Regime II growth of polyethylene single crystals from dilute solution in n-octane

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The lateral growth of polyethylene single crystals has been investigated. The dependence of the linear growth rate G on concentration C and supercooling ΔT was studied with fractionated polyethylene of relatively low molecular weight ($M_n = 1.1 \times 10^4$ and $M_w/M_n = 1.16$). The crossover of concentration dependence of growth rate was clearly observed; the exponent γ ($G \propto C^{\gamma}$) varies from 1/2 to 1 with decreasing concentration. The variation of growth with concentration and supercooling is discussed in terms of a kinetic theory taking into account finite molecular length. The analysis shows that the growth is in the mode of multi-nucleation growth (regime II).

(Keywords: polymer; polyethylene; crystallization; growth rate; single crystals; regime II)

INTRODUCTION

The linear growth rate of polyethylene single crystals from dilute solution has been studied by several authors[1-7]. The following experimental results have been reported. (1) At the initial stage, crystal size increases linearly with time. (2) The linear growth rate G increases with fractional power of concentration C; $G \propto C^{1/2}$ for relatively low molecular weight materials and $G \propto C^{1/3}$ for higher ones. (3) Supercooling dependence is expressed as $G \propto \exp(-K/T\Delta T)$ where K is a constant, T is crystallization temperature and ΔT is supercooling. These observations have been explained as a secondary nucleation and growth process. While there are two kinds of growth modes, single nucleation growth (regime I) and multi-nucleation growth (regime II), the growth mode of polyethylene single crystals has been reported as regime I[8] or intermediate between regime I and II[6].

In our previous paper[9], hereafter referred to as Part I, the authors showed that the dependence of growth rate on concentration and supercooling can be consistently explained as regime II; the linear growth of higher molecular weight materials is controlled by the nucleation of cilia formed by collisions of travelling growth steps and the growth of lower ones by the nucleation of solute molecules. Further, it was shown that the growth rate of relatively low molecular weight polyethylene increases linearly with concentration ($G \propto C$) in very dilute n-octane solution. In the present paper, we will report the experimental results in detail and analyse the results in terms of the theory in Part I.

EXPERIMENTAL

The polyethylene fraction used in this work has $M_n = 1.1 \times 10^4$ and $M_w/M_n = 1.16$. For the solvent, n-octane was used. The experimental method is essentially identical to that of Blundell and Keller[2], and others[3,5-7]. The self-seeding method[10] was used in order to obtain the proper number of seeds to measure the initial growth rate. The suspension of seeds was transferred to a bath held at the crystallization temperature (±0.05°C). A small quantity of solution was transferred to another bath at a lower temperature of 75–83°C at regular intervals in order to complete crystallization. The single crystals obtained have a step on the folding surface due to the change of lamellar thickness. We measured the size of the inside of this step, which is the size of crystals at the time of sampling, by an electron microscope. Since the crystals are truncated lozenge type, the distances from the centre of the crystals to {110} and {100} faces were measured.

In order to evaluate the dependence of growth rate on supercooling, the dissolution temperature in n-octane of the extended chain crystals (ECC) of this material crystallized at about 0.5 GPa was determined by observing the dissolution of a small amount (several tens of micrograms) of the ECC in n-octane.

RESULTS

The growth was linear with time at the initial stage in all cases (*Figure 1*). The growth rate of {110} and {100} faces at several crystallization temperatures and concentrations are shown in *Table* 1. Logarithmic plots of the linear growth rate of {100} face against concentration at different crystallization temperature are represented in *Figure 2*. The concentration dependence of the growth rate of {110} face was almost the same. The lateral habit was dependent on temperature but almost independent of concentration in the range investigated.

It was determined that the dissolution temperature T_d of the extended chain crystals in n-octane is 116.4±0.1°C.

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DISCUSSION

The concentration dependence of growth rate has been expressed by the exponent γ ($G \propto C^{\gamma}$). As seen in *Figure 2*, γ is 1/2 in the concentration range 10^{-1}–10^{-3} wt%; the majority of previous experiments have been performed in this concentration range. The exponent γ increases with decreasing concentration and reaches 1 at very dilute concentration. Since this crossover of the concentration dependence can be explained by the theory of Part I, it is reviewed briefly in the following discussion, where the effects of cilia are neglected because the molecules are not so long and fold only 10 times or so.

Growth of polymer single crystals can be described as secondary nucleation and growth; the linear growth rate is determined by the rate of secondary nucleation and velocity of travelling of growth steps, which are formed by the nucleation process. For crystallization of molecules of finite chain length, there are two kinds of processes in the travelling of growth steps; one is due to crystallization of molecules with chain folding and the other is due to the attachment of solute molecules to rest steps on which other molecules have completed crystallization (*Figure 3*). The average velocity v of travelling of growth steps is

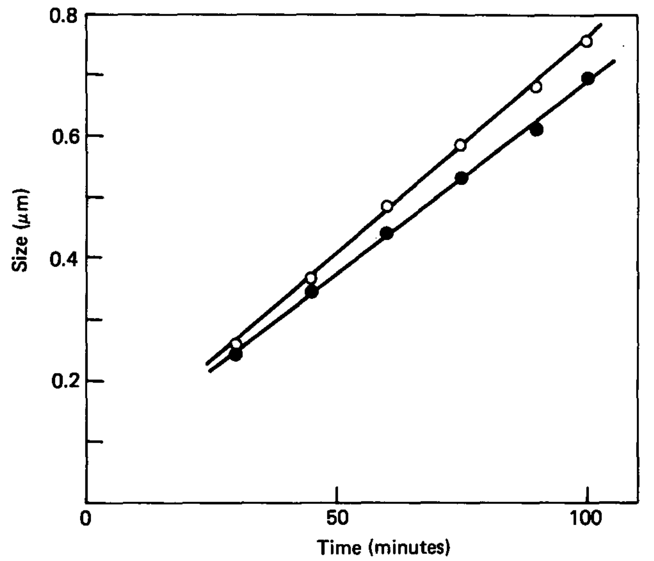

Figure 1 Growth of {100} (○) and {110} (●) faces at 88.8°C and 5.0×10^{-6} wt%

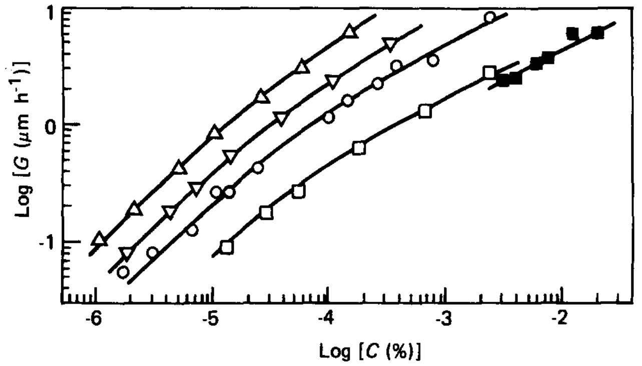

Figure 2 Logarithmic plot of linear growth rate of {100} face as a function of concentration at different crystallization temperatures: 88.8°C (△); 90.7°C (▽); 92.2°C (○); 94.2°C (□); 94.8°C (■). Full curves are calculated from equation (4) with an arbitrary unit of the ordinate under $C_0 = 4 \times 10^{-5}$ wt%

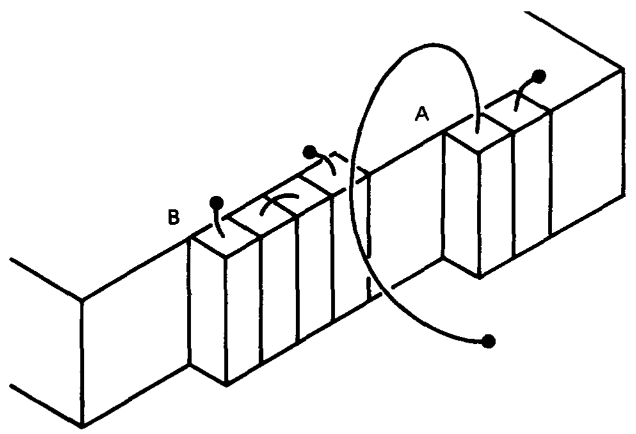

Figure 3 Schematic representation of growth steps. Step A represents a travelling step and step B a rest step. Step A travels with velocity g, and on step B a solute molecule attaches and begins to crystallize at a rate $i'a$

Table 1 Growth rate data at each crystallization temperature: C, concentration of solution (wt%); $G_{\{110\}}$ and $G_{\{100\}}$, growth rates of {110} and {100} faces (μm h^{-1})

88.8°C			90.7°C			92.2°C		
$C \times 10^4$	$G_{\{110\}}$	$G_{\{100\}}$	$C \times 10^4$	$G_{\{110\}}$	$G_{\{100\}}$	$C \times 10^4$	$G_{\{110\}}$	$G_{\{100\}}$
0.011	0.091	0.105	0.018	0.080	0.080	0.017	0.052	0.056
0.021	0.18	0.20	0.042	0.19	0.176	0.030	0.077	0.080
0.050	0.38	0.43	0.069	0.28	0.29	0.057	0.134	0.120
0.098	0.76	0.87	0.14	0.50	0.55	0.10	0.26	0.27
0.25	1.50	1.73	0.37	1.06	1.15	0.13	0.24	0.27
0.57	2.7	3.1	1.03	2.2	2.43	0.25	0.35	0.38
1.49	5.4	6.3	3.2	4.9	5.1	1.0	1.08	1.15

92.2°C			94.2°C			94.8°C		
$C \times 10^4$	$G_{\{110\}}$	$G_{\{100\}}$	$C \times 10^4$	$G_{\{110\}}$	$G_{\{100\}}$	$C \times 10^2$	$G_{\{110\}}$	$G_{\{100\}}$
1.4	1.66	1.60	0.13	0.094	0.093	0.30	2.5	2.3
2.6	2.4	2.4	0.29	0.165	0.180	0.40	2.9	2.5
3.7	3.1	3.2	0.54	0.29	0.28	0.60	3.8	3.4
7.8	3.6	3.6	1.8	0.65	0.65	0.72	4.4	3.7
23	8.2	8.2	6.5	1.38	1.31	1.2	6.7	5.7
			24	3.1	2.9	2.0	7.6	6.0

expressed as:

$$v = \frac{ha}{(1/i'a) + (ha/g)} \tag{1}$$

where a is the width of a stem, $i'a$ is the rate of attachment of solute molecules to a rest step, g is the velocity of travelling steps with chain folding and h is the number of stems made of one molecule (*Figure 3*). The linear growth rate G in regime II can be written as follows[8]:

$$G = b\sqrt{(2iv)} \tag{2}$$

where b is the thickness of a stem and i is the secondary nucleation rate per unit length. With the substitution of equation (1) into equation (2), the following expression is obtained:

$$G = b\left(\frac{2ig}{1 + (g/hi'a^2)}\right)^{1/2} \tag{3}$$

For the extreme cases:

$$G \sim ab\sqrt{(2ii'h)} \qquad hi'a^2/g \ll 1 \tag{3a}$$

$$G \sim b\sqrt{(2ig)} \qquad hi'a^2/g \gg 1 \tag{3b}$$

In the modes of equations (3a) and (3b), the process of travelling of growth steps is controlled by the attachment of a solute molecule to a rest step and folding process respectively. Since the rates i and i' are proportional to the concentration C, the dependence of growth rate on concentration is expressed as:

$$G \propto C(1 + C/C_0)^{-1/2} \tag{4}$$

where C_0 is the concentration at which $hi'a^2/g = 1$, and for the extreme cases:

$$G \propto C \qquad C \ll C_0 \tag{4a}$$

$$G \propto C^{1/2} \qquad C \gg C_0 \tag{4b}$$

Therefore, the crossover occurs at C_0. Since the supercooling dependence of the rates i' and g is negligible compared with the nucleation rate i, the supercooling dependence of equations (3a) and (3b) is the same and the condition $hi'a^2/g = 1$ or C_0 is independent of supercooling. The calculated curves in *Figure 2* are obtained from equation (4) with an arbitrary unit of the ordinate under the assumption $C_0 = 4 \times 10^{-5}$ wt%. The agreement between the experimental concentration dependence and calculated curves in *Figure 2* is good. Further, in order to confirm the prediction that C_0 is independent of supercooling, the experimental values at each crystallization temperature in *Figure 2* are translated parallel to the ordinate by the proper amount. The results are shown in *Figure 4* with the calculated curves of equation (4) under the assumption $C_0 = 4 \times 10^{-5}$ wt%. It can be seen that the translated experimental values coincide with the calculated master curve very well. The behaviour of the concentration dependence of the growth rate and the crossover concentration C_0 of {110} face are almost the same. Although in Part I the two other types of crossover of γ from 1/2 to 1 were predicted, their crossover concentrations depend on supercooling and they cannot explain the fact that data on growth rate at different supercoolings could be superimposed onto a master curve by translation along the ordinate. The similar crossover of the exponent γ was reported in the case of the growth from xylene solution by Seto and Mori[4].

The supercooling dependence of the growth rate of {110} and {100} faces is represented in *Figure 5* whose ordinate is the logarithm of growth rate interpolated at 10^{-4} wt% and abscissa is $1/T\Delta T$ ($\Delta T = T_d - T$ and $T_d = 116.4$°C). The experimental values coincide plausibly with a straight line under the present conditions ($\Delta T \sim 22.2$–27.6°C). The supercooling dependence of growth rate in regime II is included in rate i in equation (3) and expressed as follows[8]:

$$G \propto \exp\left(-\frac{K}{2T\Delta T}\right) \tag{5a}$$

$$K \equiv \frac{4b\sigma\sigma_e T_d}{k\Delta h_f} \tag{5b}$$

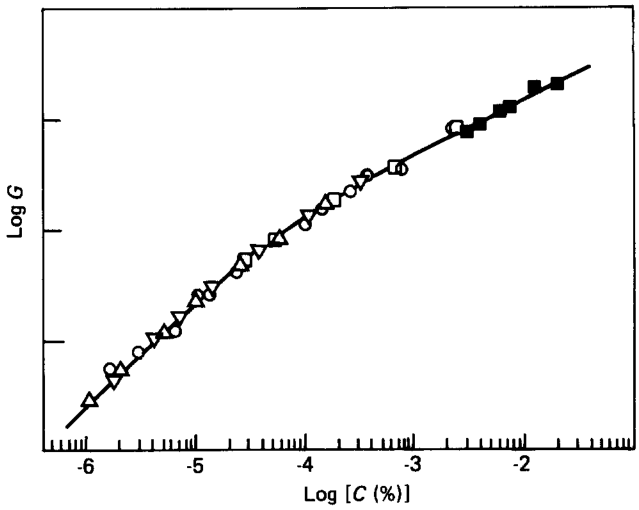

Figure 4 Plot of values obtained from the translation of growth rate in *Figure 2* parallel to the ordinate by the proper amount. The unit of the ordinate is arbitrary. Crystallization temperatures are: 88.8°C (△); 90.7°C (▽); 92.2°C (○); 94.2°C (□); 94.8°C (■). The full curve is calculated from equation (4) under $C_0 = 4 \times 10^{-5}$ wt%

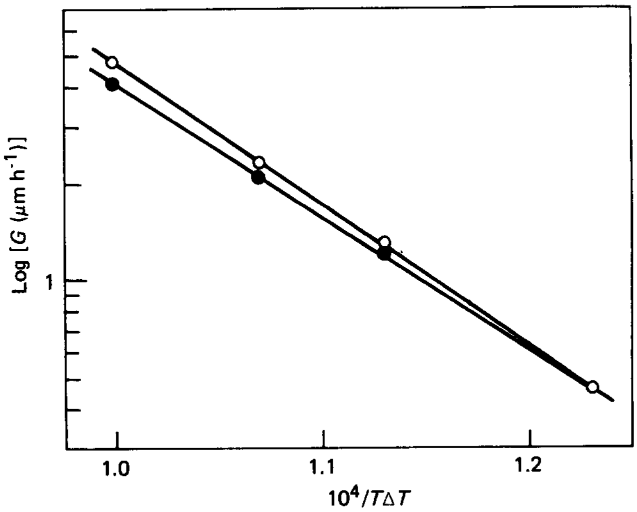

Figure 5 Linear growth rate at 10^{-4} wt% plotted against $1/T\Delta T$ using $T_d = 116.4$°C: {100} face (○); {110} face (●)

where σ and σ_e are the surface free energies of the side surface and folding surface respectively, Δh_f is the heat of fusion per unit volume of the crystal, and k is the Boltzmann constant. Corrections to the above expression may include a decrease of the heat of fusion as the temperature is lowered[8] and the heat of mixing with solvent[11,12]. But these effects are small (even cancel out each other) and are neglected hereafter. From the slope of the straight line of *Figure 5* and equation (5), the product of surface free energies $\sigma\sigma_e$ can be obtained. With the data $b_{\{110\}} = 4.14 \times 10^{-8}$ cm, $b_{\{100\}} = 3.78 \times 10^{-8}$ cm at 100°C[13] and $\Delta h_f = 2.8 \times 10^9$ erg cm^{-3}, the products $\sigma\sigma_{e\{110\}}$ and $\sigma\sigma_{e\{100\}}$ are evaluated as 1.1×10^3 erg^2 cm^{-4} and 1.3×10^3 erg^2 cm^{-4} respectively. The value $\sigma\sigma_{e\{110\}}$ is evaluated as about 1300 erg^2 cm^{-4} from the experiment[14] of growth from the melt for high molecular weight and decreases with decreasing molecular weight. Therefore, it can be said that the value of 1.1×10^3 erg^2 cm^{-4} for the present material is reasonable.

The fact that the initial growth is linear and independent of the size of the crystals also suggests regime II growth because the growth rate in regime II is independent of the substrate length $L\,(G = b\sqrt{(2iv)})$, while that in regime I is proportional to it $(G = biL)$.

CONCLUSION

The growth kinetics of the relatively low molecular weight fraction of polyethylene single crystals from dilute solution in n-octane has been investigated in terms of the kinetic theory suggested in a previous paper. The crossover of concentration exponent γ from 1/2 (at ordinary concentration range) to 1 (at high dilution) is clearly observed. This crossover is assigned to the transition of the process of travelling of growth steps in regime II; the controlling process changes from chain folding at ordinary concentration to attachment of solute molecules to rest steps, on which other molecules have completed its crystallization, at very low concentration. From the supercooling dependence of the growth rate, the products of surface free energies $\sigma\sigma_{e\{110\}}$ and $\sigma\sigma_{e\{100\}}$ are evaluated at 1.1×10^3 erg^2 cm^{-4} and 1.3×10^3 erg^2 cm^{-4}, respectively, under regime II growth. These observations, with the evidence of linear growth, confirm that the present growth is in regime II.

For further study, it is desired to observe the transition from regime II to regime I so that the microscopic rates i, i' and g are determined. Experiments at higher crystallization temperatures are required.

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