Growth rate of isotactic polystyrene crystals in concentrated solutions and in the melt*

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The growth rate of isotactic polystyrene (iPS) crystals has been investigated for crystallization in concentrated dimethyl phthalate solutions and in the melt over a wide range of supercooling from 20 to 170 K. For most of the supercoolings studied, the growth faces are rough; nucleation is not present. However, the growth rate G for each concentration shows approximately the same dependence on supercooling ΔT as growth controlled by secondary nucleation: $\log(G/\beta)$ depends linearly on $K/T\Delta T$, where β is a transport factor and K is a constant. The value of K increases with decreasing concentration. Possible mechanisms for crystal growth are discussed, taking account of the deposition of one stem on growth faces; the side surface free energy increases with decreasing concentration.

(Keywords: growth rate; isotactic polystyrene; high supercooling; transport factor; concentrated solution; rough-surface growth)

INTRODUCTION

At low supercoolings, the growth rate and morphology of polymer crystals have been successfully explained in terms of the nucleation rate and the step advancing rate[1–3]. However, since the number of stems in a critical nucleus and the free energy for the formation of a critical nucleus decrease with increasing supercooling, there should be a supercooling, at larger value, at which nucleation would not be a rate-determining process.

We have studied the growth of polymer crystals at high supercoolings through the dependence of the lamellar thickness on crystallization temperature, molecular weight and concentration; growth is not nucleation-controlled but rather is rough-surface growth at high supercoolings[4–6]. Recently one of the authors[7] has reported on the morphology and growth rate of isotactic polystyrene (iPS) crystals grown from a dilute dimethyl phthalate solution of 0.1 wt%. The growth faces are rough at crystallization temperatures lower than 130°C, but the growth rate G shows the same dependence on supercooling ΔT as the equation for secondary nucleation:

$$G = G_0\beta(T)\exp(-KT_d^0/T\Delta T) \qquad (1)$$

where G_0 and K are constants, T_d^0 is the equilibrium dissolution temperature, T is the crystallization temperature, and $\beta(T)$ is a retardation or transport factor.

It has been argued that the classical kinetic theory cannot be applied to iPS even at moderate supercoolings[8]. Sadler and Gilmer have shown that the growth rate obeys equation (1) for both rough and faceted growth faces in their simulations[9], though rough surfaces imply thermal roughening at high temperatures.

For the melt growth of iPS, G is known to obey equation (1)[1,10]. Well defined {1 1 0} growth faces were observed at crystallization temperatures higher than 200°C, while the growth faces were irregular at 190°C[11,12]. For crystallization in the 30 wt% solutions, irregular growth faces were observed at 120°C[6]. When polymer growth is controlled by nucleation, the growth faces are expected to be faceted or at most smoothly curved. Hence in the light of morphology, the growth of iPS crystals should not be controlled by nucleation at least below 190°C for melt growth and below 120°C for the 30% and 0.1% solutions.

Many investigations have been done on the growth kinetics of polymer crystals in dilute solutions and in the melt, but studies in semi-dilute and concentrated solutions are relatively few. In this paper, we report the growth rate of iPS crystals grown from concentrated solutions of 30 and 50 wt% and from the melt to examine the validity of equation (1) and the concentration dependence of K.

EXPERIMENTAL

The material used is commercial iPS ($M_w = 1.57 \times 10^6$, $M_w/M_n = 6.4$; and the tacticity is 97.2% isotactic triad)

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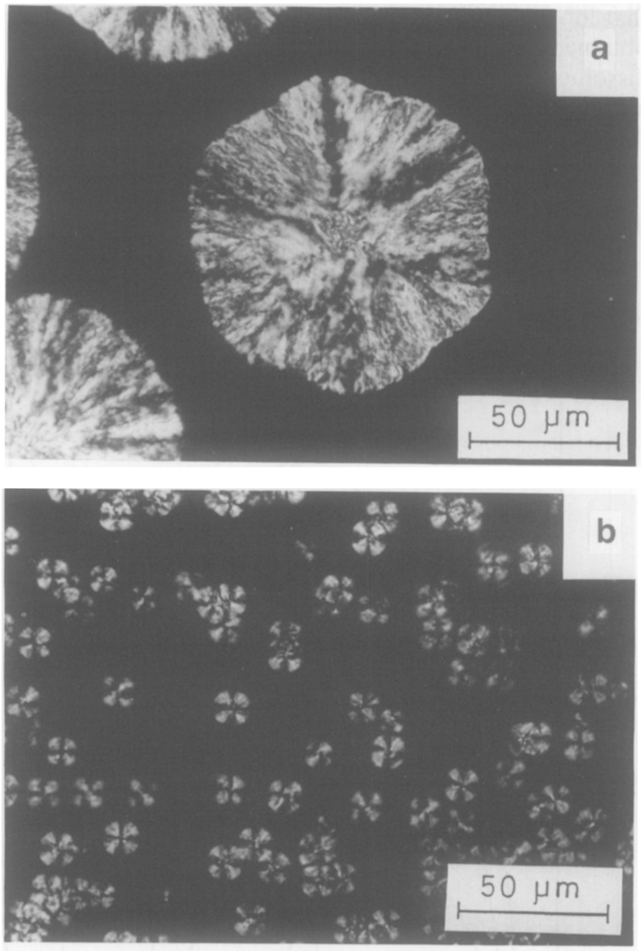

Figure 1 Optical micrographs of iPS crystallized in the melt at (a) 221.2°C and (b) 109.9°C; crossed polars

purchased from Polymer Laboratories Ltd. Dimethyl phthalate (DMP) is used as solvent.

The uniform 30 and 50 wt% solutions were prepared by dissolving at 240°C under Ar gas atmosphere. Crystallization was carried out on a hot stage (Linkam TH-600RMS) under Ar gas flow. The film samples were redissolved or melted between cover glasses at 220°C (30%), 240°C (50%) and 260°C (melt) for 3 min followed by cooling to the crystallization temperature at a rate of 90 K min^{-1}. The growth rate is determined from the time dependence of the radius of spherulites or the semi-major axis of axialites observed by an optical microscope.

The samples for differential scanning calorimetry (d.s.c.) were prepared as follows. After the crystallization in the 10 wt% solution at 100°C, the solvent was substituted by methyl ethyl ketone and the crystals were dried in vacuum. The dried powder sample was annealed under Ar gas atmosphere at 180°C (specimen A), 200°C (B), 210°C (C) or 220°C (D) to prepare specimens with different lamellar thicknesses. D.s.c. was performed by a heat-flow-type calorimeter (Rigaku 10A). Part of each specimen was melted at a heating rate of 20 K min^{-1} to prevent annealing effects during heating. Another part of the specimen was hermetically sealed in an aluminium pan with a certain amount of DMP and dissolved into 30 ± 1% solution. A slow heating rate of 1 K min^{-1} was adopted in order to dissolve into a uniform solution; higher heating rates did not give reproducible results, indicating non-uniform dissolution.

RESULTS

Growth rate

Typical optical micrographs of iPS crystals grown from the melt and from the 50% solutions are shown in *Figures 1* and *2*, respectively. At crystallization temperatures higher than about 190°C (melt) and 150°C (50%), hexagonal, oval and circular crystals were usually observed (*Figures 1a* and *2a*); they are axialites whose appearance depends on the direction of the primary crystals[11]. At low crystallization temperatures, spherulites were always observed. The size of the crystals $2R$, i.e. the diameter of spherulites or the major axis of axialites, is measured as a function of time t.

In the melt growth, dR/dt is constant except at 221.2°C, the highest crystallization temperature studied (*Figure 3*). At 221.2°C, R initially increases linearly with t, but dR/dt eventually decreases; the decrease is supposed to be due to fractionation.

In the growth from the 50% and 30% solutions below 170°C (50%) and 140°C (30%), dR/dt is initially constant and decreases with time as shown in *Figure 4*. This non-linear growth is due to the decrease in average concentration of polymer caused by crystallization or to a diffusion process near the phase boundary[13]. On the other hand, at higher temperatures, the evaporation of solvent is observed and gives rise to the apparent increase in dR/dt with time without showing any linear growth even at a short time.

The growth rate G was determined from the initial

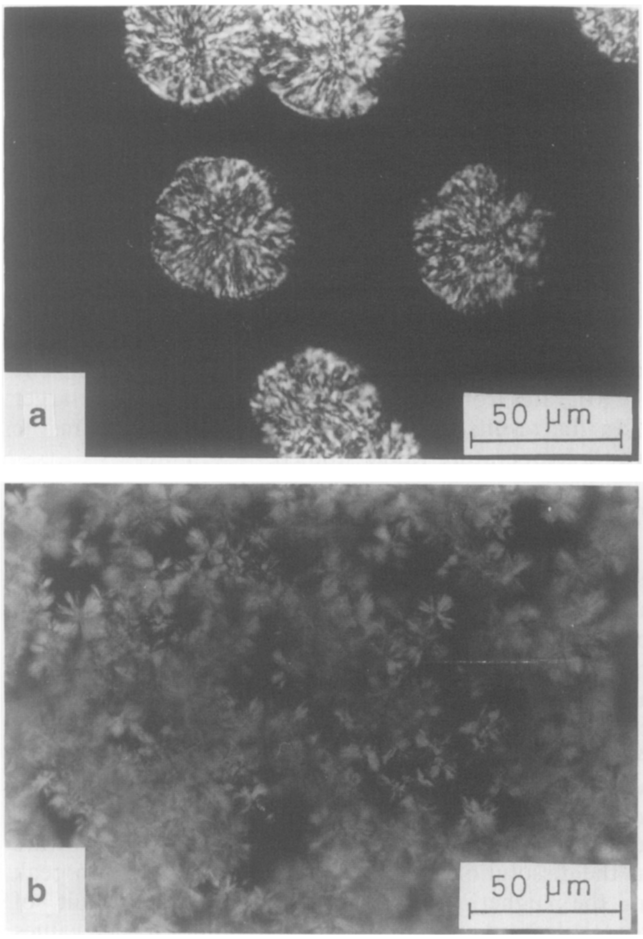

Figure 2 Optical micrographs of iPS crystallized in the 50% solution at (a) 165.6°C and (b) 70.8°C; crossed polars

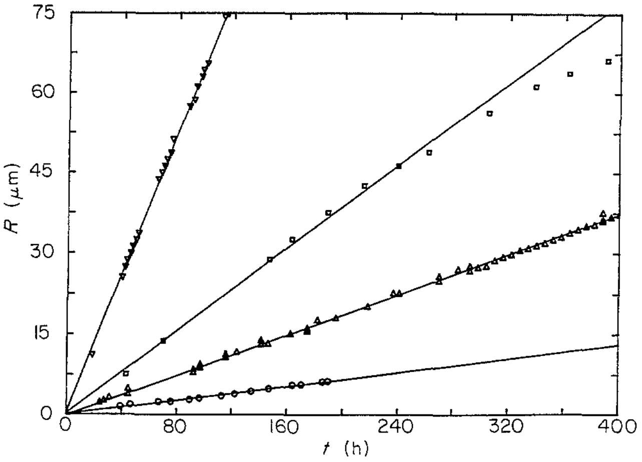

Figure 3 Time dependence of R for crystallization in the melt: (○) 109.9°C, (△) 115.1°C, (▽) 216.7°C and (□) 221.2°C

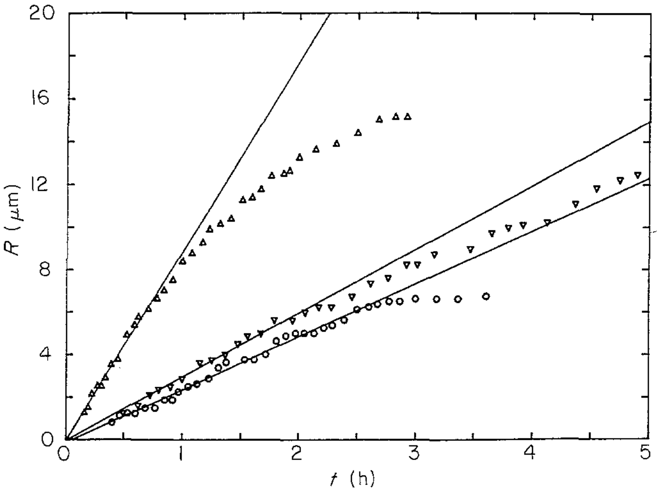

Figure 4 Time dependence of R for crystallization in the 30% solution: (○) 50.4°C, (△) 90.5°C and (▽) 130.5°C

slope in R versus t plots. The logarithm of G is plotted against crystallization temperature in *Figure 5*. The results of G for the 0.1% solution given by Tanzawa[7] are included for the sake of the following discussion. The growth rates from the melt in our study are slightly larger than the results given by Suzuki and Kovacs[10] in the whole temperature range studied.

Differential scanning calorimetry

The melting d.s.c. thermogram shows double endothermic peaks for specimens A, B and C annealed at 180, 200 and 210°C, respectively. Since the melting peak at about 220°C represents the melting of reorganized crystals, we take the lower peak temperature as the melting temperature T_m of unthickened lamellar crystals. In the dissolution thermograms for specimens A and B, two endothermic peaks were observed: the peak at lower temperature is comparatively sharp and large, and the higher one is broad and small. The ratio of peak areas is about 10:1; we take the lower peak temperature as the dissolution temperature T_d. The dissolution peak at the higher temperature may be the result of reorganization or of non-uniform dissolution. The values of T_m and T_d are shown in *Table 1* for specimens A to D. The ratio of the heat of dissolution, Δh_f (30%), to that of fusion, Δh_f (melt), is also listed in *Table 1*, obtained from the endothermic peak area in the dissolution and the melting thermograms. Taking account of the experimental accuracy, we conclude that Δh_f (30%) is approximately identical to Δh_f (melt); Δh_f is mostly a property of the polymer crystal[14].

The equilibrium dissolution temperature T_d^0 for the 30% solution is estimated by extrapolating the lamellar thickness to infinity[7]. The lamellar thickness l has been obtained from the melting temperature by use of $T_m^0 = 242$°C, Δh_f (melt) $= 9.11 \times 10^8$ erg cm^{-3} (ref. 10)

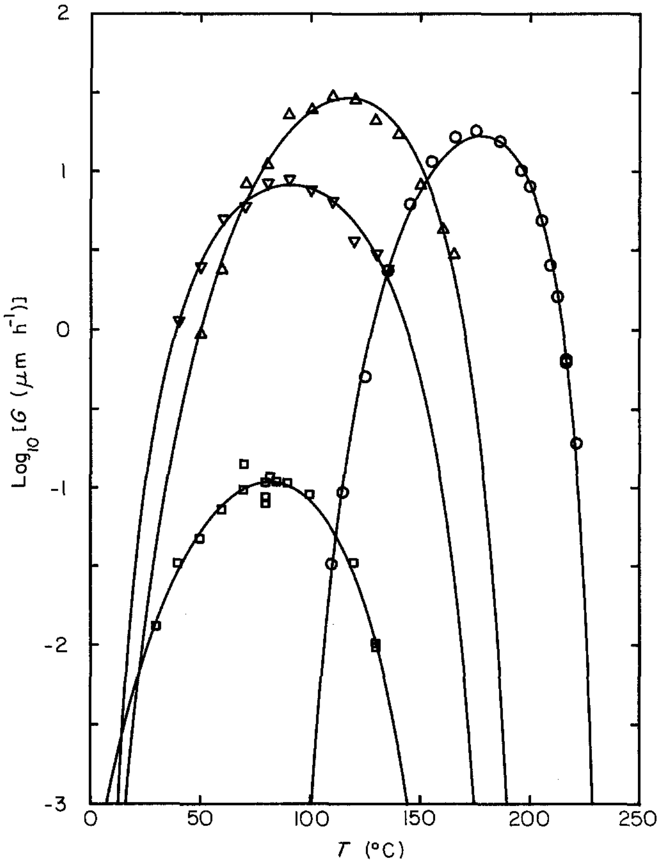

Figure 5 Growth rate *versus* crystallization temperature: (○) melt, (△) 50% and (▽) 30% solution (this work) and (□) 0.1% solution (ref. 7)

Table 1 Results of d.s.c. Melting and dissolution temperatures, and the ratio of heat of dissolution to that of fusion

Specimen	Annealing temperature (°C)	T_m (°C)	T_d (°C)	Δh_f (30%)/Δh_f (melt)
A	180	204.0 221.5	154.1 164.5 (broad)	1.3
B	200	212.0 221.5	164.2 185.0 (broad)	1.1
C	210	218.0 (shoulder) 222.0	170.0	1.1
D	220	228.5	186.0	–[a]

[a] This value could not be determined accurately, because, besides a well defined peak, a very broad peak appeared centred at about 150°C in the dissolution and at about 195°C in the melting thermograms, which are supposed to be the result of crystallization during the cooling process of the melted fraction at the annealing temperature, 220°C

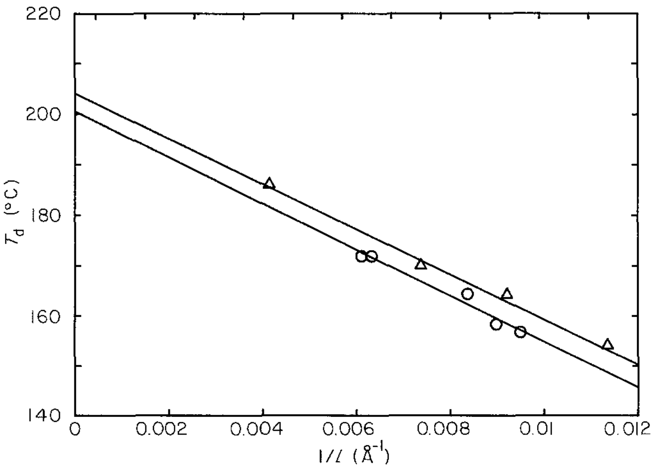

Figure 6 Dependence of the dissolution temperature on the reciprocal lamellar thickness for 30% solution (△). The results for 2% solution[7] (○) are shown for comparison

and the end surface free energy $\sigma_e(\text{melt}) = 28.8$ erg cm^{-2} (ref. 15). The dissolution temperature $T_d(l)$ of crystals with lamellar thickness l is expressed by the following equation:

$$T_d(l) = T_d^0\left(1 - \frac{2\sigma_e(30\%)}{\Delta h_f(30\%)}\frac{1}{l}\right) \qquad (2)$$

In *Figure 6*, $T_d(l)$ is plotted against $1/l$. According to equation (2), the extrapolation to zero of the straight line in *Figure 6* for $1/l$ gives $T_d^0 = 204$°C and from the slope the value of $\sigma_e(30\%)/\Delta h_f(30\%)$ is obtained to be 4.6 Å; $\sigma_e(30\%)$ is estimated as 42 erg cm^{-2}.

The present method of determination of T_d^0 was not successful for the 50% solution. We estimate that $T_d^0(50\%) = 215$°C from the interpolation of $T_d^0(30\%)$ and T_m^0. The error in this rough estimation will not affect the following discussion.

DISCUSSION

Since the driving force for crystallization increases with supercooling, the growth rate G increases with decreasing crystallization temperature; this process is described by a kinetic factor $\kappa(T)$. As crystallization temperature decreases, the transport process across the phase boundary becomes slower and the growth rate decreases. The latter process is described by a transport factor $\beta(T)$. The growth rate is expressed accordingly by these two factors:

$$G = G_0\beta(T)\kappa(T) \qquad (3)$$

where G_0 is a constant independent of temperature but dependent on concentration.

For growth controlled by nucleation, G has the form of equation (1) and hence $\kappa(T)$ is given by:

$$\kappa(T) = \exp(-KT_d^0/T\Delta T) \qquad (4)$$

For adhesive growth on the kinetically rough growth faces at high supercooling, $\kappa(T)$ is given by[4,7,16]:

$$\kappa(T) = 1 - A\exp(-\alpha\Delta T/T) \qquad (5)$$

where A and α are constants. In this case, κ hardly depends on supercooling.

The short-distance diffusion above the glass transition temperature T_g is generally described by the Williams–Landel–Ferry (WLF) equation even in solution[17]. If we adopt the WLF equation, $\beta(T)$ is given by:

$$\beta(T) = \exp[-2070/(T - T_0)] \qquad (6)$$

where T_0 is a constant. In the case of polymer crystallization, another form[1] similar to equation (6) has been proposed for $\beta(T)$:

$$\beta(T) = \exp[-U^*/(T - T_\infty)] \qquad (7)$$

where U^* and T_∞ are constants independent of temperature.

For dilute solutions, the Arrhenius equation, i.e. $T_\infty = 0$ K in equation (7), may be more appropriate for $\beta(T)$. The growth rate of iPS crystals in the 0.1% DMP solution has been analysed by applying the Arrhenius equation to β in equation (1); $U^* = 8400$ K[7]. Estimation of the transport factor is a big issue in the study of polymer crystallization, in particular at high supercooling. Since the determination of the form of $\beta(T)$ goes beyond the scope of the present paper, however, we examine the validity of equation (1) and the concentration dependence of K by using either equation (6) or (7) for β in equation (1).

First the experimental results are examined by the conventional form for $\beta(T)$, i.e. equation (7). From equations (1) and (7), G is given by:

$$G = G_0\exp\left(-\frac{U^*}{T - T_\infty}\right)\exp\left(-\frac{KT_d^0}{T\Delta T}\right) \qquad (8)$$

Four parameters, G_0, U^*, T_∞ and K, are determined for each concentration by fitting equation (8) to the growth rates in *Figure 5* by the least-squares method. The results are given in *Table 2*, and $\log\{G\exp[U^*/(T - T_\infty)]\}$ is plotted against $T_d^0/T\Delta T$ in *Figure 7*. A nearly linear relation is obtained for each concentration except for

Table 2 The best-fit values of parameters in equation (8)

Concentration (%)	G_0 (μm h^{-1})	U^* (K)	T_∞ (°C)	K (K)
Melt	8.3×10^4	570	66	190
50	4.4×10^6	1000	−38	420
30	1.7×10^4	290	−10	410
0.1	1.1×10^6	1240	−80	750

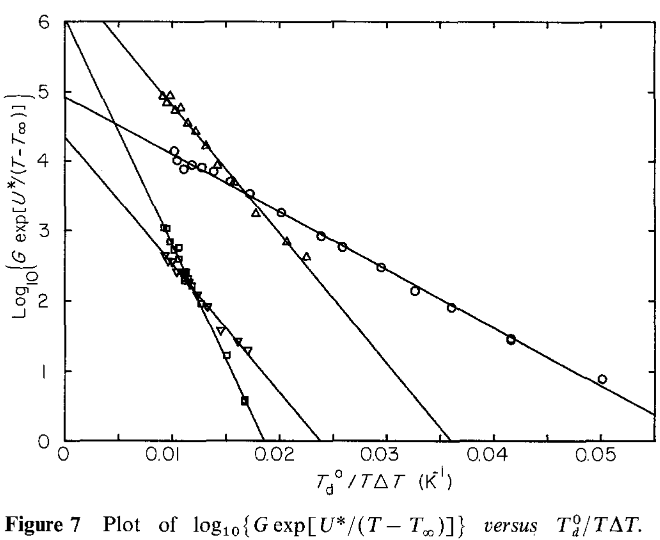

Figure 7 Plot of $\log_{10}\{G\exp[U^*/(T - T_\infty)]\}$ *versus* $T_d^0/T\Delta T$. Symbols are the same as in *Figure 5*

Table 3 The best-fit values of parameters in equation (9)

Concentration (%)	G'_0 (μm h^{-1})	T_0 (°C)	K (K)
Melt	1.9×10^8	5	230
50	3.0×10^8	-87	470
30	1.5×10^8	-120	590
0.1	3.4×10^7	-120	800

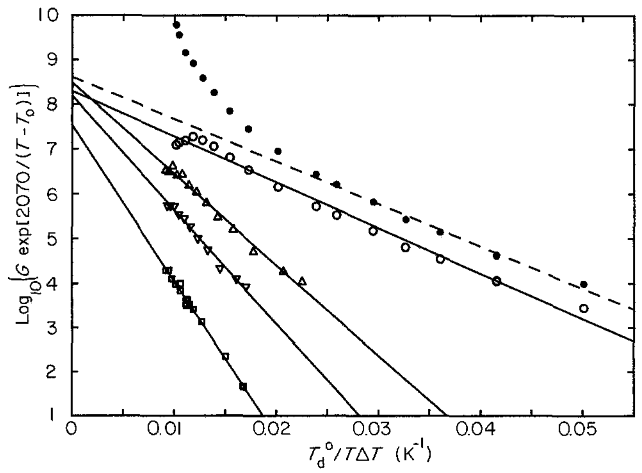

Figure 8 Plot of $\log_{10}\{G\exp[2070/(T-T_0)]\}$ *versus* $T_d^0/T\Delta T$. Symbols are the same as in *Figure 5*; (●) melt, $T_0 = 30$°C

$T < 135$°C of the melt growth. A similar deviation at high supercoolings can be observed in the results of Suzuki and Kovacs[1,10]. The value of G_0 depends on the concentration on the phase boundary, and the variation of T_∞ with concentration should be in accordance with that of T_g; G_0 and T_∞ will increase with concentration. The results shown in *Table 2* and *Figure 7* are not consistent with these anticipations. Further, the value of U^* also varies inconsistently with concentration. The large fluctuations in G_0, U^* and T_∞ are suggested to be due to too many fitting parameters, four, in equation (8). The value of K is insensitive to the fluctuations in the other parameters, because it is mainly determined by the growth rate at lower supercoolings. As shown in *Table 2*, K decreases with concentration.

Next, we examine the case in which the WLF equation is applied to $\beta(T)$. From equations (1) and (6), G is given by:

$$G = G'_0 \exp\left(-\frac{2070}{T-T_0}\right)\exp\left(-\frac{KT_d^0}{T\Delta T}\right) \qquad (9)$$

where G'_0 is a constant. The results of the least-squares method by equation (9) are given in *Table 3*. In *Figure 8*, $\log\{G\exp[2070/(T-T_0)]\}$ is plotted against $T_d^0/T\Delta T$. The number of parameters in equation (9), G'_0, T_0 and K, is three, less by one than that in equation (8). The data fitting to the experimental results by equation (9) is accordingly poorer, while the values of G'_0 and T_0 vary reasonably with concentration. The value of K decreases with concentration in this case, too.

According to the dielectric relaxation of iPS, the relaxation time of micro-Brownian motion above T_g is expressed by the WLF equation with $T_0 = 30$°C[18]. In *Figure 8*, $\log(G/\beta)$ for the melt growth with $T_0 = 30$°C is shown by full circles, and a broken straight line is drawn for the growth rates at temperatures higher than 195°C; the value of K is 220 K. The deviation from the broken line may indicate that micro-Brownian motion on boundary surfaces is different from that for primary relaxation to give a value for T_0 different from 30°C.

In the melt crystallization, no transition from regime II to regime I is observed in our sample, in contrast to the results reported by Bassett[19]. The existence of a regime transition from II to I may well depend on the molecular weight and/or the tacticity.

It can be concluded that equation (1) for secondary nucleation approximately holds for each concentration except for high supercoolings in melt growth. However, the growth faces are rough at ΔT higher than 50 K for melt growth and 80 K for the 30% and 0.1% solutions. Therefore, equation (1), which is generally regarded to be derived for secondary nucleation, is still valid at supercoolings where nucleation is not present.

In the limit of high supercooling, crystals grow by rough-surface growth. Hence κ is given by equation (5) and scarcely depends on supercooling. It seems that the limit has not been observed in the range of supercooling studied.

It is suggested in ref. 7 that there should be an intermediate growth mode between lateral growth controlled by nucleation and adhesive growth on kinetically rough growth faces; the free energy barrier for nucleation is small or zero but the probability P_α of attachment of segments creating a step of length l is still appreciably larger than that of attachment at a step, P_β. The probability P_α is proportional to $\exp[-(2bl\sigma-\Delta g)/k_BT]$ and P_β is proportional to $1-\exp[-(\Delta g-2ab\sigma_e)/k_BT]$, where σ is the side surface free energy, Δg is the free energy gain by crystallization of a stem of length l, a is the width of a crystallizing segment and k_B is the Boltzmann constant. If l is given by $\delta l + 2\sigma_e T_d^0/\Delta h_f \Delta T$, where δl is nearly constant, and further if G is proportional to $(P_\alpha P_\beta)^{1/2}$ (refs 16, 20), then G is approximately given by equation (1) and K is given by the same expression as that of regime II growth:

$$K = 2b\sigma\sigma_e/k_B\Delta h_f \qquad (10)$$

where b is the thickness of a segment. Because the value of K is rather insensitive to the form of $\beta(T)$, we use the value of K given in *Table 3*. Assuming a zig-zag fold plane[7], b is taken to be 11 Å. Under the above assumptions the value of $\sigma\sigma_e$ can be obtained by equation (10). The results are summarized in *Table 4*; $\sigma\sigma_e$ increases with decreasing concentration. This is in contrast to the case of polyethylene; little difference in $\sigma\sigma_e$ is reported between melt growth (1400 erg^2 cm^{-4} (ref. 1)) and solution growth (1300 (ref. 1), 1100 (ref. 21) erg cm^{-4}).

Table 4 Thermodynamic parameters deduced from the growth rate and d.s.c.

Concentration (%)	$\sigma\sigma_e$ (erg^2 cm^{-4})	σ_e (erg cm^{-2})	σ (erg cm^{-2})
Melt	130	28.8[a]	4.7
50	270	–	–
30	340	42	8.0
0.1	460	45[b]	10

[a] From ref. 15

[b] Estimation from the 10% and 2% solutions (ref. 7)

Even if the experimental errors are taken into account in deducing the values of σ_e from d.s.c. measurements, σ obviously increases with decreasing concentration. Because Δh_f is approximately constant with concentration, the concentration dependence of σ may result from the entropy term in σ. The larger σ gives the larger free energy barrier for crystal growth. The growth rate of iPS crystals is severely affected by the kind of solvent[22]. It is therefore suggested that, in the case of iPS, the value of σ and hence the growth rate strongly depend not only on concentration but also on the kind of solvent.

REFERENCES

1 Hoffman, J. D., Davis, G. T. and Lauritzen, J. I. Jr in 'Treatise on Solid State Chemistry' (Ed. N. B. Hannary), Plenum, New York, 1976, Vol. 3, Ch. 7
2 Toda, A., Kiho, H., Miyaji, H. and Asai, K. *J. Phys. Soc. Jpn* 1985, **54**, 1411
3 Mansfield, M. L. *Polymer* 1988, **29**, 1755
4 Kiho, H., Miyamoto, Y. and Miyaji, H. *Polymer* 1986, **27**, 1505
5 Tanzawa, Y., Miyaji, H., Miyamoto, Y. and Kiho, H. *Polymer* 1988, **29**, 904
6 Miyamoto, Y., Tanzawa, Y., Miyaji, H. and Kiho, H. *J. Phys. Soc. Jpn* 1989, **58**, 1879
7 Tanzawa, Y. *Polymer* to be published
8 Point, J. J. *Faraday Disc. R. Soc. Chem.* 1979, **68**, 167
9 Sadler, D. M. and Gilmer, G. H. *Polymer* 1984, **25**, 1446
10 Suzuki, T. and Kovacs, A. J. *Polym. J.* 1970, **1**, 82
11 Bassett, D. C. and Vaughan, A. S. *Polymer* 1985, **26**, 717; 1988, **29**, 1397
12 Keith, H. D. and Padden, F. J. Jr *J. Polym. Sci. (B) Polym. Phys.* 1987, **25**, 2371
13 Okada, T., Saito, H. and Inoue, T. *Macromolecules* 1990, **23**, 3868
14 Mandelkern, L. in 'Crystallization of Polymers', McGraw-Hill, New York, 1964, Ch. 3
15 Edward, B. C. and Phillips, P. J. *Polymer* 1974, **15**, 351
16 Sadler, D. M. *Polymer* 1987, **28**, 1440
17 Williams, M. L., Landel, R. E. and Ferry, J. D. *J. Am. Chem. Soc.* 1955, **77**, 3701
18 Fukao, K., Miyamoto, Y. and Miyaji, H. in preparation
19 Bassett, D. C. *CRC Crit. Rev. Solid State Mater. Sci.* 1984, **12**, 97
20 Sadler, D. M. and Gilmer, G. H. *Phys. Rev. (B)* 1988, **38**, 5684
21 Toda, A., Miyaji, H. and Kiho, H. *Polymer* 1986, **27**, 1505
22 Keith, H. D., Vademsky, R. G. and Padden, F. J. Jr *J. Polym. Sci. (A-2)* 1970, **8**, 1687