



Soft Matter

Effects of Structural Modification of (Alkyldiene-Imidazolium Bromide)-Based Gemini Monomers on the Formation of the Lyotropic Bicontinuous Cubic Phase

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Effects of Structural Modification of (Alkyldiene-Imidazolium Bromide)-Based Gemini Monomers on the Formation of the Lyotropic Bicontinuous Cubic Phase

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Seven homologues of an amphiphilic gemini monomer were synthesized and screened for the ability to form a bicontinuous cubic (Q) lyotropic liquid crystal phase. Four of these homologues form a Q phase with glycerol or water that can be cross-linked with retention of the nanoporous structure, with one exhibiting a well-ordered Q phase with a wider phase window than the parent monomer.

Introduction

Lyotropic liquid crystal (LLC) mesogens are amphiphilic molecules (i.e., surfactants) that self-assemble in the presence of aqueous or polar liquids to form ordered, phase-separated structures with monodisperse, nanometer-scale, hydrophilic channels (i.e., LLC phases).¹ These hydrophilic channels can have different dimensionalities and shapes, depending on the type of LLC phase formed (i.e., 1D hexagonal (H) phases, 2D lamellar (L) phases, 3D-interconnected bicontinuous cubic (Q) phases) and on whether the phase curves around the hydrophobic domains (i.e., normal/Type I) or the hydrophilic domains (inverted/Type II).¹ By using reactive amphiphiles (i.e., LLC monomers), LLC phases can be cross-linked in situ to preserve the phase microstructure to form stable, ordered polymer networks with hydrophilic nanopores.² These materials have been used for templated nanocomposite synthesis,² heterogeneous catalysis,² molecular size separations,² and enhanced ion transport.³

Q phases are particularly attractive for many materials applications compared to other LLC phases because their periodic, 3D-interconnected pores do not need to be aligned for good transport and have a low probability of being blocked

during membrane applications.⁴ The formation of a particular LLC phase is usually composition-, temperature-, and pressure-dependent,¹ but LLC phase formation can also be influenced by altering the shape or packing structure of the amphiphile.⁵ However, the design of LLC monomers that form Q phases and control of their phase behaviour have not been straightforward, historically. This is because Q phases are considered intermediate structures between the L and H phases in terms of curvature and interfacial energy,^{1, 6} and amphiphile shape-based packing approaches to LLC phase formation do not explain Q systems.⁵ Indeed, LLC monomer shape motifs known to form Q phases have ranged from symmetric gemini amphiphiles,⁷⁻¹⁰ wedge-shaped amphiphiles,¹¹ traditional lipid-like amphiphiles,¹² modified lipid-like amphiphiles,¹³ and even simple one-head/one-tail amphiphiles.¹⁴⁻¹⁶

Several years ago, our group developed an (alkyldiene-imidazolium bromide)-based gemini (i.e., bridged two-head/two-tail) LLC monomer (**1**) (Fig. 1) that forms a Type I bicontinuous cubic (Q_I) phase with water or glycerol.¹⁶ Monomer **1** is modular and economical to synthesize compared to past Q-phase LLC monomers developed in our group.¹⁷ It can also be processed into thin-film composite (TFC) membranes that perform molecular-size-based water nanofiltration and desalination¹⁷ as well as selective vapor separations.¹⁸ However, despite the versatility of monomer **1**, it has limitations in terms of utility due to its very narrow Q_I-phase window with respect to temperature and system composition.¹⁷

It has been empirically shown that the nature of the hydrophilic headgroups, the length of the linker between the headgroups, the length and type of the hydrophobic tails, and the position of the bridge linker unit relative to the ionic headgroups can affect Q phase formation/stability and nanopore size for ionic gemini LLC mesogens in general.^{1, 8-10, 19-21} However, only very preliminary studies have been conducted on the effect of structural variations on the formation of the Q_I phase for the (alkyldiene-imidazolium bromide) gemini LLC monomer platform. Specifically, only a very small number of homologues were initially synthesized in order to identify an

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Electronic Supplementary Information (ESI) available: Full details on synthesis, and structural characterization of the homologues of **1**; preparation and cross-linking of their LLC mixtures with glycerol and water; elucidation of their phase diagrams with these solvents; and identification of the phases formed. See DOI: 10.1039/x0xx00000x

initial suitable Q_i-phase candidate (i.e., monomer **1**) for polymerization and membrane studies.¹⁹ Qualitative analysis revealed that the few homologues initially synthesized had the potential to adopt a Q phase.¹⁷ However, the suspected Q phases were never confirmed, and structure-property trends for the effects of headgroup spacer length and polymerizable diene tail length on Q_i phase formation have not been elucidated for this gemini monomer platform.¹⁷

Herein, we present the synthesis and LLC phase characterization of a series of seven homologues of (alkyldiene-imidazolium bromide) gemini monomer **1** that span headgroup alkyl spacer lengths from four to nine carbons and polymerizable diene tails with a total length of either 14 or 18 carbons (Fig. 1). Five of these homologues are new compounds; the other two have been synthesized previously and showed a possible, unconfirmed Q phase but have not been fully characterized in terms of LLC phase behaviour.¹⁷ Their ability to form Q phases in glycerol and water was characterized using a combination of polarized light microscopy (PLM) and powder X-ray diffraction (PXRD) analysis to generate partial phase diagrams up to a temperature of 95 °C. It was found that four of these seven homologues formed a Q phase when blended with either glycerol or water at elevated temperatures. Of the four homologues that formed a Q phase, three were centered around headgroup alkyl spacers in the five- and six-carbon range, regardless of the two polymerizable tail lengths explored. The remaining homologue formed a weakly-ordered Q phase and had a nine-carbon headgroup spacer and an 18-carbon diene tail. Two of these four homologues had exhibited a wider Q-phase window than **1** in terms of temperature and composition range, but only one had a broader Q phase with a degree of order comparable to that of **1**. Additionally, the formed Q phases of these homologues could be radically photo-cross-linked with retention of the phase microstructure to form free-standing, transparent bulk films.

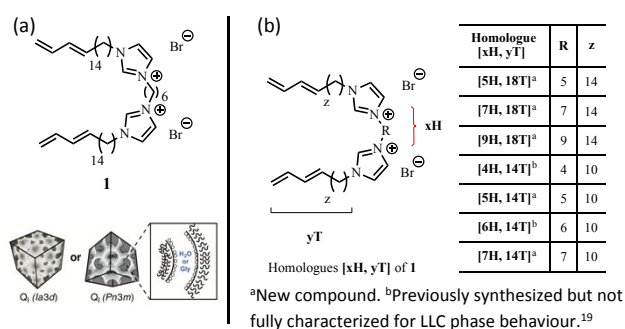


Fig. 1. (a) Structure of monomer **1** and schematic representations of the Q_i phase that it forms. (Partially reproduced from Ref. 9 with permission. Copyright American Chemical Society, 2007.) (b) Structures of the homologues of **1** prepared and studied in this work.

Results and Discussion

For simplicity of correlating structure with name, the seven monomer homologues shown in Fig. 1b are labeled as [xH, yT], where **x** refers to the total number of carbons in the headgroup spacer unit and **y** refers to the total number of carbons in the

diene tails. These homologues were synthesized via S_N2 chemistry by reacting 2.3 equivalents of the appropriate-length bromoalkyl-1,3-diene^{22, 23} with 1.0 equivalent of the desired alkyl-bridged bis(imidazole)^{24–26} in CH₃CN at 75 °C. After purification, the structure and purity of these homologues were verified by ¹H NMR, ¹³C NMR, FT-IR, and elemental analyses (see the ESI for full details). Because our main motivation in this work was to probe structure-property effects on Q-phase formation for this gemini monomer platform, we chose headgroup alkyl spacer lengths centered about the original six-carbon headgroup spacer of **1**. 14- and 18-Carbon diene tail units were chosen for this detailed homologue study because these two polymerizable tails are the most readily synthesized from economical and available starting materials of the ω-bromoalkyl-1,3-diene tail systems reported in literature.^{22, 23}

The LLC phase behaviour of these homologues was elucidated in the following manner: First, qualitative PLM-based penetration scan screening was performed on each homologue mixed with glycerol and separately water to determine which showed potential Q phase formation.^{1c} This rapid LLC phase screening technique involved placing a sample between a microscope slide and cover slip and adding solvent to the edge of the cover slip to create a concentration gradient. The sample was then heated from 25 to 95 °C, and the optical textures observed were used to identify potential LLC phases formed. Specifically, a dark, isotropic band between two birefringent LLC phases indicated a potential Q phase.¹ Partial phase diagrams were then elucidated via PLM analysis of mixtures containing either glycerol or water, with a focus on quantitatively identifying any Q phase regions. In this procedure, candidates that showed evidence of a potential Q phase by penetration scan screening were blended with glycerol or water to create a systematic series of compositions ranging from 5 to 95 wt. % monomer. Each composition was then analyzed via variable-temperature PLM from 25 to 95 °C, using changes in PLM optical texture with temperature as phase transition points in order to plot the boundaries between different phases (see the ESI for full details). The general LLC phase behaviour of the homologues was elucidated using this procedure. It should be noted that homologue [7H, 14T] was not investigated further because it is a liquid at ambient temperature and thus not a viable candidate for forming ambient- or elevated-temperature LLC phases.

Quantitative identification of suspected Q phases (and other LLC phases) was done by room-temperature PXRD analysis of radically cross-linked bulk films of compositions located in the middle of each phase region (as identified by PLM), and/or by variable-temperature PXRD (VT-PXRD) analysis of unpolymerized LLC mixtures that were near the middle of the target phase region. In particular, Q phases can be identified by the presence of a black PLM optical texture and PXRD *d*-spacings with a ratio of 1/√6: 1/√8... (see the ESI).^{1, 4} (However, the Q phase space group could not be determined due to the limited number of observable PXRD peaks). Cross-linked films of LLC mixtures (typical thickness: ca. 180 μm) were prepared by hand-mixing and centrifuging the appropriate amount of monomer and solvent with 1 wt. % 2-hydroxy-2-methylpropiophenone (HMP, a radical photo-initiator) and

irradiating the mixtures under 365 nm UV light for 1 h with heating if necessary (see the ESI for full details). PXRD of cross-linked samples allowed for convenient quantitative confirmation of LLC phases at room temperature and avoided the potential risks of perturbing LLC phase formation through solvent evaporation or ambient water uptake. PXRD of cross-linked compositions also revealed if particular LLC phases of a homologue could be retained after photopolymerization. VT-PXRD analysis of unpolymerized LLC mixtures for phase identification was used to check other non-Q-phase boundaries, or when PXRD analysis of a cross-linked composition point within a suspected Q-phase region was not informative enough to draw conclusions on the phase. To help confirm the structure of the Q phase formed by [5H, 18T] (i.e., our most promising homologue from PLM and PXRD analysis), a polymerized bulk film was sent to collaborators for more-detailed SAXS analysis, which is outside of our routine PXRD capabilities (see the ESI).

Table 1 summarizes the Q-phase formation behaviour of the homologues of monomer 1 evaluated by the aforementioned techniques. When potential Q-phase-forming homologues were mixed with glycerol, only homologues [5H, 18T] and [9H, 18T] demonstrated the ability to form a Q phase with glycerol only but not water. Relative to parent monomer 1, both [5H, 18T] and [9H, 18T] resulted in Q phases with wider phase windows in terms of temperature and lyotropic composition (Fig. 2). However, only [5H, 18T] exhibited both a wider Q-phase window and comparable Q-phase order compared to monomer 1 (see Figs. 2 and 3). These trends for glycerol mixtures suggest that longer polymerizable diene tails coupled with headgroups with shorter alkyl spacers may favor a wider Q-phase window. To our surprise, [7H, 18T] did not demonstrate the ability to form a Q phase with glycerol, despite having an alkyl headgroup spacer intermediate in length between 1 and [9H, 18T]. It should be noted that a homologue of 1 with a four-carbon alkyl headgroup spacer and 18-carbon diene tails (i.e., [4H, 18T]) was previously synthesized by our group; however, it also did not exhibit a potential Q phase in glycerol during initial screening.¹⁷

Table 1. Summary of Q-phase behaviour of monomer 1 homologues as determined by PLM and PXRD analysis of mixtures to elucidate (partial) phase diagrams.

| Homologue [xH, yT] | Glycerol | Water |
|------------------------|------------------------|---------------------------|
| [5H, 18T] ^a | Q phase | No Q phase (I phase only) |
| [7H, 18T] ^a | No Q phase | No Q phase (I phase only) |
| [9H, 18T] ^a | Weakly ordered Q phase | No Q phase |
| [4H, 14T] ^b | No Q phase | No Q phase |
| [5H, 14T] ^a | No Q phase | Weakly ordered Q phase |
| [6H, 14T] ^b | No Q phase | Weakly ordered Q phase |
| [7H, 14T] ^a | No Q phase | No Q phase |

^aNew compound. ^bPreviously made but not fully characterized for LLC behaviour.¹⁷

When the potential Q-phase-forming homologues were mixed with water, only homologues [5H, 14T] and [6H, 14T] demonstrated the ability to form a Q phase via PLM and PXRD analysis. Despite the fact that both [5H, 14T] and [6H, 14T] were able to form a Q phase with water, PXRD analysis revealed that the Q phase order was weaker than the Q phases of 1 and [5H,

18T]. Homologue [4H, 14T] demonstrated the potential to form a Q phase via initial PLM penetration scan screening (see ESI Fig. S4); however, during phase diagram elucidation via PLM and PXRD, no data indicating a pure Q phase were observed. From Table 1 and the behaviour of parent monomer 1, it appears that polymerizable diene tail length has the greatest overall impact on the ability of the (alkyldiene-imidazolium bromide) gemini monomer platform to form a Q phase in glycerol or water, with the most well-ordered Q phases centered about homologues with five- and six-carbon headgroup spacer lengths. No attempts were made to explore longer alkyl headgroup spacers because based on the observed trends, we believed that the Q phase would either not form or only less-ordered Q-phases than that of [9H, 18T] would form.

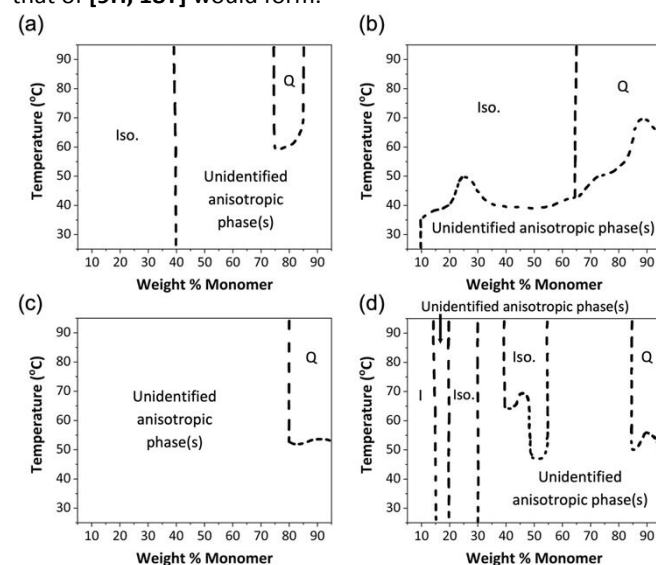


Fig. 2. Partial phase diagrams of the four Q-phase-forming homologues: (a) [5H, 18T] with glycerol; (b) [9H, 18T] with glycerol; (c) [5H, 14T] with water. (d) [6H, 14T] with water. I = discontinuous cubic phase; Iso. = amorphous isotropic phase (i.e., no order by PXRD); Q = bicontinuous cubic phase. Heterogeneous regions omitted. Note: Phase diagrams mapped out at Boulder, CO (altitude = 5,328 ft, ambient pressure = ca. 623 torr); they may be slightly different at other altitudes.

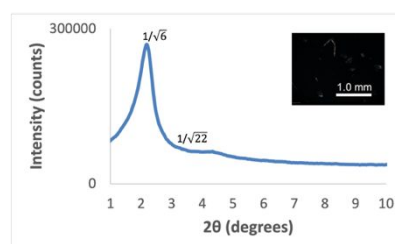


Fig. 3. PXRD profile of a bulk cross-linked Q-phase film prepared from a mixture of [5H, 18T]/glycerol/HMP (79:20:1 (w/w/w)). Inset: PLM optical texture (50x)

During the process of quantitatively determining the LLC phase boundaries, it was found that some aqueous LLC mixtures of [5H, 18T] and [7H, 18T] containing relatively low weight percentages of monomer (i.e., ca. ≤50 wt. %) also displayed some physical traits of the Q phase (i.e., black PLM optical texture, relatively viscous). However, for original LLC monomer 1, the Q_i phase forms at very high weight percentages of monomer (≥85 wt. %) relative to solvent.¹⁷ The fact that some PXRD order was observed for these low-amphiphile-content aqueous mixtures of [5H, 18T] and [7H, 18T] indicated that a

different type of an ordered, isotropic phase other than Q_i was likely present. We attributed these optically isotropic, ordered phases to be a discontinuous cubic micellar (I) phase (i.e., a cubic-packed array of spherical micelles) based on correlation of the observed PLM and PXRD data with literature information on such I phases (see the ESI for PXRD analysis).^{27, 28}

It should be noted that the Q phases identified for [5H, 18T], [9H, 18T], [5H, 14T], and [6H, 14T] are most likely a Q_i phase, based on the LLC phase behaviour of parent monomer **1** and the structural similarity of these homologues to **1**. To unequivocally confirm a Q_i or Q_{ii} phase, an L phase needs to be present in the phase diagram as a central reference point so that phases on the solvent-excessive side of the L phase can be assigned as Type I (normal) and ones on the solvent-deficient side can be assigned as Type II (inverted).¹ Unfortunately, none of the homologues investigated in this study that form a Q phase exhibited an identifiable L phase for this determination.

Conclusions

In summary, seven (alkylidene-imidazolium bromide)-based gemini monomer homologues were synthesized, and their ability to form the Q phase in glycerol and in water was explored. Although four of these monomers demonstrated the ability to form a Q phase, only homologue [5H, 18T] displayed a wider Q-phase window than the original monomer **1** while maintaining comparable Q-phase order. For this gemini imidazolium monomer platform, it appears that Q-phase formation is favored for homologues that have five- and six-carbon headgroup alkyl spacers, regardless of whether the diene tail is 14 or 18 carbons long. Additionally, well-ordered Q phases only appear to form for homologues with those headgroup spacer lengths if they also have the 18-carbon polymerizable diene tail and are blended with glycerol. Given that [5H, 18T] forms a Q phase with wider temperature and composition tolerances than monomer **1** and retains its phase structure after cross-linking, we are interested in testing TFC Q membranes of this new homologue. The next stage of this research is to determine if [5H, 18T] membranes have a different nanopore size or different separation performance compared to membranes made with monomer **1**.

Acknowledgments

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Conflicts of interest

There are no conflicts to declare.

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