

October 10th, 2018

Dear Editors,

We are submitting “Understanding the Nanoscale Structure of Inverted Hexagonal Phase Lyotropic Liquid Crystal Polymer Membranes” by Benjamin J. Coscia, Joseph Yelk, Matthew A. Glaser, Douglas L. Gin, Xunda Feng, and Michael R. Shirts, for consideration for publication as an Article in the Journal of Physical Chemistry B. We expect this work to be of significant interest to researchers who study nanostructured polymer membranes for aqueous separations.

This article examines the atomistic structure of an inverted hexagonal phase self-assembled lyotropic liquid crystal (LLC) polymer membrane. To create these materials, liquid crystal (LC) monomers self-assemble into ordered, uniform-sized and hexagonally-packed nanopores. The nm-sized pore centers are charged and hydrophilic in nature which makes this type of membrane useful for highly selective aqueous separations of small solutes. By tuning the shape, size and chemical functionality of LC monomers, one could intelligently design the pore environment. However, our current understanding of the nanoscopic pore structure is not yet adequate for us to be able to controllably design membranes for solute-specific separations.

In this paper, we used molecular dynamics (MD) simulations to model an experimentally characterized LLC polymer membrane and learn about its detailed atomistic structure. We simulated XRD patterns from the MD simulation trajectories for comparison to experimental 2D wide-angle X-ray scattering (WAXS) and 1D small-angle X-ray scattering patterns. We found that 5 columns of stacked LLC monomers are likely to pack around the hydrophilic core of each pore. These columns likely move independently of each other over time scales that we can not simulate. Some of the structure previously attributed to monomer tail tilt is likely instead due to ordered tail packing. Although the system studied has been reported as “dry”, small amounts of water appear necessary to fully reproduce all features from the experimental 2D-WAXS pattern due to asymmetries introduced by hydrogen bonds between the LLC monomer head groups and water molecules. Finally, we explored the composition and structure of the nanopores, showing there is composition gradient rather than an abrupt partition between the hydrophilic and hydrophobic regions. The clearer picture of the nanoscopic structure of these membranes provided in this study will enable a better understanding of the mechanisms of small molecule transport within these nanopores.

Some suggestions for reviewers are:

1. Menachem Elimelech is a leader in the development of membrane technologies for water desalination and water reuse (Yale University, 203-432-2789, menachem.elimelech@yale.edu).
2. Francisco Hung has used molecular simulations to study nematic liquid crystals and various nanostructured materials (Northeastern University, 617-373-8619 f.hung@northeastern.edu)
3. Eric Jankowski has experience modeling soft materials using molecular dynamics including work done simulating structure factors from simulations, much like the techniques we use in our work (Boise State University, 208-426-5681, ericjankowski@boisestate.edu)

Please send correspondence regarding this paper to Michael R. Shirts (contact details in letterhead).

Sincerely,
Michael R. Shirts
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Joseph Yelk
Matthew A. Glaser Douglas L. Gin
Xunda Feng