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Crystallization Kinetics of Low Molecular Weight Fractions of Branched Polyethylenes

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ABSTRACT: A series of cross-fractionated branched polyethylenes of M_w about 18 000 and branch contents from zero to 22 branches/1000 carbons have been studied. Both linear growth rates and bulk growth rates have been determined using optical methods. It is demonstrated that increased branching causes the regime I–regime II transition to translate to lower temperatures. This occurs through a greater reduction of the rate of secondary nucleation relative to the reduction that occurs in the rate of surface spreading. Bulk kinetic data can be used to define regimes in polyethylenes to within a few degrees but cannot be used to estimate rates of secondary nucleation and surface spreading or to determine fold surface free energies.

Introduction

Polyethylenes have found a wide range of uses today, thus making them one of the most widely studied polymers. Recently, with the advancement of synthetic processes, a commercially important class of polyethylenes has evolved, namely, linear low-density polyethylenes (LLDPE). LLDPEs are produced through the copolymerization of ethylene and comonomers such as hexane or octene, thereby producing butyl or hexyl branches, respectively. Because of the nature of the heterogeneous catalysts used and of the higher probability of a termination reaction at the comonomer, the copolymer molecules exhibit a heterogeneous composition. The branches are preferentially located in the shorter molecules; thus, to a first approximation, the bulk LLDPE behaves as if it were a blend of high molecular weight linear molecules and branched low molecular weight molecules. Upon crystallization these different species tend to fractionate making the entire crystallization process complex. The fractionation process tends to reinforce and intensify the separation of spherulitic crystallization into two processes: (1) primary crystallization of dominant lamellae forming the skeletal framework of the spherulites and (2) secondary crystallization. In the case of LLDPE the dominant lamellae are believed to be formed by the linear molecules, with secondary crystallization primarily arising from the branched molecules. The research being reported aims to further the understanding of the combined effects of microstructural defects and molecular weight on crystallization.

Understanding of the crystallization process in LLDPEs is hampered by a lack of understanding of the crystallization behavior of the branched molecules. Since there is no evidence pointing to a separation of the branched molecules from the linear molecules in the molten state, it has to be presumed that the fractionation process occurs at the growth face and is intimately related to the behaviors of the different molecules during nucleation and growth. The behavior at the growth face is a function of two separate, but related, processes. The first process is the deposition of secondary nuclei on the growth face, the second process being the subsequent growth along the face at the niches formed by the secondary nuclei. In practice, the relative rates of these two processes, secondary nucleation and surface spreading, determine the regime in which crystallization occurs.

Lauritzen and Hoffman first introduced the concept of regime transitions in 1972,[1] with experimental verification of the regime I–II transition shown in polyethylene fractions.[2] Phillips[3] shortly thereafter predicted the existence of a third regime for which Hoffman[4] derived the mathematical relationships of regime III crystallization.

The general form of the secondary nucleation theory rate equation is

$$G = G_0 \exp\left[-\frac{U*}{R(T-T_\infty)}\right] \exp\left[\frac{K_g}{T\Delta Tf}\right]$$

where G is the linear growth rate, $U*$ is the activation energy for transport of the segments to the crystallization site, R is the gas constant, T is the crystallization temperature, and T_∞ is the temperature at which all motions associated with viscous flow cease, defined as $T_g - 20$ °C. ΔT is the undercooling, $T_m° - T$. K_g is defined as $K_g = nb\sigma\sigma_e T_m°/\Delta H_f° k$ where n is 4 for regimes I and III and 2 for regime II. f is a correction factor used to compensate for changes in $\Delta h_f°$ with temperature at high undercoolings, defined as $f = 2T/(T + T_m°)$.

Regimes may most easily by envisioned as resulting from the relative rates of two competing processes: secondary nucleation and surface spreading. If the rate of deposition of secondary nuclei is i and the rate of surface spreading is g, then if expressed in units of area covered per unit time, the regimes correspond to the following conditions:

regime I	$i \ll g$
regime II	$i \sim g$
regime III	$i > g$

Molecular variables will influence the regime transition temperatures through their effects on these two rates. In the classical theories of crystal growth, $g \gg i$ because of the much lower surface free energy penalty on deposition of a crystallizing unit into a niche than onto a flat surface. Because of this effect, it can be predicted that g will be more dependent on the mobility of the polymer chain than i. The polymer chain can move into crystalline register through several possible mechanisms of chain motion.[5-8]

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One of the most important mechanisms is reptation[9] which was introduced into secondary nucleation theory by Hoffman.[10]

While the existence of regimes is now accepted, until recently little consideration had been given as to how molecular variables influence regimes and regime transition temperatures. Andrews et al.[11] used *cis*-polyisoprene to show that there is an inverse logarithmic relationship between linear growth rate and microstructural impurity levels; however, this study preceded the concept of regimes by several years. More recently, Phillips and Lambert[12] reported on the influence of cross-linking on regimes and regime transition temperatures for cross-linked linear polyethylene. It was shown that there were competing effects. Through control of the mobility of the polymer chain, reptation, or a lack of it, was of prime importance. Incorporation of microstructural impurities onto the main chain of the polymer produced copolymer effects similar to those reported by Andrews et al.[11] Phillips and Lambert interpreted their results by considering the effects of the molecular variables on the relative rates of secondary nucleation and surface spreading. It was concluded that suppression of reptation greatly reduced the rate of spreading and increasing copolymer content reduced the rate of secondary nucleation.

In the case of branching, which may be regarded as a form of copolymerization, it would be expected based on the earlier results of Phillips and Lambert[12] that the primary effect of increased branching on the crystallization process would be through a reduction of the rate of secondary nucleation, if the comonomer unit is excluded from the crystal.

There is the additional complication that the branch content might also be expected to reduce the rate of reptation through an increase in frictional resistance. However, such reptation rate changes are not documented in the literature but can be assumed to be less influential than the changes in the rate of secondary nucleation as additional frictional forces are the result of short branches, which would not be expected to influence reptation to the same degree as long chain branches, as is the case of low-density polyethylene. To a first approximation, therefore, it might be predicted that increasing the branch content should decrease the rate of secondary nucleation, i, relative to the rate of surface spreading and so should increase the range of supercooling over which a regime I exists.

In the broader application to the behavior of unfractionated LLDPEs it is recognized that the behavior at the growth face will be determined by the fastest rate of secondary nucleation, i, and the fastest rate of spreading, g. So there exists the distinct possibility that one rate could be controlled by linear molecules and the other by branched molecules. It is also recognized that the behavior will be applicable to all copolymers in which the comonomer unit is excluded from the crystal.

Bulk crystallization rates are also of importance but contain many additional changes such as those in primary nucleation rates, splaying and branching of crystals, etc. Nevertheless, they have been used by Alamo and Mandelkern et al.[13] and ourselves[12] as indicators of regime transition temperatures and are appropriate if special conditions apply. It is of considerable interest to determine the relative degrees of importance of primary and secondary crystallization to bulk kinetics in these systems where fractionation can occur in significant amounts. In this study, we will report a comparison of such data obtained from both linear and bulk growth rate studies, providing for the first time a quantitative comparison of the two approaches.

Table 1. Molecular Characteristics of the Fractions

sample	M_w	M_w/M_n	branches/1000 CH_2
H-1	18 120	1.39	0
S-4	23 600	1.47	4.22
S-1	18 600	1.12	11.17
S-7	17 500	1.15	21.75

This paper will report the behavior of a series of fractions of weight-average molecular weight ca. 18 000 and having branch contents from zero to 22 branches/1000 carbon atoms. These fractions have been produced using cross-fractionation using temperature rising elution fractionation (TREF) and gel permeation chromatography (GPC) to allow fractionation by both molecular weight and branching content independently. Because of this, segregation during crystallization, as usually occurs in LLDPEs, will not occur to any major extent in these materials. These samples have been chosen as this molecular weight is particularly well-behaved and shows a well-established regime I–regime II transition. The companion paper will consider the combined effects of molecular weight and branching content.

Experimental Section

LLDPE fractions were supplied by The Dow Chemical Co. The samples, denoted by the prefix S, contain octene as the comonomer and have been cross-fractionated using gel permeation chromatography (GPC) and temperature rising elution fractionation (TREF), which allows separation by both molecular weight and branch content. Branch contents were determined by NMR. The linear growth data for sample H-1 was taken from the work of Hoffman et al.[2] Table 1 gives the molecular weights, molecular weight distributions, and branch contents of the samples.

Crystallization kinetics were obtained through optical microscopy. Bulk growth kinetic measurements were made using the change in transmitted light intensity[14,15] measured continuously with a photomultiplier attached to the column of the Reichert-Neovar-Pol polarizing microscope with attached Mettler hot stage and temperature controller. Linear growth kinetics measurements were made using an Olympus polarizing microscope with an attached 35-mm camera and temperature-controlled Mettler hot stage. Photographs were taken as a function of time so that the change in the morphological size could be measured. Samples were held in the melt at 155 °C for 15 min prior to all experiments, before being rapidly quenched to the crystallization temperature.

Results

The effect of branching on the rate of crystallization can be seen from plots of both reciprocal half-time and the linear growth rate versus temperature. Figure 1, showing reciprocal half-time versus temperature, demonstrates that at constant temperature branching reduces the rate of bulk crystallization as seen by the leftward shift in the curves from the least branched S-4 to the most highly branched S-7 (bulk crystallization data were not reported by Hoffman et al. for the linear polymer and hence not available for comparison). It can be seen that branching reduces the rates of crystallization by a factor of 9 at 121.5 °C and the crystallization temperature at 2×10^{-2} s^{-1} by 5 °C from S-4 to S-7.

Figure 2 shows typical linear growth rate data for sample S-4, linear growth rates being obtained as the slope of such lines. The variation of linear growth rate with temperature is shown in Figure 3. The linear growth rate of S-7 is reduced by a factor of 1350 compared to H-1 at

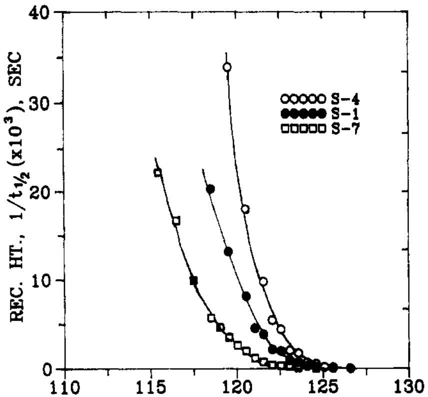

Figure 1. Reciprocal half-times as a function of crystallization temperature.

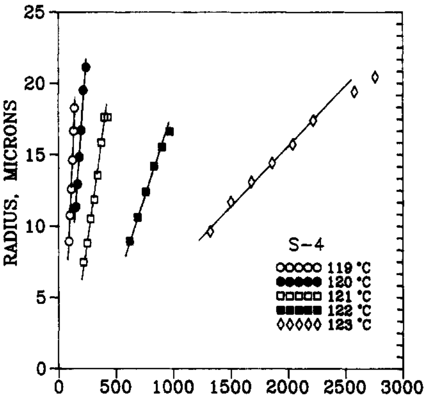

Figure 2. Radius as a function of crystallization time for selected temperatures for sample S-4.

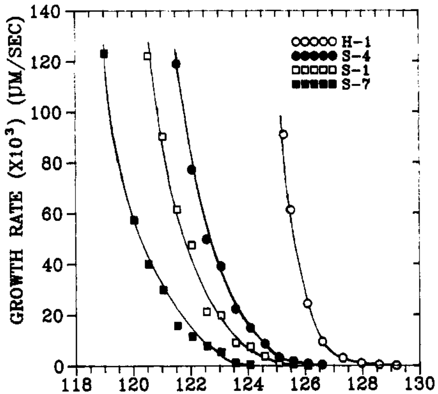

Figure 3. Linear growth rates of the fractions as a function of crystallization temperature.

124.5 °C, while the crystallization temperature is reduced at 60 × 10^{-3} μm/s from approximately 126 to 120 °C from H-1 to S-7.

Discussion

Before a discussion of the kinetics analysis can begin, consideration must be given to the values of $T_m°$ and Δh_f used in the analysis. $T_m°$ is important to secondary nucleation theory as it has a major influence on regimes and regime transition temperatures. Attempts were made at determining its value from plots of T_m versus T_c obtained from DSC experiments. As in the work of Alamo et al.,[16] extrapolations for $T_m°$ were difficult and often led to unrealistic, apparently arbitrary values of $T_m°$. For this reason, values of $T_m°$ have been calculated. There are two corrections that can be made to the equilibrium melting point of 144.5 °C characteristic of a polymer having an infinite molecular weight and no comonomer units. These are the correction of Flory and Vrij[17] and the copolymer content correction of Flory.[18] Values of $T_m°$ calculated using only the copolymer correction are designated $T_m°(1)$, and those calculated using both copolymer and molecular weight corrections are designated $T_m°(2)$. The latter are assumed to be the most accurate. The predicted values for $T_m°$ have been included in Table 2 together with experimentally determined values for $\Delta h_f°$. $\Delta h_f°$ was determined from the latent heat of melting using DSC and the percent crystallinity from wide-angle X-ray diffraction as $\Delta h_f° = 100\Delta h_f$/crystallinity. The predicted values for $\Delta h_f°$ were taken from the work of Knox[19] and correlate well with the experimentally determined values. $\Delta h_f°$ can be seen to decrease with increasing branch content, presumably due to a disruption of the crystal packing and perhaps also internal strain caused by changes in surface structure. The predicted values for $T_m°(2)$ and of $\Delta h_f°$ have been used in the secondary nucleation analysis of the series and for the plots to be found in Figure 4. A value of 1500 cal/mol has been used for U^* and −70 °C for t_∞.

Table 2. Melting Point and Latent Heat of Fusion

sample	$T_m°(1)^a$	$T_m°(2)^b$	Δh_f(exp) (J/g)	Δh_f(pred) (J/g)
H-1	144.5	142.4		288.7
S-4	143.7	142.3	256.2	256.3
S-1	142.1	140.2		238.9
S-7	139.2	137.1	188.4	212.5

[a] $T_m°(1)$ = 144.5 °C used to calculate $T_m°$ from the copolymer[18] equation. [b] $T_m°$ = 144.5 °C used in the Flory–Vrij equation[17] to calculate $T_m°$ values which were then used to calculate $T_m°$ from the copolymer[18] equation.

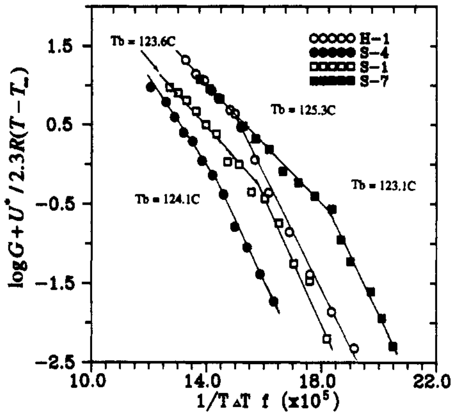

Figure 4. Secondary nucleation plots of linear growth rates using predicted input parameters and $T_m°(2)$ values.

Figure 4 shows that crystallization occurs in both regime I and regime II for the entire series of branched molecules. The regime I–II transition shows branch content dependency shifting from 125.3 °C in the linear polymer to 123.1 °C in the polymer having 22 branches/1000 methylenes. σ_e can be calculated from the slopes of the lines in regimes I and II assuming σ is equal to 11.8 erg/cm² from the work of Hoffman and Miller.[21] Table 3 gives the results of the kinetic analyses and shows σ_e to decrease with increasing branching, suggesting increased formation of loose loops and nonadjacent reentry folding. This, in turn, would lead to an increase in the thickness of the interfacial region with increased branch content, as has been suggested earlier by Mandelkern.[20] It can also be seen from Table 3 that increased branch content results at first in an increase but then in a decrease in the value of the undercooling at which the regime transition occurs.

Table 3. Parameters Derived from Kinetic Analyses

sample	log G_0	σ_e (erg·cm^{-2})	I–II transition (°C)	I–II supercooling (°C)
A. T_m°(1) = 144.5 °C for H-1, with Others Calculated from the Flory Equation				
H-1	13.16 (I)	105.6	125.3	19.2
	7.28 (II)	111.8		
S-4	11.56 (I)	88.3	124.1	19.5
	7.95 (II)	122.0		
S-1	14.12 (I)	94.5	123.6	18.4
	6.82 (II)	93.1		
S-7	15.81 (I)	86.0	123.1	16.1
	6.93 (II)	79.0		
B. T_m°(2) = 142.4 °C for H-1, with Others Calculated from the Flory and Flory–Vrij Equations				
H-1	11.32 (I)	81.0	125.3	17.1
	6.57 (II)	89.5		
S-4	10.51 (I)	75.0	124.1	18.2
	7.59 (II)	109.0		
S-1	10.79 (I)	66.2	123.6	16.6
	6.93 (II)	86.9		
S-7	13.30 (I)	63.9	123.1	14.0
	6.12 (II)	61.7		
C. T_m° = 144.5 °C, Assumed Constant for the Series				
H-1	13.16 (I)	105.8	125.3	19.2
	7.28 (II)	111.8		
S-4	12.23 (I)	109.8	124.1	20.4
	7.74 (II)	138.6		
S-1	16.54 (I)	138.4	123.6	20.9
	7.64 (II)	130.0		
S-7	22.34 (I)	220.9	123.1	21.4
	9.06 (II)	179.7		

Hoffman and Miller[21] discussed the concept of reptation in polymers and used secondary nucleation theory and experimental results to estimate the two kinetic parameters *i* and *g*. This important analysis permits the actual values of *i* and *g* to be estimated at the regime I–regime II transition temperature. We have carried out a virtually identical calculation for the series of branched polymers studied but have not been able to allow for the change in molecular viscosity with branching due to a lack of literature data. The equations used are too detailed to reproduce here; however, all calculations are the same as those of Hoffman and Miller[21] except for those used to calculate *i* and *g*. Hoffman and Miller[21] calculated G_I and G_{II} using expressions in $Z_I(\lambda)$ and $Z_{II}(\lambda)$. We have chosen to use the simple method of using the experimental value of *G* at the regime I–regime II transition and the equations[21]

$$i = G_{II}^2/2b_0^2g$$

$$L = G_I/b_0i$$

which are identical to those used by Hoffman and Miller.[21] The values of the constants used in the calculations are those of Hoffman and Miller[21] with the exception of T_0, the reference temperature of the monomeric friction coefficient, which was 455 K rather than their value of 450 K. Table 4 summarizes the results for this estimation of the kinetic parameters of the series.

Table 4. Regime Transition Analysis Results (Conditions as in Table 3)

sample	$I \times 10^{-6}$ (nuclei cm^{-1} s^{-1})	$g \times 10^5$ (cm s^{-1})	L (Å)
A. T_m° = 144.5 °C (Corrected Using the Flory[18] Equation)			
H-1	455	5.28	48.2
S-4	15.1	4.29	248
S-1	6.9	3.47	318
S-7	3.5	2.49	395
B. T_m° = 142.4 °C (Corrected Using the Flory[18] and Flory–Vrij[17] Equations)			
H-1	458	5.25	47.9
S-4	13.7	4.73	263
S-1	6.48	3.69	338
S-7	3.16	2.74	416
C. T_m° = 144.5 °C (Uncorrected)			
H-1	526	4.54	42
S-4	17.8	3.64	202
S-1	10.1	2.37	217
S-7	9.2	0.94	143

As can be seen, branching affects both *i* and *g*, but to different degrees. The introduction of branches results in a greater reduction in the rate of surface nucleation than in the rate of lateral spreading. The reduction in the rate of nucleation is due to the rejection of branches from the crystal, since only branched-free segments are able to nucleate in accord with the theory of Andrews et al.[11] Branching also reduces the rate of lateral spreading, *g*, but to a lesser degree than *i*. As more branches are added, both *i* and *g* continue to decrease, but at rates which are similar to one another. The most obvious effect on crystallization is the reduction of *i* by the initial introduction of branches. The values of the substrate width, *L*, show a clear increase with branch content for the calculations made using both corrected values of T_m°, increasing from ca. 50 Å for the linear polymer to 400 Å for the most highly branched polymer. This 8-fold increase in the niche width is quite consistent with the noted reduction in the rate of secondary nucleation, *i*, being much larger than the reduction in the rate of spreading, *g*. It is noted that our value for *L* for the linear polymer of ca. 50 Å is significantly less than the value of 210 Å computed by Hoffman and Miller.[21] As noted earlier, the only significant difference was our use of the experimental value of *G* at the regime I–regime II transition rather than computed values. The significance of the work reported lies not in the absolute calculated values but in the relative values obtained as a function of branching.

The effect of copolymerization on the rate of secondary nucleation was predicted by Andrews et al.[11] and is due to the reduction in the probability of nucleation caused by the need to find uninterrupted sequences of methylenes of a given minimum length. It is not clear why the rate of lateral spreading should be influenced to a lesser degree. It is recognized that the reptation rate is just large enough to permit the observed values of *g* and the reeling-in rate for the linear polymer. It would be reasonable to assume that the presence of branches would reduce the rate of reptation and, through it, the rate of lateral spreading, *g*, but the magnitude of the change observed here appears excessive. In the absence of literature data on the influence of branching on reptation rates the situation cannot be critically examined. An alternative mechanism for the reduction in rate is plausible. In the case of lateral spreading the branches must be excluded from the crystal as in secondary nucleus formation, but specifically the necessary uninterrupted length of the chain needed is a single stem length. Presumably the effect is related to the likelihood of the additional stem coming from the same molecule through adjacent reentry folding or from an adjacent molecule. The intrinsic probability of the stem from the same molecule containing a branch unit must be greater than that of the stem from another molecule containing a branch unit, simply because an uninterrupted sequence of methylene units of at least one stem length was used in the preceding deposition. On an a priori basis, therefore, it would be anticipated that a strictly adjacent reentry folding process would give rise to a rate of surface spreading that decreased at a more rapid rate with increasing branch content than if the surface spreading process involved other molecules. We are, therefore, led to the conclusion that an increasing concentration of branches results in an increasingly larger fraction of the surface spreading process involving adjacent molecules and hence nonadjacent reentry folding and/or ciliation.

A reduction in the rate of secondary nucleation relative to the rate of surface spreading should result in a greater fraction of adjacent reentry folding if the Hoffman–Lauritzen model[1] is strictly applied. However, studies of Voigt-Martin,[22] Mandelkern, and co-workers[16,23-25] clearly demonstrate tht the interfacial layer content increases with branch content. The conclusion reached in the preceding paragraph that an increasingly large fraction of nearby molecules add during the surface spreading process is consistent with the interfacial evidence. Branches are rejected to the folds, which may expand somewhat to accept them, or to cilia. However, it is the addition of adjacent molecules during the surface spreading process that is the major generator of interfacial volume through the production of cilia.

In order to determine the influence of the calculations made using the Flory equation on the results, a further analysis was made using a constant value of the equilibrium melting point ($T_m{}^\circ$ = 144.5 °C) for all specimens. The phenomenology was unchanged, the transition temperature decreasing from 125.3 to 123.1 °C across the series. However, when the supercooling at which the regime I–regime II transition occurs are calculated, they were found to increase across the series rather than decrease. The results of these analyses were to be found in Table 3 (part C). The use of this constant $T_m{}^\circ$ also results in the generation of values of σ_e that increase dramatically with branching, reaching a value for the highest branching content which is double that of the linear polymer. As a result of these analyses, it can be concluded that the absolute value of the equilibrium melting point of the linear polymer has only a moderate influence on the quantitative results and virtually no influence on the phenomenology of the process. However, the use of equilibrium melting points which vary or do not vary with copolymer composition and molecular weight is important. There are no differences generated in the shapes of the secondary nucleation plots or on the temperatures at which the regime transitions occur. Significant differences do arise when the transition supercoolings and fold surface free energies are calculated. It was, however, demonstrated in the early studies of the regime I–regime II transition[1,2] that the use of equilibrium melting points corrected for molecular weight dependence led to the observation that the transition occurred at a constant supercooling. So the principle of structure-dependent equilibrium melting points has generally been used in regime studies. The problem that arises here is whether or not the use of the Flory equation to estimate values of $T_m{}^\circ$ is appropriate. The question may be answered when ongoing determinations of $T_m{}^\circ$ using small-angle scattering studies are completed.

Bulk kinetic data has been used in Figure 5 to analyze the kinetic behavior of this low molecular weight series using the $T_m{}^\circ(2)$ values predicted from the Flory and Flory–Vrij equations. As was the case of the linear growth data, crystallization occurs in both regime I and regime II, but the regime I–II transition temperatures differ from those in Figure 4 by 2 °C at most. The curves in Figure 5 show only horizontal shifts, as opposed to both horizontal and vertical shifts for the curves in Figure 4. Presumably these effects are caused by different influences of branch content on the mechanisms of primary nucleation, in-filling, branching, and secondary crystallization, all of which are included in the bulk crystallization measurements. Nucleation density studies (Figure 6) show that the nucleation density decreases with increasing branch content and may be partially responsible for the effect. However, the changes seen in Figures 4 and 5 are seen on a logarithmic plot, whereas in Figure 6 it is a linear plot. It therefore appears that the reductions in rate observed for the branched polymers may be attributed largely to branching and/or in-filling processes. Thus, while the bulk kinetic data may be used to assign regimes and to estimate regime transition temperatures with some small errors in this case, the bulk data may not be used to calculate the relative rates of i and g or important kinetic parameters such as the fold surface free energy, σ_e.

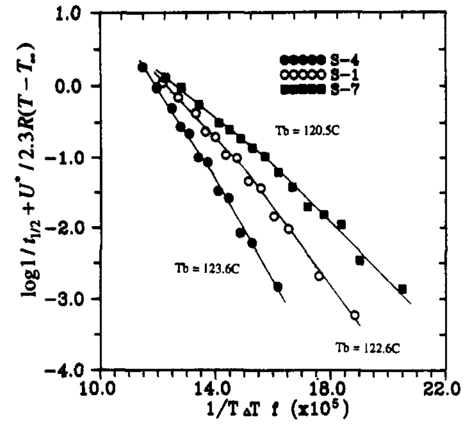

Figure 5. Secondary nucleation plots of bulk growth rates assuming heterogeneous nucleation and $T_m{}^\circ(2)$ values.

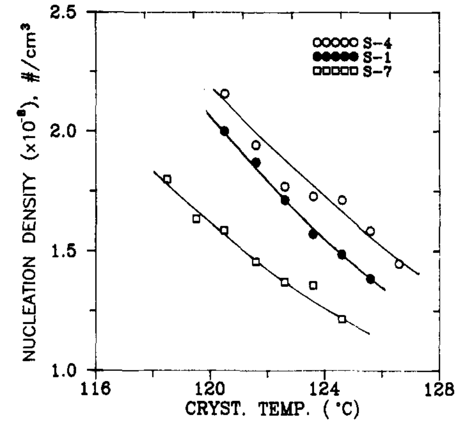

Figure 6. Nucleation density versus crystallization temperature for the branched fractions studied.

The results of the study reported here constitute a second example of the effects of chain microstructure on crystallization. In the case of cross-linked polyethylene, cross-links eliminate the ability of the chains to reptate, enabling the secondary nucleation process to dominate the growth process. Branching, on the other hand, reduces the rate of nucleation and, to a lesser degree, the rate of surface spreading. In both cases, microstructure plays an important role in determining the crystallization behavior of the branched molecules through changes in the relative rates of surface nucleation and lateral spreading. In an upcoming paper, the effect of molecular weight on the crystallization behavior of a branched polyethylenes will be discussed together with the results presented here. The results lead to a better understanding of the effects of microstructure on crystallization and the crystallization process itself.

Conclusions

1. The regime I–regime II transition translates to lower temperatures as branching increases.

2. Branching reduces the rates of secondary nucleation and of surface spreading, but to different degrees, on the basis of the analysis conducted.

3. Regime transition temperatures calculated from bulk kinetic data agree with those determined directly from linear growth rate data to within a few degrees, for polyethylenes.

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