

Differential Polymorphic Transformation Behavior of Polybutene-1 with Multiple Isotactic Sequences

Ya-Ping Ma, Wei-Ping Zheng, Chen-Guang Liu, Hua-Feng Shao, Hua-Rong Nie*, and Ai-Hua He*

Shandong Provincial Key Laboratory of Olefin Catalysis and Polymerization, Key Laboratory of Rubber-Plastics (Ministry of Education), Qingdao University of Science and Technology, Qingdao 266042, China

Abstract For the solid-solid transformation from form II to form I of isotactic polybutene-1 (iPB), the temperature dependence of form I nucleation and growth was deemed to control the transformation process. However, the relationship between form I formation and form II disappearance in the transformation process is not clear. In this work, the spontaneous crystal transformation from form II to I of iPB with 81 mol% mmmm sequence concentration is studied firstly by tracking the two processes, the decay of form II and the yielding of form I in a wide range of temperature spanning from 0 °C to 50 °C and in a long transformation time ranging from 5 min to 65 days with *in situ* FTIR and WAXD. Unlike the literature reports, the decay rate of form II is firstly found to be lower than the yielding rate of form I at all studied temperatures, especially at low transition temperature. This is attributed to the amorphous chains which locate near crystal lamella participating into the nucleation of form II. The regular chain folding and growth of iPB form I from amorphous chains containing short isotactic sequences also lead to an increase in crystallinity of form I compared with that of initial form II crystallized at 60 °C. An increase in the annealing temperature results in decrease in crystallinity and increase in lamellae thickness of iPB form I.

Keywords Polybutene-1; Polymorphic transformation; Isotactic sequence; Crystallinity; Lamellae thickness

Citation: Ma, Y. P.; Zheng, W. P.; Liu, C. G.; Shao, H. F.; Nie, H. R.; He, A. H. Differential polymorphic transformation behavior of polybutene-1 with multiple isotactic sequences. *Chinese J. Polym. Sci.* 2020, 38, 164–173.

INTRODUCTION

Isotactic polybutene-1 (iPB) with superior creep resistance, toughness, and modulus at high temperature has attracted great attention for hot water pipes.^[1] A striking feature of iPB that arouses research interest but also causes trouble in utilization is the spontaneous but slow crystal transition from metastable form II to stable form I in solid state.^[2–8] The transition leads to irreversible changes in physical properties, including not only the good profits, like the enhanced hardness, stiffness, and strength, but also the bad results, like shrinkage of the molded objects.^[1,9–11] Work to date from research groups has been carried out to accelerate the transition^[12–20] and understand the kinetics of the process.^[21–24]

Form I crystal of iPB, the thermodynamically stable one, is a twined hexagonal/trigonal form with 3/1 helix, and tetragonal form II, the metastable one, is an 11/3 helix.^[25–27] The spontaneous transformation (II to I) has been reported to be temperature and time dependent,^[28–30] and the formation of form I is a nucleation controlled process.^[31,32] A rapid transformation has been observed at room temperature.^[33–35] Low

temperature (–20 °C) contributes to fast nucleation of form I while high temperature (+20 °C) favors rapid growth of form I.^[36,37] Therefore, a previous nucleation at low temperature prior to annealing at high temperature enables a rapid transition.^[22]

Unlike the melting crystallization where chain segments pull out of the disordered melt and sequentially attach to the growth front, the formation of form I *via* solid-solid crystal transition just involves a local fine tune of chain segments,^[38] progressing as the rearrangements of lamellae and lamellar stacks.^[21] Under such transition conditions, form I nuclei are sometimes found to appear on the twisting point of lamellae in form II crystal, and a few form I crystals could form within one form II crystal.^[39] The difference in thermal expansion coefficients between crystalline lamellae and amorphous phase leads to the occurrence of internal stress, which was considered to induce the nucleation of form I.^[37] When temperature is above glass transition temperature, the chain segments in amorphous region, including the defects in chain-folded structure, tie molecules, chain entanglements, *etc.*, are still in motion.^[36] It is found that faster nucleation of form I occurs in iPB with high molecular weights due to the existence of more tie molecules.^[23] However, the movements of crystal form II was limited by intercrystalline links and entanglements in high molar mass iPB samples, and thus the transformation from metastable form II to form I was retarded.^[40]

* Corresponding authors, E-mail: niehual@qust.edu.cn (H.R.N.)
E-mail: ahhe@qust.edu.cn, aihuah@iccas.ac.cn (A.H.H.)

Received May 16, 2019; Accepted July 19, 2019; Published online October 6, 2019

Nevertheless, polymer molecules with different regularities allow chains to pack in different degrees of tightness, so *i*PB copolymers show different crystallization behaviors and transition processes.^[41–46] Notably, the kinetic controlled crystallization process may let some chains less folded during the primary formation of form II. Prolonging the crystallization time or changing the crystallization conditions, amorphous chains which locate near the interface between amorphous and crystal lamella are constrained by two phases and may crystallize under some external driving force.^[41] So far, however, the temperature dependence of the amorphous chains has not been taken into account in the solid transition.

In order to understand the transformation process deeply, both stages including form II vanishing and form I formation were instantaneously tracked at constant annealing temperature ranging from 0 °C to 50 °C in a long transformation time ranging from 5 min to 65 days. *In situ* FTIR, WAXD, DSC, and SAXS are used to clarify the dependence of transition process on time and temperature. Recruiting amorphous chains to form I crystallization is firstly observed in the solid crystal transition process, which leads to the inconsistency between the decay rate of form II and the yielding rate of form I. The crystallinities of form I decreased with the increasing annealing temperature while lamellar thickness increased. Hopefully, this study will give a plentiful understanding on phase transformation of *i*PB which benefits the enrichment of current crystal transition theory to guide the application of *i*PB materials.

EXPERIMENTAL

Materials

Isotactic polybutene-1 (*i*PB) (isotacticity from boiling ether extraction: 97.7 wt%, $M_w = 548 \text{ kg}\cdot\text{mol}^{-1}$, PDI = 3.9 (obtained by GPC), melt flow rate (MFR, 190 °C, 2.16 kg): 4.32 g/10min) was kindly supplied by Shandong Dongfang Hongye Chemical Co., Ltd. China.

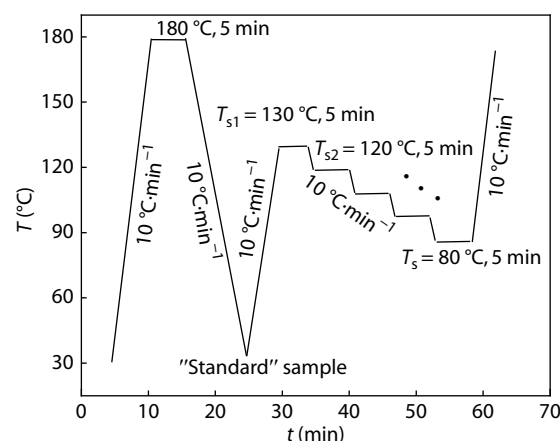
Sample Preparation

The *i*PB sample was compression molded at 180 °C under 16 MPa for 5 min to obtain the designed film with 100 μm in thickness. As-obtained *i*PB films with dimensions of 10 mm $\times$ 10 mm were melted at 180 °C for 5 min to erase thermal history, and then cooled to 60 °C for 5 min to assure the complete isothermal crystallization of *i*PB for the collection of form II. Subsequently, the temperature dropped from 60 °C to the given annealing temperature ranged from 0 °C to 50 °C at a cooling rate of 50 °C $\cdot\text{min}^{-1}$ for different time. The crystallinity and crystal structure of form II at different temperatures when samples were cooled from 60 °C to the selected annealing temperature and of form I after *i*PB underwent 65 days of crystal transition at the selected annealing temperature were measured.

Structure Characterization and Stepwise Crystallization (SC) of *i*PB

Structure characterization of *i*PB was conducted by ^{13}C -NMR measurement with a Bruker AVANCE III spectrometer at 120 °C with 1,2-dichlorobenzene- d_4 as solvent. The SC measurement was performed using a differential scanning calorimeter (DSC-8500, Perkin Elmer) according to the following procedure: (1) About 5–10 mg of sample sealed in an aluminum pan was melt-

ed at 180 °C for 5 min to erase thermal history prior to cooling to 30 °C at a rate of 10 °C $\cdot\text{min}^{-1}$ to create an initial "standard" crystalline process; (2) The "standard" sample was heated to a prescribed first stepwise crystallization temperature ($T_{s1} = 130$ °C) at a rate of 10 °C $\cdot\text{min}^{-1}$ and kept at that temperature for 5 min; (3) The sample was subsequently cooled to the second stepwise crystallization temperature ($T_{s2} = 120$ °C) at a rate of 10 °C $\cdot\text{min}^{-1}$ and isothermally maintained at this temperature for 5 min; (4) The above procedures were repeated at intervals of 10 °C till the temperature reached 80 °C. Finally, the sample was heated to 180 °C at a rate of 10 °C $\cdot\text{min}^{-1}$, and the endothermic curve of sample was recorded.^[47] The main thermal protocols are present in Scheme 1.



Scheme 1 SC thermal profiles of *i*PB.

The *in situ* FTIR spectra of samples were recorded on a Bruker VERTEX 70 FTIR spectrometer from 400 cm^{-1} to 4000 cm^{-1} at a resolution of 4 cm^{-1} with 32 scans. The sample stage was assembled with a thermostat to control the sample temperature.

WAXD analysis was operated on a Rigaku/XRD-Utima IV device using Cu K α radiation ($\lambda = 0.154 \text{ nm}$) at a generator voltage of 40 kV and a current of 40 mA. All measurements were conducted at the selective time. The form I diffraction peaks of *i*PB corresponding to crystallographic planes of (110), (300), and (220 + 211) can be observed at 2θ of about 10.0°, 17.5°, and 20.4°, respectively. The form II diffraction peaks at 12.0°, 16.9°, and 18.5° can be assigned to the (200), (220), and (213) lattice planes of crystalline structure of *i*PB, respectively. The crystallinity of the transformed form I (X_{cI}) was calculated from the ratio of total intensity of form I crystal to that of the total scattering including the amorphous background areas.

The crystallinity of *i*PB sample was measured on a differential scanning calorimeter (DSC-8500, Perkin Elmer). Samples that were obtained after 65 days of transformation at different temperatures were heated to 180 °C at a rate of 10 °C $\cdot\text{min}^{-1}$ to record the melting curves of form I. Subsequently, all melting samples were isothermally maintained at 180 °C for 5 min prior to cooling to 60 °C at a rate of 10 °C $\cdot\text{min}^{-1}$ and maintained at this temperature for 5 min for a complete isothermal crystallization to obtain form II. Next, samples continued to cool to the annealing temperature (0–50 °C) at a cooling rate of 50 °C $\cdot\text{min}^{-1}$ prior to heating to

180 °C at a rate of 10 °C·min⁻¹ to obtain the melting curves of form II. All measurements were performed under a nitrogen atmosphere with a flow rate of 50 mL·min⁻¹.

The small-angle X-ray scattering (SAXS) technique (Xeuss of Xenocs, France) was used to measure the long spacing d_{ac} , crystalline lamellar thickness d_c , and amorphous layer thickness d_a of form I crystals which were analyzed at room temperature after 65 days of transformation at different annealing temperatures. The distance of sample-to-detector was 2430 mm, the wavelength of X-ray was 0.154 nm, and each pattern was collected within 3600 s, which was then background corrected and normalized using the standard procedure. The fitting electron density correlation function $K(z)$ can be derived from the inverse Fourier transformation of the experimental intensity distribution $I(q)$ as follows:^[48,49]

$$K(z) = \frac{\int_0^\infty I(q)q^2 \cos(qz) dq}{\int_0^\infty I(q)q^2 dq} \quad (1)$$

where z denotes the location measured along a trajectory normal to the lamellar surfaces, and the multiplication of $I(q)$ with q^2 (Lorentz correction) was performed. Specific structural parameters d_{ac} , d_a , and d_c were calculated via the correlation function.

RESULTS AND DISCUSSION

Chain Structure Characterization and Stepwise Crystallization (SC) of *i*PB

¹³C-NMR spectroscopy was used to characterize the chain sequence structure of *i*PB. As shown in Fig. 1(A), the concentration of mmmm pentad sequences of *i*PB based on the signal at 27.5 ppm assigned to CH₂ is 81 mol%,^[50] and the total concentration of mmmr/rmmr/mmmr/mmmr/rmmr/rmmr/rrrr/mrrr/mrrm sequences of *i*PB with relatively high stereoregular defects is about 19 mol%, which indicate the existence of short isotactic sequences in the *i*PB chains.

As an effective method for analyzing the crystalline segments of polymer sample, stepwise crystallization (SC) procedure was used to analyze *i*PB crystalline segments that have different thermodynamic stabilities.^[47] For the employed *i*PB, multiple melting peaks are observed, and each endothermic peak represents a population of crystals (Fig. 1B).^[51] This indicates that *i*PB consists of different crystalline domains. The strong melting peak at high temperature of 118.3 °C arises from the relatively perfect crystalline domains containing relatively long isotactic sequences of *i*PB. On the other hand, the melting peaks at low temperatures of 112.2 and 106.1 °C originate from those crystalline domains with more crystalline defects, which are attributed to the crystallization from relatively short isotactic sequence of *i*PB. It is expected that *i*PB with multiple isotactic sequence segments should receive a systematic view for the understanding of crystal transition in solid state.

In Situ FTIR

FTIR is a facile and effective technique to monitor the changes in form II and form I of *i*PB based on their characteristic adsorption bands at 905 and 925 cm⁻¹, respectively.^[17,28] Especially, the FTIR equipped with thermostat is well suitable for *in situ* observation of the dependency of *i*PB crystal transition on time and temperature. Samples labeled with 0 h refer to those consisting of only crystal form II after isothermal crystallization at

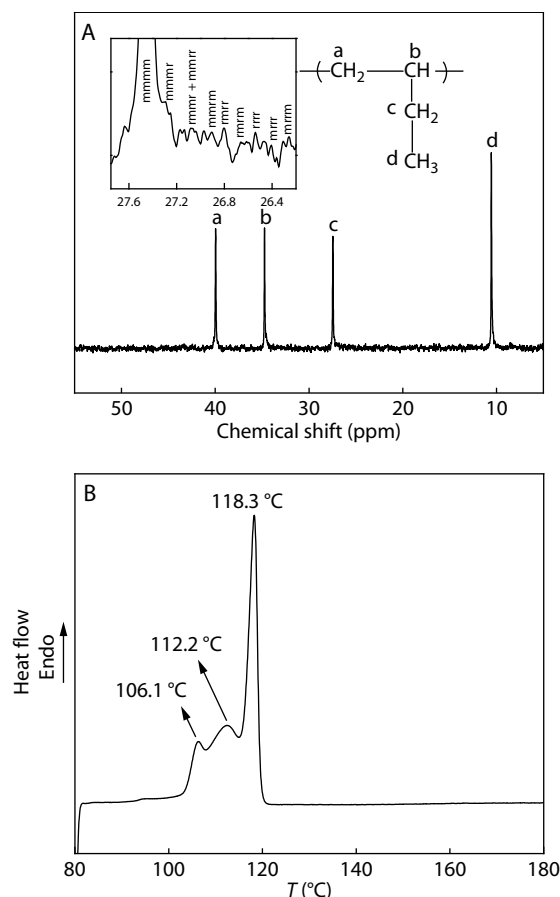


Fig. 1 (A) ¹³C-NMR spectrum and (B) DSC thermal curve after SC treatment of *i*PB.

60 °C. The other samples labeled with different time are those having been annealed for the selective time at given temperatures. Because of the existence of crystal form II, a sharp band at 905 cm⁻¹ is conspicuously observed when samples are cooled from melt (Fig. 2). With the spontaneous transition (II to I) at different temperatures, a tiny band at 925 cm⁻¹ appears and becomes stronger, while the ones at 905 cm⁻¹ gradually disappear with annealing time increasing. Obviously, the band at 925 cm⁻¹ first reaches a high value at 25 °C and then levels off ahead of other temperatures.

The band at 1152 cm⁻¹ remains unchanged during crystal transition, and the peak height ratios of H_{905}/H_{1152} and H_{925}/H_{1152} denoted as H_{II}/H_C and H_I/H_C can therefore express the variations of crystal form II and form I, respectively.^[52] As shown in Figs. 3(a) and 3(b), no matter what the annealing temperature is, all samples exhibit a sharp decrease in H_{II}/H_C and a prompt increase in H_I/H_C in the early stage of transformation. Although the H_{II}/H_C gap for samples annealed at different temperatures is small in the first 150 h, the value drops faster when samples are annealed at 25, 10, and 35 °C, and relatively slowly when samples are annealed at 0 and 50 °C. The H_{II}/H_C values of samples that are annealed at 25, 10, and 0 °C reach nearly zero after 600 h annealing, while that of the sample annealed at 50 °C is still high after 1300 h annealing. Notably, form I being absent in the sample annealed at 50 °C for 24 h indicates the difficult nucleation of form I. In the first

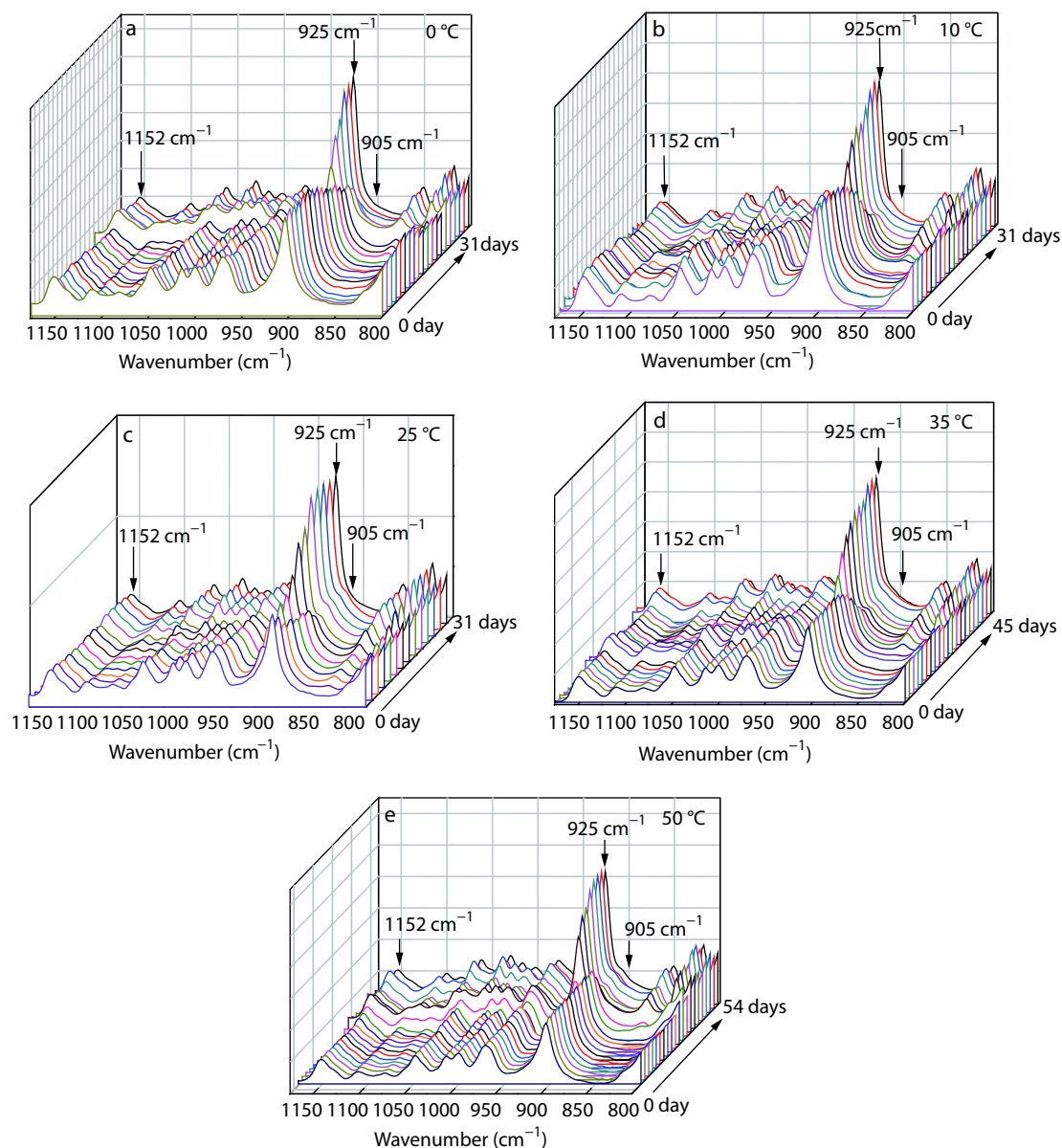


Fig. 2 FTIR spectra of *i*PB samples annealed at different temperatures of (a) 0 °C, (b) 10 °C, (c) 25 °C, (d) 35 °C, and (e) 50 °C for different time after melting at 180 °C for 5 min and then crystallized at 60 °C for 5 min.

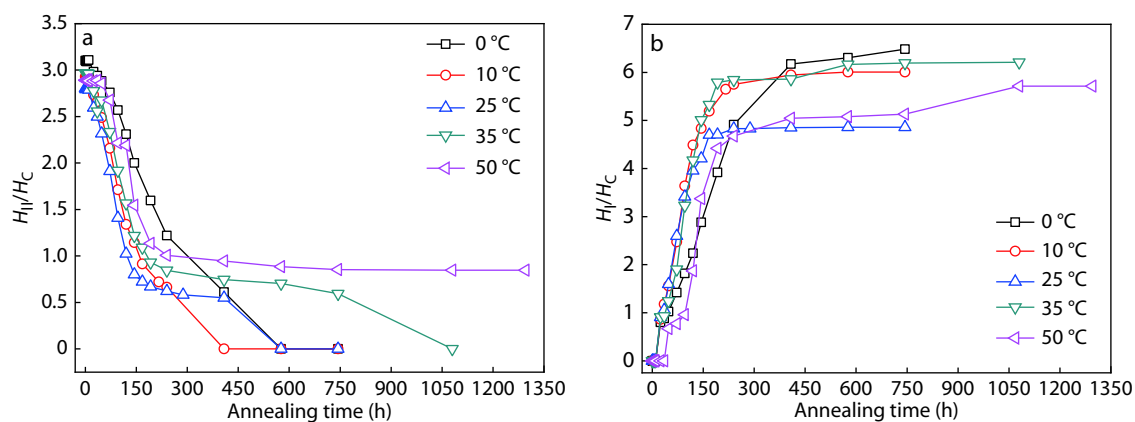


Fig. 3 Contents of (a) form II and (b) form I at different annealing temperatures as a function of annealing time.

150 h of annealing, the rapid increase in H_i/H_c is shown in samples that are annealed at 25, 10, and 35 °C. In particular, samples annealed at 0 and 50 °C show relatively slow formation of form I in the first 150 h of annealing. However, after 750 h annealing, samples at 0 °C have the highest value of H_i/H_c , while samples at 25 and 50 °C show the lowest values of H_i/H_c . This means that the dependency of the decay tendency of form II and the formation trend of form I on temperature is inconsistent.

It is noted here that form II decaying and form I yielding both proceed fast when samples are annealed at 25, 10, and 35 °C in the first 150 h annealing. Among them, samples annealed at 25 °C have the biggest decay rate of form II and yielding rate of form I, signifying the highest transition rate in the first 150 h annealing. This can be ascribed to the formation of form I actually controlled by two processes, nucleation and crystal growth. A low temperature contributes to the fast nucleation while high temperature favors the fast growth.^[23,36] High temperature leads to the difficulty in form I nucleation, thus form I is absent at 50 °C in the initial transition stage (24 h).

In Situ WAXD

In the late stage of crystal transition, adsorption bands of form II and form I are overlapped in FTIR spectra, which leads to the difficulty in discerning crystal forms. Comparatively, WAXD pattern is more distinct to identify the crystal structure (Fig. 4). Peaks at $2\theta = 12.0^\circ$ representing (200) lattice plane of form II appear strongly and clearly in samples that are annealed at 0–50 °C for 6 h and first disappear for samples annealed at 10 °C for 840 h. Peaks at $2\theta = 10.0^\circ$ representing the (110) lattice planes of form I are observed for all samples annealed at different temperatures for 6 h and grow gradually with annealing time. Peaks at $2\theta = 12.0^\circ$ are always observed even after samples are annealed at 35 and 50 °C for 1560 h. This indicates that the annealing at high temperature contributes negatively to the transformation.

Fig. 5 clearly shows the relative fraction of form I in the crystals (X_i) that is calculated through the following equation:

$$X_i = I(110)_i / [I(110)_i + R I(200)_{ii}] \quad (2)$$

where $I(110)_i$ and $I(200)_{ii}$ are the integrated intensities of form I (110) and form II (200) lattice planes, respectively. Here, a correlation parameter $R = 0.67$ proposed by Men is introduced,^[53] in which the crystal structure is showing space groups of form I and form II crystals as $P\bar{3}$ and $P4b2$ are referred.^[24] Samples annealed at 10 °C first reach the unity of X_i because of the fast transition (II to I). The higher temperature makes the remnant of form II higher in late transition stage (Fig. 5a). Samples annealed at 50 °C exhibit the slowest growth of form I as well as the relatively low X_i . The intensity changes of form II (200) lattice plane and form I (110) lattice plane with time represent the decay rate of form II and yielding rate of form I, respectively. The relative intensities of form II and form I in samples annealed at different temperatures and for different periods of time are calculated from the real-time value of form II to its original value and the real-time value of form I to its ultimate value which are shown in Fig. 5(b). Obviously, the rapid decay of form II and rapid yielding of form I are both observed in the first 150 h annealing time, and then the variations of form II and form I become slow. The half-life time ($t_{1/2}$), defined as the time for the

intensity change to reach one half the original value of form II ($t_{1/2,ii}$) or one half the ultimate value of form I ($t_{1/2,i}$), is demonstrated in Table 1. A greater value of $t_{1/2}$ indicates a lower variation rate. So, the yielding rate of form I is slightly higher than the decay rate of form II for samples annealed at 0–50 °C while a big difference between $t_{1/2,i}$ and $t_{1/2,ii}$ is observed at annealing temperature of 50 °C. This inconsistency between the yielding rate of form I and decay rate of form II was also found in our previous work.^[2] The crystallinity of form I ($X_{c,i}$) slightly decreased with increasing annealing temperature (max. 1.7%) during 0–25 °C (Fig. 5c), while a higher annealing temperature ranging from 35 °C to 50 °C led to a rapid decrease in $X_{c,i}$. We attribute this phenomenon to the unneglectable residual form II in these samples at higher annealing temperature.

Semi-crystalline polymers have a stacked structure composed of alternatively arranged crystal lamellae and amorphous region. The cilia and tie molecules in amorphous regions are in motion state at high temperature.^[38] The short isotactic sequences of *i*PB samples as proved in Fig. 1 would not crystallize at 60 °C, but may undergo crystallization when the temperature further falls to a lower point.^[32] In such a case, a few crystals of form II that originate from short isotactic sequence would somewhat counteract the disappearance of original form II. As a result, we observe a slightly quicker yielding of form I than decay of form II. Moreover, the lower annealing temperature amplifies the difference of thermal expansion between amorphous region and crystal lamellae, which induces the stronger internal stress and faster nucleation of form I in the late transformation stage.

Crystal Structure of the *i*PB before and after Transformation

Fig. 6 shows the melting behaviors of crystal form I (Fig. 6a) and crystal form II (Fig. 6b). Form I is obtained by samples undergoing 65 days of crystal transition at different annealing temperatures. Crystal form II is obtained by *i*PB melts directly cooled to 60 °C for isothermal crystallization. The crystallinities of form I and form II measured by DSC were determined from the melting enthalpies of form I and form II according to $X_c = \Delta H_m / \Delta H_m^0$ with $\Delta H_m^0(I) = 141 \text{ J} \cdot \text{g}^{-1}$ and $\Delta H_m^0(II) = 62 \text{ J} \cdot \text{g}^{-1}$.^[22] Clearly, all samples have the similar crystallinity (39%) of form II. After solid-solid crystal transition, the crystallinities of samples, dominantly in form I, are higher than the initial values of form II. Moreover, lower annealing temperature is accompanied with higher increment in crystallinity (Fig. 6c), which is in accordance with WAXD results. We attribute the increase in *i*PB crystallinity to the crystallization of shorter isotactic sequences which may be in the amorphous state before annealing. When form II is transformed to form I, short isotactic sequence would be crystallized into crystal II. The lower annealing temperature is beneficial to recruiting more amorphous chains to form crystal form II due to more strong driving force of super-cooling. A non-negligible phenomenon is that the weak melting peaks of untransformed form II are not observed for samples annealed at 35 and 50 °C. This is due to the re-crystallization of remnant form II in the heating process. No significant differences can be found in the melting peaks of form I and form II for samples annealed at different temperatures, which suggests that the stability of form I in annealed samples and that of the initial form II should be the same.

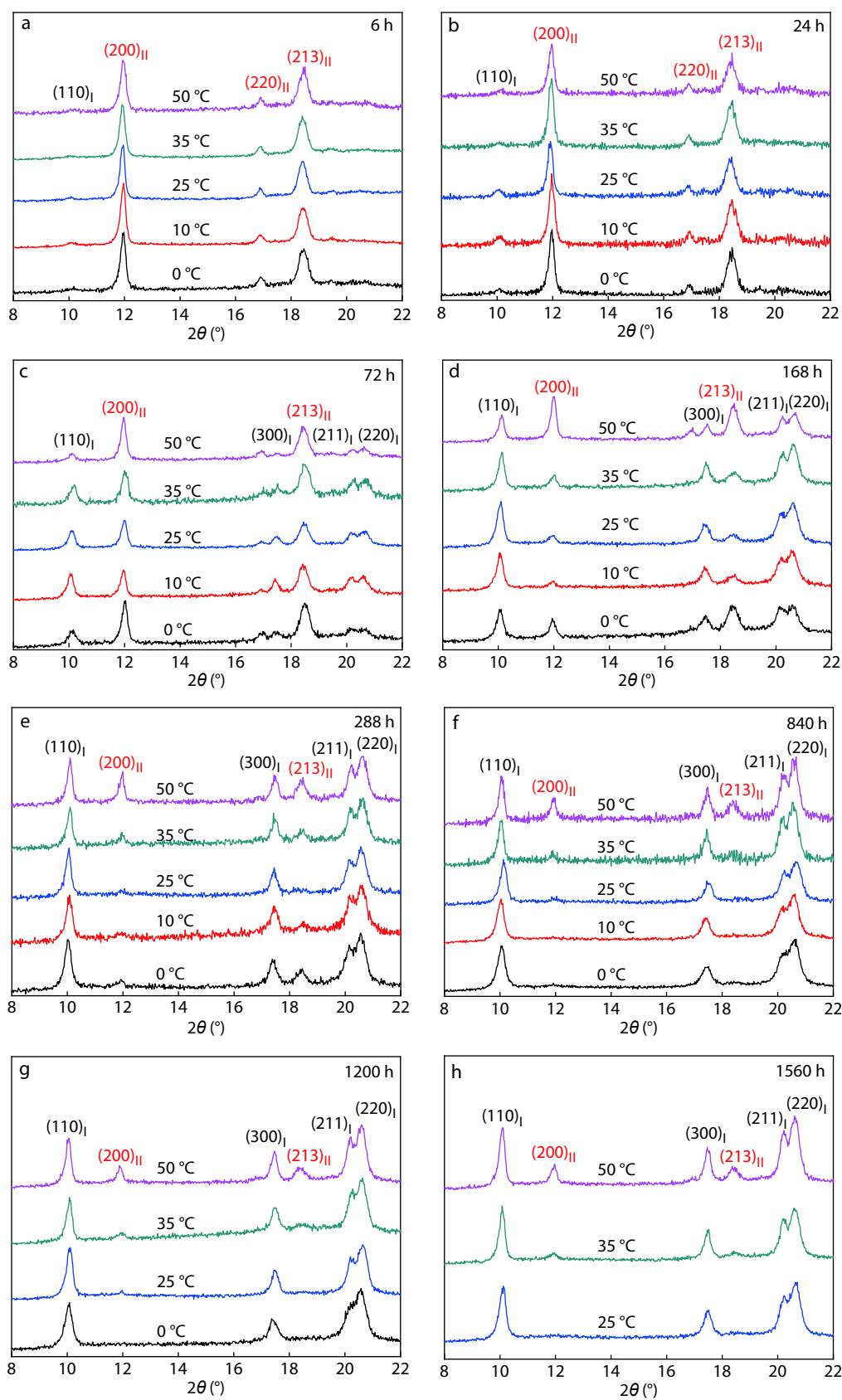


Fig. 4 WAXD patterns of *iPB* samples annealed at different temperatures for (a) 6 h, (b) 24 h, (c) 72 h, (d) 168 h, (e) 288 h, (f) 840 h, (g) 1200 h, and (h) 1560 h after melting at 180 °C for 5 min and then crystallized at 60 °C for 5 min.

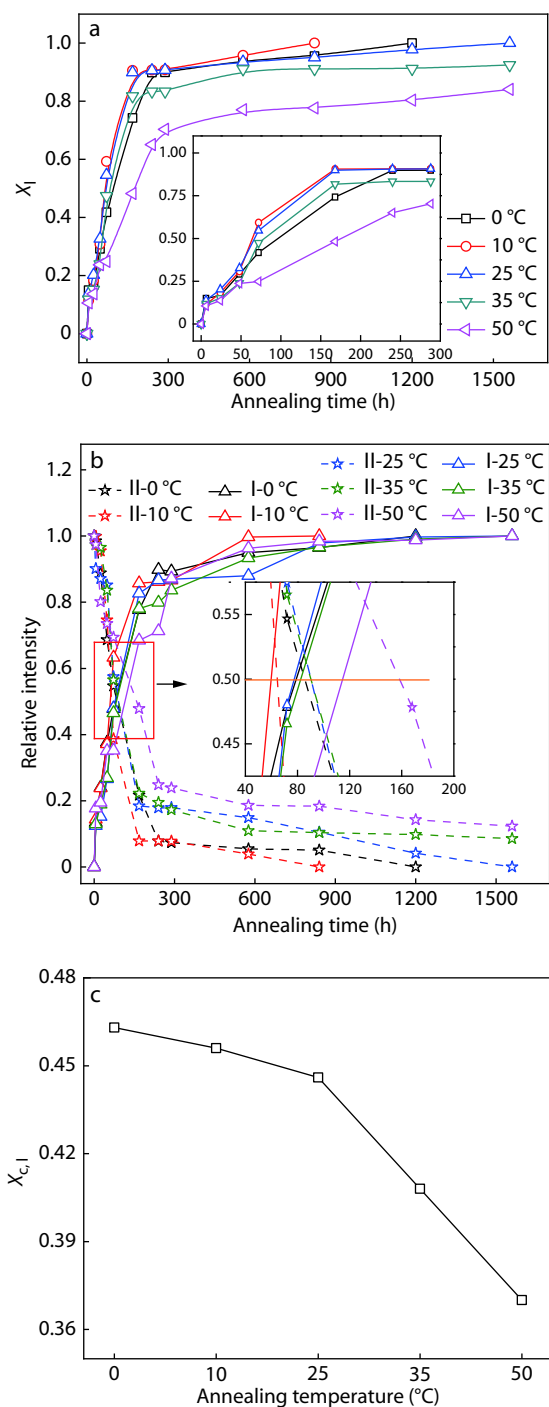


Fig. 5 (a) Fraction of crystal form I (X_I) for samples annealed at different temperatures for different time periods, (b) relative intensities of form II and form I for samples annealed at different temperatures, and (c) crystallinity of form I ($X_{c,I}$) for samples annealed at different temperatures for 65 days after melting at 180 °C for 5 min and then crystallized at 60 °C for 5 min.

SAXS

To explore the changes in crystal structure, the long space d_{ac} , crystalline lamellar thickness d_c , and amorphous layer thickness d_a of form I obtained at different temperatures are analyzed (Fig. 7). It is seen that the values of d_{ac} and d_c of form I (obtained at

Table 1 Crystal transformation half-life time $t_{1/2}$ of form II and form I for samples annealed at different temperatures.

Annealing temperature (°C)	$t_{1/2,II}$ (h)	$t_{1/2,I}$ (h)	$t_{1/2,II} - t_{1/2,I}$ (h)
0	85	79.5	5.5
10	64.5	60	4.5
25	87.5	77	10.5
35	90	82.5	7.5
50	158	102	56

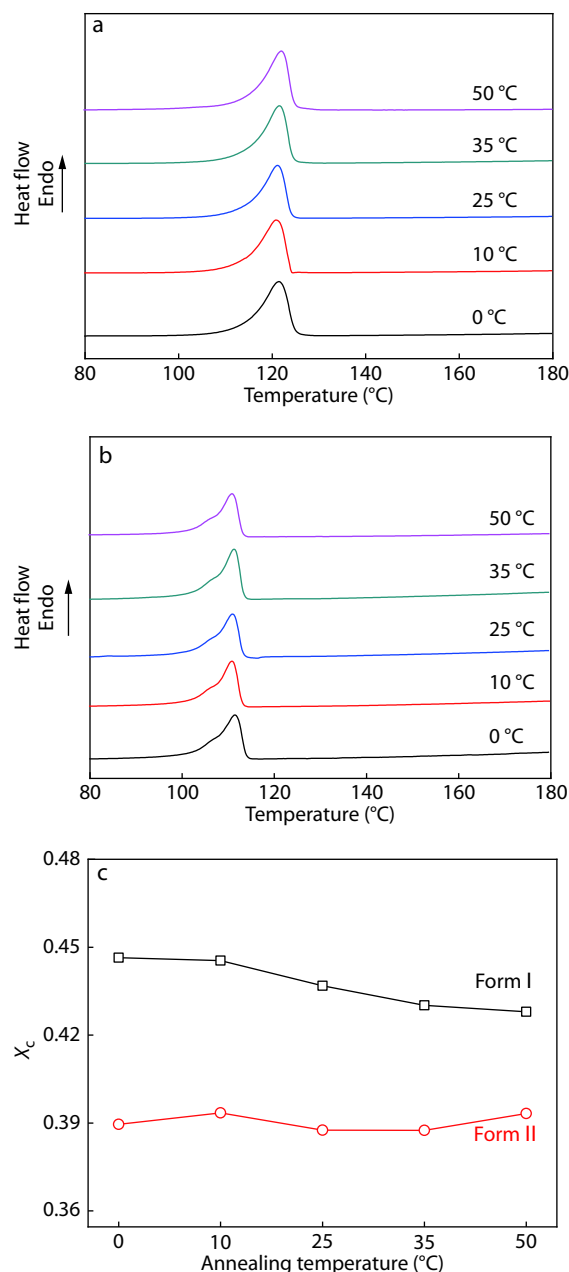


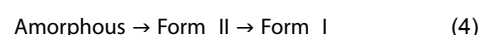
Fig. 6 DSC melting curves of iPB samples: (a) form I obtained at different temperatures after 65 days of transformation and (b) form II annealed at different temperatures for 0 h after melting at 180 °C for 5 min and then crystallized at 60 °C for 5 min; (c) Crystallinity of form I and form II.

0–50 °C) (Fig. 7c) slightly increase with the transition temperature increased. As mentioned above, some amorphous chains of

*i*PB are still in motion state at high temperature, and may crystallize to produce form II during solid transition process. The lower transition temperature contributes to the secondary crystallization that makes the amorphous chains recruited more easily to yield more form II crystals, which successively insert into the stack of original form II.^[47,54] Since each crystal of form II could induce the production of a few crystals of form I,^[39] the

ultimate form I with thinner average lamella thickness is reasonable.

Crystal transition in solid state is revealed as the conformation and packing mode change of polymer chains in the confined space. Herein, the yielding of form I could arise from the solid transition of not only the primary form II but also the newly formed form II from short isotactic sequence *via* recruiting amorphous chains which locate near crystal lamella. Therefore, two steps as follows are used to describe the process:



Step 1 refers to the direct crystal transition from form II to form I, and form II originates from the primary isothermal crystallization at 60 °C of relatively long isotactic sequences of *i*PB. The different annealing temperatures lead to different yielding rates of form I and decay rates of form II, particularly at the early stage of transformation. Samples annealed at 10, 25, and 35 °C have higher transformation rate due to the synergy effect of nucleation and growth. However, owing to the existence of multiple crystalline sequences in employed *i*PB, some amorphous chains with shorter isotactic sequence, especially those locates near the crystal lamella, participate in regular arrangement to yield form II in the transition process. Step 2 dominantly increases the crystallinity of the samples. A higher undercooling offered at lower annealing temperature enables an easier rearrangement of amorphous chains to form II. Therefore, compared to the decay of form II, a faster yielding of form I is observed, and a slight increase in crystallinity of form I is found, particularly at low temperature.

CONCLUSIONS

In summary, crystal transition of *i*PB with 81 mol% mmmm sequence concentration was studied in a wide range of temperatures by tracking the decay of form II and the yielding of form I. Different annealing temperatures lead to different yielding rates of form I and decay rates of form II, particularly at the early stage of transformation. The fast transformation rate was observed at annealing temperatures of 10–35 °C in the first transformation stage due to the synergistic effect of nucleation and growth, while more remnant of form II existed at higher annealing temperatures in late stage. Owing to the formation of form II crystals by recruiting the surrounding amorphous chains arising from the short isotactic sequences of *i*PB which locates near the crystal lamella, a higher yielding rate of form I is observed compared to the decay rate of form II. Meanwhile, an increase in the crystallinity of form I after crystal transformation is also found and its lamellar thickness increases with the temperature increased.

ACKNOWLEDGMENTS

This work was financially supported by the Major Science and Technology Innovation Project of Shandong Province (No. 2019JZZY010352), Natural Science Foundation of Shandong Province (ZR2019MB072) and Taishan Scholar Program. Special thanks to Prof. Yongfeng Men for his kind suggestions and discussions.

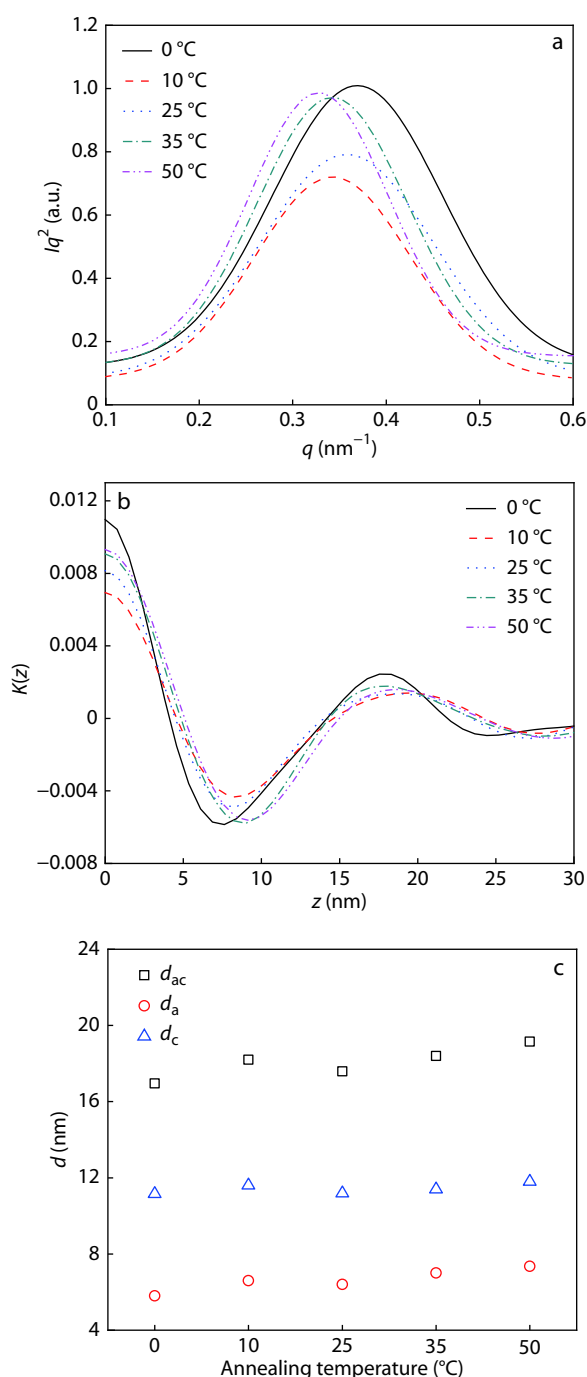


Fig. 7 (a) Temperature dependencies of selected one-dimensional scattering intensity distribution profiles, (b) the resultant correlation function curves, and (c) long spacing d_{ac} , crystalline lamellae thickness d_c , and amorphous layer thickness d_a of form I at different temperatures ranging from 0 °C to 50 °C for 65 days of transformation.

REFERENCES

- Luciani, L.; Seppala, J.; Lofgren, B. Poly-1-butene: its preparation, properties and challenges. *Prog. Polym. Sci.* **1988**, *13*, 37–62.
- He, A. H.; Xu, C. S.; Shao, H. F.; Yao, W.; Huang, B. C. Effect of molecular weight on the polymorphic transformation of isotactic poly(1-butene). *Polym. Degrad. Stab.* **2010**, *95*, 1443–1448.
- Wang, Y. T.; Liu, P. R.; Lu, Y.; Men, Y. F. Mechanism of polymorph selection during crystallization of random butene-1/ethylene copolymer. *Chinese J. Polym. Sci.* **2016**, *34*, 1014–1020.
- Wang, Y. T.; Lu, Y.; Zhao, J. Y.; Jiang, Z. Y.; Men, Y. F. Direct formation of different crystalline forms in butene-1/ethylene copolymer via manipulating melt temperature. *Macromolecules* **2014**, *47*, 8653–8662.
- Choi, S. Y.; Rakus, J. P.; O'Toole, J. L. Time dependent crystallinity of polybutene-1. *Polym. Eng. Sci.* **1966**, *6*, 349–352.
- Miller, R. L.; Holland, V. F. On transformations in isotactic polybutene-1. *J. Polym. Sci., Part B: Polym. Lett.* **1964**, *2*, 519–521.
- Xu, Y.; Liu, C. G.; Nie, H. R.; He, A. H. Fractionated and confined crystallization of polybutene-1 in immiscible polypropylene/polybutene-1 blends. *Chinese J. Polym. Sci.* **2018**, *36*, 859–865.
- Nie, H. R.; Xiao, W. J.; Ma, Y. P.; Liu, C. G.; He, A. H. High-performance isotactic poly(1-butene)/isotactic polypropylene alloys with *in-situ*-synthesized poly(propylene-co-butene). *Ind. Eng. Chem. Res.* **2019**, *58*, 6919–6924.
- Azzurri, F.; Flores, A.; Alfonso, G. C.; Sics, I.; Hsiao, B. S.; Calleja, F. J. B. Polymorphism of isotactic polybutene-1 as revealed by microindentation hardness. Part II: correlations to microstructure. *Polymer* **2003**, *44*, 1641–1645.
- Azzurri, F.; Flores, A.; Alfonso, G. C.; Calleja, F. J. B. Polymorphism of isotactic poly(1-butene) as revealed by microindentation hardness. 1. Kinetics of the transformation. *Macromolecules* **2002**, *35*, 9069–9073.
- Rubin, I. D. Relative stabilities of polymorphs of polybutene-1 obtained from melt. *J. Polym. Sci., Part B: Polym. Lett.* **1964**, *2*, 747–749.
- Tanaka, A.; Sugimoto, N.; Asada, T.; Onogi, S. Orientation and crystal transformation in polybutene-1 under stress relaxation. *Polym. J.* **1975**, *7*, 529–537.
- Cavallo, D.; Kanters, M. J. W.; Caelers, H. J. M.; Portale, G.; Govaert, L. E. Kinetics of the polymorphic transition in isotactic poly(1-butene) under uniaxial extension. New insights from designed mechanical histories. *Macromolecules* **2014**, *47*, 3033–3040.
- Xu, Y.; Liu, T.; Li, L.; Li, D. C.; Yuan, W. K.; Zhao, L. Controlling crystal phase transition from form II to I in isotactic poly-1-butene using CO₂. *Polymer* **2012**, *53*, 6102–6111.
- Wanjale, S. D.; Jog, J. P. Crystallization and phase transformation kinetics of poly(1-butene)/MWCNT nanocomposites. *Polymer* **2006**, *47*, 6414–6421.
- Liu, Y.; Cui, K.; Tian, N.; Zhou, W.; Meng, L.; Li, L.; Ma, Z.; Wang, X. Stretch-induced crystal-crystal transition of polybutene-1: an *in situ* synchrotron radiation wide-angle X-ray scattering study. *Macromolecules* **2012**, *45*, 2764–2772.
- Shao, H. F.; Ma, Y. P.; Nie, H. R.; He, A. H. Solvent vapor annealing induced polymorphic transformation of polybutene-1. *Chinese J. Polym. Sci.* **2016**, *34*, 1141–1149.
- Chen, W.; Li, X. Y.; Li, H. L.; Su, F. M.; Zhou, W. M.; Li, L. B. Deformation-induced crystal-crystal transition of polybutene-1: an *in situ* FTIR imaging study. *J. Mater. Sci.* **2013**, *48*, 4925–4933.
- Li, L.; Liu, T.; Zhao, L.; Yuan, W. K. CO₂-induced crystal phase transition from form II to I in isotactic poly-1-butene. *Macromolecules* **2009**, *42*, 2286–2290.
- Jones, A. T. Cocrystallization in copolymers of α -olefins II butene-1 copolymers and polybutene type II/I crystal phase transition. *Polymer* **1966**, *7*, 23–29.
- Marigo, A.; Marega, C.; Cecchin, G.; Collina, G.; Ferrara, G. Phase transition II→I in isotactic poly-1-butene: wide- and small-angle X-ray scattering measurements. *Eur. Polym. J.* **2000**, *36*, 131–136.
- Qiao, Y. N.; Wang, Q.; Men, Y. F. Kinetics of nucleation and growth of form II to I polymorphic transition in polybutene-1 as revealed by stepwise annealing. *Macromolecules* **2016**, *49*, 5126–5136.
- Qiao, Y. N.; Men, Y. F. Intercrystalline links determined kinetics of form II to I polymorphic transition in polybutene-1. *Macromolecules* **2017**, *50*, 5490–5497.
- Tashiro, K.; Hu, J.; Wang, H.; Hanesaka, M.; Saiani, A. Refinement of the crystal structures of forms I and II of isotactic polybutene-1 and a proposal of phase transition mechanism between them. *Macromolecules* **2016**, *49*, 1392–1404.
- Jones, A. T. Polybutene-1: type II crystalline form. *J. Polym. Sci., Part B: Polym. Lett.* **1963**, *1*, 455–456.
- Natta, G.; Corradini, P.; Bassi, I. W. Crystal structure of isotactic poly-alpha-butene. *Nuovo Cimento* **1960**, *15*, 52–67.
- Hu, J.; Tashiro, K. Relation between higher-order structure and crystalline phase transition of oriented isotactic polybutene-1 investigated by temperature-dependent time-resolved simultaneous WAXD/SAXS measurements. *Polymer* **2016**, *90*, 165–177.
- Su, F. M.; Li, X. Y.; Zhou, W. M.; Chen, W.; Li, H. L.; Cong, Y. H.; Hong, Z.; Qi, Z. M.; Li, L. B. Accelerating crystal-crystal transition in poly(1-butene) with two-step crystallization: an *in-situ* microscopic infrared imaging and microbeam X-ray diffraction study. *Polymer* **2013**, *54*, 3408–3416.
- Hu, J.; Tashiro, K. Time-resolved imaging of the phase transition in the melt-grown spherulites of isotactic polybutene-1 as detected by the two-dimensional polarized IR imaging technique. *J. Phys. Chem. B* **2016**, *120*, 4689–4698.
- Azzurri, F.; Gomez, M. A.; Alfonso, G. C.; Ellis, G.; Marco, C. Time-resolved SAXS/WAXS studies of the polymorphic transformation of 1-butene/ethylene copolymers. *J. Macromol. Sci., Part B: Phys.* **2004**, *43*, 177–189.
- Maruyama, M.; Sakamoto, Y.; Nozaki, K.; Yamamoto, T.; Kajioka, H.; Toda, A.; Yamada, K. Kinetic study of the II-I phase transition of isotactic polybutene-1. *Polymer* **2010**, *51*, 5532–5538.
- Gohil, R. M.; Miles, M. J.; Petermann, J. On the molecular mechanism of the crystal transformation (tetragonal-hexagonal) in polybutene-1. *J. Macromol. Sci., Part B: Phys.* **1982**, *21*, 189–201.
- Powers, J.; Hoffman, J. D.; Weeks, J. J.; Quinn, F. A. Crystallization kinetics and polymorphic transformations in polybutene-1. *J. Res. Natl. Bur. Stand., Sect. A* **1965**, *69*, 335–345.
- Danusso, F.; Gianotti, G. Isotactic polybutene-1: formation and transformation of modification 2. *Makromol. Chem.* **1965**, *88*, 149–158.
- Boor, J.; Mitchell, J. C. Apparent nucleation of a crystal-crystal transition in poly-1-butene. *J. Polym. Sci.* **1962**, *62*, S70–S73.
- Chvátalová, L.; Beníček, L.; Berková, K.; Čermák, R.; Obadař, M.; Verney, V.; Commereuc, S. Effect of annealing temperature on phase composition and tensile properties in isotactic poly(1-butene). *J. Appl. Polym. Sci.* **2012**, *124*, 3407–3412.
- Di Lorenzo, M. L.; Androsch, R.; Righetti, M. C. The irreversible form II to form I transformation in random butene-1/ethylene copolymers. *Eur. Polym. J.* **2015**, *67*, 264–273.
- Hoffman, J. D.; Miller, R. L. Kinetic of crystallization from the melt and chain folding in polyethylene fractions revisited: theory and experiment. *Polymer* **1997**, *38*, 3151–3212.
- Chau, K. W.; Yang, Y. C.; Geil, P. H. Tetragonal→twinned hexagonal crystal phase transformation in polybutene-1. *J. Mater. Sci.* **1986**, *21*, 3002–3014.
- Qiao, Y. N.; Yang, F.; Lu, Y.; Liu, P. R.; Li, Y. S.; Men, Y. F. Spontaneous form II to I transition in low molar mass polybutene 1 at crystallization temperature reveals stabilization role of

- intercrystalline links and entanglements for metastable form II crystals. *Macromolecules* **2018**, *51*, 8298–8305.
- 41 De Rosa, C.; Ruiz de Ballesteros, O.; Auriemma, F.; Di Girolamo, R.; Scarica, C.; Giusto, G.; Esposito, S.; Guidotti, S.; Camurati, I. Polymorphic behavior and mechanical properties of isotactic 1-butene-ethylene copolymers from metallocene catalysts. *Macromolecules* **2014**, *47*, 4317–4329.
 - 42 De Rosa, C.; Auriemma, F.; Ruiz de Ballesteros, O.; Esposito, F.; Laguzza, D.; Di Girolamo, R.; Resconi, L. Crystallization properties and polymorphic behavior of isotactic poly(1-butene) from metallocene catalysts: the crystallization of form I from the melt. *Macromolecules* **2009**, *42*, 8286–8297.
 - 43 Azzurri, F. G.; Alfonso, C. Polymorphic transformation in isotactic 1-butene/ethylene copolymers. *Macromolecules* **2004**, *37*, 3755–3762.
 - 44 Lou, Y. H.; Liao, Y. L.; Pan, L.; Wang, B.; Li, Y. S.; Ma, Z. Effect of linear and ring-like co-units on the temperature dependence of nucleation and growth in II-I Phase transition of butene-1 copolymers. *Chinese J. Polym. Sci.* **2018**, *36*, 72–79.
 - 45 He, L. L.; Wang, B.; Yang, F.; Li, Y. S.; Ma, Z. Featured crystallization polymorphism and memory effect in novel butene-1/1,5-hexadiene copolymers synthesized by post metallocene hafnium catalyst. *Macromolecules* **2016**, *49*, 6578–6589.
 - 46 Zheng, L.; Liu, L.; Shao, C. G.; Wang, W.; Wang, B.; Pan, L.; Li, Y. S.; Ma, Z. Phase transition from tetragonal form II to hexagonal form I of butene-1/4-methyl-1-pentene random copolymers: molecular factor versus stretching stimuli. *Macromolecules* **2019**, *52*(3), 1188–1199.
 - 47 Müller, A. J.; Arnal, M. L. Thermal fractionation of polymers. *Prog. Polym. Sci.* **2005**, *30*, 559–603.
 - 48 Strobl, G. R.; Schneider, M. J.; Voigt-Martin, I. G. Model of partial crystallization and melting derived from small-angle X-ray scattering and electron microscopic studies on low-density polyethylene. *J. Polym. Sci., Part B: Polym. Phys.* **1980**, *18*, 1361–1381.
 - 49 Wang, Y. T.; Lu, Y.; Jiang, Z. Y.; Men, Y. F. Molecular weight dependency of crystallization line, recrystallization line, and melting line of polybutene-1. *Macromolecules* **2014**, *47*, 6401–6407.
 - 50 Asakura, T.; Demura, M.; Nishiyama, Y. Carbon-13 NMR spectral assignment of five polyolefins determined from the chemical shift calculation and the polymerization mechanism. *Macromolecules* **1991**, *24*, 2334–2340.
 - 51 Tian, Z.; Gu, X. P.; Wu, G. L.; Feng, L. F.; Fan, Z. Q.; Hu, G. H. Effects of switching frequency of a periodic switching polymerization process on the microstructures of ethylene-propylene copolymers in polypropylene/poly(ethylene-co-propylene) in-reactor alloys. *Ind. Eng. Chem. Res.* **2012**, *51*, 2257–2270.
 - 52 Luongo, J. P.; Salovey, R. Infrared characterization of polymorphism in polybutene-1. *J. Polym. Sci., Part A: Polym. Chem.* **1966**, *4*, 997–1008.
 - 53 Qiao, Y. N.; Wang, H.; Men, Y. F. Retardance of form II to form I transition in polybutene-1 at late stage: a proposal of a new mechanism. *Macromolecules* **2018**, *51*, 2232–2239.
 - 54 Sun, Y. Y.; Fu, L. L.; Wu, Z. H.; Men, Y. F. Structural evolution of ethylene-octene copolymers upon stretching and unloading. *Macromolecules* **2013**, *46*, 971–976.