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Letter

Comment on 'Linear radial growth velocity of isolated spherulites in polymer free solidification'

Dear Sir

In the recent paper 'Linear radial growth velocity of isolated spherulites in polymer free solidification' by Huang *et al.*[1], the growth of spherulites in poly(ethylene oxide) (PEO) and isotactic polypropylene (i-PP) was accurately measured and interpreted. Thin (10 μm) films of polymer were formed between two glass slides. Spherulites 140–1200 μm in diameter were grown in these films in a heating stage on an optical microscope. In their interpretation, Huang *et al.*[1] calculate $(T_i - T_c)$ where T_i is the temperature of the interface between the growing crystal and the melt and T_c is the control temperature[2]. They use a model with three-dimensional radially symmetric flow of heat outward from a sphere crystallizing with a constant linear growth rate. The model predicts a significant value for $(T_i - T_c)$ that increases with time. The thin-film samples used are not in a condition of three-dimensional radial symmetry, and some of the latent heat produced at the interface will escape through the glass. Because heat escapes through the glass, the true increase in T_i will be much smaller and it will be almost constant with time. A large rise of interfacial temperature is not consistent with kinetic secondary nucleation-controlled growth at a constant rate, because the kinetic growth rate depends strongly on the local supercooling $\Delta T = (T_m - T_i)$. Huang *et al.*[1] use the expression $(T_m - T_c)$ for supercooling in the kinetic growth rate equation, and therefore do not realize that their prediction of a significant rise of interfacial temperature is inconsistent with a constant linear growth rate.

The data (e.g. Figure 1 of ref. 1)[3] are as follows. There is a short time when the growth is not at a constant rate. After this there is a long period of time when the spherulite radius increases linearly. The growth then slows and eventually stops as the spherulites touch each other and crystallization is over. Huang *et al.*[1] are concerned with the thermal effects of a constant rate of growth. They assume that the latent heat of crystallization must diffuse radially outward into a static polymer melt. To take this into account they draw on the results of Piorkowska and Galeski[4]. This previous work was a calculation of the temperature change at the interface which would occur during solidification at a constant rate. The interface was taken to be infinite in extent and flat. Huang *et al.*[1] made a similar calculation for the constant rate motion of a spherical growth front, which predicts that the temperature of the interface must rise during growth. The predicted temperature rise increases with the growth rate, and for the experimental conditions considered it is in the range of a few tenths of a degree to a few degrees.

Linear growth for polymer spherulites is a well known phenomenon[5–7] and is accepted as being due to kinetically controlled secondary nucleation at the interface. A simple form for the linear growth rate of crystals under these conditions, v, is[7]:

$$v = A\exp\left(\frac{-\Delta G}{kT}\right)\exp\left(\frac{-C}{(T-T_0)}\right) \qquad (1)$$

Here ΔG is the change of free energy on crystallization, usually taken to be $\Delta G = \Delta H_f T_m/\Delta T$, where ΔT is the supercooling $(T_m - T)$, T_m is the equilibrium melting point of the infinite perfect crystal and ΔH_f is the heat of fusion. The second exponential term comes from mass transport across the interface. T_0 is the temperature (below the glass transition temperature T_g) where such transport stops and C is a constant. The pre-exponential term, A, varies slowly with temperature compared with the exponential terms. What is T? Since the nucleation kinetics deal with processes that are entirely localized at the interface, the relevant temperature for the phase transformation can only be the temperature at the surface where the phase transformation is occurring, T_i. The phase transformation is a local event, and the molecule cannot be affected by the temperature of some distant material. Thus:

$$v = A\exp\left(\frac{-\Delta H_f T_m}{T_i(T_m - T_i)}\right)\exp\left(\frac{-C}{(T_i - T_0)}\right) \qquad (2)$$

Comparing this with equation (2) of ref. 1, we see that it has essentially the same form, but in ref. 1 T_i is replaced by T_c, 'a preset crystallization temperature', that is, the control temperature, which is the temperature of the melt at a large distance from the crystal. It is true that most descriptions and derivations of the kinetic growth rate formula use $\Delta T = (T_m - T_c)$ where T_c is called 'the isothermal crystallization temperature', and the external control temperature is used in calculations of supercooling[7–9]. However, these derivations all assume that, when kinetics are in control of crystal growth, heat flow is not important and there is no need to distinguish between T_c and T_i as the temperatures are essentially the same. Since T_c is known while T_i is not, T_c is used as 'the' temperature. When we are specifically considering the temperature gradients in the melt, $T_c \neq T_i$, and the temperature at which crystallization is actually occurring, T_i, must be used. To take an extreme example to make the point, if T_c is used in the kinetic growth formula and thermal conditions are chosen that make $T_i - T_c$ very large (e.g. long times, large latent heat), the prediction is that crystal growth will continue undiminished even if the crystal surface temperature is greater than the crystal melting point.

Growing crystals must simultaneously meet the conditions imposed by heat transfer, mass transfer and the kinetic attachment of units at the interface. There must always be some temperature gradient at the interface of a growing crystal, and the interfacial temperature must affect the growth rate, through the kinetics of crystallization. Thus for growth at a constant rate, it is clear that kinetics requires that the interface stay at a constant temperature, and that heat flow (with radial symmetry and no flow in the melt) requires that the interface temperature increase[1,5]. Similarly, if the growth rate decreases so that the spherulite radius $R \propto \sqrt{t}$, then solution of the heat flow equation (under the same conditions) requires a constant interface temperature[10], while kinetics requires that the local supercooling is reduced by an increase in interface temperature. These requirements are inconsistent in principle.

For the case of the constant linear growth rate, there are two possibilities. Either the temperature rise at the interface $(T_i - T_c)$ remains small enough to cause little change in local supercooling and thus little difference in the growth rate, or the heat flow does not follow the model being used. If there is convection in the melt or a lack of radial symmetry, T_i can be constant, so that the growth rate remains constant. When $R \propto \sqrt{t}$, the kinetically required increase in interface temperature must be much smaller than the temperature difference $(T_i - T_c)$ caused by latent heat. Then the heat flow equations are not significantly affected by the small change in T_i and heat flow is important to the growth rate. It is possible for both heat transfer and interface kinetics to be important at the same time, and then neither simple model for the growth rate will be correct.

The growth rate of a polymer spherulite always follows the kinetic equation (2), and so depends strongly on $T_m - T_i$. If heat flow is important it is through its effect on T_i. More commonly, mass flow of impurities is important, and this acts by the effect of impurity concentration on T_m. The term 'kinetically controlled growth' means that heat flow is not important, not that it has no effect. However, if heat flow does have a large effect on the process, then the process can no longer be called kinetically controlled. Huang *et al.*[1] describe a situation of constant growth rates as kinetically controlled, and apply the heat flow equation to it. *Table 1* shows an example for PEO crystallizing at $T_c = 49.5$ and 51°C, where constant linear growth rate is established after about 10 s of crystallization[1]. If the predicted increase of interface temperature shown in *Table 1* actually occurred, the interface temperature at $T_c = 51$°C and short crystallization times would be the same as that at $T_c = 49.5$°C and long crystallization times. This would imply that the 'kinetically controlled' radial growth rate at the interface could have two different values at the same value of interface temperature. From equation (2) there should be a significant slowdown of crystallization because of the predicted rise of T_i. Because Huang *et al.*[1] use T_c and not T_i in the expression for kinetically controlled growth rate, they do not realize this problem.

Table 1 Some data for the growth of PEO spherulites, derived from Figures 3 and 8 in Huang *et al.*[1]

Control temperature T_c (°C)	Predicted interface temperature, T_i (°C)		Observed radial growth rate (μm s^{-1})	
	after 10 s	after 150 s	after 10 s	after 150 s
49.5	49.6	51.5	3.79	3.79
51	51	51.8	2.23	2.23

The error in Huang *et al.*[1] lies in applying the theoretical calculation of a symmetric situation to the experimental results obtained, treating the spherulites as though they were truly isolated in the melt. In fact they are contained in a thin film, 10 μm thick, in contact with two glass sheets. No allowance is made for the certainty that heat can pass out of the polymer through the glass. The extent to which this occurs can be estimated from the thermal diffusivity D_T of the material (given in ref. 1 as 6.6×10^{-4} cm^2 s^{-1}) and the timescale of the experiment. With the time between data points, 5 s, as the timescale, a characteristic length for heat flow is $D_T = (3 \times 10^{-3})^{0.5} = 0.06$ cm or 600 μm. Using the total time of the experiment described above, 150 s, this length becomes 3 mm. This rough estimate is good enough to show that no significant thermal gradients can be maintained in a 10 μm thick polymer film during crystallization experiments. Any thermal gradient in the glass slide that encloses the film will also be small, and will not build up over time because each part of the glass has a similar thermal contact with the heating stage. Thus the interface will be close to the temperature of the heating stage, controlled to within ±0.1°C. Piorkowska and Galeski[4] explicitly mention that their theory assumes that no heat is transferred through the glass coverslip, and that the temperature rise they calculate can only be an upper limit when a thin film is used. Similarly, Frank[10], describing early experiments with similar geometry, states that radial diffusion of impurities will be important, while thermal effects will be small.

The observed spherulite growth is therefore isothermal, and no special explanations are required for the observed constant growth rate. Explanation of the changes in growth rate at the beginning and at the end of the experiment may be found in impurity segregation and in constraints acting on the melt.[6] It is not the intention of this note to attempt a detailed explanation of solidification kinetics. It is to point out that the constant growth rate of spherulites in thin films is simple isothermal crystallization; isothermal means that not only the control temperature T_c but also the crystal–melt interface temperature T_i remain essentially constant with time. Calculation of the increase of interface temperature that would occur under different circumstances is not relevant. For the calculations given by Huang *et al.*[1] to be relevant, there would have to be three-dimensional spherulites developing within a large body of melt. The melt pool would have to be several centimetres across to allow neglect of heat transport at the boundary in the modelling[11]. There would have to be negligible flow in the melt, no convection or settling of the denser spherulites. If these conditions could be met, heat flow would be radial into the melt, and a non-linear growth rate should be observed.

REFERENCES

1 Huang, T., Rey, A. D. and Kamal, M. R. *Polymer* 1994, **35,** 5434

2 Huang *et al.* use both T_c and T_0 for the 'control' or 'crystallization' temperature; see Figures 3 and 4 of ref. 1

3 The actual growth rates for i-PP in ref. 1 are not completely clear, as the plots in Figures 1 and 6 do not agree with the data given in Figures 5, 6 and 7, but this is not important to the present argument

4 Piorkowska, E. and Galeski, A. *Polymer* 1992, **33,** 3985

5 Keith H. D. and Padden, F. J., Jr *J. Appl. Phys.* 1963, **34,** 2409

6 Keith, H. D. and Padden, F. J., Jr *J. Appl. Phys.* 1964, **35,** 1270, 1284

7 Wunderlich, B. 'Macromolecular Physics', Academic Press, New York, 1976, Vol. 2, Chs 5 and 6

8 Hoffman, J. D., Davis, G. T. and Lauritzen, J. I., Jr in 'Treatise on Solid State Chemistry' (Ed. N. B. Hannay), Plenum, New York, 1976, Vol. 3

9 Hoffman, J. D. and Miller, R. L., *Macromolecules* 1988, **21,** 3038

10 Frank, F. C. *Proc. R. Soc. (A)* 1950, **201,** 586

11 Pawlak, A. and Galeski, A. *J. Polym Sci., Polym Phys. Edn.* 1990, **28,** 1813

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