	Experiment title: from nano to microstructure of new sulfonated polyimide membrane for fuel cell application	**Experiment number:** SC1398
Beamline: ID02	**Date of experiment:** from: 11/03/04 7h00 to 15/03/04 7h00	**Date of report:** August 03 *Received at ESRF:*
Shifts: 12	**Local contact(s):** T. Weiss	

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Report:

As observed in previous SAXS and SANS experiments, the bidimensional SAXS patterns of rigid sPI are isotropic in parallel configuration whatever the polymer composition and the process of casting used to prepare the membrane from the polymer solution. The distribution of the scattered intensity is identical whatever the azymuthal angle in the detector plane.

Figures present the variation of the scattering intensity along the parallel directions for different sulfonated polyimide samples varying the sequence length for a given IEC. On radially averaged scattering curves, these scattering profiles are characterised first by a broad shoulder at low q-values. This shoulder is sometimes clearly visible sometimes not due to an intense scattering upturn at smaller angles. This upturn is usually related to large scales heterogeneities (about 100 nm) in ionic polymers. Concerning the shoulder, it can be assimilated to an ionomer peak, the main scattering feature for ionomer films, which originates from constructive interferences from scattering objects. These objects can be considered in a very schematic frame as domains rich in sulfonated groups separated by domains containing hydrophobic blocs. For this system, the peak is quite large due to a supramolecular ionic domains organisation. With increasing the number of X units (keeping X/Y constant), its position shifts to the lower q-values. These characteristic distances are of the same order than lengths that could be estimated summing X and Y block chains lengths. Nevertheless, it is important to point out that this determination remains quite dependent on the way to extract the q-position of the shoulders since they appear over a strong intensity upturn.

The differences with the usual ionomer spectra concerns first the position of the ionomer peak which is located at lower angles and indicates the existence of three to five times larger ionic clusters or larger distances between ionic domains in the polymeric matrix compared to perfluorosulfonated systems. Second, we can observe a second broad and isotropic maximum at larger scattering angles (q_{max} □ 0.4 Å^{-1} with multiple order), which does not exist in perfluorosulfonated polymeric systems and could be attributed to the sequential form of the polymer.

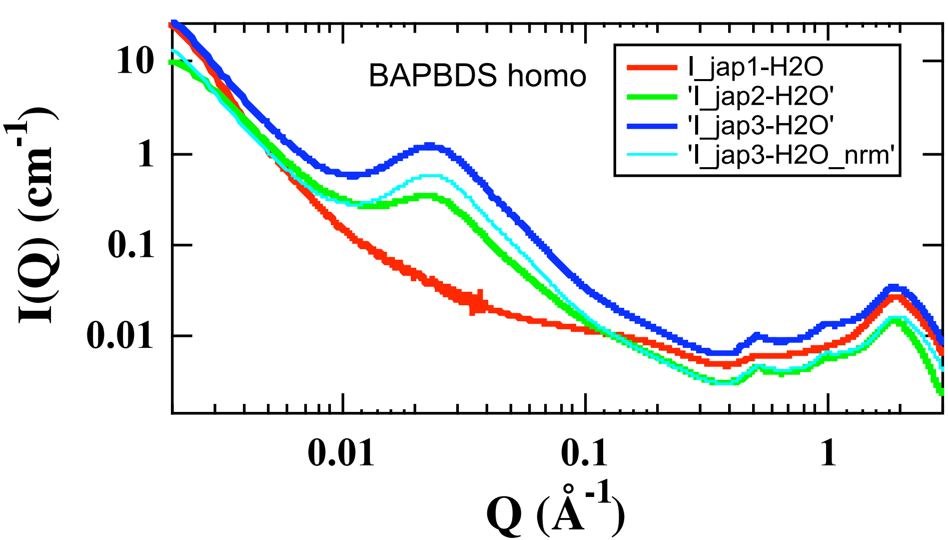

Figure 1: SAXS-WAXS resu

homopolymers in H2O

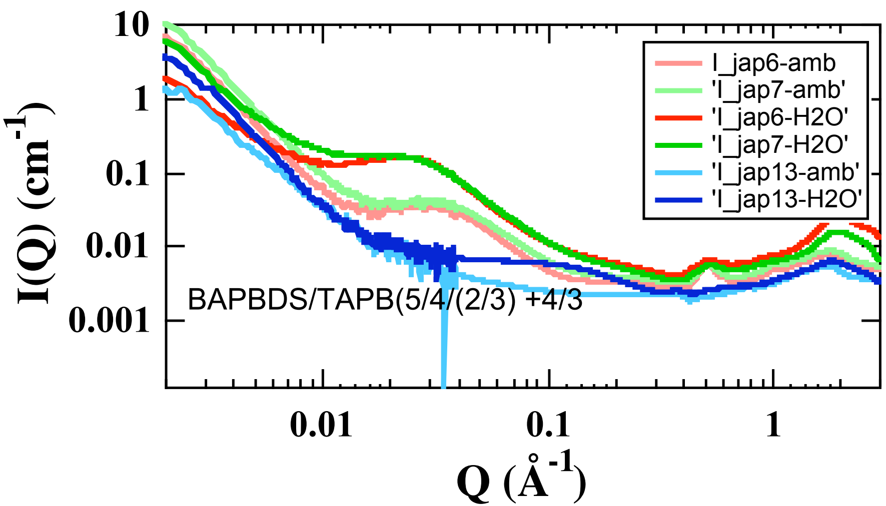

Figure 2: SAXS-WAXS resu

copolymers in H2O and
humidity

By analysing the position of these maxima, it suggest a lamellar molecular organisation which is not surprising in polyimide system.

An interesting feature concern the shoulder which appear in the intermediate q-range around 0.1 Å^{-1}. This shoulder is dependant on the water content. Two way are explored in order to analyse this intensity variation. Either it correspond to a contrast variation in the scattering length density modulation or to something which is the signature of the interaction between the polymer and looks like a sol-gel transition. This analysis is in progress. A lot of data was collected as a function of charge content and distribution. Unfortunetly no experiment were performed on ID18f in order to probe the molecular and ionic organisation along the membrane thickness.