

## ORIGINAL ARTICLE

# Melt memory of a spherulite nucleus formed through a seeding process in the crystal growth of isotactic polystyrene

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The melt memory effect on the crystal growth of isotactic polystyrene is investigated using optical microscopy. After a spherulite is melted at a slightly higher temperature than the melting point and completely disappears, a polymer crystal nucleates and grows at the same position as the original spherulite when the temperature is decreased below the melting point. After the melting–recrystallization processes are repeated by raising and lowering the temperature, the melt memory effect becomes weak. This effect completely disappears at  $\sim 40$  °C above the equilibrium melting point when the melt temperature is gradually increased during the melting–recrystallization processes. The formation of spherulite nuclei is promoted by the seeding process, which consists of the following consecutive procedures: quenching a sample to a temperature below the glass transition temperature and annealing the sample slightly above the glass transition temperature. At the initial stage, the number density of spherulites rapidly decreases with the cumulative melting time. After the initial stage, the number density of spherulites exponentially decays with the cumulative melting time and approaches a finite value. This asymptotic value decreases with the melt temperature.

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## INTRODUCTION

What type of phenomenon is the ‘melt memory effect’ in crystal growth? There have been few reports of this phenomenon for low-molecular weight materials, and it is considered to be peculiar for high-molecular weight materials. Because a polymer molecule is long, it is less mobile than a low-molecular weight molecule in the melt. Therefore, polymer molecules in the melt take a long time to reach thermal equilibrium. In polymer systems, molecular orientations and conformations are not necessarily random, depending on the sample treatment in the melt, even under identical experimental conditions, such as temperature and pressure. Melt memory effects have often been observed in the crystallization of polymer materials and have become one of the major research subjects in polymer science.<sup>1–11</sup> However, little detailed research has been performed regarding the memory of the positions of spherulites. Although there are several discussions of melt memory on the number of spherulite nuclei,<sup>12–14</sup> there is little discussion of the melt memory of spherulite positions. It is empirically well known that a spherulite is formed at the same position as the original spherulite when a polymer is crystallized after the original spherulite is melted at a slightly higher temperature than the melting point. Self-nucleation is similar phenomenon to melt memory in polymer crystallization. This phenomenon has been used to effectively realize polymer crystal growth.<sup>15–18</sup>

Understanding the melt memory effect is important to clarify the crystal growth mechanisms of polymers. In particular, the melt memory of general-purpose polymers, such as polyethylene, polypropylene and polystyrene, is academically and industrially interesting. In this study, we investigate the melt memory of isotactic polystyrene (iPS), which is a crystalline general-purpose polymer. iPS has a high glass transition temperature ( $\sim 100$  °C) and a notably slow crystallization rate (the maximum radial growth rate is  $14 \mu\text{m h}$  at  $180$  °C<sup>19</sup>). These characteristic features are convenient to study the melt memory of polymer crystal growth. Spherulite nuclei observed at  $T > 170$  °C can be regarded as those that were only formed by the melt memory effect because the primary nucleation rate of iPS spherulites is practically zero at  $T > 170$  °C.

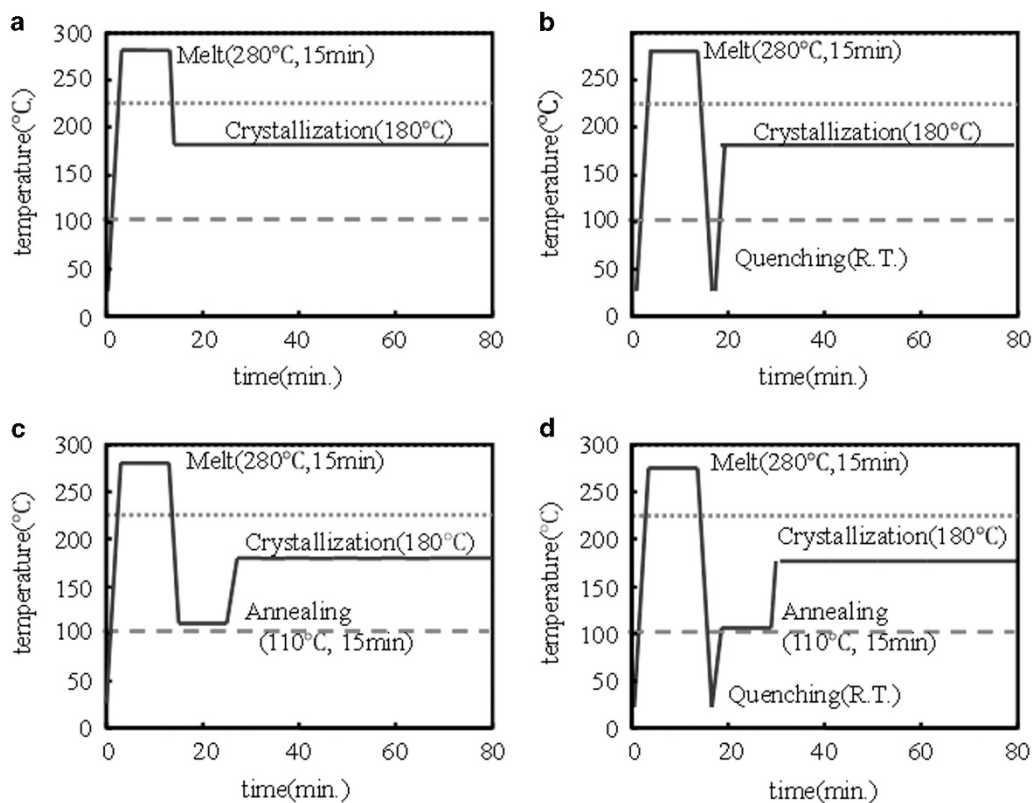
Several works have investigated iPS spherulite nucleation.<sup>12–14</sup> In Hay's<sup>12</sup> experiment, the samples were melted at  $260$  °C, but this temperature is believed not to be high enough to erase the melt memory of iPS spherulite nuclei. Boon *et al.*<sup>13,14</sup> performed dilatometry experiments of iPS spherulites and discussed iPS spherulite nucleation from the melt in detail. They made a clear distinction between the ‘resistant’ nuclei that remained above the melting point and the ‘induced’ nuclei that formed at high supercooling. Mumum *et al.*<sup>20,21</sup> performed various experiments on melt memory using iPS spherulites, but experiments were not performed for various melting times.

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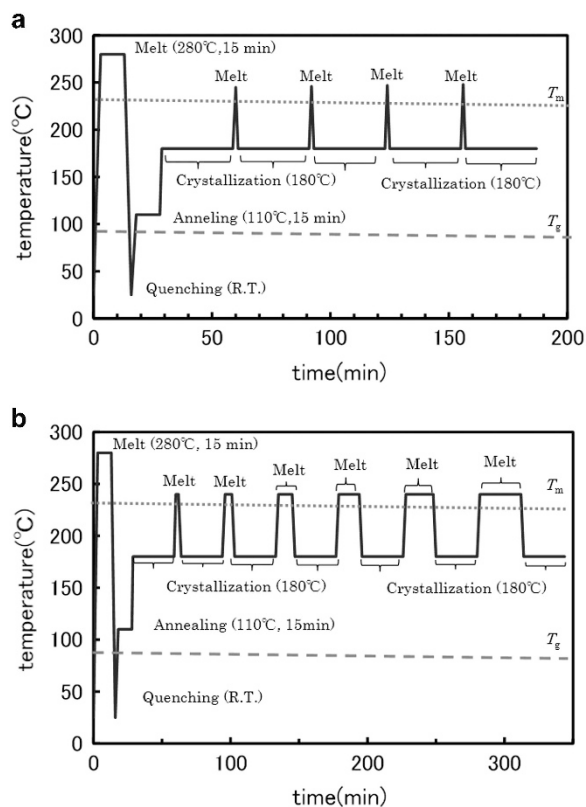
**Figure 1** Diagram of the thermal histories used in this experiment (a) with no seeding process, (b) with seeding process B, (c) with seeding process C and (d) with seeding process D. The melting point (222 °C) and glass transition temperature (~100 °C) are indicated with a dotted line and a broken line, respectively. Seeding processes B, C and D are explained in the text. A full color version of this figure is available at *Polymer Journal* online.

As a background to our experiments, we describe the ‘reset’ of the melt and the ‘seeding process’. A powder sample of iPS was melted at 250 °C, which is higher than the equilibrium melting point (242 °C),<sup>19</sup> and crystallized at 180 °C for 30 min; this sample was filled with many small crystallites. Another sample was melted at 280 °C and quenched at 180 °C, but it was not subsequently crystallized. Thus, melting at  $T \geq 280$  °C is called the ‘reset’ of the melt. This fact suggests that the apparent melting point becomes higher than the equilibrium melting point. Next, we explain the ‘seeding process’. The seeding process is the quenching process before crystallization. As a result of the seeding process, the primary nucleation of spherulites is promoted. There are several empirical methods to generate the primary nuclei of spherulites, one of which is the seeding process. Figure 1 shows the thermal histories with or without the seeding processes in this experiment: (A) directly quenching the melt to the crystallization temperature (no seeding process); (B) quenching the melt to room temperature, which is below the glass transition temperature ( $T_g$ ; ~100 °C), and subsequently heating the sample to the crystallization temperature (seeding process B); (C) quenching the melt to the annealing temperature, which is slightly higher than the glass transition temperature for a few minutes and subsequently heating the sample to the crystallization temperature (seeding process C); and (D) quenching the melt to room temperature, heating the sample to the annealing temperature, annealing it for a few minutes at a temperature slightly above the glass transition temperature and heating it to the crystallization temperature (seeding process D). The melting point (222 °C) and glass transition temperature (~100 °C) are indicated by a dotted line and a broken line, respectively.

In this study, the melt memory of the iPS samples was ‘reset’ by heating to 280 °C. We generated primary spherulite nuclei using various seeding processes and examined the dependence of the melt memory on the cumulative melting times, melt temperatures and seeding processes using a polarized optical microscope.

## EXPERIMENTAL PROCEDURE

The sample that we used is iPS ( $M_w = 55.6 \times 10^4$ ,  $M_w/M_n = 1.9$ ), which was purchased from Polymer Laboratory (Church Stretton, UK). iPS powder was interlaid between two pieces of cover glass, which were ~150- $\mu\text{m}$  thick, was placed on a hot stage (LINKAM THM600, Linkam Scientific Instruments, Surrey, UK). The samples were melted for 15 min at 280 °C to reset them. The estimated thickness of a sample was ~10  $\mu\text{m}$ . The glass transition temperature of the iPS sample, which was measured using a DSC (5200 differential scanning calorimeter SSC thermal analysis system, Seiko Instruments, Chiba, Japan) was 104 °C. All of the samples were crystallized at 180 °C, which led to the fastest crystal growth rate. The thermal histories used in this experiment are shown in Figure 2. The illustrated thermal histories in Figures 2a and b were used to investigate the melt temperature dependence and cumulative melting time dependence of spherulite nucleation. It is noteworthy that the melting time at each melt temperature is a few seconds, as shown in Figure 2a, and the melting times shown in Figure 2b are 2, 5, 10, 15, 20, 30, 40, 60 and 90 min, which leads to cumulative melting times of 2, 7, 17, 32, 52, 82, 122, 182 and 272 min. We also used the thermal histories shown in Figure 3 to investigate the seeding process dependence of spherulite nucleation. In Figure 3, the melting times are 1, 5, 10, 15, 20, 30 and 40 min, which leads to cumulative melting times of 1, 6, 16, 31, 51, 81 and 121 min. The samples were observed *in situ* using a polarized optical microscope with a hot stage. Photographs of the samples were taken through the microscope. The number of spherulites that appeared in the view of the microscope was counted in this experiment. The area of the view of the microscope was 0.156 mm<sup>2</sup>, and the sample thickness was ~10  $\mu\text{m}$ , which led



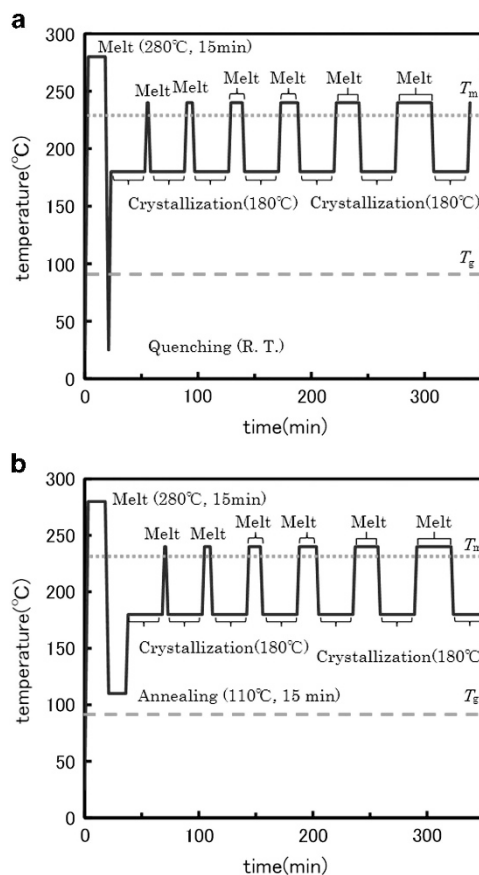
**Figure 2** Diagram of the thermal histories used in this experiment to investigate (a) the melt temperature dependence and (b) cumulative melting time dependence of the spherulite nucleation. The dotted and broken lines denote the melting point and glass transition temperature, respectively. A full color version of this figure is available at *Polymer Journal* online.

to an observable volume of  $\sim 1.56 \times 10^{-3} \text{ mm}^3$ . Approximately a few hundred spherulites were typically counted in the experiment.

## RESULTS AND DISCUSSION

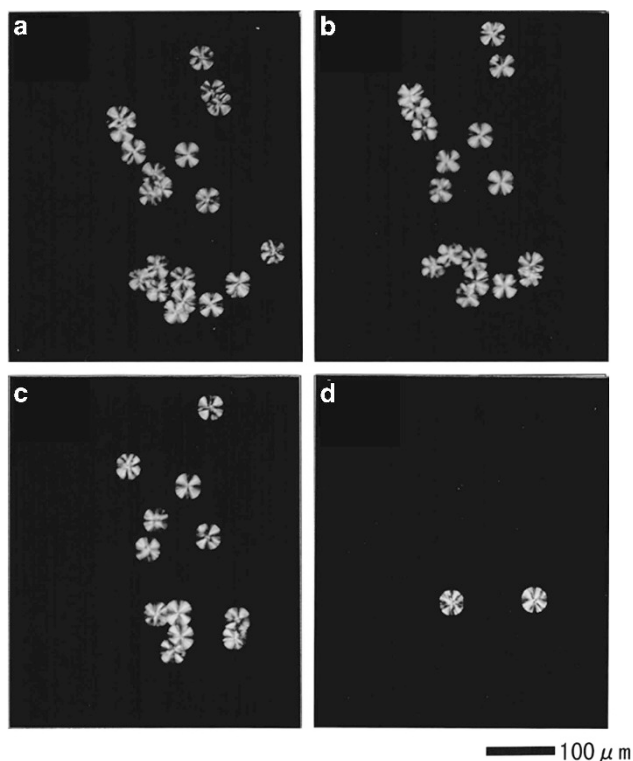
A thermal history with seeding process D, which is shown in Figure 2a, was provided for an iPS sample to investigate the melt temperature dependence of the number of spherulites. Figure 4 shows the polarized optical micrographs of iPS spherulites that were recrystallized at 180 °C for 1 h for each melt temperature. Figure 4 shows that the recrystallized spherulites for each melt temperature appear in the same location as the original spherulites, and the number of recrystallized spherulites decreases with the melt temperature. The morphologies of the recrystallized spherulites for each melt temperature are not necessarily identical to those of the corresponding original spherulites. Therefore, a spherulite does not possess the entire memory of the original spherulite, but possesses the memory of its position only. The pre-experiment confirms that the growth rate of spherulites does not depend on the melt temperature. The number of spherulite nuclei does not decrease when the melt temperature is below 245 °C. No spherulite is recrystallized when the melt temperature is above 248 °C. All spherulites disappear in a polarized optical microscope at 222 °C for all of analyzed samples. This temperature is identical to the melting point of our iPS sample, which was evaluated using the DSC measurement.

Next, we studied the melting time dependence of the number of spherulites at various constant melt temperatures. A thermal history with seeding process D, which is shown in Figure 2b, was provided for

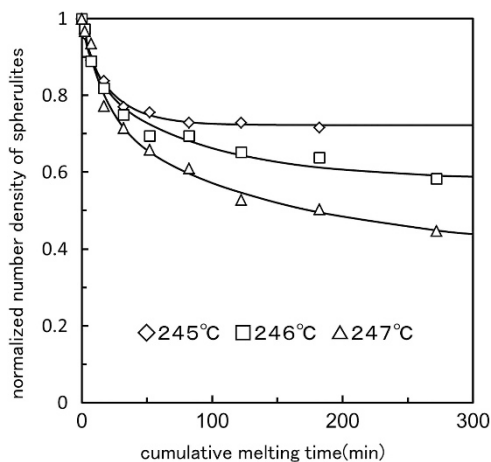


**Figure 3** Diagram of the thermal histories (a) with seeding process B and (b) with seeding process C instead of seeding process D in Figure 2b. The dotted and broken lines denote the melting point and glass transition temperature, respectively. A full color version of this figure is available at *Polymer Journal* online.

an iPS sample. Figure 5 shows the cumulative melting time dependence of the number density of crystallized spherulites for various melt temperatures. In Figure 5, the number densities are normalized by those at the cumulative melting time of zero. The numbers of spherulites that were first crystallized in the area of  $0.156 \text{ mm}^2$  are 74, 72 and 123 for the melt temperatures of 245, 246 and 247 °C, respectively. At the initial stage, the number density of spherulites rapidly decreases with the cumulative melting time, which indicates that the rapidly decreased nuclei do not significantly contribute to the melt memory. After the initial stage, the number density of spherulites exponentially decays with the cumulative melting time and approaches a certain finite value. This asymptotic value decreases with the melt temperature. The experimental data points are successfully fitted by the sum of two exponential terms with different characteristic times, as shown by the solid curves in Figure 5. The two characteristic times are 3.7 and 24.4 min for the melt temperature of 245 °C, 10.6 and 87.0 min for 246 °C and 17.4 and 150 min for 247 °C. When the melt temperature is below 245 °C, all of the spherulites recrystallize at the identical position as the original spherulites and number of spherulite nuclei does not decrease. When the melt temperature is above 247 °C, no spherulites recrystallize. The latter fact appears to be slightly inconsistent with the aforementioned experimental results using the thermal history of Figure 2a, where the spherulite nuclei remain even at the melt temperature of 248 °C. This discrepancy arises from the



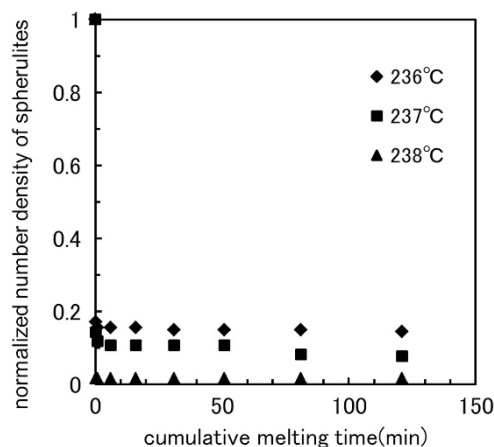
**Figure 4** Polarized optical micrographs of iPS spherulites that were recrystallized at 180 °C for 1 h for each melt temperature: (a) 245 °C, (b) 246 °C, (c) 247 °C and (d) 248 °C. The thermal history with seeding process D, which is shown in Figure 2a, is provided for an iPS sample.



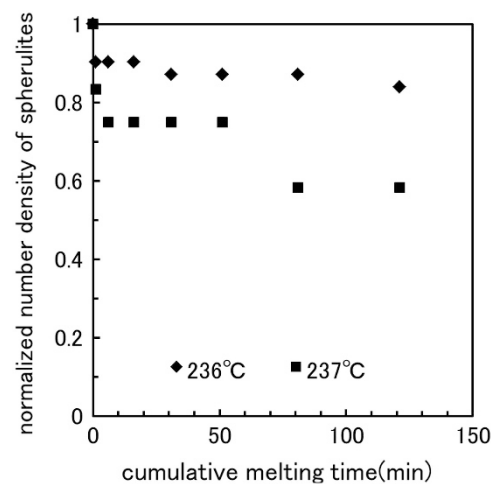
**Figure 5** Cumulative melting time dependence of the number density of the crystallized spherulites for various melt temperatures (open diamond: 245 °C; open square: 246 °C; open triangle: 247 °C). A thermal history with seeding process D (Figure 2b) is used. The solid curves represent the least squares fit to the sum of two exponential terms with different characteristic times.

difference in melting time. The melting time in the aforementioned experiment is too short in comparison with this experiment.

Next, we investigated the seeding process dependence of the number of spherulites. Here, an iPS sample was given a thermal history with seeding processes B or C instead of seeding process D, as shown in Figure 2b. These thermal histories are shown in Figure 3. In Figure 6, we show the cumulative melting time dependence of the

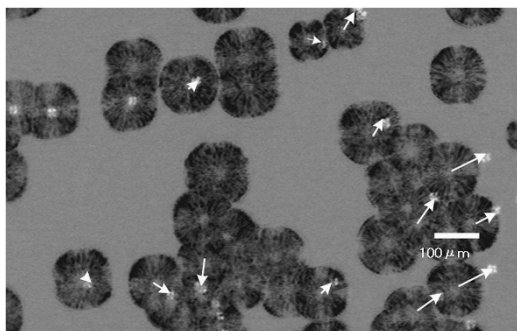


**Figure 6** Cumulative melting time dependence of the number density of the crystallized spherulites for various melt temperatures (filled diamond: 236 °C; filled square: 237 °C; filled triangle: 238 °C.) through a thermal history with seeding process B (quenching temperature: room temperature), which is shown in Figure 3a.



**Figure 7** Cumulative melting time dependence of the number density of the crystallized spherulites for various melt temperatures (filled diamond: 236 °C; filled square: 237 °C) through a thermal history with seeding process C (annealing temperature: 110 °C, annealing time: 15 min), which is shown in Figure 3b.

number density of crystallized spherulites for various melt temperatures according to the thermal history with seeding process B (quenching temperature: room temperature), which is shown in Figure 3a. The numbers of spherulites that first crystallized in the area of 0.156 mm<sup>2</sup> are 186, 168 and 178 for melt temperatures of 236, 237 and 238 °C, respectively. Figure 6 indicates that the normalized number density of spherulites instantaneously decreases to a certain value below 0.2 and becomes an almost constant. Note that the melt temperatures studied in this experiment (236–238 °C) are lower than the equilibrium melting point of iPS (242 °C). The number of spherulite nuclei does not decrease when the melt temperature is below 236 °C. No spherulites are recrystallized when the melt temperature is above 238 °C. Next, in Figure 7, we show the cumulative melting time dependence of the number density of crystallized spherulites for various melt temperatures according to the thermal history with seeding process C (annealing temperature:



**Figure 8** Stacked polarized micrograph of a negative image taken before remelting and a positive image taken during crystallization after remelting. The arrows represent the displacements of spherulite nuclei before and after remelting.

110 °C, annealing time: 15 min), which is shown in Figure 3b. The numbers of spherulites that first crystallized in the area of 0.156 mm<sup>2</sup> are 31 and 24 for melt temperatures of 236 and 237 °C, respectively. Similar experimental results were obtained for the cumulative melting time dependence of the normalized number density of spherulites, except that the normalized number density reaches a certain value above 0.6. The number of spherulite nuclei does not decrease when the melt temperature is below 236 °C. No spherulites are recrystallized when the melt temperature is above 237 °C. Note that the melt temperatures studied in the cases of thermal histories with seeding processes B and C are ~10 °C lower than those with seeding process D. This fact indicates that the spherulite nuclei that form according to the thermal history with seeding process D (both quenching and annealing) are more stable than those that form according to the thermal histories with seeding process B (quenching only) or C (annealing only). This phenomenon is not necessarily a predictable result but can be reasonably interpreted by the following simple arguments. The spherulite nuclei that form immediately after quenching below  $T_g$  are considered to be unstable but can be stabilized by annealing above  $T_g$ . By contrast, those that form immediately after quenching above  $T_g$  are also unstable but cannot be stabilized by annealing above  $T_g$ . The existence of these unstable spherulite nuclei and their stabilization behavior should be ascertained in future work. These experimental results lead to the conclusion that the crystallite composed of a high-molecular weight component can remain without melting at lower melt temperatures, which is considered to be a cause of the melt memory of spherulite nuclei that form according to the thermal histories with seeding process B or C.

The primary nuclei of iPS spherulites are only generated on the walls of the cover glass when the sample thickness is as thin as ~10 μm. Here, we confirm whether the spherulite nuclei are always generated at specific sites on the walls of the cover glass. After the reset of an iPS sample, the sample is given seeding process D, crystallized for 3 h at 180 °C, remelted for 30 min at 247 °C and recrystallized for a short time at 180 °C. Figure 8 shows a stacked optical micrograph of a negative image that was taken before remelting and a positive image that was taken during recrystallization after remelting. The arrows represent the displacements of spherulite nuclei before and after remelting. Figure 8 shows that several spherulite nuclei randomly moved, that is, the magnitudes and directions of their displacement vectors were random. Thus, there is no specific site on the cover glass for spherulite nuclei. On the basis of the detailed analyses of the average mean square displacement of the nuclei at each melting time,

it is ascertained that the average mean square displacement increases with the melting time and reaches a constant value at a certain time.

Here, we discuss the reason why the apparent melting point (~280 °C) is higher than the equilibrium melting point (242 °C) for powder samples of iPS. According to the experimental work on iPS by Kanaya's group,<sup>22</sup> an anisotropic-oriented ordered structure is formed even above the equilibrium melting point and melts at ~270 °C, which is far above the equilibrium melting point. Their experimental results are similar to our experimental results, whereby the sample cannot be reset unless the temperature is raised to 280 °C, which is far above the equilibrium melting point (242 °C). In our experiment, the iPS sample was interlaid between two pieces of cover glass, which generated shear flow. Because such shear flow empirically remains for a notably long period of time, the apparent melting point becomes higher than the equilibrium melting point.

The number of spherulites can be controlled by effectively using the melt memory, although the position of a spherulite cannot be controlled.

## CONCLUSION

We obtained the following new results using optical microscopy on iPS spherulites from the melt. (1) After an iPS spherulite is melted at a slightly higher temperature than the melting point and completely disappears, a polymer crystal nucleates and grows at the same position as the original spherulite when the temperature is decreased below the melting point. (2) After the melting–recrystallization processes are repeated by raising and lowering the temperature, the melt memory effect becomes weak and completely disappears at ~40 °C above the equilibrium melting point when the melt temperature is gradually increased during the melting–recrystallization processes. (3) The apparent melting point (~280 °C) is higher than the equilibrium melting point (242 °C) for powder samples of iPS. (4) The formation of spherulite nuclei is promoted by the seeding process which consists of the following consecutive procedures: quenching a sample to a temperature below the glass transition temperature and annealing it at slightly above the glass transition temperature. (5) The number density of spherulites rapidly decreases with the cumulative melting time and subsequently exponentially decays to a certain finite value with the cumulative melting time. This asymptotic value decreases with the melt temperature. These experimental results lead to the conclusion that the number of spherulites can be controlled if the melt memory is effectively used.

For practical purposes, it is worth discussing whether the absolute number of spherulites that form according to thermal histories with a seeding process depends on the type of seeding process (B, C and D). As previously described, the absolute numbers of spherulites that first crystallize in the area of 0.156 mm<sup>2</sup> are ~180, 30 and 90 for seeding processes B, C and D, respectively. This fact indicates that the absolute numbers of spherulites may be controlled by choosing the appropriate seeding processes. However, it should be noted that the absolute numbers of spherulites can vary depending on which area in the sample is viewed through the microscope.

For future work, we will investigate the morphologies of the iPS crystals formed according to thermal histories with various seeding processes using optical microscopy.

- 1 Overbergh, N., Berghmans, H. & Smets, G. Influence of thermal history on the melting behavior of isotactic polystyrene. *J. Polym. Sci. :Part C* **38**, 237–250 (1972).
- 2 Turska, E. & Gogolewski, S. Study on crystallization of nylon 6 (polycapramide). III. Effect of "crystalline memory" on crystallization kinetics. *J. Appl. Polym. Sci.* **19**, 637–644 (1975).

- 3 Chivers, R. A., Barham, P. J., Martinez-Salazar, J. & Keller, A. A new look at the crystallization of polyethylene. II. Crystallization from the melt at low supercoolings. *J. Polym. Sci.: Polym. Phys. Ed.* **20**, 1717–1732 (1982).
- 4 Khannna, Y. P. & Reimschuessel, C. Memory effects in polymers. I. Orientational memory in the molten state; its relationship to polymer structure and influence on recrystallization rate and morphology. *J. Appl. Polym. Sci.* **35**, 2259–2268 (1988).
- 5 Moser, K., Ohm, H. & Zwilling, W. The use of thermal analysis and optical microscopy to investigate the memory effect in nylon 12 caused by processing history. *J. Appl. Polym. Sci. Appl. Polym. Symp.* **48**, 459–472 (1991).
- 6 Alfonso, G. C. & Scardigli, P. Melt memory effects in polymer crystallization. *Macromol. Symp.* **118**, 323–328 (1997).
- 7 Häfele, A., Heck, B., Hippler, T., Kawai, T., Kohn, P. & Strobl, G. Crystallization of poly(ethylene-co-octene): II Melt memory effects on first order kinetics. *Eur. Phys. J. E* **16**, 217–224 (2005).
- 8 Zhang, W. & Martins, J. A. Evaluation of the effect of melt memory on shear-induced crystallization of low-density polyethylene. *Macromol. Rapid Commun.* **27**, 1067–1072 (2006).
- 9 Zhang, W. & Martins, J. A. Shear-induced nonisothermal crystallization of low-density polyethylene. *Polymer* **48**, 6215–6220 (2007).
- 10 Lorenzo, A. T., Aranal, M. L., Sa'nchez, J. J. & Müller, A. J. Effect of annealing time on the self-nucleation behavior of semicrystalline polymers. *J. Polym. Sci.: Part B: Polym. Phys.* **44**, 1738–1750 (2006).
- 11 Martins, J. A., Zhang, W. A. & Brito, M. Origin of the melt memory effect in polymer crystallization. *Polymer* **51**, 4185–4194 (2010).
- 12 Hay, J. N. Crystallization kinetics of high polymers: Isotactic polystyrene. *J. Polym. Phys.:Part A* **3**, 433–447 (1965).
- 13 Boon, J. The effect of extreme supercooling on the number of spherulitic centers in isotactic polystyrene. *J. Polym. Sci.:Part C* **16**, 1739–1749 (1967).
- 14 Boon, J., Challa, G. & van Krevelen, D. W. Crystallization kinetics of isotactic polystyrene. II. Influence of thermal history on number of nuclei. *J. Polym. Sci.:Part A2* **6**, 1835–1851 (1968).
- 15 Fillon, B., Lotz, B., Thierry, A. & Wittman, J. C. Self-nucleation and enhanced nucleation of polymers. Definition of a convenient calorimetric “efficiency scale” and evaluation of nucleating additives in isotactic polypropylene ( $\alpha$  phase). *J. Polym. Sci.: Part B: Polym. Phys.* **31**, 1395–1405 (1993).
- 16 Fillon, B., Wittmann, J. C., Lots, B. & Thierry, A. Self-nucleation and recrystallization of isotactic polypropylene (alpha phase) investigated by differential scanning calorimetry. *J. Polym. Sci.:Part B: Polym. Phys.* **31**, 1383–1393 (1993).
- 17 Fillon, B., Thierry, A., Wittmann, J. C. & Lotz, B. Self-nucleation and recrystallization of polymers. Isotactic polypropylene,  $\beta$  phase:  $\beta$ - $\alpha$  conversion and  $\beta$ - $\alpha$  growth transitions. *J. Polym. Sci.:PartB: Polym. Phys.* **31**, 1407–1424 (1993).
- 18 Carfagna, C., Rosa, C. D., Guerra, G. & Petraccone, V. Recrystallization kinetics of isotactic polypropylene ( $\alpha$ -form). *Polymer* **25**, 1462–1464 (1984).
- 19 Suzuki, T. & Kovacs, A. J. Temperature dependence of spherulitic growth rate of isotactic polystyrene. A critical comparison with the kinetic theory of surface nucleation. *Polym. J.* **1**, 82–100 (1970).
- 20 Mamum, A., Umemoto, S., Ishihara, N. & Okui, N. Influence of thermal history on primary nucleation and crystal growth rates of isotactic polystyrene. *Polymer* **47**, 5531–5537 (2006).
- 21 Mamum, A., Umemoto, S. & Okui, N. Self-seeding effect on primary nucleation of isotactic polystyrene. *Macromolecule* **40**, 6296–6303 (2007).
- 22 Hayashi, Y., Matsuba, G., Zhao, Y., Nishida, K. & Kanaya, T. Precursor of shish-kebab in isotactic polystyrene under shear flow. *Polymer* **50**, 2095–2103 (2009).