## **Crystallization Regimes and Reptation in Polypropylene Molecular Weight Fractions**

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ABSTRACT: Crystal growth rate data based on the kinetic nucleation theory of chain folding and the effect of reptation, have been used to predict the rate of crystal growth at moderate to high supercoolings in iPP molecular weight fractions. Growth rate data obtained for the fractions seem to be in agreement with the theoretical predictions of the regime theory. However, an extension of the gambler ruin treatment to the iPP data has not been successful with regard to the dominant morphology in regime II. The variable cluster model suggested as the morphology for polyethylene in regime II does not appear to be evident from this study. The effect of polydispersity, molecular weight, and tacticity on the crystallization behavior of iPP fractions have also been studied and correlated with the structure of polymer samples investigated. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 579–584, 1999

Key words: reptation; molecular weight crystallization; regime; fractions

#### INTRODUCTION

The morphology and crystallization regimes of some polymers, principally polyethylene (PE), have been studied in some detail. Values of the interfacial free energies, as well as the regime rate constants, have been reported for various polyethylene fractions.<sup>1-4</sup> I have observed from study of the crystallization behavior of bulk polypropylene (PP) samples that the spherulite morphology, and indeed the growth rate, are stereoregularity and molecular weight dependent.

From my study of the effect of stereoregularity on crystallization kinetics in PP, I observed that highly tactic samples crystallize faster than samples of low tacticity. However, the Avrami values obtained are lower than values predicted theoretically. This suggested that low Avrami values, in effect, can be attributed to molecular weight fractionation due to the morphologies of the crystal-

lites formed. On the other hand, my study has also revealed the absence of the so-called "regime effect" in bulk crystallized PP samples.<sup>5</sup>

Hoffman has observed that the regime effect is more likely to be obscured by polymer polydispersity than by any other factor. On the other hand, reasonably monodisperse PE fractions of various molecular weight exhibit this effect. This study thus sets out to examine the presence, or absence, of the regime effect in PP, the case of PE having been studied. In addition, the effect of molecular weight and reptation on the crystallization of PP was also investigated. This meant that I had to use narrow molecular weight fractions,  $M_W 1.03 \times 10^5$  to  $M_W 1.7 \times 10^4$ , obtained by gel permeation chromatography fractionation in my study.

#### **Regime Theory**

The kinetics of crystallization from the melt involves three growth regimes,<sup>3-6</sup> which defer with respect to the rate at which chains are deposited on the crystal surface. The observed growth rate results from two processes: nucleation and growth. By a process known as reptation, both take molecules from the melt, and, depending on the crystallization temperature, one will predominate over the other to give one of three crystallization regimes.

In regime I, the substrate growth is faster than the rate of nucleation. The growth surface is relatively smooth, and, in iPP, coarsely branched axiallites are formed. In regime II, the rate of nucleation is faster than the substrate completion rate. Each molecule is assumed to fold back and forth to give adjacent reentry. PP spherulites formed in regime II are closer textured, presumably due to the multiple nucleation that occurs. In regime III, the rate of crystallization is very fast, and the niche separation characteristic of regime II approaches the width of the stem. Here, chains do not undergo adjacent reentry.

In regime I, one primary nucleation act, occurring sporadically in time, causes completion of the entire substrate of length L, such that

$$G_{\rm I} = b_0 i L = b_0 i n_s a_0 \tag{1}$$

and for regime II multiple nucleation occurs on the substrate and

$$G_{\rm II} = b_0 (2ig)^{1/2} \tag{2}$$

In eqs. (1) and (2), G is the growth rate in cm s<sup>-1</sup>;  $b_0$  is the thickness of the layer being added; i is the surface nucleation rate in nuclei s cm<sup>-1</sup>;  $L = n_s a_0$ , the length of the substrate in cm;  $n_s$  is the number of stems of width  $a_0$  that make up this length; and g is the substrate completion rate in cm s<sup>-1</sup>. Evaluation of eqs. (1) and (2) results in

$$g = G_{\rm III} L/2b_0 = G_{\rm III} n_s a_0/2b_0 \tag{3}$$

where g is an experimentally determined parameter. The absolute growth rate in regime I can then be expressed from eq. (1) as

$$G_{\rm I} = b_0 i n_s a_0 = (C_1/n) \exp[-Q_D^*/RT] x$$
$$\times \exp(-4b_0 \sigma \sigma_e / (\Delta f) kT) \quad (4)$$

The preexponential factor  $C_1/n$  falls as 1/n due to the effect of reptation. Thus, an increase in molecular weight at a given undercooling  $\Delta T$  will decrease the absolute growth rate represented by eq. (4) in a manner that is inversely proportional to 1/n, where *n* is the number of monomer units

l'able l	Molecular	Weight Averages	

Sample	$M_W  imes 10^{-3} \ { m g mol}^{-1}$	$\begin{array}{c} M_n \times 10^{-3} \\ {\rm g \ mol}^{-1} \end{array}$	Dispersity
PP123	12	5	2.6
PP124	600	52	11.7
PP127	618	71	8.7
PP128	17	6	2.8
PP129	592	80	7.5
PP159	373	37	9.9
PP160	577	64	9.1
PP161	488	64	7.7
PP162	630	65	9.9
SH6	103	22	4.6

in the chain. Similar but more complicated expressions can be written for regimes II and III.

#### **EXPERIMENTAL**

Polymer samples used were synthesized in our laboratory using a new generation of supported Ziegler–Natta catalysts consisting of magnesium chloride, titanium tetrachloride, and triethylaluminium. Table I summarizes the molecular weight averages of the isotactic polypropylene (iPP) fractions as determined by a gel permeation chromatograph, Waters Associates 150C, in orthodichlorobenzene at 413 K. A Perkin Elmer DSC 2 interfaced to a computer was used to collect and analyze crystallization data of samples. The thermal response of the calorimeter was calibrated with the heat of fusion of ultrapure indium, 28.4 J/g, and the temperature from the melting points of indium, tin, and zinc. Experiments were carried out in an atmosphere of nitrogen.

Samples weighing approximately 10 mg were encapsulated in aluminium pans and melted for 5 min at between 460 and 480 K. They were then quenched at 160 K/min and crystallized between 400 and 420 K. A melter hot stage polarizing microscope at a maximum magnification of 400 was used to study the nucleation characteristics, growth behavior, and morphology of spherulites. In general, polymer samples were subjected to the same crystallization conditions, to enable comparison of crystallization data.

#### **RESULTS AND DISCUSSION**

Spherulite growth rate studies and isothermal crystallization kinetics were carried out as out-

	$t_{1/2}$		$Z imes 10^4$ /
$T_c$ (K)	(min)	$n \pm 0.2$	$\min^{-n}$
Sample PP123			
400	6.2	2.4	62
402	7.5	2.8	21.4
403	9.2	2.6	21.8
404	15.5	2.6	5.6
406	19.7	2.4	5.4
407	30.7	2.7	1.43
Sample SH6			
395	4.8	2.5	140
400	7.4	2.5	47.1
401	8.20	3.2	8.07
402	8.35	3.5	4.35
404	23.67	3.8	4.15
405	23.69	4.0	0.022
406	25.1	4.1	$0.0047 \pm 10$

Table II Crystallization Parameters

lined in the experimental section. Table II gives the isothermal crystallization results for two fractions, the highest and the lowest molecular weights. The plot of the growth rate against the undercooling,  $\Delta T$  and  $1/T\Delta T$ , shown in Figures 1 and 2, exhibited breaks at two points corresponding to the transition between the regimes. The regime I to II transition occurred at  $\Delta T$  of about 35 K, whereas the regime II to III transition occurred at  $\Delta T$  of about 47 K, which gives a  $\Delta T_r$  of 12 K, where  $T_r$  is the regime transition temperature.

The slope of the plot of the growth rate against temperature yields the regime rate constant, Kg. The values obtained in this study are in agreement with the theoretical predictions of the regime theory, which requires that  $Kg_{\rm I} = 2Kg_{\rm II}$  =  $Kg_{\rm III}$ . The results indicate that the slope of the plot of log *G* against temperature in regime III is twice that of regime II, but the same as regime I.

The values of the rate constants obtained when substituted into eq. (4) yield values of the lateral and fold surfaces energies,  $\sigma\sigma_e$ , and the preexponential factors in the growth expression. These parameters were determined by using the literature values of the following parameters for PP<sup>7-9</sup>:  $b_0 ext{ is } 5.0 \times 10^{-8} ext{ cm}$ ,  $a_0 ext{ is } 4.55 \times 10^{-8} ext{ cm}$ ,  $L_u ext{ is } 2.2 \times 10^{-8} ext{ cm}$ , and K' = 9.0. It was also assumed that

$$\sigma = 0.1\Delta H = q/2A_0 \tag{5}$$

where q is the work of chain folding taken as 20.580 kJ mol<sup>-1</sup>. The lateral and fold surface energies,  $\sigma \sigma_e$ , and the preexponential factors were substituted into eq. (2) to obtain an estimate of the growth rate G in each regime.



**Figure 1** Regime I–III kinetics: log of the growth rate as a function of undercooling  $(\Delta T)$ .



**Figure 2** Regime I–III kinetics: log of the growth rate as a function of reciprocal undercooling  $(1/\Delta T)$ .

# Effect of Molecular Weight and the Theory of Reptation

Several studies have been conducted on the effect of molecular weight on the crystallization behavior of polymeric systems,<sup>10</sup> and as such here only a brief discussion is presented on the effect of molecular weight on the crystallization behavior of iPP. On the other hand, attention is paid to the relatively new and somewhat complicated theory of reptation invoked by Hoffman to explain the effect of molecular weight on the crystallization behavior of some polymers.

In this study, a general decrease in the Avrami value n with molecular weight from above 3.0 toward 1.0 at high molecular weight, was observed (Fig. 3). In addition, values as high as 3.0 were obtained for the narrowest fractions. This represents a primary process of spherulitic growth for which n = 3 and a secondary process of annealing or interlamella growth occurs with nvalues between 1.0 and 1.8.<sup>11,12</sup> An Avrami value of 1.8 is characteristic of a crystallization process with one-dimensional growth, linear growth, and heterogeneous nucleation.<sup>13,14</sup> This suggests that molecular weight fractionation or rejection in broad distribution samples and impurity segregation in low stereoregular samples could result in low n values. In addition, low n values could be

obtained in high stereoregular samples if such samples had broad distributions, and although theories predict interger n values, fractional values are obtained in practice due to primary and secondary crystallization process occurring within a given system.

The plot of the molecular weight as a function of the half-life of crystallization (Fig. 4) reveals a trend of increasing half-life with increased molecular weight at a constant crystallization temperature. At the highest temperatures, a maximum crystallization rate was observed that corresponds to a minimum in the plot of molecular weight against halflife. The rate of crystallization increases with decreasing crystallization temperature irrespective of the molecular weight. This points to a nucleation phenomenon occurring in the crystallization process, as has been observed in other studies.<sup>11,12</sup> At higher molecular weights, crystallization rates increase due to their increased equilibrium melting points-higher undercooling. The melt viscosity decreases with decreasing molecular weight, which could lead to faster rates of crystallization.

Spherulite growth rate measurement and its variation with molecular weight follow the pattern of growth rate against log molecular weight and the half-life of crystallization plots, as discussed in the previous section. This observation is



Figure 3 Effect of molecular weight on Avrami value.

similar to those already reported for other polymeric systems by Barrels et al.<sup>12–16</sup> and thus is not discussed further herein.

#### **Reptation Theory and Its Effect on Crystallization** of PP Fractions

In discussing the effect of reptation on the crystallization behavior of iPP, it must be noted that crystal growth rate is a result of two processes or factors: the nucleation rate of initiating stems on the substrate and the rate at which the substrate is covered by new stems that begin at the initial stem. Both of these processes are molecular weight dependent, because the longer molecules must be extracted from the melt unto the growth front, a process that requires energy.



Figure 4 Effect of molecular weight on crystallization kinetics.

Reptation is thus the process that permits a molecule to be removed from the tangled melt by the force of crystallization and be pulled into the growth front. In a study of the effect of crystallization on PE fractions of various molecular weight, Hoffman<sup>4</sup> observed that reptation caused a decreased growth rate with an increased molecular weight from regimes I–III. The effect of reptation on the crystallization process is to lower the growth rate in a manner that is inversely proportional to the molecular weight at any given  $\Delta T$  by reducing the nucleation and substrate completion rates. This implies that shorter PP molecules enter the substrate faster than longer ones because of their faster substrate completion rates.

Thus the observed effect of molecular weight on the crystallization behavior, as deduced from the plots of the growth rate against the Avrami value and the half-life of crystallization (Figs. 3 and 4), could actually be explained by the theory of reptation. Reptation plays a role in the crystallization of both bulk and molecular weight fractions. However, the regime effect manifested by the breaks in the plot of the growth rate against temperature was observed only in molecular weight fractions.

The transitions in the plot of growth rate against temperature correspond to three different morphologies of the same polymer: positive spherulites, axiallites, and then negative spherulites. The regime I–III rate constant obtained for iPP are in reasonable agreement with the values of Monasse et al. obtained from studies of the morphology and crystallization regimes of bulk crystallized iPP.<sup>17</sup> The rate constant values obtained in this work for GPC fractions are  $Kg_{\rm I}$  is  $5.30 \times 10^5 \,{\rm K}^2$ ,  $Kg_{\rm II}$  is  $2.51 \times 10^5 \,{\rm K}^2$ , and  $Kg_{\rm III}$  is  $5.35 \times 10^5 \,{\rm K}^2$ .

#### CONCLUSIONS

The results of this study confirm the results of studies conducted for other polymeric systems, principally polyethylene, that the regime effect is obscured by polymer polydispersity. Growth rate data show that reptation is responsible for slowing the rate of crystallization in a manner inversely proportional to the molecular weight.<sup>18–20</sup> Successful application of the theory of reptation to the crystallization in iPP suggests that the theory can be applied to other semicrystalline materials that may not necessarily crystallize in a similar manner to that of iPP.

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