RECLAMATION

Managing Water in the West

Desalination and Water Purification Research
and Development Program Report No. 180

Evaluation and Development of a New Type of Polymer-based Water Desalination Membrane Containing Uniform Molecular-sized Ion Pores

U.S. Department of the Interior
Bureau of Reclamation
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Water and Environmental Services Division
Water Treatment Engineering Research Team
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Prepared for Reclamation Under Agreement No.
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by

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Glossary

CU	University of Colorado at Boulder
FT-IR	fourier-transform infrared
GE	General Electric
H_{II}	type II (inverted) hexagonal
LLC	lyotropic liquid crystal
MeOH	methanol
NF	nanofiltration
PES	poly(ether sulfone)
PLM	polarized light microscopy
PSf	polysulfone
PXRD	powder X-ray diffraction
Q_I	type I (normal) bicontinuous cubic
Reclamation	Bureau of Reclamation
RO	reverse osmosis
SAXS	small-angle X-ray scattering
TEM	transmission electron microscopy
TFC	thin-film composite
TSC	Technical Service Center
UF	ultrafiltration

1. EXECUTIVE SUMMARY

In many parts of the U.S., the demand for fresh water is projected to exceed supply. Consequently, development of new or improved methods for producing fresh water from salted and/or contaminated water sources in a facile, economical manner is of paramount importance to the U.S. Bureau of Reclamation (USBR), especially membrane-based technologies which have a smaller equipment footprint, lower energy consumption, and can be deployed more rapidly than distillation systems. Membrane-based water desalination is currently accomplished using reverse osmosis (RO) membranes that can remove 99+% of hydrated salt ions (<1 nm diameter) from water via "size-exclusion" through the voids between the polymer chains. In contrast, ***porous*** nanofiltration (NF) membranes can remove larger solutes and contaminants from water via size-exclusion but through nanopores ***in the 1–10 nm size range***. NF membranes can only partially perform desalination because their pores are much larger than most hydrated salt ions, and NF membranes do not have well-defined pore pathways or uniform pore sizes to afford clean molecular size separations. Currently, RO and NF membrane fabrication methods provide very little control over the size and distribution of the interstitial voids or nanopores for tuning rejection selectivity and permeability. Also, current RO and NF membranes suffer from low resistance to aqueous ClO– used in water treatment and membrane cleaning, as well as exposure to high or low pH conditions. They are also easily fouled by organic and biological contaminants in water.

Recently our research team developed a new type of nanoporous water purification membrane material that rejects inorganic salts and neutral organic molecules from water better than current NF membranes and comparable to conventional RO membranes. It also has a thickness-normalized water permeability comparable to that of current RO active layer materials. This new material is a water-based, type I bicontinuous cubic (QI) lyotropic liquid crystal (i.e., surfactant) (LLC) polymer network with 3D-interconnected, uniform-size, annulus-like, cationic water nanopores. Preliminary fouling studies showed that these initial systems have excellent resistance to nonspecific protein adsorption and ClO– degradation as a result of their unique chemical and morphological structures. We recently designed a new LLC monomer (**3**) that forms a cross-linkable QI-phase with the low volatility and environmentally benign solvent, glycerol, instead of water. This new **3**/glycerol QI monomer phase can be readily fabricated into defect-free, 1-inch-diameter, thin-film composite (TFC) membranes via solution casting from MeOH (methanol) onto porous polysulfone supports, with minimal glycerol loss and retention of the QI composition after MeOH evaporation and photopolymerization. After pre-filtration to exchange the glycerol in the pores with water, these TFC membranes were found to reject *uncharged* molecular solutes consistent with size-exclusion through ***uniform, 0.96 nm-wide pores*** in small stirred dead-end filtration tests. In addition, the rejection of smaller hydrated salt ions was found to be at the high level of RO membranes (≥98%) due to repulsive interactions between the cationic pore walls and the cationic metal ions.

Pursuant to Task IV (Expanding Scientific Understanding of Desalination Processes) of USBR DWPR FOA # R13SF80004, we will investigate two aspects of this new TFC QI LLC polymer membrane system in the context of developing it as a new, innovative, alternative desalination process. Specifically, we propose to: (1) scale up the preparation of this new water NF/desalination membrane material and perform cross-flow water desalination, ClO– resistance, and protein/organic matter fouling tests under more real-world operating conditions of relevance to the USBR; and (2) design more economical and easily synthesized/scalable LLC monomers based on 3 but with acrylate or methacrylate tails instead of the specialized 1,3-diene tails currently in use.

2. BACKGROUND

The removal of dissolved salts and molecular contaminants from seawater, brackish water, or wastewater to obtain clean drinking water is of great importance in regions lacking readily available fresh water sources (Short, 2007; U. N. Millenium Project, 2005). In many parts of the U.S., the demand for fresh water is projected to exceed supply (U.S. Dept. of the Interior, Bureau of Reclamation, 2012). Consequently, development of new or improved methods for producing fresh water from salted and/or contaminated water sources in a facile, economical manner is of paramount importance to the Bureau of Reclamation (Reclamation) (U.S. Dept. of the Interior, Bureau of Reclamation, 2012). The use of membranes is one approach that has many benefits over other water desalination/purification methods such as distillation, especially when a small equipment footprint, lower energy consumption, and/or rapid deployment are needed (Shannon and Semiat, 2008).

Membrane-based water desalination is currently accomplished using reverse osmosis (RO) membranes that can remove 99+% of hydrated salt ions (<1 nm diameter) from water irrespective of their charge (Fell, 1995; Vainrot et al., 2008). RO membranes are typically thin-film composite (TFC) membrane comprised of an ultrathin (ca. ≤0.1–0.2 µm), ***dense***, non-charged separating layer (usually a cross-linked poly(aryl amide)) coated on top of a more porous support (Fell, 2005; Vainrot et al., 2008). This TFC configuration provides the mechanical strength needed for the membrane to withstand the applied pressures for filtration, while the presence of an extremely thin separating layer affords respectable absolute water fluxes (i.e., thinner = less resistance to flow) (Fell, 2005; Vainrot et al., 2008). Mechanistically, RO is believed to occur via “size-exclusion” of hydrated salt ions (e.g., $Na^+(aq)$: 0.72 nm diameter) (Nightingale,1959) through the ≤0.5 nm voids between the polymer chains, while smaller water molecules (0.27 nm) (Schatzberg, 1967) can pass through (Fell, 1995; Williams, 2003).

In a complementary fashion, ***porous*** nanofiltration (NF) membranes are used to remove larger solutes and contaminants from water (e.g., large molecules/ions, macromolecules, microparticles) through a similar size-exclusion process but via actual nanopores (Bhattacharya and Ghosh, 2004). NF membranes are typically asymmetric or TFC structures; however, the thin (usually charged) separating layer is not dense but contains ***discrete, engineered pores in the 1–10 nm size range*** (Bhattacharya and Ghosh, 2004). NF membranes can only partially perform water desalination (even with charge repulsion effects) because their pores are much larger than most hydrated salt ions (Bhattacharya and Ghosh, 2004). In addition, current NF membranes do not have well-defined pore pathways or uniform pore sizes on the nanometer scale to afford clean molecular size separations (Bhattacharya and Ghosh, 2004).

Unfortunately, traditional RO and NF membrane production methods (e.g., immersion precipitation (Bhattacharya and Ghosh, 2004; Matsuura, 1993), interfacial polymerization (Fell, 1995), etc.) provide little control over the size and distribution of the interstitial voids or nanopores for tuning rejection selectivity and permeability. Also, current poly(aryl amide)-based RO and NF membranes suffer from low resistance to the chlorine (i.e., ClO^{-}) used for municipal water disinfection and membrane cleaning, as well as exposure to high or low pH conditions (Vainrot, 2008; Cadotte et al, 1980). In addition, they are easily fouled by organic and biological contaminants in water (Vainrot, 2008; Cadotte et al, 1980).

One of the major objectives in new membranes research is developing novel technologies for water desalination, NF, and other purposes based on membranes with nm-scale pores that have higher selectivity and permeability, plus better resistance to harsh chemicals and biofouling (Vainrot, 2008). Unfortunately, there are inherent difficulties in making polymers with uniform pores on the size of small ions and molecules due to the lack of convenient building blocks and/or methods for controlling pore architecture on this size regime. Only a handful of methods have been reported in the literature that affords *polymer-based* materials with *uniform, molecular-size (ca. ≤1 nm) pores* for potential membrane applications (Gin and Noble, 2011). These include controlled deposition to reduce the pore size of commercial, nanoporous track- etch membranes (Jirage et al, 1997); blending of polymers with nanoporous additives such as zeolites (Bowen et al., 2004; Jeong et al. 2007), metal-organic framework compounds (Perez et al., 2009; Bae et al. 2010), carbon nanotubes (Hinds et al., 2004; Kim et al., 2007), and peptide nanotubes (Xu et al., 2011); polymerization of thermotropic (i.e., solvent-free) liquid crystal phases with functionalized transport domains (Beginn et al., 2000; Hemni et al., 2012); and use of "molecular squares" (Czaplewski et al., 2001) and macrocyclic surfactants (Yan et al., 2002). Other recent methods for making nanoporous polymer membranes such as gel template leaching of polymers (Gankema et al., 1996), selective domain etching of phase-separated block copolymers (Liu and Ding, 1998; Wolf and Hillmyer, 2003; Yang et al., 2006); and the use of nanophase- separated amphiphilic graft copolymers (Akthuakul et al., 2004) typically afford pores larger than 6–7 nm (making them incapable of small molecule sieving) (Liu and Ding, 1998; Wolf and Hillmyer, 2003; Yang et al., 2006), or pores with irregular structures and some size variance (Gankema et al., 1996; Akthuakul et al., 2004). Of the methods that afford materials with uniform, molecular-size pores, most yield 1D cylindrical pores that must be aligned/processed in the flow direction and packed closely together before they can achieve high permeabilities (Jirage et al, 1997;

Hinds et al., 2004; Kim et al., 2007; Xu et al., 2011; Beginn et al., 2000; Czaplewski et al., 2001; Yan et al., 2002). Only a few give materials with 3D-interconnected nanopores that have good pore continuity and density without need for alignment (Bowen et al., 2004; Jeong et al. 2007; Perez et al., 2009; Bae et al. 2010; Hemni et al., 2012).

Recently, our research team at the University of Colorado, Boulder (CU) developed a new type of nanoporous polymer membrane material based on lyotropic liquid crystals (LLCs) that has *uniform*, sub-1-nm size, ionic pores (Zhou et al., 2007; Hatakeyama et al., 2010; Hatakeyama et al., 2011; Carter et al., 2012). This new material rejects neutral organic molecules from water via molecular sieving, and inorganic salts from water via a combination of molecular sieving and electrostatic effects in the nanopores. The result is a solute rejection level better than current NF membranes and comparable to or just below that of conventional RO membranes when tested under the same dead-end filtration conditions (Zhou et al., 2007; Hatakeyama et al., 2010; Hatakeyama et al., 2011; Carter et al., 2012). Examples of this new material were also found to have a thickness-normalized water permeability comparable to current RO active layer materials (Zhou et al., 2007; Hatakeyama et al., 2010; Hatakeyama et al., 2011; Carter et al., 2012).

In terms of background, LLCs are amphiphilic molecules that aggregate into ordered, phase-separated assemblies containing uniform aqueous domains with feature sizes in the 1–5 nm range (Figure 1) (Tiddy, 1980). The geometry of the LLC phase formed depends on the shape/packing properties of the amphiphiles (Israelachvili, 1985), their interfacial curvature energy (Gruner, 1989), as well as the composition, temperature, and pressure of the system (Tiddy, 1980). The periodic LLC aqueous domains can range in geometry from planar bilayers to 1D cylindrical pores to 3D-interconnected channels. Consequently, the phases are termed lamellar (L), hexagonal (H), bicontinuous cubic (Q), and discontinuous cubic (I), based on their symmetry (Tiddy, 1980). They are also subdivided into type I or type II phases depending on whether they are on the water-excessive (type I) or water-deficient (type II) side of the phase diagram relative to the central L phase (Tiddy, 1980). By using polymerizable LLCs, these ordered assemblies can be stabilized by cross-linking to afford useful, robust, nanoporous polymer networks (Gin et al. 2001; Gin et al., 2006).

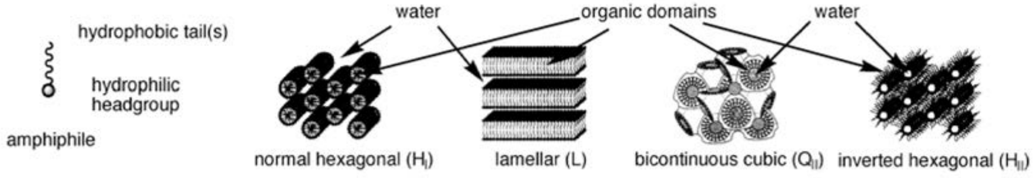


Figure 1.—Schematic representations of some common LLC phases formed by amphiphiles in water.

The new LLC membrane material we recently developed is a type I bicontinuous cubic (Q_I)-phase polymer network with ordered, 3D-interconnected (i.e., no need for pore alignment) annulus-like, cationic water pores. The first two examples of this new material were prepared from monomer **1** in water and monomer **2** in water to give cross-linked polymers with uniform ionic pores 0.75 nm and 0.86 nm in width, respectively (Figure 2) (Zhou et al., 2007; Hatakeyama et al., 2010; Hatakeyama et al., 2011). Because of the compositional sensitivity of these initial Q_I monomer systems to evaporative water loss during processing (leading to phase changes), thin-film processing to make TFC membranes was not possible (Zhou et al., 2007; Hatakeyama et al., 2010; Hatakeyama et al., 2011). Supported Q_I polymer membranes of **1**/water and **2**/water for initial testing had to be prepared by heating (60–70 °C) and pressing (10–12 tons force) these initial Q_I-phase monomer mixtures (plus radical photo-initiator) into a 35-µm thick, microporous support. The infused LLC monomer gels were then photo-cross-linked at ca. 65 °C to chemically lock-in the Q_I phase (as confirmed by powder X- ray diffraction (PXRD) and Fourier transform-infrared (FT-IR) analyses) ((Zhou et al., 2007; Hatakeyama et al., 2010; Hatakeyama et al., 2011). Dead-end water NF studies showed that the resulting flexible, melt-infused, supported Q_I membranes of cross-linked **1**/water and **2**/water reject dissolved neutral molecules and hydrated salt ions consistent with size-exclusion through uniform nanopores (Zhou et al., 2007; Hatakeyama et al., 2010; Hatakeyama et al., 2011). In fact, the non-charged solute rejection performance of these initial cross-linked Q_I membranes was found to better than that of a commercial NF membrane (with non-uniform nanopores) but slightly below that of a commercial RO membrane, when tested under the same conditions (Zhou et al., 2007; Hatakeyama et al., 2010; Hatakeyama et al., 2011). Similarly, the salt rejection of the cross-linked Q_I membranes of **1**/water and **2**/water was found to be substantially better than that of a commercial NF membrane but slightly below that of a commercial RO membrane. The *uncharged solute* rejection data of these nanoporous LLC membranes was found to fit the Ferry equation (i.e., $\%R = 100 \text{ x } [1 - (1 - [d_{solute}/d_{pore}])^2]^2$), which was originally developed to model the steric rejection of spherical particles by uniform circular pores (no charge effects) (Zeman, 1981; Aimar et al., 1990). The physical pore size of the cross-linked Q_I phase of **1**/water and **2**/water was determined by fitting the uncharged solute rejection data (no charge-charge interactions in the pores) with the Ferry equation after adapting it for uniform annulus pores instead of circular pores (Zhou et al., 2007). The *thickness-normalized* water permeability values of these two initial Q_I polymer membranes were found to be similar to that reported for commercial RO membranes (Bhattacharya and Williams, 2001), assuming a 0.1 µm RO active layer thickness (an upper limit) (Zhou et al., 2007; Hatakeyama et al., 2010). Preliminary protein and ClO^- fouling studies on the supported Q_I membranes of **1**/water also showed that these initial systems have excellent resistance to nonspecific protein adsorption and ClO^-

degradation as a result of their unique chemical and morphological structures (Hatakeyama et al., 2011).

Although these two initial cross-linked Q_I-phase systems based on **1** and **2** showed excellent promise as a new type of water NF/desalination membrane material, the inability to perform thin-film solution processing and fabricate TFC membranes limits Q_I membrane preparation to small, melt-infused samples with a very thick separating layer (ca. 35 µm thick). This not only severely restricts the absolute water flux obtainable, but it also limits the size and amount of membrane that can be prepared for testing (as well as potential industrial production/scale-up in the future). Consequently, Q_I membranes of **1**/water and **2**/water have ***not*** yet been evaluated under more real-world filtration and fouling testing conditions (i.e., via cross-flow studies that require larger size samples). Moreover, this processing limitation greatly increases the amount of relatively expensive LLC monomer needed to make membranes on a per area basis. As with commercial composite RO and NF membranes, the ideal membrane configuration would be a TFC architecture (i.e., a very thin separation layer on top of a more porous support), which yields the highest water flux while providing the mechanical stability needed to withstand the pressures required for passage through very small pores (Fell, 1995).

In addition to processing needs, more easily synthesized and cost-effective LLC monomers are also needed. The starting materials cost alone for making monomer **1** on the laboratory scale is approximately $79/(g of **1** produced) (Hatakeyama et al., 2010). The synthesis of **1** also involves an expensive phosphine-sulfide starting material, formation of a pyrophoric phosphine intermediate, a Na metal/liquid NH_3 reduction step, and a rather elaborate polymerizable 1-3-diene tail preparation (Carter et al., 2012; Pindzola et al., 2003), thus making **1** only suitable for small-scale, academic research. Although newer, ammonium-based monomer **2** utilizes more cost-effective, commercially diamine starting materials instead of phosphines (thereby reducing the materials costs to ca. $14/(g **2** produced)) (Hatakeyama et al., 2010), the synthesis of **2** still requires the same elaborate1,3-diene tails.

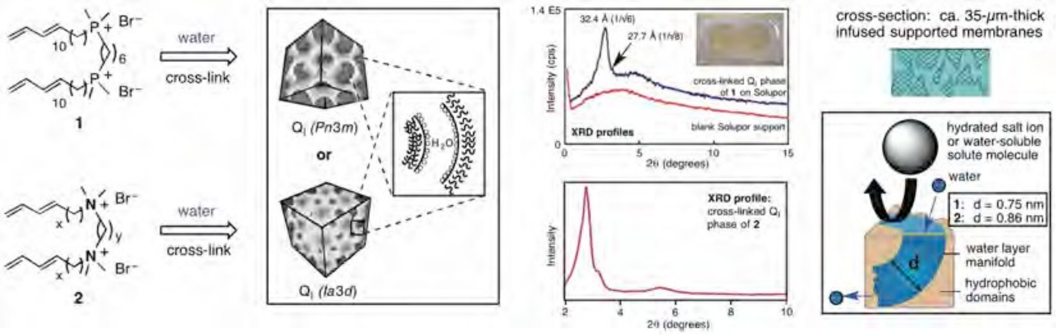
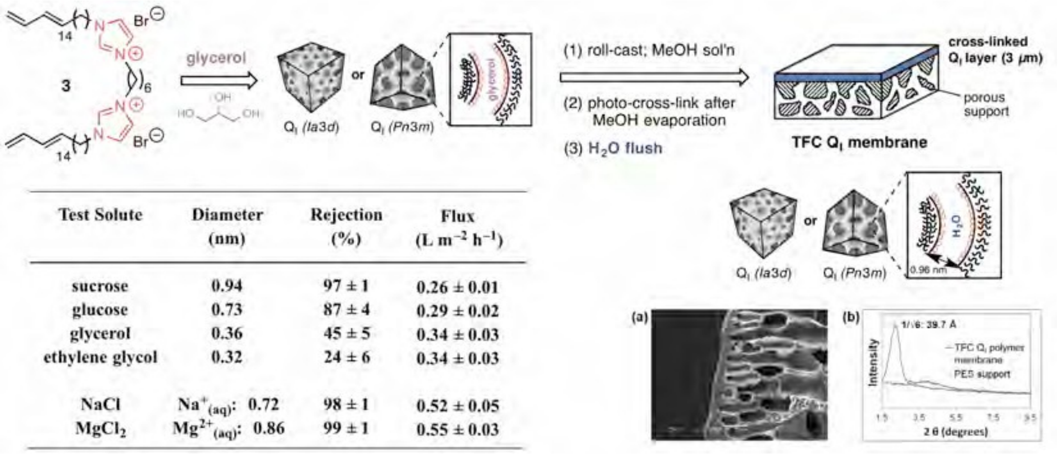


Figure 2.—Cross-linked Q_I phases of 1/water and 2/water; some characterization data for their *melt-infused* composite membranes; and the molecular size-exclusion mechanism of water desalination and NF through the materials with their physical pore sizes indicated (Zhou et al., 2007; Hatakeyama et al., 2010).

In order to develop a more economical LLC system that can be solution-processed into higher absolute-throughput TFC membranes, we very recently designed a new LLC monomer (**3**) that forms a cross-linkable Q_I-phase with the low volatility and environmentally benign solvent, glycerol, instead of water (Carter et al., 2012). In terms of laboratory scale materials costs, **3** costs only ca. $7/(g synthesized) because it uses the abundant and inexpensive natural product, imidazole, as a starting material (Carter et al., 2012). This new **3**/glycerol Q_I monomer phase can be readily fabricated into defect-free, 1-inch-diameter, TFC membranes via solution-casting from MeOH onto porous poly(ether sulfone) (PES) supports, with minimal glycerol loss and retention of the Q_I composition after MeOH evaporation and photo-initiated radical cross-linking (Figure 3) (Carter et al., 2012). We demonstrated proof-of-concept for this new processing approach by showing that a Q_I-phase [**3**/**glycerol**/radical photo-initiator (HMP)] mixture [79.7/19.8/0.5 (w/w/w)] can be roller-cast from a 60 wt % MeOH solution to generate defect-free, ca. ***3-μm-thick*** films on top of a custom-made, porous PES support (Carter et al., 2012). Retention of the Q_I phase after MeOH evaporation and photo-cross-linking was confirmed by powder XRD analysis (Figure 3) (Carter et al., 2012). After pre-filtration to exchange the glycerol in the pores with water, the resulting cross-linked TFC Q_I membranes were found to reject ***uncharged*** molecular solutes consistent with size-exclusion through ***uniform 0.96 nm pores*** in stirred dead-end filtration tests (as determined via by Ferry equation fitting) (Carter et al., 2012). However, the observed water fluxes were ca. 10 times greater than the prior melt-infused Q_I membranes of **1** and **2** (Carter et al., 2012). Interestingly, these new TFC Q_I membranes were also found to reject salts near or at the high level of RO membranes (>98%), even though the hydrated ions were substantially smaller than the nanopore size (Figure 3) (Carter et al., 2012). Compared to Dow SW30HR (a commercial high-performance RO membrane) and Dow NF-270 (a commercial porous NF membrane with non-uniform pore sizes) tested under the same conditions, the **3**/glycerol TFC Q_I membrane rejected uncharged solutes better than NF-270 but not quite as well as SW30HR. However, its salt rejection was much higher than that of NF-270 and on par with that of SW30HR (Carter et al., 2012). This higher-than-expected salt rejection may be the result of repulsive interactions between the new/different cationic headgroups in the pore walls and the approaching salt cations, or due to the new TFC membrane configuration where the Q_I phase is a pure top layer instead of infused in the support (Carter et al., 2012). This “dual-mode” rejection behavior makes this new membrane system quite unique in terms of its water purification performance (i.e., water NF via uniform nanopores but with high desalination capabilities). The thickness-normalized pure water permeability of the **3**/glycerol TFC Q_I membrane was found to be (6.6 ± 0.5) x 10^{-2} L m^{-2} h^{-1} bar^{-1} µm (based on a 3-µm-thick active layer), which is comparable to that measured for SW30HR under the same test conditions (Carter et al., 2012). It was also observed that exposure of the new **3**/glycerol TFC Q_I membranes to salt feed solutions (or aq. NaCl pre-treatment) increases their fluxes in uncharged solute filtrations by a factor of 1.5–2 without altering rejection selectivity (Carter et al., 2012). This unexpected beneficial effect may be due to some sort of anion exchange in the nanopores or interaction between the incoming salts and the ionic membrane pores/surface. Consequently, the ionic nature of these new nanoporous TFC Q_I membranes clearly requires more investigation.



Test Solute	Diameter (nm)	Rejection (%)	Flux (L m^{-2} h^{-1})
sucrose	0.94	97 ± 1	0.26 ± 0.01
glucose	0.73	87 ± 4	0.29 ± 0.02
glycerol	0.36	45 ± 5	0.34 ± 0.03
ethylene glycol	0.32	24 ± 6	0.34 ± 0.03
NaCl	$Na^+_{(aq)}$: 0.72	98 ± 1	0.52 ± 0.05
$MgCl_2$	$Mg^{2+}_{(aq)}$: 0.86	99 ± 1	0.55 ± 0.03

Figure 3.—Summary of the structure, fabrication procedure, and water NF and desalination performance of nanoporous, cross-linked Q_I TFC membranes made from 3/glycerol (Carter et al., 2012).

This new, processable Q_I-phase LLC monomer system based on ***3****/glycerol has the potential to be a transformational new type of water purification membrane material that can perform at the separation level of RO membranes but with more predictability based on size-sieving through uniform nanopores.* An intriguing advantage of this new material is the possibility of tuning the nanopore size and cation charge density uniformly on the 0.5–1 nm scale via monomer modification or changes in LLC phase-forming conditions. However, more research focused on evaluating, understanding, and controlling the structure and water filtration performance of this new type of water desalination/NF membrane is needed before it can be developed in a commercially viable alternative to conventional RO and NF membranes.

12-month Research Plan for the USBR Desalination and Water Purification Research (DWPR) Program:

Pursuant to Task IV (Expanding Scientific Understanding of Desalination Processes) of the USBR DWPR FOA # R13SF80004, we will investigate two aspects of this new Q_I LLC polymer membrane system in the context of evaluating and developing it as a new, innovative, membrane-based desalination process. Specifically, we propose to:

(1) scale up the preparation of this new water NF/desalination membrane material and perform ***cross-flow*** water desalination, ClO^- resistance, and protein/organic matter fouling tests under more real-world operating conditions of relevance to the USBR;

(2) design and synthesize more economical and easily synthesized/scalable LLC monomers based on monomer **3** but with acrylate or methacrylate polymerizable tails instead of the specialized 1,3-diene tails currently in use.

Accomplishing Objective 1 will help determine whether this new water NF/desalination membrane has performance characteristics that will make it viable and competitive in more real-world operating conditions. Accomplishing Objective 2 will replace the most expensive and time-consuming part of the LLC monomer **3** synthesis (i.e., the 1,3-diene tails) with a much more economical and scalable polymerizable tail alternative. According to a recent CU-funded independent economic analysis on this new Q_I LLC membrane technology, reducing the cost of the monomer is key to making this technology competitive with current RO membranes (Buschmann, 2012). We will contract with the USBR Denver Technical Service Center (TSC)/Denver Water Treatment Lab (Denver, CO) to perform the cross-flow membrane testing studies described above, based on the USBR's experience and facilities. Objective 1 will be evaluation/characterization research that is more practical in nature, and will require the use of standardized procedures for evaluating RO membrane performance from the literature (ASTM D 1494-03, 2003; Sagle et al., 2009; La et al., 2010; Park et al., 2008; Ju et al., 2008; La et al., 2012) and/or standardized membrane testing protocols currently used at USBR laboratories. Objective 2 will involve more fundamental, exploratory chemical design and materials engineering research that will be performed at CU.

3. CONCLUSIONS AND RECOMMENDATIONS

(for the entire duration of this project, including a 1-month no-cost extension: 09/19/2013 to 10/31/14)

Objective 1:

(1) Successfully scaled-up solution roll-casting fabrication of TFC Q_I membranes of cross-linked **3**/glycerol to prepare 2” x 4” test samples with a 3–4 µm thick Q_I top layer on a commercial porous PSf UF support from General Electric.

(2) Delivered multiple 2” x 4” TFC Q_I test membranes at regular intervals to the USBR Denver TSC for cross-flow filtration testing.

(3) USBR Denver TSC successfully performed cross-flow water flux and salt rejection tests on the TFC Q_I test membranes with pure water and a 2000 ppm aq. NaCl feed solution.

(4) Found that the cross-flow water flux and NaCl rejections for the TFC Q_I membranes of cross-linked **3**/glycerol were found to be very close to the flux and salt rejection values observed in prior dead-end filtration studies at CU.

(5) Found that the time needed for cross-flow filtration testing of the TFC Q_I membranes was very long because of the low flux resulting from the still relatively thick 3–4 µm thick Q_I top layer.

(6) Recommend as future work trying to prepare TFC Q_I membranes of cross- linked **3**/glycerol with thinner Q_I top layers (≤1 µm) to increase flux and speed of cross-flow testing

(7) Recommend as future work completing ClO^- resistance studies on the TFC Q_I membranes (in progress at USBR Denver TSC) and performing protein/organic matter fouling studies as proposed in the project.

Objective 2:

(8) Successfully synthesized and qualitatively screened the LLC phase behavior of 12 homologues (**4a–l**) of new ***acrylate-tail*** gemini imidazolium monomer platform (**4**)

(9) Several homologs of **4** exhibited a Q_I phase with glycerol when screened by the PLM solvent penetration scan method; however, none showed Q phases when tested in bulk for full phase diagram elucidation.

(10) Lack of Q_I phases in the bulk formulations of homologs **4a–l** indicates the sensitivity of the Q_I phase in this new acrylate platform and/or a very narrow composition window for the Q_I phase to exist.

(11) Successfully synthesized and qualitatively screened the LLC phase behavior of 8 homologues of a new ***methacrylate-tail*** gemini imidazolium monomer platform (**5**)

(12) None of the 8 homologs of **5** (i.e., monomers **5a–h**) synthesized showed clear evidence of Q_I phase formation with water or glycerol using the PLM solvent penetration scan method (although other thermotropic LC and LLC phases were observed).

(13) Both the acrylate- and methacrylate-tail systems are not conducive to Q_I phase formation when applied to the gemini imidazolium LLC monomer platform.

(14) Recommend as future work examining other economical, modular, polymerizable tail groups (e.g., sorbate).

(15) Recommend as future work examining other LLC phases made from convenient monomers as an alternative high-throughput NF separation layer (e.g., a macroscopically aligned inverted hexagonal (H_{II}) phase formed via an economical prior LLC monomer from CU).

Body of Report

Objective 1:

In the first quarter of this project, a new procedure for solution roll-casting and then photo-cross-linking the Q_I-phase of **3**/glycerol on top of a commercial, porous, polysulfone (PSf) ultrafiltration (UF) membrane from General Electric (GE) was developed, This updated method allows for the use of a commercial ultraporous support instead of a custom-made, microporous poly(ether sulfone) (PES) material as in the past (Carter et al, 2012), thereby reducing fabrication time as well as cost. Using this new method, membrane fabrication at CU was successfully scaled up to generate 2” x 4” TFC Q_I membranes of **3**/glycerol with a 3–4 µm-thick Q_I top layer. In the second quarter of the project, multiple 2” x 4” TFC Q_I membranes made from **3**/glycerol were delivered to the USBR Denver TSC, and initial salt rejection testing was performed with a 0.01 M NaCl feed solution using a small area (1” x 3” membrane area) cross-flow test cell (Figure 4). (The 2” x 4” size TFC Q_I membranes were cut down to 1” x 3” at the USBR Denver TSC for testing in this cell.) The flux measured was very close to that observed previously by CU using 1-inch-diameter dead-end filtration cells (Carter et al, 2012). However, the cross-flow salt rejection measured was negative (i.e., the=conductivity of the permeate was higher than that in the feed). It was hypothesized this was the result of leftover salt in the permeate volume of the USBR Denver TSC test cell from previous experiments. Control experiments performed at the USBR Denver TSC with a commercial TFC RO membrane confirmed that this was indeed the case. A protocol for cleaning and rinsing the USBR cross-flow test cell was consequently enacted to ensure that all subsequent salt rejection results collected on the system were accurate and consistent.

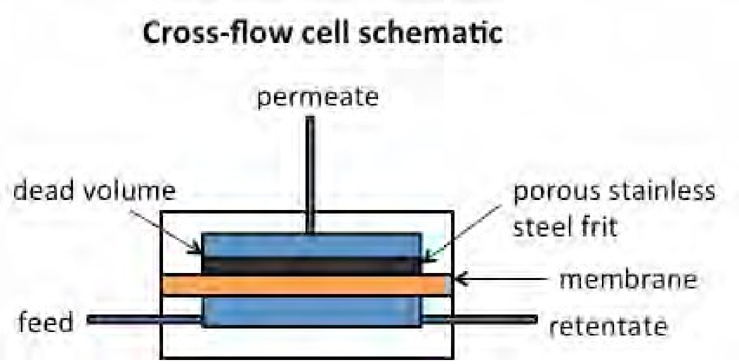
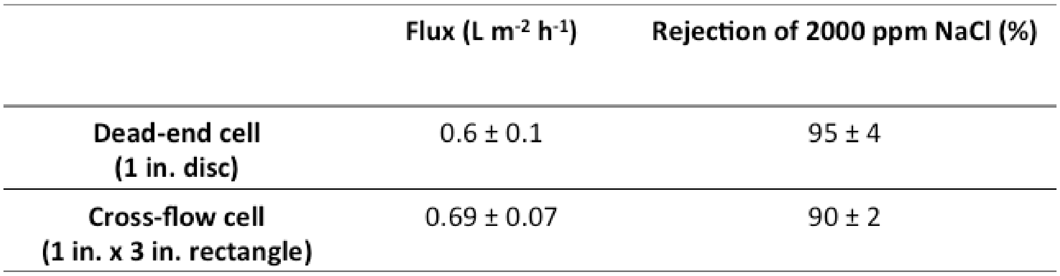


Figure 4.—Schematic of small-test-area (1” x 3”) cross-flow filtration cell used at the USBR Denver TSC. The 2” x 4” size TFC Q_I membranes were cut down to 1” x 3” at the USBR Denver TSC for testing in this cell.

In the third quarter, additional 2” x 4” TFC Q_I membranes of cross-linked **3**/glycerol were made and delivered to the USBR Denver TSC for cross-flow water flux and salt rejection testing with a 2000 ppm aq. NaCl feed solution. The test protocol that was followed was the one developed in the second quarter to ensure that the results collected were accurate, reproducible, and did not show any unaccounted salinity. The TFC Q_I membranes tested showed cross-flow water flux and rejection values comparable to what was observed in CU’s dead-end filtration units previously (see Table 1).

Table 1.—Comparison of cross-flow (USBR Denver TSC) vs. dead-end (CU) aq. NaCl filtration results for the TFC Q_I membranes made from **3**/glycerol. The values listed are the average values of three independent measurements with standard deviation error bars shown.



	Flux (L m^{-2} h^{-1})	Rejection of 2000 ppm NaCl (%)
Dead-end cell (1 in. disc)	0.6 ± 0.1	95 ± 4
Cross-flow cell (1 in. x 3 in. rectangle)	0.69 ± 0.07	90 ± 2

The only cross-flow testing difficulty noted was the long time required to complete a cross-flow study on a TFC Q_I membrane sample because of the low absolute water flux afforded by the membranes. Testing the TFC Q_I membranes (which have a 3–4 µm thick Q_I top layer) with DI water and 2000 ppm aq. NaCl took over two weeks. Reducing the Q_I active layer thickness will significantly reduce future cross-flow experiment time.

In fourth quarter of the project (including a 1-month no cost-extension), additional TFC Q_I membranes with the current 3–4 µm top layer thickness were prepared and delivered to the USBR Denver TSC to begin cross-flow ClO^- resistance testing of the membranes. Results from these most studies are pending. Preliminary modified processing/fabrication studies at CU to try and reduce the TFC membrane Q_I top layer thickness to ≤ 1 µm were also initiated. Unfortunately, no significant progress has been made on this front yet.

No stand-alone publications, patents, or conference presentations have been generated based on this part of the project work yet. These cross-flow NF results are anticipated to be included in a future manuscript focused on other filtration characterization work on the TFC Q_I membranes. Recommendations for future work in this area include: (1) developing methods for preparing TFC Q_I membranes of cross-linked **3**/glycerol with thinner Q_I top layers (≤ 1 µm) to increase flux and speed of cross-flow testing; (2) completing the cross-flow ClO^- resistance studies on the TFC Q_I membranes (recently started at the USBR Denver TSC); and (3) performing protein/organic matter fouling studies on the TFC Q_I membranes.

Objective 2:

In the first quarter, twelve homologs (**4a–l**) of the proposed new ***acrylate- tail*** gemini imidazolium monomer platform **4** were successfully synthesized using the procedure shown in Figure 5 below. These new monomers were also successfully purified and their structures were confirmed by standard chemical spectroscopic methods.

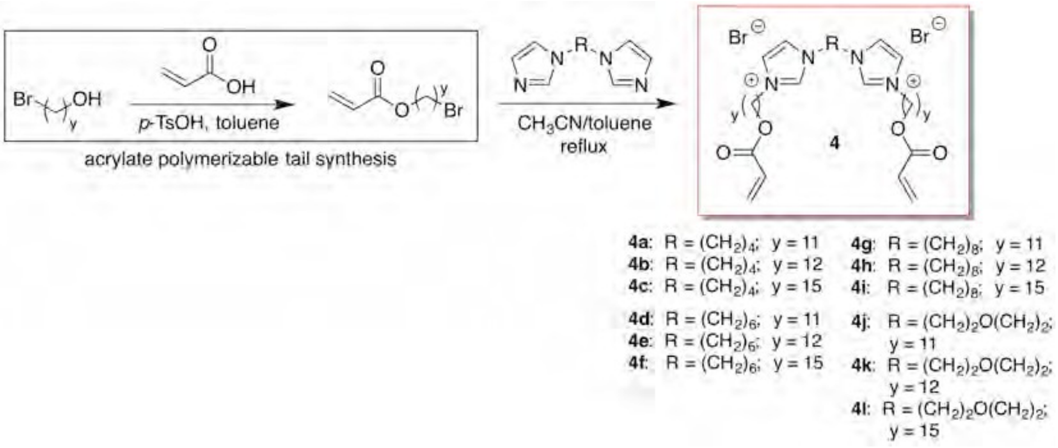


Figure 5.—Synthesis and structures of new acrylate-tail gemini imidazolium monomers 4a–l.

Using the PLM solvent penetration scan visual screening technique (Tiddy, 1980 Carter et al., 2012), monomers **4a**, **4b**, **4c**, **4e**, and **4f** were found to exhibit potential Q_I phases with glycerol at different elevated temperatures (Figure 6). Since Q_I phases are black (i.e., isotropic) under PLM cross-polarizers and typically found between birefringent (i.e., bright) lamellar (L) and normal hexagonal (H_I) phases, a dark isotropic band between two birefringent LLC phases indicates a potential Q_I phase (Carter et al., 2012; Tiddy, 1980). The other seven homologs of **4** did not show a black band between two bright regions under PLM penetration scan conditions indicative of Q-type phase formation.

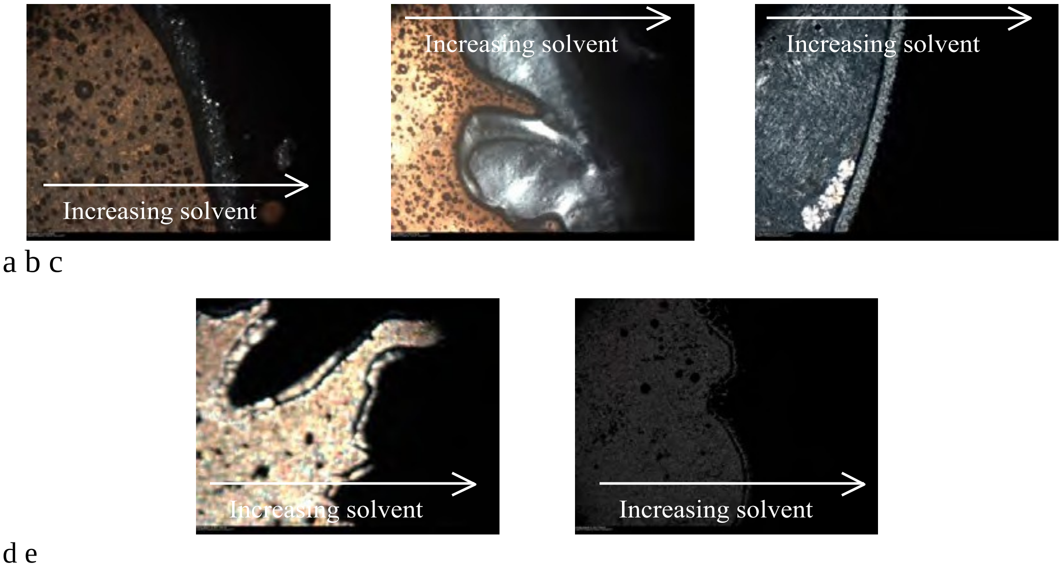


Figure 6.—Representative PLM LLC penetration scan images of the homologs of new acrylate-tail monomer platform 4 that exhibited a potential Q_I phase with glycerol: (a) PLM penetration scan of 4a at 75 °C. (b) PLM penetration scan of 4b at 80 °C. (c) PLM penetration scan of 4c at 64 °C. (d) PLM penetration scan of 4e at 49 °C. (e) PLM penetration scan of 4f at 52 °C.

Unfortunately, when phase diagrams of bulk samples of several of these acrylate monomers with glycerol were elucidated, no Q phases were observed by PLM. This result suggests that the Q_I phases in these new acrylate monomers are very sensitive to environment, and/or there is only a very narrow composition window/range for the Q_I phase to exist, making it impractical for processing of the Q_I phases of these acrylate monomers into TFC membranes.

In the second and third quarters of this project, the focus on new monomers was shifted to the synthesis of ***methacrylate***-based monomers as an alternative to the acrylate system described above. Eight homologs (**5a–h**) of methacrylate-tail gemini imidazolium monomer platform **5** were successfully synthesized using the procedure shown in Figure 7. Initially, only small amounts of **5a–h** were prepared to just demonstrate proof-of-concept for the synthesis approach.

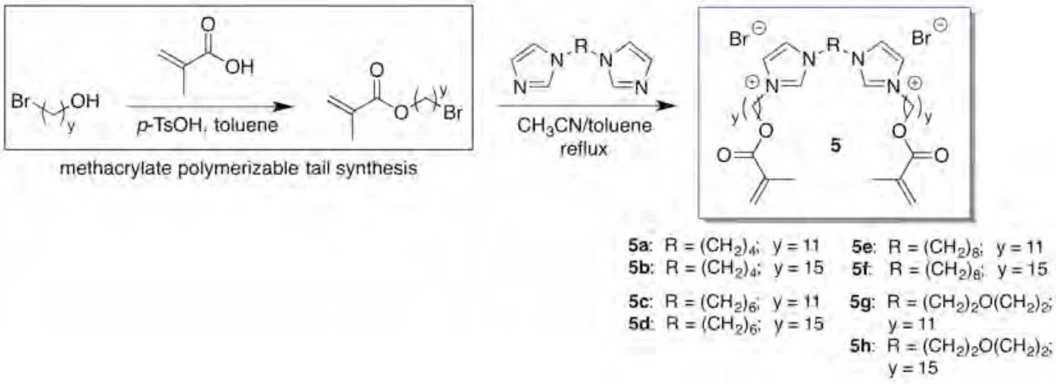


Figure 7.—Synthesis and structures of new methacrylate-tail gemini imidazolium monomers 5a–h.

Using the PLM solvent-gradient penetration scan technique (Tiddy, 1980; Carter et al., 2012), the LLC behaviors of three homologs (**5a**, **5b**, and **5c**) with water and with glycerol were screened in the second quarter. Monomer **5b** showed preliminary evidence of a possible Q phase with water at elevated temperatures (i.e., a dark band between two bright regions), but this could not be confirmed later on with bulk formulation phase analysis. In the third quarter, **5f** and **5h** were screened for potential Q_I phase formation, but neither showed a Q phase with water or glycerol. Their mixtures did not show a dark band between two bright regions under PLM penetration scan conditions that is indicative of Q- type LLC phase (Carter et al., 2012). In the fourth quarter, larger amounts of the remaining monomers in the **5** series were synthesized for LLC phase screening with water and glycerol. Unfortunately, none of the eight homologs of **5** showed clear evidence of Q_I phase formation in water or glycerol by visual PLM penetration scan analysis. Consequently, their full phase diagrams were not elucidated via bulk formulations due to the extensive time needed to systematically elucidate a two-component phase diagram with temperature variation.

Because of the lack of positive results in finding Q_I LLC phases in the new acrylate- and methacrylate-tail monomer systems, no publications, patents, or conference presentations have been generated based on this part of the project work. Recommendations for future work in this area in investigating examining the use of other economical, modular, polymerizable tail groups (e.g., sorbate ester) on the gemini imidazolium LLC monomer platform.

In light of the rather disappointing new monomer results described above, additional related work was undertaken during the last two quarters to investigate the possibility of using LLC-acrylate monomer **3** (previously developed by the Gin group) as an alternative, inexpensive, high-throughput nanoporous LLC membrane platform. LLC monomer **3** forms a columnar hexagonal thermotropic LC phase, as well as an inverted hexagonal (H_{II}) LLC phase in water that contains with close-packed 1-D cylindrical nanopores that are ca. 1.2 nm in diameter. The latter H_{II} LLC phase of **3** has been prepared as TFC water NF membranes but only as a collection of unaligned, discontinuous H_{II} domains that afford law water permeability (Zhou et al, 2005). The Osuji research group in the Chem. Eng. Dept. at Yale University contacted our groups with a collaborative idea to explore magnetic field alignment to generate macroscopically aligned (i.e., monodomain) columnar hexagonal and H_{II} films of **3** for subsequent cross-linking into high-flux polymeric NF membranes (Figure 8). Specifically, some synthesis work at CU was performed to prepare sufficient quantities of monomer **3** for the Osuji group at Yale to explore the viability of this idea.

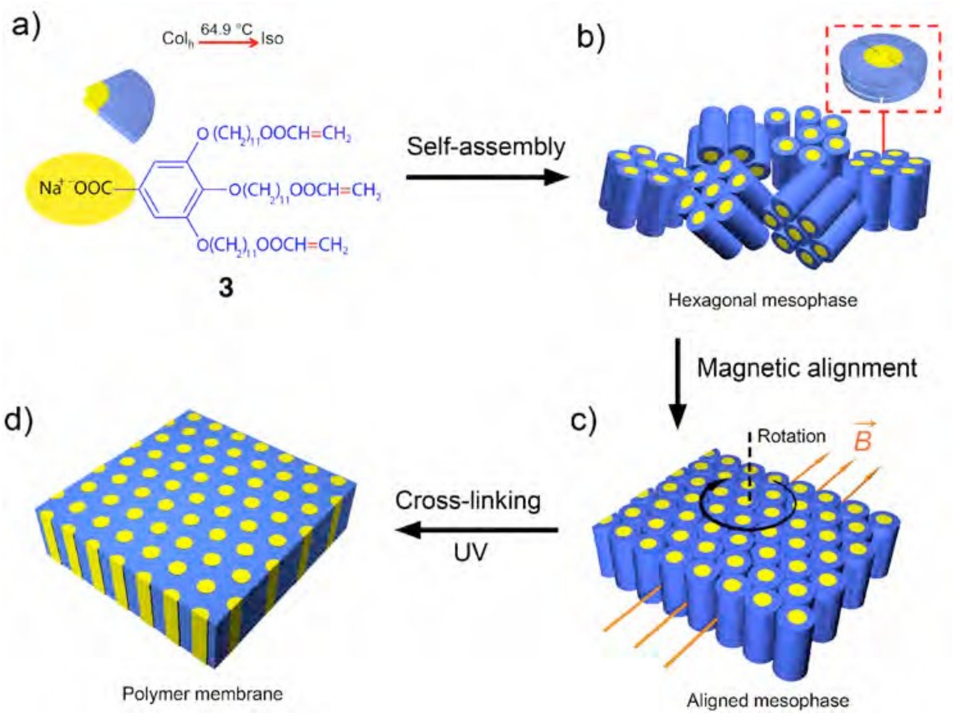


Figure 8.—Schematic of newly developed procedure for magnetic field alignment of the columnar hexagonal thermotropic LC phase of 3, followed by in situ photo-cross-linking, to form uniformly aligned nanoporous polymer films. Partially reproduced from (Feng et al., 2014). Copyright 2014 American Chemical Society.

Proof-of-concept for this idea was successfully demonstrated a couple of months ago by the Osuji group. They successfully formed free-standing (bulk) cross-linked columnar hexagonal and H_{II}-phase films of **3** containing uniformly aligned 1-nm-diameter nanopores, as confirmed by both 2-D small-angle X-ray scattering (SAXS) and transmission electron microscopy (TEM) analysis (Figure 9). Although no water filtration/permeation measurements have been performed on these magnetically aligned films yet, preliminary ion conductivity measurements showed that the aligned columnar hexagonal polymer films have a ca. 85 times higher ionic conductivity than an unaligned, polydomain film sample.

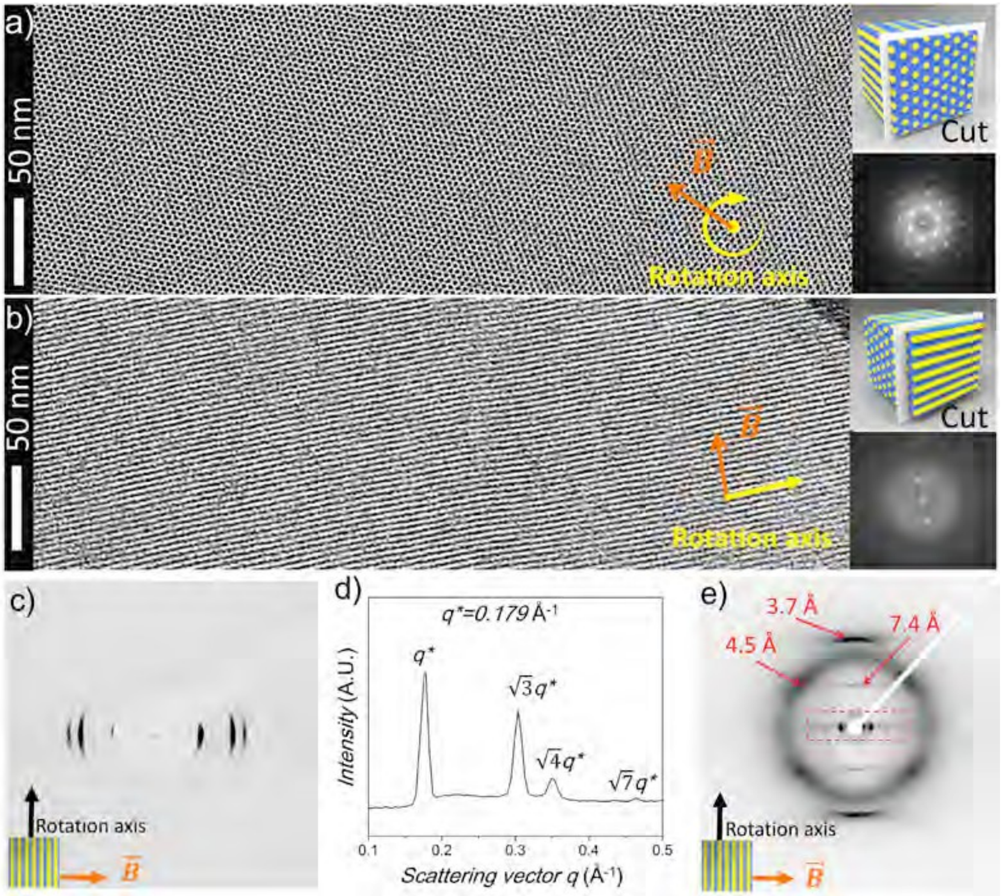


Figure 9.—TEM images of the magnetically aligned and cross-linked columnar hexagonal thermotropic LC films of 3 perpendicular and parallel to the alignment direction, and their associated SAXS profiles. Reproduced from (Feng et al., 2014). Copyright 2014 American Chemical Society.

Based on these very promising results, a joint publication by the Osuji, Gin, and Noble groups was submitted to the journal *ACS Nano* last month and just accepted for publication (Feng et al., 2014). This new joint paper acknowledges partial financial support from this USBR grant. Recommendations for future work in this area include: (1) preparing supported TFC versions of these aligned columnar hexagonal thermotropic LC and H_{II}-phase LLC polymer membranes, and (2) examining their water NF permeability/flux and salt rejection performance.

List of titles and dates of presentations or publications made; academic degrees granted; patents applied for or granted

Presentations:

(none)

Publications:

Feng, X., M. A. Tousley, M. G. Cowan, B. R. Wiesenauer, S. Nejati, Y. Choo, R. D. Noble, M. Elimelech, D. L. Gin, and C. O. Osuji, *ACS Nano* **2014**, Just Accepted Manuscript (published on-line October 26, 2014; DOI: 10.1021/nn505037b).

Academic degrees granted:

Carter, B. M., Ph.D. (Chemical Engineering), University of Colorado, Boulder, May 2014 (successfully defended April 9. 2014).

Patents applied for or granted:

(none)

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