Cross-Linkable Liquid Crystal Monomers Containing Hydrocarbon 1,3-Diene Tail Systems

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ABSTRACT: The unprecedented use of polymerizable hydrocarbon tail systems containing 1,3-diene groups for the design of thermotropic and lyotropic liquid crystal (LC) monomers is described. Cross-linkable LC dienes are synthesized by attaching LC core units to modular ω-bromoalka-1,3-diene tails of variable length. These modular diene tails are synthesized by the oxidation of long chain ω-bromoalkan-1-ols to the corresponding ω-bromoalkanals. Reaction of the ω-bromoalkanals with Matteson's reagent, followed by treatment with triethanolamine and deoxysilylation under Peterson elimination conditions, affords the desired ω-bromoalka-1,3-diene tails. The effect of the 1,3-diene group on the mesogenic behavior of certain thermotropic and lyotropic LC systems was determined by examining 1,3-diene analogues of a thermotropic calamitic LC diacrylate and a taper-shaped lyotropic LC triacrylate. Compared to their diacrylate analogues, the thermotropic LC bis(1,3-diene)s exhibit the same progression of nematic and smectic phases but with higher smectic C to nematic transition temperatures and higher clearing temperatures. Replacement of the three acrylate groups in the tapered-shaped lyotropic LC monomer with 1,3-diene moieties had little effect on its tendency to form the inverted hexagonal phase at room temperature in the presence of water. The lyotropic LC diene phases also exhibit higher clearing temperatures than the corresponding LC triacrylate. The 1,3-diene group was found to be an efficient cross-linking unit for the photopolymerization of lyotropic LC phases at ambient temperature because of its hydrophobicity, minimal phase perturbation, and the high degree of photopolymerization. With thermotropic LC systems, however, Diels−Alder dimerization of adjacent diene units was found to occur upon heating the thermotropic LC bis(diene) monomers to ca. 90 °C or higher. Thus, as a photopolymerizable group in LC monomer design, the practical utility of the 1,3-diene group appears to be limited to temperature regimes below 90 °C.

Introduction

Anisotropic networks based on liquid crystals (LCs) are a class of robust organic materials that have recently received considerable attention in the area of materials chemistry.[1,2] Anisotropic networks formed via the cross-linking of thermotropic LC monomers can be used as nonlinear optical materials,[3] piezoelectric organic transducers,[4] and tunable optical filters and polarizers.[5] These systems have also been considered for use as stable orientation layers for LC displays.[1] Ordered polymer networks based on cross-linked lyotropic (i.e., amphiphilic) LC assemblies have been used for the formation of nanoporous organic materials,[6−8] nanostructured composites,[9,10] and most recently catalytic organic analogues to molecular sieves.[11] The self-organizing nature of the LC starting materials in these systems affords a high degree of control over aspects of nanometer-scale architecture and geometry via judicious monomer design. This architectural control on the microscopic scale can be extended to the macroscopic scale by orienting the samples prior to cross-linking (e.g., via electrical, mechanical, or magnetic fields).[1] The high cross-link density in these materials not only stabilizes the ordered structures on both levels but also imparts a high degree of mechanical, thermal, and temporal stability to any anisotropic properties designed into the networks.

LC networks are usually prepared by either photochemically or thermally initiating the chain addition polymerization of reactive mixtures containing LC monomers possessing at least two polymerizable groups.[1,2] Anisotropic networks can also be formed by first preparing linear LC side chain polymers and then cross-linking the macromolecules in their ordered states.[1,12−14] Photoinitiated polymerization is commonly the method of choice for preparing cross-linked LC assemblies because it provides greater control over the final state of the network by performing the chemistry isothermally. In addition, it can be employed at a specified temperature.[1] This latter factor is particularly important for LC systems because of their inherent temperature sensitivity.

One of the most important considerations in this area of research is monomer design. The shape and physical properties of the LC building blocks ultimately determine the geometry and properties of the anisotropic networks. The nature of the polymerizable group is an important factor in LC monomer design because the reactive groups must be not only capable of rapid and efficient polymerization to trap the LC state but also conducive to LC phase formation. Reactive groups that have been employed in polymerizable thermotropic LCs have been acrylate,[1,3] methacrylate,[1] epoxide,[15] vinyl ether,[16,17] and dienoyl[18] units. These groups offer convenient preparation of polymerizable alkyl tails with the lengths necessary to induce LC behavior in the monomers. In addition, they can be photopolymerized with the appropriate initiator at the temperatures required for LC phase formation. For cross-linkable lyotropic LC systems, acrylates, dienoyl groups, and diacetylenes are the preferred reactive groups[2] due to their convenient synthesis, high photoreactivity at low or ambient temperatures, and high degree of conversion in the presence of water. Other reactive groups such as styrenes, terminal olefins, isocyanides, acrylamides, and cinnamoyl groups have also been employed in various polymerizable amphiphile designs.[19]

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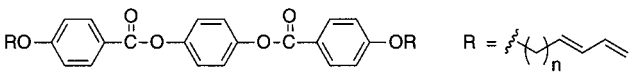
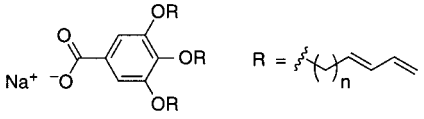
Unfortunately, many of these reactive groups have inherent drawbacks in LC design. For example, the majority of the aforementioned polymerizable groups are either polar (e.g., acrylates, acrylamides, dienoyl groups) or relatively bulky (e.g., styrenes, cinnamoyl groups), making them very different in character from the flexible hydrocarbon tails typically found on non-polymerizable LCs. Consequently, these groups are sometimes detrimental to mesogenic behavior when incorporated into a LC molecule. In addition, acrylate and methacrylate groups tend to give mesogenic systems with relatively high melting (T_m) and clearing (T_c) points.[1] LC systems with different T_m and T_c ranges can be achieved by using epoxide,[15] vinyl ether,[16,17] or dienoyl[18] groups. However, epoxides and vinyl ethers require photoinduced cationic polymerization, which is slow compared to radical photopolymerization.[1] Alkyl tails containing terminal olefins are physically more similar to linear alkyl chains; however, they are unactivated and difficult to polymerize without using transition-metal catalysts or extreme conditions (e.g., ionizing radiation). Diacetylene-containing tails are also similar to alkyl chains in hydrophobic character, but the diacetylene unit imparts more conformational rigidity to the chain. Although diacetylenes can be efficiently polymerized in the crystalline state and in ordered amphiphilic assemblies (e.g., bilayers, vesicles),[2,19] the structural changes incurred upon diacetylene polymerization are sometimes not conducive to retention of order in certain thermotropic LC systems.[20]

During the course of our research in designing polymerizable analogues of new functional LCs, we encountered the need for polymerizable groups that are more similar in hydrophobicity, size, and conformational character to typical alkyl tail units, yet reactive enough to undergo facile radical photopolymerization. This combination of characteristics was necessary for obtaining stable polymerizable analogues of some sensitive LC phases. Herein, we describe the synthesis of novel cross-linkable LCs with modular hydrocarbon tail systems containing a terminal 1,3-diene group. The use of hydrocarbon diene tail systems not only addresses these LC monomer design issues but also offers certain advantages in terms of materials properties in the cross-linked materials. For example, polydiene networks have different thermal stabilities than polyacrylate networks and would not be susceptible to hydrolytic degradation. The general effect of this reactive hydrocarbon diene tail system on mesogenic behavior and its effectiveness for cross-linking in the LC state were determined by synthesizing and studying diene analogues (**1** and **2**) of representative thermotropic and lyotropic LC acrylate monomers (**3** and **4**) (Figures 1 and 2).



1

1a n = 5
1b n = 8
1c n = 10



2

2a n = 8
2b n = 10

Experimental Section

General Considerations. All manipulations involving air- and/or water-sensitive materials were performed using standard vacuum-line techniques. Nitrogen was purified by passage through columns of Q-5 catalyst (Englehard) and 13X molecular sieves (Aldrich). All purified and liquid reagents were degassed by repeated freeze−pump−thaw cycles and stored under N_2 in flasks fitted with PTFE valves. Reaction mixtures and chromatography fractions were monitored with Whatman 250 μm silica gel F_{254} TLC plates. All column chromatography was performed using 40 μm flash silica gel purchased from J.T. Baker. Unless otherwise specified, organic extracts were dried over anhydrous Na_2SO_4, and the volatile components were removed using a rotary evaporator at aspirator pressure, followed by full vacuum on the Schlenk line (10^{-4} Torr).

Materials and Reagents. All reagents and solvents were obtained from commercial suppliers and used without further purification unless noted otherwise. Triethylamine was distilled from K_2CO_3 and stored under N_2. Thionyl chloride was distilled and stored under N_2. Tetrahydrofuran (THF) was vacuum-transferred from sodium/benzophenone. Methylene chloride was vacuum-transferred from calcium hydride prior to use.

Instrumentation. Fourier transform infrared (FT-IR) spectra were obtained using a Perkin-Elmer 1616 FT-IR spectrometer at a resolution of 4 cm^{-1} and recorded as neat films on KBr plates or as KBr mulls. ^1H NMR spectra were obtained using a Bruker AMX-300 (300 MHz), AMX-400 (400 MHz), or DRX-500 (500 MHz) FT spectrometer. Proton-decoupled ^{13}C NMR spectra were obtained at 101 MHz using a Bruker AMX-400 or at 126 MHz using a Bruker DRX-500 spectrometer. NMR spectra were obtained in $CDCl_3$ (Cambridge Isotope Laboratories). Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ. Polarized light microscopy (PLM) images were obtained using a Leica DMRXP POL microscope equipped with a Linkam THMSE 600 hot stage controlled by a Linkam TP92 temperature controller (accuracy ±0.1 °C). Differential scanning calorimetry (DSC) traces were obtained using a Perkin-Elmer DSC-7. Low-angle X-ray diffraction profiles were obtained with an Inel CPS 120 powder diffraction system using monochomatic Cu Kα radiation. This system was equipped with an Inel programmable capillary oven (accuracy ±3 °C) for variable-temperature studies. An IEC Centra CL2 centrifuge was used for mixing lyotropic LC samples. A Cole-Parmer 9815 series 6 W UV (365 nm) lamp was used for photopolymerization experiments.

Photopolymerization Sample Preparation and Methods. For thermotropic LCs **1a** and **1b**, each monomer was dissolved in CH_2Cl_2 and mixed with 1.5 mol % of 2,2-dimethoxy-2-phenylacetophenone. The volatile components were removed in vacuo affording the doped mixture of thermotropic LC monomer and photoinitiator. Thin films suitable for FT-IR analysis were cast on KBr plates and exposed to UV light (intensity of 2200 $\mu W/cm^2$ at 365 nm) through a quartz window on the N_2-flushed Linkam THMSE 600 hot stage at the appropriate temperature (126 °C for **1a** and 95 °C for **1b**) for 4 h.[21] For IH mixtures of lyotropic LCs **2a** and **2b**, 70.0 mg (86 wt %) of the monomer, 4.9 mg (6 wt %) of a 1.05 M solution of 2,2-dimethoxy-2-phenylacetophenone in *n*-dodecane, and 6.5 mg (8 wt %) of deionized H_2O were combined in a 10 × 75 mm test tube. The mixture was then centrifuged at 3800 rpm for 10 min and manually mixed with a spatula. This procedure was repeated twice before sealing the test tube with a rubber septum and allowing the mixture to equilibrate overnight at ambient temperature. Thin films suitable for FT-IR analysis were prepared on Ge plates and exposed to UV light (intensity of 2200 $\mu W/cm^2$ at 365 nm) in a N_2-flushed chamber at ambient temperature overnight.[21] The extent of polymerization in these systems was estimated by quantifying the decrease in the integrated peak intensity of the characteristic 1650 cm^{-1} stretching band of the diene groups before and after photolysis, using the absorbance mode of the FT-IR spectrometer and Beer's law.

Synthesis of ω-Bromoalkanals. ω-Bromoalkanals were prepared by Swern oxidation of ω-bromoalkan-1-ols according to literature procedures[22] and purified by column chromatography on silica gel (see below for appropriate conditions for the individual compounds). Spectroscopic data for the ω-bromoalkanal products were consistent with that reported for the same compounds made by alternate methods, as referenced below.

6-Bromohexanal.[23] Chromatography: 88:12 hexanes/ethyl acetate. Yield: 5.35 g (83%).

9-Bromononanal.[24] Chromatography: 90:10 hexanes/ethyl acetate. Yield: 8.40 g (88%).

11-Bromoundecanal.[25] Chromatography: 88:12 hexanes/ethyl acetate. Yield: 7.74 g (88%).

2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.[26] This reagent was prepared according to literature procedures[26] and purified by distillation (bp 61−62 °C at 7.5 Torr) to afford a clear, colorless liquid (72.0 g, 91%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.12 (d, J = 6.1 Hz, 6H), 1.17 (s, 12H), 4.31 (sept, J = 6.2 Hz, 1H). Spectroscopic data were consistent with that published in the literature.[26]

4,4,5,5-Tetramethyl-2-[(2*E*)-3-(trimethylsilyl)-2-propenyl]-1,3,2-dioxaborolane (Matteson's Reagent).[27] To a 500 mL, two-neck, round-bottom flask equipped with a 50 mL pressure-equalizing funnel was added tetramethylethylenediamine (19.6 mL, 0.13 mol), THF (80 mL), and *sec*-butyllithium (100 mL of 1.3 M solution in cyclohexane, 0.13 mol) under N_2 flush. The pressure-equalizing funnel was charged with allyltrimethylsilane (20.7 mL, 0.13 mol) and added dropwise to a stirring solution at −78 °C. The reaction mixture was stirred at −78 °C for 30 min and at −40 °C for an additional 2 h. This solution was added at −78 °C to a 1000 mL three-neck, round-bottom flask, equipped with an overhead stirrer and N_2 outlet, and charged with isopropyl pinacolborate (24.2 g, 0.13 mol) and THF (60 mL). The reaction mixture was stirred for 14 h, allowed to warm to ambient temperature, and then transferred to a 2000 mL beaker containing CH_2Cl_2 (300 mL), saturated aqueous NH_4Cl (150 mL), and 1 N HCl (150 mL). This solution was extracted with diethyl ether (300 mL) and washed with H_2O (3 × 150 mL) and brine (1 × 100 mL). The organic layer was dried, and the volatile components were removed in vacuo. The crude product was purified by fractional distillation at reduced pressure (48 °C at 0.1 Torr) to afford the pure product as a clear, colorless liquid (23.0 g, 74%). Spectroscopic data were consistent with that published in the literature.[27] ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.02 (s, 9), 1.24 (s, 12), 1.81 (d, J = 7.1 Hz, 2H), 5.61 (dt, J = 18.4, 1.5 Hz, 1H), 6.06 (dt, J = 18.4, 7.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ −0.90, 24.89, 83.35, 130.86, 142.26. IR (cm^{-1}): 2979, 2955, 1612, 1468, 1371, 1352, 1326, 1272, 1247, 1214, 1165, 1145, 1104, 986, 968, 886, 846, 837.

General Procedure for the Preparation of a ω-Bromoalka-1,3-dienes (5). To a 100 mL round-bottom flask was added the appropriate ω-bromoalkanal (34 mmol), Matteson's reagent (9.3 g, 39 mmol), and diethyl ether (50 mL). The reaction mixture was stirred at ambient temperature for 60 h after which time triethanolamine (6.1 g, 41 mmol) was added. The mixture was stirred for an additional 6 h during which time a white precipitate formed. After washing with saturated sodium bicarbonate (2 × 75 mL), H_2O (1 × 50 mL), and brine (1 × 50 mL), the organic fraction of the reaction mixture was dried, and the volatile components were removed. The remaining crude material was partially purified by column chromatography (75:25 v/v hexanes:ethyl acetate) to afford the (±)-(*R**,*S**)-3-trimethylsilyl-4-hydroxy-1-alkenes. This material was added to a 50 mL round-bottom flask with THF (25 mL) and concentrated H_2SO_4 (5 drops). The reaction mixture was stirred at ambient temperature in the absence of light for 12 h, washed with saturated sodium bicarbonate (1 × 50 mL) and brine (1 × 50 mL), and then dried. The volatile components were then removed, and the resulting crude product was purified by column chromatography (100% hexanes) to afford a clear, colorless liquid. For two of the compounds which were previously made using different starting materials and approaches, spectroscopic data were consistent with that published.

9-Bromo-1,3-nonadiene (5a).[28] This compound was synthesized from 6-bromohexanal and Matteson's reagent. Yield: 3.04 g (54%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.43 (m, 4H), 1.86 (m, 2H), 2.10 (m, 2H), 3.40 (t, J = 6.8 Hz, 2H), 4.96 (d, J = 10.1 Hz, 1H), 5.09 (d, J = 17.0 Hz, 1H), 5.69 (dt, J = 15.2, 7.0 Hz, 1H), 6.05 (dd, J = 15.2, 10.4 Hz, 1H), 6.31 (ddd, J = 17.0, 10.4, 10.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 27.89, 28.48, 32.48, 32.84, 34.01, 115.12, 131.41, 135.03, 137.37. IR (cm^{-1}): 3084, 3035, 3006, 2927, 2855, 1799, 1652, 1602, 1459, 1437, 1415, 1350, 1301, 1260, 1238, 1197, 1003, 951, 899, 729. Anal. Calcd for $C_9H_{15}Br$: C, 53.22; H, 7.44. Found: C, 52.96; H, 7.83.

12-Bromo-1,3-dodecadiene (5b).[29] This compound was synthesized from 9-bromononanal and Matteson's reagent. Yield: 5.3 g (64%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.30 (m, 6H), 1.40 (m, 4H), 1.85 (m, 2H), 2.08 (m, 2H), 3.40 (t, J = 6.9 Hz, 2H), 4.96 (d, J = 10.2 Hz, 1H), 5.08 (d, J = 16.9 Hz, 1H), 5.70 (dt, J = 15.2, 6.8 Hz, 1H), 6.04 (dd, J = 15.2, 10.4 Hz, 1H), 6.31 (ddd, J = 16.9, 10.5, 10.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 28.33, 28.88, 29.24, 29.30, 29345, 32.69, 32.99, 34.15, 114.80, 131.09, 135.61, 137.49. IR (cm^{-1}): 3084, 3035, 3006, 2926, 2854, 1792, 1652, 1602, 1464, 1436, 1415, 1352, 1298, 1248, 1217, 1003, 950, 898, 735. Anal. Calcd for $C_{12}H_{21}Br$: C, 58.78; H, 8.63. Found: C, 58.74; H, 8.99.

14-Bromo-1,3-tetradecadiene (5c). This compound was synthesized from 11-bromoundecanal and Matteson's reagent. Yield: 5.87 g (70%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.28 (m, 10H), 1.40 (m, 4H), 1.85 (m, 2H), 2.07 (m, 2H), 3.40 (t, J = 6.9 Hz, 2H), 4.96 (d, J = 9.7 Hz, 1H), 5.08 (d, J = 16.9 Hz, 1H), 5.70 (dt, J = 15.2, 7.0 Hz, 1H), 6.05 (dd, J = 15.2, 10.4 Hz, 1H), 6.31 (ddd, J = 16.9, 10.4, 9.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 28.37, 28.96, 29.37, 29.63, 29.65, 32.74, 33.03, 34.22, 114.77, 131.05, 135.76, 137.55. IR (cm^{-1}): 3084, 3034, 3006, 2926, 2853, 1797, 1652, 1602, 1464, 1438, 1415, 1369, 1352, 1299, 1252, 1003, 950, 897, 722. Anal. Calcd for $C_{14}H_{25}Br$: C, 61.53; H, 9.22. Found: C, 61.21; H, 9.05.

General Procedure for the Synthesis of 4-(Alkadienyl)oxybenzoic Acids (6). Methyl 4-hydroxybenzoate (0.83 g, 5.5 mmol) and ω-bromoalka-1,3-diene (5.9 mmol) were dissolved in methyl ethyl ketone (25 mL) in a 50 mL round-bottom flask. To this solution was added K_2CO_3 (2.3 g, 16.4 mmol). The flask was then fitted with a reflux condenser, and the reaction mixture was heated at reflux for 48 h under N_2 flush. The reaction mixture was then poured into a 250 mL separatory funnel, extracted with hexanes (100 mL), washed with water (3 × 50 mL) and brine (1 × 50 mL), and dried over Na_2SO_4. The volatile components were then removed with a rotary evaporator. The crude product was placed in a 250 mL round-bottom flask to which was added ethanol (85 mL), H_2O (15 mL), and finally NaOH (0.88 g, 21.9 mmol). After heating this mixture at reflux for 12 h, 3 N HCl (11 mL, 33 mmol) was added, generating the product as an off-white solid precipitate. The product was isolated by vacuum filtration, washed with cold hexanes, and dried in vacuo.

4-((6,8-Nonadienyl)oxy)benzoic Acid (6a). This compound was synthesized from **5a** and methyl 4-hydroxybenzoate as described above. Yield: 1.29 g (90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.49 (m, 4H), 1.82 (m, 2H), 2.13 (m, 2H), 4.02 (t, J = 6.5 Hz, 2H), 4.97 (d, J = 10.1 Hz, 1H), 5.10 (d, J = 16.5 Hz, 1H), 5.71 (dt, J = 14.5, 7.0 Hz, 1H), 6.07 (dd, J = 14.9, 10.7 Hz, 1H), 6.31 (ddd, J = 16.5, 10.7, 10.1 Hz, 1H), 6.93 (d, J = 8.9 Hz, 2H), 8.06 (d, J = 8.8 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 25.73, 29.06, 29.14, 32.60, 68.34, 114.38, 115.09, 121.63, 131.40, 132.55, 135.18, 137.42, 163.84, 172.29. IR (cm^{-1}): 3084, 3002, 2931, 2851, 1669, 1607, 1578, 1513, 1468, 1430, 1332, 1308, 1294, 1258, 1169, 1128, 1064, 1003, 972, 949, 898, 844, 772. Anal. Calcd for $C_{16}H_{20}O_3$: C, 73.82; H, 7.74. Found: C, 73.57; H, 7.52.

4-((9,11-Dodecadienyl)oxy)benzoic Acid (6b). This compound was synthesized from **5b** and methyl 4-hydroxybenzoate as described above. Yield: 0.75 g (96%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.33 (m, 8H), 1.46 (m, 2H), 1.81 (m, 2H), 2.08 (m, 2H), 4.02 (t, J = 6.5 Hz, 2H), 4.95 (d, J = 10.1 Hz, 1H), 5.09 (d, J = 16.9 Hz, 1H), 5.71 (dt, J = 15.2, 6.9 Hz, 1H), 6.05 (dd,

J = 15.2, 10.4 Hz, 1H), 6.31 (ddd, J = 16.9, 10.3, 10.1 Hz, 1H), 6.93 (d, J = 9.0 Hz, 2H), 8.06 (d, J = 8.9 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 26.16, 29.28, 29.30, 29.35, 29.48, 29.58, 32.73, 68.47, 114.40, 114.83, 121.58, 131.11, 132.54, 135.71, 137.54, 163.90, 172.15. IR (cm^{-1}): 3081, 2997, 2922, 2851, 1668, 1606, 1578, 1513, 1466, 1428, 1331, 1307, 1293, 1258, 1169, 1147,1128, 1064, 1037, 1002, 954, 904, 844, 772. Anal. Calcd for $C_{19}H_{26}O_3$: C, 75.46; H, 8.67. Found: C, 75.40; H, 8.51.

4-((11,13-Tetradecadienyl)oxy)benzoic Acid (6c). This compound was synthesized from **5c** and methyl 4-hydroxybenzoate as described above. Yield: 0.39 g (80%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.28 (m, 12H), 1.37 (m, 2H), 1.80 (m, 2H), 2.07 (m, 2H), 4.02 (t, J = 6.6 Hz, 2H), 4.95 (d, J = 10.8 Hz, 1H), 5.09 (d, J = 16.8 Hz, 1H), 5.70 (dt, J = 15.2, 6.9 Hz, 1H), 6.04 (dd, J = 15.2, 10.4 Hz, 1H), 6.31 (ddd, J = 16.8, 10.8, 10.4 Hz, 1H), 6.93 (d, J = 8.9 Hz, 2H), 8.05 (d, J = 8.8 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 26.19, 29.31, 29.40, 29.55, 29.68, 29.71, 29.74, 32.76, 68.51, 114.43, 114.79, 121.51, 131.08, 132.54, 135.82, 137.59, 163.89, 171.38. IR (cm^{-1}): 3078, 3006, 2922, 2852, 1674, 1607, 1580, 1514, 1469, 1429, 1393, 1304, 1256, 1171, 1108, 1038, 1003, 949, 896, 847, 773. Anal. Calcd for $C_{21}H_{30}O_3$: C, 76.32; H, 9.15. Found: C, 76.53; H, 9.29.

General Procedure for Synthesis of Thermotropic LC Bis(dienes). To a 50 mL air-free flask was added the 4-(alkadienyl)oxybenzoic acid (**6**) (3.83 mmol), CH_2Cl_2 (25 mL), and $SOCl_2$ (0.50 mL, 6.81 mmol). The flask was fitted with a reflux condenser, and the reaction mixture was heated at reflux under N_2 for 16 h. The volatile components were then removed in vacuo affording an off-white oil. To the same reaction flask was added CH_2Cl_2 (25 mL), $N(C_2H_5)_3$ (2.6 mL, 18.7 mmol), and hydroquinone (0.19 g, 1.7 mmol) in that order. The mixture was then heated at reflux for 48 h and poured into a 250 mL separatory funnel. After extraction with diethyl ether (125 mL), the organic layer was washed successively with 1 N HCl (2 × 50 mL) and brine (2 × 50 mL). The organic extracts were then concentrated in vacuo to afford the crude product. Trituration with hexanes and isolation of the resulting solid via vacuum filtration afforded the pure product as an off-white powder.

Thermotropic LC Bis(diene) Monomer (1a). This compound was synthesized from **6a** and hydroquinone using the procedure described above. Yield: 0.77 g (75%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.49 (m, 8H), 1.83 (m, 4H), 2.13 (m, 4H), 4.04 (t, J = 6.5 Hz, 4H), 4.96 (d, J = 10.1, 2H), 5.09 (d, J = 16.9 Hz, 2H), 5.71 (dt, J = 15.2, 7.00 Hz, 2H), 6.06 (dd, J = 15.2, 10.4 Hz, 2H), 6.31 (ddd, J = 16.9, 10.4, 10.2 Hz, 2H), 6.96 (d, J = 8.9 Hz, 4H), 7.25 (s, 4H), 8.14 (d, J = 8.9 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 25.74, 29.07, 29.15, 32.60, 68.39, 114.51, 115.10, 121.65, 122.85, 131.42, 132.55, 135.18, 137.42, 148.61, 163.73, 165.05. IR (cm^{-1}): 3081, 3008, 2916, 2853, 1725, 1607, 1582, 1513, 1466, 1420, 1299, 1264, 1256, 1185, 1172, 1099, 1003, 886, 848, 760. Anal. Calcd for $C_{38}H_{42}O_6$: C, 76.74; H, 7.12. Found: C, 76.93; H, 7.39.

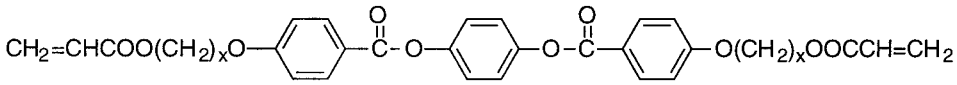
Thermotropic LC Bis(diene) Monomer (1b). This compound was synthesized from **6b** and hydroquinone using the same procedure described above, except for a final column chromatography purification step (77:23 hexanes/ethyl acetate). Yield: 0.40 g (66%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.34 (m, 16H), 1.48 (m, 4H), 1.82 (m, 4H), 2.09 (m, 4H), 4.03 (t, J = 6.5 Hz, 4H), 4.96 (d, J = 10.1, 2H), 5.09 (d, J = 16.9 Hz, 2H), 5.71 (dt, J = 15.1, 7.00 Hz, 2H), 6.06 (dd, J = 15.1, 10.4 Hz, 2H), 6.32 (ddd, J = 16.9, 10.4, 10.1 Hz, 2H), 6.97 (d, J = 8.9 Hz, 4H), 7.26 (s, 4H), 8.15 (d, J = 8.9 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 26.10, 29.22, 29.25, 29.29, 29.43, 29.52, 32.67, 68.41, 114.44, 114.79, 121.52, 122.77, 131.07, 132.43, 135.60, 137.47, 148.53, 163.70, 164.92. IR (cm^{-1}): 3082, 3009, 2917, 2850, 1725, 1608, 1582, 1513, 1467, 1420, 1299, 1260, 1186, 1171, 1101, 1004, 950, 886, 848, 760. Anal. Calcd for $C_{44}H_{54}O_6$: C, 77.84; H, 8.02. Found: C, 77.75; H, 8.14.

Thermotropic LC Bis(diene) Monomer (1c). This compound was synthesized from **6c** and hydroquinone as above and purified by recrystallized from hexanes/ethyl acetate: Yield: 0.17 g (44%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.29 (m, 24H), 1.47 (m, 4H), 1.82 (m, 4H), 2.08 (m, 4H), 4.04 (t, J = 6.6 Hz, 4H), 4.95 (d, J = 9.6, 2H), 5.08 (d, J = 17.0 Hz, 2H), 5.71 (dt, J = 15.3, 6.8 Hz, 2H), 6.05 (dd, J = 15.3, 10.4 Hz, 2H), 6.31 (ddd, J = 17.0, 10.4, 9.7 Hz, 2H), 6.97 (d, J = 9.0 Hz, 4H), 7.25 (s, 4H), 8.14 (d, J = 8.9 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 26.17, 29.29, 29.38, 29.54, 29.66, 29.69, 32.75, 68.53, 114.52, 114.79, 121.56, 122.85, 131.06, 132.51, 135.79, 137.56, 148.60, 163.80, 165.10. IR (cm^{-1}): 3076, 3007, 2916, 2848, 1726, 1607, 1581, 1514, 1467, 1420, 1299, 1270, 1256, 1184, 1170, 1083, 1003, 886, 848, 760. Anal. Calcd for $C_{48}H_{62}O_6$: C, 78.44; H, 8.50. Found: C, 78.17; H, 8.32.

3,4,5-Tris((9,11-dodecadienyl)oxy)benzoic Acid (7a). Methyl gallate (0.56 g, 3.02 mmol) and **5b** (2.44 g, 10.0 mmol) were dissolved in methyl ethyl ketone (50 mL) in a 100 mL round-bottom flask. To this solution was added K_2CO_3 (4.59 g, 33.2 mmol). The flask was then fitted with a reflux condenser, and the reaction mixture was heated at reflux for 48 h. The reaction mixture was then poured into a 500 mL separatory funnel, extracted with ethyl acetate (200 mL), washed with water (3 × 75 mL), and dried over Na_2SO_4. The volatile components were then removed with a rotary evaporator, and the crude product placed in a 500 mL round-bottom flask to which was added ethanol (120 mL), H_2O (20 mL), and finally NaOH (0.85 g, 21.3 mmol). This mixture was subsequently heated at reflux for 12 h. After heating, 3 N HCl (11.2 mL, 33.5 mmol) was added, generating an off-white solid precipitate. The product was isolated by vacuum filtration and washed with hexanes to afford a white powder. Yield: 1.63 g (82%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.33 (m, 24H), 1.48 (m, 6H), 1.75 (m, 2H), 1.82 (m, 4H), 2.08 (m, 6H), 4.03 (m, 6H), 4.95 (d, J = 10.1 Hz, 3H), 5.08 (d, J = 16.9 Hz, 3H), 5.71 (dt, J = 15.1, 6.9 Hz, 3H), 6.05 (dd, J = 15.1, 10.5 Hz, 3H), 6.31 (ddd, J = 16.9, 10.5, 10.1 Hz, 3H), 7.33 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 26.24, 29.35, 29.38, 29.43, 29.49, 29.64, 29.73, 30.50, 32.74, 69.36, 73.70, 108.78, 114.78, 123.85, 131.09, 135.68, 137.53, 143.36, 153.02, 172.12. IR (cm^{-1}): 3084, 3009, 2925, 2852, 1682, 1652, 1601, 1587, 1505, 1466, 1432, 1384, 1335, 1276, 1226, 1152, 1125, 1001, 973, 955, 899, 863, 767. Anal. Calcd for $C_{43}H_{66}O_5$: C, 77.90; H, 10.04. Found: C, 78.04; H, 10.02.

3,4,5-Tris((11,13-tetradecadienyl)oxy)benzoic Acid (7b). This compound was synthesized from **5c** and methyl gallate by the same procedure used for **7a**. Yield: 3.55 g (96%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.29 (m, 36H), 1.48 (m, 6H), 1.75 (m, 2H), 1.82 (m, 4H), 2.07 (m, 6H), 4.02 (m, 6H), 4.95 (d, J = 10.1 Hz, 3H), 5.11 (d, J = 16.9 Hz, 3H), 5.70 (dt, J = 15.1, 7.0 Hz, 3H), 6.04 (dd, J = 15.2, 10.4 Hz, 3H), 6.31 (ddd, J = 17.0, 10.4, 10.1 Hz, 3H), 7.33 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 26.23, 26.26, 29.40, 29.47, 29.57, 29.70, 29.75, 29.79, 29.83, 29.89, 30.52, 32.76, 69.38, 73.73, 108.78, 114.75, 123.79, 131.05, 135.78, 137.56, 143.38, 153.04, 171.94. IR (cm^{-1}): 3084, 3037, 3002, 2921, 2850, 1683, 1649, 1587, 1505, 1467, 1431, 1384, 1334, 1275, 1226, 1125, 1002, 973, 950, 899, 864, 765. Anal. Calcd for $C_{49}H_{78}O_5$: C, 78.77; H, 10.52. Found: C, 78.62; H, 10.28.

Sodium 3,4,5-Tris((9,11-dodecadienyl)oxy)benzoate (2a). To a 50 mL round-bottom flask was added **7a** (0.25 g, 0.38 mmol), THF (25 mL) and 0.53 M NaOH in methanol (0.71 mL, 0.38 mmol). After stirring the reaction mixture for 1 h at ambient temperature, the volatile components were removed in vacuo to leave a pale yellow gel. Acetone (10 mL) was then added and removed in vacuo (3×) in order to remove any H_2O or methanol as an azeotrope. The product was isolated as an off-white flaky solid. Yield: 0.26 g (99%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.26 (m, 24H), 1.49 (m, 6H), 1.65 (m, 6H), 2.05 (m, 6H), 3.62 (m, 4H), 3.77 (m, 2H), 4.94 (d, J = 10.1 Hz, 3H), 5.06 (d, J = 16.9 Hz, 3H), 5.66 (dt, J = 14.8, 6.7 Hz, 3H), 6.01 (dd, J = 15.0, 10.5 Hz, 3H), 6.31 (ddd, J = 16.9, 10.6, 10.1 Hz, 3H), 6.89 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 26.53, 26.69, 29.60, 29.69, 29.97, 30.50, 30.84, 32.88, 69.00, 73.23, 107.42, 114.88, 129.41, 131.12, 135.45, 137.47, 140.73, 152.51, 175.32. IR (cm^{-1}): 3324, 3084, 3034, 3007, 2924, 2852, 1652, 1602, 1576, 1551, 1501, 1466, 1412, 1380, 1313, 1225, 1129, 1002, 950, 897, 788. Anal. Calcd for $C_{43}H_{65}NaO_5$: C, 75.40; H, 9.57. Found: C, 75.02; H, 10.16.



3

3a	x = 4
3b	x = 5
3c	x = 6
3d	x = 8
3e	x = 10
3f	x = 11

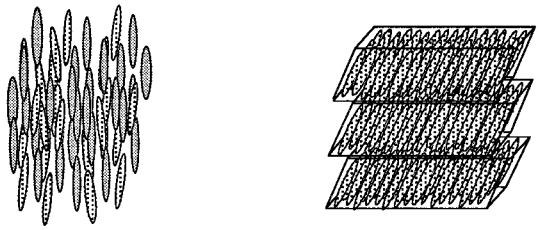


Figure 1. Thermotropic LC acrylate monomers **3** and their representative phases.

Table 1. Transition Temperatures and Phase Behavior of Thermotropic LC Diacrylate Monomers 3[a]

monomer	*x*	LC phases and transition temp (°C)						
3a	4	K	107			N	165	I
3b	5	K	92			N	170	I
3c	6	K	108	SmC	(88)	N	155	I
3d	8	K	82	SmC	108	N	148	I
3e	10	K	87	SmC	112	N	137	I
3f	11	K	81	SmC	114	N	134	I

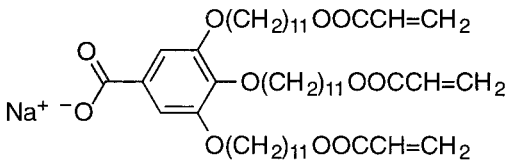
[a] K = crystalline, SmC = smectic C, N = nematic, I = isotropic. Parentheses denote transition temperatures for monotropic phases that appear only on cooling.

Sodium 3,4,5-Tris((11,13-tetradecadienyl)oxy)benzoate (2b). This compound was synthesized from **7b** using the same procedure as that for **2a**. Yield: 0.13 g (97%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.24 (m, 36H), 1.48 (m, 6H), 1.70 (m, 6H), 2.07 (m, 6H), 3.64 (m, 4H), 3.76 (m, 2H), 4.95 (d, J = 10.1 Hz, 3H), 5.07 (d, J = 16.9 Hz, 3H), 5.69 (dt, J = 15.1, 6.9 Hz, 3H), 6.01 (dd, J = 15.0, 10.4 Hz, 3H), 6.31 (ddd, J = 16.9, 10.3, 10.1 Hz, 3H), 6.90 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 26.55, 26.72, 29.48, 29.54, 29.62, 29.73, 29.88, 29.99, 30.26, 32.34, 69.05, 73.21, 107.68, 114.87, 129.52, 131.24, 135.57, 137.42, 140.88, 152.60, 175.03. IR (cm^{-1}): 3323, 3084, 3034, 3006, 2926, 2855, 1651, 1601, 1577, 1551, 1501, 1466, 1410, 1381, 1313, 1224, 1130, 1002, 951, 898, 787. Anal. Calcd for $C_{49}H_{77}NaO_5$: C, 76.52; H, 10.09. Found: C, 76.20; H, 10.57.

Results and Discussion

To study the feasibility of hydrocarbon 1,3-diene tail systems in the design of polymerizable mesogens, diene analogues of two well-known LC acrylate monomers, **3** and **4**, were examined (Figures 1 and 2). Monomers **3a**−**f** are cross-linkable thermotropic LC monomers designed by Broer et al.[30] that have been used extensively in the formation of anisotropic networks, gels, and plasticized networks.[4a,31−38] All compounds in the series exhibit the nematic phase (N), and the longer tail homologues also exhibit a smectic C (SmC) phase (Table 1).[30] The T_c values of the LC diacrylates decrease as the tail lengths increase.

Monomer **4** is a cross-linkable amphiphilic LC with a tapered shape which allows it to adopt a inverted hexagonal (IH) lyotropic mesophase at room temperature in the presence of a small amount of water (Figure 2). The important features of the lyotropic LC behavior



4

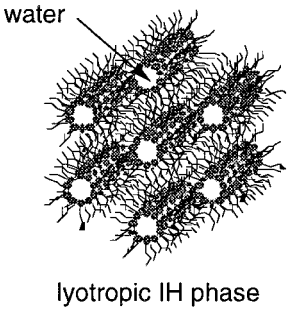


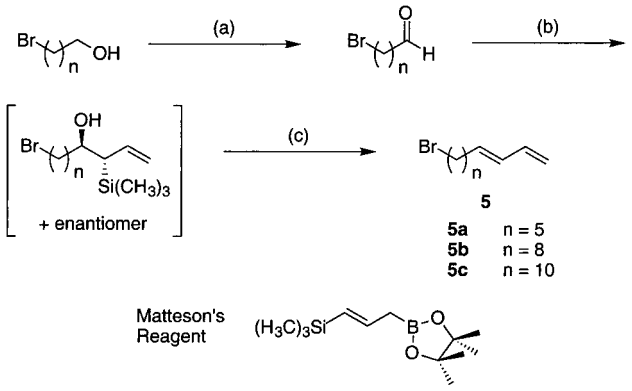
Figure 2. Lyotropic LC acrylate monomer **4** and the IH lyotropic phase.

Table 2. Lattice Dimensions of the Inverted Hexagonal Phase of 4 (88/8/4 (w/w/w) 4/H_2O/Xylene Initiator Solution) before and after Cross-Linking, As Determined by Powder X-ray Diffraction

compound	lattice constant (Å)	*d* spacing obsd (calcd) (Å)	Miller indices
4	42.5	36.8 (36.8)	100
(unpolymerized)		21.3 (21.3)	110
		18.4 (18.4)	200
4	41.8	36.2 (36.2)	100
(cross-linked)		21.0 (20.9)	110
		18.0 (18.1)	200

of **4** are summarized in Table 2. Photoinitiated radical cross-linking of **4** in the IH phase proceeds at room temperature with retention of phase microstructure, affording nanostructured polymer networks with close-packed aqueous channels. In addition, the IH phase of **4** containing ca. 5 wt % water has a T_c of approximately 60 °C,[39] thereby allowing a degree of thermal processability via the isotropic melt. Because of these properties, **4** has recently been used as a matrix molecule for the synthesis of ordered organic−organic and organic−inorganic nanocomposites with hexagonal symmetry.[9]

Scheme 1



(a) Oxalyl chloride, DMSO, $N(C_2H_5)_3$; (b) (i) Matteson's reagent, (ii) $N(CH_2CH_2OH)_3$; (c) H_2SO_4 (cat.).

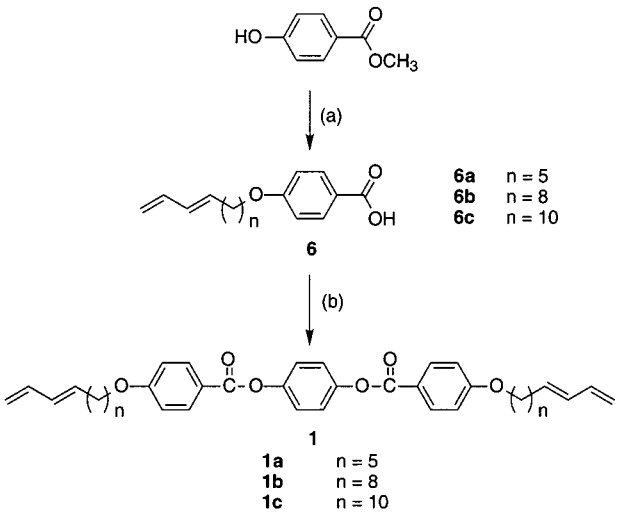
(a) LC Diene Monomer Synthesis. LC diene analogues of **3** and **4** with comparable tail lengths were synthesized by connecting long chain ω-bromoalka-1,3-diene tail units onto the appropriate LC cores. The general synthesis of modular diene tails with different lengths is detailed in Scheme 1. An appropriate length ω-bromoalkan-1-ol is first oxidized under mild Swern conditions[22] to generate the corresponding long chain ω-bromoalkanal. Subsequent reaction of the long chain ω-bromoalkanal with Matteson's reagent,[27] followed by treatment with triethanolamine, yields (±)-(*R**,*S**)-3-trimethylsilyl-4-hydroxy-1-alkenes, which were used without purification. Deoxysilylation under acidic (catalytic H_2SO_4) Peterson elimination conditions affords the desired ω-bromo-1,3-diene tail unit (**5**) in good overall yields with an *E*:*Z* ratio of 20:1 (as determined by ^{1}H NMR spectroscopy). The cis isomer is accessible with *Z*:*E* ratios of approximately 10:1 under basic (potassium hydride) Peterson elimination conditions. Using this procedure, commercially available 6-bromohexan-1-ol, 9-bromononan-1-ol, and 11-bromoundecan-1-ol were transformed into 9-bromonona-1,3-diene (**5a**), 12-bromododeca-1,3-diene (**5b**), and 14-bromotetradeca-1,3-diene (**5c**), respectively. Although compounds **5a** and **5b** have previously been made using different methods and starting materials,[28,29] our new general synthetic scheme to molecules of this type not only is convenient but also affords excellent control over the configuration of the diene.

A homologous series of thermotropic LC monomers with the general structure **1** was then synthesized by first performing a Williamson ether synthesis with 1 equiv of ω-bromo-1,3-diene (**5a**−**c**) and methyl 4-hydroxybenzoate using potassium carbonate as the base. Subsequent saponification of the resulting compound affords the corresponding carboxylic acid intermediates **6**. Reaction of intermediates **6** with thionyl chloride, followed by coupling with half an equivalent of hydroquinone in the presence of triethylamine, affords the final bis(diene) compounds **1a**−**c** in good to moderate overall yields (Scheme 2).

Lyotropic LC monomers with the general structure **2** were synthesized by reacting methyl gallate with 3 equiv of **5** in the presence of potassium carbonate to attach the three diene tails via ether linkages. Saponification of the resulting intermediates **7**, followed by titration with aqueous NaOH, affords **2a** and **2b** in excellent overall yields (Scheme 3).

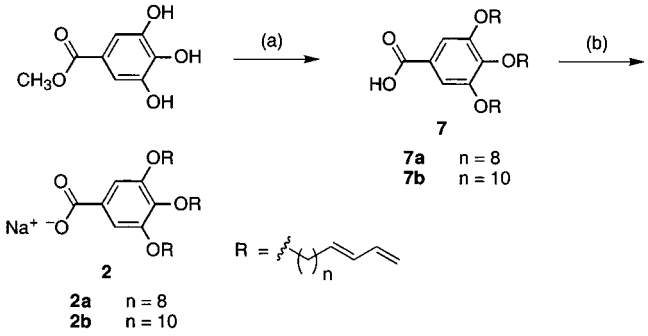
(b) Mesogenic Behavior of LC Diene Monomers. Table 3 summarizes the thermotropic LC behavior of

Scheme 2



(a) (i) **5**, K_2CO_3, Δ; (ii) NaOH; (iii) HCl; (b) (i) $SOCl_2$, Δ; (ii) 0.5 equiv hydroquinone, NEt_3, Δ.

Scheme 3



(a) 3 equiv **5**, K_2CO_3, Δ; (ii) (i) NaOH, H_2O; (iii) HCl; (b) NaOH

Table 3. Transition Temperatures and Phase Behavior of Thermotropic LC Bis(diene) Monomers 1[a]

monomer	*n*	LC phases and transition temp (°C)						
1a	5	K	120			N	206	I
1b	8	K	81	SmC	123	N	166	I
1c	10	K	86	SmC	146[b]	N	163[b]	I

[a] K = crystalline, SmC = smectic C, N = nematic, I = isotropic. [b] Denotes transitions measured after large exotherm.

compounds **1a**−**c** based on differential scanning calorimetry (DSC) and polarized light microscopy (PLM). The identities of the observed LC phases were verified by X-ray diffraction. For this series of thermotropic LC compounds, it should be noted that the enthalpy changes (ΔH) associated with each thermal transition could not be measured accurately. The high temperatures required to achieve the isotropic phase (I) during thermal cycling caused some reaction of the 1,3-diene moieties. Consequently, the intensities of the thermal transitions progressively dropped and even their positions varied with cycling. In some instances, the transition temperatures had to be estimated upon initial heating using variable temperature PLM rather than DSC as indicated.

As can be seen from Table 3, the bis(diene) homologue **1a**, with a tail length roughly equivalent to diacrylates **3b** and **3c**, only exhibits an enantiotropic N phase. The identity of the N phase was confirmed by the characteristic Schlieren optical texture observed upon both heating and cooling and the absence of X-ray diffraction

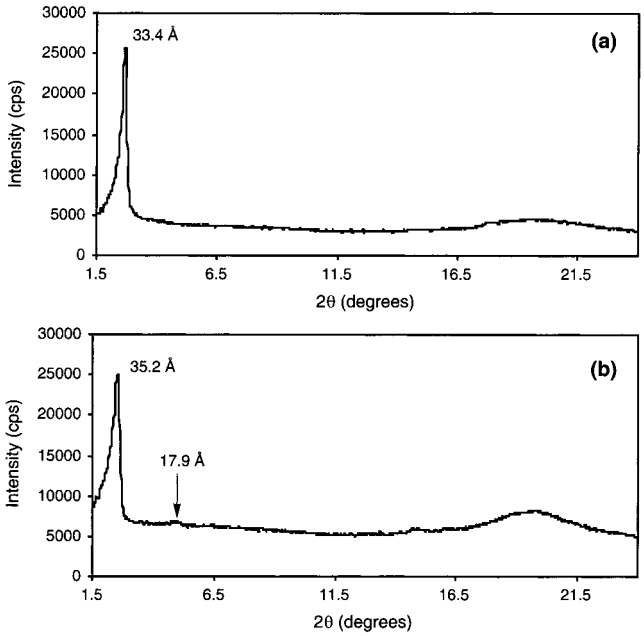


Figure 3. X-ray diffraction profiles of the smectic C phase of (a) **1b** at 96 °C and (b) **1c** at 110 °C.

peaks in the LC temperature regime. The most pronounced differences between the thermal behaviors of **1a** and **3b**−**c** are the much higher transition temperatures exhibited by the diene analogue. Compound **1b** has tails with a length approximately that of diacrylate **3d**, and it exhibits similar enantiotropic N and SmC phases. Although the T_m's of these compounds are roughly the same, **1b** exhibits a broader SmC range. The presence of a layered smectic (Sm) phase for **1b** was confirmed by the presence of a primary (d_{100}) X-ray diffraction peak at 33.4 Å when the sample was heated and subsequently cooled to 96 °C (Figure 3a). Since the calculated extended length of **1b** is ca. 44 Å,[40] the observed interlayer spacing of 33.4 Å is consistent with a SmC phase with a tilt angle of 40.9°, assuming minimal interdigitation of the tails. Electrostatic modeling calculations of the mesogenic core and van der Waals modeling of dimers suggest that the most favorable interaction between two molecules is when they are shifted with respect to one another.[41] This shifted arrangement extended throughout the LC layer macroscopically translates into the SmC phase. The last bis(diene) compound in the series (**1c**) has tails of similar overall length to diacrylates **3e** and **3f** and exhibits a transition to a LC phase at 86 °C upon initial heating, whereas **3e** and **3f** display enantiotropic SmC and N phases. However, at higher temperatures, thermal reaction of the diene groups was observed, as indicated by a massive exotherm with an onset of ca. 90 °C. The presence of two diffraction peaks at 35.2 Å (d_{100}) and 17.9 Å (d_{200}) for polymerized **1c** at 110 °C correlate to a layered Sm phase (Figure 3b). Comparison of the calculated extended length of **1c** (49 Å)[40] with the observed layer spacing (35.2 Å) is again consistent with a SmC phase but with a slightly larger tilt angle of 44.1°.

Comparison of thermal behavior of the LC bis(diene)s and diacrylates suggests several features of the diene tail system in thermotropic LC design. The first is that alkyl tails with terminal 1,3-dienes afford similar LC phase behavior compared to acrylate tails of comparable length. However, the SmC to N transition temperatures and the T_c's of the LC bis(dienes) are significantly higher than their diacrylate analogues. This fact suggests that the amount of entropy or fluidity contributed by terminal diene tails is much less than that of tails of similar total length containing more bulky polar acrylate end groups The second feature is that the 1,3-diene group appears to be more thermally sensitive than the acrylate group. LC diacrylates can be repeatedly cycled past the clearing point without premature reaction in the presence of a radical inhibitor;[42] however, the LC dienes tend to react at temperatures approaching 90−100 °C upon initial heating, even in the presence of added inhibitor. This behavior is consistent with the tendency of 1,3-dienes to undergo thermally induced [4 + 2] cycloaddition (i.e., Diels−Alder reaction) with one another, which is a concerted process. Similar thermally induced "dimerization" and polymerization side reactions have also been reported for LCs containing dienoyl systems.[18a] In addition, 1,3-dienes with substituents at the 2-position have also been observed to undergo Diels−Alder cyclodimerization at ca. 80 °C during thermally initiated radical polymerizations.[43]

Table 4. Lattice Dimensions of the Inverted Hexagonal Phase of 2 (86/8/6 (w/w/w) 2/H_2O/*n*-Dodecane Initiator Solution)

monomer	*n*	lattice constant (Å)	*d* spacing obsd (calcd) (Å)	Miller indices
2a	8	38.6	33.3 (33.4)	100
(unpolymerized)			19.4 (19.3)	110
			16.7 (16.7)	200
			12.6 (12.6)	210
2b	10	42.0	35.9 (36.4)	100
(unpolymerized)			21.2 (21.0)	110
			18.3 (18.2)	200

The phase behavior of the lyotropic monomers **2a** and **2b** were compared to that of the amphiphilic LC triacrylate **4**. Compounds **2a** and **2b** were mixed with H_2O and 2,2-dimethoxy-2-phenylacetophenone (1.05×10^{-2} M in *n*-dodecane) in an 86/8/6 ratio by weight. This composition and the wedgelike shape and amphiphilic nature of **2a** and **2b** predict the formation of the IH phase similar to **4**. Indeed, **2a** and **2b** spontaneously form the IH phase at ambient temperature with unit cell parameters slightly smaller than that of the acrylate analogue, as determined by X-ray diffraction. The lattice dimensions of the IH phases of **2a** and **2b** (unpolymerized) are listed in Table 4. In addition, the observed T_c's of unpolymerized IH phases of **2a** and **2b** (75−85 °C) are roughly 15−20 °C higher than that of the triacrylate **4** (ca. 60 °C),[39] paralleling the trend observed for the thermotropic LCs.

(c) Cross-Linking Studies. The thermotropic LCs **1a** and **1b** and lyotropic LCs **2a** and **2b** were photopolymerized in their respective mesophases, and the materials were characterized by PLM, low-angle X-ray diffraction, and FT-IR analysis to determine (1) whether order was retained after reaction and (2) the extent of polymerization. Compound **1c** was not considered in this study because of its tendency to undergo significant side reactions at elevated temperatures. The thermotropic LCs **1a** and **1b** were doped with 1.5 mol % of 2,2-dimethoxy-2-phenylacetophenone (a radical photoinitiator) and heated above their respective melting temperatures directly into their LC regimes. The samples were then subjected to UV irradiation (365 nm, 2200 $\mu W/cm^2$) for 4 h isothermally under a N_2 atmosphere.[21] The lyotropic LC mixtures of **2a** and **2b** were prepared with the photoinitiator in the form of an *n*-dodecane

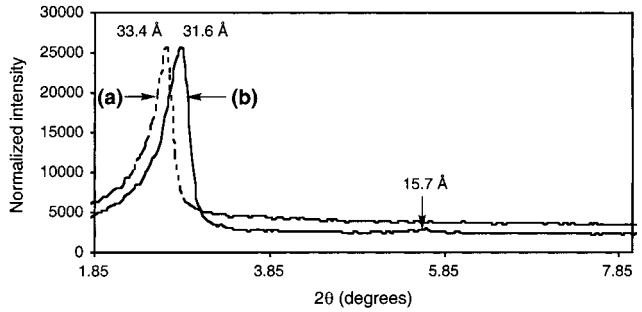


Figure 4. X-ray diffraction profiles of **1b**: (a) prepolymerization and (b) postpolymerization.

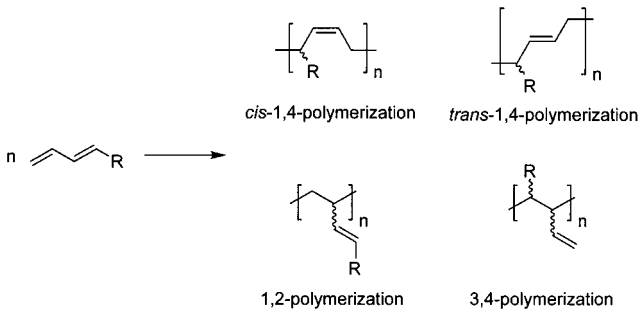


Figure 5. Possible regiochemical additions of 1,3-dienes upon radical polymerization.

solution that was added to the lyotropic mixture. Their polymerizations were performed at ambient temperature under a N_2 atmosphere via UV irradiation (365 nm, 2200 μW/cm^2) for 14 h.[21]

The optical and structural characteristics of the pre- and postpolymerization samples were compared in order to determine whether the LC order was retained after cross-linking. The Schlieren optical textures of the SmC phases of **1a** and **1b** did not change appreciably after polymerization, indicating that the LC order is maintained after photoinitiated cross-linking. This was confirmed by comparison of the X-ray diffraction profiles of the heated LC samples before photolysis and after photolysis. The cross-linked sample of **1b** maintains the characteristic X-ray diffraction profile of a Sm phase even when cooled to ambient temperature (Figure 4b). As a result of cross-linking, a slight contraction of 1.8 Å in the layer spacing occurs compared to the unpolymerized SmC phase (cf. parts a and b of Figure 4). It should be noted that pure, unpolymerized **1b** exhibits a crystalline X-ray diffraction profile marked by numerous sharp peaks in the wide angle region at ambient temperature.

Similar results were obtained for the lyotropic LC tris(diene) samples. Optical textures for the IH phases of both **2a** and **2b** remained relatively unchanged after photopolymerization, and these textures did not disappear even up to 90 °C, well above the T_c's of the unpolymerized LC mixtures. In addition, a lattice constant contraction was also observed in the IH phases of **2a** and **2b** upon cross-linking (Table 5). The lyotropic IH networks of the diene analogues apparently experience more unit cell contraction upon polymerization than that of the acrylate analogue **4** (0.7 Å) (cf. Tables 2 and 5).

The extent of polymerization for the diene LC monomers was ascertained using FT-IR analysis of thin films of the LC phases before and after polymerization. During the course of cross-linking, the conjugated 1,3-

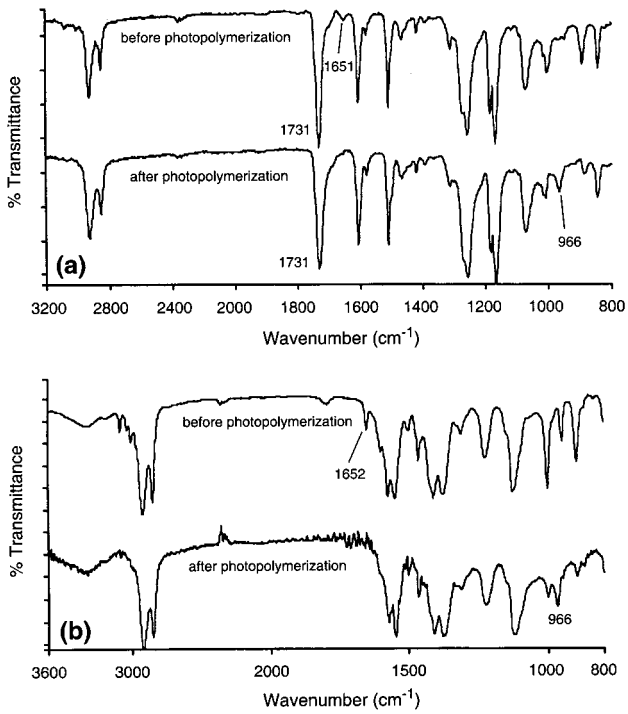


Figure 6. FT-IR spectra before and after UV photopolymerization of (a) **1b** and (b) **2a**.

Table 5. Lattice Dimensions of the Cross-Linked Inverted Hexagonal Phase of 2 (86/8/6 (w/w/w) 2/H_2O/*n*-Dodecane Initiator Solution)

monomer	*n*	lattice constant (Å)	*d* spacing obsd (calcd) (Å)	Miller indices
2a	8	37.8	32.7 (32.7)	100
(cross-linked)			19.2 (18.9)	110
			16.1 (16.4)	200
2b	10	40.2	34.5 (34.8)	100
(cross-linked)			20.3 (20.1)	110
			17.4 (17.4)	200

diene units on the monomers react and become single olefin moieties in the network backbone. Monosubstituted 1,3-dienes can undergo a number of different regiochemical and stereochemical additions during radical chain polymerization (Figure 5),[44] which makes determination of the network connectivity extremely difficult without the aid of additional analytical techniques, such as solid-state NMR spectroscopy. However, unsymmetrical, 1-substituted conjugated dienes (e.g., 1,3-pentadiene) have a characteristic IR stretching band at 1650 cm^{-1}, which will decrease in intensity during the course of polymerization.[44] Utilizing the carbonyl stretching band of the ester groups in **1a** and **1b** as an internal standard, the integrated *absorbance* intensities of the 1650 cm^{-1} band were compared before and after polymerization to determine the extent of diene polymerization using Beer's law. For compounds **1a** and **1b**, the extent of polymerization was estimated at 88% and 95%, respectively. Determination of the extent of polymerization for the lyotropic LC diene systems was much more difficult to gauge because the carbonyl stretching band for the hydrated carboxylate group is shifted to less than 1600 cm^{-1}, where it overlaps with other IR bands. A conservative estimate puts the degree of polymerization for the lyotropic systems at greater than 75% due to the essentially complete disappearance of the IR band at 1650 cm^{-1} (Figure 6). Because the strength of this 1,3-diene carbon−carbon stretch is

relatively weak, these numbers must be considered with caution for all systems. However, even considering the error associated with these calculations, both the thermotropic and lyotropic LC diene systems undergo a high degree of radical polymerization.

Conclusions

A novel, polymerizable, hydrocarbon diene tail system has been developed for use in cross-linkable LCs. The synthesis of this polymerizable tail system allows for easy modification of tail length, as well as excellent control over the *E*/*Z* configuration of the internal double bond. The 1,3-diene tail system compares well with the frequently employed acrylate-based tails in LC monomer synthesis, exhibiting very similar phase behavior when incorporated in calamitic thermotropic LCs and taper-shaped lyotropic LCs. The T_m's and T_c's of calamitic thermotropic bis(diene) monomers are higher than those of their diacrylate analogues, translating into broader LC ranges. However, the terminal 1,3-diene group suffers from thermal dimerization and polymerization side reactions at temperatures of ca. 90 °C or higher, resulting in potential processing difficulties with thermotropic LCs that exhibit higher temperature mesophases. The taper-shaped lyotropic diene LCs mirror the behavior of the analogous triacrylate system with slight variations in the dimensions of the IH phase and slightly higher T_c's. The hydrocarbon diene tails undergo a high degree of photoinitiated radical polymerization in both the thermotropic and lyotropic LC phases.

Although these hydrocarbon diene tails are best suited for use with LC systems that exhibit mesogenic behavior below 100 °C, they do have properties that make the resulting LC networks ideal for certain applications. As alluded to in the Introduction, polymerized 1,3-diene networks are not susceptible to hydrolytic degradation in acidic or basic aqueous environments, like LC networks containing residual ester linkages are (e.g., acrylate, methacrylate, or dienoyl-based polymers). This issue of environmental robustness is likely to be of consequence in the continuing development of lyotropic LC networks as nanostructured reaction catalysts and nanocomposite matrices.[9−11] In addition, the similarity of the diene tails to typical alkyl chains, coupled with their high polymerization reactivity, makes them ideal for the synthesis of polymerizable analogues of sensitive LCs that are not tolerant of bulky or polar polymerizable end groups. This latter consideration will be the subject of a forthcoming paper dealing with the synthesis of polymerizable analogues of emissive hexacatenar LCs[45] that are very sensitive to the nature of the polymerizable group.

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