ESRF	**Experiment title:** In situ study of the influence of flow induced molecular orientation on the crystallization behavior of a set of well defined i-PP's with different molecular weights (distributions)	**Experiment number**: **26-02-218**
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Report:

Two dimensional SAXS synchrotron studies have been performed in order to determine the influnce of flow and thermal histoty on crystallization behavior of isotactic polypropylene (iPP).

EXPERIMENTAL

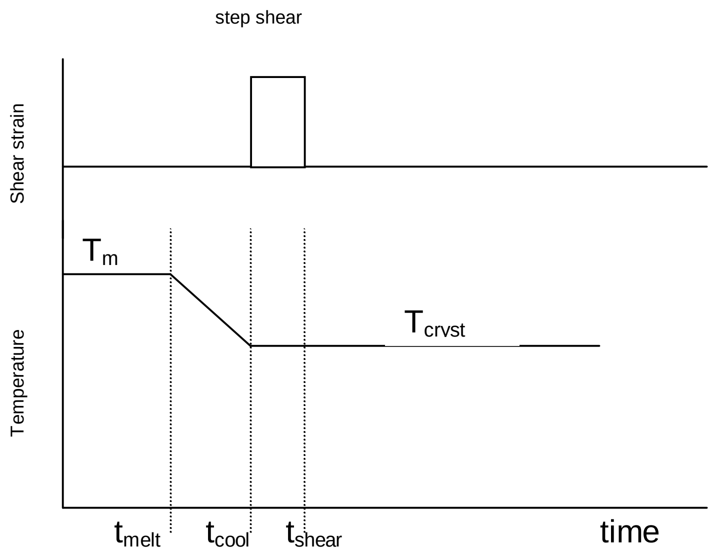


Figure 1. Experimental protocol for the shear experiments

A linear isotactic polypropylene (iPP, HD120MO, Borealis) was used. Its molecular parameters are M_w=365 000 g/mol and M_w/M_n=5.4. Disk shaped samples with a thickness between 100-500μm were prepared by compression molding.
For the in-situ SAXSexperiments a shear cell device (Linkam, CSS450) was used to apply a well-defined thermo-mechanical history to the melt. The samples were inserted between the two parallel plates of the shear cell and a shear flow with a certain strain (varying from 6000 until 36000%) was applied immediately after the chosen crystallization temperature Tc was reached (Fig.1).

RESULTS

A set of experiments was performed where the shear strain was kept constant while varying the shear rate and the shear time (Fig.2). In this way the effect of different flow parameters on the structure formation can be clearly separated.

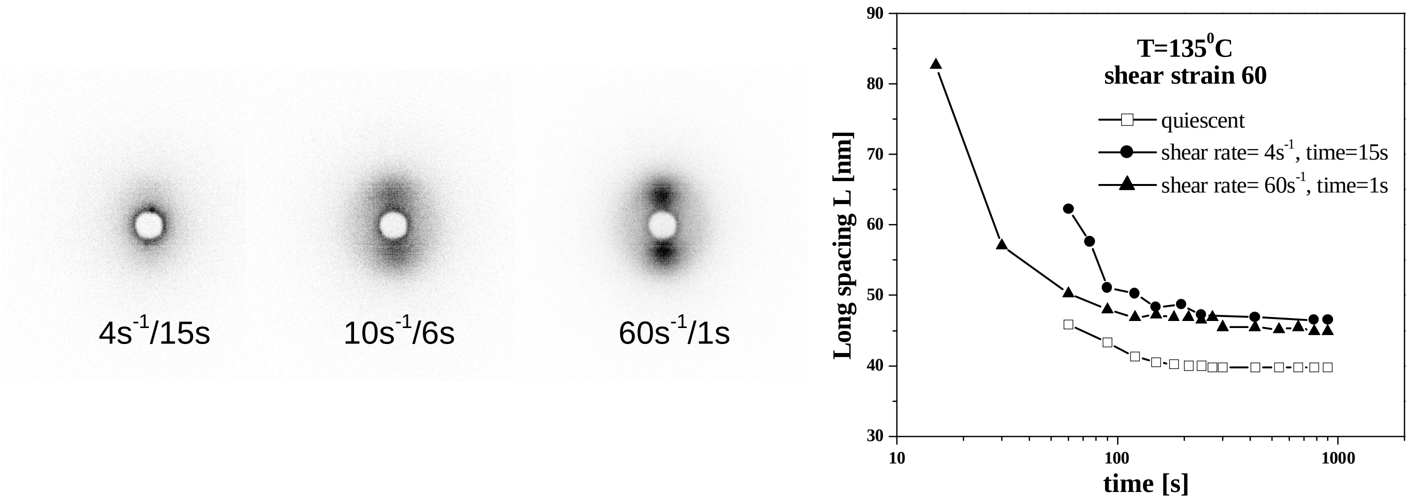


Figure 2. SAXS patterns of iPP (left) and the corresponding time evolution of the long spacing (right) during crystallization at T_c=135^{0}C and constant total strain of 6000%, for different shear rates and time. SAXS patterns are taken 60 sec after the beginning of crystallization.

Fig. 2 and Fig. 3 show that at a certain strain the parameter that has a dominant influence on the crystallization is the shear rate. A higher rate leads to a faster structure formation and to a stronger orientation. Moreover, formation of the "shishes" (equatorial streaks on Fig.3 - left) can be observed only at high enough shear strain and shear rate.

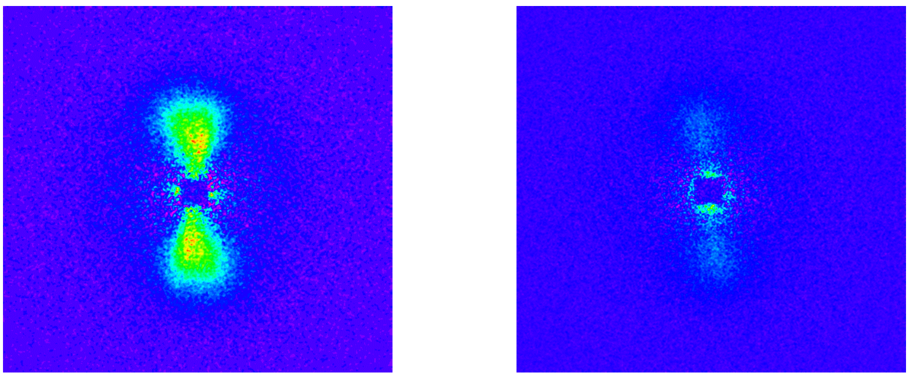


Figure 3. SAXS patterns taken 10s after applying shear with a total strain of 30000%, for different shear rate and time: 60s^{-1}/5s (left) and 10s^{-1}/30s (right), T_c=140^{0}C

The effect of thermal treatment of the polymer melt was studied. Even at temperature close to the melting point strongly oriented patterns were observed (Fig.4) with a larger space between the oriented lamellae.

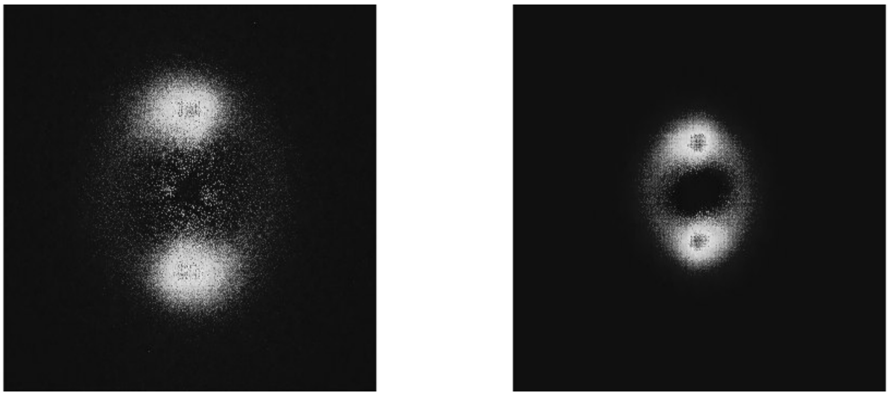
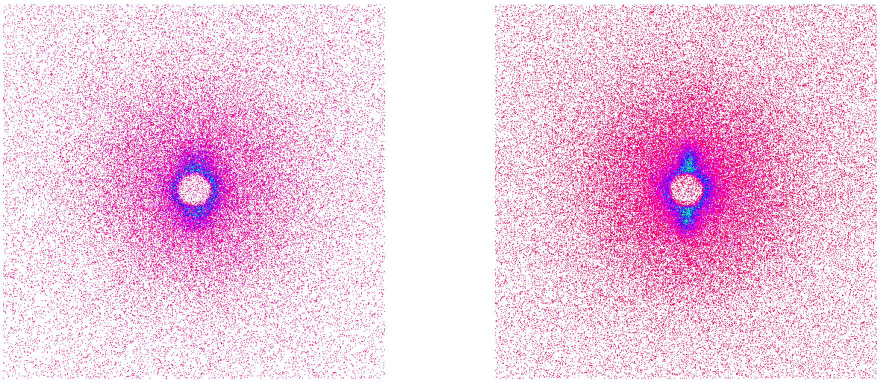


Figure 4. Oriented SAXS patterns of iPP during crystallization at different temperatures: 140^0C (left) and 165^0C (right) after shear with $60s^{-1}/5s$

A series of experiments were done in order to study the melt memory effect, i.e the presence of flow effects after re-melting the sample. Results from these experiments (Fig.5) clearly indicate that when a strong flow field is applied to the melt, some of the oriented structures created during the first shear survive the subsequent melting and after the second shear they accelerate the following quiescent crystallization.



first shear second shear

Figure 5. Images from SAXS experiments of flow induced crystallization at 145^0C and shear $60s^{-1}/3s$. Both patterns are taken 40 s after the first (left) and the second (right) shear.

SUMMARY

Shear flow influences to a high degree the crystal nucleation – it not only changes the number but also the type of the nuclei.
At a certain total strain, increasing the shear rate influences structure development more then an increase of the shear time.
Due to the melt memory, the thermal history of the polymer melt is an important factor for the kinetics of flow induced crystallization.