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Synthesis, Characterization and Thermal Degradation Studies of Copolymer Resin Derived from 8-Hydroxyquinoline 5-sulphonic acid and Thiosemicarbazide.

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ABSTRACT

Copolymer (8-QSTF) has been synthesized using the monomers 8-hydroxyquinoline 5-sulphonic acid, thiosemicarbazide and formaldehyde in 1:1:2 molar proportions. The structure of 8-QSTF copolymer has been elucidated on the basis of elemental analysis and various physicochemical techniques, i.e. UV-Visible, FT-IR and ¹H-NMR spectroscopy. Detailed thermal degradation study of the new copolymer has been carried out to ascertain its thermal stability. Thermal degradation curve is discussed which shows three decomposition steps. The activation energy (E_a) and thermal stability calculated by using the Sharp-Wentworth, Freeman-Carroll and Friedman's methods. Thermodynamic parameters such as entropy change (ΔS), apparent entropy change (S^*) and frequency factor (z) have also been evaluated on the basis of the data of Freeman-Carroll method. The order of reaction (n) is found out to be 0.98.

Keywords: 8-QSTF copolymer; Freeman-Carroll method; Synthesis; characterization; Sharp-Wentworth method; Thermal degradation.

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INTRODUCTION

Copolymers, very special classes of polymers, are known for their versatile uses and are found to be amorphous, crystalline or resinous in nature. Phenolic resins have been the workhorse as matrix resins in composites for structural and thermal applications in aerospace because of their ease of processability, thermal stability, versatile characteristics and cost effectiveness. A considerable attention has been paid in the past two decades to the synthesis of copolymer resin due to their exciting features such as high thermal stability. Tang and coworkers [1] studied the thermal decomposition kinetics of thermotropic copolyesters made from *trans*-*p*-hydrocinnamic acid and *p*-hydrobenzoic acid. Copolymers occupy an intermediate position between organic and inorganic compounds and it is hoped that the study of copolymers will lead to the production of polymer, which are both thermally stable and useful as fabricating materials. P. E. P. Michael et al. studied synthesis, characterization and thermal degradation of 8-hydroxyquinoline–guanidine–formaldehyde terpolymer [2]. Rahangdale and coworkers studied thermal degradation of terpolymers derived from 2, 4-dihydroxy-acetophenone, dithioamide and formaldehyde [3, 4].

Terpolymer resins are derived from 2,4-dihydroxypropiophenone, biuret, and formaldehyde in hydrochloric acid as catalyst and studied their thermal degradation [5, 6]. Thermal degradation of *m*-nitroaniline, *m*-chloroaniline and *m*-aminophenol has been studied by Dash *et al.* [7] and 2-hydroxyacetophenone, oxamide and formaldehyde [8].

S. L. Oswal et al synthesized and studied thermal properties of copoly(maleimide-methylmethacrylate), terpoly (maleimide- methylmethacrylate- acrylicacid), and terpoly- (maleimide-methylmethacrylatemethylacrylic acid). The thermal behaviour was studied by TG and DSC techniques [9]. Thermoanalysis and rheological behavior of copolymers of methyl methacrylate, N-phenylmaleimide and styrene studied by G. Jungang et al [10]. In order to synthesize polymers having numerous practical applications, there is a need to investigate the effect of heat on the polymers in order to establish their thermal stability. It must be pointed out that all the methods proposed have been developed by assuming that both activation energy and kinetic model do not change along the process. However, it has concluded from free- model kinetic methods of analysis that the activation energy is a function of the reacted fraction [11-14].

However, the literature studies have revealed that no copolymer has been synthesized using the monomer 8-hydroxyquinoline 5-sulphonic acid, thiosemicarbazide and formaldehyde. Therefore, in the present communication we report the synthesis, structural characterization and thermal degradation studies of 8-QSTF copolymer. The elemental analysis has been carried out to ascertain the molecular formula and the spectral studies have been used to characterize the complete structure of the 8-QSTF copolymer. After treating the thermal degradation data with Sharp–Wentworth (S-W) and Freeman–Carroll (F-C) methods, activation energy and kinetic parameters such as ΔS , z , S^* and n (order of reaction) have been evaluated [15].

MATERIALS AND METHOD

Materials and samples

All the chemicals used were of analytical grade. 8-hydroxyquinoline 5-sulphonic acid, thiosemicarbazide and formaldehyde which are purchased from Merck Chemicals, India. Solvents like N,N-dimethylformamide and dimethylsulphoxide purchased from SD Fine Ltd, Mumbai, India, were used after distillation.

Synthesis of 8-QSTF copolymer resin

The 8-QSTF copolymer was prepared by condensing 8-hydroxyquinoline 5-sulphonic acid (0.1 mol) and thiosemicarbazide (0.1 mol) with formaldehyde (0.2 mol) in the presence of 2M HCl as a catalyst at 122 ± 2 °C in an oil bath for 4 hr (Fig.1).

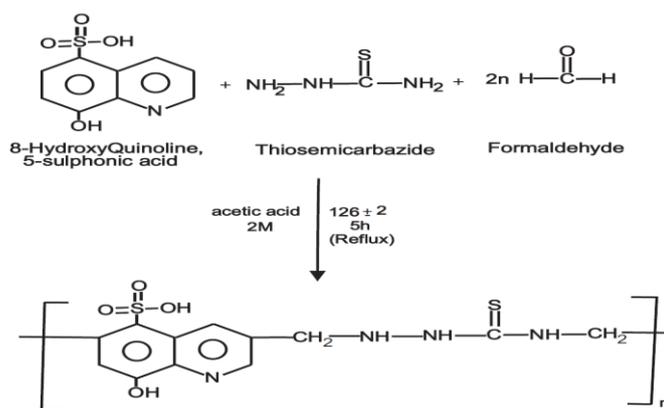


Figure 1: Synthesis of 8-QSTF copolymer resin

The brown colored solid product obtained was immediately removed and extracted with diethyl ether to remove excess of 8-hydroxyquinoline 5-sulphonic acid-formaldehyde copolymer, which might be present along with the 8-QSTF copolymer. It was further purified by dissolving in 8 % NaOH and then filtered. The copolymer was then reprecipitated by drop wise addition of 1:1 (v/v) conc. HCl / water with constant stirring and filtered. The process was repeated twice. The resulting copolymer sample was washed with boiling water and dried in a vacuum at room temperature. The purified copolymer resin was finely ground to pass through 300-mesh size sieve and kept in a vacuum over silica gel. The yield of the copolymer was found to be about 82-88 %.

Analytical and physicochemical studies

The elemental analysis was carried out on a Perkin Elmer 2400 Elemental Analyzer instrument. The UV-Visible studies were out carried using Scimadzu 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. $^1\text{H-NMR}$ studied using Bruker Avance-II FT-NMR Spectrometer in DMSO-d_6 solvent. All the analytical and spectral studies for the newly synthesized copolymer were carried out at Sophisticated Testing Instrumentation Centre (STIC), Kochi.

Instrumentation

The nonisothermal thermogravimetric analysis was performed in air atmosphere with heating rate of $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ using 5 - 6 mg of samples in platinum crucible from temperature of $40\text{ }^\circ\text{C}$ to $800\text{ }^\circ\text{C}$ and thermograms are recorded for 8-QSTF sample at Sophisticated Testing Instrumentation Centre (STIC), Kochi. With the help of thermogravimetric data the thermal activation energies (E_a) 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 1.

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, Freeman- Carroll and Freidman.

Freeman-Carroll method

The straight-line equation derived by Freeman and Carroll [16], which is in the form of

$$\frac{\Delta \log dW / dt}{\Delta \log W_r} = n - \frac{E_a}{2.303R} \cdot \frac{\Delta(1/T)}{\Delta \log W_r} \dots\dots\dots(1)$$

Where,

dW/dt = rate of change of weight with time.

W_r = $W_c - W$

W_c = weight loss at completion of reaction.

W = fraction of weight loss at time t .

E_a = energy of activation.

n = order of reaction.

The plot between the terms $\frac{\Delta \log dW/dt}{\Delta \log W_r}$ vs $\frac{\Delta 1/T}{\Delta \log W_r}$ gives a straight line from which slope we obtained energy of activation (E_a) and intercept on Y-axis as order of reaction (n). The change in entropy (ΔS), frequency factor (z), apparent entropy (S^*) can also be calculated by further calculations.

Sharp–Wentworth method

Using the equation derived by Sharp and Wentworth [17],

$$\log \frac{dC/dT}{1-C} = \log A/\beta - \frac{E_a}{2.303R} \cdot \frac{1}{T} \dots\dots\dots (2)$$

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 (E_a) from its slope.

Friedman method

Friedman [18] provides the following expression for thermal degradation kinetic studies based on Arrhenius equation:

$$\ln \left(\frac{d\alpha}{dt} \right) = \ln(z) + n \cdot \ln(1 - \alpha) - \left(\frac{E_a}{RT} \right) \dots\dots\dots (3)$$

Where α is the conversion at time t , R is the gas constant ($8.314 \text{ J.mol}^{-1}.\text{K}^{-1}$) and T is the absolute temperature. The plot of $\ln.(d\alpha/dt)$ vs $1/T$ should be linear with the slope E_a/R , from which E_a can be obtained. The plots give the activation energies at different stages of degradation reaction takes place.

This isoconversional (model-free) kinetic methods use to check the variation of the apparent activation energy values with degree of degradation. This kinetic analysis should be a starting point for obtain the useful information on the behavior of the sample (Table 2).

RESULTS AND DISCUSSION

The resin sample was brown in color, insoluble in commonly used solvent, but was soluble in DMF, DMSO, THF, pyridine, concentrated H_2SO_4 . No precipitation and degradation occurs of resin in all the solvents. These resins were analyzed for carbon, hydrogen and nitrogen content.

Characterization of copolymer

Molecular weight of copolymer was estimated by conductometric titration. The number average molecular weight (\overline{Mn}) could be obtained by multiplying the \overline{Dp} by the formula weight of the repeating unit

[19]. The result of the molecular weight of copolymer samples prepared using higher proportion of two monomers (8-QS and T) has the highest molecular weight in the series. The molecular weight for 8-QSTF is 5250 (Fig.2.).

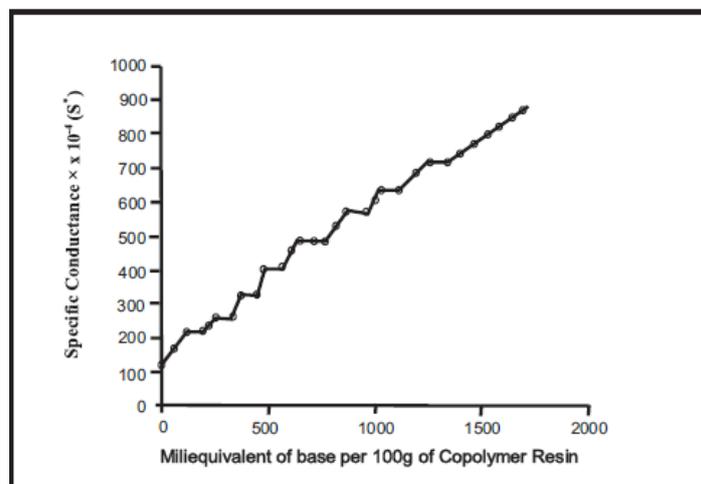


Figure 2: Conductometric titration curve of 8-QSTF polymer resin.

The composition of copolymer (represented in scheme 1) obtained on the basis of the elemental analysis data was found to be in good correlation to that of the calculated values:

- Calculated for $C_{11}H_{10}N_2O_5$: C: 52.8 %; H: 4.0 %; N: 11.2 %.
- Found for $C_{11}H_{10}N_2O_5$: C: 52.66 %; H: 4.03 %; N: 11.17 %.

A broad the UV-visible spectra of 8-QSTF copolymer is shown in Fig.3. UV-visible spectra of all the purified copolymer has been recorded in pure DMF. The perusal of the UV-visible spectra of copolymer showed almost similar nature. The spectra of this copolymer exhibit two absorption maxima in the region 240 nm and 280 nm. These observed positions of the absorption bands indicate the presence of thio carbonyl group (ketonic) processing double bond, which is in conjugation with the aromatic nucleus and hydroxyl group. The appearance of former band (more intense) can be accounted for $n \rightarrow \pi^*$ transition while the later band (less intense) may be due to $\pi \rightarrow \pi^*$ electronic transition. The shift from the basic value (viz. 280 nm and 280 nm respectively) may be due to conjugation effect, and presence of phenolic hydroxy group (auxochromes) is responsible for hyperchromic effect i.e. ϵ_{max} higher values [20, 21]. This observation is in good agreement with the proposed most probable structure of this copolymer.

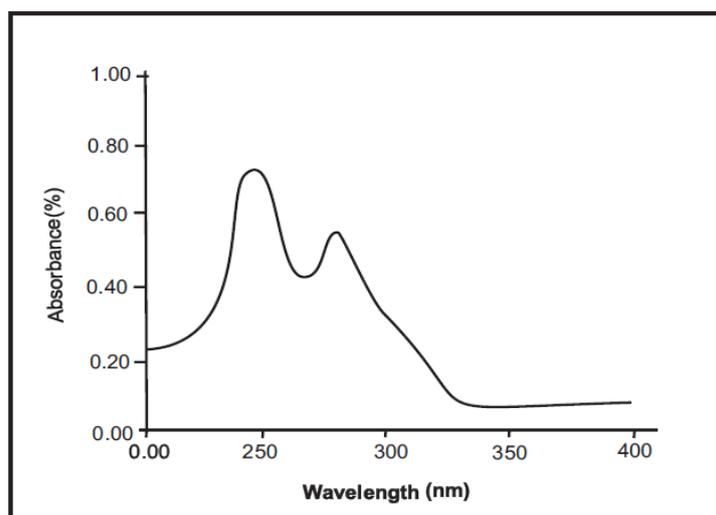


Figure 3: Electronic spectra of 8-QSTF copolymer resin

The IR-spectra of 8-QSTF copolymer is presented in Fig.4. The IR-spectra revealed this copolymer give rise to nearly similar pattern of spectra. A band appeared in the region 3444 cm^{-1} may be assigned to the stretching vibration of the phenolic hydroxy groups exhibiting intermolecular hydrogen bonding [21]. The presence of weak peak at 3000 cm^{-1} 2975 cm^{-1} describes the -NH- in biuret moiety may be ascribed in the copolymeric chain [21]. The sharp band displayed at 1631 cm^{-1} may be due to the stretching vibration of thiocarbonyl group of both, ketonic as well as thisemicabazide moiety [22]. The sharp and weak bond obtained at 1380 cm^{-1} suggests the presence of $\text{-CH}_2\text{-}$ methylene bridges [22] in the copolymer chain. The band obtained in the range of $1652\text{-}1622\text{ cm}^{-1}$ suggests the presence of $\text{-SO}_3\text{H}$ group.

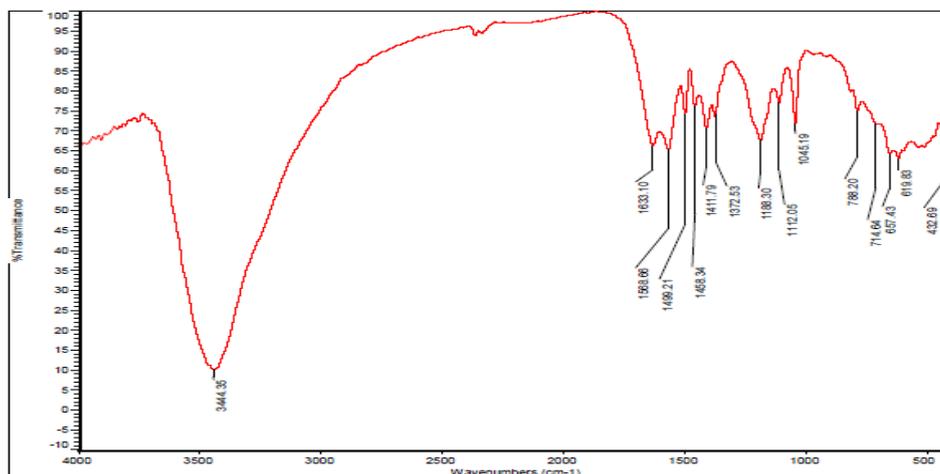


Figure 4: FTIR spectrum of 8-QSTF copolymer resin

$^1\text{H-NMR}$ spectra of 8-QSTF copolymer show a medium singlet peaks appeared at 9.51 - 9.53 ppm may be assigned to sulphonic acid protons of Ar-COOH [15]. A weak singlet signals in the region 7.37 - 7.38 ppm which due to aromatic proton (Ar-H) [22]. Also the weak singlet signal appearing at 7.06 - 7.08 ppm may be due to proton of Ar-OH (phenolic -OH) [22]. The medium triplet signal appeared at 6.64 - 6.66 ppm may be due to amido protons $\text{-CH}_2\text{-NH-CO-}$ of polymer chain [22, 23]. Also the medium doublet signal in the range of 6.42 - 6.44 ppm is attributed to the protons of methylenic bridge $\text{Ar-CH}_2\text{-NH-}$ of polymeric chain [22, 23, 24].

Thermogravimetric analysis of the copolymer

The thermal stability of copolymer is evaluated by dynamic thermo-gravimetric analysis in air atmosphere with heating rate of $10\text{ }^\circ\text{C min}^{-1}$.

Thermogram of TG of 8-QSTF copolymer is shown in Fig. 5. Thermogram of copolymer depicts three steps decomposition after loss of water molecule in the temperature range $40\text{ }^\circ\text{C} - 800\text{ }^\circ\text{C}$. The initially decomposition takes place between $40\text{ }^\circ\text{C} - 170\text{ }^\circ\text{C}$ corresponds to 5.89 % loss which may attributed to loss of a water molecule against calculated 5.02 % present per repeat unit of the polymer. The first step decomposition starts from $170\text{ }^\circ\text{C} - 320\text{ }^\circ\text{C}$ which represents degradation of sulphonic acid group and hydroxyl groups (32.90 % experimental and 32.40 % calculated). The second step which is start from $320\text{ }^\circ\text{C} - 540\text{ }^\circ\text{C}$ corresponding to 71.80 % loss of aromatic ring along with two methylenic groups against calculated 71.40 %. The third step starts from $540\text{ }^\circ\text{C} - 800\text{ }^\circ\text{C}$ corresponding to loss of thiosemicarbazide moiety (100% loss).

Thermo-analytical data

A plot of percentage mass loss versus temperature is shown in the Fig. 5 for a representative 8-QSTF copolymer. To obtain the relative thermal stability of the copolymer, the method described by Sharp-Wentworth, Freeman-Caroll and Freidman was adopted. The thermal stability of copolymer, based on the initial decomposition temperature, has also been used here to define their relative thermal stability, neglecting the degree of decomposition.

By using thermal decomposition data and then applying above methods the activation energy (E_a) is calculated which are not perfectly in agreement with each other. But the 'average E_a ' calculated by Freeman-Carroll and Freidman is nearly same and 'average E_a ' by Sharp-Wentworth is nearly double than both methods. The activation energy calculated by these methods is depicted in Table 2. However the error in activation energies obtained from the Sharp-Wentworth isoconversional method is significant and largely increases as far as conversion increases. On the other hand, it has been considered of interest to analyze the behavior of the process constitute by two competitive reactions that would lead to an apparent dependence between E_a and α when analyzed by isoconversional method, in spite such dependence is not real [25].

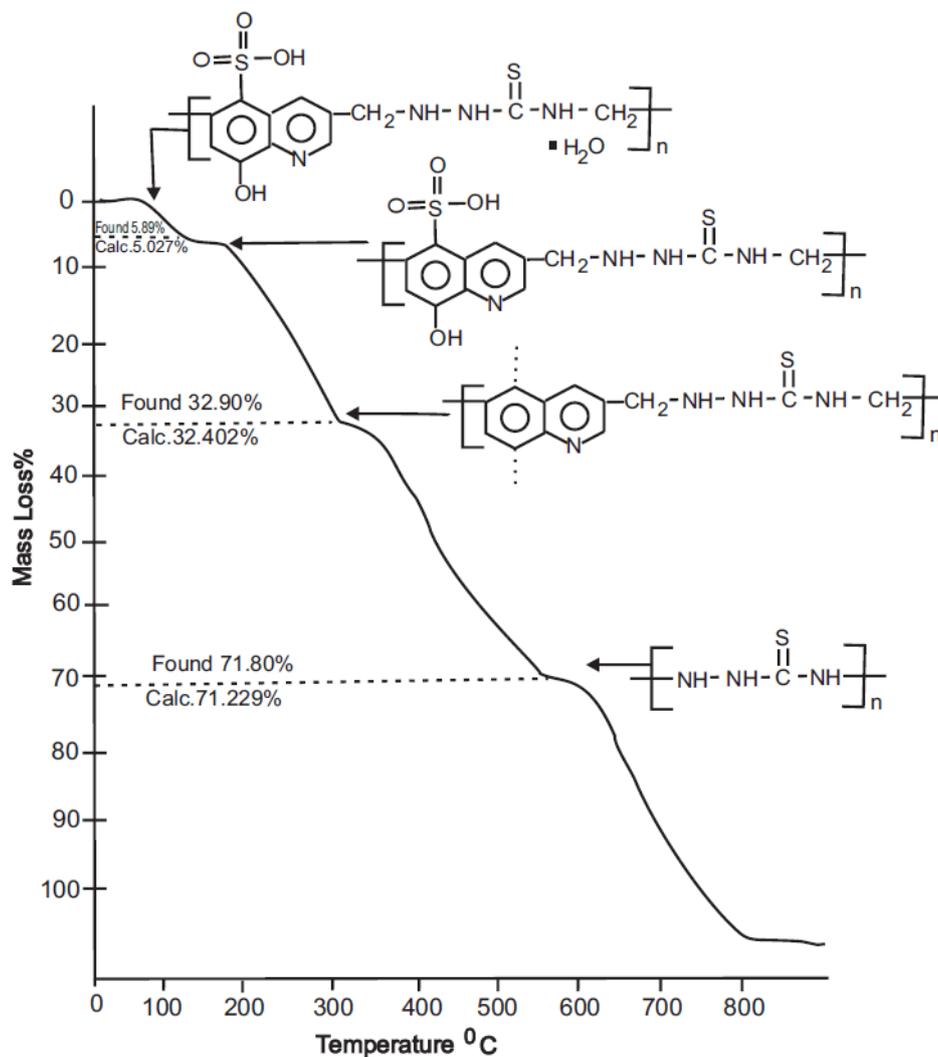


Figure 5: Decomposition pattern of 8-QSTF copolymer resin

A representative thermal activation energy plot of Sharp-Wentworth (Fig. 6), Freeman-Carroll (Fig. 7-8) and Freidman (Fig. 9) 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 (E_a) using equations (3), (4), (5). These values are given in (Table 1).

i. Entropy Change (ΔS):

$$\text{Intercept} = \log \frac{kR}{h\phi E_a} + \frac{\Delta S}{2.303R} \dots\dots\dots (3)$$

Where,
 $k = 1.3806 \times 10^{-16} \text{ erg.deg}^{-1}.\text{mol}^{-1}$,
 $R = 1.987 \text{ cal.deg}^{-1}.\text{mol}^{-1}$,
 $h = 6.625 \times 10^{-27} \text{ erg.sec}$,
 $\phi = 0.166$,

ΔS = entropy change,
 E_a = activation energy from graph.

ii. Frequency Factor (z):

$$B_{2/3} = \frac{\log z \cdot E_a}{R\phi} \dots\dots\dots (4)$$

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

Where, z = frequency factor,
 B = calculated from eq [a],
 $\log p(x)$ = calculated from Doyle table corresponding to activation energy.

iii. Apparent entropy change (S^*):

$$S^* = 2.303R \log \frac{zh}{RT^*} \dots\dots\dots (5)$$

Where, T^* = temp at which half of the compound decomposed.

The abnormally low value of frequency factor, it may be concluded that decomposition reaction of 8-QSTF copolymer can be classed as a 'slow' reaction. There is no other obvious reason [26, 27]. 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 [28, 29].

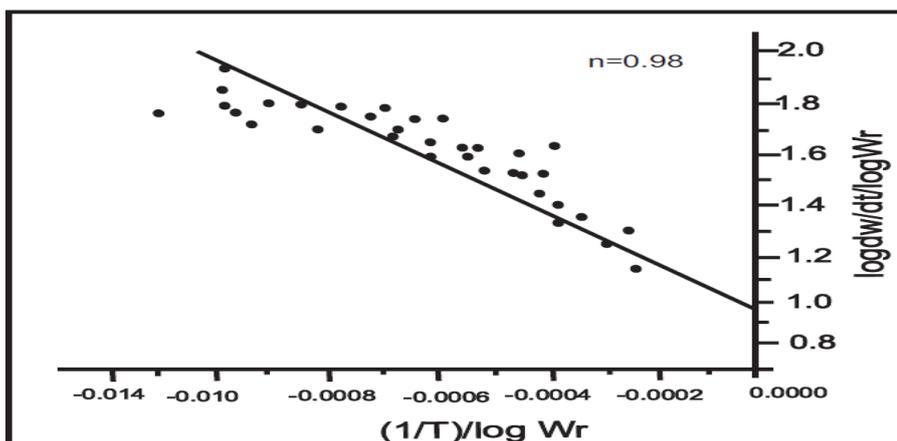


Figure 6: Sharp-Wentworth plot of 8-QSTF copolymer resin

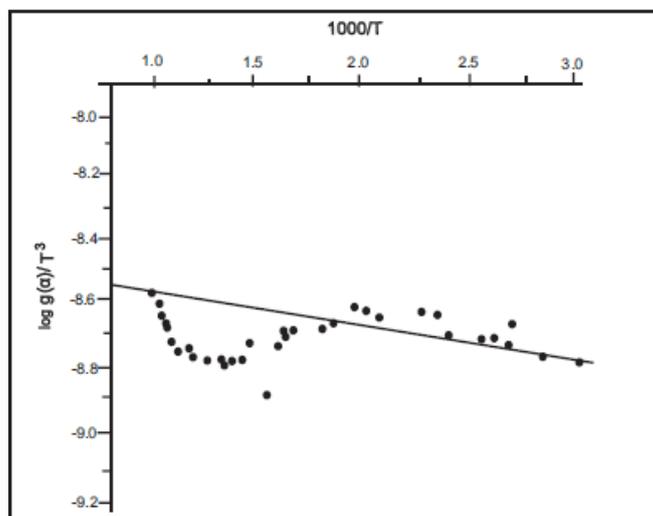


Figure 7: Freeman-Carroll plot of 8-QSTF copolymer resin

Table 1: Thermogravimetical Parameters Corresponding to Heating Rate of 10⁰C/min. of 2,4-DHBOF-I copolymers

| Terpolymers | T* (°C) ^a | ΔS | Z | S* | n |
|-------------|----------------------|------|--------|--------|------|
| 8-QSTF | 446.43 | 8.95 | 870.64 | -21.89 | 0.98 |

^aHalf decomposition temperature

Table 2: Comparison of Activation Energy (Ea) of Degradation at Different Stages by Different Methods of 8-QSTF Copolymers

| Terpolymer | Stages | Temp Range | Group loss | Wt. loss (%) | Activation (Ea) (KJ/mol.) | | |
|------------|-----------------|------------|--------------------------------------------------------------------|--------------|---------------------------|----------------|----------|
| | | | | | Sharp-Wentworth | Freeman-Caroll | Freidman |
| 8-QSTF | 1 st | 40.0-170 | H ₂ O molecule entrapped | 06.71 | 25.06 | 25.38 | 25.63 |
| | 2 nd | 170-320 | degradation of -COOH group with -OH group | 30.45 | 28.99 | 28.39 | 26.41 |
| | 3 rd | 320-540 | loss of aromatic quinoline ring along with -CH ₂ groups | 69.40 | 12.18 | 12.31 | 13.96 |
| | 4 th | 540-800 | loss of thiosemicarbazide moiety. | 84.00 | 36.16 | 36.02 | 35.67 |

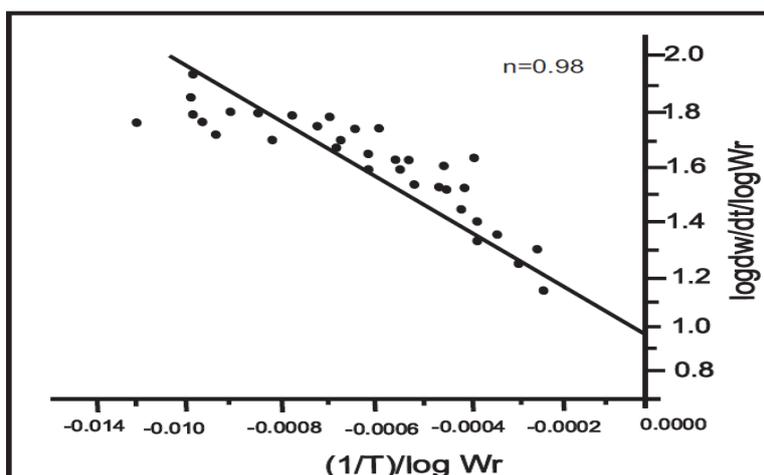


Figure 8: Freeman-Carroll plot of 8-QSTF copolymer resin for activation energy and order of reaction

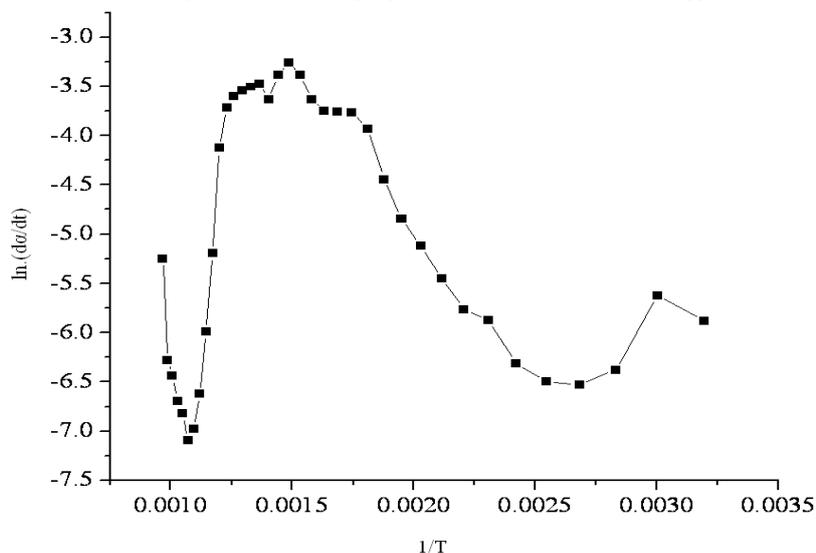


Figure 9: Friedman plot 8-QSTF copolymer resin

CONCLUSIONS

The 8-hydroxyquinoline 5-sulphonic acid–thiosemicarbazide–formaldehyde (8-HQTF) copolymer was synthesized with good yield. The copolymer have been successfully characterized to propose their plausible structure by various spectral techniques.. The thermal stability of the copolymer was found to be good. The calculated activation energies of the copolymer and its metal complexes are in good agreement with each other and their values are in accordance with their order of thermal stability. Based on the comparative Ea values calculated by SW, FC and Fridman methods, the thermal degradation mechanism for both the 8-HQTF copolymer was proposed. The order of reaction indicated that the copolymer follow nearly a first order kinetics.

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REFERENCES

- [1] Gurnule WB, Bisen VR. Res J Pharm Biol Chem Sci 2014; 5(4): 1283.
- [2] Mandavgade SK, Gurnule WB. Res J Pharm Biol Chem Sci 2014; 5(4): 737.
- [3] Rahangdale SS, Zade AB, Gurnule WB. J Appl Polym Sci 2008; 108(2): 747.
- [4] Rahangdale SS, Zade AB, Gurnule WB. J Ultra Sci 2007; 19(2): 213.
- [5] Tarase MV, Zade AB, Gurnule WB. J Ultra Sci 2007;3(1):41.
- [6] Tarase MV, Zade AB, Gurnule WB. J Appl Polym Sci 2008; 108(2): 738.
- [7] Dash DK, Sahu SK, Nayak PL. J Therm Anal Cal, 2006; 86: 517.
- [8] Gurnule WB, Juneja HD, Paliwal LJ. J Prog Cryst Growth Char Mater 2002; 45: 155.
- [9] Oswal SL, Sarkar NS, Bhandari VK, Oza HB, Patel CB. Iran Polym J 2004; 13(4): 297.
- [10] Jungang G, Guodong L, Liting Y, Liucheng Z. Polym Engg Sci 2000; 40(5): 1226.
- [11] Chen H, Liu N, Fang W. Polym Degrad Stab 2006; 91: 1726.
- [12] Vlase T, Vlase G, Birta N, Doca N. J Therm Anal Cal 2007; 88: 631.
- [13] Khawam A, Flanagan DR. Thermichin Acta 2005; 429: 93.
- [14] Joraid AA. Themochim Acta 2007; 456: 1.
- [15] Khobragade JV, Ahamed M, Gurnule WB. J Chem Pharma Res 2014; 6(8): 364.
- [16] Freeman ES, Caroll BJ. Chem Rev 1958; 62: 394.
- [17] Freidman HL. J Polym Sci 1964; C6: 183.
- [18] Sharp JB, Wentworth SA. Anal Chem 1969; 41: 2060.
- [19] Zsago J. J Phys Chem 1968; 7(72): 2406.
- [20] Patle DB, Gurnule WB. Emerg Mat Res 2014; 4(5): 01.
- [21] Patel KD, Patel MM. Proc Ind Acad Sci (Chem Sci) 1990; 102(1): 31.
- [22] Kemp W. Organic Spectroscopy, The Macmillan Press, Hong Kong; 1975.
- [23] Stuart B H. Infrared Spectroscopy: Fundamentals and Applications. John Wiley and Sons: U. K; 2004. pp 74.
- [24] Silverstein RM, Basslel GC. Spectrometric Identification of Organic Compounds. 2nd ed. Wiley: New York; 1987.
- [25] Criado JM, Sanchez-Jimenez PE, Perez-Maqueda LA. J Them Anal Cal 2008; 92: 199.
- [26] Tonbul Y, Yardakoc K. Turk J Chem 2001; 25: 332.
- [27] Zhao H, Wang YZ, Wang DY, Wang B, Wu B, Chen DQ. Polym Degrad Stab 2003; 80: 135.
- [28] Singru RN, Zade AB, Gurnule WB. J App Polym Sci 2008; 109(2): 859.
- [29] Rahangdale SS, Gurnule WB. Desl Wat Treat 2014; 4(5): 1.