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Supporting Information

Effects of tacticity and chiral center-to-dipole distance on mesogen-free liquid crystalline self-assembly of sulfonyl-containing comb-like polymers

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I. Syntheses of starting materials



n = 8: 5-(octylsulfonyl)pentyl ethanethioate n = 12: 5-(dodecylsulfonyl)pentyl ethanethioate

Scheme S1. Synthesis of 5-(octylsulfonyl)pentyl ethanethioate and 5-(dodecylsulfonyl)pentyl ethanethioate.

Synthesis of 5-(*n*-alkylthio)pentanol. *n*-Octanethiol (5.892 g, 40.3 mmol) and sodium ethoxide (5.523 g, 81.2 mmol, delivered from a stock solution of sodium ethoxide in ethanol with a concentration of 11.3 wt%) were weighed into a 250-mL two-necked round bottom flask equipped with an addition funnel and a magnetic stir bar. The flask was placed under an N_2 environment, and the mixture was stirred for 2 h at room temperature. 5-Bromopentanol (6.727 g 40.3 mmol) was added dropwise into the flask through the addition funnel, and the reaction mixture was stirred at room temperature overnight. The solvent was removed by rotary evaporation under reduced pressure, and the concentrated mixture was dissolved in dichloromethane (15 mL). The mixture was then transferred to a 250 mL separatory funnel and washed with 3 M HCl ($100 \text{ mL} \times 2$). The organic phase was dried with anhydrous sodium sulfate. After filtering off the solid and removing the solvent using a rotavapor and under vacuum, a paleyellow liquid was obtained. The product was further purified by silica gel chromatography using a mixture of ethyl acetate and hexanes (1:3, v/v) initially and then a mixture of dichloromethane and methanol (1:1, v/v) to elute the product out from the column. The solvents were evaporated and the product was dried under high vacuum, yielding a clear viscous liquid (8.001 g, 85.0% yield). ¹H NMR (CDCl₃, 500 MHz), δ (ppm) = 3.69 – 3.62 (m, -CH₂OH, 2H), 2.54 – 2.48 (m, -CH₂SCH₂-4H), 1.65 – 1.54 (m, -CH₂CH₂SCH₂CH₂CH₂CH₂CH₂OH 6H), 1.51 – 1.43 (m, -CH₂(CH₂)₂OH, 2H), 1.40 – 1.20 (m, CH₃(CH₂)₅CH₂-, 10H), 0.87 (t, CH₃CH₂-, 3H). ¹³C NMR $(CDCl_3, 126 \text{ MHz}), \delta (ppm) = 62.54, 32.21, 32.10, 31.97, 31.72, 29.61, 29.35, 29.12, 29.09, 28.85,$ 24.97, 22.54, 13.98.

29.70, 29.63, 29.61, 29.58, 29.52, 29.43, 29.32, 29.24, 28.94, 25.03, 22.66, 14.09.

Synthesis of 5-(*n*-alkylsulfonyl)pentanol. 5-(*n*-Octylthio)pentanol (8.001 g, 34.4 mmol) was weighed into a 250 mL two-necked round bottom flask fitted with a magnetic stir bar and an addition funnel. *meta*-Chloroperoxybenzoic acid (*m*-CPBA, 24.441 g, 99.1 mmol) was added into a separate 150 mL Erlenmeyer flask and dissolved with chloroform (50 mL). The *m*-CPBA solution was added dropwise into the flask for a period of 15 min, and the mixture was stirred at room temperature for 3 h. The reaction mixture was transferred into a separatory funnel and washed with 1 M NaOH (100 mL × 2). The organic layer was collected in an Erlenmeyer flask and dried with anhydrous sodium sulfate. After the solid was filtered off and the solvent was evaporated, a white crystalline powder was obtained as the pure product (7.436 g, 81.7% yield). ¹H NMR (CDCl₃, 300 MHz), δ (ppm) = 3.67 (t, -CH₂OH, 2H), 3.05 – 2.83 (m, -CH₂SO₂CH₂-, 4H), 2.02 – 1.72 (m, -CH₂CH₂SO₂CH₂-, 4H), 1.65 – 1.19 (m, -(CH₂)₂CH₂OH, CH₃(CH₂)₅CH₂-, 14H), 0.88 (t, CH₃CH₂-, 3H). ¹³C NMR (CDCl₃, 126 MHz), δ (ppm) = 61.90, 52.68, 52.41, 31.81, 31.54, 28.88, 28.77, 28.35, 24.69, 22.43, 21.78, 21.56, 13.91.

5-(*n*-Dodecylsulfonyl)pentanol was prepared and purified in the same manner as for 5-(*n*-octylsulfonyl)pentanol. Yield: 69.0%. ¹H NMR (CDCl₃, 600 MHz), δ (ppm) = 3.65 (t, -CH₂OH, 2H), 2.98 – 2.90 (m, -CH₂SO₂CH₂- 4H), 1.91 – 1.78 (m, -CH₂CH₂SO₂CH₂CH₂-, 4H), 1.63 – 1.20 (m, -(CH₂)₂CH₂OH, CH₃(CH₂)₉CH₂-, 22H), 0.87 (t, CH₃CH₂-, 3H). ¹³C NMR (151 MHz, CDCl₃), δ (ppm) = 62.82, 52.83, 52.52, 31.94, 31.85, 29.54, 29.53, 29.45, 29.27, 29.22, 29.02, 28.47, 24.81, 22.63, 21.91, 21.68, 14.06.

Synthesis 5-(*n*-alkylsulfonyl)pentyl methanesulfonate. 5-(nof Octylsulfonyl)pentanol (7.436 g, 32.0 mmol) and triethylamine (4.321 g, 42.7 mmol) were added into a 150 mL two-necked round bottom flask equipped with a magnetic stir bar and an addition funnel and dissolved in dichloromethane (20 mL). A solution of methanesulfonyl chloride (4.225 g, 36.9 mmol) in dichloromethane (20 mL) was transferred to the addition funnel and added dropwise for 15 min. The reaction mixture was stirred overnight at room temperature and then decanted into a separatory funnel. After washing with 3 M HCl (30 mL \times 3) and a saturated sodium bicarbonate solution (30 mL \times 3), the organic phase was dried with anhydrous sodium The solid was filtered off, and the volatiles were removed first by rotary evaporation and sulfate. then under high vacuum. The product was obtained as a pale-yellow liquid (9.356 g, 97.1%) ¹H NMR (CDCl₃, 300 MHz), δ (ppm) = 4.23 (t, -CH₂OSO₂CH₃, 2H), 3.00 (s, -OSO₂CH₃, 2H) vield). CH₂OSO₂CH₃, 6H), 1.64 – 1.53 (m, -CH₂(CH₂)₂OSO₂CH₃, 2H), 1.48 – 1.21 (m, CH₃(CH₂)₅CH₂-, 10H), 0.86 (t, -CH₂CH₃, 3H). ¹³C NMR (75 MHz, CDCl₃), δ (ppm) = 69.22, 52.91, 52.11, 37.31, 31.58, 28.91, 28.81, 28.59, 28.39, 24.46, 22.48, 21.86, 21.23, 13.96.

5-(*n*-Dodecylsulfonyl)pentyl methanesulfonate was prepared and purified in the same manner as for 5-(*n*-octylsulfonyl)pentyl methanesulfonate. Yield: 87.4%. ¹H NMR (CDCl₃, 600 MHz), δ (ppm) = 4.24 (t, -CH₂OSO₂CH₃, 2H), 3.01 (s, -OSO₂CH₃, 3H), 2.98 – 2.91 (m, -CH₂SO₂CH₂-, 4H), 1.93 – 1.78 (m, CH₂CH₂SO₂CH₂CH₂CH₂CH₂CH₂OSO₂CH₃, 6H), 1.64 – 1.58 (m, -CH₂(CH₂)₂OSO₂CH₃, 2H), 1.46 – 1.21 (m, CH₃(CH₂)₉CH₂-, 18H), 0.87 (t, -CH₂CH₃, 3H). ¹³C NMR (151 MHz, CDCl₃), δ (ppm) = 69.18, 53.04, 52.19, 37.42, 31.87, 29.56, 29.55, 29.46,

29.29, 29.23, 29.03, 28.68, 28.48, 24.56, 22.65, 21.95, 21.29, 14.08.

Synthesis of 5-(*n*-alkylsulfonyl)pentyl ethanethioate. 5-(*n*-Octylsulfonyl)pentyl methanesulfonate (9.356 g, 27.3 mmol) and triethyl amine (5.044 g, 49.8 mmol) were added along with chloroform (15 mL) into a 100 mL single-necked round bottom flask with a magnetic stir bar. The flask was then fitted with an addition funnel. After thioacetic acid (0.847 g, 55.8 mmol) in chloroform (10 mL) was added dropwise to the flask, the addition funnel was replaced with a reflux condenser and a gas flow control adaptor. The mixture was then heated in an oil bath to 70 °C and refluxed for 36 h. The reaction mixture was transferred into a separatory funnel; the organic phase was washed with 1 M HCl ($30 \text{ mL} \times 3$) and a saturated sodium bicarbonate solution $(30 \text{ mL} \times 3)$. The organic phase was then dried with anhydrous sodium sulfate. After the removal of the solid and the volatiles, a deep red solid was obtained. Recrystallization of the product was performed by adding the crude product and n-hexane (60 mL) into a 250 mL Erlenmeyer flask, heating the mixture at 65 °C to fully dissolve the solid, and allowing it to cool naturally to room temperature. The flask was then placed in a freezer with a temperature of -14 °C overnight. The precipitated crystals were collected using vacuum filtration and washing with cold hexanes (30 mL \times 2). The recrystallization was repeated one more time; the product was subsequently dried under high vacuum to yield a light pink crystal (5.000 g, 57% yield). ¹H NMR (300 MHz, chloroform-d), δ (ppm) = 2.97 – 2.83 (m, -*CH*₂SO₂C*H*₂-, -*CH*₂SC(O)CH₃, 6H), 2.31 (s, -CH₂SC(O)CH₃, 3H), 1.91 – 1.75 (m, -CH₂CH₂SO₂CH₂CH₂-, 4H), 1.68 – 1.17 (m, -(*CH*₂)₂CH₂SC(O)CH₃, CH₃(CH₂)₅CH₂-, 14H), 0.87 (t, CH₃CH₂-, 3H). ¹³C NMR (126 MHz, $CDCl_3$), δ (ppm) = 195.88, 52.98, 52.52, 31.81, 30.76, 29.22, 29.14, 29.04, 28.67, 28.63, 27.64, 22.70, 22.08, 21.60, 14.18. MS: m/z calc $C_{15}H_{30}O_3S_2$ [M+H]⁺: 323.1636; found: 323.1669; mass

error: 3.3 ppm.

5-(*n*-Dodecylsulfonyl)pentyl ethanethioate was prepared and purified in the same manner as for 5-(*n*-octylsulfonyl)pentyl)ethanethioate. Yield: 58.9%. ¹H NMR (500 MHz, chloroformd), δ (ppm) = 2.95 - 2.90 (m, -*CH*₂SO₂C*H*₂-, 4H), 2.86 (t, ,-*CH*₂SC(O)CH₃, 2H), 2.31 (s,

-CH₂SC(O)CH₃, 3H), 1.89 - 1.77 (m, -CH₂CH₂SO₂CH₂CH₂-, 4H), 1.65 - 1.58 (m,

-CH2CH2SC(O)CH3, 2H), 1.55 - 1.48 (m, -CH2(CH2)2SC(O)CH3, 2H), 1.45 - 1.39 (m,

-C H_2 (CH₂)₂SO₂CH₂-, 2H), 1.34 – 1.19 (m, CH₃(C H_2)₈CH₂-, 16H), 0.87 (t, C H_3 CH₂-, 3H). ¹³C NMR (126 MHz, CDCl₃), δ (ppm) = 195.86, 52.96, 52.49, 32.00, 30.74, 29.69, 29.68, 29.60, 29.42, 29.36, 29.20, 29.17, 28.65, 28.62, 27.62, 22.78, 22.06, 21.58, 14.22. MS: m/z calc C₁₉H₃₈O₃S₂ [M+H]⁺: 379.2341; found: 379.2343; mass error: 0.5 ppm.

Synthesis of isotactic poly[(R)-(-)-epichlorohydrin] (iPECH) by ring opening polymerization. The ring opening polymerization of (R)-(-)-epichlorohydrin was performed in a nitrogen-filled glovebox with flame dried glassware. A representative polymerization is shown in the following as an example. (R)-(-)-Epichlorohydrin (1.50 mL, 19.2 mmol) and modified methylaluminoxane (MMAO-12, 1.2 mL of the solution in toluene with an aluminum concentration of 7 wt %, corresponding to approximately 73 mg aluminum) were added via micropipette into a 10 mL Schlenk tube that contained dry diethyl ether (5 mL). The polymerization mixture was stirred with a magnetic stir bar at room temperature in the glove box. Shortly after the addition of MMAO-12, a precipitate started to appear and gradually increased in

quantity as the reaction proceeded. After 24 h, the Schlenk tube was removed from the glovebox, and 2,4-pentadione (2 mL) and methanol (3 mL) were added while stirring to extract the aluminoxane species from the precipitated polymer. After stirring at room temperature for an additional 2 h, the mixture was poured into methanol (30 mL), and the solid polymer was collected by vacuum filtration using a Büchner funnel. The polymer was soaked with methanol (20 mL) and filtered again. This process was repeated once more to purify the polymer. Finally, the washed polymer was dried under vacuum, yielding a white solid (0.287 g, 19.1% yield). ¹H NMR (300 MHz, chloroform-*d*), δ (ppm) = 3.80 – 3.50 (m, -CH₂CH(CH₂Cl)O-, 5H).



Figure S1. ¹H NMR spectrum of iPECH in CDCl₃. Peaks labeled with * are from impurities.

II. ¹H and ¹³C NMR, SEC, and TGA characterization data for the mono- and di-sulfonylated polyethers



Figure S2. (A) 1 H and (B) 13 C NMR spectra of aPOP-SC₅SO₂C₈ in CDCl₃.



Figure S3. Size-exclusion chromatography curve of aPOP-SC₅SO₂C₈ using CHCl₃ as eluent.



Figure S4. 13 C NMR spectrum of aPOP-SC₅SO₂C₁₂ in CDCl₃.



Figure S5. Size exclusion chromatography curve of aPOP-SC₅SO₂C₁₂ using CHCl₃ as eluent.



Figure S6. (A) 1 H and (B) 13 C NMR spectra of iPOP-SC₅SO₂C₈ in CDCl₃.



Figure S7. Size exclusion chromatography curve of iPOP-SC₅SO₂C₈ using CHCl₃ as eluent.



Figure S8. ¹³C NMR spectrum of iPOP-SC₅SO₂C₁₂ in CDCl₃.



Figure S9. Size exclusion chromatography curve of iPOP-SC₅SO₂C₁₂ using CHCl₃ as eluent.



Figure S10. ¹H NMR spectra of (A) aPOP-SO₂C₅SO₂C₈ and (B) iPOP-SO₂C₅SO₂C₈ in CDCl₃.





Figure S11. Size exclusion chromatography curves of (a) $aPOP-SO_2C_5SO_2C_8$, (b) $iPOP-SO_2C_5SO_2C_8$, (C) $aPOP-SO_2C_5SO_2C_{12}$, and (D) $iPOP-SO_2C_5SO_2C_{12}$ using CHCl₃ as eluent.





Figure S12. Thermogravimetric analysis (TGA) curves of (A) aPOP-SC₅SO₂C₈, (B) iPOP-SC₅SO₂C₈, (C) aPOP-SC₅SO₂C₁₂, (D) iPOP-SC₅SO₂C₁₂, (E) aPOP-SO₂C₅SO₂C₈, (F) iPOP-SO₂C₅SO₂C₈, (G) aPOP-SO₂C₅SO₂C₁₂, and (H) iPOP-SO₂C₅SO₂C₁₂. TGA was performed in a dry N₂ atmosphere at a heating rate of 20 °C/min.



III. PLM and XRD of atactic and isotactic POP-SC₅SO₂C₈ and POP-SO₂C₅SO₂C₈

Figure S13. PLM micrographs of (A) aPOP-SC₅SO₂C₈ and (B) iPOP-SC₅SO₂C₈ at different temperatures during the first heating and cooling cycle. The scale bar is $10 \mu m$.



Figure S14. PLM micrographs of (A) aPOP-SO₂C₅SO₂C₈ and iPOP-SO₂C₅SO₂C₈ at different temperatures during the first heating and cooling cycle. The scale bars is 20 μ m in (A) and 10 μ m in (B).

Figures S13 and S14 show the polarized light microscope (PLM) images of atactic and isotactic POP-SC₅SO₂C₈ and POP-SO₂C₅SO₂C₈ during heating and subsequent cooling processes, respectively. The temperatures were selected based on the DSC results in Figure 10 in the main text. From these PLM images, all the samples showed birefringent with small domains, except that aPOP-SO₂C₅SO₂C₈ exhibited fan texture after recrystallization at 25 °C (Figure S14A(a)-(f)). However, these textures did not show obvious changes before the isotropization temperatures (T_is), above which the birefringence disappeared.



Figure S15. (A) 2D XRD pattern for the aPOP-SC₅SO₂C₈ fiber at room temperature. (B) 1D XRD profiles for the fiber at room temperature and the powder at 61 °C. The inset shows the schematic double layer structure. The * symbols indicate reflections from the Kapton window. (C) 1D XRD profiles of the aPOP-SC₅SO₂C₈ powder sample during heating and cooling processes.

The XRD results of aPOPSC₅SO₂C₈ is shown in Figure S15. From the fiber pattern (Figure 15A), the lamellar reflections were seen on the equator with the *q* ratios being 1:2:3:4:6 (the 5th order reflection is very weak). The inter-side chain crystalline reflection (0.43 nm) was centered on the meridian. The crystalline lamellar spacing was 4.24 nm, consistent with a double layer structure (see the inset of Figure S15B). At 61 °C, the powder sample showed multiple (hk0) reflections in the wide-angle region, together with the lamellar reflections (Figure 15B). Therefore, the phase structure was determined to be smectic E (SmE). Upon heating and cooling in Figure 15C, reversible K \leftrightarrow SmE \leftrightarrow I (isotropic) phase transitions were observed.



Figure S16. (A) 2D XRD pattern for the iPOP-SC₅SO₂C₈ fiber at room temperature. (B) 1D XRD profiles for the fiber at room temperature and the powder at 70 °C. The inset shows the schematic double layer structure. The * symbols indicate reflections from the Kapton window. (C) 1D XRD profiles of the iPOP-SC₅SO₂C₈ powder sample during heating and cooling processes.

XRD results for iPOP-SC₅SO₂C₈ are shown in Figure S16. The fiber pattern was similar to that of the atactic counterpart, except that the crystal orientation was poorer (Figure 16A). The crystalline lamellar spacing was 4.20 nm, consistent with a double layer structure (see the inset in Figure S16B). At 70 °C, multiple (hk0) reflections were seen at the wide-angle region (Figure 16B), suggesting the SmE phase. Upon heating and cooling, reversible K \leftrightarrow SmE \leftrightarrow I phase transitions were observed (Figure 16C).



Figure S17. (A) 2D XRD pattern for the aPOP-SO₂C₅SO₂C₈ fiber at room temperature. (B) 1D XRD profiles for the fiber at room temperature and the powder at 150 and 180 °C. The inset shows the schematic double layer structure. The * symbols indicate reflections from the Kapton window. (C) 1D XRD profiles of the aPOP-SO₂C₅SO₂C₈ powder sample during heating and cooling processes.

XRD results for the aPOP-SO₂C₅SO₂C₈ are shown in Figure S17. From the XRD pattern in Figure S17A, crystalline lamellar structure was observed with the spacing being 4.15 nm. Although fibers could be drawn from the melt, no obvious crystal orientation was observed. This is probably due to the fast crystallization rate of the sample. At 150 °C, multiple (hk0) reflections were seen at the wide-angle region, suggesting the SmE phase. At 180 °C, these wide-angle reflections disappeared and the structure was consistent with the SmA structure (Figure S17B). Upon heating and cooling, reversible K \leftrightarrow SmE \leftrightarrow SmA \leftrightarrow I phase transitions were observed (Figure S17C).



Figure S18. (A) 2D XRD pattern for the iPOP-SO₂C₅SO₂C₈ fiber at room temperature. (B) 1D XRD profiles for the fiber at room temperature and the powder at 170 °C. The inset shows the schematic double layer structure. (C) 1D XRD profiles of the iPOP-SO₂C₅SO₂C₈ powder sample during heating and cooling processes.

XRD results for the iPOP-SO₂C₅SO₂C₈ are shown in Figure S18. From the XRD pattern in Figure S17A, crystalline lamellar structure was observed with the spacing being 4.24 nm (i.e., double layer structure; see the inset of Figure S18B). Again, no crystal orientation could be obtained for the drawn fiber due to fast crystallization rate. At 170 °C, the crystalline structure retained with the lamellar spacing being 4.07 nm and the *q* ratios being 1:2:3:4:6:8 (Figure S18B). Upon heating and cooling, only the K \leftrightarrow I phase transition was observed (Figure S18C).