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Semiconducting Studies of 8-Hydroxyquinoline-Biuret-Formaldehyde Terpolymer Resins

WASUDEO B. GURNULE*, H.D. JUNEJA† and L.J. PALIWAL‡
Department of Chemistry
Kamla Nehru College, Nagpur-440 009, India

Terpolymer resins (8-HQBF) have been prepared by the condensation of 8-hydroxyquinoline and biuret with formaldehyde in the presence of acid catalyst and using varied molar ratios of reacting monomers. The electrical properties of 8-HQBF-1, 8-HQBF-2, 8-HQBF-3 and 8-HQBF-4 terpolymer resins have been studied over a wide range of temperature (313 to 423 K). From the electrical conductivity of these terpolymer resins, activation energies of electrical conduction have been evaluated and values lie in the range 14.1×10^{-20} to 19×10^{-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 $\sigma = \sigma_0 \exp(E_a/kT)$ is obeyed. On the basis of the above studies these terpolymers can be ranked as semiconductors.

INTRODUCTION

The semiconducting properties of terpolymer resins have gained sufficient ground in recent years. Electrically conducting terpolymers are undoubtedly one of the focal points of current interest in solid state physics and chemistry. Their discovery has led to the emergence 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. are in close connection with their physical and chemical structures. In this connection, studies were made to establish a correlation between the chemical structure and characteristics defining semiconducting properties[1].

Perkin and Kotosonov[2] have studied the electrical conductivity of phenol-formaldehyde resin. An industrially useful semiconducting material has been reported by Dewar *et al.*[3] The conductivities of 8-hydroxyquinoline-oxamide-formaldehyde terpolymer resins have been reported over a wide range of temperature[4]. Pal *et al.*[5–7] have reported electrical conductivity of salicylicacid-biuret/dithiooxamide/dithiobiuret-trioxane terpolymer resins. Patel and Manavalan[8] reported the electrical properties of *p*-hydroxybenzoic acid-thiourea-triox-

†Department of Chemistry, Nagpur University, Nagpur-440 010, India.
‡Department of Chemistry, Hislop College, Nagpur-440 001, India.

ane terpolymers. The electrical resistivities of 2-hydroxyacetophenone- oxime-thiourea-trioxane resins have been reported and these polymers are ranked as semiconductors[9]. Since delocalised electrons and their conjugation impart semi-conducting properties to compounds, the present study deals with electrical properties of some terpolymer resins which may serve as potential semiconductors.

EXPERIMENTAL

The chemicals used were all of AR or chemically pure grade. 8-HQBF terpolymers were synthesized by condensing 8-hydroxyquinoline, biuret and formaldehyde in a mole ratio of 1 : 1 : 2, 2 : 1 : 3, 3 : 1 : 4 and 4 : 1 : 5 in the presence of 2M HCl as a catalyst at 130°C for 8 h as described elsewhere[10]. All the terpolymers in the form of yellow coloured powders were found to be insoluble in common organic solvents.

The electrical conductivities of terpolymer resins were measured over a wide range of temperature (313–423 K) in their pellet form using Million Megohmmeter, Model RM-160 IIIA, BPL, India and Universal Bridge TF-2700. The instrument could read and measure up to 10 MΩ to 10^6 MΩ and 0.1 Ω to 10 MΩ respectively. Test voltage is varied from 50 to 500 volts in electrical conductivity measurements.

To prepare the pellets, the purified terpolymer resins were thoroughly ground with an agate pestle and mortar. The powdered sample was passed through a 300 mesh size sieve. The well powdered terpolymers were pelletized isostatically in a steel die at 5 t/cm^2 with the help of a hydraulic press. Pellets of 1.2 cm diameter and nearly 0.2 to 0.3 cm thickness were prepared. A pellet of the test sample was put in a typical simple holder fabricated in this laboratory and resistance was measured using conductivity bridge over a 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 D.C. conductivity measurements several errors creep in. Grain boundaries are developed during compression; metallic particles of the die may get adhered to pellets during pelletisation or there may be an imperfect contact of the electrodes to the pellet due to slight deformation during pellet formation. In the present work we applied several compression cycles before taking the final results of the conductivity measurements and only limiting values were chosen as standard. The metallic particles, possibly adhered to the pellet, were gently removed by scrapping the pellet with a stainless steel blade so as not to disturb the physical dimensions. On both sides of the pellets, a thin layer of colloidal graphite in acetone was applied to ensure good contact with the electrodes. Care was also taken not to apply very high voltages to avoid any leakages across the border.

RESULTS AND DISCUSSION

The thermal activation evergy and the values of electrical conductivity at different temperatures are given in Table-1. The resistance values of the pellets of the terpolymers ranging from 313 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 (1.270 cm) since the same die was used and the thickness varied from 0.250 to 0.290 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 equations.[11]

$$\sigma = \sigma_0 \exp(-\Delta E/kT)$$

where

k = Boltzmann constant

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

σ = electrical conductivity at temperature T

ΔE = thermal activation energy of electrical conduction

This relation has been modified as

$$\log \sigma = \log \sigma_0 + (-\Delta E/2.303\,kT)$$

TABLE-1
ELECTRICAL CONDUCTIVITY DATA OF 8-HQBF TERPOLYMERS

No.	Terpolymers	Electrical Conductivity, S		ΔT	ΔE
		313 K	423 K	(K)	(J/K)
1.	8-HQBF-1	1.428×10^{-11}	5.400×10^{-7}	313–423	19.00×10^{-20}
2.	8-HQBF-2	5.889×10^{-11}	1.030×10^{-6}	313–423	15.80×10^{-20}
3.	8-HQBF-3	3.722×10^{-10}	1.142×10^{-6}	313–423	14.60×10^{-20}
4.	8-HQBF-4	1.381×10^{-9}	7.799×10^{-5}	313–423	14.10×10^{-20}

According to this relation, a plot of log σ *vs.* 1000/T would be linear with a negative slope. The results of the D.C. conductivities are presented here in the form of plots of log σ *vs.* 10^3/T for each set of data, as the range of conductivities was found to be 7.238×10^{-6} to 1.428×10^{-11} ohm^{-1} cm^{-1}.

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 from 313 to 423 K. This trend is a characteristic of semiconduction[12]. The activation energies were determined from the curves log σ *vs.* (10^3/T). The temperature dependence of the electrical conductivity in pellets of all the terpolymers is of the same type. The plots of log σ *vs.* 10^3/T are found to be linear (Fig. 1) over a wide range of temperatures which indicates the semiconducting nature of terpolymers.

From the analysis of our results it can be assumed that the difference in

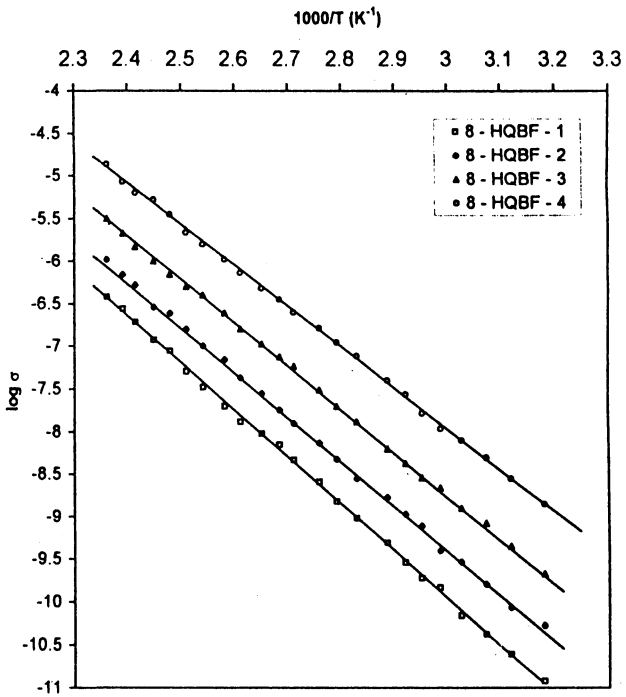

Fig. 1. Electrical conductivity plots of 8-HQBF terpolymer (temperature dependence of log σ)

electrical properties of terpolymers studied is mainly due to their chemical structure[13]; over the whole temperature range the values of electrical conductivity vary between 7.799×10^{-5} to 1.428×10^{-11} ohm^{-1} cm^{-1}. The activation energy increases in the order 8-HQBF-1 < 8-HQBF-2 < 8-HQBF-3 < 8-HQBF-4. The conductivities are in the order of 10^{-6} to 10^{-11} ohm^{-1} cm^{-1} due to comparatively small intra- and intermolecular charge transfer of terpolymers[14]. The nature of conduction (n or p type) in the terpolymers investigated could not be established because of lack of instrumentation for measuring Hall coefficients and the difficulty in getting the terpolymers as well defined crystals.

Conclusion

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

1. The electrical conductivity of 8-HQBF terpolymers at room temperature lies in the range of 1.4×10^{-11} to 1.38×10^{-9} siemen.
2. The plot of log σ *vs.* 1/T is found to be linear in the temperature range under study, which indicates that Wilson's exponential law $\sigma = \sigma_0 \exp(-\Delta E/kT)$ is obeyed.
3. Electrical conductivity of each of these terpolymer resins increases with increase in temperature. Hence, these terpolymers may be ranked as semiconductors.

4. The energy of activation is found to decrease in the order 8-HQBF-1 > 8-HQBF-2 > 8-HQBF-3 > 8-HQBF-4 and electrical conductivity is found to increase in the order: 8-HQBF-1 < 8-HQBF-2 < 8-HQBF-3 < 8-HQBF-4. The resistance of the polymeric material depends upon uncalculable parameters[15] 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[16]. The magnitude of activation energy depends on the number of π-electrons present in the semiconducting 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 a 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 decreasing order of activation energy of electrical conductivity as shown above may be due to introduction of more and more aromatic skeleton (and therefore more 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 8-HQBF terpolymer resins under study. The nature of conduction (n or p type) in the terpolymers investigated could not be established because of lack of instrumentation for measuring Hall-coeffi-cients and the difficulty in getting the terpolymers as well defined crystals.

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