Crystallization Kinetics of High Molecular Weight *n*-Alkanes

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ABSTRACT: The growth rate data reported by Bassett and collaborators (Sutton, S. J.; Vaughan, A. S.; Bassett, D. C. *Polymer* 1996, 37, 5735) for the *n*-alkane $C_{246}H_{494}$ have been analyzed using nucleation theory pertinent to chain molecules of low molecular weight. The same value for the interfacial free energy governing nucleation was found irrespective of whether the mature crystallites that developed were chains folded, with a spherulitic superstructure (low-temperature crystallization), or were non-spherulitic with extended chain (high-temperature crystallization). Reasons for this behavior are advanced and the important implications to polymer crystallization discussed.

Introduction

In a recent series of papers, Bassett and collaborators have reported on the crystallization behavior of a set of monodisperse *n*-alkanes, namely, $C_{294}H_{590}$, $C_{246}H_{494}$, and C_{198} H_{398}.[1−3] They studied the supermolecular structures that develop and also measured the growth rates of these structures, as a function of the crystallization temperature. The range of crystallization temperatures encompassed was such that crystallites formed with extended chains developed at high temperatures, while a folded chain structure, close to once folded, developed at the lower crystallization temperatures. Major changes in superstructure accompanied these changes in chain structure.

Examination by transmission electron, as well as polarizing optical, microscopy revealed that at the low crystallization temperatures conventional, spherulitic type superstructures are formed with folded chain crystallites.[1−3] On the other hand, spherulites do not develop with extended chain crystallites. Rather, in this case long crystallites are observed that are not organized into spherulites. The microstructure consists of parallel stacks of continuous lamella.[3] These structural observations have important consequences. As was pointed out by Bassett *et al.*, they demonstrate that spherulites can be formed with very pure chain molecules. Impurities are thus not a requirement for spherulite formation of chain molecules.[4−6] This observation for chain molecules confirms an earlier report that other pure, monomeric organic compounds can also form spherulites.[7] These works make clear that it is the crystallization conditions that determine whether spherulites are formed.[1−3] In addition, the data that were presented[1] also allow for an analysis of how the distinctly different superstructures, which are formed in the different temperature ranges, affect the crystallization kinetics. The analysis of the kinetic data is the purpose of the present paper. For this objective it will be helpful to briefly outline nucleation theory that is appropriate to low molecular weight chain molecules. Some unique features are found that are not encountered in conventional nucleation theory.[8,9]

Background

In the conventional manner, the growth rate, G, can be expressed quite generally as

$$G = G_0 \exp\left\{-\frac{E_D}{RT} - \frac{\Delta G^*}{RT}\right\} \tag{1}$$

Here G_0 is a constant, E_D the activation energy for segmental transport, and ΔG^* the free energy change required to form a critical size nucleus. Over the small temperature interval that will be of interest for the *n*-alkanes, the transport term can be considered to be independent of temperature. Hence, eq 1 can be written as

$$\ln G = \text{constant} - \frac{\Delta G^*}{RT} \tag{2}$$

In formulating an expression for ΔG^*, it needs to be recognized that there is a fundamental difference between the nucleation of chain molecules of finite molecular weight and other type monomeric substances. With monomers, the complete molecule participates in the nucleus. On the other hand, for a chain molecule beyond a small number of repeating units, only a portion of the molecule will be involved.[10,11] This distinction must be taken into account in calculating ΔG^*. For present purposes, we take as an illustrative example the coherent monomolecular deposition of chains on the surface of an already existing crystallite, i.e., a Gibbs type two-dimensional nucleus.[12] Although this particular nucleation mode has been popularly used in analyzing polymer crystallization, other types of nucleation can be treated equally well in a similar manner.[8] The general conclusions that are reached in the ensuing analysis do not depend on the specific kind of nucleation that is selected.

In developing nucleation theory appropriate to chain molecules, the same basic procedure is adopted as that

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which has been classically used for monomeric systems. The free energy change that accompanies the formation of a monomolecular nucleus, ζ units long and ρ sequence in breadth, from a collection of chains in the pure melt, each of which is X units long, can be expressed as[9,13]

$$\Delta G = 2\zeta\sigma_u + 2\rho\sigma_e - \zeta\rho\Delta G_u + \frac{RT}{X}\zeta\rho - \rho RT \ln\left(\frac{X - \zeta + 1}{X}\right) \quad (3)$$

Here σ_u is the lateral interfacial free energy per chain unit, σ_e is the excess free energy associated with the interface, or boundary, between the ordered and disordered chain units, and ΔG_u is the free energy of fusion per repeating unit characteristic of the infinite chain. The first two terms in eq 3 represent the positive contribution to the total free energy change of the interfaces that are present. The third term represents the contribution of the bulk free energy of fusion of the $\zeta\rho$ units. The first three terms in this equation are thus the same as the classical formulation of monomeric nucleation theory. The last two terms represent the special features of chain molecules. The first of these expresses the entropy gain that results from the increased volume available to the molecular ends after melting. The last term results from the fact that only a portion of the chain units of a given molecule participates in the formation of a nucleus. It represents the entropy gain that results from the number of different ways a sequence of ζ units can be located in a chain X units long, with the terminal units being excluded from the sequence in question.[13,14] This term is of prime importance to the present discussion for it introduces the effect of finite chain length. We should also note that ΔG_u represents the free energy of fusion per repeating unit of an infinite chain. The reason for this is that the $\zeta\rho$ units that were selected to participate in the nucleus do not recognize the chain ends, except for the corrections embodied in the last two terms of eq 3.

The surface described by eq 3 does not possess either a maximum or minimum. However, it does contain a saddle point, the coordinates of which define the dimensions of a critical size nucleus.[15] By appropriate definition and substitution, the coordinates of the saddle point are found to be[9]

$$\rho^* = 2\sigma_u \Big/ \left(\Delta G_u - \frac{RT}{X} - \frac{RT}{X - \zeta + 1}\right) \quad (4)$$

$$\zeta^* = \left[2\sigma_e - RT \ln\left(\frac{X - \zeta^* + 1}{X}\right)\right] \Big/ \left(\Delta G_u - \frac{RT}{X}\right) \quad (5)$$

This leads to

$$\Delta G^* = 2\sigma_u\left[2\sigma_e - RT \ln\left(\frac{X - \zeta^* + 1}{X}\right)\right] \Big/ \left(\Delta G_u - \frac{RT}{X}\right) = 2\sigma_u\zeta^* \quad (6)$$

As X approaches infinity

$$\Delta G^* = \frac{4\sigma_e\sigma_u}{\Delta G_u}; \quad \zeta^* = \frac{2\sigma_e}{\Delta G_u}; \quad \rho^* = \frac{2\sigma_u}{\Delta G_u} \quad (7)$$

and the classical result is obtained.[15] This reduction reflects the fact that for an infinite chain there is no influence of end groups in the selection and nucleation process.

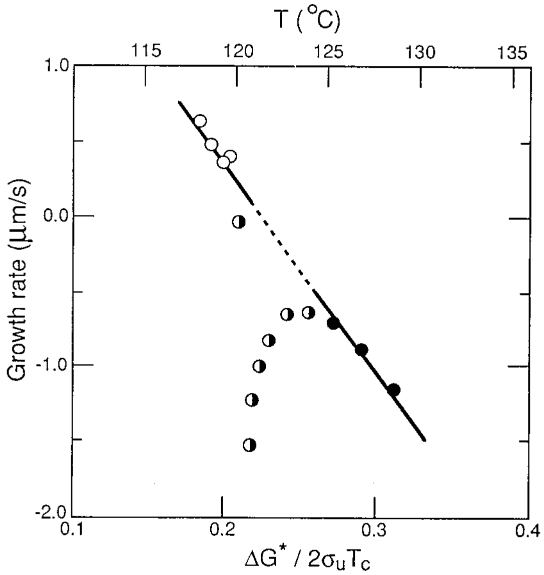

Figure 1. Plot of ln G against $\Delta G^*/2\sigma_u T_c$ according to eqs 2, 5, and 6 (lower horizontal axis). Upper axis gives corresponding crystallization temperature, T (°C).

Since the complete chain molecule does not participate in the nucleus, ΔG^* represents a selection process.[10,11] The selection of the critical number of units from a chain, ζ^*, is the first step in forming a nucleus of critical size. Subsequently, if deemed necessary, additional conditions or restraints can be added to the nucleation process. However, the sequences selected initially can serve as a nucleus by themselves.

The quantity ΔG_u is the free energy of fusion per repeating unit of the infinite chain. In the vicinity of the equilibrium melting temperature $T_m°$, it can be expressed in the usual manner as

$$\Delta G_u = \Delta H_u(T_m° - T)/T_m° \quad (8)$$

Here, ΔH_u is the enthalpy of fusion per repeating unit. Thus, the temperature dependence of the growth rate of each of the morphological forms that have been reported for $C_{246}H_{494}$[1] can be analyzed in terms of eqs 2, 5, 6, and 8. In this analysis the value of σ_e cannot be determined independently. However, it has been found that similar conclusions are reached irrespective of the value chosen for σ_e.[16] The primary concern here is whether or not the σ_e value depends on the specific superstructure that is being formed.

Results and Discussion

The growth rate data for $C_{246}H_{494}$, reported by Sutton *et al.*,[1] are plotted in Figure 1 according to the aforementioned analysis. For illustrative purposes we have selected a value of 2000 cal/mol of sequences for σ_e. Changing the σ_e value just shifts the data along the horizontal axis.

Our interest here is in analyzing only the kinetic data that represent well-defined structures that are formed directly from the pure melt. The extended chain crystallites that thus develop at the high crystallization temperatures $T_c \geq 125$ °C, are represented by the closed circles in the figure. The folded chain, spherulitic structures, formed at $T_c \leq 120$ °C, are represented by the open circles. Crystallizations at intermediate temperatures, the region where a maximum in the rate is observed, are represented by half-filled circles. In this region of crystallization, it has been directly demonstrated that rapid isothermal thickening of the initially formed folded structures takes place.[10,17] Thus, in this temperature region the measured growth rates will be affected by the thickening. In turn they will not represent the structures that were initially formed from the melt. It has also been postulated that the folded structures poison the growth surface for the crystallization of extended chains and gives rise to the maximum.[18] Whatever the reason, or reasons, this intermediate crystallization temperature region does not represent structures that were directly formed from the melt. Consequently, the growth kinetics in this region, although of general interest, are not pertinent to our present discussion. Here, we are only concerned with structures, extended or folded, that are formed directly from the pure melt.

The important and significant conclusion from Figure 1 is that the growth rate data for both extended and folded chain crystallites, which correspond respectively to nonspherulitic and spherulitic morphological superstructures, adhere to the same straight line. Thus, for a constant value of σ_u, the interfacial free energy associated with the basal plane of the nucleus, σ_e, is the same for the two different chain configurations and the accompanying morphologies that are associated with the mature crystallites. A similar conclusion was reached previously from studies of the overall crystallization kinetics of the *n*-alkanes, $C_{168}H_{338}$, $C_{192}H_{386}$, and $C_{240}H_{482}$, by means of differential scanning calorimetry.[10,16] This earlier conclusion can now be extended to include the morphological forms that develop. We are not concerned here with the absolute value of σ_e. The fact that the same value of σ_e applies implies that the interfacial structure of the nucleus is the same irrespective of the chain configuration within the nucleus and of the supermolecular structure of the actual mature crystallites that develop. This may appear to be a surprising conclusion at first glance.. However, there is no rule, or law, of crystal growth that requires the structure of the macroscopic crystallite that develops to be the same as that of the nucleus from which it evolves. This point has been made and discussed many times with respect to polymer crystallization.[11,16,19−23] Calvert and Uhlmann[22] have shown in detail how a coherent Gibbs type nucleus comprised of unfolded ordered chain units can develop into a stable mature lamellar-like crystallite.

It has also been pointed out that the ratio ζ^*/X is crucial in determining the thickness of the ultimate crystallite.[11,16] When ζ^* is comparable to X, chain growth in the longitudinal direction can take place without undo difficulty. This will result in extended chain crystallites and the supermolecular structures that Bassett *et al.* have reported.[1−3] In contrast, when ζ^*/X is small, longitudinal growth along the chain axis will be severely impeded because of the large numbers of entangled chain units that have to eventually be incorporated into the crystallite. Under these circumstances, crystallization can still proceed by a lamellar growth mechanism, leading to some type of folded chain crystallite and the spherulitic superstructure described by Bassett *et al.*[1−3] The magnitude of ζ^* depends on the crystallization temperature. Thus, at high crystallization temperatures extended chain crystallites will develop, while at lower ones folded crystallite will form, both evolving from the unfolded chain nucleus. These considerations explain the appearance of either folded chains, or extended ones as a function of the crystallization temperature.[1−3,11,16]

The approach outlined above applies equally well to polymer crystallization. It leads to lamellar structures and the development of spherulites. It is not necessary to postulate that nuclei are comprised of regularly folded chains in order for lamellar-like crystallites to evolve. The fact that the same nucleation process and nucleus structure is involved for both extended and folded chain crystallites does not allow for this postulate. Hence, the free energy of making a fold or bend cannot be calculated from the nucleation interfacial free energies that are deduced from studies of the temperature dependence of spherulite growth rates.[6]

The growth rate data by Organ et al.,[24] for the same *n*-alkane, are displaced slightly from those in Figure 1. However, these data give the same temperature dependence of the growth rate. The growth data given by Sutton et al. for $C_{294}H_{590}$ scatter slightly at the high crystallization temperatures.[1] They are, however, in qualitative accord with the plot in Figure 1. The data reported for $C_{198}H_{398}$ only cover the high-temperature, extended form, crystallization range.[1] Growth rate measurements below 118 °C were not carried out. Presumably the crystallization rate was too rapid for measurement by the technique used. However, studies of the overall crystallization kinetics with $C_{192}H_{386}$ give straight lines with the same slopes for both the folded and extended crystallites.[16]

Similar studies and analysis of the morphology and temperature dependence of the overall crystallization rates of low molecular weight fractions of linear polyethylene will be reported shortly.[25]

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