

# TRANSFORMATION OF ISOTACTIC POLY-1-BUTENE FORM II TO FORM I UNDER SUBCRITICAL AND SUPRERCritical CO<sub>2</sub>

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**Abstract** The CO<sub>2</sub>-assisted transformation of isotactic poly-1-butene (iPB-1) unstable Form II to stable Form I was studied by the high pressure differential scanning calorimetry (DSC) and wide angle X-ray diffraction (WAXD). The results showed the CO<sub>2</sub> significantly accelerated the transformation. Under CO<sub>2</sub> atmosphere, the Form II transformed to Form I totally during the heating process when the pressure was higher than 6 MPa. At the same temperature condition, the higher pressure increased, the more Form II transformed to Form I. The in-situ high pressure fourier transform infrared spectroscopy (FTIR) was also applied to monitor the transformation process under CO<sub>2</sub> pressure. The results showed that the crystal form transformation complete in few minutes under the subcritical and supercritical CO<sub>2</sub>. The mechanism of the form transformation under CO<sub>2</sub> was analyzed by Avrami equation. The Avrami exponents demonstrated that the phase transformation mechanism at lower temperature under higher pressure is changed and at higher temperature under higher pressure the mechanism is not changed.

## Introduction

Isotactic poly-1-butene (iPB-1) has many outstanding properties including higher impact strength, flexibility, abrasion resistance, creep and pressure resistance compared to the other polyolefins[1]. It has five different crystal forms: I, II, III, I' and II'[2-6]. Form I and I' are the 3/1 helix conformations, Form II is the 11/3 helix conformation[7], and Form III is the 4/1 helix conformation. Form I' and Form II' can be obtained from crystallization from melt under high pressure. Form III is usually generated from the dilute solution in the certain solvent. The Form II (melting temperature: 110-120°C) crystallized from melt, and it can transform to Form I (melting temperature: 120-135°C). The crystal form transformation substantially enhances the polymer mechanical, thermal and physical properties. However, a main drawback of iPB-1 is the slow transformation kinetics of Form II to Form I [8, 9]. Completion of the transformation normally needs several days or weeks. How to accelerate the transformation had been studied by lots of methods [10-15].

Hydrostatic pressure could enhance the crystal transition. Nakafuku and Miyaki[16] studied the effect of pressure on the melting and crystallization behavior of iPB-1 under high hydrostatic pressure up to 5 Kbar. They reported above 900 bar Form II transform to Form I totally during the heating process. Kishore and Vasanthakumari[17] published a investigation of melting process of Form I in high pressure N<sub>2</sub> and Ar from atmospheric pressure to 0.07 kbar by DSC. In their study they only discussed the melting temperature decrease with the pressure increasing, they did not discuss the inert gas pressure on the crystal transformation to Form I.

However, there is no study on the effects of the sub- and supercritical CO<sub>2</sub> on the crystal form transformation. The purpose of this article is to study whether the CO<sub>2</sub> can accelerate the

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transformation or not. For this purpose DSC and WAXD measurements are used to detect the iPB samples before and after CO<sub>2</sub> treating. The second goal of this work is to recognize the effects of CO<sub>2</sub> pressure and temperature on the transformation process and further find the relationship between the CO<sub>2</sub> pressure and the half-time of the transformation. A high pressure in-situ infrared spectrum is used to trace the formation process of iPB-1. The Avrami equation is also applied to understand the form transformation mechanism.

## Experimental

*Materials.* iPB-1 (PB 0110M) used in this study was pellets obtained from Basell Polyolefins. The sample was purified by acetone at least 24 hours, and was dried in vacuum for 2 days at room temperature before used. The films of Form II for DSC and FTIR were prepared by melting the pellets at 160°C, then pressing, finally quenching in the liquid nitrogen.

*Wide Angle X-ray diffraction.* WAXD patterns were recorded by the Rigaku D/max 2550 VB/VC in the diffraction angular range 3-50° 2 $\theta$ . The scan rate was 1° ( $\theta$ )/min.

*High Pressure DSC measurements.* A NETZSCH 204 HP was used for the high pressure DSC measurements. The 5-10 mg samples were heated under CO<sub>2</sub> atmosphere from 30°C to 170°C. The heating rate of the DSC experiments was 10°C/min. N<sub>2</sub> was used for atmosphere DSC measurements. The heating rate and temperature range were also 10°C/min and from 30°C to 170°C.

*High pressure FTIR measurements.* For in-situ FTIR measurements a BRUKER EQUINOX-55 with a high pressure view cell (TFC-M13) were used. The FTIR spectral were collected by signal averaging 32 scans at a resolution of 4 cm<sup>-1</sup> in the wave number range of 4000-400 cm<sup>-1</sup>.

## Results and discussion

*Effect of CO<sub>2</sub> pressure on the crystal transformation.* Figure 1 shows the high pressure DSC measurements of melting process of iPB-1 Form II under different CO<sub>2</sub> pressure. As shown in Figure 1, there is only one endothermic peak in the curves under 0.1 and 0.5 MPa CO<sub>2</sub> atmosphere. However, under a higher pressure, 2 or 4 MPa, the other peak higher than the Form II melt peak appears. When the the CO<sub>2</sub> pressure is up to 5 MPa, only one peak exits on the DSC curve indicating Form II transform to Form I totally before melting. The results indicate that the crystal transformation can be accelerated by applying CO<sub>2</sub>.

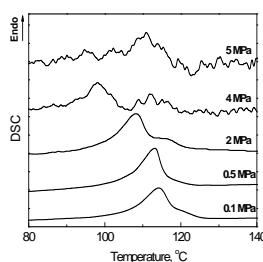


Fig.1 DSC scan measurements of iPB-1 Form II at different CO<sub>2</sub> pressures.

To investigate the effect of the pressure on the form transformation, the samples of Form II are annealed at 60°C under 5, 4 and 2 MPa for 4, 5 and 8 hours respectively. The WAXD

patterns and DSC curves of iPB-1 samples annealed under CO<sub>2</sub> and unannealed are shown in Figures 2 and 3. The WAXD pattern of Form I shows four major peaks in 9.9, 17.3, 20.2 and 20.5°[18-20]. For Form II it has three major peaks in 11.9, 16.9 and 18.4°[21, 22]. We can see that with the treated CO<sub>2</sub> pressure increasing the Form II characteristic peak decrease abruptly. From DSC curves we see clearly that after high pressure CO<sub>2</sub> treated no Form II melting peak exists. That means there is slight Form II in the samples that annealed after high pressure (4 MPa and 5 MPa) CO<sub>2</sub> treated. At the higher pressure (5MPa), the Form I that formed from sample annealed 4 hours is more than that annealed 5 hours at 4 MPa. It demonstrates that the pressure has a significant influence on the form transformation. Higher pressure CO<sub>2</sub> can accelerate the phase transition.

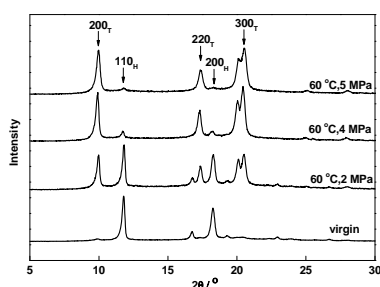


Fig. 2 WAXD patterns of virgin iPB-1 Form II and treated by CO<sub>2</sub> at 60°C under different pressure

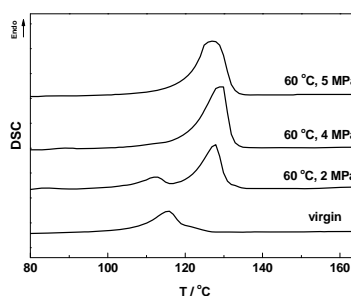


Fig.3 DSC melting scans of virgin iPB-1 Form II and treated by CO<sub>2</sub> at 60°C under different pressure

*In-situ FTIR measurements of the form transformation.* To better understand the crystal transformation, in-situ FTIR is used to detect the form transformation under high pressure CO<sub>2</sub>. There are distinct differences among the infrared spectra range in 750-950 cm<sup>-1</sup>. The 905 cm<sup>-1</sup> and 925 cm<sup>-1</sup> correspond to CH<sub>2</sub> and CH<sub>3</sub> rocking vibrations[23]. The band at 905 cm<sup>-1</sup> is known to be characteristic of form II and 925 is characteristic of Form I[24-27].

The form transition at 40°C under 4 MPa is shown in Figure 4. The absorbance of band at 905 cm<sup>-1</sup> reduces abruptly after the sample annealed in CO<sub>2</sub>. At the same time Form I generates rapidly as the absorbance of band at 925 cm<sup>-1</sup> is increasing. After the sample annealed 6 minutes, there is slight Form II in the sample as shown in the Figure 4.

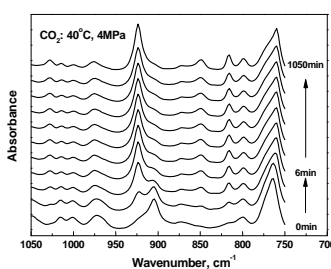


Fig. 4 Infrared spectra of iPB-1 form II during its CO<sub>2</sub> treatment at 60 and 6MPa

For both 905 cm<sup>-1</sup> and 925 cm<sup>-1</sup> correspond to CH<sub>2</sub> and CH<sub>3</sub> rocking vibration, we define the half time of the form transformation as Figure 5 shows.

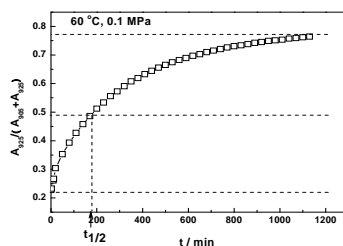


Fig. 5 The definition of  $t_{1/2}$

$A_{925}$  and  $A_{905}$  are peak areas of the band at  $925\text{ cm}^{-1}$  and  $905\text{ cm}^{-1}$ , respectively. The form transformation half time ( $t_{1/2}$ ) is defined as the characteristic band ( $925\text{ cm}^{-1}$ ) area of form I (corresponding to  $\text{CH}_2$  and  $\text{CH}_3$  rocking vibrations) changes to the half of the whole  $\text{CH}_2$  and  $\text{CH}_3$  rocking vibrations of the band ( $905\text{ cm}^{-1}$  and  $925\text{ cm}^{-1}$ ) areas.

The  $t_{1/2}$  at different temperature and pressure are shown in Figure 6.

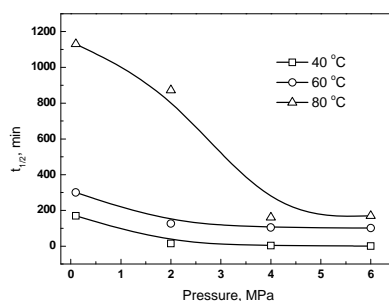


Fig. 6 The effect of  $\text{CO}_2$  pressure on  $t_{1/2}$  at different temperature

At  $40\text{ }^\circ\text{C}$  and  $60\text{ }^\circ\text{C}$  the effects of pressure on the  $t_{1/2}$  are similar. When the temperature is  $80\text{ }^\circ\text{C}$ , the pressure has a significant influence on the  $t_{1/2}$ . Higher pressure can substantially reduce the half time of the form transformation. This phenomenon also infers that higher pressure is favorable to the phase transition. The trend of the curve at  $80\text{ }^\circ\text{C}$  is different from the trends at  $40\text{ }^\circ\text{C}$  and  $60\text{ }^\circ\text{C}$ . Danusso and Gianotti[28] had reported that beyond  $65\text{ }^\circ\text{C}$  the form transformation was never observed under atmosphere and the polymorph might be in a true metastable state. The crystal transformation mechanism beyond this temperature must be different from that below this temperature.

*Analysis of form transformation kinetics using the Avrami Equation.* Many pervious studies have applied the Avrami equation to analyze the Form II to Form I form transformation in poly-1-butene[29-30]. We assume the degree of the crystal transformation,  $x$ , changes with time according to the equation:

$$1-x=\exp(-kt^n) \quad (1)$$

where the  $k$  and  $n$  are the rate constant and the Avrami exponent, respectively. Taking the logarithm of this equation twice gives:

$$\log[-\log(1-x)]=\log(k)+n\log(t) \quad (2)$$

$x$  is obtained from the infrared data and defined as

$$x=A_{925}/(A_{925}+A_{905}) \quad (3)$$

where the  $A_{925}$  and  $A_{905}$  are the infrared absorbance areas of the band at  $925\text{ cm}^{-1}$  and  $905\text{ cm}^{-1}$ , respectively.

Figures 7-10 show typical plots according to the equation (2). And the Avrami exponents of

the crystal transformation under CO<sub>2</sub> are shown in Table 1.

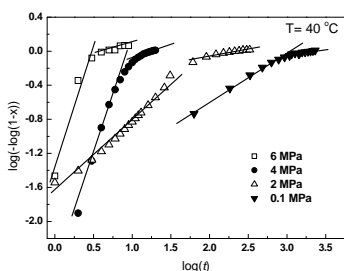


Fig. 7 Avrami's plot for the transformation at 40°C

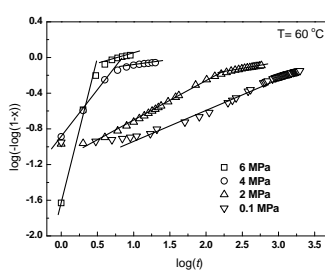


Fig.8 Avrami's plot for the transformation at 60°C

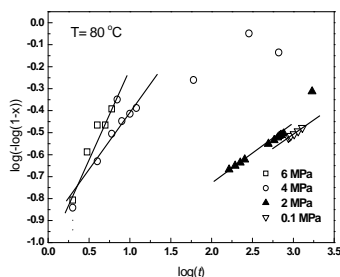


Fig. 9 Avrami's plot for the transformation at 80°C

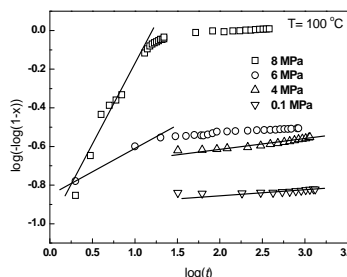


Fig. 10 Avrami's plot for the transformation at 100°C

Tab.1 Results of Avrami analysis of the Form II to Form I crystal transformation under CO<sub>2</sub>

| Temperature, °C | Avrami exponent n |         |         |         |         |
|-----------------|-------------------|---------|---------|---------|---------|
|                 | 8 MPa             | 6 MPa   | 4 MPa   | 2 MPa   | 0.1MPa  |
| 40              |                   | 3.08138 | 3.06719 | 0.83187 | 0.61703 |
| 60              |                   | 3.04276 | 0.98815 | 0.46514 | 0.41696 |
| 80              |                   | 1.14256 | 0.54723 | 0.2484  | 0.25267 |
| 100             | 0.98515           | 0.36943 | 0.0387  |         | 0.03682 |

Hong et al.[31] investigated the effect of certain processing variables on the Form II to Form I phase transformation in iPB-1. At room temperature they found the fact that n near to 1 mean that the transformation mechanism involved instantaneous (predetermined) nucleus formation and a one-dimensional growth process. Form the table 1 we can see clearly that at 40°C under higher pressure (6 MPa and 4 MPa) and at 60°C under 6 MPa the Avrami exponents nearly equal to 3. Such a value is in the more restricted range of the three-dimensional propagations of the transformation. At 80°C when the CO<sub>2</sub> pressure is 6MPa, the fact that n near to 1 means that the mechanism of the form transformation is same as the mechanism of iPB-1 at room temperature under atmosphere. The rapid phase transition under high pressure is not caused by the changing of the crystal transformation mechanism but by the molecular chain motion. Avrami exponents are decrease as the temperature increasing under the same pressure. This observation demonstrates that the increasing of the temperature can disturb the normal phase transformation. At 100°C the values of n are very small. The subcritical and supercritical CO<sub>2</sub> can change the phase transformation mechanism at lower temperature under higher pressure and enhance the phase transformation at higher temperature by increasing the molecular chain motion under higher pressure.

## Conclusions

In this work, the form transformation under subcritical, supercritical and low pressure CO<sub>2</sub> is studied. During the melting process of the Form II under higher pressure, Form II can

transform to Form I completely. After the samples of Form II annealed in CO<sub>2</sub> for certain hours, the CO<sub>2</sub> can promote the form transformation. The higher pressure the more Form II transformed to Form I. From the in situ FTIR measurement results, under sub- and supercritical CO<sub>2</sub> the Form II can transform to Form I completely in few minutes. The relationship between the half-time of the crystal transformation and the CO<sub>2</sub> temperature at same pressure is not the same. The phase transformation mechanism at different temperature under same pressure is not same. From the Avrami equation, the results demonstrate that at lower temperature under subcritical CO<sub>2</sub> the phase transformation is changed from a one-dimensional growth to a three-dimensional form growth process. And at higher temperature the phase transformation is disturbed, only under sub- and supercritical CO<sub>2</sub> the transformation can complete by increasing the molecular chain motion without changing the mechanism of the crystal transformation.

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