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Structure and Properties of the Mesophase of Syndiotactic Polystyrene IV. Release of Guest Molecules from δ form of Syndiotactic Polystyrene by Time Resolved FT-IR and WAXD Measurement

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ABSTRACT: Syndiotactic polystyrene(sPS) forms clathrates with organic solvent molecules between helical chains of *trans–trans–gauche–gauche*(TTGG) conformation, so called δ form complex. By annealing or extraction, the δ form transforms to the mesophase which has highly regulated molecular cavities between helical chains. Time resolved FT-IR spectra of the sPS films containing δ form complex with toluene were obtained to clarify the relationship between the release of toluene from the δ form and conformational changes of sPS backbone chain. From the results of FT-IR, content of TTGG conformation decreased with annealing time, and increased with extraction time by acetone, indicative of the formation of γ form from amorphous phase. The mesophase extracted holds high content of TTGG conformation and is stable, compared to annealed sample. The solvent extraction method is thus a better technique to make mesophase membranes containing molecular cavities.

KEY WORDS Syndiotactic Polystyrene / Mesophase / Time Resolved Measurement / WAXD / FT-IR / Conformation / Characterization / Molecular Cavity /

Syndiotactic Polystyrene (sPS) forms four crystalline polymorphisms, α, β, γ, and δ. α and β forms have backbone chains in *trans–trans*(TT) planer zigzag conformation with identity period 5.1Å. γ and δ forms show *trans–trans–gauche–gauche*(TTGG) helical chains of s(2/1)2. Although α and β are crystallizable through molten and amorphous sPS, the δ form is formed from sPS solution and sPS helical chain clathrates regularly with used solvent molecules as guests, so called "δ form complex". γ with no guest molecules is derived from δ by annealing above approximately 150 °C, and the packing of TTGG helical chains of γ becomes dense. Guest molecules of δ can be removed from the clathrate δ complex crystal remaining almost constant structure, resulting in a mesophase with molecular cavities whose crystalline structures have been described.[1–6] The "mesophase" means an intermediate phase between δ and γ and is the same as empty δ.[7]

The previous article describes two methods to prepare mesophase.[8] One is thermal annealing of δ form, meaning of the removal of guest solvent, above glass transition temperature of sPS. The other is step wise extraction method. The first step is extraction by acetone, relatively poor solvent to sPS which performs the exchange of guest solvent of δ form. The second step is extraction by methanol: methanol exchanges acetone and methanol is evaporated thoroughly under vacuum without structural change. One can obtain mesophase sPS with molecular cavities.

Crystalline structure and conformational change of sPS membrane were examined during the release of guest molecules from δ by annealing and extraction. The release of toluene, guest molecules, in sPS δ was investigated by Fourier Transform Infrared Spectrophotometer (FT-IR) spectroscopic *in situ*.[9–13] The characterization of δ and *in situ* observation of conformational and structural change were carried out by time resolved FT-IR and wide angle X-Ray diffraction (WAXD). Mesophase data by step wise extraction are discussed in relation to formation of γ (TTGG) from amorphous phase.

EXPERIMENTAL

Pellet-type sPS (M_w = 200000) was kindly supplied by Idemitsu Petrochemical Co., Ltd. The sPS δ membrane was prepared by casting from toluene solution of sPS at room temperature (cast RT). WAXD results were recorded at room temperature with a Rigaku RAD-RC diffractometer using Cu-$K\alpha$ as the radiation source and Ni filter at 2θ of 5 to 30°. The conformation of sPS and release of toluene molecules were studied with a Perkin-Elmer 2000 FT-IR spectrometer at the resolution of $1.0\,\text{cm}^{-1}$ and $4000–400\,\text{cm}^{-1}$. Time resolved FT-IR were performed on as-cast membranes during

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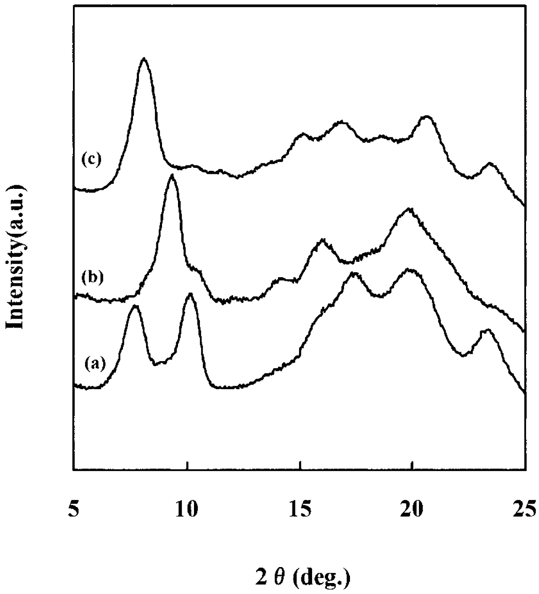

Figure 1. X-Ray diffraction of (a) δ form of cast RT, (b) mesophase by annealing, and (c) mesophase by extraction.

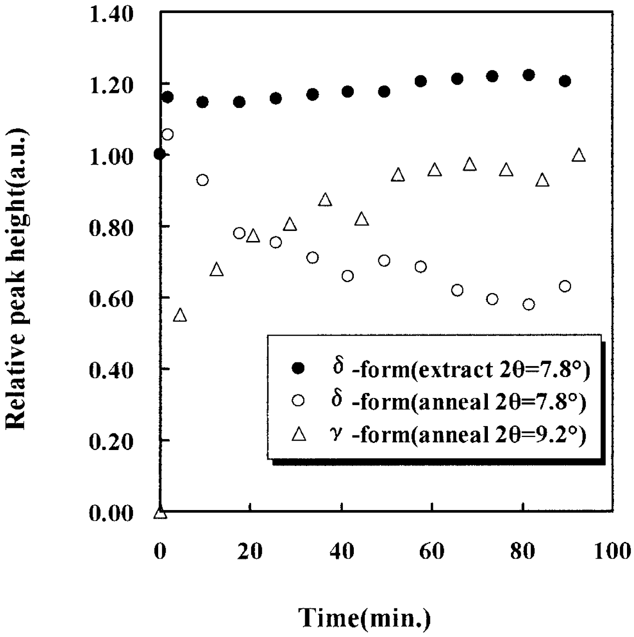

Figure 2. Annealing time dependence of relative peak height at $2\theta = 7.8°$ and 9.2° in WAXD; annealing temperature is 150 °C.

annealling at 120, 140 °C and extraction by saturated vapor of acetone (first step) using a hand-made sample cell with windows of KBr and temperature controller. Desorption from δ was monitored until the disappearance of the toluene IR peak. Time resolved WAXD was performed by the hand-made sample cell using Be window composed of a part of introduction of vapor pressure of guest molecules and temperature controller.

RESULTS AND DISCUSSION

Transformation to the Mesophase

Wide angle X-Ray diffraction (WAXD) of the crystalline structures of δ, γ, and mesophase composed of TTGG conformation was done during annealing and extraction. Figure 1 shows WAXD profiles of as-cast (a) and mesophase (b,c) sPS membranes. A typical WAXD profile of sPS δ form is shown in Figure 1 (a): diffraction peak observed at 2θ of 7.8°, 10.5°, 17°, 20°, and 23°, corresponding to b-axis lattice constants (010), $(\bar{2}10)$, (020), $(\bar{2}30)$, and $(\bar{4}11)$ of δ form, respectively. Annealed sample of δ provided a typical WAXD profile with a peak at $2\theta = 9.2°$ (Figure 1 (b)). δ thus transforms partly into γ by annealing. Therefore, annealing is not a suitable method to prepare mesophase sPS membrane. Figure 1 (c) shows a typical WAXD profile of extracted mesophase structure. Crystalline structural change during annealing and extraction was *in situ* monitored by time-resolved X-ray diffraction. Figure 2 shows annealing time dependence of relative peak height at a typical peak of $2\theta = 7.8°$ (δ form) and $2\theta = 9.2°$ (γ form). Peak height of δ ($2\theta = 7.8°$) gradually decreased with annealing time. Another peak of γ form ($2\theta = 9.2°$) appeared simultaneously. This means a slight breakdown of δ and formation of γ by thermal annealing at 150 °C. Peak height of $2\theta = 7.8°$ was still kept or much larger in the case of mesophase prepared by step-wise extraction, resulting in the removal of guest molecules from δ. There is thus little change of crystal unit lattice during formation of the mesophase.

Evaluation of Conformational Change

Conformational change was *in situ* observed by time-resolved FT-IR spectra. Conformation-active IR absorption bands characteristic to sPS were noted. In the present work the absorption bands of 933 and 841 cm^{-1} assigned to TTGG and random coil conformation, respectively, confirmed the conformation of sPS. Absorbance at 933 and 841 cm^{-1} should be normalized by the conformational independent band at 1180 cm^{-1} as internal standard to correct membrane thickness. Relative absorbance at 933 cm^{-1} to that at 1180 cm^{-1} corresponds to content of TTGG conformation. We used relative peak height instead of relative absorbance to examine more precisely conformation of TTGG. From FT-IR spectra of as-cast membrane at room temperature, membrane includes both TTGG and random coil conformations.

Figure 3 shows the time dependence of relative peak height of TTGG and random coil conformation during extraction and annealing at 120 and 140°C. The content of TTGG conformation decreased with annealing time at 120 and 140 °C and leveled off to approximately half the initial relative peak height in *c.a.* 25 min. The content of random coil conformation did

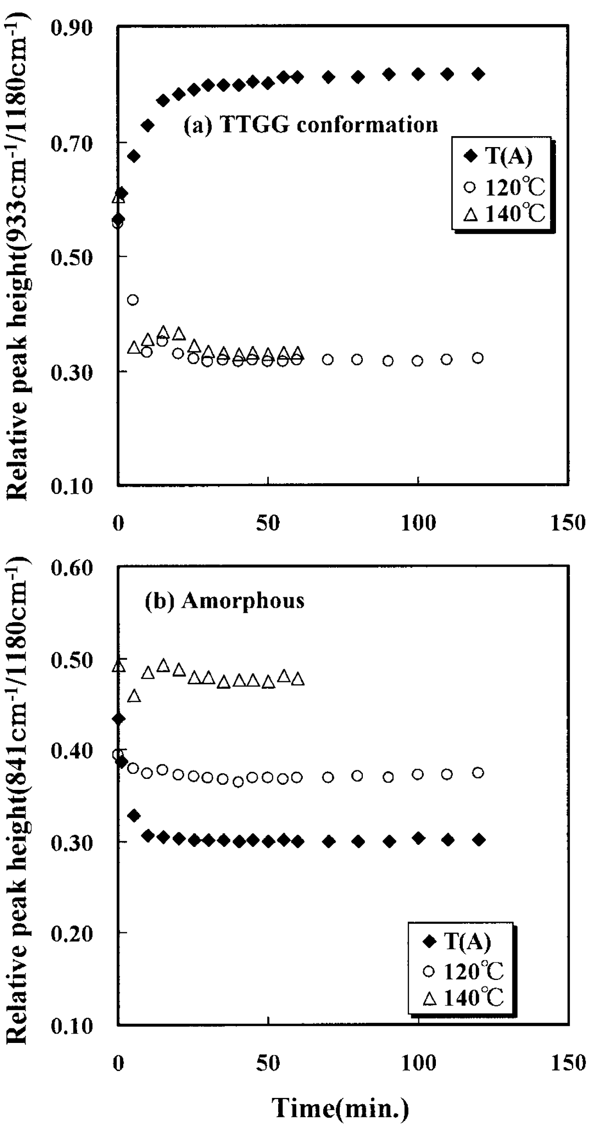

Figure 3. Time dependence of relative peak height at 933 cm^{-1} of (a) TTGG conformation and at 841 cm^{-1} of (b) amorphous phase.

not change remarkably with annealing time. This indicates that TTGG conformation of δ becomes unstable and breakd down to short helical conformation and transforms to TTGG conformation of γ. With extraction by saturated vapor of acetone of δ cast from toluene (T(A)), the TTGG conformation increased with extraction time, becoming constant at 30 min, random coil conformation reduced simultaneously, and the toluene IR peak of guest molecules in δ disappears completely at 2 h (Figure 4). Random coil conformation may thus change to TTGG conformation from amorphous phase of sPS, due to extraction by acetone vapor. Stability of mesophase possibly increases due to γ of TTGG conformation in a matrix amorphous phase. This is a probable reason of high content of mesophase by stepwise extraction. It is reasonable that increase of TTGG conformation by extraction leads to the enhanced crystallinity of δ as shown by WAXD. TTGG conformation decreased quickly with annealing time, although the toluene peak disappeared gradually (Figure 4). Annealing at 120 or 140 °C activates micro Brownian motion in amorphous phase because annealing temperature is higher than the glass transition temperature of sPS amorphous phase, *c.a.* 100 °C. TTGG conformation is influenced by micro Brownian motion and reduced considerably. Observed desorption of toluene molecule from δ form leads to unstable TTGG conformation. TTGG conformation of δ thus becomes unstable. Transformation of δ to γ should occur simultaneously by annealing. Such conformational changes by annealing should balance each other. Unstability of conformation prevails and decreased TTGG conformation is observed in Figure 3. In the case of extraction, guest molecules of toluene were exchanged at room temperature by extraction solvent. Acetone, a smaller molecule than toluene showed very low ability of complexation. TTGG conformation of δ is considered stable under exchanged state with guest molecules, acetone at 25 °C. A second extraction by methanol was carried out. Stable mesophase with high TTGG conformation was obtained.[3, 14]

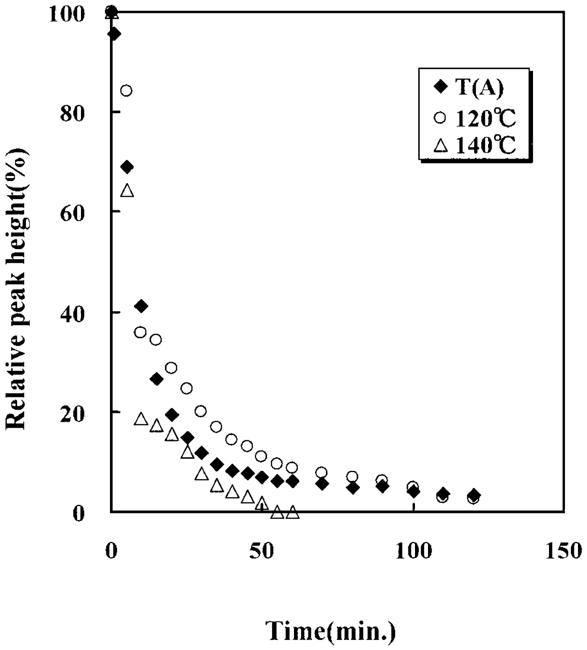

Figure 4. Time dependence of relative peak height at 465 cm^{-1} assigned to toluene molecule.

A schematic representation of phase transformation of the sPS is shown in Figure 5. Annealed sample is a mixture of γ and mesophase, and extracted sample is composed mostly of mesophase. The mesophase obtained by extraction may be stable owing to the TTGG conformation.

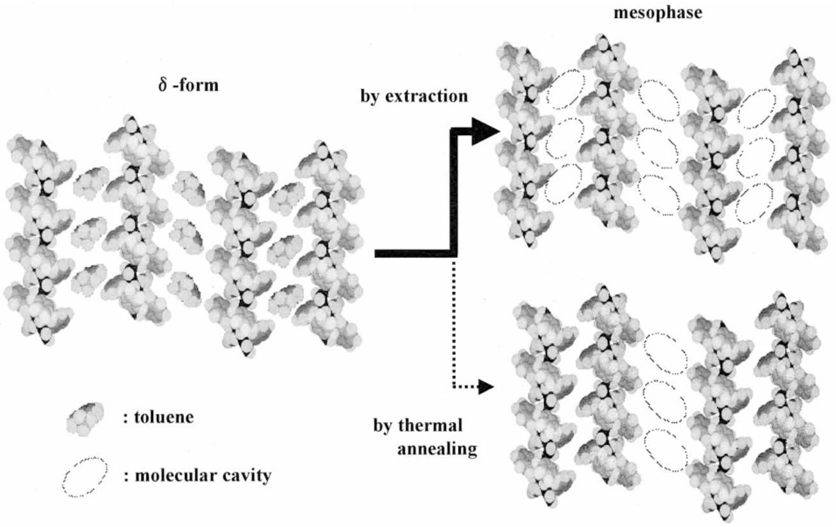

Figure 5. Schematic representation of phase transformation in sPS.

CONCLUSIONS

Thermal annealing at 120 or 140 °C and solvent extraction at room temperature were done to obtain more stable mesophase with molecular cavities. WAXD and FT-IR were done to examine crystal structure and main chain conformation of sPS during thermal annealing and extraction. From FT-IR, the content of TTGG conformation decreased with annealing, but increased with acetone extraction because of transformation to γ of TTGG conformation from random coil in the amorphous phase. Solvent extraction is thus a better technique to prepare the mesophase containing many molecular cavities in comparison with annealing.

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