In situ dialysis monitoring of block copolymer self-assembly by time-resolved SANS

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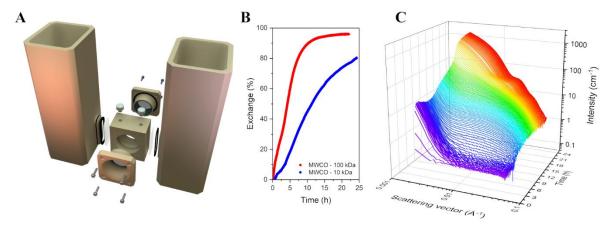
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Scattering techniques (neutron, X-ray or light scattering) are well-suited to study the selfassembly of polymers and surfactants in solution. However, the reproducibility of sample preparation and the monitoring of kinetics are often difficult to achieve in good conditions. The Large Scale Structures Group of the Institut Laue-Langevin (ILL, Grenoble), in collaboration with our team (CRPP-LCPO, Bordeaux), has recently developed a dialysis cell that allows the continuous monitoring of samples by various scattering techniques. This setup makes possible experiments where different parameters can be changed in a controlled manner (solvent composition, ionic strength, osmotic pressure, ...) with a better reproducibility than preparing samples for each condition. The diffusion rate is mainly controlled by the molar weight cut-off of the dialysis membrane used with characteristic mixing times ranging from a few minutes to several hours. As an illustration, a typical selfassembly experiment of copolymers will be presented. PDMS-b-PEG copolymer forming vesicular structures was studied by solvent displacement (also called nanoprecipitation), taking advantage of the slow exchange rate of the dialysis process to reach near equilibrium conditions. Vesicles formation was followed by time-resolved SANS and DLS. The data will be confronted to the two main mechanisms described in the literature, namely the formation of intermediate structures based on worm-like micelles [1] or hollow aggregates [2].

[1] Bernardes, A. T. J. Phys. II 1996, 6 (2), 169-174.

[2] He, X.; Schmid, F. Macromolecules 2006, 39 (7), 2654-2662.



A- Dialysis cell (exploded view). **B-** Exchange rate of D_2O (+ 1 mM NaCl) between the cell and the reservoirs followed by conductivity measurements. **C-** SANS kinetics of a PDMS-*b*-PEO self-assembly by solvent displacement.