Unified theory of nucleation of folded-chain crystals and extended-chain crystals of linear-chain polymers

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A unified theory is presented to explain the growth of folded-chain crystals (FCC) and extended-chain crystals (ECC) of linear-chain polymers. It should be emphasized that a secondary nucleus tends to thicken and grow two-dimensionally, in a thermodynamic sense, through 'sliding diffusion' of a chain within a nucleus, but thickening is suppressed if the crystal is ordered because the activation barrier for sliding diffusion is high. The nucleation rate for this model is formulated by expanding Frank and Tosi's kinetic theory, by which a transition from ECC to FCC with increasing order of a crystal and the temperature dependence of the lamellar thickness of FCC are explained.

(Keywords: crystal growth kinetics; folded chain crystals; extended chain crystals; sliding diffusion; nucleation rate)

INTRODUCTION

It is well known that, in solid polymers, two different kinds of morphological texture are universally seen, named folded-chain crystals (FCC), first studied by Keller[1], and extended-chain crystals (ECC), first found by Wunderlich[2]. It has been an important and interesting problem in polymer physics why such different textures grow on changing the crystallization conditions.

Lauritzen and Hoffman[3] and Frank and Tosi[4] explained the crystallization temperature dependence of the lamellar thickness of FCC using theories (henceforth referred to as LH and FT) based on Turnbull and Fisher's kinetic theory[5]. The latter assumes that the process of attaching 'the first molecular stem' (including the first stem after the stem length alters only once) is longer than a 'critical length' for the substrate corresponding to 'the first stage' necessary for the maximum free energy to form a secondary nucleus. The theory also assumes that the length of the stem after 'the second stem' is the same as that of the first, which results in one-dimensional growth.

A problem has been pointed out for LH and FT theories, namely that the stem length diverges for a large value of the degree of supercooling ΔT, which is named the 'δl catastrophe'. Point[6] showed that this 'δl catastrophe' can be avoided by assuming that the occupation number of 'the first stem' of length l decreases with l, but the physical reason for this assumption has not been made clear.

Besides, three questions remain for these theories. The first is why the secondary nucleus does not grow by passing through a so-called 'saddle point', which is the lowest path of the free energy for forming a secondary nucleus. The second is why the length of the stem after the second is strongly forced to be the same as that of the first one. The third is why a whole nucleus is forbidden to thicken or grow two-dimensionally in spite of the thermodynamic prediction that such growth is more stable.

Bassett *et al.*[7] suggested on the basis of their thermal analysis and X-ray observations of polyethylene (PE) under high pressure that crystallization into the orthorhombic phase from the liquid gave the FCC texture and that into the hexagonal phase from the liquid gave the ECC texture.

Yamamoto *et al.*[8] showed by the X-ray method at high pressure that interchain coherence in the hexagonal crystal of PE is very weak compared with that in the orthorhombic crystal.

We observed the growth of ECC of PE under isobaric and isothermal conditions directly by optical microscopy and the X-ray method, and found that a slight cooling of PE melt under pressure yields lozenge-shaped extended-chain single crystals (ECSC) of the order of micrometres thick[9]. We also suggested from measurements of the growth rate normal to the sides of the plate-like crystal of ECSC that the rate-determining process is nucleation of a two-dimensional nucleus, which is often called the secondary nucleus[10].

We proposed a growth theory of ECSC[11] based on Bassett's suggestion, Yamamoto's observation and our observation. In the theory, the sliding diffusion of chain molecules within a nucleus (which may be very violent in the hexagonal phase) was shown to play an important role and the theory succeeded in explaining the observed growth rate.

It is the purpose of the present paper to expand our previous theory[11] in order to derive an expression for the nucleation rate of the two-dimensional secondary nucleus based on the kinetic theory given by Turnbull and Fisher[5] and in Frank and Tosi's theory, by considering the sliding diffusion of chain molecules within the nucleus.

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We shall explain why FCC and ECC are grown under their own crystallization conditions. We also answer the three questions with respect to growth of FCC mentioned above.

BASIC VIEWPOINTS FOR THIS PROBLEM

Thermodynamic stability of a nucleus

Here we treat crystal growth whose growth rate is mainly controlled by nucleation and growth of the secondary nucleus. We assume in this paper, for simplicity, that the nucleus is a monolayer type and grows on a sufficiently wide substrate.

It is considered that, under thermal equilibrium, the secondary nucleus grows so as to minimize the ratio of its excess surface area to its volume, which leads to 'two-dimensional growth'. It is also noted that this tendency is the basic driving force in determining the shape of a growing nucleus. Thus, the 'two-dimensional' nucleus is more stable thermodynamically than the 'one-dimensional' nucleus. It may be roughly considered that the former leads to 'ECC' type growth and the latter to 'FCC' type growth. Therefore, ECC type growth may be explained as growth under thermal (local) equilibrium. But FCC type growth cannot be explained using this consideration, and it must be explained by introducing some kinetic factors that suppress the thickening of the nucleus and lead to one-dimensional growth.

Local equilibrium of a small nucleus

It is reasonable to consider, even in FCC type growth, that, before a nucleus grows larger than a so-called critical nucleus, many microscopic states of the nucleus may be seen, which can be regarded as in local equilibrium. Therefore, in both types of growth, the generation of the critical nucleus should be treated on the assumption of local equilibrium, that is, a nucleus grows two-dimensionally through or near the so-called 'saddle point' on the free energy (for forming a nucleus) contour map.

Nucleation rate based on kinetic theory

As the nuclei grow, exceed their critical size and become larger and larger, the nuclei cannot always grow under thermal equilibrium, that is, they do not always take all their possible microscopic states. In this case, growth (containing both FCC and ECC type growth) should be treated generally by the kinetic theory given by Turnbull and Fisher[5] and in FT theory, and so we start from their kinetic theory.

It is considered that macroscopic crystals grow through nuclei for which the growth rate is larger than for many other types of nuclei. In considering crystal growth, the growth rate is mainly determined by the nucleation rate, and so the nucleus with the largest nucleation rate will be observed. Therefore, the question why the FCC or ECC texture is seen under given conditions of crystallization may be answered by finding factors that determine the nucleation rate.

Elementary process of growth

We will treat in this paper, as has been discussed in our previous paper[11], the elementary process of growth of the nucleus as the attaching or detaching of one repeating unit (for example, CH_2 in the case of PE) on the surface. This treatment is very different from the treatments in LH and FT theories, where the elementary process has been defined as the attaching or detaching of one stem.

We will assume, as has also been assumed in our previous paper[11], that the shape of a nucleus is rectangular, as illustrated in *Figure 1*, with n stems of mean length l, which are folded ciliated. Here l is defined as the number of repeating units. The end surface of the nucleus is considered uneven generally. The unevenness may be slight in FCC and may be great in ECC. The number of repeating units in the nucleus is

$$N = ln \tag{1}$$

This treatment implies that l (or n) increases by $1/n$ (or $1/l$) when one repeating unit attaches to the end (or side) surface of a nucleus.

Free energy of activation for sliding diffusion of chain molecules

In this paper, all free energies and energies are expressed in terms of unit thermal energy kT. The nucleation rate formulated by Turnbull and Fisher[5] and in FT theory contains the free energy of activation for diffusion of atoms or molecules, denoted ΔE. In this paper, we consider two types of ΔE for the polymer nucleus, which are needed to add one repeating unit on the side surface and on the end surface of a nucleus. If we denote them ΔE_s and ΔE_e, respectively, ΔE is written as

$$\Delta E = p\Delta E_e + (1-p)\Delta E_s \tag{2}$$

where p is the probability of attaching a repeating unit to the end surface.

ΔE_s for diffusion of one repeating unit from the liquid to the side surface of a nucleus may be given by the free energy of activation for 'reeling in' of a cilia chain. This has been estimated by Dimarzio *et al.*[12] and is much smaller than the thermal energy kT under the usual conditions of crystallization[12]:

$$\Delta E_s \ll 1(kT) \tag{3}$$

and so it is not so important in the expression for the nucleation rate.

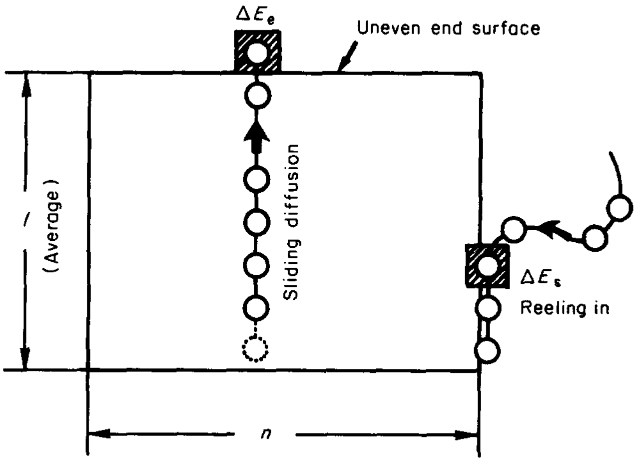

Figure 1 Model for the monolayer growth of a nucleus of a linear chain molecule. Here ΔE_e and ΔE_s are the free energies of activation for diffusion of a chain defined in the text

It is difficult, on the other hand, for a repeating unit of a new chain diffused from the liquid to the end surface to be included stably into the nucleus, for attachment to the end surface is not strong because of its wrong fitting compared with that to the side surface. Therefore, in thickening of the nucleus, most repeating units must diffuse from the inside of the nucleus to its end surface, and so ΔE_e may be given by the free energy of activation for 'sliding diffusion' of a chain within the nucleus. ΔE_e depends strongly on the situation of the nucleus, such as its lattice structure, its defect density, its chain conformation and so on.

When the crystal is close-packed and rather ordered, as in the case of orthorhombic phase of PE, ΔE_e may be given by the work to pull up the chain from the nucleus, overcoming the potential energy, which may be proportional to its 'friction constant κ' and thickness l and may be larger than $1(kT)$:

$$\Delta E_e = \kappa l > 1(kT) \tag{4}$$

Therefore, ΔE_e will become large with thickening of a nucleus and cannot be neglected in the expression for the nucleation rate, which will inhibit further thickening and the lamellae will thus grow into the FCC texture.

When the crystal is loose-packed and defect-rich, as in the case of the hexagonal phase of PE, the sliding of chains within a nucleus may be very easy, because very many point defects or dislocations continuously introduced in the nucleus will make sliding diffusion very easy. In this case, ΔE_e does not depend on l and

$$\Delta E_e \ll 1(kT) \tag{5}$$

Therefore, ΔE_e can be neglected in the expression for the nucleation rate and the nucleus can grow two-dimensionally under the local equilibrium condition, and will thus grow into the ECC texture.

In general, ΔE_e may be written

$$\Delta E_e = \kappa l^{\nu} \tag{6}$$

where ν is

$$0 < \nu \leq 1 \tag{7}$$

In this expression, κ and ν can be regarded as order parameters of the crystal, that is, κ and ν are large (small) when a crystal is ordered (disordered). Thus, ΔE is rewritten as

$$\Delta E = p\Delta E_e = p\kappa l^{\nu} \tag{8}$$

We will show in this work that ΔE is the kinetic factor that plays an essentially important role in determining the growing texture of polymers.

SEQUENTIAL PROCESS

Sequential process

We assume after FT theory that the nucleation process can be treated by a sequential process in which stages are indexed $i = 0, 1, \ldots, i, \ldots$. In this process, we will take the first stage $i = 1$ as the stage of forming the critical nucleus with n^* stems of mean length l^*, for which the free energy necessary for nucleus formation $G(N)$ takes the maximum value G^*:

$$G^* = G(N^*) = G(N)_{\max} \qquad \text{for } i = 1 \tag{9}$$

where $N^* = l^* n^*$.

As the elementary process of growth of the nucleus has been defined as the attaching or detaching of one repeating unit on the surface, stages $i = 2, 3, \ldots$ are taken as stages increasing the number of repeating units one by one. This sequential process is illustrated in *Figure 2*. The index i is combined with N by a relation

$$N = N^* + (i - 1) \tag{10}$$

The net flow j (which equals the nucleation rate) given by equation (13) in FT theory can be applied to our case and is

$$j = \frac{\alpha_0 \eta_0}{\sum\limits_{m=0}^{\infty} \prod\limits_{i=0}^{m} (\beta_i/\alpha_i)} \tag{11}$$

where η_0 is a constant and α_i and β_i are the forward and backward transition rates from the ith stage. In this paper, energy is expressed in units in which the thermal energy kT equals 1. We assume in this work that

$$\begin{aligned} \alpha_0 &= (1/h)\exp(-G^* - \Delta E_0) \\ \beta_1 &= (1/h)\exp(-\Delta E_0) \\ \alpha_i &= (1/h)\exp(-\Delta E_i) \qquad \text{for } i \geq 1 \\ \beta_i &= (1/h)\exp(-\Delta E_{i-1} - \Delta f_i) \qquad \text{for } i \geq 2 \end{aligned} \tag{12}$$

where h is Planck's constant and Δf_i is defined by

$$\Delta f_i = G(N_{i-1}) - G(N_i) \tag{13}$$

Here ΔE_i is the ΔE (defined earlier) necessary for transition from the ith stage to the $(i+1)$th stage, and β_0 is a dummy factor equal to α_0. It must be noted that Δf_i and ΔE_i are functions of i in this work, whereas they were constant in LH and FT theories.

Substitution of (12) into $\prod\limits_{i=0}^{m} (\beta_i/\alpha_i)$ gives

$$\begin{aligned} \sum_{i=0}^{m} (\beta_i/\alpha_i) &= 1, \qquad \text{for } m = 0 \text{ and } 1 \\ &= \exp(-\Delta E_0)\exp\left(\sum_{i=2}^{m} \Delta f_i + \Delta E_m\right), \\ &\qquad \text{for } m \geq 2 \end{aligned} \tag{14}$$

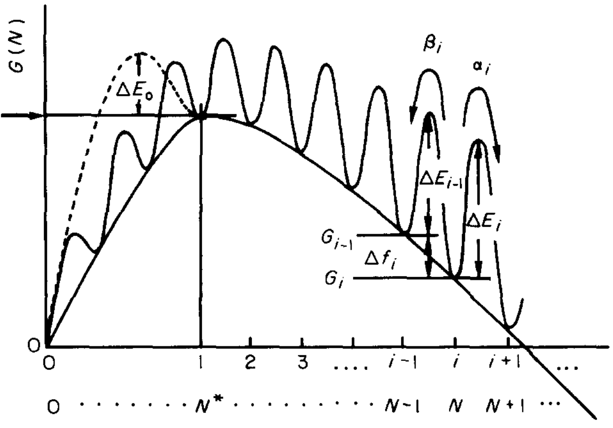

Figure 2 Reaction path of our sequential process. Here i and N are the number of the stage and the number of repeating units in a nucleus

Substituting (14) into (9) gives

$$j\approx\frac{\eta_0}{h}\,\frac{\exp(-G^*)}{\sum\limits_{m=2}^{\infty}\exp\left(-\sum\limits_{i=2}^{m}\Delta f_i+\Delta E_m\right)}\tag{15}$$

This is the basic expression for the nucleation rate j.

Free energy for formation of a nucleus $G(N)$

The energy of a nucleus of repeating number $N=ln$ is

$$E_N(l)=2(l+\gamma n)\sigma-N\Delta g\tag{16}$$

where σ is the side surface free energy, γ is the ratio of the end surface free energy σ_e and σ

$$\gamma=\sigma_e/\sigma\begin{cases}>1 & \text{for anisotropic}\\ =1 & \text{for isotropic}\end{cases}\tag{17}$$

and Δg is the free energy of fusion. In this paper, σ_e, σ and Δg are defined per repeating unit. Δg is given in LH theory and is in proportion to ΔT, and σ_e or γ has been shown to be related to the effect of unevenness of the end surface in our previous paper[11].

The free energy for formation of a nucleus $G(N)$ for the general case is given in Appendix I, but here we will assume for simplicity that $G(N)$ is approximated by

$$G(N)\simeq E_N(l)\tag{18}$$

Here we also approximate $G(N)$ of the critical nucleus by the maximum term approximation. The shapes (l^*, n^*) and $G(N^*)$ of the critical nucleus are given by (A.8) in Appendix II as

$$l^*=\gamma(2\sigma/\Delta g),\qquad n^*=2\sigma/\Delta g,\qquad N^*=n^*l^*$$
$$G(N^*)=4\gamma\sigma^2/\Delta g\tag{19}$$

In this approximation, the entropy effect caused by taking many microscopic states in (l,n) phase space is neglected, but this may be a good approximation for our purposes of qualitative discussion.

Paths in (l,n) phase space

It is convenient to describe the growth process of nuclei by 'paths' in (l,n) phase space, which is defined as the trace of a phase point (l,n)†, drawn schematically in *Figure 3*.

In order to describe the tendency that a nucleus grows more or less two-dimensionally, as discussed earlier, we may write l of the ith stage as

$$l_i=An_i^{\chi}\tag{20}$$

where n_i is n at the ith stage, χ is a path parameter constant and A is a constant, which is assumed to satisfy the boundary condition

$$l^*=An^{*\chi}\tag{21}$$

because a nucleus is considered to grow through the critical nucleus. From equations (20) and (21), we obtain

$$l_i=(\gamma n^{*1-\chi})^{1/(1+\chi)}N^{\chi/(1+\chi)}\tag{22}$$

Path parameter χ describes the type of growing nucleus, as illustrated in *Figure 3*. For example, when χ is nearly 1, the nucleus grows two-dimensionally, which corresponds to ECC type growth; and when χ is nearly 0 (smaller than 1), the nucleus grows one-dimensionally, which corresponds to FCC type growth. Therefore, the problem in this paper is to show what factors determine the value of the path parameter χ. As the shape of a nucleus is assumed to be rectangular, it may be reasonable to define the probability of attaching a repeating unit of the ith stage to the end surface as

$$p_i=l_i/(l_i+n_i)\tag{23}$$

Path parameter χ or ω

We may also describe a path by a symmetric formula $n_i=A'l_i^{\chi'}$ instead of $l_i=An_i^{\chi}$ where A' is a constant and χ' is a symmetric path parameter. In order to describe this symmetry, we will introduce another path parameter ω, which is

$$\omega\begin{cases}=\chi-1 & \text{for}\ \chi\leqslant 1\\ =(-\chi+1)/\chi & \text{for}\ \chi\geqslant 1\end{cases}\tag{24}$$

ω is 0 for $\chi=\chi'$ (ECC), -1 for $\chi\to 0$ (FCC) and 1 for $\chi'\to 0$ (needle-like).

RESULTS

(κ, ν) dependence of j

Here we will show that the texture transforms from ECC to FCC only by increasing the values of the order parameters (κ, ν) keeping other parameters constant. For

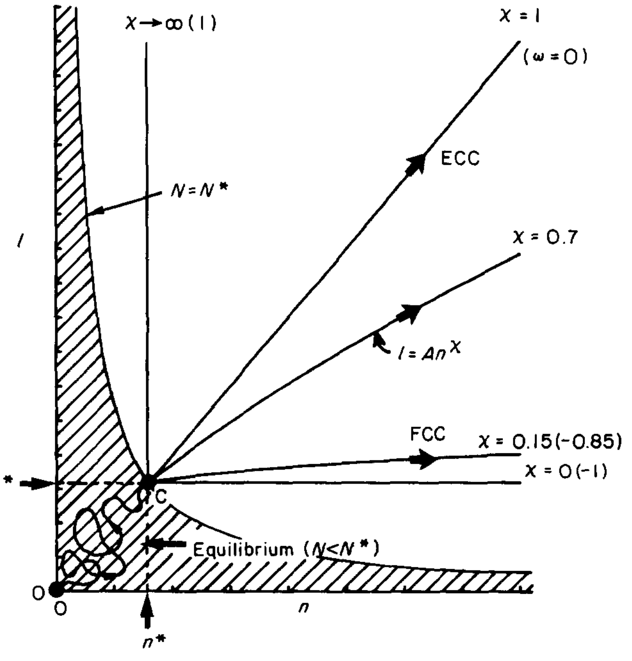

Figure 3 Paths for secondary nucleation in (l n) phase space for various values of path parameter χ (or ω). Here C indicates the critical nucleus. The region where a small nucleus is treated as a system in thermal equilibrium is indicated by oblique lines

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† It is noticed that, more generally, the 'path' should be defined as the trace of an 'average' phase point given by ($\langle l\rangle$, $\langle n\rangle$), which is defined in Appendix I

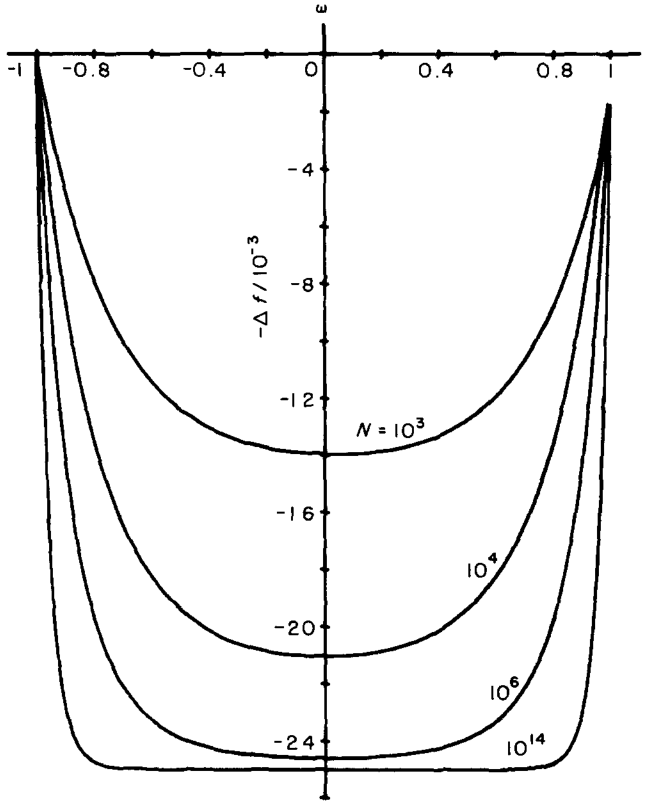

Figure 4 Plot of $-\Delta f$ against ω for $\Delta T = 15$ K and for four values of N, the number of repeating units in a nucleus. It is seen that $-\Delta f$ swiftly saturates to $-\Delta g = -0.25$ near $\omega \simeq 0$ for $N > 10^6$

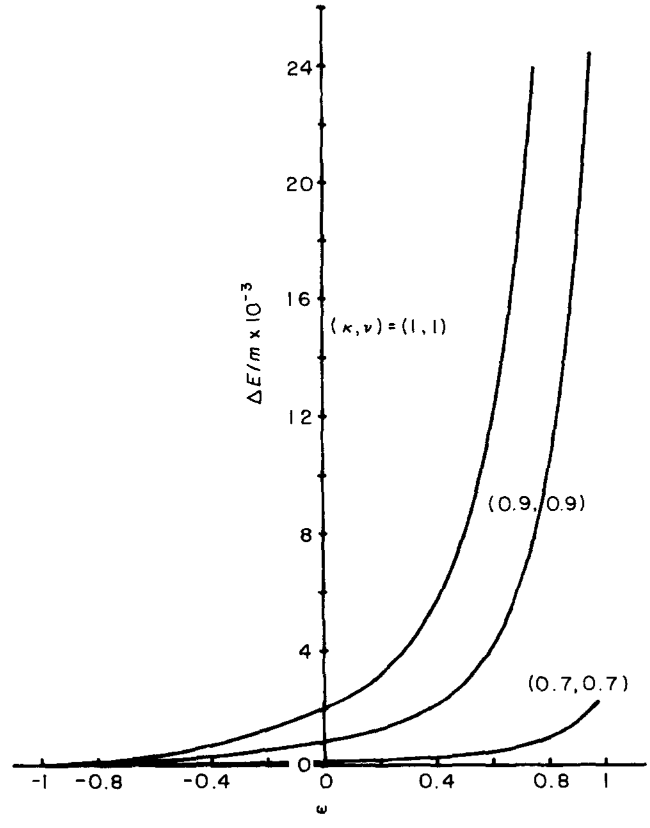

Figure 5 Plot of $\Delta E/m$ against ω for $\Delta T = 15$ K and for three values of order parameters (κ, ν)

example, those used in this paper are

$$\sigma = 0.1, \qquad \gamma = 4, \qquad \Delta g = \Delta T/600 \tag{25}$$

which are roughly taken by averaging the values of FCC and ECC of PE[11].

Now we can evaluate various quantities related to the nucleation by using the equations obtained in the previous section and the parameters above, where the nucleation rate j is given as a function of ω (or χ), ΔT and (κ, ν):

$$j = j(\omega, \Delta T, \kappa, \nu) \tag{26}$$

From equations (13), (18) and (19), $-\Delta f_m$ (driving force for crystallization) is plotted in *Figure 4* as a function of ω for a degree of supercooling such that $\Delta T = 15$ K. It shows that $-\Delta f_m$ depends strongly on the path parameter ω; that is, when ω is nearly zero, $-\Delta f_m$ swiftly decreases and approaches its minimum value of $-\Delta g$, whereas when ω is nearly 1 or -1, it decreases and approaches its minimum very slowly.

The free energy of activation for sliding diffusion of a chain ΔE_m *versus* ω is plotted in *Figure 5* from equations (8), (22) and (24) for $\Delta T = 15$ K. The figure shows that it swiftly increases with ω when the order parameters (κ, ν) are large, which will suppress thickening of the nucleus.

From these two factors, we plot in *Figure 6* the ω dependence of $(-\Delta f_m + \Delta E_m/m)$ by the full curve, which is an important factor in the formula for the nucleation rate j of equation (15). In the figure, $-\Delta f_m$ and $\Delta E_m/m$ are also plotted by a chain curve and a broken curve for comparison. This shows that the value of ω for which $(-\Delta f_m + \Delta E_m/m)$ is a minimum decreases from 0 to -1 with increasing order parameters (κ, ν), which indicates the deviation from thermal equilibrium growth of the nucleus. Here the values of the order parameters (κ, ν)

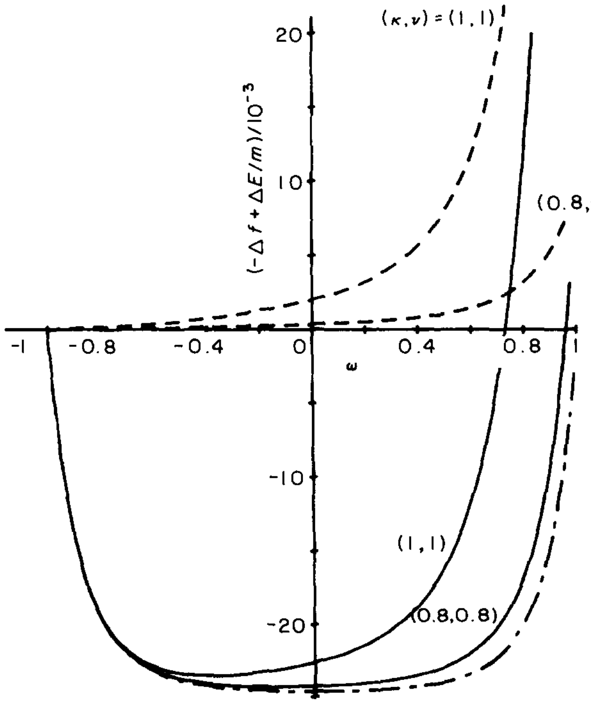

Figure 6 Plot of $(-\Delta f + \Delta E/m)$ against ω for $\Delta T = 15$ K and $N = 10^6$ (full curve) for two values of (κ, ν). The chain curve and the broken curve are plots of $-\Delta f$ and $\Delta E/m$

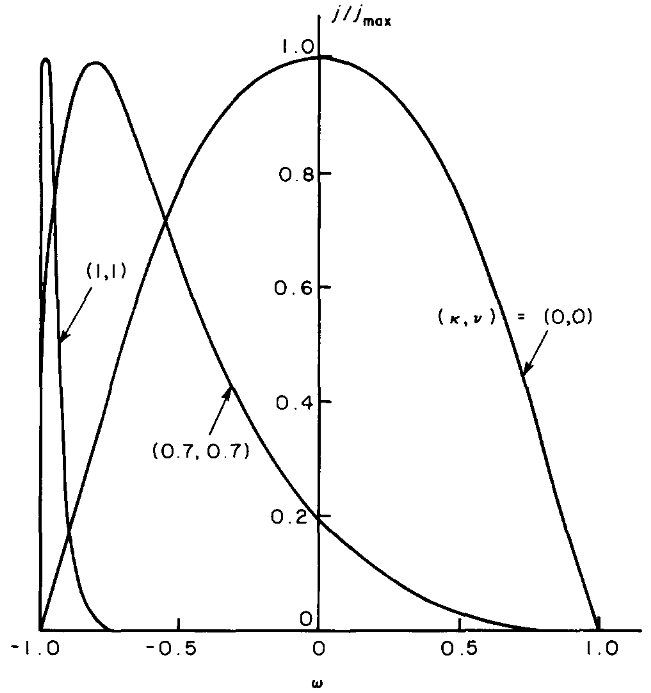

Figure 7 Plot of nucleation rate $j(\omega)$ normalized by the maximum value j_{max} against ω for $\Delta T = 15$ K for three values of (κ, ν)

necessary for the deviation are shown to be less than (1, 1), which will be shown in the 'Discussion' to be reasonable.

Thus the corresponding nucleation rate j is plotted in *Figure 7* as a function of ω for $\Delta T = 15$ K. The order parameters are shown in the figure by (κ, ν). It is clearly shown that, when the order parameters (κ, ν) are small enough and nearly (0, 0), the distribution of j is broad and its peak is seen at $\omega = 0$, which indicates that the growth is of two-dimensional type and leads to the formation of ECC. It is also shown that the distribution of j becomes sharp and its peak approaches $\omega = -1$ when the order parameters (κ, ν) increase and approach (1, 1), which indicates that the growth is of one-dimensional type and leads to formation of FCC. These results indicate that the texture transforms from ECC to FCC with increasing order parameters (κ, ν).

In order to make this transition clear, we will obtain the average value of χ and study the order parameter dependence of it. Here we will define the average value of ω by

$$\langle \omega \rangle = \int \omega j \, d\omega / \int j \, d\omega \qquad (27)$$

Then $\langle \chi \rangle$ can be obtained by substituting $\langle \omega \rangle$ into equation (24). The result is plotted in *Figure 8* as a function of the order parameters (κ, ν) for $\Delta T = 15$ K. In the figure, it is assumed that $\kappa = \nu$ for simplicity. It clearly indicates that $\langle \chi \rangle$ shows a rather sharp transition from 1 to a small value with increasing order parameters (κ, ν), which corresponds to the transition from ECC to FCC, as illustrated in *Figure 3* by the 'path' in (l, n) phase space. The transition is seen at rather large values of $(\kappa, \nu) = (0.7, 0.7)$ and it is noted that this transition is seen for constant values of σ and γ, which will be discussed again in the 'Discussion'. This result indicates that, when the crystal is ordered and (κ, ν) are large, 'sliding diffusion' of a chain within a nucleus is rather difficult and, as a result, the nucleus cannot thicken, which leads to the formation of FCC. It also indicates that, when the crystal is disordered and (κ, ν) are small, on the other hand, 'sliding diffusion' of a chain within a nucleus is rather easy and, as a result, the nucleus can easily thicken, which leads to the formation of ECC.

Thus it is concluded that the kinetic factor related to the 'sliding diffusion' of a chain plays an essential role in determining the texture of the growing polymer, which is very characteristic of a material composed of linear chains.

ΔT *dependence of the lamellae thickness for FCC*

The ΔT (or crystallization temperature T_c) dependence of the lamellae thickness of FCC can also be explained from this work. From equations (24) and (27), $\langle \chi \rangle$ is plotted in *Figure 9* by a chain curve as a function of ΔT for order parameters $(\kappa, \nu) = (1, 1)$. It shows that it has roughly a small constant value of 0.1 for a wide range of ΔT. Because l is regarded as a function of χ for a given N (as shown in equation (22)), $\langle l \rangle$ may be defined by

$$\langle l \rangle = l(\langle \chi \rangle, N) \qquad (28)$$

which is plotted in *Figure 9* by full curve I as a function of ΔT for $(\kappa, \nu) = (1, 1)$, $N = 10^6$ and the same parameter values as in the previous figures. The experimental curve given by Nakajima *et al.*[13] and the theoretical curve given in FT are also plotted by a broken curve and a full curve. The figure indicates that $\langle l \rangle$ of this work is nearly constant for large ΔT and increases swiftly for small ΔT, which agrees qualitatively with the temperature dependence of the observed curves. It is easy to show better agreement with the experimental curves by appropriate choice of the values of the parameters; for example, theoretical curve II is plotted for $\sigma = 0.2$, $\gamma = 10$. It is also shown that our curves do not show the so-called δl catastrophe even for large ΔT.

When $\langle \chi \rangle$ is very small, $\langle l \rangle$ can be roughly approximated from the definition of equations (20) and

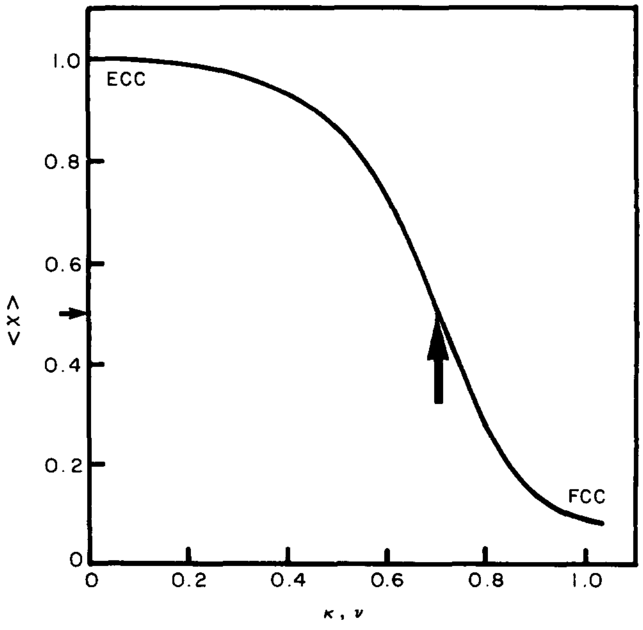

Figure 8 Plot of the path parameter $\langle \chi \rangle$ against the order parameter κ or ν for $\Delta T = 15$ K. The transition from FCC to ECC at about $(\kappa, \nu) = (0.7, 0.7)$ is indicated by the arrows

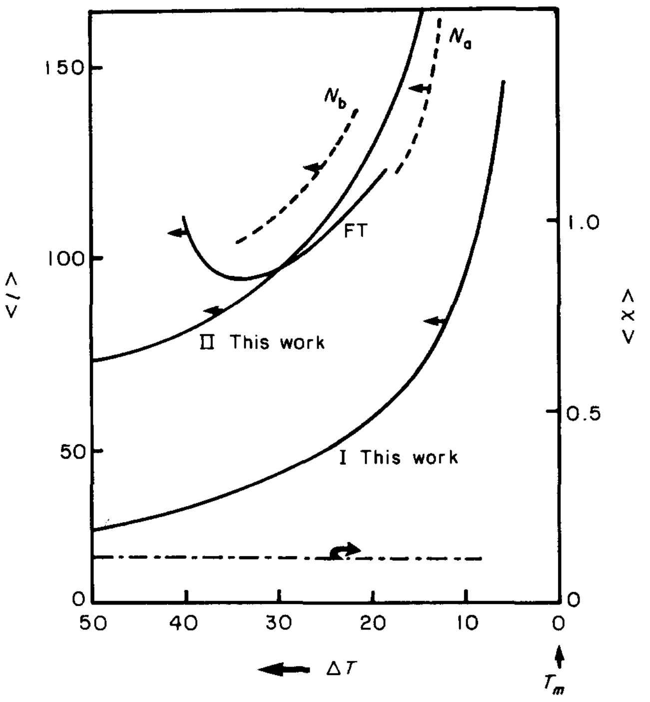

Figure 9 ΔT dependence of $\langle l \rangle$. The theoretical curves from this work and from Frank and Tosi (FT) are shown by full curves. The curve from FT is plotted for $\sigma = 0.06(kT)$ and $\sigma_e = 3.6(kT)$. Experimental curves given by Nakajima *et al.*[13] (N) are drawn by broken curves for linear polyethylene single crystals crystallized from dilute solutions: N_a (diphenyl ether) and N_b (*p*-xylene). The ΔT dependence of $\langle \chi \rangle$ is also shown by a chain curve.

(A.8) to

$$\langle l \rangle \simeq \gamma n^* \propto 1/\Delta T \qquad (29)$$

where the relation $\Delta g \propto \Delta T$ in LH theory is used. Thus the ΔT dependence of $\langle l \rangle$ can simply be understood by that of n^*, which may be the main reason why $\langle l \rangle$ rapidly increases for small ΔT.

DISCUSSION

ECC–FCC transition

We showed in the previous section that the texture transforms from ECC to FCC with increasing order parameters (κ, v) and it was concluded that the degree of order of the crystals plays an essential role in determining the texture, because it is closely related to the kinetic factor that determines the thickening rate. Now we can explain why, in PE, crystallization from the liquid to the orthorhombic form gives the formation of FCC and that from the liquid to the hexagonal form gives the formation of ECC[7], by using the well known facts that the crystal of the former is rather ordered and the crystal of the latter is rather disordered[8].

Origin of FCC formation and 'δl catastrophe'

The origin of FCC formation in LH and FT theories is that the probability (denoted q_l) of finding 'the first stem' of length l (including the case l can be altered only once in FT theory) is assumed to be given by ordinary equilibrium thermodynamic relations. They showed that q_l is an increasing function of l, which is true only when ΔT is much smaller than a critical value. When ΔT increases and approaches a critical value, the probability q_l rapidly increases with l, which leads to the so-called 'δl catastrophe'. Therefore, the essential origin of the 'δl catastrophe' in LH and FT theories is that the probability q_l is assumed to be given by thermodynamic relations even for very large l.

The origin of formation of FCC and the reason for avoiding the 'δl catastrophe' proposed by Point[6] is that the probability q_l is assumed to decrease with l for 'some' kinetic reason, but the reason behind this assumption or, in other words, the molecular image for the kinetic factor has not been made clear. We propose in this paper that the origin of formation of FCC and the reason for avoiding the 'δl catastrophe' is that the free energy of activation for 'sliding diffusion' of a molecular chain necessary for thickening is assumed to be an increasing function of the thickness of the nucleus, especially if the order of the crystal is high, as in the orthorhombic form of PE. Thus it is concluded that the kinetic factor plays an essential role in the formation of FCC.

Variation of the stem length

Another important difference between our theory and LH, FT and Point's[6] theories is whether the length of all the stems within the secondary nucleus can vary or not during the growth process. In their theories, the length of stems within the nucleus (except for the special 'first stem') is assumed to be unaltered, as if they were 'frozen'. In our theory, on the other hand, the length of all the stems is assumed to vary and to fluctuate through 'sliding diffusion' of a chain within a nucleus. We consider that the whole shape of a nucleus is determined by opposing factors, thermodynamic and kinetic, which depend closely on the degree of order of the crystal.

In this work, the degree of order of the crystal is assumed to be invariant throughout growth. But in reality, the degree of order of a nucleus may increase when the nucleus becomes larger and larger and, as a result, 'sliding diffusion' of a chain becomes more difficult. Therefore, in reality, χ may be a decreasing function of the size of a nucleus N. This may be the reason why the mean length l of FCC does not diverge even when the nucleus becomes very large and the extended-chain single-crystal (ECSC) of PE grows to a plate-like crystal micrometres thick[9].

Comparison of our theory with FT and our previous one

This theory is an expansion of FT and our previous one[11]. Therefore, it is easy to show that the formula for the nucleation rate j of both theories can be obtained as a special case of this theory. If we put $G^* = E_1$ and Δf_i and ΔE_i constant in our expression for j in equation (15), then j of equation (19) in FT is obtained, where E_1 is the energy of 'the first stem'. The assumption that Δf_i is constant corresponds to the assumption that the stem length after the second stem is kept the same as the first one.

The j of equation (3.2) in our previous theory[11] is shown to be obtained if we put $\Delta f_i = \Delta g$ and ΔE_i constant, which corresponds to the limiting case that sliding diffusion is very easy. Therefore, it is easy to show that this theory can explain the growth rate of ECSC by choosing appropriate values of the parameters.

Physical meaning of the order parameters κ and v

The parameter κ is defined as a kind of friction constant necessary for pulling up a chain, and so it is related to the lattice energy per repeating unit, to various defects or entanglements of chains in the nucleus, and so on. Therefore, the result that its order is equal to (or less than) the thermal energy $1(kT)$ shown earlier is reasonable because the order of the lattice energy per repeating unit is $1(kT)$ (Ref. 14).

The other order parameter v is a kind of scale factor representing the coherence length within which repeating units are directly linked and arranged in order. It is large when crystals are ordered and small when they are disordered, and the order of v may be 1 or 0.1. Therefore, the result that the value of v was larger than 0.7 for FCC and smaller than 0.7 for ECC shown in *Figure 8* is reasonable.

The values of these order parameters depend closely on the character of the polymer molecules, which is the reason why some polymers can grow into ECC and other polymers cannot.

Crystal order dependence of σ and γ

The ECC–FCC transition was shown by assuming constant values of σ and γ. This assumption is used only for simplicity and is not essential. In the real case, the values of the surface free energy σ and σ_e (or $\gamma\sigma$) increase with the order of the crystals, as has been discussed by Oyama[15] and in our previous paper[11], which makes the ECC–FCC transition with increasing order parameters very sharp. A more detailed comparison of our theory with the observed facts, such as the ΔT dependence of the growth rate, should be done by considering these effects.

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APPENDIX I

Free energy for formation of a nucleus $G(N)$

When a nucleus grows under thermal equilibrium, the free energy for forming a nucleus $G(N)$ is obtained by the usual thermodynamic procedure. The partition function for nuclei that contain N repeating units is written as

$$Z(N)=\sum_{l=1}^{N} P_N(l) \qquad (A.1)$$

where $P_N(l)$ is the probability given by

$$P_N(l)=\exp[-E_N(l)] \qquad (A.2)$$

$G(N)$ can be obtained from equations (A.1), (A.2) and

$$G(N)=-\ln Z(N) \qquad (A.3)$$

The free energy for forming a critical nucleus $G(N^*)$ is found by calculating

$$\mathrm{d}G(N)/\mathrm{d}N=0 \qquad (A.4)$$

where N^* is the critical value of N.

The statistical average shape of the nuclei is given by

$$\langle l\rangle=\frac{\sum_{l=1}^{N} lP_N(l)}{Z(N)} \quad \text{and} \quad \langle n\rangle=\frac{N}{\langle l\rangle} \qquad (A.5)$$

When a nucleus grows under non-equilibrium conditions, that is, a nucleus cannot take all its possible microscopic states, the range of the summation in the above equations must be changed from $\sum_{l=1}^{N}$ *to* $\sum_{l=l_{\min}}^{l_{\max}}$, where $l_{\min}$ and $l_{\max}$ are the minimum and maximum values of the stem length that the nucleus can take.

APPENDIX II

Maximum term approximation

If the distribution of $E_N(l)$ is sharp, $G(N)$ can be approximated by the maximum term of $E_N(l^+)$, for which

$$\delta E_N(l)/\delta l=0 \qquad (A.6)$$

is satisfied. By solving (A.6), we obtain

$$\begin{aligned} l^+ &= (\gamma N)^{1/2} \\ G(N)=E_N(l^+) &= 4\sigma(\gamma N)^{1/2}-N\Delta g \end{aligned} \qquad (A.7)$$

The critical nucleus is then obtained by solving (A.4), which leads to

$$\begin{aligned} l^* &= \gamma(2\sigma/\Delta g) \\ n^* &= 2\sigma/\Delta g, \qquad N^*=l^*n^* \\ G(N^*) &= N^*\Delta g=4\gamma\sigma^2/\Delta g \end{aligned} \qquad (A.8)$$

where l^* and n^* are the critical values of l and n.

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