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Der Pharmacia Lettre, 2013, 5 (5):43-51
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ISSN 0975-5071
USA CODEN: DPLEB4

Non-isothermal studies of terpolymer resin derived from 2,4-dihydroxyacetophenone and catechol

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ABSTRACT

The terpolymer (2,4-DHACF) synthesized from the polycondensation of 2,4-dihydroxyacetophenone and catechol with formaldehyde in an acidic medium. The terpolymer was characterized by UV-Visible spectra, FTIR and NMR spectroscopy. The thermal stability of the polymer was determined by TGA. In addition, the activation energy for the formation of terpolymer resin was calculated using TGA data by Freeman-Caroll method and Sharp-Went-worth method. Thermal activation energy (Ea) calculated with above two methods are in close agreement. The surface features of the polymer were analyzed by scanning electron microscopy (SEM). The thermodynamic parameter such as free energy change (ΔF), entropy change (ΔS), Apparent entropy change(S) and frequency factor Z are also determined on the basis of TGA curve and by using data of Freeman-Carroll method.*

Keywords: Synthesis, TGA, Resin, Terpolymer, Thermodynamic parameter, Kinetics.

INTRODUCTION

Polymers having good thermal stability and catalytic activity have enhanced the development of polymeric materials. Copolymer acquired a renewed research interest in the recent past because of their interesting properties, such as thermal stability, ability to bind toxic metal ions, exhibition of catalyst, pholuminescence properties [1-3]. The homopolymer and copolymer of 4-chloro-3-methyl phenyl methacrylate possesses excellent antimicrobial activity due to the presence of free chlorine in the polymeric structure [4]. Metal complexes of Schiff bases derived from 2-furancarboxaldehyde and o-phenylenediamine, 2-thiophenecarboxaldehyde and 2-aminothiophenol were screened for their antibacterial activity, which clearly establishes that the metal complexes have more potent antibacterial activity than the parent Schiff base ligand [5]. Terpolymer involing anthranilic acid and thiourea with paraformaldehyde resin was synthesized and reported [6]. Chelate polymers of azelaoyl bis-N-pheylhydroxamic acid with Mn(II),Co(II), Ni(II) and Zn(II) were synthesized and found that the Mn(II) and Zn(II) chelates possess a tetrahydral geometry, whereas Co(II) and Ni(II) chelates exhibit octahedral geometry [7]. Schiff base polymers such as poly(N,N-p-phenylene/ethlenebis(salicylideneimine)) were synthesized and the thermal stability of Cu(II) and Ni(II) complexes were reported [8]. Chand and Bailor [9] 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). Ozawa [10] suggested the method of analyzing the thermoanalytical data for nonisothermal degradation of calcium oxalate and nylon-6.

This article describes the preparation of new polymer involving 2, 4-dihydroxyacetophenone, catechol and formaldehyde monomers. The terpolymer was characterized by various spectral methods and studied by non-isothermal and tested for their thermal stability.

MATERIALS AND METHODS

Materials

2, 4-dihydroxyacetophenone and catechol were procured from Merck, India and purified by rectified spirit. Formaldehyde (37%) were of AR grade, Merck and used as received. Solvents like N, N-dimethyl formamide and dimethylsulphoxide were used after distillation.

Preparation of Terpolymer 2, 4-HACF Resin

The terpolymer was synthesized by the polycondensation reaction of 2, 4-dihydroxyacetophenone (1.52gm, 0.1mol) and catechol (1.10gm, 0.1mol) with formaldehyde (7.5ml, 0.2mol) using hydrochloric acid as the reaction medium at 124±2°C in an oil bath for 5 hrs under refluxed condition with occasional shaking. The reaction mixture was then cooled, poured into crushed ice with constant stirring and left overnight. The dark brown coloured polymer separated out was washed with warm water and extracted with diethyl ether. The dried sample was then purified by dissolving in 8 % aqueous NaOH and regenerated using 1: 1 (v/v) HCl/water with constant and rapid stirring to avoid lump formation. The process of reprecipitation was repeated twice. The polymer 2,4-HACF thus obtained was filtered, washed with hot water, dried in air, powered and kept in vacuum desicator over silica gel. The yield of the polymer was found to be 82% and the reaction route for the synthesis is shown in Fig. 1.

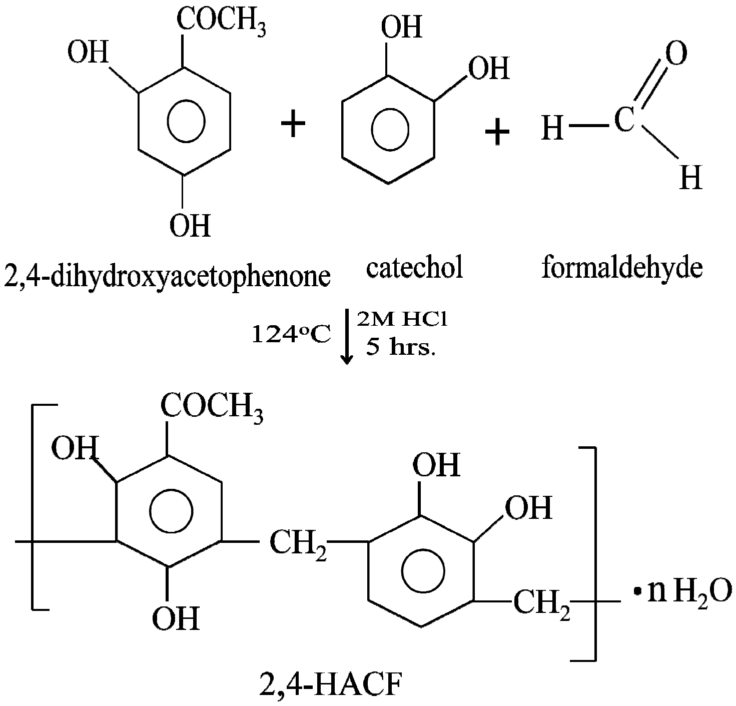

Fig. 1: Reaction and suggested structure of 2, 4-HACF Terpolymer

Characterization

The electronic spectra of the 2,4-HACF polymer sample in pure DMSO was recorded in the region 200-800 nm by Perkin Elmer UV Winlab. By Perkin-Elmer-983 spectrophotometer an infra-red spectrum of polymer resin was recorded in KBr pallets in the wave number region of 4000 - 400 cm-1 at SAIF, Punjab University, Chandigarh. A Nuclear Magnetic Resonance (^{1}H NMR) spectrum has been scanned on Bruker Advanced 400 NMR spectrometer using DMSO-d_6 at sophisticated Analytical Instrumentation Facility Punjab University, Chandigarh. The surface morphology of 2, 4-HACF polymer resin was established by scanning electron microscopy at Visvesvarya National Institute of technology (VNIT), Nagpur. From the thermo gravimetric data, which is reported in Table 1, the thermal activation energies (Ea) and order of reaction (n) calculated. Also other thermodynamic parameter such as free energy change (ΔF), entropy change (ΔS), Apparent entropy change(S*) and frequency factor Z are determined.

RESULTS AND DISCUSSION

The synthesized and purified 2, 4-HACF terpolymer resin was found to be dark brown in colour. The terpolymer is insoluble in commonly used solvent, but it is soluble in DMF, DMSO, pyridine and conc. H_2SO_4. The terpolymer resin which has been used in the present investigation was prepared by the reaction given in Fig. 1.

UV-Visible spectra of 2, 4-HACF Terpolymer Resin

The UV-Visible spectra (Fig. 2) of the 2,4-HACF terpolymer sample in pure DMSO was recorded in the region 200-800 nm at a scanning rate of 100 nm min^{-1} and a chart speed of 5 cm min^{-1}. This terpolymer sample gave two characteristics bands at 320-350nm and 240-260 nm. These observed positions for the absorption bands have different intensities. The band at 240-260 nm more intense band which may be accounted for a $\pi \rightarrow \pi^*$ transition while the less intense band at 320-350 nm may be due to $n \rightarrow \pi^*$ transition [11]. $\pi \rightarrow \pi^*$ transition indicates the presence of aromatic nuclei and $n \rightarrow \pi^*$ transition indicates presence of –OH group. The hyperchromic effect is due to the presence of – OH group.

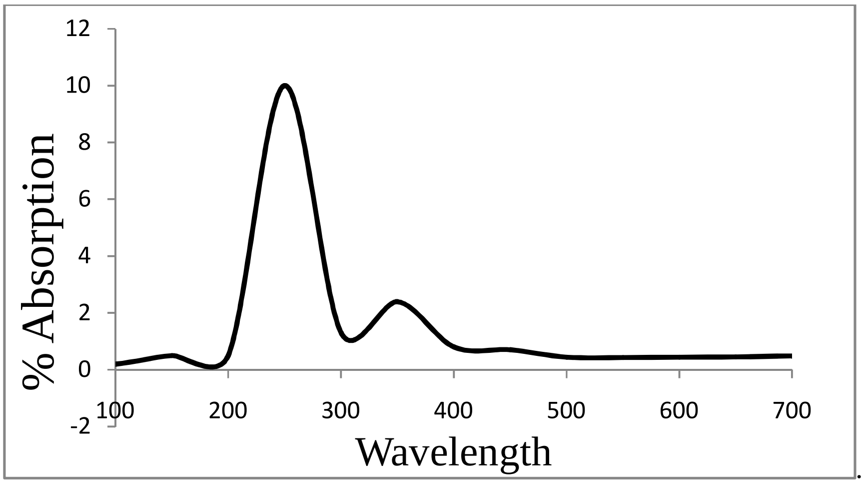

Fig. 2: UV- spectra of 2, 4-HACF Terpolymer

IR spectra of 2, 4-HACF Terpolymer:

Fig. 3 shows the infrared spectra of polymer 2, 4-HACF resin. From the spectra it has been revealed that the polymer shows broad absorption band appeared at 3280 cm^{-1} may be assigned to the stretching vibrations of phenolic hydroxyl (-OH) groups exhibiting intramolecular hydrogen bonding [12]. A sharp strong peak at 1623 cm^{-1} may be ascribed to aromatic skeletal ring. The bands obtained at 1198 cm^{-1}suggest the presence of methylene ($-CH_2$) bridge [13]. The sharp and weak band obtained at 1284 cm^{-1} suggests the presence of $Ar-CH_2-Ar$ bridge in polymer. The 1,2,3,6 substitution of aromatic benzene ring recognized by the sharp, medium / weak absorption bands appeared at 564, 798, 985, 1021 and 1069 cm^{-1} respectively. This band seems to be merged with very broad band of phenolic hydroxyl group.

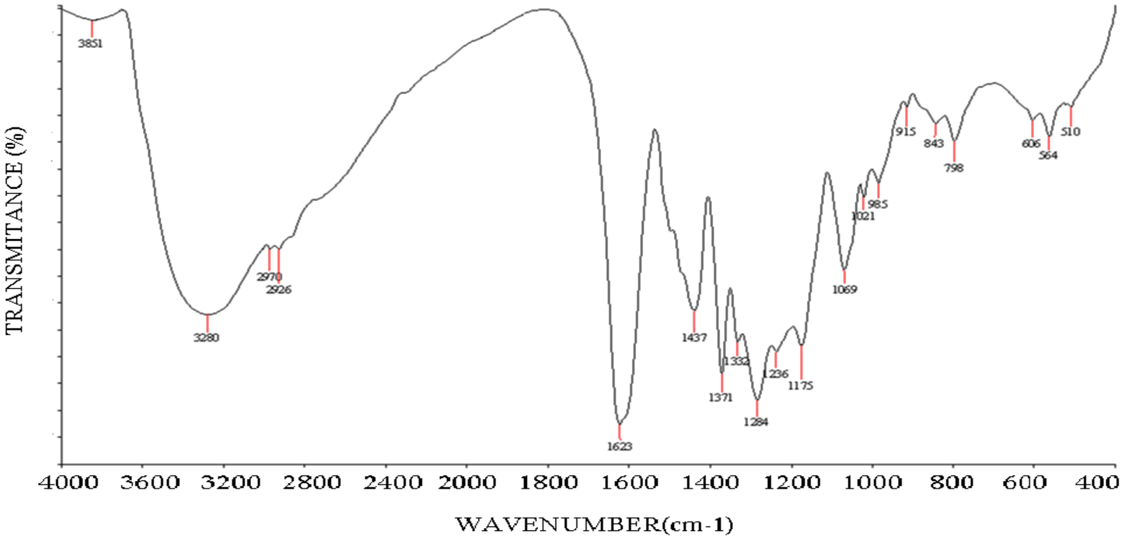

Fig. 3: IR spectrum of 2, 4-HACF Terpolymer

^{1}H NMR spectra of 2, 4-HACF Terpolymer:

Fig.4 shows the ^{1}H NMR spectra of 2, 4-HACF polymer was scanned in DMSO-d_6 solvent. The chemical shift (δ) ppm observed is assigned on the basis of data available in literature [14, 15]. From the spectral data, the singlet appearing at 3.84(δ) ppm may be due to the methylene proton of Ar-CH_2-Ar moiety. The weak multiple signals (unsymmetrical pattern) in the region of 6.39(δ) ppm may be attributed to aromatic proton (Ar-H). The signals appearing at 8.19(δ) ppm may be due to phenolic hydroxyl protons. The signals in the range of 3.2(δ) ppm are due to the proton of –$COCH_3$ groups. The much downfield chemical shift for phenolic –OH indicates clearly the intermolecular hydrogen bonding of -OH group [15, 16]. The signal appeared in the region at 2.28(δ) ppm is due to the methylene proton of Ar-CH_2 bridge [17].

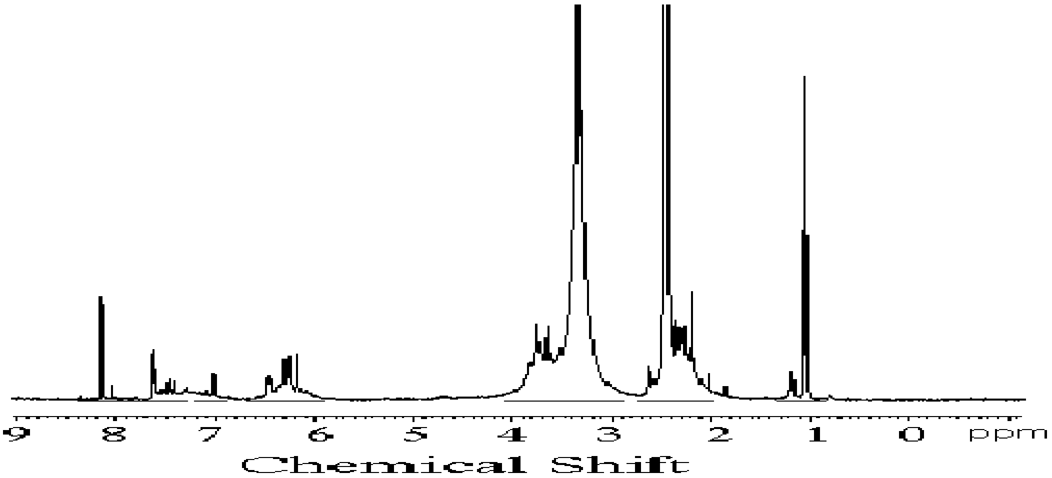

Fig 4: ^{1}H NMR spectral data of 2, 4-HACF Terpolymer

Scanning Electron Microscopy of 2, 4-HACF Terpolymer:

Fig. 5 shows the SEM image of the polymer **2,** 4-HACF. The morphology of the reported resin sample 2, 4-HACF was investigated by scanning electron micrographs at different magnification. It gives the information of surface topography and defect in nature. At lower magnification the polymer shows spherulites and friged model in which the crystals are arranged smaller in area with more closely packed structure. This indicates the crystalline nature of the polymer. Surface analysis has found great use in understanding the surface features of the materials. However, more predominantly the polymer is amorphous and this change of crystalline into amorphous is due to the condensation [18]. The image of polymer clearly indicates a less close packed structure with high porosity or voids. The amorphous character indicates that resin thus possesses higher exchange for metal ions. The morphology thus identified by SEM as crystalline as well as amorphous or transition between crystalline and amorphous, showing more or less good ion exchange capacity.

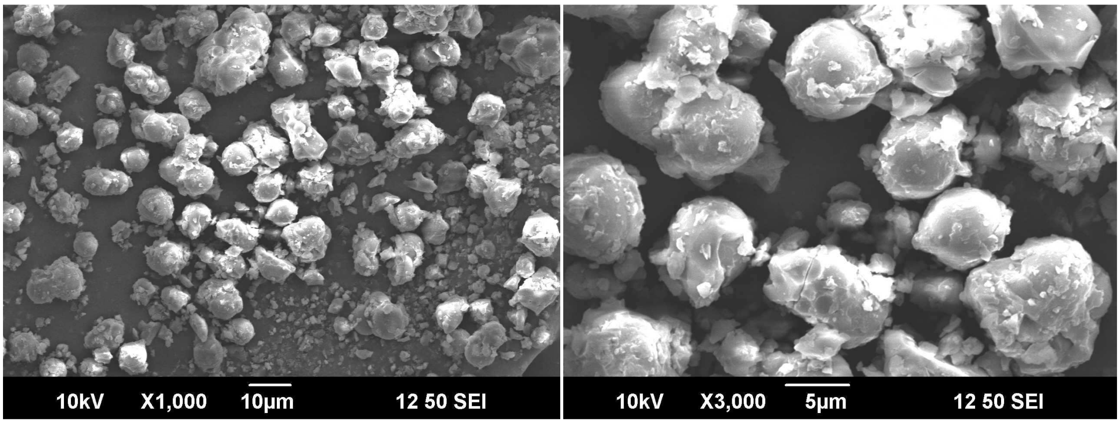

Fig 5: SEM micrographs of 2, 4-HACF Terpolymer

THERMOGRAVIMETRIC ANALYSIS (TGA)

Thermal decomposition of 2, 4-HACF terpolymer sample has been carried out using Perkin-Elmer thermo gravimetric analyser in air atmosphere with heating rate of 10°C/min. A brief account of thermal behavior of 2,4-HACF terpolymer is given in Fig. 6.

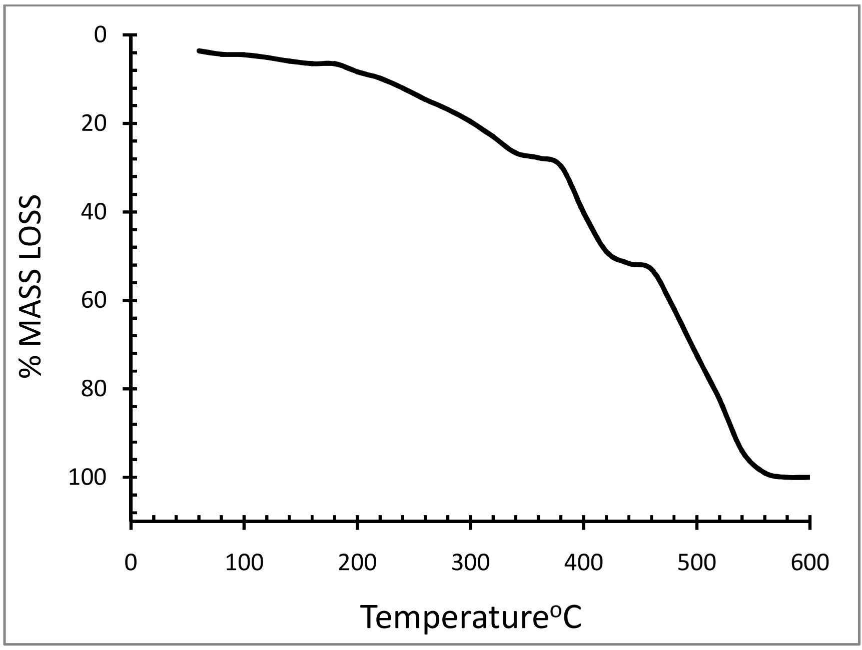

Fig. 6: Thermogram of 2, 4- HACF Terpolymer

TGA of 2, 4-HACF Terpolymer

Thermogram of TGA of this polymer is shown in Fig. 6. In order to explore the thermal degradation study of 2,4-HACF terpolymer resin, the thermo gram has been studied minutely. Thermogram of 2, 4-HACF terpolymer resin depicts four step decomposition in the temperature range 50-540°C . The first step is slow decomposition between

50 – 90^{o}C corresponds to loss of water molecule (4.8% found and 4.77% calculated). The second step decomposition start from 90-240^{o}C corresponds to degradation of three hydroxyl group which is attach with aromatic and benzene ring (18.30% calculated and 18.34% found). The third step which is in the range 240-400^{o}C corresponds to the loss of benzene ring, one sulphonic group along with two methylenic groups (66.84% calculated and 66.90% found). The fourth step corresponds to loss of complete polymer (100% calculated and 100% found) which represent total loss of remaining quinoline moiety in the range 400-540 ^{o}C.

In the present investigation Sharp-Wentworth and freeman-Carroll methods have been used to determine the kinetic parameters of 2, 4-HACF terpolymer sample.

Sharp-Wentworth method:
Using the equation derived by Sharp-Wentworth [1],

$$\text{Log}\,[(dc/dT)/(1-c)] = \log(A/\beta) - [Ea/2.303R].1/T \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

Where,
dc / dT = rate of change of fraction of weight with change in temperature.
β = linear heating rate dT / dt.

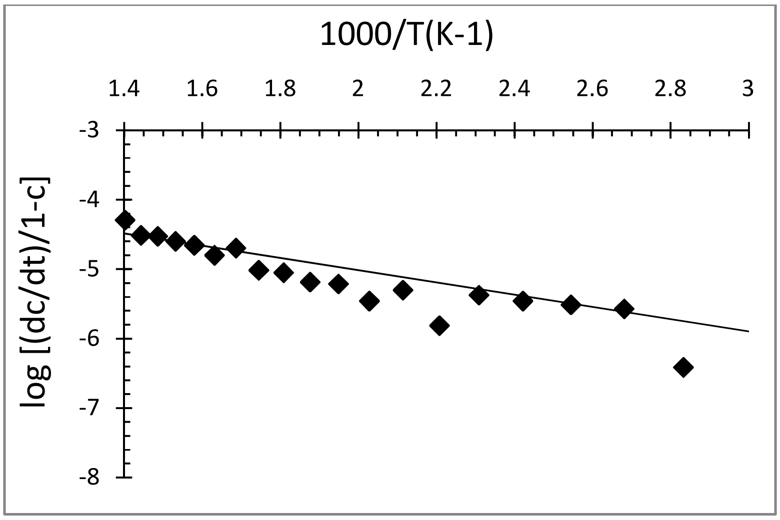

Fig 7: Sharp-Wentworth plot of 2, 4-HACF Terpolymer

By plotting the graph between (dc/dT)/(1-c) vs 1/T we obtained the straight line which gave energy of activation (Ea) from its slope. Where β is the conversion at time t, R is the gas constant and T is the absolute temperature. The plots Fig. 7 give activation energies at different stages of degradation reaction take place.

Freeman-Carroll method:
The straight- line equation derived by Freeman and Carroll, which is in the form of n

$$[\Delta \log(dw/dt)] / \Delta \log Wr = (-E/2.303R) - \Delta(1/T)/\Delta \log Wr + n \qquad \text{--------------}(2)$$

Where,
dw / dt = rate of change of weight with time.
Wr = Wc-W
Wc = weight loss at completion of reaction.
W = fraction of weight loss at time t.
Ea = energy of activation.
n = order of reaction

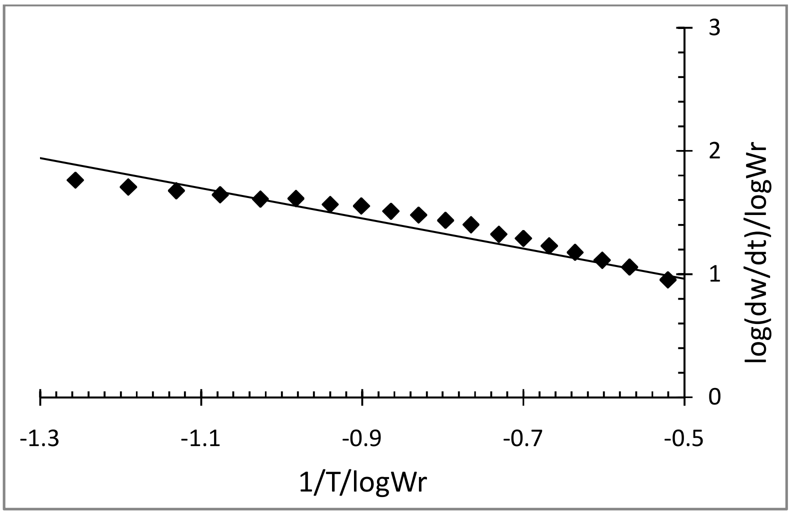

Fig. 8: Freeman-Carroll plot of 2, 4-HACF Terpolymer

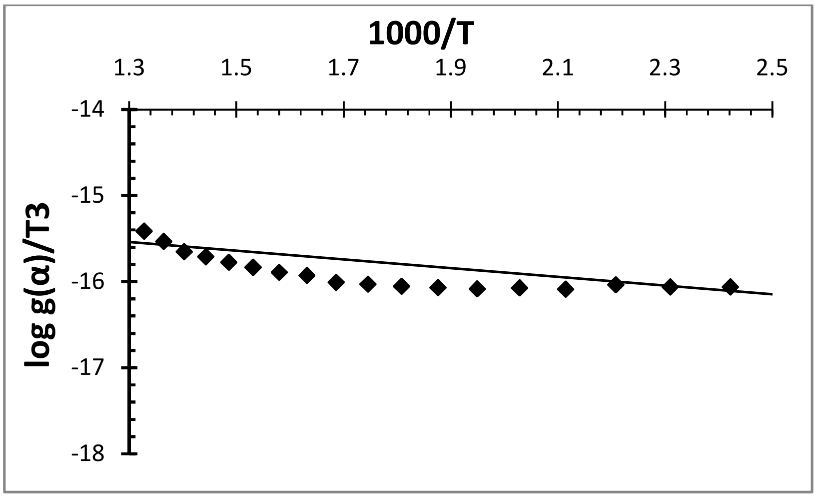

Fig. 9: Freeman-Carroll plot of 2, 4-HACF Terpolymer

A graph of percentage mass loss versus temperature is shown in Fig. 6 for 2, 4-HACF terpolymer. From the TG curve, the thermo analytical and the decomposition temperature were determined (Table 1) to obtain the thermal stability of the polymer. The method described by Sharp –Wentworth was adopted. Based on the initial decomposition temperature, the thermal stability of the polymer has been used here to define its thermal stability, neglecting the degree of decomposition.

Table 1: Results of Thermo gravimetric Analysis of 2, 4-HACF Terpolymer

Copolymer Resin	Half decomposition temp. (K)	Activation energy (KJ/mol)		Entropy change ΔS (J)	Free energy change ΔF (KJ)	Frequency factor Z (sec^{-1})	Apparent entropy S* (J)	Order of reaction found (n)
		FC	SW					
2,4-HACF	533	22.78	23.93	-298.58	181.92	339	-13.67	0.98

With the help of thermal decomposition data and the Sharp-Wentworth method Fig. 8, activation energy is calculated which is in agreement with the activation energy calculated by Freeman-Carroll method, Fig.8. Thermal activation energy plot of Sharp-Wentworth method (Fig. 7) and Freeman-Carroll method (Fig. 8) for the polymer have been shown. Thermodynamic parameters such as entropy change (ΔS), free energy change (ΔF), frequency factor (Z) and Apparent entropy (S*) calculated on the basis of thermal activation energy are given in Table 1.

DISSCUSSION

Using thermal decomposition data and then applying the Sharp-Wentworth method Fig. 7, activation energy is calculated which is in agreement with the activation energy calculated by Freeman-Carroll method, Fig. 8 [19]. Thermal activation energy plot of Sharp-Wentworth method (Fig. 7) and Freeman-Carroll method (Fig. 8) for the polymer have been shown. Thermodynamic parameters such as entropy change (DS), free energy change (DF), frequency factor (Z) and Apparent entropy (S*) calculated on the basis of thermal activation energy are given in Table 1, By using the data of the Freeman-Carroll method, various thermodynamics parameters have been calculated (Table 1). From the abnormally low values of frequency factor, it may be concluded that the decomposition reaction of 2,4-HACF terpolymer can be classed as a 'slow 'reaction. There is no other obvious reason. Fairly good straight line plots are obtained using the two methods. This is expected since the decomposition of polymer is known not to obey first order kinetics perfectly [20, 21].

CONCLUSION

Terpolymer 2,4-HACF based on the condensation reaction of 2,4-dihydroxyacetophenone and catechol with formaldehyde in the presence of acid catalyst, was prepared. In TGA the kinetic parameters evaluated from the Sharp-Wentworth and Freeman-Carroll methods are found to be similar, indicating the common reaction mode. The resins undergoes degradation at high temperature, indicates that the copolymer resins under study are thermally stable at elevated temperature. Low value of frequency factor may be concluded that the decomposition reaction of 2,4-dihydroxyacetophenone -catechol-formaldehyde polymer can be classified as 'slow reaction'.

Acknowledgement
The authors express their sincere thanks to Principal, Priyadarshini college of Engineering, Nagpur, India for cooperation and for providing necessary laboratory facilities.

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