Characterization of Crystallization in Syndiotactic Polystyrene Thin Film Samples

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Received November 23, 1999
Revised Manuscript Received September 25, 2000

Introduction. Plurality crystallizations and how they affect polymorphic behavior of syndiotactic polystyrene (s-PS) have received considerable interest, mainly in bulk samples.1,3 Also having been extensively studied is the development of α- or β-form crystals in s-PS, favored either kinetically or thermodynamically during the crystallization. Upon heating at several scanning rates, the relative fraction of α- and β-form crystals varies in bulk samples. This phenomenon favors the formations of α-form by heating at a high scanning rate. In contrast, the β-form crystal is a preferred means packing over α-form by heating at a low scanning rate and/or by crystallizing at higher temperatures closer to its Tm.4,6 The above observations suggest that the crystal—crystal transformation indeed occurs when s-PS bulk sample contains the α-form as mentioned in previous literature.1,6

Our earlier study investigated the crystallization mechanism of s-PS bulk samples using conventional absorbance FTIR spectroscopy in our previous report.7 FTIR was performed to distinguish the crystal form and crystallinity of s-PS. This work elucidates the effect of s-PS sample thickness on crystallization behavior in melt-, cold-, and heat-scanning crystallizations using FTIR spectroscopy.

Experimental Section. The syndiotactic polystyrene (s-PS) was kindly donated by the Industrial Technology Research Institute (HsinChu, Taiwan) and was used without further purification. The stereoregularity of the syndiotactic polystyrene consists of [rr] = 99% and is identified by the solution 13C NMR spectrum.8 The s-PS thin film samples were prepared by solution casting on a KBr disk, and its thickness was controlled to less than 10 μm, followed by covering with another KBr. The s-PS bulk sample was also obtained from solution casting on KBr disk with a thickness more than 100 μm. Isothermal cold- and melt-crystallization of various time intervals were performed on samples in an environmental chamber with a temperature programmable controller within an accuracy of ±0.1 °C. Next, the s-PS samples were pretreated at 320 °C for 20 min to eliminate the residual crystal memory in the melt-crystallization and then quenched by liquid nitrogen to obtain the amorphous (crystal-free) s-PS as the starting material. For cold-crystallization, the quenched s-PS sample was placed directly into the chamber at 264 °C. For the melt-crystallization, the s-PS sample was heated to 320 °C and quickly cooled (−100 °C/min) to 264 °C. All samples were prepared under a continuous nitrogen flow to minimize sample oxidation or degradation.

The crystal form and crystallinity of the s-PS were characterized by infrared spectroscopy (Nicolet AVA-

TAR 320 FTIR spectrometer, U.S.A.) with a resolution of 1.0 cm−1 at 30 °C, ranging from 940 to 820 cm−1. The frequency scale was internally calibrated using a He–Ne laser, and 32 scans were single-averaged to reduce the noise. The absolute crystallinity of α- and β-forms of s-PS can be calculated from the following equations:7

\[ C_\alpha = \frac{A_{851/\alpha}}{A_{841/\alpha} + A_{851/\alpha} + A_{858/\beta}} \times 100\% \]  

\[ C_\beta = \frac{A_{858/\beta}}{A_{841/\alpha} + A_{851/\alpha} + A_{858/\beta}} \times 100\% \]  

where \( C_\alpha \) and \( C_\beta \) represent the crystallinities of α- and β-forms, respectively, \( A_{841/\alpha} \), \( A_{851/\alpha} \), and \( A_{858/\beta} \) are the area fractions of amorphous, α-, and β-form, as obtained by the absorbance areas ranging from 865 to 820 cm−1. The conversion coefficients \( a_\alpha \) and \( a_\beta \) (0.178 and 0.272) obtained from a previous investigation7 are the ratios of absorptive coefficients of \( A_{851/\alpha} \) and \( A_{858/\beta} \) for α- and β-form crystal absorbances, respectively.

Results and Discussion. Table 1 summarizes the specific absorbance of s-PS in the IR spectrum ranging from 940 to 820 cm−1.9,10 The specific peaks of amorphous phase appear at 905 and 841 cm−1. The specific peaks of α-form are at 901 cm−1 (shifted from 905 cm−1) and 851 cm−1 (shifted from 841 cm−1),7 while the specific peaks of β-form are at 911 cm−1 (shifted from 905 cm−1) and 858 cm−1 (shifted from 841 cm−1).

Figure 1a shows the IR spectrum of the bulk s-PS sample isothermal at 320 °C for 20 min and then cooled to 30 °C at a rate of −10 °C/min. The peaks corresponding to the amorphous phase and α- and β-form crystal are apparent, implying that s-PS crystallizes to α- and β-form crystals during the cooling process. This finding corresponds to the well-known DSC trace results where two endothermic peaks corresponding to α- and β-form crystals always appear simultaneously in a normal cooling rate from the melt.3,11–13 Parts b and c of Figure 1 show the IR spectra of the s-PS in bulk and in thin films which have been heated to 264 °C from 30 °C with a scanning rate of 10 °C/min and then quenched by liquid nitrogen, respectively. Both α-form peaks (901 and 851 cm−1) and β-form peaks (911 and 858 cm−1) appear in FTIR spectra of bulk samples as shown in Figure 1b. The mechanism of crystal growth has been described as follows:11 The α-form nuclei formed at lower temperatures (less than −240 °C) induce the growth of α-form crystal during heating scanning. In addition to the heating scan, the α-form crystal converts into the thermodynamically favored β-form crystal at higher temperatures (greater than −240 °C) in s-PS bulk samples. Therefore, it leads to that s-PS crystallizes into α- and β-form crystals during heating to 264 °C in the bulk samples.

In contrast, only α-form peaks at 901 and 851 cm−1 appear after heating scanning up to 264 °C in thin film s-PS samples as shown in Figure 1c. This finding suggests that α-form crystals transforming to β-form crystals may be physically retarded at a high temperature (above −240 °C) in s-PS thin films with thickness less than 10 μm. Therefore, the s-PS thin film sample does not provide a favorable condition to overcome the energy barrier in order to induce the crystal transfor-
information from $\alpha$-form to a thermodynamically favored $\beta$-form. A critical film thickness must be met to make the $\alpha-\beta$ transformation feasible at a high temperature.

Figure 2 shows the FTIR spectra ranging from 940 to 820 cm$^{-1}$ of the thin film s-PS sample which is melt-crystallized at 264 °C at various isothermal time durations. Notably, only two main peaks located at 905 and 841 cm$^{-1}$ corresponding to the amorphous phase appear in Figure 2a–d where the crystallization process has not begun. The $\beta$-form characteristic peaks, 911 and 858 cm$^{-1}$, begin to emerge when the s-PS thin film sample is melt-crystallized at 264 °C for 20 min. Apparently, the intensity of $\beta$-form peaks gradually increases with an increasing crystallization time. Meanwhile, the relative intensity of amorphous phase peaks gradually decrease. The specific $\alpha$-form peak of $\sim$901 cm$^{-1}$ seems to be observed when the s-PS thin film sample is melt-crystallized at 264 °C for more than 40 min. However, the specific $\alpha$-form peak of $\sim$851 cm$^{-1}$ is not decomposed out after curve fitting. It is noted that the $\alpha$-form may appear, but it is too weak to be apparent in the spectra. This feature corresponds to numerous earlier studies on the s-PS crystallization mechanism which shows that crystallization favors the $\beta$-form crystal at a higher temperature (i.e., above 240 °C) for thermodynamic reasons.\(^3\)

Figure 3 shows the FTIR spectra ranging from 940 to 820 cm$^{-1}$ of the thin film s-PS sample which is cold-crystallized at 264 °C for various isothermal time durations. The peak's intensity at 901 and 851 cm$^{-1}$ reveals that the $\alpha$-form crystal increases with an increasing crystallization time; meanwhile, the relative intensity of the amorphous phase at 905 and 841 cm$^{-1}$ decreases. From this observation, we can infer that the original $\alpha$-form crystal becomes more perfect with an increasing crystallization time at 264 °C, which is reflected by the sharpening of 901 and 851 cm$^{-1}$ peaks. However, this crystal does not convert into the thermodynamically favored $\beta$-form crystal as well as the bulk sample does in the cold-crystallization process. In other
words, the individual lamellae of \( \alpha \)-form crystals can extend upon annealing at 264 °C in s-PS thin film samples.

Comparing Figure 2 and Figure 3 reveals that the intensity of \( \beta \)-form peaks grows more rapidly than the corresponding \( \alpha \)-form. Results obtained from curve fitting ranging between 865 and 820 cm\(^{-1} \) exhibit two main Gaussian peaks that provide an adequate fit with standard deviation square less than 10\(^{-8} \) for systems of melt- and cold-crystallization at 264 °C for 240 min, as shown in the upper-right corners of Figure 2 and Figure 3, respectively. Table 2 summarizes the curve-fitting results of Figure 2j and Figure 3h. The absolute crystallinity of the \( \beta \)-form is 43.2% in the melt-crystallization; meanwhile, that of the \( \alpha \)-form is 60.8% in cold-crystallization, calculated from eqs 1 and 2, as the s-PS is crystallized isothermally at 264 °C for 240 min. Notably, the crystallization rate of the \( \beta \)-form appears to be slower than that of \( \alpha \)-form in thin film samples.

**Conclusions.** In s-PS bulk samples, the \( \alpha \)-form can convert into the thermodynamically favored \( \beta \)-form packing when the temperature is close to the \( T_m \). In s-PS thin film samples, the \( \alpha \)-form crystal formed at lower temperatures continues to grow along with an elevating temperature during cold-crystallization. The usually observed \( \alpha \)-to-\( \beta \)-form transformation at higher temperatures (above 240 °C) does not occur in thin film s-PS samples. The energy barrier of \( \alpha \)-to-\( \beta \)-form transformation cannot be overcome, possibly owing to the physical hindrances in very thin film samples; therefore, such a transformation of crystal form is inhibited.

Results obtained from crystallinity indicated that the crystallization of the \( \beta \)-form has an activation energy exceeding that of the \( \alpha \)-form in thin film samples.

**Acknowledgment.** The authors thank the National Science Council, Taiwan, for financially supporting this research under Contract NSC-88-2116-E-009-006.

**References and Notes**

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MA919763

### Table 2. Results of Curve Fitting Ranging between 865 and 820 cm\(^{-1} \), Absolute Crystallinity of Melt-Crystallized, and Cold-Crystallized s-PS at 264 °C for 240 min; Results from Figure 2j and Figure 3h

<table>
<thead>
<tr>
<th>isothermal time of 240 min</th>
<th>amorphous phase</th>
<th></th>
<th>crystal phase</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>area</td>
<td>freq. a cm(^{-1} )</td>
<td>width b</td>
<td>area</td>
</tr>
<tr>
<td>cold-crystallization</td>
<td>0.410</td>
<td>840.81</td>
<td>10.836</td>
<td>0.113</td>
</tr>
<tr>
<td>melt-crystallization</td>
<td>0.366</td>
<td>840.85</td>
<td>10.699</td>
<td>0.076</td>
</tr>
</tbody>
</table>

a Wavenumber. b Width at half-height, cm\(^{-1} \). c Absorptivity ratio of \( \text{A}_{851}/\text{A}_{841} = 0.178 \). d Absorptivity ratio of \( \text{A}_{858}/\text{A}_{841} = 0.272 \).