

FOCUS REVIEW

Nanoporous polymer materials based on self-organized, bicontinuous cubic lyotropic liquid crystal assemblies and their applications

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The bicontinuous cubic (Q) lyotropic liquid crystal (LLC) phases formed by the phase-separation and self-organization of amphiphilic molecules in water are intriguing structures for a number of transport-related applications because they possess ordered, uniform, 3D-interconnected water channels on the size of single molecules. Polymeric materials formed from either the templated polymerization or cross-linking of conventional monomers around Q phases, or the direct polymerization or cross-linking of Q phases formed by reactive amphiphiles retain the desired LLC nanostructure but are more robust for true application development. The structures of Q LLC phases were only elucidated in the late 1980s, and the first successful preparation of polymers based on Q phases was reported soon after. However, the development and demonstration of these nanoporous polymers for material applications were not realized until the first decade of the twenty-first century. This focus review provides an overview of work in the area of Q LLC phase-based polymer materials, with a focus on the work of our research group and that of our collaborators on polymer networks prepared by the direct polymerization of reactive Q phases and their development as functional materials for several engineering applications.

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INTRODUCTION

Lyotropic liquid crystals (LLCs) are amphiphilic molecules typically composed of a hydrophilic headgroup section and a hydrophobic tail section that have the ability to phase-separate and self-organize into nanostructured assemblies in the presence of water. The resulting fluid, ordered LLC phases have varying degrees of average order, different levels of hydrophilic and hydrophobic domain interconnectivity, and uniform periodic features in the circa 1–10 nm size range (For general reviews on LLC phases and their classifications, see: refs 1–3). LLC phases have recently attracted a great deal of attention because of their benefits as a versatile platform for the design of functional, nanoporous polymer materials. For example, by employing reactive LLCs (that is, monomers), the desired phase can be locked-in directly via chemical cross-linking to afford robust, nanoporous polymer networks (For reviews on the synthesis and applications of nanostructured polymers made from polymerizable LLCs, see: refs 4–6). LLC networks made by this approach have been used for applications such as templated nanocomposite synthesis, drug delivery, molecular transport/separation and heterogeneous catalysis.^{7,8} Alternatively, non-polymerizable LLC phases have been used as nanostructured templates for the polymerization of conventional monomers dissolved in either the hydrophilic or hydrophobic domains. Subsequent

extraction of the LLC components affords nanoporous polymer ‘replicas’ of the original LLC phases that can also be used for a number of material applications.⁹

In both approaches, much of the utility stems from the ability to vary the LLC phase over a wide range of architectures via amphiphile design and composition control.^{1–3} (For overviews of how amphiphile shape/packing and system composition can determine the type of LLC phase formed, see: refs 10,11). These architectures range from ordered, 1D-hexagonal (H) and 2D-lamellar (L) phases to 3D-bicontinuous cubic (Q) phases with ordered interconnected pores in all directions (Figure 1).^{1–3} Within each of these LLC phase designations are more specific classifications (Type I or II) that relate to the mean curvature of the hydrophobic/hydrophilic interface. Type I (that is, normal) phases curve around the hydrophobic domains and Type II (that is, inverted) phases curve around the aqueous domains, with the L phase (zero mean curvature) serving as the central point of an ideal LLC phase progression. Consequently, Type I and II LLC phases of the same geometry can be considered reflections across the L phase and ‘inside-out’ with respect to one another. Q phases exist between the low-curvature L and the high-curvature H phases, and are also classified as Type I or II (For a review on bicontinuous Q LLC phases, see: ref. 12). Q phases are

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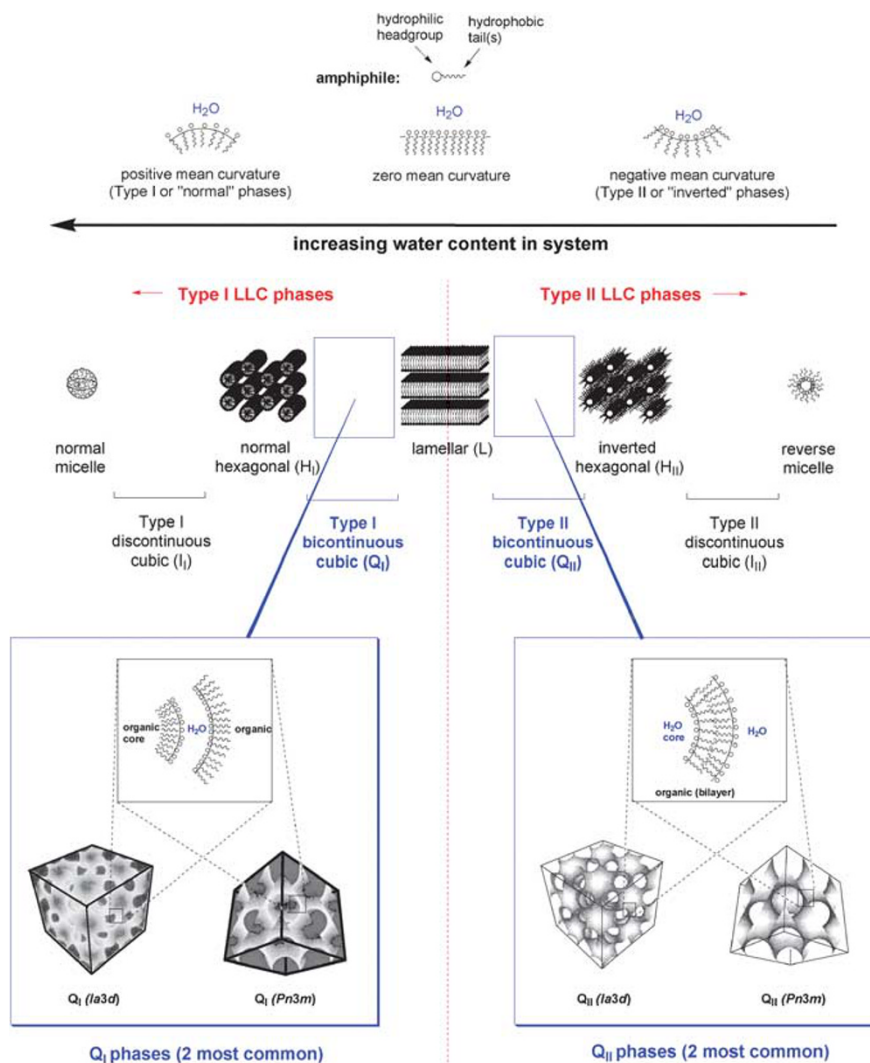


Figure 1 Schematic representations of the LLC phases formed by amphiphiles in water in an ideal phase progression, with a focus on the Type I and II Q phases. In the Q-phase representations, the gray/shaded areas represent the hydrophobic domains formed by the tails of the amphiphiles, and the open/white areas represent the water domains. Partially reproduced from ref. 34 with permission. Copyright (2003) American Chemical Society.

deemed bicontinuous because they consist of two non-connected but intertwined hydrophobic and hydrophilic regimes that exist with overall Q symmetry.¹² There are believed to be six different Q-phase geometries possible from X-ray diffraction studies,¹³ with the *Ia3d* and *Pn3m* architectures (Figure 1) being the most common.

Polymeric materials derived from LLC phases provide several distinct benefits for material applications. The ordered, open nanochannels can provide directionality for enhanced molecular transport or for molecular size discrimination. In addition, they can also provide confinement and access to interior reactive sites for catalysis. However, creating robust, polymer materials via LLC assemblies in an efficient manner can be problematic. In the direct polymerization approach, the LLC monomers must be connected quickly before disruption of the desired phase occurs, as the degree of entropy of the initial monomeric LLC phase (at equilibrium) drastically changes upon polymerization. Likewise, the LLC phase-templated polymerization of included monomers requires rapid polymerization to retain the desired phase. This latter approach is more forgiving because the non-LLC monomers being polymerized are not bonded to the amphiphiles making up the LLC phase template, thereby allowing

the entropy decrease upon polymerization to have less impact on the 'decoupled' LLC phase. Nanoporous polymers have also been synthesized via the selective domain etching of stabilized phase-separated block copolymers or via templated monomer polymerization in the domains of these copolymer assemblies (For examples of nanoporous polymers formed by phase-separated block copolymer nanostructures, see: refs 14,15). However, the materials derived from block copolymer nanostructures have much larger pores (10–50 nm).

The Q phases (Figure 1) are a particularly intriguing subset of LLC phases that are highly desirable for nanomaterial applications because they can assuage some of the issues that lower-dimensionality LLC phases have with respect to internal access and transport. The interpenetrating water channels within the Q phases provide better access to interior reactive sites compared with H and L phases, which is important for catalysis and drug-delivery applications. The interconnectivity of the Q-phase nanopores also affords a pore system that is difficult to completely block. Finally, the 3D-interconnected nature of the nanopores alleviates the need for bulk alignment of the material to obtain high throughput for transport applications. These features make polymers based on Q phases much more amenable to transport

and membrane applications. The only drawback to Q-phase polymers is that travel through the pores is more tortuous for molecular transport applications.

Surprisingly, although Q phases have been recognized to exist for many decades, their detailed structures were only postulated and confirmed experimentally within the last 25 years.¹³ Despite the attractiveness and potential benefits of Q LLC phase-based polymers for engineering applications, these materials have only been realized within the last circa 20 years. Moreover, the material properties and performance benefits of Q-phase polymers have only been demonstrated within the last 10 years. In this 'focus review', we provide an overview of work in the area of Q LLC phase-based nanoporous polymer materials, with a specific focus on the work of our group and that of our collaborators in the direct polymerization of Q-phase assemblies and their development for specific applications.

NANOPOROUS POLYMER MATERIALS VIA TEMPLATED POLYMERIZATION OF NON-LLC MONOMERS IN Q-PHASE ASSEMBLIES

In 1991, Anderson and Ström were the first researchers to demonstrate that nanoporous polymers based on Q LLC phases could be formed. They showed that methyl methacrylate can be radically polymerized within the organic regions of a Q_{II} (*Pn3m*) phase based on a didodecyldimethylammonium bromide/decane mixture, in order to form a polymeric replica of the initial LLC phase.^{16,17} They proposed that the resulting Q_{II}-phase polymer replicas may be useful for applications such as bioseparations or use as soft-tissue substitutes, burn dressing, suture coatings, and drug-delivery patches.¹⁷

Another reported attempt at Q-phase-templated polymerization involved the polymerization of the reactive organic anions (for example, acrylates) of pre-formed H- and Q-phase LLC systems formed by modified dodecylammonium surfactants.¹⁸ In this work, Hartmann and Sanderson observed that the polyacrylate and polymethacrylate formed from the templated Q phases changed into the L phase following polymerization, implying that a change in the packing parameter of the surfactant upon oligomer formation early in the polymerization can lead to LLC phase disruption.

In the past decade, much of the work in Q-phase-templated polymerization of conventional monomers has been performed by Guymon and co-workers. One of their primary goals was to investigate the effects of LLC-phase order on the photopolymerization kinetics of incorporated conventional monomers. In 2001, they demonstrated that upon photopolymerization of acrylamide within a templated Q_{II}-phase architecture of the commercial non-ionic surfactant Brij 58 (Figure 2) and water, the polymerization rate doubled compared with a micelle-templated system, and a 10-fold increase was observed over the original isotropic homogeneous mixture.¹⁹ These results were replicated 2 years later with Brij 56 surfactant system (Figure 2).²⁰ It was theorized that such LLC phase-templated polymerizations could lead to enhanced polymer-based separation materials. Related work performed by the Guymon group^{21–23} has centered around determining to what extent polymerization conditions and LLC-phase architecture influence the nanostructure and the physical properties of the templated linear polymers and cross-linked hydrogels formed by different included monomers. In general, they found that the polymerization rate in the Q-phase-templated systems,²² as well as the mechanical strength and diffusive transport properties of the resulting polymers,²³ were significantly higher than those in corresponding isotropic, homogeneous surfactant/water mixtures. These Q_{II}-templated polymers were proposed to be useful

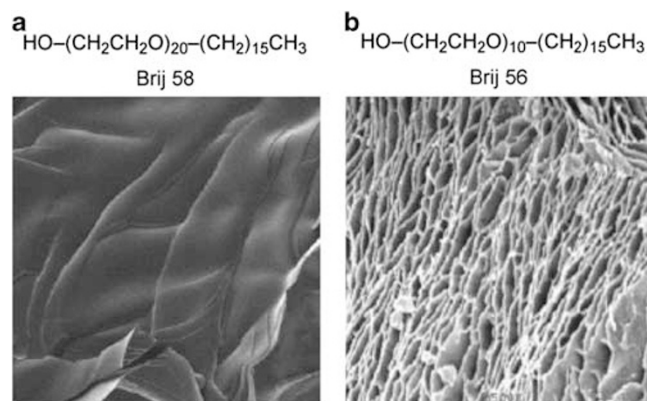


Figure 2 Structures of the surfactants used for Q_{II}-phase-templated polymerization of conventional monomers by Guymon and co-workers, along with s.e.m. images of the polyacrylamide formed in their (a) isotropic Brij 56, and (b) Q_{II}-phase Brij 56 mixtures. Partially reproduced from ref. 22 with permission. Copyright (2006) American Chemical Society.

for fabrication of advanced hydrogel materials and synthetic biomaterials, but these applications have not been realized yet.

NANOPOROUS POLYMER MATERIALS VIA THE DIRECT POLYMERIZATION OR CROSS-LINKING OF REACTIVE Q-PHASE ASSEMBLIES

Although polymers fabricated via templated polymerization of monomers within Q phases present intriguing properties, nanoporous polymers prepared via the direct polymerization or cross-linking of reactive Q phases have been highly sought-after because they have several unique features. Compared with templated polymer replicas, one of the advantages of directly polymerized or cross-linked Q phases is that the hydrophilic headgroups of the LLC monomers are all localized in the walls of the water channels. This feature allows for better control over nanopore environment and incorporation of specific functional groups in the pores if they are present in the LLC monomers. Unfortunately, one of the biggest challenges in this approach is the design of Q-phase-forming monomers that can be rapidly polymerized with retention of the phase structure. Because Q phases are considered saddle points between L and H phases,^{1,12} LLC shape- and packing parameter-based approaches^{10,11} have not been very reliable in designing amphiphiles that predictably form Q phases. The most successful approaches to designing Q-phase LLC monomers have been (1) preparing reactive variants of non-polymerizable surfactants known to form Q phases, and (2) using mixtures of LLC monomers and temperature variations to fine-tune system curvature and interfacial energy. Only a very limited number of LLC monomer platforms have been designed that reliably form Q phases.

Pioneering work in the synthesis of directly polymerizable Q phases was performed by O'Brien and co-workers in 1995.²⁴ They developed the first example of an LLC monomer system (**1a** + **1b**) that could assemble into Q_{II} phases and then be polymerized with retention of the desired nanostructures (Figure 3). Monomers **1a** and **1b** were synthesized from natural phospholipids and cross-linked by thermally-initiated radical polymerization.²⁴ Unfortunately, this monomer design approach required small-scale, elaborate syntheses and expensive starting materials.²⁴ Subsequent work resulted in two glycerol-based Q_{II}-phase LLC monomer systems (**2a** + **2b**) and **2c** (Figure 3) that are more economical and easier to produce in larger quantities than **1a** and **1b**.^{25–27} However, as for (**1a** + **1b**), careful

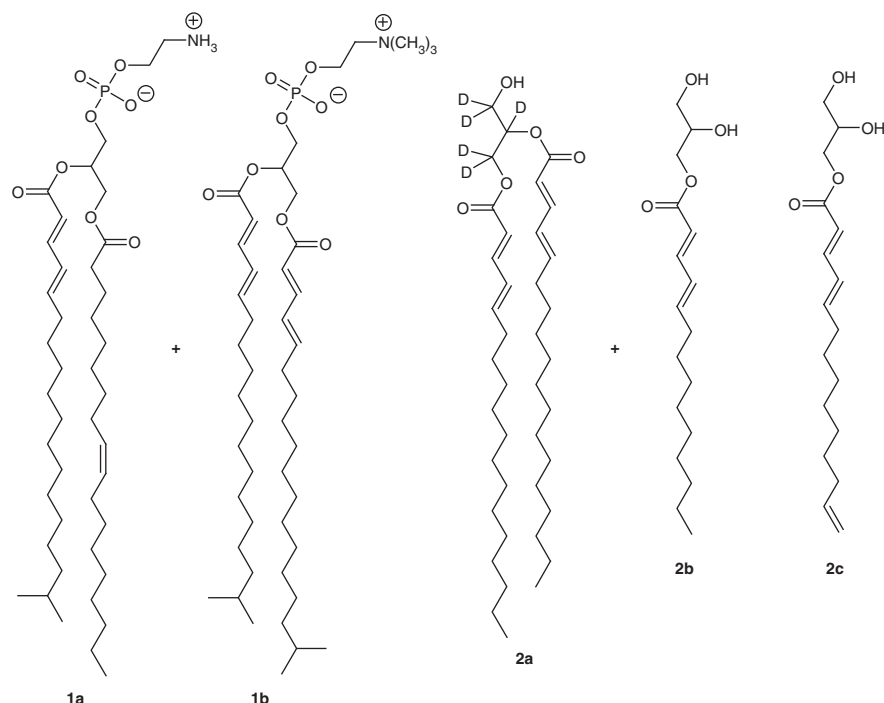


Figure 3 Structures of LLC monomer systems designed and used by O'Brien and co-workers that form Q_{II} phases in water.

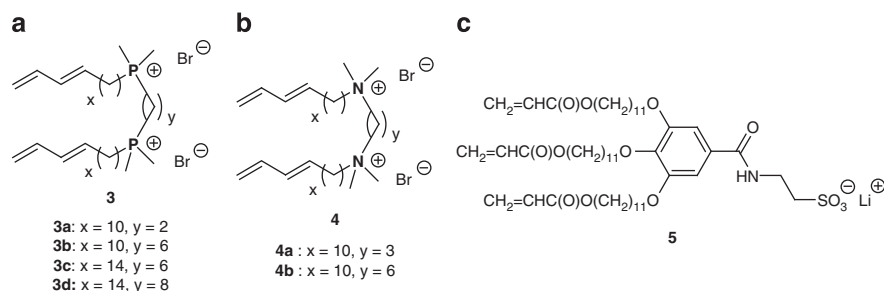


Figure 4 Structures of LLC monomers developed by the Gin group that form and can be cross-linked in Q phases: (a) gemini phosphonium monomers **3a–d** that form Q_I phases in water, (b) gemini ammonium monomers **4a** and **4b** that form Q_I phases in water, and (c) taper-shaped Li-sulfonate salt monomer **5** that forms a Q_{II} phase in propylene carbonate (PC).

blending of **2a** and **2b** is required to obtain the desired Q_{II} phases. Monomer **2c** can form a Q_{II} phase without co-monomers and is intrinsically cross-linkable, but the doubly-reactive single tail is synthetically complex to produce.²⁵ These papers, as well as other papers by O'Brien and co-workers on these polymerizable Q_{II} -phase systems,^{28–31} focused mostly on fundamental studies of chain-addition polymerization in Q phases. They also studied the diffusion of dendrimers in the water channels of the cross-linked Q_{II} -phase mixed-lipid systems and found that it was sufficiently rapid for the materials to be potentially useful for controlled release applications of encapsulated large drugs and macromolecules.³²

DESIGN AND DEVELOPMENT OF DIRECTLY CROSS-LINKED Q-PHASE LLC ASSEMBLIES AS FUNCTIONAL POLYMER MATERIALS FOR ENGINEERING APPLICATIONS

Over the last 10 years, the Gin group has performed extensive work on the design and synthesis of directly cross-linkable Q-phase LLC assemblies. With the aid of collaborators, we have also demonstrated that the resulting nanoporous polymers can be employed in a number

of transport-related applications with performance benefits. The distinguishing features of most of this work are the use of 'gemini' LLC monomer platforms and the formation and cross-linking of Q_I LLC phases. The gemini surfactant platform consists of two hydrophilic headgroups tethered by a spacer, and attached to each headgroup unit is a flexible hydrophobic tail. In terms of surfactant behavior, gemini amphiphiles are theorized have lower critical micelle concentrations, and therefore, a wider range of more attainable phase-separated architectures.³³ In terms of monomer design, this motif allows for two chain-polymerizable tails to be placed within the same monomer unit (that is, intrinsically cross-linkable), thereby allowing rapid formation of robust networks at fairly low degrees of conversion without the need for added cross-linkers. These LLC monomers (monomer platforms **3** and **4**) and the resulting cross-linked polymers set themselves apart from the host of Q-phase monomers and polymers previously reported because of their ability to form Q_I phases rather than the more common Q_{II} phases. The Gin group also developed a new subclass of cross-linkable LLC monomers (**5**) that forms Q_{II} phases in non-aqueous polar solvents and can be

cross-linked with retention of the phase structure. The structures of these LLC monomers are all shown in Figure 4.

Initial work in the area of Q_I -phase-forming gemini LLC monomers was performed by Pindzola *et al.*³⁴ It was the first example of a cross-linkable, Q_I -phase LLC system. In this work, a series of nine different gemini phosphonium monomers with alkyl-1,3-diene tails were synthesized and their LLC phase behavior with water was examined. Of the nine homologous monomers synthesized, eight were found to exhibit diverse LLC-phase behavior with water, and four of them (**3a–d**) displayed a Q_I phase in water somewhere between 55 and 90 wt% monomer over a range of temperatures. They also were able to retain their Q_I nanostructure after photo-initiated radical cross-linking, as confirmed by both polarized microscopy and powder X-ray diffraction.³⁴ No applications were initially proposed for these rather exotic materials.

The first application explored for these polymers was their use as a selectively permeable membrane material that allows water vapor transport but blocks the passage of chemical warfare agent (CWA) simulants in the vapor phase.³⁵ The impetus for this work was to develop a new type of protective garment material for military personnel and first-responders that allows water vapor 'breathability' for effective personal cooling while completely blocking toxic CWAs (For a review of CWAs and their chemistry, see: ref. 36). Currently, only a very limited number of examples of 'breathable' CWA barrier materials are known. Most economical CWA barrier materials are based on dense polymers, such as cross-linked butyl rubber (BR), that block the passage of all vapors (For a recent review of CWA- and biological warfare agent-protective garment materials and needs, see: ref. 37). The lack of water-vapor breathability can quickly lead to heat exhaustion for the wearer. The Gin group and collaborators believed that a Q_I -phase LLC polymer-BR blend with hydrophilic nanopores would allow good water-vapor transport while being able to size-reject larger, more hydrophobic CWA molecules and related molecules (Figure 5).

Lu *et al.*³⁵ found that when monomer **3b** was blended with commercial-grade BR in the presence of water, a surprisingly broad Q_I -phase region was observed at 65 °C in a **3b**/BR/ H_2O -phase diagram. In order to test the water vs CWA vapor-permeation selectivity of this LLC-BR composite material, a method was developed for making melt-infused, supported Q_I -phase membrane films of photo-cross-linked **3b**/BR/ H_2O on a 25–30- μm thick microporous polymer support. In cross-flow vapor transport studies, these supported membranes exhibited a substantial thickness-normalized water-vapor flux of $(5.9 \pm 0.3) \times 10^3 \text{ g m}^{-2} \text{ day}^{-1} \mu\text{m}$.³⁵ Thus for a 4- μm thick film of this material, the water-vapor flux exceeds the generally accepted military breathability requirement of $1500 \text{ g m}^{-2} \text{ day}^{-1}$, and is almost 300 times more permeable to water vapor than pure, vulcanized BR on the same support material. In contrast, the thickness-normalized vapor flux of 2-chloroethyl ethyl sulfide, a sulfur mustard (that is, blister agent) CWA simulant, through this material was observed to be $(2.86 \pm 0.05) \times 10^2 \text{ g m}^{-2} \text{ day}^{-1} \mu\text{m}$. These permeation values represent a vapor molar selectivity for H_2O /2-chloroethyl ethyl sulfide of 150, which is 500 times higher than the H_2O /2-chloroethyl ethyl sulfide selectivity seen through pure, vulcanized BR on the same support.³⁵

This same Q_I -phase cross-linked **3b**/BR/ H_2O polymer material was later examined as a breathable barrier for protection against nerve agent CWAs (that is, highly toxic, reactive organophosphorus esters that disrupt neurochemical pathways and cause the loss of autonomic functions³⁶).³⁸ Using dimethyl methylphosphonate (DMMP) as a nerve agent simulant, it was found that the cross-linked, Q_I -phase

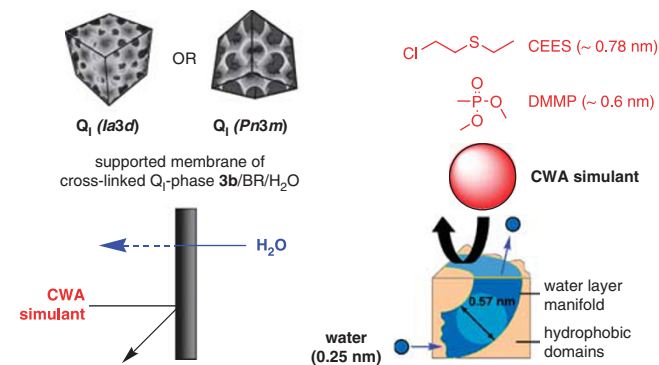


Figure 5 Schematic representation of selective 2-chloroethyl ethyl sulfide and DMMP vapor rejection and water-vapor transport through a supported, Q_I -phase, cross-linked **3b**/BR/ H_2O composite membrane.

3b/BR/ H_2O composite worked extraordinarily well for the rejection of DMMP while maintaining high water-vapor breathability. This barrier membrane rejected 99.91% of the DMMP vapor while allowing a thickness-normalized water vapor permeability of circa $5900 \text{ g m}^{-2} \text{ day}^{-1} \mu\text{m}$, giving a H_2O /DMMP molar selectivity of 1600.³⁸ Because DMMP is very water soluble, the mechanism for rejection of DMMP through the Q_I -phase composite cannot occur by solubility-based rejection the water pores, but rather must proceed by a molecular size-exclusion mechanism via the nanopores. From estimates of DMMP molecular size and its observed percent rejection, it was inferred that this cross-linked Q_I -phase LLC-BR membrane has an effective water nanopore size of circa 0.57 nm (Figure 5).³⁸ As discussed in the following sections, separate liquid-phase molecular-sieving filtration studies on the cross-linked Q_I -phase of **3b**/water revealed that it has a uniform, effective water nanopore size of circa 0.75 nm, thereby corroborating a molecular-sieving mechanism for the selective CWA vapor rejections.

The Q_I phase of **3b**/ H_2O (no BR) has also been extensively studied as a platform for synthesizing a new type of liquid water-desalination and purification membrane. Current water-purification membranes are either dense, reverse osmosis (RO) polymer membranes with circa 0.5 nm inter-chain voids that completely size-exclude larger hydrated salt ions or dissolved molecules from water molecules (0.25 nm) (For an overview of RO membranes, see: ref. 39), or nanoporous nanofiltration (NF) membranes that have non-uniform pores on the 1–10 nm scale (For a recent review on NF membranes, see: ref. 40). The lack of selectivity control in the former type of membrane and the compromises in molecular selectivity in the latter type of membrane mean that there is room for improvement. Polymers with uniform, interconnected molecular-size pores, such as those in Q -phase LLC networks, may be able to function as molecular-sieving membranes that have most of the capabilities of RO and NF membranes but none of their liabilities. To this end, water NF and desalination studies on the cross-linked Q_I phase of **3b**/ H_2O were first examined in the Gin group by Zhou *et al.*⁴¹ In this study, **3b** was found to form a Q_I phase with water at ratios between 80 and 90 wt% monomer and temperatures up to 85 °C. Supported, 35–40- μm thick, Q_I -phase membranes of cross-linked **3b**/ H_2O were prepared by heating and pressing the initial monomer mixture into a hydrophilic, microporous support and then photo-cross-linking the Q_I phase in place. Dead-end water NF and desalination studies (400 psi pressure, 2000 p.p.m aq. feed solutions) showed that the resulting supported Q_I -phase polymer membranes can almost completely (95 to >99.9%) reject dissolved salt ions and neutral

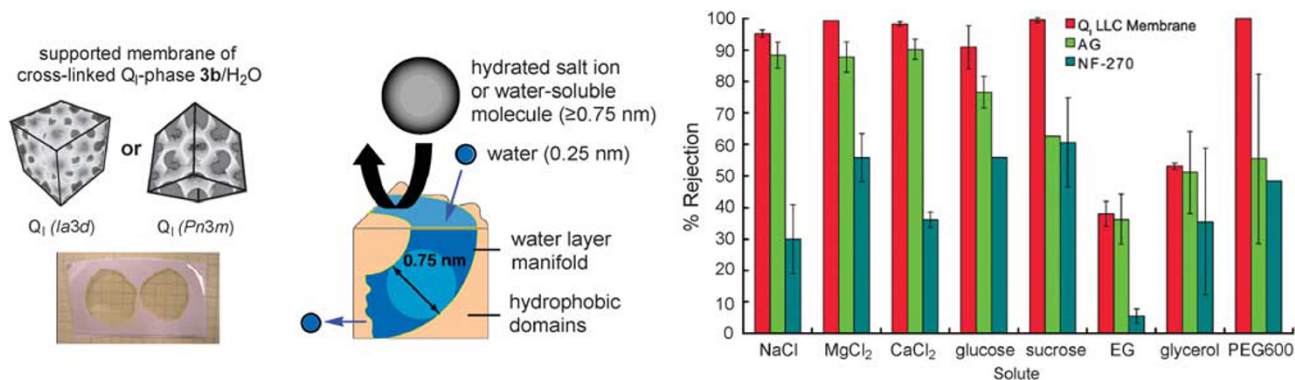


Figure 6 Mechanism of water NF/desalination through a supported Q_1 phase of cross-linked $3b/H_2O$ and comparison of its solute rejection vs those of two commercial RO and NF membranes. Partially reproduced from ref. 41 with permission. Copyright (2007) American Chemical Society.

molecules in the 0.7–1.2-nm size range in one pass. They exhibited solute rejections comparable to a commercial RO membrane (AG membrane produced by the General Electric Company) and better than a commercial NF membrane (NF-270 membrane produced by the Dow Chemical Company) (Figure 6).⁴¹ From the rejection performance of different-size neutral solutes, the effective ‘pore’ or water layer gap size of the cross-linked Q_1 phase of $3b/H_2O$ was calculated to be 0.75 nm using a modified Ferry equation model.⁴¹ The thickness-normalized water permeability of these Q_1 membranes was found to be similar to that reported for the active layer of commercial RO membranes. Having high solute rejections, as well as permeation performance comparable to that of a commercial RO membrane, mean that this nanoporous Q_1 -phase polymer shows promise as a new type of water purification membrane.

More detail on the nanopore size and water NF performance of this material was further elucidated by Hatakeyama *et al.*⁴² in 2011 via more extensive water filtration studies using a wider range of test solutes, a more appropriate pore model, static aqueous chlorine and protein fouling analysis, and comparisons against other commercial RO membranes. Membrane preparation for these more extensive experiments was the same as previously described, but a new set of small, non-charged organic molecules and more environmentally-relevant inorganic salts (including borates and arsenates) were used in the rejection studies. Two different Donnan-steric pore models were used to estimate the pore radius based on rejection values for this new set of solutes. The initial Ferry equation pore model adapted to this work was based on a lateral ensemble of uniform cylinders, whereas the new pore model was based on uniform, straight slit pores that more closely resembles the annulus channels of the Q_1 phase but without the curvature. Results from these more detailed studies provided support that this Q_1 -phase polymer membrane material has uniform-size nanopores and a water NF performance that is slightly below that of commercial RO membranes but substantially better than that of current NF membranes.⁴² This phosphonium-based Q_1 -phase polymer was also found to be tolerant to aq. ClO^- and fairly resistant to nonspecific protein adsorption, making it an intriguing candidate as a new type of chlorine- and protein-resistant water filtration membrane material.

One more research goal pursued by the Gin group in the gemini LLC monomer area was the development of cheaper, more easily synthesized Q_1 -phase-forming LLC monomers for polymer membrane applications. Gemini phosphonium monomer $3b$ worked exceptionally for its desired applications, however, there were several drawbacks to this initial monomer system, one being the rigorously

of the synthesis and the other was the cost of synthesis. The synthesis of $3b$ requires expensive phosphorus-based reagents and involves pyrophoric intermediates, as well as an Na metal/liquid NH_3 -reduction step, thus limiting it to small-scale laboratory preparations. The cost for starting materials alone (excluding solvents and chromatographic supplies) is also upwards of $\$79 g^{-1}$.⁴³ Consequently, $3b$ is not viable for scale-up or potential industrial production, and only serves as a proof-of-concept prototype. These problems need to be solved if a Q_1 -phase monomer system is to be scalable, easily modifiable and potentially commercially viable. Recent work by Hatakeyama *et al.*⁴³ resulted in the successful development of a new ammonium-based gemini LLC monomer platform 4 (Figure 4b) that is significantly cheaper, easier to synthesize and more scalable compared with phosphonium platform 3 . The synthesis of these gemini ammonium monomers is much simpler, involves non-air-sensitive intermediates and reagents, and relies on commercially available, inexpensive tetramethyl alkylamines to form the cationic gemini headgroup. A set of six homologs were generated, and two of them, $4a$ and $4b$ (Figure 4b), were found to form Q_1 phases with water above $55^\circ C$. Dead-end water NF studies on supported, melt-infused, Q_1 -phase membranes made from cross-linked $4a/H_2O$ showed that they also afford high salt and organic solute rejections. From the rejection data, it was calculated that the effective pore size of this material is 0.86 nm.⁴³ The cost to synthesize $4a$ in terms of starting materials and reagents is roughly $\$13 g^{-1}$,⁴³ which is a significant cost reduction compared with $3b$, and with only a slight penalty in membrane performance. This new gemini monomer system represents a promising new design for Q_1 -phase monomers.

One other piece of Q-phase polymer research that has come out of the Gin group is the synthesis of a new type of LLC monomer (5) that forms a Q_{II} phase with a Li salt-doped organic liquid electrolyte, propylene carbonate.⁴⁴ It has been shown that nanostructured LC-based ionic materials can be used to enhance and even direct ion conductivity for potential device applications (For a recent review of LC-based ion-conducting materials, see: ref. 45). Monomer 5 is a taper-shaped molecule containing three long acrylate tails at one end and a hydrophilic lithium sulfonate ionic headgroup at the other (Figure 4c). After photo-initiated radical cross-linking, the resulting flexible Q_{II} -phase network contains 3D-interconnected, liquid propylene carbonate/Li salt nanochannels for enhanced Li^+ conductivity, allowing it to function as a new type of separator membrane for Li batteries. Room-temperature ion conductivities measured for free-standing Q_{II} -phase films of cross-linked 5 containing 15 wt% (0.245 M $LiClO_4$ in propylene carbonate) were $(9 \pm 4) \times 10^{-3} S cm^{-1}$,

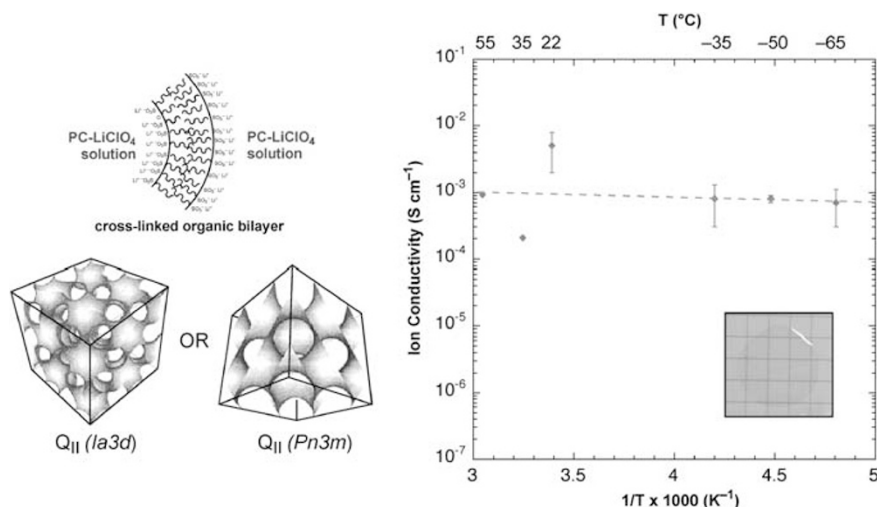


Figure 7 Structure of a cross-linked Q_{II} phase of **5** containing 15 wt% (0.245 M LiClO_4 in PC) and its ion conductivity performance as a function of temperature. Partially reproduced from ref. 44 with permission. Copyright (2009) American Chemical Society. A full color version of this figure is available at *Polymer Journal* online.

as determined by AC impedance studies.⁴⁴ Control experiments showed that the LiClO_4 dopant was necessary to provide adequate room-temperature Li^+ conductivity. An interesting observation is that this material displays significant liquid-like mobility in the nanochannels even at low temperatures. It only loses an order of magnitude of ion conductivity when cooled from room temperature to -65°C (Figure 7),⁴⁴ leading to the possibility of good Li battery performance even at very low temperatures. This relatively ‘flat’ ion conductivity with decreasing temperature is very rare in conventional polymer and gelled-polymer electrolytes but is highly desired for low-temperature Li battery operation. Optimization of these new polymer/liquid electrolyte composites and demonstration of their effectiveness in working Li-metal batteries are in progress. Recently, cross-linked bicontinuous cubic Li^+ -conducting materials based on thermotropic (that is, solvent-free) LC monomers have been developed by researchers in Japan as a complementary approach to the use of polymerizable Q-phase LLC assemblies.⁴⁶

SUMMARY

Robust, nanoporous polymer materials with 3D-interconnected, molecular-size pores can be formed via the direct cross-linking of Q phases formed by reactive LLCs or via the templated polymerization of conventional monomers included in Q phases. These materials have exceptional potential for use in a number of transport applications. Our research group has primarily focused on the design of gemini LLC monomers to form directly cross-linked Q_I -phases with sub-1-nm pores as a new material-development direction. We have shown that these new Q_I -phase networks can be used for a wide array of membrane-based molecular-sieving applications, including water NF desalination, and selective vapor transport. We have also made initial inroads into the design of LLC monomers that can form Q_{II} phases with non-aqueous polar organic solvents instead of water as the LLC solvent. Li salt-doped versions of these latter Q_{II} -phase polymer/liquid nanocomposites show enhanced ion conductivity properties, making them potentially useful for better-performing Li batteries. Current research directions in our group include developing methods for controlling the effective size of the nanopores in these Q-phase polymer materials and developing processing techniques for fabricating high-quality, thin ($\leq 5\text{-}\mu\text{m}$ thick) films of the Q-phase monomer mixtures to make superior, high-throughput membranes.

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