ELECTRICAL CONDUCTANCE STUDIES OF NEWLY SYNTHESIZED COPOLYMER RESINS DERIVED FROM DITHIOOXAMIDE AND 2,4-DIHYDROXY BENZOIC ACID.

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ABSTRACT

Copolymer resins have been synthesized by reacting 2,4-dihydroxy benzoic acid with dithiooxamide and formaldehyde in presence of 2M HCl as catalyst, proved to be semiconducting in nature. The electrical properties of DBDF-1, DBDF-2, HDBDF-3 and HDBDF-4 copolymer were measured over a wide range of temperature (313-423K). From the electrical conductivity of these copolymers, activation energies of electrical conduction have been evaluated and values lies in the range 3.76×10^{-8}- 4.45×10^{-8} J/K. The plots of log σ vs $10^3/$ T are found to be linear over a wide range of temperature, which indicate that the Wilson's exponential law $\sigma = \sigma_o \exp (Ea/kT)$ is obeyed. On the basis of above studies these copolymers can be ranked as semiconductors.

INTRODUCTION

Semiconducting studies of copolymer resins have gained sufficient ground in recent years. Electrically conducting copolymer 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. In fact, their conductivity and other properties such as thermoconduction, photoconduction, luminescence, etc in close connection with their physical and chemical structure. In this connection, studies were made to establish a correlation between the chemical structure and characteristics defining semiconducting properties[1].

Work on organic conducting polymers is carried out extensively due to their wide applications[2], in areas such as chemically modified electrodes, sensors etc. Pekaln and Kolosonov[3] have studied the electrical conductivity of phemol-formaldehyde resin. An industrially useful semicdonducting materials has been reported by Dewar et al[4]. The conductivity of a 8-hydroxyquinoline-oxamide-formaldehyde terpolymer resins have been reported over a wide range of temperature[5]. Pal et al.[6-8] have reported electrical conductivity of salicylic acid-biuret/dithiooxamide/dithiobiuret-trioxane terpolymer resins. Patel and Manavalan[9] reported the electrical properties of p-hydroxybenzoic acid-thiourea trioxane terpolymers. The electrical resistivity of 2-hydroxyacetophenoneoxime-thiourea trioxame resin were reported and these polymers are ranked as semiconductors[10]. Since delocalized electrons and conjugation impart semiconducting properties to compounds, the present study deals with electrical properties of some terpolymer resins which may serve as potential semiconductors. The electrical properties of 2,4-dihydroxyacetophenone-dithioxamide-formaldehyde copolymer have been studied by Rahandale et al.[11]

EXPERIMENTAL

Chemicals

All the chemicals used were of A.R or chemically pure grade. 2,4-dihydroxy benzoic acid (Ranbaxy Fine Chemicals, Dithiooxamide (Merck India) and formaldehyde (37%) (Qualigence fine chemicals, Mumbai) was used as received.

Synthesis of copolymer resin

The new copolymer resin DBDFF-I was synthesized by condensing 2,4-dihydroxy benzoic acid and dithiooxamide with 37% formaldehyde (7.5 ml) in a mol ratio of 1:1:2 in the presence of 2M 200 ml HCI as a catalyst at 120°C ± 2°C for 6h in an oil bath with occasional shaking to ensure thorough mixing[11]. The separated brown copolymer resin was washed with hot water and methanol to remove unreached monomers. The properly washed resin was dried, powdered and then extracted with diethyl ether and then with petroleum ether

to remove unreached monomers which might be present along with DBDF-copolymer.

The copolymer was purified by dissolving in 8% 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 copolymer sample DBDF-thus obtained was filtered, washed several times with hot water, dried in air, powdered and kept in vacuum desicator over silica gel. The yield of the copolymer resin was found to be 90%.

Conductivity Measurements :

The electrical conductivity of copolymer resins was measured over a wide range of temperature (311-420K) in their pellets form using Million-Megohmmerter, Model RM-160IIIA, BPL, India and Universal bridge TF-2700. The instrument could read and measure upto 10 MΩ to 10^5 MΩ and 0.1 MΩ to 10 MΩ respectively. Test voltage is varied from 50 to 500 volts in electrical conductivity measurements.

To prepare the pellets, the purified copolymer resins was thoroughly ground with an agate pestle and mortar. The powdered sample was pass through a 300 mesh size sieve. The well powdered copolymers was pelletalized isostatically in a steel die at 5 t/cm^2 with the help of a hydraulic press. Pellets of 1.73 cm in diameter and nearly 0.4 cm thickness were prepared. The pellet of the test sample was put in a typical sample holder fabricated in this laboratory and resistance was measured using conductivity bridge over wide range of temperature.

For this purpose, the sample pellet was heated in a tubular furnace in which D.C. conductivity cell snugly fitted, the temperature of the furnace being increased by steps from room temperature to about 423 K and regulated by using Dimmerstat and sunvic dial.

During the DC. conductivity measurements several errors crop in grain boundaries are developed during compression, metallic particles of the die may

get adhered to during pelletisation or these may be an imperfect contact of the electrodes to the pellet due to slight deformation during pellet formation. In the present work another applied several compression cycles before taking the final results of the conductivity measurements and only limiting values were chosen as standard. The metallic particles, possible adhered to the pellet, were gently removed by scrapping the pellet with stainless steel blade as to not disturb the physical dimensions of it. On both sides of the pellets, a thin layer of colloidal graphite in acetone was applied to ensure a good contact with the electrodes. Care was also taken not to apply very high voltages to avoid any leakage's across the border.

Results and Discussion

The thermal activation energy and the values of electrical conductivity at different temperatures are given in Table 1. The resistance values of the pellets of the copolymers ranging from 311 K to 420 K were converted into conductivity values (σ) by taking into account the thickness of the pellet and its diameter and evaluating thickness area parameters of the pellet of a particular copolymer. Generally the diameter of the pellet remained constant (1.73 cm) since the same die was used and the thickness varied from 0.418 to 0.428 cm according to the amount of sample present. The temperature dependence of the electrical conductivity of the copolymers are shown in Fig. 1. In the electrical conduction domain, the temperature dependence of the electrical conductivity obeys the well known equation[12].

$$\sigma = \sigma_0 \exp^{(\Delta E/kT)}$$

where,

k = Boltzmann constant

σ_0 = electrical conductivity at temperature $T \to \infty$

σ = electrical conductivity at temperature T.

ΔE = thermal activation energy electrical conduction.

This relation has been modified as Electrical Properties of …. copolymers.

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

According to this relation, a plot of log σ Vs. 1000/T would be linear with a negative slope. The result of the D.C. conductivities are presented here in the form of plots of log σ Vs. 1000/T for each set of data, as the range of conductivities was found to be 1.82×10^{-8} to 1.97×10^{-11} ohm^{-1} cm^{-1}.

It will be seen from the plots (Fig. 1) of copolymers that there is a consistent increase in electrical conductivity as the temperature rises roughly from 311 K to 420 K. These trend is a characteristic of semiconduction[13]. The activation energies were determined from the curves log σ Vs. $(10^3/ T)$. The temperature dependence of the electrical conductivity in pellet of all the terpolymers is of the same type. The plot of log σ Vs. $10^3/ T$ are found to be linear (Fig.1) over wide range of temperature which indicates the semiconducting nature of copolymers.

From the analysis of our results it can be assumed that the difference in electrical properties of copolymers studied are mainly by their chemical structure[14], over the whole temperature range the values of the electrical conductivity vary between 1.82×10^{-8} to 1.97×10^{-11} ohm^{-1} cm^{-1}. The activation energy increased in the order DBDF-1 < DBDF -2 < DBDF -3 < HDBDF -4. The conductivities are in the order of 10^{-8} to 10^{-11} ohm^{-1} cm^{-1} due to comparatively small intra intermolecular charge transfer of copolymers[15]. The nature of conduction (n or p type) in the copolymers investigated could not be established because of lack of instrumentation for measuring Hall-Coefficients and the difficulty in getting the copolymers as well defined crystals.
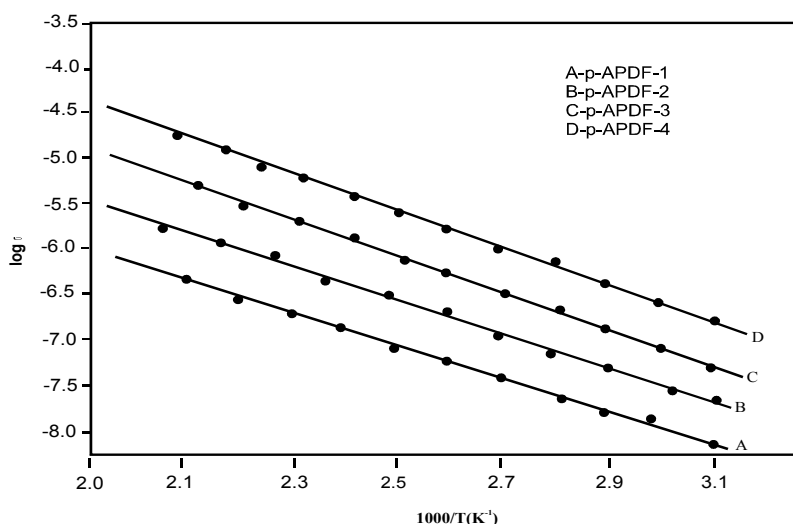
Table 1

Table 1. Electrical Conductivity Data of DBDF Copolymers

Sr. No.	Copolymers	Electrical Conductivity		ΔT (K)	ΔE (J/K)
		311 K	420 K		
1.	DBDF -1	1.82×10^{-8}	8.48×10^{-7}	313 - 423	3.45×10^{-10}
2.	DBDF -2	1.76×10^{-8}	7.82×10^{-7}	313 - 423	3.19×10^{-10}
3.	DBDF -3	1.64×10^{-8}	7.75×10^{-7}	313 - 423	2.80×10^{-10}
4.	DBDF -4	1.59×10^{-8}	6.36×10^{-7}	313 - 423	2.76×10^{-10}

CONCLUSIONS

From the results of electrical conductivity of these copolymers the following conclusions can be drawn :

1. The electrical conductivity of DBDF copolymers at room temperature lies in the range of $1.54 \times 3.82 \times 10^{-8}$ to 4.97×10^{-8} Siemen.

2. The plots of log σ vs 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.

3. Electrical conductivity of each of these copolymer resins increases with increase in temperature. Hence, these copolymers may be ranked as semiconductors.

4. The energy of activation is found to decrease in the order: DBDF -1 > DBDF -2 > DBDF -3 > DBDF -4 and electrical conductivity is found to increase in the order : DBDF -1 < DBDF -2 < DBDF -3 < DBDF -4. The resistance of the polymeric material depends upon incalculable parameters[16] such as porosity, pressure, method of preparation, atmosphere etc., but these parameters do not affect the activation energy (ΔE) and therefore, it is fairly reproducible[17]. The magnitude of activation energy depends on the number of π-electrons present in the semiconduc ting material. The more the number of π-bonds, the lower 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. Moreover, the

increasing order of electrical conductivity and decreathg order of activation energy of electrical conductivity as shown above may be due to introduction of more and more aromatic skeleton (and therefore and more π- electrons) in the structure of repeat unit of copolymers, which is in good agreement with the most probable structure proposed for the newly synthesized p-APDF copolymer resins under study. The nature of conduction (n or p type) in the copolymers investigated could not be established because of lack of instrumentation for measuring Hall-coefficients and the difficulty in getting the copolymers as well defined crystals.

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