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# Scattering from Precursors of Primary Nucleation in Sheared Isotactic Polypropylene Melt

R. Somani, B. Hsiao, L. Yang (SUNY, Stony Brook), H. Fruitwala, S. Srinivas, A. Tsou (ExxonMobil Chemical Company, Baytown Polymers Center, Texas)

Beamline(s): X27C

**Introduction:** In crystallization of polymer melts, the initial development of microstructure determines the final morphology and product properties of crystallized polymer. The aim of the present study is to probe the nature of structures induced by flow in a polymer melt before the formation of primary nuclei. The results of small-angle X-ray scattering (SAXS) experiments showed that the oriented structures or aggregates (precursors of primary nuclei) form and are stable for a long-time in the i-PP melt at high temperatures. Although the detection of structural details of the aggregates was still not possible, the SAXS data provided insight into the morphological features of the large-scale structure induced by flow before crystallization.

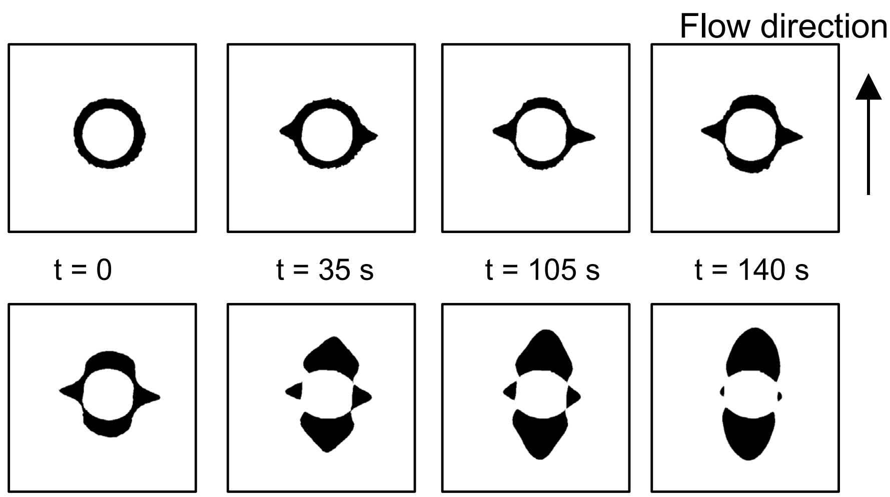


**Figure 1.** SAXS patterns of i-PP melt at 165 $^0$C before and after shear (shear rate = 60 s $^{-1}$, $t_s$ = 5 s).

**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**: Figure 1 shows a series of 2D SAXS patterns of the polypropylene melt at 165 $^0$C (slightly above the melting point temperature of 162 $^0$C) before and after application of shear (60 s $^{-1}$ shear rate and shear duration, $t_s$ = 5 s). The first pattern (t = 0, before shear) of the initial amorphous melt consists of diffuse scattering indicating the absence of any detectable structures and/or preferred orientation. The SAXS patterns in Figure 1 show the evolution of an oriented structure in hundreds of angstroms induced by flow in the polymer melt at 165 $^0$C. The emergence of equatorial streak (note that meridian is in the flow direction, shown in Figure 1) was observed immediately after shear as seen in the SAXS pattern at t = 35 s. The emergence of meridional maxima was observed in the SAXS pattern corresponding to t = 105 s after shear. As one might expect, the intensity of the maxima is relatively weak in the initial SAXS patterns (such as t = 140 and 210 s in Figure 1); however, the patterns at t = 11, 22 and 69 min clearly show the strong meridional maxima. SAXS patterns of the i-PP melt at 175 $^0$C under identical conditions of shear (rate = 60 s $^{-1}$, $t_s$ = 5 s) were similar and showed evolution of the equatorial streak immediately after shear and the meridional maxima soon afterwards.

**Discussion**: The scattering maxima along the equator (Figure 1) suggest formation of the elongated structures parallel to the flow direction and the meridional maxima perpendicular to the flow direction indicates formation of slab-like structure (or layers with different electron-density) perpendicular to the flow direction. The electron-density contrast between the layers can be attributed to two populations of chains resulted from the different relaxation responses to flow, one containing unoriented chain segments and molecules (especially the low molecular weight species that relax in a short time) and the other containing oriented clusters of aligned chain segments (due to the long relaxation of chains). These observations suggest presence of the oriented chain aggregates or precursors of primary nucleation in the polymer melts at the early stages of crystallization.

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