Electronic Supplementary Material (ESI) for Soft Matter

Formation and dissolution of phospholipid domains with varying textures in hybrid lipo-polymersomes

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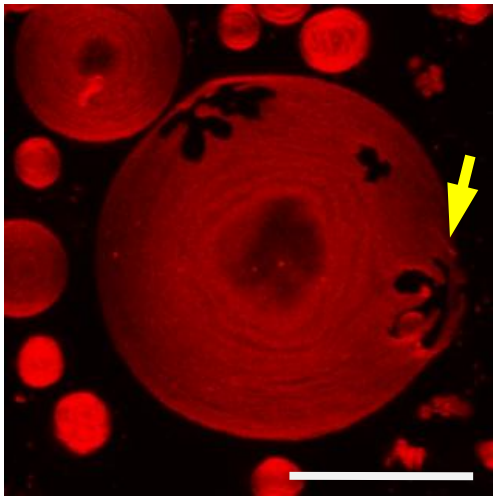
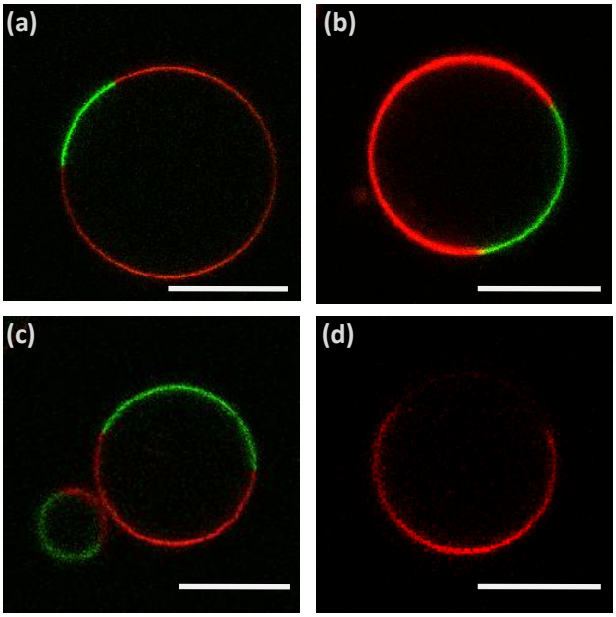
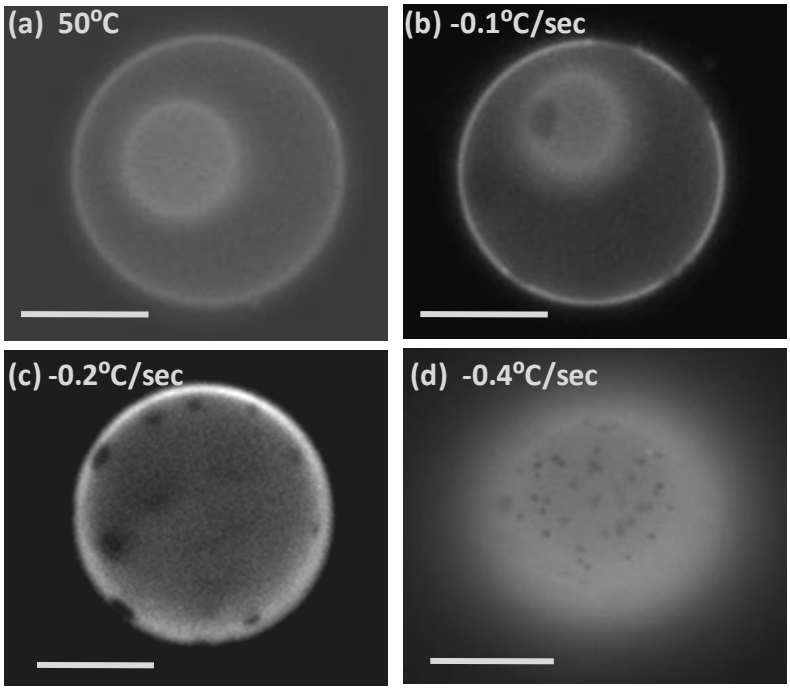
Supporting Information



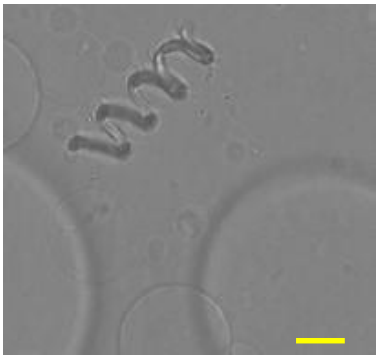
Supporting Figure S1. Confocal microscopy image of a PBdPEO:DPPC (6:4) HLP-GUV at room temperature demonstrating the irregular, star-shaped, DPPC-rich domains that form. The ordered lipid domains are more rigid than the copolymer-rich matrix and can 'bulge' out from the smoothly curved polymer shell because they would prefer to have a flatter membrane than the curvature of the GUV allows. The arrow highlights this subtle but noticeable effect. The scale bar represents 10 μm.



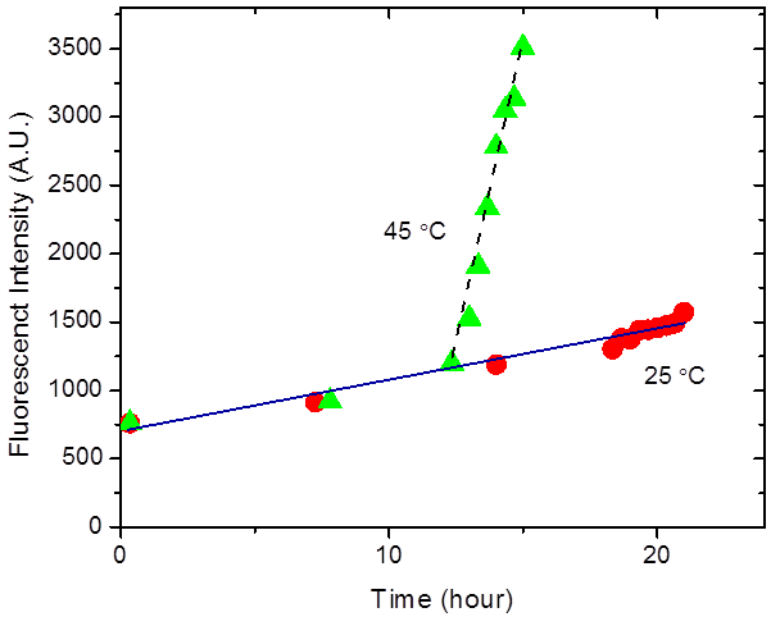
Supporing Figure S2. Confocal microscopy images of HLP-GUVs at room temperature: (a) PBdPEO:POPC:Chol (5:3:3); (b) PBdPEO:POPC:Chol (3:3:3); (c) PBdPEO:POPC:Chol (3:5:2); (d) PBdPEO:DLPC:Chol (4:3:3). All are superpositions of the red channel (Rh-DOPE), which represents the copolymer-rich matrix, and the green channel (OG-DHPE), which represents the lipid-rich domain (except (d), which shows the red (Rh-DOPE) channel only). The scale bars represent 10 μm.



Supporting Figure S3. Epi-fluorescence microscopy images of PBdPEO:DPPC:Chol (5:3:2) HLPs (labelled with Rh-DOPE) prepared at different cooling rates. (a) Homogeneously mixed membrane of a HLP at 50 °C (above the T_m of the hybrid membrane), prior to cooling; (b-d) HLPs at room temperature: faster cooling results in smaller domains, while their quasicircular domain shapes are conserved. It is worth noting that Figure S3a and S3b are of the same HLP which, as sometimes happens, contains another vesicle within its interior. The scale bar represents 10 μm.



Supporting Figure S4. A phase contrast microscopy image of the helical ribbon structure of a chol−β-CD supramolecular complex coexisting with HLP-GUVs. The scale bar represents 10 μm.



Supporting Figure S5. Effect of temperature increase on PLA_2 (0.05 mg/ml) activity on 3:2 PBdPEO:DPPC HLPs. At 25 °C a slow increase in fluorescence is observed due to slow release of protease from the HLPs. When the temperature is increased to 45 °C a more rapid increase in fluorescence is observed over time. At this temperature, the solid lipid DPPC domains melt and redisperse into the block copolymer matrix; however during this process the domains become more susceptible to PLA_2 hydrolysis causing a sharp release of encapsulated proteinase K. This in turn leads to an increased rate of proteolysis of the bodipy-BSA substrate. However there will also be a contribution of increased enzymatic kinetics at the higher temperature that also contributes to the increased rate of proteolysis observed.