First Direct Observation of Nano-Nucleation by Small Angle X-ray Scattering on Polymers

Crystallization from the melt (or gas) is an important phenomena in any material, and it significantly determines the structure and physical properties of the material. The initial stage of crystallization has been assumed to be nucleation in classical nucleation theory (CNT) since the 1930s [1], but it could not be confirmed experimentally for a long time due to technical difficulties. To solve the nucleation mechanism is important in understanding the structure and physical properties of any material, and also results in interesting applications for industry.

Although nuclei of nm order which we will refer to as nanonuclei have been previously generated, the number density of nuclei in the melt was too small to be detected by small angle X-ray scattering (SAXS) [2], where the nuclei include 2-10^6 atoms, particles or repeating units. Hence, alternative experimental nucleation studies have been performed on macroscopic crystals (macrocrystals) using optical microscope (OM) or a bubble chamber. Recently, simulation studies have been also carried out on colloid systems. However these studies cannot presume the direct observation of nano-nucleation, because macrocrystals and colloids are considerably different from the real image of nanonucleus. Therefore a long-standing and important unsolved problem is the observation of nano-nucleation and the determination of the size distribution $f(N,t)$ of nanonuclei under isothermal melt-crystallization, where N is the number of atom, particle or repeating unit (hereafter, referred to as particles) in a nucleus and t is crystallization time. $f(N,t)$ should clarify the real image of nano-nucleation, i.e., how the number
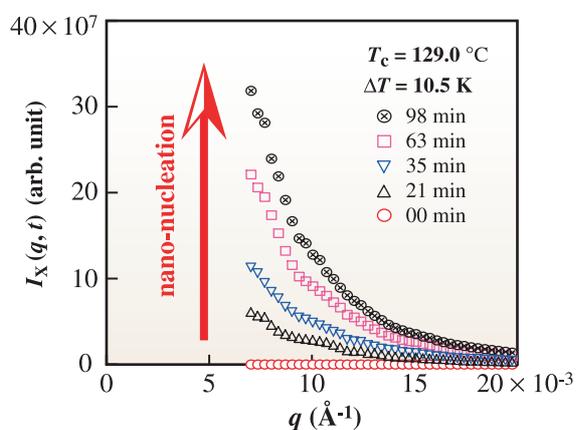
Fig. 1. Plots of $I_X(q,t)$ against q as a parameter of t at $T_c = 129.0$ °C. $I_X(q,t)$ increased with the increase of t, which is the direct evidence of nano-nucleation.
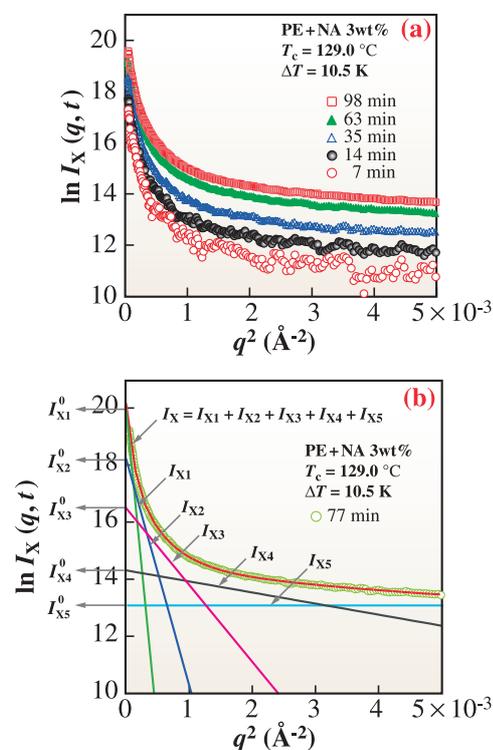
Fig. 2. Plots of ln $I_X(q,t)$ against q^2. (a) ln $I_X(q,t)$ against q^2 as a parameter of t. (b) Typical result obtained from "extended Guinier plot method". ln $I_X(q,t)$ was separated by five straight lines (I_{X1}, I_{X2},... I_{X5}). $f(N,t)$ and N were obtained from the vertical intercept and slope of the straight lines, respectively, where j indicates the different nuclei of size N_j.

and N of nanonuclei increase with t. To overcome the above difficulties, we added a nucleating agent (NA) to a polymer, by which the scattering intensity (I_x) from nanonuclei increased by as much as a factor of 10^4. We succeeded in detecting I_x for polyethylene (PE) in 2003 for the first time, as discussed in Ref. [3]. Since polymers are long chainlike molecules, their topological character is added to the fundamental nucleation mechanism. The NA is a crystalline material that accelerates nucleation and has been widely used in industry. An advantage of observing nucleation in polymers is the existence of an effective NA. Here, we report that we succeeded in observing $f(N,t)$ and in clarifying the real image of nano-nucleation using PE by SAXS [4].

We used PE (NIST, SRM1483a, $M_n = 32 \times 10^3$, $M_w / M_n = 1.1$), where M_n and M_w are the number-average molecular weight and the weight-average molecular weight, respectively, and M_w / M_n is the index of dispersion. Sodium 2,2'-methylene-bis- (4,6-di-t-

butylphenylene) phosphate (ADEKA Corp., NA-11SF) was used as a NA. The sample was melted at 160°C for 5 min within a thin evacuated glass capillary (φ1 mm) and then isothermally crystallized at its crystallization temperature (T_c = 129.0°C). The SAXS experiment was carried out at beamline **BL40B2**. The range of the scattering vector (q) was ($7 \times 10^{-3} - 2 \times 10^{-2}$) Å^{-1} and the wavelength (λ) was 1.5 Å.

Figure 1 shows plots of excess scattering intensity $I_x(q,t)$ against q as a parameter of t, where $I_x(q,t)$ indicates the net increase in I_x counted from I_x at $t = 0$. $I_x(q,t)$ increased with increasing of t. Therefore nano-nucleation was confirmed, because this increase in $I_x(q,t)$ should result from nano-nucleation.

Plots of ln $I_x(q,t)$ against q^2 as a parameter of t are shown in Fig. 2(a). We applied the extended Guinier plot method for q^2 = ($0.05 \times 10^{-3} - 1.50 \times 10^{-2}$) Å^{-2} [5]. Figure 2(b) shows part of the typical result of obtained from the extended Guinier plot method for t = 77 min. ln $I_x(q,t)$ was separated by five straight lines I_{xj} for each t, where j = 1, 2, …, 5. The $f(N,t)$ and N of the nanonuclei were obtained from the vertical intercept and slope of the straight lines, respectively.

Figure 3 shows log $f(N,t)$ against log N as a parameter of t. $f(N,t)$ increased with increasing t at a fixed N and stopped increasing after 10^2 min. The increase in $f(N,t)$ and the stop of the increase correspond to the induction and steady periods, respectively. $f(N,t)$ decreased with increasing N for any t. From this result, we can clarify two points as follows. One is that the nanonucleus exhibits considerable fluctuation with respect to the shape and/or size, i.e., it can take all possible shapes, has a large entropy and should be generated and disappear

(a)

(b)

$t = 7'$ $t = 35'$ $t = 100'$

Fig. 4. **(a)** Time evolution of $f(N,t)$ as a parameter of N. The right axis indicates $f(N,t)$ for N_5 and the left axis indicates that of the other N_i. Induction times (τ_i) were shown. **(b)** Illustration of real image of nano-nucleation.

frequently. The other is that only a small fraction of nanonuclei can survive and develop to macrocrystals.

The time evolution of $f(N,t)$ as a parameter of N is shown in Fig. 4(a). $f(N,t)$ for smaller N increased significantly faster and saturated with the increase of t. $f(N,t)$ for larger N increased much more slowly and saturated with the increase of t. We clarified the real image of nano-nucleation for the first time in Fig. 4(b). At first, smaller nanonuclei are generated up to t = 7 min. Many nanonuclei are generated and some of them grow into larger nuclei up to t = 35 min. Many more and larger nanonuclei are generated and grow up to $t \cong 100$ min.

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Fig. 3. Plots of log $f(N,t)$ against log N as a parameter of t. N^* indicates N of the critical nucleus, when it is in an activated state because of free energy of nucleation. $f_{st}(N)$ is $f(N,t)$ in the steady state.

References

[1] V.R. Becker and W. Döring: Ann. Phys. **24** (1935) 719.
[2] Y.A. Akpalu and E.J. Amis: J. Chem. Phys. **111** (1999) 8686.
[3] M. Hikosaka et al.: J. Macromol. Sci. Phys. B **42** (2003) 847.
[4] K. Okada, K. Watanabe, I. Wataoka, A. Toda, S. Sasaki, K. Inoue, M. Hikosaka: Polymer **48** (2007) 382.
[5] M.H. Jellinek and I. Fankuchen: Ind. Eng. Chem. **37** (1945) 158.