Free Volume Changes, Crystallization, and Crystal Transition Behavior of Syndiotactic Polystyrene in Supercritical CO_2 Revealed by Positron Annihilation Lifetime Spectroscopy

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ABSTRACT: The free volume of syndiotactic polystyrene (sPS) conditioned in supercritical CO_2 was investigated by using positron annihilation lifetime spectroscopy (PALS). Supercritical CO_2 increased the free volume cavity size of amorphous sPS and made the formation of γ crystal occur. The orthopositronium (o-Ps) intensity I_3 was correlated well with the crystallinity of γ form sPS, revealed by its gradual decrease with the increase of crystallinity. Furthermore, the treatment atmosphere affected the crystallization behavior of amorphous sPS. The increased free volume cavity size of amorphous sPS treated in supercritical CO_2 was larger than those treated in ambient air and supercritical N_2. Among these treatment conditions, supercritical CO_2 increased the free volume size of amorphous sPS more effectively and thus resulted in the formation of γ crystals. PALS measurements indicated that supercritical CO_2 helped remaining a constant high free volume level of the amorphous parts of the semicrystalline sPS. Likely, the crystalline parts were also affected by the $scCO_2$ as a transition from the γ form to the β form was revealed at high temperatures by WAXD.

1. Introduction

Syndiotactic polystyrene (sPS) possesses a complex polymorphism in its crystalline region, which has been extensively studied by using wide-angle X-ray diffraction (WAXD), Fourier-transform infrared spectroscopy (FTIR), and differential scanning calorimetry (DSC).[1–7] It is well-known that sPS has four polymorphic forms: α, β, γ, and δ. The α and β forms, both containing planar zigzag chains having a TTTT all-trans conformation, can be obtained from the melt or glassy state of sPS under different thermal crystallization conditions.[4,7–13] They are further classified into two limiting disordered modifications, α' and β', and two limiting ordered modifications, α'' and β''.[1,2] The γ and δ forms, with TTGG helical conformation, can be formed from solvent swelling of glassy or semicrystalline sPS.[1,14–16] Crystal transitions of sPS under ambient pressure have been extensively studied.[17] It is well-known that the γ form can transform into the α'' form by thermally annealing at temperatures above 200 °C under ambient pressure.[5,6,18,19] Usually, the β form can be obtained by slow cooling from the melt or by casting from an *o*-dichlorobenzene solution at 170 °C.[2] No direct transformation from the γ form to β form under ambient pressure has been reported.

Supercritical CO_2 (T_c = 31.1 °C, P_c = 7.37 MPa) or compressed CO_2 has been extensively studied as a solvent in terms of commercial application and fundamental understanding of solution behavior.[20] It can swell and plasticize glassy polymers, leading to a depression of the glass transition temperature (T_g) as is known from vapors or liquids.[21] The plasticization of the amorphous phase increases the mobility of the polymer chains and results in induced crystallization and concomitant change in the morphology. In addition, this effect leads to the decrease of the energy barriers, thus making some solid–solid transitions possible at much reduced temperatures. Furthermore, the presence of CO_2 can bring about some new transitions that cannot occur under ambient pressure. Phase transitions of sPS in the presence of CO_2 have been reported by Handa et al.[18] and He et al.[22–24] In supercritical CO_2, amorphous sPS can crystallize into the γ form with helical conformation, which was usually induced by certain solvents. Supercritical CO_2 can also bring about some new transitions, such as $\gamma \rightarrow \beta$, $\delta \rightarrow \beta$, $\delta \rightarrow$ empty δ, and $\alpha \rightarrow \beta$.[23,24,26,27]

In our previous papers,[25–28] new phenomena of the crystallization and crystal transitions of sPS treated in supercritical CO_2 were reported. In these articles the commonly accepted explanation was that these phenomena occurred due to a change of free volume characteristics, an increase of chain mobility of crystallizable polymers, and a decreased energy barrier for crystal form transition by plasticization of supercritical CO_2. However, up to now this reasoning only comes from limitedly available data of decreased glass transition temperatures of polymers treated in compressed CO_2 and lack other experimental evidence. The details of these mechanisms remain unclear. Positron annihilation lifetime spectroscopy (PALS) has been employed to determine the free volume cavity size, fraction, and their distribution in a variety of polymers. It should be noted that the PALS technique probes the free volume cavity sizes of the amorphous part of semicrystalline polymers. The orthopositronium is not believed to be able to form and annihilate in the crystalline regions of polymers and therefore reveals no information about those parts. Jean et al.[29] have reported that the presence of CO_2 can change the free volume of polycarbonate. To our knowledge, no work has been performed concerning the change of free volume of sPS treated in the presence of CO_2. Olson et al. have investigated the free volume properties of α and β semicrystalline sPS.[30] Dammert et al. compared the free volume size and size distributions of sPS with different tacticities by PALS and molecular modeling.[31]

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In the present study, PALS was used to characterize the free volume size of sPS treated in supercritical CO_2. The changes in free volume were correlated with the variation in treatment conditions. The mechanism of crystallization and crystal transition of sPS treated in supercritical CO_2 was further elucidated by WAXD and FTIR measurements.

2. Experimental Part

2.1. Materials and Sample Preparation. The syndiotactic polystyrene (sPS) was obtained as a commercial material from Dow Chemicals with its syndiotacticity 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 of thickness about 300 μm were obtained by forming a thin melt film pressed at 290 °C and then rapidly quenching in an ice−water bath. CO_2 with a purity of 99.95% was supplied by Beijing Analytical Gas Factory, China.

2.2. Sample Treatment. A high-pressure apparatus was used for the treatment in supercritical CO_2. The amorphous sPS films were loaded into a 25 mL high-pressure vessel which was then flushed with low-pressure CO_2 for about 2 min before reaching the chosen temperature and pressure. After the treatment of sPS sample at the desired temperature and pressure for a certain time, the vessel was quickly cooled to room temperature and depressurized slowly at an approximate rate of 0.5 MPa/min. Thermal treatments in ambient atmosphere were made in the same vessel but without the presence of the CO_2. All measurements conducted in ambient atmosphere were treated in air unless differently indicated. The γ form sPS was obtained by treating amorphous sPS at 100 °C and 16 MPa for 6 h in supercritical CO_2.

2.3. Measurement. Wide-angle X-ray diffraction (WAXD) measurements were conducted on a Rigaku D/max 2500 with Cu Kα radiation (40 kV, 300 mA). The scanning 2θ ranged between 5° and 40° with a step scanning rate of 4°/min.

Positron annihilation lifetime spectroscopy (PALS) measurements were carried out at room temperature using a fast−fast coincidence system based on Canberra modules: model 3002 D high-voltage power supply, two 2129 constant fraction differential discriminators, 2058 ns delay, model 2143 time analyzer, and a 8701 analog-to-digital converter. The Ortec module Match Maker etherNIM acquisition interphase was used together with the MAESTRO spectrum software. The two identical γ-ray detectors, placed at ≈160° to each other and at least 5 cm apart to minimize backscattering, consisted of CsF crystals mounted on Hamamatsu photomultiplier tubes. The spectrometer had a resolution function composed of a sum of two Gaussians with relative intensities 70% and 30% and with fwhm of 340 and 350 ps, respectively, and a channel width of 0.0240 ns. A 2.8 MBq ^{22}Na source, with an effective count rate of ≈500 cps, was sandwiched between 1 mm pieces of polymer sample. Five positron lifetime spectra, each containing 2.5 million counts, were collected for each sample and evaluated with PATFIT using no source correction and no fixed lifetimes or intensities. All spectra were evaluated using three lifetimes. For several representative samples, evaluations of four lifetimes were conducted. However, these analyses did not reveal any information about a longer lifetime present in the samples. It appears as if the second lifetimes were split into a second and a third lifetime when using the four-lifetime evaluation. These results confirmed that an additional long lifetime is not present in sPS, as was also concluded by Olson et al.[30] The PALS measurements were all performed within 2−4 weeks after the treatment in $scCO_2$. All measurements were conducted consecutively. The Tao−Eldrup equation (eq 1) describes the relation between the o-Ps lifetime τ_3 and an equivalent spherical cavity radius, R.

$$\tau_{o-Ps} = 0.5\left(1 - \frac{R}{R_0} + \frac{1}{2\pi}\sin\left(\frac{2\pi R}{R_0}\right)\right)^{-1} \quad (1)$$

$R_0 = R + \Delta R$, and ΔR is a fitted parameter with a value of 1.66 Å.

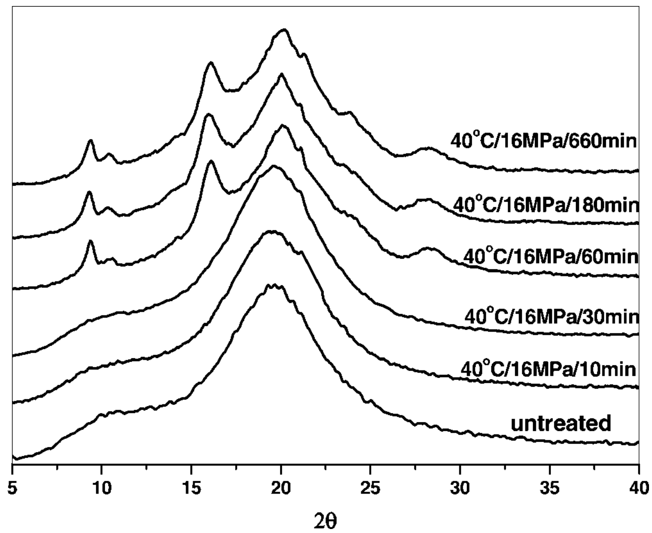

Figure 1. WAXD patterns of amorphous sPS treated at 40 °C for different time periods in supercritical CO_2 of 16 MPa.

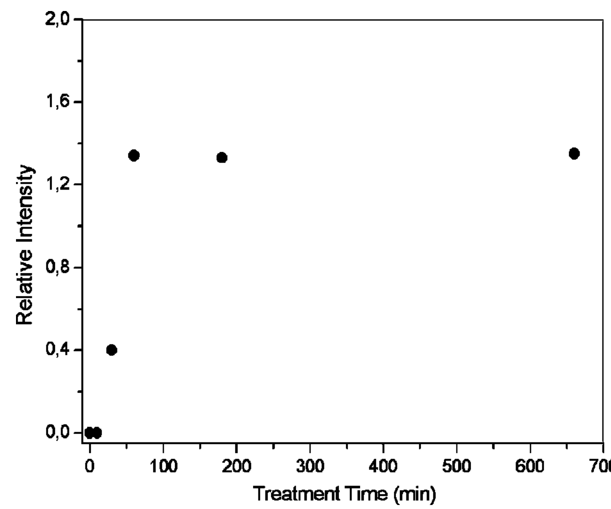

Figure 2. Change of relative intensity of the 572 cm^{-1} band with treatment time in supercritical CO_2 of 16 MPa at 40 °C.

3. Results

3.1. Free Volume Changes by γ-Crystal Formation in sPS. *3.1.1. Effect of the Treatment Time.* Figure 1 shows the WAXD patterns of amorphous sPS treated at 40 °C for different intervals of time in supercritical CO_2 of 16 MPa. As shown in this figure, the broad peak reveals the original sample to be amorphous.[18] There are no changes of X-ray diffraction for sPS sample treated in 16 MPa of CO_2 at 40 °C for 10 and 30 min. When the time is increased to 1 h, the reflection peaks at $2\theta =$ 9.2°, 10.3°, 16.0°, 20.0°, and 28.3°, attributed to the typical characteristics of the γ form crystal in sPS,[25,32] are present in the WAXD pattern of the sPS samples. Further increase of the treatment time did not increase the intensity of these peaks, indicating the maximum crystallinity reached after 1 h annealing at 16 MPa CO_2 at 40 °C. According to Yoshioka et al.,[33] the X-ray diffraction intensity starts to increase almost in parallel to the intensity increment of the 572 cm^{-1} band (FTIR), which is assigned to the γ crystal, indicating that the 572 cm^{-1} band is proportional to the degree of crystallinity.[25] Figure 2 shows the change of the intensity of 572 cm^{-1} band with the treatment time. As shown in Figure 2, the intensity of 572 cm^{-1} band increases gradually with increasing the treatment time and reaches the maximum after 1 h treatment. The combination of

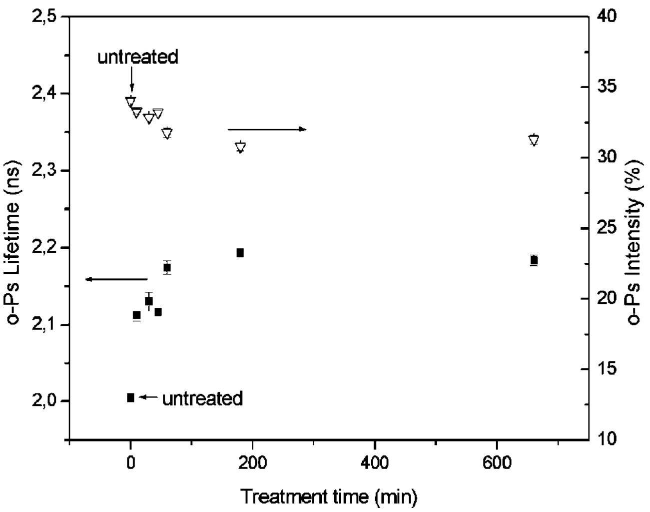

Figure 3. Change of τ_3 and I_3 with treatment time in supercritical CO_2 of 16 MPa at 40 °C.

WAXD and FTIR results showed that with increasing treatment time in supercritical CO_2 amorphous sPS crystallized into the γ form and reached the maximum crystallinity after 1 h.

PALS was used to characterize the free volume of sPS treated at 40 °C in supercritical CO_2 of 16 MPa for different intervals of time. Figure 3 shows the change of o-Ps lifetime τ_3 with the treatment time. As shown in the figure, the value of τ_3 increases gradually with the increase of treatment time and reaches the maximum value after 1 h treatment. This trend is similar to that of the intensity of 572 cm^{-1} band. As also shown in Figure 3, o-Ps intensity I_3 decreases with increasing treatment time; i.e., at higher degrees of crystallinity the o-Ps intensity is smaller. This is not surprising since I_3 is the probability of o-Ps formation, and this quantity has been correlated to the degree of crystallinity, where a decrease in intensity corresponds to an increase in crystallinity. The long-term radiation effects were investigated by measuring the o-Ps intensity over 40 h for an amorphous syndiotactic polystyrene sample; the intensity then decreased from 34.2% to 33.1%, comparable with the decrease reported by Olson et al.[30] It should be noted that the free volume size of sPS increased even when treated for a very short time of 10 min in supercritical CO_2.

3.1.2. Effect of the Annealing Temperature. To further investigate the crystallization behavior of amorphous sPS in supercritical CO_2, amorphous sPS was annealed at different temperatures. Figure 4 shows the WAXD patterns of amorphous sPS treated at different temperatures for 11 h in supercritical CO_2 of 16 MPa. As shown in the figure, the treated samples show the features of γ crystals appears clearer and clearer when the annealing temperature increased from 40 to 100 °C.

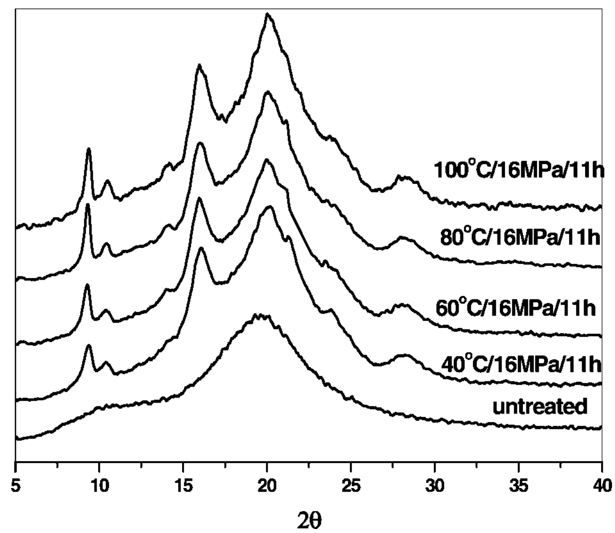

Figure 4. WAXD patterns of amorphous sPS annealed at different temperatures for 11 h in supercritical CO_2 of 16 MPa.

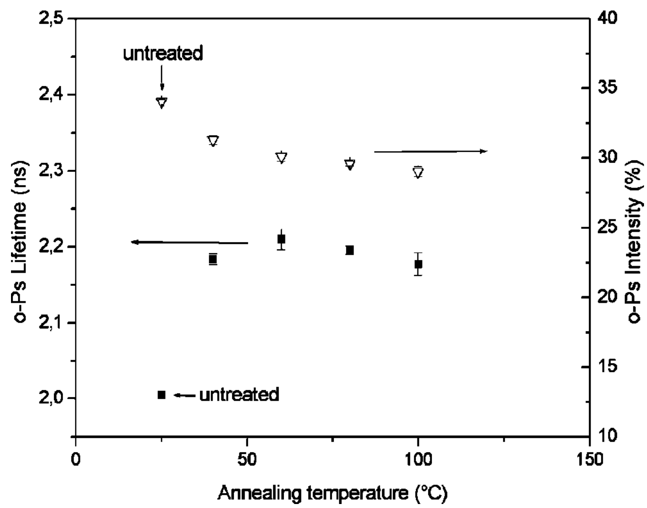

Figure 5. Change of τ_3 and I_3 with annealing temperature in supercritical CO_2 of 16 MPa for 11 h.

Figure 5 shows the change of τ_3 and I_3 with the annealing temperature. The τ_3 value first increases and then decreases along with the increase of the annealing temperature. Combining all the results of PALS with those of FTIR of samples treated for different time periods (Figure 2) and at different temperatures (not presented here) led to the trend in Figure 6. It reveals a linear relation between the I_3 and the relative intensity of 572 cm^{-1} band representing qualitatively the degree of crystallinity. This relation suggests, after calibration, a possible way of determining the absolute degree of crystallinity of sPS by PALS.

3.1.3. Effect of the Treatment in Supercritical CO_2 and Supercritical N_2. In this part of the study, amorphous sPS was treated in different surroundings to investigate its crystallization behavior. WAXD patterns (Figure 7) of amorphous sPS treated at 100 °C for 11 h in supercritical CO_2, supercritical N_2, and atmospheric air reveal that sPS crystallization occurred only in supercritical CO_2. Obviously, the treatment surrounding affected the crystallization behavior of amorphous sPS. Compared with ambient air and supercritical N_2, supercritical CO_2 provided a condition to allow amorphous sPS crystallize into γ crystals.

Figure 8 shows the change of τ_3 and I_3 with the treatment surroundings. The value of τ_3 is different for samples treated under different conditions. Compared with supercritical N_2, supercritical CO_2 increased the free volume size of amorphous sPS significantly. As also shown in Figure 8, I_3 decreased after the treatment of amorphous sPS in $scCO_2$, while it remained almost unchanged after the treatment in supercritical N_2. Consequently, according to the above discussion, supercritical CO_2 generally increased the free volume size of the amorphous regions of sPS.

3.2. Free Volume Changes by γ-Crystal Transitions in sPS at High Temperatures. *3.2.1. Effect of the Annealing Temperature.* Figure 9 shows the WAXD patterns of sPS samples initially containing only γ crystals and subsequently annealed at different temperatures for 11 h under ambient condition and in supercritical CO_2 of 12 MPa. The γ crystals in sPS were transformed into different crystal forms when treated under these conditions.[27,28] The treatment under ambient condition made the γ crystals transform into the α crystal form (Figure

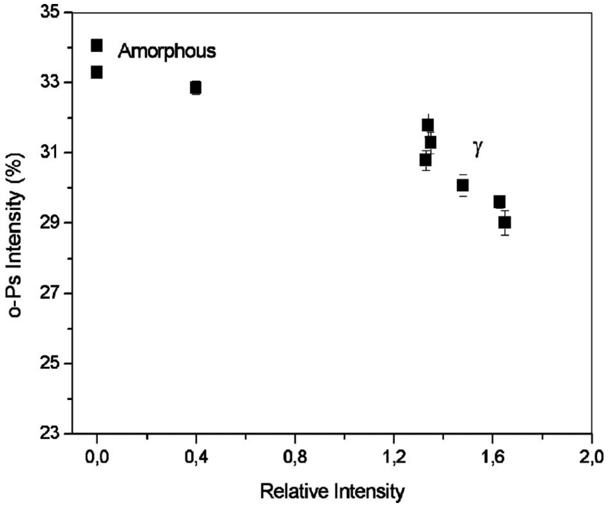

Figure 6. Change of I_3 with the relative intensity of the 572 cm^{-1} band in supercritical CO_2 of 16 MPa at different temperatures and for different times.

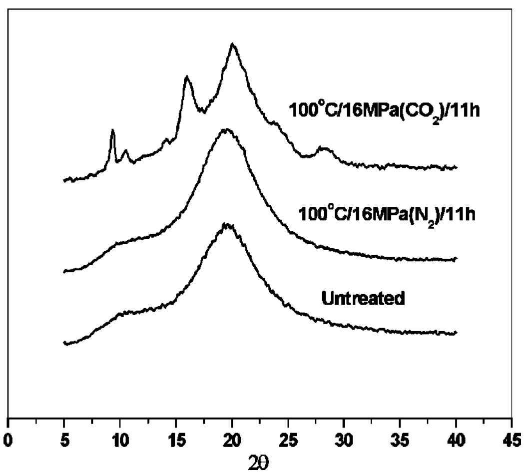

Figure 7. WAXD patterns of amorphous sPS treated at 100 °C for 11 h under the conditions indicated.

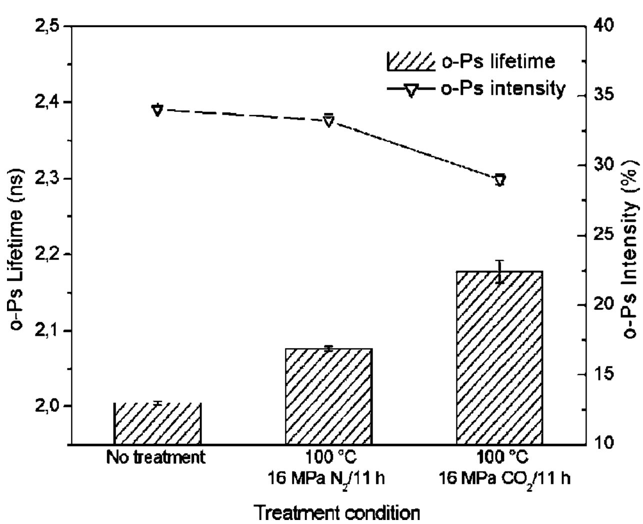

Figure 8. Change of τ_3 and I_3 with treatment atmosphere at 100 °C for 11 h.

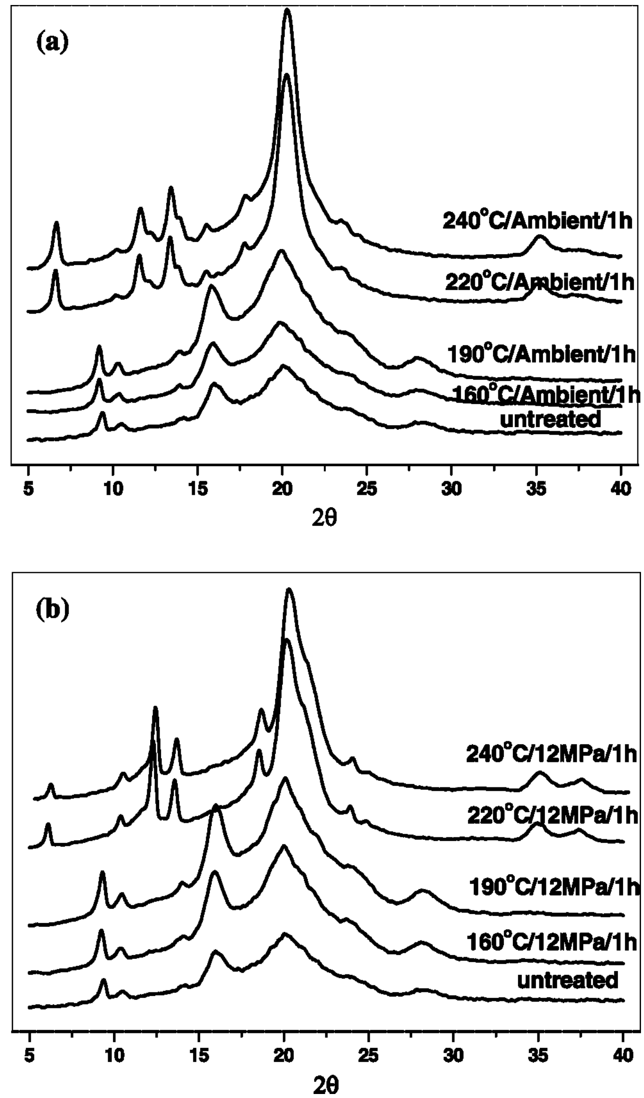

Figure 9. WAXD patterns of γ crystal sPS annealed at different temperatures for 11 h under ambient condition (a) and supercritical CO_2 of 12 MPa (b).

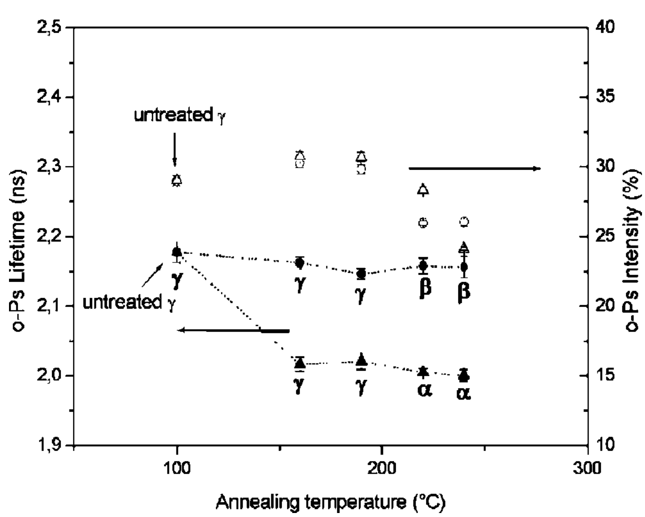

Figure 10. Change of τ_3 and I_3 with annealing temperature in supercritical CO_2 (circles) of 12 MPa for 11 h and in ambient air (triangles).

9a), while the treatment in $scCO_2$ at 12 MPa made the γ crystals transform into the β crystals (Figure 9b).

To clarify the mechanism of the crystal transition of sPS in supercritical CO_2, Figure 10 shows the change of τ_3 and I_3 with the annealing temperature under the conditions indicated. Treatment in CO_2 and air as a function of temperature has clearly

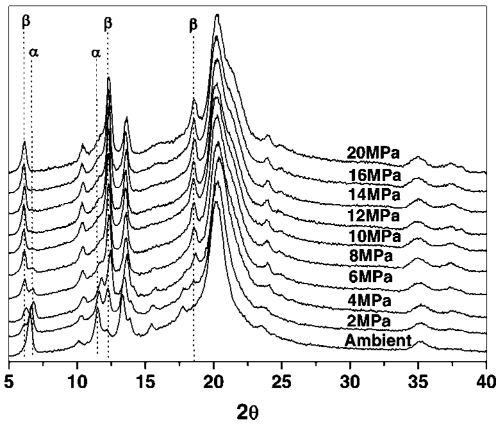

Figure 11. WAXD patterns of γ crystal sPS treated at 240 °C for 1 h in CO_2 at different pressures.

different effects on the free volume size and crystal structure of sPS. Treatment in CO_2 results in large free volume sizes, and at high temperatures a transition from γ to β crystals is observed by WAXD. On the other hand, treatment in air results in a transition from γ to α crystals at high temperatures and a reduction of free volume size to the level of untreated amorphous sPS (τ_3 = 2.005 ns) for all annealing temperatures. The thermodynamically favorable β crystalline sPS thus formed in the system with the highest mobility, and the kinetically favorable α crystals is typically observed when treating at ambient conditions. Using the Tao−Eldrup equation (eq 1), the two levels of o-Ps lifetimes correspond to equivalent spherical hole diameters of 5.98 and 5.72 Å, respectively. Following the transition from both γ to β and γ to α a decrease of o-Ps intensity is observed, indicating a further decrease of the amount of amorphous phase of the semicrystalline polymer.

3.2.2. Effect of the Treatment Pressure. sPS samples were also treated at different pressures in order to further investigate the crystal transition behavior of γ crystal sPS. Figure 11 shows WAXD patterns of γ semicrystalline sPS samples treated at 240 °C for 1 h in CO_2 of different pressures. As shown in this figure, the γ crystal transformed into α crystal at ambient pressure. Successively with the increase of the treatment pressure, the β crystal appeared gradually. After the treatment above 7.37 MPa, i.e., in supercritical CO_2, the γ crystal completely transformed into β crystal. Obviously, supercritical CO_2 at higher pressures was favorable for the formation of β crystals.

Figure 12 shows the change of τ_3 and I_3 with the treatment pressure. With the increase of the treatment pressure, the free volume size of sPS increased gradually. That is to say, compared with ambient pressure, supercritical CO_2 increased the free volume of γ semicrystalline sPS and thus made the formation of β crystal occur. As also shown in the figure, no clear change of I_3 was found when the treatment pressure was changed, indicating a constant fraction of amorphous phase in the semicrystalline polymer.

4. Discussion

From the results above, it is evident that supercritical carbon dioxide increased the free volume cavity size of syndiotactic polystyrene and promoted the transition from amorphous sPS to the γ form crystal. In the following discussion one should however bear in mind that the PALS measurements were performed at room temperature after the treatment in $scCO_2$. According to Hong et al.,[29] τ_3 decreases during depressurization of polycarbonate but never returns to its original value. It is thus believed that the free volume cavity size of sPS during treatment in supercritical CO_2 is larger than the value obtained afterward at room temperature.

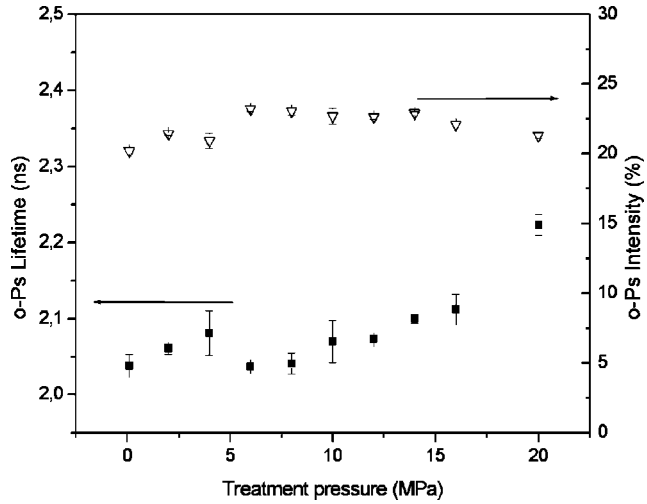

Figure 12. Change of τ_3 and I_3 with treatment pressure at 240 °C for 1 h in CO_2.

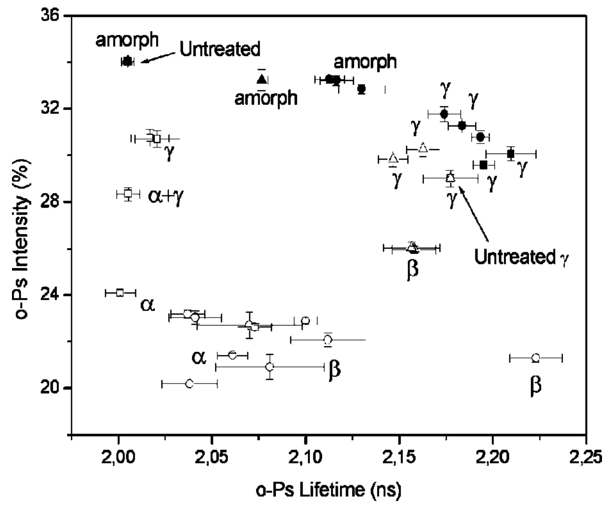

Figure 13. I_3 as a function τ_3 for all the sPS samples. Filled symbols represent a series starting from untreated amorphous sPS, where filled circles (●) are samples treated at different times, filled squares (■) are samples annealed at different temperatures, and filled triangles (▲) are samples treated with different gases. Open symbols represent series starting from γ-crystalline sPS, where open circles (○) are samples treated at different pressures, open squares (□) are samples annealed at different temperatures under ambient conditions, and open triangles (Δ) are samples treated at different temperatures under $scCO_2$ conditions.

Supercritical CO_2 can increase the free volume of the amorphous parts of sPS, if treated during sufficient time and temperature, as could be seen in Figure 3, where the o-Ps lifetime increased continuously with treatment time. In Figure 5, however, there is a tendency of decrease of o-Ps lifetime toward higher annealing temperatures. This could be caused by a decreasing sorption capacity of CO_2 in sPS with increased annealing temperature.

In Figure 13 all τ_3 values were plotted against all I_3 values to show the complex relation between free volume size, crystallinity, and crystal structure. All measurements conducted in ambient atmosphere resulted in a low level of free volume size, i.e., on the left-hand side of Figure 13. Furthermore, $scCO_2$ treatment in general increased the free volume size and crystallinity and decreased the o-Ps intensity. Some of the γ semicrystalline samples were remeasured with PALS after 1 year annealing at room temperature. The results revealed a 2.7−4.1% decrease of free volume size and a 0.5−1.5% increase of o-Ps intensity pointing at structural relaxation of the amorphous phase.

Our results of o-Ps lifetimes and intensities correspond well to literature values by Dammert et al.[31] and by Olson et al.[30] In this work o-Ps lifetime values of between 2.01 and 2.22 ns for syndiotactic polystyrene were obtained. The exact value of the lifetimes was determined by the treatment history of the sample. Dammert et al. presented a τ_3 value of 2.10 for sPS, which is high compared to the results of our untreated amorphous sPS (see Figure 13). However, Dammert et al. used a different sample treatment which resulted in a different free volume situation.

In the present study, o-Ps intensities in the range of 20−34% were obtained for sPS, depending on the degree of crystallinity of the samples. The relation between crystallinity and o-Ps intensity is clear (see Figures 6 and 13), where a high I_3 is obtained for all amorphous samples whereas lower values of I_3 were obtained for semicrystalline sPS. Dammert et al. obtained a low o-Ps intensity of 22.9% for sPS. This was argued to be caused by crystallinity of the sPS, which fits well with our results.

In the work of Olson et al., it was investigated whether o-Ps could form in the crystalline regions of α-crystalline and β-crystalline sPS. Apart from the fact that Olson et al. used four lifetimes to fit their spectra, as compared to three lifetimes which we used, the main difference between their work and ours is that they could not observe a decrease in o-Ps intensity with increasing crystallinity of sPS. Their o-Ps lifetimes and intensities all lie in the range of what we have obtained for sPS; however, the intensity of amorphous sPS was not significantly larger than for semicrystalline sPS in their work. On the basis of their results, Olson et al. concluded that o-Ps indeed could form in the crystalline regions of sPS but annihilates in the amorphous regions. On the contrary, all our results indicate that o-Ps form only in the amorphous phase of sPS demonstrated by the decreasing o-Ps intensity with increasing crystallinity.

5. Conclusions

Positron annihilation lifetime spectroscopy was used to investigate the crystallization and crystal transition behavior of sPS in supercritical CO_2. The change of free volume of sPS was correlated well with these behaviors. Generally, supercritical CO_2 increased the free volume of amorphous sPS and thus made the formation of γ crystal occur. With the increase of the crystallinity of γ crystal, I_3 decreased gradually. Furthermore, the treatment surrounding affected the crystallization behavior of amorphous sPS. The increased amount of free volume of amorphous sPS treated in supercritical CO_2 was higher than those untreated and treated in supercritical N_2. Compared with other conditions, supercritical CO_2 increased the free volume cavity size of amorphous sPS effectively and made the formation of γ crystal occur. This correlation can be used to clarify the mechanism of crystallization behavior of amorphous sPS in supercritical CO_2.

On the other hand, supercritical CO_2 also affected the crystal transition behavior of sPS. Compared with ambient condition, supercritical CO_2 increased the free volume of γ crystal sPS so that led to the formation of β crystal. The pressure of supercritical CO_2 affected the crystal transition of γ crystal sPS. The free volume of β crystal was relatively higher than that of α crystal.

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