Research Article

SYNTHESIS, CHARACTERIZATION AND THERMAL DEGRADATION STUDIES OF COPOLYMER DERIVED FROM 2, 4-DIHYDROXY PROPIOPHENONE AND 4-PYRIDYLAMINE

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ABSTRACT

The copolymer DHPPAF has been synthesized by condensation of 2,4-dihydroxypropiophenone,4-pyridyl amine with formaldehyde in the presence of 2M HCl as a catalyst at125 ± 20C in 1:1:2 molar proportion of reactants. The structure of newly synthesized copolymer has been elucidated and confirmed on the basis of elemental analysis and various spectral techniques, that is, UV-Visible, FT-IR, and 1H-NMR spectroscopy. The thermal degradation kinetics of the copolymer has been investigated by thermo gravimetric analysis (TGA) in a static nitrogen atmosphere at a heating rate of 100 C/min. Sharp-Wentworth and Freeman-Carroll methods have been used to evaluate the kinetic and thermodynamic parameters such as thermal activation energy (Ea), entropy change (ΔS), free energy change (ΔF), apparent entropy change (S*), frequency factor (Z) and order of reaction(n). The activation energy calculated by Sharp-Wentworth and Freeman-Carroll methods are in close agreement with each other. The order of decomposition reaction is found to be 0.96.

INTRODUCTION

The copolymer resin has been attracting much attention of polymer chemist due to interesting superior properties that can fulfill the demand of modern society[1]. Since last two decades, emphasis has been given on synthesis of thermally stable copolymeric resins with reference low production cost and ease of manufacture. The thermal degradation study of copolymer which primarily decides the thermal stability, processability andimportant information about its practical applicability. A large number of copolymers have been synthesized and find many applications such as adhesives, packaging, coating in electrical sensors, catalyst, activators, thermal stable materials [2,3], ion-exchangers[4,5], high dielectric constant for energy storage capacitors [6] and semiconductors [7].The considerable afford has been made to improve the quality of copolymer either by introduction of avarietyof functional monomers or by modifying methods. The thermal stability of copolymer have been studied by using the method of thermo gravimetric analysis (TGA) by several authors [8-15].

P. U.Belsare and coworkers studied the thermal degradation of terpolymer derived from 2-aminothiophenol, hexamethylenediamine with formaldehyde [16].Synthesis and thermal degradation studies of melamine formaldehyde resin has been reported by S.Ullah *et al* [17]. The thermal behavior of newly synthesized copolymer derived from salicylic acid and thiosemicarbazide has been studied by Kamlakar *et al* [18]. A. Gupta and coworkers studied the thermal degradation and kinetics of terpolymer resin derived from p-hydroxybenzaldehyde, succinic acid with ethylene glycol [19]. Thermo gravimetric analysis of terpolymer resin derived from salicylic acid, hexamethylenediamine with formaldehyde by D. T.Masram [20], 8-hydroxyquinoline and formaldehyde by P. E. P. Michael *et al* [21] and salicylic acid, diaminonaphthalene with formaldehyde by D. T.Masram [22] have been reported. The study of non-isothermal decomposition and kinetic

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analysis of 2,4-dihydroxybenzoic acid, melamine-formaldehyde copolymer has been reported by S.Butoliya *et al* [23].

The present research paper deals with synthesis, characterization and thermal behavior of newly synthesized copolymer resin derived from 2,4-dihydroxypropiophenone,4-pyridyl amine and formaldehydewhich has not been studied so far in literature. The Sharp-Wentworth and Freeman-Carroll methods have been applied to evaluate the thermodynamic and kinetic parameters.

MATERIALS AND METHODS

Materials

All thechemicals were AR grade and chemically pure grade. 2,4-Dihydroxypropiophenone(Alpha Aesar, India), 4-pyridylamine(Himedia, Mumbai, India) and formaldehyde(S. D. Fine Chemicals, India) were procured from market. Double distilled water was used for all experiments.

Synthesis of DHPPAF Copolymer Resin

The copolymer resin was synthesized by refluxing mixture of 2,4-dihydroxypropiophenone (0.1 mol), 4-pyridyl amine (0.1 mol) and formaldehyde (0.2 mol)in the presence of 2M, 200ml HCl as a catalyst at $125\pm2\ ^0C$ for about 5hrs in an oil bath with occasional shaking. The separated brown color solid products were washed with hot water to remove the unreacted monomers. The air dried product was extracted with diethyl ether to remove the 2,4-dihydroxypropiophenone-formaldehyde copolymer along with the 2,4-dihydroxypropiophenone. It was further purified by dissolving in 8% NaOH and then filtered. The copolymer was then reprecipitated by dropwise addition of 1:1 (v/v) con HCl/water with constant stirring and filtered. The process of reprecepitation was repeated twice. The copolymer sample thus obtained was filtered, washed several times with hot water, dried in air, powdered and kept in vacuumdesiccator over silica gel. The yield of the copolymer resin was found to be 83-84%. The reaction and suggested structure of 2, 4-DHP-4-PAF-I copolymer resin has been depicted in Figure 1.
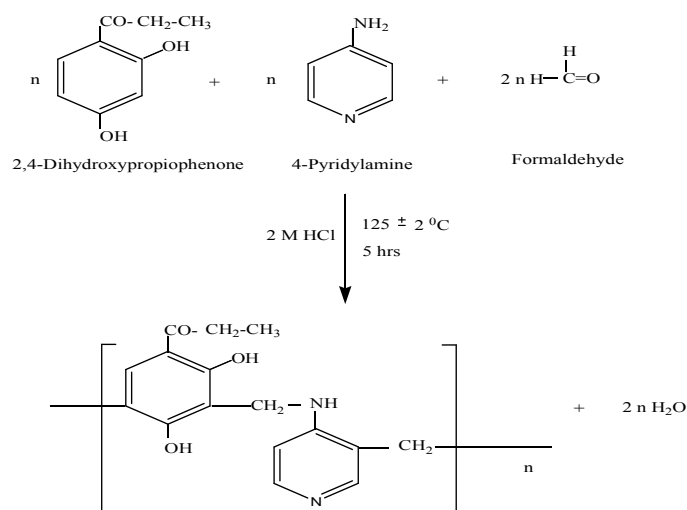

Figure 1 Synthesis of DHPPAF copolymer resin

Analytical and Physicochemical Studies

The elemental analysis of DHPPAF copolymer resin was recorded on Elemental Vario EL III Carlo Erba 1108 elemental analyzer instrument. The UV-Visible spectra of the copolymer was carried out at room temperature in DMF on double beam spectrophotometer fitted with automatic pen chart recorder in the range of 200nm – 850nm. Infrared spectra of copolymer has been scanned innajol mull on Perkin-Elmer-Spectrum RX-I, FT-IR Spectrophotometer in KBr pellets in the range of 4000-500 cm^{-1}.The proton NMR spectrum of copolymer was carried out using DMSO-d$_6$ as a solvent on Bruker Advance -II 400 MHz NMR spectrophotometer. The surfaceanalysis of the sample was examined by scanning electron microscope (SEM) using JEOL-JSM-6380 at different magnification. The TGA has been scanned by using Perkin Elmer diamond TGA/DTA analyser. All the analytical and spectral studies for the newly synthesized copolymer were carried out at Sophisticated Analytical Instruments facility (SAIF), STIC, Cochin University, Cochin, India.

Thermal Studies

Thermal analysis method is associated with a change in weight with respect to temperature. Heating is performed under strictly controlled conditions and can reveal changes in structure and other important properties of the material being studied. The non-isothermal thermogravimetric analysis was performed in air atmosphere with heating rate of 10^{0}C min^{-1}using 5-6 mg of samples from temperature range 40^{0}C to 800^{0}C and thermogram was recorded.

Theoretical Consideration

Thermogram was interpreted and analyzed to obtain information about the percentage weight loss at different temperatures which gives information about sample composition, product formed after heating and kinetic parameters. Thermodynamic and kinetic parameters have been evaluated using Sharp-Wentworth and Freeman-Carroll methods as follows

Freeman-Carroll Method

The followingexpression was given by Freeman-Carroll [24] to evaluate activation energy(E_a) and order of reaction(n) for the decomposition of copolymer

$$\frac{\Delta\log\,(dW/dt)}{\Delta\log Wr} = n - \frac{Ea}{2.30\ \Re}\cdot\frac{\Delta(1/T)}{\Delta\log Wr} \qquad (1)$$

Where, dW/dtis the rate of change of weight with time; Wr= Wc-W, where,Wc is the weight loss at completion of reaction andW is the fraction of weight loss at time t;$E_a$is the energy of activation;n is the order of reaction, T and R is the temperature and gas constant respectively.

The plot between the terms$\frac{\Delta\log\,(dW/dt)}{\Delta\log Wr}$versus$\frac{\Delta(1/T)}{\Delta\log Wr}$ gives a straight line. The slope of the line -Ea/2.303R, gives energy of activation (Ea) and intercept on Y-axis as order of reaction (n) where x=0.The change in entropy (ΔS), frequency factor (Z), apparent entropy change (S*) can also be calculated by further calculations.

Sharp–Wentworth method

The equation derived by Sharp and Wentworth [25] has been used to determine activation energy, free energy change and entropy change for the copolymer decomposition

$$\log \frac{dC/dT}{1-C} = \log(A/\beta) - \frac{Ea}{2.30\,R}\cdot\frac{1}{T} \tag{2}$$

Where, dC/dT is the rate of change of fraction of weight with change in temperature and β is the linear heating rate dT/dt. Thus a linear plot of $\log\frac{dC/dT}{1-C}$ versus $\frac{1}{T}$ is obtained, whose slope-Ea/2.303R gives activation energy (E_a) and 'A' may be calculated from the intercept on y-axis at x=0. The linear relationship confirms that the assumed order (n=1) is correct.

RESULTS AND DISCUSSION

Elemental and Physico-chemical Analysis

Elemental analysis is a technique to determine the molecular structure of polymer. The as been analyzed for carbon, hydrogen and nitrogen content. The empirical formula and empirical formula weight has been assigned by the result of elemental analysis which is presented in table 1.The % of element determined by elemental analysis is found good agreement with the calculated values.

Table 1 Elemental analysis and empirical formula of copolymer resin

Copolymer	% of C		% of H		% of N		Empirical Weight
Resin	Expt.	Calc.	Expt.	Calc.	Expt.	Calc.	formula
DHPPAF	66.80	67.60	5.85	5.63	9.80	9.85	$C_{16}H_{16}O_3N_2$ 284

The number average molecular weights ($\overline{Mn}$) of the copolymer has been determined by conductometric titration method in non-aqueous medium using ethanolic potassium hydroxide (0.05M) as a titrant. The specific conductance was plotted against milliequivalents of ethanolic KOH required for neutralization of 100g of copolymer. It revealed that there were many breaks in the plot. The first break at 448milliequivalents of base and the last break at 1344milliequivalent of base were noted (Fig. 2). The calculation of $\overline{Mn}$ by this method is based on the following considerations, (1) The first break corresponds to neutralization by more acidic phenolic hydroxyl group; (2) The break in the plot beyond which a continuous increase is observed represents the stage at which phenolic hydroxyl group of all the repeating units are neutralized [26]. On the basis of the average degree of polymerization ($\overline{DP}$), the number average molecular weight has been determined by the following relations

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

$$\overline{Mn} = \overline{DP} \times \text{Repeat unit weight}$$

The number average molecular weight ($\overline{Mn}$) has been found to be 852 and average value of $\overline{DP}$ is 3.0
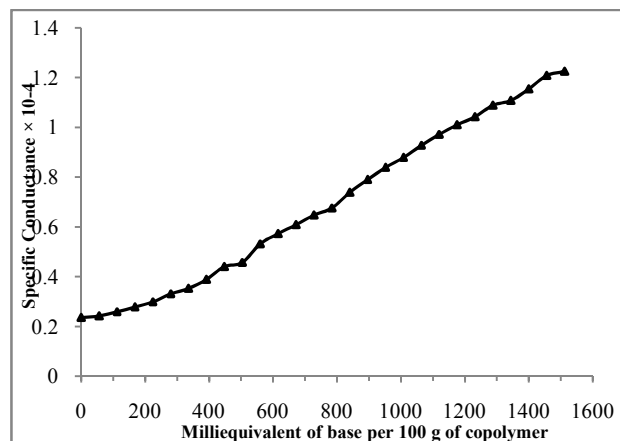

Figure 2 Conductometric titration curve of DHPPAF copolymer resin

UV-Visible Spectra

The UV-visible spectra of DHPPAF copolymer resin is presented in figure 3.UV-visible spectra of copolymer sample has been recorded in pure DMF in the region 200–800 nm. The spectrum exhibits two absorption maxima in the region 280 nm and 320 nm. These observed position of absorption band indicate the presence of carbonyl group (ketonic) having a carbon- oxygen double bond which is in conjugation with aromatic nucleus. The appearance of former band (more intense) can be accounted for π→π* transition while the letter band (less intense) may be due to n→π* electronic transition. The shift from the basic value (viz. 240 nm and 310 nm respectively) may be due to conjugation effect and presence of phenolic hydroxyl group (auxochrome) is responsible for hyperchromic effect i.e. ∈ max higher value.
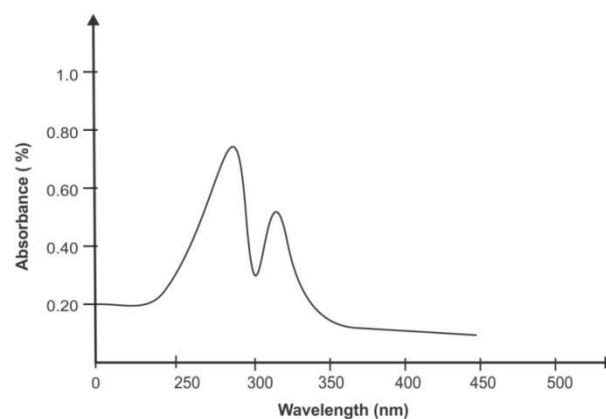

Figure 3 UV-visible spectra of DHPPAF copolymer resin

FT-IR Spectra

The FT-IR spectra of DHPPAF copolymer is presented in figure 4 and spectral data are specified in the table 2. The assignment of vibration frequency is based on the data available in the literature. A broad and strong band which appeared in the region 3290 cm^{-1} may be assigned to the stretching vibration of the phenolic hydroxyl group exhibiting intramolecularhydrogen bonding-NH group. The presence of methyl and methylene vibration at 2970 cm^{-1} gives sharp and strong peak. The sharp and weak band at2939 cm^{-1} may be due

to -NH- in pyridine moiety.The strong band at1628 cm^{-1} may be assigned due to stretching vibration of Ar-CO- group. A sharp band appearing at1482cm^{-1} describes the presence of >C=C< (aromatic) group. The sharp and strong band observed at 1373cm^{-1} suggest the presence of -CH$_2$- methylene bridge in the copolymer chain. The presence of 1,2,3,4and 5-pentasubstituted aromatic ring is recognized from weak band appearing in the region905-860cm^{-1}[27].
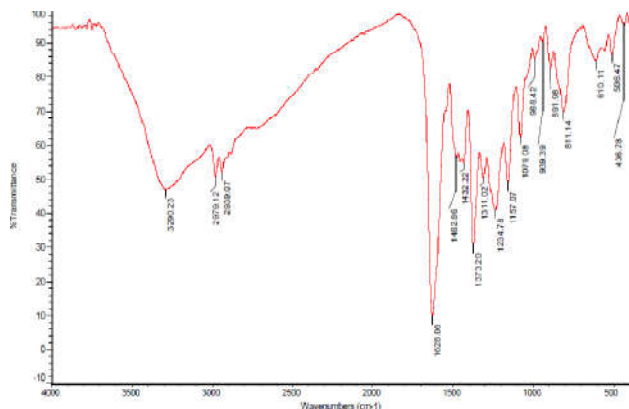

Figure 4 FT-IR Spectra of DHPPAF copolymer resin

Table 2 FT-IR data of DHPPAF copolymer resin

Observed band frequencies (cm^{-1})	Assignment	Expected band frequencies (cm^{-1})
3290 (b,st)	–OH phenolic intramolecular hydrogen bonding	3750-3200
2979(sh, St)	-CH$_2$,-CH$_3$ stretching	3500-2800
2939(sh, w)	-NH- moiety in pyridine	3450- 2795
1447(Sh)	Aromatic ring	1445-1485
1344(sh,st)	-CH$_2$- bridge	1380-1350
1628(sh, st)	Ar-CO- group	1670-1630
891(m)	1,2,3,4,5-substitution	905-860

b=broad, st= strong, sh= sharp, w= weak, m=medium

^{1}H-NMR Spectra

The ^{1}H-NMR spectra of DHPPAF copolymer is depicted in figure 5and spectral data are incorporated in the table 3. The spectrum reveals different pattern of peaks, since each of them possesses a set of protons having different proton environment. The weak multiplicity signals (unsymmetrical pattern)in the region δ 7.1ppm which is due to aromatic proton (Ar-H). A significant singlet signal appearing at δ 6.4ppm is attributed to phenolic -OH proton in intramolecular hydrogen bonding. The medium triplet signal observed at δ 7.6 ppmmay be due to amido proton Ar-CH$_2$-NH- of copolymer chain. The proton of methylenic bridge Ar-CH$_2$- NH- may be recognized from doublets signal which appears in the region δ 2.6 ppm. The presence of quartet peaks in the region δ 3.0 ppmreveals the presence of methylene proton of Ar-CO-CH$_2$-CH$_3$.A peak appeared in the region δ 1.2 ppmmay be due to methyl proton of Ar-CO-CH$_2$-CH$_3$ group [28]
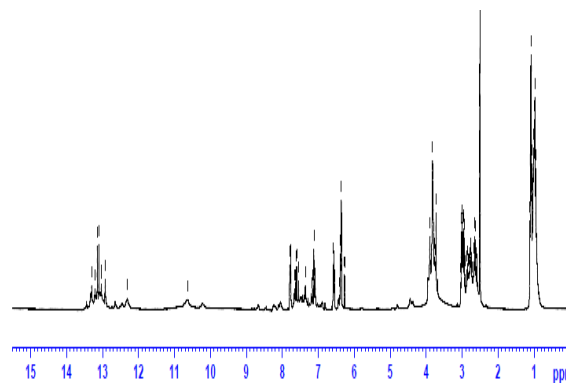

Figure 5 ^{1}H-NMR Spectra of DHPPAF copolymer resin

Table 3 ^{1}H-NMR spectra of DHPPAF copolymer resin.

Observed shift δ (ppm)	Nature of proton assigned	Expected chemical shift δ (ppm)
6.4	sProton of phenolic-OH involving intramolecular hydrogen bonding	8.0 to 12.0
7.1 m	Aromatic proton (Ar-H)	6.2 to 8.5
7.6	tProton of –NH bridge	5.0 to 8.0
2.6	dProton of Ar-CH$_2$-N moiety	2.0 to3.0
3.0 q	Methylene proton of Ar-CO-CH$_2$-CH$_3$	1.8 to 4.5
1.2 t	Methyl proton of Ar-CO-CH$_2$-CH$_3$	0.9 to 1.5

S= singlet, d= doublet, t=triplet, q= quartet, m=multiplets

Scanning Electron Microscopy

The surface morphology of DHPPAF copolymer resin was studied by scanning electron micrograph at different magnification which is presented in figure 6. It gives information about surface topography and defects in the structure. The investigated copolymer appeared to be dark brown in color. At lower magnification it shows spherules in which the crystals are arranged more closely in smaller surface area. It indicates the crystalline nature of resin and this property exhibits low ion exchange capacity for higher hydrated size metal ion. At higher magnification it shows more amorphous character with less close packed surface having deep pits. The amorphous nature of the resin indicates higher ion exchange capacity for metal ion. Thus resin is crystalline as well as amorphous or transition between crystalline and amorphous,showing less or more good ion exchange capacity[29].
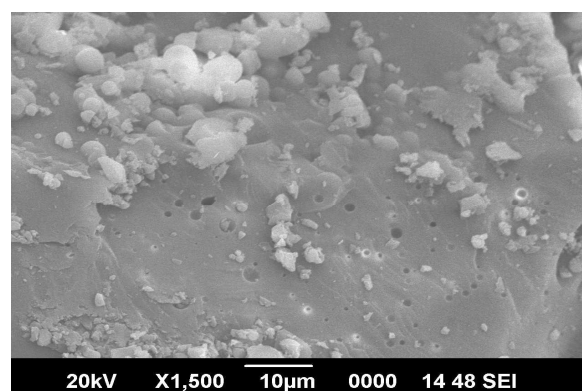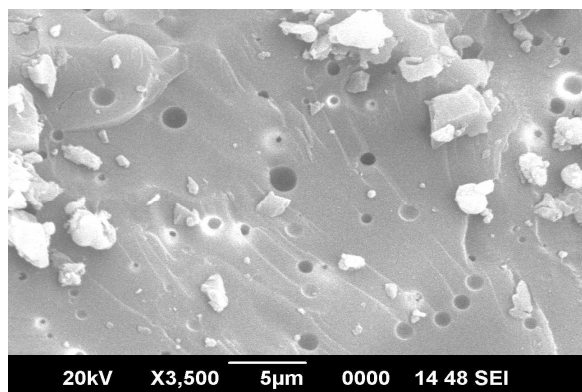
Figure 6 SEM Microgram of DHPPAF copolymer resin

Thermogravimetry Analysis of the Copolymer

The copolymer DHPPAF has been subjected to thermo gravimetric analysis and data used to assess the degradation pattern. The thermal decomposition behavior curve for the resin is depicted in figure 7 which exhibits four stage decomposition and its ranges are incorporated in the table 4.The first stage decomposition was slow and ranged between 40-260 ^{0}C corresponds to mass loss of 5.68% found and 5.96% calculated which may have been due to entrapped water molecule. The second stage decomposition starts from 260 ^{0}C to 370 ^{0}C,corresponding the gradual mass loss of 36.07% found and 36.09 % calculated which represents the degradation of two hydroxyl group and –$COCH_2CH_3$ group attached to aromatic benzene ring. The third stage decomposition at370-570 ^{0}C, corresponding to 70.45%   rapid mass loss of aromatic nucleus with two methylene group against calculated 70.52% . The fourth stage starts from 570 ^{0}C to 640 ^{0}C corresponding to removal of pyridylamine moiety with observed mass loss of 99.88% against calculated 100%. The half decomposition temperature for 2, 4-DHP-4-PAF-I copolymer is found to be 470^{0}C.
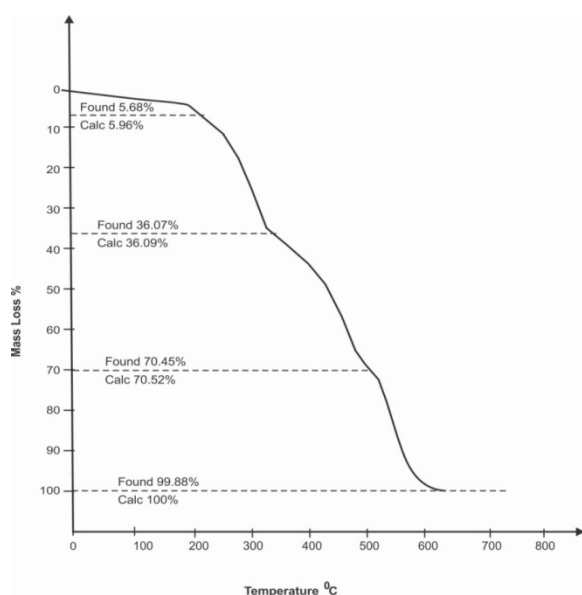

Figure 7 Decomposition pattern of DHPPAF copolymer resin

Table 4 Thermal degradation behavior of DHPPAF copolymer resin

Copolymer resin	Stages of decomposition	Temp range ^{0}C	Group degraded	% Weight loss	
				Observed	Calculated
DHPPAF	First	40 – 260	One water molecule	5.68	5.96
	Second	260 – 370	Two -OH and - $COCH_2CH_3$ group	36.07	36.09
	Third	370 – 570	Benzene ring along with two -CH_2 group	70.45	70.52
	Fourth	570 – 640	Pyridylamine moiety	99.88	100

Thermoanalytical Data

For the copolymer DHPPAFa plot of percentage mass loss versus temperature is presented in the Figure 6. To obtain the relative thermal stability of the copolymer, the method described by Sharp-Wentworth and Freeman-Carroll were 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 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 Sharp-Wentworth methods is nearly same. A representative thermal activation energy plot of Sharp-Wentworth (Figure 8) and Freeman-Carroll (Figure 9, 10) method for the copolymer have been shown. Thermodynamic parameters such as entropy change (ΔS), free energy change (ΔF), frequency factor (Z), apparent entropy change (S*), calculated on the basis of thermal activation energy (E_a) using equations (3), (4), (6) and (7). These values are incorporated in the table 5.

Entropy change

$$\text{Intercept}=\log\frac{KR}{h\Phi Ea}+\frac{\Delta S}{2.30\ R} \qquad (3)$$

where,

K= 1.3806 × 10^{-16} erg/deg/mole,
R = 1.987 cal/deg/mole,   h= 6.625 × 10^{-27} erg sec, Φ = 0.166,
ΔS = change in entropy,

Ea= activation energy from graph.

Free energy change

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

where,

ΔH = activation energy ,
T = temperature in Kelvin
ΔS = entropy change from equation (3)

Frequency factor

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

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

where,

Z= Frequency factor,
B= Calculated from (6),
log p(x) = Calculated from Doyle table corresponding to activation energy.

Apparent entropy change

$$S*=2.303R\log\frac{Zh}{RT_*} \qquad (7)$$

Where,

T_* = Temperature at which half of the compound decomposed from its total loss

Fairly good straight line plots are obtained using the two methods by ignoring some abnormal points. This indicates the decomposition of copolymer does not obey the first order kinetics perfectly. Due to abnormally low value of frequency factor, it may be concluded that the decomposition reaction of 2,4-DHP-4-PAF-I copolymer can be classed as a 'slow' reactionThe slow reaction is also predicted by negative values of entropy change. The negative values means the disorder is less and the reaction in carried out by more order manner, making it slower.There is no other obvious reason [30].

Table 5 Result of thermogravimetric analysis of DHPPAF I copolymer resin

Copolymer resin	Half decomposition temperature (T*),⁰C	Activation energy (Ea), KJ/mol		Entropy change (ΔS), (J)	Free energy change (ΔF),(KJ)	Frequency factor(Z) (sec⁻¹)	Apparent entropy (S*),(KJ)	Order of reaction (n)
		FC	SW					
DHPPAF	470	28.82	27.15	-285.41	240.66	46.89	-676.09	0.96

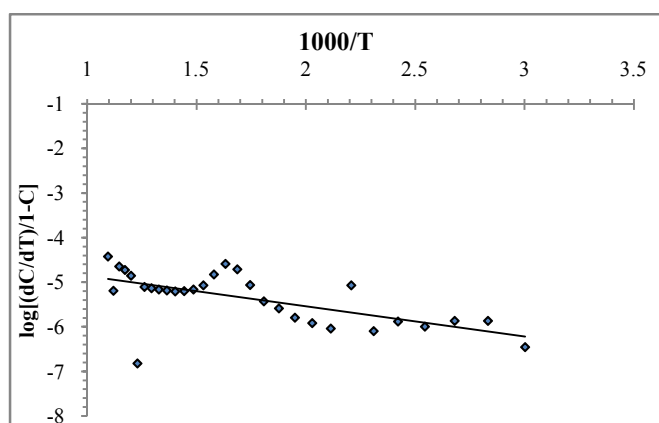FC=Freeman-Carroll,   SW= Sharp-Wentworth

Figure 8 Sharp-Wentworth plot of DHPPAFcopolymer resin
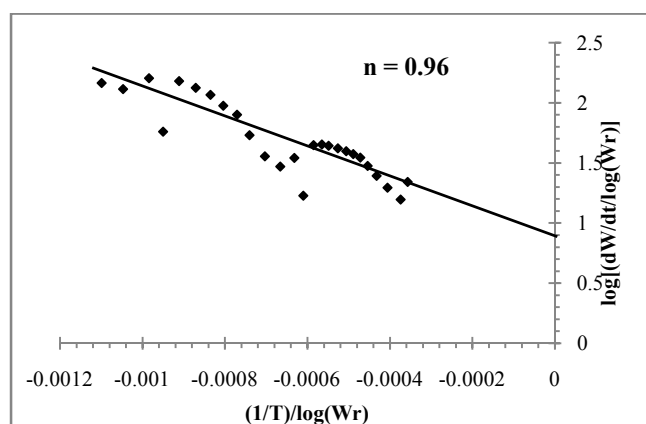

Figure 9 Freeman-Carroll plot of DHPPAF copolymer resin for activation energy and order of reaction
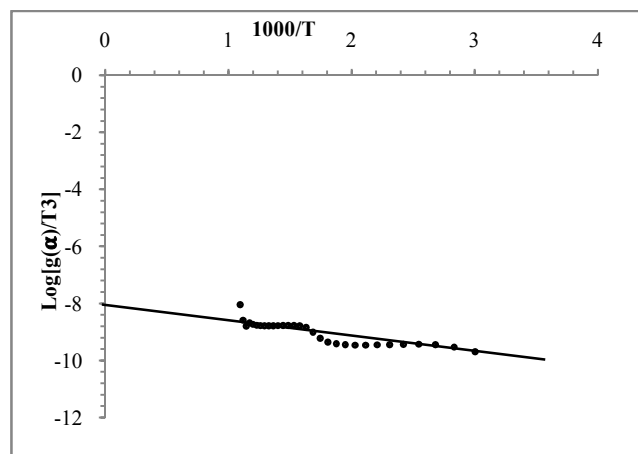

Figure10 Freeman-Carroll plot of DHPPAF copolymer resin

CONCLUSION

DHPPAF copolymer resin was prepared from 2,4-dihydroxypropiophenone,4-pyridylamine with formaldehyde in the presence of acid catalyst by condensation polymerization technique. The proposed structure of the synthesized copolymer has been confirmed from the elemental analysis,FT-IR and¹H-NMR spectral studies.Thermogram of targeted copolymer depicts four stages of decomposition. The values of activation energy evaluated by both Sharp-Wentworth and Freeman-Carroll methods are in good agreement with each other.Positive values of activation energy corresponds to energy of activation due to oxidation-reduction process of copolymer in the higher temperature range. The negative values for entropy indicate that the activated polymer has more ordered structure than the reactants. Low value of frequency factor may be concluded that the decomposition reaction of copolymer can be classified as slow reaction. Thermo gravimetric study reveals that DHPPAF copolymer resin is thermally stable even at high elevation temperature.

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