Thermal Studies of 4- Hydroxy benzaldehyde-Phenyl Hydrazine - Formaldehyde Polymer Resin

Meena Kshetrapal[1], **Manish Tiwari**[2], **Kiran S. Vajpai**[1] and **W. B. Gurnule**[3]*
[1]*Department of Chemistry, Govt. Bilasa Girls PG College, Bilaspur-495001 (CG)*
[2]*Department of Chemistry, D. P. Vipro College, Bilaspur-495001*
[3]*Post Graduate Department of Chemistry, Kamla Nehru Mahavidyalaya,*
Nagpur-440024, India
`E-mail: wbgurnule@yahoo.co.in`

Abstract-- **Polymericresin 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 ^{1}H NMR spectroscopy. The elemental analysis technique was used to determine empirical formula and empirical weight of the resin and non-aqueous conductometric titration method was used to determine average molecular weight of the newly synthesized copolymer resin. Thermal stability of the 4-HBPHF copolymer was evaluated by thermal degradation study and from the thermal degradation curve obtained, their mode of decomposition, order of reaction, apparent activation energy, frequency factor, free energy change, entropy change and apparent entropy change has been discussed . The thermodynamic and kinetic parameters were calculated by different methods like Freeman-Carroll, Sharp-Wentworth, Friedman, Chang and Coat Redfern method.**

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

I. INTRODUCTION

Copolymers which are made up of two or more monomer species, found useful in wide variety of products. They may be amorphous, crystalline or resinous in nature. Phenolic resins because of their ease of processability, thermal stability, versatile characteristics and cost effectiveness are useful for structural and thermal applications in aerospace. Thermotyropiccopolyesters were prepared by W. Tang and coworkers[1] from trans-p-hydrocinnamic acid and p- hydrobenzoic acid and studied their thermal decomposition kinetics. By the study of copolymers it will be possible to produced polymers with thermal stability and it will be useful fabricating materials as well. Synthesis, characterization and thermal degradation study of 8-hydroxyquinoline–guanidine–formaldehyde copolymer[2] was done by P. E. P. Michael et al. Thermal degradation of polymers derived from 2, 4-dihdroxy-acetophenone, dithioxamide and formaldehyde[3-4] was studied by Rahangdale and coworkers.

Copolymer resins were derived from 2,4-dihydroxypropiophenone, biuret, and formaldehyde in hydrochloric acid as catalyst and studied their thermal degradation[5-6].

The synthesis and study of thermal properties of copoly(maleimide-methylmethacrylate), terpoly(maleimide-methylmethacrylate- acrylicacid), and terpoly-(maleimide-methyl Methacrylatemethylacrylic acid) has been carried out by S. L. Oswal et al TG and DSC techniques were used to study the thermal behavior[7].

Copolymers of methyl methacrylate, N-phenylmaleimide and styrene were studied by G. Jungang et al [8] for thermoanalysis and rheological behavior. Its necessary to investigate the effect of heat on the polymers in order to establish their thermal stability to synthesize polymers having numerous practical applications. It has concluded from free- model kinetic methods of analysis that the activation energy is a function of the reacted fraction[9-15] though all the methods have been developed by assuming that both activation energy and kinetic model do not change along the process..

Synthesis, structural characterization and thermal degradation studies of 4- HBPHF copolymer is presented in this paper. This copolymer is synthesized using the monomer of 4-hydroxybenzaldehyde, phenyl hydrazine with formaldehyde. As reveled from literature survey no copolymer was synthesized using these monomers.

II. EXPERIMENTAL

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

Synthesisof 4-HBPHFCopolymer Resin

4-hydroxybenzaldehyde (0.4mol) and phenyl hydrazine (0.1mol) were condensed with formaldehyde (0.7mol) using 2M HCl. Temperature was maintained at 124 ± 2 ^{0}C in an oil bath for 5 hrs[16]. After completion of reaction solid product with brown color was obtained. The resulted product was extracted with diethyl ether to remove excess of 4-hydroxybenzaldehyde -formaldehyde 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 purified and ground finely 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. Non-aqueous conductometric titration in DMF using ethanolic KOH as the titrant was used to determined the number average molecular weights. 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 ^{0}C. Intrinsic viscosity was calculated by the Huggins Eq. (1) and Kraemer Eq. (2)

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

$$\text{In}\eta_{sp} / C = [\eta] + K' [\eta]^2 C \ldots\ldots\ldots(2)$$

Infrared spectra of 4-HBPHF copolymer resin were recorded on IR AffinityShimadzu spectrophotometer in KBrin the range of 4000– 400 cm. Proton NMR spectra were recorded on Varian-EM-360A 60 MHz proton NMR Spectrophotometer DMSO-d_6 was used as a solvent. ^{13}C NMR spectrum was recorded using Bruker 100 MHz.

Thermogravimetric analysis

The modes of thermal degradation of the copolymers 4-HBPHF were analyzed using thermogravimetricanalyzer (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 (PuXiTongYong Instrument Co. Ltd., Beijing) equipped with CuKα radiation (λ=0.15406nm).

III. RESULTS AND DISCUSSION

The prepared brown colored resin sample was soluble in DMF, DMSO, THF, pyridine, concentrated H_2SO_4, but insoluble in commonly used organic solvent. The elements, such as carbon (%C), hydrogen (%H) and nitrogen (%N) content were analyzed for the 4-HBPHF resin and presented in Table 2 Based on the analytical data, the empirical formula of the repeating unit for the 4-HBPHF-III copolymer resin is found to be $C_{32}H_{30}N_2O_7$.

Conductometric titration were carried out in DMF against ethanolic KOH by using 50 mg of sample and estimated the molecular weight of copolymer. A plot of the specific conductance against the milli equivalents 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 number average molecular weight (Mn) can be estimated by this method is based on the consideration that the first break corresponds to neutralization of the more acidic phenolic hydroxy group of all the repeating units and 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[17-18].

The average degree of polymerization DP is given by the following relation.

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

The multiplication of *Dp* by the formula weight of the repeating unit gives the number average molecular weight (Mn)[19]. The molecular weight for 4-HBPHF is 3878. Viscosity measurements were carried out in DMSO at 30°C. The resin showed normalbehaviour. The intrinsic viscosity was determinedby the Huggins[20] equation:

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

And Kraemers[21] equation:

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

The viscometric plot are shown in Fig. 3. In accordance with the above relations the plots of η_{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 [η] values in both the plots. The values of [h] 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[21].

Nearly same pattern of IR spectra was observed for all these polymer resins. A board absorption band appeared in the region 3366 cm^{-1} represents the stretching vibrations of phenolic hydroxyl (-OH) groups having intramolecular hydrogen bonding[22]. The presence of weak band at 2927 indicates the >NH stretching. The sharp band at 1672 cm^{-1}represents –C=O (aldehydic moiety) stretching vibrations. The band appeared at 1594 cm^{-1} may be due to aromatic –C=C bending and stretching . A peak at 1501 cm^{-1} corresponds aromatic skeletal ring. The 1,2,3,5 substitution of aromatic benzene ring recognized by the sharp, medium/ weak absorption hands appeared at 830 cm^{-1}, 1131- 1110 cm^{-1}respectively. The presence of sharp and strong band 1284 cm^{-1} indicates the presence of (C–N) stretching of $Ar–NH_2$. The bands obtained at 1440 cm^{-1} and at 1386 cm^{-1} may be due to -NH bending of secondary amide and ($-CH_2-$) bridge[22] respectively

The proton NMR spectra of all 4-HBPHF copolymer resin were scanned in DMSO-d_6 solvent. The chemical shift (δ) ppm observed is assigned on the basis of data available in literature. The 4-HBPHF copolymer resins show an intense weakly multiplate signal at 3.91 (δ) ppm may be attributed to methyl proton of $Ar-CH_2-N$ moiety. The medium signal at 2- 4 (δ) ppm may be due to proton of -NH bridge. The weak multiplate signal (unsymmetrical pattern) in the region of 6.46-7.31 (δ) ppm may be attributed to aromatic proton (Ar-H). The signal in the range of 5(δ)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 at9.87(δ) ppm may be ascribed to presence of Proton of Aldehydic group[23].

The ^{13}C NMR spectrum shows the corresponding peaks at 127.0- 151.5 ppm with respect to carbonatom the aromatic ring of 4-hydroxybezaldehyde moiety. The corresponding peaks appears at 158.5, 112.1, 142.1, 118.7, 129.8, 110.7 ppm with respect to carbon atom of the aromatic ring of phenyl hydrazine moiety. Peak at 191.0 ppm may be due to the –C=O of aldehyde moiety. The peak appeared at 35.9,45.2, 26.0 ppm is assigned to the $–CH_2$ bridge in the copolymer[24].

On the basis of the nature and reactive position of the monomer elemental analysis, IR, ^{1}H-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 $^{0}C.min^{-1}$.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^{0}C–600 ^{0} C. The initially decomposition takes place between 50^{0}C-70 ^{0}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 secondstep decomposition starts from $70^{0}C–340^{0}C$ 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^{0}C - 510 ^{0}C corresponding to 94.66 % loss of aromatic ring along with two methylenic groups against calculated 94.58 %. The final step starts from 510^{0}C – 560 ^{0}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.

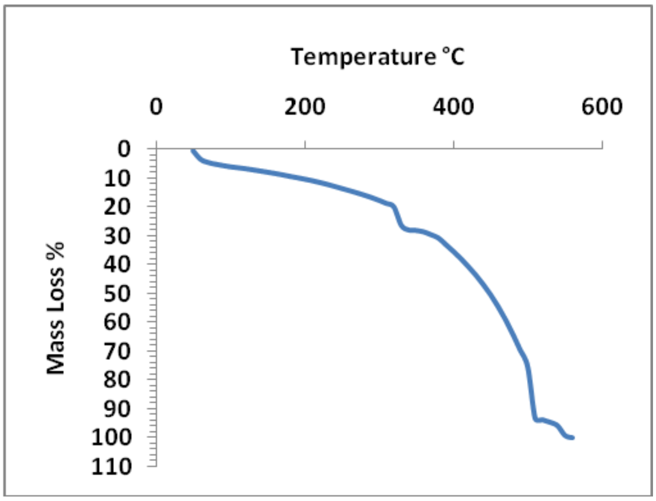

Fig. 1. TG Curve of 4-HBPHF copolymer

Freeman–Carroll Method

The straight-line equation as derived by Freeman and Carroll[25] is -

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

Where

dW/dt = rate of change of weight withtime.

Wr = *Wc-W*

Wc= weight loss at completion ofreaction.

W = fraction of weight loss at time t.

Ea= energy of activation.

n = order of reaction.

When graph was ploted between the terms [(log dW/dt)/ log] and [(1/T)/log Wr] obtained a straight line. The slope of this line represents energy of activation (*Ea*) and intercept(Figure.10) on Y-axis represents order of reaction (*n*). The change in entropy (*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[26].

$$\log\frac{dC/dT}{1-C} = \log A/\beta - \frac{Ea}{2.303R}\cdot\frac{1}{T} \ldots\ldots\ldots\ldots(5)$$

Here, dC/*dT* is the rate of change of fraction of weight with change in temperature and β represents the linear heating rate *dT/dt*.

A straight line is obtained when graph is plotted (Fig. 10) between $\log \frac{dC/dT}{1-C}$ *vs.* $\frac{1}{T}$.

Energy of activation (*Ea*) is obtained from slope of this line.

Coats - Redfern method:

Coats and Redfern provides an approximation[27-29]. This is an integral form of the rate equation. The simplified form of the equation is

$$\ln \frac{g(\propto)}{T^2} = \ln \frac{AR(1-2\,RT/E_a)}{\emptyset E_a} - \frac{E_a}{RT} \text{---}(6)$$

Where,
T = Temperature
A = Pre-exponential term
R = Gas constant
Ea = Energy of activation
ϕ= Heating rateand
α is given by

$$\propto = \frac{W_0 - W_t}{W_0 - W_f} \text{---}(7)$$

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(α) is equal to –ln (1-α) for n = 1 and ([1-(1-α)^n]/(1-n)) for n # 1.
Thus a plot (Figure 12) of either ([1-(1-α)$^{1-n}$]/T^2(1-n)) vs (1/T) or [–ln(1-α)/ 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 $\ln \frac{AR(1-2\,RT/E_a)}{\emptyset E_a}$ is constant.

The variation of the apparent activation energy values with degree of degradation can be check by this isoconversional (model-free) kinetic methods.

The expressions shown are used to calculate the entropy change (ΔS), free energy change (ΔF), apparent entropy (S*), and frequency factor (Z).

i. Entropy Change (*ΔS*):

$$Intercept = \log \frac{kR}{h\phi Ea} + \frac{\Delta S}{2.303R} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (10)$$

Where, $k = 1.3806 \times 10^{-16}$ erg.deg^{-1}.mol^{-1},

$R = 1.987$ cal.deg^{-1}.mol^{-1},

$h = 6.625 \times 10^{-27}$erg. sec,

$\phi = 0.166$,

ΔS = entropy change,

Ea = activation energy.

ii. Frequency Factor (z):

$$B_{2/3} = \frac{\log z.Ea}{R\phi} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(11)}$$

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

Where, z is frequency factor,

B = calculated from eq [a],

$\log p(x)$ = calculated from Doyle table corresponding to activation energy.

iii. Apparent entropy change (S*):

$$S^* = 2.303R \log \frac{zh}{RT^*} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \textit{(12)}$$

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

Thermo-analytical Data

Fig. 1 shows graph between percentage mass loss versus temperature for a representative 4-HBPHF copolymer. The relative thermal stability of the copolymer was described by using Sharp-Wentworth, Freeman-Caroll and Coat Redfern methods. 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.

Though the activation energy (Ea) calculated by using thermal decomposition data and by applying above methods are not perfectly in agreement with each other but the ‘average *Ea*’ calculated by Freeman-Carroll and Sharp- Wentworth is nearly same.

However due to similarity in mathematical analogy the activation energies obtained from the Coat Redfern method is significantly similar.

Thermal activation energy and thermodynamic parameters for all the copolymers resins have been calculated by using the thermal degradation data. The similarity of the thermodynamic parameters indicates a common reaction mode. From 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. Jacobs and Tompkins coats and Redfern[30] observed that the decomposition of copolymer resins does not obey first order kinetics perfectly. The activated polymer has more ordered structure than the reactants, and the reactions are slower, than normal as indicated by the negative value of S.

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[30]. The morphology of resin 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.

IV. CONCLUSION

The 4-HBPHF copolymer has been prepared by condensation polymerization of 4-hydroxybenzaldehyde and phenyl hydrazine with formaldehyde using acid catalyst. The structure of the 4-HBPHF copolymer has been confirmed from the elemental analysis, FTIR and ^{1}H NMR, ^{13}C NMR spectral studies. Similarity in determination of activation energy were observed in Freidman, Chang and Coat Redfern methods while Freeman-Carroll and Sharp-Wentworth provide accurate values 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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