

# Research Journal of Pharmaceutical, Biological and Chemical Sciences

## Thermal Degradation Studies Of Copolymer Resin Derived From 8-Hydroxyquinoline, Hexamethylene Diamine With Formaldehyde.

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### ABSTRACT

The copolymer (8-HQHMDAF) was synthesized by condensation of 8-hydroxyquinoline, hexamethylene diamine with formaldehyde in the presence of 2M HCL as a catalyst at  $124 \pm 2$  °C for 5 hrs in (1:1:2) molar proportion of reactants. The terpolymer resin composition has been determined on the basis of elemental analysis. The number average molecular weight of this resin was determined by non-aqueous conductometric titration. Thermogravimetric analysis of copolymer resin in present study has been carried out by non-isothermal thermogravimetric analysis technique in which sample is Thermal study of the resins was carried out to determine their mode of decomposition and relative thermal stabilities. The thermal activation energy determined with the help of these methods was in good agreement with each other. The copolymer (8-HQHMDAF) was characterized by FT-IR, <sup>1</sup>H-NMR Spectroscopy. SEM was used to establish the surface morphology and nature of the copolymer.

**Keywords:** Synthesis, condensation, thermogravimetric analysis, activation energy, resin.

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## INTRODUCTION

Polymers are inevitable entity in modern era of information age, because of its versatile utility in various fields. Polymeric materials are continuously replacing all the traditional materials in field of textile, packaging, adhesive commodity, engineering materials, lithography, electronics and biomaterials etc. polymeric metal complexes shows exciting features such as high thermal stability and antimicrobial action The thermal degradation study of copolymers has become a subject of interest. Study of thermal behaviour of copolymers in air at different temperature provides information about the nature of species produced at various temperatures due to degradation. Copolymers having good thermal stability and catalytic activity have enhanced the development of polymeric materials. [1-3].

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However no work seems to have been carried out on synthesis and physico-chemical technique used for the characterization of copolymer using 8-hydroxyquinoline, hexamethylene diamine with formaldehyde The present paper deals with the synthesis, characterization, and non-isothermal thermogravimetric analysis of copolymer derived from of 8-hydroxyquinoline (8HQ), hexamethylene diamine (HMDA), with formaldehyde (F)

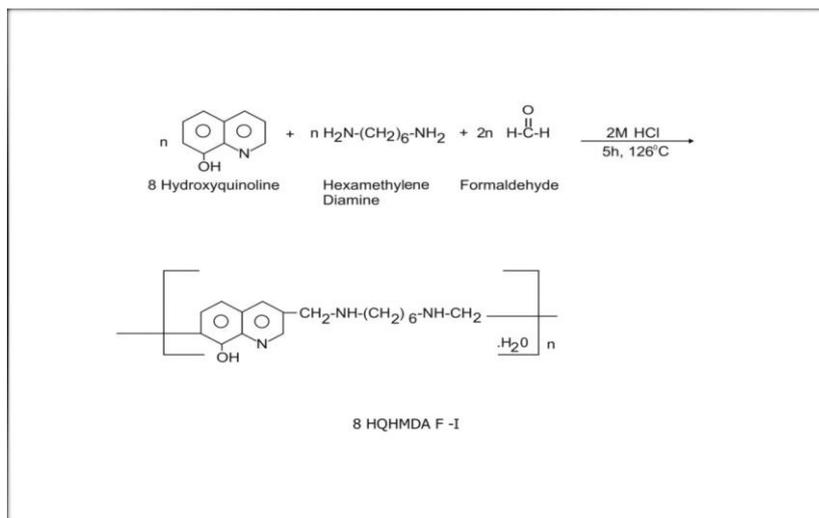
## MATERIALS AND METHODS

### Materials

All the chemicals used were of analytical grade. 8-hydroxyquinoline, hexamethylene diamine and formaldehyde are purchased from Merck Chemicals, India. Solvents like N,N-dimethyl formamide and dimethyl sulphoxide purchased from S D Fine Ltd, Mumbai, India, were used after distillation.

### Synthesis of 8-HQHMDAF Copolymer Resin

The new copolymer resin 8HQHMDAF was synthesized by condensing 8-hydroxyquinoline (0.1 mol) and hexamethylene diamine (0.1 mol) with formaldehyde (0.2 mol) in a mol ratio of 1:1:2 in the presence of 2 M 200 ml HCl as a catalyst at  $126 \pm 2^\circ\text{C}$  for 5h, in an oil bath with occasional shaking, to ensure thorough mixing. The separated copolymer 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 diethyl ether and then with petroleum ether to remove 8-hydroxyquinoline, hexamethylene diamine, formaldehyde copolymer which might be present along with 8-HQHMDAF copolymer. The yellow colour resinous product was immediately removed from the flask as soon as reaction period was over and then purified. The reaction and suggested structure of 8-HQHMDAF is shown in Fig. 1.



**Fig 1: Synthesis of 8-HQ5SAHMDAF copolymer resin.**

The copolymer was purified by dissolving in 8% aqueous sodium hydroxide solution, filtered and reprecipitated by gradual drop wise addition of ice cold 1:1 (v/v) concentrated hydrochloric acid / distilled water with constant and rapid stirring to avoid lump formation. The process of reprecipitation was repeated twice. The copolymer sample 8-HQHMDA-I thus obtained was filtered, washed several times with hot water, dried in air, powdered and kept in vacuum desiccator over silica gel.

### Characterization

The elemental analysis was carried out on a Perkin Elmer 2400 Elemental Analyzer instrument. An infra-red spectrum of copolymer resin was recorded on Perkin-Elmer-983 spectrophotometer in KBr pallets in the wave number region of 4000-400  $\text{cm}^{-1}$  Spectrophotometer.  $^1\text{H-NMR}$  studied using Bruker Advance-II FT-NMR Spectrometer in DMSO- $d_6$  solvent at STIC Analysis, Cochin. The number average molecular weight ( $M_n$ ) was determined by conductometric titration in non aqueous medium such as dimethylsulphoxide (DMSO) using ethanolic KOH as a titrant. From the graph of specific conductance against milliequivalents of base, first and last break were noted from which degree of polymerization (DP) and the number average molecular weight ( $M_n$ ) has been calculated for the terpolymer resin.

The non isothermal thermogravimetric analysis was performed in air atmosphere with heating rate of  $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$  using 5 - 6 mg of samples in platinum crucible from temperature of  $40\text{ }^\circ\text{C}$  to  $800\text{ }^\circ\text{C}$  and thermograms are recorded for 8-HQHMDAF sample at STIC, Cochin. With the help of thermogravimetric data thermal degradation curve is discussed which shows three decomposition steps. The activation energy ( $E_a$ ) and thermal stability calculated by using the Sharp-Wentworth, Freeman-Carroll and Freidman's methods. Thermodynamic parameters such as entropy change ( $\Delta S$ ), apparent entropy change ( $S^*$ ) and frequency factor ( $Z$ ) have also been evaluated on the basis of the data of Freeman-Carroll method. The thermal activation energies ( $E_a$ ) and order of reaction ( $n$ ) calculated.

### RESULTS AND DISCUSSION

The newly synthesized purified 8-HQHMDAF copolymer resin was found to be yellow in colour. The copolymer is soluble in solvents such as DMF, DMSO and THF, pyridine, concentrated  $\text{H}_2\text{SO}_4$ . No precipitation and degradation occurs of resin in all the solvents, while insoluble in almost all other organic solvents. The melting point of the terpolymer was determined by using electrically heated melting point apparatus and is found to be of 482 K. This resin was analyzed for carbon, hydrogen and nitrogen content given in Table 1. The copolymer which has been used in the present investigation was prepared by the reaction given in Fig. 1.

**Table 1: Elemental analysis and empirical formula of 8-HQHMDAF copolymer resin**

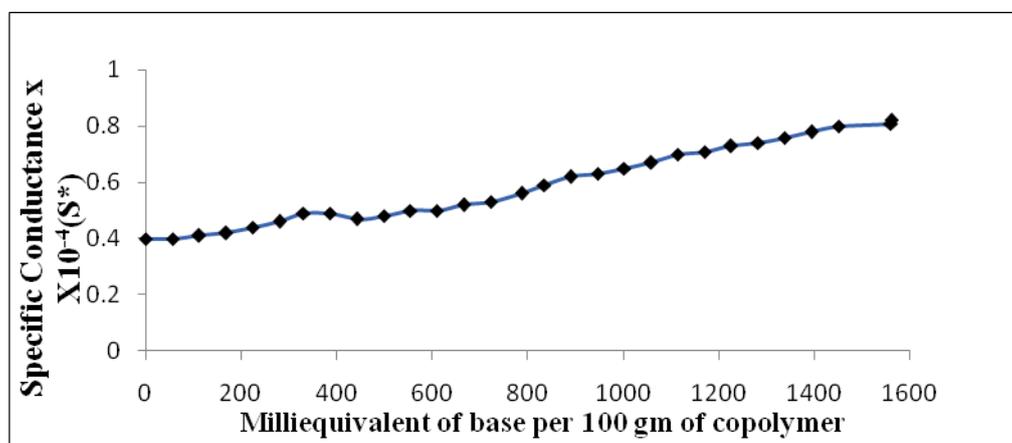
Copolymer	% of C found (cal.)	% of H found (cal.)	% of N found (cal.)	Empirical Formula	Formula Weight
8-HQHMDAF	67.65 (67.32)	8.10 (8.25)	13.60 (13.86)	C <sub>17</sub> H <sub>25</sub> N <sub>3</sub> O <sub>2</sub>	303

The number average molecular weight (Mn) of this copolymer has been determined by conductometric titration method in non-aqueous medium and using standard potassium hydroxide (0.05 M) in absolute ethanol as a titrant. The results are presented in Table 2. The specific conductance was plotted against milliequivalents of ethanolic KOH required for neutralization of 100 gm of terpolymer. There are several breaks before the complete neutralization of all phenolic hydroxyl groups. The first break in the plot was the smallest break and assumed that this corresponds to a stage in titration when an average one phenolic hydroxyl group of each chain was neutralized.

**Table 2: Molecular weight determination data of the 8-HQHMDAF copolymer resin**

Copolymer	First stage of neutralization (Meq/100gm sample)	Final stage of neutralization (Meq/100gm sample)	Degree of polymerization (DP)	Empirical Weight (gm)	Number average molecular weight (Mn)
8-HQHMDAF	96	1500	15.625	303	4734.375

From the plot (Fig.2) the first and final breaks were noted. The average degree of polymerization (DP) and hence the number average molecular weight (Mn) of the copolymer has been determined using the formula. This observation is in agreement with the trend observed by earlier workers [12].


**Fig 2: Conductometric plot of copolymer resin 8-HQHMDAF**

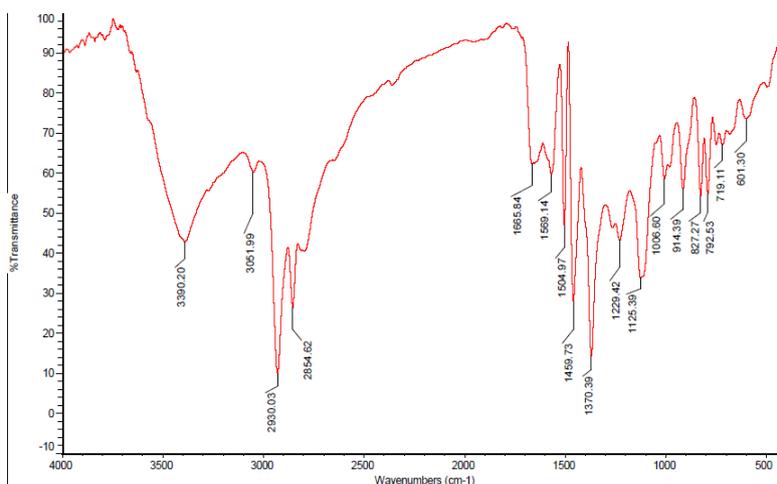
$$\overline{DP} = \frac{\text{Total milliequivalents of base required for complete neutralization}}{\text{Mill equivalents of base required for smallest interval}}$$

$$\overline{Mn} = \overline{DP} \times \text{Repeat unit}$$

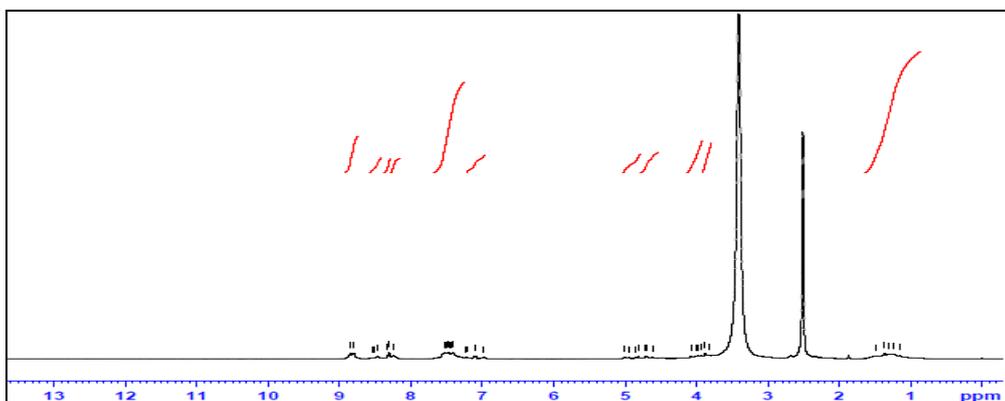
The IR-spectra of 8-HQHMDAF copolymer is presented in Fig. 3. A broad band appeared in the region 3390 cm<sup>-1</sup> may be assigned to the stretching vibrations of phenolic hydroxy (-OH) groups exhibiting intermolecular hydrogen bonding [13]. The broad band displayed at 1569 cm<sup>-1</sup> may be due to the aromatic ring with aldehyde moiety and 1459 cm<sup>-1</sup> may be due to bending of (C-H) in methylene group [14] The presence of

-NH in hexamethylene diamine moiety may be assigned due to sharp band at  $2930\text{ cm}^{-1}$ . A strong sharp peak at  $3051\text{ cm}^{-1}$  may be ascribed to aromatic skeletal ring. The bands obtained at  $1370\text{ cm}^{-1}$  suggest the presence of methylene bridges in the polymer chain. The weak band appearing at  $720 - 760\text{ cm}^{-1}$  is assigned to C – OH bond. 1,3,8 substitution of aromatic ring is recognized from the bands appearing at 712, 1125, and  $1229\text{ cm}^{-1}$  respectively [15]

The NMR Spectra of the 8-HQHMDAF copolymer resin was scanned in DMSO- $d_6$  solvent. The spectrum has been given in Fig.4. The chemical shift ( $\delta$ ) ppm observed is assigned on the basis of data available in literature [16]. Weak signal in the range of 8.45 ppm is attributed to phenolic -OH proton. [17, 18]. The NMR spectra of 8HQHMDAF-I copolymer resins show a weak multiplate signal (unsymmetrical pattern) in the region 7.55 ( $\delta$ ) ppm which is due aromatic protons. A medium singlet peak appeared at 3.93 ( $\delta$ ) ppm may be assigned to methyl protons of Ar-CH<sub>2</sub>-N group. Intense signal appeared in the region 2.52 ( $\delta$ ) ppm may be due to Ar-CH<sub>2</sub>-Ar .signal appeared in the region 7.11( $\delta$ ) ppm can be assigned to proton of N-H bridge of Ar-CH<sub>2</sub>-NH.



**Fig.3: FTIR Spectra of copolymer resin 8-HQHMDAF**

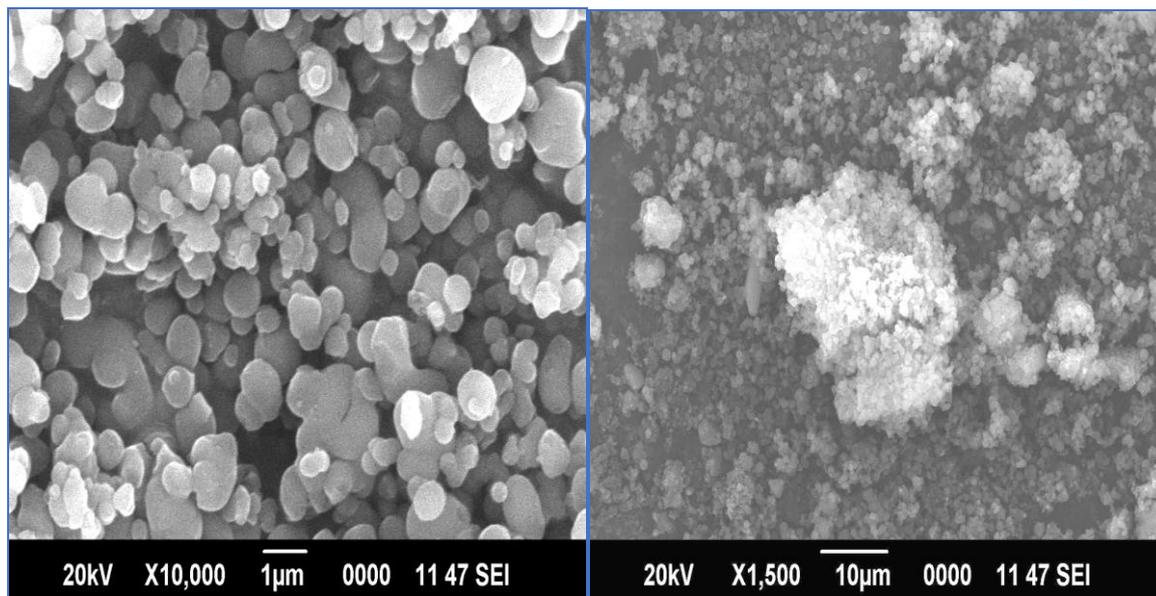


**Fig 4: NMR Spectra of copolymer resin 8-HQHMDAF**

The SEM micrographs Fig.5 A&B of 8-HQHMDAF copolymer resin sample exhibits spherulites with deep corrugation . The spherulites are typical crystalline formation and they grow in high viscous and concentrated solution. In the present case, the spherulites are complex polycrystalline formation composed of simplest structural formula having smoothest surface free from defects of growth. The crystals are smaller in surface area with less closely packed structure. Thus the spherulites morphology of resin exhibit crystalline structure of resin with deep corrugation which is clearly visible in SEM photographs of resin.

These evidences indicate that more or less the resin shows amorphous character with less close packed surface having deep pits. The resin thus possesses amorphous nature and showing higher exchange

capacity for metal ions. Thus SEM study shows that the 8-HQHMDAF copolymer resin has crystalline and some amorphous characters. Thus it has the transition structure between crystalline and amorphous.



**Fig 5 : SEM micrographs of 8-HQHMDAF copolymer resin**

On the basis of the nature and reactive position of the monomer elemental analysis, FTIR, <sup>1</sup>H-NMR spectra and molecular weight, the most probable structure have been proposed for copolymer resin as shown in Fig. 1.

#### Thermogravimetric Analysis of the Copolymer

The thermogravimetric data provide information regarding the thermal stability of a polymer. The thermograms were obtained by heating resin sample in air at 10<sup>0</sup> C/min. The results of percentage weight loss of the copolymer resins depicts three steps decomposition in the temperature range 140-600°C and are furnished in Figure 6. The slow decomposition between 0-180°C corresponds to 5.0 % loss which may be attributed to loss of water molecule against calculated 4.8 % present per repeat unit of the polymer. The first step decomposition start from 180-260°C which represents loss of hydroxyl group and acid group (38.00 % found and 37.86 % cal.). The second step decomposition start from 260-520°C corresponding to 78.00 % removal of aromatic nucleus and methylene bridge against calculated 78.4 %. The third step decomposition side chain from 480-580°C corresponding to removal of Thiosemicarbazide moiety (100.00 % found and 98.4 % cal.). With the help of thermogravimetric data the thermal activation energies (E<sub>a</sub>) and order of reaction (n) calculated [20]. Also other thermodynamic parameters such as entropy change (ΔS), apparent entropy change (S\*) and frequency factor (Z) are determined and reported in the Table 3& 4. To provide further evidence regarding the degradation system of analyzed compounds, we derived the TG curves by applying an analytical method proposed by Sharp-Wentworth and Freeman-Carroll. The 'average E<sub>a</sub>' calculated by Freeman-Carroll (24.51 KJ/mole) and 'average E<sub>a</sub>' by Sharp- Wentworth (24.85 KJ/mole) is nearly same. [21, 22].

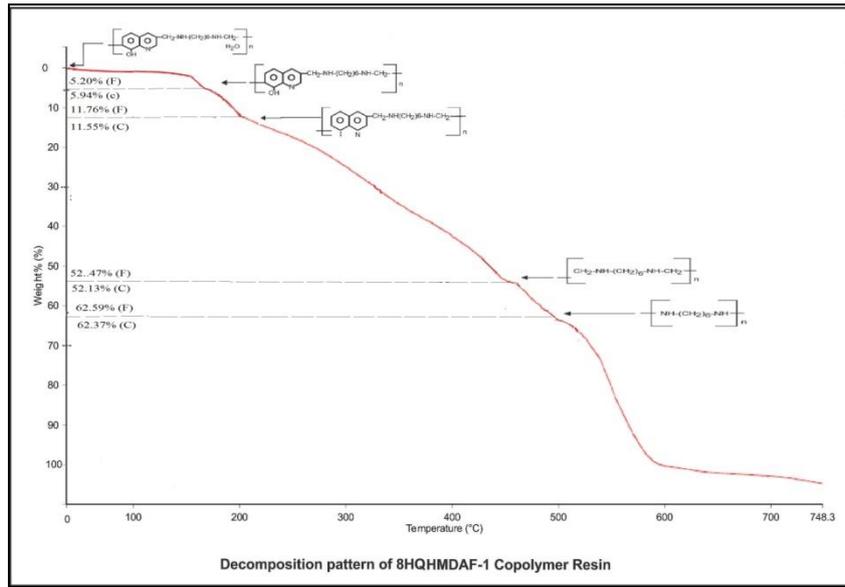


Fig 6: Decomposition Pattern of 8-HQHMDAF copolymer Resin

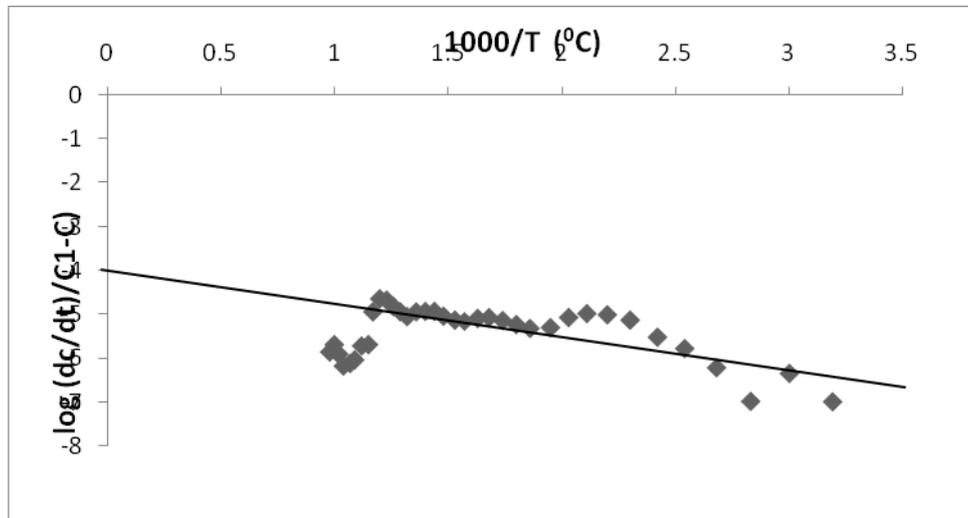


Fig 7: Sharp-Wentworth plot of 8-HQHMDAF copolymer Resin.

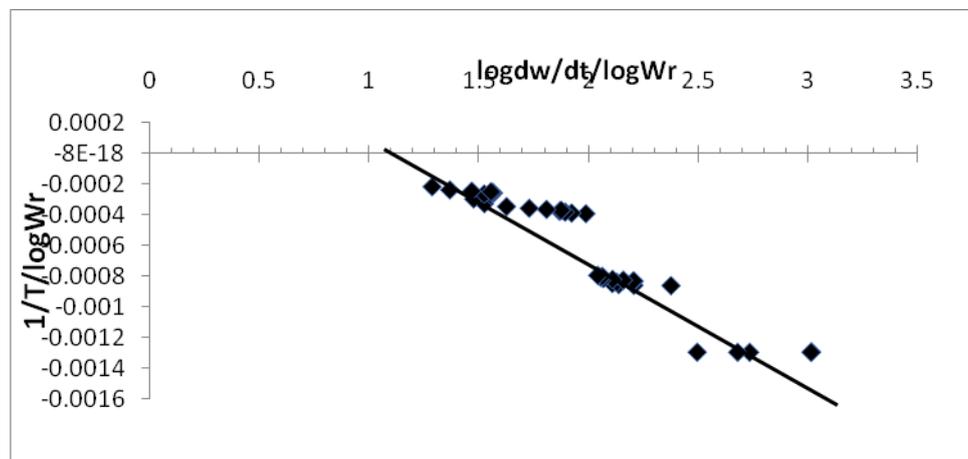


Fig 8: Thermal activation energy plot of 8-HQHMDAF copolymer resin.

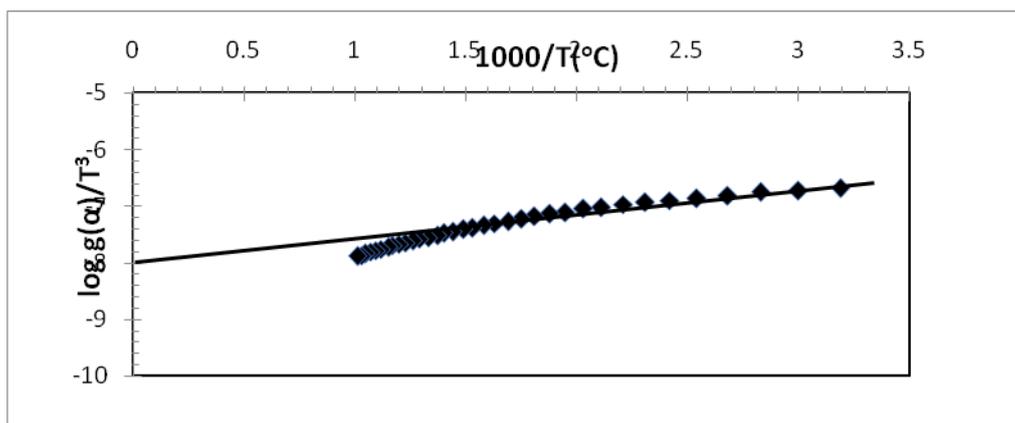


Fig 9: Freeman-Carroll plot of 8-HQHMDAF copolymer Resin

Table 3: Results of thermogravimetric Analysis of 8-HQHMDAF copolymer resins copolymer

Copolymer	Half Decomposition Temp. T*K	Activation Energy (kJ/mol)	
		F.C	S.W
8-HQHMDAF	433	24.51	24.85

**Sharp -Wentworth method:**

Using the equation derived by Sharp and Wentworth [1],

$$\log [(dc/dT)/(1-c)] = \log (A/\beta) - [Ea/2.303R] \cdot 1/T \dots\dots\dots(1)$$

Where,

dc/dT = rate of change of fraction of weight with change in temperature  
 $\beta$  = linear heating rate dT/dt.

By plotting the graph between (log dc/dt)/(1-c) vs 1/T we obtained the straight line which give energy of activation (Ea) from its slope. Where  $\beta$  is the conversion at time t, R is the gas constant (8.314 J mol<sup>-1</sup> K<sup>-1</sup>) and T is the absolute temperature. The plots Fig.7 give the activation energies at different stages of degradation reaction take place.

**Freeman-Carroll method:**

The straight-line equation derived by Freeman and Carroll as in Fig.8, which is in the form of n

$$[\Delta \log (dw / dt)] / \Delta \log Wr = (-E / 2.303R) \cdot \Delta (1/ T) / \Delta \log Wr + n \dots\dots\dots(1)$$

**Where,** dw/dt = rate of change of weight with time.

- Wr = Wc-W
- Wc = weight loss at completion of reaction.
- W = fraction of weight loss at time t.
- Ea = energy of activation., n = order of reaction.

The plot Fig.9 between the terms  $[\Delta \log (dw/dt)] / \Delta \log Wr$  Vs  $\Delta (1/T) / \Delta \log Wr$  gives a straight line from which slope we obtained energy of activation (Ea) and intercept on Y-axis as order of reaction (n). The change in entropy (S), frequency factor (z), apparent entropy (S\*) can also be calculated by further calculations. [23, 24].

**Entropy Change:**

$$\text{Intercept} = [\log KR/h\phi E] + S / 2.303 R \text{ ----- (2)}$$

Where,  $K = 1.3806 \times 10^{-16}$  erg/deg/mole,  $R = 1.987$  Cal/deg/mole

$h = 6.625 \times 10^{-27}$  erg sec. ,  $\phi = 0.166$

$S$  = Change in entropy,  $E$  = Activation energy from graph.

**Free Energy Change:**

$$\Delta F = \Delta H - T\Delta S \text{ ----- (3)}$$

Where,  $\Delta H$  = Enthalpy Change = activation energy

$T$  = Temperature in K

$S$  = Entropy change from (i) used.

**Frequency Factor:**

$$Bn = \log ZEa / \phi R \text{ ----- (4)}$$

$$B1 = \log [ \ln 1 / 1 - \alpha ] - \log P (x) \text{ ----- (5)}$$

Where,  $Z$  = frequency factor,  $B$  = calculated from equation (5)

$\log P(x)$  = calculated from Doyle's table corresponding to activation energy.

**Apparent Entropy Change:**

$$S^* = 2.303 \log Zh / KT^* \text{ ----- (6)}$$

$Z$  = from relation (4)

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

**Table 4: Kinetic parameters of 8-HQHMDAF copolymer resins**

Copolymer	Entropy Change $-\Delta S(J)$	Free Energy Change $\Delta F (kJ)$	Frequency factor $Z (S^{-1})$	Apparent Entropy Change $(S^*)$	Order of reaction $(n)$
8-HQHMDAF	300.67	165.71	438	-23.97	0.92

**CONCLUSION**

A copolymer resin, 8-HQHMDAF based on the condensation reaction of 8-hydroxyquinoline, hexamethylene diamine, formaldehyde in the presence of acid catalyst was prepared. From the FT-IR and <sup>1</sup>H NMR spectral studies the proposed structure of the 8HQHMDAF-I copolymer resin has been determined. In TGA the energy of activation evaluated from the Sharp-Wentworth and Freeman-Carroll methods are found to be nearly equal and the kinetic parameters obtained from Freeman-Carroll method are found to similar, indicating the common reaction mode. However, it is difficult to draw any unique conclusion regarding the decomposition mechanism. Low values of collision frequency factor ( $Z$ ) may be concluded that the decomposition reaction of 8-hydroxyquinoline, hexamethylene diamine, formaldehyde copolymer can be classified as 'slow reaction'. The decomposition reaction was started at higher temperature, indicating a copolymer 8-HQHMDAF is thermally stable at higher temperature.

**ACKNOWLEDGEMENT**

The authors express their sincere thanks to Principal, Kamla Nehru College, Nagpur, India for cooperation and for providing necessary laboratory facilities. to the Director, STIC Analysis Cochin for carried out spectral analysis thermal analysis

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