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Synthesis and semiconducting behaviour of amberlite XAD-4 functionalized with melamine

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ABSTRACT

Commercial amberlite XAD-4 resin was functionalized with melamine moiety through $-SO_2$ *spacer and abbreviated as AXAD-*SO_2*-MLN. Resulting intermediate products were characterized by FTIR method and functionalized resin was characterized by elemental analysis and FTIR. Electrical conducting behavior of resin found to be in the range* 0.0115×10^{-6} *to* 0.0389×10^{-6} *mho* cm^{-1} *for temperature range 305-593 K. The activation energy* (E_a) *of conduction was evaluated by Wilson's law and found to be 1.774 kJ* mol^{-1}*. The resin was found to exhibit semiconducting behavior.*

Keywords: Amberlite XAD-4, Electrical conductivity, Wilsons law, Organic semiconductors, Functionalization.

INTRODUCTION

Polymer supported synthesis and fabrication of functionalized polymeric material have been attracting much attention owing to fulfil the demands of polymer chemist, physicist, environmentalist and analysts within the domain of desired properties and applicability such as high stability at elevated temperature, good conducting ability, ion exchange selectivity and high sorption capacity [1,2]. Amberlite XAD series resins have efficient support for anchoring chelating ligands due to their good porosity, uniform pore size distribution, high surface area. Amberlite XAD resins have superior physical properties like durability and chemical stability towards harsh environments [3]. These resins, including XAD-2 and XAD-4 have been ideal for the preparation of functional resins based on their porosity and surface area [4,5]. Faber and co-workers modified XAD-2 and XAD-4. They found by transmittance infrared spectroscopy that XAD-2 was composed of styrene, divinylbenzene and ethylvinylbenzene, whereas XAD-4 was composed of divinylbenzene and ethylvinylbenzene [6].

Two methods have been frequently reported in literature to design good functionalized chelating resin with improved properties. First involve sorption of chelating ligands onto the polymeric matrix and other is based on covalent coupling of a ligand with polymer backbone through a spacer arm, generally azo (-N=N-) [7,8], methylene ($-CH_2$) group [9]or other groups [10].

The commercially available resins of amberlite series have been found to be very promising as support for designing chelating resins. Some important and recently reported chelating matrices developed using such supports are: amberlite XAD-2 functionalized with o-vanillinthiosemicarbazone [11], salicylic acid [12], o-aminophenol [13], pyrocatechol [14], and 2,3-dihydroxypyridine [15], which were used for the analysis of heavy metal ions in various matrices of environmental importance. 1-(2-pyridylazo)-2-naphthol [16], 4-(2-Pyridylazo)resorcinol [17], o-aminobenzoic acid [3], ammonium morpholine dithiocarbamate, and piperidine dithiocarbamate [18] were functionalized with amberlite XAD-4 (AXAD-4) and applied for the determination of metal ion status in various water samples.

Holding *et al* have used amberlite XAD-2 for the extraction of organic contaminants from water [19]. Nanoti *et al* reported that pH 1 is the best operating pH for the removal of furfural from aqueous solution by using AXAD-4 [20]. It is crucial that the resin can be regenerated for reuse for in economical process. Thus it could be much more completely regenerated with acetone studied by Weil *et al* [21]. Islam *et al* reported that a chelating resin of better sorption capacity by loading 1-(2-pyridylazo)-2-naphthol on AXAD-4 resin through surface modification and characterize in a systematic manner and used for the preconcentration and separation of Cd(II), Zn(II), Co(II), Cu(II), Ni(II), Mn(II), and Pb(II) from various real matrices prior to their determination by flame atomic absorption spectrometry (FAAS) [22].

In conjugated polymers, the chemical bonding leads to one unpaired electron from p orbital per carbon atom. Moreover, p bonding, in which the carbon orbitals are in the sp^2p_z configuration and in which the orbitals of successive carbon atoms along the backbone overlap, leads to electron delocalization along the backbone of the polymer. This electronic delocalization provides the ‘highway’ for charge mobility along the backbone of the polymer chain. As a result of this, the electronic structure in conducting polymers can be determined by the chain symmetry (i.e. the number and kind of atoms within the repeating unit), with the result that such polymers can exhibit semiconducting or even metallic properties [23]. Recently, it has been reported that the organic conjugated polymer resin like amberlites can be used as a semiconductors by using photo-doping and this doping involving no dopant ions [24].

When undoped, all of them 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. The best known example of such a polymer is a polyisothianaphthene (PITN), which can be considered as a derivative of polythiophene (PT) [25, 26]. Another strategy of decreasing the band gap consists in synthesising conjugated polymers with alternating strong electron-donor and strong electron-acceptor fragments [51]. 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.

Recently Hiwase *et al* have characterized p-hydroxybenzaldehyde-resorcinol-formaldehyde and p-hydroxyacetophenone-hexamine-formaldehyde [27]. Dharkar *et al* studied the conductivities of melamine-aniline-formaldehyde terpolymer resins and its polychelates. The activation energy values were found to be in range of 0.847 to 1.156 eV [28]. perkin *et al* studied the electrical conductivity of phenol-formaldehyde resin [29]. Khedkar *et al* studied structural and semi conducting behavior of terpolymeric ligand derived from m-cresol, hexamine and formaldehyde [30].

The present communication deals with synthesis of AXAD-4-SO_2-MLN and its electrical conducting behaviour with rise in temperature.

MATERIALS AND METHODS

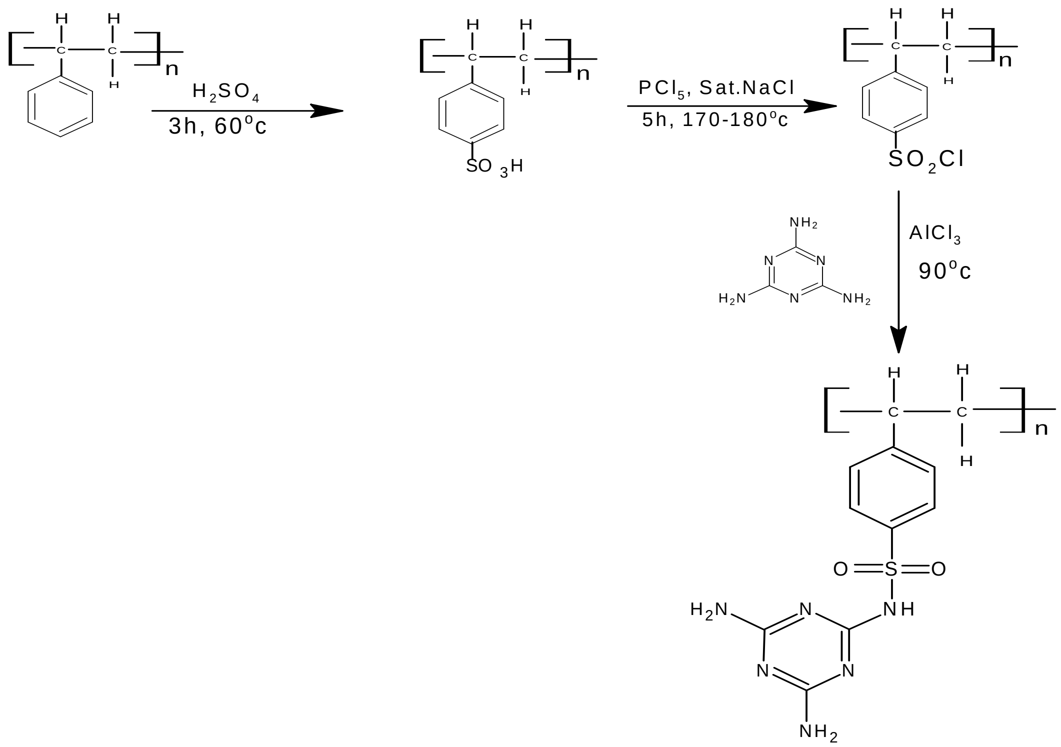
The chemicals used for the synthesis were chemically pure and analytical grade.

Amberlite XAD-4, Melamine, Conc. H_2SO_4, $AlCl_3$, NaCl and DMSO were obtained from Merck, SD Fine Chemicals, India Ltd.

Synthesis of AXAD-4-SO_2-MLN

AXAD-4 (7g) was sulphonated with conc. sulphuric acid by refluxing the mixture at 60°C for 3 hrs. The blackish colored sulphonated resin (AXAD-4-SO_3H) was collected by filtration. The product was repeatedly washed with water until free from acid and dried. In a second step the sulphonated resin was chlorinated by PCl_5 in the presence of saturated sodium chloride and refluxed it for 5 hr at 170-180^{0}C. The product (AXAD-4-SO_2Cl) was filtered and washed with hot water several times and dried it [31-32].

Resin AXAD-4-SO_2Cl refluxed with melamine in the presence of 0.2 M $AlCl_3$ as a catalyst at 90^{0}C for 6 hrs. The dark yellow colored final product (AXAD-4-SO_2-MLN) washed with water followed by DMSO. Finally, it washed with water until the test for Cl^- ion was absent for filtrate. Dry in the air and stored in vacuum desiccator. The complete reaction is shown in scheme.



Scheme. Synthesis of AXAD-4-SO_2-MLN

RESULTS AND DISCUSSION

Characterization of AXAD-4-SO_2-MLN

Elemental analysis (C, H, N, S)

Elemental analysis of AXAD-4-SO_2-MLN was carried out at C.I.M.F.R., Nagpur (M.S.), India by analytical Functional Testing Vario MICRO CHNS elemental analyzer (Germany), Serial no-11083059. Data is incorporated in Table 1.

Table 1. Elemental Analysis of AXAD-4-SO_2-MLN

Resin	%C Found (Calc.)	%H Found (Calc.)	%N Found (Calc.)	%S Found (Calc.)
AXAD-4-SO_2-MLN	62.85 (62.85)	5.93 (5.71)	19.85 (20.00)	3.99 (3.81)

IR Spectra of intermediate products and AXAD-4-SO_2-MLN

Infrared spectrum of intermediated products (Fig. 1 and 2) and AXAD-4-SO_2-MLN (Fig. 3) were recorded using FTIR Spectrophotometer, Perkins Elmer spectrum-one at the Department of Material Science, V. N. I. T., Nagpur, (M. S.) India.

The band appeared at 1178 cm^{-1} assigned to S=O Stretch (Fig. 1 and 2). The bands appeared at 626 and 1091 cm^{-1} attributed to C-S stretch (Fig.1). The bands appeared at 620 and 1085 cm^{-1} attributed to C-S stretch (Fig.2).

In IR spectrum of AXAD-4-SO_2-MLN (Fig.3), absorption bands appeared at 617, 750 and 1087 cm^{-1} attributed to C-S stretching [33]. The peaks appeared at 1172 and 1350 cm^{-1} attributed to S=O symmetric and asymmetric stretching in SO_2 [34]. The absorption bands appeared at 891, 792 and 966 cm^{-1} assigned to S-N Stretching vibration. The bands appeared at 441 and 465 cm^{-1} were attributed to O=S-N bending and SO_2 wagging respectively [35]. The peaks appeared in the region 3140-3500 and 600-900 cm^{-1} were assigned to N-H deformation and N-H wagging respectively. The peak appeared at 1016 and 687 cm^{-1} were attributed to C-H bending in aromatic ring (in plane) and C-H bending in aromatic ring (out of plane) respectively. The absorption bands appeared at 1474 and 419 cm^{-1} were attributed to C=C stretching in aromatic ring (in plane) and C=C bending in aromatic ring (out of plane) respectively

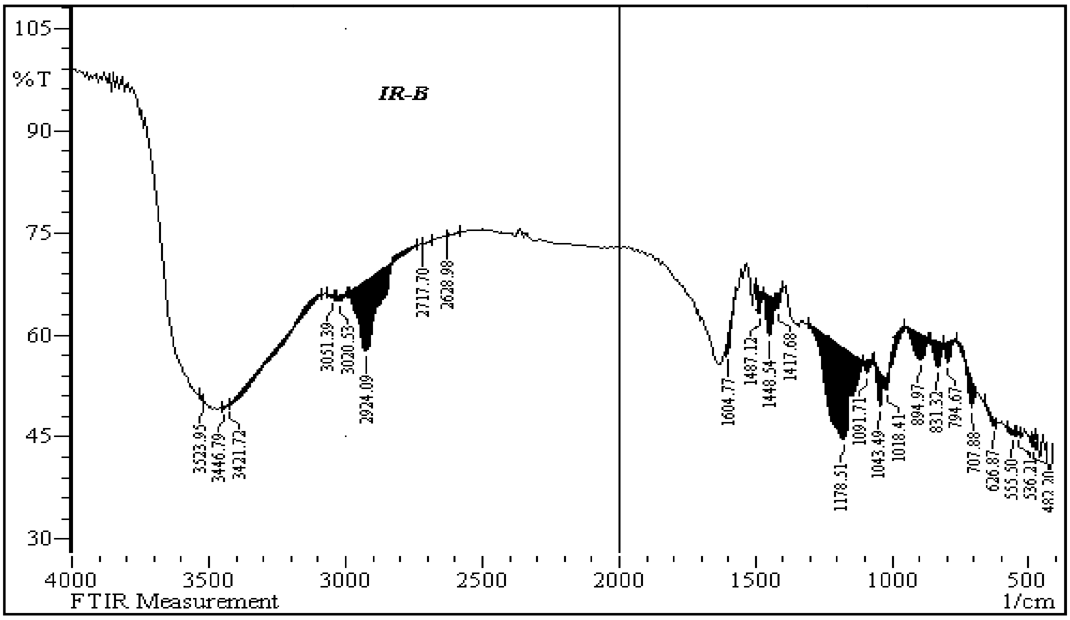


Fig.1. FTIR spectrum of AXAD-4-SO_3H (Intermediate product)

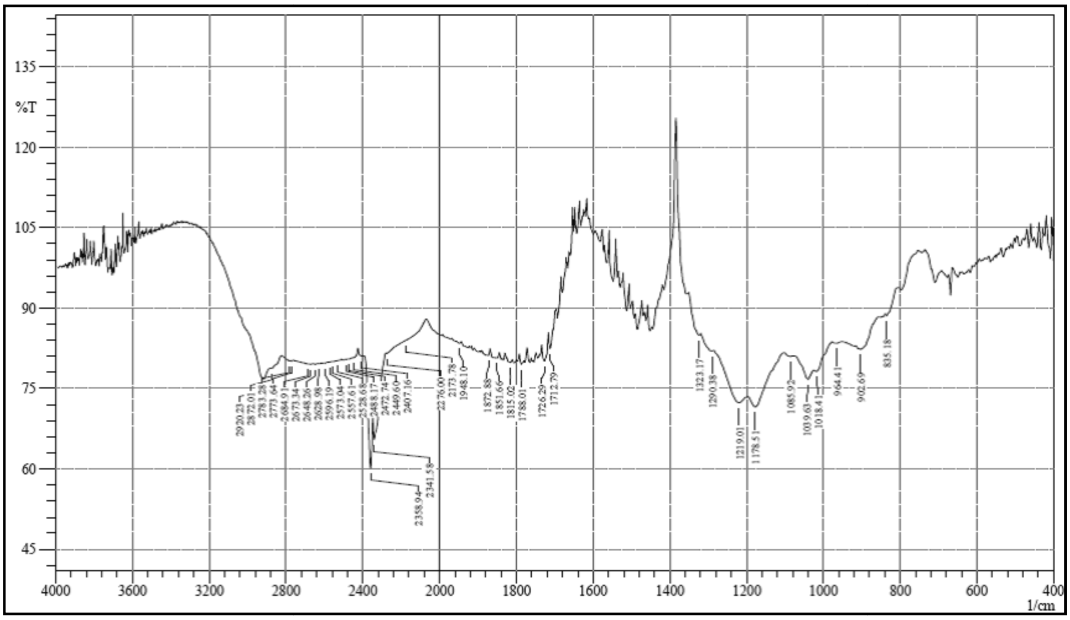


Fig.2. FTIR spectrum of AXAD-4-SO_2Cl (Intermediate product)

Electrical conductivity of AXAD-4-SO_2-MLN

The DC conductivities of AXAD-4-SO_2-MLN resin was studied for temperature range 305-593 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-SO_2-MLN resin was palatalised 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 [36]. The electrical conductivity for resin found to be in the range 0.0115×10^{-6} to 0.0389×10^{-6} mho cm^{-1}. The activation energy (E_a) of electrical conduction was found to be 1.774 kJ mol^{-1} which was calculated from the slope of the plot by using Wilson's exponential law,

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

Where;

σ = electrical conductivity at temperature T
σ_o = electrical conductivity at temperature T= ∞
E_a = activation energy of electrical conduction

K = Boltzmann constant (1.387 x 10^{-23} J mol^{-1} K^{-1})
T = absolute temperature

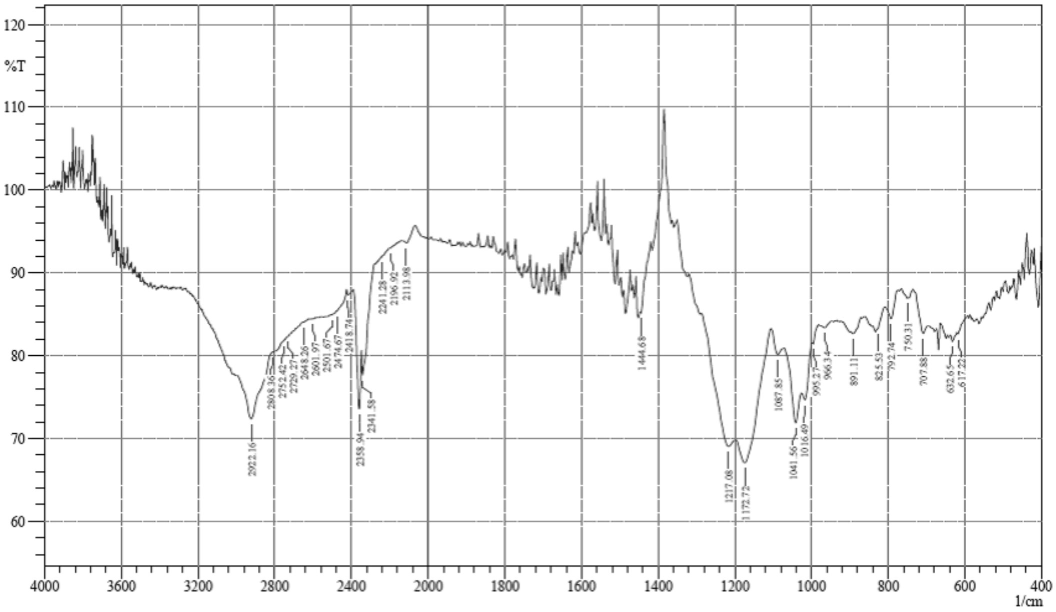


Fig.3. FTIR spectrum of AXAD-4-SO_2-MLN

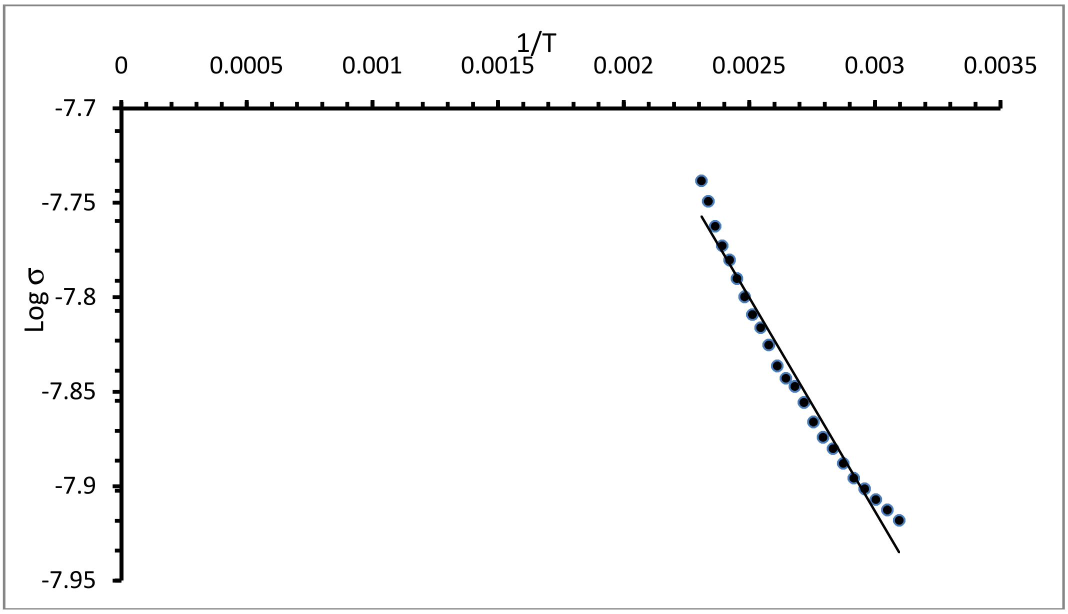


Fig. 4. Electrical conductivity Plot of AXAD-4-SO_2-MLN

The plot of log σ versus 1/*T* was found to be linear in the temperature range under study, which indicate that the Wilson's exponential law was obeyed. Electrical conductivity plot of AXAD-4-SO_2-MLN resin is shown in Figure 4 and data is given in Table 2.

Table 2: Activation energy of AXAD-4-SO_2-MLN resin

Resin	Activation energy (kJ mol^{-1})	Activation energy (eV)
AXAD-4-SO_2-MLN	1.774	11.072×10^{21}

CONCLUSION

The functionalized amberlite XAD-4 product (AXAD-4-SO_2-MLN) is confirmed by elemental analysis, FTIR spectra and it is in good agreement with the reaction scheme shown above. The plot of log σ Vs. $1/T$ is linear with negative slope hence satisfy with Wilson's equation.

Electrical conductivity of AXAD-4-SO_2-MLN resin increases by increasing temperature. Hence this resin may be ranked as semiconductor. The low activation energy of conduction of resin may be due to presence of large number of delocalized p-electrons in the polymer chain. The presence of MLN (melamine) moiety was containing three electron donating substituents with electron rich hetero atom nitrogen and the presence of –SO_2 spacer with melamine moiety extends the conjugation further support to the conduction of electrons. Due to this, highly increases the electronic charge on polymer matrix therefore showing conducting behaviour. We believe the AXAD-4-SO_2-MLN 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.

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