Study on the Crystalline Structure Transition of Syndiotactic Polystyrene Film During Heat Treatment by Two-Dimensional Infrared Correlation Spectroscopy

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The crystal structure transition of syndiotactic polystyrene film from the helical conformation to the more stable planar zigzag conformation during a heating process was studied using Fourier transform infrared (FT-IR) spectroscopy in combination with two-dimensional (2D) correlation analysis and perturbation-correlation moving-window 2D analysis. The sequence of different conformations during the transition was investigated by analyzing two-dimensional FT-IR correlation spectra in the spectral ranges of 800–700 cm⁻¹ and 600–500 cm⁻¹. It was observed that the conformation of δ helical changes prior to γ helical, and the γ helical phase is faster than the α' planar zigzag phase. By utilizing the 2D asynchronous correlation spectra, the 744 cm⁻¹ band, which is usually incorporated in the broad 750 cm⁻¹ band, can now be uniquely attributed as the α' zigzag configuration for the first time. Furthermore, by employing thermal perturbation, the shorter helical segments consisting of \( m = 7–12 \) and \( m = 12–20 \) monomeric units were disturbed in a shorter time than the longer helical segments \( m = 20–30 \) during the heating process.

Index Headings: Syndiotactic polystyrene; Two-dimensional correlation; 2D-COS; Phase transformation.

INTRODUCTION

Structural changes occurring in the ordering process of crystalline polymers have attracted considerable interest in recent years. This interest is related to the mechanical properties of polymers, which are sensitive to the change of their crystalline conformations, strongly dependent on external conditions. Syndiotactic polystyrene (sPS) is a well-known engineering polymer with many advantages, such as high crystallization rate, high melting point, high chemical stability, and in particular the polymorphism phenomenon, which was first synthesized by Ishihara in 1986.1–5 A key issue in the property of sPS is the inability to change its high glass transition temperature5 to improve its ductility. By controlling the crystallization conditions,6–8 it is possible to overcome the low ductility.

It has been demonstrated that syndiotactic polystyrene shows a very complex polymorphism6–18 as crystallization conditions are varied. α and β, which are characterized by stable planar zigzag conformations, are found in the melt or glassy state of sPS under different thermal-crystallization conditions. δ, δ', and γ, which adopt unstable T₃G₂ helical chains, are obtained from solvent crystallization. The δ form16–18 can be prepared by solvent casting or sorption of suitable compounds into amorphous or semicrystalline sPS at room temperature. The mesoform δ' form or the “emptied” δ form of sPS can be formed by proper extraction procedures on the δ form with boiling acetone. The δ form can be transformed to the γ form by annealing at 120–130 °C. The crystal transitions from unstable helical phase to stable planar zigzag phase (δ-type → γ-type → α'-type, or δ-type → β-type) can be obtained by elevating the temperature.13–15

Fourier transform infrared (FT-IR) spectroscopy is a sensitive method for detecting the conformational transition from both helical and planar zigzag crystal forms. Most of the IR work16–24 was focused on the spectral differences between the various crystalline forms of sPS upon heating or annealing. At present, two-dimensional correlation FT-IR spectroscopy (2D-COS) proposed by Noda25,26 is an excellent technique to look into the spectral intensity fluctuation under variable perturbations such as time, temperature, pressure, concentration, or electric field strength.27–29 Therefore, the specific order of events and the dynamical mechanism of the system in the perturbing process can be discerned. Through spreading the peaks over the second dimension, 2D spectra can reveal subtle information not obvious in 1D spectra, help to ascertain the unknown assignments, and efficiently improve the spectral resolution.30 These characteristics can give us lots of interesting information about the sequential order of the crystal forms with increase of temperature. Perturbation-correlation moving-window two-dimensional correlation spectroscopy (PCM2W2DCOS) was developed by Noda and Morita et al.31–33 in 2006. The main advantage of this mathematical method is that it can reveal a spectral intensity variation at a typical point on the plane between a spectral variable axis and a perturbation variable axis, such as a melting temperature at an index band of crystallinity.

Thus, with the application of 2DCOS and PCM2W2DCOS, the mechanism of the complex polymorphism in the crystalline region of sPS, which is closely related to the sequential order of the transitions of various crystal conformations during the temperature elevation process, can be probed. In this work, the crystal structure transitions of sPS film from δ helical to γ helical phase and γ helical to stable α' planar zigzag phase were detected by 2D correlation FT-IR spectroscopy in the spectral ranges of 800–700 cm⁻¹ and 600–500 cm⁻¹.

EXPERIMENTAL

Sample Preparation and Fourier Transform Infrared Spectroscopy. Syndiotactic polystyrene was kindly supplied by Professor Rastogi from Eindhoven University of Technology, with a weight-averaged molar mass (Mw) of 400 kg/mol. The 1% sPS solution was prepared by dissolving 0.1 g of sPS into 10 mL of chloroform at the boiling temperature of chloroform. The sPS solution was cast onto the KBr window.
and was dried under an infrared ray light to ensure complete removal of the solvent. Afterward, the sample was transferred to a temperature cell in the spectrometer at 60 °C. It was checked that there were no apparent solvent signals in the IR spectra at 60 °C, followed by a cooling step to 40 °C before starting the heating process.

The FT-IR measurements were performed at a resolution of 4 cm⁻¹ with a Nicolet FT-IR spectrometer equipped with a DTGS detector. Variable-temperature spectra were recorded in a temperature cell between 40 °C and 200 °C with intervals of 5 °C. The spectra used for analysis were obtained from the subtraction of the background and the sample spectra at varying temperatures.

**Two-Dimensional Correlation Spectroscopic Analysis.** Several spectra at equal temperature intervals were selected for the 2D correlation analysis using the 2D shige software composed by Shigeaki Morita (Kwansei-Gakuin University, Japan). The 2D correlation spectrum is shown in the center of the map, while the averaged 1D reference spectrum is shown at the side and top for comparison. In the 2D correlation maps, the lighter gray-scale shaded regions are defined as the positive correlation intensities, whereas the darker gray-scale shaded ones are regarded as the negative correlation intensities.

**PCMW2D Analysis.** The PCMW2D analysis was performed by the 2D shige software. The window (2m + 1) was selected as 7, which means 7 spectra were selected every time to calculate an average spectrum. The lighter gray-scale shaded regions are defined as the positive correlation intensities, whereas the darker gray-scale shaded ones are regarded as the negative correlation intensities. The spectral variations could be interpreted using the rules of PCMW2D correlation spectroscopy proposed by Morita et al. 31–32 for the cases of linear increment perturbation in Table I.

**RESULTS AND DISCUSSION**

**Crystallization Characteristics from Fourier Transform Infrared Spectra.** Fourier transform infrared spectroscopy is a sensitive method to distinguish structural changes, which has been shown by so much remarkable work on crystalline conformations. 16–20 Figure 1 shows the IR spectrum of sPS film at room temperature in the range of 1000–500 cm⁻¹, which is highly sensitive to the conformation changes. There exist several bands at 941, 931, 906, 769, 757, 572, and 547 cm⁻¹ in the spectrum, which are assigned to a typical δ helical conformation. A summary of the frequency positions and their assignments is listed in Table II.

<table>
<thead>
<tr>
<th>Region (cm⁻¹)</th>
<th>Peak (cm⁻¹)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>800–700</td>
<td>769</td>
<td>δ helical</td>
</tr>
<tr>
<td></td>
<td>765</td>
<td>γ helical</td>
</tr>
<tr>
<td></td>
<td>750</td>
<td>Amorphous</td>
</tr>
<tr>
<td></td>
<td>744</td>
<td>α¹ zigzag</td>
</tr>
<tr>
<td>600–500</td>
<td>572, 547</td>
<td>δ helical</td>
</tr>
<tr>
<td></td>
<td>538</td>
<td>α¹ zigzag</td>
</tr>
<tr>
<td></td>
<td>536</td>
<td>Amorphous</td>
</tr>
</tbody>
</table>

![Fig. 1. FT-IR spectrum of syndiotactic polystyrene film at room temperature in the spectral range 1000–500 cm⁻¹.](image-url)

The predominant δ helical conformation in solvent-induced sPS film changed to γ helical and then to more stable all-trans zigzag conformation during the heating process at 100 °C and 170 °C, respectively, which can be observed in the variable-temperature IR spectrum. In this work, IR spectra are divided into two regions of 800–700 cm⁻¹ and 600–500 cm⁻¹, which are usually chosen to distinguish the helix and zigzag conformations. With two-dimensional correlation analysis, additional information such as complex or overlapped spectral features could be obtained by spreading peaks along the second dimension.

**The 800–700 cm⁻¹ Region.** Figure 2 shows the relevant IR spectra of an sPS film in the range of 800 to 700 cm⁻¹ collected from 40 °C to 200 °C. This region corresponds to the C–H out-of-plane bending of the phenyl ring. The position of the absorbance band at 769 cm⁻¹ shifted gradually down to 765 cm⁻¹ and the intensity slightly decreased with increasing temperature until 100 °C, which is the result of the transition from the δ helical to a more closely packed γ-crystal conformation after complete removal of the solvent molecules. The slight change of the intensity is attributed to the intramolecular interaction of the helical chains packed in the monoclinic crystals. There was a sudden enhancement of the
absorbance of 765 cm\(^{-1}\) at 100 °C due to the transition. Afterward, the intensity was almost constant before disappearing at the transition temperature of \(\gamma \rightarrow \alpha'\) 170 °C. The intensity of the disordered phase band at 750 cm\(^{-1}\) was continuously decreasing between 40 and 100 °C, followed by a constant plateau before a rapid increase at 160 °C.

The intensity variation information can be observed by PCMW2D correlation analysis. Figure 3a shows a synchronous PCMW2D correlation spectrum constructed from the temperature-dependent IR spectra in the region of 800 to 720 cm\(^{-1}\) of sPS thin film. It is apparent that there are two remarkable changes of vibration intensity at around 100 °C and 160 °C in the result of two apparent transitions of \(\delta \rightarrow \gamma\)-crystal and \(\gamma \rightarrow \alpha'\)-crystal. Furthermore, the trend of intensity variation changes of the two peaks of 769 and 750 cm\(^{-1}\) is totally different before and after 130 °C (as the dotted line shows); therefore the analysis is separated into two temperature ranges of 40 °C to 120 °C and 120 °C to 200 °C in the following study. Since the PCMW2D correlation spectra were calculated from a series of 1D spectra with intervals of 10 °C, the position of the temperature point can deviate by a few degrees. In the temperature range of 40–130 °C, one positive and one negative correlation peak are identified at (769 cm\(^{-1}\), 90 °C) and (750 cm\(^{-1}\), 85 °C). These correlation peaks indicate that the increase and the decrease in the intensities of the bands at 769 cm\(^{-1}\) and 750 cm\(^{-1}\) became maximum at around 90 °C. The peaks at (769 cm\(^{-1}\), 160 °C) and (750 cm\(^{-1}\), 160 °C) become negative and positive in the temperature range of 130–200 °C. The intensity changes of 769 cm\(^{-1}\) and 750 cm\(^{-1}\) correspond with the results from 1D IR spectra.

More details of the intensity variation along the perturbation direction can be collected from the asynchronous correlation spectra in Fig. 3b. The asynchronous correlation values at 750 cm\(^{-1}\) change from positive to negative at the temperature 70 °C and 110 °C. Based on the rules of PCMW2D correlation analysis in Table 1, since the synchronous correlation value at (750 cm\(^{-1}\), 85 °C) is negative, the intensity of the band at 750 cm\(^{-1}\) concavely increased around 75 °C and concavely decreased around 110 °C. That means the intensity of the amorphous band at 750 cm\(^{-1}\) started to decrease sharply when the temperature arrived at 90 °C. In the temperature range of 130 °C to 200 °C, the positive correlation peak (765 cm\(^{-1}\), 150 °C) and negative correlation peak (750 cm\(^{-1}\), 150 °C) demonstrate that the intensity of the band at 765 cm\(^{-1}\) convexly decreased and the intensity of the band at 750 cm\(^{-1}\) concavely increased. The intensity change of 765 cm\(^{-1}\) shows that the decrease of the \(\gamma\) helical conformation becomes rapid around 150 °C. However, the increase of 750 cm\(^{-1}\) can not be explained as the amorphous phase was increasing in the range of 130–200 °C. Since PCMW2D can only give information on a spectral intensity variation at a typical point on a perturbation axis, it is inadequate to analyze the spectra with subtle peaks incorporated in a broad band. The explanation of the increase of the intensity of the band at 750 cm\(^{-1}\) will be shown in the following 2DCOS analysis.

With the help of 2DCOS spectra, subtle information, which is not obvious in the 1D spectra, can be revealed to help ascertain the unknown assignments and efficiently improve the spectral resolution. For particular software problems, the position of some bands in the 2D spectra can deviate by a few wavenumbers.

The synchronous 2D spectrum in the range 800–700 cm\(^{-1}\) generated from the temperature-dependent spectra between 40 °C to 120 °C is displayed in Fig. 4a. The 2D synchronous spectra are symmetric with respect to the diagonal line in the correlation map. Auto peaks appearing along the diagonal, which are always positive, represent the autocorrelation of perturbation-induced molecular vibrations. Cross-peaks \(\phi(v_1, v_2)\) located at off-diagonal positions may be positive or negative, and represent the simultaneous or coincidental
changes of spectra intensity variations measured at \( m_1 \) and \( m_2 \). Positive synchronous cross-peaks indicate that the intensity variations upon temperature increase at wavenumber \( v_1 \) and \( v_2 \) proceed in the same direction, while negative synchronous cross-peaks show that the changes are in the opposite direction, i.e., the intensity of one band is increasing and that of the other is decreasing. Figure 4a shows one strong auto-peak at 750 cm\(^{-1}\) that is attributed to the amorphous phase. The positive synchronous cross-peak (769, 750 cm\(^{-1}\)) means that the intensity of both the 769 cm\(^{-1}\) and 750 cm\(^{-1}\) bands, which is characteristic of the \( \delta \) helical configuration and amorphous phase, decreased with increasing temperature. The negative cross-peak (765, 750 cm\(^{-1}\)) shows that the intensity of 765 cm\(^{-1}\) attributed to the \( \gamma \) helical configuration changed in the opposite way compared with the amorphous phase. This result corresponds with 1D IR spectra, which means that the intensity of the \( \gamma \) helical configuration was increasing in the temperature region of 40 °C to 120 °C; on the other hand, the intensities of the \( \delta \) helical and amorphous conformation were decreasing. Figure 5a shows the synchronous 2D spectrum generated from 120 °C to 200 °C. The negative cross-peak (765, 744 cm\(^{-1}\)) shows that the band at 744 cm\(^{-1}\) increased in this temperature range. The band at 744 cm\(^{-1}\) can be assigned to the \( \alpha' \) zigzag configuration, which is incorporated in the broad amorphous band at 750 cm\(^{-1}\) and can not be observed in the 1D IR spectrum. There is an immediate increase of the intensity of the broad amorphous band at 750 cm\(^{-1}\) at the transition temperature of the \( \gamma \) helical to \( \alpha' \)-crystal phase, which denotes the increase of the intensity of the band at 744 cm\(^{-1}\) or the formation of \( \alpha' \)-crystal phase.

Figures 4b and 5b show the asynchronous spectra of sPS collected from the temperature-dependent spectra of 40–120 °C and 120–200 °C. An asynchronous spectrum represents sequential or successive changes of spectral intensities measured at \( v_1 \) and \( v_2 \). The 2D asynchronous spectra are asymmetric with respect to the diagonal line in the correlation map. Unlike the synchronous spectra, only cross-peaks located at off-diagonal positions appear in the asynchronous spectra. The intensity of the asynchronous spectrum \( \psi(v_1, v_2) \) represents sequential or successive changes of spectral intensities observed at \( v_1 \) and \( v_2 \). Asynchronous cross-peaks can probe the specific order of the spectral intensity changes taking place while the sample is subjected to an environmental perturbation. According to Noda’s rule,\(^{37} \) if synchronous correlation \( \phi(v_1, v_2) > 0 \) and the asynchronous correlation intensity \( \psi(v_1, v_2) \) is positive, the intensity of band \( v_1 \) varies prior to band \( v_2 \); then if \( \psi(v_1, v_2) \) is negative, band \( v_1 \) varies behind band \( v_2 \). This order, however, is reversed if \( \phi(v_1, v_2) < 0 \).

On the basis of this feature of the asynchronous spectra, more information about the sequential order of the band intensity changes in the process of elevated temperature can be obtained. According to the interpretation rules of such signs by
cross-peaks (769, 765 cm\(^{-1}\)) > 0, (765, 750 cm\(^{-1}\)) < 0, and (750, 744 cm\(^{-1}\)) > 0 can be obtained in Fig. 4b. The positive cross-peak (769, 765 cm\(^{-1}\)) indicates that the change of the \(\delta\) helical configuration occurs predominately before the \(\gamma\) helical configuration between 40 \(^\circ\)C and 120 \(^\circ\)C. And the cross-peaks (765, 750 cm\(^{-1}\)) < 0 and (750, 744 cm\(^{-1}\)) > 0 indicate that the intensity change of the amorphous band at 750 cm\(^{-1}\) varied faster than that of the bands at 765 cm\(^{-1}\) and 744 cm\(^{-1}\), which are attributed to the \(\gamma\) helical and \(\alpha'\) zigzag configurations, respectively. Furthermore, the asynchronous correlation spectrum in Fig. 5b, collected from 120 \(^\circ\)C to 200 \(^\circ\)C, shows four cross-peaks (769, 765 cm\(^{-1}\)) > 0, (765, 750 cm\(^{-1}\)) < 0, and (750, 744 cm\(^{-1}\)) > 0. The cross-peaks (765, 750 cm\(^{-1}\)) < 0 and (750, 744 cm\(^{-1}\)) > 0 can be observed in both Figs. 4b and 5b. Thus, the same results can be obtained showing that the amorphous phase is the fastest phase in the entire process, which can be induced at the lowest temperature. And cross-peaks (769, 765 cm\(^{-1}\)) > 0 and (769, 744 cm\(^{-1}\)) > 0 indicate that the change of the \(\delta\) helical configuration occurs prior to the \(\gamma\) helical and zigzag configurations during the transition of \(\gamma\) helical to stable \(\alpha'\) planar zigzag.

The sequence of the bands of different crystal conformations in the heating process is shown below:

- Amorphous phase
  - \(\delta\) helical configuration
  - \(\gamma\) helical configuration, \(\alpha'\) zigzag configuration

The 600–500 cm\(^{-1}\) Region. Figure 6 displays the variable-temperature IR spectra of sPS in the range of 600 to 500 cm\(^{-1}\) collected from 40 \(^\circ\)C to 200 \(^\circ\)C, which reveals that there was an apparent change of the spectrum at 170 \(^\circ\)C. Both of the bands at 572 cm\(^{-1}\) and 547 cm\(^{-1}\) disappeared at this phase transition temperature. The band at 536 cm\(^{-1}\) shifted to 538 cm\(^{-1}\) with a rapid enhancement of intensity at 170 \(^\circ\)C. This shift is attributed to the transition of the amorphous phase to zigzag conformation. It is obvious that the \(\alpha'\) spectrum didn’t show a difference at the transition temperature of 100 \(^\circ\)C (\(\delta\) helical \(\rightarrow\) \(\gamma\) helical). Since there is no special information in PCMW2DCOS, the spectrum isn’t shown here. Thus, this region is only sensitive to the transition of the helical phases to the stable planar zigzag phase. Depending on the transition temperature, the 2D correlation analysis is focused on the whole temperature range between 40 \(^\circ\)C and 200 \(^\circ\)C. Additionally, different critical sequence lengths can be distinguished from this region. The assignment of the vibration bands is listed in Table III.

The synchronous 2D spectrum generated from the temperature-dependent spectra of the range 600–500 cm\(^{-1}\) between 40 \(^\circ\)C to 200 \(^\circ\)C is shown in Fig. 7a. The negative cross-peaks (572, 538 cm\(^{-1}\)) and (549, 538 cm\(^{-1}\)) indicate that the intensities of the bands at 572 and 549 cm\(^{-1}\) decreased, which are assigned to the helical configuration, and the \(\alpha'\) zigzag band at 538 cm\(^{-1}\) increased with elevated temperature. This kind of transition can be detected by asynchronous spectra in Fig. 7b.

### Table III. Critical sequence lengths \(m\) evaluated for the IR bands of sPS crystalline forms.8

<table>
<thead>
<tr>
<th>(T_2G_2) conformation</th>
<th>(m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>502 cm(^{-1})</td>
<td>12–20</td>
</tr>
<tr>
<td>549 cm(^{-1})</td>
<td>7–12</td>
</tr>
<tr>
<td>572 cm(^{-1})</td>
<td>20–30</td>
</tr>
</tbody>
</table>

![Fig. 6. FT-IR spectra in the spectral range 600–500 cm\(^{-1}\) collected from 40 \(^\circ\)C to 200 \(^\circ\)C.](image)

![Fig. 7. (a) Synchronous and (b) asynchronous 2D correlation spectrum in the spectral range 600–500 cm\(^{-1}\) from 40 \(^\circ\)C to 200 \(^\circ\)C.](image)
The positive cross-peaks at (536, 503 cm\(^{-1}\)) and (549, 538 cm\(^{-1}\)) (the rule is opposite when the band appearing at the same position in the synchronous spectrum is negative) show us that the amorphous band at 536 cm\(^{-1}\) responded faster than the helical band at 503 cm\(^{-1}\) and the change of the helical band at 549 cm\(^{-1}\) occurred prior to the zigzag band at 538 cm\(^{-1}\) when induced by the heating process. As mentioned in the literature,\(^6\) the concept of critical sequence length \(m\) is defined as the length of a regular sequence with a specific conformation, which can be determined by the various vibration bands shown in Table III. In the asynchronous spectrum shown in Fig. 6b, the two negative cross-peaks (572, 549 cm\(^{-1}\)) and (572, 503 cm\(^{-1}\)) show that the intensity of the band at 572 cm\(^{-1}\) decreased faster than that of the bands at 549 and 503 cm\(^{-1}\). Therefore, it can be supposed that the shorter helical sequence segments \(m\) containing 7–12 and 12–20 monomeric units had a quicker response than that of the 20–30 monomeric units when induced by heat.

The results demonstrate that generalized 2D-IR correlation spectroscopy is a powerful method to study the ordering of different crystal segments in the induction period of polymer crystallization.

CONCLUSION

With the application of 2DCOS and PCMW2DCOS, the evolution of crystalline structural was observed in the solvent cast sPS film during thermal perturbation. Two conformational transitions were detected: \(\delta\) helical to \(\gamma\) helical configuration and \(\gamma\) helical to the more stable \(\alpha\) planar zigzag phase. Two regions of the IR spectra, 800–700 cm\(^{-1}\) and 600–500 cm\(^{-1}\), were chosen to be studied, which are sensitive to the helix and zigzag conformation.

Region of 800–700 cm\(^{-1}\): The sequential order of various crystal conformations of sPS was probed during the temperature elevation process. The change of the \(\delta\) helical configuration occurs faster than the \(\gamma\) helical configuration between 40 °C and 120 °C. The \(\delta\) helical configuration occurs faster than the \(\gamma\) helical and zigzag configuration during the transition between 120 °C and 200 °C. In the whole process, the amorphous configuration always changed earlier than both the helical and zigzag configuration. The band at 744 cm\(^{-1}\), which is usually incorporated in the broad 750 cm\(^{-1}\) band, can be split via 2D correlation analysis and can now be uniquely attributed as the \(\alpha\) zigzag configuration.

Region of 600–500 cm\(^{-1}\): The order of different helical sequence segments was investigated, showing that the shorter helical segments consisting of \(m = 7–12\) and \(m = 12–20\) monomeric units were disturbed in a shorter time than the longer helical segments \(m = 20–30\) during the heating process.

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