Crystallization Condition of Glassy Syndiotactic Polystyrene in Supercritical CO$_2$

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ABSTRACT: Polymorphism of syndiotactic polystyrene (sPS) induced by supercritical CO$_2$ (scCO$_2$) was investigated as functions of temperature and pressure by using infrared spectroscopy and X-ray diffraction. When a glassy sPS was incubated in scCO$_2$ at 18 MPa, a modification with the trans-trans-gauche-gauche (t$_2$g$_2$) conformation appeared between 40 °C and 80 °C, and the planar zigzag form appeared above 60 °C. Both forms coexisted between 60 °C and 80 °C. Below the critical temperature of CO$_2$ (31.1 °C) no crystallization occurred at any pressure. When the pressure of CO$_2$ is below the critical pressure (7.2 MPa), the t$_2$g$_2$ form did not appear at any temperature but the planar zigzag form appeared above 90 °C. These results indicate that incubation in supercritical CO$_2$ is necessary for the formation of the t$_2$g$_2$ form. On the other hand, the planar zigzag form was obtained irrespective of the physical states of CO$_2$, but depended on the incubation temperature and pressure. This indicates that the conformational stability of the planar zigzag form depends only on the thermal factors. The crystallization temperature into the planar zigzag form decreased with increasing pressure of CO$_2$ due to the plasticizer effect of CO$_2$.

KEY WORDS   Crystallization / Syndiotactic Polystyrene / Supercritical CO$_2$ / Infrared Spectroscopy /

Syndiotactic polystyrene (sPS) exhibits polymorphism. So far four crystal modifications and two mesomorphic phases have been reported, since Ishihara *et al.*[1] succeeded the synthesis of highly syndiotactic polystyrene.[2—8] The molecular conformation of the α and β forms is planar zigzag but that of the γ and δ forms is t$_2$g$_2$. Kobayashi and his coworkers revealed the characteristic vibrational modes for these conformations using the infrared and Raman spectroscopies.[9—13] It is worth noting that the formation of the modifications with the t$_2$g$_2$ sequence requires the assistance of an organic solvent. Several methods are known to obtain the t$_2$g$_2$ crystal forms, *i.e.*, casting from an organic solution, soaking the glassy sPS in an organic non-solvent, and exposing the glassy sPS in vapor of an organic solvent. For example, chloroform, benzene, toluene, and other many aromatic compounds were found to induce the δ-form.[5, 9] Since the δ-form is one of the host–guest type crystals formed by the sPS chains and solvent molecules, the cavity created by the sPS chains in the crystal is believed to play an important role to form the complex structure.[8, 14] The γ-form also takes the t$_2$g$_2$ conformation but is formed without solvents.[5, 11]

These crystal structures have been investigated in terms of various methods. Among them, the infrared spectroscopy is very sensitive to conformational changes and provides information not only on the local vibrations such as the stretching and bending modes but also on the molecular symmetry defined by the factor group analyses. The symmetries of the planar zigzag and the t$_2$g$_2$ conformations of sPS are represented by C$_{2V}$ and D$_2$, respectively. Since the number of the monomer units included in the repeating period of those conformations is different, the number of the modes for the t$_2$g$_2$ conformation is about twice of that for the planar zigzag conformation. Accordingly, the infrared spectroscopy is a powerful tool to distinguish the molecular conformations of sPS.

Nowadays, a supercritical CO$_2$ (scCO$_2$) is widely used for synthesis, selective extraction, and so on. Since the supercritical state of CO$_2$ is realized under a relatively mild condition (31.1 °C and 7.2 MPa), it allows us to control easily the higher order morphology of crystalline polymers. In addition, scCO$_2$ is an eco-friendly solvent. The phase transition and polymorphism of sPS induced by CO$_2$ were reported by Handa *et al.*[15] They found that sPS undergoes the solid–solid phase transition which cannot be induced by ordinary organic solvents. They also found that the phase transition and glass transition temperatures in compressed CO$_2$ are lower than those in ambient states, indicating that a compressed or a supercritical CO$_2$ is an effective plasticizer for sPS. Reverchon *et al.* found that scCO$_2$ is efficient to remove the solvents included in the δ-form consisting of sPS and toluene or styrene.[16]

The objective of this paper is to elucidate the molecular structure induced in the atmosphere of the gas, liq-

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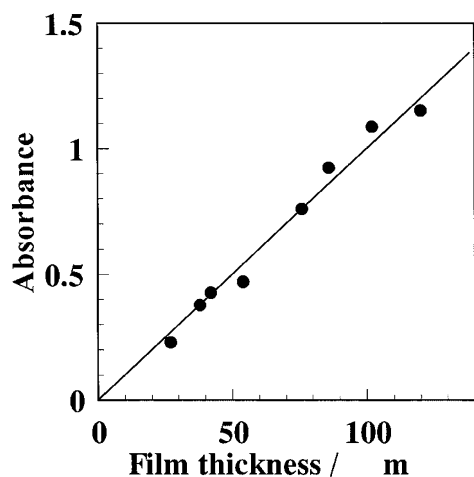[†]To whom correspondence should be addressed.

Figure 1. Dependence of the absorbance at 1028 cm^{-1} band of glassy sPS on film thickness.

Figure 2. Reduced absorbance at 572 cm^{-1} against hold-time in scCO$_2$.

uid, and super critical states of CO$_2$. Infrared spectroscopy has been used to elucidate the effects of temperature and pressure on the molecular structure.

EXPERIMENTAL

The sPS sample was synthesized by the procedure proposed by Ishihara *et al.*, that is styrene monomer and Kaminsky catalyst (cyclopentadienyl titanium trichloride and methylalumoxane) dissolved in toluene was allowed to stand at 0 °C for 24 h.[1, 17]

A glassy sPS was prepared by quenching in ice-water from the melt at 280 °C. The film thickness was about 30 μm. In order to compare the films with different thickness, a 1028 cm^{-1} band was used as the internal standard. This band is considered to be the in-plane mode of C–H bending for the phenyl group and is a local mode with no correlation with the main chain conformation. In Figure 1, the absorbance at 1028 cm^{-1} is plotted against the film thickness. The relationship of absorbance (A) and film thickness (l μm) is represented by the following equation.

$$A = 0.01004 \times l \tag{1}$$

The absorbance at 1028 cm^{-1} was experimentally observed, then the film thickness can be estimated by eq 1. In order to compare the absorbances at the same film thickness, the absorbance of the vibrational modes were reduced to that at the thickness of 50 μm.

The glassy sPS film was allowed to crystallize in scCO$_2$ by using an apparatus made of stainless steel with the capacity of 10 mL.

The infrared spectra were recorded on a spectrometer equipped with a DTGS detector (JASCO FT-IR 660 Plus). For the each spectrum, 32 transients were collected at room temperature. The absorbance o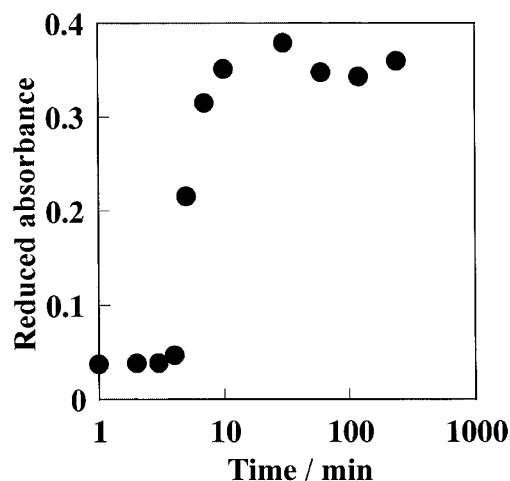f CO$_2$ under various conditions was measured by a hand-made infrared cell. Wide-angle X-ray diffraction patterns were recorded on an automatic diffractometer (RIGAKU) with Ni-filtered CuKα radiation.

RESULTS AND DISCUSSION

Several infrared bands characteristic of the t$_2$g$_2$ helical conformation were reported by Kobayashi *et al.*[9] In order to monitor the crystallization process of this modification, we chose the 572 cm^{-1} band, because this band is very sharp and is comparatively isolated from the other bands. This band is assigned to the out-of-plane mode of C–H bending of the phenyl group, and is very sensitive to the conformation.

Figure 2 represents the dependence of the reduced absorbance at 572 cm^{-1} on the incubation time in scCO$_2$ (50 °C, 18 MPa).

The crystallization occurred quickly and the absorbance reached the equilibrium within 10 min. Therefore the incubation time of 30 min was adopted. This change indicates that the glassy sPS transforms into the t$_2$g$_2$ form in scCO$_2$.

Dependence of Molecular Structure on Temperature

In order to clarify the effect of the incubation temperature (T_i) on the structure, the glassy sPS was incubated in CO$_2$ between 0 and 160 °C under the incubation pressure (P_i) of 18 MPa. Figure 3 shows the infrared spectra for the films prepared at T_i = 50, 70, and 90 °C. The spectral profile for the film incubated at 50 °C is identified as the crystal having the t$_2$g$_2$ conformation. However, the film incubated at 70 °C provided the characteristic bands for the planar zigzag form as well as those for the t$_2$g$_2$ form. At 90 °C, the 572 cm^{-1} band disappeared completely, and the film was found to be consisting of only the planar zigzag form. This
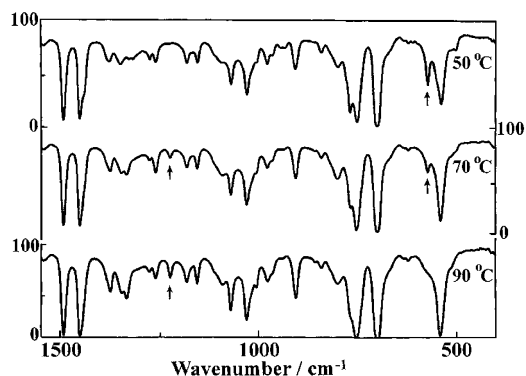
Figure 3. Infrared spectra for the sPS film incubated in scCO$_2$ at 50, 70, and 90 °C and at 18 MPa.
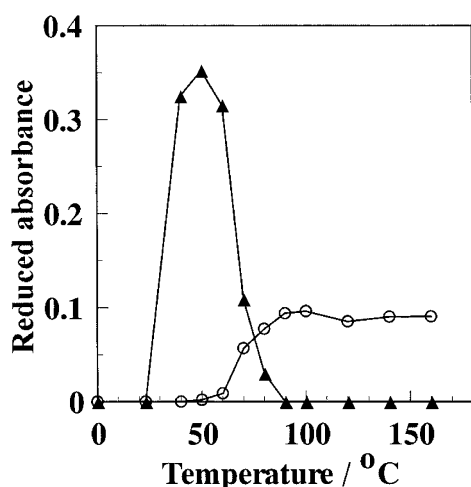

Figure 4. Dependence of the reduced absorbance for the 572 (▲) and 1223 cm^{-1} (○) bands on incubation temperature at 18 MPa in compressed CO$_2$.

Figure 5. Reduced absorbance at 572 (▲) and 1223 (○) cm^{-1} bands versus incubation temperature at 5 MPa.

temperature is much lower than the crystallization temperature of the glassy sPS reported previously (about 140 °C).[9] According to the result by Handa et al., the crystallization temperature decreased with increasing pressure of CO$_2$.[18–20] This effect is explained by plasticization due to CO$_2$ dissolved in the film. The glass transition temperature (T_g) is depressed and therefore the crystallization occurs at lower temperature.

The reduced absorbances for the 572 cm^{-1} and 1223 cm^{-1} bands are plotted against the incubation temperature in Figure 4. Below 30 °C, no trace of crystallization was recognized. In the range of 40 < T_i < 60 °C, only the bands characteristic to the t_2g_2 conformation were observed. The bands due to the two crystal modifications coexisted in the range of 60 < T_i < 80 °C. Finally only the bands due to the planar zigzag form were observed above 90°C. As the critical point of CO$_2$ is 31.1 °C and 7.2 MPa, the experimental condition of P_i = 18 MPa and T_i > 40 °C corresponds to the supercritical state of CO$_2$. According to the phase diagram reported by Starling et al., the con-
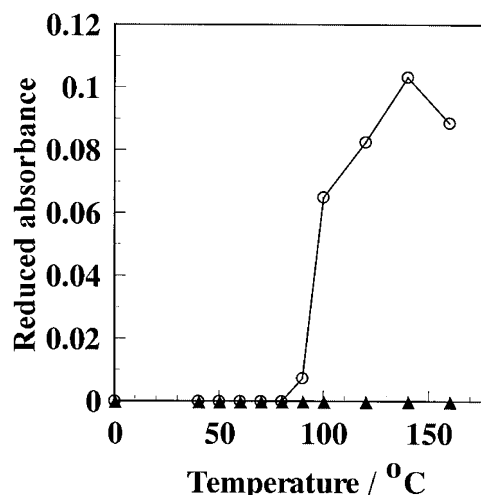
dition of 23 °C and 18 MPa corresponds to the liquid phase.[21] The infrared spectrum obtained at T_i = 23 °C is identified as that for the glassy state, indicating no crystallization occurred. Those facts indicate that the liquid phase of CO$_2$ does not induce the t_2g_2 conformation. In order to examine the behavior in the gas phase of CO$_2$, the incubation temperature and pressure were changed into 5 MPa, which is below the critical pressure of CO$_2$. In Figure 5, the reduced absorbances at 572 and 1223 cm^{-1} were plotted against T_i. As expected, no crystallization to the t_2g_2 form occurred in the range from 0 to 160 °C. These results lead us to conclude that the super critical state of CO$_2$ is the key factor to induce the t_2g_2 conformation. It is well known that the δ-form appeares in the liquid or gas phases of organic solvents. In contrast, the gas and liquid phases of CO$_2$ do not induce the t_2g_2 conformation.

Above 80 °C the 1223 cm^{-1} band increased in intensity. This temperature is a little higher than that at 18 MPa (see Figure 4). This effect is also explained by the difference in the degree of plasticization by CO$_2$.

The molecular mobility and density of CO$_2$ might affect the crystallization to the t_2g_2 conformation. Therefore we examined the correlation between the density of CO$_2$ and the absorbance at 1281 cm^{-1}, which is not the normal mode but probably the overtone or combination modes. The intensity of normal modes in scCO$_2$ was too strong to detect the absorbance. The result is shown in Figure 6. With increasing temperature under the constant pressure, the density of CO$_2$ decreases. The densities calculated from the reference 21 are also plotted in Figure 6 in which we see that the temperature dependence of the absorbance coincide with that of the density. This indicates that the band intensity can be used to determine the density of CO$_2$. In spite of the low density of CO$_2$ above the critical point, the
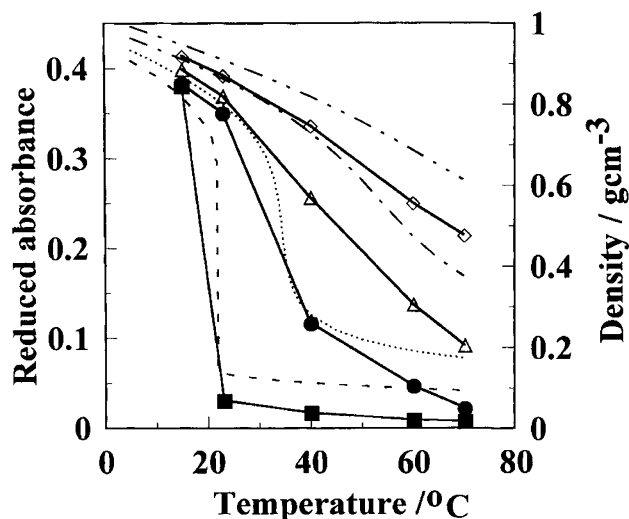
Figure 6. Temperature dependence of absorbance for the 1281 cm^{-1} band of CO$_2$. ■: 5.2 MPa, ●: 8.2 MPa, △: 12.5 MPa, ◇: 18 MPa. The theoretical densities calculated from ref 21 were also depicted in the Figure. ----: 5 MPa, ······ ; 8 MPa, −·−·−·−: 10 MPa, −·−·−·−: 18 MPa.
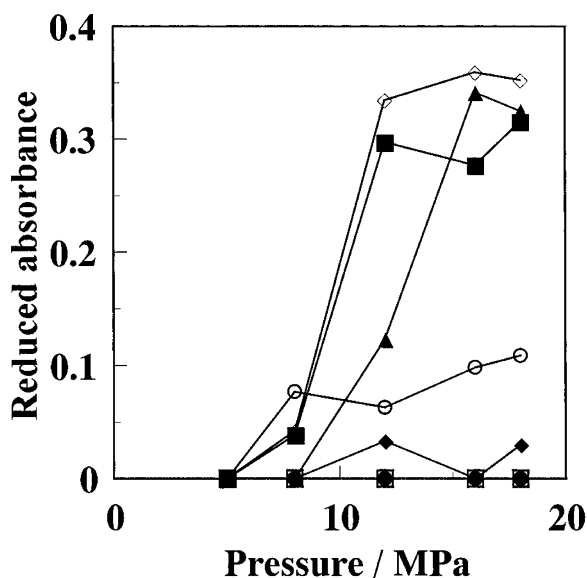

Figure 7. Pressure dependence of the reduced absorbance at 572 cm^{-1} band on pressure. ●: 0 °C, □: 23 °C, ▲: 40 °C, ◇: 50 °C, ■: 60 °C, ○: 70 °C, ◆: 80 °C.
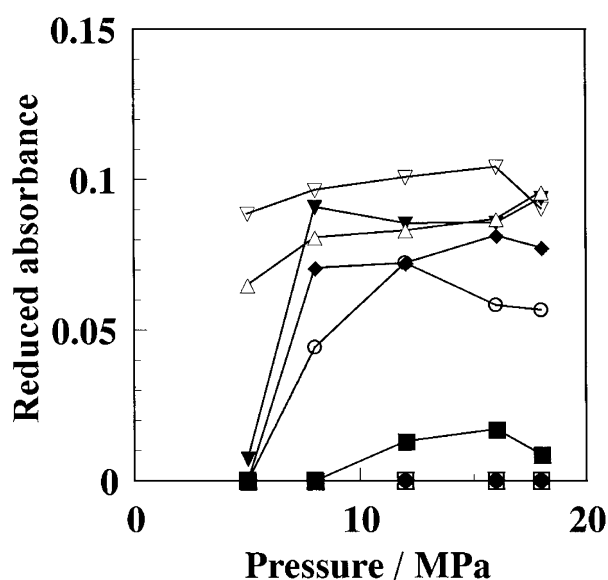

Figure 8. Dependence of the reduced absorbance at 1223 cm^{-1} on pressure in compressed CO$_2$. ●: 0 °C, □: 23 °C, ■: 60 °C, ○: 70 °C, ◆: 80 °C, ▼: 90 °C, △: 100 °C, ▽: 160 °C.

crystallization with the t$_2$g$_2$ conformation was induced. Therefore the density of CO$_2$ is irrelevant to the formation of the t$_2$g$_2$ conformation. We speculate that in the liquid phase of CO$_2$ below 31.1 °C, the molecular mobility of CO$_2$ is too small to induce the t$_2$g$_2$ conformation.

Dependence of Molecular Structure on Pressure

Figure 7 shows the reduced absorbance at 572 cm^{-1} plotted against the incubation pressure (P_i). As mentioned in the above section, the super critical state is important factor to induce the t$_2$g$_2$ conformation. When the glassy sPS was incubated below the supercritical temperature, e.g., 23 °C, no 572 cm^{-1} band was ob-

served in the range of P_i from 5 to 18 MPa. Above the critical temperature and pressure, the crystal with the t$_2$g$_2$ conformation appeared. At pressure of 8 MPa, the 572 cm^{-1} band was weak but above 12 MPa, the absorbance increased and reached to the equlibrium. The highest absorbance of this band was observed at 50°C and above 70 °C, decreased.

The pressure dependence of the intensity of the 1223 cm^{-1} band characteristic of the planar zigzag form is shown in Figure 8.

At 5 MPa, the crystallization into the planar zigzag form commenced at 90 °C. With increasing pressure, the onset temperature of crystallization decreased, i.e., 70 °C at 8 MPa and 60 °C at 12 MPa. This result is
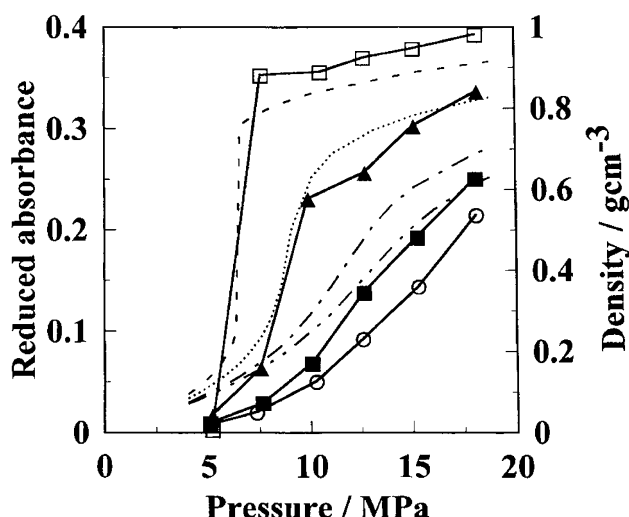
Figure 9. Pressure dependence of absorbance for the 1281 cm⁻¹ band of CO_2. □: 23 °C, ▲: 40 °C, ■: 60 °C, ○: 70 °C. The theoretical densities calculated from ref 21 are also depicted in the Figure. ----: 23 °C, ⋯⋯: 40 °C, −⋅−⋅−⋅−: 60 °C, −⋅⋅−⋅⋅−; 70 °C.

also explained by the plasticization effect of CO_2. The reduced absorbance reached a plateau with increasing pressure. The plateau value strongly depended on the incubation temperature. For instance the absorbance was about 0.015 at 60 °C, but increased with incubation temperature and reached about 0.10 at 160 °C, indicating the increment of crystallinity with incubation temperature.

The absorbance due to CO_2 at 1281 cm⁻¹ is plotted against pressure in Figure 9. With increasing pressure the absorbance being proportional to the density increased steeply around the critical pressure of 7.2 MPa. This behavior corresponds well to the formation of the t_2g_2 conformation shown in Figure 7 except for the results below 31.1 °C. This suggests that not only the molecular mobility but also the density of CO_2 plays an important role on the crystallization into the t_2g_2 form. However the driving force to induce the t_2g_2 conformation is unclear, and we need to investigate the mechanism of the formation of the t_2g_2 conformation in scCO₂ as well as organic solvents.

CONCLUSION

The structure of the polymorphs formed in scCO₂ was investigated as functions of temperature and pressure by using infrared spectroscopy and X-ray scattering. The characteristic bands for the planar zigzag and the t_2g_2 conformation observed at 1223 and 572 cm⁻¹, respectively, were monitored to determine the amount of the modifications formed in the film treated in scCO₂. The t_2g_2 conformation was induced between 40 and 80 °C at 18 MPa. Below the critical temperature of CO_2 (31.1 °C), no crystallization was observed at any pressure. In addition, below the critical pressure (7.2 MPa), no crystallization was observed, neither. These results indicate that the supercritical state is the key factor for generation of the t_2g_2 conformation.

The planar zigzag form was yielded above 60 °C at 18 MPa in scCO₂. Both conformational structures of the planar zigzag and the t_2g_2 conformation coexisted in the range between 60 °C and 80 °C. The temperature of the formation of the planar zigzag form varied depending on pressure. As the CO_2 molecules operate as a plasticizer, the glass transition temperature was depressed and hence the crystallization was also depressed.

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