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Thermogravimetric Analysis of *p*-Hydroxy-Benzoic Acid Melamine-Formaldehyde Tercopolymers

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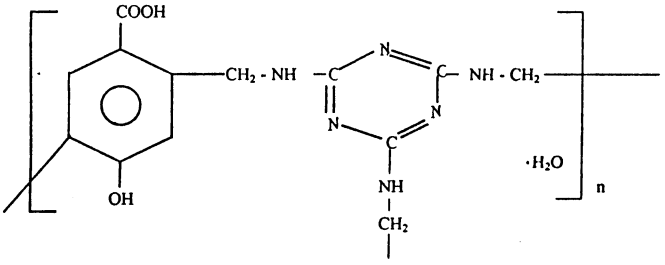
Polymers were prepared by the condensation of *p*-hydroxy benzoic [PB], melamine [M] and formaldehyde [F] in the presence of hydrochloric acid (2 M) as catalyst with varying molar ratios of reacting monomers. Polymers were characterised by their IR spectra, elemental analysis, TGA, DTA and Mn as determined by vapour pressure osmometry as well as non-aqueous conductometric titrations. The kinetic and thermodynamic parameters such as, order of reaction, energy of activation, frequency factor, entropy change, free energy change and apparent entropy change have been determined. Freeman-Carroll and Sharp-Wentworth methods have been applied for the calculation of kinetic parameters, while the data from the Freeman-Carroll method have been used to determine various thermodynamic parameters.

INTRODUCTION

A wide variety of thermally stable polymers have been synthesized and the sequence of their thermal stabilities have been predicted from their TG-data. 8-Hydroxyquinoline or phenol derivatives like *o*-aminophenol, resorcinol condensed with formaldehyde have been reported[1,2]. The salicylic acid/*p*-chloro-(bromo)-formaldehyde resins have been reported as showning chelation ion-exchange capacity[3–5]. The salicylic acid-urea-formaldehyde resins show a chelation ion-exchange capacity[6]. Resins were also synthesized by the condensation of salicylic acid and thiourea with trioxane in presence of 2 M HCl as catalyst and their ion-exchange capacity studied[7]. These studies inspired us to prepare *p*-hydroxybenzoic acid-melamine-formaldehyde tercopolymers PBMF (1).



PBMF-(1) [1 : 1 : 3]

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The Freeman-Carroll[8] and Sharp-Wentworth[9] methods have been used to evaluate various kinetic parameters for these tercopolymers. Methods for estimating kinetic parameters from dynamic TG studies are mostly based as the assumption that the Arrhenius equation is valid and that the thermal and diffusion barriers are negligible.

EXPERIMENTAL

All the chemicals used were of AnalaR grade.

Synthesis of *p*-Hydroxybenzoic Acid (PB)-Melamine (M)-Formaldehyde (F) Polymer

A mixture of *p*-hydroxybenzoic acid (0.1 mol) melamine (0.1 mol) with formaldehyde (0.2 mol) in the ratio 1 : 1 : 3 respectively was heated in the presence of 2 M hydrochloric acid (HCl) as a catalyst in an oil bath at 126°C for 4 h. The separated white resin product (PBMF) was washed with hot water and methanol to remove unreacted monomers. The resin was purified by dissolution in 8% NaOH and reprecipitation by dropwise addition of 1 : 1 (v/v) HCl. The precipitated resin product was filtered off, washed with hot water until it was free from chloride ions and dried at 60°C. Different resin samples, *viz.*, PBMF-(2) [2 : 1 : 3], PBMF-(3) [3 : 1 : 5] and PBMF-(4) [4 : 2 : 7] were prepared employing different molar ratios of reactants.

Tercopolymers obtained have been characterized by elemental analysis, UV-visible, IR, NMR spectral studies. All tercopolymers are soluble in DMF, DMSO, THF, however, are insoluble in common organic solvents.

Thermal Studies

Freeman-Carroll Method: The dynamic (non-isothermal) analyses of all the tercopolymer prepared have been carried out in air atmosphere with a heating rate 5°C/min. in a platinum crucible. The thermocouple used was chromel-alumel in the temperature range 20–600°C.

In the Freeman-Carroll method, the following expression is used to evaluate various kinetic parameters.

$$\frac{\Delta \log (dw/dt)}{\Delta \log Wr} = \left(\frac{-E_a}{2.303R}\right)\frac{\Delta(1/T)}{\Delta \log W} + n$$

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 a definite time and W is the total weight loss up to time t; T is the temperature, R the gas constat and n the order of reaction. Hence by plotting

$$\frac{\Delta \log (dw/dt)}{\Delta \log W_r} \quad vs. \quad \frac{\Delta\, 1/T}{\Delta \log W_r}$$

n is obtained as the intercept on the former axis and E_a is the slope of the line. The detailed procedure is clearly laid out for E_a representative sample as an illustration.

Sharp-Wentworth Method: Using the Sharp-Wentworth method the following expression is used to evaluate the activation energy.

$$\log\left(\frac{dc/dT}{1-c}\right) = \log(A/\beta) - \frac{E_a}{2.303R} \cdot \frac{1}{T}$$

where β is the linear heatng rate, dT/dt. Thus, a linear plot of

$$\log\left(\frac{dc/dt}{1-c}\right) \quad vs. \quad \frac{1}{T}$$

is obtained whose slope gives the value of E_a and A may be evaluated from the intercept. The linear relationship confirmed that the assumed order (n = 1) is correct.

RESULTS AND DISCUSSION

The composition of the polymeric unit was assigned on the basis of detailed study of the elemental analysis of the polymers and IR spectral studies. The thermogravimetric analyses of all tercopolymers prepared have been carried out, but for reason of economy of space the thermal data and kinetic plots for only one representative case have been given (Fig. 1–4).

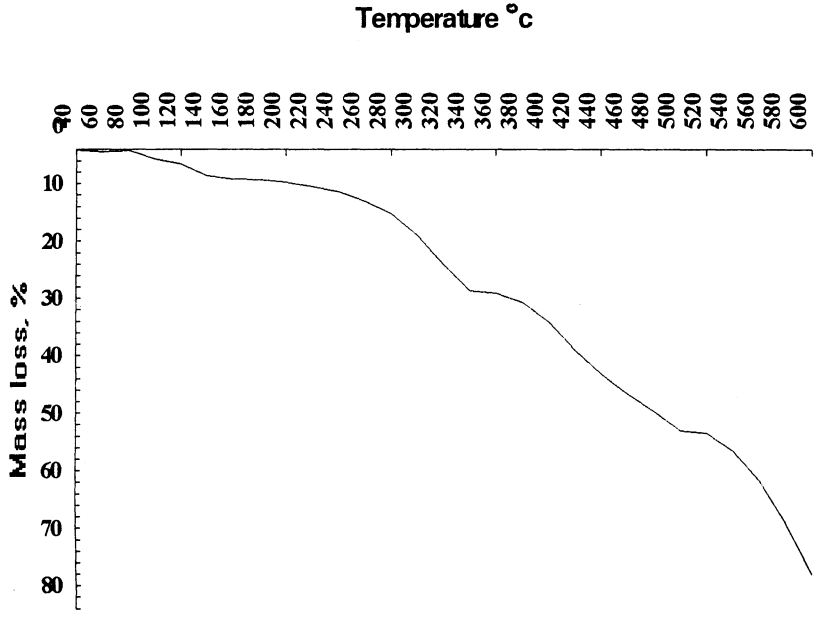

Fig. 1 TG plot of a representative polymer PBMF (1)

TG of PBMF-(1) *Polymer:* Thermogram of this tercopolymer resin is shown in Fig. 1. Thermogram of this tercopolymer resin depicts four step decomposition in the range 40–600°C. The first step shows slow decomposition from 40–180°C corresponding to 5.0% loss may be attributed to loss of a water molecule against the calculated 5.6%, present per repeat unit of polymer. The second step decomposition start from 180–340°C which represents the degradation of the side

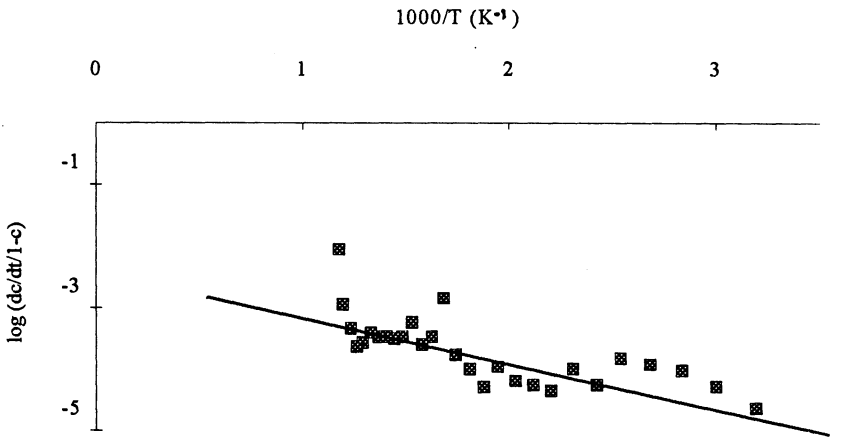

Fig. 2 Sharp-Wentwoth plot for PBMF (1) polymer

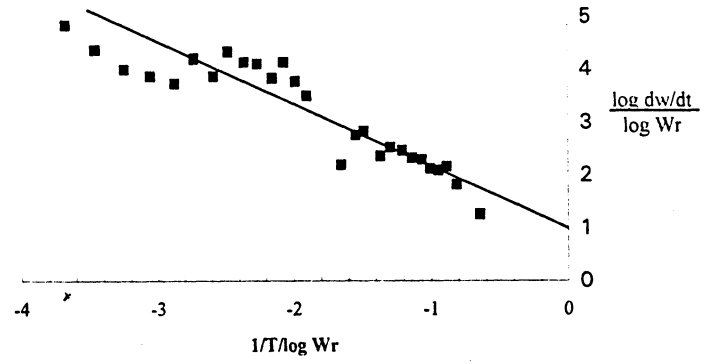

Fig. 3 Thermal activation energy PBMF (1) polymer

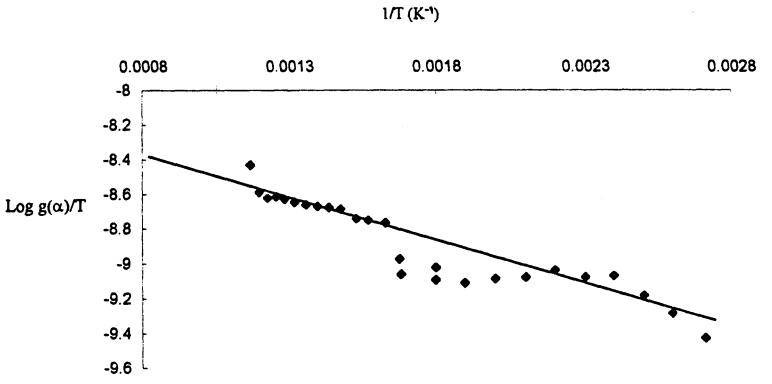

Fig. 4 Freeman-Carroll plot for PBMF (1) polymer

chain attached to aromatic nucleus in polymer, *i.e.*, phenolic —OH and carboxylic —COOH groups (24.50% found and 25.23% calcd.). The third step decomposition starts from 340–500°C corresponding to 49.00% loss of aromatic nucleus agaisnt calcualted 49.84%. The fourth step of decomposition starts from 500–600°C Corresponding to removal of side chain of triazine polymer (74% found and 75.39% calcd.) and consequently the residue remained may be assigned as 1,3,5-S-triazine (26.00% found and 25.50% calcd.).

TG of PBMF-(2) *Polymer:* Thermogram of this tercopolymer depicts four-step decomposition in the range 40–600°C. The first step shows slow decomposition between 40–180°C corresponding to 7.5% mass loss, which may be due to loss of two water molecule against calculated 7.61% mass loss per repeat unit of the polymer. The second step decomposition starts from 160–400°C which represents degradation of side chain attached to aromatic nucleus in polymer, *i.e.*, phenolic —OH and carboxylic —COOH groups (34.00% found and 33.82% calcd.). The third step gradual decomposition start from 400–500°C corresponding to loss of aromatic nucleus (67.00% found and 66.80% calcd.). The fourth step of decomposition starts from 500–600°C and represents the removal of side chain of triazine polymer (82.50% found and 83.13% calc.) and consequently residue remained may be assigned as 1,3,5-S-triazine (17.50% found and 17.12% calcd.).

TG of PBMF-(3) *Polymer:* Thermogram of this tercopolymer depicts four-step decomposition. The first step shows slow decomposition between 40–140°C corresponding to 5.5% mass loss may be due to loss of two water molecule against the calculated 5.66%. The second step decomposition starts from 140–440°C corresponding to 70% loss of aromatic nucleus against calculated 71.69%. The fourth step decomposition starts from 560–600°C represents the removal of side chain of triazine polymer (85.00% found and 84.43% calcd.) and consequently the residue may be ascribed as 1,3,5-S-triazine (15.00% found and 12.73% calcd.).

TABLE-1
ACTIVATION ENERGY AND DECOMOSITION TEMPERATURE OF PBMF TERCOPOLYMER

Sr. No.	Tercopolymer	Decomposition temp. °C	Activation energy	
			FC	SW
1.	PBMF-(1)	180	35.89	36.94
2.	PBMF-(2)	160	31.75	30.62
3.	PBMF-(3)	140	35.06	33.93
4.	PBMF-(4)	130	47.86	44.60

FC—Freeman Carrol; SW—Sharp Wentworth.

TG of PBMF-(4) *Polymer:* Thermogram of this tercopolymer resin depicts four-step decomposition. The first step shows slow decomposition between 40–130°C corresponding to 4.0% mass loss against calculated 3.90% which may

be attributed to loss of two water molecules. The second step decomposition starts from 130–400°C which represents degradation of side chain attach to aromatic nucleus in polymer, *i.e.*, phenolic —OH group and carboxylic —COOH groups (31.0% found and 30.76% calcd..). The third step decomposition start from 400–560°C corresponding to complete loss of aromatic nucleus (66.0% found and 64.57% calcd.). The fourth step decomposition starts from 560–600°C corresponding to removal of side chain of triazine polymer (79.50% found and 78.00% calcd.) and consequently 1,3,5-s-triazine may be suggested as *residue* (20.50% found and 17.50% calcd.).

TABLE-2
KINETIC PARAMETERS OF PBMF TERCOPOLYMERS

Sr. No.	Tercopolymer	Entropy change ΔS(J)	Free energy change ΔF (kJ)	Frequency factor Z (sec^{-1})	Apparent entropy change S (kJ)	Order of reaction n
1.	PBMF-(1)	8.48	32.05	498	–24.09	0.97
2.	PBMF-(2)	8.22	28.19	430	–24.21	0.95
3.	PBMF-(3)	8.30	31.63	408	–24.32	0.93
4.	PBMF-(4)	8.19	44.56	427	–24.22	0.90

RESULTS AND DISCUSSION

By using thermal decomposition data and then applying the Sharp-Wentworth method (a representative Sharp-Wen worth plot for the tercopolymer is shown in Fig. 2) activation energy is calculated which is in agreement with the activation energy calculated by Freeman-Carroll method (Table-1). A representative thermal activation energy plot (Fig. 3) and Freeman-Carroll plot (Fig. 4) for the tercopolymer has been shown. Thermodynamic parameters have been calculated on the basis of thermal activation energy. These values are incorporated in Tables 1 and 2. Thus the order of thermal activation energy is

PBMF (1) < PBMF (2) < PBMF (3) < PBMF (4).

These calculations were done after devising two computer programmes so as to reduce the personal errors. From the data given in Tables 1 and 2, it can be concluded that the values of thermodynamic parameters are comparable. The similarity of the thermodynamic parameters indicates a common reaction mode. Due to abnormally low values of frequency factor (z), it may be concluded that the reaction of decomposition of tercopolymers can be classified as a slow reaction and no other obvious reason can be given.

The decomposition of tercopolymers is known to obey first order kinetics but not perfectly, as observed by Jacobs and Tomplins[10] and by Coats and Redfern[11].

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