

SHORT COMMUNICATIONS

Effect of Entanglement on Nucleation Rate of Polyethylene

Shinichi YAMAZAKI, Masamichi HIKOSAKA,^{*,†} Fangming GU, Swapan K. GHOSH,^{*}
Motoki ARAKAKI,^{*} and Akihiko TODA^{*}

*Venture Business Laboratory, Hiroshima University, 2–313 Kagamiyama,
Higashi Hiroshima 739–8527, Japan*

**Faculty of Integrated Arts and Sciences, Hiroshima University, 1–7–1 Kagamiyama,
Higashi Hiroshima 739–8521, Japan*

(Received April 26, 2001; Accepted September 22, 2001)

KEY WORDS Nucleation / Entanglement / Topology / Extended Chain Crystal (ECC) / Folded Chain Crystal (FCC) / Polymer /

Recently, present authors found a power law of nucleation rate (I) of single crystals of polyethylene (PE), $I \propto M^{-H}$, where M is molecular weight and H is a constant.^{1,2} This indicates that the topological nature of polymer chain plays an important role on nucleation of polymers. Topological nature is related to the chain entanglement and chain sliding diffusion.^{3,4} Polymer chains should be disentangled within interface between the melt and a nucleus during nucleation. Therefore, if number density of entanglement (ν_e) is small, it is expected that I becomes large. This expectation was confirmed in our preliminary study⁵ that I decreases with increase of keeping time at a temperature above melting temperature (Δt). This result was speculated that when the melt is kept above melting temperature, ν_e gradually increases with increase of Δt and approaches to thermal equilibrium ν_e ($\nu_e = 1$), which can be regarded as “melt relaxation”. However, any experimental evidence of the expectation has not been reported yet, therefore it is important to show the evidence.

Purpose of this work is to show an experimental evidence that I increases with decrease of ν_e within the melt. It is reasonable that a giant extended chain single crystals (ECSCs) includes little entanglement ($\nu_e \sim 0$), while thin lamellae of folded chain crystals (FCCs) do a lot of entanglements. Therefore, when the giant ECSC and thin FCCs are melted, the melt should have small ν_e and large ν_e , respectively for small Δt , because the above “melt relaxation” process takes long time, *i.e.*, we showed that it takes about several hours or a few days depending on the conditions and molecular weight.⁵ This suggests that ν_e should decrease with increase of lamellar thickness (l). In the case of polyethy-

lene, l can be changed easily from several nm to several μm by changing crystallization conditions, such as degree of supercooling (ΔT) and pressure.

According to classical nucleation theory by Becker and Döring and Turnbull and Fisher, I is expressed by two competing factors as

$$I = I_0 \exp(-C/\Delta T^2) \propto D \exp(-\Delta G^*/kT) \quad (1)$$

where k is the Boltzmann constant and T is temperature, I_0 and C are constants. I_0 is proportional to diffusion constant D and C does to free energy necessary for forming of a critical nucleus ΔG^* , respectively. In the previous study, we have shown that D is a function of M , *i.e.*, $D = D(M)$ and ΔG^* is independent of M . This conclusion means that the topological nature for nucleation of polymers appears in D and not in ΔG^* .

EXPERIMENTAL

Sample Preparation

Fractionated PE (NIST, SRM1483, $M_w = 3.2 \times 10^4$, $M_w/M_n = 1.11$) was used in this work. In order to prepare ECSCs with different l , PE was isothermally crystallized at $\Delta T = 4\text{--}6$ K under the high pressure, $P = 0.4$ GPa using high pressure-differential thermal analysis (DTA) apparatus.⁶ FCCs were isothermally crystallized thin lamellae under the atmospheric pressure. l was measured on transmission electron micrographs.

Measurements of Nucleation Rate (I)

Both ECSCs and FCCs were melted at 160°C for 5 min at atmospheric pressure. After that, the samples were isothermally crystallized at various crystalliza-

[†]To whom correspondence should be addressed (E-mail: hikosaka@hiroshima-u.ac.jp).

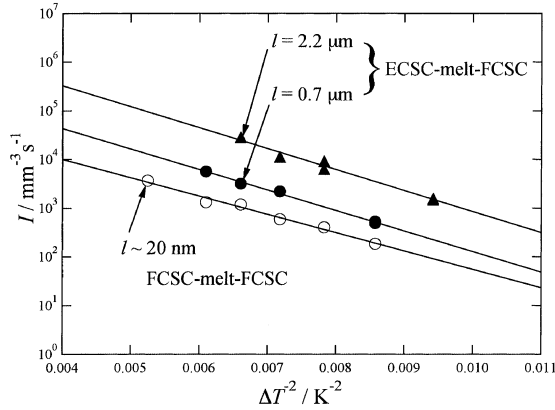


Figure 1. Plots of $\log I$ against ΔT^{-2} for $l = 20$ nm, $0.7 \mu\text{m}$, and $2.2 \mu\text{m}$, respectively. The solid lines show the best fit of the plots.

tion temperatures T_c s. Hereafter, we abbreviate these processes as ECSC-melt-FCSC and FCSC-melt-FCSC, respectively, where FCSC means folded chain single crystal. The range of $\Delta T \equiv T_m^0 - T_c$ was about $10\text{--}14^\circ\text{C}$ where T_m^0 is the equilibrium melting temperature. We used the value of T_m^0 (139.5°C) reported by Okada *et al.*⁷

We counted a number of FCSCs by means of polarizing optical microscope. The number density of nucleus ν corresponds to the number of single crystals per unit volume of the melt. Therefore, I is defined as $I \equiv d\nu/dt$, where t is the crystallization time.

RESULTS

Figure 1 shows the plots of $\log I$ against ΔT^{-2} for different l . It was found that $\log I$ showed straight lines and the slopes of the straight lines were almost similar ($C = 992, 970$, and 867 K^2 for $l = 2.2 \mu\text{m}$, $0.7 \mu\text{m}$, and ~ 20 nm, respectively). The straight line was shifted to upward with increase of l . For example, I for ECSC with $l = 2.2 \mu\text{m}$ was about 10 times as large as that for FCC with 20 nm for the same ΔT . Figure 2 shows the plot of I against l at $\Delta T = 11.5 \text{ K}$. I gradually increases at first and then rapidly does with increase of l . Thus, it is concluded that I increases significantly with increase of l . On the other hand, C does not depend on l . Therefore, ΔG^* which is proportional to C is also independent of l .

DISCUSSION

Since the spatial size of entanglement is large, entanglements cannot be included within crystalline lattice as a point defect. As shown in Figure 3, in other words, the entanglements which is expressed by cross in this figure exist on the surface of crystal or amorphous layers between lamellae and are not included within crys-

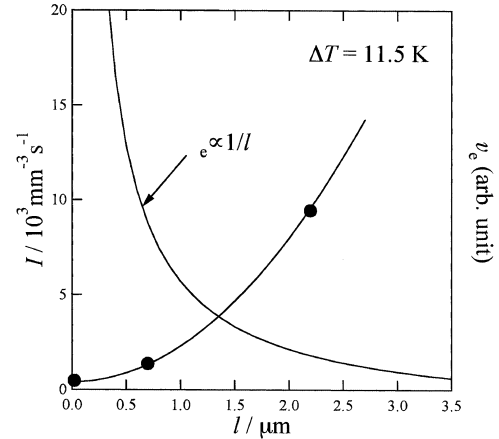


Figure 2. Plots of I against l for $\Delta T = 11.5 \text{ K}$. The solid curve shows best fit of the data. The other solid curve shows the equation $\nu_e \propto 1/l$.

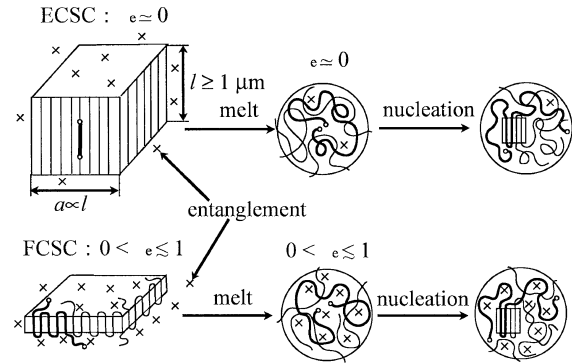


Figure 3. Schematic illustrations of melting and nucleation processes. ECSC and FCSC were melted. The cross mark denotes the entanglement.

tal. Therefore, it is considered that ν_e is expressed by the ratio of volume of crystal to surface of it as below,

$$\nu_e \propto \frac{\text{surface area}}{\text{volume}} = \frac{4al + 2a^2}{a^2l} \quad (2)$$

where a is the lateral size of ECSC. Here, it is assumed from our preliminary results⁵ that the ν_e in the melt does not change so much from that in the started crystals. In the previous study,⁸ we have shown that l is proportional to a in the case of ECSC, that is,

$$l \propto a \quad (3)$$

Combining eqs 2 and 3, we obtained

$$\nu_e \propto \frac{1}{l} \quad (4)$$

Figure 2 also plots the eq 4, *i.e.*, $\nu_e \propto 1/l$. It was found that increasing of I with increasing l correspond to decreasing of ν_e with increasing l . Therefore, it is concluded for the first time that I increases with decrease of ν_e , which is important to solve the topological mechanism of nucleation of polymers.

The fact that C is almost constant for different l means that ΔG^* is almost constant irrespective of ν_e .

The reason may be that all nucleus are the same “fold type” one,⁹ which will be shown in the following paper.

CONCLUSION

1. Nucleation rate (I) increases with increase of lamellar thickness (l), which is an experimental evidence that I increases with decrease of number density of entanglement (ν_e) within the melt.
2. Free energy necessary for forming of a critical nucleus (ΔG^*) is almost constant and does not depend on ν_e .

Acknowledgment. This work was partly supported by Grant-in-Aid for Scientific Research on Priority Areas B2 (No. 12127205) and Scientific Research A2 (No. 12305062).

REFERENCES

1. M. Nishi, M. Hikosaka, S. K. Ghosh, A. Toda, and K. Yamada, *Polym. J.*, **31**, 749 (1999).
2. S. K. Ghosh, M. Hikosaka, A. Toda, M. Arakaki, S. Yamazaki, F. Gu, and K. Yamada, *Macromolecules*, submitted.
3. M. Hikosaka, *Polymer*, **28**, 1257 (1987).
4. M. Hikosaka, *Polymer*, **31**, 458 (1990).
5. M. Hikosaka, F. Gu, and S. Yamazaki, Abstract, Conference of the European Physical Society (EPS 2000), Guimarães, Portugal, Sep. 24–28, 2000.
6. M. Hikosaka, S. Minomura, and T. Seto, *Jpn. J. Appl. Phys.*, **19**, 1763 (1980).
7. M. Okada, M. Nishi, M. Takahashi, H. Matsuda, A. Toda, and M. Hikosaka, *Polymer*, **39**, 4535 (1998).
8. M. Hikosaka, K. Amano, S. Rastogi, and A. Keller, *Macromolecules*, **30**, 2067 (1997).
9. F. P. Price, in “Nucleation”, Marcel Dekker, Inc., New York, N.Y., 1969, chapt. 8.