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Direct Formation of γ Form Crystal of Syndiotactic Polystyrene from Amorphous State in Supercritical CO₂

Weiming Ma, Jian Yu, and Jiasong He*

CAS Key Laboratory of Engineering Plastics, Joint Laboratory of Polymer Science and Materials, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China

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ABSTRACT: The crystallization behavior of amorphous syndiotactic polystyrene (sPS) in supercritical CO₂ was investigated in detail by using wide-angle X-ray diffraction, Fourier transform infrared spectroscopy, and differential scanning calorimetry. The pure γ form crystal was obtained directly after treating amorphous sPS in supercritical CO₂ in a range from 8 to 20 MPa and from 35 to 100 °C. This transformation in supercritical CO₂ was accelerated by increasing temperature. Supercritical CO₂ provided a moderate condition to crystallize the amorphous into the γ form, while liquid CO₂ could not induce the γ form even at the pressure as high as 20 MPa.

Introduction

Syndiotactic polystyrene (sPS) has received considerable interest since the successful synthesis of highly stereoregular sPS by using a homogeneous Ziegler–Natta catalyst in 1986.¹ It is a potential engineering plastic due to its high melting temperature, favorable crystallization kinetics, and good chemical resistance.² sPS possesses a complex polymorphism in its crystalline region involving four crystalline forms: α , β , γ , and δ .^{1–6} The α and β forms have an all-trans planar zigzag TTTT backbone conformation with two different submodifications, while the γ and δ forms consist of an s(2/1)₂ helical backbone conformation of regular repetition of TTGG. Two mesomorphic forms of sPS, having TTTT or TTGG conformations, also have been reported.^{7–9} Woo et al.¹⁰ have summarized the polymorphism and thermal behavior of sPS in detail.

Phase transformation of sPS within the complex polymorphism has been widely reported.¹¹ The α form can be obtained by heating the helical mesomorphic or crystalline forms.^{12,13} It can also be obtained by rapidly cooling from the molten state² or by annealing the amorphous sPS above the glass transition temperature (T_g).^{14,15} The α form can exist in α' and α'' modifications with different degrees of structural disorder. Crystallization from the glassy state at temperatures below 200 °C usually leads to the limit disordered α' modification, while at temperatures above 200 °C to the limit ordered α'' modification.^{10,16–18} The β form can be obtained by slow cooling from the melt or by casting from an *o*-dichlorobenzene solution at 170 °C.¹⁹ In addition, the formation of the β form is favored by melt-crystallized at high temperatures.^{20–22} It is worth noting that the γ and δ forms can be formed from solvent treatment of glassy sPS.^{9,23–25} The δ form in sPS is obtained by solvent casting at temperatures below 100 °C or so, while the solvent-free crystalline γ form is obtained by subjecting the δ form to thermal annealing at medium temperatures to drive out the solvent molecules.^{12,26–28} Moreover, acetone²⁵ or 1,1,2,2-tetrachloroethane²⁹ can induce sPS to develop a crystalline γ form directly.

Supercritical CO₂ ($T_c = 31.1$ °C, $P_c = 7.37$ MPa) or compressed CO₂ is extensively studied nowadays as a

solvent in terms of commercial application and fundamental understanding of solution behavior.³⁰ They can swell and plasticize glassy polymers.^{31–34} The plasticization of the amorphous phase increases the mobility of the polymer chains, which allows the chains to rearrange into a more ordered conformation, resulting in induced crystallization and concomitant changes in the morphology. This effect also leads to the decrease of the energy barriers, thus making some solid–solid transitions possible at much reduced temperatures. Furthermore, polymers absorbed with CO₂ can undergo some solid–solid transitions that cannot be induced under ambient pressure. Handa et al.³⁴ studied the effect of compressed CO₂ on the phase transition and polymorphism in sPS. They found that sPS treated with compressed CO₂ underwent the planar mesophase to β , α to β , and γ to β transitions that only occurred in the presence of liquid solvents. They also found that the phase transitions of glassy sPS to the planar mesomorphic and to the α form, and γ to α transition occurred at lower temperature in compressed CO₂ than those under ambient pressure. Glassy sPS was directly transformed into the γ form when treated with 57 atm (5.8 MPa) of CO₂ at 90 and 175 °C. However, the conditions of the previous experiments did not reach the supercritical condition of CO₂.³⁴ He et al.³⁵ found the solid-phase transition of the α form crystal to the β form of sPS in supercritical CO₂.

Supercritical CO₂ exhibits hybrid properties of a typical gas and liquid, such as low viscosity, high compressibility, and adjustable density from vaporlike to liquidlike. Thus, the conditions of phase transformation in supercritical CO₂ must be different from those in nonsupercritical CO₂. In this study, wide-angle X-ray diffraction (WAXD), Fourier transform infrared spectroscopy (FTIR), and differential scanning calorimetry (DSC) were used to identify the direct formation of γ form crystal of sPS from the glassy state. Some influencing factors such as time and temperature were investigated in detail.

Experimental Section

Syndiotactic polystyrene was kindly supplied by Dow Chemicals with its stereoregularity about 99% determined by high-resolution NMR. The average molecular weight (M_w) is 2.1×10^5 , and the polydispersity (M_w/M_n) is 2.3. Amorphous films

* Author for correspondence: Tel +86-010-62613251; Fax +86-010-62559373; e-mail hejs@sklep.icas.ac.cn.

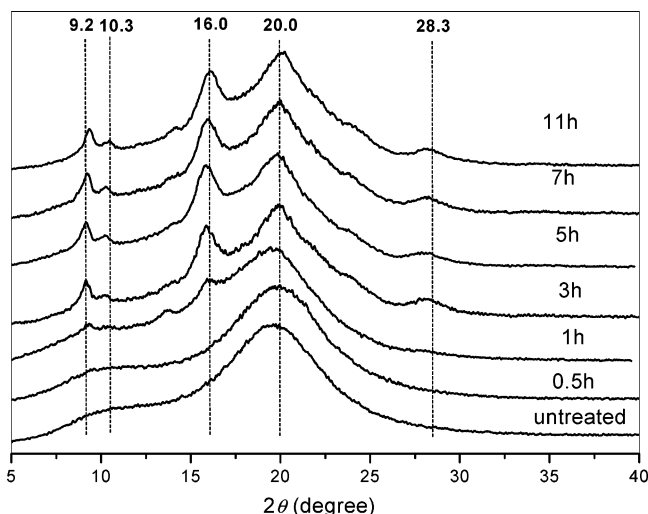


Figure 1. WAXD patterns of glassy sPS after treating in supercritical CO₂ at 12 MPa and 35 °C for different intervals of time.

of thickness about 300 μ m were obtained by forming a thin melt film pressed at 290 °C and then rapidly quenching in an ice–water bath. X-ray analysis revealed the films to be completely amorphous. CO₂ with a purity of 99.95% was supplied by Beijing Analytical Gas Factory, China.

A high-pressure apparatus was used for the treatment in supercritical CO₂. The amorphous sPS films were loaded into a 25 mL high-pressure vessel which was then flushed with low-pressure CO₂ for about 2 min. After the treatment of sPS samples at the desired temperature and pressure for a certain time, the vessel was quenched to room temperature and depressurized slowly. The amorphous films looked transparent and colorless before the CO₂ treatment and turned into opaque and milk white upon the CO₂ treatment.

FTIR measurements were carried out on a Perkin-Elmer FTIR System 2000 in the standard wavenumber range of 370–4000 cm⁻¹ for the investigation of the chain conformations and crystalline forms in sPS. WAXD measurements were conducted on a Rigaku D/max 2500 with Cu K α radiation (40 kV, 300 mA). The scanning 2θ ranged between 5° and 40° with a step scanning rate of 4°/min. A Perkin-Elmer DSC-7 was used for the analysis of the thermal behavior of sPS samples in a dry nitrogen environment. sPS has a high crystallization rate and exhibits a multiple melting behavior during DSC scans. To avoid the recrystallization of sPS during the DSC measurement, all the samples were scanned at a heating rate of 80 °C/min.³⁶ The T_g of untreated sPS sample is 103 °C.

Results and Discussion

Effect of the Treatment Time on the Phase Transition. Figure 1 shows the WAXD patterns of sPS samples treated in supercritical CO₂ (35 °C and 12 MPa) from the glassy state for different time. The broad peak reveals the original sample to be amorphous.³⁴ There are no changes of X-ray diffraction for sPS sample treated in 12 MPa of CO₂ at 35 °C for 30 min. Some indistinct peaks appear after 1 h treatment. When the time is increased to 3 h, the reflection peaks at $2\theta = 9.2^\circ$, 10.3° , 16.0° , 20.0° , and 28.3° , attributed to the typical characteristics of γ form,^{29,37} are present in the WAXD pattern of sPS samples. Further increase of the treatment time does not increase the intensity of these peaks, indicating the maximum crystallinity reached after 3 h annealing at 12 MPa of CO₂ at 35 °C. All the sPS samples treated at 35 °C in supercritical CO₂ show broader reflection peaks of the γ form. This means that the existence of the γ form crystal has either poor order or very small crystalline domains.²⁹ It should be noted

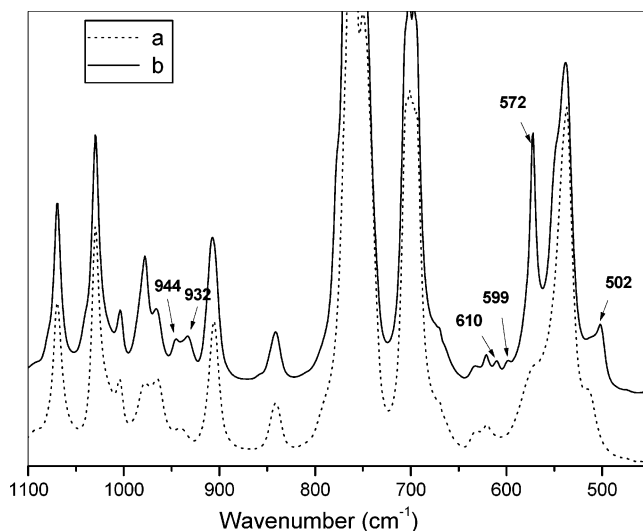


Figure 2. FTIR patterns of sPS samples of (a) amorphous and (b) treated in supercritical CO₂ (35 °C and 12 MPa) for 5 h.

that the γ form has usually been obtained by heating the δ form or solution casting with certain solvents.^{26–29} In the present study, after the treatment in supercritical CO₂, amorphous sPS was directly transformed into the γ form. The sPS samples were intensively plasticized due to the sorption of supercritical CO₂, and the mobility of polymer chains was increased such that their rearrangement into γ crystal became kinetically possible at 35 °C. By comparison, the mesomorphic or crystalline forms with all trans conformation were obtained by annealing amorphous samples under ambient pressure only above T_g .^{14,15,34} It should be noted that the temperature at 35 °C using for the amorphous sPS treatment is moderate and close to ambient temperature, much lower than the original T_g at 103 °C of glassy sPS sample. Obviously, supercritical CO₂ is responsible for the direct transformation of amorphous sPS into the γ form.

Besides WAXD, FTIR is also a useful tool to identify and characterize the change of chain conformation associated with the different polymorphic crystal forms. The above-described phase transition was further analyzed by using the characteristic bands of γ form sPS in the FTIR spectrum.³⁸ Figure 2 shows a typical spectrum of sPS treated in supercritical CO₂ (35 °C, 12 MPa), along with the spectrum of glassy sPS as a reference. Some remarkable changes and new bands appear after treating in supercritical CO₂. The bands at 502 and 572 cm⁻¹, which are absent in the spectrum of the sample before the treatment, are attributed to the mesomorphic or crystalline forms with helical conformation. Furthermore, the characteristic bands at 599 and 610 cm⁻¹ assigned to the γ form of sPS³⁸ along with the bands at 932 and 944 cm⁻¹¹⁹ indicate that the polymer chains in the amorphous phase rearrange into γ form with helical conformation. It is reported that the X-ray diffraction intensity started to increase almost in parallel to the intensity increment of the 572 cm⁻¹ band.³⁹ Therefore, after the crystalline form was confirmed by other bands, the sharp band of 572 cm⁻¹ was chosen to estimate the relative crystallinity of the γ form in the following discussion. The band of 1028 cm⁻¹ is used as the internal standard for comparison.

The treatment temperature affects the isothermal crystallization kinetics of sPS in supercritical CO₂.

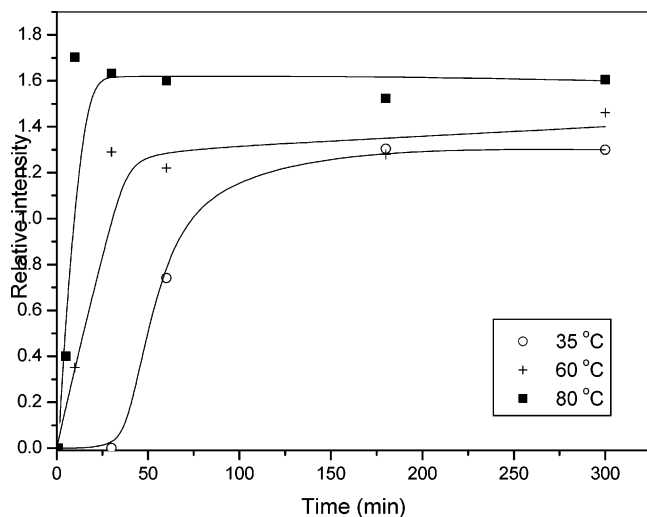


Figure 3. Relative intensity of the 572 cm^{-1} band as a function of time in 12 MPa of supercritical CO_2 at various temperatures.

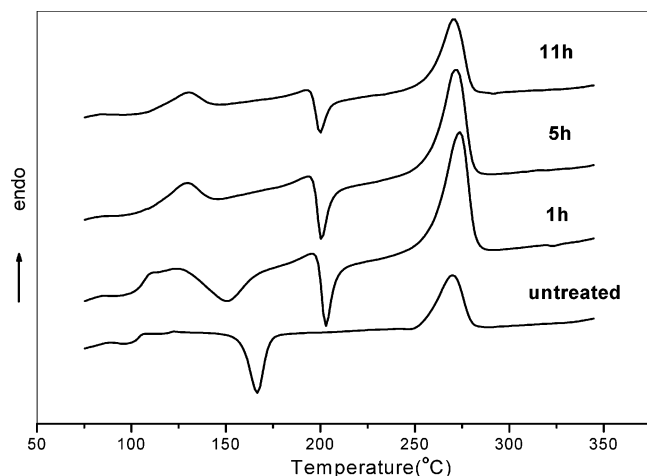


Figure 4. DSC patterns of sPS sample treated in supercritical CO_2 at 35 °C and 12 MPa for different time.

Figure 3 shows the relative intensity of the 572 cm^{-1} band as a function of time for samples treated in 12 MPa of CO_2 at various temperatures (35, 60, and 80 °C). From the trend in Figure 3, it is clear that the increase of the treatment temperature reduces the induction time and increases the transformation rate of γ crystal formation from amorphous sPS in supercritical CO_2 . The crystallinity of the γ form reaches the maximum after 3 h treatment at 35 °C, 30 min at 60 °C, and 10 min at 80 °C. In fact, at higher temperatures, the crystallization rate was so fast that the samples achieved their maximum crystallinity before the temperature of the high-pressure vessel had been stabilized. Therefore, the formation of the γ form sPS in supercritical CO_2 is significantly accelerated by increasing the treatment temperature.

Figure 4 shows the DSC patterns of sPS samples treated for different times in supercritical CO_2 at 12 MPa and 35 °C. In the heating scan of the untreated sample, some thermal peaks are evident. The DSC curve displays the typical cold crystallization and melting peaks of sPS at about 167 and 270 °C, respectively. After the treatment in supercritical CO_2 for 1 h, the DSC pattern shows a remarkable change. The cold crystallization peak moves to lower temperature, and some new peaks appear, i.e., a very small endotherm at about

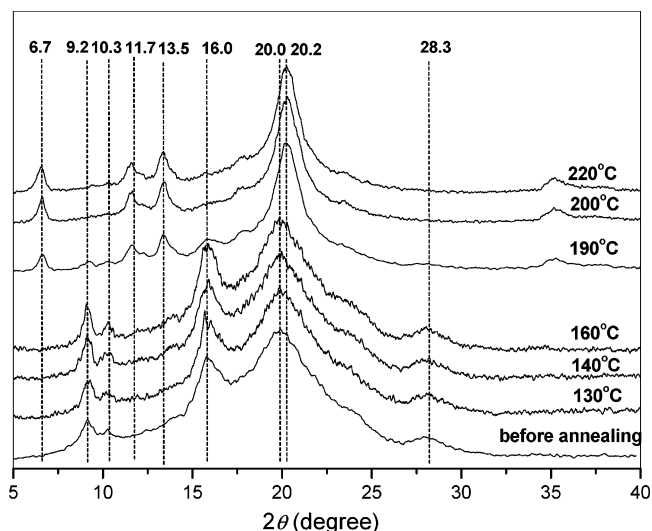


Figure 5. WAXD patterns of the samples treated in supercritical CO_2 and further annealed under ambient pressure at different temperatures.

193 °C and a sharp exothermic peak at 200 °C. The DSC patterns of sPS samples treated in supercritical CO_2 for 5 h and longer show the typical pattern of the γ crystal form with an endotherm just above the glass-transition region.²⁹ In this study, the endotherm at about 130 °C is attributed to the reorganization of the γ crystal form. By comparison with the results in the literature that the γ form melts in a temperature range of 180–200 °C,^{12,26,29} the thermal peak at about 193 °C is assigned to the melting of crystalline γ form. Following this endotherm, an exothermic peak at 200 °C shows the transition of the γ form into the α form. At an even higher temperature of about 270 °C, the broad endothermic peak is associated with the melting of the α form. The fact that the samples with prolonging treatment time have similar DSC patterns is consistent with the WAXD results shown above.

To follow the crystal structure transformation of the sPS samples of γ form during the heating scan, the samples treated in CO_2 for 5 h at 35 °C and 12 MPa were further annealed at various temperatures above T_g for 10 min under ambient pressure. The WAXD patterns of these annealed samples are shown in Figure 5. The original sample treated in supercritical CO_2 shows the typical characteristics of the γ form.^{29,37} The samples annealed between 130 and 160 °C kept their γ form without the change of the crystal structure. Furthermore, the crystallinity of the γ form increased after annealing at 130 and 140 °C; as shown in Figure 5, the diffraction peaks at $2\theta = 9.2^\circ$, 10.3° , and 28.3° of the typical γ form increase upon such thermal treatment. Even after the long treatment and sufficient plasticization in supercritical CO_2 , the γ form obtained was an imperfect crystal with a poor order because of low treatment temperature. After annealing at 130 °C and higher temperature, the γ form reorganized into a more perfect one with relatively higher degrees of crystallinity. All the information above supports the attribution of the DSC endotherm at about 130 °C to the reorganization. The DSC patterns of the samples after annealing between 130 and 160 °C are shown in Figure 6. For the sample annealed at 130 °C the reorganization endotherm peak is seen at 146 °C, which is higher than that before annealing. The postannealing increases the perfection of the crystallites and makes

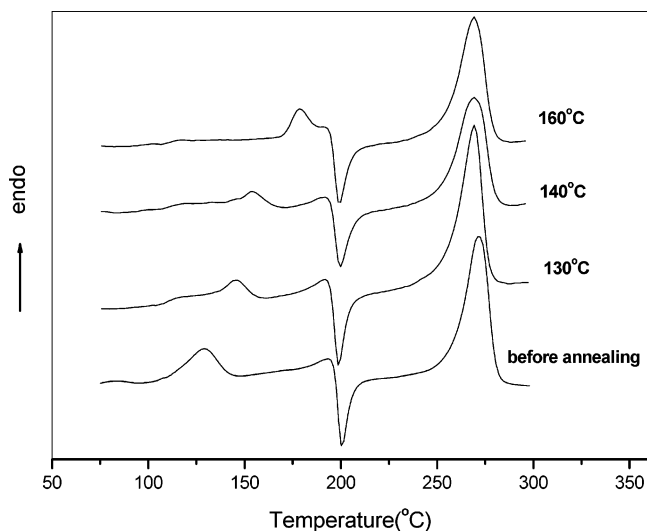


Figure 6. DSC patterns of the samples treated in supercritical CO_2 and further annealed under ambient pressure at different temperatures.

the reorganization peak move to higher temperatures. The reorganization is related to the annealing temperatures³⁴ and moves to much higher temperatures when increasing the annealing temperature to 140 and 160 °C. As also shown in Figure 5, some new peaks ($2\theta = 6.7^\circ$, 11.7° , 13.5° , and 20.2°) attributed to the α form⁴⁰ appear for the sample annealed at 190 °C. At the same time, the significant decrease of the intensity of characteristic peaks of the γ form shows that the occurrence of transformation from γ form with helical conformation into the α form with all-trans conformation in 10 min at 190 °C. The γ form has a lower stability than the α form,⁴¹ and the crystal transition from γ to α form can take place via a melting and recrystallization process upon annealing. At higher annealing temperatures of 200 and 220 °C, all the obtained crystals are the α form without any trace of the γ form.

Previous studies have shown that the solvent-free crystalline γ form sPS is always obtained by heating the solvent-cast δ form.^{26–28} Certain solvents also induce the γ form directly.^{25,29} In the present study, verified by different characterizations, the crystalline γ form has been obtained directly from amorphous phase of sPS in supercritical CO_2 . The plasticization with supercritical CO_2 provides sPS with the relaxation time essentially similar to those solvents such as acetone and 1,1,2,2-tetrachloroethane do. After the depressurization, CO_2 escapes from the sPS matrix directly and leaves no any residual. The whole process favors the formation of the γ form. Thus, that the transition from the amorphous to γ form occurred at moderate temperature indicates that supercritical CO_2 -plasticized sPS chains possess sufficient mobility to undergo such a transformation. However, because of the experimental difficulty at the present, there is no experimental evidence to show the transition of sPS from the amorphous to the γ form through the δ form or not.

Effect of the Treatment Temperature on the Phase Transition. To clarify the phase transition of amorphous sample to the γ form, the sPS samples were treated at different temperatures in 12 MPa of supercritical CO_2 . Figure 7 shows the FTIR spectra in the wavenumber range 590–620 cm^{-1} for these sPS samples. The band profile in this region is associated with the volume and polarity of the solvent molecules and the

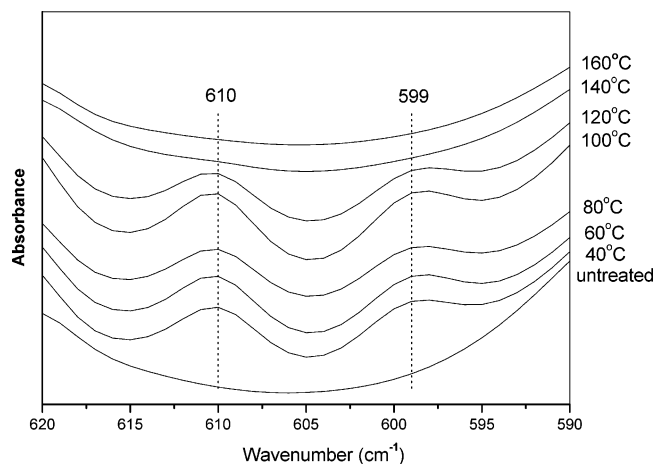


Figure 7. FTIR patterns of sPS sample treated at various temperatures with 12 MPa CO_2 for 5 h.

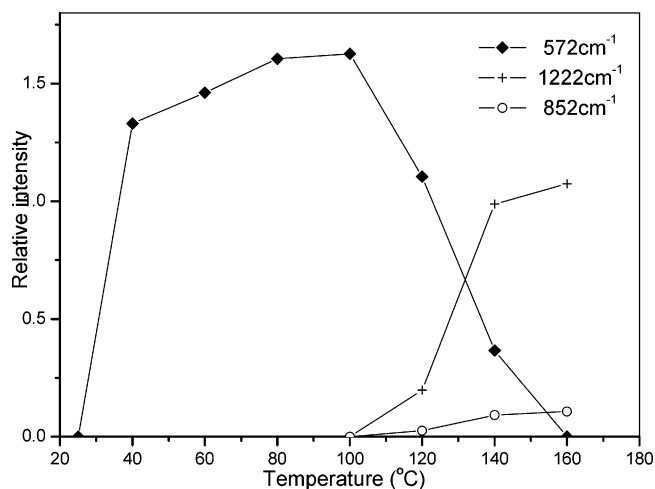


Figure 8. Effect of the treatment temperature on the reduced absorbed intensity of the 572, 852, and 1222 cm^{-1} bands in 12 MPa of supercritical CO_2 for 5 h.

interaction strength between sPS and solvent.³⁸ The remarkable changes in the 599 and 610 cm^{-1} bands assigned to the γ form³⁸ for the treated samples mean that the supercritical CO_2 induces the formation of γ form from the glassy sPS just like a solvent does. The γ form is obtained in the temperature range between 40 and 120 °C. At 140 and 160 °C, the disappearance of these bands indicates the crystallization of amorphous sPS into other structures.

The relationship of the relative intensity of the 572 cm^{-1} band with the treatment temperature is plotted in Figure 8. No γ form is obtained at 25 °C after being treated in 12 MPa of supercritical CO_2 for 5 h. The glassy sPS did not crystallize at this temperature even under a pressure as high as 20 MPa. The fact that the 572 cm^{-1} band appears at 40 °C indicates the crystallization of glassy sPS to the γ form. The slight increase of the intensity at 572 cm^{-1} from 40 to 100 °C shows a steady increase of the crystallinity with increasing treatment temperature. The γ form of the sPS sample reaches its maximum crystallinity at 100 °C. However, this band decreases abruptly at about 120 °C and higher temperatures. As shown in Figure 9, the IR bands at 932 and 944 cm^{-1} assigned to the γ form²⁹ exist in the temperature range between 40 and 120 °C, while new bands appear at 852 and 1222 cm^{-1} and the 907 cm^{-1} band shifts to 902 cm^{-1} at 140 and 160 °C. All the

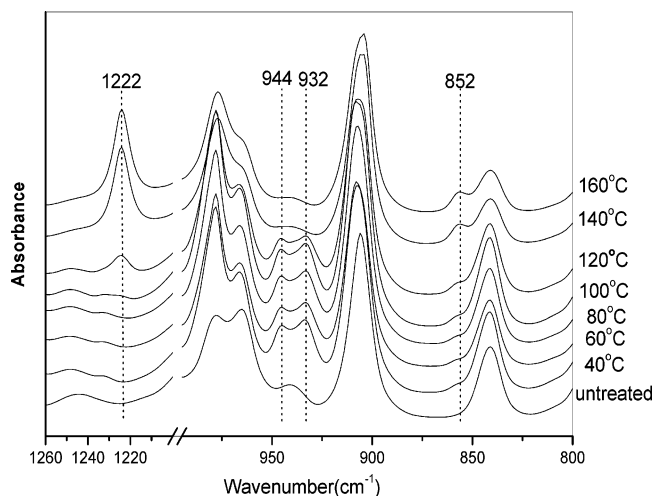


Figure 9. FTIR patterns of sPS sample treated with 12 MPa of CO₂ at various temperatures for 5 h.

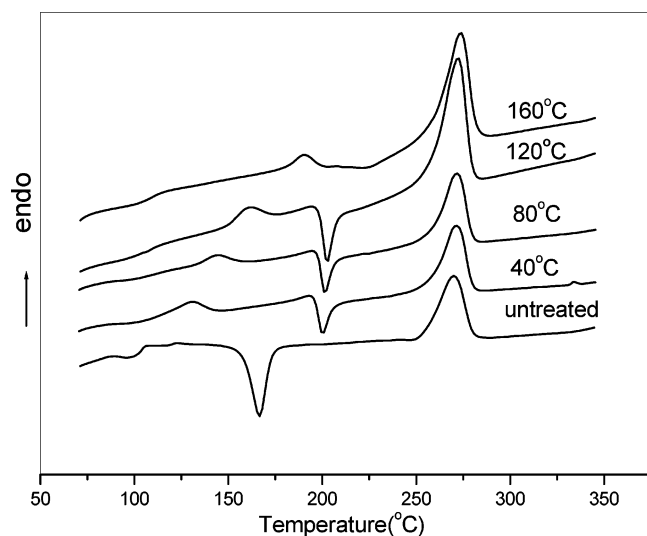


Figure 10. DSC patterns of sPS sample treated in 12 MPa of supercritical CO₂ at different temperatures for 5 h.

information indicates that the α form is obtained from amorphous sPS in supercritical CO₂ at higher treatment temperatures. Usually, the α form is obtained by annealing above the glass transition temperature,^{14,15} and the γ form can also transform into the α form at about 190 °C.^{12,13,27,28} The intensity of the 852 and 1222 cm⁻¹ bands associated with the α form (Figure 8) indicates that the γ and α forms coexist in sPS samples treated at 120 °C. A weak band of 572 cm⁻¹ at 140 °C reflects the presence of a small amount of the γ form. At 160 °C, only the α form exists with no trace of the γ form. Consequently, together with the above discussion, the γ form of different crystallinity is obtained directly from glassy sPS in supercritical CO₂.

The DSC patterns of sPS samples treated in supercritical CO₂ at different temperatures are shown in Figure 10. The reorganization peak moves from 131.5 to 190.7 °C with the increase of the treatment temperature from 40 to 160 °C. The melting peak of the γ form remains at 193 °C, and the peak of the transition from the γ to α form remains at 200 °C after treating with 12 MPa of CO₂ in the temperature range 40–120 °C. The absence of both peaks in the DSC pattern for the sample treated at 160 °C indicates that the treated sample has only the α form, which is also confirmed by

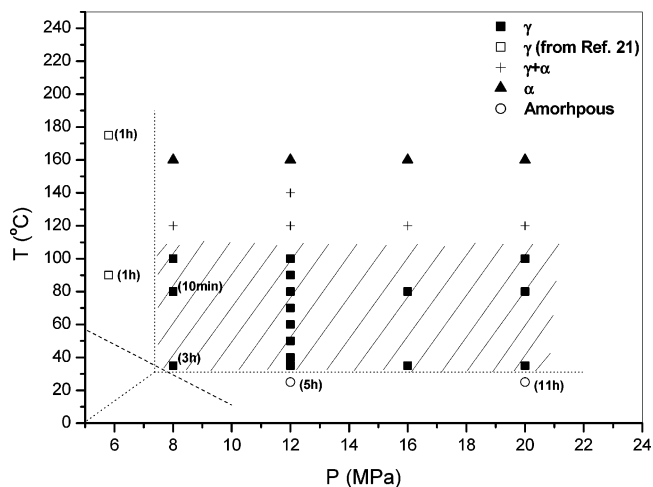


Figure 11. Variation of sPS crystal forms with the temperature and pressure of CO₂. The dotted lines represent the critical pressure (7.37 MPa) and critical temperature (31.1) of CO₂, and the dashed line is the T_g of sPS extrapolated from the data in ref 34.

the WAXD patterns (not shown here). The FTIR and DSC results consistently demonstrate that the γ form with different crystallinity can be obtained at moderate temperature from 40 to 140 °C in 12 MPa of supercritical CO₂. At 160 °C, the pure α form is obtained in supercritical CO₂. The details of the crystalline transition from the amorphous to the α form in supercritical CO₂ will be discussed by the authors in a later paper.

Conditions for the Formation of γ Form from Glassy State. The crystallization of amorphous sPS treated in CO₂ with various temperatures and pressures is summarized in Figure 11. Handa et al.³⁴ reported that glassy sPS was directly transformed into the γ form in 57 atm of CO₂ at 90 and 175 °C. This transformation was induced by gaseous CO₂.

When decreasing the temperature below the critical value (31.1 °C), CO₂ reaches its liquid state. As shown in Figure 11, no γ crystal form was detected after treating amorphous sPS in CO₂ as long as 11 h at 25 °C and 20 MPa. In contrast to this, the γ crystal was formed after treating amorphous sPS in CO₂ as short as 1 h at 35 °C and 20 MPa. The same contrast was found between the treated glassy sPS samples; one was treated for 5 h at 25 °C and 12 MPa and the other for 1 h at 35 °C and 12 MPa. The former had no γ form crystal, while the latter γ form crystal. These results indicate clearly that the liquid CO₂ could not induce the formation of the γ form from amorphous sPS even for a longer time and at much higher pressures.

In supercritical CO₂, the conditions for the formation of the γ form vary in a wide range, as shown by the shadow area in Figure 11. The γ form is obtained at 8 MPa and 35 °C, which are just a little higher than the critical pressure (7.37 MPa) and temperature (31.1 °C) of CO₂. Out of the shadow area, the $\gamma + \alpha$ mixed crystals and the α crystal were formed, which will be reported in another paper later. The plasticization effect of supercritical CO₂ depressed the T_g of sPS and lead to its crystallization at relative low temperatures. However, because of the experimental difficulty, the change of T_g of sPS in supercritical CO₂ could not be tracked. Here, the value -0.92 °C/atm of the T_g depression with the pressure³⁴ is used to estimate the T_g of sPS in supercritical CO₂. As shown by the dashed line extrapolated from the data of the literature,³⁴ supercritical CO₂

at 8 MPa can decrease the T_g of sPS below 35 °C, thus leading to the direct transformation of glassy sPS into the γ form. In the vicinity of the critical temperature and pressure of supercritical CO₂, the γ form crystal with higher crystallinity was obtained with increasing temperature and pressure, respectively.

Figure 11 suggests that the formation of γ form crystal is determined by the state of CO₂. Exhibiting hybrid properties of a typical gas and a liquid, supercritical CO₂ has its viscosity similar to a gas and the fluidity better than a liquid, so that it can diffuse much more readily into a solute just like a gas. The unique properties of supercritical CO₂ provide a moderate condition to transform the amorphous sPS directly into the γ form.

Conclusions

The γ form of sPS is usually obtained by heating the δ form or solution-casting with certain solvents such as acetone or 1,1,2,2-tetrachloroethane. In the present study, the pure γ crystal form was obtained after the treatment of the amorphous sPS in supercritical CO₂ at 8 MPa and 35 °C, just above the critical pressure and temperature of CO₂. The pure γ form crystal was obtained directly after treating glassy sPS in supercritical CO₂ in a range from 8 to 20 MPa and from 35 to 100 °C. Only a 3 h treatment at 12 MPa and 35 °C brought the γ form to its maximum crystallinity at such a low temperature, and for the same effect the shorter intervals of time were needed with increasing treatment temperature. The plasticization by supercritical CO₂ provided the sPS with an enough relaxation time and resulted in a direct crystallization from the amorphous sPS to the γ form at temperatures from 40 to 140 °C. The liquid CO₂ could not induce the γ form at any pressure. In addition, the α crystal form with the all-trans planar conformation was obtained when further increasing the treatment temperature above 140 °C.

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