



Crystallization and melting behaviors of the β -nucleated isotactic polypropylene with different melt structures – The role of molecular weight



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ABSTRACT

To elucidate influence of molecular weight on crystallization behavior of β -nucleated isotactic polypropylene (β -nucleated iPP) with different melt structures, a series of β -nucleated iPP with varying molecular weights were prepared. Results revealed that higher iPP molecular weight was more favorable for formation of high β -phase proportion (β_c). By tuning heating temperature (T_f), the melt structure (content of ordered structures within melt) of β -nucleated iPP was controlled. It was found that for all samples, β_c evidently elevated with decrease of T_f , indicating occurrence of synergetic effect between ordered structures and β -NA (ordered structure effect, OSE); with decrease of iPP molecular weight, β_c triggered by OSE increased gradually and T_f temperature range for occurrence of OSE gradually decreased. Moreover, as holding time at T_f increased from 1 to 120 min, subsequent melting curves of samples stayed unchanged, reflecting very high thermal stability of the ordered structures, being independent to iPP molecular weight.

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1. Introduction

Isotactic polypropylene (iPP) is a polymorphic semicrystalline polymer which has wide applications in many fields due to its excellent physical and chemical properties, sharing three crystal modifications, i.e., α -[1,2] β -[3–5] and γ -modifications [6]. Compared with other modifications, β -phase received most attention due to its excellent impact toughness and elongation at break [7,8]. However, β -phase is thermodynamically metastable and can only be obtained under special crystallization conditions such as in the presence of β -nucleating agents (β -NA) [9–12], in a temperature gradient [13], or under the influence of shear stress or oriented fibers [14,15]. During the past decades, intensive works have been carried out to understand the mechanism in the early stage of β -phase crystallization of iPP under various crystallization conditions, however, no general mechanism have been proposed.

In the early stage of polymer crystallization, the existence of ordered structure in the melt before the occurrence of real crystallization or not is still an important issue under debate [3,16–19]. A widely accepted viewpoint claims that polymer chains in the melt are in a random coil state at high temperature, which will not form any ordered structures before the occurrence of the real crystallization. However, more and more experimental results and computational simulations indicate that some ordered structures may exist in supercooled polymer melt before real crystallization takes place, and play a very important role in the crystallization process [18–24]. In the induction period, Kaji et al. [19] proposed the spinodal assisted crystallization mechanism; at the growth front of crystal, Strobl [18] proposed a multistage process model, claiming that there exists a transient mesomorphic layer at the crystal growth front. Li and co-workers [25,26] studied the growth front of iPP spherulites using in-situ micro-analyzing techniques and found the existence of conformational ordering long helices outside the growth front of spherulite.

Moreover, the content of ordered structures can be intentionally controlled by the so-called self-nucleation (SN) experiment through tuning the heating temperature (fusion temperature, T_f) applied on the polymer [20,27–34]. When T_f is not high enough to make the polymer melt fully molten, an amount of ordered

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structures survive within the melt, which can serve as self-nucleating agent during the crystallization process and enhance the nucleation density and crystallization rate. The SN experiment provides a practical way to explore the role of ordered structures in the early stage of crystallization. Using this method, Li et al. [20] studied role of ordered structures from mesomorphic iPP melt in the crystallization process.

Moreover, the ordered structures are found to be important in the early stage of β -crystallization of iPP. Yan and co-workers [15,35–38] introduced partially melting iPP fiber to homogeneous supercooled iPP melt and systematically investigated the β -crystallization of iPP/iPP fiber single composite. They claimed that the partly melting of orientated iPP fibers may provide the locally ordered structures within certain orientation window, which is very important to the β -crystallization; Alfonso and co-workers [39–42] studied the formation and relaxation of shear-induced nucleation and found that shear flow and partially molten fiber have similar effect on the formation of β -phase; Shen and co-workers [43,44] explored the combined effect of ordered structures and shear flow on polymorphic nature of β -cylindrites, and observed that only in the presence of ordered structures can iPP melt form β -cylindrites under the influence of shear flow, showing that ordered structures under shearing is crucial to the β -crystallization of iPP. The above studies proved that under specific conditions such as the influence of oriented fiber or shear stress, the ordered structures in certain orientation played an important role in the early stage of β -phase crystallization.

Recently, by tuning the heating temperature (T_f), we [45–47] tuned the amount of ordered structures in iPP respectively nucleated with several types of β -NA and studied the resulting polymorphic crystallization behavior. Surprising synergetic effect was observed between the dual-selective β -NAs (such as the rare earth based β -NA with the trade name of WBG-II, and the widely used N,N' -dicyclohexyl-2,6-naphthalenedicarboxamide, DCNDCA) and ordered structure of iPP, resulting in evident increase of crystallization temperature, β -nucleation efficiency and the β -phase proportion (Scheme 1), which was called the ordered structure effect (OSE). According to the variations of crystallization peak temperature T_c and the relative percentage of β -phase (β_c) with T_f , the whole T_f range was divided into three regions: regions I, II and III, when T_f was higher than 189 °C, the complete melting was achieved and only low β_c was obtained. The corresponding T_f range

was defined as region I ($T_f > 189$ °C in this study); when T_f was in 168–189 °C, the ordered structures survived in the partial melt exhibited high β -nucleation efficiency under the influence of β -NA and encouraged β -crystallization. Both T_c and β_c increased evidently compared with that in region I. The corresponding T_f range of 168–189 °C was denoted as region II and the special synergetic behavior described above was called the OSE; when T_f decreased to lower than 168 °C, OSE did not take place due to the existence of survived α -ordered entities, which can induce α -crystallization and thus have a negative effect on the β -crystallization. The corresponding T_f range was named as region III ($T_f < 168$ °C).

The study provided first evidence that for the system of iPP nucleated with dual-selective β -NA, ordered structures play a determining role in the early stage of β -nucleation. Under the influence of dual-selective β -NA, the ordered structures exhibit β -nucleation efficiency and therefore strongly encourage β -nucleation. A two-stage β -crystallization model was proposed there.

Since the ordered structures survived in the melt are thermodynamically unstable, which will gradually disappear due to the intensive molecular relaxation at this high T_f [15,31], the thermal stability of ordered structures is closely related to the holding time at T_f and the molecular weight of iPP. However, the role of iPP molecular weight in the occurrence of OSE behavior, and the thermal stability of ordered structures with β -nucleation efficiency are still unknown.

To investigate the role of iPP molecular weight in the OSE behavior, the preparation of β -nucleated iPP with different average molecular weight should be the prerequisite. For this purpose, the widely used peroxide degradation technology provided a practical and reliable way, which has been applied for PP homopolymers and copolymers [47]: in this process, iPP and peroxide were mixed and reacted through the reactive extrusion or banburying, where iPP molecular chains reacted with the peroxide-generated radicals and broke up into shorter chains, resulting in the final product with reduced molecular weight and higher melt flow index. By tuning the concentration of the peroxide additives, the molecular weight of the product can be well controlled and thus a series of iPP samples with different molecular weight can be obtained.

The aim of this study is to investigate the role of iPP molecular weight in the OSE behavior and provide deeper understandings in the OSE behavior of iPP.

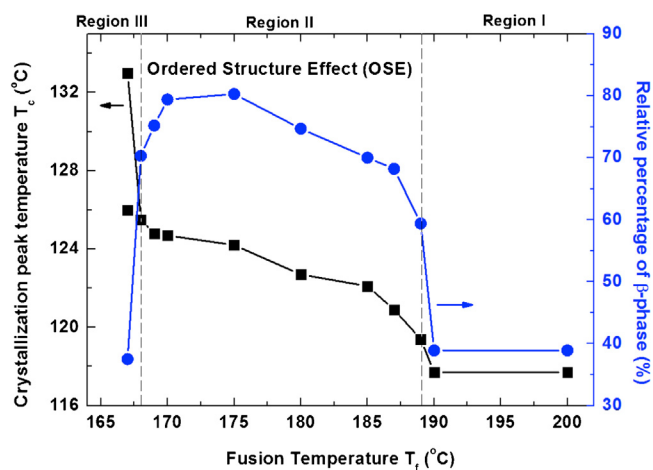
2. Experimental

2.1. Materials

iPP, trade name T38F (Lanzhou Oil Chem., Corp., China) with average isotacticity 97.6%, weighted average molecular weight 347,200, polydispersity index = 3.63, was used.

The β -NA (trade name WBG-II) was supplied by Guangdong Winner Functional Materials Corp. (China), which is a rare earth based high efficiency β -NA with α -/ β -dual polymorphic selectivity. WBG-II is heteronuclear dimetal complex of lanthanum and calcium with some specific ligands, which is a kind of irregular block-like crystal whose single crystal diameters is about tens of nanometers. WBG-II has a general formula of $\text{Ca}_x\text{La}_{1-x}(\text{LIG1})_m(-\text{LIG2})_n$, where x and $1-x$ are the proportion of Ca^{2+} and La^{3+} ion in the complex, while LIG1 and LIG2 are respectively a dicarboxylic acid and amide-type ligand with coordination numbers of m and n [48].

The peroxide used was dicumyl peroxide (DCP) provided by China National Medicine (Group) Shanghai Chemical Reagent Corp. (China) in powder form with density of 1.01 g/cm³, whose half-life time is about 0.25 min at 200 °C.



Scheme 1. Variations of crystallization peak temperature on DSC cooling curves (T_c) and relative percentage of β -phase on DSC heating curves (β_c) as a function of fusion temperature (T_f) of β -nucleated iPP (rare earth based β -NA, trade name WBG-II, concentration 0.03 wt%).

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