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Synthesis, characterization and thermal degradation study of copolymer resin

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ABSTRACT

The copolymer 2-H,4-MBP-1,5-DANF-III has been synthesized by the condensation polymerization of 2-hydroxy, 4-methoxybenzophenone (2-H,4-MBP) and 1,5-diaminonaphthalene (1,5-DAN) with formaldehyde (F) in an acidic medium with 3:1:5 M ratio of reactants. Copolymer resin has been characterized by elemental analysis, Ultraviolet, infrared (IR) and nuclear magnetic resonance (NMR) spectroscopy. The morphology of copolymer was studied by scanning electron microscopy (SEM). The thermogravimetric analysis (TGA) has been performed to evaluate the thermal degradation characteristics and to ascertain its thermal stability. Freeman-Carroll and Sharp-Wentworth methods have been used for the evaluation of kinetic parameters. Thermal activation energy Ea determined by Freeman-Carroll and Sharp-Wentworth methods are in close agreement with each other.

Selection and peer-review under responsibility of the scientific committee of the International Conference on Advanced Functional Materials (Innovations in Chemical, Physical and Biological Sciences).

1. Introduction

Study of thermal degradation behaviour and computation of kinetic parameters by implementing modern developing thermal degradation kinetic techniques is the subject of interest for many investigators. The interest is fully recognized because the kinetics is related with the decomposition mechanisms in which the thermal degradation takes place [1]. Phenolic resins have a wide number of applications in ion exchangers, semiconductors, insulating materials, activators, protective adhesive, catalysts etc. because of their chemical and heat resistance, high thermal stability and electrical insulation properties [2–4]. To improve the thermal stability at elevated temperature, many researchers have synthesized the copolymer by changing the monomer compositions. Thermogravimetric analysis (TGA) method was applied to study the thermal stability of wide variety of copolymers by several authors [5–9].

Thermal degradation study of copolymer derived from 2,4-dihydroxypropiophenone, 4-pyridylamine with formaldehyde was carried out by Rahangdale et al. [10]. Niley et al. have studied the thermal degradation and electrical conductivity of 4-hydroxyacetophenone, ethylenediamine and formaldehyde terpolymer resin [11]. Gurnule and co-worker studied the non-isothermal degradation of copolymer resin derived from 1,5-diaminonaphthalene, 2,4-dihydroxypropiophenone and formaldehyde [12]. Thermal degradation of 2,4-dihydroxyacetophenone - propylenediamine - formaldehyde terpolymer has been reported by Jiwatode et al. [13]. Dontulwar and coworkers have been studied the kinetics of thermal decomposition of resin resulted from 1-naphthol-4-sulphonic acid, hexamethylenediamine and formaldehyde [14]. Nandekar K. and Mandavgade S. have synthesized copolymer by condensation of salicylic acid and thiosemicarbazide with formaldehyde and TGA method was applied to study the non-isothermal kinetics [15].

The present communication deals with the synthesis, characterization and thermal degradation study of 2-H, 4-MBP-1,5-DAF-III copolymer. The Sharp-Wentworth and Freeman-Carroll methods have been used for the evaluation of activation energy and kinetic parameters such as entropy change (ΔS), free energy change (ΔF), apparent entropy change (S^*), frequency factor (Z) and order of reaction (n).

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2. Materials and methods

All the chemicals were of analytical grade and chemically pure grade. 2-Hydroxyl, 4-methoxybenzophenone, 1,5-diaminonaphthalene and formaldehyd were purchased from Sigma Aldrich, Himedia and S. D. Fine, India respectively. The solvents like N,N-dimethylformamide, dimethylsulphoxide, Tetrahydrofuran and diethyl ether were purchased from Merck, India.

2.1. Synthesis of 2-H, 4-MBP-1, 5-DAF-III copolymer

The 2-H, 4-MBP-1, 5-DAF-III copolymer resin was synthesized by condensing 2-hydroxy, 4-methoxybenzophenone and 1,5-diaminonaphthalene with formaldehyde in a molar ratio 3:1:5 in the presence of 200 ml, 2 M hydrochloric acid as a catalyst in an oil bath at 126 ± 2 °C for about 5 hr with occasional shaking. The brown colored copolymer resin obtained was washed with hot water and methanol to remove unreacted acid monomers and starting materials. The resin was dried, powdered and extracted with diethyl ether to remove 2-hydroxy, 4-methoxybenzophenone formaldehyde copolymer along with 2-H, 4-MBP-1, 5-DAF-III copolymer.

The resin was purified further by dissolving in 8% aqueous NaOH and regenerated by gradual drop wise addition of 1:1 (v/v) concentrate HCl/distilled water. The resulting copolymer sample was then filtered off, washed several times with hot water, dried in a vacuum at room temperature. The purified resin was finally ground to pass through 300-mesh size sieve and kept in a vacuum over silica gel. The percentage yield of the copolymer sample was found to be 84%. The reaction and proposed structure of synthesized 2-H, 4-MBP-1,5-DAF-III copolymer has been shown in Fig. 1.

2.2. Analytical and physico-chemical studies

Microanalysis for hydrogen, carbon and nitrogen content of copolymer sample was carried out on Elementar Vario EL III CARLO ERBA 1108 Elemental Analyzers instrument. The UV–visible spectra of the copolymer in DMSO was scanned on automatic recording double beam spectrophotometer (UV–VIS-NIR Spectrometer) in the region of 200–800 nm. Infrared spectra was carried out on Thermo Nicolet Avatar 370, FT-IR spectrometer in KBr pellets in the region of 4000–500 cm^{-1}. Proton NMR spectra was recorded on Bruker 400 Advance-III, FT-NMR spectrometer using DMSO d_6 as a solvent.

SEM has been carried out at different magnification using JEOL 6390LV, scanning electron microscope. The TGA of the copolymer was carried out using Perkin Elmer Diamond TGA/DTA thermal analyzer. All the spectral and analytical studies for the synthesized copolymer sample were carried out at Sophisticated Analytical Instruments Facility, SAIF, Cochin University, Cochin, India.

2.3. Thermal studies

TGA method is in connection with a change in weight with respect to temperature. Heating is executed under rigorous controlled conditions and can concede changes in structure and other important properties of the material being studied. In dynamic thermogravimetric analysis, the sample is exposed to state increase in temperature at linear rate [16].The TGA was performed using 5–6 mg of samples in air atmosphere with heating rate at 10 °C min^{-1} in platinum crucible in the temperature range 40 °C–800 °C and thermogram was recorded for 2-H, 4-MBP-1, 5-DAF-III. Thermogravimetric data was used to evaluate the thermal activation energies Eà and order of reaction (n). The further thermodynamic parameters specifically entropy change (ΔS), apparent entropy change (S^*) free energy change (ΔF) and frequency factor (Z) were determined.

3. Results and discussion

The newly synthesized copolymer sample was found to be brown color. The resin is soluble in solvents like dimethylformamide (DMF), Tetrahydrofuran (THF), Dimethylsulphoxide (DMSO) and concentrate H_2SO_4 while insoluble in just about all organic solvents.

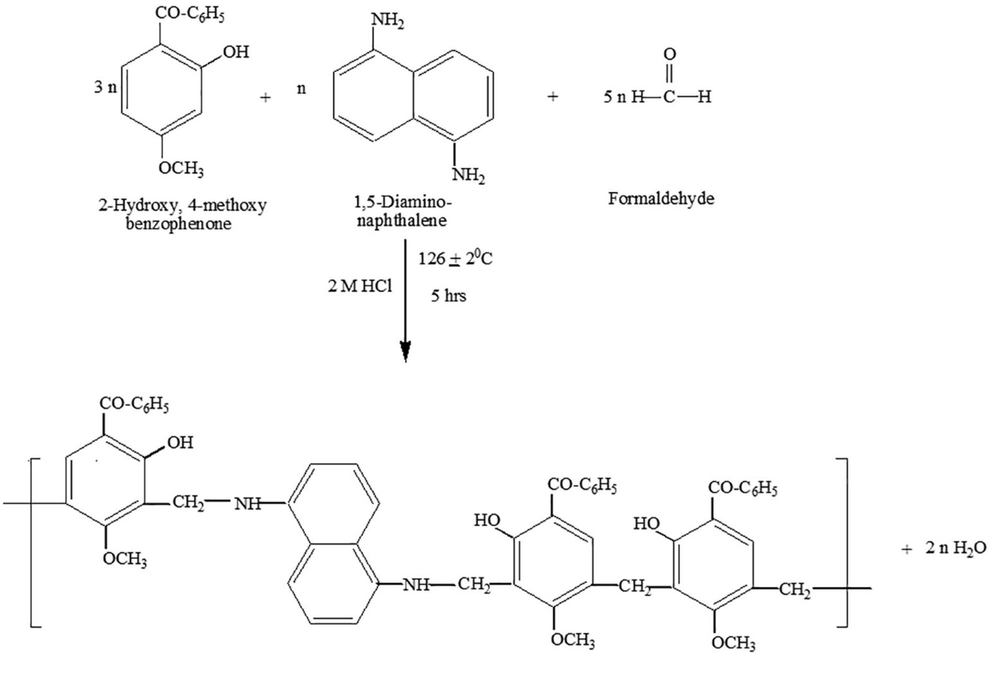

Fig. 1. Synthesis of 2-H, 4-MBP-1,5-DAF-III copolymer resin.

Table 1
Elemental analysis and empirical formula of copolymer resin.

Copolymer resin	% of Carbon Observed (cal.)	% of Hydrogen Observed (cal.)	% of Nitrogen Observed (cal.)	% of Oxygen Observed (cal.)	Empirical Formula of repeated unit	Empirical Formula weight
2-H,4-MBP-1, 5-DAF-III	74.02 75.50	5.67 5.16	3.65 3.14	15.87 16.17	$C_{56}H_{46}N_2O_9$	890

Table 2
Determination of $\overline{Mn}$ of 2-H,4-MBP-1,5-DAF-III copolymer resin.

Copolymer resin	First stage of neutralization	Final stage of neutralization	Degree of polymerization $(\overline{DP})$	Empirical formula weight (n)	Number average molecular weight $\overline{Mn}$
2-H,4-MBP-1, 5-DAF-III	504	1344	2.66	890	2373

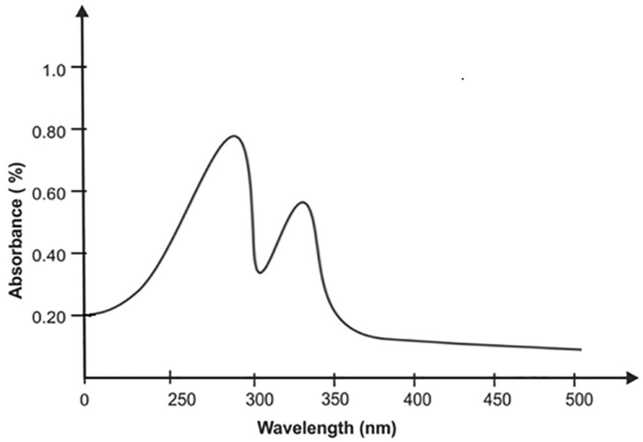

Fig. 2. UV–visible spectra of 2-H, 4-MBP-1,5-DAF-III copolymer resin.

3.1. Elemental analysis

The 2-H, 4-MBP-1,5-DAF-III copolymer was analyzed for the hydrogen, carbon and nitrogen content. From the result of elemental analysis, the empirical formula and empirical formula weight of the copolymer resin have been assigned and presented in the Table 1.

3.2. Molecular weight by non-aqueous conductometric titration

Number average molecular weight $\overline{Mn}$ of the copolymer has been determined by conductometric titration method in non-aqueous medium using standard ethanolic 0.05 N potassium hydroxide as a titrant. The specific conductance was plotted against milliequivalents of ethanolic KOH required for neutralization of 100 g of each copolymer. Examination of corresponding a plot exhibits the number of breaks in the plot. The first break at 504 and the last break at 1344 milliquivalents of base were found. The determination of $\overline{Mn}$ by this method is based on the following deliberation; (1) The first break correlated to neutralization by more acidic phenolic hydroxyl group of all the repeating units; (2) The break in the plot far off which a continuous increase is noticed, indicates the stage at which phenolic hydroxyl group of all the repeating units are neutralized [17]. By using average degree of polymerization $(\overline{DP})$, the number average molecular weight has been determined by the following relations

$$\left(\bar{DP}\right) = \frac{\text{Total milliequivalents of base for complet neutralization}}{\text{Milliequivalents of base required for smaller intervals}}$$

$$\bar{Mn} = \bar{DP} \times \textit{Repeat unit weight}$$

The results are incorporated in the Table 2.

3.3. UV–visible spectra

The electronic absorption spectra of 2-H, 4MBP-1,5-DAF-III copolymer has been scanned in pure DMSO in the range 190–800 nm and presented in Fig. 2. The spectra exhibit two absorption maxima at 285 nm and 340 nm. These observed position of absorption bands represent the presence of a carbonyl group containing a carbon oxygen double bond which is in conjugation with the aromatic nucleus.

The appearance of more intense band can be account for $\pi \rightarrow \pi^*$ electronic transition while the less intense band may be due to $n \rightarrow \pi^*$. The extra shift of absorption to the longer wavelength region from basic value (viz. 240 nm and 310 nm respectively) may be because of conjugation effect and existence of phenolic hydroxyl group which is responsible for hyperchromic effect i.e. max higher value [18].

3.4. FT-IR spectra

Infrared spectra of 2-H, 4-MBP-1, 5-DAF-III copolymer resin has been shown in Fig. 3. A very broad and strong band appeared at 3389 cm^{-1} may be due to the stretching vibration of the phenolic hydroxyl (–OH) group shows intramolecular hydrogen bonding. The strong band observed at 2934 cm^{-1} suggest the stretching vibrations of –NH (imide) group. A sharp and strong band at 1618 cm^{-1} may be assigned to the stretching vibration of >C=O group. The strong band observed at 1106 cm^{-1} region is may be due to the Ph-O-CH_3 ether linkage. The weak band at 1344 cm^{-1} may be ascribed to –CH_2 methylene bridge. The presence of 1, 2, 3, 4, 5- pentasubtitutted aromatic ring is identified from the band appeared in the region 1016, 922, 802, 696, 591 cm^{-1} [19,20].

3.5. ^{1}H NMR spectra

The ^{1}H NMR Spectra of 2-H, 4-MBP-1,5-DAP-III copolymer has been presented in Fig. 4. The weak multiplet signal appeared in the region at δ 7.5 ppm, which may be because of aromatic proton

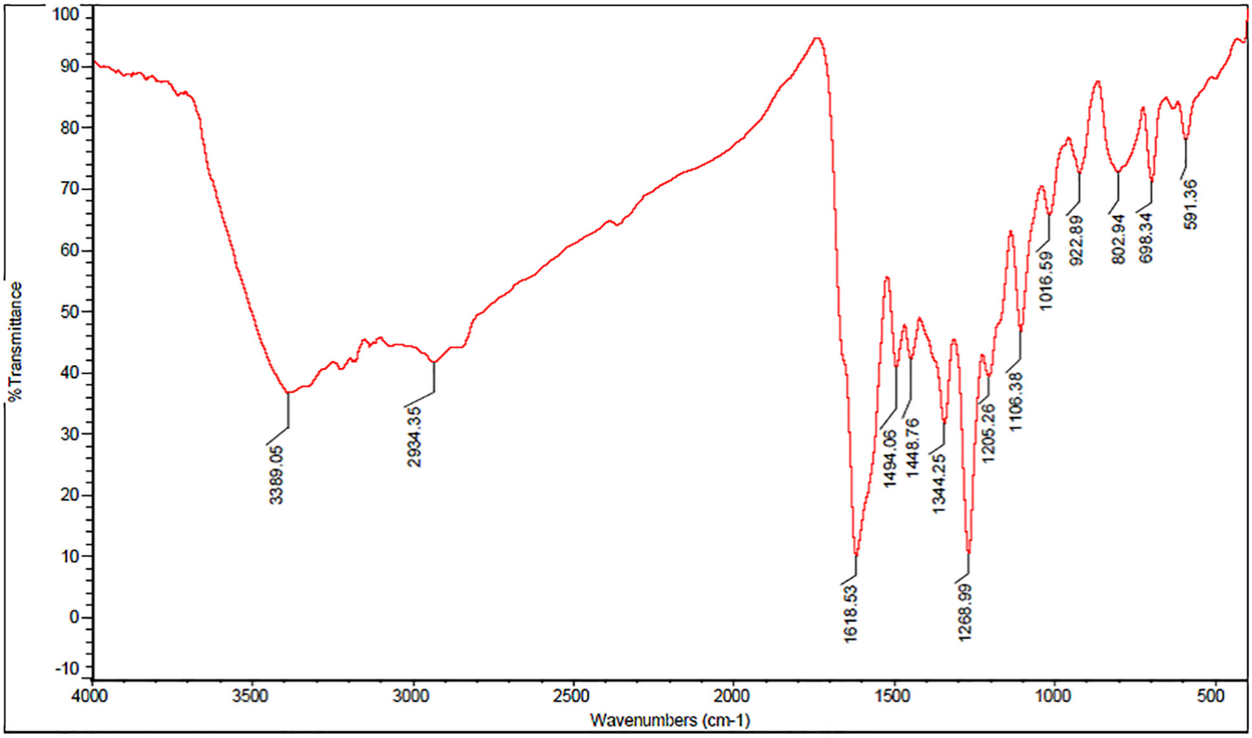

Fig. 3. FT-IR spectra of 2-H, 4-MBP-1,5-DAF-III copolymer resin.

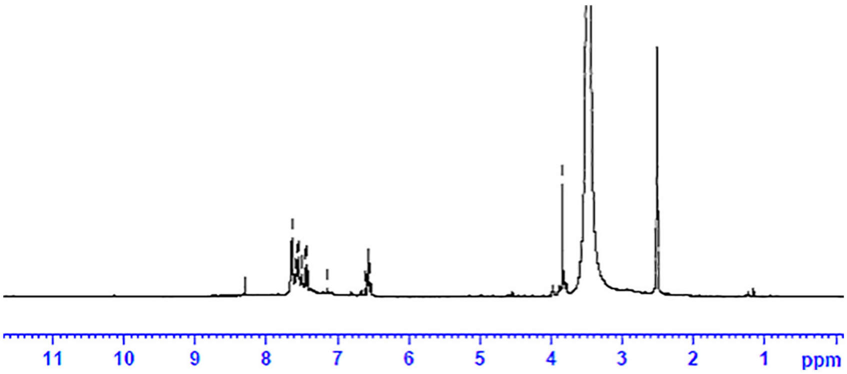

Fig. 4. ^{1}H NMR spectra of 2-H, 4-MBP-1,5-DAF-III copolymer resin.

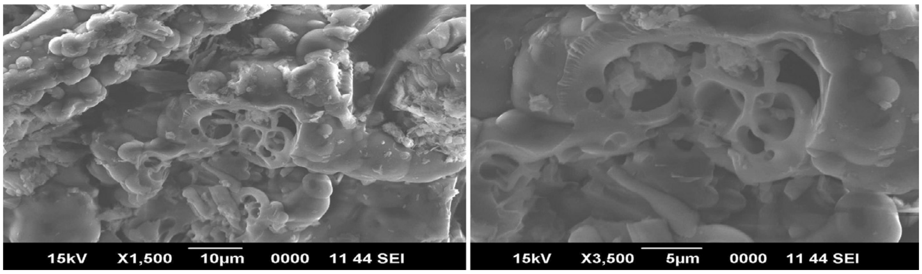

Fig. 5. SEM micrograph of 2-H, 4-MBP-1, 5-DAF-III copolymer resin.

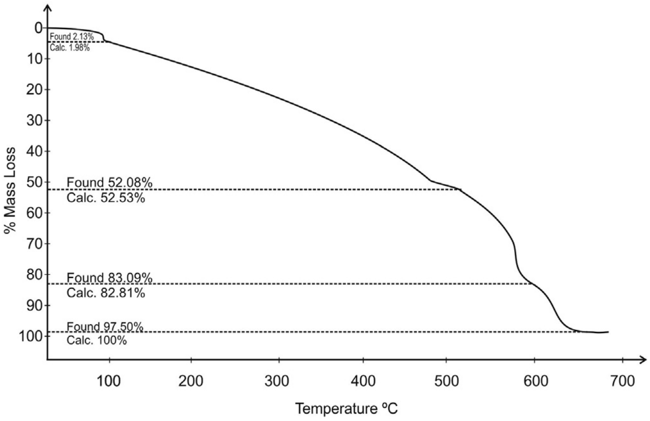

Fig. 6. Decomposition pattern of 2-H, 4-MBP-1,5-DAF-III copolymer resin.

(Ar-H). The signal in the region δ 7.2 ppm may be assigned to phenolic –OH proton in intramolecular hydrogen bonding (Ar-OH).

The presence of singlet at δ 3.5 ppm indicates the presence of Ar-O-CH_3 proton. The methylenic proton of Ar-CH_2-NH linkage may be recognized from dublet signal which appears in the region of δ 3.8 ppm. The triplet signal in the region δ 6.6 ppm may be assigned to proton of –NH bridge [21].

3.6. Scanning electron microscopy

The morphology of the synthesized 2-H, 4-MBP-1, 5-DAF-III copolymer was studied by scanning electron micrograph at distinct magnification which is presented in Fig. 5. The morphology of the resin displays spherules and fringed model. The spherules are complex polycrystalline formation smooth surface. This shows the copolymer resin is crystalline in nature. It also shows a fringes model of the amorphous-crystalline structure. The level of crystalline character depends on the acidic nature of monomer. The copolymer shows a additional amorphous character with closed packed surface having deep pits and the reactivity of active sites buried in the copolymer matrix. The existence of few holes and cracks are noted which may be because of air voids useful for ion exchange studies [22].

3.7. Thermogravimetry of 2-H,4-MBP-1,5-DAF-III copolymer resin

Thermogram of copolymer 2-H,4-MBP-1,5-DAF-III is presented in Fig. 6 and shows three steps in degradation reaction, after loss of one crystalline water molecule entrapped in the copolymer molecule, in the temperature range 40 °C–100 °C.

The initially decomposition take place between 40 °C–70 °C corresponds to 2.13% loss which may be due to loss of water molecule against calculated 1.98% present per repeat unit of the polymer. The first stage degradation starts from 70 °C–520 °C which may be due to gradual loss of phenolic –OH, –CO–C_6H_5 and –O–CH_3 groups (found 52.08% and calculated 52.53%) attached to aromatic benzene ring. The second step of decomposition begins from 520 °C–595 °C corresponding to 83.09% due to degradation of aromatic ring along with methylene group against calculated 82.81%. The third step of degradation begins from 595 °C–660 °C corresponding to removal of naphthalene moiety (97.50% found and 100% calculated). The half decomposition temperature for copolymer resin is found to be 520 °C (Table 3).

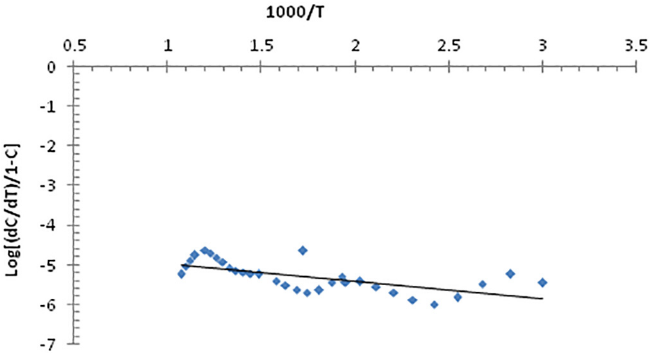

Fig. 7. SW plot of 2-H, 4-MBP-1,5-DAF-III copolymer.

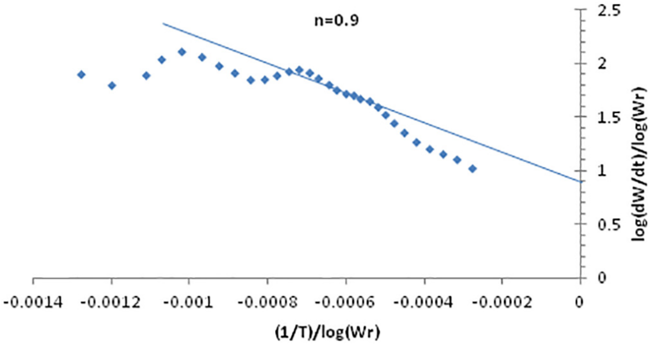

Fig. 8. FC plot of 2-H, 4-MBP-1,5-DAF-III copolymer.

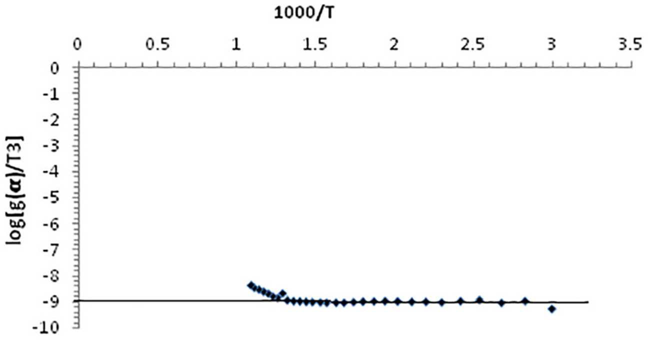

Fig. 9. Freeman-Carroll graph of 2-H, 4-MBP-1,5-DAF-III copolymer.

Table 3
Thermal degradation behaviour of 2-H, 4-MBP-1, 5-DAF-III copolymer resin.

Copolymer resin	Stages of de- composition	Temperature range (°C)	Group degraded	% Weight loss	
				Observed	Calculated
2-H,4-MBP-1,5-DAF-III	First	40–70	One water molecule	2.13	1.98
	Second	70–520	Three –OH, three –COC_6H_5, three –OCH_3 group	52.08	52.53
	Third	520–595	Three aromatic ring, four –CH_2 group	83.09	82.81
	Fourth	595–660	Naphthalene moiety	97.50	100

Table 4
Kinetic and thermodynamic parameters of 2-H, 4-MBP-1, 5-DAF-III copolymer.

Copolymer resin	Half decomposition temperature (T^*), °C	Activation Energy KJ mol^{-1}		Entropy change (ΔS), (J)	Free energy change (ΔF), (KJ)	Frequency factor (Z) (sec^{-1})	Apparent entropy (S^*), (J)	Order of reaction (n)
		FC	SW					
2-H, 4-MBP-1,5-DAF-III	520	30.52	30.00	−232.46	213.97	586	−655.40	0.90

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

3.8. Kinetics based interpretation

From the TG data of the copolymer resin and by applying Freeman-Carroll and Sharp-Wentworth methods, the activation energy Ea is calculated which is in agreement with each other. A typical thermal activation energy plot of Sharp -Wentworth (Fig. 7) and Freeman-Carroll (Figs. 8 and 9) methods for the copolymer have been shown. Thermodynamic parameters such as entropy change (ΔS), free energy change (ΔF), frequency factor (Z), and apparent entropy change (S^*) evaluated based on activation energy are given in Table 4 using the expression shown in Eq. (3), (4), (6) and (7).

(i) Entropy change

$$\text{Intercept} = \log \cdot \frac{KR}{h\Phi Ea} + \frac{\Delta S}{2.303R} \qquad (3)$$

(ii) Free energy change

$$\Delta F = \Delta H - T\Delta S \qquad (4)$$

(iii) Frequency factor

$$B_{2/3} = \frac{\log ZEa}{R\Phi} \qquad (5)$$

$$B_{2/3} = \log(3) + \log\left[1 - 3\sqrt{1-\alpha}\right] - \log p(x) \qquad (6)$$

(iv) Apparent entropy change

$$S* = 2.303R \log \frac{zh}{RT^*} \qquad (7)$$

By using data of Freeman-Carroll method, various thermodynamic parameters have been calculated (Table 4). On the basis of the initial decomposition temperature, the thermal stabilities of the copolymer resin has also been used here to define thermal stability, neglecting the degree of decomposition. The low value of frequency factor indicates that the degradation of 2-H, 4-MBP-1,5-DAF-III copolymer is slow reaction. This fact is further supported by the negative value of the entropy change. However, in the graph, a few points do not fall on the straight line which indicates the degradation of copolymer do not obey the first order kinetics perfectly [23,24].

4. Conclusion

Copolymer 2-H, 4-MBP-1,5-DAF-III has been by synthesized by condensation polymerization of 2-hydroxy,4-methoxybenzophenone and 1,5-diaminonaphthale in the presence of acid catalyst. The proposed structure of copolymer resin has been elucidated by elemental analysis, infrared (IR), nuclear magnetic resonance (NMR) and UV–Visible spectral studies. Activation energy evaluated by the both Freeman-Carroll and Sharp-Wentworth methods are in close agreement with each other. Low value of frequency factor indicates that the degradation of copolymer is slow reaction. The negative values for entropy change concluded that the activated copolymer has more ordered structure than the reactants. The TGA study predicts that the copolymer resin is stable even at high elevation temperature.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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