Empty δ Crystal as an Intermediate Form for the δ to γ Transition of Syndiotactic Polystyrene in Supercritical Carbon Dioxide

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ABSTRACT: The crystal transition behavior of δ form syndiotactic polystyrene (sPS) in supercritical CO_2 was investigated in detail by using Fourier transform infrared spectroscopy and differential scanning calorimetry. The empty δ_e form sPS was obtained after treating the δ form in supercritical CO_2 of 12 MPa in a range from 35 to 80 °C. At higher temperatures, the δ form transformed into the δ_e form transiently and then into the γ form. The existence of the intermediate δ_e form lowered the temperature for the δ to γ transition. At 240 °C, supercritical CO_2 of 12 MPa transformed the δ crystal form into more stable β form without passing through the δ_e form. Increasing the pressure of supercritical CO_2 made the δ to δ_e transition occur easily and decreased the temperature for the δ to β transition.

Introduction

Syndiotactic polystyrene (sPS) possesses a complex polymorphism in its crystalline region, which has been extensively studied by using wide-angle X-ray diffraction (WAXD), Fourier transform infrared spectroscopy (FTIR), and differential scanning calorimetry (DSC), etc.[1−7] The α and β forms, both containing planar zigzag chains having a TTTT all-trans conformation, can be obtained from the melt or glassy state of sPS under different thermal crystallization conditions.[4,7−13] They are further classified into two limiting disordered modifications, α′ and β', and two limiting ordered modifications, α″ and β''. The δ and γ forms, with a TTGG helical conformation, can be formed from solvent swelling of glassy or semicrystalline sPS.[1,14−16] Generally, the δ form contains solvent molecules entrapped in the crystal structure whereas the γ form is free of solvent. The γ form can be obtained by immersing the amorphous sPS into acetone[17] or 1,1,2,2-tetrachloroethane,[18] while the sorption of suitable solvents (methylene chloride, toluene, chloroform, iodine, dichlorobenzene, decalin, etc.) in amorphous sPS or samples having the α or γ forms usually gives the δ form. By washing the δ form in boiling acetone and further rinsing in methanol, the empty δ form (δ_e) is obtained.[19−21] The δ_e form sPS takes the same TTGG helical conformation as the original δ form does, but the solvent is taken away and the spaces occupied by solvent molecules are kept vacant. Usually, the solvent-induced crystalline δ form with the helical conformation is unstable upon heating. The δ form transforms into the γ form directly at about 130 °C and further into the α form above 200 °C.[6,19,22] Fast annealing above 150 °C can transform the δ form directly into the β form.[1]

It is well-known that FTIR is a useful tool to identify and characterize the change of chain conformation associated with different polymorphic crystal forms. FTIR has been extensively used to study the polymorphic behavior of sPS.[6,23−25] The infrared bands at 1222 and 538 cm^{-1} are associated with the trans conformation, while the features at 572 and 502 cm^{-1} represent the helical structure.[23] Moyses et al.[26] studied the region between 920 and 960 cm^{-1} to identify the δ and γ crystal forms. The infrared patterns of the α and β are different in the frequency range of 900−910 cm^{-1}.[27] Particular attention has recently been given to the infrared frequency region (590−620 cm^{-1}) where the spectroscopic data are useful for the examination of the δ, δ_e, and γ forms.[6,28] The band positions of the δ form depend on the solvent type due to the different polymer−solvent interactions, while the δ_e and γ keep the bands at almost the same positions irrespective of the kind of the solvent. The gap between the bands around 600 and 610 cm^{-1} is different among the δ, δ_e, and γ forms. The δ_e form has a smaller gap than the δ form as long as the solvent is the same type, while the γ form has the largest separation between these bands.

Supercritical CO_2 (T_c = 31.1 °C, P_c = 7.37 MPa) or compressed CO_2 has been extensively studied nowadays as a solvent in terms of commercial application and fundamental understanding of solution behavior.[29] It can swell and plasticize glassy polymers, leading to a depression on glass transition temperature to almost the same extent as affected by vapors or liquids.[30] The plasticization of the amorphous phase increases the mobility of the polymer chains and thus induces crystallization and concomitant change in the morphology. In addition, this effect leads to the decrease of the energy barriers, thus making some solid−solid transitions possible at much reduced temperatures and bringing about some new transitions that cannot occur at ambient pressure. The phase transitions of sPS in the presence of CO_2 have been reported by Handa et al.[31] and He et al.[32−34] The phase transition of the γ form sPS to the α form occurred at lower temperatures in compressed CO_2 than those at ambient pressure.[31] sPS treated with compressed CO_2 underwent some new transitions (amorphous to γ, the planar mesophase to β, α to β, and γ to β) that only occurred in the presence of liquid solvents. It is also found that the completely empty δ form (δ_e) can be obtained by extracting the δ form in supercritical CO_2.[35] Compared with the previous procedures based on boiling solvents, supercritical CO_2 allows a moderate condition to generate the δ_e crystal form.[35] Furthermore, supercritical CO_2 provides the polymer with different crystal transition behaviors from those of gaseous and liquid CO_2.[33,34] Exhibiting hybrid

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properties of a typical gas and liquid, supercritical CO_2 has its viscosity and fluidity similar to a gas, and the density and solvent strength similar to a liquid, so that it can diffuse much more readily into a matrix. The unique properties provide supercritical CO_2 much more plasticizing effect than the gaseous and liquid ones, thus bringing about more stable crystal forms and making some crystal transitions occur more easily.[33,34]

Although it has been widely investigated at ambient atmosphere, the crystal transition behavior of the δ form sPS still lacks study in the presence of supercritical CO_2 up to now. The aim of this paper is to catch the δ_e form and find the crystal transition related to the δ_e form in the presence of supercritical CO_2. Some influencing factors such as temperature, time, and pressure were investigated in detail by using FTIR and DSC.

Experimental Section

The syndiotactic polystyrene was obtained as a commercial material from Dow Chemicals with its syndiotacticity about 99% determined by high-resolution NMR. The average molecular weight (M_w) is 2.1×10^5, and the polydispersity (M_w/M_n) is 2.3. The CO_2 with a purity of 99.95% was supplied by Beijing Analytical Gas Factory, China. Toluene was of reagent grade and used as received.

Amorphous sPS films of thickness about 100 μm were obtained by forming a thin sPS melt film pressed at 290 °C and then rapidly quenching in an ice–water bath. The film sample in the δ form was obtained by immersing the amorphous one in toluene for 1 day and then kept under ambient conditions until they became touch dry.

A high-pressure apparatus was used for the treatment in supercritical CO_2. The δ form sPS films 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 sPS samples at the desired temperature and pressure for a certain time, the vessel was quenched to room temperature and depressurized slowly. Thermal treatments under ambient atmosphere were made in the same vessel but without the introduction of CO_2 specifically. All the media of ambient atmosphere are air unless indicated.

FTIR measurements were carried out under ambient conditions on a Perkin-Elmer FTIR System 2000 in the standard wavenumber range of 370–4000 cm^{-1} for the investigation of the chain conformations and crystalline forms in sPS. A Perkin-Elmer DSC-7 was used for the analysis of the thermal behavior of sPS samples with a heating rate of 10 °C/min in a dry nitrogen environment.

Results and Discussion

Effect of the Temperature on the δ_e Formation. Lower Temperature Range. The information on the infrared bands between 590 and 620 cm^{-1} is sensitive to the different crystalline forms of δ, δ_e, and γ with the TTGG helical conformation, which is important for tracing the structural changes occurred in the crystal transition.[6,28] Therefore, the infrared bands of this range are adopted to study the crystal transition behavior of the δ form subjected to the certain treatment in this paper. Figure 1 shows the change of FTIR wavenumbers with the temperature of the δ form sPS treated under ambient atmosphere for 5 h. The untreated sample with bands at 608.5 and 600.8 cm^{-1} shows the typical patterns of the δ form with toluene.[28] On heating, the δ form does not show any obvious changes up to 100 °C. At 110 °C, the separation of the two bands becomes wider, indicating the transition of the δ form into the γ form. This transition covers the range from 110 to 140 °C, and the obtained is all the γ form above the temperature of 140 °C. These two bands disappear above 220 °C, indicating the disappearance of the TTGG helical conformation, which will be discussed later.

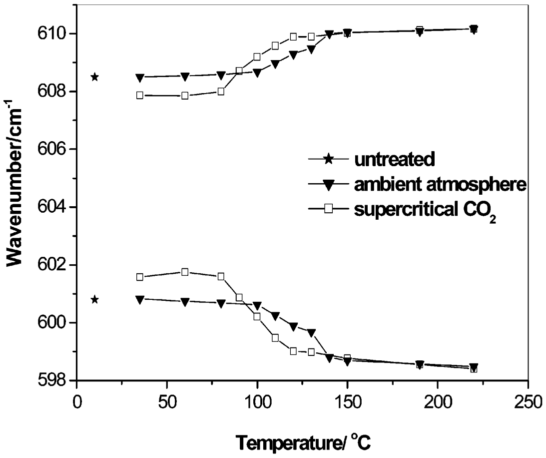

Figure 1. Variation of FTIR band position with temperature after treatment in ambient atmosphere and in supercritical CO_2 of 12 MPa for 5 h.

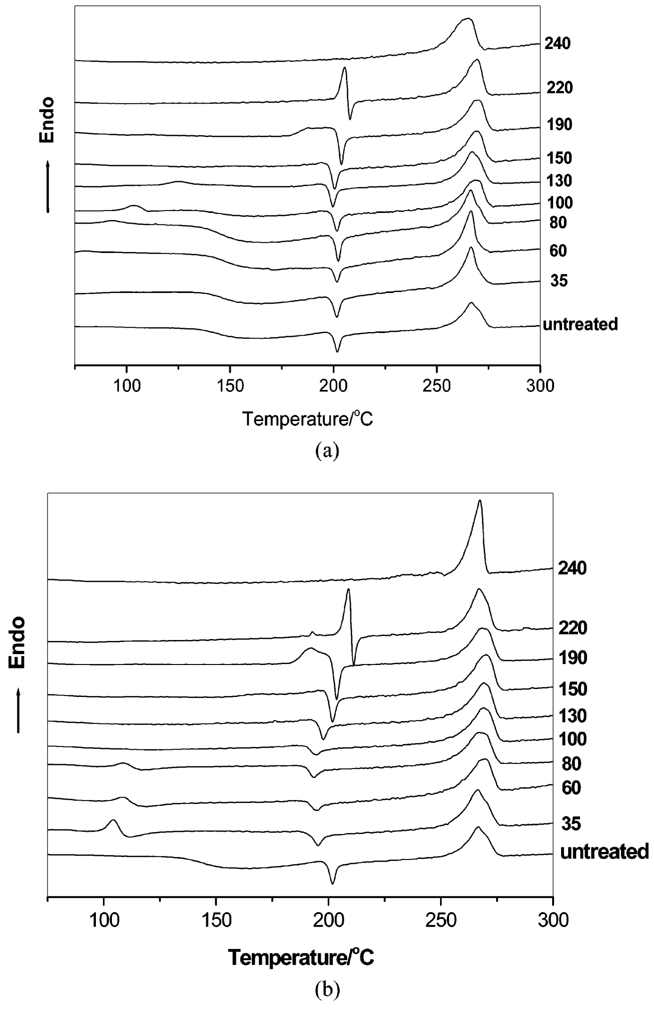

Figure 2. DSC patterns of the δ form sPS treated at different temperatures (a) under ambient pressure and (b) in supercritical CO_2 of 12 MPa for 5 h.

To analyze the thermal behavior of the δ form sPS samples treated under ambient atmosphere, the DSC patterns of the samples are shown in Figure 2a. The untreated sample shows the typical DSC patterns of the δ form. The peak associated with the δ to γ form transition is overlapped by a broad endotherm due to the solvent (toluene) evaporation during the heating of the δ form. The endotherm at 193 °C followed by the exotherm at 200 °C is corresponding to the γ to α form transition. The endotherm at 273 °C is clearly due to the melting of the α form. The DSC patterns do not show any obvious changes with the treatment temperature up to 80 °C, indicating that the solvent in the δ form crystals remains almost the same under these conditions. The almost disappearance of the broad endotherm after treating at 100 °C indicates the solvent evaporation with this treatment. The existence of the endotherm peak at about 130 °C indicates the remaining of the δ form after the treatment at 130 °C at ambient pressure. The sample after treating at 150 and 190 °C shows the typical DSC patterns of the γ form.[33] Consequently, the FTIR and DSC results shown above are consistent with the previous results.[6,22]

Different results were obtained when the δ form was treated at the same temperature and time in supercritical CO_2 of 12 MPa. Figure 1 also shows the change of wavenumber of the δ form samples treated in supercritical CO_2. The band at 608.5 cm^{-1} shifts to 607.9 cm^{-1} and at 600.8 cm^{-1} to 601.6 cm^{-1} when treated at 35 °C in supercritical CO_2 of 12 MPa for 5 h. The narrower gap between these bands clearly indicates that the empty δ_e form was obtained. It is well-known that supercritical CO_2 can swell and plasticize polymers, increasing the mobility of the polymer chains. Therefore, supercritical CO_2 diffused easily into the sPS sample and pushed out the solvent (toluene) in the crystalline lattice, thus transforming the δ form into the δ_e form totally without the collapse of the structure due to the absence of a liquid−vapor interface. Moreover, supercritical CO_2 can dry the polymer rapidly with no traces of organic solvents. Therefore, the δ_e form was obtained in "one pot" without any additional posttreatments. The separation of the bands does not change further up to 80 °C, indicating the crystal transition from δ to δ_e form occurred under this condition.

It is interesting to find in Figure 1 that the separation becomes wider again after treating the sample at 90 °C in supercritical CO_2 of 12 MPa for 5 h. This result indicates that the δ form started to transform into the γ form under this condition, where the transition temperature was about 20 °C lower than that at ambient pressure. To further identify this transition process, the δ form was treated in both atmospheres at 100 °C for different intervals of time, the FTIR patterns of which are shown in Figure 3. As shown in this figure, the δ form bands at 608.5 and 600.8 cm^{-1} do not change after 1 min treatment at ambient pressure. The gap between these bands gets a little wider when increasing the treatment time. No bands characteristic of the δ_e form appeared during this course. These results clearly indicate that the δ form transformed directly into the γ form without passing through the δ_e as an intermediate form in ambient atmosphere. The similar result has been confirmed by Gowd et al.[22] and Yoshioka et al.[28,36] However, when the treating condition was changed into supercritical CO_2, different results were obtained. As shown in Figure 3, the gap between these bands becomes narrower at first and then gets wider in the γ region after 30 min. This clearly shows that the δ form transformed into the δ_e form once and later to the more stable γ form in the presence of supercritical CO_2. Existing transiently as the intermediate form, the δ_e crystal was caught in our experiments.

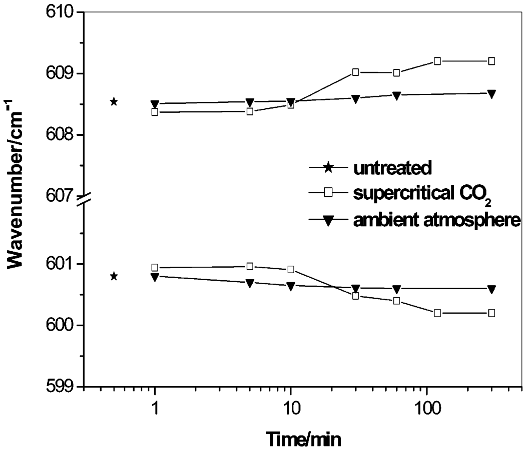

Figure 3. Variation of band position with the treatment time at 100 °C in ambient atmosphere and in supercritical CO_2 of 12 MPa.

It is reported that the transition temperature from the δ to γ form depends on the amount of solvent absorbed in the system.[22] The less amount of solvent remained in the system, the lower the transition temperature will be. Supercritical CO_2 transformed the δ form into the δ_e form transiently due to the extraction or replacement effect of supercritical CO_2, thus decreasing the transition temperature from the δ to γ form. As also shown in Figure 1, the resultant crystals were all of the γ form at 130 °C when being treated in supercritical CO_2. This temperature was also lower than that 140 °C under ambient pressure. The two bands also disappeared above 220 °C, which will be discussed in a later section.

Figure 2b shows the DSC patterns of the δ form sPS treated at different temperatures for 5 h in supercritical CO_2 of 12 MPa. After being treated at 35 °C and in 12 MPa supercritical CO_2, the sample shows a different DSC pattern from that under ambient pressure. The broad endotherm due to the solvent evaporation does not appear, while an endotherm at 104 °C accompanied by an exotherm at 111 °C corresponding to the δ_e to γ form transition is clear.[22] These peaks due to the δ_e to γ form transition remain unchanged until up to 80 °C, indicating that the obtained crystal was the δ_e form under this condition. On further keeping at 100 °C, the almost disappearance of these peaks indicates the decreasing amount of the δ form. The DSC patterns from 130 to 220 °C indicating the obtained γ form are consistent with those results of FTIR shown above.

Higher Temperature Range. As shown in Figure 1, both the bands at 608.5 and 600.8 cm^{-1} disappear when increasing the treatment temperature to 240 °C. These results show that the δ form transformed into another crystal form at this temperature at ambient pressure and in the presence of supercritical CO_2. Another band appearing at 1222 cm^{-1} (not shown here) indicates the obtained crystal form having a TTTT all-trans conformation. Figure 4 shows the FTIR patterns in the range of 820−920 cm^{-1} of samples treated at 240 °C for 5 h under different atmospheres. Depending on the treatment conditions, the δ form transformed into different crystal forms. Under ambient pressure, a new peak of 852 cm^{-1} appears, and the peak 907 cm^{-1} shifts to 902 cm^{-1}, indicating that the δ form transformed into the α form under this condition.[27] However, dramatically different results were obtained when the treatment condition was changed into supercritical CO_2. As shown

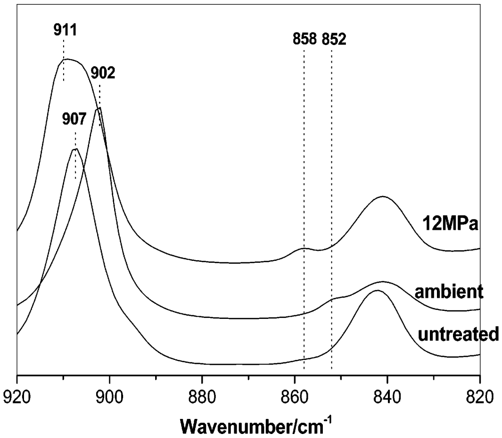

Figure 4. FTIR patterns of the δ form sPS treated at 240 °C and different pressures.

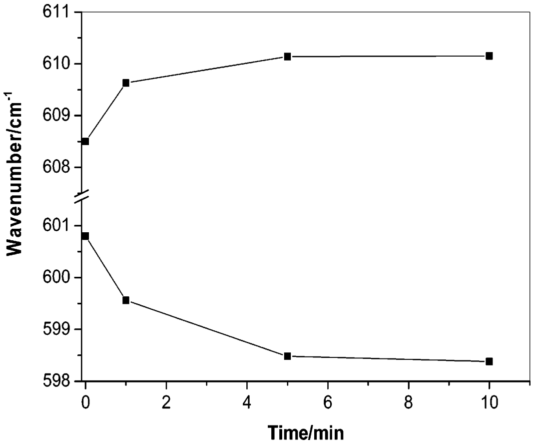

Figure 5. Variation of band position with the time in the treatment at 240 °C in supercritical CO_2 of 12 MPa.

in Figure 4, the peaks of 858 and 911 cm^{-1} (shift from 907 cm^{-1}) indicate the β form was obtained.[27] It is well-known that the β form can be obtained by slowly cooling from the melt or casting from an *o*-dichlorobenzene solution at 170 °C.[2] Usually the thermal treatment does not bring the δ form to the β form. In our study, the transformation from the δ to β form was found in the presence of supercritical CO_2.

To further identify this transition in detail, the δ form was also treated at 240 °C for different intervals of time in supercritical CO_2, the results of which are shown in Figure 5. These bands are getting a wider separation with the time and disappear after a 10 min treatment. This clearly indicates that the δ form transformed into the β form through the γ form. No bands characteristic of the δ_e form are found any more, indicating that the δ_e crystal did not exist as the intermediate form under this condition. It was shown from a previous study that plasticization effect of supercritical CO_2 lowered the energy barriers of sPS and induced the transition from the γ to β form.[34] Therefore, the presence of supercritical CO_2 made the transition from the δ to β crystal form possible. As also shown in Figure 2, the DSC shows different patterns at 240 °C under different treatment conditions. The melting peak of the β crystal form obtained in supercritical CO_2 is narrower and sharper than that of the α crystal form obtained under ambient pressure.

Consequently, together with the previous discussion, the crystal transition behavior of the δ form under different conditions is summarized in Figure 6. The solid lines show the transitions that occur under ambient atmosphere, while the dashed lines represent the transitions that are brought about only by supercritical CO_2. The crystal transition behavior of the δ form is different, depending on the treatment condition. Thermal treatment under ambient atmosphere did not produce any δ_e crystal form. Exhibiting hybrid properties of a typical gas and a liquid, supercritical CO_2 diffused into the sPS sample and transformed the δ form into the δ_e form. The δ_e crystal existed as the intermediate form for the δ to γ form transition, thus decreased the transition temperature. Furthermore, much higher treatment temperature in supercritical CO_2 did not favor the existence of the δ_e crystal. The excellent plasticization of supercritical CO_2 transformed the δ form finally into the more stable β form through the γ form.

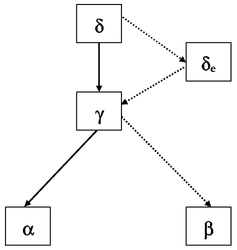

Figure 6. Crystal transition behavior of the δ form under different conditions. The solid lines show the transitions that occur under ambient pressure, and the dashed lines represent the transitions that are brought about only by supercritical CO_2.

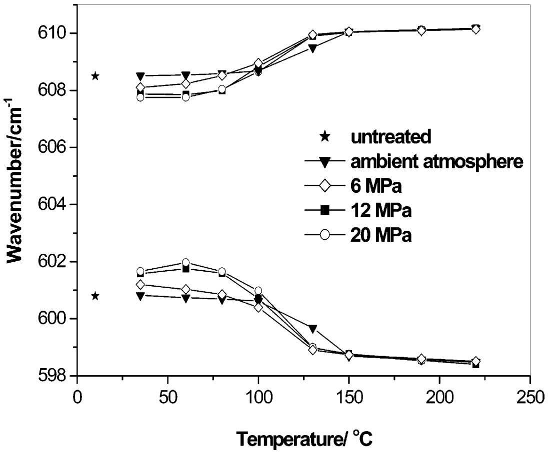

Figure 7. Variation of band position with the treatment temperature under different conditions.

Effect of the Pressure on the δ_e Formation. To further clarify the formation of the δ_e form, the sPS samples were treated at different pressures in the presence of CO_2. The variation of characteristic bands with temperature at different pressures is shown in Figure 7. The change of the band position after the treatment in supercritical CO_2 of 20 MPa is similar to that of 12 MPa, while the gap between the bands is slightly narrower in the range of 35−80 °C. This result indicates that the δ_e crystal form was easily obtained when the sample was treated in supercritical CO_2 with higher pressure. At 6 MPa, CO_2 is in its gaseous state. As shown in Figure 7, the change of the band position in the range of 35−80 °C at 6 MPa is close to that at ambient pressure, indicating that the δ_e crystal is difficult to be obtained under this condition. Compared to the supercritical CO_2, gaseous CO_2 exhibited less

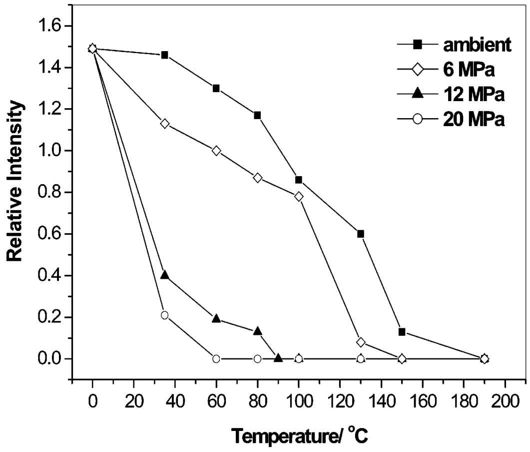

Figure 8. Relative intensity of the 462 cm^{-1} band with the treatment temperature at different pressures for 5 h.

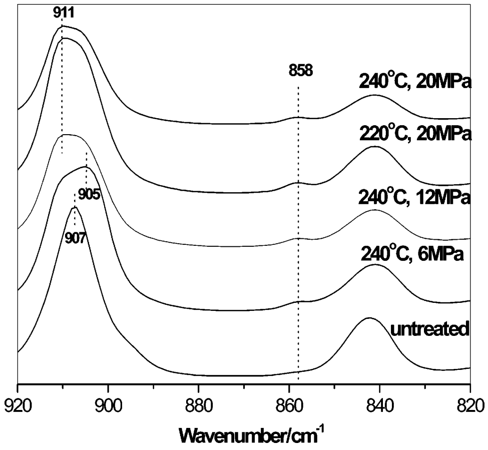

Figure 9. FTIR patterns of the δ form sPS treated under the conditions indicated.

diffusing ability and plasticizing effect and thus made the δ to δ_e transition difficult.

This phenomenon was also explained by the relative amount of toluene remained in the sPS during the treatment. In our experiments, the sharp band at 462 cm^{-1} was used to identify the relative amount of toluene that remained in sPS samples during the treatment; the band of 1028 cm^{-1} was used as the internal standard for comparison. Figure 8 shows the relative intensity of the 462 cm^{-1} band with the treatment temperature under different conditions. In the presence of gaseous CO_2 of 6 MPa, toluene could not easily be pushed out. A small amount of toluene remained even at higher temperature of 130 °C. The higher the treatment pressure, the less amount of toluene remains in the sPS sample. In the atmosphere of supercritical CO_2 at 20 MPa, toluene was pushed out completely at 60 °C, indicating that the δ form transformed completely into the empty δ_e form under this condition. Therefore, increasing the pressure of supercritical CO_2 can enhance the plasticizing and diffusing ability and thus obtain the empty δ_e form more easily.

As discussed above, higher treatment temperature in supercritical CO_2 of 12 MPa did not favor the formation of the δ_e crystal. Figure 9 shows the FTIR patterns of the δ form sPS treated at different pressures and higher temperatures. The peaks of 858 and 911 cm^{-1} (shifted from 907 cm^{-1}) indicate the β form was obtained after the treatment at 240 °C in supercritical CO_2 of 20 MPa. It is found that the β form was also obtained at lower temperature of 220 °C at this pressure, which indicates the plasticization effect was enhanced by increasing the pressure of supercritical CO_2. In the gaseous CO_2 of 6 MPa, the band at 907 cm^{-1} shifted to 905 cm^{-1} and a new band at 858 cm^{-1} appeared, indicating the finally obtained form was a mixture of the α and β crystals. This was the result of a weaker plasticization ability of the gaseous CO_2 than that of the supercritical CO_2 at the same temperature.[34] Increasing the pressure of the CO_2 at higher temperatures did not produce the δ_e crystal, indicating this was an unfavorable condition to obtain the δ_e crystal form.

Consequently, it is suggested that the pressure of CO_2 affected the formation of the δ_e form sPS. In the range of 35−80 °C, the increase of the treatment pressure made the CO_2 diffuse much more readily into the δ form crystal and push out the solvent much more easily, thus providing a moderate condition to obtain the δ_e crystal. High treatment temperature of 240 °C did not favor the existence of the δ_e crystal at any pressures. Increasing the pressure of supercritical CO_2 at this temperature only decreased the temperature for the δ to β transition and did not produce the δ_e crystal. Furthermore, with its unique properties, supercritical CO_2 provided a much stronger plasticizing effect than the gaseous one did and thus increased the mobility of the polymer chains and transformed the δ form completely into the more stable β form.

Conclusions

In this study the FTIR and DSC measurements were used to identify the formation of the δ_e form and the crystal transition related to it in the presence of supercritical CO_2. At ambient pressure, the δ crystal form transformed directly into the γ form at about 140 °C and further into the α form at higher temperatures. No δ_e form was found during the thermal treatment under ambient pressure. In the presence of supercritical CO_2 of 12 MPa, the transition from the δ to δ_e form occurred in the treatment temperature range from 35 to 80 °C. At higher temperatures, supercritical CO_2 transformed the δ form into the δ_e form transiently due to the extraction effect and thus made the temperature for the δ to γ transition lower than that at ambient pressure. At 240 °C, supercritical CO_2 further transformed the δ crystal form into the more stable β form through the γ form without passing through the δ_e form.

Furthermore, compared to gaseous CO_2, supercritical CO_2 diffused into the polymer more easily and plasticized the polymer much more effectively, thus provided much more moderate condition to obtain the δ_e and β crystal forms. Increasing the pressure of supercritical CO_2 also enhanced the plasticizing ability and induced the δ to δ_e transition more easily and decreased the temperature for the δ to β transition.

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