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Power law and scaling for molecular weight dependence of crystal growth rate in polymeric materials

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Abstract

The molecular weight (M) dependence of the linear crystal growth rate (G) and the influence of the super-cooling on the relationship between M and G were studied. The molecular weight dependence of G has been expressed generally as $G \propto M^{\alpha}$ at a given super-cooling. The temperature dependence of G shows a bell shape with the maximum growth rate (G_{max}). The value of α was -0.5 at the temperature (T_{cmax}) of G_{max}. However, the small super-cooling and the small molecular weight gave a large negative value of α. In other words, the value of α was dependent not only on the degree of super-cooling (ΔT) but also on the molecular weight. The effect on α by these two factors (ΔT and M) goes off to zero at T_{cmax} and α yields to -0.5. G_{max} can be defined as a characteristic intrinsic value to the crystal growth behavior. The molecular weight dependence of G_{max} was scaled and expressed as a -0.5 power to molecular weight for all crystalline polymers.
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Keywords: Crystal growth rate; Power law; Scaling

1. Introduction

Molecular weight (M) dependence of physical properties is one of the most common characteristics in polymeric materials. For examples, melt viscosity shows remarkable molecular weight dependence and can be scaled and expressed as a 3.4 power of molecular weight for molecular chains with entanglements. The influence of molecular weight on polymer crystallization rate has been the most interesting subject of various papers [1–14]. Data existing in the literature for spherulite growth rate of several crystalline polymers have been analyzed as a function of molecular weight expressed as a power law of M^{α}. For example, the exponent α for poly(ethylene) lies in the range of -1.3 [10] to -1.8 [13] at relatively small super-cooling. On the other hand, for relatively large super-cooling, α is nearly -0.5 [7–9,12]. The value of α depends strongly on the degree of super-cooling. The large differences in the values of α have been reported for a large number of polymers [15]. The differences are attributed to the reference crystallization temperature such as a constant super cooling or a constant crystallization temperature. The characteristic reference value for the molecular weight dependence of crystal growth rate should be employed just as to zero shear viscosity for the molecular weight dependence of melt viscosity. The objective of this paper is to make clear the molecular weight dependence of the crystallization rate as a function of the degree of super-cooling.

2. Experiments

Poly(ethylene succinate) (PESU), poly(ethylene adipate) (PEAD), poly(ethylene terephthalate) (PET) and isotactic poly(propylene) (i-PP), which were commercially available by Scientific Polymer Products Inc. were used. PESU and PEAD were fractionated into several fractions in the range of 10^3–10^4 by GPC method. PET was hydrolyzed with ammonia gas at 150 °C for various period of time in order to get several low molecular weight samples. Details in sample preparations for PESU are reported in elsewhere [15]. Details in sample preparations for PEAD, PET and i-PP will be reported in separate papers. All these samples were isothermally crystallized on a slide glass at various temperatures from the melt. The fractionated samples of

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PESU and PEAD were melted on a hot stage at above the equilibrium melting temperature for 5 min. The molten specimens were subsequently cooled down on the same hot stage to a given crystallization temperatures with cooling rate of 30 °C/min by temperature controlling device in Linkam LK-600 under an optical microscope. The samples of PET and i-PP were also melted on a hot stage at above the equilibrium melting temperature for 5 min and then slid to another hot stage kept at a constant temperature in Linkam LK-300 under an optical microscope. LK-300 has two hot stages in the equipment and could be possible to cool down a specimen by sliding from the molten state to a set-up temperature at rates of about 5000 °C/min. Linear crystal growth rate was measured by measuring spherulite radius as a function of time. Such high cooling rate from the molten state to a given crystallization temperature enables to measure high-speed crystallization rate for i-PP. In fact, the spherulite growth rate of i-PP enabled to measure in a wide crystallization temperature range encompassed through the maximum crystallization temperature (T_{cmax}), yielding a bell shaped temperature dependence of the crystal growth rate. Small angle X-ray diffraction patterns of the crystallized PESU samples were recorded with a conventional θ–2θ diffractometer (Rigaku Rad-B) in order to measure a crystal lamellar thickness. Melting temperature was recorded on a Shimazu T40 (DSC) at a heating rate of 20 °C/min. Equilibrium melting temperature (T_m^0) was determined by the DSC melting temperature as a function of the lamellar thickness according to Gibbs–Thomson's equation. Thus obtained equilibrium melting temperatures for PESU showed molecular weight dependence as expressed by $T_m^0 = 404.4 - 12,587/M$, whereas 404.4 K is the equilibrium melting temperature for infinitive molecular weight of PESU.

3. Results and discussion

3.1. Temperature dependence of crystal growth rate

Crystal growth data are often analyzed with a classical crystallization theory, which is secondary nucleation controlled, proposed by Lauritzen and Hoffman [16]; it is given by Eq. (1)

$$G = G_0 \exp\left[-\frac{\Delta E}{RT} - \frac{\Delta F}{RT} \right] \qquad (1)$$

where G_0 is a constant for a given molecular weight and ΔE is the activation energy for the transport process at the interface between the melt and the crystal surface. ΔF is the work required to form a secondary nucleus of critical size and commonly expressed as $\Delta F = KT_m^0/(T_m^0 - T)$ yielding Eq. (2). K is a secondary nucleation parameter. In Eq. (1), ΔE and ΔF terms have opposing temperature dependence; thereby bring about a maximum (G_{max}) in the growth rate.

The transport term can be expressed in terms of an equation of either the Arrhenius type ($\Delta E_{arh}/RT$) or the WLF type ($\Delta E_{wlf}/R(T-T_0)$), where T_0 is a hypothetical temperature at which the macro-Brownian motion of polymer molecules

$$G = G_0 \exp\left[-\frac{\Delta E}{RT} - \frac{KT_m^0}{RT\Delta T} \right] \qquad (2)$$

ceases. The molecular transport term is of considerable importance in the lower temperature ranges especially below T_{cmax} at which the growth rate is the maximum; therefore, the molecular transport term employed is often the WLF expression. The transport term expressed by the WLF increases significantly when the crystallization temperature decreases to near T_0. However, its temperature dependence in the vicinity of T_{cmax} approximately in the regions of $T_{cmax}(1 \pm 0.15)$ becomes very small [17,18] compared to that near T_0. In other words, the activation energy for the molecular transport is expressed by either the WLF or the Arrhenius type in a wide crystallization temperature range encompassed through T_{cmax} [18,19].

Fig. 1 shows the temperature dependence of the linear crystal growth rate as a function of molecular weight for fractionated PESU samples. Each molecular weight fraction shows crystal growth rate with a bell shaped curve. Solid and broken lines in Fig. 1 are results for the best fitting by the Arrhenius and the WLF expressions, respectively. It is clear that the both expressions can fit the data sufficiently. The maximum crystal growth rate (G_{max}) and its temperature (T_{cmax}) vary with molecular weight. The crystal growth rate (G) remarkably decreases with the molecular weight. Molecular weight dependence of T_{cmax} shows similar molecular weight dependence of T_m^0 which will be discussed in the latter section.
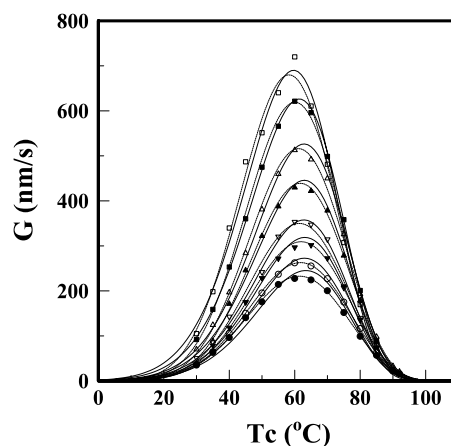

Fig. 1. Temperature dependence of spherulite growth rate (G) as a function of molecular weight for PESU. Solid and broken lines are results for best fitting by the Arrhenius and the WLF expressions, respectively. Molecular weight are indicated as ($\square$) 3,380, ($\blacksquare$) 4,660, ($\triangle$) 6,670, ($\blacktriangle$) 8,770, ($\triangledown$) 10,980, ($\blacktriangledown$) 13,660, ($\bigcirc$) 18,340, ($\bullet$) 21,210.

3.2. Molecular weight dependence of G_0, ΔE and K

Molecular weight dependence of crystal growth rate can be expressed to be a function of adsorption of polymer molecules (A) on to the crystal-growing surface, diffusion of the adsorbed molecules (D) on the crystal surface and secondary (surface) nucleation based on the adsorbed molecules. Lauritzen and Hoffmann have introduced the probability parameter of adsorbed molecules on the crystal-growing surface prior to surface nucleation but not considered the molecular weight dependence on it [20]. Accordingly, the growth rate is expressed as follows [15],

$$G \propto AD \exp\left[-\frac{KT_m^0}{RT\Delta T}\right] \quad (3)$$

Adsorption of polymer molecules is a function of molecular conformation on the crystal surface (substrate) as given by the following equation.

$$A \propto M^a \exp\left[-\frac{\Delta E_a}{RT}\right] \quad (4)$$

The exponent a lies between 0 and 1 depending on the molecular conformation on the substrate surface [21]. For example, when polymer molecules are attached with a number of contacts on the surface (loop-train adsorption), a is 0.5.

Molecular diffusion constant of the adsorbed molecules is a function of molecular weight based on reptation or sliding diffusion mechanism on the surface as given by the following equation.

$$D \propto M^d \exp\left[-\frac{\Delta E_d}{RT}\right] \quad (5)$$

According to reptation mechanism, d equals to -1 for without entanglement molecules and to -2 with entangled molecules. Taking account these factors, the crystal growth rate is expressed as follow.

$$G \propto M^{a+d} \exp\left[-\frac{\Delta E}{RT} - \frac{KT_m^0}{RT\Delta T}\right] \quad (6)$$

The pre-exponential factor of G_0 in Eq. (1) can be expressed as a function of molecular weight as given by M^{a+d}. The molecular transport term (ΔE) involves two activation energies for the molecular adsorption (ΔE_a) and the molecular diffusion ΔE_d on the crystal surface. These activation energies could be dependent on molecular weight. In addition, the parameter of K and T_m^0 in the nucleation term should be dependent on molecular weight. These factor of G_0, ΔE and K are evaluated as a function of molecular weight.

Fig. 2 shows a typical plot of natural logarithm of G (ln(G)) $+\Delta E/RT$ against $T_m^0/T\Delta T$ according to Eq. (2) for fractionated PESU with $M=4590$. The straight line was calculated to obtain the best fit to the data by a linear least square procedure. Thus obtained parameters for G_0, ΔE and
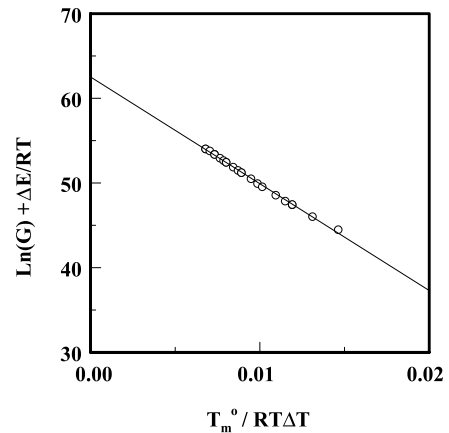

Fig. 2. Plots of natural logarithm of growth rate (G) plus molecular transport term $\Delta E/RT$ against $\left(T_m^0/RT\Delta T\right)$ for PESU with $M=4590$. Solid line results from the best fitting procedure for Eq. (2).

K are plotted against molecular weight as shown in Figs. 3 and 4. G_0 depends remarkably on molecular weight and can be expressed as a power law of $G_0 \propto M^{-0.5}$. The exponent value of -0.5 can be explained in terms of $a+d$ given in Eq. (6). The loop-train adsorptions of polymer molecules occur in polymers with relatively high molecular weight that forms chain-folding crystallization. The molecular weight dependence of the loop-train adsorption gives that the exponent a equals to 0.5. The adsorbed molecules could be migrated on the surface based on the reptation mechanism without chain entanglements, which gives d to be -1. Thus, the estimated value for $a+d$ is -0.5 [15].

On the other hand, ΔE and K show slightly molecular weight dependence and express as a power law of $M^{0.0081}$ and $M^{0.0082}$, respectively. The ratio of $\Delta E/K$ gives almost the constant value of 24 yielding no molecular weight dependence. These molecular weight dependencies were also true for the estimated values based on the WLF expression for the molecular transport term [19].

3.3. Molecular weight dependence of G_{max}
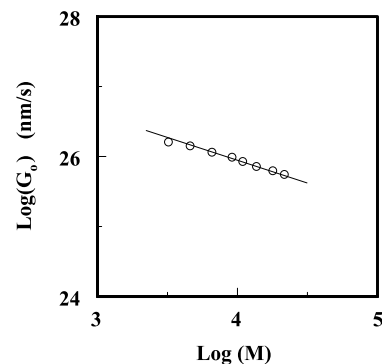
Maximum growth rate (G_{max}) can be formulated by

Fig. 3. Plots of common logarithm of the pre-exponential term of G_0 against common logarithm of molecular weight (M) for PESU.
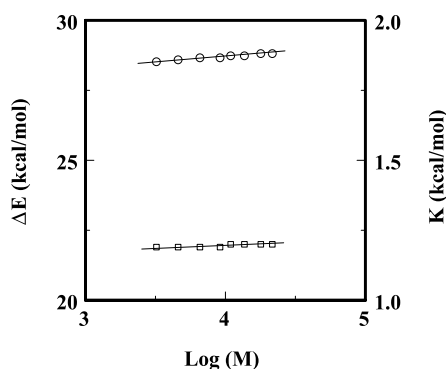
Fig. 4. Plots of the activation energy for molecular transport (ΔE) ($\bigcirc$) and the nucleation parameter of K ($\square$) against common logarithm of molecular weight (M) for PESU.

equating to zero the derivative of Eq. (2) with either the Arrhenius or the WLF expression used for the molecular transport term [18]. The crystal growth rate (G) can be formulated as a function of the maximum crystal growth rate and the reduced super-cooling (Z) based on Eq. (2) with the Arrhenius expressions in the molecular transport term, as follows,

$$G = G_{\max}\exp\left[W\frac{(1 - Z - A)^2}{Z(1 - Z)}\right] \qquad (7)$$

where $W = \ln(G_{\max}/G_0)$, $Z = \Delta T/T_m^0$ and $A = T_{\text{cmax}}/T_m^0$. Fig. 5 shows a typical plot of natural logarithm of G against the whole term of Z function in the right hand side of Eq. (7). A single straight line is observed, giving $\ln(G_{\max})$ at the intercept and the ratio of $\ln(G_{\max}/G_0)$ for the slope. Thus obtained $G_{\max}$ are plotted against molecular weight in Fig. 6, as expressing by a power law of $G_{\max} \propto M^{-0.5}$ yielding in the same power law of G_0 as given above. On the other hand, the ratio of $\ln(G_{\max}/G_0)$ gave almost the constant value of -53.8. In other words, the molecular weight dependence of $G_{\max}$ is mainly a consequence of the molecular weight dependence of G_0. It is much more
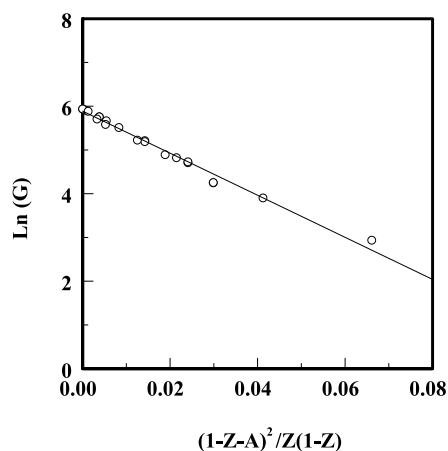
Fig. 5. Plots of natural logarithm of linear crystal growth rate (G) against the reduced super-cooling function given in Eq. (7) for PESU with $M = 4950$.
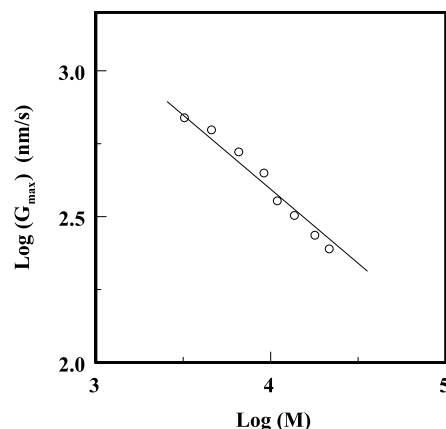
Fig. 6. Plots of common logarithm of maximum crystal growth rate ($G_{\max}$) against common logarithm of molecular weight (M) for PESU.

advantageous to use $G_{\max}$ rather than G_0 for studying molecular weight dependence, because G_0 is a derived parameter, whereas $G_{\max}$ can be measured by directly.

The equilibrium melting temperature (T_m^0) and the maximum crystallization temperature (T_{cmax}) increased with molecular weight for the fractionated samples. However, the ratio of T_{cmax}/T_m^0 yielded almost a constant value of 0.83. In general, the ratio of T_{cmax}/T_m^0 shows a constant value for a wide variety of polymers, showing ca. 0.83 [22]. The ratio of T_{cmax}/T_m^0 has been formulated on the basis of Eq. (2) as a function of the ratio of $\Delta E/K$ [22]. The constant value of T_{cmax}/T_m^0 indicates that the ratio of $\Delta E/K$ remains constant as discussed above.

3.4. Evaluation for exponent value in a power law

The molecular weight (M) dependence of the crystal growth rate can be expressed as a function of the molecular weight dependencies of ΔE, K, G_0, $G_{\max}$, T_m^0 and ΔT. When we evaluate the molecular weight dependence of G according to Eq. (2), we must estimate the each molecular weight dependence of ΔE, K, G_0, and T_m^0. This procedure comes with difficulty to determine the each molecular dependency. However, Eq. (7) involves a few factors such as $G_{\max}$, T_m^0 and ΔT, whereas $G_{\max}$ can be determined directly by experiment. In other words, the molecular weight dependence of G is associated only with T_m^0 and ΔT. This is much advantage and worth to use Eq. (7) rather than the usage of Eq. (2). The molecular weight dependence of G based on Eq. (7) can be formulated as follows.

$$\frac{d(\ln(G))}{d\ln(M)} = \frac{d(\ln(G_{\max}))}{d\ln(M)}$$

$$+ \frac{d(W(1 - Z - A)^2/Z(1 - Z))}{d\ln(M)} \qquad (8)$$

Here, we put $\alpha = d(\ln(G))/d\ln(M)$, $\beta = d(W(1 - Z - A)^2/Z(1 - Z))/d\ln(M)$, $\lambda = d(\ln(G_{\max}))/d\ln(M)$. The molecular weight dependence of G can be expressed by power law

as the following equation:

$$G \propto M^{\alpha} \propto M^{\lambda+\beta} \qquad (9)$$

As already mentioned above, the ratio of G_{max}/G_0 shows no molecular weight dependence, yielding W is the constant. G_{max} can be determined directly by experiment and its molecular weight dependence is expressed as $G_{max} \propto M^{-0.5}$, that is $\lambda = -0.5$. The exponent of β is only the unknown factor. The β is a function of T_m^0 and ΔT, because Z is a function of T_m^0 and ΔT, whereas the value of A is almost the constant for the most polymers as discussed above. The molecular weight dependence of T_m^0 can be given as $T_m^0 = T_m^{\infty} - \kappa/M$, where T_m^{∞} and κ are the equilibrium melting temperature of infinitive molecular weight and a constant, respectively. Thus, the β can be formulated as following.

$$\beta = \frac{\kappa\big(\Delta T + (1-A)\kappa/M - (1-A)T_m^{\infty}\big)\big((1-2A)\Delta T + (1-A)\kappa/M - (1-A)T_m^{\infty}\big)}{M\Delta T\big(T_m^{\infty} - \Delta T - \kappa/M\big)^2} \qquad (10)$$

The value of β can be estimated by numerically based on the molecular weight dependence of T_m^0 as drawing three-dimensional plots in Fig. 7 for PESU. It is clear that the β is strongly dependent on both the molecular weight and the super-cooling. The small super-cooling and the small molecular weight give the large negative value of β. However, the β goes to zero at the temperature (T_{cmax}) of the maximum crystal growth rate (G_{max}). The results indicate that the exponent of α at T_{cmax} can be expressed simply by the λ, which can be determined directly by experimental data at the maximum crystal growth rate in the bell shaped crystal growth curve. That is, the maximum crystal growth can be defined as an intrinsic (or reference) growth rate for crystallization behavior, just like molecular weight dependence of melt viscosity based on zero shear viscosity as an intrinsic property. The zero shear viscosity is expressed as a
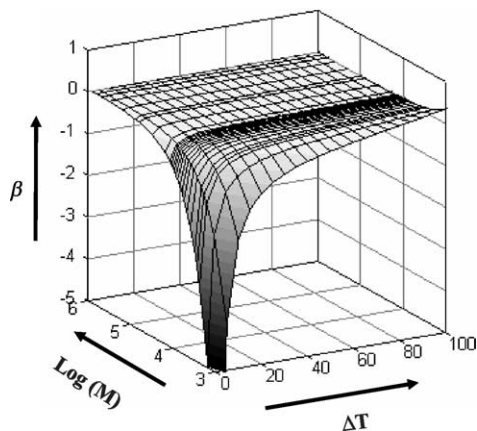
power law of $M^{3.4}$ for entangled polymers. We can thus conclude that the molecular weight dependence of the linear crystal growth rate must be evaluated by G_{max}, otherwise α depends strongly on the degree of super-cooling and molecular weight.

Fig. 8 shows the molecular weight dependence of the maximum crystal growth rate for various polymers. Data for PESU [15], PET [23], i-PP [24] and PEAD [25] are observed by our laboratory and those for poly(tetramethyl-p-silphenylene siloxane) (PTMPS) [1], isotactic polystyrene (i-PS) [6], poly(L-lactic acid) (PLLA) [8,12], cis-polyiso-prene (cis-PIP) [26] and cis-1,4-polybutadiene (cis-PBD) [27] are reported in literatures. The temperature dependence of the growth rate of i-PP was achieved with a bell shape curve with G_{max} on the first time. In general, it is difficult to measure the growth rate of i-PP in the wide range of temperature encompass through G_{max}, because of its rapid crystallization rate. The previous reference data for PET [15] showed in the narrow molecular weight range and their data were scattered. The present data for PET were achieved in the relatively wide molecular weight range. All the data of G_{max} shown in the figure are observed experimentally. All polymers show a good linear relationship with a slope of -0.5. These results indicate that the molecular weight dependence of maximum growth rate can be scaled and expressed as a -0.5 power of molecular weight to all crystalline polymers.
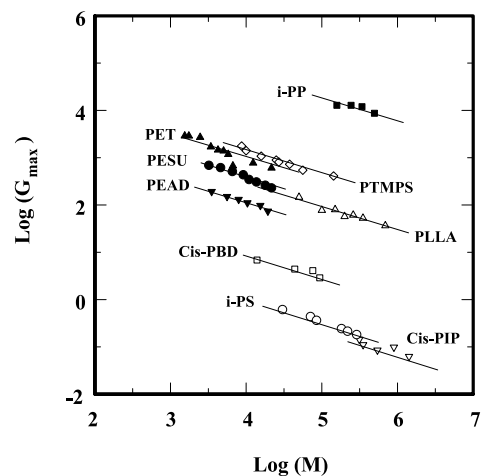

Fig. 7. Three-dimensional plots for exponents β in Eq. (8) as a function of common logarithm of molecular weight (M) and the degree of super-cooling.

Fig. 8. Plots of common logarithm of the maximum crystal growth rate (G_{max}) against common logarithm of molecular weight (M) for various polymers. All the data in the figure are observed experimentally. ($\diamond$) PTMPS [1], ($\circ$) i-PS [6], ($\triangle$) PLLA [8,12], ($\bullet$) PESU [15], ($\blacktriangle$) PET [23], ($\blacksquare$) i-PP [24], ($\blacktriangledown$) PEAD [25], ($\triangledown$) cis-PIP [26], ($\square$) cis-PBD [27].

4. Conclusions

Molecular weight dependence of linear crystal growth rate and influence of super-cooling were studied. The molecular weight dependence of G has been expressed as $G \propto M^{\alpha}$ at a given super-cooling. The temperature dependence of G shows a bell shape with the maximum growth rate (G_{max}). The value of α was -0.5 at the temperature (T_{cmax}) of G_{max}. However, the small super-cooling and the small molecular weight gave a large negative value of. In other words, the value of α was dependent not only on the degree of super-cooling (ΔT) but also on the molecular weight. The effect on α by these two factors (ΔT and M) goes off to zero at T_{cmax} and α yields to -0.5.

The activation energy (ΔE) for molecular transport and the nucleation factor (K) for surface nucleation were depended slightly on molecular weight. However, the ratio of $\Delta E/K$ showed no molecular weight dependence. The pre-exponential term of G_0 showed remarkable molecular weight dependence as express by a power law of $G_0 \propto M^{-0.5}$.

G_{max} can be defined as a characteristic intrinsic value to the crystal growth behavior. The molecular weight dependence of G_{max} was scaled and expressed as a -0.5 power to molecular weight for all crystalline polymers.

Acknowledgements

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