

# Thermal Effects Due to Polymer Crystallization

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**ABSTRACT:** The problem of dissipation of latent heat of fusion by thermal conductivity in polymer crystallizing in bulk is discussed. It is shown that the liberation of latent heat of fusion causes the increase of the temperature at the crystallization front. The increase of thermal conductivity and diffusivity of a polymer due to phase transition decreases while the presence of another crystallization front increases the temperature elevation. The temperature buildup is limited by the decrease of growth rate with temperature, directly related to the release of latent heat of fusion. The thermal effects due to crystallization of numerous spherulites in a plate are also estimated. It is shown that the crystallization causes a significant increase of the temperature inside the material as the crystallization proceeds, which slows the rate of conversion of melt into spherulites. The temperature increase in the interior of material depends on the initial temperature and on the sample sizes. The predictions were confirmed by the measurements of the temperature in bulk samples of isotactic polypropylene during crystallization at isothermal ambient conditions. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 1015–1028, 1997

**Key words:** heat of fusion; crystallization; isotactic polypropylene

## INTRODUCTION

First-order phase transformations are accompanied by the release or the absorption of latent heat of fusion. Hence, the initial temperature distribution inside the material undergoing melting or solidification changes. In metals and other low molecular substances, the interphase, at which the transformation occurs, follows the isotherm of melting point. The process of transformation is then controlled by heat dissipation; hence the position of interphase boundary is proportional to the square root of time. There are several different treatments of the that problem: for example, the solutions of Neumann,<sup>1</sup> Schwarz,<sup>2,3</sup> Stefan,<sup>1</sup> and Lightfoot.<sup>4</sup> The essential feature of those approaches is that the solidified material has a temperature equal to the melting point.

One of the main differences in crystallization

of polymers is that it proceeds at large undercoolings; solidified material is well below its melting point. This is because the crystallization of polymers is controlled by primary and secondary nucleations rather than by the dissipation of latent heat of fusion. After the primary nucleation event, the crystalline aggregate–spherulite grows radially until impingement with neighboring spherulites. The latent heat of fusion is liberated in a narrow zone of interfaces of spherulites with melt. The temperature near the crystallization front might be increased by liberation of the latent heat of fusion, but still may be well below the melting temperature of crystals because polymers usually crystallize at quite large undercoolings. In contrast to low molecular substances, the spherulite growth rate is usually constant in time and so is not proportional to the square root of time. Hence, it was concluded that the crystallization in polymers is not influenced by the dissipative transport of latent heat of fusion away from the growth front. However, the measurements of spherulite

growth rate are usually performed on polymer thin films kept at constant and uniform temperature imposed externally. Polymers are poor heat conductors; hence while not in thin films, the temperature increase could be expected during crystallization in bulk.<sup>5</sup>

In Piorkowska and Galeski,<sup>6</sup> the solution of the problem of a moving continuous plane heat source was applied to the estimation of a possible increase of the planar temperature near the crystallization front. It was shown that at the crystallization front of infinite sizes, moving with a constant velocity  $G$ , the temperature increase  $\Delta T$  at time  $t$  elapsed from the beginning of crystallization equals

$$\Delta T = s \Delta h_f d_c (d_a c_p)^{-1} \operatorname{erf}(0.5 G t^{0.5} a^{-0.5}) \quad (1)$$

where  $s$ ,  $\Delta h_f$ ,  $d_a$ ,  $d_c$ ,  $c_p$ , and  $a$  are the crystallinity degree, the heat of fusion, the density of melt, the density of crystalline phase, the specific heat capacity, and the thermal diffusivity of melt, respectively; while  $\operatorname{erf}(z) = 2\pi^{-0.5} \int_0^z \exp(-z^2) dz$ . For  $t \rightarrow \infty$ , the temperature increase  $\Delta T$  reaches tens of degrees, but it would take months or even years of crystallization to reach the equilibrium. In a reasonable time scale,  $\Delta T$  is a fraction of a degree for growth rates up to  $20 \mu\text{m min}^{-1}$ . For faster growth of spherulites,  $\Delta T$  reaches quickly several degrees because of the strong dependence of  $\Delta T$  on  $G$  as expressed by eq. (1). For the temperature range where the growth rate decreases strongly with the increasing temperature, the temperature elevation would cause a significant drop of  $G$ , which, in turn, would depress further increase of temperature. Hence, eq. (1) can hardly be applied for high undercoolings and fast crystallization.

Equation (1) was obtained assuming the same thermal properties of crystalline and amorphous phases. Higher heat conductivity and thermal diffusivity of a solidified polymer may influence the temperature distribution near the crystallization front. The crystallizing fronts of neighboring spherulites approaching each other enhance the temperature increase due to accumulated release of latent heat of fusion. The growing spherulites impinge with their neighbors forming boundaries; hence parts of their surfaces become excluded from further growth. The heat release in crystallizing polymer is then proportional to the momentary area of growing surfaces of spherulites, which is equivalent to the rate of conversion of

melt into spherulites. The increase of temperature in a crystallizing polymer related to the overall rate of crystallization is then expected. Hence, a part of the material will crystallize at temperature higher than expected, which will be reflected in its properties. According to the well-known Kolmogoroff–Avrami–Evans theory<sup>7–11</sup> and its further developments,<sup>12–15</sup> the conversion of melt into spherulites at time  $t$  elapsed from the beginning of crystallization,  $\alpha(t)$ , is described by the following equation:

$$\alpha(t) = 1 - \exp \left[ - \int_0^t F(\tau) v(\tau, t) d\tau \right] \quad (2)$$

where  $F(\tau)$  denotes the nucleation rate and  $v(\tau, t)$  is the extended volume (at time  $t$ ) occupied by spherulite nucleated at time  $\tau$  dependent on spherulite growth rate  $G$ . Since both the nucleation rate and the spherulite growth rate depend on the temperature, one can expect that the liberation of latent heat of fusion will influence the conversion rate of melt into spherulites and the time necessary for accomplishing crystallization. For the crystallization rate decreasing with increasing temperature, a slower and longer crystallization could be expected.

This article is devoted to the estimation of the thermal effect connected with the liberation of latent heat of fusion during polymer crystallization in bulk, and it is divided into two parts. The concern of the first part of the article is the temperature increase at the planar crystallization front regarding the change of thermal properties due to crystallization and the temperature dependence of growth rate. Also, the case of two crystallizing fronts approaching each other is considered. The second part is devoted to the estimation of thermal effects due to crystallization of numerous spherulites in a polymer plate. The temperature increase and the conversion degree in the interior of a sample are determined. Isotactic polypropylene physical data were used for computations, and all crystallization experiments were performed using various brands of isotactic polypropylene.

## TEMPERATURE NEAR CRYSTALLIZATION FRONT FOR DIFFERENT THERMAL PROPERTIES OF MOLTEN AND SOLIDIFIED POLYMER

The formulation of the problem of heat conduction will be recalled here only briefly since it is similar

to that described in Piorkowska and Galeski.<sup>6</sup> It is assumed that at time  $t = 0$ , the infinite sample being at the temperature  $T_0$  consists of two phases: solid for  $x < 0$ , and liquid for  $x > 0$ . The heat conductivity, the thermal diffusivity, the specific heat capacity, and the density are  $K_1, a_1, c_{p1}$ , and  $d_a$ , respectively, for a melt; and  $K_2, a_2, c_{p2}$ , and  $d_s$ , respectively, for a solid. At  $t = 0$ , the plane separating the two phases begins to move along  $x$ -axis with a velocity  $G$  equal to the spherulite growth rate. The amount of heat released per time unit and per unit area of a crystallizing front equals the following product:  $\Delta LG$ , where  $\Delta L$  denotes the amount of heat released during crystallization of a unit volume of the material,  $\Delta L = s\Delta H_f d_c$ ;  $s$  denotes the volume degree of crystallinity;  $\Delta H_f$  is the latent heat of fusion; and  $d_c$  is the crystalline phase density.

Because of infinite sizes of the crystallizing front, there are no heat fluxes in the directions perpendicular to  $x$ -axis. In the system of coordinates moving with the velocity  $G$  and with the origin of coordinates at the crystallizing front, the heat conduction equations take the following forms:

$$\alpha \frac{\delta^2 \Delta T}{\delta x^2} + G \frac{\delta \Delta T}{\delta x} - \frac{\delta \Delta T}{\delta t} = 0 \quad (3)$$

where  $a = a_1$  for  $x > 0$ , and  $a = a_2$  for  $x < 0$ ;  $x$  denotes a distance from crystallizing front; and  $\Delta T(x, t) = T(x, t) - T_0$ . The function  $\Delta T$  has to assume zero value initially and also for  $x \rightarrow \mp \infty$ . At  $x = 0$ , the conditions of continuity of the temperature function and the law of conservation of heat flux have to be fulfilled. The subsidiary equation obtained by Laplace transformation of eq. (3) has the solution in the following form<sup>6</sup>:

$$F(x, p) = B \exp\{0.5a_1^{-1}[-G - (G^2 + 4a_1p)^{0.5}]x\} \quad \text{for } x > 0 \quad (4a)$$

$$F(x, p) = B \exp\{0.5a_2^{-1}[-G + (G^2 + 4a_2p)^{0.5}]x\} \quad \text{for } x < 0 \quad (4b)$$

$$B = 2a_1a_2G\Delta Lp^{-1}\{K_2a_1[(G^2 + 4a_1p)^{0.5} - G] + K_1a_2[(G^2 + 4a_2p)^{0.5} + G]\}^{-1} \quad (4c)$$

where  $p$  denotes the transformation parameter.

For a substantial simplification of the form of the solution with little loss in the precision, it is assumed that the increase of polymer density due to crystallization is approximately the same as

the decrease of specific heat capacity; hence  $d_s c_{p2} = d_a c_{p1}$ . Therefore, the increase of thermal diffusivity of the polymer due to crystallization is determined primarily by the increase of heat conductivity  $K_2 K_1^{-1} = a_2 a_1^{-1}$ . Hence, the temperature increase,  $\Delta T(x, t)$ , is expressed as follows.

$$\begin{aligned} \Delta T(x, t) &= 0.5C \int_0^t \{\operatorname{erfc}\{x/[4a_1(t - \tau)]\}^{0.5} \\ &\quad + [\gamma_1(t - \tau)]^{0.5} + \exp(-xG/a_1) \\ &\quad \times \operatorname{erfc}\{x/[4a_1(t - \tau)]\}^{0.5} \\ &\quad - [\gamma_1(t - \tau)]^{0.5}\} R(\tau) d\tau \quad \text{for } x > 0 \quad (5a) \end{aligned}$$

$$\begin{aligned} \Delta T(x, t) &= 0.5C \int_0^t \{\operatorname{erfc}\{-x/[4a_2(t - \tau)]\}^{0.5} \\ &\quad + [\gamma_2(t - \tau)]^{0.5} + \exp(-xG/a_2) \\ &\quad \times \operatorname{erfc}\{-x/[4a_2(t - \tau)]\}^{0.5} \\ &\quad - [\gamma_2(t - \tau)]^{0.5}\} [-R(\tau)] d\tau \\ &\quad \text{for } x < 0 \quad (5b) \end{aligned}$$

where  $\operatorname{erfc}(z) = 1 - \operatorname{erf}(z)$ , and

$$C = a_1 K_1^{-1} \Delta LG (a_1 - a_2)^{-1} \quad (5c)$$

$$\begin{aligned} R(\tau) &= 0.5G \{\operatorname{erf}[(\gamma_1\tau)^{0.5}] - \operatorname{erf}[(\gamma_2\tau)^{0.5}]\} \\ &\quad + (\pi\tau)^{-0.5} [a_2^{0.5} \exp(-\gamma_2\tau) - a_1^{0.5} \exp(-\gamma_1\tau)] \quad (5d) \end{aligned}$$

$$\gamma_1 = 0.25G^2 a_1^{-1} \quad (5e)$$

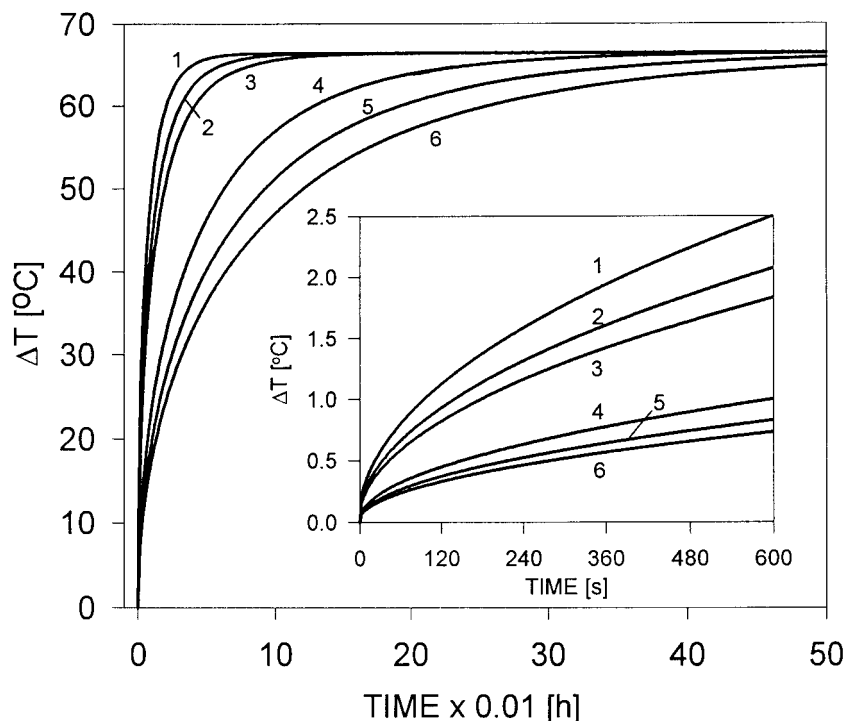
$$\gamma_2 = 0.25G^2 a_2^{-1} \quad (5f)$$

For  $x = 0$ , the above expressions describe the time dependence of temperature increase at the crystallization front, as follows:

$$\begin{aligned} \Delta T(0, t) &= C \{(t/\pi)^{0.5} [a_2^{0.5} \exp(-\gamma_2 t) - a_1^{0.5} \exp(-\gamma_1 t)] \\ &\quad + (Gt/2 + a_2 G^{-1}) \operatorname{erf}[(\gamma_2 t)^{0.5}] \\ &\quad - (Gt/2 + a_1 G^{-1}) \operatorname{erf}[(\gamma_1 t)^{0.5}]\} \quad (6) \end{aligned}$$

For  $t \rightarrow \infty$ , the temperature difference at the crystallizing front achieves the following limit:

$$\Delta T(0, \infty) = \Delta L (d_a c_{p1})^{-1} \quad (7)$$

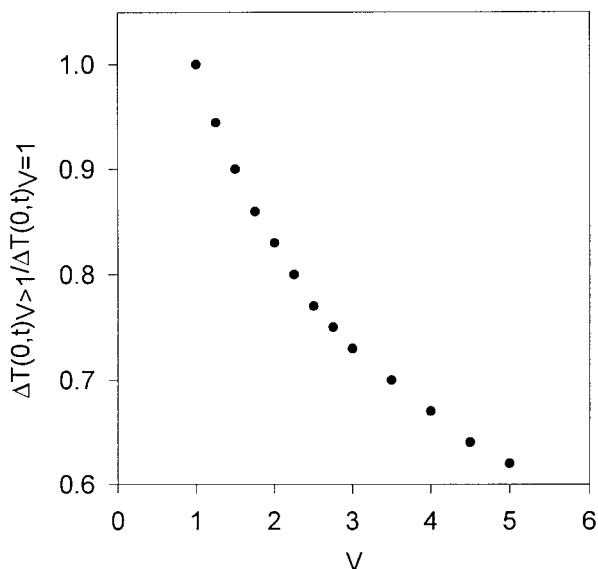


**Figure 1** Time dependencies of the temperature increase,  $\Delta T$ , at the crystallization front for the following values of growth rate  $G$  and ratio  $V = K_2/K_1$ . (1)  $G = 50 \mu\text{m min}^{-1}$ ,  $V = 1$ ; (2)  $G = 50 \mu\text{m min}^{-1}$ ,  $V = 2$ ; (3)  $G = 50 \mu\text{m min}^{-1}$ ,  $V = 3$ ; (4)  $G = 20 \mu\text{m min}^{-1}$ ,  $V = 1$ ; (5)  $G = 20 \mu\text{m min}^{-1}$ ,  $V = 2$ ; (6)  $G = 20 \mu\text{m min}^{-1}$ ,  $V = 3$ .

which appears to be independent of  $V = K_2/K_1$  ratio. For the calculations, physical parameters for polypropylene were assumed, i.e.,  $\Delta L = 119 \text{ J cm}^{-3}$ , which corresponds to  $s = 0.6$  for  $d_c = 0.946 \text{ g cm}^{-3}$  and  $\Delta H_f = 209.5 \cdot 10^3 \text{ J kg}^{-1}$ .<sup>16</sup> It should be emphasized here that  $\Delta L$  in eqs. (5)–(7) is only a proportional coefficient; hence all results could be easily recalculated for any other value of  $\Delta L$ . The typical values of  $K_1$  and  $c_{p1}$  for polypropylene melts were assumed, as follows:  $0.17 \text{ W m}^{-1} \text{ K}^{-1}$  and  $2.095 \text{ J kg}^{-1} \text{ K}^{-1}$ ,<sup>17,18</sup> respectively, and  $d_a = 0.854 \text{ g cm}^{-3}$ .<sup>16</sup> According to refs. 19 and 20, the estimated ratio of  $c_{p1}$  to specific heat capacity of crystalline phase,  $c_{ps}$ , for polypropylene is approximately 1.13 at  $120^\circ\text{C}$  and decreases to 1.07 at  $177^\circ\text{C}$ ; while the  $d_c/d_a$  ratio equals 1.11. If the partial crystallinity of a solid phase, the very weak dependence of  $d_c$  and  $d_a$  on temperature and also the range of crystallization temperature for polypropylene are taken into account, the values of heat capacity of a unit volume of a melt and a solid phase do not differ more than 2%.

In Figure 1, the increase of the temperature at the crystallization front,  $\Delta T$ , is plotted for  $G = 20 \mu\text{m min}^{-1}$  and  $50 \mu\text{m min}^{-1}$  for the ratio  $K_2/K_1$

equal 1, 2, and 3. At the beginning of the growth process,  $\Delta T$  increases with time, but it is lower for increasing  $K_2/K_1$ . For longer time elapsed from the beginning of crystallization,  $\Delta T$  reaches the level determined by  $\Delta L$  and independent of the  $K_2/K_1$  ratio. The time of achieving this steady-state increases with the increase of  $K_2/K_1$  ratio. At the temperature at which the spherulite growth rate is  $20\text{--}50 \mu\text{m min}^{-1}$ , the crystallization of a polymer is completed within several minutes; hence  $\Delta T$  in 10 min scale is also drawn in Figure 1. It is worthy to note that the ratio of  $\Delta T(0, t)_{V>1}$  (for  $V = K_2/K_1 > 1$ ) to the  $\Delta T(0, t)_{V=1}$  (for  $V = K_2/K_1 = 1$ ) remains nearly constant during first 10 min of crystallization and depends only on the ratio  $K_2/K_1$ . In Figure 2, the ratio  $\Delta T(0, t)_{V>1}/\Delta T(0, t)_{V=1}$  is drawn against  $K_2/K_1$  ratio. The higher the value of  $K_2/K_1$ , the lower the ratio  $\Delta T(0, t)_{V>1}/\Delta T(0, t)_{V=1}$ . The ratio  $K_2/K_1$  usually does not exceed 3 for many polymers; for example, it is 1.4 for polypropylene at  $25^\circ\text{C}$ , from 1.6 to 3 for various polyethylenes at  $90^\circ\text{C}$ , and 2.5 for poly(methylene oxide) at  $90^\circ\text{C}$ .<sup>21,22</sup> Even lower values of the  $K_2/K_1$  ratio can be expected at polymer crystallization temperatures



**Figure 2** Dependence of the ratio  $\Delta T(0, t)_{V>1}/\Delta T(0, t)_{V=1}$  on the ratio  $V = K_2/K_1$ .

since the heat conductivity of the crystalline phase follows the  $T^{-1}$  dependence above 100 K while the temperature dependence of heat conductivity of amorphous phase is rather weak.<sup>21-23</sup> Hence, as it is seen from Figure 2, higher conductivity of the solidified phase may lower the  $\Delta T(0, t)$  at the crystallization front by no more than 30%; for example, for iPP, it lowers only by 6%. In Figure 3, the temperature increase is plotted against the distance from the crystallizing front for  $K_2/K_1 = 1, 2,$  and  $3,$  after 1 and 10 min of crystallization at the rate  $20 \mu\text{m min}^{-1}$ . The distance at which the apparent temperature increase is visible increases with time: from 1 mm after 1 s (not shown in Fig. 3), to 8 mm after 1 min, and to 25 mm after 10 min. The increase of  $K_2/K_1$  lowers the temperature elevation and introduces asymmetry of the temperature distribution with respect to the crystallization front position.

#### TEMPERATURE DISTRIBUTION NEAR CRYSTALLIZATION FRONT WITH TEMPERATURE DEPENDENCE OF SPHERULITE GROWTH RATE

Similarly, as in Piorkowska and Galeski,<sup>6</sup> the assumption is made that the heat conduction coefficient and the thermal diffusivity behind the crystallization front are equal to those of a polymer melt,  $K_1$  and  $\alpha_1$ . For the temperature changing with time, both  $G$  and  $\Delta L$  can be expressed as

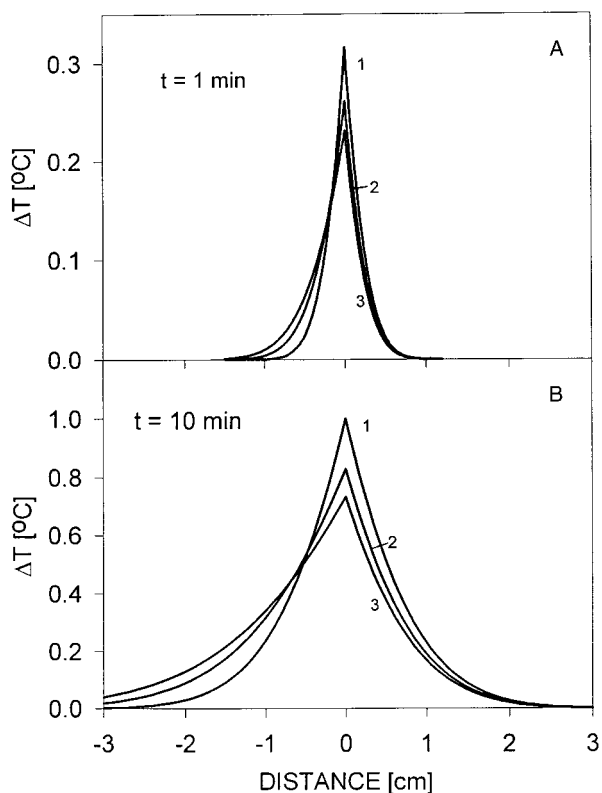
time-dependent functions, as follows:  $G = g(T(t)) = G(t)$ , and  $\Delta L = \Delta l(T(t)) = \Delta L(t)$ . Let us assume that the amount of heat  $Q(\tau)d_a c_{p1} = G(\tau)\Delta L(\tau)$  per time unit and per area unit of the plane is liberated at time  $\tau$  and  $x = x_s$  in the plane parallel to  $x = 0$ . Momentarily, the crystallization front is equivalent to the instantaneous plane source in an infinite medium at an initially uniform temperature. The temperature increase at the point  $x = x'$  at time  $t$  due to such instantaneous source of heat is described by the following formula<sup>24</sup>:

$$\Delta T_s(x', x_s, t, \tau) = 0.5Q(\tau)[\pi\alpha_1(t - \tau)]^{-0.5} \times \exp\left\{-\frac{(x' - x_s)^2}{4\alpha_1(t - \tau)}\right\} \quad (8)$$

The total temperature increase at point  $x'$  at time  $t$  due to continuous source moving and emitting heat from  $t_0 = 0$  onwards can be obtained by the following integration:

$$\Delta T'(x', t) = \int_0^t \Delta T_s(x', x_s(\tau), t, \tau) d\tau \quad (9)$$

where  $x_s(\tau)$  denotes the position of the source at time  $\tau$ .



**Figure 3** Temperature profiles near the crystallization front for  $G = 20 \mu\text{m min}^{-1}$  for  $K_2/K_1$  equal 1, 2, and 3; (A) after 1 min and (B) 10 min of crystallization.

In a system of coordinates moving with the velocity  $G(t)$  along the  $x'$  axis, with the origin at the crystallization front, the point  $x'$  will be at time  $t$  at the position  $x$ , defined by the following relationship:

$$x' = x + \int_0^t G(z) dz \quad (10)$$

Finally, the temperature increase at position  $x$  with respect to moving crystallization front at time  $t$  can be derived from eq. (9) with the help of eqs. (8) and (10) in the following form:

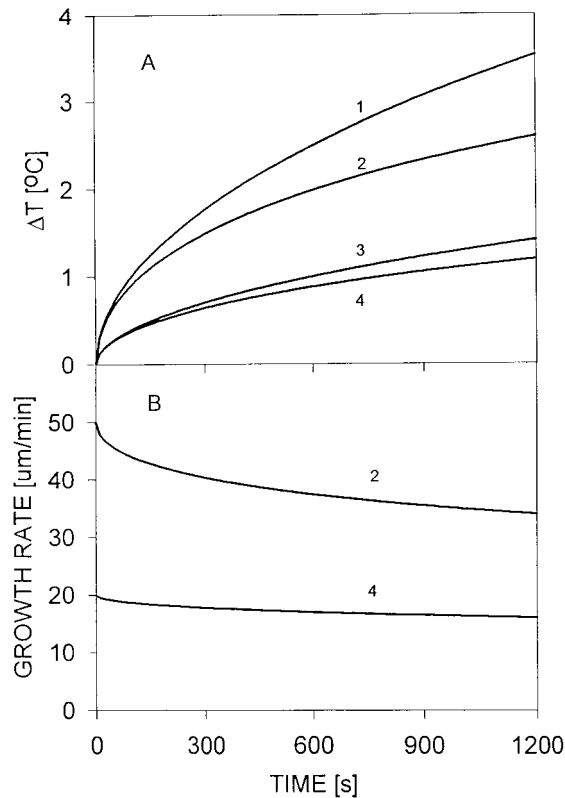
$$\begin{aligned} \Delta T(x, t) &= 0.5(\pi K_1 d_a c_{p1})^{-0.5} \int_0^t \Delta L(\tau) G(\tau) (t - \tau)^{-0.5} \\ &\times \exp \left\{ - \left[ x + \int_\tau^t G(z) dz \right]^2 / \right. \\ &\quad \left. [4a_1(t - \tau)] \right\} d\tau \quad (11) \end{aligned}$$

The temperature increase in isotactic polypropylene at the crystallization front,  $\Delta T$ , moving with temperature-dependent velocity is calculated from eq. (11) for  $x = 0$ . For computer calculations, the assumption is made that  $G$  is changing with time according to  $g(T(t))$  but constant within short time intervals,  $\Delta\tau$ . In the calculations, the spherulite growth rate temperature dependence  $g(T)$  in regime III of crystallization for  $\alpha$ -spherulites of isotactic polypropylene RAPRA iPP1 ( $M_w = 307,000$ ;  $M_w/M_n = 20$ ; melt flow index =  $3.9 \text{ g}/10 \text{ min}$ )<sup>25,26</sup> was used, as follows:

$$\begin{aligned} g(T) &= g_0 \exp \{ -U[R(T - T_\infty)]^{-1} \} \\ &\times \exp \{ -K_g[T(T_m^0 - T)]^{-1} \} \quad (12) \end{aligned}$$

where  $g_0 = 8009 \text{ cm s}^{-1}$ ,  $U = 1500 \text{ cal mol}^{-1}$ ,  $K_g = 358,400 \text{ K}^2$ ,  $T_\infty = 231.2 \text{ K}$ ,  $T_m^0 = 458.2 \text{ K}$ , and  $T$  is the crystallization temperature.

The computations were conducted for two values of  $T_0$ , 123.83 and 117.97°C, for which the respective  $G_0$  values are 20 and  $50 \mu\text{m min}^{-1}$  according to eq. (12). Since the expected values of  $\Delta T$  for reasonable time scale were within limits of several degrees, constant  $\Delta L$  was assumed. The time intervals,  $\Delta\tau$ , were chosen to be 0.5 s.  $\Delta T$  and resulting  $G$  are plotted in Figure 4 for the first 20 min of crystallization. For comparison,  $\Delta T$  for constant  $G$  is also drawn in Figure 4(A). While



**Figure 4** (A) Time dependencies of the temperature increase,  $\Delta T$ , at the crystallization front. (1)  $G = 50 \mu\text{m min}^{-1}$ , constant; (2)  $G$  initially  $50 \mu\text{m min}^{-1}$ , dependent on temperature; (3)  $G = 20 \mu\text{m min}^{-1}$ , constant; (4)  $G$  initially  $20 \mu\text{m min}^{-1}$ , dependent on temperature. (B) Time dependencies of the growth rate in which the numbers have the same meaning as in Figure 4(A).

at the very beginning of crystallization, the variable growth rate influences the temperature only slightly, it later causes slower buildup of the temperature. After 10 min of crystallization at 123.83°C and after 5 min of crystallization at 117.93°C,  $\Delta T$  is lower than that obtained for  $G = \text{constant}$  by 12 and 16%, respectively; and  $G$  is reduced by 15 and 19%, respectively. Both effects, the inhibition of the temperature buildup at the crystallization front,  $\Delta T$ , and the decrease of the growth rate,  $G$ , are more pronounced for the crystallization at lower temperature due to higher initial growth rate and stronger decrease of the growth rate with temperature.

## TEMPERATURE DISTRIBUTION BETWEEN TWO CRYSTALLIZATION FRONTS

Let us consider the temperature at the point between two approaching crystallization fronts, be-

ing apart by the distance  $d_0$  at  $t = 0$ . At time  $t$ , the point being at the distance  $x$  from the first front is at the distance  $x_a$  from the second crystallization front, as follows:

$$x_a = -x + d_0 - 2 \int_0^t G(z) dz \quad (13)$$

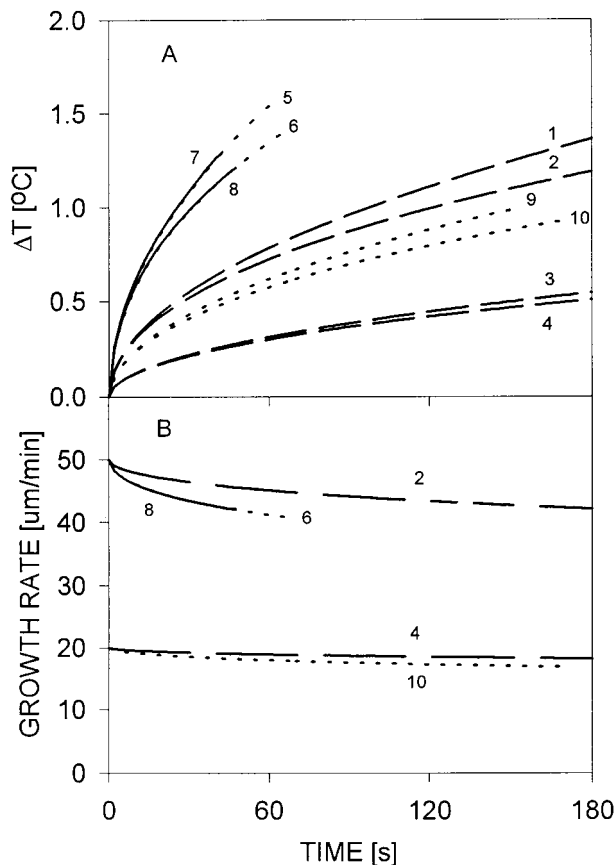
The total increase of the temperature is caused by a sum of two heat fluxes from both crystallization fronts, which is equivalent in this case to

$$\Delta T'(x, t) = \Delta T(x, t) + \Delta T(x_a, t) \quad (14)$$

where  $\Delta T$  is given by eq. (11). The two values of  $T_0$ , 123.83 and 117.97°C [corresponding to  $G = 20$  and  $50 \mu\text{m min}^{-1}$  according to eq. (12)], were considered. The computations were conducted for constant  $G$  and for temperature dependent  $G$ , for the following values of  $d_0$ : 100  $\mu\text{m}$  at 123.83°C, and 100 and 70  $\mu\text{m}$  at 117.97°C, which are close to the average diameter of spherulites in iPP crystallized at those temperatures. For temperature-dependent  $G$ , the values of the  $\Delta T'(x, t)$  and  $G$  were computed in subsequent time intervals until the impingement of crystallization fronts as it was described in the previous section. In Figure 5, the temperature increase at the crystallization front,  $\Delta T$ , and the growth rate,  $G$ , are plotted against time.  $\Delta T$  and  $G$  for an isolated crystallization front are also drawn for comparison.  $\Delta T$  at the crystallization front being approached by another one is greater than for an isolated crystallization front at the same time, at the end of crystallization by the factor 2.0 for constant  $G$ , while for temperature-dependent  $G$  by the factor 1.73 at 123.83°C and 1.86 at 117.97°C. The decrease of  $G$  is also greater than for an isolated crystallization front at the same of time;  $G$  is decreased with respect to  $G_0$  by 15–18% at the end of crystallization. The influence of the second crystallization front on  $\Delta T$  is stronger for  $T_0 = 117.97^\circ\text{C}$  than  $T_0 = 123.83^\circ\text{C}$ , but also the growth inhibition due to the temperature dependence of  $G$  is more pronounced. The two cases considered with  $d_0$  of 70 and 100  $\mu\text{m}$  almost do not differ, except for the fact that when the crystallization ends earlier  $\Delta T$  and the decrease of  $G$  are smaller.

### THERMAL EFFECTS DUE TO CRYSTALLIZATION OF NUMEROUS SPHERULITES IN A POLYMER PLATE

From the previous sections, it follows that the temperature increase due to the release of latent



**Figure 5** (A) Time dependencies of the temperature increase,  $\Delta T$ , at the crystallization front. Isolated (1)–(4) and being approached by another one (5)–(10). (1)–(4) have the same meaning as in Figure 4. In (5) and (7),  $G = 50 \mu\text{m min}^{-1}$ , constant, and  $d_0$  equals 100 and 70  $\mu\text{m}$ , respectively. In (6) and (8),  $G$  was initially  $50 \mu\text{m min}^{-1}$ , dependent on temperature, and  $d_0$  equals 100 and 70  $\mu\text{m}$ , respectively. In (9),  $G = 20 \mu\text{m min}^{-1}$ , constant, and  $d_0 = 100 \mu\text{m}$ . In (10),  $G$  was initially  $20 \mu\text{m min}^{-1}$ , dependent on temperature, and  $d_0 = 100 \mu\text{m}$ . (B) Time dependencies of the growth rate in which the numbers have the same meaning as in Figure 5(A).

heat of crystallization is strongly enhanced by a presence of neighboring crystallization fronts. On the other hand, the higher the temperature increase, the more pronounced the decrease of the growth rate.

The aim of this section is to evaluate the temperature increase during polymer crystallization in bulk, where numerous spherulites grow at the same time, taking into account the influence of the temperature increase on the crystallization kinetics.

Heat release in bulk samples where many heat sources are active can be approximated with bulk heat generation function. Let the bulk sample of

a polymer be in a form of a thick plate. In a plate of thickness  $d$ , initially at the temperature  $T_0$ , bounded by two parallel planes at  $x = 0$  and  $x = d$  kept at  $T_0$  for  $t > 0$  and where the bulk heat production rate depends on time and on the  $x$ -coordinate,  $A(x, t)$ , the increase of the temperature,  $\Delta T(x, t)$ , is described by the following formula<sup>27</sup>:

$$\begin{aligned} \Delta T(x, t) = & 2a(Kd)^{-1} \sum_{n=1}^{\infty} \sin(n\pi x/d) \\ & \times \int_0^t \int_0^d \sin(n\pi x'/d) A(x', \tau) \\ & \times \exp\{-a(n\pi/d)^2(t - \tau)\} dx' d\tau \quad (15) \end{aligned}$$

where  $a$  and  $K$  are the thermal diffusivity and heat conductivity of material. The bulk heat generation function can be assumed in the form

$$A(x, t) = \Delta L \frac{\delta\alpha(x, t)}{\delta t} \quad (16)$$

where  $\alpha(x, t)$  denotes the local, momentary conversion degree of melt into spherulites, dependent on the nucleation and spherulite growth rates.

The calculations were conducted for RAPRA iPP1 polypropylene because the temperature dependencies of spherulite growth rate and primary nucleation are well known for this polymer. The temperature dependence of  $\alpha$  spherulite growth rate in Regime III is described by eq. (12).<sup>25,26</sup> The increase of the number of spherulites in 1 mm<sup>3</sup> of isothermally crystallized sample of RAPRA iPP1,  $\Delta N$ , due to decrease of the crystallization temperature by 1°C is shown in Galeski<sup>28</sup> for a wide range of crystallization temperatures. Based on those data, the phenomenological formula for the number of nucleation centers in 1 mm<sup>3</sup> of RAPRA iPP1 for 110°C <  $T$  < 132°C takes the form

$$N(T) = 6215 \cdot 10^8 \exp(-0.1567T) \quad (17)$$

The calculations were conducted assuming the following two model modes of crystallization: with instantaneous nucleation and isokinetic when the ratio of nucleation rate to spherulite growth rate  $F(t)/G(t) = P$  remains constant.

The density of nuclei,  $D$ , for instantaneous nucleation and the ratio  $P$  for isokinetic mode of crystallization were estimated from eq. (17) as<sup>15</sup>

$$D = N(T_0) \quad (18a)$$

$$P = 3\pi^{1/3} \{ [4N(T_0)] [3\Gamma(0.25)]^{-1} \}^{4/3} \quad (18b)$$

In the Avrami equation,

$$\alpha(t) = 1 - \exp[-E(t)] \quad (19a)$$

$E(t)$  assumes the forms for crystallization with instantaneous nuclei and for isokinetic crystallization, as follows<sup>14</sup>:

$$E(t) = (4/3)\pi D \left[ \int_0^t G(z) dz \right]^3 \quad (20b)$$

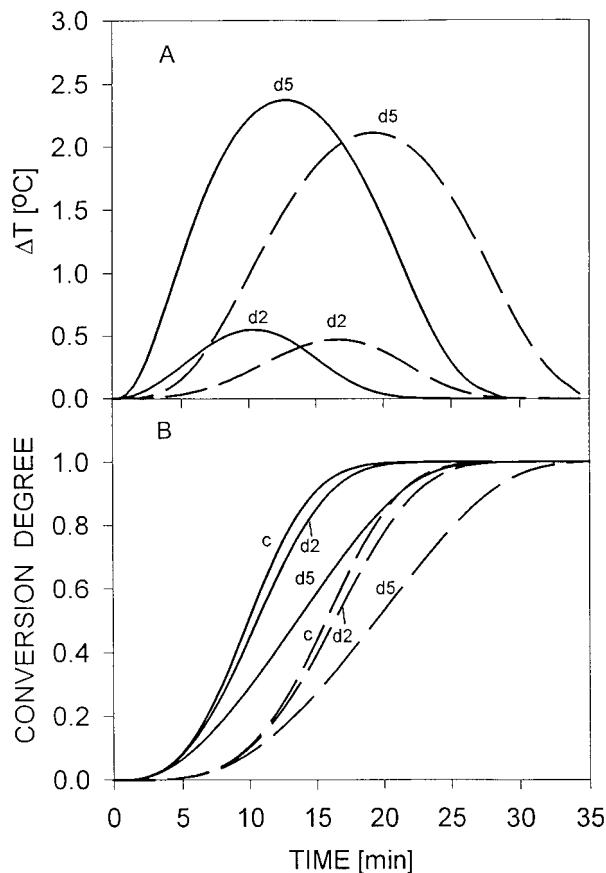
$$E(t) = (1/3)\pi P \left[ \int_0^t G(z) dz \right]^4 \quad (20c)$$

The calculations were conducted for  $T_0 = 130, 122.5, \text{ and } 120^\circ\text{C}$ . It should be emphasized that the  $\beta$ -spherulites content in RAPRA iPP1 crystallized isothermally at 120–130°C is below 5%, so the formulas derived for samples containing only  $\alpha$ -spherulites can be applied with little error. The thickness of the sample chosen for calculations was 2 and 5 mm for 130°C and 2 mm for 122.5 and 120°C. The values of thermal diffusivity,  $a$ , and heat conductivity,  $K$ , were assumed to be equal to those of a polymer melt; specifically,  $a = a_1$  and  $K = K_1$ . Such assumptions are justified by only a slight increase of heat conductivity and thermal diffusivity of polypropylene due to crystallization.<sup>21,22</sup> Preliminary calculations have shown that the temperature increase would not exceed 4°C; hence constant  $\Delta L$  was assumed. The calculations were performed for  $\Delta L$  equal 119 J cm<sup>-3</sup> at 130°C, and 119 and 89 J cm<sup>-3</sup> at 122.5 and 120°C. Those values of  $\Delta L$  correspond to volume crystallinity degree of 0.6 and 0.45 and  $\Delta H_f = 209.5 \text{ J g}^{-1}$ . It was assumed that  $G$  follows eq. (12) but is constant within short time intervals,  $\Delta\tau$ . For 130°C,  $\Delta\tau$  was chosen 0.5 s, while for 122.5 and 120°C  $\Delta\tau$  was 0.2 s. After  $t = \Delta\tau_1$  the temperature,  $T(x, \Delta\tau_1)$ , was calculated according to eqs. (15)–(20). This helped to find new values of  $G$ , as follows:

$$\begin{aligned} G(x, t) = & g(T(x, \Delta\tau_1)) \\ & \text{for } \Delta\tau_1 < t < \Delta\tau_2 \quad (21) \end{aligned}$$

The new value of  $G$  was applied then for calculation of the heat production function  $A(x, t)$  and conversion degree, respectively. The procedure



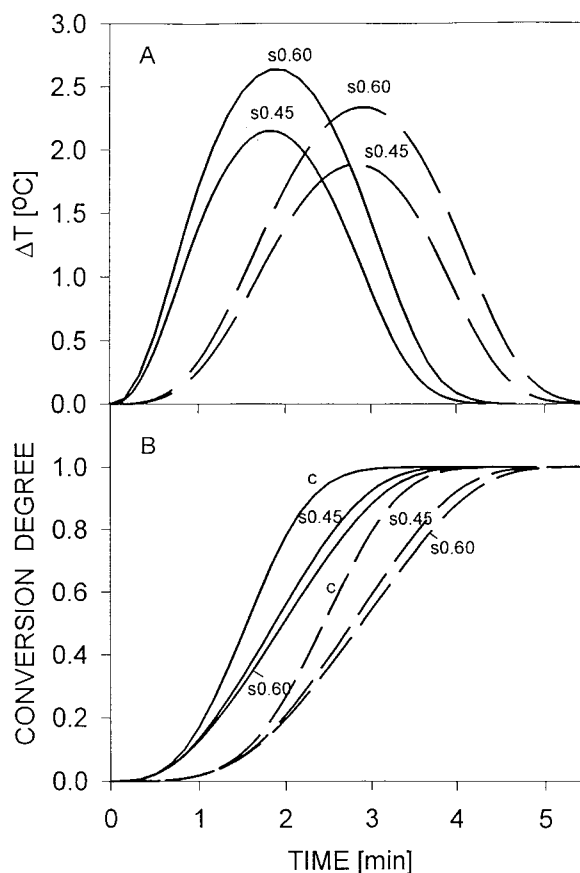


**Figure 6** (A) Time dependencies of the temperature increase in the middle of crystallizing iPP samples of thickness 2 mm (d2) and 5 mm (d5), with  $T_0 = 130^\circ\text{C}$ , crystallization from instantaneous nuclei (solid line), and isokinetic crystallization (dashed line). (B) Time dependencies of the conversion degree at the constant temperature  $T_0$  (c) and in the middle of iPP samples 2 (d2) and 5 mm (d5) thick.

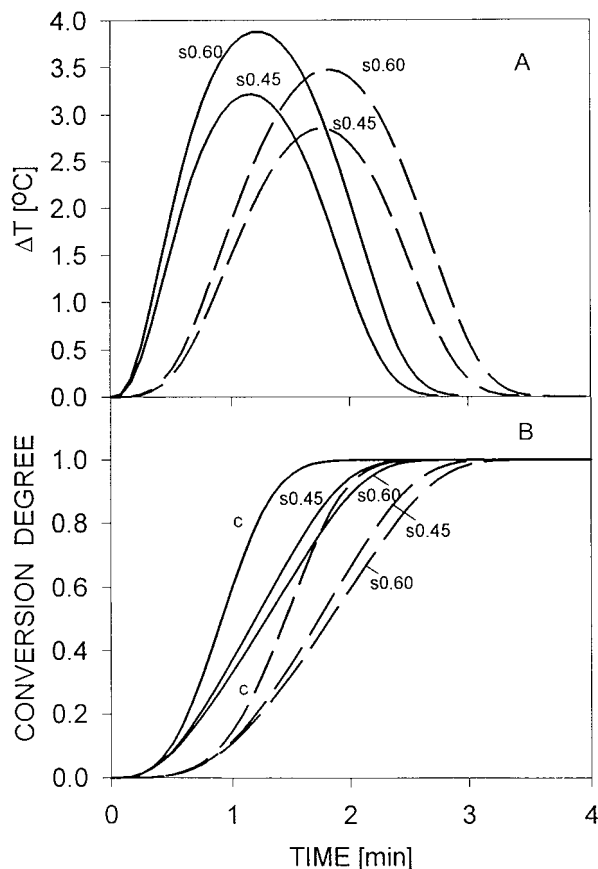
was repeated until the temperature dropped again to the initial value,  $T_0$ , in the entire sample, i.e., well after the end of crystallization. In the presented approach, the influence of the sample boundaries and local temperature gradients on the conversion rate was neglected.

The time dependencies of temperature increase in the middle of sample ( $x = d/2$ ) are plotted in Figures 6(A), 7(A) and 8(A), for the two crystallization processes considered. The time dependencies of the conversion degree in the middle of sample (and also at respective temperature  $T_0$ ) are drawn in Figures 6(B), 7(B), and 8(B) showing a significant slowing of crystallization in the central part of a sample due to the temperature increase. In Table I, the values of maximum temperature increase and the ratio  $t_h/t_{hc}$  are listed, where  $t_h$

and  $t_{hc}$  denote the crystallization half times, in the middle of sample and at constant temperature  $T_0$ , respectively. It follows that the lowering of temperature of crystallization, the increase of sample thickness and crystallinity degree enhance the temperature buildup and the slowing down of crystallization. The isokinetic crystallization, which is usually slower than crystallization from instantaneous nuclei, results in a lower temperature increase. The temperature increase and conversion degree for  $0 < x < d$  are drawn in Figure 9 for the time at which the maximum temperature is achieved in a center of a sample. The distance dependencies of temperature and conversion degree are symmetric with respect to the center of a sample ( $x = d/2$ ). The temperature in-



**Figure 7** (A) Time dependencies of the temperature increase in the middle of crystallizing iPP samples for crystallization degrees 0.45 (s0.45) and 0.6 (s0.6), with  $T_0 = 122.5^\circ\text{C}$ , crystallization from instantaneous nuclei (solid line), and isokinetic crystallization (dashed line). (B) Time dependencies of the conversion degree at constant temperature  $T_0$  (c) and in the middle of iPP samples of crystallinity degree 0.45 (s0.45) and 0.6 (s0.6).



**Figure 8** (A) Time dependencies of the temperature increase calculated for the middle of crystallizing iPP samples for crystallization degrees 0.45 (s0.45) and 0.6 (s0.6), with  $T_0 = 120^\circ\text{C}$ , crystallization from instantaneous nuclei (solid line), and isokinetic crystallization (dashed line). (B) Time dependencies of the conversion degree calculated at constant temperature  $T_0$  (c) and in the middle of iPP samples of crystallinity degree 0.45 (s0.45) and 0.6 (s0.6).

crease  $\Delta T$  divided by maximum temperature increase  $\Delta T_{\max}$  achieved in the middle of a sample drawn against  $x/d$  follows the same curve independently of the sample thickness, initial temperature, and type of crystallization process considered. For all processes considered, the temperature increases while the conversion degree decreases with the distance from sample boundary.

#### MEASUREMENTS OF TEMPERATURE INCREASE DUE TO CRYSTALLIZATION IN A THICK PLATE

To verify the above predictions, the measurements of the temperature inside a crystallizing

plate of iPP were carried out for several brands of polypropylene: RAPRA iPP1 ( $M_w = 307,000$ ,  $M_w/M_n = 20$ , melt flow index = 3.9 g/10 min); Moplen S30G, Montedison (melt flow index = 1.75 g/10 min); and Malen P-B-200 from Petrochemia-Plock, Poland (melt flow index = 0.4–0.8 g/10 min). The 1-mm-thick disks of radius 10 mm of iPPs were obtained by compression molding. A nichrom–constantan thermocouple made of wires of diameter of 0.127 mm was inserted between the two identical iPP plates. The sandwich was placed in a 2-mm-thick aluminum mold, melted at  $220^\circ\text{C}$ , melt annealed for 5 min, and then quickly placed between two polished aluminum blocks with electronically controlled steady temperature (with the precision  $0.1^\circ\text{C}$ ) for crystallization. The temperature in the middle of a sample was measured by means of embedded thermocouple connected to a meter until the steady temperature was achieved. For the determination of cooling characteristic of the system, the whole procedure was repeated with noncrystallizing atactic polystyrene (aPS) samples (thermal diffusivities of iPP and PS melts are very similar). The temperature was monitored in that way during 30 crystallization experiments. After crystallization, the samples were cut to check and determine the position of the thermocouple. Only the experiments with thermocouple embedded in the sample center were considered. The resulting thickness of iPP samples was 1.9–1.95 mm. Thin sections were examined in light microscope showed that samples of all three iPP contained predominantly  $\alpha$  phase spherulites;  $\beta$ -phase content was within 5% limit. In order to determine the crystallinity, differential scanning calorimetry measurements were conducted at a heating rate 10 K/min in a Du Pont TA 2000 apparatus on 6–7.5 mg samples cut out from the plates. Assuming the same values of  $\Delta H_f$ ,  $d_c$ , and  $d_a$  as for theoretical predictions, and recalculating mass crystallinity for volume crystallinity, the following volume crystallinity degrees were obtained: 0.43 for RAPRA iPP1, 0.47 for Moplen S30G, and 0.41 for Malen P B200.

In Figure 10, the temperature in the middle of iPP plates against time is plotted as the samples are quenched and crystallized at  $120.7^\circ\text{C}$  for RAPRA iPP1,  $121.4^\circ\text{C}$  for Moplen S30G, and  $120.6^\circ\text{C}$  for Malen P B200. The aPS plate quenching is shown for reference. It is seen that time dependencies of temperature recorded inside iPP plates differ significantly from those for aPS plates due to crystallization process in iPP. While in aPS, the temperature drops down; in iPP, the temperature

**Table I** The Maximum Temperature Increase,  $\Delta T_{\max}$ , and the Ratio  $t_h/t_{hc}$  in the Middle of a Polymer Sample for Isokinetic Crystallization (IS) and Crystallization from Instantaneous Nuclei (IN) at Various Crystallization Temperatures,  $T_o$ 

$T_o$ (°C)	$d$ (mm)	$s$	$\Delta T_{\max}$ (°C)	$t_h/t_{hc}$	
130	IN	2	0.6	0.55	1.07
		5	0.6	2.4	1.37
	IS	2	0.6	0.47	1.04
		5	0.6	2.1	1.24
122.5	IN	2	0.6	2.7	1.30
		2	0.45	2.2	1.21
	IS	2	0.6	2.3	1.18
		2	0.45	1.9	1.14
120	IN	2	0.6	3.9	1.41
		2	0.45	3.2	1.31
	IS	2	0.6	3.5	1.26
		2	0.45	2.9	1.20

decreases quickly during quenching and then increases to a maximum as crystallization continues. At the end, the ambient temperature is reached. The values of the maximum temperature increase are 1.8, 2.1, and 1°C for RAPRA iPP1, Moplen S30G, and Malen P B200, respectively. Also, the time dependencies of temperature increase in the middle of the sample differ, the time of duration of temperature increase is the longest in Malen P B200 and the shortest in Moplen S30G. To characterize the crystallization kinetics, the egzotherms during isothermal crystallization at respective temperatures of 0.45–0.5 mm thick films of RAPRA iPP1, Moplen S30G, and Malen P-B-200 in DCS apparatus were recorded. The films were obtained by compression molding. Prior to crystallization, the samples were melted at 220°C, melt annealed for 5 min, and quickly cooled to the crystallization temperature. The total amount of heat liberated during isothermal crystallization in DSC was within a 5% limit equal to that absorbed during melting of thick samples. In Figure 11, the heat flow and temperature recorded during isothermal crystallization of iPP samples at corresponding temperatures are plotted. The fastest crystallization occurs in Moplen S30G, slower in RAPRA iPP1, and the slowest in Malen P B200. It follows then that faster crystallization causes greater temperature increase but for a shorter time than in the slower crystallization. Comparison of Figures 10 and 11 shows also that the temperature increase in the middle of a thicker sample is still significant while crystallization at the

same temperature in thin sample is already completed.

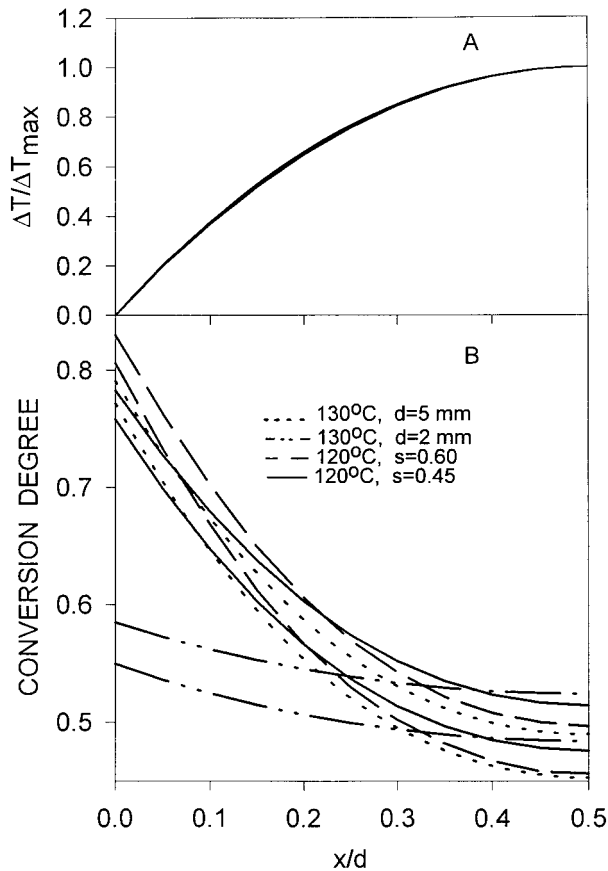
From the comparison of Figures 7(A) and 8(A) with 10(A), it follows that the temperature increase inside the RAPRA iPP1 plate is slightly lower but lasts longer than that predicted theoretically. However, it should be noted here that the secondary crystallization process and the increase of the crystallinity degree of spherulites with crystallization temperature was neglected. Neglecting the increase of crystallinity with temperature, one decreases the expected temperature buildup. In iPP, secondary crystallization contribution becomes pronounced after half-time of conversion,<sup>29</sup> when the rate of primary crystallization decreases. Attributing the entire heat released until the end of primary crystallization to primary crystallization, one only overestimates somewhat the expected initial temperature increase. Also the thermocouple made of metal wires slightly cools down the surrounding polymer because of high heat conductivity and thermal diffusivity of metals [see Appendix]. All three effects, although leading to lower temperature elevation, cannot be the reason of longer duration of the temperature increase. Both effects could be explained only by slower than predicted RAPRA iPP1 crystallization with primary nucleation differing from the two model processes considered.

## CONCLUSIONS

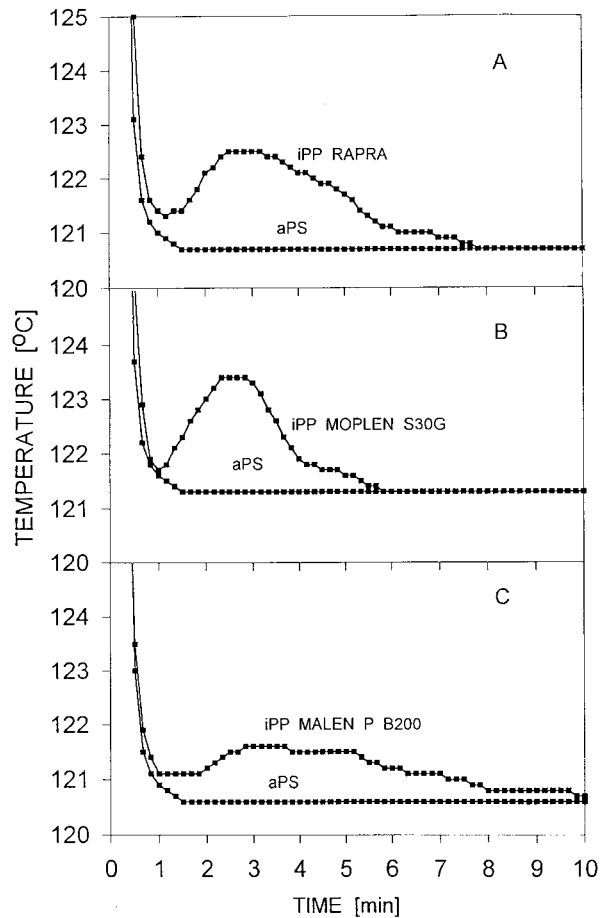
It was shown that the change of polymer thermal properties during crystallization and the decrease

of growth rate with temperature decreases while the presence of the second, approaching crystallization front increases the temperature buildup at crystallization front caused by the release of latent heat of fusion. The higher the temperature increase at the crystallization front, the more significant the influence of  $g(T)$  dependence on temperature buildup. The major effect, however, is the enhancement of the temperature increase if two crystallization fronts approach each other.

The crystallization of iPP in bulk, where heat production rate is determined by the overall rate of crystallization causes the increase of the temperature in sample interior accompanied by slower conversion of melt into spherulites. The effect depends on sample thickness, crystallinity degree, and on crystallization kinetics.



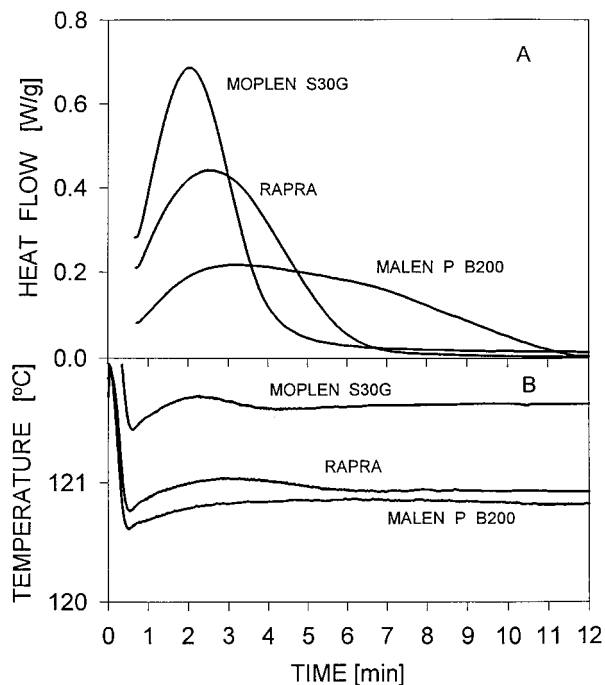
**Figure 9** (A,B) Temperature increase at the time when maximum temperature is achieved in the middle of sample, scaled to maximum temperature increase, and conversion degree against distance scaled to the sample thickness. In (B), the upper curve from each pair of curves represents the isokinetic crystallization, and the lower curve represents crystallization from instantaneous nuclei.



**Figure 10** Time dependencies of the temperature measured in the middle of 2-mm-thick plates of iPP and aPS quenched and kept at constant temperature: (A) RAPRA iPP1; (B) Moplen S30G; (C) Malen P B200.

The measurements of the temperature inside crystallizing iPP confirm the significant increase of the temperature due to release of heat of fusion, predicted theoretically.

The results indicate that the dissipation of latent heat of fusion is a controlling factor of the polymer crystallization in bulk. Polymers crystallize isothermally only in thin films and/or at low undercoolings. In other cases, one has to account for the temperature increase due to crystallization. The considerations were limited to polypropylene and to initially isothermal conditions but one can expect similar effects in other polymers and also in the course of crystallization during cooling. The strong dependence of the temperature increase of thickness implies that significant temperature elevation influencing polymer properties might be expected during both laboratory and industrial processing of thick elements.



**Figure 11** Time dependencies of heat flow and temperature during isothermal crystallization of iPP samples in DSC apparatus.

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## APPENDIX

A need to estimate the error of temperature measurements in the temperature monitoring experiment arises from the conditions of that experiment, with a small amount of polymer and the necessity for the thermocouple wire to pass through a metal mold being at ambient temperature. To estimate exactly the effect of heat flow through metal wire embedded in a polymer plate on the temperature of that wire, one has to solve the differential equation of heat conduction accounting for shape of a polymer plate, a presence of metal wires inside a plate, and thermal contacts between polymer, wires, and mold. However, to estimate an order of magnitude of the effect, a much simpler approach to that problem is possible by application of the solution for heat generation or absorption in a cylinder of perfect conductor surrounded by an infinite medium of the thermal conductivity  $K$  and the thermal diffusivity  $a$ .<sup>30</sup> The temperature decrease  $\Delta V$  in the cylinder of

radius  $r$  resulted from an absorption of heat at the rate  $Q$  per length unit per time unit for large values of time  $t$  is

$$\Delta V = Q(4\pi K)^{-1} \ln(2.2458atr^{-2}) \quad (22)$$

The heat  $2K_m\Delta T(hR)^{-1}(\pi r^2)$ , which flows through the thermocouple wires to the mold due to temperature difference  $\Delta T$  along the wire length  $hR$ , is subtracted from the polymer by a wire of length  $2(h-1)R$ , where  $\Delta T$  is the temperature difference between the central part of the plate and the mold,  $R$  is a distance from the polymer plate center to the mold, and  $K_m$  is the wires thermal conductivity. Hence, the decrease of the temperature of the thermocouple wire is

$$\Delta V/\Delta T = K_m r^2 [4KR^2 h(1-h)]^{-1} \times \ln(2.2458at/r^2) \quad (23)$$

It should be noted that, in general,  $Q$  depends on a distance from the mold and on time and is governed by local momentary value of  $\Delta T - \Delta V$ . So eq. (23) is an approximate expression for rather small values of  $\Delta V$ . It follows from eq. (23) that for better precision of temperature measurement, one has to decrease the  $r/R$  and  $K_m/K$  ratios. In the experiment of concern, the thermocouple was made of wires of  $2r = 0.127$  mm extended through the middle part of polymer sample. Constantan–nichrom wires were chosen because of their relatively low  $K_m = 20$  W m<sup>-1</sup> K<sup>-1</sup>. For  $R = 10$  mm,  $a = 10^{-7}$  m<sup>2</sup> s<sup>-1</sup>,  $K = 0.2$  W m<sup>-1</sup> K<sup>-1</sup>, and  $t = 2$  min (the time for which the maximum temperature increase due to crystallization was recorded in RAPRA iPP1 plate), the decrease of temperature in wires was only of order of several percent for various  $h$  values. One has to mention, however, that for copper wires of  $K_m$  near 400 W m<sup>-1</sup> K<sup>-1</sup>, the error due to the heat transport through the wires increases significantly. The measurements of temperature increase due to iPP crystallization by means of copper–constantan thermocouple gave considerably lower values than those obtained using constantan–nichrom thermocouple made of wires of the same diameter.

## REFERENCES

1. H. S. Carslaw and J. C. Jaeger, *Conduction of Heat in Solids*, Clarendon, Oxford, 1959, pp. 282–296.
2. C. Schwarz, *Arch. Eisenhuttew.*, **5**, 139 (1931).

3. C. Schwarz, *Z. Angew. Math. Mech.*, **13**, 202 (1933).
4. N. M. H. Lightfoot, *Proc. Lond. Math. Soc.*, **31**, 97 (1930).
5. A. Wasiak, *Chemtracts-Macromol. Chem.*, **2**, 211 (1991).
6. E. Piorkowska and A. Galeski, *Polymer*, **33**, 3985 (1992).
7. A. N. Kolmogoroff, *Izv. Akad. Nauk SSSR, Ser. Math.*, **1**, 355 (1937).
8. M. J. Avrami, *J. Chem. Phys.*, **7**, 1103 (1939).
9. M. J. Avrami, *J. Chem. Phys.*, **8**, 212 (1940).
10. M. J. Avrami, *J. Chem. Phys.*, **9**, 177 (1941).
11. U. R. Evans, *Trans. Faraday. Soc.*, **41**, 365 (1945).
12. T. Ozawa, *Polymer*, **2**, 150 (1971).
13. N. Billon, J. M. Esclaine, and J. M. Haudin, *Colloid Polym. Sci.*, **267**, 668 (1989).
14. K. Nakamura, K. Katayama, and T. Amano, *J. Appl. Polym. Sci.*, **17**, 1031 (1973).
15. E. Piorkowska, *J. Phys. Chem.*, **99**, 14,007–14,031 (1995).
16. B. Wunderlich, *Macromolecular Physics, Vol. 1, Crystal Structure, Morphology, Defects*, Academic, New York, 1973, pp. 388–389.
17. T. R. Fuller and A. L. Fricke, *J. Appl. Polym. Sci.*, **15**, 1729 (1971).
18. S. Pattnaik and E. V. Thompson, *Am. Chem. Soc. Polym. Prepr.*, **22**, 199 (1981).
19. D. W. Van Krevelen, *Properties of Polymers*, Elsevier, Amsterdam, 1976, Chap. 5.
20. D. R. Gee and T. P. Melia, *Polymer*, **3**, 286 (1962).
21. K. Eiermann, *Kolloid Z.*, **3**, 201 (1964).
22. K. Eiermann, *J. Polym. Sci., Part C*, **6**, 157 (1964).
23. C. L. Choy, *Polymer*, **18**, 984 (1977).
24. H. S. Carslaw and J. C. Jaeger, *Conduction of Heat in Solids*, Clarendon, Oxford, 1959, pp. 256–270.
25. E. Martuscelli, C. Silvestre, and G. Abate, *Polymer*, **23**, 229 (1982).
26. E. Clark and J. D. Hoffman, *Macromolecules*, **17**, 878 (1984).
27. H. S. Carslaw and J. C. Jaeger, *Conduction of Heat in Solids*, Clarendon, Oxford, 1959, p. 363.
28. A. Galeski, in *Polypropylene*, J. Karger-Kocsis, Ed., Chapman and Hall, London, 1994.
29. E. Martuscelli, M. Pracella, and L. Crispino, *Polymer*, **24**, 693 (1983).
30. H. S. Carslaw and J. C. Jaeger, *Conduction of Heat in Solids*, Clarendon, Oxford, 1959, p. 345.