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	Experiment title: GISAXS Study of the Structure and State of Ion Aggregation in the Surface Layer of Nafion Exposed to Water Vapor	**Experiment number**: SI-1868
Beamline:	**Date of experiment**: from: 11/03/2009 to: 18/03/2009	**Date of report**: 1/3/2010
Shifts: 18	**Local contact(s)**: Dr. Amarjeet Singh	*Received at ESRF:*

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Report:

Schmidt-Rohr and Chen [1] has concluded recently that the bulk scattering of Nafion reported by Gebel, Diat and co-workers [2] is best explained by assuming a 2D morphology, in which water and hydrated ionic groups form long channels stabilized by long crystallites of the matrix (see Fig. 1). The most characteristic feature in scattering of Nafion and similar materials is the ionomer peak observed at $q \sim 0.1 - 0.2$ Å^{-1} that is assigned to hydrated ionic aggreagates of a typical size of a few nm that varies with hydration.
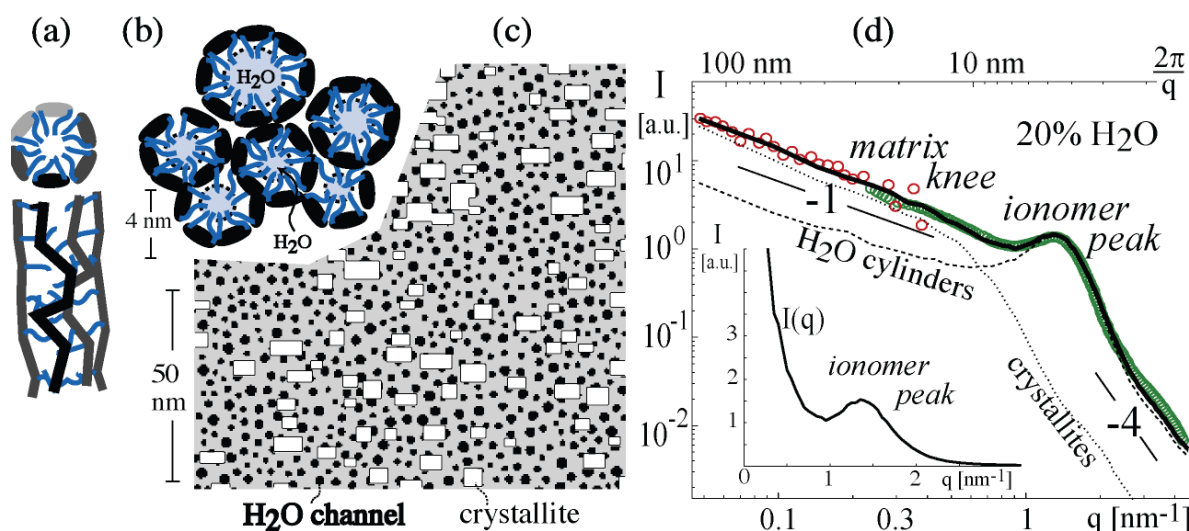

Fig. 2. The anisotropic bulk structure of hydrated Nafion comprising elongated channels stabilized by long matrix crystallites: (a) shape of aggregates, (b) aggregate packing, (c) suggested bulk morphology, (c) scattering curve in Fig. 1 as superposition of scattering by aligned water channels and crystallites. After Schmidt-Rohr and Chen [1].

The above results on bulk structure of Nafion were obtained for Nafion containing a given amount of water. However, a significant controversy often arises when the chemical potential of water rather than its content is fixed, i.e., Nafion-water equilibrium is considered. It is known that dilute solutions of Nafion, in which Nafion assumes the configuration of rod-like micelles, are infinitely stable. However, equilibration of Nafion with water yields only a swollen polymer over any realistic timescales. Moreover, many reports suggested that equlibration with a saturated vapor often yields a still more puzzling result, Schroeder's paradox [3], a swollen polymer with a lesser water content than in water, even though this result was questioned recently [4].

A few recent reports suggest that the above controversies may be related to extremely slow relaxation of Nafion, which prevents this material from reaching a true equilibrium with water [4]. In this respect, the surface of Nafion presents a special region, where relaxation can proceed much faster. In addition, this region is subject to additional surface forces, arising from surface tensions between the external medium (liquid or vapor) and the two microphases of Nafion (aqueous phase and hydrophobic matrix), which are absent in the bulk [1, 3-5]. As result, the surface may adopt quite different (metastable) confomations depending on whether it is exposed to water or vapor, as schematically shown in Fig. 2. While in vapor the surface tension balance forces the bundles of water nanochannels ("fused macaroni") get buried under a thin perfluorinated "crust" [6] and align parallel to the surface, in water such bundles are expected to break up to rod-like "spaghetti" and randomly stick out of the surface [7]. This is consistent with sharp change in the contact angle (form highly hydrophobic to hydrophilic) and roughening of Nafion surface under water observed by AFM [6].

In our first series of experiments (see report SI-1692 and ref. [7]) GISAX was used to examine the surface of Nafion in vapor. The samples were thin films of Nafion (ca. 100 nm thick) spin coated on Si wafers. We indeed observed clear signs of enhance alignment of micelles (macaroni bundles) nears the surface, which could be inferred both from a larger anisotropy of the GISAX pattern and a shift in the position of ionomeric peak for about half-critical incidence angle as compared to near critical angle (see Fig. 3a and b).

In the present experiments the purpose was to similarly examine Nafion surface under water. Using water as the external medium required a few changes in the procedures and setup compared to the first GISAXS experiment in vapor:

(1) the beam energy was increased from 8 keV to 22 keV in order to minimize scattering by water;

(2) a liquid cell with two windows made of perfluorinated polymer was used in place of a humidity chamber;

(3) since Nafion films cast on bare Si quickly detach in water, new samples, stable under water, were cast on "silanized" hydrophobic Si wafers capped with a dense layer of C18 groups aligned normal to the Si surface. Silinization was accomplished by reacting Si wafers having a native oxide layer with a solution of octadecyltrichorosilane (OTS) in dry toluene.
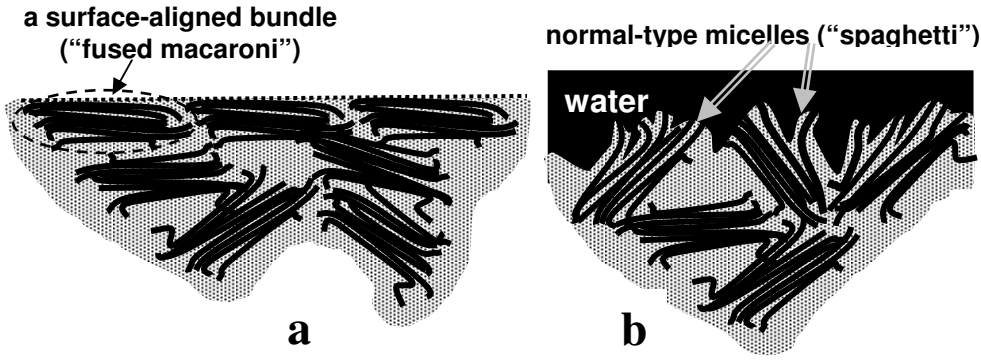
Fig. 2. Schematic representation of the surface structure of Nafion in various environments: (a)–arrangement of aligned "fused macaroni" bundles near the vapor-polymer surface; (e) roughening of the Nafion surface in liquid water accompanied by random misalignment and break-up of bundles to "spaghetti". Black and grey colors designate the aqueous phase and the perfluorinated matrix, respectively.
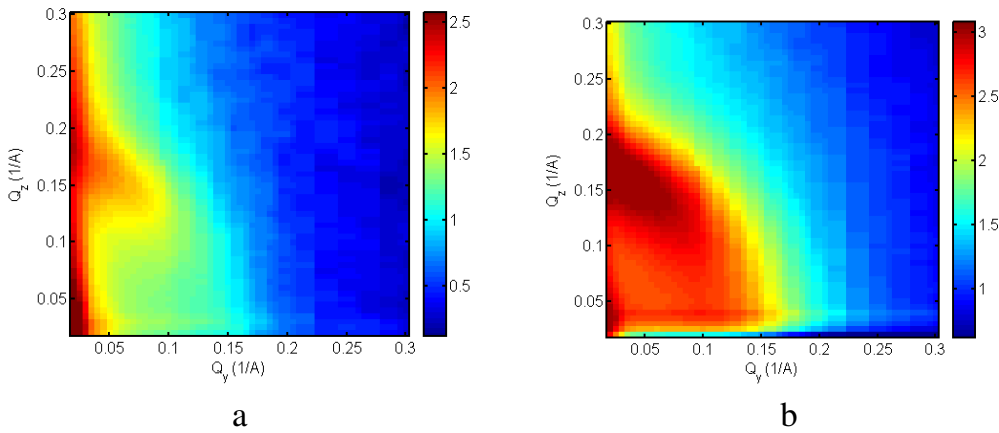

Fig. 3. 2D maps for Nafion surface in vapour: (a) incidence angle 0.11º; (b) incidence angle 0.20º.Sample: a ca. 100 nm thick Nafion film spin-coated onto a bare Si wafer. Beam energy 8 keV. Critical angle ca. 0.20º.

The sample was mounted in the liquid cell, which was then filled with water, and let equilibrate for about 1 hour prior to GISAXS measurements. GISAXS spectra were recorded for each sample at 5-6 incident angles α_i including sub-, near- and over-critical ones. To minimize the artifacts due to radiation damage the sample was laterally translated and re-aligned for each incident angle. The critical angle for Nafion(p)-water(w) interface at 22 keV was calculated using the formula

$$\alpha_{p/w}^2 = \sqrt{\alpha_p^2 - \alpha_w^2} \approx 0.05º,$$

where $\alpha_p \approx 0.07º$ is the critical angle of Nafion in air or vapor at 22 keV, as was deduced from $\alpha_p \approx 0.20º$ at 8 keV and the fact that the critical wavenumber $Q_c = 4\pi\alpha_c/\lambda$ does not depend on the beam energy, and $\alpha_w \approx 0.05º$ is the critical angle for water-air interface at 22 keV. The spectra were corrected for the backgound scattering from water and windows that was measured using a direct beam. The correction was performed by subtracting from the measured scattering for each point in the 2D map the intensity of the background scattering multiplied by a factor between 0.5 and 1. The factor was calculated so as to eliminate the

background scattering in the range $2 < Q < 3$ A^{-1} dominated by the diffraction peaks of the window polymer and some scattering from water. The resulting maps are shown in Fig. 4.

$\alpha_i = 0.03°$

$\alpha_i = 0.04°$

$\alpha_i = 0.045°$

$\alpha_i = 0.05°$
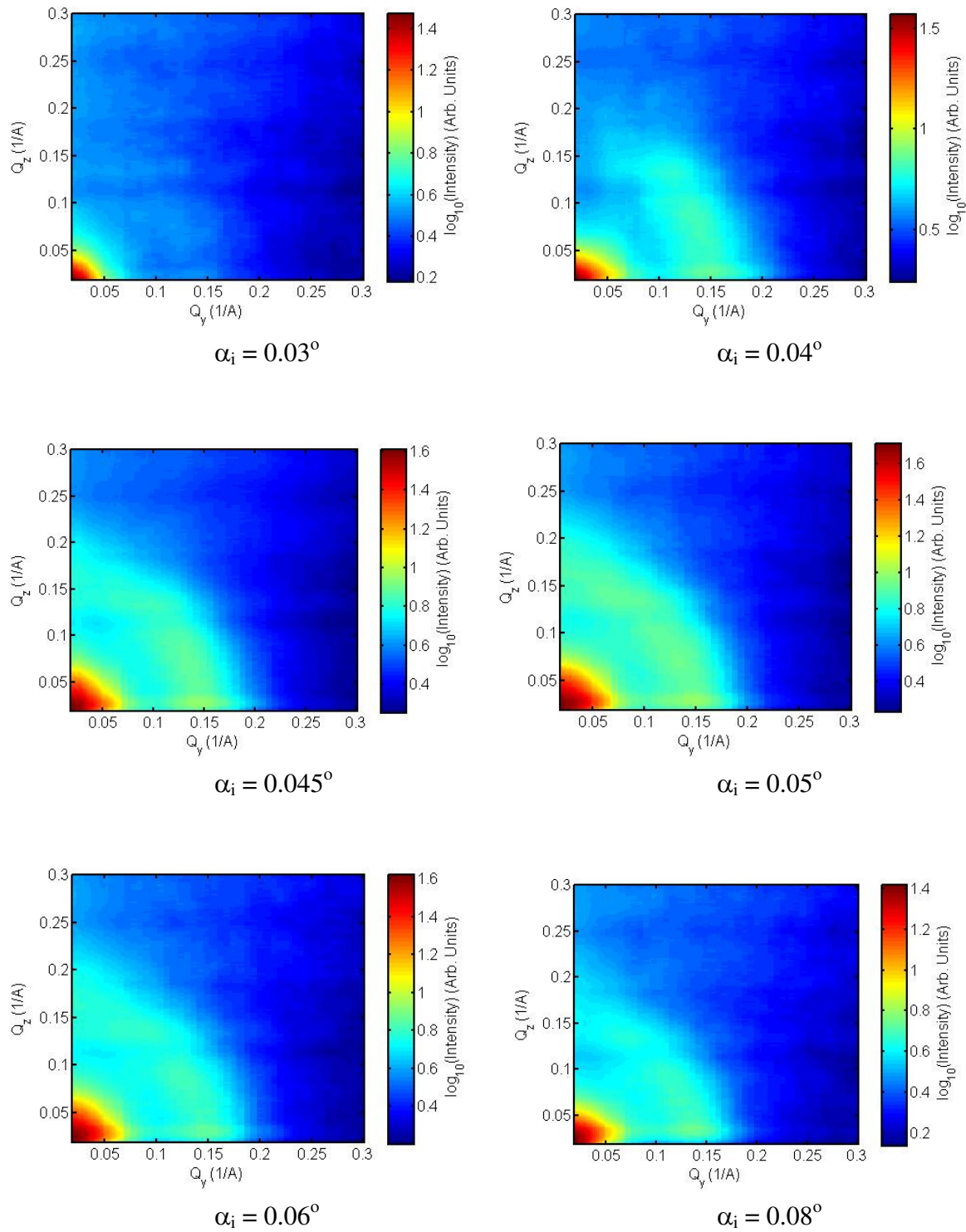
$\alpha_i = 0.06°$

$\alpha_i = 0.08°$

Fig. 4. 2D maps for Nafion surface under water. Sample: a Nafion film spin-coated onto an OTS-treated Si wafer. Beam energy 22 keV. Critical angle $\alpha_c \approx 0.07°$.

The measurements at subcritical angles proved very difficult and only a vanishingly weak ionomer could be obtained for $\alpha_i = 0.03°$ (about $0.6\alpha_c$). However, for $\alpha_i = 0.04°$, about $0.8\alpha_c$, at which the penetration depth

still only about 60% above minimum, the intensity was reasonably high and the anisotropy was clearly seen. The anisotropy was visibly weaker as α_i approached α_c. This seems to agree well with what was expected from the model (Fig. 2). However, as α_i rose above α_c the anisotropy re-appeared, which suggest some degree of alignment also existed in the film bulk.

$$\alpha_i = 0.04^o \qquad\qquad\qquad \alpha_i = 0.06^o$$

$$\alpha_i = 0.07^o \qquad\qquad\qquad \alpha_i = 0.075^o$$

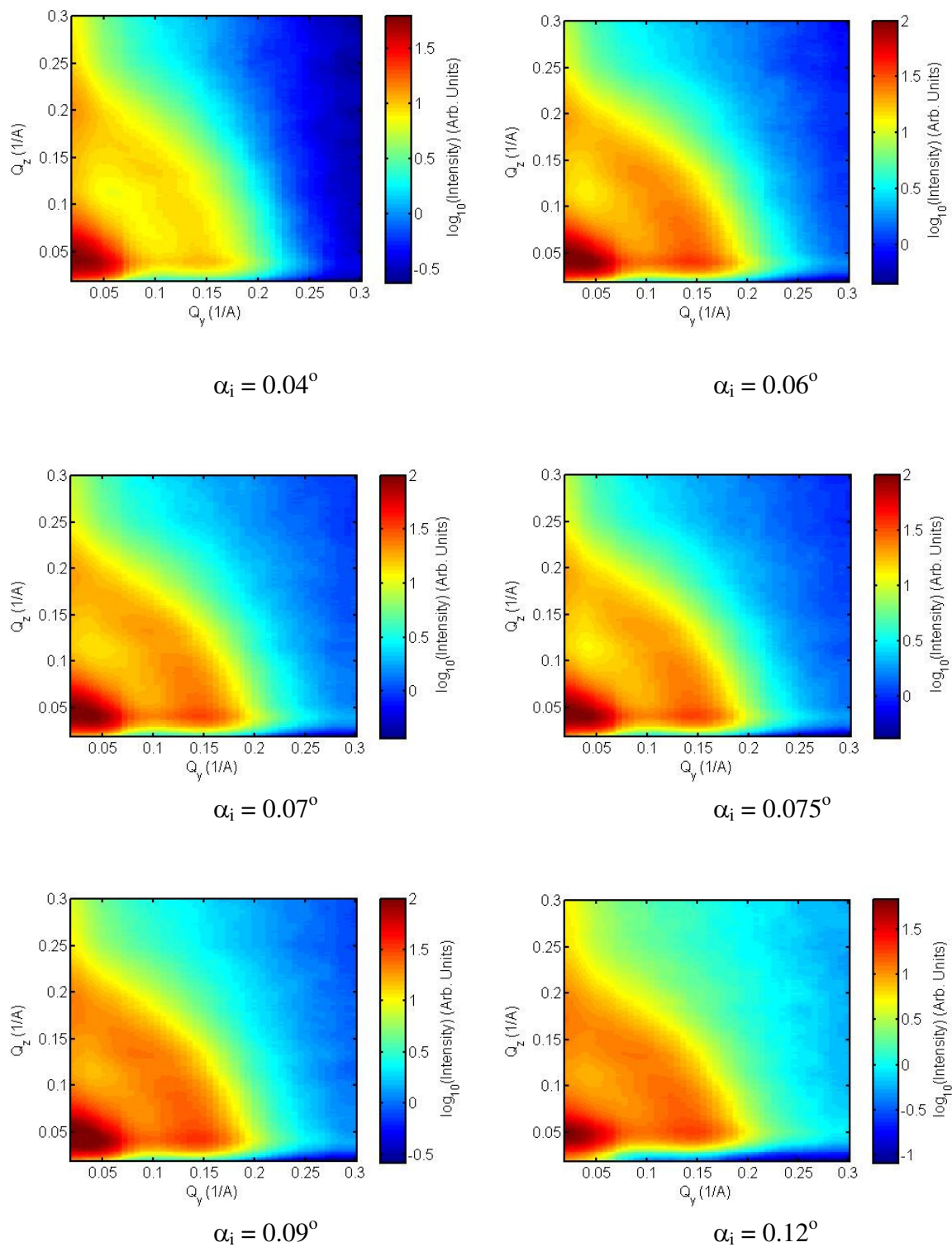$$\alpha_i = 0.09^o \qquad\qquad\qquad \alpha_i = 0.12^o$$

Fig. 5. 2D maps for Nafion surface in vapor. Sample: a Nafion film spin-coated onto an OTS- treated Si wafer. Beam energy 22 keV. Critical angle $\alpha_c \approx 0.07^o$.

In order to verify that the difference between vapor- and water-exposed samples (Figs. 3 and 4) was due to different external medium (water vs. vapor) rather than a different substrate (bare Si vs. OTS-treated) and wavelength (8 vs. 22 keV), GISAXS spectra were recorded for Nafion films on OTS-treated wafers exposed to vapor as well. The resulting 2D maps are shown in Fig. 5.

The anisotropy at the lowest incidence angle $\alpha_i = 0.04° \approx 0.55\alpha_c$ in Fig. 5 could indeed indicate some preferred in-plane micelle alignment, similar to Fig. 3a. It was also distinctly different from the pattern at lowest α_i under water in Fig. 4, pointing to different micelle arrangement in the two situations in agreement with the model picture in Fig. 2.

However, the GISAXS pattern for near- and overcritical incidence angles in Fig. 5, representing the bulk of the Nafion film on OTS-treated substrate, was distinctly different from the first experiment on bare Si substrate (Fig. 3b). It was actually more similar to the patterns observed for a similarly prepared sample under water. This suggests that it was the substrate rather than the external medium that had the most significant effect on the film morphology and micelle orientation within the film bulk. This result was unexpected in the sense that the more hydrophobic *external medium* (vapor) seems to promote an in-plane surface-alignment of micelles, whereas a more hydrophobic *substrate* seems to promote a micelle orientation perpendicular to the substrate. One may speculate that the intrinsic about-normal-to-interface orientation of the C18 groups of OTS could make the difference in the latter case, similar to interface-induced orientation of liquid-crystalline polymers. Since the film thickness is commensurate with typical dimensions of a micelle bundle, the orientation could span the whole film thickness.

This suggests attractive possibilities of controlling micelle orientation and enhancing conductivity of Nafion films in desired direction. However, the experimental evidence is clearly too limited and a more systematic examination is necessary. GISAXS would be the most suitable way to carry out such experiments to systematically elucidate this point. Since it is important to understand how it affects the behavior of Nafion films in vapor as well in liquid water, it will be beneficial to carry out examination of Nafion films on different substrates both in water (whenever possible) and in vapor (controlled humidity chamber) using the setups developed in this and preceding experiments.

In conclusion, we have seen that the GISAXS pattern at the low subcritical incidence angle indicate that the in-plane orientation presumably characteristics of the a few nm thick topmost of Nafion exposed to vapor is destroyed or even reoriented normal to the surface upon exposure to vapor. This agrees with the model proposed. However, noticeable differences between the two types of conditions were observed for the bulk scattering patterns, in particular, their anisotropy. Since the samples used for examining vapor- and water-exposed Nafion films were prepared on different substrates, the effect of substrate warrants an in-depth examination. The outcome of such examination could, on one hand, confirm and strengthen conclusion regarding the effect of the external media in general, on the other hand, may offer appealing practical possibilities of controlling the orientation and transport properties of thin Nafion films and membranes.

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