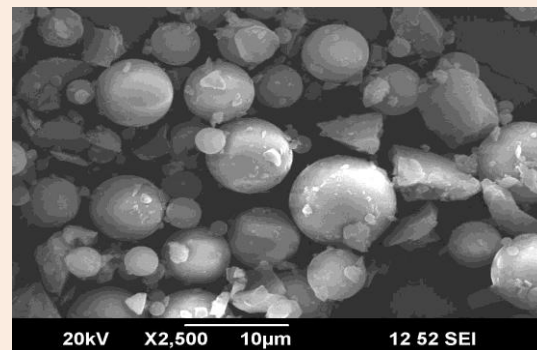


Research Article

Synthesis, Spectral, Morphology and Thermal Degradation Kinetics Studies of Copolymer

W. B. Gurnule^{1*}, Jyotsana Khobragade² and Mudrika Ahamed²¹Department of Chemistry, Kamla Nehru Mahavidyalaya, Sakkardara, Nagpur 440024, Maharashtra, India²Department of Chemistry, Priyadarshani College of Engineering, Hingna Road, Nagpur-440 019, India**Abstract**

Copolymer (8-HQ5-SASF-II) has been synthesized using the monomers 8-hydroxyquinoline 5-sulphonic acid, semicarbazide and formaldehyde in 2:1:3 molar proportions. The structure of 8-HQ5-SASF-II copolymer has been elucidated on the basis of elemental analysis and various physicochemical techniques, i.e. UV-Visible, FT-IR and ¹H-NMR spectroscopy. Scanning electron microscopy (SEM) and X-ray diffraction (XRD) analysis were used to establish the surface morphology and nature of the copolymer. Detailed thermal degradation study of the new copolymer has been carried out to ascertain its thermal stability. 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 (ΔS), 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 0.93.



Keywords: Copolymer, Freeman-Carroll method, Synthesis, Spectroscopic characterization, Sharp-Wentworth, Thermal degradation

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Introduction

In the recent years, we have witnessed a great deal of interest in the synthesis and characterization of copolymers due to their application as catalysts, semiconductors, drugs, biocides, ion-exchanger, luminescent materials and also models for enzymes [1,2]. 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. Tang and coworkers [3] studied the thermal decomposition kinetics of thermotropic copolyesters 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 [4]. Rahangdale and coworkers studied thermal degradation of terpolymers derived from 2, 4-dihydroxy-acetophenone, dithioamide and formaldehyde [5,6].

Terpolymer resins are derived from 2,4-dihydroxypropiophenone, biuret, and formaldehyde in hydrochloric acid as catalyst and studied their thermal degradation [7,8]. Thermal degradation of *m*-nitroaniline, *m*-chloroaniline and *m*-aminophenol has been studied by Dash *et al.* [9] and 2-hydroxyacetophenone, oxamide and formaldehyde [10]. Oswal et al synthesized and studied thermal properties of copoly(maleimide-methylmethacrylate), terpoly(maleimide-

methylmethacrylate-acrylic acid), and terpoly- (maleimide-methylmethacrylatemethylacrylic acid). The thermal behaviour was studied by TG and DSC techniques [11]. Thermoanalysis and rheological behavior of copolymers of methyl methacrylate, N-phenylmaleimide and styrene studied by G. Jungang et al [12]. 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 [13-16].

However, the literature studies have revealed that no copolymer 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-II copolymer. 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-II copolymer. After treating the thermal degradation data with Sharp–Wentworth (SW) and Freeman–Carroll (FC) methods, activation energy and kinetic parameters such as ΔS , ΔH , Z , S^* and n (order of reaction) have been evaluated [17].

Experimental

Materials and Reagents

All the chemicals used were of analytical grade. 8-hydroxyquinoline 5-sulphonic acid, semicarbazide and formaldehyde are purchased from Merck Chemicals, India. Solvents like N,N-dimethylformamide and dimethylsulphoxide purchased from SD Fine Ltd, Mumbai, India, were used after distillation.

Synthesis of 8-HQ5-SASF-II Copolymer

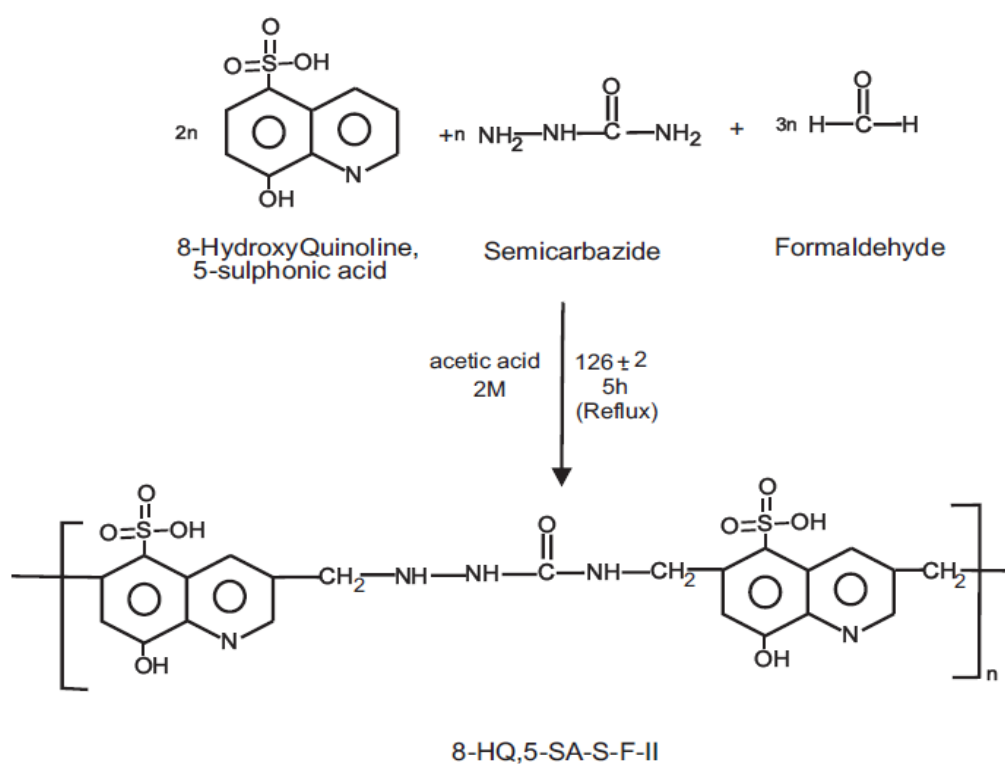


Figure 1 Synthesis of 8-HQ5-SASF-II copolymer

The 8-HQ5-SASF-II copolymer was prepared by condensing, 8-hydroxyquinoline 5-sulphonic acid, (0.2 mol) and semicarbazide (0.1 mol) with formaldehyde (0.3 mol) in the presence of 2M HCl as a catalyst at 126 ± 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 8-hydroxyquinoline 5-sulphonic acid,-formaldehyde copolymer, which might be present along with the 8-HQ5-SASF-II copolymer. 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) conc. HCl / water with constant stirring and filtered. The process was repeated twice. The resulting copolymer sample was washed with boiling water and dried in a vacuum at room temperature. The purified copolymer resin was finely ground to pass through 300-mesh size sieve and kept in a vacuum over silica gel. The yield of the copolymer was found to be about 86 %.

Analytical and Physicochemical Studies

The elemental analysis was carried out on a Perkin Elmer 2400 Elemental Analyzer instrument. 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^{-1} on Shimadzu IR Affinity Spectrophotometer at Department of Chemistry, Kamla Nehru Mahavidyalaya, Nagpur. $^1\text{H-NMR}$ studied using Bruker Avance-II FT-NMR Spectrometer in DMSO-d_6 solvent at STIC Analysis, Kochi. All the analytical and spectral studies for the newly synthesized copolymer were carried out at STIC Analysis centre, Kochi.

Instrumentation

The nonisothermal thermogravimetric analysis was performed in air atmosphere with heating rate of 10 °C.min $^{-1}$ using 5 - 6 mg of samples in platinum crucible from temperature of 40 °C to 800 °C and thermograms are recorded for 8-HQ5-SASF-II sample at STIC, Kochi. With the help of thermogravimetric data the thermal activation energies (E_a) and order of reaction (n) calculated. Also other thermodynamic parameters such as entropy change (ΔS), apparent entropy change (S^*) and frequency factor (z) are determined and reported in the **Table 1**.

Table1 Thermogravimetric Parameters Corresponding to Heating Rate of 10 °C/min. of 8-HQ5-SASF-II copolymer

Copolymer	T^* (°C) ^a	ΔS	Z	S^*	n
8-HQ5-SASF-II	456.43	8.95	880.62	-20.89	0.93

^aHalf decomposition temperature

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 [18], which is in the form of

$$\frac{\Delta \log dW / dt}{\Delta \log Wr} = n - \frac{Ea}{2.303R} \cdot \frac{\Delta(1/T)}{\Delta \log Wr} \dots\dots\dots(1)$$

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 between the terms $\frac{\Delta \log dW / dt}{\Delta \log Wr}$ vs $\frac{\Delta(1/T)}{\Delta \log Wr}$ 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 (ΔS), frequency factor (z), apparent entropy (S^*) can also be calculated by further calculations.

Sharp–Wentworth Method

Using the equation derived by Sharp and Wentworth [17],

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

Where,

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

Friedman Method

Friedman [18] provides the following expression for thermal degradation kinetic studies based on Arrhenius equation:

$$\ln \left(\frac{d\alpha}{dt} \right) = \ln(z) + n \cdot \ln(1 - \alpha) - \left(\frac{Ea}{RT} \right) \dots\dots\dots(3)$$

Where, α is the conversion at time t, R is the gas constant ($8.314 \text{ J.mol}^{-1}.\text{K}^{-1}$) and T is the absolute temperature. The plot of $\ln(d\alpha/dt)$ vs $1/T$ should be linear with the slope Ea/R , from which Ea can be obtained. The plots (**figure 8**) give the activation energies at different stages of degradation reaction takes place.

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 (**Table 2**).

Table 2 Comparison of Activation Energy (Ea) of Degradation at Different Stages by Different Methods of 8-HQ5-SASF-II Copolymer

Copolymer	Stage s	Temp Range	Group loss	Wt. loss (%)	Activation (Ea) (KJ/mol.)		
					Sharp-Wentworth	Freeman-Carroll	Freidman
8-HQ5-SASF-II	1 st	40.0-150	H ₂ O molecule entrapped	3.29	25.06	25.38	25.63
	2 nd	150-320	degradation of –SO ₃ H group with two -OH groups	36.70	28.99	28.39	28.41
	3 rd	320-480	loss of aromatic ring along with two -CH ₂ groups	59.20	12.18	12.31	13.96
	4 th	480-710	loss of quinoline and semicarbazide moiety.	85.03	86.16	86.02	87.67

Results and Discussion

The resin sample was brown in color, insoluble in commonly used solvent, but was soluble in DMF, DMSO, THF, pyridine, concentrated H₂SO₄. No precipitation and degradation occurs of resin in all the solvents. These resins were analyzed for carbon, hydrogen, sulphur and nitrogen content.

Characterization of Copolymer

Molecular weight of copolymer was estimated by conductometric titration. The number average molecular weight (\overline{Mn}) could be obtained by multiplying the \overline{Dp} by the formula weight of the repeating unit [19]. The result of the molecular weight of copolymer samples prepared using higher proportion of two monomers (8-HQ5-SA and S) has the highest molecular weight in the series. The molecular weight for 8-HQ5-SASF-II is 6345.

The composition of copolymer obtained on the basis of the elemental analysis data was found to be in good correlation to that of the calculated values:

- .Calculated for C₂₂H₁₉N₅O₉S₂: C: 47.05 %; H: 3.38 %; N: 12.47 %., O: 25.66%, S: 11.40%
- Found for C₂₂H₁₉N₅O₉S₂: C: 47.90 %; H: 3.03 %; N: 12.17 % . O: 25.45%, S: 11.12%

A broad the UV-visible spectrum of 8-HQ5-SASF-II copolymer is shown in Figure 2. UV-visible spectra of all the purified copolymer has been recorded in pure DMF. The spectra of this copolymer exhibit two absorption maxima in the region 2400 nm and 280 nm. These observed positions of the absorption bands indicate the presence of carbonyl group (ketonic) processing double bond, which is in conjugation with the aromatic nucleus. The appearance of former band (more intense) can be accounted for $\pi \rightarrow \pi^*$ transition while the later band (less intense) may be due to $n \rightarrow \pi^*$ electronic transition. The shift from the basic value (viz. 240 nm and 310 nm respectively) may be due to conjugation effect, and presence of phenolic hydroxy group (auxochromes) is responsible for hyperchromic effect i.e. ϵ_{\max} higher values [20, 21]. This observation is in good agreement with the proposed most probable structure of this copolymer.

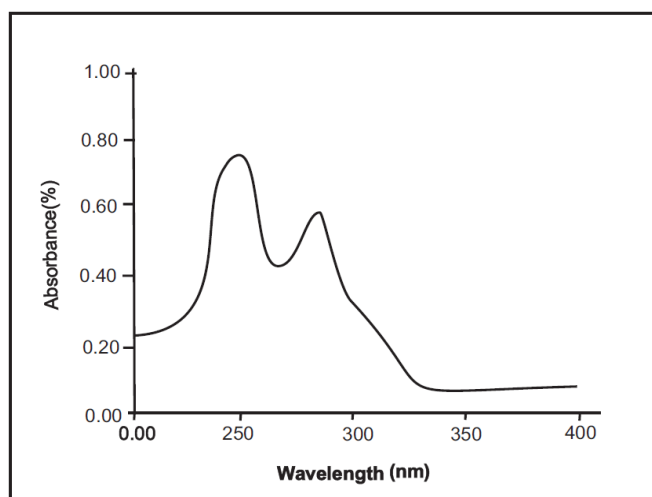


Figure 2 UV-visible spectrum of 8-HQ5-SASF-II copolymer

The IR-spectra of 8-HQ5-SASF-II copolymer is presented in Figure 3. A band appeared in the region 3435.5 cm^{-1} may be assigned to the stretching vibration of the phenolic hydroxy groups exhibiting intermolecular hydrogen bonding [21]. The presence of weak peak at 3000 cm^{-1} - 2975 cm^{-1} describes the $-\text{NH}-$ in semicarbazide moiety may be ascribed in the copolymeric chain [21]. The sharp band displayed at 1631.4 cm^{-1} may be due to the stretching vibration of carbonyl group of both, ketonic as well as semicarbazide moiety [22]. The sharp and weak bond obtained at 1380 cm^{-1} suggests the presence of $-\text{CH}_2-$ methylene bridges [22] in the copolymer chain. The band obtained in the range of $1652\text{-}1622\text{ cm}^{-1}$ suggests the presence of $-\text{SO}_3\text{H}$ group. The 1,2,3,5 substitution of aromatic benzene ring recognized by the sharp, medium / weak absorption bands appeared at $592\text{-}557$, $971.2\text{-}970$, $1098\text{-}1087$ and 1162 cm^{-1} respectively. This band seems to be merged with very broad band of phenolic hydroxyl group [22].

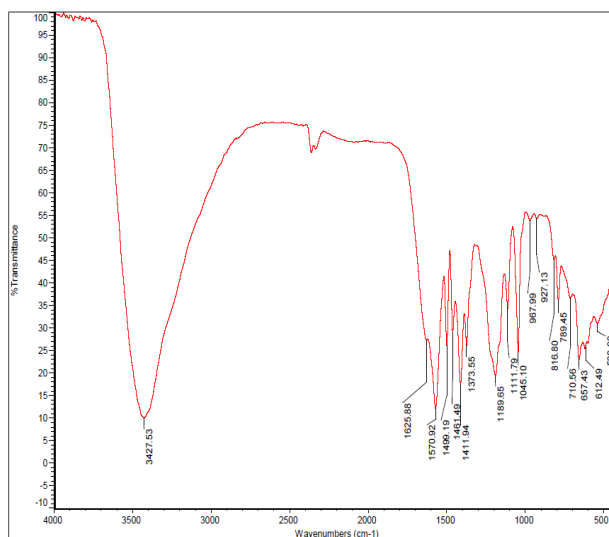


Figure 3 FT-IR spectrum of 8-HQ5-SASF-II copolymers

$^1\text{H-NMR}$ spectra of 8-HQ5-SASF-II copolymer is shown in Figure 4. A singlet signals in the region $5.02 - 5.10$ (δ) ppm which are due to methylene proton of the $\text{Ar-CH}_2\text{-Ar}$ bridges [46]. $^1\text{H NMR}$ spectra of 8-HQ-5-SACF copolymer show a weak multiple signal (unsaturated pattern) in the region $8.17\text{-}8.20$ (δ) ppm that is due to aromatic protons [44,47]. Weak signal in the range of 9.06 to 9.09 (δ) ppm is attributed to phenolic $-\text{OH}$ proton (intramolecular H -

bond) [44,47]. The methylenic protons of Ar-CH₂-N linkage may be recognized from signals which appeared in the range 2.16 to 2.23 (δ) ppm [45]. The signal appears in the range of 9.86 – 9.94 indicate the proton of SO₃H group. [22, 23, 24].

On the basis of the nature and reactive position of the monomer elemental analysis, electronic, IR, ¹H-NMR spectra and molecular weight, the most probable structure have been proposed for copolymer.

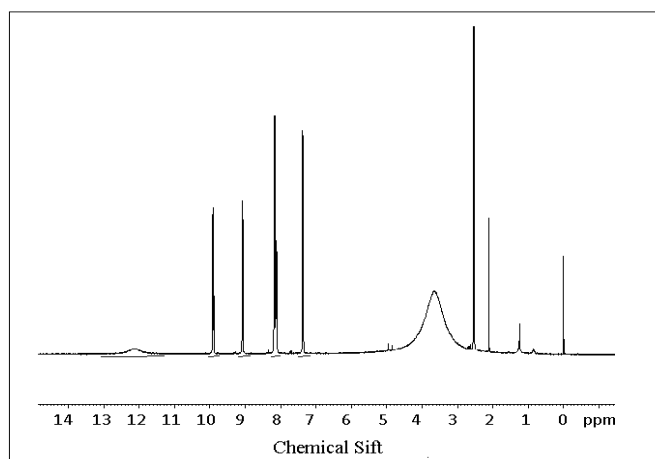


Figure 4 ¹H NMR Spectrum of 8-HQ5-SASF-II copolymer

Thermogravimetric Analysis of the Copolymer

The thermal stability of copolymer is evaluated by dynamic thermo-gravimetric analysis in air atmosphere with heating rate of 10⁰C.min⁻¹.

Thermogram of TG of 8-HQ5-SASF-II copolymer is shown in **Figure 5**. Thermogram of copolymer depicts three steps decomposition after loss of water molecule in the temperature range 40⁰C – 800⁰C. The initially decomposition takes place between 40⁰C - 150⁰C corresponds to 3.29 % loss which may attributed to loss of a water molecule against calculated 3.71 % present per repeat unit of the polymer.

The first step decomposition starts from 150⁰C – 320⁰C which represents degradation of two sulphonic acid group and two hydroxyl groups (36.70 % experimental and 36.20 % calculated).

The second step which is start from 320⁰C - 480⁰C corresponding to 59.20 % loss of aromatic ring along with two methylenic groups against calculated 59.72 %.

The third step starts from 480⁰C – 710⁰C corresponding to loss of quinoline ring and semicarbazide moiety (85.03% experimental and 85.61% calculated).

Thermoanalytical Data

A plot of percentage mass loss versus temperature is shown in the **Figure 5** for a representative 8-HQ5-SASF-II copolymer. To obtain the relative thermal stability of the copolymer, the method described by Sharp-Wentworth, Freeman-Carroll and Freidman was adopted. The thermal stability of copolymer, 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_a) is calculated which are not perfectly in agreement with each other. But the 'average E_a ' calculated by Freeman-Carroll and Freidman is nearly same and 'average E_a ' 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 iso-conversional 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_a and α when analyzed by iso-conversional method, in spite such dependence is not real [25].

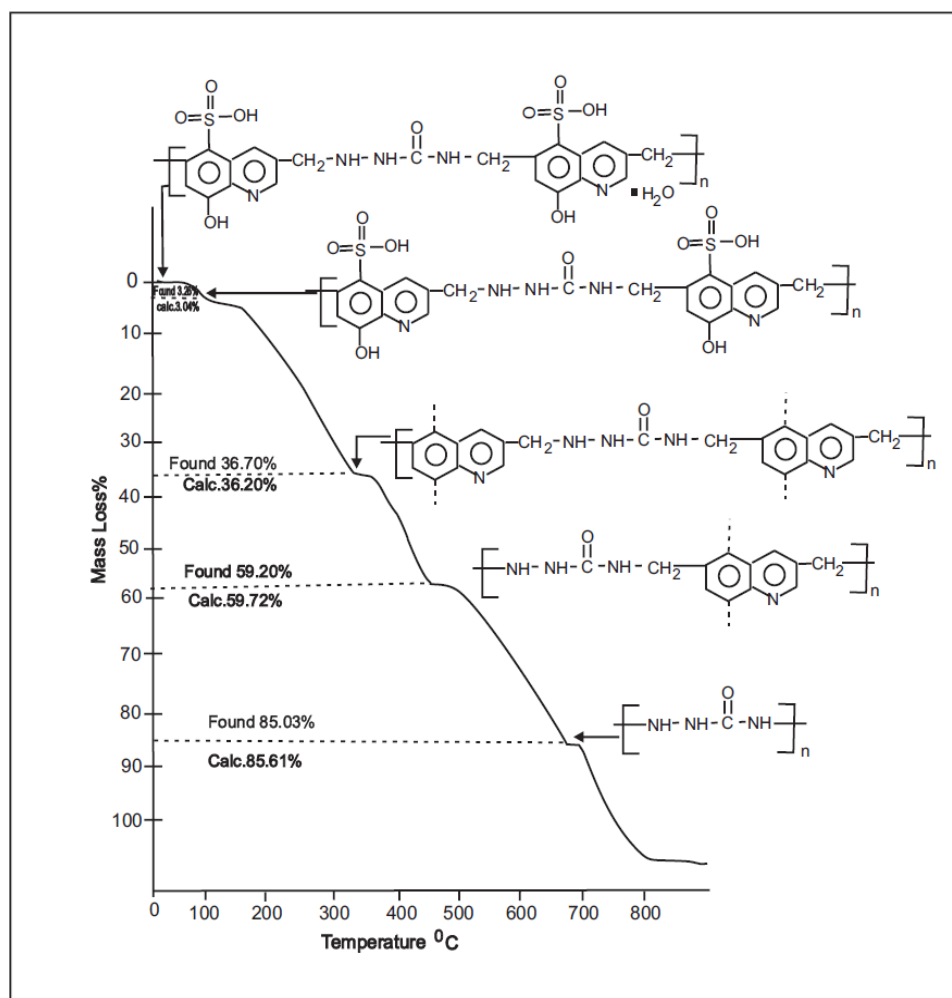


Figure 5 Thermal degradation of 8-HQ5-SASF-II copolymers

A representative thermal activation energy plot of Sharp-Wentworth (Figure 6), Freeman-Carroll (Figure 7-8) and Freidman (Fig. 9) method for the copolymer has been shown. Thermodynamic parameters such as entropy change (ΔS), frequency factor (z), apparent entropy change (S^*) calculated on the basis of thermal activation energy (E_a) using equations (3), (4), (5). These values are given in (Table 1).

i. Entropy Change (ΔS):

$$\text{Intercept} = \log \frac{kR}{h\phi E\alpha} + \frac{\Delta S}{2.303R} \dots \dots \dots (3)$$

Where,

$$\begin{aligned}
 k &= 1.3806 \times 10^{-16} \text{ erg.deg}^{-1}.\text{mol}^{-1}, \\
 R &= 1.987 \text{ cal.deg}^{-1}.\text{mol}^{-1}, \\
 h &= 6.625 \times 10^{-27} \text{ erg.sec}, \\
 \phi &= 0.166, \\
 \Delta S &= \text{entropy change}, \\
 E_a &= \text{activation energy from graph.}
 \end{aligned}$$

ii. Frequency Factor (z):

$$B_{2/3} = \frac{\log z \cdot E_a}{R\phi} \dots\dots\dots (4)$$

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

Where, z = frequency factor,

B = calculated from eq [a],

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

iii. Apparent entropy change (S^*):

$$S^* = 2.303R \log \frac{zh}{RT^*} \dots\dots\dots (5)$$

Where, T^* = temp at which half of the compound decomposed.

The abnormally low value of frequency factor, it may be concluded that decomposition reaction of 8-HQ5-SASF-II copolymer can be classed as a 'slow' reaction. There is no other obvious reason [26, 27]. Fairly good straight-line plots are obtained using the two methods. This is expected since the decomposition of copolymer is known not to obey first order kinetic perfectly [28-31].

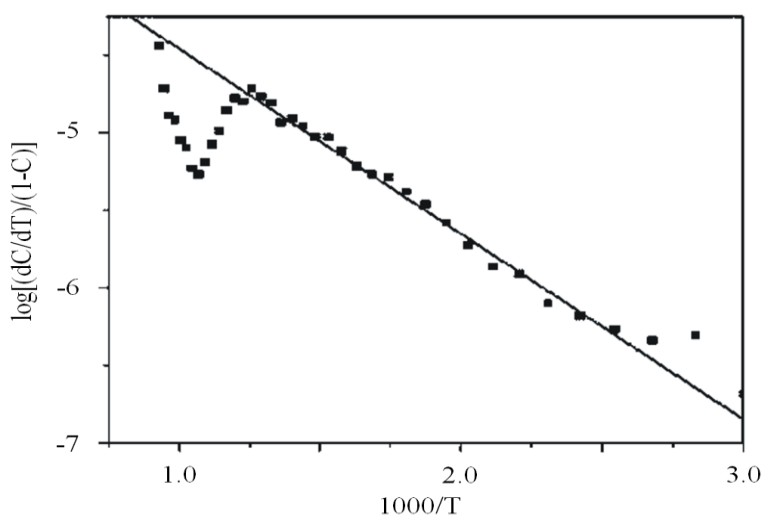


Figure 6 Activation energy plot by Sharp–Wentworth plot for 8-HQ5-SASF-II copolymer.

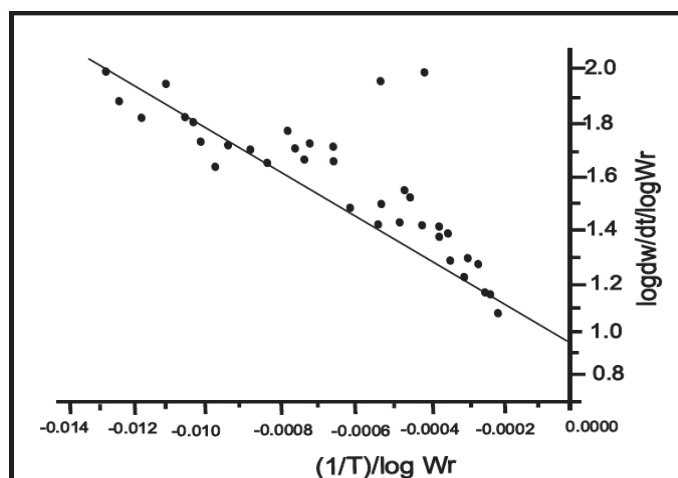


Figure 7 Activation energy plot by Freeman-Carroll of 8-HQ5-SASF-II copolymer

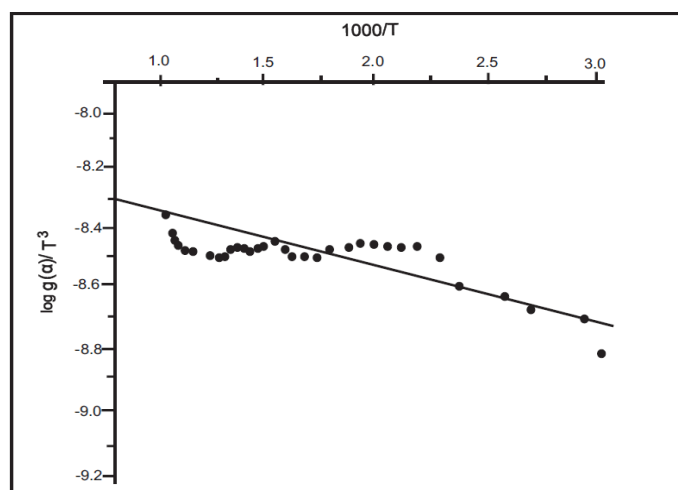


Figure 8 Freeman-Carroll plot of 8-HQ5-SASF-II copolymer

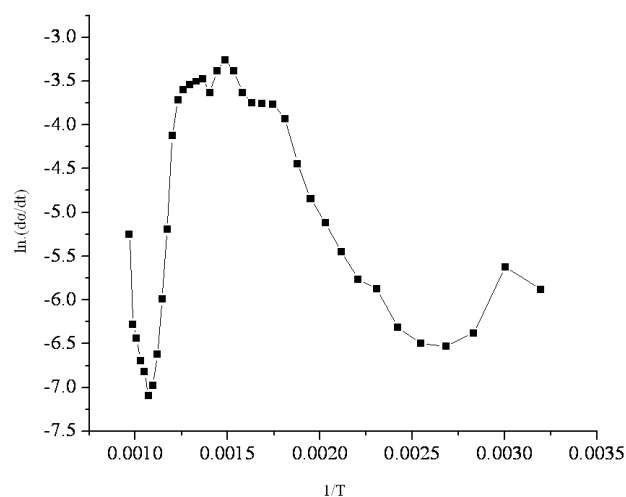


Figure 9 Activation energy plot by Friedman plot for 8-HQ5-SASF-II copolymer

Conclusion

The 8-HQ5-SASF-II 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 elemental analysis, UV-visible, FT-IR and ¹H NMR spectral studies the proposed structure of the 8-HQ5-SASF-II copolymer 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 resins undergoes degradation at high temperature, indicates that the copolymer resins 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, Friedman and Freeman Carroll methods are good agreement with each other.

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