Poly(ethylene terephthalate)
I—Heat of Fusion

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Literature values for the heat of fusion of poly(ethylene terephthalate) are reviewed and compared with values obtained using differential scanning calorimetry and from the melting point depression produced by dibutyl phthalate diluent. The heat of fusion is discussed in relation to known heats of fusion of similar aromatic polyesters.

SINCE polymers can normally only be obtained in a partially crystalline state, indirect methods must be used to determine the heat of fusion of the crystal, ΔH_f. These can vary from a simple calorimetric determination of the sample heat of fusion, ΔH, coupled with an independent measurement of the degree of crystallinity, to methods involving the measurement of a property, the magnitude of which is related to ΔH_f. The latter usually consists of the measurement of the depression of the melting point brought about by a diluent which can be a random copolymer unit, plasticizer or simply the polymer chain end groups[1]. These two basic methods can give widely varying results chiefly due to experimental uncertainties in melting point determinations, the final melting being especially difficult to detect[2]. Hence, heats of fusion determined by the diluent method can be underestimated and indeed, undue reliance on such results has led to the erroneous conclusion that the heats of fusion of polyesters are higher than those of similar polyamides[3].

We present here measurements of the heat of fusion of poly(ethylene terephthalate), PET, from the depression of the melting point brought about by di-*n*-butyl phthalate diluent and from measurements of the heat of fusion by differential scanning calorimetry, DSC, of samples of varying degrees of crystallinity.

EXPERIMENTAL

PET was originally in the form of amorphous extruded 1 mm film. An intrinsic viscosity of 0·59 dl g^{-1} determined in *o*-chlorophenol at 25°C corresponded[4] to an average molecular weight, $\bar{M}_v = 19\,000$.

A DuPont 900 differential thermal analyser, DTA, was used to determine the depressed melting points. Polymer–diluent mixtures of total weight about 20 mg were weighed directly into thin-walled glass sample tubes which were then quickly sealed. After annealing in the DTA cell the top of the tube was cut off, a thermocouple inserted into the mixture and a DTA scan performed in air at a heating rate of 20 deg. C/min. The melting point was taken as the peak of the fusion endotherm.

The heats of fusion of annealed samples of varying crystallinities were determined using a Perkin–Elmer model 1B differential scanning calorimeter. Scans were carried out under nitrogen at 16 deg. C/min, peak areas of the fusion endotherms measured by planimeter and heats of fusion computed by comparison with similar endotherms of high purity indium.

The densities of the polymer samples were measured at 23°C in aqueous calcium nitrate density gradient columns of average gradient $5{\cdot}5 \times 10^{-4}$ g cm^{-3} cm^{-1}.

RESULTS

The melting point depression produced by a simple diluent of volume fraction, ϕ_1, has been derived by Flory[1] as

$$1/T_m - 1/T^0_m = (RV_2/\Delta H_f V_1)\,[\phi_1 - \chi_1 \phi_1^2] \qquad (1)$$

where T^0_m and T_m are the melting points of the homopolymer and polymer–diluent mixtures, respectively, V_2 and V_1 are the molar volumes of the polymer repeat unit and diluent, respectively, χ_1 is a dimensionless quantity characterizing the solvent–polymer interaction energy and R is the gas constant.

An alternative form of equation (1) is

$$1/T_m - 1/T^0_m = (RV_2/\Delta H_f V_1)\,(1 - BV_1\phi_1/RT_m)\,\phi_1 \qquad (2)$$

where $B\,(=RT\chi_1/V_1)$ is the interaction energy density of the solvent–solute pair.

Volume fractions of diluent were calculated at T_m using the following densities, ρ, and expansion coefficients, α, where the subscripts 1 and 2 refer to diluent and polymer, respectively: $\rho_1 = 1{\cdot}043$ at 20°C, $\alpha_1 = 8{\cdot}08 \times 10^{-4}$ deg^{-1} and $\rho_2 = 1{\cdot}39$ at 20°C, $\alpha_2 = 2{\cdot}6 \times 10^{-4}$ deg^{-1}. A plot of the quantities $(1/T_m - 1/T^0_m)/\phi_1$ and ϕ_1/T_m according to equation (2) is shown in *Figure 1*. V_2 and V_1 were calculated from densities and expansion coefficients[5] using the above quantities for the diluent and $\rho_2 = 1{\cdot}335$ at 20°C, $\alpha_2 = 1{\cdot}6 \times 10^{-4}$ deg^{-1} from 20° to 70°C, $\alpha_2 = 3{\cdot}7 \times 10^{-4}$ deg^{-1} above 70°C. The intercept and slope of the 'least squares' line of *Figure 1* lead to values of $\Delta H_f = 29{\cdot}0$ cal. g^{-1} and $B = -1{\cdot}2$ cal. cm^{-3}.

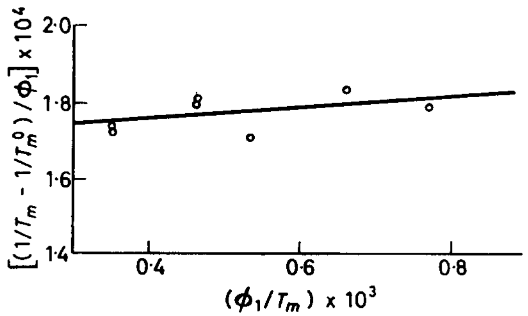

Figure 1—Plot of $(1/T_m - 1/T^0_m)/\phi_1$ versus ϕ_1/T_m for PET–dibutyl phthalate

By appropriate annealing, samples were prepared having densities between 1·34 and 1·42. Degrees of crystallinity, x, were computed using the relation

$$\rho_2 = x\rho_c + (1 - x)\,\rho_a \qquad (3)$$

where the crystalline density, ρ_c, was taken to be[6] $1{\cdot}455$ g cm^{-3} and the amorphous density, ρ_a as $1{\cdot}334$ g cm^{-3}. Observed heats of fusion measured by DSC were then divided by the degree of crystallinity to obtain ΔH_f. The mean value of ten such determinations of ΔH_f was $27{\cdot}0 \pm 2$ cal g^{-1}.

DISCUSSION

Literature values for the heat of fusion of PET are collected in *Table 1*. It can be seen that the heats obtained using copolymer or end group melting point depressions are consistently lower than those obtained using the other methods and are indeed lower than observed values of the heat of fusion of partially crystalline samples. These underestimations of ΔH_f are the result of too large observed melting point depressions.

Table 1. Literature values of ΔH_f of PET

Method	ΔH_f *cal* g^{-1}	*Ref.*
T_m depression—copolymers ethylene adipate and sebacate	11·5	7
Adiabatic calorimeter $\Delta H = 17{\cdot}9$ cal g^{-1} $\rho = 1{\cdot}404$ g cm^{-3}	31·1	8
$\Delta H = 21{\cdot}4$ cal g^{-1} $\rho = 1{\cdot}423$ g cm^{-3}	29·2	
T_m depression—copolymer ethylene isophthalate	15·2	9
—copolymer *p*-hydroxymethylbenzoic acid	15·2	
—by end groups	21·5	
—caprolactam diluent	28·6	
—diethylene glycol diluent—calculated from ref. 6	22·6	
DTA $\Delta H = 16{\cdot}7$ cal g^{-1} $\rho = 1{\cdot}41$ g cm^{-3}	26·7	10
Estimation of entropy of fusion	30·7	3
T_m depression—dibutyl phthalate diluent	29·0	This work
DSC determination of ΔH	27 ± 2	

This could possibly indicate that the copolymer units tend to alternate along the chain reducing the number of crystallizable sequences or more probably, as has been discussed by Mandelkern[2], that the melting point depression has been overestimated due to difficulties in detecting the disappearance of the last traces of crystallinity. Since PET is known to develop only intermediate crystallinity it is likely that ΔH_f is substantially greater than 21·4 cal g^{-1}, the highest observed heat of fusion. If we therefore arbitrarily consider only those reported values greater than 25 cal g^{-1} we obtain a mean value of 28·9 cal g^{-1} with a standard deviation of 1·5 cal g^{-1}.

Consider now the fusion of higher homologous polymethylene terephthalates, $\text{—[(C}_6\text{H}_4\text{) COO (CH}_2)_n\text{OCO]—}$, whose properties[3,12] are listed in *Table 2*.

Table 2. Fusion properties of polymethylene terephthalates

Polymer *n*	T_m °C	ΔH_f *cal* g^{-1}	ΔH_f *cal* $mole^{-1}$	ΔS_f *cal* deg^{-1} $mole^{-1}$	ΔS_f *cal* deg^{-1} $mole^{-1}$ $bond^{-1}$
2	275	29	5 600	10·2	1·7
4	232	35	7 700	15·2	1·9
6	161	34	8 400	19·4	1·9
10	138	36	10 900	26·7	1·9

The last column gives the entropy of fusion considered on the basis of number of chain bonds rotation about which, on a simple lattice, would lead to different conformations. The entropy of fusion of PET on this basis is seen to be lower than that of the other members. An entropy of fusion of 1·9 cal mole^{-1} deg^{-1} bond^{-1} would correspond to $\Delta H_f = 32{\cdot}6$ cal g^{-1} which is outside the limits found here.

The entropy of fusion may be considered to consist of two parts[11], an entropy of fusion at constant volume, $(\Delta S_f)_v$, caused by the polymer chains being able to assume different conformations in the liquid state and an entropy change caused by expansion of the melt, ΔS_{exp}. The former would be expected to decrease with methylene content whilst ΔS_{exp} will depend on the volume change on melting. At present data are not available for the calculation of these components of ΔS_f for the higher members of the series. As is shown in Part II[13], extremely careful annealing is needed to achieve high melting PET and the possibility thus exists that the reported melting points of the higher members are too low and hence the entropies of fusion too large.

The author wishes to thank Miss M. Luxford for experimental assistance.

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(Received January 1968)

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