## ORIGINAL ARTICLE

# Temperature dependence of crystallization of nano-oriented crystals of iPP and the formation mechanism

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We have studied the melt-elongational crystallization of isotactic polypropylene. In 2010, we observed that 'nano-oriented crystals (NOCs)' were formed when the elongational strain rate ( $\dot{\epsilon}$ ) exceeded a critical value ( $\dot{\epsilon}^*$ ). In this study, we have clarified the formation mechanism of NOCs using the crystallization temperature ( $T_c$ ) dependence of the formation of NOCs and structural studies using small angle X-ray scattering, SAXS, wide angle X-ray scattering, WAXS, and optical microscopy. We propose a 'chain reaction model' for the formation of NOCs; the locally oriented melt is formed by the melt elongation, which significantly accelerates nucleation. The generated nuclei accelerate the formation of the locally oriented melt, which further accelerates the nucleation. We formulate a relationship between  $\dot{\epsilon}^*$  and the nucleation rate (I) based on the above model. We have confirmed that NOCs are formed in the range of  $T_c = 150-167$  °C. We have obtained the degree of supercooling ( $\Delta T$ ) dependence of I from the  $T_c$  dependence of  $\dot{\epsilon}^*$ . Here, we estimated an equilibrium melting temperature in the oriented melt  $T_m^0 = 220$  °C from the observation of NOC formation, where the error in  $T_m^0$  was a few tens of K. The observed I was well-fitted with the well-known equation of  $I \propto p[-C/\Delta T^2]$  for homogeneous nucleation from classical nucleation theory (CNT), where C is a constant. Therefore, we conclude that the formation of NOCs is primarily controlled by a homogeneous nucleation process, which confirms the chain reaction model.

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## INTRODUCTION

Studies of polymer crystallization from the bulky melts can be divided into two categories: crystallization under quiescent conditions and that under flow fields. The former has been thoroughly studied for many years,<sup>1</sup> whereas the latter is not well understood. It has been hypothesized that an intense flow field should elongate the polymer chains, which significantly changes the conformation of the polymer chains within the melt from a Gaussian conformation to an elongated conformation. This conformation change causes a significant change in the crystallization behavior and physical properties of crystalline polymeric materials. Therefore, studies on elongational crystallization are of critical importance because this is one of the most important, unsolved problems in polymer science and technology.

Flow can be divided into shear and elongational flow. A considerable number of studies have focused on the shear induced polymer crystallization<sup>2,3</sup> following the discovery of the formation of 'shish' of polyethylene (PE) from solution by Pennings and Kiel<sup>4</sup> in 1965. The authors demonstrated that the shish is a type of extended chain crystals.<sup>4</sup>

McHugh<sup>5</sup> proposed a rheological theory to explain the shish formation. This theory is based on the hydrodynamics of linear macromolecules, which was reported by Peterlin.<sup>6</sup> The theory is clearly constructed for steady elongation or shearing, not for the transient state, which means that the strain  $(\varepsilon)$  and the time interval of the elongation or shearing  $(\Delta t)$  should be sufficiently large. McHugh<sup>5</sup> considered that the shish will be formed when the polymer chains are extended and oriented within the solution, and he demonstrated that one polymer chain is extended under a large elongational strain rate ( $\dot{\epsilon}$ ) or shear rate ( $\dot{\gamma}$ ). He calculated a type of 'degree of extension of a polymer chain' against  $\dot{\epsilon}$  or  $\dot{\gamma}$  for a 0.2 wt% PE solution in xylene. We can evaluate  $\dot{\epsilon}$  required for an 80% extension of one polymer chain  $(\dot{\epsilon}^{\dagger})$  from Figure 1 in McHugh:<sup>5</sup>  $\dot{\epsilon}^{\dagger} \simeq 10^5 \mathrm{s}^{-1}$  for the same molecular weight  $M = 3 \times 10^5$  as us. McHugh presented an interesting result: the elongational flow can more effectively extend polymer chains than shear flow (Figure 1 in McHugh<sup>5</sup>). However, the melt-elongational crystallization with a large  $\dot{\epsilon}$  remains an important and unsolved problem because determination of the melt elongation has been experimentally difficult.<sup>7</sup>

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**Figure 1** Schematic explanation of the chain reaction model. (a) Model of elongation of a part of one polymer chain between entanglements. (i) Small  $m_e < \langle m_e \rangle$ . Part of the polymer chain is easily extended, which contributes to the formation of the locally oriented melt. (ii) Large  $m_e > \langle m_e \rangle$ . Part of the polymer chain is not extended. (b) Schematic illustration of the chemical potential, *g*, against temperature *T*.  $\Delta h$  of the oriented melt is larger than that of the isotropic melt, and the entropy, *s*, of the oriented melt is smaller than that of the isotropic melt. Therefore,  $T_m^0$ (om) becomes larger than  $T_m^0$ (im). (c) Model of chain elongation between a nucleus and an entanglement or between nuclei. (d) Schematic illustration of  $v_{om}$  against  $\dot{\epsilon}$ . (a and c) Direction of the elongational flow is horizontal.

We succeeded in the melt-elongational crystallization of isotactic polypropylene (iPP) (2010).8 The weight averaged molecular weight  $(M_w)$  was  $3 \times 10^5$ , and the crystallization temperature  $(T_c)$  was 150 °C. We overcame the technical difficulty in the melt elongation by compressing the supercooled melt with a pair of plates or rolls. The added strain ( $\varepsilon$ ) was as small as the order of unity. When the  $\dot{\epsilon}$  became larger than a critical value ( $\dot{\epsilon}^* \cong 2 \times 10^2 \, \text{s}^{-1}$ ), the morphology and structure of the iPP transformed from the well-known spherulite structure with stacked lamellae of folded chain crystals (FCCs) to that of a 'nano-oriented crystal (NOC)' structure. The crystallization rate significantly and discontinuously increased by 10<sup>6</sup> times at  $\dot{\epsilon} \ge \dot{\epsilon}^*$ , from which we concluded that the nucleation transformed from heterogeneous to homogeneous nucleation.9 From the above experimental findings, we proposed a model for the formation of the NOCs in which the oriented melt will appear by compressing the supercooled melt and then homogeneous nucleation would be accelerated within the oriented melt. The verification of this model remains an important task.

The observed  $\dot{\epsilon}^* \cong 2 \times 10^2 \text{s}^{-1}$  was ~10<sup>3</sup> times smaller than the value of  $\dot{\epsilon}^{\dagger} = 10^5 \text{ s}^{-1}$  given by McHugh, that is, the ratio  $\dot{\epsilon}^{\dagger}/\dot{\epsilon}^*$  is as large as 10<sup>3</sup>. As the former ( $\dot{\epsilon}^*$ ) is obtained for the melt crystallization of iPP for the transient elongation, and the latter ( $\dot{\epsilon}^{\dagger}$ ) is calculated for the solution crystallization of PE for the steady elongation, we discuss

the ratio as follows: (1) because the former was obtained for a rather small  $\varepsilon$  and  $\Delta t$ , the elongation is in a transient state. Therefore, the  $\dot{\epsilon}^{\dagger}/\dot{\epsilon}^*$  ratio should significantly increase; (2) PE and iPP are similar flexible polymers because the number of monomers between two entanglements ( $N_e$ ) (within the melt) of these polymers is similar (100 (Wu<sup>10</sup>) and 164 (Eckstein et al.,<sup>11</sup>), respectively). Therefore, we may compare the  $\dot{\epsilon}^{\dagger}$  of PE with the  $\dot{\epsilon}^*$  of iPP; and (3) as  $N_e$  in the solution with the concentration of c (=0.2 wt%) should be replaced by  $N_e/c$ ,<sup>12</sup> the topological effect on  $\dot{\epsilon}^{\dagger}$  is diluted by an order of 1/c (=50). This dilution of the topological effect decreases the  $\dot{\epsilon}^{\dagger}/\dot{\epsilon}^*$  ratio but will not result in a two-digit decrease. Therefore, we may summarize from the above statements (1), (2) and (3) that  $\dot{\epsilon}^{\dagger}/\dot{\epsilon}^* \gg$  1, which means that the observed  $\dot{\epsilon}^*$  is not sufficiently large for the full extension of the polymer chains. Therefore, we have to assume that the bulky melt transforms into a 'locally oriented melt' rather than a completely oriented melt, even for  $\dot{\epsilon} \ge \dot{\epsilon}^*$ . It is important to determine how the 'locally oriented melt' is formed.

In the study of stress-induced crystallization of vulcanized rubbers from the amorphous solid, Toki *et al.*<sup>13</sup> demonstrated that the crystallization begins from the locally oriented amorphous solid. Tosaka *et al.*<sup>14</sup> suggested that the locally oriented amorphous solid is preferentially formed by an effective extension of the shorter partial chains that have a smaller  $M_c$  than the averaged  $M_c$ , where  $M_c$  is the *M* between two cross-links. Valentin *et al.* directly showed the distribution of  $M_c$  using nuclear magnetic resonance.<sup>15</sup> Although the mechanisms for the crystallization from the melt and from the amorphous solid are significantly different, especially in the effect of diffusion, the similarity between the locally oriented amorphous solid and the locally oriented melt is notable.

The objectives of this paper are as follows: (1) To propose a mechanism for the formation of the NOCs, which is called the 'chain reaction model of NOC formation'; (2) To observe the crystallization temperature ( $T_c$ ) dependence of the NOC formation; and (3) To confirm the proposed mechanism for the formation of NOCs by showing that the formation of NOCs is primarily controlled by the nucleation process.

Here, we will present a strategy on how to achieve the objectives of this paper.

(1) Propose a 'chain reaction model of NOC formation.'

(2) Based on the chain reaction model, formulate the relationship between  $\dot{\epsilon}^*$  and the nucleation rate (denoted by *I* or *I*( $\Delta T$ )) of NOCs, that is,  $\dot{\epsilon}^* = \dot{\epsilon}^*(I)$  or  $I = I(\dot{\epsilon}^*)$ .

(3) Observe the  $T_c$  dependence of the NOCs formation and obtain the degree of supercooling ( $\Delta T$ ) dependence of  $\dot{\epsilon}^*$ ,  $\dot{\epsilon}^*_{obs}$ .  $\Delta T$  is defined by  $\Delta T \equiv T_m^0 - T_c$ , where  $T_m^0$  is an equilibrium melting temperature.

(4) By combining (2) and (3), we will have the  $\Delta T$  dependence of the observed *I*,  $I_{obs}$ .

(5) If the obtained  $I_{obs}$  fits the following formula of  $I(\Delta T)$  for a homogeneous nucleation, which is well known in classical nucleation theory (CNT),<sup>9,16–18</sup> we can conclude that the formation of NOCs is primarily controlled by the nucleation process:

$$I(\Delta T) = I_0 \exp[-C/\Delta T^2] \text{ for homogeneous nucleation,}$$
(1)

where  $I_0$  is a pre-factor and C is defined as

$$C = \frac{32\sigma^2\sigma_{\rm e}(T_{\rm m}^0)^2}{kT\Delta h^2} \tag{2}$$

where  $\sigma$  is the side surface free energy of a nucleus,  $\sigma_e$  is the end surface free energy of a nucleus, kT is the thermal energy and  $\Delta h$  is the enthalpy of fusion.<sup>9</sup>  $\sigma$  and  $\sigma_e$  are called the kinetic parameters.

When studying the crystallization mechanism of any material, determining the primary rate determining process, such as nucleation or diffusion, is the most important step.<sup>9</sup> This determination is accomplished by observing how the crystallization process depends on  $T_c$  or  $\Delta T$ .

It is well known that the  $T_m^{0}$  in the oriented melt  $(T_m^{0}(\text{om}))$  should be considerably higher than that in the isotropic melt  $(T_m^{0}(\text{im}))$ ,

$$T_{\rm m}^0(\rm om) > T_{\rm m}^0(\rm im) \tag{3}$$

due to the reason shown below. Thermodynamics defines  $T_{\rm m}^{0}$  as

$$T_{\rm m}^0 = \Delta h / \Delta s, \tag{4}$$

where  $\Delta h$  and  $\Delta s$  are the enthalpy of fusion and the entropy of fusion, respectively.<sup>19</sup> Because  $\Delta s$  in the oriented melt is less than that in the isotropic melt, whereas  $\Delta h$  in the oriented melt is greater than that in the isotropic melt due to excess kinetic energy for extension, we obtain Equation 3. Although the determination of  $T_{\rm m}^{0}(\text{om})$  is important when studying flow-induced crystallization, no studies have experimentally determined reliable  $T_{\rm m}^{0}(\text{om})$  on any polymers, as far as the authors know. We will experimentally estimate a probable figure of  $T_{\rm m}^{0}(\text{om}) = 220 \,^{\circ}\text{C}$  in this paper by observing the  $T_{\rm c}$  dependence of the formation of NOCs.

Determining the mechanism for the formation of NOCs will contribute to developing a new field of research into the melt-elongational crystallization in polymer science and to exploring new polymeric materials with high performance in the polymer industry.

## THEORY: CHAIN REACTION MODEL OF NOC FORMATION Chain reaction model

It is well known in rheology that entanglements cannot be solved within a timeframe that is considerably shorter than the longest relaxation time  $(\tau_{max})^{20}$  Therefore, when the melt is elongated with a  $\dot{\epsilon}$  that is larger than  $\tau_{\text{max}}^{-1}$ , that is,  $\dot{\epsilon} \gg 1 \text{ s}^{-1} \gg \tau_{\text{max}}^{-1}$ , the number density of entanglements, ve, should be conserved. In other words, the entanglements should behave as a type of chemical cross-linkings for large  $\dot{\epsilon}$ . The entanglements are classified into two types, knots and linkings, when an entanglement is formed within one chain or between a few chains, respectively,<sup>21</sup> and there are various types of entanglements with different topological complexities,<sup>22</sup> which are sometimes described by Gauss' linking number, Ie.23 In the case of large  $\dot{\epsilon}$ , all types of entanglements should contribute to the extension of the polymer chains. The entanglements are described by the topological distribution function known as the knotting or linking probability  $P(I_e; M; d)$ , where d is the distance between the centers of mass of two chains. Therefore, the types of entanglements and the entanglement molecular weight  $(M_e)$  are functions of  $I_e$ , M and d. Therefore, the  $M_e$  should have a significant distribution within the real melt, and the reported  $M_e$  is an averaged one,  $\langle M_e \rangle$  (Private communication with Professor Isono, Y). However, the actual distribution of the Me has not been well studied and remains an unsolved problem in polymer science.

Therefore, some parts of the chains (composed of some numbers of segments) between two entanglements with a smaller  $M_e$  should be preferentially extended and should form 'the locally oriented melt' as schematically illustrated in Figures 1ai, whereas the other parts of the chains with larger  $M_e$  will not be extended (Figure 1aii)). The  $\langle M_e \rangle$  of iPP is  $\sim 7 \times 10^3$ , which corresponds to a mean number of monomers of  $\langle N_e \rangle = 1.6 \times 10^{2.11}$  Because the length of one monomer along the c axis in the unit cell is  $\sim 0.22$  nm,<sup>24</sup> the extended partial chain length with  $\langle N_e \rangle$  equals  $\sim 30$  nm; here, the size of an entanglement (composed of  $\sim 35$ –40 carbon atoms) has been omitted.<sup>25</sup> Therefore, the preferentially extended length of a partial chain with a considerably smaller  $\langle M_e \rangle$  may be < 30 nm. From this result, the scale of the oriented melt formed during the initial stage may be significantly < 30 nm.

In CNT, I is given as

$$I \equiv I_0 \exp[-\Delta G^* / kT], \tag{5}$$

where  $\Delta G^*$  is the activated free energy required for the formation of a critical nucleus.<sup>9</sup>  $\Delta G^*$  is given as

$$\Delta G^* = \frac{32\sigma_s^2 \sigma_e}{\Delta g^2} \text{ for homogeneous nucleation,}$$
(6)

where  $\Delta g$  is the free energy of fusion.  $\Delta g$  is approximated as

$$\Delta g = \Delta h \Delta T / T_{\rm m}^0. \tag{7}$$

Thus, we obtain Equation 1.

On the basis of thermodynamics, the chemical potential g of the crystals, the isotropic melt and the oriented melt against T is illustrated in Figure 1b. Here, the enthalpy, h, corresponds to the intercept of the vertical axis at T = 0 K. The h of the crystals, h(c), should be the minimum. Here, we do not distinguish between the h of the NOCs and the FCCs. The h of the melt, h(m), should be greater than the h(c). The h(m) of the oriented melt, h(om), should be

greater than that of the isotropic melt h(im) because the formation of the oriented melt requires excess kinetic energy (work) to extend the polymer chains by overcoming the entropic force. Thus, we have the following relationship:

$$h(\mathrm{om}) > h(\mathrm{im}) > h(\mathrm{c}). \tag{8}$$

It is clear that

$$\Delta h(\text{om}) > \Delta h(\text{im}),$$
 (9)

where  $\Delta h(\text{om}) = h(\text{om})-h(\text{c})$  and  $\Delta h(\text{im}) = h(\text{im})-h(\text{c})$ . The entropy of the melts and the crystals, *s*(om), *s*(im) and *s*(c), should have the relationship

$$s(\mathrm{im}) > s(\mathrm{om}) > s(\mathrm{c}). \tag{10}$$

We constructed the g vs T diagram (Figure 1b) by combining the above relationships. In Figure 1b, the  $T_{\rm m}{}^0$  in the isotropic melt and in the oriented melt,  $T_{\rm m}{}^0(\text{im})$  and  $T_{\rm m}{}^0(\text{om})$ , are shown. The thermodynamic driving forces,  $\Delta g$ , for nucleation from the oriented and isotropic melts at a  $T_c$ ,  $\Delta g(\text{om})$  and  $\Delta g(\text{im})$ , are shown in Figure 1b. It is clear that

$$\Delta g(\text{om}) > \Delta g(\text{im}) \text{ for } T = T_c.$$
 (11)

This result is a thermodynamic prediction that nucleation from the oriented melt should be significantly faster than that from the isotropic melt.

Next, we will focus on the kinetics of the nucleation process. The nucleus from the oriented melt should be a bundle type because there is no reason for the chains to regularly fold back during nucleation. We have shown that the end and side surface free energies,  $\sigma_e$  and  $\sigma$ , respectively, in a nucleus are similar:<sup>26</sup>

$$\sigma_{\rm e} \cong \sigma. \tag{12}$$

The  $\sigma_e$  and  $\sigma$  in the oriented melt,  $\sigma_e(\text{om})$  and  $\sigma(\text{om})$ , should be considerably smaller than those in the isotropic melt,  $\sigma_e(\text{im})$  and  $\sigma(\text{im})$ , that is,

$$\sigma_{\rm e}({\rm om}) \ll \sigma_{\rm e}({\rm im}) \text{ and } \sigma({\rm om}) \ll \sigma({\rm im}).$$
 (13)

The decrease of  $\sigma$  and  $\sigma_e$  takes the dominant role in Equation 6 because the increase of  $T_m^{0}(\text{om})$  and the increase of  $\Delta h(\text{om})$  are relatively small. Therefore, the  $\Delta G^*$  in the oriented melt,  $\Delta G^*(\text{om})$ , becomes considerably smaller than that in the isotropic melt,  $\Delta G^*(\text{im})$ , that is,

$$\Delta G^*(\text{om}) \ll \Delta G^*(\text{im})$$
 for the same  $\Delta T$ . (14)

Therefore, some quantity of nuclei should be instantaneously generated within the locally oriented melt. The size of a critical nucleus along the c axis is given by

$$l^* = 2\sigma_{\rm e}/\Delta g. \tag{15}$$

Considering Equations 11, 13 and 15, we obtain the relationship

$$l^*(\text{om}) \ll l^*(\text{im}). \tag{16}$$

As we showed  $l^*(\text{im}) = 88/\Delta T \text{ nm}$  for the  $\alpha_2$  form of iPP,<sup>27</sup> we have  $l^*(\text{om}) \ll /\Delta T \text{ nm}$ . Therefore, the  $l^*(\text{om})$  is < 1 nm for  $\Delta T = 53-70 \text{ K}$ , which will be shown later. Therefore, the above scale of the oriented melt should be sufficiently large for the nucleation of a critical nucleus.

After nucleation, some parts of the polymer chains included within the nucleus should be topologically 'pinned' (Figure 1c). Therefore, the pinned parts of the chains should behave as a type of chemical cross-linkings and accelerate to form 'the locally oriented melt' (private communication with Professor Watanabe H). After nucleation, the usual knots will transform into tight knots due to reeling in between the growing nucleus (=crystals), as de Genes reported.<sup>25</sup> Therefore, the increase of the tight knots will also accelerate the formation of the locally oriented melt.

The newly formed locally oriented melt significantly accelerates the nucleation rate again, which also results in the formation of the locally oriented melt. Thus, both the formation of the oriented melt and the acceleration of the nucleation process repeat again and again, just like a type of 'chain reaction,' and finally the NOCs will be formed. Therefore, we will call this model the 'chain reaction model of NOC formation.'

### Relationship between $\dot{\epsilon}^*$ and I

The chain reaction model proposes that the nuclei of the NOCs should be generated from the locally oriented melt with some probability of a nucleation rate of NOCs, *I*. This result is similar to the nucleation from the solution or the heterogeneous nucleation studied in CNT.<sup>9</sup> Therefore, the number density of nuclei of NOCs,  $v_{\text{NOC}}(\dot{\epsilon})$ , can be defined as the product of the number density of the locally oriented melt,  $v_{\text{om}}(\dot{\epsilon})$ , and  $I(\Delta T)$ , that is,

$$\nu_{\rm NOC}(\dot{\epsilon}) \equiv I(\Delta T) \, \nu_{\rm om}(\dot{\epsilon}). \tag{17}$$

Here, the 'number density' is used rather than the 'volume fraction' because number density is commonly used in CNT. From the chain reaction model, we assume that the necessary condition for NOC formation is when  $v_{\text{NOC}}(\dot{\epsilon})$  becomes larger than a critical  $(v^{\dagger}_{\text{NOC}}(\dot{\epsilon}^*))$ , that is

$$\nu_{\text{NOC}}(\dot{\epsilon}) \geqslant \nu_{\text{NOC}}^{\dagger}(\dot{\epsilon}^*),\tag{18}$$

where equal (=) holds for  $\dot{\epsilon} \equiv \dot{\epsilon}^*$ , as for  $\dot{\epsilon} > \dot{\epsilon}^*$ , NOCs should be dominantly formed. After passing through the critical condition, the formation of NOCs will be automatically accelerated by the chain reaction mechanism.

The  $v_{om}(\dot{\epsilon})$  corresponds to McHugh's degree of chain extension.<sup>5</sup> McHugh demonstrated that the degree of chain extension begins increasing at some  $\dot{\epsilon}$  or  $\dot{\gamma}$  and saturates at large  $\dot{\epsilon}$  or  $\dot{\gamma}$ , as shown in Figure 1 of McHugh.<sup>5</sup> Therefore, we assume that the  $v_{om}(\dot{\epsilon})$  similarly increases with the increase of  $\dot{\epsilon}$ , as shown in Figure 1d. Following McHugh, the  $v_{om}(\dot{\epsilon})$  may be insensitive to  $T_c$  and  $\Delta T$ . In Figure 1d, the  $\dot{\epsilon}^*$  should correspond to around the middle part in the  $v_{om}(\dot{\epsilon})$  we  $\dot{\epsilon}$  curve because  $v_{om}(\dot{\epsilon})$  should significantly increase around  $\dot{\epsilon}^*$  and then saturate to approximately unity. Therefore, we may approximate  $v_{om}(\dot{\epsilon})$  around  $\dot{\epsilon}^*$  by a tangential line, that is:

$$v_{\rm om}(\dot{\epsilon}) \cong a\dot{\epsilon} - b \text{ for } \dot{\epsilon} \cong \dot{\epsilon}^*,$$
(19)

where a and b are coefficients. Therefore, from Equation 19,

$$v_{\rm om}(\dot{\epsilon}^*) \cong a\,\dot{\epsilon}^* - b \text{ for } \dot{\epsilon} = \dot{\epsilon}^*.$$
 (20)

It is natural to consider that the formation of NOCs becomes difficult with the decrease of  $\Delta T$ , from which it is logical to consider that  $\dot{\epsilon}^*$  significantly increases with the decrease of  $\Delta T$ , as will be shown in Results. The combination of the above considerations and Equation 20 reveals that  $v_{\rm om}(\dot{\epsilon}^*)$  significantly decreases with the increase of  $\Delta T$ , whereas *I* significantly increases with the increase of  $\Delta T$ . As  $v_{\rm om}(\dot{\epsilon}^*)$  and *I* show an opposite  $\Delta T$  dependence, the product of  $v_{\rm om}(\dot{\epsilon}^*)$  and *I* becomes insensitive to a limited range of  $\Delta T$  in this study. Therefore, we may assume as the zeroth approximation that

 $v_{\text{NOC}}^{\mathsf{T}}(\dot{\epsilon}^*) = I v_{\text{om}}(\dot{\epsilon}^*) \cong \text{ const. for a limited range of } \Delta T.$  (21)

Combining Equations 20 and 21, we obtain the  $\Delta T$  dependence

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of  $\dot{\epsilon}^*$ ,  $\dot{\epsilon}^*(\Delta T)$ ,

$$\dot{\epsilon}^*(\Delta T) \cong \frac{1}{a} \cdot \left(\frac{\text{const.}}{I(\Delta T)} + b\right).$$
 (22)

Thus, we finally obtain the relationship between  $\dot{\epsilon}^*(\Delta T)$  and  $I(\Delta T)$ ,

$$\dot{\epsilon}^*(\Delta T) \cong \frac{A}{I(\Delta T)} + B,$$
(23)

or

$$I(\Delta T) \cong \frac{A}{\dot{\epsilon}^*(\Delta T) - B} \propto \frac{1}{\dot{\epsilon}^*(\Delta T) - B'}$$
(24)

where A = const./a and B = b/a.

## How to demonstrate that nucleation mainly controls NOC formation

Now we can obtain the observed  $I(\Delta T)$ ,  $(I_{obs})$ , as a function of  $\Delta T$  from the observed  $\dot{\epsilon}^*$  ( $\dot{\epsilon}^*_{obs}$ ) by using Equation 24. Therefore, we can verify that the formation of NOCs is primarily controlled by the nucleation process by confirming that the  $\Delta T$  dependence of  $I_{obs}$  satisfies Equation 1. Note that determining the constant A in Equation 24 is not required in this confirmation.

#### EXPERIMENTAL PROCEDURE

### Sample and condition of the melt-elongational crystallization

We used commercial iPP  $(M_w = 27 \times 10^4, M_w/M_n = 8, \text{tacticity} [mmmm] = 0.98$ , SunAllomer Ltd., Tokyo, Japan). The  $T_m^{0}$  of the  $\alpha_2'$  form<sup>24</sup> under a quiescent field was 187 °C.<sup>28</sup> We used a roll-type crystallization apparatus for the one-dimensional compression-type crystallization.<sup>8</sup> The sample was melted within an extruder at a temperature (the maximum temperature  $(T_{max}) = 210$  °C) greater than the  $T_m^{0}(\text{im})$ , cooled to a crystallization temperature ( $T_c = 150-172$  °C) and then rolled to elongate the supercooled melt into a sheet between a pair of rotating rolls with a diameter of 250 mm. The temperature of the rolls was also maintained at the  $T_c = 150-172$  °C. The roll gap was changed from 0.1 to 1 mm. The lowest  $T_c$  used was 150 °C because stable crystallization of NOCs was difficult at  $T_c \leq 145$  °C. The range of  $\dot{\epsilon}$  was changed from  $0-6 \times 10^2$  s<sup>-1</sup>.

We determined  $\dot{\epsilon}^*$  using an optical microscope, small angle X-ray scattering (SAXS) and wide angle X-ray scattering (WAXS) according to the methods presented in Okada *et al.*<sup>8</sup> We will denote by  $\dot{\epsilon}(S)$ ,  $\dot{\epsilon}(M)$  and  $\dot{\epsilon}(L)$  the cases  $\dot{\epsilon} \ll \dot{\epsilon}^*$ ,  $\dot{\epsilon} < \dot{\epsilon}^*$  and  $\dot{\epsilon} > \dot{\epsilon}^*$ , respectively.

#### Instruments

The optical morphology of the sample was observed using a polarizing optical microscope (Olympus, Tokyo, Japan, BX51N-33P-OC) and a Digital CCD camera system (Olympus, DP25). Because the morphology observed with the polarizing optical microscope was the same as that in ref 8, we will not present it here.

The SAXS and WAXS measurements were performed using synchrotron radiation at the BL03XU and BL40B2 beamlines of SPring-8 at the Japan Synchrotron Radiation Research Institute (JASRI) in Harima city. The X-ray wavelength was 0.1–0.2 nm, the camera length was 0.3–7.7 m, and we used an imaging plate as a detector. We obtained the SAXS and WAXS intensity of the sample by correcting for the background intensity. The sample was exposed to the incident X-ray beam along the through, edge and end directions. Here, the through direction is parallel to the compressed direction, the edge direction is perpendicular to the through direction and the elongational direction, and the end direction is parallel to the elongational direction.

#### RESULTS

#### $T_c$ and $\dot{\epsilon}$ dependence of SAXS patterns

The typical  $\dot{\epsilon}$  dependence of the SAXS patterns at  $T_c = 150$ , 160 and 167–170 °C is shown in Figure 2. These patterns were all collected in the through direction. Furthermore, these patterns all exhibited



**Figure 2**  $\dot{\epsilon}$  dependence of SAXS patterns at four  $T_c$ s. Through-view. (a)  $T_c = 150 \,^{\circ}$ C. (i and ii)  $\dot{\epsilon}(S) = 9 \, s^{-1}$ . (iii and iv)  $\dot{\epsilon}(M) = 82 \, s^{-1}$ . (v and vi)  $\dot{\epsilon}(L) = 510 \, s^{-1}$ . The printed intensity of (ii), (iv) and (vi) is increased by 4, 12 and 23 times from (i), (iii) and (v) to show relatively weak reflections, respectively. (b)  $T_c = 160 \,^{\circ}$ C. (i and ii)  $\dot{\epsilon}(S) = 30 \, s^{-1}$ . (iii and iv)  $\dot{\epsilon}(M) = 116 \, s^{-1}$ . (v and vi)  $\dot{\epsilon}(L) = 314 \, s^{-1}$ . The printed intensity of (ii), (iv) and (vi) is increased by 6, 6 and 28 times from (i), (iii) and (v), respectively. (c) (i and ii)  $T_c = 170 \,^{\circ}$ C and  $\dot{\epsilon}(M) = 334 \, s^{-1}$ . (iii and iv)  $T_c = 167 \,^{\circ}$ C and  $\dot{\epsilon}(L) = 494 \, s^{-1}$ . A beam-stop was placed asymmetrically to increase the angular resolution. The printed intensity of (ii) and (iv) is increased by 14 and 4 times from (i) and (iii), respectively.

intense oriented 'two-point patterns' along the elongational direction, as shown in Okada  $et al.^8$ 

Figure 2a presents the SAXS patterns at  $T_c = 150 \text{ °C}$ , which is the lowest  $T_c$  in this study. (i) and (ii), (iii) and (iv) and (v) and (vi) correspond to the patterns for  $\dot{\epsilon}(S)$ ,  $\dot{\epsilon}(M)$  and  $\dot{\epsilon}(L)$ , respectively. The distance between the two-points (2q) was almost the same for all

 $\dot{\epsilon}s$ , where *q* is the wave-vector of a reflection. This result indicates that the size of the NOCs does not depend on  $\dot{\epsilon}$ . When we observe the patterns in detail, the shape of the two-point region exhibited a change from a glob-type to a round-type with the increase of  $\dot{\epsilon}$ . The glob-type pattern sometimes exhibited doublet peaks or one primary peak with a plateau or shoulder. The  $\dot{\epsilon}(S)$  and  $\dot{\epsilon}(M)$  patterns also exhibited the superimposition of a ring pattern (Figure 2aii and iv), whereas  $\dot{\epsilon}(L)$  did not exhibit any rings (Figure 2avi). The presence of the rings indicated some un-oriented structures. Details of the above will be analyzed in the Analysis.

Figure 2b presents the SAXS pattern at the middle  $T_c$ ,  $T_c = 160$  °C. (i) and (ii), (iii) and (iv) and (v) and (vi) correspond to patterns for  $\dot{\epsilon}(S)$ ,  $\dot{\epsilon}(M)$  and  $\dot{\epsilon}(L)$ , respectively. The shape of the two-point pattern changed with the increase of  $\dot{\epsilon}$  (Figure 2bi, iii and v). The pattern exhibited a glob-like two-point for  $\dot{\epsilon}(S)$ , a rounded two-point and shoulder-like one for  $\dot{\epsilon}(M)$  and a rounded two-point for  $\dot{\epsilon}(L)$ . The patterns exhibited a ring for  $\dot{\epsilon}(S)$  and  $\dot{\epsilon}(M)$ , but did not exhibit a ring for  $\dot{\epsilon}(L)$  (Figure 2bii, iv and vi, respectively).

Figure 2c presents the SAXS patterns at a rather high  $T_{\rm c}$ . (i) and (ii) and (iii) and (iv) correspond to patterns for  $\dot{\epsilon}({\rm M})$  at 170 °C and for  $\dot{\epsilon}({\rm L})$  at 167 °C, respectively. There is not a pattern for  $\dot{\epsilon}({\rm S})$  because crystallization was difficult at this high  $T_{\rm c}$ .<sup>29</sup> The pattern for  $\dot{\epsilon}({\rm M})$  exhibited a rounded two-point pattern and a ring pattern (Figure 2ci and ii). The pattern changed to only two-point patterns at  $\dot{\epsilon}({\rm L})$ , and the two-point exhibited a doublet (Figure 2cii and iv).

Another characteristic of the  $\dot{\epsilon}({\rm L})$  pattern was a streak on an equatorial line.

#### $T_c$ and $\dot{\epsilon}$ dependence of WAXS patterns

We present the  $\dot{\epsilon}$  dependence of the WAXS patterns on the  $T_c$  in Figure 3. All of these patterns are through-view. The patterns for  $\dot{\epsilon}(L)$  exhibited a highly oriented fiber pattern along the elongational direction for all  $T_c$  (Figures 3a, d and g). These patterns belonged to the ordered form of the  $\alpha_2$  form because the intense characteristic reflections of the  $\alpha_2$  form,  $\bar{2}31$  and  $\bar{1}61$  (shown by arrow), were observed.<sup>24</sup> The patterns for  $\dot{\epsilon}(M)$  exhibited a superimposed pattern of spots, arcs and a Debye–Scherrer rings (Figures 3d, e and f). The oriented patterns of the spots and arcs belonged to the  $\alpha_2$  form, but the Debye–Scherrer ring pattern belonged to the disordered form of the  $\alpha_1$  form due to the lack of  $\bar{2}31$  and  $\bar{1}61$  reflections. The patterns for  $\dot{\epsilon}(S)$  primarily exhibited an un-oriented Debye–Scherrer ring pattern (Figures 3g and h). These patterns primarily belonged to the  $\alpha_1$  form.

## $T_c$ dependence of $\dot{\epsilon}^*_{\rm obs}$

Figure 4 presents plots of  $\dot{\epsilon}_{obs}^*$  against  $T_c$ . Because the NOCs cannot be crystallized at  $T_c \ge 170$  °C due to the technical limits of the present crystallization apparatus, the maximum  $\dot{\epsilon}(M)$  was alternatively plotted at  $T_c = 170$  °C. Therefore, the plot at  $T_c = 170$  °C ( $\Delta$ ) underestimates the correct  $\dot{\epsilon}_{obs}^*$ . The obtained  $\dot{\epsilon}_{obs}^*$  significantly increased with the increase of  $T_c$ , which suggests that the formation of NOCs is primarily controlled by a nucleation process. This result will be confirmed in the Discussion.

## ANALYSIS

## Six reflections in SAXS pattern

As mentioned in the Results, the two-point pattern in the SAXS pattern is sometimes composed of a few peaks, plateaus or shoulders (Figure 5). To qualitatively analyze the SAXS pattern and identify the structure, we will separate them into six reflections, including ring patterns, as shown below. As these reflections were observed at q =



**Figure 3**  $\dot{\epsilon}$  dependence of WAXS patterns at four  $T_c$ s. Through-view. The printed intensity is increased by 2–3 times for  $q > 15.8 \text{ nm}^{-1}$  to show relatively weak reflections. (a)  $\dot{\epsilon}(L) = 510 \text{ s}^{-1}$ . (b)  $\dot{\epsilon}(L) = 314 \text{ s}^{-1}$ . (c)  $\dot{\epsilon}(L) = 494 \text{ s}^{-1}$  and  $T_c = 167 \text{ °C}$ . (d)  $\dot{\epsilon}(M) = 82 \text{ s}^{-1}$ . (e)  $\dot{\epsilon}(M) = 116 \text{ s}^{-1}$ . (f)  $\dot{\epsilon}(M) = 334 \text{ s}^{-1}$  and  $T_c = 170 \text{ °C}$ . (g)  $\dot{\epsilon}(S) = 9 \text{ s}^{-1}$ . (h)  $\dot{\epsilon}(S) = 30 \text{ s}^{-1}$ . (a, d and g)  $T_c = 150 \text{ °C}$ . (b, e and h)  $T_c = 160 \text{ °C}$ . (a–c) Arrows indicate  $\overline{2}31$  and  $\overline{1}61$  reflections.



**Figure 4**  $\dot{\varepsilon}^*_{obs}$  against  $T_c$ .  $\dot{\varepsilon}^*_{obs}$  determined by polarizing optical microscope, SAXS and WAXS observations.  $\Delta$  is the maximum of  $\dot{\varepsilon}(M)$ .

 $q_1$ ,  $q_2$ ,  $q_3$ ,  $q_4$ ,  $q_R$ (NOC) and  $q_R$ (FCC), we will name them q1, q2, q3, q4,  $q_R$ (NOC) and  $q_R$ (FCC) (Figure 5). FCC refers to a folded chain crystal.

The first four reflections were oriented ones (Figures 5a, b and c), and the last two reflections were un-oriented ones (Figures 5d and e). These reflections were not always observed together. For example, a doublet of q1 and q2 was observed in Figure 5a, whereas q1 was a singlet and q2 was absent in Figure 5c. q2 was sometimes a plateau or shoulder. q3 exhibited a rather weak and broad peak (Figure 5b). q4 was observed at a rather high  $T_c$ ,  $T_c \ge 165$  °C, and exhibited a peak, plateau or shoulder (Figure 5c).  $q_R(NOC)$  and  $q_R(FCC)$  were observed for  $\dot{\epsilon}(S)$  and  $\dot{\epsilon}(M)$ . 76



**Figure 5** Typical SAXS patterns defining six types of reflections, q1, q2, q3, q4, q<sub>R</sub>(NOC) and q<sub>R</sub>(FCC). (a)  $T_c = 170 \,^{\circ}\text{C}$  and  $\dot{\epsilon}(M) = 540 \, \text{s}^{-1}$ . (b)  $T_c = 150 \,^{\circ}\text{C}$  and  $\dot{\epsilon}(L) = 510 \, \text{s}^{-1}$ . We see a weak reflection for q3. (c)  $T_c = 172 \,^{\circ}\text{C}$  and  $\dot{\epsilon}(M) = 526 \, \text{s}^{-1}$ . (d)  $T_c = 155 \,^{\circ}\text{C}$  and  $\dot{\epsilon}(S) = 9 \, \text{s}^{-1}$ . We see an un-oriented ring pattern of nano-crystals q<sub>R</sub>(NOC). (e)  $T_c = 165 \,^{\circ}\text{C}$  and  $\dot{\epsilon}(S) = 81 \, \text{s}^{-1}$ . Typical ring pattern of FCC is shown as q<sub>R</sub>(FCC). (a and c) The pattern is magnified by four times compared with the others.



**Figure 6** Plots of  $q_1$ ,  $q_2$ ,  $q_3$ ,  $q_4$ ,  $q_R(NOC)$  and  $q_R(FCC)$  against  $T_c$  for all  $\dot{e}$ .  $q_1$ ,  $q_2$ ,  $q_3$  and  $q_4$  show nearly the same  $T_c$  dependence. The values linearly decrease with the increase of  $T_c$ .  $q_R(FCC)$  is nearly constant.

#### $T_c$ and $\dot{\epsilon}$ dependence of q and scattering intensity

The q of the six reflections plotted against  $T_c$  for all  $\dot{\epsilon}$  exhibited a significant  $T_c$  dependence (Figure 6).  $q_1$ ,  $q_2$ ,  $q_3$  and  $q_4$  linearly decreased with the increase of  $T_c$ , whereas  $q_R(FCC)$  was nearly constant.  $q_R(NOC)$  scattered and did not exhibit any systematic  $T_c$  dependence. Note that these  $q_1$  and  $q_3$  did not depend on  $\dot{\epsilon}$  (Figure 7) for any  $T_c$ , which means that the size of the NOCs does depend on  $\dot{\epsilon}$ . The relative ratios of  $q_2/q_1$  and  $q_3/q_1$  plotted against  $T_c$  were nearly constant (Figure 8).

The relative scattering intensities of q1 and q2,  $I_X(q_1)/I_X(q_2)$ , plotted against  $T_c$  for all  $\dot{\epsilon}$  (Figure 9) were unity, that is,  $I_X(q_1) \approx I_X(q_2)$  for all  $T_c$ . The relative scattering intensities of q1 and q3,  $I_X(q_1)/I_X(q_3) \approx 15-50 \gg 1$  were obtained for all  $T_c$  and  $\dot{\epsilon}$ .



**Figure 7** Plots of *q* against  $\dot{\epsilon}$  for two  $T_c$ s,  $T_c = 150$  and 165 °C. The values are constant, independent of  $\dot{\epsilon}$ .



**Figure 8** Plots of  $q_2/q_1$  and  $q_3/q_1$  against  $T_c$  for all  $\dot{c}$ . The values are constant, independent of  $T_c$ .

Therefore,  $I_X(q_3)$  was considerably smaller than  $I_X(q_1)$ . The relative scattering intensity of q1 and q<sub>R</sub>(FCC),  $I_X(q_1)/I_X(q_R(FCC)) \approx 10-60 \gg 1$ , was obtained for  $\dot{\epsilon}(S)$  and  $\dot{\epsilon}(M)$ .

### Identification of six reflections in SAXS pattern

From the Results and Analysis, the six reflections in the SAXS pattern can be identified as follows:

As  $I_X(q_1) \approx I_X(q_2)$  for all  $T_c$  (Figure 9), both q1 and q2 should have the same structural origin. Based on the 'YOROI model' proposed in Okada *et al.*,<sup>8</sup> both q1 and q2 can be identified as the first peak of the diffraction pattern of the so-called one-dimensional liquid-like arrangement of NOCs.<sup>30</sup> q2 represents the distribution of the size of the NOCs. In the case of the q1 singlet, the distribution is rather



Figure 9 Plots of  $l_X(q_1)/l_X(q_2)$  against  $T_c$  for all  $\dot{c}$ . The value is roughly unity, independent of  $T_c$ .

sharp, whereas in the case of the doublet, plateau or shoulder of q1 and q2, the size distribution is broad. It is reasonable that the former was observed for  $\dot{\epsilon} \gg \dot{\epsilon}^*$ .

The weak reflection of q3 can be identified as the secondary peak or shoulder of the diffraction pattern of the so-called one-dimensional liquid-like arrangement of NOCs.<sup>30</sup> This result provides evidence for the YOROI model of NOCs.

The weak reflection of q4 can be associated with the incomplete formation of NOCs at a rather high  $T_c$ , where the formation of NOCs becomes difficult.

The  $q_R(FCC)$  should be a reflection of the FCCs because the  $T_c$  dependence of q was quite different from that of the NOCs (Figure 6). FCCs are formed from the isotropic melt. Because FCCs are formed at a high  $T_c$  up to 172 °C where they cannot be crystallized within a short amount of time in quiescent conditions, the nucleation of FCCs should be significantly accelerated during elongational crystallization.

As the  $q_R(NOC)$  did not exhibit any systematic change in both q and Ix, the isotropic NOCs were not common but accidentally crystallized due to some disturbed flow during the compression process.

Thus, we confirmed that the NOCs are crystallized in the range of  $150 \le T_c \le 167$  °C, where we can obtain a reliable  $T_c$  dependence of  $\dot{\epsilon}_{obs}^*$ .

## Estimation of $T_m^0(\text{om})$

As shown in the Experimental Procedure section,  $T_{\rm m}^{0}({\rm om}) > T_{\rm m}^{0}({\rm im}) = 187 \,^{\circ}{\rm C}$  is the minimum required condition of  $T_{\rm m}^{0}({\rm om})$ . It is natural that the formation of NOCs becomes difficult when  $T_{\rm c}$  approaches  $T_{\rm m}^{0}({\rm om})$ , where the  $\dot{\epsilon}^*$  should become infinitely large in Figure 4. Therefore,  $T_{\rm m}^{0}({\rm om})$  should be considerably  $> 200 \,^{\circ}{\rm C}$ , based on the rough extrapolation of the  $\dot{\epsilon}^*_{\rm obs}$  vs  $T_{\rm c}$  in Figure 4.

The observed q of the NOCs,  $q_1$ ,  $q_2$ ,  $q_3$  and  $q_4$ , linearly decreased with the increase of  $T_c$  (Figure 6). This finding indicates that the size of the NOCs increases with the increase of  $T_c$ <sup>8</sup> which corresponds to the basic prediction in CNT that the lateral size of a critical nucleus changes in proportion to  $1/\Delta T$ . Therefore, the size of the NOCs should approach an infinite size at  $T_m^0(\text{om})$ ; that is, the observed q of NOCs should approach zero at  $T_m^0(\text{om})$ . The lowest estimation of the  $T_m^{0}(\text{om})$  is obtained by a simple extrapolation of the fitted straight lines of q1, q2 and q3 in Figure 6. This extrapolation roughly gives  $T_m^{0}(\text{om}) = 195-210$  °C. Because the size of a critical nucleus increases in proportion to  $1/\Delta T_s^9$  the q of the NOCs should approach zero very slowly. Thus, we roughly estimate in this paper,

$$T_{\rm m}^0({\rm om}) = 220^{\circ}{\rm C}.$$
 (25)

However, because this value has ambiguity, it may be safe to state that  $T_{\rm m}{}^{0}({\rm om}) = 210-250 \,^{\circ}{\rm C}$ . Therefore, the determination of a reliable  $T_{\rm m}{}^{0}({\rm om})$  remains an important problem.



**Figure 10** Plot of  $\ln(I_{obs}/A)$  against  $\Delta T^{-2}$ .  $\Delta$  is the maximum of  $\dot{\epsilon}(M)$ . (a) Theoretical nucleation rate, *I*, given by Equation 1 well fitted to  $I_{obs}$ , which is evidence that the nucleation process primarily controls the formation of the NOCs. (b) Plots of  $\ln(I_{obs}/A)$  against  $\Delta T^{-2}$  as a parameter of  $T_{\rm m}^{-0}$ . These plots are well fitted by the line.

## DISCUSSION

## Confirmation that NOC formation is mainly controlled by the nucleation process

By inserting the observed  $\dot{\epsilon}_{obs}$  (Figure 4) into Equation 24, we have  $I_{obs}$ . ln( $I_{obs}/A$ ) was plotted against  $\Delta T^{-2}$  (Figure 10a). Here, the constant A was not determined because A does not affect the next conclusion. As the plots were well-fitted to Equation 1, it is concluded that  $I_{obs}$  satisfies the well-known formula of I in CNT. This result means that the formation of NOCs is primarily controlled by the nucleation process. Therefore, the chain reaction model of NOC formation is confirmed.

As mentioned in the Results, the error in  $T_{\rm m}^{0}({\rm om})$  was a few tens of °C. Therefore, we plotted the  $\ln(I_{\rm obs}/A)$  against  $\Delta T^{-2}$  for  $T_{\rm m}^{0}({\rm om}) = 210$ , 220 and 250 °C, respectively (Figure 10b). As all of these plots exhibited straight lines, the conclusion above was not significantly affected by the present range of  $T_{\rm m}^{0}({\rm om})$ .

It is logical that  $\dot{\epsilon}(\Delta T)$  in Equation 23 and  $I(\Delta T)$  in Equation 24 are equivalent to each other. Although we will not show the actual result in this paper, the  $\dot{\epsilon}^*_{obs}(T_c)$  in Figure 4 was well-fitted using  $I(\Delta T)$  of CNT.

#### Large $\Delta T$ and homogeneous nucleation

The range of  $\Delta T$  where the formation of NOCs was confirmed in this paper was

$$\Delta T = 53 - 70 \mathrm{K}. \tag{26}$$

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This temperature range is extremely large. As mentioned in the Theory, the kinetic parameters  $\sigma$  and  $\sigma_e$  become small in the locally oriented melt. Therefore, the combination of the large  $\Delta T$  and the small kinetic parameters yields the conclusion that the  $\Delta G^*$  becomes very small during the nucleation of NOCs. This result is the reason why the nucleation of NOCs is homogeneous and why the formation of NOCs is completed within a very short time, as short as several ms.8 Note that the homogeneous nucleation from the bulky melt is interesting because this is the first observation of this process in any material (as far as the authors know).<sup>31</sup> Until now, homogeneous nucleation has only been observed from the small droplet melt.31

## CONCLUSIONS

We studied the melt-elongational crystallization of iPP by changing the elongational strain rate ( $\dot{\epsilon}$ ) and crystallization temperature ( $T_c$ ).

(1) We proposed a 'chain reaction model' of NOC formation: some parts of polymer chains between entanglements are extended by the melt elongation, which should form the locally oriented melt; nucleation in the locally oriented melt is significantly accelerated; when  $\dot{\epsilon}$  is larger than a critical value ( $\dot{\epsilon}^*$ ), the generated nuclei accelerate the formation of the locally oriented melt; nucleation is further accelerated, and the NOCs are finally formed.

(2) We formulated a relationship between  $\dot{\epsilon}^*$  and the nucleation rate (I) based on the above model. We obtained  $I = A/(\dot{\epsilon}^* - B)$ , where A and B are constants.

(3) We clarified the  $T_c$  and  $\dot{\epsilon}$  dependence of the structures of NOCs using SAXS, WAXS and optical microscopy and confirmed that NOCs are formed in the range of  $T_c = 150-167$  °C. We obtained  $T_c$ dependence of  $\dot{\epsilon}^*$ .  $\dot{\epsilon}^*$  increased significantly with the increase of  $T_c$ .

(4) The degree of supercooling  $(\Delta T)$  dependence of observed I  $(I_{obs})$  was obtained using the above equation. Here, we estimated an equilibrium melting temperature in the oriented melt  $T_{\rm m}^{0}({\rm om}) = 220$ °C from the observation of the NOC formation. However, it may be safe to say that  $T_{\rm m}^{0}({\rm om}) = 210-250$  °C because there is ambiguity in this value. The Iobs was well fitted with the well-known equation of  $I \propto \exp[-C/\Delta T^2]$  for homogeneous nucleation from CNT, where C is a constant. Therefore, we conclude that the formation of NOCs is primarily controlled by the nucleation process, which confirms the chain reaction model.

## CONFLICT OF INTEREST

The authors declare no conflict of interest.

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