

Ultrafast Form II to I Transition of Isotactic Polybutene-1

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 Electronic Supplementary Information

Abstract Isotactic polybutene-1 (*i*PB-1) is a semi-crystalline polymer with polymorph and puzzled structural transitions. The stable form I of *i*PB-1 with excellent physical and mechanical properties can hardly be obtained directly from the melt; instead, metastable form II will spontaneously and slowly transform into form I. Bypassing the unstable form II formation is of great significance in polymer processing, which inspires extensive research on seeking the pathways to direct formation of form I. Methods for accelerating form II to I transition are another main focus in terms of practical approach for directly obtaining form I. Taking advantage of the solvent, an ultrafast transition of *i*PB-1 from form II to I within minutes has been achieved at room temperature. Such an ultrafast transition is detected after treating with dichloromethane (DCM) at 30 °C, though the framework of isothermally crystallized *i*PB-1 spherulite morphology could not be fully modified. The ultrafast II-I transition of *i*PB-1 is attributed to the solvent-induced packed-mesophase and temperature-selected chain conformation adjustment. This ultrafast transition would shed light on understanding the mechanisms of polymorphic transitions in *i*PB-1.

Keywords Polybutene-1; Ultrafast transition; Mesophase; Conformation

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Isotactic polybutene-1 (*i*PB-1), known as “gold plastics” with excellent mechanical performances including cracking and creep resistance, is of great industrial interest as compared to other polyolefins and is also a fantastic model to understand polymer crystallization.^[1,2] However, the applications have been greatly limited in the past decades due to slow but spontaneous II-I transition with increase in density, hardness, rigidity, toughness, and tensile strength at room temperature.^[3,4] When cooling from the melt, *i*PB-1 firstly settles itself into metastable form II instead of stable form I. The metastable form II has 11/3 helices loosely packed in the tetragonal unit cells. On the other hand, the stable form I contains more dense 3/1 helices packed in twinned hexagonal cells.^[5,6] During the process of cooling from melt, the system intrinsically selects the lower free energy barrier to undergo phase transition rather than arriving directly at the most stable state, so it needs to cross a free energy barrier along with thermal and density fluctuations to reach the stable structure.^[7] Consequently, when *i*PB-1 crystallizes from the melt, it is difficult to directly form the stable form I bypassing the metastable form II.

Crystallization from solution can be performed at low temperatures bypassing the crystallization temperature of form II. Form III or form I' will be formed in amyl acetate solvent about or below 50 °C respectively, and solvents,

temperatures, and concentrations of solutions have noticeable effects on the final crystal structures of *i*PB-1 when it is crystallized from solution.^[8] It is also troublesome to form stable form I under high hydrostatic pressure: form I' is formed under pressure above 100 MPa, while it still be form II under 100 MPa.^[9,10] What is more, instead of form II, form I' can be directly crystallized from melts in copolymers, but not form I.^[11] During the vast majority of form I being transformed from form II, spontaneous transition rate is the fastest at room temperature. High-pressure,^[10] pressurized CO₂,^[12] external stress,^[13,14] and solvent annealing^[15] are reported as effective approaches to accelerate the II-I transformation.

The II-I transition of *i*PB-1 was believed to start randomly as a solid-solid process with a rate-determining nucleation process followed by a fast growth process.^[16–21] The initial nucleation was supposed to start in crystalline regions, especially at positions of a crystalline lamella with defects,^[19,22,23] and the inner stress was speculated to be able to accelerate the II-I transition.^[16] However, this is contrary to the fact that form II without inter-crystalline links transformed much faster than the higher molecules with inter-crystalline links did.^[24] Researchers have tried to propose other II-I transition mechanisms.^[25] It is quite evident that the lack of the knowledge about the crystal transition process has restricted the development and appearance of novel and highly efficient accelerating techniques, thus limiting industrial applications of *i*PB-1.

In fact, a polymer crystal consists of chain helices packed

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into a particular geometry, revealing that its formation must be based on prior chain conformation adjustments. No matter what conformation is formed, the essential process of polymer crystallization is the transition of polymer chain conformation from amorphous to crystalline, which is determined by the temperature-dependent chain entropy as well as the concerned enthalpy changes along with the energy barrier due to the flexible polymer chains.^[1,26,27] The *i*PB-1 chain conformation adjustments and thus the II-I transition may depend on the chain motion and chain segment diffusion, for example, in the amorphous regions.^[23] However, a few reports have been focused on this.

Our previous work experimentally revealed that *i*PB-1 could be directly crystallized into form I at temperatures below 35 °C owing to the prior formation of temperature-selected 3/1 helix conformation as proposed.^[28] Therefore, it can be assumed that if the molecular chain mobility is enhanced to overcome the energy barrier of the chain conformation adjustment from 11/3 to 3/1 helices at low temperatures, the II-I transition would be accelerated, or even form I is possible to be directly obtained from the special mesophase composed of woken-up *i*PB-1 chains. In order to verify this hypothesis, we have established a method without damaging *i*PB-1 materials but with the molecular chain dynamics woken-up to adjust chain conformations which may be a key factor to efficiently accelerate the II-I transition. For example, a suitable solvent for *i*PB-1 treatment is expected to be efficient if it can accelerate II-I transition at low temperatures by promoting the appearance of the form I favored mesophase composed of woken-up *i*PB-1 chains. In this work, dichloromethane (DCM) is dripped on the isother-

ally crystallized *i*PB-1 films and an ultrafast form II-I transition within minutes (less than 2 min) has been successfully achieved at 30 °C.

To look into the solvent effect on crystalline morphology evolutions, the spherulite morphologies of *i*PB-1 films with fresh form II isothermally crystallized at 100 °C before and after DCM dripping are observed by polarizing optical microscopy (POM, Olympus BX51). The recorded POM images with respect to changes in time at 30 °C are shown in Fig. 1. It shows no obvious change of the *i*PB-1 spherulite morphology before and after dripping DCM at 30 °C. WAXD and DSC measurements are further performed to confirm the changes after DCM dripping at 30 °C. Fig. 2 proves that after dripping DCM at 30 °C, form II of the *i*PB-1 film transits rapidly into form I (not form I'). WAXD diffraction patterns of untwinned 3/1 helix form I' and twinned 3/1 helix form I are the same, but their melting points are different. T_m of form I' is around 99 °C while T_m of form I is higher than 120 °C.

In addition, as shown in Fig. 1, after DCM dripping at 30 °C, the *i*PB-1 spherulite suddenly becomes vague, while the vision is still bright. Two minutes later, ultrafast II-I transition occurrence is detected without obvious spherulite morphology change. The spherulites in the *i*PB-1 film after DCM dripping at 30 °C seem to remain macroscopically visible during the occurrence of II-I transition. This II-I transition within the time span of 2 min is worthy of exploring. The current experimental results are different from solution crystallization, as only form I' or form III can be formed *via* solution crystallization.^[8] The result of form I indicates that there exists a definite structure in the system, which is differ-

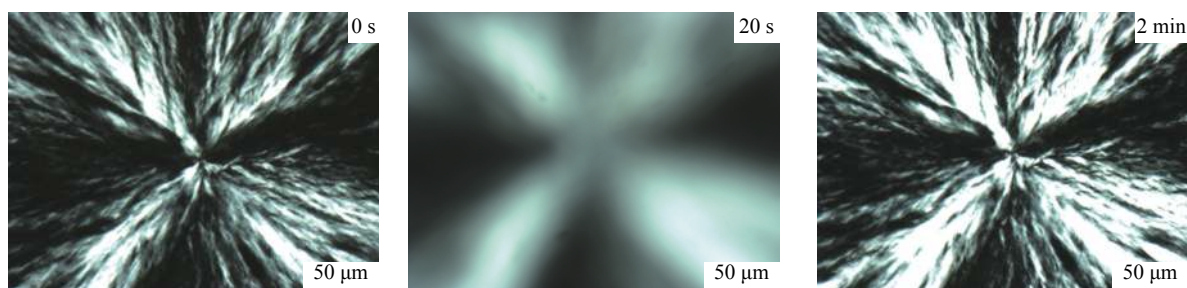


Fig. 1 POM images of DCM-treated thin *i*PB-1 films at 30 °C for different time

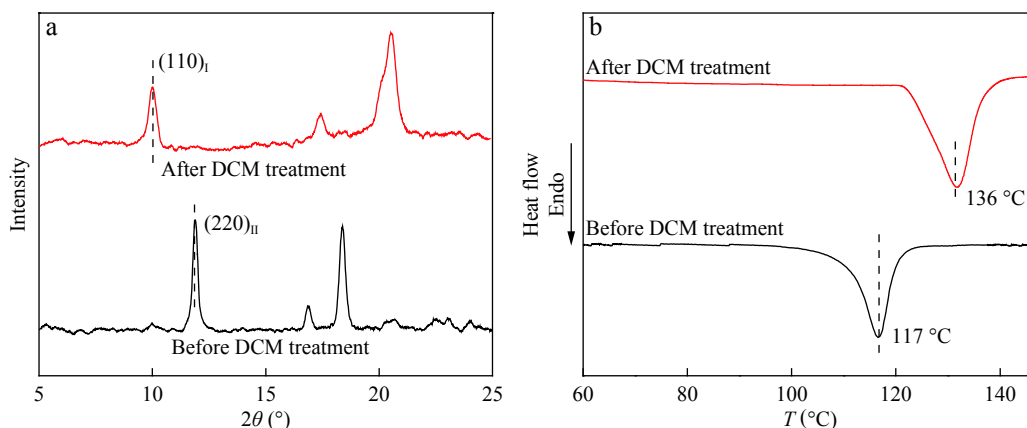


Fig. 2 (a) WAXD patterns and (b) DSC curves of *i*PB-1 films before and after DCM treatment at 30 °C

ent from the amorphous structure both in the solution and the bulk *i*PB-1.

The POM image demonstrating a bright blurred spherulite can be speculated as it corresponds to a packed-mesophase state between the crystalline and the amorphous phase, in which the molecular chains can be woken up to choose exactly the 3/1 helix conformations and recrystallize into form I *via* packed-mesophases. Furthermore, it is not that the stronger the mobility of *i*PB-1 chains, the better. When a solvent with high boiling point is used, such as paraxylene, the lamellar would dissolve into loose-mesophase which is close to the state of solution crystallization, whereas the dripped DCM would induce packed-mesophase for form I with the woken-up chains that can adjust conformation.^[29]

Fig. 3 presents FTIR spectra of the II-I transition process after dripping DCM on the comparatively thick samples at 30 °C. As shown in Fig. 3, the absorption bands at 905 and 924 cm⁻¹ correspond to form II and form I, respectively. It can be seen that form I appears with a very strong absorption band at 924 cm⁻¹ as revealed by the first FTIR spectrum collected at 2 min for the sake of lens protection after dripping DCM as solvent. It indicates that most of the form II crystals in the *i*PB-1 film have transited into form I within 2 min just after DCM dripping at 30 °C. It can be concluded that if the film is too thick for the solvent to spontaneously

penetrate into and distribute uniformly in it, part of the form II crystals in the film may not have chances to encounter the solvent plasticization effect. Form II and form I will appear in the same sample unlike the film above that has transformed within a few minutes. It is very easy to associate it with the solid-solid transition, but is it really the truth? The thin sample is equivalent to the portion of the thicker one that is permeated by the solvent, so the II-I transformation in a thick sample may follow the same principle as that in the thin sample. The solvent that penetrates into the sample induces a packed-mesophase structure, and the chain activity is between the crystalline and the amorphous region, so they can adjust conformation rapidly to form a stable 3/1 helix form I at room temperature. The primary cause of the II-I transformation acceleration is that the solvent helps to induce a special packed-mesophase along with a certain chain activity.

As known, *i*PB-1 is chiral but racemic. Analyzing “backwards” *via* a critical inspection of the crystal structures of forms I and II with a viewpoint that formation of various crystal forms is based on the prior chain conformational rearrangements. It has been reported previously that direct formation of form I in bulk *i*PB-1 from the amorphous phase or melt can occur at temperatures below 35 °C due to the 3/1 helix conformations favored by prior form I or mesophase formation.^[28] Hence, the chain conformation adjustment has been proved to be temperature dependent. At room temperature, *i*PB-1 can crystallize into an untwinned form I' (also with 3/1 helices packed in its crystal cells) by solution crystallization.^[8] Based on these experimental results, the solvent-induced ultrafast II-I transition of *i*PB-1 at 30 °C, with almost fixed spherulite morphology, can be attributed to the solvent-induced packed-mesophase but the temperature-selected adjustment of chain helix conformation. The first appearance of those directly formed form I crystals may act as the so-called initial nuclei of II-I transition whose formation could be promoted by mechanical forces, solvent effect, and being cooled to low temperatures.

In summary, *i*PB-1 with unstable form II can transit into the stable form I within 2 min at 30 °C in the presence of DCM, showing an ultrafast II-I transition rate but without obvious spherulite morphology changes. The ultrafast II-I transition mechanism of *i*PB-1 can be attributed to the solvent-induced packed-mesophase and the temperature selected chain conformation adjustment, so 3/1 helix form I can be directly crystallized from mesophase at 30 °C. The experimentally observed ultrafast II-I transition in the presence of solvents at low temperatures matches the time span of *i*PB-1 injection processing and would shed lights on fast developments of *i*PB-1 industrial applications. The phenomenon also provides a new insight to reconsider the II-I transition mechanism which is of great value to understand polymer crystallization and crystal transition mechanisms.

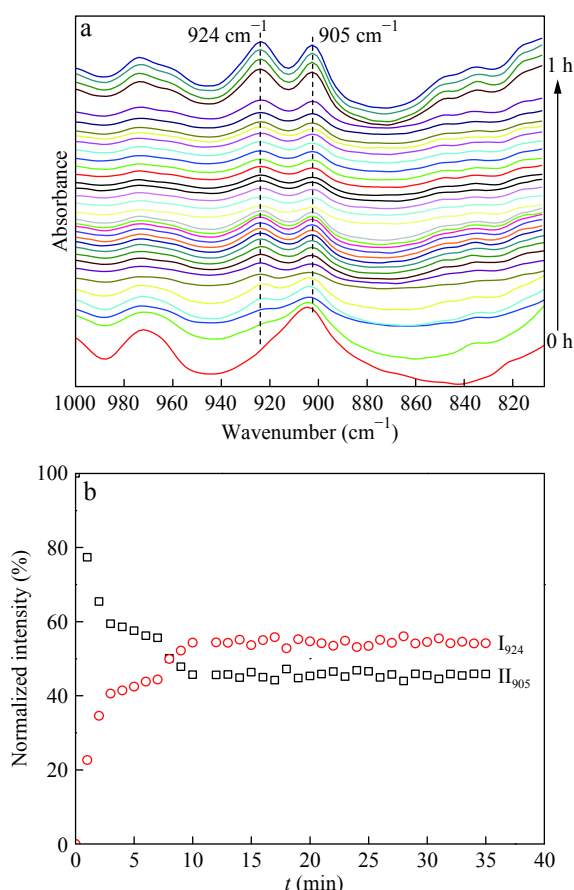


Fig. 3 (a) Selected FTIR spectra of 10 multiples *i*PB-1 film after dripping dichloromethane at 30 °C; (b) Absorbance evolution of form I and form II as a function of time after dripping dichloromethane on the 10 multiples *i*PB-1 film at 30 °C

Electronic Supplementary Information

Electronic supplementary information (ESI), which includes the experimental section, is available free of charge in the online

version of this article at <http://dx.doi.org/10.1007/s10118-019-2273-5>.

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