Isothermal Growth of Low Molecular Weight Polyethylene Single Crystals from Solution. 3. Kinetic Studies

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ABSTRACT: Single crystals of four polyethylene fractions ranging in molecular weight from 3100 to 11 600 were grown isothermally from xylene solution by using the self-seeding technique. Growth rates of the crystals were measured as a function of solution concentration, molecular weight, and temperature of crystallization. The most interesting results concern the temperature dependence of the growth rates. For the higher molecular weight fractions the growth rate decreases monotonically when the crystallization temperature increases. In contrast for fractions in the molecular weight range of 3000–4000 the growth curves show a notched appearance in which two branches can be distinguished. These branches intersect at a transition temperature where the temperature coefficient of the growth rates changes discontinuously. This behavior is interpreted to mean that the transition temperatures correspond to changes in the conformation of the chains deposited on the growth faces. Thus, as the crystallization temperature decreases, there is a transition from extended- to once-folded-chain growth, for a fraction with a molecular weight of 3100, and from once-folded to twice-folded for crystals with a molecular weight of 4050. This interpretation of the growth transitions is rationalized with the observed continuous temperature variation of the lamellar thickness by invoking a model of the growth process in which the chain ends are preferentially rejected to the exterior of the lamellae as cilia. With decreasing crystallization temperature the pendant cilia become longer and form a fold when their length becomes equal to the lamella thickness. In accordance with the kinetic theory of polymer crystal growth based on coherent surface nucleation, the growth rate data for the four fractions were analyzed by plotting log G vs. $1/T\Delta T$, where G is the growth rate, T is the crystallization temperature, and ΔT is the supercooling. Values of the basal surface free energies σ_e derived from the analysis are compared with those obtained by two independent methods and discussed in relation to the molecular structure of the crystals. It is shown that theory and experiment are consistent for crystals in which n (the average number of folds per molecule) > 1 and acceptable values of σ_e are obtained. Values of σ_e for once-folded-chain crystals are too low, possibly reflecting inadequacies in the theory. On the other hand, for extended-chain crystals the growth kinetics follow a completely different law in which $G \propto \Delta T$. These results pose a challenge to derive the correct theory for the case of extended and once-folded chains and account for the transition between them.

Introduction

Flexible macromolecules with a sufficiently regular structure characteristically crystallize from dilute supersaturated solutions or from the melt in the form of thin lamellae. Since the chains are normal to the plane of the lamellae and the chain length greatly exceeds the lamellar thickness, it has been proposed that the chains must fold on themselves many times.[1]

For most polymers it has been observed that the lamellar thickness generally increases monotonically with the temperature of crystallization T_c so that the mean number of folds per chain decreases as T_c increases.[2] This observation forms the basis for most theoretical analyses of the chain-folding problem. Several kinetic theories have been advanced to account for the chain-folding phenomenon.[3-12] These theories are usually based on a modification of coherent nucleation theory and predict that both the rate of growth and lamellar thickness vary with the supercooling ΔT. The theories generally imply sharp molecular folds with adjacent reentry; it is assumed that the fold length and hence the crystal thickness are equal to the critical nucleus size and are therefore determined by the interfacial energies and the bulk free energy of crystallization. Analysis of data on the isothermal crystallization rate for a variety of polymers has established that nucleation theory holds.[11,13]

These remarks are valid for polymers whose chain length greatly exceeds the lamellar thickness. They are, however, only partially applicable to chains whose length is of the same order of magnitude as the lamellar thickness. A particularly interesting case in point is the behavior of low molecular weight fractions of hydroxy-terminated poly(ethylene oxide). For these fractions the increase of lamellar thickness with T_c occurs in a discontinuous or stepwise manner and the lamellar thickness assumes discrete values which are integral multiples of the length of the chain.[14-17] This stepwise variation of the lamellar thickness is due to the localization of the chain ends in the lamellar surface as a result of hydrogen bonding between the end groups.

Kovacs and Gonthier[17] have measured the isothermal growth rates of hydroxy-terminated poly(ethylene oxide) single crystals from the melt using low molecular weight fractions. Their results show abrupt variations in the temperature coefficient of the growth rate corresponding to sudden changes in the number of folds per molecule and therefore of the lamellar thickness. Application of kinetic theories to the growth rates and lamellar thickness of these low molecular weight poly(ethylene oxide) fractions has revealed a series of fundamental inconsistencies apparently contradicting the model of coherent surface nucleation resulting in a sequential deposition of chain segments of fixed length.[18] In particular it was found that the lateral surface free energy (σ) appears to vary as the inverse of the lamellar thickness instead of remaining invariant as required by the theoretical model.

The work of Kovacs et al. invites the question whether the observed phenomena are general or arise from end-group pairing in the special case of hydroxy-terminated poly(ethylene oxide). It therefore seems of obvious interest

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Table I
Characteristics of the Polyethylene Fractions

fraction	$\bar{M}_w$	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	$T_d°$, K	T_s, K
PE11600	11600	11100	1.05	382.0	369.7
PE6750	6750	6100	1.10	376.8	368.4
PE4050	4050	3900	1.04	371.5	367.6
PE3100	3100	2900	1.07	367.4	365.9

to extend the observations to a polymer such as polyethylene where strong attractive forces do not exist between the end groups. Accordingly the purpose of the present work is to further probe the origins of the chain-folding phenomenon by studying the growth rates of polyethylene single crystals from solution as a function of molecular weight, crystallization temperature, and solution concentration. Sharp molecular fractions have been used covering the range from 3000 to 11 000. In this range the transition from extended- to folded-chain crystallization should be observable. Solution growth has permitted a wider range of supercoolings to be encompassed than would be possible in crystallization from the melt. The results have been analyzed in combination with data on the equilibrium dissolution temperature of the fractions and the temperature variation of the lamellar thickness as presented in parts 1 and 2.

Finally it may be noted that several authors have previously studied the growth rates of single crystals from solution. Holland and Lindenmeyer[19] found that the isothermal growth rate of single crystals of polyethylene crystallized from xylene decreases with decreasing molecular weight and with decreasing concentration; Keller et al.[20,21] and Cooper and Manley[22] found that the growth rate of polyethylene single crystals from xylene is proportional to the concentration raised to a power less than unity, and Johnson and Lehmann[23] found a similar concentration exponent for poly(3,3-bis(chloromethyl)oxetane) (penton) crystallized from *m*-xylene. In all of these cases the molecular weights of the samples were in excess of 10 000. As indicated above, the present work covers a lower range of molecular weights.

Experimental Section

The samples were the same low molecular weight linear polyethylene fractions used in the previous work (parts 1 and 2). The molecular weights, polydispersities, and equilibrium dissolution temperatures $T_d°$ are listed in Table I. The solvent was commercial *p*-xylene distilled before use.

Solutions of the desired concentration (usually about 0.1%; w/w) were prepared by mixing carefully weighed amounts of polymer and solvent and refluxing under nitrogen for 15 min. The solutions were crystallized at 75 °C and then cooled to room temperature. These crystal suspensions were used as stock samples in the crystallization kinetics experiments.

The self-seeding method[24,25] was used to initiate crystal growth at the desired temperature and concentration. Approximately 5 mL of the crystal suspension, contained in a test tube equipped with a ground-glass stopper, was immersed in an oil bath at 75 °C. The temperature was increased to some value T_s at a rate of 8 °C/min and held at this temperature for 30 min. T_s is the temperature at which only tiny fragments of the original crystals (seeds) remain in suspension. The sample tube containing the seeds was transferred to a thermostat at the desired crystallization temperature T_c and a suitable amount of pure solvent, previously equilibrated at T_c, was immediately added with gentle stirring. In this way thermal equilibrium was rapidly attained and growth immediately commenced on the seeds. The growth rate of the crystals was then uniform throughout any one preparation so that at any time all the crystals had reached the same size. Measurement of about a dozen crystals at each sampling time during the growth indicated that the individual measurements were within 1% of the average. As found previously by Holland and Lindenmeyer[19] and Blundell and Keller[20] the growth of the crystals is initially linear and then falls off as the polymer becomes depleted. The measurement of the initial growth rate is of particular interest since it is related to the initial concentration. The T_s value has a direct influence on the duration of the linear growth phase.

At a low T_s more seeds will exist and the polymer molecules in solution will be consumed more rapidly during the crystallization process. Thus, the duration of the linear growth phase will be shorter. Ideally, a low density of seeds should be used so that constant growth rate can be maintained over a long period. However, a compromise was sought in order to obtain a suitable number of crystals on sampling the preparation for electron microscopy. Values of T_s were chosen such that the growth rate was linear during the initial 1000 nm of growth as measured from the center of a crystal to any {110} face. The T_s values used for each fraction in the present work are listed in Table I.

The crystal population was sampled at any required stage of growth by using the method described by Blundell and Keller.[20] Using a preheated micropipet, we transferred a few drops from the crystallizing solution to a test tube containing pure solvent at a lower temperature T_{c2}. At this stage, the solutions contained self-seeded crystals grown to a certain size and the remaining uncrystallized polymer. On quenching into pure solvent at a lower temperature T_{c2}, the crystals continued to grow but with a thickness appropriate to crystallization at the lower temperature. Thus, a discontinuous downward step on the crystal surface was formed and this defined the size of the crystals at the time of sampling. The actual observation of the growth rates was made from measurements in the electron microscope after depositing drops of the crystal suspension on specimen grids and shadowing with platinum. The linear crystal dimensions, as measured from the center of a crystal up to the step on a {110} growth face, were plotted against the crystallization time. Linear growth with time, during the initial stages of growth, was observed in most cases. For very rapid crystallization rates, where the linear phase of growth was short, the initial slope of the curve was used for the measurements. The slope of a plot of crystal size vs. time gave the growth rate which was studied as a function of crystallization temperature, solution concentration, and molecular weight.

The quench temperature T_{c2} was mainly determined by the molecular weight of the sample. Ideally, the lowest practical quench temperature should be used since the larger the difference of the lamellar thickness characteristic of the two temperatures T_c and T_{c2}, the more clear and easily observed the step will be. Too low values of T_{c2} give rise to the formation of undesirable multilayer crystals. For the fractions PE11600 and PE6750, it was found that simple monolayer growth occurred when $60 < T_{c2} < 70$ °C. For the fractions PE4050 and PE3100, T_{c2} was conveniently set at 50 °C for monolayer growth.

The measurement of the size of a given crystal could be made within 2% from calibrated electron micrographs. On considering other possible sources of error, such as fluctuations in the temperature of the oil baths used for crystallization and the precision of the timing of the crystal sampling, we estimate that the uncertainty in the growth rates is about ±3%.

Results and Discussion

Concentration and Molecular Weight Dependence of the Growth Rate. Growth rate data for the four fractions studied are shown in Tables II–V as a function of solution concentration and crystallization temperature. It has previously been shown[21,22] that the concentration dependence of the growth rate may be described by the empirical relation

$$G \propto C^{\alpha}$$

where G is the growth rate, C is the concentration, and α is a constant, hereafter referred to as the concentration exponent. In the present work a pronounced concentration dependence was observed in all cases. As seen in Figure 1 for the higher molecular weight fractions (PE11600 and PE6750), logarithmic plots of growth rate against concentration show a good linear relationship over the entire concentration range investigated. Thus, for these cases

Table II
Growth Rate Data for the {110} Faces of Polyethylene Single Crystals from Xylene Solution, Fraction PE3100

0.05 wt %		0.01 wt %		0.005 wt %		0.001 wt %	
T_c,[a] °C	G, nm/s	T_c,[a] °C	G, nm/s	T_c,[a] °C	G, nm/s	T_c,[a] °C	G, nm/s
70.45	7.67	68.90	5.77	68.90	3.93	70.45	1.06
72.93	6.53	70.45	5.11	69.90	3.57	71.20	1.01
74.05	5.27	72.10	4.83	71.20	2.88	72.93	0.89
76.10	4.41	72.93	3.98	73.06	2.42	74.05	0.69
77.00	4.40	74.05	2.39	74.05	1.68	74.95	0.64
78.25	2.93	74.95	2.24	74.95	1.27	76.10	0.56
79.80	1.16	76.10	2.09	76.10	1.20	77.00	0.48
81.00	1.25	77.00	2.03	77.00	1.11	78.25	0.47
83.00	0.72	77.70	1.51	78.40	0.96	79.80	0.32
84.00	0.60	79.80	0.88	79.80	0.73	81.00	0.20
85.00	0.36	81.00	0.71	80.30	0.54	83.00	0.17
86.25	0.18	82.40	0.54	83.20	0.34	85.00	0.10
		84.00	0.35	84.00	0.21	86.40	0.05
		85.00	0.25	86.25	0.10		
		86.25	0.13	87.70	0.03		
		87.70	0.06				

[a] ±0.01 °C.

Table III
Growth Rate Data for the {110} Faces of Polyethylene Single Crystals from Xylene Solution, Fraction PE4050

0.05 wt %		0.01 wt %		0.005 wt %		0.001 wt %	
T_c,[a] °C	G, nm/s	T_c,[a] °C	G, nm/s	T_c,[a] °C	G, nm/s	T_c,[a] °C	G, nm/s
70.85	9.93	68.90	6.04	68.90	4.43	69.10	1.21
73.40	6.67	69.90	5.80	69.10	4.29	71.00	1.16
74.85	5.41	70.85	4.62	70.85	3.63	73.40	0.82
77.00	3.21	72.10	4.80	73.06	2.71	75.00	0.58
77.50	2.91	74.00	3.01	75.00	1.52	77.00	0.30
78.05	2.18	74.85	2.57	76.00	1.17	77.60	0.30
78.90	1.93	77.00	1.42	77.00	1.13	78.90	0.22
80.00	1.88	77.70	1.28	78.40	0.70	80.00	0.21
81.60	1.26	78.05	0.97	78.90	0.67	81.60	0.16
82.00	1.22	78.90	0.86	80.30	0.57	82.00	0.13
83.00	0.72	80.00	0.79	81.60	0.41	82.95	0.12
84.10	0.52	80.50	0.71	82.00	0.38	85.00	0.05
85.00	0.30	81.60	0.63	83.20	0.28	86.70	0.03
86.10	0.24	82.40	0.59	84.10	0.17		
88.00	0.07	85.00	0.26	85.00	0.13		
		86.70	0.12	86.70	0.06		
		87.70	0.05	87.70	0.03		

[a] ±0.01 °C.

Table IV
Growth Rate Data for the {110} Faces of Polyethylene Single Crystals from Xylene Solution, Fraction PE6750

	G, nm/s		
T_c,[a] °C	0.05 wt %	0.01 wt %	0.001 wt %
75.50	21.60	11.25	3.40
77.80	13.10	5.55	1.50
78.95	11.33	3.79	0.96
81.60	3.33	1.09	0.35
83.60	1.08	0.36	0.13
86.00	0.25	0.13	0.05
88.10	0.07	0.04	0.02

[a] ±0.01 °C.

Table V
Growth Rate Data for the {110} Faces of Polyethylene Single Crystals from Xylene Solution, Fraction PE11600

	G, nm/s		
T_c,[a] °C	0.05 wt %	0.01 wt %	0.001 wt %
76.00	26.67	14.56	6.79
78.00	16.33	8.49	3.20
80.00	10.83	4.96	1.71
81.40	7.17	2.83	1.19
83.00	4.01	1.82	0.61
86.00	0.99	0.42	0.17
87.40	0.38		
88.00	0.24	0.10	0.04
89.10	0.07	0.03	0.01

[a] ±0.01 °C.

a reliable value of α can readily be derived. On the other hand, for the lower molecular weight fractions (PE4050 and PE3100), the plots are curved, indicating that the concentration exponent is not a constant if the whole concentration range is considered (Figure 2). Nevertheless, if we choose to ignore the point at the highest concentration a straight line can readily be drawn throught the remaining points. Values of the concentration exponent thus obtained are listed in Table VI together with the values for the two higher fractions. It is seen that under the conditions employed fractional-order growth kinetics is observed, the values of α being in the range 0.3 to 0.7.

As illustrated in Figure 3 the variation of α with crystallization temperature depends upon the molecular weight of the sample. For molecular weights of 3100 and 4050, α decreases monotonically with increasing crystallization temperature. On the other hand, for the samples with molecular weights of 6750 and 11 600, α first increases with crystallization temperature, and then it passes through a maximum and decreases. These observations may be compared with earlier work[22] using polyethylene samples with molecular weights in the range 15 700–450 000 where the value of α was found to increase with crystallization

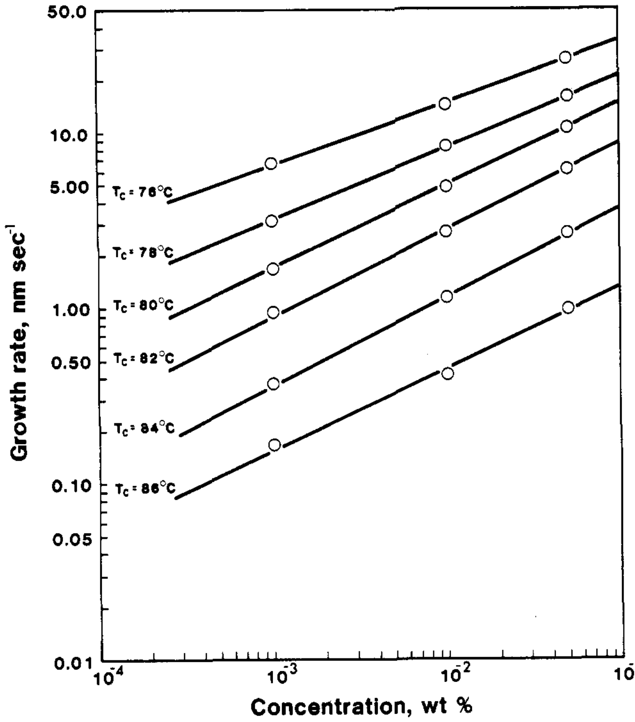

Figure 1. Typical logarithmic plots of the linear growth rate, G, of the {110} faces as a function of concentration for fraction PE11600 at different temperatures.

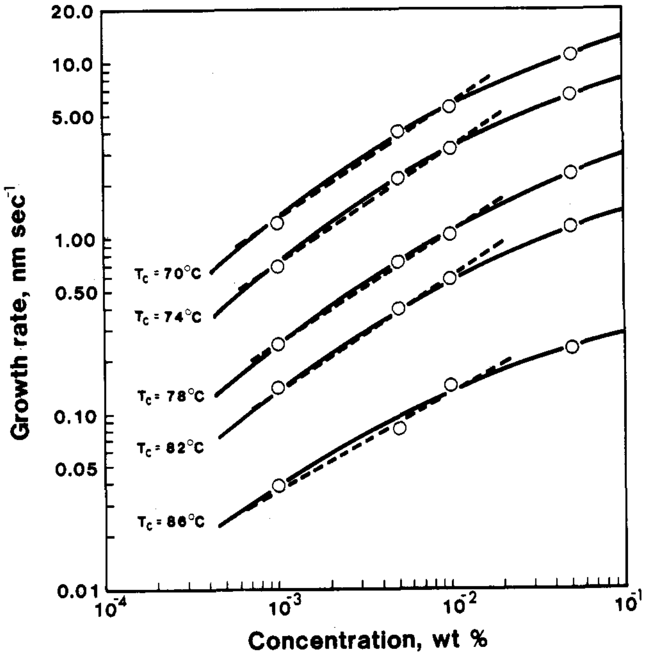

Figure 2. Typical logarithmic plots of the linear growth rate, G, of the {110} faces as a function of concentration for fraction PE4050 at different temperatures.

temperature for all but the sample of highest molecular weight for which α remained essentially constant.

When considering the values obtained for α with the different fractions at fixed crystallization temperature, we see that α first increases and passes through a maximum as the molecular weight increases (Figure 4). By contrast, it has previously been shown experimentally that for high molecular weight samples α decreases with increasing molecular weight.[22]

The variation of growth rate with molecular weight is shown in Figure 5 for various crystallization temperatures and solution concentrations. The characteristic feature of these isotherms is that as the molecular weight increases the growth rate passes through a minimum and then increases sharply. The increase in growth rate with molecular weight at higher molecular weights is in agreement with the observations of Jackson and Mandelkern[30] and Blundell and Keller,[20] who found that higher molecular weight fractions crystallize faster than low molecular

Table VI
Values of the Concentration Exponent α as a Function of Crystallization Temperature T_c

T_c, °C	α for fraction PE3100	PE4050	PE6750	PE11600
70	0.652	0.673		
72	0.634	0.673		
74	0.612	0.669		
76	0.571	0.650	0.503	0.348
78	0.552	0.625	0.554	0.417
80	0.522	0.621	0.602	0.471
82	0.506	0.611	0.605	0.474
84	0.457	0.604	0.575	0.452
86	0.413	0.544	0.493	0.443

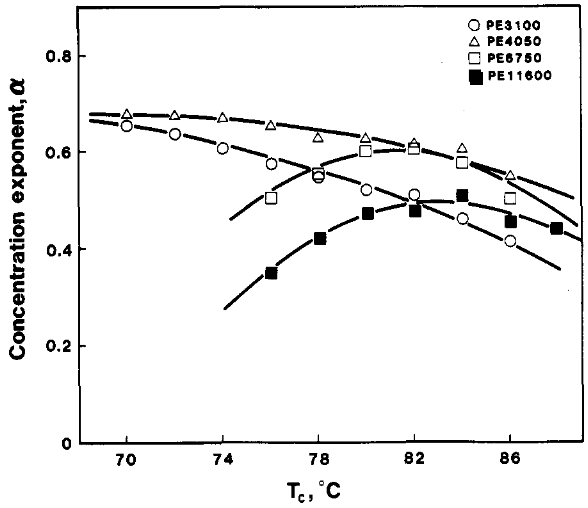

Figure 3. Variation of the concentration exponent α with the temperature of crystallization T_c for the different molecular weight fractions.

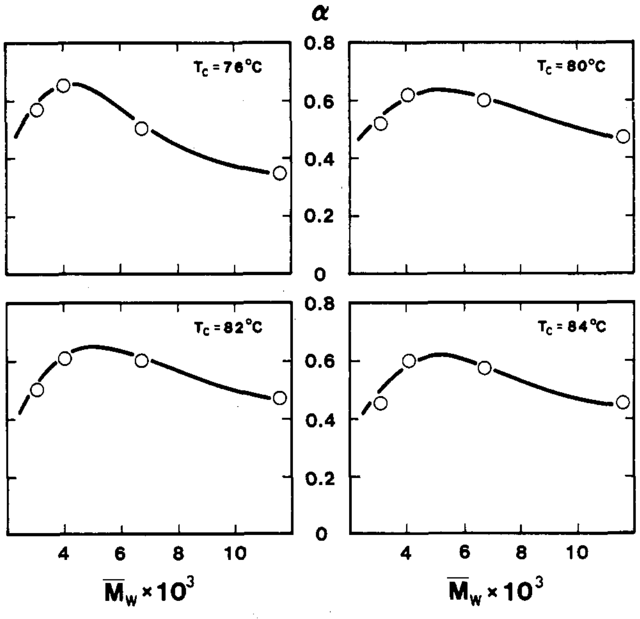

Figure 4. Examples of the variation of the concentration exponent α with molecular weight for four crystallization temperatures T_c.

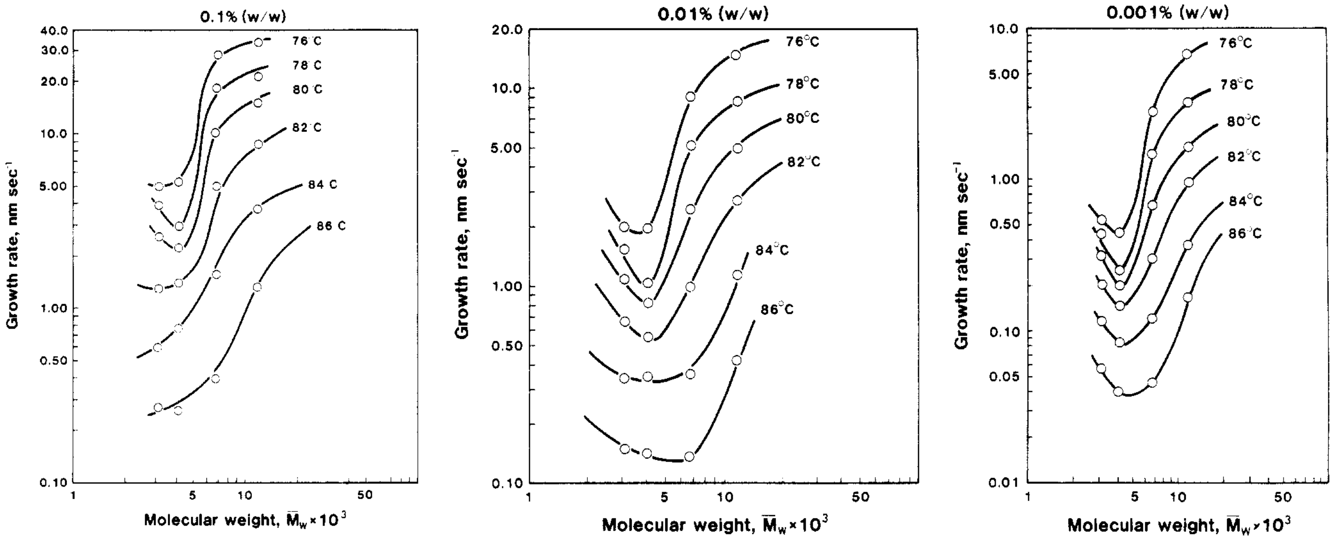

Figure 5. Growth rate as a function of molecular weight at various crystallization temperatures as indicated and solution concentrations.

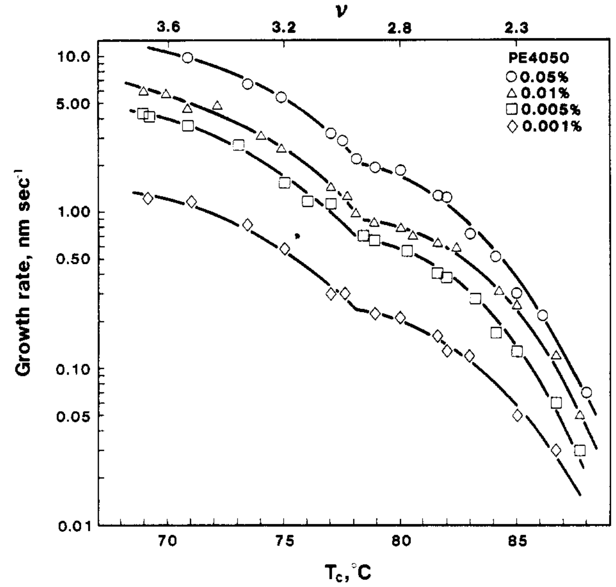

Figure 6. Temperature dependence of the growth rate for fraction PE4050 at various concentrations. The upper abscissa scale shows the number of stems per molecule (ν) corresponding to the temperature scale.

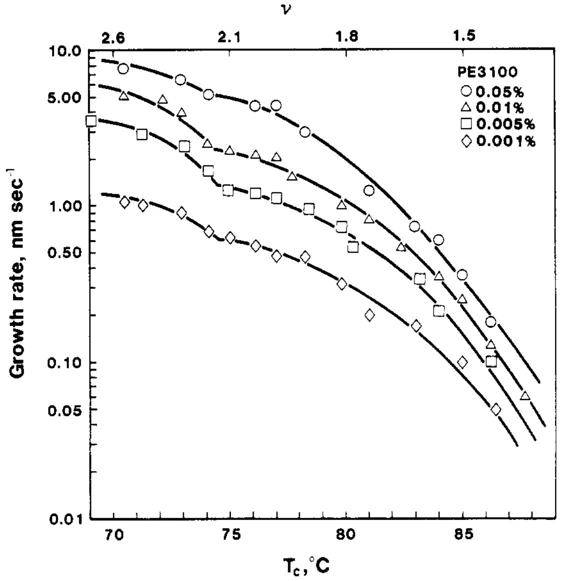

Figure 7. Temperature dependence of the growth rate for fraction PE3100 at various concentrations. The upper abscissa scale shows the number of stems per molecule (ν) corresponding to the temperature scale.

weight fractions. This effect can be qualitatively explained in terms of the increase in supercooling ($\Delta T = T_d° - T_c$) with molecular weight, since the growth rate is proportional to $\exp(-K_g/\Delta T)$, where K_g is the nucleation parameter,[10] and the equilibrium dissolution temperature $T_d°$ increases with molecular weight. The existence of a minimum in the growth rate/molecular weight isotherms has not previously been reported, presumably because measurements were not made at sufficiently low molecular weights.

At this point it must be said that there is at present no sound theoretical basis for quantitatively interpreting the observed concentration effects in structural or molecular terms. Sanchez and DiMarzio[12] have proposed a dilute-solution theory of polymer crystal growth which predicts the effects of molecular weight, solution concentration, and crystallization temperature on the growth rate of single crystals from solution. It is considered that the secondary nucleation required for continued growth of a crystal may involve cilia as well as solution molecules. Cilia are the dangling ends of molecules that are partially incorporated into the crystal lattice. Sanchez and DiMarzio proposed that these cilia can participate in nucleating a new growth strip (fold plane) on the crystal surface by a kind of "self-nucleation" mechanism. However, the theory cannot be used for quantitative analysis and discussion because it breaks down when applied to the very low molecular weight samples used in the present work. We therefore refrain from commenting further on the concentration effects, more especially so since we are of the opinion that they are not the main issue of the current study. In fact, as will be seen later the essential kinetic effects are independent of the concentration dependence.

Temperature Dependence of the Growth Rates. Figures 6–8 show growth rate data as a function of crystallization temperature for the fractions PE4050, PE3100, and PE11600, respectively. For PE11600 the growth rate decreases monotonically with the temperature of crystallization T_c. This behavior is typical of high molecular weight melt-crystallized polyethylene samples.[10] Similar results were obtained with PE6750. In contrast, for fractions PE3100 and PE4050 the growth curves show a notched appearance in which two branches can be distinguished. These branches appear to intersect at a definite temperature T^* (78 °C for PE4050 and 74 °C for PE3100)

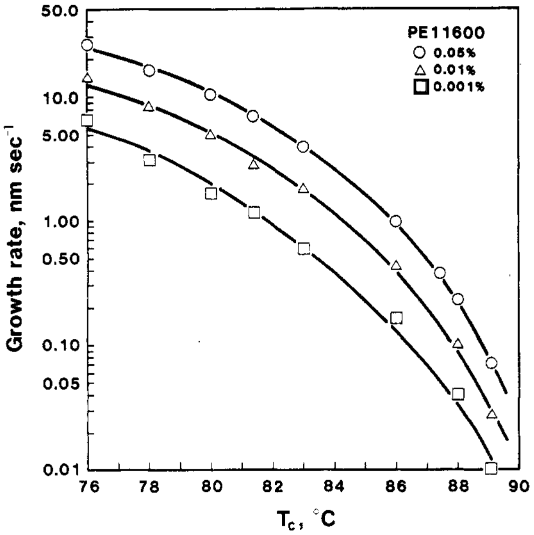

Figure 8. Temperature dependence of the growth rate for fraction PE11600 at various concentrations.

where the temperature coefficient of the growth rate d(log G)/dT changes discontinuously with T_c. For a fixed molecular weight the transition temperature T^* seems to be independent of the concentration of the polymer solution.

The results obtained with the lower molecular weight fractions are strikingly similar to the behavior exhibited by low molecular weight melt-crystallized fractions of poly(ethylene oxide) as investigated by Kovacs et al.[17] In that case the transition temperatures were shown to correspond to discontinuous changes in the conformation of the chains deposited on the growing faces. Thus, above the transition temperature growth proceeds by deposition of n-times-folded chains, whereas below the transition temperature, growth consists of the deposition of (n + 1)-times-folded chains.

In the case of the polyethylene samples studied in the present work, there are two lines of evidence suggesting that, as in the case of poly(ethylene oxide), the transition temperatures correspond to changes in the conformation of the molecules deposited on the growth faces. First, as described in part 2, the temperature variation of the heat of fusion follows a sigmoidal pattern for samples with molecular weights in the range of 3000–4000. This has been interpreted to mean that there is an abrupt change in the structure of the interfacial regions of the crystals as T_c increases, corresponding to a transition in the number of folds per molecule deposited on the growth faces. The second line of evidence in support of the proposed interpretation of the apparent growth transitions comes from an examination of the morphology of crystals of PE3100 grown at various temperatures and filtered and washed with pure solvent at the crystallization temperature. As illustrated in Figure 9 the crystals grown at high supercooling below the transition temperature exhibit sectorization which is an inherent consequence of chain folding. On the other hand, crystals grown at low supercooling above the transition temperature are not sectorized, indicating that they are principally composed of extended chains. Clearly there must be a temperature at which there is a transformation from one form of growth to the other.

Having presented evidence in support of the interpretation that the growth transitions correspond to changes in the conformation of the molecules deposited on the growth faces, we now consider the molecular nature of the transitions. As discussed in part 1, for all the fractions electron diffraction experiments show that the chain molecules are oriented normal, or nearly so, to the lamellar surfaces. Therefore, from the measurements of the tempeature variation of the lamellar thickness (l) described in part 1 together with the known extended-chain length ($L = 1.25(M_n/14)$) the number of stems per molecule can be readily estimated as $\nu = L/l$. On the basis of the observations of Jackson and Mandelkern[26] it is assumed that at the temperatures involved in crystallization from dilute solution there is no isothermal thickening of the lamellae. It is well-known that the SAXS measurements of lamella thickness correspond to the crystalline core plus a disordered surface layer. A correction for the specimen crystallinity was therefore introduced by multiplying the observed lamella thickness (l) by $\Delta H/\Delta H_u$, where ΔH is the observed enthalpy of fusion at the temperature of crystallization (see part 2) and ΔH_u = 70 cal/g is the enthalpy of fusion per segment for extended-chain crystals of infinite molecular weight.[27,28] It turns out that the number of stems per molecule increases as T_c decreases and the transition temperatures observed in the growth curves for PE3100 and PE4050 correspond respectively to 2.2 and 3.0 stems per molecule (see Figures 6 and 7). Accordingly, assuming that the incorporation of ν stems into the crystal results in the formation of $\nu - 1$ chain folds, the growth transitions can, to a good approximation, be interpreted as corresponding to a change from once-folded- to extended-chain growth for PE3100 and from twice-folded- to once-folded-chain growth for PE4050. Thus, according to this interpretation the observed growth transitions are attributed to a quantized change in the fold length of the depositing chains. At first sight this interpretation would seem to be at variance with the observation that the lamellar thickness (of mature crystals as revealed by SAXS) increases continuously with T_c as demonstrated in part 1. It should be noted, however, that a similar situation exists in the growth of poly(ethylene oxide) single crystals from the melt as investigated by Arlie et al.[15] and Kovacs and Gonthier.[17] In this case their lower molecular weight samples (2000 and 3000) do not display any discontinuous changes in the SAXS investigations, whereas they show a very sharp and well-defined transition temperature in the growth rate data. Furthermore, even for the higher molecular weight samples, where quantized changes in lamellar thickness have been observed by SAXS, the transition temperatures are always located at much lower values of T^* than the actual growth transition temperatures determined from crystal growth measurements. As shown by Kovacs and Gonthier[17] these discrepancies originate from structural rearrangements (i.e., chain unfolding) that occur during isothermal crystallization from the melt.

In the present work with polyethylene, as already mentioned above, there is reason to assume that isothermal thickening does not occur during crystallization and this assumption will later be shown to be justified. Thus, the conformation of the chains deposited on the growth faces, as experienced by growth rate measurements, and the lamellar thickness of mature crystals as revealed by SAXS are thought to be essentially the same. If this is so, then the question arises as to how the quantized change in fold length can be rationalized with the continuous change in lamellar thickness. Three models of the crystallization process can be envisaged, viz. (a) chain ends localized on the surface of the lamellae, (b) chain ends rejected to the exterior of the lamellae as cilia, and (c) chain ends incorporated within the crystal lattice. According to the proposed interpretation of the growth transitions, model a would require a stepwise change in lamellar thickness as T_c increases, in contrast to the observed continuous in-

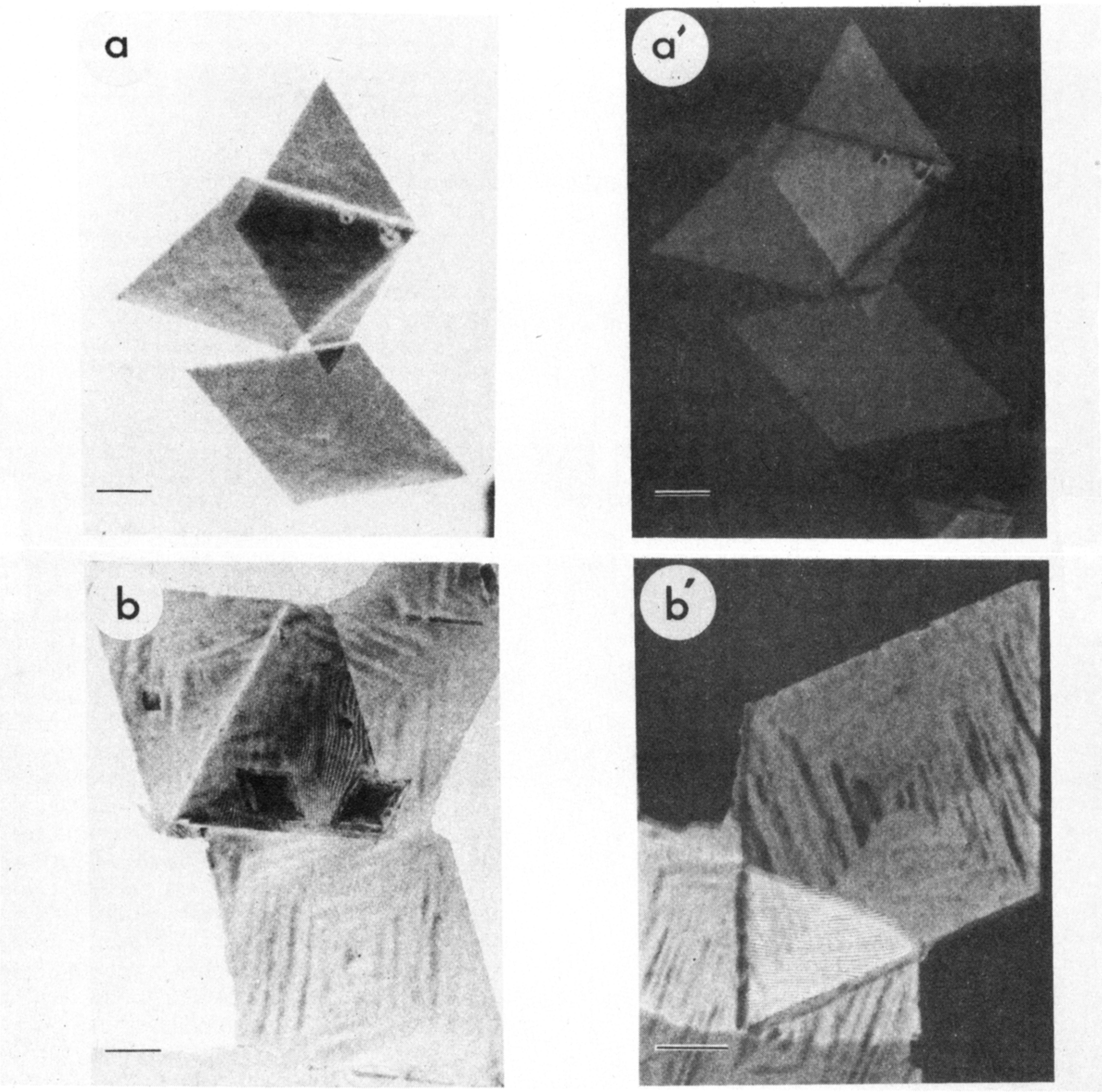

Figure 9. Bright-field (left) and dark-field (right) electron micrographs of single crystals of PE3100 grown from dilute xylene solution and filtered from solution at the crystallization temperature, which is 81 °C in part a and 55 °C in part b. The crystals in part a are typical of those grown above the growth transition temperature (74 °C) and are not sectorized, indicating they are composed of extended chains. The crystals in part b are typical of those grown below the growth transition temperature and exhibit the characteristic sectorization which is an inherent consequence of chain folding. The dark-field micrographs were taken by using a {110} reflection. Bar lines represent 1 μm.

crease (see Figure 10). For model c as pointed out by Sanchez and DiMarzio[12] the surface energy product $\sigma\sigma_e$ would tend to increase with decreasing molecular weight, which, as will be seen later, is the opposite of what is observed. We are therefore left with model b, which assumes that fractional stems are rejected from the crystal lattice as cilia. In this case, as illustrated in Figure 10, it is evident that as T_c decreases the pendant cilia would become longer and, following Hoffman et al.,[10] it can be postulated that a fold will appear when the length of the cilium becomes equal to the lamellar thickness. In this process the temperature variation of the lamellar thickness would be expected to be continuous. Thus, according to this model a quantized change in the conformation of the molecules deposited on the growth faces can occur even though the lamellar thickness changes continuously with temperature.

In concluding this section it may be of interest to note that growth transitions of the type described above have not previously been observed in studies of the growth kinetics of low molecular weight polyethylene samples. Hoffman et al.[10] and Labaig[29] have measured the growth rates of polyethylene fractions crystallized from the melt covering the molecular weight range from 3600 to 17 000. The results show that log G decreases monotonically with temperature over the range of T_c explored. The failure to observe the growth transitions in these experiments is presumably related to the relatively low supercoolings accessible in melt crystallization as compared to crystallization from solution.

Basal Surface Free Energies. We now wish to analyze the growth rate data in order to estimate basal surface free energies for the crystals of the various fractions. The kinetic theory of nucleation controlled growth of polymer crystals with infinitely long folded chains leads to an expression for the growth rate G[10]

$$G = G_0 \exp(-\Delta H^*/kT) \exp[-K_g/T(\Delta T)f] \qquad (1)$$

where ΔH^* is the activation energy for transport of chain segments to the crystal–solution interface; G_0 contains factors not strongly dependent on temperature; T is the crystallization temperature; ΔT is the supercooling $T_d^\circ - T$; f, which is given by $2T/(T_d^\circ + T)$, is a factor near unity that accounts for the slight diminution of the heat of fusion

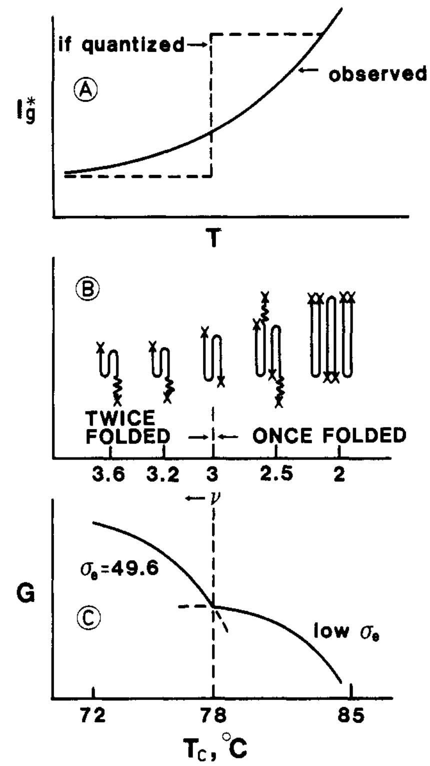

Figure 10. Schematic diagrams illustrating (for fraction PE4050) the relationship between the lamellar thickness/crystallization temperature curve (A), the model for the molecular structure of the crystals (B), and the growth curves (C). The growth transition occurs at a temperature of 78 °C. The symbol ν denotes the number of stems per molecule corresponding to the temperature scale. Above and below the growth transition temperature the crystals grow in the once-folded and twice-folded mode, respectively. The upper diagram (A) shows the observed continuous lamellar thickness/temperature relation (solid line) and the expected relation if the lamellar thickening occured in a stepwise manner (dashed line).

Δh_f as the temperature falls below the equilibrium temperature $T_d°$; and k is the Boltzmann constant. The nucleation parameter K_g has the general form

$$K_g = xb\sigma\sigma_e T_d°/(\Delta h_f)k \qquad (2)$$

where b is the thickness of the depositing growth layer; $T_d°$ is the equilibrium dissolution temperature which is molecular weight dependent; σ and σ_e are respectively the lateral and basal surface free energies; and Δh_f is the heat of fusion. The value of x depends on the nucleation regime. In regime I growth, where the formation of a surface nucleus is followed by rapid completion of the entire substrate, x has a value of 4. For regime II growth, where numerous nuclei form on the substrate and spread slowly, x has a value of 2.

By plotting log G against $1/T(\Delta T)f$ one should obtain a linear relationship if eq 1 is obeyed and the numerical value of K_g can be derived from the slope. Hence, the important parameter σ_e can be estimated, if the lateral surface free energy is known. In carrying out the analysis one needs a precise knowledge of the equilibrium dissolution temperature $T_d°$ since K_g and the supercooling ΔT are very sensitive to it. In the present work, which involves chains of finite length, $T_d°$ has been determined experimentally by measuring the dissolution temperature of large extended-chain crystals, as described in part 1. For the four fractions studied, the values of $T_d°$ used throughout the data analysis are listed in Table I.

Figures 11–13, respectively, show plots of log G vs. $1/T(\Delta T)f$ for fractions PE4050, PE3100, and PE11600 at various concentrations. For PE11600 and PE6750 linear relationships are obtained over the entire range of supercoolings investigated. On the other hand, for the two lowest molecular weight fractions, PE3100 and PE4050, one can distinguish two ranges of supercooling in which the slopes of the plots have substantially different values. According to eq 1 and 2, if there is no change in regime, the change in slope of these log G curves must be due to a change in σ_e since all the other parameters, ΔH^*, b, σ, and Δh_f, are independent of chain length and conformation. For the various fractions, values of nucleation constant K_g derived from the slopes of the log G vs. $1/T(\Delta T)f$ plots are collected in Table VII. Differences in the value of K_g for growth at the various concentrations do not ap-

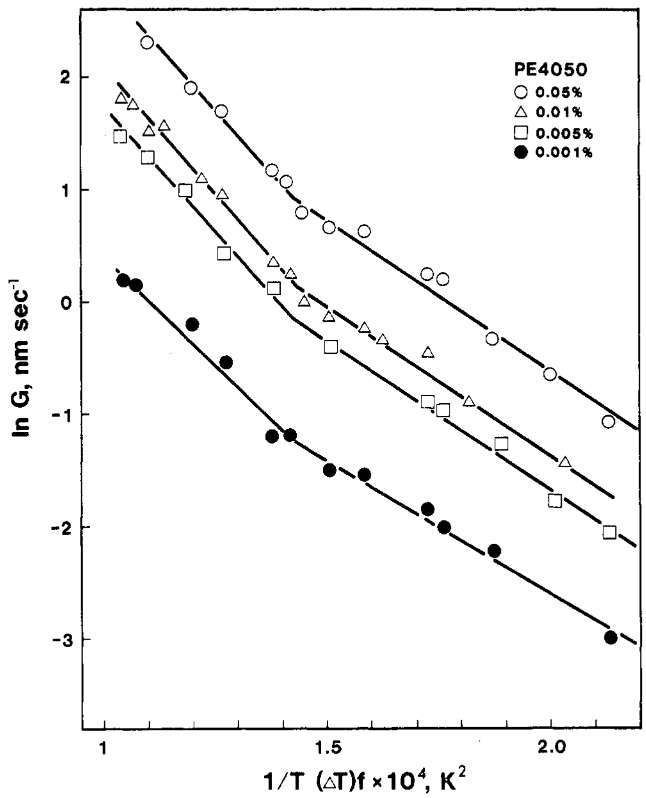

Figure 11. Plots of the logarithm of the linear growth rate G against $1/T(\Delta T)f$ for fraction PE4050 at various concentrations.

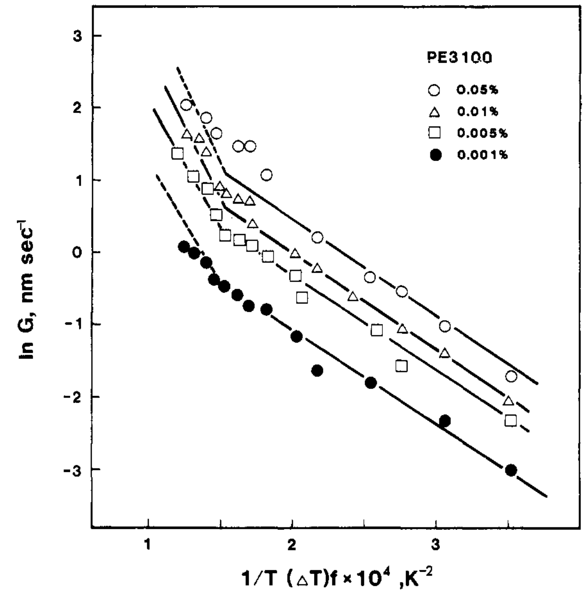

Figure 12. Plots of the logarithm of the linear growth rate G against $1/T(\Delta T)f$ for fraction PE3100 at various concentrations.

Table VII
Values of K_g Calculated from Plots of log G vs. $1/T(\Delta T)f$

fraction	temp range, °C	K_g, K^2				
		0.05 wt %	0.01 wt %	0.005 wt %	0.001 wt %	av
PE3100	70–74	27 000	25 000	26 000	23 200	25 300
	74–86	16 900	17 000	16 300	15 200	16 300
PE4050	69–78	45 300	45 300	44 800	41 300	44 200
	78–86	27 600	26 700	26 700	23 300	26 100
PE6750	75–88	80 000	77 000		74 200	77 200
PE11600	76–89	90 900	88 600		87 300	88 900

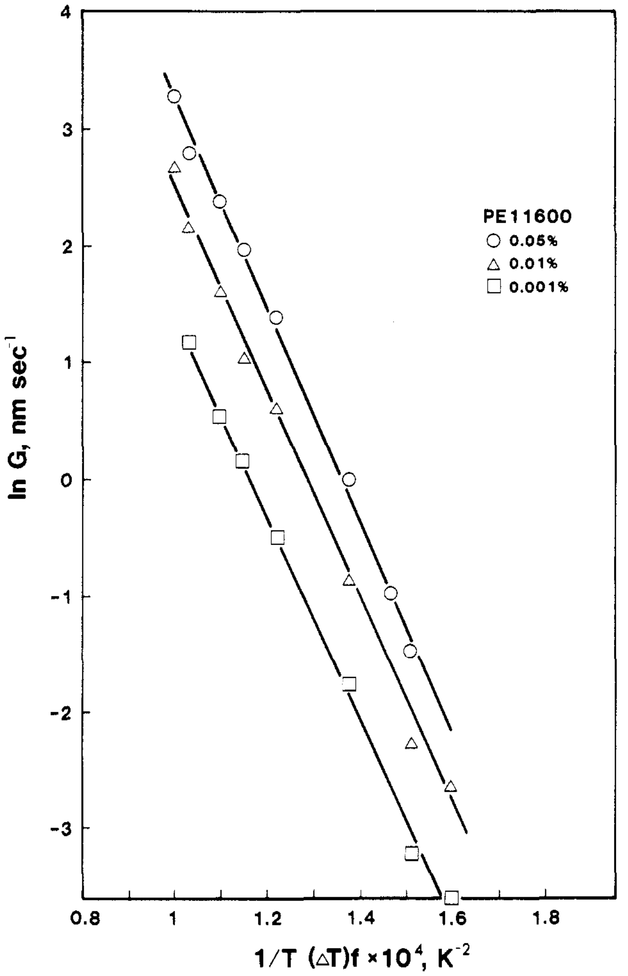

Figure 13. Plots of logarithm of the linear growth rate G against $1/T(\Delta T)f$ for fraction PE11600 at various concentrations. Fraction PE6750 shows similar behavior.

pear to be significant; consequently it was assumed that K_g is independent of concentration and the average value was used in the calculations to follow. In order to estimate whether the observed values of K_g for a given fraction correspond to regime I or regime II kinetics, we have used the so-called Z criteria proposed by Lauritzen.[31] According to this proposal the parameter governing the distinction between regime I and regime II is the dimensionless quantity

$$Z = iL^2/4g \tag{3}$$

where i is the surface nucleation rate, g is the spreading rate, and L is the substrate length. If $Z \ll 0.1$, regime I behavior holds, while for regime II behavior, $Z \gg 1$. From the experimental value of K_g the Z parameter can be estimated from the approximate expression

$$Z = \frac{iL^2}{4g} \cong z(L/2a)^2 \exp[-X/T\Delta T] \exp[2ab\sigma_e/kT] \tag{4}$$

where z is the number of CH$_2$ units corresponding to the lamellar thickness, a and b are the molecular width and layer thickness, respectively, and k is the Boltzmann constant and where $X = K_g$ when $Z \ll 0.1$ (regime I) and $X = 2K_g$ when $Z \gg 1$ (regime II).

From eq 4 it is possible to estimate the range of L values that are consistent with regime I or regime II behavior. Usually the correct choice of regime can be made by considering whether the value of L is reasonable or unrealistic. The value of L must be consistent with morphological information: for example, L cannot exceed the known lateral dimensions of the single crystals and it should be at least several times larger than the molecular width.

The following input data were used in the calculations: molecular width $a = 4.55 \times 10^{-8}$ cm; layer thickness $b = 4.15 \times 10^{-8}$ cm; $T_d°$ values as listed in Table I; z was estimated from the lamellar thickness at a given crystallization temperature divided by the projected length of the CH$_2$ unit, which is 1.25 Å; values of the basal surface free energies as estimated in parts 1 and 2.

To illustrate the results of the calculations we consider two examples. First for fraction PE11600 assuming that the observed value of K_g refers to regime I kinetics we calculate using $\Delta T = 21.8$ °C, $T = 85$ °C, and $Z < 0.1$ that $L < 8$ Å. This value is too small to be realistic since it is of the same order of magnitude as the molecular width. A recalculation assuming regime II kinetics gives $L > 750$ nm, which is considered to be too large in comparison with the observed dimensions of crystals grown at the chosen temperature. We are thus led to the conclusion that for these crystals the growth kinetics is intermediate between regime I and regime II so that $K_g = 3b\sigma\sigma_e T_d°/(\Delta h_f)k$ must apply; this implies mixed regime I and regime II behavior. A similar conclusion is reached for fraction PE6750.

Considering now the calculation for fraction PE4050 in the low-temperature range, a test for regime I behavior at $T_c = 75$ °C and $\Delta T = 23.3$ °C gives $L < 0.73$ Å, which is clearly absurd. For the test of regime II behavior we obtain $L > 12.4$ Å, which is considered to be a reasonable substrate length. For the high-temperature range at $T = 83$ °C and $\Delta T = 15.3$ °C, $L < 0.5$ Å for regime I behavior and $L > 17$ Å for regime II behavior. It is thus concluded that for this fraction the growth follows regime II kinetics, so that $K_g = 2b\sigma\sigma_e T_d°/(\Delta h_f)k$. The calculations for fraction PE3100 in the low-temperature range lead to conclusions similar to those for fraction PE4050.

Table VIII summarizes the conclusions concerning the assigned growth regimes and lists the corresponding values of the product $\sigma\sigma_e$ for each fraction. In order to extract the kinetic value of σ_e from the product $\sigma\sigma_e$ we need to know the value of the lateral surface energy σ. For polyethylene, values of this parameter ranging from 11 to 14 erg/cm^2 have been reported.[11,33] However, recent work[34] seems to favor a value of $\sigma = 11.2$ erg/cm^2 independent of chain length, and this will be used in the discussion that follows. It is emphasized, however, that small changes from this value will not alter the basic conclusions drawn here. For the four fractions studied, values of σ_e, calculated as

Table VIII
Values of the Surface Energy Product and the Basal Surface Energies

fraction	temp range, °C	growth regime	av $\sigma\sigma_e$, erg^2/cm^4	σ_e, erg/cm^2 kinetic	σ_e, erg/cm^2 from T_d (or T_m) vs. $1/l$ plots	σ_e, erg/cm^2 from l vs. $1/\Delta T$ plots
PE3100	70–74[a]	II	320	28.6	41.5	48.9
	74–86[b]	II	208	18.5	41.5	48.9
PE4050	69–78[c]	II	555	49.6	45.5	48.5
	78–86[a]	II	327	29.2	45.5	48.5
PE6750	75–88	mixed I and II	636	56.7	48.9	51.7
PE11600	76–89	mixed I and II	727	64.9	61.7	60.1

[a] Once-folded-chain crystals. [b] Extended-chain crystallization. [c] Twice-folded-chain crystals.

$\sigma\sigma_e/11.2$, are given in Table VIII. For purposes of comparison the table also includes values of σ_e derived by the two independent methods described in parts 1 and 2.

When we consider these results, several points of interest emerge. First, it is seen that all the values of σ_e are considerably lower than the accepted value of about 90 erg/cm^2 obtained for high molecular weight chain-folded lamellae.[32] As indicated earlier (see part 2) the difference is probably caused by the inclusion of chain-end effects in the effective value of σ_e due to the finite molecular weight of the samples. It is further seen that for the two highest fractions and for PE4050 in the low-temperature range, which corresponds to the deposition of twice-folded chains, the three values of σ_e agree within less than 15%, which considering the errors and approximations is satisfactory. This inspires confidence in the assignment of the growth regimes that was made on the basis of the Z criterion. From eq 2 it is obvious that no other assignment would have given acceptable values for σ_e. These results clearly imply that eq 1 is applicable down to the molecular weight range where twice-folded-chain crystals are formed. Furthermore, these data have an important bearing on the question of isothermal thickening to which reference has been made earlier in these papers. The σ_e values derived from the growth rate measurements correspond to the native or initial fold length of the crystals and would not have been affected by isothermal thickening. On the other hand, the other two methods relate to older or mature crystals and the σ_e values derived from them should reflect isothermal thickening if it had occurred. Accordingly the close correspondence between the three σ_e values for the fractions PE11600, PE6750, and for PE4050 crystallized in the twice-folded mode support the assumption made earlier, namely that there is no isothermal thickening of the crystals over the temperature range investigated. This means that the measured lamellar thickness corresponds to the initial fold length, which is the value the theories predict.

It is also interesting to note that for fraction PE4050 the value of σ_e for the high-temperature branch is essentially equal to the σ_e derived from the low-temperature branch of fraction PE3100. This suggests that the structure of the interfacial regions of the crystals of these fractions is similar in the temperature ranges in question. This is consistent with the interpretation discussed above, that the high-temperature branch of fraction PE4050 and the low-temperature branch of PE3100 correspond to the growth of crystals in which once-folded-chain deposition prevails. It is, however, important to observe that for these two cases there is a substantial discrepancy (30–40%) between the kinetic values of σ_e and those derived from the other two methods. This implies that the coherent surface nucleation theory, as expressed by eq 1, is not adequate when applied to once-folded chains.

For fraction PE3100 the high-temperature branch, which corresponds to extended-chain crystallization, yields a value of σ_e that is in complete disagreement with the values from the other methods; indeed, it is of such low magnitude (18.6 erg/cm^2) that it must be regarded as fictitious. These considerations lead to the inference that eq 1 is not applicable to the growth of extended-chain crystals, notwithstanding the linearity of the log G vs. $1/T\Delta T$ plots.

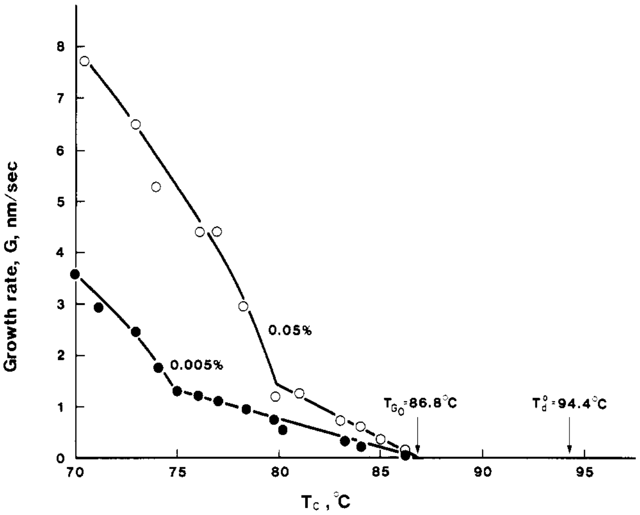

Figure 14. Growth rate as a function of crystallization temperature for fraction PE3100 at two solution concentrations. The linear portion of the curves corresponds to the temperature range where extended-chain crystallization is thought to occur. Note that the growth rate goes to zero at a temperature T_{G_0} that is well below the equilibrium dissolution temperature $T_d{}^\circ$.

In fact, for extended-chain crystallization there are compelling theoretical grounds for expecting that the growth kinetics follows a completely different law. Lauritzen, Passaglia, and DiMarzio[35] have calculated the growth flux for the paraffins C-24 and C-26, and their mixtures, and have demonstrated that G decreases linearly with increasing T_c at small values of ΔT. Following the implications of this theory it is of interest to plot the data for fraction PE3100 as G vs. T_c rather than in accordance with eq 1. (We are indebted to Professor J. D. Hoffman for suggesting this approach.) Figure 14 shows such plots for data at two concentrations. It is seen that the plots are linear over an appreciable temperature range and that there is a definite temperature at which the growth rate changes abruptly. The linear region of the plots encompasses the range where extended-chain growth occurs and the transition temperature corresponds to the onset of the growth of crystals with once-folded chains. It should be noted that the growth transition temperature is concentration dependent. This is surprising because it is counterintuitive. However, the explanation must await the development of an appropriate theory. In passing, it may be noted that similar plots of the data for the higher molecular weight fractions (none of which involve extended-chain growth) show a continuous curve with no

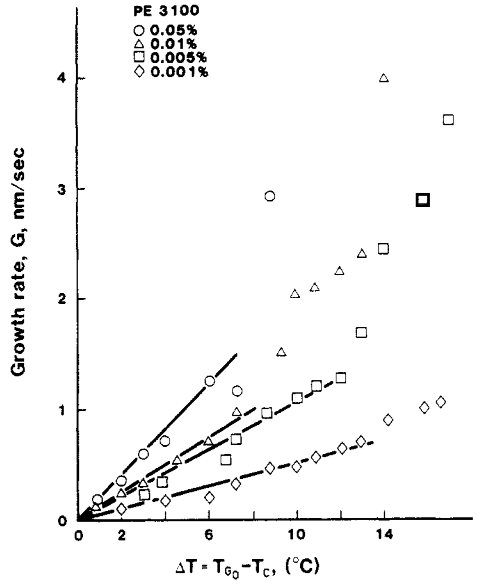

Figure 15. Growth rate as a function of effective undercooling $\Delta T = T_{G_0} - T_c$ for fraction PE3100 at four solution concentrations. T_c is the crystallization temperature and T_{G_0} is the temperature where the growth rate goes to zero. Linear relations are obtained in the region of low ΔT where extended-chain growth prevails. This shows that the growth law for extended-chain crystallization is $G = K(\Delta T)$.

temperature range of linear behavior. Returning to Figure 14 it is also striking that the linear portions of the plots converge to a temperature T_{G_0} where the growth rate goes to zero and that T_{G_0} is far below $T_d°$. The critical supercooling ($T_d° - T_{G_0}$), below which there is no crystallization, is 7.6 °C. Thus, the correct temperature from which the supercooling should be measured is not $T_d°$ but T_{G_0}. Figure 15 shows plots of G vs. $\Delta T = T_{G_0} - T_c$ from which it becomes evident that the growth law for the extended-chain crystals is $G = K(\Delta T)$. We are therefore led to the conclusion that expressions of the form of eq 1, valid for the "fold" case, do not apply to extended-chain crystallization.

Finally we wish to consider briefly a possible alternative explanation of the growth transitions observed in the log G vs. $1/T\Delta T$ plots for the fractions PE3100 and PE4050. Hoffman[36] has recently shown that with decreasing temperature at moderately large supercooling there is an abrupt change in the slope of the growth vs. temperature curve, such that the slope increases at the transition. This is essentially the effect that is observed in Figures 11 and 12. According to Hoffman this effect can be identified as a transition from regime II to regime III. "Regime III is entered when the niche separation characteristic of the substrate in Regime II approaches the molecular width. In Regime III the crystallization rate is controlled by the rate of deposition on the substrate i, rather than $i^{1/2}$ as in Regime II."[36] From our experimental data on fractions PE3100 and PE4050 we find that the ratio of the nucleation constants $K_g(\text{III})/K_g(\text{II}) = 1.55$ and 1.69, respectively, which may be compared to the theoretical prediction $K_g(\text{III})/K_g(\text{II}) = 2$. The difference (20% and 15% for fractions 3100 and 4050, respectively) is greater than the experimental error in the K_g values, which is estimated to be about 10%. On this ground the regime II → regime III transition can be rejected as an explanation for the observed growth transitions.

Conclusions

The present work has contributed new information on the growth rates of low molecular weight polyethylene single crystals and has demonstrated experimentally that folded- and extended-chain crystal growth follow different laws. The principal observations and conclusions are as follows:

(1) For solution-grown polyethylene single crystals, with molecular weights in the range of 3000–4000, the temperature coefficient of the growth rate undergoes a sharp transition. This has been interpreted to mean that at the transition temperature there is an abrupt change in the conformation of the molecules deposited on the growth faces. For a fraction with a molecular weight of 3100 the change is from extended to once-folded chains, while for a molecular weight of 4050 the transition temperature corresponds to a change from once-folded to twice-folded chains, as T_c is decreased. The observed growth transitions are thus attributed to a quantized change in the fold length of the depositing chains. These observations confirm and generalize the results of Kovacs et al. on low molecular weight hydroxy-terminated poly(ethylene oxide) fractions crystallized from the melt. Since the same basic phenomenon (i.e., the existence of growth transitions) is observed not only in polyethylene, but also in solution crystallization, it is evident that the behavior of poly(ethylene oxide) is neither special nor unique.

(2) The quantized change in the fold length of the depositing chains has been rationalized with the observed continuous temperature variation of the lamellar thickness by invoking a model of the growth process in which fractional stems, i.e., chain ends, are rejected to the exterior of the lamellae as cilia. These pendant cilia become longer as T_c decreases and form a fold when their length becomes equal to the lamellar thickness.

(3) The growth rate data for the various fractions ranging in molecular weight from 3000 to 11 000 have been analyzed by plotting ln G vs. $1/T(\Delta T)f$ in accordance with the infinite-chain kinetic theory based on coherent surface nucleation. The central issue here is whether it is valid to apply this theory to fractions of such low molecular weight. This question has been approached by comparing the values of the basal surface free energy σ_e derived from the growth kinetics with those obtained from two other methods, one of which is thermodynamic (T_d or T_m vs. $1/l$) and the other essentially kinetic (l vs. $1/\Delta T$). For very high molecular weight samples, where the number of folds per molecule is very large and chain-end effects are negligible, a value of $\sigma_e \simeq 90$ erg/cm^2 is expected. For the present samples the two independent methods give values of σ_e that are in good agreement and lie in the range of 40–60 erg/cm^2. The difference is ascribed to chain-end effects due to the finite molecular weight of the samples. When all three methods are compared, it is found that good agreement is obtained when n, the average number of folds per molecule, >1. For these cases it is concluded that the coherent surface nucleation theory gives an adequate description of the growth kinetics. When $n = 1$, the kinetically derived σ_e values, although not unreasonable, are too low in magnitude, indicating that the theory is inadequate. Finally for extended-chain crystals the kinetic σ_e values are absurdly low, which strongly suggests that the theory is not applicable.

(4) The most striking results were obtained for fraction PE3100, which crystallizes in the extended-chain mode at higher crystallization temperatures. When the growth data are plotted as G vs. T_c, it is found that the plots are linear down to a temperature corresponding to the onset of once-folded-chain growth; at that point there is an abrupt increase in the growth rates. The linear portion of the plots extrapolates to zero growth rate at a temperature T_{G_0} that

is about 7.6 °C below the equilibrium dissolution temperature $T_d°$. Plots of the growth rate vs. the effective undercooling $\Delta T = T_{G_0} - T_c$ are linear and lead to the important conclusion that the growth rate law of extended-chain crystals is $G = K(\Delta T)$.

It would be useful to verify this conclusion by studying the growth rates of more extended-chain polyethylene fractions. The effect of polydispersity on the growth rates also needs to be clarified. Although questions remain concerning the detailed interpretation of the concentration dependence of the growth rates in molecular or structural terms, the essential kinetic effects are independent of that consideration. Finally there is an immediate challenge to provide the theoretical basis for understanding extended-chain crystallization and the transition from extended- to folded-chain growth with decreasing crystallization temperature. Efforts in this direction have recently been made by Hoffman.[37]

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