Isoconversional and Thermal Methods of Kinetic Analysis of 2,4-Dihydroxybenzophenone Copolymer Resin

Wasudeo B. Gurnule,[1] S. S. Butoliya[2]

[1]Department of Chemistry, Kamla Nehru Mahavidyalaya, Sakkardara square, Nagpur-440009, India
[2]Department of Chemistry, Laxminarayan Institute of Technology, R.T.M. Nagpur University, Nagpur-440010, India

ABSTRACT: A copolymer (2,4-DHBPOF) synthesized by the condensation of 2,4-dihydroxybenzophenone and oxamide with formaldehyde in the presence of acid catalyst with varying the molar proportions of the reacting monomer. Composition of the copolymer has been determined by elemental analysis. The copolymer has been characterized by UV–visible, FTIR, and ^{1}H NMR spectroscopy. The morphology of synthesized copolymer was studied by scanning electron microscopy (SEM). The activation energy (E_a) and thermal stability calculated by using Sharp-Wentworth, Freeman–Carroll, and Freidman's method. Thermogravimetric analysis (TGA) data were analyzed to estimate the characteristic thermal parameters. Freeman–Carroll and Sharp Wentworth methods have been used to calculate activation energy and thermal stability. The activation energy (E_a) calculated by using the Sharp-Wentworth has been found to be in good agreement with that calculated by Freeman–Carroll method. Thermodynamic parameters such as free energy change (ΔF), entropy change (ΔS), apparent entropy change (S^*), and frequency factor (Z) have also been evaluated based on the data of Freeman–Carroll method. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 122: 2181–2188, 2011

Key words: copolymer; thermogravimetric analysis; degradation; kinetics; activation energy

INTRODUCTION

A wide variety of thermally stable polymers have been synthesized and the sequences of their thermal stabilities have been predicted from their thermogram (TG) data. Michael et al.[1] studied the thermal degradation of 8-hydroxyquinoline–guanidine–formaldehyde terpolymers. Sharp-Wentworth and Freeman–Carroll methods have been used to calculate the activation energy and thermal stability of the terpolymer. Thermodynamic parameters and order of reaction have also been calculated on the basis of data of Freeman–Carroll method.

Polymeric chelates of azelaoyl bis-*p*-chlorophenyl urea have been synthesized by Bonde et al.[2,3] Thermal data of these polychelates have been analyzed by Freeman–Carroll and Sharp Wentworth methods to find out various kinetic and thermodynamic parameters. Shah et al.[4] have studied the thermal analysis of the salicylic acid–formaldehyde–resorcinol polymer at the heating rate of 10°C min^{-1} in N$_2$ atmosphere. The activation energy (E_a) of various steps has also been calculated.

Jadhao et al.[5] and Michael et al.[6] carried out thermal studies of the resins to determine their mode of decomposition, activation energy, order of reaction, frequency factor, entropy change, free energy, and apparent entropy change. Freeman–Carroll and Sharp-Wentworth methods have been applied for the calculation of kinetic parameters, whereas the data from Freeman–Carroll method has been used to determine various thermodynamic parameters. To synthesize polymers having numerous practical applications, there is a need to investigate the effect of heat on the polymers to establish their thermal stability. It must be pointed out that all the methods proposed have been developed by assuming that both activation energy and kinetic model do not change along the process. However, it has concluded from free-model kinetic methods of analysis that the activation energy is a function of the reacted fraction.[7–10]

In an earlier communication[11–13] from this department, number of such copolymers has been reported. However, no work has been carried out on the synthesis, characterization, and thermal degradation studies of the copolymer from 2,4-dihydroxybenzophenone, oxamide, and formaldehyde. The synthesized resin may be used as semiconducting material, ion-exchanger, and luminescent materials.

EXPERIMENTAL

Chemicals

2,4-Dihydroxybenzophenone, oxamide, and formaldehyde (37%) were purchased from Merck, India. Solvent such as *N,N*-dimethyl formamide and dimethylsulphoxide were used after distillation. All other chemicals used were of chemically pure grade.
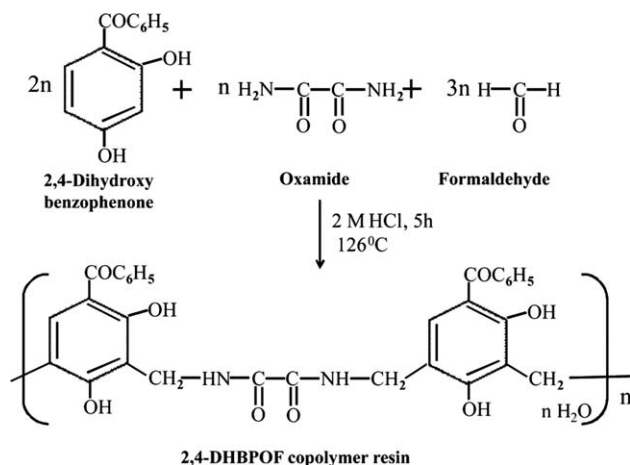
Scheme 1 Synthesis of 2,4-DHBPOF copolymer.

Synthesis of 2,4 DHBPOF copolymer

The 2,4-DHBPOF copolymer was prepared by condensing 2,4-dihydroxy benzophenone (4.28 g, 0.2 mol), oxamide (0.88 g, 0.1 mol), and formaldehyde (10.5 mL, 0.3 mol) with the molar ratio of 2 : 1 : 3 in the presence of 2M HCl as a catalyst (Scheme 1). The reaction mixture was heated at 126 ± 2°C in an oil bath for 5 h. The solid product obtained was immediately removed from the flask as soon as the reaction period was over. It was repeatedly washed with hot water to remove unreacted monomers. The air-dried copolymer was extracted with ether to remove excess of 2,4-dihydroxy benzophenone–formaldehyde copolymer, which may be present along with 2,4-DHBPOF copolymer. It was further purified by dissolving in 8% NaOH solution and filtered. It was then precipitated by dropwise addition of 1 : 1 (v/v) conc. HCl/water with constant stirring and filtered. The process was repeated twice. The resulting polymer sample was washed with boiling water and dried in vacuum at room temperature. The purified copolymer was finally ground well to pass through a 300-mesh size sieve and kept in vacuum over silica gel. The yield of this copolymer resin found to be 86.38% (Table I).

Characterization of copolymer

The copolymer was subjected to elemental analysis for C, H, N on a Colemann C, H, N analyzer. The number average molecular weight ($\overline{M_n}$) was determined by nonaqueous conductometric titration in dimethyl formamide (DMF) using ethanolic KOH as the titrant. A plot of the specific conductance against the milliequivalent potassium hydroxide required for neutralization of 100 g of copolymer was plotted.

Electronic absorption spectrum of the copolymer in DMF was recorded on Shimadzu double beam spectrophotometer in the range of 190–700 nm. Infrared spectra of copolymer was recorded in nujol mull on Perkin-Elmer-spectrum RX-I spectrophotometer in the range of 4000–500 cm^{-1}. Proton NMR spectra of newly prepared copolymer has been scanned on a Bruker Advance–II 400 MHz NMR spectrophotometer and DMSO-d_6 was used as a solvent. The surface analysis was performed using scanning electron microscope at different magnifications. Scanning electron microscopy (SEM) has been scnanned by JEOL JSM-6380A analytical scanning electron microscope at VNIT, Nagpur (M.S.).

The nonisothermal thermogravimetric analysis was performed in air atmosphere with heating rate of 10°C min^{-1} using 5–6 mg of samples in platinum crucible from temperature of 40 to 800°C, and thermogram was recorded for 2,4-DHBOF copolymer sample at Sophisticated Instrumentation Center for Analytical Research Testing (SICART), Vallabhvidya Nagar, Gujarat.

Theoretical considerations

To provide further evidence regarding the degradation system of analyzed compounds, we derived the TG curves by applying an analytical method proposed by Sharp-Wentworth, Freeman–Carroll and Freidman.

Friedman method

Friedman[14] provides the following expression for thermal degradation kinetic studies based on Arrhenius equation:

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln(Z) + n \cdot \ln(1 - \alpha) - \left(\frac{Ea}{RT}\right) \quad (1)$$

where α is the conversion at time t, R is the gas constant (8.314 J mol^{-1} K^{-1}), and T is the absolute

TABLE I
Physical and Elemental Data of 2,4-DHBPOF Copolymer

Copolymer	Reactants					Elemental analysis (%)					
	2,4-DHBP (mol.)	Oxamide (mol.)	Formaldehyde (mol.)	Catalyst 2M HCl (aq) (mL)	Yield (%)	C		H		N	
						Calc.	Found	Calc.	Found	Calc.	Found
2,4-DHBPOF	0.2	0.1	0.3	200	86.38	67.26	67.86	4.52	4.55	5.06	5.87

temperature. The plot of $\ln(d\alpha/dt)$ versus $1/T$ should be linear with the slope E_a/R, from which E_a can be obtained. The plots (Fig. 8) give the activation energies at different stages of degradation reaction takes place.

This isoconversional (model-free) kinetic methods use to check the variation of the apparent activation energy values with degree of degradation. This kinetic analysis should be a starting point for obtaining the useful information on the behavior of the sample.

Freeman–Carroll method

The straight-line equation derived by Freeman and Carroll,[15] which is in the form of

$$\frac{\Delta \log dW/dt}{\Delta \log W_r} = n - \frac{E_a}{2.303\ R} \cdot \frac{\Delta(1/T)}{\Delta \log W_r} \tag{2}$$

where

dW/dt = rate of change of weight with time.
$W_r = W_c - W$
W_c = weight loss at completion of reaction.
W = fraction of weight loss at time t.
E_a = energy of activation.
N = order of reaction.

The plot between the terms $\frac{\Delta \log dW/dt}{\Delta \log W_r}$ versus $\frac{\Delta 1/T}{\Delta \log W_r}$ gives a straight line from which slope, we obtained energy of activation (E_a) and intercept on Y-axis as order of reaction (n). The change in entropy (ΔS), frequency factor (Z), and apparent entropy (S^*) can also be calculated by further calculations.

Sharp–Wentworth method

Using the equation derived by Sharp and Wentworth,[16]

$$\log \frac{dC/dT}{1-C} = \log A/\beta - \frac{Ea}{2.303R} \cdot \frac{1}{T} \tag{3}$$

where

dC/dT = rate of change of fraction of weight with change in temperature.
β = linear heating rate dT/dt.
By plotting the graph between $\log \frac{dC/dT}{1-C}$ versus $\frac{1}{T}$, we obtained the straight line, which give energy of activation (E_a) from its slope.

RESULTS AND DISCUSSION

The newly synthesized and purified 2,4-DHBPOF copolymer was found to be yellow in color. The copolymer was soluble in DMF, DMSO, THF, concentrated H_2SO_4, and NaOH solution and insoluble in almost all other organic solvents. The melting point
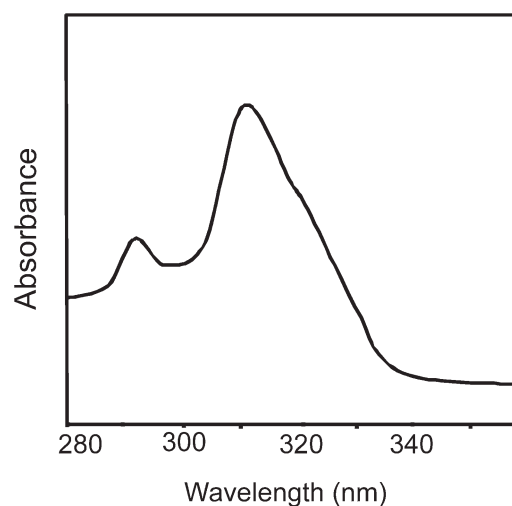

Figure 1 UV-Visible spectra of 2,4-DHBPOF copolymer.

of these copolymers is in the range of 350–400°C. This resin was analyzed for carbon, hydrogen, and nitrogen content (Table I).

Molecular weight of copolymer has been estimated by conductometric titration in nonaqueous media. The number average molecular weight ($\overline{M_n}$) could be obtained by multiplying the ($\overline{DP}$) by the formula weight of the repeating unit.[17] The molecular weight for 2,4-DHBPOF copolymer found to be 10,507.

The UV–visible spectra (Fig. 1) of the 2,4 DHBPOF copolymer samples in pure DMF was recorded in the region 190–700 nm at a scanning rate of 100 nm min^{-1} and at a chart speed of 5 cm min^{-1}. The copolymer sample displayed two characteristic broad bands at 220–260 and 270–320 nm. These observed positions for the absorption bands indicate the presence of a carbonyl group (ketonic) having a carbon–oxygen double bond that is in conjugation with the aromatic nucleus. The latter band (more intense) can be accounted for $\pi \rightarrow \pi^*$ transition, whereas the former bond (less intense) may be due to $n \rightarrow \pi^*$ electronic transition.[18]

The bathochromic shift (shift toward longer wavelength) from the basic values of the C=O group viz. 320 and 240 nm, respectively, may be due to the combined effect of conjugation and phenolic hydroxyl group (auxochromes).[19,20] The ε_{max} values may be due to introduction of more and more chromophores (carbonyl group) and auxochromes (phenolic —OH groups) in the repeated unit of the copolymer.[21,22]

Infrared spectra of the 2,4-DHBPOF copolymer is shown in Figure 2, and the IR spectral data are tabulated in Table II. From the IR spectral studies, it has been revealed that a very broad band appeared in the region 3277–3422 cm^{-1} and may be assigned to the stretching vibration of phenolic OH groups
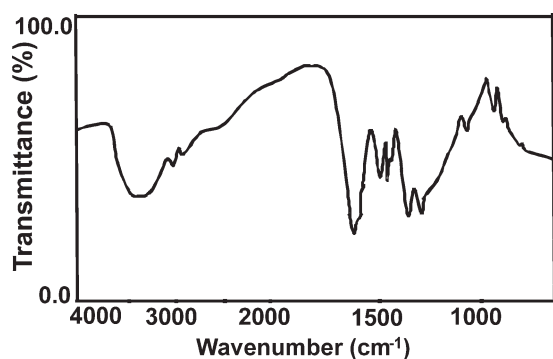
Figure 2 Infrared spectra of 2,4-DHBPOF copolymer.

exhibiting intermolecular hydrogen bonding with carbonyl (C=O) groups present in oxamide moiety.[11,12] The bands observed at 1280–1287 cm^{-1} suggest the presence of methylene (—CH$_2$—) bridges.[11] A sharp strong peak at 1490–1498 cm^{-1} may be ascribed to aromatic skeletal ring. The presence of —NH bridge of oxamide moiety may be assigned to the sharp strong band[23] at 2362–2384 cm^{-1} that seems to be merged with the very broad band of the phenolic hydroxy group. The band observed at 1619–1623 cm^{-1} may be ascribed to C=O group. The 1,2,3,4,5 pentasubstitution of 2,4-dihydroxybenzophenone rings can be recognized from sharp and medium absorption bond appearing at 914–914.6 cm^{-1}.[12]

The ^{1}H NMR spectra of copolymer was scanned in DMSO-d_6. The spectral data is given in the Table III, and the spectrum is presented in Figure 3. From the spectrum, it is revealed that 2,4-DHBPOF copolymer gave rise to different patterns of ^{1}H NMR spectra, as the 2,4-DHBPOF copolymer possesses sets of proton having different electronic environment. The weak multiplate signals (unsymmetrical pattern) in the region δ 9.2–9.5 ppm are due to aromatic protons. The methylenic protons of the Ar-CH$_2$-N- moiety may be recognized as signal appearing in the region δ 0.9–1.9 ppm.[23,24] The medium triplet signal appeared at 3.3–4.6 ppm may be due to amido protons —CH$_2$—NH—CO— polymer chain. The signals in the range of δ 7.6–7.9 ppm are attributed to phenolic hydroxy proton. This significant downfield chemical

TABLE III
^{1}H NMR Spectral Data of 2,4-DHBPOF Copolymer in DMSO-d_6

Nature of proton assigned	Chemical shift (δ) ppm of 2,4-DHBPOF copolymer	
	Observed chemical shift	Expected chemical shift
Aromatic proton (unsymm. pattern)	7.4	9.2–9.5
Proton of Ar-OH (phenolic)	7.68	7.0–7.8
Amido proton of —CH$_2$—NH—CO— linkage	3.3–4.2	3.0–4.5
Methylene proton of Ar-CH$_2$-NH moiety	1.1–1.5	1.0–2.0

shift of the protons of the phenolic OH groups, clearly indicate intermolecular hydrogen bonding of —OH with the carbonyl group present in the oxamide moiety.[11,23,24]

Scanning electron microscopy

Surface analysis has found great use in understanding the surface features of the materials. The morphology of the reported resin sample was investigated by scanning electron micrographs at different magnification, which are shown in Figures 4(a,b), respectively. It gives the information of surface topography and defect in the structure. The resin appeared to be dark drawn in color. The morphology of polymer resin shows spherulites and fringed model. The spherules are complex polycrystalline formation having as good as smooth surface. This indicates the crystalline nature of 2,4-DHBPOF copolymer resin sample. The morphology of resin
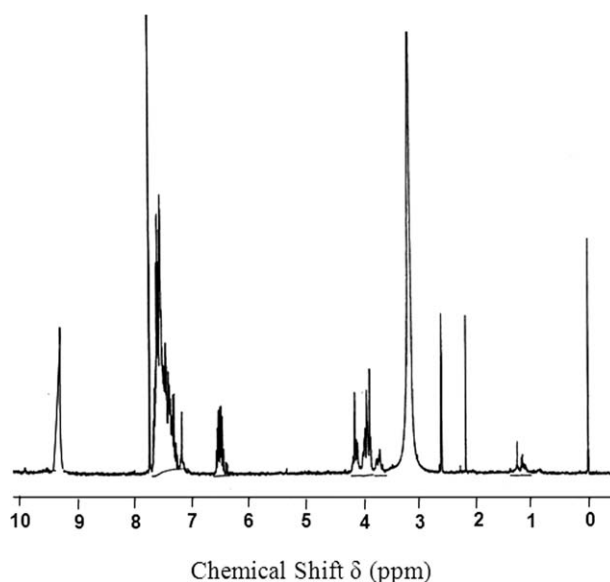
TABLE II
IR Frequencies of 2,4-DHBPOF Copolymer

Assignments	Observed wave number	Expected wave number
—OH (phenolic)	3,422.3 b,st	3,200–3,500
=NH (amido)	2,362.8 sh,w	2,250–2,450
=C=O (oxamide moiety)	1,619.5 sh,st	1,600–1,650
Aromatic ring	1,498.7 sh,w	1,450–1,545
=CH$_2$ (methylene bridges	1,287.8 sh,m	1,200–1,330
1,2,3,4,5 substitution in benzene skeleton	914 sh,w	850–950

sh, sharp; b, broad; st, strong; m, medium; and w, weak.

Figure 3 NMR spectra of 2,4-DHBPOF copolymer.
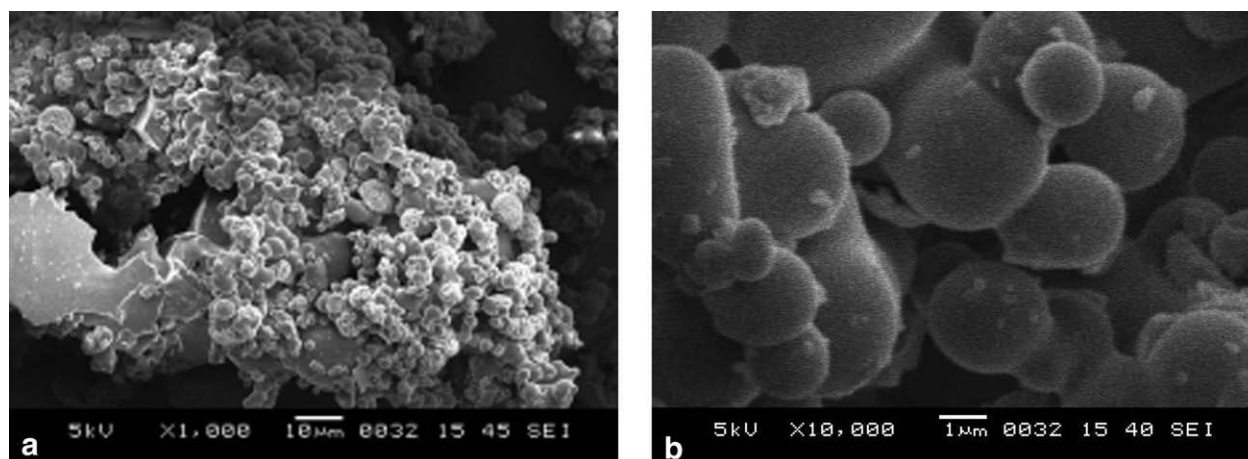
Figure 4 (a) SEM of 2,4-DHBPOF copolymer and (b) Optical photograph of 2,4-DHBPOF copolymer.
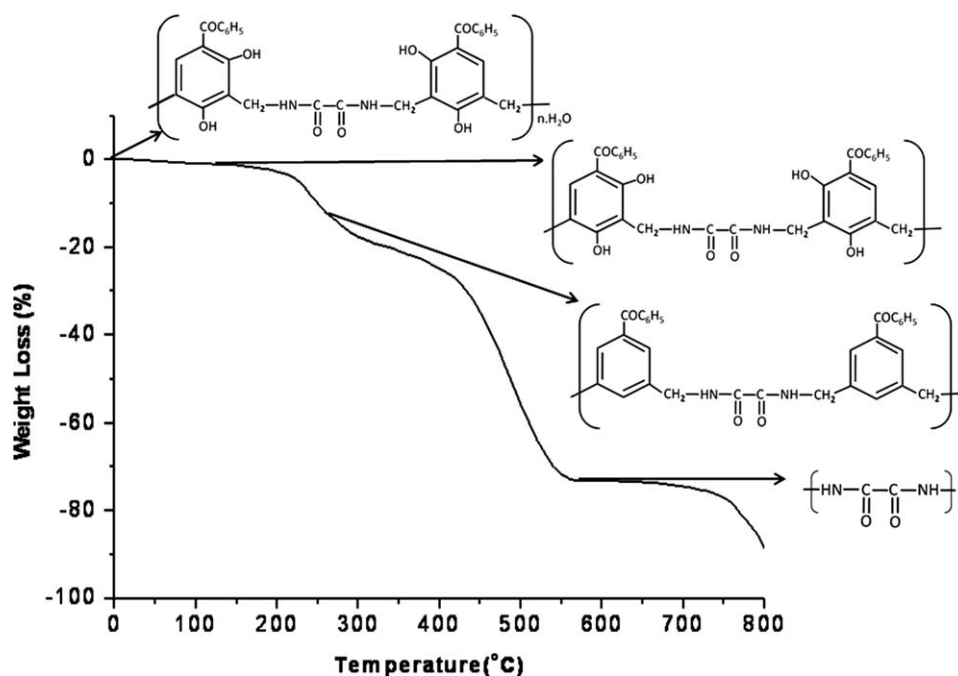

Figure 5 TG curve of 2,4-DHBPOF copolymer.

polymer shows also a fringes model of the crystalline amorphous structure. The extent of crystalline character depends on the acidic nature of the monomer. However, the photograph shows the fringed and scatted nature having shallow pits represent the transition between crystalline and amorphous. The resin exhibits more amorphous characters with closed packed surface having deep pits. Thus, by SEM micrographs morphology of the resin shows the transition between crystalline and amorphous nature, when compare to the other resin, the 2, 4-DHBPOF copolymer resin is more amorphous in nature, hence, shows higher metal ion exchange capacity.

TABLE IV
Thermogravimetric Data of 2,4-DHBPOF Copolymer Corresponding to Heating Rate of 10°C min^{-1}

Copolymer	Percentage of weight loss at various temperature (°C)				T_{half} (°C)	E_a (KJ mol^{-1})		Thermodynamic parameters			
	110	290	530	800		FC	SW	ΔS	Z	S^*	n
2,4-DHBPOF	3.26	15.5	53.6	87.6	490	21.88	21.03	8.42	749.22	−23.00	0.891

TABLE V
Comparison of Activation Energy (E_a) at Different Stages by Different Methods for 2,4-DHBOF Copolymer

Copolymer	Temperature range	Groups	Wt. loss (%)	Activation (E_a) (KJ mol^{-1})		
				Sharp-Wentworth	Freeman–Carroll	Freidman
2,4-DHBPOF	50–110	Loss of H$_2$O molecule	03.26	14.91	16.02	25.32
	110–290	Degradation of ⁻OH group	15.50	74.22	14.61	12.53
	290–530	Loss of Phenone group attached to aromatic ring	53.60	28.20	10.91	08.76
	530–800	Loss of aromatic ring along with methylene group	87.60	21.15	46.96	15.51

The polymer under study is copolymer, and hence, it is very difficult to assign their exact structures. Based on the nature and reactive, position of the monomer, elemental analysis, electronic, FTIR, H^1 NMR spectra, SEM, and molecular weight, the most probable structures have been proposed for these copolymer resins as shown in Scheme 1.

Thermogravimetric analysis of 2,4-DHBPOF copolymer

Thermogram of thermogravimetric analysis (TGA) of this copolymer is shown in Figure 5. Thermogram of copolymer depicts three-step decomposition after loss of water molecule in the temperature range 100–800°C. At first, upto 100°C corresponds to loss of 3.26%, which is due to loss of water molecule against calculated (3.84%). The first step of slow decomposition between 100 and 320°C corresponds to 15.57% mass loss, which may attribute to loss of hydroxy groups against calculated 15.09% loss present per repeat unit of the polymer. The second-step decomposition starts from 345 to 558°C that represents degradation of phenone group attached to aromatic nucleus (56.63% found and 57.98% calculated). The third step of decomposition starts from 558 to

800°C corresponds to 87.6% loss of aromatic nucleus, along with methylene bridges against calculated 86.91% loss (Table IV).

Thermoanalytical data

A plot of percentage mass loss versus temperature is shown in the Figure 5 for a representative 2, 4-DHBPOF copolymer. To obtain the relative thermal stability of the copolymer, the method described by Sharp-Wentworth, Freeman–Carroll, and Freidman was 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 using thermal decomposition data and then 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 Freidman is nearly same and "average E_a" by Sharp-Wentworth is nearly double than both methods. The activation energy calculated by these methods is depicted in Table V. However, the error in activation energies obtained from the Sharp-Wentworth isoconversional method is significant and largely increases as far as conversion increases. On the
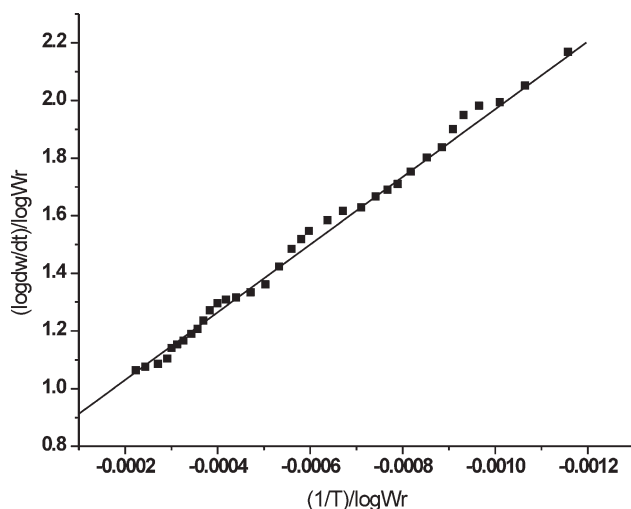

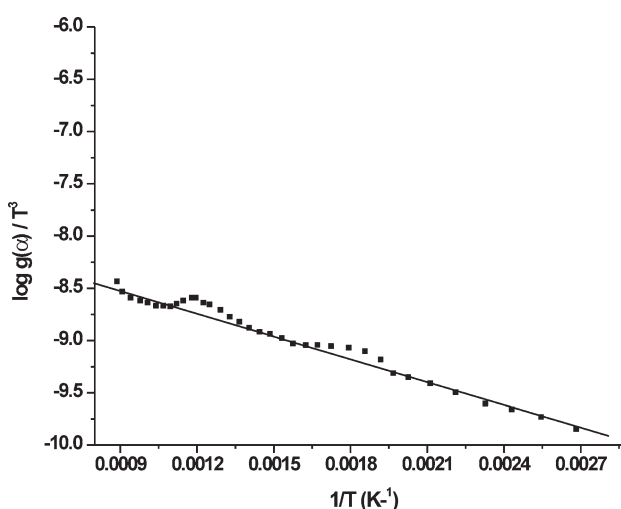**Figure 6** Sharp-Wentworth plot of 2,4-DHBPOF copolymer.

Figure 7 Freeman–Carroll plot of 2,4-DHBPOF copolymer.

other hand, it has been considered of interest to analyze the behavior of the process constitute by two competitive reactions that would lead to an apparent dependence between E_a and α when analyzed by isoconversional method, despite such dependence is not real.[25]

A representative thermal activation energy plot of Sharp-Wentworth (Fig. 6), Freeman–Carroll (Figs. 7 and 8), and Freidman (Fig. 9) method for the copolymer has been shown. Thermodynamic parameters such as entropy change (ΔS), frequency factor (Z), and apparent entropy change (S^*) calculated based on thermal activation energy (E_a) using eqs. (3)–(5). These values are given in (Table V).

(i) Entropy Change (ΔS):

$$Intercept = \log \frac{kR}{h\phi E_a} + \frac{\Delta S}{2.303R} \quad (4)$$

where,
$k = 1.3806 \times 10^{-16}$ erg deg^{-1} mol^{-1}
$R = 1.987$ cal deg^{-1} mol^{-1}
$h = 6.625 \times 10^{-27}$ erg sec
$\phi = 0.166$
ΔS = entropy change
E_a = activation energy from graph

(ii) Frequency Factor (Z):

$$B2/3 = \frac{\log Z.E_a}{R\phi} \quad (5)$$

$$B_{2/3} = \log 3 + \log 1 - 3 \sqrt{1 - \alpha} - \log p(x) \quad (a)$$

where, z = frequency factor,
B = calculated from equation (a)
$\log p(x)$ = calculated from Doyle table corresponding to activation energy

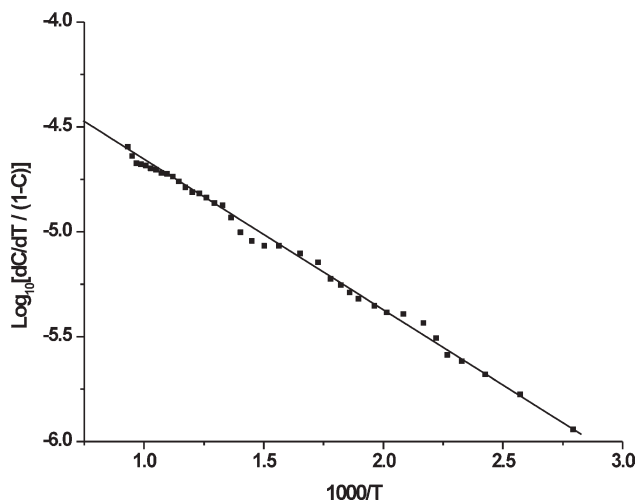(iii) Apparent entropy change (S^*):

Figure 8 Freeman–Carroll plot for activation energy of 2,4-DHBPOF copolymer.
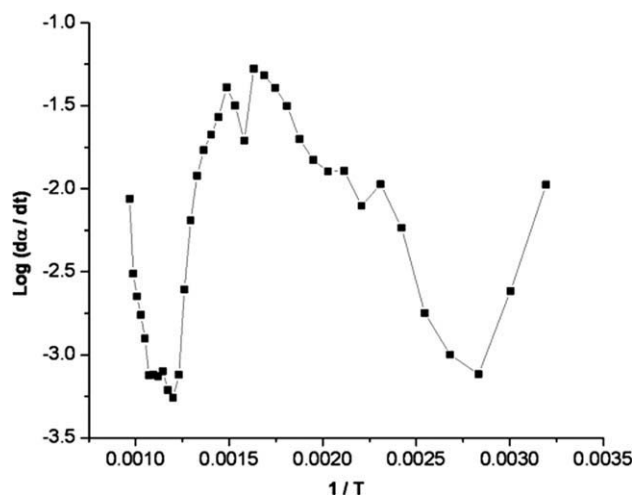

Figure 9 Freidman's plot for activation energy of 2,4-DHBPOF copolymer.

$$S* = 2.303R \ \log \frac{Zh}{RT} \quad (6)$$

where, T^* = temperature at which half of the compound decomposed.

The abnormally low value of frequency factor, it may be concluded that decomposition reaction of 2,4-DHBPOF copolymer can be classed as a "slow" reaction. There is no other obvious reason.[26] Fairly good straight-line plots are obtained using the two methods. This is expected since the decomposition of copolymer is known not to obey first order kinetic perfectly.[26]

CONCLUSIONS

1. The 2,4-DHBPOF copolymer based on the condensation polymerization of 2,4-dihydroxybenzophenone and oxamide with formaldehyde in the presence of acid catalyst has been prepared.
2. From the elemental analysis, UV–visible, FTIR, and ^{1}H NMR spectral studies the proposed structure of the 2,4-DHBPOF copolymer has been determined.
3. In TG, the energy of activation evaluated from the Freeman–Carroll and Sharp-Wentworth 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.
4. Low values of frequency factor (Z) may be concluded that the decomposition reaction of 2,4-dihydroxybenzophenone-oxamide-formaldehyde copolymer can be classified as "slow reaction."

References

1. Michael, P. E. P.; Barbe, J. M.; Juneja, H. D.; Paliwal, L. J. Eur Polym J 2007, 43, 4995.
2. Bonde, A. D.; Ukay, V. V.; Juneja, H. D.; Ghubde, R. S.; Husain, R. Mater Sci Eng B 2006, 132, 16.
3. Singru, R. N.; Zade, A. B.; Gurnule, W. B. J App Polym Sci 2008, 109, 859.
4. Shah, B. A.; Shah, A. V.; Bhatt, R. Iranian Polym J 2007, 16, 173.
5. Jadhao, M. M.; Paliwal, L. J.; Bhave, N. S. J App Polym Sci 2006, 1001, 227.
6. Michael, P. E. P.; Lingala, P. S.; Juneja, H. D.; Paliwal, L. J. J Appl Polym Sci 2004, 92, 2278.
7. Chen, H.; Liu, N.; Fang, W. Polym Degrad Stab 2006, 91, 1726.
8. Vlase, T.; Vlase, G.; Birta, N.; Doca, N. J Therm Anal Calorim 2007, 88, 631.
9. Khawam, A.; Flanagan, D. R. Thermichin Acta 2005, 93, 429.
10. Joraid, A. A. Themochim Acta 2007, 1, 456.
11. Rahangdale, S. S.; Zade, A. B.; Gurnule, W. B. J Appl Polym Sci 2008, 108, 747.
12. Tarase, M. V.; Zade, A. B.; Gurnule, W. B. J Appl Polym Sci 2008, 108, 738.
13. Gurnule, W. B.; Singru, R. N. J Therm Anal Calorim 2010, 100, 1027.
14. Freidman, H. L. J Polym Sci 1964, C6, 183.
15. Freeman, E. S.; Carroll, B. J Chem Rev 1958, 62, 394.
16. Sharp, J. B.; Wentworth, S. A. Anal Chem 1969, 41, 2060.
17. Jadhao, M. M.; Paliwal, L. J.; Bhave, N. S. J Appl Polym Sci 2008, 109, 508.
18. Silverstein, R. M.; Bassler, G. C. Spectrometric Identification of Organic Compounds; 2nd ed.; Wiley: New York, 1967, p 80.
19. Gurnule, W. B.; Juneja, H. D.; Paliwal, L. J. React Funct Polym 2002, 50, 95.
20. Gurnule, W. B.; Rahangdale, P. K.; Paliwal, L. J.; Kharat, R. B. Synth React Inorg Met-Org Chem 2003, 33, 1187.
21. Gurnule, W. B.; Rahangdale, P. K.; Paliwal, L. J.; Kharat, R. B. React Funct Polym 2003, 55, 255.
22. Gurnule, W. B.; Tarase, M. V.; Zade, A. B. J Appl Polym Sci 2010, 116, 619.
23. Lenka, S.; Parija, A.; Nayak, P. L. Polym Int 2007, 29, 103.
24. Gurnule, W. B.; Tarase, M. V.; Zade, A. B. J Appl Polym Sci 2010, 116, 619.
25. Tonbul, Y.; Yardakoc, K. Turk J Chem 2001, 25, 332.
26. Zhao, H.; Wang, Y. Z.; Wang, D. Y.; Wang, B.; Wu, B.; Clen, D. Q. Polym Degrad Stab 2003, 80, 135.