Linear isothermal crystal growth rate of i-polypropylene by differential scanning calorimetry

Atanas Milkov Atanassov

Higher Institute of Electrical and Mechanical Engineering, Laboratory of Electron and Light Microscopy, 1156 Sofia, Bulgaria

ABSTRACT

In the present work equations are derived that enable us to calculate the linear crystal growth rate using DSC-isothermal peaks. The primary nuclei density is taken into account by measuring the average spherulite radius of already crystallized samples by means of polarization microscopy. The results, thus obtained, show that the isothermal crystallization process of i-polypropylene proceeds in two stages, the second one being of higher rate.

INTRODUCTION

The crystal growth rate, G, in the equation of Hoffman et al. (1) has a dimension (cm/s), while using differential scanning calorimetry (DSC) and Avramy-isotherms (2) one obtains the crystallization rate in (1/s). Futhermore, crystallizing a sample in a DSC, one investigates the overall crystallization rate, i.e. no account is made of the number of spherulites in a unit of volume. Most frequently, the increased overall crystallization rate is not due to increased radius growth rate but only to a larger number of the growing spherulites. This results in incorect conclusions about the value of σ_e, the fold surface free energy of the secondary nucleus, which controls the crystallization rate at a constant primary nucleation rate.

The aim of the present work is to describe a new approach to the spherulite radius growth rate calculation using DSC-isothermal crystallization data.

EXPERIMENTAL

150 µm films of i-polypropylene (i-PP), an industrial product of HERCULES Company (USA), (94% isotacticity,and an viscosity average molecular weight M_v = 500 000) are studied. The crystallization experiments were conducted by a DSC-equipment, product of the Academy of Sciences of USSR (DSM-2), the temperature scale being calibrated with standart pure indium and tin samples. Isothermal crystallization is realized in the following way: 10 mg samples of i-PP are heated at 3 K/min heating rate until the temperature of T=463 K (190°C) is reached. Having kept the samples at this temperature for 5 minutes, cooling begins at the same cooling rate down to the desired

temperature for isothermal crystallization. A relatively low cooling rate is applied to avoid undercooling effects, attending the nonstationary processes of establishing constant temperature in the cell as well as in the polymer sample.

RESULTS AND DISCUSSION

Method for calculating the linear crystal growth rate G

The mass M_n of density ρ (g/cm^3), crystallized up to the instant t_n in a spherulitic polymer sample is:

$$M_n = a N \rho (4/3) \pi r_n^3 \qquad (1)$$

where: N is the number of spherulites in the DSC-pan; r_n is the average spherulite radius at $t=t_n$ (t in seconds); a is the average crystallinity.

Assuming that the spherulite radius growth rate of i-PP is a constant value ($G=dr/dt$) for a given crystallization temperature, one can write:

$$r_n = G.t_n \qquad (2)$$

Thus:

$$M_n = a N \rho (4/3) \pi G^3.t_n^3 \qquad (3)$$

The amount of crystal phase formed per a unit of time:

$$(dM/dt)_n = 4 a . \rho. \pi .N.G^3.t_n^2 \qquad (4)$$

In Eq.4 the quantity N can be expressed as:

$$N = C \int_0^\infty (dH/dt)dt \Big/ a . \rho .(4/3) \pi .R^3 \qquad (5)$$

(C in g/J is a constant, converting the amount of heat into amount of mass; R is the final spherulite radius and $\int_0^\infty (dH/dt)dt$ is the heat of the whole crystallization process).

Taking into account that the rate of mass transfer is proportional to the rate of heat evolution, i.e.

$$(dM/dt)_n = C (dH/dt)_n \qquad (6)$$

and combining Eqs.4-6, one obtains:

$$(dH/dt)_n = (3G^3t_n^2/R^2).\int_0^\infty (dH/dt)dt \qquad (7)$$

Eq.7 is correct in the very beginning of the crystallization process. In the later stages of the process, the completion of the polymer, able to crystallize strongly reduces the value of $(dH/dt)_n$. Hence, the heat evolution rate normalized to the

unit of mass is:

$$(dH/dt)_n \cdot \int_0^\infty (dH/dt)\,dt \bigg/ \int_{t_n}^\infty (dH/dt)\,dt \qquad (8)$$

Then, Eq.7 takes the form of:

$$\left[\frac{(dH/dt)_n}{\int_{t_n}^\infty (dH/dt)\,dt}\right]^{0.5} = (3G^3/R^3)^{0.5}\, t_n \qquad (9)$$

The respective quantities are shown in Fig.1.

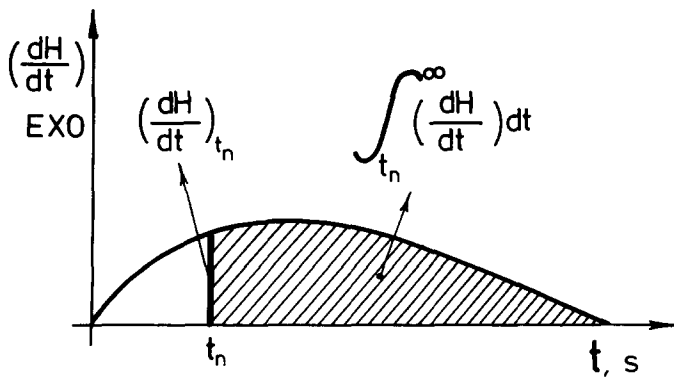Fig.1. The quantities, entering Eq.9, marked on a DSC-scan.

With:

$$\left[(dH/dt)_n \bigg/ \int_{t_n}^\infty (dH/dt)\,dt\right]^{0.5} = F_n \qquad (10)$$

and

$$(3G^3/R^3)^{0.5} = C*$$

Eq.9 gives:

$$F_n = C* \cdot t_n \qquad (11)$$

Calculation procedure

The time axis of a DSC-scan is devided at intervals of 30 sec and at the end of each interval (t_n=30; 60; 90; 120, etc.)the quantity F_n is calculated according to Eq.10. For this purpose

the respective quantities, $(dH/dt)_n$ and $\displaystyle\int_{t_n}^{\infty} (dH/dt)dt,$

are measured, the former being the distance between the base-line and the DSC-trace (in J/s) and the latter-the peak area from the specified value of t_n up to the end of the crystalliz-ation (in J). The linear crystal growth rate G (in cm/s) is determined from the slope of the plot F versus t (R is measured by means of polarization microscopy or small-angle light scattering.

Some experimental results

The DSC-isothermal crystallization peaks of i-PP in the temper-ature range of 391-398 K are worked out following the calcul-ation procedure just mentioned. The results are presented in Fig.2 (a and b). For all crystallization temperatures studed, a well-defined break is observed in the isothermal plots F vs t. According to Eqs. 9-11, the different slopes dF/dt at a constant value of the spherulite radius R=0.0075 cm (established exam-ining microtom thin sections by a polarizing microscope) means that two different values of the rates (G_I and G_{II} respectively) are involved. In the temperature range under investigation,the ratio, G_{II}/G_I, increases when the crystallization temperature increases, being $G_{II}/G_I=1.41$ at T=391 K and $G_{II}/G_I=1.73$ at T=398 K. The second, higher growth rate, stage could not be identified as a secondary crystallization because: a)the second-ary crystallization rate is lower than the primary one; b)many authors found that for i-PP secondary crystallization is lack-ing altogether (3).

Padden and Keit have established (4) that at low temperatures

the ratio $(G_\beta/G_\alpha)=1.2$ (G_β and G_α are the growth rates of

β-hexagonal and α-monoclinic i-PP phases), while Lovinger

et al. (5) reported that at higher temperatures $(G_\beta/G_\alpha)=1.7$.

Then, if such a speculation is permitted, the two slopes might be assigned to the α and β-phase crystallization processes, respectively.

The linear growth rate of spherulites is a secondary-nucleation controlled process and depends on the temperature T and under-cooling ΔT as in the following equation (1):

$$\log G = (\log G_o - E_d/2.3kT) - 4b_o \cdot \sigma \cdot \sigma_e \cdot T_m^o/2.3k \cdot \Delta H_f^o \cdot T \cdot \Delta T \qquad (12)$$

where G_o is accepted to be a constant (10^{13} 1/s), E_d is the activation energy for transport across the liquid-crystal interface, k is the Boltzman's constant, T_m^o is the equilibrium melting enthalpy in ergs per cc, σ and σ_e are the lateral and fold surface free energy of the secondary nucleus, respect-ively, in ergs/cm^2, b_o is the thickness of a monomolecular layer in cm.
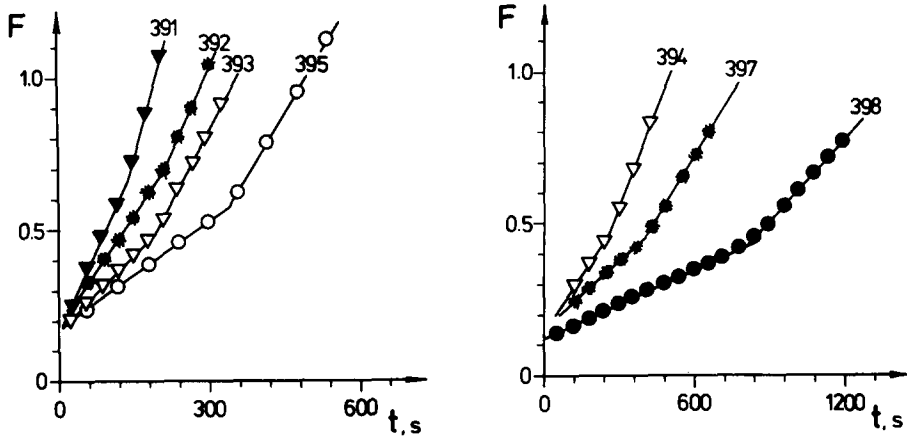
Fig.2. The function F plotted against the time t, according to
equation 11. The numbers indicate the crystallization
temperatures.

The isothermal crystallization is conducted at temperatures
highly exceeding (T_g+100), T_g being the glass transition temper·
ature of i-PP $(T_g=285$ K) where the validity of Williams-Landel-
Ferry Eq. for E_d is not proved. Since in this region the
process is secondary-nucleation controlled, the term $(E_d/2.3kT)$
can be regarded as constant and it is to be calculated from
the intercept on the ordinate of the plot logG vs $(T_m^O/T.\Delta T)$.

For i-PP the following values for ΔH_f^O and T_m^O are used:
$\Delta H_f^O=62$ cal/g $(233.8\times10^7$ergs/cc$)$; $(T_m^O)_a$ $=493$ K; $(T_m^O)_\beta$ $= 473$ K.
The value of σ is estimated following Hoffman (1):

$$\sigma = 0.11\Delta H_f^O(a_o.b_o)^{0.5} \tag{13}$$

With crystal dimensions $a_o=5.46\times10^{-8}$ cm and $b_o=6.56\times10^{-8}$ cm one
obtains $\sigma =15.4$ ergs/cm^2.

In Fig.3 three lines are drawn, line 1 being the plot of logG
vs the temperature variable $(T_m^O/T.\Delta T)$ when G is calculated
from the first part of the plots F vs t $(T_m^O=493$ K is accepted).
a -monoclinic form is considered to be first to begin crystal-
lizing, which was supported by polarization microscopy observ-
ations. By taking $logG_o=13$ s^{-1} and the above mentioned values
of the quantities entering Eq.12, respective values of both
energies for this stage are obtained: $E_d=11.1$ kcal/mol (46.5
kJ/mol) and $\sigma_e=203$ ergs/cm^2 (203 mJ/m^2).

Line 2 represents the logG vs $(T_m^O/T.\Delta T)$ data of the second
part of the plots F vs t accepting that structure II is β -

hexagonal modification of i-PP. In the same way the values
E_d = 18.8 kcal/mol (78.8 kJ/mol) and σ_e=100 ergs/cm^2
(100 mJ/m^2) have been estimated from the intercept and the
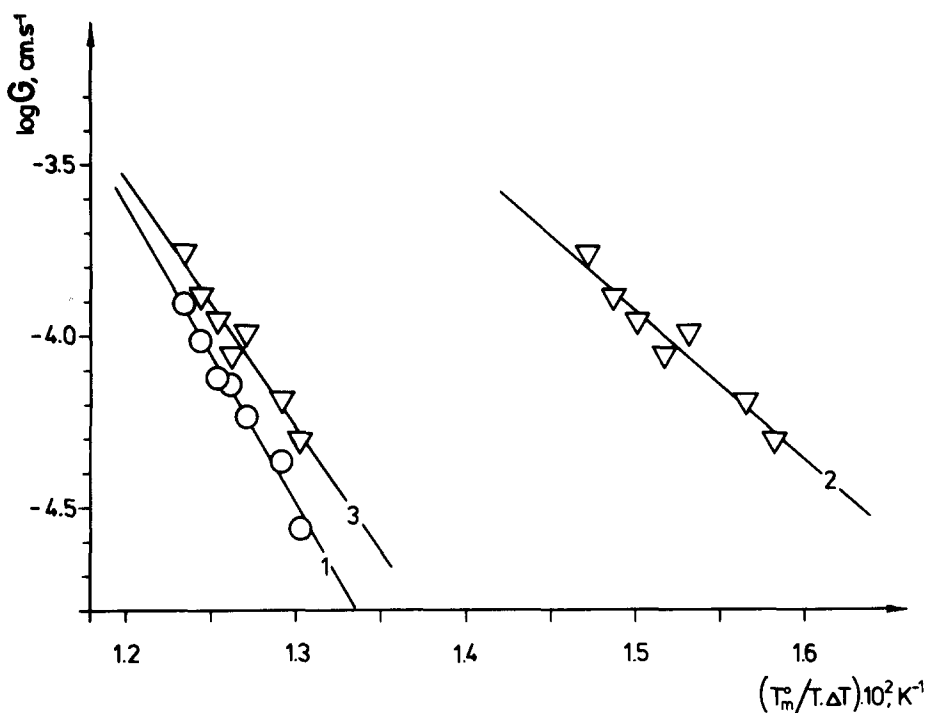slope, respectively.

Fig.3. Plot of logG versus $(T_m^o/T.\Delta T)$ for crystallization of:
1) α -monoclinic i-PP (first part of the plots F vs t);
2) β -hexagonal i-PP crystallizing in the second part,
T_m^o=473 K;
3) α -monoclinic i-PP crystallizing in the second part,
T_m^o=493 K.

It is important to comment on the fold surface and transport
energies obtained for both structures. The temperature coef-
ficients of the growth rates differ by a factor of two, being
in this case less for the second stage. E_d for crystallization
of structure II is much higher than that of structure I.
Apparently, the viscosity in the second stage is highly
increased because of the physical network existing in a 63%

crystallized polymer matrix.

Checking the assumption, that the break in the F vs t plots represents a real morphological transition, the relative extend of crystallization up to the break point, $X_{b.p.}$, has been determined by integration of the DSC-scans. $X_{b.p.}$ was then compared with the ratio of the peak intensity of β-phase (I_β) with respect to the sum of the intensities of α-phase (I_α) following the formula of Turner-Jones (6), the intensities being obtained by wide-angle X-ray scattering measurments. The former one ($X_{b.p.}$) has been estimated to be about 63% (±5%) while the ratio (I_β/I_α) does not exceed 15% in all samples investigated, i.e. only a small amount of the crystal phase, formed in the second stage is due to β-phase crystallization. Obviously, in spite of the fact that the ratio of both fold surface energies is two, the break in the F vs t plots is not related to a morphological transition. Then, within a small error, it can be accepted that α-phase crystallizes in the second stage as well. Line 3 in Fig.3 represents the second stage growth rate data assuming that structure II is α-phase. The resulting energies are: σ_e =167 ergs/cm^2 (167 mJ/m^2) and E_d=14.4 kcal/mol (60.3 kJ/mol).

Following Hoffman et al.(1) the lamellae thicknesses, l, have been calculated to be l_I=107x10^{-8}cm and l_{II}=92x10^{-8}cm, i.e. thinner crystalline lamellae are formed in the second stage. Possibly, this is caused by the higher value of E_d in the physically crosslinked melt.

In brief, the new approach presented here gives a method of growth rate calculations, using DSC-isothermal crystallization data. The main result is that this calculation procedure reveals stages in the crystallization process of different growth rates, a phenomenon which is not reported to be observed analysing the crystallization kinetics of i-PP either by DSC and dilatometry or by hot-stage microscopy measurements.

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