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Polymerizable hexacatenar liquid crystals containing a luminescent oligo(*p*-phenylenevinylene) core

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Polymerizable hexacatenar mesogens containing a photo-active oligo(*p*-phenylenevinylene) core were successfully synthesized by replacing the traditional *n*-alkoxy tails on the molecules with polymerizable hydrocarbon tails containing terminal isoprenyl or 1,3-dienyl units. It was found that for this particular liquid crystal (LC) platform, the incorporation of conventional radical polymerizable groups such as acrylates in the tails was not conducive to the formation of thermotropic LC phases, presumably due to their polar nature. The resulting photoluminescent isoprenyl and 1,3-dienyl hexacatenar monomers were found to form columnar hexagonal phases at elevated temperatures (*c*. 45–75°C), as determined by powder X-ray diffraction. Unfortunately, photoinitiated radical polymerization studies revealed that the mesogens are susceptible to photodegradation in the LC state at elevated temperatures, resulting in the loss of both LC order and emission properties during photopolymerization. Thermally initiated radical polymerization in the absence of light, however, afforded effective crosslinking with retention of both LC order and the desired emission properties. The resulting crosslinked columnar hexagonal phases were found to exhibit emission maxima at nearly identical wavelengths, with comparable intensities relative to the unpolymerized starting materials. The effect of the different polymerizable groups on the mesogenic behaviour, polymerization characteristics, and emission properties of the hexacatenar compounds is presented.

1. Introduction

Emissive liquid crystals (LCs) are intriguing systems for materials research because they couple molecular self-assembly with intrinsic light generation capabilities. This unique combination of properties offers the possibility of novel optical device applications for LC materials, such as emissive LC displays [1–4], polarized dye lasers [5–7], anisotropic organic light-emitting diodes [8–10], and ordered electron transport systems [8, 11]. Emissive LC systems are also valuable as molecular probes for studying the effect of order on photophysics and energy transfer in organic materials [12, 13]. The majority of research in the field of emissive LC systems has been focused on guest–host systems, in which a non-mesogenic fluorophore is dissolved in a thermotropic LC matrix [1–4]. However, some efforts have also been made in the design of intrinsically luminescent thermotropic LCs, of which only a small number are known [8, 12–18]. Research in this latter area has been hampered, in part, to the difficulty of incorporating a luminescent functional group in a LC while retaining the desired mesogenic properties.

Recently, our research group managed to incorporate intrinsic luminescence properties into a family of modular hexacatenar LCs [17]. Hexacatenar (i.e. six-tailed) LCs are a relatively new class of thermotropic mesogens with a hybrid structure consisting of a rod-like central core and two half-disk end units each containing three flexible tails (figure 1) [19]. Hexacatenar LCs are known to form columnar hexagonal (Φ_h) phases, in addition to the traditional nematic (N) and smectic (Sm) phases commonly formed by rod-like LCs. By employing a conjugated (*E*,*E*)-1,4-bis[2-(3,5-dimethoxy-4-hydroxyphenyl)ethenyl]benzene unit as the rod-like central core, a series of luminescent hexacatenar LCs (**1**) were formed that adopt Φ_h and columnar nematic phases [17, 20]. These novel emissive mesogens were found to have characteristics that illustrate not only the effect of molecular order on emission behaviour in these systems, but also the potential of these novel materials for device applications. For example, preliminary experiments by photophysics collaborators revealed an efficient stimulated emission mechanism in

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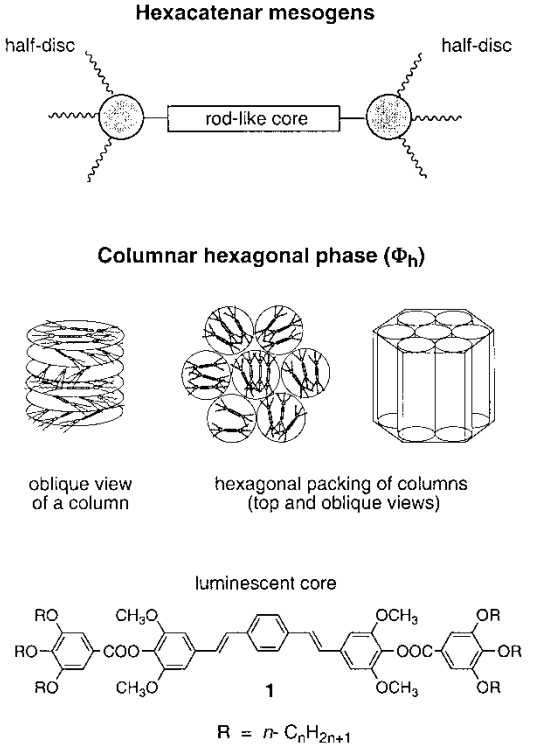


Figure 1. Structure of a hexacatenar mesogen, the Φ_h phase, and emissive hexacatenar mesogen **1**.

the Φ_h phases of **1**, which is uncommon in typical oligo(*p*-phenylenevinylene)s [21]. In addition, weak electroluminescence (EL) at high applied electrical potential was also observed when thin films of **1** in the Φ_h phase were tested in ITO/Al cells [22]. Unfortunately, one of the inherent drawbacks with these emissive hexacatenar systems is their sensitivity to thermal effects. The luminescent LC phases melted near the onset of the observed EL due to resistive heating, resulting in degradation of the active material [22]. In order to remove the temperature dependence and improve the robustness of these intriguing LC materials, polymerizable derivatives of **1** were desired so that stabilized networks of these emissive materials could be obtained.

Herein, we describe the design, synthesis, and characterization of crosslinkable derivatives of luminescent hexacatenar mesogen **1**. In order to obtain an intrinsically crosslinkable hexacatenar LC that retains the desired mesogenic and emission properties, three different sets of radically polymerizable derivatives (acryloyloxy, isoprenyl, and 1,3-dienyl) were synthesized and studied. Of the three polymerizable tail systems surveyed, it was found that only the isoprenyl and alkyl-1,3-dienyl tail systems in combination with a slightly modified oligo(*p*-phenylenevinylene) core were successful in generating hexacatenar monomers with the desired LC and luminescence properties. The effects of these different polymerizable tail systems on the mesogenic, emission, and crosslinking behaviour of the hexacatenar compounds are discussed.

2. Experimental

2.1. *General procedures and materials*

All manipulations involving air- and/or water-sensitive materials were performed using standard vacuum line techniques. Reagents 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 and oxalyl chloride were distilled and stored under N_2. 2-(1,3-Butadienyl)magnesium chloride was prepared according to literature procedures [23]. Tetrahydrofuran (THF) was vacuum-transferred from sodium/benzophenone ketyl. Methylene chloride was vacuum-transferred from calcium hydride. Reactions were monitored by thin layer chromatography (TLC) on EM Science 250 micron silica gel F_{254} plates. NMR spectra were obtained with a Bruker AMX-300 (300 MHz), AMX-400 (400 MHz), or DRX-500 (500 MHz) spectrometer. Fourier transform infrared (FTIR) spectra were obtained using a Perkin-Elmer 1616 FTIR spectrometer at a resolution of $4\,cm^{-1}$ and recorded as neat films on KBr plates or as KBr mulls. Powder X-ray diffraction (XRD) profiles (monochromatic CuKα radiation) were obtained using an Inel CPS 120 powder diffraction system equipped with an Inel programmable capillary oven (accuracy: $\pm 3^{\circ}C$). Polarizing optical microscopy (POM) was performed using a Leica DMRXP polarizing light microscope equipped with an Optronix digital camera assembly. UV-Vis spectra were obtained using a Hewlett-Packard HP 8425A spectrophotometer. Emission and excitation spectra were obtained using a ISA Spex Fluoromax-2 fluorimeter. A Cole-Parmer 9815 series 6 watt UV (365 nm) lamp was used for photopolymerization experiments. UV light fluxes were measured using a Spectroline DRC-100X digital radiometer equipped with a DIX-365 UV-A sensor. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ.

2.2. *Synthesis of hexacatenar monomers*

2.2.1. *(E,E)-1,4-Bis([2-(3,5-dimethoxy-4-hydroxyphenyl)-ethenyl]benzene*

This compound was synthesised from *p*-xylylene-bisphosphonic acid tetraethyl ester and syringaldehyde as described previously in the literature [17].

2.2.2. *3,4,5-Tris(ω-hydroxyalkoxy)benzoic acids*

Methyl gallate (2.00 g, 10.9 mmol) and the appropriate ω-bromoalkanol (6.12 g, 33.8 mmol) were dissolved

in methyl ethyl ketone (100 ml). To this solution was added K_2CO_3 (15.1 g, 109 mmol). The flask was then fitted with a reflux condenser, and the reaction mixture heated at reflux for 48 h. The reaction mixture was then extracted with ethyl acetate (200 ml), washed with water (3×75 ml), and dried over Na_2SO_4. The volatile components were removed with a rotary evaporator. The crude product was then treated with ethanol (120 ml), H_2O (20 ml), and finally NaOH (3.05 g, 76.3 mmol); this mixture was heated at reflux for 12 h. After heating, 3N HCl (40 ml, 119 mmol) was added, generating an off-white solid precipitate. The resulting solid was filtered off and washed with hexanes.

3,4,5-Tris[6-(hydroxy)hexyloxy]benzoic acid. Yield 3.61 g (70%). ^{1}H NMR (400 MHz, d_6-DMSO): δ 1.43 (m, 18H), 1.70 (m, 6H), 3.40 (m, 6H), 3.92 (t, $J = 6.3$ Hz, 2H), 3.98 (t, $J = 6.2$ Hz, 4H), 4.35 (t, $J = 5.1$ Hz, 3H), 7.18 (s, 2H), 12.84 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 25.63, 25.78, 28.41, 28.46, 28.81, 29.03, 29.23, 30.61, 63.06, 69.43, 73.20, 107.67, 126.21, 141.47, 152.35, 167.21. IR (cm^{-1}): 3336, 3234, 2918, 2848, 1681, 1587, 1502, 1467, 1430, 1331, 1221, 1210, 1122, 1060.

3,4,5-Tris[11-(hydroxy)undecyloxy]benzoic acid. Yield 7.10 g (96%). Spectral data agreed with those reported in the literature [24].

2.2.3. *General preparation of 3,4,5-tris[(acryloyloxy)-alkoxy]benzoic acids*

To a 100 ml Schlenk flask was added 3,4,5-tris(ω-hydroxyalkoxy)benzoic acid (2.0 g, 4.3 mmol), NEt_3 (2.40 ml, 17.2 mmol), and dry CH_2Cl_2 (50 ml) under a N_2 atmosphere. The Schlenk flask was fitted with a 10 ml pressure-equalizing funnel charged with acryloyl chloride (1.15 ml, 14.2 mmol) and CH_2Cl_2 (5 ml). The acryloyl chloride solution was added over 20 min, and the reaction mixture was stirred for 3 h in the absence of light. The reaction mixture was extracted with hexanes/ethyl acetate (120 ml/40 ml) and the combined extracts washed with 1N HCl (3×50 ml), H_2O (2×100 ml), and brine (2×25 ml). The organic extracts were concentrated *in vacuo* to afford the crude product, which was transferred into a 25 ml round-bottom flask with pyridine (5.0 ml), H_2O (2.5 ml), and THF (25 ml). The reaction mixture was stirred for 30 min in the absence of light and then poured into a 250 ml separating funnel. The reaction mixture was extracted with hexanes/ethyl acetate (120 ml/40 ml) and washed with 1N HCl (3×50 ml), H_2O (2×100 ml), and brine (2×25 ml). The organic extracts were concentrated *in vacuo*, again to afford a crude product, which was purified by column chromatography (50:50 hexanes/ethyl acetate) and recrystallisation from ethyl acetate to afford a white powder.

3,4,5-Tris[6-(acryloyloxy)hexyloxy]benzoic acid. Yield 2.45 g (91%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.53 (m, 12H), 1.71 (m, 8H), 1.84 (m, 4H), 4.03 (m, 6H), 4.17 (m, 6), 5.82 (dd, $J = 10.4$, 1.5 Hz, 3H), 6.12 (dd, $J = 17.5$, 10.4 Hz, 3H), 6.40 (dd, $J = 17.3$, 1.5 Hz, 3H), 7.31 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 25.68, 25.54, 25.73, 28.81, 28.90, 29.33, 30.14, 64.45, 64.58, 69.39, 73.77, 108.75, 123.84, 130.17, 130.87, 143.38, 153.08, 166.35, 172.06. IR (cm^{-1}): 3236, 2918, 2846, 1723, 1684, 1585, 1502, 1466, 1431, 1409, 1385, 1331, 1296, 1272, 1226, 1221, 1210, 1189, 1125, 1062, 810. Anal: calcd for $C_{34}H_{48}O_{11}$, C 64.54, H 7.65; found, C 64.14, H 8.10%.

3,4,5-Tris[11-(acryloyloxy)undecyloxy]benzoic acid. Yield 2.04 g (92%). Spectral data agreed with those reported in the literature [24].

2.2.4. *General preparation of hexacatenar acrylate derivatives* ***2***

To a 50 ml air-free flask (flame-dried) was added the appropriate 3,4,5-tris[ω-(acryloyloxy)alkoxy]benzoic acid (1.99 mmol), CH_2Cl_2 (25 ml), and $SOCl_2$ (0.55 g, 4.60 mmol). The flask was fitted with a reflux condenser, and the reaction mixture gently heated at reflux under N_2 for 16 h. The volatile components were then removed *in vacuo* affording an off-white solid or oil. To the same reaction flask was added THF/CH_2Cl_2 (1/1 v/v) (50 ml), NEt_3 (0.51 g, 50.7 mmol), and (*E*,*E*)-1,4-bis[2-(3,5-dimethoxy-4-hydroxyphenyl)ethenyl]benzene (0.20 g, 0.46 mmol) in that order. The reaction mixture was heated at reflux for 48 h and then poured into a 500 ml separating funnel. It was extracted with a mixture of diethyl ether (125 ml) and ethyl acetate (50 ml), and the organic extracts were washed successively with 1N HCl (2×50 ml) and brine (2×50 ml). Concentration *in vacuo* then afforded the crude product, which was purified by column chromatography.

Hexacatenar acrylate monomer ***2a***. (Chromatography: 50/50 hexanes/ethyl acetate); yield 0.29 g (51%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.46 (m, 12H), 1.54 (m, 12H), 1.71 (m, 12H), 1.85 (m, 12H), 3.88 (s, 12H), 4.06 (m, 12H), 4.17 (m, 12H), 5.81 (dd, $J = 10.4$, 1.5 Hz, 6H), 6.12 (dd, $J = 17.3$, 10.4 Hz, 6H), 6.39 (dd, $J = 17.3$, 1.5 Hz, 6H), 6.81 (s, 4H), 7.07 (d, $J = 16.2$ Hz, 2H), 7.12 (d, $J = 16.1$ Hz, 2H), 7.45 (s, 4H), 7.54 (s, 4H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 25.67, 25.70, 25.77, 28.55, 28.61, 29.15, 30.13, 56.18, 64.43, 64.52, 68.96, 73.22, 103.31, 108.88, 123.88, 126.87, 128.54, 128.72, 130.37, 130.40, 135.73, 136.54, 142.69, 152.54, 152.77, 164.26, 166.21. IR (cm^{-1}): 2939, 2861, 1723, 1684, 1652, 1635, 1616, 1593, 1558, 1540, 1506, 1457, 1429, 1408, 1336,

1296, 1273, 1193, 1149, 1130, 1062, 985, 967, 811. Anal. calcd for $C_{94}H_{118}O_{26}$, C 67.85, H 7.14; found, C 68.07, H 7.20%.

Hexacatenar acrylate monomer ***2b***. (Chromatography: 70/30 hexanes/ethyl acetate); yield 0.75 g (63%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.30 (m, 72H), 1.48 (m, 12H), 1.67 (m, 12H), 1.76 (m, 4H), 1.82 (m, 8H), 3.88 (s, 12H), 4.05 (t, $J=6.5$ Hz, 12H), 4.15 (m, 12H), 5.81 (dd, $J=10.4$, 1.5 Hz, 6H), 6.12 (dd, $J=17.4$, 10.4 Hz, 6H), 6.39 (dd, $J=17.3$, 1.5 Hz, 6H), 6.81 (s, 4H), 7.07 (d, $J=16.2$ Hz, 2H), 7.12 (d, $J=16.3$ Hz, 2H), 7.45 (s, 4H), 7.54 (s, 4H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 26.17, 26.19, 26.30, 28.86, 28.88, 29.50, 29.54, 29.56, 29.60, 29.74, 29.78, 29.80, 29.81, 29.84, 29.91, 30.58, 56.48, 64.94, 69.46, 73.76, 103.62, 109.14, 123.90, 124.03, 127.15, 128.75, 128.91, 129.06, 130.57, 135.98, 136.84, 143.11, 152.85, 153.14, 164.62, 166.54. IR (cm^{-1}): 2926, 2854, 1725, 1635, 1619, 1593, 1504, 1465, 1429, 1407, 1386, 1335, 1295, 1271, 1191, 1149, 1131, 1059, 985, 964, 811. Anal. calcd for $C_{124}H_{178}O_{26}$, C 71.43, H 8.60; found, C 71.51, H 8.45%.

2.2.5. *2-(10-Chlorohexyl)buta-1,3-diene* [23]

To a mixture of 6-chloro-1-iodohexane (prepared from 6-chlorohexanol) [25] (1.00 g, 4.06 mmol), 0.1M Li_2CuCl_4 (1.62 ml, 0.16 mmol), and THF (20 ml) was added 0.625M 2-(1,3-butadienyl)magnesium chloride under a N_2 atmosphere. The reaction mixture was stirred at ambient temperature for 18 h after completion of the addition, and the volatile components were removed *in vacuo*. The crude oil was taken up in hexane and washed with H_2O (2×50 ml), saturated NH_4Cl (4×25 ml), and brine (2×25 ml). The organic layer was dried over Na_2SO_4 and concentrated to give the crude product which was purified by column chromatography (100% hexanes); yield 0.62 g (89%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.54 (m, 6H), 1.78 (m, 2H), 2.21 (t, $J=7.3$ Hz, 2H), 3.53 (t, $J=6.6$ Hz, 2H), 4.98 (s, 1H), 5.00 (s, 1H), 5.05 (d, $J=10.8$ Hz, 1H), 5.22 (d, $J=17.6$ Hz, 1H), 6.37 (dd, $J=17.6$, 10.8 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 26.96, 28.13, 28.99, 31.42, 32.79, 45.28, 113.29, 115.79, 139.14, 146.53. IR (cm^{-1}): 3089, 2934, 2859, 1634, 1594, 1464, 1446, 1308, 992, 895, 728.

2.2.6. *2-(10-Bromodecyl)-buta-1,3-diene* [23]

This compound was synthesized from 11-bromo-1-iodoundecane (which was prepared from 11-bromoundecanol) [26] and 2-(1,3-butadienyl)magnesium chloride by the procedure used for 2-(10-chloro-hexyl)-buta-1,3-diene; yield 2.68 g (56%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.28 (m, 12H), 1.45 (m, 4H), 1.85 (m, 2H), 2.20 (t, $J=6.7$ Hz, 2H), 3.41 (t, $J=6.9$ Hz, 2H), 4.98 (s, 1H), 4.99 (s, 1H), 5.05 (d, $J=10.8$ Hz, 1H), 5.22 (d, $J=17.3$ Hz, 1H), 6.37 (dd, $J=17.6$, 10.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 28.35, 28.38, 28.97, 29.63, 29.72, 29.76, 29.80, 31.55, 33.04, 34.20, 113.21, 115.63, 139.24, 146.80. IR (cm^{-1}): 3089, 3004, 2938, 2854, 1634, 1595, 1465, 1468, 1389, 1369, 1294, 1249, 1232, 991, 893, 722.

2.2.7. *3,4,5-Tris[(7-(methenyl)-8-nonenyloxy]benzoic acid*

This compound was synthesised from 2-(10-chlorohexyl)-buta-1,3-diene and methyl gallate by the procedure used for homologues of **2**, except that NaI was added as catalyst during the etherification of the tails; yield 0.78 g (72%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.51 (m, 18H), 1.83 (m, 6H), 2.22 (m, 6H), 4.12 (m, 6H), 4.98 (s, 3H), 5.00 (s, 3H), 5.05 (d, $J=10.8$ Hz, 3H), 5.22 (d, $J=17.6$ Hz, 3H), 6.37 (dd, $J=17.6$, 10.8 Hz, 3H), 7.32 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 26.39, 28.95, 29.24, 29.52, 29.74, 30.35, 32.10, 69.44, 73.76, 108.82, 113.23, 115.64, 123.99, 139.31, 143.43, 146.96, 153.12, 172.13. IR (cm^{-1}): 3088, 3001, 2926, 2854, 1684, 1595, 1506, 1466, 1432, 1388, 1329, 1271, 1230, 1120, 990, 890, 866, 769, 723. Anal: calcd for $C_{37}H_{54}O_5$, C 76.78, H 9.40; found, C 76.69, H 9.41%.

2.2.8. *3,4,5-Tris[12-(methenyl)-13-tetradecenyloxy]-benzoic acid*

This compound was synthesized from 2-(10-bromodecyl)buta-1,3-diene and methyl gallate by the procedure used for homologues of **2**; yield 1.83 g (96%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.30 (m, 36H), 1.49 (m, 12H), 1.83 (m, 6H), 2.19 (m, 6H), 4.03 (m, 6H), 4.98 (s, 3H), 5.00 (s, 3H), 5.04 (d, $J=10.8$ Hz, 3H), 5.23 (d, $J=17.6$ Hz, 3H), 6.37 (dd, $J=17.6$, 10.8 Hz, 3H), 7.34 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 22.85, 26.25, 26.28, 28.38, 29.49, 29.59, 29.75, 29.84, 29.90, 30.54, 31.57, 31.79, 69.39, 73.73, 108.80, 113.18, 115.60, 123.87, 139.25, 143.40, 146.81, 153.05, 172.09. IR (cm^{-1}): 3089, 3003, 2928, 2853, 1685, 1594, 1506, 1466, 1432, 1388, 1329, 1270, 1229, 1120, 990, 892, 866, 769, 723. Anal: calcd for $C_{52}H_{84}O_5$, C 79.13, H 10.73; found, C 79.40, H 10.53%.

2.2.9. *Hexacatenar isoprene monomer* ***3a***

This was synthesised from 3,4,5-tris[7-(methenyl)-8-nonenyloxy]benzoic acid and (*E*,*E*)-1,4-bis[2-(3,5-dimethoxy-4-hydroxyphenyl)ethenyl]benzene by the procedure used for homologues of **2**. (Chromatography: 80/20 hexanes/ethyl acetate); yield 0.34 g (63%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.53 (m, 36H), 1.84 (m, 12H), 2.21 (t, $J=7.3$ Hz, 12H), 3.88 (s, 12H), 4.06 (m,

12H), 4.98 (s, 6H), 5.00 (s, 6H), 5.05 (d, $J=10.8$ Hz, 6H), 5.22 (d, $J=17.6$ Hz, 6H), 6.37 (dd, $J=17.6$, 10.8 Hz, 6H), 6.82 (s, 4H), 7.07 (d, $J=16.2$ Hz, 2H), 7.13 (d, $J=16.2$ Hz, 2H), 7.46 (s, 4H), 7.54 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 26.35, 28.87, 29.23, 29.54, 29.75, 30.36, 32.15, 56.31, 69.47, 73.78, 103.61, 108.83, 113.35, 115.61, 123.90, 127.03, 128.61, 128.73, 128.97, 135.56, 136.73, 139.07, 142.90, 146.59, 152.54, 153.13, 164.47. IR (cm^{-1}): 3087, 3002, 2935, 2858, 1737, 1631, 1593, 1503, 1463, 1429, 1390, 1335, 1232, 1190, 1149, 1130, 991, 958, 896, 840, 754. Anal: calcd for $C_{100}H_{130}O_{14}$, C 77.18, H 8.42; found, C 76.91, H 8.37%.

2.2.10. *Hexacatenar isoprene monomer* ***3b***

This compound was synthesized from 3,4,5-tris[12-(methenyl)-13-tetradecenyloxy]benzoic acid and (*E*,*E*)-1,4-bis[2-(3,5-dimethoxy-4-hydroxyphenyl)ethenyl]benzene by the procedure used for homologues of **2**. (Chromatography: 78/22 hexanes/ethyl acetate); yield 0.25 g (43%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.31 (m, 72H), 1.49 (m, 24H), 1.82 (m, 12H), 2.21 (t, $J=7.6$ Hz, 12H), 3.88 (s, 12H), 4.06 (m, 12H), 4.99 (s, 6H), 5.00 (s, 6H), 5.05 (d, $J=10.6$ Hz, 6H), 5.24 (d, $J=17.7$ Hz, 6H), 6.38 (dd, $J=17.6$, 10.8 Hz, 6H), 6.82 (s, 4H), 7.07 (d, $J=16.1$ Hz, 2H), 7.12 (d, $J=16.3$ Hz, 2H), 7.47 (s, 4H), 7.54 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 26.26, 27.53, 28.33, 29.49, 29.57, 29.74, 29.81, 29.85, 29.89, 30.06, 30.48, 30.53, 31.52, 56.35, 69.32, 73.70, 103.42, 108.92, 113.20, 115.64, 123.93, 127.08, 128.63, 128.72, 128.92, 135.90, 136.72, 139.21, 142.92, 146.76, 152.72, 153.06, 164.60. IR (cm^{-1}): 3088, 3002, 2925, 2852, 1736, 1632, 1593, 1504, 1464, 1429, 1388, 1336, 1231, 1190, 1149, 1130, 990, 960, 893, 838, 754. Anal. calcd for $C_{130}H_{190}O_{14}$, C 78.98, H 9.69; found, C 78.73, H 9.31%.

2.2.11. *3,4,5-Tris(9,11-dodecadienyloxy)benzoic and 3,4,5-tris(11,13-tetradecadienyloxy)benzoic acids*

These compounds were synthesized as described previously in the literature [27].

2.2.12. *Hexacatenar alkyl-1,3-diene monomer* ***4a***

This compound was synthesized from 3,4,5-tris(9,11-dodecadienyloxy)benzoic acid and (*E*,*E*)-1,4-bis[2-(3,5-dimethoxy-4-hydroxyphenyl)ethenyl]benzene by the procedure used for homologues of **2**; yield 0.38 g (38%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.33 (m, 48H), 1.48 (m, 12H), 1.76 (m, 4H), 1.83 (m, 8H), 2.07 (m, 12H), 3.88 (s, 12H), 4.05 (m, 12H), 4.95 (d, $J=10.1$ Hz, 6H), 5.08 (d, $J=16.6$ Hz, 6H), 5.70 (dt, $J=15.2$, 6.9 Hz, 6H), 6.05 (dd, $J=15.1$, 10.4 Hz, 6H), 6.31 (ddd, $J=16.9$, 10.3, 10.1 Hz, 6H), 6.82 (s, 4H), 7.07 (d, $J=16.2$, Hz 2H), 7.12 (d, $J=16.2$ Hz, 2H), 7.46 (s, 4H), 7.54 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 26.23, 29.34, 29.36, 29.41, 29.49, 29.63, 29.67, 29.73, 30.51, 32.72, 32.75, 56.37, 69.33, 73.68, 103.47, 108.98, 114.76, 123.95, 127.08, 128.65, 128.74, 128.90, 131.06, 135.68, 135.91, 136.74, 137.52, 142.96, 152.74, 153.06, 164.58. IR (cm^{-1}): 3083, 3005, 2925, 2853, 1737, 1698, 1651, 1593, 1504, 1463, 1429, 1387, 1335, 1232, 1190, 1148, 1131, 1003, 950, 896, 863, 838, 754, 732. Anal: calcd for $C_{112}H_{154}O_{14}$, C 78.01, H 9.00; found, C 78.15, H 9.16%.

2.2.13. *Hexacatenar alkyl-1,3-diene monomer* ***4b***

This compound was synthesized from 3,4,5-tris(11,13-tetradecadienyloxy)benzoic acid [27] and (*E*,*E*)-1,4-bis[2-(3,5-dimethoxy-4-hydroxyphenyl)ethenyl]benzene by the procedure used for homologues of **2**; yield 0.23 g (39%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.30 (m, 72H), 1.49 (m, 12H), 1.84 (m, 12H), 2.09 (m, 12H), 3.87 (s, 12H), 4.06 (m, 12H), 4.96 (d, $J=10.1$ Hz, 6H), 5.09 (d, $J=16.9$ Hz, 6H), 5.71 (dt, $J=15.2$, 6.9 Hz, 6H), 6.06 (dd, $J=15.2$, 10.4 Hz, 6H), 6.32 (ddd, $J=17.0$, 10.3, 10.0 Hz, 6H), 6.82 (s, 4H), 7.07 (d, $J=16.2$ Hz, 2H), 7.12 (d, $J=16.2$ Hz, 2H), 7.46 (s, 4H), 7.54 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 26.24, 29.36, 29.39, 29.44, 29.47, 29.55, 29.67, 29.73, 29.77, 29.81, 29.88, 30.51, 32.73, 56.32, 69.30, 73.68, 103.40, 108.91, 114.72, 123.92, 127.06, 128.61, 128.69, 128.83, 131.01, 135.74, 135.90, 136.71, 137.52, 142.91, 152.71, 153.05, 164.58. IR (cm^{-1}): 3084, 3005, 2923, 2852, 1738, 1651, 1593, 1504, 1463, 1429, 1387, 1336, 1240, 1190, 1148, 1131, 1002, 950, 896, 863, 839, 754, 733. Anal: calcd for $C_{124}H_{178}O_{14}$, C 78.69, H 9.48; found, C 78.42, H 9.76%.

2.2.14. p-*Xylylene-bis-phosphonic acid tetraethyl ester*

This compound was synthesized from α,α'-dibromo-*p*-xylene and two equiv of triethylphosphite, as described previously. Spectral data agreed with those reported in the literature [17].

2.2.15. *(*E,E*)-1,4-Bis[2-(4-hydroxyphenyl)ethenyl]-benzene* [*28*]

To a 500 ml air-free flask containing *p*-xylylene-bis-phosphonic acid tetraethyl ester (10.00 g, 26.4 mmol) was added THF (100 ml) via a cannula, DMF (75 ml), and potassium *tert*-butoxide (14.1 g, 126 mmol) as a powder. The reaction mixture was stirred for 4 h at ambient temperature during which time it became reddish-brown. The reaction mixture was then cooled to 0°C, and a solution of 4-hydroxybenzaldehyde (6.68 g, 54.7 mmol) in DMF (50 ml) was added dropwise. The reaction mixture became cloudy orange, was stirred for 15 min at 0°C, and was allowed to warm to

ambient temperature over 3.5 h. The reaction mixture was quenched by addition of H_2O (200 ml) and 1N HCl (200 ml). The crude product was isolated by filtration and washed with methanol to afford an olive powder; yield 3.93 g (47%). ^{1}H NMR (400 MHz, d_6-DMSO): δ 6.77 (d, $J=7.87$ Hz, 4H), 7.08 (d, $J=16.37$ Hz, 2H), 7.15 (d, $J=16.29$ Hz, 2H), 7.51 (s, 4H), 9.60 (s, 2H). ^{13}C NMR (101 MHz, d_6-DMSO): δ 115.56, 124.82, 126.34, 127.82, 128.04, 128.18, 136.28, 157.28. IR (cm^{-1}): 3386, 3014, 1603, 1592, 1515, 1446, 1376, 1247, 1173, 1104, 961, 834. Anal: calcd for $C_{22}H_{18}O_2$, C 84.05, H 5.77; found, C 83.87, H 5.92%.

2.2.16. *Non-methoxy core hexacatenar acrylate monomer **5a***

This compound was synthesized from 3,4,5-tris[6-(acryloyloxy)hexyloxy)benzoic acid and (*E*,*E*)-1,4-bis[2-(4-hydroxyphenyl)ethenyl]benzene by the procedure used for homologues of **2**. (Chromatography: 70/30 hexanes/ethyl acetate); yield 0.43 g (59%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.43 (m, 12H), 1.47 (m, 12H), 1.72 (m, 12H), 1.74 (m, 4H), 1.86 (m, 8H), 4.06 (t, $J=6.7$ Hz, 12H), 4.17 (t, $J=6.7$ Hz, 12H), 5.81 (dd, $J=10.4$, 1.5 Hz, 6H), 6.12 (dd, $J=17.3$, 10.4 Hz, 6H), 6.40 (dd, $J=17.3$, 1.5 Hz, 6H), 7.09 (d, $J=16.3$ Hz, 2H), 7.15 (d, $J=16.2$ Hz, 2H), 7.20 (d, $J=8.6$ Hz, 4H), 7.42 (s, 4H), 7.52 (s, 4H) 7.58 (d, $J=8.7$ Hz, 4H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 25.66, 25.69, 25.76, 28.55, 28.60, 29.13, 30.13, 64.41, 64.51, 69.05, 73.26, 108.65, 121.96, 123.97, 126.83, 127.43, 127.62, 128.47, 128.56, 130.38, 135.12, 136.62, 142.91, 150.41, 152.84, 164.85, 166.20. IR (cm^{-1}): 2940, 2862, 1724, 1684, 1636, 1617, 1586, 1558, 1506, 1472, 1457, 1430, 1408, 1336, 1296, 1273, 1192, 1120, 1061, 984, 965, 858, 811. Anal: calcd for $C_{90}H_{110}O_{22}$, C 70.02, H 7.18; found, C 69.95, H 6.98%.

2.2.17. *Non-methoxy core hexacatenar acrylate monomer **5b***

This compound was synthesized from 3,4,5-tris[11-(acryloyloxy)undecyloxy]benzoic acid and (*E*,*E*)-1,4-bis[2-(4-hydroxyphenyl)ethenyl]benzene (**12**) by the procedure used for homologues of **2**. (Chromatography: 70/30 hexanes/ethyl acetate and recrystallized from ethyl acetate); yield 0.23 g (37%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.30 (m, 72H), 1.49 (m, 12H), 1.66 (m, 12H), 1.76 (m, 4H), 1.84 (m, 8H), 4.05 (m, 12H), 4.15 (t, $J=6.7$ Hz, 12H), 5.81 (dd, $J=10.4$, 1.5 Hz, 6H), 6.12 (dd, $J=17.3$, 10.5 Hz, 6H), 6.39 (dd, $J=17.3$, 1.5 Hz, 6H), 7.09 (d, $J=16.2$ Hz, 2H), 7.15 (d, $J=16.4$ Hz, 2H), 7.20 (d, $J=8.4$ Hz, 4H), 7.41 (s, 4H), 7.53 (s, 4H) 7.58 (d, $J=8.6$ Hz, 4H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 25.88, 25.90, 26.00, 28.57, 29.20, 29.24, 29.31, 29.45, 29.52, 29.54, 29.62, 30.27, 30.83, 64.63, 69.25, 73.51, 108.63, 121.98, 123.83, 126.82, 127.41, 127.63, 128.44, 128.62, 130.28, 135.09, 136.62, 144.45, 150.45, 152.92, 164.93, 166.25. IR (cm^{-1}): 2919, 2850, 1727, 1635, 1585, 1504, 1467, 1430, 1408, 1386, 1338, 1295, 1271, 1192, 1121, 979, 964, 854, 809. Anal: calcd for $C_{120}H_{170}O_{22}$, C 73.36, H 8.72; found, C 73.19, H 8.51%.

2.2.18. *Non-methoxy core hexacatenar isoprene monomer **6***

This compound was synthesized from 3,4,5-tris[12-(methenyl)-13-tetradecenyloxy]benzoic acid and (*E*,*E*)-1,4-bis[2-(4-hydroxyphenyl)ethenyl]benzene by the procedure used for homologues of **2**. (Chromatography: 91/9 hexanes/ethyl acetate); yield 0.62 g (59%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.30 (m, 72H), 1.49 (m, 24H), 1.84 (m, 12H), 2.20 (t, $J=7.7$ Hz, 12H), 4.06 (m, 12H), 4.98 (s, 6H), 5.00 (s, 6H), 5.05 (d, $J=10.8$ Hz, 6H), 5.23 (d, $J=17.6$ Hz, 6H), 6.37 (dd, $J=17.6$, 10.8 Hz, 6H), 7.09 (d, $J=16.3$ Hz, 2H), 7.16 (d, $J=16.3$ Hz, 2H), 7.21 (d, $J=8.54$ Hz, 4H), 7.42 (s, 4H), 7.53 (s, 4H), 7.58 (d, $J=8.70$ Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 26.29, 28.38, 29.51, 29.60, 29.76, 29.80, 29.84, 29.91, 30.56, 31.57, 69.48, 73.78, 108.80, 113.23, 115.64, 122.25, 124.06, 127.08, 127.68, 128.68, 135.33, 136.85, 139.25, 143.25, 146.82, 150.69, 153.18, 165.21. IR (cm^{-1}): 3088, 3005, 2924, 2852, 1732, 1635, 1594, 1502, 1467, 1430, 1386, 1336, 1192, 1165, 1121, 1014, 990, 962, 892, 754. Anal: calcd for $C_{126}H_{182}O_{10}$, C 81.50, H 9.88; found, C 81.43, H 10.01%.

2.2.19. *9-Bromo-1,3-nonadiene*

This compound was synthesized as described previously [27].

2.2.20. *3,4,5-Tris(6,8-nonadienyloxy)benzoic acid*

This compound was synthesized from 9-bromo-1,3-nonadiene and methyl gallate by the procedure described in the literature for 3,4,5-tris(9,11-dodecadienyloxy)benzoic acid and 3,4,5-tris(11,13-tetradecadienyloxy)benzoic acid [27]; yield 0.78 g (60%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.50 (m, 12H), 1.72 (m, 2H), 1.84 (m, 4H), 2.13 (m, 6H), 4.03 (m, 6H), 4.96 (d, $J=10.1$ Hz, 3H), 5.09 (d, $J=16.9$ Hz, 3H), 5.71 (dt, $J=15.1$, 6.8 Hz, 3H), 6.06 (dd, $J=14.8$, 10.8 Hz, 3H), 6.31 (ddd, $J=17.0$, 10.5, 10.1 Hz, 3H), 7.33 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 25.82, 29.07, 29.23, 29.27, 30.32, 32.66, 32.75, 69.18, 73.53, 108.66, 114.95, 115.04, 123.91, 131.19, 131.34, 135.23, 135.46, 137.41, 137.47, 143.16, 152.95, 172.16. IR (cm^{-1}): 3084, 3008, 2943, 2847, 1684, 1651, 1600, 1585, 1505, 1467, 1431, 1384,

1335, 1276, 1223, 1150, 1125, 1003, 972, 955, 898, 862, 767. Anal: calcd for $C_{34}H_{48}O_5$, C 76.08, H 9.01; found, C 75.98, H 9.40%.

2.2.21. *Non-methoxy core hexacatenar 1,3-diene monomer **7a***

This compound was synthesized from 3,4,5-tris(6,8-nonadienyloxy)benzoic acid and (*E*,*E*)-1,4-bis[2-(4-hydroxyphenyl)ethenyl]benzene by the procedure used for homologues of **2**. (Chromatography: 85/15 hexanes/ethyl acetate); yield 0.36 g (52%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.51 (m, 24H), 1.77 (m, 4H), 1.85 (m, 8H), 2.12 (m, 12H), 4.06 (m, 12H), 4.96 (d, $J=10.0$ Hz, 6H), 5.09 (d, $J=16.8$ Hz, 6H), 5.72 (dt, $J=15.1$, 6.4 Hz, 6H), 6.06 (dd, $J=15.4$, 10.4 Hz, 6H), 6.31 (ddd, $J=16.8$, 10.4, 10.0 Hz, 6H), 7.09 (d, $J=16.2$ Hz, 2H), 7.16 (d, $J=16.2$ Hz, 2H), 7.20 (d, $J=8.6$ Hz, 4H), 7.41 (s, 4H), 7.53 (s, 4H), 7.58 (d, $J=8.7$ Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 25.83, 29.07, 29.24, 29.31, 30.35, 32.66, 32.75, 69.29, 73.56, 108.73, 114.95, 115.04, 122.23, 124.12, 127.06, 127.67, 127.84, 128.66, 131.21, 131.35, 135.21, 135.31, 135.45, 136.82, 137.41, 137.47, 143.07, 150.63, 153.09, 165.15. IR (cm^{-1}): 3083, 3034, 3005, 2934, 2856, 1730, 1652, 1585, 1501, 1461, 1430, 1386, 1336, 1191, 1165, 1119, 1002, 952, 897, 856, 818, 754. Anal: calcd for $C_{90}H_{110}O_{10}$, C 79.96, H 8.20; found, C 80.12, H 8.53%.

2.2.22. *Non-methoxy core hexacatenar 1,3-diene monomer **7b***

This compound was synthesized from 3,4,5-tris(9,11-dodecadienyloxy)benzoic acid and (*E*,*E*)-1,4-bis[2-(4-hydroxyphenyl)ethenyl]benzene by the procedure used for homologues of **2**. (Chromatography: 85/15 hexanes/ethyl acetate); yield 0.26 g (63%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.36 (m, 48H), 1.52 (m, 12H), 1.86 (m, 12H), 2.10 (m, 12H), 4.08 (m, 12H), 4.97 (d, $J=10.0$ Hz, 6H), 5.11 (d, $J=16.8$ Hz, 6H), 5.72 (dt, $J=15.1$, 6.8 Hz, 6H), 6.06 (dd, $J=15.1$, 10.5 Hz, 6H), 6.31 (ddd, $J=16.9$, 10.4, 10.0 Hz, 6H), 7.10 (d, $J=16.2$ Hz, 2H), 7.16 (d, $J=16.3$ Hz, 2H), 7.23 (d, $J=8.3$ Hz, 4H), 7.45 (s, 4H), 7.53 (s, 4H), 7.58 (d, $J=8.5$ Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 26.20, 27.89, 29.33, 29.40, 29.42, 29.46, 29.60, 29.63, 29.70, 30.49, 32.70, 32.72, 69.34, 73.66, 108.67, 114.77, 122.18, 124.01, 127.01, 127.62, 127.76, 128.59, 131.05, 135.25, 135.63, 136.76, 137.48, 143.11, 150.60, 153.09, 165.10. IR (cm^{-1}): 3084, 3034, 3007, 2922, 2850, 1734, 1652, 1586, 1514, 1504, 1466, 1430, 1385, 1336, 1221, 1198, 1166, 1127, 1097, 1002, 964, 950, 898, 857, 812, 748. Anal: calcd for $C_{108}H_{146}O_{10}$, C 80.85, H 9.17; found, C 80.69, H 9.46%.

2.2.23. *Non-methoxy core hexacatenar 1,3-diene monomer **7c***

This compound was synthesized from 3,4,5-tris(11,13-tetradecadienyloxy)benzoic acid and (*E*,*E*)-1,4-bis[2-(4-hydroxyphenyl)ethenyl]benzene by the procedure used for homologues of **2**. (Chromatography: 88/12 hexanes/ethyl acetate); yield 0.41 g (61%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.30 (m, 72H), 1.50 (m, 12H), 1.78 (m, 4H), 1.85 (m, 8H), 2.09 (m, 12H), 4.06 (m, 12H), 4.96 (d, $J=10.1$ Hz, 6H), 5.10 (d, $J=16.9$ Hz, 6H), 5.72 (dt, $J=15.1$, 6.9 Hz, 6H), 6.06 (dd, $J=15.1$, 10.5 Hz, 6H), 6.31 (ddd, $J=16.7$, 10.5, 10.1 Hz, 6H), 7.10 (d, $J=16.2$ Hz, 2H), 7.16 (d, $J=16.3$ Hz, 2H), 7.22 (d, $J=8.4$ Hz, 4H), 7.44 (s, 4H), 7.53 (s, 4H), 7.59 (d, $J=8.7$ Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 26.21, 27.86, 29.33, 29.37, 29.41, 29.43, 29.52, 29.65, 29.70, 29.75, 29.79, 29.86, 30.50, 32.70, 69.32, 73.64, 108.64, 114.70, 122.14, 123.99, 126.98, 127.58, 127.72, 128.56, 131.01, 135.20, 135.61, 136.72, 137.47, 143.11, 150.59, 153.08, 165.03. IR (cm^{-1}): 3084, 3034, 3007, 2922, 2850, 1734, 1652, 1586, 1514, 1504, 1466, 1430, 1385, 1336, 1221, 1198, 1166, 1127, 1097, 1002, 964, 950, 898, 857, 812, 748. Anal: calcd for $C_{120}H_{170}O_{10}$, C 81.31, H 9.67; found, C 80.98, H 9.22%.

2.2.24. *Non-methoxy core hexacatenar mesogen **8***

This model compound was prepared from the coupling of two equivalents of 3,4,5-tris(decyloxy)benzoic acid [17] with one equivalent of (*E*,*E*)-1,4-bis[2-(4-hydroxyphenyl)-ethenyl]benzene using the same protocols outlined for the synthesis of homologues of **2**. (Recrystallized from hexanes/ethyl acetate); yield 0.65 g (69%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (m, 18H), 1.28 (m, 72H), 1.49 (m, 12H), 1.76 (m, 4H), 1.84 (m, 8H), 4.06 (m, 12H), 7.09 (d, $J=16.23$ Hz, 2H), 7.16 (d, $J=16.35$ Hz, 2H), 7.20 (d, $J=8.56$ Hz, 4H), 7.41 (s, 4H), 7.53 (s, 4H), 7.58 (d, $J=8.66$ Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 14.33, 22.91, 26.31, 29.53, 29.57, 29.62, 29.81, 29.86, 29.90, 29.96, 30.58, 32.14, 32.17, 69.51, 73.82, 108.83, 122.27, 124.07, 127.10, 127.69, 127.91, 128.69, 135.34, 136.88, 143.30, 150.72, 153.20, 165.23. IR (cm^{-1}): 3025, 2930, 2856, 1734, 1585, 1502, 1467, 1430, 1385, 1336, 1194, 1164, 1116, 1098, 1016, 964, 921, 856, 750. Anal: calcd for $C_{96}H_{146}O_{10}$, C 78.97, H 10.07; found; C 79.13, H 10.18%.

2.3. *Polymerization methods*

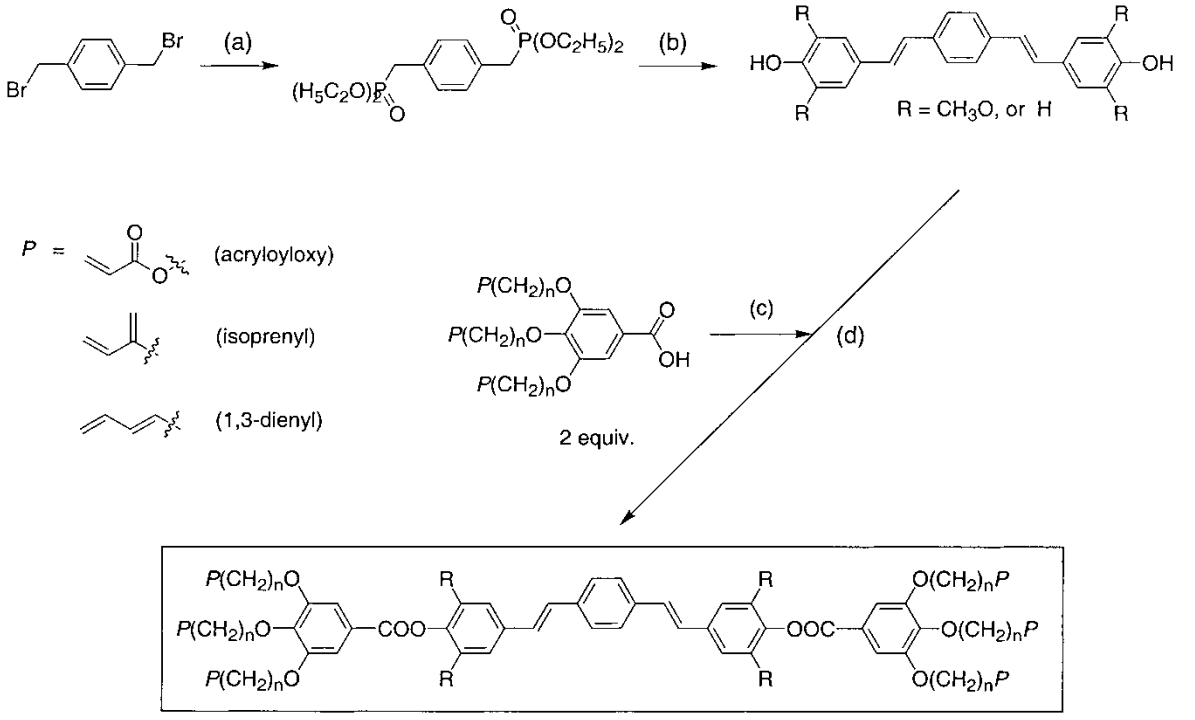
For hexacatenar LC monomers **6** and **7b**, each monomer was dissolved in CH_2Cl_2 and mixed with either 1.5 mol% of 2,2-dimethoxy-2-phenylacetophenone or 1.5 mol% of 2,2′-azobisisobutyronitrile (AIBN). The volatile components were removed *in vacuo* affording the initiator-doped solid state mixture. For

photopolymerization experiments on **7b** and subsequent control experiments using **8**, thin films were cast on glass slides and exposed to UV light (intensity $2.2\,mW\,cm^{-2}$ at 365 nm) through a quartz window in the Linkam THMSE 600 hot stage under a N_2 flush at the appropriate temperatures. For thermally initiated polymerizations, thin films suitable for FTIR analysis were cast on KBr plates, heated to 80°C, and immediately cooled to the appropriate mesophase temperature (53°C for **6** and 66°C for **7b**) on the N_2-flushed Linkam THMSE 600 hot stage. Average values for extent of polymerization by IR were obtained from three separate films of **6** and **7b**. XRD profiles of the resulting crosslinked films were obtained at ambient temperature with flat pan sample holders on the Inel CPS 120 powder XRD system.

3. Results and discussion

3.1. *Emissive hexacatenar LC monomer design and synthesis*

Our general design for crosslinkable analogues of luminescent hexacatenar mesogen **1** is presented in scheme 1. A symmetric target monomer containing six radically polymerizable tail units (i.e. activated olefins) is the preferred design for several reasons. First, the attachment of six identical reactive tails would be the simplest from a synthesis perspective. Second, six reactive groups per monomer capable of chain-addition polymerization would be more than adequate to attain a highly crosslinked system even at relatively low degrees of conversion [29]. For example, if only an average of two polymerizable groups per hexacatenar molecule react, the resultant network would be identical



2a: R = OCH_3; n = 6; *P* = acryloyloxy
2b: R = OCH_3; n = 11; *P* = acryloyloxy

3a: R = OCH_3; n = 6; *P* = isoprenyl
3b: R = OCH_3; n = 11; *P* = isoprenyl

4a: R = OCH_3; n = 8; *P* = 1,3-dienyl
4b: R = OCH_3; n = 10; *P* = 1,3-dienyl

5a: R = H; n = 6; *P* = acryloyloxy
5b: R = H; n = 11; *P* = acryloyloxy

6: R = H; n = 11; *P* = isoprenyl

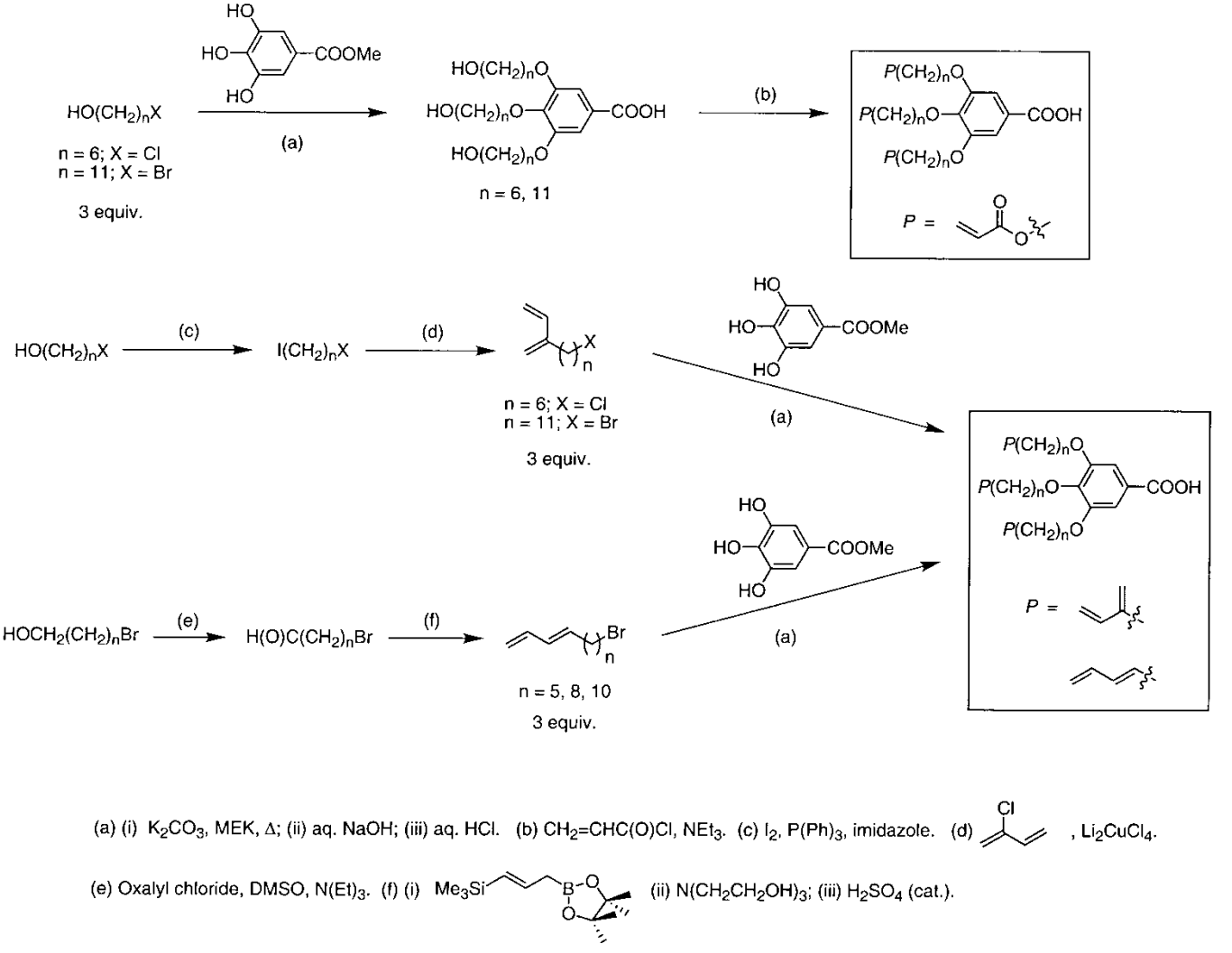
7a: R = H; n = 5; *P* = 1,3-dienyl
7b: R = H; n = 8; *P* = 1,3-dienyl
7c: R = H; n = 10; *P* = 1,3-dienyl

(a) $P(OEt)_3$, Δ. (b) (i) *t*-BuOK; (ii) 2 equiv. syringaldehyde or 4-hydroxybenzaldehyde. (c) $SOCl_2$, Δ. (d) NEt_3, Δ.

Scheme 1. General synthetic route to crosslinkable hexacatenar derivatives containing emissive oligo(*p*-phenylenevinylene) cores.

to that of a bifunctional monomer that is 100% crosslinked. Radical polymerizable moieties are the reactive groups of choice for these hexacatenar monomers because such groups are commonly employed in the design of crosslinkable rod-like LCs [30], and radical polymerization is more tolerant of organic functional groups than are other chain polymerization methods [29]. The polymerizable groups are appended at the end of the *n*-alkoxy chains in order to minimize interference with the core packing and mesophase formation [31, 32].

The general synthesis scheme for generating polymerizable analogues of **1** is also outlined in scheme 1. The photoactive (*E*,*E*)-1,4-bis[2-(4-hydroxyphenyl)ethenyl]-benzene-based central core was first synthesized via an Arbuzov reaction of α,α′-dibromo-*p*-xylene with triethyl phosphite to yield a bis(phosphonate), followed by reaction of the bis(phosphonate) with 5.25 equiv. of sodium *t*-butoxide and the appropriate 4-hydroxybenzaldehyde derivative in a Horner–Emmons reaction. The core was then coupled to two polymerizable 3,4,5-tris(*n*-alkoxy)-benzoic acid derivatives in their acyl chloride forms. The different polymerizable 3,4,5-tris(*n*-alkoxy)benzoic acid derivatives were prepared as outlined in scheme 2. The 3,4,5-tris(ω-acryloxy)benzoic acid derivatives were synthesized under Williamson ether synthesis conditions by reacting methyl gallate with an excess of the ω-bromoalkan-1-ols in the presence of potassium carbonate, followed by reaction with acryloyl chloride to introduce the acrylate end groups [24]. The 3,4,5-tris(*n*-alkoxy)benzoic acid derivatives containing isoprenyl and 1,3-dienyl tails were synthesized by reacting methyl gallate directly with an excess of the ω-bromo derivatives of the isoprenyl and 1,3-dienyl



Scheme 2. Preparation of different polymerizable derivatives of 3,4,5-tris(*n*-alkoxy)benzoic acids for the construction of crosslinkable hexacatenar LC derivatives.

tail systems in the presence of potassium carbonate. The ω-bromoisoprenyl tails were prepared by converting commercially available ω-chloroalkan-1-ols or 11-ω-bromoalkan-1-ols to the corresponding α,ω-haloiodoalkanes in excellent yields using triphenylphosphine and iodine [33]. Copper-mediated coupling of the Grignard reagent 2-(1,3-butadienyl)magnesium chloride with the haloiodoalkanes occurred preferentially at the iodocarbon at −78°C to afford the desired ω-bromoisoprenyl tails [34]. The ω-bromoalkyl-1,3-diene tails were synthesized from α,ω-haloalkanols according to literature procedures [27].

3.2. *LC behaviour of crosslinkable hexacatenar compounds*

Initial attempts at developing crosslinkable analogues of **1** focused on hexa(acrylate) derivatives. The primary reason for this choice was that the acrylate moiety is the most frequently employed polymerizable group in polymerizable thermotropic LCs, due to their facile synthesis and efficient photopolymerization [30]. In order to gauge the effect of acrylate groups on the mesogenic properties of **1**, two homologous hexa(acrylate) derivatives with two different tail lengths (**2a**, $n=6$ and **2b**, $n=11$) were synthesized according to schemes 1 and 2. Unfortunately, both **2a** and **2b** exhibited no LC transitions when analysed by DSC and POM. Instead, they simply melted from a polycrystalline state to an isotropic phase at 31 and 35°C, respectively. Similar phase disruption effects have been observed when comparing acrylate derivatives of rod-like organic mesogens and discotic metallomesogens with their nonpolymerizable analogues [35–40]. This destabilizing effect may be attributed to the branching structure and/or the dipolar interactions near the end of the acrylate tails, both of which are absent in the parent *n*-alkoxy mesogens **1**.

Derivatives of **1** containing isoprenyl tails were subsequently synthesized in order to eliminate the dipolar interactions and isolate the effect of tail end branching on mesogenic behaviour. The isoprenyl unit is structurally similar to the acrylate group but lacks the polar ester functionality. Two hexa(isoprenyl) derivatives with different tail lengths (**3a**, $n=6$ and **3b**, $n=11$) were synthesized to determine the effect of isoprenyl groups on mesogenic behaviour. Unfortunately, both **3a** and **3b** also exhibited no appreciable LC behaviour. After initial melting (**3a** at 44 and **3b** at 53°C), these materials maintained the isotropic phase as seen by POM and DSC analysis. Even in the absence of a polar ester group, the steric demands of the branched isoprenyl end groups apparently still disrupt chain packing and prevent formation of a stable LC phase in this hexacatenar platform.

In order to eliminate the undesirable effects of both terminal tail branching and polar interactions (while retaining good radical polymerization activity), two derivatives of **1** containing linear alkyl-1,3-diene tails (**4a**, $n=8$ and **4b**, $n=10$) were synthesized and studied. As in the case of the two previous sets of polymerizable hexacatenar derivatives, **4a** and **4b** also exhibited no appreciable mesogenic properties Compounds **4a** and **4b** exhibited melting points of 53 and 60°C respectively, and cooled into an isotropic glass. These initial results underscore the importance of the van der Waals interactions of the alkyl chains in enhancing thermotropic LC behaviour. In addition to polarity and branching, unsaturation in the tails can also greatly diminish these interactions [40, 41].

If crosslinkable derivatives of **1** with intrinsic LC properties are to be generated, other intermolecular interactions in the molecule must compensate for those lost by affixing terminal polymerizable groups onto the tails. One possible avenue for accomplishing this goal is removal of the four methoxy sidegroups from the conjugated central core. The resulting 'non-methoxy' core should increase the ability of the hexacatenar molecules to pack together and order. To test this supposition, three different sets of crosslinkable derivatives containing acryloyloxy, isoprenyl, and 1,3-dienyl groups were subsequently synthesized but with an oligo(*p*-phenylenevinylene) core lacking the four methoxy sidegroups. These three sets of monomers (series **5**, **6**, and **7**) were prepared using the same procedures used to produce **2**, **3** and **4**, except that (*E*,*E*)-1,4-bis[2-(4-hydroxyphenyl)ethenyl]benzene was used as the central core instead of (*E*,*E*)-1,4-bis[2-(3,5-dimethoxy-4-hydroxyphenyl)ethenyl]benzene (see schemes 1 and 2). The thermotropic LC behaviour of homologues of **5**, **6**, and **7** was investigated by POM, DSC and powder XRD; the results are summarized in the table.

As can be seen in the table, only the isoprenyl (**6**) and 1,3-dienyl (**7a**–**c**) derivatives with the unsubstituted core exhibited LC behaviour, as determined by POM, DSC, and XRD. The more polar hexa(acrylate) derivatives **5a** and **5b** showed no mesogenic behaviour, although they did exhibit reproducible melting and crystallization transitions. Such behaviour again illustrates the destabilizing effect of the acrylate group on LC formation in this particular hexacatenar platform. In general, compounds **5**, **6**, and **7** exhibited considerably higher melting points than the corresponding monomers **2**, **3**, and **4** containing the tetramethoxy core (20–30°C higher). These results demonstrate the greater ability of the unsubstituted oligo(*p*-phenylenevinylene) core to pack and aggregate.

The non-methoxy core hexa(1,3-diene) derivatives **7a** and **7b** exhibited the most interesting LC behaviour.

Table. Physical properties of crosslinkable analogues of **1** containing a non-methoxy core Cr = crystal, Φ_h = columnar hexagonal phase, I = isotropic phase. [H] = heating run, [C] = cooling run, n/a = not applicable, [P] = transition observed by POM. Ramp rates of 1.0°C min^{-1}.

	DSC			X-ray diffraction			
Compound	Transition	T/°C	ΔH/kJ mol^{-1}	T/°C	Lattice constant (a)/Å	d-spacing obs.(calc.)/Å	Miller indices
5a	Cr→I$^{[H]}$	56.4	27.5				
	I→Cr$^{[C]}$	38.9	−28.9				
5b	Cr→I$^{[H]}$	69.6	131.4				
	I→Cr$^{[C]}$	58.4	−138.6				
6	Φ_h→Cr$^{[H]}$	40.9	−23.6	53	47.3	40.3 (41.0)	(1 0 0)
	Cr→$\Phi_h^{[H]}$	52.8	20.4			24.1 (23.7)	(1 1 0)
	Φ_h→I$^{[H]}$	57.4	0.5				
	I→$\Phi_h^{[C]}$	53.6	−0.9				
7a	Φ_h→I$^{[H]}$	60.6$^{[P]}$	n/a	27	40.3	34.3 (34.9)	(1 0 0)
	I→$\Phi_h^{[C]}$	58.0$^{[P]}$	n/a			20.3 (20.1)	(1 1 0)
						17.6 (17.4)	(2 0 0)
7b	Cr→$\Phi_h^{[H]}$	65.1	30.9	66	46.1	38.2 (39.8)	(1 0 0)
	Φ_h→I$^{[H]}$	72.0$^{[P]}$	n/a			23.0 (23.0)	(1 1 0)
	I→$\Phi_h^{[C]}$	67.6	−2.1				
	Φ_h→Cr$^{[C]}$	44.9	−22.0				
7c	Cr→I$^{[H]}$	77.9	65.0				
	I→Cr$^{[C]}$	61.1	−69.6				

XRD analysis was the primary phase characterisation tool for these compounds because their LC phases exhibited only finely grained but colourful optical textures that unfortunately were not very helpful in identifying the LC phases. The individual domains in the observed optical textures did however exhibit good fluid flow under applied pressure, so the samples are definitely LC in nature and not polycrystalline. Using XRD, compound **7b** ($n = 8$) was found to exhibit a fairly well-defined Φ_h phase. The XRD profile observed for **7b** has two d-spacings that match the expected ratio of $1{:}1/\sqrt{3}{:}1/\sqrt{4}{:}1/\sqrt{7}\ldots$ (i.e. the d_{100}, d_{110}, d_{200}, $d_{210\ldots}$ diffraction planes) for a two-dimensional hexagonal array of cylinders [17]. The observed d-spacings for **7b** are consistent with a Φ_h phase with a hexagonal unit cell lattice spacing of 47.3 Å. In contrast, the longer tail non-methoxy diene homologue **7c** ($n = 10$) only showed a crystalline to isotropic phase transition. However, decreasing the overall tail length from twelve to nine carbons generated a surprising result. Upon cooling from the isotropic melt, **7a** ($n = 5$) formed a LC phase at 58°C, persisting down to 25°C. The enthalpy of this LC transition was too weak to be measured by DSC, but XRD analysis of **7a** confirmed the presence of a well defined Φ_h phase with three d-spacings that proceed in the ratio $1{:}1/\sqrt{3}{:}1/\sqrt{4}$ at ambient temperature (figure 2). The temporal stability of this ambient temperature Φ_h phase is quite limited, however. It reverts to the polycrystalline state over the course of a few hours at room temperature.

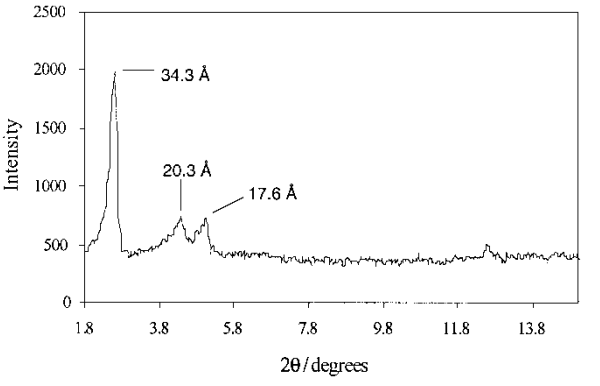


Figure 2. XRD profile of the Φ_h phase of **7a** upon cooling from the isotropic melt to 25°C.

The only non-methoxy hexa(isoprenyl) test compound synthesized, **6** ($n = 11$), exhibited LC behaviour similar to that of **7b**. Upon cooling from the isotropic melt, a somewhat uninformative grainy optical texture similar to that observed for **7b** appeared. Compound **6** also tends to supercool into the Φ_h phase. The clearing point of **6** was lower than **7b** by 15°C, and the enthalpy change was also slightly smaller (−0.9 vs. −2.1 kJ mol^{-1}). However, the XRD profiles of **6** and **7b** are similar, with intense d_{100} peaks; broad and somewhat coalesced d_{110} and d_{200} peaks; and approximately the same calculated Φ_h lattice constant.

3.3. *Crosslinking studies in the LC state*

In order to examine the effect of mesogenic order and luminescence properties on the polymerization behaviour of these emissive hexacatenar LC monomers, preliminary photo- and thermally-initiated cross-linking studies were performed on representative hexacatenar compounds. Initial photopolymerization studies were performed on monomer **7b** ($n=8$). Photoinitiated cross-linking of **7b** in the Φ_h phase was conducted using the microscope heating stage (accuracy: $\pm 0.1^{\circ}C$) and monitored by POM. The photopolymerization samples were prepared by mixing **7b** with 1.5 mol% of 2,2-dimethoxy-2-phenylacetophenone (a radical photoinitiator), annealing the mixture above its melting point at 66°C for 30 min, and then cooling the sample into the desired LC phase. The observed mosaic optical texture confirmed the presence of the Φ_h phase, and the film was exposed to UV light (intensity 2.2 mW cm^{-2} at 365 nm) for 1 h. After UV irradiation, it was observed by POM that the LC optical texture had disappeared. Extraction of the polymerized sample with various organic solvents, such as THF and chloroform, did not liberate any soluble components. Thus, the film was effectively crosslinked but with loss of the LC microstructure.

The loss of anisotropy during photopolymerization of **7b** can be rationalized in two different ways. First, a photochemical reaction of the oligo(*p*-phenylenevinylene) core or diene moiety may have occurred to alter the structure/shape of the hexacatenar LC substantially and consequently its mesogenic behaviour. Alternatively, excessive crosslinking may have disrupted the Φ_h phase. Most crosslinkable thermotropic LCs possess only two polymerizable groups per mesogen [30], and a slight contraction of the lattice spacing is associated with the crosslinking of these systems [42]. However, **7b** has six reactive groups per molecule; and as more covalent bonds are generated, the LC phase may be adversely affected by more extensive volume contraction during polymerization.

In order to determine whether a detrimental photochemical reaction was the cause of the loss of LC order during polymerization, a control experiment was performed using a mixture of compound **8**, a non-polymerizable non-methoxy model LC that exhibits the Φ_h phase between 78 and 114°C (figure 3); (*E*)-1,3-octadiene (10 equiv.); and photoinitiator, to ascertain the tolerance of the different functional groups in the system to the irradiation conditions. After exposing the control mixture to UV light (2.2 mW cm^{-2} at 365 nm) at ambient temperature for 3 h, the mixture remained highly luminescent, suggesting that the conjugated core was unaffected by UV light and radicals at room temperature. Subsequently, the temperature was raised to 75°C to reproduce the actual polymerization conditions of **7b** in the Φ_h phase, and the control sample was irradiated for an additional 4 h. This irradiation at elevated temperature resulted in a substantial yellowing of the mixture, and diminished emission intensity that was obvious to the naked eye. The resulting material was extracted with $CDCl_3$, and the soluble components were analysed by ^{1}H NMR spectroscopy. The 6.0–8.0 ppm region showed substantial decomposition of the oligo(*p*-phenylenevinylene) core, and definitive ^{1}H NMR peaks could not be identified. Components of the mixture were then systematically omitted to ascertain which factors were primarily responsible for the degradation of the oligo(*p*-phenylenevinylene) core. In subsequent irradiation control experiments, the photoinitiator was first omitted, and then the samples of **8** and (*E*)-1,3-octadiene were irradiated in the crystalline state (25°C) for 3 h and in the Φ_h phase (95°C) for 30 min. Fluorescence measurements showed that the emission intensity decreased substantially only when the samples were irradiated in the fluid ordered LC state, but not the crystalline state, even in the absence of radicals (figure 4). These results, coupled with the solvent extraction results, indicate that the non-methoxy oligo(*p*-phenylenevinylene) core is susceptible to photodegradation processes in the LC state at elevated temperatures.

In order to circumvent photodegradation in the LC state, thermally initiated radical polymerization was employed as an alternative crosslinking mechanism. 2,2′-Azobis(isobutyronitrile) (AIBN) is generally employed as

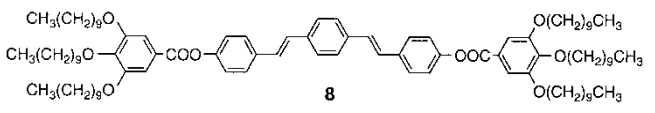


Figure 3. Structure of non-methoxy core, hexacatenar model mesogen **8**.

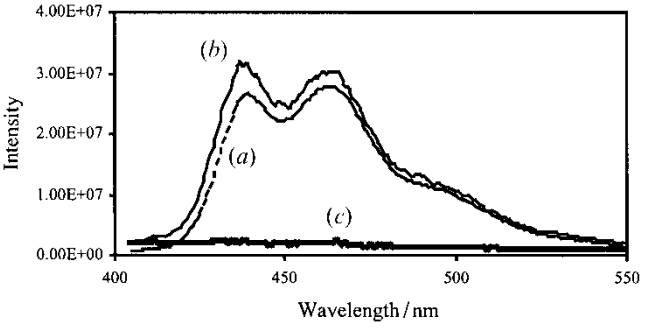


Figure 4. Emission spectra of 8: (*a*) before irradiation; (*b*) after irradiation for 3 h in the crystalline phase at 25°C; (*c*) after irradiation for an additional 0.5 h in the Φ_h phase at 95°C. Irradiation at 365 nm; all emission spectra taken at ambient temperature.

a thermal initiator for radical polymerizations between 50 and 70°C [29], making it an ideal candidate to initiate polymerization near the LC temperature regimes of the hexacatenar monomers. Consequently, test reactions on **6** and **7b** in the presence of AIBN were performed to determine whether radical crosslinking with retention of both LC order and emission properties is possible. For the thermal polymerization studies, films of **6** and **7b** containing 1.5 mol% AIBN were prepared on glass slides, heated above their clearing points to 75°C, and then cooled into their respective Φ_h ranges (53°C for **6**; 66°C for **7b**). Each film was maintained at these temperatures overnight (8 h for **6** and 14 h for **7b**) under a N_2 atmosphere and in the absence of light. The resulting films were then analysed to determine the effectiveness of thermally initiated radical polymerization. After overnight thermal polymerization, the optical textures of **6** and **7b** were virtually identical to those of the initial monomers in the Φ_h phase, indicating that phase microstructure was retained. When resulting films were raised to 100°C (well above the clearing points of **6** and **7b**), the optical textures of the samples remained unchanged, consistent with extensive crosslinking and retention of the Φ_h order. The absence of any discernible phase transitions in the polymerized samples by DSC also supports this supposition. XRD analysis revealed that the Φ_h structure of **6** and **7b** after thermal radical polymerization (figure 5) undergoes only a minor contraction of the hexagonal unit cell, compared with the monomeric LC phase. Unfortunately, secondary XRD peaks could be only barely resolved in the polymerized samples.

The extent of polymerization in the resulting insoluble materials was estimated by FTIR spectroscopy to be approximately 23% for the 1,3-diene system and *c.* 14% for the isoprene system. Monosubstituted 1,3-dienes such as 1,3-pentadiene have two characteristic IR bands near 1650 and 1600 cm^{-1} which are attributed to the symmetric and asymmetric stretches of one of the carbon–carbon double bonds the characteristic spectroscopic changes observed upon polymerization of 1,3-pentadiene were used as the basis of analysis for the polymerization of the 1,3-diene tail systems [43]. Utilizing the strong carbonyl stretch at 1734 cm^{-1} as an internal standard, the absorption intensities of the 1650 cm^{-1} band of **7b** were compared before and after polymerization to estimate the extent of conversion using Beer's Law. The extent of polymerization for overnight thermal polymerization of **7b** at 66°C was estimated to be $23 \pm 9\%$. Because of the numerous polymerization modes possible with 1,3-diene-based moieties (i.e. 1,4-addition, 1,2-addition, or 3,4-addition), it is difficult to gauge an accurate degree of polymerization from the carbon–hydrogen wagging bands.

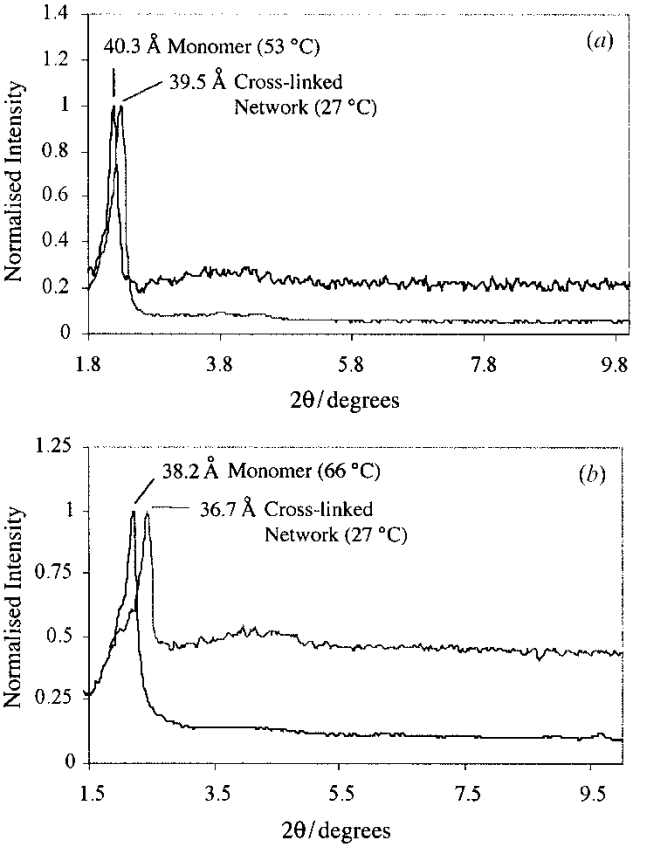


Figure 5. XRD profiles of the unpolymerized and crosslinked Φ_h phases of (*a*) compound **6** and (*b*) compound **7b**.

Similarly, the extent of thermal radical polymerization of **6** was estimated to be $14 \pm 4\%$ by monitoring the decrease of one of the carbon–carbon double bond stretching bands for isoprene at approximately 1630 cm^{-1}. Although these degrees of conversion are relatively low, extensively stabilized crosslinked structures are still achieved. For the chain-addition polymerization of a monomer containing two chain-polymerizable groups, an extent of conversion greater than 5% is typically needed to reach the gel point [30]. In the case of our hexacatenar monomers with six polymerizable groups per molecule, the degree of conversion needed to reach the gel point of the system should be even lower [30]. Since the rigidity of crosslinked networks increases dramatically as crosslinking progresses and segmental chain movement becomes more hindered, very high extents of polymerization for these highly functionalized monomers would not be expected.

3.4. *Effect of cross-linking and LC order on bulk emission properties*

Preliminary emission studies on the crosslinked Φ_h films revealed that the presence of LC order does not appreciably affect the wavelength of the emissive core.

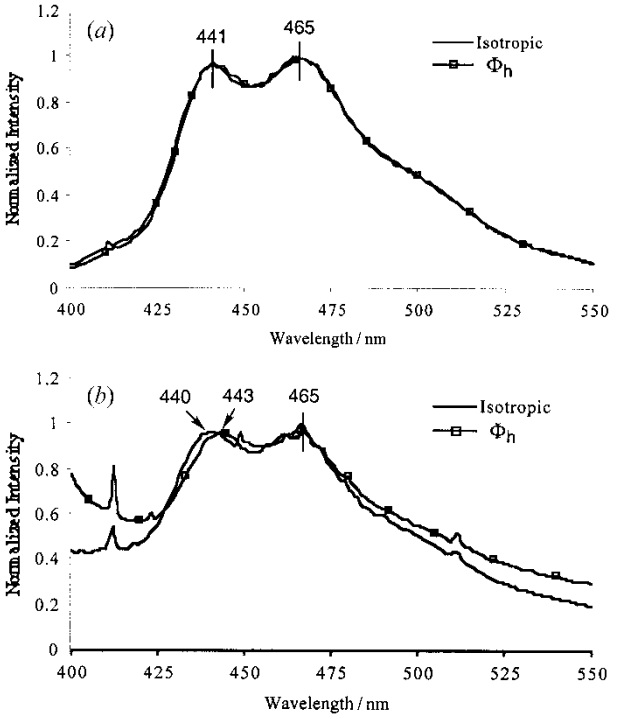


Figure 6. Ambient temperature emission spectra of films of (*a*) **6** and (*b*) **7b**, crosslinked in the isotropic and Φ_h states. Excitation at 365 nm. (Note: the sharp peaks in figure 6 (*b*) are instrument artifacts.)

Figure 6 shows the room temperature emission spectra of **6** and **7b** that were crosslinked in the Φ_h phase and in the isotropic state at elevated temperatures. As can be seen in the spectra, both the crosslinked isotropic and Φ_h forms of **6** and **7b** show two emission bands at approximately 440 and 465 nm, and the emission profiles are virtually identical regardless of the polymerizable group or the sample morphology. The excitation spectra were also identical with maxima at 397–398 nm. Comparison of the pre-polymerized samples and polymerized samples also revealed that the emission intensity does not appear to be adversely affected by the thermally initiated radical polymerization process. More detailed photophysical studies are currently underway with the aid of collaborators to determine the stabilities, lifetimes, and quantum efficiencies of these materials with respect to the crosslinked morphology.

4. Conclusions

A series of polymerizable hexacatenar compounds containing acrylate, isoprene, and 1,3-diene tail systems, and with either a luminescent (*E*,*E*)-1,4-bis[2-(3,5-dimethoxy-4-hydroxyphenyl)ethenyl]benzene or (*E*,*E*)-1,4-bis[2-(4-hydroxyphenyl)ethenyl]benzene core, were synthesized and investigated for mesogenic properties. Unfortunately, none of the hexacatenar monomers containing the tetramethoxy-substituted central core exhibited any mesogenic behaviour with the three polymerizable tail systems studied. Apparently, the packing affinity of the tetramethoxy-substituted core is insufficient to offset the destabilizing effects associated with having a polymerizable moiety at the end of each tail. However, by removing the four methoxy sidegroups on the oligo(*p*-phenylenevinylene) core to improve molecular packing ability, mesogenic behaviour was observed in the isoprenyl and alkyl-1,3-dienyl derivatives with the unsubstituted (*E*,*E*)-1,4-bis[2-(4-hydroxyphenyl)ethenyl]benzene core. These luminescent hexacatenar monomers were characterized by POM, DSC, and XRD and found to form the Φ_h phase in the *c*. 45–75°C range. These photoactive LC molecules are insensitive to radicals generated during polymerization, but they are susceptible to UV photodegradation at elevated temperatures in the LC state. As a result, the mesogenic and luminescent properties of these materials are lost upon photopolymerization. However, retention of LC order and emission properties can be achieved during crosslinking via thermally initiated radical polymerization in the absence of light. Emission behaviour is apparently unaffected by the ordering or radical crosslinking of these LCs.

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