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Electrical conductivity study of resin synthesized from 1-naphthol-4-sulphonic acid and hexamethylene diamine and formaldehyde

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ABSTRACT

A terpolymer 1-N-4-SAHDF-Resin-II was synthesized from 1-Naphthol-4-sulphonic acid and Hexamethylene diamine with formaldehyde by polycondensation method in an acidic medium with molar proportion of reactants (2:1:3). To reveal the structure of the resin, the resin was characterized by elemental analysis and spectral methods, i.e. composition of terpolymer has been determined on the basis of its elemental analysis. The terpolymer resin has been characterized by UV-Visible, FT-IR and NMR (¹H & ¹³C) spectra and by SEM. The DC conductivity of sample was determined by four probe method. The conductivity of 1-N-4-SAHDF-Resin-II was found to be in the range of 1.021×10^{-7} to $9.247 \times 10^{-5} \text{ ohm}^{-1} \text{ cm}^{-1}$ in the temperature range 313K-433K. The activation energy of the conduction for 1-N-4-SAHDF-Resin-II was found to be $1.14 \times 10^{-20} \text{ J/K}$.

Keywords: Synthesis, characterization, polycondensation, electrical conductivity.

INTRODUCTION

The synthesized terpolymer resins with highly conjugated chains have attracted much attention of scientist and introduce the recent innovations in the polymer chemistry in the last few years. The terpolymers offer novelty and versatility; hence they occupy the pivotal position in the field of material science. The terpolymer resins can be used as high energy material, ion-exchanger, semiconductors, antioxidants, fire proofing agent, optical storage data, binders, molding materials etc [1,2,3]. The semiconducting properties of terpolymer resins have gained sufficient ground in recent years. Electrically conducting polymer resins are undoubtedly one of the focal points of current interest in solid-state physics and chemistry. Their discovery has led to the emergency of not only new types of materials capable of replacing metals but also new concepts to explain their high conductivity. Work on organic conducting polymers is carried out extensively due to their wide applications in areas such as corrosion protection and antistatic coatings [4], in biosensors for coupling of electron transfer [5], fabrication of electrochemical windows and gas sensors, development of individual electronic devices and whole integrated circuits [6,7] etc. Delocalized electrons and conjugation impart semiconducting properties to the polymer resins. Kanda et al reported the rubeanato-copper semiconductive polymers and studied their AC and DC conductivity [8]. Dhawan and coworkers reported the conducting polymers predicted to be the futuristic materials for the development of light emitting diodes, antistatic and EMI materials, sensors, optoelectronic devices and rechargeable batteries due to their unique conduction mechanism and greater environmental stability [9]. This article describes the synthesis, structural characterization of a new terpolymer synthesized from salicylic acid, butylenediamine with formaldehyde and its electrical conductivity measurement study.

MATERIALS AND METHODS

2.1 Materials

The chemicals used in the synthesis of new terpolymer resin were procured from the market and were Sigma-Aldrich or chemically pure grade. Whenever required they were further purified by standard procedure.

2.2 Synthesis of 1-N-4-SAHDF-Resin-II terpolymer

The new terpolymer 1-N-4-SAHDF-Resin-II was synthesized by condensing 1-Naphthol-4-sulphonic acid (0.2 mol) and Hexamethylene diamine (0.1 mol) with 37% formaldehyde (0.3 mol) in a mol ratio of 2:1:3 in the presence of 2M 200 ml HCl as a catalyst at $140^{\circ}\text{C} \pm 20^{\circ}\text{C}$ for 6h in an oil bath with occasional shaking to ensure thorough mixing. The separated terpolymer was washed with hot water and methanol to remove unreacted starting materials and acid monomers. The properly washed resin was dried, powdered and then extracted with diethyl ether and then with petroleum ether to remove 1Naphthol-4-sulphonic acid formaldehyde copolymer which might be present along with 1-N-4-SAHDF-Resin-II terpolymer. The reddish brown coloured powdery product was immediately removed from the flask as soon as reaction period was over and then purified. The reaction and suggested structure of 1-N-4-SAHDF-Resin-II in shown in Fig. 1.

The terpolymer was purified by dissolving in 10% aqueous sodium hydroxide solution, filtered and reprecipitated by gradual drop wise addition of ice cold 1:1 (v/v) concentrated hydrochloric acid / distilled water with constant and rapid stirring to avoid lump formation. The process of reprecipitation was repeated twice. The terpolymer sample 1-N-4-SAHDF-Resin-II thus obtained was filtered, washed several times with hot water, dried in air, powdered and kept in vacuum desiccators over silica gel. The yield of the terpolymer resin was found to be 75%.

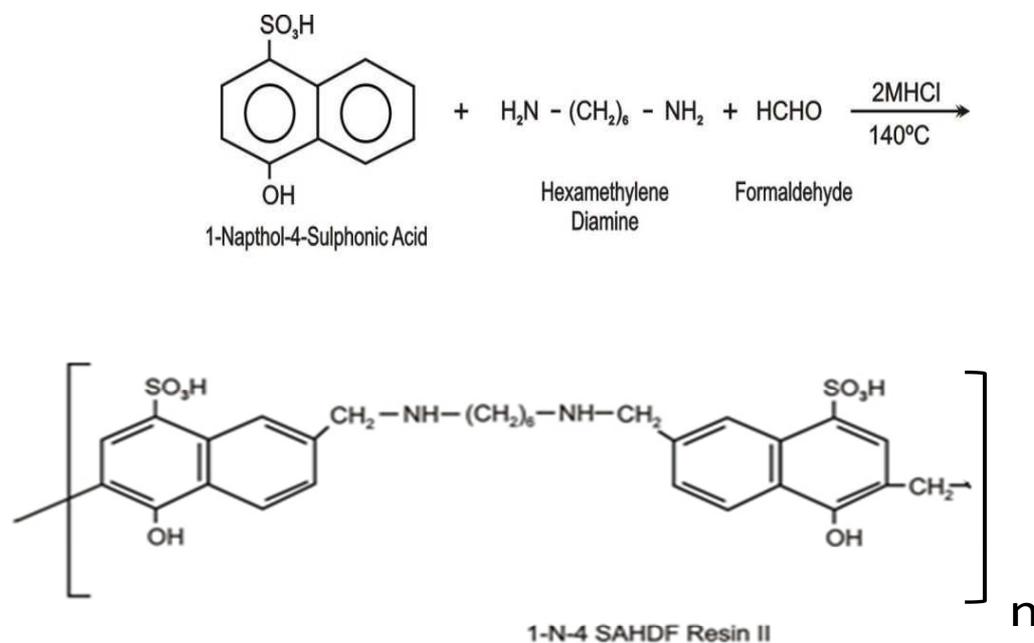


Figure 1: Reaction and suggested structure of representative 1-N-4-SAHDF-Resin-II terpolymer

2.3 Characterization:

1-N-4-SAHDF-Resin-II terpolymer resin was subjected to microanalysis for C, H, S and N at STIC, Cochin. The number average molecular weight (M_n) was determined by conductometric titration in non aqueous medium such as dimethylsulphoxide (DMSO) using ethanolic KOH as a titrant. From the graph of specific conductance against milliequivalents of base, first and last break were noted from which degree of polymerization (DP) and the number average molecular weight (M_n) has been calculated for terpolymer resin under investigation. An infra-red spectrum of p-COF-II terpolymer resin was recorded on Perkin-Elmer-R-XR Spectrophotometer in KBr pallets in the wave number region of $4000-400\text{ cm}^{-1}$ at Sophisticated Analytical Instrumentation Facility (SAIF), Punjab University; Chandigarh. Both ^1H & ^{13}C NMR spectrum of newly synthesized terpolymer resin has been scanned on Bruker

Avance II 400 MHz NMR spectrometer using DMSO-d₆ at Sophisticated Analytical Instrumentation Facility, Punjab University, Chandigarh. SEM has been scanned by FEI-Philips XL-30 electron microscope.

3. Electrical Conductivity

The resins are well known for their behavior as semiconductors though carrier mobility in them usually is very low. This is due to the difficulty which electrons experience in jumping from one molecule to another and so the carrier mobility in compounds of these kind increases with increase in molecular size [10-14]. The electrical conductivity of newly synthesized terpolymer resin was studied by Precision Impedance Analyser- 6500B. The measurements involved following steps.

3.1 Preparation of Pellet

The terpolymer samples were dried properly and thoroughly ground to a fine powder in agate mortar and pestle. The pellets were prepared of the well powdered terpolymer resins isotectically in a steel die at under a pressure of 10 metric tons cm⁻² with the help of hydraulic press. The pellets thus obtained were hard and crack free. The average diameter of the pellets and their thickness were measured using screw gauge by taking mean of three different positions. Thin layer silver coat was applied on both sides of the pellet to avoid short circuits

3.2 Measurement of Resistivity

Precision Impedance Analyser- 6500B was used to measure the electrical conductivity of 1-N-4-SAHDF-Resin-II terpolymer. The temperature variations of resin were studied by placing the sample holder along with the pallet in the electric furnace and were then heated slowly. The slow rate of heating 1 to 10 °C per minute was maintained throughout the investigation. Connection wires from the furnace were connected to the terminals of the instrument. The resistances of the sample pallet were measured by four probes (terminals) method.

Resistivity (ρ) was then calculated using the relation:

$$\rho = R \cdot \frac{A}{l}$$

Where, R= resistance of the pellet

A = Surface area of pellets and

l = Thickness of pellet.

The DC resistivities were measured from 313 to 423 K. The electrical conductivity (σ) varies exponentially with the absolute temperature according to the well-known relationship.

$$\sigma = \sigma_0 \exp\left(-\frac{\Delta E}{kT}\right)$$

Where, σ = electrical conductivity at room temperature (T)

σ_0 = electrical conductivity at temperature constant

E_a = Activation energy of electrical conduction.

K= Boltzmann constant (1.3817x10⁻²³ J mole⁻¹k⁻¹)

T= Absolute temperature

The relationship has been modified as

$$\log \sigma = \log \sigma_0 + \frac{-\Delta E}{2.303kT}$$

According to this relation, a plot of Log σ Vs 1/T would be linear with negative slope. From the Slope of the plots, the activation energy was calculated [10-14, 19].

RESULTS AND DISCUSSION

Newly synthesized, purified 1-N-4-SAHDF-Resin-II was found to be amorphous and coffee brown in colour. The terpolymers are soluble in solvents such as DMF, DMSO, THF and aq. NaOH while insoluble in almost all other organic solvents. The resin synthesise did not show sharp melting point but undergo decomposition above 240°C. These resins were analyzed for carbon, hydrogen, nitrogen and sulphur content. The Mn of the terpolymer resin was determined by non-aqueous conductometric titration in DMSO against KOH in 50% (v/v) DMSO-Alcohol mixture using 100mg of resin sample. A plot of specific conductance against the milliequivalents of potassium hydroxide required for neutralization of 100 g of terpolymer was made. Inspection of such a plot revealed that there are many breaks in plot. From this plot the first break and the last break were noted. The calculation of (Mn) by this method is

based on the following considerations. (1) The first break corresponds to neutralization of the more acidic phenolic hydroxy group of all the repeating units and (2) the break in the plot beyond which a continuous increase in conductance is observed represents the stage at which phenolic hydroxy group of all repeating units are neutralized. On the basis of the average, degree of polymerization (DP) is given by the following relation.

$$DP = \frac{\text{Total meq. of base required for complete neutralization}}{\text{Meq. of base required for smallest interval}}$$

$$(M_n) = (DP) \times \text{Repeat unit weight}$$

On the basis of degree of polymerization (DP), the average number molecular weight (M_n) is calculated by multiplying the (DP) by the formula weight of repeating unit.

The details of Elemental analysis, molecular weight determination are incorporated in Table 1.

Table 1:

Empirical formula of repeat unit	Carbon%	Hydrogen%	Nitrogen%	Sulphur%	Empirical weight of repeat unit, g	Average degree of polymerization (DP)	Average molecular weight (M_n)
$C_{29}H_{30}O_8S_2N_2$	58(Cal)	5.33(Cal)	4.66(Cal)	10.66(Cal)	600	17.50	10500
	57.84 (F)	5.43(F)	4.56(F)	10.78(F)			

4.1. Infrared spectra

Infrared spectrum of the 1-N-4-SAHDF-Resin-II has been shown in Fig. 2. Very broad band appeared in the region 3229 cm^{-1} may be assigned to the stretching vibration of phenolic -OH groups exhibiting intermolecular hydrogen bonding between -OH and $>C=O$ and NH group of amide. The band obtained at 1371 cm^{-1} suggests the presence of methylene (-CH₂-) bridges. A sharp and strong peak at 1607 cm^{-1} may be ascribed to aromatic skeletal ring. The 1,2,3,5 tetra substitution of aromatic benzene ring can be recognized from sharp and medium absorption bands appeared at 912, 1098, 1149 cm^{-1} respectively. The presence of C-H stretching of aromatic ring may be assigned as a sharp and strong band at 3011 cm^{-1} which seems to be merged with very broad band of phenolic hydroxyl group [15]. A sharp and strong peak at 1379 cm^{-1} may be ascribed to -CH₂- symmetrical deformation. A sharp peak at 2917 cm^{-1} may be ascribed to $>CH_2$, -NH, -CH₃ stretching. A sharp and strong peak at 1743 cm^{-1} may be due to $>C=O$ stretching (oxamide moiety). A broad and sharp peak at 1481 cm^{-1} may be ascribed to -NH bending of secondary amide. A sharp peak at 1286 cm^{-1} may be ascribed to -CH₂ bending (wagging & twisting). The band obtained at 1231 cm^{-1} suggests the presence of -CH₂- plane bending. The band obtained at 784 cm^{-1} suggests the presence of -CH₂ bending (rocking) and -NH deformation out of plane of secondary amide respectively.

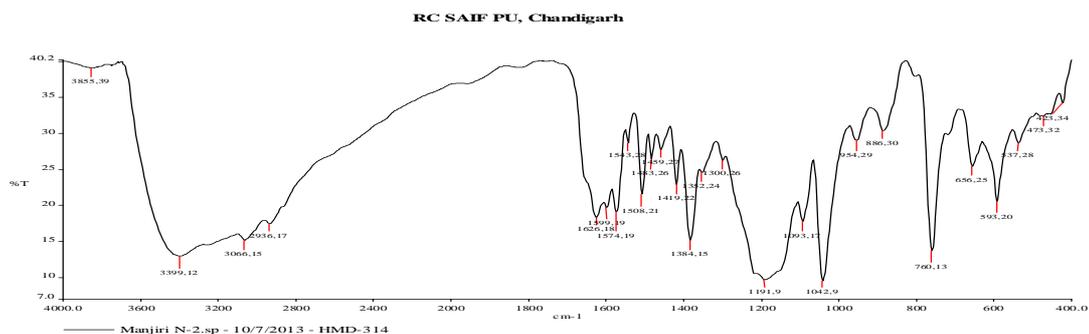


Fig 2 : Infrared spectra of 1-N-4-SAHDF-Resin-III

4.2. ¹H Nuclear magnetic resonance spectra

The ¹H NMR spectrum of 1-N-4-SAHDF-Resin-II terpolymer was scanned in DMSO-d₆ and has been shown in Fig.3. The chemical shift (δ) in ppm has been assigned on the basis of data available in literature [16]. The 1-N-4-SAHDF-Resin-II terpolymer resin shows an multiplet signals at δ 2.56 ppm which may be attributed to methyl proton of Ar-CH₃ group. The singlet obtained in the region of δ 3.46 ppm may be due to the methylene proton of Ar-CH₂-N moiety. The signal in the region of δ 6.2 ppm is attributed to protons of bridge -NH. The weak multiplet signal (unsymmetrical pattern) in the region of δ 6.62 ppm may be due to terminal methylene group. The signals in the range at δ 10.21 ppm may be due to phenolic hydroxyl protons. The much downfield chemical shift for

phenolic -OH indicates clearly the intramolecular hydrogen bonding of -OH group[16]. The multiplets at δ 1.29 ppm and 1.55 ppm may due to -CH₂-CH₂- moiety of amine. The signal at δ 7.52 ppm may due to aromatic proton (Ar-H). The singlet obtained at 9.41 ppm may assigned to sulphonic group.

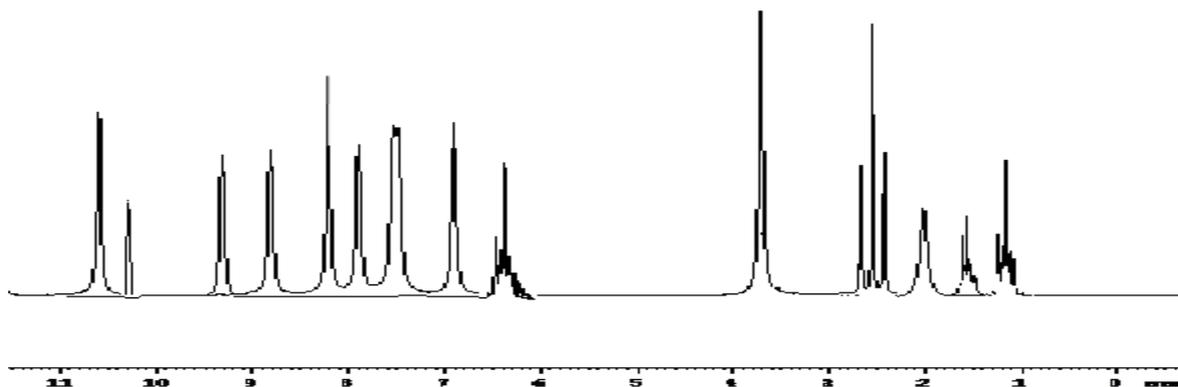


Fig. 3. ¹H Nuclear Magnetic Resonance Spectra of 1-N-4-SAHDF-Resin-III

4.3. ¹³C Nuclear magnetic resonance spectra

¹³C NMR spectrum of 1-N-4-SAHDF-Resin-II has been recorded as shown in Fig. 4. ¹³C NMR spectra display signals arising from all the carbon atoms and hence provide direct information about the carbon skeleton of the terpolymer. The ¹³C NMR spectrum of 1-N-4-SAHDF-Resin-II shows the corresponding peaks at 155.56, 107.8, 126.1, 133.89, 130.2, 126.6, 127.4, 126.32, 122.45, 126.21 ppm with respect to C₁ to C₁₀ of the aromatic naphthalene ring. The shifting of signals is due to the substitution in naphthalene ring. More electronegative group is bonded to Carbon atom, deshielding shifts increases[17]. Thus, the peak of C₁ at 155.56 may be because of deshielding effect by -OH grp. The signal at 42.1 may be assigned to -C-NH- grp. Of hexamethylene diamine moiety. Two peaks more are obtained for hexamethylene diamine, out of which peak at 26.5 may be because of methylene -CH₂- grp. The ¹³C NMR spectrum after analysis minutely confirmed that the monomers are arranged in a straight manner, giving the linear structure for terpolymer, which we have proposed is obviously correct given in Fig. 4.

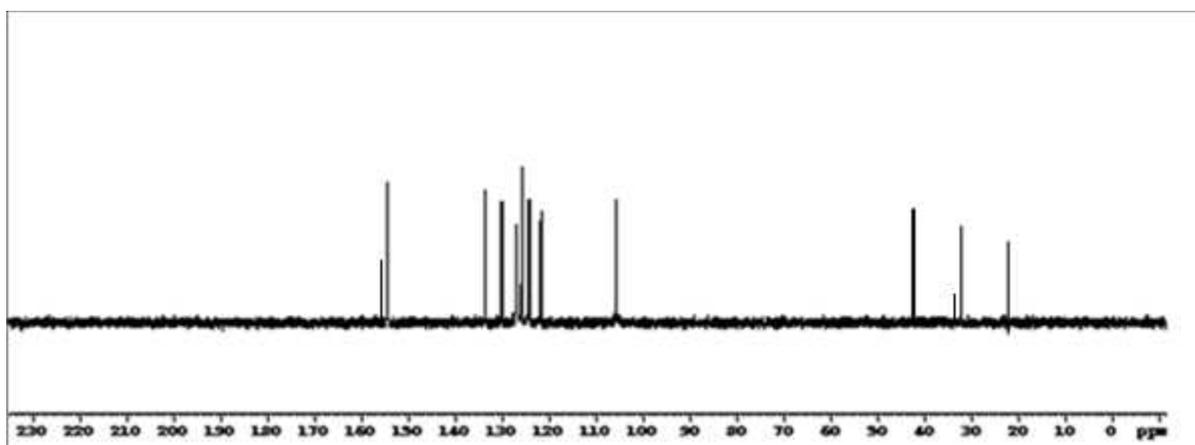


Fig. 4. ¹³C Nuclear Magnetic Resonance Spectra of 1-N-4-SAHDF-Resin-III

4.4. Scanning electron microscopy (SEM)

Scanning electron micrographs of the 1-N-4-SAHDF-Resin-II has been recorded as shown in Fig. 5. The SEM micrographs of 1-N-4-SAHDF-Resin-II sample exhibits spherulites with deep corrugation. The spherulites are typical crystalline formation and they grow in high viscous and concentrated solution. In the present case, the spherulites are complex polycrystalline. The crystals are smaller in surface area with less closely packed structure. The spherulites morphology of resin exhibit crystalline structure with deep corrugation which is clearly visible in SEM photographs of resin. These evidences indicate that more or less the resin shows amorphous character with less close packed surface having deep pits. The resin thus possesses amorphous nature and showing higher exchange capacity for metal ions [18]. Thus SEM study shows that the p1-N-4-SAHDF-Resin-II has crystalline and some amorphous characters. Thus it has the transition structure between crystalline and amorphous.

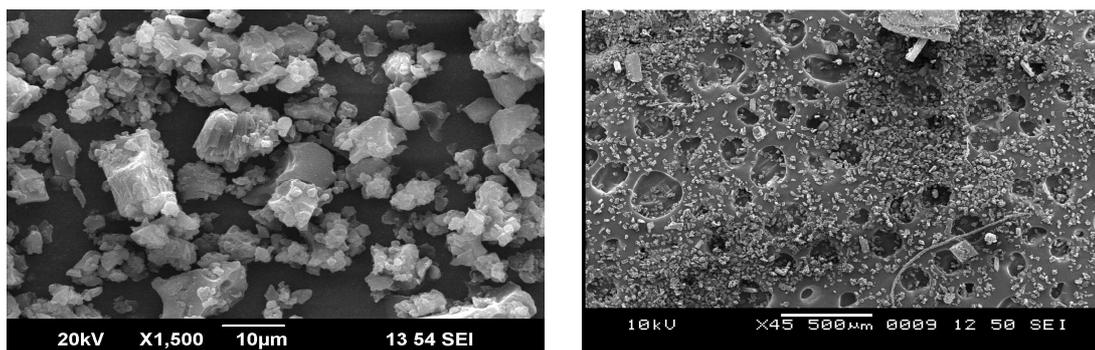


Fig. 5: SEM micrographs of 1-N-4-SAHDF-Resin-II

The polymer under study is a terpolymer hence it is very difficult to assign its exact structure. However on the basis of the nature and relative position of the monomers, elemental analysis, IR, ^1H NMR, ^{13}C NMR studies and taking into consideration the linear structure of other phenol-formaldehyde resin and the linear branched nature of urea-formaldehyde polymers, the most probable structure has been proposed for 1-N-4-SAHDF-Resin-II (Fig. 1).

4.5. Electrical Conductivity Measurement of 1-N-4-SAHDF-Resin-II

The results of electrical conductivity and activation energy are incorporated in Table 2. The temperature dependence of the electrical conductivity of the resin has been mentioned in Fig. 6. The electrical conduction of polymeric material depends upon incalculable parameters such as porosity, pressure, method of preparation, atmosphere etc; activation energy (E_a) is not affected by these parameters and, therefore, it is fairly reproducible [19,20]. The magnitude of activation energy depends on the number of electrons present in semiconductor materials. The more the number of π – electrons lowers the magnitude of activation energy and vice versa. Generally polymers containing aromatic nuclei in the backbone exhibit lower activation energy than those with aliphatic system. Thus, the low magnitude of activation energy may be due to the presence of large number of π -electrons in the polymer chain. This is in good agreement with the most probable structure proposed for the newly synthesized resin under investigation [10-14, 19,20]. The carrier motilities of the organic semiconductors might decrease due to:

- A. The forces between the adjacent molecules are relatively weak as organic compounds from molecular crystals.
- B. Due to little electronic coupling that exists between the adjacent molecules, it becomes difficult for the electrons to jump from one molecule to other.
- C. As a consequence of the disordered structure which is due to amorphous nature, the electrons get scattered while traveling through the materials, when they try to flow through it and hence lowers the conductivity.

The study shows following results of electrical conductivity-

- 1) The electrical conductivity of 1-N-4-SAHDF-Resin-II lies in the range of 1.021×10^{-7} to $9.247 \times 10^{-5} \text{ ohm}^{-1}\text{cm}^{-1}$.
- 2) The plots of $\log \sigma$ versus $1/T$ is found to be linear in the temperature range under study, which indicate that the Wilson's exponential law $\sigma = \sigma_0 \exp(-\Delta E/kT)$ is obeyed.
- 3) The energy of activation (E_a) of electrical conduction calculated from the slopes of the plots is found to be $1.14 \times 10^{-20} \text{ J/K}$.

These observations and results are in harmony with the findings of other earlier workers [10-14, 19,20]. It has been found under investigation that the order of thermal activation energy is just the reverse of electrical conductivity. The temperature dependence of electrical conductivity shows that conductivity increases with temperature. As the conductivity is found very low in the range of 10^{-7} to $10^{-5} \text{ ohm}^{-1} \text{ cm}^{-1}$ even at higher temperature. This indicates the semiconducting nature of the 1-N-4-SAHDF-Resin-II.

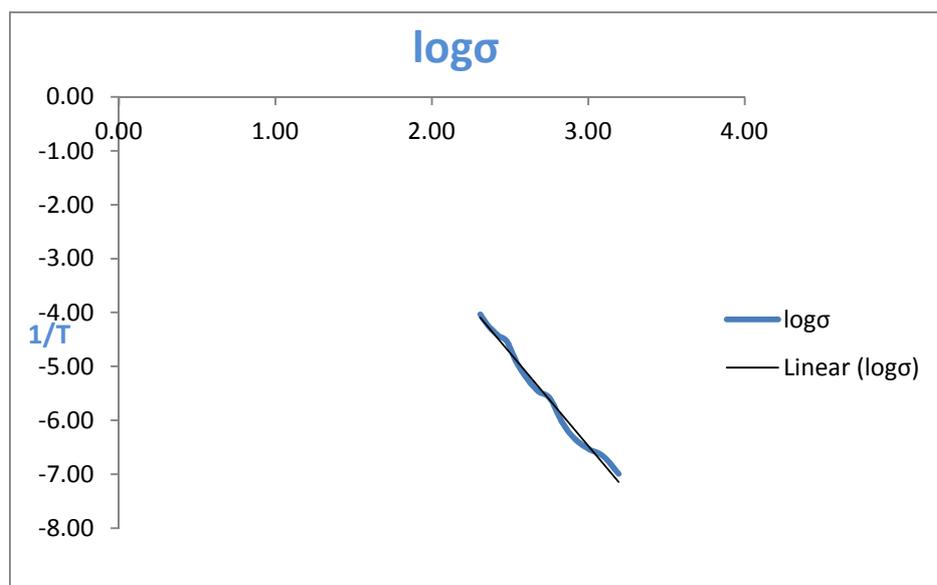
Fig. 6: Plot of $\log \sigma$ Vs $1/T$ for 1-N-4-SAHDF-Resin-II

Table 2: Evaluation of Activation Energy and Electrical Conductivity of 1-N-4-SAHDF-Resin-II

Diameter of the pellet: 1.20cm

Surface area of the pellet (A) = $\pi r^2 = 3.142 \times (D/2)^2 = 1.13 \text{ cm}^2$

Thickness of the pellet (l) = 0.21 cm

$A/l = 5.380 \text{ cm}$

Temperature (C)	Temperature (K)	$1/T \times 10^{-3}$	Resistance (Ohm)	Resistivity [C]= $R \cdot A/l \text{ ohm.cm}$	Conductivity $\sigma =$ $1/R$	$\log \sigma$
40	313	3.19	1.82E+06	9.79E+06	1.0213E-07	-6.991
50	323	3.10	8.57E+05	4.61E+06	2.1689E-07	-6.664
60	333	3.00	6.32E+05	3.40E+06	2.941E-07	-6.531
70	343	2.92	4.12E+05	2.22E+06	4.5115E-07	-6.346
80	353	2.83	2.01E+05	1.08E+06	9.2474E-07	-6.034
90	363	2.75	7.22E+04	3.88E+05	2.5744E-06	-5.589
100	373	2.68	5.40E+04	2.91E+05	3.4421E-06	-5.463
110	383	2.61	3.19E+04	1.72E+05	5.8268E-06	-5.235
120	393	2.54	1.63E+04	8.77E+04	1.1403E-05	-4.943
130	403	2.48	6.47E+03	3.48E+04	2.8729E-05	-4.542
140	413	2.42	4.88E+03	2.63E+04	3.8089E-05	-4.419
150	423	2.36	3.37E+03	1.81E+04	5.5155E-05	-4.258
160	433	2.31	2.01E+03	1.08E+04	9.2474E-05	-4.034

CONCLUSION

The data of elemental analysis, FT-IR spectra, ^1H and ^{13}C NMR spectra, supports to the above tentative structure of 1-N-4-SAHDF-Resin-II. Electrical conductivity of 1-N-4-SAHDF-Resin-II increases with increase in temperature, which is the important property for the resin. The plot of $\log \sigma$ versus $1/T$ is found to be linear in the temperature range under study, which indicates that the Wilson's exponential law is obeyed. Hence this terpolymer may be ranked as semiconductor for temperature range 313 to 433 K. The low activation energy of conduction of resin may be due to presence of large number of delocalized π -electrons in the polymer chain. This is in good agreement with the tentative structure of terpolymer resin.

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