Aliphatic polyesters as models for relaxation processes in crystalline polymers: 1. Characterization

P. A. Aylwin and R. H. Boyd

Department of Materials Science and Engineering and Department of Chemical Engineering, University of Utah, Salt Lake City, UT 84112, USA
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Syntheses and characterization of poly(pentamethylene pimelate), poly(1,6 hexamethylene adipate), poly(1,6 hexamethylene sebacate) and poly(2,5 hexamethylene adipate) are described. The first three are semicrystalline and the last completely amorphous. Dilatometry is used to establish volume-temperature curves (in both the solid and liquid regions in the first three). Liquid densities at 25°C are respectively 1104, 1096, 1033 and 1076 kg m^{-3}. Powder and fibre X-ray diffraction patterns on poly(pentamethylene pimelate) and poly(hexamethylene adipate) are indexed as monoclinic ($a = 0.614$, $b = 0.737$, $c = 1.716$ nm, $\beta = 54.6°$) and orthorhombic ($a = 1.008$, $b = 0.732$, $c = 0.1683$ nm), respectively. Under the assumption of 2 and 4 chains/cell, respectively, these lead to crystal densities of 1198 and 1222 kg m^{-3}, respectively, for these two polymers. The density of poly(1,6 hexamethylene sebacate) is known from the literature. Differential scanning calorimetry is used to establish crystal heats of fusion for the first three polymers as 151, 151, and 134 kJ kg^{-1}, respectively. The melting and crystallization temperatures of poly(1,6-hexamethylene adipate) are measured as a function of pressure up to 275 MPa. The heat of fusion derived from these data and the density data using the Clausius–Clapeyron equation is 167 kJ kg^{-1}.

Keywords Aliphatic polyesters; X-ray diffraction; unit cell; crystal density; amorphous density; heat of fusion

INTRODUCTION

Aliphatic polyesters were among the first high polymers to be synthesized using well-understood chemical reactions and have their structures characterized[1,2]. Because of lack of technological applications, however, they have not been studied extensively in more recent times. For reasons to be discussed in detail in Part 2 of this series[3], crystalline linear polymers of this family make interesting model systems for studing relaxation processes in crystalline polymers in general. However, to interpret the dielectric and mechanical relaxation behaviour studied in the succeeding papers of this series (2–4)[3–5] some fundamental physical properties of several of the polyesters selected need to be established. It is the purpose of this paper, the first in the series, to present the results of such characterization. The polymers studied will be designated by the same notation that has been generally accepted for the chemically analogous linear aliphatic polyamides, the latter being in addition of course the direct progeny historically of the aliphatic polyesters[1]. Thus 6–10 polyester refers to the condensation polymer of 1,6 hexane diol and sebacic acid:

$$(-O-(CH_2)_6-O-\overset{O}{\overset{\|}{C}}-(CH_2)_8-\overset{O}{\overset{\|}{C}}-)_n$$
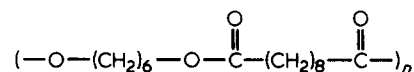
In the course of these studies it has been useful to control the degree of crystallinity through the synthesis of copolymers containing units of a non-crystallizable diol of chemically non-linear structure as well as linear diol units. The diol used was 2,5-hexane diol which is designated as 6B. The homopolymer of the 6B diol with adipic acid:

$$(-O-\overset{CH_3}{\underset{|}{CH}}-(CH_2)_2-\overset{CH_3}{\underset{|}{CH}}-O-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-)_n$$
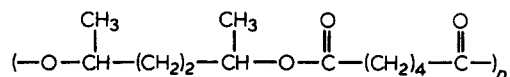
is referred to as 6B–6 polyester.

The polymers studied in the following papers are 6–6, 5–7, 6–10 and 6B–6 polyesters. The first three being semicrystalline require the densities of the crystal and amorphous fractions to establish crystallinity scales. To establish amorphous densities for the three, via dilatometry, volume *versus* temperature curves were measured through the melting points and into the liquid region. The non-crystallizing 6B–6 homopolymer was measured as a liquid also. Crystal density was established for the 6–6 and 5–7 polyesters (the 6–10 being already known[6]) by means of X-ray diffraction determination of unit cell dimensions. Heat of fusion *versus* crystallinity scales were also established through differential scanning calorimetry (d.s.c.) experiments.

To provide a basis for studying the effect of pressure on degree of crystallinity, the melting and crystallization temperatures of 6–6 polyester were determined as a function of pressure. In addition, these data were used along with the density data to establish, through the Clausius–Clapeyron equation, an independent value of the heat of fusion for this polymer.

EXPERIMENTAL

Polymer synthesis

The polyesters described in this work were synthesized using the transesterification reaction of a diol and a diester[1]. The polymerization reaction starts out as a direct esterification reaction but ends up as an ester interchange

because an excess of the glycol is normally used. Copolymers of certain compositions were obtained by adjusting the initial mol ratio of the glycols. A mass balance of the starting and final materials was carried out to determine the actual composition of the copolymers. The molecular weight of the polyesters synthesized in this work were determined by gel chromatography to be between 20 and 30 kg mol^{-1}. Further details of the synthesis may be found in the Ph.D. dissertation of P. A. Aylwin[7].

Amorphous density

It is common procedure to determine the density of the amorphous phase of a semicrystalline polymer by extrapolating the density of the melt to room temperature (25°C). The density of the polymer sample was determined by dilatometry. This technique also provides information about the melting point, the volume of expansion on melting and coefficient of thermal expansion. In the present work two dilatomers were designed and built[7], one (mercury filled) was used for solids and the other (entirely sample filled) for liquid samples (6B–6 polyester). Both dilatometers were calibrated with mercury. The solid samples were compression moulded at 10°C above melting point at ≈ 40 MPa after going through a degassing cycle under vacuum. The liquid samples were degassed inside the dilatometer by centrifugation.

Crystal density and unit cell

The crystal densities of 6–6 and 5–7 polyesters were obtained from the volume of their unit cells, as determined from X-ray data, and the molecular weight of the chain repeat units involved. Fibre and powder patterns obtained with Debye–Scherrer and Weissenberg cameras were used to determine the unit cell parameters. The Debye–Scherrer and Weisenberg cameras were attached to a Phillips X-ray unit operating at 35 kV and 20 mA. A copper target and nickel filter providing monochromatic $K\bar{\alpha}$ radiation was used. Exposure times were varied from 15 min to 16 h to allow accurate measurement of both weak and strong reflections.

The samples used to obtain powder photographs were crystallized and annealed under vacuum at 10°C below their melting point for 9 days. The samples used to obtain fibre patterns, however, were extruded from the melt through a syringe into a quenching bath of ethanol and dry ice ($\approx -80°C$). These samples were then stretched using an Instron tensile tester model TM at a rate of 0.5 mm min^{-1} to a stretch ratio of $\approx 1000\%$ at 30°C. The stretched samples were annealed under tension for 10 days at 10°C below melting point. In many previous studies on aliphatic polyesters[8-10] chain coupling with isocyanates to make polyurethanes was necessary to obtain samples that could be sufficiently oriented. However, the samples and the drawing procedure used here produced good fibre patterns without resorting to this expedient.

The fibre repeat (c) of each polymer was determined directly from the spacing between layer lines in the fibre pattern (*Figures 1a* and *1b*). The d-spacings were calculated from the diffraction lines of the powder pattern presented in *Figures 2a* and *2b*. These lines were correlated one by one to their equivalent in the powder patterns obtained with the Weissenberg camera (*Figures 3a* and *3b*). By superimposing the fibre patterns (*Figures 1a* and *4a* and *Figures 1b* and *4b*) on the respective powder patterns (*Figures 2a* and *3a* and *Figures 2b* and *3b*) the l index corresponding to each diffraction line (d-spacing) was determined. An orthorhombic and a monoclinic cell were assigned to the 6–6 and 5–7 polyesters, respectively, by determining the values of the unit cell parameters, a, b and β ($\beta = 90°$ for orthorhombic), that best fit the diffraction lines. The indices assigned to the observed and calculated interplanar spacings for 5–7 and 6–6 polyesters are presented in *Tables 1* and *2*, respectively.

Differential scanning calorimetry

The melting point, the heat of fusion of fusion and the glass transition temperature (6B–6 polyester only) of the various polyesters were determined by differential scanning calorimetry. The measurements were carried out in a Perkin–Elmer calorimeter (DSC II) using indium and cyclohexane as standards for temperature calibration. Indium was also used to calibrate the heat of fusion. The heat of fusion of 100% crystalline material was determined by calibration against degrees of crystallinity obtained from density measurements. Tests were made on four specimens crystallized from the melt at room temperature
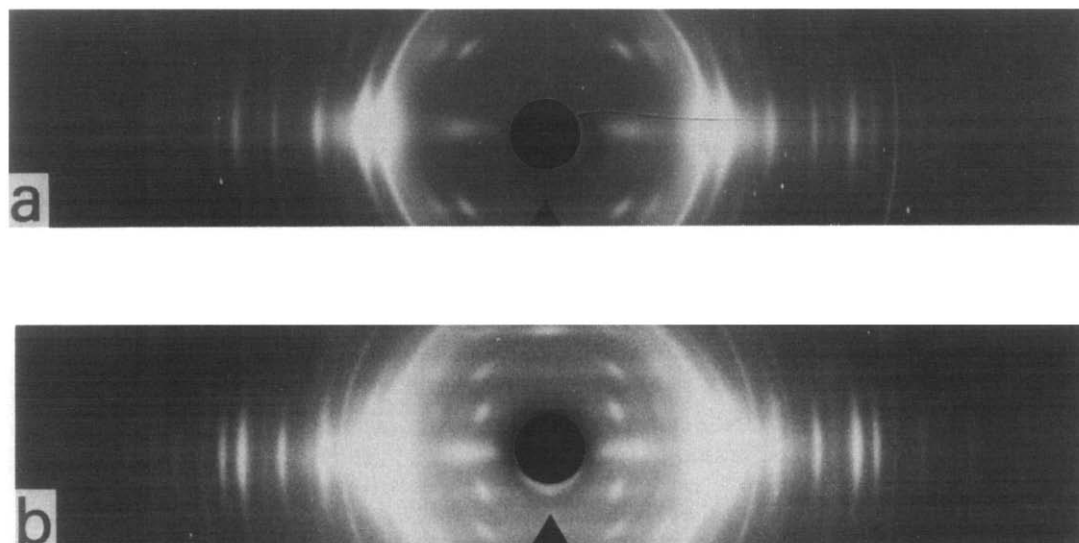

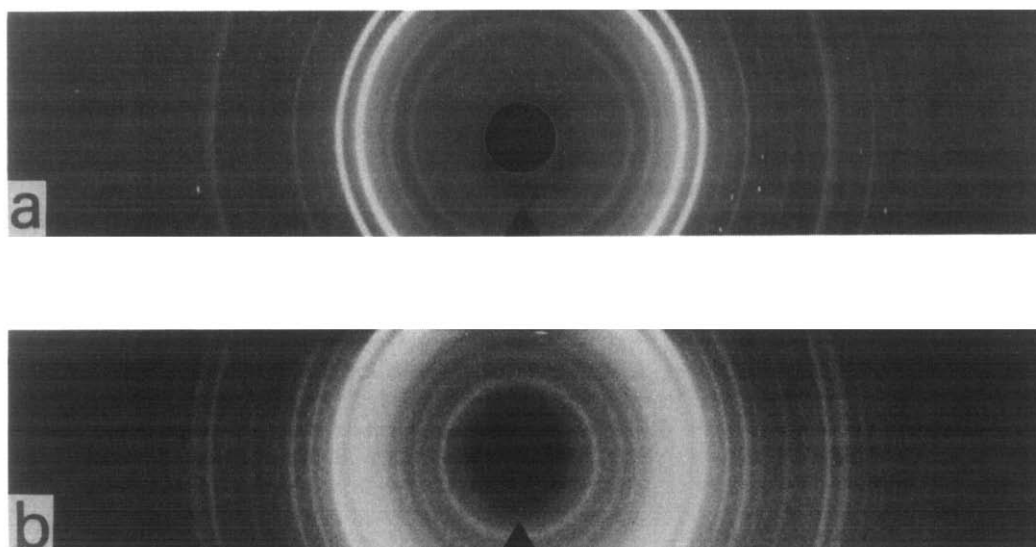*Figure 1* Fibre pattern from Debye–Scherrer camera for (a) 5–7 polyester and (b) 6–6 polyester

Figure 2 Powder pattern from Debye–Scherrer camera for (a) 5–7 polyester and (b) 6–6 polyester
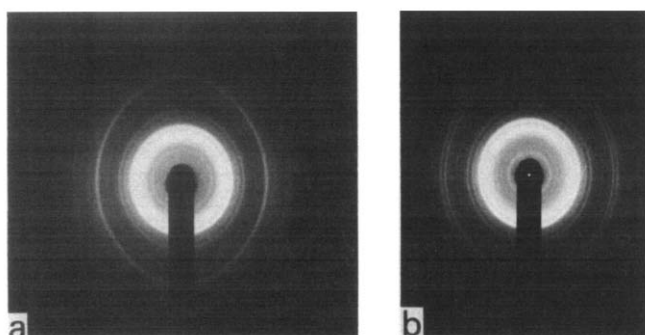

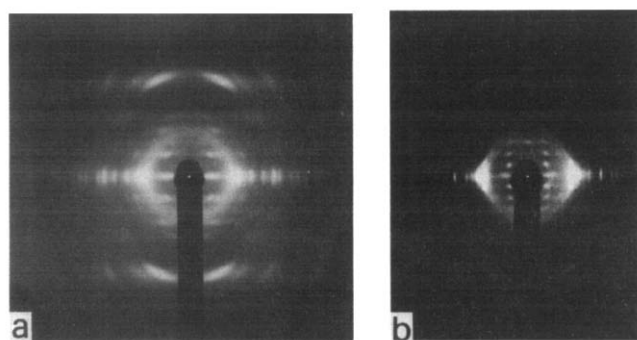*Figure 3* Powder pattern from Weissenberg camera for (a) 5–7 polyester and (b) 6–6 polyester

Figure 4 Fibre pattern from Weissenberg camera for (a) 5–7 polyester and (b) 6–10 polyester

Table 1 Observed and calculated interplanar spacings for 5–7 polyester

d (observed) (nm)	d (calculated) (nm)	Indices
0.737	0.737	010
0.606	0.606	102
0.508	0.507	$01\bar{2}$
0.414	0.414	110
0.368	0.369	020
0.366	0.368	114
0.327	0.327	$10\bar{2}$
0.315	0.315	122
0.312	0.311	115
0.312	0.307	203
0.303	0.303	204
0.296	0.297	120
0.283	0.280	214
	0.278	124
0.270	0.272	$10\bar{3}$
0.265	0.267	215
0.250	0.250	200
0.237	0.237	210
0.235	0.236	223
0.228	0.226	225
0.221	0.221	130
0.207	0.207	220
0.207	0.205	305
0.198	0.201	127
	0.200	007
	0.199	227
	0.195	307
0.187	0.189	317
0.184	0.184	040
0.172	0.173	327
	0.171	137
	0.171	237
0.163	0.163	310

and annealed at $\approx 6°C$ below their melting point for two days.

Crystallization and melting point verus pressure of 6–6 polyester

To investigate the pressures and temperatures required to crystallize 6–6 polyester, the dependence of melting and crystallization temperatures on pressure were measured. These relations were obtained by using an optical turbidimetric technique developed by Phillips and Dalal[11]. The melting (or crystallization) of a crystalline polymer is determined by a sharp increase (or decrease) of the intensity of a light beam transmitted through the sample being studied. The melting and crystallization processes were studied under heating and cooling rates of $0.2°C$ min^{-1} at a number of pressures between 0 and 275 MPa of pressure. Preliminary experiments indicated that at $0.2°C$ min^{-1} the results were reproducible to $<0.5°C$. The melting point at a given pressure was determined on a sample first crystallized at 25°C at atmospheric pressure. The crystallization temperature was determined in the same scan after keeping the sample for 10 min at 5°C above the temperature where the last traces of crystallinity disappeared. A complete description of the

Table 2 Observed and calculated interplanar spacings for 6–6 polyester

d (observed) (nm)	d (calculated) (nm)	Indices
0.861	0.865	101
0.650	0.646	102
0.560	0.561	003
	0.559	111
0.488	0.490	103
	0.485	112
0.449	0.445	013
0.415	0.415	210
0.388	0.388	104
0.366	0.366	020
0.338	0.337	121
	0.337	005
0.322	0.323	204
0.296	0.296	220
0.278	0.279	222
0.251	0.252	400
0.219	0.220	230
0.208	0.208	217
	0.208	420
0.189	0.189	512
0.183	0.183	040
0.164	0.164	610

amorphous densities of the semicrystalline polyesters (i.e., 5–7, 6–6 and 6–10 polyesters) the specific volume of the melt was extrapolated to room temperature (25°C). The melting point of each of these polymers was taken as the temperature where the last traces of crystallinity disappeared. As the 6B–6 polyester is an amorphous polymer its amorphous density was determined by direct measurement of the specific volume at different temperatures (*Figure 8*). The results obtained through this technique are summarized in *Table 3*.

Crystal density and unit cell

The unit cell parameters determined from X-ray diffraction for 5–7 and 6–6 polyesters are presented in

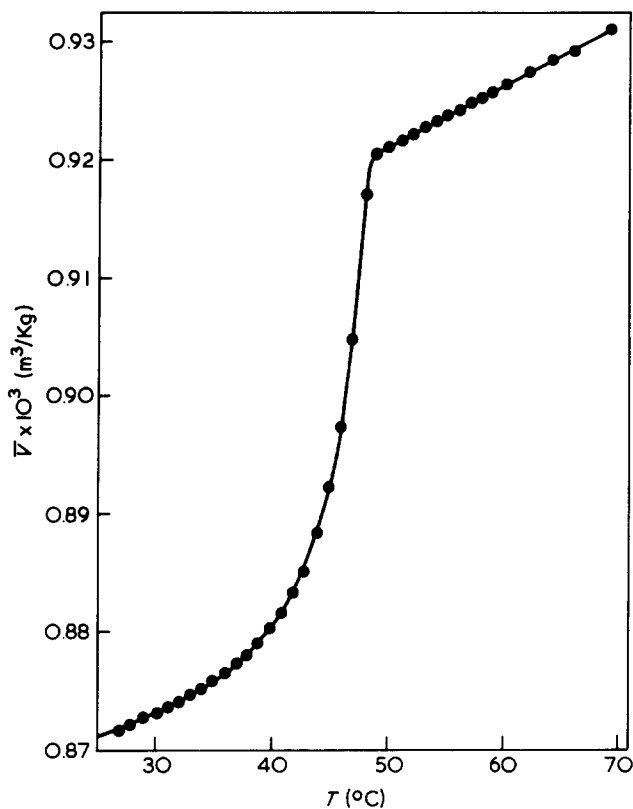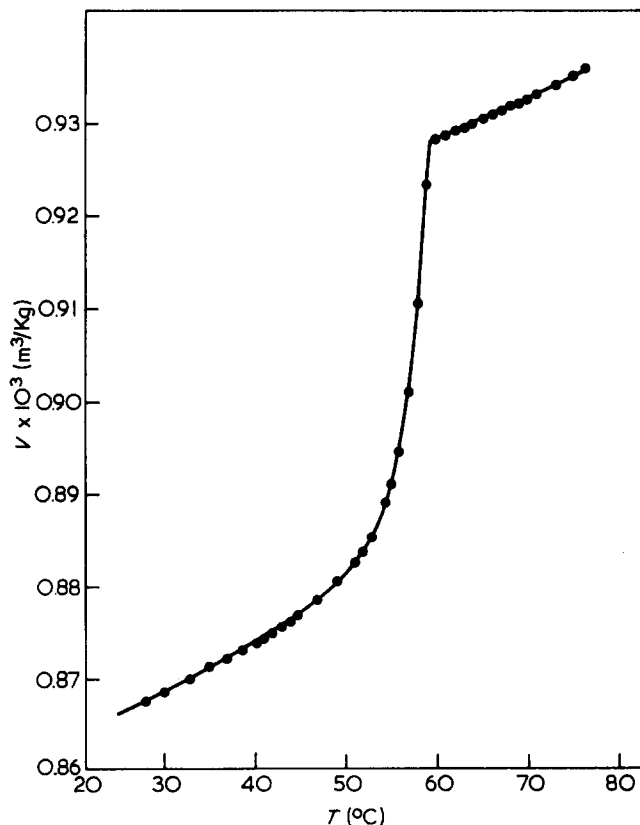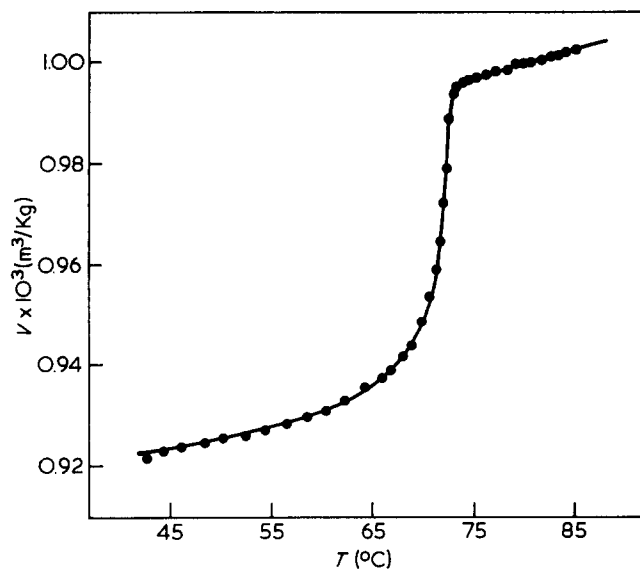Figure 6   Specific volume *versus* temperature for 6–6 polyester

Figure 5   Specific volume ($m^3 \ kg^{-1} \times 10^3$) *versus* temperature for 5–7 polyester

technique and the equipment utilized in this work may be found in the Ph.D. dissertation of E. N. Dalal[12].

RESULTS AND DISCUSSION

Amorphous density

The specific volume *versus* temperature relations obtained by dilatometry for the four homopolymers studied are presented in *Figures 5–8*. To obtain the

Figure 7   Specific volume *versus* temperature for 6–10 polyester

Table 4., the former being monoclinic and the latter orthorhombic. The observed sample densities indicate that the cell of 6–6 polyester has four chains while the unit cell of 5–7 polyester has two.

Comparison of these cells with literature results on other aliphatic polyesters is of interest. According to the summary of published unit cell dimensions of polyesters reported by Minke and Blackwell[8] many linear aliphatic polyesters crystallize in a monoclinic structure with two chains per unit cell and some with orthorhombic structures with 4 chains per unit cell. An interesting example is poly(tetramethylene adipate) (PTMA or 4–6 polyester). Kim[13] and Minke and Blackwell[8] find two forms, an α monoclinic form and a β orthorhombic one. The orthorhombic cell found by Kim[13] (as reported by Minke and Blackwell[8]) has $a = 1.005$, $b = 0.811$, $c = 1.466$ nm, $\beta = 90°$ and indicates 4 chains/cell. Streaking of the layer lines lead Minke and Blackwell[8] to

conclude that the chains are disordered along the *c*-axis in this structure. The β orthorhombic form has been reported by Minke and Blackwell[8] to transform spontaneously to the α form (monoclinic structure $a = 0.670$, $b = 0.800$, $c = 1.420$ nm, $\beta = 45.5°$, 2 chains/cell) at room temperature. This conclusion was reached by comparing the fibre patterns of quenched samples (4–6 polyester) samples before and after annealing (1 week at room temperature). In this work, however, even though the unannealed stretched samples of 6–6 polyester gave fibre photographs similar to the one reported by Minke and Blackwell[8] (their Figure 2) for melt quenched 4–6 polyester (not annealed) films, the continuous streaks over the layer lines that they report were transformed in the 6–6 polyester samples here into sharp reflections (indexed with an orthorhombic cell) upon annealing (see *Figure 1b*). In addition, in contrast to the behaviour noted by Minke and Blackwell[9] for 4–6 polyester, the d.s.c. measurement of 6–6 polyester obtained in this work did not show any evidence for the occurrence of a second crystalline phase.

Another linear polyester with an orthorhombic structure and four molecules per unit cell found in the literature[6] is poly(ethylene succinate) (or 2–4 polyester). The orthorhombic cell reported by Veda *et al.*[9] for 2–4 polyester ($a = 0.760$, $b = 1.075$, and c (fibre axis) = 0.833 nm) is very similar to the one determined by Kim[13] for 4–6 polyester and the one obtained in this work for 6–6 polyester. The three of them all have four molecular chains per unit cell.

The crystallographic structure determined for 5–7 polyester is similar to the unit cells reported for other monoclinic linear aliphatic polyesters[8]. The $a \sin \beta = 0.500$ and $b = 0.737$ nm determined for this polymer is close to the interspacings found in polyethylene (0.493, 0.740 nm) and linear parafins.

Finally, it is interesting to discuss the chain (*c* axis) shortening often observed in aliphatic polyesters; i.e., the fibre repeat distances are often less than expected for the planar zig-zag conformation (and assumed bond lengths and angles). This was first noted by Fuller and Erickson[14] in the series of ethylene glycol polyesters 2–4, 2–6, 2–9 and 2–10. In 2–4 polyester the shortening, Δc, was ≈ 0.14 nm and ~ 0.05 nm in the others. Subsequently, Veda *et al.*[9] in an X-ray structure determination attributed the 0.14 nm shortening in the 2–4 polyester to the occurrence of a *gauche* bond, G, at the C–C bond in the glycol unit and one of opposite sense, $\bar{G}$, at the centre C–C bond in the acid unit so that the chain conformation is $TTT\ G\ TTT\ \bar{G}$ in a repeat unit. Turner-Jones and Bunn[10] in an X-ray structure determination on 2–6 and 2–8 (where 0.05 nm shortening also occurs), attribute the (0.05 nm) shortening to a distortion of the chain bond internal rotational angles, primarily at each $C(H_2)$–O bond in the glycol
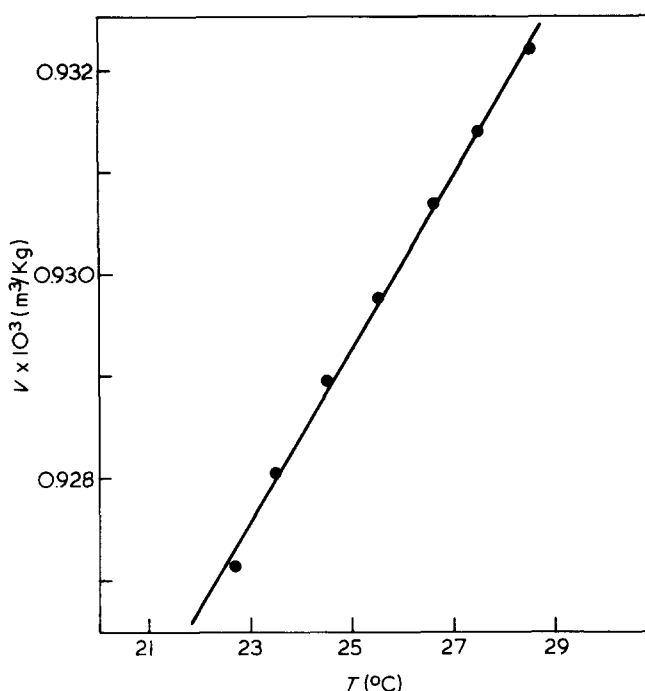

Figure 8 Specific volume *versus* temperature for 6B–6 polyester

Table 3 Amorphous density and melting point

Polyester	Amorphous density at 25°C (kg m^{-3})	Melting point (°C)
5–7	1104	49
6–10	1033	72
6–6	1096	59
6B–6	1076	–

Table 4 Unit cell dimensions and crystal densities

Polyester	*a* (nm)	*b* (nm)	c^a (nm)	$c_{calc}{}^b$ (nm)	β	Chains per unit cell	Crystal density^c at 25°C (kg m^{-3})
5–7	0.614	0.737	1.716	1.732	54.6	2	1198
6–6	1.008	0.732	1.683	1.732	90.0	4	1222

^{a} *c* is the fibre axis
^{b} c_{calc} is the length of the repeat unit when a planar zig-zag conformation is assumed
^{c} The crystal density of 6–10 polyester is 1151 kg m^{-3} (ref. 6)

Table 5 Heat of fusion (100% crystalline) and melting point

Polyester	Crystalline heat of fusion (kJ kg⁻¹)[a]	Melting point (°C)
5–7	151	47
6–10	134	70
6–6	151	58
6B–6	0	–

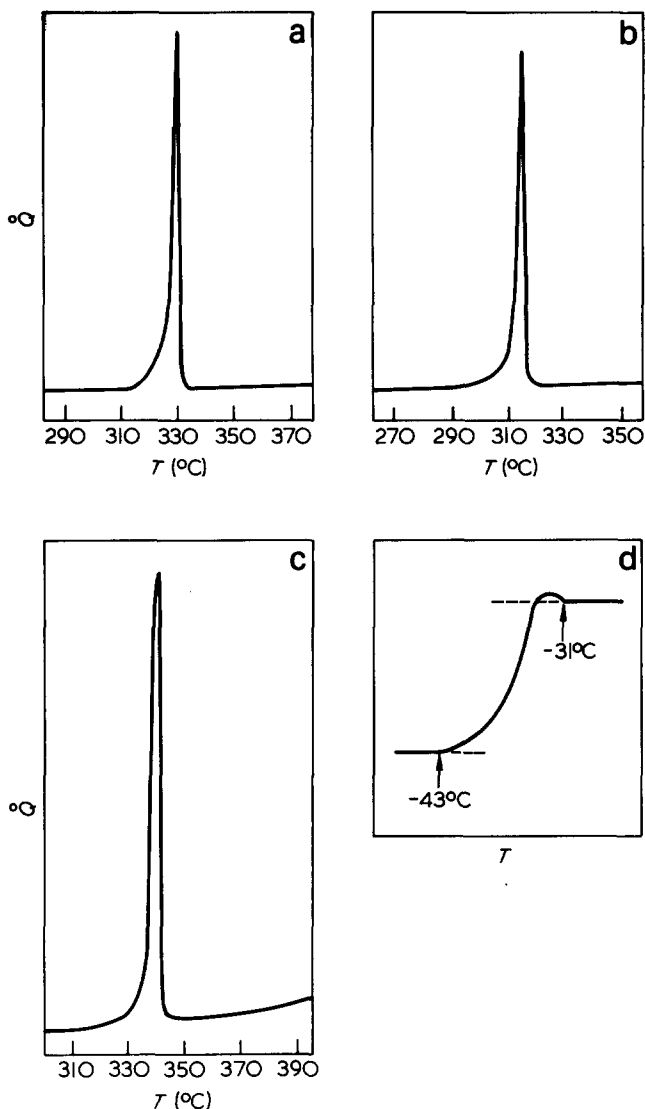[a] By comparison of heat of fusion of ≃50% crystalline specimens with density crystallinity

Figure 9 D.s.c. traces for (a) 6–6 polyester, (b) 5–7 polyester, (c) 6–10 polyester and (d) 6B–6 polyester

residue. The distortion is such that these two bonds are nearly eclipsed between T and G. In the series of 10–4, 10–6, 10–8 polyesters Fuller and Frosch[15] found the shortening to be negligible indicating an all *trans*-planar zig-zag conformation. This led them to speculate that the shortening is peculiar to the residues in the glycol units in the ethylene glycol series (however, cf. the Veda *et al.*[9] structure for 2–4 polyester). That this was not necessarily true is also shown by the results of Minke and Blackwell[8] for the 4–6 polyester and the results here for 6–6 polyester were 0.05 nm shortening is found in both cases. In contrast, the results here for 5–7 polyester and those of Bittiger and Marchessault[16] for polycaprolactone (6 polyester) show negligible shortening indicating an all

planar conformation. Judging from this, all that can be definitely said is that the effect is real (the fibre repeats are relatively accurate and straightforward to determine) and that three cases are commonly observed, negligible shortening, 0.05 nm shortening and 0.14 nm shortening. The interpretation of the shortening where it occurs, in terms of conformational or structural concepts makes no sense at all at present in a unified context.

Differential scanning calorimetry

The results obtained with this technique are summarized in *Table 5* and in *Figure 9*. The heat of fusion determined for 5–7 and 6–6 polyesters are the same and larger than the one obtained for 6–10. The melting points determined by d.s.c. (*Table 5*) and dilatometry (*Table 3*) for 5–7, 6–6 and 6–10 polyesters are in good agreement.

Crystallization and melting point versus *pressure of 6–6 polyester*

Because the transition between the solid state and molten state in polymers does not occur at a specific temperature but over a temperature range, the first step in determining the melting or crystallization point is to define in the transmitted light intensity trace the temperatures that will best represent and reproduce these phenomena. As the transmitted light intensity trace *versus* temperature has a sigmoidal shape with the solid (below the crystallization point) and the molten (above the melting point) phases being approached assymptotically, three temperatures, corresponding to the point of maximum slope (T_2), the intercepts between the rectilinear extrapolated maximum slope (at the inflection point of the trace) and the solid (T_1) and melt (T_3) base lines, were chosen for the purposes of this work. The inflection point (maximum slope) corresponds to the temperature at which the largest amount of sample goes through the transition. For the other two temperatures, T_1 corresponds approximately to initial melting and T_3 to final melting and for crystallization T_3 corresponds to onset of crystallization and T_1 to its completion. The melting and crystallization temperatures as a function of pressure are presented in *Figures 10* and *11*, respectively. In both cases, the three temperatures (T_1, T_2, T_3) are in a 2°C bracket across the pressure range covered. An average difference of 12°C (with a maximum of 14°C) between melting and crystallization temperatures across the pressure range studied can be observed.

By using the pressure dependence of the melting and crystallization temperature in conjunction with the amorphous and crystal densities and the Clausius–Clapeyron relation:

$$\frac{dP}{dT} = \frac{\Delta H}{(T\Delta V)} \tag{1}$$

(where dP/dT is the slope of the equilibrium curve between two phases, ΔV, ΔH and T are, respectively, the volume change, the enthalpy change and the absolute temperature associated with the transition between the two phases), the enthalpy change associated with the phase change was calculated. By solving for ΔH, equation (1) yields:
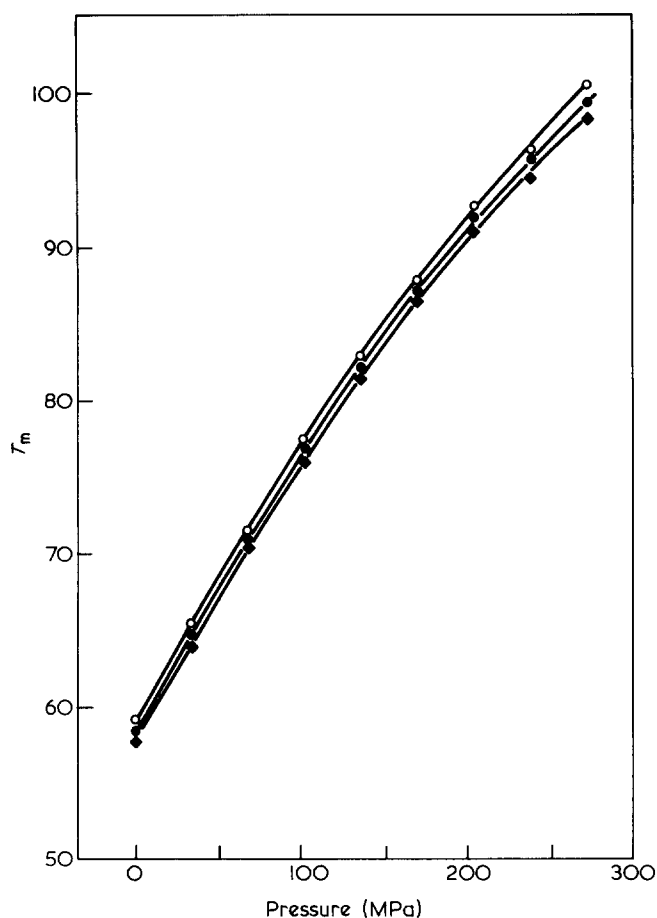
$$\Delta H = \frac{dP}{dT} \cdot T \cdot \Delta V \tag{2}$$

Figure 10 Melting temperature *versus* pressure for 6–6 polyester. ○, Start of melting; ●, maximum melting rate; and ◆, finish of melting

Figure 11 Crystallization temperature *versus* pressure for 6–6 polyester. ○, Start of crystallization; ●, maximum crystallization rate; and ◆, finish of crystallization

$$\Delta V = 1/\rho_a - 1/\rho_c$$

$\rho_c = 1222$ kg m^{-3} (crystal density determined by X-ray diffraction)

$\rho_a = 1096$ kg m^{-3} (amorphous density determined by dilatometry)

The enthalpy change (ΔH) at T_m calculated from the slope of the melting temperature *versus* pressure curve (*Figure 10*, T_2) (at $P = 0$, and neglecting the temperature change of ΔV from 25°C) was 167 kJ kg^{-1} while the one determined from the crystallization data (*Figure 11*, $T = T_2$) was 168 kJ kg^{-1}. These two numbers compare with 151 kJ kg^{-1} obtained for the heat of fusion of 6–6 polyester by d.s.c. calibrated *via* density. The final melting temperature (T_3) determined at atmospheric pressure by this technique was 59.0°C. This result compares with 58.0 and 59.0°C determined by d.s.c. and dilatometry, respectively.

The melting and crystallization temperatures *versus* pressure data were used to investigate the degree of crystallinity obtained by crystallization under pressure. It was of particular interest to establish whether densities indicating extended chain crystallization could be attained. However, it was established that the degree of crystallinity obtained by crystallization at pressures up to 60 mPa were only marginally higher than specimens slowly crystallized at atmospheric pressure. Furthermore, no higher melting component was noticed in d.s.c. scans.
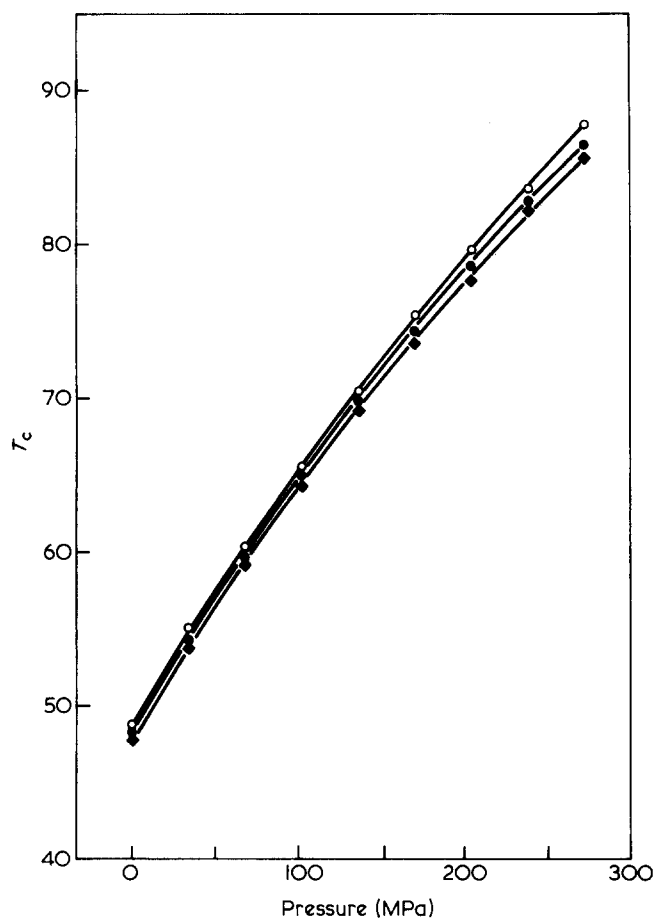
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