Hydroxyquinoline copolymers synthesis, characterization and thermal degradation studies

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Abstract. In the flow research article, we report the amalgamation of a new natural copolymer of 8-hydroxyquinoline-5- sulphonic acid, guanidine, and formaldehyde in the molar proportion 1:1:2 inside seeing 2 M hydrochloric corrosive as an impetus by polycondensation strategy. The copolymer 8-HQ-5-SAGF was portrayed by elemental examination, Ultra-Visible, Infrared spectra, ¹H and ¹³C Nuclear magnetic resonance spectroscopy. Furthermore, we have examined the non isothermal thermogravimetric examination for assurance of relative warm stability and their mode deterioration, Energy of initiation, frequency factor and request of response was measured by Freeman-Carroll (FC) and Sharp-Wentworth (SW) techniques. Energy of enactment controlled by Sharp-Wentworth and Freeman-Carroll strategies are in acceptable concurrence with one another. The surface component of copolymer is inspected by filtering electron microscopy.

Keywords. copolymer resin, polycondensation, morphology, thermal analysis, spectral studies, sharp-wentworth

1. Introduction

The thermal analysis research comprises a collection of techniques where the physical property of the substances is measured as a function of temperature when exposed to a controlled substance temperature programme. Thermally stable copolymers have been boon for polymer chemist because of their high efficiency and superior utility. They find applications as lubricants, adhesives, coating materials, catalysts, semiconductors, ion exchangers, fire resistant materials [1-4]. Rahangdale and coworkers prepared copolymers resulting from 4-pyridylamine, 2, 4- dihydroxypropophenone with formaldehyde and warm corruption was completed [5]. To examine thermal properties and degradation parameters of the terpolymer thermogravimetric analysis technique was used by Liu et al. [6]. Kinetics and warm deterioration of 2-hydroxy, 4-methoxybenzophenone, formaldehyde and 1,5- diaminonaphthalene within the sight of acid with different feed ratio of reactants has been readied. It was found from the outcomes that the deterioration was gradual reaction and order are considered to be almost identical [7]. FC and SW techniques were utilized to study the thermodynamic and kinetic parameters of terpolymer [8]. The copolymer tar was blended by the buildup polymerization including monomers like phenylhydrazine (0.1 mol), 2,4-dihydroxy benzoic corrosive, and formaldehyde in 3:1:5 ratios
within the sight acid catalyst and its warm stability were accounted [9]. Azarudeen et al. was introduced environmentally benign method for the preparation of a terpolymer involving monomers containing thiourea, formaldehyde with anthranilic acid and thermogravimetric analysis results demonstrate that the terpolymer was thermally steady [10].

The warm detonation analysis of terpolymer have became a topic of current attention, Become an significant commodity which primarily defines processability and thermal stability. Karunakaran et al. prepared terpolymer resin starting from resorcinol, thiourea with formaldehyde and measured metal particle binding, thermal properties [11]. A copolymer obtained from 2,4-dihydroxybenzoic acid, melamine with formaldehyde and non isothermal disintegration, and kinetic investigation have been accounted for [12]. Terpolymeric gum blends from salicylic acid, anthranilic acid, formaldehyde, urea, and reported for excellent warmath stability and biological screening [13-14]. Patel M and colleagues blended terpolymer resin and its polychelates. From the examination, it was discovered that the inclusion of the metal particle in the polymeric backbone lowers the warm solidity [15]. Gurnule and Patle synthesized a novel chelating copolymer with a different feed ratio of monomers [16]. Anenormous number of research works was done by different analysts on the amalgamation, spectral, and stability of different terpolymers [17-18]. Thermogravimetric analysis and differential scanning calorimetry technique is utilized to investigate the thermal stability of terpolymer [19].

SW and FC strategies are utilized to evaluate thermal decomposition parameters of terpolymer resin derived from semicarbazide, formaldehyde, and p-hydroxybenzoic acid. The findings show that terpolymers were thermally stable and the degradation reaction followed first order kinetics [20]. Different scientists orchestrate copolymers [21], graft copolymers of natural polysaccharide and results show that the warm dependable qualities are fluctuates regarding vinyl monomers [22-26].

In present communication, our main objective of this analysis is to synthesize a new copolymer resin 8-hydroxyquinoline-5-sulphonic acid-guanidine-formaldehyde (8-HQ-5-SAGF) by polycondensation method and to study thermal analysis behavior. The terpolymer resin was characterized by elemental analysis and spectral studies. The surface feature was analyzed through scanning electron microscopy. From Thermogravimetric analysis thermal behavior of copolymer resin is evaluated. Further the kinetic and thermodynamic parameters like energy of acivation (Ea), apparent entropy ($S^*$), entropy change ($\Delta S$), order of reaction (n) free energy change ($\Delta F$), and frequency factor (Z) were calculated.

2. Experimental

2.1. Materials
8-Hydroxyquinoline-5-sulphonic acid, guanidine (Sigma Aldrich), formaldehyde (SD Fine) was procured from central scientific company Nagpur. The solvents like hydrochloric acid, N,N-dimethylformamide, dimethyl sulfoxide was procured from Himedia. Entire chemicals are analytical grade and are utilized as received.

2.2. Synthesis of Copolymer resin
8-Hydroxyquinoline-5-sulphonic acid-guanidine-formaldehyde (8-HQ-5-SAGF) copolymer resin was synthesized by polycondensation of 8-hydroxyquinoline-5-sulphonic acid, formaldehyde, guanidine within 2M HCl medium in the molar ratio 1:1:2 in an oil bath at a temperature of 122 °C with intermittent shaking, to ensure detailed activity for about 5 hours. The resinous substance was obtained in yellow shading. The product procured wash with diethyl ether and hot distilled water to expel contaminations. Further, the copolymer gum was cleansed by dissolving in 8% watery NaOH and recovered by slow drop savvy expansion of 1:1 (v/v) conc. HCl/refined water. At last, the copolymer pitch was ground to
go through 300-work size sifter and kept in a vacuum over a silica gel. The proposed structure and response has appeared in Figure 1.

![Figure 1. Preparation of copolymer 8-HQ-5-SAGF](image)

2.3. Characterizations
The copolymer resin is characterized by a variety of experimental approaches. Elemental analysis was done by utilizing the Perkin Elmer 789N QP-2010 instrument. The range of FTIR in KBr pellets inside the scope of 4000-5000 cm$^{-1}$ has been inspected. The $^1$H NMR spectra were measured using DMSO-d$_6$ solvent in a 400 MHz Bruker spectrometer. The surface morphology was derived using a scanning electron microscope (JEOL6390LV). The thermal analysis of copolymer resin was carried using Perkin Elmer TGA/DTA thermal analyzer.

3. Elemental examination
Microanalysis of the contents of 8-HQ-5-SAGF copolymer resin for C, H, N, and S was performed. The findings obtained are considered to be well in line with the measured values. The empirical weights of a single repeating unit are determined from the empirical formula are presented in Table 1.

| Copolymer Resins | % of C observed (Cal.) | % of H observed (Cal.) | % of N observed (Cal.) | % of S observed (Cal.) | Empirical formula of repeated unit | Empirical formula weight |
|------------------|------------------------|------------------------|------------------------|------------------------|------------------------------------|-------------------------|
| 8-HQ-5-SAGF      | 45.82 (39.8)           | 5.39 (4.31)            | 16.41 (18.6)           | 9.17 (10.6)            | C$_{13}$H$_{18}$N$_2$O$_4$S         | 342.37                  |

3.1. UV-Visible Spectra
The Ultraviolet-Visible spectrum of 8-HQ-5-SAGF copolymer resins were recorded into unadulterated dimethysulfoxide in the assortment 190-800 nm and shown in Figure 2. The range demonstrated two
retention groups at 244 nm and 311 nm. The existence of the preceding band might be expressed as π-π* transition, while the latter weak band could be expected n-π* transition. The π-π* transition is permissible transition of benzene ring whereas the n-π* transition accounted for phenolic-OH group (auxochrome) [27].

![Ultraviolet-Visible spectrum of copolymer 8-HQ-5-SAGF](image)

**Figure 2. Ultraviolet-Visible spectrum of copolymer 8-HQ-5-SAGF**

### 3.2. IR Spectra
The IR spectra of copolymer resin 8-HQ-5-SAGF provide valuable data about the functional groups and linkages present in the copolymer gum Figure 3. In the area 3537-3590 cm⁻¹ a wide band of absorption ascribed to extending vibration of Ar-OH gatherings [28]. A sharp peak at 3102-3081 cm⁻¹ stretching vibrations of the –NH linkage (imide) and 819 cm⁻¹ shows twisting vibrations [29]. Band emerged out at 2786 cm⁻¹ assign to aromatic –CH stretching. The presence of bands within the range 1389-1420 cm⁻¹ because of the –CH₂ bridges in the polymeric chain. A band displayed at 1626 cm⁻¹ ascribed to the –C=N (imines). The tetra substitution 1,5,6,8 of quinoline moiety is affirmed with the bands at 970 cm⁻¹, 1043 cm⁻¹, 1136, and 1235 cm⁻¹ respectively.
3.3. $^1H$ NMR Spectroscopy

The proton nuclear magnetic resonance spectra are presented in Figure 4. Methylene proton that trigger signal at $2.5(\delta)$ ppm possibly assigned to $\text{Ar-CH}_2\text{-N}$ [30]. The locale within the region $7.3-8.3 (\delta)$ ppm can be allocated to aromatic ring proton. A phenolic hydroxyl group shows a sharp signal at $9.2(\delta)$ ppm. A powerless locale at $6.97(\delta)$ ppm may be due to $-\text{NH}$ bridging protons [31]. A singlet at $9.8(\delta)$ ppm suggests the presence of the $-\text{SO}_3\text{H}$ group.

3.4. Surface analysis

The surface features of copolymer resin have been at present used to decide the morphology and the grain size by SEM and are presented in Figure 5. The SEM pictures it was noted there is a uniform network in the copolymer. The copolymer exhibits a close packed arrangement having more active sites and deep pits. The copolymer display a rod like morphology [32].
3.5. Thermal Analysis of 8-HQ-5-SAGF copolymer resin

Thermal study of the 8-HQ-5-SAGF was analyzed using thermogravimetry. The thermogravimetric curve of copolymer resin is displayed in Figure 6 and their proportion of mass reduction at diverse temperatures tabulated in table 2. In the temperature range of 40°C-700 °C, the copolymer resin thermogram of produced three phases. Warm decomposition reaction, by extracting the initial H₂O fragment at temperatures between 40 ºC to 120 ºC entrapped in the crystalline type of the macromolecule (5.64% observed and 5.69% measured). Throughout the primary step of degradation with stable reduction in mass removal beginning 120 ºC to 380 ºC, leading to 56.27% mass removal was found and 56.35% mass reduction measured as a consequence of removal of -OH, -SO₂H and –CH₂-NH-C=NH-CH₂- moiety. The second stage begins from the temperature range 290 ºC to 460 ºC with the weight removal 71.85% observed and 70.33% calculated. Step 3rd disintegration initiates from the temperature range 520ºC to 700 ºC is most likely because of removal of the whole molecule.

Sharp-Wentworth method

Subsequent expression is used given by Sharp and Wentworth method.

\[
\log[(dc/dT)/(1-c)]=\log(A/\beta)-[Ea/2.303R] \frac{1}{T}
\]

Where,

dc/dT=rate of change of fraction of weight with change in temperature
\[ \beta = \text{linear heating rate } \frac{dT}{dt}. \]

The graph plotted between \( \frac{\log dc}{dt}/(1-c) vs 1/T \) gives straight line from which activation energy (Ea) is determined from its slope Figure 7. Where \( \beta \) is the conversion at time t, \( R \) is the gas constant, \( T \) is the absolute temperature.

**Freemann-Carroll method**

The Freeman and Carroll equation is

\[
\Delta \log \left( \frac{dw}{dt} \right)/\Delta \log Wr = (-E/2.303R) \Delta (1/T)/\Delta \log Wr + n \tag{2}
\]

Where, \( dw/dt = \text{rate of change of mass with time.} \)

\( Wr = W_c - W \)

\( W_c = \text{weight reduction at end of reaction.} \)

\( W = \text{fraction of weight loss at time } t. \)

\( Ea = \text{energy of activation} \)

\( n = \text{order of reaction.} \)

Based on Thermogravimetric details of the copolymer resin and by executing Freeman-Carroll Figure 8-9 and Sharp-Wentworth strategies for activation energy \( (E_a) \) is determined in conjugation with each other.

| Copolymer     | Activation Energy (Ea) (KJ mol\(^{-1}\)) | Entropy Change \( (\Delta S) \) (J) | Free Energy Change \( (\Delta F) \) (KJ) | Frequency factor \( (Z) \) (Sec\(^{-1}\)) | Apparent Entropy Change \( (S^*) \) (KJ) | Order Of Reaction (n) |
|---------------|------------------------------------------|-----------------------------------|----------------------------------------|-------------------------------------------|----------------------------------------|----------------------|
| 8-HQ-5-SAGF   | 25.3                                     | -210.71                           | 107.57                                 | 546                                       | -60.24                                 | 0.9                  |

Thermodynamic boundaries, for example, free vitality change \( (\Delta F) \), entropy change \( (\Delta S) \), Clear entropy change \( (S^*) \), and recurrence factor \( (Z) \) have been determined and are consolidated in Table 2 Utilizing articulation given in condition (3), (4), (5), (6), and (7). Vitality of initiation determined by using FC [33] and SW [34] techniques are seen as acceptable in harmony with one another. From a strangely low recurrence factor \( (Z) \) it tends to be presumed that the disintegration response of 8-HQ-5-SAGF copolymer tar can be as a moderate response. Negative estimation of entropy \( (\Delta S) \) proposes that the terpolymer is a more arranged organization as compared to the reactant.

![Figure 7. Activation energy plot of 8-HQ-5-SAGF](attachment:image.png)
4. Conclusions

The copolymer tar 8-HQ-5-SAGF was set up by including guanidine, 8-hydroxyquinoline-5-sulphonic acid, and methanal inside corrosive medium. The composition of copolymer resin was affirmed by microanalysis examination, IR, NMR, and Ultraviolet-Visible spectral studies. From the findings, it may be concluded that the energy of activation dictated by Freeman-Carroll and Sharp-Wentworth methods are in harmony with one another. The estimation of low recurrence factor implies that the deterioration of copolymer tar is classed as a moderate response. The negative worth entropy move proposes that copolymer gum has a more sorted out composition as compared to monomers. The Thermogravimetric analysis considers that the copolymer is thermally steady even at high temperatures.
5. References

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