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14. ABSTRACT

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RPPR Final Report
as of 24-May-2023

Agency Code: 21XD

Proposal Number: 75326SM **Agreement Number: W911NF-19-2-0182**
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Report Date: 31-Dec-2022 Date Received: 28-Dec-2022
Final Report for Period Beginning 01-Jul-2019 and Ending 30-Sep-2022
Title: Chemical Modification of Nanoporous Lyotropic Liquid Crystal Polymer Membranes to Improve Stretchability
Begin Performance Period: 01-Jul-2019 **End Performance Period:** 30-Sep-2022
Report Term: 0-Other

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STEM Degrees: **STEM Participants:**

Major Goals: The overall goal of this collaborative research project with the Combat Capabilities Development Command Soldier Center (CCDC SC) was to perform fundamental research to demonstrate proof-of-concept that the nanoporous, cross-linked Type I bicontinuous cubic (QI) membrane system based on lyotropic liquid crystal (LLC) monomer 1 can be chemically modified to increase the degree of stretchability of the bulk material compared to the original formulation. The ultimate stretchability target was 20% reversible isotropic elongation in the (x-y) plane of prepared bulk films with retention of the QI nanostructure.

This project began in 2019 as an initial, short-term, fundamental research grant (i.e., 12 months + a 3-month option) that was awarded to the Gin + Noble group at the University of Colorado Boulder (CU Boulder) to demonstrate proof-of-concept that the QI system of 1 can be chemically modified to increase the degree of stretchability in the bulk cross-linked polymer material. Work in Year 1 of this project (2019–2020) was entirely experimental in nature and performed by researchers in the Gin + Noble group. The CU Boulder team's specific goals in Year 1 were the following: (1) measure mechanical properties of unmodified bulk QI-phase LLC films made from monomer 1 (i.e., glass-transition temperature (Tg), % strain-at-failure, storage modulus, loss modulus); (2) Increase strain-at-failure (or strain at which permanent deformation occurs) while not significantly increasing storage modulus; (3) gain fundamental understanding of how film composition and polymer network properties affect mechanical properties; and (4) assess whether the modifications to the films affect QI phase retention.

Beginning on July 1, 2020, Years 2 and 3 of this project at CU Boulder became an expanded, multi-year fundamental research effort. The project was expanded to include a computational research component led by additional CU Boulder Co-PI, Prof. Michael Shirts. The goal of this expanded effort was to employ a combination of atomic-level simulation, macroscopic modeling, and experimental synthesis and characterization to obtain a better fundamental understanding of (a) the design guidelines governing the QI-phase formation behavior of gemini LLC monomers based on 1, and (b) the molecular transport and mechanical properties of the cross-linked QI polymers formed by these monomers. Specifically, starting in Year 2, the Shirts group used computational atomistic molecular modeling to do three things: (1) construct models of QI phase structures formed by original LLC monomer 1; (2) examine how systematic changes to the gemini LLC monomer structure (e.g., headgroup bridge unit, the counteranion associated with the cationic headgroups, the length of the polymerizable tails, and the nature

of the tail polymerizable group will affect QI phase formation, QI pore size and environment, and chemical warfare agent (CWA) simulant and water vapor transport; and (3) examine how the addition of additives, co-monomers, and reactive hydrophobic elastomers affect QI phase formation and polymerized film stretchability. The results of these atomistic molecular simulation studies would then be used to help inform material design and guide additional experimental work.

In Years 2 and 3, experimental work in the Gin + Noble group continued to focus on the original improved QI film stretchability goals, and also supported the new modeling effort in the Shirts group by preparing and charactering new monomer variants derived from the simulation results to test their accuracy. New bulk QI polymer materials with improved stretchability generated from this combined theoretical and experimental effort were fabricated into membranes and tested at CU Boulder for moisture vapor transport rate (MVTR) and CWA simulant vapor rejection using dead-end vapor permeation cells. Membrane samples of new formulations that showed promising results in these initial screening tests were then sent to the CCDC SC for more detailed mechanical property and vapor permeation testing that included stretchability and flexibility measurements, MVTR evaluation, and CWA simulant diffusion studies via attenuated total reflectance Fourier-transform infrared (ATR-FTIR) flow spectroscopy. The experimental results from the Gin + Noble group and the CCDC SC would provide feedback to the Shirts group to improve the simulation studies and inform the next round of molecular and compositional design via an iterative cycle. The data collected from this combined effort would then be used to inform a multi-variate analysis to identify the most important chemical and structural variables of the membranes to optimize the required balance between protective performance (water vapor transport with simultaneous CWA rejection) and physical performance (e.g., durability, stretchability).

Accomplishments: (See attached / uploaded PDF document for full details and findings to-date.)

Training Opportunities: Six graduate students and three undergraduate students were fully or partially supported by this grant and trained to do monomer synthesis, polymer synthesis, and polymer film mechanical property testing during period of performance of this grant. (It should be noted that some of the undergraduate students worked on this project as part of an independent study course that they took during the teaching semesters.) One full-time postdoctoral researcher was supported by this grant for two years and trained to do atomistic simulation work on LLC phases. One other postdoctoral researcher was partially supported by this grant to assist with training of students to do QI-phase polymer membrane fabrication.

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Results Dissemination: Five peer-reviewed research papers (see below) were published on results generated with funding from this project. The first of these papers (listed chronologically by publication date) describes the synthesis and LLC phase characterization of several homologs of the original gemini LLC monomer 1, and lists some molecular structure – phase formation relationships found for this monomer platform. The second and fourth papers listed are on a side-project with collaborators at the Univ. of Pennsylvania related to the overall project goals: the design and synthesis of a new, simpler QI-phase LLC monomer system for nanoporous membrane applications. The third paper listed describes experimental results showing that the mechanical compliance and stretchability of cross-linked bulk QI films made with original cross-linkable monomer 1 can be improved by blending and copolymerization with controlled amounts of a non-cross-linkable monomer analog. The last paper listed describes computational simulation results for the development of an atomistic model of the QI phase consistent with experimental detail for gemini LLC monomer 1.

Li, P.; Reinhardt, M. I.; Dyer, S. S.; Moore, K. E.; Imran, O. Q.; Gin, D. L.* “Effects of Structural Modification of (Alkyldiene-Imidazolium Bromide)-Based Gemini Monomers on the Formation of the Lyotropic Bicontinuous Cubic Phase,” Soft Matter 2021, 17 (41), 9259–9263.

Imran, O. Q.; Li, P.; Kim, N. K.; Gin, D. L.; Osuji, C. O.* “Stable cross-linked lyotropic gyroid mesophases from single-head/single-tail cross-linkable monomers,” Chem. Commun. 2021, 57 (83), 10931–10934.

Bodkin, L. N.; Li, P.; Dyer, S. S.; Krajnak, Z. A.; Malecha, J. J.; Noble, R. D.; Gin, D. L.* “Improved Mechanical Compliance in Bicontinuous Cubic Lyotropic Membranes Based on a Cross-Linking Gemini Monomer via Copolymerization with a Non-Cross-Linkable Analog,” ACS Appl. Polym. Mater. 2022, 4 (11), 8026–8031.

Li, P.; Johnson, C.; Dyer, S. S.; Osuji, C. O.;* Gin, D. L.* “A pH- and Light-responsive Nanoporous Lyotropic Gyroid Polymer Network,” Adv. Mater. Interfaces 2022, 2201761. (https://doi.org/10.1002/admi.202201761)

Sahu, S.; Schwindt, N. S.; Coscia, B. J.; Shirts, M. R.* “Obtaining and Characterizing Stable Bicontinuous Cubic Morphologies and Their Nanochannels in Lyotropic Liquid Crystal Membranes,” J. Phys. Chem. B 2022, 26 (48), 10098–10110.

Honors and Awards: Nothing to Report

Protocol Activity Status:

Technology Transfer: Two patent applications were filed jointly with collaborators at the University of Pennsylvania on the new QI-phase LLC monomer results described in two of the papers listed in the Dissemination section:

Gin, D.; Li, P.; Osuji, C.; Imran, O. “Stable Cross-linked Lyotropic Gyroid Mesophases from Single-head/Single-tail Cross-linkable Monomers,” Provisional U.S. Patent Application 63/246,143, filed September 20, 2021.

Gin, D.; Li, P.; Osuji, C.; Imran, O. “Lyotropic Gyroid Mesophase Compositions, Polymer Compositions Comprising the Same, Methods of Preparation Thereof, and Methods of Using the Same,” U.S. Patent Application 17/949,072, filed September 20, 2022.

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Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Co PD/PI
Participant: Michael Shirts

Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Graduate Student (research assistant)
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Person Months Worked: 2.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Graduate Student (research assistant)
Participant: Gregory Dwulet
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Project Contribution:
National Academy Member: N

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Institution: University of Colorado Boulder
Date Received: 21-Sep-2020 Completion Date: 4/1/20 8:40PM
Title: i Nanoporous, Ionic, Lyotropic Liquid Crystal Polymer Membranes: Permanent Pore Modification, Characterization of Ion Exchange Properties, and Fabrication of Ultrathin Films
Authors: Michael James McGrath
Acknowledged Federal Support: **Y**

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as of 24-May-2023

Partners

,

I certify that the information in the report is complete and accurate:
Signature: Douglas Gin
Signature Date: 12/28/22 6:37PM

Final Report for ARO
(1 July 2019 – 30 September 2022)

Cooperative Research Agreement Award: W911NF-19-2-0182

"Chemical Modifications of Nanoporous Liquid Crystal Polymer Membranes to Improve Stretchability"

PI: Prof. Douglas L. Gin; Co-PI: Prof. Richard D. Noble
Dept of Chemistry, University of Colorado Boulder

Co-PI: Prof. Michael R. Shirts
Dept of Chemical & Biological Engineering, University of Colorado Boulder

Period of Performance: 1 July 2019 – 30 September 2022
Total Award Amount: $823,400; Funded Amount: $823,400

Overview:

This final report summarizes the major CU Boulder research activities and findings for this subcontract grant with the Combat Capabilities Development Command Soldier Center (CCDC SC) for the entire period of performance of 1 July 2019 to 30 September 2022. Specifically, this final report summarizes information that was included in all prior informal progress reports to the CCDC SC and interim progress reports (IPRs) to the Army Research Office (ARO), plus new findings since the most recent reports to the CCDC SC and ARO.

Project Goals:

The overall goal of this collaborative research project with the CCDC SC was to perform fundamental research to demonstrate proof-of-concept that the nanoporous, cross-linked Type I bicontinuous cubic (Q_I) membrane system based on lyotropic liquid crystal (LLC) monomer **1** (see Figure 1) can be chemically modified to increase the degree of stretchability of the bulk material compared to the original formulation. The ultimate stretchability target was 20% reversible isotropic elongation in the (x-y) plane of prepared bulk films with retention of the Q_I nanostructure.

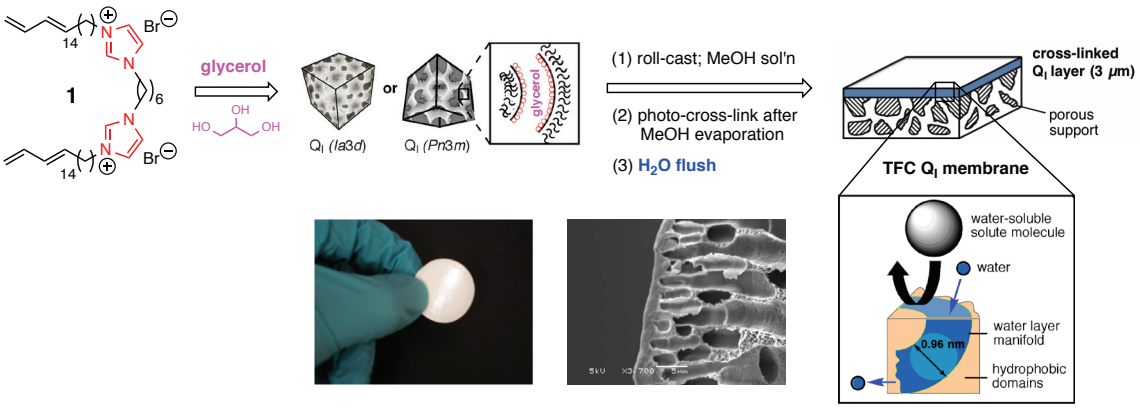


Figure 1. Structure, fabrication, and molecular-size-selective transport of nanoporous, cross-linked Q_I-phase polymer membranes made via self-assembly of LLC monomer **1**.

This project began in 2019 as an initial, short-term, fundamental research grant (i.e., 12 months + a 3-month option) that was awarded to the Gin + Noble group at the University of Colorado Boulder (CU Boulder) to *demonstrate proof-of-concept* that the Q_I system of **1** can be chemically modified to increase the degree of stretchability in the bulk cross-linked polymer material. Work in Year 1 of this project (2019–2020) was entirely experimental in nature and performed by researchers in the Gin + Noble group. The CU Boulder team's specific goals in Year 1 were the following: (1) measure mechanical properties of unmodified *bulk* Q_I-phase LLC films made from monomer **1** (i.e., glass-transition temperature (T_g), % strain-at-failure, storage modulus, loss modulus); (2) Increase strain-at-failure (or strain at which permanent deformation occurs) while not significantly increasing storage modulus; (3) gain fundamental understanding of how film composition and polymer network properties affect mechanical properties; and (4) assess whether the modifications to the films affect Q_I phase retention.

Beginning on July 1, 2020, Years 2 and 3 of this project at CU Boulder became an expanded, multi-year fundamental research effort. The project was expanded to include a computational research component led by additional CU Boulder Co-PI, Prof. Michael Shirts. The goal of this expanded effort was to employ a combination of atomic-level simulation, macroscopic modeling, and experimental synthesis and characterization to obtain a better fundamental understanding of (a) the design guidelines governing the Q_I-phase formation behavior of gemini LLC monomers based on **1**, and (b) the molecular transport and mechanical properties of the cross-linked Q_I polymers formed by these monomers. Specifically, starting in Year 2, the Shirts group used computational atomistic molecular modeling to do three things: (1) construct models of Q_I phase structures formed by original LLC monomer **1**; (2) examine how systematic changes to the gemini LLC monomer structure (e.g., headgroup bridge unit, the counteranion associated with the cationic headgroups, the length of the polymerizable tails, and the nature of the tail polymerizable group will affect Q_I phase formation, Q_I pore size and environment, and chemical warfare agent (CWA) simulant and water vapor transport; and (3) examine how the addition of additives, co-monomers, and reactive hydrophobic elastomers affect Q_I phase formation and polymerized film stretchability. The results of these atomistic

molecular simulation studies would then be used to help inform material design and guide additional experimental work.

In Years 2 and 3, experimental work in the Gin + Noble group continued to focus on the original improved Q_I film stretchability goals, and also supported the new modeling effort in the Shirts group by preparing and charactering new monomer variants derived from the simulation results to test their accuracy. New bulk Q_I polymer materials with improved stretchability generated from this combined theoretical and experimental effort were fabricated into membranes and tested at CU Boulder for moisture vapor transport rate (MVTR) and CWA simulant vapor rejection using dead-end vapor permeation cells. Membrane samples of new formulations that showed promising results in these initial screening tests were then sent to the CCDC SC for more detailed mechanical property and vapor permeation testing that included stretchability and flexibility measurements, MVTR evaluation, and CWA simulant diffusion studies via attenuated total reflectance Fourier-transform infrared (ATR-FTIR) flow spectroscopy. The experimental results from the Gin + Noble group and the CCDC SC would provide feedback to the Shirts group to improve the simulation studies and inform the next round of molecular and compositional design via an iterative cycle. The data collected from this combined effort would then be used to inform a multi-variate analysis to identify the most important chemical and structural variables of the membranes to optimize the required balance between protective performance (water vapor transport with simultaneous CWA rejection) and physical performance (e.g., durability, stretchability).

The following sections summarize the major activities completed and the findings/results obtained for the two stages of this project at CU Boulder: the initial Year 1 exploratory effort (2019–2020), and the expanded effort in Years 2–3 (2020–2022) involving computational and experimental work.

Summary of Major Research Activities and Findings

Year 1 (July 1, 2019 to June 30, 2020); [experimental work by Gin + Noble group only]:

(a) Measurement of baseline mechanical properties of unmodified bulk Q_I polymer films of monomer 1

Tasks completed and major findings:

The mechanical properties of the unmodified bulk, cross-linked Q_I polymer films of monomer **1** were successfully measured using dynamic mechanical analysis (DMA) to establish a set of baseline properties that were used to establish which methods could improve them in terms of compliance and stretchability. These properties are

summarized in Table 1 below. Figures 2 and 3 show example DMA profiles and stress-strain curves, respectively, of unmodified bulk Q_I polymer films of monomer **1**.

Table 1. Mechanical properties of unmodified, bulk, cross-linked Q_I polymer films of monomer **1**.

Storage Modulus (*E*', MPa)[a]	Loss Modulus (*E*'', MPa)[a]	% Strain-at-Failure[a]	T_g (°C)	
as-fabricated (glycerol)			as-fabricated (glycerol)	glycerol removed, dried
43 ± 6	1.5 ± 0.4	10 ± 2 (range: 7.9 –13.2)	–33[b]	71[c]

The reported average and one sample standard deviation include data from both different pieces of same film and pieces of different films. a: room temperature (22–28 °C), b: broad with shoulder peak at ca. 8 °C, c: sharper than with glycerol in pores (tan δ peak width at half-maximum ≈ 22 °C)

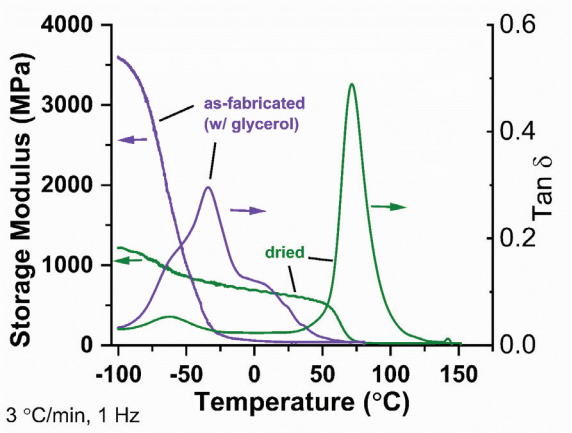


Figure 2. DMA profiles showing the T_g values for a baseline (unmodified) Q_I polymer film with glycerol in the nanopores (purple; T_g = –33 °C) and one with the glycerol removed and the film vacuum-dried (i.e. 'dried' pores, green; T_g = 71 °C).

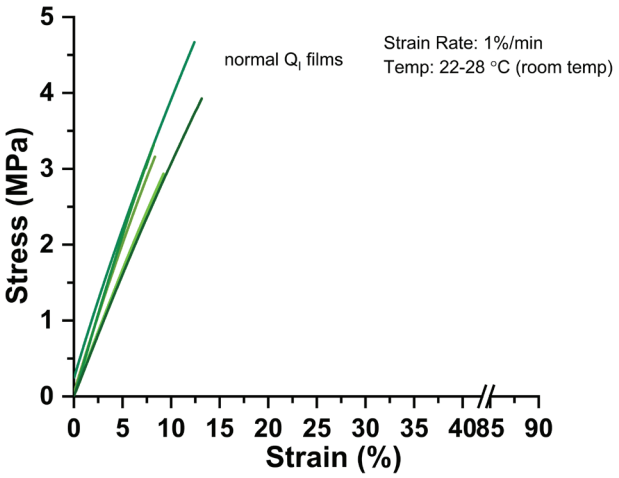


Figure 3. Stress-strain curves of unmodified bulk Q_I polymer films of **1** taken at room temperature with an applied strain rate of 1%/min.

Note: Because of a breakdown in the cooling unit on the initial DMA instrument used for this work in early 2020, it was not possible to take sub-ambient T_g measurements in Years 2–3 of this project.

(b) Testing of initial methods for improving the stretchability of bulk, cross-linked Q_I polymer films of monomer 1

Tasks completed and major findings:

(i) Addition of polybutadiene elastomers

Low-molecular-weight (LMW) polybutadiene (PBD) elastomer has been previously added into brittle photo-cured cross-linked acrylates to improve their toughness.[1] To test if this approach can be used to improve the mechanical properties and stretchability of the bulk Q_I polymer films of **1**, 8–40 wt% amounts of LMW PBD (i.e., MW: 1600 g/mol) that contained high (ca. 80%) vinyl group content were initially blended into the original monomer **1**/glycerol mixture (Figure 4).

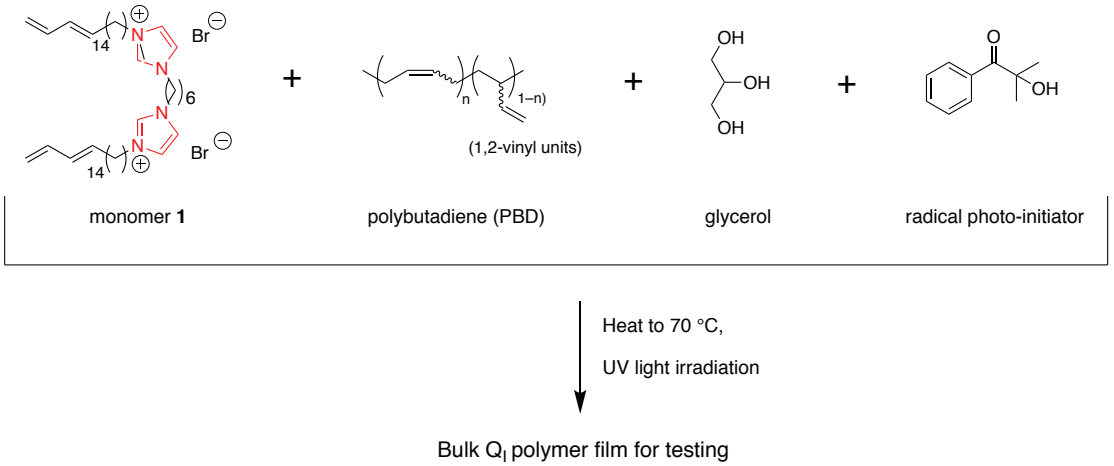


Figure 4. Blending of PBD elastomers into the original (monomer **1** / glycerol / radical photo-initiator) mixture to make blended films.

The LMW PBD was found to be completely miscible with the Q_I matrix up to ca. 30 wt% and did not affect the powder X-ray diffraction (PXRD) primary *d*-spacing of the Q_I nanostructure, suggesting that the PBD fills in the void spaces in between the Q_I cross-linked polymer. DMA experiments indicated that the storage modulus, loss modulus, and stress-strain curves of Q_I samples with this PBD additive did not show a significant difference from the baseline Q_I samples. *This set of experiments indicated that blending of LMW PBD elastomer additives alone is not a promising approach for mechanical property improvement in this system.*

(ii) Addition of disulfide compounds with and without PBD elastomers

Disulfide compounds such as tetramethyldithiuram disulfide (TMTD), 4,4 dithiomorpholine (DTM), and tetrabutylthiuram disulfide (TBTD) are known to radically cross-link (i.e., vulcanize) residual double bonds on commercial hydrocarbon elastomers (Figure 5).[2] Q_I samples containing 1600 MW high-vinyl-content PBD and some of these disulfide compounds were prepared in an attempt to cross-link the PBD with the LLC polymer matrix (Figure 5), so that the resulting material would be a copolymer with overall more rubber-like mechanical properties than the baseline Q_I samples. An extra step to the free-standing Q_I film fabrication was added after the 1-h UV irradiation with 365 nm light: The film was then heated at 160 °C on an open benchtop for 2 h because this disulfide cross-linking reaction occurs most efficiently under these conditions.[2]

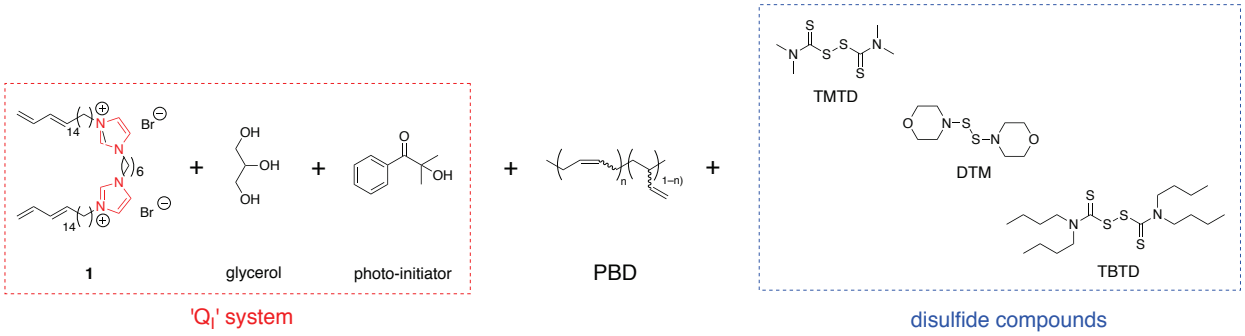


Figure 5. The components explored in blending different disulfide compounds with the Q_I-phase (monomer **1** + glycerol + radical photo-initiator) system and added PBD.

DMA showed that the resulting cross-linked (Q_I/PBD/disulfide compound) films had a storage modulus that was significantly lower than that of the original Q_I samples, with ca. 3 times the elongation at break. As seen in Figure 6 below, Q_I films containing PBD, TMTD, and/or DTM that were UV-irradiated for 1 h and then heated at 160 °C for 2 h showed a substantially lower storage modulus and an increase in % strain-at-failure compared to unmodified cross-linked Q_I films.

In addition, it was found that added PBD is not necessary to observe this change in the stress-strain behavior*: Use of just the disulfide additives and the extra post-photopolymerization 160 °C heating step can afford a similar change in the bulk stress-strain behavior (*see the stress-strain curve for the 100 monomer **1**: 2.5 TMTD: 2.5 DTM (mol:mol:mol) sample in Figure 6).

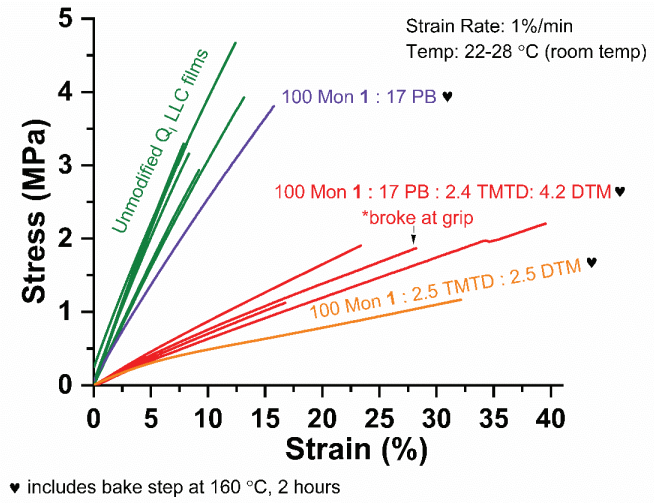


Figure 6. Stress-strain tensile test for LLC films containing various moles of PBD (1600 MW) (labelled as "PB" in figure), TMTD, and DTM on a 100-mole % basis of monomer **1**. Curves are from different pieces of same sample and also from pieces of different samples.

These disulfide additives on their own may be acting as radical chain-transfer agents or iniferters that slow down free radical polymerizations, leading to a shorter kinetic chain length, more loose-ends in the cross-linked network, and a lower storage modulus.[3,4] *Control experiments employing Fourier-transform infrared (FTIR) spectroscopy as a function of disulfide loading, followed by DMA on the cross-linked films, confirmed that the disulfide additives reduce the degree of diene conversion and improve the resulting polymer film's mechanical compliance.*

Since a reduction in the degree of diene polymerization in monomer **1** apparently can improve the mechanical compliance of the resulting cross-linked Q_I films, an experiment was performed to see if this can be done without the use of any additives, by simply reducing the amount of photopolymerization time. A control experiment with a bulk Q_I sample of **1** containing no disulfides or PBD was UV irradiated for a very short time of 4 min (i.e., 0.067 h vs. the normal irradiation time of 2 h). The resulting Q_I polymer film was found to have a similar degree of diene conversion as a film containing 100 monomer **1**: 4.6 TBTD irradiated for 1 h, as well as a similar shallower stress-strain curve and a higher % strain-at-failure value relative to unmodified Q_I films (see blue and purple traces in Figure 7). *This experiment shows that a similar improvement in mechanical properties compliance can be achieve in an additive-free fashion by simply reducing the degree of polymerization (and hence extent of cross-linking) of monomer **1** via reducing the UV photopolymerization time.*

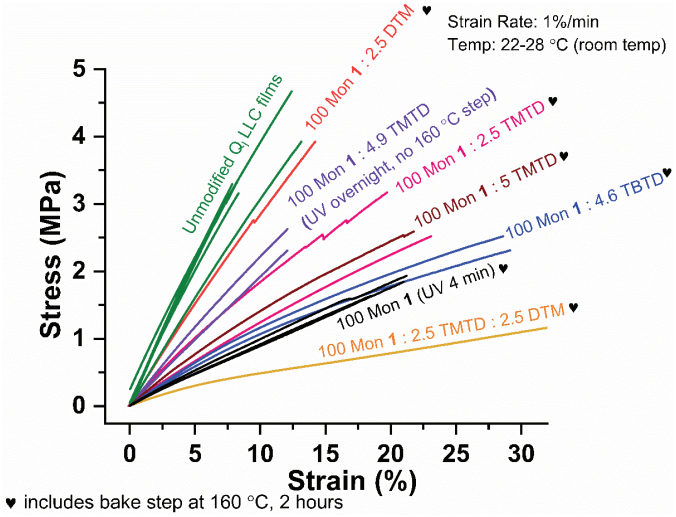


Figure 7. Stress-strain tensile curves for bulk Q_I polymer films with no added PBD containing various mole ratios of disulfides TMTD, DTM, or TBTD on a 100-mole % basis of monomer **1**, and of polymer film containing no disulfides or PBD that was UV-irradiated for 4 min (0.067 h) to achieve similar diene conversion to films containing disulfides after 1 h of UV irradiation. Curves are from different pieces of same sample and also from pieces of different samples.

The main finding from these additive studies and control experiments is that the most promising method for reducing the modulus and increasing the % strain-at-failure of bulk

*cross-linked Q_I films of **1** is reducing the degree of polymerization of the cross-linkable monomer. If methods can be found / developed to controllably lower of the degree of diene conversion on monomer **1** in a facile manner, the extent of cross-linking and the mechanical properties of the resulting Q_I polymer network can then be tailored.*

(iii) Other related approaches

Addition of other types of elastomers and other methods for limiting the degree of diene conversion on LLC monomer **1** were also explored briefly, as summarized below. *None of these related approaches were sufficiently promising to warrant further investigation*.

(a) Blending with poly(dimethylsiloxane) (PDMS) elastomer: It was hypothesized that other hydrophobic polymers such as PDMS elastomer might be blended and radically cross-linked into a Q_I-phase sample of **1** without loss of the phase to produce Q_I networks with more mechanical compliance and stretchability. Initial **1**/PDMS blends investigated were opaque but still showed a Q_I phase by PXRD and high diene conversion by FTIR analysis. However, multiple polymer samples made with different wt% loadings of uncured PDMS and monomer **1** exhibited either mechanical properties similar to those of unmodified, baseline Q_I polymer films, or a lower storage modulus but similar % strain-at-failure compared to the unmodified Q_I films. *This approach was not sufficiently promising to be explored further*.

(b) Use of thiol-based radical chain-transfer agents instead of disulfides: Thiols such as dodecanethiol can act as chain-transfer agents and be added to acrylate systems to reduce storage modulus, due to increased number of loose chain ends (i.e., smaller kinetic chain length). Unfortunately, addition of dodecanethiol (at 0.23 g per 100 g of monomer **1**) did not significantly change the strain-at-failure or storage modulus of the resulting cross-linked Q_I film from the unmodified Q_I film values. Also, dodecanethiol did not reduce the polymerization rate significantly (and thus did not change kinetic chain length). *This approach was not explored further*.

(c) Ozonolysis of an unmodified Q_I polymer film to induce chain scission and decrease average cross-link density: The radical polymerization of the 1,3-diene tails of monomer **1** results in the formation of one residual C=C double bond per diene unit polymerized. It was hypothesized that treatment of a polymerized film with O_3 (ozone) gas may perform a degree of oxidative scission of the residual double bonds to form aldehydes, thereby reducing cross-linking density and hopefully improving strain-at-failure. *Unfortunately, initial ozonolysis trials were not promising*: Although some (surface?) aldehyde formation was detected by FTIR analysis, the observed storage modulus and % strain-at-failure of one film that underwent ozonolysis were similar to those of an unmodified Q_I film. *This approach was not sufficiently promising to be explored further*.

(iv) Blending of non-polymerizable and single-polymerizable-tail analogs of monomer 1 to lower / control extent of Q_I LLC monomer cross-linking

Unfortunately, it is difficult to control the degree of radical polymerization (and the extent of cross-linking) for a cross-linkable monomer such as **1** by addition of chain-transfer agents or use of shorter photopolymerization times. The amount of chain-transfer additive and/or the length of UV irradiation time cannot predictably, reliably, or reproducibly target a specific degree of diene polymerization because of variability in chain-transfer and photo-initiation efficiency from run to run and with slight changes in reaction conditions.

To obtain better level of control over the mechanical properties of the resulting Q_I network, it was hypothesized that cross-linking density would be decreased controllably if monomer **1** (a cross-linkable monomer) were blended with specific molar amounts of either a nonpolymerizable analog (i.e., nonpolymerizable plasticizer **3**) or a non-cross-linkable, single-polymerizable analog (i.e., monomers **2** or **4**) (see Figure 8). The addition of controlled amounts of these structurally similar analogs to **1** would allow miscibility and retention of the desired Q_I phase, and lead to lower cross-linking density that would afford a lower storage modulus and higher % strain-at-failure.

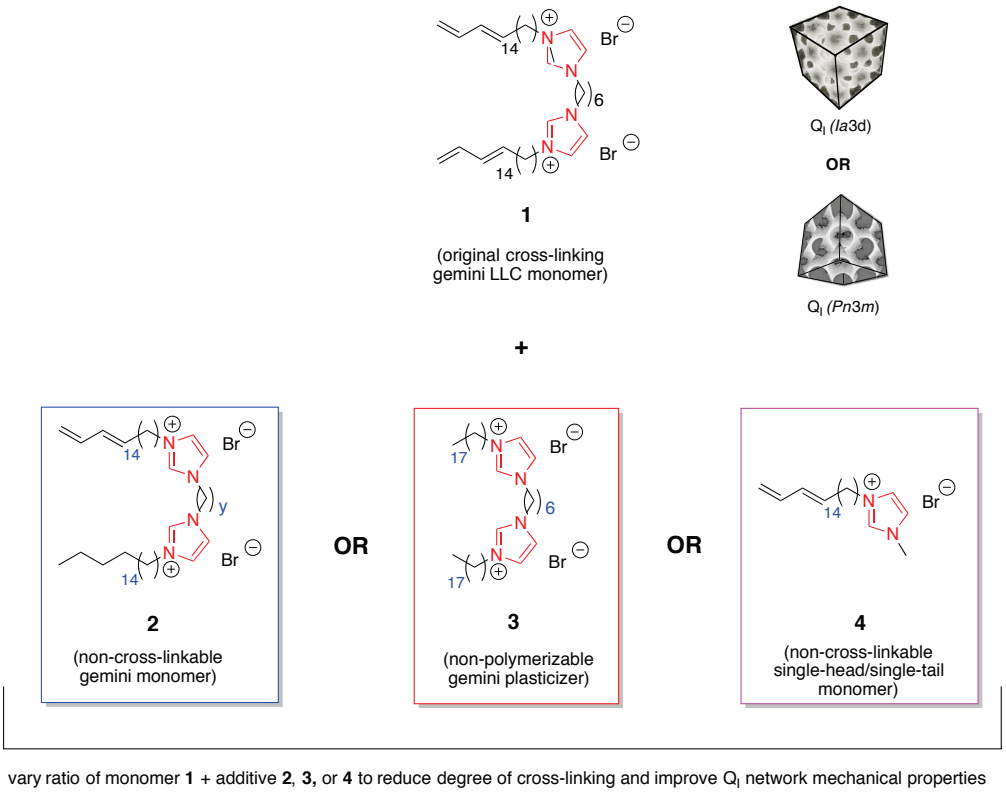


Figure 8. Proposed blending and/or copolymerization of cross-linkable gemini LLC monomer **1** with several non-cross-linkable or nonpolymerizable additives to controllable lower the overall extent of cross-linking and increase stretchability/mechanical properties in the resulting Q_I polymer networks.

However, studies with a small amount of nonpolymerizable gemini plasticizer **3** and a standard mixture of **1** / glycerol / photo-initiator showed that the resulting photopolymerized mixture lost the Q_I phase over time, presumably because **3** is not covalently locked-into the network and can relax out of the Q_I nanostructure arrangement. The storage modulus of this sample was lower than that of the unmodified Q_I polymer films (presumably because the cross-linking density was lower), but the % strain-at-failure did not increase. *Consequently, blending of a nonpolymerizable plasticizer analog of monomer **1** (i.e., compound **3**) was not explored further***.**

Blending of a small amount of a non-cross-linkable, (single-head/single-tail) monomer **4** into the standard Q_I system of **1** revealed some miscibility problems: **4** and **1** required extended mixing time to form a Q_I phase, and the resulting Q_I phase was not always completely homogeneous by PLM analysis. Also, after UV photopolymerization, the Q_I phase was retained, but the storage modulus and % strain-at-failure were essentially unchanged from those of the unmodified Q_I polymer films. This difficulty in Q_I phase formation and lack of change in mechanical properties in the polymerized blend is likely due to the fact that **4** is effectively only one-half of gemini monomer **1** and not that similar in size/shape, leading to phase separation. *Because of this very limited Q_I-phase compatibility with dimensionally dissimilar additives, blending of a non-cross-linkable, (single-head/single-tail) monomer such as **4** with gemini monomer **1** was not explored further**.*

At the end of Year 1, the focus of the experimental effort at CU Boulder shifted to the synthesis of non-cross-linkable monomer additive **2,** for blending with **1** to controllably reduce the extent of cross-linking in a Q_I mixture. Non-cross-linkable target monomer **2** has the same overall gemini amphiphile shape (i.e., two joined headgroups + two tails) and size as **1** and thus expected to be more miscible and compatible with **1** for better Q_I phase formation / less phase separation. A synthesis scheme for non-cross-linkable monomer **2** was conceptualized at this point in the project, in order to circumvent the blending shortcomings encountered with additives **3** and **4**.

(d) DCH vs. CEES vapor testing at CU Boulder

Tasks completed and major findings:

Currently, the CCDC SC evaluates a material's sulfur mustard vapor protection performance using 1,6-dichlorohexane (DCH) as a surrogate, whereas CU Boulder uses chloroethyl ethyl sulfide (CEES) as a surrogate. In addition, each lab uses a different testing method for relative vapor permeability. However, there have been no studies to determine if there is any difference between the use of CEES or DCH, using the same test material and testing method. To this end, the vapor fluxes of CEES and DCH were measured at CU Boulder for thin-film composite (TFC) Q_I membranes of **1** consisting of the Q_I LLC polymer and UP150, a poly(ether sulfone) ultrafiltration support membrane.

Vapor fluxes were determined using a simple dead-end permeation cell apparatus as previously reported in our prior paper (Figure 9).[5]

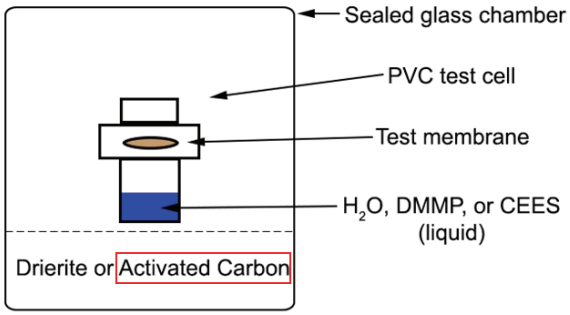


Figure 9. Schematic of the PVC test cell inside a sealed glass chamber setup that is used for vapor transport experiments at CU Boulder. Reproduced from ref. 5, Supp. Info.

It was found that CEES and DCH vapor permeabilities ((18 ± 1) and (15 ± 5) g m^{-2} day^{-1}, respectively) through the same material are similar, using the same test method and apparatus. *This study indicated that the vapor permeabilities measured at CU Boulder with CEES and at the CCDC SC with DCH can be considered comparable indicators of blister agent vapor protection performance.*

Years 2–3 (July 1, 2020 to September 30, 2022) [computational work by Shirts group; experimental work by Gin + Noble group]:

(a) Molecular modeling [Shirts group]

Tasks completed and major findings:

The main simulation task undertaken by the Shirts group during this time was development of an atomistic model of the Q_I phase consistent with the experimental detail with monomer **1**. Direct self-assembly using molecular dynamics with the GAFF2 atomistic force field and self-assembly using Martini 3 coarse-grained forcefield followed by back-mapping to atomistic structures were attempted, but neither resulted in stable Q_I structures.

Instead, a procedure was developed based on assuming that the Q_I phase was a distorted bilayer and searching for the structure geometrically most consistent with a bilayer thickness.[6] Atomistic simulations of the bilayer were carried out, which were fully stable, and identified the bilayer thickness. With these bilayer simulations, the atomistic bilayer thickness of 3.5 nm was measured, which with the estimated pore diameter enabled estimation of the average distance between the interfaces to be 4.6 nm (see

Figure 10). With the bilayer simulations, it was possible to refit the coarse-grained force field to better match the distribution function obtained from the atomistic simulation.

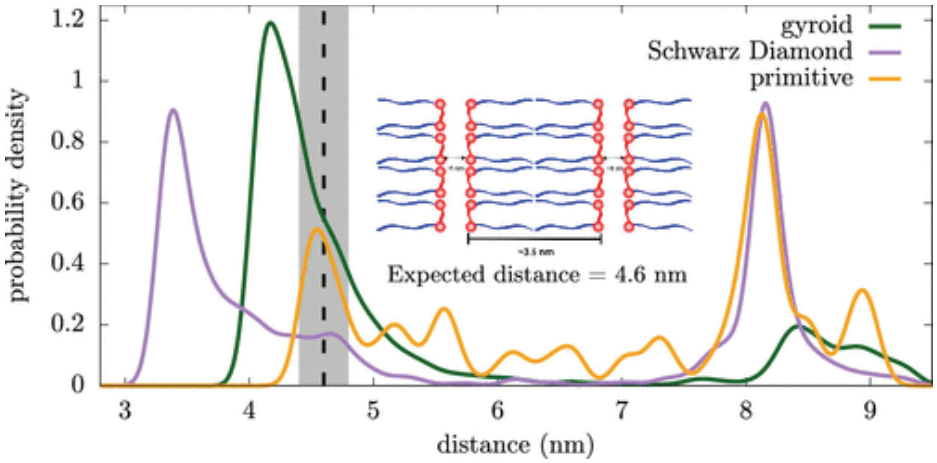


Figure 10. Gyroid structures are significantly more consistent with the observed bilayer thickness than diamond or primitive structures in the experimentally determined unit cell length. Reproduced from ref. 6.

Although this refit coarse-grained model was still unable to spontaneously self-assemble, the Shirts group placed monomers of the coarse-grained model with the headgroups at the mathematically estimated gyroid structure, filled the void with coarse-grained glycerol, and equilibrated this structure. At temperature of 300 K, the structure remained in the gyroid phase out to 1 ns (see Figure 11). This structure was then back-mapped to the corresponding atomistic structure, where it remained stable out to 500 ns. The simulated chain polymerization between the diene groups was then simulated, reaching above 90% polymerization, and the glycerol replaced with water.

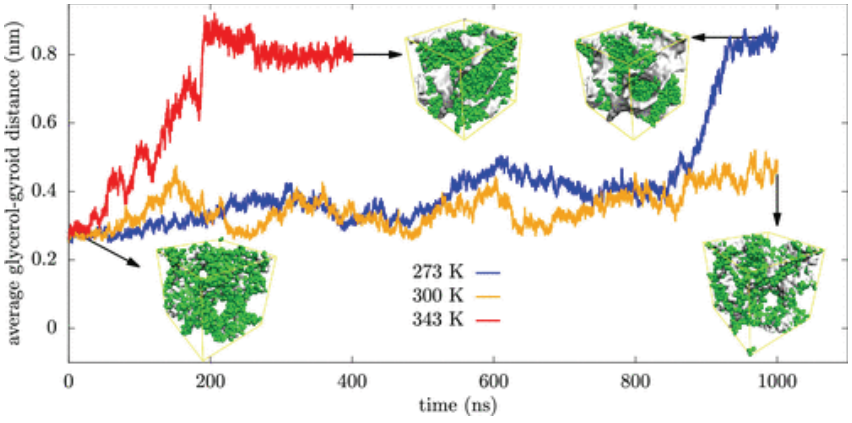


Figure 11. Refit coarse-grained simulations at 300 K showing maintenance of a stable gyroid Q_I phase. Reproduced from ref. 6.

It was found that although the system remained in the gyroid phrase, the pores were not well-defined, with significant impingement of monomers into the aqueous volume,

resulting in solvent-only pores that were significantly smaller than experiment, but that if part of the polar headgroup volume was also considered as pore, the permeable channels were consistent with experimental permeability observations. The resulting atomistic nanostructure was then analyzed for transport of water and neutral molecules. It was also found that water in the Q_I network nanopores moved approximately 120 times slower than bulk self-diffusion, but neutral molecules such glycerol moved approximately 4000 times slower than diffusion in water.

These results were published in the journal, *The Journal of Physical Chemistry B*, in late 2022.[6]

(b) <u>Monomer synthesis and characterization [Gin + Noble group]</u>

Tasks completed and major findings:

(i) Synthesis of sufficient amounts of LLC monomer 1 for planned studies

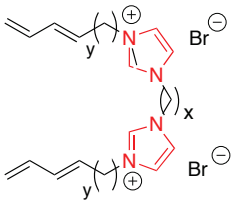
Multi-gram quantities of Q_I-phase LLC monomer **1** were needed in order to prepare sufficient bulk and TFC Q_I membrane samples for the planned vapor transport tests at CU Boulder, as well as for the ATR-FTIR-based CWA simulant diffusion experiments at the CCDC SC. Sufficient amounts of monomer **1** were synthesized according literature procedures[7] and stored in the Gin + Noble group at CU Boulder to complete all planned studies and membrane sample preparations in Years 2–3 of this project.

(ii) Synthesis and LLC characterization of variants of LLC monomer 1 with different-length headgroup spacers and different-length polymerizable diene tails

Two of the goals in Years 2–3 of the project were the synthesis and LLC phase characterization of a systematic series of LLC monomer **1** variants with different headgroup spacer and polymerizable diene tail lengths in order to determine the effect of these structural changes on Q_I phase formation. This experimental information would be used to help guide the modeling effort in the Shirts group on effects of monomer structure on Q_I phase.

Seven homologs of monomer **1** with several headgroup bridge alkyl spacer lengths and two different polymerizable diene tail lengths (i.e., monomers **1a–1g**) were successfully synthesized in multi-gram quantities and characterized (see Figure 12).[8] Polarized light microscopy (PLM)-based penetration scan screening of these new monomers blended with water or glycerol indicated that majority of them form potential Q phases (see Table 2). Verification of Q-phase formation by PXRD and elucidation of variable-temperature phase diagrams of these variants with water and glycerol were completed. These results showed that monomer homologs **1a**, **1c**, **1e**, and **1f** form a Q phase with either water or glycerol (see Figure 13). However, only homolog **1a** was found

to form a Q phase with a wider temperature and composition range with than the original monomer **1** while maintaining a similar degree of Q-phase order.



Homolog:

1a: x = 5; y = 14
1b: x = 7; y = 14
1c: x = 9; y = 14
1d: x = 4; y = 10
1e: x = 5; y = 10
1f: x = 6; y = 10
1g: x = 7; y = 10

Figure 12. Structures of the homologs of gemini LLC monomer **1** synthesized and characterized for LLC phase behavior.

Table 2. Summary of the Q phase formation behavior of the seven homologs of gemini LLC monomer **1** synthesized and studied. Data from ref. 8.

Monomer Homolog	x	y	Glycerol	Water
1a	5	14	*Q phase*	No Q phase (discontinuous cubic phase only)
1b	7	14	No Q phase	No Q phase (discontinuous cubic phase only)
1c	9	14	*Weakly ordered Q phase*	No Q phase
1d	4	10	No Q phase	No Q phase
1e	5	10	No Q phase	*Weakly ordered Q phase*
1f	6	10	No Q phase	*Weakly ordered Q phase*
1g	7	10	No Q phase	No Q phase

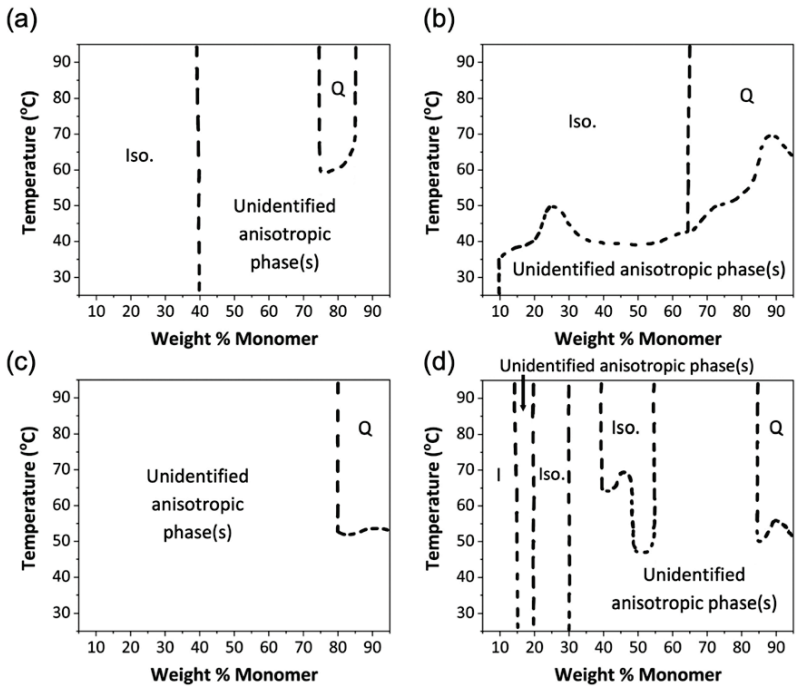


Figure 13. Partial phase diagrams of the four Q-phase-forming homologs of monomer **1**: (a) **1a** with glycerol; (b) **1c** with glycerol; (c) **1e** with water; and (d) **1f** with water. I = discontinuous cubic phase; Iso. = amorphous isotropic phase (i.e., no order by PXRD); Q = bicontinuous cubic phase. Heterogeneous regions omitted. Note: phase diagrams mapped out at Boulder, CO (altitude = 5328 ft, ambient pressure = ca. 623 torr); they may be slightly different at other altitudes. Reproduced from ref. 8.

For this cross-linkable gemini amphiphile platform, it appears that Q-phase formation is favored for homologs that have five- and six-carbon headgroup alkyl spacers, regardless of whether the diene tail is 14 or 18 carbons long. Also, well-ordered Q phases only appear to form for homologs with those headgroup spacer lengths if they also have the 18-carbon polymerizable diene tail and are blended with glycerol. *These trends indicate that the monomer **1** platform has very limited structural tunability in terms of forming and adjusting the range of the Q phase desired for membrane applications.*

These results were communicated to the Shirts group to help guide their computational efforts on the effects of changes in gemini LLC monomer structure on Q phase formation. These results were also published in the journal, *Soft Matter*, in 2021.[8]

(iii) Improved stretchability of bulk Q_I polymer films of monomer 1 via copolymerization with a non-cross-linkable monomer derivative

In the latter part of project Year 1 (2019–2020), researchers in the Gin + Noble group began working on synthesizing a *non-cross-linkable* analog to gemini LLC monomer **1** that contains only one polymerizable tail (i.e., monomer **2**). The goal was to blend controlled amounts of this non-cross-linking monomer in mixtures with cross-linkable

monomer **1** as another means of reducing the degree of cross-linking (and increasing stretchability) (Figure 14). Unfortunately, because of the physical and chemical similarities between target monomer **2** and the monomer **1** byproduct formed in the synthesis scheme, it was not possible to isolate pure monomer **2**.

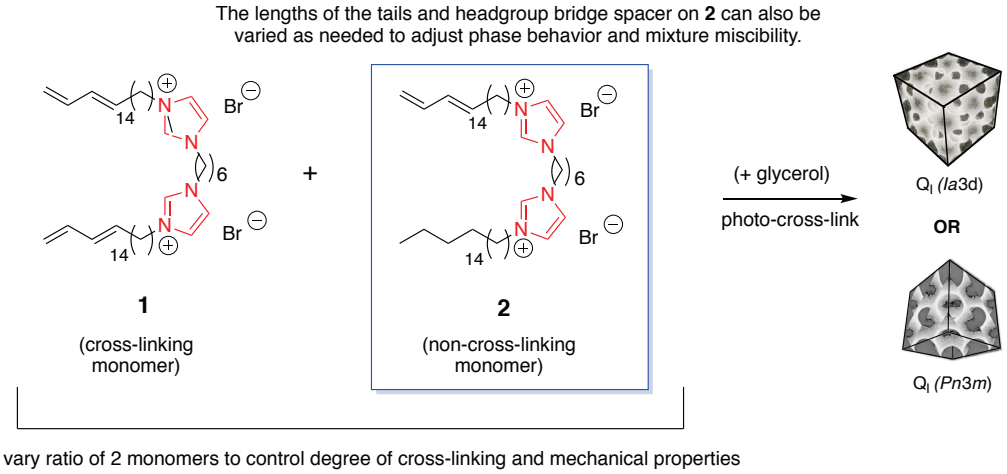


Figure 14. Co-polymerization of non-cross-linking LLC monomer **2** with cross-linkable monomer **1** to controllably reduce the extent of cross-linking / lower cross-link density.

In project Years 2–3, researchers in the Gin + Noble group successfully developed and optimized a process to reproducibly prepare a 7:93 (mol/mol) mixture of monomers **1** and **2,** respectively, containing no other impurities (Figure 15(a)). By adding appropriate amounts of pure **1** to this base 7:93 (mol/mol) (**1** + **2**) monomer mixture, a series of targeted **1**:**2** (mol:mol) blends were systematically prepared that would afford lower degrees of cross-linking upon full conversion (Figure 15(b)).[9]

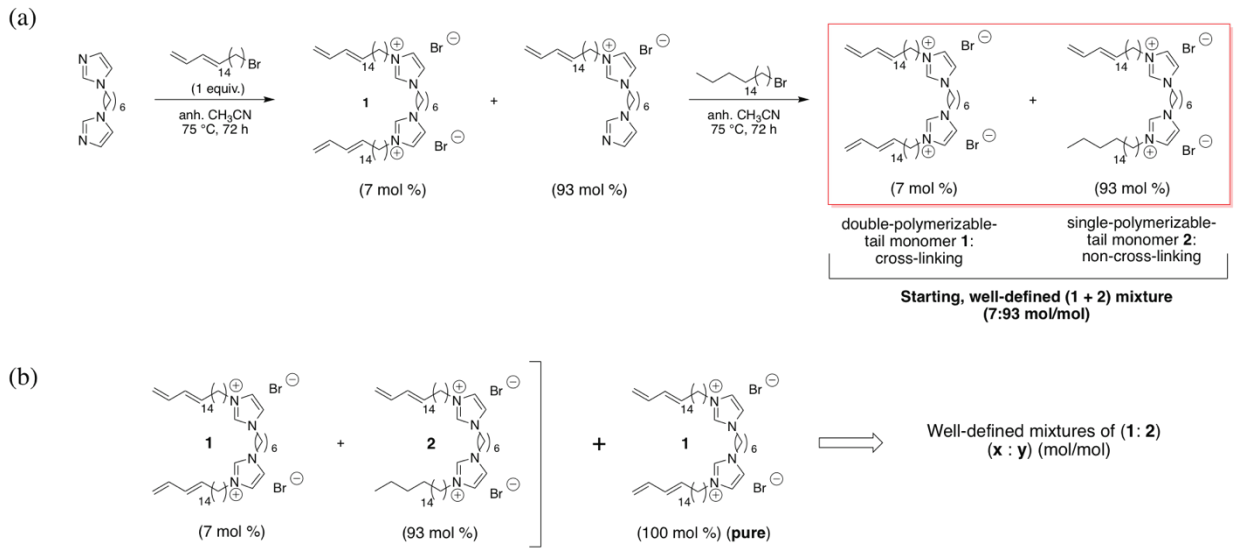


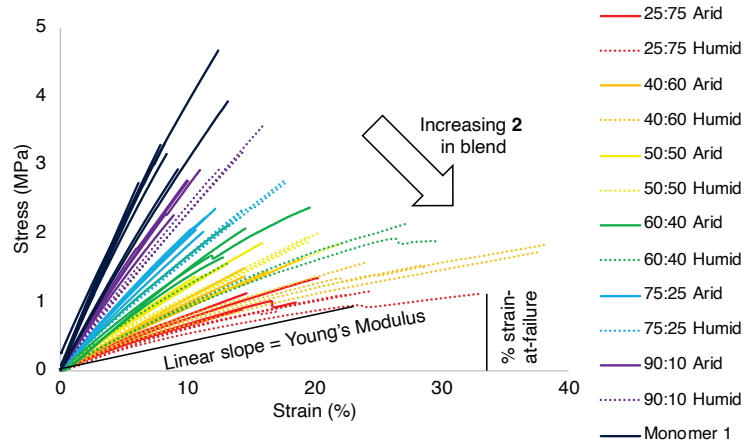
Figure 15. (a) Synthesis of a set 7:93 (mol:mol) mixture of monomers **1** and **2;** and (b) general strategy for making controlled compositions of monomers **1** + **2** with controlled lower degrees of cross-linking using this 7:93 (mol:mol) mixture of **1** and **2.**

Many of these mixtures of **1** and **2** were found to form Q phases in glycerol via PLM and PXRD analysis while showing high conversion of the polymerizable diene groups by FTIR analysis (see Table 3). DMA studies on the mechanical properties of the various cross-linked Q_I-phase **1**:**2** blends demonstrated that both *the storage modulus and the % strain-at-failure can be controlled by adjusting the molar ratios of these two monomers in the blend.*[9] *Using this approach, it was possible to produce bulk polymer Q_I films with lower degrees of cross-linking that exhibit a linear stress-strain profile with a low modulus (i.e., shallow slope) and a % stain-at-failure value exceeding 20% (see Figure 16 and Table 4).*[9] *Several of these values meet or exceed the original project target parameters for a film with 20% stretchability, depending on the conditions.*

Table 3. Summary of structural characterization data from PLM, PXRD, and FTIR analysis for cross-linked Q_I films of the **1**:**2** blends. Data from ref. 9.

Monomer Blend Composition (mol:mol)	**7:93 (1:2)**	**25:75 (1:2)**	**40:60 (1:2)**	**50:50 (1:2)**	**60:40 (1:2)**	**75:25 (1:2)**	**90:10 (1:2)**
Black PLM of bulk film:	no	yes	yes	yes	yes	yes	yes
Q_I PXRD of bulk film:	no	yes	yes	yes	yes	yes	yes
1,3-Diene Conversion (%):	73%	92%	89%	91%	93%	92%	94%

(a)



(b)

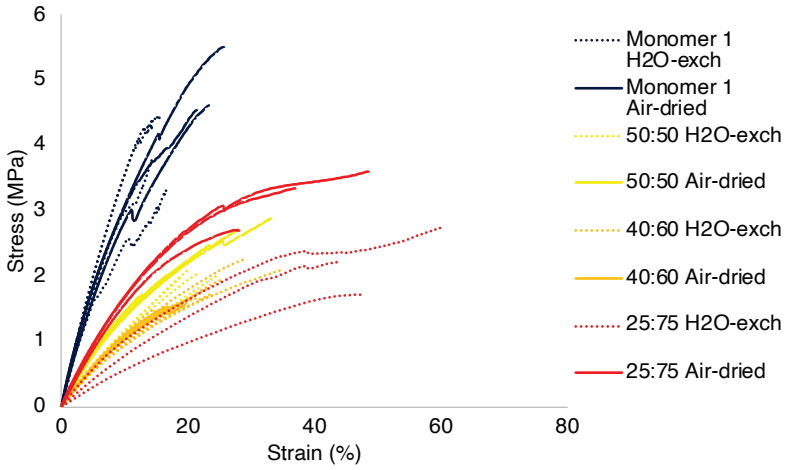


Figure 16. (a) Stress-strain plots for the cross-linked Q_I-phase **1**:**2** blends tested under arid (<30% RH; solid lines) and humid (>30% RH; dotted lines) conditions in Study 1. Labels are included to show how the % strain-at-failure and Young's modulus values were determined for each plot. (b) Room temperature (RT) stress-strain plot from Study 2, showing plastic behavior for the most-pliable Q_I films of the **1**:**2** blends as well as for the Q_I films of monomer **1** after water-for-glycerol exchange in the sample nanopores. Reproduced from ref. 9.

Table 4. Compiled RT % strain-at-failure and Young's modulus values of cross-linked Q_I-phase **1**:**2** bulk films and cross-linked Q_I bulk films of **1** tested under different RH conditions. The values shown are the average values from measurements on at least 3 different pieces from the same large film with 1 std. dev. error bars. Data from ref. 9.

Composition of Cross-linked Q_I Film (1:2 (mol:mol)):	**100:0**	**90:10**	**75:25**	**60:40**	**50:50**	**40:60**	**25:75**	**7:93**
% Strain-at-Failure (arid, <30% RH):	8 ± 3	10 ± 1	11 ± 1	15 ± 3	13 ± 2	20 ± 10	17 ± 3	N/A: (No Q phase)
% Strain-at-Failure (humid, >30% RH):	N/A	14 ± 2	16 ± 2	23 ± 9	20 ± 1	32 ± 7	24 ± 7	
Young's Modulus (arid, <30% RH) (MPa):	0.39 ± 0.05	0.27 ± 0.01	0.19 ± 0.01	0.14 ± 0.02	0.12 ± 0.01	0.09 ± 0.01	0.07 ± 0.01	
Young's Modulus (humid, >30% RH) (MPa):	N/A	0.23 ± 0.01	0.159 ± 0.004	0.09 ± 0.03	0.10 ± 0.01	0.05 ± 0.01	0.05 ± 0.01	

Two separate mechanical property studies were performed on these cross-linked Q_I films: Study 1 examined the effects of less cross-linking and external RH (i.e., arid (<30% RH) vs. humid (>30% RH) conditions) on the mechanical properties of as-prepared Q_I bulk films with glycerol in the nanopores. Study 2 examined the effect of decreased cross-linking in conjunction with replacement of the glycerol in the film nanopores with water.

From these two studies, several structure-property relationships were observed:

*(1) As mentioned before, bulk Q_I films with lower amounts of cross-linking **1** relative to non-cross-linkable analog **2** exhibit a progressively lower Young's modulus and higher % strain-at-failure values (see Figure 16). This is consistent with a decrease in cross-link density and an increase in chain segment mobility. Thus, the Young's modulus of these Q_I-phase LLC networks appears to mainly depend on the cross-link density controlled by the relative amounts of **1** and **2** in the formulation; specifically, showing an exponential relationship with increasing content of **1**.*

(2) Moisture content in the atmosphere has a significant effect on the durability of each sample: humid conditions (>30% RH) increase the % strain-at-failure value of the films by ca. 7% compared to arid conditions (<30% RH) across all of the compositions tested. However, external RH has little influence on the slope of the stress-strain curves, revealing that RH mostly affects % strain-at-failure.

(3) Changing the liquid in the Q_I pores from glycerol to water transitioned the bulk films from mostly elastic to some degree of plastic stretching behavior, as indicated by a change from linear to curved stress-strain plots (see Figure 16). Also, allowing the water-exchanged films to air-dry at RT has a larger effect on the Young's modulus of the three

*most-compliant **1**:**2** blend films (i.e., 25:75, 40:60 and 50:50 (mol/mol)) than for films made with **1** alone. It appears that the more monomer **2** in the blend, the more the internal water content of the nanopores acts as a plasticizer, affecting the stress-strain behavior of these cross-linked Q_I materials.*

In order to determine if the vapor transport properties of the films are affected by the decrease in cross-link density and increase in stretchability, the three most-pliable water-exchanged Q_I bulk films (i.e., 25:75, 40:60, and 50:50 (mol/mol) **1**:**2**) were tested and compared to baseline Q_I films made with just **1** (i.e., 100:0). Preliminary water and CWA simulant vapor fluxes were determined via a screw-cap-vial dead-end permeation cell method that involved monitoring the evaporative mass loss of a liquid reservoir below the membrane as a function of time. *All of the more-pliable **1**:**2** blends tested exhibited very high water vapor fluxes (similar to the MVTR of **1** film)* and approximately one-third of that through an open cell (see Table 5). *However, all of the more-pliable **1**:**2** blend Q_I films also displayed higher DMMP fluxes and a ca. 7-fold decrease in (water/DMMP) molar selectivity compared to the baseline film of **1**, indicating a trade-off between stretchability and DMMP rejection.* This is probably due to increased chain segment mobility and more free volume in the hydrophobic regions, resulting in more bulk flexibility but also easier passage of the larger, less-hydrophilic DMMP species through the less-cross-linked hydrophobic domains. Fortunately, *the (water/DMMP) molar selectivity values are still ca. 8 times higher than the open-cell control, signifying that these less-cross-linked films still reject DMMP vapor to a good degree*. Predictably, the more-pliable **1**:**2** blend films and the film of **1** exhibited CEES vapor fluxes and (water/CEES) molar selectivity values similar to those of an open cell. *It appears that these Q_I films – regardless of cross-link density – do not reject CEES vapor, similar to what was seen for unmodified TFC Q_I membranes of **1**.*[5] Application of a PDA coating onto these materials will be required if better CEES vapor rejection is desired.

Table 5. Water and DMMP vapor transport results for water-exchanged, cross-linked Q_I bulk films with different **1**:**2** ratios. The values shown are average values from measurements on ≥3 different pieces from the same large film with 1 std. dev. error bars. Data from ref. 9.

Membrane Sample	Average Membrane Thickness (μm)	H_2O Vapor Flux (g m^{-2} day^{-1})[a]	DMMP Vapor Flux (g m^{-2} day^{-1})[a]	(H_2O/DMMP) Molar Selectivity
100:0 (**1**:**2**):	160	$(1.83 \pm 0.10) \times 10^3$	3 ± 1	4.7×10^3
50:50 (**1**:**2**):	180	$(1.86 \pm 0.03) \times 10^3$	17 ± 3	7.6×10^2
40:60 (**1**:**2**):	205	$(1.79 \pm 0.06) \times 10^3$	19 ± 9	6.4×10^2
25:75 (**1**:**2**):	191	$(1.82 \pm 0.02) \times 10^3$	20 ± 7	6.4×10^2
Open Cell:	No membrane	$(6.6 \pm 0.3) \times 10^3$	$(5.5 \pm 0.5) \times 10^2$	8.5×10^1

[a]Permeability values are not reported because the pressure differential across the membrane for each species is assumed to be close to its partial pressure under the test conditions but could not be accurately controlled or measured in this simple testing setup.

*In summary, copolymerization of cross-linkable gemini LLC monomer **1** with controlled amounts of non-cross-linkable analog **2** allows for the formation of nanoporous Q_I polymer membranes with lower Young's modulus values and higher % strain-at-failure values that meet or exceed the desired 20% value while retaining a high WVTR. External RH and the amount of water in the nanopores of these films also affect their mechanical properties and should be considered when employing these cross-linked Q_I materials. Although DMMP rejection decreases with reduced cross-link density, increased pliability was achieved, demonstrating that the mechanical properties of these LLC-based breathable CWA-barrier materials can be modified in this fashion.*

These results were communicated to the Shirts group to help guide their computational efforts. These results were also published in the journal, *ACS Applied Polymer Materials*, in Oct. 2022.[9] The information summarized above was extracted from that publication.

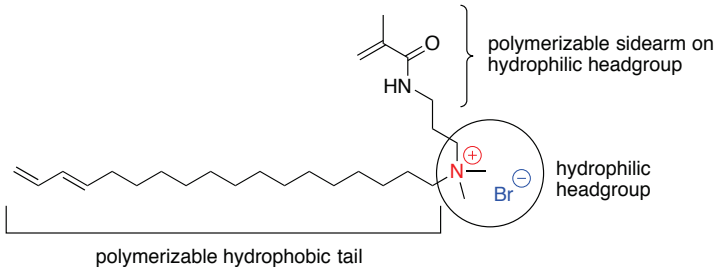
(iv) Design and synthesis of a new, Q_I-phase, cross-linkable LLC monomer platform with a simpler (single-head/single-tail) architecture

One of the limitations of the original Q_I-phase-forming LLC monomer **1** is that its synthesis is very elaborate and time-intensive.[7] Also, the monomer **1** gemini platform has limited structural tunability in terms of forming the Q phase, as well as limited compatibility with additives for Q_I phase formation, as mentioned in earlier sections of this report.

In Year 2 of the project, the Gin group undertook additional collaborative research with Prof. Chinedum Osuji's group at the University of Pennsylvania to explore the design of a new, cross-linkable Q_I-phase LLC monomer platform with a simpler architecture that

would be easier and more economical to synthesize than **1**. This research was not part of the original ARO project goals; it was an unplanned opportunity that came to light during Prof. Gin's Spring 2021 sabbatical leave that ended up being very successful and productive.

The Osuji and Gin groups collaboratively designed and demonstrated a new, structurally simpler, (single-head/single-tail) amphiphile with a polymerizable group at each end (**5**) that can be radically photo-cross-linked as a single-monomer system to form highly stable Q-phase networks (Figure 17).[10] Monomer **5** is prepared via a much less elaborate and more economical synthesis than gemini monomer **1**, making scale-up of **5** much easier. In addition, PLM and small-angle X-ray scattering (SAXS) revealed that **5** forms a gyroid-type Q phase with water at room temperature (RT) instead of at elevated temperatures like **1**. Partial phase diagram analysis suggested that the Q phase formed by **5** with water is a Q_I phase. After photopolymerization, the resulting Q-phase network is very stable with respect to long-term exposure to acidic and alkaline solutions as well as to a number of organic solvents. Vapor permeation studies have yet to be performed on the resulting Q-phase network. However, preliminary experiments involving liquid uptake of charged solutes and pressure-driven filtration of neutral solutes in aqueous solution showed that it has a nanopore diameter in the range of 1.5 nm. This collaborative work was published in the journal, *Chemical Communications*, in late 2021.[10]



5

Figure 17. Structure and behavior of monomer **5**, the new, structurally simpler, (single-head/single-tail) Q_I-phase LLC monomer jointly developed by the Osuji group and the Gin group.

In addition, follow-up collaborative work between the Gin and Osuji groups in 2022 showed that monomer **5** can also be blended and cross-linked in the Q_I phase with a spiropyran-containing dopant monomer (**6**) – in either its spiropyran (**6SP**) or protonated-merocyanine (**6M-HBr**) form (Figure 18).[11] The resulting polymer material is the first reported example of a Q-phase network with additional functional properties: It responds reversibly and colorimetrically to changes in external solution and vapor pH with retention of its Q-phase architecture but with internal physical changes. Preliminary studies also showed that this new Q_I network material is capable of strongly binding to aq. Pb^{2+} ions when activated by UV light, allowing it to function as a potential colorimetric sorbent or gated response material. This work was published in the journal, *Advanced Materials Interfaces*, in Nov. 2022.[11]

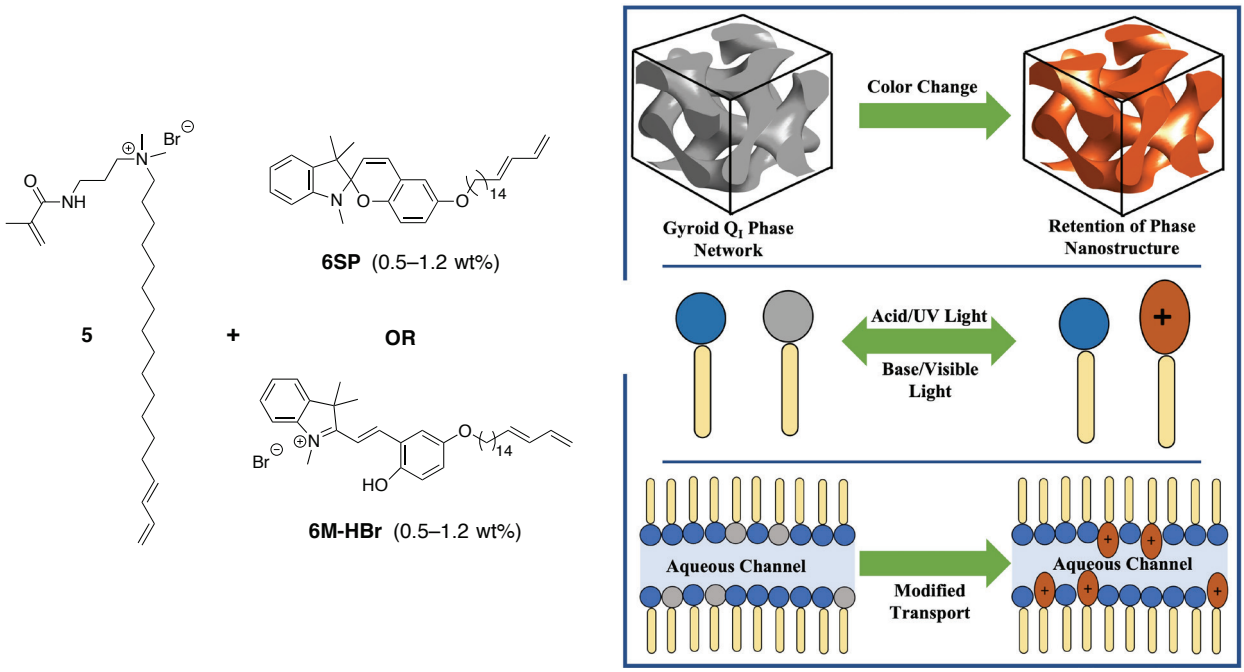


Figure 18. Structures of Q_I-phase-forming LLC monomer **5** and novel non-LLC co-monomer **6** in its spiropyran form (**6SP**) and its protonated-merocyanine form (**6M-HBr**). Various blends of (**5** + **6SP**) and (**5** + **6M-HBr**) self-assemble into gyroid-type Q_I phases that can be cross-linked in situ with retention of the phase order. The resulting nanoporous polymer networks undergo reversible physical changes in color and unit cell dimensions. Partially reproduced from ref. 11.

*Collectively, the results from this unplanned collaboration between the Gin and Osuji groups show that new cross-linkable (single-head/single-tail) monomer **5** may be a better future option for development of nanoporous LLC polymer membranes with improved stretchability for selective vapor separations.*

(3) Membrane synthesis and characterization [Gin + Noble group]

Tasks completed and major findings:

(i) Fabrication of samples of Q_I membranes based on monomer 1 for vapor transport testing at the CCDC SC

Four small bulk Q_I membrane samples made from monomer **1** (original formulation) were sent to the CCDC SC in the 4th quarter of 2020 for initial trials on the new ATR-FTIR flow system being set up there. In addition, several TFC Q_I membranes of monomer **1** (original formulation) were also prepared and sent to the CCDC SC in December 2020 for initial trials on the new ATR-FTIR flow system there.

Three Q_I TFC membrane samples were made with monomer **1** coated with polydopamine (PDA) for water and CWA simulant vapor diffusion testing at the CCDC SC. These samples have not requested by the CCDC SC yet, but they can be shipped immediately to the CCDC SC upon request.

Multiple Q_I TFC membranes of monomer **1** roll-cast and photopolymerized on ultraporous PS35 support were sent to the CCDC SC in May 2022 for CWA simulant diffusion analysis trials on the ATR-FTIR vapor flow system there. In addition, samples of just uncoated PS35 membrane support film were also sent to the CCDC SC at that time as reference samples for the flow analysis. The goal of these trials at the CCDC SC with TFC membranes of **1** were to determine the best placement orientation of the single-side-coated TFC membranes on the ATR crystal relative to the vapor flow direction, in order to obtain the best ATR-FTIR signal.

(ii) Coating of monomer 1 and its variants on ATR crystals for FTIR-based CWA simulant diffusion experiments at the CCDC SC

A procedure was needed to coat, polymerize, and then remove a thin, cross-linked Q_I film of monomer **1** from a specially cut ATR Ge crystal used on the CCDC SC's ATR-FTIR flow instrument, without damaging the Ge crystal for re-use. The following proof-of-concept experiment showed that this could be accomplished: Monomer **1** was successfully drop-cast from MeOH solution and photo-cross-linked onto an inexpensive Ge crystal disc (without formation of the Q_I phase as an initial test). The degree of polymerization was measured on the Gin + Noble group's FTIR instrument. The thin polymer film was able to be removed without damage to the Ge crystal by soaking the coated crystal in a 50/50 (v/v) MeOH/H_2O solution and allowing the polymer film to slowly lift off.

The Gin + Noble group also designed an apparatus that allows the Ge ATR crystal to be nestled within a heat-conductive sample holder. This set-up allows solution roll-casting and heating of the cast monomer **1** solution onto the top of the Ge crystal, so that a controlled-thickness Q_I-phase layer can be formed prior to photo-cross-linking. Note: PDA-coated Q_I polymer films of **1** on ATR crystals for vapor diffusion testing have not been requested yet by the CCDC SC and consequently have not been prepared yet.

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Publications and patents/patent applications generated from project:

(a) Peer-reviewed publications:

Li, P.; Reinhardt, M. I.; Dyer, S. S.; Moore, K. E.; Imran, O. Q.; Gin, D. L.* “Effects of Structural Modification of (Alkyldiene-Imidazolium Bromide)-Based Gemini Monomers on the Formation of the Lyotropic Bicontinuous Cubic Phase,” *Soft Matter* **2021**, *17* (41), 9259–9263.

Imran, O. Q.; Li, P.; Kim, N. K.; Gin, D. L.; Osuji, C. O.* “Stable cross-linked lyotropic gyroid mesophases from single-head/single-tail cross-linkable monomers,” *Chem. Commun.* **2021**, *57* (83), 10931–10934.

Bodkin, L. N.; Li, P.; Dyer, S. S.; Krajnak, Z. A.; Malecha, J. J.; Noble, R. D.; Gin, D. L.* "Improved Mechanical Compliance in Bicontinuous Cubic Lyotropic Membranes Based on a Cross-Linking Gemini Monomer via Copolymerization with a Non-Cross-Linkable Analog," *ACS Appl. Polym. Mater.* **2022**, *4* (11), 8026–8031.

Li, P.; Johnson, C.; Dyer, S. S.; Osuji, C. O.;* Gin, D. L.* "A pH- and Light-responsive Nanoporous Lyotropic Gyroid Polymer Network," *Adv. Mater. Interfaces* **2022**, 2201761. (https://doi.org/10.1002/admi.202201761)

Sahu, S.; Schwindt, N. S.; Coscia, B. J.; Shirts, M. R.* "Obtaining and Characterizing Stable Bicontinuous Cubic Morphologies and Their Nanochannels in Lyotropic Liquid Crystal Membranes," *J. Phys. Chem. B* **2022**, *26* (48), 10098–10110.

(b) <u>Patents/Patent Applications:</u>

Gin, D.; Li, P.; Osuji, C.; Imran, O. "Stable Cross-linked Lyotropic Gyroid Mesophases from Single-head/Single-tail Cross-linkable Monomers," Provisional U.S. Patent Application 63/246,143, filed September 20, 2021.

Gin, D.; Li, P.; Osuji, C.; Imran, O. "Lyotropic Gyroid Mesophase Compositions, Polymer Compositions Comprising the Same, Methods of Preparation Thereof, and Methods of Using the Same," U.S. Patent Application 17/949,072, filed September 20, 2022.