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Abstract: While the ability of proteins to self-assemble makes them powerful tool in nanotechnology, in biological systems protein-based structures ultimately depend on the context in which they form. We combine the self-assembling properties of synthetic diblock copolymers and proteins to construct intricately ordered, three-dimensional polymer protein structures with the ultimate goal of forming nano-scale devices. This hybrid approach takes advantage of the capabilities of organic polymer chemistry to build ordered structures and the capabilities of genetic engineering to create proteins that are selective for inorganic or organic substrates. Here, microphase-separated block copolymers coupled with genetically engineered heat shock proteins are used to produce nano-scale patterning that maximizes the potential for both increased structural complexity and integrity.
Diblock copolymers

Depending on the composition of the blocks, diblock copolymers can display ordered arrays of spherical, cylindrical, lamellar or bicontinuous microdomains.
A specific example: polystyrene polyethylene oxide diblock copolymer, P(S-b-EO), spun cast from benzene and microphase separated into cylindrical domains.
Chaperonin proteins from *S. Shibatae*

*Trent et al.*
Chaperonin self-assembly
Combining the two self-assembling systems

Hierarchical structures

Greater control and predictability

Increased complexity

Novel material structures

Novel properties
Interaction between diblock copolymers and chaperonins

surface charge
red=negative, blue=positive, white=neutral

hydrophilic amino acids shown in blue

GRASP models by Yi-Fen Li
Preparation of Hybrid Polymer/Protein Thin Films

- P(S-b-EO) films with protein were prepared by first combining a solution of P(S-b-EO) in benzene with an aqueous solution of chaperonin protein.
- Samples were gently mixed and stored at 4 °C for several days.
- The aqueous layer was then spun cast at 2500 rpm to produce the polymer/protein hybrid film

Note: The films were spun cast from the aqueous phase due to the visual observation that some of the polymer was dragged into the aqueous phase. We speculate that micelle formation in the aqueous phase was aided by the presence of the chaperonin protein.
Result: Hybrid Polymer and Protein Thin Film

Optical micrograph of polymer and protein hybrid thin film, 50x

AFM phase image of polymer and protein hybrid thin film
P(S-b-EO) with and without chaperonin

Polymer only

chaperonin

Polymer plus protein
P(S-b-EO) and GroEL hybrid film

height 5 nm
2 μm 0

phase 30°
Future Directions

- Explore other diblock copolymer and protein mixtures; vary surface characteristics of the protein, such as hydrophilicity and charge; vary the chi parameter of the diblock copolymer.
- Use site-directed mutagenesis to impart new functional characteristics to the chaperonin and therefore to the hybrid material.
- Develop analytical techniques capable of imaging chemical properties including composition, viscoelasticity, surface energy, etc. comparable to the domain sizes of the composite polymer/protein material.
Conclusions

- Chaperonin proteins and synthetic polymers can be physically mixed to form novel hybrid materials.
- By combining self-assembling proteins with structure-forming block copolymers, the proteins can affect the ordering of the block copolymers, and similarly, the structural evolution of the polymers can affect the self-assembly of the proteins, thus exhibiting a novel synergy.
- Cooperative interactions between the two self-assembly processes opens new avenues to design unique, functional hybrid materials. Hierarchical materials formed by this method have potential use as the functional component in nanoscale devices.