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Electrical Conductivity of Newly Synthesized Copolymer Resin-IV from 2, 4-Dihydroxypropiophenone, 1, 5-Diaminonaphthalene and Formaldehyde

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Abstract: *The copolymer 2,4-DHP-1,5-DANF-IV has been synthesized by condensation of 2,4-dihydroxypropiophenone, 1,5-diaminonaphthalene with formaldehyde in the presence of 2M hydrochloric acid as a catalyst with 4:2:7 molar ratio of reacting monomers. The copolymer has been characterized by elemental analysis, UV-Visible, FT-I 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 2.05×10^{-10} to 1.15×10^{-8} ohm^{-1} cm^{-1} in the temperature range 313-428 K. The activation energy of electrical conduction has been found to be 6.48×10^{-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, Synthesis, Characterization, Morphology, Electrical Conductivity

I. INTRODUCTION

The synthesized copolymer 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 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 day to day application in modern electronics including gas sensors, telephones, radios, computers, antistatic coating, corrosion protection, in biosensors for coupling of electron transfer and many other electronic devices include transistors, solar cells, the silicon controlled rectifier, light-emitting diodes, and digital and analog integrated circuits [1-4].

Gupta has studied the electrical conductance behaviour of terpolymer resin-II derived from p-hydroxybenzaldehyde, urea and ethylene glycol [5]. Gabal et al. have reported the synthesis, characterization and electrical conductivity of polyaniline-$Mn_{0.8}Zn_{0.2}Fe_2O_4$ nano-composites [6]. Chinchamalatpure and coworker have reported the electrical conductivity of some copolymers and its polychelates [7]. Electrical conductivity study of thermally stable newly synthesized terpolymer has reported by Niley and coworker [8]. Thakre [9] has synthesized the resins of 4-hydroxybenzoic acid, adipamide and formaldehyde and also studied the electrical conductance properties. Khedkar et al. [10] have studied the electrical conducting behaviour of newly synthesized m-cresol-hexamine-formaldehyde terpolymeric resin and its polychelates. Electrical conductivity measurement of salicylic acid-hexamethylenediamine-formaldehyde resin has studied by Masram et al. [11]. The present investigation deals with study of electrical conductivity of 2,4-dihydroxypropiophenone, 1,5-diaminonaphthalene with formaldehyde copolymer which has not been reported so far in literature.

II. MATERIALS AND METHODS

All the chemicals used were of A. R. grade. The 1,5-diaminonaphthalene , 2,4-dihydroxypropiophenone, and formaldehyde, dimethylformamide (DMF), dimethylsulphoxide (DMSO), tetrahydrofuran (THF), acetone and dimethyl ether were purchased from market, India.

2.1 Synthesis of 2, 4-DHP-1, 5-DANF-IV Copolymer

The copolymer 2, 4-DHP-1,5-DANF-IV was synthesized by condensing 2,4-dihydroxypropiophenone and 1,5-diaminonaphthalene with formaldehyde in the presence of 2M HCL as a catalyst in 4:2:7 molar proportion of reactants in an oil bath for about 5 hrs at temperature 126 $\pm$ 2 ^{0}C. The brown color product was obtained and washed with hot water several times. The product obtained was extracted with diethyl ether to remove 2, 4-dihydroxypropiophenone formaldehyde copolymer which might be present along with 2,4-DHP-1,5-DANF-IV copolymer. It was further purified by dissolving in 8% NaOH and then filtered.The copolymer was then reprecipitate by drop wise addition of 1:1 concentrate hydrochloric acid and water with rapid stirring to avoid the lumping formation. The purified sample was dried, powdered and kept in vaccum desiccators. The yield of the resin was found to be 86 %. The reaction of above synthesis has been depicted in Figure-1.

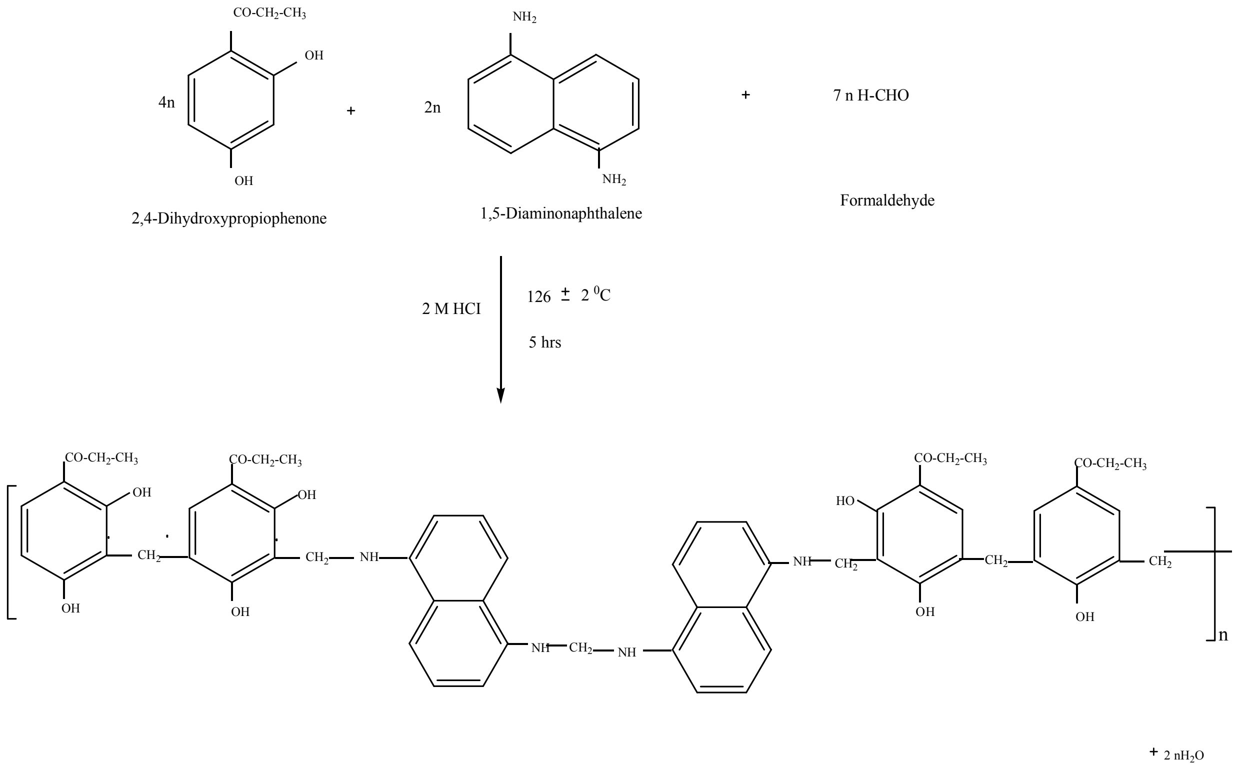

Figure 1. Synthesis of 2,4-DHP-1,5-DANF-IV copolymer resin

2.2 Analytical and Physico-Chemical Studies

The elemental analysis of the resin 2,4-DHP-1,5-DANF-IV was carried out on Elemental Vario EL III Carlo Erba 1108 elemental analyzer instrument. The UV-Visible spectra was recorded at room temperature in dimethyl sulphoxide in the range of 190 nm - 850 nm on double beam spectrophotometer. FT-IR spectra has been carried out on Perkin-Elmer Spectrum RX-I, FT-IR Spectrophotometer in the range of 4000-500 cm^{-1} in KBr pellets. The ^{1}H- NMR spectrum of the resin was recorded using DMSO-d$_6$ as a solvent on Bruker Advance -II 400 MHz NMR spectrophotometer. All the analytical and spectral studies were recorded at Sophisticated Analytical Instruments Facility, STIC, Cochin University, Cochin, India.

2.3 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 were 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 [12, 13].

III. RESULTS AND DISCUSSION

The synthesized copolymer resin was found to be brown color. The copolymer is soluble in solvent such as dimethyl sulphoxide (DMSO), dimethylformamide (DMF) and tetrahydrofuran (THF) but insoluble in almost all other inorganic and organic solvents.

3.1 Elemental Analysis

The copolymer 2, 4-DHP-1,5-DANF-IV has been analyzed for carbon, hydrogen and nitrogen contents. The empirical formula and empirical formula weight has been evaluated based on the analytical data and is presented in the Table-1.The values of percentage of elements determined are in good agreement with calculated values.

Table 1: Elemental analysis and empirical formula of copolymer resin

Copolymer resins	% of Carbon observed calculated	% of Hydrogen observed calculated	% of Nitrogen observed calculated	Empirical formula of repeat unit	Empirical formula of repeat unit
2,4-DHP-1,5-DANF-IV	69.08 70.02	6.01 5.70	6.67 5.32	$C_{62}H_{60}N_4O_{12}$	1052

3.2 UV-Visible Spectra

The UV spectra of the copolymer 2,4-DHP-1,5-DANF-IV is shown in Figure-2. The spectrum of resin has been scanned in pure DMSO in the region 190-800 nm. The spectrum exhibits two characteristics absorption maxima in the region 280 nm and 330 nm. The observed position of absorption bands indicate the presence of carbonyl group (>C=O) having carbon-oxygen double bond which is in conjugation with aromatic nucleus. The appearance of more intense band can be accounted for π→π* transition while the less intense band may be due to n→π* electronic transition. The shift from basic value (viz. 240 nm and 310 nm respectively) may be due to combined effect of conjugation and phenolic hydroxyl group (auxochrome) [14].

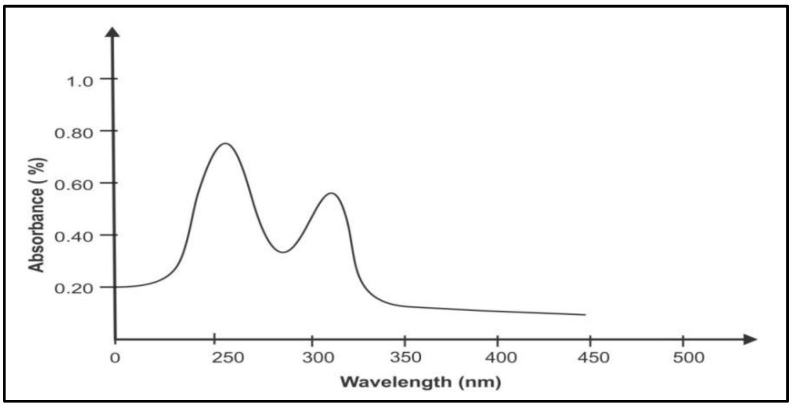

Figure 2: UV-visible spectra of 2,4-DHP-1,5-DANF-IV copolymer resin

3.3 FT-IR Spectra

The FT-IR spectra of 2,4-DHP-1,5-DANF-IV copolymer is shown in Figure-3. The band appeared at 3284 cm^{-1} may be due to the stretching vibration of phenolic hydroxyl group exhibiting intramolecular hydrogen bonding. The sharp and strong band observed at 1626 cm^{-1} may be on account of stretching vibration of carbonyl group (Ar-CO group). The medium band in the region 2978 cm^{-1} suggest the –NH- group in naphthalene moiety.

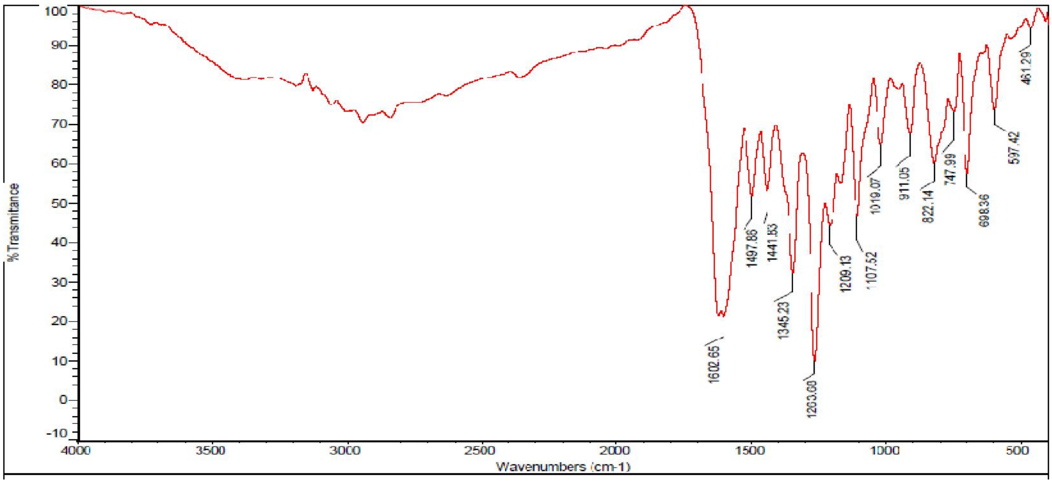

Figure 3: FT-IR-Spectra of 2,4-DHP-1,5-DANF-IV copolymer resin

The presence of methylene vibration has been indicated by the band at 2938 cm^{-1}. A weak band observed at 1455 cm^{-1} indicates the presence of >C=C< (aromatic) group. The sharp and strong band appeared at 1373cm^{-1} suggested the presence of –CH_2- methylene bridge in copolymer chain [15, 16].

3.4 ^{1}H-NMR Spectra

The ^{1}H-NMR spectra of 2,4-DHP-1,5-DANF-IV is shown in Figure 4. NMR spectra shows weak multiplicity signal at 6.4 (δ) ppm which is due to aromatic protons (Ar-H). A singlet signal appeared in the region 7.1(δ) ppm is due to the phenolic -OH proton in intramolecular hydrogen bonding. The methyl proton of Ar-CO-CH_2-CH_3 is recognized by the triplet signal in the region 1.1 (δ) ppm. The quartet signal appeared at 2.9 (δ) ppm reveals the presence of methylenic proton of Ar-CO-CH_2-CH_3 group. The proton of methylenic bridge Ar-CH_2-NH- may be identified as doublet signal observed at 2.6 (δ) ppm. The triplet signal in the region 7.6 (δ) ppm may be due to proton of –NH- bridge (amido) of copolymer chain [17, 18].

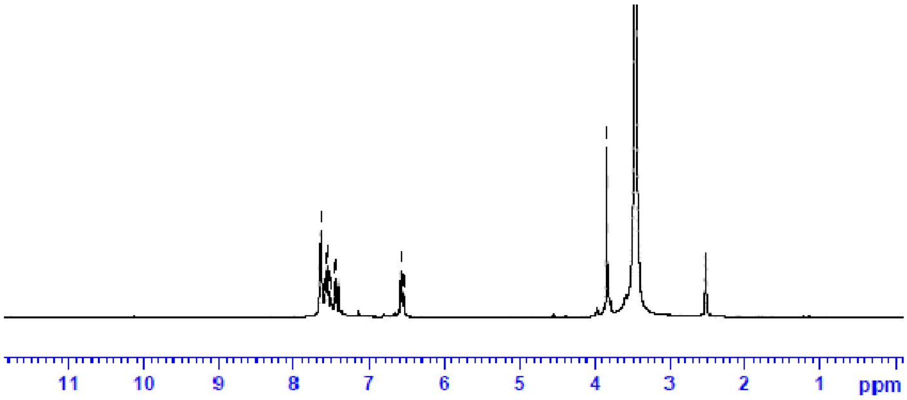

Figure 4: H^1-NMR-spectra of 2,4-DHP-1,5-DANF-IV copolymer resin

3.5 Electrical Conductivity of 2, 4-DHP-1, 5-DANF-IV Resin

The temperature dependence of the electrical conductivity of the copolymer is shown in Figure 5.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.

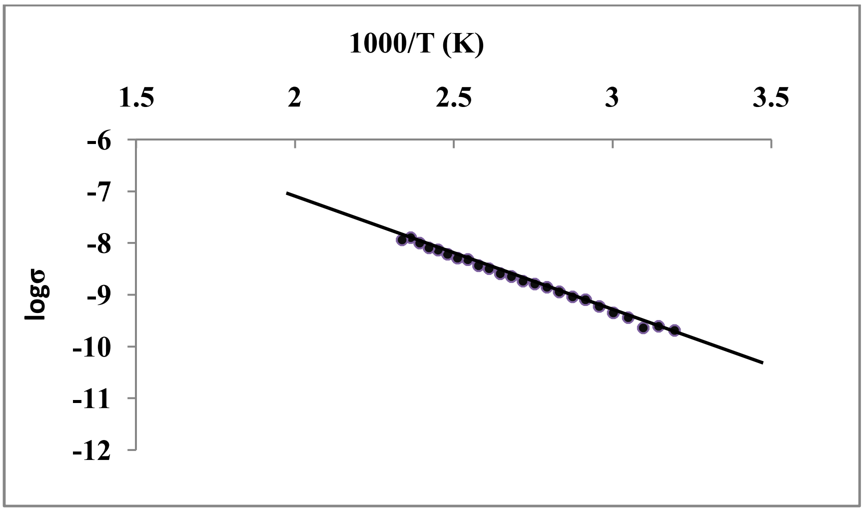

Figure 5: Electrical Conductivity Plot of 2, 4-DHP-1, 5-DANF-IV Resin

The 2,4-DHP-1,5-DANF-IV copolymer shows the electrical conductivity in the range of 2.05×10^{-10}- 1.15×10^{-8} 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 6.48×10^{-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. This is in good agreement with the most probable structure proposed for the newly synthesized resin under investigation [19].

IV. CONCLUSION

The data of elemental analysis, UV-Visible, FT-IR spectra, ^{1}H - NMR spectra, supports to the above tentative structure of 2,4-DHP-1,5-DANF-IV resin. Electrical conductivity of the copolymer resin increases with increase in temperature (2.05×10^{-10}- 1.15×10^{-8} $ohm^{-1}cm^{-1}$). The low activation energy of conduction (6.48×10^{-20}J/K) of resin may be due to presence of large number of delocalized π-electrons in the copolymer chain. The plot of log σ versus1/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.

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