

10/1/2018

Dear Editors,

We are submitting “Understanding the Nanoscale Structure of Inverted Hexagonal Phase Lyotropic Liquid Crystal Polymer Membranes” by Benjamin J. Coscia (graduate student), Joseph Yelk (graduate student), Matthew A. Glaser (professor), Douglas L. Gin (professor), Xunda Feng (post-doc) and Michael R. Shirts (professor), 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 studies 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 can 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 in order to model an experimentally characterized LLC polymer membrane and learn about its atomistic structure in detail. 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. While trying to match our simulated patterns to experimental patterns, we found that 5 columns of stacked LLC monomers are likely to pack around the hydrophilic core of each pore. We learned that these columns likely move independently of each other over time scales that we can not simulate. We also found that 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”, we show that small amounts of water are necessary to fully reproduce all features from the experimental 2D-WAXS pattern due to asymmetries introduced by hydrogen bonds between the LC monomer head groups and water molecules. Finally, we explored the composition and structure of the nanopores and reveal that there exists a 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. Chinedum Osuji has published work related to the synthesis and physical properties of the same inverted hexagonal phase LLC membrane studied in our work (University of Pennsylvania, 215-573-3608, cosuji@seas.upenn.edu).
2. 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).
3. Arun Yethiraj has studied molecular simulations of the self-assembly of liquid crystals into ordered nanostructures, including the type studied in our work. (University of Wisconsin Madison, 608-262-0258, yethiraj@chem.wisc.edu)

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

Sincerely,
Michael R. Shirts
Benjamin J. Coscia
and co-authors