ELECTRICAL CONDUCTIVITY STUDY OF THERMALLY STABLE NEWLY SYNTHESIZED TERPOLYMER

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Abstract
The present paper reports the thermal and electrical conductivity study of a resin. The resin 4-hydroxyacetophenone ethylenediamine and formaldehyde (4-HAEDF-I)) was synthesized by the condensation of 4-hydroxyacetophenone and ethylenediamine with formaldehyde in the presence of a hydrochloric acid catalyst with molar proportion 1:1:2. The purity of newly synthesized terpolymer has been tested and confirmed by thin layer chromatography (TLC) technique. Terpolymer resin was characterized by elemental analysis, infrared (IR) spectroscopy, nuclear magnetic resonance (NMR) spectroscopy and UV-Visible spectral studies. The thermal decomposition behavior of 4-HAEDF-I terpolymer was studied using Freeman-Carroll and Sharp-Wentworth methods. Electrical conductivity measurements have been carried out to ascertain the semiconducting nature of the terpolymer resin. SEM studies of the terpolymer revealed the microporous structure and it is found to be biologically active.
Keywords: Synthesis, Terpolymer, Thermal and Electrical conductivity, SEM, antimicrobial activity.

I. Introduction

The use of terpolymers in all spheres of life has been abundantly increased in recent years because of novelty and versatility. They occupy the pivotal position in the field of polymer science. The progress in this field has been extremely rapid, as they are generally useful in packaging, adhesives and coatings in electrical sensors, ion-exchangers, organometallic semiconductors, activators, catalyst and thermally stable materials, high temperature flame-resistant fibers [1-12]. Due to global applications of polymeric materials polymer science and technology have been developing rapidly and attracted much attention of the polymer scientists. Varieties of researches regarding the thermal studies of polymers are emerging out to investigate their renewed applications for the betterment of mankind. Area of polymer reaction kinetics is enhanced by applying various model fitting kinetic equations in order to study its kinetic and thermodynamic aspects [13]. Much attention has been focused to synthesize the terpolymers by applying various synthetic techniques to examine its advanced applications. In the recent past, appreciable progress has been made in many ternary systems such as acrylonitrile-methylmethacrylate-methacrylic acid [14], methylmethacrylate-styrene-butadiene [15], acrylonitrile-methyl acrylate-itaconic acid [16], styrene-acrylonitrile-methyl- acrylate [17], butadiene-acrylonitrile-chlorocyclo-vinylketone [18], maleic anhydride terpolymers [19], 2,4-dihydroxyacetophenone-dithiooxamide-formaldehyde [20], and 8-hydroxyquinoline-guanidine-formaldehyde [21]. Shah *et al*. have reported the chelating ability of resin synthesized by a microwave irradiation technique involving salicylic acid and formaldehyde with resorcinol [22]. Patel and Manavalan [23] have prepared the terpolymer of salicylic acid p-hydroxybenzoic acid and thiourea with trioxane in presence of acid catalyst with different molar proportion of monomers. Jadhav *et al.* have reported the synthesis, characterization, and thermal degradation kinetics of copolymers derived

from 2,2'-dihydroxybiphenyl-formaldehyde [24], and terpolymer synthesized from 2,2'-dihydroxybiphenyl, urea, and formaldehyde [25]. Paik and Kar [26] studied the kinetics of thermal degradation and estimation of lifetime for polypropylene particles and its effect on particle size involving the use of single and multiple heating rate techniques. Electrical properties of p-hydroxybenzoic acid – thiourea – trioxane terpolymers was studied by Patel and Manavalan [27]. Perkin and Kotosonax have studied the electrical conductivity of phenol-formaldehyde resin [28].

The electrical properties of some polychelates of polymeric ligands which may serve as potential semiconductors was reported by Aswar and Bhave [29]. Dewar *et al*. reported an industrially useful semiconducting material [30]. Pal *et al*. reported electrical conductivity of salicylic acid-biurate / dithioxamide / dithibiurate-trioxane terpolymer resins [31-33].

II. Experimental

A. Materials

All the Chemicals used were of AR grade or chemically pure grade. 4- hydroxy acetophenone purchased from Aldrich Chemical, formaldehyde from Merck while DMF and DMSO (HPLC grade) were used.

B. Synthesis of Terpolymer Resins

A mixture of 4-hydroxyacetophenone (0.1 mol), ethylenediamine (0.1 mol) and formaldehyde (0.2 mol) in molar ratio of 1:1:2 in the presence of 2M (200 ml) HCl as a catalyst has been prepared in round bottom flask. The resultant mixture was refluxed over an oil bath for heating at 120ºC ± 2ºC for 5 hrs with occasional shaking to ensure thorough mixing. The temperature of oil bath was controlled electrically with the help of dimmerstat. The resinous yellowish solid mass obtained was immediately removed from the flask as soon as the reaction period was over. The separated terpolymer resin was washed with hot water and methanol to remove unreacted starting materials and acid monomers. The properly washed resin was dried, powdered and then extracted with ether to remove 4-hydroxyacetophenone-formaldehyde copolymer which might be present along with 4-HAEDF terpolymer and then it is purified. Excellent yield of terpolymer resin was obtained by the reaction given below. Terpolymer was characterized by IR, NMR and UV-Visible spectral studies [34].

Reaction Scheme

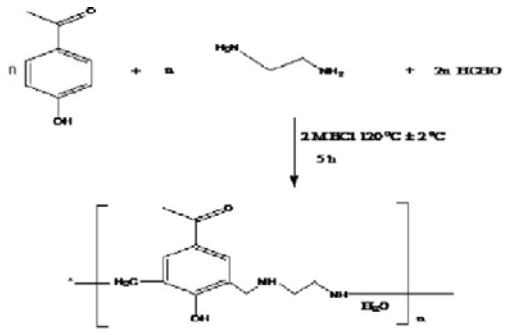

Fig. 1. Reaction Scheme for 4-HAEDF-I Terpolymer resin

2.3 Thermogravimetric analysis

The thermal method is associated with a change in weight with respect to temperature. Heating is performed under strictly controlled conditions and can revel changes in structure and other important properties of the material being studied. In non-isothermal or dynamic TGA the sample is subjected to conditions increase in temperature at linear rate.

2.4 Electrical Conductivity

Resin was palatalized and thin layer of colloidal graphite in acetone was applied on both sides of the pellets. The colloidal graphite on either side of pellets functioned as electrode. A typical sample holder was designed for the purpose of resistivity measurement and pellet is mounted on it. For measurement of resistivity at different temperature, a suitable electrical furnace was used. The temperature variations of resin was studied by placing the sample holder along with the pallet in the electric furnace that was then heated slowly. The resistances of the sample pallets were measured by two probes (terminals) method. Resistivity

(ρ) was then calculated using the relation: ρ = R. x A/l The DC resistivities were measured from 303 to 423 ^{0}K. The electrical conductivity (σ) varies exponentially with the absolute temperature according to the well-known relationship: σ = σ 0 exp –Ea/kT. The relationship has been modified as:

$$\text{Log } \sigma = \log\sigma 0 + -Ea/2.303kT$$

According to this relation, a plot of Log σ Vs 1/T would be linear with negative slope. From the Slope of the plots, the activation energy was calculated.

2.5 Antibacterial activities

Pure culture of pathogenic bacteria, viz., *Escherichia coli*, *Staphylococcus aureus*, *B. subtilis* and *Pseudomonas aeruginosa* were used for antibacterial activity. Agar diffusion method was used for antibacterial studies. Nutrient agar medium was used for culture of the bacteria. The composition was peptone (10.0 g), sodium chloride (10.0 g), yeast extract (5.0 g) and agar (20.0g) in 1000 ml of distilled water. Initially, the stock cultures of bacteria were revived by inoculating in broth media and grow at 37 ^{0}C for 18 hrs. The agar plates of the above media were prepared and wells were made in the plate. Each plate was inoculated with 18 hrs. Old cultures (100 µl, 10-4 cfu) and spread evenly on the plate. After 20 min the well were filled with of compound at different concentrations. The control wells with Gentamycin were also prepared. All the plates were incubated at 37^{0}C for 24 hrs and the diameter of inhibition zone was noted. Concentration of samples for antibacterial activity was taken as 800 µg/ml[35,36]. In order to explore antibacterial activity against *Escherichia coli*, *Staphylococcus aureus* and *Basillus subtilis. Pseudomonas aeruginosa*. Diameters of inhibition zone with respect to standard antibacterial drug (Gentamycin) were measured and results shown in table 3.

3 Results and Discussion

3.1 Solubility

The solubility of synthesized and purified terpolymer resin have been checked in various organic as well as in inorganic solvents. Resin found to be soluble in dimethyl sulphoxide (DMSO), concentrated aqueous NaOH and KOH.

3.2 Determination of Molecular weight

The molecular weight (Mn) of the terpolymer was determined by non-aqueous conductometric titration in DMF against ethanolic KOH by using 50 mg of sample. The resistance of solution was measured and a plot of the specific conductance against the miliequivalents of potassium hydroxide required for neutralization of 100g of terpolymer was made (Figure.2). Inspection of such a plot revealed that there were many breaks in the plot. From this plot the first break through and the last break were noted. The calculation of (Mn) by this method is based on the following considerations. The first break corresponds to neutralization by the more acidic phenolic hydroxyl group of all the repeating units; second break in the plot beyond which a continuous increase is observed represents the stage at which phenolic hydroxyl group of all the repeating units are neutralized.

The average degree of polymerization (DP), which is given by the following relation, is found to be the number average molecular weight (Mn) is 2975 which is obtained by multiplying the DP by the formula weight of the repeating unit.

$$\overline{DP} = \frac{\text{Total milliequivalents of base for complete neutralization}}{\text{Milliequivalents of base required for smallest intervals}}$$

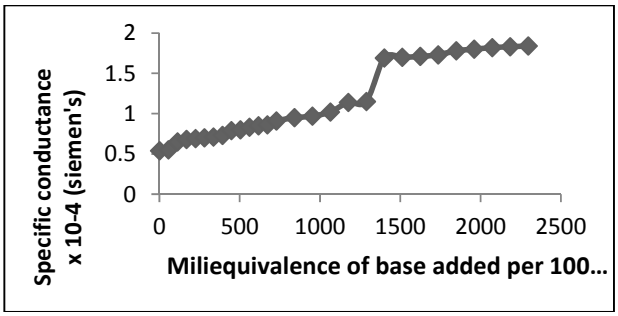

Fig. 2. Plot of the specific conductance against miliequivalents of potassium hydroxide

3.3 Thermogravimetric Analysis

The TGA and DTA analysis of the prepared terpolymer have been carried out in air atmosphere from room temperature to 1000 ^{0}C with a heating rate of 10 ^{0}C/min. for 4-HAEDF-I resins are shown in [Fig. 6 and Fig.7]. The results of thermogravimetric analysis of 4-HAEDF-I resin are tabulated in [Table. 1.] It is observed from TGA data of these resins that the sample lost 7.56 %. This weight loss may be due to loss of water of crystallization associated with terpolymer resins[15-17].

Thermogram of a 4-HAEDF-I shows two stage of decomposition after loss of water molecules. Second decomposition stage in case 4-HAEDF-I corresponds to loss of side chain attached to aromatic nucleus (-CH_2-NH-CH_2-CH_2-NH-,$COCH_3$,OH,-CH_2) and partial degradation of aromatic ring..In DTA curve second stage of decomposition of the terpolymer resin exhibit exotherm.

Third exothermic decomposition step of 4-HAEDF-I terpolymer resin corresponds to partial degradation of aromatic nucleus. The results of thermogravimetric analysis of resins and species degraded with their corresponding % mass loss are summarized in [Table. 1]. From the thermal decomposition data, thermal activation energy [Fig.3] and thermogravimetric parameters of all resins have been calculated. These values are incorporated in [Table. 2]. The activation energy calculated by using Sharp-Wentworth [Fig. 5] and Freeman-Carroll method [Fig.4] are in agreement with each other [Table. 2]. Thermogram of 4-HAEDF-I terpolymer resin depicts three stage of decomposition. The 4-HAEDF-I resin has one molecule of water associated with repeat unit of polymer. The thermal decomposition can be explained tentatively by considering one repeating unit of the terpolymer resin. The initial decomposition temperature is frequently used to define the relative thermal stability of terpolymer resin. From the abnormally low value of Z, it can be concluded that the reaction of decomposition of terpolymer can be classified as slow reaction and no other obvious reason can be given[11]. The negative value of [ΔS] indicate that the activated polymer has more ordered structure than the reactants and that the reaction are slower, than normal [18,19]. The decomposition of terpolymer is known to obey first-order kinetics but not perfectly, as by Shrivastava and Juneja [20].

Table.1 Results of Thermogravimetric Analysis of 4-HAEDF-I Terpolymer Resin

Terpolymers	Temperature Range (^{0}C)	Stage of Decomposition (DTA Peak)	Species degraded	% mass loss	
				Found	Calc.
4-HAEDF-I	40-150	First	Loss of H_2O molecule	7.5	8.44
4-HAEDF-I	160-520	Second	Loss of side chain (-CH_2-NH-CH_2-CH_2-NH-,$COCH_3$,OH,-CH_2) and partial degradation of aromatic nucleus	86.96	87.76
4-HAEDF-I	750-860	Third	Partial degradation of aromatic nucleus.	96.02	96.45

Table.2. Thermogravimetric Data and Decomposition Temperature range of 4-HAEDF-I Terpolymer Resins

Terpolymer	Decompo Temp T (^{0}C)	Half Decomp Temp (^{0}C)	Activation Energy kJ/mole		Kinetic Parameters by FC				
			FC	SW	ΔS (J)	ΔF (kJ)	Z (S^{-1})	S* (J)	n
4-HAEDF-I	160^{0}C	420	32.14	30.23	-145.21	78.32	47.07	-25.88	0.93

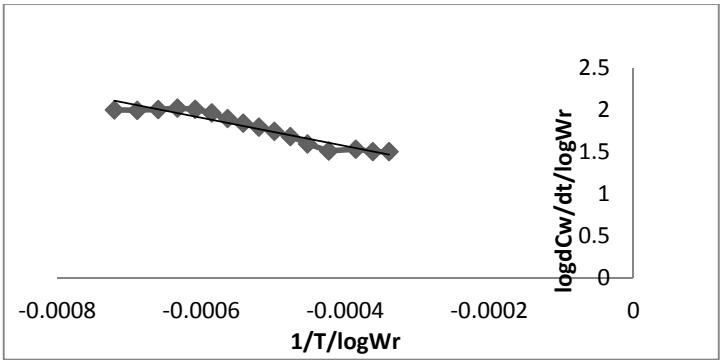

Fig.3.Thermal Activation Energy Plot of 4-HAEDF-I Terpolymer Resin

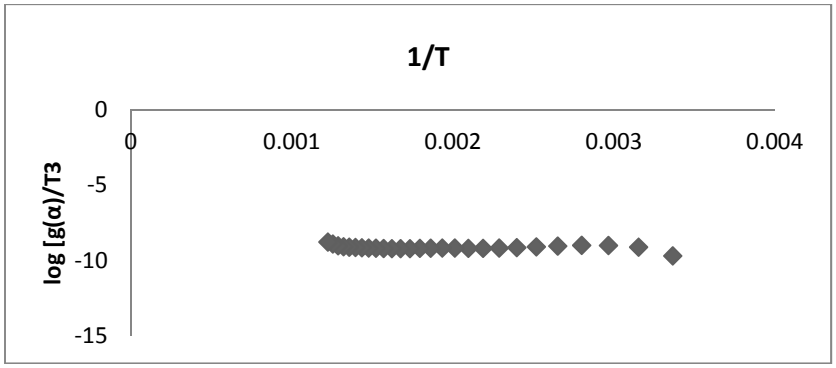

Fig. 4: Freeman-Carroll plot of 4-HAEDF-I-I Terpolymer Resin

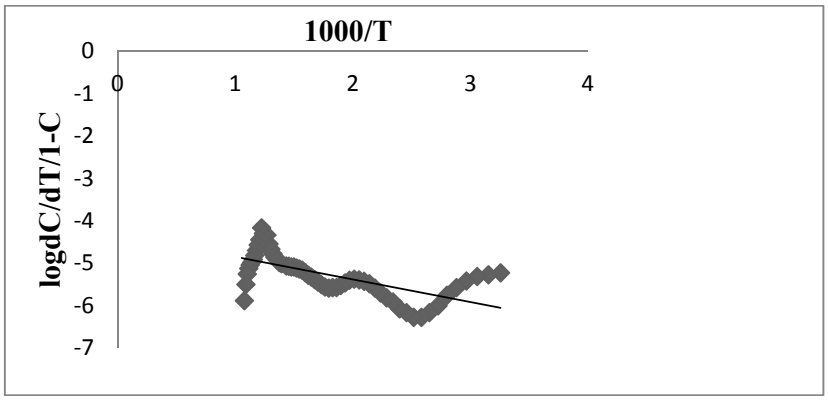

Fig.5. Sharp-Wentworth plot of 4-HAEDF-I Terpolymer Resin

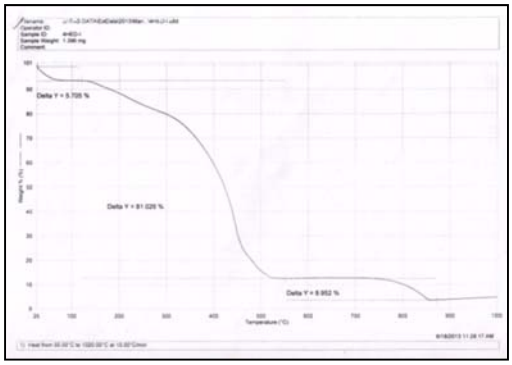

Fig. 6 : TGA curve for 4-HAEDF-I

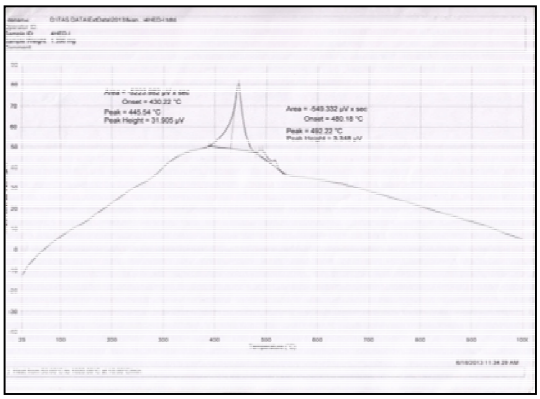

Fig. 7: DTA curve for 4-HAEDF-I

Electrical Conductivity of 4-HAEDF-I Terpolymer Resin

The DC resistivity of the 4-HAEDF-I terpolymer was measured in the temperature range of 303 – 423 K. The electrical conductivity of the terpolymer samples at room temperature varies from 2.62 $x10^{-11}$ $ohm^{-1}cm^{-1}$. The temperature dependence of the electrical conductivity shown in Fig.8.0 is found to be linear in the temperature range under study showing thereby that Wilson potential law is obeyed. Examination of the plots also revealed that the electrical conductivity of the polymers increases with the increase in temperature. Hence, these terpolymer can be termed as semiconductors.

The activation energy calculated from the slope of the plots was found to be $6.931x10^{-20}$ JK^{-1}.

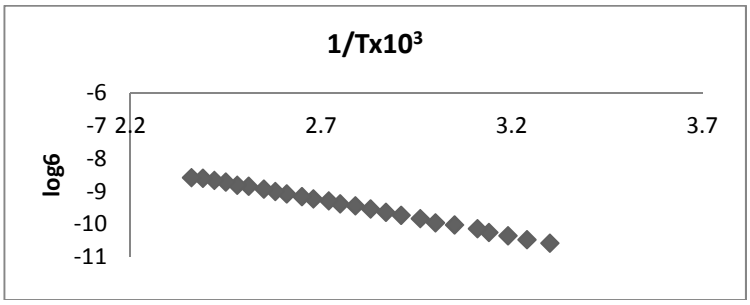

Fig.8 Electrical Conductivity plot of HAEDF-I Terpolymer Resin.

Antibacterial activities

Diameters of inhibition zone with respect to standard antibacterial drug (Gentamycin) was measured and result shown in table 3.

Table 3: Relative antibacterial activity of different resin

Sr. No.	Compound	Diameter of inhibition zone in mm			
		E. coli	*P. aruginosa*	*S. aureus*	*B. subtilis*
1	4-HAEDF-I	2	NF	4	NF
2	Gentamycine	3.1	14	3.4	--

The synthesized resin show biological activity against *E.coli, S.aureus* bacteria and *bioinactive against P.aruginosa and B.subtilis.* The terpolymer has not shown any inhibition zone for fungi *C. albicans* and *Aspergillus niger*

SEM Analysis

The scanning electron microscopic studies clearly shows the porous morphology of the terpolymer and found to contain microporous structures as well (Fig.9). These microporous structure clearly indicate that polymers may be useful in catalytic applications and adsorption phenomena.

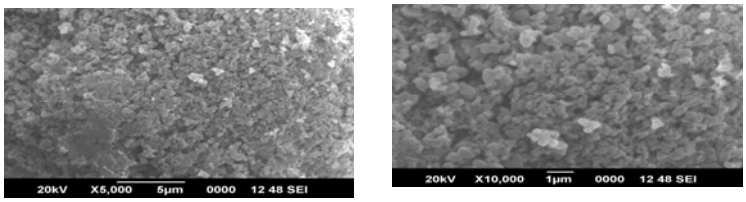

Fig.9: SEM images of 4-HAEDF-I Terpolymer Resin

Conclusions:

- Terpolymer involving 4-hydroxyacetophenone, ethylenediamine and formaldehyde was synthesized in the presence of HCl as a catalyst at 120 ^{0}C for 5 h.
- The TGA curves shows that the terpolymer resin had good thermal stability.
- The activation energy calculated by Freeman-Carroll and Sharp-Wentworth methods was found to be in good agreement with each other.
- The low frequency factor and negative entropy values calculated from Freemam-Carroll method suggested that the thermal decomposition would be slow reaction.
- Conductivity of the polymers increases with the increase in temperature. Hence, these terpolymer can be termed as semiconductors.
- Synthesized terpolymer is biologically active and shows microporous structure.

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