SYNTHESIS, THERMAL AND ELECTRICAL PROPERTIES OF COPOLYMERS BASED ON 4,4'-BIPHENOL

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Abstract: A series of copolymer resins (4,4'-BP-TETA-F) have been synthesized by condensation polymerization of 4,4'-biphenol and triethylenetetramine with formaldehyde in presence of base catalyst. Thermal analysis was carried out in air atmosphere at the heating rates of 10 ^{0}C/min for studying its thermal degradation behavior and kinetics.

Thermal degradation curve depicts three stages of decomposition and has been discussed with minute details by applying Freeman-Carroll, Sharp-Wentworth and Coat-Redfern equations to evaluate the kinetic parameters i.e., activation energy (Ea), order of reaction (n) and frequency factor (z). The data from Freeman-Carroll method has been used to determine various thermodynamic parameters i.e., entropy change (ΔS), free energy change (ΔF) and apparent entropy (S*). The electrical property of 4,4'-BP-TETA-F copolymer resin was measured over a wide range of temperature (313 – 423 K). Electrical conductivity of the copolymer resin was found to be in the range of 8.8457 x 10^{-23} to 6.7959 x 10^{-23} ohm^{-1} cm^{-1}.

Keywords: **Polymer synthesis, Thermal properties, Freeman-carroll, Kinetic parameters, Electrical conductivity.**

I. Introduction

The study of thermal degradation behavior and estimation of kinetic parameters by implementing modern developing thermal degradation kinetic techniques is the subject of interest for many investigators. The interest is fully recognized because the kinetics is related with the decomposition mechanisms in which the thermal degradation takes place. Their mechanisms allow to study the salient features of kinetic equations and kinetic study is the initiative to postulates mechanisms for the thermal decomposition [1]. Variety of thermally stable copolymers has been synthesized in order to study their thermal degradation behavior and reaction kinetics for more and more advanced applications. Literature contains large information regarding the copolymerization of binary monomer systems however; researches are developing on investigation of modern methods of synthesis of terpolymers/copolymers, its characterization and thermal studies for its high performance utility. Terpolymers exhibited renewed applications as semiconductors [2], high energy materials [3], thermally stable materials [4], antioxidants [5], optical lithography and microelectronics [6], fungicides in plants and tissues [7], biosensors [8], additives [9], ion exchangers/chelating agent [10] etc. Appreciable progress has been made by polymer scientists in many ternary systems such as linalool- styrene-methylmethacrylate [11], indene-

methylmethacrylate-acrylonitrile [12], styrene-acrylonitrile-chromium acrylate [13], isobutylene-acrylic ester – alkylboron halide [14], 2-ethoxyethyl methacrylate-styrene-maleic anhydride [15], styrene-acrylonitrile-maleic anhydride [16], anthranilic acid-thiourea-formaldehyde [17] etc. A comprehensive kinetic model for high temperature free radical production of styrene, methylmethacrylate and acrylate resins have been reported by wei wang and robin hutchinson[18]. Boztung and Basan [19] have reported the synthesis and characterization of maleic anhydride-styrene-vinyl acetate terpolymer ester derivative.

The thermal properties of emulsion terpolymers of *N*- p-tolylmaleimide/butadiene-styrene latex/acrylonitrile/styrene have been studied in detail by liting yang et al [20]. Also, number of paper has been published by our researchers from our laboratory on thermal degradation kinetics of terpolymers [21-25]. Jadhav M M have reported the synthesis, characterization and thermal degradation kinetics of copolymers derived from 2,2'-dihydroxybiphenyl- formaldehyde [26] copolymer and 2,2'-dihydroxybiphenyl, urea, formaldehyde [27] terpolymer. A detailed study has been done by Pradip Paik and Kamal K. Kar [28] on kinetics of thermal degradation and estimation of lifetime for polypropylene particles and its effect on particle size, involving the use of single as well as multiple heating rate techniques.

In the present communication, the synthesis and thermal degradation behavior and kinetics by TGA under nonisothermal conditions of copolymer derived from 4,4'-biphenol, triethylenetetramine and formaldehyde (4,4'-BP-TETA-F-I) has been studied. Activation energy (Ea), pre-exponential factor [ln(z)] and order of reaction (n) were determined. Subsequently, the electrical conductivity of 4,4'-BP-TETA-F copolymer have been studied.

Experimental

Starting Materials

The chemicals 4,4'-biphenol and triethylenetetramine are of analytical grade purity which is purchased from Acros Chemicals, Belgium. Formaldehyde (37%) was purchased from S. D. Fine Chemicals, India. All the metal nitrates, electrolytes, indicators and solvents were procured from Merck, India.

Synthesis

4,4'-BP-TETA-F-I copolymer was synthesized by condensation polymerization method by using the molar proportion 1:2:4 of reacting monomers i.e. 4,4'-dihydroxybiphenyl (1.86 gm, 0.1 mol) and triethylenetetramine (3.006 gm, 0.2 mol) with formaldehyde (15 ml, 0.4 mol) in presence of 2M NaOH as a catalyst at 160 ^{0}C in an oil bath for about 10 hrs of continuous heating with occasional shaking. The temperature of electrically heated oil bath was controlled with the help of a dimmerstat. The resinous dark reddish brown colored solid product was immediately removed, filtered and repeatedly washed with cold-distilled water, dried in air and powdered with the help of an agated mortar and pestle. The resulting polymer sample was washed several times with boiling water and dried in a desiccator at room temperature. Further dried polymeric sample extracted with diethyl ether to remove the excess 4,4'-dihydroxybiphenyl-formaldehyde copolymer, which might be present along with the 4,4'-BP-TETA-F copolymer. Finally the copolymer was passed through 300-mesh size sieve and kept in a vacuum over silica gel. Similarly, other copolymer resins, viz. 4,4'-BP-TETA-F -II and III was synthesized by varying the molar proportions of starting

materials in a ratio of 1:3:6 and 1:4:8 respectively [29, 30]. The purity of newly synthesized and purified polymer resins has been tested and confirmed by thin layer chromatography. The resin sample showing any sign of impurity was again purified by known standard methods like extraction, reprecipitation etc. and used for further studies only after the confirmation of 100 % purity of sample.

II. Theoretical considerations

Non-isothermal thermogravimetric analysis of prepared copolymer has been carried out using Perkin Elmer, Pyris1 Thermogravimetric Analyzer, in air atmosphere with a heating rate 10 ^{0}C.min^{-1} in the temperature range 40-1000 ^{0}C. TGA was carried out at VNIT, Nagpur. Thermogram represents the relationship between change in mass on the temperature which gives information about sample composition, product formed after heating and kinetic parameters [30, 31]. Kinetic parameters have been determined using Sharp-Wentworth, Freeman-Carroll and Coat- Redfern techniques as given below.

Sharp-Wentworth technique

$$log\frac{dC/dt}{1-c} = log\left(\frac{A}{\beta}\right) - \frac{Ea}{2.303R}\cdot\frac{1}{T} \qquad (1)$$

Where,

dC/dT = rate of change of fraction of weight with change in temperature

β is linear heating rate, dT/dt.

Thus, a linear plot of $log\frac{dc/dt}{1-c}$ versus $\frac{1}{T}$ is obtained whose slope gives the value of Ea and A may be evaluated from the intercept. The linear relationship confirmed that the assumed order is correct.

Freeman and Carroll technique

$$\frac{\Delta log(dw/dt)}{\Delta log Wr} = \left(-\frac{Ea}{2.303\,R}\right)\cdot\frac{\Delta(\frac{1}{T})}{\Delta log Wr} + n \qquad (2)$$

Where

dw/dt = rate of change of weight with time.

Wr = Wc – W

Wc = Weight loss at the completion of reaction

W = Total weight loss upto time t

Ea = Energy of activation

n = order of reaction

The Δlog (dw/dt) and Δlog Wr values are taken at regular intervals of 1/T. In this case $\frac{\Delta log(\frac{dw}{dt})}{\Delta log Wr}$ vs $\frac{\Delta(\frac{1}{T})}{\Delta log Wr}$ gives a straight line. The slope and intercept are equal to - (Ea/R) and n, respectively.

Coat Redfern technique

$$ln\left[\frac{g(\alpha)}{T^2}\right] = ln\left\{\frac{AR}{qE_a}\left[1 - \frac{2RT}{E_a}\right]\right\} - \frac{E_a}{RT} \qquad (3)$$

Where, q and A is the heating rate (^{0}C/min) and frequency factor respectively.

g(α) is equal to –ln(1-α) for n=1 and ([1-(1-α)^n]/(1-n) for n≠1.

Thus a plot of either $\ln[(1-(1-\alpha)^{1-n})/(T^2(1-n))]$ vs $(1/T)$ or $\ln[-\ln(1-\alpha)/T^2]$ vs $(1/T)$ should results in straight line of slope $[-Ea/R]$ for correct value of n, since it may be shown that for most values of Ea and for the temperature range over which reaction generally occurs the expression $\ln[(AR/qEa)\ (1-(2RT/Ea))]$ is constant.

Electrical conductivity:

The copolymers are well known for their behaviour as semiconductors. Although a variety of conjugated organic molecules are known as semiconductors, having low carrier mobility. This is due to the difficulties in electrons jumping from one molecule to another and so carrier mobility in the compound of this kind increases with increase in molecular size and temperature. Autocompute LCR-Q Meter 4910 was used to measure electrical conductivity of newly synthesized copolymers in the temperature range of 303 K to 453 K at constant voltage of 50 volts across the pellets prepared from copolymer resins. Sample holder with pellet was placed in electric furnace to measure the resistance with the help of above apparatus. Pellets were prepared by using hydraulic press by applying appropriate pressure.

a) Preparation of pellets for resistance measurements:-

Copolymer samples were dried properly and thoroughly ground to a fine powder in agate mortar and pestle. The pellets were prepared by well-powdered copolymer resins isostatically in a steel dia at certain pressure using hydraulic press and obtained pellets were hard and crack free. A thin layer of silver metal was applied on both sides of pellets and dried at room temperature for 4-6 hours. The silver layer on either side of pellet functioned as electrode and surface continuity of pellet was tested by means of multimeter. Average diameter of this pellet and its thickness were measured using a Screw Gauge.

b) Sample holder: -

A simple spring loaded sample holder was fabricated by copper on which pellet was mounted between two copper electrodes, one of which spring loaded while other electrode rested on copper platform.

c) Furnace for heating the sample: -

For resistivity measurement of copolymer at different temperature, a small furnace was used. Current supplied to a furnace was recorded by means of A. C. ammeter and controlled by a rheostat. To ensure the uniformity of temperature inside the furnace, a thin metal cylinder was inserted inside it. Temperature of a furnace was recorded by means of chrome-alumel thermocouple connected with digital multimeter in which millivolts can be measured. The connected wires of two electrodes insulated with porcelain beads were taken out for connections.

d) Measurement of DC electrical conductivity

The connecting wires from the sample holder kept in the furnace were connected to the terminals of LCR-Q tester model 4910. Corresponding resistance was measured keeping the pellet in sample holder at different temperatures starting from 303 K to 453 K. Resistivity (σ) was then calculated using the relation as follows,

$$\sigma = \frac{rA}{l}$$

Where,

r = Resistance of the pellet; A = Surface area of pellet;

l = Thickness of the pellet; σ = Resistivity

Conductivity was measured over a wide range of temperature. It was observed that the electrical conductivity (σ) varies exponentially with absolute temperature according to well known relationship as follows,

$$\sigma = \sigma_0 \, exp.\left(-\frac{E_a}{kT}\right)$$

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,

$$log\sigma = log\sigma_0 - \frac{E_a}{2.303kT}$$

Arrhenius, behavior can be regarded as a good approximation to band theory related to small temperature. According to this relation, a plot of log σ vs 1/T would be linear with –ve slope. Such plots were made on the basis of each set of data. From the slopes of plots, activation energy (Ea) and electrical conductivity can be calculated.

III. Result and Discussion

Thermogravimetric Analysis

Data of thermogravimetric analysis of all the three copolymers were used to determine the kinetic parameters like activation energy (Ea) and order (n) of the decomposition reaction. The kinetic parameters computed by the above mentioned kinetic equations and thermodynamic parameters such as entropy change (ΔS), free energy change (ΔF) and apparent entropy change (S*) calculated on the basis of thermal activation energy calculated by Freeman-Carroll method are shown as follows.

Entropy change

$$\text{Intercept} = log\frac{KR}{h\Phi E} + \frac{\Delta S}{2.303R} \qquad (4)$$

Where, K = 1.3806×10^{-16} erg/deg/mole;

     R = 1.987 cal/deg/mole;

     h = 6.625×10^{-27} erg sec;

     Φ = 0.166; ΔS= change in entropy;

     E = activation energy from graph

Free energy change

$$\Delta F = \Delta H - T\Delta S \qquad\qquad (5)$$

Where,

ΔH = Enthalpy change

T = Temperature in K ΔS = Entropy change {from (4) used}

Frequency factor

$$B_{2/3} = \frac{\log Z E_a}{R\Phi} \qquad\qquad (6)$$

$$(B_{2/3} = \log 3 + \log[1 - 3\sqrt{1-\alpha}] - \log p(x) \qquad (7)$$

Where, Z = Frequency factor, B = Calculated from equation (7); log p(x) = Calculated from Doyle table corresponding to activation energy.

Apparent entropy change

$$S^* = 2.303 R \log \frac{Zh}{RT^*} \qquad\qquad (8)$$

Where, Z = from relation [6],

T* = Temperature at which half of the compound is decomposed from it total loss.

Degradation patterns of these three copolymers are shown in Figure 1. Thermogram of all three copolymers exhibited three stages of decomposition without any loss of water molecules. Temperature range of first, second and third decomposition stages for different copolymers are found to be different. First stage of decomposition represents decomposition of all the hydroxyl groups (-OH) attached to the biphenyl moiety. Second stage of decomposition corresponds to loss of triethylenetetramine moiety. Third stage of decomposition may be attributed to degradation of remaining biphenyl moieties along with methylene groups.
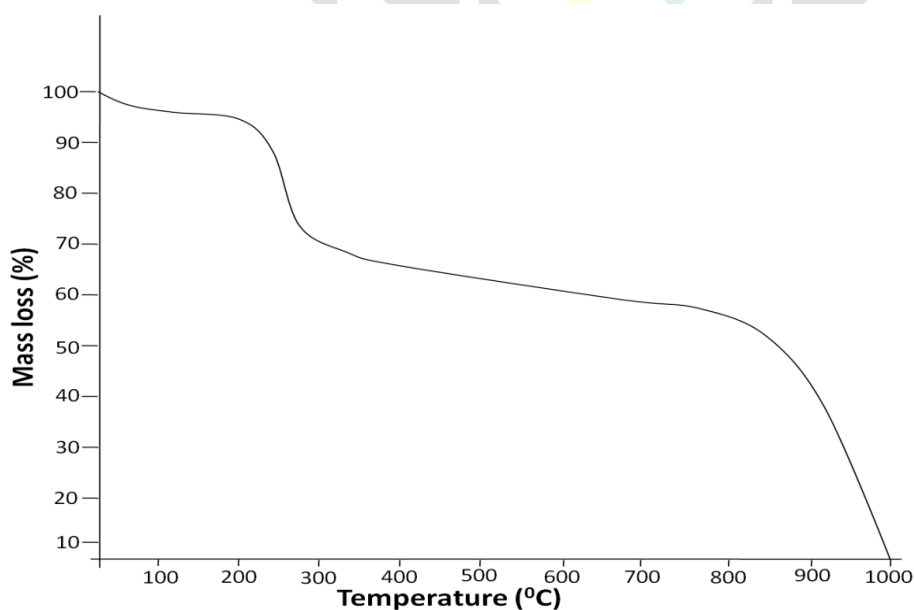

Fig. 1. Decomposition pattern of 4,4'-BP-TETA-F-I copolymer

The decomposition is due to pyrolysis of straight chain linked structure of copolymer resulted into complete degradation at 960ºC. The thermal stability of 4,4'-BP-TETA-F-I copolymer is concluded to be higher, maybe due to the stronger intermolecular hydrogen bonding present in the polymer structure because of

water of crystallization which would be more difficult to break and more resistant to higher temperature or it may be due to the possibility of almost linear structure of copolymer chain which gives stability to the polymer chain.

From the results of kinetic parameters, it is concluded that copolymers prepared from higher molar ratio of reacting monomers exhibited lower rate of decomposition suggesting the order of stability as: 4,4'-BP-TETA-F-I < 4,4'-BP-TETA-F-II < 4,4'-BP-TETA-F-III. This fact is further supported by increasing order of melting point like 4,4'-BP-TETA-F-I < 4,4'-BP-TETA-F-II < 4,4'-BP-TETA-F-III of these copolymer resins. Above mentioned order of stability may be due to possibility of branched structure of copolymer having higher molar ratio of 4,4'-biphenol which may give rise to a stable structure to the copolymer chain.

Activation energy has been calculated by the Sharp-Wentworth method which is in good agreement with activation energy calculated by the Freeman–Carroll method (Table 1). Thermodynamic parameters have been calculated on the basis of thermal activation energy and these values are cited in Table 1. Similarity of values indicates a common reaction mode. From abnormally low values of frequency factor (z), it may be concluded that decomposition reaction of 4,4'-BP-TETA-F-I copolymer resins can be classed as a "slow" reaction [30]. The low positive values of entropy (ΔS) indicate that the activated polymer has a more ordered structure than the reactants and the reactions are slower than normal which were further supported by low z values.

Table 1. Kinetic and thermodyanamic parameters corresponding to the heating rate of 10ºC/min of 4,4'-BP-TETA-F

Copoly mer	T* (^{0}C)	Activation Energy (KJ/mol.)			ΔS(J)	ΔF(KJ)	z(sec^{-1})	S*(J)	n
		F-C	S-W	C-R					
4,4'-BP-TETA-F-I	355	16.82	17.54	10.41	9.069	9980.07	125.97	-24.85	0.92
4,4'-BP-TETA-F-II	378	18.75	20.68	9.46	8.759	16126.37	383.88	-23.73	0.95
4,4'-BP-TETA-F-III	410	19.78	21.96	9.87	8.759	17074.23	557.82	-23.36	0.98

F-C = Freeman-Carroll; S-W = Sharp-Wentworth;
T* = Half Decomposition Temp. (^{0}C); n = Order of reaction.

However, in Freeman-Carroll (Figs. 3 and 4), Sharp-Wentworth (Fig. 5) and Coat-Redfern (Fig. 6) methods, some abnormal points were ignored to get a clear picture of most of the points. It is expected that decomposition of the copolymer is not obeying first order kinetics perfectly. These observations are in harmony with the findings of Jacobs and Tompkin, Coat Redfern and other earlier workers [28].
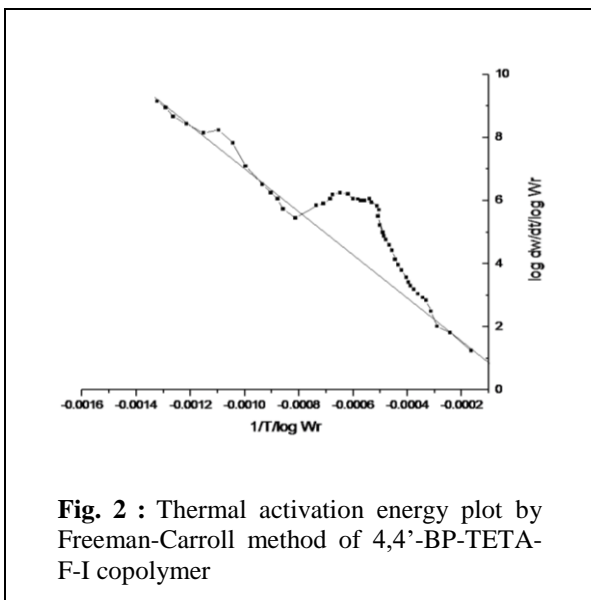
Fig. 2 : Thermal activation energy plot by Freeman-Carroll method of 4,4'-BP-TETA-F-I copolymer
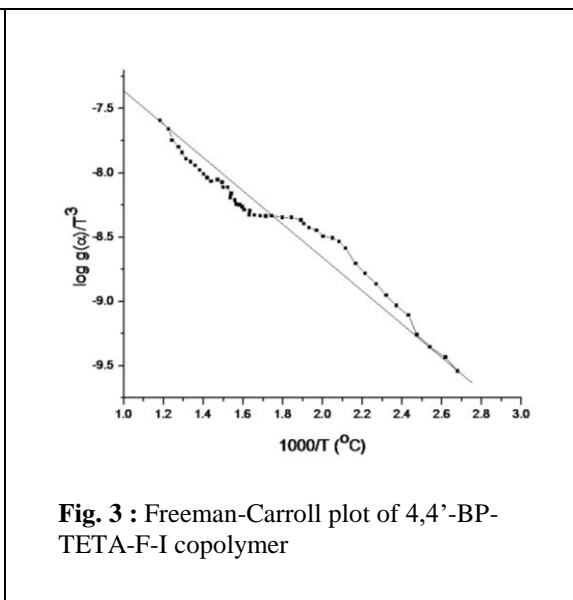
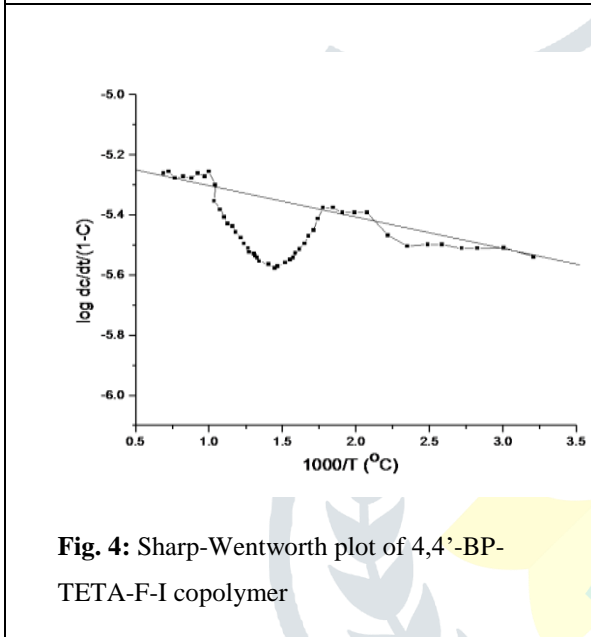**Fig. 3 :** Freeman-Carroll plot of 4,4'-BP-TETA-F-I copolymer

Fig. 4: Sharp-Wentworth plot of 4,4'-BP-TETA-F-I copolymer
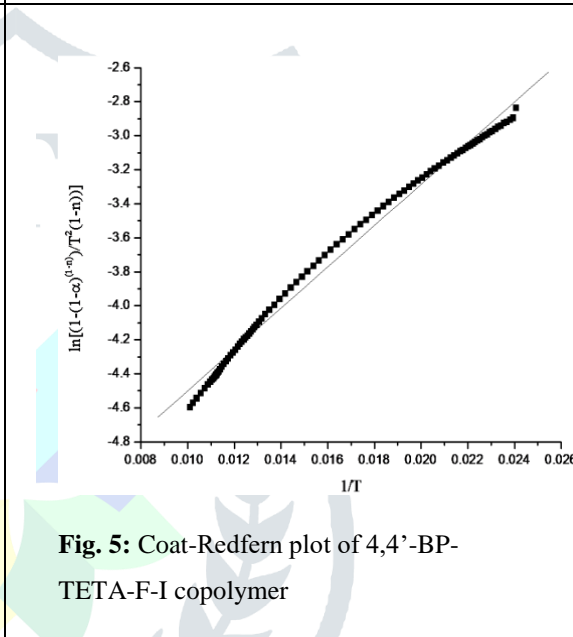
Fig. 5: Coat-Redfern plot of 4,4'-BP-TETA-F-I copolymer

Electrical conductivity:

The electrical conductivity of all newly synthesized copolymer resins were determined by two probe methods in the temperature range of 303 K to 453 K by auto compute LCR-Q meter 4910. Electrical conductivity measurement of all copolymers was carried out from room temperature to 453 K by applying a constant voltage (50 volts) across pellets. A plot between temperature dependence (1000/T) versus electrical conductivity log (σ) of these copolymers is also shown in Figure 7.

The electrical conductivity of 4,4'-BP-TETA-F copolymer resins at room temperature were found in the range of 8.8457×10^{-23} to 6.7959×10^{-23} ohm^{-1} cm^{-1}. As the temperature increases from room temperature, electrical conductivity of polymers was also found to increase uniformly and it attains the lowest value of conductivity 1.64×10^{-11} Siemen.cm^{-1}. The sequence of electrical conductivity for three different copolymer was found to be 4,4'-BP-TETA-F-I < 4,4'-BP-TETA-F-II < 4,4'-BP-TETA-F-III.

Table 2: Electrical conductivity data of 4,4'-BP-TETA-F copolymers

Sr. No.	copolymer	electrical conductivity (σ) Siemen.cm^{-1}.	T (K)	ΔT (K)	ΔE (J/K)

1.	4,4'-BP-TETA-F-I	2.04×10^{-12} 7.94×10^{-10}	303 423	303-423	8.8457×10^{-23}
2.	4,4'-BP-TETA-F-II	5.49×10^{-12} 1.70×10^{-09}	303 423	303-423	7.4415×10^{-23}
3.	4,4'-BP-TETA-F-III	1.64×10^{-11} 3.76×10^{-09}	303 423	303-423	6.7959×10^{-23}

This increase in conductivity of the polymers indicates that as molar ratio of reacting monomer increases corresponding conductivity also increases and hence electrical conductivity may depend on the concentration of the reacting monomer. As the more number of aromatic rings increases, which increases the π electrons, conjugation and delocalization in the structure which results in increasing conductivity by decreasing forbidden energy gap between valence band and conduction band.
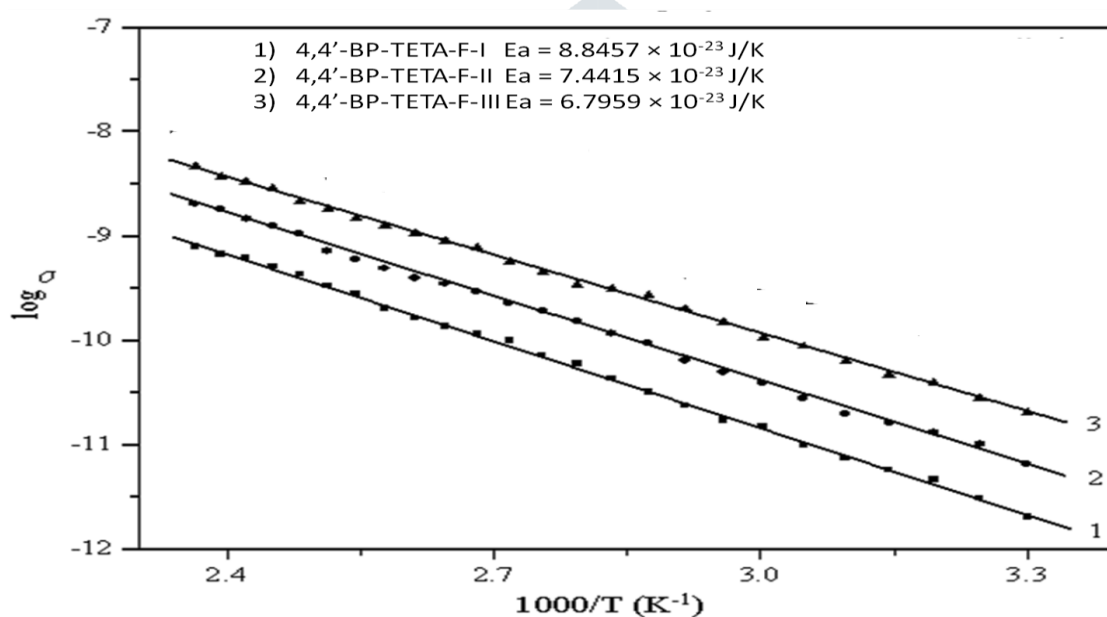

Fig 6- Electrical conductivity plots of 4,4'-BP-TETA-F copolymer resins.

Activation energy of conduction for all copolymer resins was found to decrease from I to III. This decrease in activation energy may due to the increasing concentration of reacting monomer. As conjugation in polymer increases which reduce the forbidden energy gap between valence band and conduction band and less activation energy is required to overcome the energy barrier. Plots of log σ vs 1000/T is found to be linear in temperature range under study, which indicates that Wilson's exponential law $\sigma = \sigma_0 . exp\left(\frac{\Delta E}{k.T}\right)$ is obeyed. The temperature dependence of electrical conductivity shows that conductivity increases with increase in temperature. However, there are deviations at lower temperature due to moisture content. This indicates the semiconducting nature of copolymer resins. As the conductivity is found very low even at higher temperature indicates that the 4,4'-BP-TETA-F copolymer resins have low charge carrier intramolecular transfer.

IV. Conclusion:

A synthesis of new copolymer 4,4'-BP-TETA-F, based on the condensation reaction of 4,4'-biphenol and triethylenetetramine with formaldehyde in the presence of base catalyst. The energy of activation evaluated from Sharp-Wentworth and Freeman-Carroll methods are found to be nearly equal, indicating common reaction

mode. The low positive values of entropy (ΔS) indicate that the polymer has a more ordered structure than the reactants and the reactions are slower than normal which were further supported by low z values. The copolymer resin started degradation at a high temperature, indicating that polymer is thermally stable at an elevated temperature. Electrical conductivity of each of these copolymer resins increases with increase in temperature. Hence, these copolymers may be ranked as semiconductors.

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