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Vesicular structure of amphiphilic block copolymers studied by SANS

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Amphiphilic diblock copolymers self-assemble in water solution in stable and robust polymersomes (vesicles), which combined to a chemical design flexibility make them excellent candidates as drug or imaging agent carriers. The introduction of actuator in polymersomes and the engineering of their targeted cell adhesion are critical issues for the applications of disease imaging and therapy. Functionalized polymersomes may respond to physical or chemical stimuli by permeability change, bursting or by other structural modifications of the membrane or of the whole polymersome. Stimuli can be temperature or pH changes, magnetic field application, light irradiation or osmotic shocks...

Small Angle Neutron Scattering (SANS) is perfectly suited to the determinations of the vesicles size and of the thickness and membrane structure of polymersomes. The first example concerns polymersomes with photo-responsive Liquid Crystalline (LC) polymers as hydrophilic block. External stimuli (heating or UV irradiation) have been applied to induce modifications of the LC polymersomes membrane at the molecular level (i,ii). Polymersomes prepared for biological applications could be prepared via osmHybrid vesicles resulting from the self-assembly of amphiphilic copolymers (P) and phospholipids (L) could integrate the bio-functionality of lipids and the improved stability and various coupling chemistries of polymers in a single hybrid vesicular structure. Composition (Polymer/Lipid ratio) and polymer architecture (graft copolymer vs. diblock or triblock) can be varied to obtain either homogeneous or nanostructured membranes. By varying the block length of the hydrophobic polymer, we can tune the thickness mismatch between lipid polymer membranes and play with the conformational constraints of the polymer chains at the L/P boundary. Using the contrast matching method, we could determine the homogeneous or nanostructured character (iii) within the membranes of hybrid vesicles.

- i. Structural changes induced by temperature variation and magnetic field in liquid crystal polymer vesicle. S. Hocine, A. Brûlet, L. Jia, J. Yang, A. Di Cicco, L. Bouteiller, M.H. Li *Soft Matter*, 2011, 7 (6), 2613 – 2623.
- ii. Polymersomes with PEG Corona: Structural Changes and Controlled Release Induced by Temperature Variation. S.Hocine, D. Cui, M.-N. Rager, A. Di Cicco, J.-M. Liu, Wdzieczak-Bakala, A. Brûlet, and M.-H. Li. *Langmuir*, 2013, 29, 1356–1369.
- iii. Mixing Block Copolymers with Phospholipids at the Nanoscale: From Hybrid Polymer/Lipid Wormlike Micelles to Vesicles Presenting Lipid Nanodomains, Dao, TPT. ; Brûlet A.; Fernandes, F ; Er-Rafik, M ; Ferji, K ; Schweins, R ; Chapel, JP ; Schmutz, FM ; Prieto, M Sandre, O *Langmuir* 33,7 (2017) 1705-1715. Phase Separation and Nanodomain Formation in Hybrid Polymer/Lipid Vesicles, T. P. Tuyen Dao, F. Fernandes, M. Er-Rafik, R. Salva, M. Schmutz, A. Brûlet, M. Prieto, O. Sandre and J.-F. Le Meins, *ACS Macro Lett.* 2015, 4, 182–186.

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