

Supporting Information

Reverse Hexosome Dispersions in Alkane – The Challenge of Inverting Structures

Franz Pirolt[†], Otto Glatter[‡], Gregor Trimmel[†]*

*[†] Institute for Chemistry and Technology of Materials, Graz University of Technology,
Stremayrgasse 9, 8010 Graz, Austria*

*[‡] Institute for Inorganic Chemistry, Graz University of Technology,
Stremayrgasse 9, 8010 Graz, Austria*

Number of pages: 13

Number of figures: 8

Number of tables: 1

Screening of Bulk Phases from E4–E9. Two-component systems of primary surfactant and water (δ value) were prepared in a number of different ratios. The samples were heated to 80°C to allow homogeneous mixing. Characterization was done by SAXS and polarization microscopy after cooling with an airgun during vortexing. Figure S1 and S2 show the results for the Genapol® samples E4–E9 with ethylene oxide unit numbers between 4 and 9.

E4 to E6 showed primarily the formation of a lamellar phase recognizable by the Maltese crosses in the polarization microscope pictures, and equidistant reflexes in the SAXS curve.

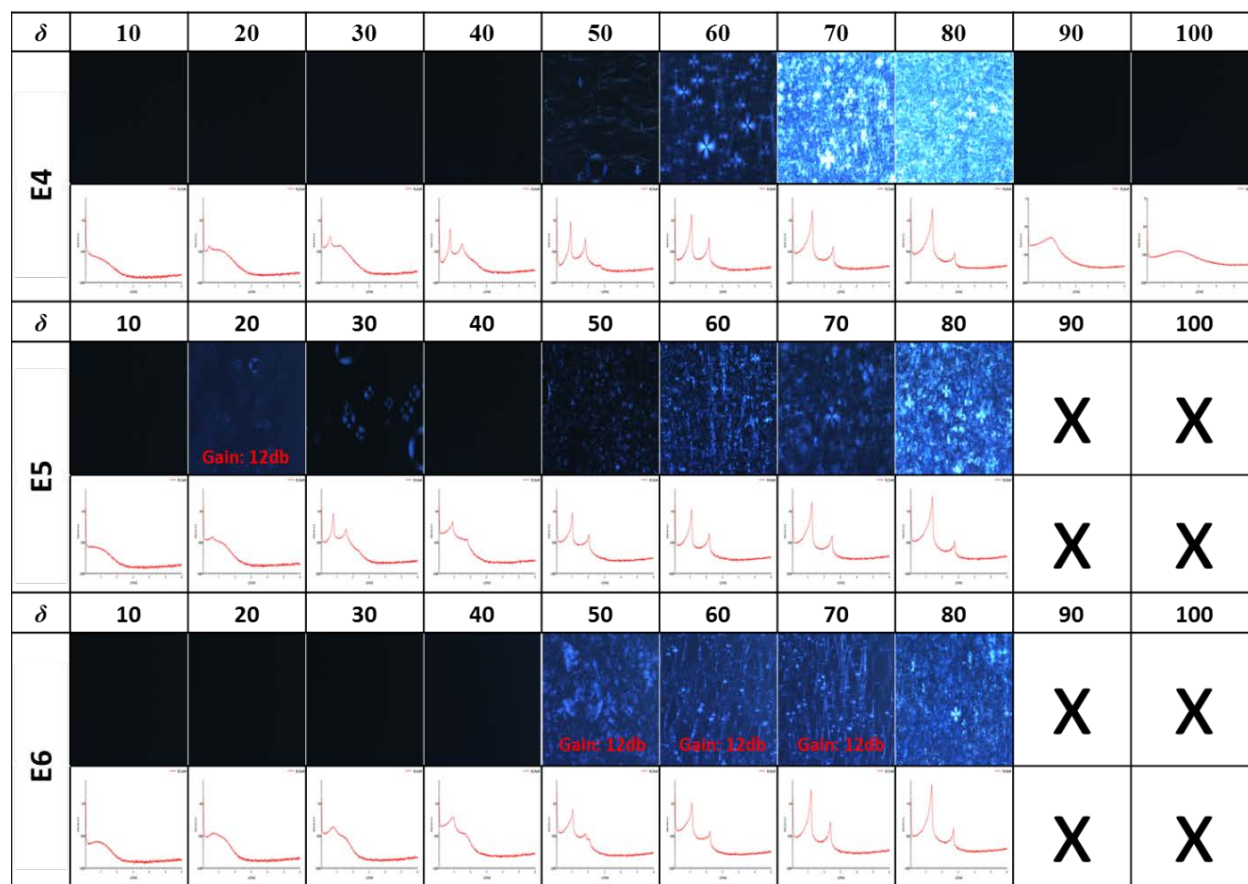


Figure S1: 1) Screening of bulk phases, results for E4–E6. **X**: insufficient sample for measurement. Upper rows: polarization-microscope pictures; lower rows: SAXS curves (log(intensity) vs. q)

E7–E9 exhibit different behavior from that shown by E4–E6: A hexagonal phase appears when δ lies between 40 and 60. The lattice parameter of E7–E9 is estimated to be between 7.20 nm at $\delta = 40$ and 6.17 nm at $\delta = 60$.

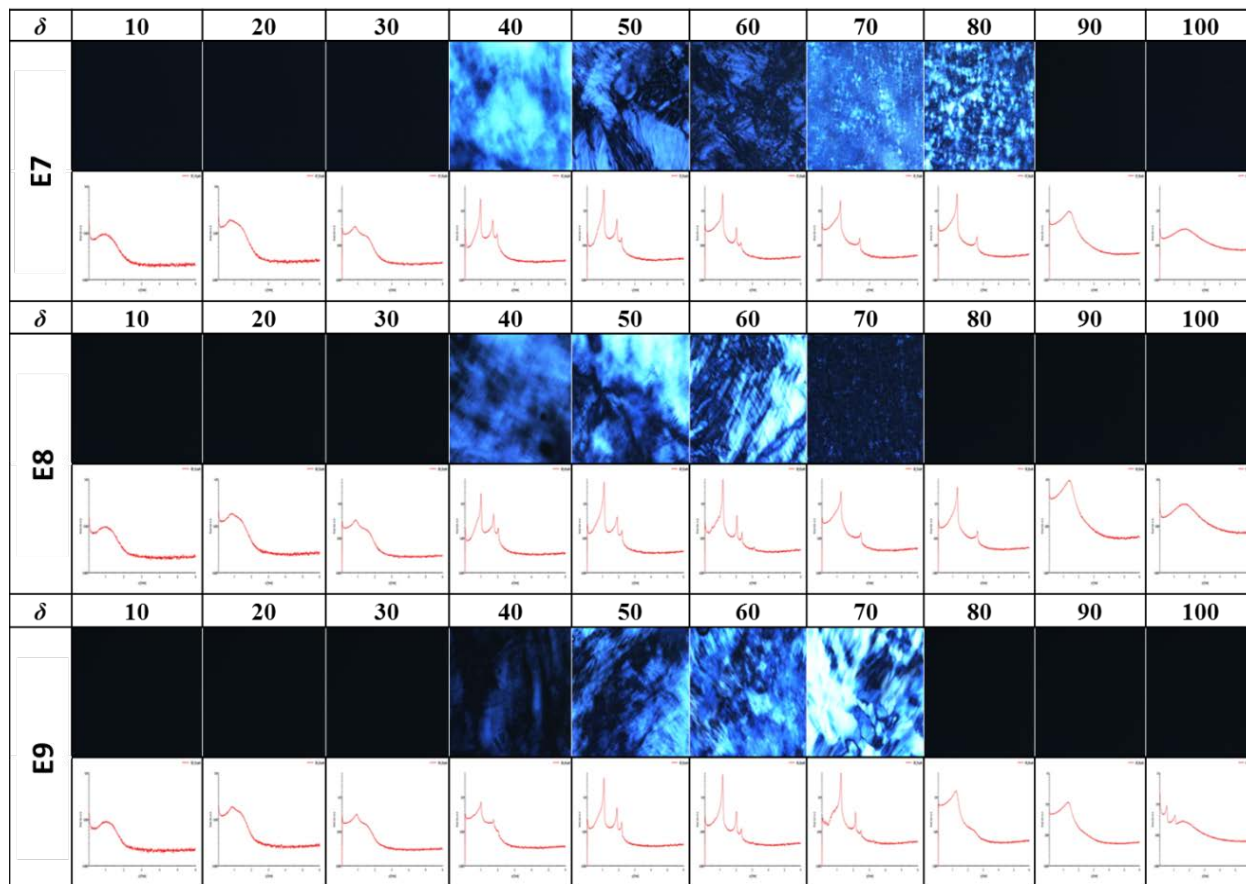


Figure S2: Screening of bulk phases for E7–E9. Upper rows: polarization-microscope pictures; lower rows: SAXS curves (log(intensity) vs. q)

L64 showed a H_I hexagonal phase at δ 55. Starting at δ 65 a weak lamellar phase ($L\alpha$) was formed and vanished above δ 80 .

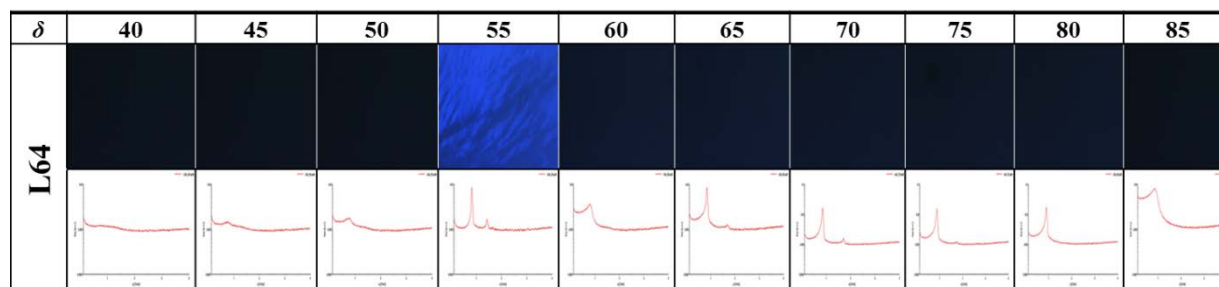


Figure S3: Screening of bulk phases for L64. Upper rows: Polarization-microscope pictures; lower rows: SAXS curves (log(Intensity) vs. q)

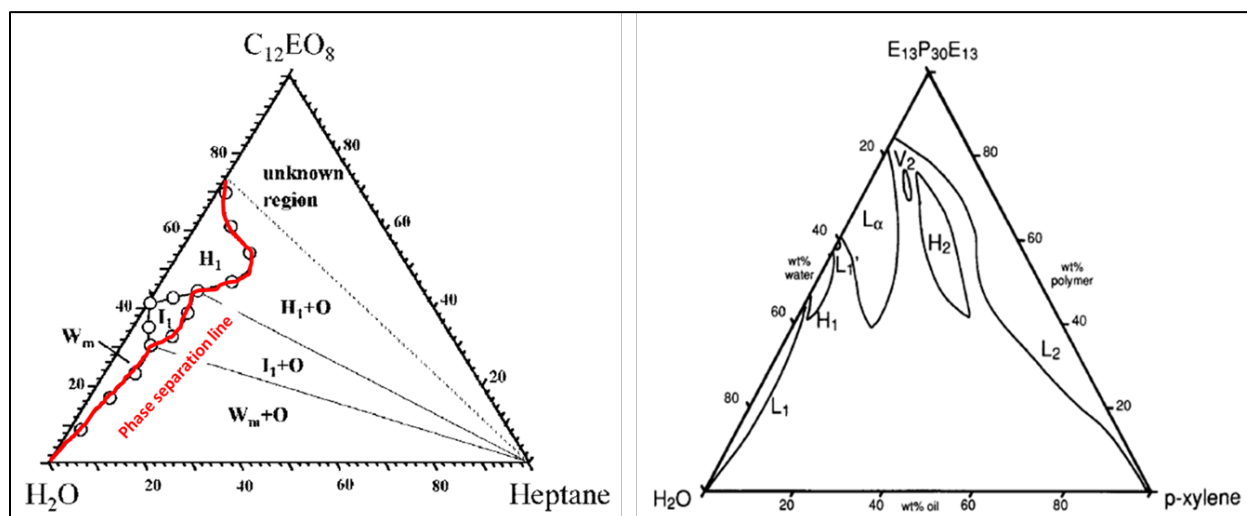


Figure S4: Phase diagrams. Left side: Brij $C_{12}EO_8$ (8 ethylene oxide units) adapted from Aramaki et al.¹ Right side: L64 from Alexandridis et al.²

1) Oil Loading

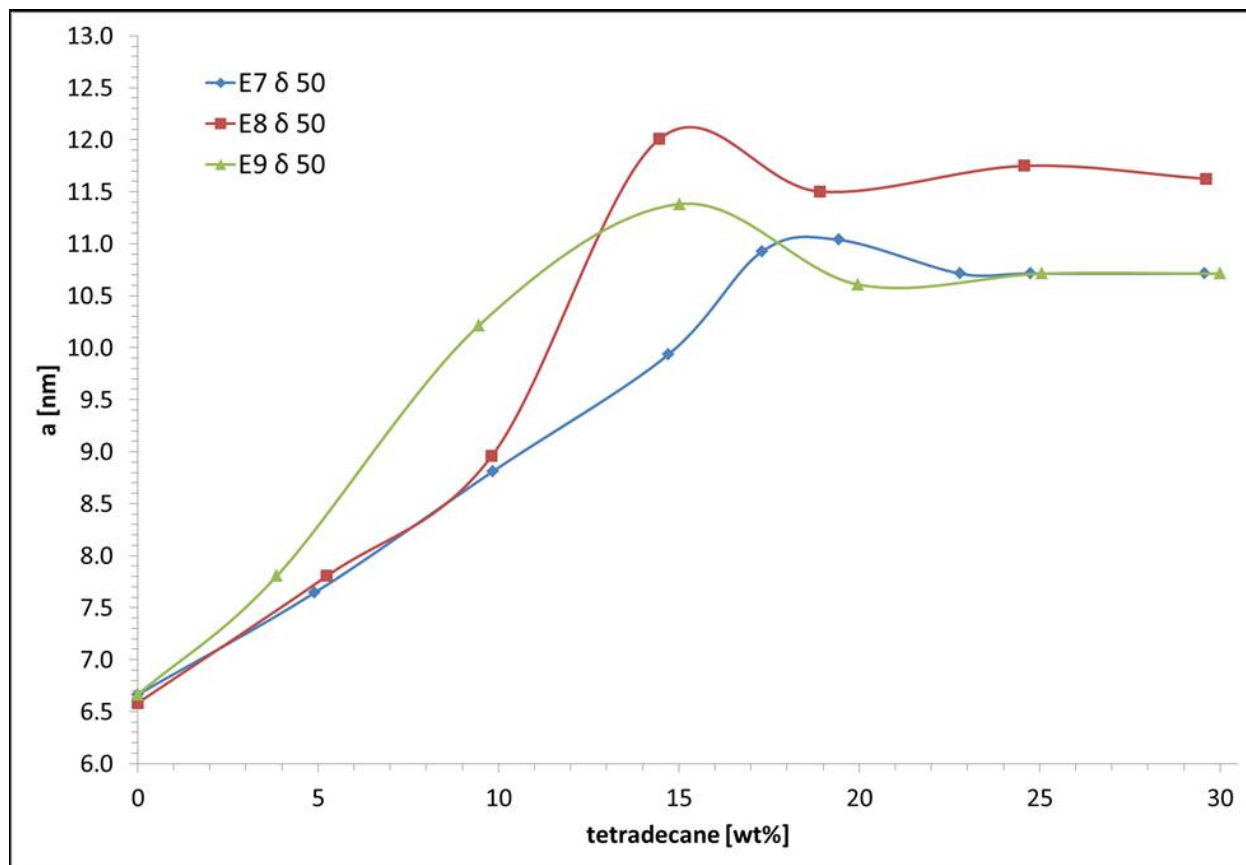


Figure S5: Oil-loading capacity of E7–E9: swelling of the lattice constant a .

Tetradecane was added successively to the bulk samples consisting of primary surfactant and water. At each step, the samples were heated to 80°C to melt the liquid crystal and to allow the oil to be incorporated. After accelerated cooling with an airgun during vortexing to ensure homogeneity, the samples were characterized with SAXS, and the lattice parameter a was estimated from the SAXS curves.

2) Monomer Synthesis

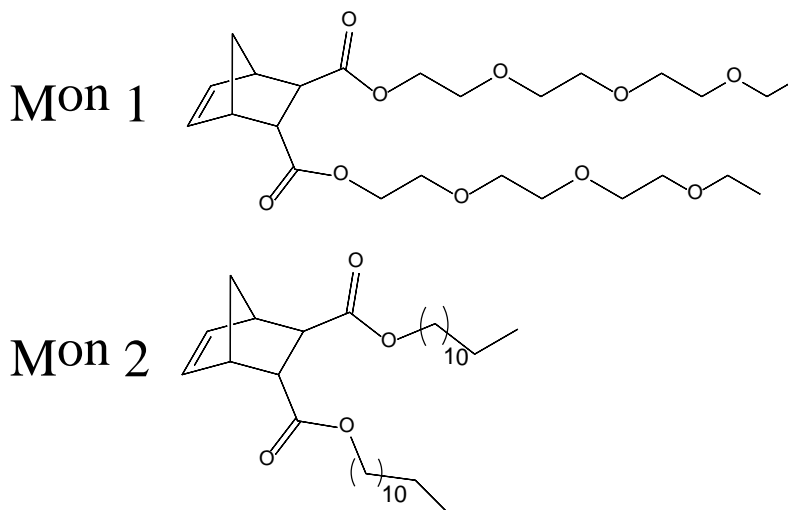


Figure S6: Monomeric units.

Mon1: Norbornene-2,3-di-carboxylic acid-di-2-(2-(2-ethoxyethoxy)ethoxy)ethylester, hydrophilic unit.

Mon2: Norbornene-2,3-di-carboxylic acid-di-dodecylester, lipophilic unit

Synthesis procedures and characterization

The reaction apparatuses were dried by heating, repeated evacuation and purging with N₂ gas. All reagents and solvents were purchased from commercial sources like Sigma Aldrich (Switzerland) or ABCR (Germany) and were used as received.

Complex M31 [1,3-bis (2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro-(3-phenyl-1H-inden-1-ylidene) (pyridyl) ruthenium(II) was obtained from UMICORE AG Co.

¹H NMR spectroscopy was performed on a Bruker Avance 300 MHz spectrometer. Deuterated solvents (chloroform-d, DMSO-d₆, D₂O) were obtained from Cambridge Isotope Laboratories Inc. Remaining solvent peaks were referenced according to the literature³. Peak shapes are specified as follows: s (singlet), bs (broad singlet), d (doublet), dd (doublet of doublets),

t (triplet), q (quadruplet) and m (multiplet). Silica gel 60 F254 was used for thin layer chromatography (TLC), purchased from Merck. Bands were visualised under UV light or by dipping into an aqueous solution of KMnO_4 (0.1 wt%).

Synthesis of Norbornene-2,3-di-carboxylic acid-di-2-(2-ethoxyethoxy)ethoxyethylester (Mon1)

The synthesis was adapted from Sandholzer et al.⁴ A 150 mL round bottom flask was filled with norbornene-2,3-di-carbonyl chloride (0.50 g, 2.30 mmol) and dichloromethane (10 mL; dry). To the mixture were added 2-(2-(2-ethoxyethoxy)ethoxy)ethanol (0.65 g, 4.82 mmol; predried by lyophilisation) and 4-(dimethylamino)-pyridine (0.01 g, 0.11 mmol) before the mixture was cooled in an ice bath. Pyridine (0.38 g, 4.82 mmol) was dissolved in dichloromethane (10 mL; dry) and added dropwise to the cooled mixture, after which the mixture was stirred for 24 h at room temperature. The reaction was monitored by TLC. Water (2 mL) was added to quench the remaining carbonyl chloride. The resulting white precipitate was filtered, and the reaction mixture was extracted with hydrochloric acid (3 x 10 mL; 2M) to remove the pyridine. The organic layer was dried with Na_2SO_4 and filtered. The solvent was removed *in vacuo*. The product was purified by column chromatography (SiO_2 / dichloromethane : acetone, 10 : 1) to afford a colorless oil in 46% yield. $^1\text{H-NMR}$ (δ , 20°C, CDCl_3 , 300 MHz): 1.41–1.46 (d, $^3J_{\text{HH}} = 9.0$ Hz, 1H, H_{nb7a}), 1.58–1.64 (d, $^3J_{\text{HH}} = 9.0$ Hz, 1H, H_{nb7b}), 2.72–2.74 (m, 1H, H_{nb3}), 3.14 (bs, 1H, H_{nb4}), 3.28 (bs, 1H, H_{nb1}), 3.41–3.44 (t, $^3J_{\text{HH}} = 3.81$ Hz, 1H, H_{nb2}), 3.48–3.73 (m, 12H, 2x -O-CH₂-CH₂-O-), 4.12–4.31 (m, 4H, 2x -OOC-CH₂-), 6.04–6.09 (m, 1H, H_{nb6}), 6.25–6.28 (m, 1H, H_{nb5}).

Synthesis of Norbornene-2,3-di-carboxylic acid-di-dodecylester (**Mon2**)

The procedure was analogous to the synthesis of monomer 1, but using norbornene-2,3-di-carboxylchloride (0.5 g, 2.30 mmol), and dodecan-1-ol (0.90 g, 4.82 mmol). The product was purified by column chromatography (SiO₂ / dichloromethane) to afford a colorless oil in 36% yield. ¹H-NMR (δ, 20°C, CDCl₃, 300 MHz): 6.27–6.06 (m, 2H, H_{nb5,6}), 4.09–4.02 (m, 4H, 2*[COO-CH₂-CH₂]), 3.37, 3.25, 3.11, 2.67 (t,s,s,d, 4H, H_{nb1-4}), 1.61 (m, 5H, 2*[COO-CH₂-CH₂], H_{nb7b}), 1.44 (m, 1H, H_{nb7a}), 1.26 (m, 36H, 2*[-CH₂-(CH₂)₉-CH₃]), 0.88 (m, 6H, 2*[-CH₂-CH₃])

ROM Polymerization

Diblock copolymer (DB)

Mon2 (0.20 g, 0.39 mmol) was dissolved in THF (5 mL; dry) in a 50 mL round bottom flask. A solution of M31 catalyst (3.21*10⁻³ M) in THF (2 mL; dry) was prepared and added all at once. The reaction mixture was stirred at room temperature until TLC showed complete conversion. **Mon1** (0.05 g, 0.13 mmol) was dissolved in THF (2 mL; dry) and added to the reaction mixture, which was stirred until TLC showed full conversion. The reaction was quenched by addition of ethyl-vinylether (50 μL). After 30 min, the solvent was partially removed *in vacuo* and the product was precipitated three times in cold MeOH. The product was dried *in vacuo* to afford a highly viscose, slightly brown resin in ca. 90% yield, and was used without further purification. The slight coloration of the product was due to residual catalyst. ¹H-NMR (δ, 20°C, CDCl₃, 300 MHz): 5.59–5.15 (m, 2H, CH₂), 4.25–3.88 (m, 1H, H_{Cp4}, 4H, -COOCH₂-), 3.71–3.45 (m, 3H, -O-CH₂-CH₂-O), 3.29–2.84 (2x bs, 3H, H_{Cp1-3}), 1.95 (bs, 1H,

H_{Cp5a}), 1.66–1.39 (m, 1H, H_{Cp5b}, 4H, –COO-CH₂-CH₂), 1.36–1.00 (m, 19H, –CH₂-), 1.21–1.13 (m, 1H, –CH₃), 0.90–0.84 (t, 3H, –CH₃)

Gel permeation chromatography showed a molecular weight of 37,315 g/mol (PDI: 1.18), which is in good agreement with the theoretic value of 39,418 g/mol. Differential scanning calorimetry showed no glass temperature T_g , but an apparent melting temperature T_m at 0°C⁴.

Triblock copolymer (TB)

Mon2 (0.50 g, 0.96 mmol) was dissolved in dichloromethane (5 mL; dry) in a 50 mL round bottom flask. A solution of M31 catalyst (0.01 M) in dichloromethane (2 mL; dry) was prepared and added all at once. The reaction mixture was stirred at room temperature until TLC showed complete conversion. To the mixture was added a solution of **Mon1** (0.13 g, 0.32 mmol) in dichloromethane (2 mL; dry). The reaction mixture was stirred until TLC showed full conversion. This step was repeated with **Mon2** (0.50 g, 0.96 mmol). The reaction was quenched by addition of ethyl-vinylether (50 μ L). After 30 min, the solvent was partially removed *in vacuo* and the product was precipitated three times in cold MeOH. The product was dried *in vacuo* to afford a highly viscose, slightly brown resin in ca. 80% yield, and was used without further purification. The slight coloration of the product was due to residual catalyst. ¹H-NMR (δ , 20°C, CDCl₃, 300 MHz): 5.59–5.15 (m, 2H, CH₂), 4.25–3.88 (m, 1H, H_{Cp4}, 4H, –COOCH₂-), 3.71–3.45 (m, 3H, –O-CH₂-CH₂-O-), 3.29–2.84 (2x bs, 3H, H_{Cp1-3}), 1.95 (bs, 1H, H_{Cp5a}), 1.66–1.39 (m, 1H, H_{Cp5b}, 4H, –COO-CH₂-CH₂-), 1.36–1.00 (m, 29H, –CH₂-), 1.21–1.13 (m, 1H, –CH₃), 0.90–0.84 (t, 3H, –CH₃)

Gel permeation chromatography showed a molecular weight of 59,470 g/mol (PDI: 1.23). Differential scanning calorimetry showed no T_g , but an apparent melting temperature at -1.5 °C.

E7–Stabilizer Influence

The influence of stabilizers on the formation of the liquid crystal is shown for samples with a δ value of 50 (hexagonal crystal).

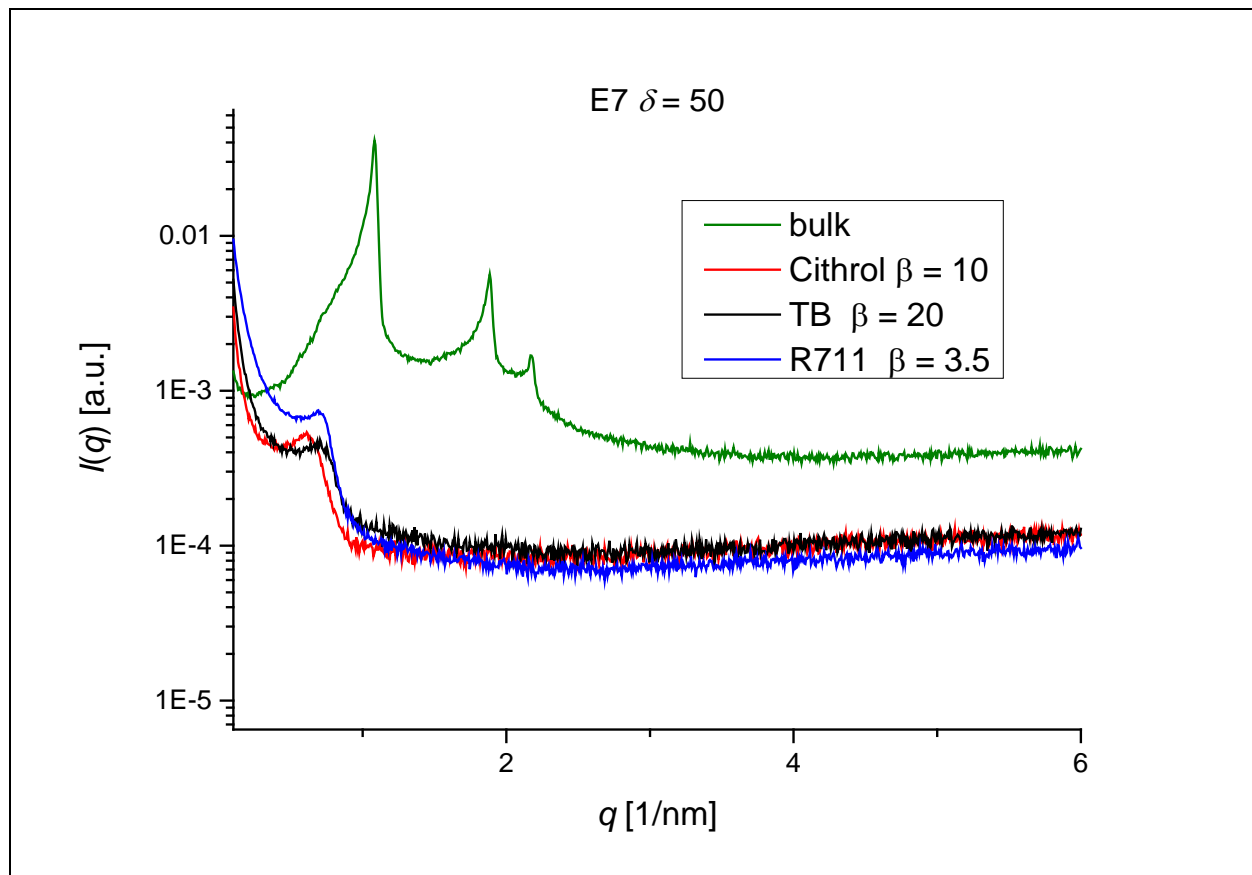


Figure S7: SAXS results for dispersions from E7 at $\delta = 50$, with different stabilizers

The bulk sample clearly shows the presence of the hexagonal crystal. The formation of a microemulsion in the dispersion instead of the expected hexagonal phase indicates an interaction between the primary surfactant and the stabilizers.

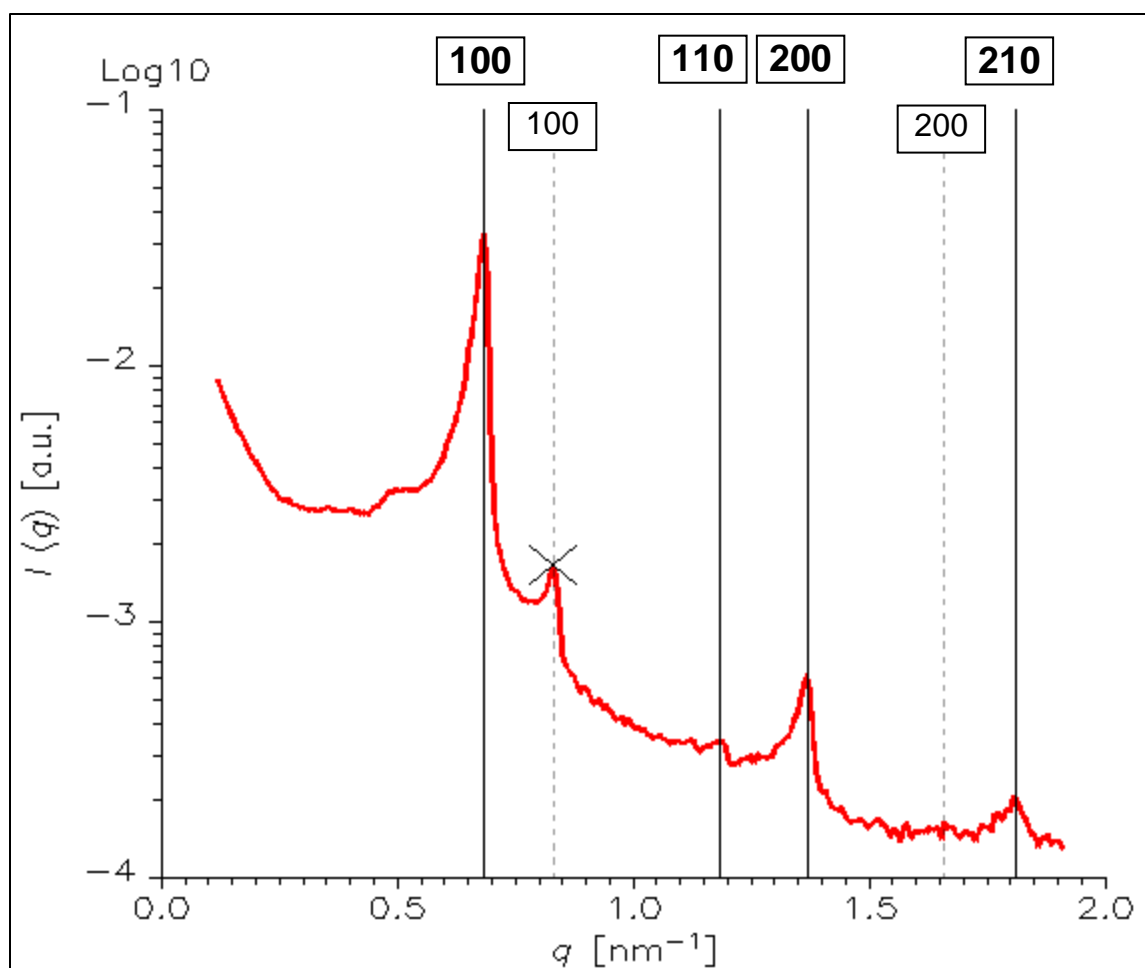


Figure S8: E7 $\delta = 60$ stabilized with Aerosil R711 $\beta = 2$. The space group indexing shows the coexistence of the dominating H_I phase (full lines) with a weak lamellar phase (L_α , dotted line) See also Fig. S2, $\delta = 70$.

Long-Term Stability Test of Water Stabilized in Tetradecane. The samples were prepared by dissolving the corresponding stabilizer in tetradecane, and adding water to this solution. The samples were ultrasonicated for 10 min. (0.2 ON / 2 OFF, 120 W). The samples were measured by using dynamic light scattering directly after preparation, and again after 1, 5, 10 and 20 days. Before the measurement, the otherwise turbid samples were diluted with tetradecane and hand-

shaken (no further ultrasonication was used). The R_H value was determined using the cumulant method.

Table S1: long-term stability test of water stabilized in tetradecane. Stabilizer concentration is 1 wt% for all samples. DB = diblock; TB = triblock; DPHS = (PEG-30) Dipolyhydroxystearate; X: large agglomerates

Stabilizer	R_H [nm]					Water Content
	0 days	1 day	5 days	10 days	20 days	
DB	122 ± 2	559 ± 10	155 ± 1	178 ± 1	239 ± 2	1 %
TB	176 ± 1	176 ± 4	111 ± 1	132 ± 2	103 ± 3	
DPHS	82 ± 0.2	121 ± 1	125 ± 3	129 ± 1	116 ± 1	
DB	422 ± 4	503 ± 4	1182 ± 14	1150 ± 13	X	5 %
TB	384 ± 8	1324 ± 8	695 ± 7	397 ± 8	201 ± 6	
DPHS	158 ± 1	222 ± 1	128 ± 1	227 ± 8	134 ± 2	
DB	508 ± 3	1632 ± 22	1583 ± 32	X	X	10 %
TB	962 ± 5	1653 ± 37	628 ± 13	1568 ± 91	188 ± 4	
DPHS	169 ± 1	159 ± 1	127 ± 1	145 ± 1	162 ± 4	

References

1. Alam, M. M.; Aramaki, K., Hexagonal Phase Based Gel-Emulsion (O/H1 Gel-Emulsion): Formation and Rheology. *Langmuir* 2008, 24 (21), 12253–12259.
2. Alexandridis, P.; Olsson, U.; Lindman, B., Self-Assembly of Amphiphilic Block Copolymers: The (EO)₁₃(PO)₃₀(EO)₁₃-Water-p-Xylene System. *Macromolecules* 1995, 28, 7700-7710.
3. Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I., NMR chemical shifts of trace impurities: Common laboratory solvents, organics, and gases in deuterated solvents relevant to the organometallic chemist. *Organometallics* 2010, 29 (9), 2176-2179.
4. Sandholzer, M.; Fritz-Popovski, G.; Slugovc, C., Synthesis and self assembly of eosin functionalized amphiphilic block-random copolymers prepared by ring opening metathesis polymerization. *J. Polym. Sci. A* 2008, 46, 401-413.