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Topological Mechanism of Nucleation of Cyclic Polyethylene

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Abstract

In order to clarify the effects of entanglement species on nucleation of polymers, we studied the nucleation rate I of cyclic and linear polyethylenes (C-PE and L-PE) from the melt as a function of degree of supercooling ΔT by means of polarizing optical microscope. We prepared several C-PEs with different weight average molecular weights $M_w=4600-114800$. I of all the sample were obeyed the equation, $I=I_0\exp(-C/\Delta T^2)$. I_0 s of C-PE with $M_w=114800$ and L-PE with $M_w=35400$ were almost the same. This indicates that C-PE is easier to nucleate than L-PE due to lack of knot entanglements. On the other hand, C s for C-PE significantly increased with increasing M_w . This tendency is quite different with L-PE previously reported. The increase of C indicates that folding regularity of end surface of nucleus increases. Since topological constraint of C-PE arose from the lack of chain ends is relatively decreased with increasing M_w , it was implied that the nucleation behavior of C-PE approaches that of L-PE.

1. Introduction

It is well known that the nucleation and growth of polymers are significantly suppressed by chain entanglements [1]. Because polymer chains should be disentangled within the interface or the melt and slide within the crystalline lattice during the nucleation and growth [2]. However, “what kind of entanglement species dominantly control the nucleation of polymer” remains unclear. In previous paper, one of the authors (SY) has proposed the hierarchized model of chain entanglements based on the melt annealing time Δt dependence of nucleation rate I [3]. They concluded that simple entanglements such as “twist entanglements” are formed within small Δt (<20 min) and then complicated entanglements such as “knot entanglements” are gradually formed. It is natural to consider that twist entanglements should be easily disentangled comparing with knot entanglements. Though it is expected that the suppression effect of the former on the nucleation should be smaller than that of the latter, this has never been confirmed experimentally yet. In order to clarify the effect of entanglement species on the nucleation of polymers, it is useful to study the nucleation of cyclic polymers. Because cyclic polymer can not physically form the knot entanglements participated with

the chain ends. By the comparison the nucleation behavior between cyclic and linear polymers, we can make clear the role of the knot entanglements in the nucleation. The main purpose of this work is to show the role of knot entanglement in the nucleation of polymers through the observation of ΔT dependence of I of cyclic and linear PE.

Theoretical background of classical nucleation theory

According to the classical nucleation theory, I is expressed by,

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

where I_0 and C are constants, ΔT is the degree of supercooling, k is the Boltzmann constant and T is the temperature. ΔT is defined by $\Delta T = T_m^0 - T_c$, where T_m^0 is the equilibrium melting temperature and T_c is a crystallization temperature. I_0 is related to diffusion constant D as $I_0 \propto D$. Whereas, C is proportional to free energy necessary for forming a critical nucleus ΔG^* as below in the case of heterogeneous nucleation,

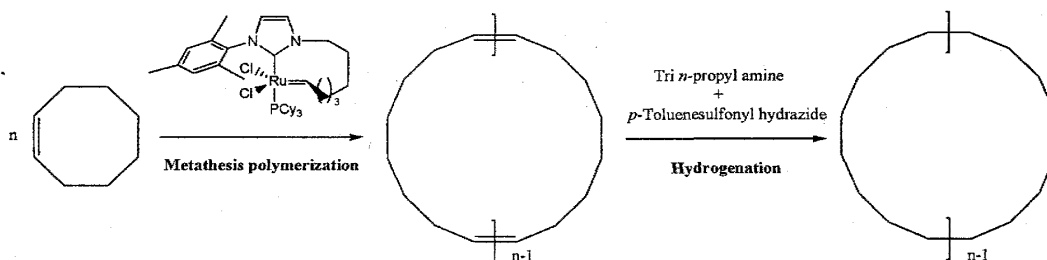
$$\Delta G^* \propto \frac{C}{\Delta T^2} \equiv \frac{16\sigma\sigma_e\Delta\sigma}{\Delta g^2} \quad (2)$$

where Δg is the free energy of fusion, σ and σ_e are the side and end surface free energy, respectively. $\Delta\sigma$ is a constant related with efficiency between nucleus and heterogeneity. It is well known for folded chain crystal that σ_e is larger than σ . Since it is natural to consider that σ of C-PE and L-PE are the same, the difference of C mainly arise from σ_e and $\Delta\sigma$. Assuming that $\Delta\sigma$ for C-PE and L-PE are the same, the difference of C reflects the difference of the shape of nucleus such as aspect of chain folding on the end surface. In this study, we will discuss the values of I_0 and C of C-PE and L-PE.

2. Experimental

Sample preparation

C-PE and L-PE were prepared by the same method reported in literatures [4]. Scheme 1 shows how to prepare C-PE. At first, cyclic and linear polyoctenes (PE precursors) were synthesized via ring opening polymerization of *cis*-cyclooctene catalyzed by modified and 1st generation Grubbs catalysts, respectively. Both PE precursors were hydrogenated by *p*-toluenesulfonyl hydrazide to corresponding PE. The weight average molecular weights M_w of C-PE and L-PE were determined by the measurements of intrinsic viscosity of PE precursors.



Scheme 1. Preparation of C-PE via olefin metathesis and hydrogenation

Measurements of nucleation rate I

C-PE and L-PE samples were softly sandwiched by cover glasses. The observations of isothermal crystallization were carried out through a polarizing optical microscope (Olympus, BX-51) equipped with a hotstage (Linkam LK600PM). After melting the starting material at a maximum annealing temperature $T_{\max}=150^{\circ}\text{C}$ for $\Delta t=1$ min, the sample was quenched to a T_c . In order to avoid the sample degradation at high temperature, the sample was purged with a running stream of nitrogen gas during the observation. Isothermal crystallization behaviors were recorded by digital video camera. The nucleation rate I was evaluated as a function of ΔT . I was defined by $I=d\nu/dt$ where ν is the number density of crystal within the melt. The details were reported in elsewhere [1].

3. Results

3.1. Comparison of I between C-PE and L-PE

Fig. 1 shows the plot of $\log I$ against ΔT^2 for C-PE with $M_w=114800$ and L-PE with $M_w=35400$. I obeyed well known equation $I=I_0\exp(-C/\Delta T^2)$, i.e, nucleation control process. These straight lines were parallel each other. This indicates that the slope of the straight line C is almost constant irrespective of topological nature of polymers. In order to compare both samples with same M_w , the data of L-PE was reduced using power law of I reported previously [5]. Reduced data of I of L-PE is also shown in same figure. It was found that intercept I_0 of C-PE was significantly larger than that of L-PE at same M_w . This indicates that the former is easier to nucleate than the latter.

3.2. Molecular weight dependence of I of C-PE

Fig. 2 shows the plot of $\log I$ against ΔT^2 for C-PE with different M_w . I also obeyed the equation $I=I_0\exp(-C/\Delta T^2)$. However, it was found that the slope C increased with increasing M_w . This result was quite differ with that of L-PE. In L-PE, it was reported that C was almost constant for M_w . Above $M_w\sim 50000$, it was found that C approaches to a constant value.

4. Discussion

4.1. Model of nucleation of C-PE and L-PE

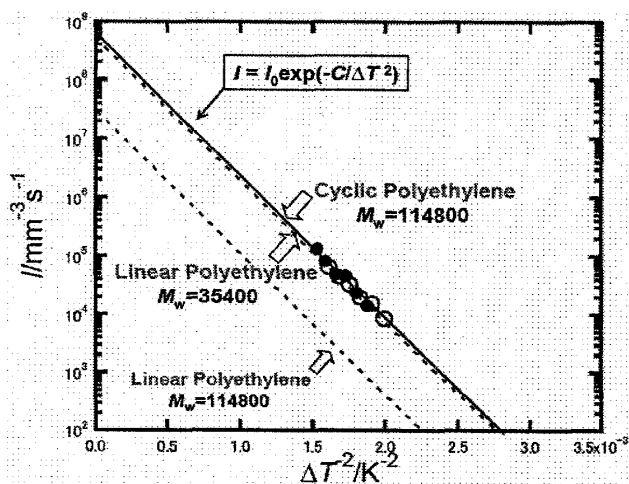


Fig. 1. Plots of $\log I$ vs. ΔT^2 for C-PE with $M_w=114800$ and L-PE with $M_w=35400$. Data of L-PE with $M_w=114800$ is reduced one using the relation reported previously.

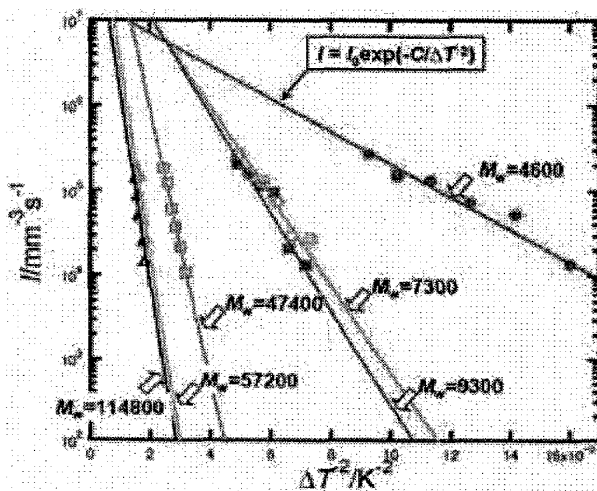


Fig. 2. Plots of $\log I$ vs. ΔT^2 for C-PE with different M_w .

Let us consider the reason why C-PE is easier to nucleate than L-PE. Fig. 3 shows schematic illustration of the nucleation from the melt of C-PE (top) and L-PE (bottom), respectively. In C-PE, since there are no complicated entanglements such as “knot”, it is easy to disentangle and to do the sliding diffusion during the nucleation. Whereas, L-PE has a lot of knot entanglements and they will act as pinning effect during the nucleation. Therefore, L-PE is more difficult to nucleate than C-PE.

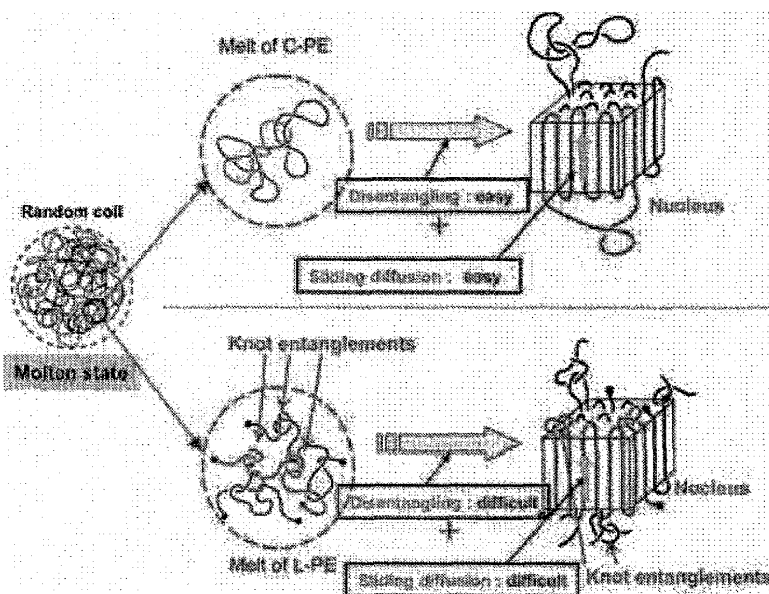


Fig. 3. Schematic illustration of the nucleation from the melt of C-PE and L-PE.

4.2. Topological constraint of C-PE

In C-PE, it was found that C increased with M_w . This implies that end surface of nucleus becomes to be ordered with increasing M_w . Fig. 4 shows schematic illustration of the nucleation with small and large C-PE. Since topological constraint of conformation and restriction of chain rearrangement during the nucleation for small ring polymer is stronger than that for large analogue, chain folding at end surface becomes disorder. In this case, there are a lot of loose loop foldings. On the other hand, since the constraint and restriction in large ring polymer are relatively small, end surface will be occupied by regular folding.

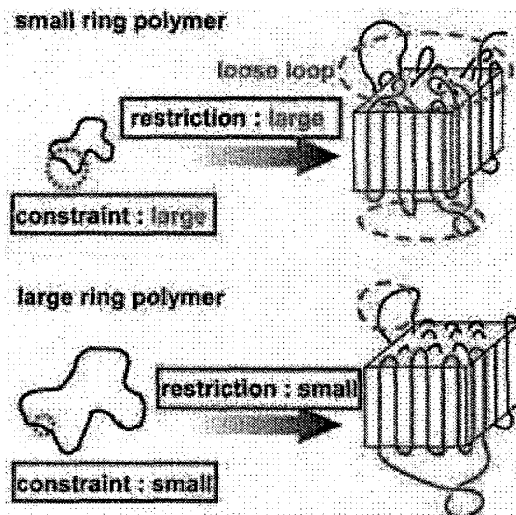


Fig. 4. Schematic illustration of the nucleation of small and large C-PE.

5. Conclusion

Topological mechanism of nucleation of cyclic polyethylene was studied. Knot entanglements are crucially suppressed the nucleation. Topological constraint determines the shape of nucleus.

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