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Two equilibrium melting temperatures and physical meaning of DSC melting peaks in poly(ethylene terephthalate)

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ABSTRACT

For poly(ethylene terephthalate), two equilibrium melting temperatures, 262 °C and 276 °C, were found with DSC. They should be assigned to two forms of crystals with the infinite crystal length, respectively. This finding made it possible every crystal form to derive the end surface free energy per unit area of crystals and the transition enthalpy of the ordered parts in the amorphous regions and using these thermodynamic quantities to convert DSC melting curves into the crystal length distribution. Through the derivation of them, the participation of the crystallization temperature on cooling in the thermal analysis of DSC melting curves was revealed thermodynamically.

1. Introduction

The analysis of the thermal properties of polymers has been advanced with the improvement in DSC (Differential Scanning Calorimetry) (Wunderlich [1]). As one of them, the conversion of DSC melting peaks into the crystal length (ζ) distribution has been tried expecting the roles of the supplement for X-ray analysis (Wlochowicz and Eder [2]). The conversion by using Gibbs–Thomson equation (Eq. (6) shown below) needs previously the equilibrium melting temperature, T_m^∞, and the end surface free energy per unit area for the crystals, σ_e. Recently, for poly(ethylene terephthalate) (PET), two values of T_m^∞ have been found with DSC. One is 262 °C for the crystals formed on cooling from the melt or after annealing and the other is 276 °C for the crystals formed during annealing. They should be assigned to two crystalline phases of the conformational disorder model of $-OCH_2CH_2O-$ but with a chain axis parallel to *c*-axis of a cell and the smectic-c model with stretched sequences, respectively (Allegra [3]). T_m^∞ of 280 °C reported already for PET is restricted only to the extended chain crystals (Wunderlich [1]). In this paper, for PET, the ζ distribution of two crystalline phases is derived from the respective DSC melting curves.

2. Experimental

2.1. Samples and thermal analysis

The heat-pressed films of PET (Scientific Polymer Products) were used for the thermal analysis with DSC3200S (Bluker). First the film set in DSC was heated to 300 °C and then cooled to 50 °C at 5 °C $\min^{-1}$. DSC was further used for annealing them at several temperatures of T_a for 1 h. After annealing, the samples were cooled to 50 °C at 5 °C $\min^{-1}$. Subsequent DSC measurements were carried out at the heating rate of 10 °C $\min^{-1}$ under the nitrogen gas flow (100 ml $\min^{-1}$). The correction of the melting temperature, T_m, in DSC curves was performed according to the means developed by us (Gunma University [4]).

3. Results and discussion

Fig. 1 shows DSC curves for PET films annealed at T_a for 1 h (a–e). For the sample annealed at 223.1 °C, two melting peaks were observed (a); one in the lower temperature side is due to the crystals formed during annealing and the other in the higher temperature side is due to the crystals formed already on cooling from the melt before annealing, although they should be reorganized without changing the form on annealing, because the crystals could not be melted perfectly at $T_a < T_m^\infty$ (=262 °C, shown below). For the sample annealed at 249.0 °C, only the sharp single melting peak of the crystals formed during annealing was observed (b). For the samples annealed at 257.0 °C and 263.0 °C, two peaks were also observed; one in the higher temperature side is due to the melting of crystals

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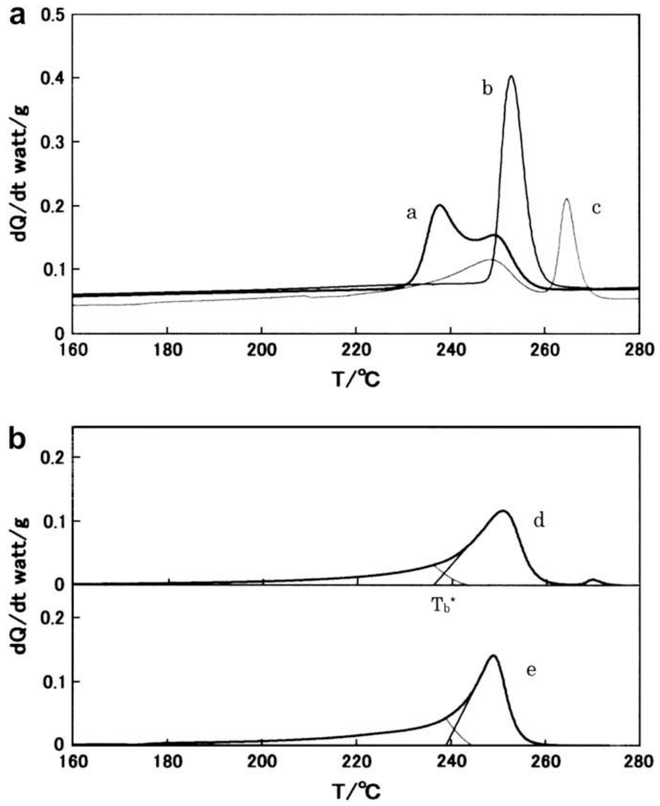

Fig. 1. DSC curves for PET films annealed at T_a for 1 h. T_a; a: 223.1 °C, b: 249.0 °C, c: 257.0 °C, d: 263.0 °C and e: 265.0 °C. dQ/dt; the heat flow. T_b^* is the onset temperature of a melting peak expected for the crystals with a form.

formed during annealing and the other in the lower temperature side is due to the melting of crystals formed on cooling after annealing (c and d). In the curve d of $T_a = 263.0$ °C, the peak in the higher temperature side was very small and off the other peak. For the sample annealed at 265.0 °C, only the single melting peak in the lower temperature side was observed (e). T_b^* of the intersection between the extrapolation line (thick) from the part with a highest slope in the lower temperature side of the large melting peak and the base line in the curve d shows the onset temperature of a melting peak expected for the crystals with a form. The subtraction of this expected melting peak area from the total endothermic peak area gives the peak with a subtracted line (thin) of lower temperature side in the curve d. The extrapolation line (thick) and the subtracted line (thin) are also shown in the curve e.

Fig. 2 shows DSC curves of crystallization on cooling from the melt (A) and after annealing (a–e). The curves a–e are linked to the melting curves a–e in Fig. 1, respectively. For the samples of curves a and b ($T_a = 223.1$ °C and 249.0 °C), the crystallization should occur during annealing at T_a. For curve A, the onset temperature of crystallization, T_c, was 217.9 °C and the heat of crystallization, h_c, was 8.37 kJ/mol. The peak temperature, T_p^c, of crystallization on cooling after annealing at 257.0 °C, 263.0 C and 265.0 °C decreased from 235.2 °C to 226.9 °C and 220.5 °C with T_a.

Fig. 3 shows DSC curves on cooling from the melt (A), after annealing (B) and on subsequent heating (C) for PE films annealed at 223.1 °C. The dashed schematic line shows the free energy, f, being equal to each other in the melt and the crystals or mesophases. The right-hand side region of the line is the melt or supercooled melt phase. For this sample, T_c/T_e is 0.92, where T_e is the end temperature of a double melting peak (C) and T_c is of curve A.

Fig. 4 shows the plots of T_m ($=T_b$, T_p^1, T_p^2 or T_e) against T_a. Where T_b is the onset temperature of a melting peak of the crystals formed during annealing, T_p^1 is the melting peak temperature of the crystals formed during annealing, T_p^2 is the melting peak temperature of the crystals formed on cooling from the melt before annealing and then reorganized on annealing or the crystals formed on cooling after annealing at above $T_a = 253$ °C. T_b and T_p^1 increased with T_a. T_b was 2–3 °C higher than T_a. Over $T_a = 240$ °C, T_p^1 peak overlapped with T_p^2 peak, which subsequently disappeared leaving T_p^1 peak. For the samples annealed at above 253 °C, the melting peak of the crystals formed on cooling after annealing appeared in the lower temperature range than T_p^1. Its peak temperature, T_p, was almost as same as T_p^2 for the samples annealed at below 240 °C. Over $T_a = 265$ °C, only T_p ($=T_p^2$) peak appeared on DSC curve without any annealing peak. To $T_a = 240$ °C, T_e was nearly 262 °C. Over $T_a = 240$ °C, T_e increased with T_a, but in the range of T_a from 260 °C to 265 °C, T_e was nearly 276 °C. Two points of T_m^∞ which two lines of $T_m = T_e$ in both ranges of below $T_a = 240$ °C and $T_a = 260$–265 °C intersect with a $T_m = T_a$ line each other were of course 262 °C and 276 °C. Although the crystals formed during annealing at below 240 °C belong to the crystal group of $T_m^\infty = 276$ °C, T_p^1 peak appeared in the lower temperature range than T_p^2, suggesting that ζ of crystals formed during annealing at below 240 °C was smaller than that of crystals showing T_p^2 peak. Below, the crystals formed on cooling from the melt or after annealing and the crystals formed during annealing are called the form I and II ones, respectively.

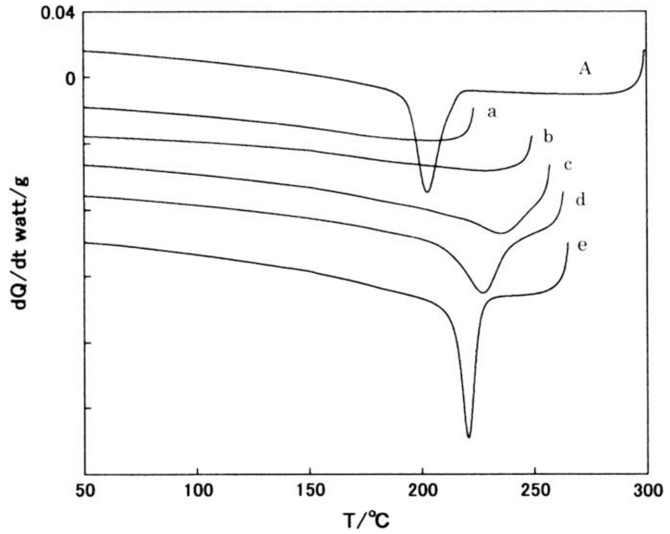

Fig. 2. DSC curves of crystallization on cooling from the melt at 300 °C (A) and after annealing at T_a for PET films. T_a; a: 223.1 °C, b: 249.0 °C, c: 257.0 °C, d: 263.0 °C and e: 265.0 °C.

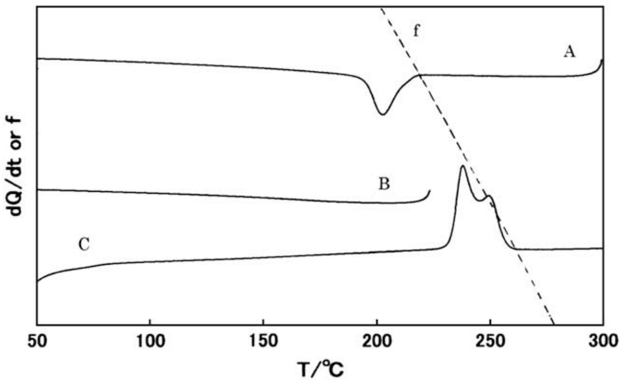

Fig. 3. DSC curves on cooling from the melt (A), cooling after heating to T_a (B) and subsequent heating (C) for PE films annealed at 223.1 °C. The dashed schematic line is the free energy (f) being equal to each other in the melt and the crystals or mesophases.

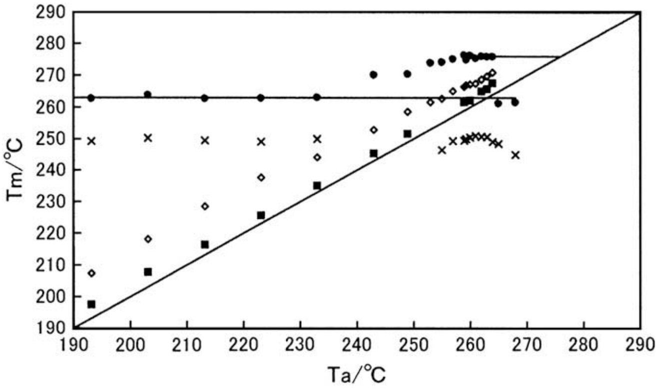

Fig. 4. Plots of T_m ($=T_b$ (■), T_p^1 (◇), T_p^2 (×) and T_e (●)) against T_a for PET films.

Next for the crystals of forms I and II, the value of σ_e is derived from (Tanaka and Fujii [5]):

$$\sigma_e = h_u^* b\left[\{RT_m^2 + (H_x - h_x)(T_m^\infty - T_m)\}/\{2(H_x - h_x)T_m^\infty\}\right] \quad (1)$$

with $H_x = 2h_u - Q_m$, where h_u^* is the heat of fusion per unit volume, b is the cell length of c-axis, h_x is the transition enthalpy per molar structural unit due to the ordered parts in the amorphous regions, h_u is the heat of fusion per molar structural unit, Q_m is the heat per molar structural unit due to the melting of crystals and R is the gas constant. The term in square bracket in Eq. (1) is no dimension. h_x is given by (Tanaka [6,7]):

$$h_x = h_g + \Delta h \quad (\Delta h > 0) \quad (2)$$

where h_g ($\approx H_g^a - H_g^c$) is the glass transition enthalpy per molar structural unit, H_g^a is the enthalpy per molar structural unit for the super-cooled melt at T_g, H_g^c is the enthalpy per molar structural unit for the crystals at T_g and Δh is the heat per molar structural unit needed to melt the ordered parts in the amorphous regions above T_g. When the ordered parts melt up to a temperature higher than the onset temperature of crystallization, T_c, observed previously on cooling from the melt, Δh is given by:

$$\Delta h = (H_m^a - H_c^a) - Q \quad (3)$$

where H_m^a is the enthalpy per molar structural unit for the melt at T_m^∞ and H_c^a is the enthalpy per molar structural unit for the super-cooled melt at T_c, Q is the heat per molar structural unit corresponding to the total area of DSC endothermic peak. $\Delta h < 0$ ($h_g > h_x$) should be the case for the glasses with T_g higher than that of primary amorphous glasses (Kwon et al. [8], Pak and Wunderlich [9], Wunderlich [10]).

Table 1 shows the values of h_x from Eqs. (2) and (3) for the samples annealed at 249 °C and 265 °C, together with the values of T_c, T_m^∞, Q, ΔH ($=H_m^a - H_c^a$), Δh and h_g used to calculate h_x, respectively. For both samples, the value of h_x was almost equal to h_u every form (see Table 2). Thus σ_e was evaluated from Eq. (1) using the values of h_x obtained above.

Table 1
The numerical values of h_x, T_c, T_m^∞, Q, ΔH, Δh and h_g for PET films annealed at 249 °C and 265 °C

Sample (T_a/°C)	T_c °C	T_m^∞ °C	Q kJ/mol	ΔH kJ/mol	Δh kJ/mol	h_g kJ/mol	h_x kJ/mol
(265)	217.9	262	10.1	16.6	6.5	16.1	22.6
(249)	217.9	276	11.1	22.6	11.5	16.1	27.6

Table 2
The numerical values of σ_e, T_m^∞, T_p, h_u, h_x, Q_m and ΔQ for PET films annealed at 249 °C and 265 °C

Form (T_a/°C)	T_m^∞ °C	T_p °C	h_u kJ/mol	h_x kJ/mol	Q_m kJ/mol	ΔQ kJ/mol	σ_e at T_p J/m^2
I (265)	262	248.5	23.0	22.6	6.0	4.1	32.2×10^{-3} (22.9×10^{-3})
II (249)	276	258.1	28.5	27.6	7.9	3.2	27.5×10^{-3} (15.1×10^{-3})

The value in () is σ_e at T_m^∞ ($Q_m = 0$). T_p is corrected by 0.2 °C for form I (248.7 °C → 248.5 °C) and 0.6 °C for form II (258.7 °C → 258.1 °C). h_u: Tanaka [11].

Table 2 shows the values of σ_e for the samples annealed at 249 °C and 265 °C, together with the values of T_m^∞, T_p, h_u, h_x, Q_m and ΔQ ($=Q - Q_m$) used to calculate σ_e, respectively. Q_m is the heat per molar structural unit corresponding to the area of a melting peak from T_m^* (see Fig. 1B). ΔQ is the heat per molar structural unit due to the melting of other parts. The value of σ_e at T_p was larger than that at T_m^∞ ($Q_m = 0$) for the crystals of forms I and II, adding σ_e (form I) > σ_e (form II).

Succeedingly for the sample annealed at 263 °C, which showed the curve d with large and small peaks (see Fig. 1B), the value of σ_e for the crystals of forms I and II contained in the same sample was evaluated from Eq. (1). The large peak in the lower temperature side is due to the melting of the crystals of form I and the small peak in the higher temperature side is due to the melting of the crystals of form II. Table 3 shows the value of σ_e every form, together with the values of T_m^∞, T_p, h_u, h_x, Q_m and ΔQ used to calculate σ_e. The value of σ_e at T_p for the crystals of form I was 2.2 (1.4) times larger than that for the crystals of form II, where 1.4 in () is that at T_m^∞. h_u refers to the crystals of a form hoping to evaluate the value of σ_e. h_x was calculated from Eqs. (2) and (3), using the value of H_m^a at T_m^∞ of the crystals of other form.

Table 3
The numerical values of σ_e, T_m^∞, T_p, h_u, h_x, Q_m and ΔQ for PET films annealed at 263 °C

Form	T_m^∞ °C	T_p °C	h_u kJ/mol	h_x kJ/mol	Q_m kJ/mol	ΔQ kJ/mol	σ_e at T_p J/m^2
I	262	250.5	23.0	28.0	6.9	3.5	37.0×10^{-3} (23.0×10^{-3})
II	276	269.1	28.5	22.0	0.2*	–	17.1×10^{-3} (16.1×10^{-3})

The value in () is σ_e at T_m^∞ ($Q_m = 0$). *: The total heat from the small melting peak. T_p is corrected by 0.2 °C for form I (250.7 °C → 250.5 °C) and 0.7 °C for form II (269.8 °C → 269.1 °C). h_u: Tanaka [11].

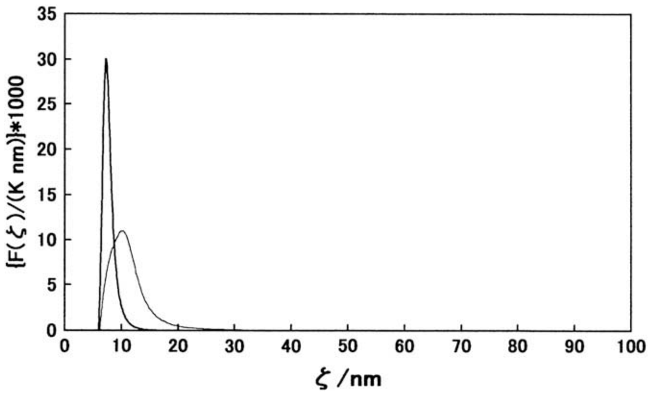

Fig. 5. $F(\zeta)$ of the single melting peak from T_b^* for PET films annealed at 249.0 °C (thick line) and 265.0 °C (thin line).

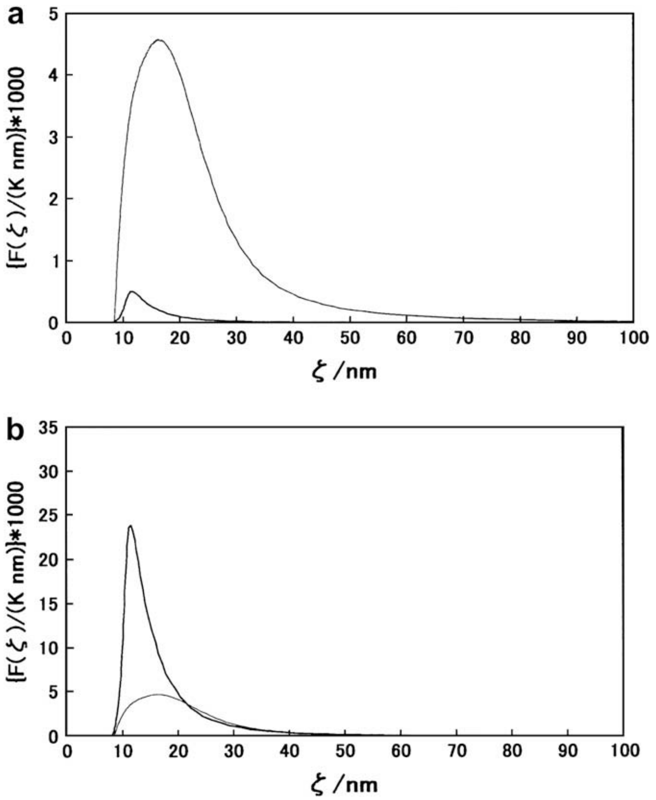

Fig. 6. $F(\zeta)$ of the small and large melting peaks from T_b^* in Fig. 1Bd for PET films annealed at 263 °C. a: $F(\zeta)$ considered the area ratio of two melting peaks, b: $F(\zeta)$ converted from each melting peak separately. The thin line is from a large melting peak of the crystals of form I and the thick line is from a small melting peak of the crystals of form II.

Last using the values of T_m^∞ and σ_e obtained above, the ζ distribution function, $F(\zeta)$, for the crystals of forms I and II is evaluated from:

$$F(\zeta) = (\Delta Q_m/Q_m)/\zeta = n_\zeta/\{N_c(T_e - T_b)\} \tag{4}$$

where ΔQ_m ($=\zeta n_\zeta Q_m/\{N_c(T_e - T_b)\}$) is the heat change per molar structural unit per K, n_ζ is the number of crystal sequences with ζ and N_c is the number of structural units of crystals melted in the temperature range from T_b to T_e. Q_m is defined in Eq. (1). $\Delta Q_m/Q_m$ is rewritten as:

$$\Delta Q_m/Q_m = (dQ/dt)/\int_{Tb}^{Te}(dQ/dt)dT \tag{5}$$

where dQ/dt is the heat flow in DSC curves. ζ is given by Gibbs–Thomson equation:

$$\zeta = \{T_m^\infty/(T_m^\infty - T_m)\}\left(2\sigma_e/h_u^*\right) \tag{6}$$

Fig. 5 shows $F(\zeta)$ of the single melting peak from T_b^* for the samples annealed at 249.0 °C and 265.0 °C (Fig. 1Ab and Be). For the sample of $T_a = 249$ °C, the sharp peak (thick line) with the ζ range of 6.0–20.3 nm and $\zeta_p = 7.2$ nm, reflecting the effective annealing and for the sample of $T_a = 265$ °C, the broad peak (thin line) with the ζ range of 6.2–72.2 nm and $\zeta_p = 10.1$ nm were obtained, respectively, where ζ_p is ζ at the maximum of $F(\zeta)$.

Fig. 6 shows $F(\zeta)$ of the large and small melting peaks from T_b^* for the sample annealed at 263 °C (see Fig. 1Bd). In $F(\zeta)$ of Fig. 6a, the area ratio of two melting peaks is considered. $F(\zeta)$ of Fig. 6b, which is converted from each melting peak separately, shows the broad peak (thin line) with the ζ range of 8.4–4230 nm and $\zeta_p = 16.2$ nm for the crystals of form I and the sharp peak (thick line) with the ζ range of 7.5–85.6 nm and $\zeta_p = 11.6$ nm for the crystals of form II. The partial overlapping of $F(\zeta)$ of thin and thick lines over $\zeta = 30$ nm in Fig. 6b suggests that the crystals of forms I and II might be mixed uniformly because the small crystals of form II worked as the nucleus on cooling after annealing.

4. Conclusion

For PET, two values of T_m^∞ which should be assigned to two crystalline phases, 262 °C and 276 °C, were found with DSC. This finding made it possible for every crystal form to convert DSC melting curves into $F(\zeta)$. The participation of T_c on cooling in the thermal analysis of DSC melting curves was revealed thermodynamically.

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References

[1] Wunderlich B. Thermal analysis of polymeric materials. Berlin: Springer; 2005.
[2] Wlochowicz A, Eder M. Polymer 1985;25:1268–70.
[3] Allegra G. Interfaces and mesophases in polymer, crystallization II. Berlin: Springer; 2005. p. 88.
[4] Japanese Patent P2007-254577A (Gunma University).
[5] Tanaka N, Fujii HJ. Macromol Sci Phys 2003;B42:621–8.
[6] Tanaka N. Polymer 1992;33:623–6.
[7] Tanaka N. Polymer 1993;34:4941–4.
[8] Kwon YK, Boller A, Pyda M, Wunderlich B. Polymer 2000;41:6237–49.
[9] Pak J, Wunderlich B. Thermochim Acta 2004;421:203–9.
[10] Wunderlich BJ. Appl Polym Sci 2007;105:49–59.
[11] Tanaka N. J Soc Fiber Sci Tech Japan 1988.