

Supporting Information

Unusually Stable Aqueous Lyotropic Gyroid Phases from Gemini Dicarboxylate Surfactants

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Experimental

Materials. All materials and reagent grade solvents were purchased from Sigma-Aldrich Chemical Co. (Milwaukee, WI) and used as received unless otherwise noted. 1,4-dibromobutane and 1,6-dibromohexane were distilled and stored under nitrogen. Diisopropylamine (Sigma-Aldrich) was distilled from CaH_2 and stored under nitrogen. Hexamethylphosphoramide (HMPA) was distilled from CaH_2 and stored over 4 Å molecular sieves. 2.5 M *n*-Butyllithium in hexanes was titrated against diphenylacetic acid in THF. Anhydrous and anaerobic THF was obtained by sparging analytical grade solvent with nitrogen for 30 minutes followed by cycling through a column of activated alumina in a Vacuum Atmospheres Solvent purification system.

Molecular characterization. ^1H NMR and ^{13}C NMR spectra were recorded in $\text{DMSO}-d_6$ or methanol- d_4 at 25 °C on both Varian MercuryPlus 300 and Bruker AC+ 300 spectrometers and were referenced to residual protiated solvent peaks in the samples. Mass Spectrometry was performed using a Waters (Micromass) LCT[®] electrospray ionization time-of-flight mass spectrometer operating in negative ion detection mode. Samples dissolved in methanol were sprayed with a sample cone voltage of 20 V. IR spectra were recorded on a Bruker Tensor FT-IR from 4000-500 cm^{-1} , using a diamond crystal attenuated total reflectance (ATR) stage. Elemental analysis (C, H, N) were performed by Columbia Analytical Services (Tuscon, AZ), using Combustion / TC and IR detection.

General Gemini Surfactant Synthesis. We employed a procedure adapted from Pfeffer et. al.¹ A 500ml 2-necked round bottom flask fitted with an addition funnel was charged with a stirbar, THF, (104 mL) and diisopropylamine (17.05 mL, 121 mmol) under nitrogen. This solution was

cooled to -15 °C in an ethanol/water/dry ice bath and *n*-BuLi (42.7 mL of a 2.71M solution in hexanes, 115 mmol) was added dropwise via addition funnel. The reaction mixture was stirred for 30 min, after which a solution of decanoic acid (10.0027g, 58.07 mmol) in THF (58 mL) was added dropwise via addition funnel. HMPA (10.1 mL) was added, and the stirred reaction mixture was warmed to 22 °C for 30 min. The reaction mixture was again cooled to -15 °C, and 1,4-dibromobutane (3.45 mL, 29.0 mmol) was added dropwise. The reaction was then allowed to warm to room temperature and stirred for 4 h. The reaction was quenched by the addition of cold 10% HCl (*aq*) (100 mL), transferred to a separatory funnel, and the aqueous and organic layers were separated. The aqueous layer was extracted with ether (3 x 50 mL) and the combined organic layers were washed with 10% HCl (3 x 50 mL), water (50 mL), and saturated NaCl(*aq*) (50 mL). After drying over MgSO₄(*s*), all volatiles were removed under vacuum. The crude solid was purified by recrystallization from EtOH.

Docosane-9,14-dicarboxylic acid. Synthesized from decanoic acid (10.0027g) and 1,4-dibromobutane (3.45ml); Yield: 9.2816g (80.4%); ¹H-NMR: (299.7 MHz, DMSO-*d*₆) δ 11.968 (COOH, s, 2H), 2.158 (CH-COOH, m, 2H), 1.557-1.018 (CH₂, m, 36H), 0.849 (CH₂-CH₃, t, J = 7.0 Hz, 6H). ¹³C-NMR: (75.4 MHz, DMSO-*d*₆) δ 177.32 (C=O), 45.18 (CH), 32.21 (CH₂), 32.09 (CH₂), 31.67 (CH₂), 29.37 (CH₂), 29.26 (CH₂), 29.04 (CH₂), 27.25 (CH₂), 27.20 (CH₂), 22.48 (CH₂), 14.30 (CH₃). MS (ESI-TOF) calcd. *m/z* for C₂₄H₄₅O₄⁻ 397.3, found: 397.4.

Tetacosane-9,16-dicarboxylic acid. Synthesized from decanoic acid (10.0021 g) and 1,6-dibromohexane (4.42 ml); Yield: 8.3526g (68.2%); ¹H-NMR (299.7 MHz, DMSO-*d*₆): δ 11.951 (COOH, s, 2H), 2.160 (CH-COOH, m, 2H), 1.557-1.082 (CH₂, m, 40H), 0.847 (CH₂-CH₃, t, J = 7.0 Hz, 6H). ¹³C-NMR (75.4 MHz, DMSO-*d*₆): δ 177.34 (C=O), 45.26 (CH), 32.25 (CH₂x2),

31.68 (CH₂), 29.39 (CH₂), 29.27 (CH₂), 29.04 (CH₂), 27.27 (CH₂), 27.21 (CH₂), 22.49 (CH₂), 14.28 (CH₃). MS (ESI-TOF) calcd. *m/z* for C₂₆H₄₉O₄⁻ 425.4, found: 425.4

General procedure for Gemini dicarboxylate salt synthesis.² In a flask equipped with a stirbar, the Gemini diacid (1 mol eq.) and alkali carbonate were suspended in methanol (0.1-0.2M). The mixture was stirred at ambient temperature until it became homogeneous, and then stirring was continued for one additional hour. All volatiles were removed under vacuum and residual water and methanol azeotropically distilled using benzene three times under vacuum. All yields were quantitative.

Sodium Docosane-9,14-dicarboxylate (Na-74). ¹H-NMR (299.7 MHz, CD₃OD): δ 2.144 (CH-COO⁻, m, 2H), 1.529 (CH-CH₂, m, 4H), 1.431-1.158 (CH₂, m, 32H), 0.889 (CH₂-CH₃, t, J = 7.1 Hz, 6H). ¹³C-NMR (75.4 MHz, CD₃OD): δ 184.09 (C=O), 49.49 (CH), 33.41 (CH₂), 33.26 (CH₂), 31.60 (CH₂), 29.59 (CH₂), 29.30 (CH₂), 28.99 (CH₂), 28.19 (CH₂), 27.70 (CH₂), 22.24 (CH₂), 12.96 (CH₃); IR (powder) 2933, 2853, 1551, 1455, 1415, 1320, 1120, 861, 721, 680, 641 cm⁻¹; *Anal.* Calc.: C₂₄H₄₄O₄Na₂•0.5H₂O: C, 63.83; H, 10.04; Found: C, 64.21; H, 10.01.

Potassium Docosane-9,14-dicarboxylate (K-74). ¹H-NMR (299.7 MHz, CD₃OD): δ 2.141 (CH-COO⁻, m, 2H), 1.526 (CH-CH₂, m, 4H), 1.427-1.160 (CH₂, m, 32H), 0.890 (CH₂-CH₃, t, J = 7.1 Hz, 6H). ¹³C-NMR (75.4 MHz, CD₃OD): δ 184.02 (C=O), 49.50 (CH), 33.40 (CH₂), 33.28 (CH₂), 31.60 (CH₂), 29.59 (CH₂), 29.29 (CH₂), 28.99 (CH₂), 28.19 (CH₂), 27.70 (CH₂), 22.25 (CH₂), 12.95 (CH₃). IR (powder) 2924, 2853, 1549, 1456, 1403, 1316, 1120, 951, 721 cm⁻¹; *Anal.* Calc.: C₂₄H₄₄O₄K₂•H₂O; C, 58.49; H, 9.41; Found: C, 58.43; H, 10.99.

Tetramethylammonium Docosane-9,14-dicarboxylate (NMe₄-74). ¹H-NMR (299.7 MHz, CD₃OD): δ 3.194 (s, 24H), 2.143 (CH-COO⁻, m, 2H), 1.532 (CH-CH₂, m, 4H), 1.432-1.148 (CH₂, m, 32H), 0.891 (CH₂-CH₃, t, J = 7.1 Hz, 6H). ¹³C-NMR (75.4 MHz, CD₃OD): δ 183.82

(C=O), 54.39 ($^+N(CH_3)_4$), 49.56 (CH), 33.46 (CH₂), 33.27 (CH₂), 31.60 (CH₂), 29.61 (CH₂), 29.31 (CH₂), 29.00 (CH₂), 28.28 (CH₂), 27.73 (CH₂), 22.25 (CH₂), 12.96 (CH₃). IR (powder) 3017, 2923, 2851, 1563, 1462, 1384, 1312, 1120, 961, 842, 806, 724, 667, 628 cm⁻¹; *Anal.* Calc.: C₃₂H₆₈O₄N₂•3.5H₂O ; C, 63.22; H, 12.43; N, 4.61; Found: C, 63.72; H, 12.79; N, 4.81.

Sodium Tetracosane-9,16-dicarboxylate (Na-76). ¹H-NMR (299.7 MHz, CD₃OD): δ 2.148 (CH-COO⁻, m, 2H), 1.519 (CH-CH₂, m, 4H), 1.423-1.150 (CH₂, m, 36H), 0.891 (CH₂-CH₃, t, J = 7.1 Hz, 6H). ¹³C-NMR (75.4 MHz, CD₃OD): δ 184.08 (C=O), 49.39 (CH), 33.40 (CH₂), 33.29 (CH₂), 31.60 (CH₂), 29.73 (CH₂), 29.58 (CH₂), 29.29 (CH₂), 28.99 (CH₂), 27.83 (CH₂), 27.70 (CH₂), 22.24 (CH₂), 12.94 (CH₃). IR (powder) 2923, 2853, 1549, 1455, 1415, 1322, 1120, 851, 721, 679, 642 cm⁻¹; *Anal.* Calc.: C₂₆H₄₈O₄Na₂ ; C, 66.35; H, 10.28; Found: C, 66.40; H, 10.45.

Gemini LLC Sample Preparation. Aqueous lyotropic liquid crystal (LLC) samples were prepared for X-ray analysis by weighing appropriate amounts of rigorously dried Gemini salt and doubly distilled water into a vial and centrifuging the tightly capped mixture for 10 min, manual mixing using a spatula, and an additional 10 min of centrifugation. Post-centrifugation, the samples were allowed to rest at room temperature for at least 12 h before X-ray diffraction analysis. Samples were stored in tightly sealed vials whenever possible during sample preparation in order to minimize water loss through evaporation.

X-Ray Diffraction. Synchrotron small-angle X-ray scattering (SAXS) measurements were performed at the 12-ID-B beamline at the Advanced Photon Source (Argonne, IL). Experiments employed a beam energy of 12 keV ($\lambda = 1.034$ Å) and a 2.550 m sample-to-detector distance, which was calibrated using a silver behenate standard sample with $d = 58.38$ Å. Two-dimensional SAXS patterns were recorded on a Pilatus 2M detector (25.4 cm x 28.9 cm rectangular area) with 1475 x 1679 pixel resolution. Samples were placed in aluminum DSC

pans with Kapton windows and placed in a Linkam DSC stage. Samples were heated to the desired temperature in a Linkam DSC and allowed to equilibrate for 5 min before data collection (exposure time ~ 1 s). 2D patterns were azimuthally integrated to obtain intensity $I(q)$ v. q plots using DataSqueeze software package (<http://www.datasqueezesoftware.com/>).

Laboratory SAXS measurements were performed in the Materials Science Center at the University of Wisconsin-Madison. Cu- K_α X-rays generated by a Rigaku Micromax 002+ microfocus source were collimated using a Max-Flux multilayer confocal optic (Osmic, Inc.) followed by passage through three pinholes to collimate and trim the final beam diameter to < 0.5 mm. Samples were mounted in a vacuum chamber on a Linkam temperature-controlled hot-stage with a 10 min thermal equilibration time (typical exposure times ~ 3 -5 min). Two-dimensional XRD patterns were recorded on a Gabriel X-ray detector (150mm diameter active circular area) using a sample-to-detector distance of 31.19 cm (calibrated using a silver behenate standard sample with $d = 58.38$ Å).

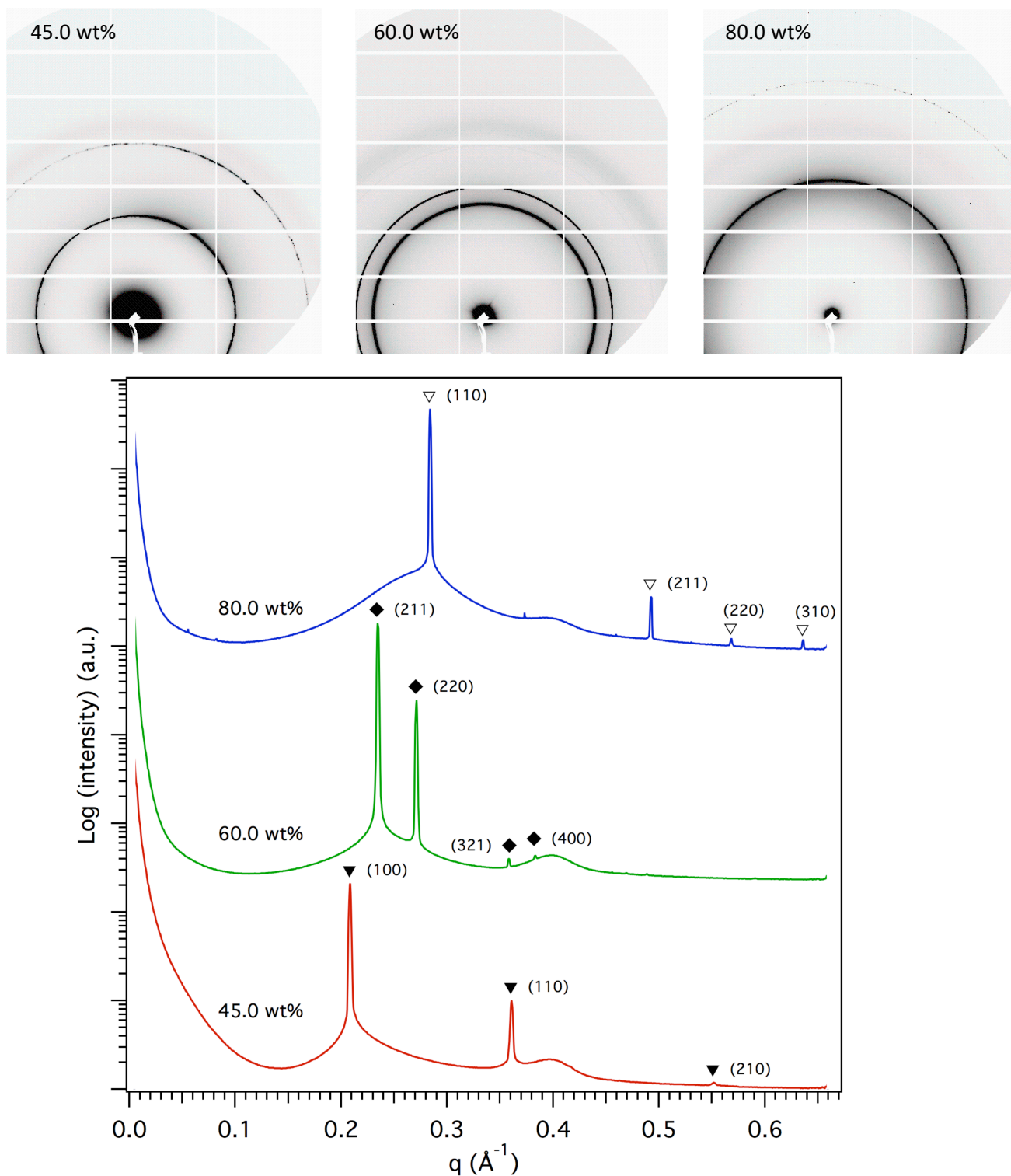


Figure S1. Two-dimensional and azimuthally integrated XRD pattern of **Na-76** at various compositions at 25 °C. Markers on each trace indicate calculated positions for Bragg reflections of the H_1 (∇ , red), G_1 (\blacklozenge , green), and P_1 (∇ , blue) morphologies. The broad low intensity peak at $\sim 0.4 \text{ \AA}^{-1}$ is an artifact resulting from the Kapton windows of the XRD sample holder.

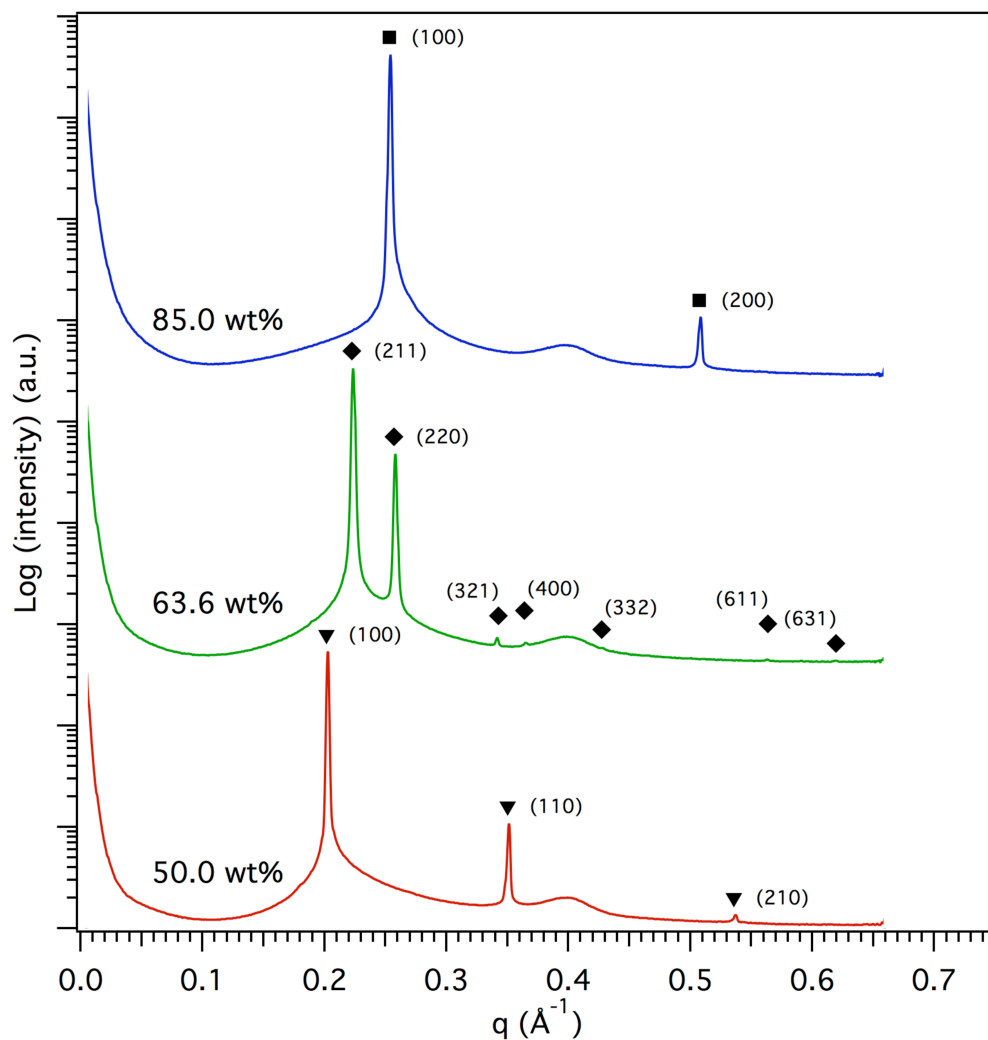
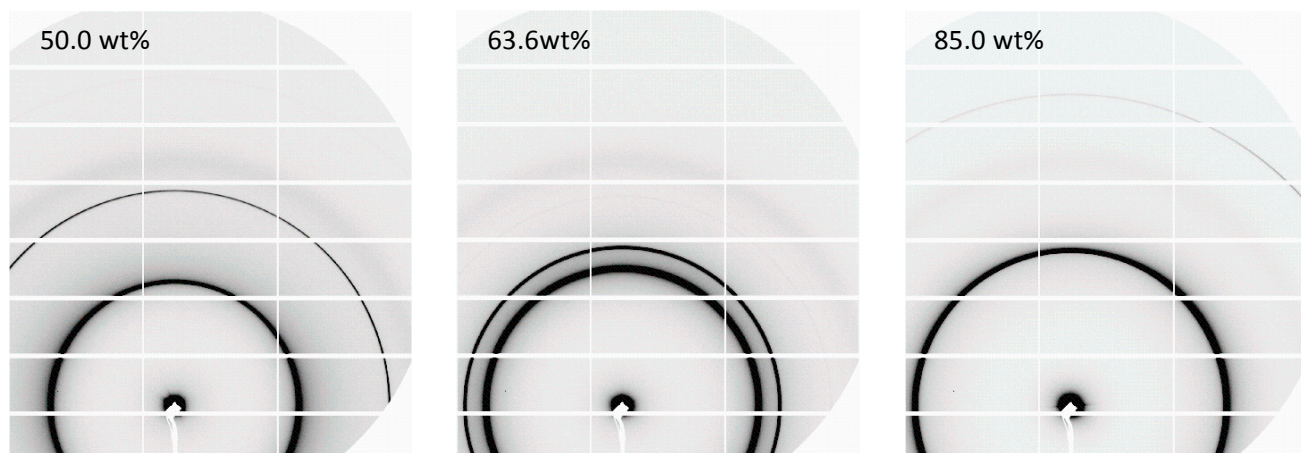


Figure S2. Two-dimensional and azimuthally integrated XRD pattern of **K-74** at various compositions at 25 °C. Markers on each trace indicate calculated positions for Bragg reflections of the H_I (∇ , red), G_I (\blacklozenge , green), and L_α (\blacksquare , blue) morphologies. The broad low intensity peak at $\sim 0.4 \text{ \AA}^{-1}$ is an artifact resulting from the Kapton windows of the XRD sample holder.

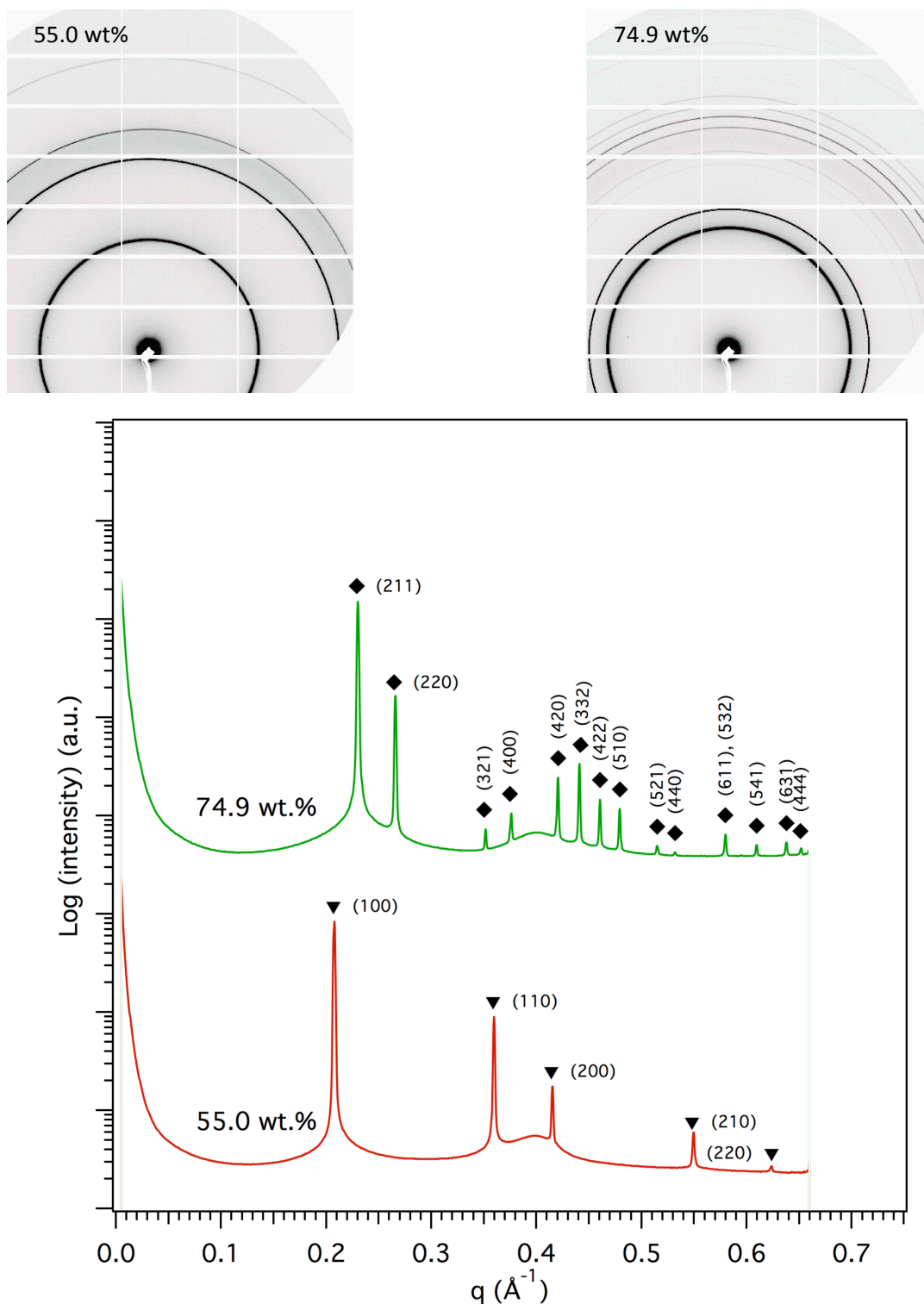


Figure S3. Two-dimensional and azimuthally integrated XRD pattern of $\text{NMe}_4\text{-74}$ at various compositions at 25 °C. Markers on each trace indicate calculated positions for Bragg reflections of the H_1 (\blacktriangledown , red) and G_1 (\blacklozenge , green) morphologies. The broad low intensity peak at $\sim 0.4 \text{ \AA}^{-1}$ is an artifact resulting from the Kapton windows of the XRD sample holder.

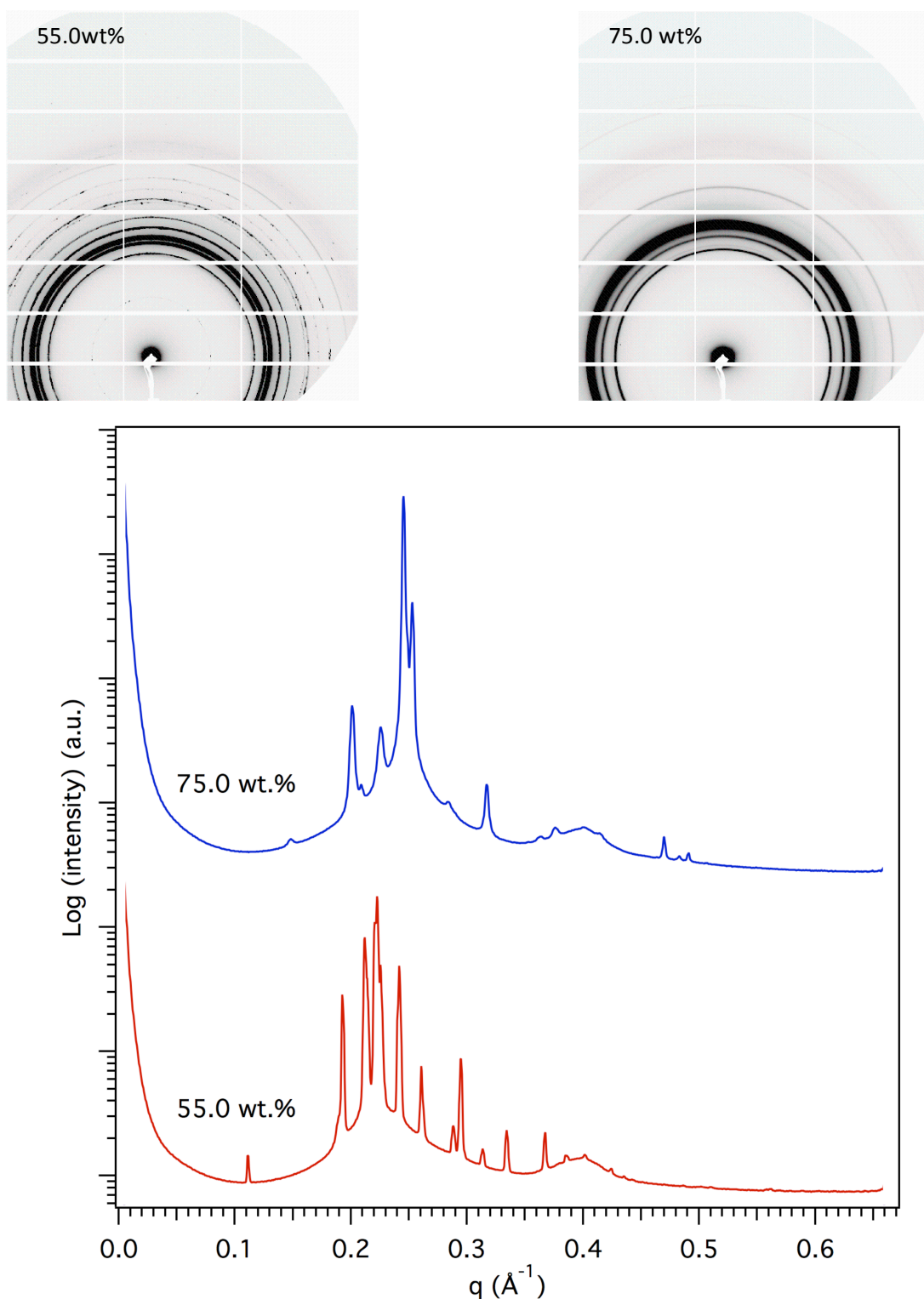


Figure S4. Two-dimensional and azimuthally integrated XRD patterns of **Na-74** unidentified LLC phases at 25 °C. The broad low intensity peak at $\sim 0.4 \text{ \AA}^{-1}$ is an artifact resulting from the Kapton windows of the XRD sample holder.

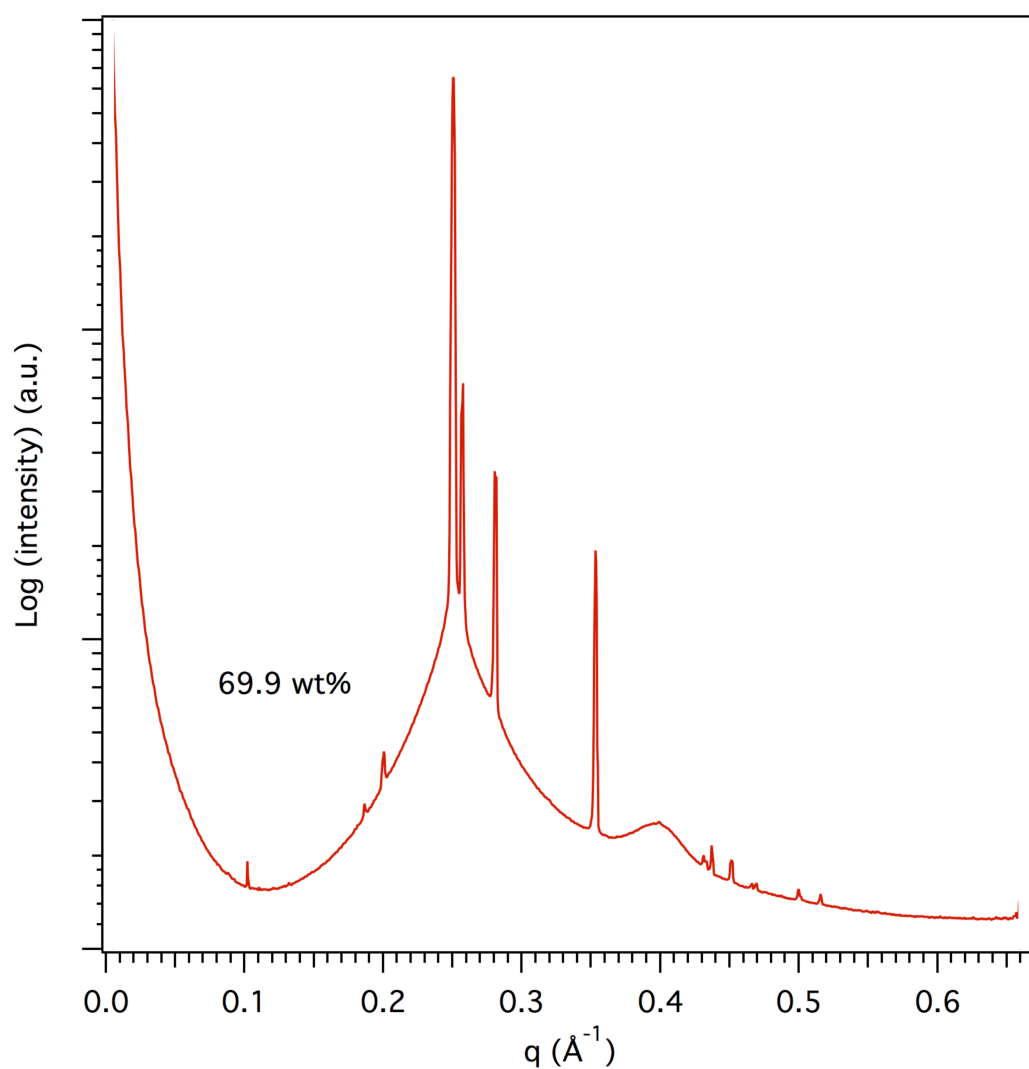
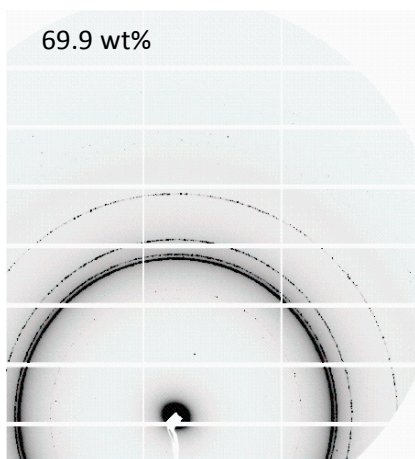


Figure S5. Two-dimensional and azimuthally integrated XRD patterns of **Na-76** unidentified LLC phases at 25 °C. The broad low intensity peak at $\sim 0.4 \text{ \AA}^{-1}$ is an artifact resulting from the Kapton windows of the XRD sample holder.

References:

- (1) Pfeffer, P. E.; Silbert, L. S.; Chirinko, J. M. *J Org Chem* **1972**, 37, 451.
- (2) Hoag, B. P.; Gin, D. L. *Macromolecules* **2000**, 33, 8549.