Charged nanopore membranes by amphiphilic random copolymer micelle assembly

Membranes that can separate solutes based not only on their size but also their chemical features (e.g. charge, hydrophobicity, specific functional groups) can potentially broaden the applications where membranes are used, replacing less energy-efficient methods such as chromatography and extraction. However, finding an easy and scalable approach which confers the membrane with high permeability, selectivity, and systematic tunability is still a great challenge. Integration of chemical functionalities into membrane nanopores requires engineering the pores and functionalizing them with specific groups to induce desired chemical interactions with the target molecule. Biological pores are the best representative of this specific interaction. For example, ion channels feature pores slightly larger than the target solute, mostly lined with hydrophobic residues but also featuring selectivity regions with charged functional groups. These characteristics bring about superior selectivity and permeability for target solute in these pores.

Inspired by these biological channels, we designed a new and easy approach for charge-based separation of sub-nanometer size molecules, with potential for further functionalization. We prepared an amphiphilic random copolymer that combines highly hydrophobic, fluorinated repeat units of 2,2,2-trifluroethyl methacrylate (TFEMA) with charged, hydrophilic repeat units of methacrylic acid (MAA), PTFEMA-r-PMAA, by free radical polymerization. The copolymer consists of 45% MAA and is insoluble in water. We found that this copolymer forms micelles in methanol. When a solution of this copolymer containing micelles are coated onto the surface of a porous support membrane a thin selective layer is formed. Using this method, we achieved membranes with pure water permeabilities up to ~6 L/m^2.h.bar by tuning the copolymer composition. The resultant membranes exhibited rejection properties expected from negatively charged membranes with ~2 nm pore size, as indicated by the relative rejections of monovalent and divalent salts as well as polyethylene glycol (PEG) with different molecular weights. The membrane showed charge-based selectivity between organic dye molecules, with a negatively charged dye being retained by >85% whereas a positively charged dye with a similar molecular size as retained by <30%. This is the first demonstration of a new approach to forming membrane selective layers by the self-assembly of easily synthesized random copolymers with highly incompatible repeat units. We believe this approach can be adapted to address various pore sizes and pore surface chemistries, leading to novel membranes with promising selectivity.