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Process analysis of phase transformation of α to β-form crystal of syndiotactic polystyrene investigated in supercritical CO_2

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Abstract

Mechanism of solid phase transformation of α to β form crystal of syndiotactic polystyrene (sPS) was investigated in supercritical CO_2. The phase transformation occurred in the original pure α and mixed (α+β) form sPS in supercritical CO_2 was traced as a function of temperature and pressure by means of wide angle X-ray diffraction (WAXD), differential scanning calorimetry (DSC). At appropriate temperature and pressure, sPS underwent solid phase transitions from α to β form. Higher temperature or higher pressure favored this transformation. Compared to the original pure α form sample, the original β form crystal in the mixed (α+β) form sample acted as the nucleus of β form crystal, so that reduced the transition temperature and pressure.

Keywords: Solid phase transition; Syndiotactic polystyrene; Supercritical CO_2

1. Introduction

Since its successful synthesis by using stereo-specific polymerization in the mid-1980s [1], syndiotactic polystyrene (sPS) has received considerable attention as a potential engineering plastic, due to its high melting temperature, fast crystallization rate, low dielectric constant and good chemical resistance [2,3]. Particular interest is its very complex polymorphism [4–8]. Depending on thermal history and/or solvent treatment, four types of crystal forms, α, β, γ, and δ can exist. The γ and δ forms, characterized by the chains in the s(2/1)2 helical conformation with an identity period of 0.78 nm, are thermally unstable [9,10]. The most stable α and β forms, characterized by chains in the all-*trans* planar zigzag conformation with an identity period of 0.51 nm [2,11], are commonly obtained by thermal crystallization procedure.

Normally, the formation of α and β forms is depending upon thermal histories and crystallization conditions, such as maximum melting temperature, melting time, cooling rate, crystallization temperature, crystallization time, and so on [7,12–18]. It was found that crystallization of sPS from melt state produces different fractions of α and β forms. The α form is obtained by cooling the molten sample to room temperature at relatively high rate, while the β form by cooling at lower rate. In addition, the melt crystallization process favors β form at temperatures above 230 °C, while the α form at temperatures below 230 °C [13,14,16,18–21]. On the other hand, works have been done on the cold crystallization of sPS from glassy state [7,12,20–22]. The cold crystallization process produces only α form crystal under most conditions [7,20–22], while mixed (α+β) form is obtained, where the β form was transformed from the α form at a high temperature (264 °C) [12]. These results have indicated that the α form is kinetically favorable, while the β form is thermodynamically stable [7,15–19,21,23]. The α form can transform into β form during isothermal crystallization from melt state [16,24] or glassy state [12].

The conditions to obtain α and β form, and the transformation between α and β form is more concerned with practical applications, since it is directly related to the final properties of sPS products [3]. The α form crystal, as well as γ form and amorphous sPS, will transform into δ form crystal by treatment with suitable solvents, whereas this transition never occurs in the β form crystal [25–27].

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Supercritical carbon dioxide (CO_2) has shown great advantages in promoting crystallization of polymers over conventional organic solvents. Supercritical CO_2 has liquid-like densities and solvent strength, and gas-like viscosities and diffusion rate. The solvent strength of supercritical CO_2 can be tuned over a wide range through small changes in temperature, pressure, or both in the vicinity of the critical point ($T_c = 31.1$ °C, $P_c = 7.38$ MPa), resulting in adjustable degree of polymer swelling. After experiment the fluid is easily removed from the polymer matrix by simply depressurizing the system. Moreover, carbon dioxide is nontoxic, nonflammable, nonexplosive, relatively inexpensive, and environmentally benign.

Although supercritical CO_2 is a weak solvent for polymers except of some fluoropolymers and silicones [28], it has substantial solubility in many polymers. The absorbed CO_2 decreases the glass transition temperature (T_g) of polymer because of an increase in the free volume fraction. This facilitates the motion of polymer chains in amorphous region and reorganizes them into the more thermodynamically stable crystalline state at lower temperature. Supercritical or compressed CO_2 can induce and promote the crystallization in the crystal growth controlled temperature region [29–40], and decreases the crystallization rate in the nucleation controlled temperature region in some polymer systems [41,42]. Not only the crystallization process of polymers from melt and glassy state, but also the phase transition between different crystal forms is influenced in the presence of high pressure CO_2. Up to now, most the works about phase transition under CO_2 are proceed in sPS system [34,43,44]. However, the relationship between the effect of the existing β form and the phase transformation has not been investigated in supercritical CO_2, even though most of the factors controlling the crystallization of α and β forms at ambient pressure have been clarified.

In the present paper, we systematically investigated the phase transition behaviors from the α form to β form by thermal treatment under supercritical CO_2, and the effect of initial crystal form on the transformation. In order to reach this goal, samples with different initial crystal forms, namely the pure α and mixed (α+β) crystal sPS, were treated at various temperatures and pressures, and characterized with WAXD and DSC to clarify the transition process.

2. Experimental section

2.1. Materials

Syndiotactic polystyrene ($M_w = 2.1 \times 10^5$, $M_w/M_n = 2.2$) used in the present study was kindly supplied by Dow Chemicals with its stereo-regularity about 99%. CO_2 with a purity of 99.95% was supplied by Beijing Analytical Gas Factory, China.

2.2. Sample preparation

Samples of pure α form were prepared by pressing sPS pellets under 20 MPa and 280 °C for 5 min into sheets of thickness about 0.8 mm, then rapidly quenching in cold water. Samples of mixed (α+β) form were obtained with similar procedure, by using compression temperature of 320 °C and slow cooling in the air. The sample sheets were then cut into pieces of proper sizes for various supercritical CO_2 treatments. The WAXD patterns confirmed the crystal forms of these samples.

2.3. Supercritical CO_2 treatments

A high-pressure apparatus was used for supercritical CO_2 treatment. The original pure α form and the mixed (α+β) form sPS samples were enclosed in the autoclave that had been preheated to the experimental temperature. The autoclave was flushed with low-pressure CO_2 for about 3 min, and then filled with more CO_2. Once the CO_2 pressure reached the desired value, the timing began.

2.4. Analysis

Differential scanning calorimetry (DSC) measurements were conducted with a Perkin–Elmer DSC-7 that had been calibrated with indium. sPS exhibits a multiple melting peaks in the DSC thermograms because of different crystal structures and/or re-crystallization during the DSC scan. A rapid heating rate, 80 °C/min, was found to minimize the re-crystallization [45]. Therefore, all the samples were scanned at 80 °C/min in a dry nitrogen atmosphere in this study in order to avoid the influence of re-crystallization during the DSC measurement on the melting behaviors of sPS. The total degree of absolute crystallinity of sPS samples, C_t, was calculated from the integration of melting peak of DSC and using 53.2 J/g [46] for the heat of fusion of 100% crystalline sPS, which was found to be suitable for both the α and β form sPS [47].

Wide angle X-ray diffraction (WAXD) patterns were measured with a Rigaku D/max 2500 diffractometer with Cu Kα radiation, operating at 40 kV and 300 mA at room temperature. The scanning 2θ angle ranged between 5 and 40° with a scanning rate of 4°/min. The diffraction peak positions and widths observed from WAXD experiments were carefully calibrated with silicon crystals with known crystal size. The percentage of the α form in the crystalline fraction, P_α, was evaluated by the method suggested by Guerra et al. [7]. The 2θ region of 10–15° was considered, and a base line between the two intensity minima located at $2\theta = 10.8$ and 14.8° was drawn. The P_α was obtained from the areas (A) of the two peaks located at $2\theta = 11.8$ and 12.3° and by the approximate relation:

$$P_\alpha = \frac{1.8A(11.8)/A(12.3)}{1 + [1.8A(11.8)/A(12.3)]} \times 100 \quad (1)$$

where 1.8 is the ratio between the intensities (measured under the same experimental conditions) of the peaks at 11.8 and 12.3° for samples of equal thickness and degree of crystallinity in the pure α and β forms, respectively. The contents of the α form, C_α, and the β form, C_β, in the samples were estimated from the C_t and the P_α.

3. Results and discussion

3.1. Effect of treatment temperature

3.1.1. From the original pure α form sPS

Fig. 1 shows the WAXD patterns of the samples by treating the original pure α form sPS ones in supercritical CO_2 at various temperatures at 20 MPa for 8 h, respectively, along with the original pure α form sample. The crystal form of original sample was confirmed by the presence of the diffraction peaks at $2\theta=6.8$ and 11.8°, typical of the α form, and the absence of the peaks at $2\theta=6.2$, 12.3 and 18.7°, typical of the β form. More exactly, the crystal form of the original sample was the α'' form, as indicated by the characteristic peaks at $2\theta=6.8$, 10.3, 11.7, 14.0, 15.6, 17.0 and 20.2°, with higher degree of crystal perfection [7]. The samples treated at lower temperatures of 140 and 200 °C exhibited the same patterns as the original one, indicating that only the α form was present. After the treatment at higher temperatures of 220, 240 and 260 °C, the appearance of the characteristic peaks of the β form revealed that a mixture of the α and β forms was obtained. With increasing treatment temperature, the amount of the β form in the crystalline phase increases and the α form decreases, respectively, as shown by the change of the intensity of diffraction peaks.

Table 1 shows the crystallinity C_t, calculated from DSC thermograms, and the content percentage of the α form, P_α, calculated from WAXD results, of the original pure α form and the samples treated in supercritical CO_2 at various temperatures at 20 MPa for 8 h, respectively. As shown in Table 1, the C_t of the sPS samples increases after thermal treatment in supercritical CO_2, and the increment levels off at the temperature above 200 °C. According to the WAXD results (Fig. 1), the increase of the degree of crystallinity at the temperatures below 200 °C is due to the crystallization of the amorphous phase into the α form, which is more favorable at 200 °C than at 140 °C. However, the new emerged β crystal of samples treated at higher temperatures may come from two originations: the crystallization of the amorphous sPS and the phase transition from the α form. It needs further analysis of the content of the α form and the β form in these samples.

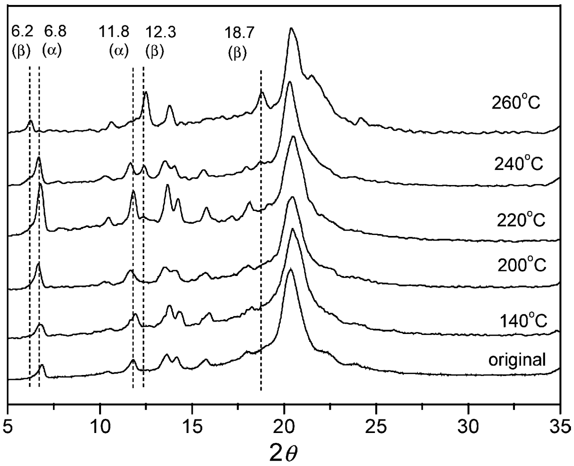

Fig. 1. X-ray diffraction patterns of the samples after treating the original pure α form sPS in supercritical CO_2 at 20 MPa for 8 h at different temperatures.

Table 1
Degree of crystallinity of the samples after treating the original pure α form sPS in supercritical CO_2 at different temperatures at 20 MPa for 8 h

Temperature (°C)	C_t	P_α (%)	C_α	C_β
Original	0.51	100	0.51	0
140	0.53	100	0.53	0
200	0.66	100	0.66	0
220	0.65	91	0.59	0.06
240	0.59	70	0.41	0.18
260	0.66	29	0.19	0.47

As shown in Table 1, both the C_α (0.59) and the C_β (0.06) in the sample treated at 220 °C are higher than those of the original sample (0.51 and 0), respectively. This result indicates that the β crystals were produced with the accompanying of the formation of new α crystals in supercritical CO_2 treatment at 20 MPa and 220 °C. Under ambient pressure, the cold crystallization of sPS only generated α form at temperatures up to 260 °C [20]. From the cold crystallization of sPS at 264 °C, Wu and Chang [12] found that β form was produced by transforming from the α form, not from the amorphous phase directly, which indicated that the phase transition from α form to β form could take place under this condition. From the point of kinetic, the crystallization of the α form, which is highly nucleated, has different nucleation mechanisms with that of the β form, which is homogeneous nucleation with a lower rate [17]. In addition, the α form has lower activation energy than the β form does from the thermodynamic point. Therefore, it is assumed that the amorphous phase crystallizes into α form preferentially because of the low energy barrier of nucleation, especially in the case of the initial α form available as the nuclei. In other words, the formation of β crystal was more possible from α form than from glassy state directly in this work. The analysis in details is still under investigation. Comparing with the result under ambient pressure, the transformation of α form into β form would occur at lower temperature, namely 220 °C, in the presence of 20 MPa supercritical CO_2.

On the other hand, Table 1 shows that the samples treated above 240 °C have C_α values lower than the original sample, although the C_t increases in the former. It means that partial amorphous fraction crystallized into α form and more α form transformed into β form, resulting in the decrease of the C_α. The increment of the C_β is higher than that of the C_t, which becomes more obvious at higher treatment temperature of 240 and 260 °C. The melting temperatures of semi-crystalline polymer would be reduced by the solubility of CO_2 in the polymer. Zhang and Handa [35] reported about 12 °C of depression in the melting temperature of sPS in the presence of high pressure CO_2 at 8 MPa. However, they also found that the depression tended to level off at the pressures beyond the critical pressure of CO_2 because of the anti-plasticization effect of hydrostatic pressure. Therefore, it can be inferred rationally that all the treatment temperatures used in this work are below the equilibrium melting temperature of sPS in the presence of supercritical CO_2 at 20 MPa, in consideration of the equilibrium melting temperature of the α form, 281.7 °C, and the β form, 288.7 °C under ambient pressure [17]. Consequently, the increasing of the C_β resulted from the solid–solid transition from the α form directly instead of the melt-crystallization process.

3.1.2. From the original mixed (α+β) form sPS

Fig. 2 shows the X-ray diffraction patterns of the samples by treating the original mixed (α+β) form sPS ones in supercritical CO_2 at various temperatures at 20 MPa for 8 h, respectively, along with the original mixed (α+β) form sample. For the sample annealed at 140 °C, the intensity of reflections of the α form ($2\theta=6.8$ and 11.8°) increases, indicating that the content of α form in the crystalline fraction increases. By further increasing temperature, the intensity of α form peaks gradually decreases and β form peaks increases, respectively. The degree of crystallinity of the original and the treated samples is shown in Table 2. It can be found that the samples treated in supercritical CO_2 have almost a constant C_t, which is higher than that of the original one, in the temperature range of 140–260 °C. The C_α (0.43) for the sample treated at 140 °C is higher than that of the original one, while the C_β keeps constant (0.19 vs. 0.17) within the error range. This means that the amorphous phase crystallized to the α form and α form did not transform further into β form. At 200 °C, the treated sample has the same C_α as the original one, while the C_β increases after treatment. It is suggested that those new crystals with β form were transformed from α form during supercritical CO_2 treatment of (α+β) sample at 200 °C. Meanwhile, same amount of α form was generated from amorphous phase. At higher temperature of 220, 240 and 260 °C, the C_α decreases after treatment although the C_t increases. However, the increase of the C_β is higher than that of the C_t, implying that there are more crystals with α form transforming into β form than those obtained from the crystallization of amorphous phase at these temperatures under 20 MPa. This transition behavior at higher temperatures is similar to that of the original α form sample. It can be concluded that the transformation of the α to β form took place at higher temperatures with the lower limit at least at 200 °C in the original (α+β) sample in the presence of supercritical CO_2 at 20 MPa.

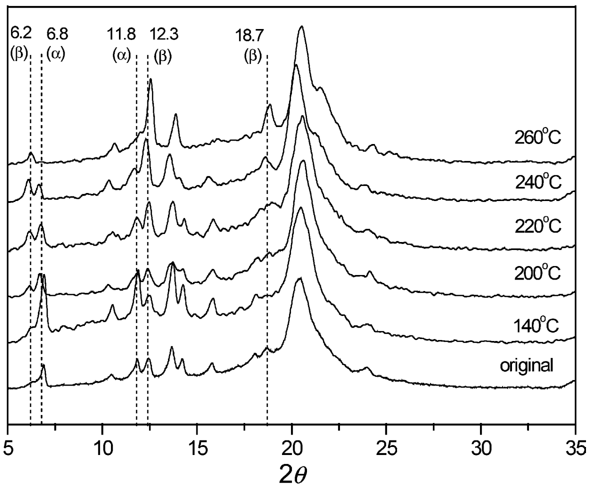

Fig. 2. X-ray diffraction patterns of the samples after treating the original mixed (α+β) forms sPS in supercritical CO_2 at 20 MPa for 8 h at different temperatures.

Table 2
Degree of crystallinity of the samples after treating the original mixed (α+β) form sPS in supercritical CO_2 at different temperatures at 20 MPa for 8 h

Temperature (°C)	C_t	P_α (%)	C_α	C_β
Original	0.54	65	0.35	0.19
140	0.60	72	0.43	0.17
200	0.62	58	0.36	0.26
220	0.58	50	0.29	0.29
240	0.64	41	0.26	0.38
260	0.60	24	0.14	0.46

The results presented above show that the α to β transition in the original mixed (α+β) form sample occurred in supercritical CO_2 at 20 MPa and 200 °C, which was 20 °C lower than that in the original pure α sample. Both temperatures were lower than the temperature of 264 °C, where the α to β transition was reported during cold crystallization of sPS [12]. This indicates that the supercritical CO_2 facilitated the transition of α form to β form, and the existing β form crystals in the original mixed (α+β) form sample acted as the nucleus of β form crystal, so as to induce the transition at lower temperatures.

3.2. Effect of treatment pressure

The effects of pressure on the crystal transition behavior of sPS were verified by treating the original pure α form and mixed (α+β) form samples in the presence of supercritical CO_2 at 200 °C and different pressures. Fig. 3 shows the X-ray diffraction patterns of the samples by treating the original pure α form ones at 8, 12, 20 and 28 MPa for 8 h,

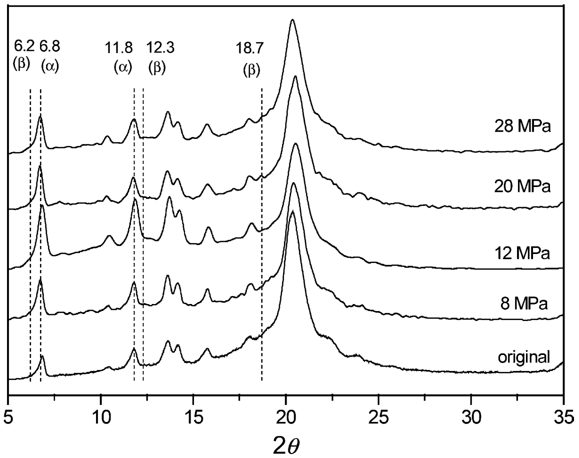

Fig. 3. X-ray diffraction patterns of the samples after treating the original pure α form sPS in supercritical CO_2 at 200 °C for 8 h at different pressures.

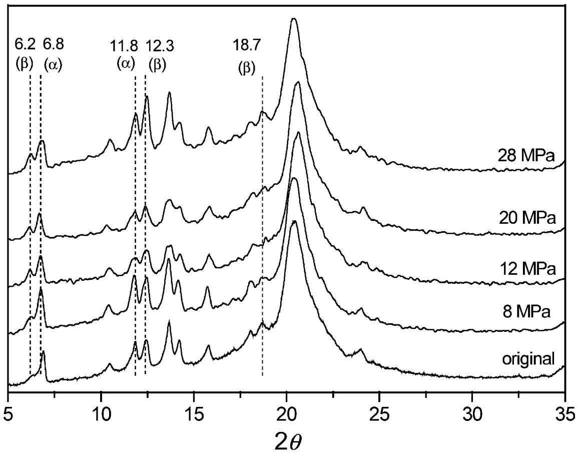

Fig. 4. X-ray diffraction patterns of the samples after treating the original mixed (α+β) forms sPS in supercritical CO_2 at 200 °C for 8 h at different pressures.

respectively. All these samples, even the one treated under 28 MPa at 200 °C, are absent of β form crystal, as indicated by the absence of peaks of the β form. Table 3 summarizes the degree of crystallinity of treated samples obtained from DSC. It shows that the C_t of samples increases after the treatment in supercritical CO_2, due to the crystallization of the amorphous phase into the α form. However, the degree of crystallinity of treated sPS is almost the same and independent of the pressure, indicating that supercritical CO_2 with higher pressure does not influence the final degree of crystallinity of the original α form sPS treated at 200 °C thermodynamically, although it may accelerate the crystallization process from the view of kinetics [40]. On the other hand, the β form was formed at 220 °C under 20 MPa (Table 1), while absent at 200 °C under a higher pressure of 28 MPa as mentioned above. It means that just increasing the pressure was insufficient to induce the solid phase transition from α form to β form below a certain temperature.

Fig. 4 shows the X-ray diffraction patterns of the samples obtained by treating the original mixed (α+β) form sample with supercritical CO_2 at various pressures at 200 °C for 8 h. At the lower pressure of 8 MPa, the P_α is higher than that of the original sample, as indicated by the increase in the intensity of diffractions at $2\theta=6.8$ and 11.8°. With increasing pressure, the intensities of α form and β form peaks decrease and increase gradually, respectively. From Table 4, it can be found that the C_t and the C_α of the sample treated at 8 MPa are higher than those of the original sample, while the C_β keeps constant. This result indicates that only the crystallization of amorphous fraction to α form occurred under this condition, and no new β form crystals were produced. At 12 MPa, the C_β of treated sample increases because of the production of new β form crystals. By further increasing the pressure, the amount of the α form transformed to the β form increases, resulting in the decrease of the P_α and C_α. Therefore, it would be required to exceed a certain pressure to induce the transition. At this moment, the chains mobility is high enough to overcome the energy barrier, because the absorption of CO_2 exerting the plasticization effect increases with increasing the CO_2 pressure. As for the original mixed (α+β) form sample, the α to β form solid phase transition pressure occurs at 12 MPa and 200 °C in the presence of supercritical CO_2 (Table 2). It can be inferred that the existing β form in the original mixed (α+β) sample accounts for the different influence of pressure on the original α form sample kinetically, where the α to β form transition had too high energy barrier to take place even at 28 MPa and 200 °C.

The results presented above show that both the treatment temperature and pressure are important in the phase transition of sPS. In other words, there is a minimum pressure at a given treatment temperature and a minimum temperature at a given pressure, respectively. The transition would not occur at lower temperature by just raising the pressure, and vice versa. For example, in the original pure α sample, the β form could not be obtained at 200 °C by increasing CO_2 pressure up to 28 MPa.

Combined with the results of α to β form solid phase transition in the original pure α sample and mixed (α+β) sample treated in the presence of supercritical CO_2 at 200 °C from 8 to 28 MPa, it can be concluded that the amorphous phase of sPS transformed to α form at first, then the new

Table 3
Degree of crystallinity of the samples after treating the original pure α form crystal sPS in supercritical CO_2 at different pressures at 200 °C for 8 h

Sample	Pressure (MPa)				
	Original	8	12	20	28
C_t	0.51	0.67	0.64	0.66	0.67

Table 4
Degree of crystallinity of the samples after treating the original mixed ($\alpha+\beta$) form sPS in supercritical CO_2 at different pressures at 200 °C for 8 h

Pressure (MPa)	C_t	P_α (%)	C_α	C_β
Original	0.54	65	0.36	0.18
8	0.59	67	0.40	0.19
12	0.56	59	0.33	0.23
20	0.62	58	0.36	0.26
28	0.53	55	0.29	0.24

crystals of β form were generated by transforming the α form. And the available β crystals in the original sample acted as the β form crystal nuclei to facilitate the production of new β crystals and the transition from the α to β form, consequently reducing the solid phase transition temperature and pressure.

3.3. Melting behavior of sPS

In order to prevent the influence of re-crystallization during the DSC measurement on the melting behaviors of sPS, all the samples were scanned at a rapid heating rate of 80 °C/min under the dry nitrogen environment. Based on the calculation by Wunderlich [48], under a heating rate of 100 °C/min, the temperature difference between the center and the outside of a sample with a diameter of 0.8 mm is only 0.65 °C. Therefore, it is reasonable to perform the thermal analysis using a heating rate of 80 °C/min for our samples.

Fig. 5 shows the melting endotherms corresponding to the samples shown in Fig. 1. The sample treated at 140 °C exhibits a similar melting behavior as that of original sample with a melting peak around 277 °C. With increasing treatment temperature to 200 °C, the sample exhibits a broad melting peak superimposing a minor shoulder endothermic at the lower temperature side, which is attributed to the melting of new crystals of α form by combining with the results of X-ray diffraction. The lower peak temperature means the less order or tiny size of new crystals. For the sample treated at 220 °C, a shoulder endothermic peak appears at the higher temperature side of the main melting peak. It could be related to the perfection of α crystals during thermal treatment because higher temperatures favor the formation of more stable crystal, which is in agreement with the cold crystallization of sPS [20,21]. The melting peak of minor β form (6%) was overlapped with the broad endotherm of α crystals. For the sample treated at 240 °C, the DSC scan shows the intensity of the peak at higher temperature side increased and the peak at lower temperature side became a small shoulder. The former is associated with the α crystals after perfecting during supercritical CO_2 treatment, while the latter is due to the melting of the β form. At the treatment temperature of 260 °C, only one melting peak at 272 °C is shown, which belongs to the β crystal. The melting of residual α crystals is overlapped with that of β crystal because the crystals in the β form dominated the crystalline fraction of sample from the result of WAXD (Table 1).

Fig. 6 shows the melting endotherms corresponding to the samples shown in Fig. 2. The original mixed ($\alpha+\beta$) sample has a lower melting peak, around 272 °C, than the original pure α form sample because of the overlap with the lower melting peak of the β form. As the treatment temperature increased from 140 to 220 °C, the peak shifts to higher temperature with an increasing breadth. At 240 °C, the shoulder peak is exhibited obviously at the lower temperature side of the main peak. The DSC thermogram of original mixed ($\alpha+\beta$) sample treated at 260 °C is similar to that met with the original pure α sample treated at 260 °C, i.e. only a narrow peak at 271 °C attributed to the β crystal.

Because the re-crystallization has been inhibited during the DSC scanning with a high heating rate, the endotherm peaks shown reflect the same crystallite state of the treated samples as those used for WAXD experiments. Therefore, above analyses based on the DSC measurements are

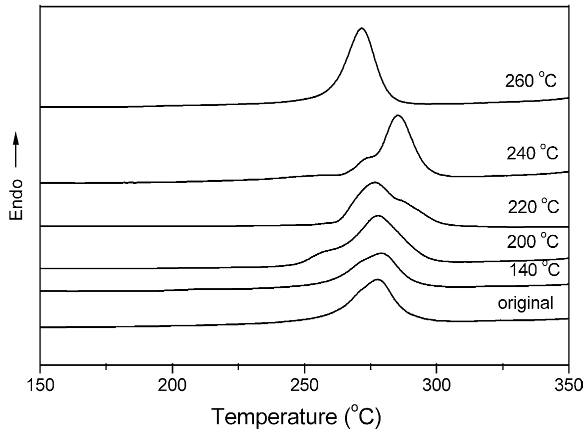

Fig. 5. Melting behavior of the samples after treating the original pure α form sPS in supercritical CO_2 at 20 MPa for 8 h at different temperatures.

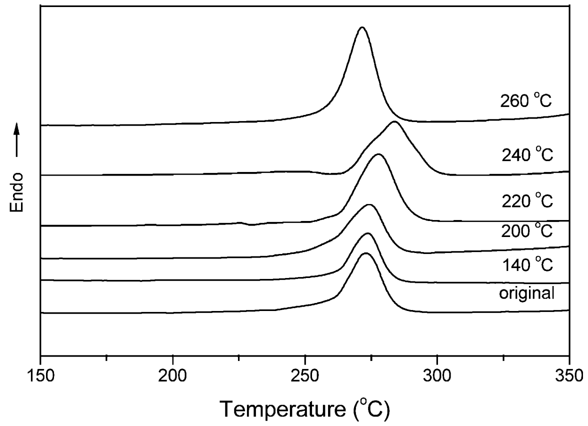

Fig. 6. Melting behavior of the samples after treating the original mixed ($\alpha+\beta$) forms sPS in supercritical CO_2 at 20 MPa for 8 h at different temperatures.

consistent with the WAXD results, further confirming the solid phase transition from the α form to the β form.

3.4. Solid phase transition in supercritical CO_2

In order to further illustrate the process of solid phase transition in the original pure α form and the mixed (α+β) form sPS in supercritical CO_2, the equilibrium crystallinity of α form and β form was drawn against the treatment temperature at 20 MPa, shown in Fig. 7. In this plot, the C_α and C_β after 1 h cold crystallization of sPS at 264 °C under ambient pressure, obtained from Ref. [12], are marked with solid and hollow asterisk, respectively. It can be found from Fig. 7 that the α form in the two groups of systems dominates at lower temperature, and the C_α begins to decrease above a certain temperature. Meanwhile, the C_β increases to compensate for the decrease of the C_α at the temperature of 220 °C for the original pure α form and 200 °C for the mixed (α+β) form sample, respectively. The differences of both the C_α and C_β between these two groups are reduced with increasing temperature. At 260 °C, the samples treated from the original pure α form and the mixed (α+β) form have similar C_α and C_β values, respectively. It is well known that the α form sPS is kinetically favorable, while the β form sPS is thermodynamically stable during normal thermal processing under ambient pressure. This feature should also be true in the presence of supercritical CO_2, due to the formation of new α form crystals at low temperatures and the increased C_β with increasing temperature. Moreover, the β form generated at lower temperatures from the original pure α form sample, and even lower temperatures from the original mixed (α+β) form sample than those in cold crystallization under ambient pressure. There are probable two main reasons: the plasticization effect of supercritical CO_2 and the depression of equilibrium melting temperature. Both favor the crystal growth for the isothermal treatment, hence promoting the formation of the β form at low temperature. Moreover, the temperature for the formation of the β form crystal decreases further, resulted from the nucleation effect of the initial β form in the original mixed (α+β) samples. At 260 °C, the polymer chains in both groups of samples have enough mobility to overcome the energy barrier during the treatment in supercritical CO_2. Therefore, the final state of treated samples is independent of the crystal forms of the original samples.

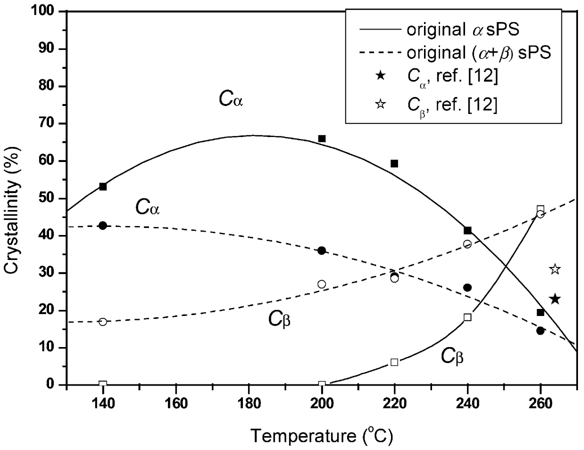

Fig. 7. The degree of crystallinity of the α form and the β form in the samples after treating the original pure α form and the mixed (α+β) forms sPS, respectively, in supercritical CO_2 at 20 MPa for 8 h.

During cold crystallization, sPS crystallizes from a solid state, where the polymer chains have higher rigidity, less flexibility, and thus less randomness than in the molten state. It has been found that melt crystallization is packed by both α and β crystal forms of various fractions depending on the crystallization conditions [18], while cold-crystallized sPS only has α crystal form whereas the packing of β form is inhibited at most temperatures [21]. But at appropriated temperature and pressure, sPS in supercritical CO_2 underwent the transformation of α form to β form. It indicated that the sorption of CO_2 lead to the increase of free volume and chains mobility, which would provide the similar relaxation time of sPS chains as it crystallized from molten state with slow cooling. This plasticization effect also resulted in decreased energy barriers of phase transition. Higher temperatures and pressures help to overcome the energy barrier of phase transition, so as to facilitate the transformation of α form to β form sPS. In addition as the final one, the initial β form crystals in the original mixed (α+β) form sample had nucleating effect, so that new β crystals were produced at a lower temperature (200 °C) in supercritical CO_2 at 20 MPa for 8 h.

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