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Synthesis, Characterization and Thermal Degradation Studies of Polymer Resin Derived From 4-Hydroxyacetophenone and Catechol

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ABSTRACT

A polymer (4-HACF) was synthesized by the polycondesation technique of 4-hydroxyacetophenone and catechol with formaldehyde in the presence of 2M HCl as a catalyst. A polymer has been characterized by UV-Visible absorption spectra, Infra-red (IR) spectra and proton nuclear magnetic resonance (^{1}H NMR) spectra. The morphology of polymer was studied by scanning electron microscopy (SEM). The thermal decomposition behavior of polymer (4-HACF) 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 (Ea) 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.

Keywords: Thermogravimetric analysis (TGA), Polymer, Morphology, Thermal degradation, Polycondensation, Synthesis

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INTRODUCTION

The non-isothermal methods are the most commonly used for performing the kinetic analysis of solid state reactions. A number of papers on this topic nave been recently published in the Journal [1-3]. These methods were originally developed by assuming‘n-order’ kinetic models. We have carried out a great effort [4-6] in generalizing the non-isothermal methods for being used for all the kinetic models describing solid state reactions. It must be pointed out that all the methods proposed have been developed by assuming that both the activation energy and the kinetic models do not change along the process. However, many authors [7, 8] have concluded from model free kinetic methods of analysis that the activation energy is a function of the reacted fraction. Phenolic resins have a large number of practical applications in electronic controls, insulating materials, protective adhesives, aerospace industries etc. because of their high thermal stability, heat and chemical resistance and electrical insulation properties [9]. Various researchers have been studied the applications of polymer resins of substituted phenols and formaldehyde [10,11]. Polymers of salicylic acid, thiourea with trioxane and p-hydroxybenzoic acid have been reported in the literature [12-14]. Manavalam and Patel [15] synthesized resins of salicylic acid, urea and formaldehyde. The present communication deals with synthetic and thermal degradation properties of a newly synthesized polymer resin derived from 4-hydroxyacetophenone, catechol and formaldehyde. The Freeman-Carroll and Sharp-Wentworth methods have been applied for the calculation of kinetic parameters [16-18]. Methods for the estimation of kinetic parameters from thermo gravimetric studies are generally based on the assumption that the Arrhenius equation is valid with thermal and diffusion barriers are negligible.

MATERIALS AND METHODS

Materials

The chemicals 4-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.

Synthesis of 4-HACF Polymer Resin

The polymer resin (4-HACF) was synthesized by the condensation polymerization reaction of 4-hydroxyacetophenone (1.36gm, 0.1mol) and catechol (1.10gm, 0.1mol) with formaldehyde (7.5ml, 0.2mol) using hydrochloric acid as the reaction medium at 122±2^{o}C in an oil bath for 5 hrs under refluxed condition with occasional shaking. The reaction mixture was then cooled. 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 polymer 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 78 % and the reaction route for the synthesis is shown in Fig. 1.

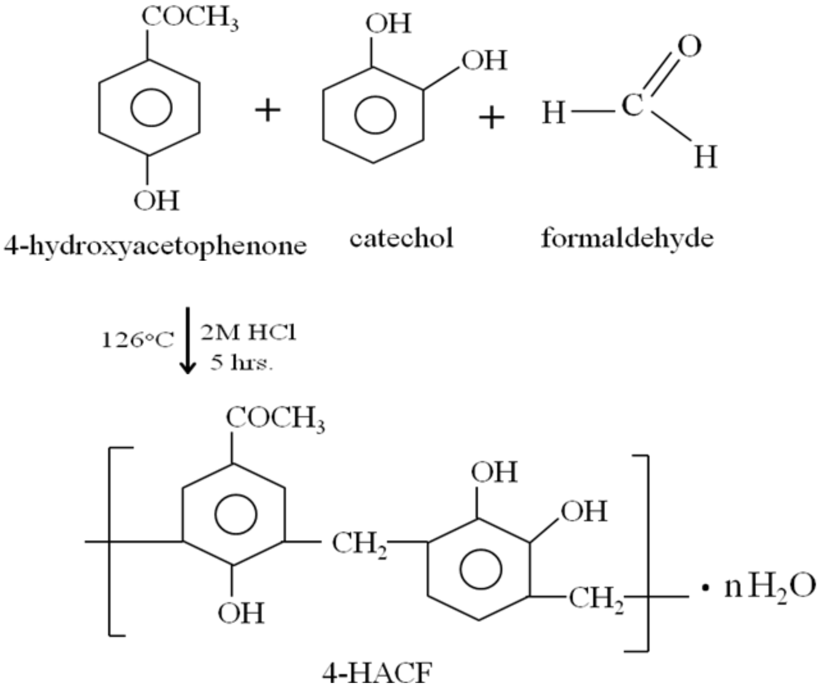

Figure 1: Reaction and Suggested Structure of 4-HACF Polymer

Characterization

Electron absorption spectra of polymer (4-HACF) were 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, and Chandigarh. An infra-red spectrum of 4-HACF polymer 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 (^{1}H NMR) spectrum of newly synthesized polymer resin has been scanned on Bruker Advanced 400 NMR spectrometer using DMSO-d_6 at sophisticated Analytical Instrumentation Facility Punjab University, Chandigarh. TGA of polymer resin has been carried out by using Perkin–Elmer TGS-II Thermogravimetric Analyzer at SICART, Vallabh Vidyanagar, Gujrat at heating rate of 10ºC per minute up to 800ºC. With the help of thermogravimetric 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 and reported in Table 1.Scanning electron micrograph of polymer has been scanned and magnification by JEOL JSM-6380A analytical scanning electron microscope at Visvesvarya National Institute of technology (VNIT), Nagpur. Study of SEM helps us to identify the exact morphology of the polymer.

Sharp-Wentworth Method:

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

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

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

Freeman-Carroll Method:

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

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

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

RESULTS AND DISCUSSION

The newly synthesized and purified 4-HACF polymer sample was found to be dark brown in colour. The polymer is insoluble in commonly used solvent, but it is soluble in DMF, DMSO, pyridine and conc. H_2SO_4.

UV-Visible Spectra of 4-HACF Polymer

The UV-Visible spectra (Fig. 2) of the 4-HACF polymer 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 4-HACF polymer sample gave two characteristics bands at 270-280nm and 220-230nm. These observed positions for the absorption bands have different intensities. The band at 270-280 nm more intense band which may be accounted for a $\pi\rightarrow\pi^*$ transition while the less intense band at 220-230 nm may be due to $n\rightarrow\pi^*$ transition [19]. $\pi\rightarrow\pi^*$ 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.

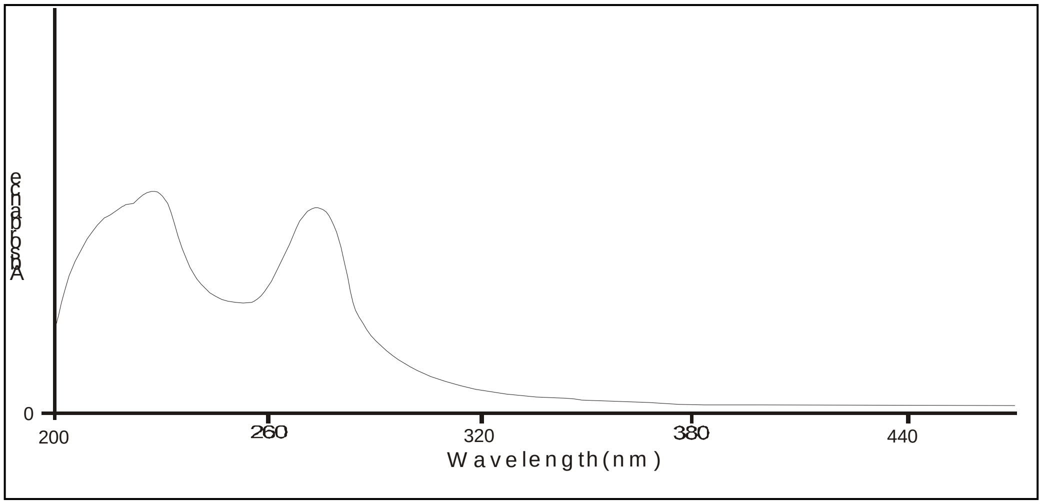

Fig 2: UV-Visible spectra of 4-HACF copolymer

IR Spectra of 4-HACF Polymer

Infrared spectra of polymer 4-HACF resin is shown in Fig. 3, From the spectra it has been revealed that the copolymer show broad absorption band appeared at 3262 cm^{-1} may be assigned to the stretching vibrations of phenolic hydroxyl (-OH) groups exhibiting intramolecular hydrogen bonding [20]. A sharp strong peak at 1592 cm^{-1} may be ascribed to aromatic skeletal ring. The bands obtained at 1360 cm^{-1}suggest the presence of methylene (-CH$_2$) bridge [21]. The sharp and weak band obtained at 1279 cm^{-1} suggests the presence of Ar-CH$_2$-Ar bridge in polymer. The sharp band displayed at 1657 cm^{-1} may be due to stretching vibration of carbonyl group attached to acetophenone moity. The 1,2,4 substitution of aromatic benzene ring recognized by the sharp, medium / weak absorption bands appeared at 827, 979 and 1018 cm^{-1} respectively. This band seems to be merged with very broad band of phenolic hydroxyl group.

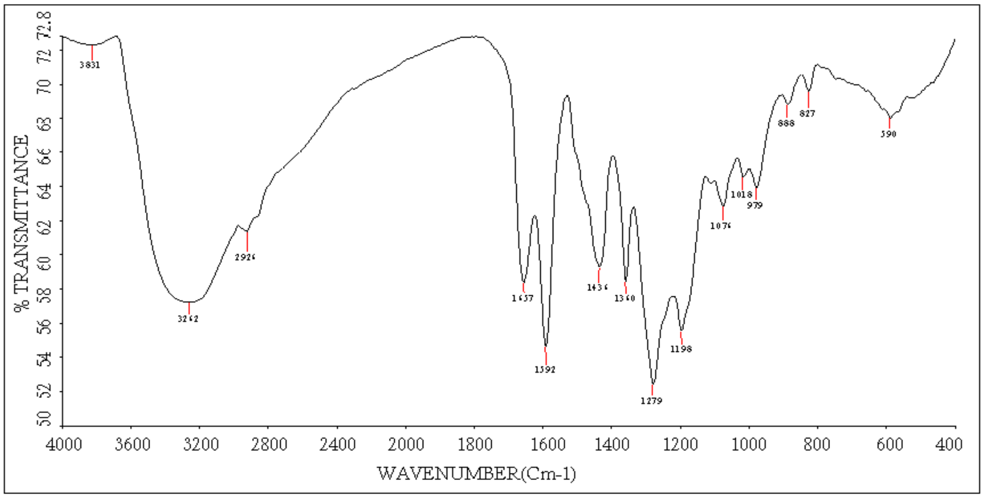

Fig 3: IR Spectrum of 4-HACF Polymer

^{1}H NMR Spectra of 4-HACF Polymer

The ^{1}H NMR spectra of 4-HACF polymer was scanned in DMSO-d_6 solvent and are shown in the Fig.4. The chemical shift (δ)ppm observed is assigned on the basis of data available in literature [22,23]. From the spectral data, The singlet obtained in the region 3.8 (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 6.9 (δ)ppm may be attributed to aromatic proton (Ar-H). The signals in the range at 8.3 (δ)ppm may be due to phenolic hydroxyl protons. The much downfield chemical shift for phenolic –OH indicates clearly the intermolecular hydrogen bonding of -OH group [23,24]. The signal appeared in the region at 2.3 (δ)ppm is due to the methylene proton of Ar-CH_2 bridge [25]. The signals in the range of 3.3 (δ)ppm are due to the proton of –$COCH_3$ groups.

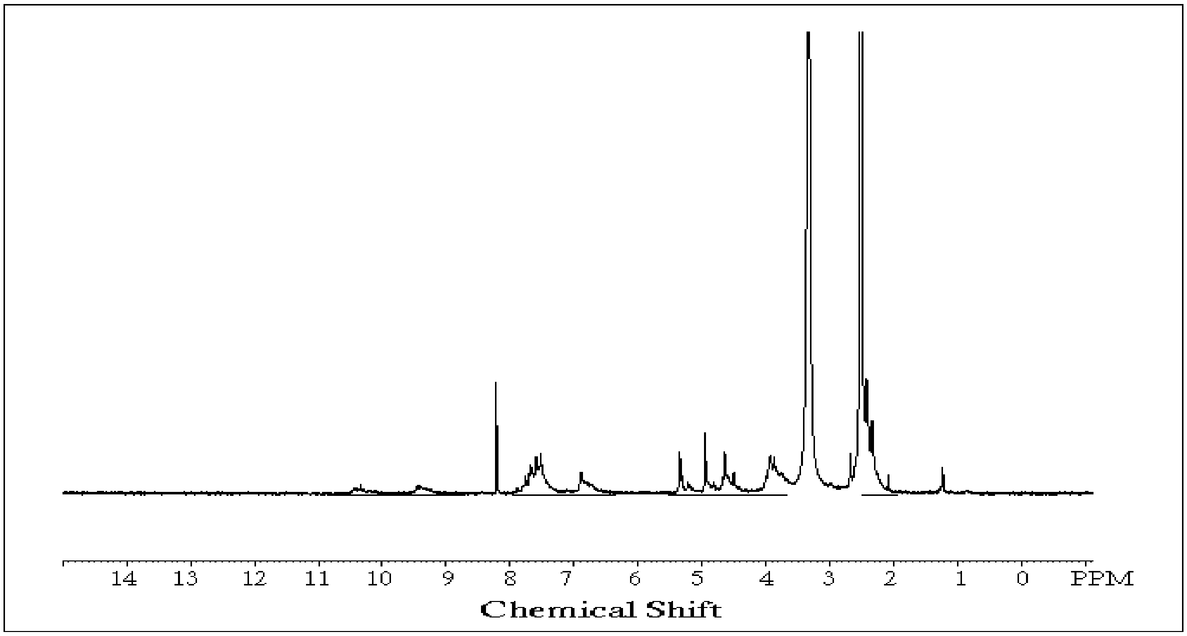

Fig 4: ^{1}H NMR Spectral Data of 4-HACF Polymer

Scanning Electron Microscopy of 4-HACF Polymer

The SEM image of the polymer 4-HACF is shown in Fig. 5. At lower magnification the polymer shows spherulites in which the crystals are arranged smaller in area with more closely packed structure. This indicates the crystalline nature of the polymer. The image also showed a transition state between amorphous and crystalline state. The crystalline form in the polymer may be due to the acidic nature of monomers. However, more predominantly the polymer is amorphous and this change of crystalline into amorphous is due to the polycondensation [26]. The image of polymer clearly indicates a less close packed structure with high porosity or voids. The voids present in the polymer may be responsible for the swelling behavior and the reactivity of the active sites buried in the polymer matrix. 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.

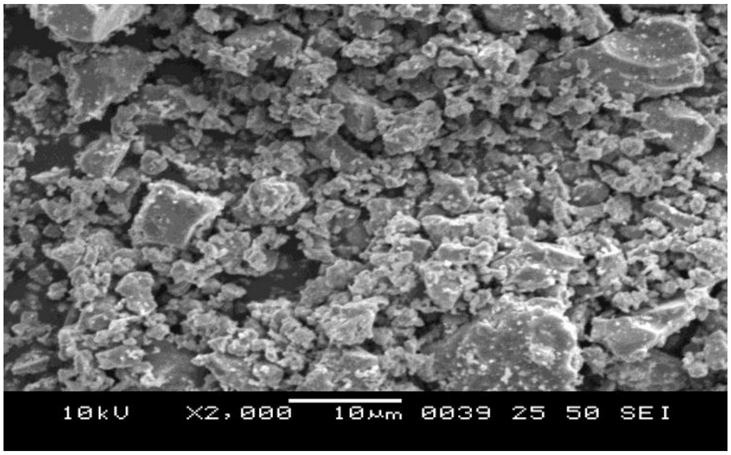

Fig 5: SEM micrographs of 4-HACF polymer

Thermogravimetric Analysis

Thermogravimetry of 4-HACF polymer 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 4-HACF polymer is given in Fig. 6.

TGA of 4-HACF Polymer Resin

Thermogravimetric analysis of 4-HACF polymer is shown in Fig. 6. In order to explore the thermal degradation study of 4-HACF polymer resin, the thermogram has been studied minutely. Thermogram of 4-HACF polymer resin depicts four step decomposition in the temperature range 50-560°C . The first step is slow decomposition between 50 – 230°C corresponds to loss of water molecule (6.26% found and 6.25% calculated). The second step decomposition start from 230-370°C corresponds to 23.95% calculated and 23.93% found which represent degradation of three hydroxyl group which is attach with aromatic ring. The third step which is in the range 370-490°C corresponds to 74.30% calculated and 74.28% 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 490-560 °C

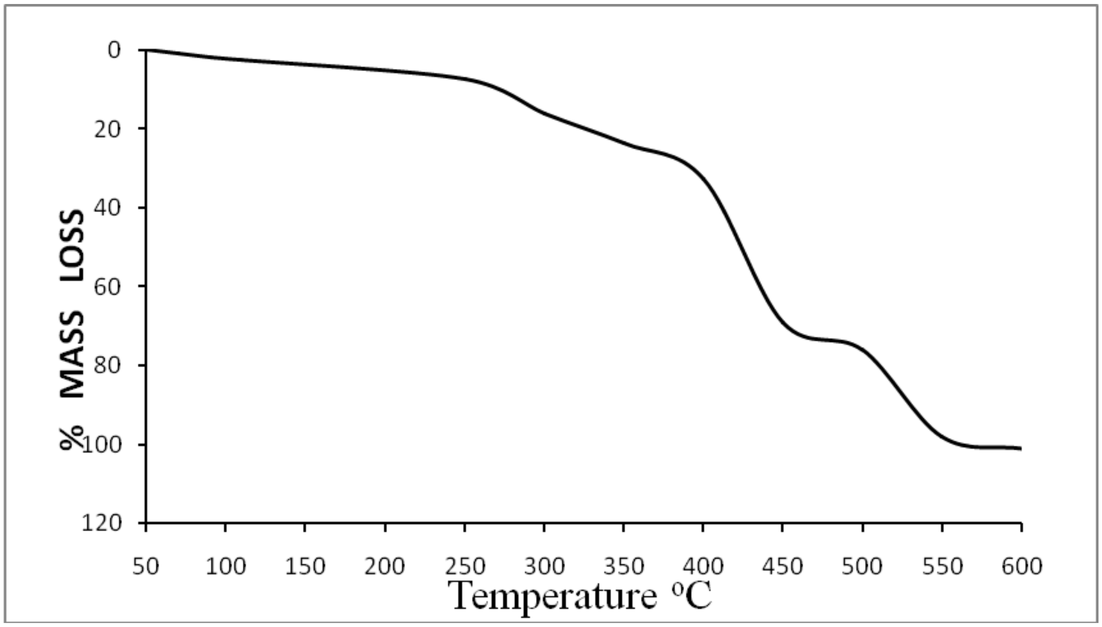

Fig 6: TGA of 4-HACF Polymer Resin

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

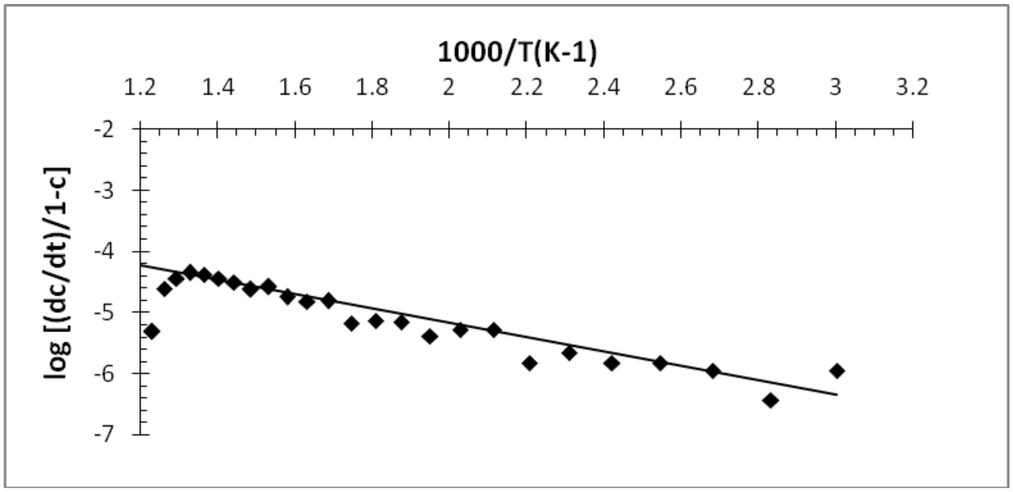

Fig 7: Sharp-Wentworth Plot of 4-HACF Polymer Resin

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.

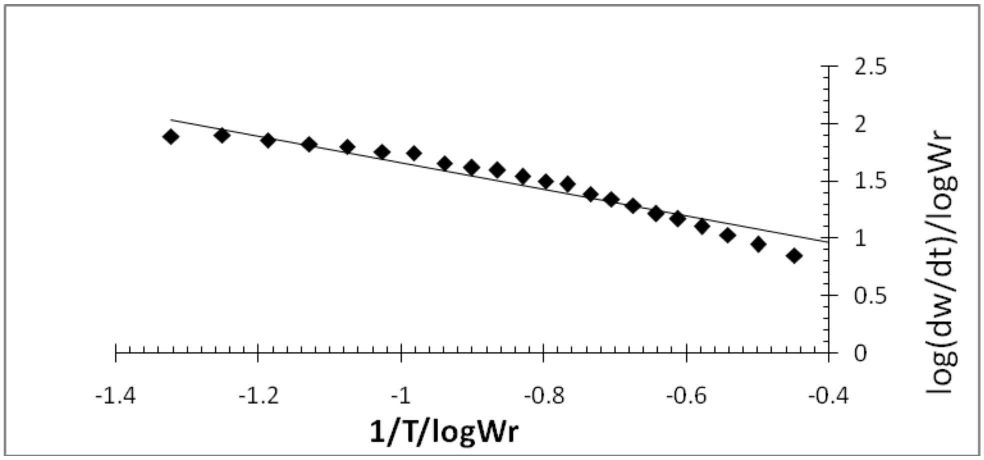

Fig 8: Freeman-Carroll plot of 4-HACF polymer resin

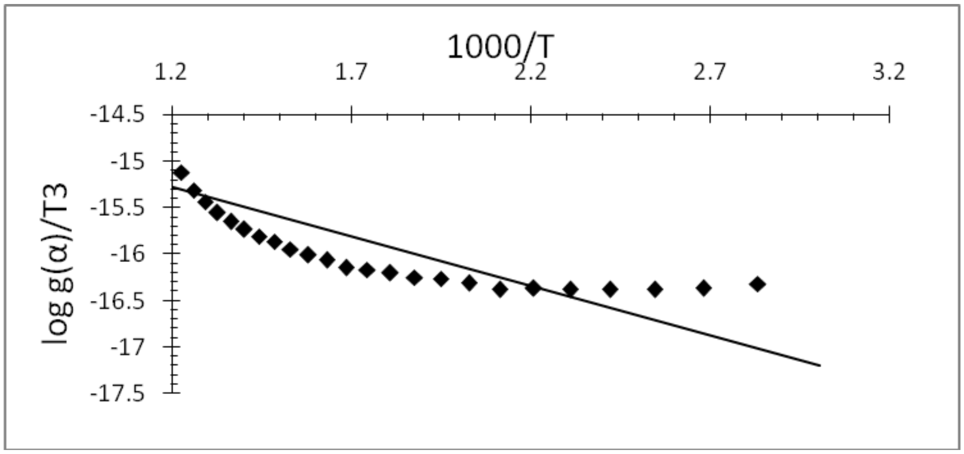

Fig. 9: Freeman-Carroll plot of 4-HACF polymer resin

A plot of percentage mass loss versus temperature is shown in Fig. 6 for 4-HACF polymer. 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 Thermogravimetric Analysis of 4-HACF Polymer Resin

Polymer 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					
4-HACF	553	20.29	21.06	-292.96	182.29	345	-13.73	0.97

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 [27]. 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 4-HACF polymer 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 [28, 29].

CONCLUSION

A polymer (4-HACF) based on the polycondesation reaction of 4-Hydroxyacetophenone and catechol with formaldehyde in the presence of 2M HCl as acid catalyst. Thermogram of 4-HACF polymer resin shows activation energy calculated by the Freeman –Carroll and Sharp-Wentworth methods are in good agreement with each other. Thermodynamic parameters have been calculated on the basis of thermal activation energy and values are given in Table 1. Due to abnormally low value of frequency factor [Z] it may be classified as a slow reaction and no other obvious reason can be given. The value of entropy [ΔS] indicates that the activated polymer has more ordered structure than the reactants and the reaction are slower than normal. It is very difficult to draw any unique conclusion from the magnitude of thermal activation energy [Ea]. Fairly straight –line plots are obtained using the two methods. However, using the Freeman-Carroll method some abnormal point ignored to get a clear picture about most of the points. Isoconversional of analysis of TGA plot indicate variation in activation energy of degradation process. The resins undergoes degradation at high temperature, indicates that the polymer resins under study are thermally stable at elevated temperature.

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