Chapter 6 Chain Length Dependence of Spherulitic Growth Rates in Poly(ethylene oxide) — Nucleation or Friction Regimes?

6.1 Introduction

Chain length plays an important, albeit still obscure role in the kinetics of polymer crystallization. Chain length influences the rate of segmental transport across the liquid/solid interface as well as the driving force for nucleation and growth processes. In recent versions of the secondary surface nucleation model initially developed by Lauritzen and Hoffman (LH model)\textsuperscript{1-4} segmental transport at the crystal growth front is described using the concept of forced steady-state reptation.\textsuperscript{5-7} In these treatments, the spherulitic growth rate, $G$, at a crystallization temperature, $T_x$, is predicted to be inversely proportional to chain length for polymer chains that are not “too long”.\textsuperscript{8} However, increasing chain length also leads to an increase in the equilibrium melting temperature, $T_m$, hence, to an increase in the undercooling, $\Delta T = T_m - T_x$, and in the driving force for crystallization. These competing effects result in the classical bell-shaped curve of spherulitic growth rate or crystallization rate vs. chain length, which has been observed for polymers such as polyethylene,\textsuperscript{9} poly(ethylene oxide),\textsuperscript{10} poly($\varepsilon$-caprolactone),\textsuperscript{11} poly(3,3-diethyl oxetane).\textsuperscript{12} In summary, current theoretical predictions suggest that the spherulitic growth rate should be inversely proportional to chain length when the undercooling is kept constant and the chain length is not “too large”.\textsuperscript{8}

The first objective of this paper is to report investigations of the chain length dependence of spherulitic growth rates for poly(ethylene oxide) and to compare our experimental results with predictions of the LH model.\textsuperscript{4} Discrepancies observed between model predictions and experiments, lead us to reexamine the long-standing controversy on the existence of crystallization regimes I and II.\textsuperscript{13-16} We then recall the Brochard-de Gennes model\textsuperscript{17-23} and propose that the I $\rightarrow$ II crystallization regime transition may be associated with different velocity or friction regimes for the dynamics of crystallizing tethered chains rather than with a change in the relative rates of secondary nucleation, $i$, and substrate completion, $g$. 

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This chapter is organized as follows: In the first part, we briefly review the basic elements of the LH theory (regime transition and chain length dependence of spherulitic growth rates) and recall relevant experimental results on the crystallization kinetics of polyethylene and poly(ethylene oxide) from the literature; In the second part, we provide our own experimental results for the dependence of spherulitic growth rates on crystallization temperature and chain length; In the third part, we analyze this growth rate data using the conventional LH theory, paying special attention to the evaluation of equilibrium melting temperatures; In the fourth part, we contrast experimental results and LH model predictions; In the fifth and last part, we propose a new approach to account for both the temperature and chain length dependence of spherulitic growth rates in flexible chain polymers.

6.1.1. LH Model

Since a thorough description of the LH model is beyond the scope of the present paper, we refer the reader to the appropriate literature for a more comprehensive overview.\textsuperscript{4,24} In the LH model, three regimes are predicted based on the relative rates of surface nucleation (\(i\)) and substrate completion (\(g\)). In regime I, surface nucleation is much slower than substrate completion. Therefore, nucleation is the rate-determining step that leads to the following expression for the growth rate:

\[
G_I = b_0 i L 
\]  

(6.1)

Here, \(b_0\) is the thickness of the crystal layer in the direction of growth and \(L\) the substrate length. In regime II, the nucleation rate is comparable to the substrate completion rate thus multiple nuclei compete to complete a new crystal layer. The growth rate in regime II is determined by the following expression:

\[
G_{II} = b_0 (2i^g)^{1/2} 
\]  

(6.2)

When the temperature is further lowered, secondary nucleation becomes much faster than substrate completion. This results in there being insufficient space for significant substrate completion. In this case, the growth rate is again controlled by the nucleation rate, \(i\). This temperature range is defined as regime III. Growth in regime III is characterized by a rate given by:

\[
G_{III} = b_0 i L' 
\]  

(6.3)
Here $L'$ is the distance between niches and is only 1.5 to 2.5 $a_0$, where $a_0$ is the width of stem. Hoffmann et al.\textsuperscript{4,24} derived expressions for $i$ and $g$, thus gave the expression for growth rate as follows:

\[
G = G_j^0 \exp\left(-\frac{U^*}{R(T_x - T_\infty)}\right) \exp\left(-\frac{K_{gj}}{T_x \Delta T}\right) \tag{6.4.1}
\]

\[
G = G_j^0 \exp\left(-\frac{Q_d^*}{RT_x}\right) \exp\left(-\frac{K_{gj}}{T_x \Delta T}\right) \tag{6.4.2}
\]

Here, eq 6.4.1 adopts the form of Vogel-Fulcher-Tammann-Hesse (VFTH) equation that describes the nonlinear behavior in the temperature region close to $T_g$ using parameters $U^*$ and $T_\infty$, while eq 6.4.2 takes the Arrhenius form using parameters $Q_d^*$ that is activation energy for the chain diffusion. It has been suggested\textsuperscript{4,24} that the eq 6.4.1 should be used when temperature is below $T_g + 100$ K and both forms can be applied when temperature is higher than $T_g + 100$ K. In eq 6.4.1, a universal value 6270 J/mol was suggested for $U^*$ and $T_\infty$ is usually taken as $T_g - 30$ K. In both equations, the third term at the right side controls the nucleation rate and depends on the undercooling ($\Delta T = T_m - T_x$). The parameter $K_{gj}$ is the secondary nucleation constant and has the following expression:

\[
K_{gj} = \frac{j b_0 \sigma_e T_m}{\Delta H_f k} \tag{6.5}
\]

where $\sigma_e$ is the basal surface free energy, $\sigma$ the lateral surface free energy, $\Delta H_f$ is the heat of fusion, $T_m$ is the equilibrium melting temperature and $k$ the Boltzmann’s constant.

The parameter $j$ varies with regime, $j = 4$ in regime I and III and $j = 2$ in regime II. Therefore it can be predicted that $K_{g(I)} = K_{g(III)} = 2K_{g(II)}$, which is an important criterion for LH theory. The quantitative relationship between $K_g$ values in three regimes is also implied by eqs 6.1 to 6.3. The $K_g$ values can be determined in the plot $\ln G + U^*/R(T_x - T_\infty)$ against $1/T_x \Delta T$, the so called LH plot. The product of surface free energy $\sigma \sigma_e$ can be calculated from $K_g$. Combined with other methods to determine the lateral surface free energy $\sigma$, $\sigma_e$ can be obtained. Therefore, by comparing this value of $\sigma_e$ with those inferred from other approaches, LH theory can be further tested.

Various polymers have been found to exhibit regime transition behavior through spherulitic growth rate measurements and/or overall kinetic studies. Three regimes have been identified in polyethylene fractions,\textsuperscript{25} cis-1,4-polyisoprene,\textsuperscript{26} isotactic poly(1-
butene), poly(3,3-dimethylthietane), and poly(L-lactic acid). Regime I/II transition has been reported for poly(ethylene oxide), and poly(1,3-dioxolane). Examples reported for regime II/III transition include isotactic polypropylene, syndiotactic polypropylene, poly(oxymethylene), poly(p-phenylene sulphide), poly(3-hydroxybutyrate), poly(pivalolactone), poly(trimethylene terephthalate), and poly(ethylene succinate).

It is noted that most studies for growth rate measurements did not use narrow fractions. It was reported by Wagner and Phillips that the Regime I/II transition temperature in one PE sample with broad molecular weight distribution shifts to lower temperature compared with narrow PE fractions. In addition, the broad molecular weight distribution leads to lower $K_{g(I)}/K_{g(II)}$ value. It was also observed by Phillips and Vatansever in the study of cis-polyisoprene that the unfractionated samples gives lower $K_{g(III)}/K_{g(II)}$ value compared with narrow fractions. The possibility of fractionation during crystallization in some mixtures of polymers with different molecular weights has been investigated by Wunderlich and Cheng. Considering these facts, the narrow fractions should be used to study the regime transition behavior especially when one tries to estimate the surface free energy by the LH equation or investigate the molecular weight dependence of the growth rate.

### 6.1.2 Role of Chain Length in the Regime Transition and Growth Rate

The detailed studies on the growth rate of polyethylene fractions by Hoffman et al. have indicated the critical role played by molecular weight in regime transitions. In the intermediate molecular weight range from 18 to 119 kg/mol defined as the B-B’ region and C-C’ region, an obvious regime I/II transition can be observed and the $K_{g(I)}/K_{g(II)}$ values remain around 2. In addition, the regime I/II transition temperature tends to increase with molecular weight. When the molecular weight exceeds region C-C’, the regime I/II transition would be lost and a single regime would be found with a mixed $K_g$ value. It is interesting to notice that there is some correlation between the evolution of regime transition behavior and crystallinity with molecular weight. In region B-B’, the crystallinity changes are very limited with molecular weight. In region C-C’, the crystallinity begins to drop significantly until the end of region D-D’. When the
molecular weight is above D-D’ region, which is defined as E-E’, the crystallinity remains almost constant. The loss of the regime I/II transition in the high molecular weight range is believed to be related to multiple nucleation on the substrate. Whether the regime II/III transition behavior in PE changes with molecular weight is still not clear. Further studies on this topic are required.

The evolution of regime I/II and II/III transition behavior with molecular weight can also be found in the study of cis-polyisoprene fractions. First, the regime I/II transition will be lost with increasing molecular weight. Then, when the molecular weight exceeds some critical value, the regime II/III transition will be lost too, leading to a single regime. It is also found that increasing the molecular weight from 313 to 543 kg/mol will produce an elevation of regime II/III transition temperature by 13 K. However, molecular weight has the opposite effect on the regime II/III transition temperature as the regime II/III transition temperature decreases with increasing poly(trimethylene terephthalate) molecular weight. An explanation of this phenomenon is still pending.

One major aim of studying the molecular weight dependence of the growth rate is to check the role of reptation theory in LH theory. Hoffman and Miller incorporated the reptation concept proposed by de Gennes into LH theory. To correlate the growth rate with the molecular weight, an expression for the “reel-in” rate $r$ was given as following:

$$r = f_c / \xi r n$$

(6.6)

where $f_c$ is crystallization force that is determined by undercooling, $\xi r$ is the monomeric friction coefficient, and $n$ is the number of repeat units. Here the concept of steady-state reptation is applied. That is, the resistance from a chain is proportional to the number of repeat units in the reptation tube confined by entanglements. Further derivation shows that, at constant undercooling $\Delta T$, the relationship between growth rate $G$ and molecular weight in regime I and II can be expressed as:

$$G_I(\text{constant } \Delta T) = n^{(1+\lambda)} = n^s$$

(6.6.1)

$$G_{II}(\text{constant } \Delta T) = n^{(1+\lambda/2)} = n^s$$

(6.6.2)

Where $\lambda = \pi/(2\Phi)$ in which $\Phi$ is the angle of sweep in radians of the first segment after it deposits on the substrate. $\Phi$ ranges from $\pi$ to $3\pi/2$. $\lambda$ should be between 1/3 and 1/2. Therefore, it can be expected that the power value in regime I will be 1.33 to 1.5 and that in regime II will be 1.17 to 1.25. Hoffman et al. analyzed growth rate data for
polyethylene fractions. The power law in eqs 6.6.1 and 6.6.2 is roughly verified. However, due to the scatter of data and the not so narrow MW distribution for some fractions, the molecular weight dependence of growth rate is still not firmly established. Higher quality data is required to eliminate potential artifacts.

Nishi et al.\textsuperscript{53} and Okada et al.\textsuperscript{54} also found a power law for molecular weight dependence of lateral growth rate for extended-chain single crystal (ECSCs) and folded-chain single crystals (FCSCs) of PE. The values of $s$ in eqs 6.6.1 and 6.6.2 were found to be 0.7 and 1.7 for ECSCs\textsuperscript{38} and FCSCs\textsuperscript{39} respectively. However, it is noted that the equilibrium melting temperatures ($T_{m0}$) they used are 4 to 5 K lower than those used by Hoffman et al. It is believed that the equilibrium melting temperature significantly affects the analysis of the kinetics data. Considering this discrepancy, their results are not comparable.

The role of entanglements on the crystal growth rate of polymers has attracted more attention recently. It is the entanglements that confine the chains and retard the transport of the chains onto the growth front. If the state of entanglement can be changed, the corresponding change of growth rate should be observed. Psarski et al.\textsuperscript{55} investigated the effect of lowered chain entanglements on the growth rate of polyethylene. In their study, the melt with low entanglement concentration is generated from melting the extended chain crystals formed under high pressure. It was believed that the low entanglement state can keep a period of time within Doi-Edwards disentanglement time.\textsuperscript{56} The decrease of the growth rate with time was observed during the growth process suggesting the gradual restorations of entanglements. The initial growth rate increases by 25 % to 45 % compared with those obtained from completely entangled melts. This effect is more significant at low undercooling.

### 6.1.3 Crystallization of PEO and its Regime Transition Behavior

The crystallization behavior of low molecular weight PEO fractions ($M_w < 11$ kg/mol) has been extensively studied by Kovacs et al.\textsuperscript{57-61} and Cheng et al.\textsuperscript{62-68} Breaks in the temperature dependence of the growth rate were observed and associated with quantized folding. Regime I/II transitions for PEO observed in either spherulitic growth rate or bulk crystallization rate data were collected by Allen and Mandelkern.\textsuperscript{32} These
authors found that the transition temperature increases steadily from 52 °C to 60 °C when the molar mass increases from 10 to $10^3$ kg/mol. Cheng et al. studied the spherulitic growth rate of three molecular weight PEO fractions (23, 56 and 105 kg/mol). They claimed the existence of three regime transitions, including a II/III transition at ca. 51 °C, a I/II transition at ca. 58 °C and a new transition between regime I back to regime II at ca. 60 °C. A change in crystallographic growth face from \{120\} to \{010\} was found at ca. 51 °C by Point and further confirmed by Marentette and Brown, leading these authors to question the existence of a II/III regime transition in PEO at this temperature. More recently, Xu reanalyzed Cheng’s growth rate data using higher $T_m$ values obtained through the non-linear Hoffman-Weeks analysis found support for a I/II regime transition at ca. 58 °C but no evidence for breaks at ca. 51 °C or 60 °C.

One should note that regime transitions which are not apparent in the raw growth rate data (plots of $G$ vs $T$) may sometimes appear in a plot of $\ln G$ vs $1/T\Delta T$ when an incorrect equilibrium melting temperature is used. It is therefore of utmost importance to evaluate as carefully as possible the equilibrium melting temperature. The $T_m$ values used in Cheng’s study (ca. 68 °C) were based on an equilibrium melting temperature for infinite molecular weight of 68.9 °C obtained by Buckley and Kovacs (BK). Experimentally observed melting temperature of 69 °C and 72 °C have been reported by Allen on the basis of dilatometry and calorimetry experiments, respectively, suggesting a much higher equilibrium melting temperature. Mandelkern et al. correctly pointed out two major errors in the BK extrapolation procedure. First, the BK extrapolation is based on experimental data for PEO fractions, not pure compounds. Hence, these fractions cannot form pure molecular crystals and application of a Flory-Vrij type treatment is inappropriate since pairing of chain-ends is prohibited in this case. Second, the BK treatment made use of an incorrect free energy expansion. Determination of the equilibrium melting temperature through the Linear Hoffman-Weeks (LHW) extrapolation yield values in the range 75 – 80 °C for intermediate to high molecular weight samples. In previous studies, one of us has already shown that the linear Hoffman-Weeks extrapolation is not justified theoretically and leads to an underestimation of the equilibrium melting temperature.
6.2 Experimental Section

Materials: Narrow poly(ethylene oxide) fractions were purchased from Scientific Polymer Products (SP$^2$) and Polymer Laboratories. These samples were kept in an evacuated dessicator in the dark prior to usage to minimize degradation. The weight-average molecular weights ($M_w$) and polydispersities ($PDI = M_w/M_n$) are listed in Table 6.1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$M_w$ (g/mol)</th>
<th>$M_w/M_n$</th>
<th>Company</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEO-11K</td>
<td>11900</td>
<td>1.05</td>
<td>SP$^2$</td>
</tr>
<tr>
<td>PEO-21K</td>
<td>21000</td>
<td>1.08</td>
<td>SP$^2$</td>
</tr>
<tr>
<td>PEO-43K</td>
<td>43500</td>
<td>1.1</td>
<td>SP$^2$</td>
</tr>
<tr>
<td>PEO-75K</td>
<td>74900</td>
<td>1.03</td>
<td>Polymer Laboratory</td>
</tr>
<tr>
<td>PEO-113K</td>
<td>113200</td>
<td>1.13</td>
<td>SP$^2$</td>
</tr>
<tr>
<td>PEO-157K</td>
<td>157000</td>
<td>1.09</td>
<td>SP$^2$</td>
</tr>
<tr>
<td>PEO-240K</td>
<td>240000</td>
<td>1.04</td>
<td>SP$^2$</td>
</tr>
</tbody>
</table>

Growth Rate Measurements: Films of PEO (20 – 40 µm) for growth rate measurements were prepared by melt pressing at ca. 100 °C and 1 MP$a$ under dry nitrogen purge and subsequent quenching in liquid nitrogen. The films were then stored in a vacuum oven until their spherulitic growth rates were measured. Isothermal spherulitic growth experiments were carried out in a Linkham hot stage purged with dry nitrogen. The temperature scale was calibrated using pure standards with sharp melting temperatures (benzoic acid, gallium and indium). Polymer samples were melted at 100 °C for 3 minutes and subsequently quenched to the appropriate crystallization temperature. To minimize degradation during slow crystallization at high temperatures, samples were initially nucleated at a lower temperature and subsequently heated up to the crystallization temperature. The spherulitic growth was recorded on a VCR using a Javelin video camera mounted on a Zeiss polarized optical microscope. Spherulite diameters were measured using a calibrated video caliper at sites in the film far away
from bubbles and film edges. The growth rate reported is the average of three measurements under identical conditions.

**Calorimetric Measurements:** The calorimetric experiments were performed in a Pyris 1 model Perkin-Elmer differential scanning calorimeter operated under dry nitrogen with an ice-water bath heat sink. For proper accounting of thermal lag effects, temperature calibration during heating was carried out using pure metal standards (gallium, indium and tin) sandwiched between two polymer films. Heats of fusion were calibrated using the latent heat of an indium standard.

Studies of the melting behavior were carried out subsequent to isothermal crystallization using a heating rate of 10 K/min. Melting temperatures reported here correspond to peak temperatures of endothermic transitions. Heats of fusion of isothermally crystallized samples were estimated through the following subtraction method. After appropriate thermal treatment to erase previous thermal history, a given sample was crystallized at a temperature $T_x$ for a period of time, $t_x$ and heated from $T_x$ to a temperature *ca.* 20 K above the final observed melting temperature. The experiment was repeated with the same sample for different times, $t_x$ at the same crystallization temperature. From each heating trace, we subtracted the thermogram obtained after a residence time at $T_x$, which was sufficiently short that it showed no evidence of melting. This approach was shown in a previous paper to yield a systematic error in the crystallinity of less than 1%.  

6.3 Results and Analysis

6.3.1 Isothermal Spherulitic Growth Rates

All spherulitic growth rate measurements were performed in the 45 – 62 °C temperature range. The plot of spherulitic growth rate, $G$, against crystallization temperature, $T_x$, is given in Figures 6.1.a and 6.1.b for samples of various molecular weights. To visualize the effect of molecular weight on the kinetics of crystal growth, we plot $G$ vs weight average molar mass for different crystallization temperatures on Figure 6.2.
Figure 6.1 The spherulitic growth rate as a function of crystallization temperature for a series of PEO fractions with molecular weight (a) 11, 43, and 113 kg/mol (b) 21, 75, 157, and 240 kg/mol
Figure 6.2 The spherulitic growth rate as a function of molecular weight at fixed temperature as indicated.

6.3.2 Determination of Equilibrium Melting Temperature and the Regime I/II Transition

6.3.2.1 Determination of Equilibrium Melting Temperature

The most important parameter in eq 6.4.2 is the equilibrium melting temperature $T_m$. The value adopted for $T_m$ will, not only, affect the linearity of such a plot, but it can also exert a significant influence on the resulting $K_g$ and $G_0$ values. As indicated above, we feel confident that the equilibrium melting temperature for infinite molecular weight PEO is significantly above the 69 °C value obtained by Buckley and Kovacs. As pointed out by Marand et al., the conventional linear Hoffman-Weeks (HW) equation neglects the $\delta l$ or $C_2$ term in the expression for the initial lamellar thickness and consequently always underestimates the equilibrium melting temperature. Application of the HW approach gives a range of $T_m$ values between 75 °C and 80 °C. While the $\delta l$ value predicted by the LH theory is generally quite small ($\delta l = \text{ca.} 1 \text{ nm for PE and PEO}$), the $\delta l$ values derived from experiments (called $C_2$) are much larger ($C_2 = 4.3 \text{ nm for PE}$).
and \( C_2 = 6.5 - 8 \text{ nm for PEO}^{68} \), and result in a non-linear relationship between crystallization temperature, \( T_x \), and observed melting temperatures, \( T_m' \).\(^{84} \) A non-linear HW analysis has been proposed by Marand et al.\(^ {39,71} \) to determine the equilibrium melting temperature. The equilibrium melting temperature obtained by this method for PEO-75K is therefore found to be 80.6 °C.\(^ {34} \)

### 6.3.2.2 Regime I/II Transition Behavior

To investigate the regime transition behavior for PEO fractions in the context of the Lauritzen-Hoffman (LH) theory, the growth rate data is plotted according to the eq 6.4.2. Here, \( Q_d' = 16 \text{ kJ/mol} \) is adopted.\(^ {85} \) The plot of \( \ln G + \frac{Q_d'}{RT_x} \) against \( 1/(T_x\Delta T) \), when linear, is characterized by its slope, \( K_g \) and intercept, \( \ln G^0 \).

First, we need to find temperature where the regime transition occurs. Fortunately, in our case the regime transition temperature is weakly affected by the choice of \( T_m \). The regime I/II transition is found in those fractions with molecular weight ranging from 11 to 157 kg/mol. Above this range, the regime I/II transition seems lost. The regime I/II transition temperature \( (T(I/II)) \) is calculated according to the cross point of two straight lines corresponding to regimes I and II in LH plot. An example is showed in Figure 6.3.a for PEO-113K. The regime I/II transition temperature \( (T(I/II)) \) increases smoothly and systematically with molecular weight as shown in Figure 6.3.b. Such a trend was also observed by Hoffman et al. in the case of PE.\(^3 \) For a series of polyethylene fractions with molecular weight ranging from 18 to 119 kg/mol, the I/II regime transition was found to occur at constant undercooling \( (\Delta T(I/II) = 16.5 \pm 0.4 \text{ K}) \). In the present study, we adopt it as a basis to determine the \( T_m \). As a consequence, the difference between \( T_m \) values should be equal to the difference between \( T(I/II) \) values. Since the equilibrium melting temperature for PEO-75K has been determined to be 80.6 °C using non-linear HW analysis as shown above, the \( T_m \) values for other fractions can be determined simultaneously as listed in Table 6.2.

The LH plots for these six fractions are shown in Figure 6.4. No break is observed around 51 °C where Cheng et al.\(^ {69} \) reported the existence of a regime II/III transition.
Figure 6.3 (a) LH plot for PEO-113K. (The regime I/II transition as indicated) (b) The regime I/II transition temperature as a function of molecular weight for PEO fractions with molecular weight ranging from 11 to 157 kg/mol.
Table 6.2: The equilibrium melting temperatures for six PEO fractions determined by assuming constant $\Delta T(\text{I/II})$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_m$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEO-11K</td>
<td>76.1</td>
</tr>
<tr>
<td>PEO-21K</td>
<td>77.4</td>
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<tr>
<td>PEO-43K</td>
<td>79.1</td>
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<td>PEO-113K</td>
<td>81.4</td>
</tr>
<tr>
<td>PEO-157K</td>
<td>81.8</td>
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</table>

Figure 6.4 LH plots for a series of PEO fractions with molecular weight ranging from 11 to 157 kg/mol. The I/II regime transition occurs at constant undercooling as indicated.
Table 6.3 The values of $K_g$, $K_g$ ratio, $\ln G^0$ in regime I and II for a series of PEO fractions showing I/II regime transition.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$K_{g(I)}$ (10$^5$ K$^2$)</th>
<th>$K_{g(II)}$ (10$^5$ K$^2$)</th>
<th>$K_{g(I)}/K_{g(II)}$</th>
<th>$\ln G_I^0$</th>
<th>$\ln G_{II}^0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEO-11K</td>
<td>1.42</td>
<td>0.957</td>
<td>1.48</td>
<td>26.41</td>
<td>20.11</td>
</tr>
<tr>
<td>PEO-21K</td>
<td>1.72</td>
<td>1.13</td>
<td>1.52</td>
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<td>21.40</td>
</tr>
<tr>
<td>PEO-43K</td>
<td>1.79</td>
<td>1.07</td>
<td>1.67</td>
<td>30.02</td>
<td>20.20</td>
</tr>
<tr>
<td>PEO-75K</td>
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<td>1.05</td>
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<td>34.74</td>
<td>19.28</td>
</tr>
<tr>
<td>PEO-113K</td>
<td>2.44</td>
<td>1.09</td>
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<td>37.62</td>
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</tr>
<tr>
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<td>1.13</td>
<td>2.40</td>
<td>40.82</td>
<td>19.55</td>
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</table>

The slope from the LH plot yields $K_g$, the nucleation constant. As shown in Table 6.3, the $K_{g(II)}$ values for these six fractions are quite close to each other. However, the $K_{g(I)}$ value increases significantly with molecular weight. Consequently, $K_{g(I)}/K_{g(II)}$ also increases with molecular weight. In the present study, since the determination of $T_m$ is still not firmly established, one needs to take great caution on how $T_m$ affects the determination of $K_g$ and $G^0$ values. In the following, the LH analysis will be performed using three other sets of $T_m$ values. In one case, the $T_m$ values by Buckley and Kovacs will be tried. In the second case, the $T_m$ value is assumed to be constant, which provides a limiting case. In the third case, the $T_m$ is determined using the criterion $K_{g(I)}/K_{g(II)} = 2$ predicted by the LH theory. Additionally, the effect of $Q_d^*$ and $U^*$ on the LH analysis will also be examined.

6.3.2.3 Study of the Regime Transition Behavior Using $T_m$ Values from Buckley and Kovacs

The $T_m$ values for the six PEO fractions are calculated using the approach suggested by Buckley and Kovacs$^{72,73}$ and are shown in Table 6.4. The LH analyses thus carried out show no I/II regime transition at the temperature where the regime I/II transition was observed using higher $T_m$ values (section 6.3.2.2). Although the data in the LH plot can be roughly fitted with a single straight line, some curvature can still be observed (see Figure 6.5.a for PEO-113K). In addition, the molecular weight dependence
of growth rates at constant undercooling does not exhibit any trend or power law (see Figure 6.5.b).

Table 6.4 The equilibrium melting temperature obtained by Buckley and Kovacs’s approach.

<table>
<thead>
<tr>
<th>$M_w$ (g/mol)</th>
<th>$T_m$ (°C)</th>
</tr>
</thead>
<tbody>
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<td>74900</td>
<td>68.42</td>
</tr>
<tr>
<td>113200</td>
<td>68.62</td>
</tr>
<tr>
<td>157000</td>
<td>68.73</td>
</tr>
</tbody>
</table>

6.3.2.4 Study of Regime Transition Behavior Using a Constant $T_m$ Value – a Limiting Case

In the present study, we investigate the limiting case where a constant $T_m$ value is assumed. Here, we chose a value of 79 °C for $T_m$. The resulting $K_{g(I)}$, $K_{g(II)}$, $K_{g(I)}/K_{g(II)}$ and prefactor $G^0$ in both regimes are listed in Table 6.5. The data shown in Table 6.5 shows that, in comparison to the case discussed in section 6.3.2.2, changes in $K_{g(I)}$ and $K_{g(II)}$ with molecular weight are limited. However, $K_{g(I)}/K_{g(II)}$ value still increases with molecular weight, suggesting that the increase in the $K_{g(I)}/K_{g(II)}$ ratio with molecular weight is an inherent property of the regime transition for PEO.

6.3.2.5 Study of the Regime Transition Behavior Assuming $K_{g(I)}/K_{g(II)} = 2$ as a Criterion for Determination of the Equilibrium Melting Temperature.

The LH theory predicts that the $K_{g(I)}/K_{g(II)}$ ratio should be equal to 2. This can be taken as a criterion to test the LH model. Here, we obtain the $T_m$ values by forcing $K_{g(I)}/K_{g(II)} = 2$. Figure 6.6.a shows the values of $T_m$ obtained by this approach. It is found that $T_m$ decreases significantly with molecular weight (from ca. 95 °C to 76 °C). Figure 6.6.b also indicates that, in both regimes, $K_g$ decreases dramatically with molecular weight.
Figure 6.5 (a) LH plot for PEO-113K using the equilibrium melting temperature from Buckley and Kovacs. (b) The growth rate as a function of molecular weight at constant undercoolings that are calculated from the equilibrium melting temperature from Buckley and Kovacs.
Table 6.5: The parameters inferred from LH analysis assuming $T_m = 79$ °C for all the PEO fractions.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$K_{g(I)}$ ($10^5$ K²)</th>
<th>$K_{g(II)}$ ($10^5$ K²)</th>
<th>$K_{g(I)}/K_{g(II)}$</th>
<th>ln $G_I^0$</th>
<th>ln $G_{II}^0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEO-11K</td>
<td>1.99</td>
<td>1.29</td>
<td>1.54</td>
<td>30.57</td>
<td>22.15</td>
</tr>
<tr>
<td>PEO-21K</td>
<td>2.13</td>
<td>1.37</td>
<td>1.55</td>
<td>32.44</td>
<td>22.88</td>
</tr>
<tr>
<td>PEO-43K</td>
<td>1.85</td>
<td>1.14</td>
<td>1.62</td>
<td>30.17</td>
<td>20.61</td>
</tr>
<tr>
<td>PEO-75K</td>
<td>1.92</td>
<td>1.00</td>
<td>1.92</td>
<td>32.28</td>
<td>19.01</td>
</tr>
<tr>
<td>PEO-113K</td>
<td>1.97</td>
<td>0.99</td>
<td>1.99</td>
<td>33.5</td>
<td>18.81</td>
</tr>
<tr>
<td>PEO-157K</td>
<td>2.08</td>
<td>0.99</td>
<td>2.11</td>
<td>35.35</td>
<td>18.69</td>
</tr>
</tbody>
</table>

Figure 6.6 (a) The equilibrium melting temperature as a function of molecular weight and (b) the $K_g$ values in regime I and II obtained by forcing $K_{g(I)}/K_{g(II)} = 2$. 
6.3.2.6 Effect of Transport Parameters \((Q_d^*, U^*)\) on the LH analysis

We note that Buckley and Kovacs\(^{72}\), Cheng et al.\(^{69}\) and Marentette et al.\(^{79}\) used \(U^* = 29.3\) kJ/mol in the analysis of their growth rate data. However, 29.3 kJ/mol is the activation energy, \(Q_d^*\), for self-diffusion in low molecular weight PEO fractions. It is therefore inappropriate to use 29.3 kJ/mol for \(U^*\) in eq 6.4.1. Furthermore, this value of the activation energy is not appropriate for intermediate molecular weight PEO fractions. Indeed, Appel et al.\(^{85}\) and Cheng et al.\(^{86}\) showed that PEO’s activation energy for diffusion, \(Q_d^*\), exhibits a sharp drop in magnitude in the 10 to 20 kg/mol molecular weight range. Above 20 kg/mol, \(Q_d^*\) reaches a limiting value of 16 kJ/mol.

In the case of PEO, both forms of the transport term (VFTH and Arrhenius) can in principle be used since \(T_x\) is around \(T_g + 100\) K. When the VFTH form is used with the universal value \(U^* = 6270\) J/mol, \(K_{g(I)}\), \(K_{g(II)}\) and \(K_g\) ratio values (Table 6.6) are very similar to those obtained with the Arrhenius form (Table 6.3). This confirms that the estimation of the secondary nucleation constant is not sensitive to the details of the temperature dependent transport term, when crystallization takes place far from \(T_g\).

Table 6.6: The parameters inferred from LH analysis using VFTH form. Here, \(U^* = 6270\) J/mol is used.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(K_{g(I)}) (10^5) K(^2)</th>
<th>(K_{g(II)}) (10^5) K(^2)</th>
<th>(K_{g(I)}/K_{g(II)})</th>
<th>(\ln G_I^0)</th>
<th>(\ln G_{II}^0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEO-11K</td>
<td>1.42</td>
<td>0.957</td>
<td>1.48</td>
<td>26.41</td>
<td>20.11</td>
</tr>
<tr>
<td>PEO-21K</td>
<td>1.72</td>
<td>1.13</td>
<td>1.52</td>
<td>29.53</td>
<td>21.40</td>
</tr>
<tr>
<td>PEO-43K</td>
<td>1.79</td>
<td>1.07</td>
<td>1.67</td>
<td>30.02</td>
<td>20.20</td>
</tr>
<tr>
<td>PEO-75K</td>
<td>2.19</td>
<td>1.05</td>
<td>2.09</td>
<td>34.74</td>
<td>19.28</td>
</tr>
<tr>
<td>PEO-113K</td>
<td>2.44</td>
<td>1.09</td>
<td>2.24</td>
<td>37.62</td>
<td>19.37</td>
</tr>
<tr>
<td>PEO-157K</td>
<td>2.71</td>
<td>1.13</td>
<td>2.40</td>
<td>40.82</td>
<td>19.55</td>
</tr>
</tbody>
</table>

6.3.3 Chain Length Dependence of the Growth Rate

In the work by Hoffman et al.,\(^3\) the chain length dependence of the growth rate is investigated by examination of growth rates at a fixed undercooling. In fact, the chain length dependence of the growth rate is also reflected in the pre exponential term \(G^0\) (eqs 6.4.1 and 6.4.2). Therefore, to investigate whether reptation concepts have been correctly
incorporated in the LH theory, one should study the chain length dependence of $G^0$. The same conclusions are obtained for studies of the molecular weight dependence of $G(\Delta T)$ and $G^0$ only if the nucleation constant $K_g$ is independent of molecular weight. In our case, since $K_g$ varies significantly with molecular weight in regime I, one should expect that these two approaches will lead to different chain length dependences in regime I. Hence, both methods will be used.

First, the growth rate data at constant undercooling ($\Delta T$) are interpolated and plotted against the logarithm of molecular weight (Figure 6.7.a). The power law exponent, $s$, in $G(\Delta T) = a(M_w)^{-s}$ is estimated from the slope of the data shown in Figure 6.7.a. It is interesting to note that $s$ exhibits different undercooling dependences in regimes I and II (Figure 6.7.b). In regime II, the $s$ value increases slightly from 0.7 to 1 with decreasing undercooling. However, a significant increase of $s$ with decreasing $\Delta T$ is observed in regime I.

The molecular weight dependence of $G^0$ in regimes I and II is shown in Figure 6.8.a and 6.8.b, respectively. While no systematic change of $G_{II}^0$ with molecular weight is observed, $\ln G_{I}^0$ increases linearly with $\ln M_w$.

### 6.4 Discussion

In the previous part, PEO growth rate data were analyzed on the basis of the LH theory. We focused on the regime transition behavior and, especially, on its chain length dependence. In this part, we will first summarize our results to determine whether they are consistent with LH theory. Second, we examine whether the calculated magnitude of the substrate length is in a reasonable range of length-scales. Third, we reexamine the incorporation of reptation concepts in the LH formalism. In this section, we introduce the Brochard - de Gennes (BD) model and propose a new interpretation for the I/II regime transition.

#### 6.4.1 Summary of Results from LH analyses

Distinct regime I/II transitions were found in six intermediate molecular weight PEO fractions. The regime I/II transition temperature increases systematically with molecular weight. To determine the equilibrium melting temperature, we assumed that
Figure 6.7 (a) Spherulitic growth rate as a function of molecular weight at constant undercooling. (the undercooling as indicated) (b) The power value $s$ as a function of undercooling.
Figure 6.8 Prefactor $G^0$ in regime II (a) and regime I (b) as a function of molecular weight inferred from the LH analysis.
the undercooling at the regime I/II transition is constant, a behavior exhibited by PE fractions. Within the uncertainty of our analysis, the nucleation constant in regime II, \( K_{g(II)} \), is independent of molecular weight. In contrast, \( K_{g(I)} \) and \( K_{g(I)}/K_{g(II)} \) increase with molecular weight. These observations are in conflict with LH theory predictions that the \( K_g \) ratio should remain equal to 2. Even in the limiting case where \( T_m \) is assumed to be independent of chain length, the \( K_g \) ratio increases significantly with molecular weight.

Equilibrium melting temperatures were also estimated following the treatment proposed by Buckley and Kovacs, although the validity of such a treatment has been questioned in the Introduction. In this case, the LH plots exhibit systematic curvature but no I/II regime transition. In addition, the growth rates at fixed undercooling do not show any meaningful chain length dependence.

To further test the LH theory, the criterion \( K_{g(I)}/K_{g(II)} = 2 \) was adopted to estimate the equilibrium melting temperature. The \( T_m \) values thus obtained decrease with increasing molecular weight, a result that is physically meaningless. Furthermore, the \( K_g \) values in both regimes decrease dramatically with increasing molecular weight, which cannot be explained by the LH theory.

We briefly recall the results reported by Hoffman et al.\(^3,4\) for eleven polyethylene fractions. A I/II regime transition was observed for all fractions and the \( K_g \) values in regimes I and II, while scattered, remain independent of chain length. The \( K_{g(I)}/K_{g(II)} \) ratio was found to be scattered about the value of 2 for all fractions.

Another objective of this study was to evaluate the incorporation of reptation concepts into the surface nucleation model. Hoffman et al.\(^3,4\) predicted a \( G(\Delta T) \sim 1/M_w \) law in regimes I and II by assuming that the chain friction coefficient is proportional to chain length and that \( K_g \) is independent of chain length in both regimes. In our analysis of PEO growth rate data, we used two different approaches to evaluate the chain length dependence of growth rates. First, we used growth rates at fixed undercoolings \( (G(\Delta T)) \). Second, we used the pre-exponential term \( G^0 \). In the first case, power laws \( G(\Delta T) \sim 1/M_w^S \) were observed in both regimes. With decreasing undercooling, the magnitude of \( s \) was found to increase slightly in regime II and rapidly in regime I. The variation of pre-exponential term \( G^0 \) with molecular weight shows no clear trend in regime II and a totally unexpected behavior\(^3\) in regime I \( (G \) increases with chain length).
In conclusion, some significant inconsistencies exist between our experimental results and predictions from the LH theory.

Here, we raise two important questions: does the inconsistency between experiments and theory arise from the inappropriate incorporation of reptation concepts into the LH theory, or does it suggest some intrinsic flaw in the premises of the theory, especially in our understanding of the I/II regime transition? In the remainder of this manuscript, we will try to answer these two questions.

6.4.2 A Test of LH Theory: Calculation of Substrate Length

It has been pointed out that the substrate length, L, defined in the LH theory must exhibit a reasonable magnitude if the LH theory is to be physically realistic.\textsuperscript{4,25,87} Until now, the substrate length has only been determined for polymers that exhibit I/II regime transition. For polyethylene, this value was found to be in the range of 55 - 90 nm (about 120 – 200 a_0),\textsuperscript{4,25} which was suggested to be associated with the range of lattice coherence.\textsuperscript{88} The general method employed in the determination of L(I/II) is given below.

In the LH theory, the prefactor \( G^0 \) is given in regimes I and II by:

\[
G_I^0 = \left( \frac{C_0 \kappa n_l}{n} \right) \left( \frac{b_0 kT}{h} \right) \left( \frac{kT b_0 \Delta H \Delta T}{4b_0 l_u \sigma^2 T_m} \right)
\]  \hspace{1cm} (6.8)

and

\[
G_{II}^0 = \left( \frac{C_0^{1/2} \kappa}{n} \right) \left( \frac{b_0 kT}{h} \right) \left( \frac{a_0 \Delta H \Delta T}{\sigma T_m} \right) \left( \frac{kT}{2b_0 \sigma l_u} \right)^{1/2} \exp \left( \frac{-q}{2kT} \right)
\]  \hspace{1cm} (6.9)

where \( C_0 \) is the configurational path degeneracy, \( \kappa \) is a numerical constant which determination is discussed below, \( n \) is the average number of repeat units in the polymer chain feeling the force of reptation during substrate completion \( (n = (2/3)(M_0 M_w)^{1/2}/M_{re}, \) where \( M_{re} \) is the molar mass of a repeat unit), \( h \) is Planck’s constant, \( l_u \) is the projected length of one repeat unit in the chain direction, and \( q \) is the work of chain folding, \( q = 2a_0 b_0 \sigma e. \) Elimination of \( C_0 \) in eqs 6.8 and 6.9 yields the substrate length at regime I/II transition temperature:

\[
L = 2a_0 \kappa \left( \frac{b_0 kT}{h} \right) \left( \frac{a_0 \Delta H \Delta T}{\sigma T_m} \right) \left( \frac{G_{II}^0}{nG_{II}^0} \right) \exp \left( \frac{-q}{kT} \right)
\]  \hspace{1cm} (6.10)
The value of $\kappa$ can be calculated by equating the substrate completion rate $g$ estimated from the LH theory to that inferred from the reptation theory, as given by:

$$
\kappa = \frac{h \exp \left( \frac{Q_d^*}{RT_0} \right) \exp \left( \frac{q}{kT} \right)}{\xi_0 l_g^* g} \tag{6.11}
$$

where $l_g^*$ is the initial lamellar thickness at the regime I/II transition temperature, and $\xi_0$ is the monomeric friction coefficient at the reference temperature $T_0$. Combination of eqs 6.10 and 6.11 gives the value of the substrate length at $T(I/II)$.

Cheng et al.\cite{86} have studied the diffusion coefficient ($D$) as a function of molecular weight and temperature for PEO. The diffusion coefficient as a function of molecular weight is classically given by:

$$
D = D_0/M^2 \tag{6.12}
$$

The parameter $D_0$ at a given temperature thus can be extrapolated using the results of $D$ as a function of $M$. The monomeric friction coefficient $\xi_0$ has been correlated with $D_0$ using the following equation:

$$
\xi_0 = \frac{kTa^2 m_0^2}{3D_0 C_x l_b^2} \tag{6.13}
$$

where $a$ is the diameter of reptation tube, $m_0$ is the molar mass of one repeat unit, $C_x$ is the characteristic ratio, and $l_b$ is the average bond length for PEO. Considering the similar microstructures of PEO and PE, $a$ is assigned the same value as polyethylene (i.e. 3 nm).\cite{4,89} Other parameters for the calculation of $L$ are listed in Table 6.7. Using the results of diffusion coefficient by Cheng et al.,\cite{86} the value of $\xi_0$ can be estimated. Here, $T_0 = 57^\circ$C was chosen as the reference temperature, since it is close to the I/II regime transition. Therefore, the substrate length $L$ at regime I/II transition can be calculated using eqs 6.10 and 6.11.

Table 6.8 lists the substrate length at the I/II regime transition for six PEO fractions. It is noted that the calculated values of $L$ are too small to be physically meaningful. However, one should note that the power law $D = D_0/M^2$, which has been used to extrapolate the value of $D_0$, is a theoretical prediction based on reptation theory. Recently, Lodge\cite{90} has shown that the diffusion coefficients for various polymers are
better fitted by the experimental power law $D = D_0/M^{2.3}$. If a 2.3 power law exponent is used, the values calculated for the substrate length at the I/II regime transition are much higher than those obtained with eq 6.12, and seem reasonable (Table 6.8).

It is noted that Cheng et al.’s study\(^{86}\) was restricted to relatively low molecular weight PEO fractions ($M_n < 21$ kg/mol) and were carried out at high temperature where crystallization can not take place. The power law coefficients determined in their study was found to depend on temperature. Furthermore, the activation energy for diffusion was also found to be molecular weight dependent. Due to the absence of high molecular weight data, one may still wonder whether the value of $D_0$ obtained by extrapolation is sufficiently reliable for use with our high molecular weight polymers.

Table 6.7 The parameters used to calculate the substrate length at I/II regime transition.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
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<td>$C_\infty$</td>
<td>5.7</td>
</tr>
<tr>
<td>$a$ (nm)</td>
<td>3</td>
</tr>
<tr>
<td>$m_0$ (g/mol)</td>
<td>44</td>
</tr>
<tr>
<td>$l_b$ (nm)</td>
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</tr>
<tr>
<td>$a_0$ (nm)</td>
<td>0.462</td>
</tr>
<tr>
<td>$b_0$ (nm)</td>
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</tr>
<tr>
<td>$\Delta H_f$ (erg/cm$^3$)</td>
<td>2.31E+09</td>
</tr>
<tr>
<td>$Q_d^*$ (J/mol)</td>
<td>16000</td>
</tr>
<tr>
<td>$k$ (erg.molecule$^{-1}$K$^{-1}$)</td>
<td>1.381E-16</td>
</tr>
<tr>
<td>$R$ (J.mol$^{-1}$K$^{-1}$)</td>
<td>8.345</td>
</tr>
<tr>
<td>$h$ (erg.s)</td>
<td>6.626E-27</td>
</tr>
</tbody>
</table>

Table 6.8 The substrate length at I/II regime transition obtained using two different power law.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$D_0 = DM^2$</th>
<th>$D_0 = DM^{2.3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>L(I/II) (nm)</td>
<td>L(I/II) (nm)</td>
</tr>
<tr>
<td>PEO-21K</td>
<td>4.65</td>
<td>93.3</td>
</tr>
<tr>
<td>PEO-43K</td>
<td>3.28</td>
<td>65.8</td>
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<tr>
<td>PEO-75K</td>
<td>3.35</td>
<td>67.2</td>
</tr>
<tr>
<td>PEO-113K</td>
<td>3.36</td>
<td>67.4</td>
</tr>
<tr>
<td>PEO-157K</td>
<td>3.2</td>
<td>64.1</td>
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</tbody>
</table>

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6.4.3 A Possible Mechanism for Regime Transitions

When discussing the chain length dependence of the crystal growth rate in the context of the current version of the LH theory, it is important to start with a brief description of how Hoffman and Miller\(^3\) introduced the concept of forced reptation in the LH theory. First, they defined the reeling-in rate of chain segments, \(r\), as the ratio of \(f_c\) of the undercooling-dependent crystallization force and \(\xi\), the friction coefficient \((r = f_c / \xi)\). Then, they assumed that the chain friction coefficient, \(\xi\), is independent of the rate of reeling-in and is proportional to the chain length. The substrate completion rate is proportional to the reeling-in rate, \(g = r (a_0 / l_g^*)\). By equating the expression of \(g\) written in terms of the reeling-in rate with that obtained in the class LH nucleation theory, they obtain an expression for the transport factor \(\beta\), which is inversely proportional to the chain length. In the standard LH theory, the same transport term, \(\beta\), is used for the rates of deposition/removal of the first stem and for these of subsequent stems. Hence, in the standard LH theory, the same chain length dependence is implicitly assumed for the substrate completion rate, \(g\), and the secondary nucleation rate, \(i\). Note, that this assumption is not physically meaningful. Indeed, Snyder and Marand\(^91\) suggested a much weaker chain length dependence for \(i\) than for \(g\), since deposition of the first stem is a very local process and should not be very sensitive to the overall length of the chain. Since both \(i\) and \(g\) are assumed to be inversely proportional to chain length in the LH theory, then, the overall growth rate \(G\) is also inversely proportional to chain length in both regimes I and II \((G(I) = b_o i L\) and \(G(II) = b_o(2ig)^{1/2}\)).

In 1992, Brochard and De Gennes (BD)\(^{17}\) proposed a model for the dynamics of a polymer chain pulled by one end through a melt of static chains. Their model predicted that the friction coefficient of the pulled chain would exhibit different chain length dependences in different velocity regimes. The BD model was developed further\(^{18-20,22,23}\) and its basic prediction were subsequently confirmed experimentally.\(^{106-110}\) In the following, the BD model is discussed in detail. Based on this model, a new mechanism for the chain length dependence of the crystal growth rate and for the origin of the I/II regime transition is given. We will therefore propose that I/II regime transitions should be interpreted as a transition in the reeling-in rate dependence of the friction coefficient rather than as a change in the relative rates of secondary nucleation and substrate
completion. Based on this interpretation, some fundamental aspects of the LH model need to be revisited.

### 6.4.3.1 Brochard-de Gennes (BD) Model

To understand crystallization, we need to understand how a chain deposits from the melt onto the crystal growth front. More specifically, we wish to investigate the dependence of the chain friction coefficient of a tethered chain on the chain length and possibly on the reeling-in rate. To discuss these issues, we consider the related process of pulling a chain by its head at a velocity $V$ with a force $F$ in an infinite melt of similar chains. This process has been discussed by de Gennes and collaborators. A chain attached to a substrate can no longer undergo free reptation and the motion of the tethered chain is constrained by the wall. Three velocity regimes have been predicted theoretically and confirmed experimentally.

At low velocity, the polymer chain is weakly deformed. In the time scale allowed for a melt chain to move an entanglement length $D^* = aN_e^{1/2}$ (where $a$ is the size of repeat unit and $N_e$ is the number of repeat units between two entanglements), the melt chain must travel along its tube to be disentangled from the tethered chain. Since this sliding time is $t_s = D^*/V = aN_e^{1/2}/V$, the sliding velocity for this melt chain is $V_{\text{tube}} = L_{\text{tube}} / t_s = D^*N/N_e(D^*/V) = (N/N_e)V$, where $N$ is the number of repeat units for the melt chain. Therefore the dissipation $T\dot{S}$ caused by sliding a melt chain is $N\xi V_{\text{tube}}^2 = (N^3/N_e^2)\xi \xi_r V^2$. This dissipation also can be expressed by the work of the force exerted by the melt chain on the tethered chain, which is $FV = T\dot{S} = (N^3/N_e^2)\xi \xi_r V^2$. Thus the force due to one single melt chain is $F = (N^3/N_e^2)\xi \xi_r V$. To estimate the friction force experienced by the tethered chain due to all the melt chains, one needs to know the number of melt chains entangled with that tethered chain ($X$). In the original model proposed by Brochard and de Gennes, a total entanglement assumption was applied, i.e., all melt chains in the volume occupied by the tethered chain are trapped. This makes $X$ proportional to $N^{1/2}$. Later, the “binary entanglement” model was proposed by Ajdari et al. This model assumes that the tethered chain only interacts with one melt chain in each entanglement blob. According to the binary model, the number of trapped chains, $X$ equals $N/N_e$ if $N <
$N_c^2$ and $N^{1/2}$ if $N > N_c^2$. In our case, the former will be applied considering the molecular weight range used. This model has been found\textsuperscript{22, 95} better than the total entanglement model as it gives a better fit to the rheological data.\textsuperscript{22} Using the binary model, one concludes that the friction force experienced by one tethered chain due to all entangled melt chains is given by:

$$F = \frac{N}{N_c}(\frac{N^3}{N_c^3})\xi_r V = \frac{N^4}{N_c^3}\xi_r V$$

(6.14)

Considering $F = \xi V$, where $\xi$ is the friction coefficient for the tethered chain, one obtains:

$$\xi = \frac{N^4}{N_c^3}\xi_r$$

(6.15)

Therefore, in this slow velocity regime, the friction coefficient is independent of velocity, but is strongly dependent of molecular weight. This regime is also called the stick regime due to the very large friction coefficient.

With an increase in velocity, the tethered chain begins to deform so that an elastic restoring force ($F_e$) develops. According to the Pincus rule,\textsuperscript{98, 99} $F_e = kT/D$, where $k$ is the Boltzmann constant and $D$ is the average blob diameter in the direction normal to the elongation. The tethered chain can be visualized as a trumpet formed by a string of blobs as shown in Figure 6.9. One can imagine that the blob size $D$ would decrease with increasing velocity until it reaches $D^*$ that is the distance between two entanglements. At this point, if one equates the friction force $F$ and the elastic force $F_e$, a threshold velocity $V^* = kTN_c^{2.5}\xi_r/(aN^4)$ is obtained. When $V > V^*$, the blob size is locked at $D^*$ and a constant elastic force $F_e = kT/D^*$ is expected. This regime is called the marginal regime. Again, equating $F_e = kT/D^*$ to $F = \xi V$, we obtain $\xi = kT/(aN_c^{1/2}V)$ is obtained. Obviously, the friction coefficient $\xi$ decreases with increasing velocity in the marginal regime, which indicates the development of slippage. Also in this regime, the tethered chain begins to disentangle which leads to lower friction. The predicted molecular weight dependence of $V^*$ was show to perfectly fit experimental results.\textsuperscript{96}

The friction in the stick and marginal regimes is mainly due to the existence of entanglements. However, the Rouse friction which acts on every monomer ($F_{Rouse} = N\xi_r V$) still contributes to overall friction force and would become dominant at high enough velocity\textsuperscript{17, 22} when $F_{Rouse} = F_e$ (marginal) = $kT/D^*$. From this equation, $V_{Rouse}$ can be derived as:

$$V_{Rouse} = (kT / aN_c^{1/2})(1 / N_c^2)$$

(6.16)
Figure 6.9 Schematic of conformational change of a chain with increasing the velocity.
The regime at $V > V_{\text{Rouse}}$ is named the Rouse regime in which the corresponding friction coefficient is:

$$\xi_{\text{Rouse}} = N \xi$$

(6.17)

Note that here as in stick regime the friction coefficient is independent of velocity but exhibit a weaker molecular weight dependence as shown in Figure 6.10.b.

![Figure 6.10](image-url)

**Figure 6.10** Evolution of (a) friction force ($F$) and (b) friction coefficient ($\xi$) with velocity in different regimes.
In summary, with increasing velocity, three regimes have been identified. In the stick regime, due to the limited deformation of the tethered chain, the entanglements contribute a lot to the friction force resulting in a very large friction coefficient, which is proportional to $N^4$. Further increasing the velocity leads to the deformation of the tethered chain, which can be described as a string of blobs with different sizes. When the blob size approaches $D^*$, the marginal regime is entered in which the tethered chains begin to disentangle, leading to a continuous decrease of the friction coefficient. Finally, the tethered chain develops into a string of blobs with size $D^*$. After that the Rouse friction $N\xi V$ becomes the dominant factor in the friction force.

In the following section, a new model for explaining the I/II regime transition in growth rate curve is proposed and applied to the case of PEO crystallization.

### 6.4.3.2 A Possible Mechanism for Regime Transition Based on Brochard–de Gennes Model

As mentioned above, the LH model assumes a weak undercooling dependence for the substrate completion rate $g$, in contrast to the strong undercooling dependence of $g$ in the Sadler, Toda, Frenkel models. If both the surface nucleation rate $i$ and the substrate completion rate $g$ exhibit an exponential dependence on undercooling suggested by Toda\textsuperscript{100}, the kinetic substrate length $L_k = (2g/i)^{1/2}$ may become insensitive to the undercooling. In this case, the mechanism for the I/II regime transition becomes suspicious and a new mechanism is desired. Obviously, considering that $g$ is related to the velocity at which a whole chain is transported from the melt onto the substrate ($V$), the variation of $g$ could be reflected in that of $V$. If $g$ changes with undercooling by several orders of magnitude, as shown by rate-equation calculations\textsuperscript{100}, $V$ may have chance to fall into different velocity regimes for which the molecular weight dependence of the friction coefficient would be different, as shown above. Recall the change in the molecular weight dependence of the growth rate in regimes I and II in the case of PEO (see Figure 6.7.b). It is possible to correlate the velocity regime with the growth rate regime to give a new mechanism for the I/II regime transition.

First we assume that there is no “regime I” in the sense defined by Hoffman er al. Second, we assume that regime II exists where the overall growth rate $G$ is expressed as
(2\(ig\))^{1/2}. In this case, the LH plot should be a straight line if the chain length dependence of the friction coefficient does not change in the experimental temperature range. We speculate that the transition observed on the LH plot results from a transition from the marginal velocity regime to the Rouse velocity regime. Such a transition is accompanied by a corresponding change in the chain length dependence of the friction coefficient. It can be seen from Figure 6.10.b that, when the marginal regime is entered, the chain length dependence of the friction coefficient becomes stronger and the friction coefficient increases significantly. This leads to a decrease in the growth rate below that expected by extrapolation of regime II (Figure 6.11.a). Therefore, it is natural to associate the marginal regime with the LH regime I and the Rouse regime with the LH regime II.

At this point, it is necessary to find the expression for friction coefficient in the marginal regime as a function of chain length. Here, we define a dimensionless parameter \(\rho\) which normalizes the velocity in the marginal regime:

\[
\rho = \frac{\ln(V) - \ln(V_{\text{Rouse}})}{\ln(V^*) - \ln(V_{\text{Rouse}})}
\]  

(6.18)

Here, \(\rho\) varies between 0 and 1. Since the friction force \(F\) is constant in the marginal regime, we can obtain \(\dot{\xi}_M V_M = \dot{\xi}_s V^* = \dot{\xi}_{\text{Rouse}} V_{\text{Rouse}}\). Using this relationship in addition to \(V^* \propto N^4\) and \(V_{\text{Rouse}} \propto N^4\), one concludes that \(\dot{\xi}_M \propto N^{3\rho+1}\), as shown in Figure 6.11.b. Obviously, \(3\rho + 1\) varies between 1 and 4. For the Rouse regime, \(\dot{\xi}_{\text{Rouse}} \propto N\).

If, like Hoffman et al., \(\rho\) we still assume that the reel-in rate, \(r\), and surface nucleation rate \(i\) are inversely proportional to \(\dot{\xi}\), then \(G\) should still be inversely proportional to \(\dot{\xi}\). Therefore, in “regime I” (corresponding to marginal regime), \(G\) should be inversely proportional to \(N^{3\rho+1}\) at fixed undercooling. The power law exponent \(s\) in regime I should be equal to \(3\rho + 1\), and take a value in the 1 to 4. The results shown on Figure 6.7 support this prediction. For the regime II, which corresponds to the Rouse regime, the \(s\) value should be 1, which is also consistent with the experimental results (see Figure 6.7).

A good linearity is observed in the LH plot for both regimes. Linearity in regime II is expected according to the new mechanism. Here, we propose an explanation for the linearity in “regime I”. According to the results of rate-equation calculations by Toda,
Figure 6.11 (a) Schematic of regime transition in growth rate due to the regime transition in friction coefficient. (b) The chain length dependence of friction coefficient (ξ) at $V^*$ and $V_{rouse}$.

$g$ is an exponential function of $1/\Delta T$. Since $i$ is also an exponential function of $1/\Delta T$, the overall growth rate $G$ in “regime I” could be expressed as following:

$$G(1) \propto N^{-(3\rho+1)} \exp\left(-\frac{K_{g(H)}}{T\Delta T}\right)$$

(6.19)
where $K_{g(II)}$ is the same nucleation constant as in regime II. Recall that since $\rho$ is velocity dependent in the marginal regime, it is also undercooling dependent. According to its definition, $\rho$ is a linear function of $\ln V$. Since $V \propto r \propto g$ and $g \propto \exp(-1/T\Delta T)$, $\rho$ should be a linear function of $1/\Delta T$. Therefore, one concludes that

$$G(I) \propto G_I^0(N)\exp\left[-(\ln(N) + K_{g(II)})/T\Delta T\right]$$

(6.20)

where $C$ is a constant. Thus linearity of the LH plot in “regime I” is explained. It is also noticed that the slope of LH plot in “regime I”, $K_{g(I)}$, should be $\ln(N) + K_{g(II)}$, which is chain length dependent. This explains the increase of $K_{g(I)}$ with chain length. This also implies that the prefactor $G_I^0$ should not follow the power law predicted by Hoffman and Miller (HM).

In summary, with the new mechanism, we are able to explain 1) the break in the LH plot, 2) the linearity of the LH plot in “regime I”, which actually should be named the marginal regime, 3) the chain length dependence of the nucleation constant in “regime I”, $K_{g(I)}$, 4) the observation that the exponential prefactor in “regime I”, $G_I^0$ does not follow the power law predicted by Hoffman and Miller. One should note that the proposal by Toda that both rates of surface nucleation and substrate completion exhibit a strong undercooling dependence, did not elaborate on the origin of regime transitions. Our new proposal therefore provides an important evidence for Toda’s model and even goes a large step further in proposing a new model for such transition.

**6.5 Conclusions**

The chain length and temperature dependences of spherulitic growth rates were studied for a series of narrow fractions poly(ethylene oxide) with molecular weight ranging from 11 to 917 kg/mol. The crystal growth rate data spanning regimes I and II crystallization temperatures were analyzed using the formalism of the Lauritzen-Hoffman (LH) theory. Our results are found to be in conflict with predictions from the LH theory. The $K_g$ ratio increases with molecular weight instead of remaining constant. The chain length dependence of the exponential prefactor, $G_I^0$, does not follow the power law predicted by Hoffman and Miller (HM). On this basis, the simple reptation argument proposed in the HM treatment and the nucleation regime concept advanced by the LH model are questioned. We proposed that the observed I/II regime transition in growth rate
data may be related to a transition in the friction coefficient, as postulated by the Brochard-de Gennes model. This mechanism is also consistent with recent calculations published by Toda in which both the rates of surface nucleation and substrate completion processes exhibit a strong temperature dependence.
6.6 Reference

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in regimes I or II and when the molecular weight is not too large. In regime III and in
the case of very high molecular weight polymers (see ref. 1), multiple secondary
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While the non-linearity may not be observable over the range of accessible crystallization temperatures, it may lead to considerable error in the estimation of the equilibrium melting temperature if a linear extrapolation is used.


(97) We will ignore for now a number of complications such as 1) the direction of this forces changes and 2) the length of the tethered chains decreases as the chain deposits on the growth front in a folded manner; 3) a given chain may not always get fully reeled-in (e.g. multiple nucleation, impingement of neighboring nuclei on a substrate, etc.); 4) the segment making first contact with the substrate may be other than a chain end.

