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Thermal Degradation Studies of High-Performance Copolymer Resin Derived From 8-Hydroxyquinoline, Acrylamide and Furfural

Megha Rangari[a], S S Rahangdale[b], Seema Shrivastava[c] , Yashpal Rathod[d], Prajkta U Waghe[e] & Wasudeo B Gurnule[a*]

[*a]Department of Chemistry, Kamla Nehru Mahavidyalaya, Nagpur 440 024, India
[b]Department of Chemistry, Jagat Arts, Commerce and Indiraben Hariharbhai Patel Science College, Gondia 441 614, India
[c]Department of Chemistry, Priyadarshini College of Engineering, Hingna Road, Nagpur 440 019, India
[d]Department of Chemistry, J M Patel College, Bhandara 441 904, India
[e]Department of Chemistry, Yashwantrao Chavan College of Engineering, Nagpur 441 110, India

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Using the polycondensation process with acid medium as the catalyst, the monomers 8-hydroxyquinoline, acrylamide, and furfural were combined to form the copolymer 8-HQAF in a molar ratio of 1:1:2. Elemental analysis method were used to evaluate the molecular weight and composition of the organic copolymer. The structure was clarified through analysis of the FTIR, proton nuclear magnetic resonance (^{1}H NMR), and UV-visible spectra. SEM analysis was done on the copolymer's crystalline behaviour and surface characteristics (SEM). For the purpose of determining their method of disintegration and relative thermal stability, non-isothermal thermogravimetric analysis The Sharp-Wentworth (SW) and Freeman-Carroll (FC) approaches have been used to compute activation energy, frequency factor, and order of response. Both the Sharp-Wentworth and Freeman-Carroll approaches for calculating activation energy agree with one another.

Keywords: Activation energy, Copolymer, Morphology, Polycondensation, ResinThermal degradation

1 Introduction

The synthesis of polymers using renewable resources has caught the interest of numerous researchers recently.[1] Numerous laboratory investigations on the synthesis, characterisation, structure, and thermal analysis of various polymers have been published.[2] Many kinetic parameters for the copolymer have been evaluated using the Freeman-Carroll and Sharp-Wentworth methods. The Arrhenius equation's assumptions that the thermal and diffusion barriers are minimal are particularly the foundation of the TGA study methodologies.[3]

Copolymers are a unique class of polymers noted for their many applications. These polymers can have crystalline, amorphous, or resinous structures in their natural state.[4] Since copolymers hold a unique place in the field of polymer science, their utilisation for the current generation has significantly increased in recent years.[5] Gupta and Co-workers have investigated the kinetics of the heat degradation of the polymers 2-amino-6-nitrobenzothiazole, melamine, and formaldehyde.[6] The heat degradation of 8-hydroxyquinoline, formaldehyde, and acrylamide terpolymer was studied by Michael *et al.*[7] Thermal degradation of polymer made from formaldehyde, dithioxamide, and 2,4-dihydrogen acetophenone was examined by Rahangdale and colleagues.[8,9] It is significant to remember that the various approaches have all been developed while keeping the kinetic model in mind. As a result, it has been determined that the kinetic analysis of is a function of the reacted fraction.[10,13] No copolymer has been synthesized utilising 8-hydroxyaquinoline, acrylamide, and furfural, according to analyses of the literature. Consequently, in this study, we describe the structural characterisation, thermal degradation tests, and copolymer production.

2 Materials and Methods

2.1 Materials

Acrylamide, furfural, and 8-hydroxyquinoline acid were purchased from Central Scientific Company in Nagpur. Solvents like DMSO and HCl were purchased from Himedia. All compounds are pure grade and analytical grade.

2.2 Synthesis of 8-HQAF Copolymer Resin

8-Hydroxyquinoline-acrylamide- furfural (8-HQAF) copolymer was synthesised by polycondnsation of

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*Corresponding author (E-mail: wbgurnule@gmail.com)

8- Hydroxyquinoline, acrylamide and furfural with 2M HCl in the ratio 1:1:2 an oil bath at a temperature of 122 °C with occasional shaking for about 5hrs as shown in Fig. 1. The copolymer obtained was black in color, washed with hot water until it was free from chloride ions. The process was repeated several times with hot water, it was filtered and dried in a vacuum at over silica gel. The dried, powdered and purified copolymer was finely crushed. The yield of the copolymer was found to about 88%.

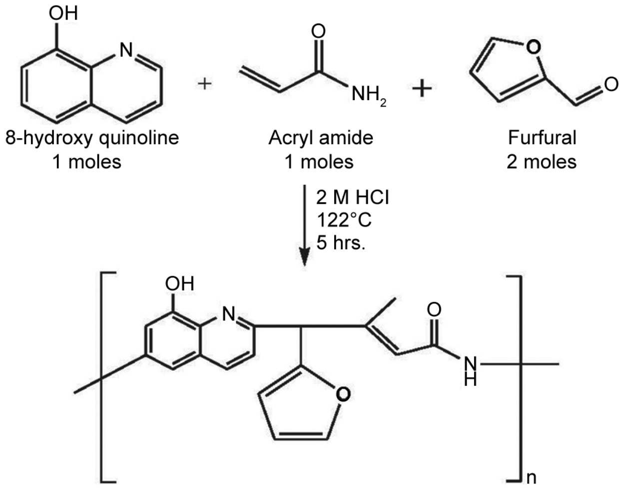

Fig. 1 — Synthesis of copolymer 8-HQAF.

2.3 Analytical and physico-chemical studies

The FTIR spectra of the copolymer resin was recorded using a Bruker (Model Tensor 27) spectrophotometer. Using a Bruker 400 MHz instrument, the proton NMR spectrum of the 8-HQAF terpolymer resin was captured. Using an elemental instrument, the elements C, H, and N contained in the 8-HQAF were identified (Model Vario EL III).

3 Results and Discussion

It was discovered that the 8-HQAF copolymer resin was a dark grey colour. In contrast to practically all other organic solvents, the copolymer is soluble in DMF, DMSO, and THF.

3.1 Elemental analysis

Table 1 displays the percentage of element present in copolymer was concluded by the calculated and experimental value found for carbon 74%, hydrogen 4.78%, nitrogen 4.33% and oxygen is 20.06% which are in good arrangement with each other. The value of elemental analysis confirm the proposed structure of copolymer $C_{36}H_{18}O_7N_2$.[14,15,16]

3.2 UV-visible spectra

8-HQAF copolymer that have been synthesised show two distinguishing bands at 280 nm and 314 nm as shown in Fig. 2. Different intensities can be seen in

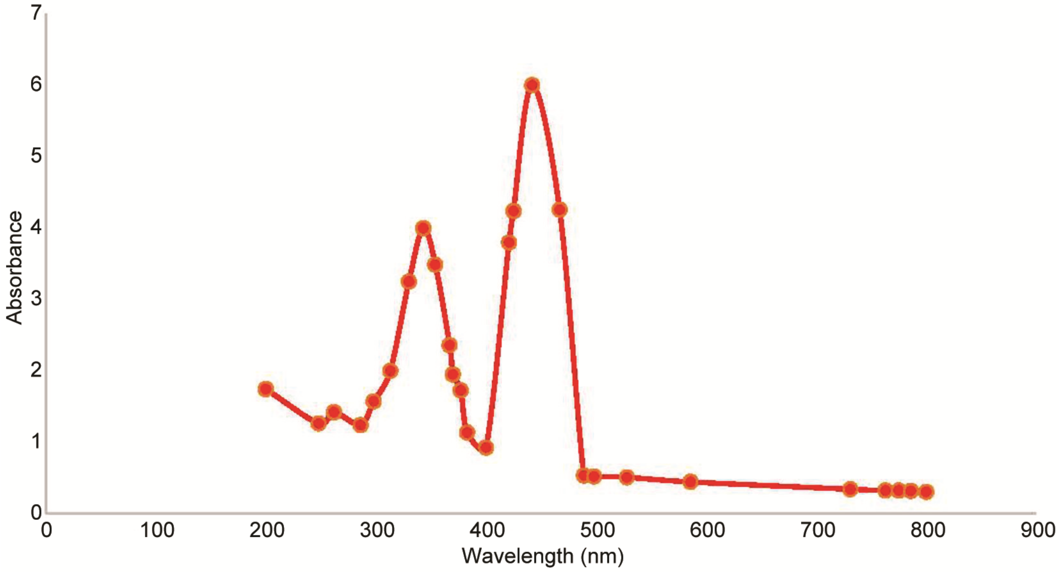

Fig. 2 — UV spectra of copolymer 8-HQAF.

Table 1 — Elemental analysis and empirical formula of copolymer resin

Copolymer resin	% of C Observed (Cal.)	% of H Observed (Cal.)	% of O Observed (Cal.)	% of N Observed (Cal.)	Emperical formula	Emperical formula weight
8- HQAF	73.90% (74%)	5.76 (4.78%)	14.98% (16.06%)	8.65% (8.53%)	$C_{19}H_{18}N_2O_3$	339

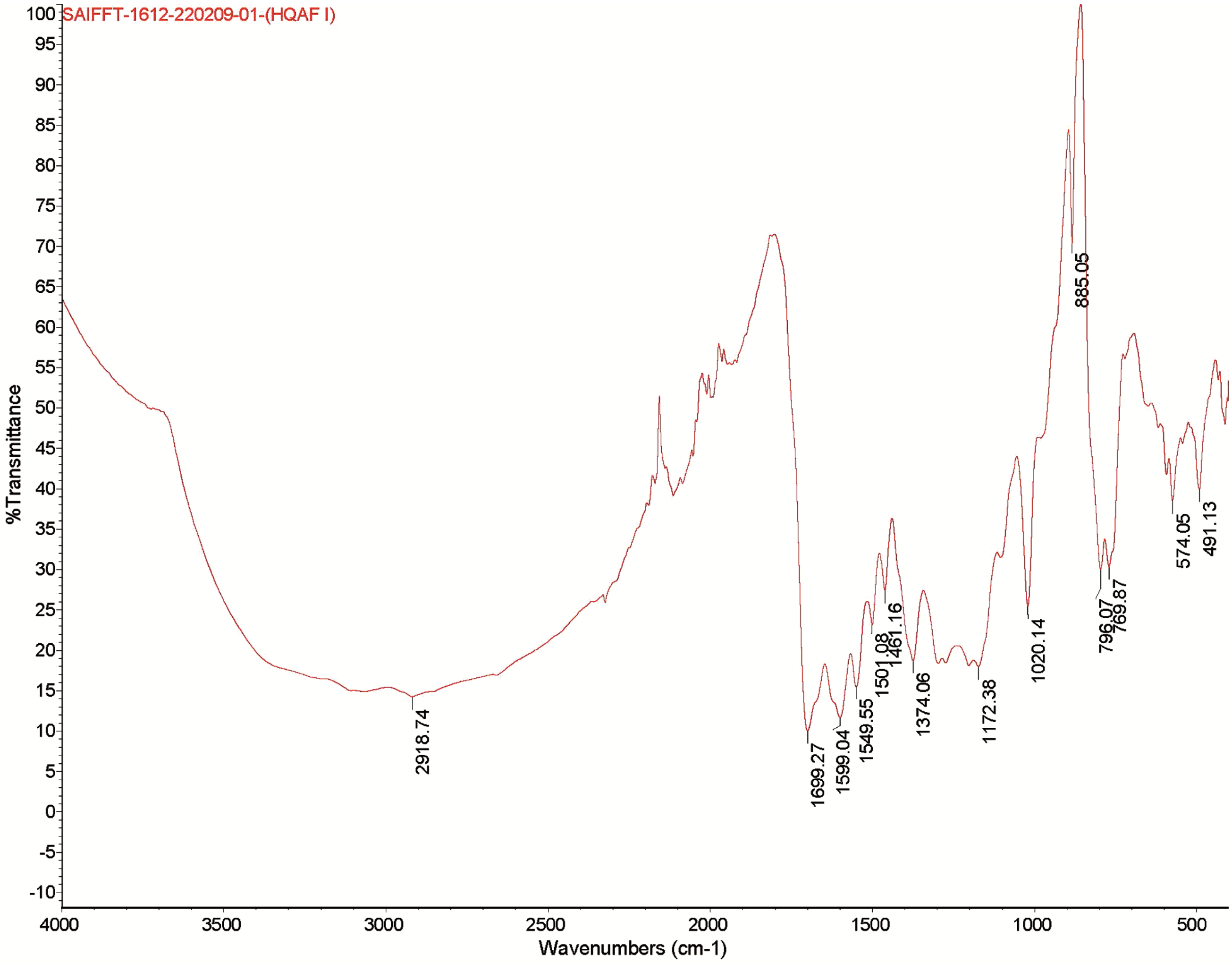

Fig. 3 — FTIR spectra of copolymer 8-HQAF.

the absorption bands' observed positions. Due to a transition that is permitted at (π-π*), the band between 280 and 320 nm is less strong.[17] The quinoline ring, which easily achieves coplanarity and shoulder merging (loss of fine structure), as well as chromophore groups like >C=C, >C=N, groups which are in conjugation with an aromatic nucleus (quinoline ring), are responsible for the permitted n-π* transition. And the reason why the band at 314 nm is stronger can be because of the (n-π*) transition, which reveals the presence of the -NH auxochrome group. As a result, the π-π* transition and n-π* the transition both confirm the existence of aromatic nuclei and -NH groups. Bathochromic changes from the fundamental values, 240 and 310 nm, can be attributed to -NH groups (auxochrome) and conjugation (caused by the chromophore).[18] Auxochromes with -NH groups cause the hyperchromic shift (Ɛ max higher levels).

3.3 FT-IR spectral analysis

The linkages and functional groups contained in the copolymer resin may be learned from the IR spectra of the 8-HQAF copolymer resin displayed in Fig. 3. The phenolic hydroxy groups that are intermolecularly hydrogen linked (O-H stretching) may be the cause of the wide band at 3423.12 cm^{-1}.[19] Possible cause of the sharp band at 1218.22 cm^{-1} is C-O stretching. The band between 3258 cm^{-1} can be caused by N-H stretching. The band at 2755 cm^{-1} might be caused by aromatic C-H stretching. A band at 2927 indicates-CH_2 stretching involved in the copolymer.[20]

3. 4 ^{1}H NMR Spectroscopy

The aromatic ring protons (Ar-H) may be the cause of the signals in the area 7.5-8 (δ) ppm (observed) and 7-8 (δ) ppm expected. The phenolic (-OH) proton is represented by a wide signal in the range of 9.10 (δ) ppm (observed) and 9.7 (δ) ppm expected.[21] The -CH_3

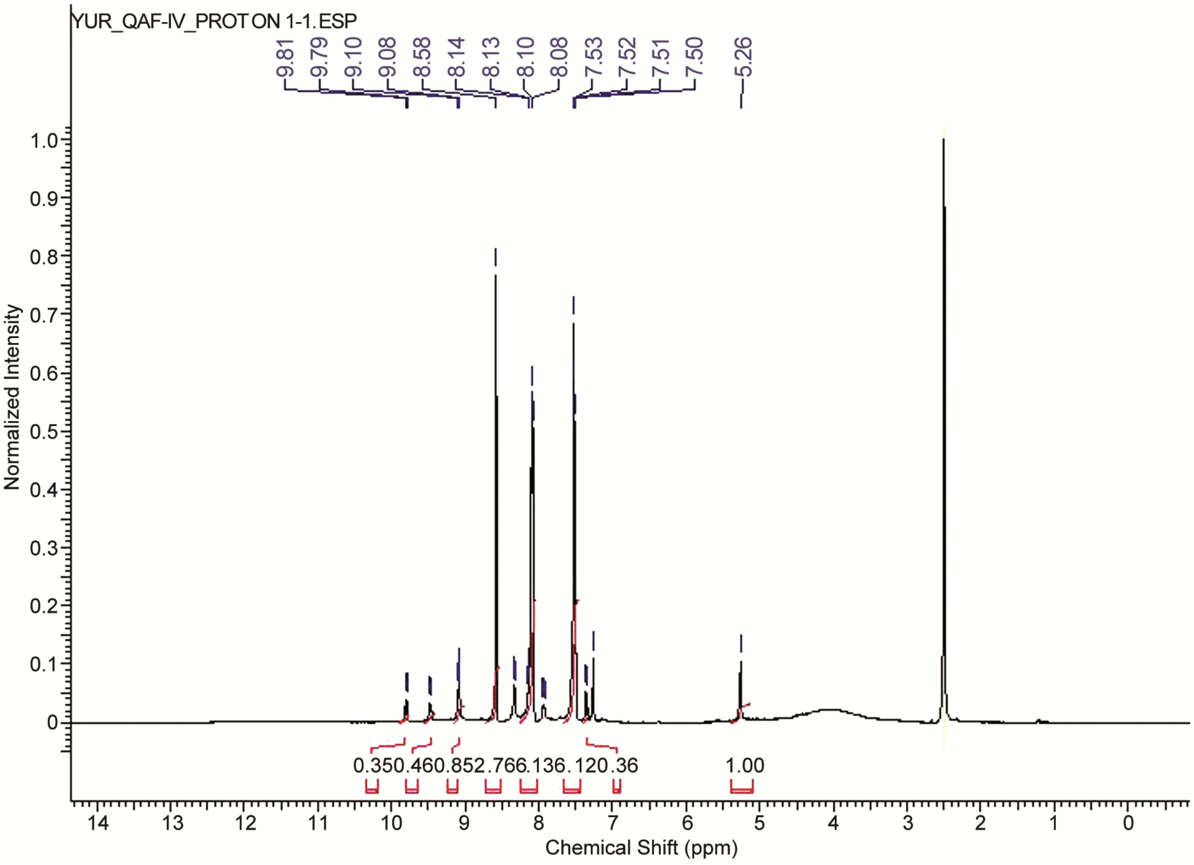

Fig. 4 — ^{1}H NMR spectra of copolymer 8-HQAF.

moiety could be the cause of the signal that appeared at δ 2.3.[22] The signal in the range at 5.26 (δ) ppm (observed) and 7.8 (δ) expected is caused by –NH as displayed in Fig. 4.

3.5 SEM morphological details

By scanning electron microscope, the copolymer resin's surface characteristics could be seen clearly. The SEM micrographs were captured at different magnifications.

Fig. 5 displays the SEM images of the 8-HQAF resin at x3500, 5um magnifications. The copolymer contains deep shallow pits with more amorphous and less densely packed surface, as shown by the pictures' spongy structure. Despite the crystalline quality of the constituent monomers, the polymerization reaction affects their crystallinity and, in the case of terpolymers, results in an amorphous output. The degree of crystallinity is 20%. It's also important to notice that the surface of the polymer has deep shallow holes and high porosity, which boosts the polymer's ability to bind metals, and this aligns with improved outcomes in experiments on metal ion separation.[23]

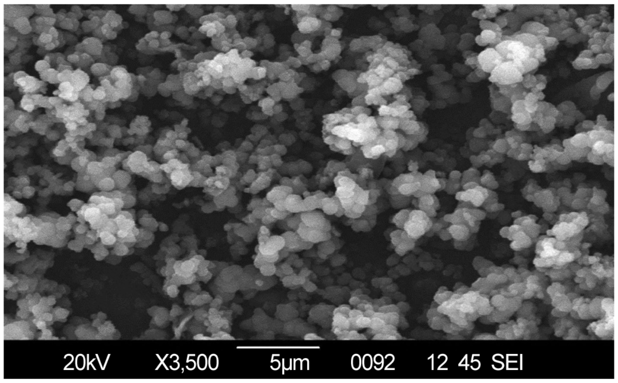

Fig. 5 — SEM of 8-HQAF Copolymer.

3.6 X-RAY Diffraction

The three major aspects of investigating the crystal structure are degree of crystallinity, crystalline orientation and lattice size. Herman, Karst and Flaschner created a quantitative approach for calculating the relative fraction of crystalline domain in a composite crystalline-amorphous structure, which is a measure of the degree of crystallinity as shown in Fig. 6.

In the above investigation Rulandand Vonk method has been employed for calculating the degree of

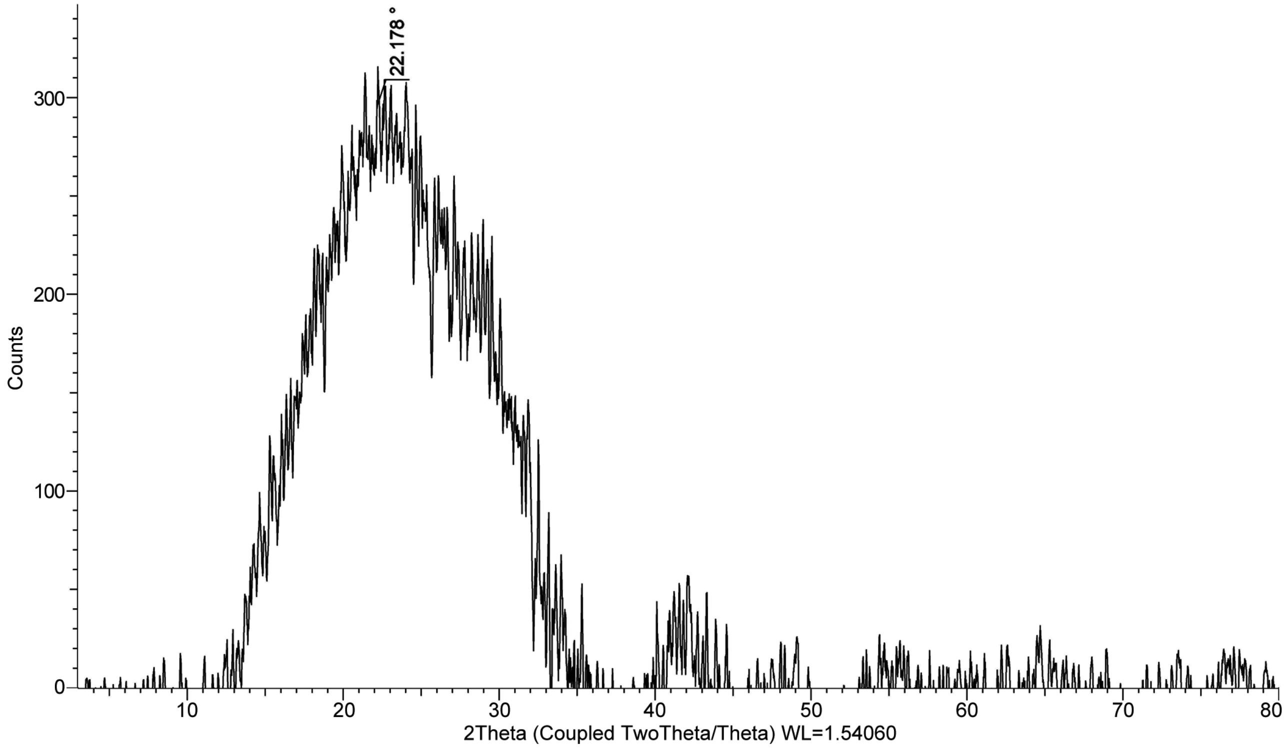

Fig. 6 — XRD spectra of 8-HQAF.

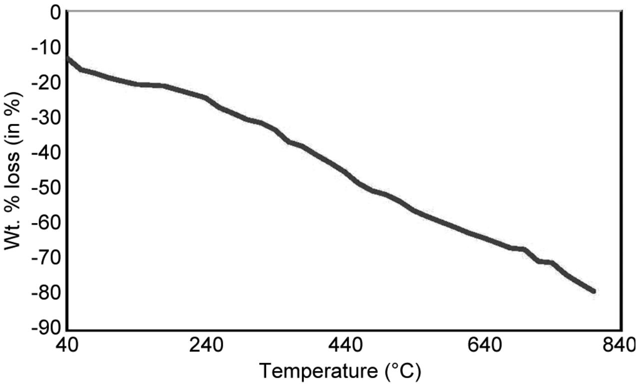

Fig. 7 — Thermogravimetric curve of 8-HQAF.

crystallinity value (20%). All sharp peaks around $2\Theta = 12^0, 14^0, 18^0, 21^0, 26^0, 28^0, 30^0$ indicates highly crystaline nature of polymeric meterial Based on data analysis the polymer synthesized can be considered as crystalline in nature.[24]

3.7 Thermal Analysis of 8-HQAF copolymer resin

Fig. 7 depicts the thermogram of 8-HQAF copolymer, while the typical percentage mass removal at various temperatures. The TG curve of the terpolymer in the current investigation did not show a sudden weight decrease, confirming their polymeric nature. Lattice water molecules are lost during the initial weight loss. For the resin, there are three stages of deterioration. The first step of deformation follows amid 110°C and 390°C, which may be caused by the loss of the terpolymer's thermally unstable amino and hydroxyl functional groups. Below this point, a progressive weight loss continues up to 610°C, where the aliphatic groups start to break down.[25] Between 510 and 800 °C, the rate of degradation was quite rapid. At this point, the resin had totally broken down. The remaining polymer weight (10%) is made up of a mixture of final pyrolysis products and some ashes.

3.8 Freeman-Carroll Method

The following Freeman-Carroll expression were utilized to compute the activation energy (Ea) and order of reaction (n) for the breakdown of copolymer.

$$\frac{\Delta \log(\frac{dw}{dt})}{\Delta logWr} = \frac{-Ea}{2.303}\left(\frac{\Delta\left(\frac{1}{T}\right)}{\Delta logWr}\right) + n \qquad \dots (1)$$

Where,

The ratio of weight change to time is known as dw/dt.

Wc is the weight loss, and Wr is the weight gain.

n is the order of the reaction, T and R are the temperature and the gas constant, respectively, and W is the total weight loss up to time t. at the conclusion of the reaction or at a specific time.

Table 2 — Thermodynamic and Kinetic parameters of copolymer

Copolymer	Activation Energy(Ea), KJ mol^{-1}		Entropy Change (ΔS), (J)	Free Energy Change (ΔF), (KJ)	Frequency Factor (Z) (sec^{-1})	Apparent Entropy Change (S*)	Order of reaction (n)
	FC	S-W					
8-HQAF	26.43	28.93	-211.81	109.07	553	-61.26	0.98

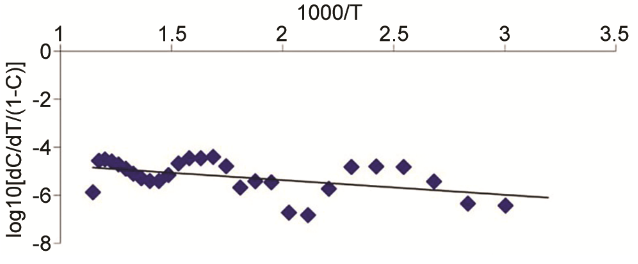

Fig. 8 — Activation energy plot of 8-HQAF copolymer.

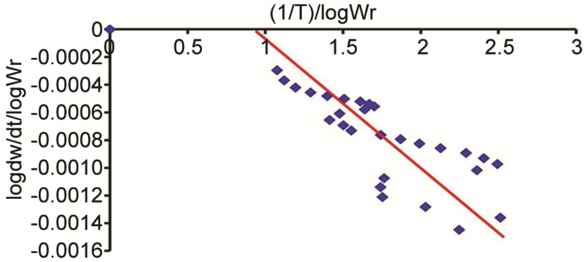

Fig. 9 — FC plot of 8-HQAF copolymer.

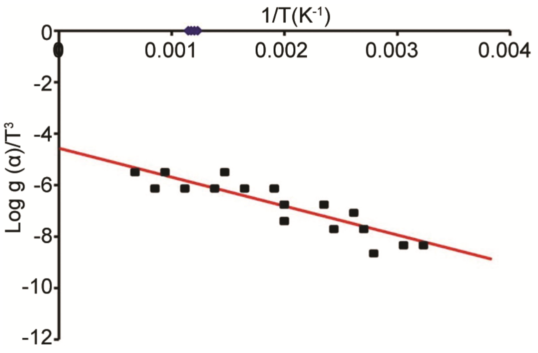

Fig. 10 — Freeman- Carroll plot of 8-HQAF copolymer.

Thus, a plot of (1/T)/logWr against (log(dw/dt)/logWr) yields a slope of -Ea/2.303R and an intercept of n on the y-axis at x = 0.

3.9 Sharp-Wentworth method

The activation energy (Ea), entropy change (S), and free energy change (F) were calculated using the Sharp-Wentworth equation.

$$\frac{\log dc/dt}{1-C} = \frac{log\alpha'}{\beta} = \frac{Ea}{2.303\,RT}$$

Based on thermogravimetric data of the copolymer resin, the activation energy (Ea) is computed in conjugation with each other using Freeman-Carroll as depicted in Fig. 8, 9 and Fig. 10 Sharp-Wentworth procedures.[26]

The formulas for the Freeman-Carroll and Sharp-Wentworth techniques of computing kinetic and thermodynamic parameters are published in Table 2. There is good agreement between the activation energies determined using the FC and SW approaches.[27] Parallel to its thermal stability, with one another. The great thermal stability of the copolymer is favoured by the attained activation energies. The copolymer has a more organised structure than its monomers, according to the negative value of entropy (S).[28,29,] Because the entropy is a measure of disorder, it is expected that the structure would be more organised if the level of disorder were to be lower. As a result, the degradation reaction slows down more than usual. The low frequency factor adds to this support.

4 Conclusion

With different ratios of the reactants, a terpolymer including 8-hydroxyqunoline, acrylamide, and furfural was synthesized at 124^{0}C for 6 hours in the presence of hydrochloric acid as a catalyst. The linear structure of the terpolymer is confirmed by its spectral characterizations. The terpolymer resin has good temperature stability, as shown by the TGA curve. It was discovered that the activation energies computed for the resins using various approaches agreed well with one another. The Freeman-Carroll method's calculated negative entropy values and low frequency factor indicated that the thermal decomposition would be a sluggish response.

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References

1 El-shazly R, Kamal R, Nassar A, Ahmed N, and Sayed G. *Appl Petro Res*, 10 (2020)115

2 Sasikala T, Greeshma K, Gnana P, Muthulingam S and Nandhakumar C, *GSC Adv Res and Rev,* 05 (2020) 19.

3 Rahangdale S S , Das N, Vajpai K and Gurnule W B, *Int J Recent Sci Res,* 10 (2019) 31772

4 Mahant R, Kongre N, Bhagat D and Gurnule W B, *Alochana Chakra J,* 9 (2020) 451.

5 Rathod Y U, Gurnule W B, *Curr Appl Polym Sci,* 4(2020) 47.

6 Rathod Y U, Zanje S B and Gurnule W B, *J Phys Conf Ser,* 1913 (2021) 1.

7 Butoliya S, Gurnule W B and Zade A, *E-J Chem,* **7** (2010) 1101

8 Burkanudeen A, Azarudeen R, Ahamed M and Gurnule W B, *Polym Bull,* 67 (2011) 1553.

9 Burkanudeen A, Ahamed M, Azarudeen R, Begum M and Gurnule W B, *Arab J Chem,* 9 (2011) S296.

10 Patel M, Kapadia M and Joshi J, *Eur Polym J,* 45 (2009) 426.

11 Gurnule W B and Patle D, *Polym Bull,* 66 (2011) 803.

12 Kushwaha A, Hiwase V and Kalambe A, *Chem Sin,* 3 (2012) 794.

13 Gurnule W B, Rahangdale P K, Paliwal L J, Kharat R B, *React Funct Polym*, 55(3) (2003) 255.

14 Spasova M, Manolova N, Markova N, Rashkov I, *Appl Surf S*ci, 363, (2016) 371.

15 Toncheva A, Mincheva R, Kancheva M, Manolova N., Rashkov I, Dubois P, Markova N, *Euro Polym J*, 75, (2016) 233.

16 Ignatova M, Manolova N, Rashkov I, Markova N, Kukeva R, Stoyanova R, Georgieva A and Toshkova R, *Polym (Basel)*, 13(16) (2021) 2690.

17 Gurnule W B, Das N, *Mater Tod Proc* 15 (2019) 611.

18 Gurnule W B, Rathod Y U. *Curr Appl Polym Sci,* 4 (2020) 1.

19 Azarudeen R and Burkanudeen A, *J Inorg Met Polym,* 22 (2012) 791.

20 Singru R N, Zade A B, Gurnule W B, *J Appl Polym Sci,* 109 (2) (2008) 859.

21 Kohad C and Gurnule W, *Mater Today Proc* 15 (2019) 438.

22 Mandavgade S K and Gurnule W B, *Mater Today Proc,* 60 (2022) 1814.

23 Tadavi S, Rajput J, Bagul S, Sangshetti J, Hosamani A and Bendre S, *Mod. Chem. Appl.* 5 (2017)1.

24 Thakre M B and Gurnule W B, *Mater Today Proc,* 15 (2019) 516.

25 Das N and Gurnule W B, *Mat Today Proc,* 15 (20190 611.

26 Rathod Y U, Pandit V U, Bhagat D S, Gurnule W B, *Mat Today Proc*, 53 (2022) 123.

27 Mishra P A, Rathod Y U, Pandit V U, Gurnule W B, *Mat Today Proc*, 53 (2022) 56.

28 Gupta P M, Rathod Y U, Pandit V U, Gupta R H, Gurnule W B, *Mat Today Proc*, 53 (2022) 101.

29 Gurnule W B and Kohad C. G, *Res. J Pharm Bio Chem Sci*, 9 (2018) 393.