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(27) Below T_g the correlated segmental motions are on a time scale >1 s, and below the β transition the time scale of even the localized segmental motions is >1 s.

On the Crystallization of High Molecular Weight Normal Hydrocarbons

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ABSTRACT: It is pointed out in this paper that the chain lengths at which low molecular weight polyethylene fractions and the recently synthesized high molecular weight *n*-alkanes no longer form extended-chain crystallites are very close to one another for crystallization from either the pure melt or dilute solution. On the basis of this observation, a nucleation theory, utilizing the Flory free energy of fusion function, which is inherent in chain molecules, has been applied to the problem. This treatment gives a natural explanation for the molecular weight at which the demarcation in crystallite form occurs. No restraints are placed on the thickness of the mature crystallite that develops.

Introduction

There have been several recent reports which describe the synthesis and properties of *n*-alkanes whose chain lengths are much higher than have been available for study heretofore.[1-3] The results of Lee and Wegner[1,2] and of Ungar et al.[3] have shown that for these compounds, depending on the crystallization mode, there is a molecular weight below which extended-chain crystallites are always formed. (It has been established that for the lower molecular weight *n*-alkanes, where all the molecules are of exactly the same size, molecular crystals are formed.) Above this molecular weight some type of folded-chain crystallite is formed. (We use the concept of folded-chain crystallites to convey the idea that the crystallite thickness is not comparable to the extended chain length. There is no implication in this phraseology as to the nature of the interfacial structure of the basal plane.) In the latter case the crystallite thickness is substantially less than that of the extended chain. Ungar et al. have concluded that the crystallite thicknesses are an integral fraction of the extended chain length, in analogy to previous reports for low molecular weight poly(ethylene oxide) fractions.[4,5] Lee and Wegner,[1,2] on the other hand, concluded that when chain folding occurs the crystal thicknesses are not exactly integral values of the extended chain length. The different conclusions are based on very similar experimental methods, namely, Raman LAM and small-angle X-ray scattering (SAXS). In one case the comparison of the Raman and SAXS results indicates a substantial, 10–15 Å, disordered overlayer for crystals formed in dilute solution.[1] In the other study it was found for similar crystallite thicknesses, involving similar techniques, that there was no disordered overlayer.[3] These differences in interpretation with undoubtedly be settled in due time by those involved. They do not directly concern us in the present work. For present purposes it is important that both schools of investigators agree as to the molecular weight range in which some type of folding occurs.

Wegner and Lee[1] report that for crystallization from the pure melt a nonextended-type crystallite is formed when the carbon number *n* is greater than 168. When crystallized from dilute solution the molecular weight range for the formation of a folded-chain type crystallite is reduced to $n = 168$ ($M = 2352$).[1] For this *n*-alkane, depending on the crystallization temperature, the ratio of crystallite thickness to extended chain length was in the range 0.55–0.67. Ungar et al.[3] found that for bulk crystallization a folded-type crystallite could be developed at $n = 246$ ($M = 3466$); while for crystallization from dilute solution a similar result is found for $n = 150$ ($M = 2102$). Thus, both studies are in substantial agreement with respect to the molecular weight at which folding occurs, for either mode of crystallization.

Recent studies have shown that low molecular weight linear polyethylene fractions display a very strong similarity to the *n*-alkanes.[6-8] Although the low molecular weight polymers are well fractionated, molecular crystals cannot be formed since all the molecules are not exactly the same chain length. For crystallization from the pure melt a fraction, $M_n = 1586$ and $M_w = 2221$, formed crystallites under all crystalline conditions with thicknesses comparable to the extended chain length.[6] However, when the molecular weight is slightly increased to $M_n = 3769$, crystallites having a thickness smaller than the extended molecular length are formed at the lower crystallization temperature. However, with only a small, 2–3 °C, increase in the crystallization temperature, thicknesses comparable to extended chain length were found. For $M_n = 5600$ the ratio of crystallite thickness to extended chain length ranged from 0.37 to 0.99. It has been quantitatively shown that the crystallite thicknesses of this fraction are *not* integral fractions of the extended chain length. For molecular weights 8000 and greater, extended-type chain crystals could not be formed. There is, therefore, almost quantitative agreement between the *n*-alkanes and polyethylene fractions with respect to the molecular weight at which nonextended crystallite structures can be developed in bulk crystallization.

Similar results are obtained with respect to crystallization from dilute solution. We have found that for polyethylene fractions with $M_n = 1586$ either folded- or extended-type crystals are formed.[7] The exact type observed

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is very sensitive to the crystallization temperatures. However, for $M_n = 2859$ only a folded-type crystallite was observed.[7,9] Leung et al.[8] report very similar results for the crystallization of low molecular weight polyethylene fractions from dilute solution. Therefore, for crystallization from dilute solution very good agreement is also obtained between the *n*-alkanes and the low molecular weight fractions with respect to the chain length at which extended-chain crystallites do not form.

The striking similarity between the *n*-alkanes and the low molecular weight polyethylene suggests that the explanation previously offered for the polymers can also apply to the *n*-alkanes.[6] The polymer behavior was explained by invoking nucleation theory appropriate to chain molecules of finite length.[10,11] The main principle in this theory involves selecting a sequence of ordered chain units and examining the results in relation to the extended chain length. Although the nuclei size is a continuous, monotonic function of the crystallization temperature, there is a temperature range of only a few degrees where a significant change in the thickness required to form a stable nucleus is observed. In this range the nucleus thickness decreases from about half the extended chain length to a much lower value. The assumption was made that when the critical size nucleus in the chain direction, ζ^*, is approximately $\geq {}^1/_2$, growth along the chain axes is sufficiently rapid to allow extended chain thicknesses to be achieved. (The value of ${}^1/_2$ is taken as a convenient reference point. We do not imply any quantitative significance to this value.) However, for smaller initial sizes, the growth in the chain direction will be retarded relative to lateral growth. Under these conditions the possibility exists for the nucleation of separate segments within the same molecule. This possibility will further retard growth to extended chain length and lead to a distribution of crystallite sizes.

Recent in situ SAXS studies of $C_{246}H_{494}$, using a synchrotron source, have revealed that the initial crystallite thickness that is detected is a noninteger fraction of the extended chain length.[12] Thus, to explain the results that have been described, including the thickness of the mature crystallites, it is not necessary to a priori assume any type of folded chain nucleus or, in particular, a quantized type of folded chain.[13,14] Therefore, by applying the same nucleation theory to the *n*-alkanes, as was used for the low molecular weight polymers, it should be possible to explain the similarities in behavior.

Results and Discussion

The calculations are based on the adoption of the Flory free energy of fusion expression[15] to nucleation theory for chains of finite molecular weight.[10,11] The theory is well suited for the problem at hand since for the *n*-alkanes the complete chain molecule is not required to participate in nucleus formation. The theory has been developed for both a three-dimensional nucleus and a coherent two-dimensional nucleus of the Gibb's type. An important ingredient in the theory is the calculation of the number of ways a critical nucleus, ζ^* units in length, can be selected from a chain x units long.

For a three-dimensional nucleus it is found that[10]

$$\frac{\zeta^*}{2}\left(\Delta f_u - \frac{RT}{x} - \frac{RT}{x - \zeta^* + 1}\right) = 2\sigma_{en} - RT \ln\left(\frac{x - \zeta^* + 1}{x}\right) \quad (1)$$

Here σ_{en} is the interfacial free energy for nucleation and Δf_u is the free energy of fusion per repeating unit of an infinite molecular weight chain. (It should be noted that σ_{en} cannot be equated with σ_{ec}, the surface free energy of a mature crystallite, or σ_e, the surface free energy of an equilibrium crystallite.) The free energy of fusion can be approximated for present purposes by

$$\Delta f_u = \Delta H_u \frac{(T_m{}^\circ - T)}{T_m{}^\circ} \quad (2)$$

In this equation $T_m{}^\circ$ is the equilibrium melting temperature of a *n*-alkane of infinite molecular weight (linear polyethylene) and ΔH_u is the enthalpy of fusion per repeating unit. The best estimates of these parameters, which are used in subsequent calculations, are $T_m{}^\circ = 145.5 \pm 1$ °C[15,20] and $\Delta H_u = 980$ cal/mol.[16] Utilizing these parameters ζ^* can be calculated for a given crystallization temperature and chain length provided the value of σ_{en} is given. Since σ_{en} has not been directly measured or calculated, it is necessary to select a range of reasonable values in order to perform an objective analysis.

In a previous study[6] of extended-chain crystallites of low molecular weight polyethylenes, the surface free energy, σ_e, of the equilibrium crystallites was calculated from the measured melting temperatures. In the low molecular weight range studied, σ_e was found to increase monotonically from 1300 to 3500 cal/mol, as the number-average chain length increased from 113 to 400. Although these values cannot be equated with the interfacial free energy for nucleation, they narrow the range of reasonable values that can be assigned to σ_{en}. It is difficult to envision a decrease in surface free energy in going from nucleation to the growth of a mature crystallite. It is possible, however, that the nucleation interfacial free energies are very close to the calculated equilibrium interfacial free energies. In this case a similar increase in the nucleation free energy would occur with increasing chain length. Alternatively, the possibility has to be considered that the nucleation interfacial free energy could be independent of molecular weight in the range of interest. The increases in σ_e that are deduced from melting point studies[6] could only be reflecting the properties of the mature crystallites. For shorter chain lengths, values of σ_{en} up to 2000 cal/mol can be considered reasonable; for chains of about 400 units or more σ_{en} could conceivably have values from a high of 4000 cal/mol to a lower value of about 1000 cal/mol. We have, therefore, performed these calculations utilizing σ_{en} values within this wide interval as the crystallization temperature and chain length were varied. With this allowable range in σ_{en} values we can only expect to ascertain general trends.

For high molecular weight polymers, crystallization does not usually occur by a homogeneous nucleation process. However, for even the largest of the *n*-alkanes, a homogeneous nucleation process is much more likely than for the high molecular weight polymers. If a heterogeneous nucleation process was operative, the model of a three-dimensional nucleus that was described would not be accurate. However, calculations with various types of heterogeneities have indicated that in many cases the nuclei thickness would not be reduced from that calculated by a homogeneous nucleation theory.[17] In the extreme, for a coherent two-dimensional nucleus, the critical nuclei thickness is given by[11]

$$\zeta^* = \frac{2\sigma_e - RT \ln\left(\dfrac{x - \zeta^* + 1}{x}\right)}{\Delta f_u - \dfrac{RT}{x}} \quad (3)$$

Nuclei thicknesses were also calculated by using this two-dimensional model.

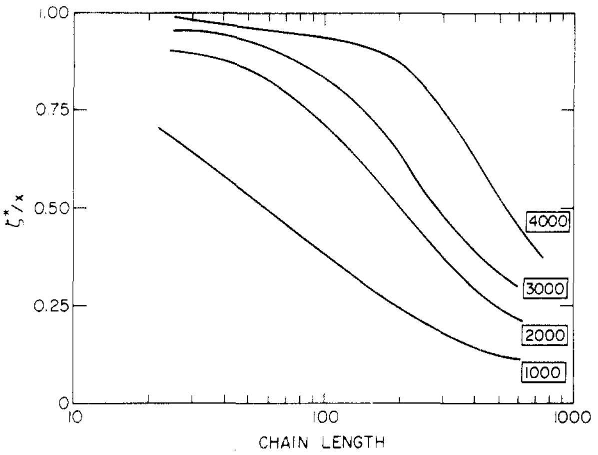

Figure 1. Plot of ζ^*/x as a function of chain length for indicated values of σ_{en} at a constant undercooling $\Delta T = 20$. Three-dimensional nucleation theory, eq 1.

For the initial calculations, in order to assess the effect of chain length, we have calculated the ratio of ζ^*/x for the range of σ_{en} values discussed, utilizing three-dimensional nucleation theory, eq 1. To make a rational comparison between molecular weights, plots of ζ^*/x as a function of chain length are given in Figure 1 for selected values of σ_{en} at an undercooling, ΔT, of 20 °C. (The undercoolings presented here were reckoned on the basis of the equilibrium melting temperature of each of the n-alkanes. These values were calculated from the Flory–Vrij theory.[18]) This undercooling is a good representation of the temperature range where crystallization would occur upon rapid cooling from the melt. As a point of reference we focus attention on the curve for $\sigma_{en} = 2000$ in this figure. Even at this fairly large undercooling the thickness of the nucleus for the shorter n-alkanes is close to the extended chain length. Hence, it is not difficult to understand why molecular crystals will form in these situations without requiring that the total molecule participate in the nucleation. However, when the chain length is increased to several hundred units, the nuclei thicknesses become significantly less than the molecular length. At a chain length of about 200 units ζ^*/x decreases below 0.5. Above this chain length multiple nucleation of an individual chain becomes possible. With increasing chain length the nuclei size becomes much less than half the molecular length, thus enhancing the possibility of multiple nucleation. These conclusions are consistent with the experimental observation that the larger n-alkanes do not form extended molecular length crystals during rapid cooling although the smaller chains do.[1,3]

Changing the value of σ_{en} does not alter the general pattern of ζ^*/x decreasing with chain length. However, the chain length at which the nuclei size reaches half the molecular length is altered. For a σ_{en} value of 4000 cal/mol the nuclei size does not decrease to half the extended length until a chain of about 500 units is reached. However, for $\sigma_{en} = 1000$ cal/mol this condition is achieved at 50 units. Quantitatively, similar results are found when comparisons are made at ΔT equal to 5 °C. At this lower undercooling ζ^*/x values are higher at corresponding chain lengths. This ratio will still decrease with x; the rate of decrease will be dependent on σ_{en}.

The influence of undercooling is illustrated more clearly in Figure 2. Here, plots of ζ^*/x against x are given for a range of undercoolings at a constant σ_{en} of 1500 cal/mol. With increased undercooling the chain length required for the nuclei thickness to achieve half chain length becomes smaller. For chains in the range 100–500 units, nuclei sizes above or below one-half can be obtained, depending on the choice of undercooling. For chain lengths greater than 500 units, nuclei sizes less than half the extended chain length are obtained for all reasonable undercoolings. The undercoolings analyzed give a good representation of the extreme in possible crystallization conditions. In a practical sense, these range from rapid quenching to very slow cooling. The results illustrated in Figure 1 and 2 can be used to predict possible structures that will be formed by the n-alkanes. The smaller chains should form extended-chain crystallites for virtually any crystallization condition. For chains several hundred units long, either extended length or much smaller sized crystallites will form, depending on the choice of crystallization conditions. For larger chains crystallites much smaller than extended length should form, irrespective of the crystallization conditions.

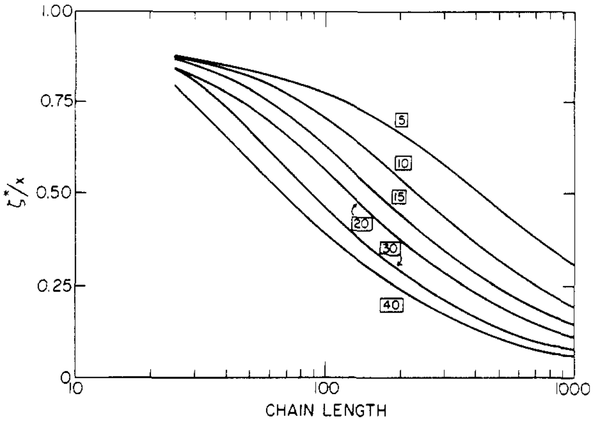

Figure 2. Plot ζ^*/x as a function of chain length for the indicated values of the undercooling ΔT for $\sigma_{en} = 1500$ cal/mol. Three-dimensional nucleation theory, eq 1.

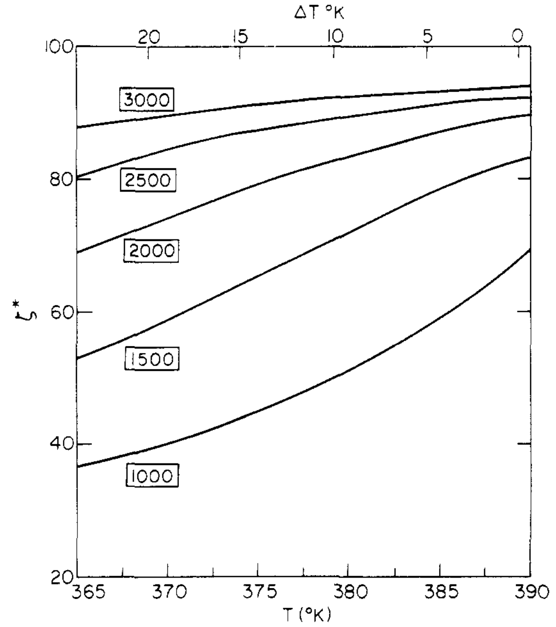

Figure 3. Plot of nucleus thickness ζ^* against temperature for $x = 100$ for different values of σ_{en}. Three-dimensional nucleation theory, eq 1.

The analysis given so far has not taken into account the possibility that σ_{en} might increase with chain length. The results of such calculations are given in Figure 3–5 where, for a fixed chain length, ζ^* is plotted against the crystallization temperature for a set of σ_{en} values. Figure 3 gives the results for a chain of 100 units where σ_{en} has been varied from 1000 to 3000 cal/mol. Nuclei sizes greater than

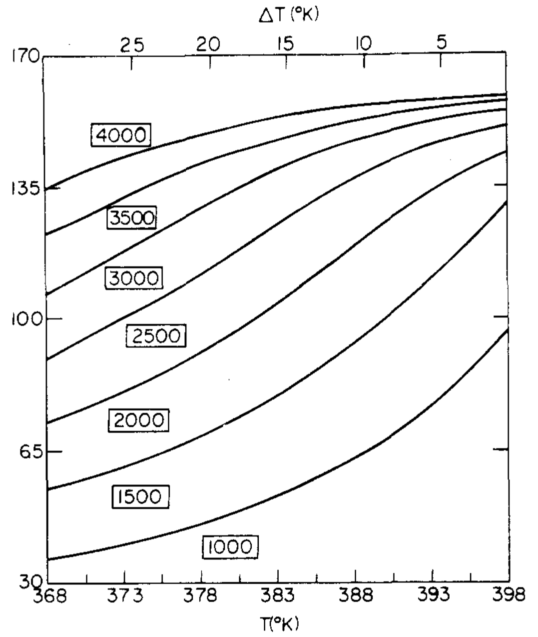

Figure 4. Plot of nucleus thickness ζ^* against temperature for $x = 168$ for different values of σ_{en}. Three-dimensional nucleation theory, eq 1.

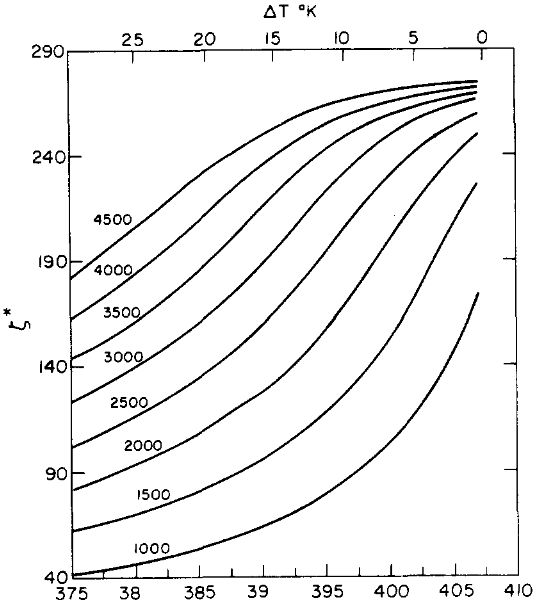

Figure 5. Plot of nucleus thickness ζ^* against temperature for $x = 288$ for different values of σ_{en}. Three-dimensional nucleation theory, eq 1.

half the extended length are obtained over a wide temperature range for σ_{en} equal to or greater than 1500 cal/mol. For the lowest σ_{en} in the plot, $\sigma_{en} = 1000$ cal/mol, ζ^* decreases below 50 units only at very large undercoolings. Solely on the basis of these results, one would predict that only extended chain crystallites would form in n-alkanes of 100 units or less, irrespective of the crystallization conditions. This expectation is in agreement with both the classical results[18] as well as the more recent ones.[1-3]

The calculations for a chain of 168 units presented in Figure 4 give less definitive conclusions. This chain length was chosen since it represents an actual experimental situation.[1] For the large σ_{en} values of 2500–4000 cal/mol ζ^* remains greater than one-half the total number of units for a wide undercooling range. For more reasonable σ_{en} values of 1000–2000 cal/mol the nuclei thicknesses decrease below one-half the extended length at high undercoolings. On the basis of these calculations this chain length forms either extended or smaller sized crystallites, depending on crystallization conditions. It was found experimentally that extended-chain crystals formed even when this n-alkane was quenched from the molten state.[1] However, when a dilute solution of this sample was quenched, nonextended crystallites with smaller thicknesses were formed.[1] Under these conditions crystallization occurs at a larger undercooling. From both the point of view of experiment and theory this chain length represents a borderline situation.

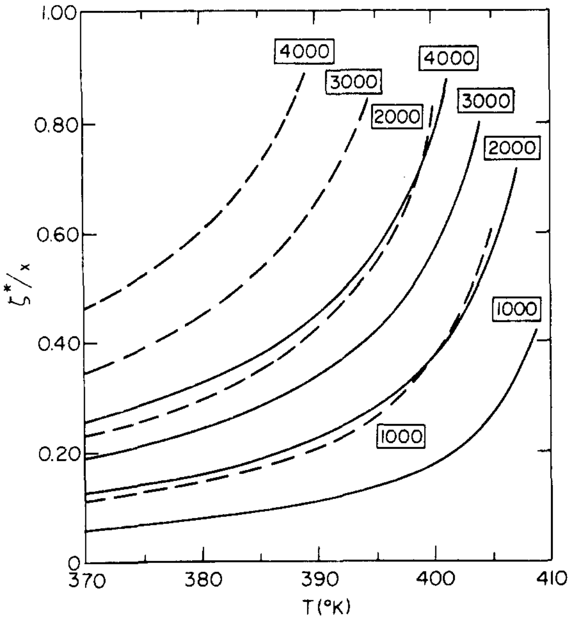

Figure 6. Plot of ζ^*/x against temperature for $x = 168$ and 288 for different values of σ_{en}. Two-dimensional nucleation theory, eq 3. $x = 168$ (- - -); $x = 288$ (—).

The results of the calculation for a chain of 288 units are summarized in Figure 5. These plots indicate that an n-alkane of this molecular weight is less likely to form an extended-chain crystallite. For σ_{en} of 1000 cal/mol the undercooling must be reduced to 5 °C before the nuclei size increases to half the molecular length. Even if σ_{en} is assigned a greater than 1000 cal/mol value, nuclei sizes greater than one-half the molecular length will only be obtained for relatively low undercoolings. As was discussed previously, σ_{en} values from 3000–4500 cal/mol yield nuclei sizes greater than one-half the extended length for a large undercooling range. The theoretical difficulty of forming extended-chain crystallites in this molecular weight range is supported by the experimental results. Cooling the n-alkane $x = 288$ in dilute solution results in the formation of crystallites that are less than extended chain length.[1] The results for chain lengths between $x = 168$ and 288 can be easily interpolated from Figures 4 and 5. When $x = 216$ is quenched from the pure melt, much less than extended-length crystallites also result.[3] When an n-alkane of 294 units was cooled in the bulk at the very slow rate of 0.2 deg/min, some extended-chain crystallites, as well as those of smaller lengths, were formed.[3]

Calculations that assume a two-dimensional coherent nucleation process are presented in Figure 6 for chain lengths of 168 and 288 units. Much smaller nuclei sizes are obtained with the two-dimensional model for comparable σ_{en} values and chain length. However, the same trends that were found for three-dimensional nucleation are still observed. Analogous to the three-dimensional case, thicknesses greater than half the extended length are obtained at the lower undercoolings and higher surface free energies. Therefore, even with this nucleus model the transition from extended to smaller size crystallites is predicted to occur within the range of chain lengths of the n-alkanes being considered.

Similar calculations of ζ^* were made previously for a chain of 400 units using relatively large values of σ_{en}.[6] For σ_{en} of 2200 cal/mol the nucleus thickness does not increase to 200 units until the undercooling is lowered to 10 °C. If σ_{en} is increased to 2800 cal/mol the nucleus size becomes greater than half the extended length only at undercoolings of 15 °C or less. This chain length is comparable to the largest n-alkane that has been studied so far, $x = 390$.[3] Even the slow cooling of this molten n-alkane does not result in the formation of extended-chain crystallites.

Calculations were also performed for the hypothetical n-alkane of 500 units. For σ_{en} of 2500 cal/mol the size of a three-dimensional nucleus only exceeds one-half the total length at very low undercoolings. The very high interfacial free energy of 3000 cal/mol or greater is required in order for the size to be greater than 250 units at reasonable undercoolings. According to the model, extended-chain crystallites would not be formed at this chain length irrespective of the crystallization conditions.

The simple nucleation theory that is presented is based on inherent properties of chain molecules.[15] The nuclei sizes are found to be very sensitive to chain length when reasonable values are assumed for the nucleation interfacial free energy. The demarcation in chain length and crystallization conditions between the extended-chain crystallites and those of smaller size becomes clear from this analysis. These conclusions are based on the relative nuclei sizes with the implication that they control the thickness of the mature crystallites.

Crystallite thickening following nucleation must also be considered as part of the total crystallization process. After formation of the nucleus, the remaining chain units of a molecule can in principle crystallize further by c-axis growth and extended-chain crystallites will be formed. This process should be operative for large values of ζ^*/x. However, for small values of ζ^*/x c-axis growth is inherently more difficult. A molecule can now participate more than once within the same crystallite and the possibility exists for multiple nucleation acts along the same chain. Under these conditions there are obvious restraints to forming extended-chain crystallites. The inability for c-axis growth to occur with crystallites having small ζ^*/x values have been observed in two low molecular weight polyethylene fractions ($M_n = 5600$ and 3769). After crystallization at low temperatures, significant crystallite thickening does not occur after long times even if the crystallization temperature is raised to the region where extended-chain crystallites would form isothermally.[6] Thus, there appears to be a correlation between the nuclei size and that of the mature crystallite. For higher molecular weights, on the other hand, crystallite thickening takes place by a quite different mechanism.[6,19-21]

Synchrotron X-ray measurements have shown that the n-alkanes begin crystallization as a nucleus whose thickness is not an integral fraction of the extended molecular length.[12] This result is clearly in close accord with the analysis presented here. The crystallites are reported to thicken with time at the higher crystallization temperatures while the size is reduced at lower crystallization temperatures. At the high temperatures, where $\zeta^* \gg {}^1/_2x$, growth along the chain axis should occur relatively easily. At the lower crystallization temperature, where $\zeta^* \leq {}^1/_2x$, multiple nucleation steps can take place. A broad crystallite size distribution will result with the possibility of a reduction in the average crystallite thickness.

The analysis given suggests that crystallization kinetic studies as a function of temperature would establish the conditions for the formation of the different types of crystallite structures and allow for estimates of the nucleation interfacial free energy. These data would enable a more quantitative analysis to be made with eq 1 and 3. Preliminary studies have indicated that the n-alkane $C_{192}H_{286}$ follows Avrami-type kinetics with a negative temperature coefficient indicative of nucleation control.[22]

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Registry No. Polyethylene, 9002-88-4.

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