

## Shear Flow Induced Crystallization of Isotactic Polypropylene - SAXS

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Beamline(s): X27C

**Introduction:** The effect of flow fields (shear, elongation, or mixed) encountered in polymer processing operations, such as extrusion, injection molding, film blowing and fiber spinning, is of interest because it has profound effect on the final product properties, such as mechanical strength, permeability, etc. One example is polyethylene fibers with highly oriented (anisotropic) crystallites have Young's modulus of 130 GPa in the direction of orientation (modulus of steel  $\sim 200$  GPa). The aim of this research project is to study the nature of the oriented structure development in isotactic polypropylene (i-PP) melt under the influence of shear flow-field using *in-situ* synchrotron SAXS (small-angle x-ray scattering).

**Methods and Materials:** A Linkam CSS-450 high temperature shearing stage modified for *in-situ* x-ray scattering studies was used to precisely control shear-field and thermal history of the polymer (i-PP) samples. Synchrotron x-ray measurements were carried at the Advanced Polymers Beamline, X27C; a 2D MAR CCD detector was used for the detection of 2D scattering patterns.

**Results:** The SAXS image (Figure 1) show strong meridional reflections in the scattering pattern of the I-PP melt at 140 °C after a brief impulse of step shear-flow field (shear rate  $102 \text{ s}^{-1}$ , strain 1428%). The meridional reflections are due to the rapid development of oriented polymer crystallites in the melt. Due to the applied shear field the polymer chain segments orient and align in flow direction and results in the formation of primary nuclei. The primary nuclei enhance growth of the oriented crystals that align perpendicular to the flow direction. The SAXS intensity profiles show that the crystallization kinetics increased by two orders of magnitude as compared to quiescent crystallization. A method was used to deconvolute the total integrated intensity into contributions arising from the isotropic and anisotropic components of the crystallized polymer. At low shear rates ( $\sim 10 \text{ s}^{-1}$ ) the oriented fraction in the polymer bulk was lower than at high shear rates ( $57, 102 \text{ s}^{-1}$ ). Only the polymer molecules above a "critical orientation molecular weight" ( $M^*$ ) can become oriented at a given shear rate due to the underlying molecular relaxation phenomenon. The critical orientation molecular weight values at different shear rates were determined from the oriented crystal fractions calculated from the SAXS data. The results suggest that the critical orientation molecular weight is sensitive at low shear rates and approach a plateau at shear rates, above  $60 \text{ s}^{-1}$ .

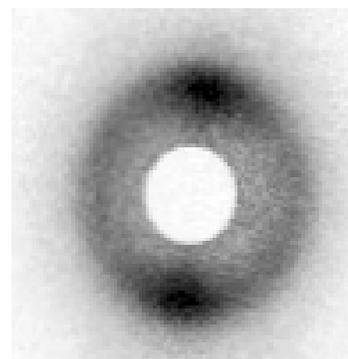
**Conclusions:** The SAXS patterns of isotactic polypropylene melt at 140 °C show the development of oriented crystallites upon application of step shear at 1428% strain and shear rates of 10, 57, and  $102 \text{ s}^{-1}$ . The results suggest that the shear induces orientation and alignment of chain segments of i-PP molecules in the flow direction, which initiate primary nuclei and the oriented crystals (kebab) grow in the perpendicular direction by the process of secondary nucleation. Due to the imposed step shear, the crystallization kinetics of (both oriented and unoriented crystals) i-PP increases by two orders of magnitude as compared to quiescent crystallization. The increase in crystallization rate is mainly due to the orientation-induced primary nuclei. The unoriented crystallites are related to the formation of  $\beta$ -form crystals. The contribution of the oriented crystals in the total crystalline phase was determined from the SAXS data. Under the imposed flow conditions, only polymer molecules having molecular weight above a critical orientation molecular weight can form oriented structures, which is about 300,000 g/mole at the present experimental conditions.

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**References:** 1) R. Somani, B. Hsiao, A. Nogales, S. Srinivas, A. Tsou, I. Sics, F. Balta-Calleja, T. Ezquerra "Structure Development During Shear Flow-Induced Crystallization of i-PP: *In-situ* Small-Angle X-Ray Scattering Study", *Macromolecules*, accepted (2000).

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**Figure 1.** SAXS pattern of I-PP at 140 °C, after step shear (rate =  $102 \text{ s}^{-1}$ , strain = 1428%); image obtained 900 s after cessation of shear.