# Crystallization and melt behaviour of isotactic poly(2-vinylpyridine)

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The crystallization and melting behaviour of highly isotactic poly(2-vinylpyridine) (it-P2VP) with $\bar{M}_v = 4 \times 10^5$ has been studied by microscopy and d.s.c.. The maximum spherulitic growth rate was found to be $250 \times 10^{-3}$ µm/min at a crystallization temperature $T_c$ of 165°C. Experimental data could be described by the growth rate theory for small supercooling, by taking the appropriate value of 75 for the constant $c_2$ of the WLF equation. The chain-folded surface free energy $\sigma_e$, was estimated at $39.5 \times 10^{-3}$ J m$^{-2}$. The melting curves showed 1,2 or 3 melting endotherms. At large supercooling, crystallization from the melt produced a small melting endotherm just above $T_c$. This peak may originate from secondary crystallization of melt trapped within the spherulites. The next melting endotherm is related to the normal primary crystallization process. Its peak temperature increased linearly with $T_c$, yielding an extrapolated value for the equilibrium melting temperature $T_m^\circ$ of 212.5°C. At normal values of $T_c$ and heating rate a third endotherm appeared with a peak temperature that was independent of $T_c$, but rose with decreasing heating rate. From the effects of heating rate and partial scanning on the ratio of peak areas, it is concluded that this peak arises from secondary crystallization by continuous melting and re-crystallization during the scan. This crystallization and melting behaviour of it-P2VP is very similar to that of isotactic polystyrene.

**(Keywords: isotactic poly(2-vinylpyridine); crystallization; melt behaviour; differential scanning calorimetry; microscopy)**

## INTRODUCTION

In 1960 Natta *et al.*[1] reported the possibility of crystallizing isotactic poly(2-vinylpyridine) (it-P2VP) by refluxing in boiling acetone. Melting temperatures between 190°C and 212°C were generally found, determined with a polarizing microscope[2]. Puterman *et al.*[3] have determined the structure from X-ray fibre utilizing rigid-body least-square refinement techniques. They found that isotactic poly(2-vinylpryidine) exists as a threefold helix with three chains through a hexagonal unit cell having the dimensions $a = b = 15.49$ Å and $c = 6.56$ Å (fibre axis).

Up to now no detailed work on the melt behaviour of it-P2VP has been published. In the present paper we report on the spherulitic growth rate from the melt and the melt behaviour of bulk-crystallized isotactic poly(2-vinylpyridine).

## EXPERIMENTAL

Isotactic (it) P2VP was prepared using an organohafnium compound as catalyst[4,10]. The polymer contained more than 98% isotactic triads and had an $\bar{M}_v$ of 400 000 and a $T_g$ of 84°C. The tacticity was measured by means of $^{13}$C n.m.r. spectroscopy using a Nicolet NT 200 machine. The $\bar{M}_v$ was determined at 25°C in methanol using the relation[5] $[\eta] = 11.3 \times 10^{-5} \bar{M}_v^{0.73}$.

Films of about 10 µm thickness were obtained by evaporation of a 3 wt% methanol solution of it-P2VP on a glass slide. Before crystallization, films were first heated at 230°C for 1 min and then cooled down to a crystallization temperature, $T_c$. This was done in order to limit the number of nuclei for detecting separate crystals. A Zeiss polarizing microscope was used to measure growth rates ($G$). Because of the low growth rate photographs of the spherulites were taken at suitable intervals sometimes covering several days ($T_c \leqslant 120$°C). After enlarging the photographs it was possible to measure the diameter of the spherulites. The magnifications were calibrated using a calibrated slide with a micrometer. For temperature control we used a hot stage plate (Mettler FP5). The temperature was constant to within 0.2°C.

Glass transition and melting temperatures were measured with a differential scanning calorimeter Perkin Elmer DSC-2 at a scan speed of 5 K/min. For the determination of $T_m$'s after crystallizing at different $T_c$'s in the d.s.c., samples were used that were first heated up to 220°C, then quenched directly to a temperature below $T_g$ (60°C) and finally heated up to the required $T_c$. Heats of fusion and melting temperatures were determined as a function of scan speed in the range of 2.5–20 K/min after crystallization via quenching to the glassy state and subsequent heating to 130°C.

Such a thermal history which differs from that applied to samples for measuring growth rates, does not affect the $T_m$ of the finally crystallized material, but strongly enhances the rate of crystallization equalling that of isotactic polystyrene (it-PS)[6]. This is of advantage in view of the rapid thermal degradation of poly(2-vinylpyridine) (it-P2VP) in the melt.

## RESULTS AND DISCUSSION

### *Crystallization behaviour*

In *Figure 1*, the average values of the spherulitic diameters are plotted against the crystallization time for

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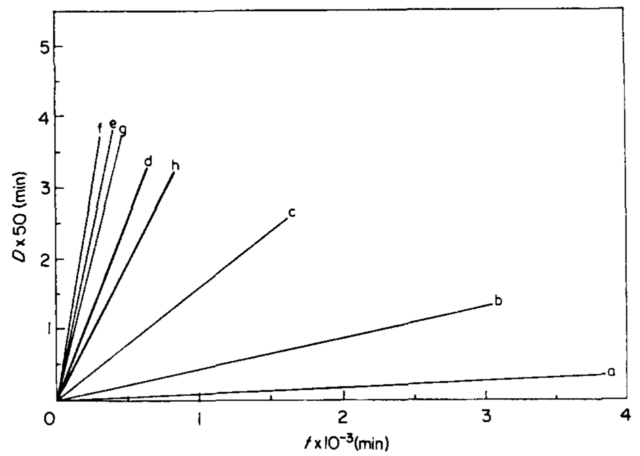

**Figure 1** Spherulitic growth of it-P2VP for various $T_c$: (a) 115°C, (b) 125°C, (c) 135°C, (d) 145°C, (e) 155°C, (f) 170°C, (g) 175°C, (h) 185°C

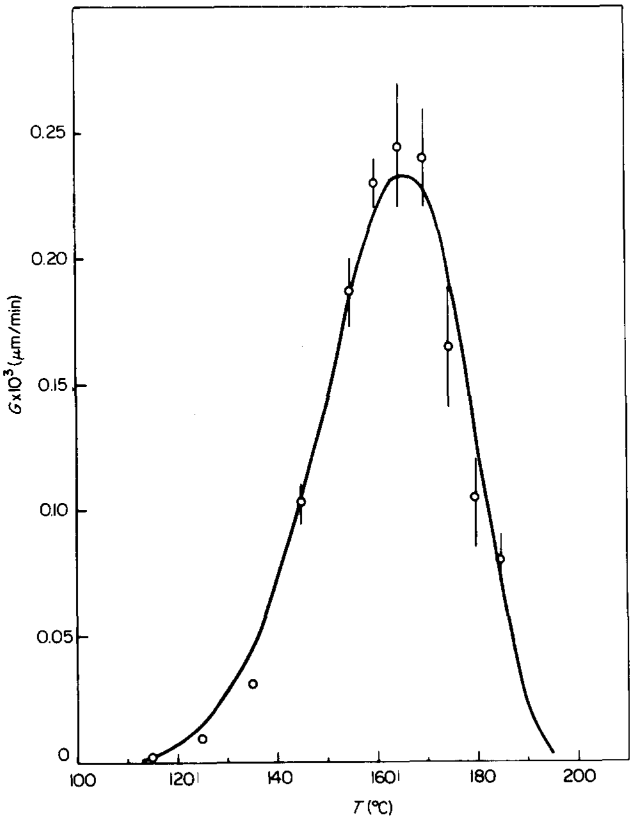

**Figure 2** Growth rate $G$ of it-P2VP as a function of crystallization temperature $T_c$. (○) Experimental values of average initial growth rate; (———) theoretical curve according to equation (4)

various $T_c$. Only initial slopes have been taken to calculate average growth rates, $G$, because of thermal degradation which increases with time, causing a decrease in growth rate. Particularly at $T_c$'s above 185°C excessive thermal degradation led to useless non-linear curves. Consequently no self-seeding procedure could be applied either. In *Figure 2* $G$ values are plotted against $T_c$. It shows a maximum value, $G_{max}$, of about $250\times10^{-3}$ $\mu$m/min for the used it-P2VP, which is nearly similar to the $G_{max}$ of $200\times10^{-3}$ $\mu$m/min of isotactic polystyrene (it-PS) of comparable $\bar{M}_v$.[7] It should be kept in mind that $G_{max}$ is influenced by molecular weight and tactic purity of the polymer.

*Figure 3* shows some typical micrographs of spherulites of it-P2VP at different $T_c$. At temperatures higher than about 160°C the spherulites had about the same diameter (*Figure 3c*). At $T_c<160$°C spherulites with different diameters appeared (*Figure 3b*) and the number of spherulites increased at decreasing $T_c$ (*Figure 3a*), but the number of nuclei seemed to reach an end value.

### *Melting behaviour*

Typical d.s.c. melting curves of it-P2VP samples crystallized in the melt at various crystallization temperatures, $T_c$, are shown in *Figure 4*. The melting points, $T_m$, are collected in a $T_m$ vs. $T_c$ diagram as shown in *Figure 5*. These melting endotherms appear after crystallization at tem-

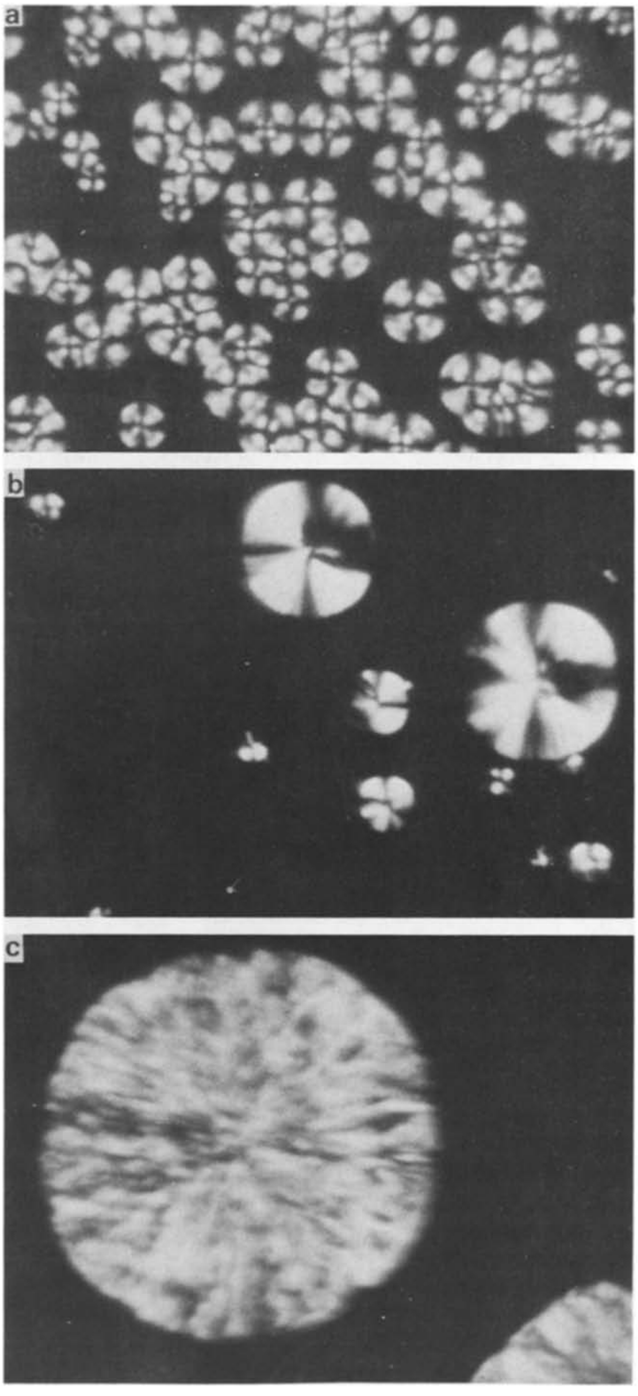

**Figure 3** Light microscopic photographs between crossed nicols of spherulites of it-P2VP at different $T_c$: (a) $T_c$=115°C, crystallization time ($t_c$)=4 days (b) $T_c$=145°C, $t_c$=8 h; (c) $T_c$=175°C, $t_c$=8 h. Magnification 500x

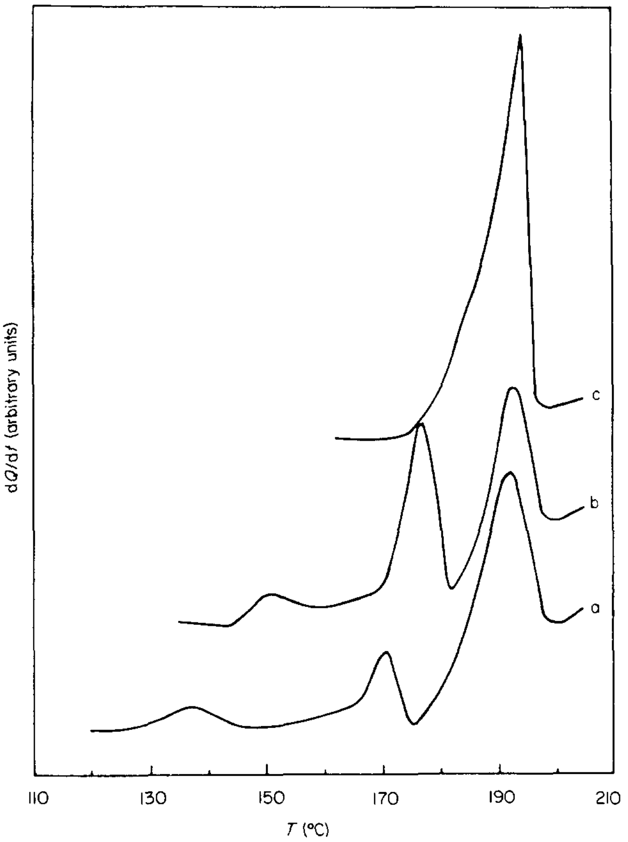

**Figure 4** D.s.c. melting endotherms of it-P2VP crystallized at different $T_c$ (a) 120°C; (b) 140°C; (c) 170°C. Heating rate: 5 K/min

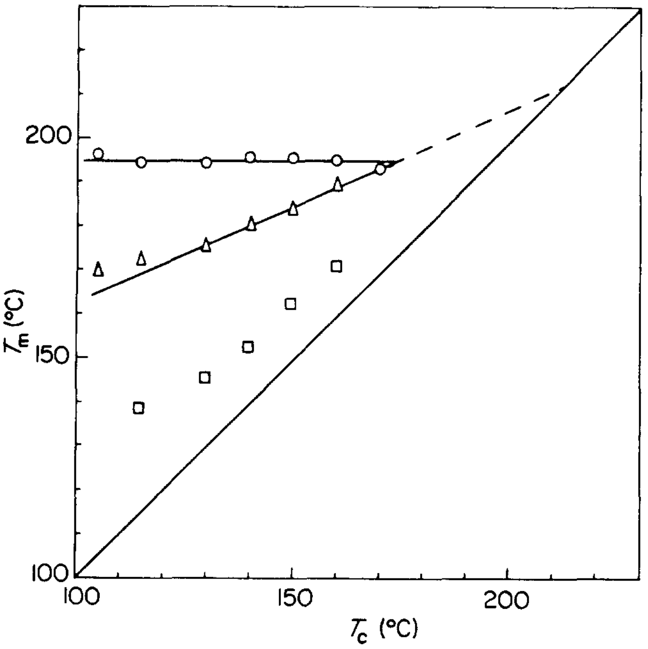

**Figure 5** Peak melting temperatures $T_m$ of it-P2VP as a function of crystallization temperature $T_c$. Heating rate: 5 K/min

peratures below 170°C: a small endotherm always lying just above $T_c$, a low melting peak (LM) at temperatures depending on $T_c$ and a high melting peak (HM) at constant temperature of 195°C. Extrapolating the $T_{LM}$-line having a slope of 0.44, to $T_m = T_c$ gives $T_m^\circ = 212.5$°C. This $T_m^\circ$ is only an approximation because of the extrapolation over a large distance. The $T_{LM}$ in *Figure 5* are recorded with a scan speed of 5 K/min. To correct for possible superheating effects, thermograms of samples crystallized at one $T_c$ of 130°C for two hours were recorded at different scan speeds. *Figure 6* shows no influence of scan speed on $T_{LM}$, so no correction is necessary in this case. $T_{HM}$, however, slowly decreased with increasing scan speed (see also *Table 1*). The areas under the HM peak increased and those under the LM peak decreased with decreasing scan speed (*Table 1*). All these results point to a recrystallization of it-P2VP. Direct proof of recrystallization during melting is the effect of partially scanning crystallized samples as shown in *Figure 7* ($T_c = 130$°C). If double melting originates from melting of two morphologically different crystal structures, one expects on rescanning only the HM peak having the same heat of fusion as the HM peak in the original sample. On the other hand, if the HM peak has a heat of fusion equal to that of the sum of the LM peak and HM peak in the original sample then this is proof that recrystallization has taken place. The latter case appeared to be valid for the it-P2VP sample.

The exhibited multiple melting behaviour of it-P2VP parallels completely that of it-PS including the small peak, melting just above $T_c$.[8] This may be expected because of the structural similarity of the two polymers. Lemstra *et al.*[9] demonstrated for it-PS that this small peak was due to secondary crystallization. They proposed the following mechanism: during crystallization numerous tie molecules are formed, especially at rather large super cooling. These tie molecules can aggregate locally to form intercrystalline links that form imperfect crystals with a low melting point. This interpretation may be applied to the present case as well.

## ESTIMATION OF GROWTH RATE PARAMETERS

The growth rate of spherulites (secondary nucleation) can be theoretically given by[11-13]

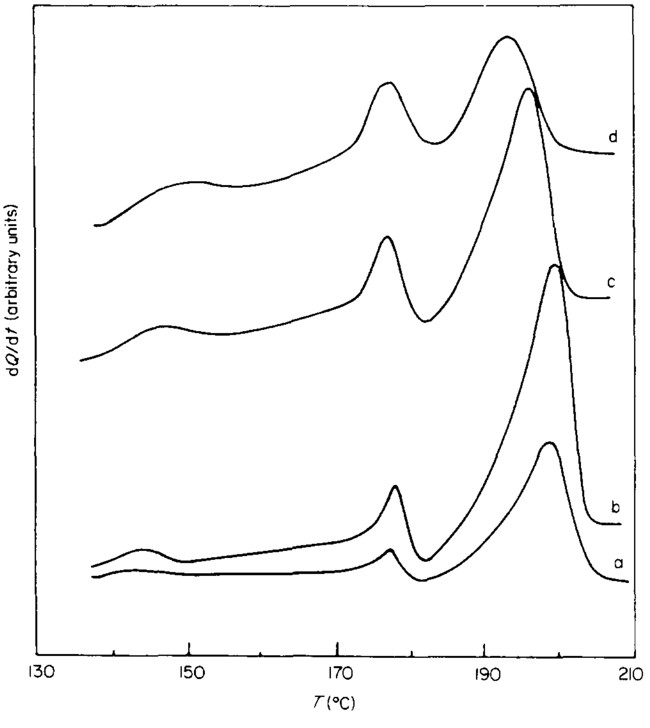

**Figure 6** Effect of heating rate on d.s.c. melting curves of it-P2VP at $T_c$=130°C: (a) 2.5 K/min; (b) 5 K/min; (c) 10 K/min; (d) 20 K/min

**Table 1** Low-melting (LM) and high-melting (HM) peak temperatures and heats of fusion as a function of heating rate of isotactic poly(2-vinylpyridine) crystallized at 130°C

| Heating rate (K/min) | $T_{LM}$ (°C) | $T_{HM}$ (°C) | $\Delta H_{LM}$ (kJ mol$^{-1}$) | $\Delta H_{HM}$ (kJ mol$^{-1}$) | $\Delta H_{LM+HM}$ (kJ mol$^{-1}$) |
|---|---|---|---|---|---|
| 2.5 | 177.5 | 198.5 | 0.14 | 1.93 | 2.07 |
| 5 | 177 | 199.5 | 0.20 | 1.72 | 1.92 |
| 10 | 177 | 190 | 0.42 | 1.56 | 1.98 |
| 20 | 177 | 199 | 0.67 | 1.02* | 1.69* |

*These lower values may be due to less recrystallization, because of the high scan speed, signifying that recrystallization is not very fast.

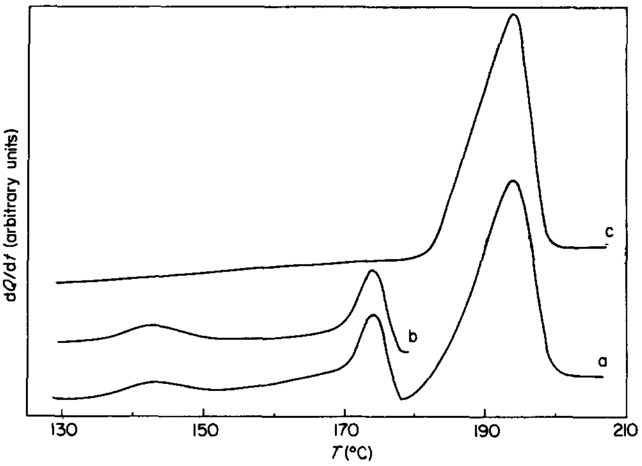

**Figure 7** Effect of partial scanning on the melting behaviour of it-P2VP crystallized at 130°C: (a) normal scan; (b) sample scanned just beyond the LM peak; (c) rescan of sample (b) after quenching to the glassy state. Heating rate: 5 K/min

$$G = G_0 \exp[-c_1c_2/(c_2 + T_c - T_g)]\exp(-4b_0\sigma\sigma_e/\Delta FkT_c) \quad (1)$$

wherein $G_0$ is a pre-exponential factor which is generally assumed to be constant or proportional to $T_c$. The first exponential factor, the transport factor, contains two constants, $c_1$ and $c_2$, originating from the empirical relationship for viscous flow given by Williams, Landel and Ferry[14]. In the second exponential factor $b_0$ is the thickness of a monomolecular layer on the crystal surface, $\sigma$ and $\sigma_e$ are interfacial free energies per unit area respectively parallel and perpendicular to the molecular chain direction of the growing crystal, $k$ is the Boltzmann constant, and $\Delta F$ is the Gibbs free energy difference per unit volume between the supercooled melt and the crystalline phase. $\Delta F$ can be approximated by[13]

$$\Delta F = \Delta H \cdot \Delta T / T_m^\circ \quad (2)$$

where $\Delta H$ is the heat of fusion per unit volume and $\Delta T$ is the degree of supercooling $T_m^\circ - T_c$. Substitution of equation (2) into equation (1) yields:

$$G = G_0 \exp[-c_1c_2/(c_2 + T_c - T_g)]\exp[-b_0\sigma\sigma_e T_m^\circ/(\Delta HkT_c\Delta T)] \quad (3)$$

When $\ln G + c_1c_2/(c_2 + T_c - T_g)$ is plotted vs. $1/T_c\Delta T$ with $T_g = 357$ K and $T_m^\circ = 485.5$ K a straight line should be obtained provided that appropriate values for $c_1$ and $c_2$ are chosen. In principle several combinations ($c_1$,$c_2$) are possible. Usually $c_1c_2 = 2060$ K.[14] The magnitude of $c_2$ was selected from values in the range of 50–100 K. *Figure 8* shows that a straight line is obtained when $c_2 = 75$ K, this value thus giving the best agreement with theory. This straight line, drawn through all experimental points excepting the three strongly supercooled ones, leads to $G_0 = 9.06 \times 10^6$ μm/min and a slope of $8.87 \times 10^4$ K$^2$. Substituting these and the relevant values for $T_g$ and $T_m^\circ$ in equation (3) yields:

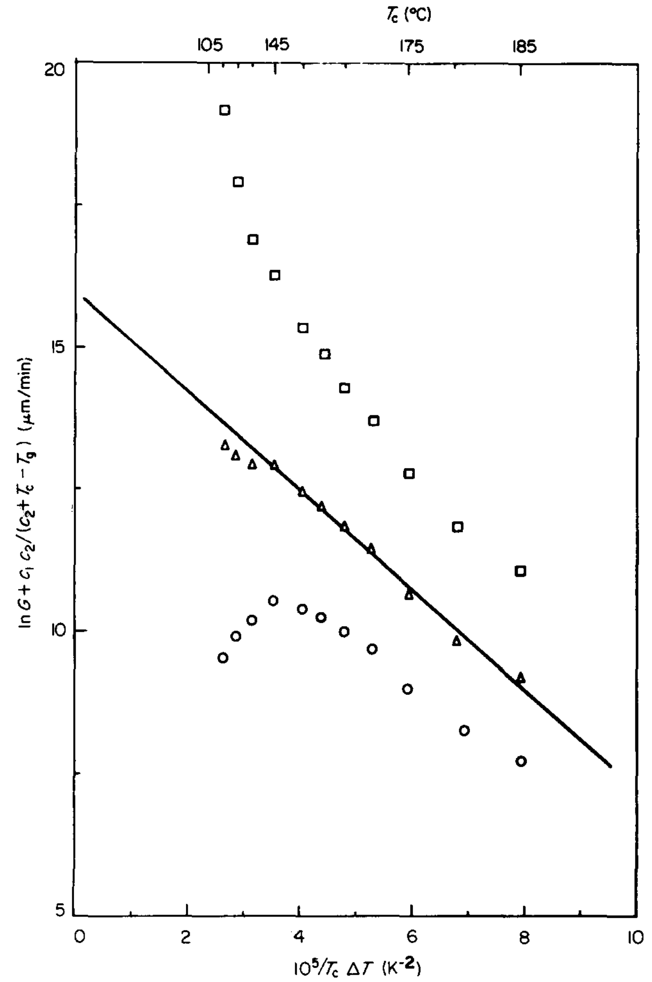

**Figure 8** Plots of $\ln G + c_1c_2/(c_2 + T_c - T_g)$ vs. $1/T_c\Delta T$ for three different values of $c_2$: (□) $c_2 = 50$ K; (△) $c_2 = 75$ K; (○) $c_2 = 100$ K. $c_1c_2 = 2060$; $T_g = 357$ K and $T_m = 485.5$ K

$$G = 9.06 \times 10^6 \exp\left[-\frac{2060}{T_c - 282}\right]\exp\left[\frac{8.87 \times 10^4}{T_c(485.5 - T_c)}\right] \quad (4)$$

In *Figure 2* the theoretical curve of $G$ is shown to fit the experimental data reasonably. From the slope of curve 2 in *Figure 8* it is possible to make an estimation of $\sigma\sigma_e$ since:

$$4b_0\sigma\sigma_e T_m^\circ / k\Delta H = 8.87 \times 10^4 \text{ K}^2 \quad (5)$$

The value of $b_0 = 4 \times 10^{-10}$ m was estimated according to

**Table 2** Growth rate parameters and other data of it-P2VP and it-PS

| | $\bar{M}_v \times 10^{-3}$ | $G_{max}$ (μm/min) | $T_g$ (K) | $T_m^\circ$ (K) | $c_2$ (K) | $b_0 \times 10^{-10}$ (m) | $\Delta H \times 10^{-6}$ (J m$^{-3}$) | $\sigma\sigma_e \times 10^4$ (J$^2$ m$^{-4}$) | $G_0 \times 10^{-3}$ (μm/min) | $\sigma \times 10^3$ (J m$^{-2}$) | $\sigma_e \times 10^3$ (J m$^{-2}$) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| it-P2VP | 400 | 0.25 | 357 | 485.5 | 75 | 4 | 81 | 1.28 | 9060 | 3.2 | 39.5 |
| it-PS[7,11] | 390 | 0.20 | 360 | 513 | 75 | 5.5 | 86 | 1.21 | 9100 | 4.7 | 25.7 |

the method proposed by Suzuki *et al.*[15] for it-PS, using the d-spacing of the 110 plane determined by Lando *et al.*[3] for the unit cell of it-P2VP. $\Delta H$ of it-P2VP was estimated from $T_m^\circ = \Delta H/\Delta S$ assuming the entropy of fusion $\Delta S$ for it-P2VP to be the same as that for it-PS. Using $T_m^\circ = 513$ K and $\Delta H = 86 \times 10^6$ J m$^{-3}$ of it-PS[11] to calculate $\Delta S$ one gets $\Delta H = 81 \times 10^6$ J m$^{-3}$ for it-P2VP. Substituting these values of $b_0$ and $\Delta H$ in equation (5) yields:

$$\sigma\sigma_e = 1.28 \times 10^{-4}\ \text{J}^2\ \text{m}^{-4} \qquad (6)$$

To calculate $\sigma$ and $\sigma_e$ use is made of the empirical relation[16]:

$$\sigma = \alpha b_0 \Delta H \qquad (7)$$

with $\alpha = 0.1$ for the lateral surface of a chain type crystal[13]. Combination of equations (6) and (7) gives $\sigma = 3.24 \times 10^{-3}$ J m$^{-2}$ and $\sigma_e = 39.5 \times 10^{-3}$ J m$^{-3}$.

The crystallization parameters and some other data of it-P2VP are listed in *Table 2* together with those of it-PS. It is seen that there are only minor differences between the growth rate parameters of the two polymers, confirming the great similarity of their crystallization behaviour.

## ACKNOWLEDGEMENT

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## REFERENCES AND NOTES

1 Natta, G., Mazzanti, G., Dall'Asta, G. and Longi, P. *Makromol. Chem.* 1964, **37**, 160

2 Natta, G., Mazzanti, G., Longi, P., Dall'Asta, G. and Bernardini, F. *J. Polym. Sci.* 1961, **51**, 487

3 Puterman, M., Kolpak, F. J., Blackwell, J. and Lando, J. B. *J. Polym. Sci., Polym. Phys. Edn.* 1977, **15**, 805

4 Meijer-Veldman, M., manuscript in preparation

5 Arichi, S. *Bull Chem. Soc. Jpn.* 1966, **39**, 439

6 Boon, J., Challa, G. and van Krevelen, D. W. *J. Polym. Sci., A-2* 1968, **6**, 1835

7 Lemstra, P. J., Postma, J. and Challa, G. *Polymer* 1974, **15**, 757

8 Lemstra, P. J., Kooistra, T. and Challa, G. *J. Polym. Sci., A-2* 1974, **10**, 823

9 Lemstra, P. J., Schouten, A. J. and Challa, G. *J. Polym. Sci., A-2* 1974, **12**, 1565

10 Highly isotactic P2VP, prepared with phenylmagnesium bromide according to Natta *et al.*[2] crystallized only extremely slowly from the melt for as yet unknown reasons. It did crystallize to some extent by treatment in boiling acetone as has been mentioned before[1]. Samples of it-P2VP, prepared with benzyl-picolyl magnesium and obtained through the courtesy of Prof. T. E. Hogen-Esch, University of Florida, Gainesville, did crystallize well from the melt, but the quantities were too small to permit a detailed study

11 Boon, J., Challa, G. and van Krevelen, D. W. *J. Polym. Sci., A-2* 1968, **6**, 1791

12 Hoffman, J. D. and Weeks, J. J. *J. Chem. Phys.* 1962, **37**, 1723

13 Hoffman, J. D. *SPE Trans.* 1964, **4**, 315

14 Williams, M. L., Landel, R. F. and Ferry, J. D. *J. Am. Chem. Soc.* 1955, **77**, 3701

15 Suzuki, T. and Kovacs, A. J. *Polym. J.* 1970, **1**, 82

16 Thomas, D. G. and Staveley, L. A. K. *J. Chem. Soc.* 1952, 4569