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# Photonic Contribution to the Glass Transition of Polymers

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Nobuyuki Tanaka

Additional information is available at the end of the chapter

<http://dx.doi.org/10.5772/59717>

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## 1. Introduction

The glass transition for polymers has been investigated for a long time as the mysterious physical phenomena of solid or liquid phases from the initial studies on the equation of state in pressure (P), volume (V), and temperature (T) to the recent thermal analyses with the temperature modulated differential scanning calorimeter (TMDSC) [1 – 9]. Polystyrene (PS) is one of polymers taking a leading part in the studies on the glass transition of polymers, so far showing the heat capacity jump of 28 ~ 31 J/(K mol) at the glass transition. The temperature modulation of TMDSC emerged the latent heat capacity jump at the glass transition temperature ( $T_g$ ), confirming the heat capacity jump data on the basis of PVT relations for PS. Also for poly(ethylene terephthalate) (PET), the abrupt heat capacity jump at  $T_g$  was observed on TMDSC curves, being not found with the standard DSC [8]. Recently, in the advances of the studies on the photonic contribution to the glass transition of polymers, the mysterious glass transition has been reasonably understood as the quantum phenomena [10 – 16]. For frozen polymer glasses, the heat capacity jump at  $T_g$  should start from the first order hole phase transition and then the glass parts should be unfrozen accompanying with the enthalpy and entropy jumps [10]. The holes are generally neighboring with the ordered parts, which are formed as pairs during the enthalpy relaxation at temperatures below  $T_g$ . First in this chapter, for isotactic PS (iPS) and PET, the heat capacity jump at the glass transition was discussed as the discontinuous change of energy in quantum state of the photon holes, followed by unfreezing of the glass parts. IPS and PET have the benzene rings being able to cause the resonance by neighboring in the side groups or the skeletal chains, respectively. Further, the details on the heat capacity jump found for iPS were also investigated for isotactic polypropylene (iPP) with methyl groups of the same 3/1 helix structure [16]. The resonance suggests the presence of remarkable photons in holes. The dimension of them is characterized by the

geometric molecular structure, e.g., the distance between reflectors such as benzene rings, affecting to the amplitude as a wave. While for the photon holes, the constant volume heat capacity could be defined as the differential coefficient of the internal energy of holes [10 – 16]. So for iPS, PET, and iPP, in order to confirm the identity in two heat capacities of ordered parts and holes in pairs, the heat capacity jump data per molar structural unit at the glass transition were compared with that per molar photon for the holes in ordered part / hole pairs. Here it should be noted that in the ordered part / hole pairs, the molar photon used for photon holes is equivalent to the molar structural unit for ordered parts numerically.

For iPS, PET, and iPP, surely the heat capacity jump at the glass transition was due to the discontinuous change of energy in quantum state of the resonant photon holes between neighboring benzene rings, but methyl groups for iPP, followed by unfreezing of the glass parts [14 – 16]. For iPS, the substance of the helix–coil transition with the enthalpy of 16.1 kJ/mol, but being smaller than the glass transition enthalpy of 18.9 kJ/mol, was shown as the ordered part / hole pairs. For PET, the ordered part / hole pairs were like the mesophase crystals with the glassy conformational disorder of ethylene glycol parts. For iPP, the helical sequences with the enthalpy of 7.4 kJ/mol or the nodules of mesophase with the enthalpy of 12.1 kJ/mol, interchanging between ordered parts and crystals automatically, were shown as the ordered part / hole pairs, depending on the presence of the crystallization upon cooling from the melt. According to above results, it could be understood that the glass transition of polymers investigated for a long time was only the collateral unfreezing phenomena of the glass parts starting by the disappearance of ordered part / hole pairs formed during the enthalpy relaxation at temperatures below  $T_g$ .

On the other hand, for iPS and iPP, from the quantum demand of hole energy at regular temperature intervals of 120 K for iPS and 90 K for iPP, the homogeneous glasses free from ordered part / hole pairs with  $T_g = 240$  K and 180 K have been predicted, respectively [15, 16].  $T_g$  of them could be understood as the first order glass phase transition temperature of the homogeneous glass [17, 18]. But, as one of other quantum possibilities for these polymers, the liquids with  $T_g = 0$  K have also been predicted. In this connection, the equilibrium melting temperature,  $T_m^\infty = 450$  K, for  $\alpha$  form crystals of iPP was corresponding to 5 times the interval of 90 K. The sift of melting from  $\alpha$  to  $\gamma$  form crystals between two peaks of a DSC double melting peak curve observed upon heating was discussed, relating to the formation and then disappearance of crystal / hole pairs.

## 2. Theoretical treatments and discussion

When the hole energy in the ordered part / hole pairs excited at the glass transition, being in equilibrium with the flow parts, is given by  $h^h (= 3C_v^{ph}T)$ , the heat capacity per molar photon for holes,  $C_p^{h*} (= C_p^{flow})$ , is given by [10 – 16] (see section 4):

$$C_p^{h*} (= C_p^{flow}) = 3C_p^{ph} \left( 1 + T \frac{d \ln J_h}{dT} \right) \quad (1)$$

where  $C_p^{\text{flow}}$  is the heat capacity per molar structural unit for the flow parts, being equal to  $C_p^x$  of the heat capacity per molar structural unit for the excited ordered parts [19],  $C_v^{\text{ph}}$  ( $= 2.701R$ ) is the constant volume molar heat capacity for photons [20],  $R$  is the gas constant,  $J_h$  is the number of holes lost by  $T$ , and 3 is the degree of freedom for photons. When  $dJ_h/dT = 0$  at  $T_g$  and the end temperature,  $T_v$ , of the glass transition,  $C_p^{h*}$  at those temperatures is given by  $3C_v^{\text{ph}}$ . Thus, the heat capacity jump per molar photon,  $\Delta C_p$ , at the glass transition is given by:

$$\Delta C_p (= C_p^{h*} - C_v^{\text{ph}}) = 2C_v^{\text{ph}} (= 44.9 \text{ J / (K mol}^*) \text{)} \quad (2)$$

In Eq. (2),  $\Delta C_p$  should be due to the discontinuous energy change from a quantum ground level for photons in the holes, that is,  $(1/2)h\nu (= h_0^h/N_A)$  to  $(3/2)h\nu (= 3h_0^h/N_A)$ , where  $h$  is Planck constant,  $\nu (= c/\lambda)$  is the frequency per second,  $c$  is the velocity of light,  $\lambda$  is the wavelength,  $N_A$  is Avogadro constant, and  $h_0^h$  is the zero-point energy per molar photon, which also is used as the energy unit below. The holes in the excited ordered part / hole pairs should be in dynamical equilibrium with the spatial tubes between a chain and neighboring chains in the flow parts [21]. At the glass transition, the sigmoidal mean heat capacity curve of  $C_p$  as shown in Fig. 1 is observed generally. Even in this case, the  $C_p$  for ordered parts should be equal to the  $C_p^h$  of the mean heat capacity for the holes in ordered part / hole pairs at the glass transition:

$$C_p = C_p^h = \alpha C_v^{\text{ph}} + (1 - \alpha) C_p^{\text{ph}} \quad (3)$$

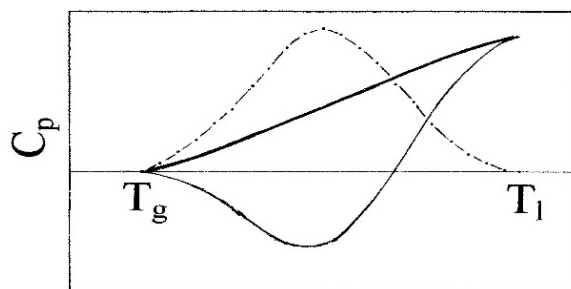
where  $\alpha$  and  $1 - \alpha$  are the fractions of ordered part / hole pairs with the respective holes of  $C_v^{\text{ph}}$  and  $C_p^{\text{ph}} (= 3C_v^{\text{ph}})$ , and  $C_p^{\text{ph}}$  is the adiabatic molar heat capacity for photons. On the other hand, the  $C_p$  for ordered parts in pairs could be divided into two components [22]:

$$C_p = \Delta C_p^x + C_p^r \quad (4)$$

under  $\int_{T_g}^{T_l} C_p dT = \int_{T_g}^{T_l} \Delta C_p^x dT$  and  $\int_{T_g}^{T_l} C_p^r dT = 0$ ,

where  $\Delta C_p^x (= C_p^{h*} - 3C_v^{\text{ph}})$  is the relative component heat capacity per molar structural unit for the excited ordered parts and  $C_p^r$  is the heat capacity change per molar structural unit due to the crystallization followed by the melting. At the glass transition,  $\Delta C_p^x$  shows a peak against  $T$ , reflecting the size distribution of ordered parts. Fig. 1 shows the representative  $C_p$  curve composed of  $\Delta C_p^x$  and  $C_p^r$  at the glass transition for polymers.

Thus, for iPS, PET, and iPP,  $\Delta C_p (= 2C_v^{\text{ph}})$  per molar photon ( $\text{mol}^*$ ) was compared with the reference value of heat capacity jump,  $\Delta C_p^{\text{exp}}$ , per molar structural unit ( $\text{mol}$ ) [8]. The results deviated from  $\Delta C_p / \Delta C_p^{\text{exp}} = 1$ . Table 1 shows the comparison of  $\Delta C_p (= 2C_v^{\text{ph}})$  with  $\Delta C_p^{\text{exp}}$  for these polymers, together with  $h^h/h_x$  at  $T_g$ , where  $h_x$  is the enthalpy per molar structural unit for ordered parts [14 – 16].



**Figure 1.** The components of the  $C_p$  curve (the thick line) at the glass transition for polymers. The dash – dotted line is the relative component  $\Delta C_p^x$  curve for the excited ordered parts with a size distribution and the thin line is the component  $C_p^r$  curve due to the crystallization and then melting.

Polymer	$T_g$ K	$\Delta C_p^{\text{exp}}$ J/(K mol)	$\Delta C_p$ J/(K mol*)	$\Delta C_p / \Delta C_p^{\text{exp}}$	$h^h/h_x$
iPS	359 <sup>*1</sup>	30.8	44.9	1.5	1.5 or 1.0
PET	342	77.8 (80.4, 46.5 <sup>*2</sup> )	44.9	0.6 (0.6)	1.0
iPP	270	19.2	44.9	2.3	1.5 or 2.5

The values in ( ): our data of Fig. 6. \*1: see Table 2. \*2:  $\Delta C_p^{\text{exp}}$  at  $T_m^\infty = 535$  K.

**Table 1.** The values of  $T_g$ ,  $\Delta C_p^{\text{exp}}$ ,  $\Delta C_p$  ( $= 2C_p^{\text{ph}}$ ),  $\Delta C_p / \Delta C_p^{\text{exp}}$ , and  $h^h/h_x$  for iPS, PET, and iPP.

However, the values of  $\Delta C_p / \Delta C_p^{\text{exp}}$  were correlated to  $h^h/h_x$  of the number of structural units holding one photon potentially (described below).  $h_x$  at  $T_g$  is given by [10, 23]:

$$h_x = h_g + \Delta h \quad (5)$$

where  $h_g \{= RT_g^2 (\partial \ln v_f / \partial T)_p\}$  is the glass transition enthalpy per molar structural unit due to the discontinuous free volume change of  $v^*$  from  $v_f = v_0$  to  $v_0 + v^*$  at  $T_g$ ,  $v_f$  and  $v_0$  are the free volume and the core free volume per molar structural unit.  $h_g$  is given approximately by three expressions; (1)  $RT_g^2/c_2$  or  $\phi_g E_a$  (in WLF equation [24],  $\phi_g \{= 1/(2.303c_1)\}$  is the fraction of the core free volume in glasses,  $c_1$  and  $c_2$  are constant, and  $E_a$  is the activation energy), (2) the molar enthalpy difference between the super – cooled liquid and the crystal at  $T_g$ :  $H_g^a - H_g^c$ , and (3) the sum of the conformational and cohesive enthalpies per molar structural unit at  $T_g$ :  $h_g^{\text{conf}} + h_g^{\text{int}}$ . For PET and iPP, the additional heat per molar structural unit,  $\Delta h$ , needed to melt all ordered parts by  $T_1$  in Fig. 1 is given by [10, 23]:

$$\Delta h = \Delta H - Q \quad (6)$$

where  $\Delta H = H_m^a - H_c^a$ ,  $H_m^a$  is the enthalpy per molar structural unit for the liquid at  $T_m^\infty$ ,  $H_c^a$  is the enthalpy per molar structural unit for the super– cooled liquid at the onset temperature,  $T_o$ , of a DSC crystallization peak upon cooling, and  $Q$  is the heat per molar structural unit

corresponding to the total area of the DSC endothermic peak upon heating. While, in the case of  $h_x^{\text{conf}} \neq h_g^{\text{conf}} = 0$  at  $T_g$ ,  $\Delta h$  is derived as [10]:

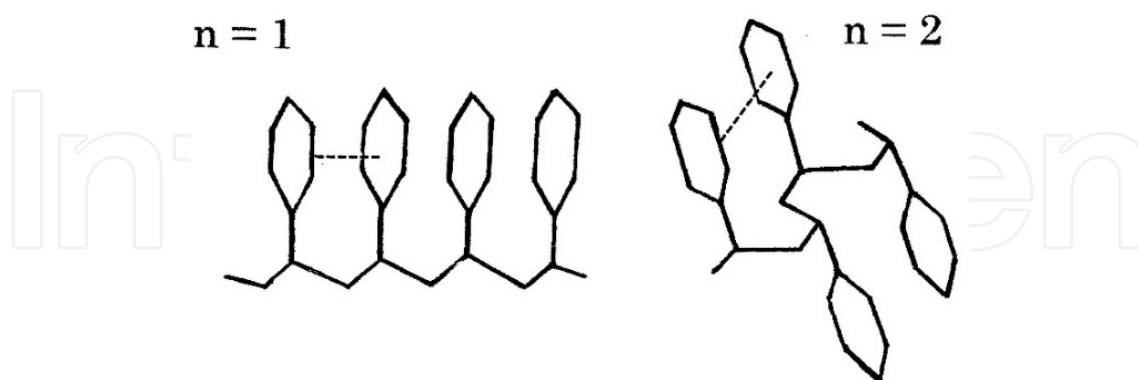
$$\Delta h = T_g \{s_g^{\text{conf}} - (R \ln Z_0) / x\} \quad (7)$$

with  $s_g^{\text{conf}} = (R \ln Z + RT_g d \ln Z / dT)$

where  $h_x^{\text{conf}}$  is the conformational enthalpy per molar structural unit for ordered parts,  $s_g^{\text{conf}}$  is the conformational entropy per molar structural unit at  $T_g$ ,  $Z$  is the conformational partition function for a chain,  $Z_0 (= Z/Z_t)$  and  $Z_t$  are the component conformational partition function for a chain regardless of temperature and depending on the temperature, respectively, and  $x$  is the degree of polymerization. For PET and iPP, the values of  $\Delta h$  from Eq. (7) were a little smaller than those from Eq. (6), respectively. In the case of  $h_x^{\text{conf}} = h_g^{\text{conf}}$ ,  $\Delta h = (RT_g \ln Z_t) / x$  was derived, applying to nylon 6 [10].

## 2.1. Isotactic polystyrene

From  $h^h = (3/2)N_A h\nu$  and  $h^h (= 3C_v T_g) = 24.2 \text{ kJ/mol}^*$  at  $T_g = 359 \text{ K}$ , the wavenumber of  $1/\lambda = 1350 \text{ cm}^{-1}$  was derived for a photon in holes [10]. This agreed nearly with the conformation sensitive band of  $1365 \text{ cm}^{-1}$  assigned to benzene rings [25, 26]. Further from the assigned relation of one photon to one structural unit numerically, the unity of  $h^h/h_x = \Delta C_p / \Delta C_p^{\text{exp}} = 1$  at the glass transition was expected [10], applying to the ordered sequences of- *TTTT*- (see Fig. 2), where *T* is the trans isomer. However,  $\Delta C_p / \Delta C_p^{\text{exp}}$  was 1.5 (see Table 1), where  $T_1$  in  $\Delta C_p^{\text{exp}}$  is  $\sim 381 \text{ K}$  [8]. Accordingly, the number of structural units holding one photon potentially in holes,  $n (= h^h/h_x)$ , is defined here necessarily. Fig. 2 shows the sequence models of- *TTTT*- ( $n = 1$ ) and unstable- *TCTC*- ( $n = 2$ ) for iPS, where *C* is the cis isomer.



**Figure 2.** The sequence models of- *TTTT*- ( $n = 1$ ) (Left) and unstable- *TCTC*- ( $n = 2$ ) (Right) for iPS. The dashed line shows one of the photon sites between benzene rings.

According to  $h^h/h_x = 1.5$ ,  $h_x (= 2h_0^h) = 16.1 \text{ kJ/mol}$  was derived. This corresponded to  $\Delta C_p T_g = 16.1 \text{ kJ/mol}^*$  of the  $C_p$  jump energy for holes at  $T_g$ . While  $h_x$  can be also derived from the solubility parameter,  $\delta \{= (h_0/V)^{1/2}\}$ , where  $h_0$  is the latent cohesive energy per molar structural unit,



corresponding to the heat of vaporization or sublimation and  $V$  is the molar volume of structural units. The relations among  $h_0$ ,  $h_u$ ,  $h_x$ , and  $h_g$  at temperatures before and after  $T_g$  are given by [19, 27]:

$$h_0 = h_g + h_x \text{ or } h_g + h_x + h_u \text{ at } T \leq T_g \tag{8}$$

$$h_0 = h_x \text{ or } h_x + h_u \text{ at } T > T_g \tag{9}$$

where  $h_u$  is the heat of fusion per molar structural unit. For crystalline polymers,  $h_u$  is contained in Eqs. (8) and (9). For iPS,  $h_0 = 35.0$  kJ/mol was derived from  $\delta = 9.16$  (cal/cm<sup>3</sup>)<sup>1/2</sup> of the mean of 12 experimental values ( $\geq 9.0$  (cal/cm<sup>3</sup>)<sup>1/2</sup>) [28], and the value of  $h_x$  from Eq. (8), 16.1 kJ/mol, agreed with that from  $h^h/h_x = 1.5$  perfectly. However it was smaller than  $h_g (= RT_g^2/c_2) = 18.9$  kJ/mol. The difference in  $h_g$  and  $h_x$ , 2.8 kJ/mol, agreed with the cohesive energy of methylene residues of  $h_m^{\text{int}} = 2.8$  kJ/mol [29], suggesting that the ordered part / hole pairs might fill softly the parts in glassy bulks.

T <sub>g</sub> K	h <sub>0</sub> kJ/mol	h <sub>g</sub> kJ/mol	Δh kJ/mol	h <sub>x</sub> kJ/mol	h <sup>h</sup> kJ/mol*	h <sup>h</sup> /h <sub>x</sub>
359 <sup>*1</sup> (360)	43.1 <sup>*2</sup>	18.9	5.3	24.2 <sup>*4</sup>	24.2	1
359 <sup>*1</sup> (360)	35.0 <sup>*2,*3</sup>	18.9	−2.8	16.1	24.2	1.5
240	1.7 <sup>*2</sup>	1.7 <sup>*5</sup>	−1.7	0	0 (16.1)	---

\*1: experimental value [30]. \*2: from Eq. (8). \*3: from  $\delta = 9.16$  (cal/cm<sup>3</sup>)<sup>1/2</sup>. \*4:  $h_x$  for the excited ordered parts or – TTTT– sequences. \*5:  $h_g = h_g^{\text{int}} + h_g^{\text{conf}}$  from  $h_g^{\text{int}} = -f_g^{\text{conf}}$  at  $T_g = 240$  K (see Fig. 4, described below). The value in ( ) of  $h^h$  column is  $h^h (= 3C_v^{\text{ph}}T)$  at 240 K.

**Table 2.** The values of  $T_g$ ,  $h_0$ ,  $h_g$ ,  $\Delta h$ ,  $h_x$ ,  $h^h$ , and  $h^h/h_x$  for iPS.

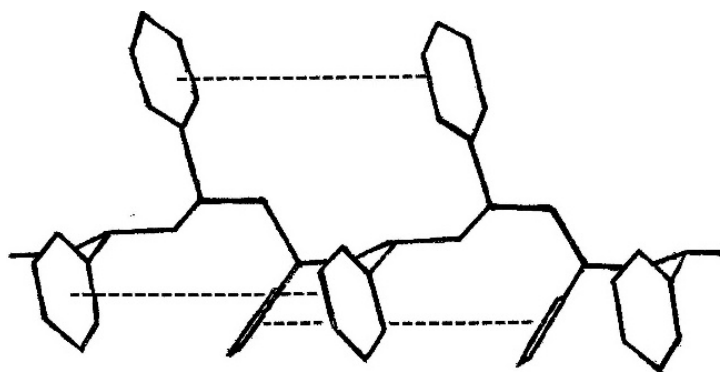
Table 2 shows the values of  $T_g$ ,  $h_0$ ,  $h_g$ ,  $\Delta h$ ,  $h_x$ , and  $h^h$  at  $h^h/h_x = 1$  and 1.5 for iPS. In the 4th line,  $h^h = h_x = 0$  and  $h_g = 1.7$  kJ/mol at 240 K are shown (discussed below). The relation of  $h^h = h_x = 0$  is brought by the energy radiation of  $2h_0^h (= 16.1$  kJ/mol\*) at  $T_g$  and the energy loss of  $h_0^h (= 8.1$  kJ/mol\*) upon cooling from  $T_g$  obeying:

$$h^h = h_0^h - 3C_v^{\text{ph}}(T_g - T) \tag{10}$$

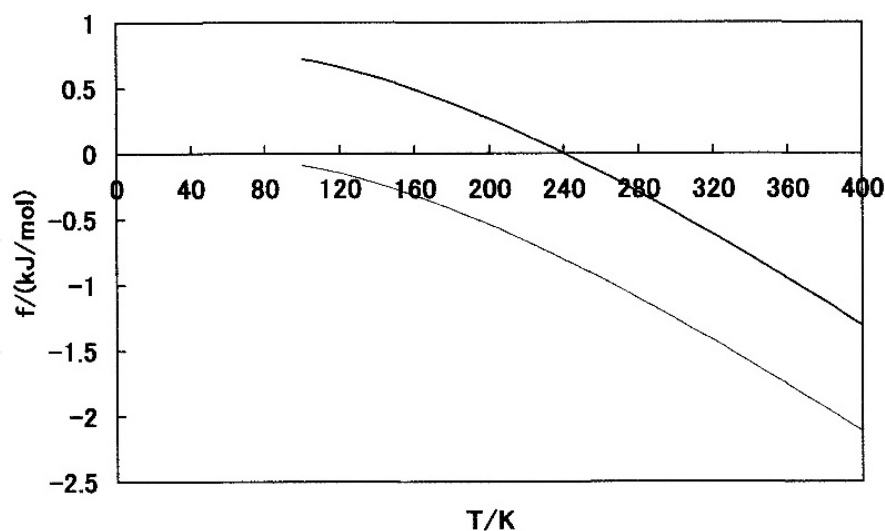
In Eq. (10), the specific temperature of 240 K at  $h^h = 0$  agreed with the hole temperature at  $h^h (= 3C_v^{\text{ph}}T) = 16.1$  kJ/mol\*. In the glasses upon heating from 0 K, the generation of ordered part / hole pairs at 240 K and succeedingly, the instant radiation of the hole energy of 16.1 kJ/mol\* should bring the same state as that of  $h^h = 0$  at 240 K upon cooling, suggesting  $T_g = 240$  K for the homogeneous glass free from the ordered part / hole pairs. Altering  $3C_v^{\text{ph}} (= C_p^{\text{ph}})$  in Eq. (10) to  $C_v^{\text{ph}}$ , the temperature at  $h^h = 0$  was  $T_g = 0$  K. While for the glasses including the ordered part /

hole pairs,  $T_g = 360$  K (see Table 2) was expected from the quantum demand of hole energy at regular temperature intervals of 120 K.

For iPS, the rotational isomeric 2-state (RIS) model of  $T$  (trans) and  $G$  (gauche) or  $G'$  (gauche') is known well [31]. Fig. 3 depicts the helix structure of  $-TGTGTG-$  ( $n = 3$ ) for iPS. From  $h^h/h_x$  ( $=n$ ) = 1.5, the intermediate sequences ( $n = 1.5$ ) between the right or left handed helical sequence ( $n = 3$ ) and the aperiodic sequence ( $n = 0$ ), displaying the helix-coil transition, were predicted as the sequences of ordered parts [14, 15]. The frequency of occurrence,  $\Gamma$ , of the helix-coil transition should be given approximately by  $h^h/h_0^h$  in Eq. (10) with  $h^h/h_0^h = 0$  at  $T = 240$  K. The  $\Delta C_p$  ( $= 3C_v^{ph}$ ) at  $T_g = 240$  K in a glassy state of  $\Gamma = 0$  was  $67.4$  J/(K mol\*) [15].



**Figure 3.** The 3/1 helix structure of  $-TGTGTG-$  ( $n = 3$ ) and the photon sites (dashed line parts) between benzene rings for iPS.



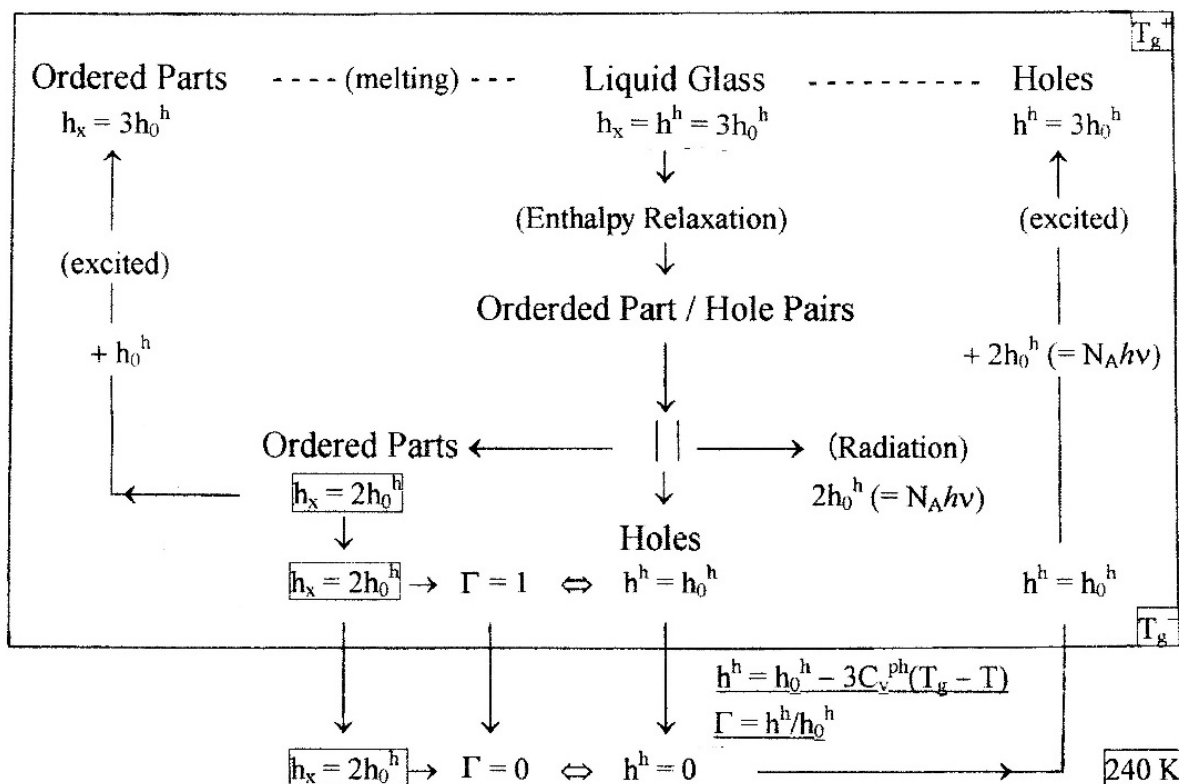
**Figure 4.** The relation between  $f$  and  $T$  calculated for the RIS model chains ( $x = 100$ ) of iPS. The thin line is  $f = f^{\text{conf}}$  and the thick line is  $f = f^{\text{conf}} + 0.81$  kJ/mol.

Fig. 4 shows the relation between  $f$  ( $= f^{\text{conf}}$  or  $f^{\text{conf}} + 0.81$  kJ/mol) and  $T$  calculated for the RIS model chains ( $x = 100$ ) with the normalized statistical weight of  $\eta = 1$  applied to  $TG$  isomer of



iPS, where  $f^{\text{conf}}$  is the conformational free energy per molar structural unit, being minus and decreasing with an increase in temperature. Adding the value of  $-f^{\text{conf}}$  ( $= 0.81$  kJ/mol) at 240 K to all values of the original thin line, the thick line of  $f^{\text{conf}} + 0.81$  kJ/mol is depicted. In the case of  $-f^{\text{conf}} = h^{\text{int}}$ , i.e.,  $(h^{\text{conf}} + h^{\text{int}}) - Ts^{\text{conf}} = 0$  at 240 K, the sum of  $-f^{\text{conf}}$  ( $= 0.81$  kJ/mol) and  $h^{\text{conf}}$  ( $= 0.89$  kJ/mol), 1.70 kJ/mol, should be the ultimate  $h_g$  at the first order glass phase transition for the homogeneous glass free from the ordered part / hole pairs (see Table 2), where  $h^{\text{int}}$  is the cohesive enthalpy per molar structural unit, and  $h^{\text{conf}}$  and  $s^{\text{conf}}$  are the conformational enthalpy and entropy per molar structural unit.

Fig. 5 shows the schematic chart of the instantaneous state changes at  $T_g$  ( $= 360$  K) upon cooling and heating as a working hypothesis. The ordered part / hole pairs formed instantaneously at  $T_g$  upon cooling have  $h^h = h_0^h$  and  $h_x = 2h_0^h$ . At  $T_g$  upon heating, the ordered part / hole pairs are excited by absorbing the photon energy of  $2h_0^h$  for the holes and adding the energy of  $h_0^h$  for the ordered parts, followed by the absorption of  $h_g$  for the glass parts. The equilibrium relation at the melting transition among the ordered parts, the holes, and the flow parts is shown by the dashed lines in Fig. 5. In order to melt the excited ordered part / hole pairs perfectly, further the latent heat of  $h_0^h$  is needed at  $T_g$ .



**Figure 5.** The schematic chart of the instantaneous state changes at  $T_g$  for iPS. The arrow marks of  $\downarrow$  and  $\uparrow$  show the cooling and heating directions, respectively.  $T_g^+$  and  $T_g^-$  are the glass transition temperatures upon cooling and heating, respectively. The  $h_x = 2h_0^h$  shows the substance of helix-coil transition between the helical sequence ( $n = 3$ ) and the aperiodic sequence ( $n = 0$ ). The arrow marks of  $\Leftrightarrow$  show the interaction between the ordered parts and the holes in the pairs. The  $\Gamma$  is the frequency of occurrence of the helix-coil transition. The dashed lines show the equilibrium relation of melting among ordered parts, flow parts, and holes in the excited state.

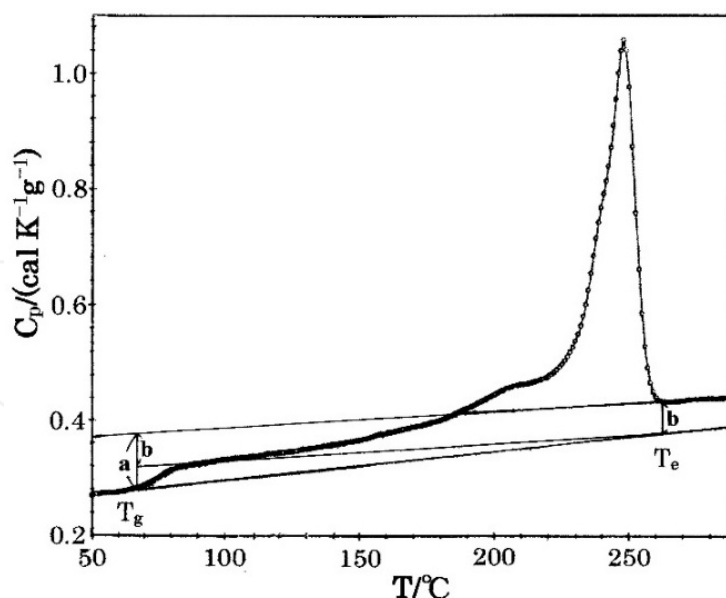
## 2.2. Poly(ethylene terephthalate)

For PET,  $h_x (= h_g + \Delta h) = 24.1$  kJ/mol was obtained from Eq. (5), being almost equal to  $h^h (= 3C_v^{ph}T_g) = 23.0$  kJ/mol\* at  $T_g (= 342$  K) [10, 23]. Thus,  $h^h/h_x (= n) = 0.95$  was shown experimentally. However as shown in Table 1,  $\Delta C_p/\Delta C_p^{exp}$  was 0.6. Table 3 shows the values of  $T_g$ ,  $h_0$ ,  $h_u$ ,  $h_g$ ,  $\Delta h$ ,  $h_x$ ,  $h^h$ , and  $h^h/h_x$  for PET. The two values of  $h_u$ , 23.0 and 28.5 kJ/mol, are assigned to the crystals with the conformational disorder of ethylene glycol parts and the smectic-c crystals with the stretched sequences, respectively [23, 32].  $\Delta C_p/\Delta C_p^{exp} = 0.6$  at the glass transition meant that one photon was situated in the neighboring phenylene residues comprising  $\sim 60$  % of the structural unit length and 40 % of  $\Delta C_p^{exp}$  was brought by unfreezing of the ethylene glycol parts in a glass state [14]. This was predicted also from the data by TMDSC [8]. From  $h^h = (3/2) N_A h\nu$  and  $h^h (= 3C_v^{ph}T_g) = 23.0$  kJ/mol\* at  $T_g = 342$  K,  $1/\lambda = 1290$  cm<sup>-1</sup> was derived, agreeing with 1288 cm<sup>-1</sup> observed for the un-oriented samples [33].

$T_g$ K	$h_0$ kJ/mol	$h_u$ kJ/mol	$h_g$ kJ/mol	$\Delta h$ kJ/mol	$h_x$ kJ/mol	$h^h$ kJ/mol*	$h^h/h_x$
342	64.7 <sup>*1</sup>	23.0 (535 K)	17.6 <sup>*3</sup>	6.5	24.1	23.0	0.95
342	70.2 <sup>*1</sup> , 68.2 <sup>*2</sup>	28.5 (549 K)	17.6 <sup>*3</sup>	6.5	24.1	23.0	0.95

\*1: from Eq. (8). \*2: from  $\delta = 10.7$  (cal/cm<sup>3</sup>)<sup>1/2</sup> [19]. \*3:  $h_g = RT_g^2/c_2^2$ . The values in () are  $T_m^\infty$  of the respective crystals [23].

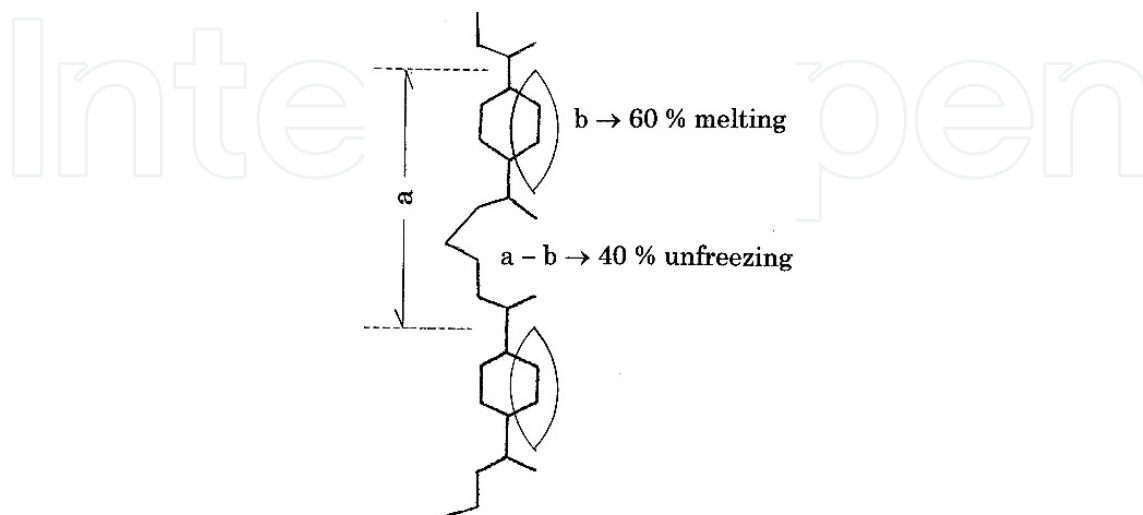
**Table 3.** The values of  $T_g$ ,  $h_0$ ,  $h_u$ ,  $h_g$ ,  $\Delta h$ ,  $h_x$ ,  $h^h$ , and  $h^h/h_x$  for PET.



**Figure 6.** The  $C_p$  curve for the non-annealed PET film. The parts of a and b show the  $C_p$  jump to the liquid line at  $T_g$  and  $T_e$ .

Fig. 6 shows the  $C_p$  curve converted from DSC curve data for the non-annealed PET film cooled to 323 K (50 °C) at 5 K/min from 573 K (300 °C).  $T_g$  agreed almost with 342 K of [8].  $T_e$  of the

end temperature of melting is 535 K (262 °C). The parts of  $a$ ,  $b$ , and  $a - b$  of  $C_p$  jump to the liquid line at  $T_g$  and  $T_e$  were correlated to the structural unit length, the lengths of phenylene and glassy ethylene glycol residues, respectively. Fig. 7 shows the parts in the structural unit related to  $a$ ,  $b$ , and  $a - b$ .

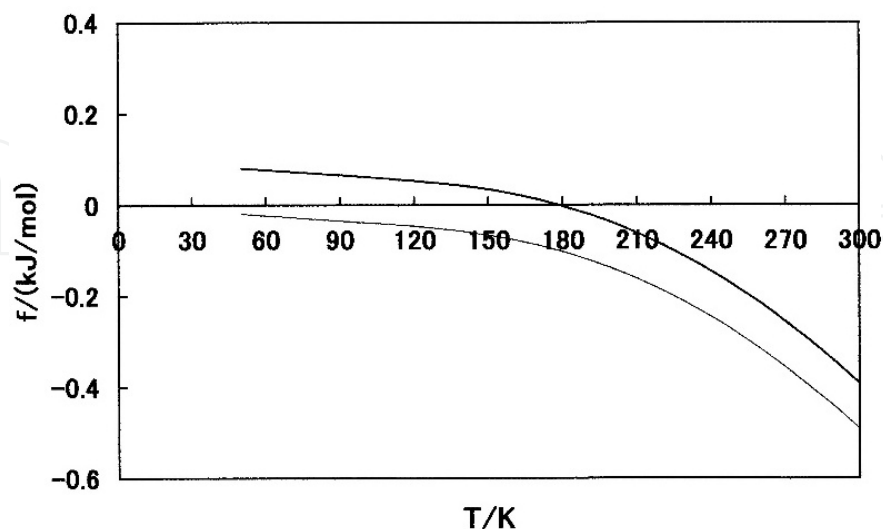


**Figure 7.** The parts in the structural unit related to the  $C_p$  jumps of  $a$ ,  $b$ , and  $a - b$  shown in Fig. 6 for PET. The part attached to the spindle mark shows the phenylene residue holding one photon together with the neighboring same residue (omitted here).

### 2.3. Isotactic polypropylene

According to the scheme of the formation of ordered part / hole pairs at  $T_g$  upon cooling (see Fig. 5), for iPP with  $T_g = 270$  K,  $h_x (= 2h_0^h) = 12.1$  kJ/mol was derived, being much larger than  $h_g \approx H_g^a - H_g^c = 6.2$  kJ/mol [34] and  $h_x (= h_g + \Delta h) = 7.4$  kJ/mol, where  $\Delta h = \Delta H - Q$ ,  $\Delta H = H_m^a - H_c^a$  (see Eqs. (5) and (6)). The used data are as follows:  $T_c = 403.6$  K,  $T_m^\infty = 450$  K for  $\alpha$  form crystals,  $\Delta H = 4.89$  kJ/mol [34], and  $Q = 3.76$  kJ/mol for the sample annealed at 461.0 K for 1 hour [10, 35]. However,  $h_0 (= h_g + h_x) = 18.3$  kJ/mol from Eq. (8) was almost equal to  $h^h (= 3h_0^h) = 18.2$  kJ/mol\*, meaning the appearance of frozen glasses with  $h_g = h_0^h + 0.1$  kJ/mol. For holes with  $C_p^{ph}$  even upon cooling from  $T_g$ , Eq. (10) showed the specific temperature of 180 K, at which all ordered part / hole pairs should be disappeared because of  $h^h = 0$ , corresponding to 240 K for iPS [15]. At temperatures below 180 K, all should be in a state of the homogeneous glass with  $T_g = 180$  K. The  $\Delta C_p (= 3C_v^{ph}) = 67.4$  J/(K mol\*) at  $T_g = 180$  K was the same as that of iPS with  $T_g = 240$  K. Fig. 8 shows the relation between  $f$  ( $= f^{conf}$  or  $f^{conf} + 0.1$  kJ/mol) and  $T$  calculated for RIS model chains ( $x = 100$ ) with the normalized statistical weight of  $\sigma = 1$  applied to  $TT$  isomer of iPP [36, 37]. The  $f^{conf}$  at temperatures below and above 180 K is minus and decreases with an increase in temperature. The absolute value of  $f^{conf} = -0.102$  kJ/mol at 180 K equaled to  $h_g - h_0^h = 0.1$  kJ/mol at 270 K. Adding the cohesive enthalpy of  $h^{int} = 0.102$  kJ/mol to  $f^{conf} (= -0.102$  kJ/mol), from  $f = f^{conf} + h^{int} = 0$  and  $h^{conf} = 0.18$  kJ/mol at  $T_g = 180$  K,  $h_g (= h^{conf} + h^{int}) = 0.28$  kJ/mol is derived as the first order glass phase transition enthalpy for the homogeneous glass composed

of isolated chains, but with the cohesive energy of  $h^{\text{int}}$  and free from ordered part / hole pairs (see Table 5).



**Figure 8.** The relation between  $f$  and  $T$  calculated for RIS model chains ( $x = 100$ ) of iPP. The thin line is  $f = f^{\text{conf}}$  and the thick line is  $f = f^{\text{conf}} + 0.1$  kJ/mol.

On the other hand, altering  $3C_v^{\text{ph}} (= C_p^{\text{ph}})$  in Eq. (10) to  $C_v^{\text{ph}}$ , the temperature at  $h^h = 0$  was  $T_g = 0$  K as well as iPS. From  $s^{\text{conf}} = 0.38$  J/(K mol) of constant at temperatures below 70 K, the sequence model of  $-TGTGTGTTG'TG'TG'T-$  in a liquid state was predicted, where  $T$  is trans,  $G$  is gauche,  $G'$  is gauche' isomer, and  $TT$  is the trans-trans isomer shifting always to the left or right direction on a sequence [38]. From  $h_x = 12.1$  kJ/mol, the nodules of mesophase interchanging between crystals and ordered parts automatically were predicted in the glasses. According to the equilibrium relation in crystals and ordered parts of this class (D in Table 4) given by  $f_x = 2f_u$  [10, 39],  $2h_u - h_x = 2.9$  kJ/mol was derived using  $h_u = 7.5$  kJ/mol for  $\alpha$  form crystals, corresponding to  $2T_m(s_u - s_x/2)$ , which was almost equal to  $h_m^{\text{int}} = 2.8$  kJ/mol of the cohesive energy of methylene residues in the sequences, where  $f_x$  and  $s_x$  are the free energy and entropy per molar structural unit for ordered parts, and  $f_u$  and  $s_u$  are those for crystals.

According to Flory's theory [40] on the melting of the fringe-type crystals with a finite crystal length of  $\zeta$ , the end surface free energy of crystals per unit area,  $\sigma_e$ , at  $(df_u/d\zeta)_\phi = 0$  is given by:

$$\sigma_e = \mu(RT\zeta/2)[1/(x - \zeta + 1) + (1/\zeta)\ln\{(x - \zeta + 1)/x\}] \quad (11)$$

where  $\phi$  is the amorphous fraction and  $\mu$  is the conversion coefficient of mol/m<sup>3</sup>. In this context:

$$2\sigma_e/\zeta = \mu(f_x - f_u) \quad (12)$$

$$f'_x = RT[(1/\zeta)\ln\{(x - \zeta + 1)/x\} - \ln P_c] \quad (13)$$

where  $P_c$  given by  $\{(x - \zeta + 1)/x\}^{1/\zeta}$  for fringe-type crystals, is the probability that a sequence occupies the lattice sites of a crystalline sequence. Moreover:

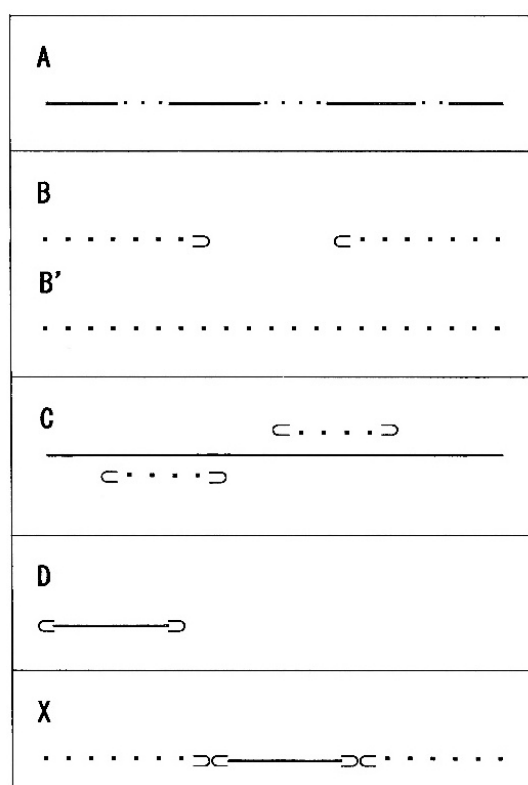
$$f_u - (f_x - f'_x) = 0 \tag{14}$$

Eq. (11) is obtained when  $\ln P_c = -1/(x - \zeta + 1)$ . From Eq. (14), the relations are derived based on  $f_u$  and  $f_x$  at  $f'_x \geq 0$ , and those can be grouped into four equilibrium classes (A ~ D) and one non-equilibrium class (X) as shown in Table 4. Class A of  $f_x = f_u$  at  $f'_x = 0$  shows the dynamic equilibrium relation between the ordered parts and the crystal parts of same fringe-type, leading to  $\sigma_e = 0$ , and that,  $\zeta = 0/0$  in Eq. (16) (described below). For class B,  $f_u = -f'_x$  from Eq. (14) with  $f_x = 0$  refers to the anti-crystal holes and  $f_x = 0$  is assigned to the ordered parts of  $\zeta = \infty$ . The interface between the anti-crystal holes and the ordered parts should work as the reflector of photons. In this case, the even interface made of the folded chain segments should be avoided through the random reflection. According to Eq. (12) with  $h_x - h_u = \sigma_e/(\mu\zeta)$ , the respective interface energies of the hole and the ordered part are compensated each other at the common interface, thus leading to  $f_x = 0$  [10]. For class C,  $f_x = f'_x$  from Eq. (14) with  $f_u = 0$  is assigned to the ordered parts of  $\zeta \neq \infty$  (i.e., a kebab structure) and  $f_u = 0$  to the crystals of  $\zeta = \infty$  (i.e., a shish structure). Class D of  $f_u (= f'_x) = f_x/2$  is related to the equilibrium in crystal and ordered parts. For those with folded chains, the reversible change from crystal or ordered parts to other parts is expected to take place automatically. The relations in class X do not satisfy Eq. (14), suggesting that the holes of class B cannot be replaced by the crystals with  $\zeta \neq \infty$ . Fig. 9 shows the schematic structure models of bulk polymers conformable to A ~ X classes in Table 4.

$f'_x$	$f_x$	$f_u$	Class
$f'_x = 0$	$f_x = f_u$	$f_u = f_x$	A
$f'_x > 0$	$f_x = 0$	$f_u = -f'_x$	B
	$f_x = f'_x$	$f_u = 0$	C
	$f_x = 2f_u$	$f_u = f_x/2 = f'_x$	D
$f'_x > 0$	$f_x = 0$	$f_u = f'_x$	X

**Table 4.** Relations of equilibrium (A ~ D) and non-equilibrium (X) in  $f_x$  and  $f_u$  at  $f'_x \geq 0$  for crystalline polymers [10, 39].

At the rapid glass transition absorbing the photon energy of  $2h_0^h$  at  $T_g$  upon heating, the ordered part / hole pairs should be excited immediately and then melted, followed by unfreezing of the glass parts. At the slow glass transition, the disappearance and then crystallization of ordered part / hole pairs should occur upon heating, bringing the new crystal parts [16]. In the closed system that the both heats of crystallization and melting should be cancelled out according to Eq. (4), those should be melted by  $T_1$  in Fig. 1. While in the open system that the heat irradiated by crystallization was escaped out of the system,  $T_1$  corresponded to  $T_m^\infty$  (450 K for  $\alpha$  form crystals) and  $h_0 (= h_g + h_x + h_u) = 21.0$  kJ/mol in Eq. (8) agreed



**Figure 9.** Schematic structure models of bulk polymers. A ~ X correspond to the classes in Table 4, respectively. •••: ordered parts,  $\frac{3}{4}\frac{3}{4}$ : crystals,  $\supset$  and  $\subset$ : folded segments, the space between  $\supset$  and  $\subset$  of B: anti-crystal hole. B is equivalent to B'.

perfectly with the value of  $h^h (= 3h_0^h) + h_m^{int}$ , where  $h_x (= h_g + \Delta h)$  is 7.4 kJ/mol, being larger than  $h_0^h (= h^h/3) = 6.1$  kJ/mol\*. In this context,  $h_g - h_0^h = 0.1$  kJ/mol,  $h_x - h_0^h = 1.3$  kJ/mol, and  $h_u - h_0^h = 1.4$  kJ/mol. The sum of them was equal to  $h_m^{int} = 2.8$  kJ/mol. Thus,  $n (= h^h/h_x) = 2.5$  was shown, almost corresponding to  $\Delta C_p/\Delta C_p^{exp} = 2.3$ . Table 5 shows the values of  $T_g$ ,  $h_0$ ,  $h_u$ ,  $h_g$ ,  $h_x$ ,  $h^h$ , and  $h^h/h_x$  for iPP. From  $h^h (= 3h_0^h) = 18.2$  kJ/mol\* at  $T_g (= 270$  K), the wavenumber of  $1/\lambda = 1022$   $\text{cm}^{-1}$  was derived for a photon in holes [10]. This agreed nearly with  $1045$   $\text{cm}^{-1}$  relating to the crystallinity [41]. Accordingly, one photon should be situated between the neighboring methyl groups in the helical sequence.

$T_g$ K	$h_0$ kJ/mol	$h_u$ kJ/mol	$h_g$ kJ/mol	$h_x$ kJ/mol	$h^h$ kJ/mol*	$h^h/h_x$
270	18.3 <sup>*1</sup>	---	6.2 <sup>*3</sup>	12.1	18.2	1.5
270	21.1 <sup>*1</sup>	7.5 <sup>*2</sup>	6.2 <sup>*3</sup>	7.4	18.2	2.5
180	0.28 <sup>*1</sup>	---	0.28 <sup>*4</sup>	0	0	---

\*1: from Eq. (8). \*2:  $h_u$  for  $\alpha$  form crystals. \*3:  $h_g = H_g^a - H_g^c$ , \*4:  $h_g = h_g^{int} + h_g^{conf}$  from  $h_g^{int} = -f_g^{conf}$  at  $T_g = 180$  K.

**Table 5.** The values of  $T_g$ ,  $h_0$ ,  $h_u$ ,  $h_g$ ,  $h_x$ ,  $h^h$ , and  $h^h/h_x$  for iPP.



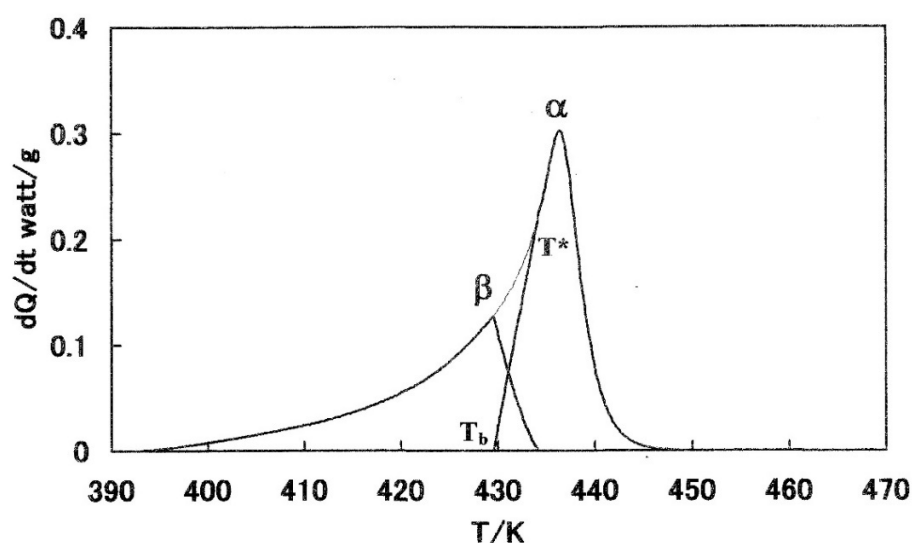
### 2.3.1. Equilibrium melting temperature, $T_m^\infty$

For PET discussed in the previous section 2.2,  $T_1$  in Fig. 1 corresponded to  $T_m^\infty = 535$  K for the crystals with conformational disorder of ethylene glycol parts, but with a chain axis parallel to c-axis of a cell. This finding in PET was also discussed in iPP with  $T_m^\infty = 435$  K, 450 K, and 462 K for  $\beta$ ,  $\alpha$ , and  $\gamma$  form crystals, respectively, which were found by DSC measurements [35]. Above all,  $T_m^\infty = 450$  K for  $\alpha$  form crystals could be  $T_1$  (in Fig.1) of the temperature expected from the quantum demand of hole energy at regular temperature intervals of 90 K. Experimentally,  $T_m^\infty$  is determined as the intersection temperature between an extrapolation line of  $T_m = T_e$  in the melting peaks without superheating and a  $T_m = T_a$  line, where  $T_m$  is the melting temperature from  $T_a$  to  $T_e$ ,  $T_a$  is the annealing (crystallization) temperature, and  $T_e$  is the end temperature of melting peak. While at  $T_m^\infty$ , the processes of melting and crystallization should occur reversibly, so that  $T_m^\infty$  equals to both temperatures of  $T_e$  and  $T_b$  of the onset temperature of melting, and that, there are two points of  $T_m^\infty$  at  $T_a (= T_e)$  and  $T_b (= T_e)$  on a  $T_m = T_e$  line. The line through two points of  $T_m^\infty$  should be parallel to the abscissa of  $T_a$ , because  $T_m^\infty$  is only one [23]. For the bulk contained  $\alpha$  form crystals with  $h_u = 7.46$  kJ/mol, the sum of  $h_g - h_0^h = 0.1$  kJ/mol,  $h_x - h_0^h = 1.3$  kJ/mol, and  $h_u - h_0^h = 1.4$  kJ/mol was equal to  $h_m^{\text{int}} = 2.8$  kJ/mol (see section 2.3). While for the bulk contained only  $\gamma$  form crystals with  $h_u = 8.70$  kJ/mol, the difference in  $h_m^{\text{int}}$  and  $(h_u - h_0^h)$  was 0.2 kJ/mol, suggesting  $h_g = h_x = h_0^h + 0.1$  kJ/mol. Figs. 10 and 11 show the DSC single and double melting peak curves for the iPP films annealed at  $T_a = 461.0$  K and 441.5 K for 1 hour, respectively. Here the single melting peak curve in Fig. 10 is divided into  $\alpha$  and  $\beta$  peaks, and the double melting peak curve in Fig. 11 is divided into  $\gamma$ ,  $\alpha$ , and  $\beta$  peaks. In both Figures,  $T_b$  is the temperature that the extrapolation line from the line segment with a highest slope in the lower temperature side of the melting peak intersects the base line. The onset temperature of the extrapolation line,  $T^*$ , is also the end temperature of the residual peak appeared by subtracting the area of single or double peak with  $T_b$  from the total endothermic peak area. The  $\beta$  peak is considered to be due to the melting of small crystals attached around the crystal lamellae of  $\alpha$  form. The mean of end temperatures in  $\beta$  peaks found for some annealing samples agreed closely with  $T_e = 435$  K of  $\beta$  form crystals [42].

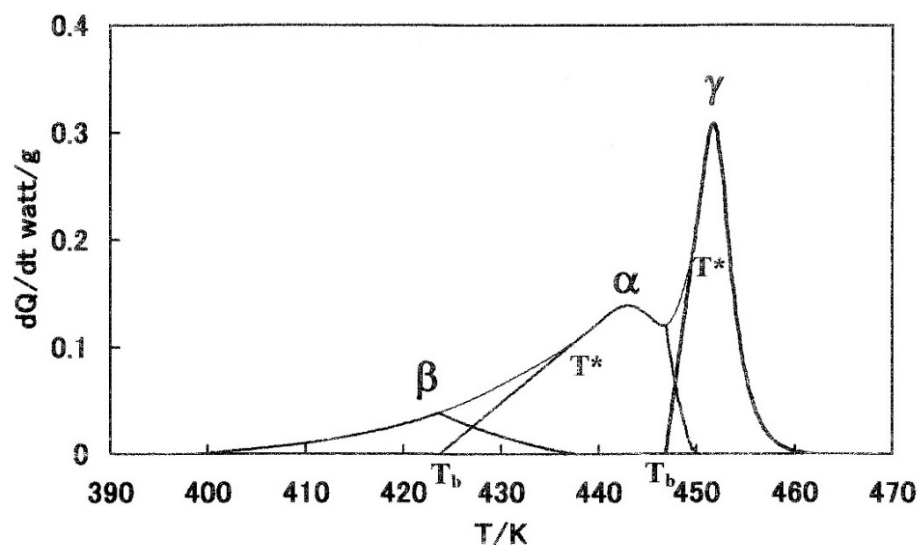
Table 6 shows the values of  $T_b$ ,  $T^*$ ,  $Q_m$ ,  $\Delta Q_m$ ,  $\Delta h^h$ , and  $\Delta h^h / \Delta Q_m$  in  $\alpha$  and  $\gamma$  peak curves for the iPP films annealed at 461.0 K and 441.5 K for 1 hour. Where  $Q_m$  is the heat per molar structural unit corresponding to the area of  $\alpha$  or  $\gamma$  peak from  $T_b$  and  $\Delta Q_m$  is the heat per molar structural unit corresponding to the area from  $T_b$  to  $T^*$  of  $\alpha$  or  $\gamma$  peak and relating to the melting of crystals recrystallized newly from  $\beta$  to  $\alpha$  form or  $\alpha$  to  $\gamma$  form. For the holes of crystal / hole pairs formed newly by recrystallization from  $T_b$  to  $T^*$  of  $\beta$  or  $\alpha$  peak, the hole energy per molar photon,  $\Delta h^h$ , is given by [10]:

$$\Delta h^h = 3C_v^{ph} (T^* - T_b) \quad (15)$$

As shown in Table 6, the small difference in  $\Delta Q_m$  and  $\Delta h^h$  could be regarded as significant for the formation and then disappearance of crystal / hole pairs from  $T_b$  to  $T^*$ . For the shift from



**Figure 10.** DSC single melting peak curve composed of  $\alpha$  and  $\beta$  peaks for the iPP film annealed at 461.0 K for 1 hour. The thin line is the part of an original DSC curve.  $T_b$  is the onset temperature of  $\alpha$  peak and  $T^*$  is the end temperature of  $\beta$  peak.



**Figure 11.** DSC double melting peak curve composed of  $\alpha$ ,  $\beta$ , and  $\gamma$  peaks for the iPP film annealed at 441.5 K for 1 hour. The thin lines are the parts of an original DSC curve.  $T_b$  is the onset temperature of  $\gamma$  or  $\alpha$  peak and  $T^*$  is the end temperature of  $\alpha$  or  $\beta$  peak.

$\beta$  to  $\alpha$  peak in Fig. 11,  $\Delta h^h/\Delta Q_m$  was 1.21 contrary to our expectation, but at  $T^* = 435$  K of the mean of  $T^*$  ( $T_m^\infty$  for  $\beta$  form crystals),  $\Delta h^h/\Delta Q_m = 0.98$  was derived. For the shift from  $\alpha$  to  $\gamma$  peak, it was 0.61, meaning the melting of original  $\gamma$  form crystals with 39 % of  $\Delta Q_m$ ; 0.13 kJ/mol. The relay of melting from  $\alpha$  to  $\gamma$  form crystals between two peaks of a DSC double melting peak curve should be done through the mediation of the formation and then disappearance of the crystal / hole pairs with 61 % of  $\Delta Q_m$ ; 0.20 kJ/mol ( $= \Delta h^h$ ), which agreed with the difference in  $h_m^{\text{int}}$  and  $(h_u - h_0^h)$  perfectly, corresponding to  $(h_g + h_x) - 2h_0^h = 0.2$  kJ/mol suggested above.

$T_a$ K	Form	$T_b$ K	$T^*$ K	$Q_m$ kJ/mol	$\Delta Q_m$ kJ/mol	$\Delta h^h$ kJ/mol	$\Delta h^h/\Delta Q_m$
461.0	$\alpha$	429.6	434.2	2.05	0.38	0.24	0.63
441.5	$\alpha$	423.7	437.7 (435)	2.16	0.78	0.94 (0.76)	1.21 (0.98)
	$\gamma$	446.9	449.9	1.64	0.33	0.20	0.61

The values in ( ) show  $T_m^\infty$ ,  $\Delta h^h$ , and  $\Delta h^h/\Delta Q_m$  at  $T_m^\infty$  for  $\beta$  form crystals.

**Table 6.** The values of  $T_b$ ,  $T^*$ ,  $Q_m$ ,  $\Delta Q_m$ ,  $\Delta h^h$ ,  $\Delta h^h/\Delta Q_m$  of  $\alpha$  and  $\gamma$  peak curves for the iPP films annealed at 461.0 K and 441.5 K for 1 hour.

### 2.3.2. $\zeta$ distribution function, $F(\zeta)$

Next, the  $\alpha$  peak curve in Fig. 10 and the two divided peak curves of  $\alpha$  and  $\gamma$  in Fig. 11 starting to melt at  $T_b$  were converted into the crystal length ( $\zeta$ ) distribution function,  $F(\zeta)$ . The  $\zeta$  is according to Gibbs–Thomson given by:

$$\zeta = \{T_m^\infty / (T_m^\infty - T_m)\} \{2\sigma_e / (\mu h_u)\} \quad (16)$$

where  $T_m$  is the corrected melting temperature. In the calculation of  $\zeta$ , the values of  $T_m^\infty$ ,  $h_u$ ,  $h_x$ ,  $\sigma_e$ , and the corrected  $T_m$  are needed previously. For  $h_u$  the reference value was used (see Table 8). The value of  $\sigma_e$  was evaluated by [43, 44]:

$$\sigma_e = \mu h_u c^* \left[ \{RT_m^2 + (H_x - h_x)(T_m^\infty - T_m)\} / \{2(H_x - h_x)T_m^\infty\} \right] \quad (17)$$

with  $H_x = 2h_u - Q_m$

where  $c^*$  is the cell length of c-axis. The term of square blanket in Eq. (17) is dimensionless.  $h_u$  refers to the heat of fusion of crystals with a crystal form liking to evaluate  $\sigma_e$ .  $h_x$  could be calculated from Eqs.(5) and (6), but in Fig. 11, using  $H_m^a$  at  $T_m^\infty$  of the other  $\alpha$  or  $\gamma$  form crystals (sub-crystals). Table 7 shows the values of  $h_x$  for the iPP films annealed at 461.0 K and 441.5 K for 1 hour, together with the values of  $T_c$ ,  $T_b$ ,  $T_e$ ,  $Q$ ,  $\Delta H$ ,  $\Delta h$ , and  $h_g$  used in the calculation of  $h_x$ .  $Q$  and  $\Delta H$  are defined in Eq. (6). The value of  $h_x$  for the iPP sample of  $T_a = 441.5$  K was smaller than  $h_u$  of the sub-crystals (see Table 8). Further, the value of  $h_x$  in the row of  $\gamma$  form, 6.85 kJ/mol, was  $\sim 0.7$  kJ/mol larger than  $h_g$  (= 6.22 kJ/mol). Also the value of  $h_x$  in the line of  $\alpha$  form, 8.07 kJ/mol, was  $\sim 0.7$  kJ/mol larger than  $h_x$  (= 7.35 kJ/mol) for the sample of  $T_a = 461.0$  K. Therefore, the value of  $h_0$  (=  $h_g + h_x + h_u$ ) in Eq. (8) for the iPP sample annealed at 441.5 K was 0.7 kJ/mol larger than that for the iPP sample of  $T_a = 461.0$  K. The cause could be attributed to  $\Delta h$  affected by  $F(\zeta)$  (see Eq. 18) of  $\alpha$  form crystals, leading the characteristic R–L image (see Fig. 15).

Form <sup>*1</sup> (T <sub>a</sub> /K)	T <sub>c</sub> K	T <sub>b</sub> K	T <sub>e</sub> K	Q kJ/mol	ΔH kJ/mol	Δh kJ/mol	h <sub>g</sub> kJ/mol	h <sub>x</sub> kJ/mol
α (461.0)	403.6	429.6	449.2	3.76	4.89	1.13	6.22	7.35
α (441.5)	403.6	423.7	449.5	4.41	6.26 (γ) <sup>*2</sup>	1.85	6.22	8.07
γ (441.5)	403.6	446.9	461.9	4.41	5.04 (α) <sup>*2</sup>	0.63	6.22	6.85

\*1: The form of main crystals liking to evaluate  $\sigma_e$ . \*2: ΔH calculated using  $H_m^a$  at  $T_m^\infty$  of the sub-crystals with the form of α or γ shown in ( ).

**Table 7.** The values of  $h_u$ ,  $T_p$ ,  $T_b$ ,  $T_e$ , Q, ΔH, Δh, and  $h_g$  for the iPP films annealed at 461.0 K and 441.5 K for 1 hour.

T <sub>a</sub> K	Form	T <sub>p</sub> K	h <sub>u</sub> kJ/mol	h <sub>x</sub> kJ/mol	h <sub>0</sub> kJ/mol	Q <sub>m</sub> kJ/mol	σ <sub>e</sub> J/m <sup>2</sup>
461.0	α	435.9	7.46	7.35	14.8	2.05	36.0×10 <sup>-3</sup> (26.7×10 <sup>-3</sup> )
441.5	α	442.8	7.46	8.07	15.5	2.16	45.2×10 <sup>-3</sup> (30.8×10 <sup>-3</sup> )
	γ	450.9	8.70	6.85	15.6	1.64	26.5×10 <sup>-3</sup> (22.2×10 <sup>-3</sup> )

The values in ( ) are σ<sub>e</sub> at  $T_m^\infty$  (Q<sub>m</sub>=0).

**Table 8.** The values of σ<sub>e</sub>, T<sub>p</sub>, h<sub>u</sub>, h<sub>x</sub>, h<sub>0</sub> (= h<sub>x</sub>+ h<sub>u</sub>), and Q<sub>m</sub> for the iPP films annealed at 461.0 K and 441.5 K for 1 hour.

Table 8 shows the values of σ<sub>e</sub> at T<sub>p</sub> for α and γ form crystals contained in the iPP films annealed at 461.0 K and 441.5 K for 1 hour, together with the values of T<sub>p</sub>, h<sub>u</sub>, h<sub>x</sub>, h<sub>0</sub>, and Q<sub>m</sub> used in the calculation of σ<sub>e</sub>, where T<sub>p</sub> is the melting peak temperature. The σ<sub>e</sub> of α form was larger than that of γ form, because according to Eq. (17), the σ<sub>e</sub> was mainly dependent on h<sub>x</sub>. For α and γ forms in the sample of T<sub>a</sub>= 441.5 K, h<sub>0</sub> (= h<sub>u</sub>+ h<sub>x</sub>) at T (> T<sub>g</sub>) of Eq. (9) was ~15.5 kJ/mol, nevertheless the values of h<sub>u</sub> were different. T<sub>p</sub> is corrected by 0.6 K (436.5 K → 435.9 K) for the sample of T<sub>a</sub>= 461.0 K and 0.2 K (443.0 K → 442.8 K) for α form and 0.8 K (451.7 K → 450.9 K) for γ form in the sample of T<sub>a</sub>= 441.5 K to the lower temperature side, according to our concept [45].

F(ζ) is defined as [23]:

$$F(\zeta) = (\delta Q_m / Q_m) / \zeta = n_\zeta / \{N_c(T_e - T_b)\} \quad (18)$$

where  $\delta Q_m$  (=  $\zeta n_\zeta Q_m / \{N_c(T_e - T_b)\}$ ) is the heat change per molar structural unit per K,  $n_\zeta$  is the number of crystal sequences with ζ,  $N_c$  is the number of structural units of crystals melted in the temperature range from T<sub>b</sub> to T<sub>e</sub>.  $\delta Q_m / Q_m$  is given by:

$$\delta Q_m / Q_m = (dQ / dt) / \int_{T_b}^{T_e} (dQ / dt) dT \quad (19)$$

where  $dQ/dt$  is the heat flow rate of DSC melting curve and  $t$  is time (see Figs. 10 and 11). Figs. 12 and 13 show  $F(\zeta)$  of  $\alpha$  and  $\gamma$  peak curves converted from the DSC single and double melting peak curves for the iPP films annealed at 461.0 K and 441.5 K for 1 hour.

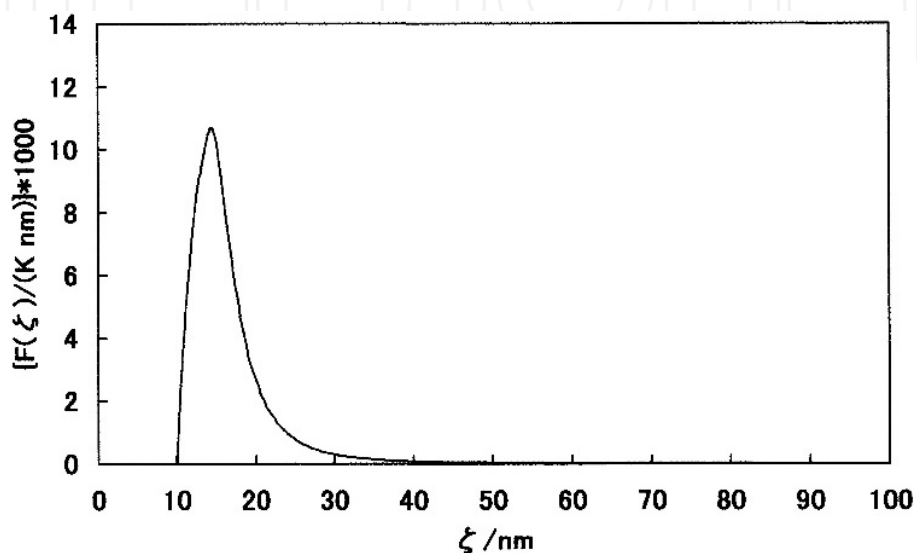


Figure 12.  $F(\zeta)$  of  $\alpha$  peak curve for the iPP film annealed at 461.0 K for 1 hour.

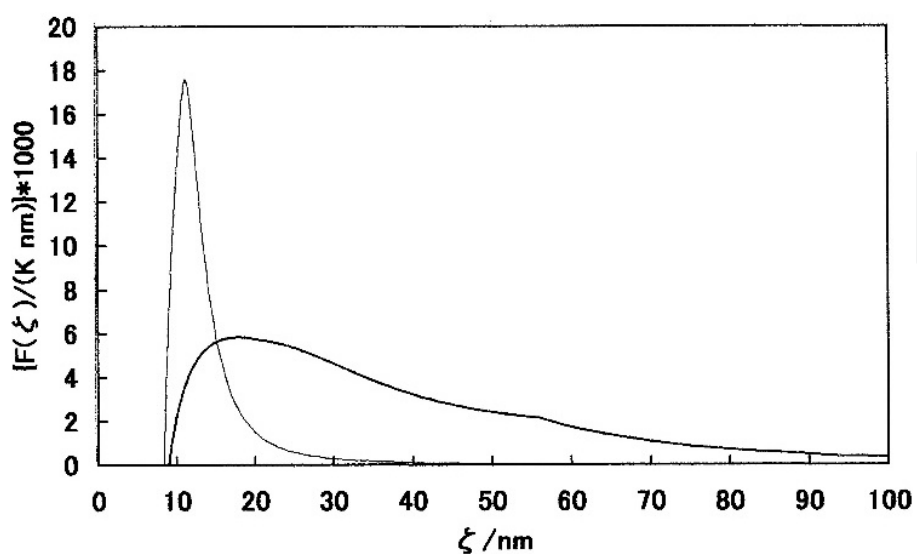


Figure 13.  $f(\zeta)$  of  $\alpha$  (thick line) and  $\gamma$  (thin line) peak curves for the iPP film annealed at 441.5 K for 1 hour.

Table 9 shows the  $\zeta$  range and  $\zeta_p$  in  $F(\zeta)$  of  $\alpha$  and  $\gamma$  peak curves obtained for the samples of  $T_a = 461.0$  K and  $441.5$  K, where  $\zeta_p$  is  $\zeta$  at the maximum of  $F(\zeta)$ . For  $\alpha$  peak,  $F(\zeta)$  in Fig. 12 showed a sharp peak with the  $\zeta$  range of  $10 \text{ nm} \sim 3870 \text{ nm}$  and  $\zeta_p = 14.6 \text{ nm}$ , and in Fig 13,  $F(\zeta)$  showed the roundish curve with the  $\zeta$  range of  $10 \text{ nm} \sim 250 \text{ nm}$  and  $\zeta_p = 19.5 \text{ nm}$ , whereas for  $\gamma$  peak,  $F(\zeta)$  showed the sharp peak with the  $\zeta$  range of  $8 \text{ nm} \sim 840 \text{ nm}$  and  $\zeta_p = 11.2 \text{ nm}$ . The maximum of  $\zeta$  was calculated using  $T_e$  ( $\sim T_m^\infty$ ) observed actually for each sample. At  $T_e = T_m^\infty$ , the maximum of  $\zeta$  should be infinite at  $\sigma_e \neq 0$ , because the melt at  $T_e$  could be interchanged in equilibrium to the imaginary crystals of  $\zeta = \infty$ . In the  $\sigma_e = 0$  of the class A in Table 4,  $\zeta = 0/0$  of indetermination at  $T_m^\infty$  is derived from Eq. (16). The refraction point at  $\zeta = 55 \text{ nm}$  on the thick line of  $\alpha$  peak in Fig. 13 is that of  $dQ/dt$  at  $T_b$  ( $= 446.9 \text{ K}$ ) in Fig. 11. For the sample of  $T_a = 441.5 \text{ K}$ , the  $\zeta$  range of  $\alpha$  peak was narrower than that of  $\gamma$  peak, because upon cooling,  $\alpha$  form crystals should be formed around  $\gamma$  form crystals. As the result, the value of  $h_x$  at the interfaces between  $\alpha$  and  $\gamma$  form crystals increased only  $\sim 0.7 \text{ kJ/mol}$  (derived above). The  $\zeta$  range of  $\alpha$  peak calculated for the sample of  $T_a = 461.0 \text{ K}$  was much larger than those of  $\alpha$  and  $\gamma$  form crystals for the sample of  $T_a = 441.5 \text{ K}$ .

$T_a$ K	Form	$\zeta$ range nm	$\zeta_p$ nm
461.0	$\alpha$	10 - 3870	14.6
441.5	$\alpha$	10 - 250	19.5
	$\gamma$	8 - 840	11.2

**Table 9.** The  $\zeta$  range and  $\zeta_p$  in  $F(\zeta)$  of  $\alpha$  and  $\gamma$  peaks for the iPP films annealed at  $461.0 \text{ K}$  and  $441.5 \text{ K}$  for 1 hour.

In the last stage, the  $\zeta$  distribution of a single-crystal like image was drawn from  $F(\zeta)$ . The number of crystal sequences in a radius direction,  $R_n$ , is given by [10]:

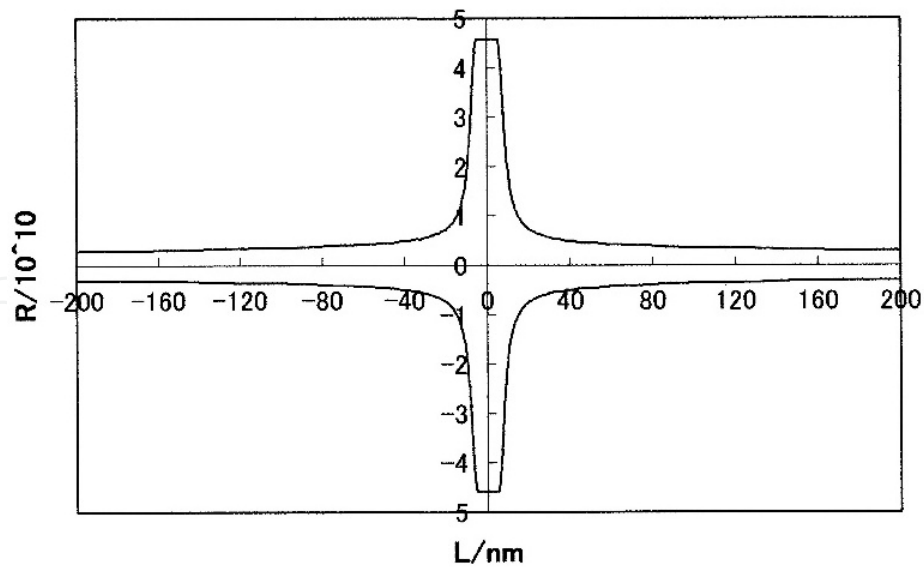
$$R_n = (\Delta N / \pi)^{1/2} \quad (20)$$

with  $\Delta N = N_c (T_e - T_b) \left( \int_{\zeta_n}^{\zeta_x} F(\zeta) d\zeta - \int_{\zeta_n}^{\zeta} F(\zeta) d\zeta \right)$

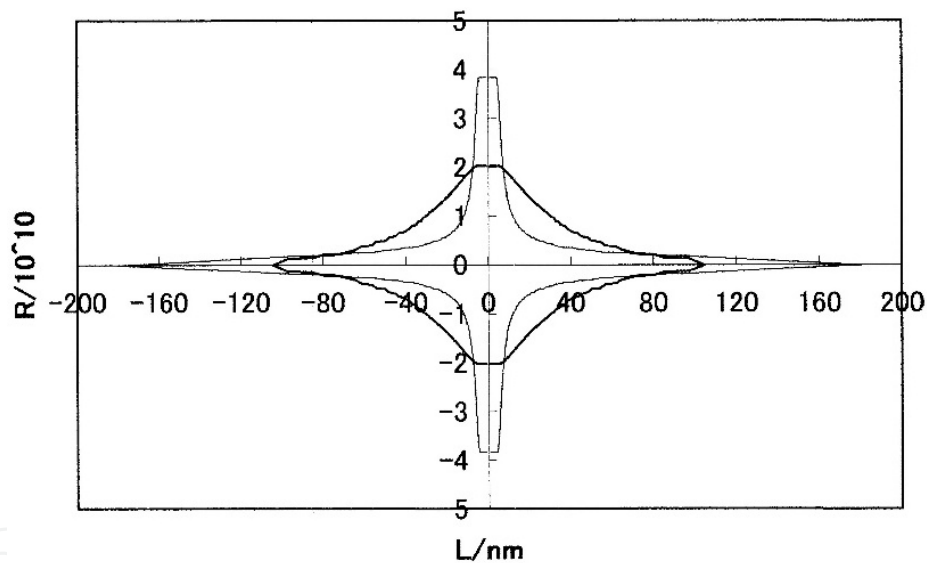
where  $\zeta_x$  and  $\zeta_n$  are the maximum and the minimum of  $\zeta$ , respectively. Figs. 14 and 15 show the representation of  $R$  ( $= \pm R_n$ ) and  $L$  ( $= \pm \zeta/2$ ) for  $\alpha$  and  $\gamma$  form crystals in the iPP films (per 1g) annealed at  $461.0 \text{ K}$  and  $441.5 \text{ K}$  for 1 hour.

From the comparison of both figures, the change of image in  $\alpha$  form crystal lamellae by annealing, and further in Fig. 15, the difference in packing states of  $\alpha$  and  $\gamma$  form crystals in same  $\zeta$  range can be seen at the view of 2D disk image.





**Figure 14.** Representation of  $R (= \pm R_n)$  and  $L (= \pm \zeta/2)$  for  $\alpha$  form crystals in the iPP film (per 1g) annealed at 461.0 K for 1 hour. The horizontal lines show  $R$  of the imaginary crystals melting from  $\zeta_n$  to  $\zeta=0$ .



**Figure 15.** Representation of  $R (= \pm R_n)$  and  $L (= \pm \zeta/2)$  for  $\alpha$  (thick line) and  $\gamma$  (thin line) form crystals in the iPP film (per 1g) annealed at 441.5 K for 1 hour. The horizontal lines show  $R$  of the imaginary crystals melting from  $\zeta_n$  to  $\zeta=0$ .

### 3. Conclusion

For iPS, PET, and iPP, the heat capacity jump at the glass transition was due to the discontinuous change of energy in quantum state of the photon holes between neighboring benzene rings, but methyl groups for iPP, followed by unfreezing of glass parts. For iPS and iPP, the homogeneous glasses free from ordered part / hole pairs with  $T_g = 240$  K and 180 K were predicted, respectively. For iPP, the cohesive energy of methylene residues was subdivided into the transition enthalpies of glasses, ordered parts, and crystals, whereas for iPS, it agreed

with the difference between the transition enthalpies of glasses and ordered parts, but the transition enthalpy of glasses was larger than that of ordered parts. The photonic contribution of 60 % to the heat capacity jump at the glass transition found for PET meant that one photon was situated in the neighboring phenylene residues comprising ~60 % of the structural unit length and the residual jump of 40 % was brought by unfreezing of the ethylene glycol parts in a glass state.  $T_m^\infty = 450$  K for  $\alpha$  form crystals of iPP could be the temperature of the quantum demand of hole energy at regular temperature intervals of 90 K. The shift of melting from  $\alpha$  to  $\gamma$  form crystals by DSC measurements was done through the mediation of the formation and then disappearance of crystal / hole pairs. The interface parts formed in  $\alpha$  and  $\gamma$  form crystals by annealing brought the excess energy of ~0.7 kJ/mol to the enthalpy of the ordered parts. This result was reflected clearly to the single crystal like image depicted on the basis of the crystal length distribution function.

#### 4. A list of abbreviations (*italic in Eqs.*)

$\alpha$  : fraction of ordered part / hole pairs with  $C_v^{ph}$

$1 - \alpha$  : fraction of ordered part / hole pairs with  $C_p^{ph}$

$C_p$  : mean heat capacity per molar structural unit for ordered parts in ordered part / hole pairs

$C_p^h$  : mean heat capacity per molar photon for holes in ordered part / hole pairs

$C_p^{ht}$  : heat capacity per molar photon for holes in excited ordered part /hole pairs

$C_p^{ph}$  : adiabatic molar heat capacity for photons

$C_v^{ph}$  : constant volume molar heat capacity for photons

$C_p^{flow}$  : heat capacity per molar structural unit for flow parts

$C_p^r$  : heat capacity change per molar structural unit due to crystallization followed by melting

$C_p^x$  : heat capacity per molar structural unit for ordered parts in excited ordered part /hole pairs

$c$  : velocity of light

$c^*$  : cell length of c-axis

$c_1$  and  $c_2$  : constants in WLF equation

$dQ/dT$  : heat flow rate of DSC melting curves

$\delta Q_m$  : heat change per molar structural unit per K

$\Delta C_p$  : heat capacity jump per molar photon at the glass transition

$\Delta C_p^{exp}$  : experimental heat capacity jump per molar structural unit at the glass transition

$\Delta C_p^x$  : relative component heat capacity per molar structural unit for excited ordered parts

$\Delta h$  : additional heat per molar structural unit needed to melt all ordered parts

$\Delta h^h$  : hole energy of crystal / hole pairs formed newly by recrystallization

$\delta$  : solubility parameter

$E_a$  : activation energy

$F(\zeta)$  : crystal length ( $\zeta$ ) distribution function

$f$  : free energy per molar structural unit

$f^{\text{conf}}$  : conformational free energy per molar structural unit

$f_g^{\text{conf}}$  : conformational free energy per molar structural unit at  $T_g$

$f_x$  : free energy per molar structural unit for ordered parts

$f_u$  : free energy per molar structural unit for crystals

$\phi$  : amorphous fraction

$\Gamma$  : frequency of occurrence of the helix–coil transition

$H_m^a$  : enthalpy per molar structural unit for the liquid at  $T_m^\infty$

$H_c^a$  : enthalpy per molar structural unit for the super–cooled liquid at  $T_c$

$H_g^a$  : enthalpy per molar structural unit for the super–cooled liquid at  $T_g$

$H_g^c$  : enthalpy per molar structural unit for the crystal at  $T_g$

$h^h$  : hole energy per molar photon for holes in ordered part / hole pairs

$h_0$  : latent cohesive energy per molar structural unit

$h_0^h$  : zero–point energy per molar photon, or energy unit per molar photon

$h_u$  : heat of fusion per molar structural unit

$h_x$  : enthalpy per molar structural unit for ordered parts

$h_g$  : glass transition enthalpy per molar structural unit

$h^{\text{conf}}$  : conformational enthalpy per molar structural unit

$h_g^{\text{conf}}$  : conformational enthalpy per molar structural unit at  $T_g$

$h_x^{\text{conf}}$  : conformational enthalpy per molar structural unit for ordered parts

$h^{\text{int}}$  : cohesive enthalpy per molar structural unit

$h_g^{\text{int}}$  : cohesive enthalpy per molar structural unit at  $T_g$

$h_m^{\text{int}}$  : cohesive energy per molar structural unit for methylene residues

$h$  : Plank constant

$\eta$  : statistical weight

$J_h$  : number of holes lost by  $T$  at the glass transition

$\varphi_g$  : fraction of core free volume in glasses

$\lambda$  and  $1/\lambda$  : wavelength and wave number

mol : molar structural unit

mol\* : molar photon

$\mu$  : conversion coefficient of mol/m<sup>3</sup>

$N_A$  : Avogadro constant

$N_c$  : number of structural units of crystals melted in the temperature range from  $T_b$  to  $T_e$

$n$  : number of structural units holding one photon potentially

$n_\zeta$  : number of crystal sequences with  $\zeta$

$\nu$  : frequency per second

$P$  : pressure

$P_c$  : probability that a sequence occupies the lattice sites of a crystalline sequence

$Q$  : heat per molar structural unit corresponding to the total area of DSC endothermic curve

$Q_m$  : heat per molar structural unit corresponding to the area of a DSC melting curve from  $T_b$

$R$  : gas constant

$R_n$  : number of crystal sequences at the radius direction of an imaginary single crystal lamella depicted on the basis of  $F(\zeta)$

$s_u$  : entropy of fusion per molar structural unit

$s_x$  : entropy per molar structural unit for ordered parts

$s^{\text{conf}}$  : conformational entropy per molar structural unit

$s_g^{\text{conf}}$  : conformational entropy per molar structural unit at  $T_g$

$\sigma_e$  : end surface free energy of a crystal per unit area

$\sigma$  : statistical weight

$T$  : temperature

$T_g$  : glass transition temperature

$T_m$  : melting temperature

$T_m^\infty$  : equilibrium melting temperature

$T_e$  and  $T^*$  : end temperature of DSC melting peak curve

$T_l$  : end temperature of the glass transition

$T_c$  : onset temperature of DSC crystallization peak curve upon cooling

$T_b$  : onset temperature of DSC melting peak curve upon heating

$T_a$  : annealing temperature

$T_p$  : DSC melting peak temperature

$V$  : volume per molar structural unit

$v_f$  : free volume per molar structural unit

$v_0$  : core free volume per molar structural unit

$x$  : degree of polymerization

$Z$  : conformational partition function for a chain

$Z_0$  : component conformational partition function for a chain regardless of temperature

$Z_t$  : component conformational partition function for a chain depending on temperature

$\zeta$  : crystal length

$\zeta_p$  : crystal length at the maximum of  $F(\zeta)$

$\zeta_n$  : crystal length at the minimum of  $\zeta$

$\zeta_x$  : crystal length at the maximum of  $\zeta$

## Acknowledgements

The author would like to thank the late Professor em. B. Wunderlich of the University of Tennessee and Rensseler Polytechnic Institute for the long time encouragement.

## Author details

Nobuyuki Tanaka\*

Address all correspondence to: thermodyna\_nt@kki.biglobe.ne.jp

Gunma University, Gunma, Japan

## References

- [1] T. G. Fox, P. J. Flory, J. Polym. Sci., 14, 315(1954).
- [2] G. Natta, P. Corradini, D. Sianesi, D. Morero, J. Polym. Sci., 51, 527(1961).

- [3] G. Gee, *Polymer*, 7, 177(1966).
- [4] A. L. Renninger, D. R. Uhlmann, *J. Polym. Sci., Phys.*, 16, 2237(1978).
- [5] R. J. Roe, A. E. Tonelli, *Macromolecules*, 12, 878(1979).
- [6] L. H. Judovits, R. C. Bopp, U. Gaur, B. Wunderlich, *J. Polym. Sci.*, 24, 2725(1986).
- [7] G. Brinke, L. Oudhuis, T. S. Ellis, *Thermochimica Acta*, 238, 75(1994).
- [8] B. Wunderlich, "Thermal Analysis of Polymeric Materials", Springer, (2005).
- [9] B. Wunderlich, *J. Appl. Polym. Sci.*, 105, 49(2007).
- [10] N. Tanaka, Y. Mastai Ed: "Advances in Crystallization Processes", InTech, p163(2012).
- [11] N. Tanaka, Preprints of 45th Japanese Conference on Calorimetry and Thermal Analysis (Hachioji), p20(2009).
- [12] N. Tanaka, Preprints of 46th Japanese Conference on Calorimetry and Thermal Analysis (Tsu), p27(2010).
- [13] N. Tanaka, Preprints of 47th Japanese Conference on Calorimetry and Thermal Analysis (Kiryu), p27(2011).
- [14] N. Tanaka, 62nd SPSJ Annual Meeting, Polymer Preprints (CD), Kyoto, 62, (2013).
- [15] N. Tanaka, Preprints of 49th Japanese Conference on Calorimetry and Thermal Analysis (Narashino), p137(2013).
- [16] N. Tanaka, 63th SPSJ Annual Meeting, Polymer Preprints (CD), Nagoya, 63, (2014).
- [17] F. Zamponi, *Nature Phys.*, 7, 99(2011).
- [18] G. Biroli, *Nature Phys.*, 10, 555(2014).
- [19] N. Tanaka, *Polymer*, 33, 623(1992).
- [20] L. H. Hill, "Introduction to Statistical Thermodynamics", Addison-Wisley, Massachusetts, p456(1960).
- [21] T. McLeish, *Physics Today*, 61, No. 8, (2008).
- [22] N. Tanaka, *Thermochimica Acta*, 374, 1(2001).
- [23] N. Tanaka, *Polymer*, 49, 5353(2008).
- [24] J. D. Ferry, "Viscoelastic Properties of Polymers", Reinhold, New York, (1961).
- [25] M. Kobayashi, S. Hanafusa, T. Yoshioka, S. Koizumi, *Japanese J. Polym. Sci. and Tech.*, 53, 575(1996).
- [26] Spectroscopic Soc. of Japan, "Infrared and Raman Spectroscopy", Kodansha Sci., Tokyo, (2011).



- [27] N. Tanaka, G. Wypych Ed: "Handbook of Solvents", ChemTech Publishing, Toronto, p253(2001).
- [28] H. Burrell, J. Brandrup, E. H. Immergut, "Polymer Handbook", Interscience, New York, (1966).
- [29] C. W. Bunn, J. Polym. Sci., 16, 323(1955).
- [30] H. Yoshida, Netsusokutei, 13(4), 191(1986).
- [31] D. Y. Yoon, P. R. Sundararajan, P. J. Flory, Macromolecules, 8, 776(1975).
- [32] G. Allegra Ed: "Interfaces and mesophases in polymer crystallization 2", Berlin, Springer, p288(2005).
- [33] J. Stokr, B. Schneider, D. Doskocilova, J. Lovy, P. Sedlacek, Polymer, 23, 714(1982).
- [34] B. Wunderlich, ATHAS databank (1992 Recommended Data).
- [35] N. Tanaka, 56th SPSJ Annual Meeting, Polymer Preprints (CD), Nagoya, 56, (2006).
- [36] P. J. Flory, J. E. Mark, A. Abe, J. Am. Chem. Soc., 88, 639(1966).
- [37] A. Nakajima, M. Hosono, "Molecular Properties of Polymers", Kagakudojin, (1969).
- [38] N. Tanaka, Polymer, 34, 4941(1993).
- [39] N. Tanaka, 58th SPSJ Annual Meeting, Polymer Preprints (CD), Kobe, 58, (2009).
- [40] P. J. Flory, J. Chem. Phys., 17, 223(1949).
- [41] J. P. Luongo, J. Appl. Polym. Sci., 3, 302(1960).
- [42] J. X. Li, W. L. Cheung, D. Jia, Polymer, 40, 1219(1999).
- [43] N. Tanaka, Proceedings of the 5th Italian Conference on Chemical and Process Engineering, Florence, 949(2001).
- [44] N. Tanaka, H. Fujii, J. Macromol. Sci., B42, 621(2003).
- [45] N. Tanaka, Gunma University, Japanese Patent 4228080.