CHEMISTRY OF
MATERIALS
Communication

Chem. Mater. **2010,** *22,* 4525–4527 4525
DOI:10.1021/cm1013027

Nanoporous, Bicontinuous Cubic Lyotropic Liquid Crystal Networks via Polymerizable Gemini Ammonium Surfactants

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Received May 8, 2010
Revised Manuscript Received July 14, 2010

Cross-linked lyotropic liquid crystal (LLC) assemblies are a class of ordered, nanoporous polymer materials that have been shown to be useful for a number of important applications.[1] These polymer materials are formed by the in situ cross-linking of reactive amphiphiles (i.e., surfactants) that self-organize in water (or other polar solvents) into microphase-separated, liquid-crystalline assemblies containing periodic, nanometer-scale, aqueous regions/pores filled with mobile water molecules. The water regions can range in shape from closed spheres to 1D cylinders, 2D lamellae, and 3D inconnected networks.[1] Unlike similar nanoporous polymers made via direct cross-linking of[2] or replica-synthesis using[3] phase-separated block copolymers, LLC networks have pores that are significantly smaller (i.e., $\leq$1 to 10 nm) and are lined with the headgroups of the amphiphiles.[1] This latter feature allows for convenient pore functionalization and tuning.[1b,c] Because of these features, LLC networks have been used in nanocomposite synthesis,[1a,c] heterogeneous catalysis,[1a,c] molecular-size-based membrane separations,[4] and enhanced ion transport.[5]

One of the most important and sought-after types of cross-linked LLC assemblies are those with a bicontinuous cubic (Q) structure.[1c,4,5] Q phases (like other LLC phases) are classified as type I (i.e., normal or water-rich) or type II (i.e., inverted or water-poor) depending on whether the hydrophilic−hydrophobic interface curves away from or toward the water regions, respectively.[1] In Q-phase systems, the open-framework and 3D interconnected pores provide better accessibility for catalysis and transport compared to lower-dimensionality LLC phases such as the 1D cylindrical hexagonal (H) and 2D lamellar (L) phases.[1c,4,5] Also, there is no need for pore alignment in these systems for transport applications because of their cubic symmetry.[1c,4,5] Recent work with $\mathrm{Q_I}$-phase LLC-based polymer membranes[4] and cubic-phase LLC[5] and thermotropic LC[6] ion-conducting materials have verified these statements. Another interesting feature of certain cross-linked $\mathrm{Q_I}$ phases is that uniform sub-1 nm pore sizes have been achieved, making them valuable for molecular sieving applications.[7,8]

Unfortunately, only a handful of LLC monomer systems are known to form polymerizable Q phases. O'Brien and co-workers pioneered two $\mathrm{Q_{II}}$-phase LLC monomer platforms based on singly- and doubly-reactive derivatives of natural phosholipids[9] and glycerol amphiphiles.[10−12] Unfortunately, the phospholipid-based systems involve fairly demanding syntheses that limit the scale of production.[9] In the case of the glycerol-based monomers, the syntheses are less demanding and use more available starting materials.[10−12] However, in both cases, mixtures of monopolymerizable and cross-linkable surfactants are typically required to obtain the desired $\mathrm{Q_{II}}$ phases and cross-linked networks.[9−11] Our research group pioneered $\mathrm{Q_I}$-phase LLC monomers based on a cross-linkable gemini phosphonium surfactant (**1**) (Figure 1).[13] This first-generation gemini LLC $\mathrm{Q_I}$ monomer can be photopolymerized into polymer membranes containing a $\mathrm{Q_I}$ network. However, its synthesis requires an expensive phosphine-sulfide starting material, pyrophoric phosphine intermediates, and a Na/$\mathrm{NH_3}$(l) reduction step to make the gemini head unit.[13] In addition, the $\mathrm{Q_I}$ phase of **1** requires processing at elevated temperatures (70 °C) to generate films for applications such as molecular-size-based water nanofiltration (NF) and desalination.[7] These features put severe limitations on the amount, cost,

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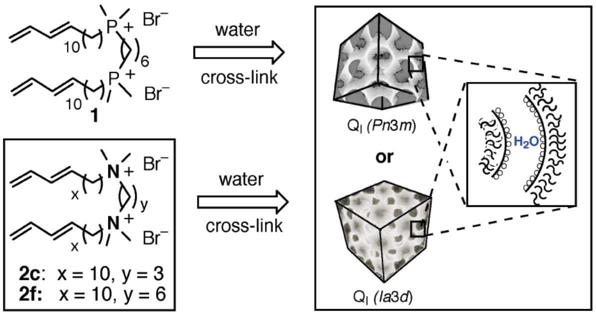

Figure 1. Structures of first- and second-generation Q_I-phase LLC monomers based on gemini phosphonium and ammonium platforms, respectively.

and scalability of this first-generation Q_I-phase material for applications.

Herein, we present a more facile route to nanoporous Q_I-phase networks using a new ammonium-based cross-linkable gemini LLC platform (**2**) that utilizes inexpensive starting materials and less demanding synthetic procedures (Figure 1). Two homologues of **2** (i.e., **2c** and **2f**) formed Q_I phases with water at ≥ 50 °C under atmospheric pressure. Processing these monomers into supported Q_I-phase polymer membranes requires milder processing conditions than the first-generation monomer **1**. Preliminary water NF and desalination studies on supported cross-linked Q_I-phase polymer membranes of **2c** show that they are able to purify water similar to Q_I membranes based on **1**.

Designing a new Q_I-phase monomer based on a gemini ammonium platform was chosen for several reasons: First, this platform is similar to the gemini phosphonium platform (**1**) that has produced several Q phases.[13] Also, several nonpolymerizable gemini ammonium surfactants in the literature exhibit a wide variety of LLC phases, including Q phases.[14−16] However, only a very small number of polymerizable gemini ammonium amphiphiles have been reported,[17,18] and polymerizable versions that afford Q (and other LLC) phases are unprecedented.

As shown in Figure 2, the synthesis of **2** utilizes a single high-yield reaction between commercially available and relatively inexpensive alkyl-bridged tetramethyldiamines with 2 equiv. of the polymerizable ω-bromoalkyl-1,3-diene tail units. In contrast, the synthesis of phosphonium monomer **1** involves multiple steps requiring high and low temperatures and expensive and/or pyrophoric phosphine reagents to make the intermediate gemini head unit, followed by the same diene tail attachment step (see the Supporting Information).[13] This new procedure represents a significant reduction in cost, effort, and synthetic complexity for Q-phase LLC monomer production compared to prior approaches.[9−13]

Six homologues of **2** were initially synthesized to investigate their LLC phase behavior with water (Figure 2).

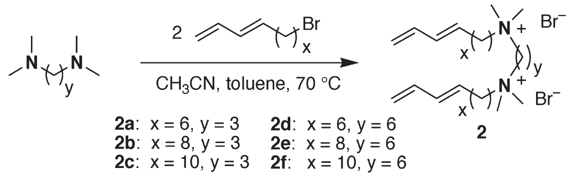

Figure 2. General synthesis scheme for homologues of monomer **2**.

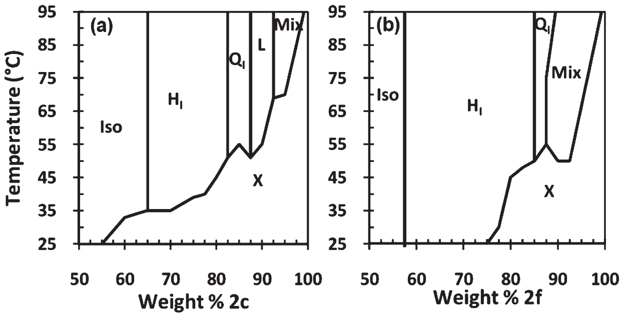

Figure 3. LLC phase diagrams of (a) **2c** and (b) **2f** with water. Iso = micellar or nonordered, H_I = type I hexagonal, Q_I = type I bicontinuous cubic, L = lamellar, Mix = LLC + crystalline, X = crystalline.

Monomers **2a**−**f** were constructed using three different length 1,3-diene-terminated tails (x = 6, 8, 10) and two different head unit spacer lengths (y = 3, 6) (see the Supporting Information for details). The phase diagrams of **2a**−**f** as a function of composition with water were mapped out over a range of temperatures using variable-temperature polarized light microscopy (PLM). The structure of each LLC phase was identified by its PLM optical texture and powder X-ray diffraction (XRD) pattern. Specifically, the desired Q phases are characterized by having completely black PLM optical textures and powder XRD pattern that typically have two prominent d-spacing peaks with the ratio $1/\sqrt{6}:1/\sqrt{8}$.[13]

Q phases were not found for four of the gemini ammonium homologues. The two compounds with the shortest tails (**2a** and **2d**) did not exhibit any LLC behavior. The two compounds with the medium length tails (**2b** and **2e**) were found to form H phases, but no Q phases were observed (see the Supporting Information). However, the two homologues of **2** with the longer tails (**2c** and **2f**) were found to form Q phases. The phase diagrams for **2c** and **2f** (Figure 3) show that a Q_I phase forms with 12.5−17.5 wt % and 12.5−15 wt % water, respectively, at temperatures of ≥ 50 °C. Figure 4 shows that mixtures of **2c** and **2f** with 15 wt % water have the characteristic Q-phase XRD d-spacing ratio of $1/\sqrt{6}:1/\sqrt{8}$, plus black PLM textures.[13] Because this Q phase appears on the water-rich side of a L phase on the phase diagram (and before a H phase), it was identified as a type I phase.[1,13]

The stabilization of the Q_I-phases of **2c** and **2f** into robust polymer networks was examined by photoinitiated radical cross-linking. In order to do this, films of the Q_I-phase mixtures containing a photoinitiator (PI) (84.2/14.8/1.0 (w/w/w) (**2c** or **2f**)/H_2O/PI) were heated to 60 °C to form the Q_I phase, and subsequently irradiated with a 365 nm UV light (8.5 mW cm^{-2}) for 1 h. The resulting materials are transparent, free-standing polymer films.

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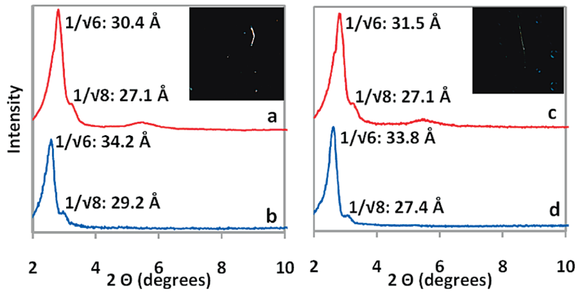

Figure 4. Powder XRD spectra of Q_I-phase mixtures of: (a) **2c** polymerized at 60 °C, (b) unpolymerized **2c** at 60 °C, (c) **2f** polymerized at 60 °C, and (d) unpolymerized **2f** at 60 °C. In all cases, the composition was 84.2/14.8/1.0 (w/w/w) monomer/H_2O/PI. Insets: PLM images of each cross-linked Q_I phase.

Table 1. Comparison of Dead-End Water NF Performance of Cross-Linked Q_I-Phase Membranes Prepared from 1 and 2c

test solute	hydrated diameter (nm)[a]	rejection (%)[b] Q_I membrane of **1**[a]	rejection (%)[b] Q_I membrane of **2c**
NaCl	0.72 ($Na^+_{(aq)}$)	95 ± 1	94 ± 2
KCl	0.66 ($K^+_{(aq)}$)	91 ± 3	92 ± 2
$MgCl_2$	0.86 ($Mg^{2+}_{(aq)}$)	> 99.3	95 ± 2
$CaCl_2$	0.82 ($Ca^{2+}_{(aq)}$)	> 99.3	96.9 ± 0.2
sucrose	0.94	> 99	97.9 ± 0.2
glucose	0.73	96 ± 2	94 ± 1
glycerol	0.36	53 ± 1	45 ± 11
ethylene glycol	0.32	38 ± 4	38 ± 3

[a] Previously published data from ref [7] and references therein. [b] All filtrations were conducted with 2000 ppm aqueous test solutions in a stirred, dead-end filtration cell with a pressure of 400 psi.

FT-IR analysis of the polymerized samples showed a diene conversion of > 95% (see the Supporting Information).[13] Retention of the Q_I-phase after cross-linking was verified by retention of the original PLM texture and XRD pattern (Figure 4). After cross-linking, a weak, broad peak sometimes appears that corresponds to the $1/\sqrt{22}$ *d*-spacing of a Q phase.[13] This peak does not correspond to a H or L phase XRD peak.

Previous studies showed that supported membranes of the cross-linked Q_I phase of phosphonium monomer **1** have uniform 0.75 nm pores and can be used as an effective water NF membrane.[7] These first-generation Q_I-phase membranes can almost completely remove small organic solutes and inorganic salts from water via a molecular-size-exclusion mechanism (Table 1).[7] In order to demonstrate that the Q_I networks formed by the new gemini ammonium monomers afford similar size nanopores and are useful for similar separations, initial water NF tests were conducted on supported Q_I membranes of cross-linked **2c**. To do this, supported cross-linked Q_I membranes of **2c** were made by melt-pressing and photopolymerizing a Q_I-phase LLC mixture containing 84.2/14.8/1.0 (w/w/w) **2c**/H_2O/PI onto the same membrane support as in prior studies.[7] However, this processing can be accomplished at lower temperatures (55−60 °C) because of the slightly different properties of the respective Q_I phase.[19] This allows for easier processing because water loss, which can disrupt the Q_I phase, is less of a factor.

Table 1 shows that the water NF rejection performance of supported Q_I-phase membranes of **2c** compared to that of **1** under the same test conditions (see the Supporting Information).[7] The Q_I-phase membranes of **2c** reject organic solutes and inorganic salts almost as well as the first-generation Q_I membranes based on **1**. The Q_I membranes of **2c** have a slightly larger nanopore width of 0.86 nm, according to modeling of the neutral solute rejection behavior using the modified Ferry Equation (see the Supporting Information).[7] These second-generation Q_I membranes also afford a similar level of throughput, with a thickness-normalized pure water permeance at 400 psi (27.6 bar) of 0.054 ± 0.003 L m^{-2} h^{-1} bar^{-1} μm, which is slightly lower than that of Q_I membranes of **1** (0.086 ± 0.001 L m^{-2} h^{-1} bar^{-1} μm) under the same conditions.[20] However, the **2c** membranes are much easier and less expensive to make in terms of the monomer.

In summary, a new Q_I-phase gemini LLC monomer system has been developed that is more easily and economically synthesized than prior examples. Two homologues of this gemini ammonium-based monomer system exhibit Q_I phases that can be cross-linked with retention of the structure. Supported membranes of these materials can be used for aqueous molecular size separations and exhibit uniform, sub-1 nm size pores. We are currently exploring systematic structural modification of the monomer **2** platform to reduce and control the effective Q_I nanopore size for targeted molecular-size separations. We are also exploring Q_I phase formation of **2** homologues with solvents other than pure water (e.g., nonaqueous solvents and ionic solutions) to see if pore size can be manipulated by solvent environment. We are also examining methods to prepare thinner films of the cross-linked Q_I phases on membrane supports to increase their flux. The more facile and scalable synthesis afforded by this new monomer platform makes these and other optimization studies viable. Finally, we are determining if these new Q_I-phase monomers can be copolymerized with commercial elastomers to make nanoporous, selective vapor barrier materials[8] in a more facile and economical fashion.

Acknowledgment. Financial support from the Colorado Center for Biofuels and Biorefining (08-5), the NSF (CBET-0853554), and the Army Research Office (W911NF-09-C-0108) is gratefully acknowledged. E.S.H. thanks the U.S. Department of Education for a GAANN Fellowship, and the National Water Research Institute and American Membrane Technology Association for a NWRI-AMTA Fellowship.

Supporting Information Available: Details on the synthesis and characterization of **2a**−**f**; phase diagrams for **2a**, **2b**, **2d**, and **2e** with water; details on the formation and polymerization of the LLC phases of **2c** and **2f**; procedures for supported Q_I membrane fabrication of **2c** and water NF testing; reagent cost comparisons for synthesis of **2c** and **1** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) The fact that the ammonium monomers **2c** and **2f** form Q_I phases at lower temperatures compared to **1** is entirely serendipitous but beneficial for processing.

(20) The lower permeance may be due to the lower water content of the new membranes (15% vs 20%), different possible surface effects, and/or lower water diffusivity due to different pore surface chemistry (N^+ vs P^+).