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# Molecular weight dependence of lateral growth rate of polyethylene (I) — an extended chain single crystal

**Mutsuo Nishi[a], Masamichi Hikosaka[a,*], Akihiko Toda[a] and Masato Takahashi[b]**
[a]*Faculty of Integrated Arts and Sciences, Hiroshima University, Higashi-hiroshima, 739 Japan*
[b]*Department of Fine Materials Engineering, Faculty of Textile Science and Technology, Shinshu University, Ueda, 386 Japan*
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Molecular weight ($M$) dependence of lateral growth rate ($V$) of an extended chain single crystal (ECSC) of polyethylene (PE) crystallized at high pressure ($P = 0.4$ GPa) was studied. We obtained a well-known relation that $V = V_0\exp(-B/\Delta T)$, where $V_0$ and $B$ are constants related to a self-diffusion constant of molecules and free energy of forming a critical nucleus and $\Delta T$ is degree of supercooling. We showed that $V_0$ decreases with increasing $M$ and $B$ does not depend on $M$, which are similar to results reported by Hoffman *et al.* for a folded chain crystal (FCC) of PE. This indicates that $M$ dependence of $V$ is controlled by the self-diffusion process of molecules, while that is not done by the nucleation process. We obtained an experimental formula, $V(M) \propto D(M) \propto M^{-H}$, where $D$ is a self-diffusion constant and $H$ is a constant, $H = 0.7$. A similar relation has been shown, reported by Hoffman *et al.* and by us in a separate paper. But the $H$ given by us was larger, $H = 1.8$. It should be noted that the $H$ of a FCC is much larger than that of an ECSC. We will propose a new mechanism from this significant difference on $H$ in a separate paper, that $M$ dependence of $V$ is mainly controlled by the surface diffusion process of chain molecules on a surface of a crystal not by the self-diffusion process within the melt. © 1997 Elsevier Science Ltd. All rights reserved.

**(Keywords: molecular weight; growth rate; extended chain crystal)**

## INTRODUCTION

It is well known that the lateral growth rate ($V$) of crystals of linear chain polymers strongly depends on molecular weight ($M$)[1]. The $M$ dependence of $V$ is an important unsolved problem for both polymer science and technology.

### *Three stages of crystal growth*

It is well known in the general nucleation theory that a crystal grows via coupling of three elementary stages after nucleation of a primary nucleus[2]. The first stage is a self-diffusion process of atoms or molecules from the isotropic phase (such as the melt, solution or gas phases) on to a surface of the crystal. The second stage is a process of absorption and diffusion of absorbed atoms or molecules on the surface. The last stage is a process of nucleation of two-dimensional nucleus and growth. The three stages are simply named the first, the second and the last stages in this paper. It should be noted that the three stages are always coupled simultaneously in the crystal growth process.

It is important to make clear which stage mainly controls the $M$ dependence of $V$. $V$ is generally expressed considering the above three stages by

$$V = V_0\exp(-\frac{B}{\Delta T}) \propto D\exp(-\frac{\Delta G^*}{\alpha kT}) \qquad (1)$$

where $V_0$ and $B$ are constants, $\Delta T$ is degree of supercooling, $D$ is a self-diffusion constant of materials, $\Delta G^*$ is free energy for forming a critical nucleus, $\alpha$ is a constant ($\alpha = 1$ and $\alpha = 2$ or 3 for single and multi nucleation processes, respectively) and $kT$ is thermal energy. In equation (1) the following relations are used

$$V_0 \propto D \text{ and } \Delta G^* \propto \frac{1}{\Delta T} \qquad (2)$$

$D$ is usually defined by

$$D \equiv D_0\exp(-\frac{\Delta E}{kT}) \qquad (3\dagger)$$

where $D_0$ is a constant $\Delta E$ is an activation energy of self-diffusion of a unit, such as an atom or a repeating unit of a polymer. It is to be noted that $\Delta E$ does not depend either on $M$, even in the case of polymers, or on $T$. We have to consider two kinds of $D$ as mentioned above, $D$ within the melt, solution or gas ($D_m$) and that on the surface ($D_s$). It is natural to consider that a much slower diffusion process mainly controls $D$, which is represented by Onsager's reciprocal relation

$$\frac{1}{D} = \frac{1}{D_m} + \frac{1}{D_s} \qquad (4)$$

### *The self-diffusion of polymer chain molecules*

It is well known in the case of self-diffusion of a linear chain polymer within the melt that $D_0$ is in proportion to

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[*] To whom correspondence should be addressed

[†] $T$ is often replaced into $T - T_g$ for a polymer system, where $T_g$ is the glass transition temperature. The difference is not important in this work.

power of $M$, therefore $D_m$ is given by

$$D_m \propto M^{-H}\exp\left(-\frac{\Delta E_m}{kT}\right) \tag{5}$$

where $H = 1$ for $M \leq M_e$ or $H = 2$ for $M > M_e$, where $M_e$ is $M$ between entanglements[3], and $\Delta E_m$ is $\Delta E$ of a repeating unit within the melt. As $\Delta E$ does not depend on $M$, equation (5) can be given by

$$D_m(M) \propto M^{-H} \tag{6}$$

It should be noted that $D_s$ has not been formulated to our knowledge, so it is not certain if equation (6) can be applied to $D_s$ or not.

### *Previous studies on* M *dependence of* V

Magill *et al.*[4] showed an experimental formula, $\log V \propto 1/\sqrt{M}$, on poly (tetramethyl-*p*-silpenyline siloxane), poly (ethylene terephthalate) and so on. Hoffman *et al.*[5] and Labaig[6] observed $M$ dependence of $V$ of a folded chain crystal (FCC) of polyethylene (PE). They found that $V$ decreased with increase of $M$. Their results agreed well for regime II but did not for regime I. Hoffman *et al.*[5] showed that the nucleation process (the last stage) does not depend on $M$. They assumed that only the self-diffusion process within the melt (the first stage) depends on $M$, and proposed a theory using a model named the 'reeling in' model[7]. They presented a theoretical relation[7,8]

$$V(M) \propto M^{-1} \text{ or } M^{-H} \tag{7}$$

where $H$ is a constant, $H$ = 1.0–1.5. This roughly corresponds to equation (6). Comparison of equation (7) with the experimental results by Hoffman *et al.* and Labaig shows that $H$ depends on $\Delta T$, and gave different values of $H$ between the two authors for regime I. Therefore, it is not certain whether the 'reeling in' model is correct or not.

### *Purpose of this study*

The purpose of this study is to solve an unsolved important problem that controls the $M$ dependence of $V$. We will submit three papers related to the study. This is the first paper (Paper I). In this paper we will quantitatively show the $M$ dependence of $V$ of an extended chain single crystal (ECSC) of PE crystallized from the melt into the hexagonal phase at high pressure ($P$ = 0.4 GPa). First, we will show in this paper that the self-diffusion process of chain molecules (the first or second stage) controls the $M$ dependence of $V$, while the nucleation process (the last stage) does not. Secondly, a reliable experimental formula of $M$ dependence of $V$ of PE, $V \propto M^{-H}$, where $H = 0.7$, for an ECSC will be experimentally shown. In the second paper (Paper II)[9] a similar experimental formula for $M$ dependence of $V$ for FCC will be shown, and in the last one (Paper III)[10], we will propose a new mechanism of $M$ dependence of $V$. These papers will give for the first time an experimental foundation to show that the surface diffusion process of absorbed chains (the second stage) controls the $M$ dependence of $V$.

### *Improved points—a single crystal*

It is well known that $V$ strongly depends on the nature of the surface of a crystal, which means that $V$ is strongly related to a crystallographic lattice plane. Therefore, it is desirable that $V$ is observed on a single crystal, where $V$ can be directly related to a definite lattice plane. We intended to observe $V$ using a single crystal in this study. It is that folded chain single crystals of PE can be formed from the melt when $M$ is not so high. One of us (AT) reported that folded chain single crystals cannot be formed at 1 atm when the number average molecular weight ($M_n$) is higher than $10^5$ [11]. The reason will be considered in the Discussion. It is expected that a single crystal will be found in the case of ECSC even for high $M_n$, such as $M_n \geq 10^5$, the reason for which is also considered in the Discussion. The second purpose of this study is to confirm a formation of an ECSC even for $M_n \geq 10^5$.

### *Previous study of an extended chain single crystal*

One of the authors (MH) reported that $V$ of an ECSC of PE with $M_n = 28.9 \times 10^3$ is given by equation (1) and, therefore, it was concluded that the lateral growth of an ECSC is controlled by the two-dimensional nucleation process[12].

They reported that an ECSC shows the following typical morphology, the cigar-like shape observed by polarizing optical microscopy[13] and the tapered shape and striation on cross section of the crystals observed by transmission electron microscopy[14].

## EXPERIMENTAL

Three kinds of fractionated PE with $M_n = 11.4 \times 10^3$ (NIST, SRM1482, $M_w/M_n = 1.19$), $M_n = 28.9 \times 10^3$ (NIST, SRM1483, $M_w/M_n = 1.11$) and $M_n = 100 \times 10^3$ (NIST, SRM1484, $M_w/M_n = 1.20$) were used in this study, where $M_w$ is a weight average molecular weight. They are named 11 K, 29 K and 100 K, respectively.

These materials were isothermally crystallized under high pressure from the melt into the metastable hexagonal phase. The pressure ($P$) was 0.4 GPa. The range of $\Delta T$ was 2.8–8.5 K. Here we defined $\Delta T$ using equilibriun melting temperature ($T_m^0$) determined by Wunderlich's method[15]. $V$ of an ECSC was measured using polarizing optical microscopy. $V$ is defined by $V \equiv \frac{1}{2}\frac{da}{dt}$, where $a$ is the lateral size of a single crystal and $t$ is the crystallization time[12]. The morphology was observed using transmission electron microscopy[16]. The experimental details were given in references 14 and 17.

## RESULTS

### *Morphology*

*Polarizing optical microscopy.* *Figure 1* shows polarizing optical micrographs of growing isolated crystals. *Figure 1*a, b and c depict growing crystals in specimens 11 K, 29 K and 100 K. Isolated cigar-like crystals were observed for all $M_n$. They showed a similar morphology of a growing ECSC to that reported for the specimen 29 K[18]. This suggests that an ECSC was formed for all $M_n$, i.e. even in the case of material with high molecular weight, such as 100 K, as mentioned in the Introduction.

*Evidence of generation of an ECSC.* The morphology of isolated crystals was observed by transmission electron microscopy to confirm the formation of an ECSC suggested above. *Figure 2* shows the transmission electron micrographs of a cross section of isolated single crystals. *Figure 2*a and b depict the morphology in specimens 29 K and 100 K. Striations have been well known to be characteristic morphology of ECSC[1]. So we can conclude that an ECSC was formed in both cases, which confirmed

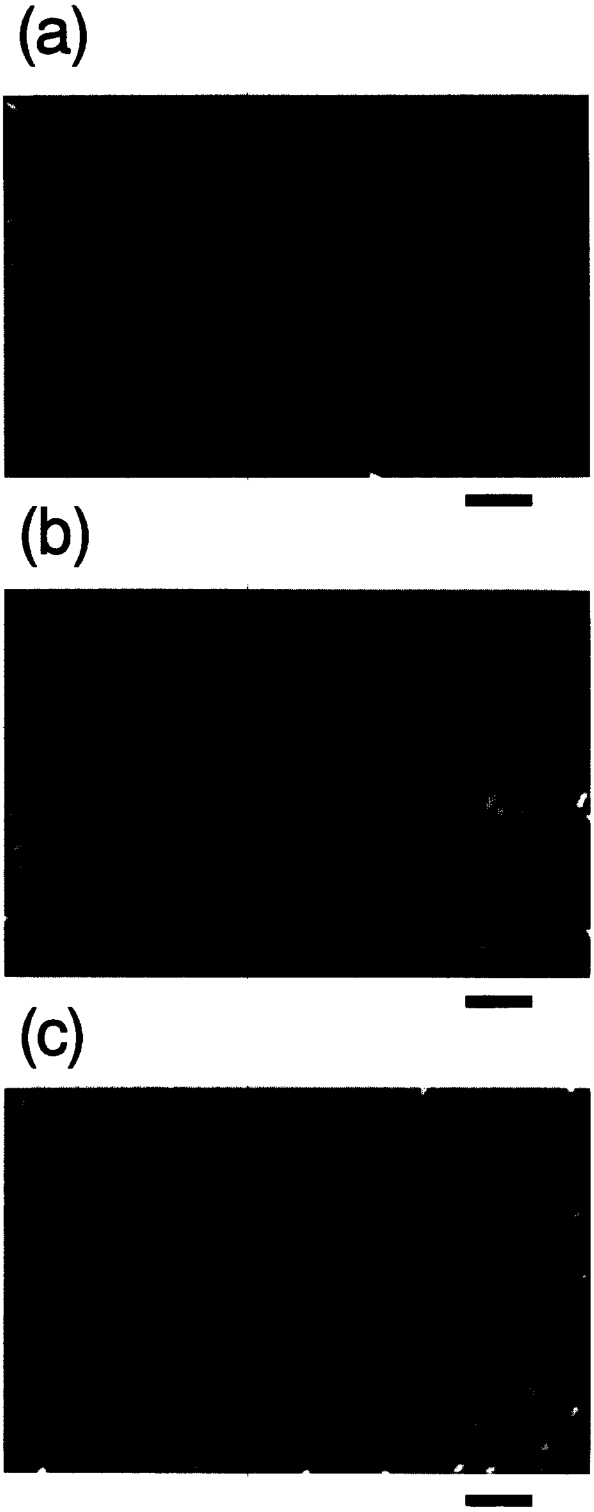

**Figure 1** Typical polarizing optical micrographs of growing ECSCs: $P = 0.4$ GPa; $\Delta T = 4.9$ K; (a) 11 K; (b) 29 K; and (c) 100 K. Scale bar = 20 $\mu$m

for the first time that single crystals can be formed even in the case of material with high $M_n$, such as $M_n = 10^5$. This is a remarkable contrast to the fact that the formation of single crystals is difficult in the case of FCCs.

This contrast confirms the prediction described in the Discussion that single crystals can be formed easily in the hexagonal phase, even in the case of material with high molecular weight, while single crystals cannot be formed easily in the orthorhombic phase.

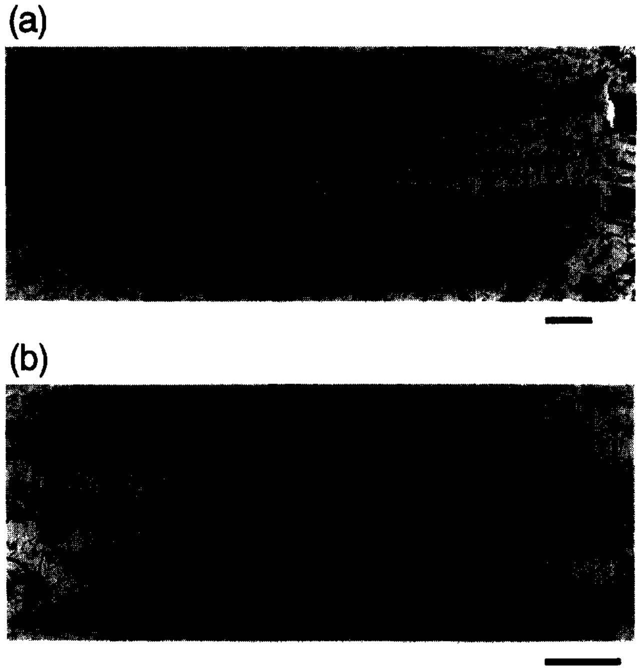

**Figure 2** Typical transmission electron micrographs of a cross section of isolated ECSCs at $\Delta T = 3.6$ K: (a) 29 K; (b) 100 K. Scale bar = 1 $\mu$m

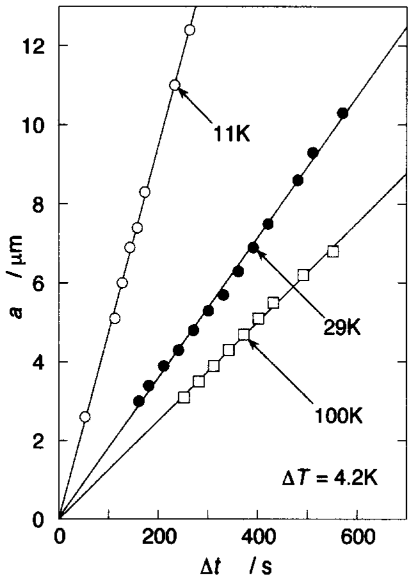

**Figure 3** $a$ as a function of $\Delta t$ at $\Delta T = 4.2$ K for $M_n$ = 11 K, 29 K and 100 K. Lines show the best fit of the plots. $\Delta t = 0$ is defined as the time when the ECSC was generated

### *Lateral growth rate*

*Steady lateral growth of an extended chain single crystal.* Typically observed $a$ of an ECSC in specimens 11 K, 29 K and 100 K is plotted against $\Delta t$ for a $\Delta T = 4.2$ K in *Figure 3*, where a parameter is $M_n$. $a$ increased linearly with increase in $\Delta t$ for all $M_n$. This shows that the growth of an ECSC was steady growth for all $M_n$, as has been reported for the specimen 29 K[12]. The slopes of the lines decreased with increasing $M_n$ where the slope was in proportion to $V$. This indicates that $V$ decreased with increase in $M_n$.

$\Delta$T *dependence of* V. *LogV* is plotted against $1/\Delta T$ for specimens 11 K, 29 K and 100 K in *Figure 4*. *LogV* decreased linearly with increase in $1/\Delta T$ for all $M_n$. Thus, we obtained the same experimental formula given by

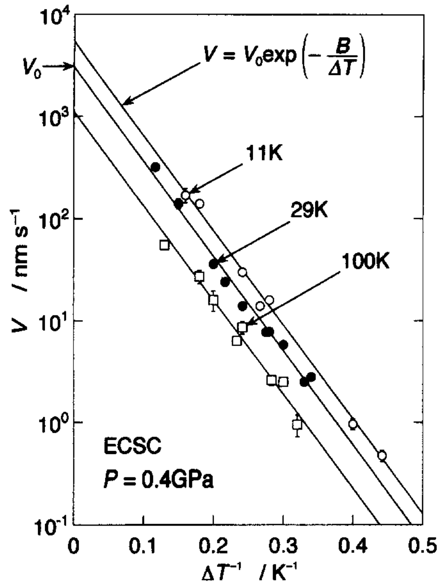

**Figure 4** log$V$ against $1/\Delta T$ for $M_n = 11$ K, 29 K and 100 K. Lines show the best fit of the plots, which correspond to equation (1)

equation (1) for all specimens as obtained on specimen 29 K, where $V_0 \propto D$ is an intercept of the vertical axis and $B$ is a slope of the line in *Figure 4*. This means that the growth of an ECSC is controlled by two-dimensional nucleation for all $M_n$.

All lines in *Figure 4* shifted downwards with increase in $M_n$. This suggests that $V$ decreases with increase in $M_n$, which will be quantitatively shown in the next section. It is to be noted that all lines were parallel, which means that the slope $B$ does not depend on $M_n$. Hence, the intercept $V_0 \propto D$ decreased with increase of $M_n$.

It should be noted that $V_0$ or $D$ given by equation (2) or equation (5) does not significantly depend on $T$ in this study, because $D_0$ does not depend on $T$ and $\exp(-\Delta E/kT)$ is nearly constant for the small change in $T$, such as $T \cong 500$ K ± 3 K, where the present experiment was carried out. $V_0$ and $B$ obtained from *Figure 4* were plotted against $M_n$ in *Figure 5*. This clearly shows that only $V_0 \propto D$ is a decreasing function of $M_n$, while $B$ does not depend on $M_n$, that is

$$V_0 = V_0(M_n) \text{ or } D = D(M_n) \text{ and } B \simeq \text{const} \qquad (8)$$

This means that the self-diffusion constant of chain molecules $D$ decreases with increase in $M_n$, while that free energy for forming a critical nucleus $\Delta G^*$ related to $B$ does not depend on $M_n$.

Thus, we have the following important relation combining equation (1) and equation (2) with equation (8),

$$V(M_n) \propto V_0(M_n) \propto D(M_n) \qquad (9)$$

This means that the $M_n$ dependence of $V$ is determined by the $M_n$ dependence of $D$. Thus, we have an important conclusion that the self-diffusion process within the melt (the first stage) or the surface diffusion process of absorbed chains on the surface of the crystal (the second stage) controls the $M$ dependence of $V$, while the nucleation process (the last stage) does not.

*Experimental formulae of* $M_n$ *dependence of* V *and* $V_0$. Log $V$ are plotted against Log $M_n$ in *Figure 6* for $\Delta T = 3$ K, 5 K and 8 K, respectively. Log$V$ decreased linearly with increasing log$M_n$. They showed almost the same slope.

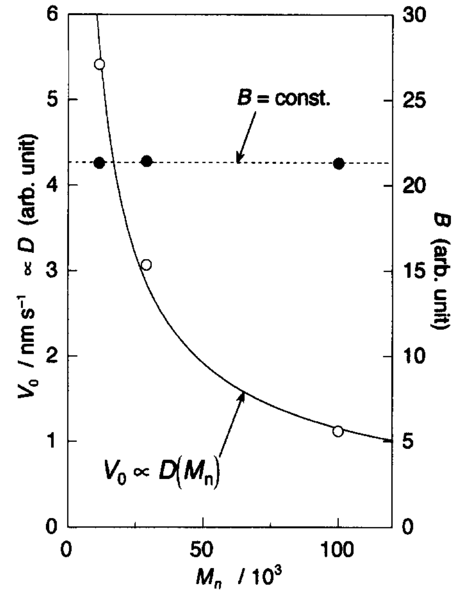

**Figure 5** Plot of $V_0$ and $B$ against $M_n$. The solid curve and the broken line show the best fit of $V_0$ and $B$, respectively. This shows that $V_0 \propto D$ is a function of $M_n$, while $B$ is constant

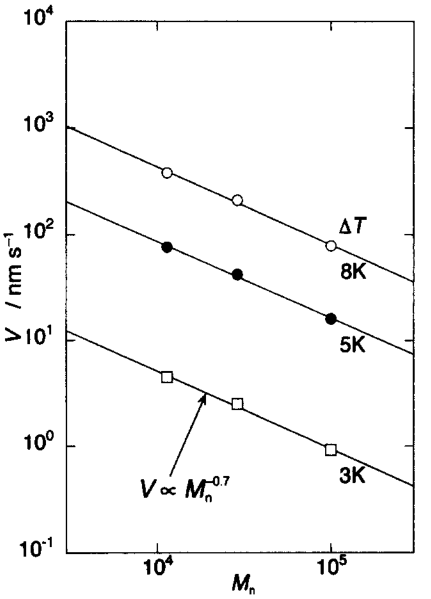

**Figure 6** Plot of log$V$ against log$M_n$ at $\Delta T = 3$ K, 5 K and 8 K. Lines show the best fit of log$V$, which corresponds to equation (10)

Thus, we have the following experimental formula

$$V(M_n) \propto M_n^{-H} \text{ where } H = 0.7 \qquad (10)$$

for $\Delta T = 3$ K, 5 K and 8 K. log$V_0$ or log$D$ also decreased linearly with increase in log$M_n$ (*Figure 7*), from which we have the following experimental formula:

$$V_0(M_n) \propto D(M_n) \propto M_n^{-0.7} \qquad (11)$$

It is obvious that equation (10) is similar to equation (7) and the slope of the line in *Figure 7* corresponds to $H$ in equation (7). Although equation (7) is given for the self-diffusion within the melt (the first stage), this similarity does not necessarily mean that the diffusion should be that within the melt, which will be made clear in a separate paper (Paper III)[10].

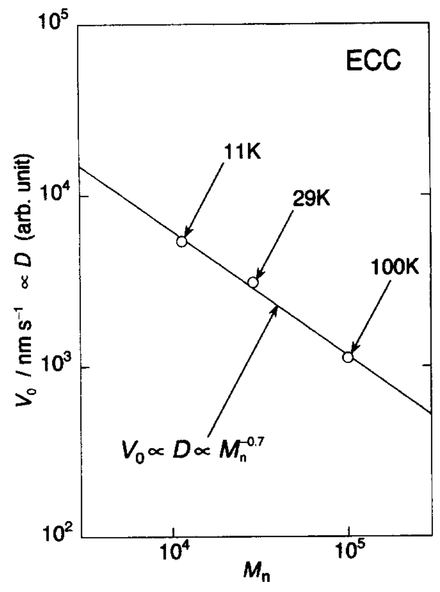

**Figure 7** Plot of $\log V_0$ against $\log M_n$. $V_0 \propto D$ was well fitted by a linear line corresponding to equation (11)

## DISCUSSION

### *Two kinds of self-diffusion stages*

We showed above that the self-diffusion process controls the $M$ dependence of $V$, while the nucleation process does not. It is an important problem next to make clear which self-diffusion process, the first or the second stage, mainly controls the $M$ dependence of $V$. It should be noted that in the experimental formula (equation (10)) $H = 0.7$ for an ECSC, while $H = 1.8$ for an FCC, which will be shown in Paper II[9]. This significant difference in $H$ strongly suggests that the $M$ dependence of $V$ is mainly controlled not by the self-diffusion process within the melt (the first stage) as proposed by Hoffman *et al.*[7] but by the surface diffusion process (the second stage) as will be shown in Paper III[10]. One of the authors (MH) showed that formation of an ECSC or a FCC is related to the order of the crystalline phase[19,20], that is, an ECSC and a FCC are formed from the melt into a disordered hexagonal and an ordered orthorhombic phase, respectively. It is natural to consider that the surface diffusion process should be controlled by the order of the crystalline phase. It is the reason why $H$ shows the significant difference between an ECSC and a FCC.

### *Why* B *does not depend on* M

It should be noted that the nucleation process does not depend on $M$ as shown above. This can be explained by our model of surface diffusion, which will be discussed in detail in a separate paper[10]. In the model a nucleus will be formed from the absorbed chains. We can estimate roughly the number of repeating units within a critical nucleus ($N^*$) using parameters $\sigma$, $\sigma_e$ and $\Delta h$ given in reference[21], where $\sigma$ and $\sigma_e$ are side and end surface free energies and $\Delta h$ is the enthalpy of fusion. $N^*$ is of the order of $10^2 - 10^3$ for the range of $\Delta T$ in our experiment, which is smaller than the number of repeating units within a molecule ($10^3 - 10^4$). This indicates that a critical nucleus should be formed by only a part of a molecular chain. Therefore, the nucleation process of the critical nucleus will not depend on $M$. Thus, it is a natural result that $B$ does not depend on $M$ in this study. This is consistent with the discussion by Hoffman *et al.*[5] on FCCs. They showed that the nucleation process of FCCs does not depend on $M$ in the case of $M > 10^4$. On the contrary, they showed that it depend on $M_n$ for $M_n < 10^4$, because $\sigma_e$ depends on $M_n$ owing to the effect of chain ends on the end surface of the critical nucleus.

### *Formation of a single crystal with high molecular weight*

It is known that folded chain single crystals cannot be formed in the case of materials with high molecular weight, such as $M_n \geq 10^5$ [11]. This can be explained by the 'sliding diffusion' theory[20,21]. The 'sliding diffusion' of chains is rather difficult in the orthorhombic phase, which results in formation of a FCC. As a result of this, cilia and/or loose loops of chain on the end surface of a crystal cannot be rearranged smoothly, but become sources of screw dislocation, which produces the overgrowth, i.e. stacked lamellae (= polycrystals). In contrast to this, the 'sliding diffusion' of chains is rather easy in the hexagonal phase at high pressure, even in the case of materials with high $M_n$, which results in the formation of an ECC. In this case the cilia and/or loose loops of chain can be dissolved easily by the significant 'sliding diffusion' of chain molecules in the hexagonal phase, which is the reason why an ECSC can be formed easily.

## CONCLUSION

(1) We obtained a well-known relation of the lateral growth rate ($V$) of an ECSC of PE that $V = V_0\exp(-B/\Delta T)$ for all kinds of molecular weight ($M$) where $V_0$ and $B$ are constants related to self-diffusion constant of molecules ($D$) and an energy of forming a critical nucleus, and $\Delta T$ is the degree of supercooling.

(2) We showed that $V_0$ decreases with increasing $M$, while $B$ does not depend on $M$, which are similar to the results of Hoffman *et al.* for FCCs of PE. Thus, we have an important conclusion that the self-diffusion of chain molecules controls the $M$ dependence of $V$, while the nucleation process does not, i.e. $V(M) \propto V_0(M)$ and $B(M) \simeq$ const.

(3) We have an experimental formula of number average $M$ ($M_n$) dependence of $V$, $V \propto V_0 \propto M_n^{-H}$, where $H = 0.7$ for an ECSC, which is similar to Hoffman *et al.*'s formula, but $H$ was less than half.

(4) We have a significant difference in $H$ between an ECSC ($H = 0.7$) and FCCs ($H = 1.8$) which will be reported in our separate paper. From this we discussed briefly a new proposal that $M$ dependence of $V$ is mainly controlled by the surface diffusion process of chain molecules not by the self-diffusion process within the melt as proposed by Hoffman *et al.*

(5) It was shown that an ECSC can be formed even in the case of PE with high $M_n$ such as $M_n = 100 \times 10^3$. This is a remarkable contrast to the fact that a single crystal of a FCC of PE cannot be formed in the case of high $M_n$. Thus, we confirmed the prediction of 'sliding diffusion' theory that an ECSC can be formed easily within the hexagonal phase owing to the high mobility of chains.

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