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ELECTRICAL PROPERTIES OF ORGANIC POLYMERS DERIVED FROM 2-HYDROXY-4-METHOXYBENZOPHENONE, 1, 5-DIAMINO NAPHTHALENE AND FORMALDEHYDE

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ABSTRACT

The organic polymer 2-hydroxy 4-methoxybenzophenone (DMB) -1,5-diaminonaphthalene (DAN) - formaldehyde (F) were synthesized by the condensation of 2-hydroxy 4-methoxybenzophenone and 1,5-diaminonaphthalene with formaldehyde in the presence of a hydrochloric acid catalyst with varied molar ratios of reacting monomers. Electrical conductivity measurements have been carried out to ascertain the semiconducting nature of the terpolymer resin. The electrical properties of DMBDANF-I, DMBDANF -II, DMBDANF -III and DMBDANF -IV polymers were measured over a wide range of temperature (314-425 K). From the electrical conductivity of these terpolymers, activation energies of electrical conduction have been evaluated and values lies in the range 15.86 x 10^{-20} – 16.44 x 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 indicate that the Wilson's exponential law $\sigma = \sigma_0 \exp\left(-\frac{E_a}{KT}\right)$ is obeyed. On the basis of above studies, these terpolymers can be ranked as semiconductors.

Key words: Electrical phoperties, Organic polymers.

INTRODUCTION

Electrical conducting 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. The terpolymers are well known for their behavior as semiconductors. 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.

Electrical conductivity measurements have been carried out to ascertain the semiconducting nature of the terpolymer resin by Dhanraj. T. Masram et al.[1] Extensive research work has been carried out on synthesis and characterization of terpolymers in our laboratory[2,3]. The terpolymers offer novelty and versatility; hence they occupy the pivotal position in the field of material science. The progress in the field

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terpolymers has been extremely rapid, as they generally useful in packaging, adhesives and coatings in electrical sensors and organ metallic semiconductors. Some other applications have been reported in the field of activators, ion exchangers, catalyst and thermally stable materials. Semiconductors are the most important ingredients of modern electronics. The terpolymer resins are well known for their behavior as semiconductors though carrier mobility in them usually is very low. Kanda et al.[4] reported the rubeanato-copper semi conductive polymers and studied their AC and DC conductivity. Dhawan and coworkers[5] 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. Pal et al.[6] have reported electrical conductivity of salicylic acid - biuret / dithiooxamide / dithiobiuret – trioxane terpolymer resins.

EXPERIMENTAL

Material

All the chemicals used were of analytical reagent grade. DMBDANF polymers were synthesized by condensing 2-hydroxy 4-methoxybenzophenone,1,5-diaminonaphthalene and formaldehyde in the mole ratios of 1 : 1 : 2, 2 : 1 : 3, 3 : 1 : 4 and 4 : 1 : 5, respectively, in the presence of 2 M HCl as a catalyst at 126^0C for 6h as described elsewhere[7]. All organic polymers are soluble in DMF, THF and DMSO, however, these are insoluble in common organic solvents. The electrical conductivity of polymers were measured over a wide range of temperature (303-423 K) in their pellets form using Million-Megohmmeter, Model RM-10 IIIA, BPL, Indian and Universal Bridge TF-2700. The instrument could read and measure up to 0.1 L to 106 ML and test voltage varied from 50-500 volts; the accuracy being at the lower range + 5 %. To prepare the pellets, the terpolymer was thoroughly ground with an agate pestle and mortar. The well powdered terpolymer was pelletalized isostatically in a steel die at 5 t/cm^2 with the help of a hydraulic press. Pellets of 1.25 cm in diameter and nearly 0.12 to 0.14 cm thickness were prepared. The pellet of the test sample was put in a typical cell fabricated in this laboratory and resistance in Megaohms was measured as a function of temperature. The sample was heated in a tabular furnace in, which D. C. conductivity cell is 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 D. C. conductivity measurements, several errors crop in as grain boundaries are developed during compression, metallic particle of the die may get adhered to pellet during pelletisation or there may be an imperfect contact of the electrodes to the pellet due to slight deformation during pellet formation. On both sides of the pellets, a thin layer of colloidal graphite in acetone was applied and the pellets were dried at room temperature in vacuum for 6 h. Care was also taken not to apply very high voltages to avoid any leakage across the border.

RESULTS AND DISCUSSION

All the samples were subjected to a thermal treatment consisting in some successive heating and cooling over a certain temperature range. This treatment was used to stabilize the structure of the sample, when the temperature dependence of the electrical conductivity becomes reversible. In order to obtain some information regarding the structure modifications, which takes place during the thermal treatment, the temperature dependence of the electrical conductivity has been studied. The resistance values of the pellets of the terpolymers ranging from 303 K to 423 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 terpolymer. Generally, the diameter of the pellet remained constant (1.25 cm) since the same die was used and the thickness varied from 0.12-0.14 cm according to the amount of sample present. The temperature dependence of the electrical conductivity of the terpolymers is shown in Fig 1. In the electrical conduction domain, the temperature dependence of the electrical conductivity obeys the well known equation (1) –

$$\sigma = \sigma_0 \exp. \left(-\frac{E_a}{KT} \right) \quad \ldots(1)$$

where

σ = Electrical conductivity at temperature T.

σ_0 = Electrical conductivity at room temperature

Ea = Activation energy of electrical conduction.

k = Boltzmann Constant (0.8625×10^{-4} ev. deg^{-1} or 1.3817×10^{-23} J. $mol.^{-1}K^{-1}$).

T = Absolute temperature.

This relation has been modified as –

$$\text{Log } \sigma = \log \sigma_0 - \frac{E_a}{2.303\, KT} \quad \ldots(2)$$

According to this relation, a plot of log σ vs 1/T would be linear with 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 2.72×10^{-08} to 1.44×10^{-12} $ohm^{-1}cm^{-1}$.

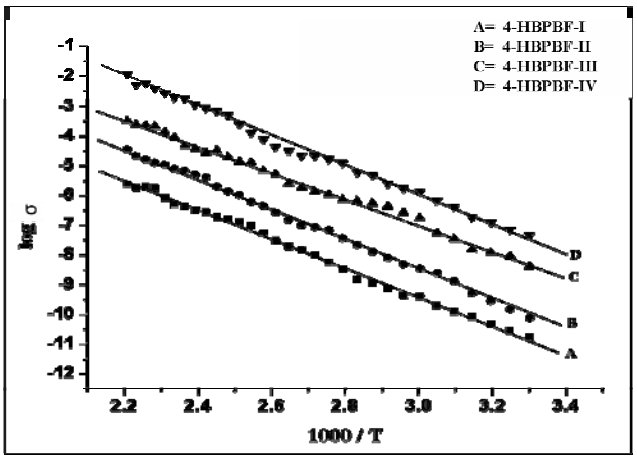

Fig. 1: Electrical conductivity plots of DMBDANF polymer resins

It will be seen from the plots (Fig. 1) of terpolymers that there is a consistent increase in electrical conductivity as the temperature rises roughly 305 K to 425 K. This trend is a characteristic of semiconduction[13]. The activation energies were determined from the curves log σ vs 1000/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 1000/T are found to be linear (Fig. 1) over a wide range of temperature, which indicates the semiconducting nature of terpolymers.

From the analysis of our results, it can be assumed that the differences in electrical properties of terpolymers studied are mainly by their chemical structure14. Over the whole temperature range, the values of the electrical conductivity vary between 2.72×10^{-08} to 1.44×10^{-12} ohm^{-1} cm^{-1}. The activation energy increased in the order DMBDANF-I < DMBDANF-II < DMBDANF-III < DMBDANF-IV. The conductivities are in the order of 10^{-03} to 10^{-12} $ohm^{-1}cm^{-1}$due to comparatively small intra intermolecular charge transfer of terpolymers[8].

Table 1: Electrical conductivity data of DMBDANF polymers

Polymers	Electrical conductivity		ΔT (K)	ΔE (J/K)
	303 K	423 K		
DMBDANF-I	1.44×10^{-12}	3.72×10^{-07}	303-423	16.443×10^{-20}
DMBDANF-II	2.49×10^{-11}	6.23×10^{-06}	303-423	16.243×10^{-20}
DMBDANF-III	2.36×10^{-09}	1.33×10^{-04}	303-423	16.023×10^{-20}
DMBDANF-VI	2.72×10^{-08}	3.40×10^{-03}	303-423	15.864×10^{-20}

CONCLUSION

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

(i) The electrical conductivity of DMBDANF polymers at room temperature lies in the range of 2.72 x 10-08 to 1.44 x 10-12 Siemen.

(ii) The plots of log σ vs 1000/T were found to be linear in the temperature range under study, which indicate that the Wilson's exponential law $\sigma = \sigma_0 \exp(-\frac{\Delta E}{KT})$ is obeyed.

(iii) Electrical conductivity of each of these terpolymer resins increases with increase in temperature. Hence, these terpolymers may be ranked as semiconductors.

(iv) The energy of activation is found to decrease in the order : DMBDANF -I > DMBDANF -II > DMBDANF -III > DMBDANF -IV and electrical conductivity is found to increase in the order: DMBDANF -I < DMBDANF -II < DMBDANF -III < DMBDANF -IV.

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 (ΔE) and therefore, it is fairly reproducible. The magnitude of activation energy depends on the number of π-electrons present in the semiconducting material. The more is the number of π-bonds, the lower is the magnitude of activation energy and vice-versa. Moreover, the increasing order of electrical conductivity and decreasing 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 terpolymers, which is in good agreement with the most probable structure proposed for the newly synthesized 4-HBPBF terpolymer resins under study.

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