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Thermal Degradation Studies of 8-Hydroxyquinoline, Adipamide and Formaldehyde Copolymer Resin.

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ABSTRACT

The paper reports the synthesis and kinetics of thermal degradation studies of resin 8-hydroxyquinoline (8-HQ) - adipamide(A) - formaldehyde (F) derived by the condensation of 8-hydroxyquinoline and adipamide with formaldehyde in the presence of catalyst hydrochloric acid in 2:1:3 molar proportions of reactants. A detail thermal degradation study of the 8-HQAF resin has been carrietd out to ascertain its thermal stability. Thermal degradation curve has been discussed in order to determine their mode of decomposition, order of reaction (n), apparent activation energy (Ea), frequency factor (z), free energy change (ΔF), entropy change (ΔS), and apparent energy change (S*). Freeman – Carroll and Sharp- Wentworth methods have been applied for the calculation of kinetic parameters while the data from the Freeman – Carroll methods have been used to determine various thermodynamic parameters.

Keywords: Freeman - Carroll, Arrhenius equation, Order of reaction, Thermal degradation, Resin, Synthesis.

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INTRODUCTION

Copolymer is made from three different monomers. Copolymers are generally resinous, amorphous, or crystalline in nature [1]. These copolymers are found to be insoluble in common organic and inorganic solvents [2]. Copolymers may be used in boiler and cooling water and in scrubber systems where corrosion and/or the formation of scale deposits problems. Other environments in which the copolymer may be used include heat distribution type sea water desalting apparatus [3], in oil field services to remove scales from pipe walls, in mining applications such as gold heap leaching, in reverse osmosis systems and as a dispersant in the pulp and paper processing industries. They also could be used as mineral beneficiation aids such as in iron ore, phosphate and potash recovery. The copolymer are found very useful applications as an adhesive [4], high temperature flame resistant[5], fibers, coating materials, semiconductors [6], catalysis and ion exchange resins [7].

TGA analysis is a tool for investigating the thermal properties of systems. The temperature can be programmed from ambient to 1000 degrees Centigrade. Thermogravimetric thermal analysis (TGA) provides testing for a wide range of materials including polymers, plastics, composites, laminates, adhesives, food, coatings, pharmaceuticals, organic materials, rubber, petroleum, chemicals, explosives and biological samples.

Thermal stability of polymeric materials is an important physical property which has led to many applications. The properties may be profoundly affected by the presence of particular sequences of co monomers as well as of quite small proportions of additives. The thermal stability of polymers and copolymers has been extensively studied employing the method of thermogravimetric analysis (TGA) by several authors. Thermogravimetric study of various phenol-formaldehyde and other coordination copolymer resin has been reported in a literature [8-9]. M. Karunakaran′ and C. Magesh [10] synthesized terpolymers by condensation of o-cresol and biuret with formaldehyde and TGA analysis was employed to study the thermal stability and the kinetic data like activation energy of the terpolymer resins. M. M. Jadhao et. al. [11] synthesized a biphenol–guanidine–formaldehyde terpolymer resin and characterized on the basis of thermogravimetric analysis/differential thermal analysis.

A thermal study of the resin was carried out to determine its mode of decomposition, activation energy, order of reaction, frequency factor, entropy change, free energy, and apparent entropy change. A. Choudhury and A. Balmurulikrishnan [12] studied the thermal degradation of the Polyamide 66/EPR-g-MA blends and analyzed by nonisothermal thermogravimetric analysis (TGA). They found that the activation energy (Ea) and overall reaction order of thermal degradation decreased with increasing EPR-g-MA content. Kole et al. [13] studied the degradation behavior of silicone/ethylene propylene diene rubber blends and discussed the effect of compatibilization of the blends on its thermal degradation characteristics. Park et al.[14] and Corrales et al.[15] reported that the Ea and overall reaction order (n) for thermal degradation of the high-density polyethylene (HDPE) were recorded higher than those of branched PE (e.g. low-density polyethylene (LDPE) and linear low-density polyethylene (LLDPE)). Dhanraj T. Mashram and co-workers [16-17] synthesized Salicylaldehyde, Ethylenediamine and Formaldehyde and reported kinetics of thermal degradation studies. Detailed thermal degradation studies of the SdEDF resin has been carried out to ascertain its thermal stability. They has been discussed Thermal degradation curve in order to determine their mode of decomposition, order of reaction, apparent activation energy, frequency factor, free energy change, entropy change, and apparent energy change. De Geiso [18] et al. synthesized 8-Hydroxyquinoline - formaldehyde polymeric ligand and their coordination polymer with Zn^{2+}, Ni^{2+}, Fe^{3+}, Al^{3+} and UO^{4+} ion and studied their thermal stabilities. Several methods have been proposed for estimating the kinetic parameters of thermal degradation reaction viz. Flynn-Wall- Ozawa, Freeman-Anderson, Coats and Redfern, Broido, Sharp-Wentworth and Freeman - Carroll method, Kiessinger method etc.

The present communication deals with synthetic and thermal degradation properties of a newly synthesized copolymer resin derived from 8-hydroxyquinoline, adipamide and formaldehyde. The Freeman-Carroll and Sharp- Wentworth methods have been applied for the calculation of kinetic parameters [19-20]. Methods for the estimation of kinetic parameters from thermogravimetric studies are generally based on the assumption that the Arrhenius equation is valid with thermal and diffusion barriers are negligible.

MATERIALS AND METHOD

Chemicals and reagents

The important chemicals (starting materials) like *8*-hydroxyquinoline (Across Organic, Fisher Scientific, India), adipamide (Across Organic, Fisher Scientific, India) and formaldehyde (S.D. Fine Chemicals) used in the preparation of new 8-HQAF 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 8-HQAF copolymer resin

The new copolymer resin 4-HBPBF was synthesized by condensing 8-hydroxyquinoline (1 mol) and adipamide (1 mol) with 37 % formaldehyde (2 mol) in a mol ratio of 1:1:2 in the presence of 2M 200 ml HCl as a catalyst at 126°C ± 2°C for 5hrs in an oil bath with occasional shaking to ensure thorough mixing. The separated cream color terpolymer resin 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-formaldehyde copolymer which might be present along with 8-HQAF copolymer. The copolymer resin was purified further by dissolving in 8% 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 copolymer sample 8-HQAF 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 polymer resin was found to be 85%. The synthesis reaction, suggested structure and physical data of 8-HQAF copolymer resin has been given in Fig. 1 and Table 1.

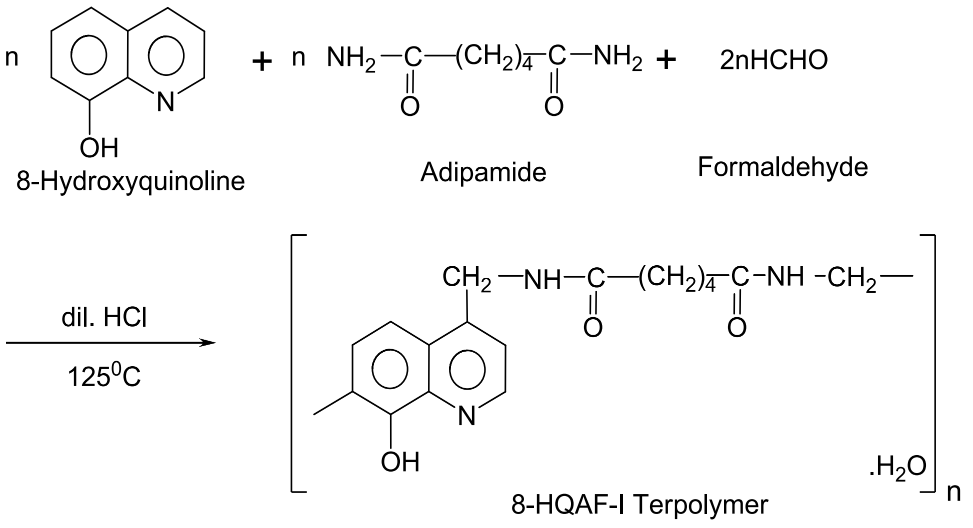

Fig. 1. Formation and suggested structure of 8-HQAF copolymer resin

Thermogravimetric analysis

Thermal analysis method is associated with a change in weight with respect to temperature. Heating is performed under strictly controlled conditions and can reveal changes in structure and other important properties of the material being studied. In non-isothermal or dynamic TGA the sample is subjected to conditions increase in temperature at linear rate [21-23].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 thermo gram is recorded for 8-HQAF sample at SICART, Vallabhvidyanagar, Gujrat. 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 and reported in the Table 3.

RESULTS AND DISCUSSION

Thermogravimetric analysis of the copolymer

Thermogravimetric analysis newly synthesized 8-HQAF copolymer has been carried out in the temperature range of 40–800ºC. The thermogravimetric data was analyzed by Sharp-Wentworth and Freeman-Carroll methods for each copolymer to calculate energy of activation (Ea), order of reaction (n) and the different kinetic parameters. Decomposition pattern of 8-HQAF copolymer resins are shown in Fig. 2-5 having different stages of thermal decomposition.

Thermogravimetry of 8-HQAF Copolymer Resin

From the thermogram the thermal degradation of 8-HQAF copolymer resin has been studied in four temperature ranges (40 – 120ºC, 120 – 280ºC, 280 – 450ºC, 450 – 800ºC). The first degradation is the initial weight loss (40 -120ºC) and showing 4.4% found and 4.46% calculated weight loss. This may be attributed due to removal of moisture retained in the sample during synthesis. As entrap water is not the part of copolymer resin, this initial loss may not be attributed being the stage of thermal degradation of the copolymer resin. The actual degradation starts from 120ºC, may be considered the first stage of thermal degradation (120 – 280ºC). By increasing temperature beyond 120ºC, the thermal vibrations of the molecules may be increased, the molecules become activated, start to attains coplannarity, loss their fine structures, the cross linking among the unreacted substituted groups of quinoline aromatic ring (-OH groups) may be increased. Cross linking may develop a strain in the macromolecule which result a weight loss of about 29.00% found and 28.50% calculated, which may be due to loss of one hydroxyl group and one sulphonic group substituted to aromatic quinoline ring. The increasing temperature beyond 280ºC, the increasing strain in the copolymer resin suffer unzipping of the cross linking, leading to a weight loss of about 60.00% found and 59.95% calculated upto the temperature 450ºC. This might be the second stage of thermal degradation of 8-HQAF copolymer resin. In the third stage of thermal degradation (450 - 800ºC), the strained copolymer resin suffer a weight loss corresponding 99.61% found and 100% calculated due to loss of 1,3,5 triazine ring with its side chain. After complete thermal degradation the rigid copolymeric part is left as the char residue which is negligible in the thermal degradation of 8-HQAF copolymer resin.

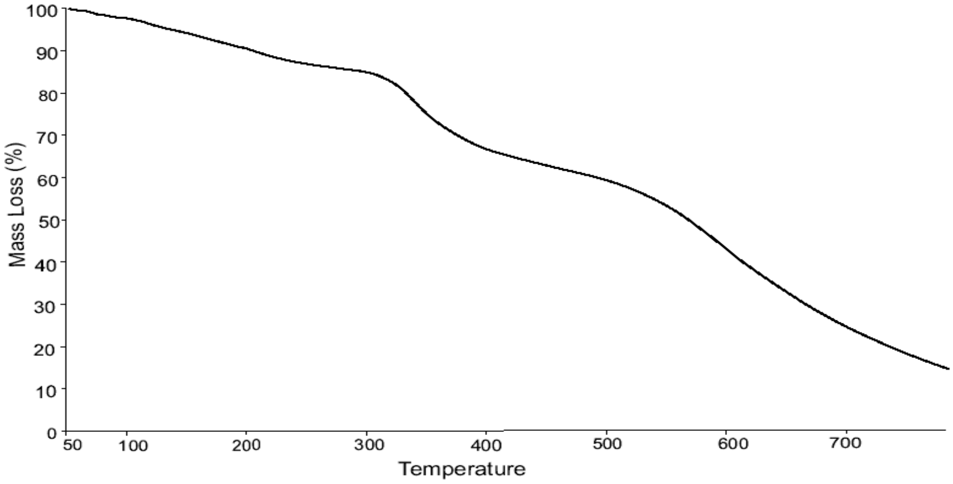

Fig. 2 : Decomposition Pattern of 8-HQAF copolymer Resin

Thermo-analytical data

A plot of percentage mass loss versus temperature is shown in the Figure 2 for a representative 8-HQAF copolymer. To obtain the relative thermal stability of the copolymer, the method described by Sharp-Wentworth and Freeman-Carroll adopted. The thermal stability of terpolymer, based on the initial decomposition temperature, has also been used here to define their relative thermal stability, neglecting the degree of decomposition. From the TG curves, the thermo analytical data and the decomposition temperatures were determined for different stages as given in Figure 2.

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

$$\frac{\Delta logdw/dt}{\Delta logWr} = n - \frac{Ea}{2.303R} - \frac{\Delta\frac{1}{T}}{\Delta logWr} - - - - - (1)$$

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.

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,

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

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.

(i) Entropy change

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

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
Δ = 0.166
ΔS= change in entropy
E = activation energy from graph

(ii) Free energy change (ΔF)

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

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

(iii) Frequency Factor (Z)

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

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

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 ($\alpha = w/W_c$)

(iv) Apparent entropy change (S^*)

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

Where, Z = from relation (6)
T^* = Temperature at which half of the compound is decomposed from it total loss.

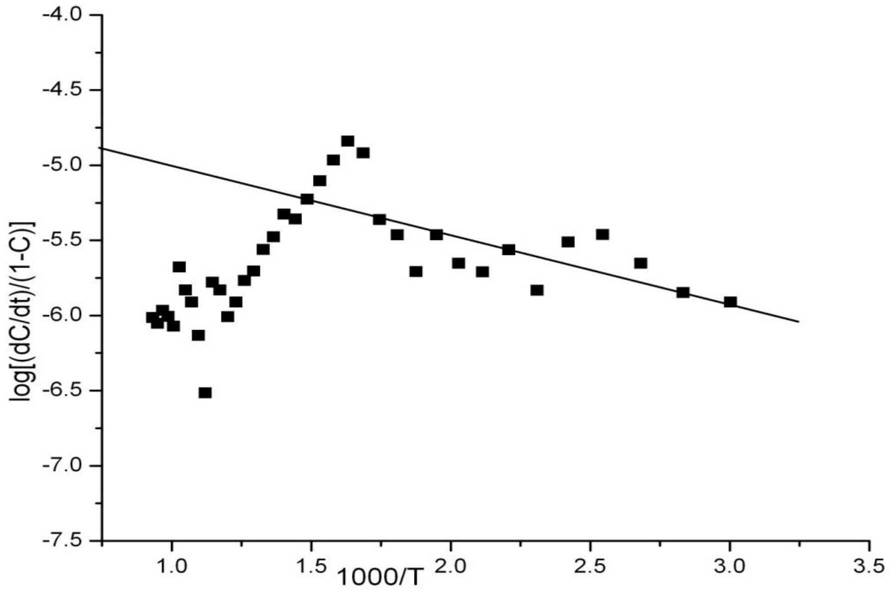

Fig. 3 : Sharp-Wentworth Plots of 8-HQAF copolymer Resin

The abnormally low value of frequency factor, it may be concluded that decomposition reaction of 8-HQAF copolymer can be classed as a 'slow' reaction. There is no other obvious reason [22-23]. 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 kinetic perfectly [24].

The 8-HQAF copolymers prepared from higher molar ratio of 8-hydroxyquinoline exhibited a lower rate of decomposition. In the present study, in case of 8-HQA copolymer 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 samples.

By using the data of the Freeman-Carroll method, various thermodynamics parameters have been calculated Table 3. The values of these thermodynamic parameters for all terpolymers are about the same. The similarity of the values indicates a common reaction mode, [25] from the abnormally low values of frequency factor, it may be concluded that the decomposition reaction of 8-HQAF copolymers can be classed as a 'slow' reaction. There is no other obvious reason [26]. 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.

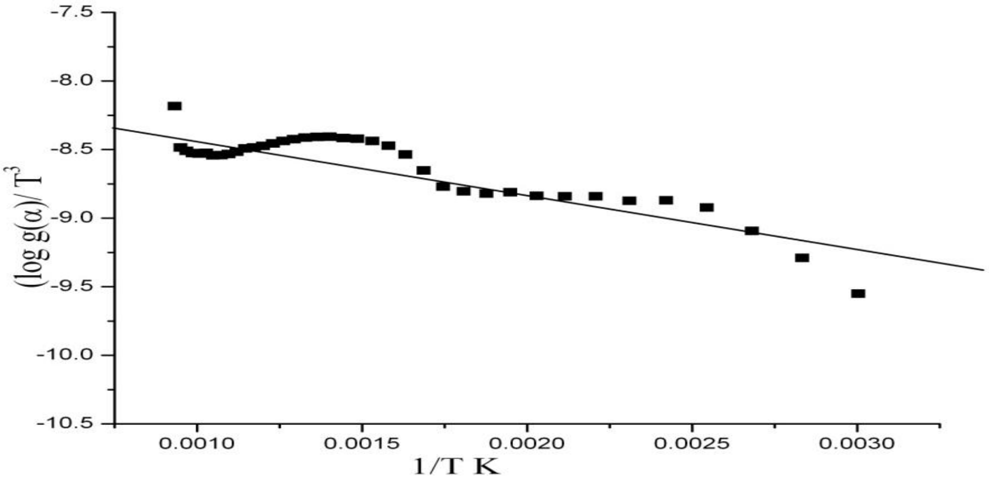

Fig. 4 : Thermal Activation Energy Plots (Freeman-Carroll Plots) of 8-HQAF copolymer Resin

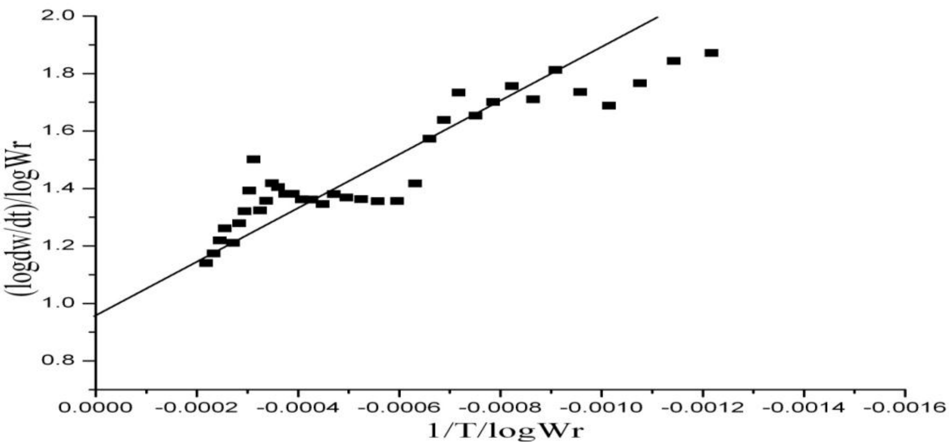

Fig. 5 : Freeman-Carroll Plots of 8-HQAF copolymer Resin

CONCLUSIONS

Thermogram of 8-HQAF copolymer resin shows activation energy calculated by the Freeman – Carroll and Sharp- Wentworth methods are in good agreement with each other. Thermodynamic parameters have been calculated on the basis of thermal activation energy and values are given in Table 3. Due to abnormally low value of frequency factor (z) it may be classified as a slow reaction and no other obvious reason can be given. The value of entropy (ΔS) indicates that the activated polymer has more ordered structure than the reactants and the reaction are slower than normal. This is further supported by low z values. It is very difficult to draw any unique conclusion from the magnitude of thermal activation energy (Ea) as decomposition mechanism is expected to be complicated. Positive values of activation energy under present investigation correspond to the energy of activation due oxidation – reduction process of terpolymer in the higher temperature range. Fairly straight-line plots are obtained using the two methods. However, using the Freeman- Carroll method some abnormal points were ignored to get a clear picture about most of the points. Similarly, in the Sharp- Wentworth method, some points at the beginning or the end did not fall on straight line. This is expected, since, the decomposition of copolymer is not obeying first order kinetics perfectly. These observations are in harmony with the findings of Jacobs and Tompkin and other earlier workers.

Table 1. Synthesis and physical data of 8-HQAF copolymer resin

Terpolymer resin	**Reactants**			**Molar ratios**	**Catalyst 2M HCl (ml.)**	**Reflux Temp. ^{0}C**	**Yield %**
	4-HBP (mol.)	**B (mol.)**	**F (mol.)**				
4-HBPBF	0.1	0.1	0.2	1:1:2	200	126 ± 2	85%

Table 2 Thermogravimetric Data and Decomposition Temperature of 8-HQAF Copolymer Resins

Copolymer Resins	Loss of molecular		Decomposition step, temperature range (ºC), mass loss (%) and species degraded				Mass of residue left over (%)
			First Step (loss of sulphonic & hydroxyl group)		Second Step (loss of aromatic quinoline nucleus)		
	Temp. range (ºC)	Mass loss (%)	Temp. range (ºC)	Mass loss (%)	Temp. range (ºC)	Mass loss (%)	
8-HQAF	40-120	5.60(F) 5.75(C)	120-260	11.05(F) 11.18(C)	260-800	51.32(F) 51.43(C)	42.27(F) 42.38(C)

Table 3 Results of Thermogravimetric Analysis of 8-HQAF Copolymer Reins

copolymer resins	Half Decomposition Temp. ºC	Activation Energy Ea (KJ)		Entropy change ΔS (J)	ree energy ΔF (KJ)	Frequency factor (Z) (Sec.$^{-1}$)	Apparent entropy (S*) (KJ)	Order reaction (n)
		FC	SW					
8-HQAF-I	613	7453.32	7253.32	160.505	97.790	685	-19.110	0.97

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

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