Thermodynamics of Enthalpy Relaxation and Hole Formation of Polymer Glasses

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1. Introduction

The enthalpy relaxation of the glassy materials has been investigated rheologically for years with a view to approaching the ideal glass. The imaginary liquid at Kauzmann temperature, $T_K$, at which the extrapolation line of enthalpy or entropy as a function of temperature for the liquid intersected the enthalpy or entropy line of the crystal, had been considered once to be the ideal glass. However, because at $T_K$, the enthalpy or entropy for the liquid was same as that of crystal, the liquid like this was hard to take thermodynamically, bringing the entropy crisis. Fig. 1 depicts the change of the enthalpy difference, $\Delta H$, between the liquid and the crystal upon cooling for a polymer. For stable liquids, $\Delta H$ should be almost constant from near $T_g$ upon cooling as described below. Therefore, the liquid line can never intersect that of the crystal. The transition from liquid to crystal or vice versa means the emission or absorption of the latent heat accompanying the enthalpy jump. Thus for polymers, $T_K$ is merely a temperature parameter.

Fig. 1. The change of $\Delta H$ for a polymer liquid or liquid crystal (solid line) upon cooling. The small arrow mark shows the direction of enthalpy relaxation. The base line is that of crystal. The dashed lines are extrapolated to $T_g$ and $T_K$, and the dot line is complementary.
For the glass transition of polymeric or other matter glasses, whether it is the phase transition or not is nowadays yet controversial\(^6\)-\(^{11}\). However for polymers, the criterion of the glass transition temperature, \(T_g\), presented by us is decisive, supporting the first order hole phase transition\(^{12}\)-\(^{14}\) and the broad heat capacity jump at the glass transition without the enthalpy relaxation has been understood successfully\(^{15}\). The cooled polymers unidentified by the criterion should belong to the liquid on the way of enthalpy relaxation even if they were glassy. When without the enthalpy relaxation at temperatures below \(T_g\), the super-cooled liquid could be stable thermodynamically. Glassy pitch\(^4\) might be the stable liquid, which is flowing still at a drop per 9 years from 1927. Recently, for poly(ethylene terephthalate) (PET)\(^{16}\), polystyrene (PS), isotactic polypropylene (iPP), polyethylene (PE) and nylon-6 (N6), it was predicted that during the enthalpy relaxation at temperatures below \(T_g\), the “ordered part / hole” pairs should generate and consequently, bringing a reduction in the relaxation time to the goal of the ideal glass, e.g., the quasi-crystals lacked periodicity but with symmetry\(^{17}\), the alternative and stable glass parts should be formed between their pairs. At \(T_g\), the unfreezing of glass parts is caused by the first order hole phase transition. Then the holes should play the free volume jump as an affair of dynamic equilibrium in the disappearance and generation of “ordered part / hole” pairs. The free volume jump at the glass transition, accompanying the enthalpy and entropy jumps, is the characteristic of the first order hole phase transition. In this chapter, introducing the constant volume heat capacity of photons to the holes\(^{16,18,19}\), the generation of “ordered part / hole” pairs during the enthalpy relaxation at temperatures below \(T_g\) and the subsequent disappearance at the glass transition, accompanied by the jumps of free volume, enthalpy and entropy, were discussed for PET, PS, iPP, PE and N6 on the basis of thermodynamics. IPP, PE and N6 were investigated as the peculiar cases for the comparison with PET and PS, which are the glassy polymers with the almost same values of the constant, \(c_2\), of WLF equation\(^{20}\), i.e., 55.3 K\(^{21}\) and 56.6 K\(^{20}\), respectively. The holes taken in the helix structure of iPP should hold the interaction of partnership with the helical ordered parts. For PE, the glasses with \(T_g\) = 135 K and 237 K depending on the structure of the ordered parts\(^{15}\) were discussed. It seems likely that from near 130 K, the growth of open space in the PE glasses occurs\(^{22}\). DSC (Differential Scanning Calorimetry) on PE films\(^{18}\) revealed that \(-38\%\) of the crystal lamella was constituted by the inter-grain aggregates containing the glass with a secondary \(T_g\). The generation of “crystal / anti-crystal hole” pairs from the secondary glass was discussed. For N6, the ordered parts were the stretched sequences of -(CH\(_2\))\(_5\)- between amido groups. The hole energy of “ordered part / hole” pairs was concerned with the frequency of absorption bands in the infrared spectrum.

2. Enthalpy relaxation and hole formation of PET, PS, iPP, PE and N6 glasses

2.1 Thermodynamics of glass transition

The glass transition temperature, \(T_g\), of polymer glasses could be identified as that of the first order hole phase transition by satisfying the criterion consisted of Eqs. (1) and (2), in which \(f_x\) has been added under the operational definition concluding that the stable glasses could not be formed easily without the generation of “ordered part / hole” pairs during the enthalpy relaxation at temperatures below \(T_g\):\(^{13}\):

\[
f_x = f_{\text{flow}} (= h_{\text{flow}} - T_g s_{\text{flow}}) = 0
\]
where \( f_x (= h_x - T_g s_x) \), \( h_x \) and \( s_x \) are the free energy, enthalpy and entropy per molar structural unit for ordered parts, \( f_{\text{flow}}, h_{\text{flow}} \) and \( s_{\text{flow}} \) are the free energy, enthalpy and entropy per molar structural unit for flow parts. The molar free energy of holes held photons at the temperature, T, is generally given by \( f^h = -RT\ln(v_i/v_0) \) and then the molar entropy of holes, \( s^h \), at a constant pressure, \( p \), is derived:

\[
s^h = -\frac{\partial f^h}{\partial T}_p = R\ln(v_i/v_0) + RT\frac{\partial \ln(v_i/v_0)}{\partial T}_p
\]

where \( v_i \) and \( v_0 \) are the molar free and core volumes of holes and R is the gas constant. When \( v_0 \) is almost constant, from \( f^h = h^h - T s^h \) and Eq. (3), the molar enthalpy of holes, \( h^h \), is derived:

\[
h^h = RT \frac{\partial \ln(v_i/v_0)}{\partial T}_p
\]

When the ordered parts at \( T_g \) are in equilibrium with the holes; \( f_x (= 0) = f^h \), from Eq. (2), the molar glass transition enthalpy, \( h_g \), is derived:

\[
h_g = RT_g \frac{\partial \ln(v_i/v_0)}{\partial T}_p
\]

In the case of \( RT_g \ln(v_i/v_0) = \Delta h \), the relation of \( h_x = h^h \) is derived from Eq. (8), because of \( RT_g \frac{\partial \ln(v_i/v_0)}{\partial T}_p = h_g \). However, when the length distribution by lengthening of ordered parts occurred during the enthalpy relaxation at temperatures below \( T_g \), as longer the length of ordered parts, the melting temperature, \( T_x \) for ordered parts should be elevated from \( T_g \) to the higher temperature\(^2\) (see Eq. (29)). Therefore the shortage of \( \Delta h (= RT_g \ln(v_i/v_0)) \) corresponding to the latent heat of disappearance for the holes at \( T_g \) is made up by the supply of the heat required to melt all ordered parts:

\[
\Delta h = \int_{T_g}^{T_f} \Delta C_p dT
\]
where $T_\ell$ is the end temperature of melting for ordered parts, $\Delta C_p$ is the difference between the observed isobaric heat capacity, $C_p^{\ell}$, for the equilibrium liquid and $C_p^s$ for the hypothesized super-heated glass at the glass transition from $T_g$ to $T_\ell$. In the equilibrium liquid, the isobaric heat capacities of ordered parts and flow parts, $C_p^x$ and $C_p^{\text{flow}}$, are equal to $C_p^{\ell}$, respectively:\(^{13}\):

\[ C_p^{\ell} = C_p^x = C_p^{\text{flow}} \]  \hspace{1cm} (10)

In the flow parts, the tube-like space exists between a chain and the neighboring chains, behaving as if it is the counterpart of a chain\(^{24}\). Therefore when the hole energy at $T (> T_g)$ is given by $\varepsilon (= 3C_{vp}T)$, $C_p^{\text{flow}}$ is represented as\(^{16}\):

\[ C_p^{\text{flow}} = 3C_{vp}(1 + Td\ln J/dT) \]  \hspace{1cm} (11)

where $C_{vp} (= 2.701R)\(^{16,18,19}\)$ is the constant volume heat capacity for photons, $J$ is the number of holes lost by $T$ and $3$ is the degree of freedom for photons.

Fig. 2 shows the schematic curves of the molar entropy, $s$, and the $v_f$ around $T_g$ upon cooling and heating for polymers. Upon cooling in Fig. 2 (upper), the dashed line is the $s$ curve for the liquid glass frozen partially from the super-cooled liquid and the solid line upon heating Fig. 2. The schematic curves of the entropy, $s$, and the free volume, $v_f$, around $T_g$ for polymers. Upper: 1: the change of $s$ for the liquid glass frozen partially from the super-cooled liquid, shown by the dashed line, 2: the entropy relaxation and 3: the change of $s$ with a jump at $T_g$ upon heating. Lower: The dashed line upon cooling is the $v_f$ curve for the same liquid glass, the solid line upon heating after relaxation shows the $v_f$ curve with a jump at $T_g$ and the dashed line shows a reversible jump of $v_f$ between $T_g$ and $T_\ell$. **Fig. 2.**
after relaxation shows the subsequent s curve with a jump at Tg. Upon cooling in Fig. 2 (lower), the dashed line is the v_f curve for the same liquid glass. Upon heating after relaxation, the solid line shows the v_f curve with a jump at T_g and the dashed line shows a reversible jump of v_f between T_g and T_l.

2.2 “Ordered part / hole” pairs

Next whether h_x agrees to h_h at T_g or not is investigated for PET, iPP, PS, PE and N6 glasses. The agreement provides one of evidences for the generation of “ordered part / hole” pairs during the enthalpy relaxation at T (< T_g). h_h at T_g is given by

\[ h_h = 3C_{\text{vph}}T_g \]  

where \( C_{\text{vph}} = 2.701R \). For PET with T_g = 342 K, h_h = 23.0 kJ/mol was derived. While h_x at T_g is given by

\[ h_x = h_g + \Delta h \]  

In Eq. (13), h_g is given approximately by three expressions\(^{(13, 25)}\): (1) \( RT_g^2/c_2 \) (c_2 is the constant of WLF equation\(^{(20)}\)), (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, \( h_{g,\text{conf}} + h_{g,\text{int}} \). \( \Delta h \) is given by either Eq. (14) or (15)\(^{(25, 26)}\):

\[ \Delta h = H - Q \]  

with \( \Delta H = H_m^a - H_c^a \), where \( H_m^a \) is the enthalpy per molar structural unit for the liquid at the equilibrium melting temperature, \( T_m^\infty \), \( H_c^a \) is the enthalpy per molar structural unit for the super-cooled liquid at the onset temperature, \( T_c \), 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. Or, rewriting Eq. (13),

\[ \Delta h = (h_{x,\text{conf}} - h_{g,\text{conf}}) + \Delta h_{\text{int}} \]  

where \( h_{x,\text{conf}} \) is the conformational enthalpy per molar structural unit for ordered parts, \( \Delta h_{\text{int}} \) is the molar cohesive enthalpy difference between the ordered parts and the glass parts. Thus when \( h_{x,\text{conf}} = h_{g,\text{conf}} \) at T_g, \( \Delta h = \Delta h_{\text{int}} = (RT_g\ln Z_0)/x \) (see Table 3 for N6) and when \( h_{x,\text{conf}} \neq h_{g,\text{conf}} = 0 \) at T_g, the another \( \Delta h \) is derived\(^{(26, 27)}\):

\[ \Delta h = T_g[s_{g,\text{conf}} - (R\ln Z_0)/x] \]  

with \( s_{g,\text{conf}} = (R\ln Z + RT_g\ln Z/dT)/x \)

where 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 as a function of temperature, respectively. The differential of Eq. (15) by temperature represents the heat capacity jump at the glass transition\(^{(15)}\).

Table 1 shows the values of T_g, \( \Delta s_g \), h_g, \( \Delta h \), h_x, h_h and h_h/h_x for PET, iPP and PS. PET showed the good agreement between h_x, i.e., 22.3 – 24.1 kJ/mol, and h_h, i.e., 23.0 kJ/mol. The values of them also agreed with the heat of fusion, h_u = 23.0 kJ/mol, for the smectic crystals of mesophase with the conformational disorder between the phenylene groups but along
Table 1. The values of $T_g$, $\Delta s_g$, $h_g$, $\Delta h$, $h_x$, $h^h$, and $h^h/h_x$ for PET, iPP and PS.

| Polymer | $T_g$ K | $\Delta s_g$ J/(K mol) | $h_g$ kJ/mol | $\Delta h$ kJ/mol | $h_x$ kJ/mol | $h^h$ kJ/mol | $h^h/h_x$ |
|---------|--------|------------------------|-------------|-------------------|-------------|-------------|------------|
| PET     | 342    | 47.1                   | 16.1*1      | 6.5*4             | 22.6        | 1.0         |
|         |        |                        | 51.5        | 17.6*2            | 6.2*5       | 23.8        | 23.0       | 1.0         |
|         |        |                        | 51.2        | 17.5*3            | 6.2*5       | 23.7        | 1.0         |
| iPP     | 270    | 23.0                   | 6.2*1       | 1.1*4             | 7.3         | 2.5 (1.0*7) |
|         |        |                        | 23.7        | 6.4*3             | 1.0*5       | 7.4         | 18.2       | 2.5 (1.0*7) |
| PS      | 359    | 52.6                   | 18.9*2      | 5.3               | 24.2*6      | 1.0         |
|         |        |                        | 56.5        | 20.3*3            | 3.9         | 24.2        | 1.0         |

*: $H_{g^a} - H_{g^c}$, *: $RT_{g^a}/c_2$, **: $h_g^{conf} + h_g^{int}$, ***: Eq. (14), ****: Eq. (16), ****: $h_x = h^h$ and ****: $(h^h/2.5)/h_x$. The data of iPP used to calculate $\Delta h$ in Eq. (14) are as follows: $T_c = 403.6$ K, $T_m^\infty = 449$ K for the $\alpha$ form crystal, $\Delta H (=H_m^\alpha - H_c^\alpha) = 4.89$ kJ/mol and $Q = 3.76$ kJ/mol for the sample annealed at 461.0 K for 1 hour.

For the smectic-c crystals with stretched sequences, $h_u$ is 28.5 kJ/mol. Further, DSC revealed that for the crystalline films of smectic-c crystals, the ordered parts in the amorphous regions were like smectic crystals and for the crystalline films of smectic crystals, the ordered parts were like the smectic-c crystals. Fig. 3 shows the sequence models of smectic crystal (A) and smectic-c crystal (B), together with the four conformations (a, b, c and d) that an isolated chain can take preferentially below 10 K. An arrow mark shows the direction of ordering or crystallization for a, b, c and d. From these results, the ordered parts are like the smectic crystal and the hole of a pair should have the free volume coming from the difference of conformation between A and a, b, c or d in Fig. 3. For iPP, $h^h$ was 2.5 times as much as $h_x$. This result suggested that the hole of a pair was the inside space of a 3/1 helical ordered part composed of 3 structural units, holding 3 photons, but each photon was concerned in the potential energy of 2.5 structural units in a helical sequence, and that, $(h^h/2.5)/h_x = 1$. This was comparable to $h^h/h_x = 1$ for PET. The value of

Fig. 3. Right: The sequence models of the smectic crystal of mesophase with a conformational disorder (A) and the smectic-c crystal with a stretched conformation (B) for PET. Left: Four conformations taken preferentially below 10 K for an isolated chain; a: TTTGT, b: TTTTGT, c: TCTTGT and d: TCTTGT, by Flory’s theory. T, G and G’ are the trans, gauche and gauche’ isomers, respectively. T and C are the trans and cis isomers of phenylene groups (lower groups). An arrow mark shows the direction of ordering or crystallization.
h_x was almost equal to h_u (= 7.6 kJ/mol for α form). Fig. 4 shows the photon sites in the helix structure and the helical conformation of an isolated sequence with an inversion defect isomer TT, taking preferentially at temperatures below 70 K.

Fig. 4. Upper: The photon sites (the dashed line parts) in the helix structure with TGTG or TG’TG’ conformation at temperatures below T_g for iPP. Large circle: C and small circle: H. Lower: The helical conformation of an isolated sequence with an inversion defect isomer TT, taking preferentially at temperatures below 70 K. The allow mark shows the shift of TT on a helical sequence.

For PS, supposing h_x = h_h, Δh was evaluated. From the value of Δh to be near that of PET, the T_f jump at T_g should be due to the release between phenyl groups. The T_g of PE 15), producing the entropy of unfreezing for the glass parts; Δs_g = h_g/T_g (see Eq. (5)), was almost dependent on h_g^int. When a value of h_g^int was that of the glass with T_g = 237 K, h_g^int/2 gave T_g = 135 K. Table 2 shows the values of T_g, Δs_g, h_g, Δh, h_u, h_h and h_h/h_x for PE glasses with T_g = 135 K (h_g^int = 2.8/2 kJ/mol) and 237 K (h_g^int = 2.8 kJ/mol). The above relation in T_g and h_g^int for the glass parts was linked to the ordered parts. For both glasses, h_h was about 5 times as much as h_g. Thus from Eq. (13), the common relations of h_x = h_h/4 and Δh = h_h/4 – h_g were predicted for the ordered parts in both glasses and shown in Table 2. Fig. 5 depicts the sequence models of ordered parts (A and B) and the schematic transition from the glassy state (C: left) to that of the “ordered part / hole” pair (C: right).

For the glass with T_g = 135 K, the coarse 4/1 helical ordered parts with GG or G’G’ conformation in Fig. 5A and as the hole of a pair, the inside space holding four photons per a helical segmental unit, -(CH_2)_4-, were predicted. Further the length distribution of helical ordered parts in the glass and as the end temperature of melting for the ordered parts, ~237 K were predicted. In this case, the same value of Δh for both glasses enabled the scheme as depicted in Fig. 6. For the glass with T_g = 237 K, the ordered part of fringe-type formed by

| Polymer | T_g/K | Δs_g/J/(K mol) | h_g/kJ/mol | Δh/kJ/mol | h_u/kJ/mol | h_h/kJ/mol | h_h/h_x |
|---------|-------|----------------|-------------|-----------|------------|------------|--------|
| PE      | 135   | 13.8           | 1.8*1       | 0.5       | 2.3*2      | 9.1        | 4 (1*)  |
|         | 237   | 14.8           | 3.5*1       | 0.5       | 4.0*2      | 16.0       | 4 (1*)  |

*1: h_g^conf + h_g^int, *2: h_x = h_h/4 and *3: (h_h/4)/h_x.

Table 2. The values of T_g, Δs_g, h_g, Δh, h_u, h_h and h_h/h_x for PE.
Fig. 5. The sequence models of ordered parts; A: the 4/1 helix structure and B: the stretched structure in the region surrounded by the dashed line. C (left): the glassy state and C (right): the state of a “ordered part / hole” pair. The plus mark (+) shows the cross section of a stretched segmental unit, -(CH2)4-. An arrow mark shows the direction of ordering.

bundling TTT parts of four sequences at least, and that, the smallest crystal of PE and the neighboring hole were predicted (see Fig. 5B and C: right), since the value of $h_x$ was almost equal to $h_u = 4.1 \text{kJ/mol}$. Fig. 6 shows the bar graph of $h_g$ at $T_g = 135 \text{K}$ and 237 K, together with $\Delta h = 0.5 \text{kJ/mol}$ at 237 K, for PE. The difference in two complementary lines suggests the supply schedule of heat over the temperature range from 135 K to 237 K in order to make up the shortage of $\Delta h$ required to melt all ordered parts in the glass with $T_g = 135 \text{K}$. For the glass with $T_g = 237 \text{K}$, the glass transition only at $T_g$ is shown. The enthalpy relaxation, accompanied by the generation of stretched segments, at temperatures over 135 K to 237 K.

Fig. 6. The bar graph of $h_g$ at $T_g = 135 \text{K}$ and 237 K (the vertical thin lines between the cross marks) and $\Delta h = 0.5 \text{kJ/mol}$ at 237 K (the thick line part) for PE. The dot and dot-dashed lines are drawn complementarily.
should vitrify or order the melted helical ordered parts and confine the larger helical ordered parts, which were not yet melted even over \( T_g = 135 \) K, in the glass. The liquid on the way of enthalpy relaxation like this should reach step by step to the glass with \( T_g = 237 \) K (\( h_{g\text{int}} = 2.8 \text{ kJ/mol} \)) at temperatures below \( T_g \). Table 3 shows the values of \( T_g \), \( \Delta s_g \), \( h_g \), \( \Delta h \), \( h_x \) and \( h^h \) for N6. For N6, \( h_{g\text{conf}} = h_{x\text{conf}} \) in Eq. (15), i.e., \( \Delta h = (RT_g \ln Z_t)/x \) was predicted, because of the strong interaction between amido groups. \( h^h \) was 4.7 times as much as \( h_x \) in the parenthesis. Accordingly a photon was concerned in the potential energy of a stretched segmental unit, \(-(\text{CH}_2)_5-\). Further \( \Delta h = 2.5 \text{ kJ/mol} \) was 0.5 kJ per molar methylene unit, \(-\text{CH}_2-\), which agreed with \( \Delta h = 0.5 \text{ kJ/mol} \) for the PE glasses with \( T_g = 135 \) K and 237 K (see Table 2). In addition, the value of \( h^h \) was almost equal to \( h_u \) of the heat of fusion. This agreement suggested that the ordered parts were the stretched segmental units in the smallest crystals of N6. Fig. 7 shows the structural unit of N6 and the photon site in the structural unit.

| Polymer | \( T_g \) K | \( \Delta s_g \) J/(K mol) | \( h_g \) kJ/mol | \( \Delta h^* \) kJ/mol | \( h_x \) kJ/mol | \( h_u \) kJ/mol | \( h^h \) kJ/mol |
|---------|-------------|--------------------------|-----------------|---------------------|----------------|----------------|----------------|
| N6 2\(^2\) | 313         | 120.1 (6.4)              | 37.6*\(^1\)     | 2.5, 0.5*\(^3\)    | 40.1 (4.5)     | 21.3           | 21.1           |

*\(^1\): \( h_x = h_{g\text{conf}} + h_{g\text{int}} \), *\(^2\): \( \Delta h = (RT_g \ln Z_t)/x \) and *\(^3\): the value of \( \Delta h \) per molar methylene unit, \(-\text{CH}_2-\). The values of \( \Delta s_g \), \( h_g \) and \( h_x \) in the parentheses are those without the cohesive energy of amido group, 35.6 kJ/mol.

Table 3. The values of \( T_g \), \( \Delta s_g \), \( h_g \), \( \Delta h \), \( h_x \), \( h_u \) and \( h^h \) for N6.

Fig. 7. The structure of N6 structural unit and the photon site (the dashed line part) in the unit. The filled circle: N, the shaded circle: O, the large circle: C, and the small circle: H.

### 3. Hole energy and a photon

A photon has the property as a boson or a wave. Therefore \( h^h \) is also represented as the vibrational energy of a wave with the quantum number \( n = 1 \) (meaning one photon) and the frequency per second (sec), \( v \):

\[
h^h = N_A(3/2)hv
\]

(17)

where \( N_A \) is Avogadro constant. Thus from Eqs. (12) and (17), the zero-point energy, \( \varepsilon_0 \) (= (1/2)\( hv \)), is derived:

\[
\varepsilon_0 = C_v h^h T_g / N_A
\]

(18)
Table 4 shows the values of \( T_g \), \( h^b \), \( \nu \), \( \lambda \) and \( 1/\lambda \) for PE, iPP, PS and PET, where \( \lambda \) is the wavelength and \( 1/\lambda \) is the wavenumber. According to the infrared spectroscopy, for PE, \( 1/\lambda = 510 \text{ cm}^{-1} \) and \( 893 \text{ cm}^{-1} \) might be concerned with \( 720 \text{ cm}^{-1} \) and \( 731 \text{ cm}^{-1} \) bands assigned to the rocking of \(-\text{CH}_2-\)\(^{32}\). For iPP, \( 1/\lambda = 1022 \text{ cm}^{-1} \) almost agreed with \( 1045 \text{ cm}^{-1} \) relating to the crystallinity\(^{33}\). Also for PS, \( 1/\lambda = 1359 \text{ cm}^{-1} \) almost agreed with one of conformation sensitive bands\(^{34}\), i.e., \( 1365 \text{ cm}^{-1} \) band. For PET, \( 1/\lambda = 1292 \text{ cm}^{-1} \) was near \( 1339 \text{ cm}^{-1} \) and \( 1371 \text{ cm}^{-1} \) bands assigned to the wagging of \(-\text{CH}_2-\) with trans and gauche conformations, respectively\(^{35}\).

| Polymer | \( T_g \) K | \( h^b \) kJ/mol | \( \nu \) sec\(^{-1}\) | \( \lambda \) \( \mu \text{m} \) | \( 1/\lambda \) cm\(^{-1}\) |
|---------|-------------|------------------|-----------------|-----------|----------------|
| PE      | 135         | 9.1              | \( 15.3 \times 10^{12} \) | 19.6      | 510            |
|         | 237         | 16.0             | \( 26.9 \times 10^{12} \) | 11.2      | 893            |
| iPP     | 270         | 18.2             | \( 30.6 \times 10^{12} \) | 9.78      | 1022           |
| PS      | 359         | 24.2             | \( 40.6 \times 10^{12} \) | 7.36      | 1359           |
| PET     | 342         | 23.0             | \( 38.6 \times 10^{12} \) | 7.74      | 1292           |

Table 4. The values of \( T_g \), \( h^b \), \( \nu \), \( \lambda \) and \( 1/\lambda \) for PE, iPP, PS and PET.

4. Conclusions and introduction to next section

For PET, PS, iPP, PE and N6 glasses, the generation of “ordered part / hole” pairs during the enthalpy relaxation at temperatures below \( T_g \) and the subsequent disappearance at the glass transition were discussed under the operational definition leading the criterion of \( T_g \). Thus it was concluded that the unfreezing of the glass parts at \( T_g \) was caused by the first order hole phase transition, accompanied by the jumps of free volume, enthalpy and entropy. \( h^b \) was concerned with the frequency of the absorption bands in the infrared spectrum. In particular, \( 1/\lambda \) for iPP and PS coincided closely with the respective sensitive bands with physical meaning. In the next section, the generation of “crystal / anti-crystal hole” pairs from the secondary glass in PE crystal lamella was discussed on the DSC curves. The secondary glass was distinguished from the primary glass discussed in the above sections. The \( C_{\gamma}^{\text{ph}} \) was also available in the discussion of the cavity radiation from the anti-crystal holes filled by photons. The anti-crystal holes were regarded as the lattice crystal made up of photons without the mass.

5. Crystallization of secondary glass in PE lamella

5.1 Thermal analysis

DSC is capable of quantitatively determining by way of standard and dynamical measurements\(^{36}\) the common thermal phenomena in polymers, e.g., the melting, the crystallization and the glass transition. Such analyses are carried out on the basis of thermodynamics, mathematics and molecular dynamics simulation\(^{36, 37}\). This section describes an attempt to understand the peculiar DSC curves of PE films containing orthorhombic crystals. DSC demonstrated two indications of the secondary glass in the crystal lamella. One of the underlying reasons was the much larger heat of melting as opposed to the heat of crystallization upon cooling and the other was the fact that the glass
transition enthalpy was larger than the molar enthalpy of the ordered parts in the amorphous regions; $\Delta h < 0$ in Eq. (14). At temperatures above its $T_g$, the generation and disappearance of the “crystal / anti-crystal hole” pairs from the secondary glass were predicted as the simultaneous phenomena in the crystallization and the melting. Hexagonal and monoclinic forms of PE crystals are also well known. However, the hexagonal crystals should not be related to the melting of the orthorhombic crystals since the DSC melting peak of the hexagonal crystals generally cannot be observed for the samples without restraints such as high pressure\textsuperscript{38}. Moreover, the DSC melting peak of monoclinic crystals disappears before the melting of the orthorhombic crystals\textsuperscript{39, 40}. Thus, when the monoclinic crystals are in the bulk state, the heat due to their melting should contribute to the activation heat required to release the secondary glass state in the orthorhombic crystal lamella.

5.2 Secondary glass

Fig. 8 depicts the DSC crystallization peak upon cooling and the two peaks divided from a DSC endothermic peak upon heating for the PE film annealed at 416.6 K (near $T_m^\infty = 415$ K) for 1 hour. The thin line in $T_b^*$ and $T_e^*$ is the curve before division. $T_c (= 391.5$ K) is the onset temperature of crystallization, $T_b^* (= T_c)$ is the intersection between the base line and the extrapolation line from the line segment with the highest slope on the lower temperature side of the melting peak, and that, the onset temperature of the higher temperature side peak and $T_e^*$ is the end temperature of the lower temperature side peak, and that, the origin of the extrapolation line, respectively. $Q_m$ is the heat per molar structural unit corresponding to the endothermic peak area of crystal lamella that starts to melt at $T_b^*$ and $h_c (= 0.89$ kJ/mol) is the heat of crystallization per molar structural unit corresponding to the area surrounded by the dashed line and the exothermic curve. $\Delta Q_m (= Q_m - h_c)$ corresponds to the area between $T_b^*$ and $T_e^*$ of the higher temperature side.

![Fig. 8](https://www.intechopen.com)

Fig. 8. The DSC crystallization peak upon cooling and the two peaks divided from a DSC endothermic peak upon heating for the PE film annealed at 416.6 K for 1 hour. $dQ/dt$ is the heat flow rate. The cooling and heating rates are 5 K/min and 10 K/min, respectively.
peak, which is equal to the area surrounded by the thin line and the lower temperature side peak curve between $T_b^*$ and $T_e^*$. The endothermic peak on the lower temperature side is due to the melting of small crystals around the crystal lamella\(^{21}\). The decrease of heat flow rate from $T_b^*$ to $T_e^*$ for the peak on the lower temperature side is believed to be due to the crystallization of secondary glass in the inter-grain aggregates belonging to the crystal lamella (see Fig. 9). This precedes the increase of heat flow rate due to the melting of newly crystallized parts from $T_b^*$ to $T_e^*$ in the peak on the higher temperature side. The equilibrium melting of the ordered parts in the amorphous regions does not show any peak. Its enthalpy, $h_\sigma$, has been represented as Eq. (13), in which $\Delta h$ given by Eq. (14) is usually positive; 6.5 kJ/mol and 11.5 kJ/mol for PET with two values of $T_m^\infty$ (535 K and 549 K)\(^{25}\), respectively. Also for iPP, $\Delta h$ (= 1.1 kJ/mol) of Eq. (14) was positive, as shown in Table 1. Nevertheless, it was found to be negative for PE (see Table 5). In order to satisfy $\Delta h < 0$ ($h_g > h_x$), the glass with a secondary $T_g$, which formed near $T_c$ upon cooling and disappeared near $T_c$ after melting of the ordered parts in the amorphous regions upon heating, must exist in the crystal lamella. When the secondary $T_g$ is approximated to $T_c$, $h_g^*$ is given by:

$$h_g^* = H_{ca} - H_{cc}$$

(19)

where $h_g^*$ is $h_g$ at the secondary $T_g$. $H_{ca}$ and $H_{cc}$ are the enthalpy per molar structural unit for the super-cooled liquid and the crystal at $T_c$. $h_x$ is given by $h_g^* + \Delta h$ ($\Delta h < 0$). Here, $\Delta H (= H_{ma} - H_{ca})$ in Eq. (14) is regarded as the heat emitted when only one single crystal lamella without deformation is formed. According to the ATHAS databank\(^{29}\), $\Delta H$ is 0.83 kJ/mol, which is close to the value of $h_c = 0.89$ kJ/mol as observed in Fig. 8. The difference in $h_c$ and $\Delta H$, 0.06 kJ/mol, might be the additive heat of emission due to the release of lamellar deformation. The spherulites observed in the films are substantially like disks\(^{42}\). The twist deformation energy of ribbon-like lamella is believed to originate from the irregular growth of lamella. Fig. 9 shows a schematic structure of the crystal lamella after release of the twist deformation from the ribbon-like lamella. The dark parts between the rectangular parallelepiped blocks correspond to the inter-grain aggregates described above. The crystal lamellae for the samples used here are described in the section 5.5 of “Crystal length distribution function”.

Table 5 shows the values of $T_c$ (= $T_g^*$), $T_b^*$, $Q$, $\Delta H$ (= $H_{ma} - H_{ca}$), $\Delta h$, $h_g^*$ and $h_x$ for the samples annealed at $T_a = 376.6$ K, 416.6 K and 426.6 K for 1 hour, where $T_g^*$ is the secondary $T_g$ and $T_a$ is the annealing temperature. $h_x$ was found to decrease with an increasing $T_a$. The values of $h_x$ for “$T_a = 416.6$ K and 426.6 K”-samples were near $h_x = 2.3$ kJ/mol for the glass with $T_g^*$ =

---

Fig. 9. A schematic structure of the crystal lamella after release of the twist deformation from the ribbon-like lamella. a, b and c (chain axis) correspond to the three cell axes of the orthorhombic crystal and the dark parts represent the inter-grain aggregates. The cell lengths of a, b and c axes for PE are 0.74 nm, 0.49 nm and 0.25 nm, respectively.
135 K in Table 2. In the amorphous region of these samples, the ordered parts with the coarse 4/1 helix structure might be formed\(^5\). The ordered parts in the inter-grain aggregates, being like the crystals of fold-type with \( h_x \) instead of \( h_x \), could also have the holes as the pair (see Eq. (28)).

| Sample \( T_a / \text{K} \) | \( T_c / \text{K} \) | \( T_b^* / \text{K} \) | \( Q / \text{kJ/mol} \) | \( \Delta H / \text{kJ/mol} \) | \( \Delta h / \text{kJ/mol} \) | \( h_g^* / \text{kJ/mol} \) | \( h_x / \text{kJ/mol} \) |
|------------------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| 376.6                  | 391.5          | 392.4          | 1.79           | 0.83           | -0.96          | 3.99           | 3.03           |
| 416.6                  | 391.5          | 392.5          | 2.38           | 0.83           | -1.55          | 3.99           | 2.44           |
| 426.6                  | 391.5          | 393.3          | 2.85           | 0.83           | -2.02          | 3.99           | 1.97           |

Table 5. The values of \( T_c (= T_g^*) \), \( T_b^* \), \( Q \), \( \Delta H \), \( \Delta h \), \( h_g^* \) and \( h_x \) for PE films annealed at 376.6 K, 416.6 K and 426.6 K for 1 hour.

5.3 “Crystal / anti-crystal hole” pairs from secondary glass

The crystal length, \( \zeta \), as a function of the melting temperature, \( T_m \), is according to Gibbs-Thomson given by:

\[
\zeta = \frac{T_m^\infty}{(T_m^\infty - T_m)}[2\sigma_e / (\mu h_u)] \tag{20}
\]

where \( \sigma_e \) is the end-surface free energy per unit area for crystals, \( \mu \) is the conversion coefficient. For PE, \( \mu = (10^6 / 14) \text{ mol/m}^3 \), \( h_u = 4.11 \text{ kJ/mol} \) and \( T_m^\infty = 415 \text{ K} \). \( \sigma_e \) is given as:

\[
\sigma_e = \mu h_u c^* \left[ \frac{(R T_m^2 + (H_x - h_x)(T_m^\infty - T_m))}{2(H_x - h_x)T_m^\infty} \right] \tag{21}
\]

where \( H_x = 2h_u - Q_m \) and \( c^* \) is the cell length of c-axis. The term of the square bracket in Eq. (21) is dimensionless. Table 6 shows the values of \( \sigma_e \) for “\( T_a = 376.6 \text{ K, 416.6 K and 426.6 K} \)”-samples, together with the values of \( T_p \), \( T_e^* \), \( h_x \), \( Q_m \), \( \Delta Q_m (= Q_m - h_c) \) and \( \Delta Q (= Q - Q_m) \) used in the calculation of \( \sigma_e \), where \( T_p \) is the melting peak temperature and \( \Delta Q \) is the heat per molar structural unit corresponding to the area of the lower temperature side peak in Fig. 8, contributing to the activation heat required to release the secondary glass state. \( \Delta Q_m \) is given by:

\[
\Delta Q_m = \int_{T_e^*}^{T_c^*} \left( \frac{dQ}{dT} \right)(1/\alpha_c) dT \tag{22}
\]

where \( \alpha_c \) is the heating rate. \( T_e^* \) was derived from Eq. (22) using \( \Delta Q_m \) in Table 6. The fact that \( T_e^* \) was almost equal to that by observation, as shown in Table 6, supported that \( h_c \) was due only to the formation of the crystal lamella, thus giving rise to the melting peak on the higher temperature side. \( T_e^* \) is also the end temperature of melting for ordered parts of fold-type in the inter-grain aggregates. Upon heating over \( T_e^* \), the flow parts in the amorphous regions should start to participate directly in the melting of crystals. With an increasing \( T_a \), \( \sigma_e \) and \( h_x \) decreased, whereas \( Q_m \), \( \Delta Q_m \) and \( \Delta Q \) increased. \( \Delta Q \) should influence \( h_x \). For all samples, the value of \( \sigma_e \) at \( T_p \) was 1.3 times larger than that at \( T_m^\infty \) (\( Q_m = 0 \)). The experimental values of \( \sigma_e \) from Eq. (20), 30 ~ 90 mJ/m^2, differed significantly from those in Table 6, probably due to the length of the lamellae after annealing and the use of cooling as the substitute of \( \zeta \) at \( T_m^{23, 44} \).
Table 6. The values of $T_p$, $T_e^*$, $h_x$, $Q_m$, $\Delta Q_m$, $\Delta Q$ and $\sigma_e$ for PE films annealed at 376.6 K, 416.6 K and 426.6 K for 1 hour.

| Sample $T_a$/K | $T_p$/K | $T_e^*$/K | $h_x$/kJ/mol | $Q_m$/kJ/mol | $\Delta Q_m$/kJ/mol | $\Delta Q$/kJ/mol | $\sigma_e$ at $T_p$/mJ/m$^2$ |
|---------------|---------|-----------|--------------|--------------|---------------------|------------------|------------------|
| 376.6         | 401.2   | 399.2 (397.7) | 3.03         | 1.37         | 0.48                | 0.42             | 16.3 (12.4)      |
| 416.6         | 401.8   | 400.1 (399.0) | 2.44         | 1.42         | 0.53                | 0.96             | 14.3 (11.1)      |
| 426.6         | 401.9   | 400.7 (389.7) | 1.97         | 1.52         | 0.63                | 1.33             | 12.9 (10.1)      |

The values in the parentheses of $T_e^*$ and $\sigma_e$ columns are the apparent $T_e^*$ by observation and $\sigma_e$ at $T_m^\infty = 415$ K ($Q_m = 0$), respectively. $T_p$ is corrected by 0.1 K to the lower temperature side.

On the other hand, according to Flory’s theory\(^{45}\) on the melting of the fringe-type crystals with a finite $\zeta$, $\sigma_e$ at $\lambda$ and $(df_u/d\zeta)_\lambda = 0$ is given by:

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

(23)

where $\lambda$ is the amorphous fraction, $f_u$ is the free energy per molar structural unit for the crystals and $x$ is the degree of polymerization. In this context:

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

(24)

$$
f_x' = RT[(1/\zeta)\ln((x - \zeta + 1)/x) - \ln P_c]
$$

(25)

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

$$
f_u - (f_x - f_x') = 0
$$

(26)

Eq. (23) is obtained when $\ln P_c = -1/(x - \zeta + 1)$. From Eq. (26), 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 7. 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 equivalent fringe-types, leading to $\sigma_e = 0$ in Eq. (24) as expected for highly oriented fibers. For class B, $f_u = -f_x'$ from Eq. (26) with $f_u = 0$ refers to the anti-crystal holes and $f_x = 0$ is assigned to the ordered parts of $\zeta = \infty$. Class C, $f_x = f_x'$ from Eq. (26) 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. (26), suggesting that the holes of class B can not be replaced by the crystals with $\zeta \neq \infty$.

When $f_u = -f_x'$ for class B, the temperature at which the anti-crystal holes disappear (melt), i.e., $T_m^h$, is given by:

$$
T_m^h = T_m^{\infty}[1 + 2\sigma_e/(\mu \zeta h_u)]
$$

(27)
where $h_u$, $\sigma e$, and $\zeta$ are imaged for the anti-crystal holes, and that, the photonic crystals made up only of photons without the mass. According to Eq. (27), $T_{m, h}$ approaches $T_m^{\infty}$ with an increasing $\zeta$. However, the interface between the anti-crystal holes and the ordered parts, which satisfy $f_x = 0$ (described below), should work as the reflector of photons attached to the anti-crystal holes. In this case, the even interface made of the folded chain segments should be avoided through the random reflection. At such an interface, from Eq. (24), the following relation of energy balance is derived:

$$h_x - h_u = T_{m, h} (s_u - s_x) = \sigma e / (\mu \zeta)$$

(28)

where $s_u$ is the entropy per molar unit for the anti-crystal holes. As well as $h_u$, one mole of units (photons) corresponds to three moles of the oscillators, since three oscillators can be coordinated to each point of the crystal lattice. According to Eq. (28) or (24), the respective interface energies of the hole and the ordered part are compensated each other at the common interface, leading to $f_x = 0$ of class B and further, $T_{m, h}$ approaches 0 K with an increasing $\zeta$. From the interface at $\zeta = \infty$, the photons are not reflected, and that, do not exist in the holes. This is exactly the real “dark hole”. Therefore when the anti-crystal hole of $\zeta = \infty$ is pairing with the neighboring crystal as shown in Fig. 11C, the crystal is set at 0 K. As opposed to Eq. (27), from $f_u = f_x'$ of class D, the $T_m$ of the crystals is derived:

$$T_m = T_m^{\infty} \{1 - 2\sigma e / (\mu \zeta h_u)\}$$

(29)

Eq. (29) is the same as Eq. (20). In Eq. (29), $T_m$ is $T_m^{\infty}$ at $\zeta = \infty$ and from Eqs. (27) and (29), $T_m^{\infty} = (T_{m, h} + T_m) / 2$ is derived. According to the pair relation, the emission of heat from the anti-crystal holes after crystallization is necessarily linked to the supply of heat of the same quantity to the newly crystallized parts. However $T_{m, h}$ should be depressed down to $T_m$ by the emission of heat to the outside. For a model of the inter-grain aggregates shown in Fig. 9, the interaction in the inter-grain aggregates and the a - c face of the crystals must be neglected and the ordered parts in the inter-grain aggregates must satisfy Eqs. (1) and (2) at $T_g^*$. It is thus presumed that over $T_g^*$, the chains that cross the glass regions give rise to the newly crystallized parts of fringe-type, whereas the folded chain segments around the glass excluded from the ordered parts give rise to the two end-surfaces of the anti-crystal hole with the same $\zeta$ as the new crystal. The $T_m$ of the crystals from the secondary glass, being equal to $T_{m, h}$, was found to change from $T_b^*$ to $T_e^*$ as a function of $\zeta$ in Eq. (29). The time spent from $T_b^*$ to $T_e^*$ was 0.73 s, in which the probability of observing a spontaneous generation of crystallization or melting should be 1/2, according to the uncertainty principle.

| $f_x'$ | $f_x$ | $f_u$ | 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 7. Relations of equilibrium (A – D) and non-equilibrium (X) in $f_x$ and $f_u$ at $f_x' \geq 0$ for crystalline polymers\(^{(46)}\).
Fig. 10 shows the schematic behaviors of sequences and photons on the way of crystallization and melting. The heat of emission, $\Delta U_h$, corresponds to $\Delta Q_m$ of the area between the observed melting curve (thin line) and the lower temperature side peak curve from $T_b^*$ to $T_e^*$ and the heat of absorption, $\Delta U_m (= \Delta U_h)$, corresponds to $\Delta Q_m$ of the under area of the higher temperature side peak curve from $T_b^*$ to $T_e^*$ in Fig. 8. Fig. 11 shows the cross sections of the glass (A) and the “crystal / anti-crystal hole” pair (C). The two end-surfaces of the anti-crystal hole in Fig. 11C contact in equilibrium those of the ordered parts. Supposing that this model of aggregates was valid for the “$T_a = 416.6$ K”-sample shown in Fig. 8, a derivation of $f_x' (= -f_u)$ = 0.13 kJ/mol was obtained from Eq. (24) using the values of $\sigma_e$ (see Table 6) and $\zeta$ (= 3.1 nm) at $T_p$ = 401.8K (see Table 9). Here, $f_x$ is rewritten as $f_x^i$ for the ordered parts in the inter-grain aggregates. Furthermore, under the assumption that the strain energy in the glass should be spent to build the interface between the anti-crystal hole and the ordered part, by substituting $h_c - \Delta H (= 0.06$ kJ/mol) for $h_x^i - h_u$, it was possible to derive $s_u - s_x^i = 0.15$ J/(K mol) at $T_c (= 391.5$ K), where $h_x^i$ and $s_x^i$ are the enthalpy and entropy per molar structural unit for the ordered parts in the inter-grain aggregates. The relation of $h_x^i - h_u = h_c - \Delta H (= 0.06$ kJ/mol) could be supported by determining $\sigma_e / (\mu \zeta) = 0.06 - 0.07$ kJ/mol in Eq. (28), which was obtained for all samples using $\zeta$ and $\sigma_e$ at $T_p$. From $f_x^i = 0$, $h_x^i = 4.17$ kJ/mol and $s_x^i = 10.7$ J/(K mol) at $T_c$ were obtained. Moreover, using $h_u = 4.11$ kJ/mol, $s_u$ was 10.9 J/(K mol) at $T_c$.

![Fig. 10. The schematic process from the glass (A) to the generation of “crystal / anti-crystal hole” pairs (B → C) by emission of $\Delta U_h$ and then the disappearance of them (M) by absorption of $\Delta U_m (= \Delta U_h)$. The filled circle (●) is the segmental unit, the arrow mark (↔) is the oscillator and the large circle is the photon.](image-url)

![Fig. 11. The cross sections of the glass (A) and the “crystal / anti-crystal hole” pair (C). The dot in large and small circles is the cross section of a segment and the blank in C is the hole. The arrow mark shows the crystallization from A to C.](image-url)
5.4 Fraction of secondary glass

The anti-crystal holes should be permeated by the photons obeying the frequency distribution function with an upper limit. This is due to the interface between the anti-crystal hole and the ordered part be able to act as a filter for the photons. The molar photon energy loss of the anti-crystal holes, $\Delta U_h$, due to the cavity radiation from $T_{b}^*$ to $T_{e}^*$ is given by:

$$\Delta U_h = 3C_v^{ph}(T_{e}^* - T_{b}^*)$$ (30)

On the other hand, the heat change per molar structural unit, $\Delta U_m$, due to the melting of the newly crystallized parts from $T_{b}^*$ to $T_{e}^*$ is given by:

$$\Delta U_m = \Gamma \Delta Q_m$$ (31)

where $\Gamma$ is the fraction of the secondary glass, contributed to the generation of “crystal / anti-crystal hole” pairs, in the inter-grain aggregates at temperatures below $T_g^*$. From $\Delta U_h = \Delta U_m$ at $T_{e}^*$, $\Gamma$ is given by:

$$\Gamma = \frac{3C_v^{ph}(T_{e}^* - T_{b}^*)}{\Delta Q_m}$$ (32)

Table 8 shows the values of $T_{e}^* - T_{b}^*$, $Q_m$, $\Delta Q_m$, $\Delta U_h (= \Delta U_m)$, $\Delta Q_m/Q_m$ and $\Gamma (= \Delta U_h/\Delta Q_m)$ for PE films annealed at 376.6 K, 416.6 K and 426.6 K for 1 hour. From $\Delta Q_m/Q_m$ and $\Gamma$, 35 – 41 % of the lamella was constituted of the inter-grain aggregates and approximately 79 – 96 % of this was the glass at $T \leq T_g^*$. The difference in $\Delta Q_m$ and $\Delta U_m$ was believed to represent the irreversible heat change due to the melting of the ordered parts of fold-type, since the folded segments have the excess defect energy. The values of $\Delta U_h$ were almost same as $\Delta h$ (= 0.5 kJ/mol) for the glasses with $T_g = 135$ K and 237 K in Table 2, giving the latent heat required to disappear the holes.

| Sample $T_a$/K | $T_{e}^* - T_{b}^*$ K | $Q_m$ kJ/mol | $\Delta Q_m$ kJ/mol | $\Delta U_h$ kJ/mol | $\Delta Q_m/Q_m$ | $\Gamma$ |
|---------------|-----------------|--------------|-------------------|-----------------|----------------|--------|
| 376.6         | 6.8             | 1.37         | 0.48              | 0.46            | 0.35           | 0.95   |
| 416.6         | 7.6             | 1.42         | 0.53              | 0.51            | 0.37           | 0.96   |
| 426.6         | 7.4             | 1.52         | 0.63              | 0.50            | 0.41           | 0.79   |

Table 8. The values of $T_{e}^* - T_{b}^*$ → $T_{e}^* - T_{b}^*$, $Q_m$, $\Delta Q_m$, $\Delta U_h (= \Delta U_m)$, $\Delta Q_m/Q_m$ and $\Gamma (= \Delta U_h/\Delta Q_m)$ for PE films annealed at 376.6 K, 416.6 K and 426.6 K for 1 hour.

5.5 $\zeta$ distribution function, $F(\zeta)$

The occurrence of $\zeta$ distribution by crystallization is one of the characteristics of bulk polymers. The conversion of a DSC melting peak into the $\zeta$ distribution by Eq. (20) needs the values of $\sigma_e$ and $T_m^\infty$. The $\sigma_e$ can be evaluated by Eq. (21) using only the DSC data. On $T_m^\infty$, the inherent temperature of the crystal form should be selected. The $F(\zeta)$ is defined as:

$$F(\zeta) = (\delta Q_m/Q_m)/ \zeta = n_\zeta/\{N_c(T_e - T_b)\}$$ (33)
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 $\zeta$, and $N_c$ is the number of structural units of crystals melted in the temperature range from $T_b (= T_b^*$ here) to $T_e$. $\delta Q_m / Q_m$ is given by:

$$\frac{\delta Q_m}{Q_m} = \frac{(dQ/dt)}{\int_{T_b}^{T_e} (dQ/dt) dT}$$ (34)

where $dQ/dt$ is the heat flow rate of the melting curve. Fig. 12 shows $F(\zeta)$ of each melting curve from $T_b^*$ for “$T_a = 376.6$ K, 416.6 K and 426.6 K”-samples. Table 9 lists the values of $\zeta$-range, $\zeta_c$ and $\zeta_p$ of $F(\zeta)$ curve for each sample, where $\zeta_c$ is $\zeta$ at $T_e^*$ and $\zeta_p$ is $\zeta$ at $T_p$. For “$T_a = 376.6$ K”-sample, $\zeta_p$ was slightly larger than for other samples. The small value of $\zeta (< \zeta_c)$ was believed to be caused by the crystallization from the secondary glass in the restricted space of inter-grain aggregates. The large $\zeta$ value at the maximum for “$T_a = 416.6$ K and 426.6 K”-samples might be related to the long period change of lamellae at the higher temperature upon heating. Whereas, the very narrow $\zeta$-range for “$T_a = 376.6$ K”-sample might be due to the effective annealing.

Fig. 12. $F(\zeta)$ for PE films annealed at 376.6 K (right), 416.6 K (middle) and 426.6 K (left) for 1 hour. $\times$; $F(\zeta_c)$.  

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Table 9. The values of ζ-range, ζc and ζp in F(ζ) for PE films annealed at 376.6 K, 416.6 K and 426.6 K for 1 hour.

| Sample T_a/K | ζ-range | ζc | ζp |
|--------------|---------|----|----|
| 376.6        | 2.1 - 14| 2.9 (2.7) | 3.3 |
| 416.6        | 1.8 - 810 | 2.7 (2.6) | 3.1 |
| 426.6        | 1.7 - 730 | 2.5 (2.2) | 2.8 |

The values in the parentheses are ζ at the apparent T_e*.

In the last stage, a single crystal-like image was drawn from F(ζ). Rewriting Eq. (33), n_ζ is given by:

\[ n_\xi = F(\xi)N_c(T_e - T_b) \]  

The number of the crystal sequences from ζ_n to ζ, N_ζ, is as follows:

\[ N_\xi = N_c(T_e - T_b) \int_{\xi_n}^{\xi} F(\xi)d\xi \]  

Accordingly, the number of the crystal sequences from -ζ (> ζ) to ζ, ΔN, is given by:

\[ \Delta N = N_c(T_e - T_b)(\int_{\xi_n}^{\xi} F(\xi)d\xi - \int_{\xi_n}^{\xi} F(\xi)d\xi) \]  

Fig. 13. The relationship between R (= ±R_n) and L (= ±ζ/2) for PE films (1 g) annealed at 376.6 K (thick line) and 426.6 K (thin line) for 1 hour. The horizontal lines show R of the crystal melting from ζ_n or ζ_c to ζ = 0.

In the last stage, a single crystal-like image was drawn from F(ζ). Rewriting Eq. (33), n_ζ is given by:

\[ n_\xi = F(\xi)N_c(T_e - T_b) \]  

The number of the crystal sequences from ζ_n to ζ, N_ζ, is as follows:

\[ N_\xi = N_c(T_e - T_b) \int_{\xi_n}^{\xi} F(\xi)d\xi \]  

Accordingly, the number of the crystal sequences from -ζ (> ζ) to ζ, ΔN, is given by:

\[ \Delta N = N_c(T_e - T_b)(\int_{\xi_n}^{\xi} F(\xi)d\xi - \int_{\xi_n}^{\xi} F(\xi)d\xi) \]  

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where $\zeta_x$ and $\zeta_n$ are the maximum and minimum of $\zeta$, respectively. When the crystal sequences are bundled, like a fringe in a circle, the number of crystal sequences in a radius direction, $R_n$, as a function of $\zeta$ is given by:

$$R_n = (\Delta N/\pi)^{1/2} \quad (38)$$

Fig. 13 shows the relationship between $R (= \pm R_n)$ and $L (= \pm \zeta/2)$ for the samples (1 g) annealed at 376.6 K and 426.6 K for 1 hour. In the $\zeta$-range of $0 \sim \pm \zeta_n/2$, $R$ at $\zeta_n/2$ is represented by a solid line, which leads to the supposition of a melting process from the end-surfaces of the crystal with $\zeta_n$ at $T_{b^*}$. The horizontal line of $R$ at $\zeta_c/2$ depicts the same imaginable melting process of the crystal with $\zeta_c$ at $T_{e^*}$. The distinct difference of $R$ or $L$ between both types of crystals should be available in order to evaluate the annealing effects. The single crystal image from $R$ and $L$ for “$T_a = 376.6$ K”-sample (thick line) was very similar to the electron microscope (EM) image of self-seeded PE crystals.

6. Conclusions

The generation and disappearance of the “crystal / anti-crystal hole” pairs from the secondary glass in PE crystal lamella were discussed on the DSC curves. Thus the fraction of the secondary glass in the lamella was derived from the molar photon energy loss of the anti-crystal holes upon heating, which agreed with the latent heat of disappearance for the holes at the primary $T_g$ of the first order hole phase transition.

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