Kinetics of Poly(ethylene oxide) Crystallization from Solution: Concentration Dependence

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ABSTRACT: Crystallization kinetics of poly(ethylene oxide) (PEO) grown from dilute solution in toluene has been investigated at various concentrations by a dynamic light scattering technique. It is found that the exponent γ ($G \propto c^{\gamma}$) varies between 0.49 and 0.73. At a given temperature, γ tends to decrease when PEO molecular weight increases from 56 300 to 325 000. For a given molecular weight, the magnitude of γ has a weak temperature dependence. We have observed a slow increase instead of an abrupt change of γ in the vicinity of the apparent regime transition temperatures. Investigation of the temperature dependence of the growth rate at several fixed concentrations confirms previous work that curvature was observed at high mass fraction but was not obvious for intermediate masses.

Introduction

In a recent paper we have investigated the temperature and molecular weight dependence of the growth kinetics of PEO crystals at a fixed concentration (0.01% w/w).[1] It was found that when the PEO molecular weight was smaller than 325 000, a plot of log G versus $1/T\Delta T$ could be fit to a line. When the molecular weight was equal to or higher than 325 000, curvature was obvious. There were two discernible linear regions in the data with slope differences of about 2. The molecular weight dependence of the growth rate was found to depend significantly on the choice of equilibrium dissolution temperature, $T_d°$, but generally the growth rate increased with molecular weight. In this paper, we continue our study of this system by focusing on the concentration dependence of the crystal growth rate.

Experimentally, Cooper and Manley found that the growth rate of PE crystals from dilute solution in xylene increased with a fractional power (0.19–0.60) of the concentration.[2] The magnitude of the concentration exponent γ at a given crystallization temperature decreased as the molecular weight increased, and it tended to increase as the crystallization temperature increased for a given molecular weight. They explained these observations by the Sanchez–Di Marzio theory of cilia nucleation,[3] where cilia, a portion of a chain dangling in the solution and not incorporating into the crystal, could nucleate a new layer. Toda et al. have a series of papers discussing the concentration dependence of PE crystal growth rate.[4-7] They found that, for high molecular weight samples (MW > 3×10^4), cilia nucleation explained the observed $^1/_3$ power dependence of the growth rate on concentration. In their most recent paper,[7] they have studied the growth kinetics of {110} twins and found that when c is less than some cutoff concentration c_0 ($c_0 \approx 1.0 \times 10^{-4}$ wt %), the crystal growth rate, G, is proportional to c and when $c > c_0$, $G \propto c^{1/2}$ for low molecular weight samples (MW < 3×10^4). They also independently measured the nucleation rate i and the step propagation rate g. It was found that i is linear with concentration at low concentrations and becomes independent of concentration in the normal dilute range. The step propagation rate g is proportional to concentration over the entire range. The concentration dependence of the nucleation rate was attributed to absorbed polymers on the growth face. The crystal growth rate G can be expressed as

$$G = biL \qquad \text{regime I} \tag{1}$$

$$G = b(2ig)^{1/2} \qquad \text{regime II} \tag{2}$$

by nucleation theory,[8] where b is the crystal stem thickness. The difference in behavior between the two regimes comes naturally from the relative importance of nucleation (regime I) and propagation (regime II).

Experimental Section

The detailed procedure for solution and seed preparation, light scattering instrumentation, kinetics measurements, and data analysis can be found in our previous papers.[1,9,10] Briefly, the procedure to obtain growth kinetics is to use dynamic light scattering (DLS) to measure the change in hydrodynamic size of crystals growing from cleaned and supercooled solutions. We initiate crystal growth by addition of a 0.01% w/w seed suspension. The weight ratio of seed suspension to polymer solution is about 1/20. The small concentration difference caused by adding seeds into polymer solutions of different concentration is taken into consideration in the calculation. For high-concentration samples (0.2% w/w), the autocorrelation function of the scattered light tends to deviate from a single-exponential decay when crystals are nearly fully grown. This is perhaps due to a significant birefringence and strong anisotropy of the large crystals where both effects can lead to nonexponential DLS autocorrelation functions. However, since we take the crystal growth rate from the early time slope in the plot of the inverse decay constant, $1/\Gamma$ ($\propto R_h$) versus time, the nonexponential decay problem for the light scattering is avoided. The experimental uncertainty in growth rates from fits to the DLS analysis is approximately ±10%. At high growth rates the uncertainty is somewhat larger.

The polydispersity and molecular weights of the PEO samples were checked by gel permeation chromatography (GPC) as described previously.[11] PEO samples were dissolved in hot THF for the GPC work. Upon cooling to room temperature, no precipitation was found. The characterization of the polymers is listed in Table I.

Results and Discussion

One of the first considerations concerning the kinetics of crystallization from solution is the role of diffusion of the dissolved polymers to the crystal surface during crystallization. This will be of fundamental importance in modeling the kinetics of the process, and it was the first

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Table I
Molecular Characterization of PEO Fractions

sample	M_p[a]	M_w/M_n[a]	M_w/M_n[b]	N_w
PEO 56	5.63×10^4	1.05	1.05	1340
PEO 105	1.05×10^5	1.03	1.09	2460
PEO 160	1.60×10^5	1.05	1.12	3820
PEO 325	3.25×10^5	1.06	1.14	7830
PEO 770	7.70×10^5	1.12	1.18	19600

[a] Molecular weight and polydispersity supplied by manufacturer.
[b] Polydispersity measured by GPC.

effect investigated in the present work. Experimentally, we have varied by 4 times the amount of seeds introduced into a 0.1% PEO 160 solution at high supercooling (T_c = 17 °C, $\Delta T \sim 22$ °C). We observed that the crystal growth rate did not change within experimental error. This is different from a diffusion-controlled rate where, for more seeds in the solution, crystal growth would be faster.

We can also assess the importance of diffusion by comparison of the nucleation time derived for the most rapid crystallization and the diffusion time of a polymer to the crystal surface. Using a fast growth rate we measure, $G = 25$ nm s^{-1}, the time for the occurrence of a nucleation event in a layer is $b/G = 1.9 \times 10^{-2}$ s (where the stem thickness b is taken as 0.465 nm, ref 8). The minimum time of the arrival of new molecules to the surface by diffusion can be estimated as follows. For the lowest concentration of 0.001% and molecular weight of 160 000, the distance, d, between the center of mass of two polymers can be estimated as $d = V^{1/3} = (M/c\rho N_a)^{1/3}$ where V is the volume of solution per polymer molecule, with M the molecular weight, c the concentration (w/w), and ρ the solution density. The average distance is then 3.1×10^{-5} cm which for a diffusion constant estimated to be[12] $D_0 = 3.6 \times 10^{-7}$ cm^2 s^{-1} leads to a diffusion time of 4.4×10^{-4} s. Even in this extreme case, i.e., very fast growth rate and very dilute solution (experimentally, we could not reach such a fast growth region at this dilution), the time of the arrival of a polymer to the crystal surface is still shorter than the time needed to nucleate a molecule on the substrate by almost 50 times. Therefore, we conclude that diffusion does not limit the crystal growth rate.

In early nucleation theory, L was identified as the substrate length of the crystals.[8] Because $G \propto L$ and $G \propto dL/dt$, this leads to an exponential growth pattern in regime I. Such nonlinear growth has not been observed experimentally. Recent improvements in nucleation theory have assigned L as the mean substrate length between defects.[13,14] However, there is disagreement concerning the value of L and indeed the actual existence of regime I.[15,16] Very recent work by Hoffman and Miller gave L to be about 50 nm for PE.[17] We have attempted to address this problem experimentally by measuring crystal growth from solutions of the same polymer concentration, initiated by seeds of varying sizes. If G is a function of seed size, the equation for growth should contain a dependence on substrate length. In our previous work,[10] we showed that seed size can be varied by changing the concentration of original seed preparation solutions. Therefore, we have prepared seed suspensions from concentrations of 0.005–0.1% and used them to seed 0.1% solutions of PEO 160 at 20 °C. These conditions appeared to show regime I growth in our previous work.[1] In these experiments we find that the crystals grow at the same rate independent of seed size. At the least, this result confirms that, if regime I growth exists, L is not given by the substrate length. Our current experiment cannot be used to estimate L for PEO, since, if L is in the range of 50 nm, it is much smaller than our seed sizes.

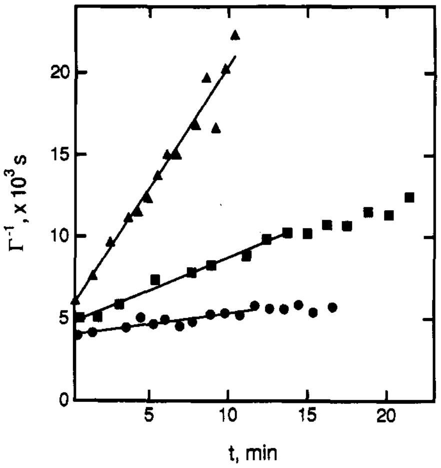

Figure 1. Crystal growth rate plot of inverse scattering decay constant versus time for PEO 160 at 20.0 °C at (▲) 0.1%, (■) 0.05%, and (●) 0.01% concentrations.

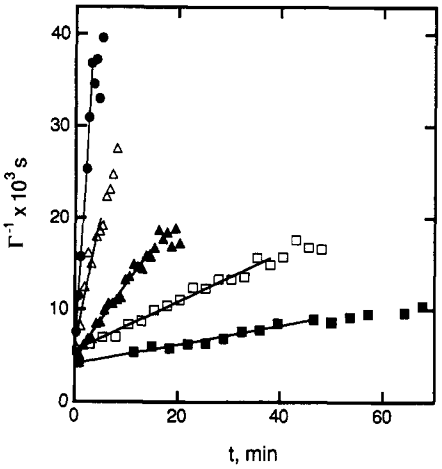

Figure 2. Plots of Γ^{-1} ($\propto R_h$) versus time at a concentration of 0.1% for PEO 325 at (●) 17.0 °C, (△) 20.0 °C, (▲) 23.0 °C, (□) 25.0 °C, $t \times 2$, and (■) 26.5 °C, $t \times 5$.

Having thus established the independence of the growth rates to both seed size and seed concentration, we can focus on the dependence on polymer concentration. At constant temperature the growth rate can be described by the relation

$$G \propto c^{\gamma} \tag{3}$$

where γ is a constant. Figure 1 is an illustrative crystal growth plot at three concentrations for PEO 160 at 20 °C by plotting Γ^{-1} versus time, where Γ^{-1}, the inverse decay constant from the DLS measurement, is proportional to R_h, the hydrodynamic radius of scattering particles. The slope of the plot can be transformed to a crystal growth rate.[1,9,10] Qualitatively, crystals grow much faster at higher concentration than at lower concentration. Figure 2 is a similar plot for PEO 325 at a concentration of 0.1% when T changes from 17 to 26.5 °C.

In accordance with our previous work,[1] we have not seen a significant decrease of the crystal growth near the end of crystallization even for our highest concentration near 0.25%. This is in contrast to Point's finding.[18] They analyzed a fall of the growth rate near the end of crystallization, which is most pronounced at shallow supercooling, in terms of mass diffusion, concentration dependence of the growth rate, and molecular weight fractionation. Their study eliminated the first two possibilities.[18] In our calculation of the crystal growth rate, the initial slope in the plot of Γ^{-1} versus time is extracted

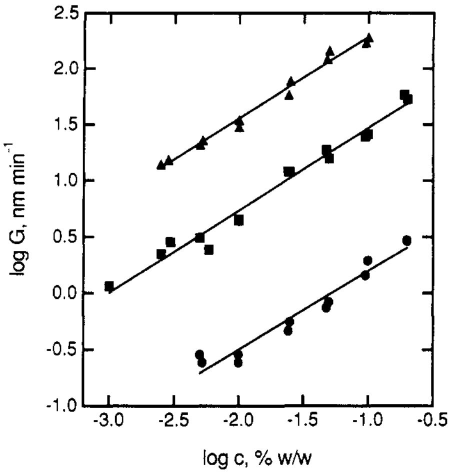

Figure 3. Concentration dependence of the crystal growth rate for PEO 56 at (▲) 17.0 °C, (■) 20.0 °C, and (●) 23.0 °C.

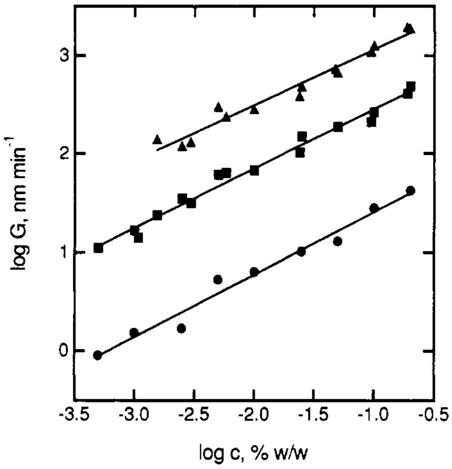

Figure 4. Concentration dependence of the crystal growth rate for PEO 160 at (▲) 17.0 °C, (■) 20.0 °C, and (●) 23.0 °C.

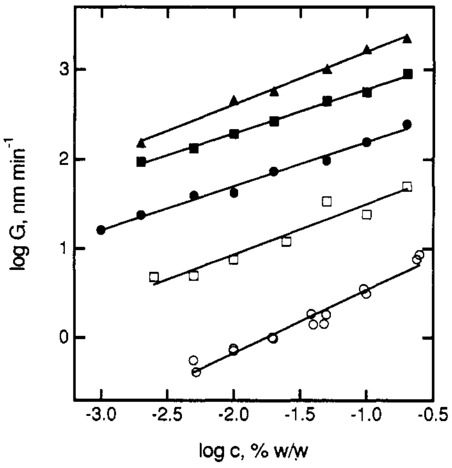

Figure 5. Concentration dependence of crystal growth rate for PEO 325 at (▲) 17.0 °C, (■) 20.0 °C, and (●) 23.0 °C, (□) 25.0 °C, and (○) 26.5 °C.

in order to avoid complications of falling growth rate toward the end of the growth. Figures 3–5 show the concentration dependence of the crystal growth for three molecular weights and several crystallization temperatures. These plots of log G versus log concentration are linear, and the slopes (γ) are listed in Table II. Two features are found. First, at fixed crystallization temperature (T_c), γ tends to increase slightly as molecular weight decreases, and, second, at fixed molecular weight, γ seems weakly dependent on the temperature. In general, these observations are consistent with Cooper and Manley's observation for PE crystals grown from dilute solution of xylene.[2] However, the magnitude of γ they measured changes more rapidly from 0.595 to 0.190 (at T_c = 90.70 °C) when the molecular weight of PE spans from 15 700 to 451 000.[2] In comparison, our data of γ are more constant and larger, for similar chain lengths.

Table II
Concentration Dependence of Crystal Growth Rate

sample	T_c, °C	regime	γ
PEO 56	17.0	II	0.73
PEO 56	20.0	II	0.73
PEO 56	23.0	II	0.69
PEO 160	17.0	I(II)	0.57
PEO 160	20.0	I(II)	0.60
PEO 160	23.0	I(II)	0.63
PEO 325	17.0	II	0.59
PEO 325	20.0	II	0.49
PEO 325	23.0	II(I)	0.49
PEO 325	25.0	I(II)	0.57
PEO 325	26.5	I	0.71

Sanchez and Di Marzio first proposed the cilia nucleation theory,[3] in which a finite chain attaches to a crystal growth front from a solution. Since the crystallization need not start from the end of the chain but can start from the middle of the chain, the longer portion of the chain folds back more readily to crystallize. It may be that the shorter portion does not crystallize on this layer but rather dangles in the solution. These portions are called primary cilia, and they may nucleate on the next layer. The nucleation rate is therefore the summation of the cilia nucleation rate (i^c) and the solution nucleation rate (i^s) with weighting factors (w_i):

$$i = w_1 i^c + w_2 i^s \tag{4}$$

While w_1 and w_2 are difficult to evaluate, i^c and i^s are found to have qualitatively the same functional dependence on temperature and molecular weight, i.e.

$$i \propto \exp(-K_g/T\Delta T) \tag{5}$$

where both i^c and i^s increase with MW and go through a broad maximum as a function of MW. The concentration dependence of i^c is weakly dependent on molecular weight at fixed crystallization temperature, and in general i^c is proportional to concentration raised to a power less than unity. In contrast, i^s is usually proportional to the concentration to the first power except for very low MW. Overall, the magnitude of the concentration exponent at a given crystallization temperature decreases as MW increases; at a given MW the exponent increases as the crystallization temperature increases. Cooper and Manley's results and our results generally agreed on this conclusion.

Toda et al. have further quantified the cilia nucleation concept.[4] In their treatment, cilia form where two steps traveling in opposite directions approach each other and collide. In this case, a pair of cilia is generated. They can nucleate on the next layer and travel out in both directions. Under this model, several equations and predictions have been derived. The key conclusions are summarized as

$$i \propto c \exp(-K_g/T\Delta T) \tag{6}$$

$$i' \propto c \tag{7}$$

$$i'' \propto \exp(-K_g/T\Delta T) \tag{8}$$

where i' relates the nucleation rate of the attachment of solution molecules to an immobile step and i'' relates the nucleation rate of a pair of cilia. When the chain length is comparatively short, cilia nucleation can be neglected. For PE, the cutoff molecular weight is 3.0×10^4. Below that limit, cilia nucleation is not important.

Regardless of whether cilia nucleation is taken into consideration, G is proportional to $c \exp(-K_g/T\Delta T)$ in regime I by Toda's model. For finite chains smaller than the cutoff MW, in regime II above and below a threshold concentration c_0 ($c_0 \approx 4 \times 10^{-5}$ wt % for PE)

$$G \propto c^{1/2} \exp(-K_g/2T\Delta T) \qquad c > c_0 \tag{9}$$

and

$$G \propto c \exp(-K_g/2T\Delta T) \qquad c < c_0 \tag{10}$$

respectively. For cilia nucleation (i.e., MW above cutoff):

$$G \propto c^{1/3} \exp(-2K_g/3T\Delta T) \tag{11}$$

Toda et al.[5] found a transition for γ from $^1/_2$ to 1 at finite chain length (MW = 1.1×10^4) when the concentration changed from greater than c_0 to smaller than c_0. The result is consistent with regime II growth. Cooper and Manley's data also seem to demonstrate the $^1/_3$ prediction by Toda's model. However, we notice that for the highest molecular weight they used (4.5×10^5), the data yield a $^1/_5$ dependence and γ also appears to vary continuously with MW. Under Toda's model, our data is not consistent with regime I growth (i.e., $\gamma < 1$) or with regime II growth. The molecular weights used in our experiments fall into the range where cilia nucleation is expected. Our values of γ are well above the $^1/_3$ dependence prediction and show very weak molecular weight dependence compared to Cooper and Manley's results.

In very recent work, Toda and Kiho discarded the previous model for the concentration dependence of i and g.[7] By studying growth kinetics of {100} twins from PE crystals, they found that g increased linearly with concentration over the whole range examined and i was proportional to c in the lower concentration range ($<1.0 \times 10^{-4}$ wt %) and became independent of concentration in the higher range ($\gg 1.0 \times 10^{-4}$ wt %). Again, the growth behavior of the crystals was attributed to regime II from the dependence of the growth rate on supercooling. Toda and Kiho suggested that the unusual dependence resulted from surface adsorption of polymers. At $c > c_0$, the growth face might be saturated with adsorbed polymers and nucleation is started by these adsorbed molecules which would make i independent of concentration. It is expected that the surface diffusion of adsorbed polymers would be very slow compared with bulk diffusion, because of the many points in the polymer chain which might stick on the surface. When chain segments stick irregularly to the surface, the completion of chain folding is frozen and the growth front immobilized. The irregular chain segments are freed only when they are knocked loose by new polymer segments attaching from solution. The implication is that the renewal of chain folding is provided by the adsorption of new polymers, which leads to a first power dependence of g on concentration.

It thus appears that surface adsorption of polymers produces a fractional power dependence of the crystal growth rate on the concentration. The existence of surface-adsorbed polymers may be supported by an indirect observation in our experiment. Dynamic light scattering measures the intensity–intensity autocorrelation function of scattering particles and relates this function to the dimensions of diffusing particles. In our system, the particles may include the crystal and a polymer-rich surface layer if it exists. We have observed that the zero time intercept of the plot of Γ^{-1} ($\propto R_h$) against time tends to be somewhat larger than the value from seeds $(\Gamma_{\mathrm{seed}})^{-1}$, especially for low crystallization temperatures. We can envisage that seeds are originally composed of crystals with a negligible adsorbed layer. After introducing them into the supercooled polymer solution, polymers begin to crystallize on the surface of seeds and also deposit a loose adsorbed layer on the seeds. The particle size thus initially expands by this thickness. The extrapolation to zero time gives the inverse decay constant obtained from scattering particles of crystals covered by this adsorbed layer. From the increase in the intercept over that for the bare seed crystals, we estimate the thickness of the adsorbed layer to be about 10 nm.

As noted above, the fractional power dependency may result from this adsorbed layer. Without it i is proportional to the collision frequency of dissolved polymers, which in turn is proportional to the first power of concentration, and g has a very weak concentration dependence. The surface layer may be composed of dangling polymer chains and partially adsorbed polymer molecules. The nucleation which leads to crystal growth is therefore controlled by absorbed molecules, cilia (in the sense of Sanchez and Di Marzio's cilia), and new molecules from solution which attach directly to the growth front. The overall nucleation rate is the summation of the three nucleation processes weighted by probability factors (similar to eq 4). Since nucleation from surface-adsorbed molecules and cilia each have only a weak concentration dependence, a fractional power dependence of i on concentration is expected. It would also be expected that cilia nucleation becomes increasingly important for higher molecular weights and that would in turn lead to a decrease in γ. We observed only a weak dependence of γ on molecular weights, suggesting that in our case cilia nucleation does not play a major role.

Toda's explanation[7] for the concentration dependence of g does not include the possibility of completion of chain-folding layers by surface mobility of the adsorbed layer. While the dynamic properties of interfaces between solids and polymer solutions have received relatively little attention[19] either from theory or from experiments, it is known that exchanges are possible between physically adsorbed polymers and other polymers free in solution, even though such processes are usually slow.[19,20] In general we expect a distribution of mobilities among adsorbed species (tails, segments in loops,[19] and segments near the crystal growth front). It may be that surface mobilities can even be enhanced by the strong thermodynamic driving force of crystallization. If step propagation is helped by desorption/readsorption of mobile segments, g might be expected to yield a fractional dependence on the concentration.

In a previous paper,[1] we found that PEO 325 at 0.01% concentration undergoes an apparent regime transition in the vicinity of $T_c = 25$ °C. It is also interesting to observe the temperature dependence of the crystal growth rate at concentrations other than 0.01%. Figures 6 and 7 are such plots at two concentrations for molecular weight 325 000 and at three concentrations for molecular weight 160 000, respectively. Again, we see pronounced curvature for the higher molecular weight sample. For PEO 160, the high-temperature end of the plots shows a slight deviation from linearity as the concentration increases. For the 0.05% and 0.1% solutions we can use the highest three points for one line and the rest of the points for a

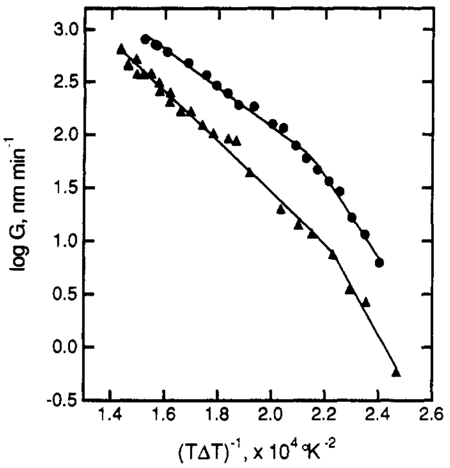

Figure 6. Temperature dependence of the crystal growth rate for PEO 325 at (●) 0.05% and (▲) 0.01% concentrations.

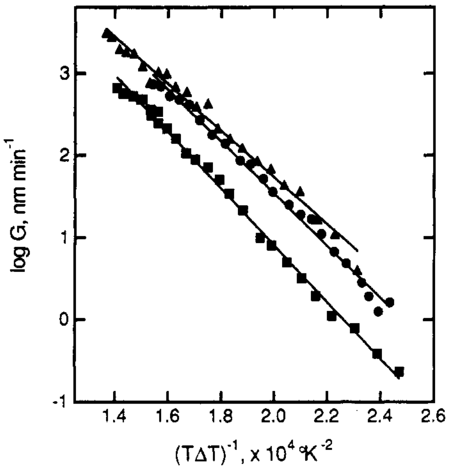

Figure 7. Temperature dependence of the crystal growth rate for PEO 160 at (▲) 0.1%, (●) 0.05%, and (■) 0.01% concentrations.

Table III
Growth Parameters at Different Concentrations and Molecular Weights

sample	*c*, % w/w	regime	$\Delta T_{\text{I-II}}$, K	ratio of slopes I/II	$K_g \times 10^{-4}$, K^2	σ_e, erg cm^{-2}
PEO 160	0.01	I(II)			7.96	43.7
PEO 160	0.05	I(II)			7.30	40.1
PEO 160	0.1	I(II)			6.51	35.7
PEO 325	0.01	I			10.55	57.7
		II	15.3	1.91	5.52	60.4
PEO 325	0.05	I			8.82	48.2
		II	16.22	2.07	4.26	46.6

second to give pairs of lines. The slope differences are less than 1.7. At the highest growth rates there is also some curvature. Given the uncertainty in the data at these higher growth rates, it is very difficult to characterize this transition but the slope differences appear to be less than 2.

For PEO 325 samples, two straight lines are used to fit the data, and based on the same suggestion as in earlier work, the lines are assigned as regime I and regime II growth. The ratios of slopes of these lines are 2.1 at 0.05% concentration and 1.9 at 0.01%. Kinetic parameters are calculated and listed in Table III. We observe that the slopes of the plots, i.e., K_g and therefore σ_e, decrease with the increasing concentration. This is in accord with the observed slight increase of γ with crystallization temperature and perhaps implies an increasing irregularity of the folding surface at higher concentration which leads to a smaller folding surface free energy.

The magnitude of γ above or below the transition region, i.e., in regime I and regime II, can also be considered. At 3.25×10^5 MW the chain is well above the 3×10^4 molecular weight cutoff for cilia nucleation, and the concentration used in this experiment is much higher than the saturation concentration, c_0. From Toda's earlier model, γ should be near $^1/_3$ in regime II and 1 in regime I. On the other hand, if g has a power 1 dependence and i is independent of concentration as found in the recent work, γ will be 0 in regime I and $^1/_3$ for regime II. Our results do not confirm any of these predictions, and further we do not see abrupt changes in γ (Table II) before and after the transition temperature. The magnitude of the observed change is not consistent with a strong distinction in the concentration dependence of g and i. Since the cilia nucleation can be neglected in our case, we are left with two possible conclusions: either i depends on concentration only slightly more strongly than g does in their fractional powers or the distinctions of the growth mechanism cannot be so sharply drawn.

Conclusion

Dynamic light scattering experiments show that the concentration dependence of PEO crystal growth rate can be expressed as $G \propto c^{\gamma}$ where γ varies from 0.73 to 0.49 when PEO MW varies from 56 300 to 325 000. At a given crystallization temperature, the magnitude of γ tends to increase as the PEO molecular weight decreases. Nevertheless, the variation of γ is small. Surface adsorption of polymers may play an important role in the concentration dependence of nucleation and step propagation and, if so, both i and g may show similar fractional power dependence on concentration. Across the observed transitions, the magnitude of γ shows only a small change.

Cilia nucleation seems to be unimportant. If cilia nucleation is taken into consideration, γ is predicted to be around $^1/_3$ in regime II. Using parameters for PE, our PEO fractions are much longer than should be necessary for cilia nucleation. Our values of γ are well above $^1/_3$ and do not have the expected strong molecular weight dependence.

The temperature dependence of crystallization for high molecular weight fractions at constant concentration shows curvature as observed previously. For intermediate molecular weight fractions, the curvature is not obvious. Changes in K_g are in accord with the change of γ and lead to the result that σ_e decreases with increasing concentration. The smaller σ_e at higher concentration implies that the folding surface tends to be more irregular at high concentration and we may expect to approach values found for melt-grown crystals. The σ_e obtained at low concentration may therefore reflect the true energetic barrier of chain folding.

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