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Synthesis and semiconducting studies of 2-Hydroxyacetophenone-formaldehyde-melamine copolymers

R. H. Gupta[a] and W. B. Gurnule[b*]

[a]Department of Chemistry, K.Z.S. Science College, Kalmeshwar, Nagpur, India.
[b,*]Department of Chemistry, Kamla Nehru Mahavidyalaya, Sakkardara Square, Nagpur – 440 009, India

Abstract

Copolymers were synthesized by condensation of 2-hydroxyacetophenone (2-HA) and melamine (M) with formaldehyde (F) in the presence of 2 M HCl as catalyst with varied molar ratios of reacting monomers. The electrical properties of 2-HAFM-I, 2-HAFM -II, 2-HAFM -III and 2-HAFM -IV copolymers were measured over a wide range of temperature (303-423 K). From the electrical conductivity of these copolymers, activation energies of electrical conduction have been evaluated and values lies in the range 7.38 x 10^{-20} – 6.52 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 $\sigma = \sigma_0 \exp^{(-\Delta E/kT)}$ is obeyed. On the basis of above studies, these copolymers can be ranked as semiconductors.

Keywords: Resin, synthesis, electrical conductivity

INTRODUCTION

The semiconducting properties of copolymer resins have gained sufficient grand in recent years. Electrically conducting copolymers 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 thermo conduction, photoconduction, luminescence, etc. are 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]. Pal et al. [2] have reported electrical conductivity of salicylic acid-biuret / dithiooxamide / dithiobiuret-trioxane terpolymer resins. Gurnule W. B. et. al. [3-5] have reported semiconducting studies of 8-hydroxyquinoline- melamine/biuret–formaldehyde terpolymer resins. Borole and co-workers [6] synthesized and characterized the poly (aniline-co-o-anisidine-co-o-toluidine) this films in inorganic and organic supporting electrolytes. The influence of inorganic and organic supporting electrolytes on electrochemical, optical properties of terpolymer thin films has been investigated. The films were characterized by conductivity measurements using four-probe technique. Borkar et. al. [7, 8] studied electrical and optical properties of conducting copolymer: poly (aniline-co-n-ethylaniline) and poly (aniline-co-m-methylaniline). The products have been characterized by solubility, spectroscopyc method, and electrical conductivity measurement. The conductivity of copolymers decreases with increasing N-ethylaniline content.

EXPERIMENTAL

Material

Melamine and 2-hydroxyacetophenone were used as received from SRL, Mumbai, India.. Formaldehyde (37 %) (Qualigens Fine Chemicals, Mumbai, India) was used as received. Solvents like N, N'-dimethyl formamide and dimethyl sulphoxide were used after distillation.

Synthesis of Copolymers

2-HAFM copolymers were synthesized by condensing 2-hydroacetophenone (2-HA) and melamine (M) with formaldehyde (F) in the mole ratios of 1:1:3, 2:1:4, 3:1:5, 4:2:7, respectively, in the presence of 2M HCl as a catalyst at 132 ± 2 ^{0}C in an oil bath for 5 h [9-12]. The cream coloured polymer obtained was washed with hot water and finally with ether to remove excess of acid monomer. The properly washed resin was dried, powdered and then extracted with diethyl ether and then with petroleum ether to remove 2-hydroxyacetophenone-formaldehyde copolymer which might be presents along with the 2-HAFM copolymer. It was further purified by dissolving in 10 % NaOH and then filtered. The copolymer was then reprecipitated by drop wise addition of 1:1 (v/v) conc. HCl / water with constant stirring and filtered. The method was repeated thrice. The resulting polymer sample was washed with boiling water and dried in a vacuum at room temperature. The purified copolymer was finely ground to pass through 300 mesh sieve and kept in a vacuum over silica gel. The yield of the copolymer was found to be about 72%. All copolymers are soluble in DMF, THF and DMSO; however, these are insoluble in common organic solvents. The resistance of copolymers was measured over a wide range of temperature (303-423 K) in their pellets form using Auto Comput LCR-Q meter 4910. The instrument could read and measure upto 0.1 ohm to 10^6 Megaohm and test voltage varied from 50-500 volts; the accuracy being at the lower range + 5 %. To prepare the pellets, the copolymer was thoroughly ground with an agate pestle and mortar. The well powdered copolymer was pelletalized isostatically in a steel die at 10 tones/inch^2 with the help of a hydraulic press. Pellets of 1.29 cm in diameter and nearly 0.13 to 0.16 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 Dimmer state 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 4-6 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 copolymers 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 copolymer. Generally, the diameter of the pellet remained constant (1.29 cm) since the same die was used and the thickness varied from 0.13-0.16 cm according to the amount of sample present. The temperature dependence of the electrical conductivity of the copolymers is shown in Fig. 1. In the electrical conduction domain, the temperature dependence of the electrical conductivity obeys the well known equation [13]

$$\sigma = \sigma_0 \exp^{(-\Delta E/\, kT)} \text{ -----------------------------------(1)}$$

Where, σ = Electrical conductivity at temperature T.
σ_0 = Electrical conductivity at temperature T O P
ΔE = Activation energy of electrical conduction.
K = Boltzmann Constant
T = Absolute temperature.

This relation has been modified as,

$$\log \sigma = \log \sigma_0 + (-\Delta E/\, 2.303\, k\, T) \text{--------------- (2)}$$

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 2.37×10^{-12} to 1.40×10^{-13} 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 303 K to 423 K.

This trend is a characteristic of semi conduction [14]. 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 copolymers 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 copolymers. From the analysis of our results, it can be assumed that the differences in electrical properties of copolymers studied are mainly by their chemical structure [15]. Over the whole temperature range, the values of the electrical conductivity vary between 2.37×10^{-12} and 1.40×10^{-13} $ohm^{-1}cm^{-1}$. The activation energy increased in the order 2-HAFM -I< 2-HAFM -II < 2-HAFM -III < 2-HAFM -IV. The conductivities are in the order of 10^{-13} to 10^{-14} $ohm^{-1}cm^{-1}$due to comparatively small intra intermolecular charge transfer of copolymers [16].

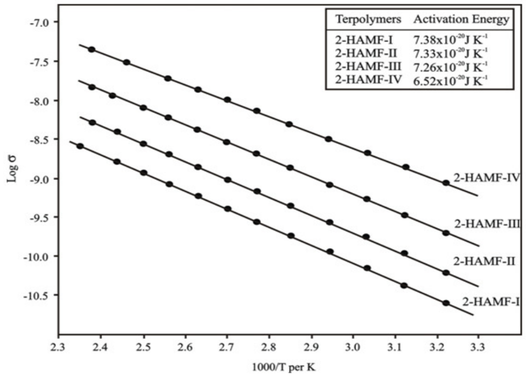

Fig 1. Electrical conductivity plots of 2-HAMF copolymers (Temperature dependence of log σ)

Table 1. Electrical conductivity data of 2-HAFM copolymers

Copolymers	Electrical conductivity		ΔT (K)	ΔE (J/K)
	303 K	423 K		
2-HAFM -I	1.49×10^{-13}	1.85×10^{-11}	303-423	7.3809×10^{-20}
2-HAFM -II	7.42×10^{-13}	5.46×10^{-11}	303-423	7.3366×10^{-20}
2-HAFM -III	1.41×10^{-12}	1.27×10^{-10}	303-423	7.2644×10^{-20}
2-HAFM -IV	2.37×10^{-12}	1.76×10^{-10}	303-423	6.5216×10^{-20}

CONCLUSIONS

The electrical conductivity of 2-HAFM copolymers at room temperature lies in the range of 1.49×10^{-13} and 2.37×10^{-12} Siemen [17]. 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 $\sigma = \sigma_0 \exp^{(-\Delta E/\, kT)}$ is obeyed. Electrical conductivity of each of these copolymer resins increases with increase in temperature. Hence, these copolymers may be ranked as semiconductors. The energy of activation is found to decrease in the order: 2-HAFM -I > 2-HAFM -II > 2-HAFM -III > 2-HAFM -IV and electrical conductivity is found to increase in the order: 2-HAFM -I < 2-HAFM -II < 2-HAFM -III < 2-HAFM - IV. The energy of activation (Ea) of electrical conduction calculated from the slopes of the plots is found to be in the range of 4.35×10^{-20} to 7.15×10^{-20} J/K.

The electrical conduction of the polymeric material depends upon uncalculable parameters [18] 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 [19-21]. 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 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 2-HAFM 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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