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Morphological transitions in polymer vesicles upon bilayer swelling with small hydrophobic molecules in water

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Attempts to scaffold surfactant based vesicles via polymerisation in the bilayer have often been shown to yield localised polymerisation and the formation of beads, due to possible phase separation between growing polymer and the molecules of the bilayer [1]. It has also been observed that other vesicle systems undergo re-arrangement and phase separation in response to the inclusion of solvents [2-3]. In order to minimise phase separation, a monomer with similar chemistry to the bilayer forming molecule can be selected. To achieve this, polymeric vesicles, also known as polymersomes, were swollen with compatible monomers, and the resulting dispersions analysed by cryogenic electron microscopy (cryo-EM). In parallel, these systems were modelled using dissipative particle dynamics (DPD) simulations and the effect of the momomer on the bilayer predicted. Through these combined approaches it was our aim to establish if phase separation occurs prior to polymerisation in polymersomes.

By the use of Cryo-EM, we have established that unilamellar polymer vesicles dispersed in water made from poly((ethylene oxide)$_{45}$-block-(methyl methacrylate)$_{164}$), poly((ethylene oxide)$_{45}$-block-(methyl methacrylate)$_{170}$), or poly(n-butyl methacrylate)$_{81}$-block-(2-(dimethylamino)ethyl methacrylate)$_{20}$ were smooth in appearance. However, when exposed to small hydrophobic molecules, here methyl methacrylate (MMA) and n-butyl methacrylate (n-BMA), they underwent morphological transitions. The monomers were added in the presence of a radical scavenger to rule out polymerisation. Upon swelling some of the bilayers increased as expected for the uptake of monomer, however, around 60% of the polymersomes lost their original simple bilayer morphology and transformed into more complex coil-like and patchy colloidal structures, which can be observed in both TEM (Figure 1&2) and SEM images (Figure 3).

The results of the DPD simulations on a model flat bilayer showed that transitions can occur upon bilayer swelling, which is accompanied by a change in the mechanical bilayer properties (Figure 4). The transition involves the formation of water pockets in the interior regions of the bilayer. Co-existence of the various morphologies in the experiments suggests an activation barrier towards morphological changes and a possibility of multiple meta-stable states. The latter indeed is supported by the existence of multiple minima in the surface tension as a function of bilayer area, as found in the simulations.

We feel that these results have an impact on, for example, the area of drug delivery, as polymersomes used in vivo as delivery vehicles may undergo such transitions, which would lead to different drug release profiles. Further details on this work are available in a recently accepted advanced preview [4].

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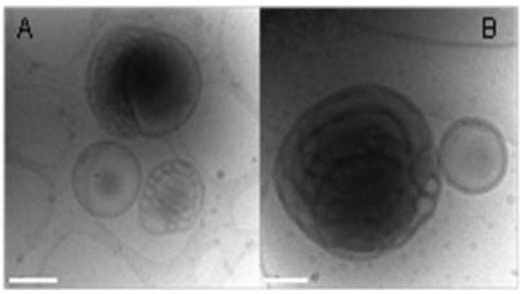

Figure 1. Cryo-TEM of PEG_{45}-b-$PMMA_{164}$ polymersomes swollen with MMA in water, showing coil and patch structures. Scale bars 500nm (A) and 200 nm (B).

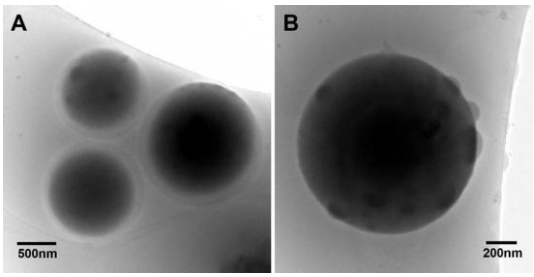

Figure 2. Cryo-TEM of PBMA-b-2DMAEMA polymersomes swollen with MMA in water displaying patchy structures.

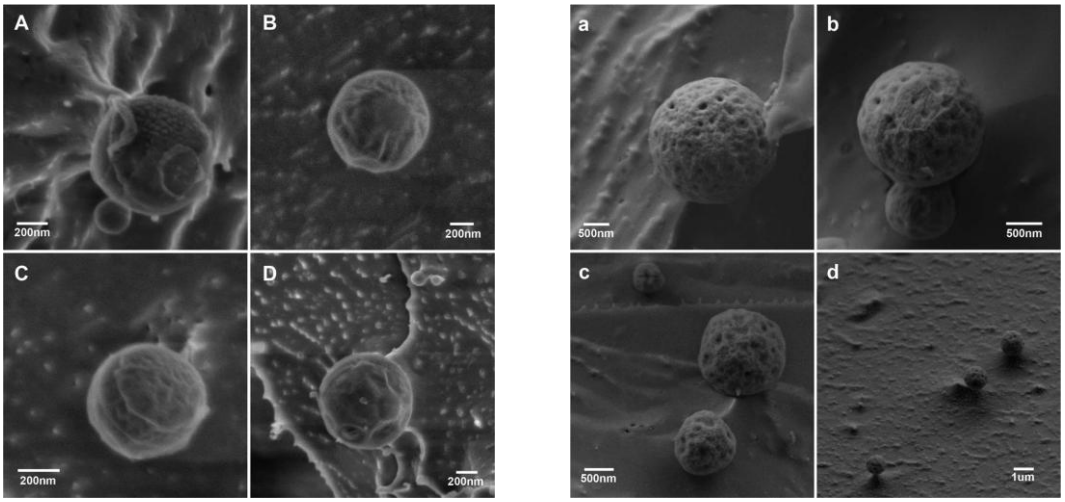

Figure 3. Cryo-SEM images of PEG_{45}-b-$PMMA_{170}$ swollen with MMA (A-D) showing coiled structures A and C and globular patchy structures D and PEG_{45}-b-$2DMAEMA_{20}$ swollen with BMA (a-d) displaying clear changes to the surface of a patchy nature.

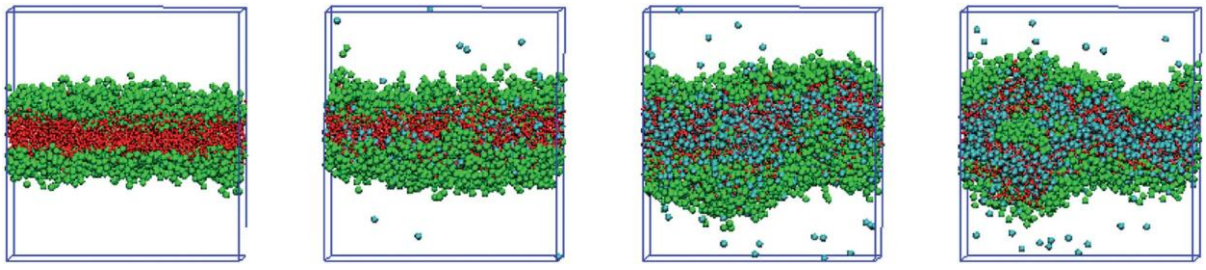

Figure 4. Simulation snapshots for 0, 500, 2500 and 3000 hydrophobic molecules (left to right). Head group beads shown in green, tail groups in red and hydrophobic monomers in blue (for clarity solvent beads not shown). As the concentration of the monomers increases they give rise to the formation of solvent pockets, which could be observed as patches and coils.