Thermally-Induced Phase Transitions in the Uniaxially-Oriented δ Form of Syndiotactic Polystyrene

*E. Bhoje Gowd, Naoya Shibayama, Kohji Tashiro**

Summary: The empty δ (δ_e) form of uniaxially-oriented syndiotactic polystyrene (sPS) samples were obtained by extracting the solvent molecules from the δ form of sPS and solvent complex in acetone and methanol. Temperature dependence of the X-ray fiber diagrams starting from the uniaxially-oriented δ_e and δ form has been measured successfully at various temperatures for the first time. The transition behavior was traced clearly by separating the equatorial and layer line reflections. The δ_e form transformed to the γ form *via* an intermediate form. The intermediate form is speculated to take disordered structure due to the empty cavities present in the δ_e form. Calorimetric studies showed an endotherm followed by an exotherm during this phase transition, which is consistant with such a speculation. On the other hand the δ form transformed to the γ form directly without passing through the intermediate form or δ_e form. During the δ to γ phase transition the solvent molecules evaporate through the columnar structure in a broad range of temperature, allowing the transition to occur smoothly.

Keywords: fiber diagrams; phase transition; polymorphism; syndiotactic polystyrene; wide-angle X-ray scattering

Introduction

Syndiotactic polystyrene (sPS) has been found to exhibit various types of crystal modifications with different molecular conformations as well as different packing structures, which are obtained by controlling the preparation conditions of the samples.[1–6] Phase transformation of sPS within the complex polymorphism has been widely studied by using various techniques. [1–6] In order to understand the phase transition mechanisms from δ_e to γ and δ to γ we have succeeded for the first time to measure the temperature dependence of the X-ray fiber diagrams starting from the uniaxially-oriented δ_e and δ forms. In the present paper we will report the structural changes during heating of the uniaxially oriented δ_e form and δ form by X-ray diffraction and calorimetric studies.

Department of Future Industry-oriented Basic Science and Materials, Toyota Technological Institute, Tempaku, Nagoya, 468-8511, Japan
Tel: (+81) 52 809 1790; Fax: (+81) 52 809 1721
E-mail: ktashiro@toyota-ti.ac.jp

δ_e - to - γ Transition

Figure 1 shows the X-ray fiber diagrams at different temperatures starting from the δ_e form of sPS and chloroform complex. The change in the equatorial patterns evaluated from fiber diagrams in the heating process is shown in Figure 2. The variation of the integrated intensity of various reflections with temperature is shown in Figure 3. It is evident from this figure that the reflection at $2\theta = 8.0^\circ$, which corresponds to the 010 reflection of the δ_e form, started to decrease in intensity from 70 °C and vanished at 100 °C. Simultaneously, a new reflection appeared at about $2\theta = 9.6^\circ$ at 70 °C and the intensity increased up to 100 °C. The disappearance of the existing peaks and the appearance of the new peaks in the broad temperature range 70–100 °C indicate a

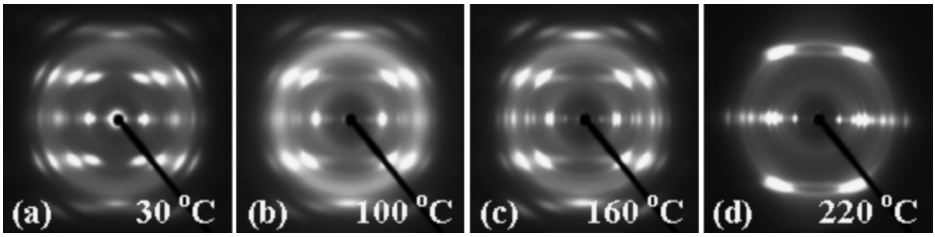

Figure 1.
Temperature dependence of the X-ray fiber diagram taken for the uniaxially-oriented δ_e form of sPS/chloroform complex in the heating process at (a) 30 °C (δ_e), (b) 100 °C (intermediate form + γ), (c) 160 °C (γ), and (d) 220 °C ($\alpha + \beta$).

phase transition and the resultant new phase is assigned as an intermediate phase. The reflections at $2\theta = 16.3^\circ$ and 20.7° were more diffusive with (increasing) temperature and could not be detected any more at 100 °C. Above 100 °C, new reflections corresponding to the γ form appeared at $2\theta = 9.1^\circ$ and 10.1° and on further heating the reflection corresponding to the intermediate form at $2\theta = 9.6^\circ$ vanished at 120 °C. That is to say, the intermediate form transformed into the γ form in a broad temperature range 100–120 °C. Above 120 °C, the intensity of the γ form reflections increased. As the temperature increased furthermore, the reflections of the γ form decreased steeply in a narrow temperature range of 190–200 °C, while those of the α and β forms increased as shown in Figures 1 and 2. The details of the crystalline transition from γ to α (β) forms will be discussed elsewhere. Based on the equatorial reflections shown in Figure 3, it is clearly evident that a new form appears in the course of transition from δ_e to γ form.

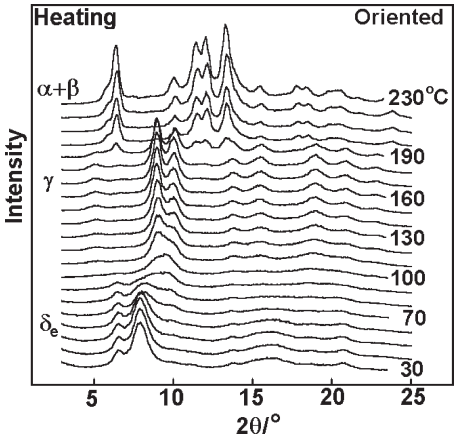

Figure 2.
X-ray diffraction profiles of the equatorial line of δ_e form of sPS/chloroform complex evaluated from fiber diagrams in the heating process.

To clarify the phase transition behavior in more detail we plotted the change in the first layer line profile with temperature as shown in Figure 4. Careful observation in the layer line profiles indicates that the δ_e phase passes through an intermediate phase before transforming into the γ form. As seen in the Figure 1 the diffuse scatterings are observed in the transition temperature range 70–120 °C by retaining a well defined layer line reflections. As a possibility we may speculate that the melting and recrystallization phenomenon occur during the phase transition from δ_e to an intermediate phase and to γ form and as a result an amorphous content increases in the transition temperature range. DSC results also confirmed such a speculation by indicating a small endotherm followed by an exotherm in a broad temperature range at 90–120 °C during the phase transition as shown in Figure 5. But we need to notice that the molecular chains maintained almost the same orientation during the phase transition as seen from the X-ray diffraction patterns. Therefore, as another possibility the δ_e form is speculated to transform transiently to an intermediate phase with the conformationally disordered

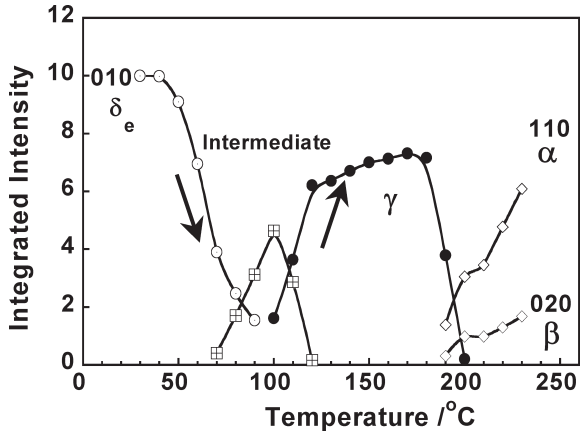

Figure 3.
Temperature dependence of the integrated intensity of the reflections at $2\theta = 8.0^\circ$ (δ_e), 9.6° (intermediate), 9.1° (γ) ,6.5° (α), and 6.0° (β) evaluated from Figure 2.

chains oriented along the draw axis, giving an endothermic peak (melting) in DSC thermogram, and then this intermediate phase transforms to the γ form by reorganizing the disordered chains giving an exothermic peak (recrystallization) in the DSC thermogram. The empty cavities present in the δ_e form may be responsible for such an intermediate form. The diffuse scatterings observed in the X-ray fiber diagram of an intermediate phase (Figure 1(b)) may support the irregular packing structure of the conformationally-disordered chains.

δ - to - γ Transition

We measured also the X-ray fiber diagrams at different temperatures starting from the δ form of toluene complex and the selected fiber diagrams are shown in Figure 6. Figure 7 gives the change in the equatorial pattern in the heating process and the variation of the integrated intensity of the various reflections with temperature. The 010 reflection of the δ form started to decrease in intensity from 100 °C and simultaneously the new reflection intrinsic of the γ form started appearing at about

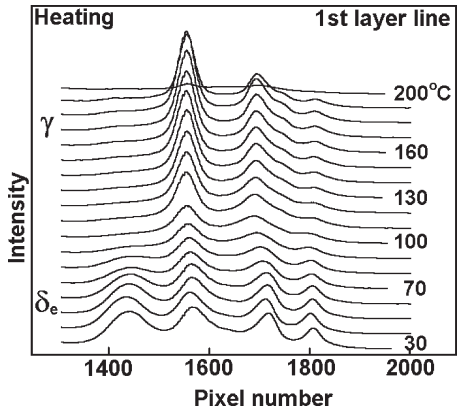

Figure 4.
X-ray diffraction profiles of the first layer line of the δ_e form of sPS/chloroform complex evaluated from the fiber diagrams in the heating process.

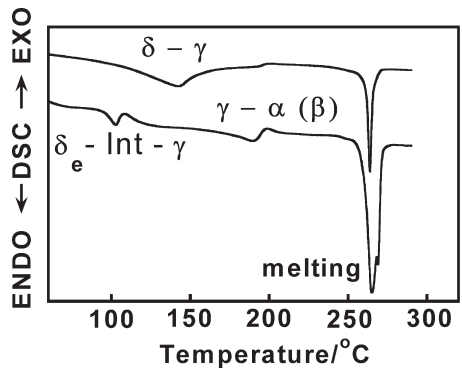

Figure 5.
DSC thermograms of δ and δ_e samples of sPS/solvent complex taken in the heating process.

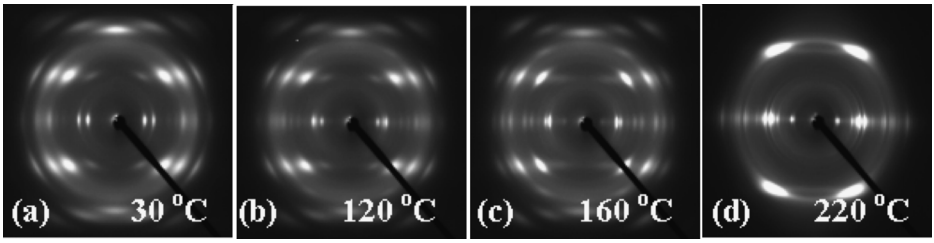

Figure 6.
Temperature dependence of the X-ray fiber diagram taken for the uniaxially-oriented δ form of sPS/toluene complex in the heating process: (a) δ (b) δ + γ (c) γ and (d) α (β).

$2\theta = 9.1^{\circ}$. Once the temperature reached above 140 °C, the 010 reflection at $2\theta = 7.7^{\circ}$ disappeared completely and pure γ form appeared above this temperature. Phase transition from δ to γ occurs over a broad range of temperature and these two forms coexist in this temperature range. It is worth recalling here that Tashiro et al.[3] speculated that by heating or by supplying new solvent, the original solvent molecules are purged away easily along the columnar axis because of the relatively weak intermolecular interactions between sPS chains and solvent molecules. The present study also confirms such a speculation that the solvent molecules evaporate through the columnar structure and the solvent evaporation occurs in a broad temperature range. Once the solvent molecules leave the crystal lattice, the structure immediately transforms to the γ form as the temperature already reachs above 100 °C. Therefore, in this temperature range both δ and γ forms coexist. These results are in good agreement with the reported data that the δ form transformed to the γ form immediately once the solvent molecules evaporated and therefore the transition occurs between only the two crystalline phases.[4–6]

DSC thermogram was investigated on the δ form. It shows a broad endotherm during the transition of δ to γ form, corresponding to the solvent evaporation as shown in the Figure 5. A broad endotherm during δ to γ form indicates the δ form transformed to the γ form without passing

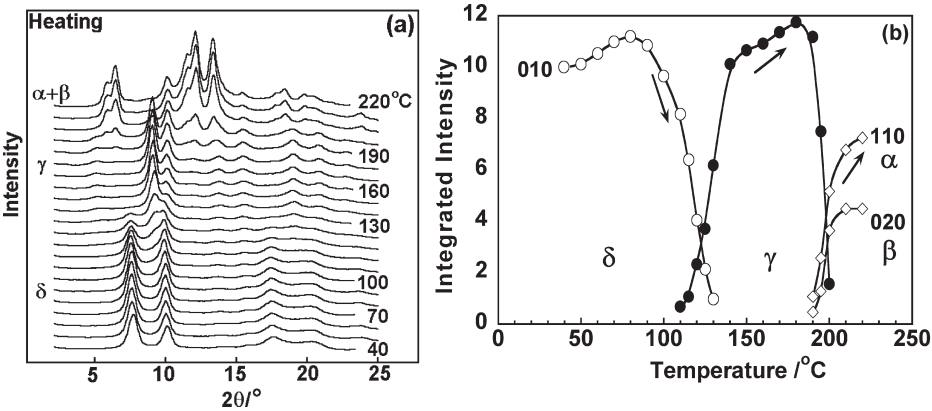

Figure 7.
(a) X-ray diffraction profiles of the equatorial line of δ form of sPS/toluene complex evaluated from fiber diagrams in the heating process and (b) the integrated intensity of the reflections $2\theta = 7.7^{\circ}$ (δ), 9.1° (γ) ,6.5° (α), and 6.0° (β) evaluated from Figure 6a.

through an intermediate form. At higher temperatures the γ form transforms to the α (β) form at 190–200 °C and at around 265 °C the melting of the α (β) form occurs. These results are in good agreement with X-ray diffraction results.

Conclusions

We measured the temperature dependence of the X-ray fiber diagrams starting from the uniaxially-oriented δ_e and δ form of sPS/solvent complex at various temperatures. By combining the experimental data of X-ray diffraction and DSC data collected during the phase transition of δ_e to γ, it has been found that the δ_e form transformed to the intermediate form transiently before transforming into the γ form. The δ form transformed to the γ form directly without passing through the intermediate form or δ_e form. This might be due to such a situation that during δ to γ phase transition the solvent molecules evaporate through the columnar structure relatively easily to make the structural change from δ to γ form smoothly. As the temperature increased furthermore, the γ form transformed to the α (β) forms in a narrow temperature range of 190–200 °C.

Acknowledgements: This work was financially supported by MEXT ''Collaboration with Local Communities'' Project (2005–2009).

[1] G. Guerra, V.M. Vitagliano, C. De Rosa, V. Petraccone, P. Corradini, *Macromolecules* **1990**, *23*, 1539.
[2] C. Manfredi,, C. De RosaG. Guerra, M. Rapacciuolo, F. Auriemma, P. Corradini, *Macromol. Chem. Phys.* **1995**, *196*, 2795.
[3] A. Yoshioka, K. Tashiro, *Macromolecules* **2003**, *36*, 3593.
[4] E. B. Gowd, S.S. Nair, C. Ramesh, *Macromolecules* **2002**, *35*, 8509.
[5] A. Yoshioka, K. Tashiro, *Macromolecules* **2003**, *36*, 3001.
[6] E. B. Gowd, S.S. Nair, C. Ramesh, K. Tashiro, *Macromolecules* **2003**, *36*, 7388.

