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Molecular weight dependence of the lateral growth rate of polyethylene

2. Folded-chain crystals

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Molecular weight (M) dependence of the lateral growth rate (V) of folded chain crystals (FCCs) of polyethylenes (PE) was investigated. This study was carried out on single (or single crystal-like) crystals using the equilibrium melting temperature (T_m^0) determined by applying Gibbs-Thomson's equation. The well-known relation $V = V_0 \exp(-B/\Delta T)$ was obtained where V_0 and B are constants and ΔT is a degree of supercooling. V_0 strongly decreased with increase of M, whereas B did not, which indicates that the self-diffusion process of polymer chains mainly controls the M dependence of V, whereas the nucleation one does not. Experimental formula that $V \propto V_0 \propto D \propto M^{-H}$ where D is self-diffusion constant and H is a constant; $H = 1.7$ was obtained. These results are similar to Hoffman *et al.*'s results but their H was rather smaller, $H = 1$–1.5. A similar study on extended-chain single crystals (ECSCs) reported in our previous paper gave the same experimental formula but H was much smaller, $H = 0.7$. From the difference in H between FCCs and ECSCs, a new proposal that M dependence of V may be mainly controlled by the surface diffusion process of chain polymers on the growing crystal surface, is discussed briefly. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

Previous studies on molecular weight dependence of growth rate

Molecular weight (M) dependence of the crystallization rate of polymer crystals is one of the most important and interesting problems in both polymer science and technology. But this has not been well solved yet as will be shown below. The M dependence of the lateral growth rate (V) of folded-chain crystals (FCCs) of polyethylene (PE) crystallized from the melt at atmospheric pressure was studied by Hoffman and co-workers[1–4], Labaig[5] and Toda[6]. They showed qualitatively that V decreased with increase of M. Hoffman *et al.*[1–4], through further quantitative studies, proposed an equation for the M dependence of V. In a previous paper, the present authors studied the M dependence of V of extended-chain single crystals (ECSCs) crystallized at a high pressure, and presented a similar equation to that of Hoffman[7]. Details will be shown later.

Purpose

This article is the second (Paper 2) of series of papers which aims to solve the mechanism of M dependence of the crystallization rate of polymer crystals. The purpose of Paper 2 is to study quantitatively the M dependence of V of FCCs of PE crystallized isothermally from the melt at atmospheric pressure. This study was carried out on single

crystals (or single crystal-like crystals) using T_m^0 determined after Wunderlich's method applying Gibbs-Thomson's equation, which will be discussed in the following part of this article. The purposes of the previous paper (Paper 1)[7] mentioned previously was to study the M dependence of V ECSCs crystallized at a high pressure, and that of the third paper (Paper 3)[8] is to propose a new mechanism of M dependence of V of PE combining the above results on FCCs and ECSCs.

Equilibrium melting temperature (T_m^0)

T_m^0 is one of the most important parameters in the study of crystal growth, because V depends on the degree of supercooling (ΔT) which is defined from T_m^0 by a relation, $\Delta T = T_m^0 - T_c$, where T_c is the crystallization temperature. There were unsolved long arguments about the following two methods with regard to how to determine the T_m^0 of orthorhombic crystals of PE. One is proposed by Broadhurst[9] and Hoffman *et al.*[1] and the other by Wunderlich[10].

In the former, T_m^0 is extrapolated from the observed M dependence of the melting temperature (T_m) of the *n*-alkane system, theoretically considering the effect of chain ends on the T_m. In the latter, T_m^0 is estimated applying Gibbs-Thomson's equation to the observed T_m of extended-chain crystals (ECCs). Gibbs-Thomson's equation is derived from thermodynamics, considering the effect of surface free energy on the free energy of a small crystal; this equation for a lamellar crystal is given by $T_m^0 = T_m + C/l$ where C is a constant and l is lamellar thickness[10]. Wunderlich[10] showed

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that the T_m of ECCs of about a few μm thick of PE is (at most) 0.3 K lower than T_m^0.

The difference of T_m^0 between the two methods is several K, which is significant and can not be negligible in this study, therefore we will re-examine on T_m^0 in this study. Although it has not been finally judged which method is correct, the latter method will be taken in this study. Hoffman *et al.*[1-4], Labaig[5] and Toda[6], on the contrary, took the former method.

Growth regime I and II or Type A and B

Hoffman *et al.*[1], Labaig[5] and Toda[6] showed that the well-known relation,

$$V = V_0 \exp(-B/\Delta T), \qquad (1)$$

was confirmed for all kinds of M where V_0 and B are constants. V_0 and B are related to the self-diffusion process of polymer chains and nucleation process, respectively.

They also showed that the plots of log V against $1/\Delta T$ showed a breaking at a $1/\Delta T$. Hoffman *et al.* observed a range of the polycrystalline morphology at the breaking point from spherulite to axialite with increase of $1/\Delta T^1$. They named the two regions separated by the breaking point, regimes I and II, respectively[1]. One of the authors (A.T.) observed V_s on single crystals and also found change of morphology at the breaking point from lenticular shape to truncated lozenge shape with curved growth {200} faces and named them Types A and B crystals, respectively[6]. In this paper the terms Types A and B will be used, because the study will be carried out on single crystals.

M_n dependence of V

Hoffman *et al.*[1] showed that V_0 decreased with increase of M, while B was nearly constant for large M[1], from which they concluded that the self-diffusion process within the melt mainly controls the M dependence of V, while the nucleation one does not. Hoffman *et al.* showed that

$$V \propto D \propto M^{-H} \quad \text{where } H = 1-1.5 \qquad (2)$$

where D is the self-diffusion constant[2-4]. Hoffman presented a theory and showed $H = 1-1.5$ introducing a model assuming that V is mainly controlled by the self-diffusion process of polymer chains from the melt to nucleus directly, which is called the 'reeling in model'[2].

The present authors also showed a similar relation on an isolated ECSC in Ref. [7] (Paper 1) that

$$V \propto V_0 \propto D \propto M^{-H} \quad \text{where } H = 0.7, \qquad (3)$$

It should be noted that the value of H was much smaller than that of FCCs given previously[7].

In this study a similar relation to that of $V_0 \propto D \propto M^{-H}$ will be reported where $H = 1.7$ for both Types A and B FCCs. From this significant difference in H between FCCs and ECSC, a new proposal (presented in a separate paper) that the M dependence of V may be mainly controlled by the surface diffusion process of polymer chains will be briefly discussed.

Polycrystals or single crystals

Hoffman and co-workers observed the V on polycrystals, such as spherulites or axialites[1-4]; Labaig observed this partly on single crystals[5]; and Toda observed this on single crystals[6]. Toda showed that single crystals could be observed at an early stage of crystallization for the samples with rather low M_n, such as 11 000 and 29 000, while they

changed easily into polycrystals due to remarkable overgrowth[6] for the sample with rather high M_n, such as 100 000. In this study, special care was taken that observation should be carried out on single crystals (or at least single crystal-like crystals). Therefore, observation was limited to the earlier stage of crystallization.

EXPERIMENTAL

Three kinds of fractionated PE used in this study were NIST, SRM1482 ($M_n = 11\,400$, $M_w/M_n = 1.19$), SRM1483 ($M_n = 28\,900$, $M_w/M_n = 1.11$) and SRM1484 ($M_n = 100\,500$, $M_w/M_n = 1.11$) where M_n and M_w are number average- and weight average-molecular weights, respectively. They are named 11, 29 and 110K, respectively, in this work.

T_m^0 was determined after Wunderlich's method[10] from the T_m of an isolated orthorhombic ECSC (T_m(ECSC)) using the relation, $T_m^0 = T_m(\text{ECSC}) + 0.3$ K which was shown in Section 1.

ECSCs were crystallized at high pressure using a high pressure cell. Details of the procedure was previously given in Ref. [11]. The formation of an isolated ECSC was confirmed by means of transmission electron microscopy (TEM). The T_m(ECSC) was estimated from a temperature where the lateral length (a) of an isolated ECSC started decreasing significantly on heating at a rate of 0.1°C/min. This was observed by means of optical microscope at atmospheric pressure.

Isothermal crystallization of an isolated folded-chain single crystal (or single crystal-like crystal) at atmospheric pressure was observed by means of a polarizing optical microscope (Olympus, BHS-751-P) using a hand-made hot stage designed by one of authors (M.H.) and recorded using a video camera system. The temperature was calibrated using standard materials and water. The sample was melted at 150°C for 3–5 min and quenched to T_c. Crystallization was carried out within nitrogen gas to prevent oxidation. The range of ΔT was from 8 to 17 K.

V was estimated by the relation $V = (1/2)(da/dt)^{11}$. Special care was taken that the observation of the growth rates was carried out on an isolated single crystal (or single crystal-like crystals), which was confirmed by morphological observation using POM or TEM after Toda's method[6].

RESULTS

M_n dependence of Tm^0

The typical morphology of a leaf-like ECSC reported in Ref. [7] was observed by means of polarized optical microscopy and TEM, from which formation of an isolated ECSC was confirmed. Observed lamellar thickness (l) was about 1 μm.

The T_m(ECSC) was estimated from a temperature where the lateral length (a) of an isolated ECSC started decreasing significantly with increase of temperature. Typical example is shown in *Figure 1*. The estimated T_m(ECSC) is shown by the arrow in *Figure 1*.

The T_m^0 estimated from T_m(ECSC) was plotted against log M_n in *Figure 2*. T_m^0 reported by Hoffman *et al.* and the T_m values of orthorhombic extended-chain crystals collected by Wunderlich[10] are also shown in *Figure 2*. The T_m^0 values obtained agreed well with Wunderlich's T_m values, while a significant deviation (about several K) from the T_m^0 reported by Hoffman *et al.* was seen.
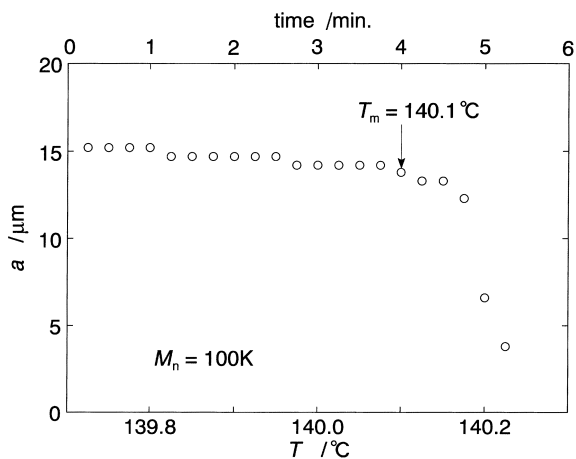
Figure 1 Typical procedure of estimation of T_m of an ECSC. T_m was estimated from a temperature where the lateral length a begins to decrease on heating at a rate 0.1 K/min
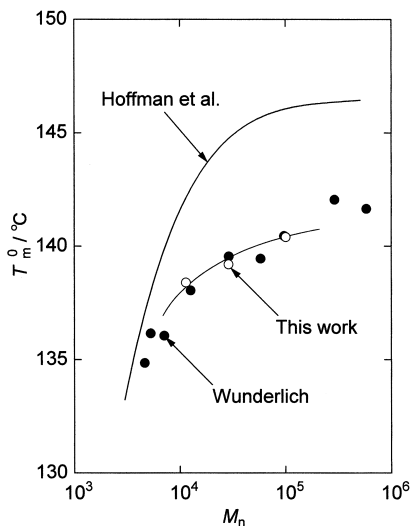

Figure 2 Equilibrium melting temperature T_m^0 plotted against log M_n. (○) this work; (●) Wunderlich[10]; solid line, Hoffman et al.[1]
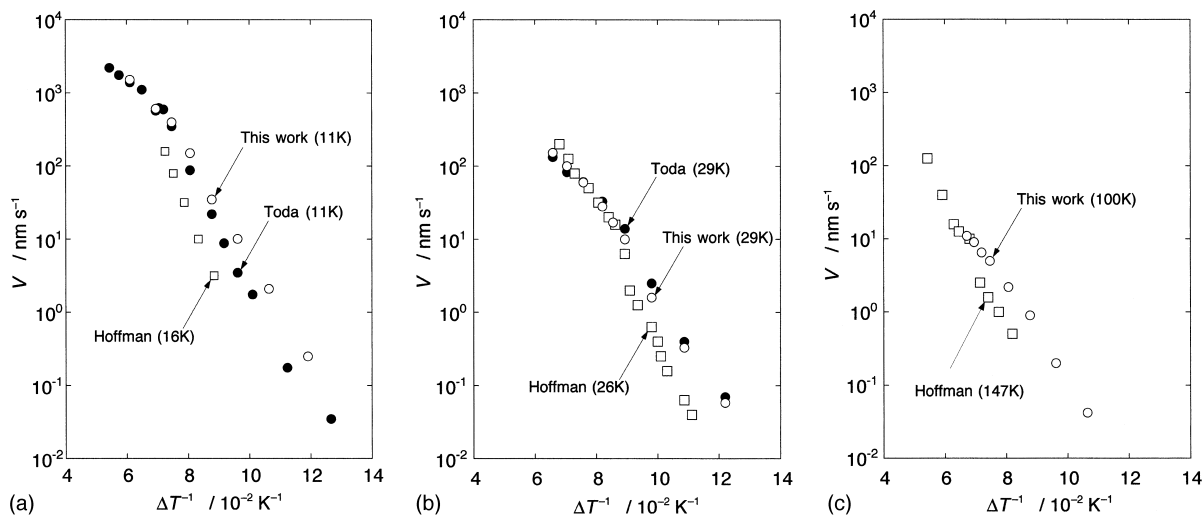
ΔT dependence of V

Formation of isolated single crystals was confirmed on samples 11 K and 29 K, but single crystal-like crystals could be obtained in the case of 100 K, as mentioned in Section 1.

The lateral growth rates (V) for samples 11 K, 29 K and 100 K were plotted against $1/\Delta T$ in *Figure 3a–c*, respectively*. In *Figure 3* the data reported by Toda[6] and Hoffman et al.[1] were also re-plotted using the new ΔT values determined from the T_m^0 in this paper. The agreement between our results and those of Toda for $M_n = 11$ K and 29 K[6] was good, while that between our results and those of Hoffman et al.[1] was good only for Type B (or regime II) but not so good for Type A (or regime I).

Plots of log V against $1/\Delta T$ obtained in this study are summarized in *Figure 4* for the three M_n values. *Figure 4* shows that they gave straight lines and breakings, therefore the well-known experimental formula, $V = V_0 \exp(-B/\Delta T)$, which is identical to equation (1), was confirmed. The breaking points were confirmed to correspond to the Type A to B transition from morphological evidence observed by optical microscopy and TEM after Toda's method[6]. The transition is shown by the dotted lines in *Figure 4*.

M_n dependence of V_0 and B

It should be noted that the slopes of plots of log V against $1/\Delta T$ for three M_n values were almost the same within the same regions, Type A or B. To clarify this, V_0 and B were plotted against M_n in *Figure 5*. This clearly showed that V_0 strongly decreased with increase of M_n, whereas B did not, as was shown by Hoffman et al. for FCCs[1] and by us, in the Paper 1, for ECSCs[7].

It should be remembered that V_0 is related to self-diffusion of polymer chains, while B is related to the activation free energy for the formation of a two-dimensional critical nucleus. Thus we have a conclusion that the self-diffusion process of polymer chains mainly controls the M dependence of V, whereas the nucleation one does not.

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* It is usual that $1/T_c\Delta T$ is taken for a horizontal axis, but we took $1/\Delta T$ in this paper. This does not affect any results, because the ratio of change in T_c (i.e. ΔT) to T_c is small enough (within a few percent) in this work. Therefore T_c in the $1/T_c\Delta T$ can be regarded to be nearly constant.
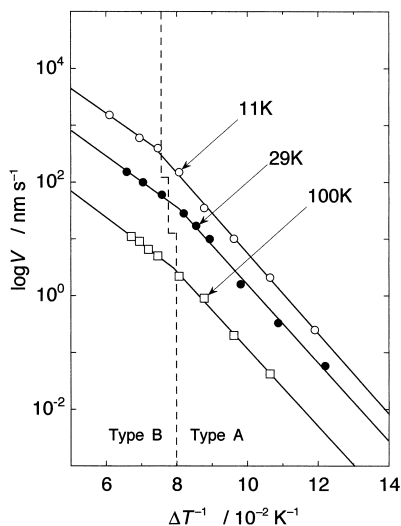

Figure 3 Lateral growth rate V against $1/\Delta T$. (a) $M_n = 11$ K, (b) $M_n = 29$ K and (c) $M_n = 100$ K. Data by Hoffman et al.[1] and Toda[6] replotted using ΔT obtained in this work were also plotted as references

Figure 4 Lateral growth rate V as a function of $1/\Delta T$ for M_n 11K, 29K and 100K
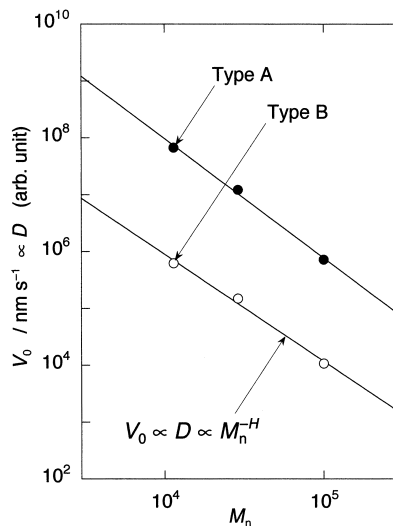

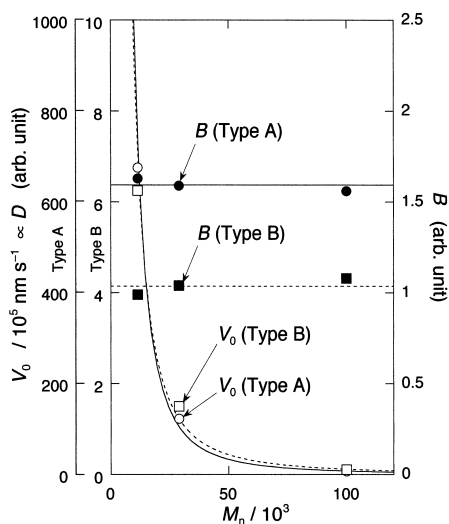**Figure 7** Log V_0 as a function of log M_n for Type A and B

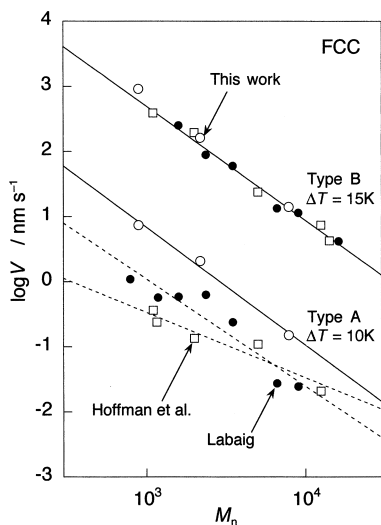**Figure 5** V_0 and B for Type A and B as a function of log M_n

Figure 6 Log V plotted against log M_n for Types A and B FCCs. The data for the Hoffman *et al.* and Labaig plots were re-plotted from the data in Refs. [2,5] using ΔT values obtained in this work

M_n dependence of V

Log V was plotted against log M_n for Types A and B FCCs in *Figure 6*, for $\Delta T = 10$ and 15 K, respectively. This showed that log V_0 linearly decreased with increase of log M_n. It should be noted that the slopes for both Types A and B FCCs were nearly the same, from which an experimental formula that

$$V \propto M_n^{-H} \quad \text{where } H = 1.7, \quad \text{for both Types A and B FCCs}$$
$$(4)$$

was obtained. This formula is similar to the previous work given by Hoffman *et al.*[1] on FCCs and by us on an ECSC[7].

Plots of log V *versus* log M_n re-plotted from the data of Hoffman *et al.*[1] and Labaig[5] are also shown in *Figure 6*, using newly determined ΔT values in this work. They showed good agreement with our result for Type B (which corresponds to regime II), while for Type A (corresponds to regime I), the data were scattered and it was difficult to estimate a correct H.

Log V_0 *versus* log M_n was also plotted for Types A and B FCCs in *Figure 7*. This showed that log V_0 linearly decreased with increase of log M_n. The slopes for both Types A and B FCCs were nearly the same, from which an experimental formula that

$$V_0 \propto D \propto M_n^{-H} \quad \text{where } H = 1.7,$$
$$\text{for both Types A and B FCCs} \quad (5)$$

was obtained. This formula is similar to the previous work by us on an ECSC[7].

DISCUSSION

Mechanism of M_n dependence of V

Here we will show that the significant difference in H ($H = 1.7$ for FCCs and $H = 0.7$ for an isolated ECSC[7]) may not been explained by self-diffusion within the melt, but may suggest that M dependence of V is mainly controlled by the surface diffusion process of chain polymers.

The formation of FCCs and ECSCs is closely related to order of crystalline phases, as has been shown by the 'chain sliding diffusion' theory presented by one of us (M.H.)[12,13], i.e. the FCCs are formed from the melt into an ordered phase, such as an orthorhombic phase, while the ECSCs are

formed into a disordered one, such as a hexagonal phase. The surface diffusion of chains is speculated to be affected by the difference of the order of the crystalline phase, which may be the reason why *H* depends on the difference in morphology of FCCs and ECSCs[8]. This point will be discussed in detail in Paper 3[8].

CONCLUSION

(1) The equilibrium melting temperature (T_m^0) was estimated experimentally applying Gibbs-Thomson's equation. This agreed well with Wunderlich's results, but was significantly different from those of Hoffman *et al*.

(2) It was shown that the self-diffusion process of polymer chains mainly controls the molecular weight (*M*) dependence of the lateral growth rate (*V*), whereas the nucleation process does not.

(3) An experimental formula that $V \propto D \propto M^{-H}$ was obtained for both Types A and B FCCs, where *D* is self-diffusion constant and *H* is a constant. It is shown that $H = 1.7$ for both Types A and B FCCs.

(4) It is shown that there is a significant difference in *H* between FCCs ($H = 1.7$) and ECSCs ($H = 0.7$), as shown by us in the previous article, from which a speculation that *M* dependence of *V* may be mainly controlled by the surface diffusion process of chain polymers, and not by self-diffusion within the melt, is briefly discussed.

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