	Experiment title: Pressure-quench of flow induced precursors of crystallization, a novel experimental technique	**Experiment number:** 26-02 564
Beamline: BM26B	**Date(s) of experiment:** From 27/06/2011 at 08:00 to 01/07/2011 at 8:00	**Date of report:** *12/09/2011*
Shifts: 9	**Local contact(s):** Dr. G. Portale	

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Report:

On-line synchrotron WAXD/SAXS during crystallization under pressure

At Beamline B26 DUBBLE of the European Synchrotron Radiation Facility (ESRF) in Grenoble a series of experiments was conducted in which WAXD patterns were acquired during crystallization under different pressures after various annealing time. The experimental protocol is shown in the Figure 1.

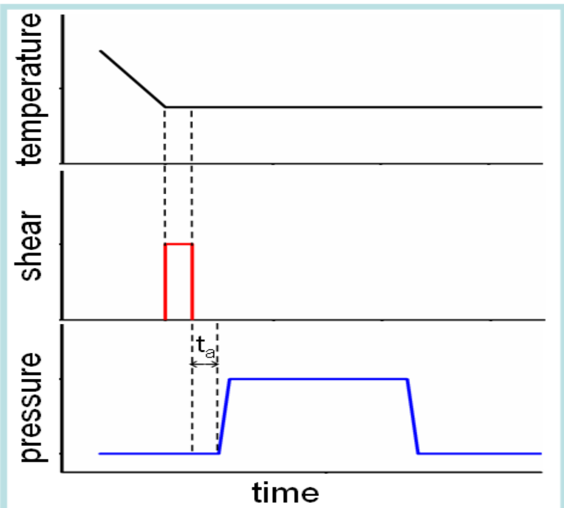


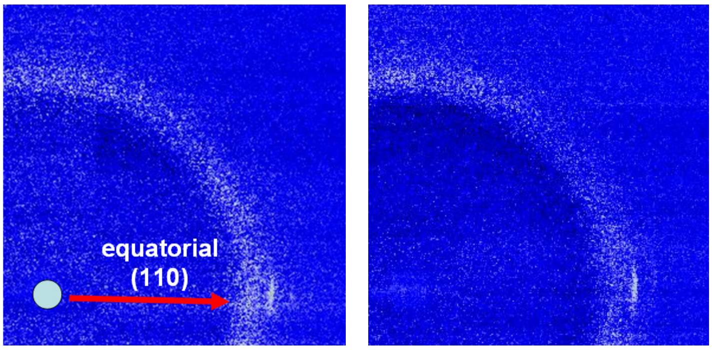
Figure 1. The experimental protocol.

In our preceding study on Pressure Quench[1], Pressure Quench was imposed right after the flow, namely annealing time t_a=0. The results conclude that Pressure Quench can effectively trigger crystallization without lowering the experimental temperature and prove the formation of flow-induced crystallization precursors. This work is going to further study time evolution of flow-induced precursors. The experimental protocol, see Figure 1, shows that Pressure Quench is introduced after an annealing process, t_a=22min, on the polymer melt sheared by the same flow as used before. Crystallizations with and without the annealing will be compared.

1. Annealing without Pressure Quench

Without Pressure Quench, no structure is observed by SAXS/WAXD (data not shown) within the annealing of 22min. No X-ray observable change concludes that these flow-induced precursors did not aggregate to form densely-packed or crystalline structures.

2. Crystallization under Pressure Quench



(a) (b)

Figure 2. Two-dimensional (2D) WAXD pattern of crystallization under Pressure Quench *a*) without annealing; *b*) after annealing

Crystallization was started by Pressure Quench to check the crystallization morphology and kinetics to understand the evolution of X-ray invisible precursors. The Pressure Quench from 50 to 300 bar was imposed on the sheared and annealed polymer melt. The equatorial (110) diffraction is clearly observed (see Fig. 2right), once Pressure Quench was researched. Appearance of highly oriented crystals, as observed in un-annealed crystallization (see Figure 2left), implies the flow-induced precursors survive after the 22-min annealing.

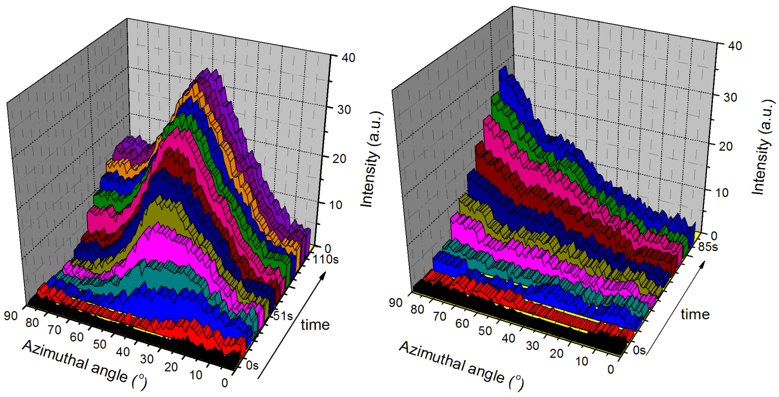


Figure 3. Change in the azimuthal distribution of (200) diffraction during Pressure Quench crystallizations for (a) un-annealed and (b) an annealed sample.

Detailed azimuthal evolutions of (200) diffractions are compared between un-annealed and annealed samples in Fig. 3, which relates to nuclei density[2] and content of twisting overgrowth[3]. Fig. 3a shows that the (200) diffraction of the un-annealed sample occurs at low azimuthal angle and moves towards higher value with time. At a crystallization time of about 50s, the majority of the (200) diffractions further develop around the azimuthal angle of 50^o. In contrast, the (200) patterns of annealed sample are mainly found at 90^o, the meridional direction in 2D, see, Fig. 3b. Due to the low crystallinity in the beginning, the azimuthal evolution can not be clearly tracked in the early stages. The different lamellar morphology must be associated to nuclei density.

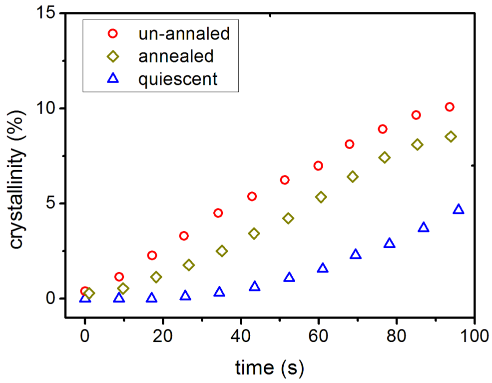


Figure 4. Crystallinity evolution for (○) unannealed; (◇) annealed (△) quiescent crystallization under Pressure Quench.

Such difference in nuclei density implies that some unstable shear-induced nuclei relaxed during annealing.

Furthermore, crystallinity development of the annealed, un-annealed samples are compared with quiescent crystallization as reference, see Fig 4. The lower crystallinity in annealed samples confirms the decrease in the total nuclei number. Application of Pressure Quench on sheared and annealed polymer melt concludes that the stable flow-induced precursors can survive after a 22-min annealing, but the average nuclei density along the whole sample does relax.

[1] Beamtime Report BM26B 26-02 519

[2] Keller, A.; Kolnaar, H. W. H. *Flow-induced orientation and structure formation.* In Processing of Polymers; Meijer, H., Ed.; Wiley-VCH: Weinheim, 1997; Vol. 18, pp 189-268.

[3] Liedauer, S.; Eder, G.; Janeschitz-Kriegl, H.; Jerschow, P. Geymayer, W.; Ingolic, E. *Intern. Polym. Proc.* **1993**, *8*, 236-244.