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Thermogravimetric studies of copolymers derived from 8-hydroxyquinoline 5-sulphonic acid, urea and formaldehyde

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ABSTRACT

Copolymer resins (8-HQ-5-SAUF) were prepared by the condensation of 8-hydroxyquinoline 5-sulphonic acid, urea and formaldehyde in the presence of hydrochloric acid as catalyst with varying the molar ratio of reacting monomers. Compositions of copolymers have been determined by elemental analysis. The number average molecular weights $(\overline{Mn})$ *have been determined by conductometric titration in non-aqueous medium. Electronic spectra, infrared spectra and nuclear magnetic resonance spectra were studied to elucidate the structure. Detailed thermal degradation study of the new copolymer resins have been carried out to ascertain its thermal stability. Thermal degradation curve is discussed which shows three decomposition steps after the loss of water molecule. Sharp-Wentworth and Freeman-Carrol methods have been used to calculate activation energy and thermal stability. The activation energy (Ea) calculated by using Sharp-Wentworth method has been found to be in good agreement with that calculated by Freeman-Carrol method. Thermogravimetric parameters such as free energy change (ΔG), entropy change (ΔS), apparent entropy change (ΔF), frequency factor (Z) have also been evaluated on the basis of the data of Freeman-Carrol method. The order of reaction (n) is found out to be 0.99.*

INTRODUCTION

Very few systems are reported showing the relation between thermal stability and structure of the copolymers. A variety of thermally stable polymers have been synthesized and the sequence of their thermal stabilities has been predicted from their TG data. 8-Hydroxyquinoline or phenol derivative like ortho-amino phenol condensed with formaldehyde have been reported [1].

8-Hydroxyquinoline (8-HQ) and its derivative are widely used as complexing agents in various applications due to their good complex forming ability [2-4]. Kannan and coworkers [5] have synthesized 8- acryloyloxy quinoline (8-AQ) and polymerized it in MEK at 70^0C using BPO initiator. Polychelates were obtained from an aqueous solution of Th (II) / Cd (II) / Zn (II) / Ni (II) and Mg (II) ions when added to the polymer in aqueous NaOH. The IR spectra of these poly-chelates suggest that metals are coordinated through oxygen atom of the ester carbonyl and with the nitrogen atom.

Liu and coworkers [6] studied the interactions of heavy metal ions and chelating ion exchange resin containing 8-hydroxyquinoline (8-HQ). The resin has good selectivity to exchangeable adsorption of heavy metal ions including Cu (II), Hg (II), Pb (II) and Mg (II) under pH 5.0 and also suggested that the chelating ion exchange resin containing

8-HQ could be used to enrich heavy metals in water and their analysis.

The study of the thermal degradation of copolymer resins have recently become a subject of interest. In the degradation of metal salt polymers, the nature of the metal ion has a major influence on the pattern of degradation [7]. The modifications induced by the presence of transition metal ions in the thermal behaviour of polymer salts which is clearly indicated in this work have been confirmed by Gabriela et al [8], revealed that the catalytic effect of cobalt ions on thermal behaviour of polymers affect the whole thermal degradation and reduced the initial thermal stability.

Gurnule and coworkers [9] have synthesized the 8-hydroxyquinoline-melamine-formaldehyde copolymer resins in the view of the interesting characteristics especially thermal analysis. From this department, a number of studies on such copolymers have been reported [10]. However, no work seems to have been carried out on synthesis, characterization, ion exchange properties and thermal stability of the copolymer resins from 8-hydroxyquinoline 5-sulphonic acid, urea and formaldehyde. The present article describes the composition of these newly synthesized resins, their characterization by elemental analysis, average molecular weight $(\overline{M}n)$ determination, intrinsic viscosity in DMSO, IR-spectra, UV-visible spectra, NMR spectra and thermal analysis giving their relative thermal stabilities.

MATERIALS AND METHODS

Experimental

Synthesis of 8-HQSUF-1 Copolymer:

A mixture of 8-hydroxyquinoline 5-sulphonic acid (2.43 gm, 0.1 mole), urea (0.606 gm, 0.1 mole) and formaldehyde (7.0 ml of 37%, 0.2 mole) in the presence of 200 ml 2M hydrochloric acid (HCl) as a catalyst was heated in an oil bath at 126 ^{0}C for 5 hrs, with occasional shaking [11, 12]. The separated resinous product (8-HQ-5-SAUF) was washed with hot water and methanol to remove unreacted monomers. The resinous product so obtained was washed with cold water, dried in air and powdered. The powder was washed with hot water and dried. Dried resins were then extracted with diethyl ether followed by petroleum ether to remove 8-hydroxyquinoline 5-sulphonic acid-formaldehyde copolymer, which might be present along with 8-HQ-5-SAUF copolymer. The resin was purified by dissolution in 8% NaOH and reprecipitation by drop wise addition of 1:1 (V/V) HCI, with constant and rapid stirring to avoid lump formation. The process reprecipitation was repeated twice. The copolymer resin 8-HQ-5-SAUF-I so obtained was filtered, washed with hot water, dried in air, powdered and stored in vacuum over anhydrous $CaCO_3$ were recorded in nujol mull with Perkin Elmer spectrum RX-I spectrophotometer in the range of 4000 -500 cm^{-1}. Proton NMR spectra were recorded with Bruker Avance-II 400 MHz proton NMR spectrophotometer and DMSO-d$_6$ was used as a solvent.

Table 1 :Synthesis of 8-HQ-5-SAUF copolymer resin

Reactants			Catalyst 2M HCl (aq) (ml)	Reflux Temp. (^{0}C)	Resin Abbreviation	Molar ratio of reactants	Yield %	Melting point of resin (decomposition temp.) (^{0}C)
8-Hydroxy-quinolene 5- sulphonic acid '8-HQSUF' (mole)	Urea 'U' (mole)	Formal dehyde 'F' (mole)						
0.1	0.1	0.2	200	126	8-HQSUF-I	1:1:2	72	238
0.2	0.1	0.3	200	126	8-HQSUF-II	2:1:3	69	246
0.3	0.1	0.4	200	126	8-HQSUF-III	3:1:4	65	255
0.4	0.1	0.5	200	126	8-HQSUF-IV	4:1:5	62	262

RESULTS AND DISCUSSION

All the newly synthesized, purified copolymer resins (8-HQ-5-SAUF) were found to be light yellow in colour. The copolymers are soluble in solvent such as DMF, DMSO and THF while insoluble in almost all other organic solvents. The resins synthesized do not show a sharp melting point but undergo decomposition above 238 ^{0}C (Table 1).

All the four 8-HQ-5-SAUF copolymer resins have been analyzed for carbon, hydrogen and nitrogen content. The elemental analysis data are in good agreement with the theoretical (calculated) data. The number average molecular weight $(\overline{Mn})$ of the copolymer resin was determined by non-aqueous conductometric titration in DMF against KOH in a 50% (v/v) DMF/alcohol mixture using 100 mg of resin sample. A plot of specific condu-ctance against the milliequivalent of potassium hydroxide required for neutralization of 100 g of copolymer was made. Inspection of such a plot revealed that there are many breaks in the plot. From this plot, the first and the last break were noted. The calculation of $(\overline{Mn})$ by this method is based on the consideration [13-14]. (1) The first break corresponds to the neutralization of more acidic hydroxy group of all the repeating units: and (2) the second break in the plot beyond which a continuous increase in conductance is observed, represents the stage at which the phenolic hydroxy group of all repeating units is neutralized. The average degree of polymeri-zation $(\overline{DP})$ is given by the relation

$$\overline{DP} = \frac{\text{Total milliequivalent of base required for complete neutralization}}{\text{Milliequivalent of base for smallest interval}}$$

The number average molecular weight $(\overline{Mn})$ could be obtained by multiplying the $(\overline{DP})$ by the formula weight of the repeating unit [11].

The electronic spectra of all the 8-HQ-5-SAUF copolymer resins give rise to a similar pattern. The spectra of these copolymers exhibit two absorption maxima in the region 240 to 260 and 320 nm. The intense band at 320 nm is due to the (π - π^*) allows the transition of 8-hydroxyquinoline 5-sulphonic acid moiety which readily attains coplanarity and shoulder merging (loss of fined structure) band at 260 nm may be due to (n - π^*) forbidden transition in aliphatic carbonyl compounds [12]. The bathochromic shift from the basic value, viz 260 and 320 nm respectively, may be due to the combined effect of conjugation and phenolic hydroxy group (auxochrome) [13].

The IR spectral studies of 8-HQ-5-SAUF resin revealed that all these copolymers give rise to nearly similar pattern of spectra. The assignment of vibrational frequencies is mainly based on the data available in the literature. A broad band appeared in the region 3406 -3449 cm^{-1} may be assigned to the stretching vibrations of phenolic hydroxy (-OH) groups exhibiting intermolecular hydrogen bonding [14]. The broad band displayed at 1630 -1632 cm^{-1} may be due to the stretching vibrations of carbonyl group (>C=O) of both ketonic as well as urea moiety [15]. The presence of -NH in urea moiety may be assigned due to sharp band at 3045 -3070 cm^{-1} [15]. The sharp band at 1549-1601 cm^{-1} may be ascribed to an aromatic skeletal ring [16]. A sharp peak at 1338 -1348 cm^{-1} may be due to the stretching vibration of sulphonic acid group [16]. The bands obtained at 790, 1184 and 1373 cm^{-1} suggests the presence of methylene bridges [16] in the polymer chain. The 3,5,7,8 tetra-substitution of aromatic ring is recognized from the bands appearing at 955, 1043, 1112 and 1231 cm^{-1} respectively [17].

Proton NMR spectra of all copolymer resin show multiple signal (unsymmetrical pattern) in the region 7.52- 7.48 (δ) ppm, which is due to aromatic protons [17]. A signal appearing in the region 8.81-8.87 (δ) ppm can be assigned to the proton of the phenolic -OH group in hydrogen bonding [17]. A weak signal at 3.63 - 4.37 (δ) ppm may be due to the proton of -NH- bridge [17, 19]. A signal at 2.53 - 2.58 (δ) ppm may be assigned to methylenic proton of an $Ar\text{-}CH_2\text{-}NH\text{-}CO$ moiety [17]. The sulphonic acid group protons of $Ar–SO_3H$ moiety may be identified by the intense peaks at 10.16-10.28 (δ) ppm [17]. A very weak signal in the region of 3.8 - 3.9 (δ) ppm may be due to the presence of HQ-5-SAUF copolymer as a impurity associated with copolymer resins.

Thermogravimetric Analysis of 8-HQ-5-SAUF Copolymers:

Examination of thermograms and TG data of these 8-HQ-5-SAUF copolymer resins revealed that the sample lost nearly 1.7 to 5.5% of its weight when the temperature was raised to 90 ^{0}C. This initial weight loss may be due to solvent or moisture entrapped in the copolymer samples [18]. Thermograms of all the 8-HQ-5-SAUF copolymers have exhibited three stages of decomposition, after loss of water molecules. The temperature range of first, second and third decomposition stage for different copolymer is found to be different. The first stage of decomposition represents degradation of hydroxyl and sulphonic acid group i.e. -OH and $–SO_3H$ groups linked to aromatic ring. The second stage of decompo-sition corresponds to loss of aromatic nucleus from the polymer. The third stage of decomposition may be assigned to removal of quinoline nucleus and methylene bridge. The degradation of species with their corresponding perce-ntage mass loss is summarized in.

TG of 8-HQSUF-1 Copolymer:

Thermogram of the copolymer resins depicts four steps decomposition in the temperature range 30-615 ^{0}C. The first step slow decomposition between 30-90 ^{0}C corresponds to 5.3% loss, which may be attributed to loss of water molecule against calculated 5.5% present per repeat unit of the polymer. The second step decomposition starts from 90-410 ^{0}C which represents degradation of hydroxyl and sulphonic moiety (35.8% found and 35.47% cal.). The third step decomposition start from 410-450 ^{0}C corresponding to 49.5% loss of aromatic nucleus against calculated 50.45%. The four step decomposition of side chain from 450-615 ^{0}C corresponding to removal of quinoline nucleus and methylene bridge of polymer (81.4% found and 82.26% cal.) and consequently residue remained may be assigned as urea moiety (18.6% found and 17.74% cal.).

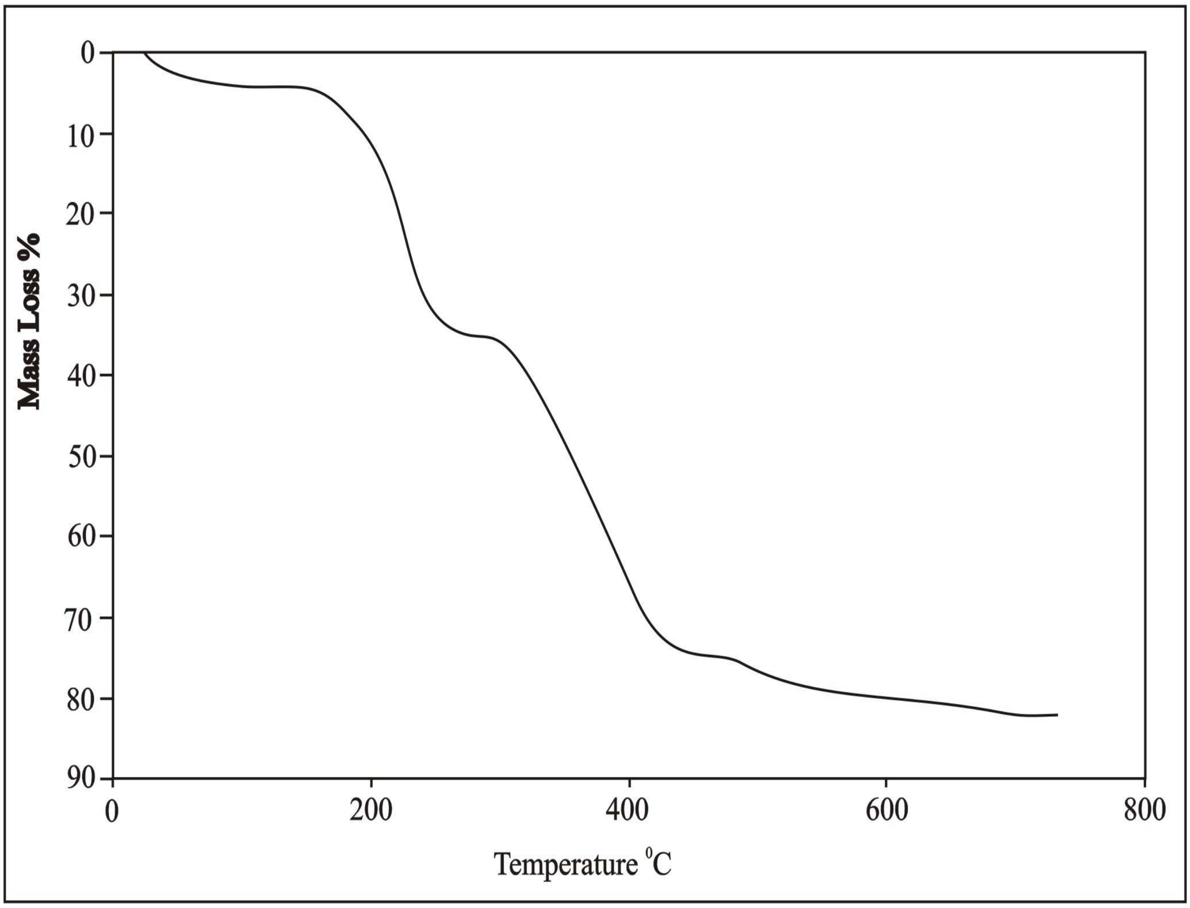

Fig. 1. Thermogravimetric Analysis of 8-HQSUF -1 copolymer

DISCUSSION

In the present study, in case of 8-HQ-5-SAUF copolymer the removal of water from the polymer is complete around 100 ^{0}C. The water is probably crystal weight loss correspond to water molecule in 8-HQ-5-SAUF-l, 8-HQ-5-SAUF-II, 8-HQ-5-SAUF-III and 8-HQ-5-SAUF-IV. The observed weight loss is a little higher than required in the region and this may be due to some other chain degradation reaction involved in the pyrolysis of the copolymers [7].

By using thermal decomposition data and then applying the Sharp- Wentworth method [26] activation energy is calculated, which is in agreement with the activation energy calculated by Freeman-Carroll method [18]. A representative thermal activation energy plot and Freeman-Carroll plot have been shown. Thermodynamic parameters have been calculated on the basis of thermal activation energy.

Fairly good straight line plots are obtained using both methods. However, in the Freeman-Carroll method some abnormal points were ignored to get a clear picture about most of the point. Similarly, in the Sharp-Wentworth method, some points at the beginning or at the end did not fall on the straight line. This is expected since the decomposition of copolymer is known not to obey first order kinetics perfectly [7, 12]. These observations are in harmony with the findings of Jacobs and Tomkin [19] and other earlier workers [19].

On the basis of all the physicochemical and thermal data and foregoing results and discussions the most probable structures have been proposed for 8-HQ-5-SAUF copolymer resins under investigation.

Table 2: Results of Thermogravimetric Analysis of 8-HQSUF-I Terpolymers

Terpolymer	**Temperature range (^0C)**	**Stage of Decomposition**	**Species degraded**	**% weight loss**	
				Found	**Calc.**
8-HQSUF-I	30-90	-	Loss of water molecule	5.3 %	5.5 %
	90-410	First	Loss of hydroxyl and sulphonic moiety	35.8 %	35.47 %
	410-450	Second	Loss of aromatic nucleus	49.5 %	50.45 %
	450-615	Third	Removal of side chain of biuret polymer	81.4 %	82.26 %

Table 3: Kinetic Parameters of 8-HQSUF-I Terpolymers

Sr. No.	**Terpolymer**	**Entropy change ΔS (J)**	**Free energy change ΔF (KJ)**	**Frequency factor Z (s^{-1})**	**Apparent entropy change S* (KJ)**	**Order of reaction N**
1.	8-HQSUF- I	-8.3866	22.58	814	-22.98	1.1
2.	8-HQSUF -II	-8.2705	16.70	457	-23.56	1.2
3.	8-HQSUF –III	-8.1751	19.11	794	-23.00	0.98
4.	8-HQSUF -IV	-8.2286	18.96	630	-23.24	0.99

FC = Freeman-Carroll Method.
SW = Sharp-Wentworth Method.

CONCLUSION

The polymer degradation is made in three stages, after loss of water molecule. The evaluating kinetic characteristics by means of Sharp- Wentworth and Freeman-Carroll methods suggest the complexity of the thermal degradation mechanism. The thermal and kinetic characteristics enabled the determination of a series of analyzed copolymer thermostability, 8-HQ-5-SAUF-IV > 8-HQ-5-SAUF-III > 8-HQ-5-SAUF-II > 8-HQ-5-SAUF-I. These copolymers can be used to prepared polychelates and also can be used as ion-exchanger for certain transition metal ions.

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REFERENCES

[1] L. D. Pennington, M. B. William, *Ind. Eng. Chem.*, **1982**, 51, 759.
[2] K. H. Faltynski, J. R. Jezorek, *Chromatographia*, **1986**, 22, 5-12.
[3] N. Yamamori, H. Ohsuyi, Y. Eguchi, Yokoi, *Eur. Polym. J.*, **1987**, 220, 965 : *Chem Abstr* **1988**, 108, 26959t.
[4] K. Janak, J. Janak, *Collect Czech Chem Commun,* **1986**, 51, 657-663; *Chem Abstr*, **1986**, 105, 43856n.
[5] T. Kaliyappan, Anupriya, P. Kannam, *Macromol New fron. Proc IUPAC, Int. Symp. Adv. Polym. Sci. Techno.*, **1998**, 1, 429-432; *Chem Abstr.*, **1998**, 309r61v.
[6] X. Liu, D. Zhu, D. Chang, *Huazhong Nongye Dauxe Xuebao.*, **2000**, 19, 15-17.
[7] P. E. P. Michael, J. M. Barbe, H. D. Juneja, L. J. Paliwal, *Eur Polym J.*, **2007**, 43(12), 4995-5000.
[8] B. A. Shah, A. V. Shah, B. N. Bhandari, *Asian J. Chem.*, **2001**, 13(4), 1305-1311; see also *Chem Abstr.*, **2002**, 136(4), 54726m.
[9] S. S. Rahangdale, W. B. Gurnule, *Der Pharma. Chemica.*, **2012,** 4(5), 1836.
[10] S. S. Rahangdale, W. B. Gurnule, *Chem. Sci. Trans.*, **2013,** 2(1), 287.

[11] R. H. Gupta, S. S. Rahangdale, W. B. Gurnule, *Bionano Frontier*, **2012,** 5, 423.
[12] R. N. Singru, A. B. Zade, W. B. Gurnule, *J. Appl. Polym. Sci*., **2008**, 109(2), 859-868.
[13] R. H. Gupta, A. B. Zade, W. B. Gurnule, *J. Appl. Polym. Sci*., **2008**, 109(5), 3315-3320.
[14] M. V. Tarase, A. B. Zade, W. B. Gurnule, *J. Appl. Polym. Sci*., **2008**, 108(2), 738-746.
[15] P. E. P. Michael, P. S. Lingala, H. D. Juneja, L. J. Paliwal, *J. Appl. Polym. Sci*., **2004**, 92(4), 2278-2283.
[16] P. S. Kalsi, Spectroscopy of Organic Compounds, 2nd ed; New Age International Publisher, New Delhi, **1995**.
[17]R. M. Silverstein, G. C. Bassle, Spectroscopic Identification of Organic Compounds, 5th ed.; Wiley: Singapore, **1991**.
[18] S. H. Maron, R. B. Reznik, *J. Appl. Polym. Sci*., **1969**, 2, 309.
[19] S. S. Rahangdale, A. B. Zade, W. B. Gurnule, *J. Appl. Polym. Sci*., **2008**, 108(2), 747-756.
[20] W. B. Gurnule, P. K. Rahangdale, L. J. Paliwal, R. B. Kharat, *Synth. React. Inorg. Met-Org. Chem*., **2003**, 33(7), 1187-1205.