| ESRF | **Experiment title:**<br>SAXS-Experiments on Smectic Superstructures | **Experiment number:**<br>SC 349 |
|---|---|---|
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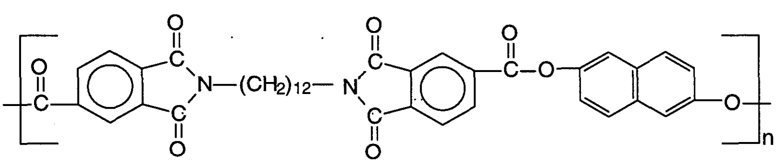
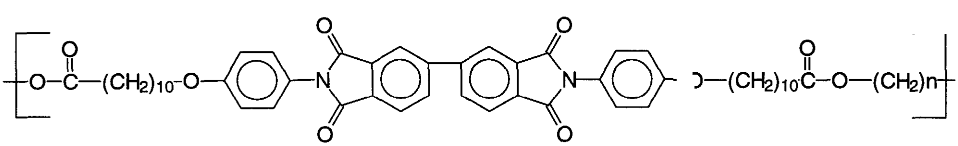
**Report:**

We obtained MAXS (low or middle angular X-ray scattering) patterns from well oriented samples of Poly(ester imide)s, which were investigated by means of X-ray-microfocus scanning experiment using a 2 μm glass capillary and determined local directors in domains of smectic structures (fibers, LC-fields and spherulites). Typical accumulation times were 16s per image at 13 keV.

Following Poly(ester imide)s consisting of long aliphatic spacers and rigid rod mesogens with smectic layer structure were examined:



**1**



**2**

The SAXS-long periods, which were proved to exist at L = 20 - 30 nm by means of large focus measurements of high ordered smectic samples of **1** and 2 at HASYLAB / Hamburg, could not be detected due to the high divergence of capillar focussed beam. For this purpose a new SAXS-setup without capillary, but with a collimator is conceivable.

Nontheless we obtained interesting results by using the normal WAXS-Setup and, in addition to this, by using a middle angular (MAXS) setup, in order to achieve a better resolution of the layer reflections at $2\Theta$-values from 1° to 8° (d = 1 nm - 8 nm). **Fig la-c)** presents three fiber patterns of 2, which show the different layer reflections in respect to the length of the spacer molecules. The Polymer with shorter spacer (here: n = 2) exhibit a smectic C layer structure and gives rise to an equatorial reflection. In contrast the molecules with longer aliphatic spacer show the maxima of $S_C$-layer reflections on the meridian, the reflection maxima give the angular $\beta$ in respect to the fiber axis if the mesogens are tilted within the smectic layers **(Fig lc and d).**

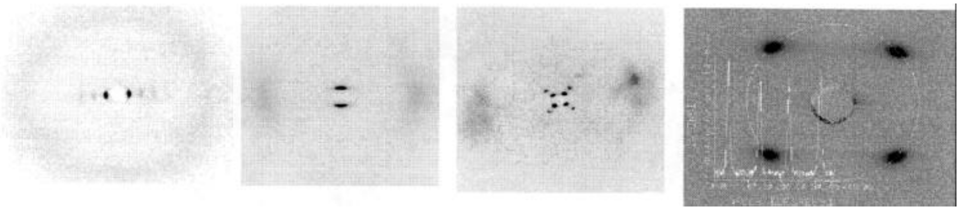
An analogous effect already reported[1,2] was found within sheared films of Polymers containing biphenylic units. Whereas Krigbaum et al.' reported the correlation of preferred orientation and molecular weights, the molecular weights of our samples in Fig. la and lb were nearly the same ($n_{inh}$=1,3 dl/g). **Fig ld)** shows an example of X-ray patterns of a 2-fiber using a middle angle setup, these reflexes are now accessable for a quantitative analysation. **Fig 2a-b)** shows first X-ray patterns with layer diffractions (d = 4 nm) within single domains of a LC-glass of 2 **(n=8),** in which the molecules show varying prefered orientations. Above sketches show the relating surface disclinations.

**Further scanning experiments will give maps of MAXS-X-ray patterns, which describe the prefered orientation in a director field of LC-polymers.**

**Detailed informations of texture in a plane will be achievable by pole figures and resulting ODFs (orientation distribution functions) using goniometer setup.**

Another interesting result is the WAXS-pattern scan through a smectic ($S_H$) spherulite of 1 shown in Fig.3. The angel between director of (001) from layer and (001) from unit cell increases to the middle of the spherulite.

[1] W.R. Krigbaum, J. Watanabe, ***Polymer 24*** (1983), 1305
[2] R. Pakull, H.R. Kricheldorf, ***Macrolmolecules*** 21 (1988), 551 and S.Buchner, Diss., Uni-Hamburg 1993



a) n = 2 , $S_C$ b) n = 12, $S_A$ c) n = 16, $S_C$ d) n = 16, $S_C$

**Fig.1:** *X-ray fiber patterns of single fibers of 2 with variable spacer length; a: n =2 equatorial layer reflection up to 3rd order, the WAXS Halo shows light anisotropy; b: n = 12 meridional layer reflection; c: n = 16 in Sc the molecules are tilted d:sample c, but received by middle angle setup, fibre axis is vertical.*

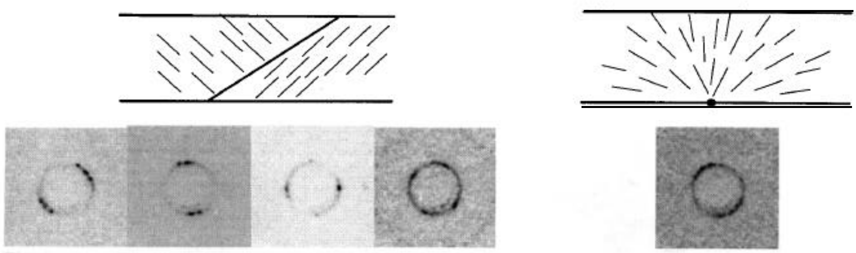


**Fig 2a-b):** *Examples* ***of*** *middle angle-X-ray patterns* ***of*** *single domains in a LC-director-field* ***of*** *2 (n=8)with relating surface disclinations.*

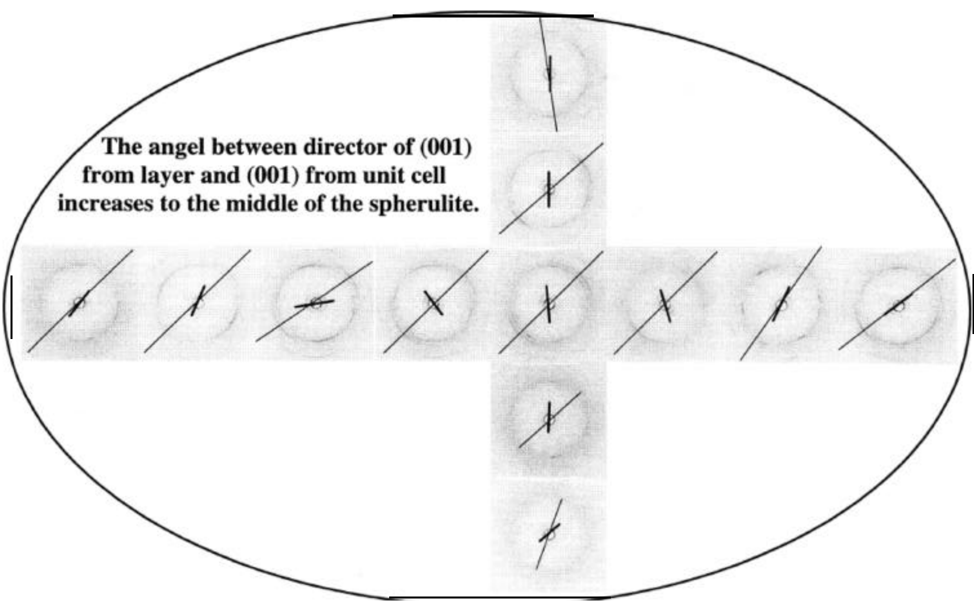



**Fig.3:** *X-ray patterns* ***of*** *in smectic spherulite* ***of 1, thin line*** *describes director* ***of*** *(001)-plane* ***of*** *unit-cell (molecular chains);* ***fat line*** *is director* ***of*** *(001)-reflection* ***of*** *the smectic layer plane.*