



Synthesis, characterization and thermal degradation studies of copolymer derived from 4-hydroxybenzophenone, melamine and formaldehyde

Wasudeo. B. Gurnule^{1*} and Sonali P. Dhote²

¹Department of Chemistry, Kamla Nehru Mahavidyalaya, Sakkardara, Nagpur, India

²Department of Chemistry, Laxminarayan Institute of Technology, RTM Nagpur University, Nagpur, India

ABSTRACT

A polymeric resin was synthesized by the polycondensation technique of 4-hydroxybenzophenone and melamine 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 (¹H NMR) spectra. The morphology of polymer was studied by scanning electron microscopy (SEM). The thermal decomposition behavior of polymer (4-HBMF) 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. The order of reaction was found to be 0.98.

Keywords: copolymer; metal complexes; thermal stability; spectral techniques, Kinetic parameters

INTRODUCTION

The foremost initiative of synthesizing Mannich base type of polymeric metal complexes based on inorganic chemistry has been tinted due to its numerous applications such as high thermal stability, complex forming ability, high thermal coating, semiconducting properties and biological applications. Polymers containing metal ions linked by organic linker showed excellent thermal stability. These coordination polymers with multidentate coordination sites are able to form complexes with metal ions. Moreover, Copolymers are generally resinous, amorphous, or crystalline in nature [1]. These copolymers are found to be insoluble in common organic and inorganic solvents [2]. Copolymers may be used in boiler and cooling water and in scrubber systems where corrosion and/or the formation of scale deposits pose problems. Other environments in which the copolymer may be used include heat distribution type sea water desalting apparatus [3], in oil field services to remove scales from pipe walls, in mining applications such as gold heap leaching, in reverse osmosis systems and as a dispersant in the pulp and paper processing industries. They also could be used as mineral beneficiation aids such as in iron ore, phosphate and potash recovery. The copolymer are found very useful applications as an adhesive [4], high temperature flame resistant[5], fibers, coating materials, semiconductors [6], catalysis and ion exchange resins [7].

Thermal stability of polymeric materials is an important physical property which has led to many applications. The properties may be profoundly affected by the presence of particular sequences of co monomers as well as of quite small proportions of additives. The thermal stability of polymers and copolymers has been extensively studied employing the method of thermogravimetric analysis (TGA) by several authors. Thermogravimetric study of various phenol-formaldehyde and other coordination copolymer resin has been reported in a literature [8-9]. M. Karunakaran and C. Magesh [10] synthesized copolymers by condensation of o-cresol and biuret with formaldehyde and TGA analysis was employed to study the thermal stability and the kinetic data like activation energy of the

copolymer resins. Manjusha M. Jadhao et. al. [11] synthesized a biphenol-guanidine-formaldehyde copolymer resin and characterized on the basis of thermogravimetric analysis/differential thermal analysis.

The present communication deals with synthetic and thermal degradation properties of a newly synthesized copolymer resin derived from 4-hydroxybenzophenone, melamine and formaldehyde. The Freeman-Carroll and Sharp- Wentworth methods have been applied for the calculation of kinetic parameters. Methods for the estimation of kinetic parameters from thermogravimetric studies are generally based on the assumption that the Arrhenius equation is valid with thermal and diffusion barriers are negligible.

EXPERIMENTAL SECTION

Chemicals and reagents

The important chemicals (starting materials) like 4-hydroxybenzophenone (Across Organic, Fisher Scientific, India), melamine (Across Organic, Fisher Scientific, India) and formaldehyde (S.D. Fine Chemicals) used in the preparation of new copolymer resin were procured from the market and were of chemically pure grade, and wherever necessary the purity was tested and confirmed by thin layer chromatography.

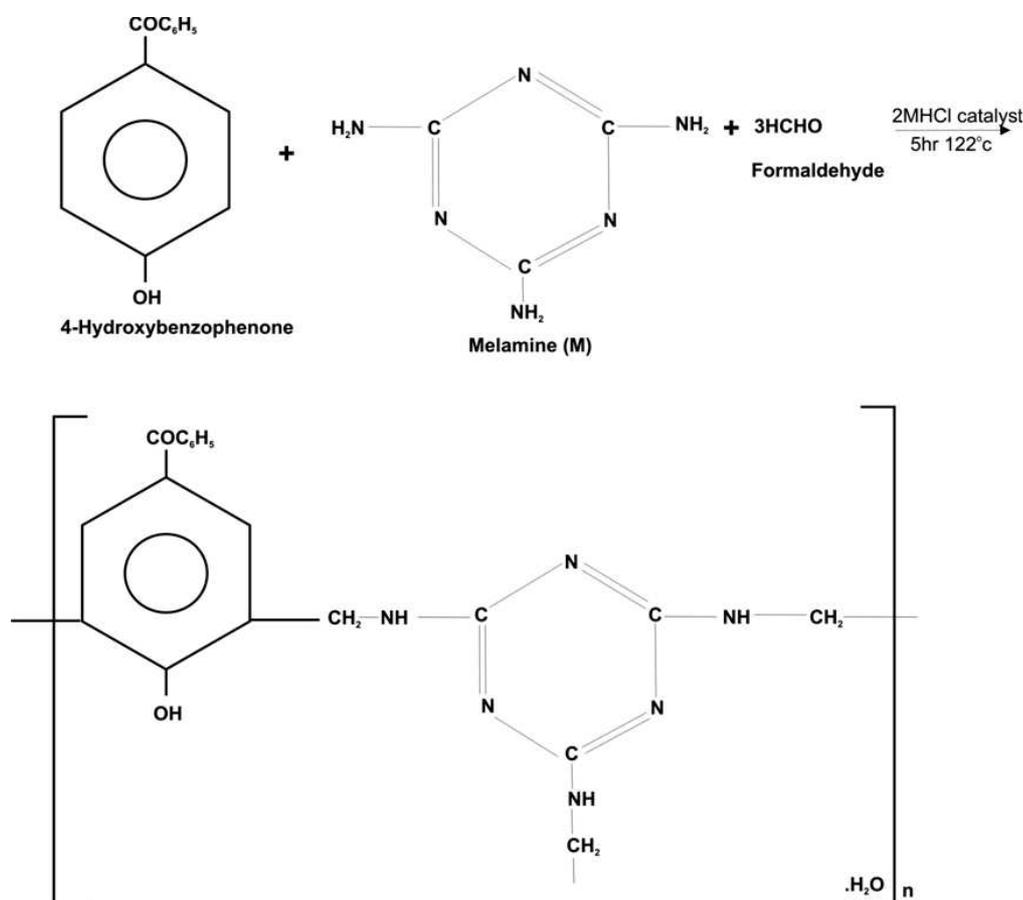


Fig. 1: Preparation of 4-HBMF Copolymer Resin

Synthesis of 4-HBMF copolymer resin

The new copolymer resin 4-HBMF was synthesized by condensing 4-hydroxybenzophenone (3.964 g, 2 mol) and melamine (1.030 g, 1 mol) with 37 % formaldehyde (11.25 ml, 3 mol) in a mol ratio of 1:1:3 in the presence of 2M 200 ml HCl as a catalyst at $126^{\circ}\text{C} \pm 2^{\circ}\text{C}$ for 5hrs in an oil bath with occasional shaking to ensure thorough mixing. The separated cream color copolymer resin was washed with hot water and methanol to remove unreacted starting materials and acid monomers. The properly washed resin was dried, powdered and then extracted with diethyl ether and then with petroleum ether to remove 4-hydroxybenzophenone-formaldehyde copolymer which might be present along with 4-HBMF copolymer. The copolymer resin was purified further by dissolving in 8% aqueous sodium hydroxide solution, filtered and reprecipitated by gradual drop wise addition of ice cold 1:1 (v/v) concentrated hydrochloric acid / distilled water with constant and rapid stirring to avoid lump formation. The process of reprecipitation was repeated twice. The copolymer sample 4-HBMF thus obtained was filtered, washed several times with hot water, dried in air, powdered and kept in vacuum desiccator over silica gel. The yield of the copolymer

resin was found to be 80-82%. The synthesis reaction and suggested structure of 4-HBMF copolymer resin has been given in Fig. 1.

Thermogravimetric analysis

Thermal analysis method is associated with a change in weight with respect to temperature. Heating is performed under strictly controlled conditions and can reveal changes in structure and other important properties of the material being studied. In non-isothermal or dynamic TGA the sample is subjected to conditions increase in temperature at linear rate [21-23]. The non-isothermal thermogravimetric analysis was performed in air atmosphere with heating rate of $10^{\circ}\text{C min}^{-1}$ using 5 - 6 mg of samples in platinum crucible from temperature of 40°C to 800°C and thermogram is recorded for 4-HBMF sample at SICART, Vallabhvidyanagar, Gujrat. With the help of thermogravimetric data the thermal activation energies (E_a) and order of reaction (n) calculated. Also, other thermodynamic parameters such as entropy change (ΔS), apparent entropy change (S^*) and frequency factor (z) are determined.

RESULTS AND DISCUSSION

4-HBMF copolymer resin has been synthesized by the condensation process and purified. These are cream color and are soluble in DMF, DMSO, aqueous KOH, and NaOH and insoluble in almost all organic and inorganic solvents.

Elemental analysis is a technique for investigating the molecular structures of polymers. Elemental analysis is often used to study the molecular structure of soluble and insoluble copolymer resins where conventional solution characterization of the insoluble polymers is impossible. Hence to investigate the molecular structures of all the prepared copolymer resins, they have been analysed for carbon, hydrogen and nitrogen content. The empirical formula and empirical formula weight have been assigned by the result of elemental analysis, given in Table 1, found in good agreement the calculated and observed elemental analysis.

Table 1 Elemental Analysis and Empirical Formula of 4-HBMF copolymer Resin

Copolymer Resins	% of C observed (Cal.)	% of H observed (Cal.)	% of N observed (Cal.)	% of O observed (Cal.)	Empirical formula of repeated unit	Empirical formula weight
4-HBMF	57.34 (57.75)	5.00 (5.05)	16.00 (16.16)	20.78 (21.12)	$\text{C}_{19}\text{H}_{20}\text{N}_6\text{O}_4$	396

Number average molecular weights (\overline{M}_n) of these polycymers have been determined by conductometric titration method in non-aqueous medium and using standard potassium hydroxide (0.5N) in absolute ethanol as a titrant. The results are presented in Table 3.50. The specific conductance was plotted against milliequivalents of ethanolic KOH required for neutralization of 100gm of each copolymer. There are several breaks before the complete neutralization of all phenolic hydroxyl groups [12]. The first break in the plot was the smallest break and assumed that this corresponds to a stage in titration when an average one phenolic hydroxide group of each chain was neutralized.

From the plot the first and final breaks were noted. The average degree number average molecular weight (\overline{M}_n) of all copolymer resins have been determined using the formula

$$\overline{DP} = \frac{\text{Total milliequivalents of base for complete neutralisation}}{\text{Milliequivalents of base required for smaller intervals}}$$

$$\overline{M}_n = \overline{DP} \times \text{Repeat unit weight}$$

It is observed that the molecular weight of copolymer resins increases with increase in 4-hydroxybenzophenone content (Table 2). This observation is in good agreement with the trend observed by earlier workers [12].

Table 2 Determination of Number Average Molecular Weight of 4-HBMF Copolymer Resin

Copolymer sample	First stage of neutralization (Meq/100gm sample)	Final stage of neutralization (Meq/100gm sample)	Degree of polymerization (\overline{DP})	Empirical weight (gm)	Number average molecular weight (\overline{M}_n)
4-HBMF	336	4144	12.33	380	4685

The UV-visible spectra (Fig. 3.46) of all four 4-HBMF copolymer samples in pure DMSO were recorded in the region 200 – 850nm at a scanning rate of 100nm min^{-1} and a chart speed of 5cm min^{-1} . The 4-HBMF copolymer resins displayed two characteristics broad bands at 270-280 nm and 320-380nm. The observed position of the

absorption bands indicate the presence of a phenone COC_6H_5 group and hydroxyl group which is in conjugation with the aromatic nucleus. -NH group. The band at $320\text{-}380\text{cm}^{-1}$ is the more intense band which may be accounted for a $\pi \rightarrow \pi^*$ transition while the less intense band at $180\text{-}300\text{nm}$ may be due $n \rightarrow \pi^*$ transition [13]. The basic value of transition for COC_6H_5 and -OH group is nearly at 320 and 240nm.

Infrared spectra of 4-HBMF copolymer resins are shown in Fig. 3.47 and IR spectral data are tabulated in Table 3.57. From the IR spectral studies, it has been revealed that all the four 4-HBMF copolymer resins show nearly similar pattern of spectra. A very broad band appeared at the region $3742\text{-}3746\text{cm}^{-1}$ may be assigned to the stretching vibration of phenolic -OH groups exhibiting intramolecular hydrogen bonding -NH group [13]. The band at $2924\text{-}2931\text{cm}^{-1}$ is due to stretching of -NH etc.. The band at $1606\text{-}1607\text{cm}^{-1}$ may be due to aromatic ring (substituted). The band at 1347 , 1283 , 1248 and 784cm^{-1} may be due to CH_2 bending (wagging and twisting), - CH_2 plane bending, - CH_2 bending (rocking 1,2,3,5 substitution in aromatic benzene ring may be due the bands appeared at $975\text{-}977\text{cm}^{-1}$, $1074\text{-}1075\text{cm}^{-1}$ and $1155\text{-}1158\text{cm}^{-1}$ [13,].

Table 3 IR Frequencies of 4-HBMF Copolymer Resin

Observed band frequencies (cm^{-1})	Assignment	Expected band frequencies (cm^{-1})
3746(b,st)	-OH phenolic intermolecular hydrogen bonding	3750-3200
2930(b,sh)	> CH_2 , -NH, - CH_3 stretching	3500-2800
1606(b,st)	Proton of aromatic ring	1600-1500
1446(sh)	- Aromatic ring	1445-1485
1347(sh,sh)	- CH_2 - bridge	1380-1350
1283(sh)	- CH_2 bending (wagging & twisting)	1370-1280
1248(b,st)	- CH_2 - plane bending	1300-1250
784(sh)	- CH_2 bending (rocking)	800-710
975(m)		950
1075(m)	1,2,3,5 substitution in aromatic ring	1058
1155(m)		1125

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

The ^1H NMR spectra of all four 4-HBMF copolymer resins were scanned in DMSO-d_6 . The spectra are given in Fig. 3.48 and the spectral data are given in Table 3.58. From the spectra it is revealed that all 4-HBMFterpolymer resins possess set of proton having different electronic environment. The chemical shift (δ) ppm observed are assigned on the basis of data available in literature [14]. The medium signal at $2.52\text{-}2.54(\delta)$ ppm may be due to the methylene proton of Ar- CH_2 bridge. The signal obtained in the region of $3.42\text{-}3.46(\delta)$ ppm may be due to the methylene proton of Ar- $\text{CH}_2\text{-N}$ moiety [14]. The singlet in the region $5.33\text{-}5.34$ (δ)ppm may be due to the proton of -NH bridge. The weak multiplet signal (unsymmetrical pattern) in the region at $6.85\text{-}6.91$ (δ) ppm may be due to the aromatic proton [13] of (Ar-H). The signals in the range $7.61\text{-}7.65$ (δ)ppm may be due to phenolic hydroxyl proton. The much downfield chemical shift for phenolic -OH group indicate clearly the intramolecular hydrogen bonding on -OH group [15].

Table 4 ^1H NMR Data of 4-HBMF Copolymer Resin

Observed Chemical Shift (δ) ppm	Nature of proton assigned	Expected chemical shift (δ) ppm
2.54	Proton of Ar-CO- C_6H_5 group	2.00 to 3.00
2.52	Methylenic proton of Ar- CH_2 moiety	2.00 to 3.00
3.42	Methylenic proton of Ar- $\text{CH}_2\text{-N}$ moiety	3.00 to 3.5
5.33	Proton of -NH bridge	5.00 to 8.00
6.85	Aromatic proton (Ar-H)	6.2 to 8.5
7.61	Proton of phenolic - OH involved intramolecular hydrogen bonding	8.00 to 10.00

Fig. 2 represents the scanning electron micrographs of 4-HBMF copolymer resin. The photographs of 4-HBMF copolymer exhibit sponge like structure derived from the aggregation of small granules. At lower magnification the resin shows spherulites in which the crystals are arranged smaller in surface area with more closely packed structures. This indicates the crystalline nature of the copolymer resin and this property shows the low ion exchange capacity for higher hydrated size metal ion. At different magnification the resins 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 copolymer sample

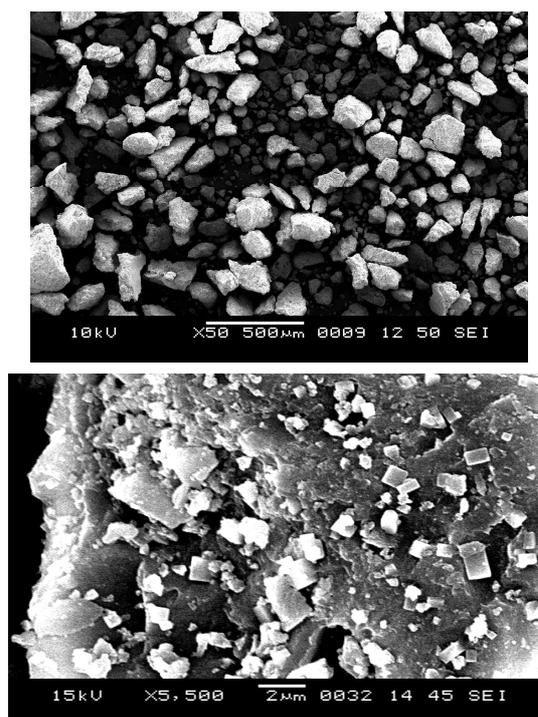


Fig. 2 SEM Micrographs of 4-HBMF copolymer Resin

The thermogravimetric analysis of all four 4-HBMF copolymer resins has been carried out in the temperature range of 40°C to 800°C. The thermograms of 4-HBMF copolymer resins are shown in Fig. 3. Thermal data of representative 4-HBMF copolymer resin has been given in Table 5, for Sharp-Wentworth method and in Table 6 for Freeman-Carroll method. The thermogram of 4-HBMF copolymer shows three steps in the decomposition reaction after initial loss of water molecular.

Thermogravimetry of 4-HBMF copolymer resin

Thermogram of 4-HBMF copolymer resin is given in Fig.3, depicts three steps in decomposition reaction, after loss of one crystalline water molecule entrapped in the polymer molecule (5.82% found and 5.94% calculated). The first step of decomposition starts from 130°C to 360°C, corresponding the gradual mass loss of 20.22% found and 20.44% calculated, which may be due to the gradual loss of one hydroxyl group and one CO group attached to aromatic benzene ring. The second step of degradation starts from 360°C to 540°C corresponding the rapid mass loss of 44.35% found and 44.56% calculated which may be due to the degradation of one aromatic benzene ring. The third step of decomposition starts from 540°C to 800°C, corresponding to slow loss of 67.37% found and 67.60% calculated, due to the degradation of side chain of melamine moiety consequently the residue is left behind, corresponding to may be of melamine moiety. The thermal degradation by increasing temperature may be due to the increasing strain and unstability and cross linking of molecule by increasing thermal vibration. To decrease the strain and to maintain stability the resin undergoes degradation.

Table 5 Thermogravimetric Data and Decomposition Temperature Range of 4- HBMF Copolymer Resin

Copolymer Resins	Loss of crystalline water molecule		Decomposition step, temperature range (°C), mass loss (%) and species degraded						Mass of residue leftover (%)
			First Step (loss of carbonyl & hydroxyl group)		Second Step (loss of aromatic phenyl nucleus)		Third Step (loss of side chain of melamine)		
	Temp. range (°C)	Mass loss (%)	Temp. range (°C)	Mass loss (%)	Temp. range (°C)	Mass loss (%)	Temp. range (°C)	Mass loss (%)	
4-HBMF	40-130	5.82(F) 5.99(C)	130-360	20.22(F) 20.44(C)	360-540	44.35(F) 44.56(C)	540-800	67.35(F) 67.60(C)	32.65(F) 32.40(C)

Table 6 Results of Thermogravimetric Analysis of 4-HBMF Copolymer Rein

Copolymer resins	Half decomposition Temp. (K)	Activation energy Ea (KJ/mol)		Entropy change ΔS (J)	Free energy ΔF (KJ)	Frequency factor (Z) (Sec. ⁻¹)	Apparent entropy (S*) (KJ)	Order reaction (n)
		FC	SW					
4-HBMF	763	23.94	23.72	-160.74	92.73	659	-23.21	0.98

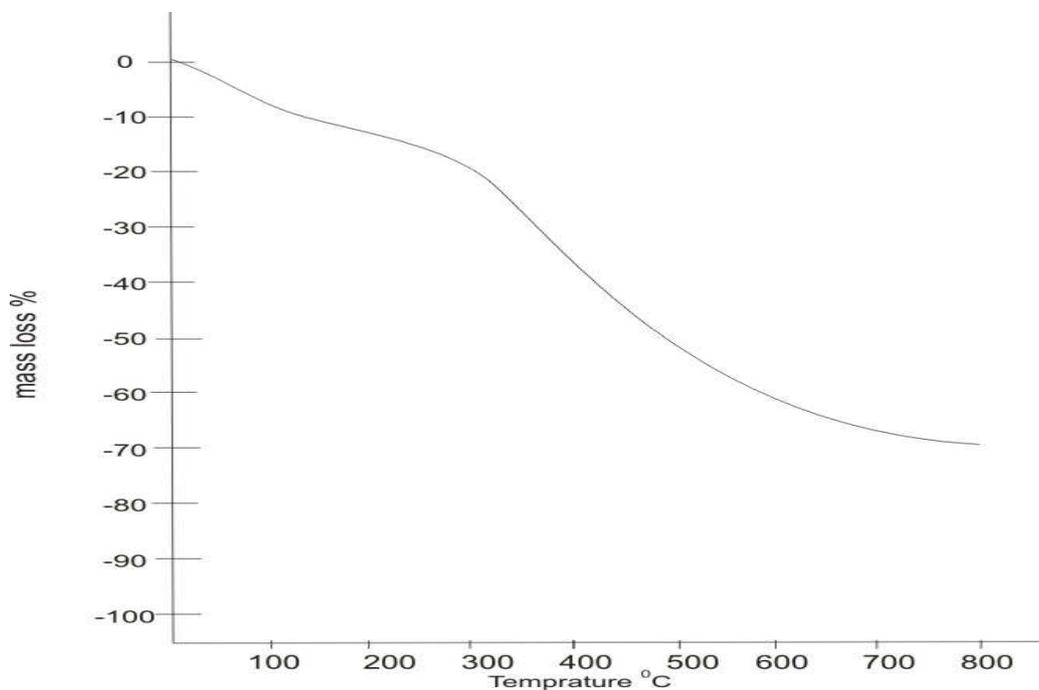


Fig. 3 Decomposition Pattern of 4- HBMF copolymer Resin

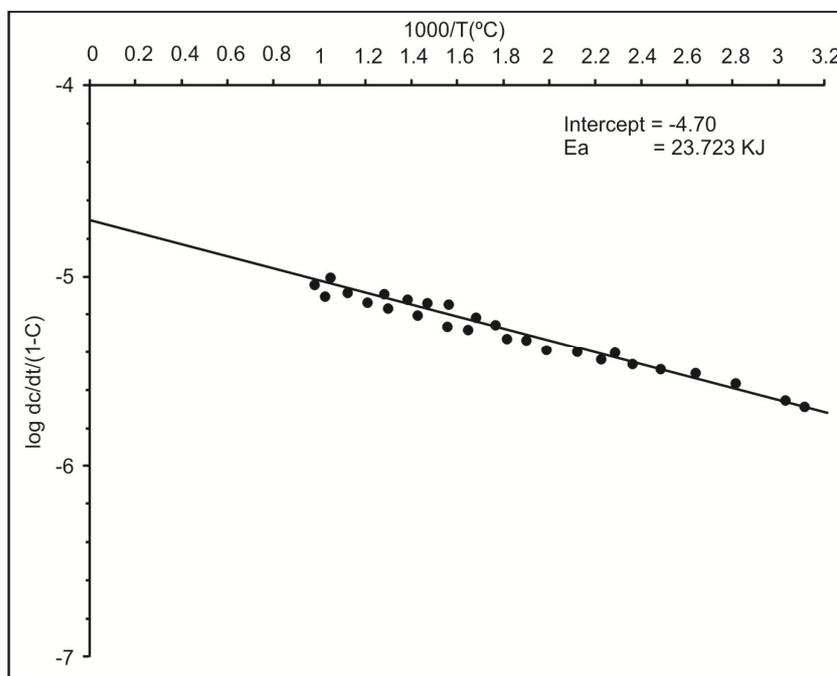


Fig. 4 Sharp-Wentworth Plot of 4-HBMF copolymer Resin

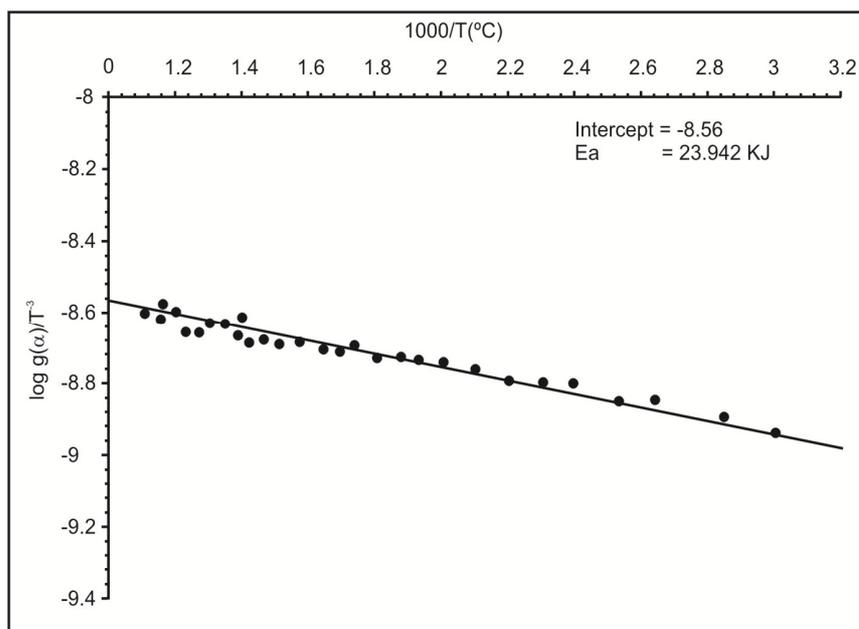


Fig. 5 Thermal activation energy plot (Freeman-Carroll plot of HBMF copolymer resin)

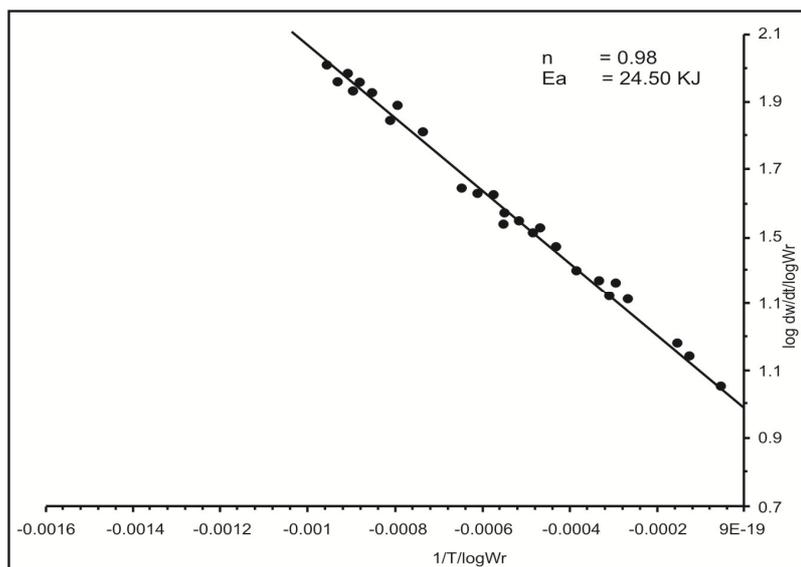


Fig.6 Freeman-Carroll Plot of 4-HBMF Copolymer Resin

The activation energy calculated by Sharp-Wentworth method and Freeman-Carroll method are in good agreement. The removal of water molecule is the initial slow mass loss, which may be due to the water entrapped in copolymer resin, hence the water is probably considered as crystal water. Finally residue remained ascribed as melamine moiety. The various kinetic parameters calculated by Freeman-Carroll method are about same, indicating common mode of decomposition reaction. Abnormally the low values of frequency factor may be indicated that the decomposition reaction can be classed as slow reaction. The slow reaction is also predicted by negative values of entropy change. The negative values mean the disorder is less and the reaction is carried by more order manner, making it slower. The graphs obtained by Sharp-Wentworth and Freeman-Carroll methods are fairly good straight lines or linear by ignoring some abnormal points, indicating that the decomposition does not obey first order kinetics perfectly [15]. However no unique conclusion can be drawn from the TGA study as the decomposition reaction perhaps is very complicated.

On the basis of all the physico-chemical and spectral evidences and foregoing results and discussion the most probable structures have been proposed for 4-HBMF copolymer resins under investigations.

Acknowledgements

The authors express their sincere thanks to Principal Priyadarshani College of Engineering, Nagpur, India for cooperation and for providing necessary laboratory facilities. One of the author (W.B. Gurnule) thanks to UGC New Delhi for financial assistance.

REFERENCES

- [1] WB Gurnule.; HD Juneja; LJ Paliwal; *Asian J Chem.*, **1999**, 11(3), 767-775.
- [2] PE Michael ; PS ; HD Juneja and LJ Paliwal; *J Appl Polym Sci.*, **2004**, 92, 2278-2282.
- [3] GC Patel; HB Pancholi and MM Patel; *High Performance Polymers*, **1991**, 3(2), 99-106.
- [4] Y Zhu; E Millan; A Sengupta; *Reactive Polymers*, **1990**. 13, 241–253,
- [5] RN Singru.; AB Zade and WB Gurnule; *J Appl polym sci*, **2008**, 109(2), 859-868.
- [6] MM. Patel; R. Manavalan, *J Molecular Science*, **1983**, 20(4) 487 – 501.
- [7] S Kole; TK Chaki; AK Bhowmick; DK Tripathy; *Polym. Degrad. Stab.* **1993**; 41: 109-116.
- [8] JW Park; SC Oh, HP Lee; HT Kim; KO Yoo; *Polym. Degrad. Stab.* **2000**; 67: 535–540.
- [9] RC DeGeis.; LG Donaruma.; EA Tomic; *J. Appl. Polym. Sci.* **1965**, 9(2), 411.
- [10] ES Freeman and DA Anderson , *J Polym Sci.*, **1961**, 54, 253.
- [11] JB Sharp and SA Wentworth, *Anal Chem.*, **1969**, 41, 2060.
- [12] T Ozawa; *J Thermal Analysis*, **1985**, 7, 601
- [13] WB Gurnule; SS Katkamwar, *J. Chem. Pharm. Res.*, **2012**, 4(4), 2193-2203.
- [14] WB Gurnule; DB Patle, *J. Chem. Pharm. Res.*, **2012**, 4(4), 2118-2121.
- [15] SS Katkamwar; AB Zade; SS Rahangdale; WB Gurnule.; *J Appl Polym Sci*, **2009**, 113, 3330 - 3335.