<u>Supplementary Information</u>:

for

Shear-Enhanced Crystallization in isotactic polypropylene.

4. In-Situ Synchrotron SAXS and WAXD

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For highly-oriented cylindrullitic growth from a central shish, the optical retardation is directly proportional to the volume of the cylindrullite. Therefore, a constant linear (viz. radial) growth rate implies that the retardation must increase as t^2. However, in short-term shearing experiments, the retardation grows linearly with time after cessation of shear. As the growth velocity of polymer crystals has been shown to be constant irrespective of the growth geometry[1], Liedauer et al. had claimed that the oriented crystals in their shear-crystallization experiment must grow as spokes off a central shish[2] so that the volume of the crystals increased linearly with time. However, we show here that this spoke-like model for crystals formed in sheared melts is not necessary to explain the optical data. To demonstrate this, we construct a "toy" model for the increase in the volume of a single cylindrullite with time in a short-term shearing experiment. The model assumes that as the cylindrullite grows radially, the geometry (viz. the degree of orientation) does not change. This is in accord with our two dimensional X-ray scattering data (Figure 8, main paper). We further assume that the linear growth velocity of the cylindrical crystal is higher during the shear pulse, as compared to the quiescent growth velocity after shearing. This too is in accord with our experiments, which show that crystallinity builds up more rapidly during shear than after shear cessation. For example, when a wall shear stress of 0.06 MPa is imposed for 12 s at 141°C, x_c □ 0.03 at the end of the shear pulse, and doubles to 0.06 only at around t_{cryst} = 150 s (Figure 15 c II, main paper), after which oriented growth is negligible (Figure 15 a II). Thus, cyllindrulites grow to impingement in approximately 150s, and approximately half of the fully impinged volume of cyllindrulitic growth is reached in 12s during shear. This suggests that the growth velocity during shear is an order of magnitude greater than the quiescent growth velocity, which pertains after cessation of shear. Therefore, the volume of the cylindrullite per unit length of the central nucleus, v is:

$$v \quad \square \quad [G_s\, t\,]^2 \qquad \text{for } t \,\square\, t_s$$

$$v \quad \square \quad [G_s\, t_s + G_q\,(t-t_s)]^2 \qquad \text{for } t > t_s$$

where □is the retardation, G_s is the linear growth velocity during shear while G_q is the linear growth velocity after shear cessation.

For $G_s = 10\ G_q$, we observe that v scales with t^2 during shear, but that the growth of v with time after shear cessation shows a quasi-linear dependence (Figure A1). Therefore, the observed linear growth of the retardation with time could arise simply from a change in the linear growth velocity after cessation of shear, rather than from spoke-like growth of crystals from the central shish. Our model can be further refined so as to consider cessation of radial growth of crystals upon impingement with neighbouring crystals, variation in inter-shish distances or shish lengths with distance from the wall of the die etc. For G_s sufficiently different [~(10 times)] compared to G_q , all variants on the model show a quasi-linear scaling of the crystal volume with time after cessation of shear.

References:

1. White, H. M.; Bassett, D. C. *Polymer* **1997**, *38*, 5515-5520.
2. Liedauer, S.; Eder, G.; Janeschitz-Kriegl, H.; Jerschow, P.; Geymayer, W.; Ingolic, E. *Int. Polym. Proc.* **1993**, *8*, 236-244.

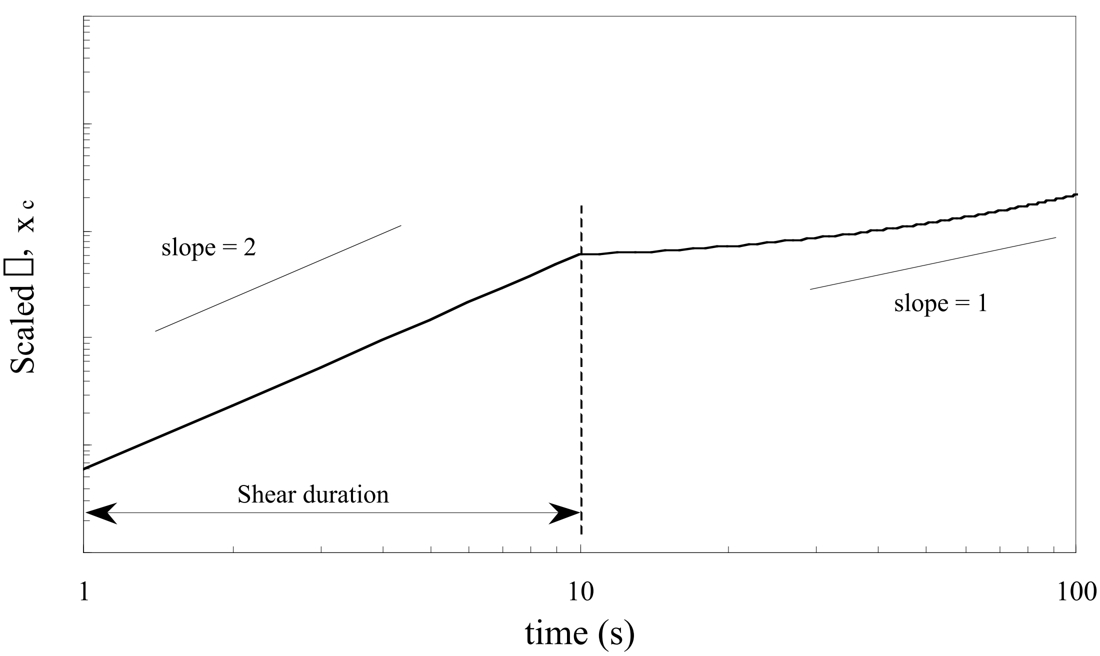

Figure A-1: Plot based on the "toy" model described in the text, of the volume of the cylindrical crystal (or the retardation observed due to that crystal) as a function of time on a log-log scale. The shearing time is 10 s, and $G_s = 10\ G_q$.