

Polymerization of a Phosphonium Diene Amphiphile in the Regular Hexagonal Phase with Retention of Mesostructure

Bradford A. Pindzola, Benjamin P. Hoag, and Douglas L. Gin*

Department of Chemistry, University of California Berkeley, California 94720-1460

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A promising approach to the design of functional, nanostructured materials is the polymerization of amphiphilic monomers in lyotropic liquid crystalline (LLC) phases (Figure 1).¹ Previous work has shown that it is possible to polymerize reactive amphiphiles in the lamellar (L),^{1c} inverted hexagonal (H_{II}),^{2–6} and bicontinuous cubic (Q_{II})³ phases with retention of nanostructure. These polymerized assemblies have been used as biomembrane mimetics,^{1c} scaffolds for functional nanocomposites,^{5–10} catalytic organic zeolite analogues,¹¹ and media for potential bioencapsulation and controlled-release applications.^{1b}

Polymerization of amphiphiles in the regular hexagonal (H_I) phase would afford ordered arrays of either linear polysoaps or, with cross-linking, polymer nanofibrils. These ordered polysoaps and nanofibrils could be useful for nanocomposite synthesis or as novel mineralization platforms, in much the same way as lipid microtubules.^{12–14} Initial work by Luzatti and co-workers employed a cross-linker to stabilize the phase but afforded network gels rather than discrete fibrils.² Additionally, a number of attempts to homopolymerize amphiphilic monomers in the H_I phase have been made but resulted in either loss of phase or low degrees of conversion.^{15–18} Friberg and co-workers observed complete conversion to the L phase when attempting to polymerize sodium 11-undecenoate in the H_I phase.^{15,16} McGrath reported radical polymerization of 11-undecenyltrimethylammonium bromide in the H_I phase with retention of mesostructure, but the reaction only proceeded to ca. 40% conversion.¹⁴ Shibasaki reported similar results with salts of 10-undecenoic acid.¹⁵

Previous homopolymerization studies in the H_I phase all employed amphiphiles with an unactivated terminal olefin as the

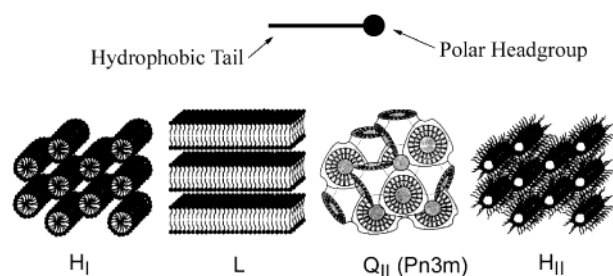
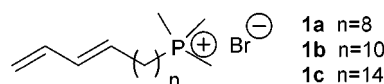


Figure 1. Schematic of a generic LLC mesogen and an illustration of some common LLC phases.

polymerizable moiety, likely contributing to the limited success of these systems. Herein, we report a new family of LLC monomers that can be homopolymerized in the H_I phase at ambient temperature with retention of phase mesostructure and with a degree of polymerization greater than 90%. The soluble polysoap from homopolymerization can be diluted to an isotropic solution or desiccated, and it reversibly re-forms the H_I phase upon returning to the original concentration.¹⁹ Additionally, the LLC monomers can be copolymerized with divinylbenzene (DVB) to generate a cross-linked structure, again with retention of the nanostructure. These amphiphiles incorporate a polymerizable hydrocarbon 1,3-diene tail and a phosphonium headgroup.²⁰ The diene tail is more reactive than a terminal alkyl olefin and is closer in character to *n*-alkyl chains than traditional (meth)acrylate and styrenic groups. Additionally, the larger phosphonium group should better direct the formation of the H_I phase²¹ and give enhanced X-ray diffraction contrast²² compared to the corresponding ammonium or carboxylate groups.



Three phosphonium diene mesogens (**1a–c**) were synthesized from the corresponding ω -bromoalkyldienes by reaction with trimethylphosphine in 2-propanol at 85 °C.²³ The ω -bromoalkyldienes were prepared from the reaction of a ω -bromoalkanal with Matteson's reagent²⁴ and subsequent acid-catalyzed elimination, as described previously.²⁵ The ω -bromoalkanal was synthesized by PCC oxidation of the appropriate ω -bromoalkanol.¹⁹

Compound **1b** demonstrated the best LLC behavior and will be the focus of this communication.²⁶ A two-component amphiphile/water, and three-component amphiphile/water/DVB phase diagram were prepared for **1b** using polarized light microscopy (PLM) to map the phase boundaries and X-ray diffraction (XRD) to confirm the identity of each phase region. The two-component phase diagram of **1b** and water exhibits the H_I phase from 50 to 75 wt % amphiphile between 25 and 80 °C. Additionally, **1b** exhibits a Q_{II} phase from 75 to 85 wt % amphiphile at 37–75 °C, and a L phase between 85 and 95 wt % amphiphile from 63

(19) See Supporting Information.

(20) Polymerizable analogues of alkyltrimethylammonium salts (which are known to form the H_I phase) containing (meth)acrylate and styrene groups were synthesized initially. However, these compounds did not exhibit significant LLC behavior.

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(26) When mixed with water, compound **1a** has a smaller H_I domain than **1b** (ca. 65–85 wt %). Compound **1c** forms phases above 30 °C but has no H_I phase.

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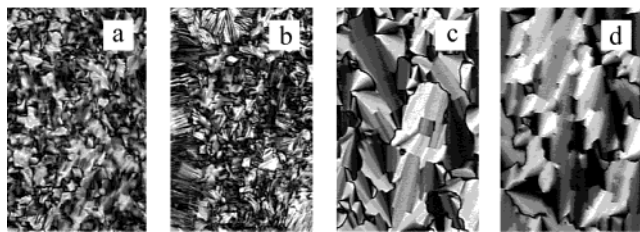


Figure 2. PLM images at 24 ± 1 °C ($12.6\times$) of (a) H_1 phase of 57/39/4 (w/w/w) (**1b**/H₂O/DMPAP) before polymerization, (b) same composition after polymerization, (c) ($25.2\times$) 55/35/1/9 (w/w/w/w) (**1b**/H₂O/DMPAP/DVB) before polymerization, and (d) same composition after polymerization.

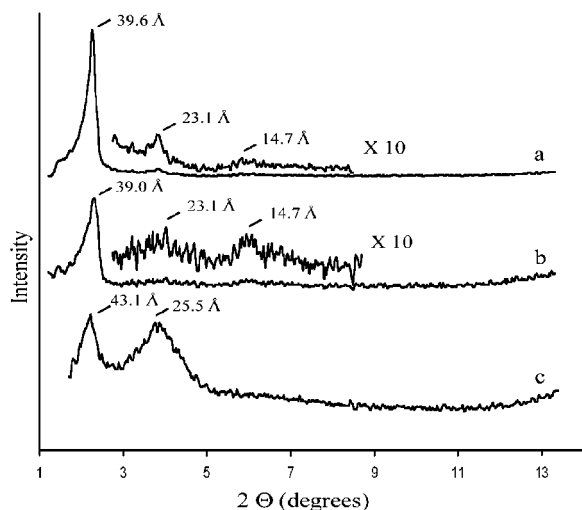


Figure 3. XRD profiles of (a) H_1 phase of 57/39/4 (w/w/w) **1b**/H₂O/DMPAP before polymerization, (b) same composition after polymerization, and (c) 55/35/1/9 (w/w/w/w) **1b**/H₂O/DMPAP/DVB after polymerization.

to at least 80 °C. From the three component mixture of **1b**, H₂O, and DVB, it can be seen that the H_1 phase can incorporate up to about 10 wt % DVB. Figure 2a shows a representative optical texture of the observed H_1 phase containing 2,2-dimethoxy-2-phenyl-acetophenone (DMPAP) as a photoinitiator, and Figure 3a shows an XRD profile of the same H_1 phase showing the expected peak ratio of $1:1/\sqrt{3}:1/\sqrt{4}:1/\sqrt{7}$.

Homopolymerization studies were performed on samples composed of 57/39/4 (w/w/w) **1b**/H₂O/DMPAP. Copolymerization studies with added DVB cross-linker were performed on samples with a composition of 55/35/1/9 (w/w/w/w) **1b**/H₂O/DMPAP/DVB. The samples were then irradiated with 365 nm light for 16–20 h at 24 ± 1 °C.

Samples polymerized without DVB remain anisotropic and display an optical texture very similar to that of the initial H_1 phase (Figure 2b). The XRD pattern shows slightly reduced peak intensities (Figure 3b) but suggests that the H_1 structure is intact. ¹H NMR analysis of the resulting homopolymer revealed almost complete disappearance of the 1,3-diene peaks at 5.04, 5.66, and 6.00 ppm, and the concomitant appearance of a broad olefin peak at 5.30 ppm, indicating ca. 90% conversion. The behavior of this

system is in contrast to the phase-change observed by Friberg,^{15,16} and the low conversions reported by Shibasaki¹⁷ and McGrath.¹⁸

Samples containing DVB cross-linker also retained their structure, as can be seen from the PLM textures (Figure 2c) and XRD profiles (Figure 3c). The optical texture changed very little. In the XRD pattern, the intensity of the primary peak decreases significantly, but a relatively strong second peak is observed corresponding to expected hexagonal spacing.²⁷ In this case, the behavior of our system is similar to that reported by Luzzati using styrene-based amphiphiles.²

The irradiated phases also display different thermal behavior compared to the initial LLC phases, consistent with a formation of polymer. Prior to photopolymerization, the optical texture of the H_1 phase of **1b** without DVB clears at 85 °C. In contrast, the homopolymerized sample does not clear, but instead the optical texture transforms at 150 °C to a lamellar mosaic texture. The optical texture of the H_1 phase of **1b** containing DVB prior to irradiation clears between 68 and 72 °C. After photopolymerization, the observed texture is stable up to 220 °C.

To obtain more information on the structure and connectivity of **1b** homopolymerized in the H_1 phase, the sample was examined by FT-IR spectroscopy. The sample exhibited a strong stretch at 983 cm^{-1} , characteristic of *trans*-1,4-polymerization, and showed no evidence of peaks at 735 or 910 cm^{-1} resulting from *cis*-1,4- and 1,2-polymerization, respectively.²⁸ The IR spectra of a control sample of **1b** photopolymerized in an isotropic aqueous phase (1 wt % amphiphile) with the same ratio of initiator also showed features indicative of solely *trans*-1,4-polymerization. Therefore, the polymer derived from polymerization in the H_1 phase appears to be structurally similar to that obtained from an isotropic polymerization.

In summary, we have developed a new polymerizable amphiphile that can be homopolymerized or copolymerized with DVB in the H_1 phase with retention of the mesostructure. To our knowledge, this is the first example of a homopolymerizable H_1 system that both retains its phase and reaches a high degree of conversion. Further studies will examine the molecular weight and polydispersity of the linear polymers, explore their potential in composite materials, and investigate the possibility of polymerization and cross-linking in the Q_{II} phase.

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Supporting Information Available: Full experimental details and characterization data for compounds and polymers synthesized in this study; phase diagrams for **1b**; ¹H NMR and IR spectra illustrating polymer conversion and structure (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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