# Rate Minimum in Solution Crystallization of Long Paraffins[†]

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ABSTRACT: Isothermal crystallization of the long alkane $n$-$C_{198}H_{398}$ from solution was studied by DSC. The maximum bulk crystallization rate ($R$) and the primary nucleation rate parameter ($1/t_{10}$) were both found to pass through a deep minimum with increasing supercooling. This behavior is in line with the equivalent, recently observed effect in melt crystallization of these compounds. The minima occur at the transition temperature between chain-extended and chain-folded crystallizations. The minimum in nucleation rate from solution is even more pronounced than the one previously observed for melt crystallization. Strong additional emphasis is thus being lent to the concept of surface "self-poisoning", apparently unique to chain-folded crystallization. The latter effect pertains both to primary nucleation and crystal growth but, as shown in the present study, to a greater extent to the former. Amongst other new effects observed in these alkanes is isothermal crystal thickening during solution crystallization, an effect absent in polyethylene.

## Introduction

Extremely pure long $n$-alkanes recently synthesized by Bidd and Whiting[1,2] provide ideal model systems for studying the early stages of chain folding. Using these materials, Ungar et al.[3] find that chains may fold if they contain 150 carbon atoms or more. The number of possible folds depends on the length of chain, with the longest $n$-alkane available, $C_{390}H_{782}$, capable of folding up to 4 times. Extensive Raman,[3,4] small-angle X-ray (SAXD),[3-5] and electron microscopic[6] studies reveal that stable crystal forms always have thicknesses equal to or very close to the extended chain length or integer fractions (IF) thereof. However, unstable noninteger fraction (NIF) forms often occur as an intermediate stage during melt crystallization,[7] subsequently thickening or thinning to produce crystals with IF thicknesses. Metastable NIF crystals may be temporarily preserved by rapidly quenching melt-crystallized samples after short crystallization times, but even at ambient temperatures these crystals may gradually transform into the most stable IF forms. Results obtained by Lee and Wegner[8] using similar materials obtained by a different preparative method are generally in agreement with the above. The single fold length measured by those authors which differs widely from an integer fraction of the extended chain length we tentatively suggest corresponds to a quenched metastable NIF form.

In addition to discrete crystal thicknesses, another unusual feature of the long-chain $n$-alkanes reported by Ungar and Keller is the existence of minima in the crystallization rate ($R$) versus crystallization temperature ($T_c$) curves.[9] Measurements on melt-grown $C_{198}H_{398}$ (C198) and $C_{246}H_{494}$ (C246) using differential scanning calorimetry (DSC) and synchrotron SAXD show that at the highest attainable $T_c$s crystallization is in the extended chain form. As $T_c$ is lowered, the rate of crystallization first increases and then, as $T_c$ is lowered further, decreases to a minimum value before again rising with increasing supercooling. For $T_c$ values below that at which the minimum in growth rate occurs, crystals grow with folded chains. Discontinuities in growth rate versus $T_c$ curves have been reported previously for low molecular weight fractions of poly(ethylene oxide)[10] and polyethylene,[11] but the actual minima obtained from the $n$-alkanes are unprecedented and have provoked new discussion of the chain-folding process.[4,12] The observed minimum in growth rate has been attributed to a "poisoning" effect[9] whereby the growth face of potentially stable extended chain crystals is blocked by the deposition of chains in folded conformations. These folded chains are not stable at temperatures above their melting point and cannot lead to productive crystal growth, yet they have a profound influence on the extended chain crystallization rates. A similar situation occurs during solution crystallization, as will be reported here.

Studies of solution crystallization have so far been confined to C198, the highest $n$-alkane of which reasonable quantities (about 80 mg) are available. C198 grown from solution in toluene may crystallize with chains either extended or folded once or twice. The different crystallization temperatures ($T_c$) and crystallization times ($t_c$) required to produce each crystal type can be clearly delineated by studying the dissolution behavior of the resultant crystals as described in ref 6. Isothermal thickening, not seen during solution crystallization of polyethylene, does occur in C198, and this too is evident from dissolution studies. Salient aspects of the dissolution behavior are repeated in more detail here and the development of the appropriate dissolution peak areas with $t_c$ is used as a measure of crystallization rates. The association of the different dissolution behaviors with crystals having a particular (IF) thickness (and hence chain conformation) has been confirmed by electron microscopic studies of the morphology and thicknesses of crystals grown under various representative conditions.[6] This previously established classification of thicknesses is fully consistent with the growth rate measurements presented here. The current results strikingly reproduce the unexpected minimum in crystallization rate previously observed during melt crystallization of long $n$-alkanes, with the minimum here even more pronounced. In addition, some unusual effects were observed near the minimum, to be described. The results are discussed in terms of possible molecular models of crystallization.

## Experimental Section

All the results presented here were obtained from a 3.85% solution of $C_{198}H_{398}$ in toluene, sealed into a DSC volatile sample pan and analyzed by using a Perkin-Elmer DSC-2 differential scanning calorimeter. Crystal growth behavior was followed by allowing the sample to crystallize in the DSC at a chosen temperature, $T_c$, for varying lengths of time, $t_c$, and then heating from $T_c$ or just below to 100 °C and measuring the peak position, $T_d$, and the area, $A$, of any dissolution endotherms thus obtained (see Figure 2 for an example). A heating rate of 10 °C min$^{-1}$ was used, which, over the small temperature intervals involved, was sufficiently fast to prevent any detectable reorganization of crystal structure during heating in the DSC. Crystallization temperatures were in the range 70–83 °C. Below 70 °C the rate of growth was so fast that considerable crystallization occurred during cooling before the desired $T_c$ could be attained. Above 83 °C, crystal-

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[†] Dedicated to the memory of Dr. David Sadler in recognition of his stimulating interest in this subject area.

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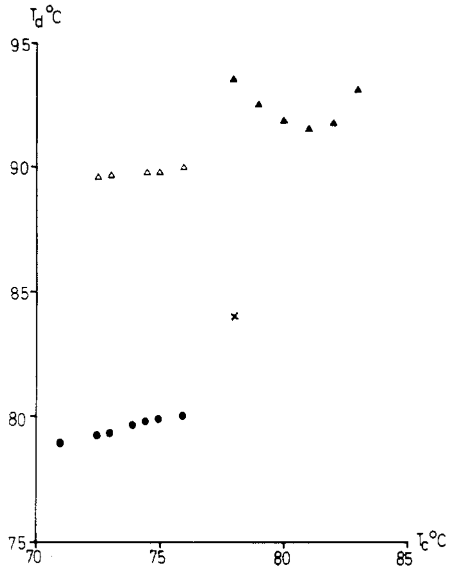

Figure 1. Dissolution temperature, $T_d$, as a function of crystallization temperature, $T_c$: (●) primary crystallization, folded chains; (△) secondary crystallization, extended chains; (▲) primary crystallization, extended chains; (×) intermediate (see text).

lization was too slow for this method of measurement to be practicable. For each value of $T_c$, the crystallization time was successively increased until no further substantial changes in either the area or the position of the dissolution endotherm(s) were observed. $T_d$ values were corrected for thermal lag arising from both the resistances between the heater and the sample pan and between the pan and the dissolving crystals. The first correction was determined from the slope of the indium melting endotherm.[13] The second correction was evaluated by recording thermograms of the same amount of fully crystallized material in suspension at different scanning rates; the thermal lag per unit mass of crystalline paraffin was obtained from the difference between the indium-corrected peak positions at 10 and 0 °C min$^{-1}$. The combined correction was applied to all $T_d$ measurements.

The $T_d$ reported for a given $T_c$ is the corrected peak position obtained when crystallization in a particular form is complete, as judged by a stable maximum value of $A$. A small increase in $T_d$ (of the order of 1 deg) was observed with time, and this was attributed to a limited increase in crystal perfection (see Discussion section). Larger, discontinuous changes in peak position, accompanied by changes in peak area, are due to recrystallization in a different crystal form. The crystallization conditions which lead to either extended chain or folded chain crystals have already been documented to some extent.[6] Crystal thickness measurements reported at that time allow us to identify the dissolution behavior observed here with either extended chain or once-folded chain crystals.

Crystallization rates were measured by plotting the area under a particular DSC dissolution peak as a function of crystallization time. The gradient of the curve thus obtained ($R$) was taken in the region where between 40% and 60% of the paraffin had crystallized in a particular form. In this region, the curve was linear and the gradient was a maximum. The parameter $R$ is a bulk property and depends both on the rates of primary nucleation and of growth of the crystals. Another parameter measured was $1/t_{10}$, where $t_{10}$ is the time needed to achieve 10% crystallization. $1/t_{10}$ is closely associated with the rate of primary nucleation.

## Results

**Dissolution Behavior.** Figure 1 shows crystal dissolution temperatures measured by DSC as a function of $T_c$.

Most of the data in Figure 1 have appeared previously (in an uncorrected form) in ref 6 but are repeated here for self-contained reading. From the results, two distinct types of crystallization can be identified. In the temperature range 70 °C < $T_c$ < 77 °C, initial crystallization produces crystals with $T_d \sim 80$ °C. The area under the dissolution endotherm, $A$, increases with $t_c$ as crystallization proceeds and the peak position also shifts slightly to higher temperatures, as discussed previously. After some time at $T_c$, a second distinct crystal population begins to form, characterized by a dissolution endotherm at around 90 °C. As $t_c$ is increased further, the area of the high-temperature endotherm increases to a stable maximum value, while the area of the low-temperature endotherm decreases correspondingly. An example is shown in Figure 2 for $T_c = 74.5$ °C. For all but the highest $T_c$ values, crystallization in the primary form is complete before any transformation takes place. By contrast, for 79 °C < $T_c$ < 83 °C, a single dissolution endotherm is obtained over the whole range of $T_c$. Crystals grown in this temperature range have $T_d \sim 92$ °C. The two types of behavior can be clearly seen in Figure 1. Behavior in the intermediate region $T_c$ = 77–78 °C and the origin of the point marked × will be considered later. From our previous morphological studies[6] and related experiments,[5] we can identify crystals grown between 79 and 83 °C as containing extended chains. The chains in crystals grown between 70 and 77 °C are folded once but will in time extend isothermally to become extended.

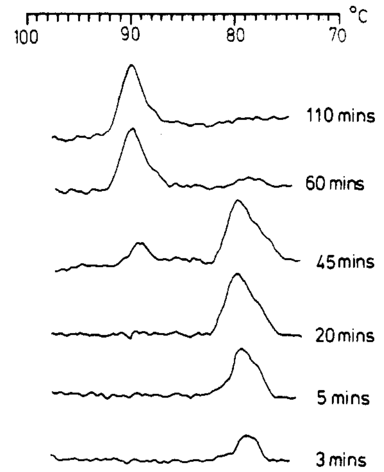

Figure 2. DSC traces obtained on heating solutions subsequent to crystallization at 74.5 °C for the times shown. Heating rate, 10 °C min$^{-1}$.

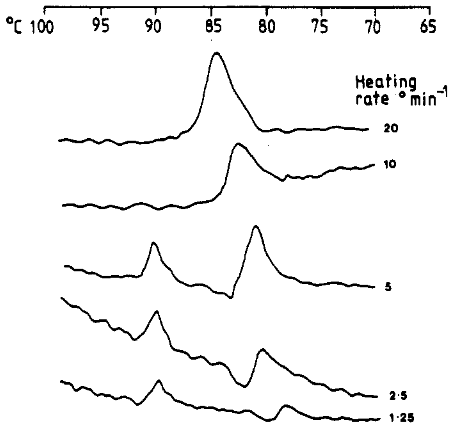

Figure 3. DSC traces obtained at the heating rates shown after crystallization for 30 min at 76.0 °C.

Figure 3 shows the DSC traces obtained using different heating rates for an example of folded chain crystals ($T_c$ = 76 °C, $t_c$ = 30 min). At the fastest rates, only one dissolution endotherm is obtained, but at rates of 5 °C min$^{-1}$ and less, reorganization occurs during heating in the DSC to give an exotherm followed by a second endotherm. No such effects were seen for extended chain crystals. The observation that no reorganization of folded chain crystals occurs during heating in the DSC at 10 °C min$^{-1}$ confirms

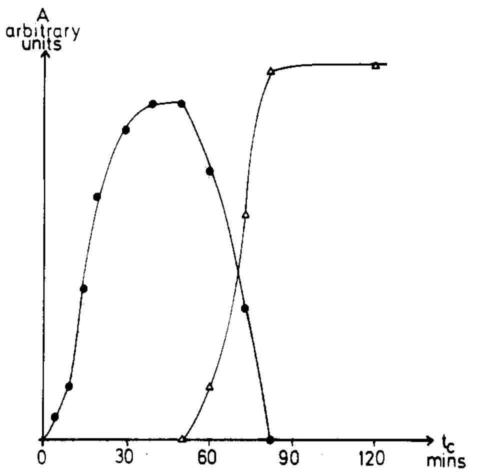

**Figure 4.** Dissolution peak area, $A$, as a function of crystallization time, $t_c$, for crystallization at 76.0 °C: (●) folded chain crystal, (△) extended chain crystal.

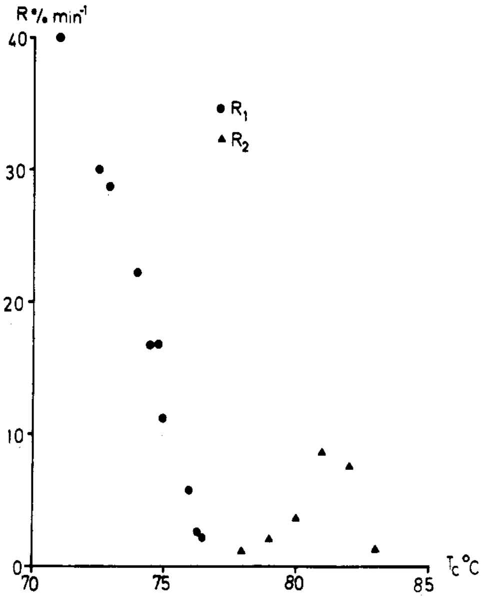

**Figure 5.** Rate of crystallization as a function of crystallization temperature, $T_c$. $R_1$ and $R_2$ refer to folded chain and extended chain crystallization, respectively.

that the second peak obtained under some conditions (and illustrated in Figure 2) is indeed due to extended chain crystals produced isothermally prior to the scan.

The maximum values of $A$, $A_{max}$, obtained for the different crystal types, give us some indication of their relative heats of dissolution. The value of $A_{max}$ increases by 5–10% when folded chain crystals become extended isothermally. Within the limits of experimental error, no difference could be detected between $A_{max}$ for isothermally thickened crystals and crystals which grew initially with their chains extended.

**Crystallization Rates.** Figure 4 shows a typical plot of dissolution peak area versus crystallization time for $T_c$ = 76.0 °C. Both the initial chain-folded crystallization and the subsequent isothermal thickening are shown. The crystallization rates measured from such curves are plotted in Figure 5 as a function of $T_c$. $R_1$ is the rate of primary crystallization in the region 70 °C < $T_c$ < 77 °C where folded chain crystals are obtained and $R_2$ is the rate of extended chain crystallization measured in the range 79–83 °C. Since the measurements refer to a bulk property, the results do not represent individual crystal growth rates and will include any effect due to changes in nucleation rate.

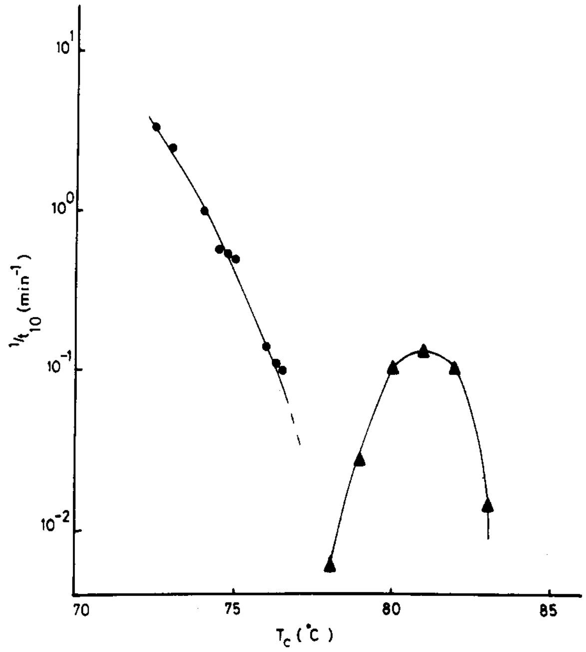

**Figure 6.** Rate parameter, $1/t_{10}$, as a function of crystallization temperature.

The parameter more closely associated with the nucleation rate, $t_{10}$, is shown as a function of $T_c$ in Figure 6. Figure 5 reveals a minimum in crystallization rate corresponding to the point at which primary crystallization changes from an extended chain to a folded chain form. This minimum is even more pronounced when the associated nucleation rates are considered, as shown in Figure 6. Thus, the surprising feature of inversion of the temperature dependence of the nucleation rate, previously reported for melt crystallization of C198 and C246,[9] is confirmed here for crystallization from solution.

**Crystallization near the Transition Point.** In the region $T_c$ = 77 °C, where the minimum in crystallization rate occurs, there is a transition from extended chain to folded chain crystal growth, and a pattern of behavior is observed which is somewhat different to that at higher or lower temperatures. Crystallization in this region proceeds very slowly at first, and the DSC traces corresponding to the early stages show a small endotherm at about 84 °C, followed immediately by an exotherm of roughly equal area and then by a slightly larger endotherm at a position corresponding to extended chain crystals. After considerable time the first endotherm and exotherm disappear, and the higher temperature endotherm grows rapidly until crystallization is complete. This behavior is illustrated in Figure 7 for $T_c$ = 78 °C, the inset showing a typical DSC trace obtained after 3 h crystallization. The low-temperature endotherm, seen only in the early stages of crystallization, is represented by the point marked × in Figure 1. It should be noted that this peak occurs at a significantly higher temperature than that obtained from chain-folded crystals grown at only slightly lower temperatures. However, the corresponding crystallization time is much longer. Similar behavior is seen for $T_c$ = 77 °C, but crystallization is much slower at this temperature. The possible origin of this peak will be discussed below.

## Discussion

In this study we use differential scanning calorimetry as a method of identifying variations in the crystallization behavior of $C_{198}H_{398}$ from solution over a range of temperatures. Distinctly different results are obtained for crystallizations above and below 77 °C. The reported

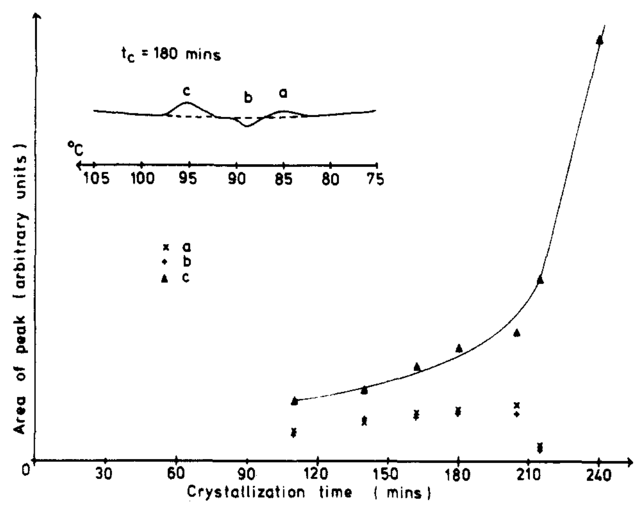

**Figure 7.** Dissolution behavior shown by crystals grown at 78.0 °C. The inset shows a typical DSC trace.

variations in dissolution temperature and crystallization rate are entirely consistent with the growth of extended chain crystals at high temperatures and with a transition to folded chain crystallization at 77 °C. This is substantiated by crystal thickness measurements obtained by different methods on crystals of $C_{198}H_{398}$ grown at several temperatures within the present range of interest, which are reported elsewhere.[6] With one possible exception,[14] for solution grown crystals, the long X-ray periods have been within 0.2 nm of calculated $L/n$ values, where $L$ is the extended chain length and $n = 1$, 2, or 3. It should be noted, however, that these measurements were made on filtered and dried crystal mats at room temperature and thus do not necessarily exclude the possibility that the primary crystallization took place in the noninteger (NIF) form. This point will be considered further below. To start with, we shall only distinguish between the chain-extended (E) and the chain-folded (F) form, the latter encompassing both integer and noninteger varieties with $l \geqslant L/2$. Crystals with twice-folded chains have not been considered here due to their instability in the DSC.

We shall first deal with the transition from extended to folded chain crystallization which occurs as the supercooling is increased and with the crystallization rate minimum associated with it. Next, we shall briefly discuss the isothermal transition from folded to extended chain crystals, observed in the temperature range 70–77 °C, with more detailed consideration in a separate publication.[15] Finally, the possible origin of the dissolution endotherm at 84 °C, recorded for crystallization at $T_c = 78$ °C (Figures 1 and 7), is discussed.

**Crystallization Rate Minimum.** Discontinuities in the gradient of growth rate versus supercooling curves have been reported previously for low molecular weight fractions of poly(ethylene oxide)[10] and polyethylene.[11] The gradient was found to step up at each transition point where the number of folds per molecule increases by 1, i.e., from 0 to 1 fold, from 1 to 2 folds, etc. The striking and novel feature of the results obtained from long *n*-alkanes, reported here for growth from solution, and elsewhere for melt growth,[9] is that in this case the crystallization rate gradient becomes negative before stepping up with increasing supercooling. To our knowledge, the existence of such negative gradients and associated rate minima has not been reported previously for any crystallizable system. Normally, for any crystallization, the rate should always increase with supercooling as the crystallization free enthalpy becomes more negative, i.e., as the driving force increases. Only on approaching the glass transition does melt crystallization start slowing down due to increased melt viscosity, but this is of no relevance to the present observations.

A possible interpretation of the retardation in extended chain crystallization has been suggested in our previous report on the crystallization rate minimum from the melt.[9] There it was assumed that the retardation is the result of two competing processes, one with a high free-energy barrier, which nevertheless is ultimately productive, and another with a low barrier yet not leading to a stable product. Such a situation can, in principle, lead to the productive process being inhibited by the other. The two processes would in this case be extended and folded chain crystallizations, respectively. According to this model, folded chain depositions are expected to occur more frequently than extended chain ones, while their residence times would increase as the melting or dissolution temperature of chain-folded crystals is reached from above. The transition point marks the temperature below which folded chains crystallize productively, as evidenced by time-resolved X-ray scattering in the case of crystallization from the melt.[9]

Incidentally,[9] the transition temperature between extended and folded chain nucleation differs from that for crystal growth. As in melt crystallization, the nucleation transition occurs at a somewhat higher temperature than the growth transition[9] (see also below). The nucleation transition occurs here at 77 °C.

The surface obstruction model proposed above is somewhat reminiscent of the poisoning of catalysts by impurities, except that in this case the "impurities" would be the paraffin molecules themselves but in a "wrong" conformation. Thus, we suggest the term "self-poisoning" to describe the effect.

We believe that an essential prerequisite for the appearance of the rate minimum is a large difference in the activation barrier between two competing processes. As the barrier for chain deposition is closely related to crystal thickness, $l$, the above requirement implies that $l$ versus $\Delta T$ is not a continuously decreasing function, as is the case for conventional polydisperse polymers, but rather a step function. This is indeed the case for melt-grown $C_{198}H_{398}$ and $C_{246}H_{494}$,[7,9,14] where observation of primary crystallization by time-resolved X-ray scattering at different temperatures revealed a large gap in the observed primary $l$ values. Thus, in the comparatively wide temperature range between the extended chain melting point ($T_{mE}$) and the temperature of the crystallization rate minimum ($T^*$), only extended chain crystals are observed.[9] At $T_c = T^*$ the NIF crystals, which appear first, have $l$ values at least 100 Å lower than $L$ (note that the $l$ values were corrected for chain tilt). This gap in $l$ values is likely to arise from the particularly low stability of lamellae with thicknesses somewhat less than $L$, caused by the difficulties of chain packing within such crystals while preserving high crystallinity.[14] As a consequence, it seems that in the temperature interval $T^* < T_c < T_{mE}$ there are indeed only two potentially viable options for lamellar thickness: either the chains are extended or they are folded with a substantially reduced $l$. These two options would have widely different activation barriers and thus fulfill the necessary condition for the minimum in growth rate.

In the first report on the rate minimum for melt crystallization,[9] it was concluded that the minimum is more pronounced for primary nucleation than for further crystal growth. This is also suggested by the present experiments. Although the two quantities have not been measured separately in either work, the above conclusion is reached indirectly: in ref 9 from the shapes of crystallization exotherms at different temperatures and in the present work from the temperature dependence of the two rate parameters $R$ and $1/t$ (cf. Figures 5 and 6). While $1/t_{10}$, the inverse time needed to reach 10% crystallization, should be largely determined by the primary nucleation rate, the second parameter, $R$, i.e., the maximum bulk heat evolution rate, is determined by both nucleation and growth rates. The minimum in $1/t_{10}$ at 77 °C is very deep indeed: its value at 78 °C, the closest measured to the minimum, is only 1/24 that of its maximum value for extended chain crystallization at 81 °C. The corresponding ratio of $R$'s is only 1/10.

The minimum in primary nucleation rate is much more pronounced in the present experimental system than in the previous case of melt crystallization of $C_{246}H_{492}$.[9] There the ratio of the $1/t_{10}$ values at the minimum to that at the maximum within the extended chain range was 1/3, as compared to the present ratio of 1/24.

The present experiment only gives a conservative indication of the maximum extent to which extended chain nucleation can be suppressed. In fact, the onset of extended chain crystallization, such as occurs at 210 min at 78 °C (Figure 7), may not be due to genuine extended chain nuclei formation directly from the solution. Since a small percentage of the material is already crystallized at that time in the folded form, the extended chain nuclei could have formed by isothermal thickening of those crystals. Thus, the rate of direct extended chain nucleation may actually be even more depressed than would appear from Figure 6.

One way of rationalizing the fact that the minimum in primary nucleation rate is deeper than that in the growth rate is by recognizing the low probability of long chains extending to form a subcritical nucleus. It is envisaged that, in the temperature region of the minimum, the nucleus will more often sidetrack into unproductive lateral growth instead of extending longitudinally as discussed in ref 4. However, if the nucleus has not yet reached the critical size, even its chain-extended part will most likely disappear with the retreat of the unproductive lateral chain-folded fluctuation. In comparison, an analogous unproductive fluctuation in the case of growth of an already stable crystal would leave the extended-chain portion of the crystal intact.

**Isothermal Crystal Thickening.** Between 71 and 77 °C, crystals grow initially with the chains folded once. However, they will subsequently transform isothermally into the more energetically favorable extended chain form. Such isothermal thickening at the crystallization temperature is well-known for polyethylene crystallized from the melt[16] but is not observed for solution crystallization, even at elevated temperatures.[17] In the case of $C_{198}H_{398}$, isothermal thickening can occur quite readily in this temperature range while the crystals are still in the solvent. From the DSC traces shown in Figure 1, the thickening appears to take place in a stepwise manner, with no visible intermediate form between the once-folded and extended chain crystals. That this is indeed the case has been confirmed by a morphological study of the thickening process, to be reported elsewhere.[15] It can be seen from Figure 2 that the dissolution temperatures of the isothermally thickened crystals are always slightly lower than those of the crystals which have grown with their chains extended. This probably reflects a lower degree of perfection in the thickened samples, and surface decoration techniques used on similar preparations indicate a more disordered surface on such crystals.[6] Other variations in dissolution temperature within a given type of crystal, apparent from Figure 1, can be directly correlated with variations in the growth rate. Lower growth rates produce crystals with higher dissolution temperatures, presumably indicative of a more perfect structure, and vice versa. This is particularly apparent for the extended chain crystals, where the maximum value of $R_2$ at 81 °C corresponds to a local minimum in $T_d$.

**Dissolution Temperatures.** The observation that $T_d$ for a particular crystal form can depend both on the crystallization time and temperature introduces some uncertainty into estimates of the true dissolution temperature of perfect folded and extended chain crystals. As compared to melting points, dissolution temperatures are more sensitive to crystal imperfections: the temperatures involved are lower and the correspondingly lower molecular mobilities do not allow as rapid healing of imperfection as occurs during a DSC melting scan. In order to extrapolate the measured $T_d$ values to infinite crystallization/annealing time, they were fitted to a function of the form $T_d(t) = (T_\infty - T_0)[1 - \exp(-t/\tau)]$. Here $T_\infty$ and $T_0$ denote the dissolution temperatures extrapolated to infinite and zero time, respectively, and $\tau$ is the time constant. $T_\infty$ values obtained at different temperatures are mutually in fairly good agreement, their averages being 80.2 ± 0.2 °C for chain-folded and 93.7 ± 0.2 °C for chain-extended crystals.

The one $T_d$ value that is not easily accounted for in this way, however, is the exceptionally high temperature (84 °C) of the small endotherm obtained for $T_c$ = 78 °C (inset, Figure 7; a similar $T_d$ was obtained for $T_c$ = 77 °C but the endotherm was too small for a reliable measurement of its position). There appears to be a definitive discontinuity between the $T_d$ for chain-folded crystals grown at and below 76.5 °C and for those grown at 77–78 °C.

At present we can only speculate about the origin of the 84 °C peak. One possibility is that below $T_c$ = 77 °C crystals grow initially with noninteger folding (NIF), while at and above 77 °C the only chain-folded crystals that can form at a finite rate are those with the chains folded exactly in two (F2 form), due to their higher $T_d$. Extended chain crystal formation, in spite of their higher growth rate, is delayed at these temperatures through lack of extended chain nuclei. Supporting this proposition is a recent study of the melting behavior of the same $n$-alkane $C_{198}H_{398}$;[14] this has clearly shown that the NIF form melts 4 °C below the melting point of the F2 form which, in turn, is 8 °C below that of the extended chain form. By analogy, taking 93.7 °C as $T_{dE}$, $T_{dF}$ of 84 °C (10 °C below $T_{dE}$) is more likely to represent the regularly folded F2 form than the lower value of $T_d$ = 80.2 °C (13.5 °C below $T_{dE}$) obtained for $T_c$ < 77 °C.

The main argument against such assignment of $T_d$ values to NIF and F2 forms, respectively, is the fact that, after filtering and drying, the mats crystallized below 77 °C give an X-ray long period $l$ = 12.5 nm,[5] which is almost exactly half the extended chain length of 25.4 nm, and thus there is no indication of the NIF form. The problem is difficult to resolve, as $l$ cannot be measured in situ with crystals in suspension. However, it may also be of relevance here to recall a previous observation on surface decoration,[6] where preferential {110} chain folding was evident only on crystals slowly grown from dilute solutions, while faster growth resulted in fairly random orientation of decorating particles. By that experience, chain-folded crystals grown from solutions as concentrated as those used here would not normally exhibit the fold regularity that would be detectable by surface decoration. On the other hand, slow crystallization as takes place at 77–78 °C might produce the highly regular folding, which is the possible cause for the high dissolution temperature of crystals grown in this temperature range. This issue is currently receiving further attention.

At this point an important general issue arises about crystal dissolution temperatures: namely, its concentration dependence. It has become customary to quote a single $T_d$ value when referring to dilute polymer solutions (<1%). The approximation of a constant $T_d$ is justified in the latter case due to the fact that the local concentration within the polymer coil becomes independent of the bulk concentration at sufficient dilution.[18] However, in the present case, neither is the molecular weight high enough nor is the concentration low enough to warrant a concentration independent $T_d$. The crystallization at 78 °C illustrates this point clearly (see Figure 7): while folded chain crystals start appearing relatively early, they do not surpass ca. 10% crystallization even after $t_c \simeq 3$ h. Only after the appearance of extended chain nuclei does crystallization take off toward completion. This indicates that for the initial concentration used (3.85%) $T_d$ of the folded form was initially sufficiently above 78 °C for nucleation and crystal growth to occur, while after only 10% of the alkane had crystallized, i.e., after the concentration decreased to ca. 3.5%, $T_d$ was reduced sufficiently to cause virtual cessation of further chain-folded crystal growth. Thus, it should be noted that all dissolution temperatures quoted in the present work refer only to the 3.85% concentration used and cannot be taken as concentration independent. We plan to expand on this issue in a subsequent publication; the present note is intended merely to indicate the problem and qualify our definition of $T_d$.

## Conclusion

The present work reaffirms the principal results on melt crystallization in the case of crystallization from solution, with several additions. Thus, the quantized variation of the dissolution temperature as a function of crystallization temperature corroborates the previously established quantized variation in fold length. Furthermore, crystal thickening (chain-folded to chain-extended transformations) is observed in solution, in contrast to the behavior of polyethylene where isothermal crystal thickening in solution never occurs. Most significantly, however, the minimum in crystallization rate with increasing supercooling was reaffirmed, in an even more conspicuous form than previously observed in melt crystallization. Thus, strong additional support is lent to the concept of surface "self-poisoning" apparently unique to chain-folded crystallization. The latter effect pertains both to primary nucleation and crystal growth but, as shown in the present study, to a greater extended to the former. This effect thus provides a unique insight into the crucial processes at the growing edge of a polymer crystal or nucleus with corresponding implications for theories of crystallization of long-chain molecules.

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**Registry No.** $C_{198}H_{398}$, 98812-29-4.

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# Deconvolution of the Excess Heat Capacity of the Brill Transition in Nylon 66

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ABSTRACT: The Brill transition in nylon 66, crystallized from solution, is a small, diffuse endotherm extending between roughly 130 and 230 °C. We have been able to deconvolute the excess heat capacity in this region using established methods of statistical mechanics. As have been found for the unfolding transitions in several globular proteins, the data can be characterized by a model having two energy states within 5% of their fractions. The transition appears to involve a mass corresponding to about 25 chemical repeat units or about five stems in a folded-chain crystal. This is much smaller than the size of the crystals calculated from small- and wide-angle X-ray data.

## Background of the Brill Transition

In 1942, Brill[1] reported that the two strongest peaks in an X-ray diffraction pattern from nylon 66, the (100) reflection and the (010,110) doublet, merge into a single peak at 160 °C. At this transition, the triclinic unit cell changes to a pseudohexagonal form. The latter is actually still

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