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A New Family of Polymerizable Lyotropic Liquid Crystals: Control of Feature Size in Cross-Linked Inverted Hexagonal Assemblies via Monomer Structure

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Abstract: An efficient and versatile synthesis of a series of polymerizable amphiphilic mesogens that affords control over tail length and position of the polymerizable group is described. The synthesis employs a novel and facile method of preparing styrene ethers. The monomers are sodium salts of styrene ether-modified fatty acids that can be used to form cross-linkable inverted hexagonal (H_{II}) lyotropic liquid crystal (LLC) phases at ambient temperature with controllable nanometer-scale dimensions. Examination of a series of regioisomers with the same alkyl chain length but with the styrene ether group at different locations along the chain revealed that the position of the styrene ether has a profound effect on the dimensions of the resulting H_{II} phase at a fixed temperature and composition. Increasing overall monomer tail length also has a significant, although smaller, effect on the unit cell dimensions of the LLC phase. By controlling the structure of the LLC monomer in this manner, cross-linked H_{II} phases with interchannel distances (ICD) ranging from 29 to 54 Å can be obtained. Furthermore, changing the counterion from Na^+ to tetraalkylammonium ions leads to further expansion of the H_{II} unit cell to a maximum ICD of 65 Å, as well as to the production of a lamellar phase. Use of these monomers affords a new and unparalleled degree of control over phase structure and dimensions for the production of nanostructured organic materials.

Introduction

The synthesis of materials with architectural control on the nanometer scale is arguably one of the greatest current challenges in the area of materials chemistry.[1] While Nature has mastered the art of synthesizing materials with that level of sophistication,[2] materials chemists are only beginning to understand the basics of performing chemistry and engineering on the nanometer size regime.[3] Many of the techniques used to obtain this degree of order in synthetic systems are based on the phenomenon of molecular self-assembly: that is, the intrinsic ability of certain chemical systems to spontaneously organize into ordered arrays on the nanometer or micrometer scale.[4]

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(1) For recent perspectives on nanometer-scale materials, see the articles in the following special journal issues dedicated to this topic: (a) *Chem. Rev.* **1999**, *99*, 9. (b) *Science* **1997**, *277*. (c) *Chem. Mater.* **1996**, *8*.

(2) Addadi, L.; Weiner, S. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 153.

(3) (a) Calvert, P. *Mater. Sci. Eng.* **1994**, *C1*, 69. (b) Peppas, N. A.; Langer, R. *Science* **1994**, *263*, 1715. (c) Heuer, A. H.; Fink, D. J.; Laraia, V. J.; Arias, J. L.; Calvert, P. D.; Kendall, K.; Messing, G. L.; Blackwell, J.; Rieke, P. C.; Thompson, D. H.; Wheeler, A. P.; Veis, A.; Caplan, A. I. *Science* **1992**, *255*, 1098.

(4) For recent reviews of nanostructure synthesis by self-assembly, see: (a) Kazmaier, P.; Chopra, K. *MRS Bull.* **2000**, *25* (4), 30. (b) Mio, M. J.; Moore, J. S. *MRS Bull.* **2000**, *25* (4), 36. (c) Stupp, S. I.; Pralle, M. U.; Tew, G. N.; Li, L.; Sayer, M.; Zubarev, E. R. *MRS Bull.* **2000**, *25* (4), 42.

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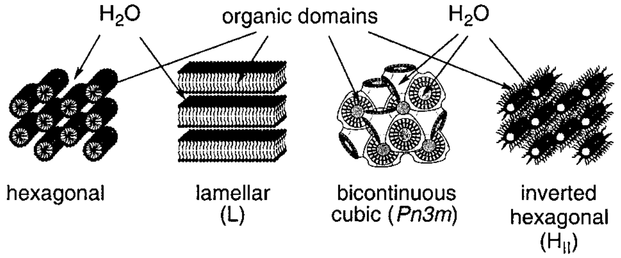

Figure 1. Representations of some common LLC phases formed by amphiphiles in the presence of water.

Langmuir–Blodgett films,[5] liquid-crystalline (LC) polymers,[6] and microphase-separated block copolymers[7] are examples of such systems that have been used as templates for the formation of nanostructured materials with interesting properties. Another very promising and versatile approach is the use of polymerizable lyotropic liquid crystal (LLC) assemblies as template media.

LLCs are amphiphilic molecules that spontaneously assemble in the presence of water to form phase-segregated assemblies with specific geometries and regular nanometer-size features (Figure 1).[8] The type of LLC phase formed depends on the concentration of the mesogen,[8] the temperature of the system,[8] and the shape of the mesogen itself.[9] LLC assemblies are intrinsically fluid in nature; thus, their ordered structures are easily distorted or disrupted by physical and chemical forces. To overcome this problem for the construction of robust materials, polymerizable or cross-linkable LLCs have been developed.[10] These reactive amphiphiles aggregate into the same types of assemblies as their nonpolymerizable analogues but the molecules can be covalently linked to their nearest neighbors in situ to form highly stable polymer networks with retention of the original microstructure.

Polymerizable LLC phases have recently been used to demonstrate that nanostructured organic materials with novel or enhanced properties can be synthesized. For example, nanoporous organic polymers,[11−13] ordered nanocomposites,[14−19] and most recently catalytic organic analogues of zeolites[20] have been prepared using polymerizable LLCs as building blocks. The inverted hexagonal (H_{II}) phase, in particular, has been employed as a preferred template for many of these new systems.[11,13,14−17,20] Cross-linking of the H_{II} phase affords a robust organic matrix with ordered, one-dimensional nanochannels that can be used for applications such as macromolecular exclusion or filtration, or as the basis for anisotropic nanocomposites if the channels are filled with reinforcing materials. Recent work in our group has shown that condensed organic and inorganic materials formed within cross-linked H_{II} assemblies exhibit properties not observed in the analogous bulk materials.[14,17] In addition, the organization of the ionic headgroups in these systems affords nanochannels with unusual chemical environments. For example, cross-linked H_{II} phases of carboxylate-containing monomers were found to have nanochannels with enhanced basicity that are capable of heterogeneous base catalysis and substrate size exclusion.[20]

One of the major advantages of using polymerizable LLC templates over other self-assembly methods is the power to modulate the nanometer-scale dimensions and geometry of the resulting materials by simply altering the temperature or composition of the system, or the structure of the monomeric building blocks.[8] The LLC behavior can be explained by considering the energetics of the amphiphiles as a collective ensemble, and/or the molecular shape of the constituent amphiphiles. Using the first theory, changes in LLC phase dimensions and geometry with variations in temperature and water content can be explained by considering the interfacial energy and intrinsic curvature of the systems.[21] Gruner and coworkers have shown that the structural dimensions of the H_{II} phase can be systematically modulated by varying system temperature.[22] However, *at a fixed temperature and system composition*, it has been proposed that the "shape" of the amphiphile has the more important role in determining which mesophase a LLC mixture will tend to adopt.[9] In an effort to create a simplified tie between amphiphile structure and preferred phase geometry under these conditions, Israelachvili[9] formulated an expression termed the "critical packing parameter," $Q = v/a_0 l_c$. This expression relates the ratio of the volume of the organic portion of the mesogen (v), the area of the amphiphilic headgroup (a_0), and average critical length (l_c) to the expected curvature, and thus geometry, of the various mesophases. For example, amphiphiles with a tapered shape (i.e., a small hydrophilic headgroup and a broad, flattened hydrophobic tail section) tend to form the H_{II} phase, whereas amphiphiles with a cylindrical shape tend to pack into low-curvature lamellar (L) phases. By modulating the size of the headgroup and varying the length and breadth of the hydrophobic tails, the unit cell dimensions of the preferred LLC phase or even the phase itself can be altered, depending on the magnitude of the changes to the monomer. For example, we have recently demonstrated that in the case of sodium 3,4,5-tris(11′-acryloyloxyundecyloxy)benzoate, which has a distinct tapered shape, the unit cell dimensions of the resulting H_{II} phases can be tuned by changing the metal counterion on the head-

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(d) Brunsveld, L.; Folmer, B. J. B.; Meijer, E. W. *MRS Bull.* **2000**, *25* (4), 49. (e) Hawker, C. J.; Hedrick, J. L.; Miller, R. D.; Volksen, W. *MRS Bull.* **2000**, *25* (4), 54. (f) Lehn, J.-M. *Pure Appl. Chem.* **1994**, *66* (10/11), 1961. (g) Whitesides, G. M.; Mathias, J. P.; Seto, C. T. *Science* **1991**, *254*, 1312.

(5) Litvin, A. L.; Valiyaveettil, S.; Kaplan, D. L.; Mann, S. *Adv. Mater.* **1997**, *9*, 124.

(6) Nelson, E. J.; Samulski, E. T. *Mater. Sci. Eng.* **1995**, *C2*, 133.

(7) (a) Zhao, D.; Feng, J.; Huo, Q.; Melosh, N.; Frederickson, G. H.; Chmelka, B. F.; Stucky, G. D. *Science* **1998**, *279*, 548. (b) Kraemer, E.; Foerster, S.; Goeltner, C.; Antionetti, M. *Langmuir* **1998**, *14*, 2027.

(8) For reviews of LLCs and their phases, see: (a) Tiddy, G. J. T. *Phys. Rep.* **1980**, *57*, 1. (b) Seddon, J. M. *Biochim. Biophys. Acta* **1990**, *1031*, 1.

(9) Israelachvili, J. N. *Intermolecular and Surface Forces with Applications to Colloidal and Biological Systems*; Academic: London, 1985; pp 249−257.

(10) For reviews of nanostructured materials synthesis using polymerizable LLCs, see: (a) Miller, S. A.; Ding, J. H.; Gin, D. L. *Curr. Opin. Colloid Interface Sci.* **1999**, *4*, 338. (b) O'Brien, D. F.; Armitage, B.; Benedicto, A.; Bennett, D. E.; Lamparski, H. G.; Lee, Y.-S.; Srisiri, W.; Sisson, T. M. *Acc. Chem. Res.* **1998**, *31*, 861. (c) Ringsdorf, H.; Schlarb, B.; Venzmer, J. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 113.

(11) Herz, J.; Reiss-Husson, F.; Rempp, P.; Luzzati, V. *J. Polym. Sci., Part C* **1963**, *4*, 1275.

(12) Lee, Y.-S.; Yang, J.-Z.; Sisson, T. M.; Frankel, D. A.; Gleeson, J. T.; Aksay, E.; Keller, S. L.; Gruner, S. M.; O'Brien, D. F. *J. Am. Chem. Soc.* **1995**, *117*, 5573.

(13) Srisiri, W.; Sisson, T. M.; O'Brien, D. F.; McGrath, K. M.; Han, Y.; Gruner, S. M. *J. Am. Chem. Soc.* **1997**, *119*, 4866.

(14) Smith, R. C.; Fischer, W. M.; Gin, D. L. *J. Am. Chem. Soc.* **1997**, *119*, 4092.

(15) Gray, D. H.; Hu, S.; Juang, E.; Gin, D. L. *Adv. Mater.* **1997**, *9*, 731.

(16) Deng, H.; Gin, D. L.; Smith, R. C. *J. Am. Chem. Soc.* **1998**, *120*, 3522.

(17) Gray, D. H.; Gin, D. L. *Chem. Mater.* **1998**, *10*, 1827.

(18) Sellinger, A.; Weiss, P. M.; Nguyen, A.; Lu, Y.; Assink, R. A.; Gong, W.; Brinker, C. J. *Nature* **1998**, *394*, 256.

(19) Werkman, P. J.; Wieringa, R. H.; Schouten, A. J. *Thin Solid Films* **1998**, *323*, 251.

(20) Miller, S. A.; Kim, E.; Gray, D. H.; Gin, D. L. *Angew. Chem., Int. Ed.* **1999**, *38*, 3021.

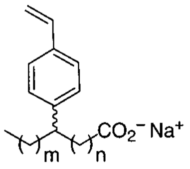
(21) Gruner, S. M. *J. Chem. Phys.* **1989**, *93*, 7562.

(22) Tate, M. W.; Gruner, S. M. *Biochemistry* **1989**, *28*, 4245.

group[16] and/or the length of the three aliphatic tails.[23] Also, below a certain tail length the monomer adopts the L phase.

The potential for control of phase architecture and dimensions in these nanostructured systems through monomer design is quite remarkable. However, at this point only loose guidelines for controlling or predicting LLC mesophases have been elucidated from the observed relationships between amphiphile structure and the properties of the resulting LLC assemblies. Furthermore, some LLC systems are comprised of mixtures of several isomers, yet still form highly ordered phases. Consequently in these systems, the structural factors that direct the formation of one phase over another and influence the unit cell dimensions are not clearly understood.

One important example of such a system is salts of styrene-substituted, long-chain carboxylic acids. These polymerizable amphiphiles adopt highly ordered H_{II} phases even though they do not possess a distinct taper shape. In 1963, Luzzati and co-workers first showed that an isomeric mixture of calcium *p*-styrylundecanoates derived from 10-undecenoic acid form an H_{II} phase at room temperature and can be cross-linked with retention of microstructure by copolymerizing the monomer with moderate amounts (5−20%) of divinylbenzene (DVB).[11] Following the work of Luzzati, our group developed a similar H_{II} forming monomer system, the sodium salt of the styryl derivative of 9-octadecenoic (i.e., oleic) acid (**1**).[15,17] Mixtures of **1**, water, and DVB can be photopolymerized with retention of phase to serve as templates for nanocomposite[15,17] and heterogeneous catalyst formation.[20] Transition-metal and alkaline earth salts were also prepared from **1** by ion exchange. The cadmium salt was used for CdS formation in the aqueous channels of the H_{II} phase, giving nanoparticles with diameters of 40 Å or less.[17]



1 m+n+3=18
(racemic mixture of
regioisomers)

Unfortunately, **1** exists as a complex mixture of regioisomers with the styrene group located at different positions along the 18-carbon backbone.[15] A key step in the synthesis of **1** is the Friedel−Crafts reaction of methyl oleate and benzene. During this step, the carbocation in the intermediate migrates up and down the chain. This results in a mixture of isomers with the phenyl ring (i.e., the styryl moiety) attached anywhere from the sixth carbon to the seventeenth carbon of the chain,[24] with no single isomer representing more than 20% of the mixture. Traditionally, LLC phases have been made with a single surfactant species, allowing aspects of mesogen shape to be correlated with the phase formed. Although **1** is a versatile platform for making functional nanostructured materials, its complex regioisomeric makeup makes it difficult to identify the structural factors that influence the formation of the H_{II} phase. In addition, these factors also make it difficult to control the unit cell dimensions of the LLC assembly via systematic monomer modification.

Herein, we present an efficient, versatile synthesis of a series of regiopure, styrene ether analogues of **1** (compounds **2**−**11**) that affords control over both overall tail length and position of the polymerizable group. By varying these parameters in a systematic fashion, we have been able to elucidate the effect of these changes on H_{II} phase formation at constant temperature for this class of monomers based on styrene-substituted, long-chain carboxylic acid salts.[25] Variation of three key structural parameters—the tail length, the point of the styrene ether attachment, and the counterion of the headgroup—resulted in a series of polymerizable LLCs. These LLCs were combined with H_2O and DVB at ambient temperature to produce cross-linked H_{II} phases with tunable interchannel distances (ICDs) in the 29−65 Å range. Theoretical studies based on neutron-scattering experiments suggest that the inner diameter of the water channels of the H_{II} phase is directly proportional to the ICD,[8b] thus control over the ICD implies control over the size domain of the reactive aqueous regions. Manipulation of the feature size of the H_{II} phase should lead to the ability to selectively tune the properties of nanostructured materials prepared from these phases.

Results and Discussions

Synthesis of Regiopure Styrene Ether Analogues of 1. To make a homologous series of single regioisomer analogues of **1**, it was desirable to have a short and modular synthetic route. The key synthetic step required is the attachment of a styrene group at a specific position along the fatty acid chain. Phenyl rings have been attached to unsaturated chains by Friedel−Crafts coupling[24a,26] and then elaborated to the styrene via the corresponding acetophenones or benzaldehydes. Unfortunately, as discussed above, Friedel−Crafts couplings have been shown to lead to mixtures of regioisomers, arising from rearrangement of the carbocation intermediates. It is also possible to create regiospecific isomers of the phenyl-branched fatty acid via addition of a phenyl Grignard reagent to a ketone/fatty acid, or by adding an alkyl Grignard to a fatty acid terminated with a phenyl ketone,[26] with subsequent reduction of the alcohol to a methine. The phenyl group must then be transformed to the styrene; overall these routes to individual isomers are too long for efficient synthesis of multiple regioisomers and homologues of **1**.

Introduction of an ether linkage between the styrenic moiety and the fatty acid backbone significantly simplifies the regiospecific synthetic route. An alternative to direct attachment of a styrene moiety to the chain is the use of a phenolic or benzylic ether linkage to give styrene or styryl ethers. Styrene ethers have been prepared by coupling either 4-hydroxybenzaldehyde[27] or 4-hydroxyacetophenone[28] to an alcohol using the Mitsunobu reaction and then transforming the carbonyl group into a vinyl

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[23] Gin, D. L.; Gray, D. H.; Smith, R. C. *Synlett* **1999**, *10*, 1509.

[24] (a) Harrison, W. J.; McDonald, M. P.; Tiddy, G. J. T. *J. Phys. Chem.* **1991**, *95*, 4136. (b) Smith, F. D.; Stirton, A. J. *J. Am. Oil Chem. Soc.* **1971**, *48*, 160.

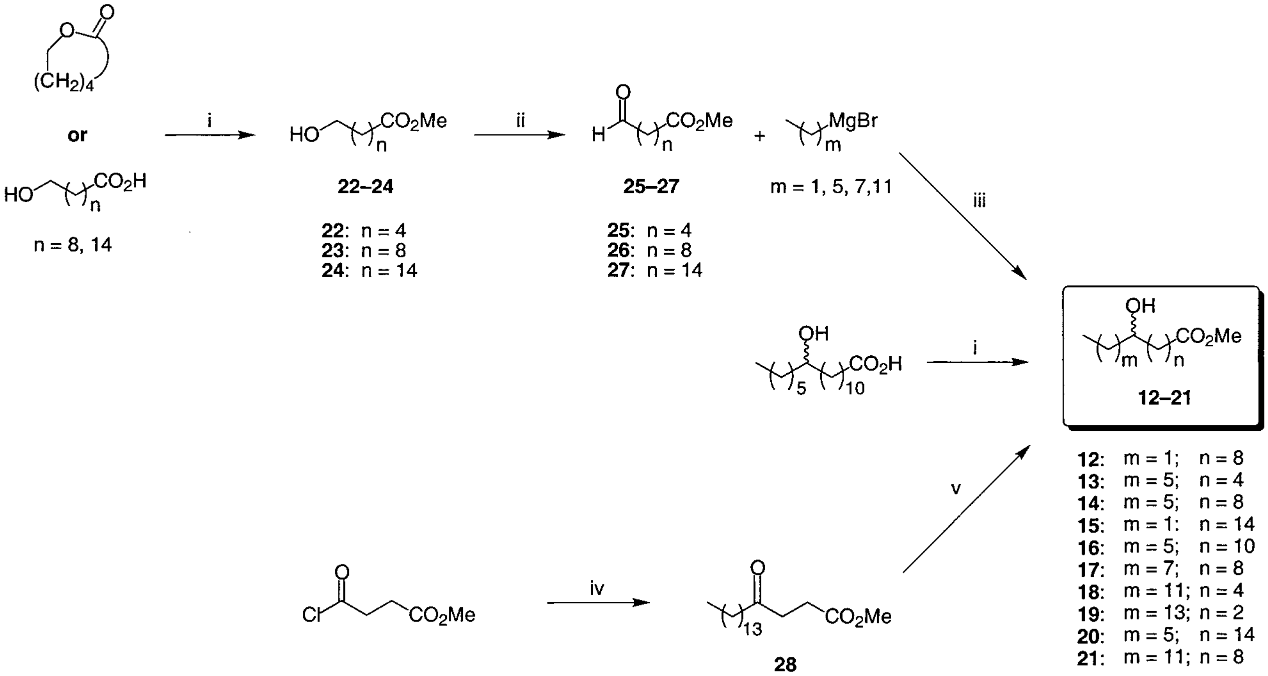
[25] Although it is known that the dimensions of the H_{II} phase are also affected by temperature (see ref 22), this paper only presents the effects of molecular structure on LC phase architecture at constant temperature (24 ± 1 °C) for this class of monomers. Preliminary studies showed that temperature changes of ca. 10 °C are necessary before changes in lattice dimension of $\geq$0.5 Å are observed in our systems (see Supporting Information). Thus, the variations in the H_{II} dimensions within the ±1 °C window of error in our measurements can be considered very small and near the limit of accuracy for our X-ray diffractometer in the low-angle region. The effect of temperature on the LC phases of these monomers will be a subject of future investigation.

[26] Freedman, H. H.; Mason, J. P.; Medalia, A. I. *J. Org. Chem.* **1958** *23*, 76.

[27] Baena, M. J.; Barberá, J.; Espinet, P.; Ezcurra, A.; Ros, M. B.; Serrano, J. L. *J. Am. Chem. Soc.* **1994**, *116*, 1899.

[28] Malamas, M. S.; Carlson, R. P.; Grimes, D.; Howell, R.; Glaser, K.; Gunawan, I.; Nelson, J. A.; Kanzelberger, M.; Shah, U.; Hartman, D. A. *J. Med. Chem.* **1996**, *39*, 237.

Scheme 1



(i) MeOH, H_2SO_4 (cat.), Δ, 90%; (ii) PCC/Al_2O_3, CH_2Cl_2, 88%; (iii) THF, 0 °C, 95%; (iv) 2 $C_{14}H_{29}MgBr$, CuI, THF, 0 °C, 94%; (v) $NaBH_4$, MeOH, 0 °C, 97%

group.[29] Alternatively, 4-chlorostyrene has been used to functionalize poly(ethylene glycol) at 70 °C with KOH.[30] The secondary alcohols used in our synthetic route were unreactive with styryl chloride, bromide, or iodide; thus, the Mitsunobu reaction was used to form the ether linkage.

The route to the styrene ethers, **2**−**11**, proceeded via the secondary alcohol/esters (**12**−**21**). The alcohols were prepared by three different routes, as shown in Scheme 1. The secondary alcohols **12**−**15**, **17**, **18**, **20**, and **21** were synthesized by first esterifying the commercially available ω-hydroxy fatty acids or corresponding lactones, and then oxidizing the resulting ω-hydroxy esters (**22**−**24**) to the corresponding aldehydes (**25**−**27**).[31,32] Addition of *n*-alkyl Grignard reagents to the crude aldehydes afforded the secondary alcohols as racemic mixtures, with the individual positions of the hydroxy groups determined by the choice of starting fatty acids and alkyl Grignard reagents. Alcohol **16** was made in one step by esterification of commercially available 12-hydroxystearic acid. Alcohol **19** was formed by coupling a tetradecanyl Grignard cuprate with an acid chloride to form the ketone (**28**),[33] followed by reduction of **28** to **19** with $NaBH_4$.

Initial attempts to attach the styrene ether onto the secondary alcohols **12**−**21** via the Mitsunobu reaction[34,35] with 4-vinylphenol using triphenylphosphine and diisopropylazodicarboxylate (DIAD) in THF only afforded the desired products in modest yields (50−60%). Unfortunately, variation of the reaction temperature, reaction time, and order of addition did not lead to significant improvements in yield.[36] However, Mitsunobu couplings with both 4-hydroxyacetophenone and 4-hydroxybenzaldehyde were found to proceed in higher yields of 70−80%. It seemed likely that 4-vinylphenol was less reactive than the carbonyl-substituted phenols due to the lower acidity of 4-vinylphenol. To address this issue, 1,1′-(azodicarbonyl)-dipiperdine (ADDP) and tributylphosphine in toluene were substituted for DIAD and triphenylphosphine in THF, following the work of Tsunoda et al.[37] with acidic carbon compounds in Mitsunobu couplings. These conditions have not been previously used for the formation of alkyl aryl ethers. Using this procedure, the desired styrene ethers **29**−**38** were produced in 75−85% isolated yields (Scheme 2). Hydrolysis of **29**−**38** to the corresponding acids **39**−**48** followed by neutralization with NaOH subsequently yielded the sodium salts **2**−**11**.

It should be noted that the success of this method has wider implications in monomer synthesis than its application to this particular series of compounds. The Mitsunobu reaction is tolerant of a wide variety of functional groups.[35,36] Thus, the development of this general method for making styrene ethers makes the attachment of a styrene group as facile as attaching an acrylate or any of the other common ester-based polymerizable groups. This reaction quickly converts primary and secondary alcohols to polymerizable styrene ether moieties with inversion of chirality at the alcohol carbon. This transformation allows the styrene group to be used in situations where the ester-based polymerizable groups are less desirable or unsuitable.

Using this synthetic route, it was possible to prepare the 10 polymerizable LLC salts **2**−**11** with overall chain lengths from 12 to 22 carbons, and with the styrene ether moiety located in a variety of positions along the chain (referred to herein as “branch points”). The 12- and 16-carbon linear styrene ether salts **49** and **50** were prepared in a similar manner from **22** and **23** by modified Mitsunobu coupling to form the terminal styrene ethers (**51**, **52**), followed by de-esterification (**53**, **54**) and formation of the sodium salts (Scheme 2). The identities of all new styrene ether compounds were confirmed by IR, ^1H ,and

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[29] Piskala, A.; Rehan, A. H.; Schlosser, M. *Collect. Czech. Chem. Commun.* **1983**, *48*, 3539.

[30] Stowe, S. C. U.S. Patent 3,190,925, 1965.

[31] Cheng, Y. S.; Liu, W. L.; Chen, S. H. *Synthesis* **1980**, 223.

[32] Piancatelli, G.; Scettri, A.; D’Auria, M. *Synthesis* **1982**, 245.

[33] Bergbreiter, D. E.; Killough, J. M. *J. Org. Chem.* **1976**, *41*, 2750.

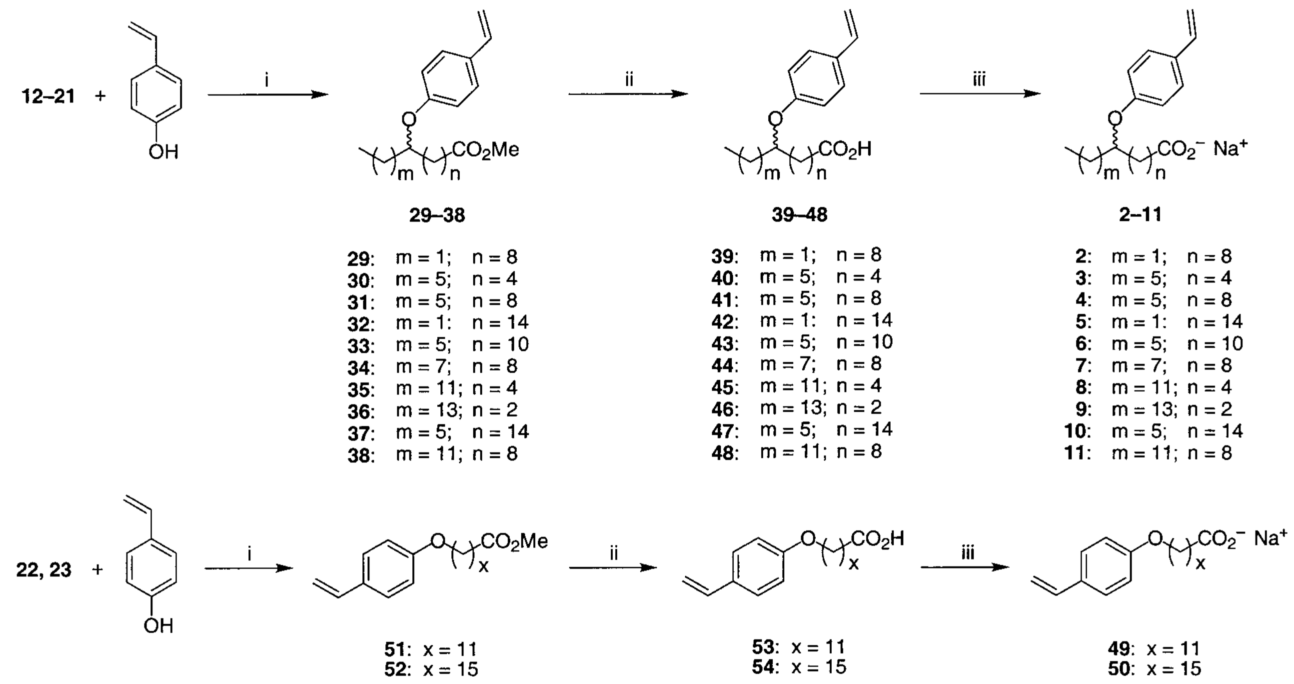
[34] Manhas, M. S.; Hoffman, W. H.; Lai, B.; Bose, A. K. *J. Chem. Soc., Perkin Trans. 1* **1975**, 461.

[35] Mitsunobu, O. *Synthesis* **1981**, 1.

[36] Hughes, D. L. *Org. React.* **1992**, *42*, 335.

[37] Tsunoda, T.; Yamamiya, Y.; Ito, S. *Tetrahedron Lett.* **1993**, *34*, 1639.

Scheme 2



(i) $P(Bu)_3$, ADDP, toluene, O °C–R.T., 84%; (ii) NaOH, 4/1 $MeOH/H_2O$, Δ, 71–94%; (iii) NaOH, $EtOH/H_2O$, 99%

^{13}C NMR and elemental analysis or high-resolution mass spectrometry. The LLC phases of the salts were characterized by polarized light microscopy (PLM) and X-ray diffraction (XRD), both in the neat form and as mixtures with water, DVB, and 2 wt % 2-hydroxy-2-methylpropiophenone (HMPP) incorporated as a photoinitiator.[15] The LLC mixtures were then photopolymerized and characterized again. All the LLC phases were prepared and studied at ambient temperature (24 ± 1 °C).

Effect of Monomer Structure on LLC Phase Dimensions. Low-angle XRD and PLM analysis of monomers **2**−**11** revealed that they all form the H_{II} phase at ambient temperature in neat form and when mixed with 6 wt % H_2O, 10 wt % DVB, and 2 wt % HMPP; however, **5** also shows some evidence of the L phase in addition to the H_{II} phase. The optical textures of **2**−**4** and **6**−**11** showed the characteristic kaleidoscopic textures of the hexagonal phases, and the positions of their observed XRD peaks were consistent with that of a hexagonal LLC phase (1, $1/\sqrt{3}$, 1/2, $1/\sqrt{7}$, ... corresponding to d_{100}, d_{110}, d_{200}, d_{210}, ...)[8b,38] (see Supporting Information for listings of all XRD data). The average interchannel distances (ICDs)[8b,38] were calculated from the average calculated d_{100} value ($\langle d_{100}\rangle$) based on all observed XRD peaks[39] (i.e., ICD = $\langle d_{100}\rangle/\cos 30°$) (see Table 1). As expected, there is a rough correlation between monomer chain length and ICD, with longer chains leading to larger ICDs. A more striking observation is that the position of the styrene ether branch point along the monomer chain has a strong effect on the ICD of the H_{II} phase formed, as illustrated by the five neat octadecanoate isomers **5**−**9** (Table 1). Figure 2 shows the XRD profiles of the H_{II} phases of neat **5**, **7**, and **9** taken at 24 ± 1 °C, showing the shift in the measured d_{100} values with the changes in isomer structure. In general, the closer the styrene ether branch point is to the end of the tail, the larger the observed ICD of the resulting H_{II} phases. It can be seen that this trend holds for the dodecanoate and docosanoate isomers as well, with the ICDs of the H_{II} phases of the neat sodium salts spanning 29−54 Å. The longer chain isomers generally form H_{II} phases with larger ICDs than their shorter counterparts. However, of the two variables, chain length and position of polymerizable group, the latter has the stronger effect upon LLC phase dimensions. When the branch point is near the headgroup (i.e., monomers **8** and **9**), the ICDs are reduced, and only the d_{100} peak has a strong intensity, suggesting a more disordered phase. In contrast to the branched salts, the linear sodium salts with the styrene ether group at the terminus of the alkyl chain (**49**, **50**) are crystalline and hydrophobic. Comparing the behavior

Table 1. Influence of Alkyl Tail Length and Styrene Ether Position on the Dimensions of the H_{II} Phases Formed by Neat LLC Sodium Salt Monomers **2**−**11** (Unpolymerized)[d]

LLC monomer	no. of C in alkyl tail	position of styrene ether attachment[a]	H_{II} phase: $\langle d_{100}\rangle$ (Å)[b]	H_{II} phase: ICD (Å)
2	12	C10	35.1	40.5
3	12	C6	24.9	28.7
4	16	C10	32.8	37.9
5	18	C16	44.6[c]	51.5[c]
6	18	C12	35.6	41.1
7	18	C10	35.3	40.8
8	18	C6	29.3	33.8
9	18	C4	30.3	35.0
10	22	C16	46.2	53.3
11	22	C10	38.4	44.3

[a] Carbon position for styrene ether attachment numbered progressively along the alkyl tail with C1 being the carboxylate carbon. [b] $\langle d_{100}\rangle$ is the average value of d_{100} based on the positions of all the XRD peaks observed for the H_{II} phase (see ref 39 and the Supporting Information). [c] Evidence of a small amount of L phase formation in the H_{II} phase. [d] X-ray diffraction measurements on the H_{II} phases were performed at 24 ± 1 °C.

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(38) Resel, R.; Thiessl, U.; Gadermaier, C.; Zojer, E.; Kriechbaum, M.; Amenitsch, H.; Gin, D.; Smith, R.; Leising, G. *Liq. Cryst.* **2000**, *27*, 407.

(39) Because of large changes in d spacing with small changes in 2θ in the low-angle region of the XRD spectrum, the primary peak d_{100} is often more accurately determined by averaging d_{100} values calculated from the positions of all the peaks in the spectrum: $\langle d_{100}\rangle = [(d_{100}\cdot 1) + (d_{110}\cdot\sqrt{3}) + (d_{200}\cdot\sqrt{4}) + (d_{210}\cdot\sqrt{7}) + ...]/n$, where n = the total number of observed XRD peaks for a hexagonal phase. Similarly, ICD is calculated from the $\langle d_{100}\rangle$ value (ICD = $\langle d_{100}\rangle/\cos 30°$). See: Johannson, G.; Percec, V.; Ungar, G.; Zhou, J. P. *Macromolecules* **1996**, *29*, 646.

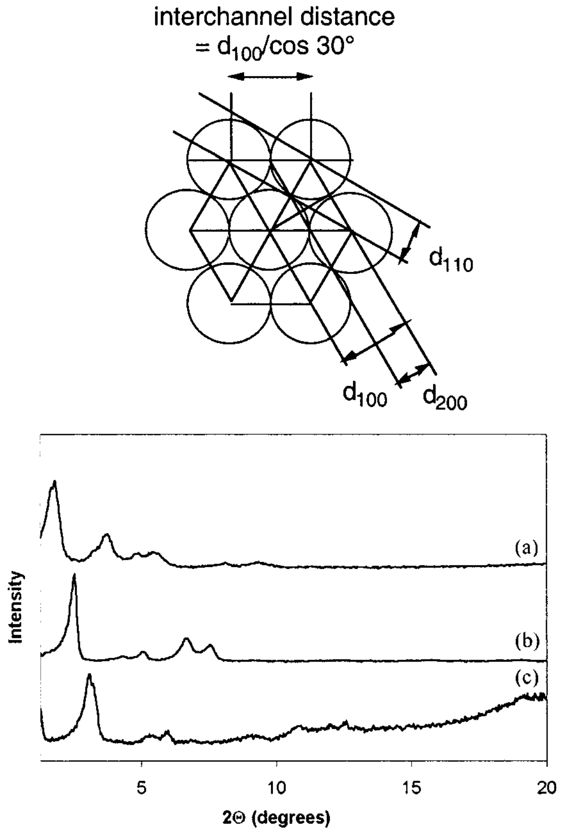

Figure 2. XRD profiles of the H_{II} phases of three unpolymerized neat monomers taken at 24 ± 1 °C: (a) **5**, (b) **7**, and (c) **9**.

of **50** to that of **5**, it can be seen that addition of just an ethyl group as a branch is sufficient to break up strong crystalline packing and induce LC behavior at room temperature. This observation is consistent with previous work on branched surfactants.[40] It should also be noted that for the neat LLC octadecanoate salt series **5**−**9**, placement of the styrene ether branch point very close to the terminus of the tail also begins to favor some formation of the L phase (Table 1).

The samples mixed with 6 wt % H_2O, 10 wt % DVB, and 2 wt % HMPP were photopolymerized with 365 nm light for 12−16 h at ambient temperature (24 ± 1 °C). The extent of polymerization was comparable to that of **1** (ca. 80%), as measured by FT-IR spectroscopy (Figure 3).[15] The resulting cross-linked polymers are slightly opaque, hard, free-standing materials that can be ground to a fine powder. They are also completely insoluble in common organic solvents and water and do not exhibit any noticeable swelling. The cross-linked samples retain the H_{II} phase as determined by PLM, and also exhibit XRD peaks characteristic of the H_{II} phase (see Figure 4 and Table 2). The H_{II} structure of the polymerized samples persists even at temperatures well in excess of 100 °C with only slight changes in unit cell dimensions (see Supporting Information). The XRD secondary peaks of polymerized mixtures from **8** and **9** were weakened significantly compared to the unpolymerized mixtures, and in the case of **9** effectively disappeared. The success of the photopolymerization showed that the individual styrene ether isomers **2**−**11** can be used in the place of **1**, to make functionalized organic nanomaterials. Phenyl ethers are stable to a wide variety of chemical conditions, being significantly labile only in the presence of powerful Lewis acids and concentrated protic acids,[41] so the polymerized matrices could be used under a range of conditions for heterogeneous catalysis, as templates for composite materials, and for nanoparticle formation.

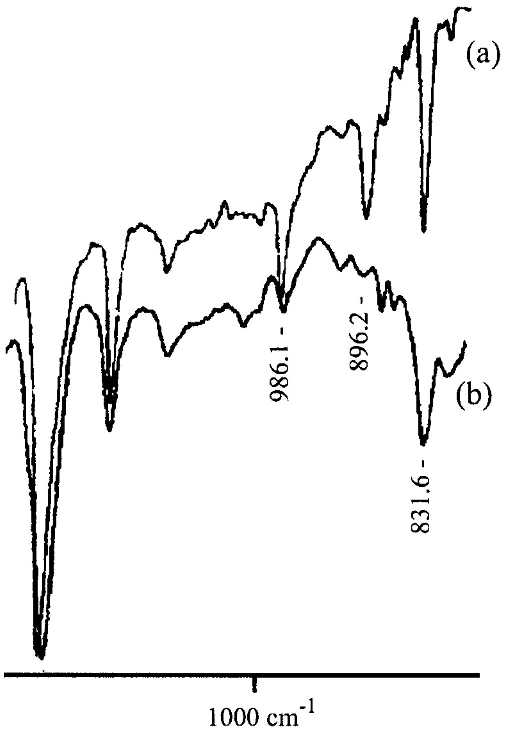

Figure 3. Representative FT-IR spectra of a H_{II} mixture of **4**/DVB/H_2O/HMPP (82/10/6/2 w/w/w/w): (a) before photopolymerization and (b) after photopolymerization.

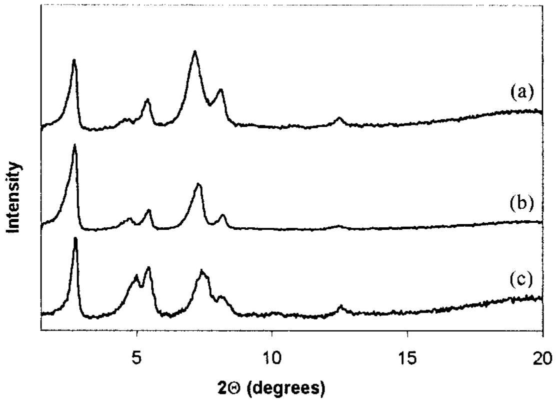

Figure 4. XRD profiles of the H_{II} phases of (a) neat **4**; (b) a mixture of **4**/DVB/H_2O/HMPP (82/10/6/2 w/w/w/w) before photopolymerization; and (c) a mixture of **4**/DVB/H_2O/HMPP (82/10/6/2 w/w/w/w) after 12 h of photopolymerization. The samples were all analyzed at ambient temperature (24 ± 1 °C).

Further studies were conducted on a selection of the LLC isomers. Three of the octadecanoate isomers, **5**, **7**, and **9**, were chosen. The effects on the phase of adding H_2O to the sodium salts were measured, and the results compared to those determined earlier for the styryl isomeric mix **1** (Table 3). Variation of the percentage of water added to H_{II} phases is known to affect the diameter of the aqueous channels[8b] and hence is another possible avenue for control of the nanodimensions. It can be seen that of the three octadecanoate isomers,

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[40] Winsor, P. A. In *Liquid Crystals and Plastic Crystals*; Gray. G. W., Winsor, P. A., Eds; Ellis Horwood: London, 1974; Vol. I, p 253.

[41] (a) Sala, T.; Sargent, M. V. *J. Chem. Soc., Perkin Trans. 1* **1979**, 2593. (b) Greene, T. W.; Wuts, P. G. M. *Protective Groups in Organic Synthesis*, 2nd ed.; John Wiley & Sons: New York, 1991; pp 426−427.

Table 2. Influence of Alkyl Tail Length and Styrene Ether Position on the Dimensions of the H_{II} Phases of LLC Monomers **2**−**11** Formed with 6 wt % H_2O, 12 wt % DVB, and 2 wt % HMPP, and Photopolymerized[d]

LLC monomer	no. of C in alkyl tail	position of styrene ether attachment[a]	cross-linked H_{II} phase $\langle d_{100}\rangle$ (Å)[b]	cross-linked H_{II} phase ICD (Å)
2	12	C10	34.6	39.9
3	12	C6	25.3	29.2
4	16	C10	31.8	36.8
5	18	C16	42.9[c]	49.6[c]
6	18	C12	36.7	42.4
7	18	C10	34.5	39.8
8	18	C6	32.7	37.8
9	18	C4	34.1	39.4
10	22	C16	46.3	53.5
11	22	C10	37.9	43.7

[a] Carbon position for styrene ether attachment numbered progressively along the alkyl tail with C1 being the carboxylate carbon. [b] $\langle d_{100}\rangle$ is the average value of d_{100} based on the positions of all the XRD peaks observed for the H_{II} phase (see ref 39 and the Supporting Information). [c] Evidence of a small amount of L phase formation in the H_{II} phase. [d] The phases were cross-linked at 24 ± 1 °C, and X-ray diffraction measurements on the H_{II} networks were all performed at 24 ± 1 °C.

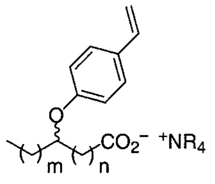
Table 3. Variation of LLC Phase Structure of Selected LLC Monomers as a Function of Water Content[d]

LLC monomer	structure of LLC phases with different amts of H_2O [phase, ($\langle d_{100}\rangle$ (Å))][a] 0% H_2O	6% H_2O	12% H_2O	24% H_2O
1	H_{II} (37.6)	H_{II} (37.9)	H_{II} (38.7)	H_{II} (38.3)[b]
5	−[c] (44.6)	L (48.2)	L (48.2)	L (47.9)
7	H_{II} (35.3)	H_{II} (34.7)	H_{II} (32.9)	H_{II} (33.0)
9	H_{II} (30.3)	H_{II} (28.6)	H_{II} (28.6)	−[c] (28.7)

[a] $\langle d_{100}\rangle$ is the average value of d_{100} based on the positions of all the XRD peaks observed for each phase. [b] Formed with 20 wt % water. [c] Mixture of H_{II} and L phases. [d] X-ray diffraction measurements were all performed at 24 ± 1 °C.

the one with the styrene ether moiety in the middle of the alkyl tail (**7**) exhibits the most stable H_{II} phase with respect to increasing water content. In this regard, **7** is most similar to **1** with respect to resistance to changes in phase structure with changes in system composition. The monomer with the styrene ether unit closest to the ionic headgroup (**9**) maintains the H_{II} phase until 24 wt % added water is reached, at which point it forms a mixture of H_{II} and L phases. In contrast, monomer **5**, with the styrene ether branch point closest to the end of the alkyl tail, seems to be the most sensitive to changes in water content. Addition of even small amounts of water to the mixed LLC phase of **5 (**predominantly H_{II} with some L phase) at ambient temperature changes the phase entirely to an L phase. Thus, depending on the structure of the LLC monomer salt, the amount of added water affects the type of LLC phase favored at ambient temperature but only has a small effect on the lattice dimensions (±1 Å) within each LLC phase formed. A similar experiment was performed by adding a mixture of 83 wt % DVB and 17 wt % HMPP. The samples were analyzed, photopolymerized, and analyzed again. Monomer **7** tolerated 20 wt % added DVB/HMPP and retained the H_{II} phase upon polymerization. Indeed, the order in the H_{II} phase of **7** appears to improve upon polymerization. Upon addition of the same amount of DVB/HMPP to neat **5** at ambient temperature, it maintained the original mixed H_{II}/L phase and was able to retain the mixed phase microstructure upon photopolymerization. In contrast, the LLC phase formed from **9** significantly deteriorated upon polymerization (see Supporting Information). This is consistent with the behavior of **9** when mixed with 12 wt % DVB/HMPP and 6 wt % H_2O and polymerized. The ability of specific isomers to accommodate more DVB cross-linker while retaining the H_{II} phase is of particular interest, as the addition of higher percentages of DVB may lead to even more robust materials.

It is clear from the studies of the styrene ether fatty acid sodium salts that changing the location of the branch point and overall tail length (and hence the alkyl tail volume) generally does not cause the salts to form phases other than the H_{II} phase. Only one of the isomeric LLC sodium salts (**5**) displays any tendency to form the L phase. Furthermore, the phase behavior of the individual octadecanoate styrene ether isomers **5**, **7**, and **9** with H_2O and DVB (Table 3) suggests that the LLC behavior of the styryl regioisomeric mixture **1** is dominated by the more abundant isomers, which have the polymerizable units near the middle of the alkyl chains.[24] To initially examine the effect of varying the headgroup size, tetramethylammonium salts (**55**−**58**) were made from styrene ether fatty acids **40**, **42**, **44**, and **46** for further examination of the effects of adding a large headgroup. Up to 50 wt % H_2O was added to the salts and the phases characterized at ambient temperature (24 ± 1 °C). All the tetramethylammonium salts formed L phases, as expected from the Israelachvili model.[9] A tetraethylammonium salt of **42** (**59**) was also prepared. It adopted an H_{II} phase when mixed with 6 and 12 wt % H_2O (ICD of 65 Å), then formed the L phase when mixed with 24 wt % H_2O.



55: m=5; n=4; R=Me
56: m=1; n=14; R=Me
57: m=7; n=8; R=Me
58: m=13; n=2; R=Me
59: m=1; n=14; R=Et

55–59

Conclusions

A new family of polymerizable LLCs has been prepared using a novel and versatile method for synthesizing styrene ethers. This homologous series of the sodium salts of styrene ether-modified fatty acids has been employed in the formation of cross-linkable H_{II} phases with control of phase dimensions. Examination of a subseries of regioisomers with the same overall chain length showed that the relative position of the styrene ether group along the alkyl chain has a profound effect upon the dimensions of the H_{II} phase at a fixed temperature and system composition. Placing the styrene ether closer to the chain end and further from the headgroup leads to H_{II} phases with systematically larger ICDs, but with a slight concomitant increase in tendency to form the L phase. Varying the total chain length of the monomer also has a significant, though smaller, effect on the unit cell dimensions of the LLC phases, with longer chains affording larger ICDs. Furthermore, changing the counterion on the monomers from Na^+ to tetraalkylammonium ions leads to further control of the unit cell dimensions. These effects in combination allow the formation of cross-linked H_{II} phases at ambient temperature with tunable ICDs in the 29−65 Å range. Manipulation of monomer structure in this fashion offers a new and unparalleled degree of control over feature size in the production of nanostructured organic catalysts and composites based on polymerizable LLC assemblies. In these systems, such control can be used to modulate substrate size exclusion in nanoporous catalyst design, or to form nanoparticles of controlled size in nanocomposite synthesis. Our group is currently engaged in studying the catalytic properties of these cross-linked materials as a function of pore size. We are also preparing transition-metal salts of these styrene ether LLC monomers for the formation of both nanoparticles and composite materials.

Experimental Section

General. All reagents and common solvents, including anhydrous THF, CH_2Cl_2, and toluene, were purchased from the Aldrich Chemical Co. and used as purchased unless otherwise noted. $NaBH_4$ was purchased from Alfa. HPLC grade methanol and $CHCl_3$ were purchased from Fisher Scientific. PCC/Al_2O_3 was prepared according to the method of Cheng et al.[31] 4-Acetoxystyrene was hydrolyzed according to the method of Corson et al.[42] to give 4-vinylphenol as a white crystalline solid that was stored at −20 °C until use. Unless otherwise specified, organic extracts were dried over anhydrous $MgSO_4$, and the solvent removed with a rotary evaporator at aspirator pressure, followed by drying under full vacuum on the Schlenk line (10^{-4} Torr). Column chromatography (flash) was performed with 40 μm silica gel (J. T. Baker). Reaction mixtures and chromatography fractions were monitored with EM Science 250 μm silica gel F_{254} plates. ^1H and ^{13}C NMR spectra were acquired at 500 and 125 MHz, respectively, using a Bruker DRX-500 spectrometer. For NMR analysis, neutral organic compounds were dissolved in $CDCl_3$, and salts were dissolved in d_4-methanol. FT-IR spectra were obtained using a Perkin-Elmer 1616 series FT-IR spectrometer. The samples were analyzed as neat compounds on NaCl or Ge crystals, or as KBr mulls. Elemental analyses were performed at Desert Analytics, Tuscon, AZ, and Quantitative Technologies Inc., Whitehouse, NJ. Optical textures were obtained using a Leica DMRXP polarizing microscope equipped with a Wild MPS 48/52 automatic camera assembly. Low-angle XRD profiles were obtained using an Inel CPS 120 powder diffraction system employing Cu Kα radiation. Photopolymerizations were performed using a Cole-Parmer 9815 series 6 W UV (365 nm) lamp under N_2 flush. Photopolymerization light fluxes were measured using a Spectroline DRC-100X digital radiometer equipped with a DIX-365 UV-A sensor.

Representative syntheses are presented below with a full listing of characterization data (^1H NMR, ^{13}C NMR, FT-IR, and elemental analysis[43]) for all new compounds. Compounds with chiral centers were synthesized as racemic mixtures. Spectral data for all new compounds and XRD peak listings for all LLC mixtures can be found in the Supporting Information. Distinct signals for all nonequivalent carbons in the alkyl backbones were not resolved in all cases due to the length of the alkyl chains. Overlapping signals are indicated as a range with the number of carbons represented.

Methyl 10-Hydroxydecanoate (23).[44] Methanol (50 mL) was added to 10-hydroxydecanoic acid (2.00 g, 10.6 mmol), followed by 10 drops of concentrated sulfuric acid. The solution was heated at reflux for 16 h, cooled to ambient temperature, diluted with water (10 mL), and then poured into ether (150 mL). The layers were separated, and the organic layer was then washed with water (3 × 25 mL), saturated $NaHCO_3$ (25 mL), and saturated NaCl (2 × 25 mL). After drying over $MgSO_4$, the solvent was removed under partial pressure, dry toluene was added (20 mL), and the solvent was removed again. The final product was dried in vacuo yielding 1.916 g (90%) of **23** as an oil which solidified at 4 °C. Spectral data were consistent with those reported in the literature.[44]

Methyl 10-Oxodecanoate (26).[45] PCC/Al_2O_3 (20.9 g, 17.0 mmol) and **3** (1.908 g, 9.43 mmol) were combined. The flask was then evacuated and filled with Ar, and anhydrous CH_2Cl_2 (20 mL) was added. The reaction mixture was stirred at ambient temperature for 5 h and then diluted with diethyl ether (60 mL). The mixture was then filtered through a ca. 4 cm plug of Florisil with extensive washing with diethyl ether (170 mL). The solvent was removed under partial pressure and the resulting oil dried in vacuo to a constant weight of 1.652 g (88% yield). Spectral data were consistent with those reported in the literature.[45]

Methyl 10-Hydroxyoctadecanoate (17).[46] Anhydrous THF (20 mL) was added to **4** (1.250 g, 6.24 mmol) under Ar and the solution chilled to 0 °C. Octylmagnesium bromide, 2.0 M in diethyl ether (4.0 mL, 8.0 mmol), was added, and the reaction was stirred at 0 °C for 1 h. After quenching with H_2O (5 mL) and 1 M HCl (15 mL), the mixture was extracted with diethyl ether (2 × 50 mL). The combined organic layers were then washed with 1 M HCl (1 × 15 mL) and saturated NaCl (2 × 15 mL), and then dried over $MgSO_4$. After removal of the solvent under partial pressure, the product was dried in vacuo to yield 1.865 g (95%) of **17** as a white solid. Spectral data agreed with those reported in the literature.[46]

Methyl 4-Oxooctadecanoate (28).[47] Anhydrous THF (10 mL) was added to CuI (1.26 g, 6.62 mmol) under Ar, and the mixture was chilled to 0 °C. Tetradecylmagnesium bromide, 1 M in THF (6.60 mL, 6.60 mmol), was then added. The resulting gray-black mixture was stirred at 0 °C for 20 min, then cooled to −78 °C, and methyl 4-chloro-4-oxobutyrate (0.45 mL, 3.6 mmol) was added. The reaction mixture was then warmed to 0 °C, stirred for 45 min, and quenched with H_2O (10 mL) and 1 M HCl (10 mL). Diethyl ether (30 mL) was then added and the cloudy organic layer separated. The organic layer was filtered through a 2.5-cm plug of Florisil to remove fine salts, then washed with saturated $NaHCO_3$ (2 × 10 mL) and saturated NaCl (2 × 10 mL) solutions, and dried over $MgSO_4$. The majority of the solvent was removed under partial pressure, and the crude product was dried in vacuo for 16 h. The resulting white solid was subsequently purified by flash chromatography, eluting with an increasing fraction of 2-propanol in $CHCl_3$. Yield: 0.965 g of a white solid (94% from 1 equiv of tetradecylmagnesium bromide). Spectral data were in agreement with the literature.[47]

Methyl 4-Hydroxyoctadecanoate (19).[46a] Compound **28** (0.472 g, 1.51 mmol) was dissolved in methanol (50 mL), and the resulting solution was chilled in an ice bath. $NaBH_4$ (0.112 g, 1.50 mmol) was added and the reaction mixture stirred at 0 °C for 30 min while H_2 gas evolved. H_2O (10 mL) was then added, followed by dropwise addition of 1 M HCl to bring the pH of the mixture to 3. After addition of diethyl ether (2 × 20 mL), the organic layer was washed with 1 M HCl (20 mL), H_2O (2 × 25 mL), and saturated NaCl (2 × 15 mL), and then dried briefly over $MgSO_4$. Removal of the solvent under reduced pressure, followed by drying in vacuo afforded 0.462 g (97%) of pure **19** as a white solid. Spectral data were in agreement with those reported in the literature.[46a]

Methyl 10-(4-Vinylphenoxy)octadecanoate (34). A Schlenk flask was charged with dry toluene (30 mL) under Ar and chilled to 0 °C. Tributylphosphine (2.3 mL, 8.9 mmol) and 1,1′-(azodicarbonyl)-dipiperdine (2.24 g, 8.89 mmol) were then added, and the resulting solution stirred for 1 h at 0 °C while the solution's bright yellow-orange color faded away. Compound **17** (1.865 g, 5.94 mmol) and 4-vinylphenol (0.800 g, 6.66 mmol) were combined and dissolved in anhydrous toluene (15 mL) in a separate vessel and added dropwise to the reaction mixture over a period of 15 min. A white solid formed during the addition. The reaction mixture was stirred at 0 °C for 1 h and then incubated without stirring at −18 °C for 24 h. After thin-layer chromatography ($CHCl_3$) indicated that the reaction had ceased, the reaction mixture was diluted with pentane (200 mL) and chilled to 0 °C for 1 h. The mixture was subsequently filtered, and the solid washed with more pentane (200 mL). The filtrate was then concentrated under

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[42] Corson, B. B.; Heintzelman, W. J.; Schwartzman, L. H.; Tiefenthal, H. E.; Lokken, R. J.; Nickels, J. E.; Atwood, G. R.; Pavlik, F. J. *J. Org. Chem.* **1958**, *23*, 544.

[43] It is extremely difficult to completely remove residual water from the amphiphilic monomer salts, the majority of which are extremely hygroscopic. Consequently, the elemental analysis results for the final salts typically do not agree within ±0.5 wt % of the calculated values for the pure salts. However, the elemental analysis results of the preceding parent carboxylic acids of the final salts (prior to titration with aqueous base) do agree to ±0.5 wt % of expected values, and all other spectroscopic data are consistent with the structures presented. Thus, the identities of the final amphiphilic monomer salts are not in question. In addition, the elemental percentages of the salts are consistent (±0.5%) with the expected values when associated water molecules are factored in.

[44] Baldwin, J. E.; Adlington, R. M.; Ramcharitar, S. H. *Tetrahedron* **1992**, *48*, 2957.

[45] Vinczer, P.; Baan, G.; Novak, L.; Szantay, C. *Tetrahedron Lett.* **1984**, *25*, 2701.

[46] (a) Tulloch, A. P. *Org. Magn. Reson.* **1978**, *11*, 109. (b) Tulloch, A. P. *Lipids* **1976**, *11*, 228.

[47] Jossang, A.; Melhaoui, A.; Bodo, B. *Heterocycles* **1996**, *43*, 755.

partial pressure to yield a crude product. Purification by column chromatography with $CHCl_3$ elution afforded 1.93 g (84%) of pure **34** as a clear oil that solidified at −18 °C. ^{1}H NMR ($CDCl_3$): δ 7.32 (d, 2H), 6.83 (d, 2H), 6.65 (dd, 1H), 5.59 (dd, 1H), 5.11 (dd, 1H), 4.20 (quintet, 1H), 3.66 (s, 3H), 2.29 (t, 2H), 1.60 (m, 6H), 1.40 (m, 2H), 1.18 (m, 20H), 0.87 (t, 3H). ^{13}C NMR ($CDCl_3$): δ 174.3, 158.5, 136.2, 130.0, 127.3, 115.7, 111.3, 78.0, 51.4, 34.1, 33.9, 33.9, 31.8, 29.7, 29.6, 29.5, 29.3, 29.2, 29.1, 29.1, 25.3, 25.3, 24.9, 22.6, 14.1. FT-IR (cm^{-1}): 2927 (s), 2854 (s), 1741 (s), 1628 (w), 1464 (m), 988 (s), 897 (s), 834 (m). Anal. Calcd for $C_{27}H_{44}O_3$: C, 77.83; H, 10.64. Found: C, 77.62; H, 10.46.

10-(4-Vinylphenoxy)octadecanoic Acid (44). A mixture of methanol/H_2O (4:1, 50 mL) and NaOH (0.500 g, 12.5 mmol) was added to **33** (1.10 g, 2.64 mmol). The resulting solution was heated at reflux for 4.5 h and then cooled to ambient temperature, at which time H_2O (5 mL) and 1 M HCl (15 mL) were added to bring the pH of the mixture to 2. The reaction mixture was extracted with 4:1 EtOAc/hexane (2 × 100 mL), and the combined organic layers were washed with saturated NaCl (2 × 50 mL). After drying over $MgSO_4$, the organic layer was concentrated under partial pressure to afford an oil. The product was then dried in vacuo to a constant weight to give 0.745 g (71%) of pure **44** as a thick oil. ^{1}H NMR ($CDCl_3$): δ 10.90 (br s, 1H), 7.32 (d, 2H), 6.84 (d, 2H), 6.65 (dd, 1H), 5.59 (d, 1H), 5.11 (d, 1H), 4.16 (quintet, 1H), 2.35 (t, 2H), 1.64 (m, 6H), 1.28 (m, 22H), 0.94 (t, 3H). ^{13}C NMR ($CDCl_3$): δ 179.5, 158.8, 136.5, 130.3, 127.6, 116.0, 111.5, 79.4, 34.1, 34.1, 33.6, 29.9, 29.9, 29.8, 29.8, 29.7, 29.7 29.5, 29.3, 26.8, 25.6, 24.9, 24.9, 9.79. FT-IR (cm^{-1}): 2927 (s), 2854 (s), 1710 (s), 1628 (w), 1465 (m), 988 (s), 897 (s), 834 (m). Anal. Calcd for $C_{26}H_{42}O_3$: C, 77.56; H, 10.51. Found: C, 77.46; H, 10.63.

Sodium 10-(4-Vinylphenoxy)octadecanoate (7). Compound **44** (0.361 g, 0.897 mmol) was dissolved in ethanol (5 mL) and then neutralized with NaOH (37 mg, 0.9 mmol) in H_2O (2 mL). The solvents were removed under partial pressure, and the product was dried in vacuo for 16 h to afford 0.377 g of **7** (99%) as a sticky, flaky white solid. ^{1}H NMR (d_4-methanol): δ 7.30 (d, 2H), 6.81 (d, 2H), 6.62 (dd, 1H), 5.58 (d, 1H), 5.04 (d, 1H), 4.25 (quintet, 1H), 2.13 (t, 2H), 1.58 (m, 6H), 1.28 (m, 22H), 0.864 (t, 3H). ^{13}C NMR (d_4-methanol): δ 183.3, 160.1, 137.8, 131.7, 128.6, 117.0, 111.6, 79.03, 39.47, 35.23, 35.18, 35.15, 33.15, 30.99, 30.95, 30.81, 30.76, 30.73, 30.49, 27.95, 26.55, 26.47, 23.86, 14.61. FT-IR (cm^{-1}): 2917 (s), 2847 (s), 1572 (s), 1508 (s), 1422 (m), 1243 (m), 987 (s), 896 (s), 833 (m). Anal. Calcd for $C_{26}H_{41}O_3Na$: C, 73.55; H, 9.73; Na, 5.41. Anal. Calcd for (**7** + H_2O) ($C_{26}H_{43}O_4Na$): C, 70.55; H, 9.79; Na, 5.19. Found: C, 71.41; H, 9.90; Na, 5.60.[43]

Tetramethylammonium 10-(4-Vinylphenoxy)octadecanoate (57). Compound **44** (85 mg, 0.21 mmol) was dissolved in ethanol (5 mL). To the resulting solution was added a 25% solution of bis(tetramethylammonium)carbonate in H_2O (85 μL, 0.11 mmol). The solvent was removed under partial pressure, and the product dried in vacuo overnight to give 0.103 g of an hygroscopic sticky solid (quantitative yield). ^{1}H NMR (d_4-methanol): δ 7.29 (d, 2H), 6.80 (d, 2H), 6.65 (dd, 1H), 5.56 (d, 1H), 5.04 (d, 1H), 4.23 (m, 1H), 3.15 (s, 12H), 2.11 (t, 2H), 1.54 (m, 6H), 1.27 (m, 22H), 0.85 (t, 3H). ^{13}C NMR (d_4-methanol): δ 183.0, 160.1, 137.8, 131.7, 128.6, 117.0, 111.7, 79.1, 56.0, 39.6, 35.2, 35.2, 33.2, 31.0, 30.9, 30.7, 30.7, 30.5, 30.5, 28.0, 26.6, 26.5, 23.9, 23.9, 14.6. FT-IR (cm^{-1}): 2919 (s), 2837 (s), 1572 (s), 1248 (s), 985 (m), 897 (m), 832 (s). Anal. Calcd for **57** ($C_{30}H_{53}O_3N$): C, 75.74; H, 11.23; N, 2.94. Anal. Calcd for (**57** + $2H_2O$) ($C_{30}H_{57}O_5N$): C, 70.41; H, 11.23; N, 2.74. Found: C, 70.06; H, 11.68; N, 3.29.[43]

Tetraethylammonium 16-(4-Vinylphenoxy)octadecanoate (59). Compound **42** (20 mg, 0.050 mmol) was dissolved in ethanol (1−2 mL). To the resulting solution was added a 20% solution of tetraethylammonium hydroxide in H_2O (35 μL, 0.050 mmol). After the majority of the solvent was removed under partial pressure, the product was dried in vacuo overnight to yield 0.027 g of a hygroscopic sticky solid (quantitative yield). ^{1}H NMR (d_4-methanol): δ 7.32 (d, 2H), 6.83 (d, 2H), 6.69 (dd, 1H), 5.60 (d, 1H), 5.07 (d, 1H), 4.21 (m, 1H), 3.29 (quartet, 8H), 2.15 (t, 2H), 1.62 (m, 6H), 1.28 (m, 34H), 0.945 (t, 3H). ^{13}C NMR (d_4-methanol): δ 181.0, 158.5, 136.2, 130.1, 127.0, 115.4, 110.1, 78.5, 51.7, 37.7, 33.1, 29.5, 29.4−29.2 (9 C signals), 26.3, 26.3, 24.9, 8.5, 6.2. FT-IR (cm^{-1}): 2920 (s), 2850 (s), 1556 (s), 1507 (s), 1393 (s), 1242 (s), 999 (m), 894 (m). Anal. Calcd for **59** ($C_{34}H_{61}O_3N$): C, 76.78; H, 11.56; N, 2.63. Anal. Calcd for (**59** + $4H_2O$) ($C_{34}H_{69}O_7N$): C, 67.62; H, 11.52; N, 2.32. Found: C, 66.98; H, 11.69; N, 2.57.[43]

Preparation of LLC Phases and Photopolymerization. LLC mixtures were prepared by first placing the appropriate amounts of the LLC monomer salt and additives (see tables) in 40-mL centrifuge tubes and mixing with a spatula by hand. The samples were then centrifuged at 2600 rpm three times with the tubes inverted after each run and allowed to equilibrate at ambient temperature (24 ± 1 °C) for a minimum of 1 h before analysis. The LLC samples were prepared as thin films on quartz plates for PLM analysis, on Al sample holders for XRD analysis, or on Ge crystals for IR analysis. Photopolymerizations were all carried out under light N_2 flush over a period of 12 h at ambient temperature with use of a 6 W UV (365 nm) lamp. The light flux at the surface of the LLC samples during photolysis was 1800 μW/cm^2. Initial conversion of the LLC monomer mixtures to a glassy cross-linked network typically occurs within the first hour of irradiation. The degree of polymerization (i.e., double bond conversion) was determined by monitoring the diminishment of the 988- and 896-cm^{-1} bands (olefin C−H out-of-plane bending) relative to the 832-cm^{-1} band (para-substituted aromatic C−H out-of-plane bending) by FT-IR spectrometry (absorbance mode).

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Supporting Information Available: Full experimental details and characterization data for all new compounds synthesized in this study; XRD data for the LLC phases of monomers **2**−**11** and **55**−**59** in neat form and as mixtures with water and DVB (before and after cross-linking); representative plots showing the small changes in the XRD peaks of the unpolymerized and polymerized H_{II} phases of **7** with increasing temperature (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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