

Partial Melting, Recrystallization and Thermal Shrinkage of Fibrous Polymers

Nobuyuki TANAKA* and Akio NAKAJIMA**

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Thermal shrinkage of fibrous polymers was thermodynamically investigated by taking into account melting of crystalline regions, presence of quasi-crosslinks in amorphous regions, and effect of elastic deformation. On these bases a thermodynamic relation was derived between the thermal shrinkage and the temperature. Experimental results on polyethylene terephthalate, Nylon 6, and methoxy-methylated Nylon 6 fibers were discussed according to the theoretical equation.

INTRODUCTION

Thermal shrinkage of fibrous polymers along the fiber axis may be caused by the decrease in orientation of amorphous chains, decrease in the number of cross-links in amorphous regions, partial melting and thickening of crystallites, and recrystallization of amorphous chains. The shrinkage behavior may also be affected by the molecular weight and its distribution of the sample.¹⁾

THEORETICAL TREATMENT

The length L of a fiber, composed of the crystalline regions oriented along the fiber axis and the amorphous regions, is, at constant force f and temperature T , given by

$$L = (1-\lambda)L_c + \lambda L_a \quad (1)$$

where L_a and L_c , respectively, are the length of the sample when it is totally amorphous and in fully oriented crystalline state; λ is the fraction of polymer in the amorphous state.

Now we define the relative shrinkage S as

$$S = \frac{L_c - L}{L_c} = \frac{L_c - L_a}{L_c} \lambda \quad (2)$$

According to Flory,²⁾ the change in Gibbs free energy $\Delta G_f/xN$ per structural unit accompanying disappearance of crystalline regions in the mixture of polymer and solvent is given by the equation:

* 田中信行: Department of Textile and Polymer Technology, Faculty of Engineering, Gunma University, Kiryu.

** 中島章夫: Department of Polymer Chemistry, Kyoto University, Kyoto.

$$\frac{\Delta G_f}{xN} = (1-\lambda)(h_u - Ts_u) + kT \left[\left\{ \left(\frac{z}{z_s} \right) \left(\frac{1-v_2}{v_2} \right) + \frac{1}{x} \right\} \ln \{1-v_2(1-\lambda)\} \right. \\ \left. + \left(\frac{1-\lambda}{\xi} \right) \left\{ \ln v_2 D + \ln \left(\frac{x-\xi+1}{x} \right) \right\} + \frac{\chi(1-v_2)^2(1-\lambda)}{1-v_2+v_2\lambda} \right] \quad (3)$$

x : total number of structural units in a polymer molecule.

N : number of polymer molecules.

h_u : heat of fusion per structural unit.

s_u : entropy of fusion per structural unit.

z : number of segments per structural unit.

z_s : ratio of molar volume of solvent to the volume of a segment.

ξ : length of crystallite in number of units.

χ : interaction free energy parameter.

D : nucleation parameter.

v_2 : volume fraction of polymer in polymer-diluent system.

Here we shall assume the presence of pseudo cross-linkages, in the amorphous regions, which are reversibly disappeared and generated. At a given temperature, thus, an equilibrium number of the pseudo-crosslinks may be preserved.

Now we introduce the changes in enthalpy h_x and entropy s_x owing to the presence of these pseudo-crosslinks in the amorphous regions. The change ΔG_a in the Gibbs free energy accompanied by disappearance of the pseudo-crosslinks may be given as

$$\frac{\Delta G_a}{xN} = \lambda(h_x - Ts_x) \quad (4)$$

Next, we shall take into account the change in free energy per structural unit, $\Delta G_{el}/xN$, for elastic deformation. Under the assumption that the entropy change with deformation is negligible, $\Delta G_{el} = -T\Delta S_{el}$ is held. When an unswollen fiber, in which the fraction of polymer in the amorphous state is λ , is swollen in diluent under a force f , the elastic entropy change per structural unit is, according to Flory's theory,³⁾ written as

$$\frac{\Delta S_{el}}{xN} = -\frac{\lambda k\nu}{xN} \left[\left(\frac{\langle \alpha \rangle}{L_{i0}} \right)^2 \left(L_a^2 + \frac{2L_{i0}^3}{L_a v_2'} \right) - 3 + \ln v_2' - 3 \ln \langle \alpha \rangle_0 \right] \\ = -\frac{\lambda k\nu}{xN} \left[\left(\frac{1}{v_2'^{2/3}} \right) \left(\alpha^2 + \frac{2}{\alpha} \right) - 3 \ln v_2' \right] \quad (5)$$

where, ν is the number of the pseudo-crosslinkages per unit volume; L_{i0} and L_i , respectively, are the isotropic lengths in the absence and presence of diluent; L_a is the length of amorphous sample under a force f ; α is the drawing ratio ($=L_a/L_i$); and $\langle \alpha \rangle_0$ and $\langle \alpha \rangle$, respectively, the linear dilation factors in the absence and presence of diluent.

$$v_2' = v_2\lambda/(1-v_2+v_2\lambda)$$

$$L_i = L_{i0}(v_2')^{-1/2}$$

and, in this case, $\langle \alpha \rangle_0 = 1$.

Hence,

$$\frac{\Delta G_{el}}{xN} = \frac{\lambda k T \nu}{xN} \left[\frac{1}{(v_2')^{2/3}} \left(\alpha^2 + \frac{2}{\alpha} \right) - 3 + \ln v_2' \right] \quad (6)$$

The force f is given by

$$f = \left[\partial \left(\frac{\Delta G_{el}}{xN} \right) / \partial L_a \right] P, T, v_2 \quad (7)$$

Integrating the equation

$$d(\Delta G_{el})_{P,T,v_2} = xN f d(L_a) \quad (8)$$

from λ to $\alpha\lambda$, we obtain the Gibbs free energy change per structural unit $(\Delta G_{el}/xN)_s$ accompanied by the drawing in swollen state.

$$\left(\frac{\Delta G_{el}}{xN} \right)_s = -f\lambda(\alpha-1) \quad (9)$$

On the other hand, the elastic entropy change only due to the swelling is given by ΔS_{el} with $\alpha=1$. Thus, the elastic entropy change from an undrawn and unswollen state to a drawn and swollen state is obtained as

$$\begin{aligned} \frac{\Delta G_{el}}{xN} &= \left(\frac{\Delta G_{el}}{xN} \right)_s - \frac{T \Delta S_{el}(\alpha=1)}{xN} \\ &= -f\lambda(\alpha-1) + \frac{\lambda k T \nu}{xN} \left(\frac{3}{(v_2')^{2/3}} - 3 + \ln v_2' \right) \end{aligned} \quad (10)$$

Here, the degree of swelling $(1/v_2')$ is assumed to be constant in the processes of deformation and partial melting.

In conclusion, the total Gibbs free energy change becomes as

$$\begin{aligned} (1/xN)\Delta G &= (1/xN)(\Delta G_f + \Delta G_a + \Delta G_{el}) \\ &= (1-\lambda)(h_u - T s_u) + kT \left[\left\{ \left(\frac{z}{z_s} \right) \left(\frac{1-v_2}{v_2} \right) + \frac{1}{x} \right\} \right. \\ &\quad \times \ln \{1 - v_2(1-\lambda)\} + \left. \left(\frac{1-\lambda}{\xi} \right) \left(\ln v_2 D + \ln \frac{x-\xi+1}{\lambda} \right) \right. \\ &\quad \left. + \frac{\chi(1-v_2)^2(1-\lambda)}{1-v_2+v_2} \right] + \lambda(h_x - T s_x) - f\lambda(\alpha-1) \\ &\quad + \frac{\lambda k T \nu}{xN} \left(\frac{3}{(v_2')^{2/3}} - 3 + \ln v_2' \right) \end{aligned} \quad (11)$$

By differentiating ΔG by λ and ξ , and introducing $(\partial \Delta G / \partial \lambda)_{\xi=0}$ and $(\partial \Delta G / \partial \xi)_{\lambda=0}$ for the state at or close to equilibrium, we obtain

$$\begin{aligned} &[(h_u - T s_u) - (h_x - T s_x) + f(\alpha-1)](1/kT) \\ &= \frac{(z/z_s)(1-v_2) + (v_2/x)}{1-v_2(1-\lambda)} + \frac{1}{x-\xi+1} \\ &\quad - \chi \left\{ \frac{1-v_2}{1-v_2(1-\lambda)} \right\}^2 + \frac{\nu}{xN} \left(\frac{3}{(v_2')^{2/3}} - 3 + \ln v_2' \right) \end{aligned} \quad (12)$$

If $v_2 = v_2' = 1$, then

$$[(h_u - T s_u) - (h_x - T s_x) + f(\alpha-1)](1/kT) = \frac{1}{x\lambda} + \frac{1}{x-\xi+1} \quad (13)$$

Substitution of Eq.(2) in Eqs.(12) and (13) leads to the relations between the relative shrinkage S and temperature T for the systems including and excluding diluent, respectively.

In the case of $v_2=1$ and $x \gg \zeta$,

$$[(h_u - Ts_u) - (h_x - Ts_x) + f(\alpha - 1)](1/kT) = \left(\frac{L_c - L_a}{xL_c} \right) \frac{1}{S} \quad (14)$$

Further, if it is approximately that

$$(h_u - h_x)/(s_u - s_x) = T_m^* \quad (15)$$

then,

$$[(h_u - h_x) + f(\alpha - 1)](1/T) = k \left(\frac{L_c - L_a}{xL_c} \right) \frac{1}{S} + \frac{h_u - h_x}{T_m^*} \quad (16)$$

The total Gibbs free energy per mole, G , of a system composed of fully oriented crystalline regions and of amorphous regions may be expressed as

$$G = (1 - \lambda)G_c + \lambda G_a, \quad (17)$$

where G_c and G_a denote the free energies for oriented crystalline regions and for amorphous regions, respectively. Comparing Eq.(17) with Eq.(1), we obtain

$$L_c = KG_c \quad \text{and} \quad L_a = KG_a, \quad (18)$$

which lead to the following relations.

$$L_c = KN_A(h_u - Ts_u) \quad (19)$$

$$L_a = KN_A(h_x - Ts_x) \quad (20)$$

where N_A is the Avogadro number. For negligibly small f , substitution of Eqs.(19) and (20) into Eq. (14) gives

$$\frac{xL_c}{KkN_A} \frac{1}{T} = \frac{1}{S} \quad (21)$$

If L_c is not largely affected by temperature, then $(1/S)$ may be proportional to $(1/T)$.

EXPERIMENTAL

Samples

(i) *Polyethylene terephthalate(PET) fiber* (150D, 30 fils)

The degree of polymerization x of the sample was estimated, from the intrinsic viscosity in a 1 : 1 (w/w) phenol-m-cresol mixture at 20°C according to the equation⁴⁾ $[\eta] = 1.7 \times 10^{-6} M_n + 0.006$, as $x = 1524$. The sample was drawn fiber and its density at 25°C was $\rho = 1.3890$.

(ii) *Nylon 6*

Two undrawn Nylon 6 yarns, *i.e.*, sample a (845D, 15 fils, $x = 97$) and sample b

Table 1. Drawing Conditions for Nylon 6

Specimen	1	2	3	4
Undrawn yarn used	a	a	a	b
Drawing temp. (°C)	120	120	20	20
Draw ratio	4	4	4	3
Drawing rate (%/min)	10	10	10	20
Relaxation time at drawing temp. (hr)	0	3	0	0
Relative shrinkage (%) at R. T. after drawing	4.95	4.00	12.5	14.8

(684D, 24 fils, $x=168$), were drawn by us to obtain specimens 1, 2, 3, and 4. The specimen 4 was further methoxymethylated to yield the specimen E. These five specimens were used for the experiments. Table 1 shows the conditions for drawing. The methoxymethylation was performed for 4.5 hrs. at 30°C in accordance with the method of Arakawa *et al.*⁵⁾ After the reaction was over, the sample was washed in water, treated by dilute NaOH solution, washed again in water, and then dried in air.

Measurement of Thermal Shrinkage

(i) Experiments at temperatures up to 160°C

Specimens were kept for 1.5 hrs in a dry oven at given constant temperatures by suspending a weight of 2.0 mg/d, and the length of the sample at that temperature was measured by a cathetometer.

(ii) Experiments at temperatures above 140°C

Specimens were heated without tension at a heating rate of 30°C/min up to given temperatures, and then quenched down to room temperature, at which the length of

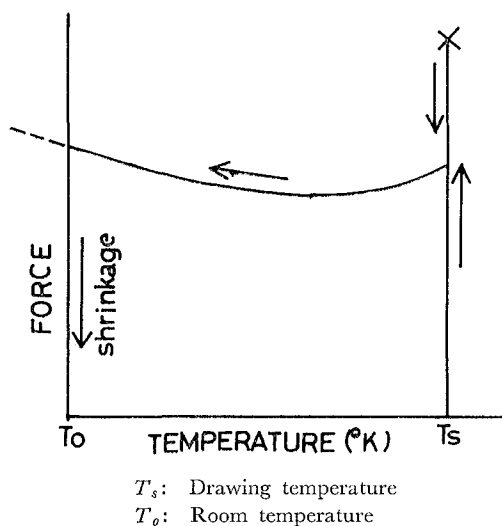


Fig. 1. Schematic diagram for fiber manufacturing process.

the sample was measured under no tension. In the temperature range from 140 to 160°C, both methods gave nearly the same value for the relative shrinkage.

The quantity L_c should be obtained with fully oriented fiber drawn as possible. However, crystallinities are generally not oriented perfectly but oriented with an orientation angle θ . Therefore, the observed value is written as $L_c \langle \cos \theta \rangle$, in which $\langle \cos \theta \rangle$ denotes the average of $\cos \theta$. Fortunately the orientation angle does not largely depend on temperature; hence in this work the observed value was regarded as L_c .

For PET fiber used here, a value of 2% may be expected for the relative shrinkage during the fiber manufacturing process as shown in Fig. 1. Therefore, the corrected value of S was obtained by adding 2% to the relative shrinkage calculated by using the length (observed value) of the original fiber at room temperature.

In the case of Nylon 6, the length of fiber, drawn as fully as possible at drawing temperatures, was regarded as L_c .

Differential Scanning Calorimetry

Thermal behavior of the PET sample was investigated by means of a differential scanning calorimeter (Rigaku Denki) at a heating rate 3°C/min.

Measurement of Crystalline Orientation

X-ray measurements were performed with a Rigaku-Denki apparatus. The degree of orientation f_c of the (100) plane of crystallite was determined from the half-width H of the maximum on the azimuthal scanning of the (100) reflection by the equation

$$f_c = \frac{180-H}{180} \quad (22)$$

Measurement of Density

The densities of the specimens were measured at 25°C using a density gradient tube composed of n-heptane and carbon tetrachloride.

Measurement of Birefringence

A polarized microscope was used to investigate the birefringence of the specimens.

RESULT AND DISCUSSION

I. Polyethylene terephthalate fiber

It is generally difficult to obtain equilibrium value of S within experimental time. Accordingly, discussion in this work will be done on the assumption that the system is in equilibrium state. Further, the force f added was so small that the term $f(\alpha-1)$ in Eq.(14) may be neglected. The reciprocal of S is plotted against the reciprocal temperature in Fig. 2. The curve obtained may be represented by a set of straight lines of different slopes; the temperatures at which slope changes were 54, 85, 112, and 143°C. The temperatures 54°C and 85°C, respectively, may correspond to the glass

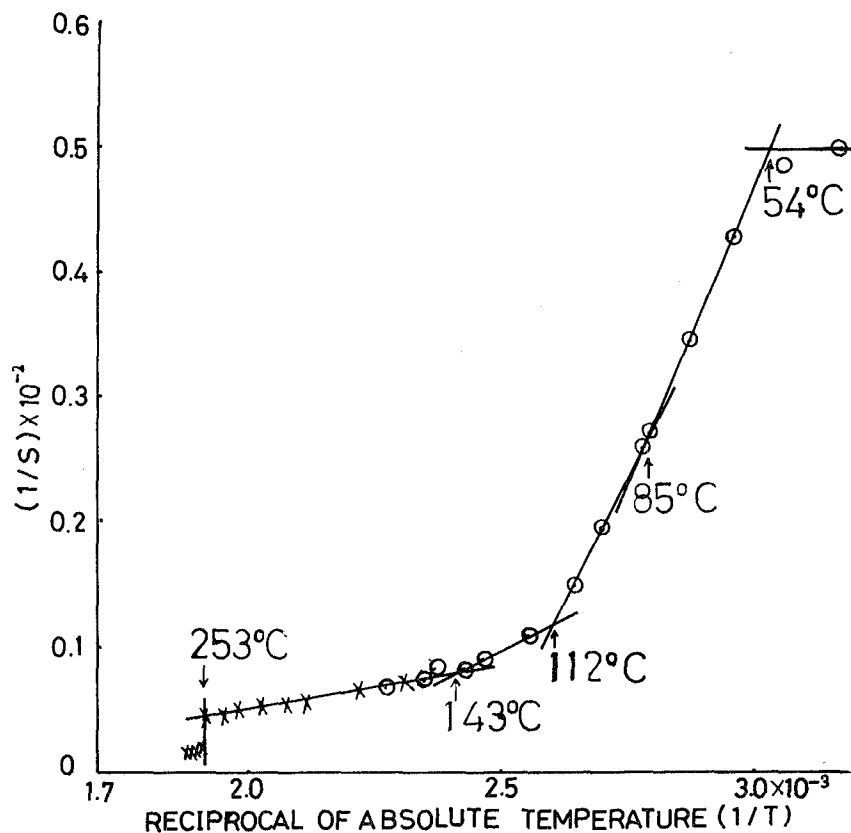


Fig. 2. Relation between the reciprocal relative shrinkage $1/S$ and the reciprocal temperature $1/T$ for PET.

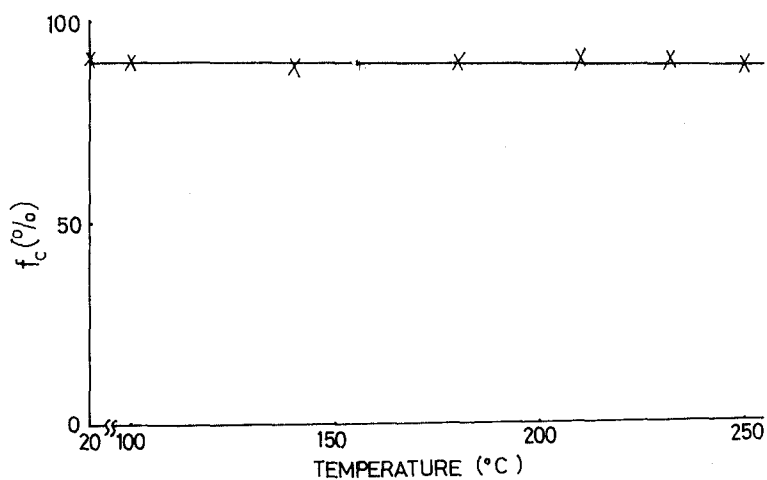


Fig. 3. Relation between the degree f_c of orientation of crystallites and the temperature ($^{\circ}\text{C}$) of heat treatment for PET.

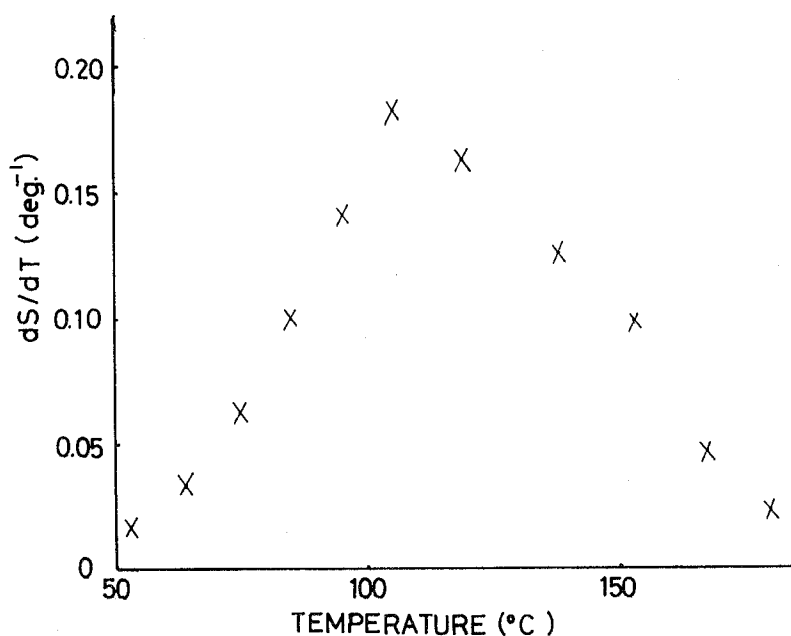


Fig. 4. Temperature dependence dS/dT of the relative shrinkage plotted against the temperature for PET.

transition temperature and presumably to the drawing temperature. The temperature range from 112°C or 140°C to 200°C is most suitable for crystallization of PET.^{6,7)} Taking into account that the degree of orientation of crystallites, f_c , was invariant in the temperature range investigated here (see Fig. 3), the linearity of $1/S$ against $1/T$ within each temperature range will be discussed later. The temperature dependence of S was shown in Fig. 4, from which we find that the maximum of the curve appears at about 105°C.

In the temperature range, 20~140°C, where the variation of λ with temperature is small (see Fig. 5), the thermal shrinkage may be caused by the decrease in the degree of orientation of molecular chains and the number of quasi-crosslinks both in the amorphous regions, *i.e.*, with increasing temperature, L_a decreases and $(G_c - G_a)$ increases.

The temperature at which $1/S$ discontinuously changes against $1/T$ is 253°C, where the abrupt endothermic spectrum begins to appear (see Fig. 6).

Now we will refer to the change in the length at above 140°C and under constant L_a , according to the fine structure model for PET given by Bosley,⁸⁾ and the mechanism for partial melting proposed by Zachermann.^{9,10)} Let $\lambda=1$ at 253°C, the apparent melting temperature, then the observed value $S^0=0.217$ of the relative shrinkage just before the discontinuous shrinkage occurs may give the following relations.

$$S^0 = \frac{L_c - L_a}{L_c} = 0.217 \quad (22)$$

$$L_a (\equiv L_a^0) = 0.783 L_c \quad (23)$$

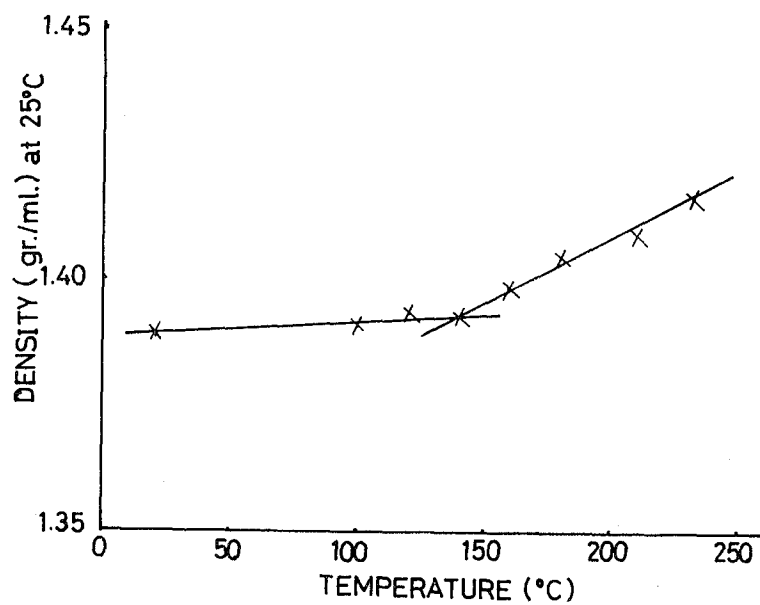


Fig. 5. Density of heat-treated sample vs. temperature of heat treatment.

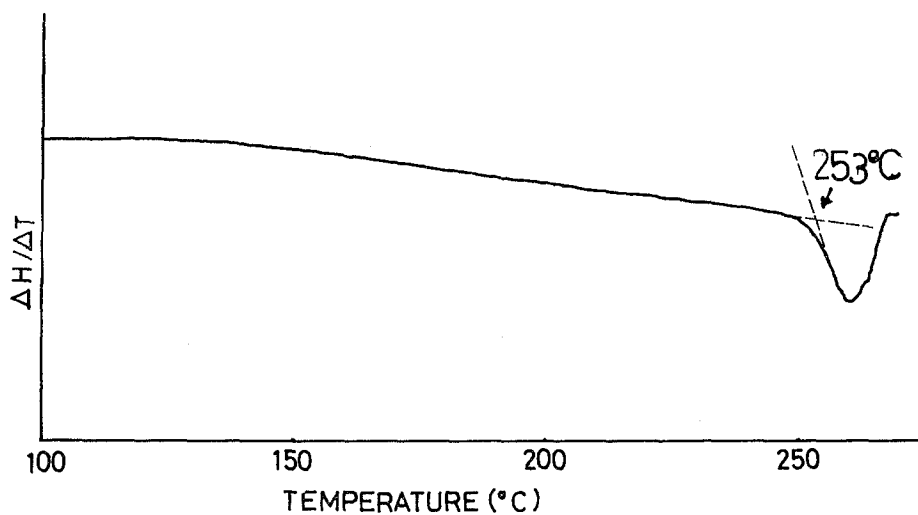


Fig. 6. DSC curve for PET.

From Eq. (14), there is obtained

$$\left(\frac{L_c - L_a}{xL_c} \right) \frac{1}{S} = (G_c - G_a) \frac{1}{RT} \quad (24)$$

which gives the slope ($\equiv A$) of the straight line for $1/S$ vs. $1/T$.

$$(G_c - G_a) \frac{xL_c}{R(L_c - L_a)} \equiv A \quad (25)$$

Thus the difference in the free energies, $G_c - G_a$ at temperatures above 143°C up to 253°C is obtained as follows

$$G_c - G_a = \frac{L_c - L_a}{L_c} \frac{RA}{x} = 0.217 \times 9.128 = 1.999 \text{ (cal/mol structural unit)} \quad (26)$$

by using the observed value of $A (= 7000^\circ\text{K})$, $R = 1.987 \text{ cal/}^\circ\text{K} \cdot \text{mole}$, and $x = 1524$. Since the L_a at 253~143°C may be assumed to be invariantly given by L_a^0 , the crystallinity, $1 - \lambda$, at 143°C is obtained as

$$1 - \lambda = 1 - S_{143} \frac{L_c}{L_c - L_a^0} = 1 - \frac{S_{143}}{S^0} = 0.1 - \frac{0.128}{0.217} = 0.416 \quad (27)$$

This figure(0.416) is in good agreement with the crystallinity ($= 0.47$) calculated from the density value at 20~140°C given in Fig. 5. The assumption that the L_a at 253~143°C is constant may be supported by the experimental result obtained by Dumbleton¹¹⁾ that the orientation of molecular chains in amorphous regions is almost unchanged in this temperature range. According to the DSC curve (Fig. 6), an endothermic phenomenon, presumably due to contentious partial melting at above 140°C with increasing temperature, was observed. Our result on birefringence shown in Fig. 7, may suggests that L_a is almost constant at 140~200°C but decreases with temperature at above 200°C.

In the next place, we'll refer to the thermal shrinkage below 143°C. If we use the λ value($= 0.53$) at below 143°C estimated from the density data shown in Fig. 5, then the relative shrinkage S_{143} at 143°C is written as

$$S_{143} = 0.53 \frac{L_c - L_a^0}{L_c} \quad (28)$$

Further, the relative shrinkage S in the temperature range 54~143°C is given by

$$S = S_{143} \frac{(L_c - L_a)/L_c}{(L_c - L_a^0)/L_c} = S_{143} \frac{L_c - L_a}{L_c - L_a^0} \quad (29)$$

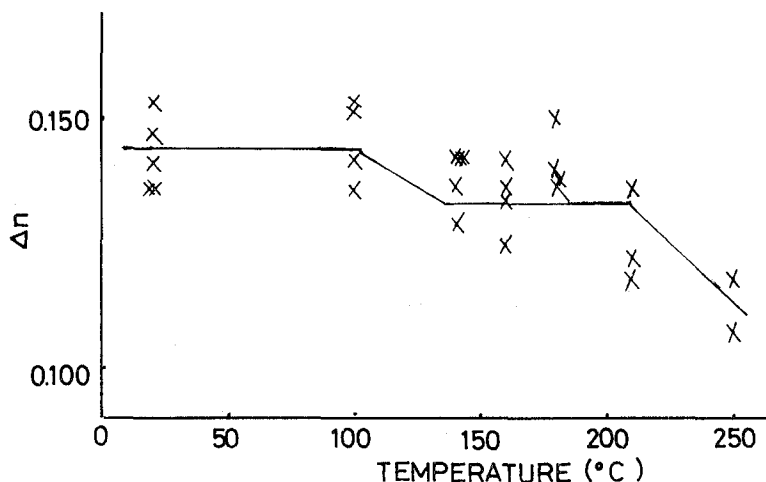


Fig. 7. Birefringence vs. temperature of heat treatment.

which leads to

$$S_{143} - S = S_{143} \left(\frac{L_a - L_a^0}{L_c - L_a^0} \right) \quad (30)$$

Eq.(29) suggests that S is proportional to L_a . The linear relationship between $(S_{143} - S)$ and $(L_a - L_a^0)$ may be compared with the empirical equation $S_w = C f_a$, given by Takagi¹²⁾ for Nylon 6, in which f_a is the orientation coefficient of molecular chains in the amorphous regions, S_w is the relative shrinkage of fibers after treatment in boiling water, and C is the constant.

As seen in Fig. 7, Δn was nearly constant at 20~100°C, hence the change of S in this region seems to depend on the change of the number of quasi-crosslinks rather than the change of orientation coefficient of molecular chains in amorphous regions. In the temperature ranges from 100 to 140°C and above 200°C, Δn decreased. Therefore, in these temperature ranges, change of the orientation coefficient may be taken in account. The increase in density of the sample with increasing heat-treatment temperature, at temperatures above 140°C, may be caused by partial melting of the crystallites and at the same time by recrystallization of amorphous chains into folded-chain or fringed micell crystals. The heat-treatment at above 200°C may cause the increase of long period.^{13,14)}

II. Nylon 6 fiber

Nylon 6 drawn fiber

The reciprocal of the relative shrinkage of Nylon 6 drawn fibers (specimens 1, 2, 3 and 4 in Table 1) was plotted against the reciprocal of the treatment temperature in Figs. 8 and 9. The refraction points obtained were listed in Table 2.

The temperature in the first column may correspond to the glass transition temperature of the specimen. This temperature was not detected for specimen 4. Similarly to the result for PET fiber, the curve for $1/S$ vs. $1/T$ can be represented by several straight lines with different slopes. Each straight line portion may be explained by the equation

$$G_c - G_a = \frac{AR}{\alpha\lambda} S \quad (31)$$

which is derived from Eq.(24). For specimens 1 and 2, λ may be expected to be constant in the temperature range up to 120°C or 140°C, because these fibers were drawn at 120°C and the most suitable temperature for crystallization of Nylon 6 is about 140°C. The drawing temperature 120°C is in between the refraction points 104.4°C

Table 2. Refraction Temperatures (°C) of Nylon 6 Drawn Fibers

Specimen				
1	39.9°C	85.4°C	104.4°C	138.5°C
2	37.0	83.8	102.9	138.5
3	50.6	—	96.0	—
4	—	84.1	—	163.6

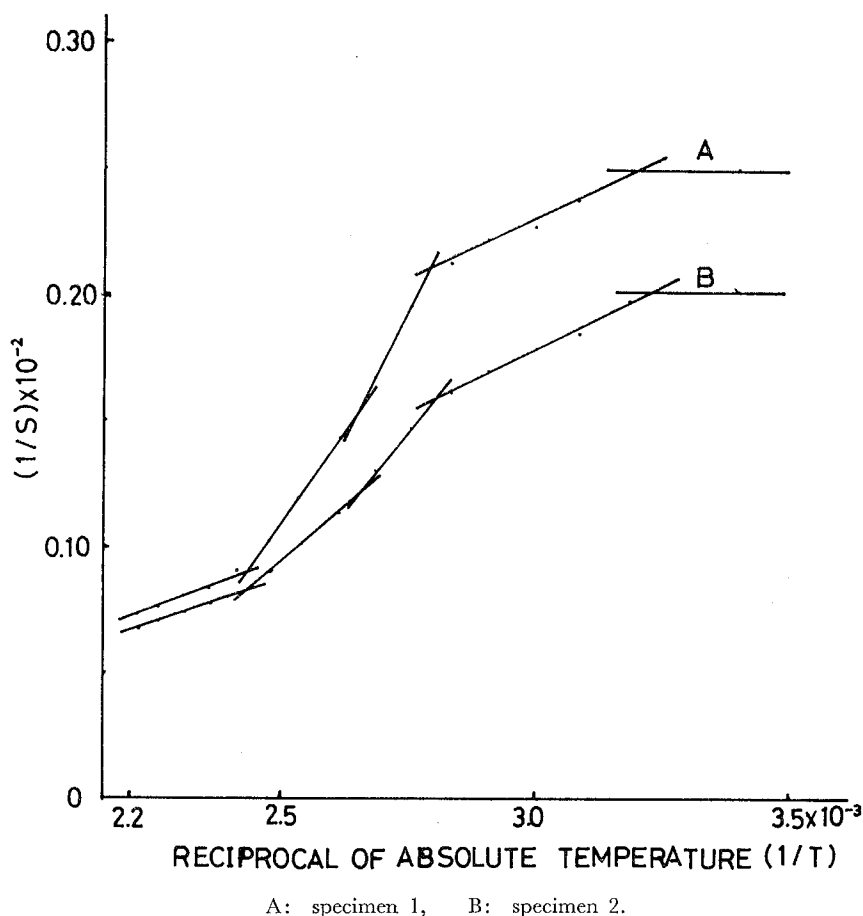


Fig. 8. Relation between the reciprocal relative shrinkage $1/S$ and the reciprocal temperature $1/T$ for Nylon 6.

(or 102.9°C) and 138.5°C. Ishibashi *et al.*¹⁵⁾ have reported that the crystallization rate of Nylon 6 is very small above 180°C. Also, Tsuruta *et al.*¹⁶⁾ showed that the partial melting occurred above 180°C. From these results, at temperatures above 140°C, the partial melting and recrystallization must be taken into account to explain the mechanism of thermal shrinkage. Also, it should be noted that,¹³⁾ on account of the partial melting and recrystallization, the small angle X-ray diffraction intensity increased with increasing temperature, and that the relative shrinkage increased, though an abrupt increase of the long period and its intensity occurred with increasing temperature in the temperature range above 180 or 190°C. For cold drawn fibers, such as the specimens 3 and 4, there are found 2 refraction points, *i.e.*, 50.6°C and 96.0°C for specimen 3, and 84.1°C and 164°C for specimen 4. But it is not clear yet what kind of characteristic temperatures of Nylon 6 correspond to these temperature.

Methoxymethylated Nylon 6 fiber

The reciprocal of the relative shrinkage of specimen E (methoxymethylated

Nylon 6 fiber) was plotted against $1/T$ in Fig. 9. A refraction point was found at 154.4°C . This temperature is also not characterized yet. The slopes of two straight lines are very small on account of the effect of permanent crosslinks introduced by methoxymethylation. In this fiber, it is reasonable to assume that the crystallization of amorphous chains in heating process is prevented. The thermal shrinkage for this kind of fiber may be resulted from the change of λ and $(G_c - G_a)$, in accordance with Eq. (31).

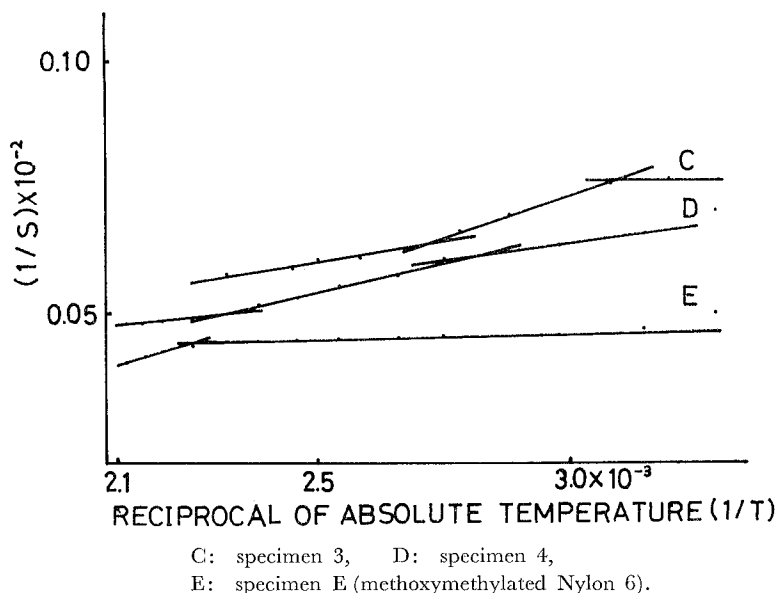


Fig. 9. Relation between the reciprocal relative shrinkage $1/S$ and the reciprocal temperature $1/T$ for Nylon 6.

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