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The mechanism of crystallization of linear polyethylene, and its copolymers with octene, over a wide range of supercoolings

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This paper is dedicated to Professor Richard S. Stein on the occasion of his 75th birthday

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Abstract

The crystallization behavior of a linear polyethylene has been studied using conventional isothermal hot stage microscopy and with the Ding–Spruiell method of rapid cooling. When studied at rapid cooling rates the polymer generates its own pseudo-isothermal crystallization temperatures, in agreement with Ding–Spruiell's studies on other systems, permitting experiments to be carried out isothermally at a temperature as low as 90°C, thus extending the range of supercooling available from the 9°C (120–129°C) typical of conventional experimentation to 29°C (90–129°C). The points generated using both the isothermal and the rapid cooling techniques form a single consistent trend, as in polypropylene. In conventional crystallization experiments it was found, as expected, that the spherulite growth rates conformed to the regime I–regime II scheme, already well established for this polymer. When analyzed using a secondary nucleation approach all three regimes are found to exist and to adequately describe the data. The regime II–regime III transition temperature was found to occur at 120.6°C. The crystallization behavior of a series of ethylene-octene copolymers synthesized using metallocene catalysts has also been studied using the same experimental methodologies. In conventional crystallization experiments it was found, as expected, that the spherulite growth rates varied with octene content and molecular weight. When studied at rapid cooling rates, at the lowest temperatures of crystallization, the spherulite growth rates of all of the copolymers studied merge with the growth rate curve of the linear polyethylene and are virtually indistinguishable. The results indicate a major breakdown of all current theories of polymer crystallization, in that the overriding equation involving the relation between crystallization rate, lamellar thickness, surface free energy and supercooling appears to be superceded in the copolymers by some hitherto unrecognized process or law. The underlying physics behind this conclusion needs to be elucidated, but appears to be consistent with the formation of a partially ordered intermediate of 3–4 stems in size on the growth face under all conditions of growth in linear polyethylene and its copolymers. The degree of disorder in the cluster is believed to be strongly dependent on supercooling, permitting incorporation of hexyl groups into the intermediate. Subsequent ordering of the cluster produces the ultimate crystal packing and ejection of hexyl groups and other impurities. The rate of formation of the cluster is suggested to be the rate controlling step in secondary nucleus formation. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Polyethylene; Ethylene copolymers; Metallocene

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1. Introduction

Linear polyethylene is one of the most important polymers, both from both academic and commercial viewpoints. It has always been taken as the paradigm of behavior for flexible polymers and the system on which most theoretical approaches have been taken. Its role as the primary model system in crystallization is undisputed, but has always been limited by its very narrow crystallization range. Having an equilibrium melting point of 144.4°C for an infinite molecular weight polymer [1,2], the isothermal crystallization temperature range that is accessible is usually from 120 to 129°C, but has sometimes been extended down to 118°C with unclear results. The narrowness of this range has limited the testing of theories of crystallization, such as regime theory. This range palls in comparison with the isothermal ranges accessible to other polymers, such as *cis*-polyisoprene (−40 to 10°C) and polyethylene terephthalate (110–210°C). This narrow range is a direct consequence of the rapid rates of crystallization that make it impossible to reach lower isothermal temperatures of crystallization using conventional hot stages without the crystallization occurring before the desired temperature is reached. In the Ding–Sprueill [3,4] approach a thin film of the polymer is cooled down at a constant rate and its actual

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temperature is monitored using a microscale thermocouple embedded in the film. The polymer behaves just like other materials and generates a plateau in temperature, through the evolution of latent heat, which is maintained as long the crystallization process proceeds. Unlike other materials, the plateau temperature is not the melting point, but is a variable determined by the cooling rate, i.e. the higher the cooling rate the lower the plateau temperature. In this paper we will report the behavior of a linear polyethylene studied under these conditions.

Ethylene copolymers, in the form of linear low-density polyethylenes (LLDPE) are a commercially important class of polyethylenes, produced through the copolymerization of ethylene and comonomers such as hexene or octene, thereby producing butyl or hexyl branches, respectively. In order to separate the effects of copolymer content from molecular weight, a series of cross-fractionated copolymers has been investigated and reported in the recent past, [5,6]. The copolymers which had been cross-fractionated for us by Dow Chemical had been synthesized using traditional slurry-based Zeigler–Natta (ZN) type catalysts, which are well-known to produce molecules in which the copolymer content varies with molecular weight. What was not well known at that time, or even now, was the sequence length distributions of the octene and ethylene mers within each molecule. It has been assumed to be random in the absence of contradictory information. Our recent studies of random copolymers of ethylene with octene [7] produced using metallocene catalysts showed that the crystallization behavior was very different from that of the ZN materials, a result which had to be a consequence of the ZN polymers being non-random within each molecule.

Quiescent crystallization is usually separated into its component parts of primary nucleation, linear spherulite (or lamellar) growth and secondary crystallization. In this paper only the linear spherulite growth rates will be considered. Regime theory, which describes linear spherulite growth in flexible polymers, comprises two separate processes. The first process is the deposition of secondary nuclei on the growth face, usually denoted as occurring at a rate i. The second process is the subsequent growth along the face at the niches formed by the secondary nuclei, often referred to as the rate of surface spreading, and denoted by the rate g. The relative rate of these two processes determines the regime at which the crystallization occurs. The concept of transitions was first introduced in 1973 by Lauritzen and Hoffman [8] being applied to linear polyethylenes, and has since been extensively evaluated by Hoffman, Phillips and others [5–12]. It is generally accepted that polyethylene, whether in the form of fractions or in unfractionated form, exhibits regime I and regime II, the transition between the two regimes occurring in the neighborhood of 127°C, being dependent on molecular weight to a small degree. The precise location of the hypothetical regime II–regime III transition has not been published for the linear polymer for experiments involving a determination of the radial growth rates of spherulites. However, Hoffman [13] has determined the value to be 121.1°C for an NBS standard linear polyethylene of $M_w = 32\,100$. The transition has been observed in cross-linked linear polyethylenes in the vicinity of 115–118°C [11], the value being dependent on the cross-link density. In bulk studies using the Ding–Spruiell technique the transition was found to be 119°C [4,14]. Using other methods Fatou et al. [15] have generated a value in the same range as the afore-mentioned studies.

The behavior of polyethylene under the, heretofore unattainable, high supercooling range is of great interest to the commercial sector, since many commercial forming operations, such as film and fiber formation, involve quenching and crystallization under dynamic rapid cooling conditions. This temperature range is thought to be 80–95°C for polyethylenes. In this paper will be reported the results of experiments carried out of cooling rates of 100s to slightly over 1000°C min^{-1} rates that are well within the range of commercial operations. It will be shown that, over this range of conditions, secondary nucleation theory can be applied to linear polyethylene with three regimes being present, the crystalline structure remaining orthorhombic. However, there is a possibility that what has been called Regime III, may really be something else, a possibility that will be explored in the discussion section of this paper.

Copolymers produced using metallocene catalysts, which are believed to produce random copolymers because of the nature of catalytic process, have also been studied [7,16,17]. Whether or not there is a non-random distribution present cannot be evaluated because of the lack of a technique to measure sequence lengths, however there are no reasons to suspect a major source of non-randomness, such as that which is well-established for the slurry-based Zeigler–Natta catalyzed polymers. There is always the possibility of chain scission occurring near a branch point, which may result in a dependence of molecular weight on comonomer content, however there are as yet no reports in the literature of such an occurrence for these copolymers. So, it is not yet known whether cross-fractionation of metallocene copolymers will assist in studies such as these. It appears at the present time that radial growth rate of spherulites is the property most sensitive to sequence length distributions.

Dow Chemical synthesized for us metallocene copolymers with molecular characteristics as near as possible identical to those of the cross-fractionated samples. Prior studies of the melting point–lamellar thickness relations [18,19] have shown that the equilibrium melting points are depressed by a factor greater than that predicted by the Flory equation [20,21]. It has been shown for one of these copolymers that the linear growth is depressed much more that in the equivalent fraction of a slurry-based Zeigler–Natta polymer, the regime I–regime II transition temperature being depressed much more, and regime III appears [7]. The conclusion resulting was that the fractions of the

Table 1
Molecular characteristics of the polymers

Sample	M_n	M_w	M_w/M_n	Branches per 1000 carbons	T_m (°C)
LPE-54/101	53 900	101 300	1.88	0	142.7
L-04	27 300	59 900	2.19	3.98	139.3
H-07	43 600	94 000	2.16	6.84	140.4
L-11	21 200	43 700	2.06	10.86	134.9

Zeigler–Natta polymer contained non-random inclusion of the octene mers and that this study generated a very important new variable for crystallization studies, namely the sequence length distribution.

In the study being reported here, an extension of previously reported preliminary studies [16,17], the studies of the metallocene copolymers have [17] been extended to the very high supercoolings characteristic of commercial processing operations. It will be demonstrated that, under such conditions, the polymer behavior changes dramatically and is no longer is dependent on comonomer content and, apparently also, molecular weight. In the preliminary study the crystallization process was envisioned as being similar to a congealing process in which the copolymer molecules wiggle into place as the growing crystal sweeps through them, the hexyl branches being included in the metastable crystals. Presumably, these crystals anneal and perfect through a variety of subsequent processes, in which some of the hexyl branches are ejected from the crystals. Although it is still believed that such processes may indeed occur, the studies of the linear polymer, when compared to those of the copolymers, indicate that the change occurring is of a much more fundamental nature, since the data for the copolymers merges with that of the linear polymer. The results indicate a major breakdown of current theories of crystallization through secondary nucleation in the copolymers, in that the underlying governing relation between lamellar thickness, surface free energy and supercooling has been superceded by a more fundamental, but heretofore, unrecognized process, or by an unknown behavioral law.

2. Experimental

The linear polyethylene studied was provided by and characterized by the Dow Chemical Company. The values of M_n and M_w are 53 900 and 101 300. Other studies of this polymer have been reported earlier, including studies of its equilibrium melting point, isothermal crystallization kinetics and lamellar thickness behavior [4,14,18,19]. LLDPE fractions, copolymers synthesized using metallocene catalysts and linear fractions were supplied and characterized by the Dow Chemical (see Table 1). All copolymers contain octene as the comonomer. The fractions have been described previously [5,6], as also have the metallocene copolymers [7,16–19]. In sample designation *L* and *H* refer to low molecular weight and high molecular weight, respectively ($M_w \sim 50\,000$, $M_n \sim 25\,000$ and $M_w \sim 98\,000$, $M_n \sim 48\,000$). The suffix M refers to materials synthesized using metallocene catalysts and ZN to materials synthesized using Zeigler–Natta catalysts (the latter are all fractions). The numbers following the letters refer to the number of hexyl branches per 1000 carbon atoms. Samples denoted by LPE are linear samples, the numbers following the LPE referring to the molecular weights in 1000s.

Linear spherulitic growth kinetics experiments were performed using an Olympus polarizing microscope with an attached 35 mm camera, or video camera, and temperature controlled hot stage. The change in the morphological size was measured by taking photographs or videos as a function of time. Samples were held at the melt temperature of 150°C for 5 min and then rapidly quenched to the crystallization temperature. Crystallization experiments at high supercoolings were carried out in the original Ding–Spruiell rapid cooling equipment [3,4], but the sample thickness was reduced to 30 μm in order to resolve the spherulites clearly at the lowest supercoolings. Crystallization was followed using a video camera in this technique.

Wide angle X-ray diffraction studies were carried out using a Rigaku Denki diffractometer using Cu Kα radiation. The melting studies were conducted in a Perkin Elmer DSC 7B instrument at a scanning rate of 10°C min^{-1}. Crystallinities were obtained using both approaches and conventional analytical techniques.

Small angle X-ray scattering studies were carried out on stacks of the thin films produced using the rapid cooling technique. Results for those films produced using conventional isothermal hot stage techniques have been reported earlier [18]. Studies were conducted at the Center for Small Angle Scattering at Oak Ridge National Laboratory using the 10 m camera [18]. A 5.115 m sample to camera length was used for specimens studied at room temperature and a 5.065 m sample to camera length at elevated temperature experimentation.

3. Results

The behavior of the linear polyethylene in the rapid cooling regime is similar to that of polypropylenes and ethylene-octene copolymers that have been studied in the past using this technique. The polymer generates a constant temperature at which crystallization occurs for a given

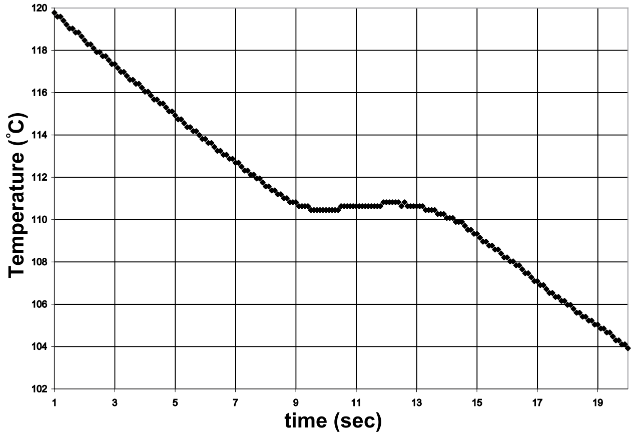

Fig. 1. Change of temperature with time in a typical rapid cooling experiment.

cooling rate. An example of the plateau generated in a rapid cooling experiment is shown in Fig. 1. Spherulites were observed throughout and were found to display a constant growth rate for a constant rate of cooling during the plateau region. The range of plateau temperatures observed reached a low point of 90°C. It is believed that much lower effective temperatures are possible, but the lower limit used in these experiments is determined by the speed of the video camera. Use was not made of the cooling device because of this limitation, only nitrogen gas from a cylinder being used in achieving the plateau temperatures reported.

In the studies at very high supercoolings, the very short time of crystallization severely restricted the time available for focusing the specimen. Generally samples were focused before melting and then refocused rapidly when the crystallization began. In some cases this procedure led to the spherulites being slightly out of focus, as evidenced by the presence of fringes around the circumference (Fig. 2). In order to generate consistent data spherulite growth rates were obtained by measuring the diameter of the black

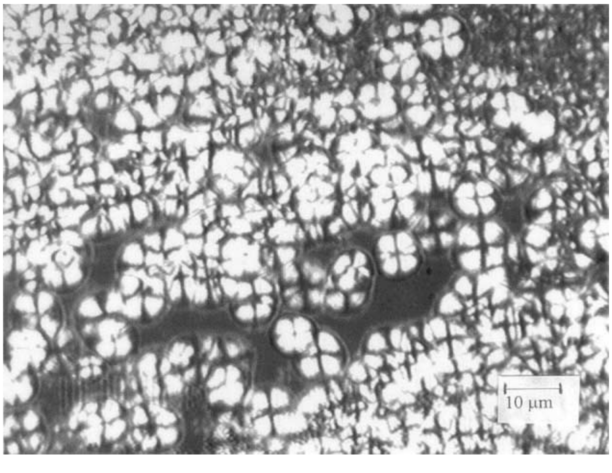

Fig. 2. Micrograph of spherulites growing under rapid cooling conditions in linear polyethylene at 122°C, showing black fringe used in growth measurements, when perfect focusing was not possible due to time constraints.

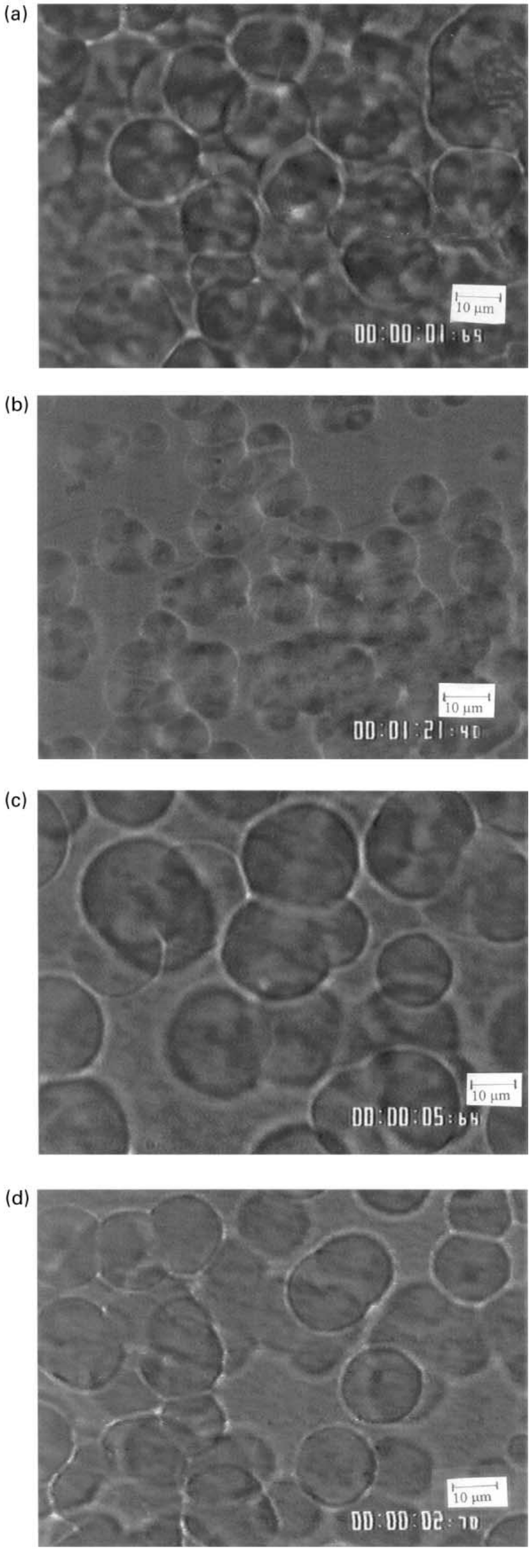

Fig. 3. Representative spherulitic morphologies present at high supercoolings: (a) linear polyethylene at 97.5°C (regime III); (b) L-04 at 92.5°C; (c) H-07 at 87.5°C; (d) L-11 at 83°C.

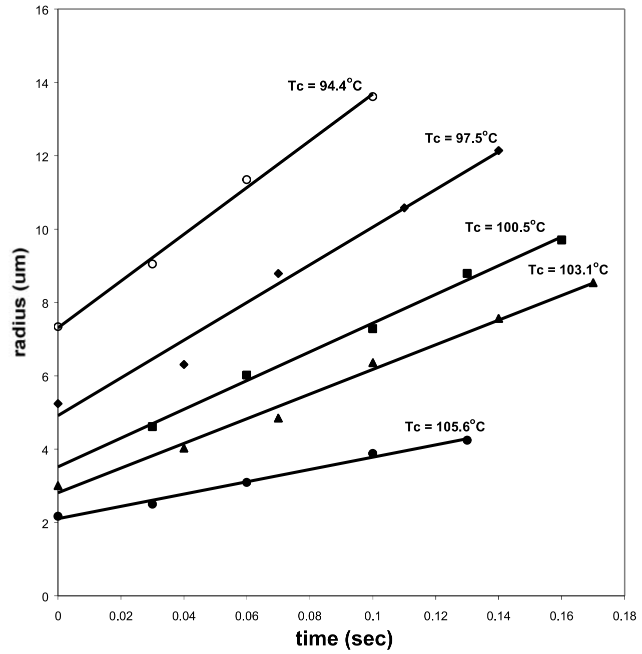

Fig. 4. Change of spherulite radius with time for linear polyethylene in the high supercooling region.

fringe, when necessary. In all the samples studied at high supercoolings (whether linear polyethylene or the copolymers) spherulites were observed. Some representative morphologies are presented in Fig. 3. Banding was present, but difficult to resolve at the highest supercoolings and will be the subject of a separate paper.

Representative examples of growth rate determinations in the rapid cooling regime are shown in Fig. 4 for linear polyethylene, where it can be seen that the growth rates were linear. It should be noted that the time scale begins when the spherulites were brought into focus, not when their growth was initiated. The lower limit of crystallization temperature was determined by the speed of the video camera. Growth rates were used only if four clear growth points could be obtained. The variation of linear growth rate with temperature for the linear polyethylene is shown in Fig. 5, where the filled symbols represent points obtained in conventional isothermal crystallization experiments. Errors on the data points are approximately the size of the symbols used for growth rates below 20 μm s^{-1} and then increases steadily with decreasing temperature to a maximum error of 5 μm s^{-1} at 70 μm s^{-1}. The open symbols represent data points obtained in rapid cooling experiments, where the polymer generates its own pseudo-isothermal crystallization temperature. The behavior is conventional, there being a clear continuation of the curve between the isothermal region and the rapid cooling region for each polymer studied. It should also be noted that the linear polymer appears to be approaching its peak, something that has not before been seen in polyethylene. This point is being explored currently in new experimentation using a faster camera. When the logarithm of growth rate is plotted against supercooling (Fig. 6) the regime I–regime II change of slope can be seen clearly in the isothermal region. There is a discontinuity, rather than a change of slope that can be assigned to a regime II–regime III transition, which can be seen between the 2nd to last and 3rd to last isothermal points on the figure.

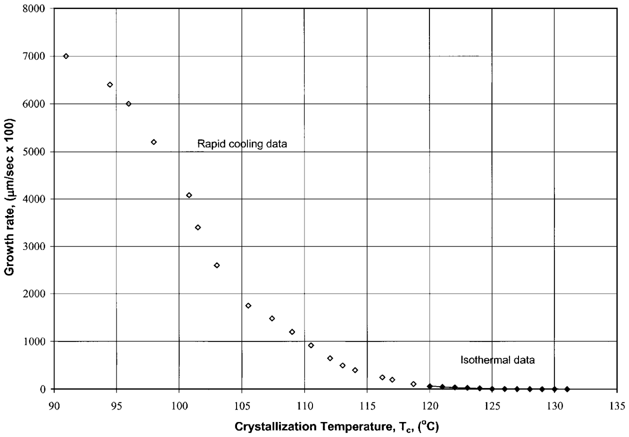

Fig. 5. Radial growth rate versus crystallization temperature for linear polyethylene (filled symbols, isothermal data; open symbols, rapid cooling data).

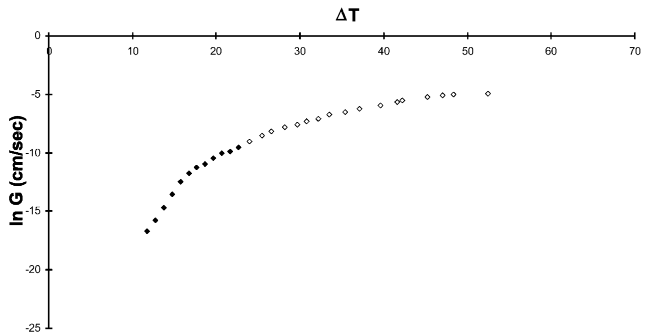

Fig. 6. Logarithm of radial growth rate versus supercooling for linear polyethylene, using the known equilibrium melting point of the polymer (isothermal data, filled symbols; rapid cooling data, open symbols).

In the case of the copolymers, the data are essentially those reported in the preliminary publications [16,17] with a few additions. The variation of the logarithm of linear growth rate with temperature is shown in Fig. 7 for several different materials, where the filled symbols represent points obtained in conventional isothermal crystallization experiments. As for the linear polymer, the open symbols represent data points obtained in rapid cooling experiments. It can be seen clearly that as high supercoolings are approached the curves of all the copolymers are tending to merge into a single curve, regardless of comonomer content or molecular weight. It has to be remembered that the equilibrium melting point is dependent on molecular weight and comonomer content and the data should be corrected for that variable using the supercooling, relative to the equilibrium melting point of each copolymer [18]. When the data are plotted as a function of supercooling (Fig. 8), the same

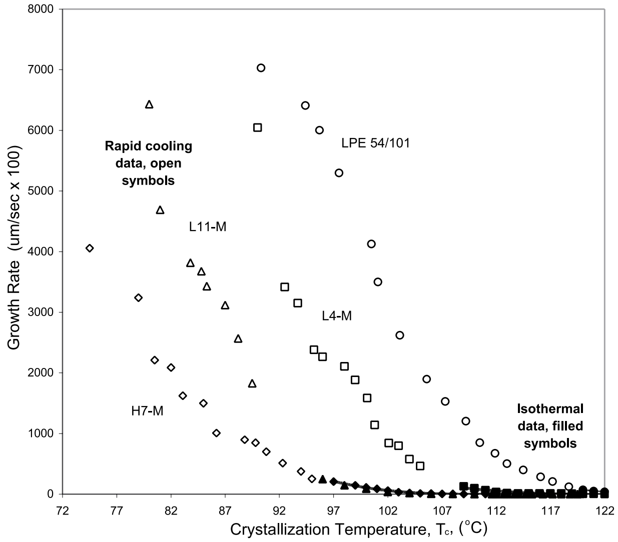

Fig. 7. Logarithm of radial growth rate versus crystallization temperature for the copolymers and linear polyethylene, as indicated.

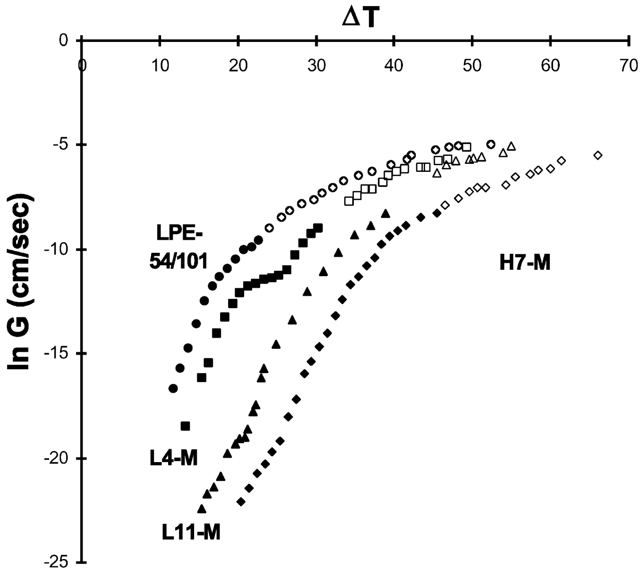

Fig. 8. Logarithm of radial growth rate versus supercooling, using established equilibrium melting points of each individual copolymer.

merging phenomenon can be seen, perhaps even more clearly.

Following crystallization the samples were stored at 0°C. Wide angle X-ray diffraction studies were later carried out at ambient temperature to determine the phase structure of the crystals formed. It was found that the conventional orthorhombic structure was formed under all conditions, although preliminary analyses indicate that there may be some minor changes in lattice parameters with crystallization temperature. It is recognized that more in-depth WAXD studies are necessary to be certain of the phases present, as the major reflections of the known crystal unit cells of polyethylene almost coincide. Differential scanning calorimetric studies were conducted at a scanning rate of 10°C min^{-1}. Again the melting curves were quite conventional, the lowest melting point achieved being 131.4°C for the plateau temperature of 90.1°C (see Fig. 9a). There are, however, some significant differences when the copolymers are considered. The polymer with four branches per 1000 atoms (L-04) shows behavior similar to the linear polymer (Fig. 9b), however, the remaining two systems show the appearance of a shoulder or second, and even, third peaks, dependent on the crystallization temperature (Fig. 9c and d). Since these copolymers are random copolymers, multiple melting peaks, such as those characteristics of fractions of the ZN copolymers, would not be expected. It will be demonstrated in a separate paper, dealing with crystallization of these materials at elevated pressures, that this second peak is likely caused by the formation of a second crystalline phase. The crystallinities of the linear polyethylene and the copolymers crystallized at selected very high supercoolings are presented in Table 2. They show the expected trends of decreasing with increasing supercooling and comonomer content. It should, however, be noted that these data were obtained by using conventional DSC scanning methods and include any changes generated during the heating cycle. In depth studies using modulated DSC are

Table 2
Crystallinities and melting characteristics of samples crystallized at selected high supercoolings

Sample	T_c (°C)	T_m (°C) peak	T_m (°C) RTB	% X_c (DSC)	% X_c (X-ray)
LPE-54/101	90.0	131.2	135.3	51.2	51.2
	109.0	131.9	135.5	56.9	57.0
	116.0	133.3	136.1	60.2	60.4
L-04	95.0	121.3	125.3	52.0	52.1
	104.0	121.5	125.0	52.9	53.9
	111.0	122.8	125.8	57.8	58.4
H-07	82.0	111.1	115.1	45.2	45.6
	89.5	110.5	114.2	49.0	48.8
	96.0	110.8	114.8	51.5	51.0
L-11	81.0	109.1	113.0	45.8	45.8
	87.5	109.0	112.7	49.0	49.2
	89.0	108.9	112.9	50.3	50.6

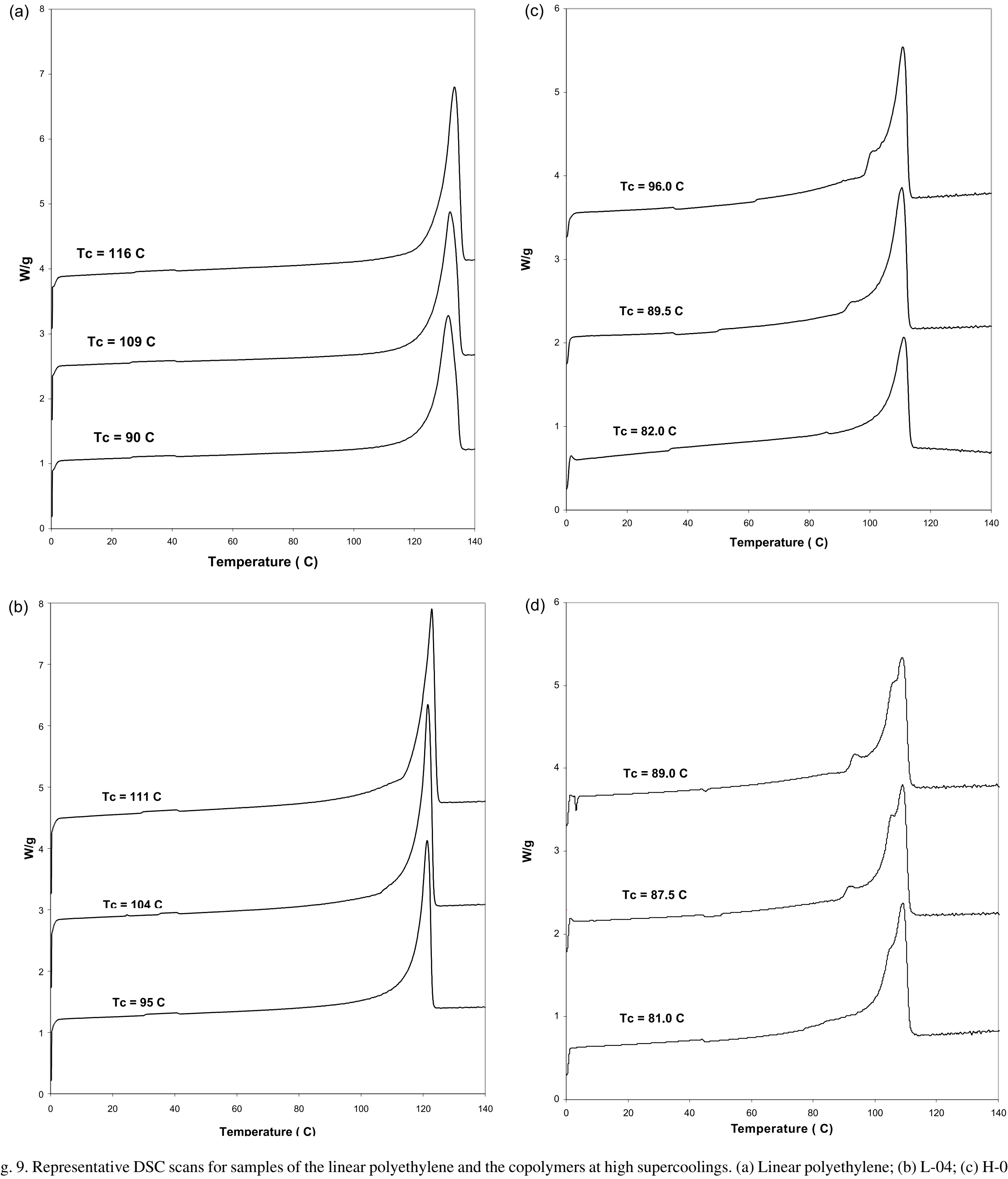

Fig. 9. Representative DSC scans for samples of the linear polyethylene and the copolymers at high supercoolings. (a) Linear polyethylene; (b) L-04; (c) H-07; (d) L-11.

currently underway to explore the phenomenon in greater depth.

Typical SAXS intensity scans for the linear polymer crystallized at several high supercoolings are shown in Fig. 10a, where it can be seen that conventional single peak profiles are obtained. An example of a Lorentz corrected curve is shown in Fig. 10b for the sample crystallized at the highest supercooling (i.e. at 90°C). There is a single prominent peak, with some evidence for a much less intense second order peak. The long period was obtained from a one-dimensional correlation function approach and multiplied by the known crystallinity (from X-ray diffraction

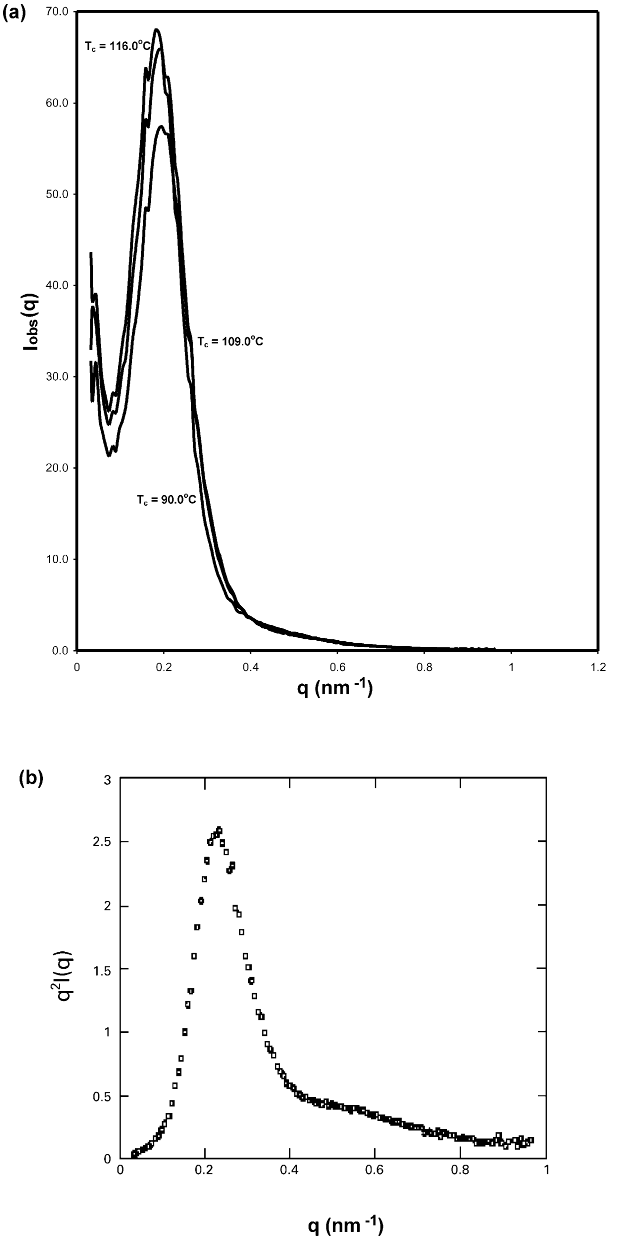

Fig. 10. SAXS studies of a linear polyethylene crystallized at high supercoolings (a) SAXS intensity curves (b) Lorentz corrected data for T_c = 91°C.

studies) to obtain the lamellar thickness. Values have been obtained for three high supercooling points and are presented in Table 3. They are also presented together with previously reported data obtained using conventional isothermal crystallizations in Fig. 11. It can be seen that a single linear dependence is obtained for both the peak melting point and the return-to-the-baseline temperatures, suggesting that there are no phase changes involved, nor any changes in mechanism, over the entire range of crystallization temperatures studied. It should, however, be remembered that the studies had been carried out on specimens, which had been cooled to room temperature and stored before study. Hence these data are typical of the final state of the films and not of the lamellar thickness dimensions occurring during crystallization. In situ SAXS or WAXD studies cannot currently be carried out because of the short time scales of crystallization involved at these very high supercoolings.

Table 3
SAXS data for linear polyethylene from 1D correlation function analysis

T_c (°C)	%X_c (X-ray)	Long period (nm)	Lamellar thickness (nm)
90.0	51.2	25.89	13.26
109.0	57.0	25.45	15.08
116.0	60.4	27.68	16.72

4. Discussion

The type of plot normally made in interpreting radial growth rate data is the secondary nucleation, or regime, plot in which the logarithm of the growth rate, less a mobility term, is plotted against the reciprocal of supercooling. It is this plot that permits the different regimes to be identified and is, in many ways, the defining plot for the crystallization behavior of a polymer. Such a plot is shown in Fig. 12 for linear polyethylene. The data that were used in this plot are those that have been used in the past by most researchers, namely $U^* = 1500$ cal mol, $T_\infty = T_g - 30$ K where $T_g = 190$ K. In this case, the known molecular weight dependent equilibrium melting point of 142.6°C, determined from SAXS studies of lamellar thickness [18] was used. The plots shown in Fig. 11 result in equilibrium melting points of 143.4°C for the peak data and 142.7°C for the return-to-the-baseline data, which compare well with the value obtained for the isothermal points alone and already published [18].

The secondary nucleation plot shows three clear slopes, as did the copolymer containing four hexyl branches per 1000 carbon atoms, which was reported earlier [16,17]. These three regions clearly correspond to the three regimes of growth, the first two having been established for over 20 years. It is worth remarking that the linearity of the fit in the regime III region suggests that traditional semi-empirical value of U^* that has been used for linear polyethylene for many years, with a very restricted range of supercoolings, is quite adequate for the data obtained at a temperature as low as 90°C. As can be seen from the data presented in Fig. 12, the slopes of the regime I and regime III regions differ by $<1\%$. The slope ratio between regime II and the other two regimes is 0.72 for regime III and 0.71 for regime I, whereas theory would predict a ratio of 0.5. It is not unusual for this ratio to be higher than theory in a bulk unfractionated polymer.

The entire crystallization behavior of the copolymers can now be analyzed, secondary nucleation plots for all the polymers studied being shown in Fig. 13. First, the filled

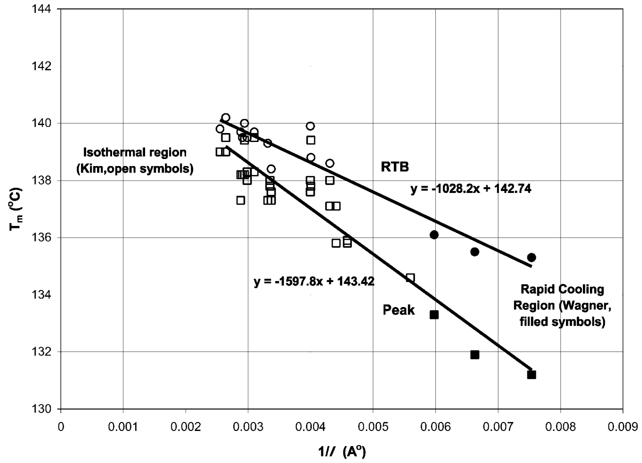

Fig. 11. Plots of melting temperature versus reciprocal lamellar thickness for linear polyethylene using both the peak temperature and the end-of melting (return to the baseline).

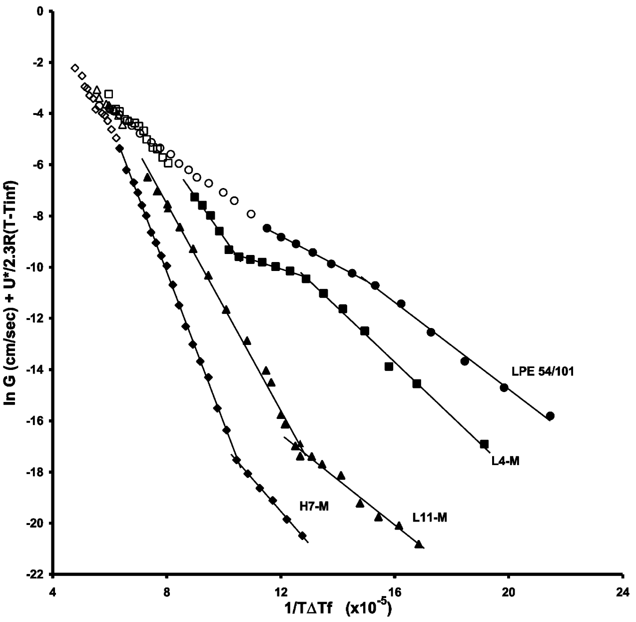

Fig. 13. Secondary nucleation plot for the linear polyethylene and the copolymers as indicated (filled symbols are isothermal crystallizations; open symbols are pseudo-isothermal crystallizations obtained from rapid cooling experiments).

points, indicative of conventional isothermal studies, show the expected decrease in crystallization rate as comonomer content is increased (e.g. compare L4 with L11). Also apparent is the decrease of crystallization rate with increasing molecular weight (e.g. H7 is slower than L11). When the open symbols, indicative of rapid cooling experiments, are considered, it can be seen that initially they continue on the same lines as the filled points. This is a very important observation, since it tells us that there is no significant difference between an experiment carried out isothermally and one that is carried out dynamically in a rapid manner, and in which the polymer film is sufficiently thin for the generation of the pseudo-isothermal crystallization condition. It is however clear that as the experiments proceed to successively higher and higher cooling rates that there is a slow downward change in the slope for all the copolymers. Ultimately, the copolymers are attaining the same growth rates. Highly significant, and not available for comment in the earlier short publication, is the fact that the data for all the copolymers are merging with the curve of the linear polymer. This cannot occur if the normal selection rules of copolymer crystallization, based on exclusion of the comonomer units, continue to apply. Nor can the merging of the curves to a common line, regardless of molecular weight, occur unless there is essentially a lack of long-range movement of the polymer chains during the crystallization process. In other words, the copolymer molecules, essentially, must freeze into place without the exclusion of molecular defects in the rate-controlling step of the nucleation process. This is a new form of crystallization, quite different from the one occurring at higher temperatures, where the molecules have time to reject the comonomer species and to diffuse in a way which is dependent on their molecular weights.

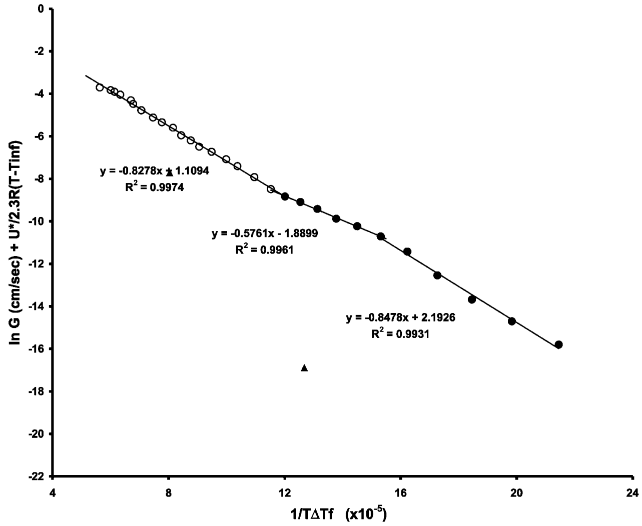

Fig. 12. Secondary nucleation plot for the linear polyethylene (isothermal data, filled symbols; rapid cooling data, open symbols).

It should be noted from Fig. 13 that the reduction in rate between L-04 and L-11 is dramatic. The orders of magnitude involved in this reduction are at least two orders of magnitude greater than would be expected on the basis of other studies (e.g. Ref. [22]). Studies of the crystallization behavior of these copolymers at elevated pressures have shown that the phase diagram of polyethylene is very sensitive to comonomer content [23]. The triple point moves to lower pressures as comonomer content is increased. For instance, the triple point of the L-04 copolymer is in the vicinity of 750 bar, whereas the triple point of the L-11 copolymer is below atmospheric pressure.

In the case of the L-11 copolymer, and presumably also for the H-07 copolymer which displays similar overall behavior, a second crystalline phase is present at atmospheric pressure alongside the orthorhombic phase. At elevated pressures, this second phase becomes stabilized producing identifiable non-spherulitic entities, which can be clearly discerned. In the atmospheric pressure studies reported here the scale of the morphology of the second phase is too small to be discerned in most optical microscopic studies. The orthorhombic spherulites being studied, and reported here, therefore are growing into or alongside a second phase (some crystals of the second phase may be seen as an indistinct granular background in Fig. 3). The crystal structure of the second phase has not yet been studied by us. It could be the hexagonal phase typical of the linear polymer at elevated pressures, the monoclinic phase, or some hitherto unrecognized unit cell. It is quite possible that the dramatic drop in lamellar growth rate observed in L-11 and H-07 is caused by interference from the second phase. The precise nature of this interference is not known at this time, could take several forms, and will be the subject of another paper concentrating on this aspect of the phenomenon.

A similar phenomenon has been seen, thoroughly investigated, and reported in *cis*-polyisoprene at elevated pressures [24–26]. In this case a disordered hexagonal phase [25] appears at pressures in excess of 2 kbar. Although this phase was identified as a poorly formed hexagonal phase on the basis of electron diffraction, it was described [26] as "similar to the more highly ordered smectic phases present in liquid crystals". Important characteristics of this phase were (a) it formed so rapidly that its growth rate could not be measured, (b) the crystals were oblate spheroids, clustered into axialites and (c) at long times it was replaced by sheaves of the conventional lamellar monoclinic phase. The growth rates of the sheaves were much lower in the presence of the pseudo-hexagonal phase than when growing alone.

The behavior of the L-11 and H-07 copolymers is therefore strongly reminiscent of the behavior of *cis*-polyisoprene in all respects. In the case of *cis*-polyisoprene [26] it was clearly demonstrated, through the use of osmium tetraoxide staining, that there was a molten region 300–400 nm ahead of the growing monoclinic lamellar sheaves. In other words, the pseudo-hexagonal crystals melted ahead of the growing sheaf. Although not suggested at that time, it would seem reasonable to suggest that this effect was caused by the heat of crystallization of the monoclinic lamellar sheaves. Hence, it appears that the rate of crystallization of the lamellar sheaves was determined by the rate of local melting of the pseudo-hexagonal crystals ahead of the growth front. As will be reported in a later publication [23], the orthorhombic spherulites of the ethylene copolymers appear to be showing similar behavior.

As can be seen from the DSC scans (Fig. 9) the L-11 and H-07 copolymers show clear evidence of multiple melting peaks, similar to what occurs at elevated pressures [23]. Presumably, this is evidence of both phases being present in what has been labeled regimes II and III of these copolymers. However, it should be noted that the secondary peaks reduce in intensity as high supercoolings are approached. Indeed, the DSC scans at the lowest crystallization temperatures of these two copolymers resemble those of the linear polyethylene and the L-04 copolymer, both of which show only the presence of the orthorhombic phase at atmospheric pressure, consistent with the phase diagram information. So, it appears that the merging of the linear growth rate curves at very high supercoolings may be partly caused by the non-existence of the second phase under these conditions.

It can also be noticed that in the isothermal regions (filled points) that the slopes of the lines are increasing as the comonomer content increases. From a simple secondary nucleation standpoint and the equations governing regime theory, this can only be a result of two possible changes. The first is an increase in the fold surface free energy, which appears in the numerator of the slope, probably caused by crowding of the rejected side branches in the interfacial regions. Secondly, there may be a reduction in the latent heat of fusion, which appears in the denominator, caused by incorporation of hexyl branches in the crystal. Although this might seem unlikely, studies of the equilibrium melting points of these copolymers crystallized isothermally at relatively low supercoolings have already shown major diversion from the Flory equation and conformation to the Sanchez Eby equation for partial incorporation of comonomers in the crystals [18,19]. Calculations of defect energies are consistent with those predicted for incorporation of methyl or ethyl groups. Presumably this is because the hexyl group is long enough for several of its methylene units to enter crystallographic register, leaving basically a branch point and a methyl group as the defects. The equilibrium melting point of the copolymers will be decreased if there exists a substantial incorporation of defects, and so the equilibrium melting points of the copolymers may be progressively decreasing as crystallization temperature decreases. Additionally, if large amounts of hexyl branches are incorporated in the crystals, rather than being excluded, then the crystal will expand, lowering the latent heat of fusion. At the same time, the crowding in the interfacial regions will be reduced, thereby causing a reduction of the fold surface free energy. All of these effects would result in a decrease in the slope. The effects are likely to be occurring simultaneously. It should also be noted that expansion of the crystal lattice, through incorporation of defects, would reduce the surface free energy by allowing more surface area per emerging chain in the fold surfaces.

However, as pointed out earlier, the orthorhombic spherulites of the L-11 and H-07 copolymers are co-existing with a second phase composed of very small crystals, which would be melting ahead of the growing spherulites, if the *cis*-polyisoprene model really applies here. Since there is no direct knowledge of the state of the melt ahead of the growing spherulites, it is quite possible that some form of order exists in the melt, retained from the now-molten crystals of the second phase. It is also possible that the crystals of the second phase could incorporate hexyl branches due to a more open structure. If so, then, on the basis of what is known about the hexagonal phase of the linear polymer at elevated pressures, they could be forming quite thick crystals. As was demonstrated clearly by Bassett [27], the lower heat of fusion of the hexagonal phase results in thicker crystals, which become chain-extended in that case. For the copolymers being considered here, the random distribution of the hexyl branches, if completely excluded from the crystals, would prevent very thick crystals from being formed. If, however, the solubility limit of hexyl branches in crystals of the second phase were much greater than the solubility limit in orthorhombic crystals, then thick crystals could be formed.

The random orientation of the small crystals of the second phase could therefore result in ordered domains being present after melting (using the *cis*-polyisoprene model), perhaps of a nematic nature, which would be misoriented with respect to the growing orthorhombic lamellae. The melt, or nematic, ordering would present an impediment to the reorientation of chains seeking to crystallize in the orthorhombic lamellae. Crystallization from such a non-random or partially ordered melt state would therefore be expected to result in quite different fold surface free energies from those found in normal quiescent crystallization. There are two likely reasons for this. First, the fold surface free energy is really an interfacial free energy representing the difference in free energy between the crystal and the melt. Secondly, it would seem unlikely in such a pre-ordered melt for the fold topology to be the same as that produced from a truly random melt.

The experimentation being reported here shows very clearly, that, not only is the linear growth rate suppressed dramatically at low supercoolings by the presence of the second phase, but also that the slope in the secondary nucleation plot in the regime III region is many times greater for the L-11 and H-7 copolymers than it is for the linear polymer and the L-04 copolymer. Can an increase in slope of such a magnitude be explained by the arguments presented in the preceding paragraph? A glance at Fig. 13 shows clearly that the rate of increase of the growth rate with supercooling in the regime III region for these copolymers is such that their growth rates should greatly exceed that of the linear polymer at high supercoolings, if the behavior were to continue. Such an event would be unique in polymer crystallization.

The phase diagram of L-11 [23], based on elevated pressure studies, suggests that the orthorhombic phase becomes the stable phase at high supercoolings. This, in itself, may be sufficient reason for the change in behavior and responsible for the slow down and merging of the curves at high supercoolings. However, it is also obvious that it cannot alone explain the behavior, since the L-04 copolymer does not form crystals of the second phase at atmospheric pressure, yet it also exhibits a change of slope and a merging with the linear polymer and the copolymers. In any case, the orthorhombic crystals have a low tolerance for hexyl group incorporation and selectivity on the basis of comonomer content would be expected.

If the afore-mentioned rationale is correct, then it seems unlikely that the regime II–III transition observed in the homopolymer is truly such a transition. The slower crystallizing copolymers all show regime II–III transitions, despite the presence of the second phase, and it is only when their crystallization rates become fast at the very high supercoolings that the change of slope occurs bringing them into conformation with the homopolymer behavior. So it appears that the phenomenon is a one associated with very fast crystallization rates and that it begins for the homopolymer at what has been identified as the regime II–III transition in that polymer. If this is indeed the case then the 'regime II–III' transition in the homopolymer may arise for some other reason. Since the behavior of the homopolymer and the copolymers is merged, and there is no discernible difference based on comonomer content, then, the implication would be that a disordered phase, which is capable of accepting the hexyl groups, is forming on the growth face of the growing lamella as an intermediate state. This phase could be a mesophase, the hexagonal phase, or simply a highly disordered orthorhombic phase containing many defects, such as buried folds, chain ends, etc. At a later time, or on cooling to ambient, this phase transforms to the orthorhombic state. Just such a phenomenon is known to occur in the crystallization of nylon 66 [28,29] where initial crystallization is into the hexagonal state, and conversion to the final structure occurs on cooling. Such an intermediate state has been suggested for polyethylene by Keller et al. [30]. In the case of nylon 66, the crystallization is now believed to occur by surface roughening, due to the presence of hydrogen bonds on the growth face, and not by secondary nucleation [29]. It is quite possible that the high linear growth rates, observed in the 'regime III' region of the linear polyethylene, are not consistent with a secondary nucleation process and correspond to the intervention of a surface roughening mechanism. If such a mechanism naturally gives rise to a mesophase or defective hexagonal structure (as it does in nylon 66) then it is indeed possible that the merging of the copolymer behavior with that of the linear polymer is also a switch to such a mechanism.

However, such an explanation, requiring a change of mechanism to a surface roughening mode, would seem to be in conflict with the observation that the plots of melting point versus reciprocal lamellar thickness are linear over the entire crystallization range. It has always been a cornerstone of regime theory that changes of regime do not affect that relationship, but that changes of mechanism cause changes of slope in that plot. There is currently no report in the polymer literature of a change from secondary nucleation to surface roughening, or vice versa. In the absence of evidence to the contrary, the linearity shown in Fig. 11

will be taken as evidence of a single mechanism operating across the entire crystallization range of linear polyethylene and that the slope changes correspond to regime transitions.

The merging of the copolymer rate data with that of linear polyethylene must then be taken as conformity with the linear polyethylene mechanism, but one in which the rate controlling formation of critical nuclei is insensitive to the presence of comonomer units. For this to be the case, the critical nucleus cannot have perfect orthorhombic packing. A plausible explanation that satisfies the criteria is that the initial deposition on the growth face is a partially ordered structure, into which the hexyl groups can be incorporated. For the trend in Fig. 11 to be observed, it would be necessary for this partially ordered surface species to be present throughout the entire crystallization range. It would therefore be the formation of this species that would control the initial lamellar thickness. Such a suggestion has been made by Keller et al. [28], but as a possible generality. Subsequent, and probably rapid, transformation to the perfect orthorhombic state would then ensue causing a change in the lamellar thickness. In the case of the copolymers this transformation would result in a change in lamellar thickness and also a rejection of the hexyl groups to the fold surface.

Such a partially ordered species on the growth front could transform to either the orthorhombic, hexagonal or monoclinic forms in the copolymers at atmospheric pressure in conformity with the applicable phase diagram. In regions where the hexagonal crystal is the preferred form it would most likely result in the hexagonal form on transformation, and vice versa. However, the probability of forming the alternative species may remain finite, perhaps due to molecular weight dependence, and should the transformation proceed to the less-preferred form then this would result in a major impediment to further growth. The errant surface species would have to return to the partially ordered state and retransform for crystallization to proceed. Such a mechanism would provide an adequate explanation for the unexpectedly low rates of linear growth of the orthorhombic spherulites in the presence of the hexagonal crystals. In other words a form of surface poisoning would occur.

A ubiquitous partially ordered intermediate on the growth face capable of transforming to either the hexagonal or orthorhombic forms would also allow for the concurrent growth of the orthorhombic species and a second crystalline form, as reported here and, observed more clearly at elevated pressures [23]. Clearly the formation of the second form is favored by the presence of hexyl groups and by the application of elevated pressures. This could arise because of the crowding in the folded surfaces making the energy of those surfaces lower in the case of the crystals of the second form. It could also result from a change in the chemical potential of the system and be much more basic in nature. If copolymers were to be treated thermodynamically as two component systems than an extra degree of freedom would be present in the phase diagrams of the copolymers. It would result in two phases being able to coexist in equilibrium over wide ranges of both temperature and pressure. As such it would generate a whole new perspective on the behavior of crystalline polymer systems. Much more extensive work aimed at exploring this possibility is currently underway.

It would seem unlikely that a metastable crystalline intermediate formed at the growth front would retain its initial structure and condition for very long. It would be expected to reduce its free energy by annealing processes, which would result, for the copolymers, in the ejection of substantial numbers of hexyl branches to the fold surfaces, or even the lateral surfaces, of the crystals. Such a process, if not occurring spontaneously from the intermediate phase and if not orthorhombic, would naturally occur when a transformation to the orthorhombic phase occurred. Such processes could be occurring immediately after the crystals are formed, if there is adequate molecular mobility, or perhaps later during storage at ambient temperature, or both. The hexagonal crystals formed at elevated pressures in both *cis*-polyisoprene [26] and linear polyethylene [27] convert to other phases on return to atmospheric pressure. The stabilization processes could occur so rapidly that they would not be detected in normal characterization experiments, or they might require some form of thermal activation and hence could be studied independently. The type and character of the stabilization processes will be controlled to some extent by the detailed structure of the folded surface. Presumably, this crystallization process is very similar to the Flory switchboard model, there being many tie-molecules. Also the number of adjacent reentry folds will be very restricted. Under these conditions, there would be very little molecular mobility, as the ability of the molecules to snake through the crystal would be very much inhibited. If this were the case the restricted molecular mobility could result in the potential annealing processes, outlined above, occurring quite slowly, or not at all. These restrictions would lead to very complex morphological structures on a micro-scale, as the crystals stabilize, involving the crystals, the interfacial regions and the interlamellar material. They would also lead to complex molecular trajectories and hence network structures. It would be these morphological-molecular features that would interact to control the resultant mechanical and physical properties. The ultimate properties, such as strain to failure and fracture toughness might be affected most by these features.

Additional information present in the kinetics data relates to the mechanism of regime transitions. The regime I–II transition is well established as a unique point at which [6] the rate of secondary nucleation equals the rate of surface spreading [12] and the data point can be analyzed to yield both quantities at that temperature. The approach was used by Lambert and Phillips, to analyze the effect of comonomer content on fractions of ethylene–octene copolymers, from slurry based Zeigler–Natta synthesis. As has been pointed out earlier these fractions are now

Table 4
Results of regime analyses

Sample	Equilibrium melting point[a]	Transition temperature (°C)	Transition supercooling (°C or K)	Growth rate at transition (cm s^{-1})	Rate i (10^6 cm^{-1} s^{-1})	Rate g (10^{-5} cm s^{-1})
Regime I–II						
LPE 13/18[b,c]	142.4	125.3	17.1	1.75×10^{-4}	458	5.2
LPE 54/101	142.7	125.6	17.1	9.46×10^{-6}	831	3.13
ZN-L-04[c]	142.3	124.2	18.1	4.47×10^{-5}	13.7	4.73
L-04	139.3	119.5	19.8	5.45×10^{-6}	199	4.34
Regime II–III						
LPE 54/101	142.7	120.8	21.9	5.45×10^{-5}	2005	4.21
L-04	139.3	113.5	25.9	1.52×10^{-5}	809	8.29
H-07	134.1	115.1	25.3	4.28×10^{-9}	6.61×10^{-4}	8.04
L-11	134.9	114.2	20.7	5.00×10^{-9}	1.59×10^{-4}	4.56

[a] Equilibrium melting points from Kim [18].

[b] NSF standard sample used by Hoffman et al. (e.g. Ref. [12]).

[c] Data from Lambert and Phillips [6].

known not to have been random copolymers [7], hence there is a need to re-evaluate the data for the polymers being considered here. The procedure followed is identical to that proposed by Hoffman et al. and used by Lambert and Phillips. Similar estimates have also been made for the regime II–III transition. It is recognized that there is not yet in the literature an analysis justifying such a procedure for this transition, so the data analysis will be very useful in indicating whether or not such an approach seems appropriate. Results obtained are presented in Table 4, together with earlier data for a lower molecular weight NBS polyethylene and a fraction of the ZN copolymers with the same comonomer content as L-04. There are several relevant observations.

First, both the regime I–II and regime II–III transitions occur at relatively constant supercoolings in accord with the original predictions of Hoffman that they are determined by thermodynamic variables, although there is more scatter for the regime II–III transition. There may be some specific trends within the scatter, which cannot be elucidated at the present time.

Secondly, when the rates of secondary nucleation are compared it is clear that the copolymers H-07 and L-11, which are subject to interference from the second phase, differ by several orders of magnitude from the other systems. This effect confirms the point made earlier that there was a dramatic suppression of crystallization rates caused by the concurrent formation of the second phase. It should be noted that this effect was not observed for the ZN fractions studied earlier [6], where it is now believed that the copolymer molecules contain non-random molecular sequences, and specifically long polymethylene sequences [7].

Thirdly, the rates of secondary nucleation at the regime II–III transition are reduced for the random copolymers compared to the linear polyethylene, similar to observations that can be made for the regime I–II transition.

Fourthly, the rates of surface spreading for all systems studied show very little variation with comonomer content, comonomer distribution or regime, or the presence of the second phase, despite significant differences in the actual regime transition temperatures. It therefore appears that this rate may be determined by some factor not currently incorporated into regime theory. Since, all the polymers have molecular weights above the entanglement limit, it may be that the rate of surface spreading is controlled by the rate of disentanglement of molecules in the vicinity of the growth front. Alternatively, it may reflect the presence of an adsorbed layer on the surface of the crystal and would be then related to the mechanism of formation of a partially ordered critical nucleus within that layer.

A further piece of information that can be gleaned from the data is the size of the critical nucleus in the regions for which secondary nucleation appears to be well-established. This procedure requires use of the Andrews' equation at a constant crystallization temperature, as derived originally [22]. This approach assumes that the critical nucleus size does not change in a copolymer if the comonomer units are excluded from the crystals. Hence a plot of logarithm of growth rate versus impurity group content leads to a slope, which is essentially the number of crystallizable units in the critical nucleus. If the lamellar thickness is known, then the number of crystallizable units in a single stem can be calculated, and from that information the number of stems in the critical nucleus can be estimated. This approach has not been used very frequently since the necessary data have generally not been available; usually due to the crystallization range moving to lower temperatures as comonomer content is increased. A lack of an adequate number of comonomer concentrations has also been a continual impediment to such studies.

Only two previous studies have been conducted but both resulted in similar conclusions: namely that (a) in *cis*-polyisoprene [22] the critical nucleus is 3 stems at −26°C and (b) in cross-linked linear polyethylene [31] the critical nucleus size ranges from 2 to 4 dependent on temperature.

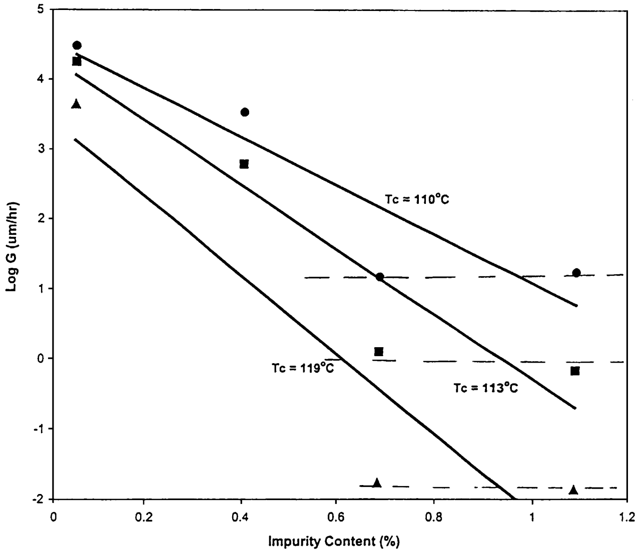

Fig. 14. Andrews' plot of logarithm of radial growth rate versus impurity content for linear polyethylene and its random octene copolymers.

In the study being reported in this publication, estimates can be made for temperatures between 110 and 119°C. In this case the analysis is complicated by the presence of the hexagonal phase in H-07 and L-11 in this temperature range. The data are plotted in Fig. 14, where lines are shown giving best fits for the data points available. The number of stems in this case corresponds to 2.9 at 119°C (regime II) and 2.1 at 110°C (regime III) with errors being in the neighborhood of 30%. This level of accuracy is typical of this type of analysis since the number of points is determined by the limited number of comonomer contents available, combined the necessity of all points corresponding to the same regime. It is, however, clear that the data for L-11 and H-07 are essentially the same, and that the growth rates are indistinguishable. The effectively zero slopes in this region of the plot would translate into an infinitely large secondary nucleus, indicating that the approach is not appropriate when the second phase is present. It also indicates that it has a pervasive influence on the crystallization process well beyond what might be expected on the basis of a simple coexistence of two phases.

If only the linear polymer and the L-04 copolymer are considered, then the slopes at 119°C and 113°C result in estimates of 3–4 stems per critical nucleus, still consistent with the data obtained from the two earlier studies [22,31]. The result, despite the magnitude of the uncertainty, is very clear and very important since it demonstrates that the critical nucleus is composed of multiple stems, whereas the most advanced forms of secondary nucleation theory, due to Hoffman et al. assume a single stem nucleus. Hence they cannot be expected to apply exactly to any polyethylene outside of regime I. The concepts of secondary nucleation theory and of regime theory remain valid, but the current versions of secondary nucleation theory cannot be expected to be quantitative in their predictions of behavior. Recent simulations of crystallization by Muthukumar et al. [32] have predicted exactly the behavior observed in the studies being reported here.

The formation of a multiple stem nucleus is completely consistent with the idea of a disordered intermediate on the growth face, and with its formation being the rate controlling step in crystallization. In other words, the formation of a monolayer cluster of three to four stems partially aligned with themselves and with the underlying crystal substrate is the rate-controlling event. They then reorganize in a subsequent step into the crystal form dictated by the phase diagram, probably in a rapid fashion. The reorganization will be aided by the well-known presence of chain mobility due to the α-relaxation process. The degree of disorder and misalignment within the cluster would be expected to vary considerably with temperature, i.e. supercooling.

At low supercoolings, the cluster might be close to perfectly aligned and the rejection of side branches would occur simultaneously with the formation of the cluster. As supercooling is increased the disorder and misalignment within the cluster would increase also, permitting the presence of buried folds, chain ends and the occasional side chain. At the highest supercoolings, side chains could be easily accommodated in the cluster on a short time scale, in accord with the experimental observations. It should be remembered that the concentration of side chains being considered here is always less than twelve per 1000 carbon atoms. At this concentration only one out of every two clusters of four stems would need to accommodate a single side chain during formation of the cluster for complete solubility of the side chains in the crystal.

The formation of such clusters on the growth front of the crystal would be expected to increase dramatically with supercooling, and give rise to increases in the rate of surface nucleation, which, in turn, lead to changes in regime. This picture is not very different from the picture developed earlier [33] of cluster nuclei with internal adjacent reentry folds. However, now, the model consists of partially aligned stems in a cluster, and the tight folds are to be regarded as loops. The fully ordered cluster of the past [33] is now achieved through completion of order within the cluster and the conversion of the loops to tight folds. It is the formation of the cluster, and the degree of order within it, that is responsible for the magnitude of the Ψ factor of secondary nucleation theory [11,12,33].

5. Conclusions

A bulk unfractionated linear polyethylene has been shown to exhibit three distinct slopes, that have been identified as regimes, of radial spherulitic growth when crystallized using a combination of isothermal studies and rapid cooling studies covering the crystallization temperature range from 90 to 129°C. It behaves conventionally over the range considered in the sense that the crystal structure observed in later experiments is orthorhombic throughout, the melting curves are not unusual and the lamellar thickness–inverse supercooling curve shows no changes of slope. The melting peak observed ranged from 131.4 to 139.5°C.

The random copolymers show up to three different ranges of radial growth rate in the isothermal temperature range studied, which can assigned to all three regimes of growth. Increasing branch content shifts regimes from the I–II transition to II–III transition and reduces the growth rate significantly. However, the behavior is significantly modified for copolymers with hexyl branch contents of seven or more per 1000 carbon atoms, through the intervention of a co-existent phase, assumed to be hexagonal or monoclinic. Analysis of growth data at regime transitions demonstrates that the principles already established for the regime I–II transition carry over to the regime II–II transition. They also show that the rate of surface spreading is relatively insensitive to comonomer content, molecular weight, regime and the presence of the second crystalline phase. It is suggested that it may be controlled by the rate of disentanglement of the molecules, which may, also, control the formation of a partially ordered intermediate on the growth face. Analysis of the behavior using the Andrews theory of copolymer crystallization in the regions that are indisputably controlled by the secondary nucleation process shows that the critical nucleus size is 3–4 stems for regimes II and III. These are consistent with previous estimates for less mobile systems and also with recent computer simulations of the crystallization process. They demonstrate that when secondary nucleation does occur outside of regime I, it does so through the formation of a multiple stem nucleus. It is suggested that this multiple stem nucleus is the partially ordered intermediate, and that its rate of formation controls the secondary nucleation process.

When studies are extended to very high supercoolings, for the copolymers, in which the polymer generates its own pseudo-isothermal crystallization temperature, the applicable existing regime III region is continued for a restricted range of temperature. When very high supercoolings are approached a new form of crystallization occurs, in which the comonomer units are no longer excluded and molecular weight dependencies appear to be eliminated. The copolymers become indistinguishable from one another on the basis of their spherulite growth rates and are also indistinguishable from the regime III region of the linear polymer.

The mechanism for this new type of behavior has not yet been established, but it appears to be due to the intervention of a partially disordered intermediate, capable of dissolving hexyl side-chains, on the growth face. However, it must do so without changing the fundamental nature of the rate-controlling process on the growth front, since the behavior conforms to that of the linear polymer in that high-supercooling range. So, the intermediate phase may indeed be simply a partially ordered orthorhombic monolayer cluster containing substantial chain ends and hexyl groups at high supercoolings, which rapidly lowers its free energy by adjusting its structure to the required crystal form.

A model has been suggested, to account for all of the experimental observations, in which secondary nucleation occurs through the formation of a partially ordered cluster of three to four stems on the growth face, in which the degree of disorder is strongly dependent on the supercooling. It is the formation of this partially ordered cluster that is the rate controlling event in secondary nucleus formation.

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