MONOPOLY: Mineral-Organic Nanostructures Organized in Polymersomes

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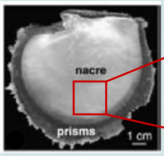
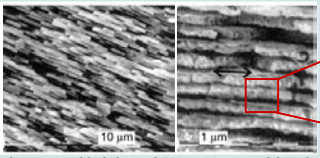
Goal: Discover synthetic route for producing artificial analog of nacre

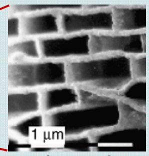
Biomineralized materials, such as nacre, exhibit superior strength and toughness



Digital image of pearl-producing *Pinctada margaritifera* oyster



TEM images of brick-and-mortar assembly of nacre: $CaCO_3$ tablets (200–900 nm thick) sandwiched between protein layers (10–50 nm thick)



TEM image of nacre membranes following dissolution of $CaCO_3$ tablets

Images adapted from reference [1]

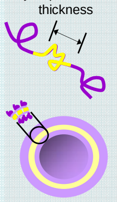
Mechanical properties of nacre can be attributed to highly ordered arrangement

- Biomineralization – process by which living organisms form minerals, often to stiffen existing tissues
  - Examples include nacre, bone, teeth
- Biomineralization of nacre occurs within extracellular compartment enclosed in membrane [2]
  - Membrane surface plays key role in growth of nacre tablets
    - Calcium crystals nucleate from polyanionic macromolecules (such as glutamate-rich proteins) deposited on organic scaffold (such as β-chitin)
- Organic membrane is found in areas surrounding and contained within the nacreous tablets

Compartmentalization during nacre growth may be key to highly ordered arrangement of $CaCO_3$

Polymer vesicles provide compartmentalized environments (nanoreactors) for controlled mineralization

Comparison of Two Polymers Used For Vesicle Formation



PDMS-PEO (Dow Corning)

Polydimethylsiloxane (Hydrophobic PDMS) | Poly(ethylene oxide) (Hydrophilic PEO)

Composition: two 12-unit PEO per 3000 m.w.

Hydrophobic core thickness: 5 nm

PB-*b*-PEO (Aldrich)

Polybutadiene (Hydrophobic PB) | Poly(ethylene oxide) (Hydrophilic PEO)

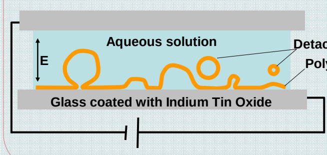
Composition PB-b-PEO: 2500-b-1300

Hydrophobic core thickness: 8 nm

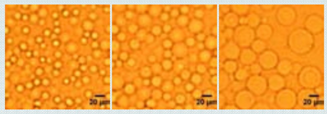
- Same hydrophilic segment (PEO)
- Comparable molecular weight (3000 vs. 3800)
- Glass transition temperature (T_g) difference for hydrophobic portion
  - T_g of PDMS = 0° C vs. T_g of PB=123° C

Preparation of Vesicles from Polymer Films

Side-View of Electroformation Setup



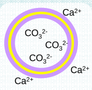
Digital image of vesicles observed by optical microscope



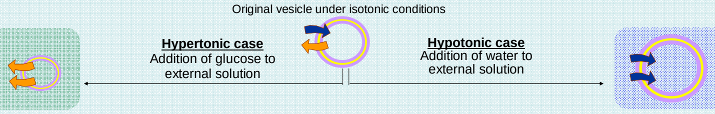
Vesicles show steady growth with time

- Electric field is applied to solution that is rehydrating film
- Proposed mechanism: Electroosmotic motion of solution creates periodic motion perpendicular to film [3]
  - Instability produces more homogeneous vesicle size dispersion

Understanding membrane permeability of polymer vesicles is vital for controlled mineralization

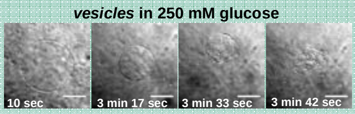


- Response of vesicle membrane to osmotic pressure differences provides fundamental information about permeability
  - Glucose-induced osmotic shock is well-established approach
- Permeability reflects relative probability for water diffusion across membrane and decreases with relative hydrophobic core thickness [4]

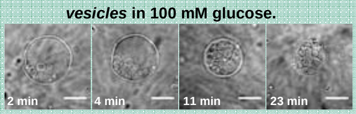


Vesicle Response to Hypertonic Stress (Increased External Glucose)

Evolution of water-filled *Dow* vesicles in 250 mM glucose



Evolution of water-filled *PB-b-PEO* vesicles in 100 mM glucose.

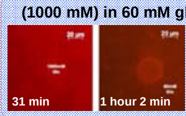


Digital images of vesicle evolution observed by optical microscope. Scale bar is 20 um.

- Both Dow and PB-PEO vesicles show internal vesiculation (daughter vesicles)
  - Similar daughter vesicle size of ~7 µm diameter may suggest similar persistence length [6]

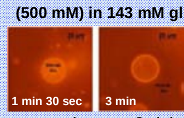
Vesicle Response to Hypotonic Stress (Decreased External Glucose)

Evolution of Glucose-Filled *Dow* vesicle (1000 mM) in 60 mM glucose environment



Diameter expands from 28 um to 34 um

Evolution of Glucose-Filled *PB-b-PEO* vesicle (500 mM) in 143 mM glucose environment



Diameter expands from 33 um to 37 um

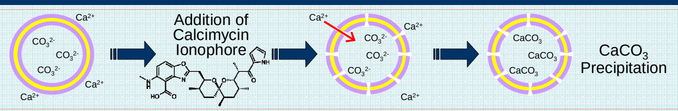
Digital images of vesicle evolution observed by fluroescence microscope. Scale bar is 20 um.

- Both Dow and PB-PEO vesicles show reduced response to hypotonic vs. hypertonic stress

Current Focus of Research

Controlled Permeability Through Use of Calcimycin Ionophore

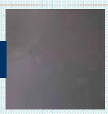
- Introduction of known calcium pathway into vesicle membrane
- Transport of calcium through membrane for reaction with carbonate



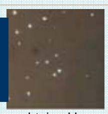
Effect of Organic Materials on Precipitation of $CaCO_3$

- Observation of $CaCO_3$ precipitation in the presence of soluble organic matrix for variation in resulting characteristics

25 mM $CaCO_3$, pH=8



25 mM $CaCO_3$ precipitated with 1000 ppm poly acrylic acid (PAA) Mw:5100, pH=8

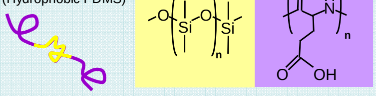


25 mM $CaCO_3$ precipitated with soluble organic matrix, pH=8

Polarized light images obtained by optical microscopy

Controlled Precipitation of $CaCO_3$ With Polyglutamate Ligands

- Acidic polymers may play significant role in deposition of $CaCO_3$ polymorphs [9]
- Synthesis is underway of PGA-PDMS-PGA copolymer for formation of vesicles
  - Incorporation of PGA in vesicle membrane mimics glutamate-rich proteins in nacre-forming membranes
  - PGA may affect calcium carbonate nucleation and growth



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