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Evaluation of kinetic parameters of dimer acid based metal-containing polyesters using thermogravimetric analysis

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Abstract

Polyesters of dimer acid, DA, have been synthesized with zinc(II) and manganese(II) salts of monohydroxyhexylphthalate (HHP). The polyesters are pale-coloured solids insoluble in common organic solvents and were characterized by elemental analysis and IR spectral studies.

Thermal stability of metal salts of HHP (metal diols) and corresponding polyesters was studied by TGA and DSC measurements. From the resulting data the kinetic parameters for thermal degradation were evaluated following the methods of Freeman and Carroll, Broido, Fuoss et al., and Dave and Chopra. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Dimer acid; Metal-containing diols; Dimer acid based metal-containing polyesters; Kinetic parameters; Thermal degradation

1. Introduction

The requirement of polymeric materials with good thermal stability and catalytic activity has enhanced the development of coordination polymers from either polymeric or monomeric ligands. The study of thermal degradation of coordination polymers has recently become a subject of interest. Coordination polymers are usually obtained in the form of insoluble and infusible powders which present a serious problem in their characterization. Molecular weight determination of coordination polymers is not possible due to their insolubility and the elemental analysis results are also not satisfactory. Therefore, thermal analysis can be of great help in establishing the structure of coordination polymers. Recently, a new elemental analysis method based on thermogravimetric data has been reported [1].

Thermogravimetry is a useful technique, which reveals the loss of mass of a given substance during the heating process [2]. The mass losses derived from the thermogravimetric curves can be correlated with the various stages of decomposition. Kinetics of thermal decomposition may be useful in calculating the important parameters, like activation energy (ΔE^*), frequency factor (Z), entropy change (ΔS^*) and free energy change (ΔG^*), for thermal reactions of a substance. These parameters directly govern the factors of thermal stability of any substance. Further, several techniques for evaluating kinetic parameters from TG [3–10], DTG [11] and DTA [12,13] traces are reported in literature. Activation energies can also be calculated from non-isothermal TG data using the

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Sharp–Wentworth method [14] as well as from isothermal TG data by difference equation method [15,16] and the Avrami–Erofeyer equation [17,18]. Some other methods are based on the peak temperature-program rate relations [19–21], the shape of the heat flow curve obtained [13] or the derivation of the peak [22]. These methods differ widely in their complexity and in the accuracy of the results which may be obtained. They have been mostly applied to organic polymers or metal complexes. However, a few reports appear on the calculation of thermal activation energies of coordination polymers [23–26]. Calculation of activation parameters for thermal reactions of a substance is important because these parameters directly govern the factors of thermal stability.

In the present study, the kinetics of thermal degradation of diols and polyesters containing Zn(II) and Mn(II) is described. Different techniques [3–5,11] have been used to elucidate the mechanism of pyrolysis in nitrogen atmosphere.

The polyesters with metal in the main chain have been synthesized by polycondensation of dimer acid, DA, with metal salts of HHP (referred to as metal diols hereafter). The metal diols in turn, have been prepared from the condensation product of phthalic anhydride and hexanediol. Dimer acid is a dimer of ricinoleic acid which is a major component of castor oil. Dimer acid based polymers are potential products of varied applications [27,28].

2. Experimental

2.1. Materials

Dimer acid, DA, was a gift from Vikram Sarabhai Space Centre, Trivandrum. Phthalic anhydride (PA) and 1,6-hexanediol (HD) were obtained from BDH, India and Wilson Laboratories, India, respectively. Acetates of Zn(II) and Mn(II) (MA) were obtained from Merck, India. Acetone, ethylacetate and other solvents were obtained from Qualigens, India. All the chemicals used were of analytical grade and were used without further purification.

2.2. Preparation of metal diols, M (HHP)

Metal salts of HHP (metal diols) were prepared from 1,6-hexanediol (HD), phthalic anhydride (PA) and metal acetate (MA) following a reported method [29] with a slight modification. 0.15 mol of hexanediol was taken in a flask fitted with a stirrer, a thermometer and a condenser. 0.05 mol of PA was added slowly over 0.5 h and was constantly stirred. Then the stirring was continued at the same temperature and a colourless liquid was obtained. 0.025 mol of MA, Zn(II) or Mn(II), were added in respective preparations and stirring was continued for 3–4 h at 90–100°C, whereby the metal diols precipitated as white solids. Unreacted HD, PA and MA were removed from the precipitate by washing thoroughly with ethylacetate, alcohol and acetone, respectively. The resulting metal diols were dried in vacuum. The metal diols were pale-coloured solids, insoluble in common organic solvents viz., benzene, chloroform, acetone, ethanol, dimethyl formamide, etc., but soluble in water. The diols do not melt up to 360°C.

Zn(HHP): Anal. calcd. for $Zn_4(CH_3COO)_8$-$(C_{14}H_{17}O_5)_2$: C, 41.79; H, 4.59; Zn, 20.70. Found: C, 42.00; H, 4.49; Zn, 19.29. IR (KBr) cm^{-1}: 3430 (OH), 2936, 2854 (CH), 1713 (C=O), 1554, 1405 (COO^-), 1491, 1435 (δ_{CH}), 1288 (C–O).

Mn(HHP): Anal. calcd. for $Mn_4(CH_3COO)_8$-$(C_{14}H_{17}O_5)_2$: C, 43.22; H, 4.74; Mn, 17.99. Found: C, 43.43; H, 1.96; Mn, 18.32. IR (KBr) cm^{-1}: 3420 (OH), 2930, 2860 (CH), 1700 (C=O), 1555, 1359 (COO^-), 1261 (C–O).

2.3. Synthesis of metal-containing polyesters of dimer acid, M(HHP)DA

Polycondensation was carried out by melt condensation technique. Equistoichiometric amounts of DA and metal diol were mixed and heated at 160±1°C. *p*-Toluene sulphonic acid was used as catalyst. The reaction was allowed to continue for 6 h and the water formed during polyesterification was continuously removed from the reaction mixture by distillation under continuous flow of nitrogen gas. Polyesterification reaction was followed by determination of unreacted carboxyl end groups in aliquots of resin ($\sim$0.2 g) withdrawn at fixed time intervals. Finally, the polyesters which were resinous solids of pale colour, were washed thoroughly with water (to remove unreacted diol) followed by acetone (to extract unreacted DA). The polyesters were dried under vacuum. The polyesters were insoluble in water as well as in organic solvents.

Zn(HHP)DA: Anal. calcd. for $[Zn_4(CH_3COO)_8\text{-}(C_{14}H_{17}O_5)_2]_{13}\text{–}(C_{36}H_{62}O_3)_{12}$: C, 52.73; H, 6.66; Zn, 15.12. Found: C, 57.71; H, 6.64; Zn, 15.03. IR (KBr) cm^{-1}: 3450 (OH), 2926, 2861 (CH), 1738, 1646 (C=O), 1552, 1405 (COO^-), 1499, 1435 (δ_{CH}), 1288 (COO), 1156 (δ_{OH}).

Mn(HHP)DA: Anal. calcd. for $[Mn_4(CH_3COO)_8\text{-}(C_{14}H_{17}O_5)_2]_2(C_{36}H_{62}O_3)$: C, 49.84; H, 5.96; Mn, 14.72. Found: C, 49.49; H, 4.22; Mn, 15.92. IR (KBr) cm^{-1}: 3435 (OH), 2925, 2853 (CH), 1710 (C=O), 1555, 1359 (COO^-), 1261 (C–O).

2.4. Measurements

IR spectra of metal diols and their polyesters were recorded on Perkin-Elmer spectrophotometer model 1430 in 4000–600 cm^{-1} range using KBr as dispersant. Elemental analyses were done on a Carlo Erba 1108 elemental analyzer. TGA were carried out on a Perkin-Elmer Thermal Analyzer TGS-4 in N_2 atmosphere at a heating rate of 15°C min^{-1}. DSC was carried out on a Mettler DSC instrument in N_2 atmosphere at a heating rate of 10°C min^{-1}.

Esterification reaction was followed by determining the acid numbers using the titrimetric method [30]. The quantitative determination of metal ions was done by complexometric methods using EDTA [31].

2.5. Determination of kinetic parameters

Detailed description of methods used for evaluating the kinetic parameters used in this report are available in literature [3–5,11]. The equations used in the various methods are listed below:

(A) Method of Freeman and Carroll [3] (from the TG curve):

$$\frac{\Delta\log \mathrm{d}W/\mathrm{d}t}{\Delta\log W_r} = x - \frac{\Delta E^*}{2.303\,R}\frac{\Delta(1/T)}{\Delta\log W_r}, \tag{1}$$

where 'x' is the order of reaction and 'W_r' is the weight fraction of the material undergoing degradation at time t, given as

$$W_r = W_c - W \tag{2}$$

where 'W_c' is the weight loss at completion of reaction and 'W' is the total weight loss up to time, t.

A plot of $\Delta\log\,(\mathrm{d}W/\mathrm{d}t)/\Delta\log W_r$ vs. $\Delta T^{-1}/\Delta\log W_r$ should result in straight lines with intercept x and slope of $\pm E^*/2.303\,R$, for any unique physical or chemical reaction.

Rate of decomposition [32]:

$$-\frac{\mathrm{d}W}{\mathrm{d}t} = \frac{Z}{\mathscr{B}}\exp\left(-\frac{\Delta E^*}{RT}\right)W_r^x, \tag{3}$$

where '$\mathscr{B}$' is the heating rate (°C/min), 'W_r' the weight fraction of the material undergoing degradation at time t, and 'Z' is the frequency factor.

(B) Method of Fuoss et al. [4] (from the TG curve):

For first-order kinetics:

$$\Delta E^* = -(RT_i^2/W_i)(\mathrm{d}W/\mathrm{d}T)_i \tag{4}$$

where 'T_i' and 'W_i' are the temperature and weight at inflection point on the TG curve and '$(\mathrm{d}W/\mathrm{d}T)_i$' is the corresponding inflection slope. Since only the ratio $\mathrm{d}W/W_i$ appears in Eq. (4), the weight may be expressed in any convenient arbitrary units. Further, the term for rate of heating, $\mathscr{B}$, does not appear in Eq. (4), it is important that the heating rate be strictly linear.

Frequency factor, Z, is computed using value of E^* determined by Eq. (4).

$$Z = -(\mathscr{B}/W_i)(\mathrm{d}W/\mathrm{d}T)_i\exp(\Delta E^*/RT_i). \tag{5}$$

Authors have claimed that their method yields values, for E and Z, of higher precision than values derived from thermogravimetry by other authors [3,33–36] because their analysis of data is much more direct and is subject to no mathematical approximations.

(C) Method of Broido [5] (from the TG curve):

$$\ln(\ln 1/Y) = \frac{-\Delta E^*}{R}\frac{1}{T} + \ln\left(\frac{R}{\Delta E^*}\frac{T}{\mathscr{B}}T_m^2\right), \tag{6}$$

where 'T_m' is the temperature of maximum reaction velocity, 'Y' is the fraction of the number of initial molecules not yet decomposed given by the equation

$$Y = (W_t - W_\infty)/(W_0 - W_\infty), \tag{7}$$

where 'W_t' is the weight at any time, t. A plot of ln(ln $1/y$) vs. $1/T$ yields a straight line whose slope is related to the energy of activation.

(D) Method of Dave and Chopra [11] (from the DTG curves):

The specific rate constant, k, for a first-order reaction, at any temperature T, can be calculated from the following equation

$$k = \frac{-\mathrm{d}W/\mathrm{d}t}{(A-a)}, \tag{8}$$

where 'A' is the total area (in mg) under DTG curve for any reaction, 'a' the area (in mg) for reaction up to time t; '$\mathrm{d}W/\mathrm{d}t$', the height of the curve at time t.

The specific rate constant k, is also given by the relationship

$$k = Ze^{-\Delta E^*/RT}. \tag{9}$$

If Eq. (9) is substituted in Eq. (8) and the logarithmic form of the resultant is differentiated and then integrated properly, the following relationship is obtained:

$$\frac{-\Delta E^*}{2.303\,R}\frac{T^{-1}}{\log(A-a)} = -x + \frac{\log(\mathrm{d}W/\mathrm{d}t)}{\log(A-a)}. \tag{10}$$

This equation is similar in form to the equation obtained by Freeman and Carroll [3]. The values of log k obtained from Eq. (8) can be plotted against $1/T$, thus yielding values of ΔE^* from slope.

3. Results and discussion

3.1. Composition

The progress of esterification reaction of the metal diols with dimer acid was followed by determining the acid number at regular intervals (Fig. 1). The degree of polymerization of the product for polyesterification may be represented by Eq. (11) [37,38].

$$D_p = (1+r)/[2r(1-p)+(1-r)]. \tag{11}$$

If this polymer, in general, is represented as an A–A–B–B type, then r is the ratio of A–A to B–B molecules and p is the extent of reaction or the fraction of end groups that has already reacted at the particular time, i.e.,

$$p = (N_0 - N)/N_0, \tag{12}$$

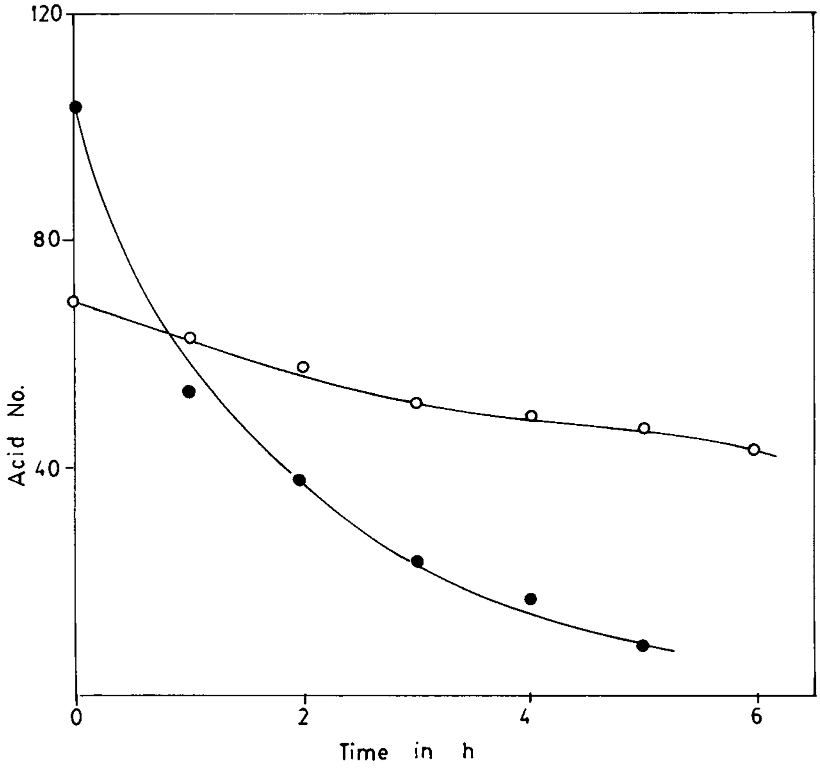

Fig. 1. Acid number vs.. time for polyesterification of DA with Zn(HHP) (●) and Mn(HHP) (○).

where N_0 is the amount of carboxylic group initially present (acid number) and N is the quantity left after a given interval of time. D_p was found to be 12.2 and 1.6 for Zn(II) and Mn(II) polyesters, respectively. A plot of extent of reaction, $1/(1-p)$ against time yielded a straight line suggesting second-order reaction kinetics which is quite consistent with the condensation reaction. The solubility of metal diols in water is suggestive of their ionic character and qualitative tests confirmed the presence of acetate ions.

The theoretical values for analysis were calculated using assumed structures keeping in view the degree of polymerization. The calculated values of elemental composition convincingly agree with the experimental ones only when a 1 : 2 mole ratio for HHP to metal is considered and two acetates are attached to each metal ion. Therefore, a structure shown in Fig. 2 is suggested where half of the acetate ions function as bridging ligands. This structure fulfils the maximum coordination number of four for tetrahedral zinc.

The pale colour of manganese diol suggests the octahedral configuration with high spin arrangement [39]. The four coordination sites of manganese are satisfied, as shown in Fig. 2 for zinc diol, and for the remaining two, bonding of each metal atom with two neighbouring metal atoms is suggested.

The deviation of the observed analysis data from the theoretical values may be attributed to the polymeric nature. The compounds may have a broad molecular weight distribution.

3.2. IR spectral studies

The IR spectra of metal diols and their polyesters are presented in Fig. 3. The perusal of these spectra suggests that metal ions have influence on the structure of diols and polyesters. The assignments are based on the literature data [40,41]. The appearance of OH stretching in 3420–3450 cm^{-1} indicates considerable hydrogen-bonding in these compounds. In Mn(II) compounds intensity of absorption due to OH stretching is lesser and the bands are broader suggesting greater H-bonding interactions.

The symmetric and asymmetric C–H stretching vibrations of CH_2 groups appear in metal diols near 2930 and 2860 cm^{-1}, respectively. In polyesters the intensity of absorption owing to CH_2 groups has enhanced indicating increased number of CH_2 groups from dimer acid. The lower degree of polymerization, in Mn(HHP)DA calculated from acid number, is further substantiated by the relatively lesser intensity of absorption due to CH_2 groups as compared to that of Zn(II) polyester.

The C–H stretching vibration of the phthalate ring is seen as absorption at 3070 cm^{-1} in all the compounds. Phthalate absorbs strongly near 1280 cm^{-1} in diols confirming the presence of ester groups conjugated with the aromatic ring.

3.3. Thermal analysis

The TG and DSC curves recorded in nitrogen for metal diols and their polyesters are shown in Figs. 4–7. The absence of melting endotherms in DSC curves indicates that all these materials have probably no crystalline structure. The TG curves show that diols and polyesters of Zn(II) exhibit two step thermal degradation whereas diols and polyester of manganese(II) exhibit one step thermal degradation. However, the thermal degradation commences at higher temperatures for Mn(II) compounds which reflects their greater ionic character as expected for the lower

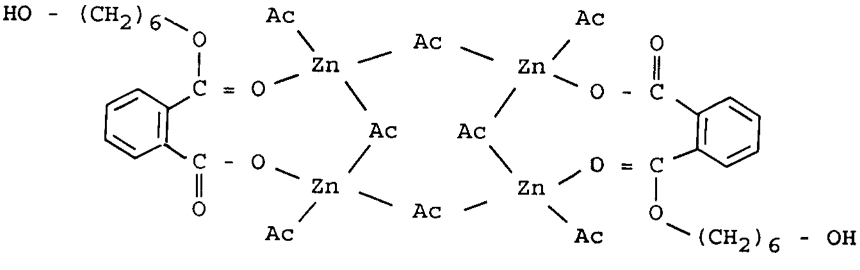

Fig. 2. Structure of zinc diol.

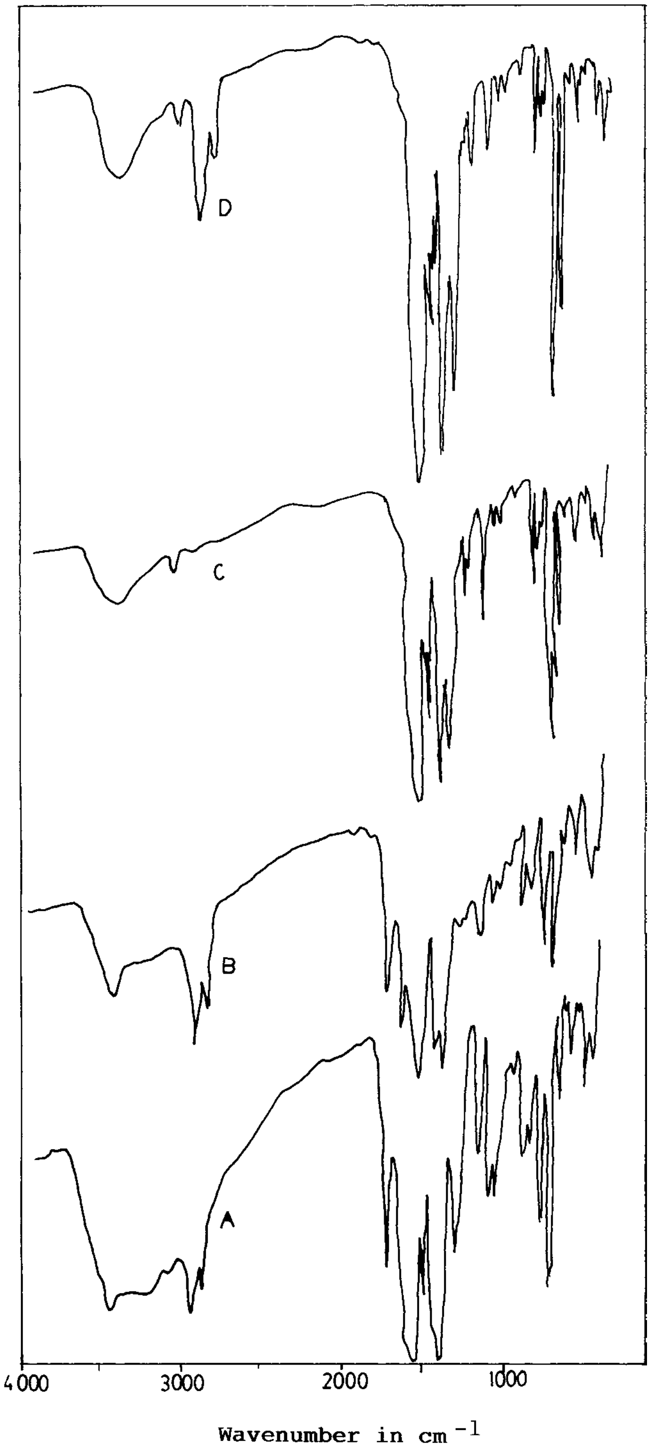

Fig. 3. IR spectra of metal diols and their polyesters (a) Zn(HHP) (b) Zn(HHP)DA (c) Mn(HHP) (d) Mn(HHP)DA.

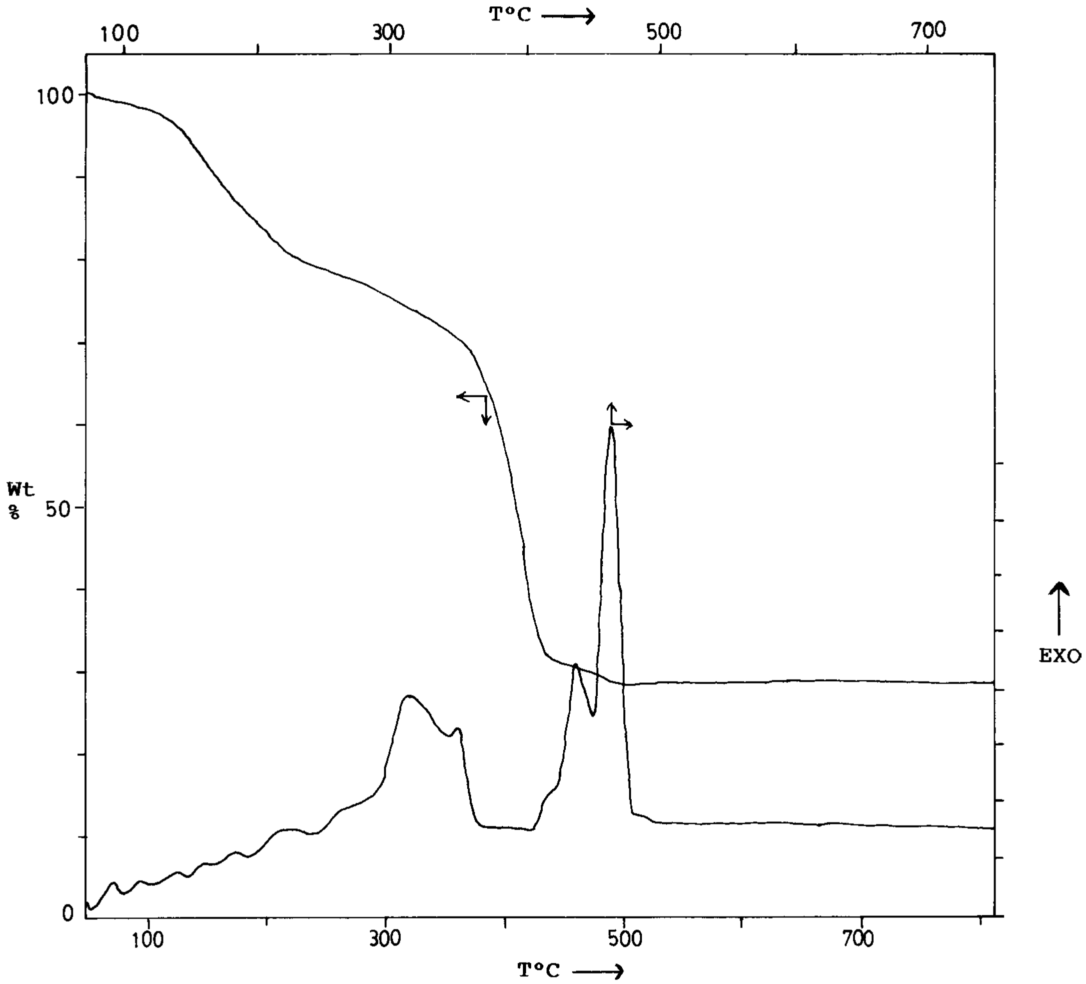

Fig. 4. DSC and TG curve of Zn(HHP).

degree of polymerization. The ionic interactions are evidenced from the IR spectral analysis also.

For all the compounds initial weight loss is almost negligible, which may be due to the adsorbed moisture. Presence of water molecules coordinated to metal ions is ruled out as the significant weight losses are observed above 200°C only, except for the Zn(II) diol. This observation is further substantiated by the DSC curves which show no endotherms for vapourization of water.

The thorough investigation of TGA and DSC curves of these metal diols and their polyesters yields interesting results about structure and stability.

For Zn diol, in the first step of decomposition ~18% weight is lost, in the temperature range 110–190°C, which is coherent with the theoretical weight corresponding to four acetate ions (calc. 18.68%). An exotherm is observed in DSC curve in 244–368°C range which corresponds to the second step of decomposition in TG curve resulting in a weight loss of ~10%. This weight loss may be attributed to the loss of a fraction of hexanediol (calc. 15.99%). The third decomposition step exhibits a steep weight loss of 39% in 370–430°C range due to loss of remaining fraction of hexanediol, bridging acetate ligands (calc. 18.68%) and a fraction of phthalate unit (calc.

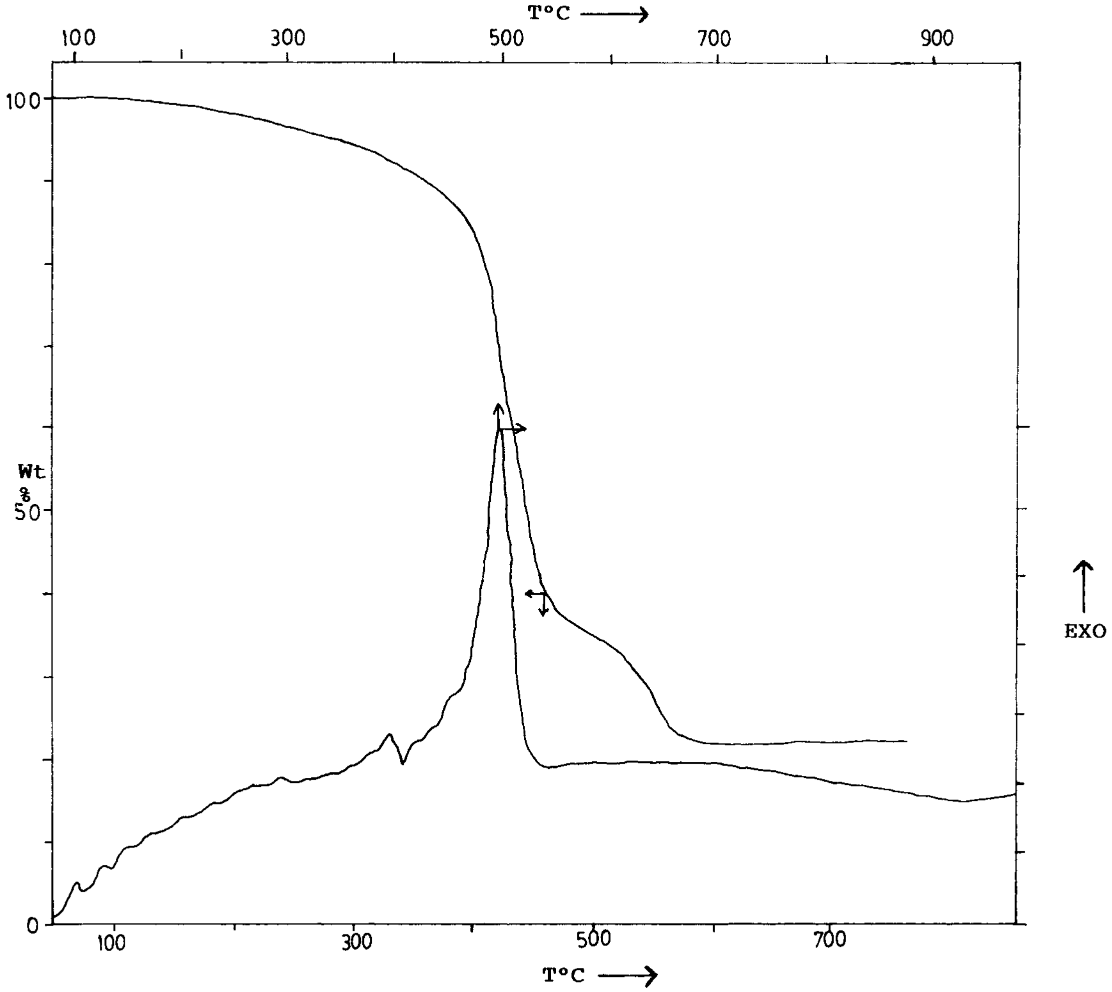

Fig. 5. DSC and TG curve of Zn(HHP)DA.

25.96%). After the final exothermic weight loss (exotherm peak maxima at 450°C) the plateau above 490°C has a weight slightly more than that for zinc oxide (calc. 25.77%).

The polyester synthesized from zinc diol and dimer acid is more thermally stable than the diol itself. The polyester decomposes gradually above 230°C and the total weight loss below 400°C may be attributed to the gradual loss of four acetate ions each of which is coordinated to a single metal atom (Fig. 2). The exotherm in DSC curve in 408–535°C range indicates the onset of major decomposition step. The degradation of main chain of polyester is observed as a sharp inflection in TG curve in 408–470°C range with a total weight loss of 47% corresponding to the loss of dimer acid (calc. 29.68%), bridging acetate ligands (calc. 13.55%) and fraction of hexanediol (calc. 11.60%). The remaining fraction of hexanediol is lost in less steeper inflection in 470–530°C, which coincides with the strong exotherm maxima at 495°C in DSC curve. The residual weight at 530°C (33%) can be attributed to the weight of zinc phthalate (calc. 33.85%) which finally decomposes in 530–580°C range and the plateau observed above this

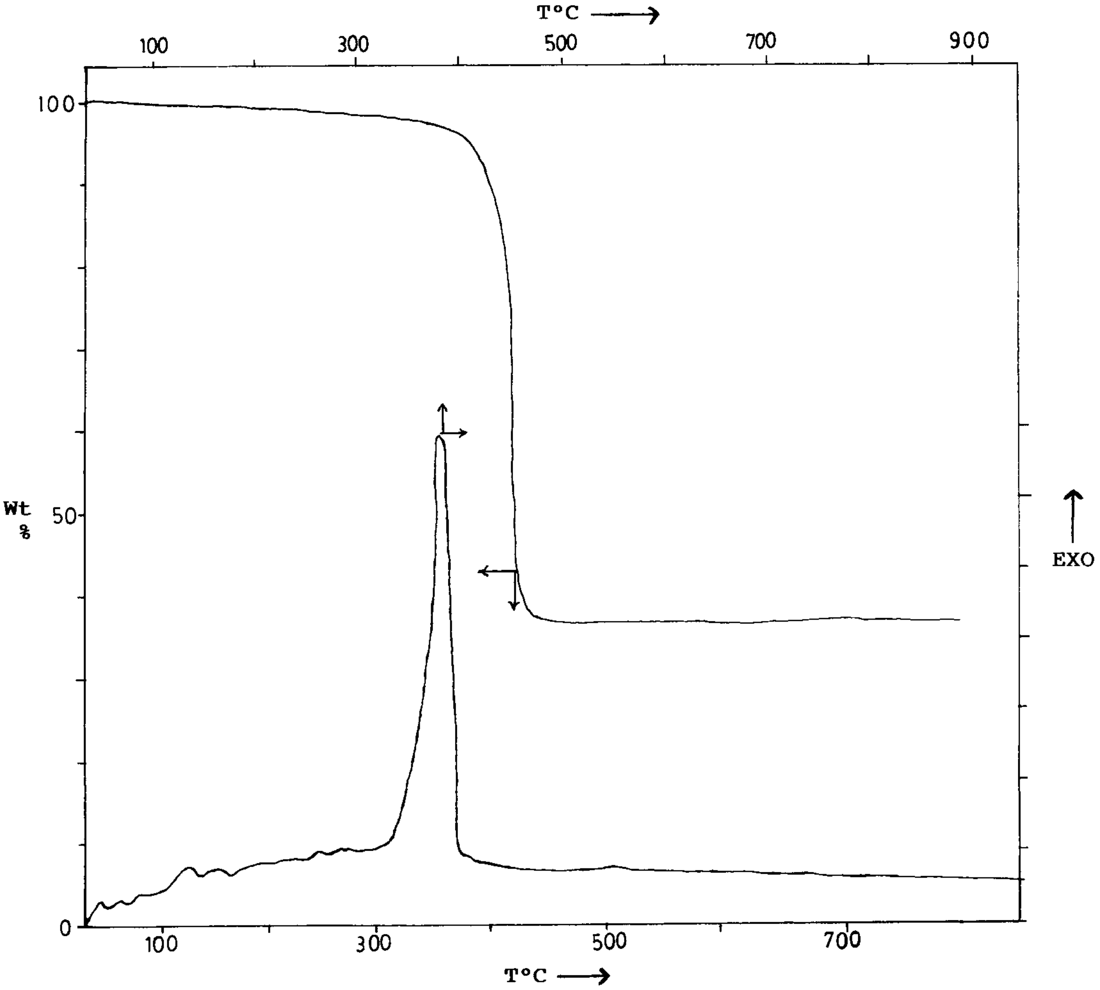

Fig. 6. DSC and TG curve of Mn(HHP).

corresponds to the formation of zinc oxide (calc. 18.69%).

Durairaj and Rao [42] reported thermal stability of manganese salt of HHP, Mn(HEP), based on the TGA and DSC studies. Decomposition pattern of Mn(HHP) in a single steep step in the present study is different from the multistep degradation reported for Mn(HEP) [42]. Mn(HHP) is not only more stable in terms of temperature of initial degradation (cf. 300°C for Mn(HEP)) but also shows greater residual weight, i.e., 37% (cf. 10% for Mn(HEP)). These authors have used metal oxides for synthesis of diol. It is suggested therefore, that the anion also plays an important role for deciding the final structure of complex.

Above 550°C the oxide of manganese is usually Mn_2O_3 formed by the decomposition of oxy salt and carbonate [43]. However, the residual weight is much higher than that calculated for Mn_2O_3 (25.84%) and somewhat lower than that for manganese phthalate (calc. 44.74%). For the polyester of Mn(HHP) the plateau is observed above 710°C which is just in agreement with the weight for metal phthalate (calc. 34.60%).

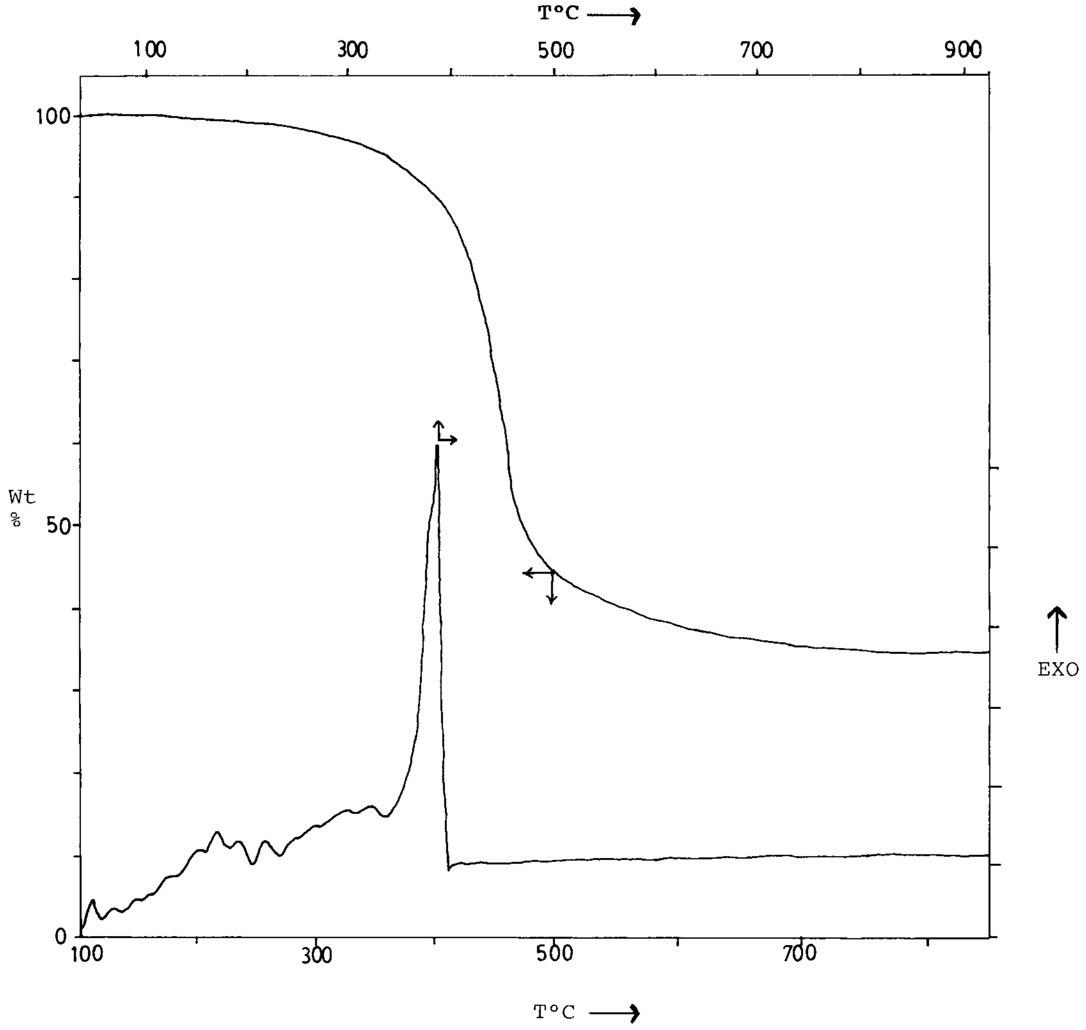

Fig. 7. DSC and TG curve of Mn(HHP)DA.

The lower stability of zinc compounds towards thermal degradation may be attributed to the greater catalytic efficiency of zinc. Zimmerman and Chu [44] in their studies on catalytic effects of metal ions on decomposition of poly(ethylene terephthalate) and its related model polyesters found the order of catalytic efficiency of individual ions towards the thermal decomposition as follows:

$$Ca < Mn < Co < Zn.$$

These authors introduced metal ions in acetate form. The multistep decomposition in case of zinc compounds against the single step degradation for manganese compounds is further indicative of complex degradation mechanism internally catalyzed by zinc acetate in the former.

The kinetic parameters for the thermal degradation of diols and polyesters were determined for the major decomposition step using the procedures described by Fuoss et al. [4], Freeman and Carroll [3], Broido [5] and Dave and Chopra [11].

1. From the slopes of the TG curves ΔE^* was calculated at the inflection point using Eq. (4).

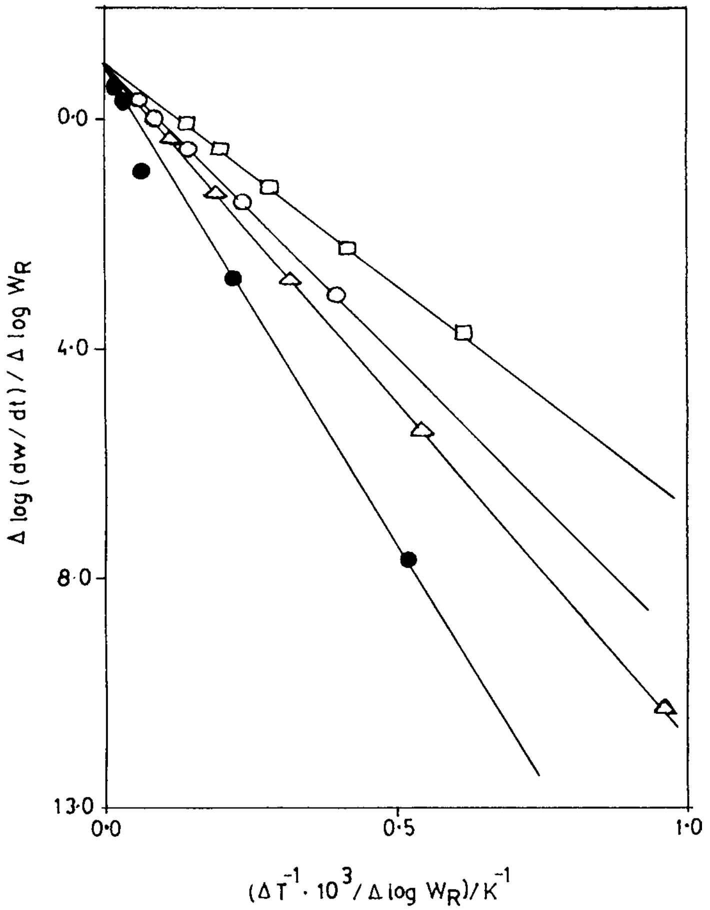

Fig. 8. Plots for the determination of kinetic parameters using Eq. (1) for the thermal degradation of Zn(HHP) (○), Zn(HHP)DA (□), Mn(HHP) (●) and Mn(HHP)DA (Δ) in nitrogen.

Frequency factor, Z, entropy, ΔS^* and free energy of activation, ΔG^* were calculated using the following equations:

$$\Delta S^* = 2.303\,R \log Zh/kT_i, \qquad (13)$$

$$\Delta G^* = \Delta E^* - T\Delta S^*. \qquad (14)$$

2. From the slopes of the TG curves values of Δlog (dW/dt) and Δlog W_r were calculated (Eq. (1)) and plots were made of Δlog (dW/dt)/Δlog W_r vs. $\Delta T^{-1}/\Delta$log W_r, as shown in Fig. 8. The energy of activation, ΔE^*, was determined from the slope. The order of reaction was determined from intercept and found to be unity for all the compounds.
3. Using Broido method plots of ln(ln 1/y) vs. 1/T, obtained from slopes of TG curves (Figs. 4–7), using Eq. (6), yielded straight lines as shown in Fig. 9. The values of ΔE^* were obtained from the slopes of these plots.
4. The values of log k were obtained from Eq. (8) using the method of Dave and Chopra. The values of log k were plotted against 1/T (Fig. 10), thus yielding values of ΔE^*.

From Table 1 it is obvious that the energy of activation for each sample varies considerably according to the different procedures adopted.

The kinetic evaluation in thermal analysis is frequently based on simple linearization technique. Vàr-

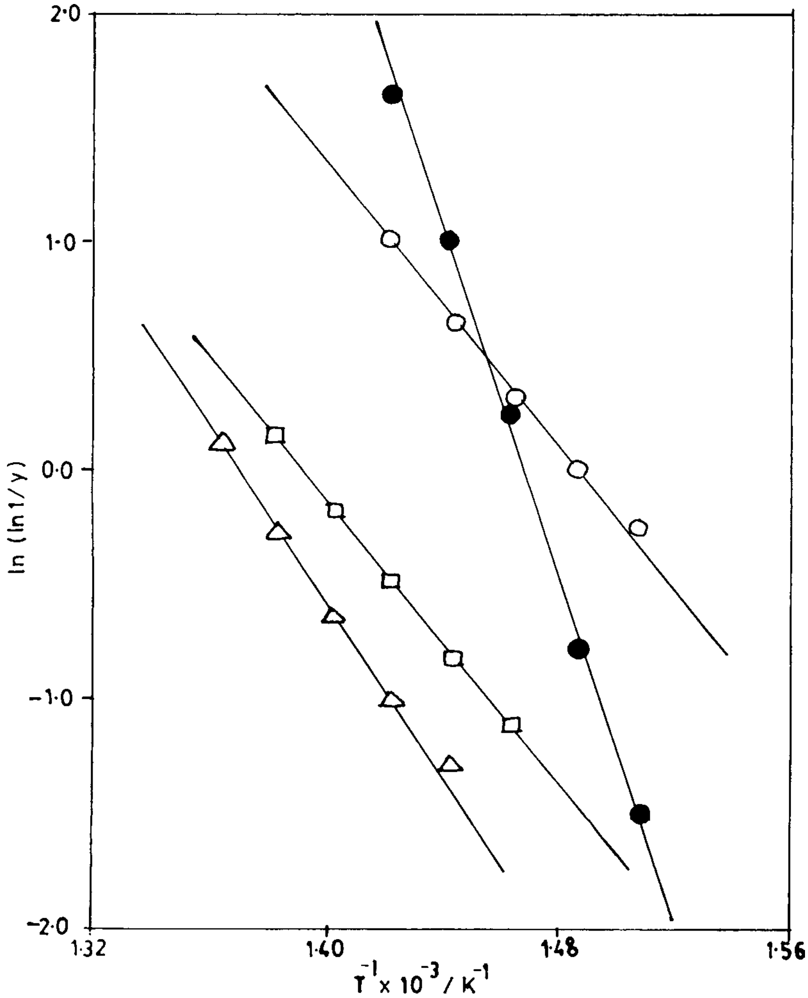

Fig. 9. Plots of ln(ln 1/y) vs.. 10^3 T^{-1}/K^{-1} using Eq. (6) for Zn(HHP) (○), Zn(HHP)DA (□), Mn(HHP) (●) and Mn(HHP)DA (Δ).

kegyi [45] mentioned the problems and disadvantages associated with these linearization procedures. Following Freeman and Carroll, Broido, and Dave and Chopra methods linear plots have to be obtained from the data derived from the TG curves, whereas in Fuoss method E^* can be directly calculated from the temperature and the weight at the inflection point on TG curve using Eq. (4). When the E^* for Zn(HHP), Zn(HHP)DA, Mn(HHP) and Mn(HHP)DA were calculated using W_i, the values were found be 82.52, 84.88, 141.12 and 88.54 kJ mol^{-1}, respectively. The values widely differed from those calculated following other methods (Table 1). In other methods W_r, weight fraction of the material undergoing degradation at time t (Eq. (2)) has been used in calculations. Therefore, E^* for all the compounds were recalculated using W_r, in place of W_i, following Eq. (4) and the values obtained (Table 1) were comparable with those from other methods.

The order of stability towards thermal degradation on the basis of kinetic parameters calculated for major decomposition step is Mn(HHP) > Mn(HHP)DA > Zn(HHP) > Zn(HHP)DA.

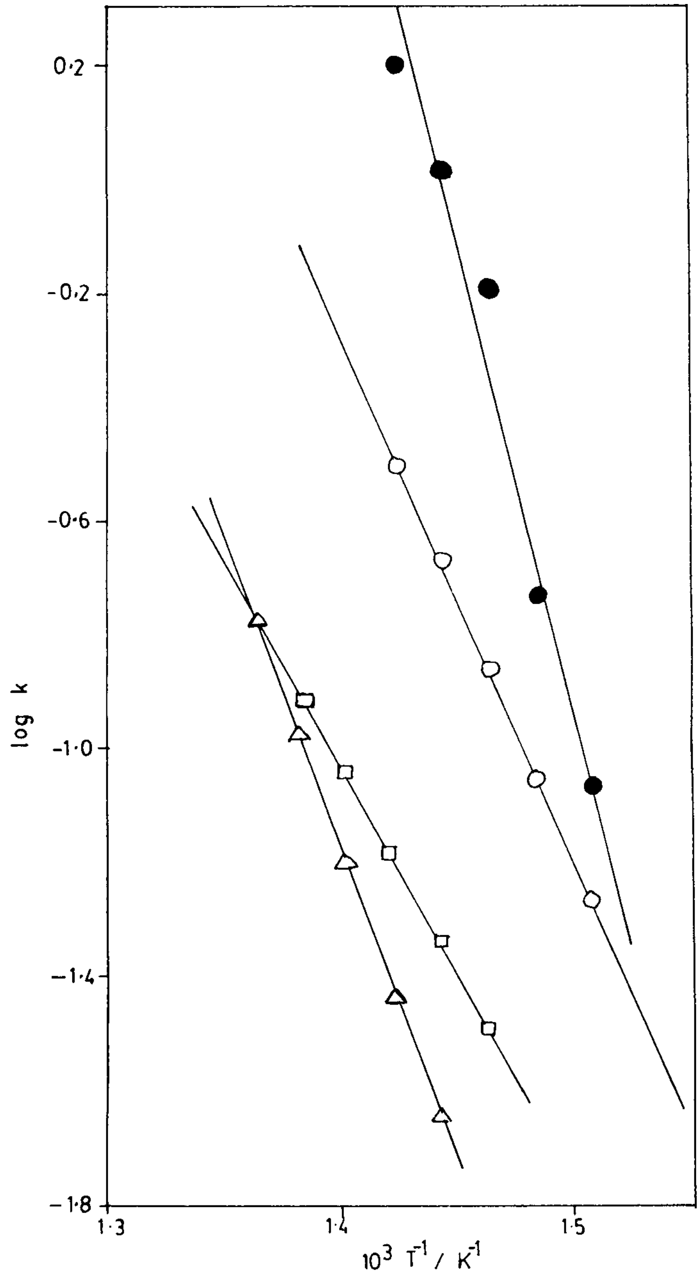

Fig. 10. Plots of log *k* vs. 10^3 T^{-1}/K^{-1} using Eq. (8) for Zn(HHP) (○), Zn(HHP)DA (□), Mn(HHP) (●) and Mn(HHP)DA (△).

4. Conclusion

Usually the determination of composition of polymeric samples from the elemental analysis data is difficult and sometimes unreliable also due to broad polydispersity of the samples. However, the thermal degradation studies may be a useful guide for deciding the composition of a polymer,

Table 1
Kinetic parameters for metal diols and their polyesters on the basis of Freeman and Carroll (FC), Broido (B), Fuoss, Salyer and Wilson (FSW), and Dave and Chopra (DC) methods

Compound	Peak temperature in DTG (°K)	Method	ΔE^* (kJ mol^{-1})	Z (min^{-1})	ΔS^* (JK^{-1} mol^{-1})	ΔG^* (kJ mol^{-1})
Zn(HHP)	683	FC	190.67	2.39×10^{14}	−636.28	625.24
		B	131.60	8.15×10^{9}	−835.44	702.21
		FSW	204.13	3.23×10^{15}	−590.87	607.69
		DC	171.57	1.81×10^{12}	−700.68	650.13
Zn(HHP)DA	718	FC	148.88	3.57×10^{10}	−802.61	725.15
		B	130.19	1.33×10^{9}	−862.54	749.50
		FSW	150.39	4.59×10^{10}	−797.75	723.18
		DC	136.40	8.67×10^{8}	−742.64	741.41
Mn(HHP)	678	FC	316.30	2.95×10^{24}	−204.67	455.06
		B	316.84	2.44×10^{24}	−202.82	454.35
		FSW	321.85	7.90×10^{24}	−185.80	447.82
		DC	319.67	1.50×10^{24}	−193.20	450.66
Mn(HHP)DA	733	FC	221.93	4.42×10^{15}	−583.27	649.46
		B	161.47	1.90×10^{11}	−773.23	728.25
		FSW	228.56	1.49×10^{16}	−562.45	640.83
		DC	213.79	2.90×10^{14}	−608.82	660.83

if used in conjunction with elemental analysis data.

The present study demonstrates that the different methods used for evaluating energy of activation from TG curves yield slightly different results. However, Fuoss method [4] seems to be the most direct and easiest one. It may have higher precision also as the authors [4] claimed, because the data is more direct and is subject to no mathematical approximations.

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