The Use of Differential Scanning Calorimetry to Study Polymer Crystallization Kinetics

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By direct comparison with dilatometry the use of a differential scanning calorimeter to determine accurate crystallization data from bulk polymers is considered. Fractions of polyethylene are used because of the high temperature dependence of their crystallization rate constants and accordingly the requirement of isothermal crystallization conditions. The accuracy of the temperature settings and the resolution of the instrument in detecting rate of heat changes are described. The requirements of the technique and choice of operating conditions are also described. The principal advantages of the method are that micro samples are required and quantitative kinetic isotherms can be rapidly obtained over a range of temperature. The values of the crystallization rate parameters so determined are discussed.

ACCURATE determination of the parameters involved in the crystallization of bulk polymer samples is limited by the high temperature dependence of the nucleation processes and the requirement of isothermal conditions. This is particularly so with polyethylene. Crystallization parameters are also very dependent on molecular weight, molecular weight distribution, degree of tacticity, and the presence of impurities or structural irregularities. There is accordingly a need for the analysis to be carried out on fractionated, well characterized polymers of which only small samples are available. These requirements are only partially fulfilled by micro-dilatometry[1,2] and hot stage polarized light microscopy[3].

Differential Scanning Calorimetry, DSC, is fundamentally a new approach to quantitative thermal analysis using micro samples. Unlike conventional techniques, however, an isothermal calorimeter measuring the thermal energy difference required to keep sample and reference at a constant temperature is used. Conventional thermal analytical techniques measure the temperature (or some other property) difference between sample and reference developed on heating (or cooling) at a fixed rate, and so they are not isothermal. DSC is potentially capable of satisfying the strict requirements of isothermal crystallization kinetic studies.

The present paper considers the usefulness and limitations of this technique in measuring meaningful and accurate crystallization data of fractionated polyethylene.

EXPERIMENTAL

Materials

Samples of polyethylene fractions, Marlex 60, were kindly supplied by Phillips Petroleum Co. Ltd. Their characteristics are listed in *Table 1*.

Dilatometry

Micro-dilatometers were used with 100–200 mg of polymer vacuum formed into a pellet and filled with mercury as described previously[2]. Precision bore Veridia tubing (0·6 mm i.d.) was used as the measuring capillary. Crystallizations were carried out by melting at 200° ± 1 °C for about 30 minutes and transferring the dilatometer to a Dewar vessel thermostat filled with polyethylene glycol-400 and controlled to ±0·04 deg. C.

Table 1. Properties of polymer samples (Phillips Marlex 60)

Serial No.	*Description*	*Inherent viscosity** dl/g	*Mol. wt†* M_w	M_n
A	Whole polymer	2·06	130 000	11 000
B	Fraction	0·83	29 000	
C	Fraction	1·80	85 000	
D	Fraction	2·47	130 000	

Dekalin at 130°C, 0·1 g/100 ml.
†From $\zeta = 5{\cdot}1 \times 10^{-4} \times M^{0{\cdot}72}$.

Differential Scanning Calorimetry

A Perkin–Elmer DSC model 1B was used, with samples (1–50 mg) of finely divided polymer accurately weighed on a micro-analytical balance to 10^{-6} g, into aluminium sample holders. The calorimeter operated with a stream of oxygen-free, dry nitrogen flowing over the sample and reference. An empty sample holder was used as the reference in the calorimeter.

The calorimeter could be used isothermally or with a constant rate of heating or cooling from 0·5 deg. C to 64 deg. C/minute. The isothermal temperature was normally obtained by reducing the temperature manually—isothermal conditions not being obtained until the detector recorded a constant baseline. The isothermal temperature was sub-divided into one degree units only from 173° to 773°A. The temperature scale required calibrating at frequent intervals and at many points, as the calibration was non-linear, using the melting points of several reference compounds.

Analysis of data

Crystallization curves are normally analysed by means of the Avrami equation

$$(1 - X_t) = \exp - Z_1 t^n \tag{1}$$

where X_t is the weight fraction of crystallized material at time t, Z_1 a rate constant and n the Avrami exponent, either from

$$n = -t \frac{\mathrm{d}X_t}{\mathrm{d}t} (X_\infty - X_t) \ln (1 - X_t)^{-1} \tag{2}$$

or graphically from a plot of log {ln (1 − X_t) } against log t, since

$$\log \{ -\ln (1 - X_t)\} = n \log t + \log Z_1 \tag{3}$$

The rate constant, Z_1, can then be calculated from the half-life, $t_{1/2}$, and the average value of n, as

$$Z_1 = \ln 2 / t^n_{\frac{1}{2}} \tag{4}$$

There is considerable doubt as to the validity of a simple Avrami equation alone describing the total crystallization isotherms of bulk polymers[1,4,5]. Despite this, however, the above analyses are justified, as a means of comparison, but the values of the parameters Z_1 and n may have no mechanistic significance.

RESULTS AND DISCUSSION

The general technique of DSC

The DSC isothermal rate curves of a sample C are reproduced in *Figure 1*. The calorimeter measures the rate of evolution of heat as a function of time and the isotherms were processed by integrating and then by analysing as above, see *Figure 2*, since it was assumed that

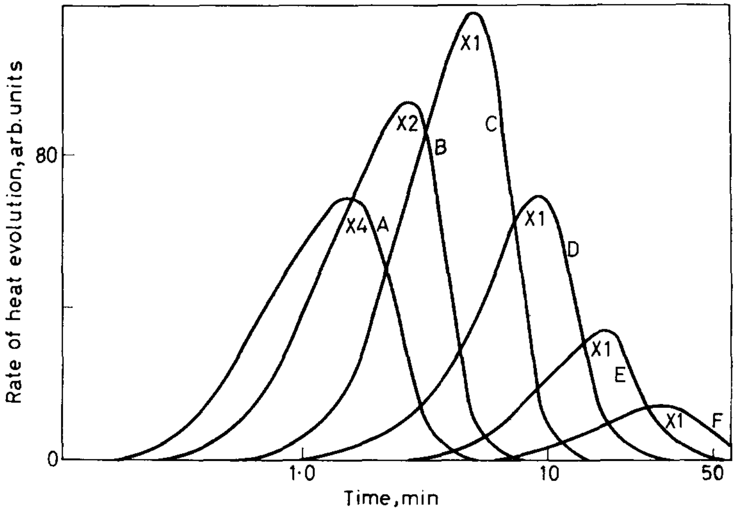

Figure 1—DSC isotherms—sample C: A—124·5, B—125·5, C—126·5, D—127·5, E—128·5, F—129·5°C

$$X_t = \int_0^t (1/\mathrm{d}t)(\mathrm{d}H_t) \Big/ \int_0^\infty (1/\mathrm{d}t)\,\mathrm{d}H_t$$

No direct determination of the absolute heat or the degree of crystallization is required.

Measurements of crystallization curves were restricted by the time required by the calorimeter to attain isothermal conditions, by the sensitivity of the instrument and the limit to sample size (~ 50 mg). This restricted the study to isotherms with maximum rates greater than two and less than 200 minutes, and to a temperature range of six or seven centigrade degrees. It was possible, however, to extend the study to higher temperatures by measuring the crystallinity developed in various time intervals from the area under the endotherm produced on subsequent melting, see *Table 2*. This method, however, was more time consuming and less accurate (say,

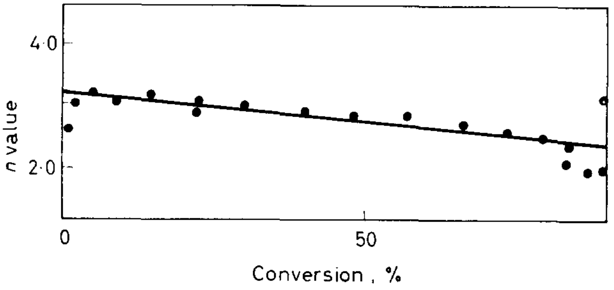

Figure 2(a)

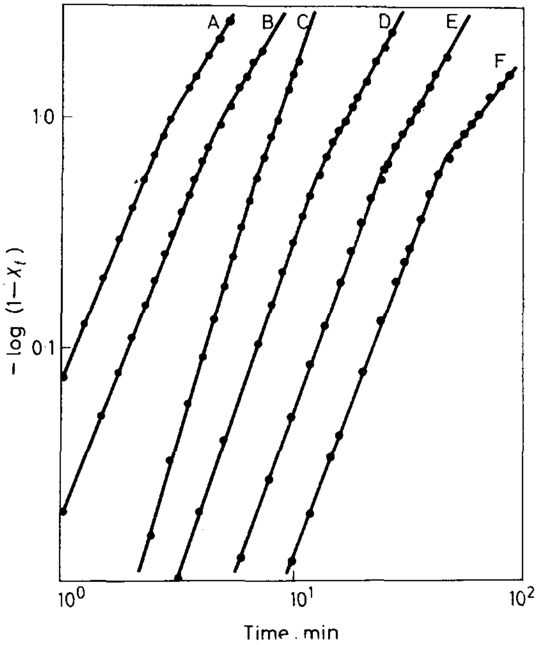

Figure 2(b)

Figure 2—Analysis of isotherms: (a) by equation (2);
(b) by equation (3), as in *Figure 1*

two per cent) but did give very similar crystallization isotherms to that of direct measurement. It was the only method of studying the crystallization rates of other polymers which were less ready to crystallize than polyethylene, e.g. isotactic polystyrene[2].

In order to test the significance of the rate curves they were compared with those obtained dilatometrically. However, differences were observed and the two sets of curves were not superposable. The dilatometer curves, see *Figure 3*, continued to crystallize to higher conversion than the DSC curves, see *Figure 4*. These differences reflected the lack of sensitivity of the calorimeter and its inability to follow the process to lower rates of crystallization. Conversion to higher degrees of crystallinity continues to occur beyond that detected as shown by melting studies, see *Table 2*.

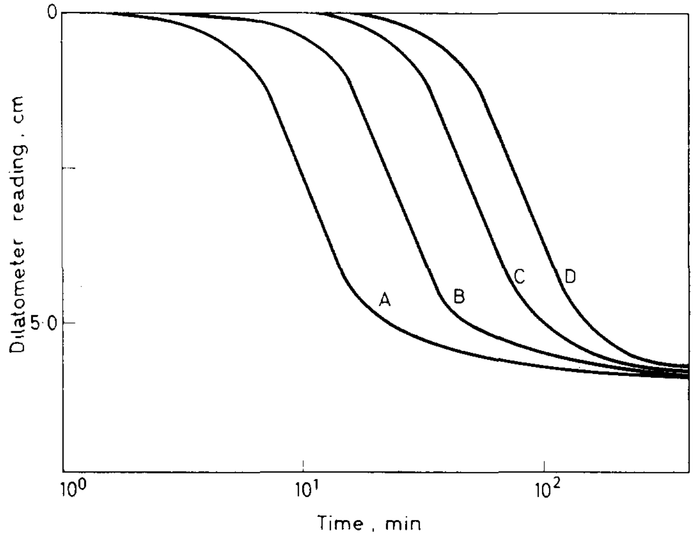

Figure 3—Dilatometric isotherms—sample C: A—126·1°, B—127·3°, C—128·4°, D—128·9°

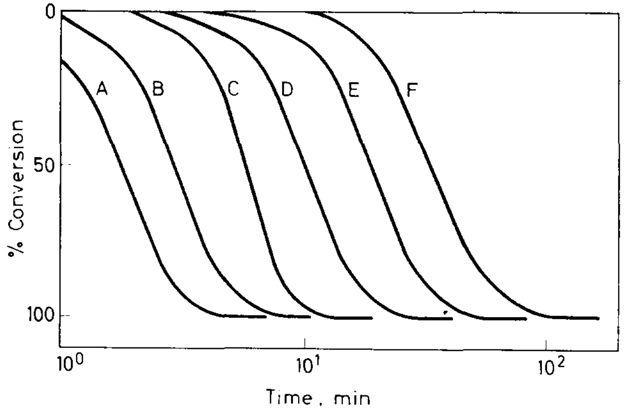

Figure 4—DSC crystallization curves—sample C, as in *Figure 1*

Analysis of the two sets of isotherms by the simple Avrami equation will give different values of the parameters Z_1 and n unless the same value is chosen for the final degree of crystallinity (X_∞). Rather than use an arbitrary value it was decided in characterizing the two techniques to use a parameter which was experimentally determinable and independent of choice of X_∞. For this purpose the time to attain maximum rate of crystallization ($T_{\text{max.}}$) was selected.

Reproducibility of crystallization isotherms

In principle, the calorimeter measures the rates under reproducibly isothermal conditions but it was observed that the rate curves showed considerable scatter. Variations were considered to be due to (1) sample size, (2) thermal history of polymer samples, and (3) variations in setting temperature.

Sample size—Measurements could conveniently be carried out on samples 1–50 mg in weight, but the observed isotherms showed the same scatter in $T_{\max.}$ values irrespective of sample size, see *Figure 5*(a). Only with the larger samples and with rapid crystallization ($T_{\max.} < 5$ min) were deviations observed—obviously due to the onset of crystallization before isothermal conditions were established.

Table 2. Comparison of techniques—Sample C

(A) *Time, min*	*DSC** *% crystn*		*Dilatometry†* *% crystn*
	Melting	Direct	
12	—	0·109	0·101
16	—	0·217	0·181
20	—	0·334	0·335
24	—	0·471	0·465
28	0·61	0·589	0·581
32	0·69	0·688	0·673
36	0·75	0·759	0·735
40	0·78	0·807	0·775
50	0·83	0·870	0·823
60	0·86	0·903	0·856
80	0·88	0·951	0·887
100	0·91	0·989	0·903
130	0·92	1·0	0·920
160	0·93	—	0·931
190	0·94	—	0·936
1240	0·99	—	0·987

(B) Crystallization parameters

DSC temp.	*n value*	$t_{1/2}$ *min*	Z_1 $(min)^{1/n}$ $\times 10^6$
127·5±0·3	2·7	20	55
128·5	2·8	36	10
129·5	2·6	68	3·2
Dilatometry			
127·50±0·05	2·8	21	62
128·35	2·9	40	7·2
128·95	2·8	70	2·9
129·10	2·8	—	1·2

*T_c=127·5°C. †T_c=127·3°C.

Sample size effects were present, however, in measuring the melting point of the samples. Melting was studied by heating at a constant rate of 0·5 deg. C/min from the crystallization temperature. This rate was sufficiently fast to prevent recrystallization at higher temperatures and so the observed melting point, $T_{\mathrm{obs.}}$, is a function of the fold period laid down at that crystallization temperature. The observed melting point increased linearly with sample size and the $T_{\mathrm{obs.}}$ obtained by extrapolation to zero sample weight.

Thermal history of polymer samples—Thermal memory, i.e. the dependence of the crystallization rate upon the length and temperature of premelting, was found to be absent as the same isotherm was obtained irrespective of the heating time (i.e. 15 minutes or 24 hours) and temperature (150° or 200°C). However, melting at 200°C for short periods was chosen as this was used in dilatometry. There was no progressive change in the polymer characteristics with repeated heating. Polymer degradation was accordingly considered to be absent under these conditions.

Variations in setting the temperature—The temperature scale of the differential scanning calorimeter is sub-divided only into units of one

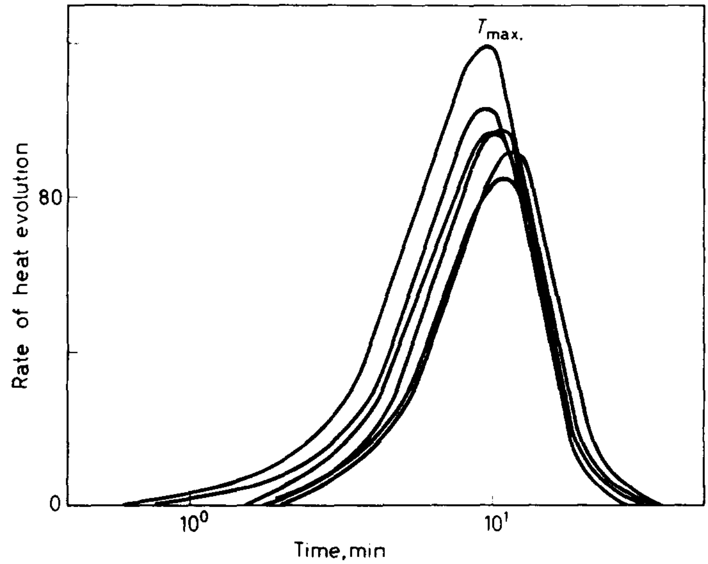

Figure 5(a). (*See caption overleaf*)

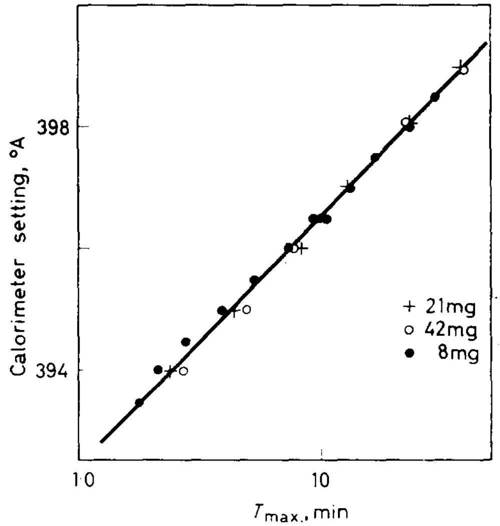

Figure 5(b)

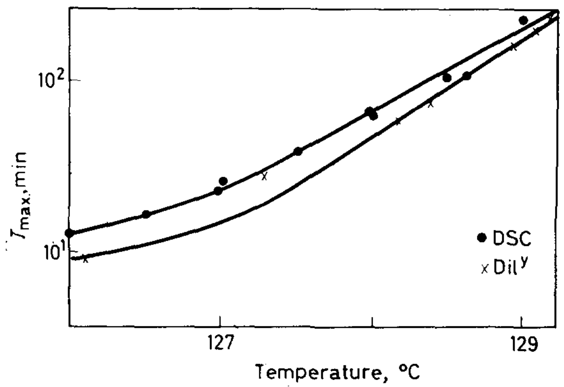

Figure 5(c)

Figure 5—Variation in $T_{max.}$ values: (a) manual setting, (b) setting by standard rate of cooling, (c) comparison with dilatometry

degree, but in the present study of polyethylene reproducible isotherms could only be produced by setting the isothermal temperature accurately and to much less than one degree. It is normal to set the temperature required manually. Isothermal conditions were then not reached instantaneously but when the detector recorded a constant response. Variations were observed in the isotherms when manual setting was adopted consistent with an error of ±0·3 deg. This error could be considerably reduced by using a standard rate of cooling (2 deg. C/min) and the temperature determined by accurate timing from a fixed temperature. This method with care reduced variations to ±0·1 deg. C, see *Figure* 5(b), but it was then not possible to measure the isothermal temperature with this degree of accuracy.

Significance of rate curves

In order to test the meaningfulness of the isotherms and gauge the accuracy of isothermal conditions within the calorimeter the rate constants and their temperature dependence, determined from the DSC and dilatometric isotherms, were compared, see *Table 2B*. Both methods gave very similar results with the same temperature dependence, *Figure* 5(c). Thus DSC, within the accuracy of setting temperature, appeared to be as accurate as dilatometry in determining isothermal crystallization curves.

The marked dependence of the $T_{max.}$ values, see *Figure 5*, and their invariance with sample size and heating effects, suggest that this is a better method of calibrating the temperature scale of the calorimeter than the melting of standard samples. Particularly since the latter is dependent on sample size and heating rates, the instrument requires frequent calibration and the former technique is rapid.

The crystallization parameters, *Table 3*, have features which have been observed in the analyses of the dilatometer rate curves[1,6]. The *n* value is non-constant and fractional. These results will be discussed later[6].

The DSC isotherms exhibit less secondary crystallization effects than were observed either on the dilatometer or from the melting curves. Deviations from the three methods only occur at quite high crystallization extents suggesting that up to 70 per cent crystallinity at least secondary crystallization is not important, and the rate constants determined initially are independent of this process. It would seem unlikely that secondary crystallization effects alone can account for the fractional n values.

Table 3. Crystallization parameters

Sample 1	*Range of n values*	*Range of Z_1 values*	*Temp. range °C*
A	3·2–3·6	10^{-3}–10^{-6}	124·5–128·5
B	2·8–3·1	10^{-3}–10^{-7}	124·5–129·5
C	2·6–3·1	10^{-3}–10^{-6}	124·5–130·5
D	3·0–3·6	10^{-3}–10^{-6}	124·5–130·5

CONCLUSIONS

Direct isothermal DSC can be applied to study the crystallization kinetics provided the rate of crystallization is sufficiently rapid. Otherwise a melting procedure has to be adopted which is more tedious than direct dilatometry. It is also less accurate due to errors in temperature settings.

Care has to be taken in setting the temperature; this is particularly true for polymers with high temperature dependent crystallizations. However, crystallization isotherms can satisfactorily be used in calibrating the temperature scale of the instrument.

DSC is, however, not as sensitive as precision dilatometry but the isotherms are meaningful and can be analysed with sufficient accuracy to test the validity of the Avrami equation. They may not be sufficiently accurate to distinguish between modified Avrami equations, as DSC cannot accurately detect secondary crystallization. It is a useful supplementary instrument to study crystallization kinetics since it is capable of measuring directly the melting points and degrees of crystallinity of partially crystalline samples.

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