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Crystallization kinetics of fractions of branched polyethylenes: 2. Effect of molecular weight

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Three series of cross-fractionated branched polyethylenes having molecular weights in the ranges 20 000, 60 000 and 110 000 and branch contents ranging from zero to 32 hexyl branches per 1000 C atoms have been studied. Both linear and bulk growth rates have been determined using optical methods. The two lower molecular weight groups show a regime I–regime II transition, which translates to lower temperatures as branching is increased. The highest molecular weight series shows either a regime II–regime III transition or simply regime III. The transition temperature also translates to lower temperatures as branching increases. The rate of secondary nucleation is reduced by branching, but the rate of reptation is reduced by increasing molecular weight causing the aforementioned effects. It is suggested that the appearance of the regime II–regime III transition is caused by a change in nucleation mechanism. Copyright © 1996 Elsevier Science Ltd.

(Keywords: crystallization; polyethylene; molecular weight)

INTRODUCTION

Linear low density polyethylenes (LLDPE) are an important class of copolymers whose behaviour is not well understood because of their *de facto* blend character. They are produced by copolymerization of ethylene with comonomers such as octene or hexene, thus generating short branches (in these cases, hexyl or butyl branches, respectively). The heterogeneous catalysts used result in the comonomer being located preferentially in short molecules. This results in the copolymers being, to a first approximation, a blend of high molecular weight, almost linear molecules and branched low molecular weight molecules. During crystallization the branched molecules are presumed to be initially rejected, leading to a fractionation problem at the growth front. This phenomenon tends to lead to the dominant lamellae of the growing spherulites being formed by linear molecules, with the branched species crystallizing as a secondary infilling process.

A lack of understanding of the behaviour of the branched molecules as a species has restrained understanding of the behaviour of the copolymers. It has generally been assumed that the fractionation process is a result of different characteristic behaviours of the linear and branched molecules at the growth front. There are two accepted processes occurring at the growth front, namely the deposition of secondary nuclei and the subsequent deposition of molecular strands in the niches formed between the secondary nuclei and the

underlying crystal plane. The regime of crystallization occurring is determined by the relative rates of these two processes.

The concept of regimes in polymer crystallization was first developed by Lauritzen and Hoffman[1] for regimes I and II with experimental verification following through studies of fractions of linear polyethylene[2]. A third regime was suggested by Phillips[3] and the necessary theory developed by Hoffman[4]. As mentioned above, the operating regime results from the relative rates of the secondary nucleation (i) and surface spreading (g) processes; when expressed in similar units regime I corresponds to $i \ll g$, regime II to $i \sim g$ and regime III to $i > g$. The classical theories of crystal growth correspond to regime I, as g is assumed to be much greater than i because of the lower amount of surface free energy created by deposition in a niche compared to deposition on a flat surface. Because of this very rapid equilibrium rate of surface spreading (g), it can be assumed that the measured value of g will be more dependent on the mobility of the polymer than will be i. There are several possible mechanisms of chain motion that come into play[5–8]; the most relevant is believed to be reptation[9,10].

All regions of regime theory result in the common equation

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

where G is the linear growth rate, U^* the activation energy for molecular transport in the vicinity of the growth front, R the gas contant and T the crystallization temperature. $T\infty$ is usually taken as $T_g - 20°C$ and is the temperature at which all relevant molecular transport

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becomes ineffective. ΔT is $T_m^\circ - T$, the undercooling, and f is a correction factor to compensate for changes in the free energy and heat of fusion with temperature and is usually written as $2T/(T + T_m^\circ)$.

K_g is defined as $nb\sigma\sigma_e T_m^\circ/\Delta h_f k$, with $n = 4$ for regimes I and III and $n = 2$ for regime II.

While the existence of regimes is now generally accepted, there has been little attention given to the influence of molecular variables on the transition temperatures. There can be little doubt that such variables will function through their influences on the values of the rates of secondary nucleation (i) and of surface spreading (g). Although it preceded the concept of regimes by several years, the study by Andrews et al.[11] of isomerized cis-polyisoprene remains the most informative in that it demonstrated for the first time that there was an inverse logarithmic relationship between linear growth rate and microscopic chain impurity levels. Since then the most comprehensive relevant study has been that reported by Phillips and Lambert[12] of the influence of crosslinking on regimes and regime transition temperatures. Two major influences were shown. Reptation, or its suppression, was of prime importance. A competing effect was a copolymer exclusion effect similar to that noted by Andrews et al.[11] in the isomerized cis-polyisoprenes. These effects were caused by crosslinks acting as both comonomer units and as suppressors of reptation. The rate of surface spreading was greatly reduced by reptation suppression, but the rate of secondary nucleation was reduced by increasing comonomer content.

Short chain branches in LLDPEs are essentially comonomer units and would be expected to reduce the rate of secondary nucleation, if the branches are excluded from the crystals on the basis of the aforementioned studies[11,12]. Branches might also be expected to reduce the rate of reptation but there are no such changes documented as yet in the literature. However, any such reductions would be expected to be on a much smaller scale than the reduction in the rate of secondary nucleation.

In the previous article[13], we reported on the crystallization behaviour of a series of fractions of low molecular weight polyethylenes, with branch contents ranging from zero to 22 branches per thousand carbon atoms. It was shown that branching affects both secondary nucleation and surface spreading, but to different degrees as predicted. The introduction of branches causes a greater reduction in the rate of secondary nucleation i than in the rate of surface spreading g due to the rejection of branches from the crystal, as only branch free segments are able to nucleate. It was also shown that increased branching causes a decrease in the regime I–regime II transition temperature as secondary nucleation is continually reduced. The combined influences of increasing molecular weight and increasing branch content are difficult to predict, since the reptation behaviour is very dependent on entanglement concentration and the time scale of disentanglement. This paper will report on the combined effects of molecular weight and branching on the crystallization behaviour of a series of branched polyethylenes.

EXPERIMENTAL

Most LLDPE fractions were supplied by Dow Chemical

Table 1 Molecular characteristics of branched polyethylenes

| 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
F-3	51 500	1.50	0
S-5	89 900	1.53	6.67
S-8	54 700	1.69	13.64
S-2	41 800	1.17	15.5
E-65	65 500	2.10	32.00
H-2	119 200	1.26	0
NBS 1484	119 600	1.19	0
S-6	174 700	1.57	2.86
S-3	117 500	1.64	5.46
S-9	104 100	1.62	11.05

Co. The samples, denoted by the prefix S, contain octene as the comonomer, and have been cross-fractionated using gel permeation chromatography (g.p.c.) and temperature rising elution fractionation (t.r.e.f.), which allows separation by both molecular weight and branch content. Branch contents were determined by nuclear magnetic resonance (n.m.r.).

Table 1 gives the molecular weight characteristics and branch contents of the samples. The fractions with molecular weight of approximately 50 000 will be referred to as IMWS (intermediate molecular weight series) and the fractions with molecular weights greater than 100 000 as HMWS (high molecular weight series). Sample F-3 is a linear fraction obtained from Dow Chemical, NBS 1484 a linear fraction from the National Bureau of Standards, and E-65 a hexene-based branched polyethylene fraction supplied by Exxon Corp. The latter sample was not cross-fractionated, but fractionated using t.r.e.f. only. The linear growth data for H-2 were taken from the work of Hoffman et al.[2] and used in the secondary nucleation analysis of the HMWS. In Table 1, data for the previously reported low molecular weight series (LMWS) are given, since comparisons involving all three series will be made later in the discussion.

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 kinetic 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 for the IMWS may be seen in Figure 1 for the linear growth data and in Figure 2 for the bulk growth data. Crystallization rate decreases with increasing branch content as seen by the leftward shift in the curves. Initial branching
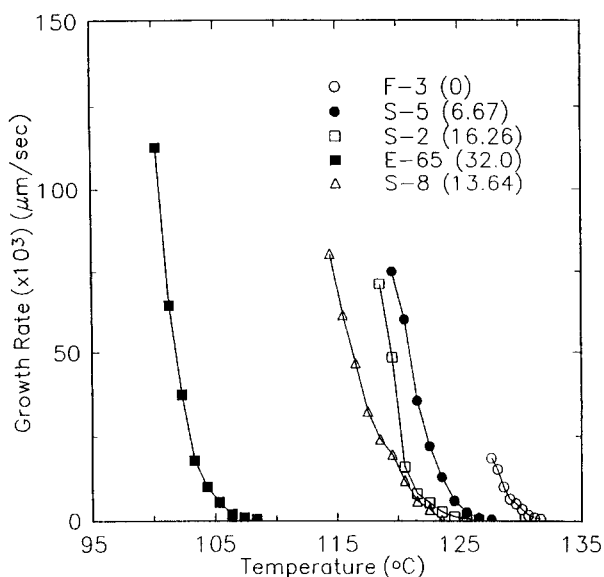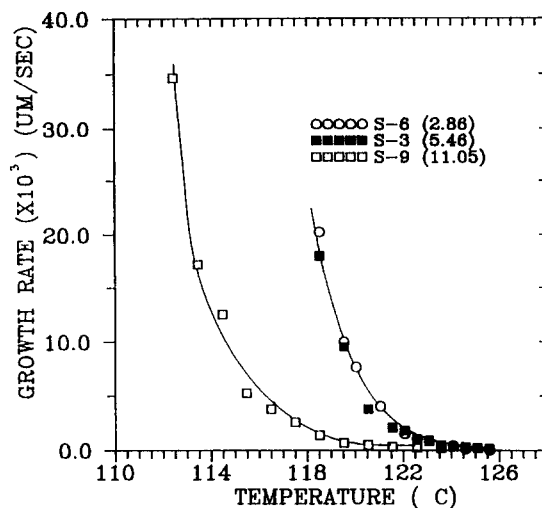
Figure 1 Linear growth rate as a function of temperature for the intermediate molecular weight series (IMWS)
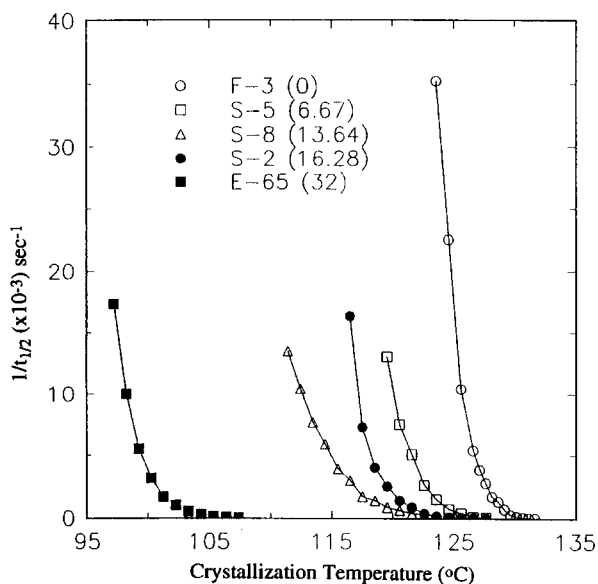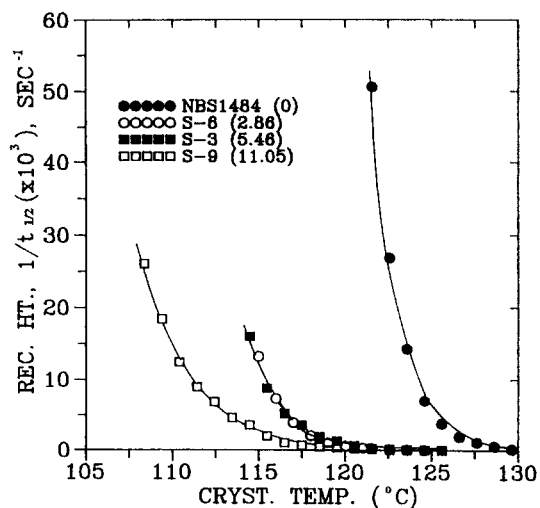

Figure 2 Bulk growth rate data expressed as reciprocal half-time for the intermediate molecular weight series (IMWS)

Figure 3 Linear growth rate as a function of temperature for high molecular weight series (HMWS)

Figure 4 Bulk growth rate data expressed as reciprocal half-time for the high molecular weight series (HMWS)

reduces the linear growth rate by a factor of 60 at 127.5°C from F-3 to S-5. The crystallization temperature is reduced by 12.5°C at $0.01\,s^{-1}$ from F-3 to S-8 in the bulk growth data. Similar results can be seen in the linear growth data in *Figure 3* and in the bulk crystallization data in *Figure 4* for the HMWS. The linear growth rate at 121°C is reduced by a factor of 360 from H-2 to S-3 and S-6, and the crystallization temperature is reduced by 16°C at $0.025\,s^{-1}$ from NBS 1484 to S-9 in the bulk growth data.

Nucleation density was calculated from the average number of nuclei per unit area of the specimen divided by the average film thickness. Plots of nucleation density *versus* crystallization temperature determined from optical microscopy are shown in *Figure 5* for IMWS and in *Figure 6* for HMWS. In all cases the nucleation density decreases with increasing crystallization temperature. There is a clear and consistent reduction

in nucleation density with increasing branch content at constant temperature.

DISCUSSION

In this section we will first consider the behaviour of the linear growth rate and its analysis. As discussed in the earlier companion paper, analysis using secondary nucleation theory requires the use of appropriate thermodynamic parameters for each polymer. For none of the specimens used, either in this paper or the preceding one, was it possible to determine equilibrium melting points using the extrapolation of a Hoffman–Weeks plot. This behaviour is believed to be due to the variation of thickening coefficients with temperature for a branched system. Consistent with the earlier report[13], equilibrium melting temperatures have been calculated using the Flory copolymer equation[16] using a T_m° of the homopolymer of 144.5°C and using the Flory–Vrij equation[17] in combination with the Flory copolymer equation. As before, the latent heats of fusion have been taken from the work of Knox[18].

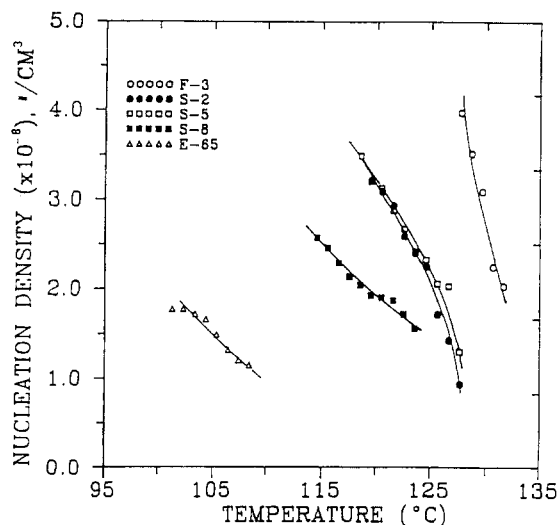Values of Δh_f° from the work of Knox[18] are shown in

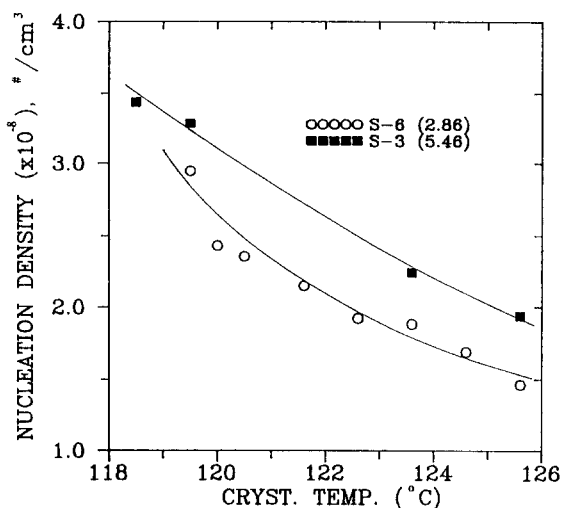**Figure 5** Nucleation density *versus* crystallization temperature for IMWS

Figure 6 Nucleation density *versus* crystallization temperature for HMWS

Table 2 Predicted values of T_m° and Δh_f°

Sample	$T_m^\circ(1)^a$ (°C)	$T_m^\circ(2)^b$ (°C)	Δh_f° pred (J g^{-1})
F-3	144.5	144.3	289.0
S-5	143.3	143.5	250.1
S-8	142.1	141.3	232.8
E-65	135.7	135.8	186.9
H-2	144.5	144.5	
NBS 1484	144.5	144.5	289.0
S-6	143.9	144.6	259.7
S-3	143.4	143.9	253.2
S-9	142.1	142.5	239.2

^{a} $T_m^\circ(1) = 144.5°C$ used to calculate T_m° from the copolymer[16] equation
^{b} $T_m^\circ(2) = 144.5°C$ used in the Flory–Vrij[17] equation to calculate T_m° values which were then used to calculate T_m° from the copolymer[16] equation
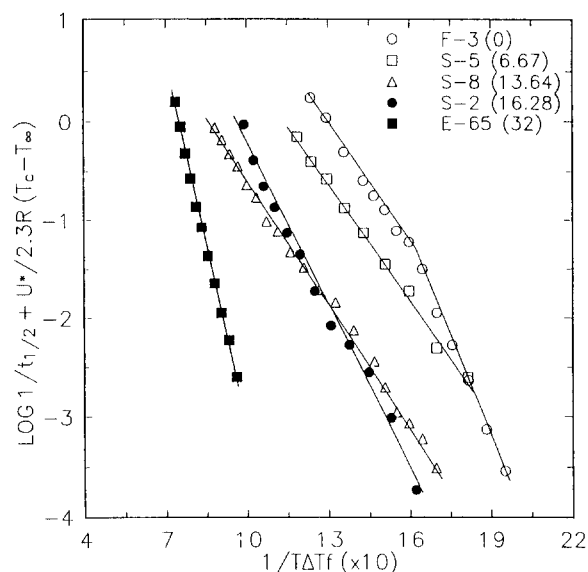

Figure 7 Secondary nucleation plot of IMWS

Table 2 together with T_m° values predicted from Flory's copolymer equation[16] and the combined Flory–Vrij[17] and Flory copolymer equation. The predicted values for T_m° and Δh_f° have been used in the kinetic analysis of the IMWS and HMWS. *Figure 7* shows that, for the IMWS, crystallization occurs in both regime I and regime II depending upon the level of branching and the crystallization temperature. F-3 shows regime I–II growth with the transition occurring at 130.1°C. S-5 shows regime II growth, this assignment being made on the basis of $\log G_0, \sigma_e$ and the calculated i values of S-8. S-8 shows regime I–II growth, with the regime I–II transition occurring at 120.5°C, a change of approximately 10°C from F-3. E-65 appears to exhibit regime I growth based on the value of the slope as calculated from the kinetic analysis.

It therefore appears that the general trend found in the study of the low molecular weight series[12], that the regime I–regime II transition temperature translates to lower temperatures with increasing copolymer content, has been repeated for F-3 and S-8 of the IMWS series. It

is noted from the molecular weight characteristics that these two fractions have M_w values of 51 500 and 54 700 respectively. S-5, which shows only regime II, has a M_w value of 89 900 and is the highest molecular weight fraction in this group. In the case of E-65, which was not cross-fractionated and has a very high branch content, it is clear that the data points are far removed from those of the other samples and that the slope is steep, corresponding to regime I.

On the basis of a comparison between S-5 with F-3, S-8 and E-65, it appears that the effect of increasing molecular weight in suppressing regime I becomes evident somewhere between M_w values of 65 000 and 89 900. This is consistent with the observations of Hoffman *et al.*[2] for linear polymers. This conclusion is further reinforced when the HMWS are considered, where the molecular weight values are all in excess of 100 000.

The HMWS shows both regime II and regime III growth, with the regime II–regime III transition exhibiting branch content dependency as shown in *Figure 8*. The regime II–regime III transition occurs in S-3 at 123.6°C and in S-9 at 120.0°C. S-6 exhibits only
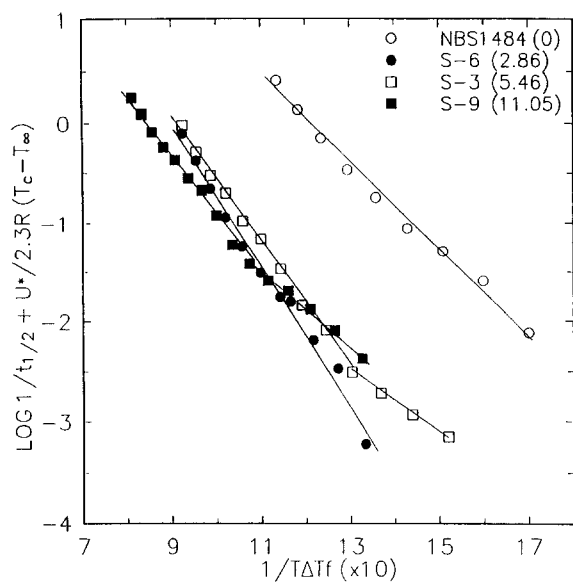
Figure 8 Secondary nucleation plot of HMWS

Table 3 Parameters derived from kinetic analyses

Sample	Log G_o	σ_e (erg cm^{-2})	Transition temperature (°C)	Supercooling at transition (°C)
(A) $T^\circ_m(1) = 144.5°C$ for F-3, H-1 and H-2 with others calculated from Flory equation				
H-1	13.16 (I)	108.6	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)			
S-7	15.81 (I)	86.0	123.1	16.1
	6.93 (II)	79.0		
F-3	11.45 (I)	77.5	130.1	14.4
	7.28 (II)	71.9		
S-5	6.14 (II)	95.5		
S-8	8.58 (I)	65.4	120.5	21.6
S-2	6.02 (II)	84.8		
E-65	11.1	95.0		
H-2	8.75			
S-6	8.16 (III)	77.6		
S-3	2.57 (II)	63.7	123.6	19.8
	6.78 (III)	63.5		
S-9	0.820 (II)	37.6	120.0	22.1
	6.34 (III)	62.7		
(B) T°_m calculated using Flory–Vrij and Flory equation				
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		
F-3	11.26 (I)	75.1	130.1	14.2
	4.70 (II)	69.9		
S-5	6.21 (II)	107.2		
S-8	8.18 (I)	60.5	120.5	20.8
	3.98 (II)	60.7		
S-2	5.49 (II)	73.7		
F-65	11.2 (I)	95.7		
H-2	9.07			
S-6	7.79 (III)	77.3		
S-3	2.69 (II)	67.0	123.6	20.3
	6.96 (III)	66.4		
S-9	0.88 (II)	39.2	120.0	22.5
	6.46 (III)	64.6		
(C) $T^\circ_m = 144.5°C$ assumed constant for 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		
F-3	11.47 (I)	77.5	130.1	14.4
	4.78 (II)	71.9		
S-5	6.58 (II)	108		
S-8	9.84 (I)	82.5	120.5	24.0
	4.54 (II)	78.4		
S-2	7.12 (II)	113.8		
E-65	14.88 (I)	157.4		
H-2	8.75			
S-6	7.73 (III)	76.3		
S-3	2.85 (II)	71.5	123.6	20.9
	7.19 (III)	70.2		
S-9	11.19 (II)	47.6	120.0	24.5
	7.07 (III)	75.1		

regime III growth owing mainly to its higher molecular weight and low branch content. The parameters derived from the kinetic analyses of the branched fractions of PE are shown in *Table 3*.

The slopes of the linear growth kinetic plots can be used to evaluate the fold surface free energy, σ_e. The calculated values for σ_e are given in *Table 3*, and show σ_e to vary with molecular weight and branch content. σ_e for the LMWS decreases with increasing branch content, indicating a change in the nature of the fold surface. Similar behaviour can be observed in *Table 3* in the HMWS. The decrease in σ_e suggests that the rejection of an increased number of branches results in an increasingly looser fold surface. This is also indicative of the increased volume fraction of the interfacial region in branched polyethylenes.

The σ_e values show a decrease from the LMWS to HMWS. The HMWS has a higher rate of secondary nucleation than the LMWS as entanglements result in increased rates of secondary nucleation. This suggests that the LMWS will have tighter folds than the higher molecular weight materials. Crystallization in the IMWS and HMWS takes place in slack portions of chain and a higher degree of non-adjacent re-entry and loose folding is expected, resulting in lower σ_e values. Again, the lower values of σ_e indicate the increased presence of the interfacial region.

The companion paper discussed the effect of branching on the crystallization in a LMWS. It was found that the introduction of branching results in a greater reduction in the rate of surface nucleation than in the rate of lateral spreading due to the rejection of branches from the crystal, necessitated by the formation of a branch-free nucleus. The regime I–regime II transition shows a branch content dependency in the LMWS.

The evaluation of the rates of secondary nucleation and surface spreading as shown in *Table 4* helps to explain the effects of branching and molecular weight on crystallization in the branched polyethylenes. The introduction of branches slows down the rate of crystallization by reducing the rate of secondary nucleation. Nucleation can only occur when a sufficient length of

Table 4 Regime transition analyses, results (conditions as in *Table 3*)

Sample	i (nuclei cm^{-1} s^{-1}) ($\times 10^{-6}$)	g (cm s^{-1}) ($\times 10^{5}$)	L (Å)
(A) $T^{\circ}_m = 144.5°C$ (corrected using Flory equation)			
H-1	455	5.3	48
S-4	15.1	4.3	248
S-1	6.9	3.5	318
S-7	3.5	2.5	395
F-3	2.8	1.1	282
S-8	21.7	1.8	130
(B) T°_m calculated using Flory–Vrij and Flory equations			
H-1	458	5.3	48
S-4	13.7	4.7	263
S-1	6.5	3.7	338
S-7	3.2	2.7	416
F-3	2.4	1.3	325
S-8	21.0	1.9	134
(C) $T^{\circ}_m = 144.5°C$ (assumed constant for series)			
H-1	453	4.5	42
S-4	17.8	3.6	202
S-1	10.1	2.4	217
S-7	9.2	0.94	143
F-3	2.8	1.1	282
S-8	24.3	1.6	116

branch-free units in sequence are able to form a critical nucleus. As more branches are added to the chain, it will become increasingly difficult for the chain to nucleate. This can be seen in the constant decrease in i from S-4 to S-7. From S-4 to S-7, i and g decrease at a constant rate with increased branch content. This helps to explain the initial large change in the regime I–II transition from 125.3 to 124.1°C from H-1 to S-4, followed by a small decrease in the transition temperature from 124.1 to 123.1°C from S-4 to S-7, this being the branch content range over which i and g change at comparable rates.

The LMWS conforms to a strict control of i and g because of its low and relatively constant molecular weight throughout the entire molecular weight series. As molecular weight is increased, the effect of entanglements on reptation becomes important. Because of entanglements and branching, longer molecules are unable to be reeled onto the growth face as easily as short molecules. This results in an increase in i as calculated for S-8 in comparison to the values for LMWS and F-3. At higher crystallization temperatures, branches reduce i so that the regime I–II transition is observed in S-8. The limited number of branches in S-5 may explain the presence of only regime II. Entanglements cause an increase in i; however, the limited number of branches does not significantly reduce i at higher crystallization temperatures in S-5 so that only regime II is observed. By contrast, the high number of branches in E-65 severely reduces nucleation so that only regime I is observed.

The effect of entanglements on reptation becomes very significant in the HMWS as seen by the presence of regime III. The molecular weight in the HMWS is greater than the critical molecular weight of entanglements so that entanglements become significant enough to dominate reptation. The long molecules are unable to reptate through the melt at high rates, resulting in reduced g, so that crystallization becomes dominated by secondary nucleation and regime III growth. The presence of branches reduces i at higher crystallization temperatures,

as was observed in the IMWS, switching growth from regime III to regime II. While S-6 shows only regime III growth due mainly to its high molecular weight and low branch content, S-3 and S-9 show both regime II and regime III caused by increased branching reducing i at higher crystallization temperatures.

The appearance of regime II–III growth is significant. Phillips and Lambert[12] observed regime II–III growth in crosslinked PE because of the elimination of lateral spreading due to crosslinking. Regime III growth in branched PE is due to entanglements serving to slow down reptation. In both systems nucleation is dominant over spreading (regime III). Phillips and Lambert[12] proposed a model for crystallization in crosslinked PE which consisted of three stem nucleus formation.

It was suggested by Phillips and Lambert[12] that high molecular weight polymers, which are above their entanglement limit, crystallize so that entanglements act as virtual crosslinks. It is also possible that high molecular weight materials nucleate in several crystals simultaneously so that all but the two nuclei generated by the two chain ends will be composed of multiple stems. Both suggestions seem to be plausible for the HMWS. It is possible, as was the case in crosslinked PE, that the regime II–III transition is accompanied by a change in nucleus size, changing from single stem to multiple stem nucleation. This in turn would suggest that the regime II–III transition is the result of a change in nucleation mechanism. Determination of the lamellar thickness of the branched samples will be necessary before calculation of the nucleus size in the branched polyethylenes can be made, so that the analysis of Andrews *et al.*[11] may be performed.

In regime III, the niche separation approaches the stem width. This means that the number of adjacent re-entry stems is limited by the niche separation, and the lamellae are expected to consist of a high number of non-adjacent re-entry stems. As pointed out by Hoffman[19], regime III crystallization results in a 'variable cluster' model where adjacently folded stems averaging about three stems are laid down interdispersed with non-adjacent re-entries. He suggests that at low crystallization temperatures 'slack' portions of chain form small clusters of stems. Thus it seems that in two cases, branched polyethylene and crosslinked polyethylene, multiple stem nucleation and regime III growth are one and the same, and that the variable cluster model is the realization of multiple stem nucleation.

Bulk kinetic data have been analysed to obtain further understanding of the kinetic behaviour of the IMWS (*Figure 9*) and the HMWS (*Figure 10*). The results for the bulk kinetics are similar to those observed for the linear kinetics. Regime I and II growth is observed in sample S-8 at 123.6°C and regime II and III growth in the HMWS with the transition occurring at 123.6°C in S-3 and at 117.0°C in S-9. Again, the correlation between regime breaks in the linear growth plots and those in the bulk growth plots is good enough to confirm that bulk kinetic data can be used to assign regimes and regime transition temperatures, as was found for the LMWS series[13]. These are fairly important conclusions since they tell us a great deal about the influence of branching and molecular weight on secondary crystallization. It is recognized that the linear growth kinetics discussed earlier reflect the growth of the dominant lamellae. This growth is limited
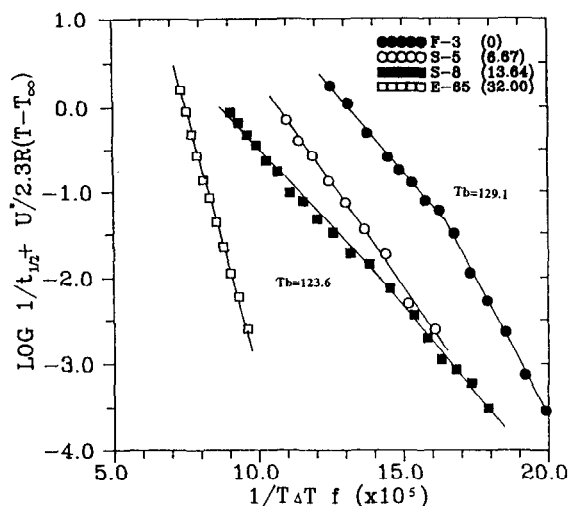
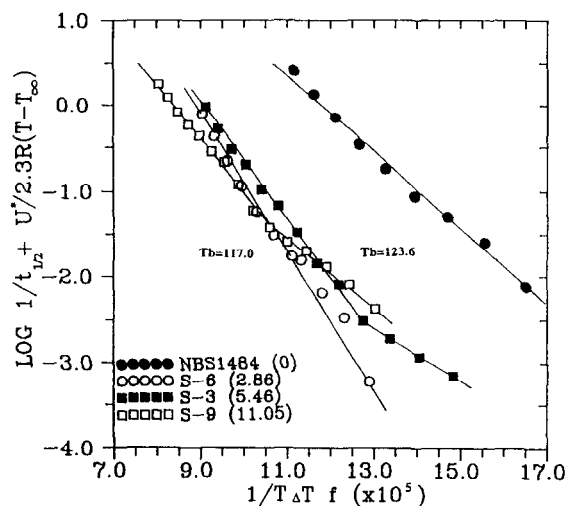**Figure 9** Secondary nucleation type analysis of bulk half-time data for IMWS

Figure 10 Secondary nucleation type analysis of bulk half-time data for HMWS

in crystallinity and, for the samples considered, rarely exceeds 15% at the isothermal temperature. The bulk kinetics must therefore be representing substantially the same phenomenon combined with the secondary crystallization occurring behind the growth front. Therefore, since the curves of *Figures 9* and *10* are similar in shape, regime behaviour, etc. to the linear growth analyses, it can be concluded that there are no major changes in the time sequence for secondary crystallization *vis a vis*

dominant lamellar growth. A similar type of behaviour was discussed for the LMWS and reported earlier[13]. The changes in nucleation density with temperature and branching referred to earlier do not have any substantial influence on the shapes of the curves. There is therefore a close relation between dominant lamellar growth and subsequent secondary crystallization, and the bulk kinetics mirror the linear growth kinetics.

CONCLUSIONS

The two papers show the combined effects of branching and molecular weight on crystallization in branched polyethylenes. Branching reduces the rate of crystallization as a result of reduced secondary nucleation. As molecular weight is increased, entanglements reduce reptation so that regime II and regime III growth is observed. The appearance of the regime II–III transition in branched polyethylene suggests that the transition is the result of a change in nucleation mechanism.

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