

Growth kinetics of polyethylene single crystals from dilute solution at low supercoolings

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(Received 13 November 1986; revised 26 December 1986; accepted 8 January 1987)

The growth rate of polyethylene single crystals is investigated in n-octane and decalin solutions for a wide range of supercoolings and concentrations. Transitions in the dependence of growth rate on supercooling and concentration are found to occur at relatively low supercooling. The transitions cannot be explained as transitions from regime II to regime I. They are discussed in terms of the effect of an impurity on the growth process: travelling steps are interrupted by an impurity on the steps. The origin of the impurity is discussed. A low molecular weight fraction segregated from the growth face or a small loop defect along the crystallizing chains will behave as an impurity. The lateral habit obtained in n-octane solution at lower supercoolings is somewhat rounded on the {100} face. The rounding of the habit is also discussed as an impurity effect.

(Keywords: polyethylene; single crystals; crystallization; regime II)

INTRODUCTION

In a previous paper¹, it was shown that regime II growth (multinucleation growth) explains well the dependence of growth rate of polyethylene single crystals from dilute xylene solution² on concentration, supercooling and molecular weight. Growth in n-octane was also explained as regime II growth³.

However, these experiments were made at relatively high supercoolings. It is expected that the growth mode changes from regime II to regime I (single-nucleation growth) as the supercooling is reduced, because the nucleation rate decreases as the supercooling is lowered. In an experiment on the lower molecular weight fraction², the supercooling dependence of the growth rate showed transient behaviour of the growth mode at lower supercooling. Further, Organ and Keller⁴ recently observed a crossover in the supercooling dependence of growth rate in poorer solvents such as hexadecane and tetradecanol. These observations suggested the transition of the growth mode from regime II to regime I at relatively low supercooling.

On the other hand, the lateral habit of single crystals in poorer solvents are macroscopically rounded.⁵ This evidence seemed to suggest that the growth surface is microscopically rough and that growth is not controlled by the nucleation process⁶.

Recently, this contradiction between growth mode and lateral habit was settled by taking account of the effect of an impurity on the crystal growth process⁷. An impurity such as solvent and defects on the growth step interrupts further crystallization on the step. This effect results in the accumulation of growth steps that are interrupted by impurities, and the lateral habit becomes macroscopically rounded although growth is still controlled by nucleation.

In the present paper, experimental results on the growth kinetics at low supercooling will be reported.

Polyethylene single crystals were crystallized in n-octane and decalin solutions; n-octane is a better solvent than hexadecane and tetradecanol and poorer than xylene, while decalin is better than xylene. In both cases, a crossover of the supercooling dependence of the growth rate was observed at low supercooling, suggesting a transition of the growth mode. However, the concentration dependence did not change in the crossover region; the concentration dependence must be changed in a transition from regime II to regime I. Similar observations on supercooling and concentration dependence of growth rate have been made by Organ and Keller^{4,8} and Leung *et al.*⁹ in tetradecanol and xylene. In this paper, these results will be explained in terms of the effect of an impurity on the crystal growth process.

EXPERIMENTAL

The polyethylene fraction used in this work was the same as that used in the previous work³: $M_n = 1.1 \times 10^4$ and $M_w/M_n = 1.16$. For the solvents, n-octane and decalin were used. Growth rates were measured at various temperatures and concentrations in n-octane and at several temperatures in decalin. The experimental method is described previously³, and is essentially identical to that of Blundell and Keller¹⁰ and others^{2,11,12}. The self-seeding method² was used to obtain the proper number of seeds. The size of crystals was measured by an electron microscope. In order to evaluate the supercooling in n-octane and decalin solutions, the dissolution temperatures of the extended-chain crystals of this fraction crystallized at about 0.5 GPa were observed by a visual method.

RESULTS AND DISCUSSION

The growth was linear with time in the initial stage for all

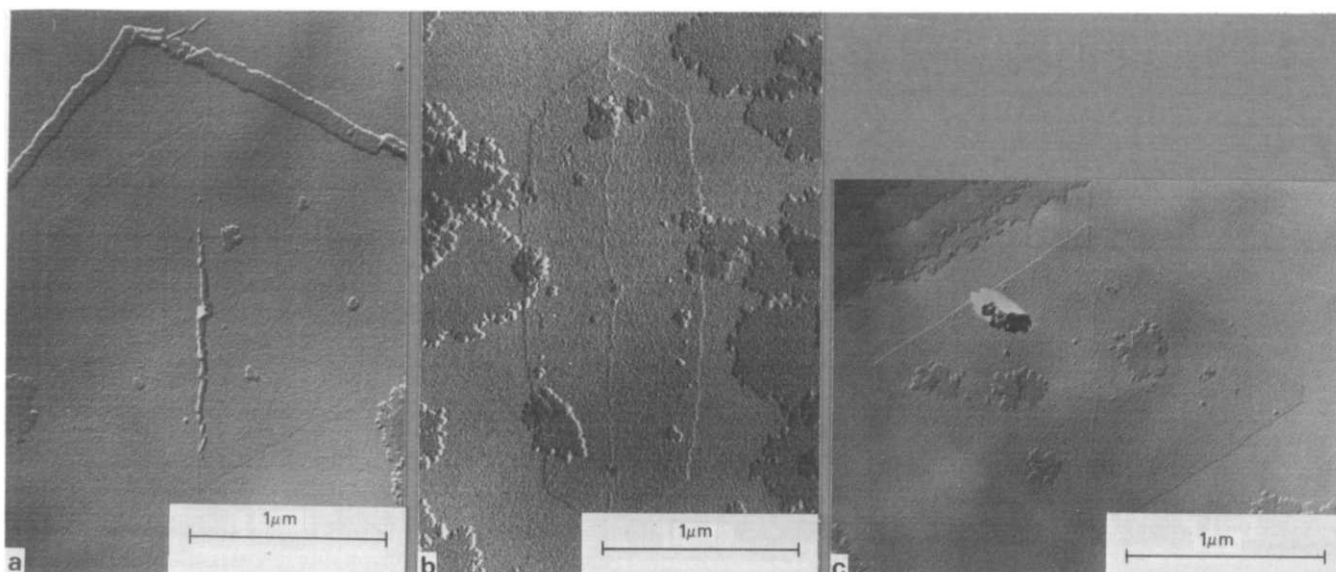


Figure 1 Electron micrographs of single crystals grown from (a) $2.0 \times 10^{-4}\%$ n-octane solution at $T = 92.0^\circ\text{C}$, (b) $2.0 \times 10^{-4}\%$ n-octane solution at $T = 98.5^\circ\text{C}$, and (c) $8.0 \times 10^{-3}\%$ decalin solution at $T = 85.0^\circ\text{C}$. All are shadowed with Pt-Pd

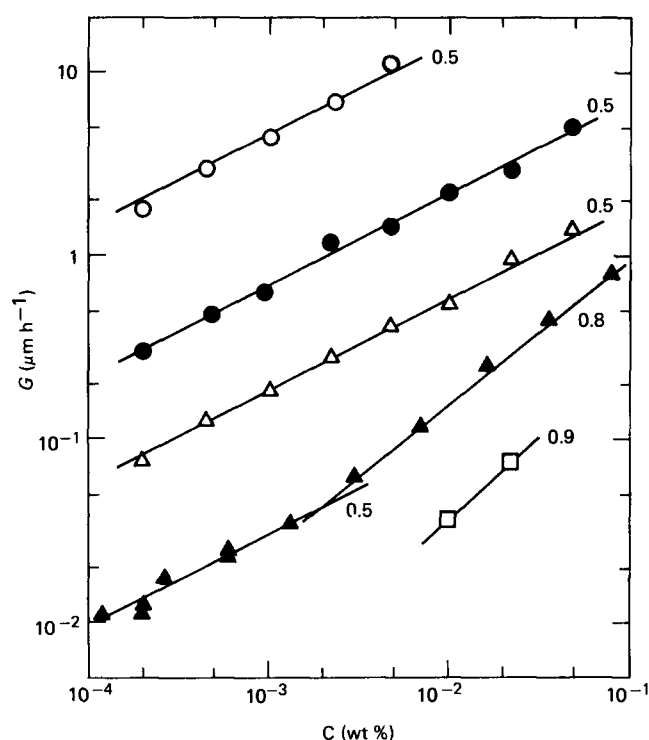


Figure 2 Logarithmic plot of linear growth rate of the $\{110\}$ face in n-octane as a function of concentration at various crystallization temperature: 92.6°C (○); 95.6°C (●); 97.0°C (△); 98.5°C (▲); 99.6°C (□). The slopes of the full lines are shown at the right

cases. The lateral habits of single crystals crystallized from decalin and n-octane solutions were of a truncated lozenge type; in decalin solution the truncation was very small. Crystals obtained at various temperatures and concentrations in decalin and n-octane solutions are shown in Figure 1.

The dissolution temperatures of extended-chain crystals were 116.4°C in n-octane and 105.4°C in decalin.

A logarithmic plot of the linear growth rate of the $\{110\}$ face in n-octane against concentration is presented in Figure 2. Plots of the $\{110\}$ and $\{100\}$ faces in n-

octane solution against $1/T\Delta T$ ($\Delta T = T_d - T$; T_d is dissolution temperature and T crystallization temperature) are shown in Figures 3 and 4. That of the $\{110\}$ face in decalin solution against $1/T\Delta T$ is presented in Figure 5.

Growth rate

We first briefly review the kinetics of polymer crystal growth. According to the regime theory of crystal growth of polymers¹³, there can be two regimes in crystal growth controlled by nucleation and growth processes. One is single-nucleation growth (regime I); where the nucleation rate is very small, nucleation occurs one by one on the growth face, and the steps generated by the nucleation sweep over the growth face before another nucleation occurs. The other is multinucleation growth (regime II); the nucleation rate is relatively large, nucleation occurs here and there, and the steps collide with other steps before they reach the edge of the growth face. The growth rate G in these regimes can be expressed by the nucleation rate i , the velocity of growth steps g and the length of the growth face L as follows¹³:

regime I, for $iL^2/2g \ll 1$

$$G = biL \quad (1)$$

regime II, for $iL^2/2g \gg 1$

$$G = b\sqrt{(2ig)} \quad (2)$$

The concentration and supercooling dependences of growth rate are determined by those of the nucleation rate and the velocity of growth steps. These dependences can be written as follows¹:

$$i \propto C \exp(-K/T\Delta T) \quad (3)$$

$$K \equiv \frac{4b\sigma\sigma_e T_d}{k\Delta h_f} \quad (4)$$

$$g \sim \text{constant} \quad (5)$$

in regime I

$$G \propto C \exp(-K/T\Delta T) \quad (6)$$

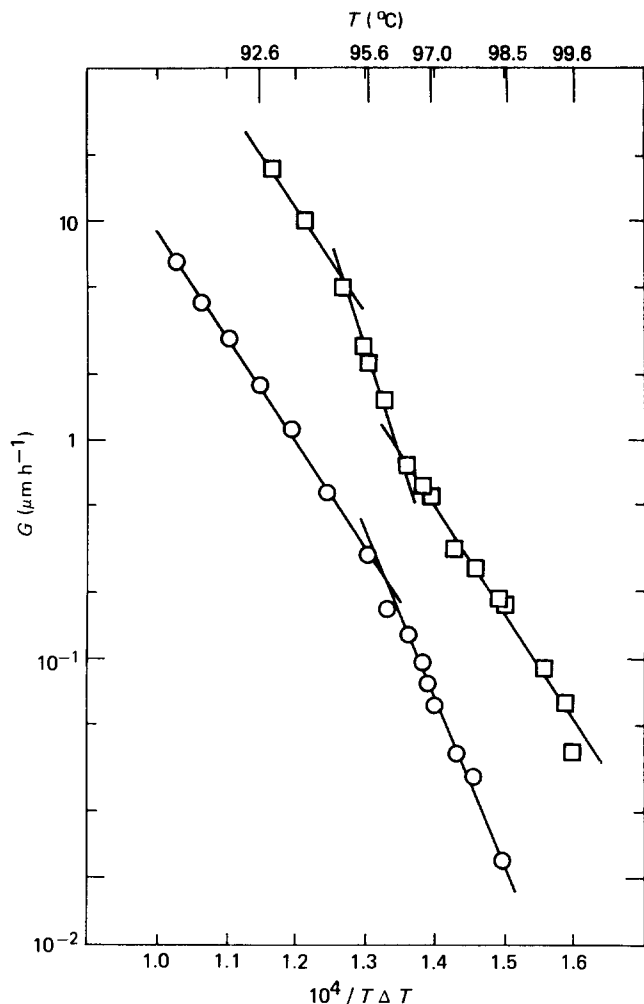


Figure 3 Linear growth rate of the {110} face in n-octane plotted against $1/T\Delta T$: at $1.0 \times 10^{-2}\%$ (□) and at $2.0 \times 10^{-4}\%$ (○)

in regime II

$$G \propto C^{1/2} \exp(-K/2T\Delta T) \quad (7)$$

Here b is the thickness of a crystalline stem, σ and σ_e are the surface free energies of the side surface and the folding surface respectively, Δh_f is the heat of fusion per unit volume of the crystal, and k is the Boltzmann constant.

In the above treatment, the contribution of cilia nucleation¹ is not considered; in crystal growth at relatively low molecular weight ($M_w \sim 10^4$), this contribution can be neglected. The velocity of steps, g , can be considered as a constant when the concentration is not so dilute ($C = 10^{-4}$ to $10^{-1}\%$)³ and the supercooling is relatively high ($\Delta T \gtrsim 20^\circ\text{C}$)⁷.

n-Octane. In the present experiments, the supercooling dependence of growth rate has two types of crossover (Figures 3 and 4). One is at higher supercooling ($10^4/T\Delta T \sim 1.27$ at concentration of $10^{-2}\%$ and 1.33 at $2 \times 10^{-4}\%$), where the supercooling dependence becomes stronger as the supercooling is lowered (type 1). The other is at lower supercooling ($10^4/T\Delta T \sim 1.35$ at $10^{-2}\%$) where the supercooling dependence becomes weaker as the supercooling is lowered (type 2). At supercooling higher than the crossover regions, the supercooling and concentration dependences of growth rate are well explained as normal regime II growth; growth is

controlled by the nucleation of solute molecules and the folding process of crystallizing chains. In regime II, the power γ expressing the concentration dependence of growth rate ($G \propto C^\gamma$) must be 0.5 as shown in equation (7). The present experiment shows that the power γ is really 0.5 in this region (Figure 2). The product of the surface free energies $\sigma\sigma_e$ is obtained from the supercooling dependence of growth rate (Figures 3 and 4) using equations (4) and (7): $1300 \text{ erg}^2 \text{ cm}^{-4}$ for the {110} face and $1600 \text{ erg}^2 \text{ cm}^{-4}$ for the {100} face. Since the product $\sigma\sigma_e$ has been evaluated as about $1300 \text{ erg}^2 \text{ cm}^{-4}$ (ref. 14), the values obtained in the present experiment will be reasonable.

The crossover of type 1 is similar to the transition from regime II to regime I in melt growth observed by Hoffman *et al.*¹⁴. If this is the case, the power γ should change from 0.5 to 1 as shown in equations (6) and (7). But, experimentally, across the crossover region of type 1, the power γ remains 0.5 (Figure 2). Further, equations (6) and (7) require that the ratio of the slopes of the curve of $\log(G)$ vs. $1/T\Delta T$ on each side of the crossover varies by a factor of 2 from regime I to regime II. However the ratio is about 1.5 in this experiment for both {110} and {100} faces (Figures 3 and 4). From all this evidence, the crossover of type 1 cannot be a transition from regime II to regime I.

If the growth still remains in regime II across the crossover of type 1, the crossover must be attributed to a transition in the supercooling dependence of the

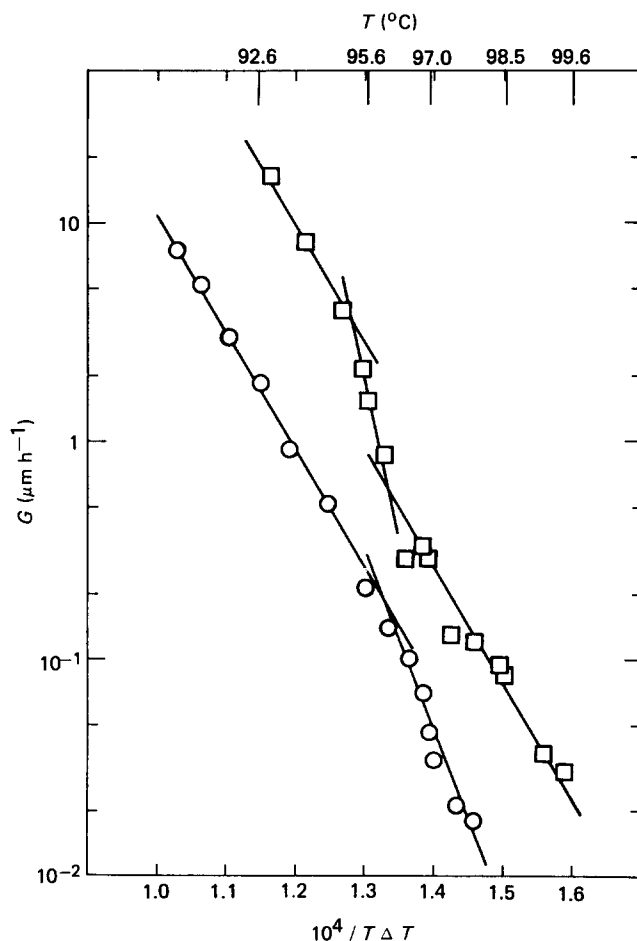


Figure 4 Linear growth rate of the {100} face in n-octane plotted against $1/T\Delta T$: at $1.0 \times 10^{-2}\%$ (□) and at $2.0 \times 10^{-4}\%$ (○)

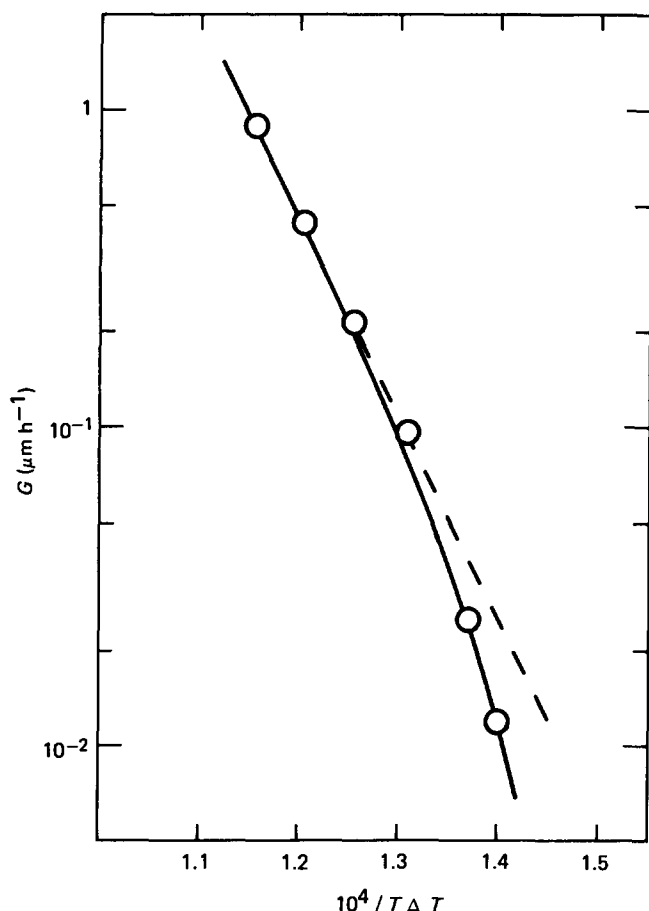


Figure 5 Linear growth rate of the {110} face in decalin at $8.0 \times 10^{-3}\%$ plotted against $1/T \Delta T$. The full curve is calculated from equation (12) with $B=27.2$ and $D=0.81$

nucleation rate i or the velocity of steps g . A transition in the nucleation rate should affect the supercooling dependence of the lamellar thickness. But the experimental evidence did not suggest such a transition. Therefore, it is reasonable to consider that the velocity of steps depends on supercooling.

In the standard model by Lauritzen and Hoffman¹⁴, the velocity of steps depends on supercooling as

$$g \propto [1 - \exp(-A \Delta T)] \quad (8)$$

$$A \equiv \frac{ab \delta l \Delta h_f}{k T T_d} \quad (9)$$

where a is the width of the stem and δl is the constant term in the formula for lamellar thickness l_g^* ($= 2\sigma_e T_d / \Delta h_f \Delta T + \delta l$). In equation (8) the first term is due to the rate of formation of a new stem on steps and the second term is due to the rate of breaking the stem. For polyethylene, typically $\exp(-A \Delta T) = 0.03$ with data $a = 4.15 \times 10^{-8}$ cm, $b = 4.55 \times 10^{-8}$ cm, $\delta l = 6 \times 10^{-7}$ cm, $\Delta h_f = 2.8 \times 10^9$ erg cm⁻³, $T_d = 116.4^\circ\text{C}$ and $T = 95^\circ\text{C}$ ($\Delta T = 21.4^\circ\text{C}$). Therefore, the term $\exp(-A \Delta T)$ can be neglected and the velocity of steps g is independent of supercooling even at relatively low supercooling.

Here we introduce impurity effects on the crystal growth process. In the following discussion, the type of impurity is not specified, but will be discussed later. The supercooling dependence of the velocity of steps g can be modified by an impurity as follows⁷. An impurity on the

growth steps will interrupt further crystallization on the growth steps, namely the travelling of the steps. However, these steps will travel again when either the impurity is buried into the crystal by a new stem crystallizing on the steps or the impurity detaches from the steps. Then, the growth rate G is expressed as⁷:

$$G = b \left(\frac{2ig}{1 + g/h^\circ i^\circ a^2} \right)^{1/2} \quad (10)$$

where $1/h^\circ$ is the probability of interruption of travelling steps and $i^\circ a$ is the rate of travelling of the interrupted steps. The probability $1/h^\circ$ will depend on the type of impurity. The rate i° is determined by the faster process, either the rate of burying or that of detachment of the impurity. In detachment, the rate i° will depend on the type of impurity but not on supercooling. In the burying process, i° will be expressed as:

$$\begin{aligned} i^\circ &\propto [\alpha - \beta \exp(-A \Delta T)] \\ &\propto [1 - B \exp(-A \Delta T)] \quad (11) \\ B &\equiv \beta/\alpha > 1 \end{aligned}$$

where α and β are constants. The factor α is smaller than 1 and is related to the decrease in the rate of formation of a new stem on the interrupted steps, and β is larger than 1 and is related to the free energy increase due to the excess surface and defects such as *gauche* configuration along the new stem which buries the impurity into the crystal. This supercooling dependence cannot be ignored when B is relatively large, while the supercooling dependence of g can be ignored. If the rate i° is determined by the burying process and $1/h^\circ$ is independent of supercooling, the supercooling dependence of the growth rate in regime II is expressed as follows, inserting equation (11) into (10):

$$G \propto \frac{\exp(-K/2T \Delta T)}{\{1 + D/[1 - B \exp(-A \Delta T)]\}^{1/2}} \quad (12)$$

where D is a constant, $g/h^\circ i^\circ a^2 \rightarrow D$ ($\Delta T \rightarrow \infty$). The supercooling dependence of equation (12) is similar to that of equation (7) at high supercoolings and becomes greater as the supercooling decreases.

The experimental data in Figure 3 at $2 \times 10^{-4}\%$ are fitted to equation (12), adjusting the parameters B and D . The result is shown in Figure 6. The agreement is good, although the calculated curve is not straight at lower supercoolings in this plot. In the fitting, the parameters are determined as $B=17$ and $D=1.0$.

As shown in equation (11), the constant B contains the factors α and β . The estimation of α will be difficult but β can be expressed as:

$$\beta = \exp\left(\frac{2bl\sigma}{kT}\right) \quad \text{or} \quad \exp\left(\frac{800n}{RT}\right) \quad (13)$$

where n is the number of *gauche* configurations on the new stem and R is the gas constant; these terms are due to the free energy increase due to excess surface or *gauche* configuration. The values of $B \sim 20$ can be obtained when $l \sim 10$ Å or $n \sim 3$ with $\sigma = 15$ erg cm⁻²; these values will not be so large. The constant D is expressed as:

$$D = 1/(\alpha h^\circ) \quad (14)$$

From this relation and the definition of B , when $B \sim 20$ and $D \sim 1$, α and β are represented by $1/h^\circ$: $\alpha = 1/h^\circ$ and $\beta = 20/h^\circ$. Since β is larger than 1, the probability $1/h^\circ$ must be larger than $1/20$.

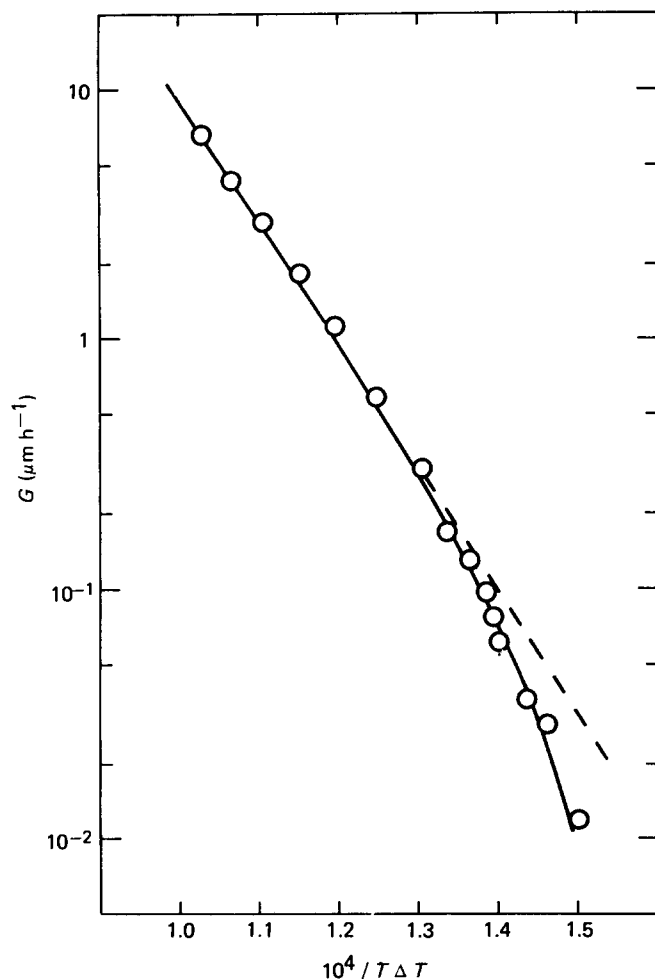


Figure 6 Fitting of equation (12) to the data at $2.0 \times 10^{-4}\%$ in Figure 3 with $B=17$ and $D=1.0$

In the crossover of type 2, the supercooling dependence of growth rate becomes similar to that at high supercooling (normal regime II); in Figures 3 and 4 the slope is parallel to that at high supercoolings. This behaviour means that the growth is still in regime II. For the concentration dependence, the power γ changes from 0.5 to about 1 as shown in Figure 2. In order to explain this dependence of growth rate, the velocity of steps, v , should be proportional to concentration and independent of supercooling:

$$G = b\sqrt{(2iv)} \quad (15)$$

$$v \propto C, \quad \text{independent of } \Delta T$$

From the concentration dependence of velocity v , it is expected that a new stem on the interrupted steps is formed when other molecules attach to the steps from solution. From the supercooling dependence of v , the process is also controlled by detachment of the impurity, not by the burying process. Therefore, the process occurs when the impurity is replaced with solute molecules that can crystallize. It is reasonable that this type of crossover occurs at higher concentrations since the process is dependent on concentration.

Decalin. The supercooling dependence of growth rate has the same behaviour as the crossover of type 1 in n-octane (Figure 5). The concentration dependence was

obtained by Cooper and Manley¹²: the power γ was 0.5 in the normal regime II. From the supercooling dependence at higher supercoolings, the product of surface free energies $\sigma\sigma_e$ is determined as $1800 \text{ erg}^2 \text{ cm}^{-4}$ for the $\{110\}$ face. The fitting of equation (12) is shown in Figure 5. The agreement is good. The parameters are determined as $B=27.2$ and $D=0.81$.

Xylene. Leung *et al.*⁹ observed the growth rate of relatively low molecular weight polyethylene at various concentrations and supercoolings. The supercooling dependence was similar to that in decalin. Although they did not explicitly discuss the behaviour at lower supercooling, from their data the crossover can be found as shown in Figure 7. For the concentration dependence, the power γ remained about 0.5 at each supercooling. The fitting of equation (12) is shown in Figure 7; the parameters are $B=25.2$ and $D=0.33$. The agreement is also good. It is noted that the crossover occurs at $1/T \Delta T \sim 1.3 \times 10^{-4}$ irrespective of the solvent: n-octane, decalin and xylene.

Hexadecane and tetradecanol. Organ and Keller observed a crossover similar to type 1 in both solvents. The power γ was less than 1 at low supercooling⁸. The fitting of equation (12) is not good with any values of parameters; at lower supercoolings across the crossover the data were almost on a straight line in the plots of $\log(G)$ vs. $1/T \Delta T$, while equation (12) rapidly decreases

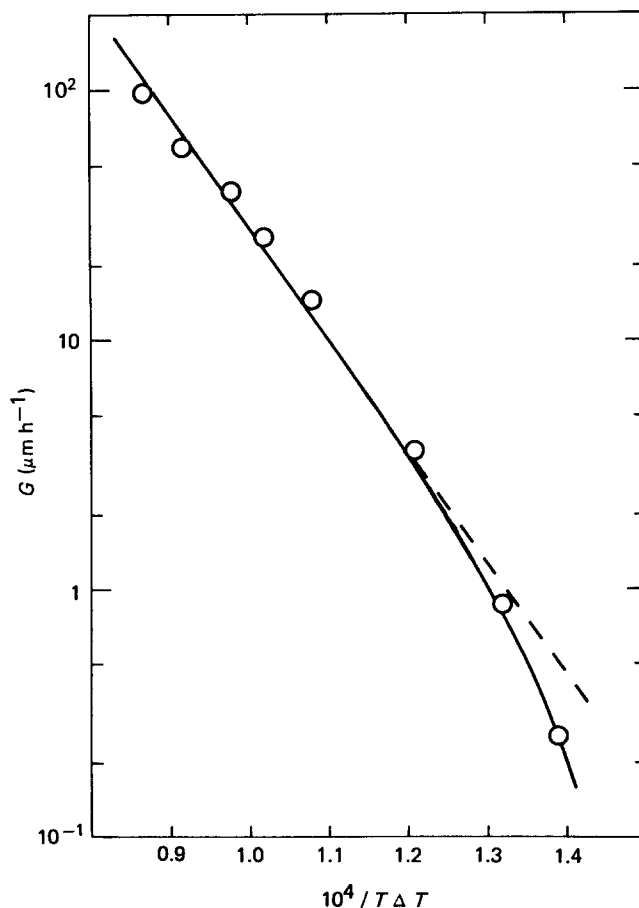


Figure 7 Linear growth rate of the $\{110\}$ face in xylene at $5.0 \times 10^{-2}\%$ plotted against $1/T \Delta T$. The data were obtained by Leung *et al.*⁹. The full curve is calculated from equation (12) with $B=25.2$ and $D=0.33$

as the supercooling decreases and becomes zero at finite supercooling $\Delta T = -\ln(B)/A$. Since the rate i° must be larger than the nucleation rate i , equation (12) will be oversimplified. If i° has the same supercooling dependence as i , namely the burying process requires nucleation on the interrupted steps,

$$i^\circ \propto \exp(-K'/T \Delta T) \quad (16)$$

where K' is a constant ($K' \leq K$), the supercooling dependence of growth rate at lower supercooling will be as follows:

$$G \propto \exp[-(K' + K)/2T \Delta T] \quad (17)$$

which is on a straight line in the plot of $\log(G)$ vs. $1/T \Delta T$. Experimentally, in the plot of $\log(G)$ vs. $1/T \Delta T$ the ratio of the slope at lower supercoolings to that at higher supercoolings was about 2. Therefore, K' will be equal to K .

Type of impurity

As shown in the above discussion, the transition of the supercooling dependence of growth rate can be explained as due to that of the velocity of steps interrupted by an impurity. In terms of the type of impurity, there can be three types: solvent adsorbed on the steps, defects along the stem and low molecular weight fraction adsorbed on the steps. First, if the solvent acts as an impurity, the supercooling of the transition will be dependent on the solvent. However, transitions similar to type 1 in *n*-octane have been observed in all the cases studied and occur at a definite supercooling irrespective of solvent, $10^4/T \Delta T \sim 1.3$. The impurity effect of the solvent will therefore be discarded, while it is known that the product of surface free energies $\sigma\sigma_e$ decreases as the solvent becomes poorer and the absolute value of the growth rate increases as the solvent becomes poorer at a given concentration and supercooling⁷. If the solvent is adsorbed on the side surface of a nucleus and reduces the surface free energy σ , the product $\sigma\sigma_e$ will decrease and the nucleation rate will be enhanced.

Secondly, Hoffman¹⁵ recently proposed a new type of defect, the Ω defect, which is made up of a hemispherical amorphous patch swelling in the stem. He showed that the persistence length of the growth face in melt growth is determined by the defects which interrupt the steps crossing over them. The probability of formation of the defects will be dependent on temperature and not on supercooling. Therefore, if the temperature dependence is weak, the probability $1/h^\circ$ will be constant within a wide range of temperature irrespective of the solvent and the transition will occur at a certain supercooling irrespective of the solvent.

Thirdly, as regards the impurity effect of low molecular weight fraction, Point *et al.*¹⁶ observed that at lower supercoolings the growth rate falls with time faster than at high supercoolings. This decrease could not be explained as being due to the depletion of the concentration; from the g.p.c. analysis it was attributed to the segregation of a low molecular weight fraction, although in the experiment a sharp fraction ($M_w/M_n \sim 1.11$) was used. The low molecular weight fraction will be rejected from the growth face and behave as an impurity. When the low molecular weight fraction crystallizes on steps, the supercooling ($\Delta T'$) is smaller than that of the higher molecular weight fraction (ΔT). The velocity of steps, g' ,

of the low molecular weight fraction has the same supercooling dependence as equation (11):

$$\begin{aligned} g' &\propto [1 - \exp(-A \Delta T')] \\ &\propto [1 - B \exp(-A \Delta T)] \\ B &\equiv \exp[A(T_d - T'_d)] > 1 \end{aligned} \quad (18)$$

where T'_d is the dissolution temperature of the low molecular weight fraction. In order to obtain the value $B \sim 20$, the difference $T_d - T'_d$ must be about 20°C; the molecular weight of the low molecular weight fraction should be several thousand. Further, this effect can also explain the fact that the transition occurs in a narrow range of supercooling irrespective of the solvent. The crossover of type 2 can also be explained by the effect. As shown in the above, in the crossover of type 2, an impurity interrupting the travelling of steps is replaced by solute molecules that can crystallize. In the present model, these processes can be interpreted as the replacement of the low molecular weight fraction by higher ones. Therefore, both crossovers, type 1 and 2, are explained by this model.

In conclusion, among the three types of impurity, defects and low molecular weight fraction are favoured.

Lateral habit

The lateral habit obtained in the present experiments is shown in *Figure 1*. In decalin the habit is well faceted, as in xylene. In *n*-octane the habit at lower supercoolings seems to be somewhat rounded on the $\{100\}$ face. It is known that in a poorer solvent such as paraffinic solvents the habit is rounded⁵ and in the limit it seems like a bamboo leaf¹⁷. The habit of crystals whose growth rate Organ and Keller measured was also rounded⁴. Since at lower supercooling below the transition in the growth rate the degree of rounding was larger than at higher supercooling in tetradecanol and hexadecane solutions, and the ratio of slope of growth rate at lower supercooling to that at high supercooling in the plots of $\log(G)$ vs. $1/T \Delta T$ was about 2 (ref. 4), in a previous paper⁷ this increase of rounding is attributed to the transition of growth rate from normal regime II to a mode similar to regime I:

$$G = bih^\circ a \quad (19)$$

In the growth mode, the interrupted steps cannot travel again and growth is controlled by the nucleation rate only. These interrupted steps accumulate on the growth face and the lateral habit becomes macroscopically rounded. However, the results on concentration dependence of growth rate recently obtained by Organ and Keller⁸ showed that the power γ is less than 1 even at lower supercoolings, which must be 1 in the mode of equation (19). Therefore, the growth will not be in the mode of equation (19) at lower supercoolings. As shown in the discussion on growth kinetics, the growth at lower supercooling is thought to be in regime II where the velocity of steps is determined by nucleation on interrupted steps. In the growth mode, the steps will not be accumulated as much as in the mode of equation (19). But accumulation will also occur if the steps pile up onto interrupted steps. The somewhat rounded lateral habits observed will result.

CONCLUSIONS

In n-octane and decalin solutions, transitions in the dependence of growth rate with supercooling and concentration have been observed at lower supercooling; a similar transition was also observed in xylene, hexadecane and tetradecanol. These transitions have been explained in terms of the effect of an impurity on the growth process. In a transition of type 1, an impurity interrupting the travelling of steps is buried into the crystal by crystallization on interrupted steps; in a transition of type 2, the impurity is detached from the steps and new polymer chains from solution crystallize on the steps; the concentration and supercooling dependence of growth rate is attributed to these processes in regime II. As the impurity, defects along the stems and a low molecular weight fraction adsorbed on the steps are favoured. In terms of lateral habit, a somewhat rounded lateral habit has been observed in n-octane at low supercoolings. The rounding of the lateral habit has some relation to the transition in the growth rate.

ACKNOWLEDGEMENTS

I am very grateful to Professor H. Kiho and Dr H. Miyaji (Kyoto University) for helpful discussions and encouragement throughout this work. I would like to

thank Dr T. Asahi (University of Yamaguchi) for preparation of ECC crystals under high pressure and Dr S. Hosomi (Idemitsu Sekiyukagaku Co. Ltd) for supply of the fractionated polyethylene.

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