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Electrical Conductivity Study of Novel Organic Copolymer Resin Synthesized from 2-Hydroxy, 4-Methoxybenzophenone, 1, 5-Diaminonaphthalene and Formaldehyde

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Abstract: *Copolymer 2-H, 4-MBP-1,5-DANF-IV has been synthesized from 2-hydroxy, 4-methoxybenzophenone, and 1,5-diaminonaphthalene with formaldehyde by polycondensation method in acidic medium with 4:2:7 molar ratios of reacting monomers. The copolymer has been characterized by elemental analysis, FT-IR and ^{1}H-NMR spectra. Electrical conductivity measurement has been carried out to ascertain the semiconducting nature of the copolymer resin. The electrical conductivity of the copolymer has been found to be 4.23×10^{-9} to 9.36×10^{-7} ohm^{-1}cm^{-1} in the temperature range 313-428 K. The activation energy of electrical conduction has been found to be 6.68×10^{-20} J/K. The plots of log σ Vs 10^3/T are found to be linear over a wide range of temperature, which obeyed the Wilson's exponential law $\sigma = \sigma_0 \exp(\Delta E/KT)$ and the copolymer can be ranked as semiconductor*

Keywords: Copolymer, Resin, Condensation, Synthesis, Electrical Conductivity Semiconductors

I. INTRODUCTION

Polymer offers versatility and novelty hence they inhabit the main roll in semiconductor. The polymer scientists are trying to improve the properties of polymeric resins such as thermal stability, high chemical resistivity, durability, conductivity in the domain of desired applicability. Semiconducting polymers have been the subject of study for many decades for day to day application in modern electronics including antistatic coating, corrosion protection, in biosensors for coupling of electron transfer, fabrication of electrochemical windows, gas sensors, radio, computers, telephones, and many other electronic devices. Such devices include transistors, solar cells, the light-emitting diode, the silicon controlled rectifier, and digital and analog integrated circuits [1-4].

Chinchamalatpure and coworker have reported the electrical conductivity of some copolymers and its polychalates [5]. Gabel et al. Have reported the synthesis, characterization and electrical conductivity of polyaniline $Mn_{0.8}Zn_{0.2}Fe_2O_4$ nano -composites [6]. Gupta has studied the electrical conductance behaviour of terpolymer resin-II derived from p-hydroxybenzaldehyde, urea and ethylene glycol [7]. Electrical conductivity study of thermally stable newly synthesized terpolymer has reported by Niley and coworker [8]. Khedkar et al. [9] have studied the electrical conducting behaviour of newly synthesized m-cresol-hexamine-formaldehyde terpolymeric resin and its polychelates. Thakre [10] has synthesized the resins of 4-hydroxybenzoic acid, adipamide and formaldehyde and also studied the electrical conductance properties. Electrical conductivity measurement of salicylic acid hexamethylene-diamine- formaldehyde resin has studied by Masram et al. [11]. Electrical conductivity of salicylidene - anthranilic acid - schiff base formaldehyde resin (R-AASA) was reported by Abbas and coworker [12]. The present study deals with synthesis, characterization and semiconducting properties of a new 2-hydroxy, 4-methoxybenzophenon, 1,5-diaminonaphthalene and formaldehyde copolymer resin.

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II. MATERIALS AND METHOD

The chemicals, like 2-hydroxyl, 4-methoxy benzophenone (Sigma Aldrich, India), 1,5-diaminonaphthalene (Himedia, India) and formaldehyde (S. D. Fine Chemicals, India) were procured from market and were of chemically pure grade.

A. Synthesis of 2-H, 4-MBP-1, 5-DAF-IV Copolymer

The copolymer 2-H, 4-MBP-1, 5-DANF-IV was synthesized by condensing 2-hydroxy, 4-methoxy benzo-phenone and 1, 5-diaminonaphthalene with formaldehyde in 4:2:7 molar ratio of reacting monomers in the presence of 2M, 200 ml HCl as a catalyst at 126 $\pm$ 2 ^{0}C for about 5 hrs. in an oil bath with occasional shaking. The separated brown

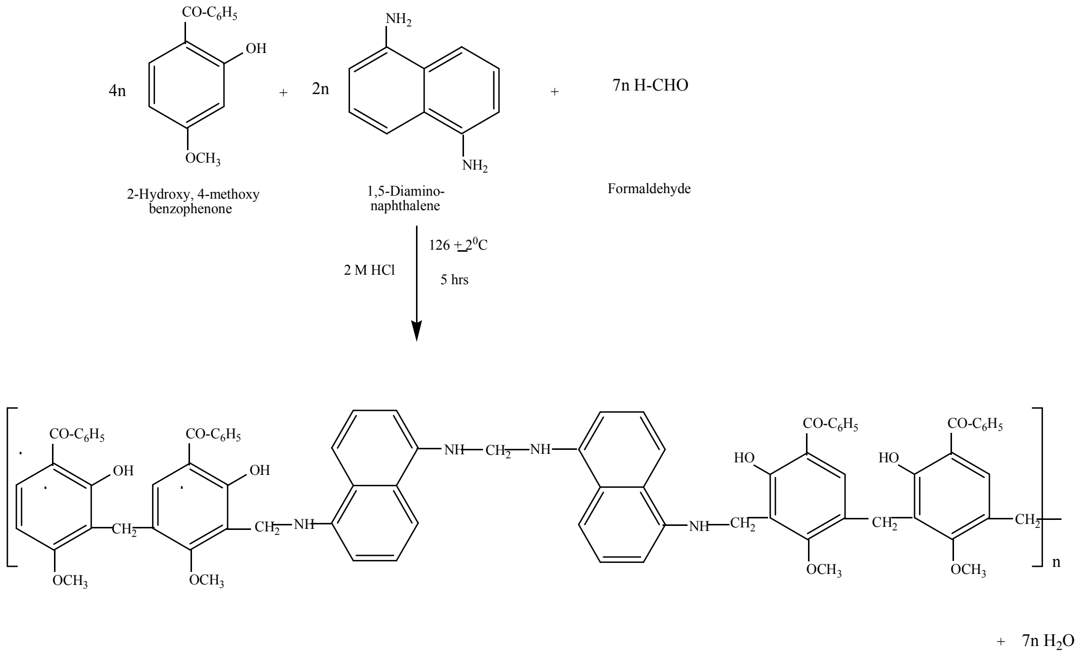

Figure 1: Synthesis of 2-H, 4-MBP-1, 5-DANF-IV copolymer resin

colour copolymer was washed with hot water and methanol to remove unreacted starting materials and acid monomers. Properly washed resin was dried powdered and then extracted with diethyl ether to remove 2-hydroxy, 4-methoxy benzophenone formaldehyde copolymer along with 2-H, 4-MBP-1, 5-DANF-IV copolymer. It was further purified by dissolving in 8% NaOH and then filtered. The purified copolymer resin was finely ground to pass through 300-mesh size sieve and kept in a vacuum over silica gel. The yield of the copolymer resin was found to be 81% .The reaction and suggested structure of 2-H, 4-MBP-1, 5-DANF-IV has been presented in Figure 1.

B. Analytical and Physico-Chemical Studies

The elemental analysis was carried out on Elemental Vario EL III Carlo Erba1108 elemental analyzer instrument. The electronic absorption spectra of the copolymer in DMSO was recorded on double beam spectrophotometer in the range of 200-800 nm. Infrared spectra of copolymer was carried out in najol mull on Perkin-Elmer-Spectrum RX-I, FT-IR spectrophotometer in KBr pellets in the range of 4000-500 cm^{-1}. Proton NMR spectrum was recorded on Bruker Advance –II 400 MHz NMR spectrophotometer using DMSO-d$_6$ as a solvent. SEM has been scanned by a JEOL JSM-6380, an analytical scanning electronic microscope. All the analytical and spectral studies were carried out at Sophisticated Analytical Instruments Facility SAIF, Cochin University, Cochin, India.

C. Electrical Conductivity

To prepare the pellet, the copolymer resin was thoroughly ground in agate pestle and mortar. The well powered copolymer was isostatically in a steel die at 10 tones /inch with the help of hydraulic press. On both sides of pellet, a thin layer of colloidal graphite in acetone was applied to ensure a good contact with the electrode. A typical sample holder was designed for the purpose of resistivity measurement and pellet is mounted on it. For measurement of resistivity at different temperature, a suitable electrical furnace was used. Auto LCR-Q meter 4910 was used to measure the electrical conductivity of copolymer resin. The temperature variations of resin were studied by placing the sample holder along with the pallet in the electric furnace that was then heated slowly. The resistances of the sample pallets were measured by two probes (terminals) method. Resistivity (ρ) was then calculated using the relation:

$$\rho = R. \times A/l$$

The DC resistivity was measured from 313 to 428 K. The electrical conductivity (σ) varies exponentially with the absolute temperature. According to the well-known relationship:

$$\sigma = \sigma_0 \exp(-Ea/kT)$$

The relationship has been modified as

$$\log \sigma = \log\sigma_0 - Ea/2.303kT$$

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 [13, 14].

III. RESULTS AND DISCUSSION

The synthesized copolymer was found to be brown color and soluble in solvents such as dimethyl formamide (DMF), Dimethyl sulphoxide (DMSO), Tetrahydrofuran (THF) and conc. H_2SO_4 but insoluble in almost all organic and inorganic solvents.

A. Elemental Analysis

The 2-H, 4-MBP-1, 5-DANF-IV copolymer was analysed for the carbon, hydrogen and nitrogen content. The composition of copolymer obtained on the basis of elemental analysis data was found to be in good correlation which is presented in Table I.

Table I. Elemental analysis and empirical formula of copolymer resin

Copolymer resin	% C Observed (cal.)	% H Observed (cal.)	% N Observed (cal.)	% O Observed (cal.)
2-H, 4-MBP-1, 5-DANF-IV	75.89	5.13	3.46	10.97
	75.69	5.23	4.30	11.07

B. FT-IR Spectra

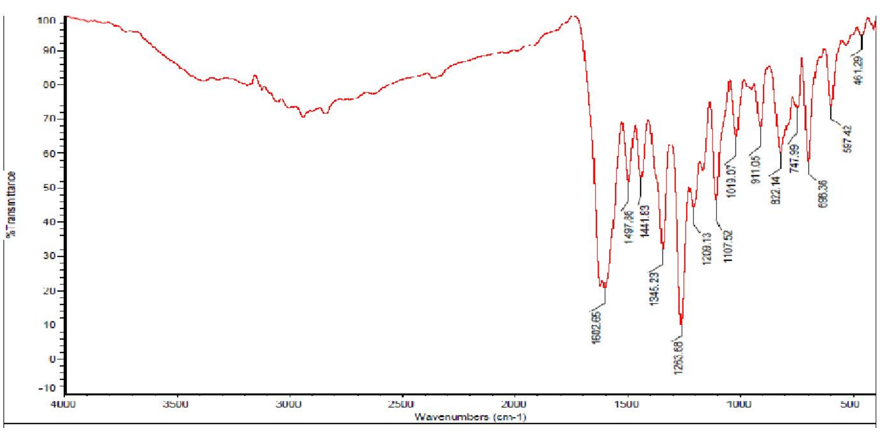

Figure 2: FT-IR spectra of 2-H, 4-MBP-1,5-DANF-IV copolymer resin

Infrared spectra of 2-H, 4-MBP-1, 5-DANF-IV copolymer resin is shown in Figure 2. A broad and strong band appeared at 3325 cm^{-1} may be due to the stretching vibration of the phenolic hydroxyl group exhibiting intramolecular hydrogen bonding with –NH group. A sharp and strong band at 1602 cm^{-1} may be assigned to the stretching vibration

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of >C=O group. The strong band observed at 2938 cm-¹ may be due to the stretching vibrations of –NH (imide) group. The strong band obtained at 1107 cm-¹ region may be due to the Ph-O-CH_3 ether linkage. The weak band at 1345 cm⁻¹ is attributed to –CH_2 methylene bridge. [15-19].

C. ¹H-NMR Spectra

The ¹H-NMR spectra of 2-H, 4-MBP-1,5-DANF-IV copolymer is presented in Figure 3. The weak multiplet signal (unsymmetrical pattern) in the region at δ 7.6 ppm, which may due to proton of aromatic ring (Ar-H). The weak signal in the region δ 7.2 ppm is attributed to phenolic –OH proton in intramolecular hydrogen bonding (Ar-OH). The presence of singlet at δ 3.4 ppm reveals the presence of Ar-O-CH_3 proton. The methylenic proton of Ar-CH_2-N linkage may be recognized from signal which appears in the region of δ 3.7 ppm. The triplet signal in the region δ 6.7 ppm may be due to proton of –NH bridge [20-23].

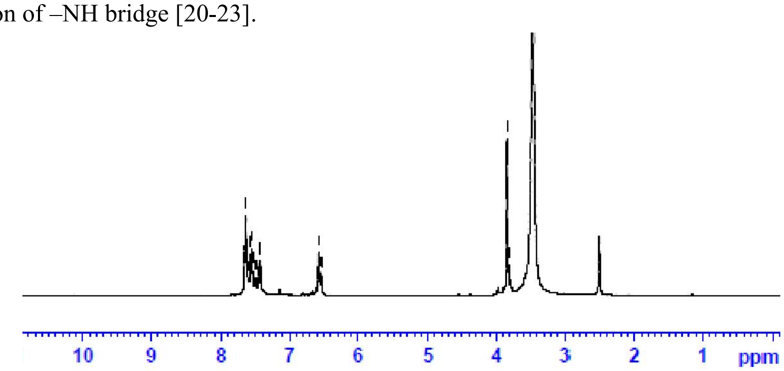

Figure 3: ^{1}H-NMR spectra of 2-H, 4-MBP-1,5-DANF-IV copolymer resin

D. Electrical Conductivity of 2-H, 4-MBP-1, 5-DANF-IV Resin

The temperature dependence of the electrical conductivity of the copolymer is shown in Figure 4.The electrical conduction of polymeric material depends upon incalculable parameters such as pressure, method of preparation, porosity, atmosphere etc. Energy of activation (Ea) is not affected by these parameters and, therefore, it is fairly reproducible. 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.

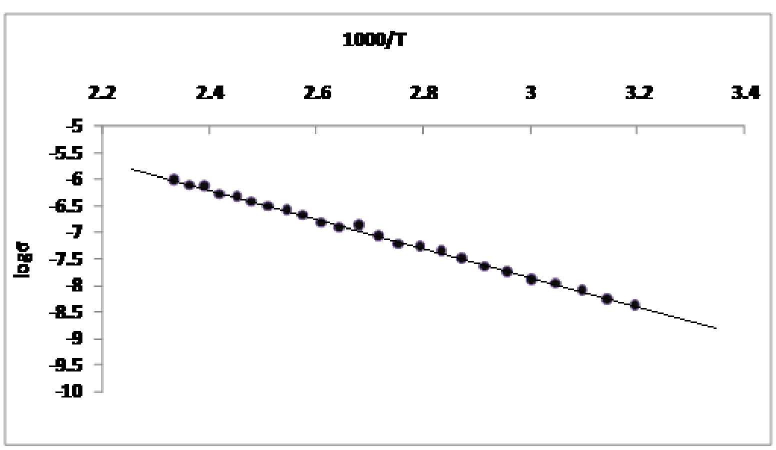

Figure 4. Electrical Conductivity Plot of 2-H, 4-MBP-1,5-DANF-IV resin

The 2-H, 4-MBP-1,5-DANF-IV copolymer shows the electrical conductivity in the range of 4.23×10^{-9} to 9.36×10^{-7} $ohm^{-1}cm^{-1}$ and the plots of log σ versus 1/T is found to be linear in the temperature range under study, which indicate that the Wilson's exponential law $\sigma = \sigma_o \exp(-\Delta E/KT)$ is obeyed. The activation energy (Ea) of electrical conduction calculated from the slopes of the plots is found to be in the range of 16.37 × 10^{-20} J/K. Thus, the low magnitude of activation energy may be due to the presence of large number of π-electrons in the polymer chain and the copolymer may be ranked as semiconductor. This is in good agreement with the most probable structure proposed for the newly synthesized resin under investigation [24-28].

IV. CONCLUSION

The data of elemental analysis, and ^1H - NMR spectra, supports to the above tentative structure of 2-H, 4-MBP-1,5-DANF-IV resin. Electrical conductivity of the copolymer resin increases with increase in temperature (4.23 × 10^{-9} to 9.36 × 10^{-7} ohm^{-1} $cm^{-1\,1}$). The low activation energy of conduction (6.68 × 10^{-20} J/K) of resin may be due to presence of large number of delocalized π-electrons in the polymer chain. The plot of log σ versus 1/T is found to be linear in the temperature range 313 -428 K, which indicates that the Wilson's exponential law is obeyed. Hence this copolymer may be ranked as semiconductor for temperature range under study.

V. ACKNOWLEDGEMENT

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