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Thermo kinetic study of 8-hydroxyquinoline 5-sulphonic acid-melamine-Formaldehyde polymer resin-III

Rajesh N. Singru[*]

Department of Chemistry, R.D College of Science, Aheri, Distt.- Gadchiroli, Maharashtra, India

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ABSTRACT

The title terpolymer (8-HQ5-SAMF-III) 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 physico-chemical 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-hydroxyacetophenonesubstituted 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 resins-III from 8-hydroxyquinoline 5-sulphonic acid-melamine and formaldehyde. The present paper describes the composition of newly synthesized resin, its characterization by elemental analysis, average molecular weight $(\overline{Mn})$, determination of intrinsic viscosity in DMSO, FTIR Spectra, UV-Visible absorption spectra, NMR spectra 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.

MATERIALS AND METHODS

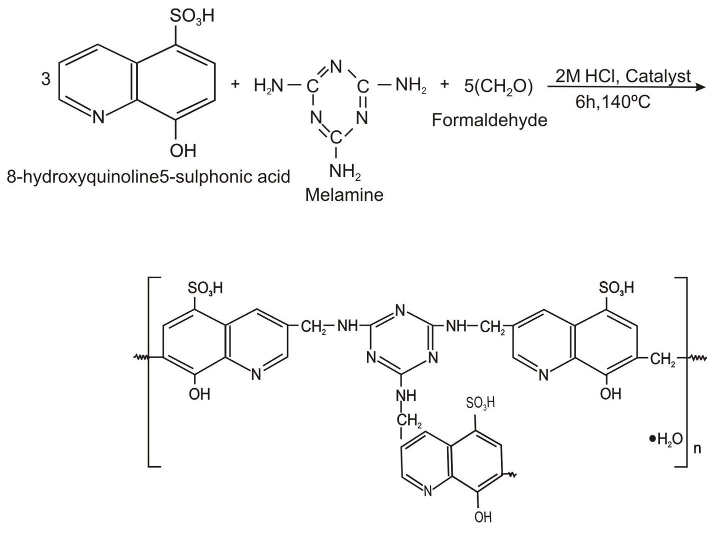
Materials

The chemicals used in the synthesis of new terpolymer resin were procured from the market and were analar or Fulka or chemically pure grade. Whenever required they were further purified by standard procedure.

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

Characterization

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 (1) and Kraemmer's equation (2).

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

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

The number average molecular weight $(\overline{Mn})$ 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 polymeriastio $(\overline{DP})$ and the number average molecular weight $(\overline{Mn})$ has been calculated for terpolymer resin.

Electron absorption spectrum of terpolymer resin was 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. An infra-red spectrum of 8-HQ5-SAMF-III terpolymer resin was recorded on Perkin-Elmer-983 spectrophotometer in KBr pallets in the wave number region of 4000 - 400 cm^{-1} at SAIF, Punjab University, Chandigarh. A Nuclear Magnetic Resonance (NMR) spectrum of newly synthesized terpolymer resin has been scanned on Bruker Advanced 400 NMR spectrometer using DMSO-d_6 at sophisticated Analytical Instrumentation Facility Punjab University, Chandigarh. TGA of terpolymer resin has been carried out by using Perkin–Elmer TGS-II Thermogravimetric Analyzer at heating rate of 10°C per minute up to 800°C.

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. This resin was analyzed for carbon, hydrogen, nitrogen and sulpher 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 Fig. 1.

The number average molecular weight ($\overline{Mn}$) of the terpolymer 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 result is presented in Table 1. The specific conductance was plotted against milliequivaletns of ethanolic KOH required for neutralization of 100 gm 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 hydroxy group of each chain was neutralized.

From the plot (Fig.2) the first and last break was noted. The average degree of polymerization ($\overline{DP}$) and hence the number average molecular weights ($\overline{Mn}$) of terpolymer has been determined using the formula.

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

$$\overline{Mn} = \overline{DP} \text{ x Repeat unit weight}$$

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 dimethyl sulphoxide (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.

Table 1 Elemental analysis, molecular weight determination and Intrinsic viscosity of 8-HQ5-SAMF-III terpolymer resin

Empirical formula of repeat unit	Empirical weight of repeat unit (gm)	Average degree of polymerization ($\overline{DP}$)	Average molecular weight ($\overline{Mn}$)	Elemental Analysis Percentage(%) of Element				Intrinsic viscosity $[\eta]$ (d1/g)
				C	H	N	S	
				Found (Cal.)	Found (Cal.)	Found (Cal.)	Found (Cal.)	
$C_{35}H_{31}N_9O_{12}S_3$	865	14.5	12542	48.55 (47.62)	3.58 (2.90)	14.56 (13.86)	11.09 (10.50)	1.31

According to the above relations, the plots (Fig.3) 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.

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 $K_1 + K_2 = 0.5$ favorably [14]. It was observed that terpolymer having higher $\overline{Mn}$ Shows higher value of [η] which is in good agreement with earlier co-workers [14, 15].

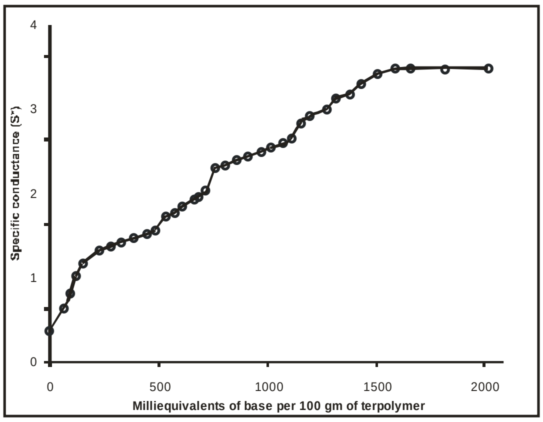


Figure2: Conductometric titration curve of 8-HQ5-SAMF-III resin

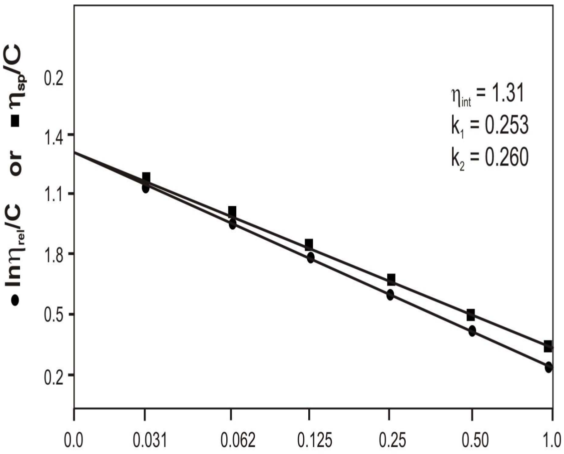


Figure 3: Viscometric curves of 8-HQ5- SAMF-III terpolymer resin

The UV-Visible spectra(Fig.4) 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].

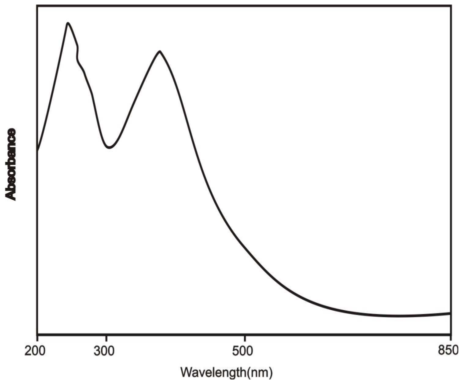


Figure 4: Uv-visible spectrum of 8-HQ5-SAMF-III terpolymer resin

The IR (Fig.5) 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.

The NMR spectrum (Fig.6) 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.

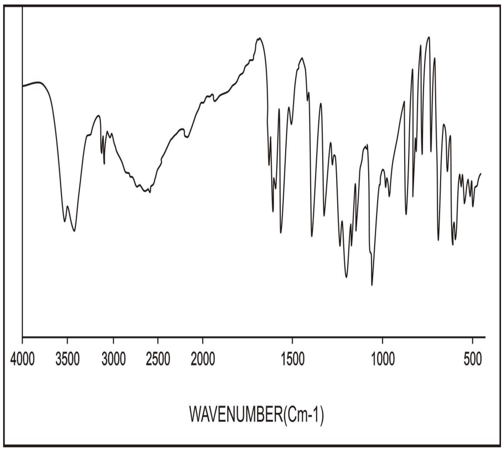


Figure2: Figure2Figure 5:IR spectrum of 8-HQ5-SAMF-III terpolymer resin

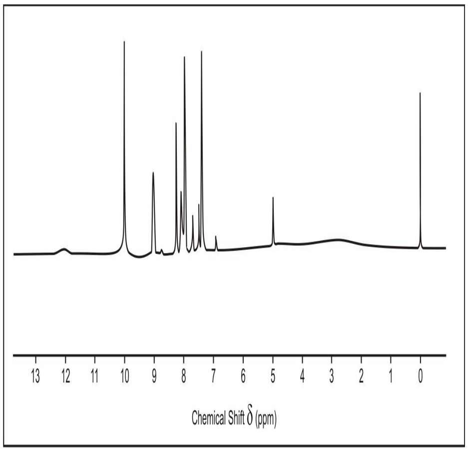


Figure 6: NMR spectrum of 8-HQ5-SAMF-III terpolymer resin

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.

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.

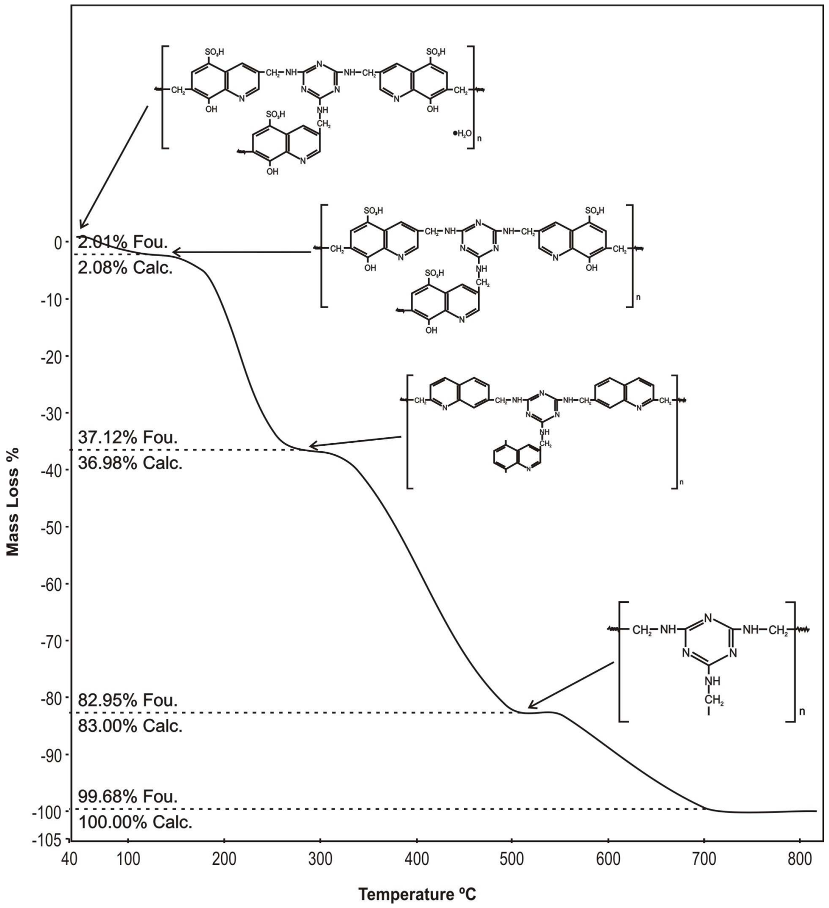


Figure 7: TGA of 8-HQ5-SAMF-III terpolymer resin

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.

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

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.

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

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

$\frac{\Delta\log(dw/dt)}{\Delta\log W_r}$ versus $\frac{\Delta(1/T)}{\Delta\log W_r}$ 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 2) 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 2).

Table 2 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 (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, Fig.9 [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

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

(ii) ΔF = ΔH - TΔS

Where,

ΔH = Enthalpy change = Activation energy

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

T = Temperature in K
ΔS = Entropy change {from (i) used}

(iii) Frequency factor

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

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

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

(iv) Apparent entropy change

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

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

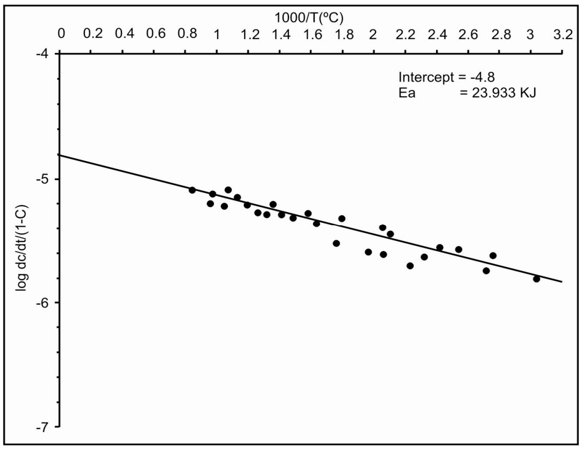


Figure 8 Sharp-Wentworth Plot of 8-HQ5-SAMF-III Terpolymer Resin

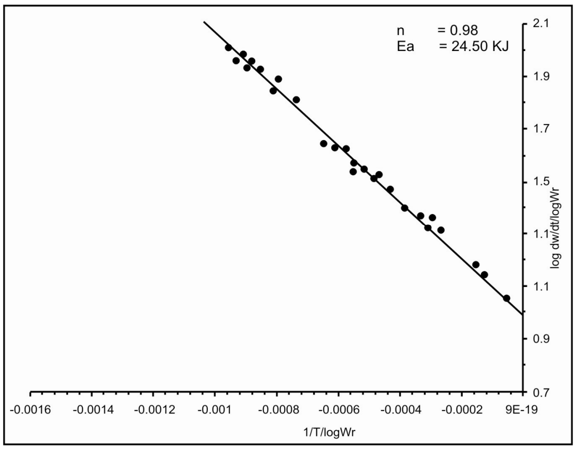


Figure 9 Freeman-Carroll Plot of 8-HQ5-SAMF-III Terpolymer Resin

By using the data of the Freeman-Carroll method, various thermodynamics parameters have been calculated (Table 2). 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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REFERENCES

[1] K Hajime; M Youchi; M Akihiro; H Kiichi; O Keido;F Akinori, *J. Apply. Polym. Sc*. **1999**, 74(9), 2266-2273.
[2] WB Gurnule ; HD Juneja; LJ Paliwal, *Indian J. Chem.* **2000**, 39(A),1110-1113.
[3] PK Rahangdale; WB Gurnule; LJ Paliwal ; RB. Kharat, *Synth. React. Inorg. Met. Org. Chem*,. **2003**, 33(7),1187-1205.
[4] DK Rath; PL Nayak; S Lenka, *J. Appl. Polym. Sci*., **1994**, 51, 1679.
[5] UK Samal; PL Nayak; S Lenka, *J. Appl. Polym. Sc*., **1993**, 47, 1315.
[6] S Zeman; LA Tokarova, *Thermochemica Acta*, **1992**, 197, 181-189.
[7] Z Hong; W Yu-Zhang; W Xui-Li; Y Ke-Ke, *Polym. Deg. Stab.* **2002,** 80(1),135.
[8] WB Gurnule; PK Rahandale; J Paliwal; RB Kharat, *J. Appl. Polym. Sci.* **2003**, 89(3), 886.
[9] WB Gurnule; P K Rahangdale; LJ Paliwal; R B Kharat, *React. Funct. Polymer*, **2003**, 55, 255.
[10] RN Singru; AB Zade; WB Gurnule, *J. of Appl. Polym. Sci*., **2008,** 109,859-868.
[11] PEP Michel; JN Barbe; HD Jureja; LJ Paliwal, *European Polym. J*., 43, **2007**,4995-5000.
[12] PK Rahangdale; WB Gurnule; LJ Paliwal; R B Kharat, *Progress in Crystal Growth and Characterization of Materials*, **2002**, 45,155-160.
[13] RM Joshi; MM Patel, *Indian J. Chem*., **1989**, 28A, 55-58.
[14] JR Patel ; DH Sutaria; , MN Patel, *High Perform Polymer*, 1994, 6, 201-208.
[15] WB Gurnule; HD Junaja;LJ Paliwal, *Asian J. Chem*., **2000**, 12(1),51-57.
[16] RM Silverstein;GC Bassler;TC Morrill,"Spectrometric Identification of organic compounds", 5th Edi. **1991**, John Wiley and Sons. Inc. Printed in Singapur.
[17] PK Rahangdale; WB Gurnule; LJ Paliwal; RB Kharat, *Synth. React. Inorg. Met. Org. Chem*., **2003**, 33(7),1187-1205.
[18] RK Samal; BK Senapati; TB Behuray, *J. Appl. Polym. Sci*., **1996,** 62, 655-660.
[19] BS Furniss; AJ Hannaford; PWG Smith; AR Tatchell, "Vogel's Text Book of Practical Organic Chemistry, Addison Westey Longman Ltd. England, First ISE Reprint, **1998**.
[20] RT Morrison; RN Boyd, "Organic Chemistry, Sixth Edition, Prentice Hall of India Pvt. Ltd., New Delhi, **1996**.
[21] G Barth Howard;W Mays Jimmy, "*Modern Methods of Polymer Characterization," A Wiley Interscience Publication, John Willey and Sons, New York*, **1991;**228.
[22] AS Aswar; RG Mahale; PR Kakde; SG Bhadange, *J. Indian Chem. Soc*. **1998,** 75, 395.
[23] NA Nadia Ahmed Mohamed; AO Abeer Obaid Hamad Al Dossary, *Polymer Degradation and Stability*, **2003**, 79(1), 6175.
[24] PK Rahangdale; LJ Paliwal; R B Kharat, *Transition of the SAEST*. **2000**, 35 (1), 16-18.