Experimental report

15/09/2016

Proposal: **9-11-1764** **Council:** 4/2015

Title: Polyelectrolytes chain conformation under confinement: electrostatic effects studied by Zero Average Contrast method

Research area: Soft condensed matter

This proposal is a new proposal

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Samples: alumina + polyelectrolyte (PSS- and P2VP+) solutions

Instrument	Requested days	Allocated days	From	To
D22	1	0		
D11	0	1	11/07/2016	12/07/2016

Abstract:

The conformation of polyelectrolytes in confined geometries is expected to be perturbated by the existence of charges inside the pore at the wall surface. Here we propose to directly access the polyelectrolyte form factor confined in non-connected 1D nanoporous anodic alumina (AA) with monodisperse pore diameter Dp using Small-Angle Neutron Scattering and the Zero Average Contrast method. By an appropriate hydrogenated/deuterated ratio of the polyelectrolyte and of the solvent one can match the scattering of confining medium and also cancel the intra and inter-chains correlations to directly measure the polyelectrolyte form factor whose analysis allows the determination of the polyelectrolyte radius of gyration Rg, contour length L and persistence length lp. In this experiment we’ll investigate the electrostatic effect on the confined polyelectrolyte chains (polystyrene sulfonate PSS-Na+ and poly-2-vinylpyridine P2VP+) by i) varying the wall charge (positive or neutral) inside the AA pore, ii) varying the Debye length and iii) varying the Dp/2Rg ratio (> and < 1). This work will provide structural information for future inelastic experiments to access the dynamics of these systems.

NB: This is a preliminary report. The experiment has been performed in July 2016.

1. Objective

The aim of this study is to gain understanding on the chain conformation of polyelectrolytes in nanoporous membranes. The experiment is divided in two parts:

- Characterization of the homemade porous alumina membranes prepared in different conditions to get the structural parameters and composition.
- Investigation of the conformation of polyelectrolyte chains in confined geometries.

2. System description

As a polyelectrolyte we used commercial sodium poly(4-styrenesulfonate) (PSS) with M_w= 70.000 kg/mol. Nanoporous alumina membranes (PAAM) were prepared by electrochemical anodization of an aluminum foil (purity 99.999%, thickness 320μm) and served as the confining medium. The membrane consists of porous channels almost perfectly arranged in a hexagonal lattice. The anodization conditions such as the voltage, temperature, duration and electrolyte will determine the final geometrical characteristics of the membrane such as diameter of the pore D_p, interpore distance D_{int}, porosity, thickness L as well as the chemical composition of the material (Fig. 1). The self-ordering of the porous channels is achieved at a certain depth after several minutes from the beginning of the anodization. For this reason the less ordered top oxide surface is removed in a mixture of chromic and phosphoric acid. In the sequel, a second anodization is performed under the same anodization conditions leading in an almost perfectly hexagonal arrangement of the pores. Post treatments such as wet chemical etching in dilute phosphoric acid and thermal annealing can further modify the geometry and composition of the material.

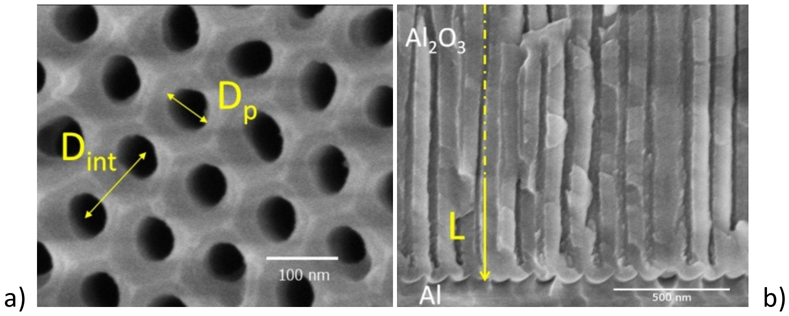

Fig. 1. SEM images for a PAAM membrane prepared at 40V, 18°C, in oxalic acid 0.3M solution. a) Top view, b) cross section.

2. Experimental Configurations

The measurements were performed at the D11 instrument at room temperature (27.7°C). The samples were aligned with the pore surface perpendicular to the beam. Alignment was achieved by tilting and rotating the sample holder while trying to obtain an isotropic pattern on the detector. The samples were measured at constant wavelength of λ=6Å at three different sample-to-detector distances (39m, 8m, 1.4m) providing a q range between $1.3x10^{-3}A^{-1}$and $0.45^{3}A^{-1}$. Both sides of the initial aluminum foil were anodized and were placed inside circular cell, in between two quartz windows. For small samples, cadmium windows with an aperture of 5mm were placed in front of the cell.

3. Results and discussion

3.1 Effect of the post treatment on the PAAM

In order to characterize the geometry and the composition of the porous medium a set of contrast variation measurements was performed for the PAAM membranes in different volume fractions of D_2O/H_2O for two kinds of samples, one without any post treatments (named "as prepared") and one etched in phosphoric acid 5%wt for 50 minutes. For the contrast variation a narrow range in D_2O volume fraction (ϕ_{D2O}) was chosen, as previous measurements conducted on PAXY spectrometer at LLB resulted in a matching point around 73% D_2O. Fig. 2 shows SANS spectra for as prepared (a) and etched (b) PAAM at three different D_2O volume fractions. From these curves we can extract D_{int}, which is given by the 1st peak position at low q, and similar value of 91 nm is obtained for both as prepared and etched conditions. The lowest scattering intensity is obtained for different ϕ_{D2O} and the oscillations near the matching point don't fully diminish, showing the existence of, at least, two different compositions in the porous membrane.

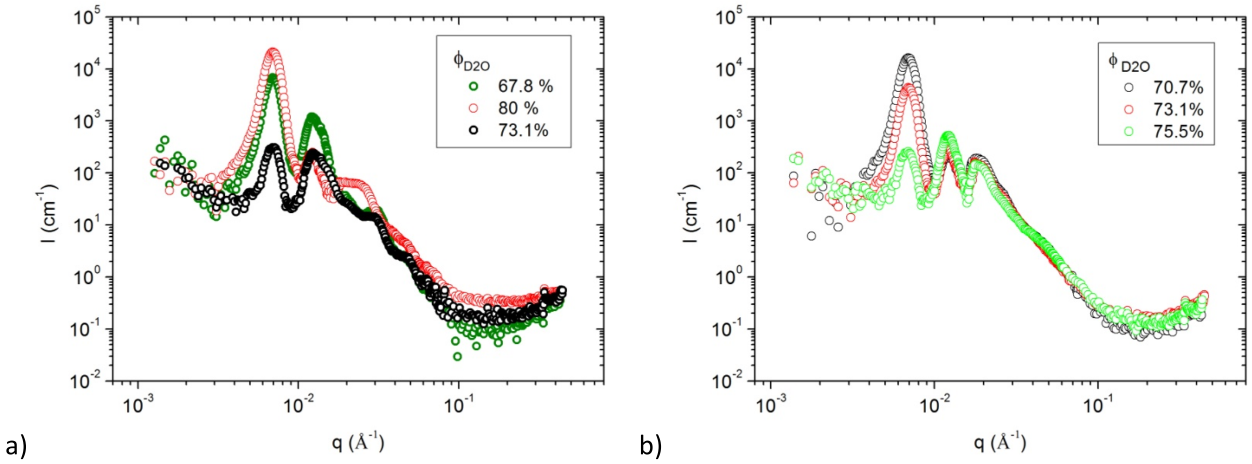

Fig. 2. SANS spectra of PAAM as anodized in oxalic acid 0.3M at 40V, T=18°C for 4 hours in different fractions of D_2O (ϕ_{D2O}): a) as prepared, b) after chemical etching in 5%wt H_3PO_4.

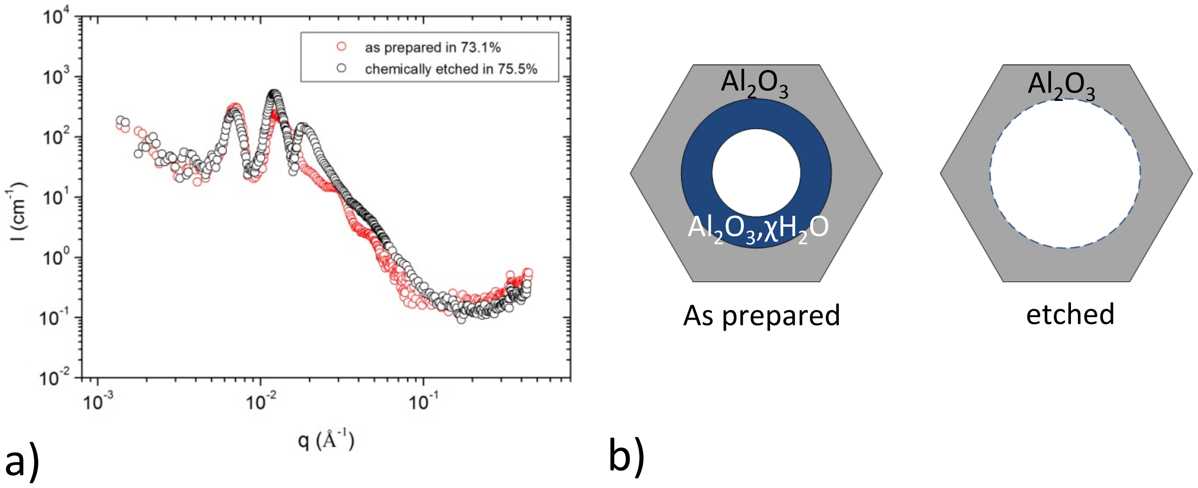

Fig. 3. a) Comparison of the SANS spectra for the as prepared sample and etched at the corresponding matching point. b) Schematic depiction porous alumina cell for the as prepared and the etched sample.

In Fig. 3a we compare the as prepared and etched sample in a contrast condition close to the matching point (73.1% for the as prepared and 75.5% for the etched). The profile of the two graphs is different as the etched sample is expected to have an enlargement in the pore diameter. The scattering length density near the matching point shifts to higher values for the etched sample. One explanation is that the as prepared sample is heterogeneous in composition with pore walls consisting of a shell of aluminum hydroxide Al_2O_3, xH_2O and bulk of amorphous alumina Al_2O_3 (Fig. 3b). The etching removes part of this layer, making the PAAM homogeneous in composition.

We are currently working on the fitting of the SANS spectra using a core/shell disc model to extract the shell thickness and its composition.

3.2 PSS inside alumina: Does it enter the nanopore?

Previous experiments showed that polyelectrolyte chains will enter if the Debye length is smaller than the pore diameter (κ^{-1}<Dp). Here we prepared a NaPSS solution at a concentration c=0.24g/mL and immersed membranes with two different diameters Dp=90nm (Fig. 4a) and Dp=25nm (Fig. 4b), to study the effect of geometrical confinement. The membranes were etched in order to have only one composition contributing to the form factor.

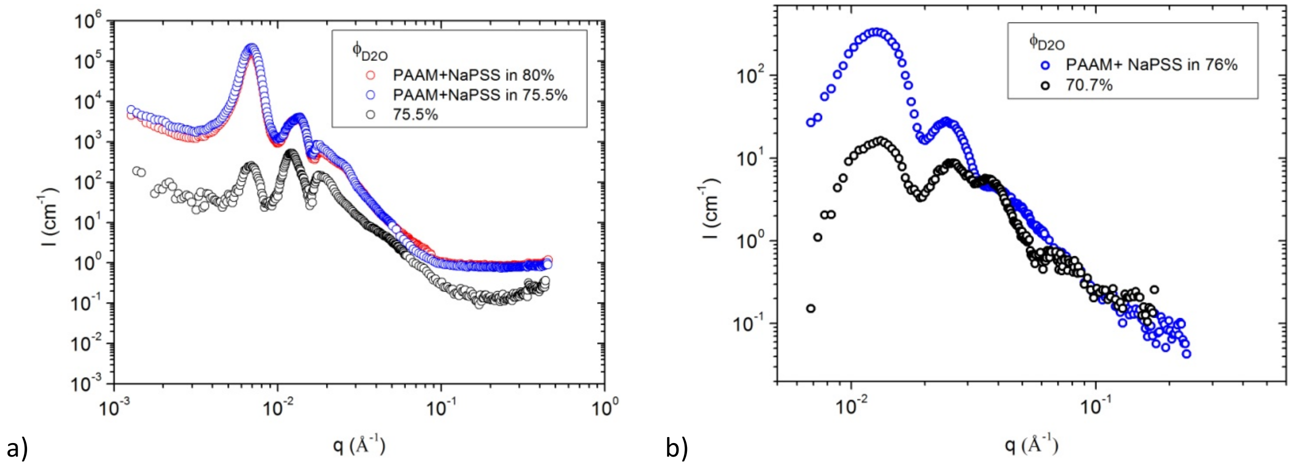

Fig. 4. SANS spectra of unfilled PAAM in D_2O/H_2O mixture and a PAAM with NaPSS, [c]=0.24 g/ml in solvent mixture of D_2O/H_2O. a) PAAM was prepared in 0.3M oxalic acid, 40V, T=18°C for 4 hours with post treatment, chemical etching in H_3PO_4 5 wt% at T=30°C for 50min (D_p=90 nm). b) Etched PAAM prepared in sulfuric acid 0.3M at 20V, T=10°C for 8 hours (D_p=25 nm).

Incubation of the membrane inside the polyelectrolyte solution lasted for 30 minutes. For the measurement of the PAAM with the NaPSS we used i) a mixture of D_2O/H_2O 75.5% in order for the solvent to contrast-match the PAAM and ii) a mixture of D_2O/H_2O 76% so as the whole NaPSS solution contrast-matches the PAAM. Fig. 4 shows the SANS spectra of unfilled PAAM (black circles) and filled PAAM with NaPSS solution (blue or red circles). The scattering intensity raises for the PAAM filled with the NaPSS indicating that the polyelectrolyte in both cases enters inside the membrane. A more quantitaive analysis of these curves is currently in progress.

4. Conculsions and perspectives

We characterized by SANS porous alumina membranes prepared under different synthesis conditions (electrolyte, voltage, etc) as well as with and without post treatments (as prepared, etched). The as prepared sample is heterogenous due to the existence of an aluminum hydroxide layer at the pore wall surface. We also investigated the penetration of polyelectrolyte chains (NaPSS) inside these membranes under contrast-matched conditions. The SANS spectra are different from the unfilled samples, indicating that NaPSS enters the porous membrane, for both diameters (90 nm and 25 nm), in less than 30 minutes of immersion. A more detailed study on the kinetics of penetration is needed in order to understand what affects this time scale.