Dynamics of precursors of fibrillar crystals

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Introduction
Fibrillar crystals can be formed from melts of flexible macromolecules applying strong deformations [1]. Control over this phenomenon is a prerequisite to tailor properties of polymeric materials, like isotactic polypropylene (iPP). However, limitations arise from incomplete knowledge of the physics involved. For instance, it is known that precursors are formed [2], but how stable are they? And, how do they evolve?

Materials and Methods
- iPP homopolymer, M_w=365 kg/mol, MWD=5.4, T_m=165 °C (HD120M0, Borealis).
- Shear experiments performed using a slit flow cell allowing for in-situ X-ray observation, see Figure 1a.
- SAXS and WAXD performed at the beamline BM26B, ESRF (Grenoble, France), see Figure 1b.

Results
Short term shear experiments together with SAXS reveal that, at 165 °C, fibrillar crystal precursors are formed when the wall stress σ_w exceeds 0.12 MPa, see Figure 2.

The time dependence of the equatorial streak intensity is shown in Figure 3. Experiments are grouped in two categories:

- σ_w≥0.12 MPa: precursors are stable and crystallize (from WAXD) increasing the scattered intensity. During crystallization their length grows ~50 nm (see Figure 4).
- σ_w<0.12 MPa: precursors are not stable and dissolve reducing the scattered intensity.

Conclusions
Fibrillar structures are formed in a melt of flexible molecules, like iPP, when stress exceeds a critical threshold. The process starts with fibrillar precursors that crystallize and lengthen with time. When the critical stress is not exceeded, precursors dissolve back to the melt.

References