CBD SET CONFERENCE
TODAY'S INNOVATION, TOMORROW'S WARFIGHTER CAPABILITIES

Advances in Fundamental Materials Research

Thiol-Functionalized Block Copolymer Membranes with Dynamic Response

Qi Zhang, Cornell University
Yuk Mun Li, Cornell University
Yibei Gu, Cornell University
Jennifer Poole, FLIR Systems, Inc.
Jeremy Walker, FLIR Systems, Inc.
Ulrich Wiesner, Cornell University

Block copolymer (BCP) membranes fabricated via SNIPS, a combination of self-assembly (SA) and non-solvent induced phase separation (NIPS), exhibit an asymmetric structure with isoporous skin layer of mesopores sitting on top of an asymmetric macroporous substructure. Membranes with poly(4-vinylpyridine) covering the mesopore walls have a switchable response to pH changes demonstrating the potential as a chemical gate. When enzymes are immobilized into the membrane pores recognizing a chemical or biological (CB) threat and in response producing strong acids, they can act as a trigger and actuate local membrane shutdown. This generates a locally closed (protective) state while maintaining high water vapor permeation everywhere else. Membranes with tunable permeability are accessible by adjusting casting parameters to control substructure between sponge-like cross-sectional morphologies or more open and permeable finger-like substructures.

In order to effectively incorporate enzymes into these switchable membranes, we designed a BCP that in addition to the P4VP block also contained covalent binding capabilities. To that end, a new triblock terpolymer, poly(styrene-block-4-vinylpyridine-block-propylene sulfide) (PS-b-P4VP-b-PPS or SVPS) was successfully synthesized with a very small poly(propylene sulfide) (PPS) block. Terminal sulfhydryl groups were introduced by terminating the PPS end block by a proton donor during anionic polymerization. Via SNIPS the terpolymer was subsequently processed into an asymmetric membrane with isoporous top surface layer. In addition to the pH responsiveness from the P4VP component, the end PPS block provided thiol functional groups for covalent bonding via thiol-ene click chemistry. This opens a pathway to numerous post-modification reactions with target molecules like enzymes covalently attached to SNIPS membranes via simple immersion in solutions containing the targets. These post-modification reactions are scalable for industrial use and more importantly minimize the risk of inactivating enzymes. The concepts described here are not limited to sulfhydryl end groups. Other functional groups including amines or carboxylic groups could be covalently attached to the end group/block of BCPs via anionic polymerization or via transformation from current thiol groups using bifunctional linkers. As more types of pore-block end-functionalized membranes emerge, the choice of incorporated enzyme receptors is expected to rapidly expand. This study therefore lays the foundation for the facile production of bio-responsive membranes.