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Two Distinct Morphologies for Semi-Crystalline Isotactic Polypropylene Crystallized after Shear Flow

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Application of shear flow to molten, highly isotactic polypropylene (iPP), results in two different morphology transitions: (1) above a certain shear rate but below a critical shear stress, flow-induced precursors nucleate many small crystallites; (2) for shear stress above, shish precursors nucleate highly oriented shish-kebab morphology. Herein we studyflow-induced crystallization (FIC) in iPP with different molecular weights, using rotational and capillary rheometry. Since precursors created by shear are quite stable, we can also use differential scanning calorimetry (DSC) and polarized optical microscopy (POM) to study crystallization, melting and morphology of iPP samples with different shear histories. Above a critical shear rate (inverse of long-chain relaxation time), the onset of crystallization on cooling shifts to higher temperatures, compared to unsheared samples. POM micrographs see a clear border between the regions affected by FIC (with) and regions crystallizing as though they had not been sheared. FIC results in much smaller crystallites, so-called rice grains of order 1 μm in size. Above a critical shear stress (~0.11 MPa) in the rotational rheometer, the morphology transitions to a shish-kebab structure. Shish appear in micrographs as highly aligned birefringent regions; in DSC, flow-induced shishfurther accelerate the onset of crystallization. In the rheometer, sheared samples with at 170°C (above T_m), behave as a viscoelastic liquid identical to unsheared samples, whereas strongly sheared samples with behave as weak gels, revealing the presence of a percolating network of shish. In capillary rheometry, samples sheared above this threshold stress likewise show anabrupt increase in apparent viscosity.