



	Experiment title: Ordering and crystallisation in sheared isotactic polypropylene	Experiment number: SC1649
Beamline: ID2	Date of experiment: from: 27 April 2005 to: 30 April 2005	Date of report: 30 August 2005
Shifts: 9	Local contact(s): Pierre Panine	<i>Received at ESRF:</i>
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Report:

A large number of iPP samples of different origin and properties was investigated, mainly Ziegler-Natta type (9 different characteristics), but also some metallocene ones. We have been chasing the origin of the smectic ordering. A series of experiments was done at room temperature (RT) on pellets as received, in a Couette-cell at temperatures in the melt, and in a standard (non-shear) temperature cell.

Summary of results

1. Pellets of 7 out of the 9 Ziegler-Natta iPP samples showed at RT a peak (let us call it the smectic peak) around a q-value corresponding to 4-5 nm in addition to the crystal peaks. However, usually only for one orientation, and weak. Probably too weak to be detected at the rotating anode.
2. In all iPP with a smectic peak, upon heating the peak did not melt and remained visible (now at about 3-4 nm) in the melt. The peak could only be made to disappear by annealing around 270°C for at least 15 minutes. If not fully annealed it reappeared again at lower temperatures.
3. Shearing usually caused alignment of the smectic peak in one direction. However, the shearing in the Couette cell was not always well-enough controlled for the present measurements, leading sometimes to ambiguous results. For example, in some cases a second peak appeared and disappeared: shearing of only part of the layer?

The shear we applied in situ was not at the origin of the smectic peak; the latter seemed to be induced by the extrusion process of the pellets. In the two samples that did not show a smectic peak in the crystalline pellets, we could not induce it by shear. When in the other cases the smectic peak was made to disappear after prolonged annealing at high temperatures, it could also not be induced again at lower temperatures in the melt.

4. One of the two samples not giving a smectic peak was treated in many ways (strong shearing, cold quenching, hot pressing plus cold quench) attempting to induce a smectic peak, either in the crystal or in the melt, but without any success.
5. The metallocene samples were all powder and some were investigated: no smectic peak.

Preliminary conclusions

1. The smectic phase in the melt of iPP originates from the crystal. If existent it can be seen already in the anisotropic pellets at RT. The shear we applied had only an orienting effect.
2. The origin of the smectic/crystal phase is still unclear. Most probably it is related to the extrusion process during the production of the pellets. A possible role of additives cannot be fully excluded yet.
3. Remarkable is that two samples ($M_n = 59k$ and $67k$ from the Sabic series) are close in properties and origin, but show a rather different behaviour: the first one shows a smectic peak, the second one not. These two samples are prime candidates for a thorough comparative chemical analysis. The absence/presence of the smectic peak potentially allows to find a clue to the origin of the smectic ordering.
4. Synchrotron measurements are essential to see the smectic peak which – if existent – is often weak. As the peak occurs in the crystal at RT for many samples from different origin, it is not clear why it has not been explicitly reported earlier (disregarded as impurity?).
5. The influence of the smectic peak on crystallisation remains to be further investigated (in quiescent conditions and with simple planar shear).