

Dependence of spherulite growth rate of poly(*p*-phenylene sulfide) on film thickness: limitation on growth rate in multinucleation regime

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A limitation on the growth rate is proposed in the multinucleation regime. Spherulite growth rates of poly(*p*-phenylene sulfide) (PPS) in thin films of 1 μm down to 0.2 μm are measured in the range of crystallization temperature from 190°C to 275°C. Dependence of the growth rate on film thickness is also measured at the crystallization temperature. Growth rates vary by 4 orders of magnitude and are independent of film thickness. Since the film thickness is nearly equal to the width of the growth surface under the conditions in this work, the growth rate is independent of the width of growth surface. This means that PPS spherulites grow in a multinucleation regime. On the basis of the limitation on growth rate we proposed in this paper, the range of growth rate has to be less than 10² under the conditions investigated. Failure of the present nucleation theory is concluded from the results. To explain these results, thermal insensitivity of step velocity must be discarded. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

The growth mechanism of polymer crystals has been explained by the nucleation theory^{1,2}, which consists of two parts: (1) the theory of the nucleus itself^{1–4} and (2) the theory of lateral growth based on the Seto–Frank model^{5,6}. The former shows that the nucleation rate *i* depends on the crystallization temperature *T_c*, or supercooling $\Delta T (= T_m^0 - T_c)$, as follows:

$$i \sim \exp\left(-K \frac{T_m^0}{T_c \Delta T}\right) \quad (1)$$

where *K* is a constant and *T_m⁰* the equilibrium melting temperature. It is deduced on the basis of the Seto–Frank model that the lateral growth rate *G* is proportional to *i* ('single nucleation regime') or to *i*^{1/2} ('multinucleation regime'). The lateral growth rate *G* is, therefore, represented as follows:

$$G = G_0 \eta \exp\left(-nK \frac{T_m^0}{T_c \Delta T}\right) \quad (2)$$

where *G*₀ and *n* are constants and η a retardation factor due to viscosity: *n* = 1 in the single nucleation regime and *n* = 0.5 in the multinucleation regime. Equation (2) has well explained dependence of *G* on temperature¹ with appropriate evaluations of η .

In addition, breaks in the plot of $\log G - 1/T_c \Delta T$ has been explained as the transition between regimes⁷. However, this explanation was strongly criticized by Point and

co-workers^{8–13}. At first, they objected to the explanation of the breaks. Recently, they also questioned the analyses and explanations of the experimental data and meanings of *K*¹³.

In another way, we have also doubted the explanation for the growth rate's dependency on temperature. According to conventional understandings^{1,14,15}, the folding rate of a chain onto a niche site, in other words, velocity of a step, is almost independent of temperature, especially at high supercoolings. Therefore, the growth rate would be almost independent of temperature if crystals grow adhesively at extremely high supercoolings. Nevertheless, experimental data of $\log G$ depended on $1/T_c \Delta T$ linearly for almost all polymers in the whole temperature range studied¹. In previous works^{16,17}, we measured the growth rate of *it*-polystyrene to study the adhesive growth. However, the adhesive growth mode was not observed as the temperature dependence of *G* up to a supercooling of 170 K. The fact suggests that *v* depends on ΔT as an exponential function like *i*. In addition, the temperature dependence of *v* was reported for solution-grown polyethylene single crystals^{18,19}. These results also suggest that *v* depends on ΔT .

In this paper, we firstly show that the growth rate in the multinucleation regime is limited by the experimental conditions and the discreteness of a crystalline lattice. This limitation has been disregarded in the conventional treatments. Next, the dependence of growth rate on ΔT and on the film thickness is reported for poly(*p*-phenylene sulfide) (PPS) spherulites in very thin films. And finally, we show that the experimental results conflict with the conventional nucleation theory at least for the spherulite growth of PPS in melt.

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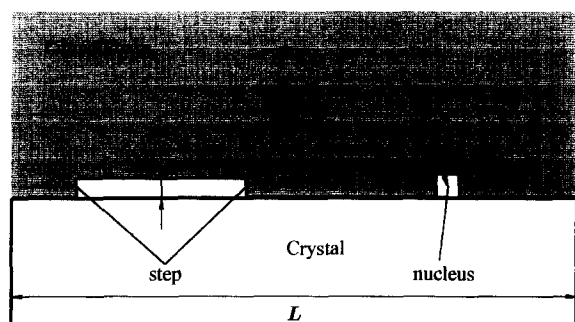


Figure 1 Schematic drawing of one-dimensional growth surface based on the Seto-Frank model

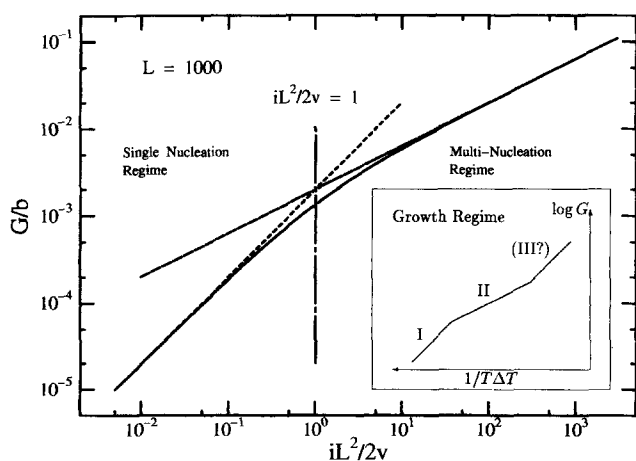


Figure 2 Exact solution by Frank with two asymptotes. It was calculated with $L = 1000$. Growth regime in $\log G - 1/T_c \Delta T$ plot is also drawn

LIMITATION ON GROWTH RATE IN MULTINUCLEATION REGIME

The Seto-Frank model treats a growth front as a one-dimensional substrate^{5,6} (Figure 1). On the substrate, a pair of steps are generated at a rate i : the process is called nucleation and i nucleation rate. The steps thus generated move along the substrate in the left and right directions with a velocity v . At a position on the substrate, the growth front advances by a height of a step b when a step passes. Therefore, the growth rate G is represented as follows:

$$G = b(l + r)v = 2bcv, \tag{3}$$

where l and r are densities of left- and right-moving steps, respectively, and $2c$ is the total density of steps (equals $l + r$). Frank⁶ solved the continuum equations of l and r under the steady-state condition and the absorbing boundary condition. The following two asymptotes were derived:

$$G = biL \quad (Z < 1 : \text{single nucleation regime}), \tag{4}$$

$$G = b\sqrt{2iv} \quad (Z \gg 1 : \text{multinucleation regime}), \tag{5}$$

where L is the width of growth surface and $Z = iL^2/2v$. The exact solution is shown in Figure 2. These equations may have led researchers to the misunderstanding that no limitations are imposed on G . However, we must recall that the growth rate is deduced from equation (3): variations in growth rate originate from those of the density of steps since it is presupposed that v is almost constant. We must

also take account of the fact that a real crystal forms a discrete lattice instead of a continuum body. If a disadvantage in the creation of steps disappears at extremely high supercoolings, a flat site and a niche site become equivalent to each other. The number of flat and niche sites become the same. (A niche site corresponds to a step.) This simple consideration shows that a maximum step density on a discrete substrate is $1/2a$, where a is the width of a site. This has been already confirmed by a Monte-Carlo simulation on a hexagonal lattice²⁰. It should be noted that adhesive growth has not been observed for polymer crystals up to the present. This means that the maximum step density of $1/2a$ is never achieved in a usual temperature range.

Next, we focus our attention on the lower limit. It is obvious that the limit is $Z = 1$ and a minimum step density is $2/L$, when L is constant during crystallization. However, this method cannot be adopted in many cases, because (1) growth surfaces spread during crystallization, i.e. L increases with crystallization time, and/or (2) transition between the single and the multinucleation regime is not observed experimentally. In the former case, it is certain that crystals grow in the multinucleation regime when the growth rate is independent of time. In the latter case, it is natural for us to assume that crystals grow in the multinucleation regime.

If it is certain that crystals grow in the multinucleation mode, we can do another estimation for the lower limit. In the multinucleation regime, the total step density $2c$ is given as $2/l_k$, where l_k is 'kinetic length' and equals $\sqrt{2v/i}$. Since l_k is a positive function of crystallization temperature, the maximum value of l_k in the temperature range studied is the one at the maximum crystallization temperature $T_c^{(max)}$. This means that $2c$ is necessarily larger than $2/l_k(T_c^{(max)})$ below $T_c^{(max)}$. Although the value of $l_k(T_c^{(max)})$ cannot be determined experimentally in many cases, we can use the upper-bounding length L^* instead of $l_k(T_c^{(max)})$ in some cases. L^* should be determined from experimental conditions so that it is assured that L^* is larger than $l_k(T_c^{(max)})$. In this case, $2/L^*$ is an alternative lower limit of the total step density. It is evident from the above procedure that the lower limit thus determined is an underestimated value.

For the growth of two-dimensional spherulites in very thin films, the maximum substrate width would be nearly equal to the film thickness, as discussed later. In this case, L^* can be determined to be the film thickness. The fact that the growth mode is the multinucleation mode assures that $l_k(T_c^{(max)})$ is smaller than the maximum substrate width. For the solution-grown single crystalline lamellae, L^* can be determined at the highest crystallization temperature as the minimum size of a lamella which grows linearly with time.

Summarizing this section, the ratio of maximum and minimum growth rates in the multinucleation regime has to satisfy the following inequality:

$$\varphi = \frac{G_{max}}{G_{min}} = \frac{c_{max}}{c_{min}} < \frac{L^*}{4a} \tag{6}$$

With $a = 0.5$ nm, $L^*/4a$ is calculated as 50, 500, 5000 for $L^* = 0.1, 1, 10$ μm , respectively. Here we emphasize again that the range is overestimated. The true range will be much narrower than the estimated one. Taking Frank's exact solution (Figure 2) into consideration, the true range where $\log G$ is a linear function of $1/T_c \Delta T$ in the multinucleation regime would be less than the above estimated values by one order of magnitude.

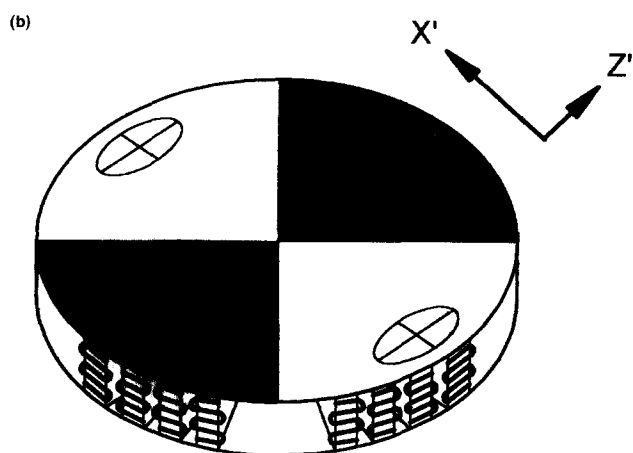


Figure 3 (a) Photograph of a two-dimensional spherulite of PPS in a thin film under a polarizing optical microscope. A $\lambda/4$ -plate was inserted between crossed polarizers. The bar is 20 μm . (b) Schematic drawing of arrangement of crystalline lamellae in two-dimensional spherulite

EXPERIMENTAL

Commercial PPS powder (Scientific Polymer Product, $M_w = 10000$ nominal) was dissolved in α -chloronaphthalene (αCN) to make a 0.08 wt% solution at 220°C. Cast films of PPS were prepared from the solution under nitrogen gas flow on a hot stage, the top surface of which was regulated at 300°C or 250°C. The casting temperature did not affect the growth rate. The solution of ca. 120 mg was typically poured onto a circular cover glass 15 mm in diameter placed on the hot stage. Using 1.35 g/cm^3 for the density of PPS²¹, the thickness of the casted film can be estimated as 0.4 μm on average. The outermost part of the film whose width was about 1 mm was very thick. The inner part was not flat and the thickness at a spherulite position was uncertain. The thickness of the inner part, however, was (1) less than 1 μm within the precision of a dial-gauge of 1 μm division and (2) less than the depth of focus of a 40 \times objective lens.

To minimize the effects of degradation, the casting process was carried out as rapidly as possible. Even for the longest case, it was completed within 3 min.

The PPS film was crystallized on a hot stage (LINKAM PH-600) under nitrogen gas flow. Crystallization

was observed by a polarizing microscope (Nikon OPTIPHOT2-POL) under crossed polarizers. A newly prepared film was used for each observation.

The film was first melted at 320°C for 1 min. The melting temperature was determined so that a spherulite did not re-appear at the same position before melting. A self-seeding technique was used at low crystallization temperatures: the film was first crystallized at 260°C for 3 min, reheated up to 290°C and kept for 1 min, then quenched to a crystallization temperature. At high crystallization temperatures, an alternative method was used to avoid degradation during induction; the induction time was about 8 h at 275°C. A film was initially quenched to 260°C from 320°C. The film was kept at 260°C for a few minutes until small spherulites were observed, then heated to a crystallization temperature. Between 260°C and 270°C, both methods were tried several times and no difference was detected. The heating and cooling rates in the above processes were 90 K/min. Figure 3a is a representative of spherulites thus obtained.

During crystallization, phase retardation due to birefringence was measured with a compensator and a green filter ($\lambda = 546 \text{ nm}$). In the usual measurement for a single crystal, the crystal was first set in a diagonal position between crossed polarizers. Instead, we observed part of a spherulite in a 45° direction with respect to the polarizers. Although a spherulite is a crystalline aggregate, the lamellae in a spherulite are arranged radially. Especially in very thin films, lamellae would be arranged parallel to each other, as shown in Figure 3b. In fact, the whole of each quadrant bounded by the Maltese cross became dark simultaneously in thin films when the analyser was rotated in the measurement. For thick films, on the other hand, the retardation could not be determined accurately because of the random orientation of lamellae.

DSC measurements were carried out to determine the equilibrium melting temperature T_m^0 . Samples were prepared as follows. At first, 5 wt% αCN solution of PPS was prepared at 220°C. After quenching the solution to room temperature, the solvent was evaporated at 300°C in Al pans under N_2 flow. PPS left in the pan was melted at 320°C for a minute and quenched to a crystallization temperature on the hot stage. To minimize isothermal thickening, the crystallization time was made as short as possible. DSC measurements were carried out at a heating rate of 20 K/min.

RESULTS

DSC measurement

Figure 4 shows DSC thermograms of PPS for five crystallization temperatures. Two melting peaks were observed in each thermogram; low temperature peaks were very small. Both peaks shifted to higher temperatures as crystallization temperature increased. A Hoffman-Weeks plot was shown in Figure 5. Low temperature peaks were not available because of inaccuracy. Using all data, a high temperature peak T_m^0 was determined as 308°C. However, the thermograms of the lowest temperatures were broader than others, as seen in Figure 4, and the Hoffman-Weeks plot was curved around $T_c = 245^\circ\text{C}$. This would be due to crystallization during the cooling processes. Except for the two data at the lowest temperatures, T_m^0 was determined as 318°C.

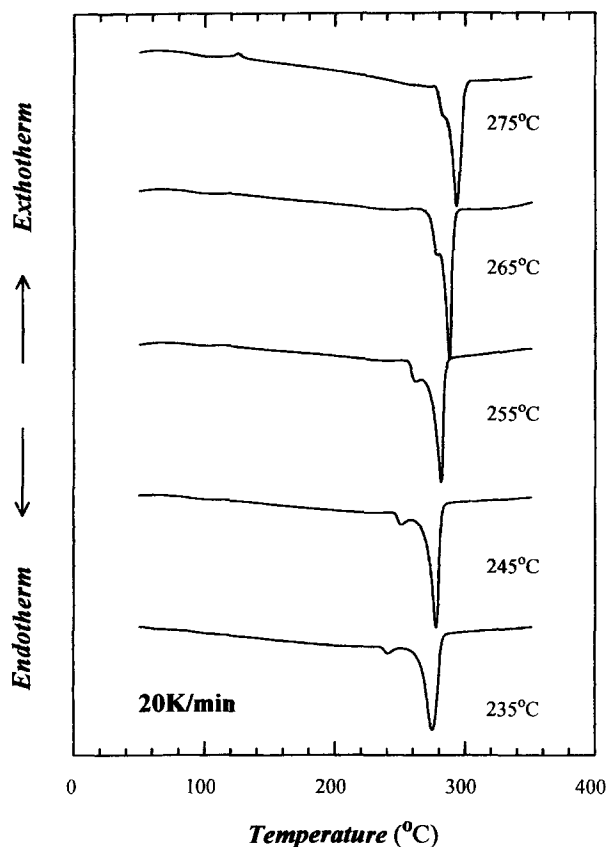


Figure 4 DSC thermogram of PPS for 5 crystallization temperatures. Crystallization temperatures are shown in the figure

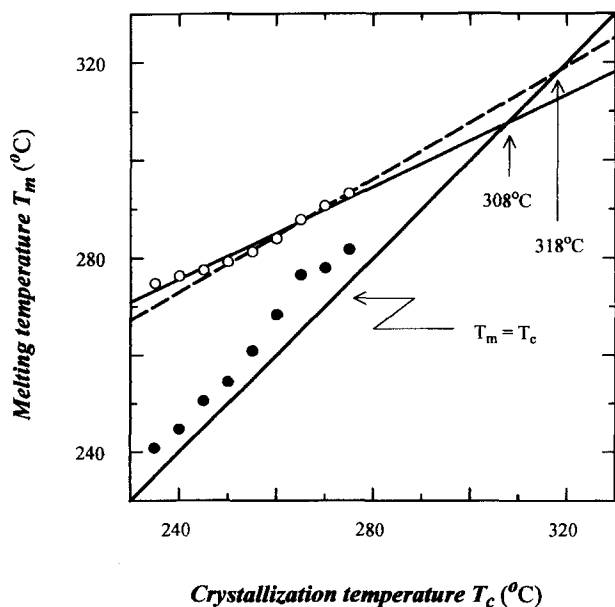


Figure 5 Hoffman-Weeks plot of PPS: ○ high temperature peak; ● low temperature peak

Spherulite growth rate

The radius of spherulites increased linearly with crystallization time from 1 to around 50 μm. In the later stages, a decrease in growth rate was observed for reasons that are unclear in some cases at high crystallization temperatures. In these cases, the growth rate was determined from its initial slope.

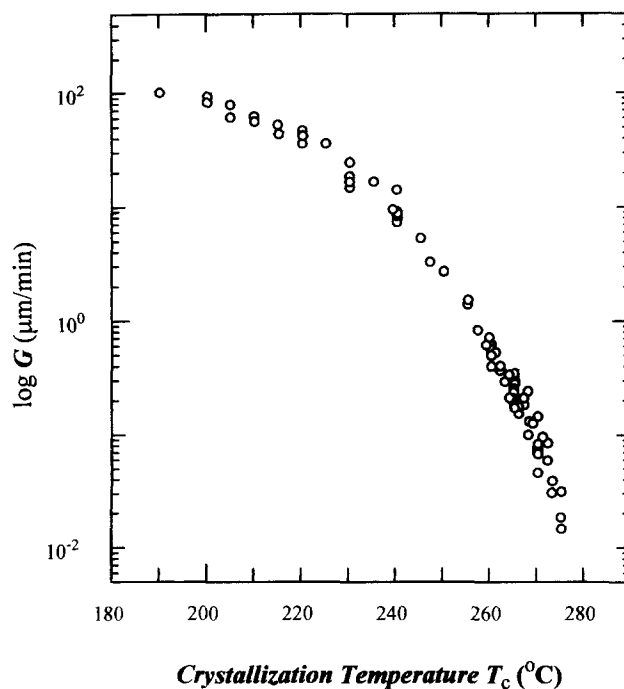


Figure 6 Growth rate of PPS spherulites as a function of crystallization temperature T_c

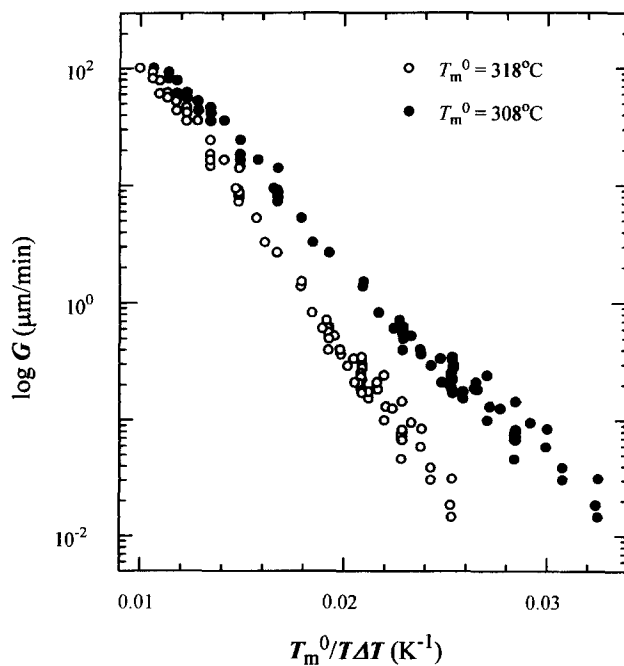


Figure 7 Growth rate of PPS spherulites as a function of $T_m^0/T_c \Delta T$. Two values of T_m^0 are used: ○ 318°C and ● 308°C

The dependence of the growth rate on crystallization temperature T_c was shown in Figure 6. The growth rate changed from 10^2 down to 10^{-2} μm/min with the increase in temperature from 190°C to 275°C: $\phi = 10^4$.

Figure 7 is a plot of $\log G - T_m^0/T_c \Delta T$ for both $T_m^0 = 308^\circ\text{C}$ and 318°C . For both values of T_m^0 , the regime transition was not observed. The only difference was its slope. Since accurate evaluation of the slope is not our concern in this paper, the uncertainty in T_m^0 does not affect subsequent discussion.

The dependence of G on phase retardation R is shown in

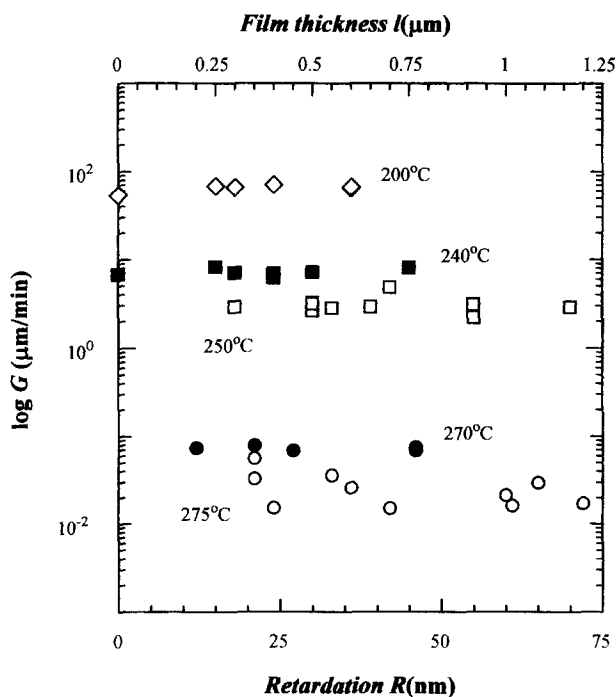


Figure 8 Growth rate of PPS spherulites as a function of phase retardation R for 5 crystallization temperatures. Crystallization temperatures are shown in the figure. The symbol on the ordinate for 200°C represents the growth rate of flat-on type lamella. The symbol on the ordinate for 240°C indicates the growth rate in very thick film where retardation could not be measured. In the cases of thin films, the phase retardation will be proportional to the width of the growth surface. The upper axis is the width of the growth surface calculated from R with $\Delta n = 0.06$, which is that for polyethylene



Figure 9 Anomalous hedrite grown isothermally at 250°C. Outer part of large retardation grew during slow cooling. The bar is 20 μm

Figure 8. It is natural for us to think that birefringence ($\Delta n = |n_e - n_o|$) is independent of film thickness l at each temperature, unless the thickness is so large that distribution of the lamellar orientation is random and that the retardation cannot be determined. Therefore, R will be proportional to l . *Figure 8* clearly shows that G was independent of l in the whole temperature range between 190°C and 275°C. The values of l with $\Delta n = 0.06$, which is the birefringence for polyethylene²², were also shown in the figure. It should be noted that the film thickness thus measured was the thickness of a growing spherulite, not the average.

In this paper, the retardation factor η was not evaluated, to avoid confusion originating from its uncertainty. The

bendings due to viscosity are left around the lowest temperatures in *Figure 7* because of this reason. If η was taken into consideration, φ could become larger than the above value. Therefore, the non-evaluation of η does not affect the later discussion.

DISCUSSION

To apply our new criterion for growth rate in the multinucleation regime, the following are required:

- (1) The maximum width of growth surface is approximately the same as the thickness of films.
- (2) Spherulites grow in the multinucleation mode.

At the beginning of the discussion, we will show that these are satisfied. Then we will discuss the applicability of the conventional nucleation theory to the results in this work in the light of our new criterion.

Width of growth surface

In the case of two-dimensional spherulites in thin films, we presuppose that crystalline lamellae are perpendicular to the film surface as shown in *Figure 3b*, since the birefringence of polymer crystals is mainly due to the difference between the refractive index in the direction parallel to the chain axis and the refractive index in the direction perpendicular to chain axis. *Figure 9* is an indirect evidence of this presupposition. The inner part of small retardation, which we call 'anomalous hedrite'²³, grew isothermally and the outer part of the large retardation grew during slow cooling. Since the retardation of the outer part is large, the small retardation of the inner part is not due to the thinness of the film. Hence, the birefringence of the inner part is very small. Except for the very rare case in which the light path coincided with the optical axis of the biaxial crystal, the fact shows that the PPS crystal is quasi-uniaxial: strictly speaking, the crystal is biaxial because its crystal system is orthorhombic²⁴. Based on this observation, we conclude that the lamellae in PPS spherulites grown in this work are arranged as edge-on types²³. Observations by electron microscope^{25,26} are other evidence of the supposition, although they were not carried out for the whole temperature range in this work. If we accept this presupposition, we can assume that L^* approximately equals the thickness of film l , except for the difference only by a factor arising from the inclination of the growth surface and the lamella itself.

Although this supposition has not been proved perfectly, it does not pose an obstacle to our discussion. Since the measurements were carried out under crossed polarizers, we only observed part of the large birefringence even if the lamellar bundles rotated about the radial direction and/or both edge-on and flat-on type lamellae co-existed. Therefore, the growth rates of the edge-on type lamellae were determined. If both types of lamellae were distributed in the direction normal to the films, the growth surface should be much narrower than the film thickness.

Growth regime

From the fact that no breaks were observed in the $\log G - 1/T_c \Delta T$ plot, it is reasonable to think that the crystals grew in one growth regime.

'Regime III' was reported for this polymer²⁷. The transition temperature reported was around 180°C. Since the lowest crystallization temperature in this work is 190°C, the growth regime is not 'regime III'.

Since the growth rate was independent of time, multi-nucleation growth is plausible. In addition, two types of single nucleation growth were also possible. One is the growth on extremely narrow growth surfaces whose width would be about 100 nm or less and constant during crystallization. The other is the growth on the growth surface whose width is equal to the film thickness. The former is the assumption introduced by Hoffman²⁸ to explain the transition from regime I to II against the claims of Point *et al.*⁸⁻¹³ The postulate of the subdivided substrate is difficult to accept for the following reasons:

- (1) The theoretical background is not clear.
- (2) There is no reason to explain the postulate that the width of each subdivided segment is the same, constant during crystallization and insensitive to crystallization temperature.
- (3) The experimental evidence has not been reported.

In addition, well-developed flat-on lamellae were observed at the central region of a spherulite of PPS by transmission electron microscope²⁶. There were no traces of the subdivision on the photograph.

The latter model is also rejected from the fact that the growth rate was independent of film thickness: growth rate in the single nucleation regime is proportional to the width of the growth surface.

Based on the above discussion, we conclude here that crystals grew in a multinucleation mode.

Failure of the conventional nucleation theory

The results are summarized as follows.

- (1) The growth rate changed by 10^4 in one growth regime ($\varphi = 10^4$).
- (2) The growth regime was the multinucleation regime.
- (3) The growth rate was independent of the film thickness down to about 0.2 μm .

In the light of the limitation on the growth rate we proposed, however, the growth rate can change only by 10^2 in a multinucleation mode. This discrepancy was too large to be explained by conventional nucleation theory, taking account of the following facts: (1) the adhesive growth is never achieved, (2) the lower limit of step density was under estimated, and (3) the range of the growth rate was underestimated because η was not evaluated. The limitation is deduced in a very simple manner, and ambiguities would arise only in the evaluation of L^* . As discussed above, the ambiguities in L^* do not affect the results. Therefore, we conclude here that conventional nucleation theory is not applicable, at least, for growth of PPS spherulites in melt.

Our discussion is based on equation (3). The equation is very simple and Frank's solution raises no doubts if we accept all the requirements for the solution. Therefore, to explain our results, only two possibilities are left: (1) equation (3), i.e. the Seto-Frank model, is not applicable, or (2) ν depends on ΔT exponentially.

If the Seto-Frank model is not applicable, the crystals do not grow laterally, including normal growth on a rough surface as a limit of lateral growth. In this case, we must introduce an alternative growth mechanism, such as the deposition of clusters, a diffuse crystal-melt interface²⁹, etc. Although these models cannot be refused, they are conjectural at present.

Next, we discuss the case in which ν depends on ΔT . There are two experimental supports for the dependence of

ν : (1) adhesive growth has never been observed as the growth rate's dependency on temperature; and (2) it was reported that ν depends on $1/T_c\Delta T$ like $i^{18,19}$. According to the usual understanding^{1,14,15}, ν is represented as follows:

$$\nu = \nu_0 \eta \exp(-\Delta F^*/kT_c)(1 - \exp(-A\Delta T)), \quad (7)$$

where ΔF^* is a free energy barrier of folding, and ν_0 and A are constants. According to the traditional sense, ΔF^* is a constant. Therefore, it has been said that ν is independent of ΔT (if $A\Delta T > 1$) or ν is proportional to ΔT (if $A\Delta T \ll 1$). The factor $(1 - \exp(-A\Delta T))$ never reveals exponential dependence on ΔT^{-1} . Then, ΔF^* would be proportional to ΔT^{-1} . If we assume the barrier is enthalpic, it would be very difficult to explain the dependence. Sadler³⁰, on the other hand, proposed an entropic barrier model in which a barrier to growth is proportional to lamellar thickness. Strobl³¹ also proposed another entropic barrier model. Strobl's model requires that a part of a chain whose length is equal to the lamellar thickness is stretched before being incorporated into the crystal. Due to the stretching, the conformational entropy decreases in proportion to the segment length which equals the lamellar thickness. If the lamellar thickness varies as a linear function of $1/\Delta T$, the barrier also varies as a linear function of $1/\Delta T$. The barrier results in the exponential dependence of the growth rate. This model presupposes that a unit incorporated is a stem. Although the issue of whether a unit incorporated is a stem or a segment is unclear at present, the entropic barrier model offers a solution to this problem.

CONCLUSION

A limitation on the growth rate in a multinucleation regime was proposed based on the discreteness of a crystalline lattice and experimental conditions. The limitation requires that the ratio of maximum and minimum growth rates in a multinucleation regime must be less than $L/4a$.

The growth rate of PPS spherulites was measured from 190°C to 275°C by a polarizing microscope. Radii of spherulites increased linearly with crystallization time. No breaks were observed in the plot of $\log G - 1/T_c\Delta T$ and the growth rate changed by 10^4 .

Phase retardation due to birefringence was also measured at crystallization temperature with a compensator. This result shows that the growth rate is independent of the retardation. Since the retardation will be proportional to the film thickness, the growth rate was independent of film thickness, or the width of the growth surface, down to ca. 0.2 μm .

Based on the criterion we proposed, the growth rate in film 0.2 μm thick can only vary within 2 orders of magnitude. This result clearly shows that the conventional nucleation theory is not applicable to the growth of PPS spherulites, and leads to the conclusion that either the Seto-Frank model or the thermal insensitivity of ν is invalid. It seems plausible that ν depends on ΔT as $\nu \sim \exp(-K'/T_c\Delta T)$ because of the facts that the dependence of ν was reported for solution-grown polyethylene crystals^{18,19} and adhesive growth has not been observed as the growth rate's dependency on temperature.

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