

On regimes I and II during polymer crystallization

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Summary

The temperature of the transition from Regimes I and II has been analyzed for several systems for which data is available for both overall crystallization rates and the direct growth rate of supermolecular structures. The same transition temperature is observed irrespective of the experimental method. In addition it is found that the Regimes do not serve as boundaries between distinct morphological forms.

Introduction

Polymer crystallization has been established to be a nucleation controlled process. This conclusion is reached on very general grounds by the analysis of the crystallization rate in the vicinity of the melting temperature. It has, however, been pointed out and strongly emphasized that because of the general nature of this conclusion it is not possible to deduce specific information about the nature and molecular structure of the nucleus. (1) Despite this shortcoming there are some important ramifications to the fact that polymer crystallization is nucleation controlled. One of these factors involves the structure, morphology and properties of the crystalline state as they relate to crystallization mechanisms. Another resides in the intrinsic interest in the analysis and interpretation of the nucleation rate itself. We address ourselves to this latter point in the present paper.

The problem that we shall consider was first analyzed by Hillig for the nucleation and subsequent growth of small molecules on an already formed substrate. (2) The conclusions that were reached could then be adapted in a straightforward manner to the crystallization of long chain molecules. (3)-(7) In this problem two extreme situations were considered. In what has been termed Regime I, the growing nucleus sweeps completely across the crystallite face before the next layer is nucleated; i.e. the rate of lateral growth of a nucleus is very much faster than the nucleation rate. In Regime II additional growth steps are allowed to nucleate before the previous layer has completely filled the substrate. The analysis of the coherent surface nucleation of long-chain molecules has shown that the temperature coefficients of the lamellar growth rates differ by a factor of two between these two extremes.

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We are interested in analyzing the factors that determine the temperature of the transition between Regimes I and II as well as any consequences of this transition on macroscopic structure and properties. We shall define this transition temperature as T_{I-II} . There are two main methods for studying crystallization kinetics in bulk systems. One of these is the study of the overall rate of crystallization; the other the growth rate of spherulites or other well-defined supermolecular structures. Since the lamellar growth rate is the fundamental quantity of interest, it has been tacitly assumed that an analysis of the overall crystallization rate is not suitable for the study of Regimes. Analysis of the growth rates of supermolecular structures has demonstrated the transition from Regime I to II in linear polyethylene (8), poly(1-3 dioxalane) (9), poly(propylene) (10), and, as discussed in the present work, poly(ethylene oxide). Presumably detailed studies of other crystalline polymers will also yield this transition between Regimes.

Since supermolecular structures are not formed over the complete molecular weight range (7)(11)(12) studies of the direct growth rate are limited in scope. The question then arises whether studies of the overall crystallization rate would not yield comparable information. In this case there are no restrictions on the molecular weights that can be investigated. Studies of the overall crystallization of linear polyethylene, over an extended molecular weight range, have shown that a change of approximately a factor of two is found in the temperature coefficient of the rate. (13) The significance of these results, in terms of Hillig's analysis, was not recognized at that time. More recently the observed change in the temperature coefficient of the overall crystallization rate in poly(1-3 dioxalane) has been recognized as corresponding to a change in Regimes. (14)

There are two primary objectives for the present paper. Sufficient data is now available to allow for a comparison of the transition temperature, T_{I-II} , between the two main methods of studying crystallization rates. There is also the interesting question as to what changes occur on the molecular and supermolecular level with the change in Regimes. Early studies suggested a causal relationship between T_{I-II} and major morphological changes on the supermolecular level. (7) (8) More extensive data is now available to examine this question in more detail. We limit ourselves to crystallization from the pure melt and analyze in detail the available data for linear polyethylene and poly(ethylene oxide) as well as those for poly(1-3 dioxalane) and poly(propylene).

Results and Discussion

The overall crystallization kinetic data of the polyethylene fractions comes primarily from an earlier report. (13) Some additional results were obtained in the present work. A molecular weight range, 4.7×10^4 to 8×10^6 , is available for analysis. Molecular weights equal to or greater than 1.2×10^6 do not show any break in the temperature coefficient over the crystallization temperature range accessible to study. However, a clearly defined transition, T_{I-II} , was

observed for all lower molecular weight fractions. Spherulite growth rates showed no transition for molecular weights greater than 1.2×10^5 over the restricted molecular weight range that could be studied. (8)

The crystallization kinetic data for poly(ethylene oxide) was taken from the literature (15)(16)(17)(18) and analyzed according to conventional nucleation theory. For this analysis the equilibrium melting temperature was taken to be 80.5°C . (12)(19) The spherulite growth rate data that are available include molecular weight fractions up to 9.5×10^5 . These data could be represented by two intersecting straight lines whose slopes are in the ratio of approximately two. Dilatometric studies of the overall crystallization kinetics included molecular weight fractions up to 6.3×10^6 . No change is found in the temperature coefficient plots for molecular weights equal to or greater than 3.8×10^6 . However, the data for lower molecular weights show a change from Regime I to II with a change in slope of about two in the temperature coefficient.

Spherulite growth and overall crystallization kinetic data are also available for poly(1,3-dioxolane) over the molecular weight range 8.8×10^3 to 1.2×10^5 . (9)(14) Both these methods show a change from Regime I to Regime II over this limited molecular weight range.

The supermolecular structures for these polymers, and for isotactic poly(propylene), have also been studied as a function of molecular weight and crystallization temperature. (7)(10)(11)(12)(14) The morphological forms have been classified by small-angle light scattering (SALS). For polyethylene and isotactic poly(propylene) the notation "a", "b" and "c" represents spherulites with decreasing order of organization; "d" and "g" represent respectively thin rods and rods whose length is comparable to its width; "h" represents randomly arranged lamellae, i.e. a disorganized superstructure. The morphological forms of polyethylene, as determined by SALS, have been confirmed by thin section electron microscopy. (20) Four different superstructures are found in poly(ethylene oxide). These have been termed hedrites, spherulites, an intermediate state and randomly arranged lamellae. (12)

In Fig. 1 we compare the results obtained for T_{I-II} by the two principal methods used in studying crystallization kinetics. In this figure T_{I-II} is plotted against molecular weight for the polyethylene and poly(ethylene oxide) fractions. The curves obtained for each of the polymers are very similar. The most important result in this figure is the fact that the spherulite growth rate and the overall crystallization rate give identical values for T_{I-II} over the molecular weight range that they coincide. Comparable kinetic studies with poly(1-3 dioxolane) give the same conclusion. (9)(14) Thus, the changes in the fundamental theoretical quantity that is involved, the temperature coefficient of the lamellar growth rate, manifests itself in exactly the same way in both spherulite growth and overall crystallization rates. Thus, there is no basic reason to restrict attention solely to the spherulite growth rate. This procedure is in fact a very restrictive one. Spherulite formation is limited with respect to molec-

ular weight for fractions of all polymers that have been studied in detail. On the other hand, overall crystallization kinetics has no such restraints and can be studied over as wide a molecular weight range as desired. This technique is particularly helpful in the study of high molecular weight fractions. The ability to carry out such studies broaden one's vistas in comprehending crystallization kinetics and mechanisms.

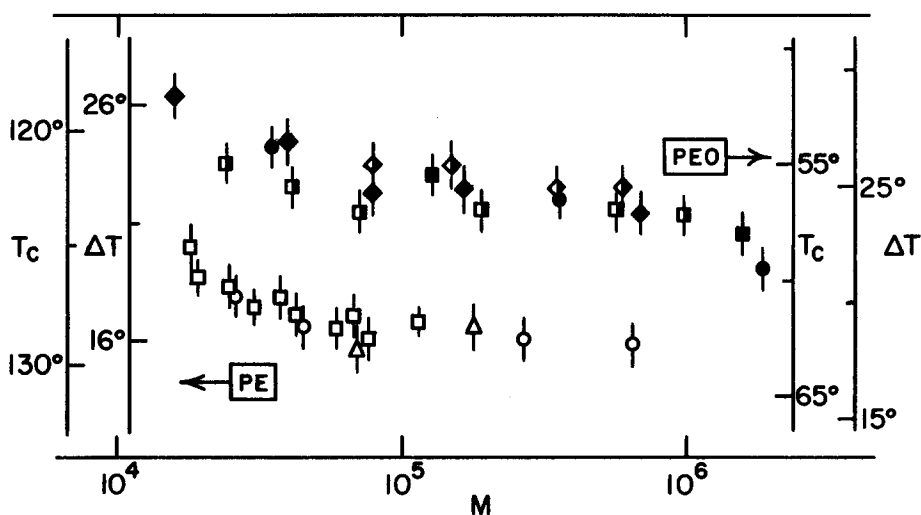


Figure 1 Plot of T_{I-II} , in terms of crystallization temperature T_c or undercooling ΔT , as a function of molecular weight of polyethylene (PE) or poly(ethylene oxide) (PEO) fractions. Polyethylene: overall rates \circ ref. (13); \triangle this work; growth rates \square ref (8). Poly(ethylene oxide): overall rates \bullet ref (15), \blacksquare ref (16) and \blacklozenge ref (18); growth rates \blacksquare ref (17), \blacklozenge ref (18).

The data given in Fig. 1 show a small increase in T_{I-II} with increasing molecular weight for both polymers. The generality of this result awaits further study on fractions of other systems. The undercooling at which the demarcation in Regimes takes place depends on the polymer type. For example, for polyethylene T_{I-II} is 17.5°C; for poly(ethylene oxide) 24°C; for poly(1,3 dioxalane) 63°C; for isotactic poly(propylene) about 56°C. (10) The result of major importance is the fact that the same values for T_{I-II} are obtained irrespective of the experimental technique.

We also examine the question if any macroscopic structural changes accompany the change from Regimes I to II. Changes in the supermolecular structure can be analyzed by studying the appropriate morphological map. Here the structures are presented as a function of molecular weight and crystallization conditions. A morphological map for isothermally crystallized linear polyethylene is given in Fig. 2. (7)(11) The locus of data points representing T_{I-II} is also plotted in

this figure. This representation makes clear that T_{I-II} does not correspond to a demarcation in any change of morphological form. Although a morphological boundary is crossed, in this case "d" to "g", for most molecular weight fractions the change from one Regime to another occurs within a particular supermolecular structure. Similar results have been observed for poly(ethylene oxide) and isotactic poly(propylene) (10) as is illustrated in Figs. 3 and 4 respectively. For poly(propylene), for example, for molecular weights equal to or less than about 10^5 , T_{I-II} occurs in a non-spherulitic region. For poly(ethylene oxide) the demarcation boundary between the Regimes traverses several morphological regions. The studies of poly(1,3-dioxalane) were limited to a relatively small molecular weight range. However, the results for this polymer still make clear that the demarcation does not correlate with any change in morphological features. The more extensive results that have been presented here do not support the earlier conclusion that the demarcation boundary coincides with a change from spherulite to non-spherulite morphology. (7)(8) Spherulite formation is almost always observed at low temperatures, i.e. below the demarcation temperature, but is not responsible for, nor is it a consequence of the change from one Regime to the other.

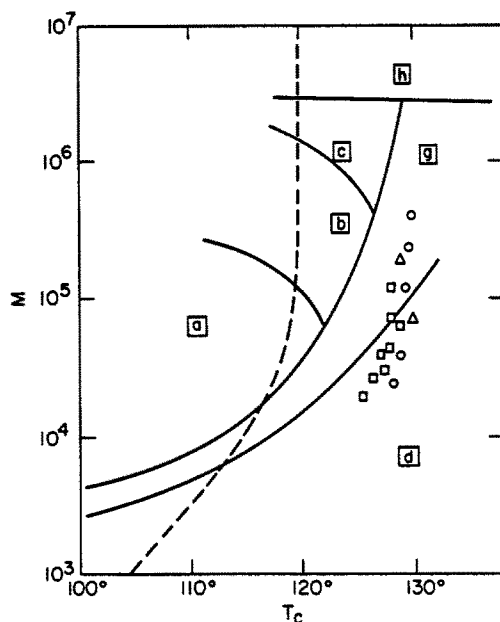


Figure 2 Isothermal morphological map of linear polyethylene from (7)(11). Supermolecular structures are indicated by notation discussed in text. Dashed curve demarcates the boundary for isothermal crystallization. The values for T_{I-II} for each molecular weight are plotted using the same symbols as in Figure 1.

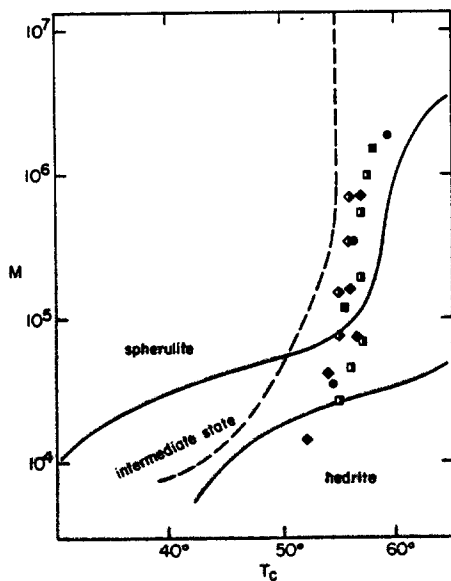


Figure 3 Isothermal morphological map of poly(ethylene oxide) from (12). Supermolecular structures are indicated. Dashed curve demarcates the boundary for isothermal crystallization. The values for T_{I-II} for each molecular weight are plotted using the same symbols as in Figure 1.

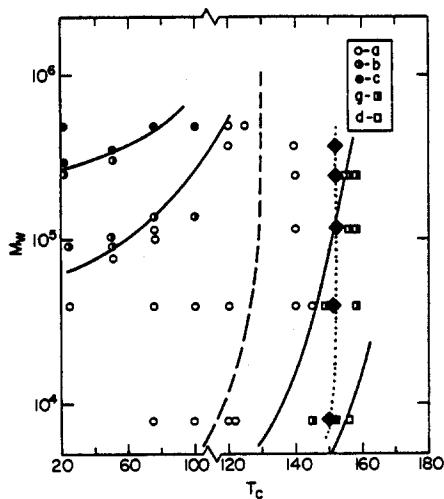


Figure 4 Isothermal morphological map of isotactic poly(propylene) from (10). Supermolecular structures are indicated by notation discussed in text. Dashed curve demarcates the boundary for isothermal crystallization. The values for T_{I-II} are indicated by \blacklozenge and the locus of points is given by dotted lines.

Analysis of electron micrographs of linear polyethylene fractions has shown that the predominant tilt angles, i.e. the angle between the chain axis and the lamellar basal plane, depends on the crystallization temperature. (21)(22) The high tilt angles appear less frequently at the higher crystallization temperatures; they predominate after crystallization at lower temperatures. The smaller tilt angles are only observed after high temperature crystallization. These data strongly suggest that the larger tilt angles disappear at crystallization temperatures at about 127°C. (21)(22) This temperature corresponds to the change from Regime I to Regime II in linear polyethylene. This change in tilt angle manifests itself in differences in the character of the lamellar structure above and below this temperature. The generality of these results and their consequences to other structures and properties remains to be elucidated.

In summary, we have found that the temperature at which the change from Regime I to Regime II is well defined. The same results are obtained irrespective of whether growth rates of spherulites or overall crystallization rates are studied. The consequences of any macroscopic structure and property changes from one Regime to the other still remain to be clarified.

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