Thermal degradation studies of high performance copolymer resin derived from 8-hydroxyquinoline 5-sulphonic acid, semicarbazide and formaldehyde

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ABSTRACT

The present investigation deals with the synthesis and thermal degradation studies of resin 8-Hydroxyquinoline 5-sulphonic acid -semicarbazide - formaldehyde derived by the condensation of 8-Hydroxyquinoline 5-sulphonic acid and semicarbazide with formaldehyde in the presence of 2M acetic acid as catalyst with varying molar proportions of reactants. Copolymer composition has been determined on the basis of their elemental analysis. The copolymer has been characterized by UV-visible, FTIR and ^1H NMR spectra. The morphology of synthesized copolymer was studied by scanning electron microscopy (SEM). The thermal decomposition behavior of some new copolymers were studied using thermogravimetric analysis in air atmosphere at heating rate of 10 ^{o}C/min. Detailed thermal degradation studies of the resin has been carried out to ascertain its thermal stability. The Freeman– Carroll and Sharp– Wentworth methods have been used to calculate activation energy and thermal stability. Thermal activation energy (Ea) calculated with the help of these methods are in agreement with each other. Thermodynamic parameters such as free energy change (ΔF), entropy change (ΔS), apparent entropy change (S*), and frequency factor (z) are also determined on the basis of the TG curves and by using data of the Freeman–Carroll method.

Keywords: Thermal degradation, Resin, Thermal stability, Morphology, Characterization, Poly-condensation.

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INTRODUCTION

The thermal degradation study of copolymer has become a subject of interest. Study of thermal behavior of copolymer in air at different temperature provides information about the nature of species produced at various temperatures due to degradation. Copolymer having good thermal stability and catalytic activity have enhanced the development of polymeric materials. In this laboratory, extensive work on the thermal degradation of copolymers has been undertaken [1-3]. It is hoped that the study of copolymer will lead to the production of polymer, which are both thermally stable and useful as fabricating materials. Patel et al. [4] studied the thermal properties of copolymer, Zeman and Tokarova[5] prepared urea–formaldehyde copolymers and studied their TGA and DTA data.

Literature survey reveals that copolymer derived from aromatic compounds with substituent's like –OH, –SO₃H– NH₂ with semicarbazide and formaldehyde show improved ion exchange properties, thermal resistance properties, coordinating properties, and good storage stability, etc.[6]. The aromatic rings offer conjugated rigid structure with high glass transition temperature and strong linkages, allowing good resistance even in harsh environment. Such terpolymers find very useful applications as adhesives, adhesive labels, high temperature flame resistant fibers, fuel hose for automobile applications, microelectronic components like compact discs [7], liquid crystal display device [8], ion exchange packs etc. Ion exchange resins have attracted much interest in recent years, as in water treatment, metal recovery from dilute solutions, hydrometallurgy, antibiotic purification and separation of radio isotopes [9], and find large application in water treatment and pollution control [10]. A chelating ion exchange resin was synthesized by Shah et al. [11] from 8-hydroxyquinoline and catechol using formaldehyde as a cross linking agent and the

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ion exchange capacity was evaluated with various metal ions say, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} as an one of industrial application. Also various kinetic characteristics such as energy of activation (Ea), order of reaction (*n*) and pre-exponential factor (*A*) of various steps of thermal decomposition have been calculated from thermogravimetric results.

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MATERIALS AND METHODS

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Materials
The important chemicals like 8-Hydroxyquinoline 5-sulphonic acid (Across Organic, Fisher Scientific, India), semicarbazide(Across Organic, Fisher Scientific, India) and formaldehyde (S.D. Fine Chemicals) used in the preparation of new 8-HQ 5-SASF copolymer resin were procured from the market and were of chemically pure grade, and wherever necessary the purity was tested and confirmed by thin layer chromatography.

Synthesis of Copolymer Resin
The 8-HQ 5-SASF resin was copolymerized by the condensation polymerization of 8-Hydroxyquinoline 5-sulphonic acid (0.1mol) and semicarbazide (0.1 mol) with formaldehyde (0.2 mol) in acetic acid medium at 124 ± 2 °C in an oil bath for 5 hrs. The solid product obtained was immediately removed from the flask as soon as the reaction period was over. It was washed with cold water, dried and powdered. The powder was repeatedly washed with hot water to remove excess of 8-Hydroxyquinoline 5-sulphonic acid - formaldehyde copolymer, which might be present along with the 8-HQ 5-SASF copolymer. The dried resin was further purified by dissolving in 8% NaOH and regenerated in 1:1(v/v) HCl/water. The purified copolymer resin was finally ground well to pass through a 300 mesh size sieve and kept in a vacuum over silica gel. The yields of these terpolymer resins found to be 88% and the melting point found to be in the range of 430K - 480 K (Table 1). The sieved resin was used for further characterization. The reaction sequence of the synthesis of 8-HQ 5-SASF copolymer resin is shown in Fig.1.
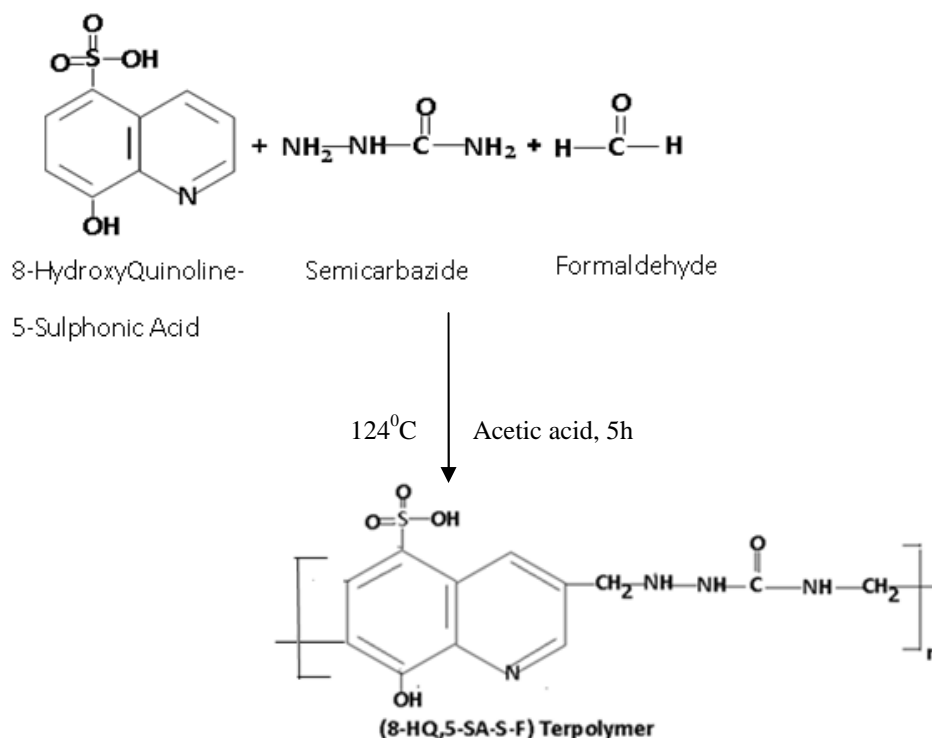

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Fig.1. Synthesis of 8 -HQ 5-SASF copolymer resin

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Characterization
The copolymer resin was subject to micro analysis for C, H and N on an Elementar Vario EL III Carlo Erba 1108 elemental analyzer. The number average molecular weight $\overline{M}n$ was determined by conductometric titration in

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DMSO medium using ethanolic KOH as the titrant by using 25 mg of sample. A plot of the specific conductance against the milliequivalants of potassium hydroxide required for neutralization of 100 gm of terpolymer was made. Inspection of such a plot revealed that there were many breaks in the plot. From this plot the first break and the last break were noted. The calculation of $\overline{M}n$ by this method is based on the following consideration [12] : (1) the first break corresponds to the stage at which the first acidic phenolic hydroxyl group is neutralized, and (2) the last break observed beyond the first break represents the stage at which phenolic hydroxyl group of all the repeating units are neutralized. On the basis of the average degree of polymerization, ($\overline{DP}$) the average molecular weight has to be determined by following eq. (1)…

$$\overline{Dp} = \frac{\text{Total milliquivalents of base required for complete neutralization}}{\text{Milliquivalents of base required for smallest interval}}$$

$$\overline{Mn} = \overline{Dp} \, x \text{ molecular weight of the repeating unit}$$

Spectral and surface analysis

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 Affinity-1 FTIR Spectrophotometer at Department of Chemistry, Kamla Nehru Mahavidyalaya, Nagpur. Proton NMR was recorded with Bruker Adanve – II 400 NMR spectrophotometer using DMSO-d_6 as a solvent, at Sophisticated Analytical Instrumentation Facility, Punjab University, Chandigarh. The surface analysis was performed using scanning electron microscope at different magnifications. SEM has been scnanned by JEOL JSM-6380A Analytical Scanning Electron Microscope at VNIT, Nagpur.

Thermogravimetric analysis

The non-isothermal 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 -HQ 5-SASF sample at STIC Cochi. With the help of thermogravimetric data the thermal activation energies (*Ea*) 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.

RESULTS AND DISCUSSION

The resin sample was light brown in color, insoluble in commonly used organic solvents, partially soluble in dimethyl formamide, tetrahydrofuran, pyridine and concentrated H$_2$SO$_4$ but completely soluble in dimethyl sulphoxide (DMSO). The melting points of these copolymer was determined by using electrically heated melting point apparatus and are found to be in the range of 430 - 480 K. These resins were analyzed for carbon, hydrogen and nitrogen content (Table 2).

The molecular weight ($\overline{M}n$) of these copolymer was determined by non-aqueous conductometric titration in DMSO against KOH in a 50% (v/v) DMSO/alcohol mixture [13]. The number average molecular weight ($\overline{M}n$) could be obtained by multiplying the $\overline{DP}$ by the formula weight of the repeating unit. The molecular weight for 8 -HQ 5-SASF copolymer is 7563. The UV-visible spectra of 8 -HQ 5-SASF copolymer samples in pure DMSO were recorded in the region 200 – 800 nm. The 8 -HQ 5-SASF copolymer resins displayed two characteristics broad band's at 230-235 nm and 335-345 nm. Both of these bands seem to be merged with each other because of their very broad nature. The observed position of the absorption bands indicate the presence of a (>C=O) group of semicarbazide having carbon oxygen double bond which is in conjugation with the -NH group. The band at 210-225 cm^{-1} is the more intense band which may be accounted for a $\pi \rightarrow \pi^*$ transition while the less intense band at 325-335 nm may be due n$\rightarrow \pi^*$ transition [14]. The UV-visible spectra of 8 -HQ 5-SASF copolymer resins show bathochromic shift i.e. the shift towards the longer wavelength in which the value of λ_{max} increases.

Infrared spectroscopy is the most direct means of identification of polymers. Through the use of the accompanying flowchart and reference to the spectral descriptions above, an unknown polymer can be quickly identified. From the IR spectral studies, it has been revealed that the 8 -HQ 5-SASF copolymer resin show broad band appeared at the region 3400-3000 cm^{-1} may be assigned to the stretching vibration of phenolic –OH groups exhibiting intramolecular hydrogen bonding with -NH group [15]. The band at 3200 - 3000cm^{-1} may be due to Aryl C-H stretching. The band at 3000-2800cm^{-1} is due to stretching of CH$_2$, -NH etc. The band at 1600-1500cm^{-1} may be due to aromatic ring with sulphonic acid group. The band at 1390-1270cm^{-1} may be of -CH$_2$ methylene bridge. The band at 1370-

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1280, and 1300-1250cm^{-1} may be due to CH$_2$ bending (wagging and twisting), -CH$_2$ plane bending. 1, 2, 3 substitution in aromatic benzene ring may be due the bands appeared at 620-250, 750-850, 800-950cm^{-1}

^{1}H NMR spectra of all 8 -HQ 5-SASF copolymer resins were scanned in DMSO-d$_6$. From the spectra it is revealed that 8 -HQ 5-SASF copolymer resin possess set of proton having different electronic environment. The chemical shift (δ) ppm observed are assigned on the basis of data available in literature [16]. The 8 -HQ 5-SASF copolymer resin show the medium signal at 2.47-2.56 (δ) ppm may be due to the methylene proton of Ar-CH$_2$ bridge. The signal obtained in the region of 3.30-3.32 (δ) ppm may be due to the methylene proton of Ar-CH$_2$-N moiety. The singlet in the region 5.25-5.32 (δ) ppm may be due to the proton of –NH bridge. The singlet in the region 6.42-6.49 (δ) ppm may be due to ortho substituted proton of –NH- group. The weak multiple signal (unsymmetrical pattern) in the region at 6.82-6.87 (δ) ppm may be due to the aromatic proton of (Ar-H). The signals in the range at 8.3-8.9 (δ) ppm may be due to phenolic hydroxyl proton. The much downfield chemical shift for phenolic -OH group indicate clearly the intramolecular hydrogen bonding on -OH group. Spectra of copolymer show a medium singlet peaks appeared at 9.51 - 9.53 ppm may be assigned to sulphonic acid protons.

Surface analysis has found great use in understanding the surface features of the materials. The morphology of the reported 8 -HQ 5-SASF resin sample was investigated by scanning electron micrographs at different magnification, which are shown in Fig. 2. respectively. It gives the information of surface topography and defect in the structure. The resin appeared to be dark in color. The morphology of polymer resin shows spherulites and fringed model. The spherules are complex polycrystalline formation having as good as smooth surface. This indicates the crystalline nature of 8 -HQ 5-SASF copolymer resin sample. The morphology of resin polymer shows also a fringes model of the crystalline amorphous structure. The extent of crystalline character depends on the acidic nature of the monomer. But the photograph shows the fringed and scatted nature having shallow pits represent the transition between crystalline and amorphous. The resin exhibits more amorphous characters with closed packed surface having deep pits. Thus by SEM micrographs morphology of the resin shows the transition between crystalline and amorphous nature, when compare to the other resin [18], the 8 -HQ 5-SASF copolymer resin is more amorphous in nature, hence shows higher metal ion exchange capacity.
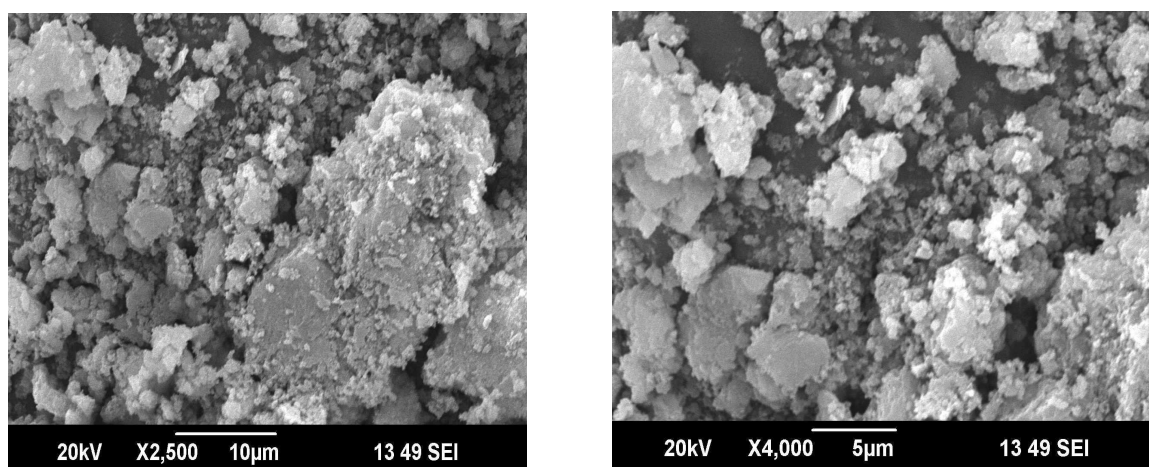

Fig. 2. SEM Micrographs of 8 -HQ 5-SASF copolymer resin

 The polymer under study is copolymer and hence, it is very difficult to assign their exact structures. On the basis of the nature and reactive, position of the monomer, elemental analysis, electronic, FT-IR, ^{1}H NMR, spectra, SEM and molecular weight, the most probable structures have been proposed for copolymer resin.

The thermal stability of copolymers is evaluated by dynamic thermogravimetric analysis in air atmosphere with heating rate of 10°C/min. Thermogram of 8 -HQ 5-SASF copolymer resin depicts three steps in decomposition reaction, after loss of one crystalline water molecule entrapped in the polymer molecule (5.23% found and 6.27% calculated). The first step of decomposition starts from 110ºC to 150ºC, corresponding the gradual mass loss of 34.01% found and 34.25% calculated, which may be due to the gradual loss of one hydroxyl group and one sulphonic acid group attached to aromatic quinoline ring. The second step of degradation starts from 150ºC to 530ºC corresponding the rapid mass loss of 74.78% found and 74.54% calculated which may be due to the degradation of one aromatic benzene ring, methylene and quinoline ring. The third step of decomposition starts from 530ºC to 800ºC, corresponding to slow loss of 98.26% found and 100.00% calculated, due to the degradation of semicarbazide moiety con-

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sequently the residue is left behind, which is of carbon moiety. The thermal degradation by increasing temperature may be due to the increasing strain and instability and cross linking of molecule by increasing thermal vibration. To decrease the strain and to maintain stability the resin undergoes degradation.

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 and Freeman- Carroll.

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

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

Where
dW/dt = rate of change of weight with time.
$Wr = Wc\text{-}W$
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. $\frac{\Delta\left(\frac{1}{T}\right)}{\Delta \log Wr}$ gives a straight line from which slope we obtained energy of

activation (*Ea*) and intercept on Y-axis as order of reaction (*n*).

Sharp–Wentworth method:
Using the equation derived by Sharp and Wentworth,

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

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 and A can be evaluated from intercept.

Where A is the conversion at time *t*, *R* is the gas constant (8.314 J.mol^{-1}.K^{-1}) and *T* is the absolute temperature. The plot of ln(dα/dt*)* vs 1/T should be linear with the slope *Ea/R*, from which *Ea* can be obtained. 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.

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Fig.3. Thermogram of 8 -HQ 5-SASF copolymer resin

By using thermal decomposition data and then applying above methods the activation energy (Ea) is calculated which are not perfectly in agreement with each other [19]. But the 'average *Ea*' calculated by Freeman-Carroll and Sharp-Wentworth is nearly same. The activation energy calculated by these methods is depicted in Table 1. A representative thermal activation energy plot of Sharp-Wentworth (Fig. 4) and Freeman-Carroll (Figure 5 and 6) 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 (*Ea*) using equations (3), (4), (5). These values are tabulated in (Table 2).

(i) Entropy change

$$\text{Intercept} = log\frac{KR}{h\Phi E} + \frac{\Delta S}{2.303\,R} \; - - - - - (3)$$

Where,
K = 1.3806 x 10^{-16} erg/deg/mole
R = 1.987 cal/deg/mole (8.314 J/K/Mol)
h = 6.625 x 10^{-27} erg sec
Φ= 0.166
ΔS= change in entropy

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Ea = activation energy from graph

(ii) Free energy change (ΔF)

$$\Delta F = \Delta H - T\Delta S - - - - - - - - - \quad (4)$$

Where, ΔH = Enthalpy change = Activation energy
T = Temperature in K
ΔS = Entropy change {from (3) used}

(iii) Frequency Factor (Z)

$$B_{\frac{2}{3}} = \frac{\log Z \, Ea}{R\Phi} - - - - - - - - - - - (5)$$

$$B_{\frac{2}{3}} = \log 3 + \log[1 - 3\sqrt{1-\alpha}] - \log p(x) ---- (6)$$

Where,
Z = Frequency factor
B = Calculated from equation (6)
log p(x) = Calculated from Doyle's table corresponding to activation energy.
α = degree of transformation (α= w/W_c)

(iv) Apparent entropy change (S*)

$$S^* = 2.303R \log\frac{Zh}{RT^*} -------------------------(7)$$

Where,
Z = from relation (5)
T* = Temperature at which half of the compound is decomposed from it total loss.

The abnormally low value of frequency factor, it may be concluded that decomposition reaction of 8 -HQ 5-SASF copolymer can be classed as a 'slow' reaction. There is no other obvious reason [20]. 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.
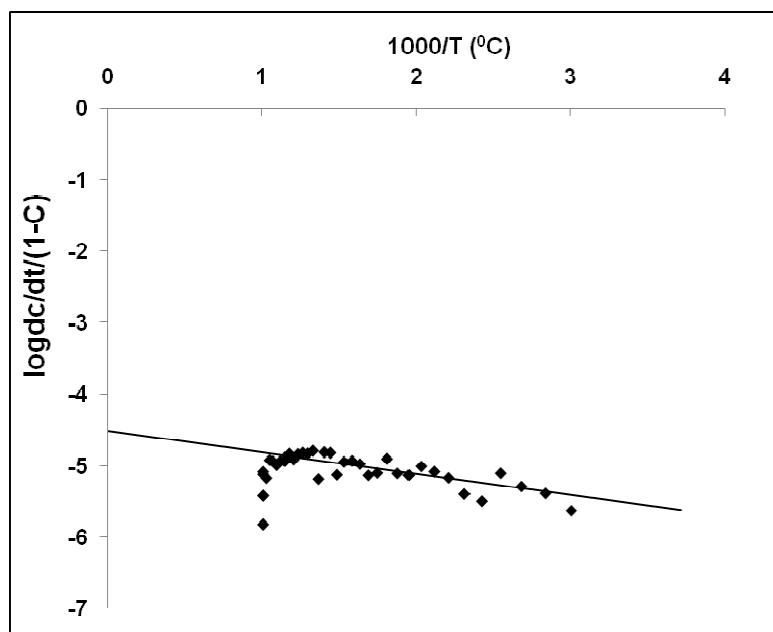

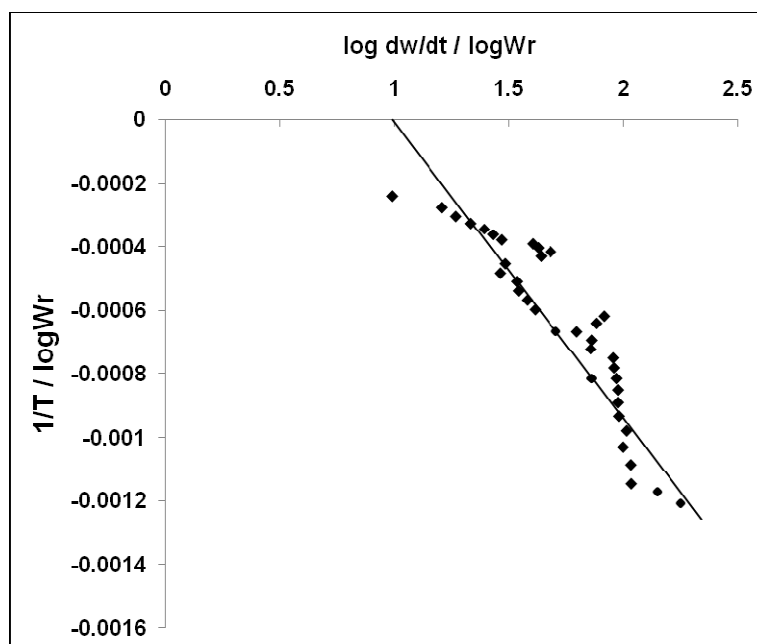**Fig. 4. Sharp-Wentworth plot of 8 -HQ 5-SASF copolymer resin**

Fig.5. Freeman-Carroll Plot of 8 -HQ 5-SASF copolymer resin for order of reaction
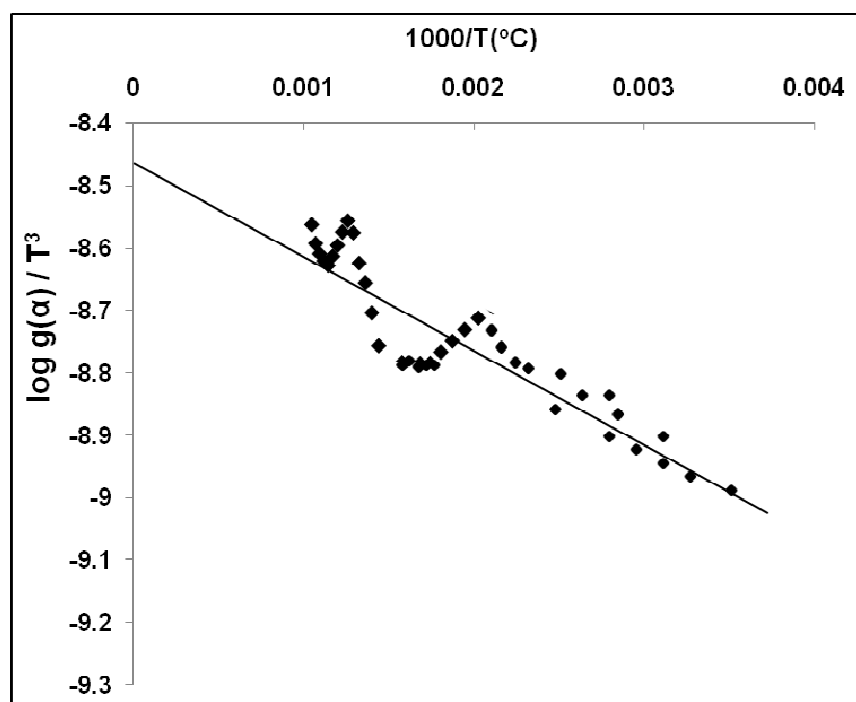

Fig. 6. Freeman-Carroll activation energy plot of 8 -HQ 5-SASF copolymer resin

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 copolymers are about the same. The similarity of the values indicates a common reaction mode, from the abnormally low values of frequency factor, it may be concluded that the decomposition reaction of 8 -HQ 5-SASF copolymers can be classed as a 'slow' reaction. There is no other obvious reason [22]. 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].

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Table 1. Results of Thermogravimetric Analysis of 8 -HQ 5-SASF copolymer Resin

Copolymer resin	Half decomposition Temp. (K)	Activation energy Ea (KJ)/mol		Entropy change ΔS (J)	Free energy ΔF (KJ)	Frequency factor (Z) (Sec.$^{-1}$)	Apparent entropy (S*) (KJ)	Order reaction (n)
		FC	SW					
8 -HQ 5-SASF	478	13.41	13.74	-63.95	97.31	659	-19.14	0.99

SW – Sharp-Wentworth Method   FC – Freeman–Carroll Method

CONCLUSION

The 8-HQ5-SASF 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 UV-visible, FT-IR and ^{1}H NMR spectral studies the proposed structure of the 8 -HQ 5-SASF copolymer has been determined. 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. Low values of frequency factor may be concluded that the decomposition reaction of 8-hydroxyquinoline 5-sulphonic acid-semicarbazide-formaldehyde copolymer can be classified as 'slow reaction'. Thermogravimetric study concluded that these copolymer is thermally stable at elevated temperature.

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