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Thermal Degradation Study of New Polymer derived from 8-Hydroxyquinoline 5-sulphonic acid and Catechol

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ABSTRACT

Polymer was synthesized from the polymerization of 8-hydroxyquinoline 5-sulphonic acid and catechol with formaldehyde (8-HQ- 5- SACF) by solution condensation in an acid medium. The polymer was characterized by elemental analysis, UV-Visible spectra, FTIR and NMR spectroscopy The thermal stability of the polymer was determined by TGA. In addition, the activation energy for the formation of polymer was calculated using TGA data by Freeman-Carroll method and Sharp-Went-worth method. The surface features of the polymer was analyzed by scanning electron microscopy (SEM). The thermodynamic parameter such as free energy change (ΔF), entropy change (ΔS) , Apparent entropy change(S^*) and frequency factor Z are also determined on the basis of TGA curve and by using data of Freeman-Carroll method .

Keywords -TGA, Resin, Synthesis, Thermodynamic parameter, Kinetics.

INTRODUCTION

The thermal degradation study of polymers has become a subject of interest. Study of thermal behavior of polymers in air at different temperature provides information about nature of species produced at various temperature due to degradation. Polymers having good thermal stability and catalytic activity have enhanced the development of polymeric materials. Copolymer acquired a renewed research interest in the recent past because of their interesting properties, such as thermal stability, ability to bind toxic metal ions, exhibition of catalyst, pholuminescence properties[1-4]. Transition metal chelated thiourea-formaldehyde resin was synthesized and reported for its good antimicrobial activity and high thermal stability [5]. The homopolymer and copolymer of 4-chloro-3-methyl phenyl methacrylate possesses excellent antimicrobial activity due to the presence of free chlorine in the polymeric structure [6]. Metal complexes of Schiff bases derived from 2-furancarboxaldehyde and o-phenylenediamine, 2-thiophenecarboxaldehyde and 2-aminothiophenol were screened for their antibacterial activity, which clearly establishes that the metal complexes have more potent antibacterial activity than the parent Schiff base ligand [7]. Terpolymer involing anthranilic acid and thiourea with paraformaldehyde resin was synthesized and reported [8]. Chelate polymers of azelaoyl bis-N-pheylhydroxamic acid with Mn(II),Co(II), Ni(II) and Zn(II) were synthesized and found that the Mn(II) and Zn(II) chelates possess a tetrahydral geometry, whereas Co(II) and Ni(II) chelates exhibit octahedral geometry [9]. Schiff base polymers such as poly(N,N-p-phenylene/ethlenebis(salicylideneimine)) were synthesized and the thermal stability of Cu(II) and Ni(II) complexes were reported [10]. An eco-friendly technique was employed for the synthesis of a terpolymer. The metal ion binding properties of the prepared polymer was also reported by our research group [11]. 8-hydroxyquinoline 5-sulphonic acid and oxamide with formaldehyde terpolymer was proved to be an excellent metal binding polymer for selective metal ions [12].

The present article described the preparation of new polymer involving 8-hydroxyquinoline -5-sulphonic acid and catechol with formaldehyde monomers. The polymer was characterized by various methods and tested for their thermal stability.

MATERIALS AND METHODS

Materials

8-hydroxyquinoline -5-sulphonic acid and catechol were procured from Merck, India and purified by rectified spirit . Formaldehyde (37%) were of AR grade, Merck and used as received. Solvents like N,N-dimethyl formamide and dimethylsulphoxide were used after distillation.

Polymerization of 8-HQ-5-SACF polymer resin

The polymer was synthesized by the condensation polymerization reaction of 8-hydroxyquinoline -5-sulphonic acid (0.1 mol) and catechol (0.1 mol) with formaldehyde (0.2 mol) using hydrochloric acid as the reaction medium at 126±2^{o}C in an oil bath for 5 hrs. under refluxed condition with occasional shaking. The reaction mixture was then cooled, poured into crushed ice with constant stirring and left overnight. The dark brown colored polymer separated out was washed with warm water and extracted with diethyl ether. The dried sample was then purified by dissolving in 8 % aqueous NaOH and regenerated using 1: 1 (v/v) HCl/water with constant and rapid stirring to avoid lump formation. The process of reprecipitation was repeated twice. The polymer 8-HQ-5-SACF thus obtained was filtered, washed with hot water, dried in air, powered and kept in vacuum desicator over silica gel. The yield of the polymer was found to be 84% and the reaction route for the synthesis is shown in Fig. 1.

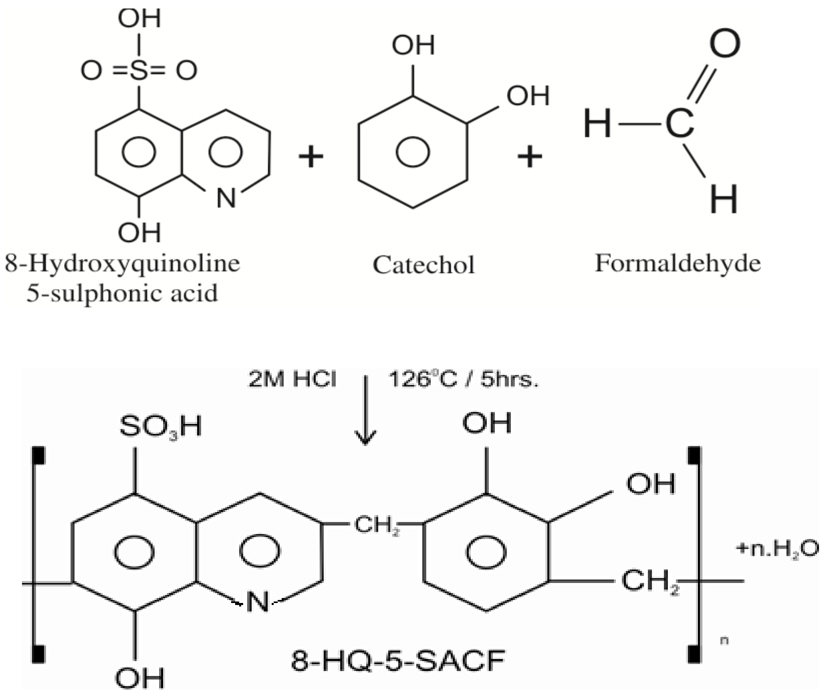

Figure 1: Reaction and expected structure of 8-HQ-5-SACF polymer

Characterization

Electron absorption spectrum of polymer 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-SACF polymer 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 polymer resin has been scanned on Bruker Advanced 400 NMR spectrometer using DMSO-d_6 at sophisticated Analytical Instrumentation Facility Punjab University, Chandigarh. TGA of polymer resin has been carried out by using Perkin–Elmer TGS-II Thermo gravimetric Analyzer at heating rate of 10ºC per minute up to 800ºC. With the help of thermo gravimetric data, which is reported in Table 1, the thermal activation energies (Ea) and order of reaction (n) calculated. Also other thermodynamic parameter such as free energy change (ΔF), entropy change (ΔS), Apparent entropy change(S*) and frequency factor Z are determined and reported in Table 1.

RESULTS AND DISCUSSION

The newly synthesized purified 8-HQ-5-SACF polymer sample was found to be dark brown in colour. The polymer is insoluble in commonly used solvent, but it is soluble in DMF, DMSO, pyridine and conc. H_2SO_4. The melting point of the polymer was found to be in the range of 391 to 394 K. The polymer which has been used in the present investigation was prepared by the reaction given in Fig. 1.

IR spectra of 8-HQ-5-SACF polymer

From IR Spectral studies (Fig. 2), it has been revealed that the polymer gave broad absorption and appeared in the region 3505-3507 cm^{-1} may be assigned to the stretching vibrations of phenolic hydroxyl (-OH) groups exhibiting intramolecular hydrogen bonding [14]. A sharp strong peak at 1556-1625 cm-1 may be ascribed to aromatic skeletal ring. The bands obtained at 1190-1220 cm-1suggest the presence of methylene (-CH_2) bridge [15]. The sharp and weak band obtained at 1279- 1344 cm^{-1} suggest the presence of Ar-CH_2-Ar bridge in polymer .The 1,2,3,5 substitution of aromatic benzene ring recognized by the sharp, medium / weak absorption bands appeared at 951-970, 1148-1044, 1183-1186 and 1321-1324 cm^{-1} respectively. This band seems to be merged with very broad band of phenolic hydroxyl group.

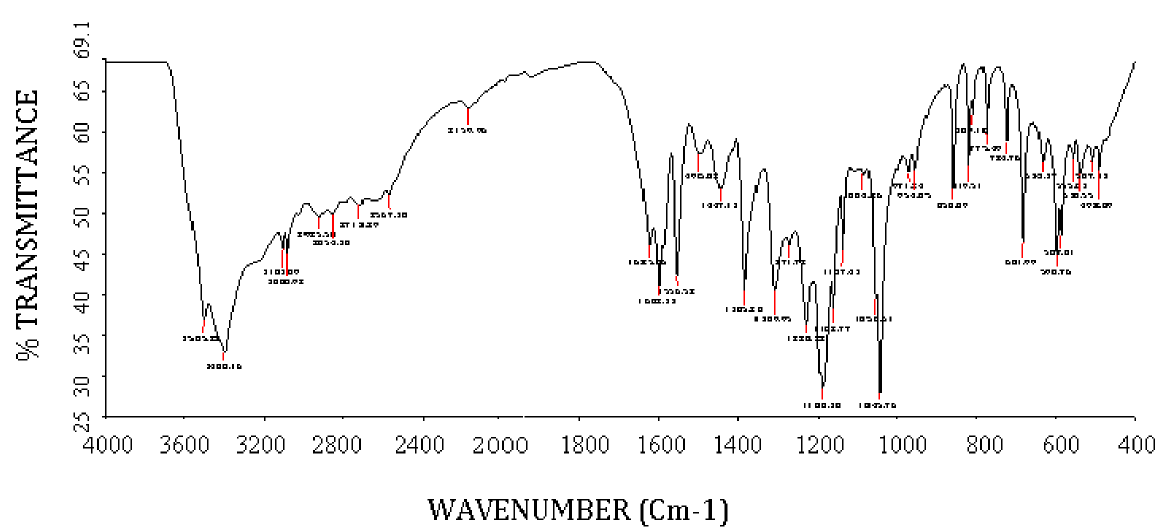

Fig 2: IR spectrum of 8-HQ-5-SACF polymer resin

^{1}H NMR spectra of 8-HQ-5-SACF polymer

The NMR spectrum (Fig. 3) of 8-HQ-5-SACF polymer was scanned in DMSO-d_6 solvent. The chemical shift (δ) ppm observed is assigned on the basis of data available in literature [16,17]. The singlet obtained in the region 3.89 - 3.94 (δ) ppm may be due to the methylene proton of Ar-CH2-Ar moiety. The weak multiple signals (unsymmetrical pattern) in the region of 8.23-8.18 (δ) ppm may be attributed to aromatic proton (Ar-H). The signals in the range at 9.11 to 9.16 (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 [17,18]. The signals in the range of 9.96 – 9.92(δ) ppm are attributed to proton of -SO_3H groups.

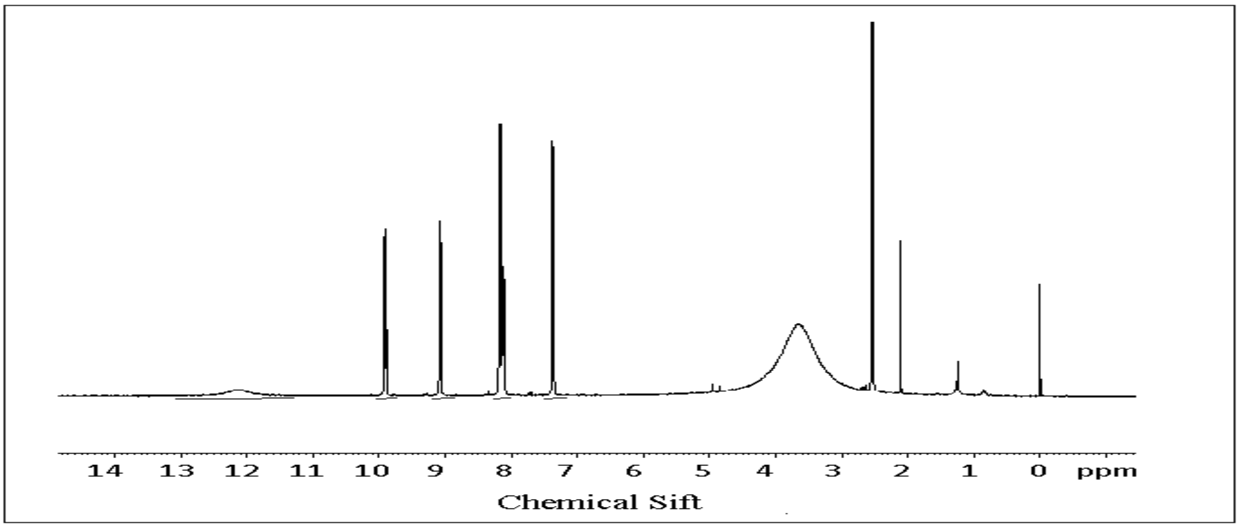

Fig 3: ^{1}H NMR spectral data of 8-HQ-5-SACF resin

SEM of 8-HQ-5-SACF polymer

The scanning electron micrographs of 8-HQ-5-SACF polymer resin have been shown in Fig. 4. The photographs of 8-HQ-5-SACF polymer exhibit sponge like structure derived from the aggregation of small granules. At lower magnification the resin shows spherulites in which the crystals are arranged smaller in surface area with more closely packed structures. This indicates the crystalline nature of the polymer resin and this property shows the low ion exchange capacity for higher hydrated size metal ion. At different magnification the resin shows more amorphous character with less closed packed surface having deep pits. The amorphous character indicates that resin thus possesses higher exchange for metal ions. The morphology thus identified by SEM as crystalline as well as amorphous or transition between crystalline and amorphous, showing more or less good ion exchange capacity. The polymerization reaction proceeds by introducing amorphous character in the polymer resin.

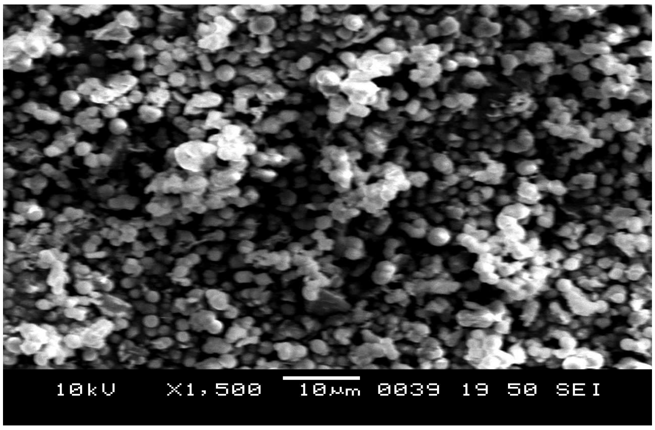

Fig 4: SEM micrographs of 8-HQ-5-SACF polymer resin

Thermo gravimetric Analysis

Thermogravimetry of 8-HQ-5-SACF polymer sample has been carried out using Perkin-Elmer thermo gravimetric analyser in air atmosphere with heating rate of 10°C/min. A brief account of thermal behavior of 8-HQ-5-SACF polymer is given in Fig. 5.

TGA of 8-HQ-5-SACF polymer

Thermogram of TGA of this polymer is shown in Fig. 5. In order to explore the thermal degradation study of 8-HQ5-SACF polymer resin, the thermo gram has been studied minutely. Thermogram of 8-HQ-5-SACF polymer resin depicts four step decomposition in the temperature range 50-540^{o}C . The first step is slow decomposition between 50 – 90^{o}C corresponds to loss of water molecule (4.8% found and 4.77% calculated). The second step decomposition start from 90-240^{o}C corresponds to 18.30% calculated and 18.34% found which represent degradation of three hydroxyl group which is attach with aromatic and benzene ring. The third step which is in the range 240-400^{o}C corresponds to 66.84% calculated and 66.90% found which represent the loss of benzene ring, one sulphonic group along with two methylenic groups. The fourth step corresponds to loss of complete polymer (100% calculated and 100% found) which represent total loss of remaining quinoline moiety in the range 400-540 ^{o}C.

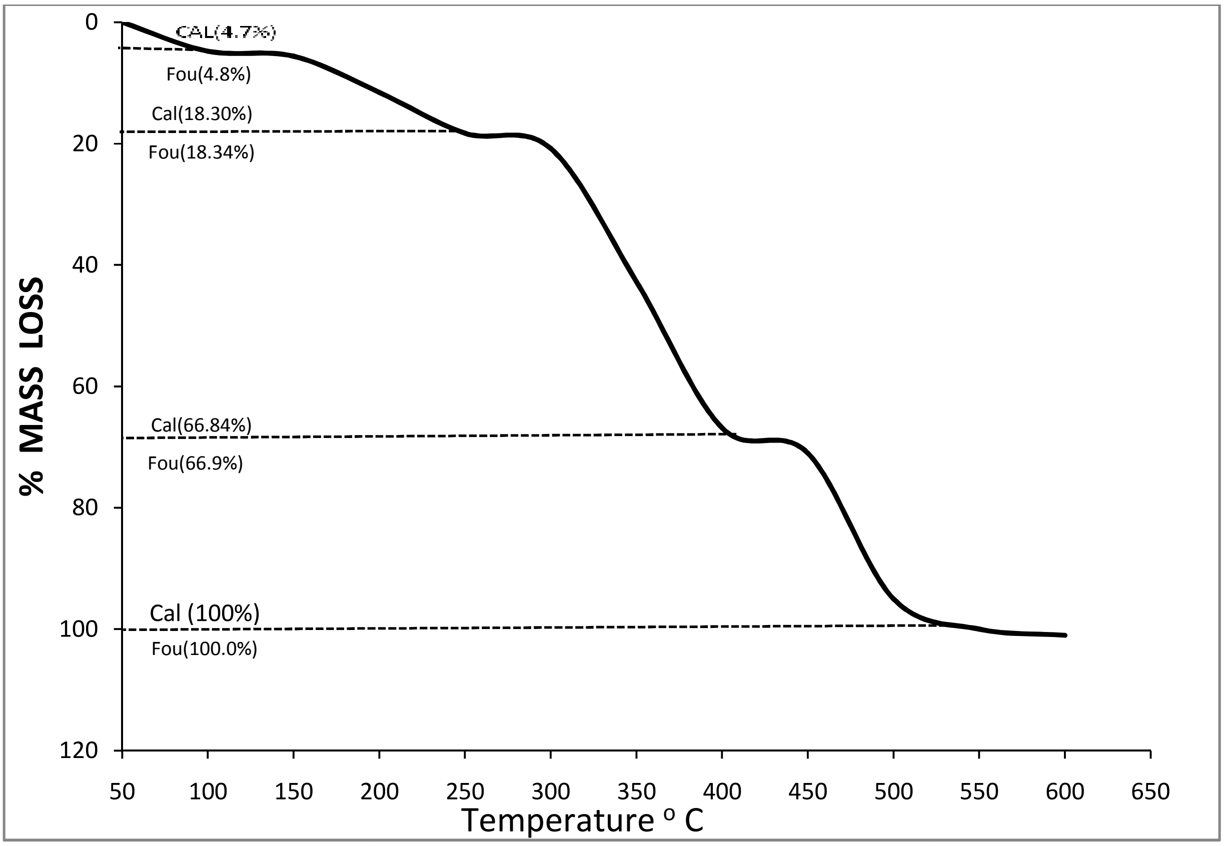

Fig 5: TGA of 8-HQ-5-SACF polymer resin

In the present investigation Sharp-Wentworth and freeman-Carroll methods have been used to determine the kinetic parameters of 8-HQ-5-SACF polymer sample.

Sharp-Wentworth method :

Using the equation derived by Sharp-Wentworth [1],

$\mathrm{Log}\,[(dc/dT)/(1-c)] = \log(A/\beta) - [E_a/2.303R].1/T$…………………(1)

Where,
dc/dT = rate of change of fraction of weight with change in temperature.
β = linear heating rate dT/dt.

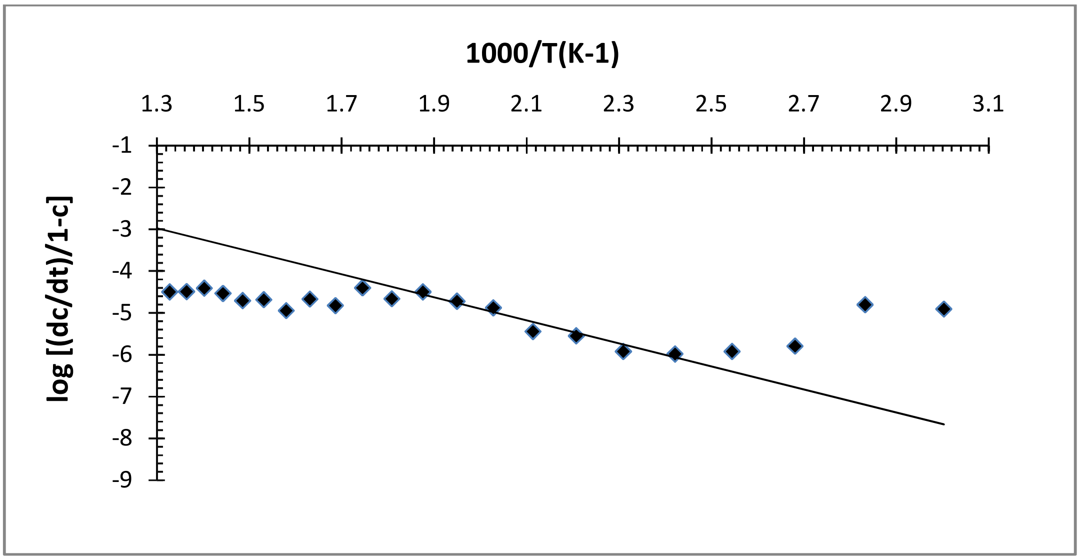

Fig 6: Sharp-Wentworth plot of 8-HQ-5-SACF polymer resin

By plotting the graph between (dc/dT)/(1-c) vs 1/T we obtained the straight line which gave energy of activation (Ea) from its slope. Where β is the conversion at time t, R is the gas constant and T is the absolute temperature. The plots Fig. 6 give activation energies at different stages of degradation reaction take place.

Freeman-Carroll method :

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

[Δ log (dw / dt)] / Δ log Wr = (-E / 2.303R)- Δ(1/T)/ Δ log Wr + n -------------- (2)

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

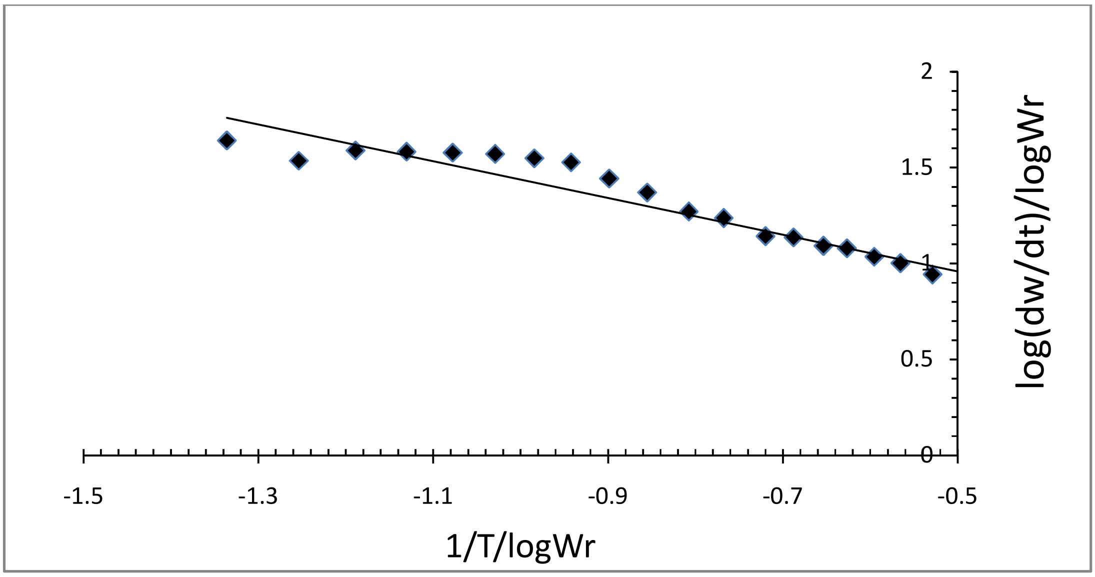

Fig 7: Freeman-Carroll plot of 8-HQ-5-SACF polymer resin

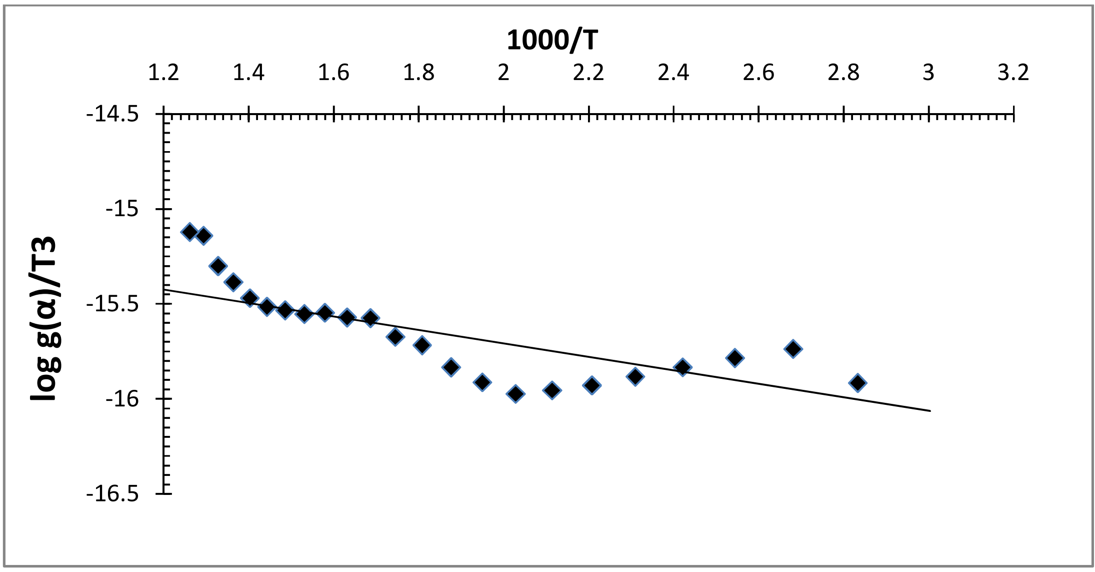

Fig. 8: Freeman-Carroll plot of 8-HQ-5-SACF polymer resin

A plot of percentage mass loss versus temperature is shown in Fig. 5 for 8-HQ-5-SACF polymer. From the TG curve, the thermo analytical 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 polymer has been used here to define its thermal stability, neglecting the degree of decomposition (Table 2).

Table 2: Results of Thermo gravimetric Analysis of 8-HQ-5-SACF polymer resin

Polymer 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-HQ-5-SACF	543	21.54	21.88	-292.96	180.61	397	-13.85	0.98

Using thermal decomposition data and then applying the Sharp-Wentworth method Fig. 7, activation energy is calculated which is in agreement with the activation energy calculated by Freeman-Carroll method, Fig. 7 [19]. Thermal activation energy plot of Sharp-Wentworth method (Fig. 6) and Freeman-Carroll method (Fig. 7) 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 KR/h ϕ E] + S/2.303 R-----------------(3)
Where,
K = 1.3806 x 10^{-16} erg/deg/mole,
R = 1.987 cal/deg/mole
h = 6.625 x 10^{-27} erg sec, ϕ = 0.166
S = change in entropy
E = activation energy from graph

ii)Free Energy Change :
ΔF = ΔH- TΔS ----------------------- (4)
ΔH = Enthalpy change
T = Temperature in K

S = Entropy change

iii) Frequency Factor :
Bn = log ZEa / ϕ R ---------------------------(5)
B1 = log [ln 1 / 1-α] – log P(x)---------------------(6)
Z = frequency factor
B = calculated from equation (6)
Log P(x) = calculated from Doyle's table corresponding to activation energy.

iv) Apparent Entropy Change :
S* = 2.303 log Zh / KT* ---------------------- (7)
Z = from relation (4)
T* = temperature at which half of the compound is decomposed from it total loss.

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-HQ-5-SACF polymers can be classed as a 'slow 'reaction. There is no other obvious reason [20, 21]. Fairly good straight line plots are obtained using the two methods. This is expected since the decomposition of polymer is known not to obey first order kinetics perfectly [20, 21].

CONCLUSION

A polymer 8-HQ-5-SACF based on the condensation reaction of 8-hydroxyquinoline -5-sulphonic acid and catechol with formaldehyde in the presence of acid catalyst, was prepared. 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-catechol-formaldehyde polymer can be classified as 'slow reaction'.

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