Reply

Response to Grubb's comment on 'Linear radial growth velocity . . .'

Dear Sir

The previous letter by D. T. Grubb[1] is a revised commentary on our paper[2] regarding spherulitic crystallization. At the end of the first paragraph of ref. 1 it is claimed that: 'Huang *et al.* 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.' And at the beginning of the seventh paragraph: 'The error . . . lies in applying the theoretical calculation . . . to the experimental results obtained.' To substantiate the claim, the author incorrectly uses Hoffman's equation[3] and offers a simplistic scaling argument. Significantly, no experimental data or any other factual evidence that would support the claim is presented in ref. 1.

Below we show that our analysis, which agrees with our experimental data, is generally sound, consistent and in agreement with classical work in the field. We also show that the claim of ref. 1 is based largely on misreading of our paper[2], and on apparently wrong assumptions. The following points summarize our response.

1. Hoffman's equation is based on thermodynamic analysis of macromolecules folding during crystallization. The supercooling $\Delta T = T_m - T$ is the driving force for crystallization, 'which corresponds to a crystallization experiment carried out isothermally at a temperature of T'; see the original definition on p. 400 in ref. 3. In Hoffman's equation, T is defined as the isothermal crystallization temperature; see p. 3040 in ref. 4. It is the preset isothermal temperature T_c in our experiments, and not the interface temperature T_i. Grubb[1] wrongly replaces T by T_i disregarding their intrinsic differences; see equation (2) in ref. 1. He confuses the surface temperature T_i and the preset crystallization temperature T_c (the temperature of the melt surrounding the spherulite). The growth velocity of the isolated spherulite is determined by the preset crystallization temperature T_c. Our experimental and theoretical results have shown that the temperature rise of the spherulite surface does not change the growth velocity. In the linear growth region, the growth velocity is constant because the melt temperature is at a preset temperature and does not change. The latent heat release during spherulitic growth is compatible with the linear growth velocity, which is determined by Hoffman's equation. It is wrong to replace the preset crystallization

temperature with the interface temperature calculated from the preset crystallization temperature. Specifically, it is not justifiable to use the calculated surface temperature of 51.1°C in the place of the preset temperature 49.5°C because the experimental measurements already show that, for $T_c = 49.5°C$, $v = 3.79\,\mu m\,s^{-1}$ and that neither of these two variables changes during growth.

2. Grubb[1] apparently misunderstands the difference between heat-transfer-controlled growth and kinetics-controlled growth. As early as 1974, the classical work of Ivantsov[5] indicated that, if the substance has a high linear crystallization rate and heat removal is rapid, a temperature difference will occur. In this case, the crystal shape will be determined by both kinetic laws and heat transfer laws. Ivantsov concluded that there are two cases for growth of a spherical crystal (see *Figure 1*):

(A) Growth at constant surface temperature (T_i = constant) or heat-transfer-controlled growth. In this case, the build-up of heat during the process of crystallization leads to slow growth and the crystal size is proportional to the square root of the elapsed time:

$$R = \sqrt{2at(St)} \qquad (1)$$

Here $St = (T_i - T_c)/(L/C_p)$ is the Stefan number, where T_i and T_c are the constant temperature at the crystallization front and melt temperature at a great distance from the crystal, respectively; C_p and a are the heat capacity and thermal conductivity of the melt, respectively; L is latent heat; R and t are the radius of the crystal and time, respectively.

(B) Growth at constant rate (V = constant) or kinetics-controlled growth. Ivantsov assumed that the latent heat L liberated at the crystal surface is taken up both within the crystal and by the surrounding melt, and that the thermal constants of the crystal and the melt are the same, the two being isotropic. The melt was assumed to have a constant temperature. He indicated that the exact solution takes on a very complex form. However, for the initial stages of growth, a simple formula was obtained:

$$(St) = (Pe) \qquad (2)$$

where $(Pe) = VR/a = (V^2t)/a$ is the Peclet number. Solving equation (2) for the difference between crystal and melt temperatures, one obtains:
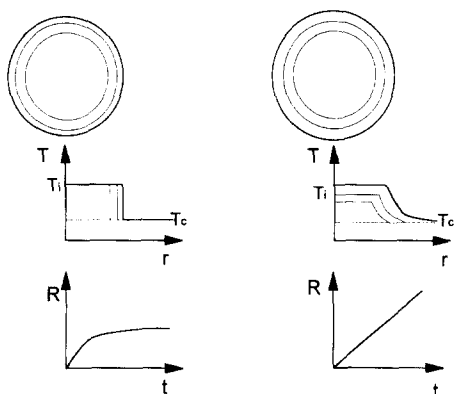
$$T_i - T_c = [(L/C_p)(V^2/a)]t \qquad (3)$$

Figure 1 Two cases of the growth and temperature distribution in circular geometry

0: spherulite
1: hot stage
2: hot stage cover
3: sample
T_c :pre-set temperature
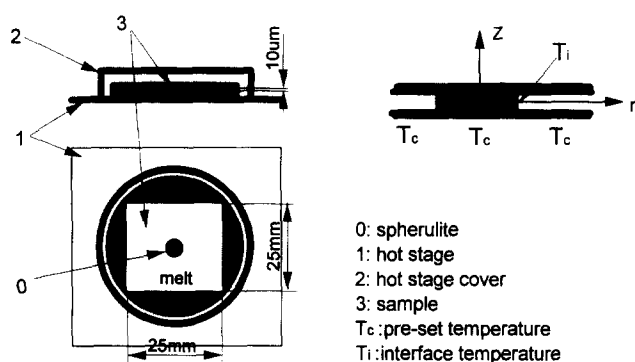T_i :interface temperature

Figure 2 The experimental set-up: hot-stage and sample

Equation (3) shows that the crystal temperature rises when one assumes a constant growth rate. That means that *temperature rise and constant growth velocity may coexist*. Polymer spherulitic crystallization follows this case.

Figure 1 shows case A on the left and case B on the right. As clearly shown in ref. 2, both the experimental data and the mathematical model for polymer solidification follow case B.

3. The analysis provided above clearly shows that spherulitic growth at constant velocity may be associated with a small increase in the temperature. Grubb[1] disregards the local polymeric solidification phenomena (case B above) and reduces the complex phase transition process to an order-of-magnitude scaling argument that totally neglects to take into account heat exchange between the sample and the environment in which it is placed. The experimental set-up is shown in *Figure 2*, which indicates the locations of the different components of the solidification cell and the relevant temperatures. According to Grubb[1], the crystallization is isothermal (i.e. constant temperature) and occurs within a heat

conductive boundary that is kept at constant temperature. This is clearly impossible since perfectly uniform and constant temperature are not compatible with heat transfer or spherulitic growth. On the other hand, the local solidification model given in case B and used in ref. 2 is compatible with the global heat transfer process, since small radial gradients will always exist whenever a moving heat source (i.e. moving crystallization front) is enclosed between glass plates kept at essentially constant temperature. The actual magnitude of sustainable temperature rise at the interface is difficult to fix, due to the complexity of the heat transfer problem (see *Figure 2*). The analysis in ref. 2 provides an indication of the maximum potential temperature rise at the interface. Most likely, the temperature rise will be significantly smaller. This may explain the misunderstanding by Grubb[1]. However, the actual magnitude of the cumulative temperature rise at the interface does not change any of the conclusions reported in our work[2]. The experimental and theoretical results of ref. 2 have shown that the temperature rise at the spherulite surface does not change the growth velocity. In the linear growth region, the growth velocity is constant because the melt is at a preset temperature that does not change. As shown above and in ref. 2, the latent heat release during spherulitic growth is compatible with the linear growth velocity, which is determined by Hoffman's equation. Grubb[1] mistakenly replaces the constant preset crystallization temperature with the variable calculated interface temperature to calculate a velocity change that is not observed experimentally. Based on this clear error, Grubb[1] then claims the growth rate must decrease.

In summary, the above shows that our analysis of the problem presented in ref. 2 is sound and that the objections of Grubb[1] represent an inconsistent qualitative scaling argument. We have also shown that these objections are based on misunderstanding of some of the fundamental aspects of the problem and of the critical parameters defined in the analysis.

REFERENCES

1   Grubb, D. T., *Polymer* 1996, **37**, 3177
2   Huang, T., Rey, A. D. and Kamal, M. R. *Polymer* 1994, **35**, 5434
3   Hoffman, J. D., Davis, G. T. and Lauritzen, J. T. Jr in 'Treatise on Solid-State Chemistry' (Ed. N. B. Hannay), Plenum, New York, 1976, Vol. 3, Ch. 7
4   Hoffman, J. D. and Miller, R. T. *Macromolecules* 1988, **21**, 3038
5   Ivantsov, G. P. *Proc. Acad. Sci. USSR* 1947, **58**, 567; 1951, **81**, 172; 1952, **83**, 573; Ivantsov, G. P. in 'Growth of Crystal, Vol 1, Consultants Bureau, New York, 1958, p. 61; in 'Growth of Crystal', Vol. 2, Consultants Bureau, New York, 1960, p. 53

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