

ORIGINAL ARTICLE

Magnetic-field-induced alignment of syndiotactic polystyrene

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Magnetic-field-induced alignment of syndiotactic polystyrene (sPS) is reported here. Isothermal crystallization of sPS samples from several annealing temperatures was conducted in a 2 or 10 T magnetic field. The isothermal crystallization of low-molecular-weight sPS samples from the annealing temperature, which induced self-seeding, achieved effective alignment of the polymer chains. Azimuthal scans of the samples crystallized in the magnetic field revealed that the *b*-axis of the β -phase unit cell was aligned parallel to the magnetic field. A low sPS molecular weight and a high magnetic field were effective for a high degree of alignment. Stepwise crystallization from the annealing temperature also induced effective alignment of the sPS.

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INTRODUCTION

The development of transition metal catalysts has made it possible to synthesize highly isotactic and syndiotactic polyolefins. Highly syndiotactic polystyrene (sPS) was first synthesized using half-sandwich titanocene catalysts. sPS is commercially produced as an engineering plastic because of its high melting temperature of ~300 °C.^{1–3} Injection molding is used mainly to form sPS products. Mechanical stretching of sPS has been investigated to study the molecular orientation process and mechanical response during the formation of sPS films.⁴

Mechanical orientation is a conventional method used to obtain films or fibers of polymers with highly ordered polymer chains. Magnetic- or electric-field-induced alignment of polymer chains has been investigated to yield oriented polymer materials without deformation of the specimens. The magnetic-field-induced alignment of some crystalline polymers, such as poly(ethylene terephthalate),⁵ poly(ethylene-2,6-naphthalate),^{6,7} polycarbonate,⁸ isotactic polypropylene,⁹ isotactic polystyrene^{10–12} and polyethylene,¹³ has been reported. The magnetic-field-induced alignment of crystalline polymers was conducted during the melt-crystallization process. The existence of ordered domains with a critical size and an anisotropic diamagnetic susceptibility in a relatively low viscosity environment is essential for alignment.¹⁴ The large diamagnetic anisotropy is one of the important factors for the effective magnetic-field-induced alignment of polymers. Slow crystallization is favorable for the preservation of the fluidity, which is important for the arrangement of the crystallizing polymers. The low melt viscosity is also required so that the mobilities of the ordered domains and polymer chains are not decreased.

Some reports of magnetic-field-induced alignment of iPS should indicate that the diamagnetic anisotropy of the polystyrene crystal

domains is enough to induce the magnetic field alignment.^{10–12} However, the magnetic-field-induced alignment of sPS faced two difficulties. The first is the high crystallization rate of sPS. The crystallization rate of sPS is much faster than that of iPS. The fast crystallization would not allow enough time for the magnetic-field-induced alignment of the polymer chains or crystals during the melt crystallization of sPS. Precise control of the melt-crystallization temperature program is necessary to achieve magnetic-field-induced alignment of sPS. The second is the high melt viscosity of commercially available sPS because of its high molecular weight. We previously reported the magnetic-field-induced alignment of low-molecular-weight polyethylene.¹³ Decreasing the molecular weight effectively decreased the melt viscosity, which made it possible to align the polyethylene crystals in the magnetic field. In this experiment, the melt-crystallization temperatures are precisely optimized. Furthermore, low-molecular-weight sPS samples were synthesized using a half-titanocene catalyst. This article reports the effects of the sPS molecular weight and different melt-crystallization temperature programs on the degree of the magnetic-field-induced alignment.

EXPERIMENTAL PROCEDURE

Materials

sPS samples were synthesized via the polymerization of styrene using a half-titanocene catalyst, (pentamethyl-cyclopentadienyl)titanium trichloride, with methylaluminoxane as a cocatalyst in toluene at 50 °C. The molecular weight of the sample was controlled by the molar ratio of the Al in methylaluminoxane to Ti. The sPS samples were melted at 300 °C and pressed under a pressure of 10 MPa in a mold with a radius of 5.5 mm and a thickness of 0.1 mm, followed by quenching in water at room temperature. The melt crystallization of the sPS samples was conducted in a 2 or 10 T magnetic field

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generated by a cryocooler-cooled superconducting magnet (Sumitomo Heavy Industries, Tokyo, Japan) in the atmosphere.

Analytical procedures

^{13}C NMR spectra of the sPS samples were recorded on an Alpha-300 spectrometer (JEOL, Tokyo, Japan) in pulse Fourier transform mode at 120 °C. The samples were dissolved in 1,1,2,2-tetrachloroethane/1,1,2,2-tetrachloroethane- d_2 (9/1 (v v $^{-1}$)), and the resonance of the 1,1,2,2-tetrachloroethane- d_2 (5.88 p.p.m.) was used as an internal reference. The number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) of the sPS samples were measured by gel-permeation chromatography PL-GPC-220 (Agilent Technologies, Santa Clara, CA, USA) using trichlorobenzene at 140 °C as the solvent and standard polystyrene samples for calibration. Thermal analysis of the sPS samples was conducted by differential scanning calorimetry (DSC) using a DSC 8230 (Rigaku, Tokyo, Japan). The melting temperature was determined at a heating rate of 10 °C min $^{-1}$ after previously heating to 300 °C and cooling to room temperature at a rate of 10 °C min $^{-1}$. The top of the endothermic peak during the second heating process is defined as the melting temperature (T_m). The viscosity of the sPS was measured with a cone and plate viscometer CAP Viscometer, Model CAP 2000+ (Brookfield, Middleboro, MA, USA) at 235 °C and 100 r.p.m. The polarized optical micrographs of the samples were observed using an optical microscope BX50 (Olympus, Tokyo, Japan) equipped with a hot-stage FP90 (Mettler Toledo, Greifensee, Switzerland). Wide-angle X-ray diffraction (WAXD) patterns of the sPS samples were recorded on a R-Axis RAPID (Rigaku, Tokyo, Japan) using Cu K α radiation.

RESULTS AND DISCUSSION

Structure and thermal properties of the sPS samples

The structures and thermal properties of the sPS samples are summarized in Table 1. The fraction of [rr] triads in the sPS samples determined by ^{13}C NMR spectroscopy was >95%. The molecular weights of the samples used in this study were relatively low, $M_n = 8200\text{--}78\,000$.

Optimization of the temperature program

Optimization of the melt-crystallization temperature program is very important for the effective magnetic-field-induced alignment of crystalline polymers. The temperature program used in the present investigation is illustrated in Scheme 1. A sample is heated from room temperature to the annealing temperature (T_{an}) at a rate of 10 °C min $^{-1}$ and held constant for 10 min. Then, the sample is cooled to an isothermal crystallization temperature (T_{itc}) at a rate of 10 °C min $^{-1}$ and held constant for 180 min. When locally ordered domains remain in the annealing state, the domains could act as heterogeneous nuclei and raise the crystallization temperature (T_c) during the cooling process. A temperature program that produces locally ordered domains at T_{an} and promotes heterogeneous slow crystallization at a higher T_{itc} is desirable to achieve the effective magnetic-field-induced alignment of crystalline polymers.^{5,9,11,12,15}

Table 1 Structure and properties of sPS samples

Sample	M_n^a ($\times 10^3$)	M_w/M_n^a	T_m^b (°C)	T_{max}^c (°C)	T_c^d (°C)	Viscosity ^e (Pa·s)
1	8.2	1.91	248.6	249.0	234.0	4.7
2	15.6	2.05	253.2	253.5	239.9	31.4
3	26.6	1.85	256.7	259.6	245.9	
4	78.0	1.74	263.7	269.5	253.6	

Abbreviations: DSC, differential scanning calorimetry; GPC, gel-permeation chromatography; M_n , number-average molecular weight; M_w , molecular weight distribution; sPS, syndiotactic polystyrene; T_c , crystallization temperature; T_m , maximum temperature.

^aDetermined by GPC using polystyrene-standard samples.

^bDetermined by DSC on the second heating process.

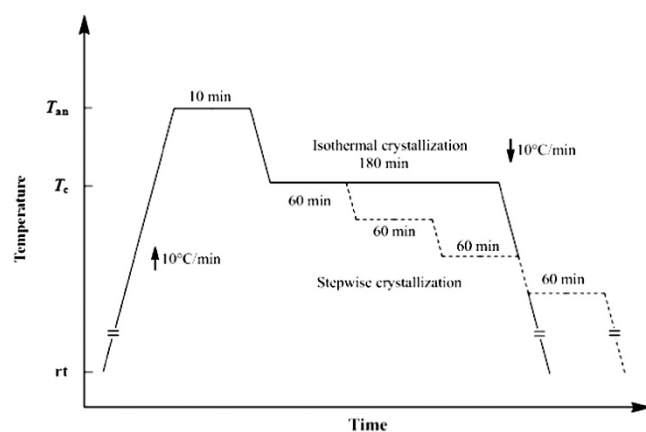
^c T_{max} which induced maximum T_c on the cooling process.

^d T_c on the cooling process from T_{max} .

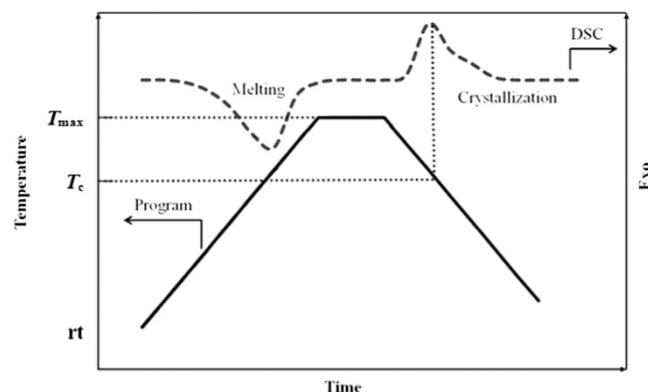
^eMeasured by a cone and plate viscometer at 235 °C with 100 r.p.m.

DSC measurements of the sPS samples were conducted using the alternative temperature program shown in Scheme 2 to optimize T_{an} and T_{itc} . The samples were heated from room temperature to T_{an} at a rate of 10 °C min $^{-1}$, held constant for 10 min and then cooled to room temperature at a rate of 10 °C min $^{-1}$; this program is shown as a solid line. The corresponding DSC profile with endothermic and exothermic peaks derived from melting and crystallization is shown as a broken line. The measurements were conducted using various heat treatment temperatures. The maximum temperature in the program (T_{max}), which is close to the T_m of the samples, was used to find the T_{an} that effectively preserves the ordered domains. Figure 1 shows the DSC profiles of sPS (Sample 3) treated at 260 or 270 °C. The crystallization profile of the sample treated at 260 °C contains two exothermic peaks at ~ 245 and 230 °C, as shown in Figure 1a. By contrast, a unimodal exothermic peak was observed at ~ 230 °C in the profile of the sample treated at 270 °C, as shown in Figure 1b.

The morphologies of the crystallized samples after the heat treatment were observed by polarization microscopy to study the effects of the treatment temperature on the texture of the crystals. The polarization microscope photographs of Sample 3 treated at 260 or 270 °C and cooled to room temperature at a rate of 10 °C min $^{-1}$ are shown in Figure 2. The photograph of Sample 3 treated at 260 °C shows small optical textures (Figure 2a). The formation of these small crystals indicates heterogeneous nucleation caused by the locally



Scheme 1 A scheme of the temperature program. The magnetic field is applied throughout the process.



Scheme 2 Schematic diagram of the differential scanning calorimetry (DSC) measurement, temperature program (solid line) and DSC profile (broken line).

ordered domains, the so-called 'self-seeding effect'.¹⁶ By contrast, large spherulites were observed in the photographs of Sample 3 treated at 270 °C (Figure 2b), indicating homogeneous crystallization from the melting state.

We are now ready to consider the DSC profiles in Figure 1 combined with the optical textures in Figure 2. The sPS Sample 3 treated at 260 °C showed two exothermic peaks derived from crystallization during the cooling process (Figure 1a). The lower exothermic peak in Figure 1a at ~230 °C was almost the same as that in Figure 1b, which was the profile of sPS Sample 3 treated at 270 °C. The exothermic peak at ~230 °C in Figure 1a should be because of the crystallization induced by homogeneous nucleation. The higher exothermic peak at 245 °C in Figure 1a should be because of the heterogeneous nucleation induced by the residual locally ordered domains.

DSC measurements of all the samples were conducted using the temperature program in Scheme 2 with some T_{\max} to optimize T_{an} and T_{itc} of the sPS samples for magnetic-field-induced alignment. When two exothermal peaks are detected, as shown in Figure 1a, the higher exothermic peak is defined as T_c because the higher crystallization temperature induced by heterogeneous nucleation is important for this experiment. In addition, the temperatures of the lower exothermic peaks were almost the same and independent of T_{\max} . The relationship between T_{\max} and T_c of the sPS samples is plotted in Figure 3 to determine the T_{an} of the sPS samples. The T_{an} that attained the maximum T_c should promote effective heterogeneous

crystallization during the cooling process via the locally ordered domains and should be suitable for use as T_{an} . For example, the T_{an} and T_{itc} of Sample 1 were determined as follows. The T_c of Sample 1 increased with increasing T_{\max} and rose to 234 °C at T_{\max} 249 °C. The T_c declined at T_{\max} above 249 °C. We determined 249 °C as the T_{an} for Sample 1. We also set the maximum T_c 234 °C of the DSC diagram as the T_{itc} in the temperature program for the magnetic-field-induced alignment.

Magnetic-field-induced alignment

The melt crystallization of the sPS samples was investigated in magnetic fields according to the temperature program shown in Scheme 1. The T_{an} and T_{itc} set in the experiments are summarized

Table 2 Magnetic orientation of sPS samples

Run	Sample	Magnet T	T_{an} (°C)	T_{itc} (°C)	Crystalline phase	$f_{\phi 0 2 0}$
1	1	2	249	243	β	0.21
2	2	2	253	238	β	0.19
3	3	2	260	245	β	0.00
4	3	10	260	245	β	0.49
5	3	10	260	252–246	β	0.65
6	4	10	271	262	α	

Abbreviations: sPS, syndiotactic polystyrene; T_{itc} , isothermal crystallization temperature; T_{an} , annealing temperature.

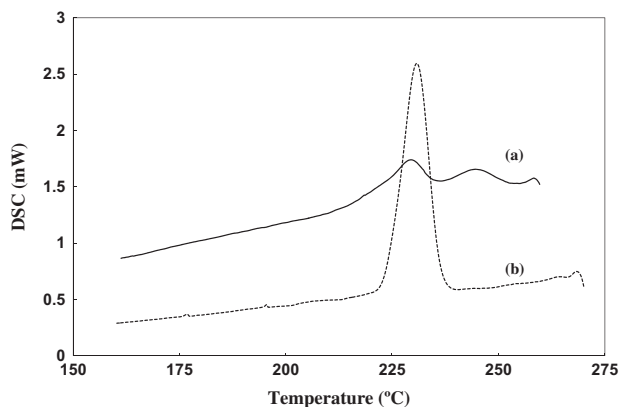


Figure 1 Differential scanning calorimetry (DSC) curves (crystallization profiles) of the syndiotactic polystyrenes (sPS) (Sample 3) cooling process from maximum temperature (T_{\max}) (Scheme 2) of 260 °C (a) or 270 °C (b).

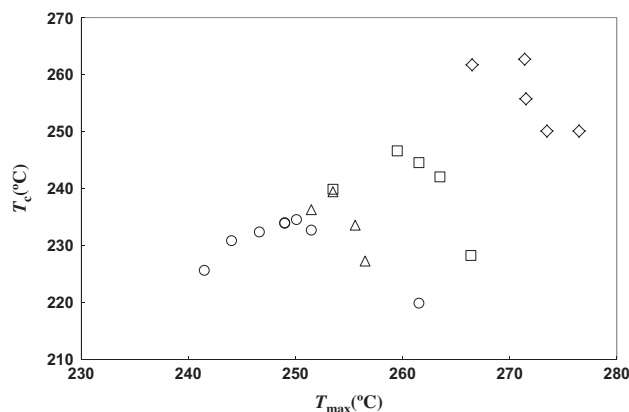


Figure 3 The relationship between maximum temperature (T_{\max}) and crystallization temperature (T_c) of the syndiotactic polystyrenes (sPS) samples: Sample 1 (○), Sample 2 (△), Sample 3 (□) and Sample 4 (◇).

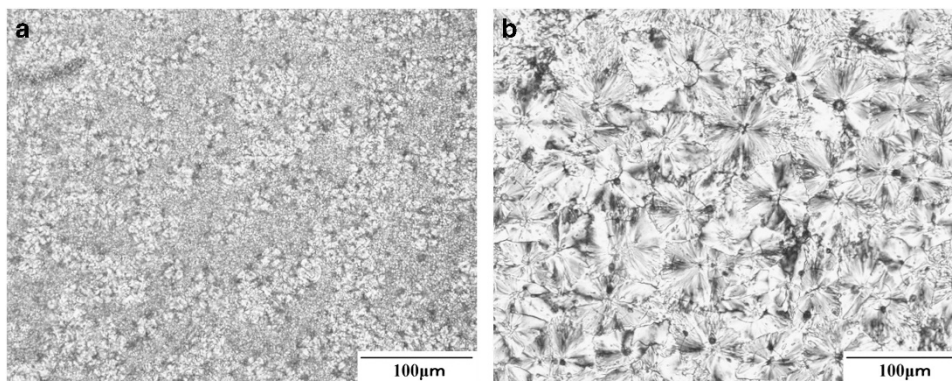


Figure 2 Polarization microphotographs of Sample 3 melted at (a) 260 °C or (b) 270 °C and cooled to room temperature at a rate of 10 °C min⁻¹.

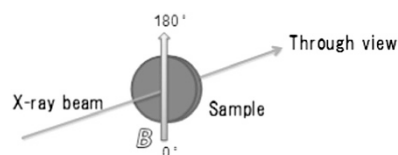
in Table 2. The WAXD pattern of sPS Sample 3 ($T_{an}=260\text{ }^{\circ}\text{C}$ and $T_{itc}=245\text{ }^{\circ}\text{C}$) with a 10 T magnetic field (Run 3) is shown in Figure 4a. The reflections derived from the (0 2 0), (1 1 0), (0 4 0), (1 3 0), (0 6 0) and (1 1 1) planes of the β phase of the orthorhombic crystal are detected at $\sim 2\theta=6.1^{\circ}$, 10.4° , 12.3° , 13.6° , 18.6° and 20.1° , respectively. The crystallized sPS Samples 1 (Run 1) and 2 (Run 2) also showed WAXD patterns derived from the β phase. Figure 4b shows the WAXD pattern of crystallized sPS Sample 4 (Run 6). The reflections derived from the (1 1 0), (2 1 0), (3 0 0), (2 2 0), (4 0 0), (4 1 0) and (2 1 1) planes of the α phase are detected at $\sim 2\theta=6.7^{\circ}$, 10.3° , 11.7° , 13.5° , 15.6° , 17.9° and 20.3° , respectively. Weak reflection peaks derived from the β phase were also detected, indicating the coexistence of a small amount of the β phase in the sample. The difference should be because of the molecular weights of the samples. Sun *et al.* studied the crystalline structures of low-molecular-weight sPS and reported that the low-molecular-weight sPS ($M_w = <63\text{ }000$) formed the β phase.¹⁷ The low-molecular-weight sPS Samples 1–3 ($M_w = 15\text{ }700$ – $49\text{ }200$) should preferentially form the β phase in our experiments. By contrast, the high-molecular-weight sPS Sample 4 ($M_n = 136\text{ }000$) would form both the α and β phases during the temperature program used in Run 6.

The X-ray diffraction pattern and azimuthal scan of the (1 1 1) and (0 2 0) planes of sPS Sample 3 melt crystallized in the 10 T magnetic field (Run 5) are shown in Figure 5. Zero azimuthal angle corresponds to the direction parallel to the magnetic field, as illustrated in Scheme 3. The azimuthal scan of the (0 2 0) plane showed maxima

at 0° and 180° , and that of the (1 1 1) plane showed maxima at 90° and 270° . The azimuthal X-ray scans of the sPS samples melt crystallized under the conditions of Runs 1–4 showed similar patterns.

In the case of an orthorhombic crystal, an axis of easy magnetization must be parallel to one of the crystal axes (a -, b - or c -axis).¹⁸ The azimuthal scan of the (0 2 0) plane indicates that the normal vector of the (0 2 0) plane, namely the b -axis, is parallel to the direction of the magnetic field. The a - and c -axis of the orthorhombic crystal inevitably align perpendicular to the direction of the magnetic field. The alignment direction of the c -axis is same as that of iPS, which forms hexagonal crystals, as reported previously.^{10–12}

The WAXD fiber pattern of the sPS β phase calculated using the reported crystal lattice,² assuming that the b -axis aligns parallel to the magnetic field, is shown in Figure 6. The Miller indices of the planes and azimuthal angles are summarized in Table 3. The calculation indicates that four points of the diffraction from the (1 1 1) plane should be detected at 81.3° (and 98.7° , 261.3° , 278.7°). However, the



Scheme 3 Illustration of the wide-angle X-ray diffraction (WAXD) measurements of the syndiotactic polystyrene (sPS) samples; B : direction of the magnetic field.

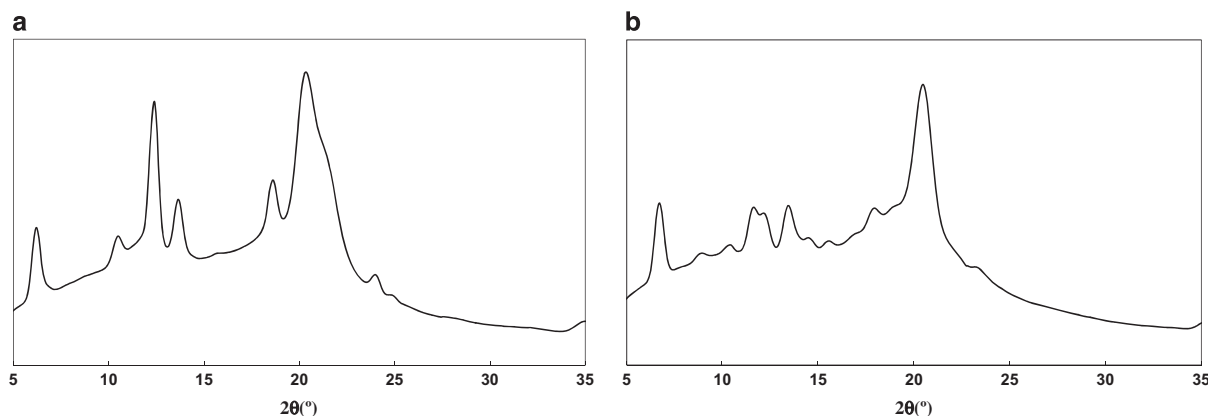


Figure 4 X-ray diffraction patterns of the syndiotactic polystyrene (sPS) samples isothermally crystallized in the 10 T magnetic field: (a) Sample 3, Run 4 and (b) Sample 4, Run 6.

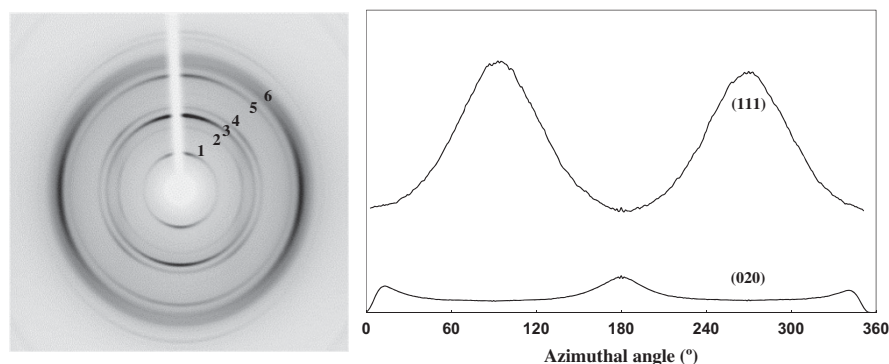


Figure 5 Oriented wide-angle X-ray diffraction (WAXD) pattern and azimuthal X-ray scan of syndiotactic polystyrene (sPS) (Sample 3, Run 4), crystallized in the 10 T magnetic field. Zero azimuthal angle corresponds to the direction parallel to the magnetic field, (0 2 0): Ring No. 1; (1 1 1): Ring No. 6.

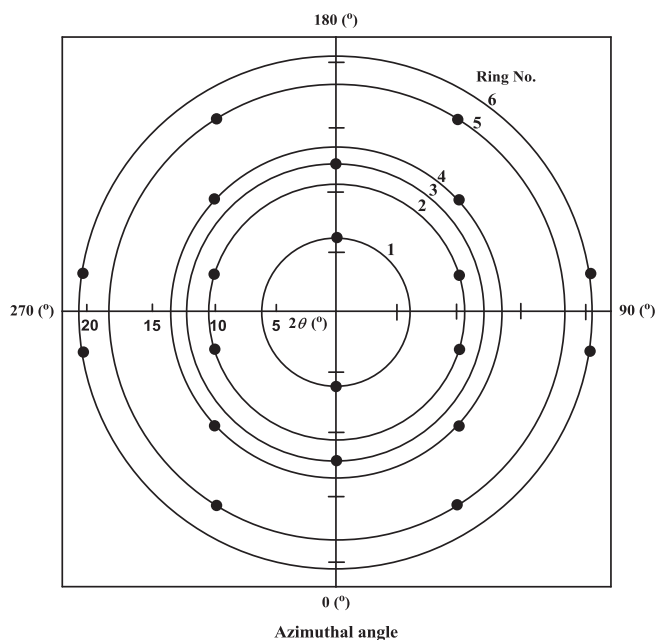


Figure 6 Calculated wide-angle X-ray diffraction (WAXD) fiber pattern of the syndiotactic polystyrene (sPS) β phase assuming that the b -axis aligns parallel to the magnetic field.

azimuthal scan of the (1 1 1) plane showed two maxima at 90° and 270° , as shown in Figure 5. The result can be explained by the broadening of the peaks. The peaks at 81.3° and 98.7° (261.3° and 278.7°) should be detected as one broad peak at 90° (270°).

The degree of the magnetic-field-induced alignment was calculated using the following equations:

$$\langle \cos^2 \phi \rangle = \frac{\int_0^{\pi/2} I(\phi) \cos^2 \phi \sin \phi d\phi}{\int_0^{\pi/2} I(\phi) \sin \phi d\phi} \quad (1)$$

$$f\phi = (3\langle \cos^2 \phi \rangle - 1)/2 \quad (2)$$

where ϕ is the azimuthal angle. The intensity of the scans ($I(\phi)$) was determined based on the baseline at the lowest point of the scans. The intensity distribution of the (0 2 0) azimuthal scan, $f_{\phi 0 2 0}$, was used to quantitatively study the alignment degree of the sPS samples. Integration of $I(\phi)$ from π to $3\pi/2$ is acceptable for the calculation of f_{ϕ} in this experiment instead of integration from 0 to $\pi/2$ because of the symmetry of the peak pattern. When the b -axis is aligned perfectly parallel to the magnetic field or perfectly randomly, $f_{\phi 0 2 0}$ is 1 or 0, respectively. The alignment degrees, the $f_{\phi 0 2 0}$ values, of the sPS samples melt crystallized at T_{an} and T_{itc} in the magnetic field are summarized in Table 2. The alignments of Samples 1 and 2 were detected in the 2 T magnetic field (Runs 1 and 2). By contrast, the alignment of Sample 3 was not observed in the 2 T magnetic field (Run 3). The high magnetic field of 10 T induced clear magnetic-field-induced alignment of Sample 3 (Run 4). The increase in the magnetic field effectively increases the degree of the sPS alignment. The alignment degree of Sample 4 was low even in the 10 T magnetic field (Run 5). The melt viscosities of Samples 1 and 2 were measured using a cone and plate viscometer at approximately T_{itc} of 235°C at 100 r.p.m. The viscosity of Sample 2 was much higher than that of Sample 1 (Table 1). The increase in the molecular weight of the sPS samples markedly increases the melt viscosity at around T_{itc} . The melt viscosities of Samples 3 and 4 were unmeasurable because the T_{itc} of

Table 3 Calculated fiber texture orientation of sPS β phase assuming that b -axis aligns parallel to the magnetic field

Ring no.	(h k l)	2θ ($^\circ$)	Azimuthal angle ($^\circ$)
1	0 2 0	6.1	0.0, 180.0
2	1 1 0	10.5	73.0, 107.0, 253.0, 283.0
3	0 4 0	12.3	0.0, 180.0
4	1 3 0	13.6	47.5, 132.5, 227.5, 312.5
5	0 6 0	18.5	33.2, 146.8, 213.2, 146.8
6	1 1 1	20.5	81.3, 98.7, 261.3, 278.7

Abbreviation: sPS, syndiotactic polystyrene.

the samples were higher compared with the maximum temperature of the heater attached to the viscometer. Although the high T_{itc} of Sample 4 would tend to decrease the viscosity, it seems reasonable to suppose that the high molecular weight of the sample greatly affects its melt viscosity according to the results of Samples 1 and 2. The increase in the molecular weight of the samples should markedly increase the melt viscosity and decrease the mobility of the locally ordered domains.

Slow crystallization should effectively improve the degree of the magnetic-field-induced alignment of crystalline polymers, as previously reported for polyethylene.¹¹ A lower crystallization rate should offer sufficient time for the alignment of the locally ordered domains and induce a high degree of alignment of the crystals. Although the slow crystallization should induce large locally ordered domains, which have large magnetic anisotropies, the mobility of the domains should be low. The formation of small domains via fast crystallization should be better for the high mobility of the domains; however, the magnetic anisotropy of the small domains should be insufficient for magnetic-field-induced alignment. The crystallization conditions that induce locally ordered domains with high mobilities and large magnetic anisotropies are contrary to each other. We tried a stepwise cooling process to solve this problem. Sample 3 was stepwise cooled from 252 to 246°C in 2°C increments in the 10 T magnetic field (Run 5), as indicated by the dotted line in Scheme 1. The sample showed a higher degree of magnetic-field-induced alignment than the samples isothermally crystallized at 245°C (Run 4). The stepwise cooling should decrease the crystallization rate, which should provide time for the alignment of the locally ordered domains and increase the alignment degree.

CONCLUSIONS

The magnetic-field-induced alignment of low-molecular-weight sPS samples was achieved by melt crystallization in a 2 or 10 T magnetic field. The melt crystallization of the sPS samples via the optimized temperature program attained effective alignment. The locally ordered domains derived from residual microcrystals at the annealing temperature promoted heterogeneous nucleation and yielded small spherulite crystals. The melt-crystallized sPS samples with low molecular weights under the optimized temperature programs formed crystals of the orthorhombic β phase. The b -axis of the unit cell of the orthorhombic crystals aligned parallel to the direction of the magnetic field. The low-molecular-weight samples showed high alignment degrees. The stepwise cooling was effective at increasing the alignment degree. The low viscosity and slow crystallization rate in the presence of locally ordered domains are favorable for a high degree of magnetic-field-induced alignment.

The conventional mechanical orientation of sPS aligns the polymer chains parallel to the conducted direction along the c -axis. Although

the degree of orientation is low, the magnetic-field-induced alignment of sPS shows the ability to align the *b*-axis of the sPS unit parallel to the conducted direction without deformation of the specimens.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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