ESRF	**Experiment title:** Design of new-generation ion-selective membranes	**Experiment number**: MA-1414
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Report:

Supramolecular assembly of low-molecular-weight compounds is known to generate a large diversity of cylindrical structures, which can be suitable for the design of ion-selective membranes. Of particular interest are wedge-shaped amphiphilic molecules bearing a polar group at the tip of the wedge and a large hydrophobic rim, which generally tends to form well-defined cylindrical superstructures with polar groups arranged along the cylinder axis. In this work, we studied the structure of a novel series of wedge-shaped sulfonates: 2,3,4-tris(11'-acryloylundecyl-1'-oxy) benzenesulfonates of Li, Na, K and Cs, which can serve as a model of the ion-selective membrane (Figure 1a). The results shown below are mainly focused on Na sulfonate (A-Na).

The A-Na fibers were prepared at room temperature with a home-made micro-extruder having an aperture size of 300μm. Temperature-dependent X-ray scattering measurements in transmission geometry were performed in order to study the thermotropic phase transitions of the material.

Two columnar mesophases were identified. At room temperature (25ºC), A-Na self assembles to form a columnar hexagonal disordered phase (Col_{hd}) while at T~ -10ºC a phase transition takes place and a columnar rectangular phase is observed (Col_r). The lattice parameters are the following: a = 39.1±0.1 Å for the case of the Col_{hd} phase and a = 38.4 ± 0.9 Å and b = 62.0 ± 2.6 Å for the case of the Col_r phase. 2D X-ray scattering patterns are shown in Figure 1b. Based on the mass density of the compound (~1.0 g/ml), the number of molecules contained in one slice of the hexagonal unit cell was estimated to be four. Therefore the molecules self-assemble in tetramers to form supramolecular disks with a hydrophilic center and a hydrophobic rim. The disks are in turn stacked on top of each other to build supramolecular cylinders, and such cylinders are eventually organized on a 2D hexagonal lattice (Figure 1c). In the pattern corresponding to -100ºC the peaks related to the ice formation show up at high scattering angles.

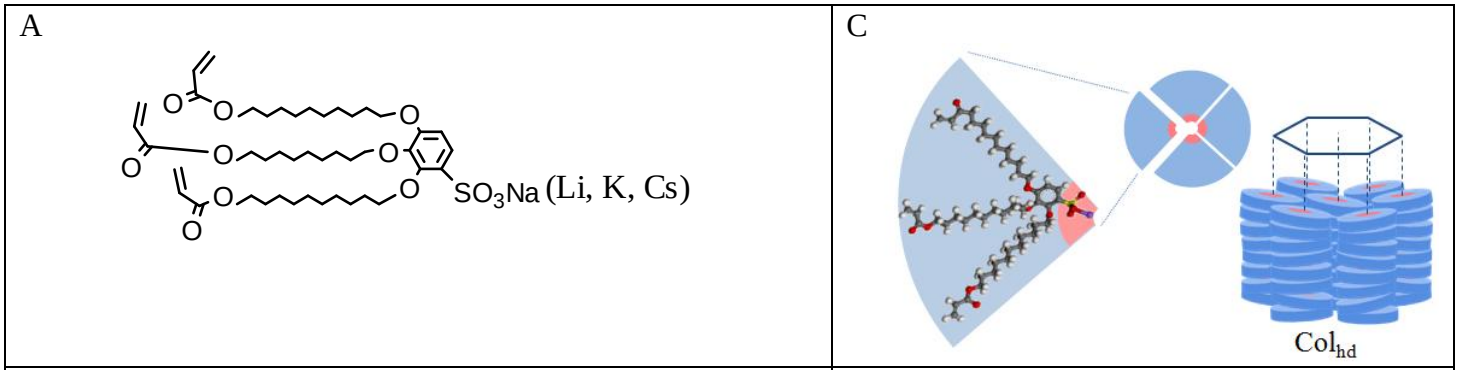

Figure 1. (a) Molecular structure of the wedge shaped acrylic sulfonates. (b) 2D X-ray patterns from oriented fibers of A-Na obtained at 25ºC (left) and -100ºC (right). The insets show in more detail the small-angle region were the peaks of the mesophase are visible. (c) Self-assembly of wedge-shaped molecules of **A-Na** to form a disordered columnar mesophase (Col_{hd}).

The presence of water drastically influences the structure and conducting properties of ion-conductive materials, such as Nafion. Here, the influence of relative humidity (RH) on the supramolecular structure of the self-assembled wedge-shaped molecules was studied. The increase of RH in a first instance results in swelling of the Col_{hd} phase. At RH=100% Col_{hd} phase disappears and scatering peaks corresponding to gyroid (G) and diamond (D) cubic bicontinuous phases were identified. Figure 2a shows the 2D X-ray pattern and the corresponding 1D curve. Schematic view of the sequence of phase transitions is shown in Figure 2b.

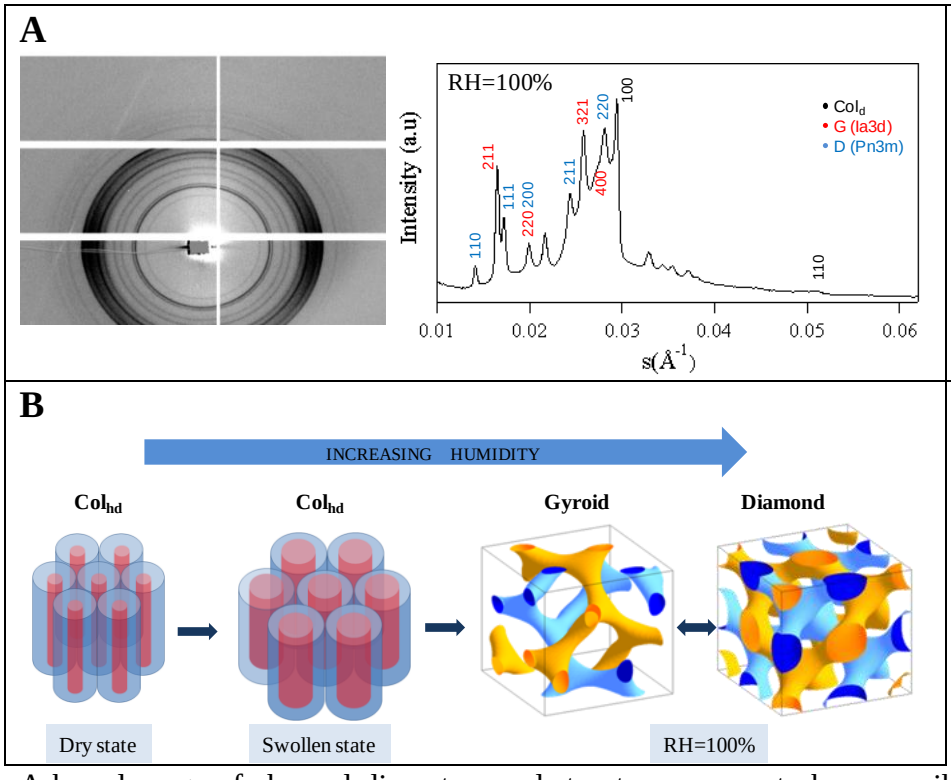

Figure 2. (a) 2D x-ray scattering pattern obtained from a A-Na fiber stabilized under RH=100% (left) and 1D Intensity vs. scattering vector curve (right). Main reflections of phases identified are indicated. (b) Evolution of supramolecular structure as a function of humidity.

A broad range of channel diameters and structures seems to be accessible simply by tuning T and RH. This opens a facile way for preparation of 3D-structured membranes with a controlled channel diameter.