



Crystalline transformation of isotactic polybutene-1 in supercritical CO₂ studied by in-situ fourier transform infrared spectroscopy

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ABSTRACT

The solid-solid crystalline transformation of isotactic polybutene-1 (iPB-1) from tetragonal form II to hexagonal form I could be accelerated by supercritical carbon dioxide (scCO₂). In this study, in-situ Fourier transform infrared spectroscopy (FTIR) and two dimensional correlation spectroscopy (2DIR) is used to observe and investigate the crystallization behaviour of iPB in scCO₂ and compressed CO₂. Based on the transform sequence given by 2DIR analysis, this transformation of helical chain structures is found to be initiated with the motion of side chains and followed by the movement of main chains. It is speculated that the motion of polymer chains was enhanced with the diffusion of CO₂. Also this crystalline transition is observed even in compressed CO₂, suggesting that CO₂ could also diffused into polymer under high pressure near the critical pressure. This diffusion of CO₂ is indicated by the growth of IR bands being assigned to the stretching vibration of C–O. A further investigation on the mechanically heating and freely cooling of iPB provides more evidences on the process of structure transition. The result implies that the nucleus of tetragonal form II formed in the melt is not affected by the existence of scCO₂, but the crystallization temperature become obviously lower.

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1. Introduction

Isotactic polybutene-1 (iPB) is a semi-crystalline polymer with outstanding mechanical properties, such as high creep resistance, low stiffness, excellent impact behaviour and elastic recovery [1–3]. Three crystalline structures of isotactic polybutene-1 have been reported in previous literatures [2,4–12]. Among which the metastable tetragonal form II with 11/3 helical chains is formed during crystallization from melt at room temperature and atmospheric pressure, then it would transform into the stable twin hexagonal form I with 3/1 helical chains spontaneously even at room temperature [11,13]. However, this transition usually undergoes at a low rate, and will finish in several days or months [3,14].

Because the crystalline transformation from form II to form I significantly alters the properties of iPB-1, and brings a considerable enhancement of the mechanical properties such as stiffness, hardness and tensile strength [1–3], it is important to learn and control this structure transition well. Several researches were carried on to induce and accelerate this transformation by kinds of mechanical stimuli, such as pressure [12,15], stress [16] and shear [11,17].

However, these studies were mainly concentrated on the phenomenon observed about the crystallization of form II from melt and the following conformational transition from form II to form I. A few achievements were made on the study of the mechanism during the crystalline transition. Some researchers studied the crystallization of form II from the melt and the solid-solid transition of iPB from form II to form I upon ageing and provided some detailed information about changes taking place during this process [3,11–13,15]. Chau et al. suggested that the nucleation of the stable crystalline phase occurred shortly after crystallization from the melt and the subsequent growth of nuclei followed a rod-like geometry [13]. Jiang et al. concluded that nucleation of the iPB-1 stable Form I crystals was the rate-determining step of the Form II to I conversion and stacking regularity of the crystalline lamellae played a very important role in generating the nuclei of the Form I crystals, based on the obtained results from AFM through in situ melting processes [3]. Generally, it is commonly believed that the nucleation and growth of the transformation plays an important role in the birth of form II from melt, and the transformation from form II to form I is possibly kinetically driven.

Recently, supercritical fluid is also found to be a good choice for inducing solid-solid transitions of several semi-crystalline polyolefin with lower temperature and pressure [18–24]. DeSimone

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et al. investigated on solvent induced crystallization behaviour of poly(bisphenol A carbonate) and the influence impacted by reaction conditions, including temperature, pressure, processing period and particle size, in which supercritical CO₂ (scCO₂) played the role as a processing aid [25]. He et al. have carried out a series of researches on the crystalline change of syndiotactic polystyrene in scCO₂ [26,27]. ScCO₂ is recognized as a superior solvent to organic vapours and liquids ascribing to its remarkable properties [28–30]. It's safe, inexpensive and comparatively friendly to the environment, as well as it is easy to be removed by depressurizing which warrants its use in polymer processing. ScCO₂ is believed to be able to swell and plasticize amorphous polymers or the amorphous phase of semi-crystalline polymers [21–23]. Also it can reduce the glass transition temperatures or melting points of semi-crystalline polymers through reducing the energy barriers, thus the transformation may take place under lower temperature and pressure. This supercritical fluid induced process is always considered as solvent induced structure transition.

For investigation on the variation of microstructure of polymers, infrared spectroscopy is widely used in application. Zhu X Y et al. studied the crystalline transformation of iPP with in-situ Fourier transform infrared (FT-IR) spectroscopy [31,32]. It is feasible to characterize the polymer backbone conformation changes by time-resolved FTIR spectroscopy. Differently crystalline structures of iPB present distinguishing bands on IR spectra, and have been clearly studied and reported before [13,33–37].

Meanwhile, as a development in vibrational spectroscopy of recent years, generalized two dimensional correlated infrared spectroscopy (2DIR) can simplify complex spectra with overlapped peaks through spreading spectra peaks over the second dimension [38–41]. Isao Noda et al. have applied this technique on studying the pressure-induced and thermally-induced transition of polyethylene [42,43], which shows the possibility of introducing this novel method into our study on the mechanism of scCO₂ induced crystalline transformation of semi-crystalline polymers.

Li B and Li L et al. has observed and reported the scCO₂ inducing or accelerating crystalline transition of iPP and iPB with the help of several experimental techniques such as DSC, XRD and FTIR [18,19,24,44]. In this paper, we take advantage of the FTIR and 2DIR technology to evaluate the influence of high CO₂ pressure on crystallization behaviours of iPB-1 and propose a possible dynamic mechanism for this supercritical fluid accelerated transition.

2. Experimental

The isotactic polybutene-1 pellets (PB 0110 M) used in this study was kindly provided by Basell Polyolefins (now Lyondell-Basell). The molecular weight is 4.39×10^5 (M_w), and the melt index is 0.4 g/10 min (190 °C/2.16 kg). 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 before the experiments. And sample pellets were heated and pressed into film with ca. 0.5 mm thickness at 170 °C and 10 MPa for 30 min, in order to adjust the thermal history and for IR measurement. Then the sample films were quenched to room temperature by liquid nitrogen.

The IR spectra were collected by a Bruker Equinox-55 FTIR spectrometer at the resolution of 4.0 cm⁻¹. The experimental spectrometer was equipped with a Harrick high-pressure demountable liquid cell and a controlling thermocouple to provide sequences of time-dependent or temperature-dependent IR spectra under different pressure and temperature. Detail of this equipment was described elsewhere [44]. At experiments, sample films were sandwiched within a pair of ZnSe plates. The spectrum collecting was started up as soon as CO₂ was added and the pressure arrived at the expected value, which took for about half

a minute. Thermal behaviour of iPB was studied by mechanically heating, operated by hot stage with a temperature controller (accuracy was ± 0.5 °C). And the heating rate was set at 1 K/min.

2Dshige software developed by Dr. Shigeaki Morita (Kwansei-Gakuin University, Japan) was used to obtain generalized 2D spectra in certain spectra ranges. In the 2D correlation maps, the red-coloured regions are defined as the positive correlation intensities, whereas the blue-coloured ones are regarded as the negative correlation intensities. The slice spectra were also plotted by the 2D Shige software to explore the intensities of cross peak with no obvious representation on 2D maps.

3. Results and discussions

3.1. 1DIR study of the time-dependent crystallization of iPB in scCO₂

According to previous literature [34–36,45], the bands at 1328, 1260, 1152, 1098, 1060, 1027, 1014, 1000, 925, 845, 815 cm⁻¹ are assigned to the band vibration of form I, while the bands at 1151, 1111, 1049, 1001 cm⁻¹ are due to the vibration of crystalline form II [9,13]. In Fig. 1 the spectrum of iPB in air is compared with the spectrum obtained at the very beginning with scCO₂ treatment (20 °C, 8 MPa). The effect of scCO₂ doesn't exhibit on the spectrum at the very beginning. And it shows that the shape and location of IR bands of iPB is not affected by the presence of CO₂. Therefore it is feasible to study the solvent induced crystallization of iPB by in situ FTIR at this spectral range from 1170 to 770 cm⁻¹.

In the experimental operation, the time-dependent FTIR spectra were collected in the time interval of 1 min at the early time and every 30 min after this transformation slowing down. The range of 1170–790 cm⁻¹ on the spectra is chosen for further study, in which most of the bands have obvious variations. IR spectra collected at 100 °C and 8 MPa in the first 20 min are shown with respect to time in Fig. 2. The variations of intensities of IR absorption bands indicate that the existing amounts of corresponding crystalline structure changes greatly in scCO₂.

It is clearly that the bands represent form II (ie. 904 cm⁻¹) varies in the opposite direction with those of form I (ie. 923 cm⁻¹). The decrease of band 904 cm⁻¹ occurs simultaneously with the growth of 923 cm⁻¹ band and a “isosbestic point” is found between them, which suggests that the crystalline structure of the sample transits directly from form II to stable form I in a solid-solid transformation. Twenty minutes after the start of this experiment, the peaks representing form II almost disappear, which indicates that the transformation should complete in a rapid rate.

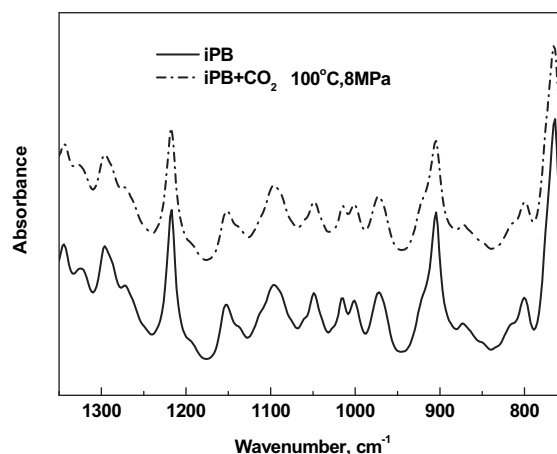


Fig. 1. IR spectra of iPB form II before and after treatment with scCO₂ at 100 °C, 8 MPa.

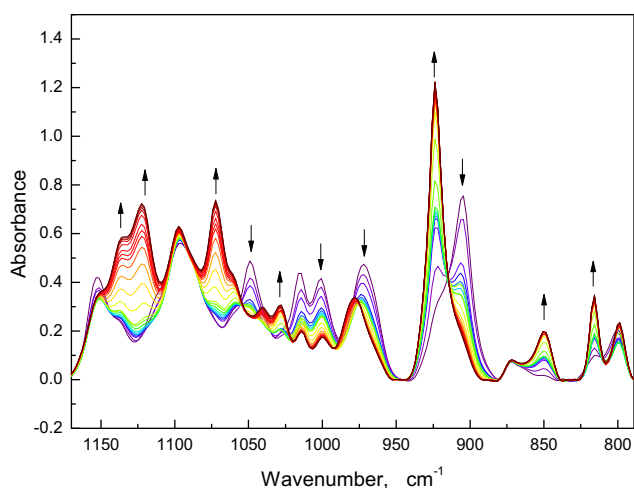


Fig. 2. The time-resolved IR spectra of isotactic polybutene-1 induced by scCO_2 (100 °C, 8 MPa) in the range of 1170–790 cm^{-1} in respect to processing time.

3.2. 2DIR study of the time-dependent crystallization of iPB in scCO_2

The 2D-IR correlation spectroscopy originally proposed by Isao Noda provides two kinds of spectra. 2D synchronous and 2D asynchronous spectrum could be obtained, which are characterized by two independent “wavenumber” axes (ν_1, ν_2) and a correlation intensity axis. Generally, the correlation intensity in the synchronous and asynchronous maps reflects the relative degree of in-phase and out-of phase response, respectively.

On synchronous spectra, peaks appearing on the diagonal are called “autopeaks” and their symbols are always positive. The intensity of autopeaks corresponds mathematically to the auto-correlation functions observed under environmental perturbations. Strong autopeaks may suggest that these regions of a spectrum change intensity to a great extent under a given perturbation. Off-diagonal peaks ($\Phi(\nu_1, \nu_2)$) are cross peaks, which may be positive or negative, and correspond mathematically to the coincidental changes of spectra intensity variations measured at ν_1 and ν_2 . Cross peaks with a positive symbol demonstrates that intensity variations of the two peaks at ν_1 and ν_2 take place in the same direction (both increase or decrease); while the negative cross peaks (the symbol of $\Phi(\nu_1, \nu_2)$ is negative) help to infer intensities of the two

peaks at ν_1 and ν_2 change in opposite directions (one increase, while the other one decrease) under environmental perturbation.

On asynchronous spectra, there are no autopeaks but only off-diagonal cross peaks, recorded as ($\Psi(\nu_1, \nu_2)$). The cross peaks appear only if the intensities of two spectral feature (ν_1, ν_2) change out of phase (delayed or accelerated). Sequential or successive changes of spectral intensities taking place under the environmental perturbation could be obtained through the considering of the symbols of the cross peaks both in synchronous and asynchronous maps. According to Noda’s rule [38,43,46], when $\Phi(\nu_1, \nu_2) > 0$, if $\Psi(\nu_1, \nu_2)$ is positive (red-coloured area), band ν_1 will vary prior to band ν_2 ; if $\Psi(\nu_1, \nu_2)$ is negative (blue-coloured area), band ν_1 will vary after ν_2 . However, this rule is reversed when $\Phi(\nu_1, \nu_2) < 0$. Be brief, if the symbols of the cross peak in the synchronous and asynchronous maps are the same (both positive or both negative), band ν_1 will vary prior to band ν_2 ; While if the symbols of the cross peak are different in the synchronous and asynchronous spectra (one positive, and the other one is negative), band ν_1 will vary after ν_2 under the environmental perturbation.

2D correlation contour maps in the region of 950–790 cm^{-1} of iPB collected in scCO_2 (100 °C, 8 MPa) and calculated by 2Dshige software are shown in Fig. 3, on which the areas coloured by red and blue represent positive and negative cross-peaks respectively. To reveal the transform sequence of these conformations, the symbols of cross peaks on synchronous and asynchronous maps are calculated by 2DIR and slice spectra, and shown in Table 1. In this analysis, slice spectra draw by Shige software are also helpful in observing cross peaks with no significant appearance.

Strong autopeaks are observed at 904 and 923 cm^{-1} in synchronous spectrum, indicating that those regions in the spectrum change intensity to a great extent under scCO_2 . Based on this observation, it is speculated that the corresponding molecular vibrations are both susceptible and undergo great changes with the environmental perturbation. Cross-peaks between band 904 cm^{-1} and all the other bands are observed negative, which supports the assignment that only the band 904 cm^{-1} represents the unstable form II, while all the others in the range 950–790 cm^{-1} should be assigned to crystalline form I.

Several cross peaks appear in the corresponding asynchronous spectrum: (923, 904), (923, 850), (923, 815), (904, 850) and (904, 815), possibly arising from the sequence of responses given by corresponding molecular vibrations towards the perturbation of supercritical fluid. To reveal the sequence of these conformations, we calculate the cross peaks among them by 2D maps and slice spectra, results of which are listed in Table 1.

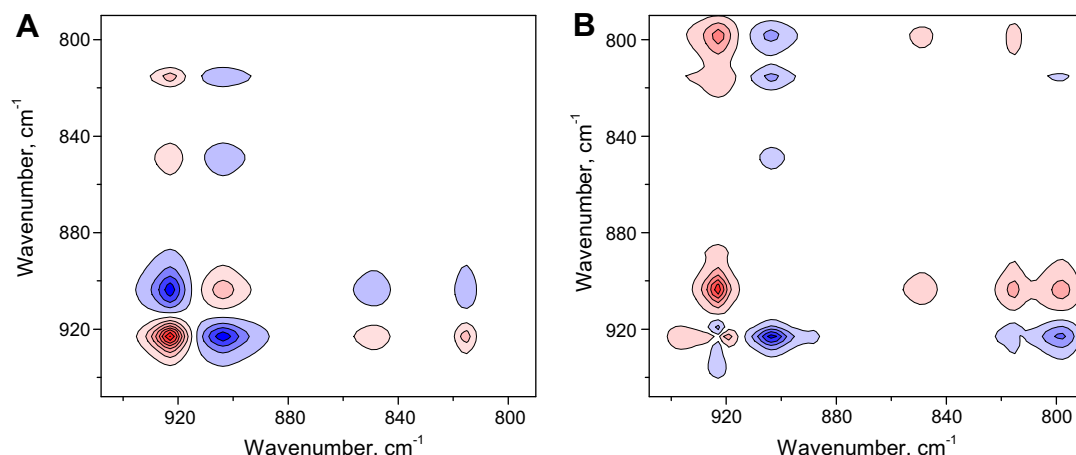


Fig. 3. 2D correlation contour map of iPB collected in scCO_2 (100 °C, 8 MPa) in the range of 950–790 cm^{-1} (A) synchronous spectrum, (B) asynchronous spectrum.

Table 1

Change Sequences within the region of 950–790 cm^{-1} , calculated from 2D maps and slice spectra of iPB during scCO_2 induced crystalline transformation process at 100 °C and 8 MPa.

$(\nu_1, \nu_2)/\text{cm}^{-1}$	Synchronous	Asynchronous	Sequence/ cm^{-1}
(923, 904)	–	+	904 → 923
(923, 850)	+	–	850 → 923
(923, 815)	+	+	923 → 815
(904, 850)	–	–	904 → 850
(904, 815)	–	–	904 → 815
904 → 923 cm^{-1} ; 850 → 923 → 815 cm^{-1}			
CH ₃ rocking and CH ₂ twisting of iPB form II → CH ₃ rocking and CH ₂ twisting of iPB form I;			
CH ₃ rocking → CH ₃ rocking and CH ₂ twisting of iPB → CH ₂ rocking and CC symmetric vibration			

Based on the results listed in Table 1, the transform order of these peaks is discerned as 904 → 923 cm^{-1} ; 850 → 923 → 815 cm^{-1} (the arrow “→” means “changes prior to”). And it is noted from the present literatures [34,37] that 904 cm^{-1} refers to the CH₃ rocking and CH₂ twisting of iPB form II, while 923 cm^{-1} represents CH₃ rocking and CH₂ twisting of iPB form I. 850 and 815 cm^{-1} should be respectively assigned to CH₃ rocking and CC symmetric vibration. Considering both the sequence and peak assignments, it is concluded that the motion of side-chain (CH₃ group) is initiated at first and then lead the twisting of main-chain, finally molecular vibration of the C–C structure responds to the

perturbation. This sequence implies how the helical crystalline transformation of this polymer changes within twenty minutes in scCO_2 .

Seen from the previous studies, the transition of form II to I involves a change in the chain conformation and requires an elongation of the helix from 0.187 to 0.217 nm per chemical repeat unit [14,47]. It is commonly believed that the motion of chains plays an important role in conformational transition and the dynamical conformational disorder. Nakafuku and Miyaki suggested that low overall degree of order and inclusion of defects into the crystalline lattice favoured the formation of the most stable structure [15]. The 2DIR analysis in our study supports their conclusion. It is speculated that the diffusion and sorption of scCO_2 into polymer chains induces the motion of side-chains and thus provides free volume for the twisting of main-chains, which ensures the occurrence of helical transformation.

For a further analysis, 2D correlation contour maps in the region of 1176–946 cm^{-1} are also calculated by 2Dshige software and shown in Fig. 4. These IR absorption bands present a intricate variation in 1DIR, however, it is easy to trace the characteristic change of these peaks in 2DIR. The symbol of the production calculated from intensities of cross peaks both from synchronous and asynchronous maps is recorded in Table 2.

Fig. 4 (A)(B) are the synchronous and asynchronous maps for two spectra ranges. From the symbols of cross peaks, it is summarized that the intensities of peaks at 1049, 968, 1002 cm^{-1}

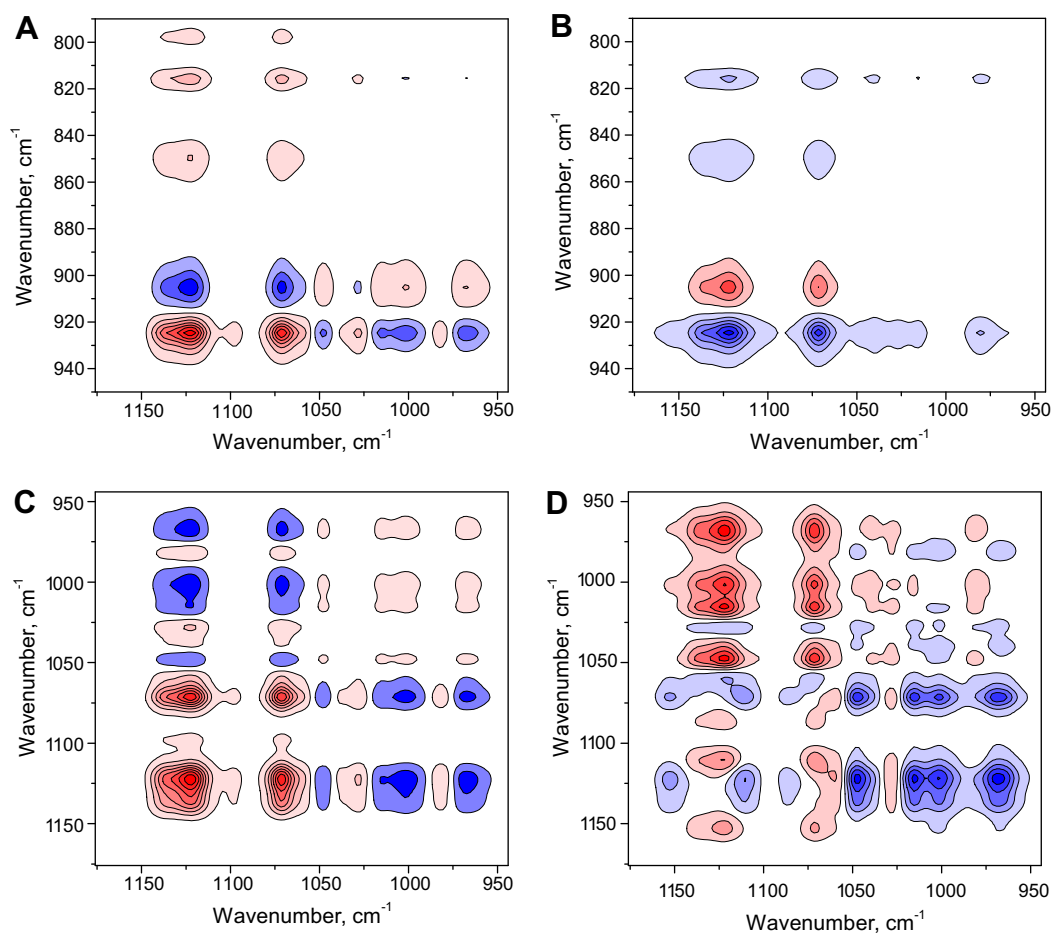


Fig. 4. 2D correlation contour maps calculated by 2DIR, based on 1D time-dependent FTIR spectra which is focus on the crystalline transformation of iPB collected in scCO_2 (100 °C, 8 MPa): synchronous spectrum in the range of (A) 950–790 cm^{-1} vs 1170–950 cm^{-1} , (C) 1170–950 cm^{-1} , and asynchronous spectrum in the range of (B) 950–790 cm^{-1} vs 1170–950 cm^{-1} , (D) 1170–950 cm^{-1} .

Table 2

Symbol of the production of the intensities calculated for the cross peaks both from 2D synchronous and asynchronous maps, during scCO₂ induced crystalline transformation processing at 100 °C and 8 MPa.

v1\v2	1135	1122	1072	1049	1029	1002	983
904	–	–	–	+	–	–	–
923	–	–	–	+	–	+	+
968	–	–	–	+	–	–	–
983	+	+	+	+	+	+	–
1002	–	–	–	+	–	–	–
1029	–	–	–	+	–	–	–
1049	–	–	–	–	–	–	–
1072	–	–	–	–	–	–	–
1122	+	–	–	–	–	–	–
1049 → 904 → 968 → 1002 → 923 → 1029 → 1072 → 1135 → 1122 → 983 cm ⁻¹							
Molecular vibration of crystalline form II → Molecular vibration of crystalline form I → stretching vibration of C–O in scCO ₂							

change in the same direction and in-phase with the peak at 904 cm⁻¹, thus could be assigned to the crystalline structure of form II, while band at 1029 cm⁻¹ has the same behaviour with 923 cm⁻¹ band. However, the intensities of 1072, 1135 and 1122 cm⁻¹ changed in the same direction but out-phase with both 904 and 923 cm⁻¹, which was probably arising from the stretching vibration of C–O in scCO₂.

The transform order of peaks in the overall range from 1176 to 780 cm⁻¹ is listed in Table 2. It is clearly noted from the sequence that in the crystalline region, IR bands representing unstable form II converses into those of stable form I and then scCO₂ keep on diffusing into the free volume of polymer chains.

3.3. 1DIR study of the thermally crystalline transformation of iPB-1 in scCO₂

To validate that the structure transition is induced by the diffusion of CO₂ and mainly caused by the motion of polymer chains, the thermally behaviour of unstable crystalline form II in supercritical CO₂ is also studied in a further step. Isotactic polybutene with crystalline structure form II is heated at a fixed rate of 1 °C/min from room temperature to 170 °C and then freely cooled. Fig. 5 is the IR spectra in the range of 950–780 cm⁻¹ obtained during this process in CO₂ with a pressure at 8 MPa.

From the IR spectra, it is observed that the sample undergoes a successive change of crystalline structure both with the increase

and decrease of temperature. Once being surrounded by supercritical CO₂ of 8 MPa, the crystalline transition starts since the very beginning, and will finish in a few minutes. Around 140 °C, the shape of IR bands representing the crystalline structure turns into a broad peak, implying that the melting behaviour of iPB occurs. This temperature well matches the melt point of form I recorded in the references [13,48,49].

During the freely cooling, IR bands referred to the crystalline structure form II appear at about 60 °C, and turn into characteristic bands of form I immediately, which could be seen from Fig. 5 (B). It seems that the existence of scCO₂ has little effect on the kind of nucleus formed in the melt, so that it is still tetragonal form II that grows from the melt. But it has a remarkable influence on the transition from form II to form I. This transition in freely cooling could be finished in a few minutes. At the same time, the crystallization temperature is found at about 60 °C. The decrease of crystallization temperature, compared to 90 °C obtained in the same kind of experiments without scCO₂, strongly suggests that the motion of polymer chains is enhanced, which is in agreement with the speculations mentioned above.

A heating-cooling-heating operation is also taken, and almost the same phenomenon is obtained except the structure transition doesn't happen at the reheating process because it has already been form I at the second beginning, which implies the reversibility of the transformations.

3.4. 1DIR study of the time-dependent crystallization of iPB in compressed CO₂

This CO₂ induced crystalline transformation is also observed within compressed CO₂. Above we propose that the influence of scCO₂ on solid-solid transformation of polymers mainly arises from the diffusion of CO₂ and the following enhanced movements of polymer chains. It is further speculated that the diffusion of CO₂ into polymer takes place not only in scCO₂, but also in compressed CO₂ with pressure near the critical pressure(7.38 MPa). This speculation is validated by the growth of IR bands at 1072, 1135 and 1122 cm⁻¹, which is assigned to the stretching vibration of C–O in scCO₂. The reference spectrum of pure scCO₂ (40 °C, 12 MPa) in the spectrum region of 1170–900 cm⁻¹ is provided in Fig. 6, which supports the assignment.

Fig. 7 compares the IR spectra collected under 40 °C with different pressures and in scCO₂. Obviously, the diffusion of CO₂ is observed in experiments with higher pressure. And the rate of transformation from form II to form I is evidently increased with

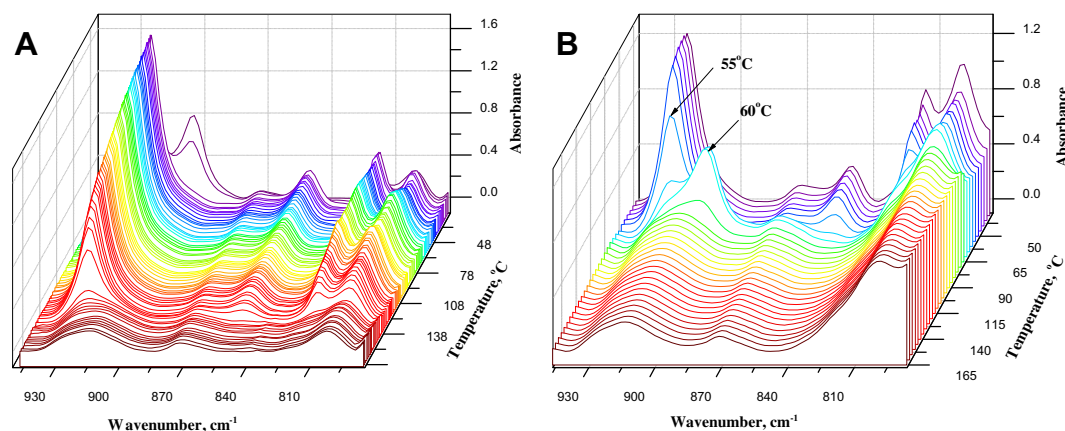


Fig. 5. The IR spectra of isotactic polybutene-1 from 950 to 780 cm⁻¹ in CO₂ (8 MPa) (A) 1D temperature dependent spectra from 20 to 160 °C at the rate of 1 °C/min. (B) 1D temperature dependent spectra from 165 to 30 °C during freely cooling.

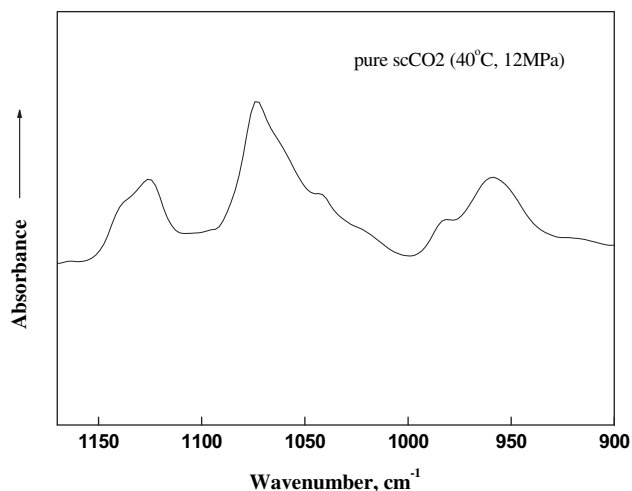


Fig. 6. Reference spectrum of pure scCO₂ (40 °C, 12 MPa) in the spectrum region of 1170–900 cm⁻¹.

the increment of pressure. It is suspected that the diffusion of CO₂ into polymer even takes place under pressures slightly below the critical pressure, and induces the crystalline transformation consequently.

In a further step, the effect of pressure on the crystalline transformation of iPB is discussed. Experiments were carried on under different pressure (ambience, 2, 4 and 6 MPa) but at a fixed

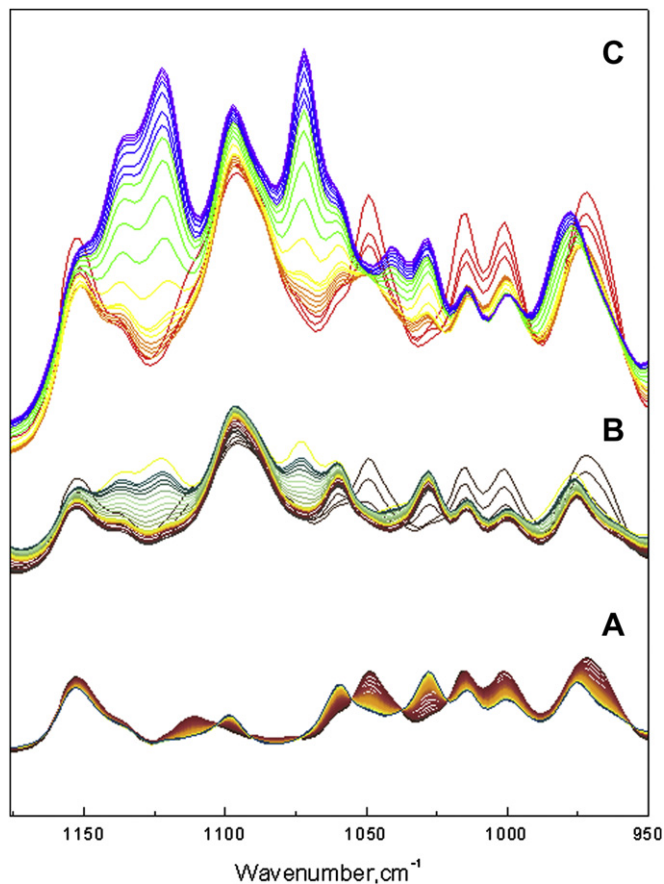


Fig. 7. Time-dependent IR spectra of iPB collected in the region of 1176–950 cm⁻¹ under different experimental condition (A) for 2542 min in CO₂ at 40 °C, ambience; (B) for 355 min in CO₂ at 40 °C, 6 MPa; (C) for 22 min in CO₂ at 100 °C, 8 MPa.

temperature (40, 60 and 80 °C). From the experimental results, it is noted that the crystalline transformation completes in shorter time when the pressure is higher. Take the series of experiments at 40 °C for example, the transition finished in 20 min in compressed CO₂ of 6 MPa, while at 2 MPa this transition only carried through a little in one day. This experimental result coincides with the statement given above. With higher pressure, the motion of polymer chains is even more enhanced, and thus speeds up the process of crystalline transformation.

4. Conclusion

FTIR and 2DIR was applied into the investigation of scCO₂ induced crystalline transformation of isotactic polybutene. The structure transition was found to be accelerated in scCO₂ or compressed CO₂, together with the diffusion and sorption of CO₂.

2DIR correlation spectroscopy technique revealed that the variation in the intensity of the band at 904 cm⁻¹ proceeded in prior to that of the band at 923 cm⁻¹, and 850 cm⁻¹ occurred in prior to those of the bands at 923 and 815 cm⁻¹. From this sequence, it is speculated that the structure transition from form II to form I starts with the motion of side chains, which goes along with the diffusion and sorption of CO₂ into the free volume of polymer. Subsequently, the main chains twist and complete the forming of the other kind of helical chain structure. In 1DIR, unstable crystalline form II turned into stable form I directly, without any mediate states, and we believed that the motion of polymer chains played an important part in the crystalline transition induced by scCO₂.

The diffusion of CO₂ was discerned by the growth of IR bands assigned to νC–O in 1DIR. Also, these IR bands were also found in compressed CO₂ with pressure slightly below the critical pressure. It provided an explanation for the occurrence of transformation from form II to form I even in compressed CO₂, that the diffusion of CO₂ enhanced the motion of polymer chains. In supercritical state, the diffusibility of CO₂ was improved, as well as the speed of the structure transition in polymers.

These speculations are further proved by the experiments of mechanically heating and freely cooling of unstable form II. It is noted unstable form II grows from the melt, showing that the kind of nucleus formed in the melt was not altered by the presence of scCO₂. However, the motion of polymer chains was enhanced, which is confirmed by the decrease of crystalline temperature in scCO₂ compared with that obtained in compressed CO₂ or in the air.

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