline index was evaluated from XRD data.

Keywords: Amberlite XAD-4 resin, Organic semiconductor, Electrical conductivity

I. INTRODUCTION

Until about 30 years ago, all carbon based polymers were rigidly regarded as an insulator and extensively have been used by the electronics industry because of their high resistivity, but now researchers are engaged in converting insulating polymers to conducting materials due to their strength, toughness, fractional resistance, plasticity, elasticity and corrosion resistance. In recent years, semiconducting property of resins gained sufficient ground and this narrow perspective is rapidly changing as a new class of polymer known as intrinsically conductive polymer or electroactive polymer is being discovered. The conducting polymer research began nearly a quarter of a century ago, when films of polyacetylene were found to exhibit profound increases in electrical conductivity when exposed to halogen vapor [1-3]. Conducting polymers opened the way to progress in understanding the fundamental chemistry and physics of π -bonded macromolecules. Polymers with spatially extended π -bonding system are known as conjugated polymers. Synthesized conjugated conducting polymers can be classified into two major categories 1) chemically polymerized materials and 2) electrochemically polymerized via chemical polymerization [4-5]. The first highly conducting organic polymer, chemically doped polyacetylene, was reported in 1977 [6]. Work on organic

conducting polymers has been carried out extensively due to wide applicability in area of electronics [7].

Undoped polymers are wide band gap semiconductors. Two approaches were mentioned in literature to minimize the band gap. The band gap can be reduced if the bond-length alternation is cancelled [8-9]. Another strategy of decreasing the band gap consists in synthesizing conjugated polymers with alternating strong electron-donor and strong electron-acceptor fragments [10]. The value of band gap can be varied by appropriate functionalization of the conjugated backbone. In particular and appropriate combination of electron donating (reducing agents) and electron withdrawing (oxidizing agents) substituent may results in the preparation of semiconducting conjugated polymers in which bond alteration is lowered by consequence they exhibits a narrow band gap and make them good conductors [11].

In conjugated polymers, the chemical bonding leads to one unpaired electron from p orbital per carbon atom. Moreover, p bonding, in which the carbon orbital are in the sp^2p_z configuration and in which the orbital of successive carbon atoms along the backbone overlap, leads to electron delocalization along the backbone of the polymer. Hybridization of the high-lying HOMO level of the donor and the low-lying LUMO level of the acceptor in the donor-acceptor unit leads to a very small HOMO-LUMO gap [12]. Undoped conjugated polymers derived by Brabecet *al* used in photovoltaic cells [13]. Motoriet *al* have studied the electrical conductivity of semi crystalline polymers as a function of temperature and time of applied voltage [14]. The effect of plasticizer on structural and electrical properties of polymer nanocomposite electrolytes was studied by Pradhan *et al* [15].

X-ray diffraction pattern of polymer contain both sharp as well as defused bands. Sharp bands correspond to crystalline orderly regions and defused bands correspond to amorphous regions. Polymer's crystallinity is expressed in terms of relative degree of crystallinity or crystallinity index, i.e. fraction of the sample which is crystalline. Degree of

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crystallinity can be estimated by integrating the relative intensities of the peaks and halos [16-18].

The present paper deals with the characterization, electrical conductivity and XRD studies of hydroquinone modified amberlite XAD-4.

II. EXPERIMENTAL

Amberlite XAD-4 resin was modified with hydroquinone moiety through the azo spacer (-N=N-) technique in four steps. First step involved nitration, second step involved amination, third step involved diazotization and final step involved coupling of hydroquinone with diazotized intermediate product. Synthesis and characterization of AXAD-4-N=N-HQ was reported in our earlier paper [19].

III. RESULT AND DISCUSSION

IR spectrum of AXAD-4-N=N-HQ

Infrared spectrum of AXAD-4-N=N-HQ was recorded using FTIR Spectrophotometer, Perkins Elmer spectrum-one at the Department of Material Science, V. N. I. T., Nagpur, (M. S.) India.

In infrared spectrum of AXAD-4-N=N-HQ (**Fig.1**), the prominent peak appeared at 3380 to 3214 cm^{-1} (broad) assigned to H bonded phenolic -OH. The peak appeared at 2928 cm^{-1} corresponds to aliphatic C-H stretching vibration. The band appeared at 1263 cm^{-1} assigned to phenolic C-O stretching vibration and band appeared at 831 cm^{-1} corresponding to p-disubstituted aromatic ring [20-22].

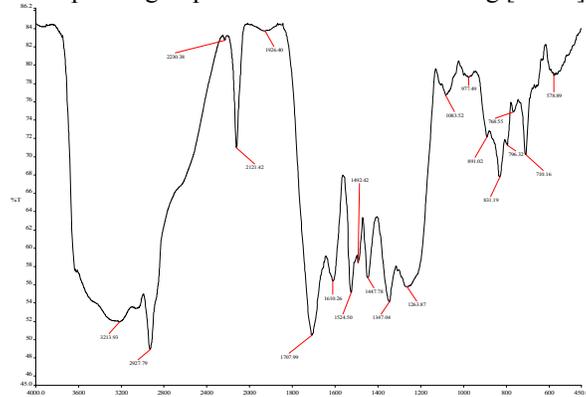
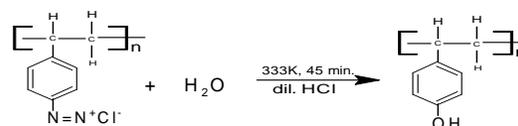


Fig.1: FTIR spectrum of AXAD-4-N=N-HQ

Determination of number average molecular weight of AXAD-4-N=N-HQ

Since sample does not have weakly acidic phenolic (Ar-OH) groups, diazotized sample was boiled with water at 333 K for 45 minutes in the slightly acidic condition (Dil. HCl) to introduce -OH group on the sample. Modified sample (AXAD-4-OH) was dried in air and stored in vacuum desiccator. Reaction is shown in **Scheme 2**.



Scheme 2: Modified AXAD-4-OH

The number average molecular weights (M_n) were determined by non-aqueous conductometric titration in DMF using 0.1M KOH in absolute alcohol as titrant. From the graph (**Fig. 2**) of specific conductance against milliequivalents of base, first and last break were noted. From which the degree of polymerization (DP) and the number average molecular weight (M_n) was calculated using following equations [23].

$$\overline{DP} = \frac{\text{Total meq. of base required for last break}}{\text{meq. of base required for first break}}$$

$$\overline{M}_n = \overline{DP} \times \text{repeat unit weight}$$

Where;

DP = degree of polymerization

M_n = molecular weight of the resin

Repeat unit weight was calculated from elemental analysis and data incorporated in **Table 1**.

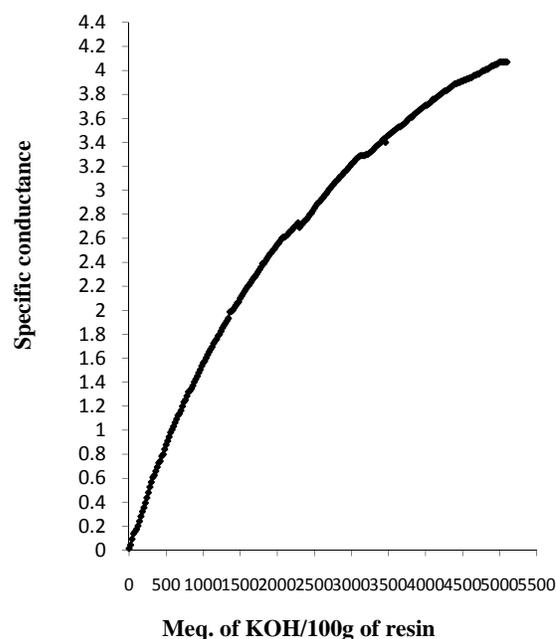


Fig.2: Non aqueous conductometric titration curve of AXAD-4-OH

Table 1: Number average molecular weight of AXAD-4-N=N-HQ

Empirical formula of repeat unit	MW of Repeat unit	DP	MW of resin
C ₂₅ H ₂₄ N ₂ O ₂	390	52	20280

Electrical conductivity of AXAD-4-N=N-HQ

For the measurement of resistance of the AXAD-4-N=N-HQ digital multimeter model DT 92080L was used. The DC conductivity of AXAD-4-N=N-HQ were studied for temperature range 300 to 598 K. The specific conductance of these resins was calculated from the values of specific resistance. The electrical conductivity as a function of temperature of the polymer was studied. The powdered samples of AXAD-4-N=N-HQ resin were palletized by hydraulic press at pressure of 17 lb inch⁻². The surface of pallet were made conducting by applying graphite paste. The diameter and thickness was measured using screw gauge. The solid state conductivity as function of temperature was recorded by two probe method [24]. The electrical conductivity for AXAD-4-N=N-HQ was found in the range of 0.01014 × 10⁻⁶ to 0.03076 × 10⁻⁶ mho cm⁻¹. The plot of log σ versus 1/T was found to be linear in the temperature range under study, which indicates that the Wilson's exponential law [25].

$$\sigma = \sigma^0 e^{(-E_a/kT)}$$

Where; σ = electrical conductivity at temperature T, σ⁰ = electrical conductivity at temperature T = ∞, E_a = activation energy of electrical conduction (eV).

Table 2: Electrical conductivity data of AXAD-4-N=N-HQ

Resin	Activation energy (kJ mol ⁻¹)	Activation energy (eV)
AXAD-4-N=N-HQ	1.879	11.728 × 10 ²¹

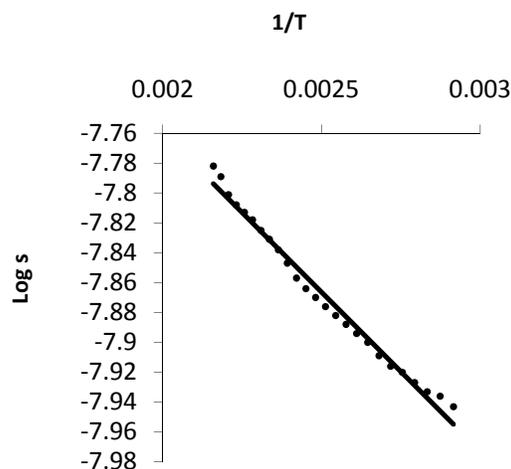


Fig.3: Electrical conductivity

Activation energy (E_a) of electrical conduction calculated from slopes of the plots was found to be 11.728 × 10²¹ eV. Electrical conductivity plots of AXAD-4-N=N-HQ resin is given in Fig. 3. Electrical conductivity data of AXAD-4-N=N-HQ resin are shown in Table 2.

XRD analysis of AXAD-4-N=N-HQ

X-Ray diffraction measurement of AXAD-4-N=N-HQ has been carried out by using X'PERT PRO PANalyticalMPD θ/θ goniometer with Cu-Kα radiation, and fixed slit incidence (0.5° divergence, 1.0°, anti-scatter, specimen length 10 mm) and diffracted (0.5° anti-scatter, 0.02 mm nickel filter) optics at the Department of Material Science, V. N. I. T., Nagpur (M.S.) India. In the XRD pattern of AXAD-4-N=N-HQ resin number of overlapping crystalline phases and amorphous halos were appeared. XRD pattern shown in Fig. 4 and data is tabulated in Table 3. The resin exhibited peak at (2θ).

Table 3: Percentage of crystallinity and crystalline index of AXAD-4-N=N-HQ

Intensity of		% crystallinity (X _c)	Crystalline index (CI)
Crystalline peak	Amorphous peak		
213	74	74.21	0.65

Percentage of crystallinity and crystalline index [26-28] were calculated using the following equation:

$$\text{Percentage of crystallinity, } X_c = \left[\frac{I_c}{(I_c + I_a)} \right] \times 100$$

$$\text{Crystallinity Index, } CI = \frac{I_c - I_a}{I_c}$$

Where; X_c = percentage of crystallinity, CI = crystallinity Index, I_c = intensity of crystalline peaks, I_a = intensity of amorphous peaks

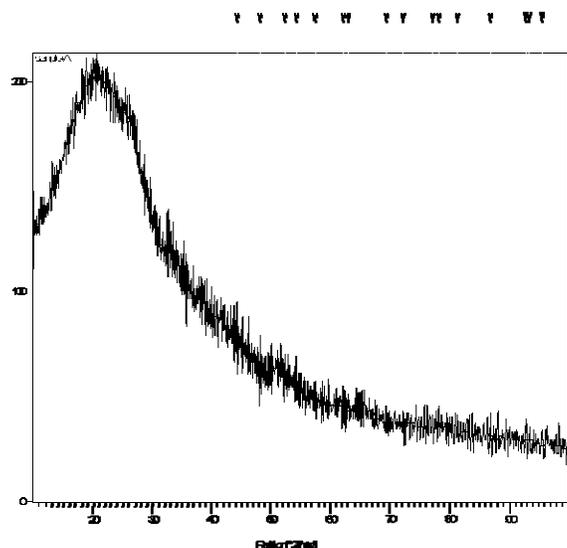


Fig.4: XRD pattern of AXAD-4-N=N-HQ

Scanning electron microscopy (SEM)

The surface morphology and internal structure of functionalized AXAD-4-N=N-HQ beads shown by the SEM photographs. These photographs reveal that arrangement of functionalized resin is disordered and it is amorphous in nature. (Fig. 5) [29].

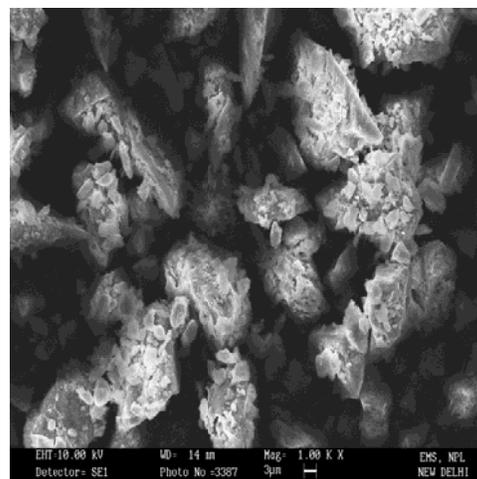
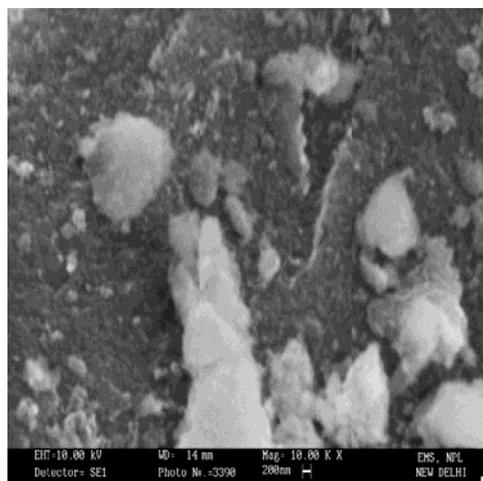


Fig.5: SEM photographs of AXAD-4-N=N-HQ

CONCLUSION

Electrical conductivity of AXAD-4-N=N-HQ resin increases by increasing temperature. Low activation energy of conduction of resin may be due to presence of large number of delocalized p-electrons in the polymer chain. Low conducting behaviour of AXAD-4-N=N-HQ is due to presence of two electron donating group ($-OH$) on the polymeric matrix per repeat unit. Hence this resin may be ranked as semiconductor. We believe the AXAD-4-N=N-HQ resin may be the forerunners of a new class of organic polymers with electrical properties which may be systematically and controllably varied over a wide range by chemical doping. XRD pattern of functionalized resin showed the number of overlapping crystalline phases (sharp peaks) and amorphous halos (broad peaks). From the XRD pattern and data it revealed that AXAD-4-N=N-HQ is not a total crystalline. Such morphological transformations are due to the addition of the amorphous content, increase in molecular weight and cross linking network. The XRD data was support to the SEM. SEM photographs showed that AXAD-4-N=N-HQ resin is in micrometer range.

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