MAR06-2005-002843

Abstract for an Invited Paper
for the MAR06 Meeting of
the American Physical Society

Polymer Vesicles in Biomimetic Applications

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The performance of phospholipid vesicles in targeted pharmaceutical delivery is greatly improved by the addition of water-soluble polymeric tethers. The resulting solvated brush resists protein adsorption and access of biological entities to the hydrophobic membrane core, evading immune response. Polymeric vesicles have, due to their increased stability and greater variability in chemical and mechanical properties, huge potential relative to lipsomes. They may ultimately form the basis for artificial cells and scavengers, or in non-biomedical applications, distributed microreactors. To this end, we explore the incorporation of biomimetic features in polymer lamellae: membrane phase separation and "rafts", bending fluctuations and budding, triggered release, and dynamic engulfment. Vesicle phase separation, bending, lamellar disruption, and lamellar wetting all are rooted in block copolymer and polymer brush physics. For instance, vesicles blended from two block copolymers, polystyrene-co-poly(ethylene oxide) (PS-PEO) and poly(butadiene)-PEO (PBD-PEO) exhibit no macroscopic phase separation, though blends of PS and PBD at the same molecular weight do. This represents either an upward shifting of the UCST or a suppression of large-scale morphology. Also interesting is the ability of PS-PEO to form robust, vesicle-sized, capsules carrying aqueous phase cargo. While we doubt the true vesicular nature of these structures, they are often robust to passing of a liquid-air contact line. Their morphology is highly dependent on copolymer composition. The capsules are subject to buckling instabilities and in some instances, glassy fracture with sudden content release. Lamellar physics also plays an important role in the scavenging and adhesion capabilities of polymer vesicles: While the density of adhesive groups on the chain ends of incorporated tethers acts in ways easy to anticipate, engulfment dynamics depends dramatically on dynamic membrane bending.