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Synthesis, Spectral Characterization and Kinetic study of 8-hydroxyquinoline 5-sulphonic acid-melamine-Formaldehyde terpolymer resin

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ABSTRACT

The title terpolymer (8-HQ5-SAMF) synthesized by the condensation of 8-hydroxyquinoline 5-sulphonic acid (8-HQ5-SA) and melamine (M) with formaldehyde (F) in the presence of acid catalyst and using varied 3:1:5 molar proportions of the reacting monomers. The synthesized terpolymer characterized by different spectral techniques. The thermogravimetric analysis of terpolymer resin prepared in present study has 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 resin was carried out to determine the mode of decomposition and thermal stability. Thermal decomposition curve was 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 resin. Thermal activation energy (Ea) 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 thermogravimetric parameters like frequency factor (Z), entropy change (ΔS), free energy change (ΔF) and apparent entropy (S) have been determined using Freeman-Carroll method.*

Keywords: Synthesis, polycondensation, resins, thermogravimetric analysis (TGA).

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 material [1], ion-exchanger [2], semiconductors [3], antioxidants, fire proofing agent, optical storage data, binders, molding materials etc. Literature survey reveals the chelation ion-exchange properties of 2,4-dinitrophenylhydrazone of 2-hydroxyacetophenone-formaldehyde resin [4], and oximes of 2-hydroxyacetophenone-substituted benzoic acid-formaldehyde resin [5] for different metal ions. Thermogravimetric analysis of urea-formaldehyde polycondensate (UFPS) has been reported by Zeman and Tokarova [6]. Terpolymer resins having good thermal stability have enhanced the scope for development of some polymeric materials.

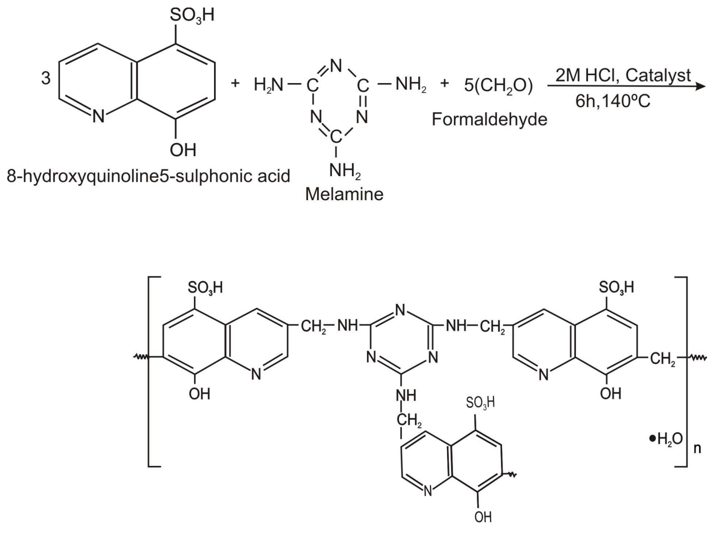
The study of the thermal degradation of terpolymer resins have recently become a subject of interest. Zhao Hong et. al. studied the thermal decomposition behaviour of phosphorous containing copolystar [7]. In an earlier communication [8-11] from this department numbers of studies on such terpolymers have been reported. However no work seems to have been carried out on synthesis, characterization and thermal stabilities of the terpolymer resin-III from 8-hydroxyquinoline 5-sulphonic acid-melamine and formaldehyde. The present paper describes the composition of newly synthesized resin; its spectral characterization by UV-Visible absorption spectra, NMR spectra ^{13}CMR spectra, morphology was studied by SEM micrographs and thermal analysis by applying the Sharp-Wentworth and Freeman-Carroll methods. Energy of activation (Ea), Kinetic parameter viz. Z, ΔS, ΔF, S*, and order of reaction (n) were determined by applying Freeman-Carroll Method.

EXPERIMENTAL SECTION

Synthesis of 8-HQ5-SAMF-III terpolymer resins

The new terpolymer resin 8-HQ5-SAMF-III was synthesized by condensing 8-hydroxyquinoline 5-sulphonic acid (0.3 mol) and melamine (0.1 mol) with 37% formaldehyde (0.5 mol) in a mol ratio of 3:1:5 in the presence of 2M 200 ml HCl as a catalyst at 140^0C ± 2^0C for 6h 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-SAMF-III terpolymer. 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-HQ5-SAMF-III in shown in Fig. 1.

The terpolymer was purified by dissolving in 10% aqueous sodium hydroxide solution, filtered and reprecipitated by gradual dropwise 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-SAMF-III thus obtained was filtered, washed several times with hot water, dried in air, powdered and kept in vacuum desicator over silica gel. The yield of the terpolymer resin was found to be 76%. The elemental analysis is tabulated in Table 1.



8-HQ5-SAMF-III

Figure1: Reaction and expected structure of 8-HQ5-SAMF-III terpolymer resin

RESULTS AND DISCUSSION

The newly synthesized purified 8-HQ5-SAMF-III terpolymer resin was found to be yellow in colour. The terpolymer is soluble in solvents such as DMF, DMSO and THF 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 in 392 K.

The UV-Visible spectra(Fig.2) of the 8-HQ5-SAMF-III terpolymer sample in pure DMSO was 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}. The 8-HQ5-SAMF-III terpolymer sample gave two characteristics bands at 360-370nm and 240-260nm. 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 presence of–NH and–OH group. The hyperchromic effect is due to the presence of –OH and -NH groups, which act as auxochrome [16].

The IR (Fig.3) spectral studies revealed that the terpolymer gave broad absorption band appeared in the region 3506-3508 cm^{-1} may be assigned to the stretching vibrations of phenolic hydroxyl (-OH) groups exhibiting intramolecular hydrogen bonding [17]. A sharp strong peak at 1556-1626 cm^{-1} may be ascribed to aromatic skeletal ring. The bands obtained at 1210-1230 cm^{-1} suggest the presence of methylene ($-CH_2$) bridge [18]. The 1,2,3,5 substitution of aromatic benzene ring recognized by the sharp, medium / weak absorption bands appeared at 953-970, 1145-1046, 1182-1188 and 1320-1321 cm^{-1} respectively. The presence of sharp and strong band at 3393-3402 cm^{-1} indicates the presence of –NH bridge. This band seems to be merged with very broad band of phenolic hydroxyl group.

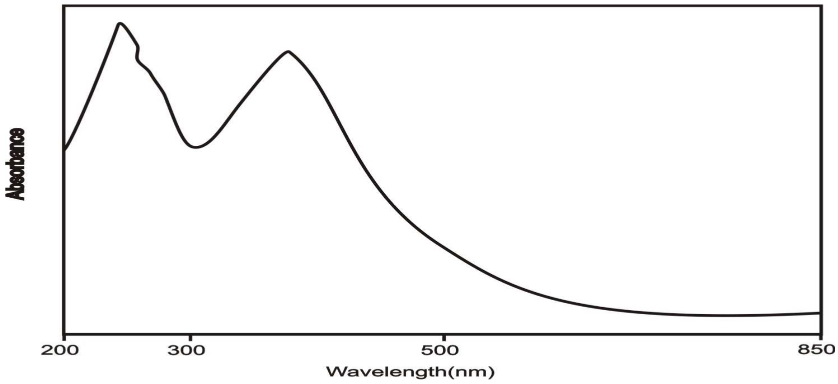


Figure 2: Uv-visible spectrum of 8-HQ5-SAMF-III terpolymer resin

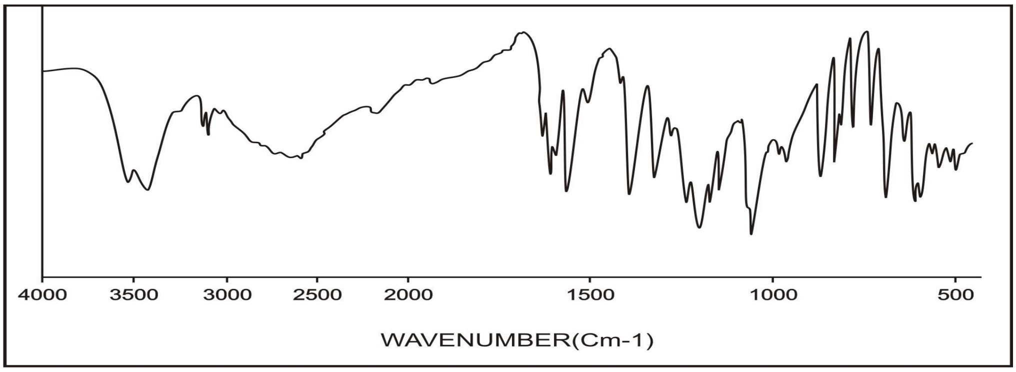


Figure 3: IR spectrum of 8-HQ5-SAMF-III terpolymer resin

The NMR spectrum (Fig.4) of 8-HQ5-SAMF-III terpolymer was scanned in DMSO-d_6 solvent. The chemical shift (δ) ppm observed is assigned on the basis of data available in literature [19, 20]. The singlet obtained in the region 4.98-4.96 (δ) ppm may be due to the methylene proton of Ar-CH_2-N moiety. The signals in the region 7.35-7.41 (δ) ppm are attributed to protons of –NH bridge. The weak multiplate signals (unsymmetrical pattern) in the region of 8.25-8.20 (δ) ppm may be attributed to aromatic proton (Ar-H). The signals in the range at 9.02 to 9.06 (δ) ppm may be due to phenolic hydroxyl protons. The much downfield chemical shift for phenolic –OH indicates clearly the intramolecular hydrogen bonding of -OH group [20, 21]. The signals in the range of 9.96 – 9.92(δ) ppm are attributed to proton of -SO_3H groups.

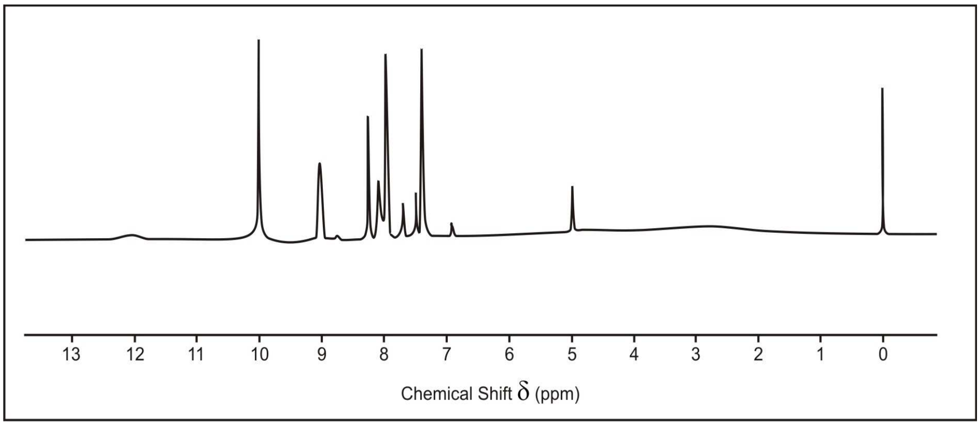


Figure 4: NMR spectrum of 8-HQ5-SAMF-III terpolymer resin

^{13}C NMR Spectra

Carbon NMR spectra of representative terpolymer resin is prescribed in Fig. 5. ^{13}C NMR spectra display signals arising from all the carbon atoms and hence provide direct information about the carbon skeleton. The ^{13}C NMR spectrum of 8-HQ5-SAMF-III terpolymer resin assigned the peak positions according to the literature. The ^{13}CNMR spectra shows the corresponding peaks at 151.00 - 165.00, 121.7 -132.3, 136.8 - 147.5,129.2 - 136.8, 134.6 - 148.9, 133.4 - 151.2, 136.2 - 149.5, 137.4 - 148.3 and 149.2 - 161.3 ppm with respect to C_1 to C_9 of the aromatic quinoline ring. Peaks at 165.00-173.2 and 161.00 - 177.3 ppm are due to C_1 to C_3 of aromatic melamine ring. The peak appeared at 115.5-126.7 ppm confirm the presence of -C-NH group in the resin. The peak appeared at 60.2-69.4 ppm may be due to the presence of -C-OH group. The peak appeared at 41.8 to 49.6 ppm may be assigned to the -CH_2 bridge in the terpolymer. The ^{13}C NMR spectra clearly established the linear structure of the terpolymer synthesized from 8-hydroxyquinoline 5-sulphonic acid-melamine-formaldehyde (Fig. 1).

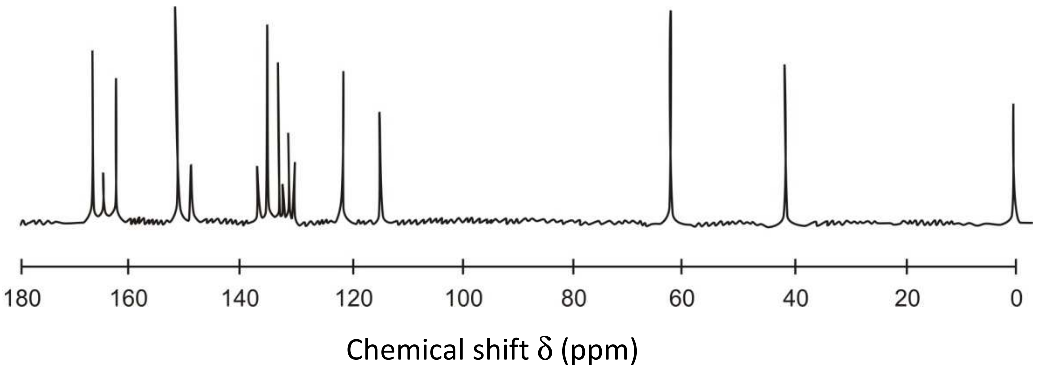
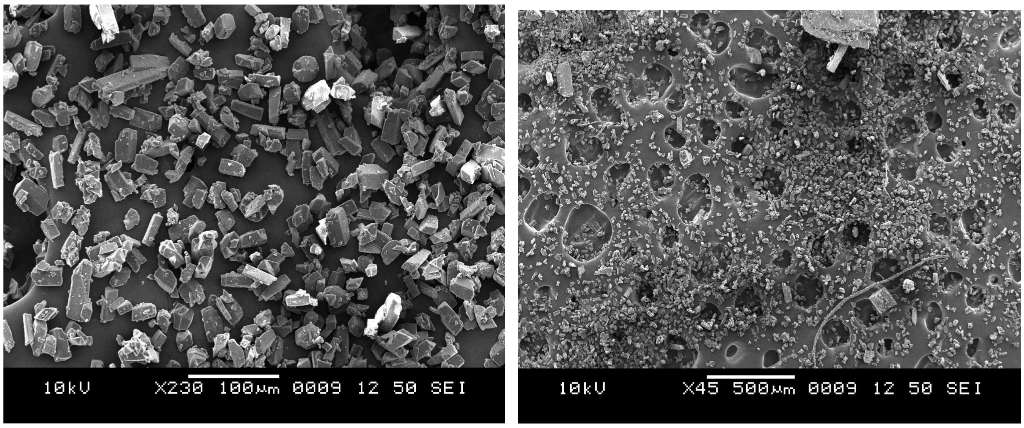


Fig. 5. ^{13}C NMR Spectra of 8-HQ5-SAMF-III Terpolymer Resin

Scanning Electron Microscopy (SEM)

SEM enables imaging to surface feature of 10-10^5 times magnification and resolution of features down to 3-100 nm depending upon the sample. Surface analysis has been found to be of great use in understanding the surface features of the materials. The morphology of the synthesized and purified terpolymer resins under investigation has been reported by scanning electron microscopy which is shown in Fig. 6. The white bar at the bottom of the SEM microscopy represents the scale. The morphology of the terpolymer resin shows fringed, scattered, miscellaneous model of the crystalline amorphous structure. The fringe and scattered structure represent transition material between the crystalline and amorphous phases. This tends to draw attention away from the details of the fine structure and gives little insight into the structure of large entities such as spherulites.

The SEM photographs exhibits such spherulties which are the aggregate of crystalline present along with the some amorphous regions. The amorphous region shows secondary structural feature such as corrugations and having shallow pits.



(A) (B)

Fig. 6: SEM micrographs of 8-HQ5-SAMF-III terpolymer resin

The spherulites structure of the 8-HQ5-SAMF-III terpolymer resin, indicates the presence of crystalline structure of the polymer. But the corrugation in the surface area with deep pits, shows the amorphous nature of the terpolymer. Thus SEM micrographs of 8-HQ5-SAMF-III terpolymer resin indicates the presence of transition structures between crystalline and amorphous. The amorphous nature depends on acidic character of reacting monomers. In the present terpolymer resins, the monomers have more acidic character (as 8-hydroxyquinoline 5-sulphonic acid is acidic in nature), therefore shows more amorphous nature. The more amorphous nature shows more ion exchange property, hence the 8-HQ5-SAMF-III terpolymer resin can be used as ion exchanger in the purification purpose.

The polymer under study is terpolymer and hence, it is very difficult to assign the exact structure. 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 structure [22] of proposed for 8-HQ5-SAMF-III terpolymer has been shown in Fig. 1.

Thermogravimetry:
Thermogravimetry of 8-HQ5-SAMF-III terpolymer resin has been carried out using Perkin-Elmer thermogravimetric analyser. A brief account of thermal behavior of 8-HQ5-SAMF-III terpolymer is given in Fig. 7-9.

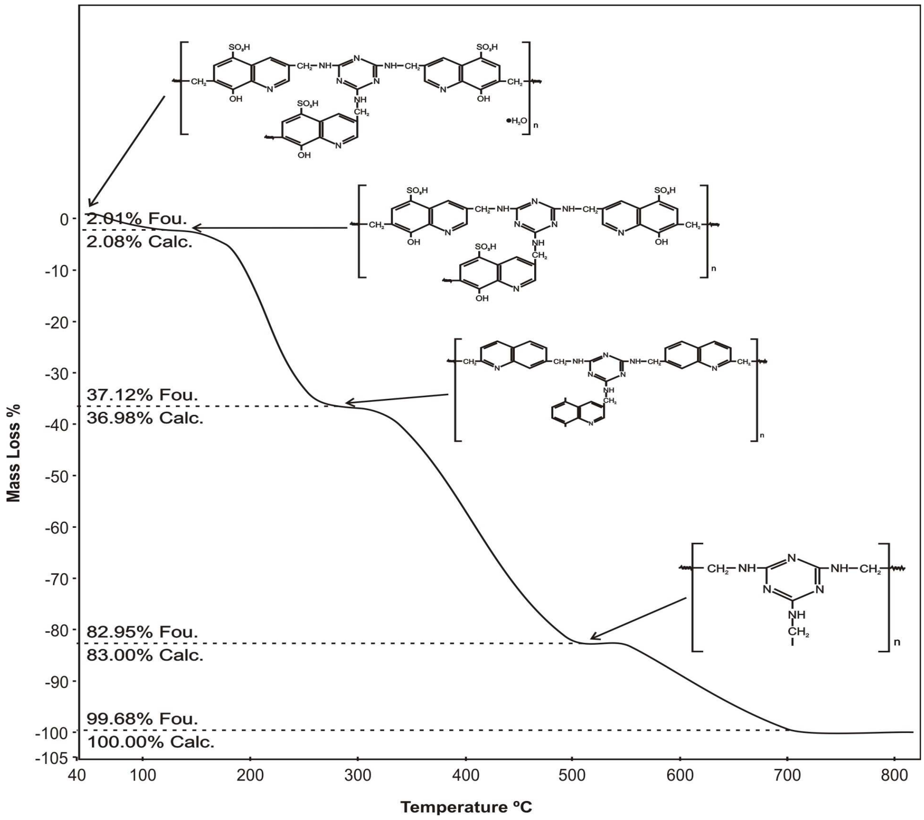


Figure 7: TGA of 8-HQ5-SAMF-III terpolymer resin

TG of 8-HQ5-SAMF-III terpolymer:
In order to explore the thermal degradation study of 8-HQ5-SAMF-III terpolymer resin, the thermogram has been studied minutely. Decomposition pattern of 8-HQ5-SAMF-III terpolymer resin is shown in Fig. 7. The data of thermogravimetric analysis revealed that the sample loss 2.01% found and 2.08% calculated weight loss when temperature was raised from 40 - 160ºC. This initial weight loss may be due to the loss of water of crystallization associated with terpolymer resin [23]. After loss of water molecule thermograph of 8-HQ5-SAMF-III terpolymer resin has depicted three stage decomposition. The first decomposition step represents degradation of three phenolic hydroxyl groups and three sulphonic groups substituted to three aromatic quinoline rings, in the temperature range of 160 - 290ºC, corresponded the weight loss of 37.12% found and 36.98% calculated. The weight loss by increasing temperature may be due to activating the macromolecules which may develop the cross linking in the molecules. Cross linking developed the strain in the macromolecule with result of weight loss to acquire the stability. The second stage of decomposition of 8-HQ5-SAMF-III terpolymer resin has been started by increasing temperature from 290 – 520ºC, when observed a rapid mass loss corresponding to 82.95% found and 83.00% calculated weight

loss, which may be due to the loss of three aromatic quinoline rings due to unzipping of cross linking, high strain, unstability and depolymerization occurred in the resin. In the third stage, the temperature has been increased from 520 – 800ºC which might increasing the strain in the molecule, cross linking increased, unstability increased, leading to weight loss of about 99.68% found and 100% calculated and the rigid prepolymeric part after the third stage is left as the char residue which is negligible in 8-HQ5-SAMF-III terpolymer resin decomposition.

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

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

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

Where, β is the linear heating rate. The graph of $\log\left[\frac{\mathrm{dc/dt}}{\Delta(1-\mathrm{c})}\right]$ versus $1/\mathrm{T}$ 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.

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

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

$\frac{\Delta\log(\mathrm{dw/dt})}{\Delta\log \mathrm{W_r}}$ versus $\frac{\Delta(1/\mathrm{T})}{\Delta\log \mathrm{W_r}}$ 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 Fig. 7 for 8-HQ5-SAMF-III terpolymer. From the TG curve, the thermoanalytical and the decomposition temperature were determined (Table 1) to obtain the thermal stability of the polymer. The method described by Sharp –Wentworth was adopted. Based on the initial decomposition temperature, the thermal stability of the terpolymer has been used here to define its thermal stability, neglecting the degree of decomposition (Table 1).

Table 1 Results of Thermogravimetric Analysis of 8-HQ5-SAMF-III terpolymer resin

Terpolymer Resin	Half decomposition temp. (K)	Activation energy (KJ/mol)		Entropy change -ΔS (J)	Free energy change ΔF (KJ)	Frequency factor Z ($\mathrm{sec^{-1}}$)	Apparent entropy S* (J)	Order of reaction found (n)
		FC	SW					
8-HQ5-SAMF -III	593	32.74	31.59	160.68	105.53	745	-19.05	0.99

FC = Freeman-Carroll, SW = Sharp-Wentworth

Using thermal decomposition data and then applying the Sharp-Wentworth method Fig. 8, activation energy is calculated which is in agreement with the activation energy calculated by Freeman-Carroll method [22]. Thermal activation energy plot of Sharp-Wentworth method (Fig. 8) and Freeman-Carroll method (Fig. 9) 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.

(i) Entropy change

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

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

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

Where,
ΔH = Enthalpy change = Activation energy
T = Temperature in K
ΔS = Entropy change {from (i) used}

(iii) Frequency factor

$$B_{2/3} = \frac{\log Z E_a}{R\Phi} \quad [1]$$

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

Where,
Z = Frequency factor
B = Calculated from equation [2]
log p(x) = Calculated from Doyle table corresponding to activation energy.

(iv) Apparent entropy change

$$S^* = 2.303R \log \frac{Zh}{RT^*} \quad [3]$$

Where,
Z = from relation [1]
T* = Temperature at which half of the compound is decomposed from it total loss.

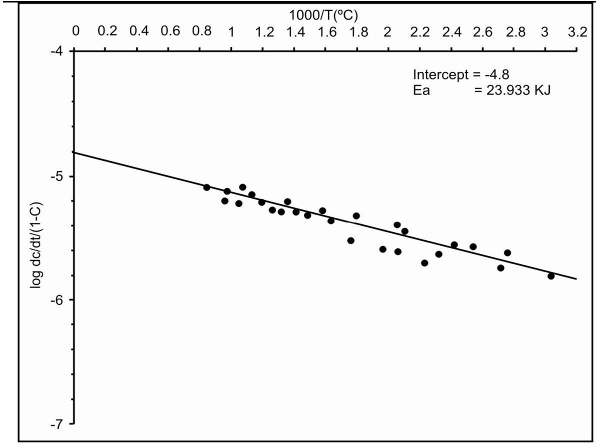


Figure 8 Sharp-Wentworth Plot of 8-HQ5-SAMF-III Terpolymer Resin

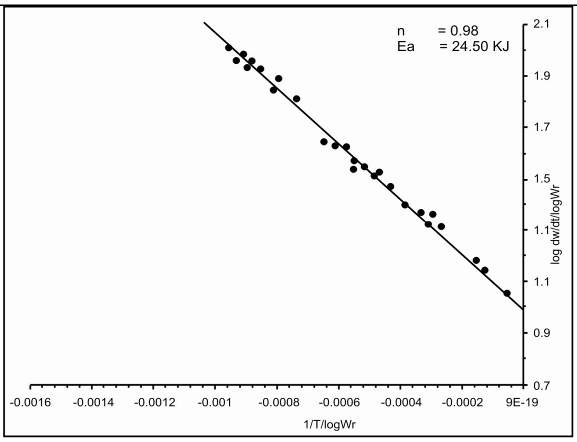


Figure 9 Freeman-Carroll Plot of 8-HQ5-SAMF-III Terpolymer Resin

By using the data of the Freeman-Carroll method, various thermodynamics parameters have been calculated (Table 1). From the abnormally low values of frequency factor, it may be concluded that the decomposition reaction of 8-HQ5-SAMF 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].

CONCLUSION

1) A terpolymer 8-HQ5-SAMF-III, based on the condensation reaction of 8-hydroxyquinoline 5-Sulphonic acid-Melamine-formaldehyde in the presence of acid catalyst, was prepared.
2) As the degradation of the terpolymer under investigation started at high temperature which indicates that the terpolymer 8-HQ5-SAMF-III is thermally stable at elevated temperature.
3) Low value of frequency factor may be concluded that the decomposition reaction of 8-hydroxyquinoline 5-sulphonic acid-melamine-formaldehyde terpolymer can be classified as 'slow reaction'.

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