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| Journal: | <i>ChemComm</i> |
| Manuscript ID | CC-COM-08-2021-004211.R1 |
| Article Type: | Communication |
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Stable cross-linked lyotropic gyroid mesophases from single-head/single-tail cross-linkable monomers

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Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

A single-head/single-tail surfactant with a polymerizable group at each end is presented as a new simplified motif for intrinsically cross-linkable, gyroid-phase lyotropic mesogens. The resulting nanoporous polymer networks exhibit excellent structural stability in various solvents and are capable of molecular size discrimination.

Cross-linked lyotropic liquid crystal (LLC) phases are nanoporous polymer materials that have been found to be useful for a number of applications, including templated synthesis, heterogeneous catalysis, molecular size filtration, and enhanced ion transport.¹ They are prepared by the direct polymerization of cross-linkable amphiphilic (i.e., surfactant) monomer systems that form periodic, phase-separated assemblies around a polar liquid such as water, with retention of the phase nanostructure. This process yields stabilized polymer structures with uniform, ca. 1-nm-wide pores in which the hydrophilic headgroups of the monomers are localized at the pore walls, thereby providing the ability to control or functionalize the pore environment for specific applications.

Although LLC phases with different pore architectures are known, bicontinuous cubic (Q) phases are highly desired for the preparation of LLC networks for selective molecular transport and uptake applications.² This is because Q phases possess 3D-interconnected pore systems with overall cubic symmetry, and thus do not require alignment for good transport performance or internal access as with lower-dimensionality LLC phases.²

Unfortunately, only a very limited number of Q-phase LLC monomer platforms have been reported that can be cross-linked with phase retention. Most of these are based on fairly elaborate monomer motifs (Fig. 1) that typically require costly and/or complicated syntheses, making them difficult to scale-

up or structurally modify. In particular, cross-linkable Q-phase monomer systems based on reactive lipid-like (i.e., single-head/two-tail),^{3,4} gemini (i.e., bridged two-headgroup/two-tail),^{5–12} taper-shaped (i.e., single-head/three-tail),^{13,14} and two-headed-lipid (i.e., two-head/two-tail)¹⁵ amphiphiles have been reported that can be radically polymerized with retention of phase architecture. Many of these were intrinsically cross-linkable single-monomer systems,^{5–9,13,14} while others were cross-linkable mixtures of LLC monomers^{3,4} or blends with co-monomers or organic additives.^{8,10–12,15} The hydrophilic headgroups in these systems ranged from uncharged⁴ to ionic^{5–8,13,14} and zwitterionic,^{3,9–11} but they all had a polymerizable group in their hydrophobic tails as a common feature.

A small number of structurally simpler, single-head/single-tail amphiphilic monomers have also been reported to form Q phases.^{16–20} Based on a 'simple surfactant' motif, they are easier to synthesize^{18,19} and chemically modify. These amphiphiles were uncharged,¹⁷ ionic,^{16,18} or zwitterionic¹⁹ in nature, but they all contained only one radically polymerizable group per molecule (either near the headgroup^{16,18} or in the tail¹⁷) and thus required cross-linking co-monomers to form stable Q networks.^{17,19} In some cases, blending with an organic additive was also required to form a Q phase.¹⁸

Herein, we present an intrinsically cross-linkable, single-head/single-tail amphiphile (**1**) that can be radically polymerized as a single-monomer system to generate highly stable Q-phase networks (Fig. 1). This new monomer motif carries a polymerizable methacrylamide group near the ionic headgroup and a polymerizable diene group in the hydrophobic tail, allowing it to be radically cross-linked without added co-monomers/cross-linkers, unlike prior Q-phase single-head/single-tail monomer systems. Monomer **1** is readily synthesized from a commercial polymerizable amine and forms a gyroid-type Q phase with water at room temperature as confirmed by polarized optical microscopy (POM) and small-angle X-ray scattering (SAXS). After photopolymerization, the resulting polymeric materials exhibit excellent retention of the mesophase nanostructure. Notably, the nanostructure is stable

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Electronic Supplementary Information (ESI) available: synthetic procedures, phase diagrams, analytical data on materials, and structure calculations. See DOI: 10.1039/x0xx00000x

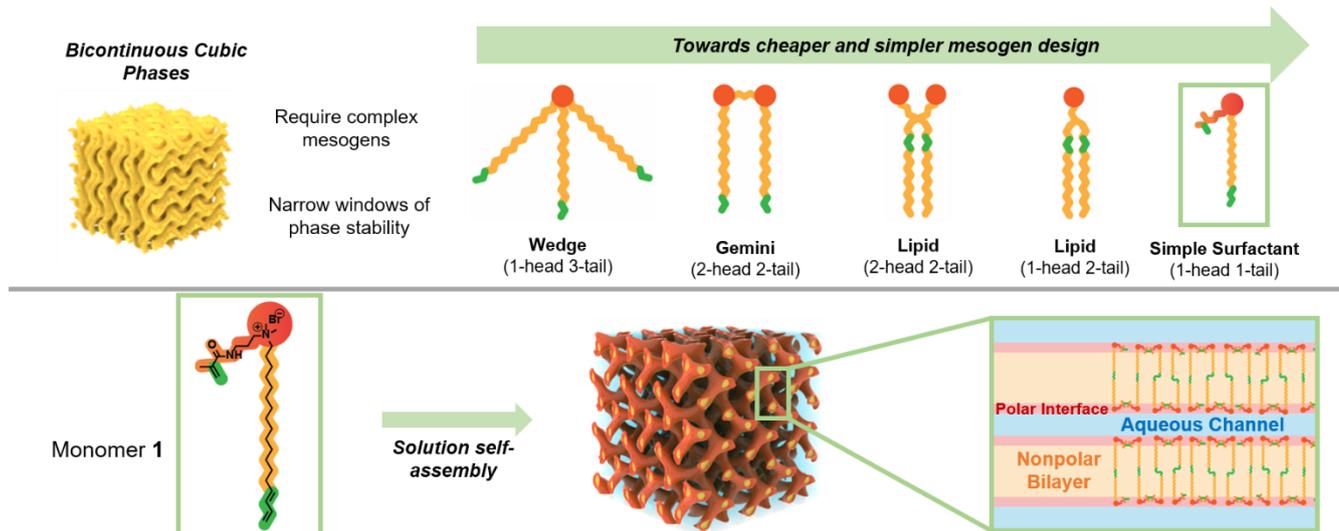


Fig. 1 Schematic of double-gyroid Q phase and typical cross-linkable LLC monomer architectures that form Q phases (red/orange = hydrophilic headgroup, yellow = hydrophobic tail, green = polymerizable group). The novel design of monomer **1**, as well its self-assembly into a nanoporous, normal-type, double-gyroid network, are also depicted.

with respect to long-term exposure to acidic and alkaline aqueous conditions, as well as to organic solvents of interest. Preliminary studies also show that the different polymerizable groups in the hydrophilic vs. hydrophobic regions of the monomer can be initiated non-selectively, or with some selectivity for one reactive group, via the use of different aqueous solutions for Q phase formation or radical photo-initiators with different solubilities. Experiments involving uptake of charged solutes and pressure-driven filtration of a neutral solute indicate the Q-phase networks have a pore diameter in the range of 1.5 nm, which agrees well with the calculated pore size based on SAXS data.

Monomer **1** was synthesized by reacting *N*-[3-(dimethylamino)propyl]methacrylamide with 18-bromooctadeca-1,3-diene²¹ in CH₃CN at 70 °C in a one-step S_N2 reaction. After purification, the structure and purity of **1** were verified by ¹H NMR, ¹³C NMR, FT-IR, and elemental analyses (see the ESI for details). The design of **1** was based on a non-cross-linkable cationic monomer with a single methacrylamide group near the head that was recently found to form a Q phase with aqueous solutions (i.e., monomer **2**, see Fig. 3 and ESI Fig. S1). By replacing the long alkyl tail on this monomer with a polymerizable diene tail, an intrinsically cross-linkable analogue was generated. The diene tail system was chosen because of its similarity in shape and hydrophobic character to regular *n*-alkyl tails compared to tail systems with bulkier or more polar polymerizable moieties,^{21,22} thereby increasing the probability of retaining the Q phase of the original monomer. Although not the focus here, **1** can also form other LLC mesophases such as lamellar and hexagonal (see ESI Fig. S6).

A Q phase was obtained at room temperature at a composition of 87.5/11.5/1.0 (w/w/w) monomer **1**/water/2,2-dimethylpropiophenone (DMPA, a radical photo-initiator). Polymer films with retention of the Q-phase structure (typical thicknesses between 50–150 μm) were obtained by photo-cross-linking the monomer mesophase with UV light under N₂ purge for ca. 3 h (Fig. 2a-c). The monomer mesophase and the resulting polymer films exhibited dark POM images, consistent

with the optically isotropic character of Q phases (Fig. 2d, e). SAXS spectra of the mesophase and polymer films (Fig. 2f) display the characteristic peaks associated with the (211) and (220) planes of the double-gyroid structure (space group *Im3d*), appearing at normalized scattering vector ratios of 1:√(4/3) (i.e., √8:√6). From these *q*-values, the lattice parameter *a* of the monomer mesophase and polymerized films was calculated to be 8.74 and 8.55 nm, respectively. No evidence of lattice swelling (i.e., change in *a*) was seen in dry vs. wet polymer films (see ESI Fig. S7).

The fabrication of a Q-phase nanostructured polymer film does not always guarantee stability of the Q-phase microstructure at the molecular level. The novel structural motif of **1**, with two chain-addition polymerizable groups at opposite ends of the molecule, affords significantly more Q-

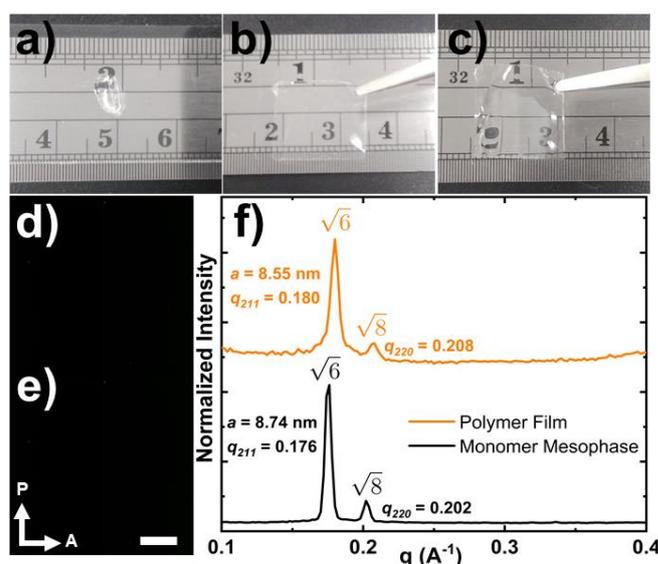


Fig. 2 Photos of (a) monomer gyroid mesophase of **1**, water, and photo-initiator, (b) dry polymer film of cross-linked gyroid phase of **1**, and (c) same polymer film of **1** after 30-min water immersion; POM micrographs of (d) monomer mesophase and (e) dry polymer film observed between crossed polarizers (scale bar = 100 μm); (f) SAXS spectra of gyroid mesophase and polymer of **1**.

phase stability when polymerized than monomer **2**, a similar Q-phase-forming monomer with only one polymerizable group (see ESI Fig. S1) or the combination of **2** and an added bifunctional cross-linker (1,10-decanediol dimethacrylate (DDMA)). Fig. 3a compares the SAXS spectra of Q-phase films made from **2** (left), **2** + DDMA (center), and **1** (right) after water immersion for ca. 24 h. In both cases involving **2**, the SAXS spectra show successful retention of the gyroid phase upon cross-linking. However, after water immersion of these gyroid polymer films, SAXS analysis shows disappearance or significant diminishment of the (220) (i.e., $\sqrt{8}$) peak, along with an increase in the primary peak width and a larger value of the lattice parameter, consistent with partial or total loss of the double-gyroid nanostructure. Speculatively, this loss of structure upon water exposure may originate from a combination of leaching of monomers that were not cross-linked to the polymer matrix, and molecular scale rearrangement for monomers linked only at a single site. In contrast, the polymer film made from intrinsically cross-linkable **1** exhibited negligible difference in the SAXS traces of as-made and water-immersed films, indicating the Q-phase structure is much more robustly locked-in at the molecular level. Further testing of the polymer films confirmed that the gyroid polymers are stable to at least 210 °C, and that they maintain their structure even after prolonged immersion in aqueous acid and base, as well as in organic and halogenated organic solvents (Fig. 3b). While there are prior reports of cross-linked gyroid structures produced from LLC monomers with more-complex structures, we are unaware of

LLC-derived nanostructured polymers with the remarkable thermal and chemical/solvent stability demonstrated here.

Preliminary studies also show that the methacrylamide and diene groups in the hydrophilic vs. hydrophobic regions of the monomer can be initiated non-selectively, or with some degree of selectivity for one reactive group over the other, with retention of the Q phase. When water was used to form the Q phase of **1** with DMPA as a hydrophobic photo-initiator, FTIR analysis showed that the diene tails were largely polymerized, but only a small fraction of the methacrylamide groups near the head was converted. However, when a 0.1 M aq. LiCl solution was used to form the phase instead of pure water, near-quantitative conversion of both the head and tail polymerizable groups was achieved (see ESI Fig.S8). We hypothesize that the increase in ionic strength of the aqueous phase may reduce the ability of the methacrylamides near the water/organic interface to reside near the aqueous phase, forcing them to reside more in the hydrophobic regions where the hydrophobic DMPA initiator and diene tails are located for more effective initiation of both groups. The use of 2-hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone (HHMP), an uncharged, water-soluble radical photo-initiator, showed complete conversion of both the head and tail polymerizable groups (see ESI Fig. S9), probably because its organic yet hydrophilic nature allows it to partition between the aqueous and organic domains and initiate groups residing in or near both. In each case, SAXS confirmed Q phase retention after partial or near-complete photopolymerization. Prior work on selective initiation of LLC monomers with two different polymerizable groups has only been demonstrated in vesicles for proof-of-concept;^{23–25} selective polymerization in a Q phase is unprecedented. Although completely independent initiation of one reactive group over the other has not been achieved yet, these results suggest that it may be possible to alter the mechanical properties of gyroid films of **1** by controlling the degree of polymerization in the head vs. tail regions.

The nanoporous nature of the cross-linked gyroid polymers makes them natural candidates for applications such as selective adsorption and nanofiltration (NF). These applications have been pursued in other polymerized LLC phases,²⁶ but the gyroid morphology is particularly valued because of its continuous percolated nature. The solvent and thermal stability of the cross-linked gyroid polymers suggest that they could be of interest in a wide range of selective transport applications, ranging from aqueous and organic solvent NF, to ion-conduction in ambient or harsh environments such as Li-ion batteries or alkaline fuel cells, respectively. The theoretical pore size of the aqueous channels separating the intertwined gyroid structures was estimated as ca. 1.5 nm, and the specific surface area is estimated to be in the ca. 500 m² g⁻¹ range (see the ESI).²⁷ Fig. 4a summarizes the uptake of various charged dyes into Q-phase polymer films of **1** immersed into aq. dye solutions for 72 h. The solute sizes reported are the calculated geometric mean dimensions of the molecules (see ESI Table S4). The films showed no discernible uptake of Methylene Blue (MB), which at 0.6 nm is smaller than the estimated aqueous channel size. This rejection is likely due to electrostatic repulsion between this

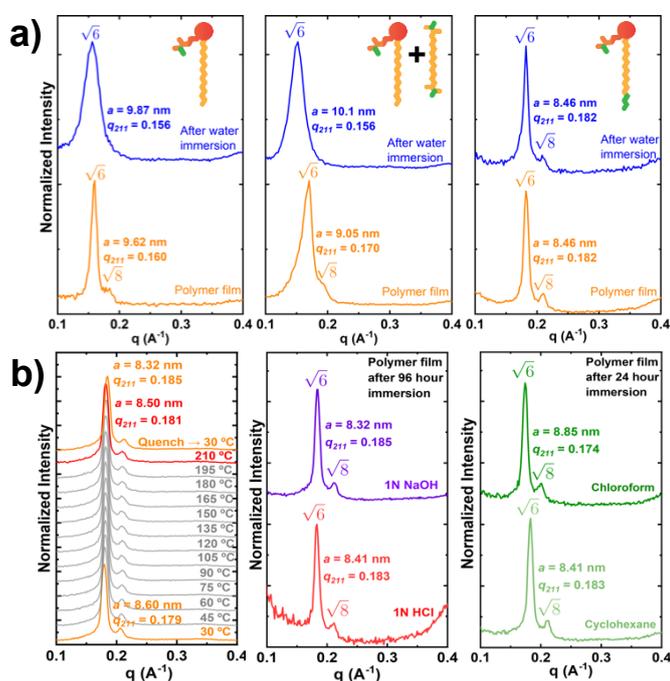


Fig. 3 (a) SAXS plots comparing degree of retention of double-gyroid phase after 24 h of water immersion for polymer films made from (left) monomer **2**; (center) monomer **2** + DDMA cross-linker; and (right) monomer **1**; (b) SAXS plots summarizing the stability of the gyroid nanostructure in monomer **1**-derived polymers at elevated temperatures, as well as in various solvent environments (at room temperature).

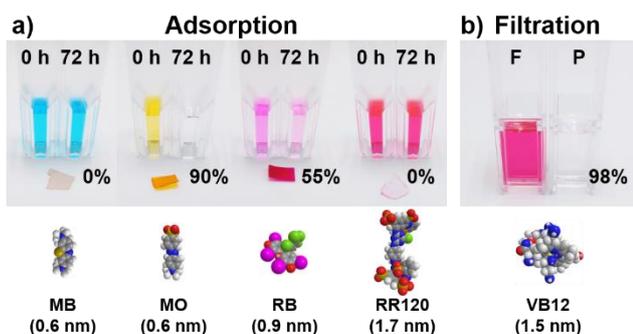


Fig. 4 (a) Photos of uptake of charged dyes into gyroid polymers. The rejection of small cationic Methylene Blue (MB) and large anionic Reactive Red 120 (RR120) indicates the polymers have charge- and size-based selectivity; (b) Photo of Vitamin B12 (VB12) feed (F) and permeate (P) obtained from pressure-driven filtration of gyroid polymer membranes of **1**, indicating 98% solute rejection.

cationic dye and the positively charged interior surfaces of the membrane pores due to the quaternary ammonium group on the surfactant. In contrast, the negatively charged dyes Methyl Orange (MO, 0.6 nm), Rose Bengal (RB, 0.9 nm), and Reactive Red 120 (RR120, 1.7 nm) were taken up by the polymer, but the amount adsorbed is a function of the size of the dye. The lack of discernible uptake of RR120 suggests that it is simply too large to enter the channels of the polymer, despite favourable electrostatic attraction. These results qualitatively indicate that the pore size lies between 0.9 and 1.7 nm. This range of length scales is of interest for NF, as recently demonstrated in other LLC-based membranes.²⁶ Fig. 4b shows a photograph of the permeate from the pressure-driven filtration of a Vitamin B12 feed (VB12, 1.5 nm) through a ca. 100- μm -thick gyroid polymer film of **1**. The near-complete (98%) rejection of uncharged VB12 suggests that the effective pore size is in the range of 1.5 nm, consistent with our estimate from SAXS data. The thickness-normalized permeability of the films is roughly $0.1 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1} \mu\text{m}$, which agrees well with previously reported NF data on cross-linked Q-phase films with similar pore sizes but made using more-complex LLC monomers.^{15, 28}

In conclusion, we report a novel intrinsically cross-linkable surfactant motif for the formation of nanoporous polymer films with a gyroid Q-phase structure. SAXS and POM data confirm the successful retention of the gyroid nanostructure in the cross-linked polymer films. The benefit of having two polymerizable groups (as opposed to one) on the monomer is illustrated by comparing the long-term stability of the polymeric films upon water exposure. The solvent and temperature stabilities of the fabricated gyroid films indicate their potential for separations applications. Lastly, the transport performance (i.e., effective pore size based on rejection, and water permeability) of the fabricated gyroid films has been studied. The results motivate further study and optimization of this platform based on a novel LLC monomer motif.

C.O.O. and O.Q.I. acknowledge NSF support through CBET 2010890. C.O.O. also acknowledges NSF support through DMR-1945966. The authors acknowledge use of the DEXS facility at the Univ. of Pennsylvania (NSF MRSEC 1720530), the purchase of which was made possible by NSF MRI 1725969, ARO DURIP W911NF-17-1-0282, and the Univ. of Pennsylvania. P.L. and D.L.G. thank the Joint Science and Technology Office for

Chemical Biological Defense (JSTO CBD) for funding under CB10872.

There are no conflicts to declare.

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