

## Studies of Copolyesters. Thermal Characterization and Kinetics of Thermal Degradation of Poly(ethylene/trimethylene terephthalate) Copolyesters<sup>†</sup>

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**ABSTRACT:** Random copolyesters of dimethyl terephthalate (DMT), ethylene glycol (EG) and propane-1,3-diol (PrG) and the homo-polyesters poly(ethylene terephthalate) (PET) and poly(trimethylene terephthalate) (PPrT) have been subjected to differential thermal analysis (DTA) and thermogravimetry (TG). Thermodynamic parameters like enthalpy of fusion ( $\Delta H_f$ ), entropy of fusion ( $\Delta S_f$ ) and percent crystallinity ( $X_c$ ) are discussed in terms of structural differences, particularly the effect of composition and chain flexibility. Kinetic order and activation energy for the thermal degradation of the copolyesters are discussed.

**KEY WORDS** DTA / Enthalpy of Fusion / Entropy of Fusion / Percent Crystallinity / TG / Kinetic Order / Activation Energy /

The synthesis and characterization of terephthalate copolyesters with varying percentage of ethylene glycol and propane-1,3-diol and the homo-polyesters poly(ethylene terephthalate) and poly(trimethylene terephthalate) were reported in a previous article.<sup>1</sup> Thermo-analytical methods, such as differential thermal analysis (DTA), thermogravimetric analysis (TG), and thermovolumetry have been employed increasingly in the investigation of chemical reactions in the liquid and solid states at elevated temperatures. DTA studies provide structural information on comonomer distribution and crystallinity of the copolymers.<sup>2</sup> Very little has been reported concerning the degradation studies of polyesters.<sup>3-8</sup> In the present study, we report the thermal and degradation kinetic phenomena of terephthalate copolyesters of ethylene glycol and propane-1,3-diol.

### EXPERIMENTAL METHODS

The synthesis and characterization of the copolyesters used in this study have been given elsewhere.<sup>1</sup>

A Mettler system TA 2000 DTA was used to record the DTA curves. Typically, 5—10 mg of the sample was encapsulated in aluminium sample pans and empty pans were used as references. The lids of the pans were perforated with a needle so that the measurements were carried out in air atmosphere. Dynamic studies were performed by heating the material at a rate of 10K min<sup>-1</sup> in a DTA cell. The heat of fusion,  $\Delta H_f$ , of the copolyesters were determined by comparing the area under the endothermic peak to the area of standard indium endotherm.<sup>1,9-11</sup> The per cent crystallinity,  $X_c$ , of the copolyesters were calculated by the following equation<sup>10-12</sup>:

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$$\%X_c = \frac{\Delta H_f(\text{EG} \times \text{M1}) + (\text{PrG} \times \text{M2})}{\Delta H_f^0(\text{EG} \times \text{M1})} \times 100 \quad (1)$$

where EG = mol% of ethylene terephthalate in the copolymer; M1 = molecular weight of ethylene terephthalate repeat unit (192); PrG = mol% of trimethylene terephthalate; M2 = molecular weight of trimethylene terephthalate repeat unit (206) and  $\Delta H_f^0$  = the heat of fusion per gram of repeat unit of poly(ethylene terephthalate) (PET) (32.2 cal g<sup>-1</sup>).

Thermal degradation of the copolyesters was studied by means of dynamic thermogravimetry with a Stanton Redcroft TG-750 model thermobalance; 5 mg of the sample were heated in nitrogen atmosphere at a heating rate of 10K min<sup>-1</sup>. A platinum-rhodium thermocouple was used to measure the temperatures.

### KINETIC TREATMENT

The order and activation energy for the major decomposition reaction steps were calculated by various methods. Most kinetic treatments are based on the following relationships:

$$\frac{dc}{dt} = kf(c) \quad (2)$$

where  $c$  is the conversion,  $t$  = time,  $k$  = a temperature dependent rate constant and  $f(c)$  = a temperature independent function of  $c$ . The constant  $k$  is generally assumed to follow a law of the form:

$$k = Ae^{-E/(RT)} \quad (3)$$

where  $A$  = pre-exponential factor,  $E$  = activation energy,  $R$  = gas constant and  $T$  = absolute temperature. In homogeneous kinetics, conversion is defined in terms of concentration, and the conversion function is assumed to have the form:

$$f(c) = (1-c)^n \quad (4)$$

where  $n$  = order of reaction. By combining eq

2-4 and including the rate of temperature rise,  $dT/dt$ , the following integral form of the equation can be written:

$$\int_0^c \frac{dc}{(1-c)^n} = \frac{A}{B} \int_0^c e^{-E/(RT)} dT \quad (5)$$

where  $A$  and  $B$  are constants. Integration of the terms on the left hand side gives:

$$\int_0^c \frac{dc}{(1-c)^n} = -\frac{[(1-c)^{1-n} - 1]}{(1-n)} \quad \text{for } n \neq 1 \quad (6)$$

$$= -\ln(1-c) \quad \text{for } n = 1 \quad (7)$$

For the right hand side of eq 5, various authors used different approximations for the calculation of the kinetic parameters: Coats and Redfern<sup>13</sup>:

$$\int_0^T e^{-E/(RT)} dT = (RT^2/E)(1 - 2RT/E)e^{-E/(RT)}$$

Plot:  $\log \{[\ln(1-c)]/T^2\}$  vs.  $1/T$

for  $n = 1$

Doyle<sup>14</sup>:

$$\int_0^T e^{-E/(RT)} dT = -2.315 - 0.4567E/(RT)$$

for  $E/(RT) \geq 20$

Plot:  $\ln(1-c)$  vs.  $1/T$  for  $n = 1$

Murray and White<sup>15</sup>:

$$\int_0^T e^{-E/(RT)} dT = (RT^2/E)e^{-E/(RT)}$$

Plot:  $[\ln \{ \ln(1-c) \} - 2 \ln T]$  vs.  $1/T$

for  $n = 1$

The activation energies are determined graphically from the above equations, assuming the correct order of the reaction ( $n = 1$  for the present system) which is established by differential methods wherever necessary.

## RESULTS AND DISCUSSION

The compositions and molecular weights of the copolyesters are given in Table I. When the copolyesters were heated at a rate of  $10\text{K min}^{-1}$  in a DTA cell, it was found that a sharp endotherm occurred around 180–240°C depending upon the comonomer contents (EG and PrG) in the copolyester (PET, 246°C; A4, 238.2°C; A3, 237.0°C; A, 186.7°C, and PPrT, 225.2°C, Table I). This endotherm was attributed to the melting of the copolyester and the corresponding temperature is the melting temperature of the copolyester. As the PrG content increases the copolyester becomes more amorphous and hence there is no melting temperature for the copolyesters A1 and A2. When the composition of PrG reaches 100 mol%, that is homopolymer, the polymer becomes crystalline again. The melting temperature–composition relations for this component follow an independent curve, so that an eutectic type minimum results at the inter-

section of the two curves.<sup>11,16–18</sup> This is a typical behavior of random copolymers when studied over a wide range of compositions.

The  $\Delta H_f$  and per cent crystallinity-composition relationship of the copolyesters are shown in Table II. As the PrG content increases in the copolyester, the  $\Delta H_f$  and per cent crystallinity decreases upto 56 mol% of PrG and then the polymer becomes amorphous. The decrease in melting temperature ( $T_m$ ) with increasing PrG content in the copolymer is in agreement with the theory of equilibrium melting of random copolymers.<sup>19</sup> This theory predicts a depression in  $T_m$  caused by the non-crystallizing units according to the equation:

$$1/T_m - 1/T_m^0 = -\frac{R}{\Delta H_f^0} \ln X_A \quad (8)$$

where  $T_m$  = the melting temperature of the copolymer;  $T_m^0$  = the melting temperature of the homopolymer;  $\Delta H_f^0$  = the heat of fusion per repeat unit of the homopolymer, and  $X_A$  = the mole fraction of the crystallizable units. The melting point depression is dependent on the heat of fusion per mole of the crystallizing unit and on the sequence propagation probability  $p$ , which is suggested in random copolymers can be identified with  $X_A$ .<sup>19</sup> Using Flory equation, the  $T_m^0$  calculated from the  $1/T_m$  vs.  $-\ln X_A$  plot was in good agreement with the DTA  $T_m$  of PET ( $T_m$  for PET by the Flory equation is 242.5°C; and by DTA is 246.0°C). The  $\Delta H_f^0$  (for PET) calculated by Flory equation is 2650 cal per mol and by DTA analysis is 11920 cal per mol. The values of  $\Delta H_f^0$  determined from an analysis of copolymer melting always differ by varying amounts from the values obtained by other methods.<sup>20</sup>

Figure 1 gives the thermogravimetry curves for the copolyester A and A1. The kinetics of thermal degradation of the copolyester was studied from the weight loss *versus* temperature curve using different approximation methods for the calculation of the kinetic

**Table I.** Compositions and molecular weight of the copolyesters

Polymer	NMR Composition/mol%		Molecular weight ( $M_n$ )
	EG	PrG	
PPrT	0	100.0	5941
A2	22.3	77.7	1490
A1	29.0	71.0	1612
A	43.8	56.2	3052
A3	74.7	25.3	1750
A4	83.5	16.5	2010
PET	100.0	0	3303

**Table II.** Effect of composition on the thermodynamic properties and crystallinity of copolyesters

Polymer	Mol% of PrG	$\Delta H_f$	$\Delta S_f$	% $X_c$
		cal g <sup>-1</sup>	cal deg <sup>-1</sup> mol <sup>-1</sup>	
A4	16.5	18.82	7.07	58.5
A3	25.3	15.35	5.78	47.8
A	56.2	12.07	5.04	38.0

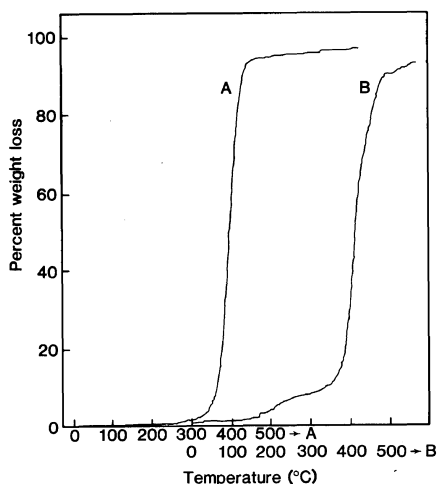


Figure 1. Thermogravimetry curves for terephthalate copolyester samples A (curve A) and A1 (curve B), cf. Table I.

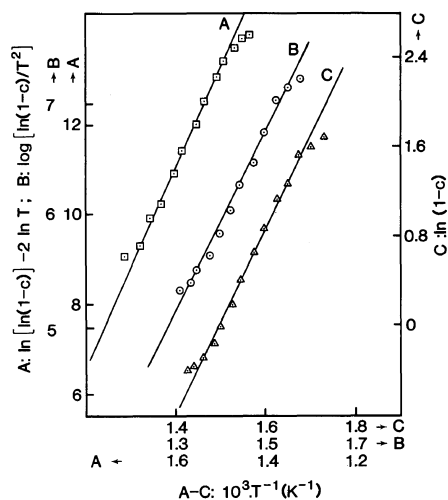


Figure 2. Calculation of activation energies  $E$  for the degradation of terephthalate copolyester sample A (cf. Table I) according to Murray and White<sup>15</sup> (plot A), Coats and Redfern<sup>13</sup> (plot B), and Doyle<sup>14</sup> (plot C).

parameters (Coats and Redfern,<sup>13</sup> Doyle<sup>14</sup> and Murray and White<sup>15</sup>). Figure 2 shows the calculations of the activation energy for the copolyester A using the above methods for a first order reaction. The mechanism for the major degradation route was found to be unimolecular. The energies of activation for

Table III. Activation energies  $E$  for the degradation of terephthalate homo- and co-polyesters of ethylene glycol and propane-1,3-diol according to different methods of evaluation

Polymer <sup>a</sup>	Temp of degradation °C	$E/\text{kcal mol}^{-1}$ <sup>b</sup>		
		Coats and Redfern <sup>13</sup>	Doyle <sup>14</sup>	Murray and White <sup>15</sup>
PET	311—448	33	36	39
A	301—457	37	37	41
A1	120—476	18	17	17
PPrT	285—448	38	38	42

<sup>a</sup> PET, poly(ethylene terephthalate); PPrT, poly(trimethylene terephthalate).

<sup>b</sup> In SI units 1 cal = 4.184 J.

the homo- and copolyesters were calculated and listed in Table III. Major decompositions start around 325°C and are completed around 450°C. From the activation energies, it is clear that as the PrG content increases in the copolymer chain, the copolymer needs less energy to degrade; that is the presence of long soft alkyl chain  $(-\text{CH}_2-\text{CH}_2-\text{CH}_2-)$  makes the polymer more susceptible to degradation because of the decrease in crystallinity. The variation of the activation energies calculated by different methods is due to various approximations employed in the calculation and lies within the experimental errors.

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