Analysis of the crystallization kinetics of isotactic polypropylene by infra-red spectroscopy

Andrzej Włochowicz and Marek Eder
Textile Institute, Technical University of Łódź, Branch of Bielsko-Biała, Bielsko-Biała, ul.P.Findera 32, 43-300 Poland
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INTRODUCTION

The intensity of the bands 1168, 998, 899, 842 and 809 cm^{-1} of the infra-red absorption spectrum of isotactic polypropylene (PP) decreases with the decreasing crystallinity of PP[1] and disappears in the i.r.-spectrum of the molten polymer (*Figure 1*). We assumed a linear relationship between the optical density of the crystalline sensitive bands and the crystallinity of the polymer and used i.r. absorption technique to follow the isothermal crystallization of polypropylene

EXPERIMENTAL

The subject of the analysis was a Polish polypropylene F-104 of isotactic index 95-97% and intrinsic viscosity $[\eta] = 1.64$ determined in decalin at 135°C.

Measurements of the crystallization rates were carried out with aid of the Beckman 4220 i.r. spectrophotometer with variable temperature cell FH-01.

The PP film was placed between two plates of crystal NaCl and the distance was fixed at 0.1 mm using teflon spacers and the system was held at 185°C for 3 min. After melting the sample, the cell was rapidly cooled to the temperature of interest with CO_2 being expanded from the cylinder. A time base record was then obtained of the 998 cm^{-1} transmission changes until crystallization was complete.

In addition the growth rate of spherulites of PP was observed. A piece of PP-film on a quartz plate was sustained for 3 min at 185°C and was quickly transferred to the heated stage of a Boetius microscope set at the desired temperature. Growing spherulites were recorded photographic in time steps depending on the diameter of spherulites.

RESULTS

The degree of phase transition was calculated from the transmission curves of the 998 cm^{-1} band using the relationship:

$$\frac{X_t}{X_\infty} = \frac{\log\frac{D_0}{D_t}}{\log\frac{D_0}{D_\infty}} \qquad (1)$$

Here D_0 denotes the transmission at the moment of beginning of crystallization, D_∞ is the transmission at the end of crystallization in the test time scale, without taking into account the secondary crystallization, D_t is the transmission at the time t, X_t and X_∞ are the crystallinities at the time t and at the termination of the crystallization, respectively.

Using the equation of Mandelkern[2] we analysed the experiment in a plot

$$\log\left[-\ln\left(1-\frac{X_t}{X_\infty}\right)\right]$$

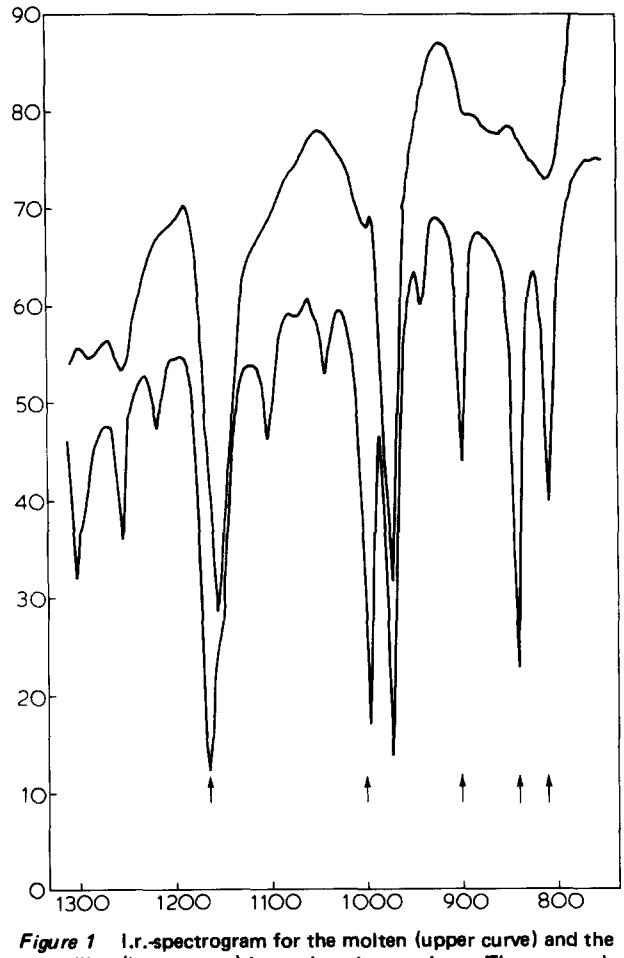

Figure 1 I.r.-spectrogram for the molten (upper curve) and the crystalline (lower curve) isotactic polypropylene. The arrows show the regular bands

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against log t (*Figure 2*) and determined the constants K and n which describe the rate and mechanism of crystallization (*Table 1*).

The exponent $n=3$ is an analogue to the results obtained by other authors from dilatometric or other data[3-10].

Microscopic examinations (*Figure 3*) reveal a linear relationship between the spherulite size and the crystallization time. Some values for the growth rate of the spherulite radius (G), calculated by the least square method, are listed in *Table 2*. We accepted the method of interpretation of temperature dependence of K and G proposed by Takayanagi *et al.*[11] and Ishizuka *et al.*[9]:

$$\log K = \log K_0 - \frac{n C_1 T}{(T-C_2)^2} - \frac{C_3 T_m^\circ}{T\Delta T} \qquad (2a)$$

$$\log G \sim \sim \log G_0 - \frac{C_1 T}{(T-C_2)^2} - \frac{C_4 T_m^\circ}{T\Delta T} \qquad (2b)$$

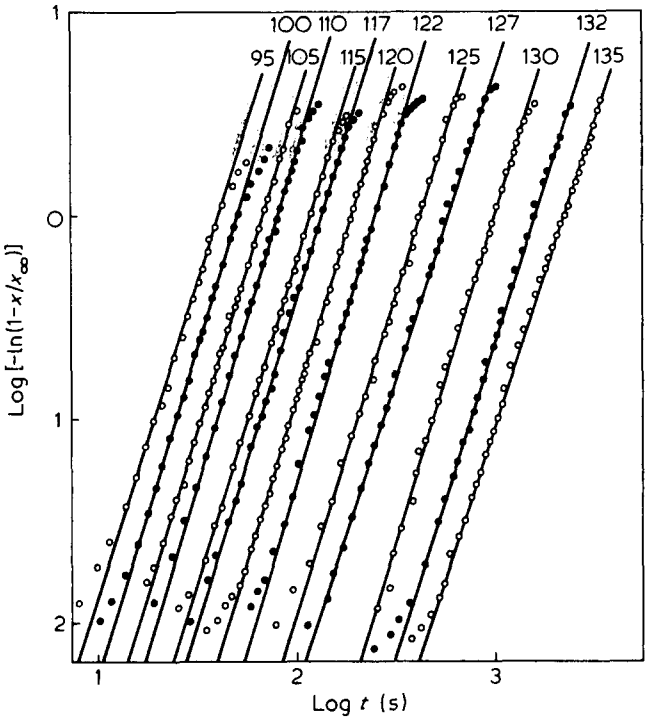

Figure 2 Avrami diagrams for polypropylene

Table 1 Kinetic parameters of isothermal crystallization

Temperature (°C)	Parameters n	log K	$t_{0,5}$ (s)
135	2.98	−10070	2073
132	3.03	−9808	1529
130	3.05	−9293	977
127	2.97	−8316	561
125	3.03	−8076	407
122	3.12	−7625	242
120	3.08	−7123	181
117	2.96	−6430	130
115	3.03	−6334	115
110	3.05	−5922	78
105	3.05	−5782	66
100	3.05	−5294	48
95	2.96	−4854	38

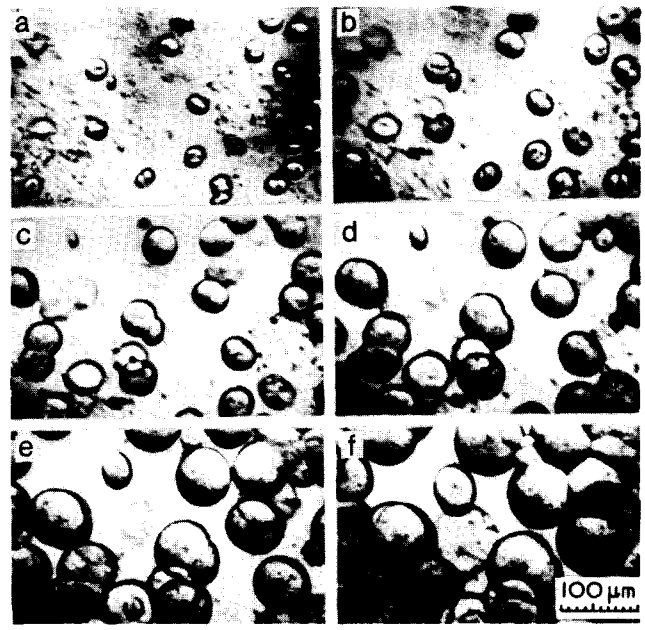

Figure 3 Photomicrographs of the spherulites created in the isothermal crystallization process at 142° C. Elapse at crystallization time: (a) 28; (b) 37; (c) 47; (d) 60; (e) 75; (f) 90 min

Table 2 Spherulitic growth rates G

Temperature (° C)	(µm/s)
142	0.0080
141	0.011
140	0.016
139	0.019
138	0.025
137	0.029
136	0.035
135	0.044
134	0.061
132	0.080
130	0.139
129	0.166
127	0.218
126	0.268
125	0.339
123	0.438

Similarly, the average velocity of crystallization ($\bar{V}_c$)[13] and the crystallization half-time ($t_{0.5}$) can be expressed as:

$$-\log t_{0.5} = 1/n \log\left(\frac{K_0}{\ln 2}\right) - \frac{C_1 T}{T-C_2)^2} - \frac{C_5 T_m^\circ}{T\Delta T} \qquad (2c)$$

$$\log \bar{V}_c = \log 0.95 + 1/n \log 0{,}334\, K_0 - \frac{C_1 T}{(T-C_2)^2} - \frac{C_6 T_m^\circ}{T\Delta T} \qquad (2d)$$

where C_1, C_2 are the constants connected with the *WLF* coefficients[12] and $T_g = 0°C$[9]; C_3–C_6 are the constants including the surface free energies of the nucleation centres and the enthalpy of melting ΔH_f; T_m° is the melting temperature of the crystalline phase, 184°C[9]; ΔT is the undercooling; n is constant depending upon the geometry of crystal growth.

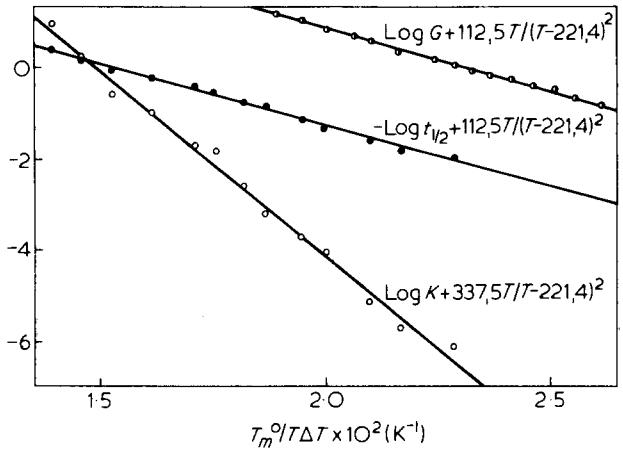

Figure 4 Diagrams of the equations (2)

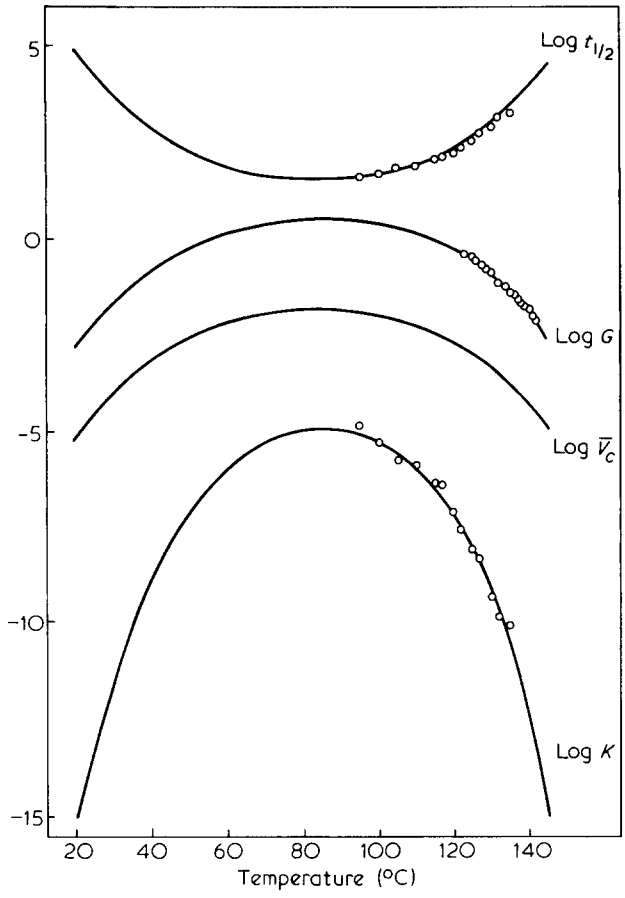

Figure 5 Log K, log G, log $t_{0,5}$ and log $\bar{V}_C$ calculated from equations (2) and experimental data as a function of temperature

The equations (2) are illustrated in *Figures 4* and *5* and show that the extremes of the parameters which characterize the isothermal crystallization process are in the temperature range 80°–90°C.

The numerical values calculated with the least square method: $C_3 = 809.8; C_4 = 267.1; C_5 = 270.3$ gave the value of surface free energy (σ_c) of crystal plane containing chain folds equal to $\sigma_c = 49.6$ erg cm^{-2}. The following values were used: $\Delta H_f = 1{,}34.10^9$ ergcm^{-3} [10], $a_0 = 5{,}46.10^{-8}$ cm, $b_0 = 6{,}56.10^{-8}$ cm[14] and relationships[15]

$$C_3 = 12 b_0 \cdot \sigma \cdot \sigma_c / 2.303 \cdot k \cdot \Delta H_f$$

$$\sigma = 0.11 \Delta H_f (a_0 b_0)^{1/2}$$

where a_0, i, b_0 are the parameters of crystal lattice and k = Boltzmann's constant.

CONCLUSIONS

(1) The crystallization of polypropylene is three-dimensional, spherical (the coefficient C_3 is nearly three times higher than C_4 and C_5).

(2) Avrami exponent $n = 3$ and micrographs imply a heterogeneous, athermal nucleation and the growth of spherulites from predetermined nuclei.

(3) The parameters of crystallization process of polypropylene are generally in accordance with the literature data but in lower temperature range K is smaller than the published values[3–10].

(4) The applied spectrophotometric method is distinguished by its accuracy. Additional advantages are its simplicity in measuring and the ease and clarity of interpretation of the results which make it useful for the analysis of polymer crystallization kinetics. The applied procedure is limited by the time constant of the i.r.-spectroscope and allows large supercoolings.

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