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# Thermogravimetric study of 8-hydroxyquinoline 5-sulfonic acid–melamine–formaldehyde terpolymer resins-II

**R. N. Singru · W. B. Gurnule**

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**Abstract** The title terpolymer (8-HQ5-SAMF-II) is synthesized by the condensation of 8-hydroxyquinoline 5-sulfonic acid (8-HQ5-SA) and melamine (M) with formaldehyde (F) in the presence of acid catalyst and using 2:1:3 M proportions of the reacting monomers. The synthesized terpolymer resin is then characterized by different physicochemical techniques viz. number average molecular mass determination, intrinsic viscosity determination, and spectral studies like UV–Visible, IR, $^1$H NMR, and $^{13}$C NMR spectra. The morphology of synthesized terpolymer was studied by scanning electron microscopy (SEM). The thermogravimetry of the terpolymer resin prepared in this study has been carried out by non-isothermal thermogravimetry technique in which sample is subjected to condition of continuous increase in temperature at linear rate. Thermal study of the resin was carried out to determine their mode of decomposition and relative thermal stabilities. Thermal decomposition curves were studied carefully with minute details. The Freeman-Carroll and Sharp-Wentworth methods have been used in the present investigation to calculate thermal activation energy and different kinetic parameter of the terpolymer resins. Thermal activation energy $E_a$ calculated with the two above-mentioned methods are in close agreement. The advantage of Freeman-Carroll method is to calculate both the order of reaction $n$ and energy of activation in one single stage by keeping heating rate constant. By using data of thermogravimetry, various thermodynamic parameters like frequency factor $Z$, entropy change $\Delta S$, free energy change $\Delta F$, and apparent entropy $S^*$ have been determined using Freeman-Carroll method.

**Keywords** Decomposition · Polycondensation · Resins · Synthesis · Thermogravimetric analysis

## Introduction

Terpolymers are useful materials in fabrication, flexibility, chemical inertness as well as being light in weights. Polymers with highly conjugated chains have attracted much attention in the last few years because they are materials of academic interest and also they are investigated as the materials of electronics [1, 2], opto-electronics [3, 4], and photonics [5]. In addition, electrically conducting polymers have a wide variety of applications ranking from electrode materials [6], microelectronic devices [7], catalysts for photo-electrochemical processes [8], organic batteries [9] to electrochemical display devices [10]. The oxidative polycondensation method is simply the reaction of compounds including –OH groups and active functional groups (–$NH_2$, –CHO, –COOH) in their structure with the oxidants as NaOCl, $H_2O_2$, and air in the aqueous alkaline and acidic medium [11]. Another class of this family is that of polyamines (PIs), which are also known as polymeric Schiff bases, polymers that are synthesized by a polycondensation reaction between an amine and hydrazine with an aldehyde or diketone [12]. Because of the properties based on their electronic structure, oligophenols, they have paramagnetism, semi-conductivity, electrochemical cell, and resistance to high energy.

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Therefore, they have been used to prepare composites with resistance to high temperature and graphite materials, epoxy oligomer and block copolymers, adhesives, photoresists, and antistatic materials [13, 14]. Schiff-based derivatives of oligophenols and electrochemical properties of some poly (Schiff) bases and their metal complexes have been studied by Kaya et al. [15, 16]. Poly (*p*-phenylene-2, 6-benzoxazole) (PBO) fiber, which is a new kind of high performance rigid-rod isotropic crystal polymers, has excellent thermal stability, solvent resistance, remarkable tensile strength and modulus [17, 18].

This article describes the compositions of newly synthesized resins 8-hydroxyquinoline 5-sulfonic acid (8-HQ5-SA) and melamine (M) with formaldehyde (F), their characterization by elemental analysis, average molecular mass $M_n$ determination of intrinsic viscosity in DMSO, FTIR Spectra, UV–Visible absorption spectra, NMR spectra, and thermal analysis giving their relative thermal stabilities by applying the Sharp-Wentworth and Freeman-Carroll methods. Energy of activation $E_a$, thermodynamic parameters viz. $Z$, $\Delta S$, $\Delta F$, $S^*$, and order of reaction $n$ were determined by applying Freeman-Carroll method.

## Experimental

### Materials

All the chemicals used in the synthesis of various new terpolymer resins were procured from the market and were analar or Fluka or chemically pure grade. Whenever required they were further purified by standard methods like thin layer chromatography, reprecipitation, and crystallization, which are generally used for the analytical purification purpose.

### *Synthesis of 8-HQ5-SAMF-II terpolymer resins*

The new terpolymer resin 8-HQ5-SAMF-II was synthesized by condensing 8-hydroxyquinoline 5-sulfonic acid (4.86 g, 0.2 mol) and melamine (1.26 g, 0.1 mol) with 37% formaldehyde (11.1 mL, 0.3 mol) in a mol ratio of 2:1:3 in the presence of 2 M 200 mL HCl as a catalyst at 130 ± 2 °C for 6 h, in an oil bath with occasional shaking, to ensure thorough mixing. The separated terpolymer 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 5-sulfonic acid formaldehyde copolymer which might be present along with 8-HQ5-SAMF-II terpolymer. The yellow color resinous product was immediately removed from the flask as soon as reaction period was over and then purified. The reaction and suggested structure of 8-HQ5-SAMF-II is shown in Fig. 1.

The terpolymer was purified by dissolving in 10% aqueous sodium hydroxide solution; it is then filtered and reprecipitated by gradual dropwise 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 terpolymer sample 8-HQ5-SAMF-II thus obtained was filtered, washed several times with hot water, dried in air, powdered, and kept in vacuum desiccator over silica gel. The yield of the terpolymer resin was found to be 75%. The elemental analysis is tabulated in Table 1. Similarly various molar 8-HQ5-SAMF terpolymer resins viz. 1:1:2, 3:1:5, 4:2:7 have been synthesized on our laboratory but due to economy of space only one 8-HQ5-SAMF-II terpolymer sample is taken as representative sample for the study in the present investigation.

### *Characterization of terpolymer resins*

The viscosities were determined using Taun-Fuoss viscometer at six different concentrations ranging from 1.00 to 0.031% of terpolymer in DMSO at 30 °C. The intrinsic viscosity $\eta$ was calculated by relevant plots of the Huggins' equation and Kraemer's equation.

$$\eta_{\mathrm{Sp}/C} = \eta + K_1[\eta]^2 C \quad (1)$$

$$\ln\eta_{\mathrm{rel}/C} = \eta + K_2[\eta]^2 C \quad (2)$$

The number average molecular mass $M_n$ was determined by Conductometric titration in nonaqueous medium such as dimethyl sulfoxide (DMSO) using ethanolic KOH as a titrant. From the graphs of specific conductance on '*X*' axis

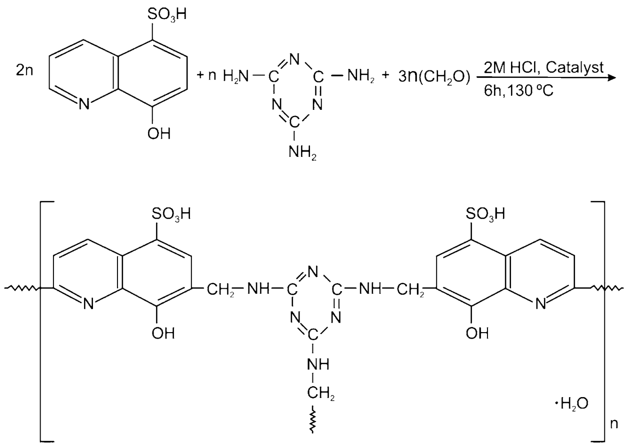

**Fig. 1** Reaction and suggested structure of representative 8-HQ5-SAMF-II terpolymer resin

**Table 1** Elemental analysis, *E*, molecular weight determination, *M*, and intrinsic viscosity, *η*, of 8-HQ5-SAMF-II terpolymer resin

| Terpolymer | Empirical formula of repeat unit | Empirical weight of repeat unit/Kg × $10^{-3}$ | Average degree of polymerization/*DP* | Average molecular weight/$M_n$ | Intrinsic viscosity $\eta$/dl $g^{-1}$ | Elemental analysis/*E* | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | C/% Found (Cal.) | H/% Found (Cal.) | N/% Found (Cal.) | S/% Found (Cal.) |
| 8-HQ5-SAMF-II | $C_{25}H_{24}N_6O_9S_2$ | 644 | 14.5 | 9338 | 0.93 | 46.58 (45.51) | 3.72 (3.15) | 17.39 (16.77) | 9.84 (9.15) |

against milliequivalents of base on '*Y*' axis, first and last breaks were noted from which degree of polymerization $D_p$ and the number average molecular mass $M_n$ have been calculated for each terpolymer resin.

Electron absorption spectrum of terpolymer resin was recorded in DMSO (spectroscopic grade) on spectrometer model AAS-4139 (ECO) double-beam type spectrophotometer having frequency as well as time base scanning in the range of 180–2600 nm at Sophisticated Analytical Instrumentation Facility, Punjab University, Chandigarh. Infrared spectra of 8-HQ5-SAMF-II terpolymer resin were recorded on Perkin-Elmer spectrophotometer model RX-I having resolution in KBr pallets in the wave number region of 4000–250 $cm^{-1}$ at SAIF, Punjab University, Chandigarh. Nuclear Magnetic Resonance (NMR) spectra of newly synthesized terpolymer resin have been scanned on FTNMR-Cryo magnet spectrum 400 MHz (Bruker) spectrometer using DMSO-d6 at Sophisticated Analytical Instrumentation Facility Punjab University, Chandigarh, $^{13}C$ NMR spectra were recorded on Bruker Advanced 400 spectrometer at National Chemical Laboratory (NCL) and scanning electron microscopy (SEM) of terpolymer resin was scanned by JEOL JSM-6380 A, Analytical scanning electron microscope at Visvesvarya National Institute of Technology (VNIT), Nagpur. TG of terpolymer resin has been carried out by using Perkin-Elmer Purix TG, DT-7 thermal analyzer at heating rate of 10 °C per minute in nitrogen atmosphere up to 800 °C.

## Results and discussion

The newly synthesized purified 8-HQ5-SAMF-II terpolymer resin was found to be yellow in color. The terpolymer is soluble in solvents such as DMF, DMSO and THF while insoluble in almost all other organic solvents. The melting point of this terpolymer was determined by using electrically heated melting point apparatus and is found to be 422 K. This resin was analyzed for carbon, hydrogen, nitrogen, and sulfur content. The details of elemental analysis are incorporated in Table 1. The terpolymer which has been used in the present investigation was prepared by the reaction given in Fig. 1.

The results of Conductometric titration method in non-aqueous medium have been presented in Table 1. The specific conductance was plotted on '*X*' axis against milliequivalents of ethanolic KOH on '*Y*' axis required for neutralization of 100 g of each terpolymer. There are several breaks before the complete neutralization of all phenolic hydroxyl groups. The first break in the plot was the smallest break and assumed that this corresponds to a stage in titration when an average one phenolic hydroxyl group of each chain was neutralized.

From the plot, the first and last breaks were noted. The average degree of polymerization $D_p$ and hence the number average molecular mass $M_n$ of all terpolymers have been determined using the formula [19].

$$D_p = \frac{\text{Total milliequivalents of base required for complete neutralization}}{\text{Milliequivalents of base required for smallest interval}}$$

$$M_n = D_p \times \text{Repeat unit mass}$$

It is observed that the molecular mass of terpolymers increases with increase in molar ratio of reacting monomers such as 8-HQ5-SAMF-I < 8-HQ5-SAMF-II < 8-HQ5-SAMF-III < 8-HQ5-SAMF-IV. This observation is in agreement with the trend observed by earlier workers [20] but due to economy of space only one representative sample 8-HQ5-SAMF-II terpolymer resin was taken in the present investigation (Table 1).

In viscosity measurements reduced viscosity versus concentration was plotted for each set of data. The intrinsic viscosity $\eta$ was determined by the corresponding linear plots. Huggins' and Kraemer's constants were determined by expressions 1 and 2. According to the above relations, the plots of $\eta_{Sp}/C$ and ln $\eta_{rel}/C$ against $C$ were linear with slopes of $K_1$ and $K_2$, respectively. By extrapolating linear plot to zero concentration, intercepts on the viscosity function axis give $[\eta]$ value in both plots. The values of intrinsic viscosity obtained from both plots have been found to be closed agreement with each other. The calculated values of the constants $K_1$ and $K_2$ in most cases satisfy the relation $K_1 + K_2 = 0.5$ favorably [21]. It was observed that terpolymer having higher $M_n$ shows higher values of $\eta$ which are in good agreement with earlier coworkers [22].

The UV–Visible spectra (Fig. 2) of the 8-HQ5-SAMF-II terpolymer samples in pure DMSO gave two characteristics bands at 350–370 and 260–260 nm. These observed positions for the absorption bands have different intensities. The more intense band is due to $\pi \rightarrow \pi^*$ transition and the less intense is due to $n \rightarrow \pi^*$ transition. Transition $\pi \rightarrow \pi^*$ indicates the presence of aromatic nuclei, and $n \rightarrow \pi^*$ transition indicates the presence of –NH and –OH groups. The hyperchromic effect is due to the presence of –OH and –NH groups, which act as auxochrome [23]. The spectra of different 8-HQ5-SAMF terpolymer resins reveal that $\varepsilon_{max}$ value gradually increases as the molar concentration of 8-hydroxyquinoline 5-sulfonic acid in terpolymer resin increases. The increasing order of $\varepsilon_{max}$ values may be due to introduction of more and more aromatic ring and auxochrome phenolic –OH and –NH groups in the repeated unit of the terpolymer resins. The observation is in good agreement with proposed structures of the above-mentioned terpolymer resins.

The IR spectral studies revealed that 8-HQ5-SAMF terpolymers gave rise to nearly similar pattern of spectra. Table 2 and Fig. 3 showed the study of representative terpolymer resin 8-HQ5-SAMF-II. Broad absorption band appeared in the region 3506 $cm^{-1}$ may be assigned to the stretching vibrations of phenolic hydroxyl (–OH) groups exhibiting intramolecular hydrogen bonding [24]. A sharp strong peak at 1556 $cm^{-1}$ may be ascribed to aromatic skeletal ring. The bands obtained at 1626 $cm^{-1}$ suggest the presence of methylene (–$CH_2$) bridge [25]. The 1,2,3,5 substitution of aromatic benzene ring recognized by the sharp, medium/weak absorption bands appeared at 971, 1045, 1137, and 1271 $cm^{-1}$, respectively. The presence of sharp and strong band at 3309 $cm^{-1}$ indicates the presence of –NH bridge. This band seems to be merged with very broad band of phenolic hydroxyl group.

The NMR spectra 8-HQ5-SAMF terpolymer resins revealed that all 8-HQ5-SAMF terpolymers gave different

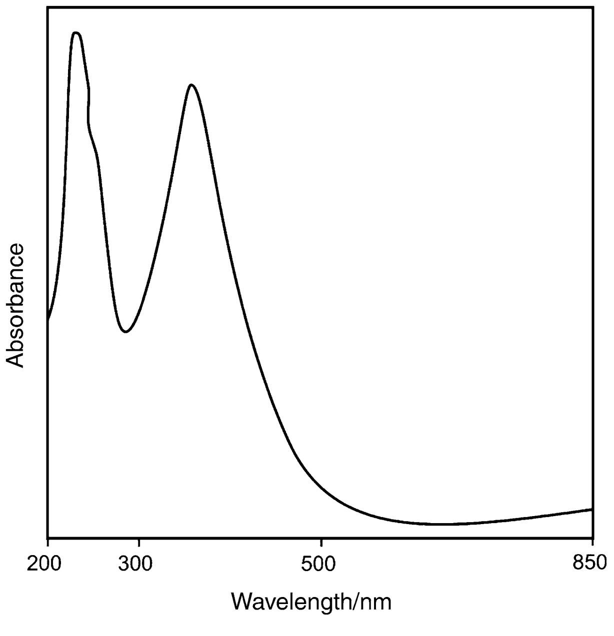

**Fig. 2** UV–Visible spectra of 8-HQ5-SAMF-II terpolymer resin

**Table 2** IR frequencies of 8-HQ5-SAMF-II terpolymer resin

| Observed band frequencies/cm$^{-1}$ | Assignment | Expected band frequencies/cm$^{-1}$ |
|---|---|---|
| $3506_{b,st}$ | –OH phenolic intermolecular hydrogen bonding | 3750–3200 |
| $3309_{sh,st}$ | >N–H stretching (amide/imide) | 3200–3000 |
| $30{,}805_{b,sh}$ | =C–H stretching | 3000–2800 |
| $2566_{b,st}$ | C–H stretching (–$CH_2$ group) | 2800–2400 |
| $1556_{sh,st}$ | Aromatic ring (substituted) | 1600–1500 |
| $1589_{sh}$ | –NH bending of secondary amide | 1570–1490 |
| $1379_{sh,sh}$ | –$CH_2$– symmetrical deformation | 1390–1370 |
| $1412_{sh,sh}$ | –$SO_3H$ Group | 1480–1350 |
| $1228_{sh}$ | –$CH_2$ bending (wagging and twisting) | 1370–1280 |
| $808_{b,st}$ | –$CH_2$– plane bending | 1000–900 |
| $1312_{sh}$ | –$CH_2$ bending (rocking) | 1423–1300 |
| $757_{sh}$ | –NH deformation out of plane of secondary amide | 800–600 |
| $858_{sh}$ | Tetrasubstituted aromatic ring | 830–860 |
| $971_{m}$ | 1,2,3,5 substitution in aromatic ring | 950 |
| $1045_{m}$ | | 1058 |
| $1137_{m}$ | | 1125 |

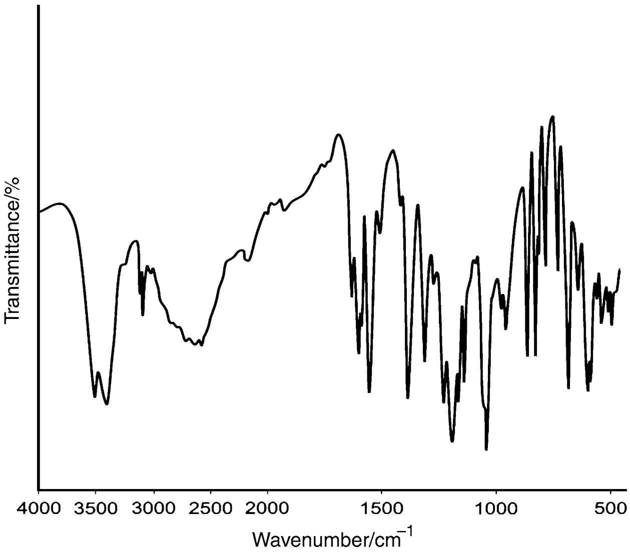

**Fig. 3** Infrared spectra of 8-HQ5-SAMF-II terpolymer resin

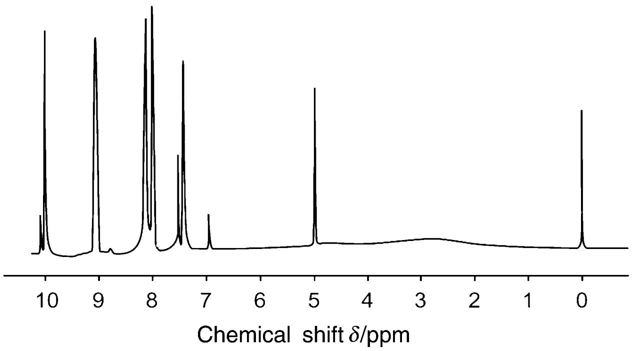

**Fig. 4** $^1$H NMR spectra of 8-HQ5-SAMF-II terpolymer resin

pattern of $^1$H NMR spectra, since each of 8-HQ5-SAMF terpolymer possesses set of proton having different electronics environment. The chemical shift $\delta$ (ppm) observed is assigned on the basis of data available in the literature [26] depicted in Table 3 and showed in Fig. 4 for 8-HQ5-SAMF-II as representative terpolymer. The singlet obtained in the region 4.49–5.01 $\delta$ (ppm) may be due to the methylene proton of Ar–$CH_2$–N moiety. The signals in the region 6.69–7.01 $\delta$ (ppm) are attributed to protons of –NH bridge. The weak multiplate signals (unsymmetrical pattern) in the region of 8.01–8.03 $\delta$ (ppm) may be attributed to aromatic proton (Ar–H). The signals in the range at

**Table 3** $^1$H NMR spectra of 8-HQ 5-SAMF-II terpolymer resin

| Observed chemical shift δ/ppm | Nature of proton assigned | Expected chemical shift δ/ppm |
|---|---|---|
| 4.49–5.01 | Methylene proton of Ar–$CH_2$ moiety | 3.00–6.00 |
| 6.69–7.01 | Proton of –NH bridge | 5.00–8.00 |
| 8.01–8.03 | Aromatic proton (Ar–H) | 6.2–8.5 |
| 9.00–9.30 | Proton of phenolic –OH involved intramolecular hydrogen bonding | 8.00–10.00 |
| 9.9–10.00 | Proton of $SO_3H$ group | 9.00–10.00 |

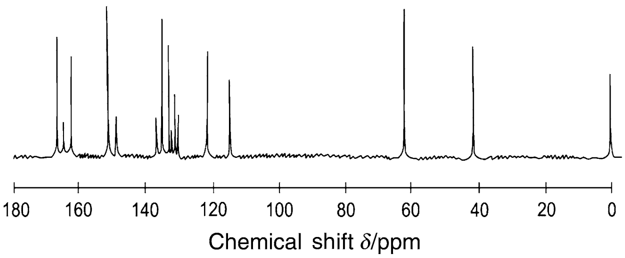

**Fig. 5** $^{13}C$ NMR spectra of 8-HQ5-SAMF-II terpolymer resin

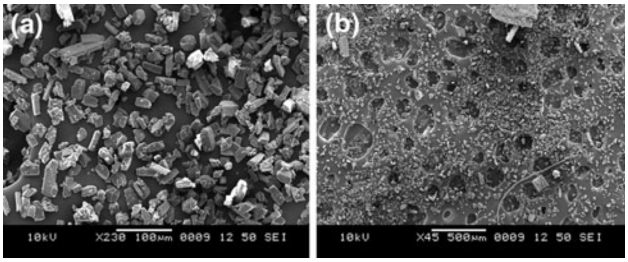

**Fig. 6** SEM of 8-HQ5-SAMF-II terpolymer resin

9.00–9.02 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 [27]. The signals in the range of 10.01–10.02 δ (ppm) are attributed to proton of $-SO_3H$ groups.

$^{13}C$ NMR spectra display signals arising from all the carbon atoms and hence provide direct information about the carbon skeleton. The $^{13}C$ NMR spectrum of 8-HQ5-SAMF-II terpolymer resin is shown in Fig. 5, and the peak positions are assigned according to the literature [28]. The $^{13}C$ NMR spectra show the corresponding peaks at 151.00, 121.7, 136.8, 129.2, 134.6, 133.4, 136.2, 137.4, and 149.2 ppm with respect to $C_1$ to $C_9$ of the aromatic quinoline ring (Fig. 5). Peaks at 165.0, 163.2, and 161.00 ppm are due to $C_1$ to $C_3$ of aromatic melamine ring. The peak appeared at 115.5 ppm confirms the presence of –C–NH group in the resin. The peak appeared at 60.2 ppm may be due to the presence of –C–OH group. The peak appeared at 41.8 ppm may be assigned to the $-CH_2$ bridge in the terpolymer. The $^{13}C$ NMR spectra clearly established the linear structure of the terpolymer synthesized from 8-hydroxyquinoline 5-sulfonic acid–melamine–formaldehyde (Fig. 1).

SEM micrographs of 8-HQ5-SAMF-II terpolymer are shown in Fig. 6. The morphology of pure sample shows spherulites with deep pits. This is the transition of crystalline and amorphous layered morphology, which is the characteristic of polymer. The monomers have crystalline structures at the beginning of the reaction, but during course of condensation polymerization the crystalline structures of monomers lost into amorphous nature in terpolymer resin.

The polymers under study are terpolymer and hence, it is very difficult to assign their exact structures. However, on the basis of the nature and reactive site of the monomers and taking into consideration the linear structure of other substituted phenol formaldehyde polymers and the linear branched nature of urea–formaldehyde polymers the most probable structures proposed for 8-HQ5-SAMF-II terpolymer have been shown in Fig. 1.

## Thermogravimetry

A brief account of thermal behavior of various 8-HQ5-SAMF terpolymers is given. But for reason of economy of space the thermal data and plots for only one representative case have been given in Figs. 7, 8, and 9.

### *TG of 8-HQ5-SAMF-II terpolymer*

Thermogravimetry is found to be a very useful method to assess the thermal stability of a polymeric resin [29]. Thermogravimetric data of the terpolymer is present in Table 4. The thermograms have been recorded in the temperature range of 40–800 °C, which is shown in Fig. 7. The 8-HQ5-SAMF-II terpolymer resin exhibits three-stage decomposition after loss of one water molecule in the temperature range of 40–140 °C (2.12% mass loss found against 2.78% mass loss calculated). The first-stage decomposition starts at 140–300 °C, with a mass loss of 33.32% found and 33.22% calculated, which may be due to the removal of one sulfonic group ($-SO_3H$) and hydroxyl

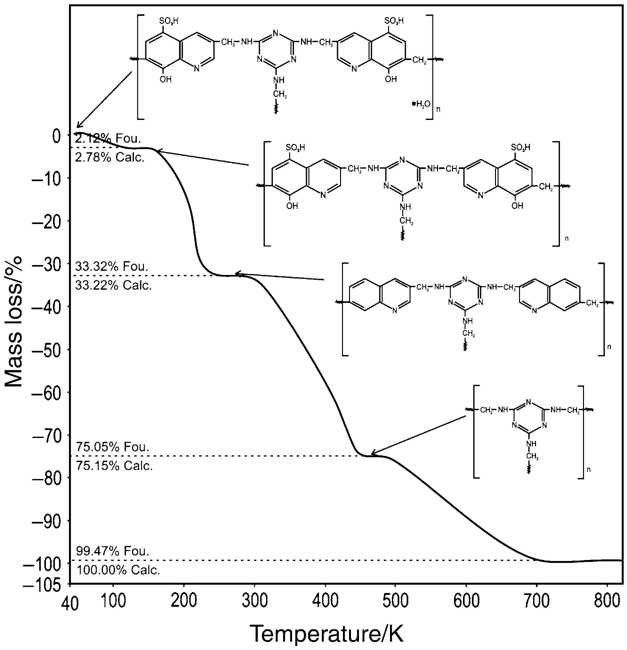

**Fig. 7** Decomposition pattern of 8-HQ5-SAMF-II terpolymer resin

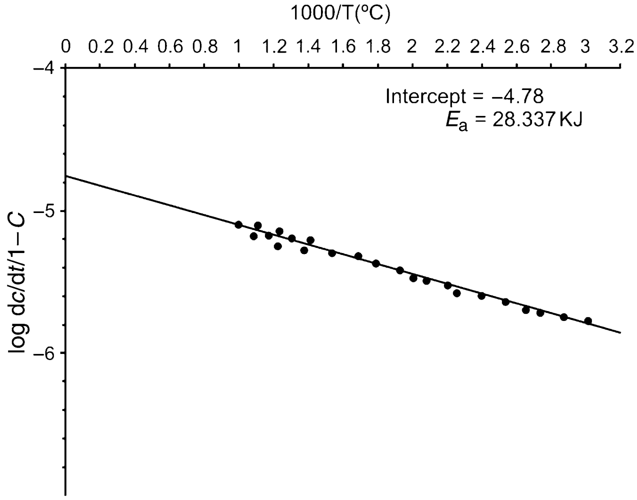

**Fig. 8** Sharp-Wentworth plot of 8-HQ5-SAMF-II terpolymer resin

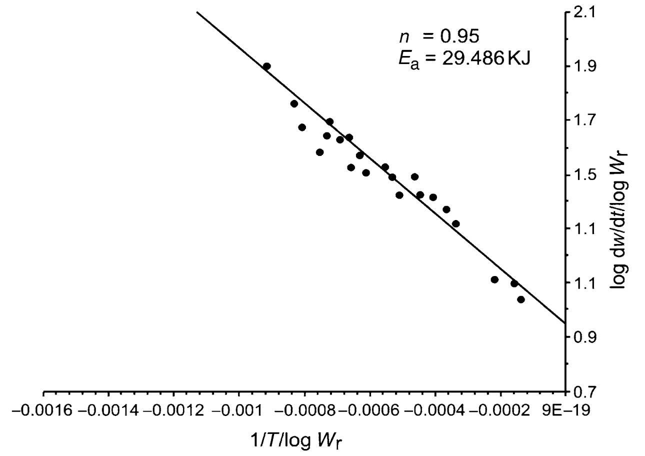

**Fig. 9** Freeman-Carroll plot of 8-HQ5-SAMF-II terpolymer resin

group (–OH) attached to aromatic quinoline ring. In the second stage, the decomposition starts at 300–480 °C, involving 75.05% mass loss found with 75.15% calculated mass loss, which corresponds to the mass loss due to aromatic quinoline ring. The third stage of decomposition starts from 480 °C and the complete decomposition of the terpolymer takes place at 800 °C involving 99.47% of the mass loss found and 100% calculated of the terpolymer sample.

In the present investigation Sharp-Wentworth and Freeman-Carroll methods have been used to determine the thermodynamic parameters of 8-HQ5-SAMF-II terpolymer sample.

*Sharp-Wentworth method*

In this method, the following expression is used.

$$\log \mathrm{d}c/\mathrm{d}T/(1-C) = \log \overset{\prime}{\alpha}/\beta = E_a/2.303RT$$

where, $\beta$ is the linear heating rate. The graph of log d$c$/d$T$/(1 − $C$) versus 1/$T$ on '$X$' axis has been plotted. The graph is a straight line with $E_a$ as slope and $A$ as intercept on '$Y$' axis. The linear relationship confirms that the assumed order $n = 1$ is correct.

*Freeman-Carroll method*

In this method, the following expression is used.

$$\Delta\log(\mathrm{d}w/\mathrm{d}t)/\Delta\log W_r = -E_a/2.303R\cdot\Delta(1/T)/\Delta\log W_r + n$$

where, d$w$/d$t$ = rate of change of mass of terpolymer sample with respect to time $W_r = W_c - W$, where $W_c$ is the mass loss at the completion of the terpolymer reaction or at definite time and $W$ is the total mass loss up to time $t$. $T$ is the temperature, $R$ is the gas constant and $n$ is the order of reaction. Hence the graph of

$$\Delta\log(\mathrm{d}w/\mathrm{d}t)/\Delta\log W_r \text{ versus } \Delta(1/T)/\Delta\log W_r$$

should give the value of the order of reaction $n$ on '$Y$' axis and the slope $m = -E_a/2.303R$. The detailed procedure is clearly laid out for one representative sample as an illustration.

A plot of percentage mass loss versus temperature (thermogram) is shown in Fig. 7 for representative 8-HQ5-SAMF-II terpolymer. From the TG curves, the thermo analytical data and the decomposition temperature were determined to obtain the relative thermal stabilities of

**Table 4** Result of thermogravimetric analysis of 8-HQ5-SAMF terpolymer resins

| Terpolymer resins | Half decomposition temp, $T_h$/K | Activation energy/KJ mol$^{-1}$ | | Entropy change $\Delta S$/J | Free energy change $\Delta F$/KJ | Frequency factor $Z$/s$^{-1}$ | Apparent entropy $S^*$/J | Order of reaction found/$n$ |
|---|---|---|---|---|---|---|---|---|
| | | FC | SW | | | | | |
| 8-HQ5-SAMF-I | 563 | 25.08 | 23.93 | 160.50 | 97.79 | 685 | −19.11 | 0.96 |
| 8-HQ5-SAMF-II | 573 | 29.10 | 28.33 | 160.68 | 101.89 | 703 | −19.09 | 0.95 |
| 8-HQ5-SAMF-III | 593 | 32.74 | 31.59 | 160.68 | 105.53 | 745 | −19.05 | 0.99 |
| 8-HQ5-SAMF-IV | 603 | 36.76 | 35.42 | 160.87 | 109.63 | 780 | −19.02 | 0.98 |

*FC* Freeman-Carroll, *SW* Sharp-Wentworth the various polymers. The methods described by Sharp-Wentworth and Freeman-Carroll were adopted. Based on the initial decomposition temperature, the thermal stabilities of the terpolymers have also been used here to define their relative thermal stabilities, neglecting the degree of decomposition (Tables 4, 5).

Using thermal decomposition data and applying the Sharp-Wentworth method, activation energy is calculated which is in agreement with the activation energy calculated by Freeman-Carroll method [30]. The activation energy $E_a$ can be calculated by using equation Slop $= -E_a/2.303R$, where, $R$ is the gas constant and slop can be calculated from the corresponding plots of Sharp-Wentworth method and Freeman-Carroll method.

A representative thermal activation energy plot of Sharp-Wentworth method (Fig. 8) and Freeman-Carroll method (Fig. 9) for the polymer has been shown. Thermodynamic parameters such as entropy change $\Delta S$, free energy change $\Delta F$, frequency factor $Z$ and Apparent entropy $S^*$ calculated on the basis of thermal activation energy are given in Table 4, using equations are given below.

(i) Entropy change
Intercept $= \log KR/H\Phi E + \Delta S/2.303R$
where,
$K = 1.3806 \times 10^{-16}$/J deg$^{-1}$ mol$^{-1}$
$R = 8.314$/J deg$^{-1}$ mol$^{-1}$
$h = 6.625 \times 10^{-27}$/J s
$\Phi = 0.166$
$\Delta S =$ change in entropy
$E =$ activation energy from graph

(ii) Frequency factor
$B_{2/3} = \log\ ZE_a/R\Phi$ (3)
$B_{2/3} = \log\ 3 + \log[1-3]\sqrt{\left(1-\acute{\alpha}\right) - \log\ P(x)}$ (4)
where,
$Z =$ Frequency factor
$B =$ Calculated from Eq. 4
$\log p(x) =$ Calculated from Doyle table corresponding to activation energy

(iii) Free energy change
$\Delta F = \Delta H - T\Delta S$
where,
$\Delta H =$ Enthalpy change $=$ Activation energy
$T =$ Temperature/K
$\Delta S =$ Entropy change {from (i) used}

(iv) Apparent entropy change
$S^* = 2.303 \log Zh/RT^*$ (5)
where,
$Z =$ from relation (3)
$T^* =$ Temperature at which half of the compound is decomposed from it total loss

The 8-HQ5-SAMF terpolymers prepared from higher molar ratio of 8-hydroxyquinoline 5-sulfonic acid exhibited a lower rate of decomposition. The thermal stability of the terpolymers predicted on the basis of the initial as well as half decomposition temperatures is in harmony with that predicted from the activation energy values. This fact is further supported by the increasing order of melting points from lower to higher molar ratio of 8-HQ5-SAMF terpolymers. This order of stability may be due to the possibility of an almost linear structure of the terpolymer having higher molar ratio of 8-hydroxyquinoline 5-sulfonic acid which may give rise to a stable structure to the terpolymer chain [30, 31]. In this study, in the case of 8-HQ5-SAMF-II terpolymer the removal of water from the polymer is completed around 140 °C, which may be due to solvent or

**Table 5** Thermogravimetric data and decomposition temperature range of 8-HQ5-SAMF-II terpolymer resin

| Terpolymer resins | Loss of crystalline water molecular | | Decomposition step, temperature range/°C, mass loss/% and species degraded | | | | | | Mass of residue left over/% |
|---|---|---|---|---|---|---|---|---|---|
| | | | First step (loss of sulfonic and hydroxyl group) | | Second step (loss of aromatic quinoline nucleus) | | Third step (loss of side chain with melamine) | | |
| | Temp. range/°C | Mass loss/% | Temp. range/°C | Mass loss/% | Temp. range/°C | Mass loss/% | Temp. range/°C | Mass loss/% | |
| 8-HQ5-SAMF-II | 40–140 | 2.12 (F)<br>2.78 (C) | 140–280 | 33.32 (F)<br>33.22 (C) | 280–480 | 75.05 (F)<br>75.15 (C) | 480–800 | 99.47 (F)<br>100.0 (C) | 0.53 (F)<br>0.00 (C) |

moisture probably crystal water entrapped in the terpolymer samples [32, 33].

The analysis of the thermograms indicates that the decomposition of the terpolymers is a three-stage process after a loss of water molecule at 140 °C. In the first step, side chain attached to aromatic nucleus and hydroxyl groups decompose. In the second step, aromatic nucleus decompose, while in the third step, side chain attached to melamine polymer and melamine itself degraded, and finally, there is no residue remained after completion of degradation. Decomposition is completed at about 800 °C in all terpolymer resins.

By using the data of the Freeman-Carroll method, various thermodynamics parameters have been calculated (Table 4). The values of thermodynamic parameters for various molar ratio terpolymers 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-HQ5-SAMF-II terpolymer can be classed as a 'slow' reaction which can also be supported by negative value of entropy change. There is no other obvious reason [34, 35].

Fairly good straight-line plots are obtained using the two methods. This is expected since the decomposition of terpolymer is not to obey first-order kinetics perfectly.

## Conclusions

(1) A terpolymer, 8-HQ5-SAMF-II, based on the condensation reaction of 8-hydroxyquinoline 5-sulfonic acid–melamine–formaldehyde in the presence of acid catalyst, was prepared.

(2) In TG the energy of activation evaluated from the Sharp-Wentworth and Freeman-Carroll methods are found to be nearly equal and the thermodynamic 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.

(3) Low values of collision frequency factor (*Z*) may be concluded that the decomposition reaction of 8-hydroxyquinoline 5-sulfonic acid–melamine–formaldehyde terpolymer can be classified as 'slow reaction'.

(4) The decomposition reaction was started at higher temperature, indicating a terpolymer 8-HQ5-SAMF-II is thermally stable at higher temperature.

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