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POLYMER CRYSTALLIZATION
Isothermal and non-isothermal spherulite growth parameters from optical microscopy and differential scanning calorimetry

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Differential scanning calorimetry (dual furnace, null-balance, DSC) and optical microscopy (OM) have been used to study the isothermal crystallization kinetics of poly(oxymethylene)-POM. The non-isothermal crystallization of the same material has also been studied by optical microscopy.

A very controversial problem is whether the isothermal kinetic parameters may be applied to describe the non-isothermal crystallization. The results show that the kinetic spherulite growth parameters obtained by non-isothermal optical microscopy are, within the experimental errors involved, the same as those obtained by isothermal optical microscopy or isothermal DSC. The importance of this finding is highlighted.

Keywords: crystallization kinetics, DSC, optical microscopy, spherulite growth parameters

Introduction and scope

The most practical and important scientific and technological challenge in the field of polymer crystallization is perhaps the accurate modelling and prediction of the non-isothermal crystallization under real processing conditions, from first principles and basic experimental data, which are normally best obtained in isothermal conditions. This long-term objective requires an increasingly closer study of the detailed mechanism and kinetics of the crystallization process, even for the simpler case of quiescent melts.

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The kinetics of polymer crystallization, from a local point of view, may be described as a nucleation-governed process, both in its initiation and growth (surface nucleation) steps. In the early work of Turbull and Fischer [1], based on the theory of absolute reaction rates, an expression was derived for the rate of nucleation of a second phase in simple condensed systems (consisting of atoms or simple molecules), i.e.

$$N^* = (N_A kT / h)\cdot\exp[-(\Delta F^* + \Delta\Phi^*)/(kT)] \tag{1}$$

where ΔF^* is the free energy of activation for the diffusion of a molecule across the phase boundary and $\Delta\Phi^*$ is the free energy required to form a nucleus with the critical size (k = Boltzmann's constant; h = Planck's constant; N_A = Avogadro's number; T = absolute temperature). Equation 1 gives N^* as the number of nuclei of critical size formed per unit time and per mole of initial phase.

In later works, Hoffman *et al.* [2, 3] applied these nucleation concepts and formalism in the study of the crystalline growth of linear polymers with chain folding. For a coherent surface nucleation process, the nucleation-controlled linear growth rate in the direction normal to the surface may be approximated by $G = bN^*/N_A$, where b is the thickness of the nucleus and, in this way, the final expression for the linear growth rate, at the crystallization temperature T, becomes

$$G \approx (b\,k\,T/h)\cdot\exp[-\Delta F^*/(k\,T)]\cdot\exp[-\Delta\Phi^*/(k\,T)] \tag{2}$$

Here, the opposite temperature dependencies of the two exponentials yield the well known and documented maximum growth rate at some temperature above the glass transition temperature, T_g and below the thermodynamic melting point, T_m^o. The exact form of the functions that describe those dependencies, in particular that of the diffusion-related exponential, however, is still not definitely established, thus raising some difficulties in the accurate correlation and understanding of the actual crystallization behaviour of polymer materials.

However, at least four possibilities have been proposed [4] for $\Delta F^*/(kT)$, two of which are:

i) $\Delta F^*/(k\,T) = U^*/[R\,(T - T_\infty)]$, with U^* = 4100 cal/mole, $T_\infty = T_g - 51.6$, and R = gas constant, for crystallization temperatures between T_g and $T_g + 100$, and

ii) for crystallization temperatures outside this range, or when the polymer has a wide molecular weight distribution, $\Delta F^*/(kT)$ is taken to have the same WLF functionality, with the appropriate material-dependent adjustable constants C_1 and C_2, i.e.

$$\Delta F^*/(k\,T) = C_1\cdot C_2/(C_2 + T - T_g) \tag{3}$$

In the case of two-dimensional coherent surface nucleation, the nucleation term $\Delta\Phi^* / (kT)$ has the form $(K_g/T\Delta Tf)$, where $\Delta T = (T_m^o - T)$, and f is the usual correction factor that takes into account the decrease of the heat of fusion with the crystallization temperature [3], i.e. $f = 2T/(T_m^o + T)$; K_g is related to the lateral (σ) and fold surface (σ_e) free energies of the surface nucleus, as may easily be obtained by a straightforward calculation of $\Delta\Phi^*$.

The use of the resulting final expression for the spherulite growth rate, G, thus requires the knowledge of the appropriate and accurate values for the pre-exponential factor $G_o = bkT/h$ (whose slight temperature dependence may usually be neglected) and for C_1, C_2 and K_g. This problem has previously been analysed in some detail by Miller [4], who clearly defined the conditions that the experimental spherulite growth data should satisfy to yield values for G_o, C_1, C_2 and K_g. While K_g should always be possible to obtain to better than ± 10% [4, 5] from data covering only a limited temperature range, C_1 and (G_o, C_2) normally require increasingly wider temperature ranges, ideally from well below to well above the maximum growth rate temperature.

While, for some polymers, such extended temperature ranges are accessible, this work concentrates on the most unfavourable situation of data obtained near T_m^o, to show that even here there undoubtedly is a fundamental compatibility and definite linkage between the isothermal and non-isothermal polymer crystallization behaviour, despite much recent controversy [6–8]. In a separate paper of this Proc. [9], we undertake to accurately predict the kinetics of the non-isothermal crystallization of POM, from basic isothermal kinetic DSC and optical microscopy data for the same polymer.

As is well known, accurate isothermal DSC traces enable a very detailed characterization of the crystallization kinetics, by means of several possible parameters, one of which is the reciprocal crystallization half-time (partial peak area = 50% of the total), $1/t_{1/2}$, which may be proved to be proportional to G (heterogeneous nucleation) or to $[G^{(n-1)} N^*]^{1/n}$ (homogeneous nucleation), for a single mechanism process, if one uses either the Avrami's [10] or Tobin's [11] model to interpret the data.

Procedure

It is difficult to measure overall crystallization and spherulite growth rates for POM for below the melting point. As a consequence, the pre-exponential factor G_o and the parameters C_1 and C_2 cannot be determined as accurately as the nucleation-related K_g parameter [4].

As for many polymers, that can be investigated over wide temperature ranges, values of $C_1 \approx 25$ and $C_2 \approx 30$ K have been obtained [5], C_1 and C_2 have been set to these same values. Then, G_o and K_g have been determined by a two-parameter fit of Eq. (2), with the above ΔF^* and $\Delta\Phi^*$, to the experimental spherulite growth data obtained by optical microscopy, in both the isothermal and non-isothermal modes. The corresponding equation for the reciprocal crystallization half-times, $1/t_{1/2}$, was also used, in the same way, with the isothermal DSC data.

Experimental

The material used in this study was a well characterized [12, 13] commercial grade in POM-Delrin 150 (T_m^o =198.3°C, T_g = –82 to –74°C, N-average mol. w. ≈70000 g/mole).

The microscopical crystallization studies were carried out on a Mettler FP82 hot stage, under a polarizing microscope fitted with a 530 nm retardation plate. Before each of the isothermal crystallization experiments, the material was melted and heated up to 200°C to erase its thermal history; no thermal degradation was ever detected (as assessed by DSC). Then, the temperature was quickly lowered to the chosen crystallization temperature, and the spherulites were photographed, at intervals, to measure their radii as functions of time. The non-isothermal measurements were carried out in a similar way, by cooling the material in the hot stage from 200°C at constant cooling rates of 1 deg·min^{-1} and 5 deg·min^{-1}. All photographs had exposure times shorter than 1 second.

The isothermal DSC experiments were carried out on a Perkin -Elmer DSC7, using a fully controlled temperature jump procedure [14], from above the melting point to the crystallization temperature. These experiments were preceeded by a thorough calibration of the instrument, using two standards at a scanning rate of 0.2 deg·min^{-1}. For each isothermal scan, blank runs were also performed with the same sample, at a temperature where no phase change did occur (above the melting point), to fully account for, and accurately eliminate, the initial transient heat capacity signal – proportional to $C_p \cdot (dT/dt)$ – that is obtained in every DSC temperature jump experiment. The use of consistent sample heat treatments prior to each run, and the high precision and accuracy of the calorimeter, ensured exactly reproducible DSC traces at each crystallization temperature, in order to accurately characterize the sample's behaviour. The DSC data were obtained to within less than 5 μW and 0.001 min.

Figure 1 shows a typical isothermal DSC trace, together with the corresponding blank trace; also shown on the same figure is a plot of the sensor's temperature, to indicate that the final isothermal run temperature has been attained well before the onset of crystallization. For data treatment purposes, time was always correctly counted since the beginning of the isothermal (i.e. since t = 1.500 min, in the case shown). The same figure also depicts the resulting subtracted (run-blank) trace, used to measure the crystallization half-times.

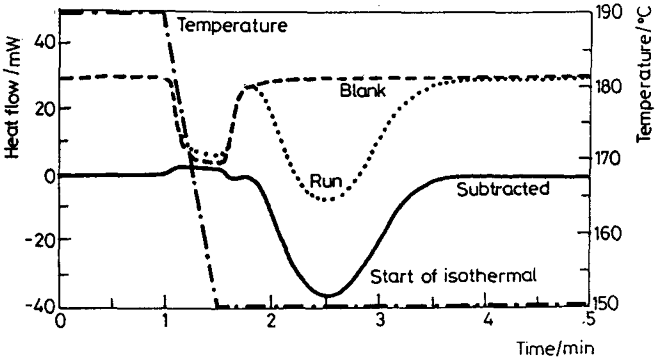

Fig. 1 Isothermal DSC traces for the crystallization of POM (150°C)

Results and discussion

The isothermal spherulite growth data are plotted in Fig. 2, for temperatures between 157° and 160°C. Different spherulites within the same optical microscopy sample yielded exactly the same results, as illustrated for the temperature of 160°C (combined o and + symbols). The linearity of the plots is beyond doubt, showing a marked negative dependence of the growth rate, G, (slope of the lines) on the temperature (experiments close to the melting point).

The non-isothermal spherulite growth data are shown in Fig. 3, for the cooling rates of 1 and 5 deg·min^{-1}. Measurements on different spherulites within the same sample yielded entirely consistent results (combined o, + and x symbols). The lines now show the expected increasing slope with time, due to the increase in the growth rate as the temperature is lowered.

The above radius data were then differentiated to yield the corresponding G values, which are plotted in Fig. 4 (ln G *vs.* $1/T\,\Delta Tf$). On the same plot and coordinates, the reciprocal of the isothermal crystallization half-times, $1/t_{1/2}$, measured by DSC, are also shown.

The most important observation to be made is that all lines have almost exactly the same slope, which is a clear indication that the nucleation-related parameter, K_g, is virtually the same for both the isothermal and non-isothermal data, obtained by optical microscopy or DSC.

Its values, $3.75\cdot10^5$ K^2 (by DSC) and $4.19\cdot10^5$ K^2 (by OM), reasonably agree with previous data [12] and computations [13]. As for the actual relative position of the lines, one should note that a small negative error of 2° to 3°C in the hot

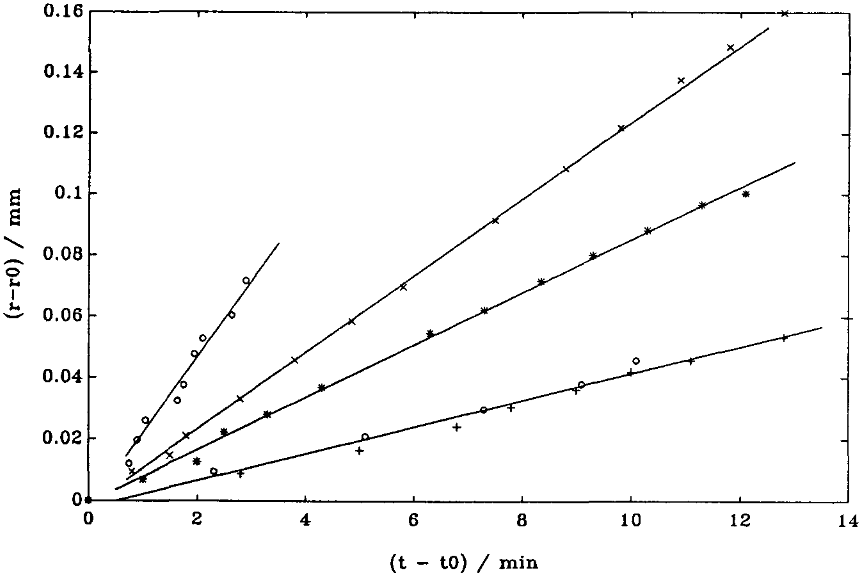

Fig. 2 Isothermal POM spherulite growth data: r_o = initial recorded radius; o 157°C; x 158°C; * 159°C; o, + 160°C

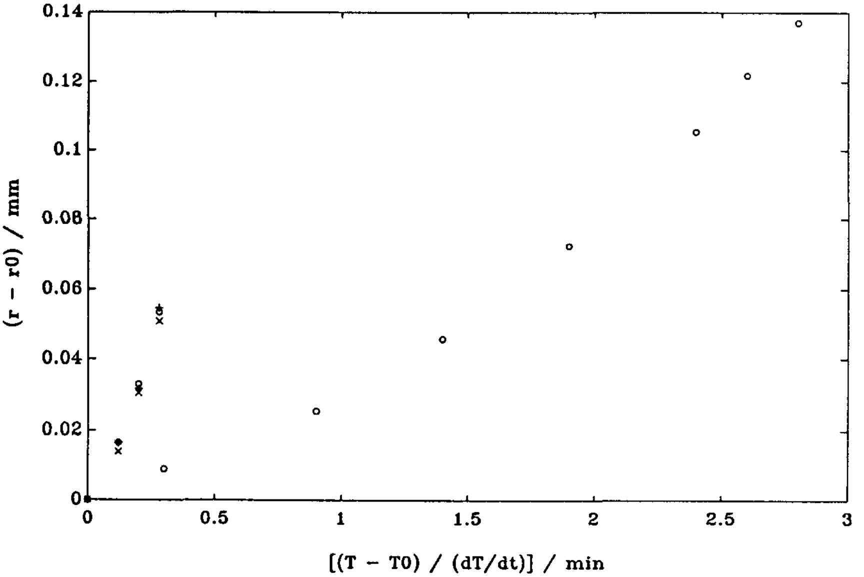

Fig. 3 Non-isothermal POM spherulite growth data: (r_o, T_o) = initial recorded radius and temperature; o 1 deg·min^{-1}; +, x, o 5 deg·min^{-1}

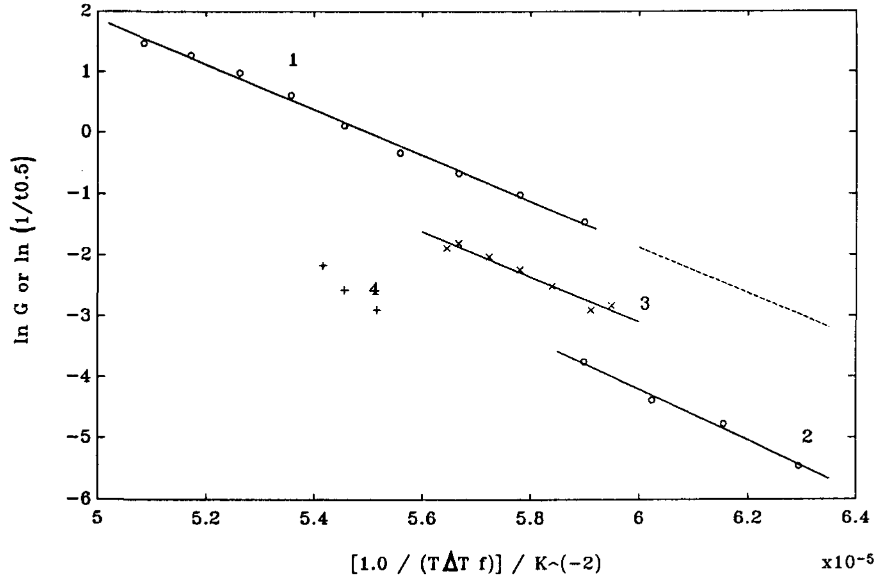

Fig. 4 Combined growth rate and half-crystallization time data: 1 - isoth. $1/t_{1/2}$ (DSC); 2 - isoth. G(OM); 3 - G at 1 deg·min^{-1} (OM); 4 - G at 5 deg·min^{-1} (OM)

stage sample temperature reading (as a result of the exothermal crystallization) is sufficient to horizontally shift the isothermal G data line (2) to an almost exact extrapolation of the DSC ($1/t_{1/2}$) data line (1), as shown; the different pre-exponential factors of G and ($1/t_{1/2}$), as well as the value of the rate of nucleation (or number of nuclei) and of some other numerical constants and phase densities, should also contribute to the shifts. This is a problem that will deserve closer analysis in the future. A temperature offset is the obvious explanation for the shift between 1 and 5 deg·min^{-1}G-lines (lower than measured sample real supercoolings, for the 5 deg·min^{-1} line); also, the fact that the isothermal and non-isothermal optical microscopy measurements were performed at very different times (at different ambient temperatures, thus affecting the hot stage calibration) should explain the unexpected sign of the nevertheless small shift between the isothermal and the 1 deg·min^{-1} G-lines.

Conclusions

1. Even for the very unfavourable case of an industrial grade of POM (non-homogeneous fast crystallizing polymer), the experimental isothermal and non-

isothermal kinetic spherulite growth parameters, namely the nucleation-related K_g parameter, show very good agreement;

2. So, despite much recent controversy, and as theoretically expected on simple physical grounds, one should indeed be able to use isothermal kinetic data (obtained by optical microscopy or DSC) to accurately model the kinetics of non-isothermal polymer crystallization. This is illustrated in detail in a separate paper of these Proceedings.

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References

1 D. Turnbull and J. C. Fisher, J. Chem. Phys., 17 (1941) 71.
2 J. D. Hoffman, SPE Transactions, 4 (1964) 315.
3 J. D. Hoffman, G. T. Davies and J. I. Lauritzen, The Rate of Crystallization of Linear Polymers with Chain Folding, in Treatise on Solid State Chemistry, 3, Plenum Press, 1976.
4 R. L. Miller, Flow Induced Crystallization (Ed. R. L. Miller), Gordon and Breach Sci. Publishers Ltd., 1979, p. 31.
5 R. D. Icenogle, J. Polym. Sci. Polym. Phys. Ed. 23 (1985) 1369.
6 R. M. Patel and J. E. Spruiell, Polym. Eng. & Sci., 31 (1991) 730.
7 C. F. Friedl and N. J. McCaffrey, SPE Antec, 1991, p. 330.
8 T. W. Chan and A. I. Isayev, SPE Antec, 1992, p. 1148.
9 J. A. Martins and J. J. C. Cruz-Pinto, Proc. ICTA-10, Vol. 2, Wiley & Sons, Chichester 1993, p.621.
10 J. M. Avrami, J. Chem. Phys., 7 (1939) 1103; 8 (1940) 212; 9 (1941) 177.
11 M. C. Tobin, J. Polym. Sci., Polym. Phys. Ed., 12 (1974) 399; 14 (1976) 2253; 15 (1977) 2269.
12 Z. Pelzbauer and A. Galeski, J. Polym. Sci., Polym. Phys. Ed., 38 (1972) 23.
13 J. D. Hoffman, Polymer, 29 (1983) 3.
14 J. A. Martins, M. Sc. Dissertation, Univ. Minho and Lisboa, Portugal (1991).

Zusammenfassung — Mittels DSC (Doppelofen, Nullwaage) und Lichtmikroskopie wurde die isotherme Kristallisationskinetik von Poly(oxymethylen)-POM untersucht. Mittels Lichtmikroskopie wurde auch die nichtisotherme Kristallisation dieses Materiales untersucht.
Ein sehr umstrittenes Problem ist, ob die isothermen kinetischen Parameter zur Beschreibung der nichtisothermen Kristallisation verwendet werden können. Die Resultate zeigen, daß die mittels nichtisothermer Lichtmikroskopie erhaltenen kinetischen Sphärolithwachstumsparameter innerhalb der Fehlergrenzen dieselben sind, die mittels isothermer Lichtmikroskopie oder isothermer DSC erhalten wurden. Die Wichtigkeit dieser Erkenntnis wird unterstrichen.