

Mesogen synthesis

All syntheses were carried out with modifications on the liquid crystal and polyesterification chemistries of Svensson et al.¹ and Moore and Stupp². All manipulations were performed under nitrogen following standard Schlenk procedure. Throughout this paper the **nBPP4** and **nBPP2F4** designation will be used to denote all final, siloxane-containing LC monomers. **P4** denotes the four carbons of the nonfluorinated LC butyl ester end group while **P2F4** denotes fluorination on the last four carbons of the LC hexyl ester group, and **n** is the length of the flexible spacer (4, 6 or 8 carbons). A detailed written procedure is provided for the synthesis of intermediates **1-3** and the product **4BPP4**.

Syntheses of the fluorinated compounds **4BPP2F4**, **6BPP2F4** and **8BPP2F4** follow identical methods except for the replacement of butanol by fluorinated hexanol. 6-Bromo-1-hexene and 8-bromo-1-octene were the respective precursors in the syntheses of **6BPP4/6BPP2F4** and **8BPP4/6BPP2F4**. All compounds were further purified following the **4BPP4** procedure unless otherwise indicated. All products and intermediates were verified via ¹H NMR spectrometry. NMR data were in accordance with the structures for all cases.

4'-(3-Buten-1-yloxy)-[1,1'-biphenyl]-4-carboxylic acid (1) Biphenyl precursor to **4BPP4**. 4'-Hydroxy-4-biphenylcarboxylic acid (6.43 g, 0.030 mol), potassium hydroxide (5.05 g, 0.090 mol) and potassium iodide (1.00 g, 6.0 mmol) were combined with 450 ml ethanol and 25 ml water in a 1 L round bottom flask. The pale yellow mixture was stirred at 50°C. 4-Bromo-1-butene (6.09 ml, 0.060 mol) was added after 1 h and the mixture was refluxed. After 24 h the reaction was cooled to 0°C and 300 ml water added. After stirring at 0°C for 1 h concentrated hydrochloric acid was added slowly (~9 ml, pH≤1). White precipitates were filtered and washed with cold water. Recrystallization was performed from ethanol. Yield: 2.78 g, 0.010 mol,

34.5%. ^1H NMR (DMSO) (δ): 2.48 (m, 2H, OCH_2CH_2), 4.05 (t, 2H, OCH_2CH_2), 5.13 (q, 2H, $\text{CH}=\text{CH}_2$), 5.87 (m, 1H, $\text{CH}=\text{CH}_2$), 7.03 (d, 2H, ArH), 7.66 (d, 2H, ArH), 7.73 (d, 2H, ArH), 7.98 (d, 2H, ArH).

4'-(5-Hexen-1-yloxy)-[1,1'-biphenyl]-4-carboxylic acid Biphenyl precursor for **6BPP4** was synthesized from 4'-hydroxy-4-biphenylcarboxylic acid and 6-bromo-1-hexene (8.02 ml, 0.060 mol). Yield: 8.07 g, 0.027 mol, 90.2%. ^1H NMR (DMSO) (δ): 1.52 (m, 2H, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2$), 1.73 (m, 2H, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2$), 2.10 (m, 2H, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2$), 4.00 (t, 2H, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2$), 5.02 (q, 2H, $\text{CH}=\text{CH}_2$), 5.83 (m, 1H, $\text{CH}=\text{CH}_2$), 7.04 (d, 2H, ArH), 7.66 (d, 2H, ArH), 7.75 (d, 2H, ArH), 7.97 (d, 2H, ArH).

4'-(7-Octen-1-yloxy)-[1,1'-biphenyl]-4-carboxylic acid Biphenyl precursor for **8BPP4** was synthesized from 4'-hydroxy-4-biphenylcarboxylic acid and 8-bromo-1-octene (10.07 ml, 0.060 mol). Yield: 8.64 g, 0.027 mol, 88.8%. ^1H NMR (DMSO) (δ): 1.41 (m, 6H, $\text{OCH}_2\text{CH}_2(\text{CH}_2)_3\text{CH}_2$), 1.75 (m, 2H, $\text{OCH}_2\text{CH}_2(\text{CH}_2)_3\text{CH}_2$), 2.05 (m, 2H, $\text{OCH}_2\text{CH}_2(\text{CH}_2)_3\text{CH}_2$), 4.02 (t, 2H, $\text{OCH}_2\text{CH}_2(\text{CH}_2)_3\text{CH}_2$), 5.00 (q, 2H, $\text{CH}=\text{CH}_2$), 5.83 (m, 1H, $\text{CH}=\text{CH}_2$), 7.05 (d, 2H, ArH), 7.67 (d, 2H, ArH), 7.76 (d, 2H, ArH), 8.00 (d, 2H, ArH).

(2R)-2-(4-Hydroxyphenoxy)propionic acid butyl ester (2a) In a 1 L round bottom flask R-(+)-2-(4-hydroxyphenoxy) propionic acid (27.3 g, 0.150 mol), butanol (54.9 ml, 0.600 mol) and DPTS (11.74 g, 0.038 mol) were dissolved in 600 ml dichloromethane (DCM) and 60 ml dimethylformamide (DMF). Diisopropylcarbodiimide (DIPC) (27.9 ml, 0.180 mol) was added. The reaction was stirred for 24 h, filtered to remove urea, washed 3 times with 0.1 M hydrochloric acid, 2 times with brine and dried with magnesium sulfate. Rotatory evaporation removed solvent. Further purification was from silica column (4:1 hexane: ethyl acetate). The product (pink-gray oil) was not air and moisture-sensitive and was stored at room temperature

for later use. Yield: 25.0 g, 0.104 mol, 69.9%. $^1\text{H-NMR}$ (CDCl_3) (δ): 0.87 (t, 3H, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.32 (m, 2H, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.58 (m, 5H, $\text{OCH}^*\text{CH}_3 + \text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 4.17 (m, 2H, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 4.68 (q, 1H, OCH^*CH_3), 6.74 (m, 4H, ArH).

(2R)-2-(4-Hydroxyphenoxy)propionic acid 3,3,4,4,5,5,6,6,6-nonafluoro-1-hexyl ester
(2b) The fluorinated hexyl ester derivative was synthesized from R-(+)-2-(4-hydroxyphenoxy)propionic acid (1.74 g, 0.0096 mol), fluorinated hexanol (10.1 g, 0.038 mol), DPTS (0.747 g, 0.0024 mol) and DIPC (1.77 ml, 0.011 mol) in 100 ml DCM and 10 ml DMF. The product was washed, dried and further purified through silica column (hexane: ethyl acetate 2:1). Yield: 2.90 g, 0.0068 mol, 70.9%. $^1\text{H-NMR}$ (CDCl_3) (δ): 1.62 (d, 3H, OCH^*CH_3), 2.46 (m, 2H, $\text{OCH}_2\text{CH}_2\text{CF}_2$), 4.48 (t, 2H, $\text{OCH}_2\text{CH}_2\text{CF}_2$), 4.70 (q, 1H, OCH^*CH_3), 6.76 (m, 4H, ArH).

4-[(1R)-2-butoxy-1-methyl-2-oxoethoxy]phenyl 4'-(3-Buten-1-yloxy)-[1,1'-biphenyl]-4-carboxylate (3) Vinyl mesogen precursor for 4BPP4. Intermediate (1) (2.60 g, 0.010 mol), (2) (2.48 g, 0.010 mol) and DPTS (0.81 g, 2.60 mmol) were dissolved in 100 ml DCM and 15 ml DMF in a 250 ml round bottom flask. DIPC (1.93 ml, 0.013 mol) was added. The reaction was stirred for 24 h, filtered to remove urea, washed 3 times with 0.1 M hydrochloric acid, 2 times with brine and dried with magnesium sulfate. Rotatory evaporation removed solvent. White to pale yellow solid was obtained from silica column (DCM). Yield: 3.91 g, 8.00 mmol, 76.9%. $^1\text{H-NMR}$ (CDCl_3) (δ): 0.93 (t, 3H, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.35 (m, 2H, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.65 (m, 5H, $\text{OCH}^*\text{CH}_3 + \text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 2.60 (q, 2H, $\text{ArOCH}_2\text{CH}_2\text{CH}=\text{CH}_2$), 4.09 (t, 2H, $\text{ArOCH}_2\text{CH}_2\text{CH}=\text{CH}_2$), 4.19 (m, 2H, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 4.76 (q, 1H, OCH^*CH_3), 5.18 (q, 2H, $\text{CH}=\text{CH}_2$), 5.94 (m, 1H, $\text{CH}=\text{CH}_2$), 6.94 (d, 2H, ArH), 7.02 (d, 2H, ArH), 7.15 (d, 2H, ArH), 7.59 (d, 2H, ArH), 7.68 (d, 2H, ArH), 8.23 (d, 2H, ArH).

4-[(1R)-2-butoxy-1-methyl-2-oxoethoxy]phenyl 4'-(5-Hexen-1-yloxy)-[1,1'-biphenyl]-4-carboxylate Vinyl precursor to 6BPP4. Yield: 8.80 g, 0.017 mol, 64.0%. ¹H-NMR (CDCl₃) (δ): 0.94 (t, 3H, OCH₂CH₂CH₂CH₃), 1.35 (m, 2H, OCH₂CH₂CH₂CH₃), 1.64 (m, 9H, OCH^{*}CH₃ + OCH₂CH₂CH₂CH₃ + ArOCH₂CH₂CH₂CH₂CH=CH₂), 1.83 (m, 2H, ArOCH₂CH₂CH₂CH₂CH=CH₂), 2.17 (q, 2H, ArOCH₂CH₂CH₂CH₂CH=CH₂), 4.04 (t, 2H, ArOCH₂CH₂CH₂CH₂CH=CH₂), 4.19 (m, 2H, OCH₂CH₂CH₂CH₃), 4.76 (q, 1H, OCH^{*}CH₃), 5.02 (q, 2H, CH=CH₂), 5.85 (m, 1H, CH=CH₂), aryl region same as 4BBP4 vinyl mesogen.

4-[(1R)-2-butoxy-1-methyl-2-oxoethoxy]phenyl 4'-(7-Octen-1-yloxy)-[1,1'-biphenyl]-4-carboxylate Vinyl precursor to 8BPP4. Yield: 9.16 g, 0.017 mmol, 57.5%. ¹H-NMR (CDCl₃) (δ): 0.93 (t, 3H, OCH₂CH₂CH₂CH₃), 1.46-1.24 (m, 6H, ArOCH₂CH₂(CH₂)₃CH₂CH=CH₂), 1.52 (m, 2H, OCH₂CH₂CH₂CH₃), 1.60 (s, 3H, OCH^{*}CH₃), 1.64 (m, 2H, OCH₂CH₂CH₂CH₃), 1.85 (m, 2H, ArOCH₂CH₂(CH₂)₃CH₂CH=CH₂), 2.09 (q, 2H, ArOCH₂CH₂(CH₂)₃CH₂CH=CH₂), 4.03 (t, 2H, ArOCH₂CH₂(CH₂)₃CH₂CH=CH₂), 4.20 (m, 2H, OCH₂CH₂CH₂CH₃), 4.77 (q, 1H, OCH^{*}CH₃), 5.00 (q, 2H, CH=CH₂), 5.84 (m, 1H, CH=CH₂), aryl region same as 4BBP4 vinyl mesogen.

4-[(1R)-2-(3,3,4,4,5,5,6,6,6-nonafluoro-1-hexoxy)-1-methyl-2-oxoethoxy]phenyl 4'-(3-Buten-1-yloxy)-[1,1'-biphenyl]-4-carboxylate Vinyl precursor to 4BPP2F4. Yield: 3.47 g, 0.0051 mol, 91.6%. Product was used in hydrosilylation without column purification. ¹H-NMR (CDCl₃) (δ): 1.08 (d, 3H, OCH^{*}CH₃), 1.55 (m, 2H, OCH₂CH₂(CF₂)₃CF₃), 2.50 (m, 2H, ArOCH₂CH₂CH=CH₂), 4.02 (t, 2H, ArOCH₂CH₂CH=CH₂), 4.42 (m, 2H, OCH₂CH₂(CF₂)₃CF₃), 4.74 (q, 1H, OCH^{*}CH₃), 5.10 (q, 2H, CH=CH₂), 5.87 (m, 1H, CH=CH₂), 6.85 (d, 2H, ArH), 6.94 (d, 2H, ArH), 7.06 (d, 2H, ArH), 7.53 (d, 2H, ArH), 7.62 (d, 2H, ArH), 8.13 (d, 2H, ArH).

4-[(1R)-2-(3,3,4,4,5,5,6,6,6-nonafluoro-1-hexoxy)-1-methyl-2-oxoethoxy]phenyl 4'-(5-Hexen-1-yloxy)-[1,1'-biphenyl]-4-carboxylate Vinyl precursor to 6BPP2F4. Yield: 13.53 g, 0.020 mol, 100%. Product was used in next hydrosilylation without column purification. ¹H-NMR (CDCl₃) (δ): 1.03 (d, 3H, OCH^{*}CH₃), 1.55 (m, 2H, OCH₂CH₂(CF₂)₃CF₃), 1.75 (m, 2H, ArOCH₂CH₂CH₂CH₂CH=CH₂), 2.07 (m, 2H, ArOCH₂CH₂CH₂CH₂CH=CH₂), 2.40 (m, 2H, ArOCH₂CH₂CH₂CH₂CH=CH₂), 3.95 (t, 2H, ArOCH₂CH₂CH₂CH₂CH=CH₂), 4.41 (m, 2H, OCH₂CH₂(CF₂)₃CF₃), 4.72 (q, 1H, OCH^{*}CH₃), 4.93 (q, 2H, CH=CH₂), 5.75 (m, 1H, CH=CH₂), aryl region same as 4BBP2F4 vinyl mesogen.

4-[(1R)-2-(3,3,4,4,5,5,6,6,6-nonafluoro-1-hexoxy)-1-methyl-2-oxoethoxy]phenyl 4'-(3-Buten-1-yloxy)-[1,1'-biphenyl]-4-carboxylate Vinyl precursor to 8BPP2F4. Product was purified through silica column (hexane: ethyl acetate 4:1). Yield: 5.50 g, 0.0078 mol, 49.9%. ¹H NMR: 1.17 (d, 3H, OCH^{*}CH₃), 1.38-1.57 (m, 8H, ArOCH₂(CH₂)₄CH₂CH=CH₂), 1.84 (m, 2H, OCH₂CH₂(CF₂)₃CF₃), 2.12 (m, 2H, ArOCH₂(CH₂)₄CH₂CH=CH₂), 4.04 (t, 2H, ArOCH₂(CH₂)₄CH₂CH=CH₂), 4.50 (m, 2H, OCH₂CH₂(CF₂)₃CF₃), 4.82 (q, 1H, OCH^{*}CH₃), 5.01 (m, 2H, CH=CH₂), 5.84 (m, 1H, CH=CH₂), 6.92 (d, 2H, ArH), 7.03 (d, 2H, ArH), 7.15 (d, 2H, ArH), 7.61 (d, 2H, ArH), 7.70 (d, 2H, ArH), 8.23 (d, 2H, ArH).

4-[(1R)-2-butoxy-1-methyl-2-oxoethoxy]phenyl 4'-[4-(1,1,3,3-tetramethyldisiloxanyl)butoxy]-(1,1'-biphenyl)-4-carboxylate 4BPP4 15 drops (~0.1 ml) of the hydrosilylation catalyst platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex in xylene (Pt ~2%) was added to a solution containing (3) (3.90 g, 8.00 mmol) in 15 ml toluene. The resulting yellow solution was added dropwise to a second, stirring solution of tetramethyldisiloxane (30 ml, 0.170 mol) in 30 ml toluene at 60°C. The reaction was stirred at 60°C for 24 hours and toluene was removed by rotatory evaporation. White to pale yellow solid

was obtained from silica column (6:1 hexane: ethyl acetate). Yield: 2.53 g, 4.06 mmol, 50.8%. 6BBP4 was purified through silica column (8:1 hexane: ethyl acetate). Yield: 3.75 g, 0.0058 mol, 33.8%. 8BBP4 was purified through silica column (10:1 hexane: ethyl acetate). Yield: 7.40 g, 0.011 mol, 64.9%. ¹H NMR of 4BBP4, 6BBP4 and 8BBP4 share several identical regions; all differences are indicated in bracket. ¹H NMR (CDCl₃, n = 1, 3, 5) (δ): 0.09 (s, 6H, SiMe₂H), 0.17 (s, 6H, SiMe₂O), 0.61 (t, 2H, CH₂Si), 0.91 (t, 3H, OCH₂CH₂CH₂CH₃), [4BBP4: 1.34 (m, 2H, OCH₂CH₂CH₂CH₂Si), 6BBP4: 1.32-1.46 (m, 6H, OCH₂CH₂(CH₂)₃CH₂Si), 8BBP4: 1.32-1.42 (m, 10H, OCH₂CH₂(CH₂)₅CH₂Si)], 1.56 (m, 2H, OCH₂CH₂CH₂CH₃), 1.64 (m, 5H, OCH^{*}CH₃ + OCH₂CH₂CH₂CH₃), 1.86 (m, 2H, OCH₂CH₂(CH₂)_nCH₂Si), 4.03 (t, 2H, OCH₂CH₂(CH₂)_nCH₂Si), 4.19 (m, 2H, OCH₂CH₂CH₂CH₃), [4BBP4 and 6BBP4: 4.72 (m, 1H, OCH^{*}CH₃), 4.78 (m, 1H, SiH), 8BBP4: 4.70 (m, 1H, OCH^{*}CH₃), 4.75 (q, 1H, SiH)], 6.93 (d, 2H, ArH), 7.03 (d, 2H, ArH), 7.15 (d, 2H, ArH), 7.59 (d, 2H, ArH), 7.70 (d, 2H, ArH), 8.23 (d, 2H, ArH).

All fluorinated compounds were purified through silica column (hexane: ethyl acetate 4:1). 4BPP2F4 Yield: 2.00 g, 0.0025 mol, 50.9%. 6BPP2F4 Yield: 3.60 g, 0.0043 mol, 22.4%. 8BPP2F4 Yield: 2.50 g, 0.0030 mmol, 20.0%. ¹H-NMR (CDCl₃, n = 1, 3, 5) (δ): 0.11 (s, 6H, SiMe₂H), 0.23 (s, 6H, SiMe₂O), 0.61 (t, 2H, CH₂Si), [4BBP2F4: 1.57 (m, 2H, OCH₂CH₂CH₂CH₂Si), 6BBP2F4: 1.56-1.20 (m, 6H, OCH₂CH₂(CH₂)₃CH₂Si), 8BBP2F4: 1.50 (m, 2H, OCH₂CH₂CH₂(CH₂)₄CH₂Si), 1.45-1.23 (m, 8H, OCH₂CH₂CH₂(CH₂)₄CH₂Si)], 1.66 (d, 3H, OCH^{*}CH₃), 1.88 (m, 2H, OCH₂CH₂(CH₂)_nCH₂Si), 2.51 (m, 2H, OCH₂CH₂(CF₂)₃CF₃), 4.04 (t, 2H, OCH₂CH₂(CH₂)_nCH₂Si), 4.51 (t, 2H, OCH₂CH₂CH₂CH₃), 4.72 (m, 1H, OCH^{*}CH₃), 4.82 (m, 1H, SiH), 6.95 (d, 2H, ArH), 7.03 (d, 2H, ArH), 7.16 (d, 2H, ArH), 7.61 (d, 2H, ArH), 7.71 (d, 2H, ArH), 8.24 (d, 2H, ArH).

Mesogen polymer attachment

4BPP4 (2.987 g, ~1:2.5 molar ratio of polymer vinyl group to mesogen SiH) was dissolved in 6.5 ml toluene and stirred at 60°C. PS-PVMS polymer (0.464 g, 60/40 molar ratio) and 7 drops (~0.05 ml) of platinum catalyst were dissolved in 3.0 ml toluene. The resulting clear solution was added dropwise to the first mesogen solution. The reaction was stirred continuously at 60°C. 2 to 3 ml of reaction mixture was removed approximately every 12 hours and precipitated into methanol. White precipitate was filtered, redissolved in the initial volume of toluene, and re-precipitated into methanol to allow complete removal of excess, unattached mesogen. White, rubbery solid was isolated by filtering. Rise in LC attachment percent was monitored with NMR.

Yield (increases with respect to reaction time): ~0.1-0.3 g. ^1H NMR (CDCl_3 , $n = 1, 3, 5$) (δ): 0.03-0.24 (m, $\text{SiMe}_2\text{OSiMe}_2 + \text{PVMS SiMe} + \text{SiCH}_2\text{CH}_2\text{SiMe}_2\text{O}$), 0.39 (s, 2H, $\text{SiCH}_2\text{CH}_2\text{SiMe}_2\text{O}$), 0.55 (s, 2H, $\text{OCH}_2\text{CH}_2(\text{CH}_2)_n\text{CH}_2\text{Si}$), 0.88 (t, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.00 (s, 2H, $\text{OCH}_2\text{CH}_2(\text{CH}_2)_n\text{CH}_2\text{Si}$), [4BPP4: 1.23-1.62 (br. m, 11H, styrene $\text{PhCHCH}_2\text{Ph} + \text{OCH}_2\text{CH}_2(\text{CH}_2)_n\text{CH}_2\text{Si} + \text{OCH}^*\text{CH}_3 + \text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 6BPP4/8BPP4: 1.25-1.71 (br. m, 13H/15H, styrene $\text{PhCHCH}_2\text{Ph} + \text{OCH}_2\text{CH}_2(\text{CH}_2)_n\text{CH}_2\text{Si} + \text{OCH}^*\text{CH}_3 + \text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$)], 1.67-2.10 (br. d, 3H, styrene $\text{PhCHCH}_2\text{Ph} + \text{OCH}_2\text{CH}_2(\text{CH}_2)_n\text{CH}_2\text{Si}$), 3.94 (s, 2H, $\text{OCH}_2\text{CH}_2(\text{CH}_2)_n\text{CH}_2\text{Si}$), 4.13 (s, 2H, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 4.70 (d, 1H, OCH^*CH_3), 5.70-6.03 (m, 3H, Si-CH=CH_2), 6.26-6.74 (m, 2H, styrene o- ArH), 6.83-7.18 (m, 9H, LC $\text{ArH} + \text{styrene m, p-ArH}$), 7.52 (s, 2H, ArH), 7.62 (s, 2H, ArH), 8.16 (s, 2H, ArH).

The same procedure was used in LC attachment to the PVMS homopolymer. Yield (increases with respect to reaction time): ~0.1-1.5 g. ^1H NMR (CDCl_3 , $n = 1, 3, 5$) (δ): 0.01-0.23 (m, $\text{SiMe}_2\text{OSiMe}_2 + \text{PVMS SiMe} + \text{SiCH}_2\text{CH}_2\text{SiMe}_2\text{O}$), 0.43 (s, 2H, $\text{SiCH}_2\text{CH}_2\text{SiMe}_2\text{O}$), 0.54

(s, 2H, $\text{OCH}_2\text{CH}_2(\text{CH}_2)_n\text{CH}_2\text{Si}$), 0.91 (m, 3H, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), [4BPP4: 1.38 (m, 2H, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.53-1.63 (br. s, 2H, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}$), 6BPP4: 1.28-1.59 (br. m, 8H, $\text{OCH}_2\text{CH}_2(\text{CH}_2)_3\text{CH}_2\text{Si} + \text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 8BPP4: 1.25-1.55 (t, 12H, $\text{OCH}_2\text{CH}_2(\text{CH}_2)_5\text{CH}_2\text{Si} + \text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$)], 1.63 (m, 5H, $\text{OCH}^*\text{CH}_3 + \text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.80 (m, 2H, $\text{OCH}_2\text{CH}_2(\text{CH}_2)_n\text{CH}_2\text{Si}$), 3.99 (t, 2H, $\text{OCH}_2\text{CH}_2(\text{CH}_2)_n\text{CH}_2\text{Si}$), 4.18 (s, 2H, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 4.75 (q, 1H, OCH^*CH_3), 5.79 (d, 1H, $\text{Si-CH}=\text{CH}_2$), 6.00 (m, 2H, $\text{Si-CH}=\text{CH}_2$), 6.97 (m, 4H, ArH), 7.13 (m, 2H, ArH), 7.58 (s, 2H, ArH), 7.67 (s, 2H, ArH), 8.22 (s, 2H, ArH).

Measurement of order-disorder transition temperatures

Temperature dependent SAXS was used to investigate the effects of increasing LC content upon the self-assembly behavior. Analyzing the reciprocal of the maximum scattering intensity ($1/I_{\text{max}}$) as a function of the reciprocal temperature ($1/T$) allows for systematic determination of the order-disorder transition temperature (T_{ODT}). Additionally, the wavelength of concentration fluctuations, above T_{ODT} , and the d-spacing, below T_{ODT} , denoted as (d) was plotted versus reciprocal temperature^{3,4}. (see Figure S1 for an example)

Additionally, rheometry was used to confirm the order-disorder transition temperatures that were determined via temperature dependant SAXS, a representative trace is shown in Figure 5. The T_{ODT} is characterized by a maxima in tan delta, which is the ratio of the loss modulus (G'') and the storage modulus (G'). (see Figure S2 for an example)

The values for the T_{ODT} obtained via rheometry were consistent with those from SAXS, however due to the faster ramp rate, $5^\circ\text{C}/\text{min}$ for rheometry compared to 30 min equilibration for SAXS, the values were typically $\sim 20^\circ\text{C}$ higher than those from SAXS (see table S1). Some

samples were not investigated via SAXS or rheometry as they had not yet been synthesized or there was not sufficient material available, respectively.

It is difficult to compare the T_{ODT} for the samples resulting in the attachment of LC to the PS61-PVMS18 backbone to the samples synthesized with PS27-PVMS14 for several reasons. Both the molecular weight and the polydispersity of these polymers differ, and this has an effect upon the T_{ODT} . Additionally, while homogeneous anchoring of the LC mesophase with the inter-material dividing surface (IMDS) is exclusively observed in this system where the PS domains form cylinders, it is expected that either homogeneous or heterogeneous anchoring could exist for lamellar morphologies⁵. As the LC anchoring is a significant driving force for the self assembly of these materials it is expected that the anchoring will influence the T_{ODT} . In depth studies into the lamellar and transitional morphologies are currently underway.

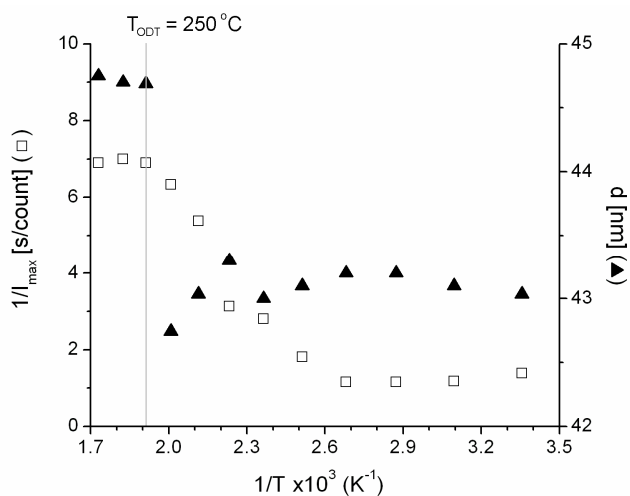


Figure S1. Plot of $1/I_{\max}$ versus $1/T$ and d versus $1/T$ for sample PS27-PVMS14. Where I_{\max} is the maximum intensity of the scattering in the q range of interest and d is the spacing of the ordered phase below the T_{ODT} and the length scale of concentration fluctuations above the T_{ODT} .

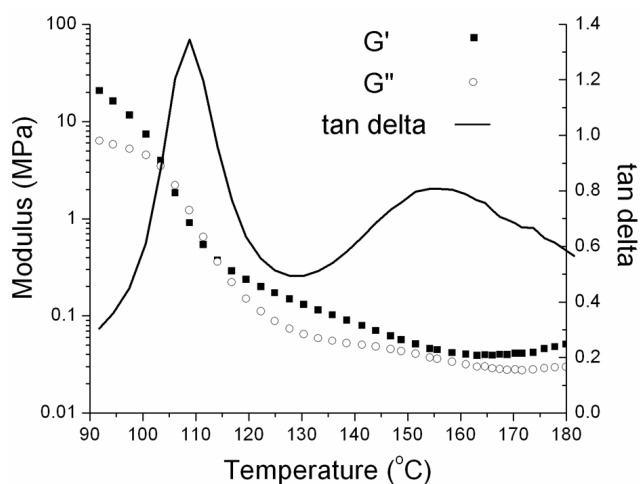


Figure S2. Rheometry for sample PS27-LCP_{4BPP446}. G' is the storage modulus, G'' is loss modulus, and $\tan \delta = G'/G''$. The polystyrene T_g is observed at 110°C and the T_{ODT} is observed at 155°C .

References

1. Svensson, M.; Helgee, B.; Skarp, K.; Andersson, G., Effects of nitro substituents on the properties of a ferroelectric liquid crystalline side chain polysiloxane. *Journal of Materials Chemistry* **1998**, 8, (2), 353-362.
2. Moore, J. S.; Stupp, S. I., Room-Temperature Polyesterification. *Macromolecules* **1990**, 23, (1), 65-70.
3. Hashimoto, T.; Shibayama, M.; Kawai, H., Domain-Boundary Structure of Styrene-Isoprene Block Co-Polymer Films Cast from Solution.4. Molecular-Weight Dependence of Lamellar Microdomains. *Macromolecules* **1980**, 13, (5), 1237-1247.
4. Mao, G. P.; Wang, J. G.; Clingman, S. R.; Ober, C. K.; Chen, J. T.; Thomas, E. L., Molecular design, synthesis, and characterization of liquid crystal coil diblock copolymers with azobenzene side groups. *Macromolecules* **1997**, 30, (9), 2556-2567.
5. Anthamatten, M.; Zheng, W. Y.; Hammond, P. T., A morphological study of well-defined smectic side-chain LC block copolymers. *Macromolecules* **1999**, 32, (15), 4838-4848.