Macromolecules **1994,** *27,* 147-156

Crystallization Kinetics of Long-Chain *n*-Alkanes from the Melt and from Solution

R. G. Alamo, L. Mandelkern,* and G. M. Stack[†]

Department of Chemistry and Institute of Molecular Biophysics, Florida State University, Tallahassee, Florida 32306

C. Kröhnke

CIBA AG, Additives Division, R-1038.5.09, CH-4002 Basel, Switzerland

G. Wegner

Max-Planck-Institut für Polymerforschung, Ackermannweg 10, Postfach 3148, D-6500 Mainz, Germany

Received July 9, 1993; Revised Manuscript Received October 8, 1993[●]

ABSTRACT: The crystallization kinetics of the *n*-alkanes $C_{168}H_{338}$, $C_{192}H_{386}$, and $C_{240}H_{482}$ have been studied for the structures formed from either the pure melt or solution. For all the *n*-alkanes studied, and independent of the crystallization medium, the rate of crystallization decreases rapidly with increasing temperature. A discontinuity is observed in the temperature interval where a specific type of folded structure is no longer formed from the original melt or solution. The effect of concentration was also analyzed for the *n*-alkane with 168 carbons. Decreasing concentration decreases the rate of recrystallization but the functional dependence with temperature is maintained. To analyze the kinetics of the crystallites formed from the initial state, distinction needs to be made between these structures and those transformed from them. If this distinction is not made, the results could show an inversion in the rate of crystallization. The nucleation process of either folded or extended crystallites is found to be the same and shows characteristics similar to those found in the low molecular weight polymers.

Introduction

Long-chain *n*-alkanes with carbon atoms between 100 and 500 units have recently been synthesized.[1-4] Because of their uniform chain length, they serve as model compounds in the study of the polyethylenes as well as other polymers. Their properties can now be studied and compared to those of low molecular weight polyethylenes. Thus, extrapolation to the infinite chain length could, in principle, predict the properties of the polymeric chain. A fundamental connection between the *n*-alkanes and polymers has already been pointed out in the very similar molecular weights at which folding occurs.[5]

In a previous paper[6] the kinetics of the isothermal thickening of folded crystallites formed by $C_{168}H_{338}$ and $C_{240}H_{482}$ crystallized from either the melt or solution were analyzed. A detailed analysis of the fusion process and the crystallization kinetics from the pure melt of $C_{192}H_{386}$ has also been reported.[7] In addition, other analyses concerned with morphology,[8-13] nucleation theory,[14-18] isothermal thickening,[6,19,20] crystallization kinetics,[7,21-23] and melting processes[5-7] have been reported for similar high molecular weight *n*-alkanes. Of particular interest is an inversion in the crystallization rate versus temperature that has been claimed to take place in melt-grown $C_{246}H_{494}$[21,23] and in solution-crystallized $C_{198}H_{398}$.[22] Theories were developed to explain this very unusual phenomenon.[16-18] A similar inversion in the growth rate has also been reported for a methoxy-terminated poly(ethylene oxide) fraction crystallized from the bulk.[24]

In the present paper, the crystallization rates of $C_{168}H_{338}$ and $C_{240}H_{482}$ from the melt and from solution, as well as the crystallization of $C_{192}H_{386}$ from the melt (previously reported), are analyzed in terms of classical nucleation theory adapted for chains of finite length. It is found that a clear distinction must be made between crystallization from the disordered state and the subsequent isothermal thickening that can also occur. From these studies the reality of the inversion in the crystallization rate can be discussed and analyzed in detail. These studies will also provide the framework for a comparison of the behavior of the *n*-alkanes and of polyethylene fractions of similar chain lengths.

Experimental Section

The *n*-alkanes $C_{168}H_{338}$, $C_{192}H_{386}$, and $C_{240}H_{482}$ were used in this study. Their synthesis has been described previously.[4,7]

Thermal analysis experiments were performed using a Perkin-Elmer differential scanning calorimeter (DSC-2B) for most of the work. Some of the crystallization kinetic experiments from the melt were followed using a Perkin-Elmer DSC-4. For the crystallizations carried out from solution, stainless-steel liquid O-ring sealed pans, specially designed for solution studies, were used. Toluene was used as a solvent and the concentration (w/v %) was adjusted in the DSC liquid pan. Isothermal crystallizations were carried out directly in the calorimeter by first melting or dissolving the *n*-alkane and then rapidly cooling the sample to the desired crystallization temperature. Temperature calibration was performed using indium as the standard.

The crystallization kinetic data were obtained either from the exothermic peaks integrated to various crystallization times or from the area of the endothermic melting peaks. In the latter case, the sample was heated subsequent to isothermal crystallization for a predetermined time. The area of the peak was used to determine the amount of transformation that had taken place. The importance of using a relatively high heating rate has already been discussed.[6] When the endotherms were used to follow the crystallization kinetics, heating was always initiated from the crystallization temperature without any further cooling.

Results and Discussion

I. Rate of Crystallization. A. Crystallization from Solution.

Crystallization rates of the lowest molecular

[†] Present address: Eastman Chemical Co., P.O. Box 1972, Kingsport, TN 37662.

[●] Abstract published in *Advance ACS Abstracts,* November 15, 1993.

0024-9297/94/2227-0147$04.50/0

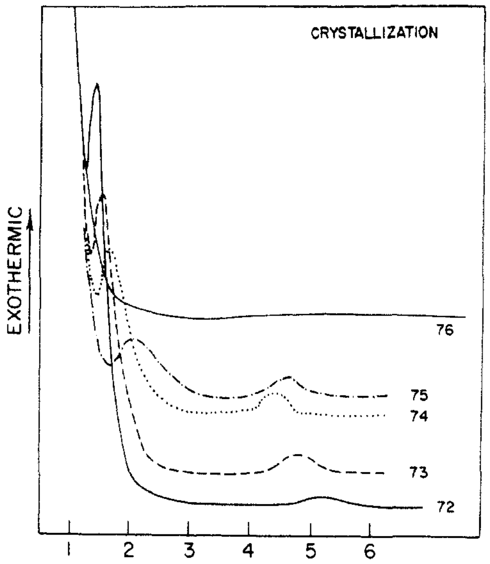

Figure 1. DSC exotherms of the crystallization of $C_{168}H_{338}$ from a 4 w/v % toluene solution at the indicated temperatures.

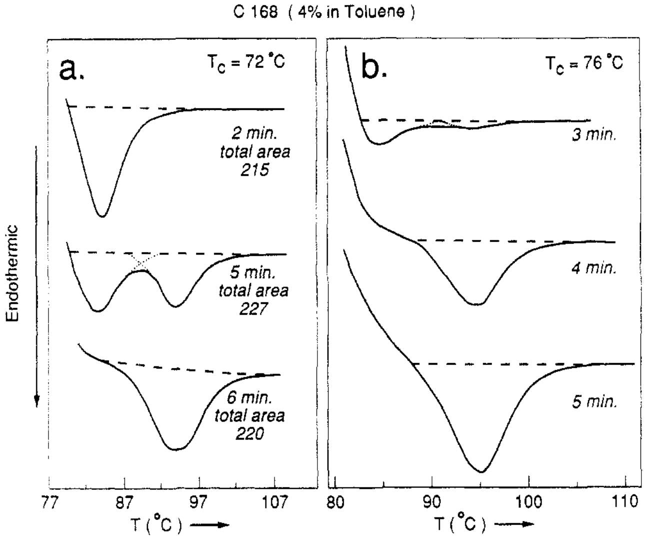

Figure 2. DSC dissolution endotherms after isothermal crystallization of $C_{168}H_{338}$ from a 4 w/v % toluene solution for the indicated times: (a) T_c = 72 °C; (b) T_c = 76 °C. The solutions were heated at 20 °C/min from the crystallization temperature.

weight n-alkane studied, $C_{168}H_{338}$, were analyzed at concentrations of 4, 1, 0.2, and 0.15% in toluene. The DSC exotherms for the crystallization of a 4% solution are shown in Figure 1. Only a narrow temperature interval, 70–76 °C, is available to study the crystallization process. For the purpose of clarity, the exotherms at 70 and 71 °C have been omitted from the figure. Below 70 °C the crystallization is too fast to be resolved by the DSC. Above 76 °C the crystallization is very slow and sufficient heat is not released to be detected in a standard DSC scan. Therefore, above this temperature, the crystallization process was monitored by plotting the area under a particular DSC dissolution peak as a function of crystallization time. An unusual feature in Figure 1 is the appearance of double exothermic peaks in the range of crystallization temperatures studied. The variation of the first exotherm (at the shorter times) with temperature follows the pattern expected for the crystallization of polymeric or oligomeric substances. It appears at longer times with increasing temperature, which is characteristic of a decreasing crystallization rate. On the other hand, the behavior of the second exotherm is quite the opposite. The process associated with this exotherm becomes faster with increasing temperature. For T_c = 76 °C both peaks overlap in a broad exotherm.

To obtain some insight into the process or processes that lead to these exotherms, the crystallization at a given temperature was interrupted at different times. For example, the crystallization was stopped at a time between the two exotherms, at a time corresponding to the maximum of the second exotherm, and after the second exotherm is completed. After each of these time intervals the crystals were rapidly melted from the crystallization temperature, T_c. The melting endotherms resulting from these interrupted experiments are given in panels a and b of Figure 2 for crystallization temperatures of 72 and 76 °C, respectively.[25] A common feature of the thermograms of Figure 2 is the disappearance with time of the initial peak found at ≈84 °C. In a previous work it was shown that this transformation is a consequence of an isothermal thickening process that is taking place during crystallization.[6] Close to once folded crystals are initially formed and are subsequently isothermally transformed to the thermodynamically more stable extended crystals. Measured and calculated dissolution temperatures of extended and once folded $C_{168}H_{338}$ crystals agreed closely with the dissolution peak temperatures of Figure 2. It was also shown that the rate of this process increases very rapidly with crystallization temperature.

If we compare the exothermic thermogram for T_c = 72 °C of Figure 1 with the melting endotherms of Figure 2a, it is clear that the second exotherm, which appears at about 5 min, must be associated with the isothermal reorganization of the once folded crystals (with a dissolution temperature $T_s \approx 85$ °C) to extended crystals ($T_s \approx 95$ °C). The extended crystals are formed at the expense of the folded crystals as implied by the conserved areas under the dissolution peaks before and after the transformation. Melting before the second exotherm starts to develop, i.e., after only 2 min at 72 °C, results in single melting peaks at temperatures which agree with the dissolution of once folded crystals. After crystallization for 5 min, where the second exotherm is developing, half of the area of the first melting peak is transformed to crystals having a dissolution temperature close to that for extended crystals. Melting after the second exotherm is observed (6 min) only results in extended crystals as shown in Figure 2a, indicative of a complete transformation.

The dissolution peaks observed at different times after crystallization at 76 °C (Figure 2b) are examples of the rapidly increasing rate of transformation of the folded to extended form with increasing crystallization temperatures. The fact that this transformation occurs during the initial stages of crystallization at 76 °C would have been difficult to ascertain by just examining the exothermic process. As Figure 1 indicates, at this temperature only one broad exotherm is perceived. Consequently, a careful examination of the dissolution peaks at the early times of crystallization is necessary in this range of temperatures in order to realize that folded crystals are formed initially from the original solution. As a corollary, it is important to recognize that when studying crystallization mechanisms, or kinetics, from either exothermic or endothermic peaks, care must be taken to establish the structure that is initially formed from the disordered state.

The crystallization kinetics can be analyzed by taking the inverse of the time to reach 10% of crystallization as a measure of the crystallization rate. For crystallization temperatures of 77 °C or higher, the dissolution temperature of the folded structure was not detected at any

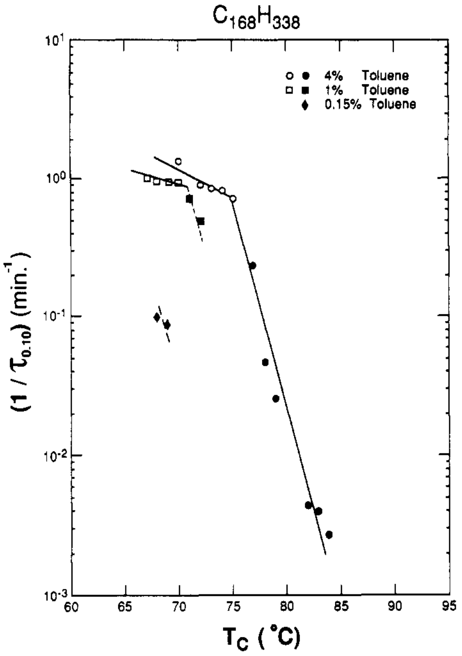

Figure 3. Rate of crystallization as a function of temperature for $C_{168}H_{338}$ crystals at the indicated concentrations in toluene. Open symbols represent data for once folded crystals. Closed symbols are data for extended crystals.

crystallization time. This observation is an indication that the folded crystallites are not formed at these temperatures. Only extended crystals were obtained at temperatures of 77 °C, or greater, and their crystallization rates were obtained from the dissolution peaks as previously noted. The crystallization rates are plotted versus crystallization temperature in Figure 3. Most of the data were obtained for a 4% solution. The sparser set of data that were obtained in 1 and 0.15% solutions are also included in this figure. All the data represent the crystallization rates of the structures that were initially formed. Thus, the crystallization rate at 76 °C from the 4% concentrated solution was not included in this figure. As was previously described in the interpretation of the broad exotherm obtained at this temperature (Figure 1), the transformation of the folded initially formed crystallites at 76 °C is very rapid and the experimental determination of the rate is complicated by the transformation. The open symbols represent folded chain crystals and the closed ones are the extended chain crystals.

The rate of crystallization decreases with increasing crystallization temperature. The data from the 4% solution show a distinct break at the crystallization temperature where folded crystals are no longer formed. Although fewer data points are available, similar trends are also observed for the 1 and 0.15% solutions. The data of Figure 3 indicate that decreasing concentration decreases the crystallization rate of both the folded and extended structural forms. If the time at which there is a maximum heat outflow is taken as representative of the overall crystallization rate ($\tau_{0.50}$), the general character of the rate of crystallization is unchanged.

An inversion in the rate of crystallization of a 3.85% solution of $C_{198}H_{398}$ has been reported from a DSC study in which dissolution peaks, after crystallization at a given temperature, were analyzed with time.[22] This inversion generates a minimum in the curve of the rate of crystallization vs temperature. The decrease of the rate of crystallization of $C_{198}H_{398}$ with decreasing temperature was interpreted as being a consequence of surface poisoning.[22] It was postulated that folded nuclei formed on the surface of extended crystals would retard their growth. Since no minimum has been found in the present study with $C_{168}H_{338}$, it is important to examine possible reasons why a minimum could have resulted from the experimental data reported for the $C_{198}H_{398}$ solution.

The minimum in the crystallization rate was observed in the temperature interval where the rate of formation of folded chain crystals is severely reduced. With only a slight increase in crystallization temperature, only extended crystals are produced from the original solution. It was shown previously[6] that the isothermal transformation (thickening) of a folded to extended structure is very rapid in this temperature range. Therefore, extreme care must be taken to separate the two processes when analyzing the crystallization rate from endotherms. If the original folded chain crystals transform rapidly to extended ones, there is the distinct possibility that only the melting of the extended crystals will show up in the DSC scans. To be consistent in the analysis and interpretation, it is important that the rate of formation of the structure that is initially formed always be recorded. Any subsequent transformation, such as from a folded to an extended form, represents a different process that should not be intermixed with crystallization from the homogeneous solution. Put another way, the kinetics of the thickening of the extended from the folded form should not replace the initial rate of formation of the folded structure. In the aforementioned study of $C_{198}H_{398}$ from a toluene solution[22] the heating thermogram after crystallization at 78 °C is shown in Figure 7 of ref 22. This thermogram makes clear that the crystallization process starts with a folded structure. This is indicated by the first (low-temperature) endotherm followed by an exotherm as a consequence of the reorganization on heating leading to a high-temperature endotherm. In the analysis of the kinetic data[22] in this temperature range, the initial formation of folded crystallites from the melt was disregarded. The crystallization rate of extended structure from the melt was taken, overlooking the fact that they develop from the folded ones. In this manner, two distinctly different processes, crystallization and transformation, were intermixed. The data plotted here in Figure 3 only represent the rate of crystallization of the form that initially develops, irrespective of whether it is folded or extended. When the kinetic data are treated in this manner, no minimum is observed in the crystallization rate. On the other hand, if the second exothermic peak in Figure 1, indicative of isothermal thickening to the extended form, is taken as a measure of the initial formation of this structure, a minimum in the rate of crystallization will be observed as is illustrated in Figure 4. In this figure the open and closed circles represent the crystallization rates of the structures that are initially formed (folded or extended, respectively); the closed triangles represent the rates of the isothermal transformation. We can conclude, therefore, that the minimum reported for $C_{198}H_{398}$ was most probably a consequence of the intermixing of crystallization rates from solution with the thickening rates.

The work of Ungar and Organ[19] was restricted to the study of only a 3.85% solution of $C_{198}H_{398}$. It was speculated, however, that the nucleation rate of extended chain crystals will increase with decreasing polymer concentration. The argument was then made that decreasing the polymer concentration will "dilute" the poisoning effect on the extended crystals and thus favor their formation and growth. The results of the crystallization rate of $C_{168}H_{338}$ shown in Figure 3 make quite clear that the rate of crystallization of extended crystals,

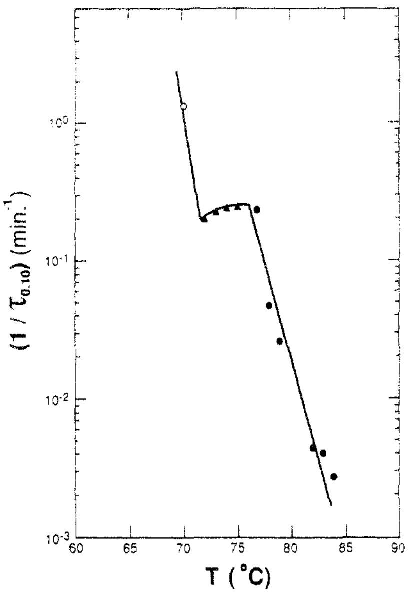

Figure 4. Rate of crystallization versus temperature for $C_{168}H_{338}$ crystals formed from a 4 w/v % toluene solution. Open circles represent data for once folded crystals. Closed circles are data for extended crystals. The closed triangles are related to the transformation from once folded to extended crystal.

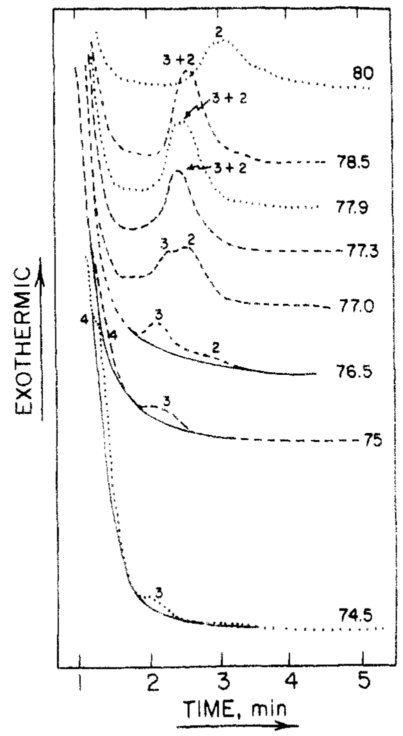

Figure 5. DSC exotherms of the crystallization of $C_{240}H_{482}$ from a 4 w/v % toluene solution. Numbers at the maximum of the exotherm indicate the number of stems per chain molecule in the crystallite; i.e., a twice folded chain crystal contains 3 stems.

as well as folded crystals, decreases rapidly with dilution. These results are contrary to the one expected from a poisoning effect.

Two exotherms were also found in the crystallization of a 4% solution of $C_{240}H_{482}$ in toluene. Some typical exotherms are shown in Figure 5 for the crystallization temperature range 74.5–80 °C.[25] The numbers inserted at the maximum of each exotherm represent the *number of stems per chain molecule in the crystallite*. Thus, if the molecule is folded once, the crystal will contain 2 stems per molecule, 3 stems if it is folded twice, etc. It is important that the exothermic peaks are assigned to a given crystallite structure in order to properly analyze the crystallization rate of the form that initially develops from the homogenous solution.

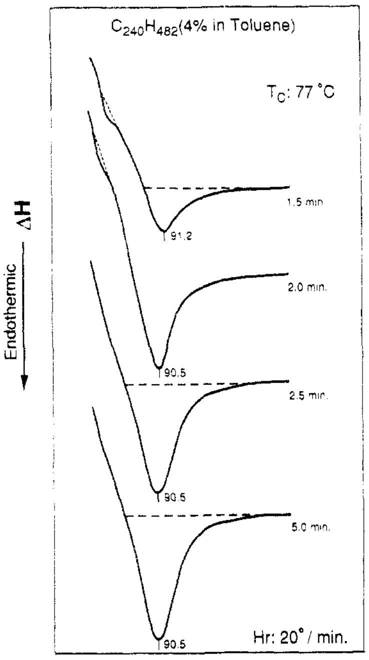

Figure 6. DSC dissolution endotherms after crystallization of a 4 w/v % solution of $C_{240}H_{482}$ at 77 °C for the indicated times. The heating rate is also indicated.

This assignment was made as follows. Single exothermic peaks were observed at crystallization at 80 °C and above. On heating these crystals, single dissolution peaks at 91 °C are observed over the complete crystallization interval.[6] This temperature is very close to the calculated dissolution temperature of a crystallite comprised of 120 carbon atoms.[6] We can, therefore, associate the exotherms obtained in this temperature range with the crystallization of approximately once folded crystals. Thus, following the above notation they are indicated by the symbol 2 in Figure 5. Crystallization temperatures in the range 78.5–76.5 °C give either one or two exothermic peaks. The dissolution temperatures shown in the endotherms of Figure 6 help assign each of the exothermic peaks observed at 77 °C to a given structure. Two endotherms are observed at the early crystallization times. The endotherm with a peak temperature of 82 °C is consistent with the dissolution of approximately twice folded crystallites. This small endothermic peak vanishes after crystallization of only 2.5 min, or after complete formation of the second exotherm. At this point only the dissolution peak of the approximately once folded crystallite is present. It was concluded previously that at the very early times twice folded crystals are formed and are transformed isothermally to once folded crystals. These are represented by 3 and 2 in Figure 5.[6] The second exotherm is, therefore, the result of this transformation. Because the transformation rate increases with increasing crystallization temperature, the second exotherm appears at decreasing times with increasing crystallization temperature. It eventually overlaps the first exotherm. This is clearly the case for the exotherms obtained at 77.3, 77.9, and probably 78.5 °C. The transformation is also taking place during the heating process; hence, the very small endotherms found for the initially formed crystals and their rapid disappearance (Figure 6).[25] At the low isothermal crystallization temperatures, $T_c \leq 75$ °C, three times folded crystals are initially formed and isothermally transform to twice folded crystals. The assignment of the observed exotherms with a given crystallite structure in this

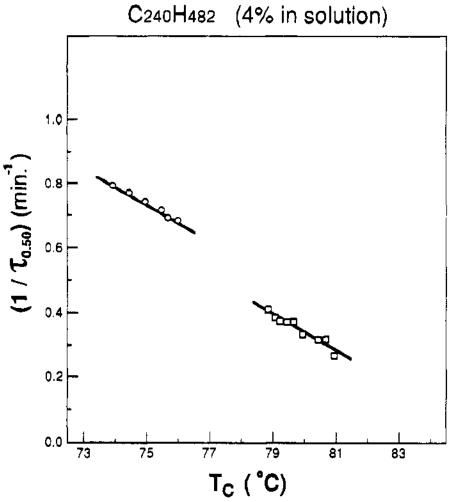

Figure 7. Rate of crystallization as a function of temperature for $C_{240}H_{482}$ crystals from a 4 w/v % solution in toluene. Open circles are data for three times folded crystals and open squares represent once folded crystals.

temperature range, as well as the isothermal transformation, was previously explained in detail in a discussion of the thickening process.[6]

With the assignment of the exotherms of Figure 5 the crystallization kinetics of the structures that are initially formed from the solution can be analyzed. We have indicated earlier that the character of the crystallization rate of $C_{168}H_{338}$ did not change if the maximum heat outflow was taken as a measure of the rate of crystallization rather than a small percentage (i.e., 10%) of the total transformation. Based on these results, the inverse of the time at which there is a maximum heat outflow was taken as a measure of the crystallization rate. This quantity, $1/\tau_{0.50}$, is plotted against the crystallization temperature in Figure 7. Despite the complexity of the transformation processes that take place during the isothermal crystallization of this *n*-alkane from solution, two well-defined regions can be distinguished. In both of these regions the measured rates of crystallization are not affected by any isothermal transformation. For crystallization temperatures below 76 °C, given by the open circles, the exothermic peak of the approximately three times folded crystals is well defined (see peak 4 in Figure 5) and separated from the peak corresponding to the transformation to twice folded structures (peak 3 in Figure 5). In the other crystallization range illustrated, between 79 and 81 °C, only once folded crystals are formed from the original solution. Therefore, in these two temperature ranges the crystallization rate of the crystallites initially formed is well established. Very similar negative temperature coefficients of the crystallization rate, as manifested by two parallel lines slightly displaced from one another, are found in both temperature ranges. The interval between these two regions, $76 \le T_c \le 78.5$ °C, represents the temperature range where twice folded crystals (represented by 3 in Figure 5) form from the original solution. However, over most of this region the transformation to once folded structures (2 in Figure 5) is very rapid. For temperatures of 76.5 and 77 °C, the exotherm corresponding to the formation of the twice folded crystals could be identified. However, this peak overlaps the one that corresponds to the isothermal transformation to the once folded structures and could be influenced by the transformation. Therefore, none of the points in the temperature interval $76 \le T_c \le 78.5$ °C are plotted in Figure 7. In this figure only the rates of crystallization of the pure structures, which develop from the original solution, are shown. It is clear that the temperature coefficients, which are directly related to the nucleation rates, are the same for the formation of either twice or once folded crystallites.

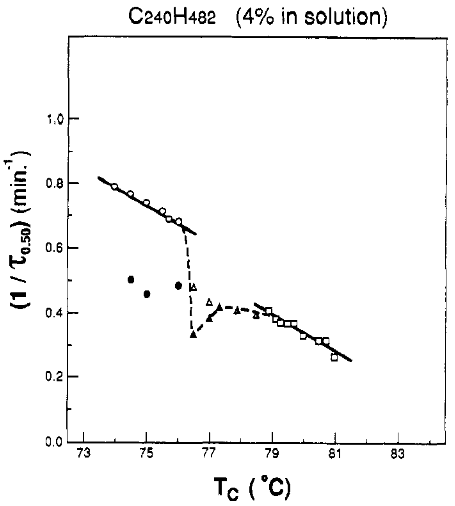

Figure 8. Rate of crystallization as a function of temperature for $C_{240}H_{482}$ crystals from a 4 w/v % solution in toluene. The following crystal structures are represented in this figure: (○) three times folded crystals; (△) twice folded crystals (see text); (□) once folded crystals; (●) transformation from three times to twice folded crystals; (▲) transformation from twice to once folded crystal s; (◭) twice folded crystals which transform very rapidly to once folded crystals.

In Figure 8, the quantity $1/\tau_{0.50}$ is plotted against the temperature using all of the exothermic data, i.e., the rate of formation of the initial structures as well as the rate of their transformation. In this figure the data points of Figure 7 are replotted using the same symbols: the closed circles represent the transformation from three times to twice folded crystallites, the closed triangles the transformation from twice to once folded crystals, and the open triangles represent the results at 76.5 and 77.0 °C that were just discussed. For most temperatures in the intermediate region, $76 \le T_c \le 78.5$ °C, the transformation takes place simultaneously, or right after the growth of the initial twice folded crystals. Separate exotherms are not resolved. The evolution of the exotherms shown in Figure 5 for T_c of 77, 77.3, and 77.9 °C is an example of this phenomenon and indicates the complication in establishing an accurate value of the rate of crystallization of twice folded crystals in this temperature range. These points are indicated by half-closed triangles in Figure 8. The data in Figure 8 indicate that the two points that can be identified with the formation of twice folded crystals must be influenced by the isothermal transformation since they fall in the region characteristic of transformed structures.

If the open triangles in Figure 8 are disregarded and we only consider the remaining data, an inversion of the crystallization rate with temperature will result, as is indicated by the dashed curve. However, it can only be obtained if the exotherms corresponding to the transformation of twice folded to once folded crystals are also considered as data points. This, however, involves the intermixing of two distinctly different types of rate processes. As was pointed out, similar exotherms are in fact found in the thermograms of the crystallization of $C_{168}H_{338}$ from solution, as well as in $C_{192}H_{386}$,[7] $C_{240}H_{482}$,[6] and $C_{246}H_{494}$[21] crystallized from the melt. They do not, however, represent the crystallization rate of the structure that is formed from the original solution. The plots in Figures 3 and 7 make quite clear that when the crystallization rate of species that are formed initially can be reliably differentiated from the transformation (thickening) process, there is no minimum in the rate of crystallization. Experimentally determined crystallization rates usually serve as the fundamental basis for the further development of theories that describe the nucleation and growth processes involved in the crystallization. In the *n*-alkane crystallization, therefore, the isothermal thickening needs to be separated from the original crystallization. Unfortunately, these two processes are very often either misinterpreted or cannot be separated from one another. The problem is compounded further by the complexities of the isothermal thickening process. This difficulty has already been pointed out in a previous study devoted to thickening[6] and is also found in the crystallization of $C_{198}H_{398}$ from solution.[19,22] Based on the results obtained here with $C_{168}H_{338}$ and $C_{240}H_{482}$, we can conclude that the folded crystals initially formed during the crystallization of $C_{198}H_{398}$ in the interval 78–81 °C[22] rapidly transformed isothermally to extended crystals. In this instance, the data reported by Organ et al.[22] in this temperature interval would need to be modified to take into account the rate of the initially formed folded crystals. The inversion in this case would most probably vanish.

An inversion in the rate has also been reported for the crystallization of $C_{246}H_{494}$ from the pure melt.[9,23] However, thickening has also been shown to take place in the temperature region where the growth rate of this alkane decreases with decreasing temperature. For example, the synchrotron experiments reported in ref 9 showed that folded crystals of $C_{246}H_{494}$ formed initially from the melt and started to thicken isothermally after approximately 2.5 min of crystallization at 120.5 °C. According to the growth rate/temperature data of the same *n*-alkane (see Figure 4 of ref 23), this temperature is in the region where an inversion of the growth rate was observed. The question immediately arises as to which of the $C_{246}H_{494}$ crystal growth rates was followed. Either the initially formed folded crystals or the isothermally thickened ones could be studied. It is also possible that these rate measurements were intermixed. Without a clear and careful delineation between these possibilities, there is no meaningful way to interpret the kinetic result.

Other examples of this type problem are found in the crystallization behavior of some other polymers.[24,26,27] One example is given in a study of the lamellar structure and crystallization behavior of a variant of poly(ether ether ketone), where some meta linkages are incorporated. It was found that this polymer undergoes melting and recrystallization in the same temperature region where the crystallization rate shows a discontinuity.[26,27] Instead of the conventional inverted U-shape plot, the rate shows a minimum at about 240 °C. Although no specific information is given as to whether melting and recrystallization are also occurring isothermally, this behavior is very similar to that found in the *n*-alkanes.[6] At a given temperature, the thinner crystals ($\approx$30 Å) that are initially formed would melt and recrystallize into the more stable thicker crystals ($\approx$55 Å). In a similar manner to that previously described, this process could enhance the overall crystallization in the temperature range where thinner crystals are initally formed.

Another example of an inversion in the growth rate was reported for a methoxy-terminated poly(ethylene oxide) sample having a molecular weight of 3000.[24] The inversion was reported in a temperature interval of less than 1 deg and based on three data points. It was clearly pointed out that a mixture of extended and once folded crystals is observed in the temperature region where the inversion is reported (see p 325 of ref 24). The optical microscopic technique that was used to measure the growth rate cannot differentiate between the growth of the two structures. The isothermal thickening, which is very rapid at these temperatures,[24] could easily influence the measured growth rate, in complete analogy to the problems just described for the *n*-alkanes.

The experimental results reported here demonstrate quite definitively that no inversion in the crystallization rate takes place for the two *n*-alkanes studied. Because two different theoretical concepts have been advocated to explain the unusual inversion of the rate of crystallization, it is, therefore, important that we examine their basis. One of these is the "poisoning" effect presented by Sadler and collaborators.[16,28,29] Although a qualitative argument can be made for this phenomenon to cause a minimum in the crystallization rate,[21,22] we have already pointed out that the observed influence of polymer concentration on the crystallization rate is just the opposite of that predicted.

The other theory, developed to explain the apparent minimum in the crystallization rate, is based on a unique version of nucleation theory.[17,18] The essence of this theory is the assumption that two types of nuclei can form; one is an extended chain nucleus (but not the complete molecule) and the other a once folded nucleus. The critical size of a chain folded nucleus and its temperature dependence are allowed to follow the dictates of classical monomeric nucleation theory. On the other hand, the critical size in the chain direction of the extended type nuclei is assumed independent of the crystallization temperature. Its rate of formation is governed by a conventional Arrhenius type temperature-dependent process. This development certainly represents a rather unusual type nucleation theory. These *ad hoc* set of assumptions of two different types of nuclei, each with a different temperature rate of formation, will obviously lead to a maximum in the nucleation rate and thus the crystallization rate. The unusual efforts that were made to adjust nucleation theory to explain a maximum in the rate were obviously unnecessary. As explained above, the rate does not show an extremal. Furthermore, it was assumed that for crystallization temperatures at the left side of the maximum in the crystallization of $C_{246}H_{482}$,[17,18] extended crystals were nucleated from the original melt. However, as we have indicated, once folded crystals are initially formed from the original melt in this temperature range.[9,25] The application of this nucleation theory to explain an inversion of the crystallization rate of extended chain crystals in a temperature region where it has been shown experimentally that they are not formed from the original state is, obviously, questionable. In fact, other analyses have demonstrated that the adaption of classical nucleation theory to chains of finite length explains in a natural manner the formation of extended and folded crystals and the thickening and thinning observed during crystal growth.[7,14,30]

B. Crystallization from Pure Melt. The crystallization rates from the melt of the long-chain *n*-alkanes have also been studied. Although the crystallization kinetics of $C_{192}H_{386}$ have already been reported,[7] the results for this *n*-alkane will be included here to allow for a more detailed analysis and comparison with those of $C_{168}H_{338}$ and $C_{240}H_{482}$. The rate of crystallization, taken as the inverse of the time needed to obtain 5% of crystallinity, is plotted as a function of the crystallization temperature in Figure 9. The curves describing each of the alkanes are very similar to one another but are displaced along the time and temperature axes. They all show a very strong

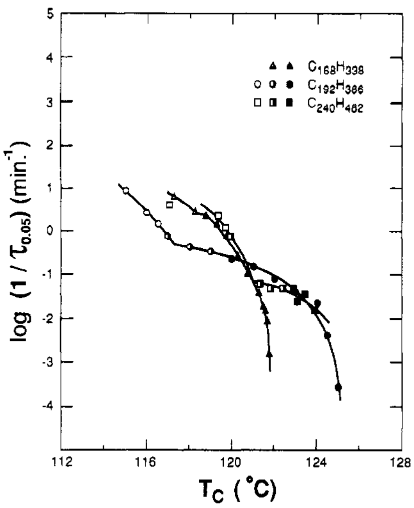

Figure 9. Rate of crystallization as a function of temperature for the indicated *n*-alkanes crystallized isothermally from the pure melt. Open symbols represent the formation of once folded crystals. Closed symbols are data for extended crystals. Half-closed symbols represent the experimental values which may be affected by a rapid transformation from once folded to extended crystals.

negative temperature coefficient indicative of a nucleation-controlled process. The kinetics of $C_{240}H_{482}$ were not followed at higher crystallization temperatures because of sample degradation and minimal sample supply. The rate of crystallization decreases with increasing temperature and shows a discontinuity in each of the curves. These occur at 117.3, 118.3, and 121 °C for $C_{192}H_{386}$, $C_{168}H_{338}$, and $C_{240}H_{482}$, respectively. Similar discontinuities have been observed in low molecular weight fractions of poly(ethylene adipate),[31] poly(ethylene oxide),[24,32,33] isotactic polypropylene,[34] and linear polyethylene.[30,35] Thus, they appear to be characteristic of the crystallization of low molecular weight chain molecules. The $C_{168}H_{338}$ and $C_{240}H_{482}$ samples crystallize at the same rate in the temperature interval 117–121 °C and crystallize faster than $C_{192}H_{386}$. However, for crystallization temperatures greater than 121 °C, $C_{168}H_{338}$ crystallizes slower, at the same temperature, than the other two alkanes. No inversion is observed in the crystallization kinetics of any of these alkanes. These features of the crystallization kinetics will be clarified in the subsequent analysis of the data where nucleation theory appropriate to chains of finite length is applied.

Before analyzing the data in terms of nucleation theory, it is important to establish the temperature regions of crystallization where the structure that initially crystallizes from the melt is well defined. As was discussed previously, it is important that complications caused by the transformation from one structure to another be avoided in this type of analysis. Following the distinction made in Figure 3 between folded and extended crystals, the crystallization rates of folded structures in the temperature interval where the thickening process does not interfere with the rate measurement are represented by open symbols in Figure 9. The crystallization rates of extended structures, formed from the initial melt, are represented by closed symbols. The temperature interval where the measurement of the rate may be affected by the transformation is represented by the half-closed symbols. The thickening process of $C_{192}H_{386}$ crystals formed from the melt has not been explicitly described.[7] However, in analogy to the interpretation given to Figure 1 of this work, the two exotherms shown at T_c = 115–117 °C in ref 7 are clear indications of a transformation. It is estimated that at slightly higher crystallization temperatures the thickening process is too fast to manifest as two distinct exothermic peaks. In this case the measured rate could not be assigned to a definite structure of the crystallite.

It is also possible that the crystallization of $C_{168}H_{338}$ at 117.3 and 118.3 °C could be initiated by folded crystals that transform rapidly to extended and, therefore, these points are also indicated by half-closed triangles in Figure 9. The break observed in this narrow temperature range is similar to the break observed in $C_{192}H_{386}$ and $C_{240}H_{482}$ where the rate measurement is affected by the thickening process.[6] Attempts to follow the possible thickening by looking at the exo- or endotherms of the crystallization of $C_{168}H_{338}$ at 117.3 or 118.3 °C were unsuccessful. However, the process could be very fast and may not be separated into two peaks in the experiments.

Each of the curves in Figure 9 shows a temperature interval where the crystallization rate does not change very much with temperature: for example, the interval between 121 and 122.5 °C for $C_{240}H_{482}$, between 117 and 120 °C for $C_{192}H_{386}$, and around 118 °C for $C_{168}H_{338}$. This is the temperature interval with most, but not all, of the half-closed symbols. It therefore indicates that the plateau shown by the rate/T_c curves of low molecular weight species needs to be, at least partially, associated to the temperature interval where the transformation of folded to extended crystals is very rapid. In this interval, two competing effects, the decrease of the crystallization rate and the increase of the transformation rate with increasing temperature, are in line with the plateau observed.

II. Temperature Coefficient of the Crystallization Process. The very marked negative temperature coefficient that is observed in Figures 3, 7, and 9 strongly suggests a nucleation-controlled crystallization process. In analyzing the problem, we adapt the very general formulation given by Turnbull and Fischer[36] for the steady-state nucleation rate. Accordingly, the steady-state nucleation rate N can be expressed as

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

for all classes of molecular substances and all nuclei types and shapes. Here N_0 is a constant, slightly dependent on the temperature; E_D and ΔG^* are the free energy for transport across the liquid-crystal interphase and the free energy required to form a nucleus of critical size, respectively. The temperature range over which the crystallization rate of the *n*-alkane can be studied is restricted to an interval in the vicinity of the true melting temperature. Therefore, the transport term remains essentially constant in these experiments. The free energy change required to form a critical size nucleus controls the nucleation and thus the crystallization rate.

In formulating an expression for ΔG^*, cognizance must be taken of a fundamental difference between monomeric species and chain molecules of finite molecular weight.[7,14,37–39] In the former case a complete molecule participates in the nucleus and one arrives at the classical result for ΔG^*. For a chain molecule, beyond a small number of repeating units, only a portion of the molecule participates in the formation of a nucleus. This distinction must be taken into account in calculating ΔG^*. The expression for ΔG^* for chains of finite length has been given[37,38] and specifically applied to the *n*-alkanes.[7,14] The analysis can be applied equally well to any type of nucleation process. We take as an example the formation of a coherent Gibbs type two-dimensional nucleus as the controlling nucleation process.[38] This type of nucleus has been commonly adapted for the crystallization of polymeric chain-like molecules. The nucleus has two different surfaces that are represented by interfacial free energies σ_u and σ_e as the lateral and end surfaces, respectively. For the crystallization from the bulk ΔG^* can be expressed as[38]

$$\Delta G^* = \frac{2\sigma_u\left[2\sigma_e - RT\ln\left(\frac{x-\xi^*+1}{x}\right)\right]}{\Delta G_u - \frac{RT}{x}} = 2\sigma_u\xi^* \qquad (2)$$

and for crystallization from solution as[40]

$$\Delta G^* = \frac{2\sigma_u\left[2\sigma_e - RT\ln \upsilon_2 - RT\ln\left(\frac{x-\xi^*+1}{x}\right)\right]}{\Delta G_u' - \left(\frac{RT}{x}\right)\upsilon_2} = 2\sigma_u\xi^* \qquad (3)$$

Here ξ^* is the number of repeating units along a chain, which is comprised of x units, that are required for the formation of a critical size nucleus. υ_2 is the effective polymer volume fraction, V_u and V_1 are the specific volumes of the repeating unit and solvent, respectively, and χ_1 is the polymer–solvent interaction parameter. The quantity ΔG_u is the free energy of fusion per repeating unit of the *infinite chain*. In the pure state

$$\Delta G_u = \frac{\Delta H_u(T_m^\circ) - T}{T_m^\circ} \qquad (4)$$

and in the polymer–solvent system

$$\Delta G_u' = \Delta G_u - RT\frac{V_u}{V_1}\{(1-\upsilon_2) - \chi_1(1-\upsilon_2)^2\} \qquad (5)$$

where T_m° is the equilibrium melting temperature of the infinite size chain. The equilibrium melting temperature characteristic of the real, finite length chain, T_m, is not directly involved in specifying the critical nucleus dimensions. The reasons for this have already been discussed in detail[14,30,38] and need not be repeated here. When conventional procedures, using T_m, are used, the error involved can be significant for small values of x. They obviously will decrease at higher molecular weights. In the expressions for ΔG^* (eq 2 or 3) the value of σ_e needs to be known. Therefore, a comparison of theory with experiment cannot be made without an *a priori* assumption of the value of σ_e. Reasonable limits can now be set for this parameter and the data can be analyzed for a set of values for σ_e. However, it has been shown that the same kind of results are obtained irrespective of the value taken for σ_e, if it is in the acceptable range.[41]

The experimental rates of crystallization of the n-alkanes from the melt are plotted in Figure 10 according to eqs 1 and 2. We have thus made the tacit assumption that the crystallization rate can be identified with the nucleation rate. In the interval of chain length of interest, the interfacial free energies of the mature crystals were found to increase slightly with chain carbon number.[5] Assuming the same values for the interfacial free energy of the nucleus as for the mature crystals, reasonable values for σ_e are 2000 cal/mol for $C_{168}H_{338}$, 2300 cal/mol for $C_{192}H_{386}$, and 2500 cal/mol for $C_{240}H_{482}$,[5] which have been used to calculate ΔG^* according to eq 2. The equilibrium melting temperature of the infinite polyethylene chain was taken as 145.5 °C and ΔH_u = 950 cal/mol.[42] The same symbols used in Figure 9 are also used in Figure 10. Thus, the half-closed symbols represent the data with some experimental uncertainty as it was previously discussed. The data for the three n-alkanes studies are well represented by sets of intersecting straight lines when analyzed in the manner described. A compilation of the slopes of the straight lines is given in Table 1. The high-temperature region, where extended crystals are formed, is termed region I and the slope described as S_I. In analogy, the low-temperature region is termed region III and the intermediate, region II. We note from Figure 10 that enough data points are available to clearly demarcate these three regions for $C_{192}H_{386}$. The data for $C_{192}H_{386}$ are, therefore, represented by a set of three intersecting straight lines. The slopes in the high and low crystallization temperature regions (regions I and III, respectively) are the same. Since extended crystallites are formed in region I and folded crystallites are formed in region III, the fact that the slopes are the same is indicative that an identical free energy of formation of the initial nucleus is involved irrespective of the eventual crystallite structure that develops from it. This implies the same nucleus structure in both cases.

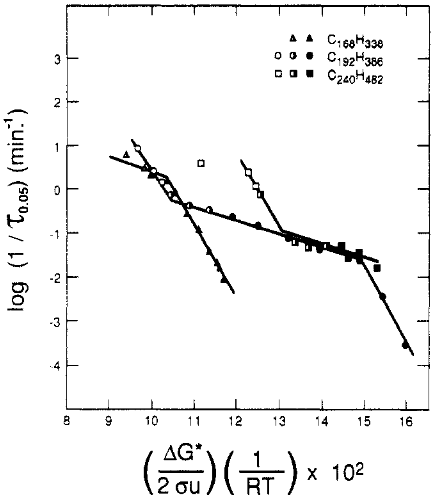

Figure 10. Plot of log (crystallization rate) against nucleation temperature function for coherent surface nucleation from eq 2 for the n-alkanes indicated. Symbols as in Figure 9.

Table 1. Compilation of Slopes from Figure 10

n-alkane	S_I	S_{II}	S_{III}	S_{II}/S_I	S_{II}/S_{III}
$C_{168}H_{338}$	−170	−35		0.21	
$C_{192}H_{386}$	−170	−30	−170	0.18	0.18
$C_{240}H_{482}$		−30	−170		0.18

The data available for $C_{240}H_{482}$ can be represented by two straight lines. Their slopes are the same as those for $C_{192}H_{386}$ in the low and intermediate crystallization temperature regions. If we consider a slightly higher value of σ_e for $C_{240}H_{482}$, the data represented by the squares in Figure 10 will be shifted to the right. However, the value of the slopes will be maintained. As was indicated previously, it was not possible to obtain data at higher crystallization temperatures because of degradation. Nevertheless, we can reasonably expect that higher T_c's for $C_{240}H_{482}$ lead to a temperature coefficient similar to the one found for $C_{192}H_{386}$ in this temperature range. The results obtained for $C_{168}H_{338}$ in the high-temperature region (filled triangles) support this expectation. The value of the slope in this region (−170) is identical to that obtained in the high-temperature region of $C_{192}H_{386}$, and in both regions extended crystals are formed. The slope characterizing the temperature coefficient of the crystallization of extended crystals is the same for $C_{168}H_{338}$ and $C_{192}H_{386}$, indicating an identical mechanism of formation of both forms irrespective of the structural form that eventually evolves from the initiating nucleus, and is also independent of the particular alkane. It is not correct to *a priori* assume a particular nucleus structure to account for the structural form that is eventually observed.[15,43] There is no scientific principle that requires the nucleus and the mature crystallite to have the same structure. It has already been pointed out and discussed in some detail how the different extended or folded forms are evolve from the same type of nucleus.[14] This theoretical development is consistent with the present results. Moreover, it can also explain the thickening or thinning of the crystallite, depending on the temperature, as the crystallization proceeds. The same type of nucleus is formed over the complete temperature range. Its size is determined by straightforward nucleation theory. In the plots of Figure 10, there is an intermediate region of a reduced sope with the same value for the three *n*-alkanes studied (see Table 1). As indicated by the half-closed symbols, some of the points in the region represent crystallization temperatures where, although folded crystals initially form, they are rapidly transformed to extended crystals. The set of intersecting straight lines found for each of the *n*-alkanes in Figure 10 is reminiscent and suggestive of regime type transitions found in higher molecular weight polyethylenes[44-46] as well as other polymers.[47,48] In polymer crystallization the regimes are labeled I, II, and III in descending order of the crystallization temperature region in which they are found. Characteristically the temperature coefficients of regimes I and III are expected to be the same. This expectation is found for the polyethylenes[30,46] without the need to introduce a transport term. The values listed in Table 1 indicate that the same results are found here for the *n*-alkanes. The identity of the temperature coefficients can be explained on the same basis as the polyethylenes, despite the fact that the crystallite structures are different. It is clear that we must have some connection between the two regions, or regimes I and III, in the alkanes even if the thickening transformation did not take place. It is tempting to assign the region with lower slope to regime II and its polynucleation character. In this region nuclei are allowed to form before the previous layer is completed. In the simplest analysis this leads to a theoretical ratio of 0.5 between the slopes of regimes II and I. However, for linear polyethylene this ratio was found to decrease with molecular weight and approached a value of 0.2 for low molecular weight fractions.[30] The ratio found here for the *n*-alkanes, 0.21–0.18 (see Table 1), is very similar to the value for the low molecular weight polymers. This result could be a natural consequence of the molecular weight dependence on the ratio. However, this conclusion has to be tempered by the complication introduced by the structural transformation that takes place during crystallization. Despite this uncertainty some conclusions can be reached with respect to the intermediate temperature region. One is that there must be a connection between the two regions where the rates of formation of only the pure forms were measured. Since the temperature dependence of the nucleation rates of the initial structures is identical, the same mechanism of formation, or minor variant thereof, must be operative. This leads to the conclusion that this region must be regime II. Preliminary results of the crystallization rates, from the melt, of low molecular weight fractions of polyethylene and poly(ethylene oxide) show striking analogies. The data and analysis will be presented in a forthcoming publication.[49]

Crystallization from Solution. The crystallization rates of $C_{168}H_{338}$ and $C_{240}H_{482}$ from a 4% solution are plotted according to eqs 1 and 3 in Figure 11. Only the data for the structures that were initially formed in the original solution are utilized. Thus, for $C_{168}H_{338}$ the rates of crystallization of nearly once folded crystallites (represented by open circles) and extended (closed circles) crystals are given in the figure. Similarly, the data for three times folded $C_{240}H_{482}$ crystallites (open triangles) and once folded ones (open squares) are also included. To compare both systems, the time corresponding to the maximum of the exothermic peak was taken as the measurement of the rate. A value of σ_e = 2000 cal/mol (73.5 erg/cm^2) was used in the analysis of both systems. v_2 was taken as the nominal concentration for both alkanes (4 w/v %) although the use of slightly higher or lower values does not change appreciably the slopes of Figure 11. Striking similarities are found in the slope of the crystallization rate data corresponding to all of the folded forms (open symbols). Thus, three, parallel straight lines, which are only slighly displaced from one another, can be drawn through the data and thus reflect almost identical temperature coefficients. This result indicates that the same type of nucleation process is involved irrespective of the different kinds of crystallites (close to three times or once folded) that are developed.

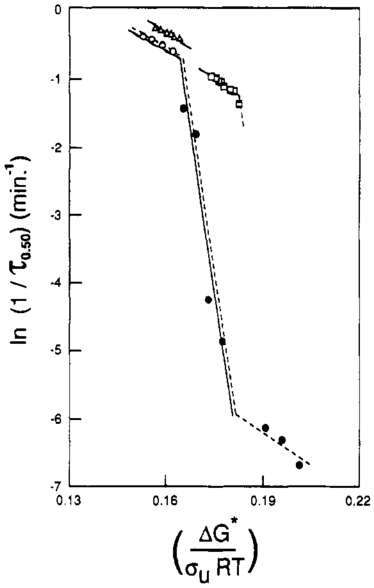

Figure 11. Plot of ln(crystallization rate) against nucleation temperature function for coherent surface nucleation from eq 3. Open and closed symbols represent folded and extended crystals, respectively. (○,●) data for $C_{168}H_{338}$ from solution; (△,□) data for $C_{240}H_{482}$ from solution. Concentration is 4 w/v % in toluene.

The interpretation of the data that correspond to the initial formation of extended $C_{168}H_{338}$ crystallites (closed circles) is more complex. There are two ways of representing the data as is indicated by the solid and dashed lines in Figure 11. A line parallel to those of the folded crystals can be drawn through the three data points obtained at the highest temperatures. This would be consistent with the analyses of the melt-crystallized system. This description of the data leaves an intermediate temperature region, indicated by the dashed line, where the rate decreases very rapidly with temperature. The experimental point obtained at the highest crystallization temperature with $C_{240}H_{486}$ seems to indicate a similar rapid decrease of the rate with increasing temperature. However, this representation can not be interpreted according to conventional regime theory. The ratio of the slopes in this case will be inverted. An alternate procedure is to neglect the data points obtained at the three highest crystallization temperatures of $C_{168}H_{338}$ and only consider the two intersecting straight lines (as drawn in the figure by solid lines). These three data points have the highest experimental uncertainty. In this case, the change in slope can be related to a regime I to II transition in analogy to the results obtained for the rates of $C_{168}H_{338}$ from the melt (see Figure 10) and a more consistent interpretation is obtained. To solve this problem larger amounts of sample for several different *n*-alkanes are needed. The availability of such materials will allow for more detailed experimental data and hence to a more precise interpretation of the kinetics of the extended structures from solution.

Conclusions

The crystallization rates of the *n*-alkanes $C_{168}H_{338}$, $C_{192}H_{386}$, and $C_{240}H_{482}$ crystallized from either solution or the melt decrease rapidly with increasing temperature and show a discontinuity in the temperature interval where a specific type of folded structure is no longer formed from the original melt or solution. Folded crystallites thicken isothermally, through a melt-recrystallization process,[6] to thermodynamically more stable structures, which are other folded or extended ones. Because the rate of thickening increases rapidly with increasing crystallization temperature, the thickening process interferes with the measurement of the crystallization rate of folded crystals that are initially formed at high temperatures. If a clear distinction is not made between the crystals formed from the initial state and those transformed, the results could show an inversion in the rate of crystallization.[21,22] However, when the study of the crystallization rate is directed only to the crystallites that are formed directly from the original disordered state, no inversion of the crystallization rate has been observed. In solution, the crystallization rate of either the folded or extended structures decreases with decreasing concentration. Moreover, the temperature variation is similar and shows a break at the transition of folded to extended crystals formed from the original solution.

Curves that describe the crystallization rate vs temperature of *n*-alkanes can be divided into three main regions: a first low-temperature region where folded structures are formed from the melt and where the thickening process is slow and does not affect the measurement of the rate of crystallization, an intermediate temperature region in which the isothermal thickening rate is very rapid and the measurement of the crystallization rate of the folded crystals will be affected in part by the transformation, and a third temperature interval in which folded structures are no longer formed and, therefore, the crystallization rate of extended crystallites is well defined. The nucleation process is the same irrespective of whether folded or extended structures are formed initially. The general characteristics of the crystallization kinetics of the high molecular weight *n*-alkanes are very similar to those of other low molecular weight chain molecules.

Acknowledgment. The authors gratefully acknowledge the support of this work by the National Science Foundation Polymers Program (Grant DMR 89-14167).

References and Notes

(1) Paynter, O. I.; Simmonds, D. J.; Whiting, M. C. *J. Chem. Soc., Chem. Commun.* **1982**, 1165.
(2) Bidd, I.; Whiting, M. C. *J. Chem. Soc., Chem. Commun.* **1985**, 543.
(3) Bidd, I.; Holdup, D. W.; Whiting, M. C. *J. Chem. Soc., Perkin Trans.* **1987**, *1*, 2455.
(4) Lee, K. S.; Wegner, G. *Makromol. Chem., Rapid Commun.* **1985**, *6*, 203.
(5) Mandelkern, L.; Prasad, A.; Alamo, R. G.; Stack, G. M. *Macromolecules* **1990**, *23*, 3696.
(6) Alamo, R. G.; Mandelkern, L.; Stack, G. M.; Kröhnke, C.; Wegner, G. *Macromolecules* **1993**, *26*, 2743.
(7) Stack, G. M.; Mandelkern, L.; Kröhnke, C.; Wegner, G. *Macromolecules* **1989**, *22*, 4351.
(8) Ungar, G.; Stejny, J.; Keller, A.; Bidd, I.; Whiting, M. C. *Science* **1985**, *229*, 386.
(9) Ungar, G.; Keller, A. *Polymer* **1986**, *27*, 1835.
(10) Ungar, G.; Organ, S. J. *Polym. Commun.* **1982**, *28*, 232.
(11) Organ, S. J.; Keller, A. *J. Polym. Sci., Polym. Phys. Ed.* **1987**, *25*, 2409.
(12) Ungar, G.; Organ, S. J.; Keller, A. *J. Polym. Sci., Polym. Lett. Ed.* **1988**, *26*, 259.
(13) Ungar, G. *Integr. Polym. Sci. Technol.* **1988**, *2*, 346.
(14) Stack, G. M.; Mandelkern, L. *Macromolecules* **1988**, *21*, 510.
(15) Hoffman, J. D. *Polym. Commun.* **1986**, *27*, 39.
(16) Sadler, D. M.; Gilmer, G. H. *Polym. Commun.* **1987**, *28*, 242.
(17) Hoffman, J. D. *Polymer* **1991**, *32*, 2828.
(18) Miller, R. L. *Polymer* **1992**, *33*, 1783.
(19) Ungar, G.; Organ, S. J. *J. Polym. Sci., Polym. Phys. Ed.* **1990**, *28*, 2353.
(20) Organ, S. J.; Ungar, G.; Keller, A. *J. Polym. Sci., Polym. Phys. Ed.* **1990**, *28*, 2365.
(21) Ungar, G.; Keller, A. *Polymer* **1987**, *28*, 1899.
(22) Organ, S. J.; Ungar, G.; Keller, A. *Macromolecules* **1989**, *22*, 1995.
(23) Keller, A.; Organ, S. J.; Ungar, G. *Makromol. Chem., Macromol. Symp.* **1991**, *48/49*, 93.
(24) Cheng, S. Z. D.; Chen, J. *J. Polym. Sci., Polym. Phys. Ed.* **1991**, *29*, 311.
(25) Figures 2a, 5, and 6 have already been published in ref 6. They have been included here solely to facilitate the description and reader's understanding of the transient structures in Figures 1 and 5.
(26) Liggat, J. J.; Staniland, P. A. *Polym. Commun.* **1991**, *32*, 450.
(27) Blundell, D. J.; Liggat, J. J.; Flory, A. *Polymer* **1992**, *33*, 2475.
(28) Sadler, D. M. *J. Chem. Phys.* **1987**, *87*, 1771.
(29) Sadler, D. M. *Polymer* **1987**, *28*, 1440.
(30) Fatou, J. G.; Marco, C.; Mandelkern, L. *Polymer* **1990**, *31*, 890.
(31) Takayanagi, M., *Mem. Fac. Eng., Kyushu Univ.* **1957**, *16*, 110.
(32) Kovacs, A. J.; Gonthier, A. *Kolloid Z. Z. Polym.* **1972**, 250, 530.
(33) Kovacs, A. J.; Gonthier, A.; Straupe, C. *J. Polym. Sci., Polym. Symp.* **1975**, *50*, 283.
(34) Janimak, J. J.; Cheng, S. Z. D. *Polym. Bull.* **1989**, *22*, 95.
(35) Leung, W. M.; Manley, R. St. J.; Panaras, A. R. *Macromolecules* **1985**, *18*, 760.
(36) Turnbull, D.; Fischer, J. C. *J. Chem. Phys.* **1949**, *17*, 7.
(37) Mandelkern, L.; Fatou, J. G.; Howard, C. *J. Phys. Chem.* **1964**, *68*, 3386.
(38) Mandelkern, L.; Fatou, J. G.; Howard, C. *J. Phys. Chem.* **1965**, *69*, 956.
(39) Mandelkern, L. *J. Polym. Sci., Polym. Symp.* **1966**, *15*, 129.
(40) Fatou, J. G.; Riande, E.; Garcia Valdecasas, R. *J. Polym. Sci., Polym. Phys. Ed.* **1975**, *13*, 2103.
(41) As has been shown previously[7,30] changing the values of σ_e only shifts the data along the horizontal axis without changing any of the major characteristics of the resulting curves.[30] It has been found that the value of σ_e for equilibrium crystallites is slightly dependent on chain length in the lower molecular weight range.[5] Consequently, it can be expected that σ_e for the nucleus will follow a similar pattern.
(42) Flory, P.; Vrij, A. *J. Am. Chem. Soc.* **1963**, *85*, 3548.
(43) Hoffman, J. D. *Macromolecules* **1986**, *19*, 1124.
(44) Hoffman, J. D.; Frolen, L. J.; Ross, G. S.; Lauritzen, J. I., Jr. *J. Res. Natl. Bur. Stand.* **1975**, *79A*, 671.
(45) Hoffman, J. D. *Polymer* **1983**, *24*, 3.
(46) Fatou, J. G.; Marco, C.; Mandelkern, L. *Polymer* **1990**, *31*, 1685.
(47) Fatou, J. G. *Crystallization Kinetics*. In *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; John Wiley & Sons: New York, 1989; Suppl. Vol., p 231.
(48) Lovinger, A. J.; Davis, D. D.; Padden, F. J., Jr. *Polymer* **1985**, *26*, 1595.
(49) Alamo, R. G.; Mandelkern, L., in preparation.