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Synthesis and Polymerization of a Chiral Liquid Crystal Diacrylate Exhibiting Smectic A* and C* Phases

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ABSTRACT: The alignment and cross-linking of chiral liquid crystal (LC) phases has been used to generate ordered noncentrosymmetric polymer networks with a variety of interesting optical and transducer properties. Typically, cross-linkable chiral LC mixtures are prepared by adding nonreactive chiral dopants to achiral LC diacrylate monomers for ease of preparation. Examples of intrinsically chiral LC diacrylates which exhibit chiral smectic phases are rare because of the difficulties associated with the design of such monomers. Herein, we present the stereospecific synthesis and subsequent photopolymerization of achiral smectic diacrylate **1**, which is derived from (*S*)-ethyl lactate. Monomer **1** exhibits an enantiotropic smectic A* phase from 49.2 to 71.0 °C upon heating at 0.5 °C/min and from 71.2 to 39.3 °C upon cooling at the same rate. The smectic A* phase of the chiral monomer can be homeotropically and homogeneously aligned and subsequently photopolymerized to yield highly uniform, noncentrosymmetric polymer films of predefined symmetry. Upon rapid cooling at 5.0 °C/min, the monomer also exhibits a metastable, monotropic ferroelectric smectic C* phase from approximately 35.5 to 33.0 °C. The cross-linking of this metastable phase will also be discussed.

A number of interesting phenomena exhibited by many solid-state materials, such as piezoelectricity, pyroelectricity, and nonlinear optical properties, arise from the fact that the materials are highly ordered and lack of a center of symmetry.[1−3] Recently, researchers have attempted to achieve control over both order and symmetry in designer organic solids by employing polymerizable liquid crystals (LCs) as building blocks for these structures.[4−6] The polymerization of LC diacrylate mixtures containing chiral dopants[7] and the polymerization of chiral LC monoacrylates[5,8] and diacrylates[9,10] have been successfully used to synthesize noncentrosymmetric polymer networks that can be employed in a number of technological applications. The unique self-assembly properties of LC monomers provide a high degree of order and processability, and the presence of the chiral components removes the center of symmetry in these molecular assemblies. Of particular interest are chiral LC diacrylate mixtures that exhibit the smectic LC phases (Figure 1).[11] For example, noncentrosymmetric networks formed from the alignment and cross-linking of LC diacrylates that adopt the ferroelectric smectic C* phase (Scheme 1) exhibit pyroelectric, piezoelectric, and nonlinear optical properties as a result of their symmetry and high degree of order.[7e,10]

For ease of synthesis, the preferred method of generating cross-linkable, chiral LC phases has typically been to add nonreactive chiral additives[7] or chiral monoacrylates[8] to LC diacrylates in order to induce asymmetry in the phases. This approach typically yields noncentrosymmetric networks with properties that lack complete thermal, mechanical, and temporal stability because the chiral components retain a high degree of mobility within the cross-linked matrices.[7] (It should also be noted that chiral monoacrylate/diacrylate mixtures have also been used to generate ferroelectric LC elastomers in which the switchable anisotropic properties of the systems are desired characteristics.[12]) *Intrinsically chiral* LC diacrylates that exhibit LC phases would generate highly ordered noncentrosymmetric networks with stable properties. However, examples of intrinsically chiral LC diacrylates that exhibit chiral smectic phases are rare because of the difficulties associated with the design of such monomers. Few methods exist for conveniently synthesizing an enantiomerically pure stereocenter close to the rigid core of a calamitic LC that also allow for connection to a flexible spacer and a terminal acrylate. Only one example of an intrinsically chiral, smectic LC diacrylate has been reported.[10] The synthesis of this monomer is elaborate and requires enantiomeric resolution with enzymes. Herein, we present the stereospecific synthesis and subsequent photopolymerization of a new chiral smectic diacrylate **1** derived from the natural product, (*S*)-ethyl lactate.

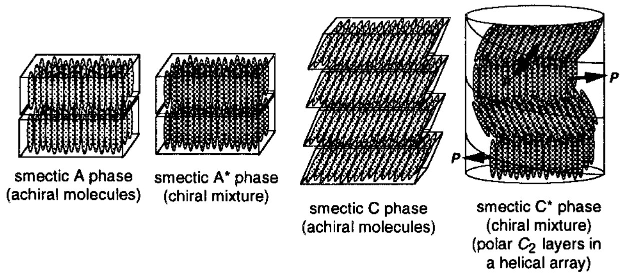
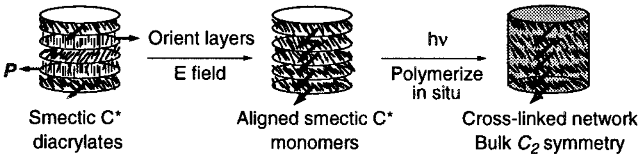


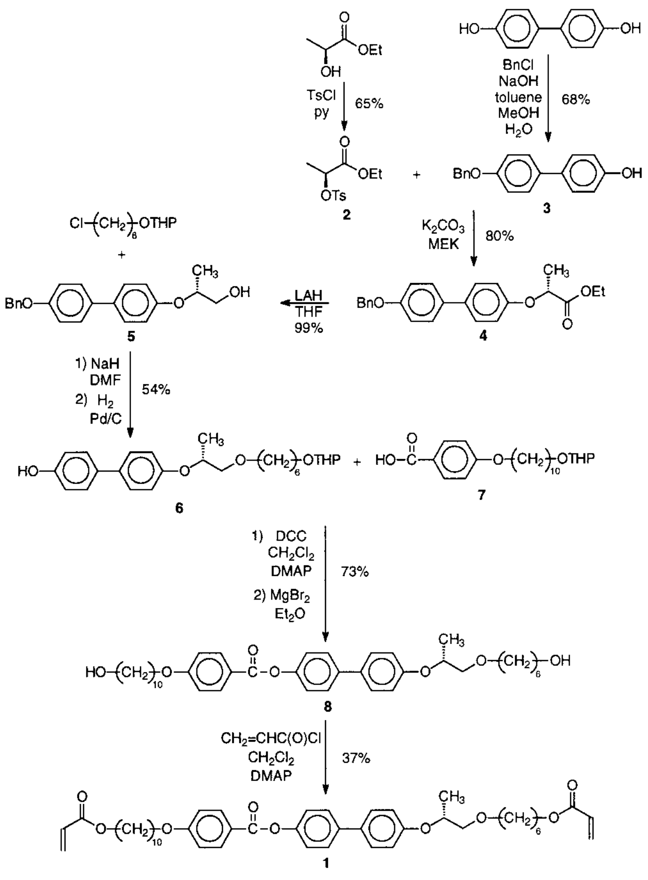
Figure 1. Schematic representations of some of the more common thermotropic smectic LC phases.

Scheme 1. Schematic Representation of the Synthesis of Noncentrosymmetric Networks for the Cross-Linking of Oriented Smectic C* LC Phases



The stereospecific synthesis of **1** is depicted in Scheme 2 below. (*S*)-Ethyl lactate is first reacted with *p*-

Scheme 2. Synthesis Scheme for Monomer 1



toluenesulfonyl chloride to afford the corresponding chiral tosylate **2**. The potassium salt of monoprotected 4,4′-biphenol **3** is then added to tosylate **2** via an S_N2 substitution reaction to yield ether **4** with complete inversion of stereochemistry. Subsequent reduction of **4** with lithium aluminum hydride affords chiral platform **5**. Tetrahydropyranyl (THP) ether protected 6-chlorohexan-1-ol is then added to **5** via another nucleophilic substitution reaction. Subsequent removal of the benzyl protecting group using standard hydrogenation techniques affords phenol **6**, which is essentially one-half of the target molecule. To obtain the other half of the target molecule, ethyl 4-hydroxybenzoate is connected to THP-protected 10-chlorodecan-1-ol via an S_N2 type reaction to yield compound **7**. Subsequent coupling of fragments **6** and **7** using dicyclohexylcarbodiimide affords the THP-protected form of the target monomer. Removal of the THP protecting groups using magnesium bromide, followed by reaction of the resulting diol **8** with acryloyl chloride affords LC diacrylate **1**.

The DSC thermogram of **1** revealed two distinct thermal transitions at 49.2 and 71.0 °C upon heating at 0.5 °C/min and two transitions at 71.2 and 39.3 °C upon cooling at the same rate. Upon heating the sample above 49.2 °C, polarized light microscopy revealed a focal conic fan texture characteristic of a smectic phase.[11] Above 71.0 °C, an isotropic melt formed. When the sample was cooled at 0.5 °C/min from the isotropic melt, a similar focal conic fan texture was observed below 71.2 °C (Figure 2), and a texture characteristic of a polycrystalline sample was observed below 39.3 °C. The broad smectic phase in this molecule was identified as a smectic A* phase. X-ray diffraction analysis of the mesophase upon cooling to 50 °C revealed a single diffraction peak at 44.3 Å, consistent with a lamellar structure with a layer thickness of this magnitude (Figure 3a). Correlation of the calculated extended length for **1** (44 Å)[13] with the observed layer spacing suggested very little if any molecular tilt in the mesophase. This phase did not respond to an applied electric field when homogeneously aligned in an antiparallel-rubbed ferroelectric LC cell. In addition, the Debye–Scherrer X-ray diffraction profile of a sample aligned in a strong magnetic field exhibited only two intense low-angle reflections along the *y*-axis and two

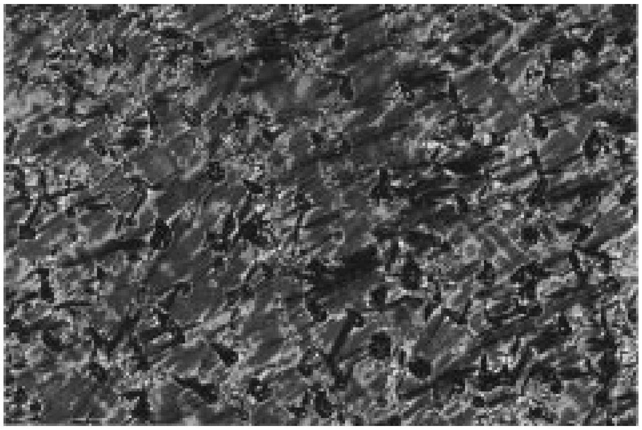


Figure 2. Optical texture observed for **1** upon cooling to 47.3 °C at 0.5 °C/min from the isotropic melt.

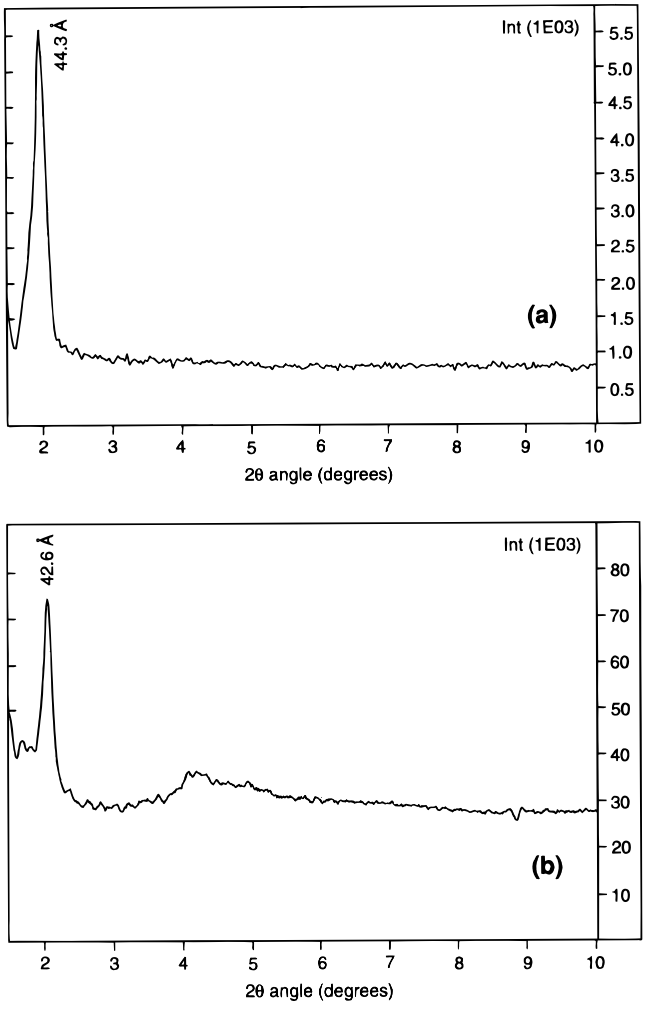


Figure 3. Powder X-ray diffraction profiles of (a) the unpolymerized smectic A* phase of **1** at 50 °C) and (b) the cross-linked smectic A* phase of **1** taken at ambient temperature.

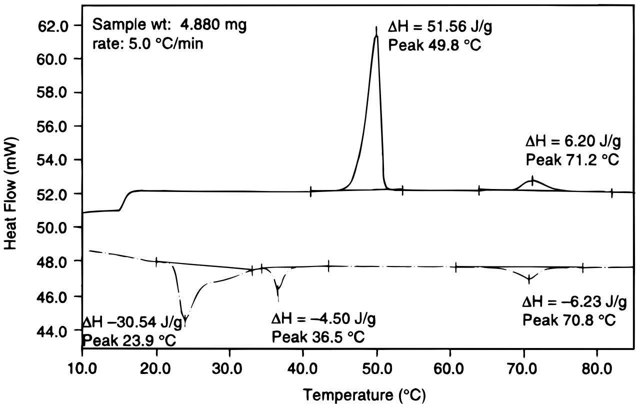
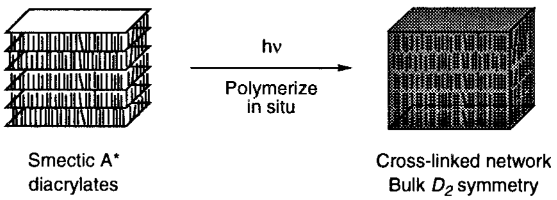


Figure 4. DSC thermogram of **1** at a heating and cooling rate of 5.0 °C/min.

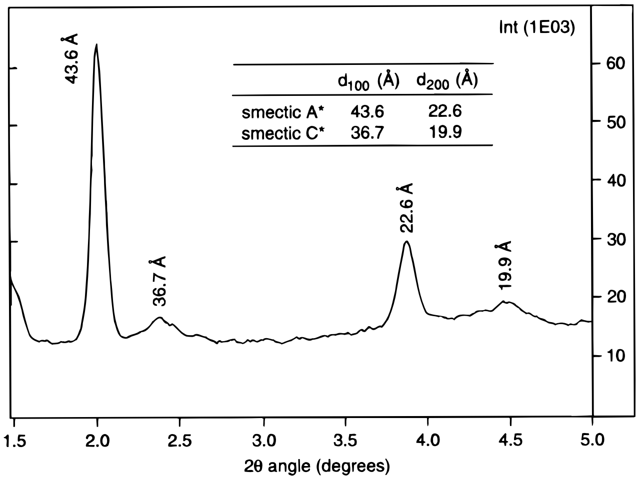
Scheme 3. Schematic Representation of the Cross-Linking of the Smectic A* Phase of 1



diffuse wide-angle reflections along the orthogonal *x*-axis. These results are consistent with a perpendicularly oriented smectic A* phase rather than a tilted smectic C* phase.[10,11a,14]

In addition to a smectic A* phase, monomer **1** also exhibits a very narrow, metastable smectic C* phase upon rapid cooling (5.0 °C/min). As can be seen in Figure 4, two closely positioned transitions appear at 36.5 and 23.9 °C when **1** is rapidly cooled at 5.0 °C/min, whereas only a single transition appears in this region at a slower cooling rate of 0.5 °C/min. The optical texture of the narrow mesophase (ca. 33.0−35.5 °C) between these two transitions was Schlieren in nature, but slightly different from that exhibited by the smectic A* phase. In contrast, this new mesophase could be flipped by an applied electric field when placed in a rubbed ferroelectric LC cell. This switching behavior is consistent with a ferroelectric, tilted smectic C* phase.[11] It was not possible to obtain X-ray diffraction data on the smectic C* phase of **1** because the mesophase tended to quickly crystallize upon standing at constant temperature,[15] and our X-ray diffractometer oven was not accurate enough to reproducibly target its narrow temperature regime (∼2.5 °C).

Monomer **1** can be cross-linked in the smectic A* phase by cooling a sample containing 2 wt % 2,2-dimethoxy-2-phenylacetophenone to the appropriate temperature and irradiating it with 365-nm light (11 000 μW/cm^2) under nitrogen (Scheme 3). During irradiation, the initially fluid LC monomer mixture became a tough, pale yellow, translucent film that is completely insoluble in common solvents. Thin films (5 μm thick) typically required only 10−15 min of irradiation time to ensure a high degree of polymerization. The loss of the characteristic acrylate absorption bands (1636 and 811 cm^{-1}) in the FT-IR spectrum of the photolyzed material indicated that a high degree of polymerization (ca. 80%) occurs under these photolysis conditions. The polymerized material exhibits an optical texture and an X-ray diffraction profile virtually identical to that of the original smectic A* phase, indicating that the order in the system is locked-in upon cross-linking. Figure 3b shows the room-temperature X-ray diffraction profile of a sample of **1** photopolymerized at 50.0 °C. The first-order diffraction peak of the photopolymerized material is slightly smaller than that of the monomer mixture, consistent with slight volume contraction upon cross-linking. The stability of these cross-linked networks can be illustrated by the fact that their X-ray diffraction profiles remained unchanged even when samples were heated well above the clearing point of the monomer. It should also be noted that the smectic A* phase of **1** can be easily aligned and photopolymerized in the homeotropic state between two glass slides, as indicated by the observation of a uniformly dark, pseudoisotropic optical texture.[11,16]



	d_{100} (Å)	d_{200} (Å)
smectic A*	43.6	22.6
smectic C*	36.7	19.9

Figure 5. Powder X-ray diffraction profile of a sample of **1** containing cross-linked smectic A* and smectic C* domains.

Unfortunately, uniform networks of **1** retaining the smectic C* phase could not be obtained by photopolymerization. With untreated glass substrates, attempts to produce uniform smectic C* samples via fast cooling generally afforded samples containing small, persistent domains with optical textures indicative of the prior smectic A* phase. The presence of distinct smectic A* and C* regions in these samples was clearly evident under the polarized light microscope. These defect domains appear to be the result of the sensitivity of the mesogen to surface imperfections on the untreated substrates. As mentioned previously, the smectic C* regions also tend to crystallize rapidly upon standing at constant temperature. Thus, rapid photopolymerization was required in order to trap the inherently unstable smectic C* phase in these mixtures. Powder X-ray diffraction analysis of the cross-linked, mixed smectic samples revealed a set of higher angle reflections, in addition to the characteristic diffraction peaks of the cross-linked smectic A* phase (Figure 5). These higher angle reflections correspond to the first and second-order diffraction spacings of a tilted smectic C* phase with a periodic layer spacing of 36.3 Å. Based on the calculated length of **1** of 44 Å,[13] this observed layer spacing is consistent with a tilt angle of 32.4° between the director and the layer normal in the cross-linked smectic C* domains.[10,11a] The use of antiparallel-rubbed ferroelectric LC cells afforded more uniform examples of the smectic C* phase; however, tiny defect domains were still observed, and crystallization tended to occur quite rapidly upon standing.[15] We are currently working on better alignment and annealing procedures to obtain uniform samples of **1** in the smectic C* phase.

Although the cross-linked smectic A* phase of **1** is noncentrosymmetric in nature,[1] the piezoelectric properties of systems with this geometry are inherently difficult to measure.[17] Since monomer **1** can be easily synthesized in a modular fashion from an abundant chiral starting material, it appears to be a viable platform for fine-tuning the architecture and properties of LC networks. We are currently performing systematic structural modifications on the monomer in order to broaden the temperature range and stability of the observed smectic C* phase. In doing so, it should be possible to polymerize monodomain samples of this mesophase to generate polar networks with C_2 symmetry, the piezoelectric properties of which are much easier to measure.[7e]

Experimental Section

General Considerations. All reactions and distillations were performed under nitrogen flush using standard Schlenk line techniques. Nitrogen was purified by passage through columns of Q-5 catalyst (Engelhard) and 13X molecular sieves (Aldrich). All solvents were purchased from Fisher Scientific (Optima grade) and used without further purification unless otherwise noted. All reagents and drying agents were purchased from either Fisher Scientific or the Aldrich Chemical Co. and used without further purification unless otherwise noted. Anhydrous *N*,*N*-dimethylformamide (DMF) was purchased from Aldrich in a Sure-Seal bottle. Anhydrous CH_2Cl_2 was distilled from CaH_2 and stored under nitrogen in a Schlenk tube. THF was vacuum-transferred from sodium benzophenone ketyl and stored under nitrogen. Reaction mixtures and chromatography fractions were monitored with EM Science 250 μm silica gel F_{254} TLC plates. All column chromatography was performed using 40 μm flash silica gel purchased from Mallinckrodt-Baker. Unless otherwise specified, organic extracts were dried over anhydrous Na_2SO_4, and the solvent was removed with a rotary evaporator at aspirator pressure, followed by full vacuum on the Schlenk line (10^{-4} Torr). All photopolymerizations were performed inside a nitrogen-filled glovebag (I^2R Corp.) using a UVP Blak-Ray long wavelength (365 nm) ultraviolet lamp, Model B100AP. KBr disks (2 × 25 mm) used for IR and photopolymerization studies were purchased from Wilmad.

Instrumentation. Infrared (IR) spectra were obtained on a Perkin-Elmer 1616 series FT-IR spectrometer at a resolution of 4 cm^{-1} and were recorded as thin films on KBr plates. Samples for IR photopolymerization studies were sandwiched between KBr plates. ^1H NMR spectra were obtained on a Bruker AMX-300 (300 MHz) or a Bruker AMX-400 (400 MHz) spectrometer. Proton-decoupled ^{13}C NMR spectra were obtained at either 75 or 100 MHz on the same instruments. NMR spectra were obtained in $CDCl_3$ or DMSO-d_6 unless otherwise specified (Cambridge Isotope Laboratories). Data for proton NMR peaks are tabulated after each chemical shift value: multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad; dd, doublet of doublets; dt, doublet of triplets). Differential scanning calorimetry (DSC) was performed using a Perkin-Elmer DSC-7. Low-angle X-ray diffraction profiles were obtained with an Inel CPS 120 powder diffraction system using Ni-filtered Cu Kα radiation. This system was equipped with an Inel programmable capillary oven with an accuracy of 1 °C for variable temperature studies. Variable temperature X-ray studies were performed on samples loaded into glass capillaries. Room-temperature X-ray analyses were performed on samples loaded either in capillaries or on flat aluminum sample pans. Polarized light microscopy was conducted on a Leica DMRXP POL microscope with a Linkam THMSE 600 hot stage controlled by a Linkam TP 92 temperature controller (accuracy ±0.1 °C). Polarized light microscope photographs were obtained with a Wild MPS 48/52 automatic camera assembly. Elemental analyses were performed at M-H-W Laboratories, Phoenix, AZ. Photopolymerization light fluxes were measured using a Spectroline DRC-100X digital radiometer equipped with a DIX-365 UV-A sensor. Electric field alignment of ferrorelectric LC samples was performed in Linkam ferroelectric LC cells with a cell gap of 5 μm. The inner surfaces of these cells were coated with ITO and rubbed polyimide layers aligned antiparallel. A KEPCO BOP 1000M bipolar power supply was used in conjunction with LabView for Windows software to generate an electric field (±40 V) for the switching of the smectic C* phase.

Ethyl (2*S*)-2-(((4-Methylphenyl)sulfonyl)oxy)propanoate (2). (*S*)-(−)-Ethyl lactate (96.0 mL, 847 mmol) and pyridine (500 mL) were added to a 1 L round-bottom flask and cooled to 0 °C. *p*-Toluenesulfonyl chloride (198.5 g, 1.041 mol) was then added in small portions over 15 min, after which time the clear solution began to get progressively cloudy. The reaction mixture was placed in the refrigerator for 12 h, and ice was added in small portions until all of the solid dissolved. The mixture was then poured into a 2 L separatory funnel and extracted with CH_2Cl_2 (3 × 450 mL). The combined extracts were acidified with 1.0 N aqueous HCl (200 mL) and then washed with 0.5 M aqueous $CuSO_4$ (150 mL), H_2O (100 mL), saturated $NaHCO_3$ (200 mL), and brine (200 mL). The organic extracts were subsequently dried over Na_2SO_4 and concentrated to afford an oily liquid. Trituration and recrystallization of the crude product with a 10:1 petroleum ether−chloroform mixture under subambient temperature conditions yielded 148.8 g (65%) of pure **2** as white crystals. ^1H NMR (300 MHz, $CDCl_3$): δ 1.19 (t, $J = 7.1$ Hz, 3H, $-OCH_2CH_3$), 1.49 (d, $J = 7.0$ Hz, 3H, $-CH_3$), 2.43 (s, 3H, Ar$-CH_3$), 4.1 (q, $J = 7.1$ Hz, 2H, $-OCH_2CH_3$), 4.9 (q, $J = 6.9$ Hz, 1H), 7.3−7.8 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.5, 17.9, 21.1, 61.3, 73.8, 127.5, 129.5, 129.5, 132.9, 144.8, 168.5. IR (cm^{-1}): 2988, 1754, 1598, 1450, 1370, 1307, 1191, 1083, 1029, 944, 888, 818, 665, 556. $[\alpha]^{\mathrm{D}}_{23}$: −37.3° (*c* 4.62, THF). Anal. Calcd for $C_{12}H_{16}O_5S$: C, 52.93; H, 5.92. Found: C, 52.75; H, 5.83.

4-(4-(Phenylmethoxy)phenyl)phenol (3).[18] To a 1 L round-bottom flask containing 4,4′-biphenol (28.0 g, 150 mmol) were added H_2O (75 mL) and NaOH (6.08 g, 152 mmol). This mixture was stirred and heated to 100 °C. Next were added in succession toluene (250 mL), benzyl chloride (27.7 g, 197 mmol), and methanol (38 mL). The resulting mixture was then heated at reflux for 24 h, during which time white crystals of the product formed. The white crystals were filtered off, heated in 300 mL of ethyl acetate to remove impurtities, and isolated by filtration. Additional portions of pure product were recovered by concentrating the filtrate and isolating the resulting white crystals repeatedly. Small portions of product were also recovered from the reaction supernatant by concentrating it and recovering the white crystals as before. The total mass of pure **3** recovered was 28.2 g (68%). ^1H NMR (400 MHz, $CDCl_3$ + DMSO-d_6): δ 5.12 (s, 2H, $-CH_2-$), 7.49−6.81 (m, 9H), 9.51 (s, 1H, $-OH$). ^{13}C NMR (100 MHz, $CDCl_3$ + DMSO-d_6): δ 69.2, 115.1, 115.6, 127.0, 127.0, 127.6, 127.8, 128.4, 130.6, 133.0, 137.2, 156.6, 157.2. IR (cm^{-1}): 3398, 2907, 1610, 1596, 1501, 1453, 1375, 1247, 1176, 1027, 1008, 918, 815, 746, 700, 604, 515. Anal. Calcd for $C_{19}H_{16}O_2$: C, 82.58; H, 5.84. Found: C, 82.33; H, 5.63.

Ethyl (2*R*)-(4-(4-(Phenylmethoxy)phenyl)phenoxy)-propanoate (4). To a 100 mL round-bottom flask containing **3** (2.75 g, 9.95 mmol) in methyl ethyl ketone (25 mL) was added tosylate **2** (2.71 g, 9.95 mmol) as a solution in 25 mL of methyl ethyl ketone, followed by K_2CO_3 (4.24 g, 30.7 mmol). After the reaction mixture was heated at reflux under nitrogen for 24 h, it was then concentrated and transferred to a 500 mL separatory funnel containing H_2O (200 mL) and diethyl ether (150 mL). The layers were separated, the aqueous layer was extracted with diethyl ether (2 × 75 mL), and the combined organic layers were then washed with saturated $NaHCO_3$ solution (100 mL), H_2O (100 mL), and brine (200 mL). The combined organic layers were dried over Na_2SO_4 and concentrated to afford crude **4** as a white powder. After continuous washing with hexane for 18 h in a Soxhlet extractor, 3.00 g

(80%) of compound **4** was isolated as a white powder. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.26 (t, $J = 7.1$, 3H, $-OCH_2CH_3$), 1.63 (d, $J = 6.8$, 3H, $-CH_3$), 4.23 (q, $J = 7.1$, 2H, $-OCH_2CH_3$), 4.77 (q, $J = 6.8$, 1H), 5.09 (s, 2H, Ar$-CH_2$), 6.9$-$7.5 (m, 13H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1, 18.5, 61.3, 70.1, 72.7, 115.1, 115.3, 127.4, 127.8, 127.9, 128.6, 133.5, 134.3, 137.0, 156.7, 158.0, 172.2. IR (cm^{-1}): 2924, 1747, 1604, 1500, 1452, 1377, 1269, 1242, 1197, 1131, 1099, 1047, 1019, 820, 732, 694, 512. $[\alpha]^{D}{}_{23}$: $+32.5°$ (c 1.43, THF). Anal. Calcd for $C_{24}H_{24}O_4$: C, 76.57; H, 6.43. Found: C, 76.32; H, 6.29.

(2*R*)-(4-(4-(Phenylmethoxy)phenyl)phenoxy)propan-1-ol (5). Lithium aluminum hydride (0.920 g, 24.3 mmol) and anhydrous THF (40 mL) were added to a dry 250 mL round-bottom flask. After the slurry was stirred and cooled to 0 °C, a solution of **4** (5.15 g, 13.7 mmol) in 100 mL of anhydrous THF was added dropwise via a 250 mL pressure-equalizing addition funnel. (Caution: H_2 was evolved upon addition of the ester.) The resulting mixture was stirred at 25 °C for 1 h and then heated at reflux for an additional 2 h. The mixture was then cooled to 0 °C, and H_2O (1 mL), 15% aqueous NaOH (1 mL), and H_2O (3 mL) were added in succession. The resulting solution was filtered through a course glass filter and concentrated to afford an off-white solid. This solid was then dissolved in CH_2Cl_2, washed with 0.1 M aqueous citric acid solution (75 mL) and brine (200 mL), dried over Na_2SO_4, and finally concentrated to give 4.54 g (99%) of pure **5** as a white powder. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.29 (d, $J = 6.2$, $-CH_3$), 2.02 (dd, $J = 7.7$, 5.3, 1H, $-OH$), 3.75 (m, 2H, $-CH_2-$), 4.52 (m, 1H, CH), 5.09 (s, 2H, Ar$-CH_2$), 6.9$-$7.5 (m, 13H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.8, 66.3, 70.1, 74.9, 115.1, 116.4, 127.5, 127.7, 127.8, 128.0, 128.6, 133.6, 134.0, 137.0, 156.8, 158.0. IR (cm^{-1}): 3426, 2905, 1608, 1499, 1378, 1243, 1177, 1063, 1044, 1010, 813, 746, 700, 514. $[\alpha]^{D}{}_{23}$: $-6.24°$ (c 1.14, THF). Anal. Calcd for $C_{22}H_{22}O_3$: C, 79.02; H, 6.63. Found: C, 79.13; H, 6.67.

4-(4-((1*R*)-Methyl-2-((6-(2-oxanyloxy)hexyl)oxy)ethoxy)phenyl)-1-(phenylmethoxy)benzene. Sodium hydride (0.985 g, 41.0 mmol) and anhydrous DMF (25 mL) were added to a dry 500 mL round-bottom flask. The flask was then fitted with a 250 mL pressure-equalizing addition funnel charged with a solution of **5** (9.09 g, 27.2 mmol) dissolved in anhydrous DMF (100 mL). This solution was added dropwise into the NaH slurry, and evolution of H_2 commenced. The reaction mixture was then heated to 95 °C, whereupon the mixture turned from cloudy yellow to a clear, dark orange color. The pressure-equalizing addition funnel was subsequently charged with a solution of 2-((6-chlorohexyl)oxy)tetrahydropyran (12.0 g, 54.4 mmol) in anhydrous DMF (125 mL), which was then added dropwise to the at 95 °C reaction mixture over 1 h. After heating at reflux for an additional 12 h, the reaction mixture was transferred to a 2 L separatory funnel and washed with H_2O (1 L). The aqueous layer was extracted with diethyl ether (4 × 400 mL), and the combined organic extracts were washed with H_2O (2 × 300 mL) and brine (300 mL). After drying over Na_2SO_4, the organic extracts were concentrated to yield an off-white solid. The crude product was dissolved in a hexane$-$ethyl acetate$-CH_2Cl_2$ mixture (50:10:40) and purified by column chromatography using a mixture of 90:10 CH_2Cl_2-ethyl acetate as the eluant to yield 9.48 g (67%) of an off-white solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.2$-$1.9 (br m, 17H), 3.3$-$4.0 (br m, 8H), 4.55 (m, 2H), 5.10 (s, 2H, Ar$-CH_2$), 6.9$-$7.5 (m, 13H). IR (cm^{-1}): 2936, 1500, 1452, 1245, 1120, 1034, 821, 732, 695, 514.

4-(4-((1*R*)-Methyl-2-((6-(2-oxanyloxy)hexyl)oxy)ethoxy)phenyl)phenol (6). To a flame-dried, 100-mL, pear-shaped Schlenk flask containing 10% Pd/C (1.00 g) in methyl acetate (30 mL) was added 4-(4-((1*R*)-methyl-2-((6-(2-oxanyloxy)hexyl)oxy)ethoxy)phenyl)-1-(phenylmethoxy)benzene (0.693 g, 20.5 mmol). The flask was charged with nitrogen, and a balloon filled with H_2 was fitted to the flask via a glass stopcock sidearm. The nitrogen was briefly evacuated from the flask, and the H_2 was allowed to enter until an atmosphere of H_2 was maintained above the liquid. The solution was stirred for 12 h under a H_2 atmosphere at ambient temperature and then filtered through a medium porosity glass frit containing a small layer of silica gel. After the collected solid was washed with excess methyl acetate, the filtrate was concentrated to yield a crude product. The crude product was subsequently purified by column chromatography using a 20:80 mixture of hexane$-$ethyl acetate as the eluant, yielding 0.463 g (81%) of pure **6** as a white paste. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.32 (d, $J = 6.2$ Hz, 3H, $-CH_3$), 1.35 (m, 4H), 1.45$-$1.95 (m, 10H), 3.4 (m, 1H), 3.5 (m, 4H), 3.65 (m, 1H), 3.75 (m, 1H), 3.9 (m, 1H), 4.6 (m, 2H), 6.8$-$7.0 (m, 4H), 7.30$-$7.45 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.0, 19.5, 25.3, 25.8, 25.9, 29.4, 29.5, 30.6, 62.3, 67.6, 71.6, 73.1, 73.9, 98.9, 115.6, 116.2, 127.5, 127.7, 132.8, 133.7, 155.2, 156.8. IR (cm^{-1}): 3341, 2938, 1609, 1500, 1444, 1376, 1241, 1118, 1076, 1023, 824, 522.

4-((10-(2-Oxanyloxy)decyl)oxy)benzoic acid (7). To a 100-mL round-bottom flask containing 2-butanone (50 mL) and K_2CO_3 (4.00 g, 28.9 mmol) was added 10-chlorodecan-1-ol (90%) (5.66 g, 26.4 mmol) and ethyl 4-hydroxybenzoate (4.40 g, 26.5 mmol). This mixture was heated at reflux for 24 h, filtered, and concentrated in vacuo. The mixture was then added to a separatory funnel with diethyl ether (200 mL) and H_2O (100 mL). After the layers were separated, the ether layer was washed with 15% aqueous NaOH (3 × 20 mL) until TLC showed the absence of starting material. The combined ether layers were then washed with brine (100 mL), dried over Na_2SO_4, and then concentrated. This crude intermediate was added to a 250 mL round-bottom flask together with 3,4-dihydro-2*H*-pyran (10 mL, 110 mmol), CH_2Cl_2 (100 mL), and a catalytic amount of PPTS (5 mg). After stirring for 1 h at ambient temperature, this reaction mixture was added to a 500 mL separatory funnel and washed with H_2O (100 mL) and then brine (100 mL). The organic layer was dried over Na_2SO_4, concentrated, and added to a 250-mL round-bottom flask containing a 3:1 MeOH$-H_2O$ mixture (150 mL) and $LiOH{\cdot}H_2O$ (10.0 g, 238 mmol). After heating at reflux for 12 h, the reaction mixture was cooled and H_2O (100 mL) was added. Aqueous 1.0 M citric acid was then added until the solution was slightly acidic (pH 5). This aqueous solution was extracted with diethyl ether (3 × 150 mL), and the combined organic extracts were washed with brine (100 mL) and dried over Na_2SO_4. After removal of the solvent in vacuo, the crude product was purified by recrystallization from hot hexanes to yield 7.00 g (an overall yield of 73%) of **7** as white, lustrous crystals. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.2$-$1.9 (m, 22H), 3.40 (dt, $J = 9.6$, 6.7, 1H), 3.5 (m, 1H), 3.75 (dt, $J = 9.5$, 6.9, 1H), 3.9 (m, 1H), 4.02 (t, $J = 6.5$, 2H), 4.6 (m, 1H), 6.9$-$8.1 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.6, 25.5, 25.9, 26.1, 26.2, 29.0, 29.3, 29.4, 29.4, 29.7, 30.7, 62.3, 67.7, 68.2, 98.8, 114.1, 121.4, 132.3, 163.6, 171.5. IR (cm^{-1}): 2935, 2851, 1679, 1606, 1579, 1514, 1466, 1430, 1298, 1256, 1174, 1120, 1076, 1032, 903, 858, 774, 646. Anal. Calcd for $C_{22}H_{34}O_5$: C, 69.81; H, 9.05. Found: C, 70.08; H, 8.91.

4-(4-((1*R*)-Methyl-2-((6-(2-oxanyloxy)hexyl)oxy)ethoxy)phenyl)phenyl 4-((10-(2-Oxanyloxy)decyl)oxy)benzoate. To a 50 mL round-bottom flask containing phenol **6** (0.476 g, 1.11 mmol) cooled to 0 °C was added CH_2Cl_2 (25 mL), acid **7** (0.434 g, 1.15 mmol), and 1,3-dicyclohexylcarbodiimide (0.264 g, 1.28 mmol). One crystal of 4-(dimethylamino)pyridine was added, and the solution was stirred for 24 h at 0 °C. The solution was then filtered, concentrated, and redissolved in diethyl ether (75 mL). After the ether solution was washed with saturated $NaHCO_3$ (50 mL), 0.4 N aqueous NaOH (50 mL), and brine (100 mL), it was then dried over K_2CO_3 and concentrated to yield 0.983 g of crude product, which was used in the subsequent step without further purification. (The NMR characterization of this compound was difficult because of the large number of similar NMR signals from the four diastereomers formed in this reaction.) IR (cm^{-1}): 2935, 2855, 1732, 1607, 1496, 1261, 1209, 1168, 1121, 1076, 1035, 845, 816, 764.

4-(4-((1*R*)-Methyl-2-((6-hydroxyhexyl)oxy)ethoxy)phenyl)phenyl 4-((10-Hydroxydecyl)oxy)benzoate (8). To a 50 mL round-bottom flask containing crude **8** (0.983 g) was added diethyl ether (30 mL) and $MgBr_2$ (0.849 g, 4.61 mmol). The flask was wrapped with aluminum foil to keep out light and stirred for 8 h at ambient temperature. The solution was then concentrated and transferred to a 250 mL separatory funnel containing CH_2Cl_2 (50 mL) and H_2O (25 mL). The organic layer was washed with brine (50 mL), dried over K_2CO_3, and then concentrated to afford a crude product. This crude product was purified by column chromatography using a mixture of 40:30:30 ethyl acetate−CH_2Cl_2−hexane as the eluant affording 0.502 g (73% over two steps) of pure **8** as a white solid. ^1H NMR ($CDCl_3$, 300 MHz): δ 1.2−1.9 (m, 27H), 3.5 (m, 3H), 3.6 (m, 5H), 4.05 (t, $J = 6.5$ Hz, 2H), 4.6 (m, 1H), 7.0 (m, 4H), 7.25 (m, 2H), 7.5 (m, 2H), 7.6 (m, 2H), 8.15 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 165.4, 163.9, 157.9, 150.3, 138.8, 133.4, 132.6, 128.4, 128.0, 122.3, 121.8, 116.6, 114.6, 74.3, 73.6, 71.9, 68.6, 63.3, 63.1, 33.1, 33.0, 29.9, 29.8, 29.8, 29.7, 29.7, 29.4, 26.3, 26.2, 26.1, 25.9, 17.5. IR (cm^{-1}): 3350, 2930, 2842, 1729, 1610, 1498, 1274, 1217, 1172, 1119, 1078, 877, 845, 801, 761. $C_{38}H_{52}O_7$: 620.82; MS (FAB) *m/z* 620 (M^+).

10-(4-(((4-(4-((1*R*)-Methyl-2-((6-(prop-2-enoyloxy)hexyl)oxy)ethoxy)phenyl)phenyl)oxy)carbonyl)phenoxy)decyl Prop-2-enoate (1). To a 50 mL round-bottom flask containing diol **8** (0.502 g, 0.809 mmol) was added anhydrous CH_2Cl_2 (25 mL) via cannula, NEt_3 (8.0 mL) via syringe, a crystal of 4-(dimethylamino)pyridine, and a few grains of 2,6-di-*tert*-butyl-4-methylphenol (radical inhibitor). This mixture was stirred and cooled to 0 °C, and then acryloyl chloride (0.6 mL, 7.4 mmol) was added dropwise via a syringe. After 15 min, the reaction was found to be complete by TLC monitoring. The reaction mixture was then quenched by pouring it into ice-cold 0.1 N aqueous HCl. The resulting mixture was extracted with CH_2Cl_2 (3×50 mL), washed with brine (100 mL), dried over K_2CO_3, and concentrated. The concentrate was separated by column chromatography using a 20:80 mixture of ethyl acetate−hexane as the eluant to afford 0.216 g (37%) of pure monomer **1** as a white solid. ^1H NMR (400 MHz, $CDCl_3$): δ 1.1−1.9 (m, 27 H), 3.51 (t, $J = 6.5$, 2H), 3.51 (dd, $J = 10.2$, 4.8, 1H), 3.65 (dd, $J = 10.2$, 5.8, 1H), 4.04 (t, $J = 6.6$, 2H), 4.14 (t, $J = 6.7$, 2H), 4.16 (t, $J = 6.7$, 2H), 4.6 (m, 1H), 5.8 (dd, $J = 10.4$, 1.5, 1h), 5.8 (dd, $J = 10.4$, 1.5, 1H), 6.1 (dd, $J = 17.3$, 10.4, 1H), 6.1 (dd, $J = 17.3$, 10.4, 1H), 6.4 (dd, $J = 17.3$, 1.5, 1H), 6.4 (dd, $J = 17.3$, 1.5, 1H), 6.9−8.2 (m, 12 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.1, 25.7, 25.8, 25.9, 28.5, 28.5, 29.0, 29.1, 29.3, 29.4, 29.4, 29.5, 64.5, 64.6, 68.2, 71.5, 73.2, 73.9, 114.2, 116.2, 121.5, 121.9, 127.6, 128.1, 128.6, 128.6, 130.4, 130.4, 132.2, 133.1, 138.4, 150.0, 157.6, 163.5, 165.0, 166.2, 166.3. IR (cm^{-1}): 3061, 3036, 2922, 2852, 1728, 1635, 1607, 1512, 1496, 1470, 1408, 1263, 1206, 1169, 1076, 1017, 986, 852, 822, 811, 759, 726, 690, 652, 516. $[\alpha]^D{}_{23}$: +5.04° (*c* 0.595, CH_2Cl_2). Anal. Calcd for $C_{44}H_{56}O_9$: C, 72.50; H, 7.74. Found: C, 72.34; H, 7.54.

Preparation of Photopolymerizable Monomer Mixtures. 2,2-Dimethoxy-2-phenylacetophenone (2 wt %) was dissolved with monomer **1** in CH_2Cl_2. The solvent was subsequently removed in vacuo to afford the reactive monomer mixture.

Photopolymerization of the Liquid Crystal Phases. A. Unoriented Thin Films of the Smectic A* and C* Phases. Photopolymerization of 1 in the Smectic A* Phase. Approximately 4 mg of the monomer mixture was placed between two KBr plates (2×25 mm disks) and heated to the isotropic melt using the microscope heating stage. The mixture was then cooled at 2.0 °C/min to 63.4 °C and subsequently irradiated with the UVP lamp (11 000 W/cm^2) for 10 min with the sample temperature maintained by the heating stage. Polymerization of the sample was monitored by IR spectroscopy to confirm the loss of acrylate bands at 1636 and 811 cm^{-1}. The degree of polymerization was quantified by comparing the absorbance of the 811 cm^{-1} band before and after photopolymerization. Retention of the LC phase architecture was confirmed by comparing the optical textures and the X-ray diffraction profiles of the sample before and after photopolymerization.

Photopolymerization of 1 in the Mixed Smectic C* and A* Phases. The above procedure was followed except the polymerization temperature was maintained at 33.0 °C using the hot stage.

B. Aligned Thin Films of the Smectic A* and C* Phases. Homogeneously Aligned Samples. A Linkam ferroelectric LC cell was heated above the clearing temperature of the monomer (ca. 80 °C) on a heating mantle. The cell was filled by adding approximately 4 mg of the monomer/photoinitiator mixture to one end of the heated cell and drawing the melted sample in by capillary action. After the filled cell was mounted into the ferroelectric LC cell attachment on the hot stage, the sample was subsequently heated to the isotropic phase. Upon cooling at 2.0 °C/min to obtain the desired mesophase, a homogeneous texture was observed under the polarized light microscope. Photopolymerization of the oriented phase at constant temperature was performed using the same procedure described above. Retention of the phase architecture was confirmed by the fact that the cross-linked samples exhibit the original optical texture even when heated above 120 °C and cooled to room temperature.

Homeotropically Aligned Samples. A similar procedure was used for the cross-linking of homeotropically aligned samples except that the samples were initially melted and annealed between two Fisher microscope slides, or two Linkam glass cover slips before cooling to the appropriate temperature. Homeotropic alignment in the unpolymerized and polymerized samples was confirmed by X-ray diffraction and the observation of a dark, pseudoisotropic optical texture.

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Supporting Information Available: Optical texture of cross-linked **1** in the unoriented smectic A* phase, Debye−Scherrer X-ray profile of a magnetically oriented smectic A* phase of **1**, FT-IR spectra of **1** in the smectic A* phase before and after photopolymerization (4 pages). See any current masthead page for ordering and Web access instructions.

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