The influence of molecular weight on the regime crystallization of linear polyethylene

J. G. Fatou and C. Marco
Instituto de Ciencia y Tecnología de Polímeros, Juan de la Cierva 3, Madrid-28006, Spain

and L. Mandelkern
Department of Chemistry, and Institute of Molecular Biophysics, Florida State University, Tallahassee, FL 32306, USA

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Overall crystallization rates of polyethylene fractions, ranging in molecular weight from 1.95×10^4 to 8.0×10^6, have been measured over the temperature range from 114 to 128°C. From kinetic analysis of these data, three distinct regimes have been detected. The assignment of the regimes has been made based on several mechanistic situations, which lead to the same temperature coefficient. The influence of molecular weight on the regime behaviour has been found to be very profound. It changes the type of regime that is observed, the slope of the temperature coefficient in regime II and the location of the transition temperature from one regime to another.

(Keywords: linear polyethylene; crystallization kinetics; regime crystallization)

INTRODUCTION

Polymer crystallization, whether manifested by observation of the overall crystallization rate, the spherulite growth rate or the growth of specific crystal faces, is a result of the rate of deposition of nuclei of a stable size (i.e. the steady-state nucleation rate) and their subsequent growth as well as the rate at which untransformed chain units are brought to the growing crystal faces. At temperatures in the vicinity of the melting temperature, the nucleation processes are so dominant that the crystallization rates can be formulated and explained solely in terms of steady-state nucleation rates[1]. Over an extended temperature range, particularly as the glass temperature is approached, the transport of chain units to the growing crystallite, i.e. their relaxation and mobility in the non-crystalline region, becomes an important factor. Under these conditions, because of the competition between the two different processes, a maximum is observed in the crystallization rate as a function of temperature[1–3].

In an analysis of nucleus formation and subsequent growth of small, non-chain-like molecules, on an already formed substrate (nucleation followed by growth), Hillig[4] pointed out that two extreme situations could exist with respect to crystallization temperature. These regions were later defined as regimes I and II. In regime I, Hillig[4] allowed the growth step, following nucleation, to sweep completely across the face of the crystal. A pause occurs before the next layer is nucleated. In other words, in this situation the rate of lateral growth of a nucleus across the crystal face is very much faster than the nucleation rate itself. In regime II, new growth steps are allowed to nucleate before the previous layer has completely filled the substrate. These two extremes manifest themselves in a difference in the slopes of the temperature coefficient of the crystallization process when the crystallization rate is plotted against the temperature function dictated by the appropriate nucleation function. For this three-dimensional growth problem, Hillig[4] and Calvert and Uhlman[5] found that the ratio of the slopes of regime II to I is 0.33.

Sanchez and DiMarzio[6] modified Hillig's work and adopted these concepts to polymer crystallization. In this case the dimensionality of the lateral growth along a crystal face is reduced by one. The height of a nucleus, or growth strip, is assumed constant, being determined only by the undercooling at which the crystallization takes place. This implies that growth along the chain axis is severely retarded relative to the lateral accretion of chain units, an assumption that is well justified for long-chain molecules. For polymers in regime I, the overall growth, or crystallization, rate is proportional to the steady-state nucleation rate. For the conditions defining regime II, the overall crystallization, or growth, rate is equal to the square root of the nucleation rate. Consequently, it turns out that the ratio of the temperature coefficient slope between regimes II and I is 0.5 for the lamellar crystallization of polymers, involving coherent nucleation[6,7]*.

Another case of interest that has also been considered is when the nucleation rate is greater than the rate at which the nucleus spreads out, or grows, on the substrate[8]. Under these conditions a crystallite does not develop much beyond the dimensions of a nucleus of critical size. The overall growth or crystallization rate will again be proportional to the nucleation rate. The temperature coefficient of the process will then be the same as for regime I. We shall call this case regime Ia, since it differs physically and mechanistically from regime

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[*] As should be self-evident, the conclusions reached above are made on very general grounds. There is no implication, or need, to assume any type of interfacial structure for the nucleus

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I, despite having the same temperature coefficient. At high crystallization temperatures and low undercoolings, this situation could be envisaged to occur with very high-molecular-weight species. In another extreme we can have the situation where the rate of nucleation is so high (large undercooling and low crystallization temperature) that the concentration of nuclei becomes so dense that there is not sufficient space for subsequent lateral growth. The crystallization rate will again be proportional to the steady-state nucleation rate and the temperature coefficient will be the same as in regimes I and Ia. This situation has been called regime III[9]†.

Another physical situation that can be envisaged is concerned with the relative rate at which chain units cross the crystal, or nuclei–liquid, interface. When the chain mobility becomes sufficiently restricted, as for example when the crystallization temperature approaches the glass temperature, then, because of the lack of chain mobility, crystallite sizes will not develop much larger than that of nuclei from which they form. We again have the situation of essentially just laying down stable nuclei. This situation, however, does not require an excessively high nucleation rate as is characteristic of regime III, although the crystallization rate is again proportional to the nucleation rate. This condition will be true for all molecular weights. We designate this case as regime IIIa and note that it will have the same temperature coefficient as regime III. We distinguish between the two cases because regime IIIa does not necessarily require very high nucleation rates, which is the physical basis that has been expounded for regime III[9]. Although our descriptions for the basis of regimes IIIa and Ia appear to be identical, it is appropriate to distinguish between them because they can occur for quite different molecular and mechanistic reasons. In addition, to analyse experimental data appropriate to regime IIIa, it is necessary to introduce the transport term into the analysis. In doing so an element of arbitrariness is introduced. However, in all the other cases that have been described, just introducing the steady-state nucleation rate into the problem suffices. We thus can describe and anticipate several different regimes, or variants thereof. For all but one (regime II) the crystallization rate is proportional to the nucleation rate; for one of these (regime IIIa) an appropriate temperature-dependent transport term needs to be introduced into the analysis.

Since the introduction of the regime concept in polymer crystallization, there has been a great deal of experimental verification of these ideas. For example, regime I–II transitions have been observed in linear polyethylene[10–12], poly(1,3-dioxolane)[13], poly(L-lactic acid)[14], i-polypropylene[15], poly(ethylene oxide)[12,16], *cis*-1,4-polyisoprene[17] and poly(3,3-dimethyl thietane)[18]. Transitions from regime II to what has been defined as regime III have been experimentally observed in i-polypropylene[19,20], polyoxymethylene[21], *cis*-1,4-polyisoprene[17], poly(3-hydroxybutyrate)[22], poly(*p*-phenylene sulphide)[23], poly(3,3-dimethyl thietane)[18] and poly(1-butene)[24]. The existence of regime III has been inferred for linear polyethylene by *estimates* of two low-temperature growth rates from data obtained from the crystallization of droplets[9,25,26]. With several exceptions and the estimates for polyethylene, regime III has often been observed in the vicinity of the temperature for the maximum growth rate. Therefore, the deduction that regime III exists (more properly IIIa in the above description) has involved the introduction of the transport function in one form or another. This function is always selected to give a regime II–III transition and is not the same for each polymer. Based on this type of analysis, three regimes have been observed in *cis*-1,4-polyisoprene[17], poly(3,3-dimethyl thietane)[18] and poly(1-butene)[24].

The major purpose of the investigation that is reported here was to explore the molecular-weight dependence of regime formation. This involves an identification of the regimes, the location of the temperature of transition from one to another and an analysis of the slopes of the temperature dependence of the crystallization rate. To accomplish this objective it is necessary to utilize fractions that cover as wide a molecular-weight range as possible. Reported studies of the influence of molecular weight on regime behaviour have been limited. Overall crystallization rates of poly(3,3-dimethyl thietane) fractions ranging from 6.5×10^3 to 1.04×10^5 have been studied and three regimes reported[18]. Studies of poly(phenylene sulphide) have been limited to two unfractionated samples[23]. For $M_w=51\,000$ a regime II–III (or IIIa) transition was observed. For $M_w=15\,000$ only regime IIIa was deduced. In studies of the spherulite growth rate of fractions of *cis*-1,4-polyisoprene the analysis, and conclusions drawn therefrom, depends crucially on the nature of the transport term introduced[17]. With this understanding of the method of analysis, one regime, defined as III, was found for the two highest molecular-weight fractions $M=8.97\times10^5$ and $M=1.12\times10^6$. When the molecular weight is decreased, a II–III transition is observed. For the two lowest molecular weights studied, $M=3.51\times10^5$ and $M=3.13\times10^5$ three regimes are observed with this type of analysis. Detailed studies of the I–II transition in linear polyethylene fractions have been reported from growth-rate studies of supermolecular structures, i.e. spherulites and axialites[10,27]. This method of observation limits the molecular-weight range that can be studied[10,28–30], so that the data reported are restricted to $M=10^4$ to 10^5.

Conventionally, studies of crystallization kinetics to observe regime behaviour have focused on measuring the growth of spherulites or other well defined supermolecular structures. Since it is now well established that supermolecular structures do not develop over the complete molecular-weight range[28–30], studies of growth rate are thus limited in scope, particularly for the purposes at hand. This restraint is most clearly illustrated for linear polyethylene and poly(ethylene oxide)[12]. Since the overall lamellar growth rate is the fundamental quantity of interest, it had been tacitly assumed that an analysis of the overall crystallization rate is not suitable for the study of regimes. However, it has been shown, in comparative studies with polyethylene and poly(ethylene oxide), that the same results are obtained from either the overall crystallization rate or the growth rate of supermolecular structures[12]. Since there is no molecular-weight limitation to the study of the overall crystallization rate, it is appropriate for present studies, since it gives a much broader database for analysis. The need for investigating a very wide range in molecular weight was indicated in earlier work cited and will become apparent from the new experimental data reported here. To accomplish the objectives that have been set forth, we report the results

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† A similar situation should also apply to the three-dimensional process studied by Hillig[4] and Calvert and Uhlman[5]

of a study of the overall crystallization rate of linear polyethylene fractions covering the range 1.95×10^4 to 8×10^6. We present data for the widest ranges in molecular weight and crystallization temperature that have been reported for the crystallization kinetics of linear polyethylene. We limit our analysis here to the consideration of regimes as described above. In a subsequent report we shall consider the more general aspects of the relation between crystallization rate, temperature and molecular weight.

EXPERIMENTAL

Materials

The linear polyethylene fractions used in this work were obtained from several sources. Fractions were obtained from Marlex 50 (a linear unfractionated polyethylene sample manufactured by Phillips Petroleum Co.) by column fractionation using the technique that has been described previously[31]. The highest molecular-weight fractions were obtained from a Hifax sample (a linear, high-density polyethylene sample, manufactured by Hercules Powder Co. with a viscosity-average molecular weight of 7×10^6) by a liquid–liquid separation method that has also been previously described[32–34]. The solvent/non-solvent system used was tetralin and a low-molecular-weight poly(ethylene glycol). *N*-Phenyl-2-naphthylamine was added to the solvent to prevent oxidation. The fractionation temperature was 130°C and through the entire fractionation process the system was kept under N_2 atmosphere, and exposure of hot solution to air was avoided as much as possible. The fractions were precipitated with acetone, previously cooled by addition of small pieces of dry ice. The sample was filtered, washed repeatedly with acetone and dried in a vacuum oven for 24 h at 40°C.

The determination of the intrinsic viscosities of the obtained fractions has been described elsewhere[11]. The intrinsic viscosities were determined in the conventional manner by extrapolating the linear plot of η_{sp}/c against concentration c to zero concentration. Viscosity-average molecular weights were obtained from the relation:

$$[\eta] = 6.20 \times 10^{-4} M_n^{0.7}$$

given by Chiang[35] for decalin at 135°C.

For fractions whose molecular weights were less than 1×10^6, the ratio of the weight- to number-average molecular weights was less than 1.1.

Besides the fractions obtained by fractionation, two fractions of linear polyethylene were obtained from the Société Nationale des Pétroles D'Aquitaine (SNPA). Their characteristics were: $M_n = 19\,000$, $M_w = 20\,400$; and $M_n = 107\,000$, $M_w = 115\,000$.

Crystallization kinetics

The crystallization kinetics studies were carried out using calorimetric techniques. The general principles have been previously described in detail[36]. All d.s.c. measurements were made on a Perkin–Elmer DSC 7 instrument. Automatic calibration was carried out with indium, $T_m = 156.60°C$, $\Delta H_u = 28.45\ J\ g^{-1}$, and zinc, $T_m = 419.47°C$, $\Delta H_u = 108.37\ J\ g^{-1}$, as standards supplied by Perkin–Elmer.

For kinetics experiments, sample sizes were 3–10 mg. The samples were all placed in aluminium pans, weighed and crimped. The sample pan was then placed in one sample holder while a reference pan was placed in the other. The samples were heated 20°C above the corresponding melting temperature for 10 min. This procedure ensured the complete melting of the sample. These conditions were used in all the experiments. Subsequently, the samples were undercooled at a rate of $64°C\ min^{-1}$ until the desired crystallization temperature was reached and the corresponding crystallization exotherms scanned as a function of time until no change in the d.s.c. energy axis was observed. The partial area corresponding to 25% of the total transformation was determined from the data points stored for each isothermal crystallization run on a PE 7700 computer by using DSC 7 kinetics software.

RESULTS AND DISCUSSION

General results

Quantitative kinetic data could be obtained in the temperature interval from 114 to 128°C depending on the molecular weight. At higher temperatures the rates become too slow to measure by calorimetry in a reasonable time period, and at lower temperatures the crystallization rates become so rapid as to preclude accurate measurements. The times required are in the range of the equipment response. The conclusion is that the region between 115 and 128°C is the most adequate for the calorimetric technique and the precision of the points in this range is higher. The crystallization times reported here range from about 4 min at the lower crystallization temperature to about 1500 min at the higher one.

The influence of molecular weight on the timescale of the crystallization process is shown in *Figure 1*. This shows a plot, on a double logarithmic scale, of the time required for 25% of the total transformation to develop, $\tau_{0.25}$, as a function of molecular weight at the given crystallization temperature.

Although there is only a very small change of $\tau_{0.25}$ with molecular weight at lower crystallization temperatures, the dependence becomes very steep at higher crystallization temperatures and lower molecular weights, and it changes monotonically between the extremes. A

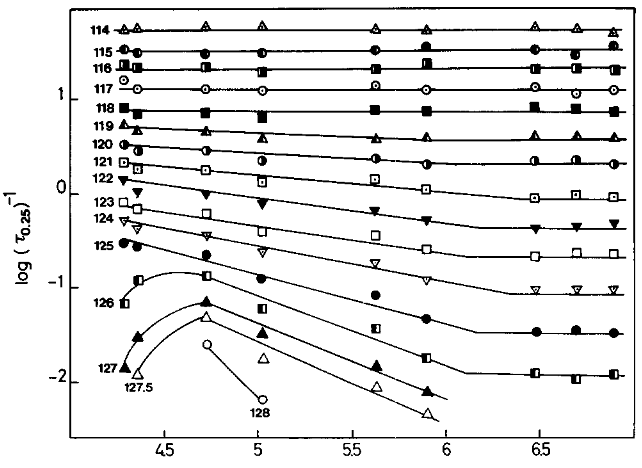

Figure 1 Plot of $\log(\tau_{0.25})^{-1}$ against $\log M_n$ at indicated crystallization temperatures

maximum in the timescale is even reached at crystallization temperatures higher than 125°C. The molecular weight at which the crystallization rate achieves its maximum value depends on the crystallization temperature. The maximum is shifted to lower molecular weights as the crystallization temperature is decreased, and it is more pronounced at the higher crystallization temperatures. For molecular weights greater than that which corresponds to the maximum, the relation between $\tau_{0.25}$ and molecular weight depends on crystallization temperature. Moreover, in the higher molecular-weight range, no dependence of the crystallization rate on chain length would be expected. These results agree with those obtained previously on the influence of molecular weight on the crystallization rate[11].

Several attempts to explain the relation between crystallization rate, molecular weight and temperature have been reported in the literature[37–39]. Most of these analyses have been for limited ranges in molecular weight and crystallization temperature. Our present purpose is to assess the influence of molecular weight on the regime behaviour. A more detailed discussion and analysis of the influence of molecular weight and crystallization temperature is currently under way and will be presented elsewhere[40].

The influence of the crystallization temperature on the timescale of the crystallization process is very pronounced. *Figure 2* shows the plot of $(\tau_{0.25})^{-1}$ as a function of the temperature of crystallization. The data for the highest molecular-weight fractions, 1×10^6 to 8×10^6, fall on only one curve. No apparent discontinuity is found in the plot. However, for the intermediate molecular-weight region (8×10^5 to 5×10^4), the plots clearly exhibit one discontinuity around $T_c=118$ to 121°C, depending on molecular weight.

An important observation is that these curves resemble those reported in growth rates[10–17]. These in turn were related to changes in regimes. Put another way, the curves for the lower molecular weights exhibit breaks. Their significance in terms of regimes will be discussed later.

Another interesting point is that a deviation is observed at high temperature for the fractions $M_n=1.95\times10^4$ and 2.3×10^4. The temperature range in which these deviations occur corresponds to the region where the crystallization rate decreases very dramatically (see *Figure 1*). The crystallization times increase over several decades as the molecular weight decreases. Since the free energy of nucleus formation is, according to nucleation theories[41,42], very dependent on molecular weight for chains of less than $M_w=5\times10^4$, the strong influence of molecular weight on crystallization rate offers a plausible explanation.

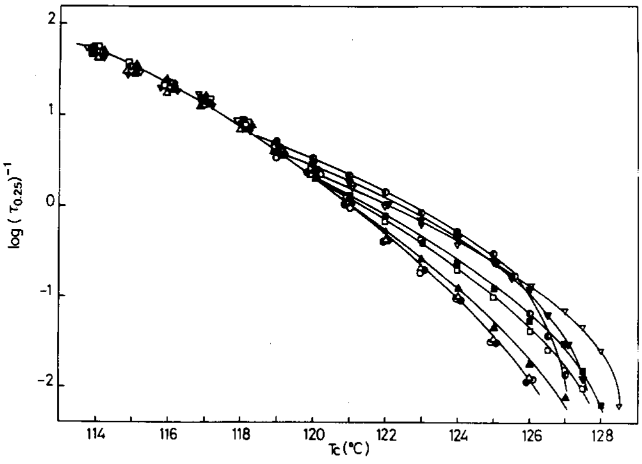

Figure 2 Plot of $\log(\tau_{0.25})^{-1}$ against crystallization temperature for indicated molecular weights: (○) 8×10^6; (●) 5×10^6; (△) 3×10^6; (▲) 8×10^5; (□) 4.25×10^5; (■) 1.07×10^5; (▽) 5.3×10^4; (▼) 2.3×10^4; (◐) 1.95×10^4

Another important observation that can be made from these data is the fact that the exponent n of the Avrami equation changes with molecular weight, as has been previously reported[11]. The value is $n=3$ for the molecular-weight range from 1.95×10^4 to 8×10^5. This value is reduced to $n=2$ for the highest molecular weights.

Crystallization temperature coefficient

Another way of analysing these data is to consider the temperature coefficients of the crystallization rate. The steady-state nucleation rate $\dot{N}$ for all nuclei types is given by[43]:

$$\dot{N}=N_0\exp\left(\frac{-E_D}{RT}-\frac{\Delta G^*}{RT}\right) \tag{1}$$

where N_0 is a constant, E_D is the energy of transport in the solid–liquid interface and ΔG^* is the free energy of forming a stable nucleus.

The equations describing the critical conditions for nucleation have, for chains of infinite molecular weight, the same analytical form as the equations derived for a collection of monomeric molecules with similar arrangement in the nucleus. However, theory pertinent to finite molecular-weight chains presents significant differences. The critical conditions have been obtained for both three-dimensional homogeneous nucleation[41] and coherent two-dimensional nucleation[42].

In the nucleation of chains of finite length, which involves the unimolecular deposition of chain sequences, the critical conditions are given by[42]:

$$\Delta G^*=2\sigma_u\xi^* \tag{2}$$

where

$$\xi^*=\frac{2\sigma_e-RT_c\ln(x-\xi^*+1)/x}{\Delta G_u-RT_c/x} \tag{3}$$

In these equations, σ_e and σ_u are the interfacial free energy per sequence as it emerges from the basal plane of the nuclei and the lateral interfacial free energy, respectively; x is the number of repeat units along the chain direction in the nucleus; and ΔG_u is the free energy of fusion per repeat unit of the infinite chain. This quantity can be approximated by:

$$\Delta G_u=\Delta H_u(T_m^\circ-T)/T_m^\circ$$

where T_m° is the equilibrium melting temperature of the infinite-size chain.

In the limit of high molecular weights and low undercooling, ΔG^* is reduced to:

$$\Delta G^*=\frac{4\sigma_e\sigma_u}{\Delta G_u}=\frac{4\sigma_e\sigma_u T_m^\circ}{\Delta H_u\,\Delta T} \tag{4}$$

where ΔH_u is the heat of fusion and ΔT is the undercooling. The result in equation (4) is the classic result for a Gibbs-type nucleus made up of small molecules and is independent of the shape of the nucleus and the chain disposition within it.

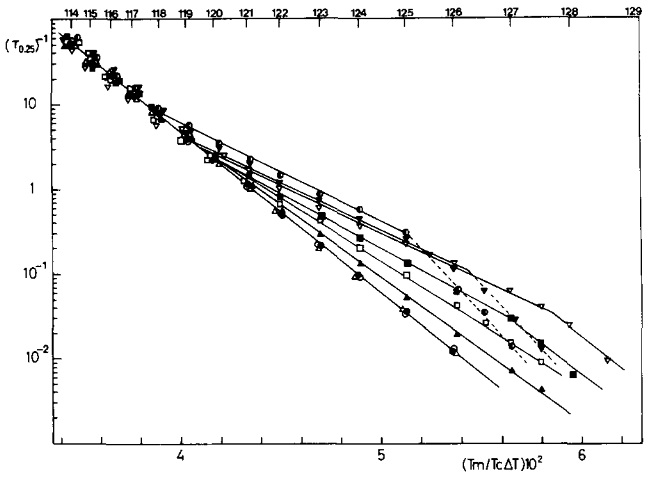

Figure 3 Plot of $\log(\tau_{0.25})^{-1}$ against $T_m^\circ/T_c\,\Delta T$ at indicated molecular weights: (○) 8×10^6; (●) 5×10^6; (△) 3×10^6; (▲) 8×10^5; (□) 4.25×10^5; (■) 1.07×10^5; (▽) 5.3×10^4; (▼) 2.3×10^4; (◐) 1.95×10^4. $T_m^\circ=145.5°C$

The analysis of the temperature coefficient can be carried out by incorporating the nucleation rate into the expression for the overall crystallization rate at low transformation levels. Since we are only dealing here with a small temperature interval in the vicinity of the melting temperature, there is no need to introduce the transport term. The validity of this assumption will be discussed subsequently in the analysis of the experimental data.

In order to avoid complications in the analysis of the temperature coefficient of the crystallization rate, we will consider first molecular-weight fractions where nucleation does not need to be corrected for finite chain length. This includes molecular weights from 5.3×10^4 up to 8×10^6. The experimental data can be treated according to equations (1) and (2) if the equilibrium melting temperature for polyethylene is defined. Despite the importance of this parameter in the analysis of crystallization kinetics, direct experimental determination has proved to be very elusive. Recourse has been made to theory and to the development of extrapolation procedures of experimental data. The theoretical treatment and suggested extrapolations give an equilibrium melting temperature for infinite molecular-weight polyethylene of $145.5\pm1.0°C$[44,45]. The equilibrium melting temperature of the real finite chain is not involved in the formulation of the critical nucleus dimensions. Consequently, plots of $\ln(\tau_{0.25})^{-1}$ against $(T_m^\circ/T_c\,\Delta T)$ should give a straight line according to equation (1).

The temperature coefficients were determined from the plots of *Figure 3*. For fractions greater than 800 000 the same linear relation is obtained for the whole range of crystallization temperatures. This result is in accord with the results that have been reported for a large number of unfractionated polymers[46] and with previous results on polyethylene[11].

An interesting feature of *Figure 3* is that, for molecular weights of 800 000 and lower, the data cannot be given by a linear representation. However, the data for 800 000 and 425 000 can be represented by two intersecting straight lines. Three intersecting straight lines give a very good representation of the lower molecular-weight data. In the same figure, fractions with $M_w=23\,000$ and 19 500 are included for comparative purposes. These molecular weights are in a range where ΔG^* changes with chain length.

The existence of breaks in the temperature coefficient has been previously described when growth rate or overall rate data[10,11] were examined in polyethylene. Results that are comparable with those reported here were published previously[11] without recognition of the relationship in terms of Hillig's analysis.

In order to analyse the low-molecular-weight region (fraction with $M_w<5.3\times10^4$), the corrections for finite molecular weight in the nucleation theory need to be brought in, according to equations (2) and (3). These corrections depend on the choice of σ_e. There is not a unique analysis for chains in this region because the parameter σ_e has to be used and cannot be deduced from the data. Reasonable values of σ_e appear to be in the range 1000 to 5000 cal mol^{-1} (299 to 1493 J g^{-1})[47].

From the slope of the highest molecular-weight fraction, the product $\sigma_e\sigma_u$ can be obtained. It is obvious that σ_e and σ_u cannot be independently determined. If a value of $\sigma_u=100$ cal mol^{-1} is assumed, comparable with the values deduced for low-molecular-weight n-paraffins from kinetics studies involving isolated droplets[48], σ_e is 2100 cal mol^{-1} (627 J g^{-1}). This value has been used in equations (2) and (3) to calculate the values of $\Delta G^*/RT_c$ used in *Figure 4*.

The major characteristics of the plots in *Figure 3* are maintained in *Figure 4*. As was found in the previous analysis (*Figure 3*), the slopes in the high-temperature region for the two lowest molecular-weight fractions are higher than those corresponding to higher molecular-weight fractions. Variations in σ_e do not affect this conclusion as is illustrated in *Figure 5*. This figure is a plot of $\ln(\tau_{0.25})^{-1}$ against $\Delta G/2\sigma_u T=\xi^*/T$ for three different values of σ_e, 1500, 2000 and 4000 cal mol^{-1}. In the three cases the slopes in the region of the highest crystallization temperatures are higher for the two lower molecular-weight fractions compared with those corresponding to the highest molecular weights. The difference only occurs at the lowest undercoolings. This is the region in which the minimum in rate was found (see *Figure 1*).

The slopes of the straight lines from *Figures 3, 4* and *5* are given in *Table 1* for each of the molecular weights. Slopes in regime I for fractions 8×10^5 and 4.25×10^5 are

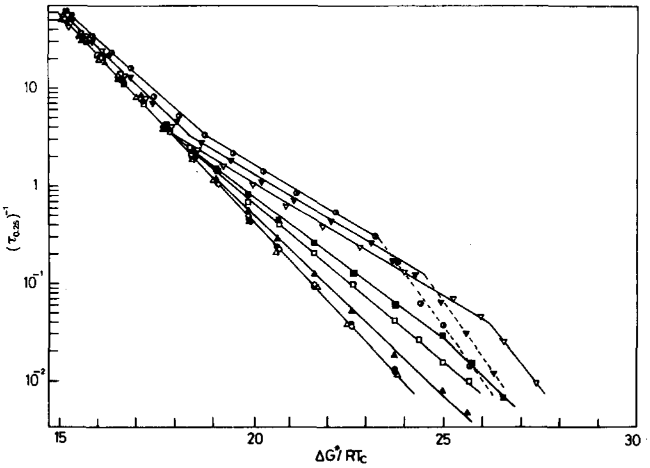

Figure 4 Plot of $\log(\tau_{0.25})^{-1}$ against $\Delta G^*/RT_c$ at indicated molecular weights: (○) 8×10^6; (●) 5×10^6; (△) 3×10^6; (▲) 8×10^5; (□) 4.25×10^5; (■) 1.07×10^5; (▽) 5.3×10^4; (▼) 2.3×10^4; (◐) 1.95×10^4. $T_m^\circ=145.5°C$; $\sigma_u=100$ cal mol^{-1}; $\sigma_e=2100$ cal mol^{-1}

Table 1 Slopes

Molecular weight	From $T_m^\circ/T\Delta T^a$			From $\Delta G^*/RT_c{}^b$			From ξ^*/T_c; $\sigma_e=1500$			From ξ^*/T_c; $\sigma_e=4000$		
	III	II	I	III	II	I	III	II	I	III	II	I
$8\times10^{6\,c}$	−181.3	−181.3	−181.3	−0.423	−0.423	−0.423	−59.9	−59.9	−59.9	−22.5	−22.5	−22.5
$5\times10^{6\,c}$	−180.2	−180.2	−180.2	−0.423	−0.423	−0.423	−59.6	−59.6	−59.6	−22.4	−22.4	−22.4
$3\times10^{6\,c}$	−188.5	−188.5	−188.5	−0.426	−0.426	−0.426	−60.4	−60.4	−60.4	−22.7	−22.7	−22.7
8×10^5	−187.8	−161.4	–	−0.424	−0.365	–	−60.0	−51.9	–	−22.5	−19.4	–
4.25×10^5	−189.4	−148.1	–	−0.428	−0.334	–	−58.3	−47.3	–	−22.5	−17.7	–
1.07×10^5	−197.8	−146.2	−218.0	−0.444	−0.328	−0.488	−62.4	−46.1	−67.2	−23.5	−17.4	−24.3
5.3×10^4	−186.5	−102.1	−210.6	−0.416	−0.227	−0.466	−59.1	−31.9	−62.6	−22.2	−12.1	−25.4
2.3×10^4	−184.5	−101.8	−210.8	−0.404	−0.213	−0.455	−57.8	−30.5	−64.9	−21.6	−11.1	−23.7
1.95×10^4	−163.6	−100.1	−239.4	−0.356	−0.210	−0.512	−50.5	−31.1	−72.3	−18.7	−11.1	−26.5

[a] $T_m^\circ=145.5°C$

[b] ΔG^* calculated with $\sigma_e=2100\,\mathrm{cal\,mol^{-1}}$

[c] Fractions from $M=8\times10^6$ to 3×10^6 do not have any change in slope and regime changes are not as indicated

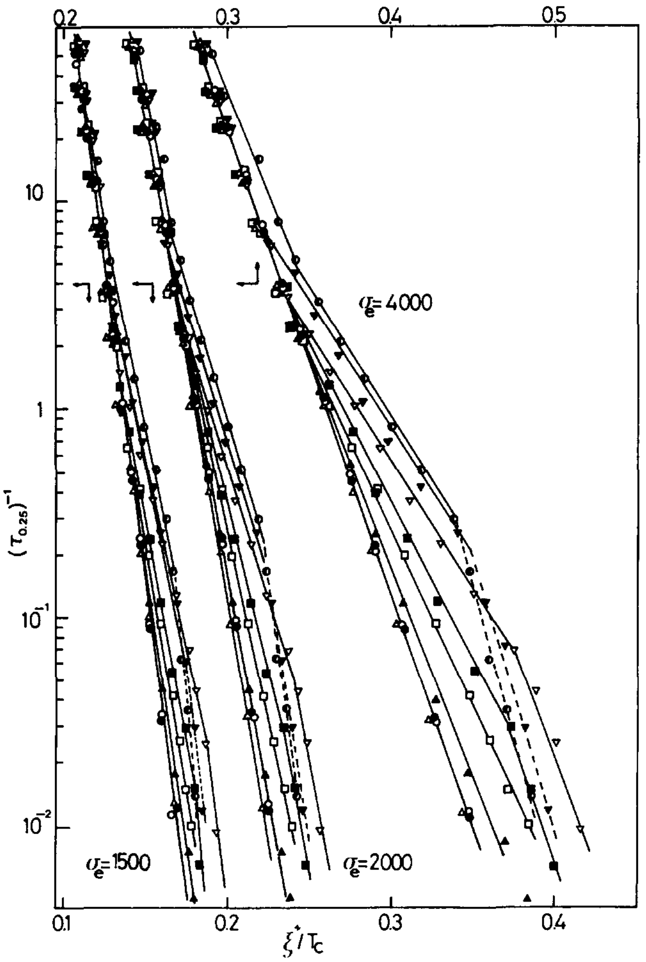

Figure 5 Plot of $\log(\tau_{0.25})^{-1}$ against ξ^*/T_c at indicated molecular weights: (○) 8×10^6; (●) 5×10^6; (△) 3×10^6; (▲) 8×10^5; (□) 4.25×10^5; (■) 1.07×10^5; (▽) 5.3×10^4; (▼) 2.3×10^4; (◐) 1.95×10^4. Three different values of σ_e are indicated

not indicated, because this regime occurs for these fractions at temperatures in which calorimetric measurements have not been obtained. One can anticipate that, based on previous observations[11], they fall in line with the lower molecular-weight fractions. The relative values of the slopes in each of the regions are the same irrespective of the specific method of analysis that leads to *Figures 3, 4* or *5*.

The fact that the data in *Figures 3, 4* or *5* can be represented by sets of intersecting straight lines (or a single straight line) is highly reminiscent of the characteristics of regime crystallization. This conclusion is readily confirmed by examining in more detail the actual values of the slopes and their ratios. The slopes are given in *Table 1* and the slope ratios are summarized in *Table 2*. The different methods of analysis yield essentially the same results. At lower undercoolings the slopes are nearly constant for all the molecular weights including the very high ones. The only exceptions, as was seen in the figures, are the slopes for the two lowest molecular-weight fractions, which are just slightly lower. The data for the three highest molecular weights are well represented by a single straight line over the whole range of crystallization temperatures, i.e. 114 to 126°C. The slope of this straight line is the same as that of the lower molecular weights (1.07×10^5 to 1.95×10^4) at higher crystallization temperatures. For the lower molecular weights, crystallization in this temperature range can be assigned in a straightforward manner to regime I. As the crystallization temperature is lowered, the transition to regime II is quite clearly discerned*. A unique observation is made here. The very interesting and important feature in these plots is that the slopes for these fractions increase continuously in this regime as the molecular weight increases. They are consistent with, and join smoothly with, the high-temperature slopes of $M=4.25\times10^5$ and 8×10^5, which are also molecular-weight-dependent, and do not show a transition to regime I within the crystallization temperature range studied. Consequently, as will be discussed further below, the ratio of the slopes from regime II to I is not a constant but varies with molecular weight.

As the temperature is lowered further, for all fractions except $M=3\times10^6$ to 8×10^6, there is another sharp break in the slopes, which indicates the domain of another regime. Since the slopes of this regime are the same, within experimental error, with those of regime I, it is assigned regime III. We have thus observed a regime II–III transition in linear polyethylene by the *direct observation* of the overall crystallization rate. There has been no need

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* Based on previous observations[11], this regime I–II transition would also be observed for higher molecular-weight fractions, up to and including $M=8\times10^5$, if the kinetic studies were extended to higher crystallization temperatures

Table 2 Slope ratios

Molecular weight	From $T_m^\circ/T\Delta T$[a]			From $\Delta G^*/RT_c$[b]			From ξ^*/T_c; $\sigma_e=1500$			From ξ^*/T_c; $\sigma_e=4000$		
	II/I	II/III	III/I	II/I	II/III	III/I	II/I	II/III	III/I	II/I	II/III	III/I
8×10^6 [c]	1	1	1	1	1	1	1	1	1	1	1	1
5×10^6 [c]	1	1	1	1	1	1	1	1	1	1	1	1
3×10^6 [c]	1	1	1	1	1	1	1	1	1	1	1	1
8×10^5 [d]	0.86	0.86	1.0	0.86	0.86	1.0	0.86	0.86	1.0	0.86	0.86	1.0
4.25×10^5 [d]	0.78	0.78	1.0	0.78	0.78	1.0	0.81	0.81	1.0	0.79	0.79	1.0
1.07×10^5	0.67	0.74	0.91	0.67	0.74	0.91	0.69	0.74	0.93	0.72	0.74	0.97
5.3×10^5	0.49	0.55	0.88	0.49	0.55	0.89	0.51	0.54	0.94	0.48	0.54	0.87
2.3×10^5	0.48	0.55	0.88	0.47	0.53	0.89	0.47	0.53	0.89	0.47	0.51	0.91
1.95×10^5	0.42	0.60	0.68	0.41	0.59	0.69	0.43	0.62	0.70	0.42	0.59	0.70

[a] $T_m^\circ=145.5°C$

[b] ΔG^* calculated with $\sigma_e=2100\,\text{cal mol}^{-1}$

[c] Fractions from $M=8\times10^6$ to 3×10^6 do not have any change in slope and regime changes are not as indicated

[d] It has been assumed that these fractions have the same slope in regime I as in regime III

to introduce any transport term, over the range of crystallization temperatures studied, in order to achieve this result. Neither was there any necessity to *estimate* growth rates to establish the existence of regime III for linear polyethylene[9,25,26]. This latter result presents an interesting dilemma. The establishment of regime III by the experimental methods described here validates the estimate of the overall growth rate made previously from droplet experiments in order to demonstrate this regime in linear polyethylene[9,26]. However, as has been pointed out by Barham *et al.*[26], this growth rate is at least six orders of magnitude greater than has been estimated as being necessary for the reeling-in of chains from the entangled melt in order to form crystallites of regularly folded chains[38]. This dilemma is thus easily resolved by discarding the reeling-in hypothesis, which has been shown to be untenable on other grounds as well[49,50].

As we have previously noted, the crystallization rate–temperature data for the three highest molecular-weight fractions can be represented by a single straight line. No discontinuities in the slope are observed. This fact does not mean that the crystallization in the temperature interval studied, which is the same as that of the other fractions, is occurring in just one regime. As was pointed out in the 'Introduction', there are several different regime modes, with different mechanisms, that give the same temperature coefficient. The slope is the same as that of regime I for the lower molecular-weight fractions. However, since no transition to regime II is observed in the appropriate temperature range for the fractions $M=(3\text{–}8)\times10^6$, we assign this crystallization to regime Ia. If the high-temperature range is in regime I, the transition to regime II should have been observed. The further rationale for this regime assignment is that the steady-state nucleation rate is not very molecular-weight-dependent. However, the rate g of lateral growth of the nucleus could show such dependence (see below). Thus, when g becomes sufficiently small, crystallization will not proceed much beyond stable nuclei size and the system will be in regime Ia. At lower crystallization temperatures, the steady-state nucleation rates of the three highest molecular-weight fractions, which are of concern at this point, should be comparable with that of the lower molecular-weight species. Consequently, crystallization is taking place in regime III. Since the temperature coefficients of regimes III and Ia are the same, a single straight line is observed in *Figures 3, 4* and *5*. There is no outward evidence of a transition in regimes.

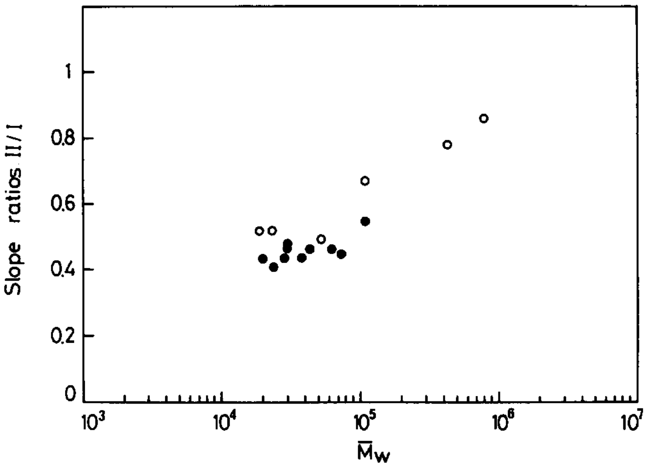

Figure 6 Plot of slope ratios II/I against molecular weight: (○) this work; (●) ref. 10

The ratios of the slopes between regime II and regime I with molecular weight are plotted in *Figure 6**. Also plotted in the figure are the corresponding data obtained from the study of growth rates of supermolecular structures. In the limited range where the molecular weights overlap, comparable results are obtained between the two experimental techniques. In this molecular-weight range the ratio is about 0.5 as was predicted in the initial analysis[10]. However, when an extended molecular-weight range is examined, based on the rate of overall crystallization, we find there is a linear increase in this ratio with molecular weight. A ratio of unity is being approached in the limit of very high molecular weight. If a linear extrapolation is extended to lower molecular weights, a value of approximately 0.3 is found for this ratio. This value is consistent with the ratio found for low-molecular-weight polyethylene fractions[51] and the high-molecular-weight n-alkane $C_{192}H_{386}$[52].

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* We assume in this plot and in *Table 2* that fractions $M=8\times10^5$ and 4.25×10^5 have the same slope in regime I as in regime III

The molecular-weight dependence of the slopes in regime II and consequently the variation in the slope ratio between regimes II and I must involve the interrelation between the steady-state nucleation rate and the rate g at which the nucleus develops, or spreads, laterally. Since the nucleation rate will not be very molecular-weight-dependent, the burden falls on the quantity g. This conclusion is to be expected since all types of growth processes should be molecular-weight-dependent. There is the direct molecular-weight effect of entanglements that limits the crystallizability of units and the indirect effect on the mobility of the chain. Our experimental results indicate that, at molecular weights of the order of $(1\text{–}5)\times10^4$, the classical description of regimes I and II are operative and the ratio of slopes is 0.5. However, at the very highest molecular weight, the quantity g becomes so small that the system is in regime Ia and the apparent slope ratio is unity. At molecular weights between these two extremes there is a steady decrease in g, which is reflected in the slope ratio. The quantity g must make a major contribution to the molecular-weight dependence of the overall crystallization rate and will of course be operative over the complete temperature range, including all regimes.

It should be emphasized that the effect of molecular weight on the slopes in regime II would not be detected if we arbitrarily restricted our measurements to the growth rate of supermolecular structures. Moreover, regime III is directly observed by determining the overall crystallization rate utilizing techniques sensitive to very rapid crystallization rates. The virtue of this classical method in studying crystallization kinetics should not be underestimated.

Another aspect of regime crystallization that can be analysed is how the temperature of the transition from one regime to another depends on the molecular weight. In *Figure 7* the transition temperature between regimes I and II, $T_{\text{I–II}}$, is plotted against the molecular weight for the work reported here, from previous studies of the overall crystallization rate by dilatometry[11] and from the growth-rate studies of supermolecular structures[10]. Over the molecular-weight range of overlap the data from all sources give the same results. However, the studies of overall crystallization rates significantly extend the molecular-weight range of interest and make clear that there is a small but significant dependence of $T_{\text{I–II}}$ on molecular weight. At the higher molecular weights $T_{\text{I–II}}$ is essentially constant at about 128–129°C. However, as the molecular weight decreases below $M=10^5$, $T_{\text{I–II}}$ decreases to 125°C. This change in $T_{\text{I–II}}$ with molecular weight can again be attributed to the variation of g with chain length.

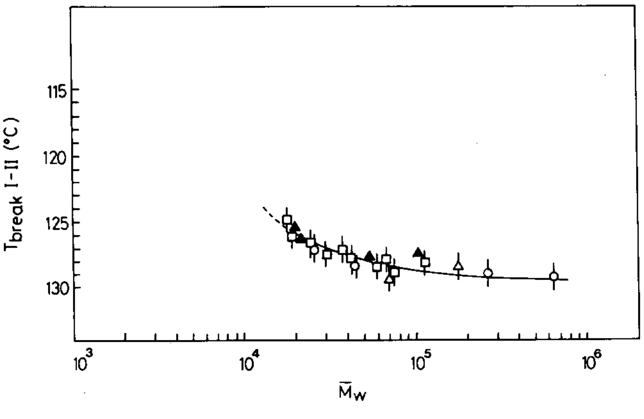

Figure 7 Plot of $T_{\text{I–II}}$ against molecular weight: (▲) this work; (○) and (△) PE overall rate, refs. 11, 12; (□) ref. 10

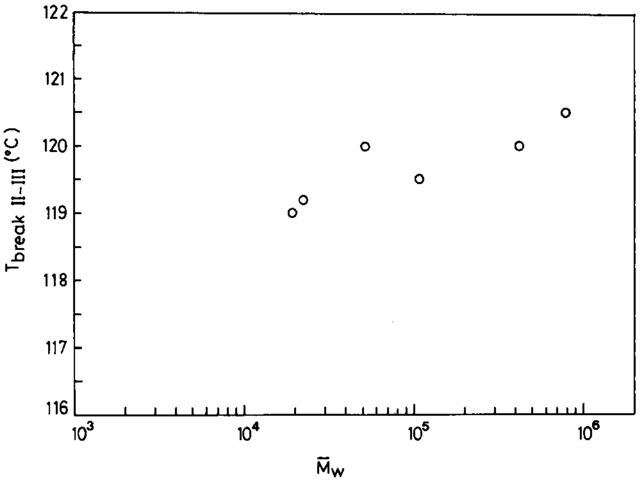

Figure 8 Plot of $T_{\text{II–III}}$ against molecular weight

The transition temperatures between regimes II and III, $T_{\text{II–III}}$, are plotted in *Figure 8* as a function of molecular weight. We find that, for the molecular-weight range within which this regime transition is observed ($<10^6$), there is a slight dependence of the transition temperature on molecular weight. The transition temperature increases with molecular weight from $T_{\text{II–III}}=$ 119°C for $M_w=1.95\times10^4$ to 120.5°C for $M_w=8.0\times10^5$. This transition has been predicted to occur[9] at $T_{\text{II–III}}=$ 121°C, a value which is very close to that observed experimentally. We should note that regime III is observed without the need to introduce any transport term. The analysis only involves the steady-state nucleation rate. However, we have found from detailed calculations that introducing any of the standard forms that have been used for the transport term does not alter any of the conclusions with regard to the regimes, their slopes and transitions.

CONCLUSIONS

In summary, by studying the overall crystallization rates of linear polyethylene fractions over a wide range in molecular weight and crystallization temperatures, we have been able to detect directly three distinct regimes. The assignment of regimes has been made from a very general point of view. Several different mechanistic situations are described, which lead to the same temperature coefficient. The influence of molecular weight on the regime behaviour is found to be profound. It influences the type of regime that is being observed, the slope of the temperature coefficient in regime II and the temperature of the transitions between regimes. The technique of measuring overall crystallization rates is shown to be quite potent in this application. Studies need not be limited to measuring the growth rates of particular supermolecular structures and in particular spherulites. This has been the conventional technique, which unfortunately limits the molecular-weight range that can be studied for this purpose. The crystallization kinetics of linear polyethylene is not unique. Therefore, similar results can be expected for fractions of other polymers.

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