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Structural Changes during Thermally Induced Phase Transitions Observed for Uniaxially Oriented δ Form of Syndiotactic Polystyrene

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ABSTRACT: The temperature dependence of the X-ray fiber diagram and polarized infrared spectra has been measured successfully for the first time for the δ form of uniaxially oriented syndiotactic polystyrene, which was obtained by dipping the uniaxially oriented samples into organic solvents, for example toluene. The δ form is known to transform to the γ form in a broad temperature range by purging out the solvent molecules. It has been confirmed that no other form like empty δ form appears during this δ to γ transition. At higher temperatures around 190−200 °C the γ form was found to transform to the mixture of α and β forms, not simply to the α form as having been reported so far. The DSC thermogram showed an endothermic peak followed by an exothermic peak in the course of transition from the γ form to α (and β) form. These thermal peaks had been speculated to reflect the melting of the γ form followed by the recrystallization into α (and β) form. But, judging from the clear X-ray diffraction diagram of highly oriented α (and β) form, the molecular chains must keep the orientation almost perfectly during this transition. The infrared spectra also show the well-oriented chain conformations of T_2G_2 and all-trans types during the transition. The γ form has been speculated to transform transiently to a disordered state without losing the chain orientation and then transform into more regular α (and β) form.

Introduction

Syndiotactic polystyrene (sPS) exhibits various types of crystal modifications with different molecular conformations as well as different packing structures of these chains, which are obtained by controlling the preparation conditions of the samples.[1−24] The application of external conditions, e.g., temperature, solvent atmosphere, etc., causes quite complicated phase transitions.[1−24] The α and β forms with all-trans planar-zigzag (T_4) conformation are obtained by cooling the melt or by heating the glass prepared by quenching the melt into ice−water bath.[3−7] The α form crystallizes into a hexagonal unit cell whereas the β form crystallizes into an orthorhombic unit cell.[6,8−11] They are further classified into the disordered forms (α′ and β') and the ordered forms (α″ and β'') depending on the disorderliness of chain packing mode.[3−7] A mesophase of all-trans planar-zigzag conformation was also reported, which can be obtained by stretching the amorphous sample around the glass transition temperature.[12] The δ form having helical conformation $[-(T_2G_2)_2-]$ can be obtained by supplying an organic solvent to the glassy samples and forms a complex between the polymer and the solvent.[1,2,13,14,25−27] The chains in the δ form are packed in a monoclinic unit cell.[30] The δ_e form (empty δ) is obtained by extracting the solvent molecules from the δ form in acetone and further rinsing in methanol or by keeping the δ form in CO_2 of the supercritical fluid state.[15−17,23] The δ_e form retains the helical structure similar to the δ form but contains the cavities, which had been occupied by solvent molecules.[15−17] Heating the δ form at around 100 °C results in the γ form by purging away the solvent molecules.[13−15,18−22] The γ form is solvent-free, and the T_2G_2 chains are packed side by side in the crystal lattice. The γ form is also obtained by dipping the glassy sample into solvents like acetone,[20] 1,1,2,2-tetrachloroethane,[24] supercritical CO_2,[28] or bulky molecules which are too big to be enclosed as a guest of sPS clathrate phase.[29]

The phase transformation of sPS among the above-mentioned crystal modifications has been widely studied by using various techniques including X-ray and electron diffraction,[13−15,18,19,31,32] infrared and Raman spectroscopy,[20,33−36] solid-state NMR,[37,38] and conformational energy analysis.[39] The δ form transforms to the γ form above 100 °C, which transforms to the α form around 190 °C. The δ form and γ form also transform into the β form directly by heating the sample in the presence of solvent molecules in the amorphous region. Most of the measurements about the crystalline transitions starting from the δ form had been carried out at room temperature after annealing the samples at elevated temperatures. Gowd et al.[19,20] carried out the in-situ measurements of X-ray diffraction and infrared spectra starting from the δ form during the heating process to understand the phase transition mechanisms. The transition from δ to γ form depends on the relative amount of solvent present in the starting δ form sample.[19] Yoshioka and Tashiro[21,22] measured the infrared spectral change in the course of heating the δ form and found that the transition occurs directly from the δ to γ form and not via the δ_e form. On the other hand, when the δ_e form is heated, it transforms to an intermediate form transiently before transforming into the γ form.[15,40−42]

Though the phase transitions from δ to γ to α, δ_e to γ were reported in this way, the detailed mechanism of these phase transitions has not yet clarified well. In most of the earlier studies the δ form samples used were unoriented. For example, the X-ray diffraction pattern of such an unoriented sample consists of the reflections overlapping in a complicated manner, making the data analysis ambiguous more or less. We need to utilize the oriented samples to avoid the overlap of reflections in the X-ray diffraction and infrared spectra, by which the data collected during the heating process should become more useful for the clarification of the phase transition behavior. In the previous paper we reported the temperature dependence of the X-ray fiber diagram and polarized infrared spectra of the δ_e form in the heating process and discussed the structural change from δ_e to γ form more clearly than before.[40] In order to make

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characteristic features of the transition behavior of the δ_e form clearer, we need to perform a similar experiment for the uniaxially oriented δ form, as will be described in the present paper. Strictly speaking, the phase transition behavior of the oriented sample might be different from that of the unoriented sample. But the essential features of the phase transitions from the δ form to γ form and α (β) form have been found to be almost the same between these two types of samples, as will be mentioned in a later section.

To our knowledge there is no article appearing in the literature on the 2-dimensional X-ray fiber diagrams measured at different temperature with a purpose to understand the structural changes during heating of the uniaxially oriented δ form. We will also report here the change in the polarized infrared spectra during heating of the uniaxially oriented δ form film, which may give us useful information about the intermolecular interactions as well as the chain conformation. We believe that the present data should make a significant contribution to better understanding of the phase transitions of sPS.

Experimental Section

Samples. sPS pellets (M_w 272 000, M_w/M_n 2.28) were kindly supplied by Idemitsu Petrochemical Co., Ltd. The glassy samples were prepared by quenching the melt into ice water. A small piece of rectangular shape was cut out from the amorphous strip and stretched by about 5 times the original length at around the glass transition temperature (~100 °C) above the hot plate. These uniaxially oriented samples were dipped in toluene for 3 days at ambient temperature to obtain the oriented δ form. The samples removed from toluene were kept at ambient temperature until they became perfectly dry. A similar method was followed to prepare thin films for FTIR studies.

Measurements. The oriented δ form sample was set into a homemade brass-block heater for the X-ray diffraction measurement. This heater was set on a goniometer head of the X-ray diffraction apparatus. The fiber diagrams were recorded using an imaging plate system DIP 1000 (MAC Science Co. Japan) with graphite-monochromatized Cu Kα line as an incident X-ray beam. The infrared spectra were measured with a Varian FTS 7000 series FT-IR spectrometer. The sample was sandwiched between a pair of KBr plates and then set to a homemade heating cell. The infrared spectral measurement was made at a resolution power 1 cm^{-1}. The IR polarization measurements were made using a KRS-5 wire grid polarizer. Two successive IR measurements, with parallel and perpendicular polarizations of the electric vector with respect to the draw direction of the specimen, were performed at every constant temperature during heating. The DSC thermograms were measured in the heating process by using a differential scanning calorimeter TA Instruments DSC Q1000 under a nitrogen gas atmosphere at the rate of 10 °C/min.

Results and Discussion

δ-to-γ Transition. At first, the DSC thermogram was investigated carefully on the uniaxially oriented δ form of the sPS and toluene complex. A broad endothermic peak was observed during the δ to γ phase transition in the temperature range of 100−150 °C, as shown in Figure 1. The endothermic peak in this temperature range is assigned to the evaporation of toluene molecules from the δ form followed by the δ to γ phase transition. It should be noted here that the δ-to-γ transition region observed for the oriented sample is essentially same as that observed for the unoriented sample as seen in the DSC data reported so far.[13] This can be said also about the temperature dependences of X-ray diffraction[13,15] and infrared spectra.[14−16] In other words, the utilization of the oriented sPS samples may allow us to perform more detailed investigation of the essential features of the δ-to-γ phase transition without any disturbance coming from the ambiguity due to the use of the unoriented samples, as will be seen below.

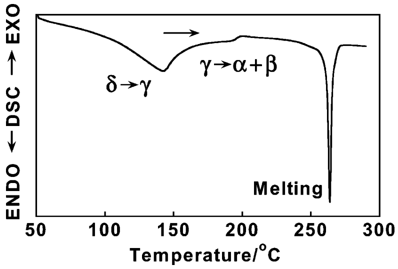

Figure 1. DSC thermogram of uniaxially oriented δ sample of sPS and toluene complex taken in the heating process.

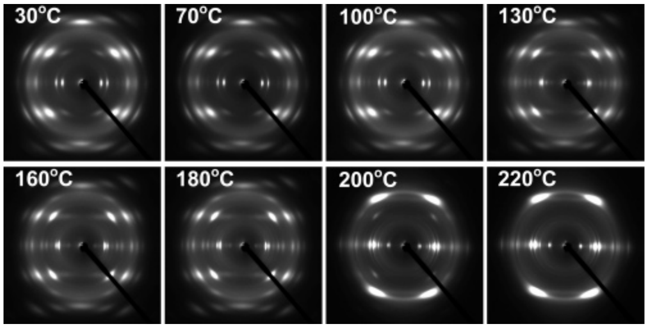

Figure 2. Temperature dependence of the X-ray fiber diagram taken for the uniaxially oriented δ form of sPS/toluene complex in the heating process.

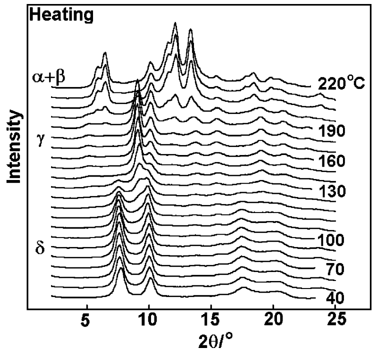

Figure 3. Temperature dependence of X-ray diffraction profile on the equatorial line of the δ form derived from the sPS/toluene complex.

Figure 2 shows a series of X-ray fiber diagrams measured at different temperatures starting from the uniaxially oriented δ form of sPS−toluene complex. The change in the equatorial line profile evaluated from the fiber diagram is shown in Figure 3. The variation in the integrated intensities of the reflections corresponding to each crystalline form was evaluated by the deconvolution method and plotted against temperature, as shown in Figure 4. The 010 reflection of the δ form at $2\theta = 8.0°$ started to decrease its intensity at 100 °C and vanished at 130 °C. Simultaneously, a new reflection characteristic of the γ form appeared at about $2\theta = 9.2°$ at 110 °C, and the intensity increased up to 130 °C. The phase transition from δ to γ occurs over a broad range of temperature, and these two forms coexist in this temperature range. The 2-D X-ray fiber diagram looks like a simple overlap of the two types of diagrams due to the δ and γ forms in this temperature region. It is worth mentioning here that in the case of the δ_e to γ transition we observed an intermediate form with halo-like diffuse scatterings in the fiber diagram because of the disordered structure due to the voids present in the δ_e form.[40] However, in the present case of δ form, the toluene molecules in the crystal lattice might play a role to

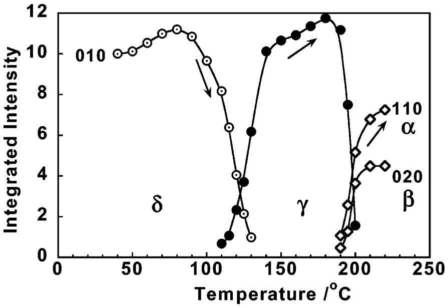

Figure 4. Temperature dependence of the integrated intensity of the reflections at $2\theta = 8.0^\circ$ (δ), 9.1° (γ), 6.5° (α), and 6.0° (β) evaluated from Figure 3.

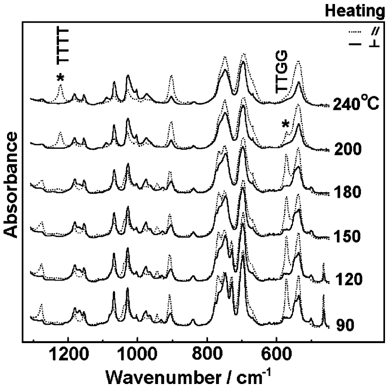

Figure 5. Polarized infrared spectra measured for the uniaxially oriented δ form of sPS and toluene complex at three different temperatures in the frequency region 450−1250 cm^{-1}. The solid and broken lines indicate the perpendicular and parallel band components with respect to the draw direction, respectively. In the spectra at 180 and 200 °C, both helical and planar-zigzag contribution is detected as seen from 572 and 1222 cm^{-1} bands (asterisks).

accelerate the phase transition from the δ to γ form without such an intermediate form. Several papers were reported from the viewpoints of experiments and computer simulation about the diffusion behavior of solvent molecules included in the crystal lattice.[21,43−45] At present, it is not concretely clear how the solvent molecules go out of the columns built up by sPS chains and solvent molecules by heating the δ form. Anyway, however, it might be speculated that the structure becomes unstable once the solvent molecules leave the crystal lattice by heating the δ form because the thermal mobility of the sPS chains is also enhanced by increasing temperature. Then such an unstable lattice transforms immediately to the γ form without any passage to the intermediate form or δ_e form.

To further understand the phase transition behavior with the eye of infrared spectroscopy, we carried out the temperature-dependent polarized infrared measurements of uniaxially oriented δ sample. Figure 5 shows the polarized infrared spectra measured at various temperatures during heating from the uniaxially oriented δ form. Figure 6a shows the extended polarized infrared spectra in the frequency region 450−620 cm^{-1}. The vibrational frequency and integrated intensity of the 572 cm^{-1} band along with the toluene band were evaluated by the spectral deconvolution method and were plotted against temperature, as shown in Figure 6b. As the temperature increased, the toluene band started to decrease in intensity around 100 °C and disappeared completely at 150 °C. The structure changed from δ to γ form in a broad temperature range from 100 to 130 °C.

Figure 7a shows the temperature dependence of polarized infrared spectra in the frequency region 595−615 cm^{-1} starting

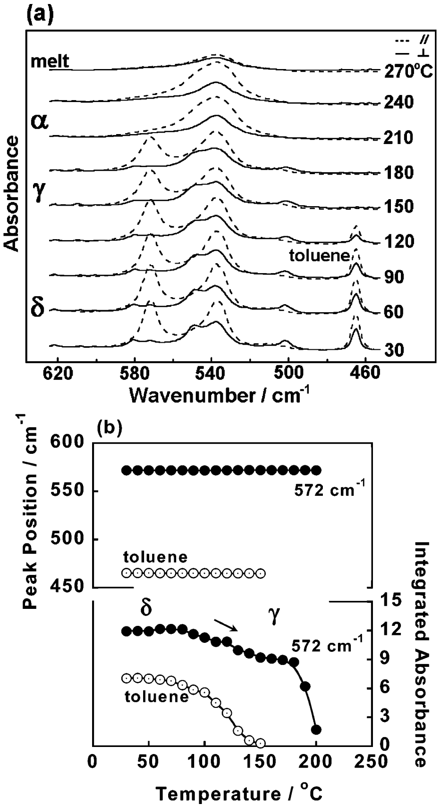

Figure 6. Temperature dependence of (a) the polarized infrared spectra in the frequency region 450−600 cm^{-1} and (b) the peak position and absorbance estimated for the bands characteristic of the δ and γ forms along with the toluene band starting from the uniaxially oriented δ sample of sPS and toluene complex. In (a) the solid and broken lines indicate the perpendicular and parallel band components with respect to the draw direction, respectively. Integrated absorbance is estimated for the perpendicular band component.

from the uniaxially oriented δ form of sPS and toluene complex. The integrated absorbance was plotted against temperature in Figure 6b. These bands were found to change only between the δ and γ forms in the transition region of 100−130 °C. The bands at 600.8 and 608.2 cm^{-1} corresponding to the δ form of the sPS−toluene complex decreased in intensity drastically in the temperature region 100−130 °C and disappeared at 130 °C. Simultaneously, the bands at 598.5 and 610 cm^{-1} appeared, which are assigned to the γ form. As already reported by Yoshioka et al.,[22] the infrared bands observed in the temperature region 100−130 °C are assumed to be a simple overlap of two pairs of the bands intrinsic to δ and γ forms. We did not observe any decrease in T_2G_2 content during the δ to γ transition unlike the case of δ_e to γ transition, where the T_2G_2 content decreased drastically because of the structural disorder during the transition.[15,40] As the temperature increased furthermore, the bands of the γ form decreased steeply in a narrow temperature range of 190−200 °C, as shown in Figure 6a. The transition from γ to α form will be discussed in a later section.

γ-to-α (β) Transition. As seen in Figures 2−4, on further heating the γ form reflection at $2\theta = 9.2^\circ$ decreased steeply in a narrow temperature range of 180−190 °C, and simultaneously new reflections appeared at $2\theta = 6.2^\circ$, 6.6°, and so on. These reflections can be assigned to both of the α and β forms. In this temperature range 180−190 °C both the γ and α (β) forms coexist. In Figure 2, the 2-D X-ray fiber patterns observed in the temperature region 180−200 °C do not indicate any disordering and ordering of the chains in the crystal during the γ to α (β) transition. Above 200 °C, the 2-D X-ray fiber patterns show well-defined reflections on the equatorial and layer lines,

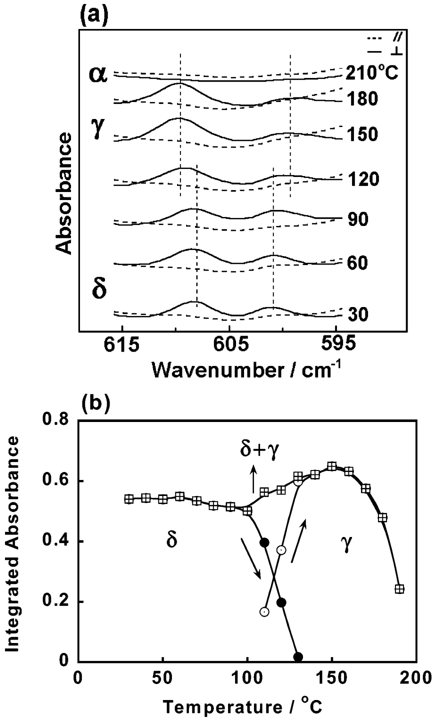

Figure 7. Temperature dependence of (a) the polarized infrared spectra in the frequency region 595−615 cm^{-1} and (b) the absorbance estimated for the bands characteristic of the δ and γ forms starting from the uniaxially oriented δ sample of sPS and toluene complex. In (a) the solid and broken lines indicate the perpendicular and parallel band components with respect to the draw direction, respectively. Integrated absorbance is estimated for the perpendicular band component.

indicating that the molecular chains maintained almost the same orientation during the phase transition.

In Figure 2 the layer line reflections corresponding to the planar-zigzag conformation are detected even at such a relatively low temperature as 140 °C. The intensity increases with increasing temperature and merges to the reflections of α (and β) form. So far, the γ form was said to transform only to the α form in a narrow temperature range above 190 °C because it is kinetically favorable.[2,3,13,14,19−21] Recently, we have found that the mixture of α and β forms can be obtained at higher temperatures by heating the thicker films of δ form or γ form.[46] By increasing the thickness of the starting sample, the solvent evaporation in the amorphous phase may be delayed, and these solvent molecules are responsible for the appearance of the β form along with the α form. Although the detailed description about this phenomenon will be made in a separate paper, the same concept may be adopted here to explain the phase transitions in the uniaxially oriented samples. The chain orientation affects the diffusion behavior of solvent molecules as it determines the path length and the resistance to diffusion through the amorphous region. These toluene molecules may plasticize the *oriented* amorphous phase, and this effect leads to the formation of more stable β form along with the kinetically favorable α form during heating. The layer line reflections intrinsic to the planar-zigzag chain may correspond to that of the β form. That is to say, the formation of the crystal forms of planar-zigzag chain conformation is considered to be made through the various routes of γ to α, γ to β, and amorphous to β transitions in the solvent atmosphere. When we look at the infrared spectra at higher temperatures, the γ form started decreasing its intensity at 180 °C and disappeared completely at 200 °C, as shown in Figures 6 and 7. Simultaneously, the bands corresponding to the all-trans conformation started appearing from 180 °C and became sharp at 200 °C. In the infrared spectra, we observed only the spectra of α form at higher temperature because no residual solvent remains in the amorphous phase of the thin films used for the analysis. A detailed discussion will be made about the solvent-induced formation of the β form elsewhere.

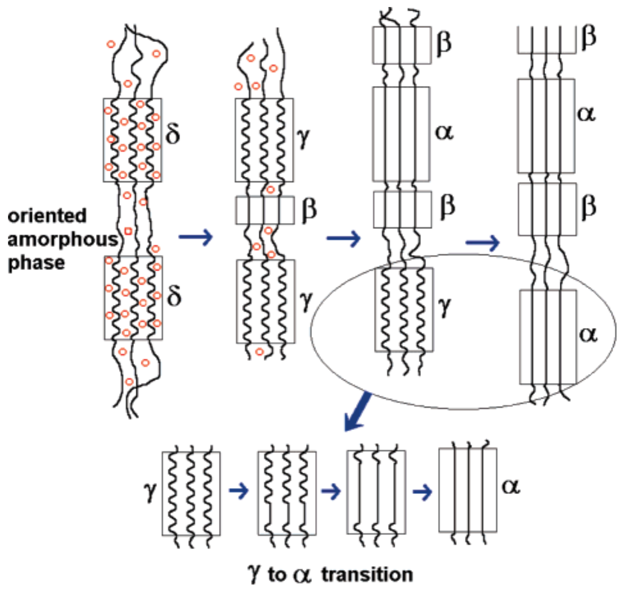

Figure 8. Schematic illustration of structural change in the phase transition from δ to γ (β) to α (β) form. The straight solid lines indicate the all-trans zigzag conformation, the curved lines indicate the helical conformation, and the small circles indicate the solvent molecules. Enlarged picture shown in the lower side illustrates the transition from the γ to α form.

As seen in Figure 1, the DSC thermogram shows a small endothermic peak followed by an exothermic peak during the transition from γ to α (and β) form. It had been speculated that these thermal peaks reflect the melting of the γ form followed by the recrystallization into the α (and β) form.[2,32,47] At this moment, however, we notice that we did not have any experimental evidence to support such a speculation. It is quite important to point out almost the perfect retention of molecular chain orientation during the drastic conformational change from the T_2G_2 type to all-trans type, as known from Figure 2. A similar observation was made for the stretched films and the uniplanar oriented films to show that the phase transition from γ to α form occurs by retaining the molecular chain orientation, although this observation was made by measuring the X-ray diffraction profiles at room temperature for the samples annealed at higher temperatures, different from our in-situ observation.[48,49] By combining all the experimental data presented in this paper, we may propose another model to explain the phase transition behavior from δ to γ to α (and β) form, as illustrated in Figure 8. The δ form transforms into the γ form. Some parts of the oriented amorphous phase may transform into the β form. By increasing temperature furthermore the γ form transform to the α and β form with keeping almost perfectly the chain orientation between $(T_2G_2)_2$ helical form and the all-trans planar-zigzag form. We might have several possibilities to explain the retention of chain orientation. For example, the γ form transforms into a phase of nematic liquid crystal type with the disorder in the relative height of the neighboring chains as well as the conformational disordering, and then this disorder phase transforms into the all-trans type form. But, the X-ray fiber diagram did not give us any experimental evidence supporting the generation of such a structurally disorder phase. Another possibility is the melt of the γ form immediately followed by the recrystallization to the oriented α (and β) form. But there is also no indication of the increment of the amorphous component during this process. Rather, it might be possible to speculate that some parts of the γ form crystallites change to the irregular conformation from the stable T_2G_2 form due to the radical thermal motion of the chains. For example, the conformational exchange between TT and TG bonds might occur:

---TTGGTTGGTTGGTTGGTTGG---
↓
---TTGGTTTTTTGGTTGGTTGG---
↓
---TTTTTTTTTTGGTTTTTTGG---
↓
---TTTTTTTTTTTTTTTTTTTT---

This type of conformational transformation in the crystallites was proposed for the phase transition from form II to form III of poly(vinylidene fluoride) in the heating process.[50,51] The small exothermic peak in the DSC thermogram shown in Figure 1 might correspond to such a process occurring during the γ to α (β) transition. Anyway, however, we need to investigate a more concrete mechanism of the γ to α (β) transition with the total reflection of the chain orientation by analyzing the X-ray diffractions in more detail.

Conclusions

In the present paper we reported the first success about the measurement of the temperature dependence of the X-ray fiber diagram and polarized FTIR spectra starting from the uniaxially oriented δ form of sPS and toluene complex at various temperatures in the heating process. We found that the δ form transforms to the γ form in a broad temperature range, and no other form is observed other than the simple overlap of δ and γ forms in this temperature range. The solvent molecules residing in the crystal lattice helps to occur the transition smoothly. This phenomenon is different from the δ_e to γ transition where the δ form transforms to an intermediate form transiently before transforming into the γ form because of the existence of many voids in the δ_e crystallites. At higher temperatures around 190−200 °C the γ form transformed to the mixture of α and β forms rather than into the α form only. The toluene molecules transiently residing in the amorphous region on the way of transition from δ to γ (because of the slow diffusion in oriented samples) are responsible for the appearance of the β form along with the α form. In the transition from the γ form to the α (and β) form the molecular chain orientation is perfectly kept unchanged, probably due to the conformational exchange between TT and TG bonds in the molecular chains, which may be caused by remarkable thermal motion at a higher temperature.

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