



## Thermal Degradation Study of Copolymer Resin Derived from 4-Hydroxybenzaldehyde, Phenyl Hydrazine and Formaldehyde

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### Abstract

Polymeric resin 4-HBPHF has been synthesized by the polycondensation of 4-hydroxybenzaldehyde, phenyl hydrazine with formaldehyde in presence of HCl catalyst in 4:1:7 molar proportion of reactants. The structure of the resin was elucidated by use of variety of special techniques, for example UV-Visible, FTIR and <sup>1</sup>H NMR spectroscopy. The average molecular weight of the copolymer resin was determined by non-aqueous conductometric titration method. The empirical formula and empirical weight of the resin were determined by elemental analysis. The thermal degradation studies of the 4-HBPHF copolymer resin have been carried out to ascertain its thermal stability. The thermal degradation curve has been discussed in order to determine their mode of decomposition, order of reaction, Apparent activation energy, frequency factor, free energy change, entropy change and apparent entropy change. Freeman-Carroll, Sharp-Wentworth, Friedman, Chang and Coat Redfern method have been applied for the calculation of kinetic parameters while the data from the Freeman-Carroll methods have been used to determine various thermodynamic parameters.

**Keywords:** Synthesis, Copolymer, Morphology, Thermal Degradation, Polycondensation, Activation Energy.

### Introduction

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 coworkers<sup>1</sup> 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 copolymer<sup>2</sup>. Rahangdale and coworkers studied thermal degradation of polymers derived from 2, 4-dihydroxyacetophenone, dithioamide and formaldehyde<sup>3, 4</sup>.

Copolymer resins are derived from 2,4-dihydroxypropiophenone, biuret, and formaldehyde in hydrochloric acid as catalyst and studied their thermal degradation<sup>5, 6</sup>. Thermal degradation of m-nitroaniline, m-chloroaniline and m-aminophenol has been studied by Dash et al.<sup>7</sup> and 2-hydroxyacetophenone, oxamide and formaldehyde<sup>8</sup>. S. L. Oswal et al synthesized and studied thermal properties of copoly(maleimide-methylmethacrylate), terpoly(maleimide-methylmethacrylate-acrylic acid), and terpoly-

(male imide-methyl Methacrylate-methylacrylic acid). The thermal behaviour was studied by TG and DSC techniques<sup>9</sup>. The thermoanalysis and rheological behavior of copolymers of methyl methacrylate, N-phenylmaleimide and styrene studied by G. Jungang et al<sup>10</sup>. 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 fraction<sup>11-15</sup>.

However, the literature studies have revealed that no copolymer has been synthesized using the monomer of 4-hydroxybenzaldehyde, phenyl hydrazine with formaldehyde. Therefore, in the present communication we report the synthesis, structural, characterization and thermal degradation studies of 4-HBPHF copolymer.

### Experimental

All the chemicals used were of analytical grade. 4-hydroxybenzaldehyde, phenyl hydrazine and formaldehyde which is purchased from Merck Chemicals, India.

#### Synthesis of 4-HBPHF Copolymer Resin

The 4-HBPHF copolymer resin was prepared by condensing 4-hydroxybenzaldehyde (0.4 mol) and phenyl hydrazine (0.1 mol) with formaldehyde (0.7 mol) in the presence of 2M HCl as a catalyst at  $124 \pm 2$  °C in an oil bath for 5 hr<sup>16</sup>. The brown colored solid product obtained was

immediately removed and extracted with diethyl ether to remove excess of 4-hydroxybenzaldehyde-formaldehyde copolymer, which might be present along with the 4-HBPHF copolymer. It was further purified by dissolving in 8 % NaOH and then filtered. The copolymer 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 copolymer sample was washed with boiling water and dried in a vacuum at room temperature. The purified copolymer resin was finely ground to pass through 300-mesh size sieve and kept in a vacuum over silica gel. The yield of the copolymer was found to be about 86 %.

**Characterization of 4- HBPHF Copolymer Resin**

The copolymer resins were subject to microanalysis for C, H and N. The number average molecular weights were determined by non-aqueous conductometric titration in DMF using ethanolic KOH as the titrant. The viscosities were determined using a Tuan-Fuoss viscometer at six different concentrations ranging from 3.0 wt.% to 5 wt.% of resin in DMF of 30 °C. Intrinsic viscosity was calculated by the Huggins Eq. (1) and Kraemer Eq. (2)

$$\eta_{sp}/C = [\eta] + K[\eta]^2C \dots\dots\dots(1)$$

$$\ln\eta_{sp}/C = [\eta] + K' [\eta]^2C \dots\dots\dots(2)$$

Infrared spectra of 4-HBPHF copolymer resin were recorded on IR Affinity Shimadzu spectrophotometer in KBr in the range of 4000–400 cm. Proton NMR spectra were recorded on Varian-EM-360A 60 MHz proton NMR Spectrophotometer DMSO-d<sub>6</sub> was used as a solvent. <sup>13</sup>C NMR spectrum was recorded using Bruker 100 MHz.

**Thermogravimetric analysis**

The modes of thermal degradation of the copolymers 4-HBPHF were analyzed using thermogravimetric analyzer (TGA Instruments Model SDT Q600) at a heating rate of 10 °C/min in a static nitrogen atmosphere. Based on the results obtained, the degradation pattern, activation energy (Ea), order of the reaction (n), entropy change (ΔS), free energy change (ΔF), apparent entropy (S\*), frequency factor (Z) were calculated by Freeman–Carroll, Sharp–Wentworth and Coat Redfern methods.

**SEM and XRD studies**

The morphology of the 4-HBPHF

copolymer was analyzed by scanning electron microscope using HITACHI instrument (Model S-3000 H). The 4-HBPHF copolymers were scanned at different magnifications. The particle size and strain of newly synthesized copolymer was identified by XRD using a XD-2 diffractometer (PuXi TongYong Instrument Co. Ltd., Beijing) equipped with CuKα radiation (λ=0.15406nm).

**Results and Discussion**

The resin sample was brown in color, insoluble in commonly used organic solvent, but soluble in DMF, DMSO, THF, pyridine, concentrated H<sub>2</sub>SO<sub>4</sub>. The elements, such as carbon (%C), hydrogen (%H) and nitrogen (%N) content were analyzed for the 4-HBPHF resin and presented in Table II. Based on the analytical data, the empirical formula of the repeating unit for the 4-HBPHF-III copolymer resin is found to be C<sub>32</sub>H<sub>30</sub>N<sub>2</sub>O<sub>7</sub>.

Molecular weight of copolymer was estimated by conductometric titration in DMF against ethanolic KOH by using 50 mg of sample. A plot of the specific conductance against the milliequivalents of potassium hydroxide required for neutralization of 100 g of copolymer was made. Inspection of such a plot revealed that there were many breaks in the plot. From this plot the first break and the last break were noted. The calculation of Mn by this method is based on the following considerations<sup>17,18</sup>: (1) the first break corresponds to neutralization of the more acidic phenolic hydroxy group of all the repeating units; and (2) the break in the plot beyond which a continuous increase is observed represents the stage at which phenolic hydroxy group of all the repeating units are neutralized. On the basis of the average degree of polymerization DP is given by the following relation.

$$(\overline{DP}) = \frac{\text{(Total milliequivalents of base required for complete neutralization)}}{\text{Milliequivalents of base required for smallest interval}} \dots\dots\dots(3)$$

The number average molecular weight Mn could be obtained by multiplying the Dp by the formula weight of the repeating unit<sup>19</sup>. The result of the molecular weight of copolymer samples prepared using higher proportion of two monomers has the highest molecular weight in the series. The molecular weight for 4-HBPHF is 3878.

Viscosity measurements were carried out in DMSO at 30°C. The resin showed normal behaviour. The intrinsic viscosity was determined by the Huggins<sup>20</sup> equation:

$$\eta_{sp}/C = [\eta] + K[\eta]^2C$$

and Kraemers<sup>21</sup> equation:

$$\ln \eta_{sp} / C = [\eta] + K' [\eta]^2 C$$

The viscometric plots are shown in Figure 3. In accordance with the above relations the plots of  $\eta_{sp} / C$  and  $\ln \eta_r / C$  against  $C$  were linear giving the slopes  $K_1$  and  $K_2$  respectively. Intercepts on the viscosity function axis gave  $[\eta]$  values in both the plots. The values of  $[\eta]$  obtained from both relations were good in agreement. The calculated values of Huggin's and Kraemer's constants  $K_1$  (0.403) and  $K_2$  (0.084) in most of the cases satisfy the relation  $K_1 + K_2 = 0.5$  favourably<sup>21</sup>.

The IR spectral study revealed that all these polymer resins gave nearly same pattern of IR spectra. A broad absorption band appeared in the region  $3366 \text{ cm}^{-1}$  may be assigned to the stretching vibrations of phenolic hydroxyl (-OH) groups exhibiting intramolecular hydrogen bonding<sup>22</sup>. A weak band appear at  $2927 \text{ cm}^{-1}$  may be due to  $>NH$  stretching. The sharp band appeared at  $1672 \text{ cm}^{-1}$  may be due to  $-C=O$  (aldehydic moiety) stretching vibrations. The band appeared at  $1594 \text{ cm}^{-1}$  may be due to aromatic  $-C=C$  bending and stretching. A peak at  $1501 \text{ cm}^{-1}$  may be ascribed to aromatic skeletal ring. The bands obtained at  $1440 \text{ cm}^{-1}$  may be due to  $-NH$  bending of secondary amide and the band at  $1386 \text{ cm}^{-1}$  may be due to  $(-CH_2-)$  bridge<sup>22</sup>. The 1,2,3,5 substitution of aromatic benzene ring recognized by the sharp, medium/ weak absorption bands appeared at  $830 \text{ cm}^{-1}$ ,  $1131-1110 \text{ cm}^{-1}$  respectively. The presence of sharp and strong band  $1284 \text{ cm}^{-1}$  indicates the presence of  $(C-N)$  stretching of  $Ar-NH_2$ .

The proton NMR spectra of all 4-HBPHF copolymer resin were scanned in  $DMSO-d_6$  solvent. The chemical shift ( $\delta$ ) ppm observed is assigned on the basis of data available in literature. The 4-HBPHF copolymer resins show an intense weakly multiplet signal at  $3.91 (\delta)$  ppm may be attributed to methyl proton of  $Ar-CH_2-N$  moiety. The medium signal at  $2-4 (\delta)$  ppm may be due to proton of  $-NH$  bridge. The weak multiplet signal (unsymmetrical pattern) in the region of  $6.46-7.31 (\delta)$  ppm may be attributed to aromatic proton ( $Ar-H$ ). The signal in the range of  $5 (\delta)$  ppm may be due to phenolic hydroxyl protons. The position of the signal of phenolic hydroxyl proton is slightly shifted to downfield, indicating clearly the intramolecular hydrogen bonding of  $-OH$  group. The signal at  $9.87 (\delta)$  ppm may be ascribed to presence of Proton of Aldehydic group<sup>23</sup>.

The  $^{13}C$  NMR spectrum shows the corresponding peaks at  $127.0-151.5 \text{ ppm}$  with respect to carbon atom the aromatic ring of 4-

hydroxybenzaldehyde moiety. The corresponding peaks appears at  $158.5, 112.1, 142.1, 118.7, 129.8, 110.7 \text{ ppm}$  with respect to carbon atom of the aromatic ring of phenyl hydrazine moiety. Peak at  $191.0 \text{ ppm}$  may be due to the  $-C=O$  of aldehyde moiety. The peak appeared at  $35.9, 45.2, 26.0 \text{ ppm}$  is assigned to the  $-CH_2-$  bridge in the copolymer.

On the basis of the nature and reactive position of the monomer elemental analysis, IR,  $^1H-NMR$  spectra and molecular weight, the most probable structure have been proposed for these copolymer.

### Thermogravimetric Analysis of the 4-HBPHF Copolymer

The thermal stability of copolymer is evaluated by dynamic thermogravimetric analysis in air atmosphere with heating rate of  $10 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$ . Thermogram of TG of 4-HBPHF copolymer is shown in Fig. 1. Thermogram of copolymer depicts four steps decomposition after loss of water molecule in the temperature range  $50 \text{ }^\circ\text{C} - 600 \text{ }^\circ\text{C}$ . The initially decomposition takes place between  $50 \text{ }^\circ\text{C} - 70 \text{ }^\circ\text{C}$  corresponds to  $3.95 \%$  loss which may attributed to loss of a water molecule against calculated  $3.25 \%$  present per repeat unit of the polymer. The second step decomposition starts from  $70 \text{ }^\circ\text{C} - 340 \text{ }^\circ\text{C}$  which represents degradation of aldehydic group and two hydroxyl groups ( $29.02 \%$  experimental and  $28.16 \%$  calculated). The third step which is start from  $340 \text{ }^\circ\text{C} - 510 \text{ }^\circ\text{C}$  corresponding to  $94.66 \%$  loss of aromatic ring along with two methylenic groups against calculated  $94.58 \%$ . The final step starts from  $510 \text{ }^\circ\text{C} - 560 \text{ }^\circ\text{C}$  corresponding to loss of imide moiety.

From the TG data, the following methods have been used to calculate the various kinetic and thermodynamic parameters and to propose the thermal degradation model.

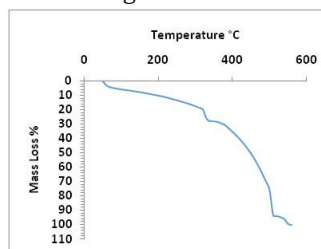


Fig. 1. TG Curve of 4-HBPHF copolymer

### Freeman-Carroll Method:

The straight-line equation derived by Freeman and Carroll<sup>25</sup>, which is in the form of

$$\frac{\Delta \log dW/dt}{\Delta \log W_r} = n - \frac{Ea}{2.303R} \cdot \frac{\Delta(1/T)}{\Delta \log W_r} \dots\dots\dots(4)$$

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 (  $\log dW/dt$  )/  $\log W_r$  vs  $(1/T)/\log W_r$  gives a straight line from which slope we obtained energy of activation ( $E_a$ ) and intercept (Figure 10) on Y-axis as order of reaction ( $n$ ). The change in entropy ( $\Delta S$ ), frequency factor ( $z$ ), apparent entropy ( $S^*$ ) can also be calculated by further calculations.

**Sharp-Wentworth Method:**

Using the equation derived by Sharp and Wentworth<sup>26</sup>

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

.....(5)

Where

$dC/dT$  = rate of change of fraction of weight with change in temperature  
 $\beta$  = linear heating rate  $dT/dt$ .

By plotting the graph (Figure 10) 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.

**Coats - Redfern method:**

Coats and Redfern provides an approximation<sup>27-29</sup>. This is an integral form of the rate equation. The simplified form of the equation is

$$\ln \frac{g(\alpha)}{T^2} = \ln \frac{AR(1-2RT/E_a)}{\phi E_a} - \frac{E_a}{RT}$$

.....(6)

Where,

$T$  = Temperature  
 $A$  = Pre-exponential term  
 $R$  = Gas constant  
 $E_a$  = Energy of activation  
 $\phi$  = Heating rate and  
 $\alpha$  is given by

$$\alpha = \frac{W_0 - W_t}{W_0 - W_f}$$

.....(7)

Where,

$W_0$  = Initial weight of the sample  
 $W_t$  = Residual weight of the sample at the temperature  
 $W_f$  = Final weight of the sample  
 $g(\alpha)$  is equal to  $-\ln(1-\alpha)$  for  $n = 1$  and  $([1-(1-\alpha)^n]/(1-n))$  for  $n \neq 1$ .  
 Thus a plot (Figure 12) of either  $([1-(1-\alpha)^n]/T^2)$  vs  $(1/T)$  or  $[-\ln(1-\alpha)/T^2]$  vs  $(1/T)$  should result

in a straight line of slope  $[-E_a/R]$  for correct value of  $n$ , since it may be shown that for most value of  $E_a$  and for the temperature range over which reaction generally occurs the expression  $\ln \frac{AR(1-2RT/E_a)}{\phi E_a}$  is constant.

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.

The expressions shown are used to calculate the entropy change ( $\Delta S$ ), free energy change ( $\Delta F$ ), apparent entropy ( $S^*$ ), and frequency factor ( $Z$ ).

i. Entropy Change ( $\Delta S$ ):

$$\text{Intercept} = \log \frac{kR}{h\phi E_a} + \frac{\Delta S}{2.303R}$$

.....(10)

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

ii. Frequency Factor ( $z$ ):

$$B_{2/3} = \frac{\log z.E_a}{R\phi}$$

.....(11)

$B_{2/3} = \log 3 + \log [1-3\sqrt{1-\alpha}] - \log p(x)$ .....(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 ( $S^*$ ):

$$S^* = 2.303R \log \frac{zh}{RT}$$

.....(12)

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

**Thermo-analytical Data**

A plot of percentage mass loss versus temperature is shown in the Fig. 1 for a representative 4-HBPHF copolymer. To obtain the relative thermal stability of the copolymer, the method described by Sharp-Wentworth, Freeman-Caroll and Coat Redfern methods was adopted. The thermal stability of copolymer, 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 are not perfectly in agreement with each other. But the 'average  $E_a$ ' calculated by Freeman-Carroll and Sharp-Wentworth is nearly same. However the activation energies obtained from the Coats Redfern method is significantly similar. This is due to similarity in mathematical analogy.

By using the thermal degradation data, thermal activation energy and thermodynamic parameters for all the copolymers resins have

#### SEM and XRD analyses

Surface analysis has found great use in understanding the surface features of the polymers. SEM gives the information of surface topology and defect in the structure. The semi crystalline nature of the 4-HBPHF copolymer resin was established by scanning electron microscopy. The polymerization reaction proceeds by introducing amorphous character in the copolymer sample. The image is a bulbous and honey-bee cluster. The resin is less close packed with high porosity on the surface. Further, the surface of the resin has deep pits with an amorphous character<sup>30</sup>. The morphology of resin

#### Conclusion

The 4-HBPHF copolymer based on the condensation polymerization of 4-hydroxybenzaldehyde and phenyl hydrazine with formaldehyde in the presence of acid catalyst has been prepared.

From the elemental analysis, FTIR and <sup>1</sup>H NMR, <sup>13</sup>C NMR spectral studies the proposed structure of the 4-HBPHF copolymer has been determined. Freeman-Carroll and Sharp-Wentworth provide accurate values of activation

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been calculated. The similarity of the thermodynamic parameters indicates a common reaction mode. With regard to the abnormally low value of frequency factor, it may be concluded that the reaction of decomposition of the copolymer resins can be classed as a "slow" reaction, and no other plausible reason can be given. The decomposition of copolymer resins is known not to obey first order kinetics perfectly, as observed by Jacobs and Tompkins coats and Redfern<sup>30</sup>. The negative value of S indicates that the activated polymer has more ordered structure than the reactants, and that the reactions are slower, than normal.

sample thus identified by SEM as crystalline as well as amorphous or transition between crystalline and amorphous, showing more or less good ion capacity. Polymer states shown schematically and representative XRD patterns. The figure shows Very broad features, not defined by a crystalline model. XRD patterns have very broad features consistent with "incoherent scatter" from an amorphous solid. Amorphous diffraction, incoherent scattering, can be described using a Debye function. Debye related scattering functions to radial distribution functions.

energy while Friedman, Chang and Coats Redfern methods would lead to similarity in determination of activation energy. From the result obtained, the values of kinetic parameters are significantly controlled by the level of degradation and calculation techniques used to analyze the experimental data. The 4-HBPHF resin started degradation at high temperature, indicating that this polymer resin is thermally stable at elevated temperature therefore may be used in industry where need the thermally stable polymer

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