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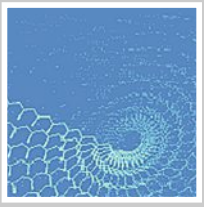

Polymer and Colloid Highlights

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Biomimetic Polymer Architectures

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Membranes play a pivotal role in biological systems as they enable locally confined and compartmentalized reactions in cells. Biological membranes are built primarily from lipids. Mimicking biological membranes with synthetic systems finds application areas as diverse as engineering, biotechnology and nanotechnology. Using polymers as building blocks for synthetic membranes is particularly appealing, because the large toolbox of chemical modifications applicable during polymer synthesis allows fine-tuning of membrane properties. Amphiphilic block copolymers can self-assemble into membranes that structurally resemble biological, lipid-based membranes. Importantly, due to the longer chain length of polymers, the resulting membranes possess a higher thickness and often increased robustness.[1]

These different properties of polymers and lipids are observed in hybrid membranes. Careful selection of materials with appropriate properties (fluidity, saturation, chain length) leads to phase separation and formation of polymer- and lipid-rich domains (Fig. 1A). Interestingly, the selective insertion of membrane proteins into the polymer or lipid domains can also be controlled by their different physico-chemical parameters.[2] Polymer membranes can also be assembled from triblock copolymers containing two chemically different hydrophilic blocks to fine-tune interfacial properties at both sides of the resulting asymmetric membrane,[3] which is of particular importance to obtain well-defined interactions with biomolecules, *e.g.* enzymes for sensing applications or stimuli-responsiveness. Polymer membranes can also assemble into vesicular structures that are stable in solution. The membrane curvature in giant unilamellar vesicles is very similar to planar membranes due to the several micrometer large diameter of these assemblies. Fig. 1B shows such a micrometer-sized polymersome where the membrane has been dye-labeled for visualization. The diameter in the micrometer range allows imaging by light microscopy techniques and it is in the same range as cells. Thus, they are ideally suited as synthetic cell mimics that can be equipped with additional functionality at the membrane and in their inner compartment.[4] Self-assembled vesicular architectures can also be generated at the nanoscale (Fig. 1C), which leads to an increased membrane curvature. The nano-size of these vesicles bears different advantages and further widens the potential of polymeric assemblies. Both hydrophobic and hydrophilic cargo such as therapeutic macromolecules can be hosted in their inner cavity (hydrophilic) and in the membrane (hydrophobic).[5] In addition, the polymersomes can act as nanocompartments to perform reactions in their confined interior environment.[6] These concepts are not limited to applications in solution, the polymer vesicles can also be covalently attached to solid substrates. A thiol-ene reaction under biocompatible reaction conditions facilitates immobilization of vesicles while maintaining structural integrity.[7] This opens up opportunities for the generation of compartmentalized 'lab-on-a-chip' designs based on self-assembled polymeric nanocompartments.

In conclusion, the biomimetic membrane structure formed by self-assembly of amphiphilic block copolymers provides enhanced properties when compared to lipid-based membranes. In particular, the tunable thickness, stimuli responsiveness and tunability of the polymers themselves stand out. Polymer membranes at interfaces can for example be employed as filtration membranes with high specificity or to generate nanostructured surfaces, whereas vesicular architectures find application as advanced cell mimics, drug delivery carriers or micro/nano reaction compartments (see refs. [4–6] and references therein). Together, this exemplifies how polymeric membranes can be finely adjusted to specific requirements, which further highlights their wide application potential.

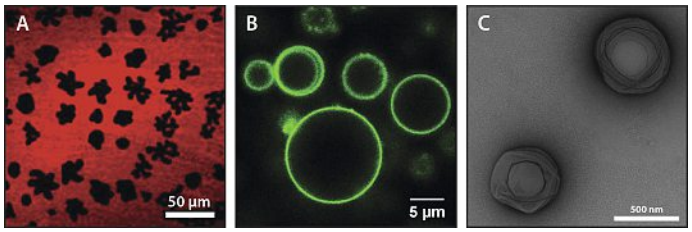

Fig. 1. Polymer architectures assembled from amphiphilic polydimethylsiloxane-polymethyloxazoline block copolymers. A. Laser scanning microscopy (LSM) image of a planar lipid/polymer hybrid membrane (polymer labeled with sulforhodamine B), reproduced with permission from ref. [2], copyright 2015 American Chemical Society. B. LSM image of giant, micrometer-sized polymersomes (membrane labeled with atto488) and C. Transmission electron microscopy image of nano-sized polymer vesicles (stained with uranyl acetate).

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