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Stability of form II of syndiotactic polypropylene confirmed by cold and melt crystallization in supercritical carbon dioxide

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Abstract

The form II of syndiotactic polypropylene (sPP) has been found more thermodynamically stable than form I when melt crystallized at pressures above 150 MPa, while the reverse occurs below 150 MPa. In the present study, through the cold and melt crystallization in supercritical CO_2 the stability of various polymorphic forms of sPP, especially form II, was confirmed by using Fourier-transform infrared spectroscopy and wide-angle X-ray diffraction. Compared with the formation of pure form I at high temperatures under ambient condition, a mixture of forms I and II was formed by both the cold and melt crystallization in supercritical CO_2. This atmosphere changed the relative stability of forms I and II, and made the form II more thermodynamically stable than form I. The increased solubility parameters of the surroundings, at which the form II was formed, also confirmed the stability of form II over form I in supercritical CO_2. The incubation pressure was the key factor affecting the formation and amount of form II. Supercritical CO_2 provides a combining severe condition to obtain the form II crystal, although its pressure was much lower than the elevated pressures (>150 MPa) reported before.

Keywords: Crystal stability; Syndiotactic polypropylene; Supercritical carbon dioxide

1. Introduction

Syndiotactic polypropylene (sPP) has attracted considerable interest since the successful synthesis of highly stereoregular sPP by using new metallocene catalysis in recent years [1]. It processes a complex polymorphism in its crystalline region involving four crystalline forms [2–9]. Forms I and II present chains in the s(2/1)2 helical conformations [2,3,8,10], whereas forms III and IV present chains in *trans*-planar and $(T_6G_2T_2G_2)_n$ conformations [11,12], respectively. Briefly, form I is the most stable form of sPP, which is obtained under the common conditions of crystallization both from the melt and the solution as single crystals [3,5,13]. The crystalline form II, on the other hand, is the metastable form obtained by stretching sPP samples of low stereoregularity, or by removing the tension in the *trans*-planar form III stretched from highly stereoregular sPP samples [8,14–20]. Furthermore, crystallization at elevated pressure also gives the form II [21]. Form II can also be obtained by annealing relaxed fibers of sPP or by solvent induced crystallization of unoriented samples initially in the *trans*-planar conformation [18,22]. Forms III and IV are also metastable phases of sPP. Form III is obtained by cold drawing of the samples quenched from the melt into an ice bath [8,13–17,23–26]. It is reported that form III can also be obtained by spontaneous crystallization at 0 °C of highly stereoregular sPP [27–30]. Finally, form IV is obtained by exposing samples of form III to certain solvent [12].

Since sPP presents complex polymorphism, the crystal transition behavior between various forms of sPP was investigated in detail. It was found that the relative stability of involved polymorphic forms can be changed by treating sPP samples under different conditions. These conditions include annealing [9,16,20,22,29,30], strain [17,18,20,23,26,31,32],

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elevated pressure [21], solvent [33] and UV irradiation [34]. Each of the parameters involved strongly influences the final crystallization behavior of sPP. The stability of different polymorphic forms with the degree of deformation was discussed in detail by De Rosa et al. [35]. Rastogi et al. [21] found that the relative stability between forms I and II changed when the sPP sample melt crystallized at high pressures. It appears that the chains in the helical form I are more stable than the chains in the helical form II, which has been verified under ambient conditions [2–9]. However, when treated at high pressures above 1.5 kbar (150 MPa), the form II was obtained, which was confirmed by the appearance of (110) reflection at 5.2 Å [21]. Compared with the formation of ordered form I below 150 MPa, it was suggested that form II was thermodynamically more stable than form I above 150 MPa. Thus resultant crystals in form II had a higher melting point than the crystals in form I at elevated pressures [21]. Obviously, the treatment condition of elevated pressure changed the stability of crystal forms I and II. It is known that the finally obtained crystal form for samples treated under certain condition was determined by the relative stability of various crystal forms under this condition. Therefore, the change of stability of various polymorphic sPP forms under various conditions, especially extreme conditions, is of great interest to be investigated. On the other hand, it is well known that supercritical CO_2 is a fluid working at a temperature and a pressure higher than its critical point ($T_c = 31.1\ ^\circ C$, $P_c = 7.37$ MPa) with certain solvent strength [36]. Since the treatment condition of thermal, elevated pressure and solvent surroundings all affects the polymorphism behavior of sPP, therefore, supercritical CO_2 exhibiting these features provides a combining condition to investigate the complex polymorphism of sPP and also the relative stability of various crystal forms.

In the present study, the initial form was obtained by molding sPP at 170 °C, followed by quickly quenching it in ice water and keeping it for 144 h. Then the initial sPP form was cold and melt crystallized in supercritical CO_2, respectively. Through the study on these crystallization behaviors of sPP, the stability of various crystal forms, especially form II, was confirmed. For comparison, the ambient condition was also chosen to treat initial sPP samples. The result was also compared with that at elevated pressures reported by Rastogi et al. [21]. WAXD and FTIR were used to identify the crystal form of sPP obtained under different conditions.

2. Experimental section

2.1. Materials and sample preparation

Syndiotactic polypropylene was kindly supplied by Atofina Company with its stereoregularity of [rrrr] 81% and [rr] 89% determined by ^{13}C NMR spectroscopy at 100 °C on a Bruker AM-300 FT-NMR spectrometer. The average molecular weight (M_w) is 8.6×10^4 and the polydispersity (M_w/M_n) is 4.1. The sPP film of 0.1 mm thick was molded in a hot press at 170 °C, followed by quenching in ice water and subsequently isothermal crystallization at 0 °C for 144 h.

2.2. Sample treatments

A high-pressure apparatus was used for the treatment in supercritical CO_2. As to cold crystallization, the original sPP samples were loaded into a 25 ml high-pressure vessel which was then flushed with low pressure CO_2 for about 2 min. After the treatment of sPP samples at the desired temperature and pressure for a certain time, the vessel was quenched to room temperature and depressurized slowly. As to melt crystallization, in supercritical carbon dioxide of a certain pressure the original sample was melted at 180 °C and kept for 1 h at this temperature, then rapidly cooled to the crystallization temperature (T_c) and kept at this temperature for 7 h to ensure complete crystallization, still in supercritical carbon dioxide of the same pressure. Isothermal crystallization from the melt and cold crystallization under ambient condition was conducted in the same procedure but without the presence of supercritical carbon dioxide.

2.3. Measurements

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.

FTIR measurements were carried out on Perkin–Elmer System 2000 FTIR in the standard wave number range of $370–4000\ cm^{-1}$ for the investigations of chain conformations and crystalline forms in sPP. Curve fitting of the spectra was conducted using the software package 'Peakfit V4.12' for the deconvoluted spectra with a mixed Gaussian–Lorenzian function in the form:

$$f(x) = (1-L)H\exp - \left[\left(\frac{x-x_0}{w}\right)^2 (4\ln 2)\right] + L\frac{H}{4\left(\frac{x-x_0}{w}\right)^2+1}$$

where x_0 is the peak position, H is the height, w is the width at half-height, and L is the Lorenzian component.

3. Results and discussion

3.1. Crystalline polymorphs and conformation structures of original sample

The original sample was obtained by molding sPP at 170 °C, followed by quickly quenching in ice water and keeping it for 144 h. The WAXD pattern of as-prepared original sPP sample is shown in Fig. 1a. It shows the typical reflection peaks at $2\theta = 12.3$, 16.0, and 20.3°. These peak positions correspond to 200, 020 and 121 diffraction planes of form I with helical conformation [20]. At the same time, the absence of 211 reflection peak at $2\theta = 18.9°$ indicates that the as-prepared original sPP sample was the disordered modification of form I [13]. As also shown in the WAXD pattern of the initial sample, a broad peak centered at about $2\theta = 17°$ appeared, which indicates the existence of another crystal form. It is known that the peak at $2\theta = 17°$ appears both in form II and in *trans*-planar

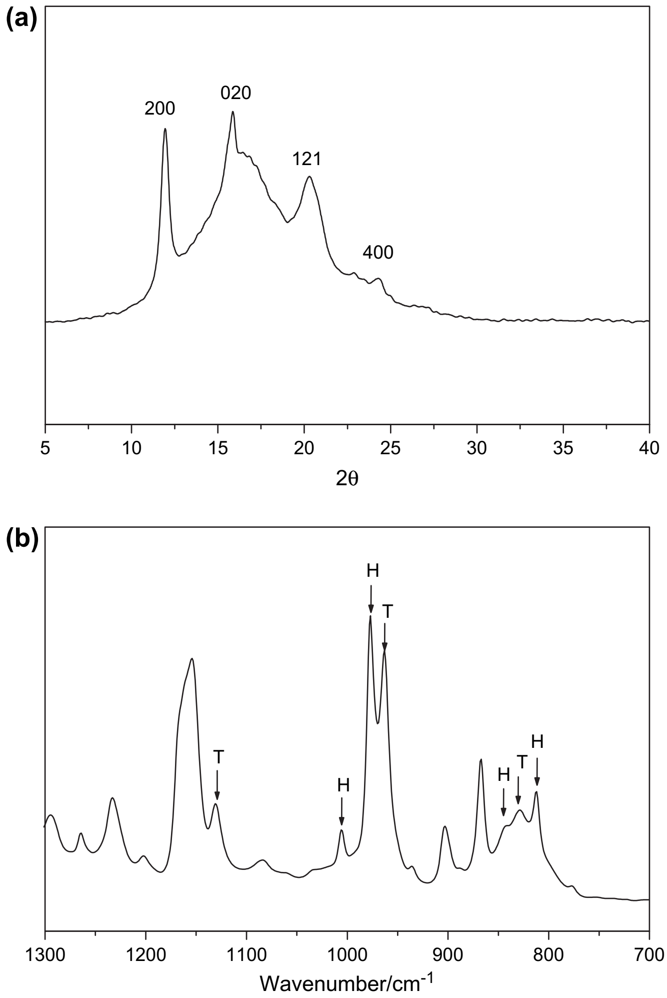

Fig. 1. WAXD patterns (a) and FTIR spectra (b) of the original sample, where the arrows indicate the helical conformation (H) and the *trans*-planar mesophase (T).

mesophase. To further clarify the attribution of this peak, the FTIR pattern of the original sample is also shown in Fig. 1b. It is observed that in the original sample, the bands of the helical conformation of sPP appear at 810, 843, 868, 977 and 1005 cm^{-1}, indicating the obtained helical conformation [24,27,37]. As also shown in the figure, the evident bands at 831, 963 and 1132 cm^{-1} appear, indicating the existence of *trans*-planar mesophase [24,27,37]. Therefore, considering the above assignments of the infrared active bands and WAXD patterns, it is concluded that the original sample was a mixture of form I and *trans*-planar mesophase.

It has been shown that the *trans*-planar mesophase could be formed by keeping the sample at 0 °C for a long time [27–30]. However, in our experiments the most obtained original form was that of form I with helical conformation. The low stereoregularity (81%) of sPP was responsible for this phenomenon. It is well known that the crystallization of the mesomorphic form depends on the degree of stereoregularity of the sPP sample [38]. The helical conformation was easily obtained because of the defects existing in sPP samples having low stereoregularity [31]. Therefore, quenching the sPP melt at 0 °C allowed the prevalent crystallization of form I with helical conformation, but also developed a small amount of *trans*-planar mesophase. Thus the obtained sample was used as an initial form to investigate its cold and melt crystallization behaviors in supercritical CO_2 in this paper.

3.2. Cold crystallization in supercritical CO_2

Fig. 2a shows the FTIR spectra of the original sPP samples cold crystallized in supercritical CO_2 of 12 MPa for 7 h at the temperatures indicated. As shown in this figure, the intensity of bands at 831, 963 and 1132 cm^{-1}, assigned to the *trans*-planar mesophase conformation, decreases after the treatment at 35 °C; and the intensity of bands at 810, 843, 868, 977 and 1005 cm^{-1}, assigned to the helical conformation, increases. These clearly indicate that the *trans*-planar mesophase transformed into the helical conformation after treating at 35 °C in supercritical CO_2 of 12 MPa. Upon further increase of the cold crystallization temperature, the intensity of the bands attributed to the *trans*-planar mesophase continues to decrease,

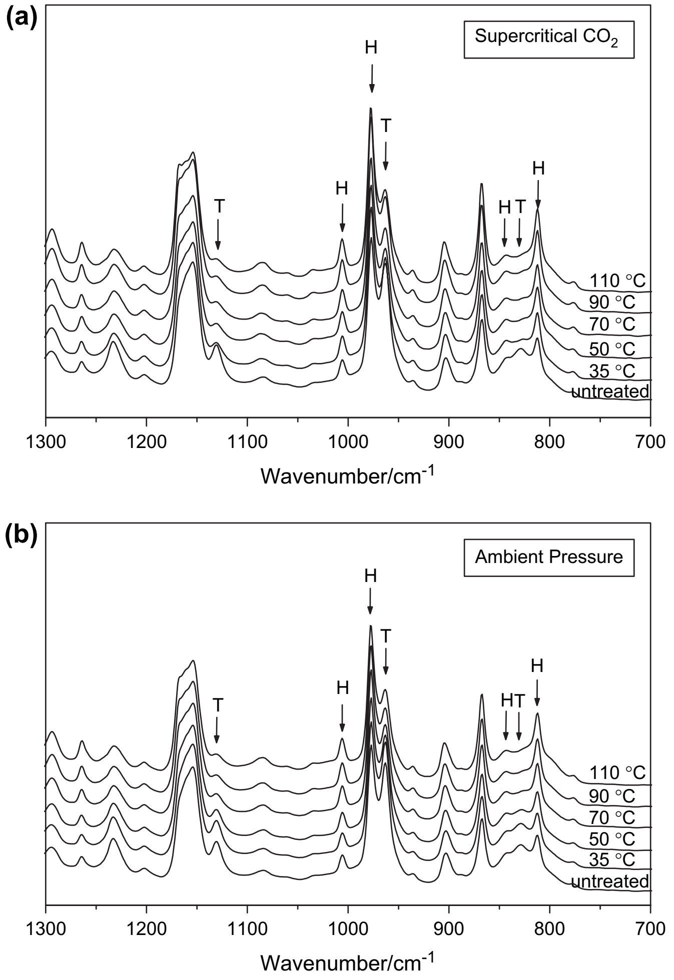

Fig. 2. FTIR spectra of the original sample treated in supercritical CO_2 of 12 MPa (a) and atmospheric pressure (b) for 7 h at the temperatures indicated, where the arrows indicate the helical conformation (H) and the *trans*-planar mesophase (T).

while the bands assigned to the helical conformation appear to dominate. At higher temperature of 110 °C, the characteristic bands, assigned to the *trans*-planar mesophase, nearly disappear. Altogether, cold crystallization of the original sPP sample in supercritical CO_2 transformed its *trans*-planar mesophase gradually into the helical conformation.

For comparison, the cold crystallization of the original sPP was also conducted under ambient condition. Fig. 2b shows their FTIR spectra after crystallization for 7 h at the temperatures indicated. No obvious change was found when the original sample was treated at 35 °C. This was different from that in supercritical CO_2, where the transformation of *trans*-planar mesophase into helical conformation occurred. By further increasing the temperature to 50 °C, the relative intensity of the bands assigned to the *trans*-planar mesophase and helical conformation, begins to decrease and increase, respectively. This indicates that the transformation of *trans*-planar mesophase into helical conformation occurred at this temperature under ambient condition. Compared with the spectra in Fig. 2a, obviously supercritical CO_2 changed the cold crystallization behavior of sPP.

In order to further understand the development of *trans*-planar mesophase and helical conformation during the annealing treatment in supercritical CO_2 and atmospheric surroundings, the peaks of 1130 cm^{-1} (*trans*-planar mesophase) and 812 cm^{-1} (helical conformation) were curved-fitted and the integral area of the two bands was calculated. The band of 1153 cm^{-1} was used as the internal standard for the comparison. Fig. 3 shows the relative area of the peaks at 1130 cm^{-1} and 812 cm^{-1} with the treatment temperature under the conditions indicated. It is observed that the relative area of band at 1130 cm^{-1} decreases at 35 °C when the sample was treated in supercritical CO_2, while it does not change until 50 °C when treated under ambient condition (Fig. 3a). Furthermore, the relative area of this band assigned to *trans*-planar mesophase in supercritical CO_2 is lower than that under ambient condition at the same temperature. This indicates that cold crystallization in supercritical CO_2 further decreased the content of *trans*-planar mesophase. After this treatment, as shown in Fig. 3b, the relative area of the band of the helical conformation began to increase at lower temperature than that under ambient condition. The supercritical CO_2-treated samples were rich of helical conformation.

In this study, the ratio of the bands at 812 and 1130 cm^{-1} was used to quantify the transformation behavior of the original sample treated under different conditions. This ratio is called the transformation index [39]. Fig. 4 shows this index as a function of the treatment temperature under the conditions indicated. It is seen that the transformation from the *trans*-planar mesophase into helical conformation occurred at lower temperature in supercritical CO_2 than that under ambient condition. Obviously, supercritical CO_2 decreased the temperature for this transformation due to its combining effect of temperature, pressure and solvent. And the helical conformation was more favorable in supercritical CO_2 than under ambient condition.

It is known that the FTIR spectra of forms I and II are similar, because they possess the same helical conformation.

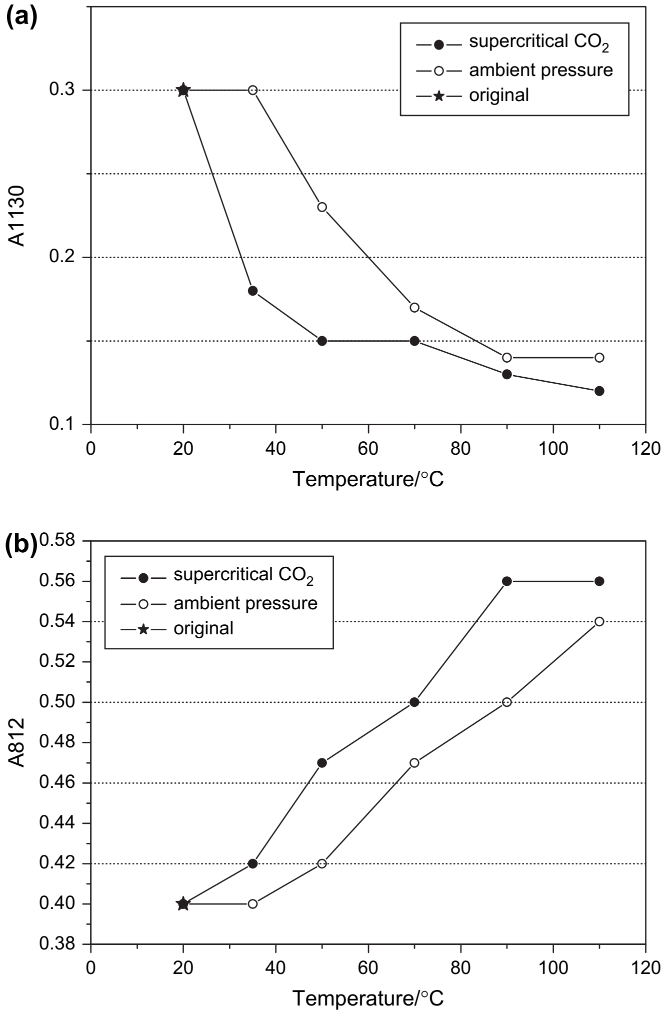

Fig. 3. Change of the relative intensity of the bands at 1130 cm^{-1} (a) and 812 cm^{-1} (b) with the treatment temperatures under the conditions indicated.

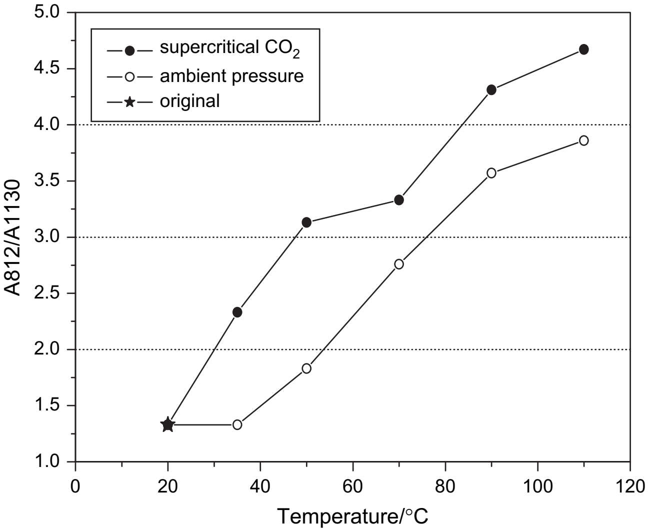

Fig. 4. Change of the transformation index with the treatment temperatures under the conditions indicated.

To further identify the conformation transformation, WAXD patterns for samples cold crystallized in supercritical CO_2 and under ambient condition are shown in Fig. 5. It is clear that at higher temperatures cold crystallization in different surroundings brings to different crystal forms. After being treated above 90 °C under ambient condition, the presence of the intensive peaks at $2\theta = 12.3$, 16.0 and 20.3° indicates the formation of all form I crystal with helical conformation (Fig. 5b) [20]. The absence of 211 reflection peak at $2\theta = 18.9°$ also indicates that the as-prepared original sPP sample was the disordered modification of form I [13]. However, after being treated at 90 °C in supercritical CO_2, a shoulder peak with lower intensity at $2\theta = 17.0°$ appears (Fig. 5a). Together with the FTIR results shown above, it indicates that a small amount of crystal form II was present in cold crystallized samples. At 110 °C the intensity increase of this shoulder peak indicates the increased amount of form II crystal. Altogether, compared with the formation of form I under ambient condition, a mixture of forms I and II was obtained at higher temperatures in supercritical CO_2. Obviously, here supercritical CO_2 was responsible for the appearance of form II crystal.

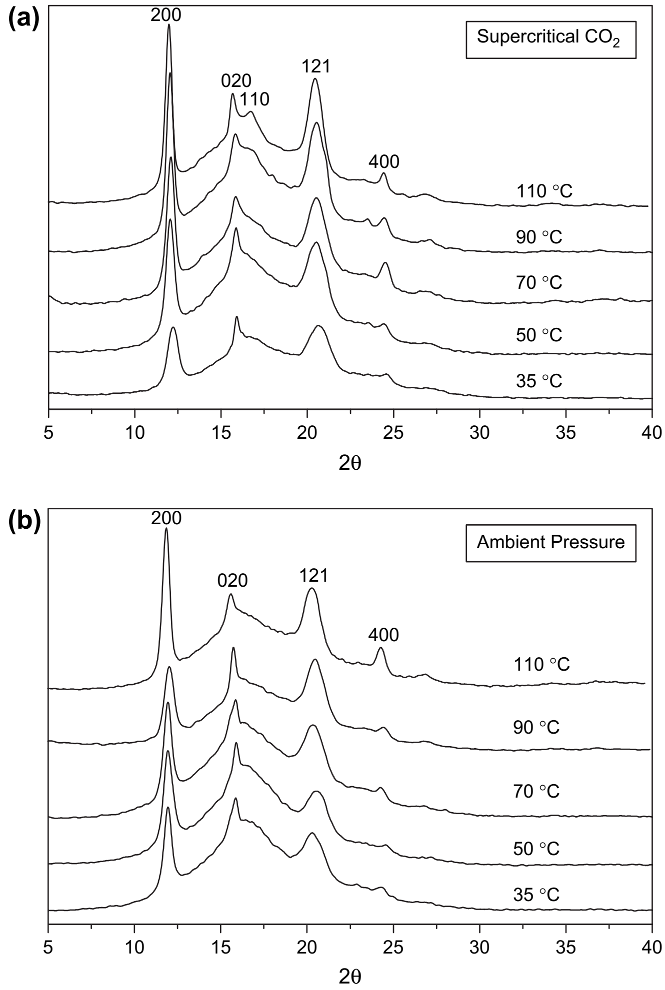

Fig. 5. WAXD patterns of the original sample treated in supercritical CO_2 of 12 MPa (a) and atmospheric pressure (b) for 7 h at the temperatures indicated.

Consequently, the cold crystallization behavior of the original sPP sample in different surroundings was different. Supercritical CO_2, as a severe surrounding with thermal, pressure and solvent effects, decreased the temperature of transformation from *trans*-planar mesophase to helical conformation. Furthermore, the treatment in supercritical CO_2 brought about the mixture of forms I and II at higher temperatures, while ambient surrounding only pure crystal form I. It is well known that chains in the helical form I are more stable than the chains in the helical form II [2–9]. Under ambient condition, form II usually transformed into form I. In our experiments, cold crystallization of the original sample under ambient condition brought about only the form I. However, cold crystallization at higher temperatures in supercritical CO_2 produced a small amount of form II. It has been reported that usually the form II was obtained by stretching sPP samples of low stereoregularity, or by removing the tension in the *trans*-planar form III stretched from highly stereoregular sPP samples [8,14–20]. It can also be obtained in powder samples by crystallization from the melt at elevated pressure above 150 MPa [21], where small traces of disordered form I coexisted with form II. In supercritical CO_2 of our study, form II together with form I was obtained when the sample cold crystallized at high temperatures in supercritical CO_2. Obviously, here supercritical CO_2 favored the formation of form II crystal.

3.3. Melt crystallization in supercritical CO_2

To further clarify the transformation behavior of original sPP samples, the melt crystallization was also conducted in different surroundings. Fig. 6a shows the WAXD patterns of sPP samples obtained by isothermal crystallization from the melt in supercritical CO_2 at various temperatures, T_c. The patterns of the melt-crystallized samples indicate that, at low temperatures from 40 to 60 °C, the crystallization into form I occurred, as indicated by the presence of intense peaks at $2\theta = 12.3$, 16.0, 20.3° [20]. The absence of 211 reflection at $2\theta = 18.9°$ in these patterns indicates that the obtained form to be disordered modification of form I [13]. With increasing the temperature to 80 °C, the appearance of the shoulder peak with low intensity at $2\theta = 17.0°$ (Fig. 6a) indicates that a small amount of crystal form II was present in the melt-crystallized samples. At 100 °C, the increased intensity of peak at $2\theta = 17.0°$ indicates the increased amount of form II crystal. At the same time, the intense peaks at $2\theta = 12.3$, 16.0, 20.3° indicate that the obtained crystal was a mixture of form II and disordered form I. This result was similar to the cold crystallized one at higher temperatures in supercritical CO_2. Both cold and melt crystallization in supercritical CO_2 brought about the mixture of forms I and II at high temperatures.

For comparison, the melt crystallization was also conducted under ambient condition. The X-ray diffraction patterns of samples treated are shown in Fig. 6b. The presence of the intense peaks at $2\theta = 12.3$, 16.0, 20.3° in all the WAXD patterns indicates the obtained form I with helical conformation [20]. No form II was found at any crystallization temperatures (T_c) under ambient condition, which was very different from

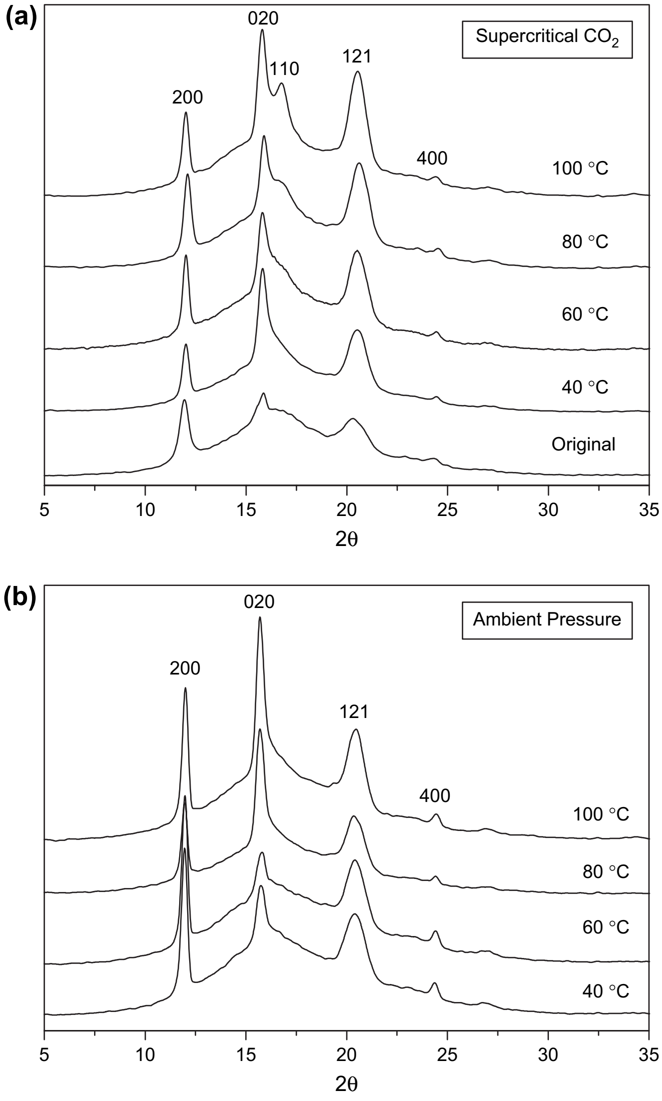

Fig. 6. WAXD patterns of sPP after isothermally crystallized at the indicated crystallization temperatures for 7 h from the melt at 180 °C in supercritical CO_2 of 20 MPa (a), and under ambient condition (b).

that in supercritical CO_2. De Rosa et al. [40] have reported that in the less stereoregular melt-crystallized samples small amounts of crystals of form II are present or a mode of packing of form II occurs as a defect in a prevailing mode of packing of form I. In our experiments, the pure form I crystal was obtained when melt crystallization occurred at any temperatures under ambient condition. Compared the melt crystallization behavior of the original sPP sample in different surroundings, it is seen that supercritical CO_2 changed the melt crystallization behavior of sPP, especially at high treatment temperatures, and was responsible for the formation of form II crystal.

3.4. Stability of form II in supercritical CO_2

The above results and discussion has shown that the cold and melt crystallization behaviors of the original sPP sample were different in different surroundings. As to cold crystallization, supercritical CO_2 decreased the temperature of transformation from *trans*-planar mesophase into the helical conformation. The helical conformation was more favorable in supercritical CO_2 than in ambient atmosphere. It is known that the helical conformation was more stable than *trans*-planar mesophase under ambient condition [2–9]. Annealing the *trans*-planar mesophase usually transformed it into the helical conformation. In supercritical CO_2, this transformation occurred at relatively lower temperatures. Obviously, supercritical CO_2 did not change the relative stability of *trans*-planar mesophase and helical conformation. The *trans*-planar mesophase remained less stable than helical conformation in supercritical CO_2.

As shown above, both the melt and cold crystallization at high temperatures in supercritical CO_2 brought about the mixture of forms I and II, while the treatment under ambient condition produced only pure form I. It is well known that forms I and II share the same helical conformation and have essentially the same density [41]. Based on the packing energy calculations, the form I is more stable than form II under ambient condition [2–9,21]. Therefore, annealing the sPP sample at high temperatures under the ambient condition usually transforms the form II into form I, i.e. the latter is more stable under such condition. In the present study, the original sample containing form I with helical conformation and *trans*-planar mesophase finally transformed into the pure form I, and no form II was obtained after both cold and melt crystallization under ambient condition. However, a certain amount of form II was found after both cold and melt crystallization at higher temperatures in supercritical CO_2. Considering the melt and cold crystallization behaviors of sPP in ambient atmosphere and supercritical CO_2, it was deduced that supercritical CO_2 changed the stability of forms I and II. The existence of form II indicated that the form II became the thermodynamically stable form in supercritical CO_2, which was very different from that under ambient condition.

Rastogi et al. [21] have reported that form II became the thermodynamically stable crystal when cooled from the melt above 150 MPa. Pure form II free from any conformational defects was obtained when the sample was crystallized at elevated pressures and temperatures from the isotropic melt. However, in the present study a certain amount of form I coexisted with form II when sPP samples cold and melt crystallized at high temperatures in supercritical CO_2. The low stereoregularity [rrrr] 81% of the sPP in our study was responsible for this phenomenon. The form I with helical conformation was easily obtained because of the defects existed in sPP samples with low stereoregularity [31]. Therefore, although form II was stable than form I in supercritical CO_2, pure form II could not be obtained because of the low stereoregularity.

To further clarify the formation and stability of form II, the initial sPP samples were melt crystallized in supercritical CO_2 by changing the incubation pressure and melt temperature. Fig. 7 shows the X-ray diffraction patterns of sPP samples obtained by isothermal crystallization at 100 °C from the melt in supercritical CO_2 at the pressure indicated. As shown in this figure, the typical peak at $2\theta = 17.0°$ attributed to form II with helical conformation is absent both under ambient condition and in compressed CO_2 of 6 MPa. Only pure form I was obtained under such conditions. With increasing the treatment pressure to 8 MPa, the appearance of the typical peak at $2\theta = 17.0°$ indicates the formation of form II, although the intensity is very weak. The intensity of this peak increases with increasing the pressure. This obviously shows that form II was favored in supercritical CO_2 with higher pressures, and its content was expected to increase with increasing the treatment pressure and to pure one at certain pressure. It is well known that form II is more likely to withstand the compressive forces when compared with the antichiral form I [21]. Therefore, the investigation of sPP crystallization in supercritical CO_2 with higher pressure confirmed the stability of form II.

Fig. 7 also shows the solubility parameters of supercritical carbon dioxide with the conditions indicated. It has been reported that supercritical carbon dioxide is a severe atmosphere combining temperature, pressure and solvent, and has its solubility parameter increased with decreasing temperature and increasing pressure [42]. A correlation was found between the solubility parameter of the media, including supercritical carbon dioxide with or without a cosolvent, and the stability of the resultant syndiotactic polystyrene (sPS) crystal forms. The higher solubility parameter the media had, the more ordered and stable crystal forms were obtained [43]. Fig. 7 clearly shows that the content of form II increases with increasing solubility parameter from 0 to 7.7 $MPa^{1/2}$. Therefore, similar to the situation happened with sPS [43], this phenomenon also confirmed that form II of sPP was more thermodynamically stable than form I in supercritical CO_2 at higher pressures.

Furthermore, the melt crystallization of sPP was also conducted in supercritical CO_2 by changing the melting temperature. Fig. 8 shows X-ray diffraction patterns of samples of sPP obtained by isothermal crystallization at 100 °C after melting at different temperatures in supercritical CO_2. No difference was found when changing the melting temperatures from 180 to 240 °C. This indicates that melting temperature did not affect the formation of form II crystal in supercritical CO_2. Therefore, the change of melting temperature was not responsible for the formation of form II.

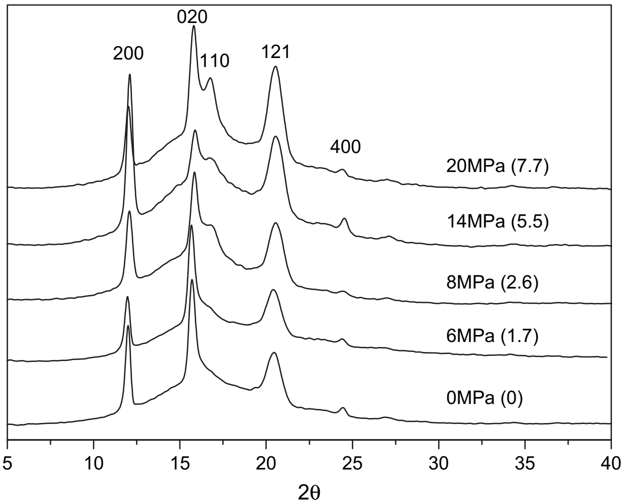

Fig. 7. WAXD patterns of sPP after isothermally crystallized at 100 °C for 7 h from the melt at 180 °C in supercritical CO_2 with the pressure indicated. Inside the parenthesis is the solubility parameter of supercritical CO_2 with the conditions indicated.

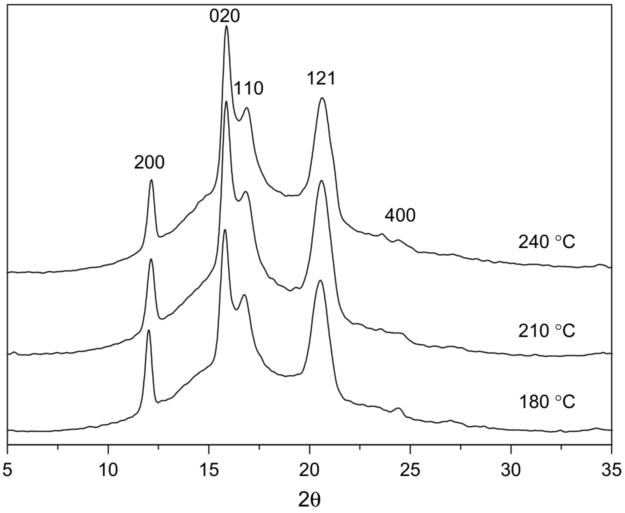

Fig. 8. WAXD patterns of sPP after isothermally crystallized at 100 °C for 7 h from the melt at temperatures indicated in supercritical CO_2 of 20 MPa.

Now it can be deduced that the incubation pressure of supercritical CO_2 was a key factor to affect the formation of form II. The increase of incubation pressure of supercritical CO_2 favored the formation of form II and increased the relative amount of form II, correlated with the increased solubility parameter of the media as well. Obviously, the crystal of form II became the relative thermodynamically stable form because of its ability to withstand the compressive forces exerted by supercritical CO_2.

In addition, it is shown that the form II crystal was obtained by cold and melt crystallization in supercritical CO_2 with a low pressure of 8 MPa. This pressure producing the form II in supercritical CO_2 was quite moderate than that in the air with elevated pressure (150 MPa). Obviously, supercritical CO_2 was responsible for this phenomenon. It is known that supercritical CO_2 exhibits hybrid properties of a typical gas and liquid, such as low viscosity, high compressibility, and adjustable density from vapor-like to liquid-like [44]. Therefore, supercritical CO_2 can diffuse easily into the sPP chains and thus provides a combining severe condition to obtain the form II crystal, although its pressure was much lower than the elevated pressures reported. However, due to the experimental difficulty, the in situ measurement in supercritical CO_2 cannot be conducted nowadays. Whatever the mechanism is, supercritical CO_2 provided a new condition to obtain the form II with helical conformation. Further experiments are needed to clarify the mechanism.

4. Conclusions

In the present study, the original sPP sample containing form I and *trans*-planar mesophase was treated in supercritical

CO_2 to conduct further cold and melt crystallization. FTIR and WAXD results consistently showed different crystallization behaviors of sPP in different surroundings. In the cold crystallization, supercritical CO_2 decreased the temperature of transformation from *trans*-planar mesophase into the helical conformation. Compared with the formation of pure form I at high temperatures under ambient condition, the mixture of forms I and II was obtained in supercritical CO_2. The similar results were also obtained from the melt crystallization in supercritical CO_2. All the results confirmed that supercritical CO_2 changed the stability of forms I and II, and made the form II more thermodynamically stable than form I. The increased solubility parameters at which the form II was formed also confirmed that form II of sPP was more thermodynamically stable than form I in this atmosphere. The incubation pressure was the key factor to affect the formation of form II crystal in supercritical CO_2, and increasing the pressure increased the amount of form II. Furthermore, supercritical CO_2 can diffuse easily into the sPP chains and thus provides a combining severe condition to obtain the form II crystal, although its pressure was much lower than the elevated pressures reported before.

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