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Supporting Information

Unexpected Role of Linker Position on Ammonium Gemini Surfactant Lyotropic Gyroid Phase Stability

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Materials. All materials and reagent grade solvents were purchased from Sigma-Aldrich Chemical Company (Milwaukee, WI, U.S.A.) and used as received unless otherwise noted. Anhydrous and anaerobic THF was obtained by sparging analytical grade solvent with nitrogen for 30 min, followed by cycling through a column of activated alumina in a Vacuum Atmospheres Solvent purification system. Dowex®-1 chloride anion exchange resin (20-50 mesh) was purified prior to use by washing with the ion exchange reaction solvent until the washes were colorless. Docosane-9,14-dicarboxylic acid (**1**) was synthesized according to our previously reported procedure.[1]

Molecular characterization. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$, $(CD_3)_2SO$, or CD_3OD at 25 °C on both Bruker Avance-400 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. Samples dissolved were in a 10 mM $CH_3CO_2NH_4$ in CH_3CN and sprayed with a sample cone voltage of 20 V. Elemental analyses (C, H, N) were performed by Atlantic Microlab Inc. (Norcross, GA). C, H, and N were quantified simultaneously using combustion with thermal conductivity and infrared detection. Combustion analysis with ion chromatography detection was used to determine the Cl content.

N,N'*-dinonyl-*N,N,N',N'*-tetramethyl-*N,N'*-butanediyl bis(ammonium) dibromide.** By a modification of the procedure of Mivehi *et al.*,[2] a 50 mL round-bottom flask was charged with a stirbar, *N,N*-dimethylnonylamine (2.002 g, 11.69 mmol), 1,4-dibromobutane (0.64 mL, 5.38 mmol), and acetone (13.5 mL). A water-cooled reflux condenser was attached to the flask and the reaction was heated to reflux for 24 h. The reaction was then cooled to -20°C to crystallize the product. The resulting white precipitate was isolated by vacuum filtration and recrystallized from Et_2O:EtOH (9:1 *v*/*v*, 20mL). Yield: 1.6431g (54.7%). ^{1}H NMR (300 MHz, $CDCl_3$, 22 °C): δ(ppm) 4.03 (CH***$_2$-NMe$_2$, *m*, 4H), 3.42 (C***H***$_2$-NMe$_2$, *m*, 4H), 3.29 (N(C***H***$_3$)$_2$, *s*, 12H), 2.18 (C***H***$_2$-CH$_2$-NMe$_2$, *m*, 4H), 1.78 (C***H***$_2$-CH$_2$-NMe$_2$, *m*, 4H), 1.45-1.18 (C***H***$_2$, *m*, 24H), 0.88 (CH$_2$-C***H***$_3$, *t*, $J^3_{\text{H-H}}$ = 6.92, 6H).

1,4-Bis(nonyl-*N,N,N',N'*-tetramethylammonium)butane dichloride (NCl-84). *N,N'*-dinonyl-*N,N,N',N'*-tetramethyl-*N,N'*-butanediyl-bis(ammonium) dibromide (1.643 g, 2.942 mmol) was taken up in MeOH (40 mL) in a 125 mL Erlenmeyer flask, and stirred over Dowex®-1 chloride anion exchange resin (20.0 g) for 4 d. The reaction solution was transferred to a column packed with additional anion exchange resin (20.0 g) and was eluted through the column dropwise using MeOH (120 mL). Removal of the solvent from the eluent furnished a white solid, which was recrystallized from CH_2Cl_2 (10 mL). Yield: 1.280 g (92.7%). ^{1}H NMR (400 MHz, CD_3OD, 22 °C): δ(ppm) 3.42 (C*H*$_2$-NMe$_2$, *m*, 4H), 3.33 (C*H*$_2$-NMe$_2$, *m*, 4H), 3.11 (N(C***H***$_3$)$_2$, *s*, 12H), 1.84 (C***H***$_2$-CH$_2$-NMe$_2$, *m*, 4H), 1.79 (C***H***$_2$-CH$_2$-NMe$_2$, *m*, 4H), 1.48-1.24 (C***H***$_2$, *m*, 24H), 0.91 (CH$_2$-C***H***$_3$, *t*, $J^3_{\text{H-H}}$ = 7.00, 6H). ^{13}C NMR (101 MHz, CD_3OD, 22 °C): δ(ppm) 65.82(NCH$_2$), 64.32(NCH$_3$), 51.26 (NCH$_2$), 33.00(CH$_2$), 30.57(CH$_2$), 30.34(CH$_2$), 30.31(CH$_2$), 27.46(CH$_2$), 23.72(CH$_2$), 23.62(CH$_2$), 20.70(CH$_2$), 14.42(CH$_3$). MS (ESI-TOF) Calcd: *m/z* for $C_{26}H_{58}N_2^{2+}$ 199.2293, Found: 199.2292; Calcd: *m/z* for $C_{26}H_{58}ClN_2^{+}$ 433.4284, Found: 433.4. Elemental Anal. Calc.: $C_{26}H_{58}Cl_2N_2$•1.4H_2O: C, 63.10; H, 12.10; N, 5.66; Cl, 14.33 Found: C, 63.33; H, 12.44; N, 5.66; Cl, 14.13.

Docosane-9,14-diamine (2). ***CAUTION: this procedure adapted from Hall et al.[3] involves the in situ generation of hydrazoic acid, which is volatile, highly toxic, and explosive. Exercise***

care while attempting this reaction! In a 50 mL round-bottom flask, **1** (1.500 g, 3.763 mmol) was dissolved in a mixture of concentrated H_2SO_4 (7.50 mL) and C_6H_6 (7.50 mL). This biphasic mixture was stirred vigorously while NaN_3 (0.739 g, 11.4 mmol) was added portionwise (4 x 0.18 g). After stirring at 22 °C for 1.5 h, the reaction flask was cooled to 0 °C in an ice water bath and 30 wt% NaOH(*aq*) (25 mL) was added dropwise. After allowing the reaction to slowly warm to 22 °C and stir for 1 h, the heterogeneous reaction mixture was diluted with H_2O until it became homogeneous. This solution was extracted with Et_2O (3 x 75 mL). The combined organic extracts were washed sequentially with H_2O (70 mL) and saturated NaCl(*aq*). After drying over $NaSO_4$(*s*), all volatiles were removed under vacuum to yield a transparent pale yellow oil. This reaction product was used in subsequent preparations without further purification. Yield 1.271 g (99.3 %). ^1H NMR (400 MHz, $CDCl_3$, 22 °C): δ (ppm) 2.68 (C***H***-NH_2, *m*, 2H), 1.70-1.00 (C$\boldsymbol{H}_2$ and N$\boldsymbol{H}_2$, *m*, 20H), 0.88 (CH2-C$\boldsymbol{H}_3$, *t*, J^3_{H-H} = 6.92 Hz, 6H).

Docosane-9,14-bis(*N,N,N*-trimethylammonium) dichloride (NCl-84α). A 200 mL round-bottom flask was charged with a stirbar, **2** (1.271 g, 3.735 mmol), K_2CO_3 (1.549 g, 11.21 mmol), CH_2Cl_2 (10.0 mL), and MeOH (20.0 mL). CH_3I (2.50 mL, 40.1 mmol) was added to the stirred heterogeneous reaction, and the reaction flask was fitted with a water-cooled condenser and heated to 50 °C for 4 h. After allowing the reaction to cool slowly to 22 °C, the reaction was further chilled in a freezer at -20°C for 16 h to crystallize the product. The resulting white crystalline solid was isolated by vacuum filtration, redissolved in MeOH (50 mL), and stirred with Dowex®-1 anion chloride exchange resin (10.0 g) for 4 h. The reaction mixture was then transferred to a column packed with additional anion exchange resin (20.0 g) and was eluted through the column dropwise using MeOH (150 mL). The volatile reaction solvent was removed under vacuum and the resulting off-white solid was thoroughly dried by lyophilization with C_6H_6 (2 x 25 mL). Yield: 1.520 g (81.8 %). This reaction product was used in subsequent preparations without further purification. ^{1}H NMR (400 MHz, CD_3OD, 22 °C): δ(ppm) 3.24 (C***H***-NMe$_3$, *m*, 2H), 3.12 (N(C***H***$_3$)$_3$, *s*, 18H), 2.15-1.90 (C***H***$_2$-CH, *m*, 4H), 1.75-1.21 (C***H***$_2$, *m*, 32H) 0.91 (CH$_2$-C***H***$_3$, *t*, $J^3_{\text{H-H}}$ = 6.83 Hz, 6H). ^{13}C NMR (101 MHz, CD_3OD, 22 °C): δ(ppm) 77.22 (CH), 51.72(N(CH$_3$)$_3$), 33.03(CH$_2$), 31.13(CH$_2$), 31.12(CH$_2$), 30.95(CH$_2$), 30.92(CH$_2$), 30.74(CH$_2$), 30.73(CH$_2$), 30.57(CH$_2$) (CH$_2$), 30.55(CH$_2$), 30.44(CH$_2$), 30.43(CH$_2$), 29.25(CH$_2$), 29.19(CH$_2$), 29.09(CH$_2$), 29.01(CH$_2$), 23.74(CH$_2$), 14.44(CH$_3$). MS (ESI-TOF) Calcd: *m/z* for $C_{28}H_{62}N_2^{+2}$ 213.2452, Found: 213.2447; Calcd: *m/z* for $C_{28}H_{62}ClN_2^+$ 461.4597, Found: 461.4. *Elemental Anal. Calc.*: $C_{28}H_{62}Cl_2N_2$•0.5H_2O: C, 66.37; H, 12.43; N, 5.53; Cl, 13.99 Found: C, 66.31; H, 12.45; N, 5.43; Cl, 13.78.

Docosane-9,14-bis(*N,N*-dimethylamide) (3). $SOCl_2$ (1.10 mL, 15.1 mmol) was added dropwise to a 100 mL round-bottom flask containing **1** (2.001 g, 5.020 mmol) and anhydrous THF (5.0 mL). Upon stirring this reaction for 3 h at 22 °C, A solution of $HN(CH_3)_2$ (15.1 mL, 2.0 M in THF, 30.2 mmol) was added dropwise, at a rate that allowed gas evolution to cease between drops. The resulting heterogeneous mixture was allowed to stir for 16 h. 2 M HCl (25 mL) was added to the reaction solution to quench the reaction, and the aqueous layer was extracted with diethyl ether (3 x 25 mL). The combined organic extracts were washed sequentially with H_2O (25 mL) and saturated NaCl(*aq*) (25 mL). After drying over $MgSO_4$(*s*), all volatiles were removed under vacuum. Yield: 2.002 g (88.1 %). ^{1}H NMR (400 MHz, $CDCl_3$, 22 °C): δ(ppm) 3.04 ((C=O)-N(C***H***$_3$)$_2$, *s*, 6H), 2.96 ((C=O)-N(C***H***$_3$)$_2$, *s*, 6H), 2.61 (C***H***-(C=O), *m*, 2H), 1.60 (C***H***$_2$-CH, *m*, 4H), 1.47-1.11 (C***H***$_2$, *m*, 32H), 0.87 (CH2-C***H***$_3$, *t*, $J_{\text{H-H}}$ = 7.0 Hz, 6H).

Docosane-9,14-bis(methyl-*N,N*-dimethylamine) (4). A 100 mL Kjeldahl flask under N_2(*g*) was charged with a solution of **3** (2.002 g, 4.422 mmol) in THF (57.5 mL). $LiAlH_4$ (0.438 g, 11.5 mmol) was carefully added under N_2(*g*) purge. The resulting heterogeneous reaction mixture was heated to 50 °C for 24 h in an oil bath. The reaction was slowly quenched by adding water (1.0 mL) dropwise, at a rate that allowed gas evolution to cease between drops. A 25 wt% solution of NaOH(*aq*) (1.0 mL) was subsequently added, followed by additional H_2O (5.0 mL). The heterogeneous mixture was filtered and the solids were washed with Et_2O (50 mL). The filtrate was also extracted with additional Et_2O (3 x 25 mL) and the combined extracts were washed with saturated NaCl(*aq*) (25 mL). After drying over $MgSO_4$(*s*), all solvents were removed under vacuum. This reaction product was used in subsequent preparations without further purification. Yield: 1.735 g (92.3%). ^1H NMR (400 MHz, $CDCl_3$, 22 °C): δ(ppm) 2.18 ($N(C\boldsymbol{H}_3)_2$, *s*, 12H), 2.06 ($CH\text{-}C\boldsymbol{H}_2\text{-}NMe_2$, *d*, $J^3_{H\text{-}H}$ = 7.00 Hz, 4H), 1.45 ($C\boldsymbol{H}$, m, 2H), 1.37-1.15 ($C\boldsymbol{H}_2$, *m*, 36H), 0.88 ($CH_2\text{-}C\boldsymbol{H}_3$, *t*, $J^3_{H\text{-}H}$ = 7.00, 6H). ^{13}C NMR (101 MHz, $CDCl_3$, 22 °C): δ(ppm) 65.16 ($N\text{-}CH_2$), 46.23 ($N(CH_3)_2$), 35.93 (CH), 32.46 (CH_2), 32.43 (CH_2), 32.08 (CH_2), 30.32 (CH_2), 29.85 (CH_2), 29.52 (CH_2), 27.28 (CH_2), 27.26 (CH_2), 26.83 (CH_2), 22.84 (CH_2), 14.28 (CH_3).

Docosane-9,14-bis(methyl-trimethylammonium) diiodide (5). In a 100 mL round-bottom flask **4** (1.735 g, 4.082 mmol) was dissolved in CH_2Cl_2 (8.0 mL), and CH_3I (0.80 mL, 12.8 mmol) was added. The flask was fitted with a water-cooled reflux condenser and heated to reflux. After refluxing for 4 h the reaction was allowed to cool and to continue stirring for 16 h. All volatiles were removed under vacuum and the crude material was recrystallized from 2:1 EtOH: Et_2O. Yield: 1.3672 g (47.2 %). ^1H NMR (400 MHz, $CDCl_3$, 22 °C): δ(ppm) 3.94 ($N\text{-}C\boldsymbol{H}_2$, *m*, 2H), 3.50 (N(C***H***$_3$)$_3$, *s*, 18H), 3.18 (N-C***H***$_2$, *m*, 2H), 1.70-1.15 (C***H***$_2$, *m*, 36H), 0.88 (CH$_2$-C***H***$_3$, *t*, $^3J_{\text{H-H}}$ = 7.00 Hz, 6H).

Docosane-9,14-bis(methyl-trimethylammonium) dichloride (NCl-74β). 5 (1.367 g, 1.929 mmol) was taken up in MeOH (25.0 mL) and stirred over Dowex®-1 chloride anion exchange resin (10.54 g) for 2 h. The reaction solution was transferred to a column packed with additional ion exchange resin (20.38 g), and this solution was eluted through the column dropwise using methanol (75.0 mL). All volatile solvents were removed under vacuum. Yield: 1.008 g (99.2 %). ^{1}H NMR (400 MHz, CD$_3$OD, 22 °C): δ(ppm) 3.30 (N-C***H***$_2$, *m*, 4H), 3.15 (N(C***H***$_3$)$_2$, *s*, 18H), 1.94 (C***H***, *m*, 2H), 1.58-1.21 (C***H***$_2$, *m*, 36H) 0.90 (CH$_2$-C***H***$_3$, *t*, $J^3_{\text{H-H}}$ = 7.04 Hz, 6H). ^{13}C NMR (101 MHz, CD$_3$OD, 22 °C): δ(ppm) 72.37 (N-CH$_2$), 53.76 (N(CH$_3$)$_3$) , 35.01 (CH), 34.87 (CH$_2$), 34.33 (CH$_2$), 33.06 (CH$_2$), 30.99 (CH$_2$), 30.71 (CH$_2$), 30.46 (CH$_2$), 27.51 (CH$_2$), 27.28 (CH$_2$), 23.74 (CH$_2$), 14.44 (CH$_3$). MS (ESI-TOF) calcd: *m/z* for $C_{30}H_{66}ClN_2^+$ 489.4910, Found: 489.4923, calcd: *m/z* for $C_{30}H_{66}N_2^{2+}$ 227.2603, Found: 227.2. Elemental Anal. Calc.: $C_{30}H_{66}Cl_2N_2$•1.35H$_2$O: C, 65.50; H, 12.34; N, 5.09; Cl, 12.89 Found: C, 65.50; H, 12.64; N, 5.08; Cl, 12.82.

Gemini LLC Sample Preparation. Aqueous lyotropic liquid crystal (LLC) samples were prepared for X-ray scattering analyses by massing appropriate amounts of rigorously dried Gemini salt and deionized water (Thermo Scientific Barnstead NANOpure™ system, 18 MΩ) into a vial and centrifuging the tightly capped mixture at 10,000 rpm for 10 min, manual mixing using a spatula, and an additional 10 min of centrifugation. The samples were allowed to rest at 22 °C for at least 12 h post-centrifugation and prior to small-angle X-ray scattering (SAXS) analyses. Samples were stored in tightly sealed vials whenever possible during sample preparation, in order to minimize water loss through evaporation.

Small-Angle X-Ray Scattering (SAXS) Experimental Conditions. 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 14 keV (λ = 0.88560 Å) and a 2.027 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 sealed in hermetic aluminum DSC pans (TA Instruments) and thermostatted in a Linkam DSC stage. Samples were heated to the desired temperature in the Linkam DSC stage and allowed to equilibrate for 5 min before data collection (typical exposure time ~1 s). 2D–SAXS patterns were azimuthally-integrated to obtain intensity I(q) *v.* q plots using MatLab software at beamline 12-ID-B. I(q) *v.* q plots were manipulated in Igor Pro 6.3 using procedures developed by Schmitt *et al.*[4]

Laboratory small angle X-ray scattering (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 the final beam with a 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 ~10 min). 2D-SAXS patterns were recorded on a Gabriel X-ray detector (150 mm diameter active circular area) using a sample-to-detector distance of 32 cm (calibrated using a silver behenate standard sample with d = 58.38 Å). 2D patterns were azimuthally integrated to obtain intensity $I(q)$ $v.$ q plots using the DataSqueeze software package.[5]

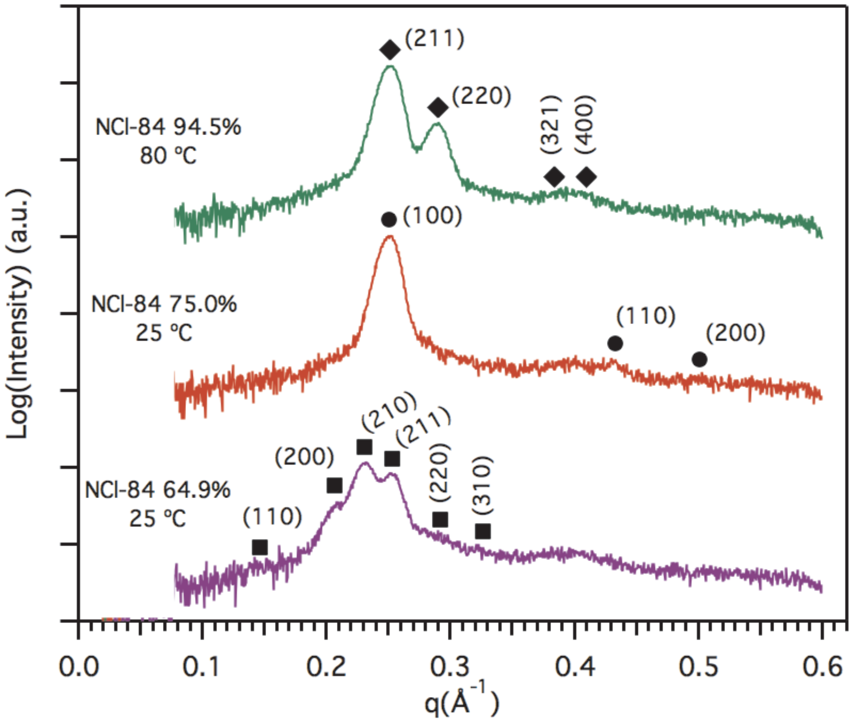

Figure S1. Laboratory source azimuthally-integrated SAXS patterns of **NCl-84** LLCs at 64.9, 75.0. and 94.5 wt% surfactant. Markers on each trace indicate the calculated peak positions for the $Pm\bar{3}n$ (■), H_I (●), and G_I (◆) LLC morphologies. The broad scattering feature at approximately 0.4 Å^{-1} is due to the Kapton® in the SAXS sample holder.

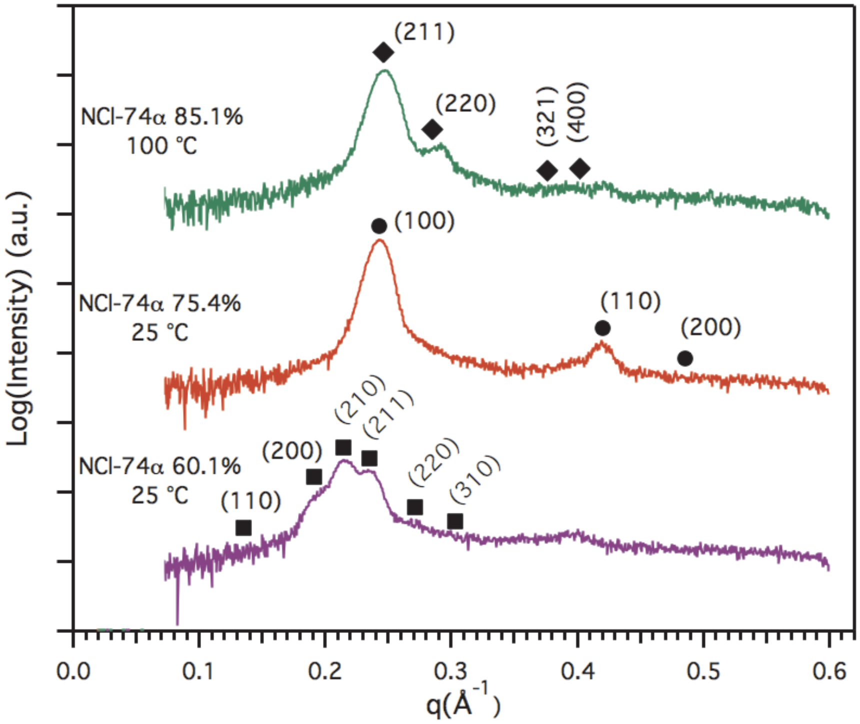

Figure S2. Laboratory source azimuthally-integrated SAXS patterns of **NCl-74α** LLCs at 60.1, 75.4, and 85.1 wt% surfactant. Markers on each trace indicate the calculated peak positions for the $Pm\overline{\mathbf{3}}n$ (■), H_I (●), and G_I (◆) LLC morphologies. The broad scattering feature at approximately 0.4 Å^{-1} is due to the Kapton® in the SAXS sample holder.

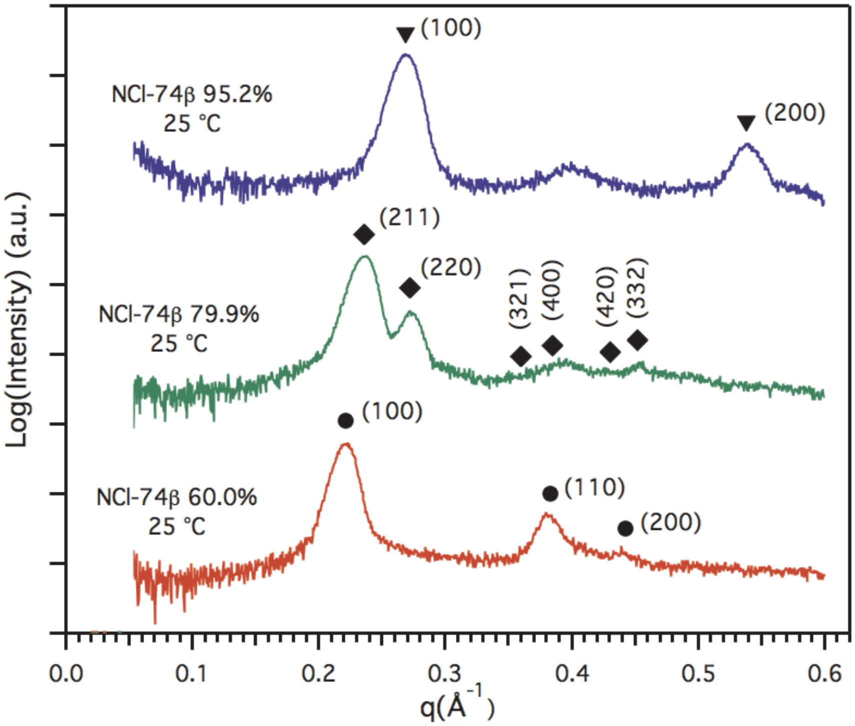

Figure S3. Laboratory source azimuthally-integrated SAXS patterns of **NCl-74β** LLCs at 60.0, 79.9 and 95.2 wt% surfactant. Markers on each trace indicate the calculated peak positions for the H_I (•), and G_I (◆), and L_α (▼) LLC morphologies. The broad scattering feature at approximately 0.4 Å^{-1} is due to the Kapton® in the SAXS sample holder.

References:

(1) Sorenson, G. P.; Coppage, K. L.; Mahanthappa, M. K. *J. Am. Chem. Soc.* **2011**, *133*, 14928.

(2) Mivehi, L.; Bordes, R.; Holmberg, K. *Langmuir* **2011**, *27*, 7549.

(3) Hall, D. M.; Mahboob, S.; Turner, E. E. *Journal of the Chemical Society (Resumed)* **1950**, 1842.

(4) Schmitt, A. K.; Mahanthappa, M. K. *Computer Code for Materials Scientists: Igor Pro Procedures for Analyzing Dynamic Light Scattering, Rheology, and Synchrotron X-ray Scattering Data*, 2013, fig**share**. http://dx.doi.org/10.6084/m9.figshare.644515

(5) Heiney, P. A. http://www.datasqueezesoftware.com/.