Quiescent Crystallization Kinetics and Morphology of i-PP Resins for Injection Molding. II. Nonisothermal Crystallization as a Function of Molecular Weight

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ABSTRACT: The quiescent nonisothermal crystallization kinetics of polypropylene resins was studied as a function of their molecular weight, M_w. Differential scanning calorimetry and polarized light optical microscopy were used to follow this kinetics. It was observed that a modified Hoffman and Lauritzen equation could describe with accuracy their nonisothermal behavior. Also it was found that the polypropylene nonisothermal growth rates, G_n, were similar to their corresponding isothermal rates, G, and also decreased with the increase in M_w. The use of a prior isothermal nucleation procedure allowed to obtain data at higher temperatures and to compare these data at higher cooling rates than the ones found in the literature. The morphology of all the samples revealed a fine and radial spherulitic texture. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 1733–1740, 1999

Key words: polypropylene; nonisothermal crystallization; crystallization kinetics; morphology; nucleation

INTRODUCTION

In the first part of this work,[1] the isothermal crystallization kinetics of various isotactic polypropylene (i-PP) resins was studied as a function of their weight-average molecular weight M_w, the amount of ethylene, and the amount of grafting. It was observed that the isothermal crystallization growth rate G decreased with the increase of M_w for the homopolymers. For the heterophasic polymers, the ones with similar M_w had their G increased as the amount of ethylene, in the chemical synthesis, increased. In the grafted polymers, as the amount of grafted maleic anhydride (MA) increased, G decreased.

Values of the fold surface-free energy σ_e were also calculated by using the Hoffman and Lauritzen theory.[2] The σ_e values of the lower M_w homopolymers were similar to the ones found in the literature. However, these values increased with the increase in M_w. Also, it was found that the heterophasic and grafted polymers had values of σ_e higher than of the homopolymers. All samples showed a spherulitic morphology, except the acrylic-acid-grafted polypropylene, which showed needle-like crystallites.

In the second part of this work, we will present data of the nonisothermal crystallization of some of the homopolymers used in the first part as a function of their molecular weight.

THEORETICAL BACKGROUND

The packing and cooling stages of the injection molding of thermoplastics are mainly nonisother-

mal processes. The cooling rates are extremely high, generally higher than 200°C/min and are not constant. Therefore, the experimental reproduction of these conditions is extremely difficult to achieve.

However, it seems that this experimental limitation will soon be overcome, as the works of Ding and Spruiell[3,4] show. They developed a new apparatus based on the standard light depolarizing microscopy technique (LDM), which allowed measurements of nonisothermal crystallization kinetics of i-PP at cooling rates up to 5000°C/min. The temperature of the polymer was measured directly by using an iron constantan thermocouple inserted into the sample, thus eliminating the lag time between the sample temperature and the surrounding temperature. During the nonisothermal experiments, they observed the formation of a plateau in the temperature versus time curves; this plateau was attributed to the fact that the rate of energy release during crystallization was higher than the rate at which energy was carried away by the cooling medium. Therefore, much of the growth process occurred under a locally isothermal condition. They also found that both isothermal and nonisothermal growth rates fell on one curve and that both data could be fitted by the traditional Hoffman and Lauritzen equation,[2] or

$$G = G_o \exp\left[\frac{-U^*}{R(T_c - T_\infty)}\right] \exp\left[\frac{-K_g}{T_c(\Delta T)f}\right] \quad (1)$$

where G is the isothermal crystallization growth rate; G_o, the pre-exponential factor (independent of temperature); U^*, the activation energy for reptation in the melt (1500 cal/mol); T_c, the isothermal crystallization temperature; T_∞, the theoretical temperature at which reptation ceases $(T_g - 30K)$; T_g, the glass transition temperature; K_g, the nucleation constant; ΔT, the degree of undercooling; f, $2T_c/T_m^o + T_c$; T_m^o, the equilibrium melting temperature.

For their nonisothermal calculation, they substituted T_c by the temperature at which the plateau was observed.

Lim et al.,[5] in a recent study of nonisothermal crystallization of i-PP in dotriacontane, also used a modified Hoffman and Lauritzen equation to fit their data. They substituted the isothermal crystallization temperature T_c of eq. (1) by $(T_m - \alpha t)$, where T_m was the temperature at which the first measurable data was recorded, and α was a constant cooling rate; therefore, eq. (1) was written as

Table I PP Resins Used in This Work

| Sample | Homopolymer | |
	M_w (g/gmol)	MFI (g/10 min)
H1	84,000	756.00
H2	240,000	18.00
H5	1,400,000	0.03
H6	493,000	1.30

$$G_n = G_{on} \exp\left[\frac{-U^*}{R[(T_m - \alpha t) - T_\infty]}\right]$$
$$\times \exp\left[\frac{-K_g\{T_m^o + (T_m - \alpha t)\}}{2(T_m - \alpha t)^2\{T_m^o - (T_m - \alpha t)\}}\right] \quad (2)$$

where G_n is the non-isothermal crystallization growth rate, and G_{on} is the pre-exponential factor containing quantities not strongly dependent on temperature.

Numerical integration of eq. (2) gave them the nonisothermal spherulite radius r_{en} as a function of time because $G_n = dr_{en}/dt$. They compared these results with their experimental data, and the agreement was found to be very good.

Equation (2) has not been tested with higher and nonconstant cooling rates as the ones used in injection molding. However, it is a good approximation for studying the nonisothermal crystallization of polymers. Therefore, this last approach will be used in this work.

EXPERIMENTAL

Materials

The i-PP resins were kindly donated by OPP Petroquimica do Brasil. The grades used in this work are listed in Table I.

Nonisothermal Crystallization

Polarized Light Optical Microscopy

The growth rate of the nonisothermal crystallization G_n was measured by using a polarized light optical microscope (PLOM) from Leica, model DMRXP, and a hot stage from Linkam, model THMS 600. To this microscope, a video camera from Kappa was attached, and the spherulitic growth of the samples was recorded in a video equipment. Therefore, the spherulites radius was

Figure 1 Hot stage and sample temperatures versus time curves for sample H6.

measured directly from the videotapes. Also, photographs of the developing morphology were taken at some temperatures. The samples were first melted at 200°C for 5 min and then cooled at −100°C/min down to 138°C (except sample H5, which was cooled down to 130°C). After the visible formation of the nuclei, at 138 or 130°C, the samples were again cooled down to room temperature, at −5°C/min. Tests were also run with an iron constantan thermocouple of $d = 75$ μm, inserted into the samples, in order to evaluate the temperature difference between the samples and the hot stage.

Differential Scanning Calorimetry

Thermal data was obtained by using a differential scanning calorimeter (DSC) from Perkin–Elmer, model DSC-7, under N_2 atmosphere. The samples were heated at 20°C/min up to 200°C, maintained at this temperature for 5 min, and then cooled down to room temperature at the following cooling rates: −5, −10, −20, −30, −40, and −50°C/min.

RESULTS AND DISCUSSION

Nonisothermal Crystallization

Figure 1 shows the hot stage and sample temperatures versus time curves for sample H6. It can be observed that the sample temperature is always lower than the programmed hot stage temperature. This lag temperature is approximately 3–4°C. However, the cooling rates are similar; in

other words, in the observed temperature range, the crystallization heat release of the sample was low enough to maintain the hot stage cooling rate.

The lag temperature between the sample and the environment is another parameter that also needs to be taken in account. However, Guo[6] measured the temperature lag for PP during crystallization in a DSC and found that the sample temperature was 0.2°C higher than the oven temperature before crystallization and 0.7°C at the maximum crystallization temperature. Therefore, we can assume that at the low cooling rates used in this work, this lag temperature is not significant.

As already pointed out in the experimental section, an isothermal nucleus was allowed to form at 138°C for some samples and at 130°C for sample H5. Therefore, the spherulite radius was measured after the visible formation of this nucleus; $t = 0$ was established as the time when the cooling rate of −5°C min begun, and the spherulite had already a small radius $r_{en,i}$. We observed, as pointed out in part I of this work,[1] that r_{en} was linear with time at the beginning of the growing process and during all the isothermal experiments. This observation allowed us to conclude that the spherulite growing process was not controlled by diffusion and that G was not dependent on the spherulite radius.

If we compare nonisothermal experiments with and without this prior isothermal nucleation procedure (PIN), we will observe that the spherulite radius in both experiments is different when com-

Figure 2 Nonisothermal experiments with and without the PIN procedure for sample H2.

Figure 3   Experimental and calculated spherulitic radius as function of time, at a cooling rate of −5°C min: Samples (a) H1, (b) H2, (c) H5, and (d) H6.

pared at the same temperature. The spherulite radius in the experiment without PIN will be smaller than the radius in the experiment with PIN because, in the first experiment, the spherulite will start to grow at a latter time. However, if the growing process of both experiments is not controlled by diffusion, the growth rate will not be a function of the spherulite radius, but only a function of temperature. Then we will be able to superimpose the plots of radius versus temperature of both experiments by shifting one of them along the radius axis. To confirm the validity of the PIN procedure, we made measurements with and without PIN. Figure 2 shows these results for sample H2. It can be observed that the agreement is excellent; therefore, the PIN procedure is valid. Also, it can be observed that the PIN procedure allows us to obtain data at higher temperatures than the experiments without PIN.

As said before, the numerical integration of eq. (2) allows one to calculate the nonisothermal

spherulite radius as a function of time. The best values for G_{on} and K_g were found by trial and error. The initial G_{on} and K_g values of the algorithm were chosen to be the corresponding isothermal G_o and K_g values, given in Table III of de Carvalho and Bretas.[1] The result is shown in Figure 3, where both experimental and calculated spherulitic radii as a function of time are shown. It can be observed that the agreement between both radii was excellent; therefore, we can conclude that eq. (2) describes very well the nonisothermal crystallization for these homopolymers, independent of their molecular weight.

After the G_{on} best value was obtained, it was possible to calculate a theoretical G_n as a function of temperature by using eq. (2). These results are shown in Figure 4. The corresponding G values, from de Carvalho and Bretas[1] and G_n (derivative) are also shown to compare to the theoretical G_n. G_n (derivative) was calculated as the derivative of the experimental radius ver-

Figure 4 Isothermal and nonisothermal crystallization growth rates of samples (a) H1, (b) H2, (c) H5, and (d) H6.

sus time curves. It can be observed that in all the homopolymers, G_n (theoretical) is similar to G_n (derivative); therefore, eq. (2) describes with accuracy the nonisothermal crystallization kinetics of these samples. Regarding the similarity between G_n and G, it can be observed that in all the homopolymers, $G_n = G$, except in sample H5, where G_n is slightly higher than G. The

Table II   Values of G_{on} as Found by Fitting of Equation (2)

Sample	G_{on} (μm/min)	G_{on}/G_o
H1	3.4×10^{10}	0.97
H2	4.08×10^{10}	0.96
H5	3.06×10^{13}	1.10
H6	4.82×10^{10}	0.89

results for samples H1, H2, and H6 are similar to the ones found by Lim et al.[5] for pure i-PP, where G_n and G were found to be the same at a 0.5°C/min cooling rate. However, they found that G_n was lower than G in i-PP–dotriacontane blends at the final stages of crystallization. This last trend was attributed to the fact that G_n was controlled by diffusion. In our case, we attributed the discrepancy between G_n and G of sample H5 to experimental errors.

Table II shows the G_{on} values found for our samples. Lim et al.[5] obtained $G_{on} = 1.37 \times 10^9$ μm/min for an i-PP of 168,000 M_w; this value gave an excellent agreement with their experimental values. Their G_{on} was also found to be in the range of G_o for regime III, 0.64×10^9 to 5.81×10^9 μm/min, from the work of Clark and Hoffman.[7] Ding and Spruiell[4] found $G_o = 7.15 \times 10^{10}$ μm/min, for i-PP of 210,850 M_w. As can

Figure 5 $(T_{onset} - T_c)$ as a function of the cooling rate of some of the homopolymers.

Figure 6 Crystallization heat as a function of the cooling rate of some of the homopolymers.

be seen from Table II, the values of G_o for the homopolymers H1, H2, and H6 are 3.5×10^{10}, 4.3×10^{10}, and 5.41×10^{10} μm/min, respectively, which are similar to the values found by Ding and Spruiell[4]; however, the G_o of homopolymer H5 is much higher than these values, indicating that G_o, and consequently, G, are dependent on the molecular weight, as already concluded in de Carvalho and Bretas.[1] The G_{on} have approximately the same values than their corresponding G_o. Therefore, G_n, as G, is dependent on the molecular weight.

If we assume that our G_o and G_{on} values are correct, the question that remains is why both change with the M_w?

G_o, for regime I, can be given by the following expression[8]:

$$G_o = C_o \kappa n_l \left[\frac{b_o kT}{h} \right] \left[\frac{kTa_o \Delta G}{4b_o l_u \sigma^2} \right] \qquad (3)$$

where C_o is a constant; κ, a numerical constant evaluated from a determination of the monomeric friction coefficient as it enters into the rate that a molecule is reeled on to the surface as given by reptation theory; b_o, the layer thickness; n, the number of —CH₂— units in the chain consistent with the appropriate moment of the molecular weight; a_o, the width of the chain; I_u, the C—C distance as projected along the chain axis; ΔG, the free energy difference between subcooled melt and crystal; h, Plancks's constant; k, Boltzmann constant; and σ, interfacial surface free energy.

For the other regimes, II and III, the dependency of G_o is similar. Thus, G_o will account for

other factors that influence the transport of the crystallizing macromolecule to the substrate; these factors are mainly structural factors. Therefore, we would expect that if G_{on} has the same dependency on these factors than G_o, then due to the high molecular weight of sample H5 (that will affect mainly n_1), the values of G_o and G_{on} for that polymer will be higher than for the lower molecular weight samples, H1, H2, and H6.

Figure 5 shows $(T_{onset} - T_c)$ as a function of the cooling rate for the homopolymers, as calculated by DSC. T_{onset} is defined as the temperature at which crystallization begins. Therefore $(T_{onset} - T_c)$ is a measure of the width of the crystallization peak, and it can be related to the global or overall crystallization rate in the same way as $(t_{1/2} - t_i)$ is in the isothermal conditions. The lower $(T_{onset} - T_c)$, the narrower the crystallization peak, and the higher the overall crystallization rate. It can be observed that sample H5 has the lowest $(T_{onset} - T_c)$, while sample H2 has the highest $(T_{onset} - T_c)$ values. These data confirm the observation that H5 has the highest overall crystallization rate, probably due to the contribution given by a high nucleation rate because its growth crystallization rate G was the lowest.[1]

Table III Heat of Melting, ΔH_m and Melting Temperatures T_m of the Samples

Sample	T_m (°C)	ΔH_m (J/g) to Crystallinity (%)
H1	163.6 (0.5)	85.4 (4.0) to 40.8
H2	164.8 (0.9)	73.8 (1.8) to 35.2
H5	163.8 (0.6)	72.1 (5.4) to 34.4

(a)

(b)

Figure 7 PLOM micrographs of sample H2, with the PIN procedure, at different temperatures and at a cooling rate of $-5°C$ min: (a) $T = 123.5°C$, 200X; (b) $T = 120.5°C$, 200X.

Figure 6 shows the heat of crystallization of the homopolymers as a function of the cooling rate. The lowest and highest molecular weight samples, H1 and H5, respectively, have crystallization heats independent of the cooling rates; however, sample H2 has its crystallization heat decreasing as the cooling rate increases. Sample H1 has also the highest heat of crystallization.

Table III shows the heat of melting ΔH_m and melting temperature T_m of the samples as obtained by DSC. It can be observed that the melting temperature was almost the same, independent of the molecular weight. Regarding the heats of fusion, samples H2 and H5 had lower heats of fusion than sample H1, indicating a lower degree of crystallinity. The percentage of crystallinity, assuming $\Delta H_m^o = 209.3$ J/g, for pure i-PP is also shown. Sample H1 has the highest percentage of crystallinity.

Morphology

Figure 7 shows polarized light optical micrographs of the spherulitic morphology of homopolymer H2 at different temperatures, after the PIN procedure; the development of a fine and radial texture can be observed. Figure 8 shows micrographs of the same sample, at different temperatures, without PIN. Again, the development of a fine and radial texture is observed; however, in this last case, due to the surging and growing of other spherulites, measurement of the radius became increasingly difficult. Figure 9 shows the development and growing of the spherulitic morphology for sample H5 at different temperatures after the PIN procedure. Again, a fine and radial texture is observed.

(a)

(b)

Figure 8 PLOM micrographs of sample H2, without the PIN procedure, at different temperatures and at a cooling rate of $-5°C$ min: (a) $T = 124.1°C$, 200X; (b) $T = 122.4°C$, 200X.

(a)

(b)

Figure 9 PLOM micrographs of sample H5 with the PIN procedure, at different temperatures and at a cooling rate of $-5°C$ min: (a) $T = 125.2°C$, 200X; (b) $T = 119.5°C$, 200X.

CONCLUSIONS

The following conclusions can be inferred from this work.

1. The PLOM nonisothermal experiments showed that the modified Hoffman and Lauritzen equation can describe with accuracy the nonisothermal crystallization of the homopolymers at a cooling rate of $-5°C$ min.

2. The nonisothermal growth rates G_n of all homopolymers were found, in general, to be similar to the corresponding isothermal rates G and also with the same dependence on molecular weight.

3. The PIN procedure allowed to obtain nonisothermal data at higher temperatures than the without PIN procedure, allowing us also to compare G_n at higher cooling rates than the ones found in the literature.

4. Thermal data by DSC showed that the lower the molecular weight, the higher the crystallization heat and the higher the amount of crystallinity.

5. The melting temperature was constant, independent of molecular weight.

6. The morphology of the samples, as seen by PLOM, revealed a fine and radial texture for all the homopolymers.

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