

Kinetics of Thermal Degradation Studies of Some New Terpolymers Derived from 2,4-Dihydroxypropiophenone, Oxamide, and Formaldehyde

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ABSTRACT: The terpolymers (2,4-DHPOF) have been synthesized by the condensation of 2,4-dihydroxypropiophenone with oxamide and formaldehyde in the presence of 2M HCl as catalyst with varying proportions of reactants. Terpolymer composition has been determined on the basis of their elemental analysis. The terpolymer has been characterized by UV-visible, IR, and ¹H NMR spectra. The thermal decomposition behavior of some new terpolymers was studied using thermogravimetric analysis in air atmosphere at heating rate of 10°C/min. Thermal decomposition curves are discussed with careful attention to minute details. The Freeman–Carroll and Sharp–Wentworth methods have been used to calculate activation energy and thermal stabil-

ity. Thermal activation energy (E_a) calculated with the help of these methods are in agreement with each other. Thermodynamic parameters such as free energy change (ΔF), entropy change (ΔS), apparent entropy change (S^*), and frequency factor (z) are also determined on the basis of the TG curves and by using data of the Freeman–Carroll method. The Friedman method evaluated the variation in the apparent activation energy changes by isoconversional (model-free) kinetic methods. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 619–627, 2010

Key words: thermogravimetric analysis (TGA); resin; polycondensation; synthesis

INTRODUCTION

The thermal degradation study of terpolymers has become a subject of interest. Study of thermal behavior of terpolymers in air at different temperature provides information about the nature of species produced at various temperatures due to degradation. Terpolymers having good thermal stability and catalytic activity have enhanced the development of polymeric materials. In this laboratory, extensive work on the thermal degradation of terpolymers has been undertaken.^{1–3} It is hoped that the study of terpolymers will lead to the production of polymer, which are both thermally stable and useful as fabricating materials. Patel et al.⁴ studied the thermal properties of copolymers and terpolymers. Zeman and Tokarova⁵ prepared urea–formaldehyde copolymers and studied their TGA and DTA data.

A wide variety of thermally stable polymers have been synthesized and the sequence of their thermal stabilities has been predicted from their TG data.

Chand and Bailor⁶ studied the thermal stabilities of metal ion- (β -diketone) polymers and suggested the sequence of thermal stabilities to be Be (II) > Cu (II) > Ni (II) > Zn (II) > Co (II). The kinetic properties of polymers have also been studied. The polycoordination of 4,4'-bis-(acetoacetyl) diphenyl ether with Be (acetyl acetate)⁷ was formed to proceed by a bimolecular mechanism. Various methods have been used to analyze the thermoanalytical data. Ozawa⁸ suggested the method of analyzing the thermoanalytical data for nonisothermal degradation of calcium oxalate and nylon-6 and considered the applicability of the method to other types of thermal analysis. They also proposed a method of analyzing thermal data by transforming them to equivalent isothermal data and utilizing linear relations to elucidate the mechanism of degradation.⁹

In the present communication, we report the relative thermal stabilities of some new terpolymers derived from 2,4-dihydroxypropiophenone, oxamide, and formaldehyde on the basis of their activation energies, calculated from nonisothermal TG data using the Sharp–Wentworth method^{10,11} as well as from isothermal TG data via (two well known methods)¹² widely used in the field of organic polymers. The tentative compositions and structures of the polymeric units have also been proposed. These

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TABLE I
Synthesis and Physical Data of 2,4-DHPOF Terpolymers

Terpolymers	Reactants			Catalyst 2M HCl (aq) (mL)	Yield (%)
	2,4-DHP (mol.)	Oxamide (mol.)	Formaldehyde (mol.)		
2,4-DHPOF-I	0.1	0.1	0.2	200	81.6
2,4-DHPOF-II	0.2	0.1	0.3	200	81.9
2,4-DHPOF-III	0.3	0.1	0.4	200	80.6
2,4-DHPOF-IV	0.4	0.1	0.5	200	82.3

display good agreement with the results of elemental analysis, electronic spectral, IR spectral, and ^1H NMR spectral studies.

EXPERIMENTAL

Chemicals

The chemicals 2,4-dihydroxypropiophenone, oxamide, and formaldehyde (37%) used are of analytical grade and chemically pure which is purchased from Merck, India. Solvents like *N,N*-dimethyl formamide and dimethylsulphoxide were used after distillation.

Synthesis of 2,4-DHPOF terpolymers

The 2,4-DHPOF-I terpolymer was prepared by condensing 2,4-dihydroxypropiophenone (1.6618 gm, 0.1 mol) and oxamide (0.8807 gm, 0.1 mol) with formaldehyde (7.5 mL, 0.2 mol) in the presence of 2M HCl as a catalyst at $126 \pm 2^\circ\text{C}$ in an oil bath for 5 h. The brown-colored solid terpolymer product obtained was immediately removed and extracted with diethyl ether to remove from excess 2,4-dihydroxypropiophenone-formaldehyde copolymer, which might be present along with the 2,4-DHPOF-I terpolymer. It was further purified by dissolving in 8% NaOH and then filtered. The terpolymer was then reprecipitated by drop wise 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 a vacuum at room temperature. The purified terpolymer wash finely ground to pass through 300-mesh size sieve and kept in a vacuum over silica gel. The yield of the terpolymer was found to be about 80–83% (Table I).

Similarly, the terpolymers viz. 2,4-DHPOF-II, 2,4-DHPOF-III, and 2,4-DHPOF-IV were synthesized by varying the molar ratios of the reacting materials, i.e., 2,4-dihydroxypropiophenone, oxamide, and formaldehyde in the ratios of 2 : 1 : 3, 3 : 1 : 4, and 4 : 1 : 5, respectively.

Characterization of terpolymers

The terpolymers were subject to microanalysis for carbon, hydrogen, and nitrogen on a Colemann C, H, and N analyzer at RSIC, Punjab University, Chandigarh. The number average molecular weight (\bar{M}_n) of the terpolymer resins was determined by nonaqueous conductometric titration in DMF against alcoholic KOH by using 25 mg of sample. A plot of the specific conductance against the milliequivalents KOH required for neutralization of 100 gm of terpolymer was made. Electronic absorption spectra of the terpolymers in DMSO was recorded on Shimadzu UV-Visible double beam spectrophotometer fitted with automatic pen chart recorder on thermosensitive paper in the range of 200–850 nm. Infrared spectra of 2,4-DHPOF terpolymers were recorded in nujol mull on Perkin-Elmer-spectrum RX-I

TABLE II
Thermogravimetric Data of Degradation of 2,4-DHPOF Terpolymer

Terpolymer	First stage			Second stage		
	$T_{\text{range } 1}^a$ ($^\circ\text{C}$)	$T_{\text{max } 1}^b$ ($^\circ\text{C}$)	W_1^c	$T_{\text{range } 2}^d$ ($^\circ\text{C}$)	$T_{\text{max } 2}^e$ ($^\circ\text{C}$)	W_2^f
2,4-DHPOF-I	221.10–300.59	272.56	12.95	300.59–532.16	529.59	70.67
2,4-DHPOF-II	203.11–297.70	269.43	14.19	297.70–612.37	541.32	76.62
2,4-DHPOF-III	175.92–359.65	274.65	19.17	359.65–623.14	520.94	83.89
2,4-DHPOF-IV	173.58–313.39	278.62	17.19	313.39–579.75	532.13	90.12

^a First degradation temperature range.

^b First temperature corresponding to the maximum degradation rate.

^c First maximum loss.

^d Second degradation temperature range.

^e Second temperature corresponding to the maximum degradation rate.

^f Second maximum loss.

TABLE III
Thermogravimetric Parameters Corresponding to Heating Rate of 10 °C/min of 2,4-DHPOF Terpolymer

Terpolymers	$T_{\text{half}}^{\text{a}}$ (°C)	E_a (KJ/mol.)		ΔS	z	S^*	n
		FC	SW				
2,4-DHPOF-I	491	23.93	16.33	8.75	1052.85	-24.65	0.88
2,4-DHPOF-II	499	26.80	24.12	8.30	994.52	-22.78	0.93
2,4-DHPOF-III	490	27.12	20.44	8.47	920.23	-22.86	0.87
2,4-DHPOF-IV	472	21.51	44.02	8.22	713.92	-23.11	0.96

^a Half decomposition temperature.

spectrophotometer in the range of 4000–500 cm^{-1} . ¹H NMR spectra were recorded on Bruker Advance-II 400 MHz proton NMR spectrometer DMSO- d_6 was used as a solvent.

Thermogravimetric analysis

The nonisothermal thermogravimetric analysis was performed in air atmosphere with heating rate of 10°C/min using 5–6 mg of samples in platinum crucible from temperature of 40–800°C, and thermograms are recorded for four samples. With the help of thermogravimetric data, which is reported in Table II, the thermal activation energies (E_a) and order of reaction (n) calculated. Also, other thermodynamic parameters such as free energy change (ΔF), entropy change (ΔS), apparent entropy change (S^*), and frequency factor (z) are determined and reported in the Table III.

RESULTS AND DISCUSSION

The resin samples were brown in color, insoluble in commonly used solvent, but it was soluble in DMF, DMSO, THF, pyridine, and concentrated H_2SO_4 . No precipitation and degradation occurs of resin in all the solvents. The melting point of these terpolymers are in the range of 540–560°C. These resins were analyzed for carbon, hydrogen, and nitrogen content (Table IV).

Characterization of terpolymers

Molecular weight of terpolymers was estimated by nonaqueous conductometric titration. The number average molecular weight (\overline{Mn}) could be obtained by multiplying the \overline{DP} by the formula weight of the repeating unit.¹³ The result of the molecular weight of terpolymers prepared using higher proportion of two monomers (2,4-DHP and O) has the highest molecular weight in the series. The molecular weight for 2,4-DHPOF-I, 2,4-DHPOF-II, 2,4-DHPOF-III, 2,4-DHPOF-IV are 5127.5, 7300.5, 8112.5, 10,337.5, respectively.

The electronic spectra of all 2,4-DHPOF terpolymers are shown in Figure 1. UV-visible spectra of all the purified terpolymers have been recorded in pure DMF. The perusal of the UV-visible spectra of terpolymers showed almost similar nature. The spectra of these terpolymers exhibit two absorption maxima in the region 280 nm and 320 nm. These observed positions of the absorption bands indicate the presence of carbonyl group (ketonic) processing double bond, which is in conjugation with the aromatic nucleus. The appearance of former band (more intense) can be accounted for $\pi \rightarrow \pi^*$ transition, whereas the later band (less intense) may be due to $n \rightarrow \pi^*$ 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 hydroxy group (auxochromes) is responsible for hyperchromic effect, i.e., ϵ_{max} higher values.¹⁴ The ϵ_{max} value gradually increases in the order: 2,4-DHPOF-I < 2,4-DHPOF-II < 2,4-DHPOF-III < 2,4-DHPOF-IV. This is in increasing order of ϵ_{max} values

TABLE IV
Elemental Analysis Data of 2,4-DHPOF Terpolymers

Terpolymers	Elemental analysis (%)					
	C		H		N	
	Calc.	Found	Calc.	Found	Calc.	Found
2,4-DHPOF-I	56.11	56.06	5.03	5.39	11.2	10.07
2,4-DHPOF-II	60.52	60.31	5.26	5.43	7.0	6.14
2,4-DHPOF-III	62.46	62.44	5.36	5.49	5.09	4.41
2,4-DHPOF-IV	63.54	63.98	5.41	5.46	4.0	3.44

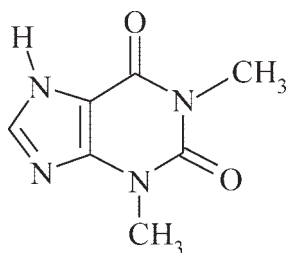


Figure 1 Electronic spectra of terpolymers: (1) 2,4-DHPOF-I (2) 2,4-DHPOF-II (3) 2,4-DHPOF-III (4) 2,4-DHPOF-IV.

may be due to introduction of more and more chromophores (carbonyl group) and auxochromes (phenolic-OH groups) in the repeat unit of the terpolymer resins.¹⁵ This observation is in good agree-

ment with the proposed most probable structures of these terpolymers.

The IR-spectra of all four 2,4-DHPOF terpolymers are presented in Figure 2. The IR-spectra revealed that all these terpolymers give rise to nearly similar pattern of spectra (Table V). A broad band appeared in the region $3700\text{ cm}^{-1} - 3250\text{ cm}^{-1}$ may be assigned to the stretching vibration of the phenolic hydroxy groups exhibiting intermolecular hydrogen bonding.¹⁵ The presence of weak peak at $3000\text{ cm}^{-1} - 2975\text{ cm}^{-1}$ describes the $-\text{NH}-$ in biuret moiety may be ascribed in the terpolymeric chain.¹⁵ The presence of methyl and methylene vibrations at $2950\text{ cm}^{-1} - 2935\text{ cm}^{-1}$ gives sharp and weak peaks. The sharp band displayed at $1640\text{ cm}^{-1} - 1615\text{ cm}^{-1}$ may be due to the stretching vibration of carbonyl group

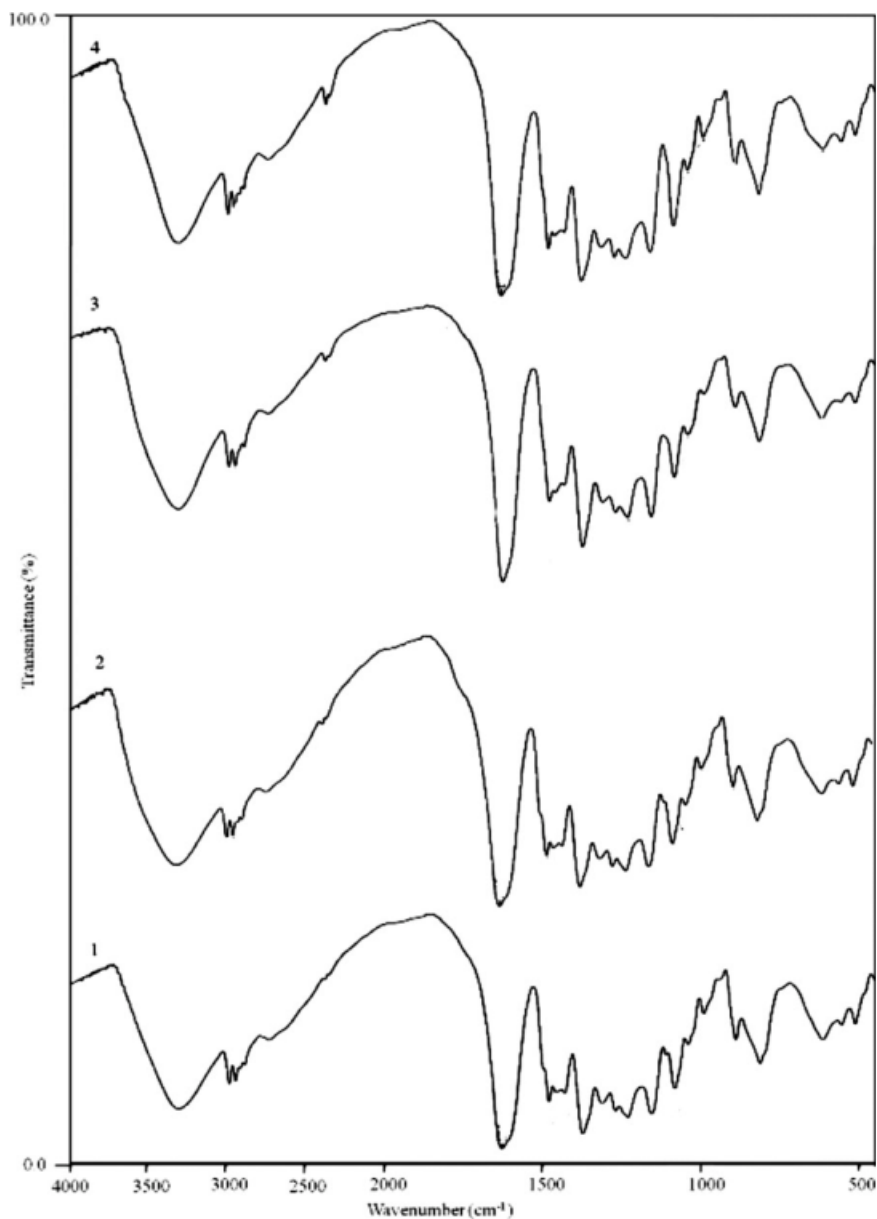


Figure 2 Infrared spectra of terpolymers: (1) 2,4-DHPOF-I (2) 2,4-DHPOF-II (3) 2,4-DHPOF-III (4) 2,4-DHPOF-IV.

TABLE V
IR Frequencies of 2,4-DHPOF Terpolymers

Assignment	Observed wave number (cm ⁻¹)			
	2,4-DHPOF-I	2,4-DHPOF-II	2,4-DHPOF-III	2,4-DHPOF-IV
—OH (phenolic)	3288.9 b, st	3300.1 b, st	3291.8 b, st	3300.2 b, st
>NH (amido)	2978.9 sh, w	2978.3 sh, w	2978.6 sh, w	2978.5 sh, w
—CH ₃ , >CH ₂ assymm., symm. vib	2939.3 sh, w	2938.6 sh, w	2938.9 sh, w	2939.0 sh, w
>C=O (ketonic and biuret moiety)	1627.5 sh, st	1626.8 sh, st	1627.5 sh, st	1628.4 sh, st
Aromatic ring	1478.8 sh, w	1478.4 sh, w	1479.0 sh, w	1479.4 sh, w
>CH ₂ (methylene bridges)	1373.7 sh, m	1374.2 sh, m	1373.9 sh, m	1373.7 sh, m
1,2,3,4,5 substitution in benzene skeleton	890.3 sh, w	890.7 sh, w	889.8 sh, w	889.8 sh, w

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

of both, ketonic as well as biuret moiety.^{15,16} The sharp and weak bond obtained at 1370 cm⁻¹ – 1275 cm⁻¹ suggests the presence of —CH₂— methylene bridges¹⁶ in the terpolymer chain. The presence of 1, 2, 3, 4, 5-pentasubstitution of aromatic ring is recognized from the weak bond appearing at 905 cm⁻¹ – 860 cm⁻¹, respectively.¹⁶

¹H NMR spectra of 2,4 DHPOF terpolymers are shown in Figure 3 and show a weak singlet signals in the region 9.46 ppm–9.22 ppm which due to aromatic proton (Ar—H)¹⁶ (Table VI). Also, the weak singlet signal appearing at 7.98 ppm–7.62 ppm may be due to proton of Ar—OH (phenolic —OH). The medium triplet signal appeared at 7.58–7.65 ppm may be due to amido protons —CH₂—NH—CO— of polymer chain.¹⁶ Also the medium doublet signal in the range of 6.52–6.54 ppm is attributed to the protons of methylenic bridge Ar—CH₂—NH— of polymeric chain. A medium quartet peaks appeared at 6.44–6.55 ppm may be assigned to methylene protons of Ar—CO—CH₂—CH₃. Also, the methyl protons of Ar—CO—CH₂—CH₃ assigned to the peaks at 2.91–2.96 ppm. The methylenic bridge in between —Ar—CH₂—Ar— is assigned in the region 3.89 ppm which is present only in 2,4-DHPOF-III and 2,4-DHPOF-IV terpolymers.¹⁷

On the basis of the nature and reactive position of the monomer elemental analysis, electronic, IR, ¹H NMR spectra, and molecular weight, the most probable structures have been proposed for these terpolymers as shown in Figure 4.

Thermogravimetric analysis

The thermal stability of terpolymers is evaluated by dynamic thermogravimetric analysis in air atmosphere with heating rate of 10°C/min.

TG of 2,4-DHPOF-I terpolymer

Thermogram of TGA of this terpolymer is shown in Figure 5. Thermogram of terpolymer depicts four-step decomposition in the temperature range 40–800°C. The first step slow decomposition between 40 and 170°C corresponds to 6.68% loss which may attributed to loss of a water molecule against calculated 6.08% present per repeat unit of the polymer. The second step decomposition starts from 170 to 460°C which represents degradation of —COCH₂CH₃

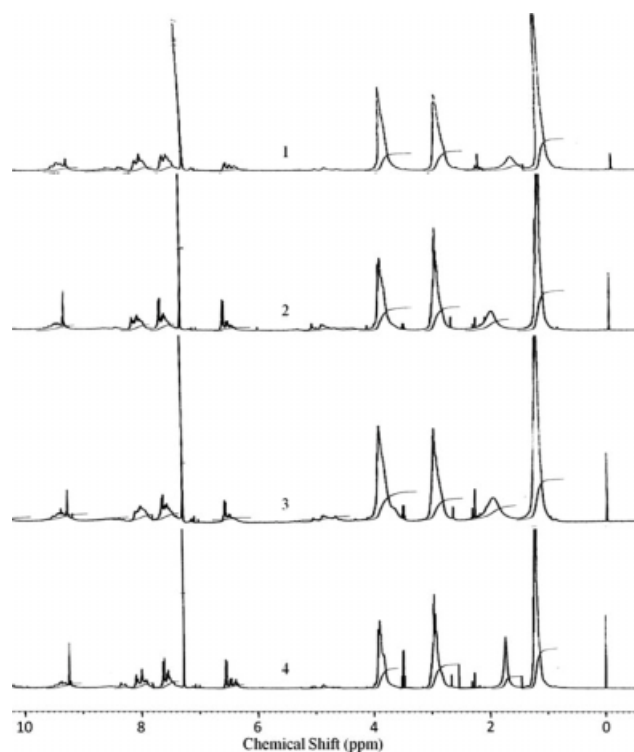


Figure 3 NMR spectra of terpolymers: (1) 2,4-DHPOF-I, (2) 2,4-DHPOF-II, (3) 2,4-DHPOF-III, and (4) 2,4-DHPOF-IV.

TABLE VI
 ^1H NMR Spectral Data of 2,4-DHPOF Terpolymers in DMSO- d_6

Chemical shift (δ) ppm of terpolymer				Nature of proton assigned
2,4-DHPOF-I	2,4-DHPOF-II	2,4-DHPOF-III	2,4-DHPOF-IV	
9.46	9.22	9.38	9.22	Aromatic proton (unssymm. Pattern)
7.98	7.87	7.65	7.62	Proton of Ar—OH (phenolic —OH)
7.58–7.61	7.60–7.62	7.59–7.65	7.60–7.62	Amido proton of —CH ₂ —NH—CO— linkage
6.52–6.54	6.52–6.54	6.52–6.54	6.52–6.54	Methylene proton of Ar—CH ₂ —NH moiety
6.44–6.54	6.52–6.55	6.52–6.55	6.52–6.55	Methylene proton of Ar—CO—CH ₂ —CH ₃
2.93–2.96	2.90–2.93	2.91–2.93	2.91–2.93	Methyl proton of Ar—CO—CH ₂ —CH ₃
—	—	3.89	3.89	Methylene proton of Ar—CH ₂ —Ar linkage

group and two hydroxyl groups (36.40% experimental and 36.82% calculated). The third step which is start from 460 to 635°C corresponding to 70.75% loss of benzene ring along with two methylenic groups against calculated 70.94%. The fourth step starts from 635 to 800°C corresponding to total loss of remaining oxamide moiety.

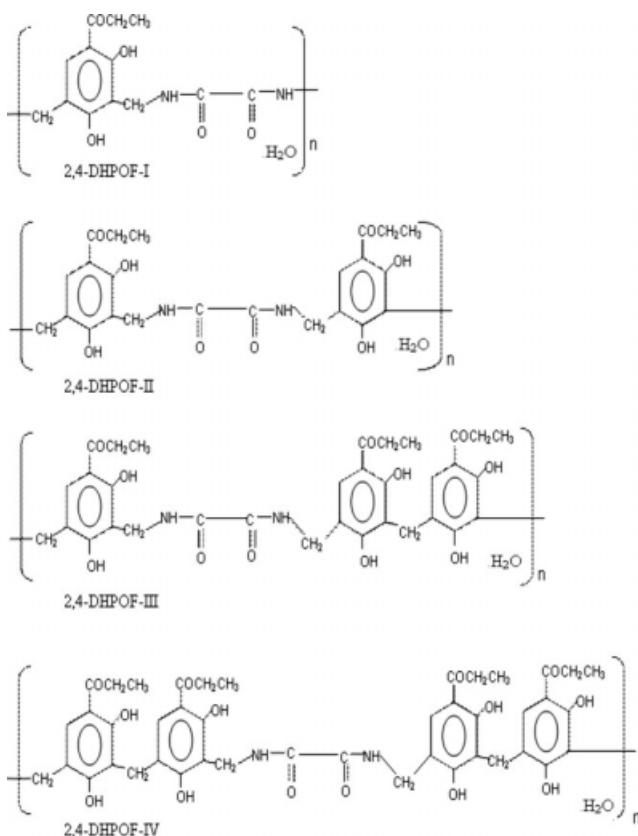


Figure 4 Suggested structures of terpolymers.

TG of 2,4-DHPOF-II terpolymer

The first step slow decomposition between 40 and 168°C corresponds to 3.51% loss which may attributed to loss of a water molecule against calculated 3.79% present per repeat unit of the polymer. The second step decomposition starts from 168 to 448°C which represents degradation of two —COCH₂CH₃ groups and four hydroxyl groups (42.03% experimental and 42.19% calculated). The third step which is start from 448 to 710°C corresponding to 81.53% loss of two benzene rings along with three methylenic groups against calculated 81.85%. The fourth step starts from 710 to 800°C corresponding to total loss of remaining oxamide moiety.

TG of 2,4-DHPOF-III terpolymer

The first step slow decomposition between 40 and 142°C corresponds to 2.62% loss which may attributed to loss of a water molecule against calculated 2.76% present per repeat unit of the polymer. The second step decomposition starts from 142 to 486°C which represents degradation of three —COCH₂CH₃ groups and six hydroxyl groups (44.33% experimental and 44.63% calculated). The third step which is start from 486 to 735°C corresponding to 86.71% loss of three benzene rings along with four methylenic groups against calculated 86.80%. The fourth step starts from 735 to 800°C corresponding to total loss of remaining oxamide moiety.

TG of 2,4-DHPOF-IV terpolymer

The first step slow decomposition between 40 and 163°C corresponds to 2.03% loss which may

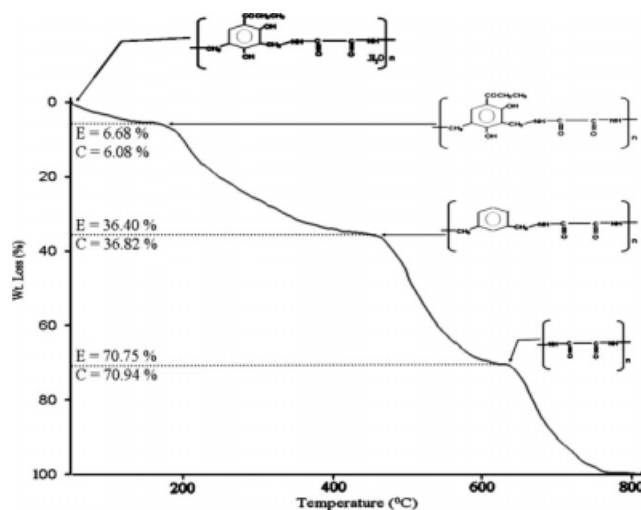


Figure 5 Freidman's isoconversional (model-free) kinetic methods for variation of the apparent activation energy values with degradation stages of 2,4-DHPOF-I terpolymer.

attributed to loss of a water molecule against calculated 2.16% present per repeat unit of the polymer. The second step decomposition starts from 163 to 440°C which represents degradation of four $-\text{COCH}_2\text{CH}_3$ group and eight hydroxyl groups (46.23% experimental and 46.02% calculated). The third step which is start from 440 to 693°C corresponding to 87.32% loss of four benzene rings along with five methylenic groups against calculated 87.46%. The fourth step starts from 693 to 800°C corresponding to total loss of remaining oxamide moiety.

To provide further evidence regarding the degradation system of analyzed compounds, we derived the TG curves by applying an analytical method proposed by Freeman–Carroll¹² and Sharp–Wentworth.¹⁰

Freeman–Carroll method

The straight-line equation derived by Freeman and Caroll, which is in the form of

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

where

dw/dt = rate of change of weight with time

$W_r = W_c - W$

W_c = wt. loss at completion of reaction

W = total wt. loss upto time t

E_a = energy of activation

n = order of reaction.

The plot between the terms $\frac{\Delta \log dw/dt}{\Delta \log W_r}$ vs. $\frac{\Delta(1/T)}{\Delta \log W_r}$ gives a straight line from which slope we obtained energy of activation (E_a) and intercept on Y-axis as order of reaction (n).

Sharp–Wentworth method

Using the equation derived by Sharp and Wentworth,

$$\log \frac{dC/dT}{1-C} = \log A/\beta - \frac{E_a}{2.303R} \cdot \frac{1}{T} \quad (2)$$

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 $\log \frac{dC/dT}{1-C}$ vs. $\frac{1}{T}$, we obtained the straight line which give energy of activation (E_a) from its slope and A can be evaluated from intercept. The change in entropy (ΔS), change in enthalpy (ΔH), frequency factor (z), and apparent entropy (S^*)¹⁸ can also be calculated by further calculations.

Friedman method

Friedman^{19,20} provides the following expression for thermal degradation kinetic studies based on Arrhenius equation as follows:

$$\ln \left(\frac{d\alpha}{dt} \right) = \ln(z) + n \cdot \ln(1 - \alpha) - \left(\frac{E_a}{RT} \right) \quad (3)$$

where α is the conversion at time t . R is the gas constant (8.314 J/mol/K) and T is the absolute temperature (K). The plot of $\ln(d\alpha/dt)$ vs. $1/T$ should be linear with the slope E_a/R , from which E_a can be obtained. From the slope of the linear plot of $\ln(1 - \alpha)$ vs. $1/T$, n can be obtained. The plots (Figs. 6 and 7) give the activation energies at different stages of degradation and respective order of reaction takes place.

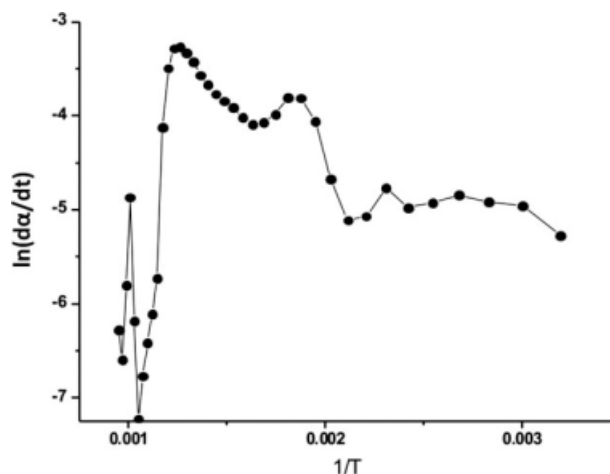


Figure 6 Freidman's isoconversional (model-free) kinetic methods for the order of reaction at differential degradation stages of 2,4-DHPOF-I terpolymer.

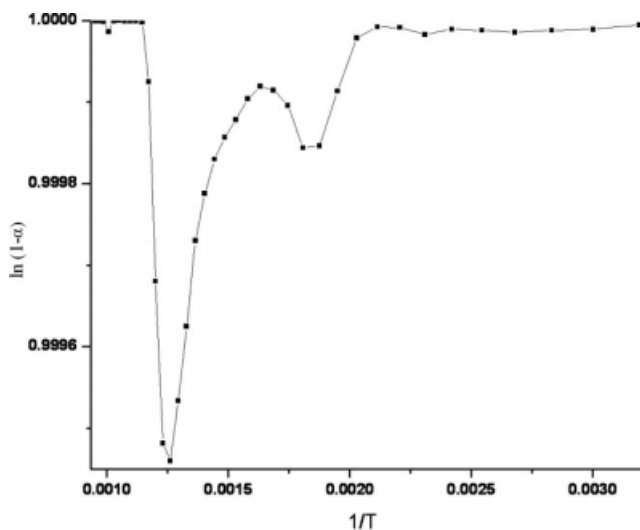


Figure 7 Friedman's isoconversional (model-free) kinetic methods for the order of reaction at different degradation stages of 2,4-DHPOF-I terpolymer.

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 to obtain the useful information on the behavior of the sample (Table VII).

A plot of percentage mass loss vs. temperature is shown in the Figure 5 for a representative 2,4-DHPOF-I terpolymer. From the TG curves, the thermo analytical data and the decomposition temperatures were determined for different stages as given in Table II. To obtain the relative thermal stabilities of the various terpolymers, the method described by Sharp-Wentworth¹⁰ was adopted. The thermal stabilities of terpolymers, based on the initial decomposition temperature, neglecting the degree of decomposition (Table III).

By using thermal decomposition data and applying Sharp-Wentworth method (a representative Sharp-Wentworth plot of 2,4-DHPOF-I polymer is

TABLE VII
Friedman's Isoconversional (Model-Free) Kinetic Methods to Check the Variation of the Apparent Activation Energy Values with Degree of Degradation of 2,4-DHPOF-I Terpolymer

Degradation temperature (°C)	% Degradation	Activation energy E_a (KJ/mol.)	Order of reaction (n)
100–140	0.98–1.60	4.98	1.0
160–200	1.85–2.46	14.96	0.9
240–340	2.46–5.18	21.28	1.0
340–520	16.99–62.74	19.70	0.9
600–680	97.11–97.18	139.84	1.0
680–720	97.18–97.20	430.41	1.0
720–760	97.20–97.56	41.57	1.0

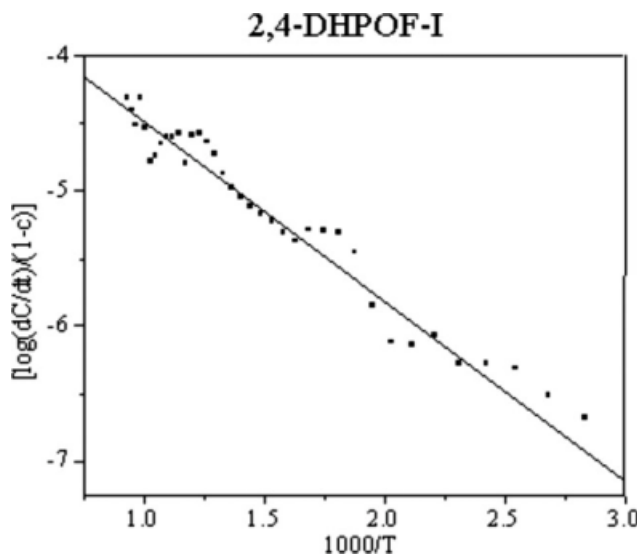


Figure 8 Thermal activation energy plot of 2,4-DHPOF-I terpolymer.

shown in Fig. 8), activation energy is calculated which is in agreement with the activation energy calculated by the Freeman-Carroll method¹² (Table III). A representative thermal activation energy plot of Sharp-Wentworth (Fig. 8) and Freeman-Carroll (Figs. 9 and 10) for the terpolymer has been shown. Thermodynamic parameters have been calculated on the basis of thermal activation energy. These values are given in (Table II).

The sequence of thermal stabilities was found to be in the order of 2,4-DHPOF-I > 2,4-DHPOF-II > 2,4-DHPOBF-III > 2,4-DHPOF-IV. The sequential order of thermal stabilities of terpolymers predicted on the basis of the initial decomposition

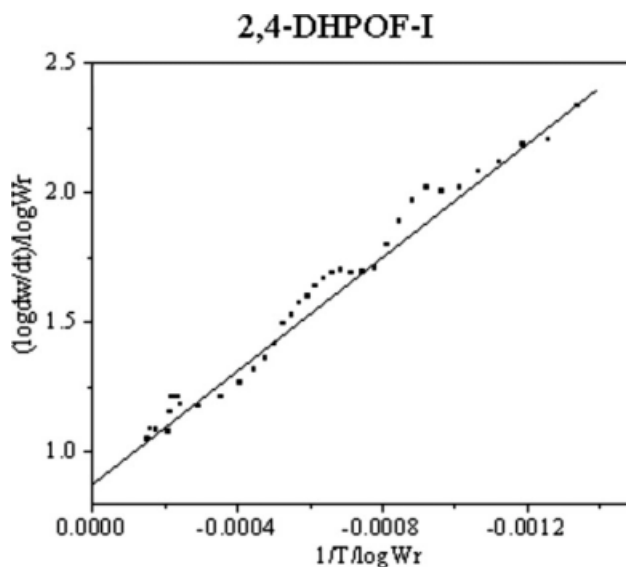


Figure 9 Freeman-Carroll plot for 2,4-DHPOF-I terpolymer.

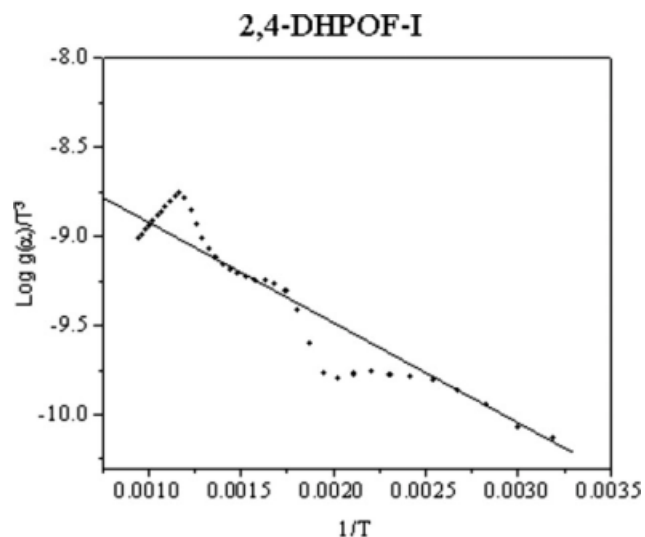


Figure 10 Freeman-Carroll plot for 2,4-DHPOF-I terpolymer.

temperatures is in harmony with that predicted from the activation energy values (Table II).

The analysis of thermograms indicates that the decomposition of terpolymers is three-step process after loss of water molecule present per repeat unit of the polymer. The first step decomposition represents degradation of four $-\text{COCH}_2\text{CH}_3$ group and eight hydroxyl groups. The second step which is corresponding to loss of four benzene rings along with five methylenic groups. The third step corresponding to total loss of remaining oxamide moiety.

By using the data of Freeman-Carroll method, various thermodynamic parameters have been calculated (Table III). The values of these thermodynamic parameters for all the terpolymers changes as their compositions. The similarity of the values indicates a common reaction mode.²¹ From the abnormally low value of frequency factor, it may be concluded that decomposition reaction of 2,4-DHPOF terpolymers can be classed as a "slow" reaction. There is no other obvious reason.²²

Fairly, good straight-line plots are obtained using the two methods. This is expected since the decom-

position of terpolymer is known not to obey first order kinetic perfectly.^{23,24}

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References

1. Rahangdale, S. S.; Zade, A. B.; Gurnule, W. B. *J Ultra Sci* 2007, 19, 213.
2. Tarase, M. V.; Zade, A. B.; Gurnule, W. B. *J Ultra Sci* 2007, 3, 41.
3. Gurnule, W. B.; Juneja, H. D.; Paliwal, L. J. *Orient J Chem* 1999, 15, 283.
4. Patel, R.; Patel, K.; Patel, R. *J Indian Chem Soc* 1984, 54.
5. Zeman, S.; Tokarova, L. A. *Thermochim Acta* 1992, 712, 181.
6. Chand, J. S.; Bailor, J. C. *J Inorg Nucl Chem* 1962, 24, 1225.
7. Vinogradova, S. K.; Korshak, V. V. *Kinetika (Kataliz)* 1964, 5, 247.
8. Ozawa, T. *Bull Chem Soc Jpn* 1965, 38, 1881.
9. Ozawa, T. *J Therm Anal* 1976, 9, 369.
10. Sharp, J. B.; Wentworth, S. A. *Anal Chem* 1969, 41, 2060.
11. Pepazian, H. A. *J Appl Polym Sci* 1972, 16, 2503.
12. Freeman, E. S.; Carroll, B. *J Phys Chem* 1958, 62, 394.
13. Pal, T. K.; Kharat, R. B. *Angew Makromol Chem* 1989, 55, 173.
14. Patel, K. D.; Patel, M. M. *Proc Indiana Acad Sci (Chem Sci)* 1990, 102, 31.
15. Kemp, W. *Organic Spectroscopy*; The Macmillan Press: Hong Kong, 1975.
16. Stuart, B. H. *Infrared Spectroscopy: Fundamentals and Applications*; Wiley: U.K., 2004.
17. Silverstein, R. M.; Bassler, G. C. *Spectrometric Identification of Organic Compounds*, 2nd ed.; Wiley: New York, 1987.
18. Jadhav, M. M.; Paliwal, L. J.; Bhave, N. S. *Proceeding of NASM-2004, Nagpur, India, 2004*; p 124.
19. Freidman, H. L. *J Polym Sci* 1964, C6, 183.
20. Cao, M. Y.; Wunderlich, B. *J Polym Sci Polym Phys Ed* 1985, 23, 521.
21. Tonbul, Y.; Yardakoc, K. *Turk J Chem* 2001, 25, 332.
22. Zhao, H.; Wang, Y. Z.; Wang, D. Y.; Wang, B.; Wu, B.; Chen, D. Q. *Polym Degrad Stab* 2003, 80, 135.
23. Zsago, J. *J Phys Chem* 1968, 72, 2406.
24. Singru, R. N.; Zade, A. B.; Gurnule, W. B. *J Appl Polym Sci* 2008, 109, 859.