Crystallization Kinetics of High Polymers. Polyethylene Oxide—Part I

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Detailed analyses of the crystallization of polyethylene oxide samples of different molecular weights have been carried out using dilatometry and hot stage polarized light microscopy, in order to establish the dependence of the kinetic parameters on molecular weight distribution.

Qualitative molecular weight distributions were determined by turbidimetric titration. In general, crystallization proceeded from randomly nucleated spherulites, the growth rates of which were dependent on the dispersity of the sample. Nucleation was predetermined, but the density varied with the preheating temperature as well as with the temperature of crystallization. Very large spherulites were produced if an elevated preheating temperature was used, 80°C and above, due to the low density of nucleation. The data are discussed in the light of the anomalies repeatedly observed in the crystallization isotherms, determined by dilatometry, of polyethylene oxide samples.

SEVERAL studies have been made of the crystallization of polyethylene oxide samples[1-4], all in different molecular weight ranges. In general anomalous crystallization behaviour is observed, and this has cast considerable doubt on the validity of using the Avrami equation[5] to describe the crystallization rate isotherms of high polymers[3,4].

The present paper is a systematic study of the crystallization of polyethylene oxide samples of very different molecular weights in order to establish why the analysis of the rate curves by the Avrami equation is misleading.

EXPERIMENTAL

Materials

The polymers were used as unfractionated industrial samples but purified by repeated precipitation from a filtered benzene solution with excess *n*-heptane. They were dried *in vacuo*. The polymer characteristics are listed in *Table 1*.

We are indebted to the Union Carbide Co. Ltd, and the Shell Chemical Co. Ltd, for the gift of samples and details of their characteristics.

Apparatus and techniques

Number average molecular weights of the lower (molecular weight) samples were measured on a Mechrolab vapour pressure osmometer, model 301 in benzene at 37°C. Attempts were also made to measure the number average molecular weight of the higher samples on a Mechrolab membrane osmometer, model 502, but this failed due to excessive diffusion. Polystyrene samples of similar molecular weights equilibrated in the osmo-

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meter after several minutes, and exhibited no decrease in osmotic pressure over several hours. By comparison with the behaviour of sample E it was considered that these higher samples contained a considerable fraction of materials with molecular weight below 10^4.

Table 1. Polymer characteristics

Serial No.	*Mol. wt (by manufacturer)* $\times 10^3$	*Intrinsic viscosity dl/g*	*Average mol. wt viscosity* $\times 10^3$	*Average mol. wt number* $\times 10^3$
A* (Poly-ox)	>6 000	8·20		
B* (WSR 305)	500	3·91		
C	500	3·13		
D* (WSR-35)	200	2·45		
E	20·0	0·36	77·0	17·7‡ 21·5
F	9·0	0·33	62·0	8·2
G†	6·0	0·16	15·0	5·8 5·2§
H†	4·0	0·10	6·0	3·25

*Union Carbide Co. Ltd.—Ucar polymers.
†Shell Chemical Co. Ltd.—polyethylene glycols (PEG).
‡Membrane osmometry.
§Ebulliometry.

Intrinsic viscosity was measured in benzene at 25°C, and the viscosity average molecular weight determined from the equation

$$\eta = 1{\cdot}29 \times 10^{-3} M_v^{0\cdot5}$$

but was only valid for the lower samples[6].

Qualitative molecular weight distributions were determined by turbidimetric titration using conventional apparatus[7]. Benzene–*n*-heptane at 35°C was used as the solvent–precipitant system.

Three types of dilatometers, differing only in bulb size and shape, were used to measure isothermal crystallization rates. Their shape and dimensions were:

Dilatometer A: cylinder, diameter 0·2 cm, height 5 cm.
Dilatometer B: thin film, diameter 5 cm, thickness 0·005–0·02 cm.
Dilatometer C: cylinder, diameter 2 cm, height 2 cm.

The measuring capillaries were 0·6 mm i.d. and the polymer samples confined over thrice vacuum distilled mercury.

200 mg samples, vacuum moulded in the form of a pellet, were used in dilatometers A. Varying weights of polymer were deposited uniformly, by evaporation of a dilute solution, on the upper surface of dilatometers B. Volatiles were removed from the samples by vacuum melting over several days. Dilatometers C were used only with low molecular weight material as the higher samples did not coalesce into a continuous sample on melting. 5 g samples were used.

A polarized light microscope—Leitz Dialux–Pol—fitted with a metal hot stage thermostatically controlled with a thermistor bridge circuit[8] to within 0·04 deg. C was used to study the crystallization characteristics of the samples. Polymer samples were studied as thin films (10^{-2} to 10^{0} mm thick) pressed between thin-wall glass microscope slides separated by thin metal washers. The size and number of nuclei were measured photographically and visually with a micrometer eyepiece. Damage to the microscope lenses by heat was minimized by using long working distance objective lenses. Temperature control was gauged from the observed scatter in the initial radial growth rates of the nuclei, and the temperature of the stage calibrated from the melting points of standard substances.

Method of analysis of isotherms

Measurement of volume contraction during isothermal crystallization is the most widespread technique for observing the process continuously with sufficient accuracy to determine the mechanism. Experimental results are conventionally interpreted in terms of the Avrami equation[5], relating extent of crystallinity (X_c) to time t

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

and for dilatometry

$$X_c=(h_0-h_t)\,/\,(h_0-h_\infty)$$

where h_0, h_t and h_∞ are the dilatometric heights initially, at time t, and finally; Z_1 is the rate constant, and n the Avrami exponent. n is required to be an integer between one and four, and is used diagnostically for the crystallization process[9,10].

Repeated discovery of non-integral n value[11–13] suggests that n cannot be used to make predictions concerning crystallization mechanisms. Indeed, Banks and Sharples[3], and later Hillier[4], from a study of the crystallization kinetics of polyethylene oxide, indicated that the value of n can be misleading. In particular, a value of $n=2{\cdot}0$ indicating growth of discs or rods, was measured dilatometrically, while microscopic observations showed the presence of growth of spheres, i.e. spherulites, and so requiring a minimum n value of 3·0. There have been several attempts to modify the Avrami equation to account for these and other observations[4,14,15].

The Avrami equation is normally analysed by one of two methods:

(*i*) a plot of log $\{-\ln(h_t-h_\infty)\,/\,(h_0-h_\infty)\}$ against log t gives a line of gradient n, and intercept at $t=1{\cdot}0$ of log Z_1, since from equation (1)

$$\log\{-\ln(h_t-h_\infty)/(h_0-h_\infty)\}=n\log t+\log Z_1 \tag{2}$$

Only an average value of n is obtained, but it is possible to determine n as a function of crystallinity from instantaneous gradients.

(*ii*) by calculation from

$$n=-t\,\frac{dh}{dt}\,\{(h_t-h_\infty)\ln(h_0-h_\infty)/(h_t-h_\infty)\}^{-1} \tag{3}$$

$$Z_1=\ln 2\times t_{\frac{1}{2}}^{-n}$$

where $t_{1/2}$ is the half-life of the crystallization.

Both methods give very similar results.

RESULTS

(1) *Equilibrium melting temperature* (T_m)

Temperature/volume curves were determined dilatometrically and used to measure the equilibrium melting temperature of the various samples, by the following procedure. Polymers were initially crystallized at a high temperature such that the crystallization isotherm could be followed over two weeks, and then left to anneal for this period at this temperature. Subsequently the temperature was raised at the rate of one degree per day. The point of final melting, where the volume curve of the partially crystalline polymer attains that of the amorphous polymer was taken as a measure of the melting point, T_m. Samples were then cooled at the same rate and the usual hysteresis of crystallization observed.

The T_m values so obtained are listed in *Table 2* and compared with the literature values. Extrapolation of the reciprocal melting temperature versus reciprocal degree of polymerization plot to infinite chain length, according to the equation[16],

$$(1/T^0_m - 1/T_m) = 2R\,(\Delta H\,X)^{-1} \tag{4}$$

where T^0_m is the equilibrium melting point of an infinite molecular chain, X the degree of polymerization, and ΔH the heat of fusion, gave $T^0_m = 69°$ in excellent agreement with the value observed for sample A. However, the value of ΔH determined was lower than that determined by Mandelkern[18], from the effect of diluents on the melting point.

Table 2. Melting characteristics

Sample	*Degree of polym*^{n} $\times 10^4$	*Melting point* °*C*	ΔH *cal/monomer mole*	*Ref.*
A	13·6	68·6		
B	1·14	67·5	540±50	
D	0·45	67·0		
E	0·045	63·0		
F	0·020	64·0		
G	0·0136	61·3		
9–10×10^3		66·0	1 980	2
	×10^0			
PEG 300	7·0	−12·0		
400	9·0	7·0		
600	13·6	22·0		
800	18·2	30·0	650±50	17
1 000	22·7	42·3		
1 500	34·0	47·0		
4 000	90·0	55·5		

Microscope melting points, as determined by the disappearance of birefringence, have been used to characterize the polymer samples[1]. These were found to be consistently three to five degrees lower than the values determined dilatometrically, and so are not quoted.

(2) *Dilatometric crystallization rates*

The isothermal rate curves of sample F were typical of the curves obtained from most samples. Crystallization proceeded at a greatly reduced rate beyond the initial region in which an Avrami equation appeared to fit. Secondary crystallization was clearly present.

Analysis of the curves by equation (3) gave non-constant n values in that the initial n value decreased from 4·0 (or 3·0) to 3·0 (or 2·0) finally, see *Figure 1* and *Table 3*. Values of n between 3·0 and 4·0 indicative of spherulitic growth from sporadic nucleation changing to instantaneous nucleation were expected and so only in part of the samples was analysis of the curves by the Avrami equation meaningful. These variations between samples were also apparent in other studies of the crystallization of polyethylene oxide samples. Mandelkern *et al.*[2] first suggested that the n value changes during crystallization from 3·0 to 2·0, and Barnes *et al.* from 4·0 to 3·0 and 2·0, while Banks and Sharples[3] and later Hillier[4], found n to be effectively constant at 2·0 throughout the crystallization. These rate characteristics are listed in *Table 3*, and compared with those determined in the present study.

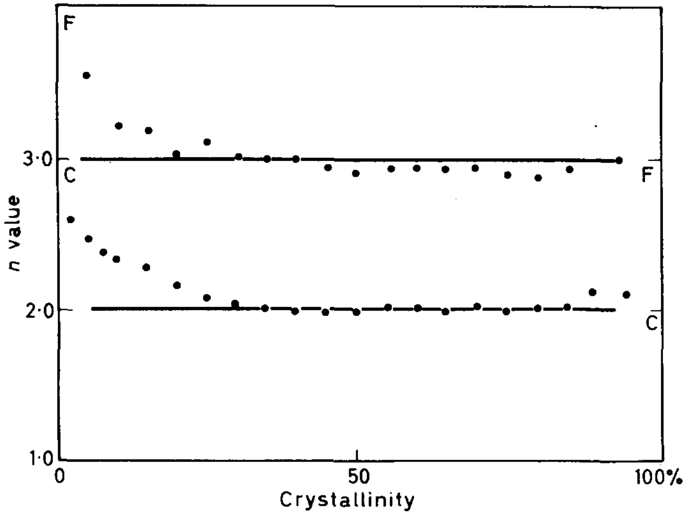

Figure 1—Variation in n value during the crystallization of samples F and C

The Avrami equation adequately describes the crystallization of a few samples but is wrong for the others; this may arise from several effects:

(*i*) assumptions inherent in the derivation of the Avrami equation,
(*ii*) assumptions inherent in analysing the rate curves,
(*iii*) dilatometric characteristics, i.e. effect of sample size, surface nucleation, etc.,
(*iv*) effect of molecular weight distribution on crystallization processes.

(*i*) *Microscope observations*—In order to test the assumptions inherent in the development of the Avrami equation, namely:

(*a*) the time dependence of the nucleation and growth processes,
(*b*) the random spacing of the nuclei, and
(*c*) the number of dimensions in which growth from the primary nuclei proceeds,

the development of crystallization within the polymer was measured with a polarized light microscope.

Table 3. Rate characteristics (dilatometers A)

(a) *Sample*	*Temp. range* °*C*	$\log Z_1$	*n values* *at* 50%	*n values* *expected*
A	54–57	2·5–3·5	3·0	3·0
B	54–57	2·5–3·5	2·0	3·0
C	52–54	2·5–3·5	2·0	3·0
D	52–54	2·5–3·5	2·4	3·0
E	52–55	2·5–3·5	2·2*	4·0–3·0
F	51–54	2·5–3·5	3·0*	3·0
G	52–55	2·5–3·5	3·0	3·0

(b) *Sample or* M_n	*Temp. range* °*C*	$\log Z_1$	*n values*	*Ref.*
4 000	46–50	3·0– 5·0	2·0*	1
6 000	50–54	3·0– 5·0	2·0*	
20M	50–56	11·0–18·0	3·0	
10 000	52–58	4·0–14·0	3·0–2·0	2
WSR 35, i.e. D	—	—	2·0	3
WSR 35, i.e. D	51–58	2·5– 4·1	1·5–2·0	4

*Initially 4·0 falling to 2·0.

Crystallization developed from the melt first as rodlike objects which developed into sheaths by lateral branching, and finally into spherulites with the characteristic Maltese cross birefringence. These spherulites were frequently very large with diameters greater than 1 mm, and with sample G greater than 1 cm. The large spherulites exhibited a coarse radial fibrillar appearance.

The spherulites of all samples grew linearly with time until just before the point of impingement with a neighbouring spherulite, when a marked reduction in rate was observed. Growth rates were reproducible from sample to sample, over the total sample and independent of the preheating temperature, provided the sample was melted above T_m. The growth rates, however, exhibited dependence on crystallization temperature and molecular weight, *Figure 2*.

Analysis of the temperature dependence ought to yield information concerning the mechanism of radial growth, and in particular whether it is nucleation controlled[18], since

$$\log G = \log G^0 + CT_m^a \{T \,.\, (T_m - T)^a\}^{-1} \tag{5}$$

where G^0 and C are constants, T the temperature of crystallization, and a a constant equal to 1·0 or 2·0 for two- and three-dimensional nucleation. No clear distinction could be made between the two nucleation processes, as the equations with $a = 1{\cdot}0$ and 2·0 fitted equally well. The C values listed in

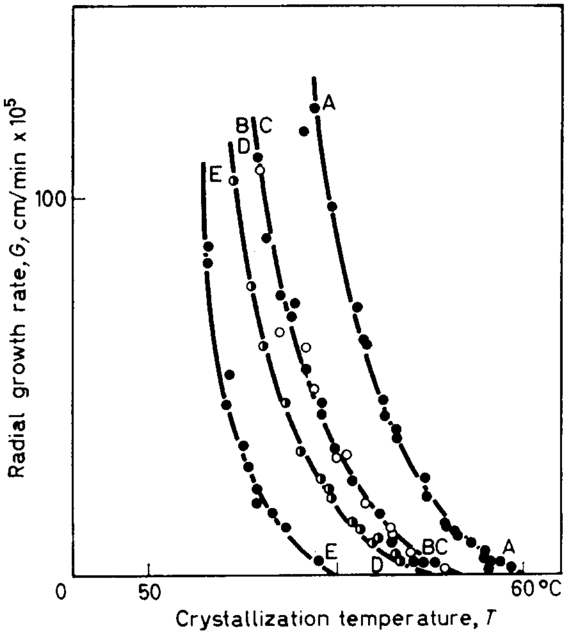

Figure 2—Temperature dependence of radial growth rates, samples A, B, C, D and E

Table 4 are quoted for both equations. They varied considerably with molecular weight of the sample.

Large variations were observed in the size of the spherulites which developed, and in all the samples the number of nuclei was dependent on the temperature of preheating but independent of the duration of preheating (up to 60 h) provided the sample was heated for a minimum period (10 to 15 min). At a fixed preheating temperature, the number of nuclei developed was independent of prior treatment and varied only with the temperature of crystallization, see *Table 5*. Prolonged treatment at elevated temperatures, i.e. above 100°C, considerably reduced the number of nuclei produced subsequently on recrystallization and remelting at lower temperatures. Preheating below 100°C did not alter the radial growth rate characteristics of the sample. No volatile evolution or molecular weight change was detected on prolonged heating at 100°C under vacuum, and so thermal degradation

Table 4. Temperature dependence of growth rates

	C values			*C values*	
Samples	$a=1{\cdot}0$	$a=2{\cdot}0$	*Samples*	$a=1{\cdot}0$	$a=2{\cdot}0$
A	43·7±5·0	0·050±0·012	E	46·5	0·075
B	46·5	0·073	F	20·0	0·026
C	46·5	0·091	G	31·0	0·037
D	50·0	0·076			

was not considered to account for these observations. Nucleation characteristics varied from sample to sample within a polymer, and were not reproducible. However, similar trends were noted within each sample.

Table 5. Nucleation characteristics

Sample	*Premelting temp.* °*C*	*Crystn temp.* °*C*	*Nucleation density no. per ml* $\times 10^{-4}$
B	70	58·0	3·7
		57·6	6·5
		56·9	10·2
		56·0	16·7
		54·9	22·2
B	64·0	56·0	14·0
	70·5		10·6
	71·5		4·8
	75·2		0·40
C	63·0	56·0	∞
	65·5		30–40
	67·8		8·3
	72·7		6·5
	76·4		2·0
	79·4		0·7
			Nucleation rate no. per ml per min $\times 10^{-4}$
E	70	54·9	0·176
		54·3	1·29
		54·2	1·63
		53·9	3·00
		53·5	9·30
		53·3	20·0
		52·4	32·0
		Preheating time min	*Relative rate*
E	65	15	3·05
		165	3·10
	70	15	1·81
		165	1·88
	75	15	1·90
		165	1·89

Nucleation was heterogeneous, as the spherulites were reproduced at randomly spaced fixed points in the field of view. The number of nuclei increased linearly and rapidly to a limiting value which remained constant throughout the remainder of the crystallization, see *Figure 3*(a). The limiting number of nuclei decreased with increasing crystallization temperature for constant preheating treatment, see *Table 5* and *Figure 3*(b). Only in sample E did heterogeneous nucleation appear sporadically with time over a major fraction of the crystallization process. This nucleation rate had a temperature dependence similar to that of the growth rate.

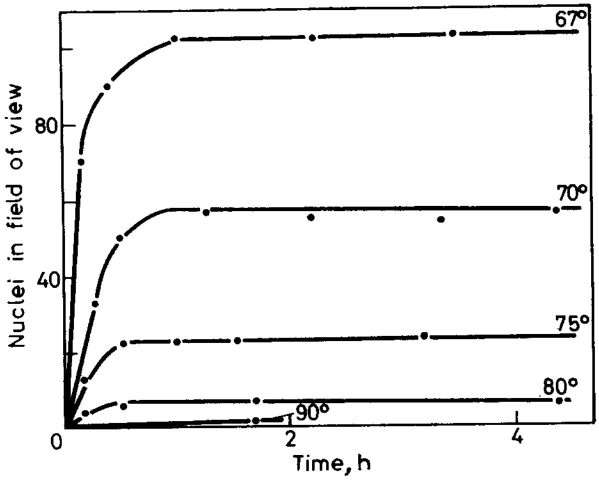

Figure 3—(a) Development of nuclei with time in sample A after preheat treatment; (b) Effect of preheating temperature on the limiting nucleation density—sample A

Microscope observations are consistent with the crystallization kinetics of all the samples being described by an Avrami equation with n values between 4·0 and 3·0. Initial and final deviations will be expected as the rodlike nuclei develop into spherulites, and as the growth rate decreases on impingement, but this will be over a small fraction of the total process.

(ii) *Assumptions in analyses of dilatometric isotherms*—In determining the average n value by equations (2) and (3) no allowances were made for:

(a) secondary crystallization or annealing processes,
(b) the presence of an induction period in which no crystallization occurs,
(c) the changing nucleation characteristics, or
(d) experimental accuracy in determining dh/dt.

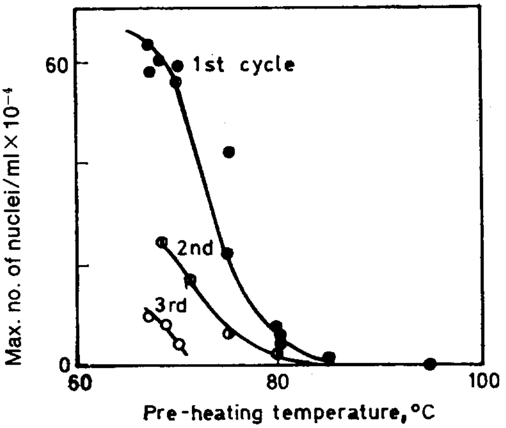

Figure 3(b)

(a) h_∞ for the initial crystallization could not be determined experimentally due to the onset of secondary crystallization. The choice of h_∞, however, did not alter the initial values of n appreciably, and with only one value of h_∞ it was possible to obtain an effective constant for n, see *Figure 4*, curves h_∞.

(b) The Avrami equation was developed to allow for the restriction to the growth of crystalline regions by their impingement but it is assumed in the derivation of the equation that the crystalline regions have a constant shape. If there is an initial period in which no nuclei are produced or in which their shape changes allowance must be made in the experimental time by an amount which is equivalent to an induction period. The corrections to the value of n by including various induction periods, less than the experimentally observed one, reduced the value of n, see *Figure 4* curves t. The effect is more noticeable in the initial values of n.

(c) The change from sporadic to instantaneous nucleation leads also to a reduction in n value (from 4·0 to 3·0). Initial variations in the value of n during crystallization of isotactic polystyrene has been attributed to this[19].

(d) In estimating n by equation (3), $\mathrm{d}h/\mathrm{d}t$ cannot be determined with the same accuracy as h_t, or t, but has to be estimated from smoothed curves of $\Delta h/\Delta t$ against t. This limited the final accuracy in n to between five and ten per cent, see *Figure 4* curve $\mathrm{d}h/\mathrm{d}t$.

Maximum variations in the value of n were gauged from addition of these effects, see *Figure 4*. The n value at 50 per cent conversion had least error. However, each of these variables alone or together could not account for the observed effectively constant n values of 2·0 from spherulitic growth.

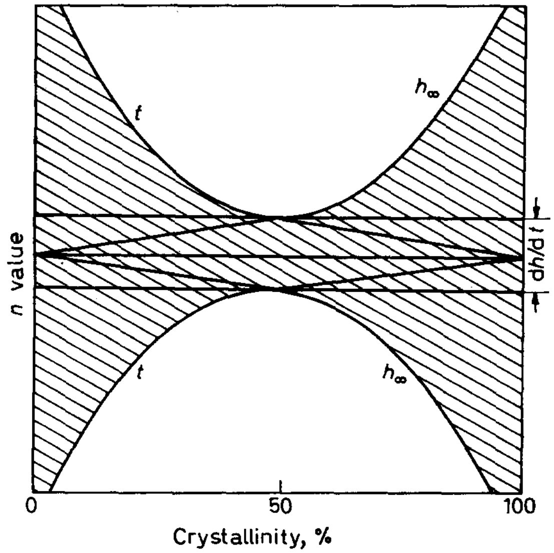

Figure 4—Error in n value produced by uncertainties in value of (a) induction period t, (b) h_∞ and (c) $\mathrm{d}h/\mathrm{d}t$

Variations which resulted in a more acceptable *n* value at one conversion, yielded non-constant values of *n*.

(iii) *Effect of dilatometer shape*—Despite the fact that isotherms were reproducible from dilatometer to dilatometer for each sample, and consistent from one set of published results to another, see *Table 3*, it was considered desirable to study the part played by sample and dilatometer shape on the course of the crystallization, using the dilatometers described above.

Dilatometers A. All previous crystallizations described were carried out in this type of dilatometer. Increasing the sample size, and varying dimensions, had no measurable effect on the kinetics.

Dilatometers B. Samples were studied as thin films, and the crystallization kinetics were dependent on the sample thickness. In general the thin films crystallized at slower rates with lower average *n* values, see *Table 6*. The *n* value changed continuously during crystallization from an initial value of 4·0 to a final value of 2·0.

The development of the spherulites within thin films during the crystallization of samples D and E, was visible to the eye and their diameters finally approached several millimetres (10^2 to $10^3 \times$ the film thickness). For most of the crystallization the spherulites were constricted to grow as discs rather than spheres, and the observed changes in the *n* value from four to two were consistent with the change from growth of sporadically nucleated spheres to predetermined discs.

Dilatometers C. Only sample G was studied. Microscope observations indicated that the nucleation density was very dependent on preheating temperature, and prolonged heating at about 100°C considerably reduced the number of nuclei. Indeed in this way it was possible to produce only five nuclei in the total volume of sample (5 ml). Nucleation proceeded in the bulk of the sample, not at the surface, but the large spherulites which eventually developed dropped under gravity to the bottom surface in contact with the mercury, giving the appearance of surface nucleation. Crystallization subsequently developed as one growing front, when the spherulites coalesced. Analysis of the crystallization isotherms gave *n* values which changed from 4·0 to 1·0, averaging about 2·3.

It is clear that because of the low nucleation density and the corresponding development of large spherulites, the temperature of preheating the shape and size of the polymer sample in the dilatometers can materially alter the crystallization kinetics. This is particularly true of the low molecular weight samples. The anomalous crystallization characteristics of the higher samples which were effectively independent of the dimensions of the samples cannot be accounted for by this effect alone.

(iv) *Molecular weight distribution*—The molecular weight distributions of the various samples were measured qualitatively by turbidimetric titration since characterized samples were not available. The integral distribution curves were determined by plotting the observed turbidity against amount of non-solvent added to the benzene solution. Under the concentration range used the turbidity increased linearly with the weight of polymer taken, but the specific turbidity varied from sample to sample. No anomalous coagulation of the polymer precipitate occurred on standing.

Integral distribution curves, obtained by plotting turbidity against per-

Table 6. Effect of dilatometer shape

Sample	*Dilatometer*	*Sample thickness cm*	*Crystn temp. °C*	$t_{1/2}$ *min*	*n values*	*Melting temp. °C*
C	A	0·20	54·0	19	2·0	100
			55·9	77	2·0	
			56·7	150	2·0	
			57·4	250	2·0	
	B	0·001	54·0	120	2·6*	70
			55·0	215	2·3*	
			56·0	635	2·5*	
		0·020	54·0	120	2·4*	70
			55·0	220	2·5*	
			56·0	640	2·4*	
D	A	0·20	50·5	34·5	2·4	100
			51·0	42·5	2·4	
			52·0	79·0	2·4	
			53·5	133	2·4	
	B	0·02	51·9	15·0	1·8	100
			52·5	24·5	1·9	
			53·2	34·0	1·9	
			53·5	47·0	1·8	
			54·0	70·0	1·9	
E	A	0·02	52·8	32	3·3*	70
			54·0	125	3·3*	
			54·6	295	3·0*	
			55·0	420	3·3*	
	B	0·003	54·0	100	2·4*	70
			55·0	450	2·0*	
			56·0	1 550	2·0*	
		0·010	54·0	87	2·7*	70
			55·0	400	2·5*	
			56·0	1 500	2·5*	
		0·020	54·0	70	3·4*	70
			55·0	290	3·4*	
			56·0	1 500	3·7*	

*n—not constant; value at $t_{1/2}$ quoted.

centage non-solvent, are shown in *Figure* 5(a) for the samples. It was clear that samples B, C, D and E were anomalous in appearing to titrate in several distinct stages over a wide range of percentage non-solvent. These samples also gave anomalously low specific turbidity values. Samples A, F, G and H titrated over a narrower volume range and clearly had narrower molecular weight distributions. By comparison with the lower samples, samples B, C, D and E contained a considerable proportion of low molecular weight material, and appeared to have the distribution of a mixture of low and high molecular weight polymers. These conclusions were to some

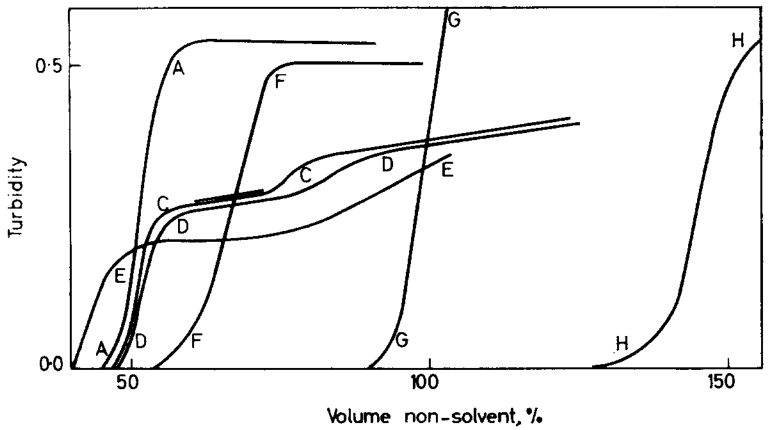

Figure 5—(a) Turbidity curves of bulk polymer samples; (b) turbidity curves of the fractions from sample E

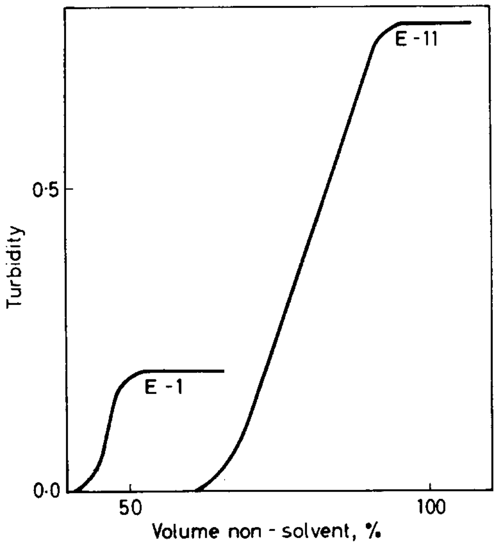

Figure 5(b)

extent substantiated by partial fractionation of samples B, D and E, using the solubility characteristics observed in the turbidity titration, see *Table 7*. Distinct separation was observed in the turbidity curves of these fractions, and to all intents and purposes these polymers behaved as mixtures of two distinct polymers of well separated molecular weight. This can best be seen from the turbidity curves of the fractions obtained from sample E, in *Figure 5*.

DISCUSSION

The anomalous crystallization behaviour of the polyethylene oxide samples cannot be attributed to any of the assumptions used in deriving the equation, or in analysing the isotherms. Yet in none of the crystallizations studied could the rate isotherms be fitted by a single Avrami equation. In general, continuously varying n values are observed, and two distinct behaviours can be distinguished. In the higher samples B, C and D the n value drops rapidly to 2·0 and is effectively constant (depending on choice of h_∞). The kinetic characteristics vary with sample dimensions and preheating temperature. These samples have broad molecular weight distribution. In the lower samples, the n value varies between 4·0 and 3·0, or between 4·0 and 2·0 according to the sample thickness and preheating treatment. This is consistent with so few spherulites being present that their dimensions approach those of the total sample and they are eventually constrained to grow as discs (for which $n = 3{\cdot}0$ or 2·0). The continuous change observed in the n value for sample E in either of the dilatometers A or B is consistent with crystallization progressively altering from sporadic nucleation of spheres to instantaneous discs.

Table 7. Fractionation

Sample	*Fraction*	*Wt%*	*Viscosity* *dl/g*
B	I	60–70	
	II	30	
D	I	61	2·60
	II	27	0·30
	III	10	0·10
			$M_n \times 10^3$
E	I	50	50
	II	50	6·6

It is likely that these effects can explain some of the characteristics of the higher molecular weight samples. Sample D was observed to grow as instantaneous spheres with growth rates 2×10^{-3} to $3{\cdot}5 \times 10^{-4}$ cm/min in the range 52·0° to 54·0°C. If no impingement has occurred the spherulites would have diameters similar to the sample thickness, see *Table 8*.

The experimental data on sample D, i.e. WSR 35 quoted by others[4], agree reasonably closely with those obtained in dilatometers B only, see *Table 8*. For this sample under these conditions the spherulites are clearly constricted to grow as discs.

Nucleation of the spherulites occurred within the bulk of the sample, and there was no preferred surface nucleation. Mercury droplets imbedded in thin polymer films, preheated to destroy most of the nuclei, i.e. at 100°C, showed no tendency to nucleate spherulites. The analysis of the crystallization isotherms in terms of surface nucleation, by Barnes *et al.*[1], is not valid especially not for the low molecular weight samples (see dilatometers C).

The higher molecular weight samples also have anomalously broad molecular weight distributions with a considerable fraction of low molecular weight material. This has an effect on the crystallization processes; the radial growth rates of partially fractionated materials are very different from

Table 8. Kinetic data

Sample D

Dilatometer	*Sample thickness cm*	*Crystn temp. °C*	*$t_{1/2}$ min*	*Spherulite diam. at $t_{1/2}$ cm*	*n values at $t_{1/2}$*
A	0·2	52·0	79	0·3	2·4
		53·5	133	0·1	2·4
B	0·02	51·9	15·0	0·06	1·8
		54·0	70·0	0·05	1·9

Comparison of sample WSR 35, i.e. D

Dilatometer	*Temp. °C*	*Z_1 $(min)^{1/n} \times 10^6$*	*n values*
B	51·9	4 080	1·8
	52·5	1 610	1·8
	53·2	853	1·9
	53·5	659	1·8
	54·0	331	1·9
Ref. 4	51·14	9 820	1·91
	53·77	1 390	1·99
	54·59	531	1·59
	55·63	23·2	1·51
	58·23	2·07	1·80

that of the unfractionated parent polymer[20]. Fractionating sample E considerably altered its crystallization rate constant but did not appreciably improve the fit of a single Avrami equation to these isotherms, see *Table 9*.

While the molecular weight distribution may have some effect on the ability of a polymer to crystallize, and on the ability to describe the overall crystallization by a single Avrami isotherm, the conclusions drawn from dilatometric results on polyethylene oxide samples concerning the applicability of the Avrami equation to describe the crystallization kinetics are suspect unless it can be conclusively shown that many spherulites are produced and their dimensions are very much less than those of the polymer

Table 9. Molecular weight distribution

Sample	*Cryst. temp. °C*	*n value*	*$t_{1/2}$ min*
E	52·8	3·3*	30
	54·0	3·3*	125
	54·6	3·0*	295
	55·0	3·3*	420
E–I	52·0	3·3*	83
	53·0	3·4*	320
	54·0	3·1*	1 330

samples used in the dilatometers. This is facilitated in polyethylene oxide by not preheating above about 70° to 80°.

R.L.T.S. is indebted to the University of Aberdeen for the award of a research studentship and M.S. thanks the Pakistan Council of Scientific and Industrial Research for leave of absence for the duration of this work.

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(*Received May 1968*)

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