

Origin of Double Melting Peaks of α -Form Isotactic Polypropylene: Recrystallization and Lamellar Thickness Hierarchy

Jinhai Yang

Department of Polymer Science and High Performance Materials, University of Southern Mississippi, Hattiesburg, Mississippi

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ABSTRACT: Isotactic polypropylene (iPP) shows both double melting peaks and single melting peak depending on cooling rates and crystallization temperatures. This manuscript reviews the related studies. These melting behaviors can be explained based on two types of spherulite structures. Type I Spherulites have predominant cross-hatched lamellae with same thickness in both tangential and radial directions. They form at low crystallization temperatures and show one melting peak at fast heating rates, while double melting peaks at low heating rates because

of recrystallization. Type II Spherulites have thinner cross-hatched lamellae in center and thicker radial lamellae in peripheral part. They form at high crystallization temperatures and show double melting peaks that can not be eliminated by fast heating rates. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 1520–1526, 2010

Key words: polypropylene; double melting peak; spherulite; crystallization; recrystallization; cross-hatched lamellae

INTRODUCTION

Isotactic polypropylene shows a very interesting double melting peak behavior, while X-ray diffraction shows that only α -form crystal exists. This behavior depends on crystallization temperatures, cooling rates and DSC heating rates.^{1–9}

Based on the studies, the isothermal crystallization temperatures can be divided into four regions: region I (below 122°C), region II (from 122 to 133°C), region III (from 133 to 152°C), and region IV (above 152°C). The ranges may be different dependent on polypropylene molecular weights and isotacticities. IPP shows double melting peaks in region I and III, while one melting peak in region II and IV. IPP also shows double melting peaks in nonisothermal crystallization with fast cooling rates.^{1,6,10,11}

The melting behavior of iPP also depends on heating rates in DSC tests. The double melting peaks can be divided into two types based on their response to heating rates. The high temperature peak of Type I double melting peaks decreases and disappears at last with increase of heating rates [as shown in Fig. 1(a)]. Usually 40°C/min is a high heating rate enough to eliminate the high temperature peak. These double melting peaks form in isothermal crys-

tallization region I^{2,12,13} and nonisothermal crystallization at fast cooling rates.^{1,10} The Type II double melting peaks can not be eliminated by fast heating rates. Figure 1(b) shows their melting behavior dependency on heating rates. They form in isothermal crystallization at region III.^{9,12–15}

At low heating rates, the low temperature peak of the double melting peaks decreases and gradually disappears.^{1,9,13–15} It was also reported that at low heating rates, the single melting peak of iPP crystallizing at region II and nonisothermally crystallizing at slow cooling rates can become double melting peaks with a new peak occurring at high temperature.^{9,11}

Two questions should be answered to understand the origin of double melting peaks. What structures are related to the two melting peaks respectively? Do the structures form during the crystallization or during the DSC heating? In this article, we will answer the two questions based on the reported results by previous publications.

When do the double melting peak structures form?

Increasing DSC heating rates can decrease sample annealing and the melting behavior trends to show the real structures forming in crystallization. Figure 1(a) shows that with the increase of heating rates, the high temperature peak of the Type I double melting peaks gradually disappears, and its peak

Correspondence to: J. Yang (shinningsea@gmail.com).

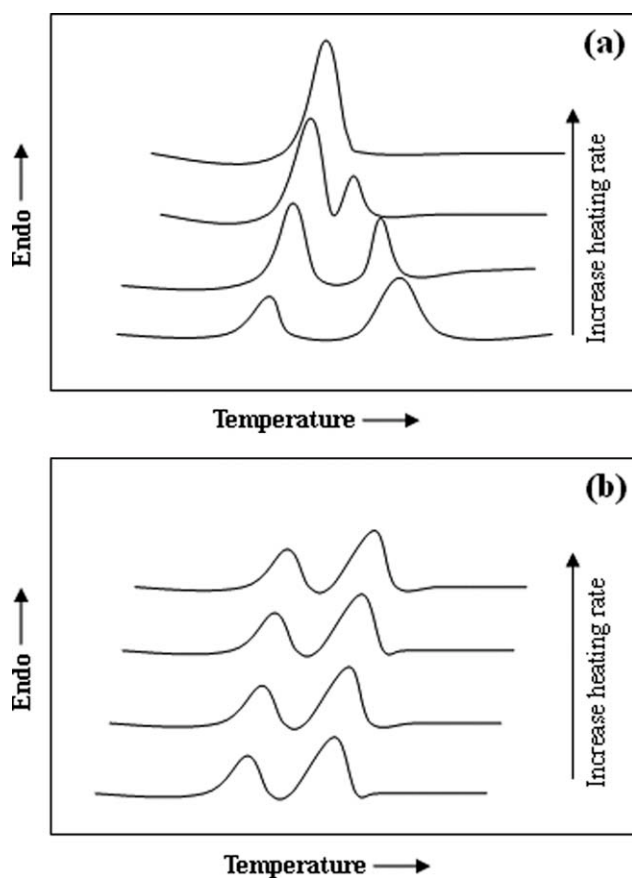


Figure 1 Sketch of heating rate effect on melting behavior of iPP: (a) Type I double melting peaks; (b) Type II double melting peaks.

temperature gradually decreases. While both the integrated peak area and temperature of the low temperature peak increase.^{1–3,10,11,13,16} These studies indicate that the high temperature peak of the Type I double melting peaks forms in the DSC heating. The original samples only have one crystal structure related to the low temperature melting peak.

Figure 1(b) shows that increasing heating rates does not eliminate the Type II double melting peaks. Both the two peak temperatures increase with heating rates because of superheating. The integrated area ratio of the two peaks does not change.^{9,13,14} This indicates that there are two kinds of crystal structures in the original samples.

Next we will discuss three crystal structures: structures leading to Type II double melting peaks; original structure showing Type I double melting peaks; new formed crystal structure in DSC annealing.

Crystal structures showing type II double melting peaks

Three structures were proposed to explain the double melting peaks: double model molecular struc-

tures, two kinds of crystal unit structures, and two groups of lamellar thicknesses.

Double model molecular structures

The melting behavior of iPP depends on both molecular weight^{17–20} and isotacticity.^{19–24} At the same crystallization conditions, the melting temperatures increase with both molecular weight^{19,20} and isotacticity.^{19–23} Isotacticity shows more obvious effect on the melting temperature than molecular weight.^{19,20} Kamide and Yamaguchi¹⁸ reported blends of two polypropylenes with different melting temperatures showed double melting peaks. Thus double model molecular structures can lead to double melting peaks. However, it was reported that polypropylene with very narrow molecular weight distribution and high isotacticity also showed double melting peaks.^{9,15,23–25} In this manuscript, most of the reported double melting peaks were not attributed to double model molecular structures.

Two kinds of crystal unit structure

iPP α form crystal was first reported by Natta and Corradini,²⁶ which was monoclinic type and belonged to C2/c space group. Mencik,²⁷ Hikosaka and Seto²⁸ reported a new diffraction peak from $\bar{2}31/\bar{1}61$ plane occurred at high temperature annealing. They suggested that the reflection was from another α crystal modification ($\alpha 2$ form), which was also monoclinic crystal but belonged to P2₁/c space group. The α crystal modification reported by Natta and Corradini was called $\alpha 1$ form. Crystallization temperatures were reported to affect α crystal modification. At low crystallization temperatures (approximately below 125°C), only $\alpha 1$ crystal formed, while at higher crystallization temperatures, $\alpha 2$ crystal modification began to occur.^{29,30} Some articles reported that $\alpha 2$ crystal could also form when the samples crystallizing at low temperatures were annealed at high temperatures.^{11,12,28,31}

Now the question is whether Type II double melting peaks are attributed to the two kinds of α form crystals. Rosa et al.³⁰ reported that when crystallizing below 125°C iPP only formed $\alpha 1$ crystal. Above 125°C, $\alpha 2$ crystal began to occur. However, iPP showed only one melting peak at high heating rates when crystallizing at temperatures up to 135°C. When crystallizing at region IV, iPP formed $\alpha 2$ crystal and showed only one melting peak. It was found that the melting temperatures of both $\alpha 1$ and $\alpha 2$ crystals versus crystallization temperatures fitted into one master curve. These results supported that both $\alpha 1$ and $\alpha 2$ crystal had the same melting temperatures. Thus two α crystal forms did not lead to double melting peaks.

Two groups of lamellar thickness

iPP showed epitaxial crystallization behavior in both solution^{32,33} and melt^{24,34–37} with a subsidiary (or daughter) lamella attaching to the primary (or mother) lamella by an 80 degree angle.^{34,38} The primary lamellae were along the spherulite radial direction and were also called radial lamellae. The subsidiary lamellae were along the tangential direction and were also called tangential lamellae. This epitaxial crystallization behavior also led to positive and negative spherulite phenomenon.^{39,40}

Weng et al.³⁷ studied the iPP structure crystallizing at 145°C with TEM. The iPP showed Type II double melting peaks. Two distinguishing lamellar morphologies were observed along the spherulite growth direction. In the spherulite center was a cross-hatched structure. To outside of the spherulites, the cross-hatched structure gradually gave way to a predominant radial lamellar structure with thinner tangential lamellae between them. Both radial and tangential lamellae in the cross-hatched structure had equal thickness. The radial lamellae outside were thicker than the center lamellae. The spherulite structure was shown in Figure 2.

With DSC, Weng et al.³⁷ heated the iPP samples crystallizing at 145°C to a temperature between the double melting peaks, and then quenched the samples. Figure 3 shows the sketch of the DSC curves. TEM showed that both the cross-hatched lamellar structure in spherulite center and the tangential lamellae between the radial lamellae outside of the spherulite disappeared because they were melted and crystallized into fine lamellae in quenching. However, the radial lamellae outside the spherulite survived. This experiment strongly supported that

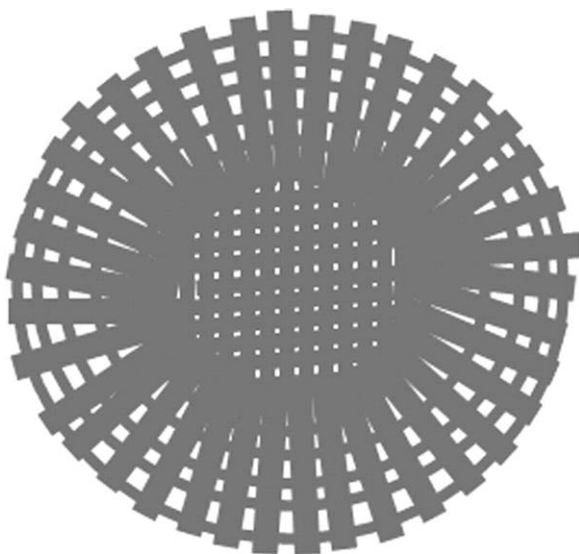


Figure 2 Sketch of spherulite structure that shows double melting peaks.

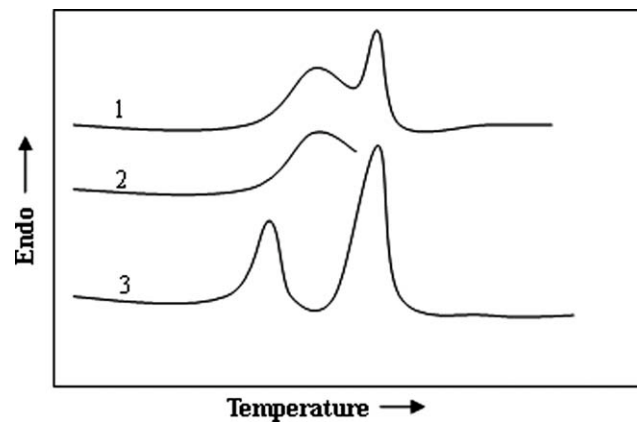


Figure 3 Sketch of DSC heating curves of: (1) iPP crystallized at 145°C for 3 h, (2) heated to between double peaks (3) quenched after partial melting.

the low temperature melting peak was attributed to the melting of the cross-hatched lamellae in the spherulite center and tangential ones outside, while the high temperature melting peak was attributed to the melting of the radial lamellae outside.

This spherulitic structure was also reported by Norton and Keller³⁵ at crystallization temperature (T_c) = 130°C, Olley and Bassett³⁶ at T_c = 130 and 150°C, Binsbergen³⁴ at T_c = 143°C. At lower crystallization temperatures, predominant cross-hatched lamellar structure was reported by Norton and Keller³⁵ at T_c = 116°C, Loos and Petermann⁴¹ at T_c = 90°C. At higher crystallization temperatures, predominant radial lamellar structure was reported by Norton and Keller³⁵ at T_c = 140–148°C, Maiti and Yamada⁷ at T_c = 153–166°C, Yamada^{9,25} at T_c = 153–166°C.

Besides TEM, SAXR studies also showed two groups of lamellar thicknesses in iPP samples crystallizing at region III which showed Type II double melting peaks; and only one group of lamellar thickness in iPP samples crystallizing at region I, II and IV which showed one melting peak or Type I double melting peaks.^{6,23,42}

Based on the morphology studies, Weng et al.³⁷ proposed the following spherulite growth mechanism. At first stage, cross-hatched lamellar structure forms [as shown in Fig. 4(a)], which includes equal thickness lamellae in both directions. At second stage, the cross-hatched lamellar structure gradually gives way to the radial lamellar structure with small amount of tangential lamellae between them [as shown in Fig. 4(b)].

Based on the spherulite growth mechanism, Weng et al.³⁷ proposed three kinds of spherulite structures dependent on the isothermal crystallization temperatures. When iPP crystallizes at both region I and region II, its spherulite sizes are so small that the cross-hatched structure does not get chance to grow

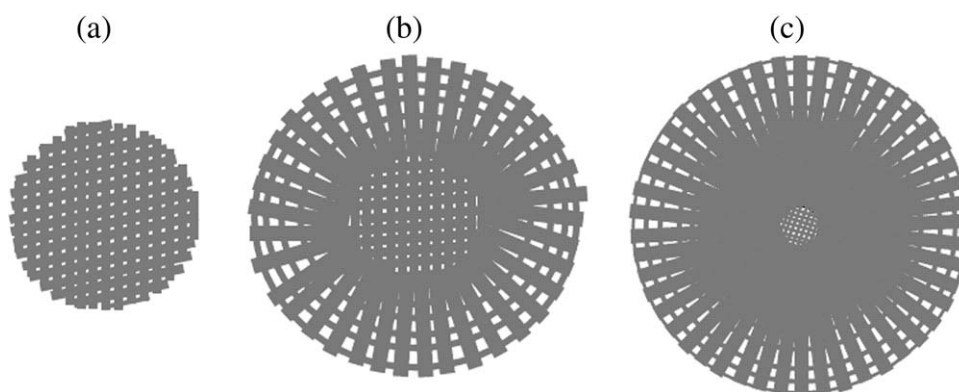


Figure 4 Three different spherulite structures. (a) cross-hatched, (b) cross-hatched lamellae surrounded by radial lamellae, (c) radial lamellae with small cross-hatched core.

into radial lamellar structure. Thus the spherulites compose of predominantly cross-hatched structure with one group of lamellar thickness. When iPP crystallizes at region III, the spherulite sizes are big enough to allow the transition from cross-hatched structure to radial lamellae. Thus the spherulites compose of two groups of lamellar thicknesses and show double melting peaks. When iPP crystallizes at region IV, it may form two possible structures. One possible structure is that the cross-hatched structure still exists but with very low amount considering the large spherulites [as shown in Fig. 4(c)]. In DSC tests, there is only one melting peak because the DSC can not detect the small amount of cross-hatched structure. Another possible structure is that the spherulites compose of only radial lamellae because the cross-hatched structure is suppressed by high temperatures. Some reports^{7,9,25} seem to support the second structure.

Studies by Marco et al.⁸ supported the above mechanism. He compared the melting behaviors of iPP and iPP nucleated by 0.5% of nucleation agents, which isothermally crystallized at various temperatures. When crystallizing between 130 and 142°C, iPP showed double melting peaks. However, the nucleated iPP showed only one melting peak and the peak position was almost equal to the low temperature peak of the double melting peaks of the iPP crystallizing at the same temperatures (as shown in Fig. 5). Based on the above mechanism, when the nucleation agent was added, the spherulite sizes decreased dramatically, thus only cross-hatched lamellae formed.

Studies by Weng et al.³⁷ about iPP self-seeding isothermal crystallization also support this mechanism. In their study, iPP was first melted at 210°C and cooled down to 50°C at 10°C/min. This sample showed double melting peaks because of recrystallization [as shown in Fig. 6(e)]. Then the iPP was heated up to various self-seeding temperatures at 10°C/min, and immediately cooled down to 145°C

at 80°C/min and isothermally crystallizing for a period time. When iPP melt crystallized at 145°C, it showed double melting peak behavior [as shown in Fig. 6(a)]. When self-seeding temperature was 172.2°C, most of the crystals melted and the seed density was very low, so iPP could form big spherulites with both cross-hatched and radial lamellar structures and showed double melting peak behavior [as shown in Fig. 6(b)]. When self-seeding temperature is 171.2°C, seed density increased, and iPP formed smaller spherulites with only small amount of radial lamellar structure. Thus iPP only showed a small peak at high temperature [as shown in Fig. 6(c)]. When self-seeding temperature was 168°C, seed density was very high and iPP could only form very small spherulites with only cross-hatched lamellar structure. Thus iPP only showed one melting peak whose position was almost same with that of the low temperature peak of the double peaks [as shown in Fig. 6(d)]. TEM study showed that only cross-hatched structure was observed when self-seeding temperature was 168°C, and both cross-hatched and radial lamellar structures were

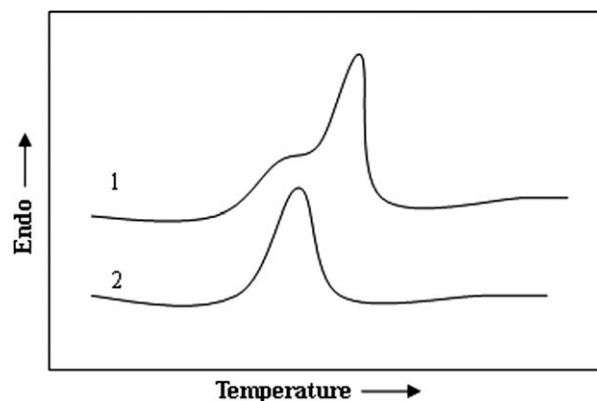


Figure 5 Sketch of DSC curves of: (1) iPP; (2) iPP with 0.5% of nucleation agent isothermally crystallizing at 142°C. The heating rate was 10°C/min.

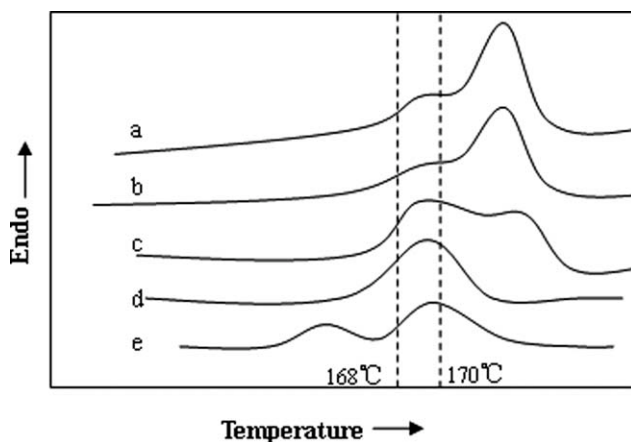


Figure 6 Sketch of DSC curves of iPP isothermally crystallizing at 145°C: (a) without self-seeding; (b) self-seeding at 172.2°C; (c) self-seeding at 171.2°C; (d) self-seeding at 168°C; (e) nonisothermally crystallizing at 10°C/min.

observed when self-seeding temperatures were 171.2 and 172.2°C.

Though the iPP double melting peak phenomena were reasonably explained by the above spherulite growth mechanism, we are still challenged to explain the following phenomenon. Based on the mechanism, radial lamellae begin to occur at outside of the cross-hatched lamellae with increase of crystallization temperatures. Thus, the new melting peak should occur at higher temperature [as shown in Fig. 7(a)]. However, all the report showed that the new formed peak occurred at lower temperature [as shown in Fig. 7(b)].^{2-5,8,14,27,28} These results seem to indicate that the melting temperatures of the cross hatched lamellae formed at higher crystallization temperatures where the radial lamellae begin to occur are lower than those formed at lower crystallization temperatures.

Structures related to type I double melting peaks

The high temperature peak of Type I double melting peaks can be eliminated by increasing heating rates, indicating this peak is formed in the annealing of

DSC heating and the origin sample only has one group of structure related to the low temperature peak. Based on the morphology studies,^{35,37,41} iPP forms cross-hatched lamellar structure at low crystallization temperatures, which composes the same lamellar thickness at both directions as shown in Figure 4(a).

Recrystallization

In DSC heating scanning, after the lamellae begin to melt, the melt can be nucleated by the remained lamellae to form new nuclei. These nuclei then grow into thicker lamellae which melt at higher temperature showing higher temperature melting peak. This process is called recrystallization.

Though iPP crystallizes very slowly at temperatures from 150 to 170°C, however, its crystallization speed can increase dramatically by the remained unmelted crystals, self-seeds. A lot of publications showed that iPP could recrystallize in a short time when annealed at around 160°C. For example, Pae and Sauer⁴³ reported 0.5 min at 160°C, Zhu⁴⁴ reported 1.5 min at 163°C, Kim¹³ reported 5 min at 162.5°C, Marco et al.⁸ reported 5 min at 164°C, Kamide and Yamaguchi¹⁷ reported below 5 min at 162°C and below 10 min at 163.5°C. When heating rates are 1, 5, 10, and 40°C/min, the heating times from 150 to 165°C are 15, 3, 1.5, 0.375 minutes respectively. Thus, at low heating rates, it is possible for iPP melt to recrystallize.

Recrystallization shows two characteristics. First, it is affected by heating rates. Increasing heating rates can decrease recrystallization. For example, iPP crystallizing at region I (below 122°C) shows recrystallization at heating rates less than 20°C/min, but not at 40°C/min. Every sample has a specific heating rate (K_s) below which it shows recrystallization behavior. Second, the specific heating rate decreases with the increase of the crystallization temperatures.¹³

We can use a simple model to explain recrystallization. We define two functions. First one is nucleation time, $\tau(T)$, which is the time to form nuclei at

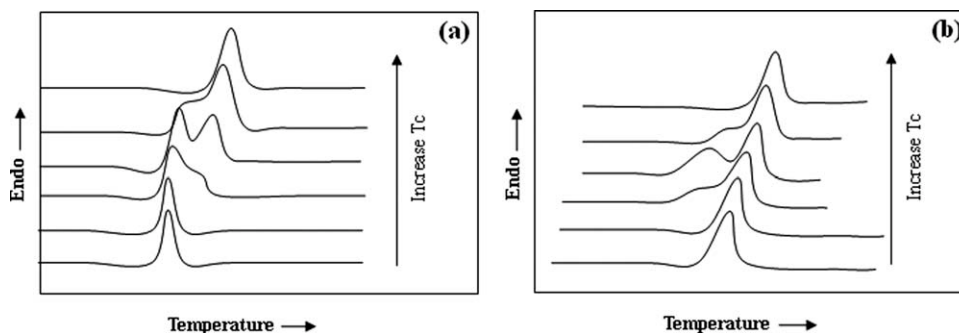


Figure 7 Sketch of DSC heating curves of iPP crystallizing at various temperatures: (a) predicted based on spherulite growth mechanism; (b) experimental results.

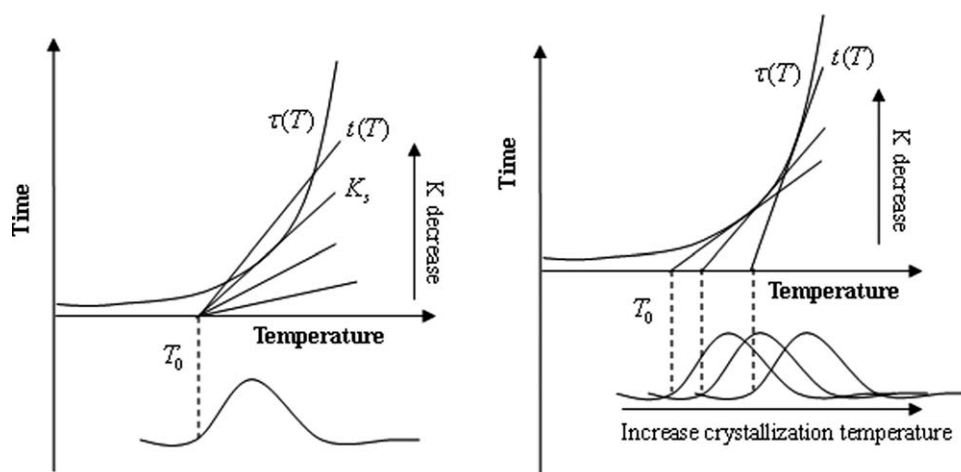


Figure 8 Sketch of relationship between $\tau(T)$ and $t(T)$.

one corresponding temperature. Second one is a simple time function, $t(T)$, which is the time from the crystal melting to the corresponding temperature. It is shown in the following equation,

$$t = (T - T_0)/K$$

where T is the corresponding temperature, T_0 is the temperature where the crystal begins to melt, and K is the heating rate of DSC.

Figure 8(a) shows the curves of both $\tau(T)$ and $t(T)$. From the melting curve, we get the initial melting temperature, T_0 . When DSC heating rates are high, $t(T)$ curve can not meet $\tau(T)$ curve. In these cases, recrystallization can not occur. With the decrease of heating rates, $t(T)$ curve begin to meet $\tau(T)$ curve at heating rate of K_s . In this case, recrystallization begins to happen. It should be mentioned that Figure 8 simplifies the process. The actual K_s should be a little bit higher than the predicted value. Suppose the two curves meet at point (T_1, t_1) , $\tau(T)$ curve tells us that it needs t_1 to initiate the recrystallization at T_1 . However, the melt experiences t_1 at temperatures from T_0 to T_1 . Thus, recrystallization must occur before T_1 or with time less than t_1 .

Figure 8(b) shows that with the increase of crystallization temperatures, the iPP melting peaks will move to high temperatures increasing the initial melting temperature, T_0 and moving the $t(T)$ curve to high temperatures. Thus, at the same heating rate, the recrystallization gradually disappears with the increase of crystallization temperature. Or it needs lower heating rates to recrystallize the iPP crystallized at high temperatures.

CONCLUSION

Melting behaviors of iPP were reviewed in this manuscript. IPP shows complicated double melting

behaviors dependent on its spherulite structures, which are determined by crystallization temperatures. At low crystallization temperatures, iPP forms cross-hatched crystal structure with epitaxially growing lamellae which have the same thickness in both directions. These iPP samples showed only one melting peak at high heating rates, but double melting peaks at low heating rates because of recrystallization. At high crystallization temperatures, iPP forms spherulites with thinner cross-hatched lamellae in center and thicker radial lamellae outside of the spherulites. The double lamellae groups form two melting peaks that can not be eliminated by increasing heating rates.

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