

Thermoanalytical Study and Kinetics of New 8-Hydroxyquinoline 5-sulphonic Acid-Oxamide- Formaldehyde Terpolymer Resins

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Abstract: The terpolymer resins (8-HQ5-SAOF) have been synthesized by the condensation of 8-hydroxyquinoline 5-sulphonic acid (8-HQ5-SA) and oxamide (O) with formaldehyde (F) in the presence of acid catalyst and using varied molar proportion of the reacting monomers. The synthesized terpolymer resins have been characterized by different physico-chemical techniques. Thermogravimetric analysis of all terpolymer resins in present study have been carried out by non-isothermal thermogravimetric analysis technique in which sample is subjected to condition of continuous increase in temperature at linear rate. Thermal study of the resins was carried out to determine their mode of decomposition and relative thermal stabilities. Thermal decomposition curves were studied carefully with minute details. The Freeman-Carroll and Sharp-Wentworth methods have been used in the present investigation to calculate thermal activation energy and different kinetic parameter of the terpolymer resins. Thermal activation energy (E_a) calculated with above two mentioned methods are in close agreement. The advantage of Freeman-Carroll method is to calculate both the order of reaction (n) and energy of activation in one single stage by keeping heating rate constant. By using data of thermogravimetric analysis, various thermodynamic parameters like frequency factor (Z), entropy change (ΔS), free energy change (ΔF) and apparent entropy (S^*) have been determined using Freeman-Carroll method.

Keywords: Polycondensation, Kinetic parameter, Activation energy, Thermogravimetric analysis.

Introduction

The synthesized terpolymer resins, showing versatile applications and properties, attracted the attention of scientist and introduce the recent innovations in the polymer chemistry.

These terpolymers can be used as high energy material¹, ion-exchanger², semiconductors³, antioxidants, fire proofing agent, optical storage data, binders, molding materials *etc.* Literature survey reveals the chelating ion-exchange properties of 2, 4-dinitrophenylhydrazones of 2-hydroxyacetophenone-formaldehyde resin⁴, and oximes of 2-hydroxyacetophenone-substituted benzoic acid-formaldehyde resin⁵ for different metal ions. Thermogravimetric analysis of urea-formaldehyde polycondensate (UFPS) has been reported by Zeman and Tokarova⁶. Terpolymer resins having good thermal stability have enhanced the scope for development of some polymeric materials. The study of the thermal degradation of terpolymer resins have recently become a subject of interest. Zhao Hong *et al.* studied the thermal decomposition behaviour of phosphorous containing copolymer⁷. In an earlier communication⁸⁻¹¹ from this department numbers of studies on such terpolymers have been reported. However no work seems to have been carried out on thermo analytical and kinetic studies of the terpolymer resins from 8-hydroxyquinoline 5-sulphonic acid-oxamide and formaldehyde. The present paper explores the thermal analysis giving their relative thermal stabilities by applying the Sharp-Wentworth and Freeman-Carroll methods. Energy of activation (E_a), Kinetic parameter *viz.* Z , ΔS , ΔF , S^* , and order of reaction (n) were determined by applying Freeman-Carroll Method.

Experimental

The entire chemical used in the synthesis of various new terpolymer resins were procured from the market and were Analar or Fulka or chemically pure grade. Whenever required they were further purified by standard methods.

Synthesis of 8-HQ5-SAOF terpolymer resins

The new terpolymer resin 8-HQ5-SAOF-1 was synthesized by condensing 8-hydroxyquinoline 5-sulphonic acid (2.43 g, 0.1 mol) and oxamide (0.88 g, 0.1 mol) with 37% formaldehyde (7.4 mL, 0.2 mol) in a mol ratio of 1:1:2 in the presence of 2 M 200 mL HCl as a catalyst at $130\text{ }^{\circ}\text{C} \pm 2\text{ }^{\circ}\text{C}$ for 6 h in an oil bath with occasional shaking to ensure thorough mixing. The separated terpolymer 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 5-sulphonic acid formaldehyde copolymer which might be present along with 8-HQ5-SAOF terpolymer. The yellow color 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-HQ5-SAOF-1 in shown in Figure 1.

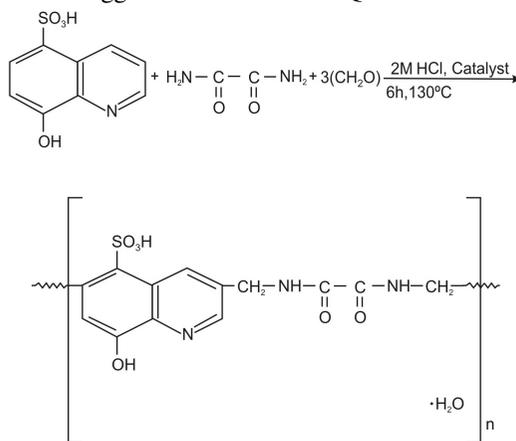


Figure 1. Reaction and suggested structure of representative 8-HQ5-SAOF-1 terpolymer resin.

The terpolymer was purified by dissolving in 10% 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 terpolymer sample 8-HQ5-SAOF-1 thus obtained was filtered, washed several times with hot water, dried in air, powdered and kept in vacuum desiccator over silica gel. The yield of the terpolymer resin was found to be 80%.

Similarly other terpolymer resins *viz.* 8-HQ5-SAOF-2, 8-HQ5-SAOF-3 and 8-HQ5-SAOF-4 were synthesized by varying the molar proportions of the starting materials *i.e.* (2:1:3), (3:1:4) and (4:1:5) respectively with little variation of experimental condition. The elemental analysis is tabulated in Table 1.

Characterization of terpolymer resins

The viscosities were determined using Taun-Fuoss viscometer at six different concentrations ranging from 1.00 to 0.031% of terpolymer in DMSO at 30 °C. the intrinsic viscosity η was calculated by relevant plots of the Huggins' equation and Kraemmer's equation.

$$\eta_{sp}/C = [\eta] + K_1 [\eta]^2 C \quad (1)$$

$$\ln \eta_{rel}/C = [\eta] - K_2 [\eta]^2 C \quad (2)$$

The number average molecular weights (\bar{M}_n) were determined by conductometric titration in non aqueous medium such as dimethylsulphoxide (DMSO) using ethanolic KOH as a titrant. From the graphs of specific conductance against milliequivalents of base, first and last break were noted from which degree of polymerization (\bar{DP}) and the number average molecular weight (\bar{M}_n) have been calculated for each terpolymer resin.

Electron absorption spectra of all terpolymer resins were recorded in DMSO (spectroscopic grade) on Shimadzu double beam spectrophotometer in the range of 200 to 850 nm at Sophisticated Analytical Instrumentation Facility, Punjab University, Chandigarh. Infra-red spectra of four 8-HQ5-SAOF terpolymer resins were recorded on Perkin-Elmer-983 spectrophotometer in KBr pellets in the wave number region of 4000-400 cm^{-1} at SAIF, Punjab University, Chandigarh. Nuclear Magnetic Resonance (NMR) spectra of newly synthesized terpolymer resins have been scanned on Bruker Advanced 400 NMR spectrometer using DMSO- d_6 at sophisticated Analytical Instrumentation Facility Punjab University, Chandigarh. TGA of all terpolymer resins have been carried out by using Perkin-Elmer TGS-II Thermogravimetric Analyzer at heating rate of 10 °C per minute up to 800 °C at SICART, Vallabhvidya nagar, Gujarat.

Results and Discussion

All the newly synthesized purified 8-HQ5-SAOF terpolymer resins were found to be yellow in colour. The terpolymers are soluble in solvents such as DMF, DMSO and THF while insoluble in almost all other organic solvents. The melting points of these terpolymers were determined by using electrically heated melting point apparatus and are found to be in the range of 436 to 449 K. These resins were analyzed for carbon, hydrogen, nitrogen and sulphur content. The details of elemental analysis are incorporated in Table 1. The terpolymer which has been used in the present investigation was prepared by the reaction given in Figure 1.

Table 1. Elemental analysis, molecular weight determination and intrinsic viscosity of 8-HQ5-SAOF terpolymer resins.

Terpolymer Resins	Empirical formula of repeat unit	Empirical weight of repeat unit, g	Average degree of polymerization (\overline{DP})	Average molecular weight (\overline{M}_n)	Elemental Analysis				Intrinsic viscosity $[\eta]$ (dL/g)
					Percentage, % of Element				
					C	H	N	S	
8-HQ5-SAOF-1	$C_{13}H_{14}N_3O_7S$	356	16.5	5874	43.11 (43.82)	3.21 (3.93)	11.36 (11.79)	8.18 (8.98)	0.81
8-HQ5-SAOF -2	$C_{23}H_{21}N_4O_{11}S_2$	592	17.00	10064	45.98 (46.62)	3.15 (3.55)	8.97 (9.46)	10.23 (10.81)	1.12
8-HQ5-SAOF -3	$C_{33}H_{28}N_5O_{11}S_3$	830	18.00	14940	47.12 (47.71)	3.05 (3.37)	8.04 (8.43)	10.85 (11.56)	1.32
8-HQ5-SAOF -4	$C_{43}H_{35}N_6O_{15}S_4$	1067	18.5	21002	47.82 (48.36)	2.96 (3.28)	7.14 (7.87)	11.68 (12.01)	1.49

The number average molecular weight (\overline{M}_n) of these terpolymers 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 1. The specific conductance was plotted against milliequivalents of ethanolic KOH required for neutralization of 100 g of each 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 neutralised.

From the plot, the first and last breaks were noted. The average degree of polymerization (\overline{DP}) and hence the number average molecular weights (\overline{M}_n) of all terpolymers have been determined using the formula.

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

$$\overline{M}_n = \overline{DP} \times \text{Repeat unit weight}$$

It is observed that the molecular weight of terpolymers increases with increase in 8-hydroxyquinoline 5-sulphonic acid content. This observation is in agreement with the trend observed by earlier workers^{12,13}.

Viscosity measurements were carried out at 300 K in freshly triple distilled dimethylsulphoxide (DMSO) using Tuan-Fuoss Viscomer, at six different concentrations ranging from 1.00% to 0.031%. Reduced viscosity versus concentration was plotted for each set of data. The intrinsic viscosity $[\eta]$ was determined by the corresponding linear plots. Huggins' and Kraemmer's constants were determined by an expression 1 and 2.

According to the above relations, the plots of η_{sp}/C and $\ln\eta_{rel}/C$ against C were linear with slopes of K_1 and K_2 respectively. By extrapolating linear plot to zero concentration, intercepts on the viscosity function axis give $[\eta]$ value in both plots. The values of intrinsic viscosity obtained from both plots have been found to be closed agreement with each other. The calculated values of the constants K_1 and K_2 in most cases satisfy the relation $K_1 + K_2 = 0.5$ favourably¹⁴. It was observed that terpolymer having higher \overline{M}_n shows higher value of $[\eta]$ which are in good agreement with earlier co-workers^{14,15}.

The UV-Visible spectra of all the 8-HQ5-SAOF terpolymer samples in pure DMSO were recorded in the region 200-850 nm at a scanning rate of 100 nm min⁻¹ and a chart speed of 5 cm min⁻¹. All the four 8-HQ5-SAOF terpolymer samples gave two characteristics bands at 310-330 nm and 230-275 nm. These observed positions for the absorption bands have different intensities. The more intense band is due to $\pi \rightarrow \pi^*$ transition and the less intense is due to $n \rightarrow \pi^*$ transition. $\pi \rightarrow \pi^*$ transition indicates the presence of aromatic nuclei and $n \rightarrow \pi^*$ transition indicates the presence of -NH and -OH group. The hyperchromic effect is due to the presence of -OH and -NH groups, which act as auxochrome¹⁶. From the spectra of 8-HQ5-SAOF terpolymer resins it is observed that ϵ_{max} value gradually increases in the order of 8-HQ5-SAOF-1 < 8-HQ5-SAOF-2 < 8-HQ5-SAOF-3 < 8-HQ5-SAOF-4. The increasing order of ϵ_{max} values may be due to introduction of more and more aromatic ring and auxochrome phenolic -OH and -NH groups in the repeated unit of the terpolymer resins. The observation is in good agreement with proposed structures of above terpolymer resins.

The IR spectral studies revealed that all these terpolymers gave rise to nearly similar pattern of spectra. A broad absorption band appeared in the region 3500-3510 cm⁻¹ may be assigned to the stretching vibrations of phenolic hydroxyl (-OH) groups exhibiting intramolecular hydrogen

bonding¹⁷. A sharp strong peak at 1500-1650 cm^{-1} may be ascribed to aromatic skeletal ring. The bands obtained at 1150-1250 cm^{-1} suggest the presence of methylene ($-\text{CH}_2$) bridge¹⁸. The 1,2,3,5 substitution of aromatic benzene ring recognized by the sharp, medium / weak absorption bands appeared at 960-980, 1120-1055, 1210-1182 and 1320-1280 cm^{-1} respectively. The presence of sharp and strong band at 3390-3410 cm^{-1} indicates the presence of $-\text{NH}$ bridge. This band seems to be merged with very broad band of phenolic hydroxyl group.

The NMR spectra of all four 8-HQ5-SAOF terpolymer were scanned in DMSO- d_6 solvent. From the spectra it is revealed that all 8-HQ5-SAOF terpolymers gave rise to different pattern of ^1H NMR spectra, since each of 8-HQ5-SAOF terpolymer possesses set of proton having different electronics environment. The chemical shift (δ) ppm observed is assigned on the basis of data available in literature¹⁹. The singlet obtained in the region 5.12-4.92 (δ) ppm may be due to the methylene proton of $\text{Ar}-\text{CH}_2-\text{N}$ moiety. The signals in the region 7.30-7.39(δ) ppm are attributed to protons of $-\text{NH}$ bridge. The weak multiplate signals (unsymmetrical pattern) in the region of 8.21-8.18(δ) ppm may be attributed to aromatic proton ($\text{Ar}-\text{H}$). The signals in the range at 9.08 to 9.02(δ) ppm may be due to phenolic hydroxyl protons. The much downfield chemical shift for phenolic $-\text{OH}$ indicates clearly the intramolecular hydrogen bonding of $-\text{OH}$ group^{20,21}. The signals in the range of 10.02-10.08(δ) ppm are attributed to proton of $-\text{SO}_3\text{H}$ groups.

The polymers under study are terpolymer and hence, it is very difficult to assign their exact structures. However, on the basis of the nature and reactive site of the monomers and taking into consideration the linear structure of other substituted phenol-formaldehyde polymers and the linear branched nature of urea-formaldehyde polymers the most probable structures of proposed for 8-HQ5-SAOF terpolymers have been shown in Figure 2.

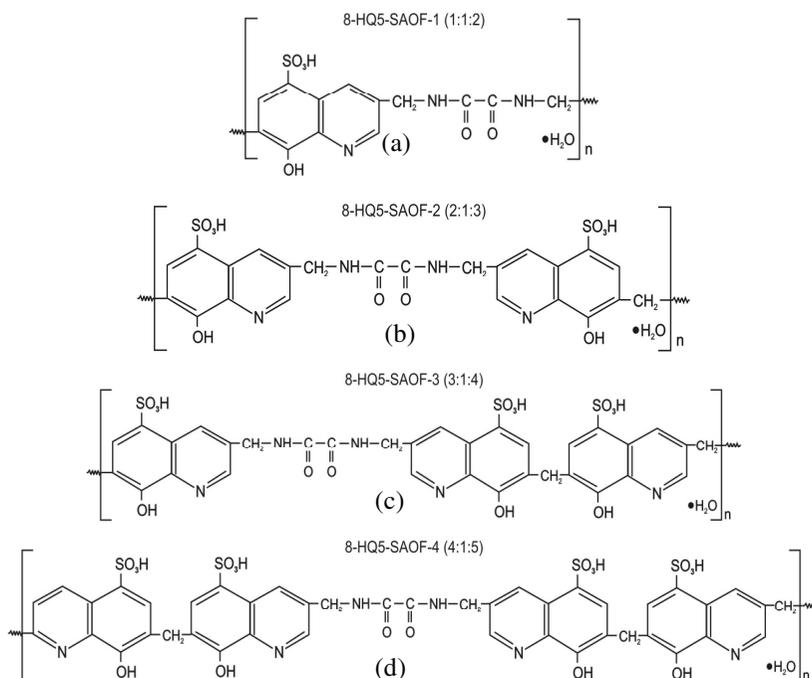


Figure 2. Suggested structure of terpolymer resins.

(a) 8-HQ5-SAOF-1; (b) 8-HQ5-SAOF-2; (c) 8-HQ5-SAOF-3; (d) 8-HQ5-SAOF-4.

Thermogram of all 8-HQ5-SAOF terpolymer resins have been recorded using Perkin-Elmer thermogravimetric analyzer. Brief accounts of thermal behaviour of these terpolymers are given. But for reason of economy of space the thermal data and kinetic plots for only one representative case have been given in Figure 3-6.

TG of 8-HQ5-SAOF-1 terpolymer

Thermogram of the terpolymer is shown in Figure 3 and depicts three steps decomposition in temperature range 40-800 °C, after loss of water molecule (5.04% found and 5.06% calculated). First step decomposition starts from 120-290 °C which represents the degradation of side chain attached to aromatic nucleus and hydroxyl group (32.13% found and 32.58% calculated). Second step decomposition starts from 290-460 °C, corresponding to 69.26% loss of aromatic nucleus against calculated 69.38%. Third step decomposition starts from 460 to 800 °C which corresponds to loss of oxamide moiety with its side chains (99.85% found and 100.00% calculated). Consequently no residue may be assigned after complete degradation.

In the present investigation Sharp-Wentworth and Freeman-Carroll methods have been used to determine the kinetic parameters of 8-HQ5-SAOF terpolymer sample.

Sharp-Wentworth method: In this method following expression is used.

$$\log \left[\frac{dc/dt}{\Delta(1-c)} \right] = \log(A/\beta) - Ea/2.303R - 1/T \quad (3)$$

Where β is the linear heating rate. The graph of $\log \left[\frac{dc/dt}{\Delta(1-c)} \right]$ versus $1/T$ has been plotted. The graph is a straight line with Ea as slope and A as intercept. The linear relationship confirms that the assumed order (n) = 1 is correct.

Freeman-Carroll method: In this method following expression is used.

$$\frac{\Delta \log(dw/dt)}{\Delta \log W_r} = (-Ea/2.303R) - \frac{\Delta(1/T)}{\Delta \log W_r} + n \quad (4)$$

Where, dw/dt = rate of change of weight of terpolymer sample with respect to time $W_r = W_c - W$, where W_c is the weight loss at the completion of the terpolymer reaction or at definite time and W is the total weight loss up to time t . T is the temperature, R is the gas constant and n is the order of reaction. Hence the graph of

$$\frac{\Delta \log(dw/dt)}{\Delta \log W_r} \text{ versus } \frac{\Delta(1/T)}{\Delta \log W_r} \quad (5)$$

Should give on Y axis ($x=0$) an intercept for the value of n , the order of reaction and the slope $m = -Ea/2.303R$. The detailed procedure is clearly laid out for one representative sample as an illustration.

A plot of percentage mass loss versus temperature is shown in Figure 3 for representative 8-HQ5-SAOF-1 terpolymer. From the TG curves, the thermo analytical and the decomposition temperature were determined Table 2 to obtain the relative thermal stabilities of the various polymers. The method described by Sharp -Wentworth was adopted. Based on the initial decomposition temperature, the thermal stabilities of the terpolymers, have also been used here to define their relative thermal stabilities, neglecting the degree of decomposition Table 2.

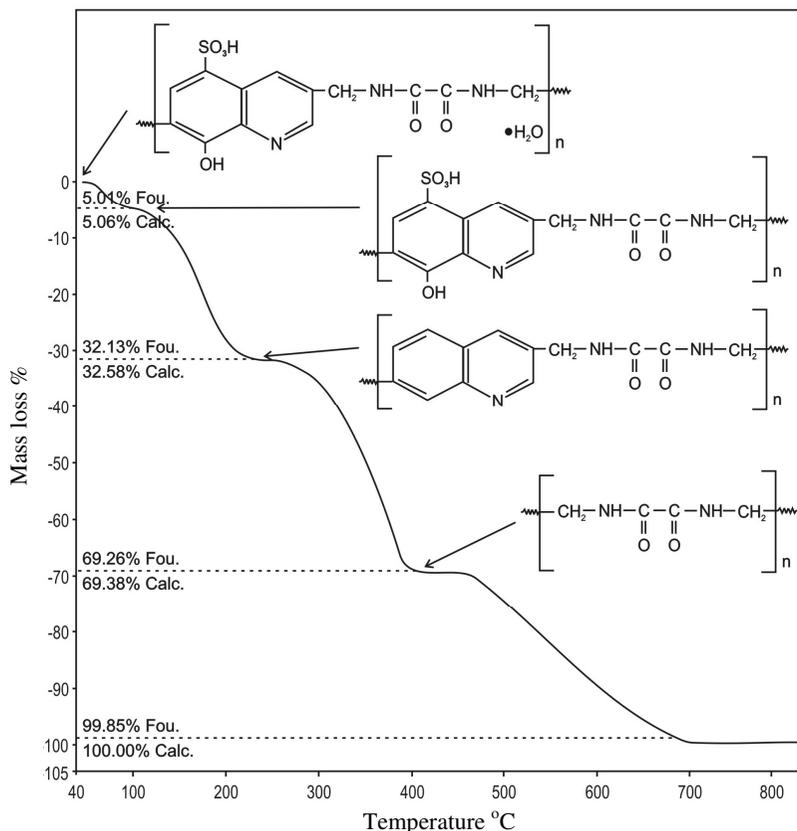


Figure 3. Thermogram of representative 8-HQ5-SAOF-1 terpolymer resin.

Table 2. Result of Thermogravimetric Analysis of 8-HQ5-SAOF terpolymer resins.

Terpolymer Resins	Half decomposition temp. K	Activation Energy, kJ/mol		Entropy change $-\Delta S$, J	Free energy change ΔF , kJ	Frequency factor Z, sec ⁻¹	Apparent entropy S^* , J	Order of reaction found, n
		FC	SW					
8-HQ5-SAOF-1	543	22.019	21.253	160.512	94.736	700	-19.076	0.96
8-HQ5-SAOF-2	583	24.508	23.167	160.698	97.304	746	-19.032	0.95
8-HQ5-SAOF-3	623	27.513	26.231	160.883	100.642	776	-19.006	0.93
8-HQ5-SAOF-4	663	31.593	30.252	159.920	104.036	846	-18.900	0.94

FC = Freeman-Carroll, SW = Sharp-Wentworth

Using thermal decomposition data and then applying the Sharp-Wentworth method (A representative Sharp-Wentworth plot of 8-HQ5-SAOF-1 terpolymer is shown in Figure 4) activation energy is calculated which is in agreement with the activation energy calculated by Freeman-Carroll method²². A representative thermal activation energy plot of Sharp-Wentworth method Figure 4 and Freeman-Carroll method (Figure 5 & 6) for the polymer have been shown. Thermodynamic parameters such as entropy change (ΔS), free energy change (ΔF), frequency factor (Z) and Apparent entropy (S^*) calculated on the basis of thermal activation energy are given in Table 2, using equations are given below.

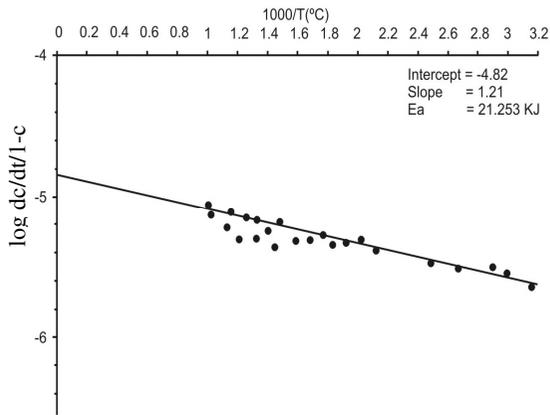


Figure 4. Sharp-Wentworth Plot of 8-HQ5-SAOF-1 terpolymer resin.

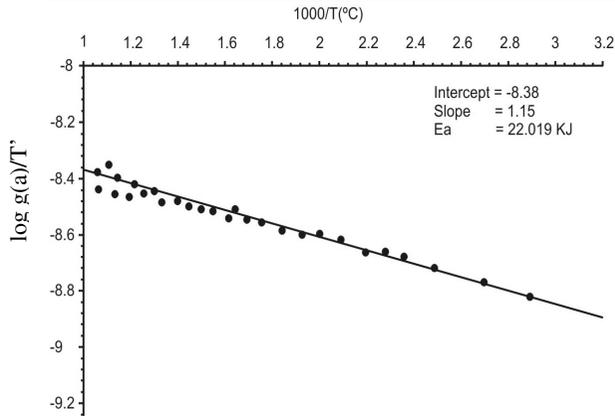


Figure 5. Freeman-Carroll Plot of 8-HQ5-SAOF-1 terpolymer resin.

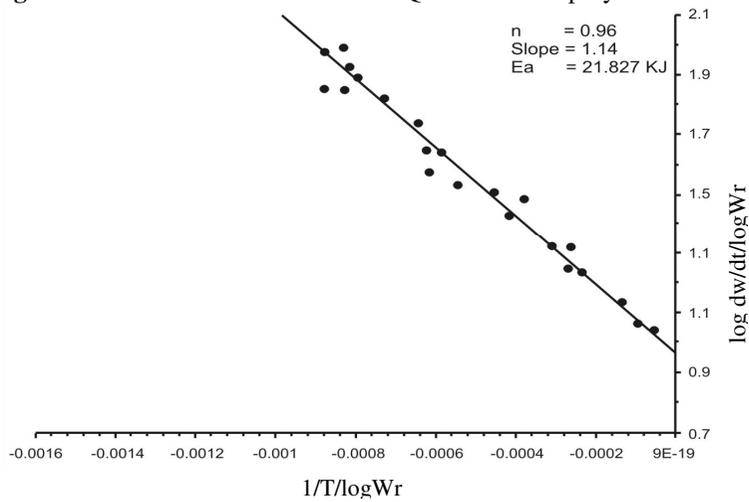


Figure 6. Freeman-Carroll Plot of 8-HQ5-SAOF-1 terpolymer resin.

(i) Entropy change

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

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

$R = 1.987$ cal/deg/mole

$h = 6.625 \times 10^{-27}$ erg sec

$\Phi = 0.166$

ΔS = change in entropy

E = activation energy from graph

(ii) $\Delta\Phi = \Delta H - T\Delta S$

Where, Δ = Enthalpy change = Activation energy

T = Temperature in K

ΔS = Entropy change {from (i) used}

(iii) Frequency factor

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

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

Where, Z = Frequency factor

B = Calculated from equation (7)

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

(iv) Apparent entropy change

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

Where, Z = from relation (6)

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

The 8-HQ5-SAOF terpolymers prepared from higher molar ratio of 8-hydroxyquinoline 5-sulphonic acid exhibited a lower rate of decomposition. Hence, the sequence of thermal stability is suggested to be 8-HQ5-SAOF-1 < 8-HQ5-SAOF-2 < 8-HQ5-SAOF-3 < 8-HQ5-SAOF-4. The sequence of thermal stability of the terpolymers predicted on the basis of the initial as well as half decomposition temperatures is in harmony with that predicted from the activation energy values. This fact is further supported by the increasing order of melting points from 8-HQ5-SAOF-1 to 8-HQ5-SAOF-4. This order of stability may be due to the possibility of an almost linear structure of the terpolymer having higher molar ratio of 8-hydroxyquinoline 5-sulphonic acid which may give rise to a stable structure to the terpolymer chain²³. In the present study, in case of 8-HQ5-SAOF-1 terpolymer the removal of water from the polymer is completed around 120 °C, which may be due to solvent or moisture probably crystal water entrapped in the terpolymer samples²⁴.

The analyses of the thermograms indicate that the decomposition of the terpolymers is three stage processes after a loss of water molecule at 120-160 °C. In the first step side chain attached to aromatic nucleus and hydroxyl groups decompose. In the second step, aromatic nucleus decompose while in the third step side chain attached to oxamide polymer and oxamide itself degraded and finally there is no residue remained after completion of degradation. Decomposition is completed at about 800 °C in all terpolymer resins.

By using the data of the Freeman-Carroll method, various thermodynamics parameters have been calculated Table 2. The values of these thermodynamic parameters for all terpolymers are about the same. The similarity of the values indicates a common reaction mode,²⁰ from the abnormally low values of frequency factor, it may be concluded that the decomposition reaction of 8-HQ5-SAOF terpolymers can be classed as a 'slow' reaction. There is no other obvious reason^{23,24}.

Fairly good straight line plots are obtained using the two methods. This is expected since the decomposition of terpolymer is known not to obey first order kinetics perfectly^{23,24}.

Conclusions

1. A terpolymer, 8-HQ5-SAOF, based on the condensation reaction of 8-hydroxyquinoline 5-sulphonic acid-oxamide-formaldehyde in the presence of acid catalyst, was prepared.
2. 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.
3. Low values of frequency factor may be concluded that the decomposition reaction of 8-hydroxyquinoline 5-sulphonic acid-oxamide-formaldehyde terpolymer can be classified as 'slow reaction'.
4. Thermogravimetric study concluded that these terpolymers are thermally stable at elevated temperature.

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