

# Stability of crystal forms of syndiotactic polystyrene correlated with their formation in different media having different solubility parameters

Weiming Ma<sup>a,b</sup>, Jian Yu<sup>a</sup>, Jiasong He<sup>a,\*</sup>

<sup>a</sup>Key Laboratory of Engineering Plastics, Joint Laboratory of Polymer Science and Materials, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China

<sup>b</sup>Graduate School of Chinese Academy of Sciences, Beijing 100080, China

Received 5 July 2005; received in revised form 23 August 2005; accepted 5 September 2005

Available online 22 September 2005

## Abstract

The formation of crystal forms of syndiotactic polystyrene having different stability was investigated in different media having different solubility parameters with the help of wide-angle X-ray diffraction, Fourier-transform infrared spectroscopy and differential scanning calorimetry. The starting sample was the  $\gamma$  form of syndiotactic polystyrene, and the solubility parameter of the media was adjusted by changing the temperature, pressure, cosolvent of supercritical carbon dioxide. With increasing solubility parameter, the stability of the resultant crystal forms was increased in the order from  $\gamma$  through  $\alpha''$  and  $\beta'$  to  $\beta''$  form.

© 2005 Elsevier Ltd. All rights reserved.

**Keywords:** Crystal stability; Solubility parameter; Syndiotactic polystyrene

## 1. Introduction

Solvent induced crystallization (SINC) in semi-crystalline polymers has been widely investigated [1–3]. The interaction between polymer and solvent could rearrange the polymeric chains into a thermodynamically lower energy state and thus induce crystallization at temperature below the glass transition temperature ( $T_g$ ) of the polymers. However, the solvent strength of single solvent in SINC cannot be adjusted in a wide range only by changing the temperature. And the using of different solvents usually introduces a new variable [4]. Supercritical CO<sub>2</sub> is a fluid working at a temperature and a pressure higher than its critical point ( $T_c=31.1$  °C,  $P_c=7.37$  MPa). Its major advantage relies on its adjustable solvent strength over a wide range through small changes in the temperature, pressure or both, resulting in different degree of polymer swelling [5]. Furthermore, exhibiting features of both thermal and solvent environments, supercritical CO<sub>2</sub> can swell and plasticize glassy polymers, leading to a depression on their  $T_g$  to almost the same extent as affected by vapors or liquids [6]. The plasticization of the amorphous phase increases the

mobility of the polymer chains and induces concomitant change in the morphology and crystallization under moderate conditions. In addition, this effect leads to the decrease of the energy barriers, thus making some solid–solid transitions possible at much reduced temperatures and bringing about some new transitions that can not occur at ambient pressure.

Syndiotactic polystyrene (sPS) has received considerable interest since the successful synthesis of highly stereoregular sPS by using a homogeneous Ziegler–Natta catalyst in 1986 [7]. It 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) and so on [8–14]. Typically, the crystalline  $\alpha$  and  $\beta$  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 [11,14–20]. They are further classified into two limiting disordered modifications,  $\alpha'$  and  $\beta'$ , and two limiting ordered modifications,  $\alpha''$  and  $\beta''$ . The crystalline  $\delta$  and  $\gamma$  forms, with TTGG helical conformation, can be formed from solvent swelling of glassy or semicrystalline sPS [8,21–23]. Crystal transition of the sPS at ambient pressure has been summarized [24]. It is well known that the  $\gamma$  form can transform into the  $\alpha$  form by thermally annealing at temperatures above 200 °C under ambient pressure [12,13,25,26]. Usually, the  $\beta$  form can be obtained by slow cooling from the melt or by casting from

\* Corresponding author. Tel.: +86 10 62613251; fax: +86 10 82612857.  
E-mail address: [hejs@iccas.ac.cn](mailto:hejs@iccas.ac.cn) (J. He).

an *o*-dichlorobenzene solution at 170 °C [9]. No direct transformation from the  $\gamma$  form to  $\beta$  form under ambient pressure has been reported. Phase transitions of sPS in the presence of CO<sub>2</sub> have been reported by Handa et al. [25] and He et al. [27–30]. The phase transition of  $\gamma$  form sPS to  $\alpha$  form occurred at lower temperature in compressed CO<sub>2</sub> than those under ambient pressure [25]. In the presence of CO<sub>2</sub> of 57 atm (5.8 MPa), the  $\gamma$  form sPS can transform into the  $\beta$  form at about 240 °C [25]. It should be noted that this phase transition is induced by gaseous CO<sub>2</sub>. However, crystal transition behavior of  $\gamma$  form sPS in supercritical CO<sub>2</sub>, especially in the temperature range covering the transition temperature of  $\gamma$  form under ambient pressure, still lacks of study. Exhibiting hybrid properties of a typical gas and liquid, such as low viscosity, high compressibility and adjustable density from vapor-like to liquid-like, supercritical CO<sub>2</sub> must provides polymers with different crystal transition behavior from that under non-supercritical condition.

On the other hand, it is well known that CO<sub>2</sub> is essentially a non-polar fluid without dipole moment [31]. Evaluated from equations in the literature [32,33], the solubility parameter of CO<sub>2</sub>,  $\delta_{\text{CO}_2}$ , is 0–15 MPa<sup>1/2</sup> in the temperature range of 30–190 °C and the pressure range of 5–30 MPa, which is much lower than those of most polymers. Therefore, although acting as an efficient plasticizer, supercritical CO<sub>2</sub> is a weak solvent for most polymers. It is reported that adding a small amount of polar cosolvent to supercritical CO<sub>2</sub> is equivalent to giving the mixed fluid an overall small dipole moment, thus increasing the solubility of CO<sub>2</sub> in the polymers [31,34,35]. The effect of the cosolvent in supercritical CO<sub>2</sub> on the crystal behavior of polymers has been reported by Handa et al. [31, 35] and He et al. [36]. The presence of polar CH<sub>2</sub>Cl<sub>2</sub> and CH<sub>3</sub>OH produced methyl-substituted poly(aryl ether ether ketone) and *tert*-butyl-substituted poly(ether ether acetone) with crystals which underwent melting at higher temperatures and over a much narrower temperature range [31,35]. The addition of a small amount of C<sub>2</sub>H<sub>5</sub>OH as a cosolvent induced the crystallization of polycarbonate at much lower temperature and pressure [36]. Overall, the existence of cosolvent in previous studies did not induce any crystal transition of polymers. The effect of the cosolvent in supercritical CO<sub>2</sub> on the crystal transition behavior of polymorphic polymers has not been reported yet.

In our previous paper [37], the preliminary WAXD results about the crystal transition behavior of the  $\gamma$  form sPS under different conditions have been reported. In the present paper, starting from the  $\gamma$  crystal and changing the solubility parameter of the media by means of adjusting temperature, pressure and cosolvent of supercritical carbon dioxide, the formation of crystal forms having different stability was investigated. The characterization of the resultant crystal forms was performed by using wide-angle X-ray diffraction (WAXD), Fourier-transform infrared spectroscopy (FTIR), and differential scanning calorimetry (DSC). Finally, the stability of these resultant crystal forms was correlated with the solubility parameter of these different media.

## 2. Experimental section

### 2.1. Materials

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  $2.1 \times 10^5$  and the polydispersity ( $M_w/M_n$ ) is 2.3. CO<sub>2</sub> with a purity of 99.95% was supplied by Beijing Analytical Gas Factory, China. Acetone was of reagent grade and used as received.

### 2.2. Sample preparation

Amorphous films of thickness about 300  $\mu\text{m}$  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.

### 2.3. Sample treatments

A high-pressure apparatus was used for sPS treatment in CO<sub>2</sub>. The method to obtain the  $\gamma$  form sPS from the amorphous state followed the procedure described in Ref. [28]. Briefly, the amorphous sPS samples were loaded into a 25 mL high-pressure vessel, which was then flushed with low-pressure CO<sub>2</sub> for about 2 min. After the treatment of sPS samples at 100 °C and 16 MPa for 6 h, the vessel was quenched to room temperature and depressurized slowly. The  $\gamma$  form sPS thus obtained was further treated by using a similar procedure. A 20 mol% of acetone according to the amount of CO<sub>2</sub> was directly added to the vessel at the beginning of the treatment where the cosolvent was indicated.

### 2.4. Measurements

WAXD measurements were conducted on a Rigaku D/max 2500 with Cu K $\alpha$  radiation (40 kV, 300 mA). The scanning  $2\theta$  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. The sPS has high crystallization rate and exhibits multiple melting behavior during DSC scans. In order to avoid the recrystallization of sPS during the measurement, all the samples were scanned at a heating rate of 80 °C/min [28,38].

FTIR measurements were carried out on a system 2000 FTIR (Perkin–Elmer) in the standard wavenumber range of 370–4000 cm<sup>-1</sup> for the investigation of the chain conformations and crystalline forms in sPS.

## 3. Results and discussion

The original  $\gamma$  form with relative high crystallinity was obtained by treating the glassy sample in supercritical CO<sub>2</sub> of 16 MPa at 100 °C for 6 h, followed by WAXD test. Its pattern referred to as the ‘original sample’ is shown in Fig. 1(a). The sample exhibits the typical characteristics of the  $\gamma$  form

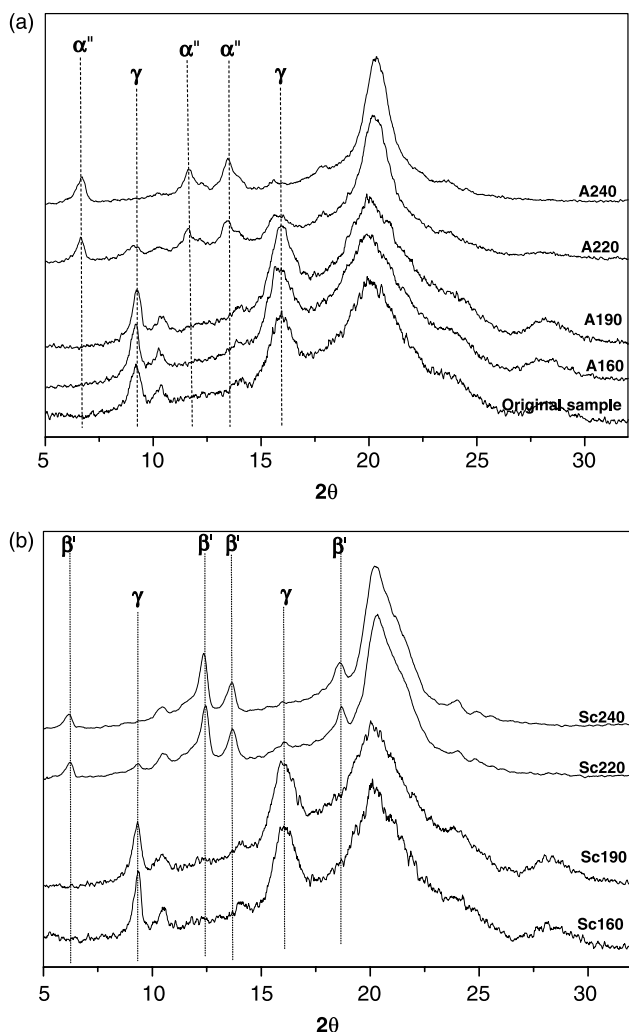


Table 1  
Description of the thermal treatment for  $\gamma$ -form samples

Sample code	Temperature (°C)	Pressure (MPa)	Time (h)	Atmosphere
A	160, 190, 220, 240	Ambient	1	Ambient atmosphere
G	160, 190, 220, 240	6	1	Gaseous CO <sub>2</sub>
Sc	160, 190, 220, 240	12	1	Supercritical CO <sub>2</sub>
HSc	160, 190, 220, 240	20	1	Supercritical CO <sub>2</sub>
SSc	160, 190, 220, 240	12	1	Supercritical CO <sub>2</sub> + 20 mol% acetone

obtained [11]. At the same time, the relative intensity of the  $\gamma$  form peaks ( $2\theta=9.2, 16.0, 28.3^\circ$ ) decreases sharply. This result implies that the  $\gamma$  form transforms into the  $\alpha$  form at about 220 °C under ambient pressure. At the higher temperature of 240 °C, the structure obtained is all that of the  $\alpha$  form with no trace of the  $\gamma$  form. Some additional peaks ( $2\theta=15.6$  and  $18.0^\circ$ ) appear in A220 and A240, indicating the structure thus obtained was  $\alpha''$  form with a higher degree of perfection [11]. The results shown above are consistent with the previous study [5,13,26].

When the original sample was treated at the same temperature in the presence of supercritical CO<sub>2</sub>, dramatically different results were obtained. Fig. 1(b) shows the diffraction patterns of the original sample treated at different temperatures with supercritical CO<sub>2</sub> of 12 MPa. Sc160 and Sc190 keep those characteristic peaks of the  $\gamma$  form. Some new peaks ( $2\theta=6.2, 12.3, 13.6, 18.6, 20.2$  and  $35^\circ$ ) appear for the sample treated at the temperature of 220 °C for 1 h, indicating that the  $\beta'$  form was obtained [11]. At the same time, the relative intensity of the  $\gamma$  form peaks ( $2\theta=9.2, 16.0, 28.3^\circ$ ) decreases sharply and almost reaches zero. These results clearly indicate that the  $\gamma$  form transformed into the  $\beta'$  form under this condition. It was reported that the  $\beta'$  form sPS could not be formed from the  $\gamma$  form by solid–solid transition during the normal thermal processes [25]. Obviously, CO<sub>2</sub> was responsible for the transformation of the  $\gamma$  form into the more stable  $\beta'$  form in supercritical CO<sub>2</sub>.

To further clarify this crystal transition process, the  $\gamma$  form samples were treated at 240 °C in supercritical CO<sub>2</sub> of 12 MPa for different intervals of time, the WAXD patterns of which are shown in Fig. 2. The samples treated for 1 and 5 min keep the pattern of  $\gamma$  form, indicating the crystal structure did not change. Some new peaks ( $2\theta=6.2, 12.3, 13.6$  and  $18.6^\circ$ ) attributed to the  $\beta'$  form appear for the sample treated for 8 min. At the same time, the significant decrease of the intensity of characteristic peaks of the  $\gamma$  form shows that the occurrence of transformation from  $\gamma$  form with helical conformation into the  $\beta'$  form with all-trans conformation. All the obtained crystals were the  $\beta'$  form without any trace of the  $\gamma$  form when the treatment time increased to 10 min. Further extending the treatment time up to 300 min did not produce any other crystal forms. The results shown above indicate that the  $\gamma$  form transformed into the  $\beta'$  form directly

Fig. 1. WAXD patterns of  $\gamma$  form sPS treated under ambient pressure (a) and supercritical CO<sub>2</sub> at 12 MPa (b) for different temperatures.

( $2\theta=9.2, 10.3, 16.0, 20.0, 28.3^\circ$ ) [12,25,28]. It is suggested that the sPS samples were intensively plasticized by swelling of supercritical CO<sub>2</sub> and the polymer chains were rearranged into the  $\gamma$  form with the helical conformation as a result of the increased molecular mobility near the  $T_g$  [28]. Subsequently, the original  $\gamma$ -form samples were treated further under different conditions to study the crystal transition behaviors of the  $\gamma$ -form. For clarity and brevity, the thermal conditions for treating  $\gamma$ -form samples are summarized in Table 1.

### 3.1. Resultant crystal forms with changing the temperature

Crystal transition of the  $\gamma$  form sPS under ambient pressure has been widely reported [5,12,13,26]. Fig. 1 shows the WAXD patterns of original sample treated at different temperatures under ambient pressure for 1 h. For A160 sample annealed at 160 °C, the diffraction pattern is still that of the  $\gamma$  form. No change is found when further increasing the temperature to 190 °C. At 220 °C, the WAXD pattern shows a remarkable change. Some new peaks ( $2\theta=6.7, 11.8, 13.5, 20.2, 35^\circ$ ) appear in A220, indicating that the  $\alpha$  form was

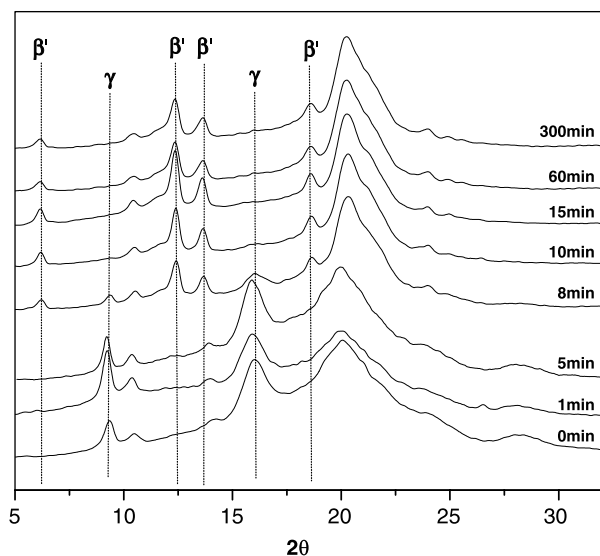


Fig. 2. WAXD patterns of  $\gamma$  form sPS treated at 240 °C in supercritical  $\text{CO}_2$  of 12 MPa for different intervals of time.

without passing through any intermediate crystal forms in the presence of supercritical  $\text{CO}_2$ . At the beginning of the experiments, the temperature and pressure in the vessel did not reach the equilibrium. Therefore, the crystal transition did not occur immediately and there existed a delay of about 5 min. After the treatment condition reached the equilibrium, the crystal transition from  $\gamma$  to  $\beta'$  form occurred very fast. This direct crystal transition was also verified by FTIR, which is shown in Fig. 3. The intensity of characteristic bands of  $\gamma$  form sPS at 932 and 945  $\text{cm}^{-1}$  decreases and the bands at 858  $\text{cm}^{-1}$  assigned to the  $\beta$  form appears after 8 min treatment, indicating the crystal transition from the  $\gamma$  form into  $\beta$  form [13,28]. Furthermore, according to the WAXD and FTIR results shown above, the treatment time of 10 min was enough to study the influence of the media on the formation of different crystal forms. Therefore, the treatment time of 1 h was adopted to treat all the original samples in this paper.

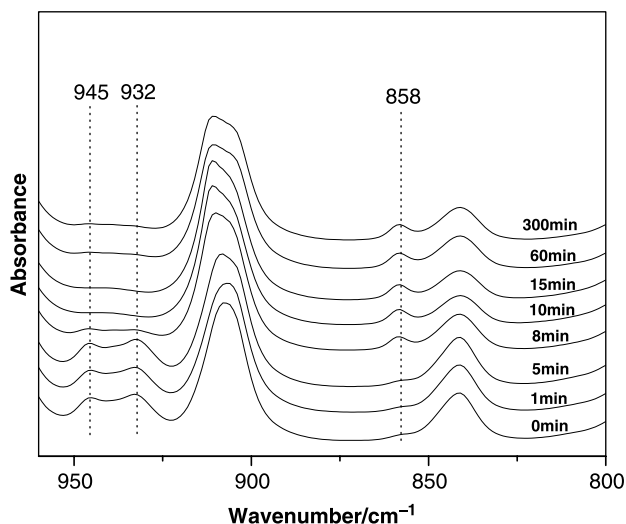


Fig. 3. FTIR patterns of  $\gamma$  form sPS treated at 240 °C in supercritical  $\text{CO}_2$  of 12 MPa for different intervals of time.

It is well established that the sorption of low molecular weight species leads to an acceleration of relaxation of the macromolecules [25]. The plasticization effect of supercritical  $\text{CO}_2$  could lower the energy barriers and thereby induce such  $\gamma$  to  $\beta'$  transformation. It is commonly accepted that the  $\alpha''$  type is a kinetically more accessible crystal, while the  $\beta'$  crystal is of a thermodynamic stable crystal packing [39]. Under ambient condition, the crystallization rate of the  $\alpha$  form is higher than that of the  $\beta$  form at low temperature, but the difference is gradually diminished as the temperature is increased. At the temperature higher than a certain temperature of 273 °C [40], the  $\beta$  form is favored. In the presence of supercritical  $\text{CO}_2$ , the curve of crystallization rate-temperature shifts to lower temperature because of decreased  $T_g$  and  $T_m$ , resulted from strong plasticization effect of supercritical  $\text{CO}_2$  [41]. So in our experiments, the  $\beta'$  form appeared in the sample of Sc220 and Sc240.

The DSC patterns of the samples treated at 240 °C for 1 h under different conditions, together with the original  $\gamma$  form sample, are shown in Fig. 4. The original sample shows the typical DSC patterns of the  $\gamma$  crystal [28]. The endotherm at about 155 °C is attributed to the reorganization of the  $\gamma$  crystal form. The endotherm at 193 °C followed by the exotherm at 200 °C corresponds to the  $\gamma$  to  $\alpha$  form transition. At an even higher temperature of about 273 °C, the broad endothermic peak is clearly associated with the melting of the  $\alpha$  form. The samples treated at 240 °C under different conditions show DSC patterns different from that of the  $\gamma$  form. The X-ray evidence in Fig. 1 has already suggested that the obtained A240 and Sc240 were  $\alpha''$  and  $\beta'$  crystals, respectively. Apparently, the  $\alpha''$  and  $\beta'$  crystals displayed different DSC patterns, as shown in Fig. 4. The melting temperature of the  $\beta'$  crystal (268 °C) is lower than that of the  $\alpha''$  crystal (272 °C), which is consistent with the reference [39]. In addition, the melting transition width of the  $\beta'$  crystal is narrower than that of the  $\alpha''$  crystal, suggesting the broader lamellar thickness distribution of the obtained  $\alpha''$  type crystal than that of  $\beta'$  crystal. Furthermore,

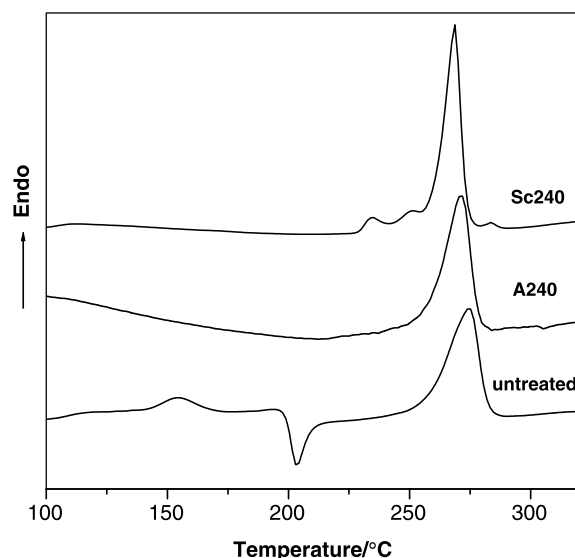


Fig. 4. DSC patterns of the samples treated under the conditions indicated.



the existence of small endothermic peaks in Sc240 sample indicates that the structural reorganization might more readily occur in the disordered  $\beta'$  crystal upon DSC scanning [25,39]. Consequently, the DSC results shown above are consistent with the WAXD results.

### 3.2. Resultant crystal forms with changing the pressure

To further study the crystal transition, the original  $\gamma$  sample was treated at different pressures in the presence of  $\text{CO}_2$ . When decreasing the pressure to 6 MPa in the temperature range of 160–240 °C,  $\text{CO}_2$  is in its gaseous state. Fig. 5(a) shows the WAXD patterns of the  $\gamma$  form sample treated in gaseous  $\text{CO}_2$  of 6 MPa. The characteristic patterns of  $\beta'$  form in both G220 and G240 samples indicate that the  $\gamma$  form transformed into the thermodynamically favorable  $\beta'$  form under these conditions. At the same time, weak peaks of 6.7 and 9.2° are still found in G220, indicating the co-existence of a small amount of the  $\alpha''$  form and  $\gamma$  form [11,28]. After a higher temperature treatment at 240 °C, the  $\gamma$  form disappears and the obtained is the typical feature of the  $\beta'$  form, together with the residual  $\alpha''$  phase in

sample G240, reflected by the weak peak at  $2\theta = 6.7^\circ$  [11]. This was probably a result of the less plasticizing ability of the gaseous  $\text{CO}_2$  than that of the supercritical  $\text{CO}_2$  at the same temperature. Generally speaking, gaseous  $\text{CO}_2$  with low pressure cannot diffuse easily into and plasticize the polymer matrix well. On the contrary, supercritical  $\text{CO}_2$  exhibits hybrid properties of a typical gas and a liquid, such as gas-like diffusivity coupled with liquid-like solubility. Therefore, supercritical  $\text{CO}_2$  has been shown to swell most polymers to a comparative degree. These unique properties provide supercritical  $\text{CO}_2$  much more plasticizing effect than the gaseous one.

Fig. 5(b) shows the WAXD patterns of the  $\gamma$  form sample treated at high pressure of 20 MPa in supercritical  $\text{CO}_2$ . HSc160 and HSc190 keep those of the  $\gamma$  form. It is found that the obtained HSc220 shows the typical patterns of the  $\beta'$  form without any trace of  $\gamma$  form and  $\alpha''$  form. This result indicates that all the  $\gamma$  form transformed into the  $\beta'$  form under this treatment condition. The crystal transition temperature was lower than that treated in supercritical  $\text{CO}_2$  of 12 MPa. It is believed that supercritical  $\text{CO}_2$  with the pressure of 20 MPa diffused into sPS samples much more readily than that of the 12 MPa. Increasing incubation pressure increased the solubility of  $\text{CO}_2$  in sPS samples and enhanced the plasticizing ability. It should be emphasized that the energy barrier for the  $\gamma$  to  $\beta'$  transition might be increased by the hydrostatic pressure when increasing the incubation pressure of supercritical  $\text{CO}_2$ . However, it seems that, compared with the plasticization effect, this hydrostatic pressure effect could be neglected for the  $\gamma$  to  $\beta'$  transition at high pressures. Therefore, supercritical  $\text{CO}_2$  with the pressure of 20 MPa overcame the energy barrier for the  $\gamma$  to  $\beta'$  transition easily, thus providing a proper condition enough to obtain the  $\beta'$  form at 220 °C.

Consequently, the pressure of  $\text{CO}_2$  affected the crystal transition of  $\gamma$  form sPS. The  $\gamma$  form transformed into the  $\alpha''$  form in ambient atmosphere (air) about 0.1 MPa. Compared with the mixture  $\alpha''$  and  $\beta'$  crystal forms obtained in gaseous  $\text{CO}_2$  of 6 MPa, supercritical  $\text{CO}_2$  of 12 MPa transformed the  $\gamma$  form completely into the  $\beta'$  crystal at 240 °C. Supercritical  $\text{CO}_2$  of 20 MPa decreased this crystal transition temperature to 220 °C. Therefore, increasing the pressure of supercritical  $\text{CO}_2$  assisted the crystal transition of the  $\gamma$  form. The higher the pressure was, the more stable crystal forms obtained.

### 3.3. Resultant crystal forms with adding a cosolvent

Evaluated from equations in the literature [32,33], the solubility parameter of  $\text{CO}_2$ , in the temperature range of 160–240 °C and the pressure of 12 MPa was about 2.0–2.9  $\text{MPa}^{1/2}$ . As shown in Table 2, the solubility parameter of polystyrene was about 17.4–19.0  $\text{MPa}^{1/2}$  [42]. Considering the large difference between  $\delta_{\text{CO}_2}$  and  $\delta_{\text{sPS}}$ , we estimated that the solubility of  $\text{CO}_2$  in syndiotactic polystyrene was very limited. On the other hand, acting as a polar fluid, acetone has a dipole moment of 2.9 D and a solubility parameter of about 20.0–20.5  $\text{MPa}^{1/2}$  [42]. Therefore, the addition of a small amount of acetone into supercritical  $\text{CO}_2$  gives the mixed fluid an overall

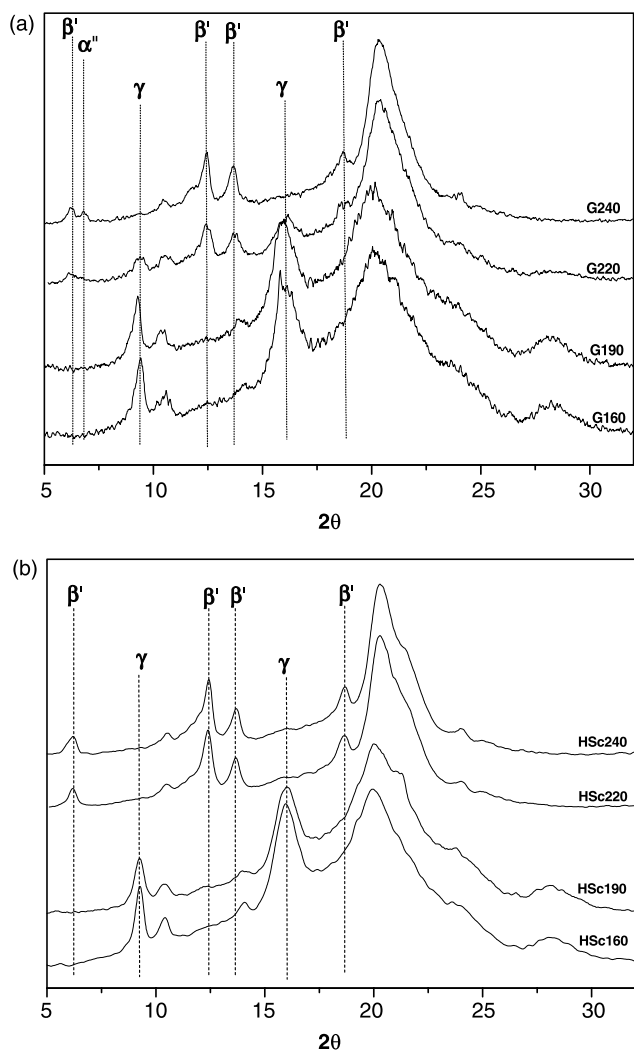


Fig. 5. WAXD patterns of  $\gamma$  form sPS treated in gaseous  $\text{CO}_2$  at 6 MPa (a) and supercritical  $\text{CO}_2$  at 20 MPa (b) for different temperatures.

Table 2  
Solubility Parameters of polystyrene, acetone and supercritical CO<sub>2</sub>

	Sc-CO <sub>2</sub> <sup>a</sup> (160–240 °C, 12 MPa)	Polystyrene <sup>b</sup>	Acetone <sup>b</sup>
$\delta$ (MPa <sup>1/2</sup> )	2.0–2.9	17.4–19.0	20.0–20.5

<sup>a</sup> Calculated from reference [32].

<sup>b</sup> Values from reference [42].

small dipole moment, hence enhances the polymer–fluid interaction and increases the solubility of CO<sub>2</sub> in polymer. It should be also noticed that acetone can only induce the amorphous sPS into the  $\gamma$  form crystal, while it can not induce the  $\gamma$  form crystal into other crystal forms [43]. So in our study, acetone was used as a cosolvent in supercritical CO<sub>2</sub> to study the  $\gamma$  crystal form transition under this condition.

Fig. 6 shows the WAXD pattern of the original sample treated with supercritical CO<sub>2</sub> + 20 mol% acetone at 12 MPa at the temperature indicated. SSc160 shows the typical of the  $\gamma$  form. It is interesting to found that some characteristic peaks ( $2\theta = 12.3, 13.6$  and  $35^\circ$ ) of the  $\beta'$  form appear at a relative low temperature of 190 °C, indicating that the  $\gamma$  form partially transformed into the  $\beta'$  form under thus moderate condition [11]. This transition temperature was lower than that treated by supercritical CO<sub>2</sub> alone at the same pressure. Obviously, the addition of acetone favored this crystal transition. Supercritical CO<sub>2</sub> with acetone as a cosolvent plasticized the sPS much more effectively than that of the supercritical CO<sub>2</sub> alone, thus leading to the transition from  $\gamma$  to  $\beta'$  at relative low temperature. At a higher temperature of 220 °C, the obtained SSc220 was all that of the  $\beta'$  form. The additional peaks of  $2\theta = 11.8$  and  $15.8^\circ$  emerging at 240 °C indicate that the SSc240 obtained was that of the  $\beta''$  form with a higher perfection [10]. To the best of our knowledge, the structurally ordered  $\beta''$  was only obtained by casting from a suitable solvent [8]. In the present study, due to its unique property and efficient plasticizing effect,

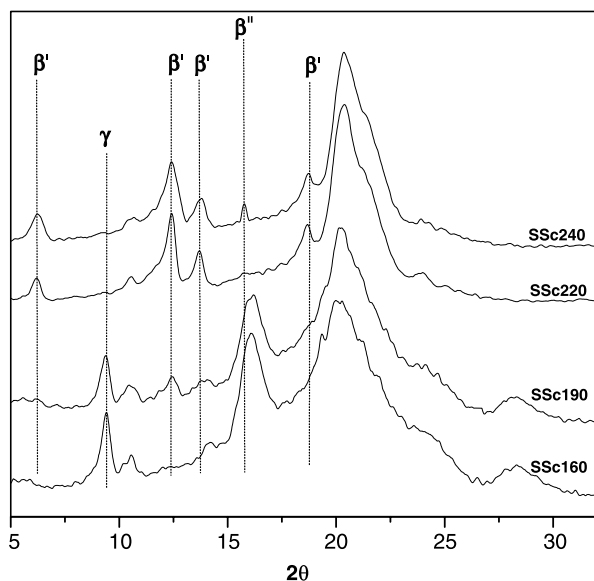


Fig. 6. WAXD patterns of  $\gamma$  form sPS treated in supercritical CO<sub>2</sub> of 12 MPa with 20 mol% acetone for different temperatures.

the supercritical CO<sub>2</sub>–acetone mixture transformed the  $\gamma$  form directly into this ordered  $\beta''$  form.

It is well known that the energy barrier for crystal transition in a polymer can be overcome by increasing its temperature or by dissolving enough diluent in it [30]. In the case of polymer–supercritical CO<sub>2</sub>, it is a subtle combination of both temperature and the solubility of the fluid which determines the plasticization of the polymer [44]. However, due to the essential property of CO<sub>2</sub>, the solubility of supercritical CO<sub>2</sub> in the polymer is relative limited. As shown above, the addition of a small amount of acetone to supercritical CO<sub>2</sub> brought about a dramatic effect in the crystal transition of the  $\gamma$  form sPS. According to the theory of corresponding states [45], the critical temperature and pressure of CO<sub>2</sub>–acetone (20 mol%) mixture were estimated to be about 65.2 °C and 6.46 MPa, respectively. Therefore, this binary fluid was in its supercritical state in our experiments. It is well established that pure acetone itself is ineffective in inducing any crystal transition of  $\gamma$  form sPS. However, it became a very effective agent when used as a cosolvent in supercritical CO<sub>2</sub>.

Increasing the treatment pressure of supercritical CO<sub>2</sub> to 20 MPa decreased the temperature for the  $\gamma$  to  $\beta'$  transition to 220 °C, while supercritical CO<sub>2</sub>–acetone further decreased this temperature to 190 °C even at a lower pressure of 12 MPa. Therefore, the existence of acetone as the cosolvent enhanced the polymer–solute interactions and provided the supercritical fluid with an efficient plasticization effect. This effect allowed a faster relaxation time for macromolecules and provided a moderate condition to obtain the  $\beta'$  crystal. Furthermore, in addition to its own plasticization effect, CO<sub>2</sub> delivered the polar acetone uniformly into the polymer matrix and thus produced the more ordered  $\beta''$  modification with a higher structural perfection.

### 3.4. A correlation of crystal stability with the solubility parameter of different media

Together with the discussion in the previous paragraphs, the crystal transition behavior of  $\gamma$  form sPS was different under various treatment conditions. The corresponding crystal forms obtained are summarized in Table 3. At ambient pressure, the  $\gamma$  form transformed into only the  $\alpha''$  form even at the temperature up to 240 °C. By increasing the pressure to 6 MPa, the  $\gamma$  crystal was transformed into  $\beta'$  form. However, the remaining of residual  $\alpha''$  form after treating the  $\gamma$  form in the presence of gaseous CO<sub>2</sub> suggested the insufficient plasticization effect. The presence of the supercritical CO<sub>2</sub> overcame the energy barrier and made the crystal transition from  $\gamma$  to  $\beta'$  possible. Increasing the pressure of supercritical CO<sub>2</sub> decreased the temperature for  $\gamma$  to  $\beta'$  transition. Furthermore, the existence of acetone in supercritical CO<sub>2</sub> provided a moderate condition to transform the  $\gamma$  into  $\beta'$  form and produced the more ordered  $\beta''$  form at high temperature. It is well known that all the phases of sPS have various degrees of stability. A plot of the free energy vs. temperature depicting the equilibrium and metastable states of various crystals has been reported [46]. Possessing a low free energy, the  $\beta$  form is the most stable and has a higher

Table 3  
The obtained crystal forms after treatment for 1 h under different conditions

Temperature (°C)	160	190	220	240
A	$\gamma$	$\gamma$	$\gamma + \alpha''$	$\alpha''$
G	$\gamma$	$\gamma$	$\gamma + \alpha'' + \beta'$	$\alpha'' + \beta'$
Sc	$\gamma$	$\gamma$	$\gamma + \beta'$	$\beta'$
HSc	$\gamma$	$\gamma$	$\beta'$	$\beta'$
SSc	$\gamma$	$\gamma + \beta'$	$\beta'$	$\beta''$

equilibrium melting temperature than the  $\alpha$  form [43]. In terms of the stability of different crystals, the sequence is  $\beta'' > \beta' > \alpha'' > \alpha' > \gamma$ .

On the other hand, with the stability of the resultant crystal forms, the solubility parameters under the conditions indicated are plotted in Fig. 7. As to supercritical or gaseous CO<sub>2</sub>, the solubility parameters were calculated by using the formula in reference [32]. When acetone was added into the supercritical CO<sub>2</sub>, the solubility parameter of the mixed fluid was calculated according to the molar concentration of acetone. The sequence of the solubility parameter at 240 °C is supercritical CO<sub>2</sub> + acetone (12 MPa) (3.9) > supercritical CO<sub>2</sub> (20 MPa) (3.2) > supercritical CO<sub>2</sub> (12 MPa) (2.0) > gaseous CO<sub>2</sub> (6 MPa) (1.0) > ambient pressure (0). Obviously, the crystal form obtained depended on the solubility parameter of the media. The higher solubility parameter the media had, the more ordered and stable crystal forms were obtained. Consequently, the media with a higher solubility parameter plasticized the sPS chains better and overcame the energy barrier easier, thus transformed the original  $\gamma$  form into a more stable crystal form. Furthermore, increasing the solubility parameter of the media provided a more moderate condition to obtain a more stable crystal form.

These results clearly showed there existed a correlation between the stability of the sPS crystal forms and the solubility parameter of the media for their formation, and suggested that the chemical resistance of sPS could be enhanced by treating it in different media having different solubility parameters.

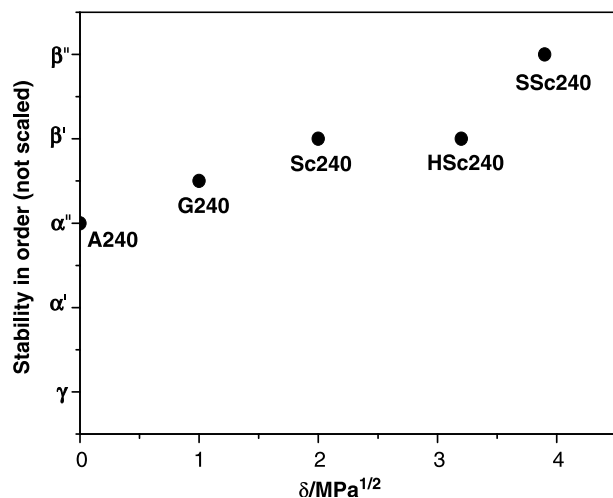


Fig. 7. A correlation of stability of sPS crystal forms with the solubility parameter of the media, in which these forms were produced at 240 °C for 1 h.

Therefore, whatever the mechanism was, the supercritical fluid treatment provided a new route to forming the  $\beta$  form sPS, which has better mechanical properties and solvent resistance [24,47].

#### 4. Conclusions

In the present paper, the starting  $\gamma$  form of sPS was treated in different media having different solubility parameters by adjusting the temperature, pressure and cosolvent of supercritical CO<sub>2</sub>. WAXD, FTIR and DSC results consistently showed that depending upon the solubility parameters the media had, the  $\gamma$  form transformed into different crystal forms with different crystal stability. A correlation was found between the solubility parameter of the media and the stability of the resultant sPS crystal forms. The higher solubility parameter the media had, the more ordered and stable crystal forms were obtained.

#### Acknowledgements

This work was supported by the National Natural Science Foundation of China (Grant 20274056). Thanks to Dr Jun Zhang for his useful discussion.

#### References

- [1] Desai AB, Wilkes GL. *J Polym Sci, Polym Symp* 1974;46:291.
- [2] Durning CJ, Russel WB. *Polymer* 1985;26:113.
- [3] Im SS, Lee HY. *J Appl Polym Sci* 1989;37:1801.
- [4] Stejny J, Whitfield AF, Pritchard GM, Hill MJ. *Polymer* 1998;39:4175.
- [5] Tomasko DL, Li HB, Liu DH, Han XM, Wingert MJ, Lee LJ, et al. *Ind Eng Chem Res* 2003;42:6431.
- [6] Handa YP, Capowski S, O'Neill M. *Thermochim Acta* 1993;226:177.
- [7] Ishihara N, Seimiya T, Kuramoto M, Uoi M. *Macromolecules* 1986;19:2464.
- [8] Guerra G, Vitagliano VM, De Rosa C, Petraccone V, Corradini P. *Macromolecules* 1990;23:539.
- [9] De Rosa C, Rapaciucolo M, Guerra G, Petraccone V, Corradini P. *Polymer* 1992;33:1423.
- [10] Auriemma F, Petraccone V, Dal Poggetto F, De Rosa C, Guerra G, Manfredi C, et al. *Macromolecules* 1993;26:3772.
- [11] Lin RH, Woo EM. *Polymer* 2000;41:121.
- [12] Sun YS, Woo EM, Wu MC, Ho RM. *Polymer* 2003;44:5293.
- [13] Gowd EB, Nair SS, Ramesh C. *Macromolecules* 2003;36:7388.
- [14] Wu SC, Chang FC. *Polymer* 2004;45:733.
- [15] Woo EM, Sun YS, Lee ML. *Polymer* 1999;40:4425.
- [16] Sun YS, Woo EM. *Polymer* 2001;42:2241.
- [17] Sun YS, Woo EM. *Macromolecules* 1999;32:7836.
- [18] Sun YS, Woo EM. *J Polym Sci, Part B: Polym Phys* 2002;40:176.
- [19] Bu WS, Li YY, He JS, Zeng JJ. *Macromolecules* 1999;32:7224.
- [20] Li YY, He JS, Qiang W, Hu X. *Polymer* 2002;43:2489.
- [21] Rastogi S, Goossens JGP, Lemstra PJ. *Macromolecules* 1998;31:2983.
- [22] Immirzi A, de Candia F, Iannelli P, Zambelli A. *Makromol Chem Rapid Commun* 1988;9:761.
- [23] Vittoria V, de Candia F, Iannelli P, Immirzi A. *Makromol Chem Rapid Commun* 1988;9:765.
- [24] Kellar EJC, Galiotis C, Andrews EH. *Macromolecules* 1996;29:3515.
- [25] Handa YP, Zhang ZY, Wong B. *Macromolecules* 1997;30:8499.
- [26] Naddeo C, Guadagno L, Acierno D, Vittoria V. *Macromol Symp* 1999;138:209.
- [27] Li YY, He JS. *Chin J Polym Sci* 2002;20:191.

- [28] Ma WM, Yu J, He JS. *Macromolecules* 2004;37:6912.
- [29] Ma WM, Yu J, He JS. *Macromolecules* 2005;38:4755.
- [30] Liao X, He JS, Yu J. *Polymer* 2005;46:5789.
- [31] Handa YP, Roovers J, Wang F. *Macromolecules* 1994;27:5511.
- [32] Pang TH, McLaughlin E. *Ind Eng Chem Process Des Dev* 1985;24:1027.
- [33] Tomohiro M, Norio S, Masahiko M, Yoshiyuki S, Hirokatsu M. *Macromolecules* 2001;34:1291.
- [34] Saucéau M, Letourneau JJ, Freiss B, Richon D, Fages J. *J Supercritical Fluids* 2004;31:133.
- [35] Handa YP, Zhang ZY, Roovers J. *J Polym Sci, Part B* 2001;39:1505.
- [36] Liao X, Li G, Sun XH, He JS. *Acta Chim Sinica* 2003;61:1697.
- [37] Ma WM, Yu J, He JS. *Macromol Rapid Comm* 2005;26:112.
- [38] Kellar EJC, Evans AM, Knowles J, Galiotis C, Andrews EH. *Macromolecules* 1997;30:2400.
- [39] Woo EM, Sun YS, Yang CP. *Prog Polym Sci* 2001;26:945.
- [40] Wang C, Chen CC, Hung CH, Lin KS. *Polymer* 2004;45:6681.
- [41] Zhang ZY, Handa YP. *Macromolecules* 1997;30:8505.
- [42] Barton AFM. *CRC handbook of solubility parameters and other cohesion parameters*. 2nd ed. Boca Raton: CRC Press; 1991.
- [43] De Candia F, Carotenuto M, Guadagno L, Vittoria V. *J Macromol Sci, Phys* 1996;B35:265.
- [44] Condo PD, Sanchez IC, Panayiotou CG, Johnston KP. *Macromolecules* 1992;25:6119.
- [45] Reid RC, Prausnitz JM, Sherwood TK. *The properties of gases and liquids*. 3rd ed. New York: McGraw-Hill; 1977.
- [46] Ho RM, Lin CP, Tsai HY, Woo EM. *Macromolecules* 2000;33:6517.
- [47] De Candia F, Romano G, Russo R, Vittoria V. *Colloid Polym Sci* 1990; 268:720.