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SHORT COMMUNICATION

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Power law of nucleation rate of folded-chain single crystals of polyethylene

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Abstract The number-average molecular weight (M_n) dependence of the primary nucleation rate (I) of polyethylene (PE) folded-chain single crystals was studied in the ordered phase. We observed that the M_n dependence of I is mainly controlled by the diffusion process of polymer chains within the interface between a nucleus and the melt and/or within the nucleus. The results show that I decreases with increasing M_n and follows a power law $I \propto M_n^{-2.3}$ for the ordered phase. It is named the power law of the nucleation rate. In a previous article we showed that for the disordered phase $I \propto M_n^{-1}$. In this article, we concluded that I decreases with increasing M_n and follows a universal power law, $I \propto M_n^{-H}$ for both ordered and disordered phases. The power H depends on the degree of order of the crystalline phase, which is related to the morphology.

Key words Nucleation rate · Topological nature · Molecular weight · Entanglements · Chain sliding diffusion

Introduction

Nucleation of polymers is very important for both basic science and technology. Several theories were proposed to elucidate the nucleation mechanism of atomic or low-molecular-weight condensed matter systems in the first half of the twentieth century [1, 2]. Further improvement was done later [3]. Early experimental studies on nucleation of polymers revealed interesting characteristics [4–8]. This added further interest in this particular field and was explained [9–11] by applying the earlier theories [1–3]. However, important mysteries such as "how a very long linear chain polymer can be rearranged into a nucleus" and "why the molecular weight (M_n) significantly controls the nucleation behavior" have not been solved yet. This is because the topological nature of polymer chains, which seriously affects the dynamical properties of the chains [12], has not been considered well in the previous nucleation studies of polymers. In the melt, polymer chains are highly entangled and they interpenetrate each others spheres of action. We have insisted that topological nature becomes much more significant and suppresses the nucleation rate with increasing M_n [13], because entanglements should be resolved in the nucleation process. We have shown that nucleation rate (I) of extended-chain single crystals (ECSCs) of polyethylene (PE) decreases with an increase of M_n and obeys a new "power law" of $I \propto M_n^{-1}$. It has been concluded that the M_n dependence of I is mainly controlled by the diffusion process and not by the formation process of a critical nucleus.

On the basis of this result, we propose that the topological nature, such as disentanglement and chain sliding diffusion, takes an important role in the nucleation process. Disentanglement and sliding diffusion within the interface between the melt and nucleus and/or within the nucleus are expected, and should be confirmed experimentally. The purpose of this study is to show that the power law of nucleation $I \propto M_n^{-H}$ is universal and that the power H increases with increasing degree of order of the crystalline phase. This will confirm that the disentanglement and chain sliding diffusion mainly control the nucleation process.

It is well known that polymer crystals show various polymorphisms. These are roughly classified into the "ordered phase", such as the orthorhombic or monoclinic phase etc., and the "disordered mobile phase", such as the hexagonal phase. We have shown that when polymers are crystallized into ordered and disordered phases, folded-chain single crystals (FCSCs) and ECSCs are formed, respectively [14, 15]. The disentanglement and sliding diffusion mentioned previously strongly depend on the degree of order of the crystalline phase, which results in that the power H depends on the degree of order of the crystalline phase. In a previous study, we showed $I \propto M_n^{-1}$ for ECSCs, which are formed in the disordered (hexagonal) phase, whereas here, we will show $I \propto M_n^{-2.3}$ for FCSCs of PE that are formed in the ordered (orthorhombic) phase.

Experimental

Samples and equipment

We investigated well-fractionated PE samples. The samples were fractionated from a single "mother sample" (Table 1) so that they contained the same type of heterogeneities. The range of the number-average molecular weight (M_n) was from 30×10^3 to 99×10^3 (named 30 K, 99 K, etc.). The samples were specially prepared and supplied by Sunallomer Ltd. The degree of supercooling, $\Delta T = (T_m^0 - T_c)$ was determined using the equilibrium melting temperature (T_m^0) presented by Okada et al. [16]. T_c is the crystallization temperature. Isothermal crystallization of an isolated FCSC at atmospheric pressure was observed using a polarizing optical microscope (Olympus, BX-50) equipped with a hot stage (Linkam) and was recorded by a video camera system. The temperature of the sample was calibrated using standard materials, In and Sn.

Method

The nucleation rate, I, is obtained by

$$I = \frac{dv}{dt} , \tag{1}$$

where v is the number density of the nuclei in the melt and t is the crystallization time. Becker and Döring [1] and Turnbull and Fisher [2] showed that I is expressed by

$$I = I_0 \exp(-\Delta G^*/kT) , \tag{2}$$

Table 1 M_n, M_w and molecular-weight distribution of polyethylene fractions fractionated from a "mother sample". Here K = 10^3

Sample	$M_n/10^3$	$M_w/10^3$	M_w/M_n
30 K	30	34	1.15
50 K	50	57	1.14
71 K	71	81	1.14
99 K	99	114	1.14
Mother	48	116	2.42

where I_0 is a constant, ΔG^* is the free energy for the formation of a critical nucleus and kT is the thermal energy. I_0 is proportional to the diffusion constant, D, and is expressed by

$$I_0 \propto D \propto \exp(\Delta E/kT) , \tag{3}$$

where ΔE is the activation energy for self-diffusion of a unit, such as an atom or a repeating unit of polymer. ΔG^* can be expressed by

$$\Delta G^* = C/\Delta T^2 , \tag{4}$$

where C is a constant related to the surface free energies and enthalpy of fusion. Substitution of Eq. (4) into Eq. (2) leads to

$$I = I_0 \exp(-\kappa/\Delta T^2) , \tag{5}$$

where $\kappa = C/kT$. Both the parameters I_0 and κ are functions of T; however, for practical purposes they can be approximated as constants. Because the change in T ($\approx$403 K $\pm$ 3 K) is small enough the changes in $\exp(-\Delta E/kT)$ and κ can be neglected.

Results

In the early stage of the nucleation v increases linearly with increasing t. I, which is the slope of the plot of v versus t, decreases with decreasing ΔT. $\log I$ is plotted against ΔT^{-2} for samples 30 K, 50 K, 71 K and 99 K in Fig. 1. log I decreases linearly with increasing ΔT^{-2}.

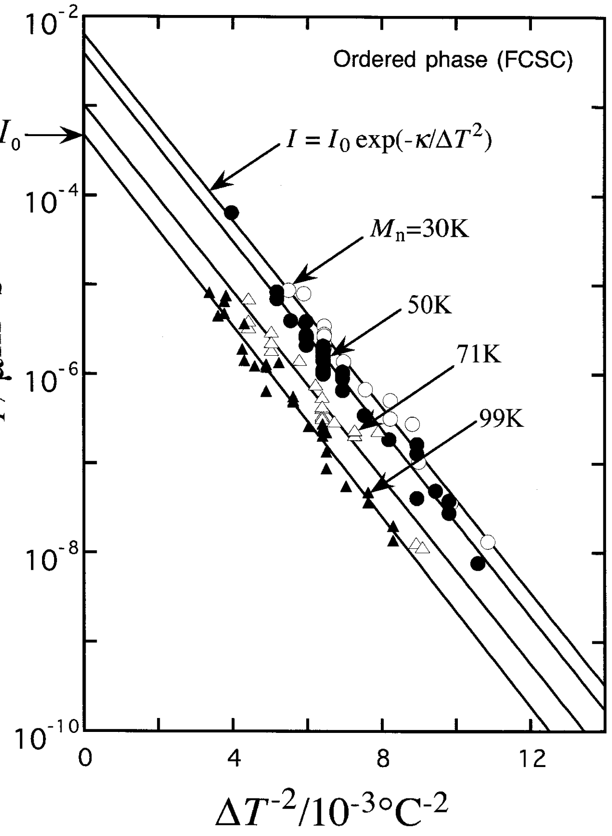

Fig. 1 Plot of log I against ΔT^{-2} for M_n = 30 K, 50 K, 71 K, 99 K in the ordered phase. The solid lines show the best fit of the data with Eq. (5). I_0 and κ were determined from the fitting

Equation (5) fits well with the experimental results. Therefore I_0 and κ can be determined as fitting parameters. Figure 1 shows that all the fitting curves are nearly parallel and shift downward with increasing M_n. It means that κ does not depend on M_n, while I_0 decreases with increasing M_n. The M_n dependences of I_0 and κ are plotted in Fig. 2. One may now summarize that

$$I_0 = I_0(M_n) \quad \text{and} \quad \kappa \approx \text{constant} \ . \tag{6}$$

Therefore, it can be concluded here that diffusion constant, D, which is proportional to I_0, decreases with an increase in M_n, while the free energy for the formation of a critical nucleus, ΔG^*, which is related to κ, does not depend on M_n. We observed the same phenomenon (Eq. 6) in the nucleation of ECSCs [13]; therefore, it might be a universal phenomenon, which leads to the conclusion

$$I(M_n) \propto I_0(M_n) \propto D(M_n) \ . \tag{7}$$

We have plotted log I_0 against log M_n in Fig. 3. We observed that the M_n dependence of I obeys a new power law,

$$I_0 \propto M_n^{-2.3} \tag{8}$$

for the ordered phase. In a previous study we showed that the M_n dependence of I is expressed by a similar power law, $I_0 \propto M_n^{-1}$, for the disordered phase [13], as described in the Introduction. Therefore, the nucleation rate can be expressed by a unique power law

$$I(M_n) \propto D(M_n) \propto M_n^{-H} \ , \tag{9}$$

where

$$\begin{aligned} &H = 2.3 \text{ for the ordered phase (FCSC)} \\ &H = 1.0 \text{ for disorderd phase (ECSC)} \ . \end{aligned} \tag{10}$$

From these experimental findings, we propose that there is a "universal power law of the nucleation rate", irrespective of the degree of order of the crystalline phase, which is related to morphology.

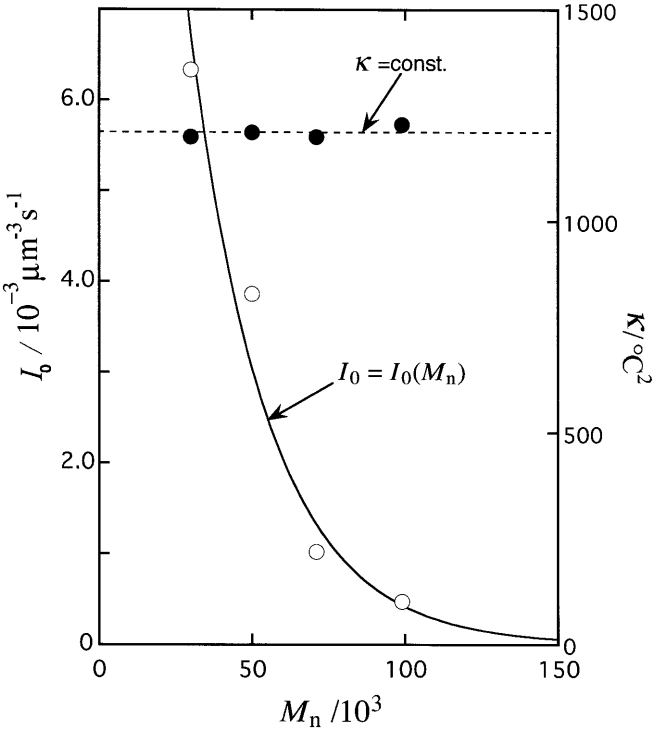

Fig. 2 Plot of I_0 and κ against M_n. The solid line represents the power law $I_0 \propto M_n^{-2.3}$. The broken lines show that κ is nearly constant

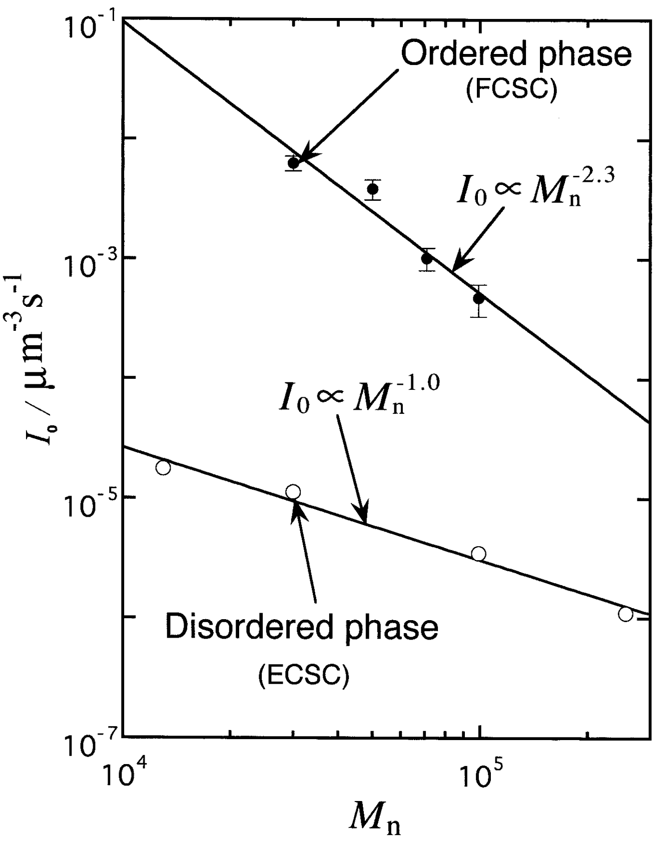

Fig. 3 Plot of log I_0 against log M_n. The solid lines represent the power law $I_0 \propto M_n^{-2.3}$ for the ordered phase and $I_0 \propto M_n^{-1.0}$ for the disordered phase

Discussion

In the melt, polymer chains are highly entangled (marked by X in Fig. 4) and have a random-coil conformation within a sphere called a "Gaussian sphere". Usually, a large number of chains are superimposed in a Gaussian sphere. In order to form a nucleus, the polymer chains rearrange themselves within the Gaussian sphere into a parallel-packed folded

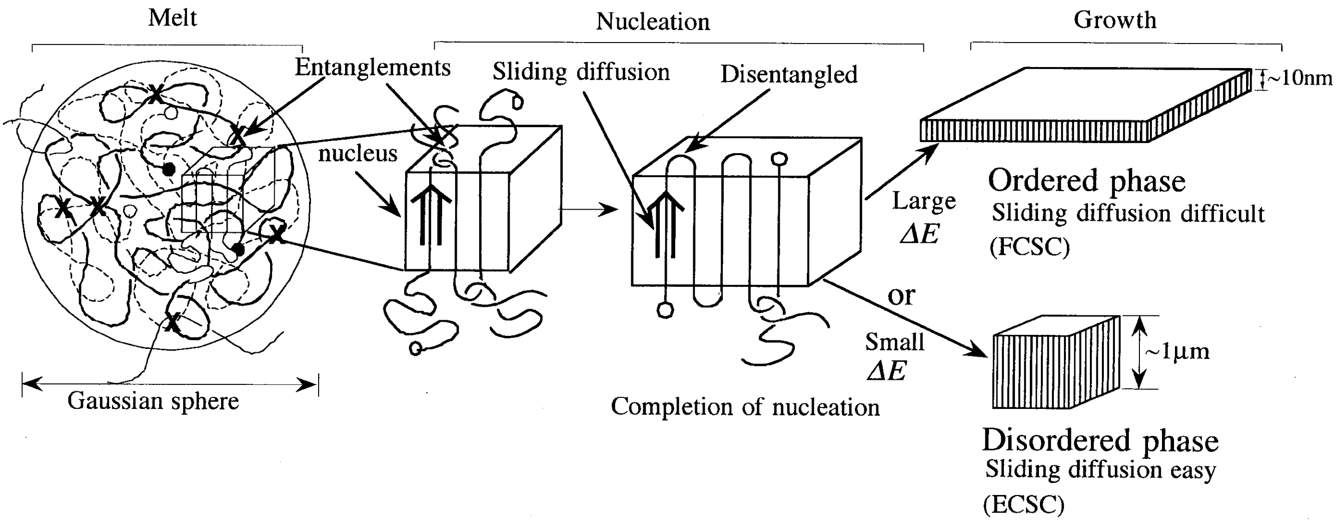

Fig. 4 Schematic diagram of the "topological nucleation mechanism". Polymer chains are rearranged from the random-coil conformation called a "Gaussian sphere" into the nucleus through disentanglement (marked by **X**) and chain sliding diffusion within the nucleus and within the interface. A nucleus only survives when it becomes sufficiently large. This corresponds to the completion of nucleation. Nuclei which survive then grow into macroscopic crystals such as folded-chain single crystals (FCSCs) or extended-chain single crystals (ECSCs) depending on ΔE

structure via disentanglement and sliding diffusion (marked by ⇑). Disentanglement and sliding diffusion are necessary for nucleation because of the topological nature. They are also required for the growth of a nucleus. For disentanglement chain ends have to pass through the entanglement. When M_n increases, the number of entanglements included within one molecule increases; therefore, disentanglement and sliding diffusion should become difficult. This is the reason why topological restrictions increase with increasing M_n, which results in I decreases with an increase of M_n.

To explain the power law we have proposed a primitive theory [13] which shows that the completion of nucleation corresponds to the stage at which a whole chain is accommodated within a nucleus. Taking into consideration both macroscopic diffusion of the center of mass of a chain molecule and the topological diffusion along chain axis, i.e. the chain sliding diffusion in the nucleation process, the theory is formulated to be

$$I(M_\mathrm{n}) \propto D(M_\mathrm{n}) \propto M_\mathrm{n}^{1-3\alpha} \; . \qquad (11)$$

Here α is a kind of order parameter related to the crystalline phase. Comparison with Eq. (9) gives $\mathrm{H} = 3\alpha - 1$, where $\alpha = 1.1$ and 0.7 for nucleation in ordered and disordered phases, respectively. An increase in the value of H corresponds to an increase in the degree of order of the crystalline phase.

It is important to consider why H increases with the increase in the order of the crystalline phase. There are three different types of diffusion, such as within the melt, within the interface between the melt and the crystals, and within the crystalline phase. It is obvious that the diffusion within the melt cannot be controlled by the degree of order of the crystalline phases, so this is not the cause of the crystalline phase dependence of H. Therefore, the difference in H should arise from the diffusion within the interface between the melt and the crystals and/or in the crystalline phase. Thus, the crystalline phase dependence of H should be experimental evidence that disentanglement and sliding diffusion (within the interface between the melt and a crystal and/or within the crystalline phase) have an important role in the nucleation process. It is obvious that the sliding diffusion and disentanglements become difficult as the degree of order of the crystalline phase increases. Figure 4 shows that a nucleus will survive after growing to a sufficiently large size, which corresponds to the "completion of nucleation". The nucleus which has survived grows into a macroscopic crystal of FCSC or ECSC depending on ΔE.

Conclusions

We observed that the nucleation rate decreases with an increase of M_n, and proposed a universal power law $I \propto M_\mathrm{n}^{-\mathrm{H}}$, where the power H depends on the degree of order of the crystalline phase that is related to the morphology of the crystals. It is shown that the formation process of a critical nucleus does not depend on M_n, whereas only the diffusion process does depend on M_n. It is concluded that the nucleation process of polymers is a process where entangled chains within the supercooled melt are rearranged into parallel-packed crystalline lattices through disentanglement and chain sliding diffusion within the interface and within a nucleus.

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References

1. Becker VR, Döring W (1935) Ann Phys 24:719
2. Turnbull D, Fisher JC (1949) J Chem Phys 17:71
3. Frank FC, Tosi M (1961) Proc R Soc Lond Ser A 263:323
4. Turnbull D, Cormia RL (1961) J Chem Phys 34:820
5. Sharples A (1962) Polymer 3:250
6. Cormia RL, Price FP, Turnbull DJ (1962) J Chem Phys 37:1333
7. Gornik F, Ross GS, Frolen LJ (1967) J Polym Sci 18:79
8. Koutsky JA, Walton AG, Baer E (1967) J App Phys 38:1832
9. Lauritzen JI Jr, Hoffman JD (1960) J Res Natl Bur Stand US 64A:73
10. Price FP (1969) In: Zettlemoyer AC (ed) Nucleation. Dekker, New York, pp 405–488
11. Wunderlich B (1976) Macromolecular physics, vol 2. Academic, New York, pp 1–105
12. Doi M, Edwards SF (1986) The theory of polymer dynamics. Clarendon, Oxford, pp 140–187
13. Nishi M, Hikosaka M, Ghosh SK, Toda A, Yamada K (1999) Polym J 31:749
14. Hikosaka M (1987) Polymer 28:1257
15. Hikosaka M (1990) Polymer 31:458
16. Okada M, Nishi M, Takahashi M, Matsuda H, Toda A, Hikosaka M (1998) Polymer 39:4535