	Experiment title: Water-swollen perfluorated Ionomer membranes: µSAXS studies	**Experiment number**: SC701
Beamline:ID13	**Date of experiment**: from: 9/06 7h00 to: 12/06 7h00	**Date of report**:
Shifts: 9	**Local contact(s)**: MÜLLER Martin	*Received at ESRF:*

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Report:

The aim of this experiment was to study, using x-ray diffraction technique, ionic conducting polymer membranes out of the film plane. Since the membrane are usually between 50 and 150 microns thick, the idea was to study them using a very tiny beam (tipycally 10-15 micron in diameter) through the side of the membrane and to compare the experiment as we shine the membrane perpendicualry to the film surface. We wanted to keep a good angular resolution for SAXS purposes. The samples were placed in a cell in which we controlled the water vapor pressure.

Two types of membranes were studied: Nafion (perfluonated membrane) as reference of a isotropic structure (usually described in the litterature) and PIS (sulfonated polyimide membrane) a system that we have developped at the CEA and for which the experiments of swelling, conductivity and preliminary SANS have demonstrated that the structure is anisotropic.

First of all, the experiments were very successful and the results unexpected. Their analysis are still in progress.

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For nafion (115), it appears that the small angle shoulder (5e-2 Å-1)which can be observed at smaller angles than the ionomer peak (2e-1 Å-1)and that we consider to be related to a superstructure in the perfluorated chains crystalline domains, is very well pronounced in this scattering geometry and looks like a peak (fig. 1. Moreover it is anisotropic, indicating an orientation of the chains perpendicular to the processing direction.

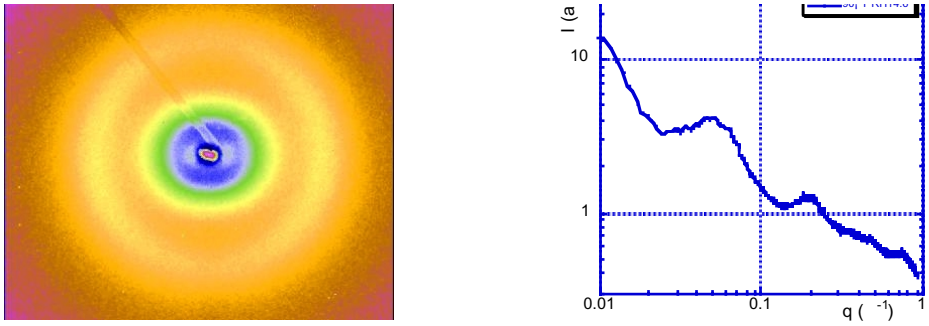

Fig 1: 2D-spectrum from Nafion in tangential configuration and the corresponding profil along the vertical direction.

For PIS, a copolymer with a an ODA3-4';4-4' diamine in the hydrophobic part we have studied different sequences variing the size of the hydrophilic bloc, keeping the total charge constant and reciprocally variing the charge keeping the size ratio betwen both blocks, constant.

Since the ionomer peak observed in the plan of the membrane do not move as we swell the membrane even though we observe a thickness variation from 20 to 30%, we expected to observe this ionomer peak shifting in this scattering geometry.

In fact we observe a different ionomer peak – at larger angles than the previous one

- which still does not shift as we swell the membrane
- but which depends on the size of the hydrophobic bloc (see Fig. 2)

The questions are now what is the origin of the ionomer peak in the plan of the film and is it really an ionomer peak ? How the system swell and at which scale.

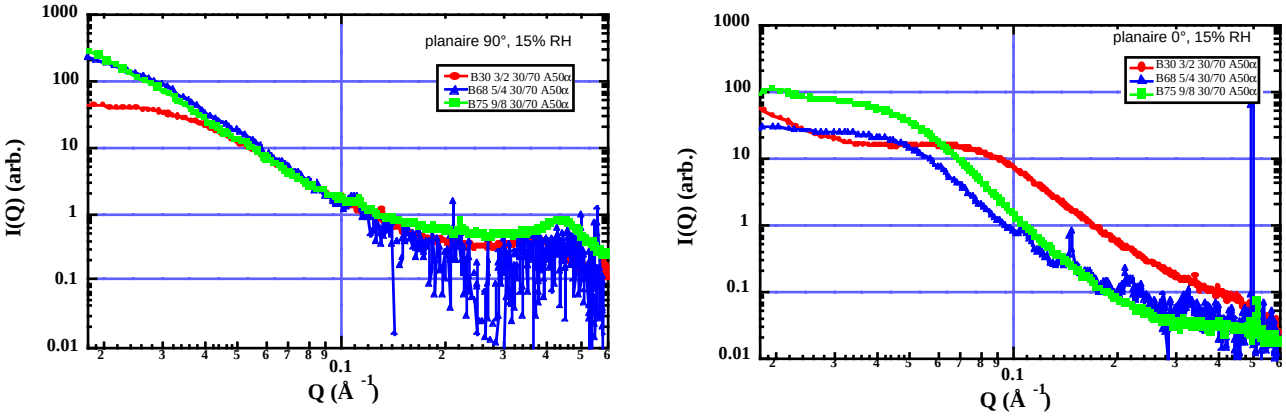

Fig. 2 left) In plane scattering profile of PIS sample for different ionic block sizes

Right) out of plane scattering profile of PIS sample for different ionic block sizes