

## Degree of Supercooling ( $\Delta T$ ) Dependence and Mass Distribution Function $Q(N,t)$ of Nano-nucleation of Polymers by SAXS

“Nucleation” was assumed to be the early stage of crystallization in classical nucleation theory (CNT) proposed by Becker and Döring [1] in 1930s. Since it is known that the nucleus has a size on the nm order, i.e., that nucleus includes  $2 - 10^6$  particles or repeating units, we call it a “nano-nucleus.” However, it has been too difficult to observe directly nano-nucleation because of the technical issues.

So far, observations with an optical microscope (OM) or a bubble chamber have mainly been done to trace macroscopic nucleation at a scale larger than  $1 \mu\text{m}$  (= macro-crystal). In these studies, it is assumed that both nano-nucleation and macro-crystallization are predominantly controlled by the “critical nano-nucleation,” which is an important but unsolved problem. In the CNT, the critical nano-nucleation corresponds to the activated state in the free energy of the nucleation process.

We succeeded in direct observation of nano-nucleation by small-angle X-ray scattering (SAXS) for the first time in 2003 [2] and obtained the size distribution  $f(N,t)$  of nano-nuclei in 2007 [3], where  $N$  is the size of a nucleus counted by the number of repeating units and  $t$  is crystallization time. But these results were obtained only for one case of the degree of supercooling,  $\Delta T$ . In the nucleation study, it is important to obtain dependence of nano-nucleation on  $\Delta T$ , as  $\Delta T$  is proportional to the free energy of melting which is the driving force of nucleation.  $\Delta T$  is defined as  $\Delta T \equiv T_m^\circ - T_c$ , where  $T_m^\circ$  is the equilibrium melting temperature and  $T_c$  is crystallization temperature.

In this study, we obtained dependence of nano-nucleation on  $\Delta T$  and then compared it with the dependence of macro-crystallization on  $\Delta T$  to confirm the predominant contribution of the critical nano-nucleation in macro-crystallization. Second, we observed the “mass distribution function  $Q(N,t) \propto Nf(N,t)$ ” directly. The  $Q(N,t)$  should exhibit the real image of nano-nucleation, which cannot be described by  $f(N,t)$ . Finally, we proposed a new nucleation theory by introducing  $Q(N,t)$  in order to solve the serious problem in CNT that the kinetic equation with respect to  $f(N,t)$  does not satisfy the mass conservation law [4].

We used polyethylene (PE) (NIST, SRM1483a,  $M_n = 32 \times 10^3$ ,  $M_w/M_n = 1.1$ ,  $T_m^\circ = 139.5^\circ\text{C}$ ), where  $M_n$  and  $M_w$  are the number-average and the weight-average molecular weight, respectively, and  $M_w/M_n$  is the index of dispersion. The nucleating agent of sodium 2,2'-methylene-bis-(4,6-di-*t*-butylphenylene) phosphate (ADEKA Corp., NA-11SF) was mixed with PE. The sample was melted at  $160^\circ\text{C}$  for 5 min within

a thin evacuated glass capillary ( $\phi 1\text{mm}$ ) and then isothermally crystallized at  $\Delta T = 10.5 - 13.0 \text{ K}$ . The SAXS experiment was carried out at beamline **BL40B2**. The range of the scattering vector ( $q$ ) was  $(7 - 214) \times 10^{-3} \text{ \AA}^{-1}$  and the wavelength ( $\lambda$ ) was  $1.50 \text{ \AA}$ .

Figure 1 shows typical  $f(N,t)$  against  $t$  as a parameter of  $\Delta T$  for  $N = 2.2 \times 10^4$  [rep. unit] which is larger than the size of a critical nano-nucleus ( $N^* = 450$  [rep. unit]). The  $f(N,t)$  was obtained by applying an “extended Guinier plot method” to excess scattering intensity  $I_X(q,t)$  which was obtained by subtracting background intensity [3]. In the figure, it was found that  $f(N,t)$  increases rapidly with an increase of  $t$  for larger  $\Delta T$ , while it increases slowly for smaller  $\Delta T$ . We determined  $\tau$  for each  $\Delta T$  by the onset time of the linearly increasing  $f(N,t)$ , where  $\tau$  is the induction time for nucleation.

The inverse of  $\tau$  is plotted as a function of  $\Delta T^{-1}$  in Fig. 2. This indicates the relationship as  $\tau^{-1} \propto \exp[-\gamma/\Delta T]$  (1), where  $\gamma$  is a constant. Thus, it is clear that nano-nucleation does not occur when  $\Delta T$  becomes significantly small. This indicates that the “induction period” of crystallization is not controlled by a so-called “spinodal decomposition” process [5] but rather by nucleation process.  $\Delta T$  dependences of nucleation rate ( $I$ ) of a macro-crystal and “net flow ( $j$ )” of nano-nucleation are also shown in Fig. 2.  $I$  is defined by the variation of the number of macro-crystals per unit volume and time. We have observed  $I$  of macro-crystals larger than  $1 \mu\text{m}$  by OM and obtained the experimental formula,  $I \propto \exp[-C'/\Delta T]$  (2), where  $C'$  is a constant. When the critical nano-nucleation is the rate-determining process, it is well known in CNT that  $j$  is given by  $j \propto \exp[-\Delta G^*(N^*)/kT] \propto \exp[-C/\Delta T]$  (3), where  $\Delta G^*(N^*)$  is the free energy of

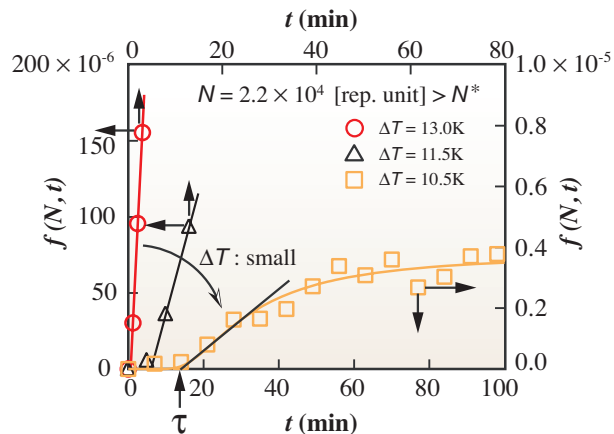


Fig. 1. Plots of  $f(N,t)$  against  $t$  as a parameter of  $\Delta T$  for  $N = 2.2 \times 10^4$  [rep. unit]  $> N^*$ . It clarified that nano-nucleation becomes impossible as  $\Delta T$  decreases.

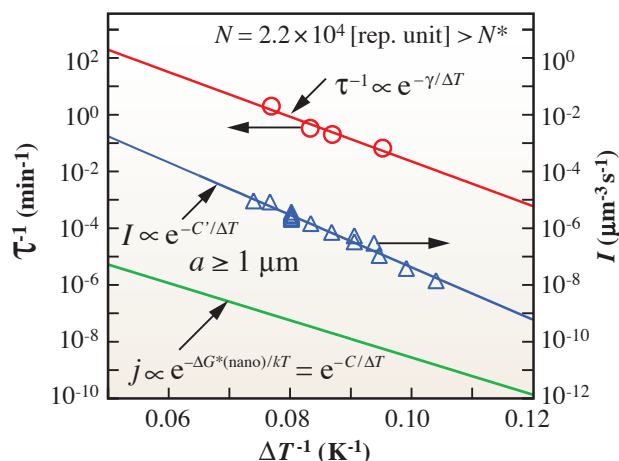


Fig. 2. Plots of  $\tau^{-1}$ ,  $I$  and theoretical  $j$  against  $\Delta T^{-1}$ . The observed  $N$  of nano-nucleus was  $N = 2.2 \times 10^4$  [rep. unit]  $> N^*$  and the lateral size of macro-crystal was larger than  $1 \mu\text{m}$ . Since  $\tau^{-1} \propto I \propto j$ , it clarified that critical nano-nucleation mainly controls macro-crystallization.

critical nano-nucleation,  $\Delta G^*(N^*) \propto \Delta T^{-1}$  for two-dimensional nucleus,  $kT$  is thermal energy, and  $C$  is a constant. It is to be noted that  $j$  is the theoretical formula. Since  $\tau^{-1} \propto I \propto j$  (4) was obtained, it clarified that the critical nano-nucleation mainly controls the macro-crystallization. Thus it is concluded that OM is a useful tool for convenient routine work in studies of nucleation.

Plots of  $\log Q(N, t)$  (right axis) and  $\log f(N, t)$  (left axis) against  $\log N$  as a parameter of  $t$  for  $\Delta T = 10.5 \text{ K}$  are shown in Fig. 3. It was found that  $f(N, t)$  decreased monotonously but  $Q(N, t)$  showed a minimum with a magnitude similar to  $N^*$  and increased with an increase of  $N$  for each  $t$ .

We plotted  $Q(N, t)$  against  $N$  as a parameter of  $t$  in Fig. 4. As  $Q(N, t)$  showed a minimum with the similar magnitude of  $N^*$  for each  $t$ , it was clearly shown that the critical nano-nucleation is the activated state in the

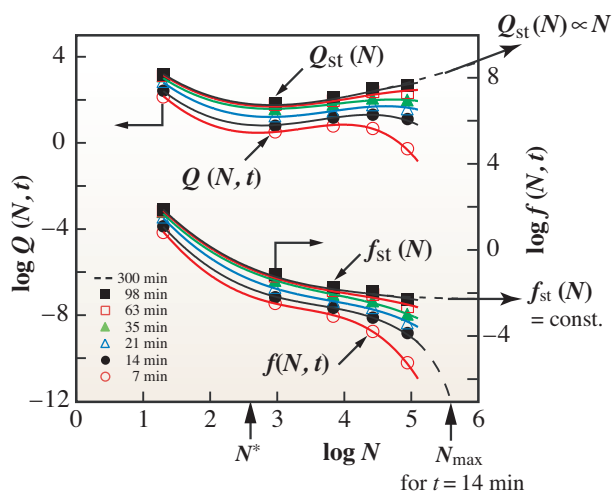


Fig. 3. Plots of  $\log Q(N, t)$  (left axis) and  $\log f(N, t)$  (right axis) against  $\log N$  as a parameter of  $t$  for  $\Delta T = 10.5 \text{ K}$ .

nucleation process.  $f(N, t)$  cannot describe this entire situation at all. Therefore, we focus the discussion on phenomena in the range of  $N \geq N^*$ .  $Q(N, t)$  had a maximum and became to 0 at  $N_{\text{max}}$  with the increase of  $N$  for a finite time. We obtained  $N_{\text{max}}$  for each  $t$  by extrapolating observed  $f(N, t)$  to larger  $N$ .  $N_{\text{max}}$  increases with as  $t$  increases. The maximum of  $Q(N, t)$  increased and shifted to larger  $N$  with the increase of  $t$ . Consequently, we found that the total mass of nano-nuclei increases for  $N \geq N^*$ . Our finding indicates that the crystallinity increases with the increase in  $t$  in the nucleation process. We showed that  $Q(N, t)$  satisfies the mass conservation law which is demanded by the basic equation of a stochastic process [4].

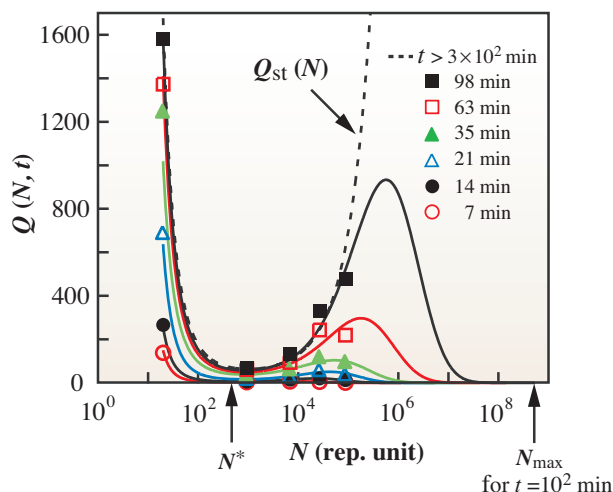


Fig. 4. Plots of  $Q(N, t)$  against  $N$  as a parameter of  $t$  for  $\Delta T = 10.5 \text{ K}$ . The total mass of nano-nuclei for  $N \geq N^*$  increases. This behavior indicates that crystallinity increases with the increase of  $t$  in the nucleation process.

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