



Memory effect of locally ordered α -phase in the melting and phase transformation behavior of β -isotactic polypropylene

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Abstract

Structural changes in β -isotactic polypropylene (β -iPP) during the heating were studied by means of differential scanning calorimetry and real-time in situ X-ray diffraction using a synchrotron source. Crystalline phase transformation and the memory effect caused by residual nuclei of α -iPP were observed during the heating of β -iPP. The memory effect observed in β -iPP during heating and crystallization is believed to be due to the existence of locally ordered α -form in the melt. The effect of local α -form order was probed by studying the behavior under heating of samples with a range of thermal histories. Samples were heated above the equilibrium melting temperature of iPP to remove all residual local order and the memory effect associated with this local order. The samples crystallized isothermally at different temperatures exhibited a significantly different melting and phase transformation behavior during heating. β -iPP is found to be an excellent material for the study of polymorphism, phase transformations, and characteristic memory effects in semicrystalline polymers.

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1. Introduction

The phase transformation from metastable β -phase to stable α -phase is a characteristic feature of β -isotactic polypropylene (β -iPP) and has been extensively studied [1–5]. Since the first report on the phase transformation in β -iPP by Padden and Keith [1], the structural changes and memory effects involved in the transformation have been widely studied [6–9]. However, these phenomena are still under debate. Recently, we investigated the melting memory effect of β -iPP during the crystallization process by means of real-time in situ WAXD experiments by using synchrotron radiation. In that study we proposed a model, which attributed the phase transformation and melting memory effect in β -iPP to the presence of locally ordered α -form in the amorphous melt [10]. Although a few studies have considered the memory effect [6], it remains unclear how the subtleties of the molecular architecture in the chain influence the memory effect. Based on the results of past

research, we assume that some local order of α -form exists in the melt above the usual melt temperature of iPP (i.e. 200 °C), and this local order post-crystallizes from the melt during crystallization. The α -form crystal (α') formed by this process induces the phase transformation observed while reheating the sample. This crystalline memory during heating is termed the melting memory. This effect is added onto the driving force because of the relative thermodynamic stability of the α -form with respect to the β -form. It is worth emphasizing that the phase transformation in the melt occurs via recrystallization during the heating procedure, whereas the phase transformation in the solid state occurs through mechanical deformation.

The newly formed α -form crystals (α' -form) are considered to have a low melting point, and they are thermodynamically less stable compared to the original α -form and the α -form formed by the recrystallization as described in this study. It was clearly explained in our previous paper that these were post-crystallized during the cooling process and exhibited a clear $\alpha(110)$ peak prior to $\beta(300)$ characteristic peak in WAXD pattern [10]. This

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post-crystallized α' -form takes on an active role and is coupled with the thermodynamic instability of β -form during the phase transformation in the heating process.

In the present work we investigate the effect of thermal history on the melting and phase transformation behavior in β -iPP under different thermal environments. The sample was heated above the equilibrium melting temperature of iPP to remove residual α -nuclei. The experiments considered the samples crystallized under controlled cooling and/or by quenching. Differential scanning calorimetry and in situ wide-angle X-ray diffraction were used to probe the effect of the heating rate and the memory effect of local order in the melt.

2. Experimental

2.1. Materials and sample preparation

The isotactic polypropylene, Daelim Poly PP, was procured from Daelim Co. Ltd, Korea, and the β -nucleating agent, NJSTAR, was obtained from New Japan Co. Ltd, Japan. The materials were used as received. The β -iPP sample was prepared in a Brabender batch mixer by adding 0.2 wt% β -nucleating agent to the iPP melt, mixing for 3 min at 220 °C and 75 rpm to homogenize the mixture. The entire experiment was carried out under a nitrogen atmosphere.

2.2. Characterization

Isothermally crystallized β -iPP samples were prepared by melting the sample at 200 °C for 10 min to obtain a uniform melt state, after which it was crystallized at the desired temperature. The samples were crystallized at a range of temperatures (e.g. 60, 80 and 100 °C), where the crystallization time at each temperature was chosen so as to attain an equal amount of crystallinity. The degree of crystallinity in the sample was estimated from the heat of fusion determined by DSC at the scanning rate of 10 °C/min.

DSC measurements were carried out under a nitrogen atmosphere on a Perkin–Elmer DSC-7. Samples were heated to 200 or 250 °C at heating rates of 3, 10 or 20 °C/min and cooled from the melt to 50 °C at the rate of 10 or 160 °C/min. The crystallized samples were reheated at the rate of 3 or 10 °C/min. The second heating thermogram was used to observe the phase transformation behavior in the sample.

Wide-angle X-ray scattering experiments were conducted using a synchrotron X-ray radiation source (4C2 beam line, wavelength 1.598 Å) under static mode at the Pohang Accelerator Laboratory, Korea. The WAXD pattern was taken in situ every 5 s during melting and crystallization, which allowed us to monitor the time dependent structural modifications in the non-equilibrium state. The heating rates used in these experiments were the same as those cited above for the DSC experiments. The scattering

intensity was corrected by subtracting the background intensity. The relative amount of β -modification in the sample was estimated from the K -value of the following equation [2]

$$K = I_{(300)\beta} / (I_{(300)\beta} + I_{(110)\alpha} + I_{(040)\alpha} + I_{(130)\alpha}) \quad (1)$$

where $I_{(110)}$, $I_{(040)}$, and $I_{(130)}$ are the intensities of the strong equatorial α -form peaks attributed to the (110), (040) and (130) planes located at $2\theta = 14.2^\circ$, 17° and 18.8° , respectively, and $I_{(300)}$ is the peak intensity due to the (300) plane in the β -form located at $2\theta = 16.2^\circ$. The K -value is zero in the absence of the β -form and unity if only the β -form is present. The conventional WAXD pattern for β -iPP shows the sample to be 91% β -form.

3. Results and discussion

3.1. Thermal analysis of β -iPP by differential scanning calorimetry

3.1.1. Melting characteristics and phase transformation behavior

Fig. 1 shows the DSC thermograms measured during the first heating of the original sample, which was prepared in a batch mixer and air-cooled to room temperature, whereas Fig. 1(b) shows thermograms measured during the subsequent heating of the crystallized β -iPP sample. These thermograms clearly show the melting characteristics of β -iPP and the effect of thermal history on the sample. The sample exhibits simultaneous melting and recrystallization phenomena while heating at low rates, particularly in the recooled sample [3,11]. The phase transformation from metastable β -form to stable α -form occurs only by recrystallization during the heating procedure. This behavior is essentially due to the thermodynamic instability of the β -form. The significance of the present study lies in its evaluation of the phase transformation behavior in semi-crystalline polymers, in which both the thermodynamically stable and unstable phases are present. β -iPP is an excellent model polymer for the study of phase stability and phase transformation.

When the sample is subjected to the first heating at the rate of 20 °C/min (Fig. 1(a)—(1)), the thermogram shows two separate broad peaks corresponding to the melting of the β -form and α -form. When the sample is heated at 10 °C/min (Fig. 1(a)—(2)), however, the thermogram exhibits sharp peaks at 146 and 165 °C/min for the melting of the β -form and α -form, respectively, and a small endotherm at around 151 °C. The endothermic peak is caused by the melting of less stable α' -form crystals that had formed during the initial stages of the heating process via $\beta\alpha$ -recrystallization within the β -phase. The small exothermic peak at 153 °C is caused by the recrystallization of newly formed α' -form into a stable α -form via $\alpha\alpha'$ -recrystallization. When the sample is slowly heated at 3 °C/min (Fig. 1(a)—(3)), a remarkably different melting

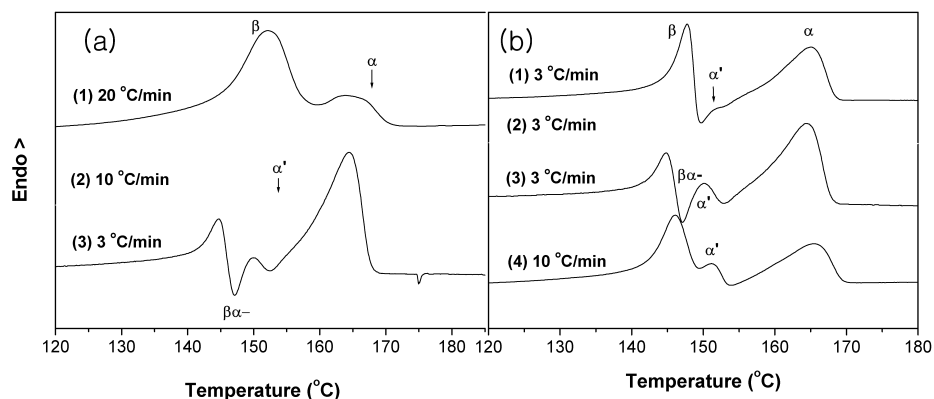


Fig. 1. DSC heating thermograms measured at a range of heating rates for β -iPP samples with different thermal histories. (a) First heating thermograms of original sample (1) 20 °C/min, (2) 10 °C/min and (3) 3 °C/min. (b) Second heating thermograms of crystallized samples: (1) 3 °C/min (crystallized from 200 °C, -10 °C/min); (2) 3 °C/min (crystallized from 250 °C, -10 °C/min); (3) 3 °C/min (quenched from 250 °C, -160 °C/min) and (4) 10 °C/min (quenched from 250 °C, -160 °C/min).

behavior is observed. In this case, the melting of the β -form occurs at 145 °C followed by an exothermic peak at around 147 °C. This recrystallization peak is caused by the phase transformation of metastable β -form to stable α -form, while the endotherm at around 150 °C corresponds to the melting of newly formed α' crystals. These two processes are superimposed in the range 147–150 °C. Finally, the melting of the α -phase occurs at around 165 °C. The dependence of the DSC peak temperatures on the heating rate is due to the kinetic and morphological effects associated with a given thermal history.

Fig. 1(b) shows the second heating thermograms measured from the samples crystallized under a range of conditions. The thermograms clearly show the effect of thermal pre-history on the memory effect and its influence on the phase transformation. On reheating at 3 °C/min the sample crystallized by cooling from 200 °C at -10 °C/min (Fig. 1(b)—(1)), the thermogram clearly demonstrated the phase transformation from $\beta \rightarrow \alpha$ -form via melting and recrystallization. The first melting peak occurred at around 148 °C, corresponding to the melting of the β -form, and was followed by the recrystallization peak at around 150 °C. The second melting peak originates from the summation of the melting of newly formed α' -form and the originally existing α -form crystals within the β -phase. These processes are superimposed in the thermogram, and they occur only if the

sample was cooled below its critical cooling temperature prior to melting. It is worth emphasizing that, in the temperature range at which the phase transformation takes place, β -iPP is in a partially molten state and β -phase behaves as a super cooled liquid for α -form and tends to recrystallize into the stable α -form. This is a general trend in the melting behavior of β -iPP, which possesses the crystalline memory effect because of the presence of residual local α -form order in the amorphous melt [10].

3.1.2. Effect of equilibrium melting temperature

To destroy residual crystal nuclei, the samples were heated above the equilibrium melting temperature of iPP (T_m°) to create a fully isotropic amorphous state. When the sample is cooled from this state, the β -nucleating agent can efficiently seed β -modification because of the absence of α -form nuclei. Fig. 1(b)—(2) shows the heating thermogram of the sample crystallized from 250 °C under controlled cooling (ca. 10 °C/min). The heating thermogram for this sample is basically the same as that in Fig. 1(b)—(1). We also measured heating thermograms for the samples prepared by rapid quenching (160 °C/min) of the melt at 250 °C. The quenched samples were heated at the rate of ca. 3 or 10 °C/min, giving the thermograms shown in Fig. 1(b)—(3) and (4). Surprisingly, these thermograms, which were obtained from samples originally heated to above T_m° , are

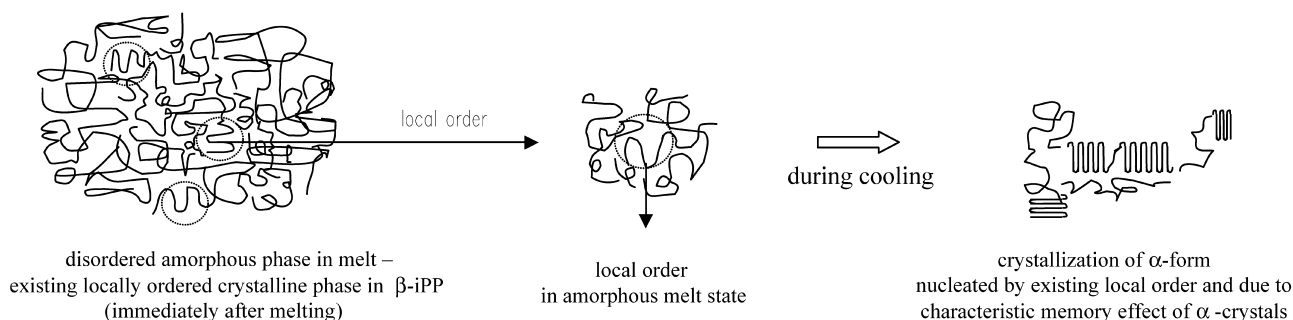


Fig. 2. Schematic representation of the locally ordered α -phase nuclei in the amorphous melt of β -iPP.

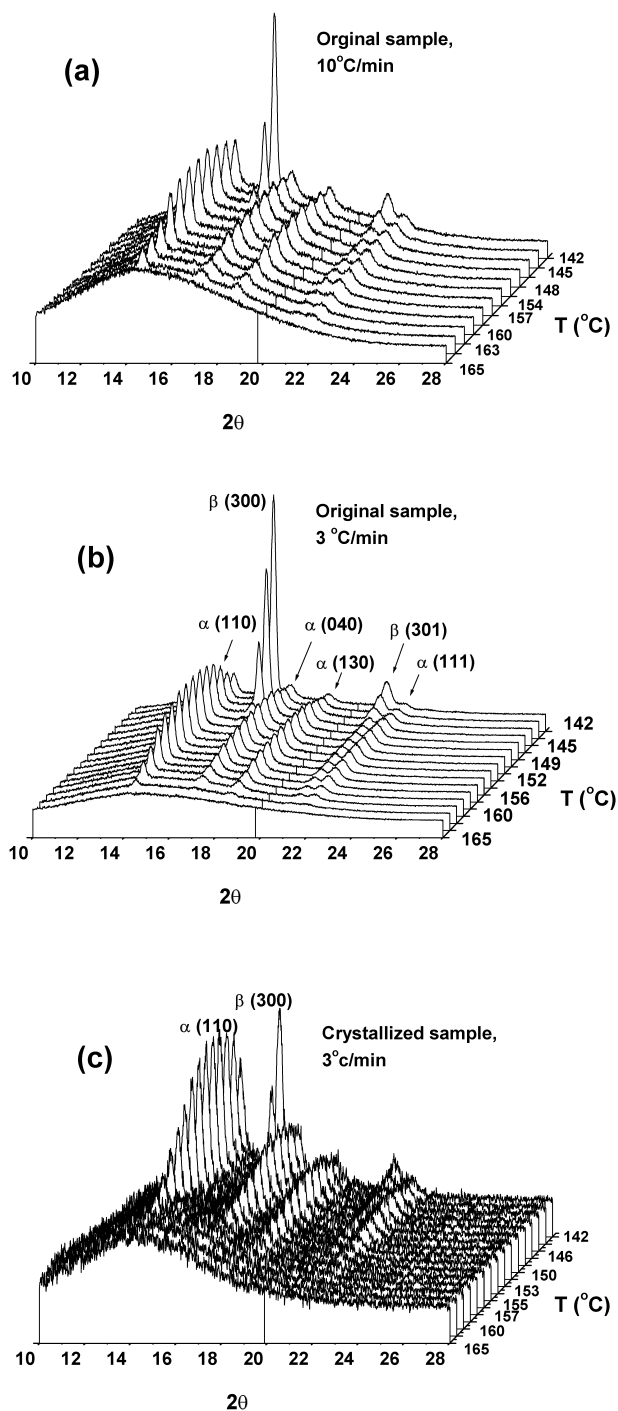


Fig. 3. WAXD pattern profile for the β -iPP sample during heating at different rates: (a) 10 °C/min, (b) 3 °C/min for the original sample and (c) 3 °C/min for the sample crystallized by cooling from 200 °C at -10 °C/min.

found to be similar to the corresponding thermograms from the first heating shown in Fig. 1(a)–(2) and (3).

3.2. Local order and its memory effect

The samples in the amorphous melt state above the melt temperature of β -iPP contained evenly dispersed

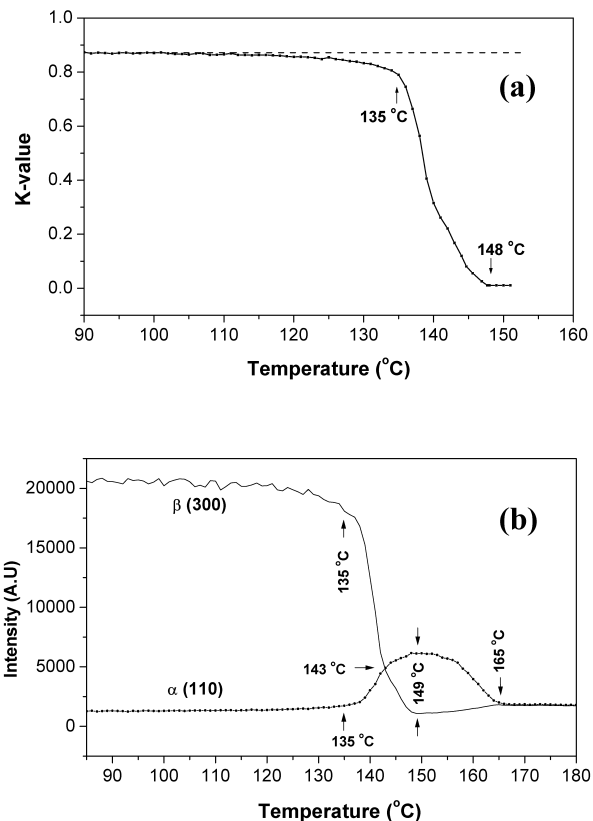


Fig. 4. (a) K -value as a function of temperature during the melting of β -iPP. (b) WAXD peak intensities of the $\beta(300)$ and $\alpha(110)$ plane peaks as a function of temperature during the melting procedure.

β -nucleating agent, and they did not contain residual α -nuclei. Hence, the controlled cooling of this amorphous state leads to complete crystallization into the β -form, as evidenced by the appearance of a single exotherm in the crystallization thermogram. When this crystallized sample is reheated, however, the β -iPP exhibits a behavior typical of simultaneous melting and recrystallization. This phenomenon is unexpected for the fully crystallized β -iPP. The phase transformation behavior observed while reheating suggests the existence of residual α -nuclei within the β -phase [9,10]. Fig. 2 shows a schematic representation of the domains of locally ordered α -phase in the amorphous state immediately after melting. The phase transformation process occurs in spite of the presence of β -nucleating agent owing mainly to the structural and thermodynamic instability of the β -phase, which exhibits a tendency to recrystallize into a thermodynamically more stable α -phase. A similar conclusion was drawn from the study of the annealing and melting behavior of β -iPP [12]. Thus, the evolution of simultaneous melting and recrystallization behavior while heating involves the melting memory effect of β -iPP, and this phenomenon is made possible by the existence of locally ordered α -form in the melt.

A number of mechanisms have been reported for the formation of α -form nuclei within β -iPP [3,9,13,14,15]. First, α -nuclei can form within β -spherulites on cooling

below the critical cooling temperature (i.e. 100–105 °C). The formation of α -nuclei within β -spherulites is also observed at around 166–170 °C while being heated, which is attributed to a high temperature β – α transition or the production of α -nuclei on partial melting of the β -phase near $T_m(\beta)$ (ca. 148 °C). This corresponds to true α -self-nucleation, which would be active if the final temperature never exceeded 157 °C [13]. The α -form nuclei could be produced more profusely within the β -spherulites than in α -spherulites, and thermal stabilization of α -nuclei occurs during the partial melting of β -phase spherulites [14,15]. As per our hypothesis outlined above, α -nuclei can form because of the characteristic memory effect of its stereo regularity induced by the existence of some local α -form order even in the isotropic melt stage, which leads to self-nucleation of α -form within the β -phase during crystallization as shown in Fig. 2. As we have shown in our previous report [10], the residual local order can be destroyed, and consequently, a high percentage of the pure and stable β -form can be obtained by holding the sample at lower melt temperatures for longer hold times, or at higher melt temperatures for shorter hold times. However, complete removal of residual α -form from the β -phase is not an easy task, because the instability of the β -phase encourages the formation of α -form in addition to the effect of the α -form hidden within the β -spherulites. This is evidenced in all existing reports by the observation of a small hump characteristic of an α -plane in the XRD pattern of fully crystallized β -iPP. This supports our hypothesis regarding the lingering presence of the memory of α -form nuclei even after heating the sample above its equilibrium melting temperature and applying various techniques to control its nucleation efficiency.

3.3. Synchrotron in situ X-ray diffraction studies

Real-time in situ WAXD studies using a synchrotron source were carried out to study the structural characteristics and crystalline transformations in β -iPP during heating and cooling [10]. Initially, the sample exhibits a full β -modification ($K = 0.91$) with a peak characteristic of the $\beta(300)$ plane. The diffraction pattern profile was recorded in situ over a time span of 5 s for each pattern.

3.3.1. Melting and phase transformation behavior

Fig. 3(a) shows the X-ray pattern profile for the heating of the original β -iPP sample at 10 °C/min. The profile shows that the maximum peak intensity at $2\theta = 16.2^\circ$, characteristic of the $\beta(300)$ plane, decreases with increasing temperature. The pattern at 142 °C exhibits a very high intensity peak because of the $\beta(300)$ plane and a low intensity peak at $2\theta = 14.2^\circ$, characteristic of the $\alpha(110)$ plane. The $\alpha(110)$ plane peak is present up to 165 °C, the final melt temperature of the α -form. The WAXD pattern profile for the sample heated at 3 °C/min is shown in Fig. 3(b) and is considered in conjunction with the DSC thermogram for the same system shown in

Fig. 1(a)–(3). The rate dependent phase transformation in the β -iPP sample with respect to change in the peak intensity and relative β -content with temperature is reported elsewhere [10].

The relative amount of β -form in β -iPP was quantitatively determined from the K -value (Eq. (1)). The temperature dependence of the K -value during the heating procedure is shown in Fig. 4(a). The K -value is constant ($K = 0.88$) up to 113 °C, and the onset of β -form melting occurs at around 114 °C. Above this temperature the K -value decreases with increasing temperature. Over the temperature range of 135–149 °C, the K -value decreases sharply from 0.79 to 0.01, after which it remains almost constant. This temperature zone, therefore, contains the sharp melting and recrystallization of β -form crystals, as supported by the DSC results (Fig. 1(b)–(1)). It is noteworthy that the K -value does not fall to zero until the final melt temperature. This may be due either to the presence of residual nuclei of β -form crystals in the polymer melt, for which there is no experimental evidence, or to the limitations in the method of calculating the K -value.

The peak intensities of the β -form (300) plane and the α -form (110) plane are plotted against the temperature during the heating process in Fig. 4(b). The β -form peak intensity begins to decrease at around 130 °C, which is followed by a sharp decrease in the region 135–149 °C. It is interesting to note the variation of the peak intensity for the $\alpha(110)$ plane. The onset of the increase in the $\alpha(110)$ plane peak intensity occurs at around 135 °C, the same temperature as the onset of the sharp decrease in the intensity of the $\beta(300)$ plane peak. The increase in the $\alpha(110)$ peak intensity as the temperature is increased beyond 135 °C is due to the transformation of β -form into α -form. The maximum intensity of the $\alpha(110)$ plane peak coincides with the minimum in the $\beta(300)$ plane peak intensity. The first intersection of these two peak intensities, which occurs at approximately 143 °C, can be termed the critical equilibrium transition temperature of the two phases. The intersection of the two peak intensities demonstrates clear evidence that a crystalline phase transformation occurs during the melting of β -iPP. The intensity of the $\alpha(110)$ plane peak reaches the maximum at 149 °C, then, decreases with increasing temperature until it meets the $\beta(300)$ plane peak intensity at 165 °C. This temperature is the same as the peak temperature of the α -form in the DSC study, which indicates that equilibrium was achieved in the melt.

Fig. 3(c) shows the in situ WAXD pattern profile measured during the heating of a sample that had been recooled from the melt state at 200 °C under a controlled cooling rate (–10 °C/min). This thermal history is the same as that used to obtain the DSC curve in Fig. 1(b)–(1). As the temperature increases, the peak intensity due to the $\beta(300)$ plane decreases while the $\alpha(110)$ plane peak intensity increases. The β – α -transition takes place at around 148 °C, as evidenced by the disappearance of the $\beta(300)$ plane peak, and a sharp increase in the α -peak intensity was observed. Although the heating rate is the same, the original

and crystallized samples exhibit different trends with temperature.

3.3.2. Effect of equilibrium melting temperature

Fig. 5(a) shows the WAXD pattern profile for the sample while crystallizing from above its equilibrium melting temperature at the fixed rate of 10 °C/min. Evidence of β -crystals begins to emerge in the pattern at around 119 °C, and the crystallization process is complete at around 105 °C. The final material contained a high proportion of β -modification ($K = 0.93$). To remove the residual α -nuclei,

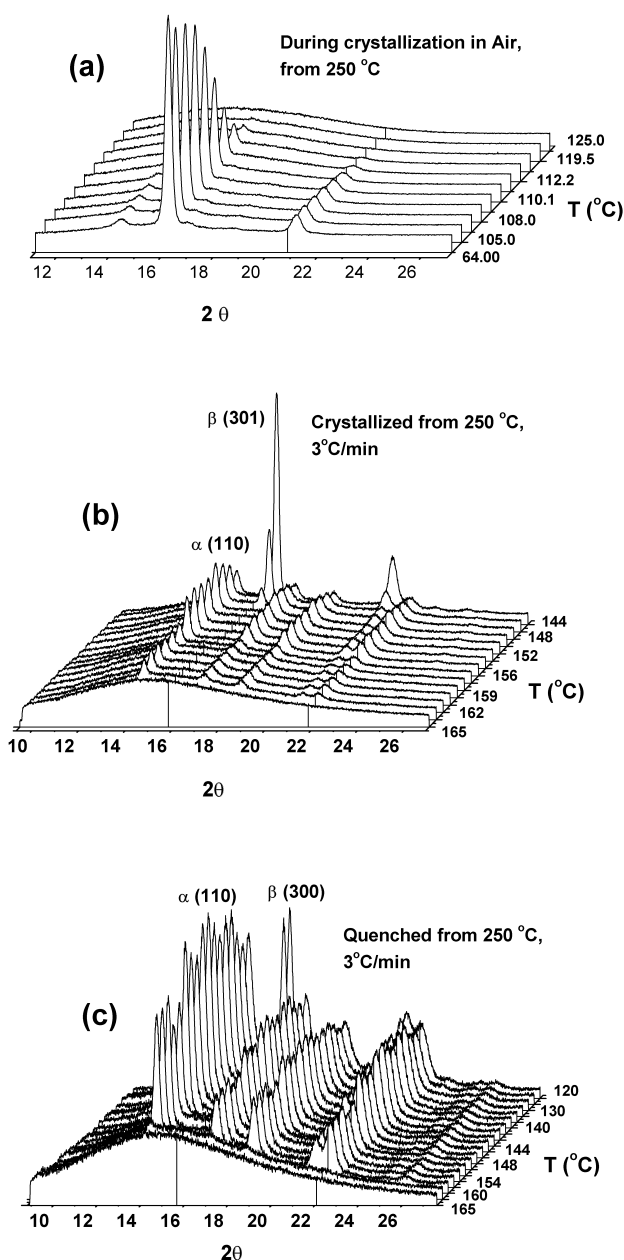


Fig. 5. WAXD pattern profile for the β -iPP samples crystallized from above the equilibrium melting temperature, 250 °C: (a) during crystallization under controlled cooling, -10 °C/min from 250 °C, and (b) 3 °C/min, second heating profile for crystallized sample, -10 °C/min and (c) 3 °C/min, ice water quenched sample from 250 °C/min.

the sample was exposed for 5 min at 250 °C, assuming left over the evenly dispersed β -nucleating agent alone, and the sample was crystallized slowly, and reheated at the rate of 3 °C/min to observe the characteristic memory effect of α -form in the absence of self-nuclei. The in situ WAXD pattern profile measured during the heating process is shown in Fig. 5(b), and the results can correlate with DSC results (Fig. 1(b)–(2)), and it evidences the clear phase transformation in the sample, even in the absence of local order. To reconfirm the results, the sample was quenched in ice water from 250 °C within 1–2 s to suppress the nucleation process and the memory effect of the α -form. Unexpectedly, the WAXD pattern of the quenched sample exhibits peaks characteristic of both the α -form and β -form. Fig. 5(c) shows the in situ WAXD pattern profile that resulted from slow heating (ca. 3 °C/min) of the quenched sample. The profile is similar to that obtained during the heating profile of the crystallized sample.

The results support our concept regarding the existence of locally ordered α -form in these systems and its characteristic memory effect. We conclude that removing the memory effect of the α -form in the β -iPP sample is almost impossible, and that the resulting phase transformation is not only caused by the thermodynamic instability of the β -form but also by the characteristic memory effect of α -form.

3.4. Memory effect and phase transformation in isothermally crystallized samples

Fig. 6 shows the DSC thermograms measured during the heating of samples that had been isothermally crystallized at a range of temperatures ($T_{cr} = 60, 80$ and 100 °C). Regardless of crystallization temperature, the samples all show of crystallinity around 80%. Fig. 6(a) and (b) shows the thermograms measured during the first heating of the samples at 3 and 10 °C/min, respectively.

When heated at 3 °C/min, the samples crystallized at $T_{cr} = 80$ and 100 °C exhibit a trend similar to that of the original sample (Fig. 1(a)–(3)), while the sample crystallized at $T_{cr} = 60$ °C shows a different behavior. The samples crystallized at 80 and 100 °C (Fig. 6(a)–(2) and (3)) show the melting peak of the β -form at around 145 °C, the $\beta\alpha$ -recrystallization peak at around 148 °C, and the melting of newly formed α' -crystals at 150 °C. It is worth noting that alongside the melting of the α' -form at 150 °C, there appears a small exothermic peak at around 153 °C, which corresponds to the recrystallization of newly formed α' -form via $\alpha\alpha'$ -recrystallization. This $\alpha\alpha'$ -recrystallization is clearly visible in the sample crystallized at 100 °C, whereas the sample crystallized at 60 °C exhibits only the peak associated with $\beta\alpha$ -recrystallization.

Fig. 6(b) shows the heating thermograms measured while heating at 10 °C/min. These thermograms differ from those measured for similar samples heated at 3 °C/min. While there is no change in the peak temperature of the original β -form crystals, a shoulder appears in the melting peak of

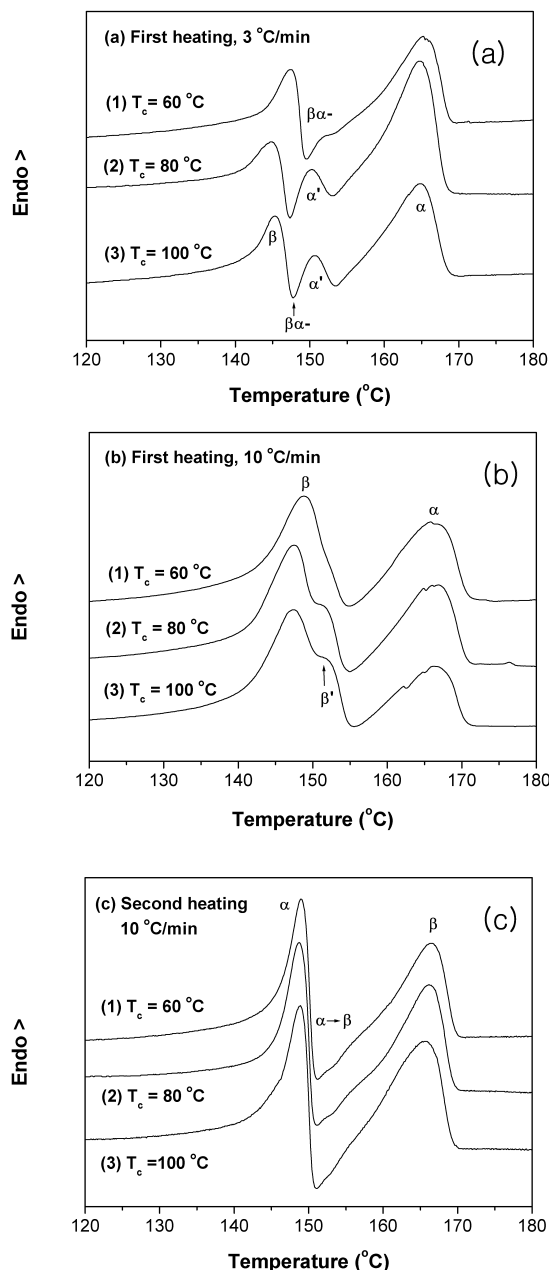


Fig. 6. DSC heating thermograms of the isothermally crystallized β -iPP samples at various temperatures: (a) first heating, (3 °C/min), (b) first heating (10 °C/min), and (c) second heating (3 °C/min).

the β -phase. This shoulder represents the presence of newly formed β' -phase via $\beta\beta'$ -recrystallization towards the local stabilization of β -phase during the melting process prior to $\beta\alpha$ -recrystallization. This phenomenon, which was not observed in the sample crystallized at 60 °C, is attributed to morphological effects during the isothermal crystallization process. Fig. 6(c) shows the second heating thermograms of the sample recooled at a rate of 3 °C/min. These thermograms exhibit a clear phase transformation via recrystallization similar to that observed for the original β -iPP sample (Fig. 1(b)).

4. Conclusions

In this study we used differential scanning calorimetry and in situ wide-angle X-ray diffraction to investigate two phenomena: (1) the crystalline phase transformation from metastable β -form to stable α -form in β -iPP, and (2) the memory effect caused by residual domains of locally ordered α -form within the β -phase and the influence of this effect on melting behavior. The marked memory effect in β -iPP observed during crystallization studies was explained on the basis of the existence of locally ordered α -form in the amorphous melt immediately after melting. The melting behavior of the samples with a range of thermal histories was studied. The results showed that, irrespective of the conditions adopted, the characteristic memory effect of α -form within the β -phase cannot be nullified. We found that the phase transformation behavior in β -iPP is determined by the presence of local order, the strong characteristic memory effect of the α -form, and the thermodynamic instability of the β -phase with respect to the α -phase.

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