

Studies on the Melt Spinning of Nylon 6. II. Effect of Heating the Threadline upon Orientation and Crystallization

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Synopsis

The effect of heating nylon 6 threadline in a spinning tube upon its orientation and crystallization behavior was studied by measuring the filament birefringence Δn_H at the outlet of the spinning tube, the conditioned filament birefringence Δn_∞ after take-up, the filament densities and crystallinities of the γ -form, and by calculating the relative crystallinity of the threadline. Results were as follows: When the filament mean temperature $\overline{\theta_s(x)}$ in the spinning tube was about 80°C, the birefringence Δn_H showed a peculiar behavior in that, at this temperature, the Δn_H value decreased due to partial melting of the semistable molecular structure of the threadline that had been formed before the inlet of the spinning tube. And, when the temperature was over about 80°C, the Δn_H value increased due to the setting in of crystallization. The relative crystallinity χ of the threadline was calculated using the kinetic theory of nonisothermal crystallization neglecting the entropy effect of molecular orientation. Assuming that the crystal growth was spherulitic rather than fibroid, the calculated χ values approximately agreed with the experimental results.

INTRODUCTION

In a previous paper,¹ the authors and co-workers measured and discussed the cooling, thinning, and orientation of nylon 6 threadline in melt spinning. In another paper,² the authors studied the orientation mechanism in the melt spinning process and proposed that the orientation mechanism was the same as in the initial orientation in the drawing of amorphous and unoriented nylon 6 undrawn filament.

Polyethylene and polypropylene are known to develop considerable crystallization in melt spinning as, for example, Nakamura's study³ using x-ray analysis has shown. But in the case of nylon 6, as the report of Ruscher et al.⁴ shows, distinctive crystallization has not been found in x-ray diffraction photographs of the undrawn filament yarn directly after take-up under industrial spinning conditions. For these conditions, no literature is available on the orientation and crystallization of nylon 6 threadline in melt spinning for the case in which the threadline is heated in the spinning tube after the completion of thinning in the conventional manner.

In the present work, the effect of heating the nylon 6 threadline in the spinning tube after cooling and thinning in a cooling chamber upon its orien-

TABLE I
Experimental Melt Spinning Conditions^a

Experimental No.	Take up velocity, v_{Tu} cm/sec	Extruding rate, $Q \times 10^2$ g/sec
1	500	1.53
2	1000	3.05
3	1667	5.08

^a Number-average molecular weight of extruded polymer, $\bar{M}_n = 19000$; diameter of nozzle, 2.5×10^{-2} cm; quench air, natural convection; diameter of filament at takeup, constant (6×10^{-4} cm).

tation and crystallization behavior was studied. Furthermore, with regard to crystallization of nylon 6 threadline in melt spinning, a theoretical calculation was carried out and discussed in comparison with experimental results.

EXPERIMENTAL

Method and Conditions of Experiments

The melt spinning apparatus shown in Figure 1 was used. This apparatus is made up of a spinning head, cooling chamber, and spinning tube and was used in a previous study.¹ Table I shows the major spinning conditions. Under these conditions, the cooling and thinning of the threadline were completed in the cooling chamber.¹ The mean temperature of the threadline in the spinning tube was varied from room temperature to 140°C by means of heating the spinning tube externally under the spinning condition shown Table I (exps. 1, 2, and 3).

Measurements

Birefringence Δn_H of Running Threadline at Outlet of Spinning Tube. The instrument for the measurement of Δn_H was set at position H, as shown in Figure 1. It is identical to the instrument in the previous paper.¹

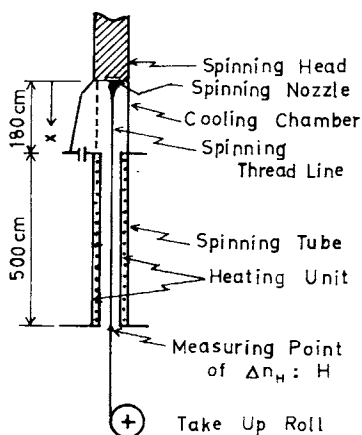


Fig. 1. Scheme of melt spinning apparatus.

Conditioned Filament Birefringence Δn_∞ After Take-up. Δn_∞ was measured by polarized microscope and Berek compensator, after conditioning the filament yarn sample for a time more than 15 hr in a 20°C, 50% R.H. atmosphere so that the sample fully develops spontaneous extension.

Filament Yarn Density. A density gradient tube was used to measure the undrawn filament yarn density at 25°C both immediately after take-up and after subsequent conditioning as mentioned above.

Crystallinity in γ -Form. An x-ray diffractometer was used to measure the crystallinity in the γ -form of the conditioned yarn. The x-ray diffraction patterns of the yarns all showed the equatorial reflection $(\frac{001}{200})$. In the x-ray diffraction method, it is difficult to distinguish between the equatorial reflection $(\frac{001}{200})$ from γ -form crystals and the reflection from the semicrystalline phases.⁵ However, it has been shown⁶ that the thermally unstable semicrystalline phase exhibits considerable transition to the α -form by boiling water treatment for 30 min, but the thermally stable γ -form crystals do not exhibit transition to other crystalline phases by the same treatment. On account of this, we took x-ray diffraction patterns of undrawn filament samples boiled in water for 30 min, by means of wide-angle x-ray diffraction method and defined the measure of the degree of crystallinity in γ -form crystals as the ratio of the intensity I_γ of the reflection from γ -form crystals over the integral intensity I_t . That is, I_t is the integral of the reflections (200) and $(\frac{002}{202})$ from α -form crystals and of the reflection $(\frac{001}{200})$ from γ -form crystals.

RESULTS AND DISCUSSION

Effect on Orientation of Heating the Running Threadline in the Spinning Tube

Figure 2 shows the Δn_H and Δn_∞ values plotted against the filament mean temperature $\bar{\theta}_s(x)$ in the spinning tube. The Δn_H -versus- $\bar{\theta}_s(x)$ curves show

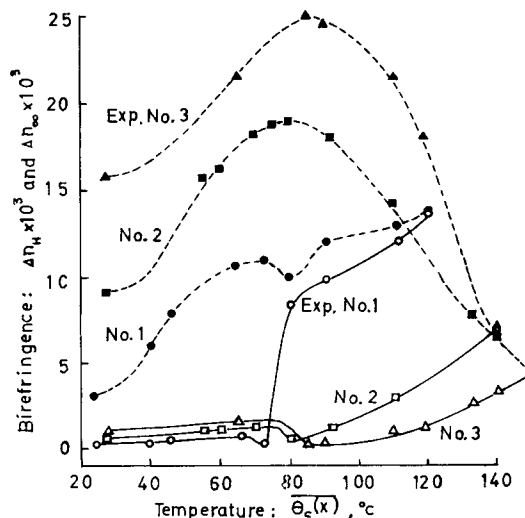


Fig. 2. Plot of birefringences Δn_H (open marks) and Δn_∞ (solid marks) against filament mean temperature $\bar{\theta}_s(x)$ in the spinning tube for different spinning conditions (exp. 1-3).

different behavior according to the temperature ranges (i) $\overline{\theta_s(x)} < 70^\circ\text{C}$, (ii) $70^\circ\text{C} < \overline{\theta_s(x)} < 85^\circ\text{C}$, and (iii) $\overline{\theta_s(x)} > 85^\circ\text{C}$. In the temperature region (i), the Δn_H value slightly increases with increasing temperature $\overline{\theta_s(x)}$ and is lowest in the case of exp. 1. However, in the temperature region (ii), the Δn_H values show a dip before they rise steeply in the temperature region (iii). This is assumed to be due to the influence of the crystallization of the threadline. Namely, the unstable structure in the threadline formed before region (ii) partially remelts in region (ii) and becomes a forerunner-like state of the crystallization; therefore, the Δn_H also decreases. It is suggested that a relatively stable crystallization proceeded in region (iii). The Δn_H for exp. 1 that was lowest of the three curves on region (i) was the highest in region (iii) because of the longest residence time in the spinning tube.

On the other hand, the Δn_∞ shown in Figure 2 by the dotted curves increased in correspondence with increasing temperature $\overline{\theta_s(x)}$, making the ratio $\Delta n_\infty/\Delta n_H$ approximately constant in region (i). This phenomenon is estimated to be identical in nature to the spontaneous extension and increases in birefringence observed on nylon 6 filament yarns after take-up in the spinning process. In the next region, (ii), the Δn_∞ has a maximum value at temperature $\overline{\theta_s(x)}$ where the minimum value in Δn_H was observed. This may be interpreted as follows. The state of molecules in region (ii) being in a forerunner-like state of crystallization is likely to increase the spontaneous extension of the thread due to moisture absorption after take-up, considering the increased mobility of the molecular chain in region (ii). Figure 3 supports the above reasoning by showing the effect of temperature $\overline{\theta_s(x)}$ on the spontaneous extension in exp. 2. Figure 3 shows further the percentage of moisture absorption in a 20°C , 50% R.H. atmosphere. Although the percentage of moisture absorption is not affected by temperature $\overline{\theta_s(x)}$, the spontaneous extension increases with temperature $\overline{\theta_s(x)}$, forms a peak region (ii), and decreases sharply in region (iii). Furthermore, in region (iii), the birefringence difference $\Delta n_\infty - \Delta n_H$ decreases with $\overline{\theta_s(x)}$, making the Δn_∞ value approach the Δn_H value as shown in Figure 2.

This fact is likely due to the development of crystallization at a temperature $\overline{\theta_s(x)} > \text{about } 85^\circ\text{C}$, temperature region (iii), inducing a relatively stable fiber structure thereby suppressing the spontaneous extension due to moisture absorption.

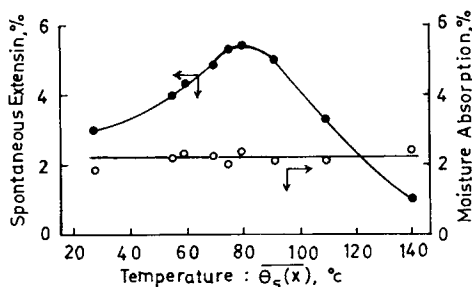


Fig. 3. Effects of temperature $\overline{\theta_s(x)}$ on spontaneous extension (solid circles) and moisture absorption (open circles) for exp. 2.

Effect on Crystallization of Heating the Running Threadline in the Spinning Tube

In the preceding section, the authors reasoned that the abrupt increase in Δn_H and decrease in the Δn_∞ in the temperature region (iii) was due to the development of crystallization. The purpose of this section is to verify the above reasoning.

Figure 4 shows the dependence of the density of yarns both nonconditioned (sampling immediately after take-up) and conditioned upon temperature $\theta_s(x)$ for the case of exp. 1. The densities suddenly start to increase at about 80°C. This behavior corresponds to the peculiarities of Δn_H , Δn_∞ , and spontaneous extension at about the same $\theta_s(x)$. Furthermore, the difference between the nonconditioned and the conditioned filament density decreases with increasing $\theta_s(x)$. These results support the reasoning in the preceding section.

Figure 5 shows the wide-angle x-ray diffraction patterns of the nylon 6 filament samples taken up under the condition of (a) $\theta_s(x) = 27^\circ\text{C}$ and (b) $\theta_s(x) = 110^\circ\text{C}$ and boiled in water for 30 min. The x-ray pattern of the former filament sample (a) shows the presence of two equatorial reflections (200) and $\begin{pmatrix} 002 \\ 202 \end{pmatrix}$ from α -form crystals, and the near absence of an equatorial reflection $\begin{pmatrix} 001 \\ 200 \end{pmatrix}$ from γ -form crystals. This means that the structure filament sample (a) before boiling water treatment is almost all semicrystalline phase. But the x-ray pattern of the latter filament sample (b) shows distinctly the equatorial reflection from γ -form crystals.

Figure 6 shows the dependence of the crystallinity I_γ/I_t in γ -form on temperature $\theta_s(x)$. The crystallinity in the γ -form suddenly starts to increase at temperature $\theta_s(x)$ of about 80°C again verifying the reasoning in the previous section. It can be reasoned that the increase in the I_γ/I_t value in the higher-temperature region, (iii), are the crystals in the γ -form formed by the heating of the spinning tube.

Calculation of Crystallinity in Melt Spinning

In developing a mathematical model for the calculation of the crystallinity in melt spinning, the following three problems have to be taken into consider-

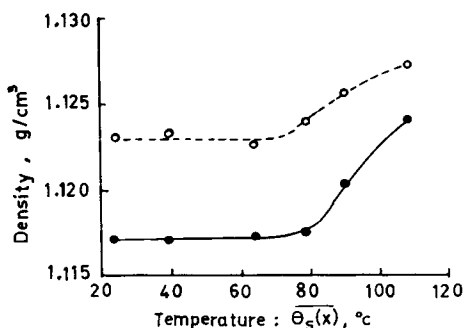
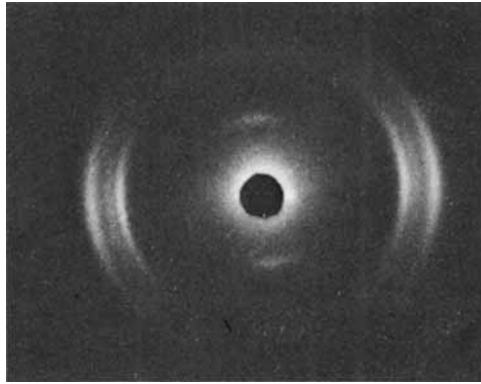
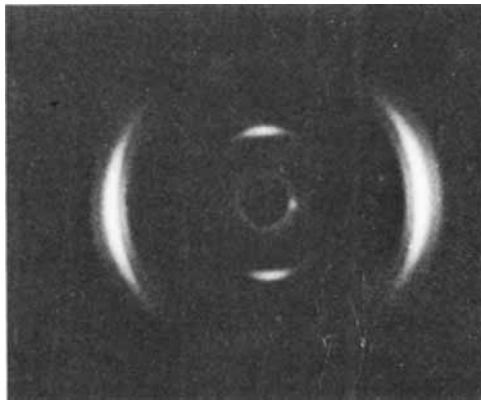


Fig. 4. Effects of temperature $\theta_s(x)$ on density for unconditioned filament (solid circles) and conditioned filament (open circles) in a 20°C, 50% RH atmosphere after take up.



(a)



(b)

Fig. 5. Wide angle x-ray diffraction patterns for $\overline{\theta_s(x)} = 27^\circ\text{C}$ (a) and $\overline{\theta_s(x)} = 110^\circ\text{C}$ (b).

ation. Problem I is that the crystallization in melt spinning occurs as a non-isothermal process. Concerning this problem, the authors analyzed the non-isothermal crystallization⁷ for water-quenched melt spinning of thick nylon 6 monofilament and have shown that relative crystallinity χ as a function of cooling time t and temperature θ is given by the following equation.

$$\begin{aligned} \chi[t, \theta(t)]_s &= 1 - \exp \left[-\frac{4}{3} \pi \int_0^t I[\theta(\tau)] \left\{ \int_\tau^t G[\theta(t)] dt \right\}^3 d\tau \right] \\ &= 1 - \exp \left[-\frac{4}{3} \pi \left\{ \sum_{i=1}^{i=n} I_i \Delta t_i \left(\sum_{j=i}^{j=n} G_j \Delta t_j \right)^3 \right\} \right] \end{aligned} \quad (1)$$

where I is homogeneous nucleation rate, G is spherulite growth rate, and i and j are integers. The dependences of G and I of nylon 6 on the temperature are⁸

$$\ln G(T) = \ln T + 3.25 - \frac{207.3T}{(T - 258.4)^2} - \frac{1.73 \times 10^5}{T(T_m - T)} \quad (2)$$

$$\ln I(T) = \ln T - 1.07 - \frac{207.3T}{(T - 258.4)^2} - \frac{2.56 \times 10^5}{T(T_m - T)} \quad (3)$$

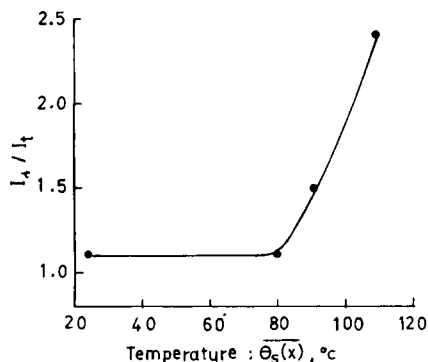


Fig. 6. Effect of temperature $\bar{\theta}_s(x)$ on I_s/I_t (γ - form crystallinity parameter) for exp. 2.

where T_m is melting point = 503°K and T is the absolute temperature. Equations (1) through (3) enable the calculation of χ_s from the temperature of threadline $\theta(t)$.

Problem II is that we do need to know whether the effect of the molecular orientation in melt spinning or the change in entropy⁹⁻¹¹ is negligible or not. Kobayashi et al.¹¹ derived the relation between the change in entropy ΔS_0 and birefringence Δn in polyethylene using Kuhn's equation¹²:

$$\Delta n = \frac{2\pi(\bar{n}^2 + 2)^2}{45\bar{n}} N(\alpha_1 - \alpha_2) \left(\lambda^2 - \frac{1}{\lambda} \right) \quad (4)$$

where \bar{n} is mean refractive index of the unoriented state, N is molecular chain number per unit volume, and $\alpha_1 - \alpha_2$ is the difference of main polarizability and from the equation of rubber elasticity

$$\Delta S_0 = -\frac{Nk}{2} \left(\lambda^2 + \frac{2}{\lambda} - 3 \right) \quad (5)$$

where k is Boltzman's constant.

Kobayashi et al. further derived theoretically the expressions for the ratios G_0/G and I_0/I , where G and I are for the case of bulk isothermal crystallization and G_0 and I_0 are for the case when molecular orientation proceeds with the crystallization. Numerical examples for polyethylene given by them are G_0/G in the order of 10^1 and I_0/I in the order of 10^4 when $\Delta n = 1 \times 10^{-3}$ and the crystallization temperature is 131°C.

Using these formulas, the estimated effect of molecular orientation on the crystallization in the melt spinning of nylon 6 may be computed. Figure 7 shows the relation between ΔS_0 and Δn obtained by substituting characteristic values of nylon 6 ($N = 3.5 \times 10^{21} \text{ cm}^{-3}$, $\bar{n} = 1.55$ and $\alpha_1 - \alpha_2 = 2.13 \times 10^{-24}$)² into eqs. (4) and (5) and by eliminating λ . On the other hand, nucleation rate is given as follows:

$$\frac{I}{T} = I_c \exp \left(-\frac{E_D}{kT} - \frac{\Delta F^*}{kT} \right) \quad (6)$$

where I_c is a constant not depending on temperature, E_D is the free energy of activation for transport across the liquid-nucleus interface, and ΔF^* is the

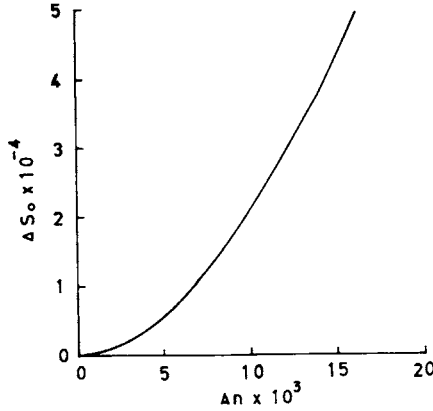


Fig. 7. Relation between birefringence Δn and change in entropy ΔS_0 .

free energy for the formation of critical nucleus. Since the $(T_m - T)^{-1}$ law holds^{8,13} on nylon 6,

$$\Delta F^* = \frac{4a\sigma_s\sigma_e}{\Delta f} \quad (7)$$

where a is a side length of crystal nucleus, σ_s is the lateral interfacial free energy, and σ_e is the interfacial free energy at the end surface. The free energy of fusion Δf is expressed as

$$\Delta f = (T_m - T)\Delta S \quad (8)$$

where ΔS is the entropy of fusion. Considering the change in entropy ΔS_0 under the molecular orientation after Kobayashi's concept,¹¹ we obtain

$$\Delta f = (T_m - T)(\Delta S - \Delta S_0). \quad (9)$$

Using eqs. (7), (8), and (9), eq. (6) becomes

$$\ln I(T) = \ln T + \ln I_c - \frac{E_D}{kT} - \frac{4a\sigma_s\sigma_e}{kT(T_m - T)(\Delta S - \Delta S_0)} \quad (10)$$

Considering that the same can be said of the spherulite growth rate G , eqs. (2) and (3) are

$$\ln G(T) = \ln T + 3.25 - \frac{207.3T}{(T - 258.4)^2} - \frac{7.98 \times 10^{11}}{T(T_m - T)(\Delta S - \Delta S_0)} \quad (11)$$

$$\ln I(T) = \ln T - 1.07 - \frac{207.3T}{(T - 258.4)^2} - \frac{1.18 \times 10^{12}}{T(T_m - T)(\Delta S - \Delta S_0)} \quad (12)$$

Since $\Delta S = \Delta h_u/T_m$, using $\Delta h_u = 23.2 \times 10^8 \text{ erg/cm}^3$ ¹³ and $T_m = 503^\circ\text{K}$ ⁸, $\Delta S = 4.16 \times 10^6 \text{ erg/cm}^3 \text{ deg}$ is obtained. Under the normal melt spinning condition, the Δn is 1.25×10^{-3} at the highest (for example, the Δn_H value of exp. 3 at the room temperature as shown in Figure 2). The ΔS_0 value corresponding to the above Δn value is $0.38 \times 10^3 \text{ erg/cm}^3 \text{ deg}$ from Figure 7. This value is negligibly small as compared with the ΔS value. In the case of the heating the spinning tube, the maximum Δn_H value is 13.6×10^{-3} (exp. 1 and $\theta_s(x) = 120^\circ\text{C}$ as shown in Fig. 2). The ΔS_0 value corresponding to this

maximum Δn_H value is 3.6×10^4 erg/cm³ deg. Using eqs. (11), (12), and (1), we calculated χ_s values under the above mentioned condition (exp. 1 and $\bar{\theta}_s(x) = 120^\circ\text{C}$). The results are as follows: χ_s is 0.75 by $\Delta S_0 = 0$ and 0.77 by $\Delta S_0 = 3.6 \times 10^4$ erg/cm³ deg. The difference is very small. After all, in the calculation of the crystallinity in melt spinning of nylon 6, the change in entropy based upon the molecular orientation is negligible. However, in the exceptional case of the higher-speed spinning condition, it is estimated that the ΔS_0 value is not negligible.

Problem III is that we do need to know the mode of crystal growth. Although eq. (1) was derived assuming that the mode of crystal growth is spherulitic, one-dimensional fibrillar growth is usually assumed in analyzing crystal growth under molecular orientation. Assuming that G and I given in eq. (1) are applicable in the case of fibrillar growth, the relative crystallinity χ_f expressed as

$$\begin{aligned} \chi[t, \theta(t)]_f &= 1 - \exp \left[-\frac{1}{2} d_c^2 \int_0^t I[\theta(\tau)] \left\{ \int_\tau^t G[\theta(t)] dt \right\} d\tau \right] \\ &= 1 - \exp - \left[\frac{1}{2} d_c^2 \left\{ \sum_{i=1}^{i=n} I_i \Delta t_i \left(\sum_{j=i}^{j=n} G_j \Delta t_j \right) \right\} \right] \end{aligned} \quad (13)$$

where d_c is the size of nucleus.

By using a d_c value of about 20 \AA ,¹³ the measured values of $\theta(t)$ ¹ for exps. 1-3 and eqs. (2) and (3), the computed values of χ_f under the unheated spinning tube ($\bar{\theta}_s(x)$ is room temperature) is less than 10^{-4} , which is negligibly small. Furthermore, under the heated spinning tube, the χ_f value is less than 10^{-4} , which also is negligibly small. Since crystallization occurs at $\bar{\theta}_s(x)$ above 80°C as the measured results of densities show, calculating the crystallinity in melt spinning assuming a fibrillar crystal growth is not valid. On account of this, eq. (1) in which spherulitic growth of crystals is assumed is used to compute the χ_s for the case of nonheated spinning tube. The computed χ_s was about 10^{-4} even for exp. 3 where the cooling of the threadline in the cooling chamber was comparatively slow. Therefore, no appreciable crystallization is estimated to have taken place in the spinning tube. But as shown in Figure 4, the measured density of the undrawn filament yarn immediately after take-up amounts to as much as 1.117 g/cm^3 even under the $\bar{\theta}_s(x)$ of room temperature. Assuming a density¹⁴ of 1.165 g/cm^3 for the γ -form crystals and an amorphous density of 1.1108 g/cm^3 (although the density of nylon 6 sample that is quenched in acetone-Dry Ice bath from the melt is¹⁵ 1.0942 g/cm^3), in the present study we defined the amorphous density as the value obtained when the nylon 6 sample was cooled in mercury bath at 25°C in order to know the contribution of the increase in density during melt spinning amounts to as much as 12%. Therefore, the theory based on the crystal growth starting from a nucleus is not applicable in the present case. It is estimated that the oriented molecular conformation that was generated in melt spinning was frozen by the cooling to take on a semicrystalline state.

Figure 8 shows the values of relative crystallinity χ_s , for the case of the heated spinning tube, calculated from eq. (1) and plotted against $\bar{\theta}_s(x)$. Although Figure 8 shows χ_s approaching 100%, the attained γ -form crystallinities of nylon 6 are 45-50% in the temperature range of 80 - 140°C .⁷ Therefore, a real γ -form crystallinity $\chi_{s,\gamma}$ is approximately expressed as

$$\chi_{s,\gamma} \doteq 0.5 \chi_s \quad (14)$$

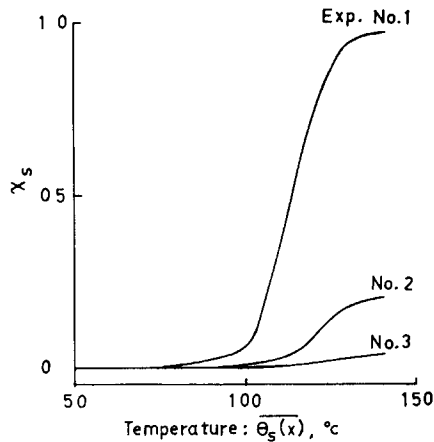


Fig. 8. Effects of temperature $\overline{\theta_s(x)}$ on crystallinity χ_s that is calculated from eq. (1).

In Figure 8, exp. 3, longest of the three curves in residence time, was largest in χ_s values corresponding to the behavior of the Δn_H in the temperature region (iii). Furthermore, the departure of the χ_s -versus- $\overline{\theta_s(x)}$ curves from the horizontal line approximately corresponds to the data for the density (Fig. 4) and the measure of γ -form crystallinity (Fig. 6).

From the above results, it is considered valid to calculate the crystallinity in the melt spinning of nylon 6 under heated spinning tube assuming a spherulitic growth of crystals.

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