Crystallization Kinetics of High Polymers. Polyethylene Oxide—Part II

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The crystallization of polyethylene oxide samples, fractionated and unfractionated, has been studied with a differential scanning calorimeter. Conclusions previously arrived at that the anomalous characteristics of the crystallization isotherms are partly attributable to the wide molecular weight distributions and low nucleation densities are confirmed. However, non-integral values of the Avrami exponent, n, are observed under conditions of high density of nuclei, and with fractionated samples, which cannot readily be explained by any of the current theories of crystallization kinetics.

THE use of a differential scanning calorimeter to determine meaningful and accurate crystallization rate constants for bulk polymers, and in particular polyethylene fractions, has been described in a previous paper[1]. The technique has the considerable advantage of requiring micro samples, and quantitative kinetic isotherms can be determined rapidly over a temperature range.

The present paper describes the application of this technique to polyethylene oxide, in order to confirm the conclusions of Part I[2], that the crystallization characteristics are limited by nucleation density and molecular weight distribution, and also to extend the observations under conditions where these factors are not limiting, in order to test the validity of the Avrami equation to polymer crystallization kinetics.

EXPERIMENTAL

Materials

The polymer samples were as listed in Part I; the same serial numbering is adopted[2].

Differential scanning calorimeter (DSC)

A Perkin–Elmer DSC, model 1B, was used with 1 to 50 mg samples of powdered polymer. The operation and sensitivity of the calorimeter in determining crystallization isotherms has been described previously[1]. The temperature scale of the calorimeter was calibrated from the melting point of standard materials, purified by zone refining; the melting points were determined by extrapolating the observed melting temperature to zero weight of sample, in order to correct for heat flow.

RESULTS

(1) *Initial considerations*

The DSC isotherms of the crystallization of sample A are reproduced in *Figure 1.* The calorimeter measured rate of heat change as a function of

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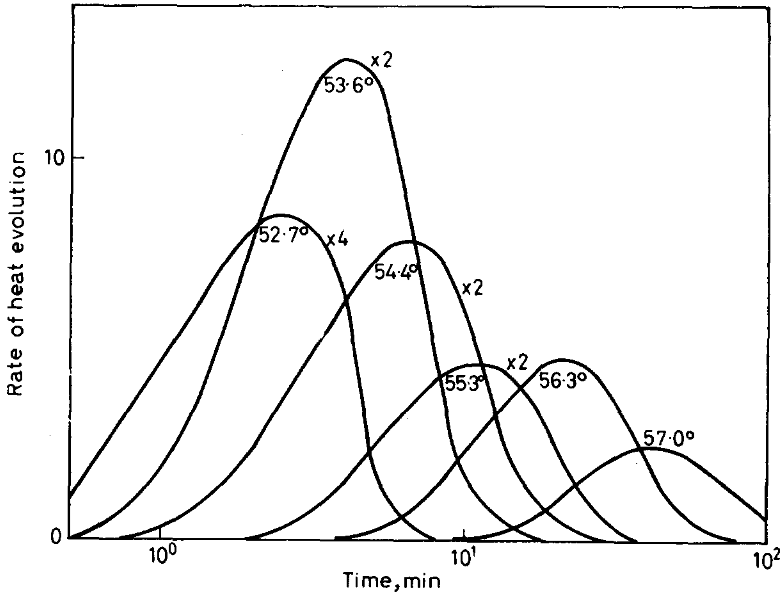

Figure 1—DSC crystallization isotherms—sample A

time, and these isotherms were processed first by integrating, and then by analysing with either equation (2) or (3) of Part I, since the extent of conversion, X_t, at time t was taken as the fraction of the heat evolved, i.e.

$$X_t = \int_0^t (\mathrm{d}h_t/\mathrm{d}t) \Big/ \int_0^\infty (\mathrm{d}h/\mathrm{d}t) \qquad (1)$$

and

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

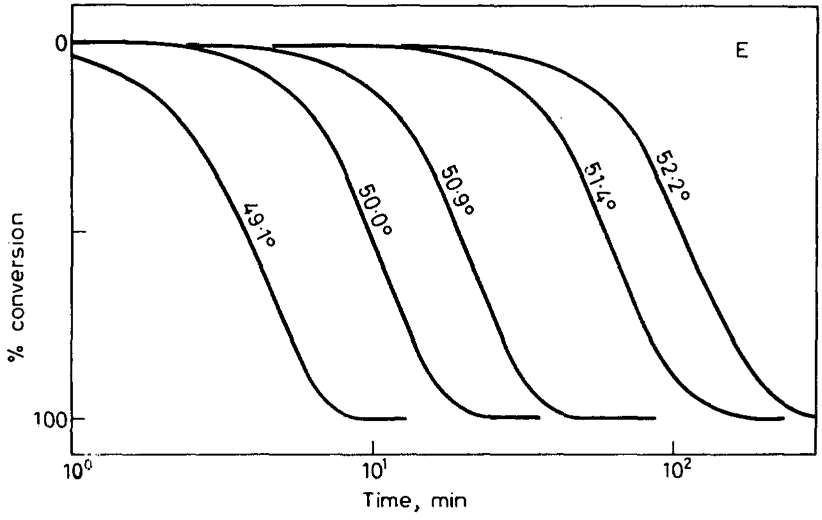

Figure 2—Integrated crystallization isotherms—sample E

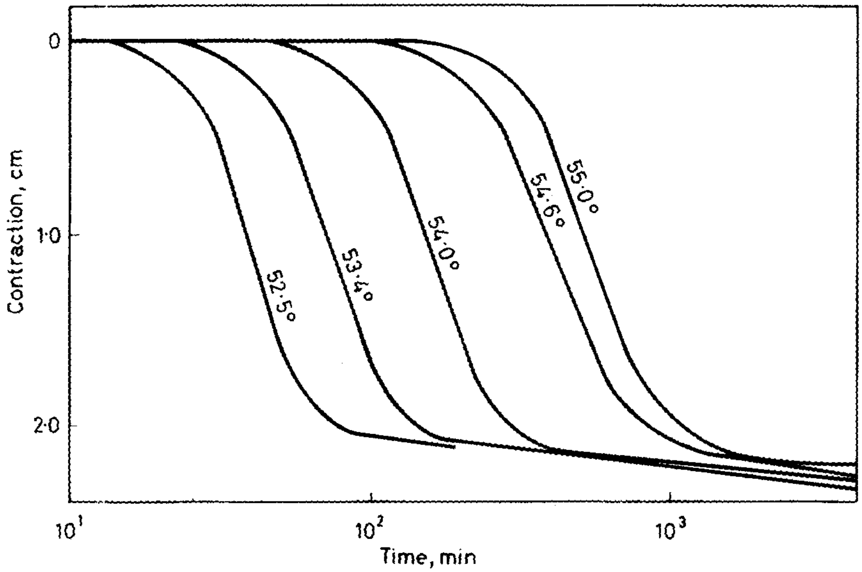

Figure 3—Dilatometric crystallization isotherms—sample E

where Z_t and n are the corresponding Avrami equation rate constant and exponent.

The integrated rate isotherms, see *Figure 2,* exhibited differences from those measured dilatometrically, see *Figure 3,* and the two sets of curves could not be superimposed. The dilatometric crystallization curves continued to higher conversion and longer time. These differences arose from the lack of sensitivity of the calorimeter and the inability to follow the process to low rates. However, measurement of the degree of crystallinity from the heat absorbed on subsequent melting confirmed that crystallization proceeded beyond the limit of detection (see also ref. 1).

Variations were also observed in the isotherms of each sample, due to difficulties in setting the isothermal temperature of the calorimeter to better than 0·3 deg. C. The variations were independent of sample size and rate of crystallization, see *Figure 4,* but could be considerably reduced (0·1 deg. C) by adopting a standard temperature setting procedure of cooling the sample at a slow standard rate of 2 deg. C/min for timed periods from a fixed temperature.

Crystallization isotherms could be determined directly rather than indirectly from a composite curve of heats of melting obtained at various crystallization times, but was limited by the time required to establish isothermal conditions, by sample size, and by the sensitivity of the detector (1 millical/sec). Accordingly satisfactory isotherms could only be obtained if the maximum rate of crystallization occurred at greater than three or four and less than 150 min and the sample size was adjusted. Crystallizations could be studied over a six or seven degree temperature range, and the technique compared favourably with that of dilatometry in this respect.

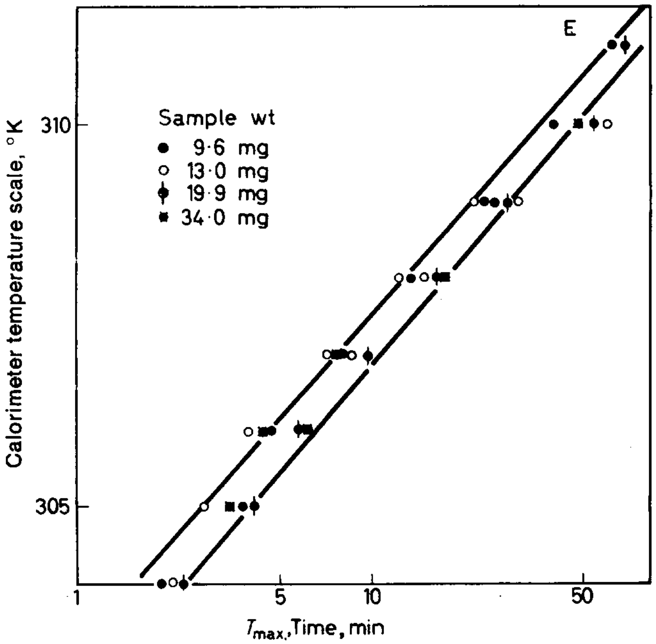

Figure 4—Variation in $t_{max.}$ in setting temperature

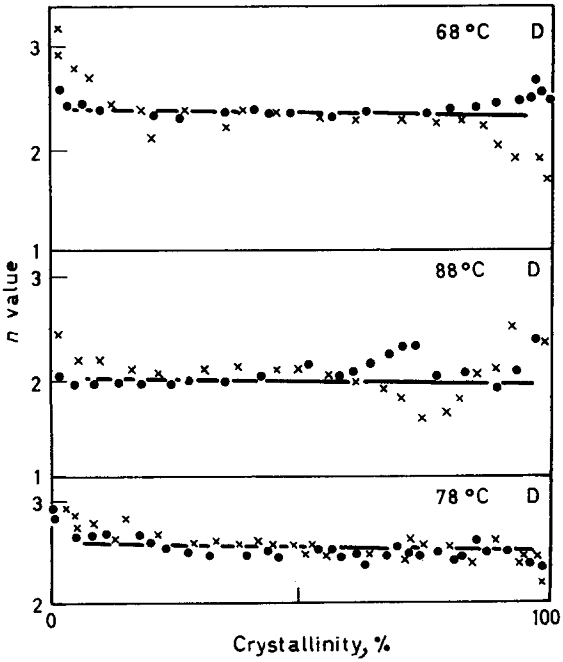

Figure 5—Variation in *n* value with preheating temperature—sample D

Table 1. Preheating temperature

Sample	*Crystn temp. °C*	*Half-life $t_{1/2}$ min*	n^* *value*	*Preheating temp. °C*
D	52·6	13·5	2·6	68
	51·6	9·4	2·6	
	50·7	6·6	2·6	
	49·8	4·4	2·5	
	49·1	3·5	2·6	
D	49·8	6·5	2·4	78
	50·7	11·5	2·5	
	51·6	16·8	2·5	
	52·6	29·0	2·5	
	53·5	49·0	2·5	
D	49·1	22·0	2·0	88
	49·8	28·0	2·1	
	50·7	32·0	2·1	
	51·6	37·0	2·0	
D	52·6	47·0	2·0	110

*Value at $t_{1/2}$.

Table 2. Crystallization parameters
(Preheating temperature 78°C)

Sample	*Crystn temp. °C*	*Half-life $t_{1/2}$ min*	n *value at* 50%
A	53·6	5·0	2·4*
	54·4	8·2	2·4*
	55·3	13·5	2·5*
	56·3	26·0	2·5*
	57·0	52·0	2·5*
B	50·7	4·7	2·6
	51·6	6·2	2·5
	52·6	11·0	2·5
	53·5	17·0	2·4
	54·4	32·5	2·4
	55·3	64·0	2·6
C	52·6	9·6	2·6*
	53·5	15·0	2·6*
	54·4	32·0	2·5*
	56·3	60·0	2·5
E	48·2	2·6	2·8*
	49·1	5·0	2·8*
	50·0	9·6	2·7*
	50·9	22·0	3·0*
	51·7	53·0	2·6*
	52·6	178·0	2·6*

*n continuously decreasing.

(2) *Rate parameters*

Previous observations on the crystallization of these polyethylene oxide samples with a polarized light microscope indicated that the density of the nuclei produced during isothermal crystallization was very dependent on the preheating temperature, and the low density of nuclei could partly account for the anomalously low value of the Avrami exponent *n* obtained on analysing the isotherms[2]. The effects of the duration and temperature of pre-melting were accordingly studied.

In general, crystallization isotherms were not reproducible unless the samples were initially preheated for a long period, say 18 hours, at each temperature. The length of subsequent preheating at this temperature, i.e. 10 min to 18 h, had no further effect and the isotherms were reproducible. Varying the preheating temperature had a very considerable effect

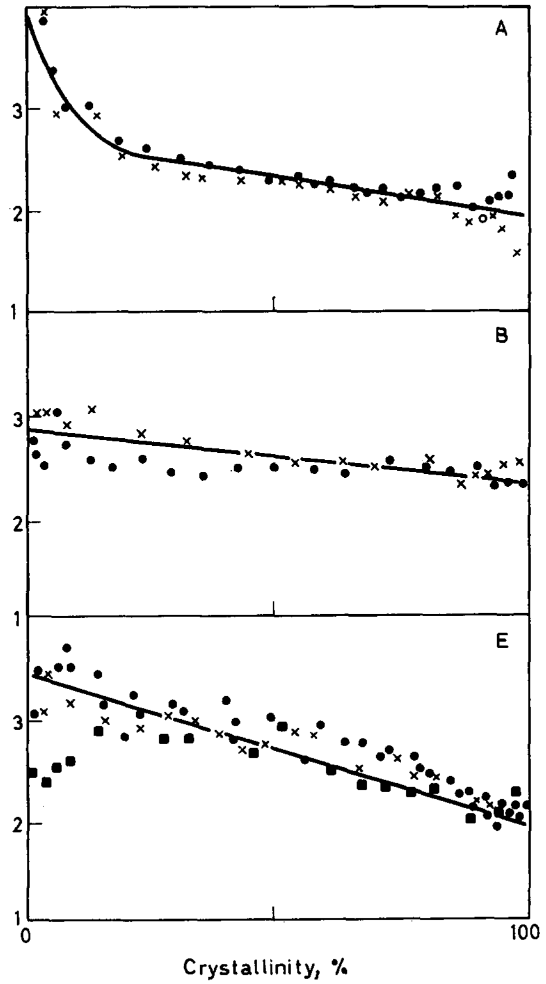

Figure 6—Variation in *n* value—unfractionated samples

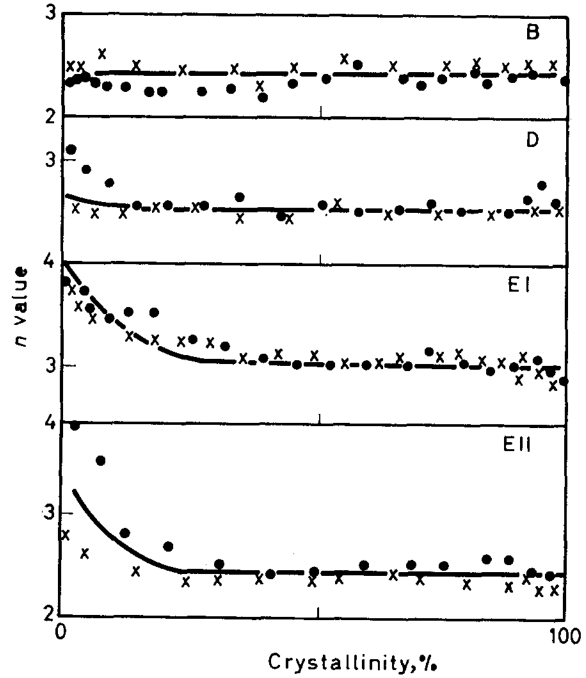

Figure 7—Variation in *n* value—fractionated samples

on the subsequent re-crystallization rate and on the value of its Avrami exponent *n*; the rate constant decreased with increasing temperature of preheating (constant crystallization temperature), and above a preheating temperature of 80°C, the Avrami exponent *n* also began to decrease appreciably. With sample D, the *n* value changed from an effectively constant value of about 2·5 ($\pm$0·2) to about 2·0 to 1·8, see *Table 1* and *Figure 5*. This change in *n* value and decrease in rate constant with increasing preheating temperature were consistent with a reduction in nucleation density and the final production of large spherulites constrained by sample size to grow as discs. Below 80°C, the observed *n* value appeared to be independent of preheating temperature. Accordingly, in order to obtain reproducible isotherms whose characteristics were independent of subsequent heating at the same or lower preheating temperature and a large number of nuclei during the crystallization a temperature of 78°C and an initial heating period of 18 h was chosen for all subsequent crystallizations.

The crystallization parameters of the isotherms determined in this way are listed in *Table 2*. All, except for sample D, exhibited a marked variation in *n* during crystallization; a progressive change from 3·0 (or 4·0) to about 2·0, see *Figure 6*. All the isotherms including those of sample D were inconsistent with the microscope observations that the crystallization process could be described by a single Avrami equation of predetermined spherulitic growth, for which a value of 3·0 was expected[2].

Table 3. Fractionated samples

Sample	*Crystn. temp. °C*	*Half-life* $t_{1/2}$ *min*	*n value*	*Preheating temperature °C*
A	59·7	50·0	2·0	88
	58·8	36·0	2·1	
	57·9	26·0	1·9	
	57·0	8·6	1·9	
	56·1	6·2	2·0	
B-1	55·2	42·0	2·5	78
	54·3	29·0	2·5	
	53·4	20·5	2·5	
	52·5	12·6	2·5	
	51·6	9·0	2·4	
	50·7	7·5	2·5	
D-1	54·3	32·0	2·5	78
	53·4	14·2	2·4	
	52·5	11·0	2·5	
	51·6	7·4	2·5	
	50·7	5·6	2·5	
E-I	48·9	28·0	3·0	78
	48·0	10·5	3·0	
	47·1	7·2	3·0	
	46·2	2·7	3·0	
E-II	48·7	26·5	2·5	78
	47·8	13·0	2·5	
	46·9	7·2	2·5	
	46·0	2·8	2·5	

(3) *Molecular weight distribution*

The polyethylene oxide samples used contained a large fraction of low molecular weight material and since this has been observed to alter the crystallization characteristics, it was considered desirable to remove this fraction. The characteristics of the fractionated sample are listed in *Table 7* of Part I.

Fractionation considerably altered the crystallization rate constants and their temperature dependence, see *Table 3.* It also had a considerable effect on the variation of *n* during the crystallization.

No marked differences were observed in crystallization behaviour of fractionated and unfractionated sample D, and these characteristics were similar to those observed in the other fractionated samples, A-1, B-1 and E-11, that is, an initial decrease in the value of *n* from 3·0 to about 2·5 where it stayed effectively constant throughout the remaining crystallization, see *Figure 7* and *Table 3.* Only in sample E-1 was the value of *n* consistent with an Avrami equation and the observed change in crystallization mechanism from sporadic to predetermined nucleation of spherulites, in that the *n* value decreased from its initial value of 4·0 to a constant one of 3·0.

The temperature and duration of preheating also had an effect on the crystallization characteristics of the fractionated samples, as prolonged heating at temperatures above 80°C reduced the value of n to an effectively constant value at 2·0, and also reduced the overall rates of crystallization.

DISCUSSION

The very low constant n values noted previously can still be attributed to a reduction in nucleation density as all the samples fractionated and unfractionated exhibited this marked trend to produce lower n values, i.e. 2·0 and lower as the preheating temperature was raised. Microscope observations indicated also that very large spherulites with diameters in excess of the sample thickness were being produced. However, despite the obvious conclusions that the general Avrami equation cannot fit the crystallization isotherms of the polyethylene oxide samples a low nucleation density cannot be invoked universally, since at the low preheating temperatures 10^4 to 10^5 nuclei per ml were present.

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