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D. C. ELECTRICAL CONDUCTIVITY AND ACTIVATION ENERGY OF p-CRESOL-MELAMINE-FORMALDEHYDE TERPOLYMERS

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ABSTRACT

Terpolymers were synthesized by the condensation of p-cresol (p-C) and melamine (M) with formaldehyde (F) in the presence of 2M HCl as catalyst with varied molar ratios of reacting monomers. The electrical properties of p-CMF-1, p-CMF-2, p-CMF-3 and p-CMF-4 terpolymers were measured over a wide range of temperature (313-423 K). From the electrical conductivity of these terpolymers, activation energies of electrical conduction have been evaluated and these values lies in the range 6.36 x 10^{-20} – 8.23 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 $\sigma = \sigma_o$exp. (Ea/kT) is obeyed. On the basis of above studies, these terpolymers cab be ranked as semiconductors.

Key words : Synthesis, Resins, Terpolymer, Semiconductor, Conduction.

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 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. have 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].

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Work on organic conducting polymers is carried out extensively due to their wide applications[2], in areas such as chemically modified electrodes, sensors etc. Pekain and Kolosonov[3] have studied the electrical conductivity of phenol-formaldehyde resin. An industrially useful semiconducting material has been reported by Dewar and Talati[4]. The conductivity of 8-hydroxyquinoline-oxamide-formaldehyde terpolymer resins have been reported over a wide range of temperature[5]. Pal and Kharat[6-8] have reported electrical conductivity of salicylic acid-biuret/dithiooxamide/dithibiuret-trioxane terpolymer resins. Patel and Manavalan[9] reported the electrical properties of p-hydroxybenzoic acid-thiourea trioxane terpolymers. The electrical resistivities of 2-hydroxyaceto-phenoneoxime-thioureatrioxane 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.

EXPERIMENTAL

All chemical used all of A. R. or chemically pure grade and procured from the market and whenever necessary, the purity was checked by standard method.

Synthesis of terpolymers

Terpolymers (p-CMF) were synthesized by condensing p-cresol, melamine and formaldehyde in a mole ratio of 1 : 1 : 3, 2 : 1 : 4, 3 : 1 : 5 and 4 : 2 : 7 in the presence of 2M HCl as a catalyst at 130°C for 5 hrs as described earlier[11]. All the terpolymers in the form of cream colored powders were found to be insoluble in common organic solvents; however, these are soluble in DMF, DMSO and THF.

Conductivity measurements

The electrical conductivity of terpolymer resins was measured over a wide range of temperature (313-423 K) in their pellets form using Million-Megohmmeter, Model RM-160 III A, BPL, India and Universal Bridge TF-2700.The instrument could read and measure up to 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 terpolymer resins were thoroughly ground with the help of an agate pestle and mortar. The powdered sample was passed through a 300 mesh size sieve. The well powdered terpolymers were pelletalized isostatically in a steel die at 5 t/cm^2 with the help of a hydraulic press. Pellets of 1.2 cm in diameter and nearly

0.2 to 0.3 cm thickness were prepared. The pellet of the test samples 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 was snugly fitted. The temperature of the furnace being increased by steps from room temperature to about 423 K and regulated by using dimmer stat and sunvic dial.

During the D. C. conductivity measurement, several errors crop in grain boundaries are developed during compression, metallic particles of the die may get adhered to 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, another applied several compression cycles before taking the final results of the conductivity measurements as standard. The metallic particles, possibly 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 leakages 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 terpolymers ranging from 313 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 (1.3 cm) since the same die was used and the thickness varied from 0.241 to 0.261 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[12].

$\sigma = \sigma_o \exp^{(\Delta\_E/kT)}$

Where,

k = Boltzmann constant

σ_o = Electrical conductivity at temperature $T \rightarrow \infty$

σ = Electrical conductivity at temperature T

ΔE = electrical conductivity energy of electrical conduction.

$$\log \sigma = \log \sigma_o + \frac{-\Delta E}{2.30\,kT}$$

Table 1 : Electrical conductivity data of p-CMF terpolymer resins

Terpolymers	Electrical conductivity (Ω^{-1} cm^{-1})		T (K)	E (J/K)
	313 K	423 K		
p-CMF - 1	4.41×10^{-11}	3.53×10^{-7}	313 - 423	8.27×10^{-20}
p-CMF - 2	3.03×10^{-10}	3.95×10^{-6}	313 - 423	7.63×10^{-20}
p-CMF - 3	3.55×10^{-9}	2.99×10^{-5}	313 - 423	7.01×10^{-20}
p-CMF - 4	2.45×10^{-8}	2.78×10^{-4}	313 - 423	6.36×10^{-20}

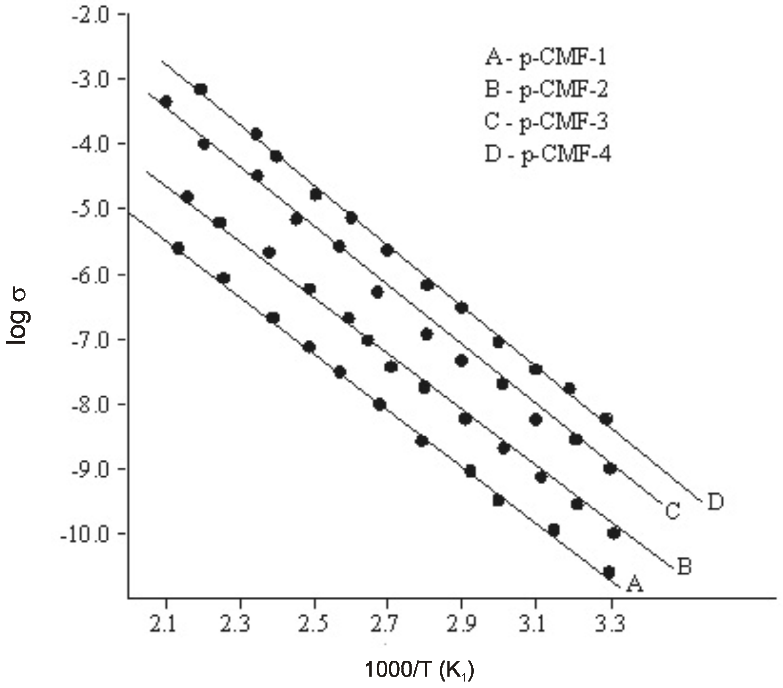

Fig. 1 : Electrical conductivity plots of p-CMF terpolymer resins (Temperature dependence of log σ)

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 2.78×10^{-4} to 4.49×10^{-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 K to 423 K. This 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 (Fig. 1) over wide range of temperature, which indicates the semiconducting nature of terpolymers.

From the analysis of our results, it can be assumed that the difference in electrical be assumed that the difference in electrical properties of terpolymers studied are mainly by their chemical structure[14]. Over the whole temperature range, the values of the electrical conductivity vary between 2.73×10^{-4} to 4.49×10^{-11} ohm^{-1} cm^{-1}. The activation energy increased in the order p-CMF-4 < p-CMF-1 < p-CMF-3 < p-CMF-4. The conductivities are in the order of 10^{-4} to 10^{-11} ohm^{-1} cm^{-1} due to comparatively small intra intermolecular charge transfer of terpolymers[15].

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.

CONCLUSIONS

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

(i) The electrical conductivity of p-CMF terpolymers at room temperature lies in the rang of 4.49×10^{-11} to 2.45×10^{-8} Siemen.

(ii) 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.

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

The energy of activation is found to decrease in the order : p-CMF-1 > p-CMF-2 > p-CMF-3 > p-CMF-4 and electrical conductivity is found to increase in order : p-CMF-4 > p-CMF-3 > p-CMF-2 > p-CMF-1.The resistance of the polymeric material depends upon incalculable parameters[16] 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[17]. 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. 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 decreasing order of activation energy of electrical conductivity as shown above may 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 p-CMF 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-coefficients and the difficulty in getting the terpolymers as well defined crystals.

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REFERENCES

1. L. Gautman and O. L. E. Lyons., Organic Semiconductors, John Wiley, New York (1967).
2. E. M. Genies, A. A. Syed and C. Tsintavis, Mol. Cryst. Liq. Cryst., **121**, 181 (1985).
3. L. A. Perkin and A. S. Kotaosonow, Konstr. Materosn Grafita, **8**, 122 (1974).
4. J. S. Dewar and A. M. Talati, J. Am. Chem. Soc., **86**, 1592 (1964).
5. J. S. Lingala, L. J. Paliwal and H. D. Juneja, National Seminar on Polymers, Chennai, **21** (1999).
6. T. K. Pal and R. B. Kharat, Die. Angew. Micromole. Chemise, **173**, 55 (1989).

7. T. K. Pal and R. B. Kharat, Indian J. Chem., **28A**, 55 (1989).
8. T. K. Pal and R. B. Kharat, J. Indian Chem. Soc., **55**, 2785 (1989).
9. M. M. Patel and R. J. Manavalan, Micromole. Sci. Chem., **19**, 951 (1983).
10. H. B. Pancholi and M. Patel, J. Indian Chem. Soc., **75**, 86 (1998).
11. R. N. Singru, A. B. Zade and W. B. Gurnule, J. Appl. Chem., **109**, 859 (2008).
12. M. M. Patel, M. A. Kapadia and G. P. Joshi, J. Appl. Polym. Sci., **106**, 1307 (2007).
13. L. Paradeshi, A. Rasheed and R. A. Bhobe, J. Indian Chem. Soc., **57**, 388 (1980).
14. M. Spiratos and G. I. Rusr, A. Airinei and A. Ciobana, Die Angew. Micromole. Chemie., **107**, 33 (1982).
15. G. Maneeks and R. Wille, Micromole. Chem., 133 (1970).
16. C. D. Sabane, A. P. Sinha and A. B. Biswas, Indian J. Pune Appl. Phys., **4**, 187 (1966).
17. W. V. Dunlop, An Introduction to Semiconductors, Wiley, New York (1957) p. 189.

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