Communication

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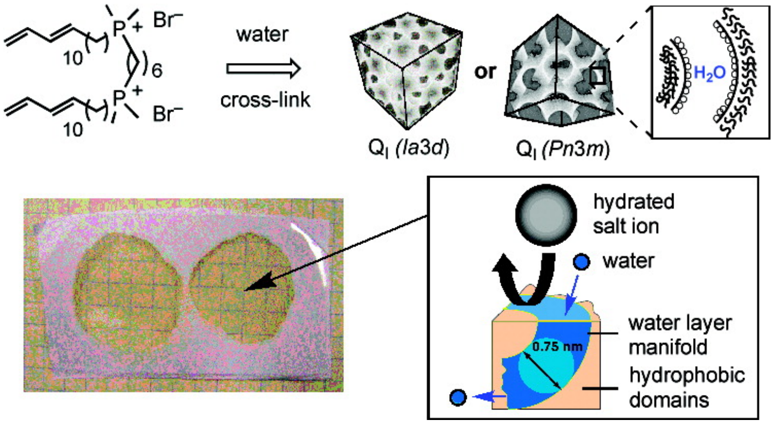

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New Type of Membrane Material for Water Desalination Based on a Cross-Linked Bicontinuous Cubic Lyotropic Liquid Crystal Assembly

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The production of pure water from seawater or brackish water is extremely important in regions and situations where clean water supplies are unavailable. Reverse osmosis (RO) is a membrane process that removes hydrated salt ions ($<$1 nm in diameter) and larger solutes from water, irrespective of their charge.[1] RO membranes typically consist of a *dense*, amorphous, ultrathin ($\leq$0.1 μm) polymer active layer (cellulose acetate,[1] poly(arylamide)s,[1] or sulfonated polymers[2]) on top of a porous support. It is believed that in RO membranes, hydrated salt ions (e.g., $Na^+_{(aq)}$: 0.72 nm diameter)[3] are "size-excluded" through the $\leq$0.5 nm interstitial voids between the polymer chains, while smaller water molecules (0.27 nm)[3] are able to pass through.[1] Nanofiltration (NF) membranes are similar to RO membranes, but the polymer active layer is *porous* (i.e., contains *discrete nanometer-size pores*) and is usually charged.[4] NF membranes can completely reject molecular solutes 1−10 nm in diameter via size- and charge-based exclusion but only partially reject small monovalent ions.[4] Current RO and NF membrane production methods (e.g., interfacial polymerization) provide little control over the size and distribution of the interstitial voids or nanopores.[1,4] Several polymer synthesis[5−7] and modification[8,9] strategies have recently been explored that generate membranes with nanopores for liquid filtration. Only one of these methods affords pores smaller than 1 nm[8] and none have been reported to be able to perform water desalination.[5−9] Herein, we present a nanoporous polymer material based on cross-linked lyotropic liquid crystals (LLCs) that rejects inorganic salts and neutral organic molecules from water as good as, and in many cases better than, conventional RO membranes under the same test conditions, with a water permeability comparable to that of current RO active layer materials. This material is a type I bicontinuous cubic (Q_I) LLC network made from monomer **1**, with an ordered 3-D interconnected water manifold system and an effective pore size of about 0.75 nm (Figure 1).[10]

LLCs are amphiphilic molecules that self-organize in water to form ordered, phase-segregated assemblies with nanometer-scale water and organic domains.[11] Recently, we showed that water NF membranes with 1.2 nm diameter cylindrical pores can be made by cross-linking the inverted hexagonal (H_{II}) LLC phase as a supported membrane.[12] These membranes are capable of molecular sieving but have low water permeability due to nonuniform alignment of the uniaxial pore domains.[12] They also cannot effectively remove small salt ions from water due to the size of the nanopores.[13,14] To overcome these limitations, the cross-linked Q_I phase of LLC monomer **1** (which was previously synthesized in our group)[15] was explored as a new type of water NF material because its interconnected water nanopore system promised superior transport properties without need for alignment. Monomer **1** forms a type I (i.e., "normal") Q phase (either the *Ia*3*d* or *Pn*3*m* structure),[15] which is believed to be composed of interpenetrating organic networks separated from one another by a continuous water layer surface with overall cubic symmetry.[15] Copolymerized with butyl rubber (BR), this material selectively rejects hydrophobic chemical agent simulant vapors but has enhanced water vapor transport due to its 3-D water manifold structure.[16] However, the cross-linked Q_I phase of **1** has not been explored for water NF, nor has its effective pore size been determined.

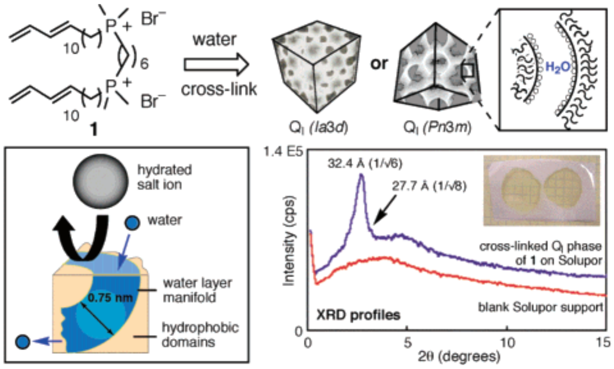

Figure 1. Structure of the cross-linked Q_I phase of **1**; XRD profile and photograph (grid = 0.25 × 0.25 in.) of a supported Q_I membrane; and proposed mechanism of water desalination and NF through the material.

Free-standing films of cross-linked **1** cannot withstand high pressures. Consequently, a hot-pressing method similar to that used to make supported Q_I-phase **1**−BR composite films[16] was employed to make supported membranes for NF testing, because solvent-casting was ineffective. This method involves heating (70 °C) and pressing (12 tons force) the initial Q_I-phase monomer mixture [80.0/19.4/0.6 (w/w/w) **1**/H_2O/radical photoinitiator] into a 35−40 μm thick, microporous, *hydrophilic*, polyethylene fiber matte support (Solupor E075-9H01A).[16] In this process, the LLC monomer gel is completely infused through the support and then radically photocross-linked at 65 °C with 365 nm light to lock-in the Q_I phase (see Supporting Information). The presence of *d*-spacings with a ratio of $1/\sqrt{6}:1/\sqrt{8}$ in the powder X-ray diffraction (XRD) profile[15,16] of the membranes (Figure 1) confirms that the Q_I phase is retained after polymerization. The degree of diene polymerization was found to be $>$95% using mid-IR spectroscopy[16] (see Supporting Information). The resulting 40-μm thick, optically transparent membranes (Figure 1) are flexible, uniform, and structurally stable under various test conditions, including sustained exposure to 400 psi water pressure or drying in vacuo (45 mtorr) for days (see Supporting Information).

Table 1 shows the inorganic salt and organic solute rejection performance of supported Q_I-phase membranes of **1** obtained using a stainless steel, 25 mm I.D., stirred dead-end filtration cell at 400

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Table 1. Filtration Performance[17] of Q_I Membranes[a]

test solute	diameter (nm)	rejection (%)	flux (L m^{-2} h^{-1})[g]
Ethidium Red	1.2[b]	>99.9	$(5.1 \pm 0.6) \times 10^{-2}$
PEG-600	1.2[c]	>99.9	$(5.1 \pm 0.2) \times 10^{-2}$
sucrose	0.94[d]	>99.9	$(5.4 \pm 0.3) \times 10^{-2}$
glucose	0.73[d]	96 ± 2	$(5.2 \pm 0.1) \times 10^{-2}$
glycerol	0.36[e]	53 ± 1	$(5.1 \pm 0.8) \times 10^{-2}$
EG	0.32[e]	38 ± 4	$(5.2 \pm 0.6) \times 10^{-2}$
NaCl	Na^+ (aq): 0.72; Cl^- (aq): 0.66[f]	95 ± 1	$(5.1 \pm 0.1) \times 10^{-2}$
$MgCl_2$	Mg^{2+} (aq): 0.86[f]	>99.3	$(5.2 \pm 0.6) \times 10^{-2}$
$CaCl_2$	Ca^{2+} (aq): 0.82[f]	>99.3	$(5.2 \pm 0.4) \times 10^{-2}$

[a] Dead-end method; 400 psi; 0.45-μm prefiltered 2000 ppm aq feed solutions; 1 pass. [b] MM2 modeling. [c] Stokes−Einstein eqn. [d] Ref 20. [e] Ref 21. [f] Ref 3. [g] For a 40 μm thick LLC active layer; pure water flux: $(5.9 \pm 0.1) \times 10^{-2}$ L m^{-2} h^{-1}.

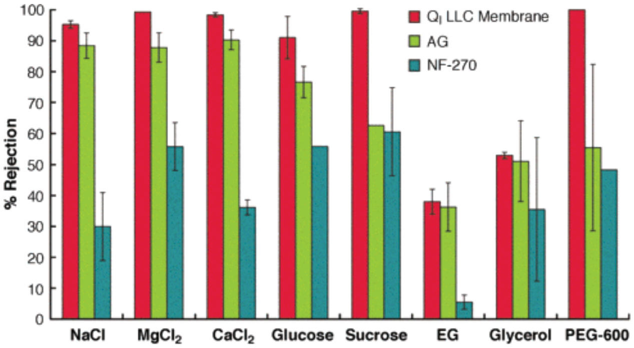

Figure 2. Comparison of rejection properties[17] of Q_I, AG, and NF-270 membranes (dead-end filtration; 400 psi; 2000 ppm aq feed solutions).

psi applied pressure, and 2000 ppm aqueous feed solutions. The percent rejections[17] were determined by analyzing the concentration of the solutes in the permeate and retentate using ionic conductivity and total organic carbon analysis (see Supporting Information). The Q_I-phase membranes can almost completely (95 to >99.9%) reject dissolved salts (NaCl, $MgCl_2$, $CaCl_2$), neutral molecules (glucose, sucrose, PEG-600), and molecular ions (Ethidium Red) in the 0.64−1.2 nm size range in one pass. Only solutes such as ethylene glycol (EG) and glycerol, which are similar in size to water, afford mediocre rejections. From these results, the effective "pore" or gap size of the water layer manifold in the Q_I membrane was calculated to be 0.75 nm using the Ferry equation (see Supporting Information).[18]

Under the same dead-end filtration conditions, a commercial RO (GE-Osmonics AG) and NF membrane (Dow NF-270) exhibited lower rejections compared to the LLC membrane for the same solutes, except for EG and glycerol (Figure 2). For glycerol, the three membranes show similar moderate rejections (ca. 40−55%). For EG, the rejections of the LLC and AG membrane are similar (ca. 40%), but NF-270 is much lower.

The thickness-normalized water permeability of the Q_I-phase membranes was determined to be 0.089 L m^{-2} h^{-1} bar^{-1} μm based on a measured LLC layer thickness of 40 μm. This value is comparable to the reported water permeabilities of commercial RO membranes (0.047−0.28 L m^{-2} h^{-1} bar^{-1} μm),[19] assuming an active layer thickness of 0.1 μm (an upper limit).[1,2] From measured water fluxes, the permeability of the LLC membrane was found to be slightly lower than that of AG, but both are much lower than that of NF-270 (assuming a 0.1 μm active layer thickness for AG and NF-270, see Supporting Information). The Q_I-phase membrane also has very stable water filtration performance. Almost full (>95%) water flux recovery after salt solution filtration and <15% water flux drop upon switching from pure water to various 2000 ppm feed solutions were observed (see Supporting Information). Control experiments with supported membranes containing an *isotropic* layer of cross-linked **1** did not show any observable water transport under the same test conditions (see Supporting Information). This result confirms that the LLC nanostructure plays an important role in the transport properties of this new water desalination material.

In summary, a new type of *nanoporous* polymer capable of efficient water desalination and NF has been demonstrated. This material, which is based on a cross-linked Q_I-phase LLC assembly, has an effective pore size of 0.75 nm and is capable of high salt rejection, with a water permeability similar to that of commercial RO membranes in dead-end filtration. We are currently exploring new processing methods that afford thin Q_I films and larger area samples so that cross-flow studies can be performed. We are also exploring whether the water manifold gap size and permeability of the material can be tuned by modifying the structure of the LLC monomer, as well as the design of more readily synthesized Q_I-phase monomers.

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Supporting Information Available: Full experimental details for the supported Q_I-phase membranes of **1**. Results of filtration and control studies for the Q_I, AG, and NF-270 membranes (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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