

# Polymerized Lyotropic Liquid Crystal Assemblies for Materials Applications

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## ABSTRACT

The development of functional materials with nanometer-scale architectures and the effect of these architectures on their chemical and physical properties are currently of great interest in materials design. Polymerizable lyotropic liquid crystal (LLC) assemblies provide a facile entry into this area by allowing one to fix the inherent order in these systems using covalent bonds to create robust, nanostructured materials. The use of the cross-linked inverted hexagonal phase in templated nanocomposite formation and heterogeneous catalysis has been demonstrated. Additionally, the polymerization of LLC mesogens in the regular hexagonal and bicontinuous cubic phases is being targeted for future developments in functional materials. Future directions for new applications of these materials are also discussed.

## Introduction

Lyotropic liquid crystal (LLC) mesogens are amphiphilic molecules containing one or more hydrophobic organic tails and a hydrophilic headgroup.<sup>1</sup> The amphiphilic character of these molecules encourages them to self-organize into aggregate structures in water, with the tails forming fused hydrophobic regions and the hydrophilic headgroups defining the interfaces of phase-separated aqueous domains. These aggregates can be relatively simple individual structures such as micelles and vesicles or highly ordered yet fluid condensed assemblies with specific nanometer-scale geometries known collectively

as LLC phases (Figure 1).<sup>1,2</sup> Unlike thermotropic LC phases, which are typically composed of a single compound and possess primarily temperature-dependent phase morphology,<sup>1</sup> LLC phases are mixtures that have wide regions of stability with respect to temperature, pressure, and system composition.

LLC phases and amphiphile self-assembly have immediate relevance in biology because of the prevalence of organized lipid structures in living systems. However, one of the most promising new research directions for LLC assemblies is their use in the construction of nonbiological, nanostructured organic materials.<sup>3,4</sup> LLC phases have many virtues that make them ideal for this role. Their architectures are well suited for the incorporation of hydrophobic and hydrophilic reagents in separate domains with well-defined nanoscale geometries. In addition, the amphiphilic self-assembly process localizes the headgroups of the LLC mesogens exclusively at the hydrophilic/hydrophobic interface with the groups oriented toward the hydrophilic domains. This arrangement presents a unique opportunity to engineer the environments in those regions for specific applications via choice of LLC headgroup and solvent. Finally, LLC mesogens offer excellent control over phase geometry and symmetry on the nanometer-scale level via molecular design. This control can be extended to the macroscopic scale through appropriate alignment techniques. With the current interest in nanoscience<sup>5</sup> and, in particular, nanostructured materials, LLC assemblies are especially attractive for the design of nanoscale systems for targeted materials applications. The only caveat with LLC phases is that they are inherently fluid, and hence lack the robustness required for many materials applications.

Polymerizable or cross-linkable LLC mesogens are a viable solution to this problem. These reactive amphiphiles aggregate into the same types of assemblies as their nonpolymerizable analogues, but they can be covalently linked to their nearest neighbors in situ to form robust polymers or networks that retain their original microstructure over a wide range of physical and chemical conditions. Micelles,<sup>6</sup> inverse micelles,<sup>7</sup> and microemulsions<sup>8</sup> are easily polymerized with retention of phase microstructure. The resulting polymeric materials have been used for applications<sup>4</sup> such as controlled colloidal particle synthesis. Lamellar assemblies such as vesicles,<sup>9</sup> lipid microtubules,<sup>10</sup> and the lamellar (L) phase<sup>9</sup> have also been successfully polymerized in the past. These polymers have found utility as biomembrane models,<sup>9</sup> drug delivery agents,<sup>9</sup> anisotropic metalization and mineralization templates,<sup>10,11</sup> and templates for layered nanocomposites.<sup>12</sup> The polymerization of the more geometrically complex, nonlamellar LLC phases, however, has been more problematic due to difficulties in phase retention upon polymerization.<sup>13</sup> The successful polymerization of amphiphiles in the normal hexagonal (H<sub>I</sub>) and inverted hexagonal (H<sub>II</sub>)

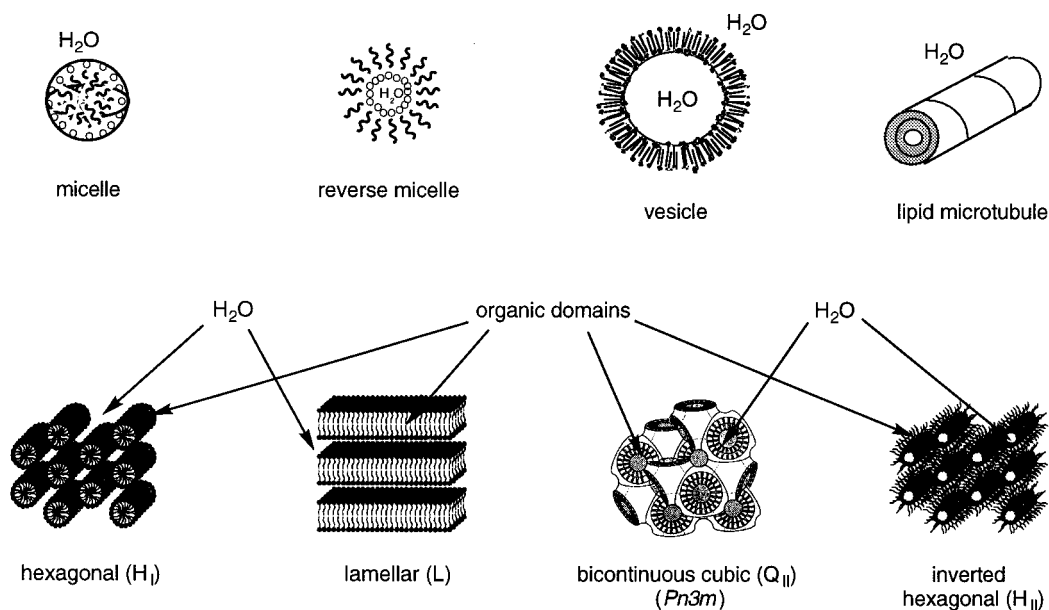
Douglas L. Gin was born in Ashcroft, BC, Canada, in 1966. He received his B.Sc. from the University of British Columbia in 1988 and his Ph.D. from Caltech with Robert H. Grubbs in 1993. After postdoctoral work with Alan G. MacDiarmid at the University of Pennsylvania, he began his independent research career in the Chemistry Department at the University of California, Berkeley, in 1994. He is currently Associate Professor of Chemical Engineering, and Chemistry & Biochemistry at the University of Colorado at Boulder.

Weiqiang Gu was born in 1966 in Jiangsu province, China. After receiving his B.S. (1988) and M.S. (1991) from Fudan University, he obtained his Ph.D. with Richard G. Weiss from Georgetown University in 2000. He is currently a postdoctoral associate with D. L. Gin, working on Lewis acid catalysis and membrane development with nanostructured materials.

Brad Pindzola was born in 1975 in Great Falls, Montana. He received his B.A. (1997) from Carleton College and is currently finishing his Ph.D. degree at the University of California, Berkeley with D. L. Gin. His work focuses on the design and synthesis of lyotropic mesogens for polymerization in nonlamellar phases.

Wen-Jing Zhou was born in Shandong, China, in 1966. After obtaining his B.S. (1989) and M.S. (1992) at Shandong University, he completed his Ph.D. at the University of California, Davis, in 1999 with Mark J. Kurth. He then did postdoctoral work with D. L. Gin and is currently with DuPont Powder Coatings.

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**FIGURE 1.** Common aggregate structures (top row) and LLC phases (bottom row) of amphiphiles in water.

phases was first reported in 1963,<sup>14</sup> but unfortunately with little characterization detail. Additional work in this area did not appear again until the 1990s.<sup>13,15–18</sup> During that time, the first reports of the successful cross-linking of the bicontinuous cubic ( $Q_{II}$ ) phases also appeared.<sup>19</sup> O'Brien et al. have recently written a comprehensive review on the polymerization of amphiphiles in nonlamellar LLC phases, concentrating primarily on fundamental aspects of polymerization in the  $Q_{II}$  and  $H_{II}$  phases.<sup>20</sup> Cross-linked nonlamellar LLC assemblies have been proposed for many applications in biological and materials sciences<sup>20</sup> because of their unique nanometer-scale architectures. However, the potential of these systems in actual applications has remained largely undemonstrated.

This Account will present an overview of our work in designing functional materials based on cross-linked nonlamellar LLC assemblies and demonstrating their utility in certain applications. Specifically, this article will focus on our efforts in developing cross-linked  $H_{II}$  phases for use as templates for nanoscale synthesis and as a novel scaffold for heterogeneous catalysis. In addition, more recent work in the design of new monomers that permit the stabilization of other nonlamellar LLC phases will be discussed, as well as the new opportunities they offer for materials applications. Finally, some new research directions will be presented with respect to new applications of these materials and new monomer designs.

## Cross-Linked $H_{II}$ Assemblies for Materials Applications

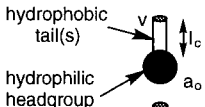

















We initially chose to demonstrate the viability of cross-linked nonlamellar LLC phases as functional nanomaterials by concentrating on the polymerization and application of the  $H_{II}$  phase. The geometry of the  $H_{II}$  phase is such that cross-linking of the fused hydrophobic tails generates a continuous polymer network around the ordered hydrophilic domains, affording excellent robust-

ness. In other LLC phases such as the  $H_I$  and  $L$  phases, the hydrophobic domains are discontinuous, and cross-linking them would not afford the same level of robustness. The  $Q_{II}$  phases were also attractive from the viewpoint of making porous, ordered nanomaterials. However, at the time we began our research in 1994, little was known about designing polymerizable amphiphiles that adopt these phases. The architecture of the  $H_{II}$  phase is reminiscent of those of zeolites and mesoporous sieves. Given the amount of materials research done inside these inorganic nanostructured materials,<sup>21,22</sup> developing tunable organic “analogues” to these systems was of great interest.

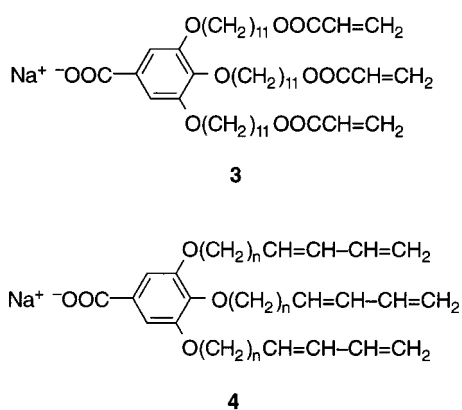
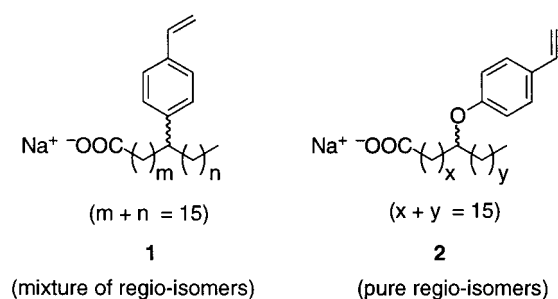
**(a) Monomer Design Considerations.** One of the most important considerations in developing cross-linked  $H_{II}$  phases into functional materials is appropriate design of the building blocks. We have taken a qualitative shape-directed approach to the design of cross-linkable LLC monomers. The ability of amphiphilic molecules to adopt LLC phases with specific geometries has been rationalized in two ways. One is a global perspective of the amphiphile–water system which considers the preferred geometry of the phase-segregated aggregate structure in the context of interfacial energy and intrinsic curvature.<sup>23</sup> The other is a more molecular approach which considers the general shape and packing preferences of the constituent amphiphiles and the relative amount of water in the system. In an effort to create a link between amphiphile structure and preferred phase geometry, Israelachvili<sup>24</sup> formulated the “critical packing parameter”,  $Q = v/a_0l_c$ , which relates the ratio of the volume of the organic portion of the amphiphile ( $v$ ), the area of the amphiphilic headgroup ( $a_0$ ), and the average critical length ( $l_c$ ) to the expected curvature, and thus geometry, of the various LLC phases (see Table 1).

These very qualitative shape guidelines were originally developed to explain the formation of micelles, reverse

**Table 1. Relationships between Amphiphile Shape, Water Content, and Preferred Aggregate Structure, Based on the Israelachvili Model<sup>24</sup>**

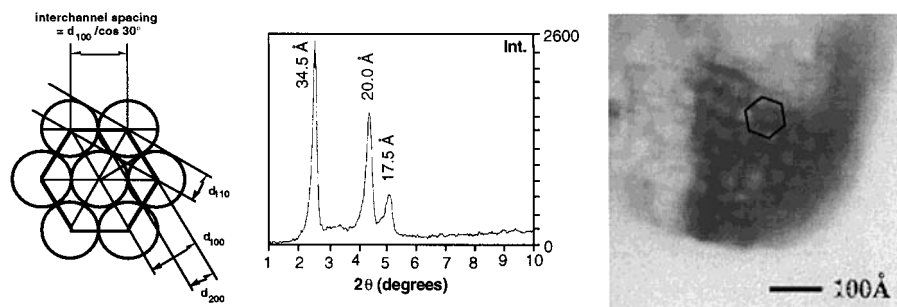
Amphiphile "shape"	Amphiphile structure	$\rho = \frac{V}{a_0 l_c}$	Rel. H <sub>2</sub> O content	Aggregate structure
 (conical)		< 1/3	high	
 (truncated cone)		1/3–1/2	medium	
 (cylindrical)		~1	medium	
 (conical)		> 1	low	
-----				
 (tapered?)			low	
 (cylindrical?)			medium	

micelles, and the H<sub>I</sub> and L phases but did not extend to the lesser known H<sub>II</sub> phase (or Q<sub>II</sub> phases) at that time.<sup>24</sup> We rationalized that amphiphiles with a tapered shape (i.e., a small hydrophilic headgroup and a broad, flattened hydrophobic tail section) should prefer to pack to form the H<sub>II</sub> phase, similar to the behavior of taper-shaped thermotropic LCs.<sup>25</sup> Using this idea, we have synthesized four polymerizable LLC systems (**1–4**) that form the H<sub>II</sub> phase at ambient temperature in the presence of ca. 5–20 wt % water. Monomers **1** and **2** are both monofunctional,

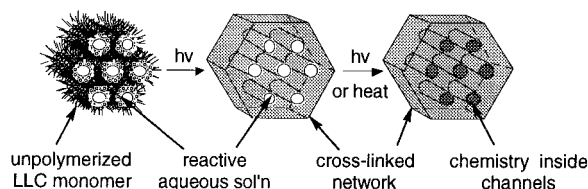


styrene-branched, long-chain carboxylate salts that require added cross-linker (e.g., 5–15 wt % divinylbenzene (DVB)) in order to form a network. Monomer **1** exists as a complex mixture of regioisomers (and stereoisomers) with the styrene group located at different positions along the 18-carbon backbone.<sup>26</sup> In contrast, **2** is a recently designed regioregular analogue of **1** in which the overall tail length and position of the polymerizable group can be changed independently.<sup>27</sup> By varying these two parameters and the nature of the headgroup counterion of **2**, the unit cell dimensions of the resulting H<sub>II</sub> phase can be modulated systematically over a wide range.<sup>27</sup> Monomers **3** and **4** also share a common platform, albeit a quite different one from that of **1** and **2**. Monomers **3** and **4** are polymerizable, three-tailed acrylate<sup>17</sup> and diene<sup>28</sup> derivatives of gallic acid salts, respectively. These monomers more clearly exhibit the desired taper shape and do not require cross-linker because they have three chain-polymerizable moieties per monomer. By varying the tail length<sup>29</sup> and the headgroup counterion,<sup>30</sup> the unit cell dimensions of the resulting H<sub>II</sub> phases can also be modulated.

With added radical photoinitiators, the H<sub>II</sub> phases of these monomers can be photo-cross-linked with retention of the microstructure. This approach yields robust, organic networks possessing hexagonally packed, monodisperse channels that are typically ca. 1.5 nm in diameter with an interchannel spacing of ca. 4 nm (Figure 2).<sup>3,4</sup> Degrees of polymerization in the 60–90% range are typically achieved in these systems under very mild photolysis conditions.<sup>17,26–28</sup> The resulting cross-linked networks are extremely robust organic materials that are completely insoluble in common solvents and do not exhibit any significant swelling. They are also very thermally stable organic materials<sup>26</sup> and exhibit mechanical properties



**FIGURE 2.** XRD profile and TEM image of the cross-linked  $H_{II}$  phase of **3** containing 5 wt %  $H_2O$ . The light circles in the TEM image are the cross sections of the cylindrical aqueous channels as seen looking down the cylinder axis; the dark areas are the cross-linked organic regions of the phase.



**FIGURE 3.** Synthesis of ordered nanocomposites using polymerizable  $H_{II}$  assemblies.

ranging from hard, brittle materials in the case of cross-linked **1** or **2**<sup>26,27</sup> to flexible thin films for polymerized **3** and **4**.<sup>17</sup>

**(b) Templates for the Synthesis of Functional Nanocomposites.** Our initial research into the use of cross-linked  $H_{II}$  assemblies for materials applications was directed at investigating them as tunable organic templates for the synthesis of functional, polymer-based nanocomposites. Our basic design strategy involved the following steps: (1) Formation of the  $H_{II}$  phase in the presence of hydrophilic precursors to functional solid-state materials, rather than pure water. (2) Photopolymerization of the matrix monomers into an ordered template network with retention of microstructure. (3) In situ conversion of the reagents trapped within the hydrophilic channels to form the “filler” materials (Figure 3).

We were able to demonstrate that a variety of organic and inorganic materials can be formed inside the channels of the cross-linked  $H_{II}$  phase, affording a range of ordered nanocomposite materials with diverse functional properties. We initially formed poly(*p*-phenylenevinylene) (PPV), a luminescent conjugated polymer, inside the cross-linked  $H_{II}$  phases to demonstrate proof-of-concept.<sup>17</sup> We then showed that silica<sup>26</sup> and CdS nanoparticles<sup>31</sup> can also be grown inside the cross-linked LLC assemblies. Table 2 lists the monomers, the reactive precursor solutions used to form the initial  $H_{II}$  phases, and the reactions used to generate the materials inside the resulting networks.

The primary goal of this nanocomposite work was to investigate whether the nanometer-scale organization imposed by the LLC matrix would enhance or modify the functional properties of the “filler materials” formed inside. It was thought that the dimensionally constrained environment would limit the degree of conversion of these materials and separate them from one another, thereby

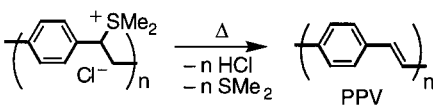
imparting them with different structures and different properties than those obtained in bulk.

The nanocomposite system that has been studied most extensively and that best exemplifies the effect of nanostructure on functional properties is the PPV system. Pure PPV typically has a photoluminescence quantum efficiency in the range of 5–27% and is sensitive to oxidation.<sup>32</sup> The hexagonal PPV nanocomposites exhibit enhanced solid-state photoluminescence quantum yields (up to 80%) with long-term stability due to chain isolation/protection in the channels.<sup>17</sup> The PPV nanocomposites can be processed into thin films and extruded fibers for device applications by applying conventional processing techniques to the fluid  $H_{II}$  phase prior to photo-cross-linking.<sup>17</sup> Recently, we have found that shear-aligning the PPV nanocomposite prior to polymerization affords macroscopically aligned  $H_{II}$  phases that exhibit polarized photoluminescence. The photophysical behavior<sup>33,34</sup> and a more detailed picture of the structure<sup>29,35</sup> of this system have recently been elucidated by collaborators. Light-emitting diodes have also recently been constructed using the PPV nanocomposite as the active emission layer.<sup>36</sup> Other potentially useful properties such as paramagnetism and metal-based luminescence have been introduced into the  $H_{II}$ –PPV system by employing transition-metal and lanthanide cations as the counterions.<sup>30</sup>

Similar confinement and size constraint effects were also observed in the formation of silica and CdS within the cross-linked  $H_{II}$  assemblies, although their influence on the functional properties of the nanocomposites has not been as thoroughly investigated. <sup>29</sup>Si MAS solid-state NMR spectroscopy indicated that only partial  $Si(OEt)_4$  conversion occurred after photoacid-catalyzed condensation in the  $H_{II}$ –silica nanocomposites, affording essentially individual silica nanoparticles in the channels.<sup>26</sup> Further silicate condensation was not possible, even upon heating of the sample at 220 °C in vacuo overnight. In contrast, similar photocondensation and heating of the same  $Si(OEt)_4$  solution used in the LLC samples but in nontemplated form yielded a fully condensed silicate sample.<sup>26</sup> These results suggest that the dimensional and diffusional constraints of the nanochannels restrict the degree of silica condensation possible, by isolating the reactive domains from one another. UV–visible characterization of the  $H_{II}$ –CdS nanocomposite also revealed that individual CdS



**Table 2. List of LLC Monomers and Reactions in the Nanochannels for Template Synthesis of Ordered Nanocomposites Using Cross-Linked H<sub>II</sub> Phases**

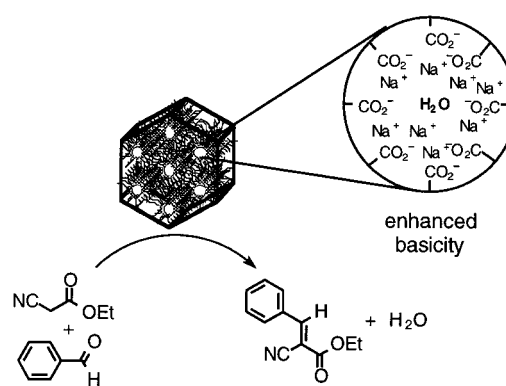
Monomer	Reaction in H <sub>II</sub> Nanochannels	Properties/Effects
3		<ul style="list-style-type: none"> <li>• higher quantum yield</li> <li>• blue shift in emission</li> </ul>
1	$n \text{ Si(OEt)}_4 + 2n \text{ H}_2\text{O} \xrightarrow{\text{photoacid}} (\text{SiO}_2)_n + 4n \text{ EtOH}$	<ul style="list-style-type: none"> <li>• limited deg. of SiO<sub>2</sub> conv.</li> </ul>
Cd <sup>2+</sup> salt of 1	$\text{Cd}^{2+} + \text{H}_2\text{S} \longrightarrow \text{CdS} + 2 \text{ H}^+$	<ul style="list-style-type: none"> <li>• control of CdS particle size</li> </ul>

nanoparticles were formed in the channels rather than bulk material. The UV–visible absorption maximum and absorption threshold indicated that CdS particles with diameters of 40 Å or less were formed.<sup>31</sup> Despite the small CdS particle size, photoluminescence from the nanocomposite was not observed. We are currently investigating the bulk properties of these two organic–inorganic nanocomposites and determining if particle size and distribution can be controlled by tuning the architecture of the ordered templates.

### (c) A Novel Platform for Heterogeneous Catalysis.

Nanostructured inorganic materials containing reactive ionic sites such as zeolites<sup>37</sup> and doped mesoporous sieves<sup>38</sup> play important roles as shape- and size-selective heterogeneous catalysts. It is believed that zeolites (and related structures) are able to facilitate reactions by localizing reactants in their pores and providing a high local concentration of active sites (typically acidic or basic). In addition, the high ionic strength and dielectric constant in the nanochannels, together with electronic confinement of the guest molecules, may contribute to preactivation of the reactants.<sup>37</sup> Many LLC assemblies such as the H<sub>II</sub>, L, and Q<sub>II</sub> phases also localize the ionic headgroups of the constituent amphiphiles exclusively into the interior of their aqueous domains. Consequently, we rationalized that cross-linked LLC assemblies may possess intrinsic size-selective catalytic properties as a result of their microstructural similarities to the nanostructured inorganic catalyst systems. They would also offer capabilities that are unobtainable with inorganic materials, namely the chemical tunability, mechanical properties, and processability of an organic polymer.

We have managed to demonstrate proof-of-concept that the cross-linked H<sub>II</sub> phase can act as a catalytic organic “analogue” to zeolites and mesoporous sieves. We recently showed that the cross-linked H<sub>II</sub> phase of **1** acts as an effective heterogeneous base catalyst for the Knoevenagel condensation of ethyl cyanoacetate ( $pK_a \approx 9$ ) with benzaldehyde in refluxing THF (Figure 4).<sup>39</sup> In fact, it is able to accelerate the reaction better than basic versions of zeolite-Y and MCM-41 mesoporous sieves



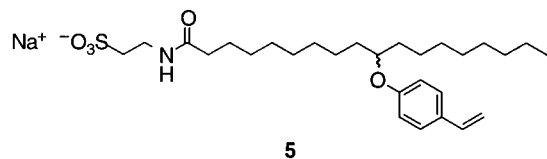
**FIGURE 4.** Base catalysis of the Knoevenagel condensation of ethyl cyanoacetate with benzaldehyde using the H<sub>II</sub> phase of **1** cross-linked with DVB.

under a variety of conditions.<sup>40</sup> The nanoporous polymer network contains closely packed, monodisperse water channels ca. 15 Å in diameter that are lined with weakly basic carboxylate anions ( $pK_a$  typically  $\sim 5$ ). As a result of the nanostructure, the H<sub>II</sub> network of **1** exhibits enhanced basicity ( $pK_a \approx 9$ ), as determined by acid titration.<sup>39</sup> It is believed the apparent increase in collective basicity results from a decrease of the dielectric constant and an increase in surface potential as the anionic carboxylates pack together in the nanochannels and destabilize one another.<sup>41</sup> The cross-linked H<sub>II</sub> of **1** was also found to reject water-soluble dyes larger than the channels,<sup>39</sup> indicating size selection capabilities consistent with its structure.

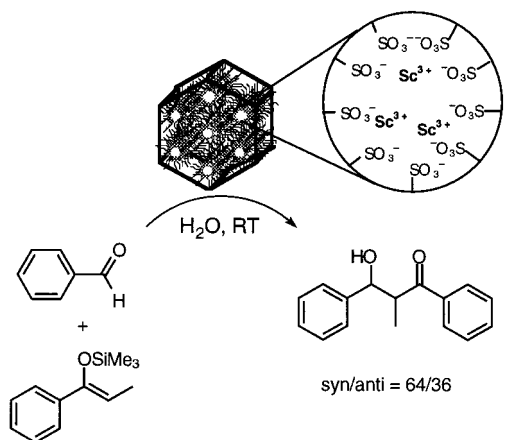
In addition to studying the intrinsic catalytic properties of the cross-linked H<sub>II</sub> assemblies, we have also used the nanoporous networks to support catalytic metal species in the channels (as a means of catalyzing other organic reactions). Polymer-supported heterogeneous catalysts employing reactive metals are advantageous because they offer a broad range of reactivity in addition to the recyclability, processability, and tunability offered by the polymeric support. The majority of polymer-supported catalyst systems are based on amorphous polymers. The structure and unique chemical environment offered by the H<sub>II</sub> phase suggested that differences in reactivity or

selectivity might be achieved if it were used as a support for metal-based catalysis.

Our initial efforts focused on forming Pd<sup>0</sup> nanoparticles in the channels<sup>42</sup> because Pd<sup>0</sup> nanoparticles stabilized in or on solid supports are known to catalyze hydrogenation and Heck coupling reactions.<sup>43,44</sup> Unfortunately, formation of Pd nanoparticles inside the cross-linked H<sub>II</sub> phase of **3** via Pd<sup>2+</sup> exchange and H<sub>2</sub> reduction resulted in loss of order in the polymer.<sup>42</sup> This revealed residual mobility in the network and an inherent weakness of these organized structures to protonation of the carboxylate headgroups. Some differences in reactivity and selectivity compared to more conventional heterogeneous Pd catalysts were observed with this Pd nanoparticle composite in hydrogenation and Heck test reactions,<sup>42</sup> but it was not possible to correlate them to nanostructure. However, we were able to successfully use the cross-linked H<sub>II</sub> phase as a nanostructured support for scandium(III)-based Lewis acid catalysis in water. Scandium(III) trifluoromethanesulfonate (Sc(OTf)<sub>3</sub>)<sup>45</sup> and polymer-supported Sc(III) catalysts<sup>46</sup> have recently garnered a great deal of attention because they can accelerate a variety of organic reactions using water as an environmentally benign solvent. To study the effect of a nanostructured support on Sc catalysis, a cross-linked H<sub>II</sub> assembly containing Sc(III) ions in the channels was synthesized.<sup>47</sup> The scandium-containing polymer was prepared by first making a cross-linked H<sub>II</sub> phase of new LLC monomer containing a sodium sulfonate headgroup (**5**) and then quantitatively exchanging Sc(III) for Na<sup>+</sup> in the polymer with retention of the hexagonal structure.<sup>47</sup>



Mukaiyama aldol test reactions of benzaldehyde with (*Z*)-1-phenyl-1-trimethylsiloxypropene in the presence of this catalyst affords 88% yield of a mixture of four stereoisomers with a *syn*/*anti* ratio of 64/36 (Figure 5).<sup>47</sup> In contrast, the same reaction catalyzed by aqueous Sc(OTf)<sub>3</sub>,<sup>45</sup> Sc-



**FIGURE 5.** Lewis acid catalysis of the Mukaiyama aldol reaction using the Sc(III)-exchanged, cross-linked H<sub>II</sub> phase of **5**.

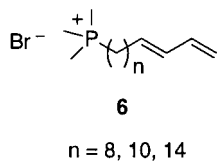
(III)-exchanged surfactants,<sup>48</sup> and amorphous polymer-supported Sc(III) catalysts<sup>46</sup> affords similar yields but essentially no diastereoselectivity (*syn*/*anti* = ca. 50/50). Other confined systems such as calix[6]arene-supported Sc(III) catalysts exhibit diastereoselectivities favoring the *anti* isomers (*syn*/*anti* = 31/69 to 40/60).<sup>49</sup> Thus, nanostructure or differences in nanostructure in the catalyst do have an effect on the stereochemical outcome of certain reactions.

## Polymerization of Other LLC Assemblies

In addition to the H<sub>II</sub> phase, our group is also investigating the polymerization and application of the H<sub>I</sub> and Q<sub>II</sub> phases because they provide entry into nanoarchitectures with potentially complementary, or even superior, materials characteristics. Polymerization of amphiphiles in the H<sub>I</sub> phase would afford surface-functionalized fibrillar structures with uniform diameters in the 1–10 nm range. Such structures could be used to form anisotropic nanocomposite materials, in much the same way that larger polymerized lipid microtubules have been employed as anisotropic metalization and mineralization templates.<sup>14,15</sup> Cross-linked Q<sub>II</sub> assemblies have even greater potential as nanoporous catalysts because they more closely resemble the interconnected channel structure of zeolites and thus provide better reactive site accessibility. A great deal is now known about polymerization in the Q<sub>II</sub> phases;<sup>19,20</sup> however, the same cannot be said about the polymerization of the H<sub>I</sub> phase, which has been only moderately successful in the past.<sup>14–16</sup> The design of new LLC systems that adopt these phases and can be stabilized by polymerization would undoubtedly help to realize their potential as functional materials.

The design considerations for monomers that can be polymerized in the H<sub>I</sub> and Q<sub>II</sub> phases are significantly different than those for the H<sub>II</sub> phase. As alluded to earlier, amphiphiles that adopt the H<sub>I</sub> phase typically have a large headgroup area relative to the volume of the tail section and a packing parameter greater than one.<sup>24</sup> Design of molecules that adopt the Q<sub>II</sub> phases is more difficult since the currently available predictive LLC theories do not adequately address this phase. The alkyltrimethylammonium bromide salts (TABs) are the best known amphiphiles that form the H<sub>I</sub> phase, and they also form Q<sub>II</sub> phases in appropriate amounts of water.<sup>50</sup> Therefore, polymerizable versions of these mesogens seemed an ideal starting point. Unfortunately, simple (meth)acrylate analogues of several TABs were not observed to display any significant LLC behavior. To develop a polymerizable amphiphile platform that permitted access to these phases, the headgroup was changed from ammonium to phosphonium, and the ester-based polymerizable moiety was replaced with a 1,3-diene group.<sup>51</sup> The larger phosphonium group better directs the formation of the H<sub>I</sub> phase.<sup>24</sup> The 1,3-diene tail moiety is closer in overall character to the *n*-alkyl chain of the TAB surfactants<sup>28</sup> and thus should not have as detrimental an effect on LLC phase formation as the more polar and bulkier (meth)acrylate groups.

Depending on the tail length, monomers based on **6** were found to adopt the desired H<sub>I</sub> and Q<sub>II</sub> phases when combined with water.<sup>51</sup> Certain homologues can be



homopolymerized in the H<sub>I</sub> phase with retention of phase microstructure and a degree of polymerization of >90%.<sup>51</sup> The resulting soluble polymer is able to maintain the H<sub>I</sub> phase up to 150 °C. In addition, it is able to reform the H<sub>I</sub> phase after being desiccated and rehydrated, or after being diluted to the isotropic state and reconcentrated.<sup>51</sup> Homologues of **6** can also be cross-linked with added DVB to afford very robust nanostructured networks with only slight disruption of the original order.<sup>51</sup> We are currently optimizing conditions for homopolymerizing and cross-linking the Q<sub>II</sub> phase formed by **6**.

## New Directions

There are two new directions that we are interested in pursuing in the immediate future, based on our success with the cross-linked H<sub>II</sub> phase and in the design of new monomers for accessing other nonlamellar phases. The first is investigation of cross-linked LLC phases as novel polymer membrane materials. From an architecture perspective, the water-based microstructures of these materials would be ideal for size-selective removal of macromolecular- and perhaps even molecular-size contaminants from water. Initial filtration and solute size selectivity experiments in our group have shown that water transport can be achieved through thin films of cross-linked **3** in the H<sub>II</sub> phase and that this transport occurs via the nanochannels and not pinhole leaks or defect sites in the films. Consequently, these materials display enticing properties as separation media that warrant more intense study. Cross-linked Q<sub>II</sub> phases possess even greater potential as membrane materials because unlike the H<sub>II</sub> phase, these interconnected systems would not require macroscopic pore alignment to facilitate transport. The second direction that we are interested in pursuing is the design of LLC monomers that can be cross-linked in H<sub>I</sub> and Q<sub>II</sub> phases without the need for added cross-linkers. Intrinsically cross-linkable monomers would greatly simplify the preparation and characterization of H<sub>I</sub> and Q<sub>II</sub> networks. We plan to investigate two strategies for generating intrinsically cross-linkable monomers based on **6**. One strategy is incorporating polymerizable counterions onto the amphiphilic monomers. Kline recently showed that when TAB surfactants are ion-exchanged with 4-vinylbenzoate, polymerization of the 4-vinylbenzoate counterion stabilizes unordered, rodlike micellar solutions.<sup>52</sup> We have established the viability of extending this approach to ordered LLC phases by demonstrating that nonpolymerizable analogues of **6** containing different polymerizable counterions can be photopolymerized in

the H<sub>I</sub> phase.<sup>53</sup> The other strategy is designing polymerizable dimeric (i.e., gemini) surfactants. The bridged dual headgroup of a gemini surfactant<sup>54</sup> should allow incorporation of two polymerizable tails without compromising the overall monomer shape considerations<sup>24</sup> for forming the H<sub>I</sub> and Q<sub>II</sub> phases. Gemini amphiphiles with two polymerizable diene tails have recently been synthesized in our group and are currently under study.

## Summary

In summary, we have demonstrated that the cross-linked H<sub>II</sub> phase can be used in materials applications ranging from templated synthesis to heterogeneous catalysis. We have also developed a novel LLC monomer platform that provides access to both H<sub>I</sub> and Q<sub>II</sub> phases. Polymerized H<sub>I</sub> and Q<sub>II</sub> phases should be able to achieve similar functional properties with appropriate forethought in the design of the monomers. One of the most intriguing issues for future investigation in this area is how differences in nanometer-scale geometry between the various LLC phases will impact the selectivity and functional properties of the polymerized materials.

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