

Rapid Communication

SOLID PHASE TRANSITION OF SYNDIOTACTIC POLYSTYRENE IN
SUPERCRITICAL CO₂

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Abstract Solid phase transition of the α form crystals to the β form crystals in syndiotactic polystyrene (sPS) samples has occurred in supercritical CO₂. This transformation is different from those detected under other conditions. The effects of some factors (e.g. time, temperature, and pressure) on the solid phase transformation of sPS in supercritical CO₂ were analyzed in detail. Experimental results show that longer time, higher temperature or higher pressure favors the transformation of the α form crystals to the β form crystals.

Keywords Solid phase transition, Syndiotactic polystyrene, Supercritical CO₂

INTRODUCTION

Polymorphism is a common and widespread phenomenon in polymers so that almost all the crystalline polymers are polymorphic if the proper conditions for the crystallization of the different forms can be found^[1]. Acquiring a good knowledge of the physical and chemical properties (mechanical, thermal and electrical properties, and solvent resistance, etc.) of different polymorphic forms of a given polymeric material can be advantageous for exploiting possible applications. One of the most remarkable cases of commercial interest is the much higher solvent resistance of the β form crystals of syndiotactic polystyrene (sPS) with respect to the other forms^[2].

sPS has received considerable attention as a potential engineering plastic, due to its high melting temperature, fast crystallization rate and good chemical resistance^[3]. Of particular interest is its complex polymorphic behavior involving four crystalline forms: α , β , γ , and δ . It has been shown that both the α and β forms have an all-*trans* planar zigzag (*tttt*)_n backbone conformation, whereas the γ and δ forms have a helical (*trans*, *trans*, *gauche*, *gauche*, (*ttg*⁺*g*⁺)_n) backbone conformation. The α form with a hexagonal unit cell and the β form with an orthorhombic unit cell, both with an identity period of $c = 0.51$ nm, can be obtained from the melt or the glassy state of sPS under different thermal conditions^[4–6]. The γ and δ forms, both with an identity period of $c = 0.78$ nm, can only be formed from solvent swelling of glassy sPS and have been shown to have the same monoclinic crystal structure. Among these four crystalline forms, the α form with $a = 2.63$ nm and the β form with $a = 0.88$ nm, $b = 2.88$ nm are the primary crystalline polymorphs.

A number of studies^[1, 4–16] have been carried out on polymorphs and solid phase transformations of sPS. Guerra and his coworkers^[4] first gave the nomenclature of the α and β crystalline forms and studied their formation from melt and glass phase of sPS in detail. Ho *et al.*^[16] discussed the polymorphs of melt-crystallized sPS, using the metastability theory given by Keller and Cheng^[17]. Since (*ttg*⁺*g*⁺)_n has slightly higher energy than (*tttt*)_n, the δ form is stable up to $\sim 120^\circ\text{C}$ and a solid phase transformation of the γ form to the α form is possible at around 180°C . In fact, the transformation between the α form and β form is of more concern for practical applications, because it is directly related to the final properties of sPS product^[5]. But, because there is almost no

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energy difference between the two known polymorphs having the all-*trans* conformation^[18], the transformation of the α form to the β form is hardly implemented under normal conditions^[1].

With increasing pressure and temperature over a certain critical temperature and critical pressure, a pure component will reach its supercritical fluid (SCF) region. A supercritical fluid has a viscosity similar to a gas and a fluidity much better than a liquid, and its surface tension is substantially lower than that of a liquid so that the fluid can diffuse much more readily into a solute material, after the manner of a gas. For example, carbon dioxide attains a supercritical state when its temperature exceeds 30.95°C, and its pressure exceeds 7.375 MPa. The moderate critical conditions for CO₂ make it a convenient fluid for experimentation. At the same time, it has “green” properties, being nonflammable, relatively nontoxic and naturally abundant^[19]. These properties of SC-CO₂ give an impetus to development of a number of new applications^[20].

In supercritical CO₂, the conditions of phase transformation must be different from those in non-supercritical CO₂. So the aim of the present work is to scrutinize the effect of supercritical CO₂ on the polymorphs and transformations of *s*PS, and investigate some of influencing factors (*e.g.* time, temperature and pressure) in detail. This research should also initiate a study of polymorphism and solid phase transition of crystallizable polymer in supercritical fluid state generally.

EXPERIMENTAL

The *s*PS was synthesized in Prof. You-liang Hu's laboratory. The polymer has a M_w of 630000 and M_w/M_n of 4.5, as determined by GPC, and a syndiotacticity of 97%, as determined by high resolution NMR. Its T_m is 272°C.

A high-pressure apparatus was used for *s*PS treatment in supercritical CO₂ (Fig. 1). The high-pressure vessel was flushed with low-pressure CO₂ for about 3 min and heated to the experimental temperature, then the *s*PS samples were loaded into it. When the CO₂ pressure reached the desired value, the timing began. At the end of annealing, CO₂ was slowly vented from the vessel.

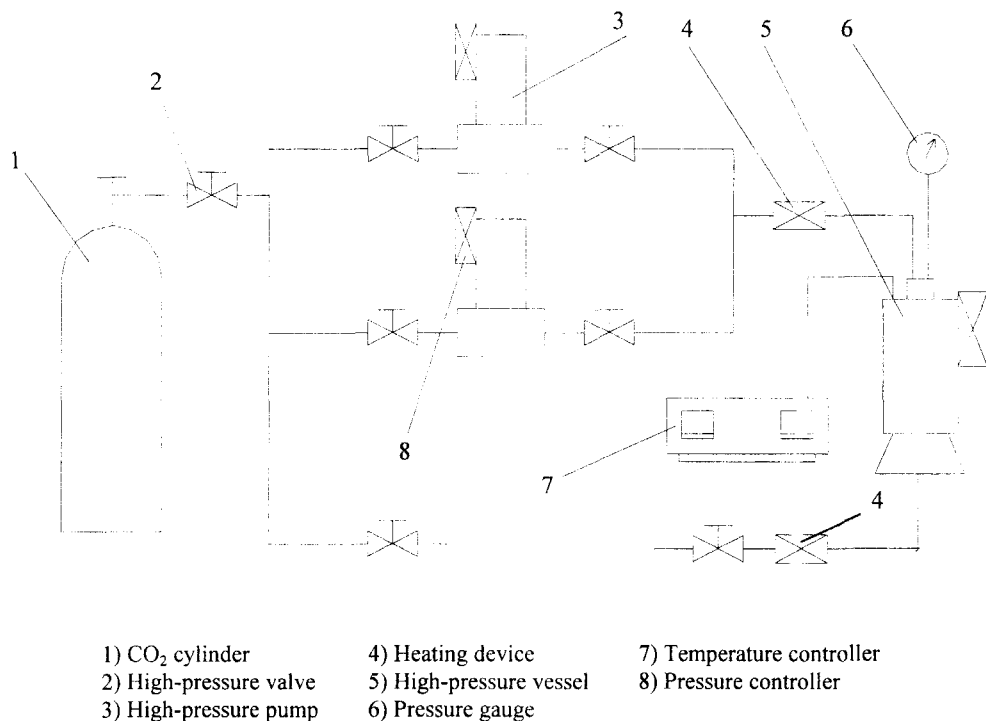


Fig. 1 Diagram of experimental device for treating *s*PS samples in supercritical CO₂

The films for wide-angle X-ray diffraction measurement were 0.05 mm in thickness and were prepared as follows. sPS powder was first sandwiched between two cover glasses of 0.16 mm thickness and heated on a hot stage at 320°C, followed by pressing into film first and conditioning for 5 min. This process was sufficient to eliminate any thermal history and the memory of the α form in the melt. Then the samples were transferred quickly (within 1 or 2 s) from the hot stage to a silicon oil bath kept at 170°C and crystallized for 1 h in order to obtain the pure α form samples^[5].

The determination of the sPS crystalline forms was conducted by wide-angle X-ray diffraction. It was shown that the α form crystal exhibits characteristic peaks at $2\theta = 6.7, 11.6^\circ$, and the β form at $2\theta = 6.1, 12.2$ and 18.6° . The measurement of the content of the α and β forms was carried out according to the method described in Ref. [4]. The 2θ region $10^\circ\text{--}15^\circ$ was considered, and a baseline between the two intensity minima located at $2\theta = 10.8^\circ$ and $2\theta = 14.8^\circ$ was drawn. The areas (A) of the two peaks located at $2\theta = 11.6^\circ$ and $2\theta = 12.2^\circ$ were measured, and the percentage of the α form in the crystalline fraction was evaluated by the approximate relation^[4].

$$P_\alpha = \frac{1.8A(11.6)/A(12.2)}{1+1.8A(11.6)/A(12.2)} \times 100$$

where 1.8 is the ratio between the intensities (measured under the same experimental conditions) of the peaks at 11.6° and 12.2° for samples of equal thickness and crystallinity in the pure α and β forms, respectively.

RESULTS AND DISCUSSION

Transformation with Respect to Exposure Time

The X-ray diffraction patterns of the sPS samples, displayed in Fig. 2, were obtained from originally pure α form samples, followed by annealing in supercritical CO₂ (200°C and 16 MPa) for different intervals of time. It can be seen that for all the samples, the α form peaks (at $2\theta = 6.7, 11.6^\circ$) disappear gradually with increasing annealing time, while the β form peaks (at $2\theta = 6.1, 12.2, 18.6^\circ$) increase gradually. During this experiment, no peaks for other crystal forms were observed. Furthermore, when the annealing time is longer than 8 h, there are no α form peaks to be seen at all.

Figure 3 shows the content of α form crystal in sPS samples annealed in supercritical CO₂ for different intervals of time. It can be seen that the amount of the α form in the samples decreases with increasing annealing time. For the first few hours, the percentage of the α form in the samples decreases slightly. After 6 h, the amount of the α form drops suddenly and is completely transformed to the β form.

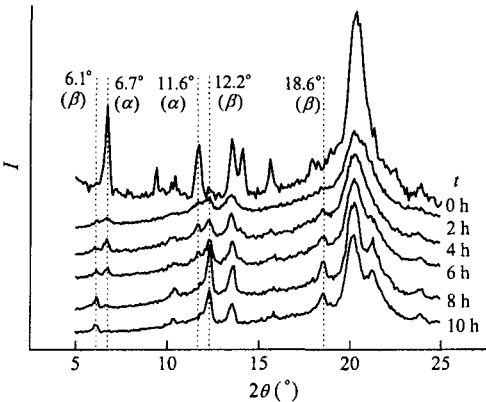


Fig. 1 X-ray diffraction patterns (CuK α) of sPS samples annealed in supercritical CO₂ (200°C and 16 MPa) for different period of time

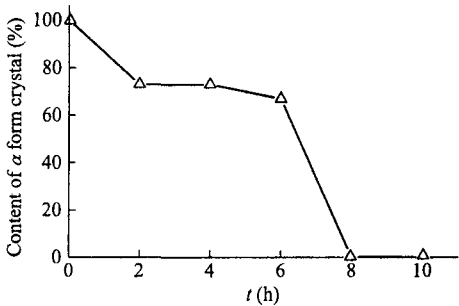


Fig. 2 Effect of annealing time on the content of α form crystal in sPS samples
Samples were annealed in supercritical CO₂ at 200°C and under a pressure of 16 MPa

The slight decrease of the α form at the beginning is due to the increased crystallinity of *s*PS caused by annealing at about 200°C^[16]. Supercritical CO₂ at high temperature and pressure induces the crystallization of polymeric materials^[21]. The results of De Rosa and co-workers^[8] have indicated that the β form crystal structure is more stable thermodynamically. These factors favor the formation of the β form crystal in the sample and inevitably reduce the amount of the α form in the same sample.

Further, the significant reduction of the α form indicates that solid phase transformation of the α form to the β form has occurred in supercritical CO₂. It is well known that the interaction between *s*PS and solvent molecules play a vital role in the formation of complex polymorphism^[4]. The sorption of low molecular weight species accelerates the relaxation rate of macromolecules. Supercritical CO₂ is also an effective plasticizer for polymers. This plasticization effect could lower the energy barriers and thereby favor the occurrence of solid-solid phase transitions at much lower temperature. Consequently, polymer can crystallize at a temperature below its normal T_g when it contacts with supercritical fluids. This means that supercritical CO₂ gradually infuses into solid polymer to plasticize it and to increase the free volume of the amorphous region in the crystallizable polymer. Therefore, the chain mobility and the degree of swelling of the polymer are increased. Supercritical CO₂ can decrease the glass transition temperature of a polymer and accelerate the relaxation of macromolecules. So new solid-solid transitions result from reduced energy barriers.

It can be seen that the transformation in supercritical CO₂ is not the same as the transformations^[10, 11, 15] from $(ttg^+g^+)_n$ to $(tttt)_n$ under other conditions. These facts indicate that all these differences result from the special properties of supercritical CO₂.

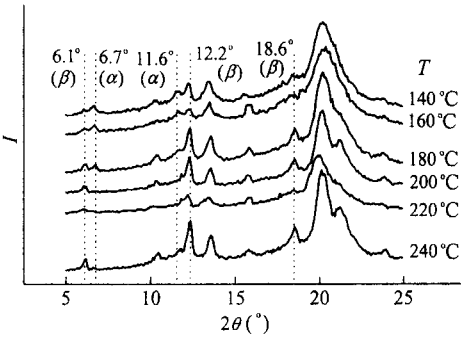


Fig. 4 X-ray diffraction patterns (CuKα) of *s*PS samples annealed in supercritical CO₂ (8 h and 16 MPa) at different temperatures

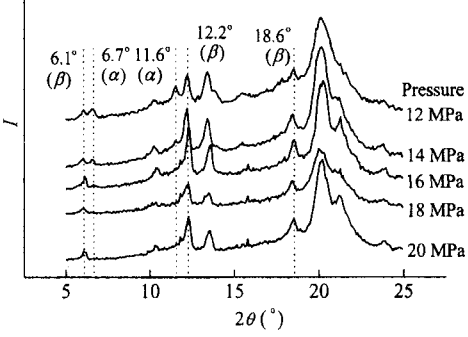


Fig. 5 X-ray diffraction patterns (CuKα) of *s*PS samples annealed in supercritical CO₂ (200°C and 8 h) at different pressures

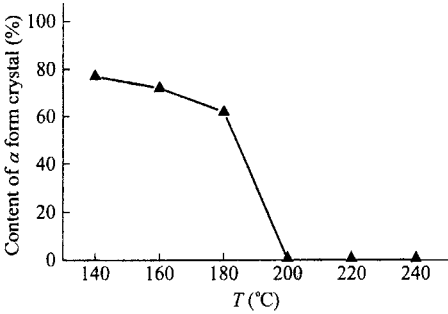


Fig. 6 Content of the α form in *s*PS samples annealed in supercritical CO₂ (8 h and 16 MPa) at different temperatures

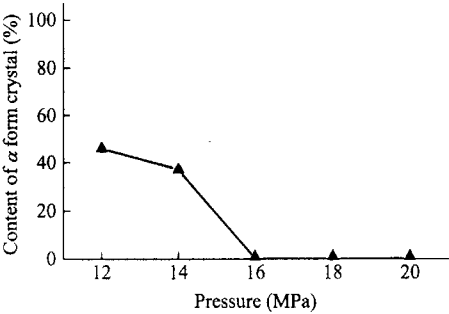


Fig. 7 Content of the α form in *s*PS samples annealed in supercritical CO₂ (200°C and 8 h) at different pressures

Transformation with Respect to Exposure Temperature and Pressure

Figure 4 shows the X-ray diffraction patterns of pure α form samples annealed in supercritical CO₂ at different temperatures. Figure 5 also shows the effect of pressure on the solid phase transformation of *s*PS in supercritical CO₂. All these diffraction patterns exhibit similar results, *i.e.*, with increasing temperature or pressure, the typical α form peaks (at $2\theta = 6.7, 11.6^\circ$) weaken gradually and β form peaks (at $2\theta = 6.1, 12.2, 18.6^\circ$) increase gradually. Figures 6 and 7 show the effects of annealing temperature and pressure on the content of α form crystal in *s*PS samples, respectively. It can be seen that higher temperature or higher pressure favors the transformation of the α form to β form.

Up to now, there is no general and adequate theory to explain the molecular mechanism of solid phase transition in polymer crystals under different conditions^[17]. In the present study, the solid phase transformation of *s*PS in supercritical CO₂ results from the increased solvent capacity, fluidity and diffusion ability of supercritical CO₂. Moreover, the increased free volume in the samples is a major factor governing the solid phase transformation of the α form of *s*PS to the β form.

When *s*PS is annealed in supercritical CO₂, there is a complex physicochemical interaction between the polymer and supercritical CO₂^[22]. Within a limited period of time, the degree of swelling of the polymer increases with the prolongation of time. Moreover, the transformation of the α form to the β form can only occur and finish within a relatively short period of time when the free volume of the sample is sufficiently large. For the same reason, the degree of swelling of the sample also increases with increasing temperature and pressure in supercritical CO₂. Only sufficiently high temperature and pressure can supply a large enough free volume for the solid phase transformation of *s*PS in supercritical CO₂. However, similar to the crystallization of polymer in compressed gas^[23], increased pressure also can weaken the chain mobility of macromolecules and decrease free volume as well, so that there should be a pressure range where a net increase of the free volume could be reached.

In conclusion, the solid phase transformation of the α form crystals to the β form crystals of *s*PS in supercritical CO₂ is solely induced and governed by the special properties of supercritical CO₂, and is different from other transitions occurring under other conditions.

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