



# Thermal Degradation and Critical Studies of the Isoconventional Methods of Kinetic Analysis of 8-HQ5-SASF-III Polymer

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## Abstract:

Polymer (8-HQ5-SASF-III) has been synthesized using the monomers 8-hydroxyquinoline 5-sulphonic acid, semicarbazide and formaldehyde in 3:1:4 molar proportions. The structure of 8-HQ5-SASF-III polymer has been elucidated on the basis of elemental analysis, various physicochemical techniques and spectral methods i.e. UV-Visible, FT-IR and <sup>1</sup>H-NMR spectroscopy. Detailed thermal degradation study of the new polymer has been carried out to ascertain its thermal stability. Thermal degradation curve is discussed which shows four decomposition steps. The activation energy ( $E_a$ ) and thermal stability calculated by using the Sharp-Wentworth, Freeman-Carroll and Friedman'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 order of reaction ( $n$ ) is found out to be 0.97.

## Keywords:

Thermal degradation, synthesis, characterization, polymer, thermal analysis, kinetic parameters.

## Introduction:

A large amount of work has been reported from these laboratories on the synthesis, characterization, structure and thermal studies of several polymers [1-2]. The Freeman-Carroll [2] and Sharp-Wentworth [3] methods have been used to evaluate various kinetic parameters for these polymer. The method for estimating kinetic parameters from dynamic TG studies suffers from the difficulty that the two parameters, temperature and time can not be continuously changed. This problem is eliminated in Freeman-Carroll method where the parameters of temperature and time can be varied. Methods for estimating kinetic parameters from dynamic TG studies [4] are mostly based on the assumptions that the Arrhenius equation is valid and that the thermal and diffusion barriers are negligible.

Copolymers, very special classes of polymers, are known for their versatile uses and are found to be amorphous, crystalline or resinous in nature. Phenolic resins have been the workhorse as matrix resins in composites for structural and thermal applications in aerospace because of their ease of processability, thermal stability, versatile characteristics and cost effectiveness. W. Tang and coworkers [4] studied the thermal decomposition kinetics of copolyester made from trans-p-hydrocinnamic acid and p-hydrobenzoic acid. Copolymers occupy an intermediate position between organic and inorganic compounds and it is hoped that the study





of copolymers will lead to the production of polymer, which are both thermally stable and useful as fabricating materials. Michael et al. studied synthesis, characterization and thermal degradation of 8-hydroxyquinoline-guanidine-formaldehyde terpolymer [5]. Polymer resins are derived from 2,4-dihydroxypropiophenone, biuret, and formaldehyde in hydrochloric acid as catalyst and studied their thermal degradation [6]. Thermoanalysis and rheological behavior of copolymers of methyl methacrylate, N-phenylmaleimide and styrene studied by G. Jungang et al. In order to synthesize polymers having numerous practical applications, there is a need to investigate the effect of heat on the polymers in order to establish their thermal stability. It must be pointed out that all the methods proposed have been developed by assuming that both activation energy and kinetic model do not change along the process. However, it has concluded from free- model kinetic methods of analysis that the activation energy is a function of the reacted fraction [7].

However, the literature studies have revealed that no polymer has been synthesized using the monomer 8-hydroxyquinoline 5-sulphonic acid, semicarbazide and formaldehyde. Therefore, in the present communication we report the synthesis, structural characterization and thermal degradation studies of 8-HQ5-SASF-III polymer. The elemental analysis has been carried out to ascertain the molecular formula and the spectral studies have been used to characterize the complete structure of the 8-HQ5-SASF-III polymer. After treating the thermal degradation data with Sharp-Wentworth (SW) and Freeman-Carroll (FC) methods, activation energy and kinetic parameters such as  $\Delta S$ ,  $Z$ ,  $S^*$  and  $n$  (order of reaction) have been evaluated [8].

## Material and Methods:

All the chemicals used were of analytical grade. 8-hydroxyquinoline 5-sulphonic acid, semicarbazide and formaldehyde which is purchased from Merck Chemicals, India.

### Synthesis of p-APDF polymer resin

The 8-HQ5-SASF-III polymer was prepared by condensing 8-hydroxyquinoline 5-sulphonic acid (0.3 mol) and semicarbazide (0.1 mol) with formaldehyde (0.4 mol) in the presence of 2M acetic acid as a catalyst at  $124 \pm 2$  °C in an oil bath for 5 hr (Figure 1)

The brown colored solid product obtained was immediately removed and extracted with diethyl ether to remove excess of p-aminophenol -formaldehyde copolymer, which might be present along with the 8-HQ5-SASF-III polymer. It was further purified by dissolving in 8 % NaOH and then filtered. The copolymer was then reprecipitated by drop wise addition of 1:1 (v/v) cone. HCl / water with constant stirring and filtered. The process was repeated twice. The resulting polymer sample was washed with boiling water and dried in a vacuum at room temperature. The purified polymer resin was finely ground to pass through 300-mesh size sieve and kept in a vacuum over silica gel. The yield of the polymer was found to be about 83 %.





### Analytical and physicochemical studies

The UV-Visible studies were out carried using Shimadzu UV-1800 Spectrophotometer in the range 200-800 nm. The Infrared spectrum was recorded in the region of 500-4000 cm<sup>-1</sup> on Shimadzu IR Affinity Spectrophotometer at Department of Chemistry, Kamla Nehru Mahavidyalaya, Nagpur. <sup>1</sup>H-NMR studied using BrukerAvance-II FT-NMR Spectrometer in DMSO-d<sub>6</sub> solvent at STIC Analysis, Kochi. All the analytical and spectral studies for the newly synthesized copolymer were carried out at STIC Analysis centre, Kochi. The nonisothermalthermogravimetric analysis was performed in air atmosphere with heating rate of 10 °C. min<sup>-1</sup> using 5 - 6 mg of samples in platinum crucible from temperature of 40 °C to 700 °C and thermograms are recorded for 8-HQ5-SASF-III sample at STIC, Kochi. With the help of thermogravimetric data the thermal activation energies (*E<sub>a</sub>*) and order of reaction (*n*) calculated. Also other thermodynamic parameters such as entropy change ( $\Delta S$ ), apparent entropy change (*S\**) and frequency factor (*z*) are determined.

### Theoretical considerations

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, Freeman- Carroll and Freidman.

### Freeman-Carroll method

The straight-line equation derived by Freeman and Carroll[25], which is in the form of

$$\frac{\Delta \log dw/dt}{\Delta \log w_r} = n - \frac{E_a}{2.30.R} \cdot \frac{\Delta(1/T)}{\Delta \log W_r} \dots\dots\dots(1)$$

Where

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

W<sub>r</sub> = W<sub>c</sub>-W

W<sub>e</sub> = weight loss at completion of reaction.

W = fraction of weight loss at time t.

E<sub>a</sub> = energy of activation.

n = order of reaction.

The plot between the terms  $\frac{\Delta \log dw/dt}{\Delta \log w_r}$  vs  $\frac{\Delta(1/T)}{\Delta \log W_r}$  gives a straight line from which slop we obtained energy of activation (*E<sub>a</sub>*)and intercept on Y-axis as order of reaction (*n*). The change in entropy ( $\Delta S$ ), frequency factor (*z*), apparent entropy (*S\**) can also be calculated by further calculations.





### Sharp-Wentworth Method

Using the equation derived by Sharp and Wentworth[26],

Log

$$\frac{dc/dt}{1-C} = \log A / \beta - \frac{Ea}{2.303R} \cdot \frac{1}{T} \dots\dots\dots(2)$$

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  $\log \frac{dc/dt}{1-C}$  vs.  $\frac{1}{T}$  we obtained the straight line which give energy of activation ( $Ea$ ) from its slope.

This isoconversional (model-free) kinetic methods use to check the variation of the apparent activation energy values with degree of degradation. This kinetic analysis should be a starting point for obtain the useful information on the behavior of the sample.

### Results and Discussion:

The newly synthesized 8-HQ5-SASF-III polymer was found to be brown in color. The polymer is soluble in solvents such as DMF, DMSO and THF while insoluble in almost all other organic solvents. The melting point of this copolymer was determined by using electrically heated melting point apparatus and is found to be 435K.

The UV-visible spectra (Figure 2) of p-APDF polymer resin in pure DMSO was recorded in the region 200-600 nm. The spectra of polymer exhibit to absorption maxima in the regions of 230-250 and 290-310 nm. The bands at 230-250 nm indicate the presence of a C = S group containing a carbon-sulfur double bond in conjugation with the aromatic nucleus, and this is characteristic of the  $\pi \rightarrow \pi^*$  transition. The later band indicates  $\pi \rightarrow \pi^*$  transition. The bathochromic shift (the shift toward a longer wavelength) from the basic values (237 nm and 310 nm) may be due to the combined effect of conjugation and the phenolic hydroxyl group (auxochrome).

IR spectra of 8-HQ5-SASF-III polymer is depicted in Figure 3. A broad absorption band appeared in the region  $3436 \text{ cm}^{-1}$  may be assigned to the stretching vibrations of phenolic hydroxyl (-OH) groups exhibiting intramolecular hydrogen bonding.[9] A sharp strong peak at  $1640 \text{ cm}^{-1}$  may be ascribed to aromatic skeletal ring. The bands obtained at  $1282 \text{ cm}^{-1}$  and  $1430 \text{ cm}^{-1}$  suggest the presence of methylene (-CH<sub>2</sub>-) bridge.[10]. The 1,2,3,5 substitution of aromatic benzene ring recognized by the sharp, medium / weak absorption bands appeared at  $913 \text{ cm}^{-1}$ ,  $1150 \text{ cm}^{-1}$ ,  $1105 \text{ cm}^{-1}$  and  $1218 \text{ cm}^{-1}$ . The presence of sharp and strong band at  $3002 \text{ cm}^{-1}$  indicates the presence of -NH bridge. This band seems to be merged with very broad band of phenolic hydroxyl group.





The NMR spectrum of 8-HQ5-SASF-III polymer was scanned in DMSO- $d_6$  solvent. The spectrum is given in Figure 4. A singlet signals in the region 5.2 - 5.10 ( $\delta$ ) ppm which are due to methylene proton of the Ar-CH<sub>2</sub>-Ar bridges [30]. <sup>1</sup>H NMR spectra of 8-HQ-5-SASF polymer show a weak multiple signal (unsaturated pattern) in the region 8.17-8.20 ( $\delta$ ) ppm that is due to aromatic protons [11]. Weak signal in the range of 9.6 to 9.9 ( $\delta$ ) ppm is attributed to phenolic -OH proton (intramolecular H - bond) [31]. The methylenic protons of Ar-CH<sub>2</sub>-N linkage may be recognized from signals which appeared in the range 2.16 to 2.23 ( $\delta$ ) ppm [32]. The signal appears in the range of 9.86 - 9.94 indicate the proton of SO<sub>3</sub>H group [12].

### **Thermogravimetric analysis of the polymer**

The thermal stability of polymer is evaluated by dynamic thermogravimetric analysis in air atmosphere with heating rate of 10 °C.min<sup>-1</sup>.

Thermogram of TG of 8-HQ5-SASF-III polymer is shown in Figure 5. Thermogram of polymer depicts four steps decomposition after loss of water molecule in the temperature range 40 °C - 750 °C. The first step decomposition takes place between 40 °C - 90 °C corresponds to 2.20 % loss which may attributed to loss of a water molecule against calculated 2.01 % present per repeat unit of the polymer. The second step decomposition starts from 90°C - 145°C which represents degradation of three -OH groups and three sulphonic acid groups attached to the aromatic ring (38.29 % experimental and 38.23 % calculated). The third step which is start from 145°C - 310°C corresponding to loss of aromatic rings and methylene groups (73.20 % experimental and 73.30% calculated ). The fourth step decomposition starts from 310°C - 750°C leaving behind semicarbazide moiety (91.68% experimental and 91.05% calculated).

### **Thermo-analytical data**

A plot of percentage mass loss versus temperature is shown in the Figure 5 for a representative 8-HQ5-SASF-III polymer. To obtain the relative thermal stability of the copolymer, the method described by Sharp-Wentworth and Freeman-Carroll was adopted. The thermal stability of polymer, based on the initial decomposition temperature, has also been used here to define their relative thermal stability, neglecting the degree of decomposition.

By using thermal decomposition data and then applying above methods the activation energy (E<sub>a</sub>) is calculated which are not perfectly in agreement with each other (Table 1). But the 'average E<sub>a</sub>' calculated by Freeman-Carroll is nearly same and 'average E<sub>a</sub>' by Sharp-Wentworth is nearly double than both methods. The activation energy calculated by these methods is depicted in Table 2. However the error in activation energies obtained from the Sharp-Wentworth isoconversional method is significant and largely increases as far as conversion increases. On the other hand, it has been considered of interest to analyze the behavior of the process constitute by two competitive reactions that would lead to an apparent dependence between E<sub>a</sub> and a when analyzed by isoconversional method, in spite such dependence is not real [13].





A representative thermal activation energy plot of Sharp-Wentworth (Figure. 6) and Freeman-Carroll (Figure. 7, 8) method for the polymer has been shown. Thermodynamic parameters such as entropy change ( $\Delta S$ ), frequency factor ( $z$ ), apparent entropy change ( $S^*$ ) calculated on the basis of thermal activation energy ( $E_a$ ) using equations (1) and (2). These values are given in (Table 2).

The abnormally low value of frequency factor, it may be concluded that decomposition reaction of 8-HQ5-SASF-III polymer can be classed as a 'slow' reaction. There is no other obvious reason [14-15]. Fairly good straight-line plots are obtained using the two methods. This is expected since the decomposition of polymer is known not to obey first order kinetic perfectly [16, 17].

**Table. 1-** Thermogravimetical Parameters Corresponding to heating rate of 10°C/min. of 8-HQ5-SASF-III polymer.

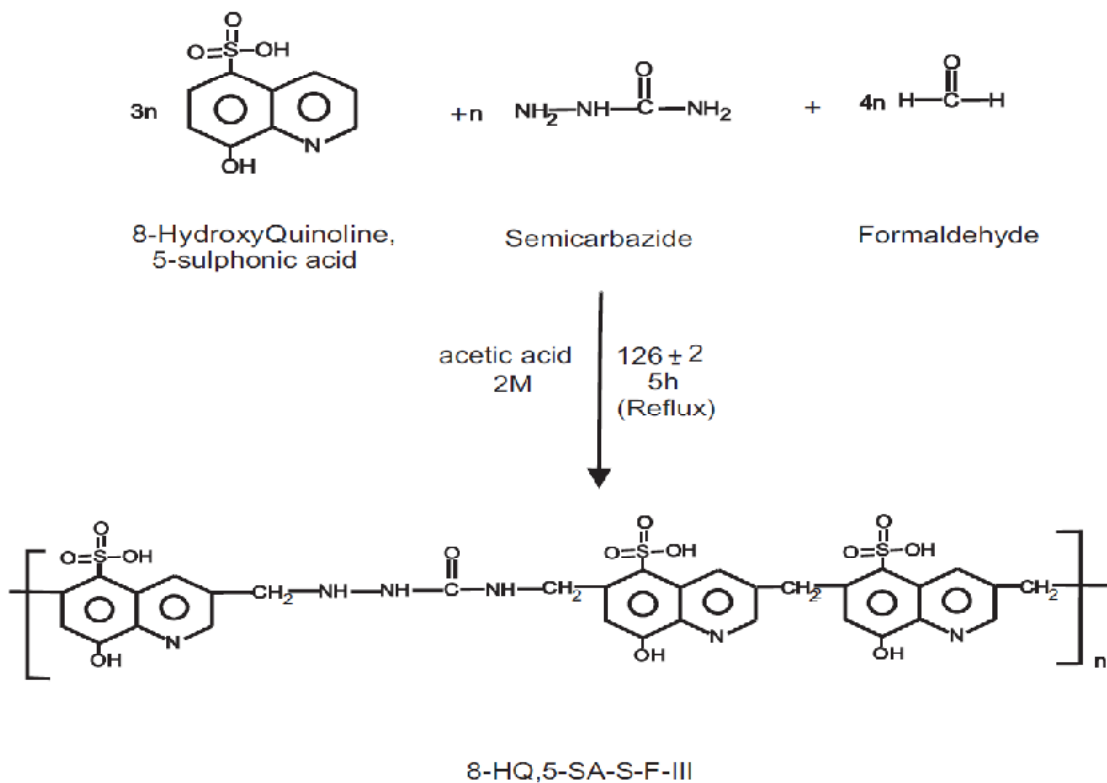
Polymers	T* (°C) <sup>a</sup>	DS	Z	S*	n
8-HQ5-SASF-III	457.82	6.94	886.72	-21.74	0.98

<sup>a</sup>Half decomposition temperature

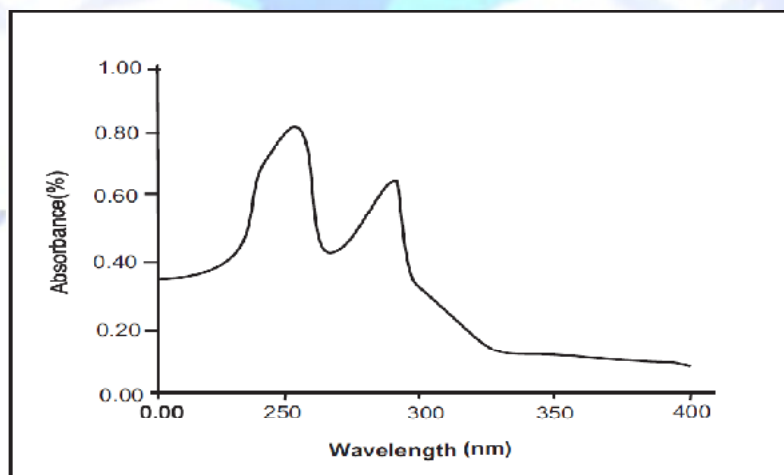
**Table. 2-** Comparison of activation energy ( $E_a$ ) of degradation at different stages by different methods of 8-HQ5-SASF-III polymer.

Polymer	Stage	Temp Range(°C)	Group loss	Wt. loss (%)	Activation ( $E_a$ ) (KJ/mol.)	
					Sharp Wentworth	Freeman Caroll
8-HQ5-SASF-III	1 <sup>st</sup>	40-90	H <sub>2</sub> O molecule entrapped	2.20	24.69	24.26
	2 <sup>nd</sup>	90-145	degradation of -OH and Sulphonic acidgroups attached to the aromatic ring	38.29	27.46	23.54
	3 <sup>rd</sup>	145-310	loss of quinoline ring and methylene groups	73.20	14.34	14.64
	4 <sup>th</sup>	310-750	loss of dithiooxamide moiety	91.68	36.76	35.74

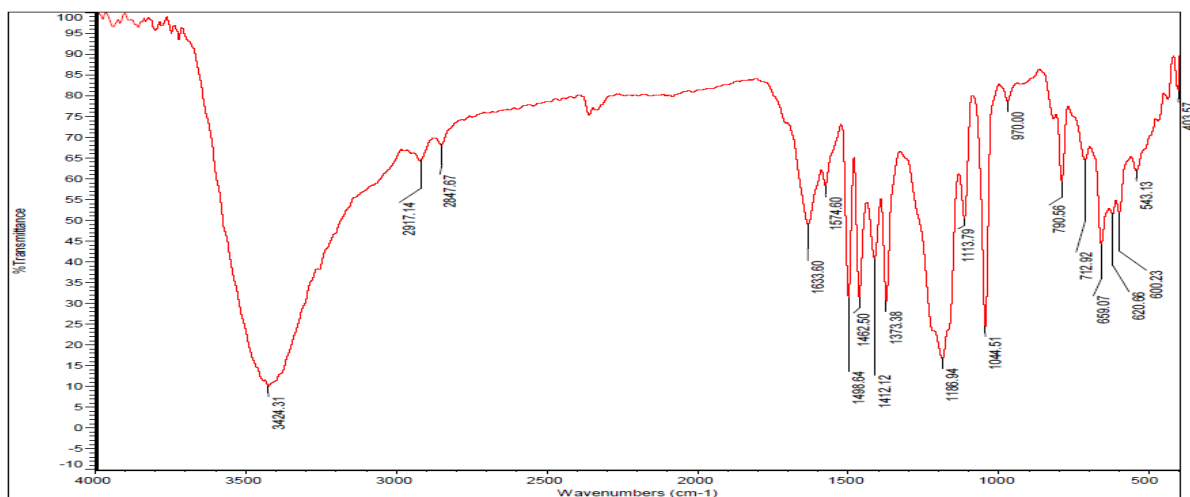




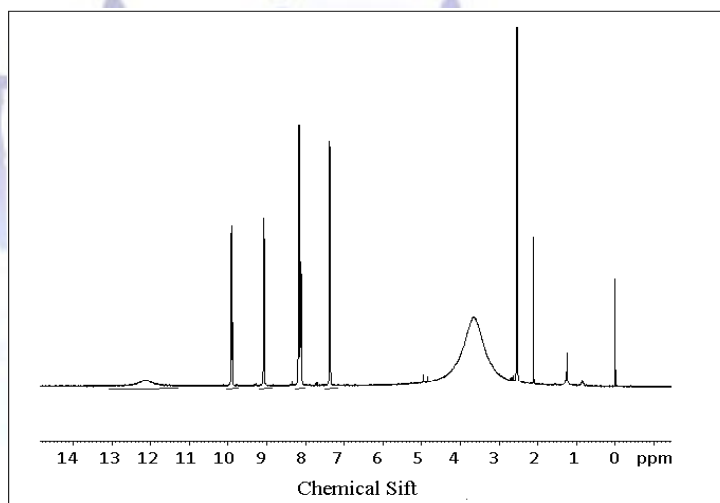
**Figure.1**-Synthesis of 8-HQ5-SASF-III polymer



**Figure. 2**-UV-Visible Spectra of 8-HQ5-SASF-III polymer



**Figure. 3-** Infra Red Spectra of 8-HQ5-SASF-III polymer



**Figure. 4-**<sup>1</sup>H NMR Spectrum of 8-HQ5-SASF-III polymer



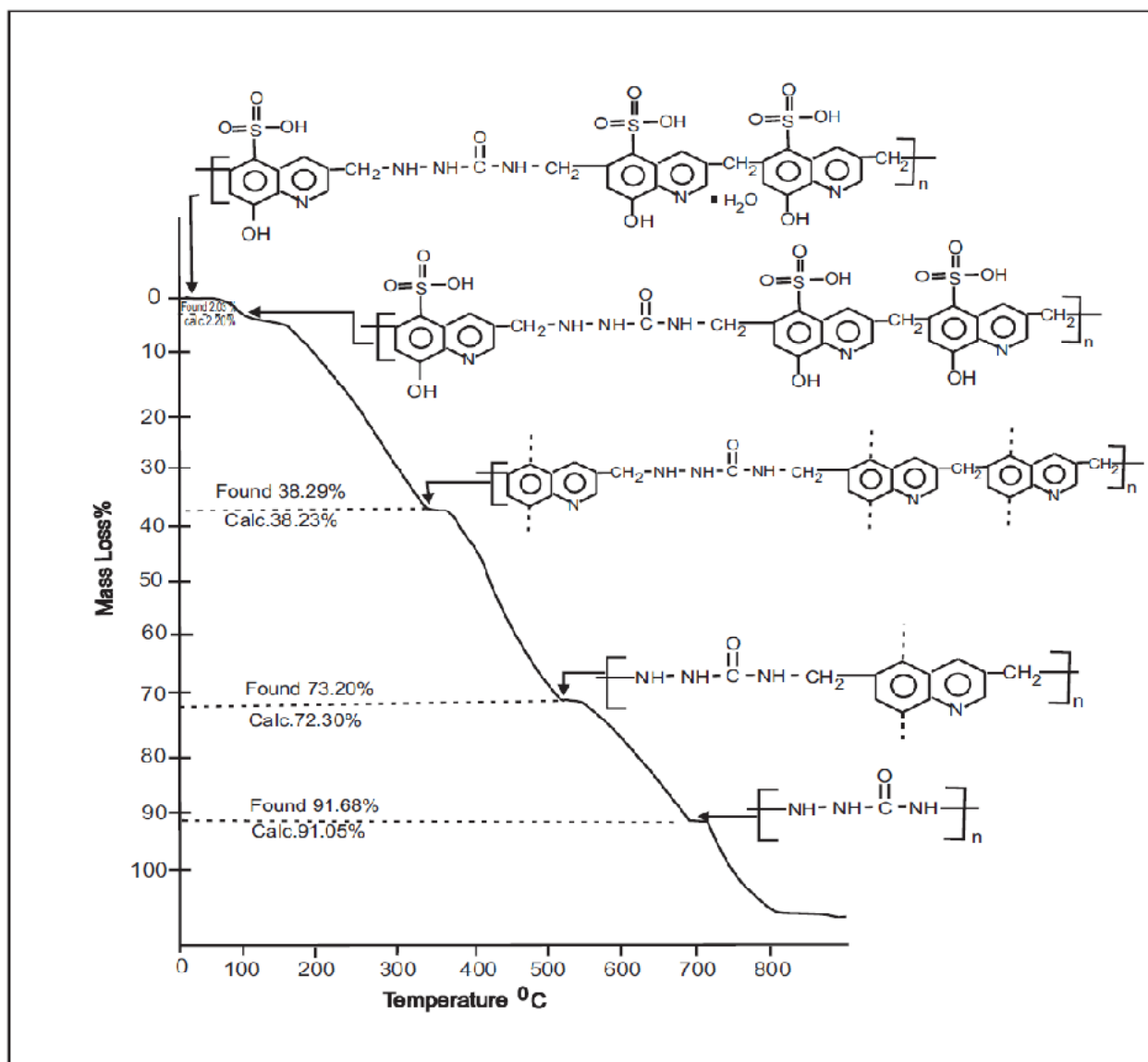


Figure. 5- Thermogram of 8-HQ5-SASF-III polymer

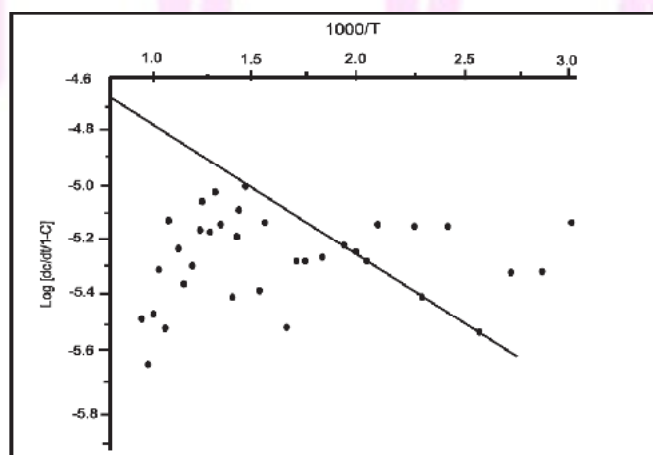
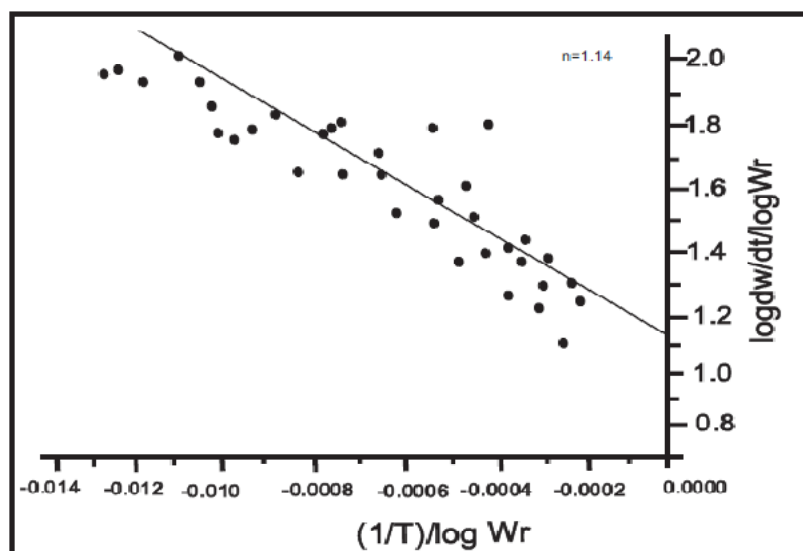
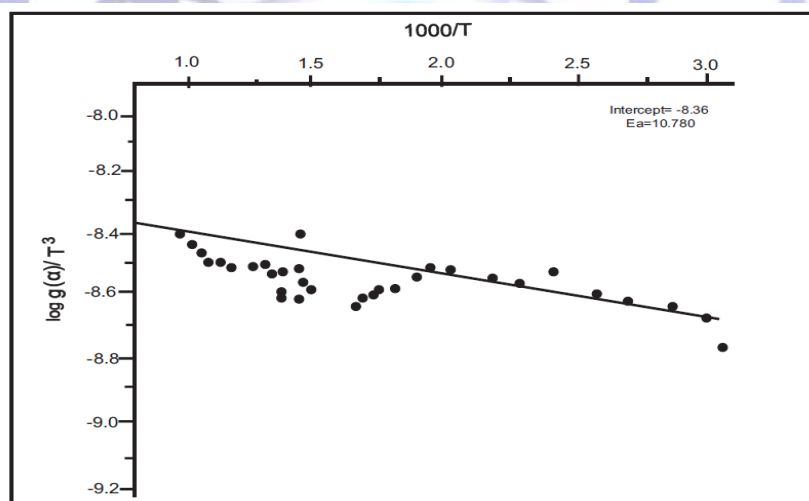


Figure. 6-Sharp-Wentworth plot of 8-HQ5-SASF-III polymer



**Figure. 7** Freeman-Carroll plot of 8-HQ5-SASF-III polymer



**Figure. 8-** Activation Energy Plot of 8-HQ5-SASF-III polymer

## Conclusion:

The 8-HQ5-SASF-III copolymer based on the condensation polymerization of 8-hydroxyquinoline 5-sulphonic acid and semicarbazide with formaldehyde in the presence of acid catalyst has been prepared. From the UV-visible, FT-IR and  $^1\text{H}$  NMR spectral studies the proposed structure of the 8-HQ5-SASF-III polymer has been determined. In TGA the kinetic parameters evaluated from the Sharp-Wentworth and Freeman-Carroll methods are found to be similar, indicating the common reaction mode. The resin undergoes degradation at high temperature, indicates that the polymer resin under study are thermally stable at elevated temperature. Low value of frequency factor may be concluded that the decomposition reaction of 8-hydroxyquinoline 5-sulphonic acid-semicarbazide-formaldehyde polymer can be classified as 'slow reaction'. The activation energy



calculated from Sharp Wentworth and Freeman Carroll methods are good agreement with each other.

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