Crystal growth rate as a function of molecular weight in polyethylene crystallized from the melt: an evaluation of the kinetic theory of polymer crystallization

J. J. Point and M. Dosière
Université de Mons, 21 avenue Maistriau, B-7000, Mons, Belgium
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The aim of this paper is a critical evaluation of the classical kinetic theory of polymer crystallization. This theory, even the most recent version of Hoffman and Miller[4] does not explain the kinetic data of Labaig[2] on crystallization of polyethylene (PE) from the melt. We define various characteristic lengths which are significant in Hoffman and Miller's approach[4] and state that their values, as calculated from the theory, are not consistent with assumptions which are basic to the model. Lastly, we recall some conceptual shortages of the theory. We conclude that the occurrence of regime I is completely hypothetical and that the use of the $\log G$ *versus* $1/T\,\Delta T$ plot to determine the product $\sigma\sigma_e$ of the macroscopic interfacial free enthalpies of the lateral and of the fold surfaces is unjustified.

(Keywords: polyethylene; classical kinetic theory of crystallization; crystallization regimes; persistence length)

INTRODUCTION

The data of Hoffman *et al.*[1] and Labaig[2] on the crystallization of polyethylene (PE) from the melt and their interpretation[3–5] are the keystone of the classical kinetic theory of polymer crystallization. The graph of the logarithm of the growth rate of polymer crystals *versus* the isothermal crystallization temperature shows a break (*Figure 1*). This fact and other similar results on other systems, which are not so well documented, are the sole presumptions that, as stated in ref. 4 'some agency breaks up the growth front into apparently independent sections of mean length L_p', a length which is independent of the crystallization temperature and of the molecular weight. This strong assumption and the numerical value of L_p are basic to the Hoffman–Lauritzen (HL) theory[3]. Until 1986 the assumed order of magnitude of the (hypothetical) persistence length L_p was 1 μm [Hoffman[6]]. In 1986, Point *et al.*[7] noted that if L_p was actually as large, nonlinear growth should be readily observed. Hoffman and Miller[4] (HM) state that their new estimate of L_p (21 nm) removes this objection. The change of the order of magnitude of this (hypothetical) length is a revolution and the theory needs to be assessed again[8–11]. This is the aim of the present paper.

We first examine the predictive ability of the HM formulae[4] when applied to the data of Labaig[2] on the crystallization of polyethylene from the melt. Then, we establish a clear distinction between mononucleation regime and regime I and we define various characteristic physical lengths which are significant in the HM model[4] in order to examine whether the calculated values of these lengths are consistent with the assumed physical description of the crystallization process. Lastly we recall[9] some conceptual shortages of the HM[4] (and HL) theory.

GROWTH RATE OF PE CRYSTALS GROWN FROM THE MELT: A COMPARISON BETWEEN PREDICTED AND OBSERVED VALUES

Figure 1 gives, for a sharp PE fraction[11] ($M_w = 35\,000$; $M_z = 39\,200$), the growth rate data of Labaig[2] and a curve calculated from the two following formulae of Hoffman and Miller[4].

$$G\,(\mu\text{m/s}) = (2.841\times10^{17})n_z^{-4/3}\,\Delta T\,\mathrm{e}^{-5736/RT}\times\mathrm{e}^{-1.91\times10^{5}/T\Delta T} \qquad (1)$$

$$G\,(\mu\text{m/s}) = (2.836\times10^{10})n_z^{-7/6}\,\Delta T\,\mathrm{e}^{-5736/RT}\times\mathrm{e}^{-0.955\times10^{5}/T\Delta T} \qquad (2)$$

where T is the isothermal crystallization temperature; $\Delta T = T_m - T$, the undercooling; T_m is the melting point and n_z the z average of the number of CH_2 units in one molecule.

Equations (1) and (2) were used when the crystallization temperature was, respectively, higher and lower than 127.8°C. Neither the calculated nor the experimental values of the growth rate depend greatly on the molecular weight and similar correlations are noted for other fractions. For the fractions of M_w equal to 23.4; 35; 50.7; 97.2; 133 and 241 K, the mean value of the ratio of the experimental and calculated value of G is found to be 0.63 ± 0.39 at 125°C and 1.43 ± 1.23 at 129.5°C. On the other hand, according to Hoffman and Miller[4], a good agreement is obtained between the data of Hoffman, Frolen, Ross and Lauritzen[1] and the values determined from equations (1) and (2). If both the experimental data of refs 1 and 2 are taken into account the HM formulae[4] do not justify the dependence of G on the molecular weight (and *a fortiori* do not support the steady-state reptation model of HM[4]). This is illustrated by *Figure 2*

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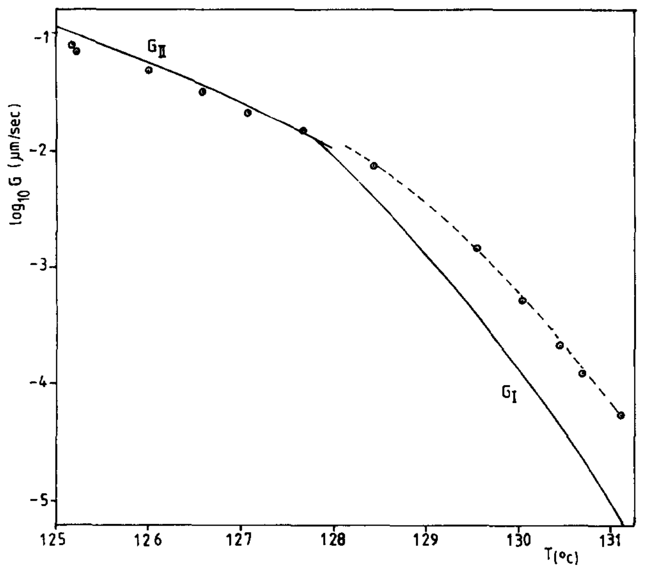

Figure 1 Growth rate of crystals grown from the melt for a PE fractin ($M_w = 35000$; $M_w/M_n = 1.12$; $n_z = 2794$). Data from ref. 2. Full line by equation (1) and (2)

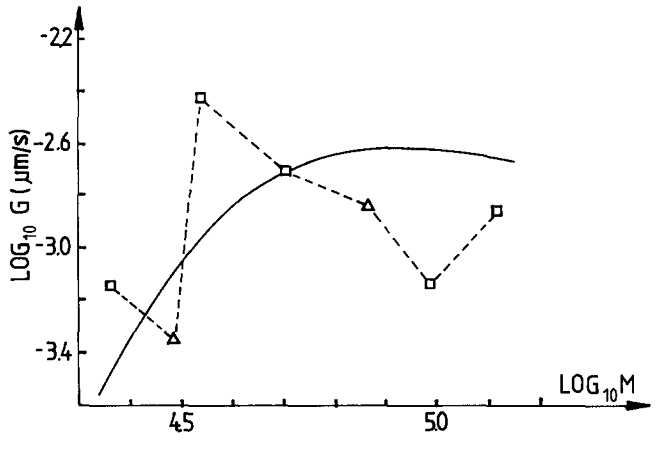

Figure 2 $\mathrm{Log}_{10} G$ *versus* $\log_{10} M_w$ at 129°C. □, data from ref. 2 and △, data from ref. (1) [selected as in ref. (5)]. Full line by equation (1)

where experimental data show unambiguously a molecular weight dependence of G other than that predicted by the equations (1) and (2).

Moreover these equations cannot be used to describe exactly the break of the log G *versus* T curves. They lead to the prediction that the graph of $\ln G + 5736/rT - \ln \Delta T$ *versus* $1/T\Delta T$ is made of two straight segments whose slopes are in the ratio 2/1. Let us consider, (*Figure 3*), in a representation proposed by HM[4], the data pertaining to the crystallization of a particular fraction ($M_w = 30600$, $n_z = 2740$). In the vicinity of the break the experimental points are near two straight segments the slope of which are in the ratio 2.44:1. This ratio appreciably differs from 2:1.

The equation of a curve made of two straight segments depends on only four parameters if, however, there is no definite relation between the slopes of these segments. We conclude from the present analysis which is based on both sets of available data[1,2], that equations (1) and (2) have a poor predictive ability.

A proper account of the HM theoretical model[4] leads to the prediction that the slope of the $\ln G + 5736/rT - \ln \Delta T$ *versus* $1/T\Delta T$ curve changes continuously over a large temperature range and that the distance between the theoretical curve and its asymptotes is of significant magnitude. The experimental points are not found on the theoretical curve, but on its asymptote.

THEORETICAL

We restrict ourselves, in this part of the paper, to a discussion of the self-consistency of the theory, without touching on the conceptual problems raised by the HM[4] [and HL[3,5]] formalism. To examine this point we adopt the following procedure. We show that the theory leads to consideration of five characteristic lengths. Then in the discussion, we examine whether the order of magnitude of these lengths, as calculated by the HM theory[4], are coherent in the framework of the model itself. Firstly, we establish a clear distinction between the mononucleation regime and regime I.

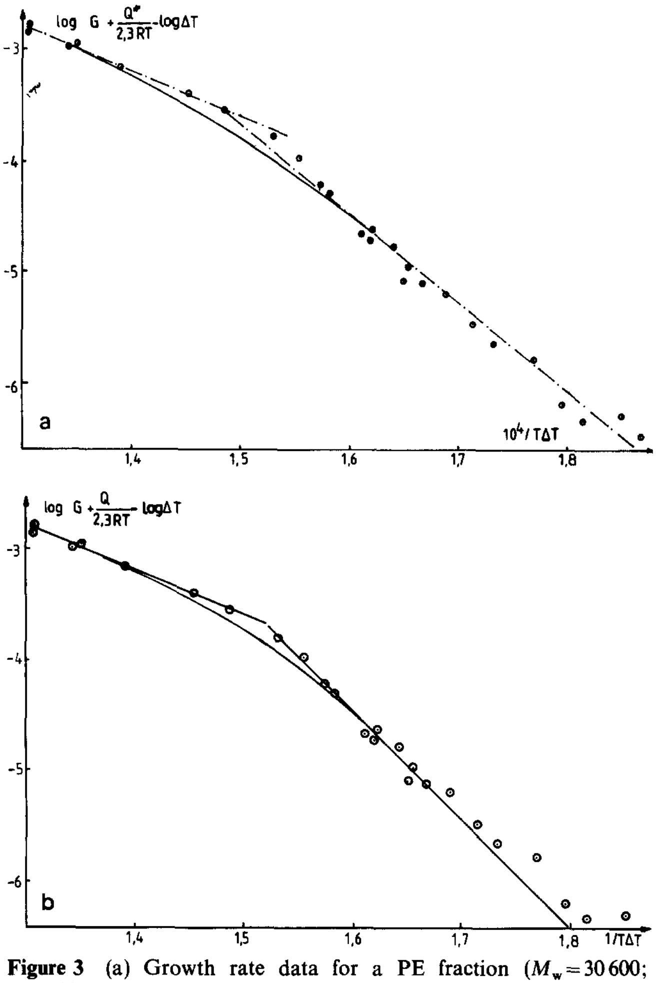

Figure 3 (a) Growth rate data for a PE fraction ($M_w = 30600$; $M_z = 38630$; $T_m = 416.8$ K); data from ref. 1. The straight segments are obtained by linear regression for data in the temperature ranges 124–127°C and 127–128.7°C. $K_{gI} = 0.919 \times 10^5$; $K_{gII} = 1.862 \times 10^5$; $K_{gI}/K_{gII} = 2.02$. The curve in full line is calculated by assuming that the break in the curve is due to a regime I–regime II transition (see text). The experimental points in the vicinity of the break are not on the curve but on its asymptotes. This shows that the observed 'transition' is sharper than that predicted on this basis. In the high temperature range the experimental points are outside the straight segment. This effect is not observed when old versions of the HL theory are tested (because in this case the term $\ln \Delta T$ is omitted). (b) Another linear regression on the same data. The temperature ranges were 124–127°C and 127–131°C. $K_{gI} = 2.245 \times 10^5$; $K_{gII} = 0.919 \times 10^5$; $K_{gI}/K_{gII} = 2.44$. In the vicinity of the 'transition', the experimental points are not on the curve, calculated by assuming a regime I–regime II transition. Therefore, this hypothesis cannot be retained

The Frank model and the kinetic length: mono and polynucleation regimes

In the Frank model[12] of growth by secondary nucleation, nuclei are initiated on a substrate of length L at a rate of i events per unit time and length. Such a nucleus spreads on the substrate at a rate g. For a sufficiently high value of the kinetic length $L_k = (2g/i)^{1/2}$ there is a high probability that a nucleus generated on the substrate covers the whole substrate before the occurrence of another nucleation event. In this situation, known as the mononucleation regime, the growth rate is

$$G = biL \tag{3}$$

where b is the thickness of the nucleus. If the substrate is an edge of a polygonal crystal, L increases with a rate proportional to G and the crystal grows exponentially with the time[7]. We have discussed this point in detail elsewhere[7]. The other extreme situation, where $L_k \ll L$, is known as the polynucleation regime (or regime II, see later). Then, a certain number of nuclei (of the order of magnitude of L/L_k, where L_k is the mean distance between the nuclei, or the 'niche separation'[5], grow simultaneously. If it is assumed that when two steps moving in the two opposite directions at the same level encounter each other, these steps are annihilated, then $G = b(2gi)^{1/2}$.

The Hoffman and Lauritzen (HL) model: thermodynamic length, persistence length and regime I

Hoffman and co-workers make use of the Frank model[12] to describe polymer crystallization. The initiation step is pictured as the attachment of a single full stem. The spreading of the nucleus results from addition of further stems. Because of the occurrence of new lateral surfaces, the initiation steps leads to an excess free enthalpy which contains a term equal to $2bl\sigma$ where l is the length of a stem and σ the interfacial surface free enthalpy. Provided that it is adjacent, the addition of a further stem decreases this excess free enthalpy if the length exceeds the thermodynamic limit $l^* = 2\sigma_e/\Delta s_f\,\Delta T$ (where σ_e is the fold surface interfacial free enthalpy and Δs_f the entropy of fusion per unit volume) by an amount which we denote δ. When the width of the nucleus is higher than the thermodynamic length $L_t = 2bl\sigma/ab\delta\ \Delta s_f\ \Delta T$, the excess free enthalpy becomes negative and the nucleus is stable.

A strong additional hypothesis leads to the concept of regimes I and II. The edge of the lamellar crystal is assumed to be subdivided into independent sections of mean length L_p. The boundaries between these sections are defects which stop the growth of the nuclei. Thus provided that $L \gg L_p$ and $L_k \gg L_p$ equation (3) must be replaced by $G = biL_p$ and the growth rate is a constant. This hypothetical situation (which differs from the mononucleation regime by the strong assumption of the existence and the constancy of L_p) is known as regime I (in contrast to regime II, which is the polynucleation regime).

In addition to the four lengths l, L_k, L_p, L_t, a fifth length is of interest. This is the width L_m of a nucleus made of one macromolecule folded adjacently in a conformation with full adjacency.

Discussion of the coherence of the HM model

Despite our conceptual reservations (see later), we examine whether the order of magnitude of l, L_p, L_t, L_k, L_m as calculated by Hoffman and Miller[4] are consistent with their own model.

For a particular fraction ($M_w = 30\,600$, $M_z = 38\,360$), we have calculated (*Table 1*) by the HM formalism[4], the values of the five lengths defined in the theoretical part of that paper.

The values of the crystal thickness l differ from the estimation given by Hoffman, Frolen, Ross and Lauritzen[1], from those measured by Labaig[2] on similar samples and from those measured more recently by Barham *et al.*[13]. Because l may change after the crystallization any discussion would be inconclusive.

We have shown[7] on experimental grounds that the previously assumed value of L_p (if such a length exists) $\simeq 1\,\mu$m was too large. As noted by Hoffman and Miller[4] the new value of L_p (21 nm) is so small that the experimental determination of this hypothetical length is not practicable.

The width (L_t) of a stable nucleus exceeds the width (L_m) of a layer made of a single molecule. This implies two types of initiation process as described by Toda[14], either the attachment of a molecule on a smooth surface or the attachment of a molecule in a niche in view to achieve the building of a stable nucleus. The ratio L_t/L_m depends on the molecular weight and on the temperature. This fact is not taken in account in the theory and was thus, for an unknown reason, considered as irrelevant by Hoffman and Miller[4].

When L_k and L_m are compared, for instance, at 124°C, the mean distance between the nuclei is calculated to be more or less 2 nm. Every molecule which attaches itself to the crystal occupies a width of 8.8 nm. Thus each molecule is shared between several layers. This cannot be taken into account by the ciliation concept[15].

In order to compare L_t and L_p, let us consider what happens at 129°C when the width of a nucleus attains L_p (21 nm). Some defect of the lattice must stop its growth, before it attains the length L_t ($\simeq 70$ nm) of thermodynamic stability. This is a puzzling situation.

Table 1 Evaluation of the kinetic theory of crystallization

t_c °C	l (nm)	L_m (nm)	L_t^a (nm)	L_t^b (nm)	L_t^c (nm)	L_k^d (nm)	L_p (nm)
121	12.4	10.7	34.8	29.0	25.0	0.4	21
122	13.0	9.6	37.9	32.0	27.7	0.7	21
123	13.6	9.2	41.5	35.2	30.9	1.2	21
124	14.2	8.8	45.6	39.1	34.5	2.1	21
125	15.0	8.4	50.4	43.6	38.7	4.0	21
126	15.8	7.9	56.1	48.9	43.8	8.0	21
127	16.7	7.5	62.8	55.2	49.7	17.7	21
128	17.7	7.0	70.7	62.7	56.9	43.2	21
129	18.9	6.6	80.4	71.9	65.7	118.7	21
130	20.2	6.2	92.3	83.1	76.5	378.0	21
130.5	21.0	5.9	99.2	89.8	82.9	720.6	21

[a] Calculated by $L_t = (\sigma/\sigma_e)(ll^*/\delta)$; $l^* = 2\sigma_e/\Delta G$; $l = l^* + \delta$; $\delta = kT/2b\sigma$

[b] Calculated by $L_t = (\sigma/\sigma_e)(ll^*/\delta) - (a/\delta)l^* + (\sigma/\sigma_e)\lambda \ln(l_0/x_0)l^*$ (ref. 4)

[c] Lower bound calculated by $L_t = (\sigma/\sigma_e)(ll^*/\delta) - (a/\delta)l^*$ (because the exact values of λ and l_0/x_0 are not given in ref. 4)

[d] Calculated by (ref. 4)

$$L_k\,(\text{nm}) = 21(T_0/T)^{1/2} \exp[K_{gII}(1/T\,\Delta T - 1/T_0\,\Delta T_0)]$$

$$\times \exp[Q/2r(1/T_0 - 1/T)]$$

[e] From ref. (4) we adopt the following values for the parameters involved. $\sigma = 11.8\ \text{mJ/m}^2$; $\sigma_e = 90\ \text{mJ/m}^2$; $\Delta s_f = \Delta h_f/T_m$; $\Delta h_f = 2.8 \times 10^8\ \text{J/m}^3$; $Q = 5736$ cal; $K_{gII} = 0.955 \times 10^5$; $T_m = 416.77$K; $T_0 = 400.36$K; $\lambda = 1/3$; $a = 0.455$ nm; $b = 0.415$ nm; $l_0/x_0 = 30\,600/14.03$

In the low temperature range, L_k is much smaller than L_t. This leads to the same perplexing difficulty, as quoted in the preceding paragraph.

From these examples, it may be concluded that the HM model[4] is not self-consistent. These various objections were presented ten years[9] ago when dealing with old versions of the theory.

FURTHER THEORETICAL DISCUSSION

Let us consider the pre-exponential factor C_0 which according to Hoffman and Miller[4] represents 'the configurational path degeneracy associated with the nucleation process'. We recognize that in any kinetic theory it is necessary to introduce a pre-exponential factor but we note that, in view of the fact that there are 'many ways ultimately leading to a first full stem'[4] the value of C_0 and its temperature and molecular weight dependence may be the crux of the problem (indeed a rather difficult problem[9,10]). Actually C_0 is chosen by Hoffman and Miller[4] to be a constant equal to 2.5×10^7. (In previous versions of the theory[5] the corresponding factor was chosen dependent on the temperature and molecular weight and its order of magnitude was 10^2.)

In addition, introduction of C_0 contradicts the assumptions which lead to the use of σ (a macroscopic free energy) in the expression of the lateral free energy. Hoffman and Miller's[4] use in the expression of the rate constant of the exponential factor of the form $\exp(-\varepsilon/kT)$ where ε/kT is unusually large (for instance larger than 30) results from the fact that the deposition of a full stem is considered as a single step. This was shown to be unjustified elsewhere[10]. For these various reasons, the developments of Hoffman and Miller[4] are not actually a theoretical calculation.

CONCLUSIONS

As is well known, when crystallization of PE from the melt is considered the plot of ln G *versus* T shows a break in slope (*Figure 4*). This may be due to molecular weight segregation[17], to a modification of the kind of the thermal dependence of the thickness of the lamellae (note that at sufficiently low temperatures the thickness of the lamellae is not inversely proportional to the supercooling but is more or less constant[16]), to a thermal dependence of the viscosity or to other physical parameters. This problem is of interest.

We have mentioned various drawbacks in the explanation given by Hoffman and co-workers[1,3–5]. Moreover, an irretrievable defect of the HM[4] and HL theories is the fact that they lead to values of L_k, L_p, L_t, L_m which are not consistent with the model itself. Similar difficulties are encountered with such models when crystallization of PE from dilute xylene solutions is considered. But in this case it may be argued that the Frank nucleation model[12] probably holds despite the fact that the analytical expressions proposed by Hoffman and Miller[4] for i and g are not valid[19].

If the expressions of G given by Hoffman and Miller[4] were considered as empirical formulae, they would require various improvements. As given in ref. 4, these formulae allow only a poor prediction of the value of G (within a factor of 5). Moreover, they cannot be used to

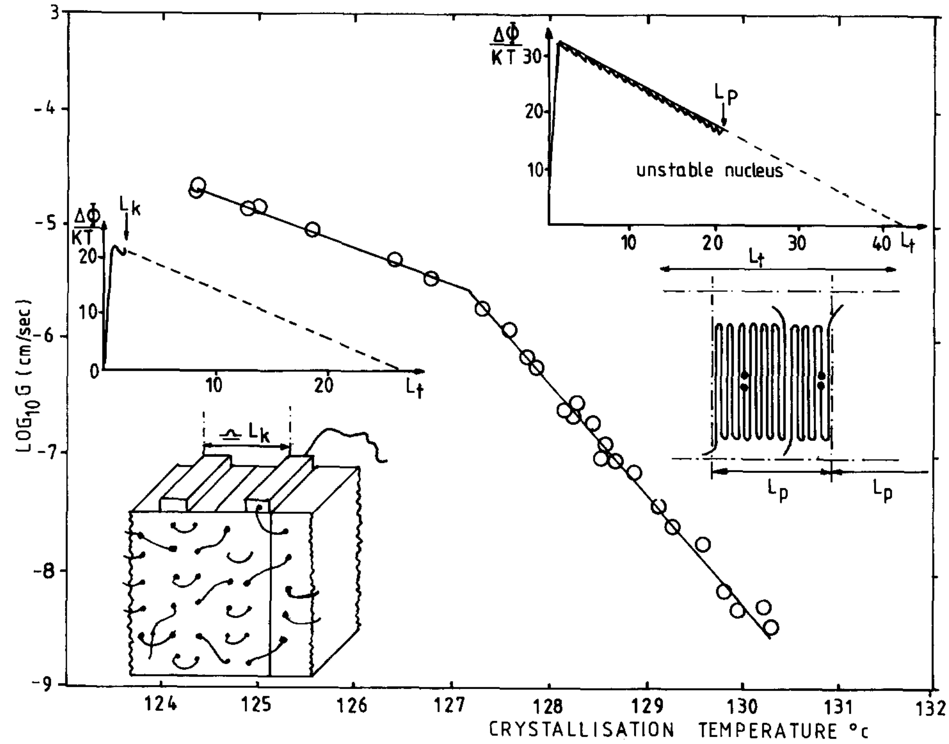

Figure 4 Growth rate data for a PE fraction ($M_w=30600$; $M_z=38360$) (data from ref. 1). This figure is, in fact, that usually shown to illustrate the HL assumption of regime I–regime II transition[3,17]. However, there are various inconsistencies. For example, the transition appears too sharp (see also *Figure 3*). As shown in the upper insert: L_m is smaller than L_t and several molecules are involved in the building of a single stable nucleus. Because $L_p<L_t$, the growth of a nucleus stops before it is stable. For clarity, the width of the first stem is enlarged. As shown in the lower insert: L_m is larger than L_k and each molecule is shared between various layers. Because both L_p and L_k are lower than L_t, development of stable nuclei is not possible.

predict the trends of the dependence of G with molecular weight, which are shown here in *Figure 2*, taking into account the experimental data of both the refs 1 and 2. From a pragmatic point of view, occurrence of regime I is completely hypothetical and the use of data on the crystal growth rate of polymer to derive information about macroscopic interfacial free energies is totally unjustified.

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