Equilibrium Melting Temperature of Isotactic Polypropylene with High Tacticity. 2. Determination by Optical Microscopy

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ABSTRACT: In part 1 of this series, we proposed a new method to determine the correct equilibrium melting temperature \( T_m^0 \). Effects of the “melting kinetics” and lamellar thickening were omitted from \( T_m^0 \). The correct \( T_m^0 \) of isotactic polypropylene (IPP) \( ([\text{mmm}]) = 99.6\% \), \( M_n = 64 \times 10^3 \), and \( M_n/M_w = 2.4 \) was observed to be 186.1 °C. In this paper, the rigorous Gibbs–Thomson plot was obtained by using the direct correspondence between the maximum melting temperature \( T_m^{\text{max}} \) and maximum lamellar thickness \( l_{\text{max}} \). \( T_m^{\text{max}} \) and \( l_{\text{max}} \) were observed by means of optical microscopy and transmission electron microscopy (TEM), respectively. The validity of the Gibbs–Thomson plot obtained by means of a differential scanning calorimeter (DSC) (part 1 of this series) was confirmed by comparing it with the rigorous Gibbs–Thomson plot in this paper. The Hoffman–Weeks plot is widely used as one of the methods to obtain \( T_m^0 \). It was shown that the Hoffman–Weeks plot is correct only when \( l \gg 1/\Delta T \), where \( \Delta T \) is the degree of supercooling, is satisfied. However, in the case of IPP, the condition is not satisfied, and so the result obtained by the Gibbs–Thomson plot is not equivalent to that obtained by the Hoffman–Weeks plot. The existence of \( \alpha^\prime \) phase was confirmed again by breakings in slopes of \( l \) and \( T_m \) against \( T_c \) at 159 °C. Furthermore, the broad bimodal distribution of \( l \) was caused by the difference between the lamellar thickening growth rate of isolated mother lamellae and the lamellae thickening rate of stacked daughter lamellae.

1. Introduction

In the previous paper (part 1), a new method to determine a reliable equilibrium melting temperature \( T_m^0 \) was proposed.1 In the method, the Gibbs–Thomson plot

\[
T_m(l) = T_m^0 - \frac{C}{l} \tag{1}
\]

was applied, where \( l \) is lamellar thickness, \( T_m(l) \) is melting temperature \( T_m^0 \) of lamellae with \( l \) and \( C \) is given by eq 1 in part 1 of this series.2 It was shown that two effects depending on heating rate \( (\beta) \), i.e., the “melting kinetics” and lamellar thickening, should be omitted from \( T_m(l) \).

In part 1, the differential scanning calorimeter (DSC) and the transmission electron microscope (TEM) were used for observations of \( T_m(l) \) and \( l \), respectively. It was shown that endothermic peak temperature \( (T_m(DSC)) \) corresponds to reciprocal averaged lamellar thickness \( (l^{-1}) \) in the Gibbs–Thomson equation. \( T_m^0 \) of isotactic polypropylene (IPP) was determined to be 186.2 °C.

DSC measurement is convenient and useful to observe \( T_m \). However, there is a problem that the Gibbs–Thomson plot made by using \( T_m(DSC) \) is not always rigorous for polymers, because the correspondence between \( T_m(DSC) \) and \( (l^{-1}) \) is reliable only when distribution of \( l (l(l)) \) and that of \( T_m \) are sharp, and not when they are broad. It is usual in polymers that \( l(l) \) is rather wide.3

In this paper (part 2), a “rigorous Gibbs–Thomson plot” will be carried out by using direct correspondence between \( T_m \) and \( l^{-1} \), i.e., maximum \( T_m \) \( (T_m^{\text{max}}) \) and maximum \( l (l_{\text{max}}) \), which can be observed by means of an optical microscope and TEM, respectively.

1.1. Effect of “Melting Kinetics” and Lamellar Thickening on \( T_m \). In part 1 of this series, it was proposed that correct \( T_m(l) \) can be obtained by omitting the two effects of the “melting kinetics” and lamellar thickening on \( T_m \).4–7 The effect of lamellar thickening can be omitted when \( l \) is thick enough, such as \( l > 15 \) nm for IPP. The effect of the “melting kinetics” of thick lamellae can be omitted by observation of isothermal melting. Therefore, the \( T_m^{\text{max}} \) of thick lamellae with \( l > 20 \) nm would be directly observed by means of an optical microscope in this paper.

1.2. Significant Lamellar Thickening in the Mobile Phase of IPP. Thick lamellae can be obtained by isothermal crystallization at high \( T_c \). Hikosaka et al. proposed a chain sliding diffusion theory that lamellae thicken significantly when polymers are crystallized in mobile phases such as the hexagonal phase, a liquid crystalline phase, or a kind of disordered phase where the lattice is expanded and chains are packed loosely.8–10 The \( \alpha^2 \) phase of IPP above \( T_{c_{\alpha^2-\alpha}} = 159 \) °C is a mobile phase, where \( T_{c_{\alpha^2-\alpha}} \) is the \( \alpha^2-\alpha^2 \) transition temperature.11,12 Lamellar thickening should be accelerated significantly in the mobile phase. In the present paper, it will be confirmed that significant thick lamellae are formed in the \( \alpha^2 \) phase.

1.3. Melting Behavior and Lamellar Morphology of IPP. The melting behavior of spherulite should be closely related to change in lamellar morphology. There
is no crosshatching lamellae when iPP is crystallized at a higher Tc than 150 °C.13–19 In part 1 of this series, we suggested that the two-stage melting endotherm of iPP crystallized at Tc ≥ 148 °C observed by means of DSC corresponds to the bimodal distribution of l. In this paper, detailed evidences of the bimodal distribution of l will be shown by means of TEM, corresponding to a change of the optical morphology of spherulites.

1.4. Problem of the Hoffman–Weeks Plot. The Hoffman–Weeks plot method has been widely used to obtain Tm,0 of polymers.20–22 Hoffman and Weeks assumed that,

\[ l = \beta l^* \propto \frac{1}{\Delta T} \quad (2a) \]

\[ l = \text{constant (on heating)} \quad (2b) \]

where \( l \) is a constant, \( l^* \) is l of a critical nucleus, and \( \Delta T \) is the degree of supercooling. By application of these assumptions to the Gibbs–Thomson equation, the following equation is obtained

\[ T_m = bT_c + c \quad (3a) \]

\[ c = (1 - b)T_m^0 \quad (3b) \]

where b and c are constants. \( T_m^0 \) can be obtained as an intersection of lines of \( T_m = T_c \) and eq 3a. The Gibbs–Thomson equation (eq 1) is equivalent to the Hoffman–Weeks equation (eq 3a) under the assumptions of eq 2, parts a and b.

\( T_m^0 \) obtained from the Hoffman–Weeks plot and that obtained from the Gibbs–Thomson plot are sometimes similar and, however, sometimes quite different. A typical example of the former is polyethylene (PE) and the one of the latter is iPP.21–28 Furthermore, in the case of polyvinylidenefluoride (PVDF), the Hoffman–Weeks plot cannot give \( T_m^0 \).29,30

The problem that the Hoffman–Weeks plot method does not always work well has not been solved yet. The reason should be that above assumptions are not correct for all polymers. It is possible that l is constant on heating (eq 2b) by using thick lamellae. Therefore, the validity of the Hoffman–Weeks plot method depends on whether eq 2a is satisfied or not. In this paper, the actual validity of the Hoffman–Weeks plot will be tested for typical cases, such as PE and iPP.

1.5. Purpose of This Study. The first purpose is to obtain the correct \( T_m^0 \) by using direct correspondence between \( T_{m,\text{max}} \) and \( l_{\text{max}}^{-1} \) in the rigorous Gibbs–Thomson plot. \( T_{m,\text{max}} \) and \( l_{\text{max}}^{-1} \) will be obtained from the results by means of optical microscope and TEM, respectively. The effect of the “melting kinetics” on \( T_m \) was directly omitted by applying isothermal melting condition (\( \beta = 0 \) K/min). Lamellar thickening was also omitted by observing thick lamellae larger than 20 nm. The validity of the convenient Gibbs–Thomson plot by means of DSC in part 1 of this series will be evaluated by comparing both results.

The second purpose is to show that significant lamellar thickening occurs when iPP crystallizes in the \( \alpha^2 \) form. Accordingly, it will be confirmed that the \( \alpha^2 \) phase of iPP is a kind of mobile phase.

The third purpose is to show that the Hoffman–Weeks plot method is correct only when \( l \propto 1/\Delta T \) is satisfied, which will be confirmed from experimental results.
2.4. Partial Melting. DSC showed double melting endotherms. To confirm that a higher DSC peak \( T_{m(I)} \) and a lower peak \( T_{m(II)} \) correspond to the melting of thick and thin lamellae, annealing was carried out. DSC measurement was carried out by using Perkin-Elmer DSC7 under nitrogen flow. The details of the DSC measurement were shown in part 1 of this series. The sample was heated to an annealing temperature between \( T_{m(II)} \) and \( T_{m(I)} \) in an oil bath at a heating rate of 5 K/min. The sample temperature was directly measured by thermocouples. When sample temperature strictly reached to the annealing temperature between \( T_{m(II)} \) and \( T_{m(I)} \), the sample was quickly transferred into frozen acetone and quenched.

3. Results

3.1. Comparison of Nonisothermal Melting Behavior Observed by Optical Microscopy and DSC. In part 1 of this series, the DSC melting endotherm showed two-stage melting, i.e., peaks II \( (T_{maz(II)}) \) and I \( (T_{maz(I)}) \) at low and high temperatures, respectively. It was shown that peaks II and I correspond to meltings of thin and thick lamellae, respectively. To make clear what kind of lamella melts corresponding to DSC peaks, change of optical morphology was observed on heating at \( \beta = 5 \text{ K/min} \).

Typical melting behaviors of a spherulite crystallized at \( T_c = 153 \) °C \( \leq T_{a2-a2} \) and \( T_c = 164 \) °C \( > T_{a2-a2} \) observed by polarized optical microscopy are shown in Figures 3 and 5, and the corresponding DSC curves are shown in Figures 4 and 6, respectively. Parts a, b, c and d in Figures 3 and 5 showed morphologies at the temperatures indicated by arrows a, b, c and d in Figures 4 and 6, respectively.

Figure 3a showed morphology before melting. At a little higher temperature \( (177.1 \) °C) than \( T_{maz(II)} \), fine texture disappeared, which indicated partial melting of thin lamellae (Figure 3b). At \( T_{maz(I)} \), 180.2 °C, the distinct texture disappeared and the spherulite melted completely, which indicated complete melting of thick lamellae (Figure 3, parts c and d).
Similar morphological change was observed for the sample crystallized at \( T_c = 164 \ °C > T_{a2-a2} \) (Figures 5). Partial melting (Figure 5b) and whole melting (Figure 5, parts c and d) were observed corresponding to \( T_{m_{a2}} \) (II) and \( T_{m_{a2}} \) (I), respectively (Figure 6).

Thus, it was concluded that the similar “two-stage melting” was observed in the morphological change, as well as in DSC. The partial and complete meltings corresponded to the meltings of thin and thick lamellae, respectively.

3.2. Isothermal Melting Behavior and \( T_m \) Observed by Optical Microscopy. Melting behavior of a spherulite was observed by phase contrast optical microscopy under isothermal condition \( (\beta = 0 \ K/min). \) Two-stage melting behavior was observed for both samples crystallized at \( T_c = 153 \ °C \leq T_{a2-a2} \) and \( T_c = 164 \ °C > T_{a2-a2} \) (Figures 7 and 8). Figures 7a and 8a showed spherulites before melting. Figures 7b (175.1 °C) and 8b (182.4 °C) showed partial melting, which should correspond to \( T_{m_{a2}} \) (II). Distinct textures were clearly observed. Figures 7c (177.1 °C) and 8c (183.3 °C) showed the start of complete melting. When the spherulites were kept at the same temperatures (Figures 7c and 8c), they melted slowly and disappeared completely (Figures 7d and 8d) after 25 and 30 min, respectively. Therefore, the temperatures of Figure 7d and 8d should correspond to \( T_{m_{a2}} \) (DSC).

\[ T_{a2-a2} = 159 \ °C \] (4)

\( T_{a2-a2} \) (DSC) was also shown as a reference in Figure 9. Both \( T_{m_{a2}} \) (OM) and \( T_{m_{a2}} \) (DSC) at \( \beta = 0 \ K/min \) showed similar tendency against \( T_c \), i.e., breakings were observed and the \( dT_m/dT_c \) in the \( \alpha' \) phase was larger than that in the \( \alpha2 \) phase. Thus, the \( \alpha2 \)–\( \alpha' \) transition was confirmed again.

3.3. \( T_c \) Dependence of \( T_{m_{a2}} \) (OM). \( T_{m_{a2}} \) (OM) was plotted against \( T_c \) in Figure 9. Open symbols indicated \( T_{m_{a2}} \) (OM) of samples crystallized into the \( \alpha2 \) form, and filled symbols indicated that of samples crystallized into the \( \alpha' \) form. \( T_{m_{a2}} \) (OM)s of all crystallized specimens were higher than \( T_{a2-a2} = 159 \ °C \) in this study. Therefore, \( T_{m_{a2}} \) (OM) was denoted as \( T_{m_{a2}} \) (OM).

\( T_{m_{a2}} \) (OM) increased with increasing \( T_c \). Breaking of the differential coefficient \( (dT_m/dT_c) \) was observed at 159 °C, which corresponds to the \( \alpha2 \)–\( \alpha' \) transition. Therefore, the breaking temperature was

\[ T_{a2-a2} = 159 \ °C \] (4)

3.4. Lamellar Morphology and Thickness. Transmission electron micrograph of an ultrathin section with low magnification is shown in Figure 10. The radial direction of the spherulite corresponded to the direction of \( a^* \) axis of lamellae. The lateral lengths of the lamellae were several hundreds of micrometers. It corresponds to the texture of spherulite observed by optical microscopy as shown in Figure 2. I was obtained from edge-on
increase of $T$ as indicated by solid curves.

sharp peaks with large $l$ (peak I) and small $l$ (peak II) as indicated by solid curves.  $f(l)$ shifted to larger $l$ with increase of $T_c$.

**a)** $T_c < T_{a_2-a_2}$. For the samples crystallized at $T_c < T_{a_2-a_2}$, $l_{max}$ increased gradually from 21 to 32 nm with increase of $T_c$ from 148 to 157 °C (Figure 13). $f(l)$ showed bimodal distribution. $f(l)$ was separated into two rather sharp peaks with large $l$ (peak I) and small $l$ (peak II) as indicated by solid curves. $f(l)$ shifted to larger $l$ with increase of $T_c$.

**b)** $T_c > T_{a_2-a_2}$. $l_{max}$ of samples crystallized at $T_c > T_{a_2-a_2}$ significantly increased from 53 to 69 nm with an increase of $T_c$ from 162 to 166 °C (Figure 14). $f(l)$ also showed bimodal distributions. It was separated into sharp peak with small $l$ (peak I) and very broad peak with large $l$ (peak II). $f(l)$ of peak I became very broad with increase of $T_c$. The sharpness of $f(l)$ of peak II did not depend on $T_c$.

3.6. **Confirmation of the Bimodal Distribution of l by Partial Melting.** DSC melting curves at heating rate of 5 K/min of sample crystallized at 162 °C is shown.
in Figure 15a. The sample temperature reached the annealing temperature, and then the sample was immediately quenched (Figure 15b).

Transmission electron micrographs of the samples before and after annealing are shown in Figure 16, parts a and b, respectively. After annealing, crosshatched very thin lamellae within a spherulite were observed (Figure 16b). It was formed by melt-recrystallization after partial melting. Thick lamellae were also observed after annealing (Figure 16b), which correspond to thick lamellae of the original sample as indicated by arrow in Figure 16a. The thickness of thick lamellae became slightly thinner due to the disordering of the end surface of lamellae. Corresponding to the morphology change, DSC melting curves of samples after partial melting showed the higher peak (Figure 15c). A melting peak of thin lamellae crystallized at cooling from the annealing temperature also observed. Therefore, the two-stage melting was confirmed by the bimodal distribution of $l_{\text{max}}$.

3.7 $T_c$ Dependence of $l_{\text{max}}$. $l_{\text{max}}$ was plotted against $T_c$ in Figure 17. $l_{\text{max}}$ of the specimens crystallized into the a2 form and the a2' form were indicated by open circles and filled circles, respectively. At $T_c \leq T_{\text{a2-a2'}},$
lmax increased slowly with increase of Tc. And at Tc > T_{R2}-R2′, lmax increased significantly with increase of Tc.

Breaking of the differential coefficient \( \frac{dl_{max}}{dT_{c}} \) was observed at Tc \( \approx 159°C \). Tm, R2′(OM) was also plotted again for comparison. Tc dependence of lmax showed similar tendency with that of Tm, R2′(OM). The breaking temperature of \( \frac{dl_{max}}{dT_{c}} \) was in good agreement with that of \( \frac{dT_{m}}{dT_{c}} \). They corresponded to the T_{R2}-R2′ observed by means of wide-angle X-ray scattering and DSC. Therefore, the very high Tm, R2′(OM) in R2′ phase was due to the very large lmax.

3.8. Equilibrium Melting Temperature. The Gibbs–Thomson plot, \( T_{m,max} = T_{m,az}(OM) \) vs l_{max}^{-1}, is shown in Figure 18. T_{m,az}(OM) increased linearly with decrease of l_{max}^{-1}. An experimental formula was obtained

\[
T_{m,az}(OM) = 186.1 - \frac{240}{l_{max}} \quad \text{°C} \quad \text{for } M_n = 64 \times 10^3
\]

(5)

The slope of the line, C in eq 1, was also obtained,

\[
C = 240 \pm 21 \text{ nm } K
\]

(6)

Thus, the rigorous Gibbs–Thomson plot and Tm0 were obtained in this study.

3.9. Validity of Gibbs–Thomson Plot Obtained by Using DSC. In this paper, the rigorous Gibbs–Thomson plot and Tm0 were obtained by means of optical microscope. The convenient Gibbs–Thomson plot obtained by means of DSC in part 1 of this series was also shown in Figure 18. The result of convenient Gibbs–Thomson plot was similar to the rigorous one. Therefore, the validity of the convenient Gibbs–Thomson plot was confirmed. The method used to obtain the plot by means of DSC is useful as a practical and convenient one.
4. Discussion

4.1. End Surface Free Energy. End surface free energy ($\sigma_e$) is obtained from $C$ in eq 1. $C$ is given by

$$C = \frac{2\sigma_e T_m^0}{\Delta h} \quad (8)$$

where $\Delta h$ was reported as between 148 and 209 J/cm$^3$ in the literature. Therefore, we obtained reliable $\sigma_e$

$$\sigma_e = (39-55) \times 10^{-7} \text{ J/cm}^2 \quad (9)$$

Most $\sigma_e$ values reported in the literature were in the range of $0.07-70 \times 10^{-7}$ J/cm$^2$. $\sigma_e$ is obtained from the Gibbs-Thomson plot or $\Delta T$ dependence of lateral growth rate. In the former case, the Gibbs-Thomson plots used in the literature were unreliable as mentioned in part 1 of this series. In the latter case, growth rate strongly depends on $\Delta T$. Therefore, the estimated $\sigma_e$ is strongly affected by $T_m^0$, and the reported $\sigma_e$s were unreliable because the $T_m^0$s of iPP in the literature were not reliable.

4.2. Broad Distribution of $l$ in the $\alpha2'$ Phase. Bimodal distribution of $l$ can be explained by the forming mechanism of lamellae. Axialite with isolated mother lamellae is formed in the initial process of crystallization at high $T_c$. One of the authors (Hikosaka) showed that the $l$ of the isolated mother lamellae increased linearly with crystallization time ($t$) (Figure 19), i.e.,

$$l = l^* + 2Ut \quad (10)$$

where $U$ is the lamellar thickening growth rate. On
the other hand, it is well-known that $I$ of stacked lamellae are given by

$$I = I^s + W \log(t - c)$$

(11)

where $W$ is the lamellar thickening rate and $c$ is a constant. $U$ is much larger than $W$.

The forming process of stacked lamellae can be explained as follows. At first, an isolated mother lamella is formed in the melt. When the end surface makes contact with the melt, significant thickening growth occurs and thick lamellae are formed. Lateral growth and thickening growth of mother lamellae occurs simultaneously. After that, overgrowth starts and new daughter lamellae stack on the mother lamella through the screw dislocation, cilia, or loop on the fold surface. When a lamella is sandwiched by other lamellae, i.e., its end surface is restricted by other lamellae, it thickens with a rather slow thickening rate $W$. Thus, thick and thin lamellae are formed.

4.3. Test of the Assumption of the Hoffman–Weeks Plot. Figure 20 illustrates the correspondence of the Gibbs–Thomson plot and the Hoffman–Weeks plot when eq 2a is satisfied. The horizontal axes indicate $\Delta T$ and $I^{-1}$. It is obvious that the both plots are equivalent and give the same $T_m^0$ under the condition of eq 2a.

In this section, one of the assumptions of the Hoffman–Weeks equation (eq 3a), $I \propto 1/\Delta T$ (eq 2a), was tested. The plots of $I$ vs $1/\Delta T$ of typical polymers, such as iPP and PE, are shown in Figure 21.

(a) iPP. The approximated line of $I$ of iPP was obtained (Figure 21)

$$I = \frac{2220}{\Delta T} - 40 \text{ nm}, \text{ for iPP}$$

(12)

The second term is large and cannot be neglected.
Figure 22 shows the Hoffman–Weeks plot of iPP using our data. $T_m$, $R_2'$ obtained by the Hoffman–Weeks plot ($T_m$, $R_2'$\textsubscript{HW}) was 17.1 °C higher than the correct $T_m$, $R_2'$\textsubscript{OM} as

$$T_m$, $R_2'$\textsubscript{HW} = 186.1 °C$$

Thus, the Hoffman–Weeks plot of iPP cannot work well.

(b) PE. In the case of PE

$$l = \frac{300}{\Delta T} + 3 \text{ nm, for PE}$$

was reported (Figure 21).\textsuperscript{41} Therefore, the second term can be roughly neglected

$$l = \frac{300}{\Delta T} + \frac{1}{\Delta T} (\text{nm})$$

This means that eq 2a is nearly satisfied. Therefore, in the case of PE, the Hoffman–Weeks plot works.\textsuperscript{2,23,24}

5. Conclusion

(1) The rigorous Gibbs–Thomson plot was obtained by using the direct correlation between $T_{m_{\text{max}}}$ and $l_{\text{max}}$. An optical microscope and TEM were used for observations of $T_{m_{\text{max}}}$ and $l_{\text{max}}$, respectively. The effects of the “melting kinetics” and lamellar thickening were omitted from $T_m$ by observing the isothermal melting at $\beta = 0$ K/min and observing thick lamellae larger than 20 nm, respectively.

(2) The rigorous $T_{m_{\text{max}}}$ of iPP ($\text{MMMM}$) = 99.6%, $M_n$ = 64 x 10$^3$) was obtained to be 186.1 °C.

(3) The $T_m^{0}$ obtained by using the convenient Gibbs–Thomson plot in part 1 of this series was similar to that obtained by using the rigorous one. Therefore, the
validity of the convenient Gibbs–Thomson plot was confirmed. The method by means of DSC is easy and useful as a practical one.

(4) It was shown that the Hoffman–Weeks plot is correct only when \( l \approx 1/\Delta T \) is satisfied. In the case of iPP, \( l \approx 1/\Delta T \) is not satisfied, and so the Hoffman–Weeks plot cannot work well.

(5) Breaks in differential coefficients of \( T_m \) and \( l \) against \( T_c \) were observed at \( T_{\alpha_2 - \alpha_2} = 159^\circ \text{C} \) by means of an optical microscope and TEM, respectively. Therefore, the existence of mobile phase of iPP, the \( \alpha_2 \) phase, and the solid-to-solid transition (the \( \alpha_2 - \alpha_2' \) transition) were confirmed again.

(6) The double melting endotherm of DSC corresponded to a bimodal distribution of lamellar thickness. The broad distribution of \( l \) was explained by the mechanism of lamellar thickening growth of isolated mother lamellae and lamellar thickening of stacked daughter lamellae.

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References and Notes

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