Toward Subtle Manipulation of Fine Dendritic $\beta$-Nucleating Agent in Polypropylene

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ABSTRACT: Dendritic $\beta$-nucleating agent ($\beta$-NA) can readily manipulate the formation of dendritic $\beta$-crystals with a unique toughening effect on polypropylene (PP) to drastically enhance the ductility. However, by the current method, the geometric size is too large to fully perform the nucleating efficiency. In this study, by comparatively investigating the effect of molecular weight of PP and diffusion of $\beta$-NAs in a PP melt, we proposed a novel carrier strategy that selective enrichment of $\beta$-NAs in a PP carrier was followed by directed migration into polymer matrix. Accordingly, the growth of NAs was controlled by the release from the PP carrier, which decreased the available amount of $\beta$-NAs during the growth stage. In this case, the viscosity difference between PP carrier and matrix determined the interfacial movement of $\beta$-NAs. When the PP carrier and matrix had same molecular weight, the diffusion and release became favorable to facilitate the formation of the dense and fine dendritic aggregates. As a result, the relative content of $\beta$-crystals reached 92%, with a drastic increase of $\sim$82% in the optimal condition compared to the directed compounded PP/$\beta$-NAs sample. This study can open a new avenue to tailor the topologies of $\beta$-NAs and the ensuing $\beta$-crystals for high-performance PP products.

INTRODUCTION

Polypropylene (PP) is a typical polymorphic material, and the crystalline compositions including crystalline modification and topological structure determine the final properties.1−3 $\beta$-Crystalline can overcome the intrinsic inferior toughness of $\alpha$-crystal and, thus, is more attractive in real practical applications.4,5 With respect to the stable $\alpha$-crystal formed under common processing conditions, $\beta$-crystal is thermodynamically metastable and can be obtained only under some specific crystallization conditions. Generally, incorporation of $\beta$-nucleating agents ($\beta$-NAs) is the most feasible industrial way to boost the number of $\beta$-crystals and enhance the toughness of PP products.6−8

In recent years, some soluble $\beta$-NAs have been found to dissolve in PP melts at high temperature and recrystallize into various morphological aggregations upon cooling, providing a facile and effective tool to tailor the crystalline morphology and the resulting performance of PP products.9−11 By adjusting the final solubility of $\beta$-NAs, Varga firstly obtained dot, needle-like, dendritic NA aggregates and revealed the template effect on the formation of dendritic $\beta$-crystals.12 Luo demonstrated that the PP sheet containing dendritic $\beta$-crystals exhibited an increment of 76% in the impact strength due to better connection between the dendritic crystallites.13 Although soluble $\beta$-NAs and their thermally induced morphologies have been widely studied,14−16 the researches on the $\beta$-NAs morphological regulation mainly focused on relatively high-molecular-weight PP resins.17,18 In these cases, dendritic $\beta$-NAs, which were generated via dissolution-recrystallization process, often existed in the form of micrometer-sized aggregates with thick stems, affording a low specific surface area for heterogeneous nucleation of $\beta$-crystals. As a result, the nucleating efficiency of $\beta$-NAs reduced and some $\alpha$-crystals were inevitably generated in the blank zone without $\beta$-NAs, which had a negative affect on the resulting mechanical properties of PP products. Therefore, it is of great importance to achieve a controllable formation of fine dendritic aggregates of $\beta$-NAs.

Two factors may be taken into consideration to seize the clue of minifying the dendritic aggregates. On the one hand, similar to polymer crystallization, the formation of dendritic $\beta$-NAs aggregates in the PP melt follows the homogeneous nucleation mechanism.19 The size of the resulting $\beta$-NAs is determined by the gap between dissolution and recrystallization temperatures, which, in turn, depends on the concentrations of $\beta$-NAs and molecular weights of PP.20−22 On the other hand, decreasing the available amount of $\beta$-NAs can restrict the furcating growth of the $\beta$-NAs to generate smaller aggregates.23 Enlightened by the diffusion-controlled release technology,24,25 a novel carrier strategy that selective enrichment of $\beta$-NAs in a carrier is followed by the directed migration into polymer matrix should be feasible to regulate the growth of the dendritic aggregates. To this end, we first study the impact of the molecular weight on the dissolution and crystallization temperatures of the PP/$\beta$-NA system by constructing a ternary experimental phase diagram of temperature/concentration/molecular weight. Then, PP resins rich in $\beta$-NAs are proposed as a novel carrier for slowly supplying $\beta$-NAs to the PP matrix via thermal diffusion, and the effects of molecular weights of PP carriers...
Figure 1. Morphological evolution of the PP2 with 0.3 wt % β-NAs when β-NAs were in (a) solid, (c) saturated, and (f) unsaturated conditions. (d, g) Morphology of the recrystallized NA aggregates for saturated and unsaturated condition, respectively. (b, e, and h) Corresponding polarized light microscope (PLM) photos after crystallization of PP at 135 °C.

Figure 2. (a) Dissolution temperature ($T_d$) and (b) recrystallization temperature ($T_c$) of β-NAs in the PP melts of different molecular weights; (c) experimental phase diagram of PP/β-NAs blends as a function of concentration of β-NAs and molecular weight of PP, where the blue surface indicates $T_d$ whereas the green one represents $T_c$. 
were investigated to reveal the diffusion mechanism. Finally, the submicro dendritic $\beta$-NAs aggregates with high nucleating efficiency were obtained, providing a practical instruction for the manipulation of PP crystalline composition and morphology by varying the topologies of $\beta$-NAs.

**RESULTS AND DISCUSSION**

**Ternary Experimental Phase Diagram of PP/$\beta$-NAs Sample: Dependence of Concentration and Molecular Weight.** To study the morphological evolution of $\beta$-NAs, it is necessary to comprehensively understand the underlying correlation between the dissolution and crystallization of $\beta$-NAs in PP melts. We first investigated the states of $\beta$-NAs in PP melts during the heating/cooling processes. As demonstrated in many studies, there are three different physical states in the corresponding PP melts based on the solubility of $\beta$-NAs, namely solid, solid-saturated solution coexistence, and unsaturated solution, determining the ensuing morphologies with the recrystallization during the cooling. A typical growth process is presented in Figure 1. When $\beta$-NAs do not dissolve in PP melt and stay in solid state at low temperature, they keep the original morphology. Once $\beta$-NAs start to dissolve with the increasing temperature, $\beta$-NA/PP solution becomes saturated. Upon cooling, the dissolved molecules are prone to crystallization on the nondissolved ones along the preferred direction under the directing effect of hydrogen bonding between the amide groups attached to $\beta$-NAs, forming the needle-like morphology. With the complete dissolution, i.e., unsaturated solution, the homogeneous nucleation and growth will result in the highly branched dendritic aggregates. The surface of the aggregates hosts a number of nuclei for the growth of $\beta$-crystal, so the topologies of the $\beta$-NAs aggregates can be transformed into the morphologies of the resulting $\beta$-crystal via epitaxial crystallization on the surface. Accordingly, three morphological $\beta$-crystals can be obtained by adjusting the solution state in PP melt: spherulite, fibrous, and dendritic crystals.

The prerequisite for dendritic $\beta$-crystals is the complete dissolution of $\beta$-NAs in the PP melts during heating, and the size is strongly dependent on the undercooling, which represents the gap between dissolution and recrystallization temperatures. Because the dendritic $\beta$-NAs are generated during the cooling process only when they are completely dissolved in PP melts, the heating temperature of the special structure forming is defined as the dissolution temperature ($T_d$). The recrystallization temperature ($T_c$) corresponds to the temperature at which the dissolving $\beta$-NAs initially re-appear. Accordingly, a ternary experimental phase diagram as function of NAs concentration and molecular weight of PP was constructed, as shown in Figure 2. One can observe that both $T_d$ and $T_c$ shift to higher values with increasing $\beta$-NAs concentration and molecular weight.

The dissolution is a substantial movement and exchange process at the interface between the given solute and solvent. It is reported that solute molecules pass through a stagnant film composed of solvent molecules surrounding the solid solute surface and then diffuse into the solvent. Therefore, the diffusion is a limiting factor determining the dissolution of $\beta$-NAs in the PP melt. On the basis of Einstein–Sutherland equation, the diffusion rate is related to the dissolution temperature and the viscosity of the polymer melt.

$$D = \frac{k_B T}{6\pi\eta r}$$

where $D$ is the diffusion constant, $k_B$ is Boltzmann’s constant, $\eta$ is the viscosity, $T$ is the absolute temperature, and $r$ is the radius of the solute particle. Accordingly, variation in the dissolution temperature at the different $\beta$-NAs concentration and PP molecular weight can be well understood. Based on dissolution equilibrium theory, at a given temperature, the solubility of $\beta$-NAs in PP melts is constant, and the thermal molecular motion is intensified and $D$ value increases with increasing temperature, which is favorable for the dissolution of $\beta$-NAs. Obviously, at high concentration of $\beta$-NAs, a higher temperature is required for dissolution. In addition, the viscosity of polymer melt is related to the molecular weight. With rise in the molecular weight of PP, the melt viscosity increases, as shown in Figure 3.

![Figure 3. Zero-shear-rate viscosities of PP resins with different molecular weights.](image)

The $D$ value decreases and the corresponding diffusion of $\beta$-NAs from the boundary layer becomes difficult. Compared to small-molecule solvent, polymer melt featuring long-chain and entanglement networks exhibits a unique cage effect on solute molecules, which need to overcome the large steric hindrance to diffuse through the boundary layer and finally dissolve into the melt. The constraining effect of the network structure on molecular motion has been well-discovered. High-molecular-weight polymer possesses a longer chain with more interand intramolecular entanglements, magnifying the cage effect to constraint the movements of $\beta$-NAs. Therefore, with the increase in the molecular weight of PP, the dissolution temperature of $\beta$-NAs also rises.

Analogous to the results investigated by Kristiansen and his co-workers for PP/α-NAs (di-benzylidene-sorbitol) mixtures, PP/$\beta$-NAs mixture follows a typical monotectic phase behavior, as the two components display totally solid immiscibility and homogeneous solution in liquid state. Upon cooling, the solubility of $\beta$-NAs in PP melts decreases, initiating recrystallization. The recrystallization of $\beta$-NAs in the PP melt is the homogeneous nucleation and growth process. The supercooling expressed by the difference between dissolution and crystallization temperatures dictates the size of the resulting $\beta$-NAs aggregates. Specially, small aggregate is only generated at high supercooling. The contour map of the gap between the $T_d$ and $T_c$ was plotted as a function of the concentration of $\beta$-NAs and the molecular weight of PP. As shown in Figure 4a, the high supercooling is only observed in the narrow region of the concentration lower than 0.2% and molecular weight less...
than \(2.5 \times 10^5\) g/mol. Therefore, fine dendritic aggregates of \(\beta\)-NAs only can be obtained in PP of low molecular weight. Here, two key issues should be noted. First, for the low-molecular-weight PP, the self-nucleation originating from quick molecular motion ability is evident, deteriorating \(\beta\)-nucleating efficiency of \(\beta\)-NAs.38 In this case, \(\alpha\)-crystals prevail over \(\beta\)-crystals, which are verified by dark \(\alpha\)-crystals featuring positive bi-refringence in Figure 4b1. Second, with increasing either molecular weight or \(\beta\)-NAs concentration, the nucleating efficiency is promoted, but it is inevitable to cause the supercooling to decrease. As a result, \(\beta\)-NAs aggregates in Figure 4b2–b5 are more than 200 \(\mu\)m and even reach 600 \(\mu\)m in the lowest supercooling. The \(\beta\)-crystals grow in the zone adjacent to the \(\beta\)-NAs, whereas \(\alpha\)-crystals appear in the blank zone without \(\beta\)-NAs. Unambiguously, it is extremely difficult for PP to generate a large number of fine dendritic \(\beta\)-crystals due to the mismatch between supercooling and nucleating efficiency.

**Morphological Manipulation of \(\beta\)-NAs via Diffusion-Controlled Release Technology.** In the conventional compounding samples, all of the NAs are dispersed homogeneously in the matrix and the size of the resulting \(\beta\)-NAs aggregates is determined by the gap between dissolution and recrystallization temperatures. However, the gap of polar \(\beta\)-NAs in a nonpolar PP, especially a high-molecular-weight one, is low, so the size of \(\beta\)-NAs often is large. Inspired by diffusion-controlled release of drug, \(\beta\)-NAs were first distributed into one kind of PP to obtain a \(\beta\)-NA carrier (c-NA); then the c-NA was added into pure PP matrix. In the diffusion-controlled release process, the growth of \(\beta\)-NA is controlled by the releasing rate of NAs from PP carrier, which can decrease the available amount of \(\beta\)-NAs during the growth stage. As a result, the smaller aggregates can be obtained. In this study, the widely used PP resin having molecular weight of 477 100 g/mol was chosen as a model because \(\beta\)-NAs can promote the crystallization in the form of \(\beta\)-crystal.39,40 Expectedly, the growth of dendritic \(\beta\)-NAs in PP matrix can be weakened via the diffusion-controlled release of \(\beta\)-NAs to obtain homogeneous fine dendritic \(\beta\)-NAs and the ensuring \(\beta\)-crystal. First, the effect of the diffusion between same molecular weight PP on the morphology of \(\beta\)-NAs was revealed. In this case, the molecular weight of \(\beta\)-NAs-loaded PP carrier and PP matrix is the same. Figure 5 displays the morphological evolution of \(\beta\)-

![Figure 4](image1.png)

**Figure 4.** (a) Contour map of the supercooling of \(\beta\)-NAs in different molecular-weight PP melts; (b1)–(b5) the typical PLM photos of the \(\beta\)-crystal in corresponding regions.

![Figure 5](image2.png)

**Figure 5.** Morphological evolution of PP3/\(\beta\)-NAs sample during cooling from 250 °C. The photos are taken at (a) 230 °C, (b) 190 °C, (c) 165 °C, (d) 155 °C, (e) 145 °C, and (f) 137 °C, respectively.
NAs during the cooling process. Initially, needle-like β-NAs appeared at the interface between the two PP phases (Figure 5b,c). With the decrease in the temperature, the fibrous β-NAs branched and large numbers of three-dimensional dendrites evolved from the melt. Compared to the conventional compounding way in which β-NAs were directly incorporated into PP matrix (Figure 4b3), the mean size of dendritic β-NAs decreased from over 500 to 88.5 μm via the diffusion-controlled release technology. Obviously, the diffusion of β-NAs from the PP carrier containing β-NAs effectively controls the growth of dendritic β-NAs.

It should be noticed that the amount of β-NAs was 1% in the carrier, where β-NAs cannot dissolve completely in the PP melts. The diffused β-NAs are possibly stemmed from two forms, namely solid aggregated particles and the dissolving molecules. It must be answered that which kind of β-NAs dominates the diffusion. Carbon nanotubes (CNTs) are insolvable and easily assemble into micrometer-sized aggregates, which are similar to the insoluble β-NA aggregates. Therefore, CNTs can be utilized as tracing elements to reveal the diffusion behavior of the β-NAs in the PP matrix. As shown in Figure 6, the interface between CNTs and pure PP stays...
discernable and unchanged in the whole heating cycle. On the contrary, for PP/NA samples, the interface extended gradually. It can be deduced that the solid β-NA aggregates have no moving ability, and the dendritic β-NA completely resulted from the diffusion of the dissolving β-NA from the PP carrier. When it happens, the physical state of β-NA-Loaded carrier is transformed from solid-saturated solution to solid-unsaturation solution, leading to the further dissolution of the aggregated particles. The dissolving β-NA are supplied sequentially and diffused into PP matrix, so the nucleation and growth of the dendritic β-NA proceed simultaneously. As a result, the resulting aggregates exhibit small size. The formation mechanism of fine dendritic β-NA controlled via diffusion-controlled release is proposed as in Figure 7.

Further, the effect of the PP carriers with different molecular weight was investigated. As shown in Figure 8, when the molecular weight of the PP carrier is higher than that of PP matrix, fine dendritic aggregates of β-NA are observed, similar to the result of Figure 5; in the case of the carrier with the molecular weight lower than that of PP matrix, only few dendritic aggregates of β-NA are confined to the interface between the carrier and PP matrix. This variation can be ascribed to the viscosity difference between the PP carrier and matrix. The viscosity of polymer melt is highly related to the molecular weight. High-molecular-weight PP exhibits high viscosity. When the viscosity of the carrier is higher than that of PP matrix, the diffusion of β-NA happens readily along the decreased-viscosity direction. On the contrary, there is the resistance effect induced by the increased viscosity on the diffusion of β-NA, which can compel the backflow to less viscous carrier in the form of favorable energy. The diffusion of β-NA out of the carrier is difficult and the resulting dendritic aggregates are few (Figure 8c). This is similar to the dispersion of polyhedral oligomeric silsesquioxane with different substituents in polystyrene bulk from Misra group, where the retardant dissolution caused the preferential surface aggregation of the diffusing particles. Additionally, comparison between Figure 8a,b demonstrates that when the carrier has the same molecular weight as the matrix, more β-NA are diffused from the carrier compared to the higher-molecular-weight carrier. This can be attributed to the strong mobility of β-NA in the less viscous PP carrier. Accordingly, we can come to a conclusion that when the PP carrier and PP matrix share the same molecular weight, the fine dendritic β-NA and β-crystals can be achieved via diffusion-controlled release technology.

Finally, the relative contents of β-crystals ($K_p$) in the samples were evaluated by differential scanning calorimetry (DSC) melting curves. The peaks below 155 °C in Figure 9 correspond to the melting of β-crystals, whereas the melting peak above 155 °C resulted from α-crystal. When β-NA are blended directly with the PP matrix, $K_p$ presents the lowest value, which should be attributed to low specific surface area of large β-NA featuring more than 300 μm size generated at the low supercooling (Figure 4b2). On the contrary, with the diffusion-released strategy, the fine aggregates are generated, providing more available nuclei for PP crystallization to facilitate the formation of β-NA; moreover, the size and content of β-NA can be controlled by regulating the molecular weight of the PP carrier. When the carrier has the same molecular weight as the PP matrix, the diffusion of β-NA from the carrier becomes more favorable, leading to dense and finer dendritic β-NA. As a result, the $K_p$ reaches 92%, with a drastic increase of ~82% compared to the directed compounded PP/β-NA sample (HPP). Moreover, it seems interesting that there are double peaks of β-crystals in the directed compounded PP/β-NA sample. As stated earlier, micrometer-sized β-NA in the sample have a low specific surface area and thus low nucleating efficiency of β-NA, resulting in imperfect β-crystals. During the heating process, the less stable β-crystal will be transformed into the stable one, thus two melting peaks of β-crystal are observed at ~155 °C. For the samples prepared via the diffusion strategy, fine β-NA exhibit a high specific surface area to facilitate sufficient crystallization of PP, generating more perfect β-crystals with single melting peak.

**CONCLUSIONS**

In this study, the experimental phase diagram for the binary system consisting of PP and β-NA was constructed to reveal the dependence of the concentration and PP molecular weight on the solubility and crystallization of β-NA in PP melts. The results showed that high supercooling was only observed in the narrow region of the concentration lower than 0.2% and molecular weight less than 2.5 × 10^5 g/mol. Nevertheless, fine dendritic β-crystals cannot be obtained in bulk matrix due to the rapid crystallization of α-form crystal. On the contrary, when β-NA were selectively distributed in the PP carrier, the growth of dendritic β-NA was determined by the diffusion of β-NA out of the carrier, which decreased the available amount of β-NA during the growth stage. As a result, submicron dendritic NAs and β-crystals were generated. Moreover, the releasing efficiency of β-NA depended on the viscosity...
difference between the carrier and matrix. Only if the PP carrier and the matrix had the same molecular weight, the dense and fine β-NAs were formed. The fine dendritic aggregates featuring high specific surface area can provide more available nuclei for PP crystallization to facilitate the formation of β-crystals, which not only drastically increases the fraction of the β-crystals but also promotes the crystallization of more perfect crystal.

**EXPERIMENTAL SECTION**

**Materials.** A series of commercial iPP resins were purchased in this study, and the detailed information is listed in Table 1. β-Nucleating agent (trade mark: TMB-5) was provided by Shanxi Chemical Industry Research Institute (China). Its chemical structure is \( \text{N},\text{N}^\prime\text{-dicyclohexylterephthalamide} \).44

| name | \( M_w \) (g mol\(^{-1}\)) | \( M_n \) (g mol\(^{-1}\)) | MI (g/10 min) | supplier |
|------|-----------------|-----------------|--------------|---------|
| PP1  | 921 400         | 145 900         | 0.5          | Aladdin reagent (China) |
| PP2  | 505 000         | 76 220          | 2.2          | Aladdin reagent (China) |
| PP3  | 477 100         | 74 500          | 4            | Aladdin reagent (China) |
| PP4  | 257 500         | 53 510          | 12           | Aladdin reagent (China) |
| PP5  | 196 900         | 46 170          | 35           | Aladdin reagent (China) |

**Samples Preparation.** To achieve a uniform dispersion of β-NAs in the matrix, a simple two-step method was applied to prepare β-NAs-containing PP in this study. First, the master batches of PP/β-NAs mixture with 1 wt % concentration were melting blended by a micro twin-screw extruder to achieve the desired dispersion. The temperature from barrel to die was set from 150 to 185 °C, with a screw speed of 25 rpm. After granulating, the master batches were then diluted to the expected concentrations of 0.1, 0.2, 0.3, 0.4, 0.5, and 0.7 wt % by adding pure PPs, and extruded again via the same mixing process. For comparison purpose, PP with 0.1 wt % carbon nanotube (CNT) was also prepared in the same way.

**Characterization.** Polarized Light Microscope (PLM). The phase behaviors of the samples were directly observed by polarized light microscope (Leica DM2500P) connected to a hot stage (Linkam THMS600, Linkam Scientific Instruments Ltd., U.K.) and a Pixelink camera (PL-A662). Samples were initially heated to the expected temperature at a rate of 30 °C/min and then held for 5 min to realize thermodynamic equilibrium. Afterward, the samples were cooled to 135 °C at a rate of 10 °C/min, and the self-assembling morphologies of β-NAs were recorded.

Figure 10 illustrates the observation process of the specimens used for diffusion behavior: (a) both pure PP and 1 wt % β-NAs-containing PP pellets were first compressed into thin film using two hot glass slides at 180 °C. The β-NAs-containing PP film (c-NA) was then cut to the appreciated size and put in the center of the pure one via hot compressing at 180 °C. (b) The specimens were heated to 250 °C to partly dissolve β-NAs, thus triggering the diffusion from c-NA to PP matrix. (c) After cooling, the diffusion was terminated, and the β-NAs self-assembled to dendritic aggregates in the PP matrix. For convenience, \( \text{PP}_{x-y} \) was defined, where \( x \) presented the kind of the carrier and \( y \) corresponded to the kind of the matrix.

In addition, the morphologies of the dendritic β-NA aggregates were first recorded by the Pixelink camera and then the Linkage software provided by Linkam Scientific Instruments was utilized to analyze the size of the dendritic aggregates. Over 100 dendritic crystalline aggregates were recorded and the average size and distribution were calculated.

**Rheological Tests.** The extruded pellets were first dried in a vacuum oven at 80 °C for 4 h and then pressed into a 2 mm thick sheet at 180 °C on a hot press. The zero-shear-rate viscosity was then measured by using a rotary rheometer (AR2000, TA instruments) in the steady sweep mode with a shear rate from 0.01 to 10 s\(^{-1}\). The plate diameter was 25 mm and the gap was 1 mm. All of the samples were in equilibrium at 250 °C in the oven for 5 min before start.

**Differential Scanning Calorimetry (DSC).** The relative fractions of β-crystal (\( K_b \)) of samples were investigated with a Q20 differential scanning calorimetry apparatus (TA), which was calibrated using indium and zinc standards. For the samples prepared via the diffusion-released technology, the content of β-NAs in the PP carrier was 1 wt %. The diffusion regions in

![Figure 10. Schematic illustration for the observing process of β-NA diffusion from the PP carrier to PP matrix: (a) placing the c-NA film in the center of the pure one; (b) heating and holding temperature to trigger the diffusion; (c) cooling to observe the self-assembling morphology of β-NAs in PP matrix.](7236)
the observed PLM specimens were cut and then heated from 40 to 200 °C at a rate of 10 °C/min. The relative fraction of β-crystal \( (K_\beta) \) is calculated according to the following equations:

\[
K_\beta = \frac{X_\beta}{X_\beta + X_\alpha}
\]

where \( X_\alpha \) and \( X_\beta \) are the crystallinities of the α- and β-crystals, respectively, and they can be obtained by

\[
X_i = \frac{\Delta H_i}{\Delta H_f^0}
\]

where \( \Delta H_i \) is the measured fusion and \( \Delta H_f^0 \) is the standard fusion heat (177 J/g for the α-crystal and 168.5 J/g for the β-crystal \( ^{15} \)).

For comparison, the homogeneous compounded one with 0.1 wt % NAs was also investigated at the same condition.

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**Notes**
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