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Isothermal Thickening of Crystals of High Molecular Weight *n*-Alkanes

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ABSTRACT: The kinetics of the isothermal thickening of folded high molecular weight *n*-alkane crystallites have been studied for $C_{168}H_{338}$ crystallized from solution and $C_{240}H_{482}$ crystallized from both the pure melt and solution. The effect of concentration on the isothermal thickening rate was also analyzed for the *n*-alkane with 168 carbons. Depending on the length of the *n*-alkane and the mode of crystallization, the isothermal thickening may proceed from initially a close to once folded crystal to an extended one or may also proceed through multiple refolding stages. The characteristics of the curves describing the relation between thickening rate and crystallization temperature are common for both of the *n*-alkanes and are independent of the mode of crystallization. The rate of thickening increases with crystallization temperature and the process is autocatalytic. Undercooling normalizes the rates obtained at different concentrations. The experimental facts and theoretical considerations favor the mechanism of the isothermal thickening being a melting and recrystallization process as opposed to solid-state diffusion.

Introduction

Among the studies of the crystallization behavior of polymers and related oligomers, polyethylene and *n*-alkanes have been the most widely studied systems. The molecular simplicity of the polyethylenic chain, and the well-established thermodynamic and structural properties, made it an ideal model system to study the intricacies of the crystallization mechanisms of polymers. Related studies with the monodisperse *n*-alkanes would, obviously, serve as a basis to further develop theoretical models. *n*-Alkanes present the same orthohombic perpendicular methylenic subcell packing and the all-trans conformation as polyethylenes. The missing gap of having available *n*-alkanes that are able to form folded structures has been overcome with the recent synthesis of *n*-alkanes with chain length between approximately 100 and 400 carbons.[1–4] It was found that *n*-alkanes with a carbon number higher than about 150 may form folded or extended crystals depending on the crystallization conditions[4–6] and that folding occurs in the same molecular weight range as low molecular weight polyethylene fractions.

It has also been reported that the folded *n*-alkane crystallites may increase or reduce their thickness in order to achieve a more thermodynamically stable structure.[6,7] Thickening can also occur at the crystallization temperature when the *n*-alkane is crystallized from the melt or from solution.[6,8,9] Isothermal thickening of lamellar crystallites is also known to occur during the crystallization of polymers from the melt. In fact, there are extensive studies of the molecular weight and temperature dependence of the thickening for unfractionated polyethylene[10–15] as well as polyethylene fractions.[15,16] In contrast, however, when the crystallization of polymers is conducted from dilute solution, thickening at the isothermal crystallization temperature has not been observed.[17–20] The molecular weight of polymer fractions studied in these works varied between 4000 and approximately 200 000.

Ungar and Organ[8] have published a study of the isothermal thickening during the crystallization of $C_{198}H_{398}$ from solution and have proposed a mechanism for this process.[21] On the basis of electron microscopic studies, it was postulated that the $C_{198}H_{398}$ crystals formed from solution thicken through a solid-state diffusion mechanism.[21] Similar studies of the $C_{198}H_{398}$ crystallites formed from the melt were not carried out. Therefore, a comparison between thickening of these crystals in the different media could not be made, and the effect of concentration was not investigated.

In this paper the results of a study of the kinetics of the thickening process in the *n*-alkane $C_{168}H_{338}$ crystallized from solution and of $C_{240}H_{482}$ crystallized from both the melt and solution are reported. The effect of concentration has also been studied for the $C_{168}H_{338}$ sample. Since the experimental methods used to study the kinetics of the thickening process in these *n*-alkanes are similar to those used by Ungar and Organ,[8] there is an overlap in certain aspects of this subject. However, in the present work we have extended the range in the number of carbons in the *n*-alkane and the thickening has been studied from solution as well as from the melt. In addition, and perhaps more important, the results obtained here are not consistent with the thickening mechanism proposed previously for $C_{198}H_{398}$.[21]

A detailed study of the thickening process of the *n*-alkanes from solution should lead us to a better understanding of why thickening has not been found in polymers under these conditions. A detailed study of the kinetics of the thickening process of the crystallites formed from the melt is important for other reasons. It could give information about the thickening mechanism in the different crystallizing media and serve as a basis of comparison with similar phenomenon observed in the polymers. These and similar studies in longer *n*-alkanes

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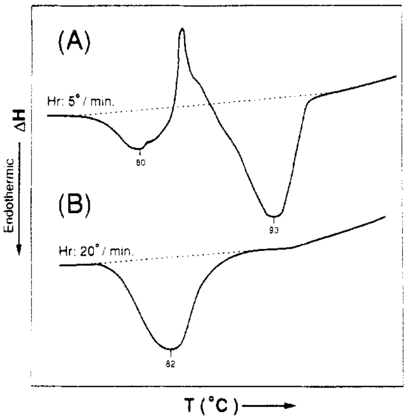

Figure 1. DSC dissolution thermograms of crystallites from a 1 w/v % toluene solution of $C_{168}H_{338}$ crystallized at 65 °C: (A) heating rate, 5°/min; (B) heating rate, 20°/min.

will provide the details that allow for the formulation of the steps that govern the thickening process. They can also be compared to the different mechanisms that have been proposed to explain the thickening observed in melt-crystallized polyethylene. One general type of mechanism involves linear growth of the chain along the *c*-axis of the crystallite, by a variety of processes, without any conformational change.[10,21-24] Another, involves a melt-recrystallization process.[25-28]

Experimental Section

The synthesis of the long-chain *n*-alkanes studied here has been described in previous publications.[4,29]

The thickening process was studied by differential scanning calorimetry, primarily using the Perkin-Elmer DSC-2B. However, some studies of the crystallization of the *n*-alkanes from solution were also carried out in a Perkin-Elmer DSC-4. Large-volume stainless steel O-ring-sealed capsules, especially designed for solution studies, were used. Temperature calibration was carried out using indium as standard. Concentrations of 4, 1, 0.2, and 0.15% were prepared in toluene in the DSC liquid pan. As will be described below heating rates had to be maintained relatively high, at least 20 K/min, to prevent transformation during the heating process. After isothermal crystallization for a specified length of time at a given temperature, the heating process was initiated from the crystallization temperature; i.e., the sample was never cooled.

Results

In the interest of clarity the results for each of the *n*-alkanes and the modes of crystallization will be studied separately.

$C_{168}H_{338}$ Crystallized from Solution. The crystallization of $C_{168}H_{338}$ from solution was studied in the temperature range 50–84 °C. Crystallization temperatures between 50 and 70 °C initially produced single endothermic peaks. With time, a higher dissolution endotherm appears. If the system was held for sufficient time, at a given crystallization temperature, the heating process resulted in only the highest dissolution endotherm. It was found that the heating rate plays an important role in identifying the endothermic peaks. An example is given in Figure 1 where crystals from a 1% solution of $C_{168}H_{338}$ in toluene were crystallized at 65 °C for 10 min. The samples were then heated, without cooling, at either 5°/min (Figure 1a) or 20°/min (Figure 1b). The thermogram at 5°/min shows an initial dissolution peak at about 80 °C, an exothermic peak as a consequence of recrystallization of the crystals previously dissolved, and finally the dissolution peak of the recrystallized material. The transformation of the initial crystals to crystals which have higher dissolution temperature by dissolution–recrystallization on heating is obvious. A quite different situation is found in the thermogram of Figure 1b. Here only the dissolution peak of the initial crystallites is present. A heating rate of 20°/min appears to be sufficiently rapid to suppress dissolution or partial dissolution of the crystals on heating. Therefore, this heating rate has been used in all the experiments carried out with $C_{168}H_{338}$. The results shown in Figure 1 have been obtained for conditions of temperature and time where thickening has not as yet begun. However, in other situations the thickening can overlap melting or dissolution and recrystallization, as will be described for the longer chain *n*-alkane.

Typical DSC endotherms of a 4% solution of $C_{168}H_{338}$ in toluene are shown in Figure 2a. In this case the crystallization was conducted at 65 °C for increasing times. After very short crystallization times of 1 or 2 min, one endothermic peak with a dissolution temperature of approximately 83 °C was obtained on subsequent melting. A single endothermic peak with no change in the heat of fusion or dissolution temperature was still obtained if the crystallization time was increased up to 30 min. However, after longer crystallization times, double-peaked endotherms are obtained as shown in the figure. Eventually only the high-temperature endotherm persists. It is important to note that the total integrated area, which is indicated in the figure with an experimental error of ±5%, is basically constant with time. This result indicates a conservation of the level of crystallinity through the transformation. Thus, no additional crystallites are formed with increasing crystallization time. Therefore, it can be concluded that the crystallites having the higher dissolution temperature develop at the expense of the lower dissolution crystallites that were formed initially. Figure 2b shows similar thermograms after isothermal crystallization of the same solution at 72 °C. After crystallization for 5 min at this temperature, half of the area corresponding to the initially formed low dissolution peak is transformed to crystallites with a higher dissolution peak. If the crystallization is carried out for 6 min, only the high-temperature endotherm is present. The total integrated area is again found constant with time. A comparison of parts a and b of Figure 2 makes clear that the isothermal transformation that is taking place is faster with increasing temperature.

It is important to relate the dissolution endotherms of Figures 1 and 2 with a given chain structure. Extended chain crystals of $C_{168}H_{338}$ were independently prepared from the melt after crystallization at 121 °C for 1600 min. Toluene was added to these crystals to form a 4% concentrated solution and the dissolution temperature determined by DSC. A peak dissolution temperature of 98 ± 2 °C was observed. This temperature represents the dissolution temperature of the extended crystals. Dissolution temperatures can also be calculated theoretically from the expression given by Flory[30,31] for polymer–diluent mixtures

$$\left(\frac{1}{T_m}-\frac{1}{T_m^{\circ}}\right)=\left(\frac{R}{\Delta H_u}\right)\left(\frac{V_u}{V_1}\right)[v_1-\chi_1 v_1^2]-\frac{R}{\Delta H_u}\left[\frac{\ln v_2}{y}+\frac{v_1}{y}\right] \quad (1)$$

with T_m° = 397.5 K (melting temperature of the undiluted pure crystal), R = 1.987 cal/mol, ΔH_u = 980 cal/mol, V_1 = 106.11 cm³/mol (specific volume of toluene), V_u = 14 cm³/mol (specific volume of polymer), v_1 and v_2 are the volume fractions of diluent and polymer, respectively. χ_1

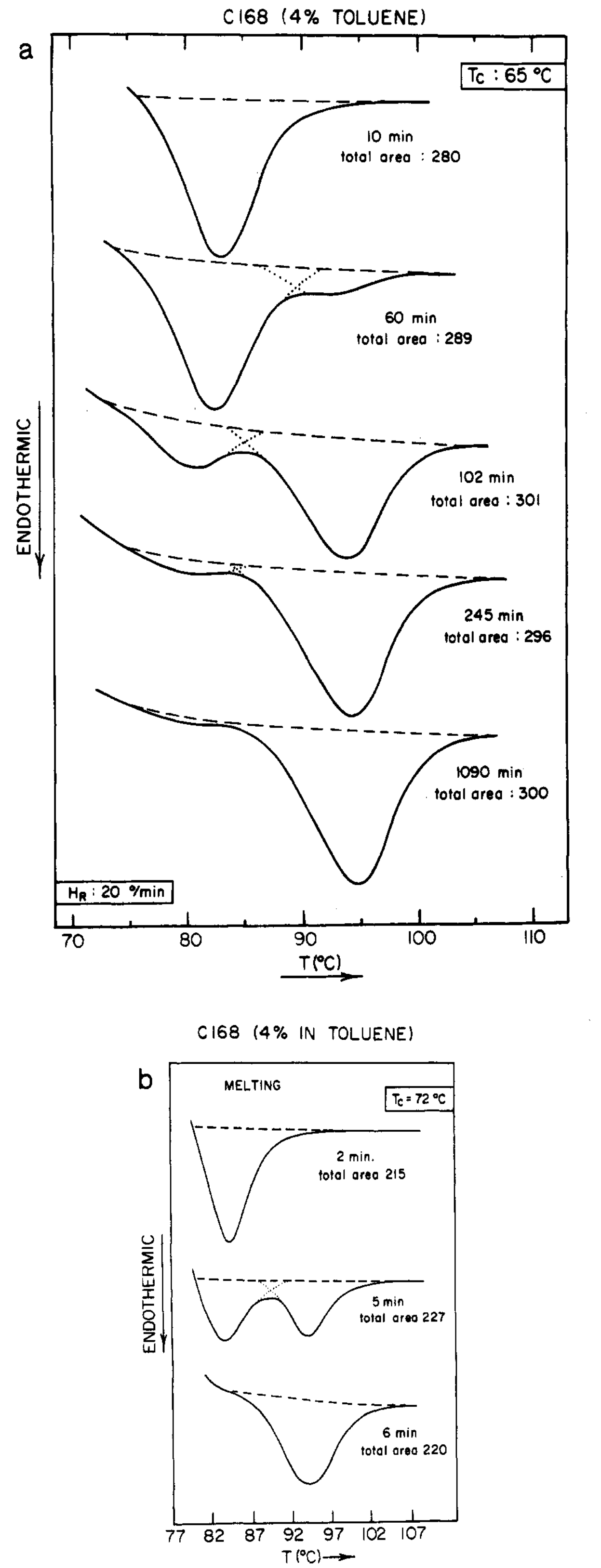

Figure 2. (a) DSC dissolution endotherms after crystallization of a 4 w/v % solution of $C_{168}H_{338}$ at 65 °C for the indicated times. (b) Same as a except after isothermal crystallization at 72 °C. Times and integrated areas, in arbitrary units, are also indicated in the figure.

is the interaction parameter, taken as 0.48 (32), and y = 168 equals the number of repeating units in the chain. This calculation gives a dissolution temperature of 99.9 °C for an extended $C_{168}H_{338}$ crystallite. This value agrees closely with the directly determined experimental value. The high dissolution peaks observed in parts a and b of Figure 2 are very close to these temperatures and thus correspond to the dissolution of extended $C_{168}H_{338}$ crystals.

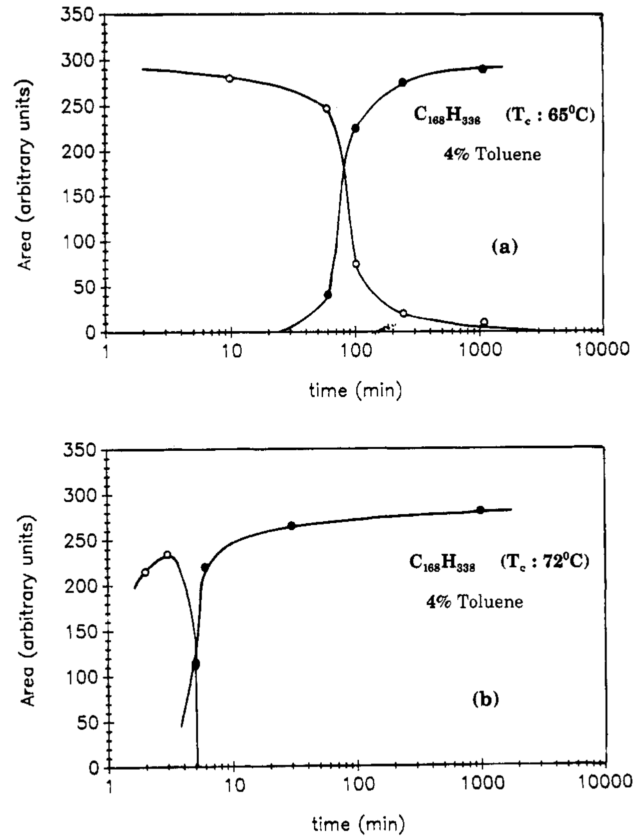

Figure 3. Integrated area under dissolution peaks versus crystallization or aging time of $C_{168}H_{338}$ crystallites formed from a 4% solution at the crystallization temperatures: (a) 65 °C; (b) 72 °C. (○) Low-temperature melting peak. (●) High-temperature melting peak.

The low dissolution temperature peak must, therefore, correspond to the dissolution of some type of folded $C_{168}H_{338}$ crystallite.[33] An idea of this latter structure can be obtained from eq 1 and the observed dissolution temperature. An estimated dissolution temperature of 85.4 °C is obtained for an *n*-alkane with a carbon number of 168/2 = 84 (4% dilution) from eq 1. This temperature is close to the peak temperature of the initial endotherms found in parts a and b of Figure 2. It is consistent with the initial folded crystals having a thickness in the vicinity of half the extended length of the molecule. This, naturally, is just an approximate calculation and does not imply that the crystallite thickness is an *exact* integral value of the extended length. The details of the folded structure are not pertinent to the present discussion.

The important result, from parts a and b of Figure 2, demonstrates that there is an isothermal transformation of crystallites from an approximately half-folded to extended form within a conserved system. Moreover, both of the dissolution temperatures remain constant with increasing time. Thus folded crystals are transformed to the extended forms in a discontinuous manner. Crystals with intermediate thickness, which would produce a series of endotherms of continuously increasing dissolution temperatures, are clearly not present.

The integrated areas of each of the endothermic peaks, taken from parts a and b of Figure 2, are plotted against time in parts a and b of Figure 3. The area corresponding to the extended crystals increases at the expense of that of folded crystals. At 65 °C more than 1000 min is needed for this isothermal transformation to be completed. However, when the crystallization temperature is increased

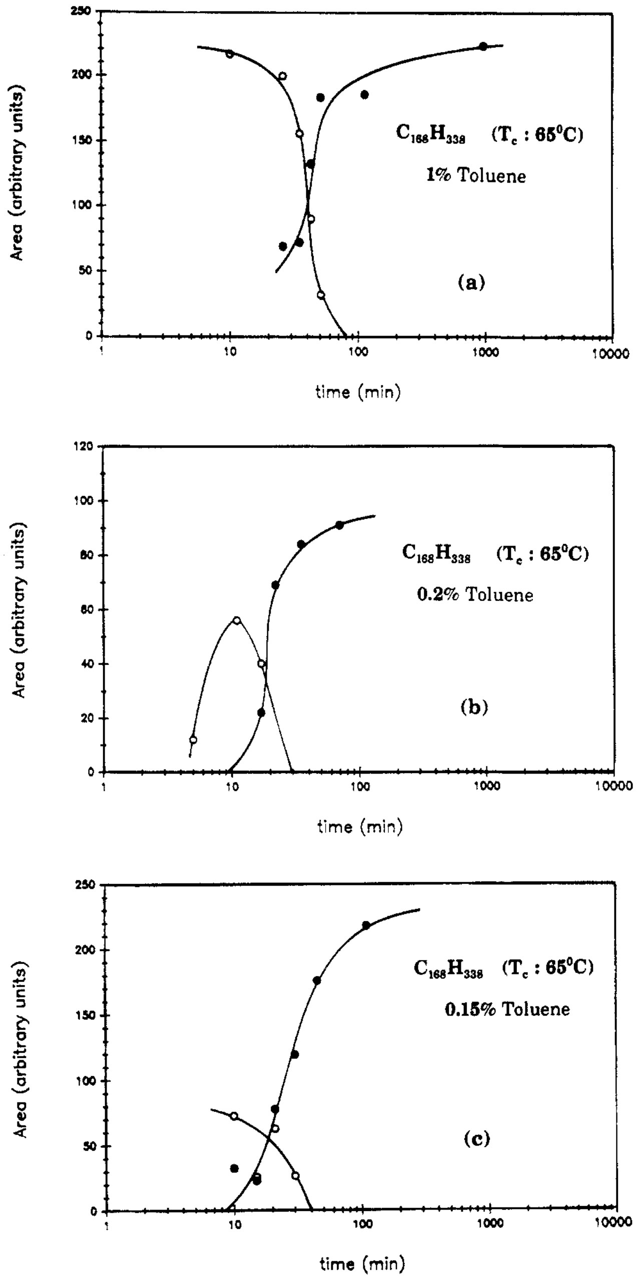

Figure 4. Integrated area under dissolution peaks versus crystallization or aging time of $C_{168}H_{338}$ crystallites formed at 65 °C with varying concentration: (a) 1 w/v % in toluene, (b) 0.2 w/v % in toluene, (c) 0.15 w/v % in toluene. (○) Low-temperature melting peak. (●) High-temperature melting peak.

to 72 °C, the folded crystallites completely disappear after approximately 5.5 min.

Isothermal crystallization of $C_{168}H_{338}$ in toluene was also studied in less concentrated solutions. A transformation of the type described in Figures 2 and 3 was always observed, independent of dilution. As an example, the integrated area of the endothermic peaks has been plotted versus log time in Figure 4 for three different concentrations (1, 0.2, and 0.15%) at the same crystallization temperature of 65 °C. The general character of the plots is the same as at higher concentrations and temperature. A comparison of the data in Figures 3a and 4 indicates that at a given isothermal crystallization temperature the transformation from the folded to extended forms became faster with dilution.

To better visualize the rate of transformation (rate of thickening), the inverse of the time required to obtain complete transformation of folded to extended forms was taken as a measure of the rate of thickening. This time was obtained from plots similar to those of Figure 3, as the intercept of the curve of the area of folded crystals with the abscissa. It is plotted on a semilogarithmic scale against the crystallization temperature in Figure 5. From this figure we find that the thickening rate is relatively slow at temperatures below 60 °C but increases very rapidly with increasing T_c. At 72 °C folded crystals are completely transformed to an extended form in 5.5 min. It takes only 2.5 min at 75 °C. Crystallization temperatures above 76 °C produced only extended chain crystallites from the initial solution. The rate of formation of folded chain crystallites in this high-temperature range, which is close to their dissolution temperature, has become very small. Since the transformation rate to the extended form is very fast at these temperatures, any folded structure that might crystallize will be very rapidly transformed to extended structures. They could very well act as sites to enhance the crystallization of the remainder of the material which will be in the extended form. Consequently, coupled with instrumental limitations, a crystallization temperature will be reached for which folded structures will no longer be observed. Therefore, the autocatalytic transformation kinetics will suddenly cease at a given T_c as illustrated by the curves of Figure 5. The crystallization temperature at which folded structures are no longer formed will depend on their dissolution temperature. They will, therefore, decrease with decreasing concentration as is indicated in Figure 5.

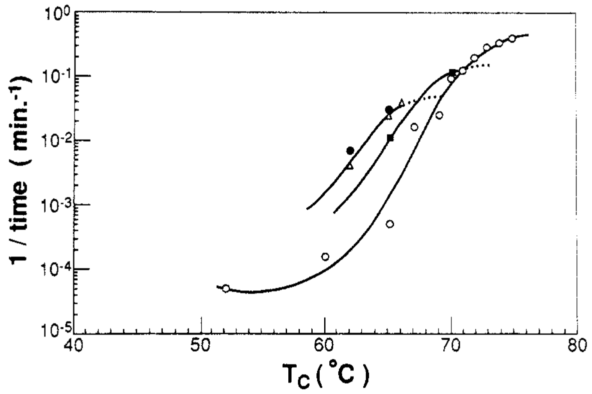

Figure 5. Rate of thickening versus crystallization temperature for $C_{168}H_{338}$ crystallites formed from toluene solutions: (○) 4, (■) 1, (●) 0.2 (△) 0.15 w/v %.

Contrary to these detailed findings, Ungar and Organ[8] have reported, using similar experimental techniques, that the n-alkane $C_{198}H_{398}$, in a 3.85% toluene solution, showed a maximum in the transformation rate at about 75 °C. The reasons for this discrepancy are difficult to determine since the results come from different laboratories, with different samples.[8] One possibility could be related to the experimental procedures. In our work, after isothermal crystallization, the sample was never cooled. The melting process was always initiated at T_c. In contrast, Organ et al. initiated the heating process either from T_c or at a temperature just below it (see the experimental part of ref 34). Unfortunately, it is not specified which crystallization temperatures they choose to melt from T_c and those which they cooled. If cooling below T_c took place after a high crystallization temperature, beyond the curve of Figure 5 in the present work, additional crystallization of folded structures would most probably develop. Therefore, the increased area of the folded peak, which would result from this procedure, could very well produce a maximum in their data.

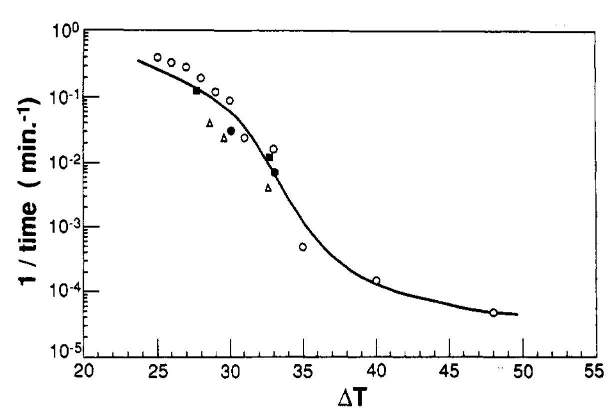

Figure 6. Rate of thickening versus undercooling for $C_{168}H_{338}$ crystallites formed from toluene solutions: (○) 4, (■) 1, (●) 0.2, (△) 0.15 w/v %.

Since the dissolution temperatures of the $C_{168}H_{338}$ crystals, either folded or extended, depend on dilution, a more rational way of examining the data might be based on the undercooling (ΔT) rather than absolute crystallation temperature. The undercooling depends on the crystallization temperature and the equilibrium dissolution temperature. The latter temperature can be calculated from eq 1 and varies from 94.5 to 99.9 °C for the concentration range of interest here. The thickening rate is plotted against the undercooling in Figure 6. Within the experimental error all of the data points can be fitted with a single curve. The differences in the rate of thickening with concentration, which was observed in Figure 5, are thus consequences of the changing undercooling and are not a direct consequence of dilution. Undercooling normalizes the thickening rate, which decreases very rapidly with increasing undercooling.

$C_{240}H_{482}$ Crystallized from the Melt. In studying the isothermal thickening of $C_{168}H_{338}$ from solution, melt-recrystallization processes were observed. For that system the problem could be completely avoided by adopting a heating rate of 20 °C/min. We now consider the same problem for $C_{240}H_{482}$ crystallized from the melt. Figure 7 gives thermograms of $C_{240}H_{482}$ crystallized at 116 °C for 1.8 min at different heating rates. All of the thermograms show the characteristics of melting and recrystallization during the heating process for all heating rates. The respective areas after peak deconvolution are plotted versus heating rate in Figure 8. The heat of fusion of the low-melting peak, open circles in the figure, remains basically constant with heating rate, and that of the high-melting peak, closed circles, decreased with increasing heating rate. Figure 8 indicates that the reorganization of folded $C_{240}H_{482}$ crystals formed from the melt, through melt-recrystallization processes, during heating is faster than for crystals of $C_{168}H_{338}$ formed from solution. Heating rates as high as 80°/min did not avoid the melt-recrystallization process of the $C_{240}H_{482}$ crystals.

Figure 7 and 8 clearly show that the melt–recrystallization process upon heating could not be experimentally avoided in studying this *n*-alkane. However, it is still possible to accurately determine the thickening rate. At a given temperature the thickening rate was taken as the inverse of the time at which only the higher endothermic peak was present in the thermogram. This condition is indicative of the complete transformation of a folded to an extended structure. A standard heating rate of 20°/min was used to follow the thickening process.

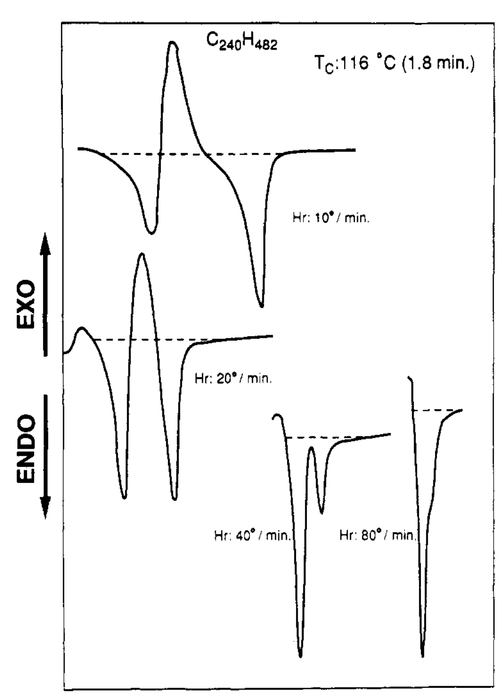

Figure 7. DSC melting thermograms for $C_{240}H_{482}$ crystallites formed from the melt at 116 °C for 1.8 min. Different heating rates are indicated in the figure.

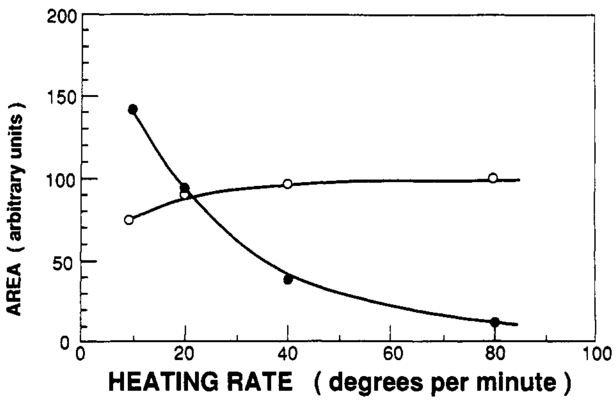

Figure 8. Integrated area under the melting peaks of Figure 7 plotted against heating rate. (○) Low-temperature melting peak. (●) High-temperature melting peak.

The crystallization of $C_{240}H_{482}$ from the melt was carried out in a temperature interval between 110 and 124 °C. A thickening process similar to the one observed in $C_{168}H_{338}$ crystallized from solution was found in a temperature interval between 112 and 120 °C. Typical DSC thermograms of the crystallization of $C_{240}H_{482}$ from the melt at 119.7 °C are shown in Figure 9. The area of the higher temperature endothermic peak increases with crystallization time at the expense of the lower endothermic peak. The different structures associated with each of the endotherms can be identified by first comparing the observed melting temperatures with that of the extended *n*-alkane. The melting temperature of an extended $C_{240}H_{482}$ in the pure melt is 129 °C.[35] This temperature is very close to the peak of the second endotherm in Figure 9. This endotherm can, therefore, be associated with melting of extended $C_{240}H_{482}$ crystals. The lower temperature endotherm in the original melt must represent a folded form that isothermally transformed to more stable extended crystals. It is worth noting that the observed melting temperature of the lower endotherm in Figure 9 is a few degrees higher than the melting temperature of an extended *n*-alkane with 120 carbons (T_m = 120 °C).[35] This analysis indicates that the initially formed crystallites may very well deviate from being integrally once folded. Furthermore, it should be noted that both of the peak melting temperatures are maintained constant with time,

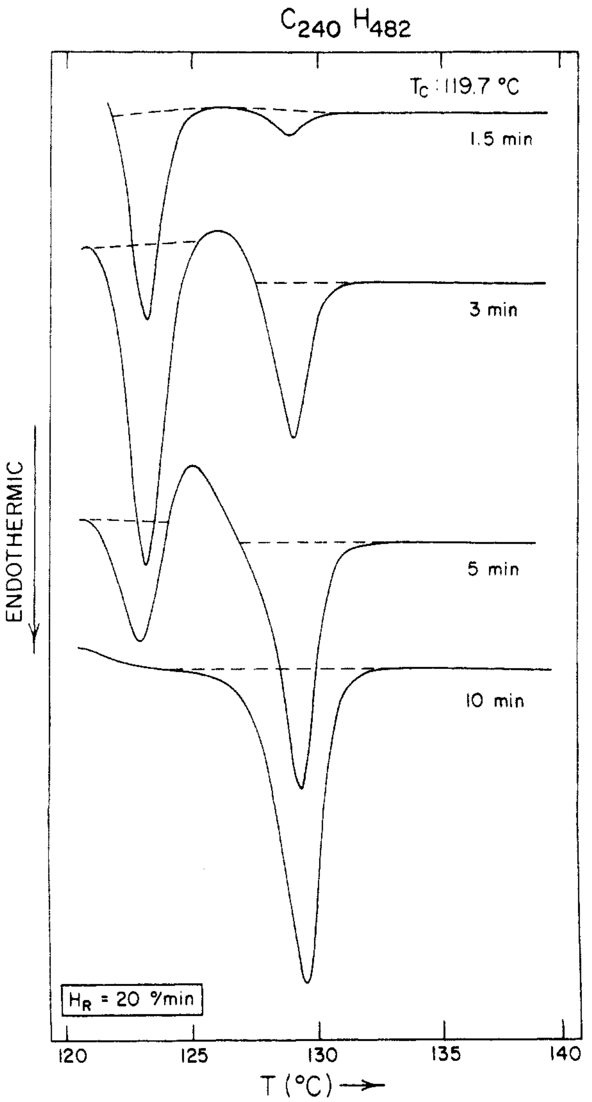

Figure 9. DSC endotherms after isothermal crystallization of $C_{240}H_{482}$ at 119.7 °C for the indicated times.

indicating a discontinuous isothermal thickening process from folded to extended $C_{240}H_{482}$ crystals, similar to the transformation observed in $C_{168}H_{338}$ from solution.

The integrated area of both peaks is plotted against log time for crystallization temperatures of 115 °C in Figure 10a and for 118 °C in Figure 10b. The overlap of the melt–recrystallization process with the isothermal thickening process is clearly reflected in the results of Figure 10a. Due to the thickening process, the heat of fusion of low-temperature peak, indicated by the open circles in the figure, decreases, since the extended crystals are formed at the expense of folded ones. However, the heat of fusion (or area) of the high-temperature peak, closed circles, is constant with time, consistent with the fact that the untransformed folded material melts and recrystallizes into the extended form upon heating. The constancy of the total area with time, observed during the thickening process in $C_{168}H_{238}$ (see Figure 2a,b), would not be expected in this case because of the melt–recrystallization complication. Parts a and b of Figure 10 differ from those of $C_{168}H_{338}$ (Figure 3a and 3b) in that the peak for the extended $C_{240}H_{482}$ is always observed at the very early times of the process due to melt/recrystallization on heating.

At higher crystallization temperatures (see Figure 10b), the rate of crystallization of the initial folded crystals is less than that at lower temperatures (Figure 10a). This is indicated by the fact that the area increases with crystallization time at the higher temperature in contrast with the lower temperature where the area decreases continuously due to the isothermal thickening. In fat, however, the thickening rate increases with temperature as is indicated by the shorter times at which the first endotherm vanishes.

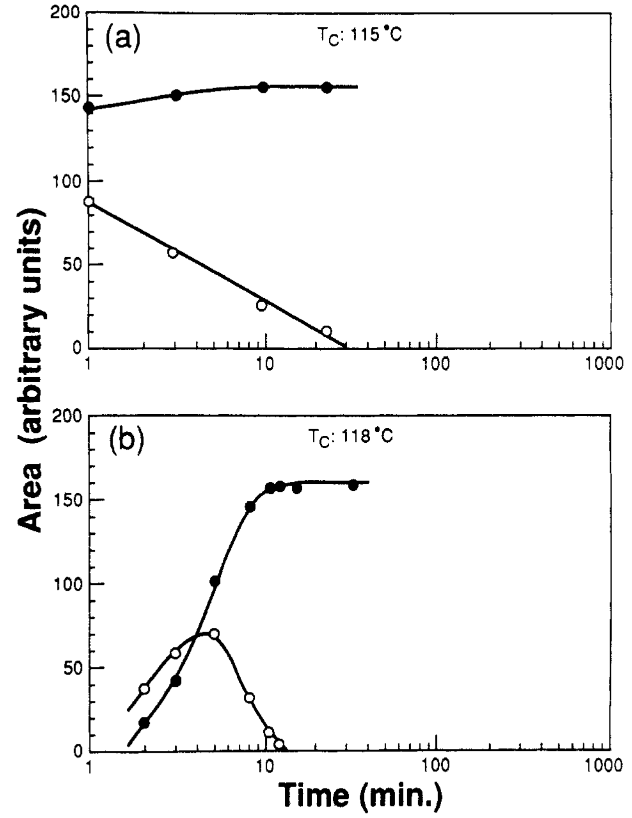

Figure 10. Integrated area under melting peaks against crystallization or aging time of $C_{240}H_{482}$ crystallites formed from the melt at the crystallization temperatures (a) 115 and (b) 118 °C. (○) Low-temperature melting peak. (●) High-temperature melting peak.

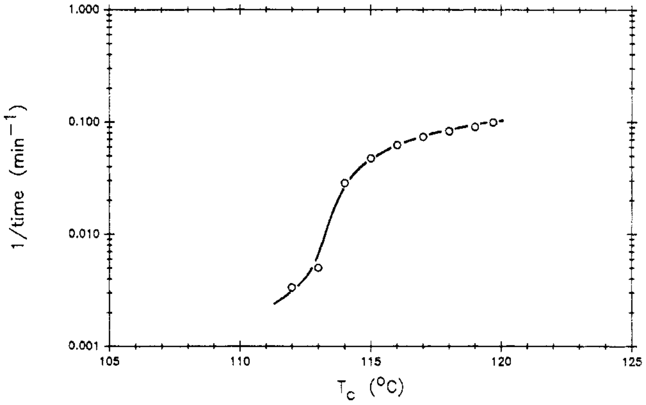

Figure 11. Rate of thickening against crystallization temperature for $C_{240}H_{482}$ crystallites formed from the melt.

The rate of thickening is plotted against the crystallization temperature in Figure 11. The shape of the resulting curve is identical to that found for the transformation of the $C_{168}H_{338}$ crystals formed from solution (Figure 5). The transformation to the extended, more stable crystals is favored with increasing crystallization temperature. This behavior appears to be a general feature of the crystallization of normal paraffins from either the bulk or solution. We find again that, for this system, there is no maximum in the rate of thickening. Crystallization temperatures higher than 120 °C only produced extended crystals.

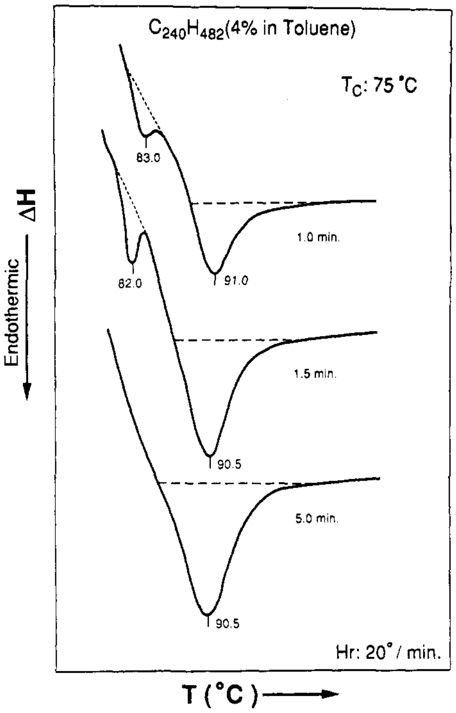

Figure 12. DSC dissolution endotherms after crystallization of a 4 w/v % solution of $C_{240}H_{482}$ at 75 °C for the indicated times.

$C_{240}H_{482}$ Crystallized from Solution. The crystallization of $C_{240}H_{482}$ was also carried out from a 4% solution in toluene in a range of temperatures between 74 and 85 °C. As an example, Figure 12 illustrates the endotherms at 75 °C, after different crystallization times. Crystallization after 1 and 1.5 min resulted in a small dissolution peak at about 82 °C and a main dissolution peak at about 90.5 °C. After 5 min at this temperature, the small peak is no longer present. The total integrated areas of the peaks of the 1.5-min thermogram and the 5-min thermogram are close to one another. These results are reminiscent of an isothermal transformation process. It remains, however, to identify the structural forms that are involved. The dissolution temperature of the extended form in a 4% toluene solution could not be determined experimentally due to shortage of material. However, an estimate of this temperature can be made from eq 1. The calculated dissolution temperature is 105 °C and is well above the dissolution temperatures that are indicated in Figure 12. Therefore, the endotherms in Figure 12 must represent a folded structure that transforms into another more stable folded structure. The isothermal thickening found in $C_{168}H_{338}$ crystallized from solution and $C_{240}H_{482}$ crystallized from the melt involved the transformation of a folded chain crystallite to one where the chains were extended. In contrast, the process illustrated in Figure 12 involves two folded chain crystallites that have different thermodynamic stabilities.

Similar thermograms are given in Figure 13 for isothermal crystallization at 77 °C. The higher temperature reduces the crystallization rate, as indicated by a lower heat of fusion after the same crystallization time. However, the first and second thermograms of this figure clearly show the presence of a small endotherm at about 83 °C which vanishes after 2.5 min of crystallization. The transformation process is accordingly faster with increasing crystallization temperature in agreement with previous results.

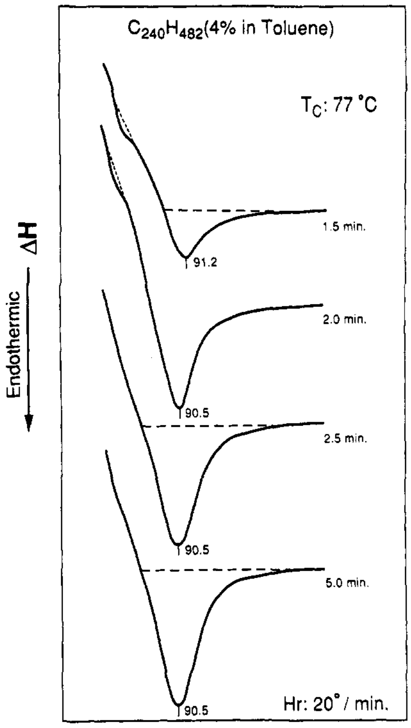

Figure 13. Same as Figure 12 except after crystallization at 77 °C for the indicated times.

Table I. Calculated Dissolution Temperatures for Different Carbon Length Chain Crystals According to Equation 1[a]

no. of carbons	T_m (°C)	no. of carbons	T_m (°C)
240	105.1	80	83.3
120	94.1	60	72.3

[a] The concentration is 4 w/v % in toluene.

An approximate measure of the kind of fold structures that are represented by the endotherms of Figures 12 and 13 can be obtained by comparing the experimental dissolution temperatures with those calculated from eq 1 for a 4% solution. The dissolution temperatures for folded structures whose thicknesses are $^1/_4$, $^1/_3$, and $^1/_2$ of the extended length have been calculated. This is obviously an approximate calculation since the fold of the folded structure, sharp or irregular, is not taken into account. A slightly lower dissolution temperature from that calculated should result from this cause. The values of T_m, given in Table I, have been calculated solely for the purpose of obtaining approximate values to compare with experiment. As a result of this calculation the small endotherm in Figures 12 and 13, whose peak temperature was at 82–83 °C, can be identified with crystallites in which the molecule is approximately twice folded. The peak at 90.5 °C can then be associated with a structure in which the molecules have been folded once.

In order to facilitate the understanding of the more complex transformation that is observed in this system, we consider a specific aspect of the isothermal crystallization kinetics. A more detailed analysis of the crystallization kinetics of $C_{240}H_{482}$ from solution, as well as for other systems, will be given in a subsequent publication. For present purposes some of the exotherms of the crystallization of $C_{240}H_{482}$ at a series of constant temperatures are given in Figure 14. The high crystallization temperature range, T_c = 80 °C or higher (not shown), only produces single exothermic peaks. Those crystallites that are formed at 80 °C melt over a very narrow range consistent with the dissolution of a single structure. The peak dissolution temperature of 91 °C that is observed on heating the crystals formed at these temperatures is consistent with an approximately once folded chain

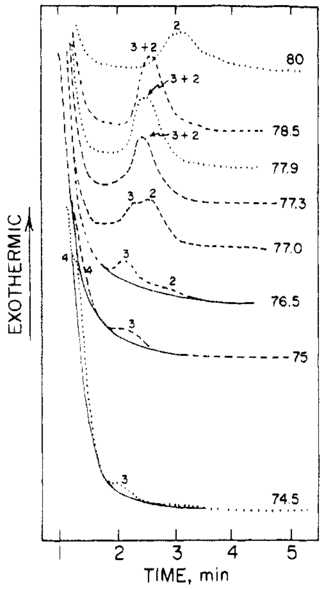

Figure 14. Crystallization exotherms at the indicated temperatures of a 4 w/v % toluene solution of $C_{240}H_{482}$. Numbers at the peak maxima indicate the number of stems in the crystal; i.e., a twice folded chain crystal contains 3 stems.

structure as was indicated previously. The crystallites formed at 84 °C, after 30 min of crystallization time (not shown in the figure), melt quite broadly at the much higher temperature ≈100 °C. This temperature is just about 5 °C below that calculated for an extended chain crystallite. It would appear that some thickening from the approximately once folded to nearly extended crystals is taking place but has not been completed.

The range of crystallization temperatures between 78.5 and 76.5 °C shows either one or two exothermic peaks. The first exotherm (appearing at the early times) is interpreted as a result of the crystallization of close to twice folded crystals. The second exotherm appears at decreasing times with increasing crystallization temperature, as is clearly shown in the 76.5 and 77 °C exotherms of Figure 14. It is interpreted as the result of the isothermal transformation of twice folded crystals to once folded crystals. According to this reasoning the transformation increases with increasing crystallization temperature and is consistent with the results obtained for the same n-alkane crystallized from the melt and $C_{168}H_{338}$ crystallized from solution. Also consistent with this reasoning are the two endotherms observed at the early crystallization times at a T_c = 77 °C in Figure 13. Because after crystallization for 2.5 min (maximum of the exotherms in Figure 14), melting resulted in a single high-temperature peak, it is concluded that the reorganization is also taking place during the heating process.

It appears that at the crystallization temperatures between 77.3 and 78.5 °C the transformation of the twice to once folded crystals is too fast to resolve itself into a separate peak. A possible enhancement of the crystallization of once folded crystals at these temperatures, due to the rapid transformation of the small amount of twice folded crystals at the beginning of the crystallization process, also needs to be considered. Hence, the small variation of the exothermic peak in this range of crystallization temperatures.

Crystallization temperatures of approximately 75 °C and lower produce crystallites with close to 3 times folded chain structures at the very early crystallization times. This structure is illustrated by the very first exotherm, less than 1.5 min, in Figure 14. To better visualize the initial exotherms, an arbitrary background has been drawn for the thermograms obtained at 74.5 and 75 °C in this figure. The second exotherm in both thermograms is also consistent with the transformation of the close to 3 times folded chain structure to a twice folded chain structure. The dissolution temperature of crystallites with thicknesses of about $^1/_4$ the length of the molecule will be very difficult to observe by differential scanning calorimetry. The reason is that the isothermal crystallization temperature is very close to the dissolution temperature of these crystals. Thickening at this temperature is very rapid and occurs during the DSC scan. Thus, the 3 times folded structure transforms very rapidly to about twice folded crystals on heating. This is the reason for observing the dissolution endotherm of the twice folded crystals, at 82 °C, at the early times of the crystallization at 75 °C in Figure 12. The twice folded crystals also reorganize on heating as evidenced by the 91 °C dissolution peak observed in the DSC heating scan in this figure. A rapid transformation on heating, of the initial close to 3 times folded crystals, to about twice folded crystals at temperatures between 74 and 75 °C also explains the similarity of the dissolution thermograms at the very early times at temperatures below ≈77 °C.[36] If, alternatively, we associate the two exotherms found either at 74.5 or at 75 °C, as shown in Figure 14, with crystallization of the twice folded crystals (the first) and thickening to a once folded crystal (the second), the transformation rate will not increase with temperature. This would be contrary to our earlier discussion of other systems as well as to the results of Figure 14 for T_c between 76.5 and 78.5 °C. These results clearly indicated that the rate of isothermal thickening for this system increases with increasing crystallization temperature.

$C_{240}H_{482}$ is, therefore, a rather unusual system when crystallized from solution. Depending on the crystallization temperature, different folded structures are initially formed and transformed isothermally to more stable crystallites. For relatively low T_c, the heating process by itself will not distinguish between these structures due to dissolution–recrystallization during heating. Therefore, the appropriate exotherms need to be examined. Crystallization temperatures about 84 °C and higher produced close to extended crystals with a dissolution temperature of about 100 °C.

Discussion

The results presented above for $C_{168}H_{338}$ and $C_{240}H_{482}$ showed a discontinuous isothermal transformation from a given crystallite structure to another more stable thicker crystallite. Because the thicker crystals are formed at the expense of the thinner ones, the process can be considered to be a thickening one that takes place isothermally. This type of thickening is observed whenever the n-alkane crystallizes in some type of folded structure. This is true for crystallizations carried out from solution or from the melt. The $C_{168}H_{338}$ n-alkane crystallized from solution, and $C_{240}H_{482}$ crystallized from the melt, whose thicknesses were approximately half of the molecular length, transformed to crystallites where the chains were completely extended. $C_{240}H_{482}$ crystallized from solution displays a discontinuous isothermal transformation from one folded crystallite structure to another. The specifics of the structures involved depend on the crystallization temperatures.

The rate of the transformation increases with temperature and generates a sigmoidal type curve. The process ceases at a temperature that corresponds to that at which only extended chain crystallites form from the melt or from the original solution. We have found no evidence in our detailed studies of several *n*-alkanes for a maximum in the thickening rate as has been reported for $C_{198}H_{398}$ crystallized from solution.[8] At a fixed temperature the transformation rate increases with dilution. The rate-concentration data are, however, normalized when comparison is made at a constant undercooling.

In analyzing endotherms in order to establish the crystallite structures, cognizance must be taken of the fact that alterations can occur on heating. These involve the melt–recrystallization process and the inability to detect small amounts of crystallites that transform very rapidly isothermally and are thus not resolved during the heating scan.

We are faced with the problem of understanding the basis for the isothermal transformation, or thickening, of one discrete structure to another. This situation appears to be unique to the *n*-alkanes. Isothermal crystallite thickening is well-documented in bulk crystallized linear polyethylene[11-16] and other polymers.[37] However, for polymers, thickening is a continuous process, rather than being a discrete one. Several different mechanisms have been proposed. One involves diffusion, or the motion of chain units, within the crystallite along the *c*-axis. This mechanism involves an Arrhenius type activated process and has been shown to be inadequate to explain thickening in polymers.[16] As far as the *n*-alkanes are concerned the sigmoidal nature of the rate–temperature plots (Figure 5) and the dependence of the rate on undercooling, with varying concentration (Figure 6), are very different to reconcile with a diffusion type process. Other thickening processes that have been proposed include the insertion mechanism of Strobl and Voigt-Martin[28] and a melting and recrystallization process.[16] These latter mechanisms require partial or total melting of the initial crystals before and during the transformation. We shall investigate the applicability of this process to the thickening of the *n*-alkanes. Before doing so, there is another phenomenon intimately related to thickening that needs to be considered.

Keller and collaborators have followed the isothermal crystallization in the bulk of $C_{246}H_{492}$ by means of syncrotron X-ray radiation. They found that, depending on the crystallization temperature, the crystallites either thickened or became thinner during the time course of crystallization.[6,38] It has also been reported that low molecular weight poly(ethylene oxide) fractions undergo either an isothermal thickening or thinning process when crystallized from the melt.[38-41] These studies have made clear that the final structure that evolves in low molecular weight species, *n*-alkanes or polymers, is quite different from that of the originating nucleus. In fact the initial crystallite thickness that can be detected is a nonintegral fraction of the extended chain length.[6,39,40] Therefore, the postulate and calculations that assume that the initial structure that is formed, and maintained in the development of the mature crystallite, is either a fully extended or an integrally folded critical sized nucleus do not apply to the *n*-alkanes and low molecular weight polymers.[42-45]

For a complete understanding of the problem, both the thickening or thinning that occurs during the isothermal crystallization as well as the isothermal transformation with time from one discrete state to another has to be explained. To simultaneously explain these two phenomena, we postulate that a free energy diagram, as is schematically pictured in Figure 15, exists. The free energy function of the crystallite has a set of minima energy wells.

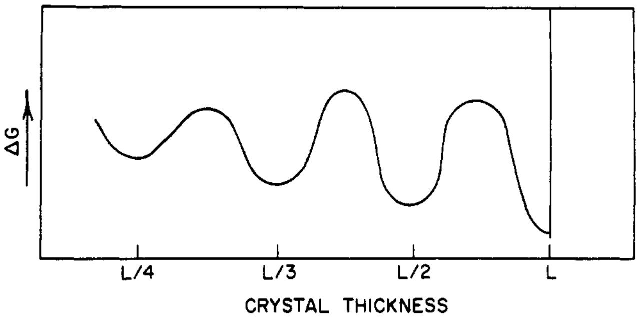

Figure 15. Schematic representation of the crystal free energy versus crystal thickness for *n*-alkanes. *L* indicates the thickness of the extended chain crystal.

The lowest energy well corresponds to extended chain crystallites. The progressively higher energy wells correspond to folded chain crystallites with thicknesses approximate half, one-third, etc., of the extended molecular length. For present purposes the specific nature of the fold structure is not pertinent. The important point is that there is a set of minima each of different energies that correspond to different folded structures. The crystallites of course will tend to seek the lowest free energy level possible.

During isothermal crystallization the critical nucleus dimension in the chain direction will determine the initial crystallite thickness and, thus, its position relative to a given well.[29,46] During crystallization the chains will seek the nearest local free energy minimum. Focusing attention on the region of such a local minimum if the initial thickness is less that the corresponding to the minimum, for example, $L < L/2$, thickening will occur from L to $L/2$. However, if $L > L/2$ but less than the length corresponding to the barrier height, then L will decrease (or thin) to $L/2$ in order to reach the nearest, local, free-energy minimum. This diagram thus explains, in a straightforward manner, the thinning or thickening that is observed during the initial isothermal crystallization. The thickness of the initial nucleus can be calculated without any a priori assumptions with regard to the structure in the local minimum.[47,48] It next remains to explain on this basis how the isothermal transformation from one discrete structure to another takes place with time.

A given crystallite structure will tend to seek the lowest free energy minimum. The question that then needs to be addressed is the feasibility of such changes in the present case and how the energy barrier between minima can be overcome isothermally. We consider this problem by analyzing energy fluctuations in such systems following the concepts used for thickening in bulk systems. The mean-square energy fluctuation is given by the expression[49]

$$\overline{\Delta E} = [(\bar{E} - E)^2]^{1/2} = (RT^2C_v/N_0)^{1/2} \qquad (2)$$

Here C_v is the heat capacity of the system and N_0 is Avogadro's number. We have used this equation to calculate the energy fluctuations that occur within a 4 × 4 segment section of a crystallite which is $(168 - 3)/2$ units thick. The C_v values given by Wunderlich et al.[50,51] have been used over the temperature range of interest (50–75 °C). The calculated energy fluctuations correspond to the thick dash line in Figure 16.

The free energy change required to dissolve this small section of a crystallite can be calculated from the expres-

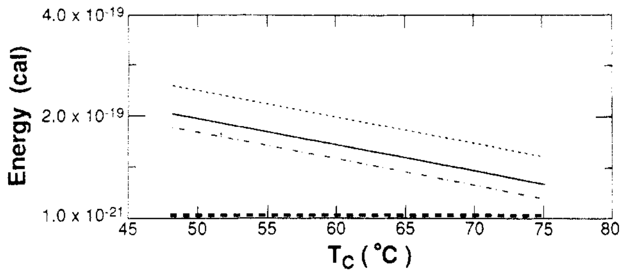

Figure 16. Thick bottom dash line ($\overline{\Delta E}$): Calculated energy fluctuations within a 4 × 4 segment section of a crystallite 83 CH_2 units thick. The upper three lines correspond to the calculated free energy change required to dissolve the former small portion of the crystal (ΔG) calculated for (- - -) $\sigma_e = 2000$ cal/mol, (—) $\sigma_e = 3000$ cal/mol, and (–·–) $\sigma_e = 3500$ cal/mol.

sion[30]

$$\Delta G = x^2 L \Delta f_u + RT \left\{ \left[\left(\frac{1}{X_1}\right)\left(\frac{1-v_2}{v_2}\right) + \frac{1}{L} \right] \ln (1-v_2) + \frac{1}{x} \left[\ln v_2 + \frac{2\sigma_{ec}}{RT} + \ln\left(\frac{L-x+1}{L}\right) \right] + \frac{\chi_1}{X_1}(1-v_2) \right\} \quad (3)$$

Here Δf_u, the free energy of fusion per repeat unit of the infinite chain, has been approximated by $\Delta H_u \Delta T / T_m°$, $T_m°$ is the equilibrium melting temperature of the infinite size chain (418.5 K), x is the number of units of the portion of the crystal to be melted, and L, in units, is the total length of the crystal. $X_1 = V_1/V_u$, and the rest of the terms in this equation have the same meaning as in eq 1. The values of the interfacial free energy, σ_{ec}, of the portion of the crystal undergoing melting is unknown. However, values to σ_{ec} within reasonable limits can be assigned. For present purposes we have allowed σ_{ec} to vary from 2000 to 3500 cal/mol. Thus, the magnitude of ΔG can be compared with that of $\overline{\Delta E}$. ΔG values have been calculated for a 4% solution of $C_{168}H_{338}$ folded crystals in the temperature interval between 50 and 75 °C. The results are given in Figure 16 by the three upper lines. Increasing σ_{ec} decreases the value of ΔG. Values for $\overline{\Delta E}$ and ΔG are of about the same order of magnitude over the whole temperature interval. They in fact become very close to one another at temperatures between 70 and 75 °C. This result is in accord with the experimental observations, summarized in Figure 5, which showed a steep increase of the thickening rate in this temperature interval. These calculations are obviously approximate since they depend on the values taken for σ_{ec} and the number of segments assumed to melt. However, they demonstrate that energy fluctuations are of sufficient magnitude to cause the melting of a portion of a crystallite and thus initiate the dissolution process.

Once a small portion of the crystal is melted, the energy necessary to melt the adjacent units will be less. Once initiated, the cooperativity of the process will bring $\overline{\Delta E}$ and ΔG even closer to one another. The autocatalytic character of the curves describing the thickening rate against temperature (Figures 5 and 11) is consistent with the proposed cooperative melt–recrystallization process as being the thickening mechanism. In addition, the normalization of the dependence of the thickening rate on concentration by the undercooling (Figure 6) is in accord with this calculation. The experimental results then agree with the theoretical analysis, with partial melting taking place isothermally by means of energy fluctuations.

A premelting process associated with the disordering of end sequences of the chain is known to occur during fusion of normal extended paraffins.[29,35,52–57] In a continuous heating of these paraffins premelting was observed at temperatures well before complete melting.[29] The same theoretical arguments, initially formulated by Flory and Vrij for extended chains[52] should apply to folded crystals. When the crystallization of the higher molecular weight n-alkanes is carried out at temperatures that are close to the melting or dissolution of the initial folded crystals, energy fluctuations might cause a similar premelting process especially when localized at the ends of the chain. Energy fluctuations could initiate a cooperative premelting process of folded crystals formed at high crystallization temperatures. The kinetically favored folded structures will thus melt and recrystallize into thermodynamically more stable forms, either one which is less folded or one which is extended. The theories underlying the premelting associated with the disordering of the ends of the chain and energy fluctuations predict an increase of these processes with temperature and, therefore, both vary in the same direction as the experimental results.

In contrast, Organ, Ungar, and Keller[21] have proposed a thickening mechanism that involves a solid-state diffusion process. According to this proposal an extended crystal usually grows at the tip of a well-developed folded crystal ("spearhead" crystal) which further thickens through solid diffusion. In this model the thickening of the n-alkane needs to begin before the complete transformation of the molten material to folded crystallite. It has been shown (see Figure 2a as an example) that, within experimental error, the total heat of fusion of the untransformed and thickened crystals remains constant before and after thickening. The total mass of the system in this example is conserved so that no additional material could have crystallized into extended crystals. Growth of extended crystals before thickening is, therefore, not consistent with these observations. In addition, as was pointed out, a solid chain diffusion process requires a smooth increase of the thickening rate, rather than the autocatalytic process that is actually observed. Furthermore, this mechanism is not consistent with the observed dependence of the thickening rate on the undercooling.

Conclusions and Summary

Folded long-chain n-alkane crystals undergo isothermal thickening. Depending on the length of the n-alkane and the mode of crystallization, the isothermal thickening may proceed from a close to once folded crystal to extended crystals. This is the situation found for $C_{168}H_{338}$ crystals from solution and $C_{240}H_{482}$ crystals formed from the melt. Isothermal thickening may also proceed through multiple refolding stages as seen for $C_{240}H_{482}$ crystals formed from solution.

The rate of thickening increases with the crystallization temperature and is autocatalytic. Undercooling is the determining variable of the rate of thickening and normalizes the rate obtained at different concentrations.

The mechanism of the isothermal thickening is consistent with a melt–recrystallization process. The initial kinetically favored folded crystals melt and recrystallize into the thermodynamically more stable extended crystals. An estimation of the energy fluctuations within the system indicates that melting of a small portion of the crystallites is, theoretically, feasible and therefore establishes the basis for the proposed mechanism.

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