Experimental Study of the Mechanism of Crystallization of Poly(ethylene oxide) and an Alternative to the Standard Kinetic Theory of Crystallization of Long-Chain Compounds

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ABSTRACT: At a definite temperature of crystallization, the structure of melt-grown lamellae of poly(ethylene oxide) (PEO) depends on the thickness of the seeds. Lamellae which are far from equilibrium with the melt grow irreversibly at constant thickness. They select in a polydisperse PEO fraction the molecules which have the adequate length. These facts are in contradiction with the predictions of the standard theory of polymer crystallization. They add conclusive experimental support to the author's recently proposed alternative approach to the mechanism of crystallization of long-chain compounds. The discussion includes the interpretation of the breaks observed in curves which give the thermal dependence of the crystal growth rate of many linear polymers.

A. Introduction

1. Scope. The experimental part of this paper is a study of the effects of various modes of seeding on the structure of melt-grown poly(ethylene oxide) (PEO) crystals. The results disagree with the predictions of the standard theory of polymer crystallization (the Hoffman−Lauritzen (HL) theory) and confirm the alternative approach proposed in ref 1. The aim of this paper is to discuss, on the basis of new data, two opposite views on the mechanism of crystallization of long-chain compounds. Indeed, the author has presented alternative views on this problem and succeeded[1] in an unprecedented quantitative prediction of the thermal dependence of the growth rate of PEO crystals isolated in the melt.

The theory presented in ref 1 predicts three behaviors which would be unexpected in the standard theory,[2] and the main goal of the experiments described in this paper is to test them on PEO. (Studies on other polymers are in progress.) These predictions are the following:

(i) At the same supercooling, it would be possible, by suitable seeding procedures, to prepare crystals of very different structures and properties. (If true, this may satisfy the scientific curiosity but also may be significant when applied to polymers of practical use.)

(ii) Segregation of the molecules according to their degree of polymerization would, to an unsuspected extent, occur in crystallization of oligomers. Moreover, in a polydisperse sample, the largest molecules would not necessarily crystallize first (inverse segregation effect). (The segregation process may have practical applications in polymer fractionation.)

(iii) The breaks in the curves giving the thermal dependence of the crystal growth rate of other polymers which were in the past[3] classified as due to regime I−regime II transitions would be explained by the onset of fractionation. (This leads one to question the currently used method of interpretation of the thermal dependence of the crystal growth rate and the estimate of lateral and/or end specific surface free energies.)

The first two conjectures disagree with the standard[2] (HL) theory:

(i) If the growth is controlled by secondary nucleation, the thickness of the lamellae is approximatively equal to the stem length. According to the HL theory, this length depends solely on the temperature of crystallization and so the behavior predicted in (i) above should not occur.

(ii) If the first stage of building up a surface nucleus is the loose attachment of the molecule to a substrate characterized by its width, *severe and in some instances inverse* segregation effects are unexpected.

(iii) Changes of regime were[3] accepted as *the* explanation of the breaks in the growth rate versus T_c curves. These are presented in a recent review[2] of the standard theory as a basic and unifying concept. If the author's views are correct, they must substitute for these considerations.

The discussion may be limited to PEO crystallization but should apply to the interpretation of the breaks observed in the growth rate curve of polyethylene[4] (PE) and *Hevea* rubber[5] (HR).

Table 1

sample	M_n	M_w	$T_m(0,p)$	$T^*(0,p)$	$T^*(1,p)$
PEO1500	1430	1486	47.65		
PEO3000	2938	3088	58.15	51.90	
PEO6000	6341	6605	63.70	60.45	56.60

B. Experimental Section

2. Materials. The studied narrow hydroxy-terminated PEO fractions range between 1500 and 6000 in number-average molecular weight (M_n) and were obtained from Hoechst. Their GPC molecular weight distributions are characterized in Table 1. Table 1 also gives the melting temperatures $T_m(0,p)$ and the growth transition temperatures $T^*(n,p)$ as defined by Kovacs.[6,7] (See Appendix A for the exact definition (with some nuances) of these notations.)

3. Crystallization of PEO from Unseeded Melts. Figure 1 shows the melting traces of the PEO6000 fraction quenched from 65 °C and then isothermally crystallized. At all the crystallization temperatures but the highest, two or three melting peaks are observed. They are denoted by X, Y, and Z (and not by E, F_1, and F_2) because the melting peaks are large and overlap. The fact that there are distinct melting peaks is related to the fact that, according to the discovery of Arlie et al.,[8] the chain ends are preferentially rejected at the surface of the lamellae. In view of the polydispersity of the fraction, these crystallized samples may however (see Table 1

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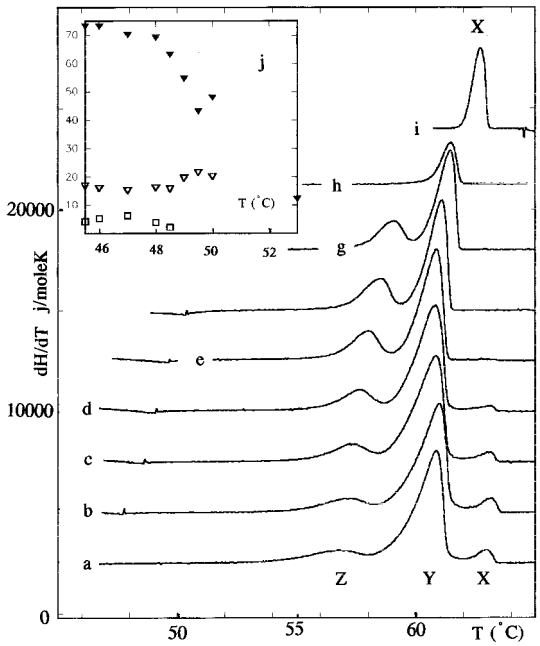

Figure 1. (a−g) DSC melting traces of samples quenched from the unseeded melt at 65.6 °C to 46.1, 47.6, 48.6, 49.1, 49.6, 50.1, and 50.6 °C and then isothermally crystallized for 15 min. In (h) and (i) the T_c are 53.6 and 54.6 °C and the crystallization times are 120 and 240 min. (d) Crystallinities in the Z, Y, and X peaks as a function of T_c (hollow squares, hollow triangles, and filled triangles).

and Figure 9) contain any sort of crystals made of subfractions of the PEO6000 sample either nearly monodisperse or polydisperse and/or made of mixtures of IF and NIF molecules. These reproducible results are only apparently in contradiction with the data of Kovacs,[6] because the results of Kovacs et al. concern crystals grown isolated in the melt from seeds prepared according to a strictly defined procedure while here the seeds are possibly stacks of lamellae.

Figure 1j gives the crystallinities related to the three observed peaks as a function of the crystallization temperature. The hypothetical large differences in the structure and properties, which were expected from the standard theory of crystallization, are at least not clearly evidenced: In three *significantly* large and overlapping ranges of temperatures, respectively E, F_1, and F_2, crystals (or X, Y, and Z) are nucleated and grown. At the same temperature of crystallization, say 50.6 °C, E nuclei and F_1 nuclei grow respectively as E and F_1 crystals. *This is in formal contradiction with the theories of continuous surface nucleation*, which predict that at a definite temperature of crystallization (say 50.6 °C, a temperature which is lower than $T^*(1,p)$), only one repliement index (2 at least at that temperature) occurs.

4. Preparation of Seeded Melts. A sample of the 6000 fraction was successively annealed at different temperatures higher than 60 °C and then fully recrystallized by slow cooling. Its DSC melting trace is given in Figure 2a and shows two major melting peaks Y and E and auxiliary melting "peaks" X′ and X″. The sharp peak E at the highest temperature is clearly the melting peak of extended-chain crystals, and the peak Y very likely corresponds to F_1 crystals. Heating such a sample to 63.4 °C and then cooling to 25 °C gives on partial remelting a seeded melt designated later as S_I seeded melt. Such S_I melts have a low crystallinity (<1% or a few percent) and the just mentioned E peak as the sole melting peak (Figure 2b). If maintained at 62.9 °C for hours, such a seeded melt appears remarkably stable. That is to say that at the precision of the calorimeter, neither the position of its melting peak nor its crystallinity changes. Even the "seeding power" is not modified. Seeded melts of quite similar histories (S_{II} seeded melts) (Figure 2c) display two sharp melting peaks E and E* revealing the presence of two distinct populations of extended-chain crystals which differ by the main molecular weight (see section 12) of the herein reported PEO molecules. Quenching S_I and S_{II} melts to room temperature and then reheating to 62.9 °C do not affect their properties. For practical reasons, they are usually quenched and then stored at room temperature. They are remelted at 63.4 °C (or at slightly lower temperature) just before use.

The half-width of the E melting peaks of the melts S_I and S_{II} being very small, it is assumed that these seeds are crystals in which the polydispersity of the PEO is nearly equal to 1. This implies some fractionation involving diffusion of the various molecular species. These phenomena depend on the full thermal history of the sample. This is why specimens differ slightly from one another. Large specimens were found to be nonhomogeneous. The experiments reported in the next sections were performed from two mother specimens of relatively small size (more or less 0.1 g) stored at room temperature (see Figure 2b,c). They are denoted in this section and later as S_I and S_{II}. Note that Kovacs and Buckley[9] have previously observed double E peaks in PEO6000 fraction, without taking advantage of this peculiarity.

5. Isothermal Crystallization of S_I and S_{II} Melts (Seeding at 63.4 °C). Figure 3 gives the DSC melting traces of samples quenched from 63.4 °C to various temperatures T_c and then isothermally crystallized at these T_c.

The thermogram (not reproduced) of an S_I melt crystallized at 45 °C (a temperature lower than $T^*(1,p)$) shows that the E seeds remain intact but allow the nucleation and growth of (very likely) F_1 and F_2 crystals. Figure 3a is from an S_{II} melt crystallized under quite similar conditions (at 45 °C) and displays the same phenomena. *At these low T_c the E seeds do not grow as E crystals On their facets, F crystals are nucleated (by a surface or by a tridimensional process) and grow. The actual formation, at the same temperature, of two types of F (F_1 and F_2) crystal would be, according to the HL theory, forbidden.*

In the thermogram (Figure 3b) of an S_{II} melt crystallized at 57.6 °C, a temperature between $T^*(0,p)$ and $T^*(1,p)$, the area of peak E* is larger than in the seeded melt, that is to say the E* seeds have grown as E* crystals. This is not the case for the E seeds. In addition, a Y peak shows the concurrent nucleation and growth of a once-folded crystal. Different attempts (at other temperatures and durations of crystallization) lead to similar results: the DSC trace shows a sharp E* peak and a large F peak.

At the highest T_c, the crystallinity as E lamellae of S_I and S_{II} samples increases with the crystallization time without significant widening of the melting peak. Figure 3c shows that at 60.6 °C the two different E* and E seeds give respectively E* and, much less efficiently, E crystals. At such high crystallization temperature, the growth rate is small and very long periods are needed to obtain a large crystallinity. In the samples which have the highest crystallinity, one wider peak replaces the two E peaks. The shape of this peak clearly shows however that crystals originate in different seeds.

6. Crystallization from Seeded Melts at Lower Temperatures. As already mentioned, the mother samples used to prepare the seeded melts may contain in addition to the well-characterized E nuclei other crystalline entities which melt at temperatures higher than $T_m(1,p)$ (Figure 2a). This suggests seeding at a lower temperature. Seeded melts are thus prepared by heating the mother samples to 62.9 or 61.9 °C (instead of 63.4 °C). Thermograms a−e of Figure 4 are related to samples crystallized by quenching the melt from 62.9 °C. They are other illustrations of the already described phenomena. However, the largest crystallinities are obtained in relatively shorter durations. Note that the crystals of low melting point ($<T_m(1,p)$) of Figure 4d are either F_1 crystals or Y crystals with only one fold per molecule which contain material of low molecular weight.

Thermograms a−g of Figure 5 concern samples crystallized by quenching melts obtained by partial melting (at 61.9 °C) of the mother sample. The new observed facts are the growth of various X crystals. These crystals are nucleated from subsidiary seeds which in the preceding experiments were irreversibly melted by heating to 62.9 or 63.4 °C. They are NIF crystals, or E crystals of relatively low molecular weight,

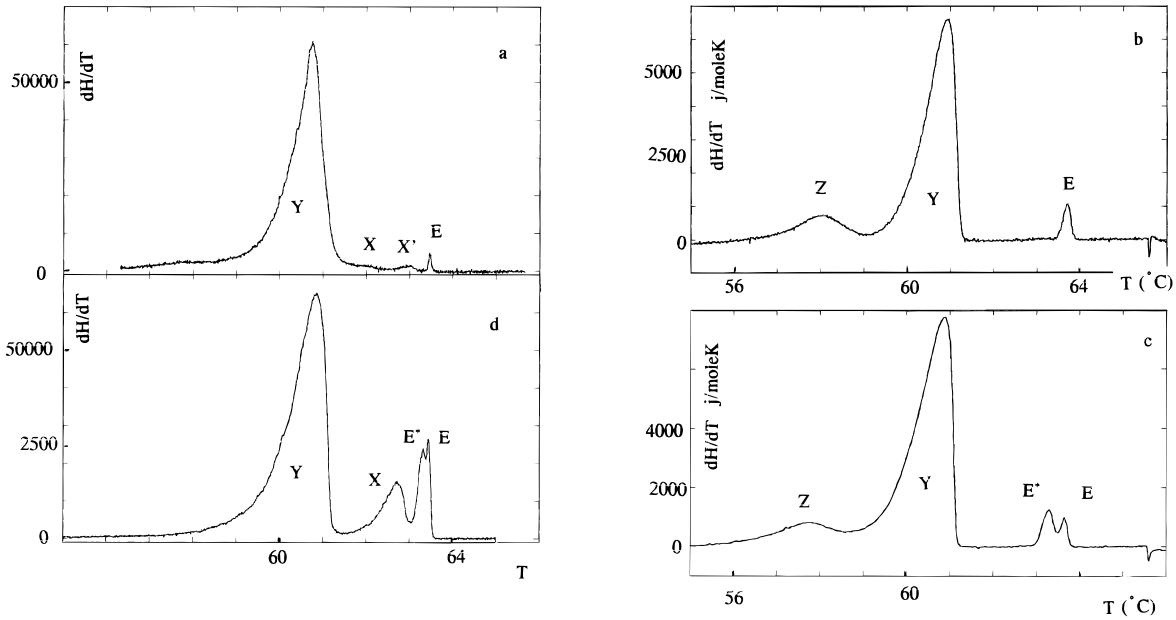

Figure 2. (a−c) DSC melting traces of a mother sample of S_I and S_{II} seeded melts after cooling to ambient temperature. (d) Thermogram of another sample showing two E peaks and an X peak; all these peaks very likely to correspond "extended-chain crystals".

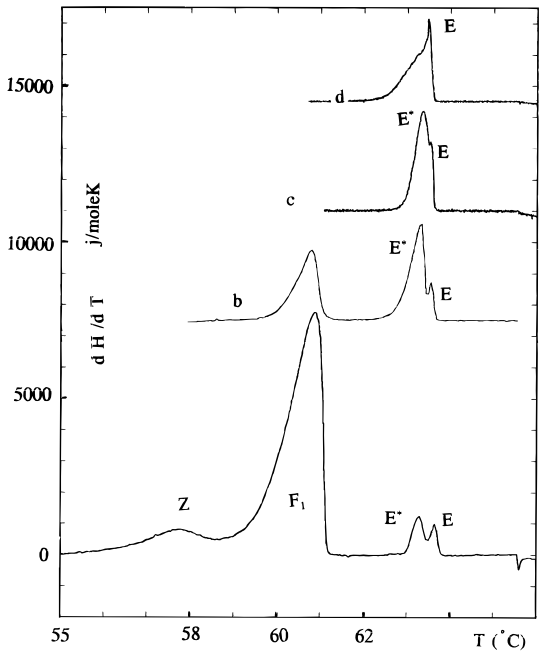

Figure 3. Thermogram of an S_{II} seeded melt after quenching to 25 °C; (b−d) after seeding at 63.4 °C and crystallization (b) at 57.6 °C for 15 min, (c) at 60.6 °C for 999 min, and (d) at 61.6 °C for 999 min.

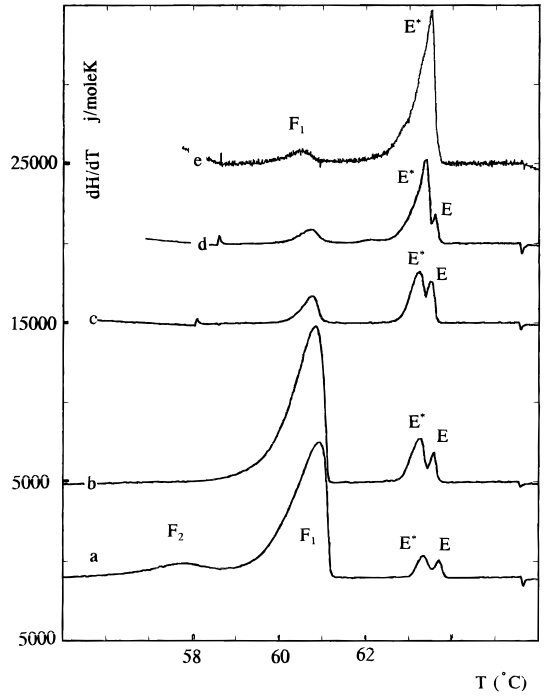

Figure 4. (a) Thermogram of an S_{II} seeded melt after quenching to 25 °C. (b−d) The sample was first melted until 62.9 °C and then quenched to T_c. The crystallization temperatures and times were (47.6 °C, 15 min), (58.1 °C, 15 min), (58.6 °C, 15 min), and (58.6 °C, 999 min).

or possibly more complicated entities. The area of one of these subsidiary melting peaks at 61.9 °C is even relatively large (Figure 3d,f). This peak may be that of crystals in which two molecules give three stems.

As a preliminary conclusion, it appears that in a very large range of isothermal crystallization, the structure of the crystal is not determined by the temperature of crystallization (a basic, but now disproved, postulate of the theories of continuous surface nucleation). These theories assume a nearly zero entropy growth of 2D crystals (see section 9). On the contrary, as shown here, tridimensional nuclei which are far from equilibrium with the melt grow irreversibly at a constant thickness, even if this thickness is much larger than the lower thermodynamic bound (as computed for 3D crystals). At one definite temperature of crystallization and depending of the mode of seeding, a large variety of crystals of different melting points and very different structures and thermodynamic properties are thus grown from a large variety of seeds.

When the temperature of seeding is decreased, the E melting peaks become wider and in the S_{II} samples the E and E* (and X?) melting peaks overlap. At the highest crystallization temperature (near $T_m(1,p)$, the E melting peaks of S_I and S_{II} give together a very large and roughly triangular trace. Crystallinity as high as 80% was obtained in a reasonably short crystallization time.

7. Crystallization by Slow Cooling a Seeded Melt. In the preceding sections, we have described the mode of preparation of partially crystallized samples containing solely E crystals having a sharp melting peak at elevated temperature.

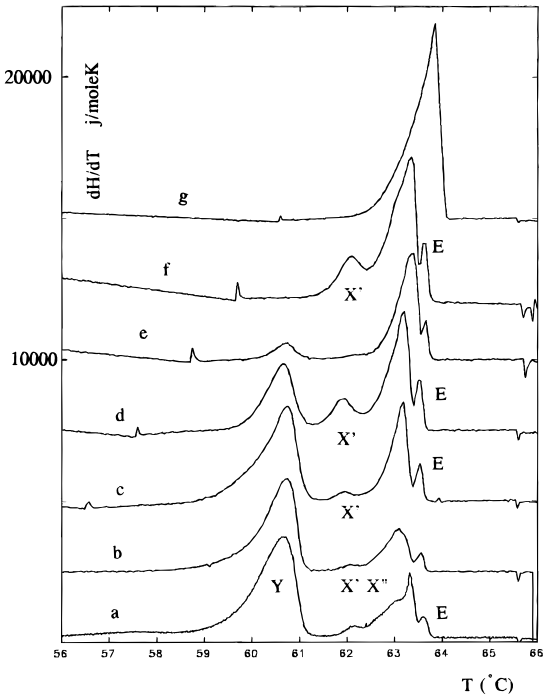

Figure 5. Same mother sample. (a−f) The seeding was at 61.9 °C and the temperatures of crystallization were 52.6, 54.6, 56.6, 57.6, 58.6, and 59.6 °C. The crystallization times were 15 min. For (g): 60.6 °C and 480 min.

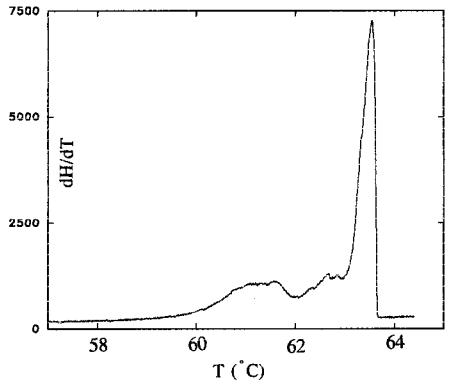

Figure 6. Echoing effect.

Such samples may be fully crystallized by subsequent quick cooling. During this cooling, F crystals are nucleated and grown. The DSC traces of such samples show then E and Y melting peaks. The shape of the Y melting peaks presents in many instances some characteristic details which repeat (or are correlated to) characteristic details of the X (or E) melting peaks. This peculiarity, shown in Figure 6, suggests that the Y crystals were actually nucleated on the facets of E (or X) crystals.

At the highest crystallization temperatures used, the shortest molecules of the fraction seem not able to crystallize onto too thick seeds or crystals. This would be why the crystallinity as E crystals is limited. Starting from a sample containing E crystals at 63 °C and by slow cooling, we have obtained highly crystalline samples with only one wide E melting peak. We assume that such a sample is made of successive peels of PEO of lower and lower molecular weight. A similar onion structure where E* seeds hide E seeds would explain the different "seeding powers" of the E and E* seeds of the S_{II} melts.

8. Sedimentation of Crystals in Partially Crystallized Samples. According to the previous sections, it appears that some of the seeded melts or partially crystallized samples are suspensions of crystals in a melt. In addition, it is very likely that the mean molecular weight and the polydispersity of the PEO in the crystals differ from the mean molecular weight

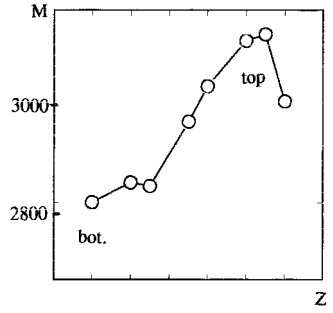

Figure 7. Variation of the number molecular weight from the bottom to the top of the test tube (PEO3000).

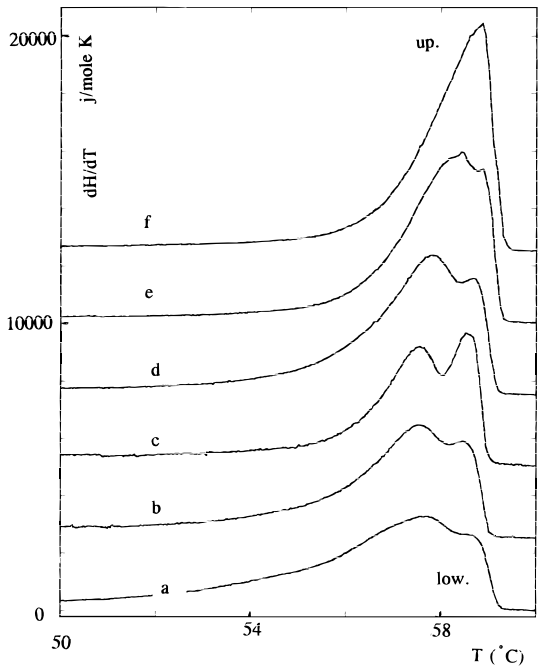

Figure 8. (a−f) Thermograms taken from the bottom to the top of the centrifuged sample (PEO3000).

and polydispersity of the whole sample. Such an observation was previously reported by the author[1] on a PEO3000 sample; the largest molecules were the first to crystallize. Sedimentation of the crystalline phase could be a method of fractionation. Work in this direction with a PEO6000 fraction is in progress but here only results pertaining to less viscous 3000 and 1500 PEO fractions are reported. We have crystallized the PEO3000 fraction in a centrifuge immersed in a thermostated bath. The temperature of the surrounding bath was successively 62 and 61° C; then the bath was slowly cooled to room temperature. A too effective sedimentation may lead to a sample where the solid phase (or a crystalline gel or a paste) separates from a liquid. If in this liquid no seeds are present, further crystallization is not possible. To seed again the liquid phase by Brownian and/or convective motion of the seeds, the rotation of the centrifuge was interrupted from time to time. Rotation of the centrifuge also leads to an unknown increase of the temperature of the rotor. For all these reasons, the sample follows a not exactly known temperature program, which nevertheless includes two isothermal parts at high T_c. At the end of the experiment, the crystallized sample was cut into slices. The mean molecular weight in these slices (Figure 7), some DSC melting traces (Figure 8), and GPC molecular weight distributions (Figure 9) are given. Separation effects were observed. They are totally unexpected and in the oppposite direction of the effects previously obtained in another similar work just recalled.[1] Now the most surprising observation is that both the mean molecular weights and the ultimate melting points of the fractions *increase* from the bottom to the top of the centrifuge tube.

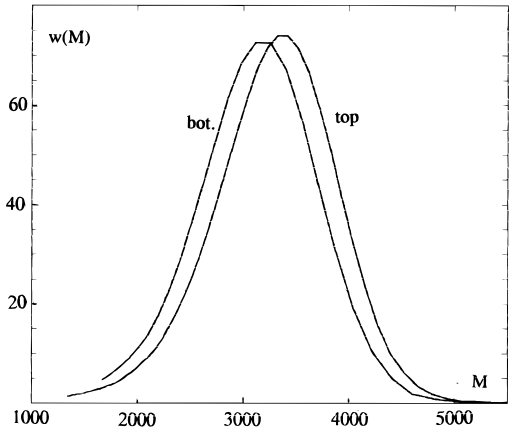

Figure 9. Molecular weight distribution in the upper and lower parts of the centrifugation tube (PEO3000).

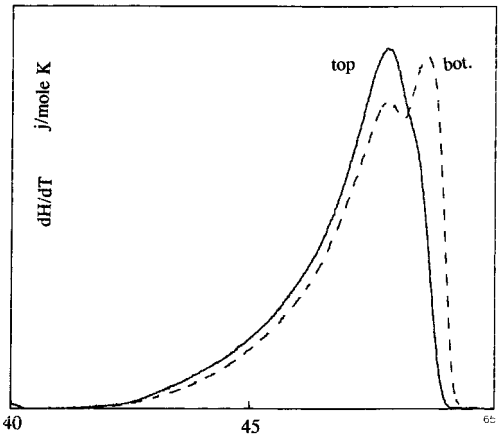

Figure 10. PEO1500 DSC melting traces taken at the bottom and the top of the test tube.

Bimodal DSC traces were obtained from the slices which came from the lower part of the centrifuge tube. The peak which appears at the *lowest* temperature is not observed in the upper slices of the sample. SAXS patterns (to be described in another paper[10]) of the bimodal specimens show two types of lamellar stacks of two different periodicities, 20.3 and 21.5 nm. These thicknesses are exactly known because the SAXS patterns of both stacks each have more than five orders. We have proceeded to a similar experiment with a PEO1500 fraction but by a simple progressive cooling of a seeded melt during its continuous centrifugation. Corresponding DSC melting traces are given in Figure 10. That of the bottom sample is bimodal. The peak at the *highest* temperature is lacking in the other DSC trace. This is now the a priori "normal result". The longer molecules crystallize first. The molecular weight distributions confirm this result (Figure 11). Further confirmation is gained from the SAXS patterns.[11]

C. Discussion

9. Background. (i) Morphological observations by Bassett,[11] Keller, and others (see for instance the results obtained on PE by the isohypse decoration method[12]) show that as currently accepted, the growth of polymer lamellae *may be* (and is apparently[3]) controlled by surface nucleation. Such observations are not conclusive because these investigations by electron microscopy are at a scale much larger than 0.5 nm (the thickness of a monomolecular layer).

(ii) From the beginning, Holland and Lindenmeyer[13] observed that the thermal dependence of the growth rate of a polymer crystal may be accounted for by assuming that the crystal growth is controlled by secondary nucleation. The standard theory[2,14] (Hoffman, Hoffman and Lauritzen (HL), Frank and Tosi, Seto and Mori) assumes that in this secondary nucleation process, the free energy barrier is proportional to the thickness of the lamellae. To the knowledge of the author, this proportionality was never directly verified (by measurement on the *same* sample of both the crystal growth rate G and the thickness of the lamellae (l_c)). A careful analysis of the original papers[4,15] shows that the few attempts to compare these, both virginal experimental data were unsuccessful. These points were reviewed elsewhere.[3,16]

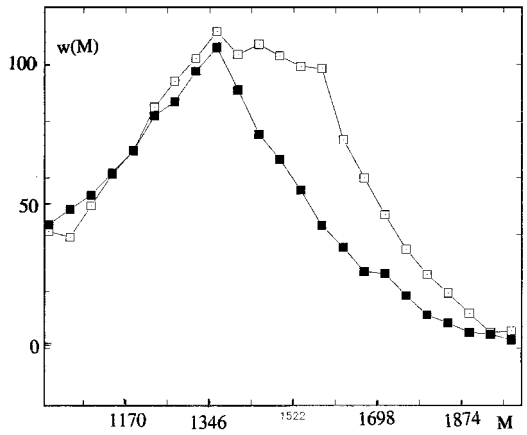

Figure 11. Electrospray mass distribution for the samples of Figure 10.

(iii) Kinetic arguments were used in the pioneering works of Hoffman and others. This is why the HL theory is said to be a "kinetic theory". Nevertheless, its major prediction is that the thickness of the growing lamellae is approximatively *equal* to its thermodynamic lower bound. Therefore the theory concludes to an exchange between two phases of polymer molecules which have in both the liquid and the crystal nearly equal chemical potentials. Therefore the theory may be objectively presented, in a not too provocative way, as *a theory of zero entropy production melting and crystallization of 2D crystals in equilibrium with a melt*. The status of two distinct phases may be refused to (i) a 2D nucleus with cilia and (ii) the melt in which these cilia are immersed. At the high supercoolings involved, crystallization from a highly viscous melt may be, *on the contrary*, pictured as a totally irreversible phenomenon. It would involve the attachment of molecules to *3D crystals*, the thickness of which is significantly larger than the thermodynamic lower bound (*calculated from usual thermodynamics for 3D crystals).* The melting of a crystal is not necessarily the reverse process of the crystallization. It may be that at the melting point the tridimensional crystal bursts and that any substrate for molecule attachment disappears. On these bases, the author has presented a new theoretical approach (scrutinized in the present paper) of the mechanism of growth of oligomer (and, with some modifications, of polymer) crystals.[1]

"The growth rate is assumed to depend on:

(i) the difference ΔT between the melting temperature T_m of a polymer of infinite molecular weight and the temperature of crystallization

(ii) the thickness of the growing crystal. More particularly all the lamellae of *any* thickness l_c larger than a critical thickness

$$l_c > l^* = A/\Delta T \qquad (1)$$

are allowed to grow (but not the thinner, which are unstable).

(iii) The molecules which are larger than l_c

$$l > l_c \tag{2}$$

are the only ones allowed to attach themselves to the growing facet. If the seeds are isolated in the melt, the growth rate of the crystals is assumed to be proportional to the cumulative fraction $C(l_c)$ of such molecules. The logarithm of the mean growth rate is also assumed to depend linearly on the inverse of the mean length of the attached molecules:

$$\log G = \log C(l_c) + B - C/\langle l \rangle \tag{3}$$

(the last term of this expression may be taken as a mean supercooling with respect to T_m. [In an alternative version (Wunderlich[17]), it may be assumed that the crystal selects the molecules which have a length approximatively equal to its thickness].”

In these views, the process of crystallization implies an exact shape and size recognition of the crystallizing molecules and the substrate. This substrate is characterized by its *initial* thickness (a free physical parameter), and not by its width L_p as in the “regime theories”. The lamellae grow at constant thickness. Their thickness may be changed only by a new 3D nucleation. Note also that a PEO fraction with a Poisson distribution of molecular weight is taken as largely polydisperse. Severe segregation according to the molecular weight is computed.

This functional dependence of the growth rate of a lamella of thickness l_c by attachment of molecules of length l

$$G = G(T_c, l_c, l) \tag{4}$$

and formulas 1−3 were used[1] to predict quantitatively, with a surprising success, the molecular weight and temperature dependence of the growth rates of isolated crystals of the PEO sharp fractions studied by Kovacs.[6]

To appreciate the differences between this approach and the standard theory, note that in the Hoffman−Lauritzen[2,14] theory of continuous surface nucleation and in *contradiction* with the new approach, formula 4 is replaced by

$$G = G_X(\Delta T(p)) \tag{5}$$

(i) G depends solely on one variable, the supercooling, which now is the difference between the (“mean?”) melting point of the PEO fraction[7] of degree of polymerization p and the temperature of crystallization. This is because all the molecules are assumed to crystallize together.

(ii) l_c does not appear explicitly (in (5)) as a free variable. This is because the initial thickness of the crystal is modified by a continuous “surface nucleation” (see HL[14] and Sadler[18]).

(iii) The molecular weight distribution does not appear explicitly in (5) because it is only used to determine the mean melting point of the fraction. More exactly in the case of PEO, the proved dependence[19] of the growth rate curve on the polydispersity of the fraction is ignored. (It is however similar to these of the fractions studied in this paper.)

(iv) The subscript X takes the value I, II, or III according to the regime of crystallization, which depends on the Lauritzen persistence length. The analytical expression of G is changed accordingly.

Let us recall that the experimental part of the present paper scrutinizes some immediate and controversial consequences of the new approach. The raised questions are: (i) Is it possible to grow lamellar crystals of different thicknesses and melting behaviors at a definite temperature of crystallization? (ii) Does severe segregation according to the molecular weight occur during the crystallization? (iii) Are the breaks observed in the curves giving the thermal dependence of the crystal growth rate related to this fractionation process?

As detailed below, the answers to the first two questions conform to the prediction of solely my model. The third problem is also discussed below because the present work adds conclusive data to those of ref 1. Moreover, it is an important question because, although the standard theory of regimes and the method of calculation of the so-called $\sigma\sigma_e$ product from data on the crystallization kinetics were previously ruled out,[3] the breaks in the growth rate curve, for instance, of polyethylene and *Hevea* rubber fractions (two paradigms) need an alternative explanation.

10. Crystallization from Unseeded Melts. The results are discussed by comparaison with data obtained by Kovacs and Gonthier[18] and Kovacs and co-workers (and others) on crystallization in a melt seeded by *large E isolated crystals*. In these experiments, the growth rate and the structure of the crystal were actually solely a function of the temperature. In successive temperature intervals $T_m(0,p)$ to $T^*(0,p)$, $T^*(0,p)$ to $T^*(2,p)$, etc., the PEO fractions crystallized as single crystals of respective thicknesses which were in the vicinity of the mean length of the molecule (E crystals), half this length (F_1 crystals), and a third of this length (F_2 crystals). These data are arguments which support qualitatively the HL theory of continuous surface nucleation because at any temperature T_c (nevertheless from *singular and identical* seeds) and in a deterministic fashion a specific type of crystals is produced. In another but similar view, Cheng et al.[20] assumed that in a deterministic way continuous surface nucleation leads to the formation of NIF crystals of exactly defined thickness (which are the precursors of IF crystals).

From a quantitative point of view, the author and Kovacs[7] concluded that the HL theory cannot be used to predict (even roughly) the values of the growth rate. However, *they did not realize at this early stage (and even recently) that the solution was to refuse the basic and nearly universally accepted postulate of surface nucleation.*

To understand the significance of the new data on crystallization of an unseeded melt (section 3), consider what according to the theories of seconday nucleation would happen in an unseeded melt for instance at temperatures slightly lower than $T^*(0,p)$. Both an E nucleus and an F_1 nucleus must be created and are created, but any surface nucleation theory predicts that they grow as F_1 crystals. *This prediction is not verified by our experiments (see Appendix B for a more detailed discussion).* At crystallization temperatures significantly lower than $T^*(0,p)$, a part of our samples crystallize as E crystals. These results on the irreversible growth of stable crystals which are far from equilibrium with the melt will now be confirmed by the analysis of the data on the growth of well-characterized nuclei.

11. Nature of the Seeds in the S_I and S_{II} Seeded Melts. The width of the melting peaks in the DSC

melting traces of the S_I and S_{II} melts is very low. Since our work to determine the relationship between the molecular weight and the melting temperature of monodisperse PEO samples is not yet complete (work still in progress in our laboratory), we use a Tamman correlation between the melting temperature and the mean molecular weight of the polydisperse fractions studied by Kovacs. From the observed melting peaks of S_I and S_{II}, a rough estimation of the molecular weight in the seeds is 6560 +150 and 6110 + 150. The crystals appear to consist of nearly monodisperse PEO. The same conclusion is applicable to the E crystals grown from these seeds. Thus in accordance with a suggestion of Wunderlich,[17] as a variant of the author's assumption, an E nucleus selects molecules which have (in their helical conformation) a length nearly equal to the thickness of the growing lamella.

12. Crystallization in Samples Quenched from 63.4 °C to T_c. The structure of the growing lamellae is in many instances, and independently of the crystallization temperature, the same as that of their tridimensional nuclei. It must be said that this is not in contradiction with the Kovacs discoveries. In the Kovacs experiments the nuclei are isolated crystals made of the largest molecules of the PEO fraction. Micrographs of the Kovacs crystals show such thick seeds. The formation of these seeds results from molecular weight segregation, the same phenomenon as highlighted by the present study. In our case, the nuclei may be stacks of lamellae. Small differences in the periodicity of adjacent stacks could destroy the phase agreement in the alternance of crystalline and amorphous regions.

All the observations reported here show that at sufficiently low temperatures, the E crystals accept only molecules of adequate length. In the PEO6000 fraction the difference of thickness of crystals melting respectively at 63.3 and at 63.4 °C may be estimated to be of the order of magnitude of 1 nm. Such difference in lengths corresponds to a variation of the molecular weight of 150, a difference in degree of polymerization of 3.5, and a difference in the number of helix turns of one. The differences observed between the lamellar thickness of the two populations of lamellae observed in another PEO fraction was also equal to 1 nm. It is strongly appealing to propose that the 7/2 helical conformation of the molecule implies a quantification of the lamellar thickness. If things happen as described above, the whole polydisperse PEO fraction cannot crystallize in a single type of E lamellae. This fits with what is observed: in a sample with only one type of lamellae, the crystallinity is indeed limited.

13. DSC Trace of Samples Crystallized by Slow Cooling and Molecular Weight Distributions. The melting points of the Kovacs PEO fractions may be approximated by a Tamman expression as efficiently as the Flory and Vrij[21] formulation used by Kovacs and Buckley. We use the formula $T_m(0,p) = 68.12 - 29270/M$ for the calculation of the melting points of "extended" and "once-folded" crystals. Starting from the differential molecular weight distribution $w(M)\,dM$, obtained from GPC, we express the differential molecular weight distribution as a function of $1/L$ with $W(1/L) = w(M)M^2(l_u/M_u)$.

$W(1/L)$ is presented in Figure 12 as a function of $1/L$. This graph is very similar to one peak of the DSC trace. The simplest interpretation of this observation is that molecular weight fractionation occurs to a large extent

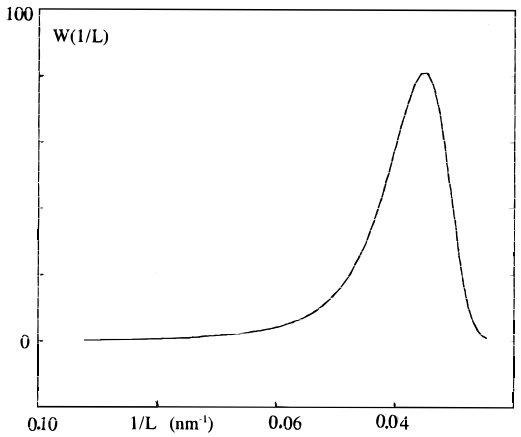

Figure 12. GPC molecular weight distribution for the PEO4000 fraction used by Kovacs[6] in a $W(1/L)$ representation.

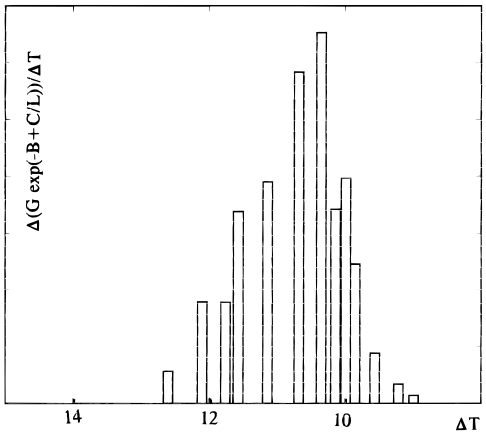

Figure 13. Molecular weight distribution from formula (3) and the crystal growth rate as measured by Kovacs[6] on his PEO4000 fraction.

during crystallization. The DSC melting peak and the GPC curve would both represent, although in a more or less distorted way, the molecular weight distribution. Thus this distribution would be directly accessible by direct experiments because, basically, crystallization and gel permeation chromatography are both fractionation methods. According to these premises, the corresponding dilatometric melting curve giving the volume of such a sample, *obtained by an ad hoc crystallization procedure*, as a function of the temperature is a representation of the integral molecular weight distribution of the sample. It is even possible to compute the molecular weight distribution from the kinetic data and formula 3 (see Figure 13 and ref 1).

14. Fractionation by Sedimentation in Partially Crystallized Samples. The observed segregation effects conform to the prediction of the author's model.[1] The segregation of the molecules of the highest molecular weight in the crystallization of the PEO1500 fraction is illustrated by the thermograms (Figure 10). We have measured by electospray the distribution in the various molecular species from two samples taken respectively from the top and bottom of the tube of the centrifuge (Figure 11). Despite the fact that the efficiency of the ionization depends certainly on the size of the molecules, these data give a definitive proof of the, a priori "normal", molecular weight segregation. Note also that apparently the shorter molecules do not crystallize at all. The right part of the mass spectra of the two samples is identical.

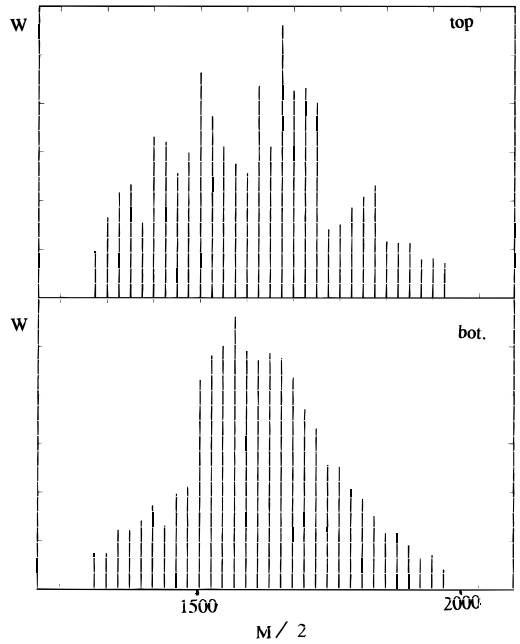

Figure 14. ESR molecular weight distribution from samples taken from the bottom and the top of the centrifuged PEO3000 sample.

It remains to explain why, in this work, an inverse effect was observed in the centrifugation of the PEO3000 sample. In the experiment with the PEO1500 fraction *but also in a segregation experiment reported previously on a PEO3000 fraction*, the largest molecules crystallize first. In the present study on the PEO3000 fraction the molecular weight is smaller in the sedimented sample than in the melt! We have initially assumed that a crystal of definite thickness may grow by attachment of (7/2 helical) molecules of length larger than this thickness:

$$l > l_c \qquad \text{(A)}$$

In the alternative assumption proposed by Wunderlich[17] (at the ACS meeting in Anaheim), this condition may be replaced by

$$l \cong l_c \qquad \text{(B)}$$

At this time we did not have conclusive reasons to make a choice between these two formulations.

The only way to explain that in the PEO3000 centrifugation both the mean molecular weight and ultimate melting point increase from the bottom to the top of the test tube is (i) to assume that the second condition (condition B) is the correct one, (ii) to assume that the mean molecular weight of PEO is lower in the sinking crystals than in the melt, and (iii) to recognize that the molecules involved in the primary nucleation are not necessarily the largest in the distribution, but may also be the most numerous. The more general explanation is that the temperature of nucleation and the molecular weight distribution are both determinant factors.

The inverse effect is the consequence of the primary nucleation (see also sections 5 and 6). The mean molecular weight in the seeds is smaller than the mean molecular weight of the whole fraction. Figure 14 (a poor document) presents the mass distribution observed by electrospray in two slices of the centrifugated specimen. The distribution of molecular weight of the sample coming from the lowest part of the tube appears to be deformed with respect to the Poisson distribution. The distribution in the other slice presents "holes" which would correspond to the species crystallized during two periods in which the temperature of the sample was maintained constant. The analysis cannot be quantitative (further progress of our electrospray technique being needed).

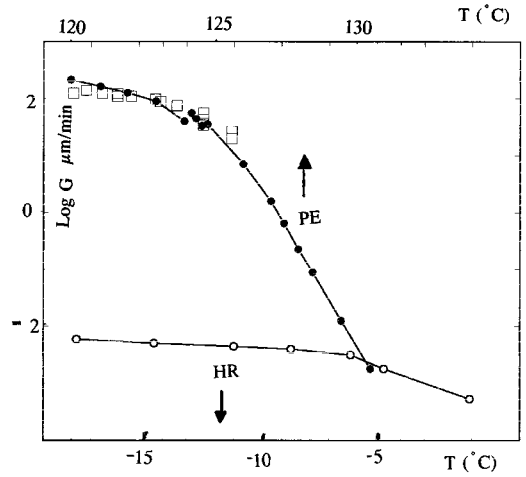

Figure 15. Thermal dependence of the growth rate (μm/min): filled circles, PE, M_n = 11 900, M_w/M_n = 1.19 (data of Toda[22]); hollow squares, C_xH_{2x+2}, x = 246, 198, 150 (data of Ungar[23] et al.); hollow circles, HR data of Phillips et al.[25]

15. Kinetic Theory of Polymer Crystal Growth. A Central Problem: "The HL theory and the breaks in the curve giving the thermal dependence of polymer crystal growth rate". The system and the problems studied in this paper are clearly peculiar but authorize general remarks. Until now, the growth rate branch of extended-chain crystals of a PEO fraction was considered as the representation of a single and coherent set of data related to the thermal dependence of a free energy barrier. In this and in a previous paper,[1] I have proposed that the thermal dependence of the growth rate of crystals only shows up in the plateau of the curve, because in the corresponding range of temperatures, all the molecules can crystallize. At increasing temperatures, higher than the break in the curve, a larger and larger part of the fraction cannot crystallize. This is now a well-etablished fact. Thus the right part of this curve of large slope reflects, also, the progressive onset of segregation of the molecules according to their molecular weight.

Labaig[5] has shown the strong similarity of the curves giving the thermal dependence of the crystal growth rate of PE and of PEO (in the extended-chain conformation). Figure 15 gives the thermal dependence of the growth rate of a polyethylene fraction (Toda[22]). The curve presents a break. On the same figure the crystal growth rates of normal paraffins, C_xH_{2x+2}, are also shown.[23] In a large temperature range, these crystal growth rates are approximatively equal to that of the PE fraction. The curves also present a plateau but end abruptly at the melting points. By similitude with the results obtained for PEO, the progressive change of the slope of the PE curve may be explained here by the onset of fractionation. (Segregation of PE molecules according to their molecular weight was largely exemplified in the past.[12,24]) Note that the molecular length dependence of the growth rate of the alkane and PE is not large. The heights of the corresponding plateau are nearly equal. This is not the case for PEO, where significant molecular weight effects are observed.

We interpret in a similar way the breaks in the growth rate curve of *Hevea* rubber[5] and of poly(lactic acid)[25] (PLL) of low molecular weight. *The explanation may be general. An alternative and "classical" explanation, in the framework of the theory of regimes of Hoffman, Lauritzen, and Phillips was critically discussed elsewhere.*[3]

16. Fractionation on Crystallization and Other Approaches of the Mechanism of Crystallization. It is known that in melts PEO molecules are associated by hydrogen bonds. Cheng et al.[20] assumed that such associated molecules may be considered as a single macromolecule, which attaches itself to a crystal in an NIF conformation. The reader should consult the original papers. We just note here that segregation of the molecules according to their molecular weight cannot be accounted for if the individual molecules are at the moment of their attachment to the crystal associated in a single entity.

In the tridimensional models of Sadler,[18] Gilmer, Goldbeck-Wood,[26] and others, the connectivity of the different parts of a molecule in the melt is not accounted for. These models are therefore not adapted to predict the influence of the molecular weight on the growth rate or to justify the observed fractionation effects.

D. Conclusions

I have proposed recently[1] an alternative approach of the kinetic theory of crystallization. In this approach, the crystal growth is assumed to occur, generally, at constant thickness and to be not controlled by secondary nucleation. Behaviors, predicted on this basis but in disagreement with the standard theory, were reported and discussed in this work.

(i) Immersed in a melt, 3D crystals, which are far from equilibrium with the liquid phase, actually grow totally irreversibly at constant thickness. It is therefore possible at a definite temperature of crystallization to grow various types of crystals presenting a large variety of structures. This was done. It is very likely that such an observation is not a great surprise for the morphologist but must retain the attention of the practitioners because samples of different structures may have different properties.

(ii) During crystal growth, there is a mutual size and shape recognition between the crystal facet and the incoming molecules, and therefore molecular weight segregation may occur to an unexpected extent. Even, in some instances, the shortest molecules in a fraction may crystallize first.

(iii) PEO crystals may be so ordered objects that lamellae of respectively 20 and 21 nm thickness have different and measurable thermodynamic properties.

(iv) The slope of the curve giving in an ad hoc representation the thermal dependence of the growth rate varies with the molecular weight distribution and cannot be used to calculate physical parameters such as surface free energy. More precisely (for PEO), the breaks of these curves show trivially the onset of fractionation.

(v) Even isothermally crystallized polymer samples may be heterogeneous. When it was assumed that the structure of the growing crystal was controlled by the supercooling, it was allowed for instance to say "this SAXS pattern gives the thickness of the crystals". The exact information given by a SAXS pattern is that the sample contains lamellae of the measured thickness.

This work raises several other questions:

(i) Why for instance is the molecular weight dependence of the crystal growth rate much more important in PEO than in PE? These differences may perhaps be associated with the helical versus trans conformation of the molecules and the motion of the self-attaching molecules on a crystal surface?

(ii) Is the suggested quantification of the thickness of PEO lamellae a valuable conclusion? This would make (even more) artificial the distinction between surface and volume free energy.

(iii) What is the role of homogeneous primary nucleation (a relatively irrelevant problem according to the standard theories).

(iv) The most important question concerns however the standard theory of polymer crystal growth. One of the main justifications of the standard theory is the occurrence of breaks in the curves which give the thermal dependence of the linear rate of crystallization, and its controversial[3] interpretation by the regimes theory. In the PEO case, my claim is that the breaks reveal trivially the onset of molecular weight segregation. This claim relies on an important amount of evidence. The same phenomenon is a plausible reason for the breaks observed in the studies of fractions of low molecular weight PE, PLL, and HR.

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Appendix A

("When crystallized from seeds isolated in the melt amd made of extended molecules of the *largest* molecular weight of the distribution, the lamellae have a thickness which may be *approximated* by

$$l(n,p) = L(1 + n)^{-1} = pl_u(1 + n)^{-1}$$

L is the *mean* value of the overal chain length in the crystal lattice). L is proportional to the average degree of polymerization p, the proportionality factor being $l_u = 0.2783$ nm, the length of a monomer along the chain axis parallel to the c axis, in the PEO subcell. A large proportion of the chain ends are rejected onto the surface layers of the crystalline lamellae and the 7/2 helical chain axis is normal to the latter. The *number of folds* (n) depends on the crystallization temperature and time. The curve giving the thermal dependence of the growth rate consists of juxtaposed "hyperbolic" branches which intersect at growth transition temperatures $T^*(n,p)$. In the temperature ranges $T_m(0,p)$ to $T^*(0,p)$, $T^*(0,p)$ to $T^*(1,p)$, $T^*(1,p)$ to $T^*(2,p)$, etc. the observed values of n are *(if the seeds are isolated crystals made of the largest molecules of the fraction)* respectively 0, 1, 2, etc.

The quoted values of the melting and growth transition temperatures were obtained by interpolation of the values given by Kovacs and Gonthier. The interpolation was made by the Tamman formula (instead of the Flory and Vrij formula,[21] which is no more efficient than the simpler Tamman expression)

$$T_n^* - T^*(n,p) = B_n/(pl_u)$$

Note that the peaks of the DSC traces or the SAXS patterns, which are usually attributed to the melting of "extended-chain crystals", correspond in many instances to crystals in which the fraction of the extended chain cannot be much larger than 50%, because more or less than 50% of the molecules are significantly longer than the crystal thickness (see the polydispersities reported in Table 1). The lamellae observed by Kovacs and others are usually designated by the symbols E, F_1, F_2, etc. and also by the symbol IF (by contradistiction to NIF) lamellae. In the present work, we make use of the symbols X ,Y, and Z instead of respectively E, F_1, and F_2 when we cannot assume with certainty that the repliement index of the molecules is mainly 0, 1, or 2. These distinctions appear necessary because the *seeds* of the Kovacs crystals and some of the crystals studied in this work are very likely IF crystals. In this eventuality, it is important to note this peculiarity because in such crystals the material is, by necessity, practicaly monodisperse (the value of p being defined within a few units; see section 11).

Appendix B

Note more particularly that the (observed) growth of E crystals at low temperatures is not an artifact because:

(i) *We do not observe a measurable exotherm of crystallization before full effective thermostatization at the quenching temperature of the very small (more or less 1 mg) specimens*. Thus the observed E crystals are not grown during quenching.

(ii) Use of different rates of DSC melting, has also shown that the E crystals do not result from the melting of F crystals and subsequent recrystallization.

(iii) In any case, it is also very likely that the nucleation of the observed E crystals occurs at temperatures lower than 60 °C, a temperature lower than $T_m(1,p)$, because attempts to nucleate and isothermally crystallize unseeded specimens during a very long stay at 60 °C (and for shorter residence time intervals at lower temperatures) were unsuccessful, while at this temperature samples seeded by E crystals grow very quickly.

When fractions of other molecular weights are used, the DSC data cannot always lead with certainty to similar conclusions: (i) For instance, F_1 crystals of sufficiently low molecular weight material are unstable and transform themselves into E crystals. (ii) E crystals of sufficiently large molecular weight are obtained solely by annealing of NIF crystals.

Finally, note that at temperatures between $T^*(0,p)$ and $T_m(1,p)$ Kovacs et al. have observed the growth of E and F_1 crystals (in different preparations). That observation was however not a definitive proof against the HL theory because in the theoretical development, the smooth substrate on which 2D crystals are nucleated is assumed to be large. This condition is not satisfied if as in the Kovacs experiments F_1 crystals are grown from F_1 nuclei. This is possible in the temperature range $[T^*(n,p), T_m(1,p)]$.

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