Two-step formation of entanglement from disentangled polymer melt detected by using nucleation rate

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Abstract

“How do chain molecules spontaneously entangle from completely disentangled polymer melt?” remains the most interesting unsolved problem. In order to solve this problem, we used the concept that the melt of “nascent” polymer crystallized during polymerization just after melting does not include any entanglements. We succeeded in detecting the increase of entanglement density $n_e$ with the increase of annealing time $\Delta t$ above the equilibrium melting temperature before isothermal crystallization. The increase of $n_e$ was detected by observing the decrease of nucleation rate $I$ from the melt of nascent polymer with different $\Delta t$s. $I$ is a very sensitive detector of entanglements because the nucleation is a rearrangement process of chains to the crystalline lattice through the disentanglement. Therefore, $I$ is significantly suppressed with the increase of $n_e$. We found a two-step decrease of $I$ with an increase of $\Delta t$ for the first time. This should correspond to a two-step increase of $n_e$ with an increase of $\Delta t$. This indicates that simple entanglements such as twist or knot with lower order (one time knot) were formed within short time and then the complicated ones such as knot with higher order (two or three times knots) or loops (entanglements by loop conformation) were formed.

Keywords: Entanglement; Nucleation; Nascent polyethylene

1. Introduction

1.1. During the melting entanglement density $n_e$ should increase

Ideal melting and crystallization of polymers can be regarded as the transitions between fully extended chain crystals without entanglements (the ideal crystal such as extended chain crystal (ECC) [1–3]) and fully entangled Gaussian chain melt [4–6] (the thermal equilibrium melt) as shown in Fig. 1 of our previous paper [7], because the crystallization process is considered to be a process where polymer chains are disentangled within the interface between a nucleus and the melt and within a small crystal and are rearranged into large ideal crystals via chain sliding diffusion [8,9]. The melting is the reverse process of crystallization. During melting, from an ideal crystal the chains will be fully entangled to the Gaussian coil due to the thermal motion.

The mechanism of how the polymer chains spontaneously entangle has also been the most important unsolved problem. Though a few theoretical approaches for this problem have been reported [10–12], it has not been clarified experimentally yet. It has been difficult so far to prepare the liquid with entanglement density $n_e \approx 0$ and to detect the change of $n_e$. In this paper, we have solved the above difficulties by melting the so-called “nascent” polymer prepared by crystallization during polymerization (reactor powder) [13–15] which does not include entanglements (Fig. 1). In this case, we can control $n_e$ within the melt by changing the “melt annealing time” ($\Delta t$) which is the annealing time at a temperature above the equilibrium melting temperature $T_m^0$. We will define that
The main purpose of this work is to show how the polymer chains within the melt form the entanglements. Based on our results, we will show the change of $n_e$ from $n_e(0)$ to large $n_e$ using reactor powder of polyethylene (reactor-PE).

1.2. How to prepare the melt with $n_e \equiv 0$

Recently, the metallocene catalysts are widely used for polymerization of polyolefines such as polyethylene (PE) or isotactic polypropylene (iPP) in order to obtain the sample with narrow molecular weight distribution and/or high tacticity [15–17]. When this polymerization is applied to a homogeneous system at low temperature below crystallization or dissolution temperature, the so-called reactor powder is obtained. Under this condition, the polymer chain will be immediately crystallized during the polymerization. Fig. 1 shows the schematic illustration of polymer chain formed from catalysis in solution and the nucleation behavior during the polymerization.

Using the reactor-PE, we can study the formation of entanglements within the melt. After melting, $n_e$ should increase with an increase of $\Delta t$. In other words, we can widely control $n_e$ within the melt from zero to unity (thermal equilibrium melt) by changing $\Delta t$. On the other hand, if the experiment will be started from the melt just after melting of folded chain crystals (FCCs), $n_e$ within the melt at $\Delta t \equiv 0$ shows a certain value between zero and unity. At this point, reactor powder is the most suitable material to explore the formation process of entanglements during the melting of polymers.

1.3. Nucleation rate $I$ is a sensitive detector of $n_e$

Since the entanglements cannot be involved to the crystal lattice, it is obvious that the entanglements within the melt will suppress the nucleation and growth of the crystal [8,9]. Fig. 2 shows the schematic illustration of how the nucleation is suppressed by the entanglements. When the nucleus will be formed from the melt, the entanglements within the interface between the melt and nucleus should be disentangled in order to grow to larger nucleus. If the entanglements are not disentangled properly, the entanglements will result in the "pinning effect" for the formation and growth of nucleus, because the sliding diffusion of the chain within the nucleus or interface should be suppressed by the entanglements. As a consequence, $I$ should become to be small. Similar pinning effects such as conformational pinning or self-poisoning effects are well known for long paraffin system or crystal growth of polymers [18,19].

Though the relation between $I$ and $n_e$ is one of the most important problem in polymer crystallization, it has not been clarified yet. In the 1980s, Rault has studied the memory effects in semicrystalline polymers by using refined method combined with annealing and quenching [20]. He showed that the entanglements play an important role in semicrystalline polymers. Psarski et al. showed that the growth rate of
spherulite of PE from the melt with lowered entanglements using the ECCs is larger than that from the ordinary melt [21]. However, though the growth rate is controlled by the “secondary” nucleation, the quantitative experimental formula between “primary” nucleation rate $I$ and $\nu_e$ remains unclear. In our previous paper, we succeeded in showing that $I$ of PE decreases with the increase of $\nu_e$ within the melt. We have prepared the melt with different $\nu_e$s by melting ECCs with different lamellar thicknesses $L$ [7,22]. We showed that $\nu_e$ is proportional to $1/l$. We proposed the experimental formula of $I$ as a function of $\nu_e$:

$$I(\nu_e) = I_0 \exp(-\gamma \nu_e)$$

(2)

where $I_0$ means $I$ at $\nu_e \equiv 0$ $(\Delta t \equiv 0)$ and $\gamma$ is the constant. Needless to say, the melt of ideal crystals at $\Delta t \equiv 0$ should correspond to the melt of ECC with $l = \infty$, whereas the melt of any crystals at $\Delta t = \sigma$ should correspond to the thermal equilibrium melt. Since $\nu_e$ within the melt increases with the increase of $\Delta t$, $I$ should decrease. The results of this work will give us an important insight on the relation between $I$ and $\nu_e$.

As $\nu_e$ should be qualitatively evaluated by rheological measurements [23], we have been measuring the time evolution of $\nu_e$ of the same reactor-PE. In our sequential paper [in preparation], the significant relationship between $\nu_e$ evaluated by $I$ and that by rheological measurements will be shown.

1.4. The origin of melt memory effects

It is well known that the melt memory effects in polymer crystallization are significant. Hashimoto and Itoh reported the melt memory effects on the nucleation of iPP and isotactic polystyrene [25]. They insisted that the effects arose from the "seeding effect" of primary nucleus. It was observed that the seeding effect was significant when the samples were melted and annealed below $T_m^0$ before isothermal crystallization. According to their experiments, if the samples are melted and annealed at a higher temperature than $T_m^0$, the seeding effect should disappear. However, in order to solve the essential mechanism of nucleation, the melt annealing before isothermal crystallization should be conducted at a higher temperature than $T_m^0$. We emphasize that the origin of melt memory effect on polymer crystallization basically arises from the change of $\nu_e$ during melt annealing and not from the seeding of primary nucleus. According to our preliminary experiments on PE, when the melt annealing temperature was increased from 150 °C to 200 °C, we found that $I$ decreased by one third at the same annealing time. Needless to say, the magnitude of melt annealing effect should be changed for the molecular weight of samples [26]. Therefore, in this paper, we will discuss that the change of $I$ against $\Delta t$ will be controlled by the change of $\nu_e$ during the melt annealing.

1.5. Purpose of this work

The purpose of this work is to show the change of $I$ of reactor-PE against $\Delta t$ and to establish an experimental formula of $\nu_e(\Delta t)$. Based on experimental facts, we will discuss how the polymer chains form the entanglements within the melt through the hierarchization of entanglements.

2. Experimental

2.1. Sample

The reactor-PE sample was supplied by Japan Polyethylene Corp. The polymerization of reactor-PE was carried out at a low temperature (ca. 70 °C) in the solvent. Weight average molecular weight $M_w$ and molecular weight distribution $M_w/M_n$ were $33.1 \times 10^5$ and 2.31, respectively, where $M_n$ is the number average molecular weight. The obtained sample did not so brittle. However, comparing with ordinary PE samples with same molecular weight, reactor-PE was easy to deform.

The reason why $\nu_e$ is almost zero just after melting of reactor-PE is shown as below. As the concentration of catalyst within the reactor is sufficiently dilute, we only need to consider the intramolecular entangling of a polymerized chain. The polymerization temperature in this work corresponds to the melting temperature of $n$-alkane which has ca. 35 carbons (C35). The molecular weight of C35 is much smaller than that between entanglements of PE [27]. At 70 °C, we can roughly estimate the number of repeating units within the heterogeneous critical nucleus of PE as $N^* \sim 100$ [28], where $N^*$ is the number of repeating units within the critical nucleus. This estimated $N^*$ is almost the same as the chain length between entanglements [27]. When the number of carbons of growing polymer chain increases to more than 35 during the polymerization, the crystals without entanglements will be formed immediately. Therefore, the reactor powder consists of stacked thin lamellae with few entanglements within the amorphous phase. Additionally, it was confirmed that the melting temperature of reactor-PE was higher than that of melt crystallized PE. Moreover, we also confirmed that the melting temperature of the first heating process was higher than that of the second heating process.

In order to decrease the statistical error for determination of $I$ [29], the nucleating agent (NA11-SF supplied by Adeka Corp) [30] was added to reactor-PE by 0.1 wt%. Then, the reactor-PE added with NA11-SF in xylene was frozen and crushed by homogenizer. The addition of nucleating agent only decreases the free energy necessary to form a critical nucleus in heterogeneous nucleation. Since it is considered that the nucleation of PE without nucleating agent should be heterogeneous, the other effect of nucleating agent such as activity or wetting will be ignored in this work. Above sample by one sequential handling was used in all the experiments for measurements of $I$ in this work. Therefore, samples used for the measurements of $I$ have the same history of preparation and can be regarded as identical ones.

2.2. Instrument

The reactor-PE sample was softly sandwiched between cover glasses. Isothermal melt annealing and crystallization
experiments were conducted on a polarizing optical microscope (Olympus, BH-2) fitted with a hotstage (Linkam LK600PM). The sample thickness during the measurements was kept almost constant (ca. 30 µm) due to the surface tension of the sample and the weight of the upper cover glass. After melting, the sample instantly (within 2 min) formed a thin circular film without any bubble. In order to avoid the sample degradation at high temperature, the sample was purged with a running stream of nitrogen gas (50 ml/min). In this work, it is assumed that no chemical reaction such as cutting of bond occurs during the melt annealing and crystallization processes. From GPC measurements, it was found that the molecular weight of PE did not change during the melt annealing with ∆t < 4 h (unpublished data).

2.3. Measurements

A typical crystallization process was schematically shown in Fig. 3. The starting sample was melted at a maximum annealing temperature $T_{\text{max}} = 150^\circ C$ for each ∆t (from 2 to 180 min) and quenched to a crystallization temperature $T_c$ (the degree of supercooling $\Delta T = 12^\circ C$). Then, $I$ was obtained one by one for each ∆t. During isothermal crystallization, $I$ was determined by $I \equiv \frac{dv}{dt}$, where $v$ is the number density of crystal within the melt and $t$ is the crystallization time [31]. The counting method of crystals is explained elsewhere [7,22]. The counts of the crystals were carried out in the center of the sample in order to eliminate the effect of surface or interface in nucleation.

3. Results

3.1. Increase of $n_e$ leads to decrease of $I$

Fig. 4 shows the typical optical micrographs of FCC formed from the melt of reactor-PE at different ∆ts. Since the spatial distribution of observed small crystals was well, the statistical error for the evaluation of $I$ was small. From these photographs, it is qualitatively evident that $I$ decreased

![Graph](image-url)

Fig. 3. Schematic illustration of heating and crystallization processes.

![Images](image-url)

Fig. 4. Typical polarizing optical micrographs of isolated crystals at the same crystallization time $t$ and $T_c = 128.4^\circ C$ with (a) $\Delta t = 2$, (b) $\Delta t = 20$, (c) $\Delta t = 120$, and (d) $\Delta t = 180$ min, respectively. The scale bar is 20 µm.
The experimental data can be divided into two regions that arose from fast and slow entanglements. Solid curve shows the best fitting with the experimental data in Eq. (3).

![Diagram of number density of nucleus](image)

**Fig. 5.** The number density of nucleus $n$ was linearly increased with the increase of $t$. The nucleation rate $I$ was defined by the slope of these straight lines.

with the increase of $n_e$, because the increase of $\Delta t$ should correspond to the increase of $n_e$.

### 3.2. $I$ decreased with increase of $\Delta t$

In order to evaluate qualitatively the decrease of $I$ with the increase of $\Delta t$, Fig. 5 shows the plot of $n$ of reactor-PE against $t$ with different $\Delta ts$. Since $n$ increased linearly with the increase of $t$, we can obtain $I$ from the slope of straight lines [22,29,31]. It is obvious that $n$ decreased with the increase of $\Delta t$.

**Fig. 6** shows the plot of $I$ of reactor-PE against $\Delta t$ at the same $T_{max}$ and $T_c$. We found that $I$ rapidly decreases with the increase of $\Delta t$ up to $\Delta t \approx 20$ min and then slowly decreases. The experimental formula of $I$ as a function of $\Delta t$ can be represented by

$$I(\Delta t) = A \exp\left(-\Delta t/\tau_f\right) + B \exp\left(-\Delta t/\tau_s\right) + I_\infty$$

(3)

where $A$, $B$ and $I_\infty$ are the constants and $\tau_f$ and $\tau_s$ are defined as the relaxation time for the formation of fast and slow entanglements, respectively. $I_\infty$ is assumed to be

$$I_\infty = \lim_{\Delta t \to \infty} I(\Delta t)$$

(4)

The fitting parameters are summarized in Table 1. It is noted here that $I_\infty$ should be logically larger than zero. Therefore, the value of $I_\infty$ was tentatively assumed to be $10^4$. In spite of this value, it was found that $\tau_f$ and $\tau_s$ were quite different. Needless to say, for further rigorous discussion, $I_\infty$ should be estimated by measurement at much larger $\Delta t$. $\Delta t$ Eq. (3) should be an evidence of two-step increase of $n_e$ against $\Delta t$. It was found for the first time that $n_e$ rapidly increases at first and then it does slowly. This suggests that simple entanglements are formed within small $\Delta t$ ($<20$ min) and then complicated entanglements are gradually formed. Therefore, it was experimentally clarified how the entanglements of the chain molecules are formed for the first time. It is of interest that the value of $\tau_s$ (188 min) obtained in this work and the long relaxation time $\tau_s$ ($\sim 10^5$ min) estimated by Rault [20] are similar in time scale. This implies that large topological movement such as disentanglement of complicated entanglements requires more time.

### 4. Discussion

#### 4.1. Change of $n_e$ against $\Delta t$

Let us derive an experimental formula of $n_e$ as a function of $\Delta t$. First, we assume that Eq. (3) can be divided into two components of fast and slow entanglements ($I_f(\Delta t)$ and $I_s(\Delta t)$),

$$I(\Delta t) = I_f(\Delta t) + I_s(\Delta t) = \{A \exp\left(-\Delta t/\tau_f\right) + I_\infty\} + \{B \exp\left(-\Delta t/\tau_s\right) + I_\infty\}$$

(5)

where $I_\infty = I_{\infty f} + I_{\infty s}$.

In our previous papers [7,22], we have obtained the experimental formula of $I(n_e)$ given by Eq. (2). According to Eq. (2), we assumed that the following equation can be applicable for each component of fast and slow entanglements ($I_{f}(n_e)$ and $I_{s}(n_e)$),

$$I(n_e) = I_{f}(n_e) + I_{s}(n_e) = I_0^{f} \exp\left(-\gamma n_e^f\right) + I_0^{s} \exp\left(-\gamma n_e^s\right)$$

(6)

and

**Table 1**

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<th>Parameters $A$</th>
<th>$B$</th>
<th>$\tau_f$</th>
<th>$\tau_s$</th>
<th>$I_\infty$</th>
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<td>(mm$^{-3}$ s$^{-1}$)</td>
<td>(mm$^{-3}$ s$^{-1}$)</td>
<td>(min)</td>
<td>(min)</td>
<td>(mm$^{-3}$ s$^{-1}$)</td>
</tr>
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<td>$5.53 \times 10^4$</td>
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From Eq. (3).
4.2. Two-step entangling model

What are simple and complicated entanglements? Let us consider a variety of the entanglements which suppressed the nucleation. The entanglements can be roughly classified into some variations such as twist, knot or loops as shown in Fig. 7. Plots of \( v_e \), \( v^f_e \) and \( v^s_e \) against \( \Delta t \) given by Eq. (7). The \( v^f_e \) rapidly increases with the increase of \( \Delta t \), while the \( v^s_e \) gradually increases with the increase of \( \Delta t \). The total \( v_e \) (summation of \( v^f_e \) and \( v^s_e \)) increases by two steps.

\[
v_e = v^f_e + v^s_e \tag{7}
\]

where \( v^f_e \) and \( v^s_e \) are \( v_e \) of fast and slow entanglements and \( I^f_0 \) and \( I^s_0 \) are the constants.

Comparing the first and second terms of Eqs. (5) and (6), we can obtain the following initial conditions

\[
\lim_{\Delta t \to 0} I^f(v_e) = I^f_0 = \lim_{\Delta t \to 0} I^f(\Delta t) = A + I^f_0
\]

\[
\lim_{\Delta t \to 0} I^s(v_e) = I^s_0 = \lim_{\Delta t \to 0} I^s(\Delta t) = B + I^s_0 \tag{8}
\]

and boundary conditions

\[
\lim_{\Delta t \to \infty} I^f(\Delta t) = I^f_\infty = \lim_{\Delta t \to \infty} I^f(v_e) = I^f_0 e^{-\gamma}
\]

\[
\lim_{\Delta t \to \infty} I^s(\Delta t) = I^s_\infty = \lim_{\Delta t \to \infty} I^s(v_e) = I^s_0 e^{-\gamma} \tag{9}
\]

Finally, we obtained an experimental formula of \( v_e \) as a function of \( \Delta t \).

\[
v_e(\Delta t) \propto -\ln\left\{C \exp\left(-\Delta t/\tau_1\right) + D\right\} -\ln\left\{C \exp\left(-\Delta t/\tau_2\right) + D\right\} \tag{10}
\]

where \( C \) and \( D \) are the constants. Fig. 7 shows the change of \( v_e \) against \( \Delta t \). In this calculation, for simplicity, we assumed as

\[
v^f_e = v^s_e \quad \text{for} \quad \Delta t = \infty \tag{11}
\]

Used parameters in this figure are summarized in Table 2. In future work, we might need to confirm the validity of assumptions for further rigorous quantitative discussion.

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>D</th>
<th>( \gamma )</th>
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<tr>
<td>Values</td>
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Fig. 8 shows the classification of entanglements such as twist, knot and loops. In this figure, toward bottom and right sides, entanglements become to be complicated.

Fig. 8. Taking into account of the topological movement, it is expected that the formation rate of twist, knot or loops is different. The twists or knots with lower order are easy to form than knots with higher order or loops. Therefore, based on the measurement of \( I \) against \( \Delta t \), we can estimate which kind of entanglements is constructed initially.

The twists mean that a part of the single chain or multichains are twisted. The twist becomes much more complicated with the increase of the number of twists, i.e., with the increase of the “order” of twist. The knot is identified that a chain end passes through a circle of the same chain. The knot becomes a “high order-complicated one” when it passes through the circle more times. The links are similar to the knot consisting of multichains and are included in the class of knot. In the chain molecules, the conformation of loose folding, i.e., the so-called “loop” can be formed. The loop conformation consists of a bound chain with folding, i.e., tip of loop. The loop itself can form the twist, knot or link as if the loop behaves as a single chain. We denote the entanglements consisting of loop to “Loops” in Fig. 8. It should be noted that no knot and link can be formed without the chain end or tip of loop, while the twist will be formed at any place of the chains.

The simple entanglements are easily formed without significant topological movement of the chains, while complicated entanglements are difficult to be formed due to large cooperative topological movement of the chains. Here, the topological movement of the chains needs the sliding diffusion along the chain axis.

In general, the molecular weight between entanglements, i.e., \( v_e \) in the thermal equilibrium state is usually obtained by rheological measurements [23]. It is noted here that the \( v_e \) obtained by rheological measurements is not necessarily coincident with that evaluated by \( I \) in this work, because it is considered that entanglements solved easily such as twists are not sensitive for rheological measurements.

Fig. 9 shows the schematic time evolution of forming entanglements between a few chains. At first, the simple entanglements will be formed within short time. Since the free
The sudden change of chain end, the formation of loops takes a longer time. Though the loop conformation shown by Loops will be formed. Therefore, the increase of knots, the formation of new knot becomes much more difficult due to the decrease in chain mobility. Therefore, the increase of knot at the center of the chain will be slow. On the other hand, the complicated entanglements of loop conformation will rarely form the Loop s.

Fig. 9. Time evolution of entanglements between two random coiled chains. (a) At $\Delta t \equiv 0$. Two chains have not been entangled yet. (b) At small $\Delta t$. The knot (A) will be formed near the chain end. The twist will be formed at any place of the chains. The loop conformation will be sometimes formed. (c) At large $\Delta t$. The knot (A) will be transported to the center of chain and new knot (B) will be introduced near the chain end. The loop conformation will rarely form the Loops.

Finally, in our preliminary test using rheometer [in preparation], the sudden change of $\nu_e$ in short $\Delta t$ clarified in this work is also being confirmed.

5. Conclusion

1. We found a two-step decrease of $I$ with an increase of $\Delta t$ for the first time. This corresponds to the two-step increase of $\nu_e$.

2. Two-step increase of $\nu_e$ indicates that simple twists or knots are formed within short time and then complicated knots or loops are formed very slowly. The difference between simple and complicated entanglements is characterized by topological restriction.

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