Non-isothermal Kinetic Study of *p*-Cresol-Dithiooxamide-Formaldehyde Terpolymer

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Abstract: Terpolymer (*p*-CDF) has been prepared by using the monomer *p*-cresol, dithiooxanude and formaldehyde in 1:1:2 molar proportions. The structure of *p*-CDF terpolymer has been elucidated on the basis of elemental analysis and various physicochemical technique like UV-visible, FTIR, ¹H NMR and TG analysis. Detailed thermal degradation curve is discussed which shows four steps decomposition. The activation energy (*E_a*) and thermal stability calculated by using the Sharp Wentworth, Freeman-Carroll methods. Thermodynamics parameters such as entropy change (ΔS), apparent entropy change (S^*) and frequency factor (*z*) have also been evaluated on the basis of the data of Freeman-Carroll method. The order of reaction (*n*) is found to be 1.05.

Keywords: Synthesis, Thermal degradation, Activation energy, Terpolymer, Kinetic Parameter.

Introduction

Terpolymers having good thermal stability and catalytic activity have enhanced the development of polymeric materials. The study of the thermal degradation of terpolymers has recently become a subject of interest.

Copolymers, very special classes of polymers, are known for their versatile uses and are found to be amorphous, crystalline or resinous in nature. Phenolic resins have been the workhorse as matrix resins in composites for structural and thermal applications in aerospace because of their ease of processability, thermal stability, versatile characteristics and cost effectiveness. W. Tang and coworkers¹ studied the thermal decomposition kinetics of thermotropic copolyesters made from *trans-p*-hydrocinnamic acid and *p*-hydrobenzoic acid. Copolymers occupy an intermediate position between organic and inorganic compounds and it is hoped that the study of copolymers will lead to the production of polymer,

which are both thermally stable and useful as fabricating materials. P. E. P. Michael *et al.* studied synthesis, characterization and thermal degradation of 8-hydroxyquinoline-guanidine-formaldehyde terpolymer². Rahangdale and coworkers studied thermal degradation of terpolymers derived from 2, 4-dihydroxyacetophenone, dithioamide and formaldehyde^{3,4}.

Terpolymer resins are derived from 2,4-dihydroxypropiophenone, biuret and formaldehyde in hydrochloric acid as catalyst and studied their thermal degradation^{5,6}. Thermal degradation of *m*-nitroaniline, *m*-chloroaniline and *m*-aminophenol has been studied by Dash *et al.*⁷ and 2-hydroxyacetophenone, oxamide and formaldehyde⁸. S. L. Oswal *et al.* synthesized and studied thermal properties of copoly(maleimide-methylmethacrylate), terpoly(maleimide-methylmethacrylate-acrylic acid) and terpoly(maleimide-methylmethacrylate-methyl-acrylic acid). The thermal behaviour was studied by TG and DSC techniques⁹. Thermoanalysis and rheological behavior of copolymers of methyl methacrylate, *N*-phenylmaleimide and styrene studied by G. Jungang *et al.*¹⁰. In order to synthesize polymers having numerous practical applications, there is a need to investigate the effect of heat on the polymers in order 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 fraction¹¹⁻¹⁴.

However, the literature studies have revealed that no copolymer has been synthesized using the monomer *p*-cresol, dithiooxamide and formaldehyde. Therefore, in the present communication we report the synthesis, structural characterization and thermal degradation studies of *p*-CDF terpolymer. The elemental analysis has been carried out to ascertain the molecular formula and the spectral studies have been used to characterize the complete structure of the *p*-CDF terpolymer. After treating the thermal degradation data with Sharp-Wentworth (S-W) and Freeman-Carroll (F-C) methods, activation energy and kinetic parameters such as ΔS , z , S^* and n (order of reaction) have been evaluated¹⁵.

Experimental

All the chemicals used were of analytical grade. *p*-cresol, dithiooxamide and formaldehyde which is purchased from Merck Chemicals, India. Solvents like *N,N*-dimethyl formamide and dimethylsulphoxide purchased from SD Fine Ltd, Mumbai, India, were used after distillation.

Synthesis of p-CDF terpolymer resin

The *p*-CDF copolymer was prepared by condensing *p*-cresol (1.081 g, 0.1 mol) and dithiooxamide (1.2020 g, 0.1 mol) with formaldehyde (7.5 mL, 0.2 mol) in the presence of 2 M HCl as a catalyst at 126 ± 2 °C in an oil bath for 5 h (Scheme 1).

The green colored solid product obtained was immediately removed and extracted with diethyl ether to remove excess of *p*-cresol-formaldehyde terpolymer, which might be present along with the *p*-CDF 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 terpolymer sample was washed with boiling water and dried in a vacuum at room temperature. The purified terpolymer resin was 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%.

Analytical and physicochemical studies

The elemental analysis was carried out on a Perkin Elmer 2400 Elemental Analyzer instrument. The UV-Visible studies were out carried using Hitachi 330 UV-Vis Spectrometer in the range 200-850 nm. The Infrared spectrum was recorded in the region of 500-4000 cm^{-1} on Perkin Elmer Spectrum RX1 FT-IR Spectrometer. ^1H -NMR studied using Bruker Avance-II FT-NMR Spectrometer in DMSO- d_6 solvent. All the analytical and spectral studies for the newly synthesized terpolymer were carried out at Sophisticated Analytical Instrumentation Facility (SAIF), Punjab University, Chandigarh.

Instrumentation

The non-isothermal thermogravimetric analysis was performed in air atmosphere with heating rate of $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ using 5 to 6 mg of samples in platinum crucible from temperature of $40\text{ }^\circ\text{C}$ to $800\text{ }^\circ\text{C}$ and thermograms are recorded for *p*-CDF sample at SICART, Vallabh vidyanagar, Gujrat. With the help of thermogravimetric data the thermal activation energies (*Ea*) and order of reaction (*n*) calculated. Also other thermodynamic parameters such as entropy change (ΔS), apparent entropy change (S^*) and frequency factor (*Z*) are determined and reported in the Table 4.

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 and Freeman-Carroll.

Freeman-Carroll method

The straight-line equation derived by Freeman and Carroll¹⁶, which is in the form of

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

Where

dw/dt = rate of change of weight with time.

W_r = $W_c - W$

W_c = 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 $\frac{\Delta \log W / dt}{\Delta \log W_r}$ vs. $\frac{\Delta(1/T)}{\Delta \log W_r}$ gives a straight line from which slope we

obtained energy of activation (*Ea*) and intercept on Y-axis as order of reaction (*n*). The change in entropy (ΔS), frequency factor (*z*), apparent entropy (S^*) can also be calculated by further calculations.

Sharp-Wentworth method

Using the equation derived by Sharp and Wentworth¹⁷,

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

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.

Friedman method

Friedman¹⁸ provides the following expression for thermal degradation kinetic studies based on Arrhenius equation:

$$\ln\left(\frac{da}{dt}\right) = \ln(Z) + n \cdot \ln(1-\alpha) - \left(\frac{E_a}{Rt}\right) \quad (3)$$

Where α is the conversion at time t , R is the gas constant (8.314 J.mol⁻¹.K⁻¹) and T is the absolute temperature. The plot of $\ln(da/dt)$ vs. $1/T$ should be linear with the slope E_a/R , from which E_a can be obtained. The plots (Figure 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 obtain the useful information on the behavior of the sample.

Results and Discussion

The resin sample was green in color, insoluble in commonly used solvent, but was soluble in DMF, DMSO, THF, concentrated H₂SO₄. No precipitation and degradation occurs of resin in all the solvents. These resins were analyzed for carbon, hydrogen, nitrogen and sulphur content.

Characterization of terpolymer

Molecular weight of copolymer was estimated by conductometric titration. The number average molecular weight ($\overline{M}_n$) could be obtained by multiplying the $\overline{D}_p$ by the formula dithiooxamide weight of the repeating unit¹⁹. The result of the molecular weight of terpolymer samples prepared using higher proportion of two monomers *p*-cresol has the highest molecular weight in the series. The molecular weight for *p*-CDF is 2270.

The composition of terpolymer (represented in scheme 1) obtained on the basis of the elemental analysis data was found to be in good correlation to that of the calculated values:

Scheme 1. Synthesis of terpolymer resin

• Calculated for $C_{11}H_{14}N_2O_2S_2$: C: 48.88 %; H: 5.18 %; N: 10.37 % S: 23.70 %

• Found for $C_{11}H_{14}N_2O_2S_2$: C: 48.26 %; H: 5.01 %; N: 10.29 % S: 23.18 %

The UV-Visible spectrum in Figure 1 of purified copolymer resin exhibits two characteristic bands at 245 nm and 270 nm. These observed positions of the absorption bands indicate $\pi \rightarrow \pi^*$ transition which may be due to C = S double bond. While the latter may be due to $n \rightarrow \pi^*$ transition for the presence of the phenolic hydroxyl group (auxochrome)²⁰. This observation is in good agreement with the proposed probable structure for the *p*-CDF terpolymer resin.

Figure 1. UV-visible spectra of *p*-CDF terpolymer resin

The IR spectral data are tabulated in Table 1 and IR spectra *p*-CDF terpolymer is depicted in Figure 2. A broad absorption band appeared in the region 3596.3 to 3322.1 cm^{-1} can be assigned to the stretching vibrations of the phenolic -OH groups²¹. A medium band at 2922.9 cm^{-1} may be due to stretching vibration of -NH- group. A weak band at 1659.5 cm^{-1} may be due to the stretching vibration of the thio (C=S) group. A sharp peak at 1601.6 cm^{-1} can be assigned to an aromatic skeletal ring. 1,2,3,5-tetrasubstitutions of the aromatic benzene ring are recognized from bands appearing at 861.9, 913.4, 1003.8 and 1231.3 cm^{-1} respectively. The band at 1483.2 cm^{-1} may be due to -CH₂- bending, 1379.3 cm^{-1} may be due to -CH₂- wagging, 813.2 cm^{-1} may be due to -CH₂- rocking.

Figure 2. IR spectra of *p*-CDF terpolymer resin

Table 1. IR spectral data of *p*-CDF terpolymer resin

Observed Band Frequency, cm ⁻¹	Assignment	Expected band frequency
3596.3 to 3322.1 b	-OH phenolic intermolecular hydrogen bonding	3700 to 3300
2922.9 m	>NH stretching	2800 to 3500
1659.5 w	>C=S stretching	1600 to 1400
1601.6 Sh	Aromatic ring	1600 to 1500
1483.2 Sh	-CH ₂ - bending	1460
1379.3 b	-CH ₂ - wagging	1280 to 1370
813.2 Sh	-CH ₂ - rocking	710 to 800
861.9, 913.4, 1003.8, 1231.3	1,2,3,5 substitution	900,1000,1100,1200

Sh = sharp, *b* = broad, *St* = strong, *m* = medium and *w* = weak

Proton NMR spectra of terpolymer resin are presented in Figure 3 and NMR spectra data are incorporated in Table 2 and the chemical shift (δ) ppm observed are assigned on the basis of data available in literature²². A signal at 1.42 (δ) ppm is due to methylene protons of Ar-CH₂-Ar moiety. A signal at 3.62 (δ) ppm is due to methylene proton of Ar-CH₂-N moiety. A signal at 4.36 (δ) ppm is due to proton of Ar-NH₂- moiety. A weak signal at 6.51 (δ) ppm may be due to protons of -NH- bridge. Proton NMR spectra of terpolymer resin show a multiplet signal (unsymmetrical pattern) 6.94 (δ) ppm is due to aromatic protons. A signal appeared in the region at 8.48 (δ) ppm can be assigned to proton of phenolic -OH group involved in hydrogen bonding.

Figure 3. NMR spectra of *p*-CDF terpolymer resin**Table 2.** ¹H-NMR spectral data of *p*-CDF terpolymer resin

Nature of proton assigned	Observed Chemical Shift (δ)ppm	Expected Chemical Shift (δ) ppm
Proton of phenolic -OH	8.48	8.0 to 12.0
Aromatic proton (Ar-H) (unsymmetric pattern)	6.94	6.2 to 8.5
Proton of Ar-NH ₂ - group	4.36	3.0 to 5.0
Methylene proton of Ar-CH ₂ - N moiety	3.62	3.0 to 3.5
Thioimide proton of -CS-NH-CS- linkage	6.51	4.0 to 8.5
Methylene proton of Ar-CH ₂ -Ar moiety	1.42	1.5 to 2.5

Thermogram of *p*-CDF is shown in Figure 4. The result of thermogravimetric analysis is shown in Table 3. Thermogram of *p*-CDF terpolymer depicts decomposition in the range 20-800 °C. The first step slow decomposition between 20-150 °C corresponds to 2.12% mass loss which may be attributed to the loss of H₂O molecule against calculated 2.78% present per repeat unit of the polymer. The second step decomposition starts from 150-250 °C which represent degradation of side chain attached to benzene ring in polymer 33.32% found and 33.22% calc. The third step decomposition starts from 250-440 °C corresponding to 75.05% loss of benzene ring against 75.15% calculated. The fourth step decomposition starts from 440-800 °C corresponding to removal of methylene and dithiooxamide moiety (99.47% found and 100% calc).

Figure 4. Thermogram of *p*-CDF terpolymer resin

Table 3. Comparison of activation energy (E_a) of degradation at different stages by different methods of *p*-CDF terpolymer

Terpolymer	Step	Temp Range	Group loss	Wt. loss, %	Activation (E _a) (kJ/mol.)		
					Sharp-Wentworth	Freeman-Caroll	Freidman
<i>p</i> -CDF	1 st	20-150	H ₂ O molecule entrapped	2.78	34.89	35.34	34.02
	2 nd	150-250	degradation of -CH ₃ group and one -OH group	33.22	35.71	32.16	9.47
	3 rd	250-440	loss of aromatic ring	75.15	18.94	10.46	17.21
	4 th	440-800	loss of dithiooxamide moiety.	100.00	84.32	70.21	69.56

Thermo analytical data

A plot of percentage mass loss versus temperature is shown in the Figure 4 for a representative *p*-CDF terpolymer. To obtain the relative thermal stability of the terpolymer, the method described by Sharp-Wentworth and Freeman-Carroll was adopted. The thermal stability of terpolymer, 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 is in agreement with each other. The 'average E_a ' calculated by Freeman-Carroll and by Sharp-Wentworth is nearly same. The activation energy calculated by these methods is depicted in Table 3. 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 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, in spite such dependence is not real²³.

A representative thermal activation energy plot of Sharp-Wentworth (Figure 5) and Freeman-Carroll (Figure 6,7) and Friedman (Figure 8) method for the terpolymer has been shown. Thermodynamic parameters such as entropy change (ΔS), frequency factor (z), apparent entropy change (S^*) calculated on the basis of thermal activation energy (E_a) using equations (3) and (4). These values are given in Table 4.

Figure 5. Sharp Wentworth plot of *p*-CDF terpolymer resin

Figure 6. Freeman Carroll plot of terpolymer resin

Figure 7. Freeman Carroll plot of *p*-CDF terpolymer resin

Figure 8. Friedman plot of *p*-CDF Terpolymer resin

Table 4. Kinetic parameters of *p*-CDF terpolymer resin

Terpolymer	Entropy Change	Free Energy Change	Frequency Factor	Apparent Entropy change	Order of Reaction
	ΔS (J)	ΔF (KJ)	Z (S^{-1})	S^* (kJ)	n
<i>p</i> -CDF	-8.1190	2.576	169	11.26	1.05

*(n) = Actual order found.*i). Entropy Change (ΔS):

$$\text{intercept} = \log \frac{k}{h \phi E_a} + \frac{\Delta S}{2.303 R} \quad (3)$$

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

ii) Frequency Factor (z):

$$B_{2/3} = \frac{\log z \cdot E_a}{R \phi} \quad (4)$$

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

Where, z = frequency factor,

B = calculated from eq [a], $\log p(x)$ = calculated from Doyle table corresponding to activation energy,

iii) Apparent entropy change (S^*):

$$S^* = 2.303R \log \frac{zh}{RT^*} \quad (5)$$

Where, T^* = temp at which half of the compound decomposed.

The abnormally low value of frequency factor, it may be concluded that decomposition reaction of *p*-CDF terpolymer can be classed as a 'slow' reaction. There is no other obvious reason^{24,25}. Fairly good straight-line plots are obtained using the two methods. This is expected since the decomposition of terpolymer is known not to obey first order kinetic perfectly^{26,27}.

Conclusion

- 1) The *p*-CDF copolymer based on the condensation polymerization of *p*-cresol and dithioxamide with formaldehyde in the presence of acid catalyst has been prepared.
- 2) From the elemental analysis, UV-Visible, FT-IR and ^1H NMR spectral studies the proposed structure of the *p*-CDF terpolymer has been determined.
- 3) Freeman-Carroll and Freidman provide accurate values of activation energy while Sharp-Wentworth would lead to important error in determination of activation energy.

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