Electrical Conductance Properties of a Copolymer Resin Derived From 4-Hydroxyacetophenone and Catechol

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Abstract– The copolymer resin 4-HACF has been synthesized by the condensation of 4-hydroxyacetophenone (4-HA) and catechol (C) with formaldehyde (F) in 2:1:3 molar ratios in presence of 2 M hydrochloric acid as catalyst. Scanning electron microscopy (SEM) was used to determine the surface features of the resin. UV-Visible, IR and proton NMR spectral studies have been carried out to elucidate the structure of the resin. Electrical conductivity measurements have been carried out to ascertain the semiconducting nature of the copolymer resin. The electrical properties of 4-HACF copolymer were measured over a wide range of temperature (313-428K), activation energy of electrical conduction has been evaluated and plot of log s vs 103/T is found to be linear over a wide range of temperature, which can be ranked it as semiconductor. This remarkable property of this copolymer resin may be used to make a wide range of semiconducting and electronic devices such as transistors, light emitting diodes, solar cells and even lasers which can be manufactured by much simpler way than conventional inorganic semiconductors.

Key Words - **Copolymers, Resin, Electric conductivity**

I. INTRODUCTION

The copolymers are well known for their behavior as semiconductors. Semiconductor materials are the foundation of modern electronics, including radio, computers, telephones, and many other devices. Such devices include transistors, solar cells, many kinds of diodes including the light-emitting diode, the silicon controlled rectifier, and digital and analog integrated circuits. Although a variety of conjugated organic molecules are known as semiconductors, the carrier mobility in them is usually low. This is due to the difficulties in, which electrons jumps form one molecule to another and hence, the carrier mobility in the compound of this type increases with increasing molecular size. The synthesized polymer resins showing versatile applications and properties attracted the attention of scientists and introduce the recent innovations in the polymer chemistry. These polymers can be used as high energy material [1], ion-exchanger [2], semiconductors [3], antioxidants [4], fire proofing agent [5], optical storage data [6], binders [7], molding materials, [8] etc. The semiconducting properties of polymer resins have gained sufficient ground in recent years. The work on organic conducting polymers is carried out extensively due to their wide applications in areas such as chemically modified electrodes, sensors etc [9,10]. An industrially useful semiconducting material has been reported by Dewar et al. [11]. The conductivity of an 8-hydroxyquinoline-oxamide-formaldehyde polymer resins has been reported over a wide range of temperature [12]. Pal et al. [13] has reported electrical conductivity of salicylic acid-biuret/dithio-oxamide / dithiobiurettrioxane polymer resins. Masram D. T. and coworkers reported the conducting polymers predicted to be the futuristic materials for the development of light emitting iodes, antistatic and EMI materials, sensors, optoelectronic devices and rechargeable batteries due to their unique conduction mechanism and greater environmental stability [14]. Since delocalized electrons and conjugation impart semiconducting properties to compounds, the present study deals with synthesis, structural characterization of a new copolymer synthesized from 4-hydroxyacetophenone, catechol with formaldehyde and its electrical conductivity measurement study.

II-EXPERIMENTATION

Starting Materials
The chemicals such as 4-hydroxyacetophenone and catechol were purified by rectified spirit, formaldehyde (37%), metal chlorides and nitrates (AR grade, Merck) were used. All other solvents and the indicators were of the analytical grade procured from India. Standardized disodium salt of EDTA was used as a titrant for all the complexometric titrations.

Synthesis of copolymer resin
The resin 4-HACF-II was prepared by the condensation polymerization of 4-hydroxyacetophenone (0.2mol) and catechol (0.1mol) with formaldehyde (0.3mol) in hydroxychloric acid medium at $124\pm2^{o}C$ in an oil bath for 5h under refluxed condition with occasional shaking. The solid product obtained was immediately removed from the flask as soon as the reaction

period was over. It was washed with cold water, dried and powdered. The powder was repeatedly washed with hot water to remove excess of 4-hydroxyacetophenone-catechol-formaldehyde resin, which might be present along with the 4-HACF-II copolymer resin.

The dried resin was further purified by dissolving in 8% NaOH and regenerated in 1:1 (v/v) HCl/H$_2$O. This process was repeated twice to separate the pure polymer. The resulting polymer resin washed with boiling water and dried in vacuum at room temperature. The purified copolymer resin was finally ground well and kept in a vacuum over silica gel. The yield of the copolymer was found to be 86 % and the reaction route for the synthesis is shown in Fig. 1.
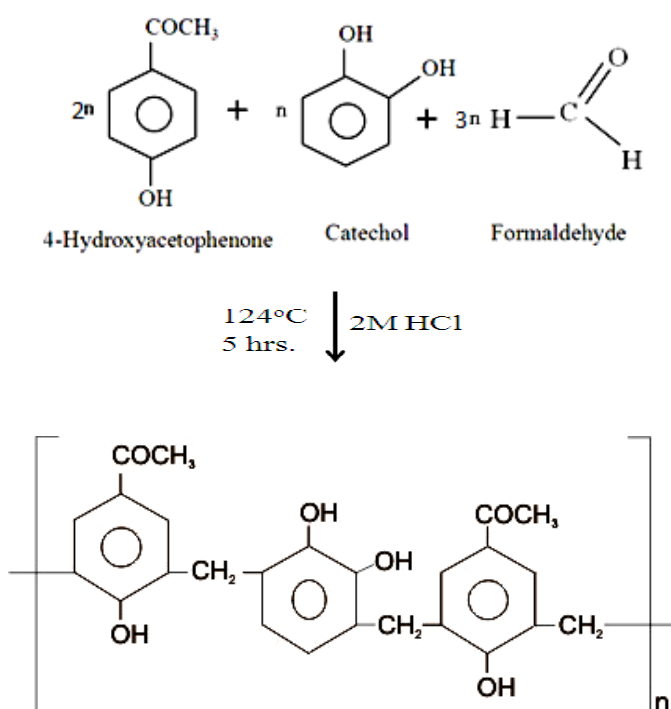

Fig. 1 Formation and suggested structure of 4-HACF-II copolymer resin

III- CHARACTERIZATION OF COPOLYMER RESIN

Physicochemical and elemental analysis

The copolymer resin was subject to micro analysis for C, H and N on an Elementer Vario EL III Carlo Ebra 1108 elemental analyzer. The number average molecular weight $\left(\overline{Mn}\right)$ was determined by conductometric titration in DMSO medium using ethanolic KOH as the titrant by using 25 mg of sample. A plot of the specific conductance against the milliequivalents of KOH requires for neutralization of 100 g of polymer was made. Inspection of such a plot revealed that there were many breaks in the plot. From this plot, the first break and the last break were

noted. The calculation of $\left(\overline{Mn}\right)$ by this method is based on the following consideration. On the basis of average degree of polymeration, $\overline{DP}$ the average molecular weight has to be determined by following equation.

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

$$\overline{Mn} = \overline{DP} \times \text{Repeat unit weight.}$$

The intrinsic viscosity was determined using a Tuan-Fuoss viscometer [15] at six different concentrations ranging from 0.3 to 0.05 wt% of resin in DMF at 30^{0}C. Intrinsic viscosity (n) was calculated by the Huggin's equation [16] and Kraemer's equation. [17].

$$[\eta_{sp}/c] = [\eta] + K_1[\eta]^2.C$$

$$\ln [\eta_r/c] = [\eta] - K_2[\eta]^2.C$$

Spectral Analysis

An infra-red spectrum of 4-HACF-II polymer resin was recorded in the region 4000 to 400 cm^{-1} were scanned in KBr pellet on Perkin Elmer Model 983 spectrophotometer at Sophosticated Analytical Instrument Facility, Panjab University, Chandigarh.Electron absorption spectra of copolymer (4-HACF-II) were recorded in 200 to 800 nm range by using Shimadzu automatic recording double beam spectrophotometer (UV-VIS-NIR Spectrometer) UV-240 at Sophisticated Analytical Instrument Facility, Punjab University; Chandigarh having 10 nm optical paths supplied with the instruments was used. A Nuclear Magnetic Resonance (^{1}H NMR) spectrum of newly synthesized polymer resin has been scanned on 90 MHz for proton using Bruker Avance II 400 NMR Sepctrometer in deuterated dimethyl sulphoxide (DMSO-d$_6$) at Sophisticated Analytical Instrumentation Facility, Panjab University, Chandigarh. Scanning electron micrograph of polymer has been scanned and magnification by scanning electron microscope at Sophisticated Test and Instrumentation Centre, STIC, Cochin University, Cochin.

Electrical conductivity

The electrical resistivity of copolymer resins was measured in a suitable sample holder designed for the purpose, in the temperatures range (i.e. from 313 to 428 K) by applying constant voltage across the pellets prepared from copolymer resins. The measurements involved following steps.

Preparation of Pellets for Resistance Measurements

First copolymer resins was dried and thoroughly ground in agate pestle and mortar and then pelletalized isostatically in a steel die at 10 tones/inch^2 with the help of hydraulic press. A thin layer of colloidal graphite in acetone was applied on both sides of the pellets and dried at room temperature for 6 hrs. The colloidal graphite on either side of pellet functioned as electrode. The surface continuity of the pellet was then tested by means of multimeter.

Measurement of dimension of the pellet

The average diameter of this pellet and its thickness were measured using Travelling Microscope (comparator type). Actual dimensions were measured as average of the three measurements taken at three places.

Sample Holder

A simple spring loaded sample holder was fabricated using brass electrodes. The prepared pellet of resin was mounted between the two brass electrodes, one of which was spring loaded while other electrode rested on the brass platform.

Furnace for Heating the Sample

For resistivity measurements at different temperatures a small furnace was used. The current supplied to the furnace was recorded by means of AC ammeter and controlled by a rheostat. To ensure a uniform temperature inside the furnace, a thin metal cylinder was inserted into it. The temperature of the furnace was recorded by means of Alumel- chromel thermocouple connected with digital multimeter in which millivolts were measured. The connection wires of two electrodes which were insulated with porcelain beads were taken out for connections.

Measurement of Electrical Resistivity

The resistance of the pellet was measured on BPL-India Million Megohmmeter RM 160 MK IIIA. The connection wires from the furnace were connected to the terminals of the instrument. In this way corresponding resistance of the pellet was measured directly by keeping the pellet in sample holder. Resistivity (σ) was then calculated using the relation as below.

$$\sigma = Rx \frac{A}{l}$$

The electrical conductivity (σ) varies exponentially with the absolute temperature according to well known relationship,

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

This relation has been modified as,

$$\text{Log } \sigma = \log \sigma_0 + \frac{-Ea}{2.303 \times k \times T}$$

According to this relation, a plot of log σ Vs l/T would be linear with negative slope. From the slopes of the plots, the activation energy (Ea) of electrical conduction was calculated.

RESULTS AND DISCUSSION

The copolymer resin 4-HACF-II was dark brown in color and soluble in solvents like N,N-dimethylformamide (DMF), tetrahydrofuran (THF), dimethylsulphoxide (DMSO), aqueous sodium and potassium hydroxide solutions and insoluble in alcohol, chloroform and carbon tetrachloride. The melting point of resin is 487K and empirical formula of the terpolymer resin is found to be $C_{25}H_{22}O_6$ which is in good agreement with the calculated values of C, H and O. The molecular weight of terpolymer resin was also determined by conductometric titration. The calculated molecular weight for 4-HACF-II resin is 3620.

Electronic Spectral Analysis

The UV-Visible spectra of the 4-HACF-II copolymer resin in pure DMF were recorded in the region 200-800 nm. The spectra have shown in Fig 2. The UV-Visible spectra of 4-HACF-II copolymer resin gave rise to two characteristic bands at about 200 to 250 nm and 290 to 360 nm. These observed positions for the absorption bands clearly indicate the presence of carbonyl group in the sample belonging to 4-dihydroxyacetophenone moiety. The former band (more intense) appeared as a result of $\pi \rightarrow \pi$*[18] transition while the latter band (less intense) may be due to n$\rightarrow \pi$* [19] electronic transition.
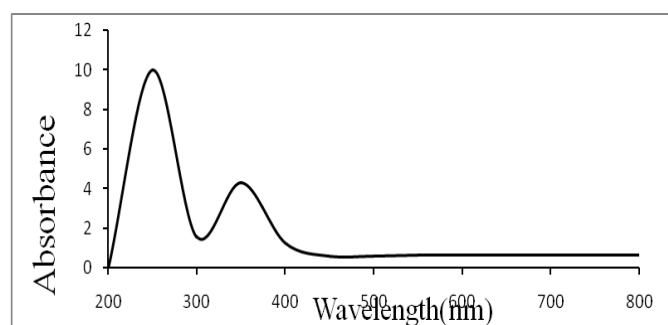

Fig. 2 Electronic spectra of 4-HACF-II copolymer resin

Infra-Red Spectral Analysis

The IR spectra of 4-HACF-II copolymer resin are presented in Fig. 3. A broad band appeared in the 3252 (b) cm^{-1} may be assigned to the stretching vibration of phenolic hydroxyl (-OH) group exhibiting intermolecular hydrogen bonding [20]. The sharp and weak band obtained at 1198 (w) cm^{-1} suggests the presence of Ar-CH$_2$-Ar bridge in polymer. The sharp strong peak at 1441(s) cm^{-1} may be ascribed to aromatic skeletal ring

[20]. The bands obtained at 1279 cm^{-1} suggest the presence of methylene (-CH$_2$) bridge [21]. The sharp band displayed at 1658 cm^{-1} may be due to stretching vibration of carbonyl group attached to acetophenone moity. The 1,2,3,5 substitution of aromatic benzene ring recognized by the sharp, medium / weak absorption and appeared at 562(st), 779(s), 977(s) and 1017(m) cm^{-1} respectively. This band seems to be merged with very broad band of phenolic hydroxyl group [20,21].
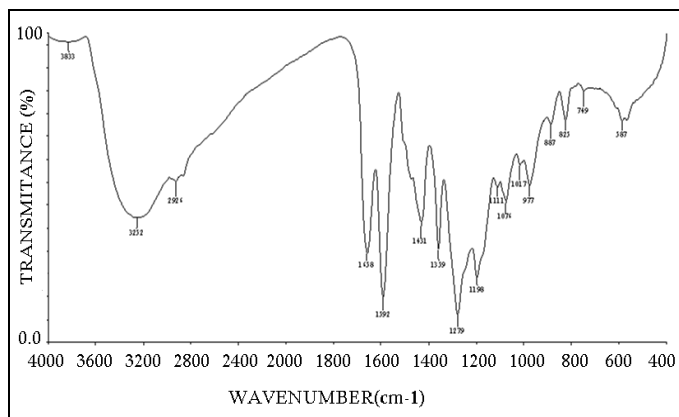

Fig. 3 Infra-red spectra of 4-HACF-II copolymer resin

^{1}H NMR Spectral Analysis

The NMR spectra of 4-HACF-II is presented in Fig. 4. The singlet obtained in the region 2.24 (δ) ppm may be due to the methylene proton of Ar-CH$_2$-Ar bridge [22]. The weak multiple signals (unsymmetrical pattern) in the region of 7.74(δ) ppm may be attributed to aromatic proton (Ar-H) [23]. The signals in the 8.09 (δ) 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 [24]. The signal appeared in the region at 3.79(δ) ppm is due to the methylene proton of Ar-CH$_2$ bridge [25]. The methyl protons of the Ar - CO - CH$_3$ moiety may be identified by the intense peak at 3.22(δ) ppm.
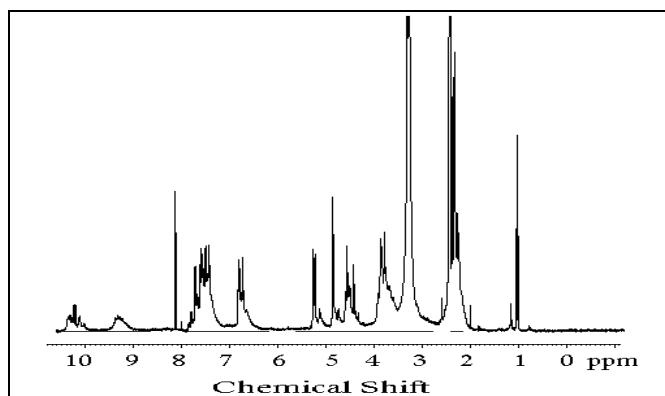

Fig. 4 ^{1}H NMR spectra of 4-HACF-II copolymer resin

Scanning electron microscopy (SEM)

The scanning electron micrograph of 4-HACFI copolymer resin have been scanned and magnification by analytical scanning electron microscope at Sophisticated Test and Instrumentation Centre, STIC, Cochin University, Cochin as shown in the Fig.5. Surface analysis has found great use in understanding the surface features of the polymers. SEM gives the information of surface topology and defect in the structure. The semi crystalline nature of 4-HACF copolymer resin was established by scanning electron microscopy. The morphology of resin sample thus identified by SEM as crystalline as well as amorphous or transition between crystalline and amorphous, showing more or less good ion capacity. The polymerization reaction proceeds by introducing amorphous character in the copolymer sample.
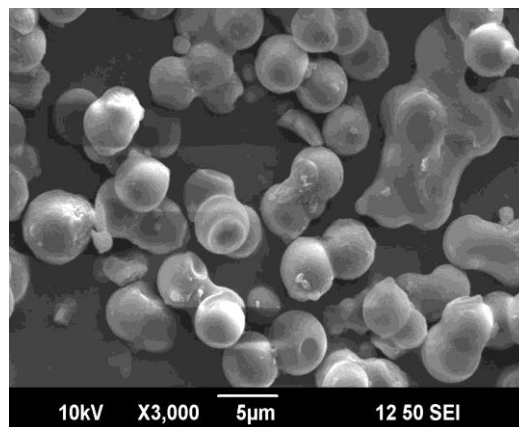

Fig. 5 Scanning electron microscopy of 4-HACF-II copolymer resin

Electrical Conductivity

The DC resistivity of 4-HACF-II copolymer resin was measured in the temperature range of 313 to 428^0 K by applying a constant voltage (50 volts) across the pellet. The temperature dependence of the electrical conductivity of these tercopolymers is plotted in Fig.6. From the result of electrical conductivity data following conclusions are drawn.

1) The electrical conductivity of 4-HACF-II copolymers at room temperature lies in the range of 3.2 x 10^{-10} to 4.4 x 10^{-9} Siemen [26].

2) The plots of log σ versus l/T is found to be linear in the temperature range under study, which indicate that Wilson's exponential law $\sigma = \sigma_0 \exp (\Delta E/kT)$ is obeyed.

3) The energy of activation (Ea) of electrical conduction calculated from the slopes of the plots is found to be 10.14 x 10^{-20} J/K.

4) Electrical conductivity of resin increases with increase in temperature. Hence, 4-HACF-II copolymer resin may be ranked as semiconductor.

The resistance of polymeric sample depends upon uncalculated parameters [27]. Such as porosity, pressure, method of preparation, atmosphere etc., but these parameters is not affect the activation energy and therefore it is fairly reproducible [28]. The magnitude of activation energy depends on the number of π – electrons present in the semiconducting material. More the number of π – bond lower is the magnitude of energy of activation (Ea) and vice-versa. Generally polymers containing aromatic nuclei in the backbone exhibit lower activation energy than those of aliphatic structure. Thus, the low magnitude of activation energy may be due to the presence of large number of π – electrons.
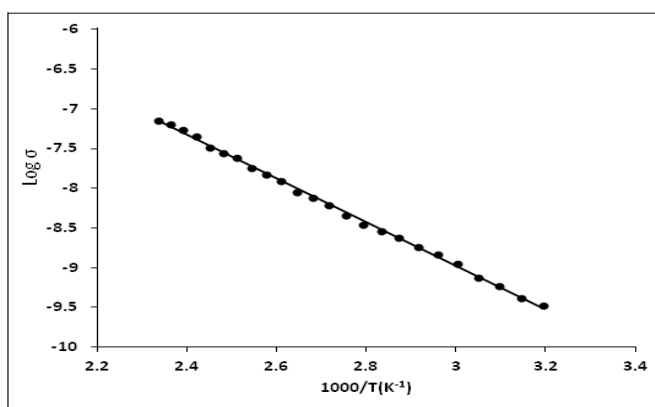

Fig. 6 Electrical conductivity of 4-HACF-II copolymer resin

CONCLUSION

A tercopolymer resin 4-HACF-II based on the condensation reaction of 4dihydroxy acetophenone and catechol with formaldehyde in the presence of acid catalyst was prepared in molar ratios 2:1:3. From the results of electrical conductivity of copolymer, electrical conductivity of 4-HACF-II copolymer at room temperature lies in the range of 3.2×10^{-10} to 4.4×10^{-9} ohm^{-1} cm^{-1}. The plots of log σ vs 1000/T was found to be linear in the temperature range under study $\sigma = \sigma_0 \exp (\Delta E/kT)$ is obeyed. . Electrical conductivity of each of resin increases with increase in temperature. Hence, these copolymers may be ranked as semiconductors. The concerted research effort was carried out to aim at developing organic materials that would possess the good electrical properties as the inorganic semiconductors. The resistance of the polymeric material depends upon incalculable parameters such as porosity, pressure, methods of preparation, atmosphere etc., but these parameters do not affect the activation energy and therefore, it is fairly reproducible. Also from the FTIR and ^{1}H NMR spectral studies the proposed structure of the 4-HACF-II copolymer resin has been determined.

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