

The Effect of Melt History, Pressure, and Crystallization Temperature on Spherulite Size in Bulk Isotactic Polypropylene

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Synopsis

Melt history, pressure, and crystallization temperature are three variables that may be used to vary spherulite size in polymer systems. In this study, bulk polypropylene samples were given various melt treatments and then isothermally crystallized under constant pressure. Spherulite size was found to increase with increasing severity (i.e., increased temperature or time at temperature) of melt treatment, explained by the thermal deactivation of nucleation sites. Spherulite size also increases with increasing crystallization temperature, owing to a smaller driving force for nucleation and the deactivation of increasing numbers of nuclei at higher crystallization temperatures. An analogous effect of pressure was also found, and a simple model to compare increased pressure and decreased crystallization temperature was derived.

INTRODUCTION

The idea of using melt history, pressure, or crystallization temperature to vary nucleus density (and thus spherulite size) in semicrystalline polymers is not new. The effect of each of these variables has been studied in several polymer systems (see, for example, references 1 through 4). However, much of the past work has dealt with thin films, and there are inherent difficulties in extending conclusions of these studies to bulk polymers. The purpose of this paper is to report preliminary results of a study of the effect of the aforementioned variables on spherulite size in bulk-crystallized isotactic polypropylene.

EXPERIMENTAL

The polymer used in this study was Hercules Profax 6623, a commercially available, general-purpose, heat-stabilized polypropylene. It has a M_w of 418,000, a M_n of 61,000, an intrinsic viscosity (Decalin 135°C) of 2.7 dl/g, and a nonisotactic (Decalin solubles) content of about 3%.

A schematic of the mold design employed is shown in Figure 1. The polymer pellets were placed in the mold and the mold sealed. A vacuum of better than 10 μ Hg was then drawn on the mold chamber. The portion of the mold containing the polymer was then immersed in a constant-temperature ($\pm 1/4^\circ$ C) wax bath at the desired melt temperature. Once the poly-

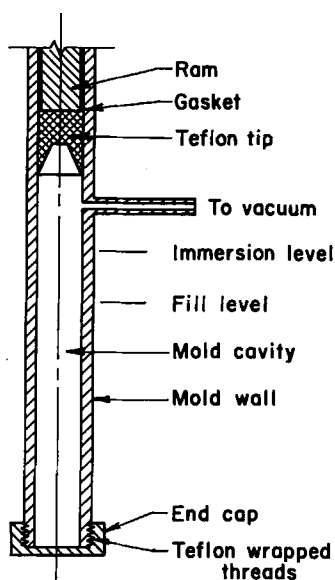


Fig. 1. Schematic of mold.

mer was molten, it was compressed by the ram and held at constant pressure (± 25 psi) throughout the treatment cycle. The pressure was monitored by strain gauges mounted on the ram. After a specified time in the melt bath, the mold was transferred to a constant-temperature ($\pm 1/4^\circ\text{C}$) oil bath for isothermal crystallization. Heat transfer in the mold was such that the polymer temperature was within 1% of the temperature of the crystallization bath within $6\frac{1}{2}$ min of insertion. Time required for crystallization varied with the melt history, pressure, and crystallization temperature employed but typically was in the range of $\frac{1}{2}$ to 2 hr. After crystallization, the mold was removed from the bath and allowed to air cool. The pressure was then released and the sample removed. The finished samples were in the form of rods, about $\frac{5}{16}$ in. in diameter and $2\frac{1}{2}$ in. long.

The rods were sectioned, mounted in "Koldmount," rough ground, and then polished through $0.05\text{-}\mu$ Linde "B" alumina. The samples were then "heat etched" to reveal their spherulite sizes by holding them in air at about 100°C for 12 to 24 hr. (This technique was developed from published work of Inoue.⁵) The average spherulite diameter was determined using the light microscope and lineal analysis.⁶ (As used here, the term "average spherulite diameter" refers to the inverse of the average number of spherulite boundaries intersected per unit length by random straight lines projected on the sample surface.)

RESULTS AND DISCUSSION

Figure 2 is a typical plot of spherulite diameter versus time at melt temperature for two different melt temperatures. As shown, spherulite diam-

eter increased with increasing time in the melt bath. (As on all plots, the lines shown are least-squares lines.)

Figure 3 is a plot of spherulite diameter versus melt temperature for a long and a short melt time. Here, spherulite diameter is seen to increase with increasing melt temperature. Both the preceding results indicate an increasing deactivation of nucleation sites with increasing severity of melt treatment.

It is generally believed that heterogeneous nucleation is far more important in polymer systems than homogeneous nucleation.⁷ Thus, the results indicated in Figures 2 and 3 are presumably due to the increasing deactivation of heterogeneous nuclei with increasing severity of melt treatment. (One could also explain the results in terms of "self-seeding,"

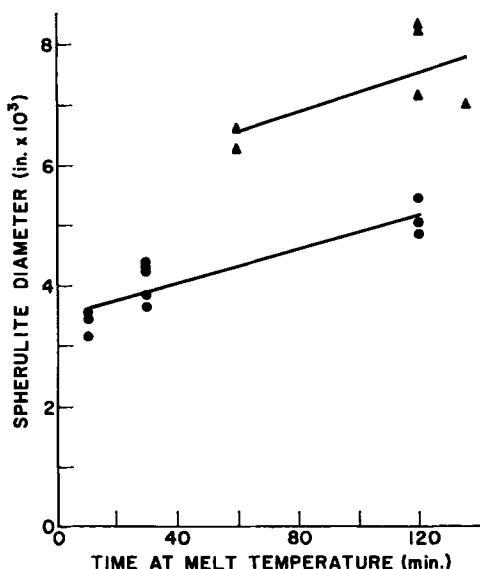


Fig. 2. Spherulite diameter vs. time at melt temperature for a crystallization temperature of 135°C and a pressure of 3770 psi. Melt temperatures: (●) 200°C; (▲) 220°C.

by proposing the persistence of small crystalline regions in the melt above the melting point. More and more of these would be destroyed by thermal energy with increasing severity of melt treatment, leaving fewer to act as seed nuclei at the crystallization temperature. However, the melt treatments employed here are probably too severe to allow for significant self-seeding.)

Figure 4 shows the effect of pressure on spherulite size for samples given various melt treatments. Note the ability of increased pressure to induce nucleation, particularly for the samples given the most severe melt treatment. The effect could conceivably be due to the increase in the thermodynamic melting point of the polymer at increased pressures resulting in a

greater effective undercooling. This in turn would cause a greater driving force and a reduced activation barrier for nucleation.

To see how melting temperature might vary with pressure, we can invoke the Clausius-Clapeyron equation to estimate the change in melting point

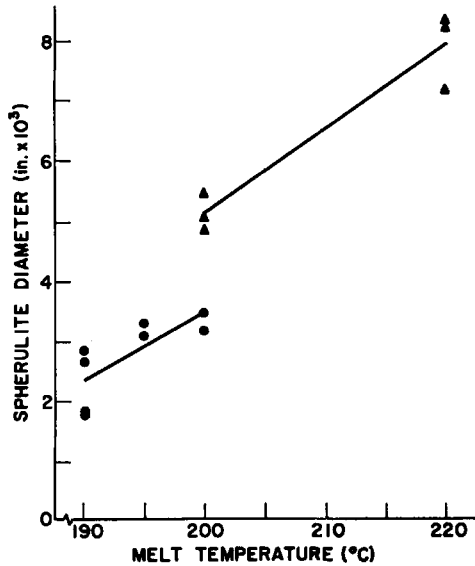


Fig. 3. Spherulite diameter vs. melt temperature for a crystallization temperature of 135°C and a pressure of 3770 psi. Time at melt temperature: (●) 11 min; (▲) 120 min.

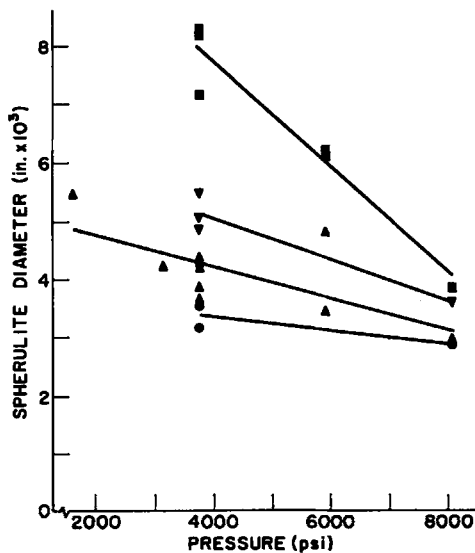


Fig. 4. Spherulite diameter vs. pressure for a crystallization temperature of 135°C. Melt treatments: (●) 11 min at 200°C; (▲) 30 min at 200°C; (▼) 120 min at 200°C; (■) 120 min at 220°C.

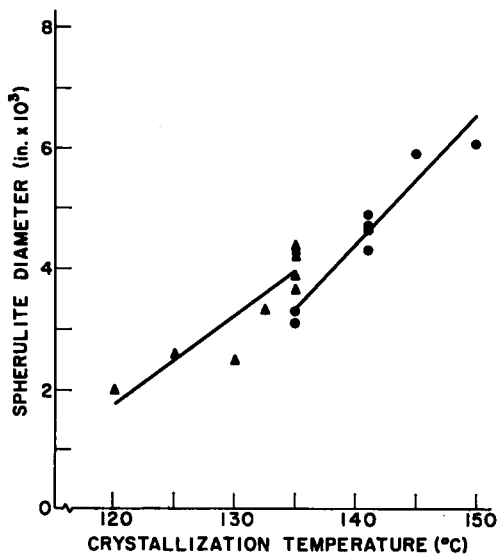


Fig. 5. Spherulite diameter vs. crystallization temperature for a pressure of 3770 psi. Melt treatments: (●) 10 min at 195°C; (▲) 30 min at 200°C.

associated with a change in pressure. (Since thermodynamic quantities are functions of structure in semicrystalline polymers, the calculation can be expected to give only order of magnitude results.) This is written

$$\frac{\Delta T_{mp}}{\Delta P} = T_{mp} \frac{\Delta V_f}{\Delta H_f}$$

where ΔT_{mp} is the change in melting temperature associated with pressure change ΔP , T_{mp} is the melting temperature at atmospheric pressure, and ΔV_f and ΔH_f the volume change on fusion and the heat of fusion, respectively. We choose the values of $T_{mp} = 473^\circ\text{K}$ (from actual measurements of Fatou,⁸ using extrapolation technique) and $\Delta H_f = -24 \text{ cal/g}$ (taken from experimental data of Kamide and Yamaguchi⁹ for samples crystallized at 135°C).

From dilatometric traces made during the runs, we estimate $\Delta V_f = -0.08 \text{ cc/g}$ for a crystallization temperature of 135°C and a pressure of 3770 psi. Thus we find $\Delta T_{mp}/\Delta P \simeq 2.6 \times 10^{-3} \text{ }^\circ\text{K/psi}$.

Even though this model is based on rather crude approximations, it is interesting to compare model and actual results. To do this, we refer to data for a melt treatment of 30 min at 200°C , followed by a crystallization treatment at 135°C with a pressure of 3770 psi. From Figure 4, note a slope of $(\Delta D/\Delta P) = -2.8 \times 10^{-4} \text{ mil/psi}$ is obtained for these conditions (D is the spherulite diameter). For identical conditions on Figure 5 (a plot of spherulite diameter versus crystallization temperature), note the slope $(\Delta D/\Delta T_{\text{cryst}})$ is $0.15 \text{ mil/}^\circ\text{K}$. As a first approximation, assume that with identical melt conditions the number of nuclei formed, and

hence the final spherulite diameter, is a function of undercooling alone. Hence, $D = f(\Delta T)$, where $\Delta T = T_{mp} - T_{xial}$. If the approximation is valid, a given increase in the melting point due to application of pressure has the same effect on spherulite diameter as an identical decrease in the crystallization temperature. Or, for the data in question,

$$\left(\frac{\Delta D}{\Delta T_{xial}}\right) = -\left(\frac{\Delta D}{\Delta T_{mp}}\right).$$

Since the relationship between ΔT_{mp} and ΔP is assumed independent of pressure or crystallization temperature, we may form the relationship

$$\left(\frac{\Delta D}{\Delta T_{mp}}\right) = \left(\frac{\Delta P}{\Delta T_{mp}}\right)\left(\frac{\Delta D}{\Delta P}\right).$$

Thus, we have

$$\left(\frac{\Delta D}{\Delta T_{xial}}\right) = 0.15 \text{ mil}/^{\circ}\text{K}$$

and

$$\begin{aligned} -\left(\frac{\Delta D}{\Delta T_{mp}}\right) &= -\left[\frac{1}{2.6 \times 10^{-3} \text{ }^{\circ}\text{K}/\text{psi}}\right](-2.8 \times 10^{-4} \text{ mil}/\text{psi}) \\ &= 0.11 \text{ mil}/^{\circ}\text{K}. \end{aligned}$$

Given the limits of the Clausius-Clapeyron equation, the questionability of the thermodynamic data employed, and the crudeness of the model, these results (30% discrepancy) show satisfactory agreement. Although the experimental data are not sufficient to warrant further refinement, it can be concluded that the effect of pressure is probably explained by its elevation of the crystalline melting point.

The increase in spherulite diameter with increasing crystallization temperature, shown in Figure 5 for two different melt treatments, is as expected. This is due to a smaller driving force for nucleation and the deactivation of increasing numbers of nucleation sites with increasing temperature. It should be noted that at crystallization temperatures much below 135°C, considerable nucleation and growth has taken place before the samples reach the desired crystallization temperature.

In general, the variation of average spherulite diameter between samples subjected to identical thermal cycles (at the same pressure) was small. For the ten conditions shown on Figures 2 through 5 for which at least one replication was made, eight show standard deviations of less than 8%. The other two (of which one represents only two samples) have standard deviations of 23% and 24%.

Thus, it appears that melt history, pressure, and crystallization temperature may be used separately, or in concert, to give a predictable and reproducible variation of spherulite size in bulk isotactic polypropylene.

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