Unified theory of nucleation of folded-chain crystals (FCCs) and extended-chain crystals (ECCs) of linear-chain polymers:

2. Origin of FCC and ECC*

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An improved formulation for the nucleation rate j of a generalized sequential process is presented. The topological nature of linear chains was formulated by introducing activation energy for chain sliding diffusion within crystals. It is shown that when chain sliding diffusion is easy extended chain crystals (ECC) will be formed from folded chain crystals (FCC) by lamellar thickening, whereas when it is difficult FCCs will be formed, which shows the origin of ECC and FCC. It indicates that there is no essential difference in formation mechanism between FCC and ECC. It is predicted that polymers crystallized from the melt into hexagonal form will change continuously from FCC to ECC with increasing crystallization temperature.

(Keywords: nucleation rate; topological nature; chain sliding diffusion within crystals; extended chain crystals; folded chain crystals; hexagonal form)

INTRODUCTION

The previous paper[1] presented a unified theory (henceforth referred to as UI) which explained the origin of formation of folded chain crystals (FCC) and extended chain crystals (ECC) of linear chain polymers. UI also explained the dependence of lamellar thickness of FCC on the degree of supercooling ΔT. UI was improved from the previous theory[2] based on experimental results on extended chain single crystals (ECSC) of polyethylene (PE) under high pressure[3,4]. UI was an extension of kinetic theories given by Turnbull and Fisher[5] and by Frank and Tosi (FT)[6].

UI started from the viewpoint that a nucleus will tend to grow two-dimensionally due to the thermodynamical driving force. Then UI introduced a topological viewpoint that the sliding diffusion of a chain within a nucleus plays an essential role. UI showed that when chain sliding diffusion is easy, the nucleation rate for a two-dimensionally growing nucleus becomes dominant, whch gives rise to ECC type growth. On the contrary, when chain sliding diffusion is difficult, the nucleation rate for a one-dimensionally growing nucleus becomes dominant, which gives rise to FCC type growth.

Recently, Hikosaka *et al.* succeeded in providing experimental evidence[7] on PE which confirmed the viewpoints of UI mentioned above. They showed that PE crystallizes first into FCC type lamellae, which then thicken into ECC type lamellae, when PE is crystallized from the melt into the disordered hexagonal phase in which chains can easily slide within a lamella. They also showed that extended chain single crystals (ECSC) can be formed and grow only in the hexagonal phase and not in the ordered orthorhombic phase.

The former confirmed Wunderlich and Davison's suggestion that ECC is formed by a lamellar thickening mechanism[8]. The latter also confirmed Bassett and Piermarini's suggestion that there should be a close relation between the formation of ECC and FCC and the hexagonal and orthorhombic phases in PE[9]. The evidence of Hikosaka *et al.*[7] gave molecular bases to the lamellar thickening mechanism and to the relation between the morphologies of FCC and ECC and the phases. In other words, this experimental evidence clearly showed the important role of chain sliding diffusion within solids (nucleus or lamella) in the formation of FCC and ECC which was stressed in UI.

However, two insufficient points remained in UI. First, the formulation of the nucleation rate, j, (UI equation (15)) was complex. Second, the definition of the average of the two activation energies (denoted as ΔE) necessary for two kinds of diffusion (diffusion of a chain in liquid or solution and sliding diffusion of a chain within a nucleus) was too simple. The oversimplification gave too large a value of ΔE for FCC. For example, ΔE became as large as $100(kT)$ for a stem 100 A long.

The aims of this paper are:

(1) to improve the formulation of j by deriving a simple form for a generalized sequential process and to redefine ΔE on the basis of the kinetic nature;

(2) to show that when a nucleus can thicken and grow two-dimensionally by chain sliding diffusion, a lamella can also thicken and grow three-dimensionally by chain sliding diffusion, which will finally result in the formation

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of ECC; the reverse (which will result in formation of FCC) will also be shown to be true;

(3) to show more clearly than UI did that the origin of formation of FCC and ECC is related to the ease or difficulty of chain sliding diffusion within crystals (nuclei or lamellae);

The paper concludes that there is no essential difference between the formation mechanisms of FCC and ECC and presents a prediction that ECC will be formed from FCC by lamellar thickening via chain sliding diffusion when polymers crystallize into the hexagonal (or pseudo-hexagonal) form and that FCC will be formed when polymers crystallize into another ordered form such as orthorhombic or monoclinic.

It will be shown that j is determined by two competing factors only, a thermodynamical and a kinetic factor. The origin of the formation of FCC and ECC will be shown to be related to which factor becomes dominant. It will be shown that j can be rewritten as a product of two probabilities, the probability of generating a critical nucleus and the survival probability of the nucleus.

It will also be shown that the formulation of j obtained in this work is apparently similar to that given in previous theories by Lauritzen and Hoffman (LH)[10] and FT. But the essential difference between them will be shown to be related to the topological viewpoint, i.e. the effect of chain sliding diffusion, which plays an important role in this work. In other words, the physical meaning of ΔE in this and the previous theories is different. ΔE in this work includes the activation energy both for chain sliding diffusion within crystals (nucleus or lamella) and for diffusion within the melt or solution, while ΔE in both LH and FT theories only includes the activation energy for diffusion within the melt or solution.

To achieve aim 2, it will be sufficient in this paper to obtain conditions for two- (or one-) dimensional growth of a nucleus to clarify the condition of formation of ECC (or FCC).

GENERALIZED NUCLEATION RATE j

Improved formulation of nucleation rate j

We will use the same 'generalized' linear sequential process as used in UI. 'Generalized' means that ΔE is a function of the stage number m, which will be discussed below. The process is illustrated in *Figure 1*. Let us start from the general form of the nucleation rate j given by FT equation (13):

$$j=\frac{\alpha_0\beta_0}{\sum_{m=0}^{\infty}\sum_{i=0}^{m}(\alpha_i\beta_i)} \tag{1}$$

α_m and β_m are the forward and backward transition rates from the mth stage and are given by UI equation (12). Note that the summation in UI equation (14) can be written as (see UI Figure 2)

$$\sum_{i=2}^{m}\Delta f_i=G^*-G_m \tag{2}$$

where Δf_i is the difference in the free energy for forming a nucleus between the $(i-1)$th stage and the ith stage defined by UI equation (13), G_m is the free energy for forming a nucleus of the mth stage and $G^*=G_m$ for a critical nucleus (see *Figure 1*). In *Figure 1*, N is the total number of repeating units within a nucleus.

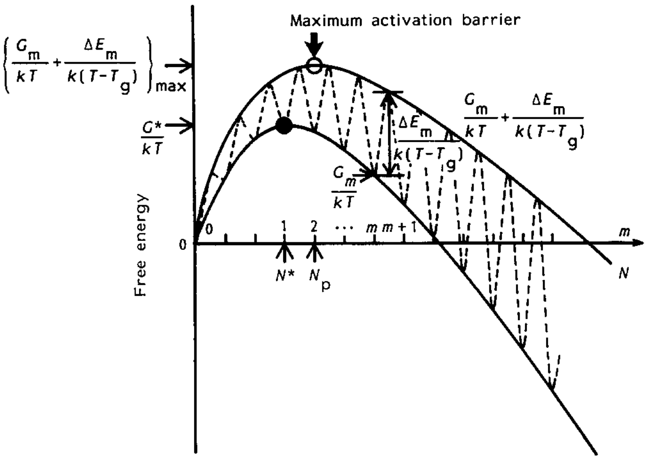

Figure 1 Generalized linear sequential process where ΔE_m is a function of m. Actual maximum activation barrier is indicated by open circle and arrow

Substitution of UI equations (13) and (14) and equation (2) into equation (1) gives

$$j=\alpha_0\eta_0/A \tag{3}$$

where η_0 is a constant and

$$A=2+\sum_{m=2}^{\infty}(h/kT)\alpha_0\exp\{G_m/kT+\Delta E_m/k(T-T_g)\} \tag{4}$$

Here h is Plancks constant, kT is the thermal energy at a temperature T, $\Delta E_m=\Delta E$ (activation energy necessary for diffusion) from the mth to the $(m+1)$th stage (*Figure 1*) and T_g is the glass transition temperature.

If we make the approximation that

$$\Delta E_0\simeq\Delta E_1 \tag{5}$$

then A can be approximated as follows:

$$A\simeq\sum_{m=0}^{\infty}(h/kT)\alpha_0\exp\{G_m/kT+\Delta E_m/k(T-T_g)\}+(1-\alpha_0/\beta_1) \tag{6}$$

Evidently, in this problem,

$$A\gg 1$$

and

$$\alpha_0/\beta_1\ll 1 \tag{7}$$

Combination of equations (6) and (7) gives

$$A\simeq\sum_{m=0}^{\infty}(h/kT)\alpha_0\exp\{G_m/kT+\Delta E_m/k(T-T_g)\} \tag{8}$$

Substitution of equation (8) into equation (3) ultimately gives a new and simple formulation for j:

$$j=\eta_0\left(\frac{kT}{h}\right)\left[\sum_{m=0}^{\infty}\exp\{G_m/kT+\Delta E_m/k(T-T_g)\}\right]^{-1} \tag{9}$$

Equation (9) shows that j is determined by only two factors, G_m and ΔE_m. G_m is a decreasing function of m for $m>1$ and will become negative when m becomes large (see *Figure 1*). ΔE_m is, on the contrary, always a positive constant or a positive increasing function of m for any m (*Figure 1*). Therefore, the two factors compete.

G_m is derived from a thermodynamic procedure, as shown in UI Appendixes I and II, whereas ΔE_m is determined by the manner of diffusion. Therefore, the nature of ΔE_m is essentially kinetic. Thus we conclude that the nucleation rate j is determined by two competing factors, a thermodynamic factor G_m and a kinetic factor ΔE_m. In this paper, the conclusion reached in UI will be confirmed: ECC will grow when the thermodynamic factor is dominant; FCC will grow when the kinetic factor is dominant.

Observable crystals should clearly be formed through the nucleus that gives the largest j. Therefore, we have to find such a nucleus to predict which type of crystals will be formed. This is why j is so important in the study of crystallization kinetics.

Physical meaning of j

We will rewrite the formula for j to make its physical meaning clear:

$$j=\eta_0(kT/h)\exp[-\{G_m/kT+\Delta E_m/k(T-T_g)\}_{\max}]P_s \quad (10)$$

where P_s is a survival probability of a nucleus defined as

$$P_s=\left\{\sum_{m=0}^{\infty}\exp[\{G_m/kT+\Delta E_m/k(T-T_g)\} -\{G_m/kT+\Delta E_m/k(T-T_g)\}_{\max}]\right\}^{-1} \quad (11)$$

Equation (10) is a new basic formulation of j corresponding to UI equation (15). Equation (10) shows that j is given by a product of two probabilities, the probability of passing through the maximum activation barrier of formation of a nucleus, $\exp[-\{G_m/kT+\Delta E_m/k(T-T_g)\}_{\max}]$, and the survival probability of the nucleus, P_s.

Note here that ΔE_m is generally not always constant but is a function of m, which is an important difference from the previous theories of Turnbull and Fisher[5], FT and LH. In this case, the so called critical nucleus cannot give a maximum activation barrier in the sequential process (see *Figure 1*). For example, when ΔE_m is an increasing function of m, the nucleus which gives the maximum activation barrier will become bigger than the so called critical nucleus. In *Figure 1*, the former is indicated by an open circle at $N=N_p$ and the latter by a filled circle at $N=N^*$.

The previous theories[5,6,10] clearly correspond to the special case $\Delta E_m=\Delta E=$constant. In this case, N_p becomes equal to N^* and equation (10) becomes

$$j=\eta_0(kT/h)\exp[-\{G^*/kT+\Delta E/k(T-T_g)\}]P_s \quad (12)$$

which agrees, of course, with the formula given in the previous theories[5,6,10]. Therefore, in this work j can be regarded as a more generalized nucleation rate than the j in the previous theories.

NUCLEATION RATE *j* OF POLYMER SYSTEM

End surface free energy σ_e

Here we will consider the same monolayer nucleus as is given in UI. *Figure 2a* shows a schematic nucleus with n stems, each of which contains l repeating units. l is an average number. We will call l (averaged) stem length. Both a fold and cilia may be seen on the uneven end surface. *Figure 2b* shows a more simplified schematic nucleus. It should be more general to consider that the end surface of the nucleus is uneven and fluctuated, i.e. the position of the folds can always slide and fluctuate. This fluctuation effect must give an entropic effect to the free energy of the system. Therefore, the entropic effect should be included in the end surface free energy σ_e, which is shown in Appendix 1. Equation (A10) in Appendix 1 shows that σ_e can be written as a function of side surface free energy σ:

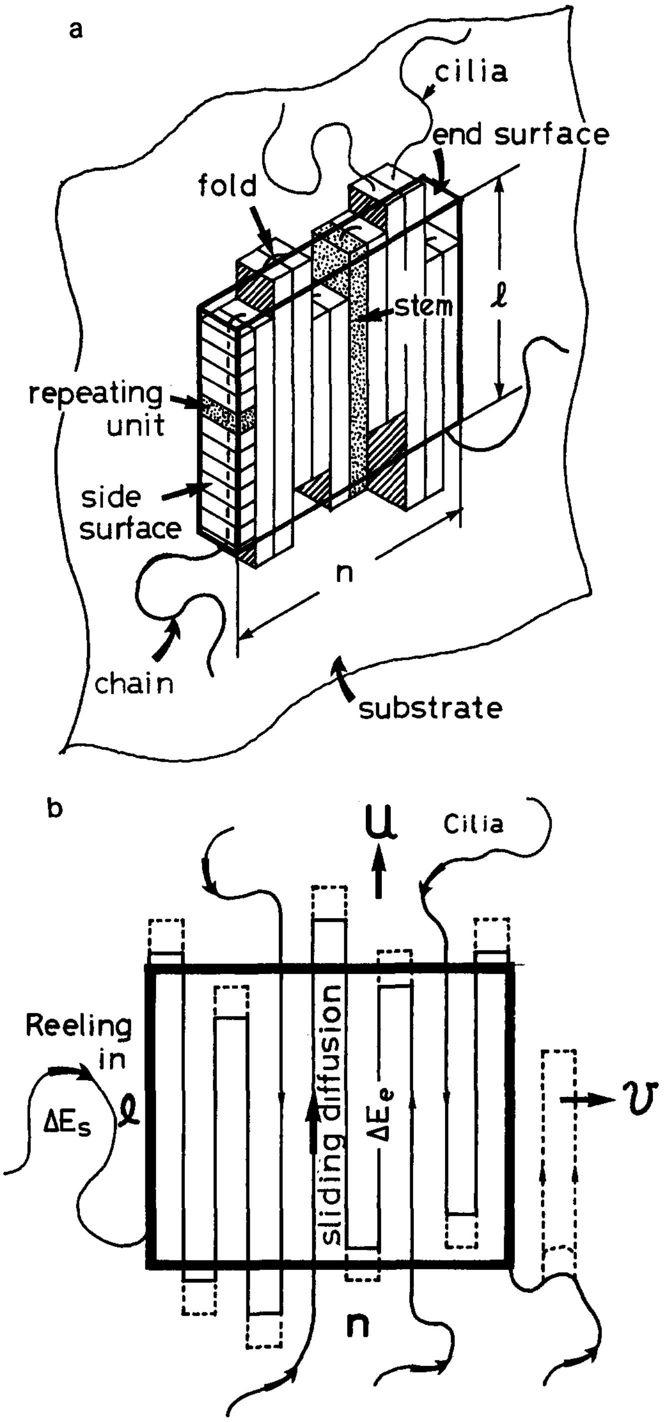

Figure 2 Monolayer nucleus with uneven end surface: (a) definition of terms; (b) definition of ΔE_e and ΔE_s, the activation free energies for chain sliding diffusion within a nucleus and for reeling from the melt or the solution, respectively. U and v are the growth rates parallel and normal to the stem axis, respectively

$$\sigma_e=1/2\{E_f-kT\ln(2kT/\sigma)\} \quad (13a)$$

where E_f is the excess free energy per fold given by

$$E_f=q+2ab(\sigma/bc) \quad (13b)$$

with q the fold energy per fold and a, b and c lattice parameters. Note that σ_e and σ are no longer independent parameters. Equation (13a) is an improved formulation of equation (4.5) in Reference 3.

Here we will use the same equation for G_m as UI equations (18) and (16).

Growth paths of a nucleus

The nucleus tends, in general, to grow two-dimensionally, as discussed in UI, due to the thermodynamic driving force. For two-dimensional growth, l has to increase. Here we will call this nuclear thickening or thickening of a nucleus, which is just an analogy of the well known lamellar thickening. A more detailed relation between the two will be shown below.

To describe two-dimensional growth, we will use the same growth path in (l, n) phase space (*Figure 3a*) as is given in UI,

$$l = A'n^{\chi(\omega)} \tag{14}$$

where A' is a constant given from UI relation (21), and χ is a parameter related to the path parameter ω as follows:

$$\chi(\omega) = \begin{cases} \omega + 1 & -1 < \omega \leqslant 0 \\ 1/1 - \omega & 0 < \omega < 1 \end{cases} \tag{15a}$$

Equation (15a) is the same as UI equation (24). From equations (14) and (15a),

$$l = \begin{cases} A'n^{\omega+1} & -1 < \omega \leqslant 0 \\ A'n^{1/1-\omega} & 0 < \omega < 1 \end{cases} \tag{15b}$$

Some examples of growth paths are shown in *Figure 3a*. Path 1, where $\omega \simeq 0$, represents typical two-dimensional growth and will give the formation of ECC. Path 2, where $\omega \simeq -1$, represents typical one-dimensional growth and will give the formation of FCC. Thus expression (14) is suitable to describe two-dimensional growth. The paths assumed in theories by LH and FT and by Point[11], which are shown in *Figure 3b*, are, on the contrary, limited to describing one-dimensional growth and cannot describe any two-dimensional growth.

UI showed that $\omega \simeq 0$ for disordered crystals and ω decreases to -1 with increasing order of the crystals. The same results will be shown in the latter part of this paper.

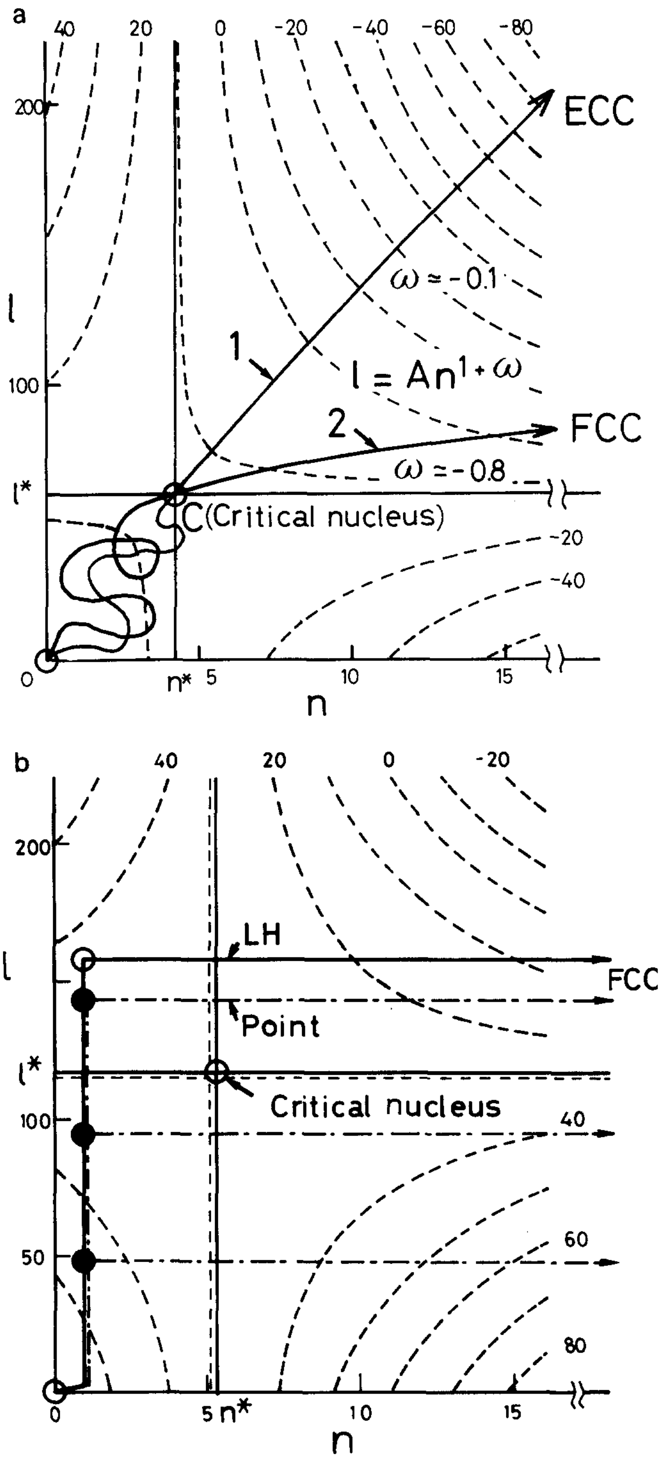

Figure 3 Growth paths of a nucleus in (l, n) phase space. ---, Contour lines of G_m. (a) Paths from this work. 1 and 2 indicate two- and one-dimensional growth, which will give formation of ECC and FCC, respectively. (b) Paths from the theories by LH and FT and by Point[11] for FCC

Averaged activation energy for diffusion ΔE_m

A nucleus grows two-dimensionally through two kinds of diffusion of chains (see *Figure 2b*) as has been discussed in UI. One is related to the 'reeling in' of a chain from the melt or the solution, which is important in increase of n. The other is related to the 'sliding diffusion' of a chain within the growing nucleus, which is important in increase of l. The activation free energies for the two types of diffusion are denoted as $\Delta E_{s,m}$ and $\Delta E_{e,m}$, respectively. $\Delta E_{s,m}$ is usually smaller than $\Delta E_{e,m}$ (see UI equation (3)). We will assume the same relation as UI equation (6) (see *Figure 4*),

$$\Delta E_{e,m} = \kappa l_{e,m}, \qquad l_{e,m} = l_m^{\nu} \tag{16}$$

where κ is a kind of friction energy per repeating unit caused by interchain friction, $l_{e,m}$ is an effective chain length for the sliding diffusion at the mth stage, l_m is the stem length at the mth stage and ν is a positive exponent which determines the l_e. $l_{e,m}$ should be shorter than l_m because there may be some point defect along a chain as shown in *Figure 4*. Therefore ν should be positive and smaller than one. Both κ and ν are increasing functions of the degree of order of the crystal. Here we will assume, as assumed in UI, that

$$\kappa \simeq \nu \tag{17}$$

They will be simply written as (κ, ν). In this paper, kT_m per repeating unit is taken as the unit of κ.

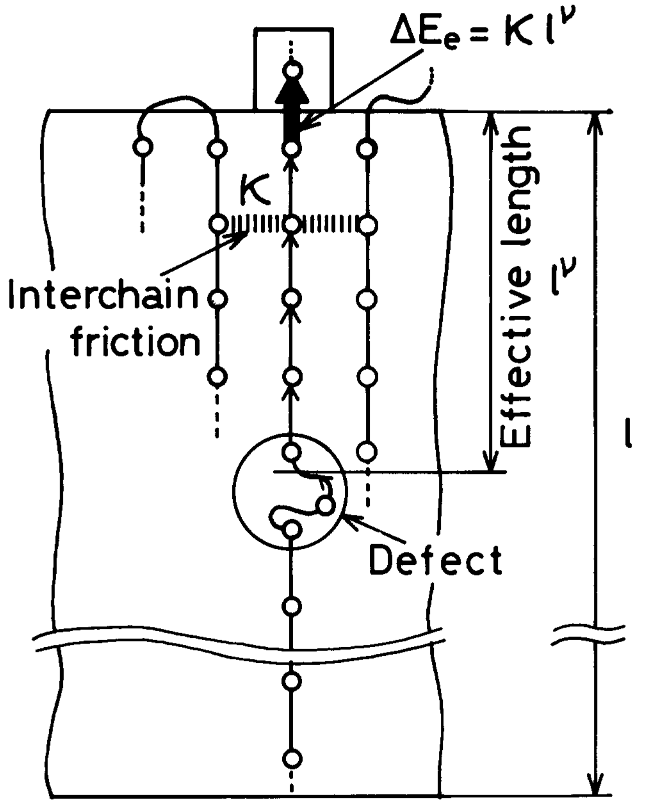

Figure 4 Definition of ΔE_e, activation energy for chain sliding diffusion within a crystal (nucleus or lamella)

The definition of the average of $\Delta E_{s,m}$ and $\Delta E_{e,m}$, ΔE_m, given by UI equation (2) is too simple. $\Delta E_{e,m}$ and $\Delta E_{s,m}$ are mixed in our sequential process. In the kinetic process, $\exp\{\Delta E_{e,m}/k(T-T_g)\}$ and $\exp\{\Delta E_{s,m}/k(T-T_g)\}$ indicate the difficulty of passing through the respective activation barriers. If $\exp\{\Delta E_{e,m}/k(T-T_g)\} \gg \exp\{\Delta E_{s,m}/k(T-T_g)\}$, then $\exp\{\Delta E_m/k(T-T_g)\}$ should be mainly determined only by $\exp\{\Delta E_{e,m}/k(T-T_g)\}$, while the reverse should be true. This is very characteristic of such a kinetic process. Therefore the 'kinetic average' of ΔE_m should be defined as

$$\exp\{\Delta E_m/k(T-T_g)\} = p\,\exp\{\Delta E_{e,m}/k(T-T_g)\} + (1-p)\exp\{\Delta E_{s,m}k/(T-T_g)\} \tag{18}$$

where p is the probability of finding a repeating unit on the end surface, which may be related to chain sliding diffusion. The physical meaning of p defined by UI equation (23) is not clear. Here we will redefine p by noticing its meaning mentioned above. From equation (A17) in Appendix 2, we have

$$p = \begin{cases} \{1+1/(\omega+1)\}^{-1} & -1<\omega\leqslant 0 \\ (2-\omega)^{-1} & 0<\omega<1 \end{cases} \tag{19}$$

Thus, ΔE_m is obtained from equations (18) and (19).

In this paper, the parameter sets I and II listed in *Tables 1* and *2* are used. Parameters in *Table 1* were obtained from our new analysis on normal growth rate and lamellar thickness of PE shown in the succeeding paper[12] (referred to as UIII). In UIII, it is shown that parameter sets I and II correspond to parameters for FCC at atmospheric pressure and parameters for ECC under high pressure (0.3 GPa) of PE, respectively.

ΔE_m is shown in *Figure 5* as a function of N_m. When (κ, ν) is large, as shown in *Figure 5a*, i.e. for set I in *Table 1*, ΔE_m increases rapidly to several tens of kT for $\omega \simeq 0$, but it remains small (less than a few kT) when $\omega \simeq -1$. This suggests that thickening of a nucleus is possible only for the latter case and nearly impossible for the former. If (κ, ν) is small, as shown in *Figure 5b*, i.e. for set II in *Table 1*, it of course remains small for almost any ω. This suggests that a nucleus can thicken for almost any ω.

Sequential process

Here we will regard G_m/kT and $\{G_m/kT + \Delta E_m/k(T-T_g)\}$ as continuous functions of m. Then the sequential process in *Figure 1* can be regarded as composed of two continuous curves. The simplified sequential processes

Table 1 Parameters obtained from analysis of the dependence on the degree of supercooling ΔT of l and normal growth rate V for FCC and ECC of PE[12]

	Set I (FCC at 0.1 MPa)	Set II (ECC at 0.3 GPa)
σ ($10^{-3}\,\mathrm{J\,m^{-2}}$)	10.9	3.3
$\sigma_e{}^a$ ($10^{-3}\,\mathrm{J\,m^{-2}}$)	43.9	6.3
κ (kT_m per repeating unit)	0.66	0.35

^{a}Calculated from Equation (13)

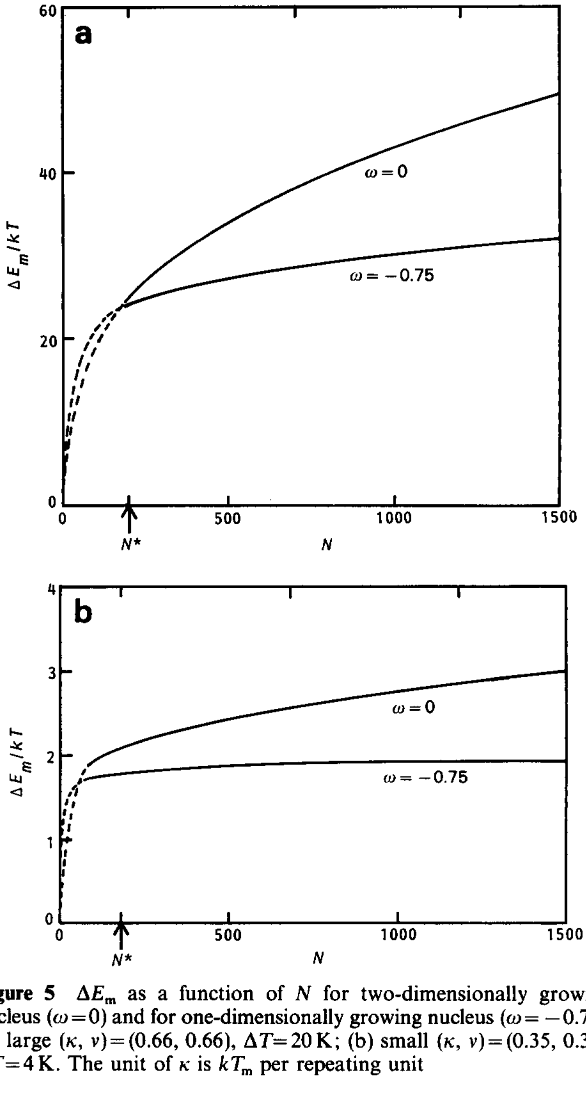

Figure 5 ΔE_m as a function of N for two-dimensionally growing nucleus ($\omega = 0$) and for one-dimensionally growing nucleus ($\omega = -0.75$): (a) large $(\kappa, \nu) = (0.66, 0.66)$, $\Delta T = 20$ K; (b) small $(\kappa, \nu) = (0.35, 0.35)$, $\Delta T = 4$ K. The unit of κ is kT_m per repeating unit

Table 2 Lattice constants and thermodynamic parameters for FCC and ECC of PE

	Set I (FCC at 0.1 MPa)	Set II (ECC at 0.3 GPa)
a $(10^{-10}\,\mathrm{m})$	4.55^{13}	$^{a}4.25^{15}$
b $(10^{-10}\,\mathrm{m})$	4.15^{13}	$^{a}4.90^{15}$
c $(10^{-10}\,\mathrm{m})$	1.274^{14}	1.215^{16}
T_m (K)	418^{13}	503^{17}
T_g (K)	250^{18}	250 (assumed)
Δg^b $(10^5\,\mathrm{J\,m^{-3}})$	$6.48\,\Delta T^{13}$	$3.23\,\Delta T^{13,19}$
q^c $(10^{-20}\,\mathrm{J}$ per fold)	2.97×10^{20}	

^{a} Orthoganol–hexagonal lattice was taken
^{b} Free energy of fusion calculated by LH equation $(28)^{10}$
^{c} (110) plane was taken

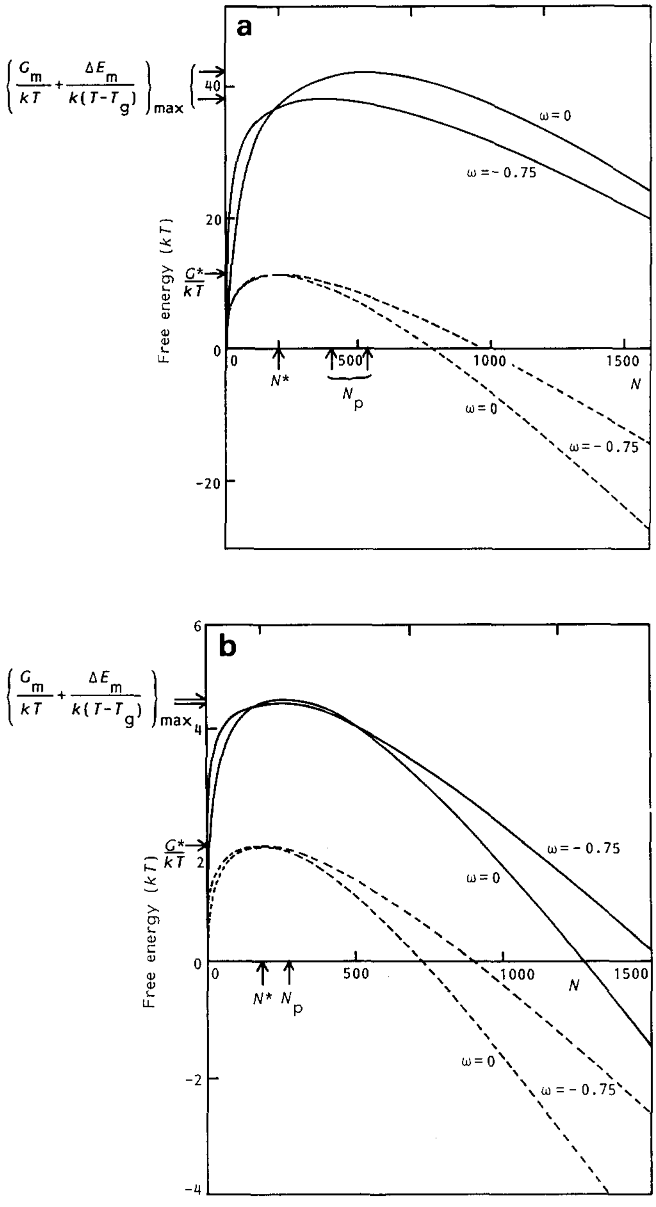

Figure 6 Simplified sequential processes: ---, G_m/kT; ——, $\{(G_m/kT)+[\Delta E_m/k(T-T_g)]\}/k(T-T_g)$. (a) Large ΔE_m, i.e. $(\kappa, \nu)=(0.66, 0.66)$, $\Delta T=20$ K. (b) Small ΔE_m, i.e. $(\kappa, \nu)=(0.35, 0.35)$, $\Delta T=4$ K

are illustrated in *Figure 6*. In *Figures 6a* and *b* parameter sets I and II in *Tables 1* and *2* are used, respectively.

Note first that in both *Figures 6a* and *b* the thermodynamic curve G_m itself showed the similar behaviour. G_m decreases faster with m (for $m>1$) for two-dimensional ECC type growth (where $\omega \simeq$ zero) than it does for one-dimensional FCC type growth (where ω is small enough, $\simeq -1$). This suggests that, from the thermodynamic viewpoint, ECC type growth will be preferred over FCC type growth.

Figure 6a shows a typical sequential process for large (κ, ν) where chain sliding is difficult. For two-dimensional growth (where $\omega \simeq 0$), the kinetic barrier of ΔE_m rapidly becomes large with increasing m (see *Figure 5a*), so $\{G_m/kT+\Delta E_m/k(T-T_g)\}$ becomes much larger with m than it does for one-dimensional growth (where $\omega \simeq -1$). Therefore the latter type growth will become favoured. This suggests that when chain sliding diffusion is difficult, one-dimensional FCC type growth (corresponding to $\omega \simeq -1$) will occur.

Figure 6b shows another typical sequential process for small (κ, ν) where chain sliding diffusion is easy. As ΔE_m always remains small and constant (*Figure 5b*) for any ω, $\{G_m/kT+\Delta E_m/k(T-T_g)\}$ is mainly determined by the thermodynamic factor G_m/kT. This suggests that when chain sliding diffusion is easy, two-dimensional type growth, i.e. ECC type growth (where $\omega \simeq 0$), will become dominant.

In the next section, these suggestions will be confirmed by calculation of j.

ORIGIN OF FCC AND ECC

(κ, ν) *dependence of* j

Let us confirm the suggestions in the previous section by calculating j given in equation (10). *Figure 7* shows $\exp[-\{G_m/kT+\Delta E_m/k(T-T_g)\}_{\max}]$, P_s and j as a function of ω or l/l^*, where l^* is l for a critical nucleus. The maximum value of N, $N_{\max}$, does not greatly affect the result if it is sufficiently large. It is sufficient for us to assume that

$$N_{\max}/N^*=200 \tag{20}$$

Figure 7a is for the typical parameter set I in *Tables 1* and *2* where (κ, ν) is large (0.66, 0.66). In this case, $\Delta E_{e,m}$ becomes large and chain sliding diffusion within the solid becomes difficult. *Figure 7a* indicates that $\exp[-\{G_m/kT+\Delta E_m/k(T-T_g)\}_{\max}]$ decreases to zero very swiftly with increase of ω. P_s, on the other hand, increases rapidly from zero and then shows a broad maximum with increase of ω. As a result, j, which is the product of P_s and the exponential function, shows a very sharp maximum at $\omega \simeq -1$, which indicates one-dimensional FCC type growth of a nucleus.

Figure 7b is for small (κ, ν), (0.35, 0.35). It is drawn by using parameter set II in *Tables 1* and *2*. In this case, $\Delta E_{e,m}$ becomes small and chain sliding diffusion within the solid becomes easy. The figure shows that $\exp[-\{G_m/kT+\Delta E_m/k(T-T_g)\}_{\max}]$ remains nearly constant for most of the range of ω, i.e. $-1<\omega<0.5$, while P_s increases swiftly from zero and then shows a broad maximum at $\omega \simeq 0$. Therefore, j shows a broad maximum at $\omega \simeq 0$, which indicates two-dimensional ECC type growth of a nucleus.

The nucleation rates j are summarized in *Figure 8* as a function of ω or l/l^* for large and small (κ, ν), i.e. large

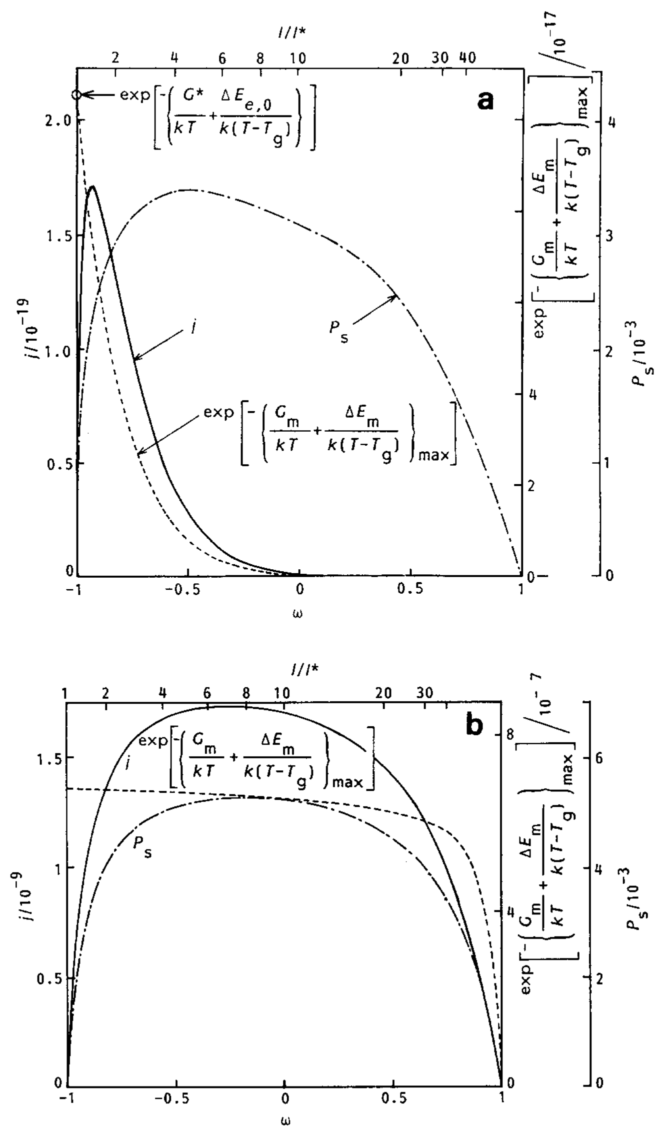

Figure 7 Plots of j, $\exp[-\{G_m/kT+\Delta E_m/k(T-T_g)\}_{max}]$ and P_s against ω or l/l^*: (a) large ΔE_m, i.e. $(\kappa, \nu)=(0.66, 0.66)$, where chain sliding diffusion is difficult, $\Delta T=20$ K; (b) small ΔE_m; i.e. $(\kappa, \nu)=(0.35, 0.35)$, where chain sliding diffusion is easy, $\Delta T=20$ K

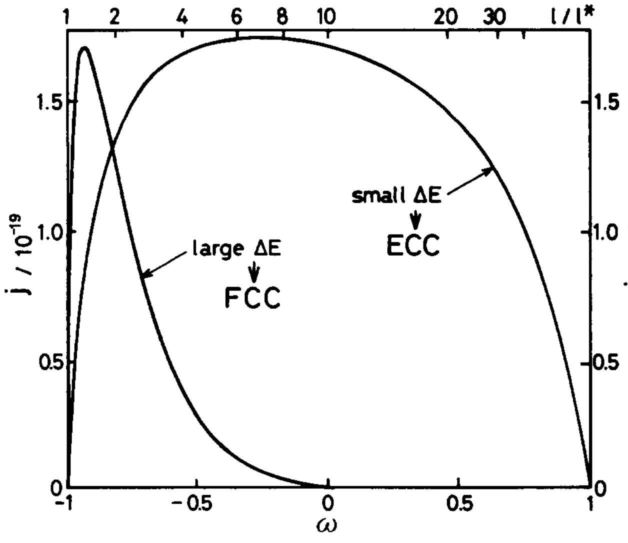

Figure 8 j *versus* ω for large and small ΔE, indicating the formation of FCC and ECC. Parameters are the same as in *Figure 7*

and small $\Delta E_{e,m}$. *Figure 8* shows a sharp maximum at $\omega \simeq -1$ and a broad maximum at $\omega \simeq 0$, which indicate FCC and ECC type growth of a nucleus, respectively.

It will be shown in the next section that the two- (one-) dimensional ECC (FCC) type growth of a nucleus can be regarded as the formation of ECC (FCC). Therefore, *Figure 8* can be considered to indicate typical conditions for formation of ECC and FCC.

Thus it can be concluded that, when chain sliding diffusion is difficult, FCC will be formed, whereas, when it is easy, ECC will be formed. This confirms the suggestion in the previous section. *Figure 8* corresponds to UI Figure 7 and FT Figure 1.

Correspondence of nuclear thickening and lamellar thickening

Both this paper and UI stress that a nucleus tends to thicken and grow two-dimensionally due to the thermodynamic driving force, which has been shown above by using the kinetic theory.

From the thermodynamic viewpoint, lamellae should also tend to thicken and grow three-dimensionally. In the lamellar thickening, chain sliding diffusion along the chain axis within a lamella should play an important role, which is essentially the same as the thickening of a nucleus.

Therefore, it is natural to conclude that nuclear thickening and lamellar thickening should correspond directly, i.e., when a nucleus can thicken easily, a lamella can also thicken easily, while, when a nucleus cannot thicken easily, a lamella cannot thicken so easily. In the former case, nucleus and lamella will grow two- and three-dimensionally, respectively, which will finally give rise to the formation of ECC. In the latter case, they will grow only one- and two-dimensionally, respectively, which will only result in the formation of FCC.

This is illustrated in *Figure 9*. When $\Delta E_{e,m}$ is small, a thin FCC type nucleus and lamella (*Figure 9a*) will thicken and finally grow into a large thick ECC type nucleus and lamella (*Figure 9c*). When $\Delta E_{e,m}$ is large, the nucleus and lamella cannot thicken and can only grow into a big thin FCC type nucleus and lamella (*Figure 9b*).

Thus, we reach the important conclusion that there should be no essential difference betwen FCC and ECC in the formation mechanism. This conclusion has recently been confirmed by our experimental results for PE showing that FCC lamella thicken into ECC lamella by remarkable lamellar thickening via chain sliding diffusion[7].

Thus it is sufficient in this paper to clarify conditions for two- (one-) dimensional growth of a nucleus to clarify the conditions of formation of ECC (FCC). Therefore, in this paper, we will regard the growth of a two- (one-) dimensional nucleus as the formation of ECC (FCC).

Transition from ECC to FCC with increase of (κ, ν)

We can estimate the average of ω by UI equation (27)

$$\langle\omega\rangle = \int \omega j \mathrm{d}\omega \Big/ \int j \mathrm{d}\omega \qquad (21)$$

$\langle\omega\rangle$ is plotted in *Figure 10* as a function of (κ, ν), which corresponds to UI Figure 8. From the conclusion in the previous section, *Figure 10* can be considered to indicate a drastic transition from ECC to FCC with increase of (κ, ν). The transition point is seen at $(\kappa, \nu)=(0.57, 0.57)$,

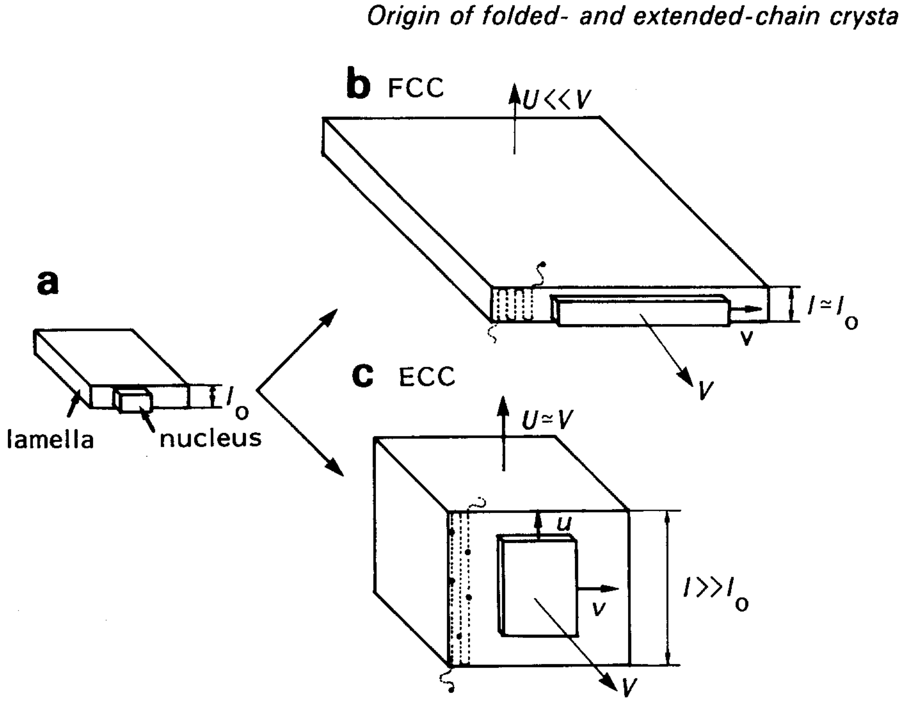

Figure 9 Model for formation of FCC and ECC: o----o, chain. (a) Initial FCC type lamella and nucleus. (b) FCC type growth for large ΔE where chain sliding diffusion is difficult and the lamellar thickening rate U is much smaller than the lateral growth rate v. (c) ECC type growth for small ΔE where chain sliding diffusion is easy and U is comparable to v

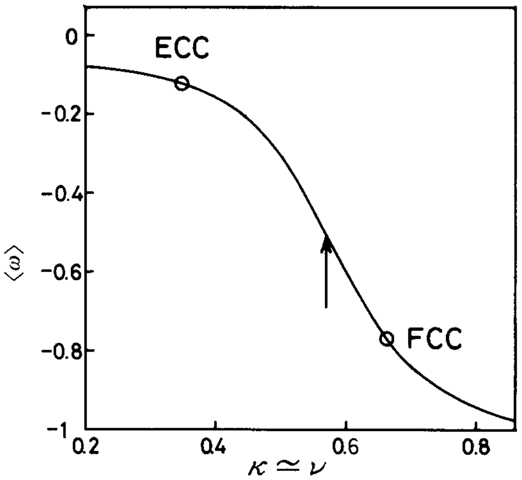

Figure 10 Transition from ECC to FCC shown by a plot of $\langle\omega\rangle$ against (κ, ν). Arrow indicates transition point. Parameter sets I and II are used, except for ω

which is smaller than the value shown in UI (0.7, 0.7). This indicates that ECC will be obtained for $(\kappa, \nu) \simeq (0.35, 0.35)$ and FCC will be obtained for $(\kappa, \nu) \simeq (0.66, 0.66)$. This result is more natural and reasonable than the results in UI, (0, 0) and (1, 1), respectively, which were too small and too large, respectively. The differences come from the improvement in the average of ΔE_m given by equation (18) and the definition of p given by equation (19) in this work.

Origin of FCC and ECC

Let us now determine the dominant factor in the formation of FCC and ECC. In *Figure 8*, j showed a sharp maximum for FCC and a broad maximum for ECC. We showed earlier that this remarkable difference in j is mainly determined by the difference in $\exp[-\{G_m/kT+\Delta E_m/k(T-T_g)\}_{\max}]$, the probability of passing through the actual maximum barrier of formation of a nucleus. This is because, as shown in *Figure 7*, this term shows a fast decrease for FCC and is nearly constant for ECC with increase of ω, while $P_s(\omega)$ shows similar broad distribution for FCC and ECC.

The probability $\exp[-\{G_m/kT+\Delta E_m/k(T-T_g)\}_{\max}]$ contains two competing factors, the thermodynamic factor, G_m, and the kinetic factor, ΔE_m. It is obvious from the discussion above that, when $\Delta E_{e,m}$ becomes large, the kinetic factor becomes dominant and, when it becomes small, the thermodynamic factor becomes dominant. Therefore we conclude, as in UI, that, when ΔE_m is small, the thermodynamic factor G_m will become dominant and ECC will be formed by the thermodynamic driving force, whereas, when the kinetic factor ΔE_m is large and dominant, FCC will be formed.

Thus we conclude that the origin of ECC and FCC is mainly related to the ease or difficulty of chain sliding diffusion within crystals (nucleus or lamella).

Lamellar thickening rate U

Note that the nucleation rate j given by equation (9) or (10) is a net flow of the generalized sequential process. Therefore it can be applied to any kinetic problem. It is applicable, of course, to formulating the lamellar thickening rate U. We have recently applied it[21] and succeeded in explaining the remarkable discrete integral lamellar thickening observed recently by Barham and Keller on isothermal crystallization from the melt on PE[22].

Prediction for formation of ECC and FCC

It is obvious, as is discussed in UI, that chain sliding diffusion is easy in a disordered crystallographic phase such as the hexagonal form (including the pseudo-hexagonal form) and difficult in an ordered phase such as the orthorhombic form, or the monoclinic or triclinic forms.

By coupling this with the conclusion on the origin of ECC and FCC reached above, we predict that ECC will be formed by lamellar thickening via chain sliding diffusion when polymers crystallize into a disordered phase of hexagonal form and that FCC will be formed when they crystallize into an ordered phase such as orthorhombic or monoclinic where lamellar thickening is difficult. This prediction is essentially similar to Bassett and Piermarini's suggestion[9].

We predict more generally that lamellae of any polymer will tend to thicken due to the thermodynamic driving force if chains can slide to some extent within the solid. We also predict that some polymers which crystallize from the melt into the hexagonal form will show a continuous change from FCC to ECC just with a change in crystallization temperature. This prediction has recently been confirmed experimentally on polychlorotrifluoroethylene and poly(1,4 transbutadiene)[23], which supports the conclusion reached above that there should be no essential difference between FCC and ECC.

Comparison with previous theories

The formulation of j obtained in this work, equation (10), is apparently similar to that given in the theories of LH and FT. But there is an essential difference between them in the physical meaning of the activation energy for diffusion, ΔE. In both LH theory and FT theory, ΔE indicates activation energy for diffusion of chains within the melt or solution, which is denoted in this theory by $\Delta E_{s,m}$. It is usually much smaller than G^*. In this work, on the other hand, ΔE given by equation (18) contains both $\Delta E_{s,m}$ and the topological effect of chain sliding diffusion within the solid (nucleus and lamella), $\Delta E_{e,m}$. This work and UI showed that the latter plays an essential role in the formation mechanism of FCC and ECC. The topological nature of the linear polymer chain is well known to play an important part in some problems in polymer science, but it has not been taken into account in any kinetic theory of nucleation before UI and this work.

Turnbull and Fisher classified ΔE into two types of activation energy for diffusion, one across the phase boundary and another within the solid solution, when the transformation involves the separation of a phase having a different composition[3]. $\Delta E_{s,m}$ corresponds to the former in their theory. $\Delta E_{e,m}$ in this theory corresponds to the latter, because neither term is the activation energy for diffusion across the phase boundary. Both terms represent the activation energy within a crystal (solid solution, lamella or nucleus).

The famous previous polymer crystallization theories, LH and FT theories, agree roughly (not quantitatively, only qualitatively) with the present theory when σ is large and chain sliding diffusion is difficult, because in this case, the effect of fluctuation of the system will become small and a nucleus will grow only one-dimensionally. The resemblance between the theories is shown by equation (12) in this work as a special case.

But the assumptions in their theories, attaching of the first stem as the first step of a secondary nucleus and its one-dimensional growth, do not seem to be natural. The generation of a two-dimensional critical nucleus by thermal fluctuation and further two-dimensional growth due to the thermodynamic driving force may become more natural, especially when σ is small and chain sliding diffusion is easy, as in the hexagonal form, as has been discussed in UI and in this work.

Point introduced the idea of the opportunity for a molecule (here the first stem was assumed) to fold back at the end of every stage. The possibility of fold back was shown to increase with increasing stem length, by which mechanism the so called δl catastrophe was avoided[11]. This effect is essentially a kinetic one. UI also succeeded in avoiding the δl catastrophe by introducing a kinetic effect of chain sliding diffusion within crystals. Both kinetic effects are similar in that they prohibit infinite increase of l at any crystallization temperature, which should be taken into polymer crystallization theory.

We first stressed in Reference 2 the important effect of fluctuation of a nucleus which is caused by chain sliding motion within the nucleus and formulated its effect by equation (4.2) in Reference 2. UI again stressed the important effect of the fluctuation of a nucleus in polymer crystallization. The present work also showed the importance of fluctuation in the formulation of σ_e (equation (13)), which indicates that fluctuation becomes more important when σ becomes smaller but is not so important for large σ. This result for large σ agrees with the conclusion of Hoffman *et al.* that the effect of the roughness of the end surface on the 'effective' or 'kinetic' end surface free energy, $\sigma_{e(k)}$, is small for large σ[24].

Sadler also stressed the importance of fluctuation and proposed an entropic barrier to crystal growth[25]. Although some essential differences exist between our theory and Sadler's, i.e. the former is based on a nucleation theory and the latter is not, both theories have a similar viewpoint on the importance of fluctuation, which needs to be studied further in future to clarify polymer crystallization kinetics.

SUMMARY AND CONCLUSION

A simple formula was derived for the generalized nucleation rate j for a linear sequential process:

$$j=\eta_0\left(\frac{kT}{h}\right)\left[\sum_{m=0}^{\infty}\exp\left\{\frac{G_m}{kT}+\frac{\Delta E_m}{k(T-T_g)}\right\}\right]^{-1}$$

It was shown that j is determined by two competing factors, a thermodynamic factor G_m and a kinetic factor ΔE_m.

The nucleation rate j was rewritten as

$$j=\eta_0(kT/h)\exp[-\{G_m/kT+\Delta E_m/k(T-T_g)\}_{\max}]P_s$$

This illustrates the simple physical interpretation that j is given by a product of two probabilities, the probability of passing through the maximum activation barrier of formation of a nucleus, $\exp[-\{G_m/kT+\Delta E_m/k(T-T_g)\}_{\max}]$, and the survival probability of the nucleus, P_s.

The free energy for the uneven end surface was derived:

$$\sigma_e=1/2\{E_f-kT\ln(2kT/\sigma)\}$$

This indicates that the entropic effect due to fluctuation of the fold position becomes important when the side surface free energy σ becomes small.

The topological nature of linear chains was taken into our theory by introducing the activation energy for sliding diffusion of chains within a crystal (nucleus or lamella), $\Delta E_{e,m}$. This nature was revealed to be the most essential factor in the formation mechanism of ECC and FCC.

The origin of ECC and FCC was shown to be related to the ease or difficulty of chain sliding diffusion within a crystal (nucleus or lamella). It was shown that, when chain sliding diffusion within a crystal is easy, both nucleus and lamella will easily thicken and grow two- and three-dimensionally, respectively, which will result in formation of ECC. When chain sliding diffusion is difficult, nucleus and lamella cannot easily thicken and thus they grow only one- and two-dimensionally, which will result in formation of FCC.

It was concluded that there should not be any essential difference between FCC and ECC in their formation mechanism.

It was predicted that, when polymers crystallize into a disordered phase of hexagonal (or pseudo-hexagonal) form, ECC will be formed by lamellar thickening via chain sliding diffusion, and that FCC will be formed when they crystallize into an ordered phase such as orthorhombic, or monoclinic where lamellar thickening is difficult. This prediction is essentially similar to Bassett and Piermarini's suggestion[9].

It was also predicted that lamella of any polymer will tend to thicken if chains can slide to some extent within the crystal. Therefore, some polymers which crystallize from the melt into the hexagonal form will show a continuous change from FCC to ECC just with a change in crystallization temperature.

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APPENDIX 1 σ_e FOR UNEVEN END SURFACE

Let us consider the nucleus shown in *Figure 2b* where the end surface is uneven. Here we will fix both the stem number n and its averaged stem length l. Each stem length l_i can vary (fluctuate) under the boundary condition

$$\sum_{i=1}^{n} l_i = nl = N \qquad \text{(A1)}$$

where i is the number of the stem within a nucleus. Here we will simply denote G_m by $G(N)$. $G(N)$ is given by

$$G(N) = -\ln Z(N) \qquad \text{(A2)}$$

where $Z(N)$ is a partition function defined by

$$Z(N) = \sum_{l}\sum_{\{l_i\}} \exp[-E_{N,l}(\{l_i\})/kT] \qquad \text{(A3)}$$

where $E_{N,i}(\{l_i\})$ is the energy of formation for a nucleus with a set of stems $\{l_i\}$. $\{l_i\}$ indicates a microscopic state with a set of stems with lengths $l_1, l_2, \ldots, l_i, \ldots, l_n$. Here we will divide $E_{N,i}(\{l_i\})$ into two terms:

$$E_{N,l}(\{l_i\}) = E_{\mathrm{N}}^{0}(l) + \delta E_{N,i}(\{l_i)\} \qquad \text{(A4)}$$

where $E_{\mathrm{N}}^{0}(l)$ is the energy of a nucleus without unevenness and $\delta E_{N,i}(\{l_i\})$ is the excess energy caused by the unevenness. The former is given by

$$E_{\mathrm{N}}^{0}(l) = 2l\sigma + nE_{\mathrm{f}} - N\Delta g \qquad \text{(A5)}$$

where Δg is the free energy of fusion given in LH theory. Substitution of equation (A4) into (A3) gives

$$Z(N) = \sum_{l} \exp[-E_{N}^{0}(l)/kT] \sum_{\{l_i\}} \exp[-\delta E_{N,l}(\{l_i\})/kT] \qquad \text{(A6)}$$

If we assume that l_i varies independently, the second summation in (A6) can be approximated as follows:

$$\sum_{\{l_i\}} \exp[-\delta E_{N,l}(\{l_i\})/kT] \simeq \prod_{i=2}^{n-1} \sum_{\delta i_i = 0} \exp(-\sigma \delta l_i/kT)$$

$$\simeq (2kT/\sigma)^n \qquad \text{(A7)}$$

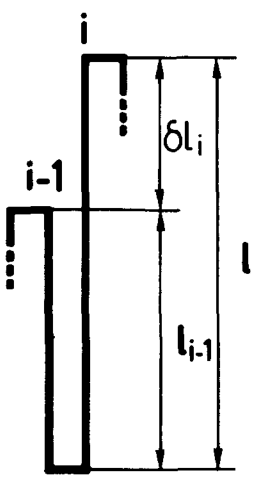

Figure 11 Definition of δl_i

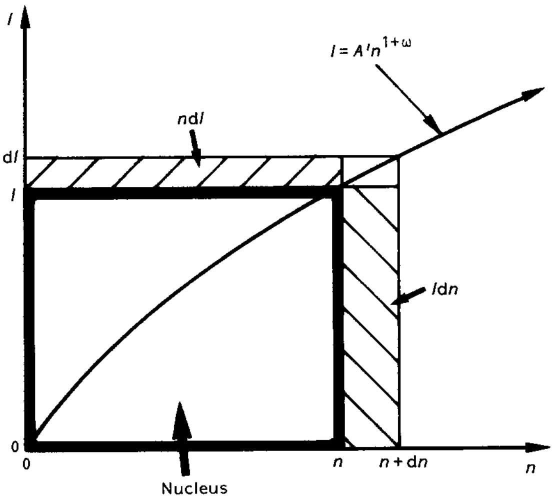

Figure 12 Growth of a nucleus along its growth path given by equation (15)

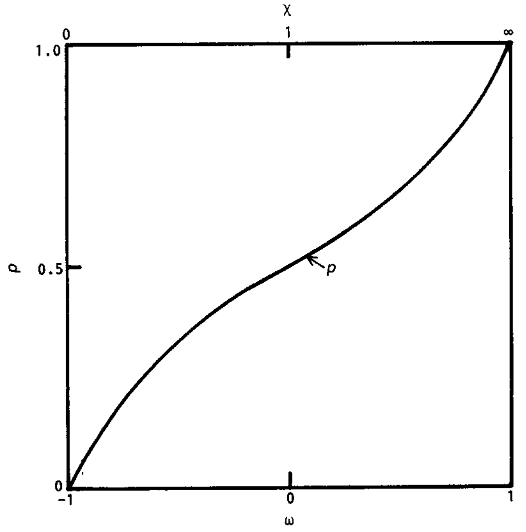

Figure 13 p as a function of ω or χ

where δl_i is defined by (see *Figure 11*)

$$\delta l_i = |l_i - l_{i-1}| \tag{A8}$$

Substitution of equation (A7) into (A6) and combination with equation (A5) gives

$$\begin{aligned} Z(N) &= \sum_l \exp[-E_N^0(l)/kT](2kT/\sigma)^n \\ &= \sum_l \exp[-\{2l\sigma + nE_f - nkT\ln(2kT/\sigma) - N\Delta g\}/kT] \end{aligned} \tag{A9}$$

Therefore we may define σ_e by the relation

$$\sigma_e = 1/2\{E_f - kT\ln(2kT/\sigma)\} \tag{A10}$$

This is a new formulation of σ_e for uneven end surface. Then $Z(N)$ becomes

$$Z(N) = \sum_l \exp[-E_N(l)/kT] \tag{A11}$$

where

$$E_N(l) = 2l\sigma + 2n\sigma_e + N\Delta g \tag{A12}$$

Equation (A12) is a popular formulation which corresponds to UI equation (16).

APPENDIX 2 DEFINITION AND DERIVATION OF p

Let us assume that a nucleus grows from size $ln = N$ to size $(l + \mathrm{d}l)(n + \mathrm{d}n) = (N + \mathrm{d}N)$, as illustrated in *Figure 12*, where $\mathrm{d}l$, $\mathrm{d}n$ and $\mathrm{d}N$ are the increases in l, n and N, respectively. The probability, p, of finding a repeating unit on the end surface is equal to the ratio of the increased number of the repeating unit on the end surface $n\mathrm{d}l$ to the total increased number $\mathrm{d}N$,

$$p = n\mathrm{d}l/\mathrm{d}N \tag{A13}$$

$\mathrm{d}N$ is approximately given by

$$\mathrm{d}N = l\mathrm{d}n + n\mathrm{d}l \tag{A14}$$

Substitution of equation (A14) into (A13) gives

$$p = 1/[1 + (l/n)(\mathrm{d}n/\mathrm{d}l)] \tag{A15}$$

From equation (14),

$$\mathrm{d}n/\mathrm{d}l = n/\chi(\omega)l \tag{A16}$$

Substitution of equations (A15) and (14) into (A16) gives

$$p = \begin{cases} [1 + 1/(\omega + 1)]^{-1} & -1 < \omega \leqslant 0 \\ [2 - \omega]^{-1} & 0 < \omega < 1 \end{cases} \tag{A17}$$

p is illustrated in *Figure 13* as a function of ω. The figure shows that p changes roughly linearly from zero to one when the path parameter ω varies from -1 to 1. p is kept constant, if ω is constant, during growth.