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Kinetics of Thermal Decomposition of Copolymer Resin-II Derived from 4-hydroxylbenzaldehyde, Phenyl hydrazine and Formaldehyde.

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ABSTRACT

Polycondensation technique was employed to synthesize copolymer resins of 4-hydroxybenzaldehyde, phenyl hydrazine and formaldehyde in acidic medium with mole proportion of 1:1:2. The copolymer was characterized by ultraviolet, infra-red, nuclear magnetic resonance (^{1}H and ^{13}C) spectroscopy, scanning electron microscopy (SEM) and X- ray diffraction analysis (XRD). The thermal decomposition pattern and the kinetics of thermal decomposition of the copolymers were investigated by thermogravimetric analysis (TGA) in a static nitrogen atmosphere at a heating rate of 10° C/min. Freeman–Carroll, Sharp– Wentworth, Freidman's, Chang and Coat Redfern methods have been adopted to evaluate the kinetic and thermodynamic parameters such as thermal activation energies (E_a), order of the reaction (n), entropy change (ΔS), free energy change (ΔF), apparent entropy (S*), and frequency factor (Z).

Keywords: Copolymer, Thermal analysis, Kinetics, Degradation model, synthesis, Thermodynamic parameters.

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INTRODUCTION

Recently, much attention has been focused on the development of copolymers which are rational alternative to conventional polymers [1, 2]. The biomedical applications of copolymers have further provoked the researchers for the synthesis of new copolymers with heteroatoms in their molecular structure. A survey of the literature reveals that the copolymers with low molecular weight exert a pull on the concentration of synthetic chemists due to their varied biological activities [3]. A comparative study of mechanical and thermal behaviors of poly(propylene cyclohexene carbonate)s and poly (propylene carbonate) have been carried out, and the poly (propylene cyclohexene carbonate) possesses higher thermal stability and mechanical strength compared to the latter [4]. Thermal degradation kinetics of poly(methylphenylsiloxane) containing methacryloyl groups was investigated that different solid-state reaction mechanism was followed at different stages of degradation [5]. Methylvinylsilylene and styrene were copolymerized at different feed ratios. The thermal study reveals that the order of the reaction increases with the increase in the molar proportions of the monomer [6]. Copolymer involving 8-hydroxyquinoline 5-sulfonic acid and melamine with formaldehyde was synthesized in the presence of an acid catalyst, and its thermal stability has also been reported. The high initial decomposition temperature of the copolymer indicates the thermal stability of the copolymer [7]. Kinetic parameters of the copolymer involving 2,2-dihydroxybiphenyl, urea, and formaldehyde were calculated by the Freeman–Carroll (FC) and Sharp–Wentworth (SW) methods. From the results, it was reported that the copolymers have good thermal stability, and the decomposition reaction follows the first order kinetics [8]. Copolymer involving salicylic acid, guanidine, and formaldehyde was prepared, and its kinetic parameters evaluation was also carried out. The order of the reaction was found to be nearly one, and thermal activation energy was found to be very low [9]. Similarly, solution polymerization of three monomers involving 8-hydroxyquinoline, salicylic acid, and formaldehyde was carried out to obtain a copolymer. From the TGA results, the copolymer was thermally stable, and the order of reaction for the thermal decomposition was found to be nearly one [10].The copolymer involving 8-hydroxyquinoline, anthranilic acid, and formaldehyde and its polychelates with few transition metals. The thermal stability and its kinetic parameters were calculated. The result of the study reveals that the polychelates possess higher thermal stability, low activation energy, and decreased order of reaction compared to their copolymer ligand [11]. 2-hydroxy-4-ethoxybenzophenone–ethylene (HEBP–1,2-PG) resin was synthesized by the condensation of 2-hydroxy-4-ethoxybenzophenone and 1,2-propylene glycol in acidic medium, and its polychelates were synthesized. It was observed that the incorporation of the metal ion into the polymeric backbone decreases the thermal stability because of breaking of an intramolecular hydrogen bonding present in the polymeric ligand [12]. The present research article discusses the synthesis and the characterization of the copolymer resin derived from 4- hydroxybenzaldehyde and phenyl hydrazine with formaldehyde. The thermal behavior of the copolymer resins was evaluated by TGA, and the kinetic and thermodynamic parameters such as activation energy (E_a), order of the reaction (n), entropy change (ΔS), free energy change (ΔF), apparent entropy (S*), and frequency factor (Z) were determined by FC and SW, Freidman's, Chang and Coat Redfern methods [16].

EXPERIMENTAL

Materials

4- Hydroxybenzaldehyde and phenyl hydrazine were procured from Merck, India and purified by rectified spirit. Formaldehyde (37%) were of AR grade, Merck and used as received. Double distilled water was used for all the experiments. All other chemicals were of analytical grade and used without further purification.

Synthesis of Resin

The copolymer resin (4-HBPHF -II) involving 4- hydroxybenzaldehyde (0.2 mol) and phenyl hydrazine (0.1 mol) with formaldehyde (0.3 mol) was synthesized using glacial acetic acid as the reaction medium at 120 ± 2 °C for 6 h [21]. The reaction mixture was then cooled, poured into crushed ice with constant stirring, and left overnight. The brown colored resin obtained was then washed with warm water and methanol. It is then filtered off to remove unreacted monomers. Finally, the copolymer resin was air dried. The yield of the copolymer was found to be 80.99% (Table1). The dried resin sample was then dissolved in 8% NaOH and regenerated using 1:1 (v/v) HCl/water. It is then filtered off and cured in an air oven at 75 °C for 24 h. The proposed reaction for the synthesis of copolymer is shown in Fig. 1. The purity of newly synthesized and purified polymer resin sample has been tested and confirmed by thin layer chromatography technique. Dimethyl sulphoxide (DMSO) was used as a solvent for developing chromatogram and was allowed to run for about 30 min, when the chromatogram was exposed to iodine chamber then we get single colour spot for resin sample. This indicates that the synthesized and purified polymer resin sample has no impurities.

Table 1: Synthesis 4 – HBPHF-II copolymers

Copolymers	Reactants			Molar ratios	Catalyst 2M HCl (ml)	Reflux Temp. 0C	Yield (%)	Time (hr)	Melting point (K)
	4-hydroxybezaldehyde (4-HB)(mol)	Phenyl hydrazine (PH) (mol)	Formaldehyde (F) (mol)						
4 – HBPHF-II	0.2	0.1	0.3	2:1:3	200	120 ±2	89.99	5	489-495

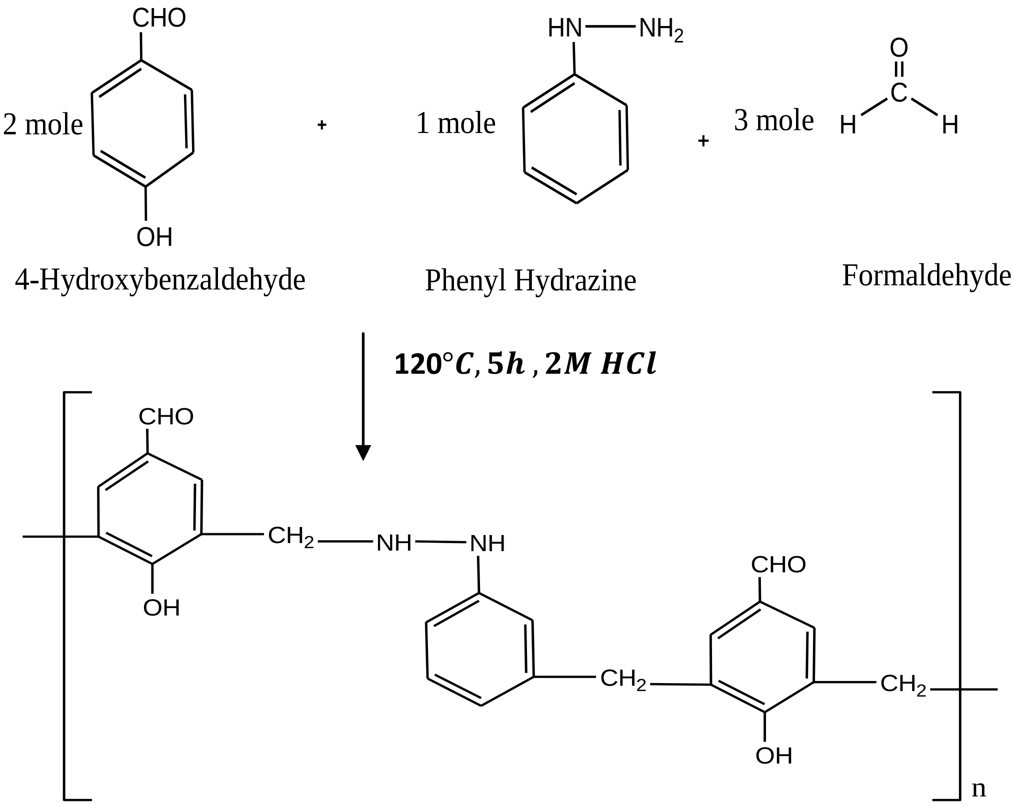

Figure 1: Reaction and suggested structure of 4 – HBPHF -II Copolymer resin

Elemental analysis

The carbon, hydrogen and nitrogen of the copolymer resin were done by microestimation technique by using Perkin Elmer 2400 Elemental analyzer.

Spectral Analyses

The UV-Visible spectra of the 4-HBPHF-II copolymer resin was recorded at room temperature in dimethyl formamide (spectroscopic grade) in 850 to 200 nm range by using UV 240 shimadzu automatic recording double beam spectrophotometer fitted with an automatic pen chart recorder. The FTIR spectrum of the copolymer had been scanned in KBr pellets on a Bruker (Model Tensor 27) spectrophotometer, and the proton NMR spectrum of the copolymer resin was recorded in DMSO-d_6 solvent using Bruker 400 MHz. ^{13}C NMR spectrum was recorded using Bruker 400 MHz.

Thermogravimetric analysis (TGA)

The modes of thermal degradation of the copolymer 4-HBPHF-II was analyzed using thermogravimetric analyzer (TA 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 (E_a), order of the reaction (n), entropy change (ΔS), free energy change (ΔF), apparent entropy (S*), and frequency factor (Z) were calculated by FC and SW, Freidman's, Chang and Coat Redfern methods.

SEM and XRD analyses

The surface analysis of the 4-HBPHF-II copolymer resin was examined by scanning electron microscope (SEM) using Hitachi (Model S-3000H) at 50009 magnification. The particle size and strain of newly synthesized copolymer was identified by XRD using a XD-2 diffract meter (PuXi TongYong Instrument Co. Ltd., Beijing) equipped with CuKα radiation (λ=0.15406nm).

RESULTS AND DISCUSSION

The 4-HBPHF-II copolymer resin was soluble in solvents like N,N-dimethylformamide (DMF), tetrahydrofuran (THF), dimethylsulfoxide (DMSO), and aqueous NaOH and KOH solutions, whereas the resins were insoluble in common organic solvents. From the Table 2, it is found that the values of the % elements determined are in good agreement with the calculated values. The elemental analysis data suggest the empirical formula and the empirical formula weight for the repeating unit of 4-HBPHF-II Copolymer resin as given in Table 2.

Table 2: Elemental Analysis and Empirical Formula of 4-HBPHF-II Copolymer Resins

Copolymer Resins	% of C observed (Cal.)	% of H observed (Cal.)	% of N observed (Cal.)	Empirical formula of repeated unit	Empirical formula weight
4 -HBPHF -II	67.59 (67.98)	5.78 (5.42)	6.98 (6.90)	$C_{23}H_{22}O_5N_2$	406

The UV-visible spectra of all the 4 –HBPHF-II copolymer samples in pure DMSO were recorded in the region 200-800 nm at a scanning rate of 100 nm min^{-1} and at a chart speed of 5 cm min^{-1}. The perusal of the UV-visible spectra of copolymers showed almost similar nature. The spectra of these copolymers exhibit two absorption maxima in the region 290-330 nm and 340-400 nm. These observed positions of the absorption bands indicate the presence of carbonyl group having a carbon-oxygen double bond and azo group which is in conjugation with the aromatic nucleus. The appearance of former band can be accounted for π→π* transition while the later bond may be due to n→π* electronic transition. The shift from the basic value may be due to conjugation effect, and presence of phenolic hydroxy group (auxochromes) is responsible for hyperchromic effect i.e. $\varepsilon_{\max}$ higher values[7, 24]. This observation is in good agreement with the proposed most probable structures of these copolymer resins

The FTIR spectrum of the 4 –HBPHF-II copolymer resin is shown in Fig. 2, and the spectral data are presented in Table 3. A strong band at 1293.1 cm^{-1} is due to (C–N) stretching of (Ar–NH$_2$) [22]. A broad band appeared in the region 3185 cm^{-1} may be assigned to the hydroxyl group [22, 23]. A peak appeared at 1595 cm^{-1} may be assigned to aromatic ring stretching modes [24]. The tetra substitution of aromatic benzene ring by sharp, medium/weak absorption bands appeared between 1163 and 800 cm^{-1} [24]. The band appeared at 1671 cm^{-1} may be due to –C=O (aldehydic moiety) stretching vibrations [25]. The band appeared at 1595 cm^{-1} may be due to aromatic –C=C bending and stretching . The band appeared at 1438 cm^{-1} may be due to –NH bending vibration of secondary amine .The presence of –NH bridge in the copolymer is confirmed by the absorption band at 2826 cm^{-1} [22]. This band seems to be merged with a broad band of –OH group. A band appeared at 2837.6 cm^{-1} may be attributed to $–CH_2$ linkage present in the copolymer resin [26].

Table 3: IR frequencies of 4-HBPHF-II polymer resin.

Observed band frequencies (cm-1)	Assignment	Expected band frequencies (cm-1)
	4 – HBPHF-II	
3185(b)	-OH phenolic intermolecular hydrogen bonding	3500-3100
2826(w)	>NH stretching	2800-2900
1671 (m)	Aromatic ring with aldehydic group	1630-1680
1595(sh)	Aromatic C=C bending and stretching	
1509(sh,b)	Aromatic ring (substituted)	1600-1500
1273(b,st)	(C–N) stretching of Ar–NH2	1200–1300
1438(w)	-NH bending vibration of secondary amide	1490-1570
1163- 831 (m)	Tetrasubtituted aromatic ring	1200- 830
759(m)	CH2 bending (rocking)	800-710
693 (m)	1,2,3,5 substitution in aromatic ring	550-600

sh=sharp; b=broad; st=strong; m=medium; w=weak

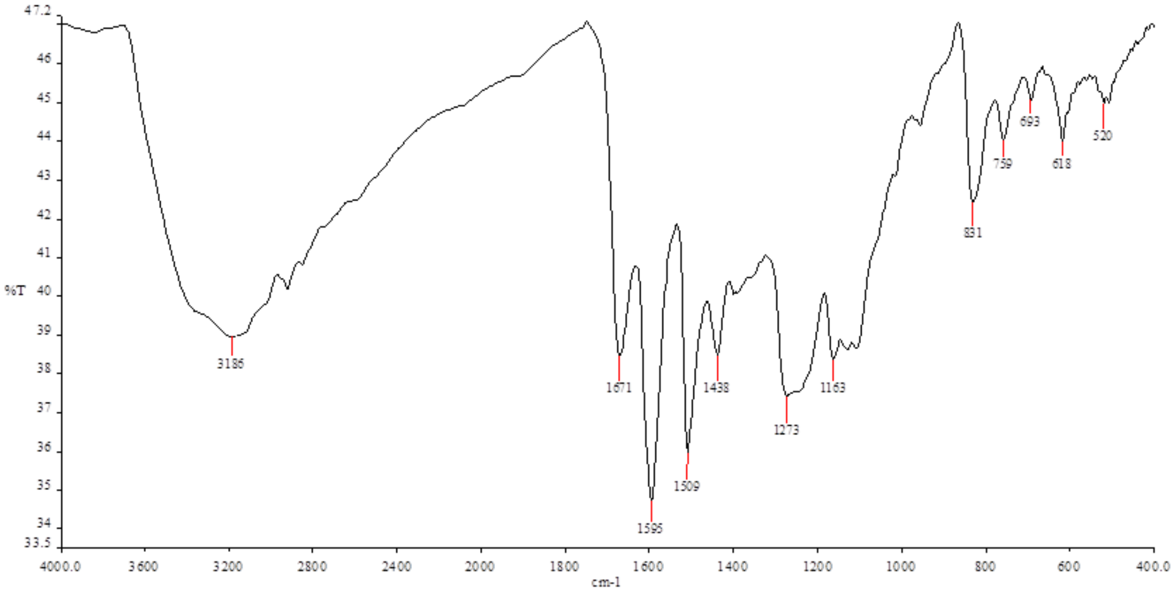

Figure 2: Infra-Red Spectra of 4 – HBPHF-II Copolymer resin

The ^1H NMR spectrum of 4 –HBPHF-II copolymer resin is depicted in Fig. 3, and the spectral data are presented in Table 4. The chemical shift (δ) ppm observed is assigned on the basis of the literature [7, 10, 24]. The medium singlet at 2.35-2.59 (δ) ppm may be due to methylene proton of Ar–CH_2 bridge. A singlet observed in the region 3.91 (δ) ppm is due to methylene proton of Ar–CH_2–N moiety. A signal observed at 4 (δ) ppm is due to Ar-NH moity. A singlet observed in the region 2 (δ) ppm may be attributed to the protons in –NH linkage. The signal at 5 (δ) ppm is assigned due to –OH group. The signal at9.87- 9.89 (δ) ppm is assigned to Ar–CHO indicates the intramolecular hydrogen bonding between Ar–CHO groups in the terpolymer resin. The signals in the region at 6.5-7.27 (δ) ppm may be assigned to the protons in the aromatic ring.

Table 4: ^{1}H NMR Spectral data of 4-HBPHF-II polymer resin.

Observed Chemical Shift (δ) ppm	Nature of proton assigned	Expected chemical shift (δ) ppm
2.35-2.59	Methylene proton of Ar-CH2 moiety	2.00 - 3.00
3.91	Methylenic proton of Ar-CH2-N moiety	3.00 - 3.50
4	Proton of Ar–NH bridge	4.00 - 8.00
6.5-7.27	Aromatic Proton (Ar-H)	6.2 - 8.5
5	Proton of phenolic-OH involved intramolecular hydrogen bonding	4.5 - 5.5
2	Proton of amines - CH2-NH-	1-2
9.87-9.89	Proton of Aldehydic group	9-10

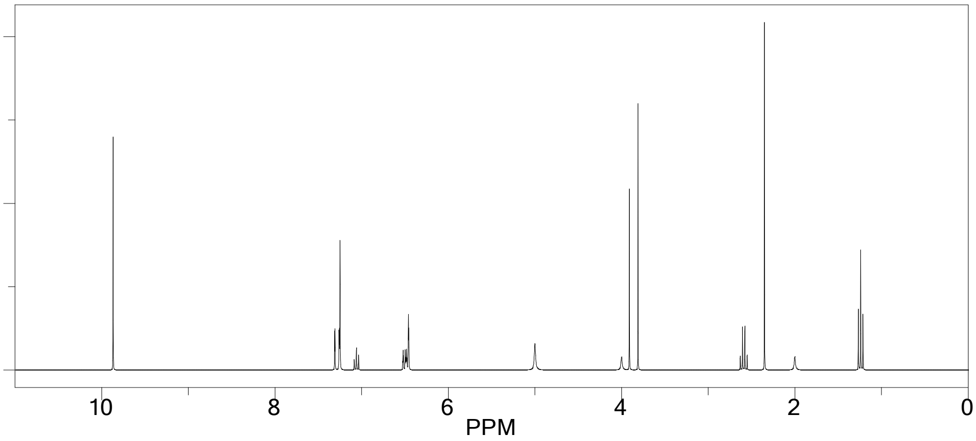

Figure 3: ^{1}H NMR Spectra of 4 – HBPHF-II Copolymer resin

The ^{13}C NMR spectrum of 4 –HBPHF-II resin, the peak positions are assigned according to the literature [27]. The ^{13}C NMR spectrum shows the corresponding peaks at 129.2-129.9, 126.5-127.8, 129.4-128.4, 158.2, 126.4-130, 129.6-128.0 ppm with respect to C_1 to C_6 of the aromatic ring of 4 - Hydroxybezaldehyde moiety. The corresponding peaks appears at 151.5, 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, 22.5 ppm is assigned to the –CH_2 bridge in the terpolymer. From the spectral analyses, (FTIR and NMR) the structure of the 4-HBPHF-II is proposed.

Thermogravimetric technique is found to be a valuable method to evaluate the thermal decomposition pattern of the polymer. Thermogram of the 4 –HBPHF-II copolymer is depicted in Fig. 4, and the data are presented in Table 5. The 4 –HBPHF-II resin exhibits the decomposition involving four stages. The first stage decompo-sition begins at 50 °C with a weight loss of 4.06% (calc. 4.43%) of the resin and ends at 60 °C which may be due to the removal of water molecule present in the copolymer. In the second stage, the decomposition starts at 60 °C with 26.20% of weight loss (calc. 27.09%) and ends up at 400 °C, and this loss may be due to the elimination of -CHO and –OH groups attached to the aromatic nucleus.

In the third stage, the decomposition starts at 400 °C with 90.05% of weight loss (calc. 92.61%) and ends up at 560 °C, and this loss may be due to the elimination of $–CH_2$ and the aromatic nucleus. The final stage of the decomposition starts at 560 °C, and the complete decomposition of the copolymer takes place at 600 °C involving 99.89% (calc. 100%) of weight loss of the remaining imides moiety of copolymer resin.

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 (Table 6, 7)

Table 5: Thermal degradation behaviour of 4-HBPHF-II polymer resin

Copolymer	Stages	Temp Range	Wt. loss(%)		Group loss
			Found	Calcd.	
4 – HBPHF-II	1st	50.0-60.0	4.06	4.43	H_2O molecule entrapped
	2nd	60.0-400.0	26.20	27.09	degradation of -CHO group with -OH groups
	3rd	400.0-560.0	90.05	92.61	loss of aromatic ring along with $-CH_2$ groups
	4th	560.0-600.0	99.89	100	loss of –NH-NH- moiety.

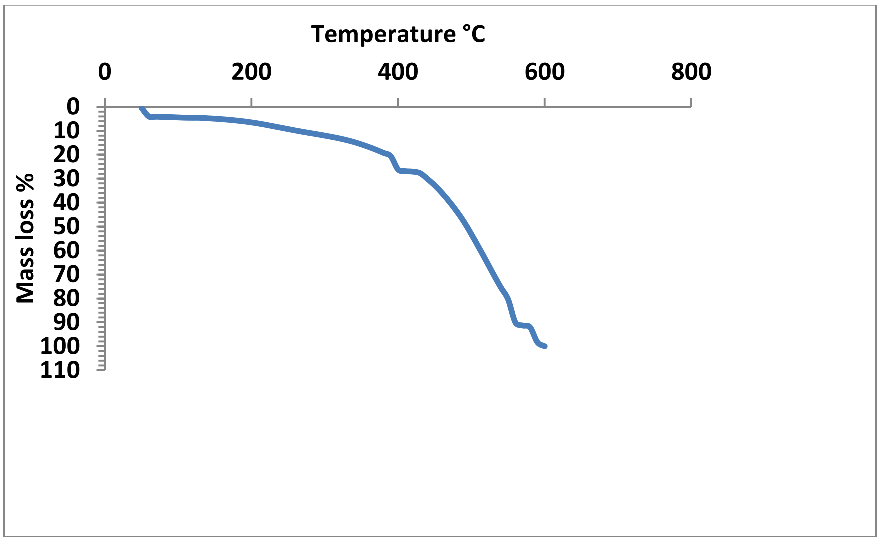

Figure 4: Decomposition pattern of 4 – HBPHF-II Copolymer resin.

Freeman Carroll method

The activation energy (E_a) and the order of reaction (n) for the terpolymer decomposition were calculated using the following expression proposed by FC.

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

where, dw/dt is the rate of change of weight with time; $W_r = W_c - W$, where W_c is the weight loss at the completion of reaction or at definite time and W is the total weight loss up to time t; n is the order of the reaction, T and R are the temperature and the gas constant, respectively.

Hence, a plot of Dlog(dw/dt)/DlogW_r versus D(1/T)/DlogW_r gives a slope of -E_a/2.303R with an intercept equals to n on the y-axis where x = 0 (Fig.5,6).

Sharp Wentworth Method

The following expression given by SW was used to determine the activation energy (E_a), entropy change (DS), and free energy change (DF).

$$\log \frac{dC/dT}{1-C} = \log A/\beta - \frac{Ea}{2.303R} \cdot \frac{1}{T} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

Where *dC/dT* is a rate of change of fraction of weight with change in temperature. $^{\beta}$ *is* linear heating rate *dT/dt*. The graph of logdc/dt/(1 - C) versus 1/T gives a slope of -E_a/2.303R with an intercept on the y-axis where x = 0 (Fig.7).

Friedman Method

Friedman provides the following expression for thermal degradation kinetic studies based on Arrhenius equation:

$$ln\left(\frac{d\alpha}{dt}\right) = ln(z) + n.ln(1-\alpha) - \left(\frac{Ea}{RT}\right) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

Where α is the conversion at time *t, R* is the gas constant (8.314 J.mol^{-1}.K^{-1}) and *T* is the absolute temperature. The plot of *ln.(dα/dt)* vs *1/T* should be linear with the slope *Ea/R,* from which Ea can be obtained. The plots give the activation energies at different stages of degradation reaction takes place (Fig.8,9).

Chang Method

Chang provides the following expression for thermal degradation kinetic studies

$$\ln\frac{d\alpha / dT}{(1-\alpha)^2} = \log(z) - \frac{Ea}{R}.\frac{1}{T}$$ ---(4)

A plot of [ln(dα)/dt)/ (1-α)n] vs 1/T will yield a straight line if the order of decomposition reaction n is selected correctly. The slope of this line provides the (-Ea/R) values, from which Ea can be obtained. The plots give the activation energies of degradation reaction takes place (Fig.10).

Coats - Redfern Method

Coats and Redfern provides an approximation. This is an integral form of the rate equation. The simplified form of the equation is

$$\ln\frac{g(\propto)}{T^2} = \ln\frac{AR(1-2\,RT/E_a)}{\emptyset E_a} - \frac{E_a}{RT}$$ ---(5)

Where, T is Temperature, Ais Pre-exponential term, R is Gas constant, Ea is Energy of activation, φ is Heating rate and α is given by

$$\propto = \frac{W_0 - W_t}{W_0 - W_f}$$ --(6)

Where, W_0 is Initial weight of the sample, W_t is Residual weight of the sample at the temperature , W_f = Final weight of the sample and g(α) is equal to –ln(1-α) for n = 1 and ([1-$(1-\alpha)^n$] /(1-n)) for n # 1.Thus a plot of either ([1-$(1-\alpha)^{1-n}$] /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(Fig.11).

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 (Table 5).

A representative thermal activation energy plot of FC, SW Freidman's, Chang and Coat Redfern method for the 4-HBPHF-II copolymer resin is shown in Figs. 5 to 11 respectively. The expressions shown in Table 7 are used to calculate the entropy change (ΔS), free energy change (ΔF), apparent entropy (S*), and frequency factor (Z).

i. Entropy Change (*ΔS*):

$$Intercept = log\frac{kR}{h\phi Ea} + \frac{\Delta S}{2.303R}$$ …………………………………………… (7)

Where, k = 1.3806 x 10^{-16} erg.deg^{-1}.mol^{-1},
R = 1.987 cal.deg^{-1}.mol^{-1},
h = 6.625 x 10^{-27} erg.sec,
ϕ = 0.166,
ΔS = entropy change,
Ea = activation energy from graph.

ii. Frequency Factor (z):

$B_{2/3} = \frac{\log z.Ea}{R\phi}$…………………………………………………………………….…… (8)

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

$S^* = 2.303R \log \frac{zh}{RT*}$…………………………………………………………………(9)

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

The similarity of the thermodynamic parameters indicates a common reaction mode. Using the FC and SW, Freidman's, Chang and Coat Redfern methods, the kinetic and thermodynamic parameters were calculated and presented in the Table 6 and 7 respectively . From the results, it is obvious that the activation energy calculated from FC and SW methods is in good agreement with each other for the 4-HBPHF-II copolymer. While Freidman's, Chang and Coat Redfern methods provide accurate values of activation energy in good agreement. The difference in activation energy by these methods is due to analogy in the mathematical model .The thermal stabilities of the copolymer resins were predicted to be high due to the low activation energies. The linear structure and the presence of intramolecular hydrogen bonding in the aromatic ring further confirm the higher thermal stability of the resin. The low frequency factor value obtained predicts that the decomposition reaction is slow [7, 28]. This is further supported by the negative entropy change. However, a few points do not fall on the straight line in the graphs which shows that the reaction does not obey the exact first-order kinetics.

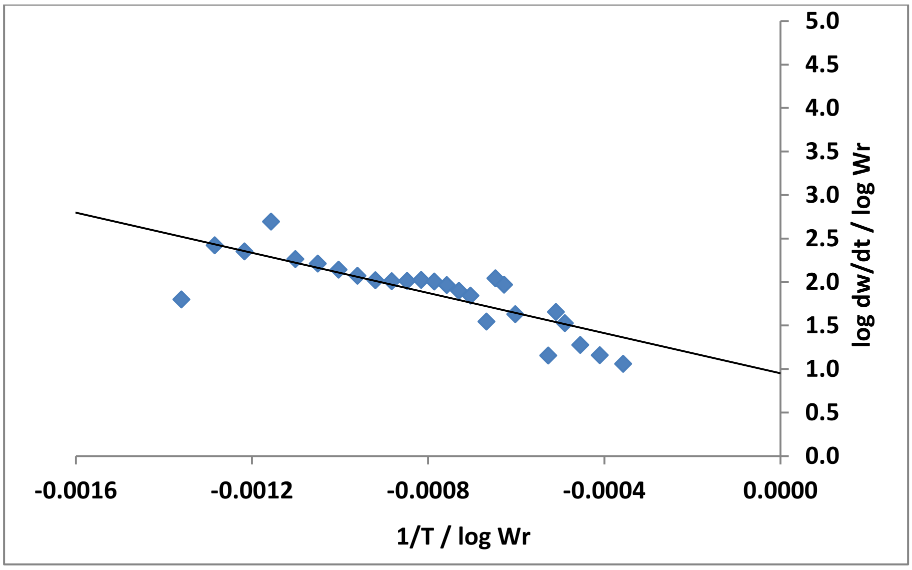

Figure 5: Freeman- Caroll plot 1 of 4 – HBPHF-II Copolymer resin for activation energy and order of reaction

SEM And XRD Analyses

The SEM image of the 4 –HBPHF-II at 50009 magnification is shown in Fig. 15. 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 [29]. The figure 16 depicts the XRD pattern of the 4- HBPHF-II Copolymer resin, a broad diffused peak and absence of well defined peak clearly pointed out the amorphous nature [30].

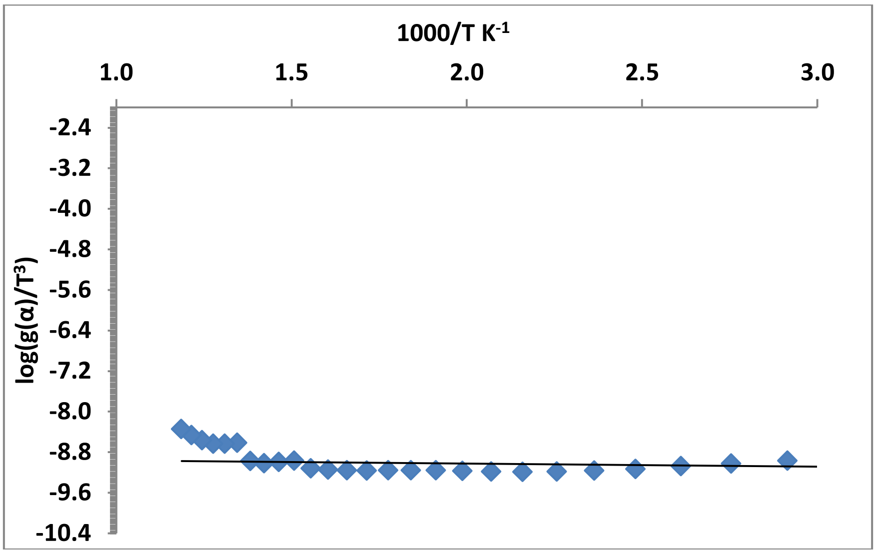

Figure 6: Freeman- Caroll plot 2 of 4 – HBPHF-II Copolymer resin for intercept

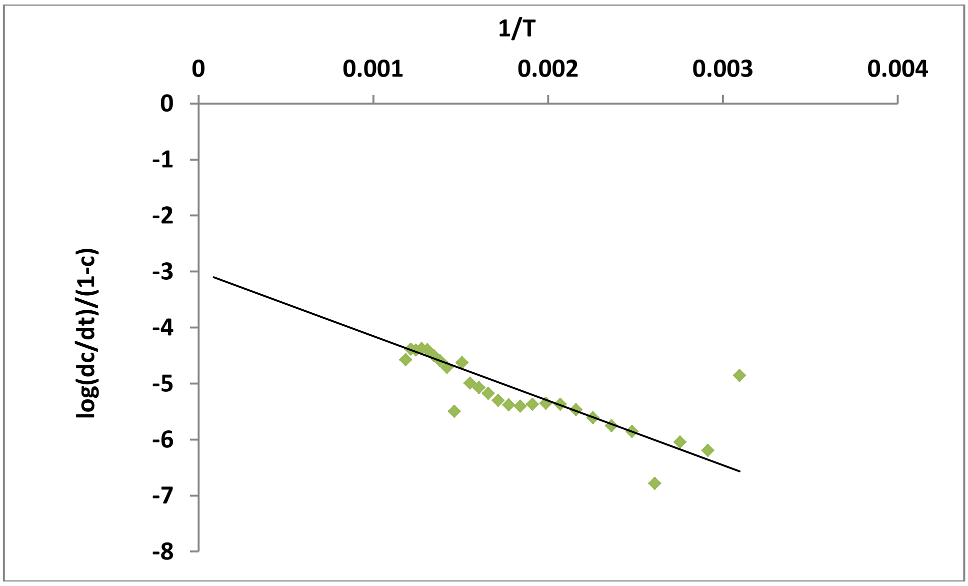

Figure 7: Sharp-Wentworth Plot of 4 – HBPHF-II Copolymer resin

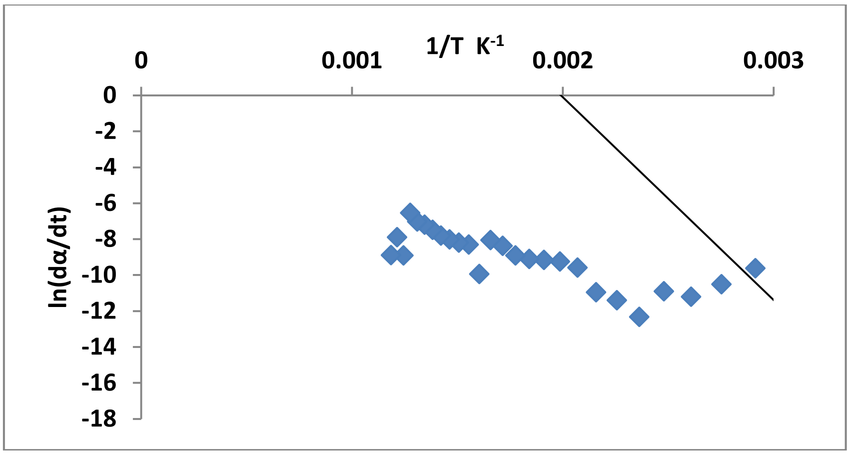

Figure 8: Friedman plot of 4 – HBPHF-II Copolymer resin for activation energy

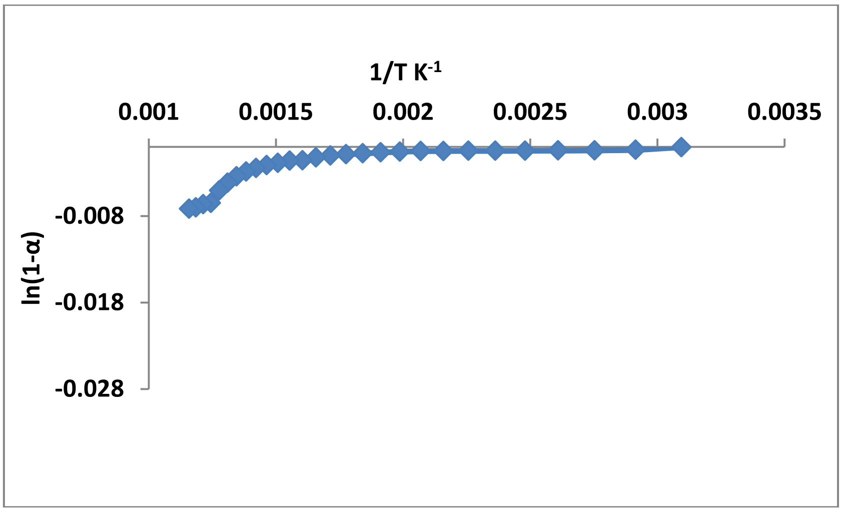

Figure 9: Friedman plot of 4 – HBPHF-II Copolymer resin for the order of reaction

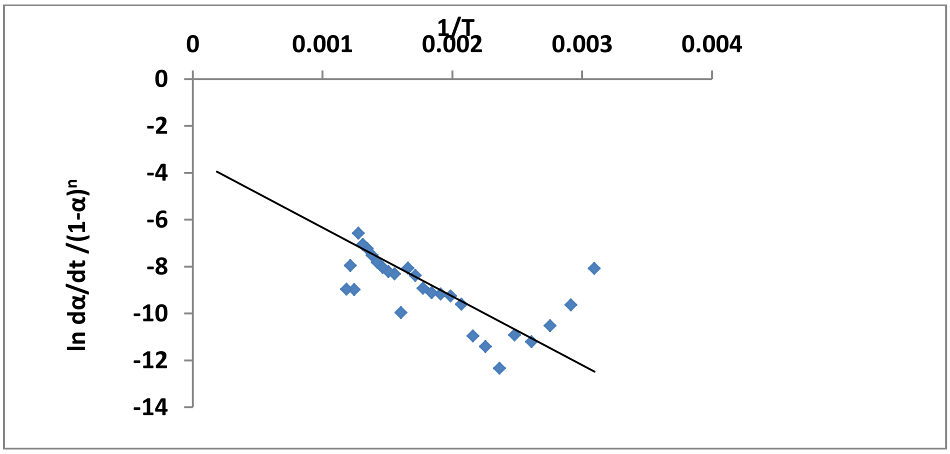

Figure 10: Chang plot of 4 – HBPHF-II Copolymer resin

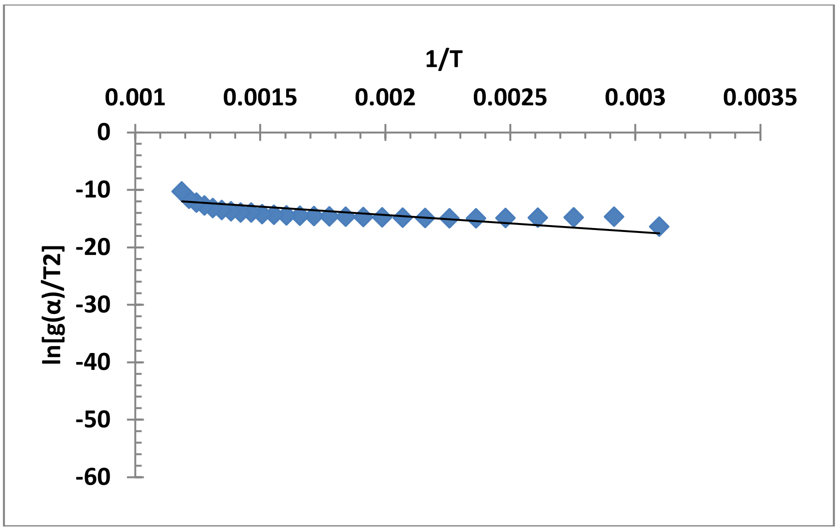

Figure 11: Coat Redfern plot plot of 4 – HBPHF-II Copolymer resin

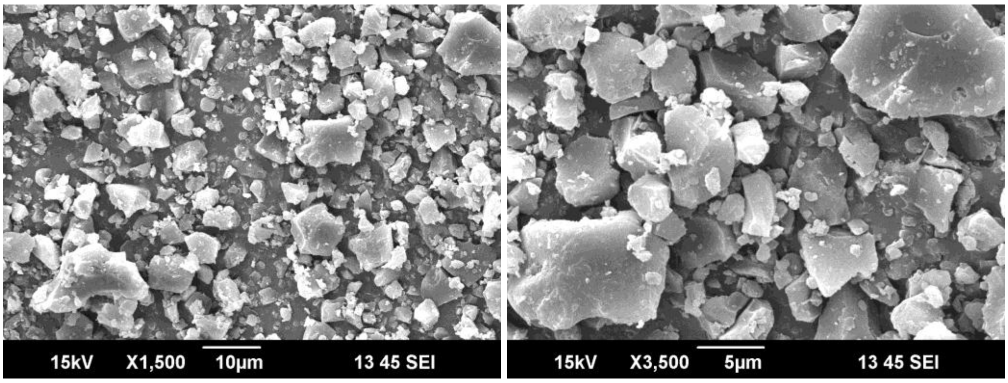

Figure 12: SEM photograph (a, b) of 4 – HBPHF-II Copolymer resin

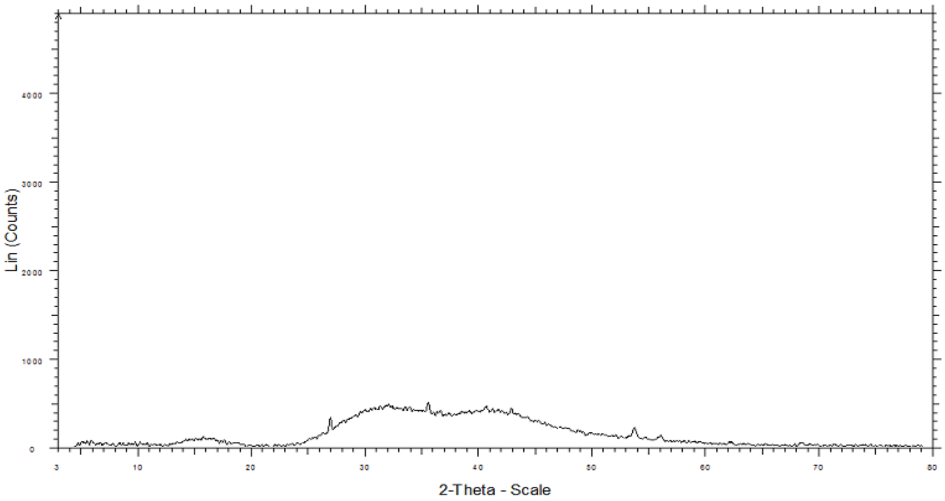

Figure 13: XRD pattern of 4 – HBPHF-II Copolymer resin

Table 6: Comparison of Activation Energy (Ea) of Degradation by Different Methods of 4-HBPHF-II Copolymers resin

Copolymer	Activation (Ea) (KJ/mol.)				
	Sharp-Wentworth	Freeman-Caroll	Chang	Freidman	Coat Redfern
4- HBPHF-II	22.0671	22.1092	24.3858	24.33258	24.37332

Table 7: Thermogravimetrical Parameters of 4-HBPHF-II copolymers

Copolymer	T* (^{0}C)[a]	ΔS(J)	ΔF(KJ)	Z (sec-1)	S*(KJ)	n
4 – HBPHF-II	500	-149.46	31.08	360.21	-24.09	0.95

[a]Half decomposition temperature

CONCLUSION

Copolymers 4 -HBPHF was synthesized from 4-hydroxybenzaldehyde and phenyl hydrazine with formaldehyde using condensation polymerization technique in presence of acid catalyst. The structure of the resin was proposed on the basis of spectral and physicochemical analysis. 4- HBPHF-II copolymer resins were thermally stable even at high temperature. The order of the reaction for thermal decomposition was nearly one, and the activation energy was found to be less for the decomposition. The activation energy calculated by different methods are agreement with each other. Further, the thermal decomposition rate was slow. Thermoanalytical data was used to calculate activation energy by Freeman-Carroll and Sharp Wentworth methods. The results indicate that given copolymer have potential as matrix resin for long term applications at temperature up to 350^{o}C.

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