

Role of epitaxy of nucleating agent (NA) in nucleation mechanism of polymers

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Abstract

The role of “epitaxy” of nucleating agent (NA) in nucleation mechanism of polymers was studied to formulate the nucleation rate (I) as a function of concentration of NA (C_{NA}) in mixture of polymer and NA and lateral size of a NA crystal (a_{NA}), $I \propto C_{NA}/a_{NA}$. It is proved that the epitaxy of NA controls nucleation mechanism by confirming above formula experimentally by observing nucleation by means of optical microscopy. We also clarified that heterogeneous nucleation is a probabilistic phenomenon by confirming that “induction time of nucleation (τ_i)” did not depend on C_{NA} . We established a method to obtain reliable I and τ_i by adding NA which has been a difficult problem in polymer science. © 2006 Elsevier Ltd. All rights reserved.

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1. Introduction

Crystallization is divided to “nucleation” and “growth” processes. Becker and Döring and Turnbull and Fisher proposed classical nucleation theory (CNT) in 1930 [1,2]. CNT divided the nucleation process to “induction” and “steady” periods. Steady period is the process when nuclei generate stationary. Induction period is the process until nucleation reaches steady period. We will focus on the steady period in this work.

1.1. Studies of epitaxy in heterogeneous nucleation

There are two kinds of nucleation, “homogeneous” nucleation and “heterogeneous” nucleation. Homogeneous nucleation is the process of birth of small regions of crystalline

phase in the pure super-cooled melt. Heterogeneous nucleation is the process of birth of small crystalline regions on or near surfaces [3]. Most nucleation from the melt is the heterogeneous nucleation. In the case of heterogeneous nucleation, the melt includes heterogeneity or impurity. The special materials that have high performance in the acceleration of nucleation are called “nucleating agents (NAs)” which play an important role industrially. NA is used to offer technical advantages, such as making rain happen and so on since early times. Polymer industry often uses NA nowadays to improve performances of polymer materials.

Two explanations have been proposed on how NA accelerates heterogeneous nucleation. The most popular one insists that “epitaxy” between NAs and crystals controls the nucleation [4]. The other insists that suppression of mobility of molecular chains by adding NAs controls the nucleation [5,6]. Yoshimoto et al. and Lotz et al. showed epitaxy structurally between α form crystals of isotactic polypropylene (iPP) and NA crystals by means of transmission electron microscopy

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(TEM) or atomic force microscopy (AFM) [7,8]. But it has not been clarified how epitaxy controls and accelerates heterogeneous nucleation by kinetic study of nucleation. We will prove that epitaxy of NA controls nucleation by kinetic study of nucleation. Hereafter we will name NA crystals as NA.

1.2. Alternative nucleation study on macroscopic crystals

In these days, kinetic studies of nucleation have been done by alternative observation on macroscopic crystals (hereafter we will call “crystals”) by means of optical microscope (OM) or bubble chamber and so on [2], because of difficulty of direct observation on nanometer order nuclei [9]. Degree of supercooling (ΔT) dependence of nucleation rate (I) and induction time (τ_i) has been studied. ΔT is defined by $\Delta T \equiv T_m^0 - T_c$, where T_m^0 is equilibrium melting temperature and T_c is crystallization temperature. I in the steady period is defined by

$$I(a \geq a_{\text{obs}}) \equiv d\nu(a \geq a_{\text{obs}}, t)/dt, \quad (1)$$

where a is lateral size of a crystal, a_{obs} is the minimum a which can be detected clearly by means of OM, $\nu(a \geq a_{\text{obs}}, t)$ is number density of nuclei in the melt and t is crystallization time. $I(a \geq a_{\text{obs}})$ and $\nu(a \geq a_{\text{obs}}, t)$ are obtained on much larger crystals with $a = a_{\text{obs}}$.

As shown in our succeeding paper, both ΔT dependence of nucleation and crystal generation are controlled by critical nucleation [10]. Hence we studied I and τ_i by means of OM in this work. τ_i is defined by a time until nucleation reaches the steady period and is given experimentally by intercept of t axis in $\nu(a \geq a_{\text{obs}}, t)$ vs. t plot of a straight line of steady $\nu(a \geq a_{\text{obs}}, t)$ after definition of Frisch [11].

1.3. Epitaxial controlling factors in I

CNT showed that I in steady period is given by a product of two factors, i.e.,

$$I = I_0 \exp[-\Delta G^*(N^*)/kT], \quad (2)$$

where I_0 is pre-factor, N is number of atom, molecule, particle or repeating unit within a nucleus, N^* is N of a critical nucleus, $\Delta G^*(N^*)$ is free energy of formation of a critical nucleus, k is Boltzmann constant and T is temperature [1]. If the epitaxy takes the important role in nucleation mechanism, then the epitaxy should affect the two factors.

The first purpose of this work is to formulate the first factor of I_0 by considering the effect of epitaxy as a function of concentration of NA in mixture of polymer and NA (C_{NA}) and lateral size of NA (a_{NA}), $I = I(C_{\text{NA}}, a_{\text{NA}})$. The second purpose is to confirm $I = I(C_{\text{NA}}, a_{\text{NA}})$ experimentally, by which we will be able to prove that epitaxy controls I .

The second factor is related to $\Delta G^*(N^*)$ that is a function of free energy of interface related to epitaxy between nucleus and NA ($\Delta\sigma$) [3], i.e.,

$$\begin{aligned} \Delta G^*(N^*) &\propto \Delta\sigma \quad \text{for } \Delta g \leq 2\Delta\sigma \text{ (three dimension nucleus)} \\ &\propto 1/(\Delta g - \Delta\sigma) \quad \text{for } \Delta g > 2\Delta\sigma \text{ (two dimension} \\ &\quad \text{nucleus)}, \end{aligned} \quad (3)$$

where Δg is free energy of fusion. $\Delta\sigma$ and Δg are counted per repeating unit. Effect of epitaxy on $\Delta G^*(N^*)$ will be studied in our separate paper [13].

1.4. Is heterogeneous nucleation a probabilistic phenomenon?

It is interesting problem that nucleation is a probabilistic phenomenon in heterogeneous nucleation. In the studies of heterogeneous nucleation, it has been sometimes assumed that nuclei nucleate on most NA immediately after quenching to T_c , i.e., $t = 0$ [4]. It is unknown whether nucleation happens all together or probabilistic. The third purpose is to clarify that nucleation is a probabilistic phenomenon, i.e., essential mechanism does not change for both heterogeneous nucleation and homogeneous one. Probabilistic phenomenon means that each nucleation should be incoherent and isolated. In this case, τ_i should be independent of C_{NA} . We will show in this work

$$d\tau_i/dC_{\text{NA}} = 0. \quad (4)$$

1.5. Improvement to obtain reliable I and τ_i

In the past nucleation studies on polymers without NA by means of OM, nuclei did not show uniform dispersion within a sample and I showed significant scatter [12], since small amount and various kind of impurities disperse nonuniformly and work as NA accidentally in the melt. Therefore we had to carry out many independent experiments to obtain reliable I and τ_i . The fourth purpose is to establish a method to obtain reliable I and τ_i by adding a NA uniformly.

1.6. Purpose

Purposes of this work are (1) to show and formulate $I = I(C_{\text{NA}}, a_{\text{NA}})$ theoretically by taking into consideration that epitaxy of NA controls nucleation, (2) to verify $I = I(C_{\text{NA}}, a_{\text{NA}})$ experimentally, which proves that epitaxy controls and accelerates nucleation by kinetic study of nucleation, (3) to clarify that nucleation is a probabilistic phenomenon in heterogeneous nucleation by showing that τ_i does not depend on C_{NA} and (4) to establish a method to obtain reliable I and τ_i by adding NA uniformly.

2. Theory

2.1. Nucleation rate and epitaxy

For the sake of simplicity, we assume that less than two nucleus nucleates on one NA. This means that nucleation is probabilistic phenomena, which will be verified in this work. When NA is fine crystal and disperses uniformly in polymer

melt, above assumption is held. a_{NA} is smaller than μm in order and we used $a_{NA} \cong 0.2 \mu\text{m}$ in this work.

We will formulate the important relation between I , C_{NA} and a_{NA} by assuming epitaxy. Assume that C_{NA} is dilute enough where all NA crystals are “active”. The meaning of “active” will be explained in Section 2.2. In our separate paper, relation between epitaxy and $\Delta G^*(N^*)$ will be described [13]. From Eq. (2), it is obtained that

$$I \propto I_0. \quad (5)$$

If epitaxy controls nucleation, I_0 should be proportional to surface area of NA (A), i.e.,

$$I_0 \propto A. \quad (6)$$

And I_0 should also be proportional to number density of NA (ν_{NA}) in the melt, that is,

$$I_0 \propto \nu_{NA}. \quad (7)$$

Hence we obtained from Eqs. (5)–(7) that

$$I \propto I_0 \propto \nu_{NA} A. \quad (8)$$

When we assume that all NAs have similar shape, A is given by

$$A \propto a_{NA}^2. \quad (9)$$

Proportionality coefficient will change according to shape of NA. ν_{NA} is defined by ratio of total weight of NA per unit volume (M_{NA}) and weight of one NA (m_{NA}), i.e.,

$$\nu_{NA} \equiv M_{NA}/m_{NA}. \quad (10)$$

As

$$M_{NA} \propto C_{NA} \text{ and } m_{NA} \propto a_{NA}^3, \quad (11)$$

ν_{NA} is given by

$$\nu_{NA} \propto C_{NA}/a_{NA}^3. \quad (12)$$

From Eqs. (8), (9) and (12), we have an important formula,

$$I \propto C_{NA}/a_{NA}. \quad (13)$$

In the case that $a_{NA} = \text{const.}$ (or given), Eq. (13) leads to

$$I \propto C_{NA}. \quad (14)$$

On the other hand, in the case that $C_{NA} = \text{const.}$ (or given), Eq. (13) gives

$$I \propto 1/a_{NA}. \quad (15)$$

Thus we can prove the important role of epitaxy in nucleation by confirming Eqs. (14) and (15) experimentally. In this work, epitaxy will be proved by showing Eq. (14). Eq. (13) or (15) means that we will be able to develop high-performance NA

by decreasing a_{NA} into nm order, which will be described in our separate paper [13].

2.2. C_{NA} dependence of I

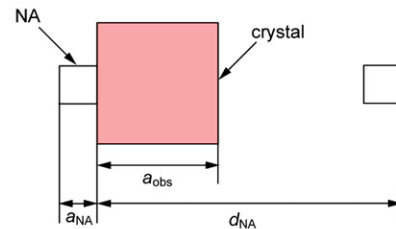
It is well known that $I(a \geq a_{\text{obs}})$ in Eq. (1) saturates with the increase of C_{NA} , i.e., $I(a \geq a_{\text{obs}})$ becomes constant for larger C_{NA} than “ C_{NA}^\dagger ”. In this section, the reason why $I(a \geq a_{\text{obs}})$ saturates for $C_{NA} > C_{NA}^\dagger$ will be shown. It is to be noted that a_{obs} is experimentally fixed. For example, $a_{\text{obs}} = 1 \mu\text{m}$ will be taken in this study. Therefore a_{obs} does not relate to lateral growth with t or with ΔT . For the sake of simplicity, a_{NA} is fixed. Fig. 1(a) illustrates a crystal with size a_{obs} on a NA. C_{NA} is given by

$$C_{NA} \propto (a_{NA}/d_{NA})^3, \quad (16)$$

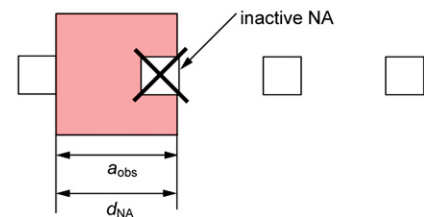
where d_{NA} is mean distance between NAs. When NA is cubic, C_{NA} is defined by

$$C_{NA} \equiv (a_{NA}/d_{NA})^3. \quad (17)$$

(a) $d_{NA} > a_{\text{obs}}$, $C_{NA} < C_{NA}^\dagger$: $I(a \geq a_{\text{obs}}) \propto C_{NA}$



(b) $d_{NA} \cong a_{\text{obs}}$, $C_{NA} = C_{NA}^\dagger$: $I(a \geq a_{\text{obs}})$ starts saturation



(c) $d_{NA} < a_{\text{obs}}$, $C_{NA} > C_{NA}^\dagger$: $I(a \geq a_{\text{obs}})$ saturates

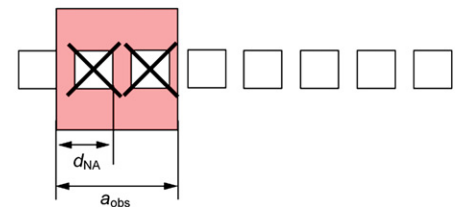


Fig. 1. Illustration of change of nucleation on a NA with the increase of concentration of NA in mixture of polymer and NA (C_{NA}). Lateral size of NA (a_{NA}) and that of crystal (a_{obs}) are given. (a) $d_{NA} > a_{\text{obs}}$. One crystal with size a_{obs} is formed on one of NA crystals. As the other NA crystals are “active”, Eq. (14) is applied. (b) $d_{NA} \cong a_{\text{obs}}$. One crystal with a_{obs} includes two NA crystals. The newly included NA crystals become “inactive”. (c) $d_{NA} < a_{\text{obs}}$. Most NAs become inactive.

Eq. (16) or (17) means that d_{NA} decreases with the increase of C_{NA} as shown in Fig. 1(b) and (c). Therefore C_{NA} dependence of $I(a \geq a_{obs})$ depends on relative relation between d_{NA} and a_{obs} (Figs. 1 and 2a).

(a) $d_{NA} > a_{obs}$

In this condition, one crystal with size a_{obs} is formed on one of NA crystals. As one crystal includes only one NA crystal, the other NA crystals can work as fresh NA, which we will name “active” NA crystals. Therefore Eq. (14) is applied (Fig. 1a) and a straight line of $I(a \geq a_{obs})$ should be expected against C_{NA} as shown in Fig. 2a. We will verify that epitaxy

controls nucleation by obtaining Eq. (14) experimentally in this work.

(b) $d_{NA} \cong a_{obs}$

When

$$d_{NA} \cong a_{obs}, \tag{18}$$

surface of other NA becomes covered by the crystal with a_{obs} . In this case, nucleation cannot happen on the covered NA crystal, i.e., the NA crystal cannot work as NA (we will name this “inactive” NA crystal) (Fig. 1b). When inactive NA crystal starts appearing, $I(a \geq a_{obs})$ starts saturating. C_{NA}^\dagger is defined by the breaking in $I(a \geq a_{obs})$ vs. C_{NA} . C_{NA}^\dagger is given by combining Eqs. (17) and (18),

$$C_{NA}^\dagger = (a_{NA}/a_{obs})^3. \tag{19}$$

(c) $d_{NA} < a_{obs}$

Most NAs except for the NA on which nucleus is generating become inactive (Fig. 1c). In this case, $I(a \geq a_{obs})$ saturates.

Hence it is concluded that

$$I(a \geq a_{obs}) \propto C_{NA} \quad \text{for } C_{NA} < C_{NA}^\dagger, \text{ i.e., } d_{NA} > a_{obs} \\ \cong \text{const.} \quad \text{for } C_{NA} > C_{NA}^\dagger, \text{ i.e., } d_{NA} < a_{obs}. \tag{20}$$

2.3. a_{NA} dependence of I

Eq. (15) means that $I(a \geq a_{obs})$ increases with the decrease of a_{NA} for $C_{NA} < C_{NA}^\dagger$, as shown in Fig. 2b. For example, when a_{NA} becomes $1/10^2$, $I(a \geq a_{obs})$ should increase 10^2 times. a_{NA} dependence of $I(a \geq a_{obs})$ will be verified in our separate paper [13].

2.4. Prediction of mean crystal size a_{max} after solidification

It is interesting to predict “mean crystal size (a_{max})” after completion of solidification. Since $I(a \geq a_{obs})$ saturates for $C_{NA} > C_{NA}^\dagger$, a_{max} should be proportional to a_{obs} , i.e.,

$$a_{max} \propto a_{obs}. \tag{21}$$

Combining Eqs. (21) and (19), we have

$$a_{max} \propto \frac{a_{NA}}{(C_{NA}^\dagger)^{1/3}}. \tag{22}$$

Hence we have

$$\log a_{max} = \log a_{NA} - \frac{1}{3} \log C_{NA}^\dagger + \text{const.} \tag{23a}$$

We showed illustration of $\log a_{max}$ against $\log C_{NA}^\dagger$ as a parameter of a_{NA} given by Eq. (23a) (Fig. 3),

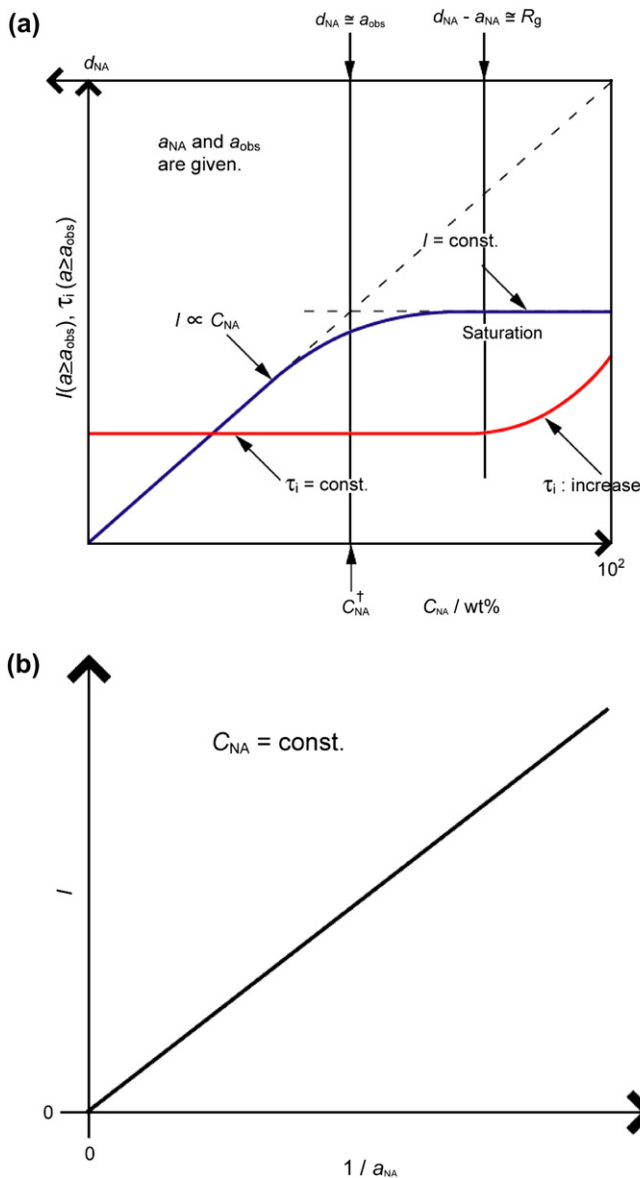


Fig. 2. (a) Prediction of C_{NA} dependence of nucleation rate (I) and induction time (τ_i) for a given a_{NA} and a_{obs} . C_{NA}^\dagger is critical C_{NA} . I increases with the increase of C_{NA} for $C_{NA} < C_{NA}^\dagger$ and should saturate for $C_{NA} > C_{NA}^\dagger$. (b) Illustration of plots of I against $1/a_{NA}$ for $C_{NA} = \text{const.}$ I increases with the decrease of a_{NA} from Eq. (15).

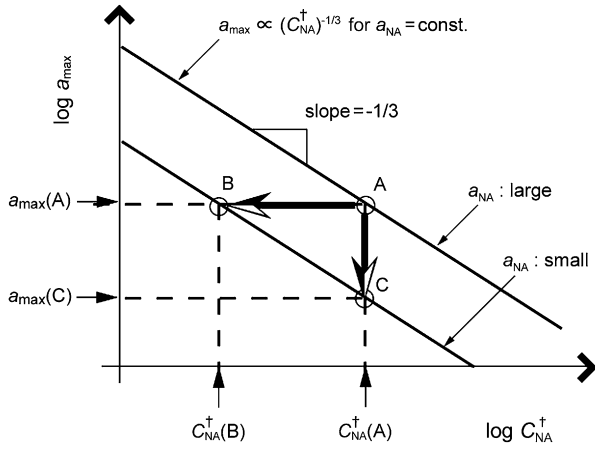


Fig. 3. Theoretical illustration of $\log a_{\max}$ against $\log C_{\text{NA}}^{\dagger}$ given by Eq. (23a) as a parameter of a_{NA} . A \rightarrow B indicates that when smaller a_{NA} is used, we need less C_{NA}^{\dagger} for the same a_{\max} . A \rightarrow C indicates that we can obtain smaller a_{\max} , when a_{NA} is smaller for the same C_{NA}^{\dagger} . Therefore we are able to predict that NA will have high-performance by decreasing a_{NA} .

$$a_{\max} \propto (C_{\text{NA}}^{\dagger})^{-1/3} \quad \text{for } a_{\text{NA}} = \text{const.} \quad (23b)$$

For example, we obtain $a_{\max}(\text{A})$ of A point when $C_{\text{NA}}^{\dagger}(\text{A})$ is used in Fig. 3. When smaller a_{NA} is used, we need less C_{NA}^{\dagger} on the same $a_{\max}(\text{A})$, $C_{\text{NA}}^{\dagger}(\text{B})$ of B point. $a_{\max}(\text{A})$ should become smaller one, i.e., $a_{\max}(\text{C})$ of C point when a_{NA} is smaller on the same $C_{\text{NA}}^{\dagger}(\text{A})$. Therefore we can predict that NA will have high-performance by breaking up significantly. If we will observe a_{\max} , we will be able to obtain relation between a_{NA} and C_{NA}^{\dagger} . However, a_{\max} was not observed in this work.

2.5. Condition of probabilistic nucleation

Polymer chains should disentangle and rearrange through chain sliding diffusion in nucleation process from the melt [14,15]. As the above chains from a nucleus are included in a “Gaussian sphere” with size of radius of gyration (R_g) [16], either nucleation is a probabilistic phenomenon or does not depend on relative relation between $d_{\text{NA}} - a_{\text{NA}}$ and R_g (Figs. 2a and 4).

$$(a) \quad d_{\text{NA}} - a_{\text{NA}} \gg R_g$$

As one Gaussian sphere touches much less than one NA, nuclei on each NA do not interact each other, i.e., each nuclei should be “incoherent” (Fig. 4a). Probability of nucleation on a NA (P_{NA}) is independent and the same on any NA in the melt. Therefore τ_i should be independent of C_{NA} , as shown in Fig. 2a,

$$d\tau_i/dC_{\text{NA}} = 0, \quad (24)$$

i.e.,

$$\tau_i = \text{const.} \quad (25)$$

This is the condition of probabilistic nucleation.

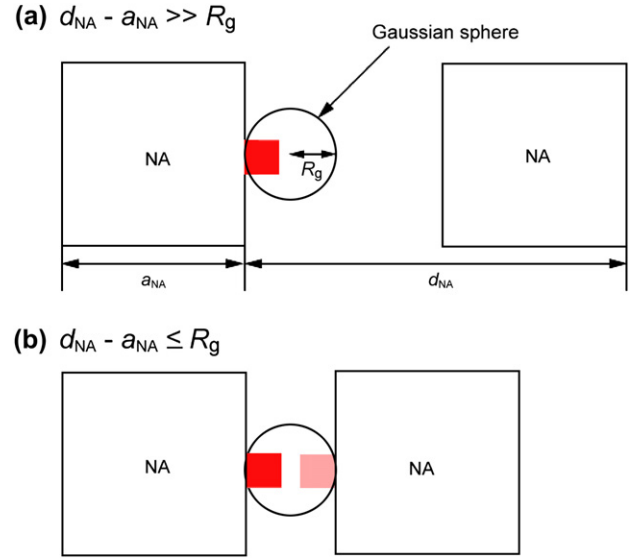


Fig. 4. Condition that nucleation is a probabilistic phenomenon. (a) $d_{\text{NA}} - a_{\text{NA}} \gg R_g$. As nuclei on each NA do not interact each other, τ_i is independent of C_{NA} . This is the condition of probabilistic nucleation. (b) $d_{\text{NA}} - a_{\text{NA}} \leq R_g$. More than two NAs are touched with one Gaussian sphere with R_g . As nucleation competes on two NAs, τ_i should increase with the increase of C_{NA} .

$$(b) \quad d_{\text{NA}} - a_{\text{NA}} \leq R_g$$

In this case, more than two NAs are included in one Gaussian sphere with R_g (Fig. 4b). The chains would like to nucleate on these NAs in the Gaussian sphere, i.e., NAs compete against each other for one nucleus. Hence nucleus becomes “coherent”, P_{NA} should decrease and τ_i will increase with the increase of C_{NA} (Fig. 2a). Therefore this case is not probabilistic nucleation.

3. Experimental

3.1. Sample

The material used in this study was fully fractionated polyethylene (PE, NIST, SRM1483, $M_w = 32 \times 10^3$, $M_w/M_n = 1.1$) and iPP (Sunallomer Ltd., JPO-A, $M_n = 15.3 \times 10^3$, $M_w/M_n = 5.6$ and [mmmm] = 99.5%). The NA of sodium 2,2'-methylene-bis-(4,6-di-*t*-butylphenylene) phosphate (ADEKA Corp., NA-11SF) was used and $a_{\text{NA}} = 0.23 \pm 0.12 \mu\text{m}$. Two kinds of samples were prepared. One is polymer mixed with NA, which is named as “PE + NA” or “iPP + NA”. The other is polymer without mixing NA, which is named as “PE” or “iPP”.

3.2. Sample preparation

We improved the following best method to mix NA uniformly in polymers. We prepared xylene suspension of NA by dispersing NA uniformly in xylene which is a solvent of PE and iPP with ultrasonic machine at room temperature. Concentration of NA in xylene suspension ($C_{\text{NA/xylene}}$) was $C_{\text{NA/xylene}} \cong 10^{-2} - 10^{-7}$ wt%. We dissolved polymer powder into the xylene suspension of NA at a temperature (T_{mix})

and agitated it to prepare xylene solution of polymer in which NA disperses uniformly. Concentration of polymer in xylene solution ($C_{\text{polymer/xylene}}$) was $C_{\text{polymer/xylene}} \cong 0.1 \text{ wt\%}$. T_{mixS} of PE and iPP were $T_{\text{mix}} = 120 \text{ }^\circ\text{C}$ and $T_{\text{mix}} = 110 \text{ }^\circ\text{C}$, respectively. Then we quenched the xylene solution of polymer with NA to $T = 0 \text{ }^\circ\text{C}$ to crystallize polymers. Xylene was evaporated using rotary pump evacuator and we collected polymer crystals with NA.

3.3. Instrument

Small amount of samples was first sandwiched by cover glasses. The thickness of sample was controlled to be $30 \text{ } \mu\text{m}$ by inserting Al spacer. Sample was put in a hot stage (Linkam L-600A). The nitrogen gas was flown at a rate of 50 ml/min to protect from oxidization decomposition of sample. Number of isolated crystals was counted using polarizing optical microscope (Olympus, BH) and recorded by means of CCD camera system. The temperature was calibrated using standard materials, In and Sn. To observe isolated single crystals, observation was limited to the earlier stage of crystallization.

3.4. Crystallization

We counted number density of nuclei which size is $a \geq a_{\text{obs}} = 1 \text{ } \mu\text{m}$ ($\nu(t)$) in this study. We observed $I(a \geq a_{\text{obs}})$ and τ_i from the plot of $\nu(t)$ against t . $I(a \geq a_{\text{obs}})$ is rewritten from Eq. (1) to

$$I(a \geq a_{\text{obs}}) \equiv d\nu(t)/dt = I. \quad (26)$$

We used samples of PE and PE + NA to observe dispersion of nuclei. C_{NA} of PE + NA was $C_{\text{NA/PE}} = 0.4 \text{ wt\%}$. They were first melted at a maximum melting temperature $T_{\text{max}} = 160 \text{ }^\circ\text{C}$ for 5 min and were then crystallized isothermally at a fixed T_{cS} , $T_{\text{c}} = 124.6$ or $126.7 \text{ }^\circ\text{C}$. Since $T_{\text{m}}^0 = 139.5 \text{ }^\circ\text{C}$ [17], $\Delta T = 12.9$ or 14.9 K .

We used samples of iPP + NA to observe C_{NA} dependence of I and τ_i . C_{NA} of iPP + NA was $C_{\text{NA/iPP}} = 10^{-4}$ to 1 wt\% . It was first melted at $T_{\text{max}} = 220 \text{ }^\circ\text{C}$ for 5 min and was then crystallized isothermally at a fixed $T_{\text{c}} = 146.7 \text{ }^\circ\text{C}$. Since $T_{\text{m}}^0 = 186.1 \text{ }^\circ\text{C}$ [18], $\Delta T = 39.4 \text{ K}$.

4. Results and discussion

4.1. Dispersion of nucleation

We showed optical micrograph of crystallization from the melt in Fig. 5. We compared crystallization of samples of PE and PE + NA side by side simultaneously at $\Delta T = 14.9 \text{ K}$. In the case of PE without mixing NA, which corresponds to previous work [12], nuclei did not show uniform dispersion and $\nu(t)$ was too small as compared with that of PE + NA at the same ΔT (Fig. 5a). The bad dispersion results in significant error of I and τ_i . In the case of PE + NA, nuclei showed uniform dispersion and $\nu(t)$ significantly increased (Fig. 5b). Thus we could obtain uniform dispersion of nucleation by adding NA to PE uniformly.

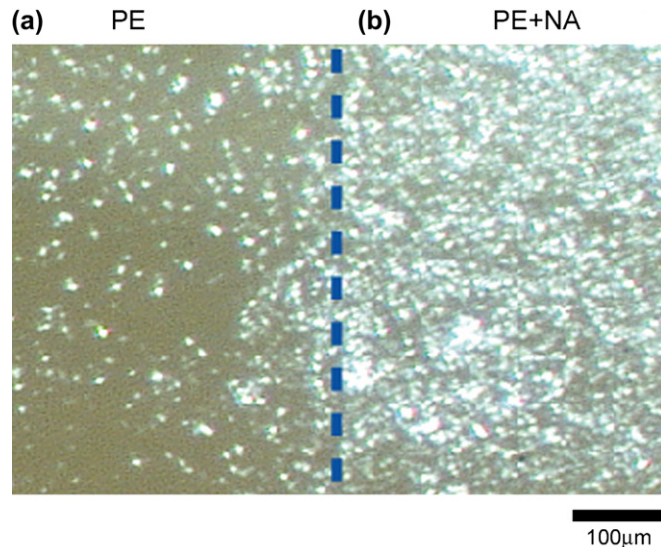


Fig. 5. Optical micrographs of crystallization in the melt. Crystallization of samples of PE without mixing NA and PE + NA was compared side by side simultaneously at $T_{\text{c}} = 124.6 \text{ }^\circ\text{C}$ and $\Delta T = 14.9 \text{ K}$. (a) PE. Nuclei did not show uniform dispersion and number density of nuclei $\nu(t)$ was small. (b) PE + NA. Nuclei showed uniform dispersion and $\nu(t)$ significantly increased.

4.2. Reliable I and τ_i

Typical comparison of $\nu(t)$ against t of PE with that of PE + NA is shown in Fig. 6a and b, respectively. We repeated four independent experiments (shown by different marks) and observed I and τ_i . In the case of PE, I and τ_i for $\Delta T = 14.9 \text{ K}$ showed significantly large scatter in the melt, i.e.,

$$I = \langle I \rangle \pm \Delta I = (9 \pm 2) \times 10^{-6} \text{ } \mu\text{m}^{-3} \text{ s}^{-1}$$

and

$$\tau_i = \langle \tau_i \rangle \pm \Delta \tau_i = 87 \pm 8 \text{ s}, \quad (27)$$

where $\langle I \rangle$, $\langle \tau_i \rangle$, ΔI and $\Delta \tau_i$ are mean of I and τ_i and scatter of I and τ_i , respectively (Fig. 6a). Thus we have large relative error of $\Delta I/\langle I \rangle$ and $\Delta \tau_i/\langle \tau_i \rangle$,

$$\Delta I/\langle I \rangle \cong 25\% \text{ and } \Delta \tau_i/\langle \tau_i \rangle \cong 10\%. \quad (28)$$

In the case of PE + NA, I and τ_i for $\Delta T = 12.8 \text{ K}$ showed significantly small scatter, (Fig. 6b), i.e.,

$$I = \langle I \rangle \pm \Delta I = (5.8 \pm 0.5) \times 10^{-6} \text{ } \mu\text{m}^{-3} \text{ s}^{-1}$$

and

$$\langle \tau_i \rangle \pm \Delta \tau_i = 232 \pm 4 \text{ s}. \quad (29)$$

Hence we have small relative error of $\Delta I/\langle I \rangle$ and $\Delta \tau_i/\langle \tau_i \rangle$,

$$\Delta I/\langle I \rangle \cong 9\% \text{ and } \Delta \tau_i/\langle \tau_i \rangle \cong 2\%. \quad (30)$$

We obtained similar results with respect to iPP. Therefore we could establish a method to obtain reliable I and τ_i by obtaining uniform dispersion of nucleation by adding NA to polymers uniformly.

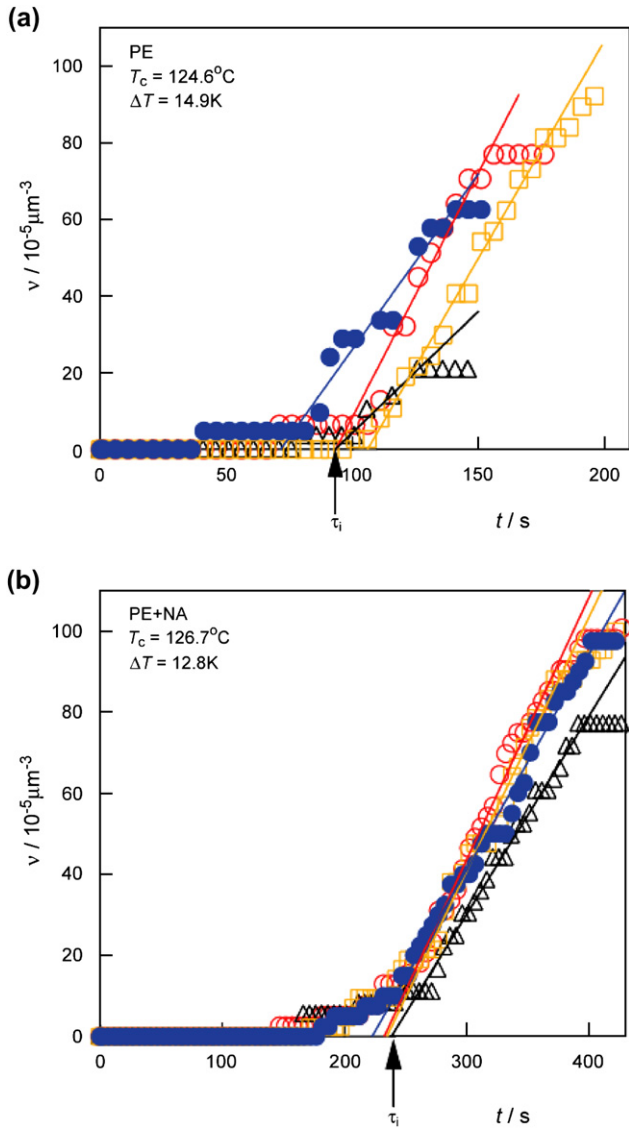


Fig. 6. Typical comparison of $\nu(t)$ against t of PE with that of PE + NA. I and τ_i were obtained from the slope and intercept of lines. Four lines indicate four independent experiments. (a) PE. $T_c = 124.6^\circ\text{C}$ and $\Delta T = 14.9\text{K}$. I and τ_i showed significantly large scatter. (b) PE + NA. $T_c = 126.7^\circ\text{C}$ and $\Delta T = 12.8\text{K}$. As I and τ_i showed significantly small scatter, we could establish a method to obtain reliable I and τ_i .

4.3. C_{NA} dependence of time evolution of $\nu(t)$

Fig. 7 shows typical C_{NA} dependence of $\nu(t)$ against t of iPP + NA at $\Delta T = 39.4\text{K}$. $C_{NA} = 10^{-3}\text{wt}\%$ is right axis and others are left axis. $\nu(t)$ increased much faster when C_{NA} increased. Thus it clarified that I was accelerated with the increase of C_{NA} . On the other hand, τ_i s were nearly the same for all C_{NA} . It also made clear that τ_i did not depend on C_{NA} .

4.4. C_{NA} dependence of I

Plots of I against C_{NA} of iPP + NA for a fixed $a_{NA} (= 0.23\ \mu\text{m})$ at $\Delta T = 39.4\text{K}$ are shown in Fig. 8. Horizontal axis on top is d_{NA} obtained by using Eq. (17). I increased with the increase of C_{NA} and saturated for $C_{NA} \geq 1\text{wt}\%$.

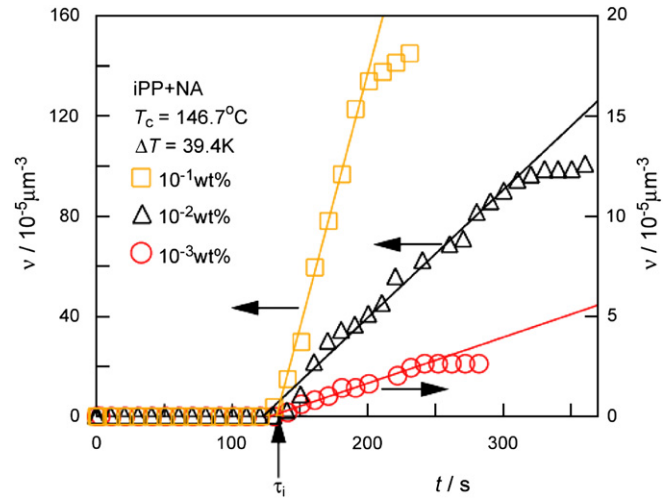


Fig. 7. Typical C_{NA} dependence of $\nu(t)$ against t of iPP + NA at $T_c = 146.7^\circ\text{C}$ and $\Delta T = 39.4\text{K}$. $\nu(t)$ increased much faster when C_{NA} increased.

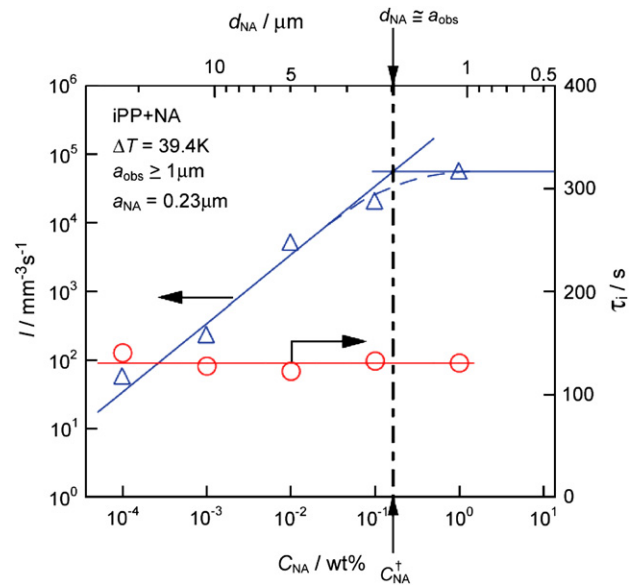


Fig. 8. Plots of I and τ_i against C_{NA} of iPP + NA for a fixed $a_{NA} = 0.23\ \mu\text{m}$ at $T_c = 146.7^\circ\text{C}$ and $\Delta T = 39.4\text{K}$. Left and right vertical axes indicate I and τ_i , respectively. Upper horizontal axis on top indicates d_{NA} obtained by using Eq. (17). It verified that $I \propto C_{NA}$ experimentally, which proved that epitaxy controls and accelerates nucleation. $d\tau_i/dC_{NA} = 0$ clarified that nucleation is a probabilistic phenomenon.

I increased 10 times when C_{NA} does 10 times. Thus we obtained the following experimental formulae,

$$I \propto C_{NA} \quad \text{for } C_{NA} \leq 10^{-2}\text{wt}\% \quad (31)$$

and

$$I \cong \text{const.} \quad \text{for } C_{NA} \geq 1\text{wt}\%. \quad (32)$$

Hence we have a breaking $C_{NA}(C_{NA}^\dagger)$ at

$$C_{NA}^\dagger \cong 10^{-1}\text{wt}\%. \quad (33)$$

The experimental formulae clarified the theoretical prediction of Eq. (14) that $I \propto C_{NA}$ for $a_{NA} = \text{const.}$ experimentally.

Therefore it is concluded that the epitaxy of NA controls and accelerates I .

In Fig. 8, $d_{NA}^{\dagger} \cong 2 \mu\text{m}$ that corresponds to $C_{NA}^{\dagger} \cong 10^{-1} \text{ wt}\%$, which satisfied condition of breaking of I . The present range of C_{NA} corresponds to $d_{NA} = 1\text{--}20 \mu\text{m}$.

4.5. C_{NA} dependence of τ_i

We obtained plots of τ_i against C_{NA} of iPP + NA for a fixed $a_{NA} (= 0.23 \mu\text{m})$ at $\Delta T = 39.4 \text{ K}$ from Fig. 7 (Fig. 8). τ_i did not depend on all observed C_{NA} . Hence we obtained experimental formula,

$$d\tau_i/dC_{NA} = 0 \text{ or } \tau_i = \text{const. for all observed } C_{NA}. \quad (34)$$

Therefore we verified the theoretical prediction of Eqs. (24) and (25) and it is concluded that nucleation is a probabilistic phenomenon.

In our sequential paper, we will show that size distribution $f(N, t)$ of nano-nucleus increased slowly with the increase of t and saturated (or became steady). It will verify again independently that nucleation is a probabilistic phenomenon, because $f(N, t)$ should decrease showing a maximum and become 0, i.e., it does not saturate, if nucleation is not probabilistic and happens instantaneously at $t = 0$ [10].

5. Conclusion

- (1) $I \propto I_0 \propto C_{NA}/a_{NA}$ is formulated theoretically by considering the effect of epitaxy between NA crystals and polymer crystals on nucleation.
- (2) $I \propto C_{NA}$ for $a_{NA} = 0.23 \mu\text{m}$ is verified experimentally. Hence it proved that epitaxy controls and accelerates nucleation.
- (3) $d\tau_i/dC_{NA} = 0$, i.e., $\tau_i = \text{const.}$ for C_{NA} was obtained, which clarified that the nucleation is a probabilistic phenomenon in heterogeneous nucleation.

- (4) We established a method to obtain reliable I and τ_i by adding NA uniformly into the melt of polymers.

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