



Terpolymerization of 2-hydroxyacetophenone, catechol and formaldehyde and its thermal studies

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ABSTRACT

The copolymer has been synthesized by the polycondensation technique of 2-hydroxyacetophenone with catechol and formaldehyde in the presence of 2M HCl as a catalyst. The copolymer has been characterized by UV-visible, IR and ¹H NMR spectra. The thermal decomposition behavior of new copolymer was studied using thermogravimetric analysis in air atmosphere. 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 stability. 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 TG curves and by using data of the Freeman-Carroll method. Scanning electron microscopy (SEM) was used to establish the surface morphology and nature of the copolymer.

Keywords: Copolymer, Morphology, Thermal degradation, Polycondensation, Resin.

INTRODUCTION

In the recent years, we have witnessed a great deal of interest in the synthesis and characterization of transition metal complexes containing copolymers as due to their application as catalysts, semiconductors, drugs, biocides, ion-exchanger and also models for enzymes [1-4]. Non-biodegradable polymer wastes can be reutilized by recycling to useful products rather than by burying them, but only a minor portion of the polymer is recyclable due to economic infeasibility and technical difficulty. Thus, the demand for degradable and biocompatible polymers is rapidly increasing because of the growing recognition worldwide of the need to reduce the global environmental pollution resulting from non-biodegradable polymer waste. For wide-spread acceptance, environmentally degradable polymers must overcome some significant obstacles not recognized earlier. Hence developments in this area require insuring a balance polymer is developed that not only has desirable properties, but also is environmentally acceptance.

The thermal degradation of polymers has been at the centre of thermal analysis studies for many years. Thermogravimetric analysis (TGA) is a common method to study the thermodegradation kinetics of polymers. Similarly differential scanning calorimetry (DSC) is also employed to elucidate the decomposition steps observed in the TGA data. Kinetic analysis may effectively assist in probing degradation mechanisms as well as in predicting the thermal stability of polymers [5].

The synthesis of functionalized copolymer is desirable for a variety of applications ranging from electronic devices to biological materials [6-12]. Many polymers with reactive functional groups are now being synthesized and used not only for their macromolecular properties, but also for the properties of functional group. These groups provide an approach to a subsequent modification of polymer for specific end application [13]. Although copolymer resin

has good thermo-oxidative resistance, extensive research has been done to improve thermal properties through modification of their structure with introduction of some functional group, such as oxadiazolic etc. [14]. It was found that the introduction of nitrogen into the polymeric skeleton can largely improve the flame resistance, adhesion, and also decrease contamination of environment on pyrolysis [15,16].

However relatively few studies have been reported on the thermostability and thermal degradation kinetics of the thermo tropic copolymers. It is considered that a more detailed study would be of value because the copolymers must encounter elevated temperatures at almost every step in the manufacturing, compounding and processing steps as well as in service and repair.

The aim of investigation is to synthesize a new kind of high performance polymer with good processing ability, high mechanical property and excellent thermal properties. The purpose of this study is to provide trustworthy kinetic data for prolonging life time estimation. Coating of this copolymer may find potential applications in inhibiting implantable biomedical device associated infections.

EXPERIMENTAL SECTION

Materials

2-hydroxyacetophenone 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.

Polymerization of 2-HACF copolymer resin

The copolymer was synthesized by the condensation polymerization reaction of 2-hydroxyacetophenone (0.1mol) and catechol (0.1mol) with formaldehyde (0.2mol) using hydrochloric acid as the reaction medium at $126 \pm 2^\circ\text{C}$ 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 colored 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 copolymer 2-HACF thus obtained was filtered, washed with hot water, dried in air, powdered and kept in vacuum desiccator over silica gel. The yield of the polymer was found to be 81% and the reaction route for the synthesis is shown in Fig. 1.

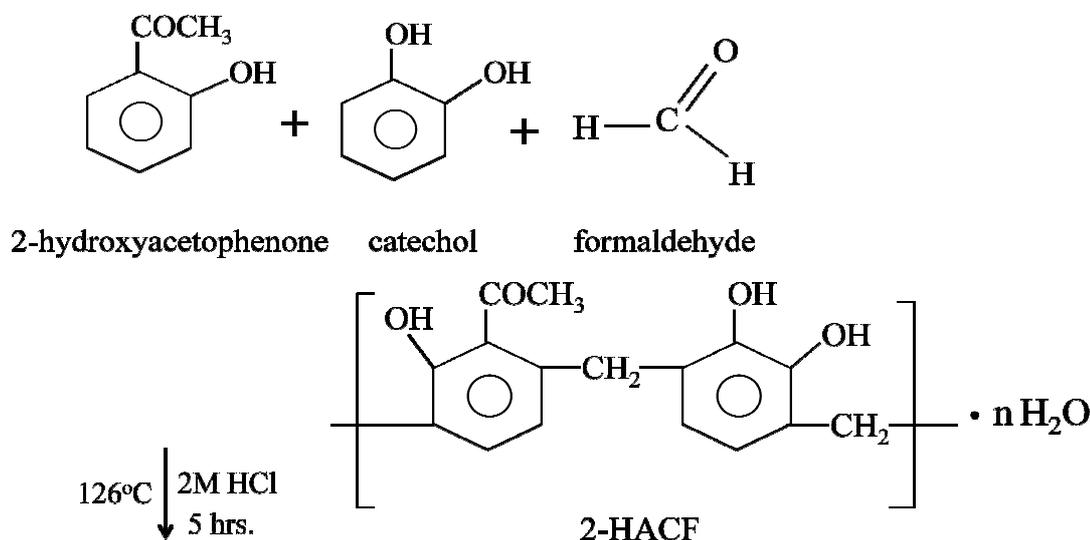


Figure 1: Reaction and expected structure of 2-HACF copolymer

Characterization

Electron absorption spectrum of copolymer resin was recorded in DMSO (spectroscopic grade) on shimadzu double beam spectrophotometer in the range of 200 to 850 nm at Sophisticated Analytical Instrumentation Facility, Punjab University, Chandigarh. An infra-red spectrum of 2-HACF copolymer resin was recorded on Perkin-Elmer-983 spectrophotometer in KBr pallets in the wave number region of 4000 - 400 cm^{-1} at SAIF, Punjab University, Chandigarh. A Nuclear Magnetic Resonance (^1H NMR) spectrum of newly synthesized copolymer resin has been scanned on Bruker Advanced 400 NMR spectrometer using DMSO-d_6 at sophisticated Analytical

Instrumentation Facility Punjab University, Chandigarh. TGA of copolymer resin has been carried out by using Perkin–Elmer TGS-II Thermo gravimetric Analyzer at SICART, Vallabh Vidyanagar, Gujrat at heating rate of 10°C per minute up to 800°C. With the help of thermo gravimetric data, which is reported in Table 1, the thermal activation energies (E_a) 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 and reported in Table 1.

RESULTS AND DISCUSSION

The newly synthesized and purified 2-HACF copolymer sample was found to be dark brown in colour. The copolymer is insoluble in commonly used solvent, but it is soluble in DMF, DMSO, pyridine and conc. H_2SO_4 . The melting point of the polymer was found to be in the range of 379 to 383 K. The copolymer which has been used in the present investigation was prepared by the reaction given in Fig. 1.

UV-Visible spectra of 2-HACF copolymer

The UV-Visible spectra (Fig. 2) of the 2-HACF copolymer sample in pure DMSO was recorded in the region 200–850 nm at a scanning rate of 100 nm min⁻¹ and a chart speed of 5 cm min⁻¹. The 2-HACF copolymer sample gave two characteristics bands at 360–370nm and 240–260nm. These observed positions for the absorption bands have different intensities. The more intense band is due to $\pi \rightarrow \pi^*$ transition and the less intense is due to $n \rightarrow \pi^*$ transition. $\pi \rightarrow \pi^*$ 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, which act as auxochrome [17].

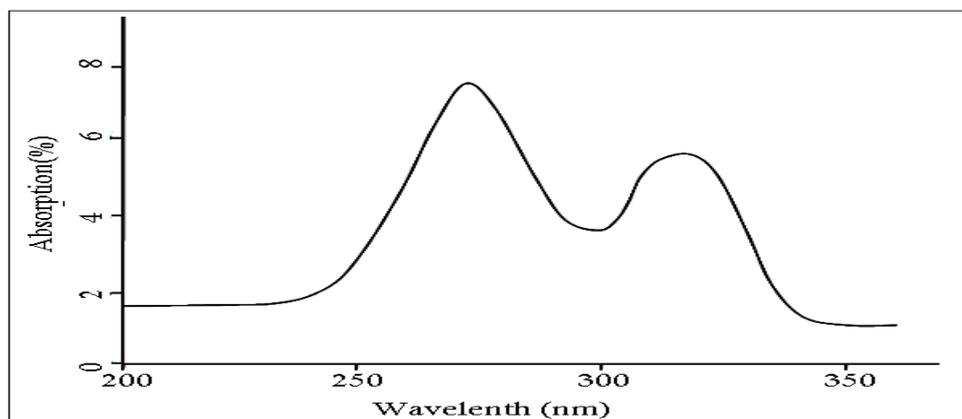


Fig 2: UV-Visible spectra of 2-HACF copolymer

IR spectra of 2-HACF copolymer

From IR Spectral studies (Fig. 3), it has been revealed that the copolymer show broad absorption band appeared in the region 3368–3370 cm^{-1} may be assigned to the stretching vibrations of phenolic hydroxyl ($-OH$) groups exhibiting intramolecular hydrogen bonding [18]. A sharp strong peak at 1613–1614 cm^{-1} may be ascribed to aromatic skeletal ring. The bands obtained at 1215–1218 cm^{-1} suggest the presence of methylene ($-CH_2$) bridge [19]. The sharp and weak band obtained at 1299–1305 cm^{-1} suggest the presence of $Ar-CH_2-Ar$ bridge in polymer. The sharp band displayed at 1636–1640 cm^{-1} may be due to stretching vibration of carbonyl group attached to acetophenone moiety. The 1,2,3,5 substitution of aromatic benzene ring recognized by the sharp, medium / weak absorption bands appeared at 949–953, 1072–1078, 1199–1208 and 1368–1374 cm^{-1} respectively. This band seems to be merged with very broad band of phenolic hydroxyl group.

¹H NMR spectra of 2-HACF copolymer

The NMR spectrum (Fig. 4) of 2-HACF copolymer was scanned in $DMSO-d_6$ solvent. The chemical shift (δ) ppm observed is assigned on the basis of data available in literature [20,21]. The singlet obtained in the region 3.86 – 3.91 (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 6.83–7.24 (δ) ppm may be attributed to aromatic proton ($Ar-H$). The signals in the range at 8.2 to 8.4 (δ) ppm may be due to phenolic hydroxyl protons. The much downfield chemical shift for phenolic $-OH$ indicates clearly the intramolecular hydrogen bonding of $-OH$ group [21,22]. The signal appeared in the region at 2.48–3.99 (δ) ppm is due to the methylene proton of $Ar-CH_2$ bridge [23]. The signals in the range of 3.2–3.6 (δ) ppm are due to the proton of $-COCH_3$ groups.

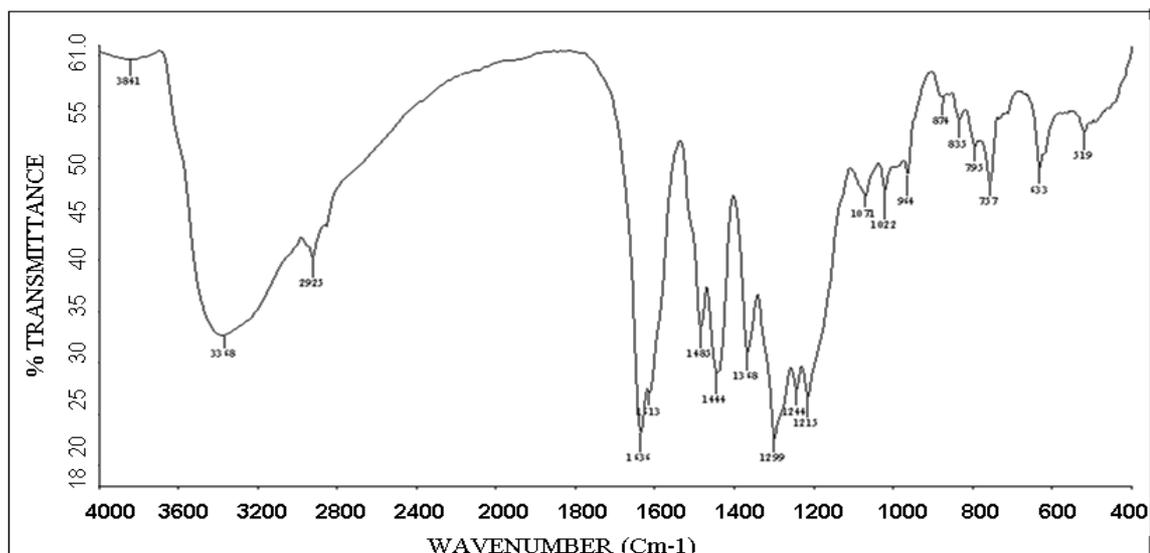
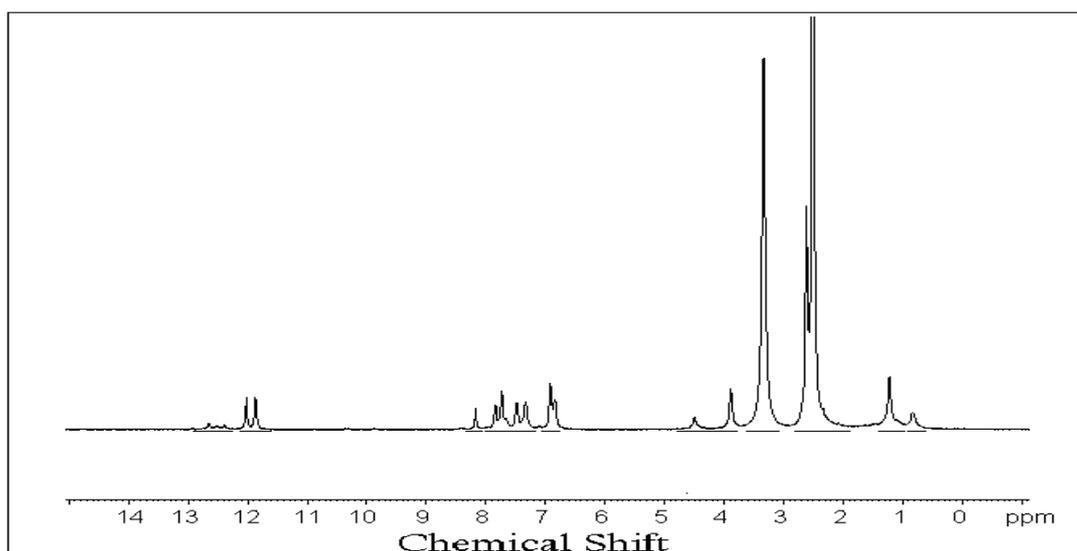


Fig 3: IR spectrum of 2-HACF copolymer

Fig 4: ¹H NMR spectral data of 2-HACF copolymer

Scanning Electron Microscopy of 2-HACF copolymer

The surface morphology of 2-HACF copolymer was established by scanning electron microscopy. The SEM image of the copolymer 2-HACF is shown in Fig. 5. The image of copolymer clearly indicates a less close packed structure with high porosity or voids. The voids present in the copolymer may be responsible for the swelling behavior and the reactivity of the active sites buried in the polymer matrix. The image also showed a transition state between amorphous and crystalline state. The crystalline form in the copolymer may be due to the acidic nature of monomers. However, more predominantly the copolymer is amorphous and this change of crystalline into amorphous is due to the polycondensation [24]. At different magnification the resin shows more amorphous character with less closed packed surface having deep pits. 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. The polymerization reaction proceeds by introducing amorphous character in the polymer resin.

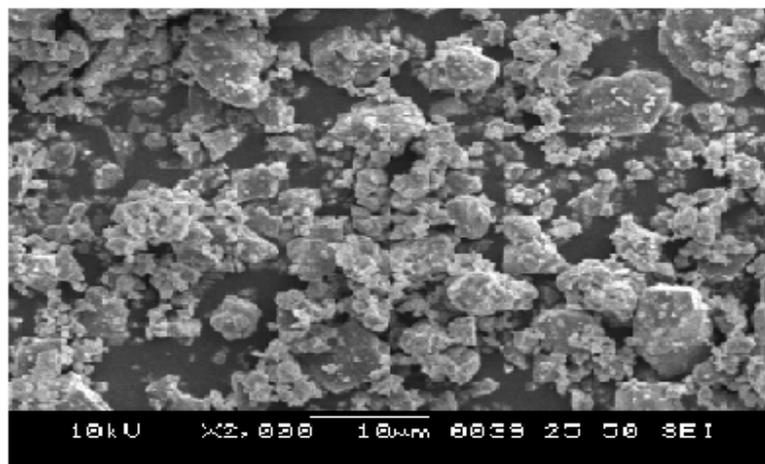


Fig 5: SEM micrographs of 2-HACF copolymer

Thermo gravimetric Analysis

Thermogravimetry of 2-HACF copolymer 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-HACF copolymer is given in Fig. 6.

TGA of 2-HACF copolymer resin

Thermogram of TGA of this polymer is shown in Fig. 6. In order to explore the thermal degradation study of 2-HACF copolymer resin, the thermo gram has been studied minutely. Thermogram of 2-HACF copolymer resin depicts four step decomposition in the temperature range 50-520°C. The first step is slow decomposition between 50 – 180°C corresponds to loss of water molecule (6.23% found and 6.25% calculated). The second step decomposition start from 180-320°C corresponds to 23.95% calculated and 23.90% found which represent degradation of three hydroxyl group which is attach with aromatic ring. The third step which is in the range 320-450°C corresponds to 74.30% calculated and 74.34% found which represent the loss of benzene ring, one acetyl group along with two methylene groups. The fourth step corresponds to loss of aromatic ring (100% calculated and 100% found) in the range of 450-520 °C

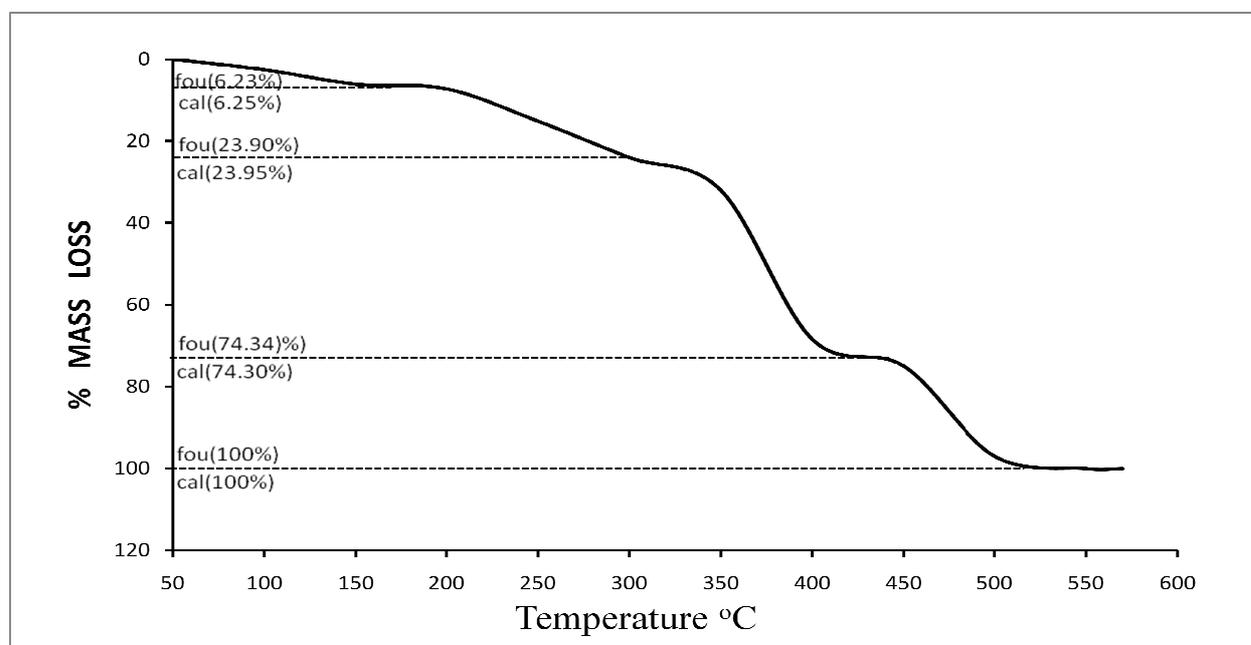


Fig 6: TGA of 2-HACF copolymer resin

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

Sharp-Wentworth method :

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

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

Where,

dc / dT = rate of change of fraction of weight with change in temperature.

β = linear heating rate dT / dt .

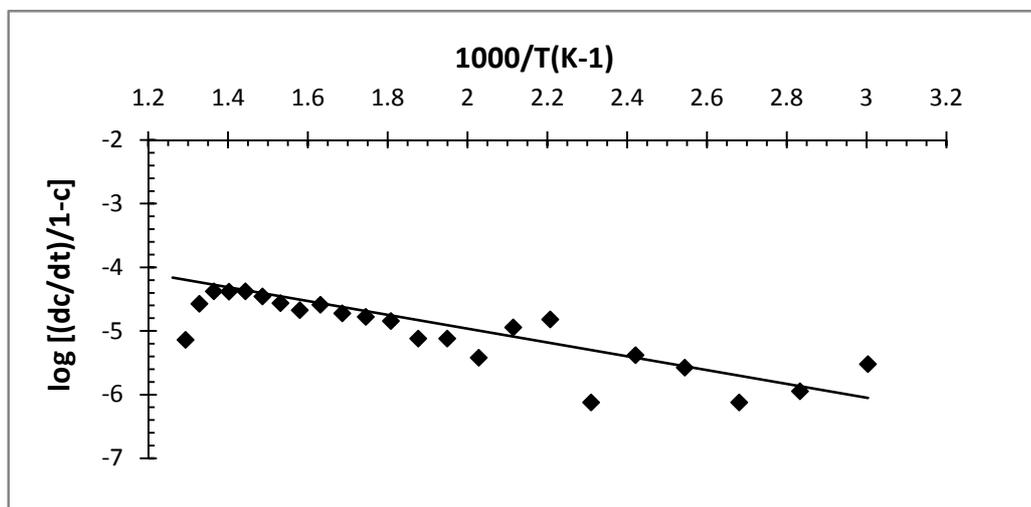


Fig 7: Sharp-Wentworth plot of 2-HACF copolymer resin

By plotting the graph between $(dc/dT)/(1-c)$ vs $1/T$ we obtained the straight line which gave energy of activation (E_a) 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

$$[\Delta \log (dw / dt)] / \Delta \log W_r = (-E / 2.303R) - \Delta(1/T) / \Delta \log W_r + n \dots \dots \dots (2)$$

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

A plot of percentage mass loss versus temperature is shown in Fig. 6 for 2-HACF copolymer. 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).

Table 1: Results of Thermo gravimetric Analysis of 2-HACF copolymer resin

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-HACF	533	20.14	20.41	-294.87	177.30	356	-13.75	0.93

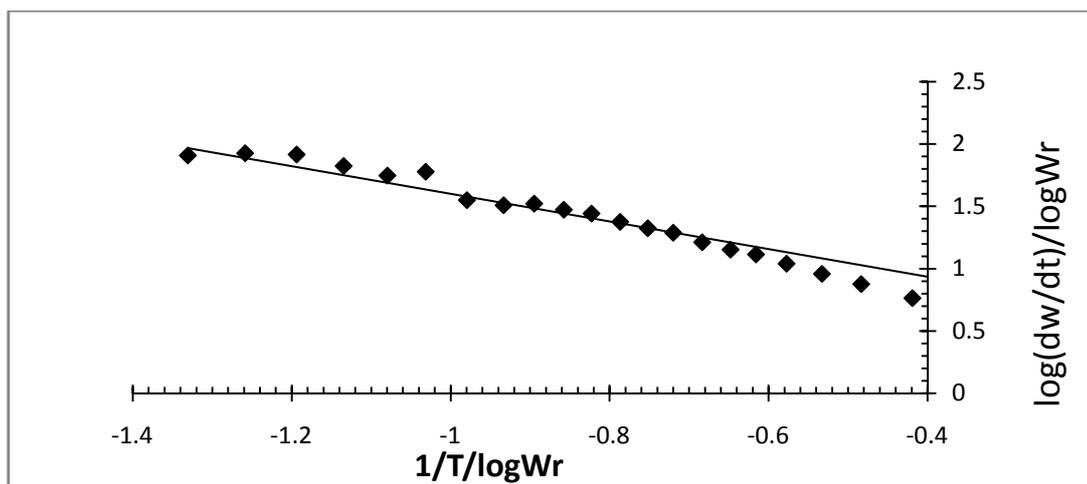


Fig 8: Freeman-Carroll plot of 2-HACF copolymer resin

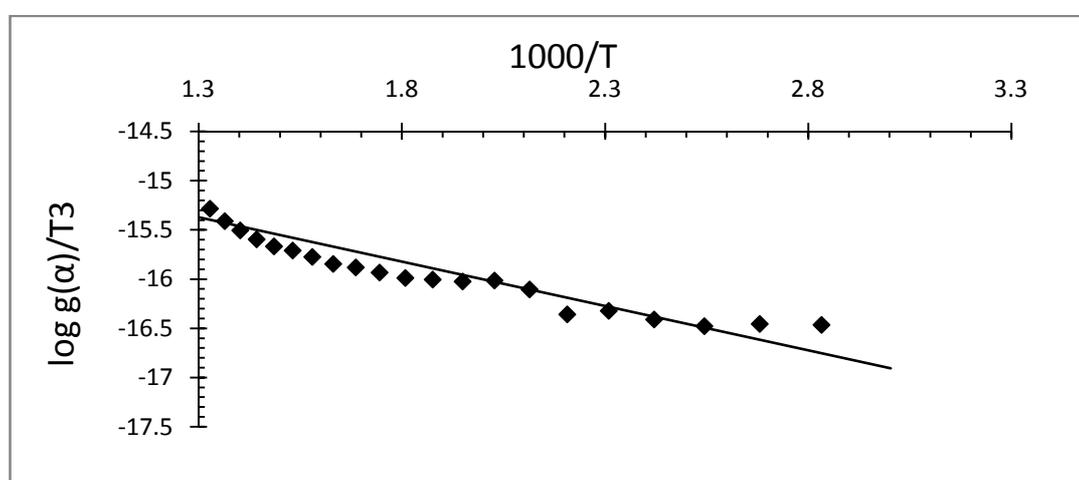


Fig 9: Freeman-Carroll plot of 2-HACF copolymer resin

Using thermal decomposition data and then applying 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 [25]. 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,

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-HACF copolymer can be classed as a 'slow' reaction. There is no other obvious reason [26, 27]. 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 [26, 27].

CONCLUSION

A copolymer containing 2-hydroxyacetophenone, catechol and formaldehyde was synthesized and characterized by various physicochemical properties like UV-Visible, FTIR, ^1H NMR and TGA. Thermal properties were determined by TGA analysis. The activation energy of thermal decomposition ($E_a = 20.41$) by Sharp-Wentworth method and ($E_a = 20.14$) by Freeman-Carroll method was investigated with thermogravimetric analysis at heating rate $10^\circ\text{C}/\text{min}$ from 50 - 520°C . Isoconversional analysis of TGA plot indicate variation in activation energy of degradation process. 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-hydroxyacetophenone-catechol-formaldehyde copolymer can be classified as 'slow reaction'.

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