	Experiment title: Correlation between mechanical deformation and structural change on ionomer membranes : SAXS-WAXS study	**Experiment number**: SC959
Beamline:ID02	**Date of experiment**: from: 12/06/02 7h00 to 15/06/02 7h00	**Date of report**:
Shifts: 9	**Local contact(s)**: P. Panine	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Diat Olivier DRFMC/SI3M/PCI, CEA Grenoble

Gebel Gérard "

Rubatat Laurent, A. de la Rosa P. van der Heijden & J-F. Blachot

B. Moore & K. Page University of Missippi

Report:

SAXS coupled with WAXS experiments were performed on Nafion-type samples under different elongation (from 0 up to 200%, to cover the entire viscoelastic regime). A stretching machine available at the ID2 beamline was incorporated in a humidity controlled box in order to vary roughly the water vapour pressure (using saturated salt solutions to yield 10, 50 and 98% R.H.). The membranes were studied in different ionic forms (i.e. Cs+, Li+, alkylammonium or H+) in order to vary the dipolar interactions between the pendant ionic groups and to change the number of water molecules per ionic sites from 1 to more than 20 [4]. Membrane samples having different ionic contents (or equivalent weights) or with different lengths of the ionic pendant chains along the polymer backbone were tested. The main objective was using an orientation mechanism to evidence the form factor of the polymeric aggregates present in the polymer film by eliminating partially (as a function of the scattering direction) the contribution of the structure factor.. Although that the analysis are preliminary, the figure 1a (2D scattering pattern for different drawn ratio; the stretching direction is parallel to the second diagonal and the shadow comes from the WAXS detector) show that:

Parallel to the stretching axis (fig. 1c), we first observe the shift to the low angle followed by the decrease in intensity until the quasi-disappearance of the ionomer peak when in the orthogonal direction we observe the increase in intensity of the same ionomer peak (fig1b). For a draw ratio greater than 1.5, the scattering intensity corresponds to the scattering of oriented cylinders in bundles (the bundles scattering contribution is observed in the scattering upturn at low q). At large scattering angles we observe also some contrary variation in intensity concerning the crystalline peaks (100 and 202 resp.) that can be analysed in term of an improvement of polymer backbones correlation perpendicularly to the stretching axis and a de-correlation between fluor atoms from chain to chain and along the stretching direction.

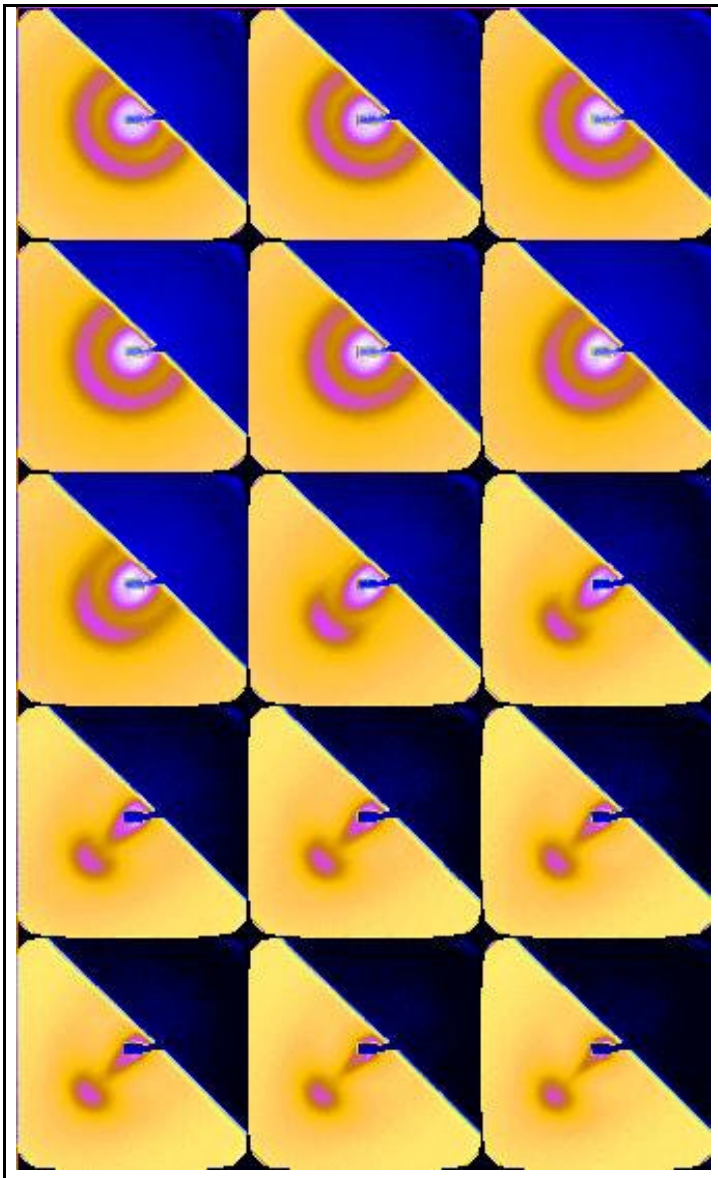

Fig.1a

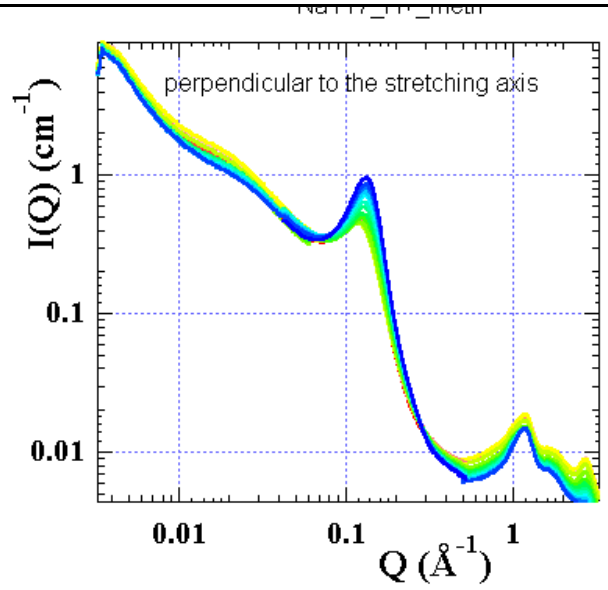

fig.1b

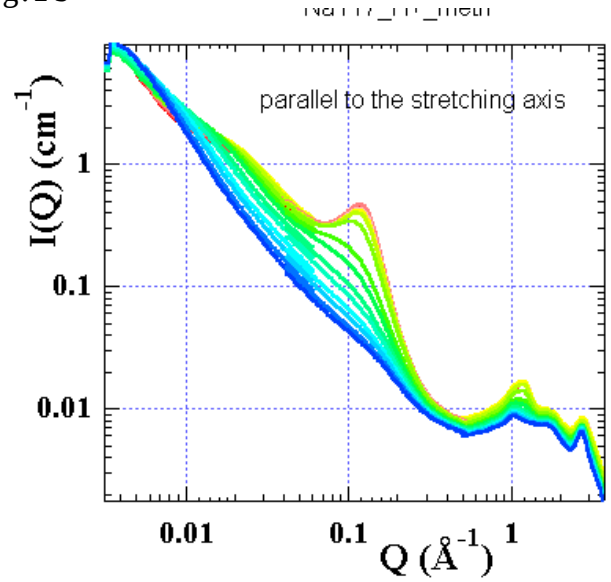

Fig.1c

The analysis at very low q was unfortunately prevented by the strong scattering of the cell windows (polymer and not mica as required by the local contact to avoid strong spot on the WAXS camera) and SANS measurements will be performed to solve this problem.

We evidenced also that the TBA+ counterions allow to increase the quality of the orientation compared to H+ due to higher dipolar interactions between aggregates. On the other hand the methanol as a solvent allows to reduce considerably the cristallinity and so to observe more clearly the form factor of cylindrical object.

Deeper analysis is still in progress (2500 files were obtained and an Igor procedure has been developed to automatically analyse the scattering variation as a function of stretching ratio).

First results are presented at SRPS II in September 2002.