Relationship between magnetic alignment and the crystallization condition of isotactic polystyrene

Masafumi Yamato *, Tsunehisa Kimura

Graduate School of Engineering, Tokyo Metropolitan University, Miami-ohsawa 1-1, Hachioji, Tokyo 192-0397, Japan

Received 13 January 2006; accepted 17 January 2006
Available online 19 May 2006

Abstract

The relationship between a magnetic alignment and crystallization conditions of isotactic polystyrene (iPS) was studied by means of DSC, POM, WAXD, FT-IR, and birefringence measurements. The onset temperature for crystallization during the cooling process was found to depend on the melting temperature. From observations using a polarized optical microscope, the proportion of spherulite decreased in cases where melting occurred at greater than 265 °C. These results suggest that melting at less than 265 °C causes self-seeding, which is known as the ‘melt memory effect’ in iPS, leading to a high nucleation density. The maximum intensity of transmitted light that could be observed by birefringence measurements was also dependent on the melting temperature. The high nucleation density that was obtained by melting at less than 265 °C was suitable for achieving higher orientations. In situ infrared measurements in a magnetic field were carried out in a home-built apparatus into which an autorotation polarizer unit had been installed. This allowed us to automatically acquire simultaneous polarized infrared spectra both parallel and perpendicular to the magnetic field. Orientation was confirmed for the crystalline band, while no orientation was observed for the amorphous band. The dichroic difference increased during isothermal crystallization with increasing crystallinity. No orientation effects were observed in the melted state in the present study.

q 2006 NIMS and Elsevier Ltd. All rights reserved.

Keywords: Magnetic alignment; Isotactic polystyrene; In situ measurement; Birefringence; FT-IR measurement; Nucleation density; Self-seeding

1. Introduction

We have been reported on the magnetic alignment of semicrystalline polymers [1–6] such as poly(ethylene-2,6-naphthalate) [1], isotactic polystyrene [2], and poly(ethylene terephthalate) [3] that occurs during melt crystallization in a magnetic field. The condition for magnetic alignment is closely related to the crystallization kinetics, but the details have not been fully clarified. We assume that some ordered structure that exists in the molten state is responsible for the alignment. This structure could cause inhomogeneous nucleation, resulting in a high nucleation density. We have studied the effects of nucleation density-dependence on the melting temperature and on the resultant magnetic alignment by means of differential scanning calorimetry and by polarized optical microscopy. Wide-angle X-ray diffraction measurements and in situ birefringence measurements during isothermal crystallization were carried out in order to clarify the dependence of the degree of orientation on the nucleation density. In situ FT-IR measurements were carried out in order to determine in which stage during the crystallization process magnetic alignment occurred.

2. Experimental

2.1. Sample preparation

We used a powdered form of isotactic polystyrene (iPS, molecular weight 400,000) purchased from Scientific Polymer Products, Inc. Film samples were prepared by hot-pressing the powder at 250 °C for 5 min, followed by quenching in iced water. The films that were obtained exhibited an amorphous halo in wide-angle X-ray diffraction (WAXD). The samples that were used for differential scanning calorimetry (DSC) measurements and WAXD had a thickness of about 0.1 mm, while for optical microscopy and FT-IR spectroscopy, samples with a thickness of less than 50 μm were used.
2.2. DSC measurement

DSC measurements were carried out using a SEIKO DSC200 equipped with a thermal analysis system SSC5200H under a dry nitrogen atmosphere. Aluminum pans were filled with about 7 mg of the sample films. The scanning rates during both the heating and cooling processes were 10 K/min.

2.3. Optical microscopy

An Olympus BX microscope was used to carry out polarized optical microscopy (POM). Pictures were taken using a digital camera.

2.4. Thermal treatment and birefringence measurements

To enable crystallization with an accurately-controlled temperature program, a heating cell that could be inserted into a cryogen free magnet (maximum \( B = 8 \) T) with an internal bore of 100-mm was built. (Schematic drawing shown in Fig. 1). An aluminum cell that could be heated by ceramic heaters was connected to a water-cooled base unit. The temperature was measured using a PT100 and was controlled by a PID controller (Shimaden FP21). The disk-shaped samples were held between two cover glasses with a Kapton frame of the same thickness inserted as a spacer. To prevent the oxidation of the sample, the chamber containing the heating cell was flooded with nitrogen. A laser, a polarizer, an analyzer and a photodiode were also built into the apparatus shown in Fig. 1, making birefringence measurements possible during the heat treatment.

2.5. FT-IR measurement

FT-IR spectroscopy was conducted using a Nicolet Magna 750 spectrometer. The system resolution was 4 cm\(^{-1}\), and 32 scans were averaged. In order to make measurements under a magnetic field, the infrared light emerging from the spectrometer was introduced into a split-type magnet (maximum \( B = 5 \) T) and was detected by an MCT/A detector that was set up outside of spectrometer. An autorotation polarizer unit allowed us to measure the dichroic difference spectra that were generated during annealing under a magnetic field. The heating cell that was used was the same one used in the birefringence measurements in order to enable crystallization with the same thermal history.

2.6. WAXD measurement

For 2D-WAXD measurements, a set-up incorporating a rotating anode (MacScience MXP18) operating at 4.5 kW and an image plate detector (MacScience DIP2020) was used. Cu K\(_\alpha_1\) radiation was selected by a graphite monochromator. The diffraction patterns were analyzed using software, which was created by the author.

3. Results and discussion

Before conducting heat treatment in a magnetic field, it was necessary to examine the thermal behavior of the prepared amorphous sample. Fig. 2 shows an example of a DSC heating scan. The quenched sample showed a glass transition around 95 \(^{\circ}\)C, a broad exothermic peak around 160 \(^{\circ}\)C that originated from cold crystallization and a broad melting range (210–230 \(^{\circ}\)C) during the heating process. Although the crystallization of iPS is very slow, these results showed that the crystallization progressed sufficiently during the heating process.

It is known that differences in melting temperature have a significant effect on nuclear density during the crystallization of iPS. Fig. 3 shows DSC thermograms obtained during the cooling process after melting at different temperatures. In those cases, where the melting temperature is above 270 \(^{\circ}\)C, no DSC signal for crystallization was observed, because crystallization is very slow under these conditions. However, when the melting temperature was below 265 \(^{\circ}\)C, the onset temperature for crystallization was shown to depend on the melting temperature. This suggests that nuclear density also depends on the melting temperature [7].

This was supported by observations made using a polarized optical microscope. Fig. 4 shows photographs of samples annealed at 180 \(^{\circ}\)C for 10 h after melting at different
temperatures. The growth of spherulites is obvious, and the concentration of spherulites decreases with increasing melting temperature. From the results of DSC and POM measurements, we found that the nucleation density strongly depended on the melting temperature, and the critical melting temperature was estimated as being 265°C. This self-seeding effect is called the 'melt memory effect', and originates from a residual structure formed by melting below an equilibrium melting point [7–9]. However, the details of this residual structure are not fully understood yet. The residual structure seems to maintain some order, similar to that of a crystal, because it serves as a crystal nucleus. Previous reports have pointed out that rotation of structures that exist in the molten state or in the initial stages of crystallization induces the magnetic alignment of semicrystalline polymers. Consequently, this means that the degree of orientation of the magnetic-aligned polymer strongly depends on the nuclear density. In order to examine the relationship between nuclear density and magnetic alignment, WAXD measurements were carried out on samples that had been prepared under the same crystallization conditions (210°C for 10 h) after being melted at different temperatures. However, for samples that were prepared by melting above 265°C, no characteristic diffraction peaks reflected by crystalline iPS were observed, only an amorphous halo. The degree of crystallinity in these samples was too low to detect any crystalline character in our WAXD system, since the crystal growth rate of iPS is very slow under these conditions, in addition to their low nuclear density. Meanwhile, in those samples prepared by melting at less than 260°C, the magnetic alignment of iPS was observed. An example of such a result is shown in Fig. 5. In the 2D image, the orientation is a little unclear. Azimuthal distributions of diffraction peaks reflected by the (220) and (211) planes of crystalline iPS show that the c-axis of the iPS was aligned toward a direction perpendicular to the magnetic field. This result agrees with previous reports for the magnetic alignment of iPS [2,7].

The effect of the nucleation density on the magnetic alignment of iPS was also studied by making birefringence measurements under a magnetic field. Fig. 6 shows the temporal changes of the transmitted light intensity under cross Nicole conditions during isothermal crystallization at 210°C after melting at different temperatures. Since, the light intensity depends on the degree of orientation, an increase in the light intensity with crystallization time indicates that magnetic alignment takes place during isothermal crystallization. Comparing the maxima of the light intensities for the different melting temperatures, we found that greater intensities were exhibited by samples melted at lower temperatures.

Fig. 3. DSC thermograms during the cooling process after melting at different temperatures.

Fig. 4. Optical micrographs (crossed polar) of iPS samples crystallized at 180°C for 10 h after melting at different temperatures (a), 250°C; (b), 260°C; (c), 265°C; (d), 270°C.

Fig. 5. Example of the magnetic alignment of iPS.

Fig. 6. Optical micrographs (crossed polar) of iPS samples crystallized at 180°C for 10 h after melting at different temperatures (a), 250°C; (b), 260°C; (c), 265°C; (d), 270°C.

M. Yamato, T. Kimura / Science and Technology of Advanced Materials 7 (2006) 337–341 339
The results obtained from birefringence measurements strongly suggest that a high nucleation density is suitable for magnetic alignment. If crystallization takes place at a low nucleation density, large spherulites grow, as shown in Fig. 4c and d. The spherulites contain a large anisotropic core consisting of a stack of lamellae that branch out, resulting in an isotropic spherical object. These characteristics remain unchanged if the crystallization takes place under a magnetic field [7]. This observation could explain the influence of melting temperature on the magnetic alignment. At high nucleation density, the anisotropic, oriented cores of the spherulites occupy most of the volume, leading to macroscopic orientation, but this effect is lost at low nucleation density because in this case, the overall random orientation of the outer parts of the spherulites dominates.

We measured FT-IR spectra under a magnetic field in order to study in which stage of the crystallization the magnetic alignment takes place. To carry out in situ FT-IR measurements under a magnetic field, we designed and built a new apparatus equipped with an autorotation polarizer unit [10]. Using this system, we could simultaneously obtain spectra for incident light impinging from both perpendicular and parallel to a magnetic field. We also obtained dichroic difference spectra, which are formed by the subtraction of a perpendicular spectrum from a parallel spectrum. The magnetic alignment and crystallization behavior could be studied by analyzing the perpendicular and dichroic difference spectra. Fig. 7 shows the perpendicular and dichroic difference spectra of iPS annealed at 210 °C for 5 h after melting at 250 °C for 10 min in a magnetic field (5 T). The sign of the absorbance in the dichroic difference spectra depends on the angle between the dipole moment and the magnetic field. The bands at 899, 1186, and 1196 cm⁻¹, which are assigned to the 31-helix structure, show large negative values in the dichroic difference spectrum. This indicates that the direction of the dipole moment of these bands is almost perpendicular to the magnetic field. On the other hand, the direction of the dipole moments of the bands at 920, 1050, and 1081 cm⁻¹, assigned to the 31-helix structure, are almost parallel, as indicated by the positive value in the dichroic difference spectrum. The peak intensities of the bands at 836, 906, and 1155 cm⁻¹, assigned to amorphous conformations, were almost zero. As a result, we could conclude that the orientation of the sample is mainly due to the crystalline part.
We also studied the orientation behavior during isothermal crystallization by using in situ infrared measurements in a magnetic field. Fig. 8 shows temporal changes of the peak intensity under perpendicular polarization during isothermal crystallization at 210 °C after melting at 250 °C for 10 min. In Fig. 9, the peak intensities of the bands assigned to the 31-helix were seen to increase. In addition, the peak intensity of the band at 906 cm⁻¹, assigned to the amorphous region, began to decrease immediately after the crystallization temperature was reached. This indicates that crystallization started immediately at 210 °C and that the crystallinity increased with increasing crystallization time. Under these crystallization conditions, crystallization was almost completed after 60 min.

We also investigated the effect of nucleation density on the magnetic alignment of iPS and tried to determine in which stage during the crystallization the magnetic alignment took place. The onset temperature for crystallization during the cooling process depended on the melting temperature. From observations made using a polarized optical microscope, the density of spherulites decreased when melting was carried out above 265 °C. The structures that occurred when the powder was melted at temperatures less than 265 °C served as nuclei, resulting in an acceleration of crystallization and an inhibition of large spherulite growth. The results of birefringence measurements during isothermal crystallization at different melting temperatures suggested that crystallization had to be initiated at a high nucleation density (as caused by the melt memory effect) in order to achieve a higher degree of orientation of the magnetic alignment. We also confirmed by in situ FT-IR measurements that alignment did not take place in the melted state, but actually started with the formation of crystalline material. The magnetic alignment strongly depended on the crystallization conditions, such as crystallization temperature and melting temperature.

4. Conclusion

We investigated the effect of nucleation density on the magnetic alignment of iPS and tried to determine in which stage during the crystallization the magnetic alignment took place. The onset temperature for crystallization during the cooling process depended on the melting temperature. From observations made using a polarized optical microscope, the density of spherulites decreased when melting was carried out above 265 °C. The structures that occurred when the powder was melted at temperatures less than 265 °C served as nuclei, resulting in an acceleration of crystallization and an inhibition of large spherulite growth. The results of birefringence measurements during isothermal crystallization at different melting temperatures suggested that crystallization had to be initiated at a high nucleation density (as caused by the melt memory effect) in order to achieve a higher degree of orientation of the magnetic alignment. We also confirmed by in situ FT-IR measurements that alignment did not take place in the melted state, but actually started with the formation of crystalline material. The magnetic alignment strongly depended on the crystallization conditions, such as crystallization temperature and melting temperature.

Acknowledgements

This work was supported by an Industrial Technology Research Grant Program in ‘01 from New Energy and Industrial Technology Development Organization (NEDO) of Japan, and a Grant-in-Aid for Scientific Research on Priority Area ‘Innovative utilization of strong magnetic fields’ (Area 767, No. 15085207) from MEXT of Japan.

References

[1] H. Sata, T. Kimura, S. Ogawa, M. Yamato, E. Ito, Polymer 37 (1996) 1879.
[2] H. Ezure, T. Kimura, S. Ogawa, E. Ito, Macromolecules 30 (1997) 3600.
[3] T. Kimura, T. Kawai, Y. Sakamoto, Polymer 41 (2000) 809.
[4] T. Kawai, T. Kimura, Polymer 41 (2000) 155.
[5] M. Yamato, T. Kimura, Trans. MRS-J. 27 (2002) 117.
[6] H. Aoki, M. Yamato, T. Kimura, Chem. Lett. (2001) 1140–1141.
[7] F. Ebert, T. Thurn-Albrecht, Macromolecules 36 (2003) 8685.
[8] Y. Sakamoto, T. Kawai, T. Kimura, Trans. MRS-J. 27 (2002) 73.
[9] T. Kawai, Y. Sakamoto, T. Kimura, Mater. Trans., JIM 41 (2000) 955.
[10] M. Yamato, T. Kimura, Abstracts of Seventh Symposium on New Magneto-Science 2003, p. 21.