Ultrafast Form II to I Transition of Isotactic Polybutene-1

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Abstract Isotactic polybutene-1 (iPB-1) is a semi-crystalline polymer with polymorph and puzzled structural transitions. The stable form I of iPB-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 iPB-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 crystalized iPB-1-spherulite morphology could not be fully modified. The ultrafast II-I transition of iPB-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 iPB-1.

Keywords Polybutene-1; Ultrafast transition; Mesophase; Conformation

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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. The 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. However, a few reports have been focused on this.

Our previous work experimentally revealed that iPB-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. 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 iPB-1 chains. In order to verify this hypothesis, we have established a method without damaging iPB-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 iPB-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 iPB-1 chains. In this work, dichloromethane (DCM) is dripped on the isothermally crystallized iPB-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 iPB-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 iPB-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 iPB-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. Tm of form I' is around 99 °C while Tm of form I is higher than 120 °C.

In addition, as shown in Fig. 1, after DCM dripping at 30 °C, the iPB-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 iPB-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. The result of form I indicates that there exists a definite structure in the system, which is differ-
ent from the amorphous structure both in the solution and the bulk iPB-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 iPB-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 iPB-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, iPB-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 I in bulk iPB-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, iPB-1 can crystallize into an unwinnted form I (also with 3/1 helices packed in its crystal cells) by solution crystallization.[6] Based on these experimental results, the solvent-induced ultrafast II-I transition of iPB-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, iPB-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 iPB-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 iPB-1 injection processing and would shed lights on fast developments of iPB-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.

Electronic Supplementary Information

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

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