Effect of Solvent Molecules on Phase Transition Phenomena of Syndiotactic Polystyrene

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ABSTRACT: The phase transitions occurring in bulk samples of the syndiotactic polystyrene−toluene complex were monitored by X-ray diffraction and infrared spectral measurements during heating. For this purpose we have chosen the δ form samples with different thickness so that the diffusion time of solvent molecules in the sample was changed. By heating the sample, the δ form transferred to the γ form in the temperature range 100−130 °C, irrespective of the thickness of starting δ form samples. In a thin sample the evaporation of solvent occurred easily after the solvent was excluded from the δ form by heating, resulting in the formation of the γ form and then the α form at higher temperature. But, the thicker sample was found for the first time to give higher content of the β form in addition to the transformation of the γ to α form. In this case the solvent molecules excluded from the δ form crystal lattice are remained in the amorphous region and enhance the formation of the β form in a relatively low-temperature region. In this way, depending on the relative content of residual solvent, the formation behavior of the β form was found to be largely different.

Introduction

Syndiotactic polystyrene (sPS) exhibits the various types of crystal modifications with the different molecular conformations as well as the different chain packing structures depending on the preparation conditions.[1−24] The application of external condition, 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 commonly obtained by thermal crystallization procedures.[3−7] The α and β forms are further classified into the disordered forms (α' and β') and the ordered forms (α'' and β'') depending on the regularity of the chain packing mode.[3−7] The δ form having helical conformation $[-(T_2G_2)_2-]$ can be obtained by supplying organic solvent molecules to the glassy samples and form a complex between the polymer and the solvent.[1,2,9,10,21−23] Annealing or heating the δ form results in the γ form by purging away the solvent molecules.[9−17] Phase transformation of sPS within the complex polymorphism has been widely studied.[9−13,24,25] In particular, the in-situ measurements of X-ray diffraction and infrared spectra during heating process were made for the δ form of sPS with different solvent complexes to understand the phase transition mechanisms.[13,14,16,26−28] The δ form transforms to the γ form above 100 °C, and on further heating at higher temperature around 190 °C, the γ form transforms to the α form. In several cases the δ form transforms into the β form directly rather than into the γ form followed by the subsequent transition to the α form.[2] Rapid heating or sudden annealing to high temperature (above 150 °C) directly transforms the δ form into the β form. On the other hand, sPS gels, whose structure of cross-link is similar to the structure of δ form, also transforms directly into the β form on heating.[29,30]

Though the phase transitions have been reported in this way, the reason for such transitions is not yet clear. For example, we may have the following questions about the phase transitions of the δ form or sPS gel during heating: Why gels are favoring the β form at 140 °C or why β form appears by rapid heating or by annealing suddenly at higher temperatures? Is it possible to get the β form not for the gel but also by heating the δ form at moderate heating rates? What are the factors influencing these phase transitions from δ to γ to α or δ to β?

In the present paper we will report the structural changes during heating of the δ form of toluene complex on the basis of X-ray diffraction (XRD) and infrared spectral data. At first time we considered the role of solvent molecules excluded from the crystal lattice during δ to γ transition on thermally induced transitions of δ, γ, α, and β. It is a rare opportunity for us to study the effect of solvent molecules at higher temperatures because the solvent molecules reside in the crystal lattice at room temperature and do not show much effect on the amorphous region. For that purpose we used the δ form samples of different thickness so that we could control the solvent diffusion rate from the amorphous phase. Also for the first time, we are showing the δ to γ to β transition by in-situ measurements of X-ray diffraction and infrared spectra on heating the δ form. These results are considered to make a significant contribution for better understanding of the phase transformations in the δ form and also that of sPS gels during heating.

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 with different thickness were prepared by quenching the molten sheets into ice water. These samples were dipped in toluene for 2 days at ambient temperature to obtain the δ form. The samples removed from toluene were kept at ambient temperature until they became perfectly dry. Samples with thickness of 100, 150, 400, 600, and 800 μm were used for temperature-dependent measurements of X-ray diffraction and infrared spectra and for the differential scanning calorimetry (DSC) measurement.

Measurements. X-ray Diffraction. The X-ray diffraction system was a Rigaku/TTR-III X-ray diffractometer with Cu Kα line as an incident X-ray beam. The X-ray diffraction profiles were measured in a reflection mode in the 2θ range of 10−30° at scanning rate of 5°/min. The sample was mounted on a homemade heating cell, and the X-ray diffraction patterns were recorded at every constant temperature during the heating process.

FTIR. The infrared spectra were measured with a Varian FTS 7000 series FT-IR spectrometer. The sample was sandwiched

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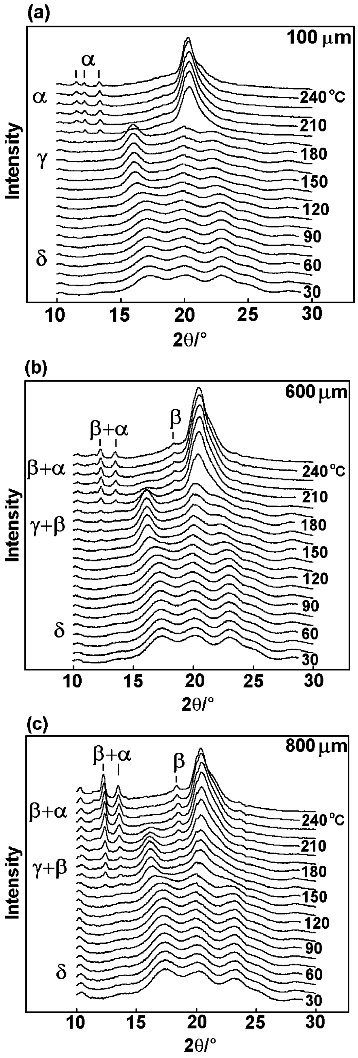


Figure 1. Temperature dependence of the X-ray diffraction profile of the δ form in the heating process: (a) 100, (b) 600, and (c) 800 μm thick samples.

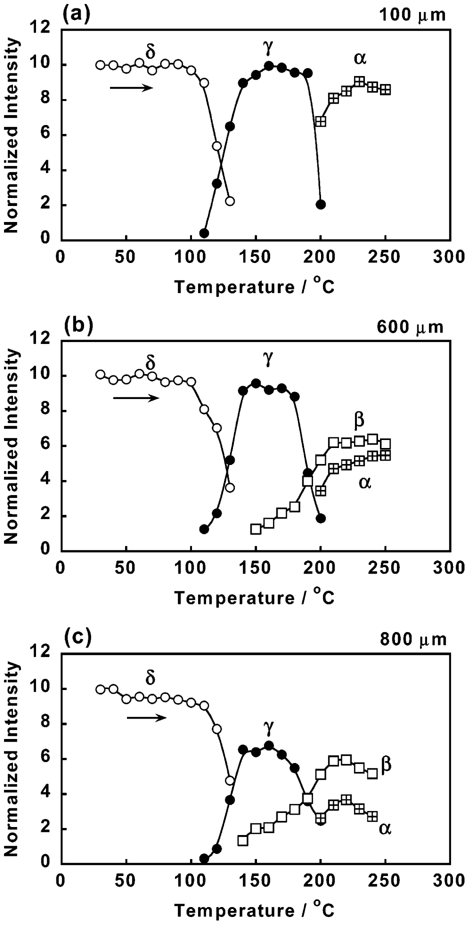


Figure 2. Temperature dependence of the integrated intensity of the reflections at $2\theta = 17.0°$ (δ), 15.9° (γ), 11.5° (α), and 12.3° (β) evaluated from Figure 1: (a) 100, (b) 600, and (c) 800 μm thick samples.

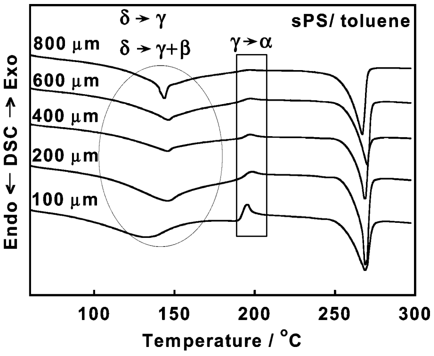


Figure 3. DSC thermograms of the δ form taken for the samples of different thickness in the heating process.

between a pair of KBr plates and then set to a homemade heating cell. The infrared spectral measurements were made at a resolution power 1 cm^{-1} at every constant temperature during heating.

DSC. The DSC thermograms were measured in the heating process by using differential scanning calorimeter TA DSC Q1000 under nitrogen gas atmosphere at a rate of 10 °C/min.

Results and Discussion

Temperature Dependence of X-ray Diffraction Pattern. The temperature dependence of the X-ray diffraction patterns of the δ form is shown in Figure 1a−c for the samples of 100, 600, and 800 μm thickness, respectively. On heating the pattern did not show any obvious change up to 100 °C. On further heating, the reflections at $2\theta = 17.0°$, 20.2°, and 23.3° corresponding to the δ form started to decrease in intensity and vanished at 130 °C. Simultaneously, new reflections at $2\theta = 15.9°$ and 19.9° appeared, and these reflections correspond to the γ form. The variation in the integrated intensity of a reflection characteristic of each crystalline form was evaluated through the deconvulation method and plotted against temperature for all the samples, as shown in Figure 2a−c. It is apparent from Figure 2a−c that the δ to γ transition occurs in the temperature region 100−130 °C irrespective of the thickness of the starting δ form samples. On further heating these samples show complicated behavior at higher temperatures. In the case of the sample with thickness 100 μm, the reflections at $2\theta = 15.9°$ and 19.9° corresponding to the γ form decreased steeply in a narrow temperature range of 190−200 °C and vanished at 200 °C, as shown in Figures 1a and 2a. At the same time new reflections corresponding to the α form appeared at $2\theta = 11.5°$, 12.2°, and 13.4°, and the intensity of these reflections increased on further heating, as indicated in Figure 1a. These results are in good agreement with the reported data.[13]

On the other hand, in the case of thicker samples (600 and 800 μm), we observed new reflections at $2\theta = 12.3°$, 13.6°, and 18.5° along with the γ form reflections above 140 °C, which were found to come from the β form. It was also observed that on further heating the γ form reflections started to decrease in intensity, and simultaneously the intensity of the β form

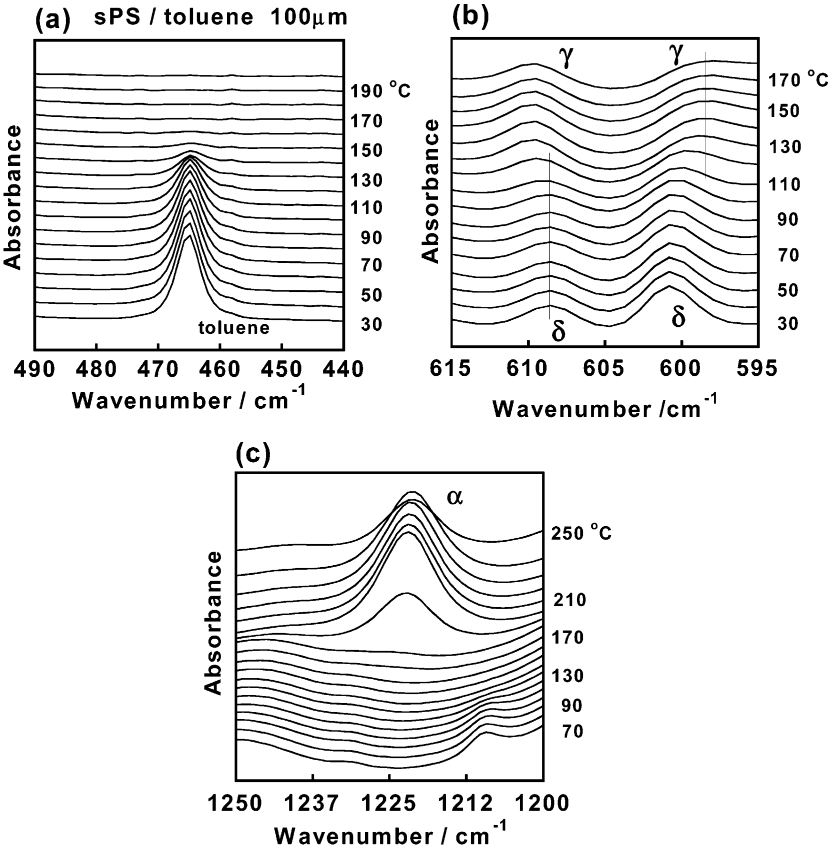


Figure 4. Temperature dependence of infrared spectra of the δ form of 100 μm thickness in different frequency regions: (a) 440−490, (b) 595−615, and (c) 1200−1250 cm^{-1}.

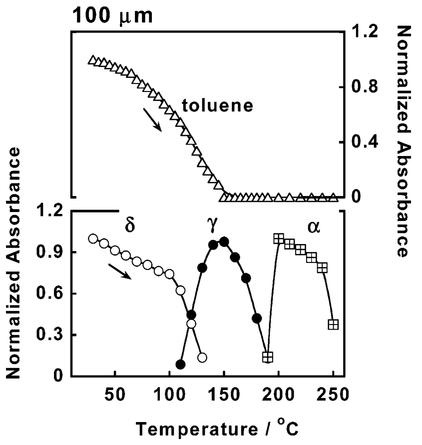


Figure 5. Temperature dependence of integrated absorbance of different bands characteristic of δ, γ, α, and toluene evaluated from Figure 4.

reflections increased in the temperature region 140−190 °C, as shown in Figures 1b,c and 2b,c. It means some parts of the γ form transforms to the β form in this temperature region. Once the temperature reached 190 °C, the remaining γ form transforms to the α form similarly to the 100 μm sample. Above this temperature both α and β forms coexist until melting.

DSC Thermograms. The DSC thermograms are studied in detail to understand the phase transition behavior starting from the δ form samples having thickness ranging from 100 to 800 μm. DSC thermograms of the various samples clearly shows the differences in the phase transition behavior as shown in Figure 3, which are consistent with the X-ray diffraction results. The transition from δ to γ form is not clear in the DSC thermograms because of the overlapping of a broad endotherm caused by the toluene evaporation. However, for the thicker samples a sharp endotherm is observed at 140 °C, which is overlapping with the broad endotherm of toluene evaporation. The endotherm, i.e., a peak at 140 °C, may be assigned to the appearance of the β form along with the γ form in thicker samples. At higher temperature, 190−200 °C, the γ form transforms to the α form as evidenced by a small endotherm followed by an exotherm. In the case of thin samples, the δ form transforms to the γ form and at higher temperature the γ form transforms to the α form. Therefore, we could see a clear endotherm followed by an exotherm because of the major structural change from γ to α transition. On the other hand, in the case of thicker samples already some parts of the δ and γ forms transformed into the β form; therefore, a weak endotherm followed by an exotherm is observed at 190−200 °C, which corresponds to the γ to α transition. The endotherm at 270 °C is due to the melting of the samples.

The X-ray diffraction and DSC results revealed that by increasing the thickness of the samples the β form is more easily observed along with the γ form at 140 °C. On further heating the γ form partially transforms to the β form, and above 190 °C the transition from the γ form to the α form is also detected although the degree of the latter transition becomes lower for the thicker sample. For further understanding of this complex phase transition behavior, we have carried out the temperature-dependent measurements of infrared spectra for the δ form samples with different thickness.

Temperature Dependence of Infrared Spectra. Though both the δ and γ forms exhibit the same helical conformation, some infrared bands are distinguished between them. Yoshioka et al.[16] reported the infrared frequency region sensitive to the chain packing mode in the crystalline forms of sPS (δ, empty δ (δ_e), and γ) having the same chain conformation. So we have

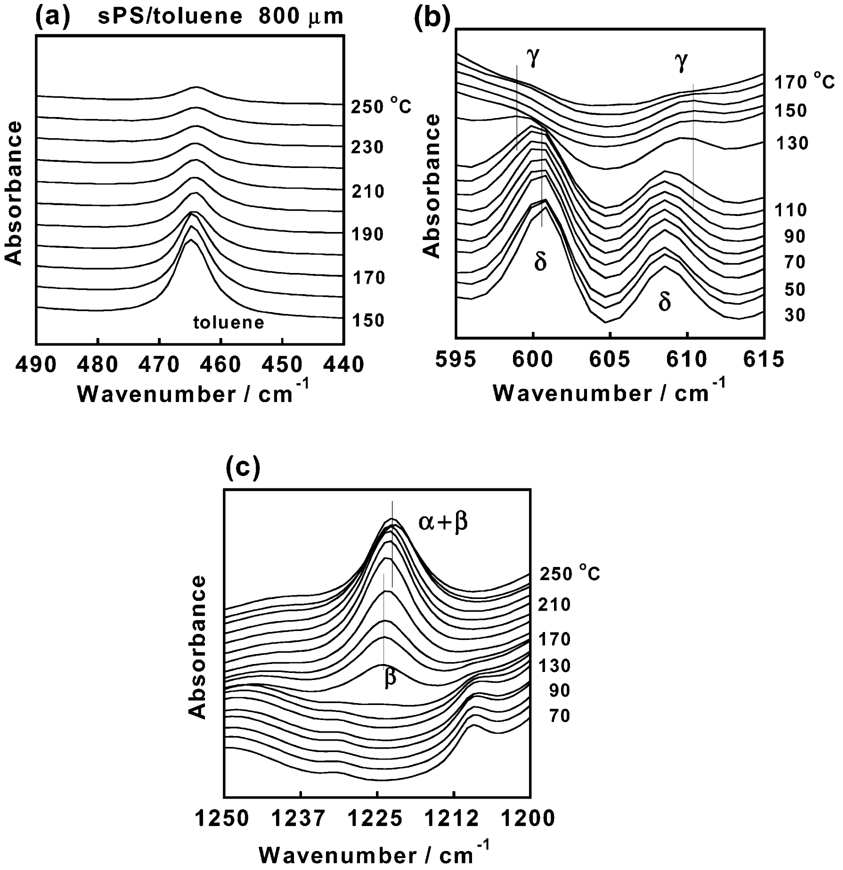


Figure 6. Temperature dependence of infrared spectra of the δ form of 800 μm thickness in different frequency regions: (a) 440−490, (b) 595−615, and (c) 1200−1250 cm^{-1}.

chosen the frequency region 595−615 cm^{-1} to distinguish the δ and γ forms during the phase transition in the present study. For all trans-zigzag conformation, the bands at 1222 cm^{-1} for the α form and 1224 cm^{-1} for the β form are chosen.

Figure 4 shows the temperature dependence of infrared spectra taken for the 100 μm thick sample in different frequency regions including the toluene band. The integrated absorbance was evaluated for several bands and plotted against temperature, as shown in Figure 5. As the temperature increased, the bands characteristic of the δ form decreased in intensity and simultaneously the bands characteristic of the γ form increased in the temperature range 100−130 °C. During the phase transition the toluene molecules, which are in the crystal lattice of the δ form, leave the crystal lattice and occupy the amorphous region transiently and then leave the sample completely at 140 °C. The disappearance of the toluene band confirms the complete evaporation of toluene molecules from the sample in the temperature region close to δ to γ transition. As the temperature increased furthermore, the bands of the γ form decreased steeply at around 190 °C, and the 1222 cm^{-1} band characteristic of the α form with all trans (TTTT) conformation increased instead. These results are in good agreement with the X-ray diffraction data. The α form bands disappeared above 260 °C due to the melting of the sample. Most of the earlier workers found the similar behavior during heating the δ form samples because most of them used very thin films or powdered samples during such experiment similarly to the present case using the 100 μm thick sample.[9,10,14,16]

The temperature dependence of infrared spectra of the 800 μm thick sample is shown in Figure 6 in different frequency regions. The δ to γ transition occurs in the temperature range 100−130 °C similar to that observed for the 100 μm thin sample.

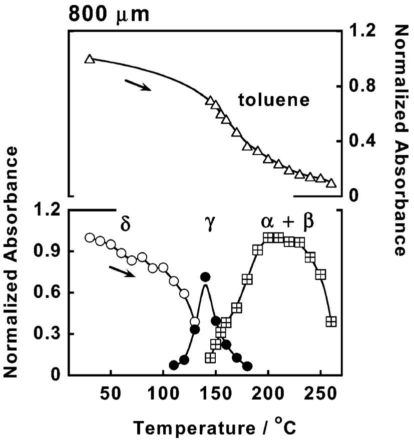
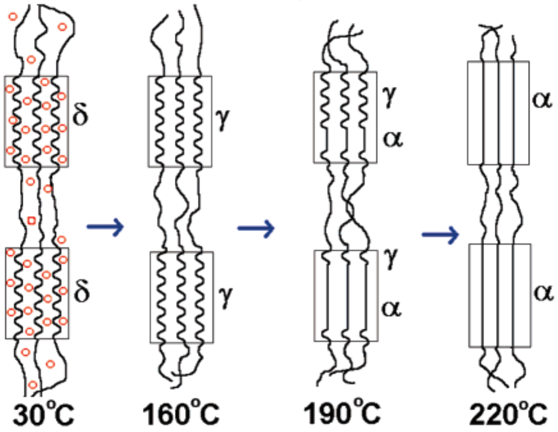


Figure 7. Temperature dependence of integrated absorbance of different bands characteristic of δ, γ, α (β), and toluene evaluated from Figure 6.

Above 140 °C, a band at 1224 cm^{-1} is noticed, corresponding to the β form, as supported by the X-ray diffraction results shown in Figure 1c. These results clearly indicate that the thicker samples behave differently from the thinner samples. In thicker samples the δ form transforms to the mixture of γ and β forms at 140 °C. The integrated absorbance was evaluated for several bands and was plotted against temperature, as shown in Figure 7. As seen here, on further heating the absorbance of the γ form bands decreases, and simultaneously the absorbance of the all-trans bands of α and β forms increase instead. These infrared results indicate that the γ to β transition occurs partially in the temperature range from 140 to 190 °C as already pointed out using the X-ray diffraction data (Figures 1 and 2). As the temperature increased furthermore, the bands of the remaining

(a) Thin sample (100 µm)



(b) Thick sample (800 µm)

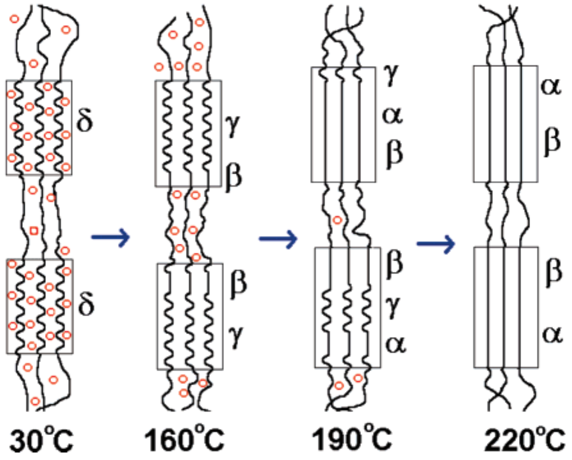


Figure 8. Schematic illustrations of structural change in the phase transition from (a) δ to γ to α form and (b) δ to γ (β) to α (β) form detected for thin and thick δ form samples. The straight solid lines indicate the all-trans zigzag conformation, the curved lines indicate the helical conformation, and the small circles indicate the solvent molecules.

γ form decreased steeply and the band characteristic of the α form increased in intensity at 190 °C, and as a result the sample changed to the mixture of the α and β forms. These results are in very much consistent with the X-ray diffraction data and the DSC data. When we looked at the behavior of toluene band in the case of thick samples, we found that toluene band exists up to the melting temperature of the sample, which is entirely different from the case of 100 μm thick sample, where the toluene band disappeared already near the transition temperature from δ to γ form. The appearance of toluene band up to the melting in thicker sample is due to the lower diffusion rate of toluene molecules in the amorphous phase. It has been known that the solvent occupies the amorphous region of the γ form after the δ to γ transition even in solvent-rich gels.[30] Therefore, in the present case also the toluene molecules are speculated to reside in the amorphous phase even after the δ to γ transition in the thick sample.

The toluene molecules residing in the amorphous phase of the γ form at higher temperature (above 130 °C) may enhance the mobility of the amorphous region vigorously and are responsible for the appearance of the β form along with the γ form above 140 °C. It is speculated that the δ form and the γ form are partially dissolved in toluene at such a high temperature and transforms to more stable β form. It is also observed that the content of the β form increased at higher temperature and simultaneously the content of the γ form decreased as the thickness of the starting sample was increased from 600 to 800 μm. By increasing the thickness of the sample further, we might observe the direct transition from δ to β form without passing through the γ form. It is also worth mentioning here that the toluene evaporation from the sample is further delayed by packing the sample in between the KBr plates for IR experiment or in a tightly packed DSC pan. Therefore, in our studies, the β form domination is more in the case of infrared spectral data and DSC data compared to the X-ray diffraction case because we performed the X-ray diffraction measurements for the sample set on an aluminum plate in an open system during heating.

We recall that the supercritical carbon dioxide can plasticize the glassy polymers, and this effect leads to the decrease of the energy barriers, thus making some solid−solid transitions possible at much reduced temperatures and bringing about some new transitions that cannot occur at ambient pressure.[17,19] Recently, Rizzo et al.[20] also showed that the presence of high boiling solvents in the amorphous phase of the γ form could induce the γ to β transition. Therefore, we can emphasize here that the solvent molecules residing in the amorphous phase may partly dissolve the δ form and act as a plasticizer at that temperature to overcome an energy barrier to induce the thermodynamically stable β form. In this way we observed for the first time such in-situ plasticization at higher temperature.

The present data may help us to understand the phase transition behavior in sPS gels. It was shown that sPS gels transforms directly into the β form without passing through the solvent-free γ form.[29] On the other hand, it was shown that in the gels of sPS/toluene sPS/chloroform directly transforms into the β form whereas the gels of sPS/benzyl methacrylate transiently passes through the γ form before transforming into the β form.[30] The difference in the phase transition behavior of sPS gels may arise because of the polymer−solvent interactions. We may say that toluene and chloroform interact strongly with the polymer compared to benzyl methacrylate. Therefore, the solvent in the amorphous region of the δ or γ form might play a crucial role in deciding the phase transition to the β form. These data showed that the δ to β and γ to β transitions favored at lower transition temperature (140−190 °C) than the usual γ to α transition at 190 °C because of the plasticization effect in the amorphous phase. The activation energy of the α form formation is said to be lower than that of the β form, suggesting that the α form is kinetically favorable.[2,31−34] However, the plasticization effect in the amorphous phase may reduce the activation energy for the transformation to the β form, thus making the δ to β and γ to β transitions easier at much reduced temperature. However, as seen in Figures 1 and 2, the transition from γ to α occurs at 190−200 °C even when the β form is obtained. Among the crystalline forms α and β, the β form is most stable and has a higher equilibrium melting temperature than that of the α form.[32] The β form is stable to solvent atmosphere and does not change to the δ form by being dissolved into solvent.[35,36] On the other hand, the α form is least stable and can easily convert into the δ form in the presence of solvent molecules.[35,36] That is the reason we always observe the stable β form in the presence of solvents instead of the α form. We also observed that by increasing the thickness of the starting δ form, the amount of toluene in the amorphous phase increased because of the slower diffusion rate, and as a consequence the content of the β form increased in thicker samples.

At this stage we might have such a question that the quenched thicker samples may contain some traces of the β form because the heterogeneous temperature distribution might occur in the thicker sample and the β form is crystallized at relatively higher temperature.[2] Since the β form is stable against the solvent,[35,36] the initially existent β form may remain in the starting δ form samples and grow during heating to higher temperature. But this possibility can be excluded perfectly in our present experiment. As shown clearly in Figures 4 and 6 (and Figure 1), there was no trace of the infrared bands corresponding to the β form, the band at 1224 cm^{-1}. Figures 4 and 6 indicate definitely that the starting sample consisted of only the δ form, and that these *pure* δ samples transferred to the β form in the cases of thicker samples with the help of solvent molecules as a kind of plasticizer.

By combining all the experimental data presented in this paper, we have given the different phase transition models for the thin and thick films as shown schematically in Figure 8 to explain the phase transition behavior from δ to γ to α and δ to γ (β) to α (β). Thickness of the sample affects the diffusion behavior of solvent molecules in the amorphous region as it determines the path length. These solvent molecules help the formation of the crystal forms of planar zigzag chain conformation at relatively lower temperature through the various routes of the δ to β, the γ to β, and the γ to α transitions in the solvent atmosphere. On the other hand, in thin films the formation of planar zigzag conformation occurs only via the γ to α transition as seen in model (a).

Conclusions

In the present paper we considered the role of solvent molecules, which are excluded from the crystal lattice of the δ form during δ to γ transition, on phase transition behavior at higher temperatures. We prepared the δ form samples of the sPS/toluene complex with different thickness. We performed the temperature-dependent measurement of X-ray diffraction and infrared spectra to understand the complex phase transition behavior of sPS. Diffusion rate of the solvent molecules in the amorphous phase was considered to vary depending on the sample thickness as seen in the temperature-dependent infrared spectra. The toluene band was observed until melting in the case of thicker samples, indicating the delay in the evaporation of solvent from the amorphous phase. X-ray diffraction measurements revealed that the δ form transforms into the γ form in the temperature range 100−130 °C, irrespective of the thickness of the starting samples. In thin samples (100−400 μm) the γ form transforms into the kinetically favorable α form in the temperature region 190−200 °C. No effect of toluene molecules was observed in thin samples because of the rapid diffusion after δ to γ transition. On the other hand, in thicker samples (500−800 μm) the β form appeared along with the γ form at 140 °C. On further heating some parts of the γ form transforms into the β form as evidenced by X-ray diffraction and infrared spectral data. At 190 °C, the remaining γ form transforms to the α form. In thicker samples, the diffusion of toluene molecules is delayed, and these toluene molecules enhance the mobility of the polymer chains in the amorphous phase and the sPS chains reorganize into the thermodynamically stable β form.

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