Role of Solvent Molecules as a Trigger for the Crystal Phase Transition of Syndiotactic Polystyrene/Solvent Complex

E. Bhoje Gowd* and Kohji Tashiro*

Department of Future Industry-Oriented Basic Science and Materials, Graduate School of Engineering, Toyota Technological Institute, Tempaku, Nagoya 468-8511, Japan

C. Ramesh

Department of Polymer Science and Engineering, National Chemical Laboratory, Dr. Homi Bhabha Road, Pune 411 008, India

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ABSTRACT: The phase transitions occurring in the syndiotactic polystyrene−norbornadiene complex were investigated by simultaneous measurements of wide-angle X-ray diffraction (WAXD) and differential scanning calorimetry (DSC). To understand the effect of norbornadiene molecules on the phase-transition behavior, the δ form samples with different contents of norbornadiene were prepared. By heating these samples, we found that the δ-to-γ transition occurred well below 100 °C in a broad temperature range, and the onset of the transition temperature depended on the content of norbornadiene included in the starting sample. The sample without norbornadiene molecules showed the δ-to-γ transition to be above 100 °C. Upon further heating, the γ form transformed into a mixture of α and β forms in the presence of norbornadiene molecules, whereas the sample without norbornadiene transformed into only the α form. In this way, it has been found that the solvent molecules, which are not completely evaporated from the sample but are transiently trapped in the amorphous region because of the slow diffusion, have a significant role in facilitating the phase transitions as well as the transition temperatures in the crystalline region. On the basis of WAXD and DSC results, a phase-transition model has been reasonably constructed.

Introduction

Syndiotactic polystyrene (sPS) shows quite complicated polymorphic behavior, and it has been extensively studied for the last two decades.[1−32] Among the four crystalline forms (α, β, γ, and δ) of sPS, the α and β forms take all-trans planar-zigzag (T_4) conformation, whereas the γ and δ forms take helical conformation [-$(T_2G_2)_2$-].[1−13] Recently, the δ form of sPS has been further classified as clathrates and intercalates. In clathrates, the low-molecular-weight compounds are trapped as guest molecules in the cavities of the host sPS and are characterized by a stoichiometric molar ratio (monomeric unit/guest) of 4:1.[11−15] In the intercalates, the guest molecules are not isolated in host cavities but are contiguous inside the layers intercalated with enantiomorphous polymer helices with a stiochiometric molar ratio (monomeric unit/guest) of 2:1.[16,17] The extraction of the solvent molecules from the δ form (clathrates) by a suitable procedure leads to the formation of the so-called empty δ (δ_e) form.[18−22] The δ_e form retains the helical structure that is similar to those of the δ and γ forms but with the cavities that had been occupied by solvent molecules. Besides these crystalline forms, a mesophase of all-trans planar-zigzag conformation and an intermediate form were also reported.[20−23]

Structural changes in thermally induced phase transitions of the δ form have been well investigated for both unoriented and uniaxially oriented samples.[20−31] It has been found that the δ form directly transforms to the γ form above 100 °C, and the transition occurs over a temperature range depending on the nature and amount of solvent residing in the crystal lattice of the δ form.[25−28] The δ_e form behaves differently from the δ form because of the cavities present in the crystal lattice. When the δ_e form is heated, it transiently transforms into an intermediate form before transforming into the γ form.[20−22] At higher temperature, the γ form transforms into the α form around 180−190 °C.[25−28] More recently, we showed that depending on the solvent included the γ form transforms into a mixture of α and β forms rather than into only the α form.[29,30] The solvent molecules in the amorphous region, which are not purged from the sample but are transiently trapped in the amorphous phase during the transition from δ to γ (because of the slow diffusion in bulky and oriented samples), are responsible for the appearance of the β form along with the α form.[29,30] That is to say, the crystalline phase transition does not occur independently of the amorphous region but is more or less affected by the molecular mobility in the crystalline−amorphous interface. Although the phase transitions have been known in this way, many questions are left unanswered. Why was the δ-to-γ transition found to occur always above 100 °C? Is it possible to observe this transition at lower temperature by plasticizing the amorphous phase? Although many authors including us reported the phase-transition behavior during heating of the δ form, no one clearly pointed out the above questions. To understand more about the crystalline transitions in sPS, we used an organic solvent of large size with a high boiling point as guest molecules. The diffusion of these guest molecules from the δ crystal lattice to the amorphous phase and to the outside of the sample could be controlled. For this purpose, we have chosen a bulky solvent norbornadiene (bicyclo[2.2.1]hepta-2,5-diene) to form the sPS-solvent complex.

In the present article, we will report for the first time the phase-transition behavior of sPS complex with a bulkier solvent, where these solvent molecules are not isolated in the cavities of the sPS chains in the lattice. It is worth pointing out that all earlier studies on the crystalline transitions of sPS have been made with smaller molecules that are trapped in the cavities of sPS chains in the lattice. These data allow us to consider for the first time the role of solvent molecules on the thermally

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* Corresponding authors. E-mail: bhojegowd@yahoo.com; ktashiro@toyota-ti.ac.jp. Tel: +81-52-809-1790. Fax: +81-52-809-1793.

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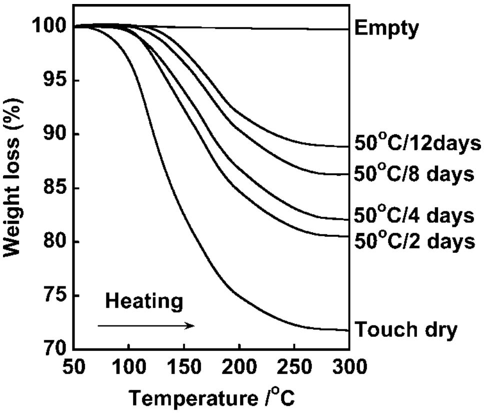

Figure 1. TGA thermograms taken for the δ form samples of the sPS−norbornadiene complex along with the extracted sample in the heating process.

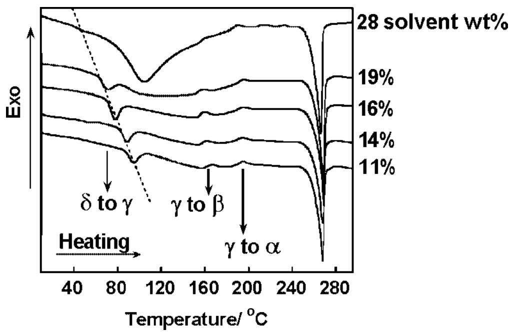

Figure 2. DSC thermograms taken in the heating process for the δ form samples of the sPS−norbornadiene complex with different norbornadiene content.

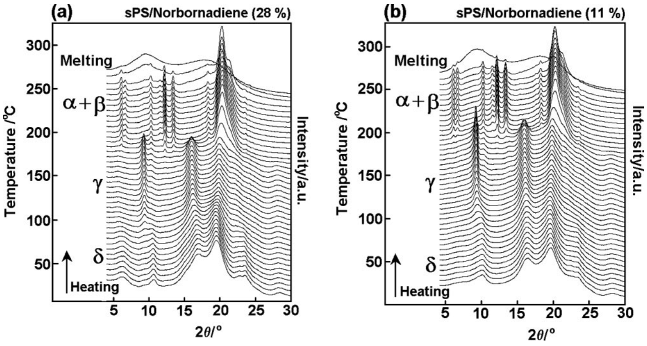

Figure 3. X-ray powder diffraction patterns observed during the heating process of the sPS−norbornadiene complex with (a) 28 and (b) 11 wt % of norbornadiene.

induced transitions of δ-to-γ and γ-to-α (β) forms. These results should make a significant contribution to the understanding of the complex phase transformations exhibited by sPS, in particular, and to the understanding of the crystalline transformation of semicrystalline polymers in general.

Experimental Section

Samples. Syndiotactic polystyrene pellets ($M_w = 272\ 000$, $M_w/M_n = 2.28$) were kindly supplied by Idemitsu Petrochemical. The glassy samples were prepared by quenching the molten sheets in ice water. The thickness of the quenched sample was maintained at around 200 μm. These samples were dipped in norbornadiene for 5 days at ambient temperature to obtain the δ form. The samples removed from norbornadiene were kept at ambient temperature until they became perfectly dry. Samples with different amounts of solvents were obtained by drying the samples at 50 °C for different intervals of time. In another case, all solvent molecules were extracted by refluxing the δ form samples in acetone for 15 h and then in methanol for 8 h.

Measurements. *Thermogravimetric Analysis.* The TGA thermograms were recorded in the heating process by the use of thermogravimetric analysis TA DSC Q5000 under a nitrogen gas atmosphere at a rate of 10 °C/min.

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

Wide-Angle X-Ray Diffraction−Differential Scanning Calorimetry. The X-ray diffraction−DSC system used in this study consists of a goniometer of Rigaku RINT/TTR-III and a DSC unit based on Rigaku/Thermo Plus DSC-II. The X-ray beam used was Cu Kα radiation. The X-ray diffraction profiles were measured in the 2θ range of 4−30° at a scanning rate of 5°/min, and the DSC heating rate was 2 °C/min during the heating process.

Results and Discussion

Figure 1 shows the TGA thermograms of the samples without any norbornadiene residue (by extraction) and the samples dried at 50 °C for different intervals of time. The initial content of norbornadiene in a touch dry sample was 28 wt % and decreased to 11 wt % depending on the drying time, as indicated in Figure 1. In a touch dry sample, the solvent molecules are considered to distribute almost evenly in crystalline and amorphous phases,[16,32,33] but, upon drying the sample at 50 °C, the amount of solvent present in the sample decreased, as indicated in Figure 1. The diffusion of norbornadiene is relatively fast during the initial drying time, and a kind of saturation occurred after reaching a certain level. The amount of solvent does not decrease below 11 wt % even after prolonged drying. Petraccone et al.[16] already studied the desorption kinetics of norbornadiene using the uniaxially stretched sample of the sPS−norbornadiene complex and showed that the desorption of norbornadiene is mostly from the amorphous phase. Therefore, it is assumed that in the case of the sample with 11% solvent all solvent molecules are located in the crystalline phase. In the case of the 28% norbornadiene-containing sample, the amount of solvent molecules present within the crystal could be >11%. Norbornadiene is an appreciably large molecule and seems to increase the free volume of sPS chains in the amorphous region as well as in the δ crystal lattice. Therefore, the diffusion of the bulkier norbornadiene is considered to be relatively slow in the amorphous phase at room temperature and stays in the amorphous phase for longer times compared with that of other small solvent molecules.

The DSC thermograms are studied in detail to understand the phase-transition behavior during heating. Figure 2 shows the DSC thermograms taken for the sPS−norbornadiene δ form starting with different amounts of norbornadiene. The remarkable changes in the DSC thermograms clearly indicate the differences in the phase-transition behavior by changing the norbornadiene content in the starting samples. To assign these complicated DSC thermograms, simultaneous WAXD−DSC measurements were performed in the heating process. The powder diffraction patterns observed during the heating process are plotted as a function of temperature for the δ form with 11 and 28 wt % of norbornadiene and are shown in Figure 3. The room-temperature WAXD patterns of 11 and 28 wt % norbornadiene-containing samples appear to be similar but show subtle differences. In particular, the intensities of 010 ($2\theta = 6.2°$) and $\bar{2}10$ ($2\theta = 10.6°$) reflections were found to change with the amount of solvent molecules trapped in the sample. The peak intensity decreases with a decrease in the solvent content in the lattice and shows that the structure factor is affected by the amount of solvent present in the crystal lattice.

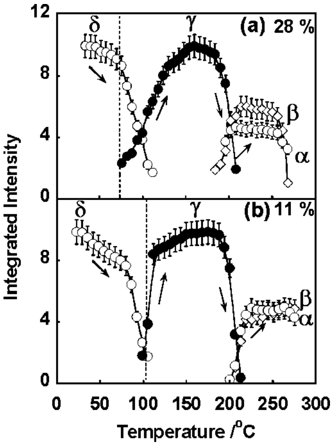

Figure 4. Temperature dependence of the integrated intensity of the X-ray reflections at $2\theta = 6.2$ (δ), 9.3 (γ), 6.6 (α), and 6.1° (β) evaluated from Figure 3.

Upon heating, the reflections at $2\theta = 6.2$ and 10.6° started to decrease in intensity at 70 °C and vanished at 120 °C. Simultaneously, new reflections corresponding to the γ form appeared at $2\theta = 9.3$ and 15.9° at 70 °C. Figure 4 shows the variation in the integrated intensity of selected X-ray reflections that is characteristic of each crystalline form plotted against temperature. It is apparent from Figure 4 that the δ-to-γ transition occurs over a broad temperature range starting at 70 °C. In the same temperature range, the DSC thermogram (Figure 2) shows a small endotherm, followed by an exotherm. On the basis of the WAXD results, we assigned the DSC peaks in the 70−100 °C temperature range to the phase transition from δ-to-γ form. A broad endotherm is also observed in the DSC thermogram after the transition point, which is due to the evaporation of excess norbornadiene molecules. Upon further heating, the γ-form reflections started to decrease in intensity; simultaneously, the intensity of the β-form reflections increased in the 170−190 °C temperature region, as shown in Figures 3a and 4. However, some amount of the γ form still coexists with the β form in this temperature region. Once the temperature reached 190 °C, the remaining γ form transformed to the α form. The DSC thermogram also clearly showed the two transition points in this temperature range of 170−200 °C, and these transition points were assigned to the γ-to-β and γ-to-α transitions on the basis of the WAXD results. Above this temperature, both the α and β forms coexist until melting. In this way we can clearly assign the transition points in the DSC thermograms.

The sample with 11 wt % of norbornadiene shows a different DSC thermogram, as seen in Figure 2. In this case the δ-to-γ transition shifted to a higher temperature than that of the sample containing 28 wt % of norbornadiene. Figure 3b shows the change in the WAXD patterns during heating for the sample containing 11 wt % of norbornadiene. The variation in the integrated intensity of selected X-ray reflections is shown in Figure 4. From the WAXD patterns, it is also clear that the reflections corresponding to the γ form started appearing above 100 °C. Upon further heating, the γ form transformed into a mixture of β and α forms similar to that of the sample containing 28 wt % norbornadiene. Although the initial contents of the norbornadiene molecules are different, the norbornadiene molecules, which are excluded from the crystal lattice of the δ form during δ-to-γ transition, are responsible for the appearance of the β form. As seen in Figure 4, the content of the β form is less in the 11-wt %-containing sample compared with that of the 28-wt %-containing sample. That is, the total content of the norbornadiene molecules in the amorphous phase of the γ form reflects on the content of the β form at higher temperature. The content of residual norbornadiene molecules in the amorphous phase of the γ form at any given temperature can be estimated from the TGA thermograms.

The above results clearly indicate that the WAXD results are very much consistent with the DSC data. The δ-to-γ transition occurs well below 100 °C. Furthermore, the δ-to-γ transition temperature depends on the initial content of norbornadiene, as seen in Figure 2. These results are different from the reported data in which the δ-to-γ transition always occurs above 100 °C in several sPS−solvent complexes.[25−31] Therefore, we emphasize that the norbornadiene molecules, which reside in the amorphous phase of the δ form, are responsible for such a reduction in δ-to-γ transition temperature. We have to consider the interaction of the solvent molecule with sPS chains to explain the δ-to-γ transition in different solvents. The small molecules such as toluene or chloroform are trapped in the cavities of the host sPS and are tightly bound in between the sPS chains. Therefore, these complexes are kinetically stable and these solvent molecules cannot diffuse out of the crystalline lattice below the glass-transition temperature. Once the amorphous phase becomes mobile upon heating, the solvent molecules diffuse out of the crystalline lattice; as a result, the δ-to-γ transition always occurs above 100 °C, which is incidentally similar to the glass-transition temperature of sPS (97 °C).[25−31] In the case of sPS−norbornadiene complexes, excess solvent molecules reside in the amorphous phase at room temperature and are considered not only to affect the mobility of the amorphous phase (glass-transition temperature) but also to reduce the transition temperature of the δ-to-γ transition to the lower temperature side. It is worth highlighting here that the bulky solvent molecules such as norbornadiene are not isolated in host cavities but reside in between the monolayers of sPS chains. In this case, the diffusion of these guest molecules from the crystal lattice may be much easier than that of the trapped molecules inside the cavities of the crystal lattice. Upon further heating, the DSC thermograms showed two transition points at 170 and 200 °C, as seen in Figure 2. On the basis of the WAXD results, we assigned these transition points to the γ-to-β and γ-to-α transitions, respectively. This is the first time that the appearance of the β form along with the α form has been detected at higher temperature in thin samples. In our previous papers, we showed that the diffusion of solvent molecules is delayed in thicker samples or uniaxially oriented samples and as a result the thermodynamically stable β form appears in such thick samples.[29,30] The present study confirms that the norbornadiene molecules present in the amorphous phase play a role in the appearance of the β form even in thinner samples. The transition temperature and the content of the β form are mainly dependent on the amount of norbornadiene molecules, which transiently reside in the amorphous region. In this way, the norbornadiene helps to overcome an energy barrier to induce the phase transitions at lower temperature as well as for the appearance of the thermodynamically stable β form.

To study the effect of solvent molecules more clearly, we prepared the δ form without any norbornadiene molecules by treating the δ form with 28 wt % norbornadiene in acetone and in methanol. The absence of solvent molecules is confirmed by the TGA, as shown in Figure 1. The room temperature WAXD pattern of the norbornadiene-removed sample (Figure 5) is different from that of the room temperature patterns shown in Figure 3. The reflections are seen at $2\theta =$ 9.5, 13.4, 16.2, 20.3, and 23.6°. This pattern is also different from the δ_e form reported for other sPS−solvent complexes.[22,31,34] The appearance of crystalline reflections at $2\theta =$ 9.5, 13.4, and 23.6° clearly indicated that the pattern belongs to the family of the δ form. Furthermore, the infrared spectra measured at room temperature (not shown here) showed TTGG

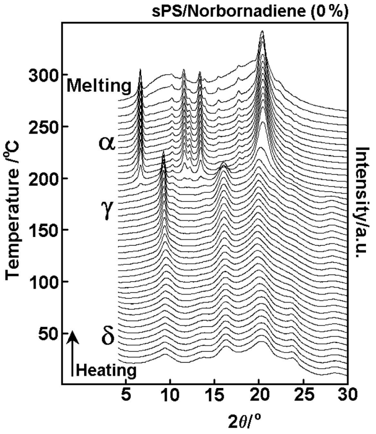

Figure 5. X-ray powder diffraction patterns observed during the heating process of the sPS−norbornadiene complex without norbornadiene (0 wt %).

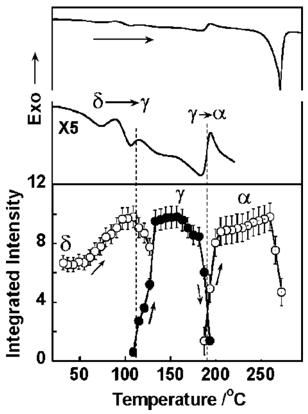

Figure 6. Temperature dependence of the integrated intensity of the X-ray reflections at $2\theta = 9.5$ (δ), 9.3 (γ), and 6.6° (α) evaluated from Figure 5. For comparison, the DSC thermogram of the extracted sample is displayed.

bands, which are characteristic of the δ form. For further understanding of these structural differences, a detailed study of the crystal structure of the sample without norbornadiene (0%) is needed, and this is beyond the scope of the present work. Figure 5 shows the WAXD patterns of the δ form without norbornadiene (0 wt %) in the heating process. The variation in the integrated intensity of X-ray reflections characteristic of each crystalline form $2\theta = 9.5$ (δ), 9.3 (γ), and 6.6° (α) is evaluated and shown in Figure 6 along with the DSC thermogram of the extracted sample. WAXD data indicate that the onset temperature of the δ-to-γ transition is 100 °C. The DSC thermogram also showed a complex behavior in the temperature range of 100−110 °C. These results indicate that the δ-to-γ transition is more complex in the case of the δ form sample without norbornadiene molecules. Upon further heating, the γ form transformed into the α form only at higher temperature different from the samples containing 28 and 11 wt % norbornadiene molecules, where the β form was also obtained along with the α form. These results clearly indicate that the solvent molecules in the amorphous region play a crucial role in triggering the crystalline phase transitions.

By combining all of the experimental data presented in this article, we propose the model that is schematically illustrated in Figure 7 to explain the phase-transition behavior from δ to γ (β) to α (β) and from δ to γ to α. The initial content of the norbornadiene molecules has a significant role in deciding the δ-to-γ transition temperature. The sample without any norbornadiene molecules shows the δ-to-γ transition above 100 °C. From these results we may say that the norbornadiene molecules residing in the amorphous phase are considered not only to affect the mobility of the amorphous phase (glass-transition temperature) but also to reduce the temperature of the δ-to-γ transition through the activated motion of the molecules in the crystalline−amorphous interfacial part. Another important point is that the sample with solvent gives the thermodynamically stable β form along with the α form at higher temperature, whereas the sample without solvent gives only the α form.

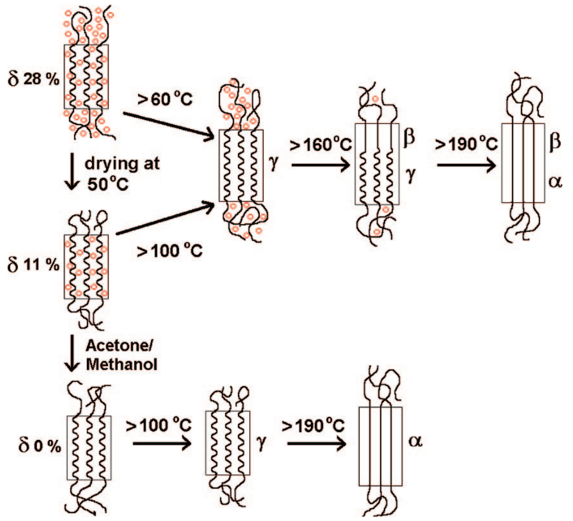

Figure 7. Schematic illustration of phase-transition behavior detected for the sPS−norbornadiene complex starting with 28, 11, and 0 wt % of norbornadiene. The straight solid lines indicate the all-trans zigzag conformation, the curved lines indicate the helical conformation, and the small circles indicate the solvent molecules.

Conclusions

In the present article, we investigated the effect of norbornadiene molecules, which reside in the amorphous phase, on the phase-transition behavior of the δ form during heating. The DSC and WAXD data obtained for the samples with different contents of norbornadiene revealed that the δ form transforms into the γ form at lower temperatures (70−120 °C), and the onset of the transition depends on the amount of norbornadiene molecules in the starting sample. The δ form without any norbornadiene transforms into the γ form above 100 °C. The thus obtained γ form was found to transform into a mixture of α and β forms when the sample contained some amount of residual solvent. It transforms into only the α form for the solvent-free sample. In this way, the solvent molecules trapped in the amorphous phase can accelerate the phase transitions at lower temperature (δ to γ) and more easily induce the γ-to-β phase transition. Bulky norbornadiene molecules may expand the cavities in the crystal lattice of the δ form and make the diffusion of norbornadiene from the lattice easier, resulting in the transition to the γ phase in the lower temperature region. The norbornadiene molecules still trapped in the amorphous region after the δ-to-γ transition may enhance the partial dissolution of the crystal lattice, followed by recrystallization to the β form.

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