Synergies among the self-assembled β-nucleating agent and the sheared isotactic polypropylene matrix

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1. Introduction

Isotactic polypropylene (iPP) is one of the most important commercial plastics owing to its low manufacturing cost and good comprehensive properties. Moreover, iPP is a typical polymorphic polymer with at least four basic crystalline phases, i.e., monoclinic α, trigonal β, orthorhombic γ and mesomorphic smectic phase [1–3]. Among them, β-phase with excellent toughness and ductility is more attractive for wide industrial applications [4–13]. Compared with γ-phase obtained under common conditions (e.g., static state), high content β-phase can be only generated under some specific conditions, such as shearing or elongation deformation [4–6], abrupt temperature gradient [7] and the addition of β-NAs [8–13]. The addition of β-NAs is the most effective and accessible method to obtain higher level β-phase iPP. In the past decades, many studies [12,14–19] have been carried out to investigate the concentration effect of β-NAs on the β-phase crystallinity and mechanical properties of iPP.

Nucleating agents (NA) will be crystallized prior to the crystallization of polymer melts and can aggregate into a certain crystalline structure. In other words, NA can be spontaneously self-assembled. As early as 1979, Roehl et al. [20] discovered that in
low-molecular-weight organic liquids, dibenzylidene sorbitol (DBS) will self-assemble into a three-dimensional percolation network through hydrogen bonding if the content of DBS is relatively low. Subsequently, Mitra et al. [21] and Ilzhoefer et al. [22] showed that DBS could self-assemble into agglomerates within poly (ethylene terephthalate) (PET) melt and fibrillar bundles in poly (dimethylsiloxane) (PDMS) polymer. Especially, some researchers have shown more interests in the self-assembly of NA for iPP [23–25]. More importantly, under quiescent conditions NA is reported to self-assemble into various aggregates, such as needle-like [24] and dendritic [23,25].

As well known, thermoplastic polyolefins (e.g., iPP) are typically fabricated into their final forms by typical polymer processing operations including injection molding, extrusion, blowing, etc. Moreover, the flow field inevitably involved in the practical processing operations can profoundly influence the crystalline structure, orientation and ultimately mechanical properties of the polymers [26–28]. As aforementioned, β-NA is widely employed to improve the toughness and ductility of iPP. Recently, it has been reported that both β-NA [29–31] and x-NA [32,33] can be self-assembled into needle-like microstructure or three-dimensional network structure in the polyolefins matrix during the polymer processing. Unfortunately, the influences of flow fields on the self-assembly of NA in the hosting iPP matrix were scarcely discussed in the open literatures, let alone the effects of self-assembled aggregates on the subsequent crystallization of the iPP matrix.

In this study, the effects of both shear temperature and shear rate on the self-assembly of β-NA were investigated via polarized optical microscopy (POM) and elaborately controlled Linkam CSS450 shear stage. Furthermore, the combined effects of shear and self-assembled aggregate of β-NA on the crystallization of iPP matrix were systematically explored by using wide-angle X-ray diffraction (WAXD) and small-angle X-ray scattering (SAXS).

2. Experimental

2.1. Materials

Commercially available iPP (T30S, melt flow index (MFI): 3.0 g/10 min (230 °C, 21.6 N), weight-average molecular weight (Mw): 39.9 × 10^5 g/mol and molecular weight distribution (MWD): 4.6) was purchased from Dushanzi Petroleum Chemical Co., China. β-NA, a heteronuclear dimetal complex of lanthanum and calcium with some specific ligands, was provided by Winner Functional Materials Co. Ltd. Its general formula is Ca_{x}La_{1−x}(LIG1)_{m}(LIG2)_{n}, where x and 1−x are the proportions of Ca^{2+} and La^{3+} ions in the complex. LIG1 and LIG2 are dicarboxylic acid and amide-type ligands with coordination numbers of m and n, respectively [10]. Its synthetic method is described in the literature [34]. The diameter and length of a single raw β-NA crystal were tens of nanometers and less than 1 μm, respectively.

2.2. Sample preparation

Solution blending method was utilized to prepare β-NA/iPP composites with different β-NA contents (0 and 0.2 wt %). Briefly, β-NA powders and iPP pellets were dissolved in xylene at 130 °C by violent stirring in an oil bath for 1 h. The mixture was remained overnight at room temperature and dried in a vacuum oven to remove excess solvent at 70 °C for 48 h. Finally, the material obtained was hot-pressed into films at 190 °C for 5 min. These films were compression molded with different dimensions: circular samples of 1 mm in thickness and 2.5 cm in diameter for rheological measurement, and 100 μm in thickness and 1.5 cm in diameter for shear experiment. For convenience, the iPP composites containing 0 and 0.2 wt % of β-NA were designated as iPP0 and iPP0.2, respectively.

2.3. Characterization

The rheological measurement, such as temperature dependent dynamic modulus at a particular frequency, is one of the most facile methods to detect the structural change and phase transition temperature of the polymer matrix and its fillers [35]. The rheological measurements were performed in a linear viscoelastic regime on a stress-controlled rheometer (AR2000, TA Instruments) using a dynamic temperature sweep mode under an oscillation frequency of 1 rad/s. The samples (1 mm in thickness, 2.5 cm in diameter) were heated to 240 °C, maintained at this temperature for 5 min to eliminate the thermal history, and then cooled down to 110 °C at a rate of 5 °C/min. A large strain was reported to be able to remarkably enhance the phase transition and impact the resultant morphology [36], therefore, a very small strain of 0.2% was employed in this study. All the rheological measurements were conducted under a nitrogen atmosphere.

The morphology evolution of all samples during shear experiments was observed by a POM (Olympus BX-51 equipped with a Linkam CSS450 shear stage). Fig. 1 illustrates the thermal and shear profiles utilized in this study. The compressed samples were put in the shear stage between two quartz slides. Subsequently, they were heated to 240 °C and maintained at this temperature for 2 min to remove the thermal history. The gap size between the quartz plates was reduced to 30 μm for convenient observations. Finally, the samples were cooled down to shear temperature (T_{shear}) with a cooling rate of 30 °C/min. At a specific T_{shear}, different shear rates (0, 20, 60, 100, 140, 180 and 220 s^{-1}) were applied. The shear time was fixed at 10 s by employing a steady mode. Once the shear was terminated, the samples were subsequently cooled down to crystallization temperature (T_{cry}) at a cooling rate of 30 °C/min for isothermal crystallization until the crystallization was finished.

The crystalline structure of the final crystallized samples was investigated by wide-angle X-ray diffraction (WAXD) and small-angle X-ray scattering (SAXS). The WAXD tests were carried out with a NanoSTAR-U X-ray diffractometer (Bruker AXS INC.). The experiment was performed using Cu Kα radiation operation at 40 kV and 60 mA. The wavelength of X-ray was 0.154 nm and the sample to detector distance was controlled at 84 mm. Scattering patterns were collected by a 2D gas-filled wire detector (Bruker Hi-
respectively. Moreover, once the temperature is further decreased to 104 °C, the onset crystallization temperature of the iPP melt is 104 °C, indicating that the onset crystallization temperature of the iPP melt is 104 °C. The data acquisition time was 60 s per frame, with each frame separated by a waiting time of 5 s.

For both WAXD and SAXS measurements, several sheared films were stacked together to obtain a total thickness of about 1 mm to achieve a maximum diffraction intensity. It is worth noting that all the films were arranged along the shear direction.

3. Results and discussion

3.1. Self-assembly behaviors of β-NA detected by rheological measurements

The self-assembly behaviors of β-NA in the polymer melt can be verified indirectly by the rheological measurements. One way to determine the self-assembly temperature is to measure the storage modulus (G'). The log G' as a function of cooling temperature is shown in Fig. 2. For iPP0, the log G' gradually increases with decreasing the temperature. When the temperature is further decreased to 104 °C, the log G' begins to dramatically increase. This indicates that the onset crystallization temperature of the iPP melt is 104 °C. However, with respect to iPP0.2, the log G' exhibits a complex temperature dependence relative to iPP0. At the beginning of the cooling process, the log G' behaves identically to that of iPP0. Subsequently, the log G' begins to increase more quickly at around 188 °C. Then the log G' increases slightly while the temperature is below 170 °C. This suggests that 188 and 170 °C represent the onset and end temperature for the self-assembly of β-NA, respectively. Moreover, once the temperature is further decreased to around 140 °C, the log G' increases abruptly, suggesting that the onset crystallization temperature for the iPP matrix in iPP0.2 is about 140 °C. Obviously, the onset crystallization temperature of the iPP matrix in iPP0.2 is much higher than that (104 °C) of the iPP0 sample. Such remarkable deviation of the onset crystallization temperature for the iPP matrix should be attributed to the heterogeneous nucleation effect of β-NA. The self-assembly process of β-NA has been verified to be completed prior to the onset crystallization of iPP matrix.

Furthermore, based on the rheological result of the iPP0.2 sample, three different regions corresponding to three different physical states of the system can be easily identified, i.e., Region I at the temperatures above 188 °C, β-NA and iPP form a homogeneous mixture; Region II at the intermediate temperatures ranging from 170 to 188 °C, β-NA is self-assembled; Region III at the temperatures below 170 °C, the self-assembly process of β-NA in the iPP matrix has been completed. Therefore, three different shear temperatures, i.e., 200, 180 and 160 °C, were selected in the following shear experiments to explore the influence of shear temperature on the self-assembled aggregate of β-NA as well as the subsequently developed supermolecular structure of the iPP matrix.

3.2. Supermolecular structure of host iPP matrix under static condition

Fig. 3 shows the supermolecular structure of iPP0 and iPP0.2 during cooling and isothermal crystallization under static conditions. For each sample, four photographs were captured at 180 °C (in the self-assembly temperature range) and 160 °C (after the completion of self-assembly) with crystallization time of 3 min (tcryst was the time for the isothermal crystallization at 130 °C), respectively. As shown in Fig. 3a and b, no crystal is observed at 180 °C and 160 °C for the iPP0 sample. When iPP0 is isothermally crystallized at 130 °C for 2 min (Fig. 3c) and 5 min (Fig. 3d), only sporadic spherulites can be clearly observed. However, in iPP0.2, snowflake-like aggregates of β-NA can be faintly observed even at 180 °C (Fig. 3e) and become clearer at 160 °C (Fig. 3f). Obviously, this POM observation is consistent with the aforementioned rheological result that the self-assembly of β-NA takes place in the temperature range from 188 to 170 °C (see Fig. 2). Moreover, as shown in Fig. 3c, the surface of the self-assembled β-NA can host a large number of sites for the nucleation of the iPP matrix. Additionally, many more nucleation sites in the iPP0.2 sample lead to a faster crystallization of the iPP matrix than that of the iPP0 sample. This case can be confirmed by the fact that the β-NA induced crystals occupy the view field faster than those in iPP0 (see Fig. 3d, d'). Meanwhile, this also indicates that the addition of β-NA results in a dramatic enhancement of crystallization kinetics, which is well consistent with the rheological result that the onset crystallization temperature of the iPP matrix in iPP0.2 is much higher than that of iPP0 (see Fig. 2).

3.3. Influence of shear rate and shear temperature on the self-assembled aggregates of β-NA

To ascertain the impact of shear on the self-assembled aggregates of β-NA in the iPP matrix, the iPP0.2 melt was sheared at different shear rates and shear temperatures (Tshear). The self-assembled aggregates of the β-NA and crystalline morphology of the isothermally crystallized iPP0.2 were observed by POM. To clearly observe the self-assembled aggregates of β-NA during the cooling process, photographs were taken at 138 °C (viz., prior to the crystallization of the iPP matrix). As clearly shown in Fig. 4, only snowflake-like assembly of β-NA is observed in the iPP matrix regardless of the shear rates when Tshear is 200 °C. At this temperature, the formed iPP/β-NA composite is still a homogeneous mixture and the effect of shear on the β-NA self-assembly can be completely removed at such a high temperature. Therefore, the self-assembled aggregate of β-NA is identical to that developed under static condition (see Fig. 3f).

As shown in Fig. 5, when Tshear is decreased to 180 °C, snowflake-like aggregates are steadily distorted. At lower shear rate, most β-NA were changed into deformed snowflake-like aggregates (see Fig. 5a). With further increasing the shear rate, the transformation from the deformed snowflake-like assembly to the needle-like structure is observed (see Fig. 5b-e). At the highest shear rate, only fine needle-like structure is observed (see Fig. 5f). Moreover,
they orient along the shear direction. According to the rheological measurement, 180 °C (in Region II shown in Fig. 2) is a temperature, where β-NA is actually self-assembled. In this region, lower shear rates can slightly deform the snowflake-like aggregates. If higher shear rate is applied, snowflake-like aggregates, which are self-assembled, will be severely dismembered; and these dismembered needle-like fragments are apt to align orderly along the shear direction.

For comparison, different shear rates were applied at lower temperature (i.e., Tshear = 160 °C). Because β-NA has already been self-assembled into snowflake-like aggregates at 160 °C under static condition (see Fig. 3b'), it is conceivable that the self-assembled aggregates will be substantially deformed once the shear is applied at this temperature. Fig. 6a demonstrates that even the shear rate is as low as 20 s⁻¹, the needle-like β-NA with short branching structure rather than snowflake-like, Fig. 3b', is developed and orients along the shear direction. Further increasing the shear rate, the needle-like β-NAs become much finer and denser, significantly different from the samples sheared at higher temperatures (Figs. 4 and 5). Combined with the rheological measurement, the development of needle-like β-NA at lower shear temperature can be understood as follows. The self-assembly of β-NA has been completed at 160 °C under static conditions, and the branches in the snowflake-like structure will be substantially scraped from the assembly once the shear is applied at this temperature. Naturally, these fine branches (i.e., single needle-like β-NA) will align along the shear direction.

To sum up, according to Figs. 4–6, three kinds of aggregates were obtained via the self-assembly of β-NA at different shear temperatures and shear rates, that is, snowflake-like aggregates, deformed snowflake-like ones with smaller branches, fine and oriented needle-like aggregates. Furthermore, with increasing the shear rate, the orientation level of needle-like aggregates becomes higher and higher, while its size (viz., length and diameter)

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Fig. 3. The POM photographs of the iPP0 (a–d) and iPP0.2 (a’–d’) samples. (a, a’): 180 °C during cooling; (b, b’): 160 °C during cooling; (c, c’): isothermal crystallization for 2 min; (d, d’): isothermal crystallization for 5 min. Scale bar is 100 μm.

Fig. 4. The POM photographs of the self-assembled aggregates of β-NA at different shear rates (Tshear = 200 °C). The subscripts represent the shear rate. These photographs were captured at 138 °C. The shear direction is vertical. Scale bar is 100 μm.
becomes smaller and smaller. Further investigation is needed to understand the mechanisms to cause the decreased size of needle-like $\beta$-NA upon increasing the shear rate.

### 3.4. Synergy of shear conditions and self-assembled $\beta$-NA on the supramolecular structure of iPP matrix

The WAXD was first adopted to obtain the information on the crystal variation, overall crystallinity and $\beta$-phase crystallinity in the $\beta$-nucleated iPP. Fig. 7 shows the WAXD spectra of the iPP0.2 sample. As shown in Fig. 7a–c, a sharp peak at $2\theta = 16.1^\circ$, and weak peaks at $2\theta = 14.1^\circ$ and $2\theta = 21.8^\circ$ are observed, characteristic diffraction peak of the (300) plane for the $\beta$-phase, the (13-1), (111) and (041) planes for the $\alpha$-phase, respectively. All these observations clearly indicate the coexistence of $\beta$- and $\alpha$-phases in the iPP0.2 sample regardless of the shear rate and shear temperature.

Through deconvoluting the peaks of one-dimensional (1D) WAXD profiles, the overall crystallinity ($X_c$) was calculated according to Equation (1):

$$X_c = \frac{\sum A_{\text{cryst}}}{\sum A_{\text{cryst}} + \sum A_{\text{amorp}}} \times 100\%$$

where $A_{\text{cryst}}$ and $A_{\text{amorp}}$ are the fitted areas of crystalline and amorphous region, respectively. The relative content of $\beta$-phase...
\((K_b)\) can be evaluated by Turner–Jones criterion \([37]\) as Equation (2):

\[
K_b = \frac{A_{b(300)}}{A_{a(110)} + A_{a(040)} + A_{a(130)} + A_{b(300)}} \times 100\% \tag{2}
\]

where \(A_{b(300)}\) represents the area of the (300) reflection peak; \(A_{a(110)}\), \(A_{a(040)}\) and \(A_{a(130)}\) are the areas of (110), (040), (130) reflection peaks, respectively. Meanwhile, the crystallinity of \(\beta\)-phase \((X_{\beta})\) is given by Equation (3):

\[
X_{\beta} = X_c \times K_b \tag{3}
\]

The calculated results are shown in Fig. 8, where \(X_c\) and \(X_b\) are plotted as a function of the shear rate. For the samples sheared at 200 °C, both \(X_c\) and \(X_b\) have no apparent change at lower shear rates, while a slight increase was observed at higher shear rates. In this case, at high shear temperatures, the molecular chains in the iPP sheared melt are prone to relax and therefore the feeble effect of the shear on the microstructure developed in the iPP matrix is understood. With respect to the samples sheared at 180 °C, \(X_c\) and \(X_b\) become constant at relative lower shear rates, and a slight decrease is observed with further increasing the shear rate, Fig. 8. However, for the samples sheared at 160 °C, \(X_c\) and \(X_b\) decrease sharply even with a relatively low applied shear rate. Moreover, \(X_c\) and \(X_b\) decrease with increasing the shear rate until it reaches 140 s\(^{-1}\). Once the shear rate exceeds 140 s\(^{-1}\), they reach plateau values. In addition, it should be noted that \(X_c\) and \(X_b\) of these samples sheared at 160 °C are much lower than those of their counterparts sheared at 180 and 200 °C. Combined with the evolution of \(\beta\)-NA aggregates under different shear conditions, the decreased \(X_b\) should be ascribed to the formation of tiny and dense needle-like aggregates (see Fig. 5e,f and Fig. 6). Specifically, these formed fine needle-like aggregates are extremely dense to cause

**Fig. 7.** The WAXD spectra for the iPP0.2 sample as a function of shear rate and shear temperature.

**Fig. 8.** (a) \(X_c\) and (b) \(X_b\) as a function of shear rate for the iPP0.2 sample sheared at different temperatures.
very small space between the adjacent aggregates. As a result, the motion of iPP chains even with an applied shear will be substantially restricted, the crystallization is steadily restrained to give a decreased $X_c$ with further increasing the shear rate. In addition, the dramatically decreased $X_b$ in the samples sheared at 160 °C is due to the fact that the shear may greatly accelerate the $\alpha$-nucleation and $\alpha$-crystal growth rate. Such a shear-induced $\alpha$-form will restrain the growth of $\beta$-form and therefore the crystallinity of $\beta$-form is decreased rapidly with increasing the shear rate [38]. On the other hand, upon applying a higher shear rate, the $\beta$-phase is mainly induced by the fine dense needle-like $\beta$-NA. As mentioned above, the adjacent needle-like $\beta$-NAs will allow a confined space for the growth of $\beta$-form crystals. In the view of these, it is understandable that $X_b$ decreases with increasing the shear rate. For the samples sheared at 180 °C, only when the shear rate is high enough, it shows impact on $X_b$. To sum up, though the coexistence of $\alpha$- and $\beta$-phases at different shear temperatures and shear rates can be observed, the ability of $\beta$-NA with different self-assembled aggregates to induce the formation of $\beta$-form shows a significant dependence on the shear temperature and shear rate.

To further explore other crystalline parameters for the samples at different shear temperatures and shear rates, two-dimensional (2D) SAXS measurements have been conducted and the corresponding 2D-SAXS patterns are shown in Fig. 9. For the iPP0.2 sample sheared at 200 °C, the 2D-SAXS patterns generally represent the isotropic scattering rings, indicating that there is no

![Fig. 9. The 2D-SAXS patterns of the iPP0.2 sample as a function of shear rate and shear temperature of (a) 200, (b) 180, and 160 °C. The numbers on the bottom of the pictures represent the shear rate. The shear direction is vertical.](image)

![Fig. 10. The Lorentz-corrected one-dimensional (1D) SAXS intensity profiles.](image)
lamellar orientation. This is understandable because the oriented structures induced by shear are prone to relax at high temperatures. For the iPP0.2 sheared at 180 °C, clearer scattering maxima on the equator can be observed only when a higher shear rate was applied, suggesting that there is a higher level of lamellar orientation along the shear direction. Whereas, for the iPP0.2 sheared at 160 °C, two distinct maxima along the equatorial and meridional directions are observed even when the applied shear rate is lower. Typically, the appearance of strong equatorial maxima can be attributed to the shear-induced α-phase lamellar stacks, which are parallel to the shear direction. Correspondingly, the appearance of a strong meridional maxima can be ascribed to a strong anisotropic epitaxial growth of iPP induced by the self-assembled needle-like β-NA.

The Lorentz-corrected intensity profiles of the circularly integrated 2D-SAXS patterns of all the samples are shown in Fig. 10. The position of scattering peak generally keeps almost constant for the samples sheared at 180 and 200 °C, while it shifts to a higher position with increasing the shear rate for the samples sheared at 160 °C. The average thickness of the amorphous (l_a) and crystalline layers (l_c) can be evaluated from the 1D electron density correlation function k(z) as shown in Equation (4) [39]:

\[ k(z) = \frac{\int_0^\infty I(q)q^2 \cos(qz) dq}{\int_0^\infty I(q)q^2 dq} \] (4)

where \( I(q) \) is the 1D intensity shown in Fig. 10. The calculated results from the 1D electron density correlation functions are shown in Fig. 11. The long period (L) listed in Fig. 12a was calculated by the z value of the first maxima of k(z). Because the crystallinity of all the

![Fig. 11. The k(z) versus z plots of iPP0.2 sheared at different temperatures.](image)

![Fig. 12. The long period calculated from (a) the one-dimensional electron density correlation function k(z) and (b) the Bragg’s law.](image)
samples is higher than 50%, the larger value is assigned as the average thickness of crystalline layers \( (L_c) \). The average thickness of the amorphous \( (L_a) \) can be calculated by \( L_a = L - L_c \).

For comparison, the long period \( L \) related with the position of the scattering peak was also calculated by the Bragg’s law as Equation (5):

\[
L = \frac{2\pi}{q_{\text{max}}}
\]

The calculated results from the Bragg’s law are shown in Fig. 12b. It should be noted that the \( L \) obtained by the \( z \) value of the first maxima of \( K(x) \) is closely identical to that calculated by the Bragg’s law. That is, with increasing the shear rate, \( L \) remains almost constant when the shear temperature is 200 and 180 °C. If the shear temperature is decreased to 160 °C, \( L \) has no obvious change at lower shear rate and shifts to lower values only at higher shear rates. It has been well established that \( L \) of \( \beta \)-phase is larger than that of \( \alpha \)-phase [40], which is relevant to different stacking manners of \( \alpha \)-phase and \( \beta \)-phase in iPP [13]. Thus, the decreased \( L \) for the samples sheared at 160 °C should be ascribed to smaller crystallinity of \( \beta \)-phase (see Fig. 8). As shown in Fig. 13, the \( L \) of the samples sheared at 200 and 180 °C remains almost constant irrespective of the shear rate. However, for the samples sheared at 160 °C, the \( L \) becomes constant when the shear rate is lower and then shifts to a smaller value with further increasing the shear rate. The evolution of \( L_a \) shows the identical trend to that of \( L_c \).

4. Conclusions

The effects of the shear rate and shear temperature on the self-assembly of \( \beta \)-NA were explored. The crystallization of the hosting iPP matrix upon the combined effects of self-assembly aggregates of \( \beta \)-NA and the shear conditions was investigated in details. The results show that, under quiescent condition, 190 and 170 °C are the onset and the end temperature for the self-assembly of \( \beta \)-NA, respectively. Moreover, the self-assembly of \( \beta \)-NA has been completed prior to the crystallization of the iPP matrix. Under shear flow, when \( T_{\text{shear}} \) is 200 °C (at this temperature, a spontaneous self-assembly of \( \beta \)-NA can not take place), the snowflake-like morphology is formed regardless of the shear rate. In this circumstance, \( X_{\beta} \), \( L \) and \( L_c \) keep almost constant with increasing the shear rate. If the shear is applied at 180 °C (at this temperature, \( \beta \)-NA is spontaneously self-assembled under static condition), the long needle-like aggregates of \( \beta \)-NA can be observed. \( X_{\beta} \) decreases while \( L \) and \( L_c \) keep almost constant with increasing the shear rate. When \( T_{\text{shear}} \) is 160 °C (at this temperature, a spontaneous self-assembly for \( \beta \)-NA has been completed under static condition), \( X_{\beta} \), \( L \) and \( L_c \) sharply decrease with increasing the shear rate. The observed different self-assembly aggregates of \( \beta \)-NA developed under shear conditions have demonstrated that the self-assembled aggregates have significant effects on the supermolecular structure of the iPP matrix.

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