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Molecular Weight Dependence of Spherulites Growth Rate of Isotactic Polystyrene

Al Mamun and Norimasa Okui

Department of Organic and Polymeric Materials, International Polymer Research Center,
Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo, Japan.

Abstract: **The molecular weight (MW) dependence of crystal growth rate (*G*) was studied for isotactic polystyrene (iPS). The samples were isothermally crystallized over a wide range of temperature (T_c) from melt. A well define spherulitic morphology of iPS crystals, linearly growing with time in all directions, is observed. The crystallization temperature dependence spherulites growth rate shows a bell-shape curve having a maximum growth rate (G_{max}) at a temperature (T_{cmax}). The maximum growth rate always appears at 175°C, regardless of molecular weight. The temperature dependence bell-shaped curve can be expressed by classical crystallization theory. The plots of the reduced growth rate (G/G_{max}) and the reduced temperature (T/T_{cmax}) showed a single master curve without MW dependence, indicating the ratio of (G_o/G_{max}) is a constant, where G_o is pre-exponential factor of the crystal growth rate. The MW dependence of G_{max} was mainly a consequence of the MW dependence of G_o. The G_{max} decreased with MW and can be expressed as $G_{max} \propto \mathrm{MW}^{-0.5}$.**

Keywords: **Molecular weight; crystal growth rate; crystallization from melt; isotactic polystyrene.**

I. INTRODUCTION

In recent years, much attention has been made in polymerization catalysis for better insight into the crystallization behavior of iPS. The recent use of highly efficient transesterification catalysts, development of chain extenders and high vacuum technology have facilitated the synthesis of high molecular weight iPS with enhanced mechanical properties. As compared to atactic polystyrene, iPS exhibit improved stiffness and higher dimensional stability due to its crystallinity [1]. For achieving a better understanding of iPS processing and properties, it is highly desirable to control both iPS molecular weight and its distribution. While extensive research has been done on polyolefins with crystallization kinetics, little is known with respect to the molecular weight effect on crystallization, processing, and properties. Molecular weight is one of the very important factors that can control the final properties. The time required for final properties is one of the most concerns in industrial application especially at higher temperatures where the crystallization process can take from few minutes to several days which is costly and complex procedure in industry. Isotactic polystyrene has seldom been investigated owing to its relatively slow crystallization rate. Nevertheless, the slow crystallization rate of iPS provides the opportunity to investigate the crystallization kinetics over the entire temperature range, especially in a lower temperature. The crystallization rate can accelerate due to melt memory effect where molecular weight is the key factor to control crystallization kinetics [2].Crystallization behaviors of polymeric materials are characterized by the crystal nucleation and crystal growth rates. Since it is well established that the rate of crystal growth is primarily a function of crystallization temperature, it can then be considered a constant when considering crystallization under isothermal conditions [3]. The influence of molecular weight on polymer crystallization process has been the most interesting subject of various papers [4, 5]. Most of the works studied the overall crystallization process, measured by dilatometry, DSC, X-ray, IR, and many other methods. The overall crystallization rate is a function of linear crystal growth rate and primary nucleation rate. For a clear understanding of molecular weight dependent crystallization rate, it is necessary to study molecular weight dependence crystal growth rate and nucleation rate separately.

Previously we reported the crystallization behavior for a specific molecular weight of iPS where crystal nucleation and growth process with time and temperatures are explained from both molten and glassy states [6]. The objective of this report is to study the MW dependence of the crystal growth rate for iPS, which is the first attempt to study the experimental results with classical theory. The growth rate was determined before their impingement by measuring the spherulites radius measured from POM micrographs taken at successive intervals during isothermal crystallization process. The temperature dependent crystal growth rate is discussed with classical theory and a single master curve of the linear crystal growth rate for iPS will be also analysis.

II. EXPERIMENTAL

Isotactic polystyrene with three molecular weights, (M_N) of 8370, 23050 and 25080 were supplied by Idemitsu Kosan Co., Ltd. The typical sample was melted between two cover glasses and a metallic spacer of 20 μm is used to get uniform sample thickness. The sample was first melted and crystallized several times in order to erase the previous thermal history. In a typical experiment, the sample was melted at 250 ^{o}C for 5 min, which is above the equilibrium melting temperature of T_m^o (242^{o}C) for iPS [6]. Subsequently, the molten polymer was cooled to preset crystallization temperatures at a 30^{o}C/min cooling rate. The crystal growth rates were measured on a temperature controlled apparatus (Linkam LK-600) under an Olympus BH-2 polarized optical microscope (POM) equipped with a CCD camera (Pixel 600ES-CU). In the isothermal crystallization experiments, the development of the spherulites was recorded as a function of time. At temperatures below 140 °C, crystallization process is slow but the number of spherulites is numerous; however, it is very slow above 200°C with few spherulites. The samples used with different molecular weight of 8370, 23050 and 25080, will be treated as sample A, sample B and sample C, respectively.

III. RESULTS AND DISCUSSION

Fig. 1 shows the typical POM micrographs for iPS sample A, crystallized at 160 and 180 ^{o}C after melt from 250 ^{o}C. A well define spherulitic structure can be seen clearly. It starts growing on an individual active site, and becomes larger with time. A CCD camera captures the images of the growing spherulites with a specific time interval. The crystal growth rates were determined by measuring the radius of the spherulites as a function of time.

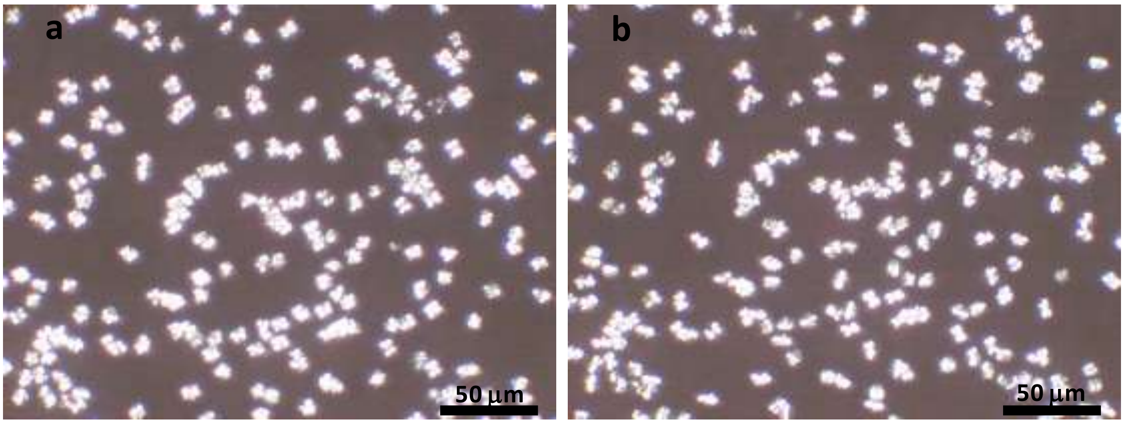

Fig. 1. Polarized optical micrographs of iPS spherulites, crystallized at: (a) 160 °C and (b) 180 °C after melt from 250 °C.

Fig. 2 shows an example of time dependent radial growth of iPS sample A, crystallized at 140, 160, 175 and 195 °C, after melt from 250 °C. A linear increase of radial growth with time was found at all crystallization temperatures. The growth rate is calculated from the slope of the linear curve. It is clear that for a certain molecular weight sample, crystallized at a temperature, the radial growth with time is always constant. It seems from Fig. 2 that the growth rate increases with crystallization temperatures, shows a maximum, and then decreases with higher temperature. For example, The growth rate increases smoothly from 3.12 nm/sec at 140 °C, passes a maximum growth rate of 10.7 nm/sec at 175°C, then decreases smoothly to 5.07 nm/sec at 195 °C for sample A.

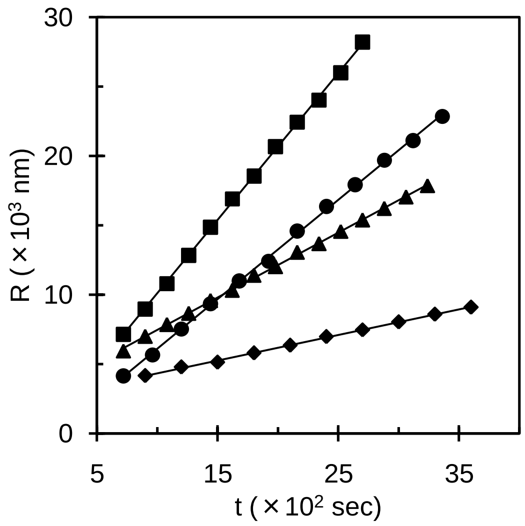

Fig. 2. Radial growth *R*, with time *t*, for sample A, crystallized at: 140°C (diamond), 160°C (circle), 175°C (square), 195°C (triangle) after melt from 250°C.

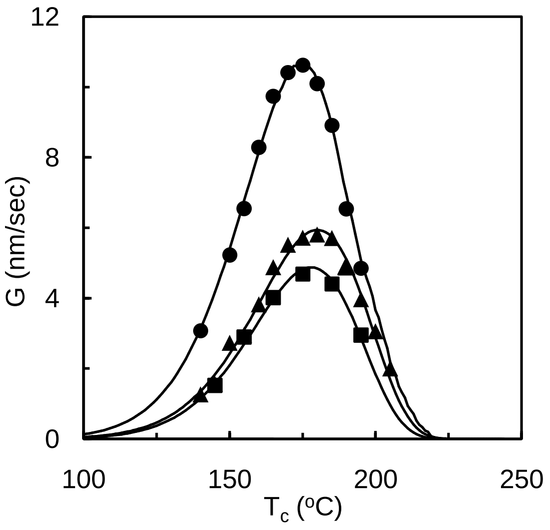

Fig. 3. Temperature dependence of spherulites growth rate as a function of molecular weight: sample A (circle), sample B (triangle), sample C (square). Solid lines represents the best fitting for Eq. (1).

Fig. 3 shows the crystallization temperature dependence growth rate from the melt as a function of molecular weight for iPS. The crystal growth rate shows bell shape temperature dependence for all MW samples. These results are consistent with almost all crystal growth behaviors reported in polymeric materials [5]. Crystal growth data are often analyzed with a classical crystallization theory, which is secondary nucleation controlled, proposed by Lauritzen and Hoffman [7]; it is given by Eq. (1)

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

where G_0 is a constant strongly dependent on molecular weight [4] 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, commonly expressed as $\Delta F = KT_m^o / (T_m^o - T)$. K is a secondary nucleation parameter as given by $K = n\sigma_e\sigma_s / \Delta H_m$. σ is the free energy and ΔH_m is the heat of fusion. The molecular transport term can be expressed in terms of Arrhenius equations [8]. The solid line in Fig. 3 is calculated by the best fit based on Eq. (1) where the molecular transport term is assumed to have an Arrhenius form. It is clear that the Arrhenius expression can fit the data quite well. From Fig. 3 it is also clear that the temperature dependence of the crystal growth rate strongly depends on molecular weight of the samples. The maximum crystal growth rate (G_{max}) decreases and its temperature (T_{cmax}) increases with

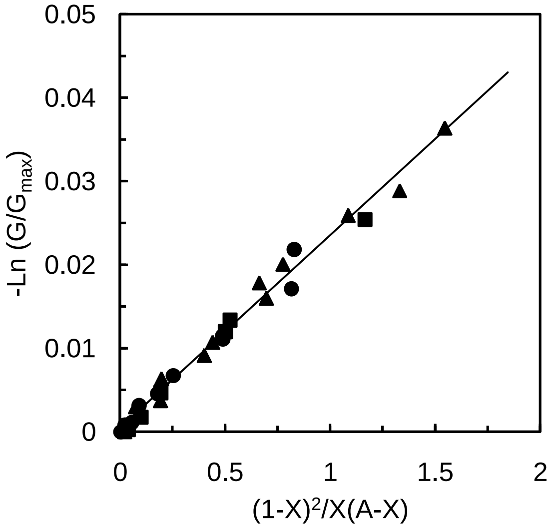

Fig. 4. Plots of the ratio of logarithm of the reduce growth rate (G/G_{max}) versus reduced temperature $[(1 - X)^2/X(A - X)]$ based on Arrhenius expression of Eq. (2). Symbols in the figure are the same in those in Fig. 3.

molecular weight, a similar phenomenon to the molecular weight dependence of equilibrium melt temperature, (T_m^o). The ratio of T_{cmax} / T_m^o is found almost independent of the molecular weight. The reduced growth rate has been formulated based on Eq. (1) with the Arrhenius expressions in the molecular transport term [9, 10], as follows,

$$\ln\left(\frac{G}{G_{\max}}\right) = \left[\ln\left(\frac{G_{\max}}{G_o}\right)\right]\left[\frac{(1-X)^2}{X(A-X)}\right] ------(2)$$

where $X = T / T_{cmax}$ and $A = T_m^o / T_{cmax}$. When the crystal growth rate data are plotted according to Arrhenius expression of Eq. 2, the reduced growth rate (G/G_{max}) shows a linear relationship with the reduced temperature of the second term $(1-X)^2/X(A-X)$ as shown in Fig. 4. This indicates no molecular weight dependence in growth rate, and the linear relation is true for other various polymers [9].

Fig. 5 shows plots of the reduced rate, G/G_{max} with the reduced temperature, T/T_{cmax}, based on the data in Fig. 3. A single master curve is observed showing no MW dependence. The single master curve indicates that the ratio of (G_{max}/G_o) is a constant. In other words, the MW dependence of G_{max} is mainly a consequence of the MW dependence of G_o. It is much more advantageous to use G_{max} rather than G_o for studying MW dependence, because G_{max} can be observed experimentally but G_o cannot.

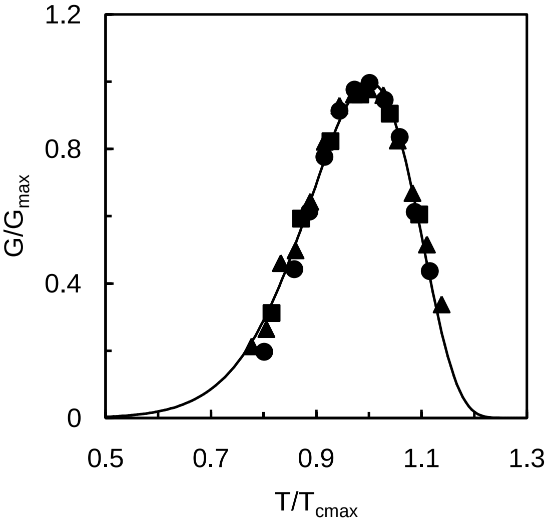

Fig. 5. Master curve of the linear crystal growth rate for iPS. Symbols in the figure are the same as those in Fig. 3. The solid curve results from the fitting procedure for Eq. (1).

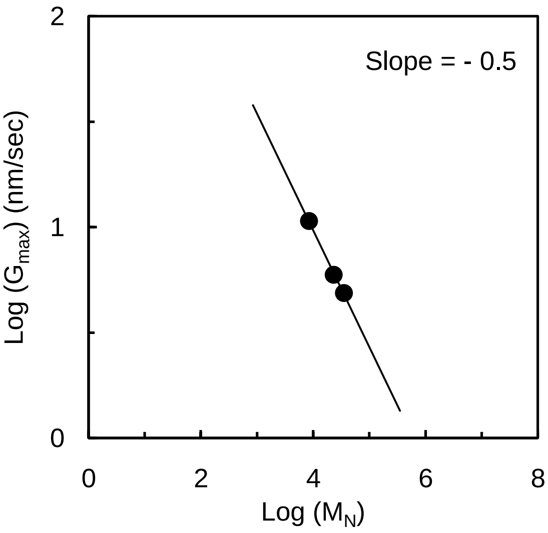

Fig. 6. Log plots of the maximum crystal growth rate against log of molecular weight for iPS.

Fig. 6 shows the log plot of MW dependence G_{max}, which decreases with increasing MW. The MW dependence of G_{max} in iPS exhibits only one characteristic point, which is neither influenced by the supercooling nor the crystallization temperature since G_{max} is a consequence of comparable weight between two factors: nucleation (ΔF) and moleculer transport term (ΔE). Therefore, the MW dependence of G_{max} is more reliable than that of G at a temperature. The logarithm of G_{max} decreases linearly with the logarithm of MW with a slope of ca. -0.5. Thus the MW dependence of G_{max} can be expressed as the power law, $G_{max} \propto \mathrm{MW}^{-0.5}$. Details of these MW dependences with a slope -0.5, can be explained on the basis of the molecular transport mechanism during the crystal growth process [9].

IV. CONCLUSION

The MW dependence of the crystal growth rate over a wide range of temperature was studied. The temperature dependence growth rate showed a bell-shape with a maximum growth rate (G_{max}), which showed remarkable MW dependence. The plots of the reduced growth rate (G/G_{max}) against the reduced temperature (T/T_{cmax}) depicted a single master curve without MW dependence. The MW dependence of G_{max} was found mainly a consequence of the MW dependence of G_o. The G_{max} decreased with MW and the dependence can be expressed as $G_{max} \propto \mathrm{MW}^{-0.5}$. Thus isotactic polystyrene has found MW dependence of crystal growth that can be tuned with crystallization temperature for optimum condition. The present paper focus mainly on the molecular weight dependence crystallization behavior of iPS, the recent studies of blends of iPS with ethylene-hexene copolymer will be report separately.

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