Thermal Properties of Stirrer Crystallized Polyethylene

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Changes in the thermal properties of polyethylene crystals grown at 95°C from a stirred, dilute xylene solution have been determined using an adiabatic calorimeter over the temperature range $-35° \rightarrow 180°C$. The bulk of the material is thermodynamically very similar to polyethylene single crystals grown at 90°C in the conventional manner. An extremely small (ca. 0·2 per cent) amount of high melting ($>141{\cdot}3°C$) component is present which it is suggested is in a fully extended chain conformation. A method is presented whereby the reversible entropy of fusion (that is, free from irreversible annealing effects) may be calculated at low ($< 90°C$) temperatures.

THERE still remain many puzzling aspects of the crystallization and morphology of polyethylene, chemically the simplest of polymers. In particular much current work is concerned with the structure when either formed or deformed under stress[1]. Possibly the simplest case that can be considered, crystallization from a stirred dilute solution, has been shown by Pennings[2] to yield unusual fibrous crystals. In these at least some of the molecules are present as fully extended chains and at the start of the work reported here it was hoped that some variant of the Pennings technique might prove suitable for the production of macroscopic quantities of this form of polyethylene. It rapidly became obvious, however, both from this and other work[3], that only a minute amount of such material was present. Digestion with nitric acid[3] showed that this was the core of the fibre—the initially formed crystal which appears to act subsequently as a nucleation centre for further growth of the more familiar single crystal type. Thus, although present to only a limited extent, the extended chain form may be of fundamental importance in such processes as fibre spinning or melt extrusion.

As noted above the emphasis of the work described here changed as it progressed—from an examination of the thermal properties of the hoped-for appreciable fraction of extended chain polyethylene, to showing that the form did exist, albeit a very small percentage. Alternative evidence for the presence of this form is essentially via the electron microscope[3]. Differential thermal analysis[4] presents an ambiguous and complex picture.

The present work reports enthalpy changes which accompany the stepwise heating of stirrer crystallized polyethylene from $-35°C$ until well into the melt.

EXPERIMENTAL

Stirrer crystallized polyethylene was kindly supplied by Dr A. Keller. It was Marlex 50 crystallized from one per cent solution in stirred (1 500 rev/min) xylene at 95°C and washed with pure solvent at this temperature.

Enthalpy changes were measured using a precision adiabatic calorimeter as previously described[5]. Modification, together with the associated calibration, to permit operation down to −40°C will be reported elsewhere. Here some features of adiabatic calorimetry particularly relevant to this investigation are emphasized. The heating rate is slow (a few degrees per hour away from transitions) especially in the melting region where it tends to zero. In this case three hours were required to raise the temperature from 128° to 141°C. When gross melting (as opposed to premelting and/or annealing) is occurring it is not possible to stop the experiment and retain adiabatic conditions. Here (128° → 141°C) a long continuous heating run was performed, monitoring power input and temperature as functions of time. This permits the construction of an enthalpy/temperature curve through the melt, although this is less accurate than for the remainder of the temperature range due to the non-equilibrium nature of the measurements (note that there is no loss of accuracy for the overall change 128° → melt). Prior to 128°C the range 95° → 128°C had been covered in normal stepwise heating runs in six hours. Obviously this is far from Wunderlich's 'zero entropy production' condition[6] and polymer has had ample opportunity for annealing in this time (in fact the rate of heat evolution was measurable at the end of each run from 95°C and above, see below). On the other hand by the same token superheating effects[4] should be completely absent.

RESULTS

General

The quantities H_t^{150} and S_t^{150} (enthalpy and entropy changes, respectively, from t to 150°C) were first calculated as described previously[5]. The reference temperature, T_R, in the present case was 150°C; at 140°C solid is still present, see below. The entropy change thus calculated is in error due to irreversible annealing processes. A correction is discussed below. The enthalpy, entropy and free energy of fusion were next computed at the various experimental temperatures using H_t^{150}, S_t^{150} and the equation

$$C_p = 2{\cdot}114 + 3{\cdot}11 \times 10^{-3}t + 1{\cdot}9 \times 10^{-6}t^2 \qquad \mathrm{J\,g^{-1}\,deg^{-1}},\ t\,°\mathrm{C} \qquad (1)$$

for the specific heat of supercooled polyethylene[7]. Free energies of fusion at temperatures below 95°C (i.e. where annealing effects were absent) were then fitted to a cubic in temperature and the resulting constants used with standard thermodynamic formulae to give the enthalpy, entropy and free energy of fusion, and the specific heat of the solid, at rounded temperatures.

Temperatures below 95°C

Following the above procedure the free energy of fusion, ΔG, at a temperature t, is given by

$$\Delta G = 75{\cdot}22 - 0{\cdot}4953t - 1{\cdot}035 \times 10^{-3}t^2 + 3{\cdot}36 \times 10^{-6}t^3 \qquad \mathrm{J\,g^{-1}},\ t\,°\mathrm{C} \qquad (2)$$

The maximum deviation of a point from this is less than 0·01 per cent in the temperature range −35° → 95°C. Experimental heats of fusion, ΔH, reproduced with trivial loss of accuracy in this range, are shown in *Figure 1*. The specific heat of solid polymer as derived via equations (2) and (1) is essentially correct in the range −10° → 80°C but outside these limits the

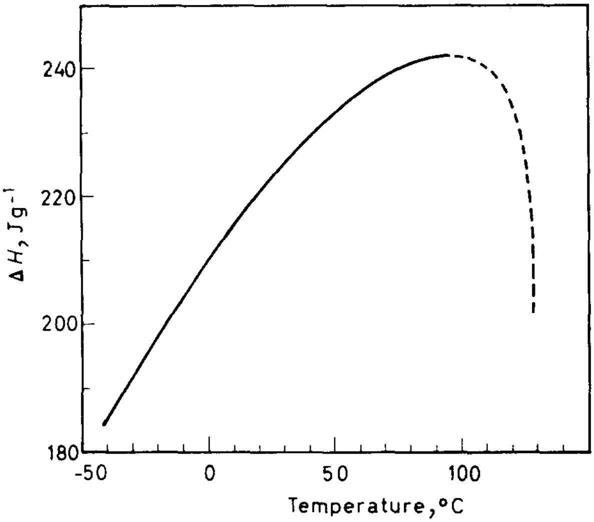

Figure 1—Heat of fusion (ΔH) of stirrer crystallized polyethylene at low temperatures. Extensive morphological changes occur in the region represented by the broken line

calculated curve is flatter than the observed. A better representation is through

$$C_p = 1{\cdot}555 + 6{\cdot}75 \times 10^{-3}t + 2{\cdot}72 \times 10^{-7}t^3 \qquad \mathrm{J\ g^{-1}\,deg^{-1}},\ t\,°\mathrm{C} \qquad (3)$$

(a squared term is superfluous) which accurately reproduces experimental points in the range $-35° \rightarrow 100°C$.

Specific heat deviations from equation (2) are not sufficient to have an appreciable effect on ΔH even at $-30°C$ but do emphasize that (2) is merely a convenient way of presenting the results and not suitable for lengthy extrapolation outside the temperature range $-35° \rightarrow 95°C$.

Here we should repeat that ΔG in equation (2) contains an irreversible entropy contribution (the heat of fusion is unaffected).

Temperatures above 95°

In the region 95°C → melt we consider only enthalpy changes. The considerable morphological changes at these high temperatures are reflected in the heat evolution at the end of each run. Experimental enthalpies of fusion are shown in *Figure 2* where most polymer is seen to melt at 131–2°C. Energy input to the calorimeter was stopped when the temperature was 141·3°C. This is close to the maximum reported melting point of 141·4°C[8]. Temperature equilibration is normally complete 10 to 15 minutes after cessation of energy input. Such was not so here. The temperature slowly fell, the rate decreasing approximately exponentially. The fall was observed for an hour (final rate: $2{\cdot}4 \times 10^{-4}$ deg. C min^{-1}, normal 'steady state' loss at this temperature $0{\cdot}4 \times 10^{-4}$ deg C min^{-1}) when another run was commenced. Steady state conditions were reached in the usual 15 minutes after the end of this run (149°C) but the overall enthalpy increase was

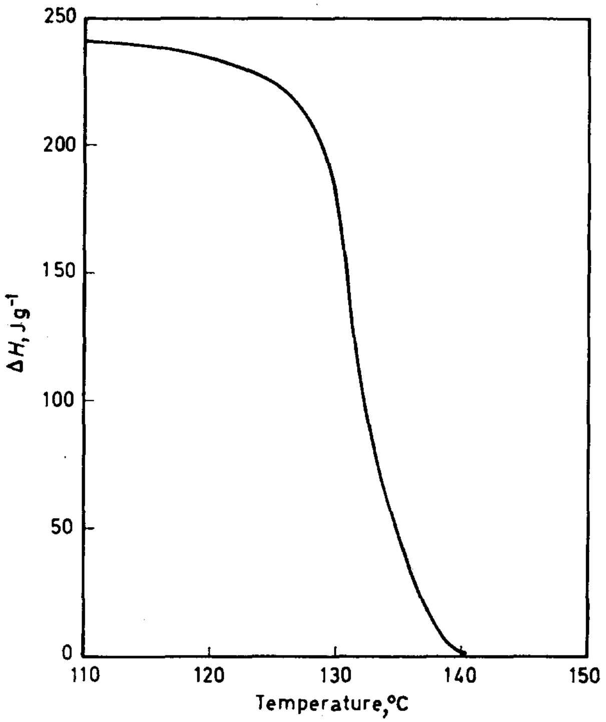

Figure 2—Heat of fusion (ΔH) of stirrer crystallized polyethylene near the melting point

significantly larger than for completely molten polyethylene. An extra 0·7 J g^{-1} was required. This represents the heat of fusion of the solid remaining at 141·3°C; the observed slow fall in temperature is due to the uptake of latent heat by melting polymer. From the observed decrease in the rate of fall of temperature the requisite 0·7 J g^{-1} could not be abstracted at 141·3°C so that there remains a very small (*ca.* 0·2 per cent) amount of polyethylene of melting point greater than 141·3°C. It is difficult to ascribe this to anything other than extended chain crystals.

As noted above heat is evolved as the temperature is raised above 95°C; *Table 1* shows the amounts.

Table 1. Rate of heat evolution

Temperature, °C	95·1	103·0	110·9	118·6	125·8
Rate, J g^{-1} min^{-1} (×10^3)	3·5	8·9	13·4	19·8	53·0

DISCUSSION

The results presented here (however calculated, see below) show that thermodynamically this stirrer crystallized polethylene is very similar to conventional 90°C solution grown material. For the latter ΔG is about 1 J g^{-1} lower. Only at the highest temperatures is there evidence for the extended chain conformation, in agreement with the suggestion[3] that this is present only as a nucleus. It is important that considerable fractionation occurs in the stirrer crystallization process. Marlex 50 is known to contain an appreciable low molecular weight fraction and without its removal this acts as a diluent; ultimate melting points are not attainable.

We next examine the effect of irreversible annealing processes on the apparent [i.e. as given via (2)] entropy change. Below a certain critical temperature, T_c, enthalpy and entropy changes are completely reversible, at least on the time scale of these experiments. Hence in *Figure 3*

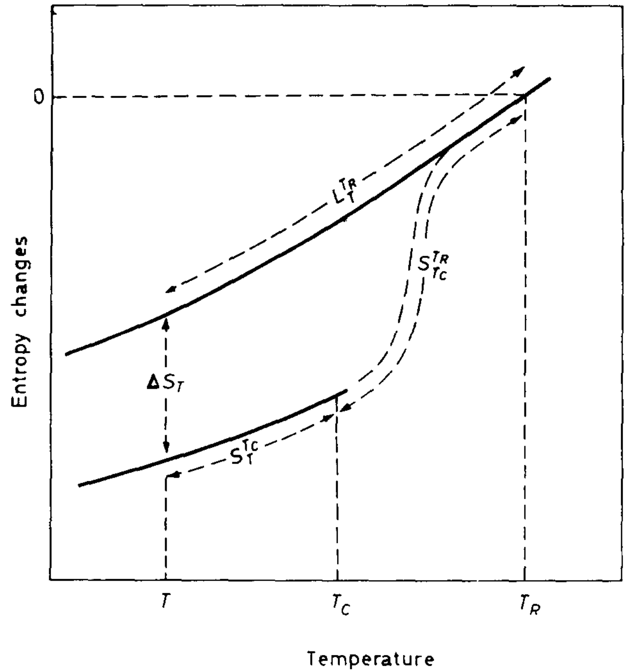

Figure 3—Entropy changes as a function of temperature

$S_T^{T_c}$ $(=S_{T_c}-S_T)$ is a meaningful thermodynamic quantity. The reversible entropy change that we seek is $S_{T_c}^{T_R}$ and the reversible entropy of fusion is ΔS_T $(=S_T^{T_c}+S_{T_c}^{T_R}-L_T^{T_R}$ where $L_T^{T_R}$ refers to entropy changes in the supercooled liquid). For polymers in general the degree of crystallinity increases rapidly with decreasing temperature below the melting point and soon attains a constant limiting value. We define a free energy degree of crystallinity $x_{G,T}=\Delta G_T/\Delta G_{\infty,T}$ where $\Delta G_{\infty,T}$ is the free energy of fusion of extended chains at a temperature T, and assume that x_G also becomes invariant with temperature sufficiently far below the melting point. In this region

$$x_G\Delta G_{\infty,T}=\Delta H_T-T\,(S_T^{T_c}+S_{T_c}^{T_R}-L_T^{T_R}) \tag{4}$$

or

$$(\Delta H_T/T)-S_T^{T_c}+L_T^{T_R}=x_G\,(\Delta G_{\infty,T}/T)+\;S_{T_c}^{T_R} \tag{5}$$

so that the LHS of (5) should be linear in $\Delta G_{\infty,T}/T$ and give both x_G and $S^{T_R}_{T_c}$. ΔH_T and $S^{T_c}_{T}$ are available from the present work, $L^{T_R}_{T}$ from (1), and $\Delta G_{\infty,T}$ from measurements, similar to those reported here, on *n*-alkanes[7] where irreversible entropy effects are absent. For polyethylene T_c is about 80°C. This may correspond to the onset of the limiting value of x but to be assured of constant x we consider, initially, the temperature range $-35° \longrightarrow 60°$C. Here equation (5) holds extremely well, deviations from linearity are trivial, $x_G = 0{\cdot}812$, and $S^{150}_{60} = 1{\cdot}1552$ J g^{-1} deg^{-1}. The 'experimental' value of S^{150}_{60} as used in (2), is 0·0162 J g^{-1} deg^{-1} *greater* and we must conclude that our assumption of a constant free energy crystallinity, at least in the temperature range of interest here, is invalid. Annealing increases the melting point, the overall enthalpy change remaining unaltered. Hence, the irreversible 'experimental' entropy change should be *less* than the true reversible value. As it is the average melting point corrected for irreversibility in the above way is 142·6°C, an absurdly high value when it is realized this refers to melting of the major chain folded component. The above comments suggest a more productive approach. The melting point of the bulk of the sample, via (2), is 131·2°C; a value of 129·5°C is found by differential calorimetry[4] using heating rates of 5 deg. C/min and this is probably accurate to within one degree. Enthalpically, the present polymer is very similar to material crystallized at 90°C under static conditions; for this melting points in the range 121° to 128°C have been reported[9]. A rather higher value for the present material is reasonable since it was grown, albeit under stirred conditions, at 95°C and the increase of lamellar thickness with growth temperature in this region is well known. The 'observed' ratio $\Delta H/\Delta S$ is constant to within 0·1 deg. C of 131·2°C in the range 90° to 130°C. Arbitrary correction of ΔS to give melting points as low as 110°C shows that, irrespective of the absolute value of $\Delta H/\Delta S$, this is the normal behaviour. Knowing the melting point we may therefore calculate ΔS at, say, 90°C below which temperature irreversible changes are absent. Reversible entropies of fusion are found to be 0·0026 J g^{-1} deg^{-1} greater than those of (2) and the reversible free energy of fusion is given by

$$\Delta G = 74{\cdot}15 - 0{\cdot}4979t - 1{\cdot}035 \times 10^{-3}t^2 + 3{\cdot}36 \times 10^{-6}t^3 \qquad \text{J g}^{-1}, t\text{°C} \qquad (6)$$

Figure 4 shows corrected values of ΔG.

From measurements of the X-ray long spacing it is known that polyethylene single crystals (that is, the main component of the material under consideration here) thicken above about 110°C. The mechanism is a matter of some dispute—whether chain mobility[10] alone is sufficient or whether partial melting and subsequent recrystallization[11] is necessary. The rates of heat evolution in *Table 1* are based on observations over the twenty minutes following the cessation of energy input to the calorimeter. In this period they are essentially linear with time in agreement with other results of our own and of Karasz and Hamblin[12] (these linear rates of heat evolution —annealing—should not be confused with the heat absorption—melting —at 141·3°C for which, as seen above, there is a relatively rapid rate of change with time) . Owing to the very different time scales of the experiments the present work cannot be compared directly with the differential

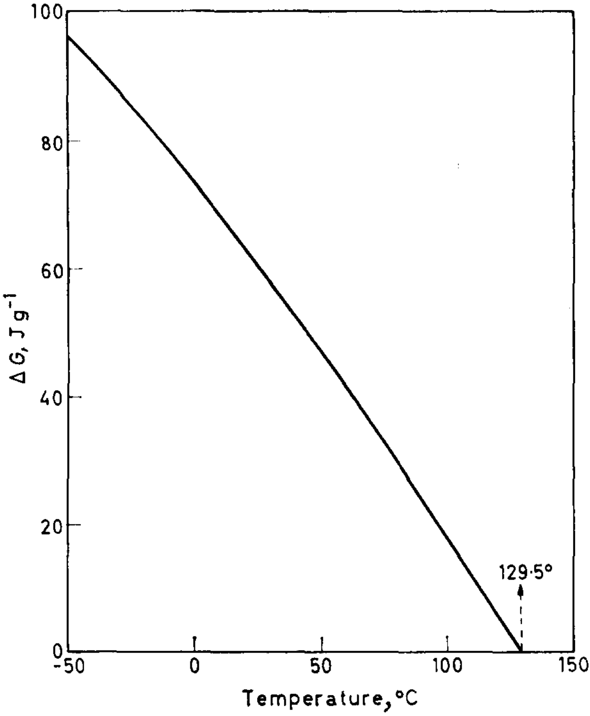

Figure 4—Reversible free energy of fusion (ΔG) of stirrer crystallized polyethylene [equation (6)]

calorimetry of Mandelkern[11]. Our observed enthalpy output increases with temperature—a rate process plot of log (rate of heat evolution) against reciprocal temperature gives a surprisingly straight line; rates are, however, considerably influenced by residual solvent[5,12]. The linear rate of heat evolution may arise in several ways. If partial melting does not occur or is relatively rapid (so that melting is essentially in 'equilibrium' with the heating rate) the effect is due to annealing or recrystallization alone. Alternatively linear or non-linear melt (recall the slow disappearances of the final traces of crystallinity) and recrystallization effects could superimpose to give the observed overall linear rate. This is unlikely, temperature effects would be expected to emphasize one or the other. The linear rate process relation implies that we are looking at one mechanism over the whole temperature range but on present evidence it cannot be said whether this refers to the annealing or recrystallization process.

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REFERENCES

[1] HAY, I. L. and KELLER, A. *J. Matls. Sci.* 1966, **1**, 41; 1967, **2**, 538

[2] PENNINGS, A. J. and KIEL, A. M. *Kolloidzschr.* 1965, **205**, 160

[3] KELLER, A. and MACHIN, M. J. *J. macromol. Sci.* 1967, **B1**, 41

[4] WUNDERLICH, B., CORMIER, C. M., KELLER, A. and MACHIN, M. J. *J. macromol. Sci.* 1967, **B1**, 93

[5] RICHARDSON, M. J. *Trans. Faraday Soc.* 1965, **61**, 1876

[6] WUNDERLICH, B. *Polymer, Lond.* 1964, **5**, 611

[7] ATKINSON, C. M. L. and RICHARDSON, M. J. Submitted for publication

[8] ARAKAWA, T. and WUNDERLICH, B. *J. Polym. Sci.* 1967, **C16**, 653

[9] WUNDERLICH, B., SULLIVAN, P. ARAKAWA, T., DICYAN, A. B. and FLOOD, J. F. *J. Polym. Sci.* 1963, **A1**, 3581
BAIR, H. E., HUSEBY, T. W. and SALOVEY, R. *Polymer Preprints,* 1968, **9**, 795

[10] RENEKER, D. H. *J. Polym. Sci.* 1962, **59**, S39

[11] MANDELKERN, L. and ALLOU, A. L. *J. Polym. Sci.* 1966, **B4**, 447

[12] KARASZ, F. E. and HAMBLIN, D. J. National Physical Laboratory *Report BP/R/15,* 1963