Effect of Pre-Existed Form I' on the Phase Transition of Isotactic Poly-1-butene Form III under High Pressure CO_2

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Summary: The CO_2 plasticization effect on the isotactic poly-1-butene (iPB-1) form III with pre-existed minority form I' was investigated by using high-pressure differential scanning calorimetry (DSC). The results showed that the form III melting peak moved to a lower temperature and the melting peak area of form II generated during heating decreased with the increased CO_2 pressure. The solid-solid transition of form III to I' in the iPB-1 was mainly studied by fourier transform infrared spectroscopy (FTIR). It was claimed that the phase transition was a thermodynamic process and the pre-existed form I' in form III inhibit the phase transition of form III into I'. The influence of the pre-existed form I' on the melting behavior of the iPB-1 was also studied by DSC. It was found that the form I' also suppressed the recrystallization of form II.

Keywords: form III; form I'; isotactic poly-1-butene; polymorphous; transitions

Introduction

Isotactic poly-1-butene (iPB-1) is one of the major commodity polymers with many outstanding properties in contrast to other polyolefin.[1–3] Depending on the formation conditions, it may exist in four different crystal structures, designated as form I, II, III and I'.[4–6] Forms I and I' have the same 3/1 helix conformation with twined hexagonal and untwined hexagonal crystal structure respectively.[7,8] Form II has the tetragonal unit cell packed by 11/3 helix conformation, and form III with 4/1 helix chain conformation has the orthorhombic unit cell.[9] Forms III and I' are usually formed by crystallization from certain dilute solution.[10–13] Form I' can also be obtained through crystallization from the melt under high hydrostatic pressure or annealing form III above 90 °C.[14–16]

The multiple phase transition of Form III has been widely studied.[17–20] By differential thermal analysis (DTA) measurement, Clampitt et al.[21] studied the form III melting behavior and pointed out that form II is generated during heating. Geacintov et al.[22] claimed the presence of an exothermal peak in the DTA thermogram peak may indicate that the recrystallization involves a short-lived molten state. Meanwhile, form III might transform into I' at certain process. Miles et al.[23] found that Form III undergoes a crystal-crystal transition to Form I' during form III melt at a very slow heating rate. Nakamura et al.[24] indicated that form III could transit into I' by a solid-state coextrusion of form III.

Supercritical carbon dioxide ($scCO_2$) has been increasingly attracted because the chemical inertness, noncombustibility, low cost and is widely used in the polymer processing such as, grafting, foaming, and impregnation of additives.[25–30] The plasticization effect of CO_2 on the polymer leads to decrease the glass transition temperature and melting temperature,[31–33] and it could also induce polymer phase transition,[30,34] crystallization,[35] and conformational transition.[36] In our previous work,[37] we investigated the phase transition of form II

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to I and found that the application of high pressure CO_2 significantly accelerate the phase transition. And high pressure CO_2 also influenced the form III melting behavior and the phase transition of form III to I'.[38] Meanwhile, we also found that the phase transition of form III with pre-existed minority form I' under CO_2 is different from that of form III.

This paper was devoted to investigate the influence of the pre-existed minority form I' in the form III on the phase transition of form III under high pressure CO_2. The plasticization effect of CO_2 on the melting behavior of form III with pre-existed minority form I' was investigated by using high-pressure differential scanning calorimetry (DSC). Fourier transform infrared (FTIR) measurement was applied to analysis the crystal-crystal transition of Form III into I'. The influence of the pre-existed minority form I' on the recrystallization of form II was studied by DSC.

Experimental Part

Materials and Sample Preparations

iPB-1 pellets (PB 0110M) were kindly supplied by Basell Polyolefins. Before used, they were purified by Soxhlet extraction in acetone for at least 24 h and then dried in a vacuum oven at 40 °C for 2 days.[37] iPB-1 was dissolved in carbon tetrachloride at a weight concentration of 3%. iPB-1 film with form III was obtained by evaporating the solvent completely in the iPB-1 solution at room temperature. The form III with pre-existed minority form I' was prepared by annealed the obtained form III at 100 °C for 1 hour under N_2, as evidenced by FTIR measurement (see Figure 2). CO_2 (purity: 99.9% w/w) was purchased from Air Products Co., Shanghai, China.

CO_2 Treatments

Treatments of iPB-1 films by using CO_2 were performed in a high-pressure vessel placed in a homemade oil bath with a temperature controller, as described elsewhere.[39] The films were placed in the vessel. After a preset period of time, the vessel was cooled to the ambient temperature, and then the CO_2 was released. Before characterized, the treated films were placed in a vacuum oven at ambient temperature for 24 h to completely evacuate the CO_2 in them.

Characterization of Polymers

DSC (NETZSCH DSC 204 HP, Germany) was used to characterize the melting behaviors of iPB-1 under ambient N_2 and high pressure CO_2. The calorimeter was calibrated by carrying out the measurement of the melting points and the heat of fusion of In, Bi, Sn, Pb, and Zn under ambient N_2 and high CO_2 pressure conditions, respectively.[39] For each DSC measurement, about 5–10 mg of the iPB-1 was heated from 30 to 170 °C at a heating rate of 10 °C/min. An FTIR of Bruker Equinox-55 was used to study the phase transition from form III to I' under CO_2. FTIR spectra were recorded at a resolution of 4.0 cm^{-1} and a rate of 1 spectrum per 32 s. The scanned wavenumber was in the range of 4000–400 cm^{-1}.

Results and Discussion

CO_2 Plasticization Effect on the Form III with Minority Form I'

Figure 1 shows the high pressure DSC measurements of form III with pre-existed minority form I' at various CO_2 pressures. Two endothermic melting peaks were detected when form III with minority I' was heated under atmospheric N_2 and in low CO_2 pressure region. The former was mainly attributed to the melting of form III, as determined by further FTIR and DSC measurements, and the latter was the melting of form II generated by the recrystallization during the heating. On saturation with CO_2, the form III melting peak moved to a lower temperature. It was ascribed to the plasticization effect of CO_2, and this phenomenon was similar to those observed in other polymers. Moreover, the plasticization effect on the form II melting

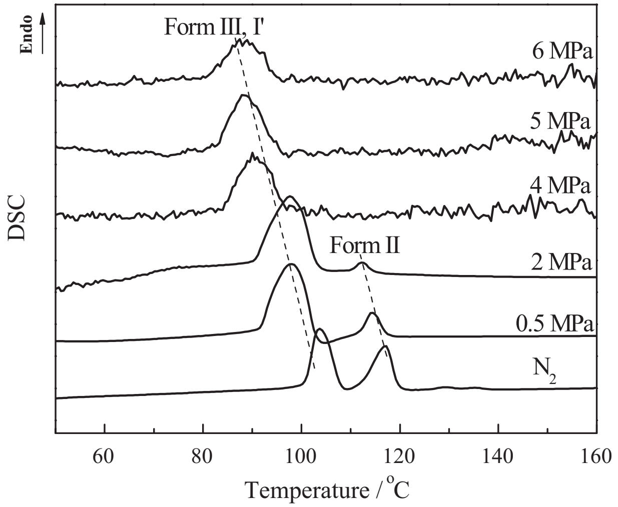

Figure 1.
DSC melting curves of form III with pre-existed minority form I' at different CO_2 pressures.

peak was significant, the endothermic peak area substantially decreased even when the pressure was 0.5 MPa. Trace form II melting peak was observed under 2 MPa. Meanwhile, no form II endothermic peak was detected with further increasing the pressure above 4 MPa, which was claimed that no form II recrystallization occurred during the sample melting. In addition, this phenomenon was also observed in the form III melting under high pressure CO_2.[38]

The melting processes of form III and I' at atmospheric pressure undergo two processes. Form III and I' melt into a short lived molten state, and then recrystallize into form II at elevated temperature.[23] The application of high pressure CO_2, could enhance the polymer chain mobility in the molten state, thus, the polymer chain could not acquire sufficient energy at the transition temperature to break interchain cohesive forces to recrystallize into Form II.

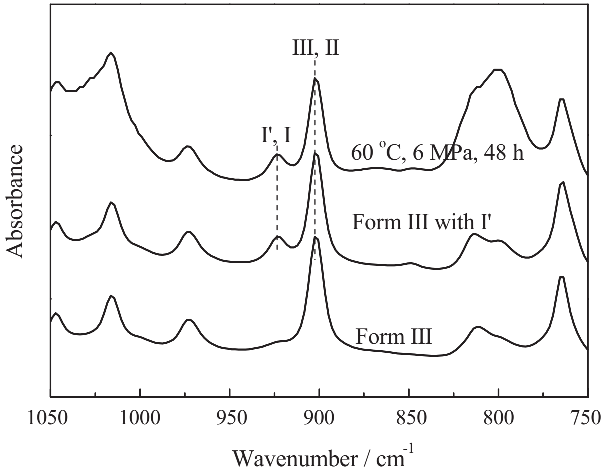

Figure 2.
IR spectra of form III, form III with pre-existed minority form I' and that treated at 60 °C and 6 MPa for 48 hours.

Effect of Pre-Existed Form I' on the Transition of Form III to I

The infrared spectroscopy was widely used to study the polymorphism crystal forms of iPB-1.[40,41] Previous work has shown there are distinct differences among the infrared spectrum range in 800–950 cm^{-1} between form III/II and I/I' of iPB-1, and the bands at 905 and 925 cm^{-1} both correspond to the CH_2 and CH_3 rocking vibrations.[42] The band at 905 cm^{-1} is known to be the characteristic of form III/II while the one at 925 cm^{-1} is characteristic of form I/I'.[43]

Figure 2 shows the IR spectra of form III with minority form I' and that annealed at 60 °C and 6 MPa for 48 h. The form I' characteristic band at 925 cm^{-1} kept the peak area even after 48 h. It was indicated that no form III was transformed into form I'.

The IR spectra of form III with minority form I' treated at 16 MPa and 60 °C for 5, 18 and 48 h are shown in Figure 3, respectively. And the top trace in Figure 3 represents the spectrum of form III annealed at the same CO_2 conditions for 48 h. A weak IR absorption band at 925 cm^{-1} was observed in form III saturated for 48 h, which revealed the formation of form I'. However, in comparison with the spectrum of form III with pre-existed form I', the IR absorption band at 925 cm^{-1} showed relatively small changes with the increasing time. It was claimed that form III could not transform into I' by further elongating the annealing time. This result was consisted with Gtacintov's and our previous work.[22,38] The form transition of III into I' was a thermodynamic selection process and only a certain amount of form III can transform into I' at a certain annealing temperature. By comparison the middle trace in Figure 2 with the tope trace in Figure 3, it was indicated that the amount form I' in form III with pre-existed form I' is higher than that in form III annealed at 60 °C and 16 MPa for 48 h. As the phase transition was a thermodynamic process, the content of form I' in CO_2-treated form III with minority form I' cannot exceed that transformed by annealing form III at the same CO_2 conditions, thus, no form I' was transformed from form III.

Then, we discuss the case that the content of from I' in the form III with pre-existed form I' was lower than that in form III could transformed under CO_2. Figure 4 displays the IR spectra of the sample treated at 80 °C under 8 and 18 MPa at various time. The tope trace in Figure 4 shows the IR spectrum of form III was annealed at 80 °C and 8 MPa for 1 h. We defined the transformed fraction of form III was derived from the ratio between the

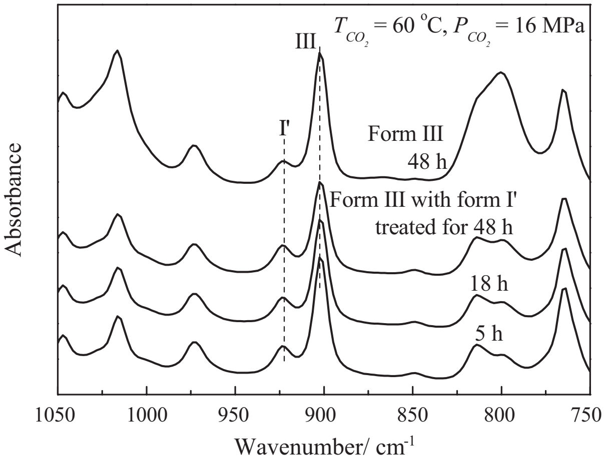

Figure 3.
IR spectra of form III with pre-existed minority form I' annealed at 60 °C and 16 MPa for various time.

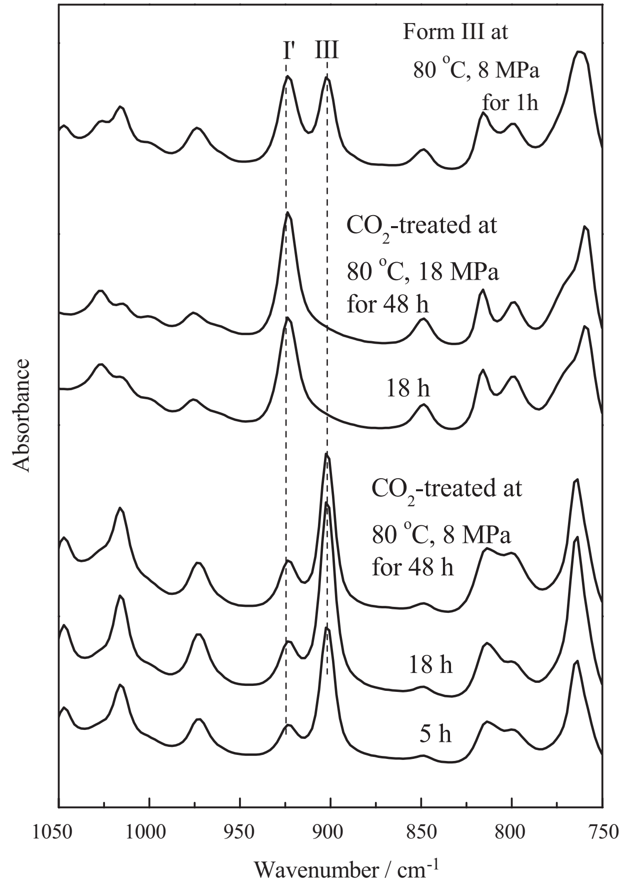

Figure 4.
IR spectra of form III with pre-existed minority form I' annealed at 80 °C, 8 and 18 MPa for various time.

absorbance band area at 925 cm^{-1} (A_{925}) and the sum of that at 905 and 925 cm^{-1} ($A_{905}+A_{925}$). More than half of form III transited into form I'. In contrast, when form III with pre-existed form I' annealed under CO_2, the peak areas of 905 and 925 cm^{-1} had no changes. The pre-existed form I' strongly inhibited the crystal phase transition of form III into I'. One of the possible reasons of such a suppression of form transition might be related to the kinetics of iPB-1 phase transition process. The phase transition of iPB-1 form II into I had been widely investigated by applying Avrami treatment to analyze the kinetic data observed during the phase transition.[20,44,45] Hong and Spruiell[46] had found that the straight lines of Avrami plots became gentle curves as the crystal transformation nears completion. They ascribed this behavior to a change of mechanism in the late stages of the transformation. Chau and Geil[45] had investigated the phase transition under atmospheric pressure by WAXD measurement, and also found the Avrami plots showed a change in slope. They believed the form transition undergoes two processes, instantaneous nucleation at the early stage of the transformation, followed by a second process of random nucleation. Thus, the inhibition of the form III to I' might be ascribed to that the pre-existed form I' disturbed the first process of the phase transition and inhibited the crystal phase transition. However, by further increasing the CO_2 pressure to 18 MPa, the IR absorption band at 905 cm^{-1} was disappeared, it was indicated that form III could transform into I' completely at a higher CO_2 pressure. Namely, the form III can undergo phase transition at a higher pressure, which might be ascribed to the increased polymer chain motion by increasing polymer free volume.

Influence of Pre-Existed Form I' on the Recrystallization of Form II

Figure 5 shows the DSC curves of the sample treated with CO_2 at 60 °C and 6 MPa for 48 h. The DSC curve of form III with pre-existed form I' after CO_2 annealed shows four endothermic peaks at 85, 100, 117 and 128 °C, corresponding to the melting of form I', III, II and I, respectively. However, no melting peak at about 85 °C was detected before CO_2 treated, which mean that the pre-existed form I' in form III was mainly in an amorphous state, and the CO_2 could induce the crystallization of the amorphous form I' into a crystalline state. As shown in Figure 5, the DSC curves of form III with minority form I' after CO_2 treated shows a smaller form II melting peak than that in form III. Meanwhile, the change in the form I' chain packing state had a significant influence on the form II recrystallization. It was claimed that better packed polymer chain in form I' might inhibit the sudden evolution of polymer chain into form II. Thus, the form III with minority form I' after CO_2 treated have a smaller form II melting peak than that before CO_2 annealing.

The DSC endotherms of the form III with form I' annealed at 60 °C and 16 MPa for various time and that of form III annealed at the same conditions for 48 h are shown in Figure 6. In comparison the melting behavior of the form III with minority form I' annealed at 60 °C and 6 MPa for 48 h in Figure 5, the melting peak of form I' moved to a higher temperature. It related to the stronger CO_2 plasticization effect on the form I', which enhanced the polymer chain arrangement into a better packing. Furthermore, the form II melting peak area was substantially decreased in the DSC curve of form III with pre-existed form I' compared with the DSC curve of the pure form III annealed for the same time. It was claimed that the form II recrystallization is also suppressed by the existence of the pre-existed form I' at a higher pressure. And the inhibition effect of the pre-existed form I' on the form II recrystallization needs further investigation.

As shown in Figure 7, when form III with minority form I' annealed at 80 °C and 8 MPa for 5–48 h, the form II recrystalliza-

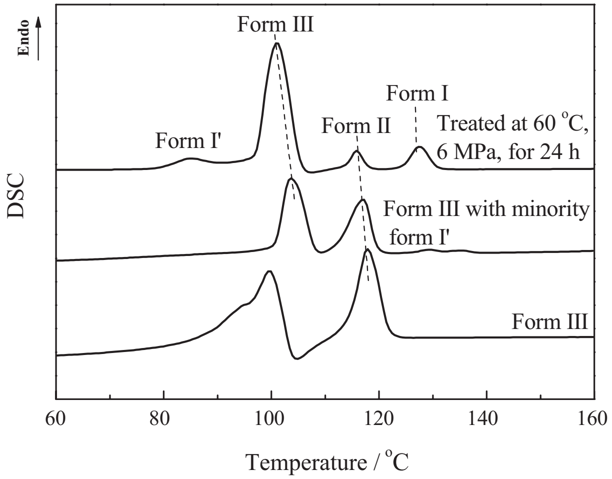

Figure 5.
DSC curves of form III with pre-existed minority form I' treated at 60 °C and 6 MPa for 48 hours.

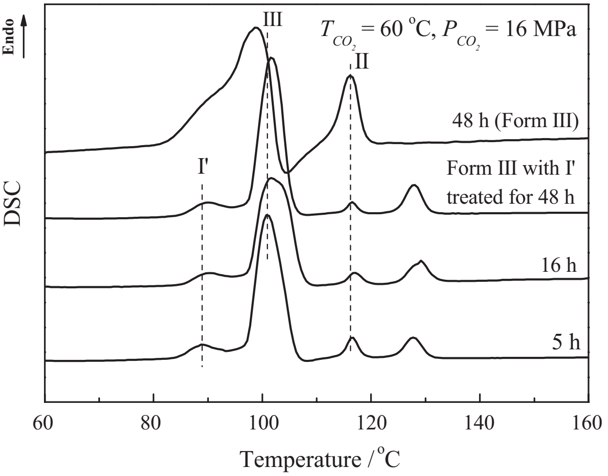

Figure 6.
Melting endotherms of form III with pre-existed minority form I' annealed at 60 °C and 16 MPa for various time.

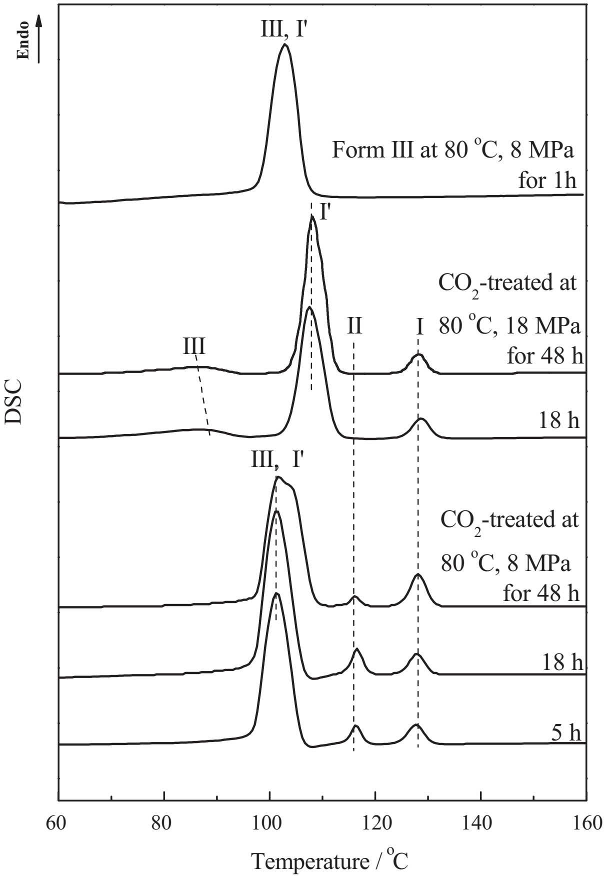

Figure 7.
DSC heating curves of form III and form III with pre-existed minority form I' annealed at 80 °C, 8 and 18 MPa for various time.

tions were also inhibited. Whereas, in the DSC curve of the form III after annealed at CO_2, no form II melting peak was detected. And when form III completely transformed into I' at 80 °C and 18 MPa in form III with pre-existed minority form I', the endothermic peaks corresponding to form II melting also disappeared. These results indicated that the form transition of form III into I' also suppressed the form II recrystallization. Furthermore, the effect of the phase transition on the inhibition of form II recrystallization was more significant than that of pre-existed form I', the effect of pre-existed form I' on the inhibition of form II recrystallization could be neglected.

Conclusion

High pressure DSC measurements revealed that CO_2 had a significant plasticization effect on the melting behavior of the sample that contained majority of form III with minority I'. The melting peak of form III moved to a lower temperature. The endothermic peak of form II that generated during the heating reduced with CO_2 pressure and no melting peak was observed when the CO_2 pressure above 4 MPa. By comparing the IR spectra of the form III with pre-existed form I' and pure form III annealed at 60 °C under 8 and 16 MPa, the pre-existed form I' inhibited the form III to I' transition, which was ascribed to the thermodynamic process of the phase transition. The inhibition of phase transition at 80 °C and 8 MPa might be due to the disturbed the first process of the phase transition. The pre-existed form I' also significantly suppressed the recrystallization of form II during the heating, but this inhibition effect was neglected when majority form III could transform into form I'.

Acknowledgements: The authors are grateful to the Shanghai Shuguang Project (08SG28), National Science Foundation of China (50703011), Shanghai Rising-Star Program (08QA1402200), Program for Changjiang Scholars and Innovative Research Team in University and the 111 Project (B08021).

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