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Curved faces in polymer crystals with asymmetrically spreading growth patches

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Polymer crystals often have curved faces. Understanding such morphology is of major interest since it allows distinction between fundamentally different theories of polymer crystallization. E.g. Sadler's "roughness-pinning" theory assumes that the curvature is a result of roughening transition on lateral faces. It has since been shown by Mansfield that the curvature can be explained quantitatively, essentially within the Lauritzen-Hoffman nucleation theory. However, the step propagation rates v implied in their treatment are substantially lower than predicted by the LH theory. The retardation appears to be due to the "self-poisoning" or "pinning" effect of incorrect chain attachment, effectively demonstrated by the extreme cases of growth rate minima in long-chain monodisperse n-alkanes. Recently crystals of poly(vinylidene fluoride) and alkanes $C_{162}H_{326}$ and $C_{198}H_{398}$ have been found with habits that can be best described as bounded by curved {110} faces. The interesting feature is the asymmetry of the curvature: while the faces are curved at one end, they are straight at the other. We carried out mathematical analysis of the curvature, generalizing the Mansfield model. We suggest that such asymmetric curvature arises from the propagation rates to the left, v_l, and to the right, v_r, being different because of the lack of mirror bisecting planes such as (110). By solving appropriate equations with moving boundaries, we obtained the shape of the growth front $y(x,t)$. Calculated crystal habits gave excellent fits to the observed growth shapes of a-axis lenticular crystals of long alkanes and PVDF, as well as of single crystals of PEO. This explains some hitherto poorly understood morphologies and, in principle, allows independent measurements of step initiation and propagation rates in all polymers.