Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Characterization of the phase behaviour of a novel polymerizable lyotropic ionic liquid crystal

Nicolas. Goujon,[a] Maria. Forsyth,[ab] Ludovic. F. Dumée,[a] Gary Bryant,[c] Nolene Byrne*[a]

Phase assignment using SAXS data

The Bragg diffraction peak positions were obtained by fitting the 1D-SAXS spectra using Origin pro software where the peak intensity was strong enough for a reliable peak fit, otherwise the maximum peak intensity was used. The lyotropic liquid crystalline phases were determined by the relative positions of the diffraction peaks.

L_α $$\left(\frac{a}{d}\right) = 1, 2, 3, 4 \ldots where\ d = 2\pi/q,\ a\ is\ the\ lattice\ parameter$$

H_1 $$\left(\frac{\sqrt{3}\cdot a}{2\cdot d_{hk}}\right)^2 = 1, 3, 4, 7, 9, 12 \ldots$$

I_1 (*Pm3n*) $$\left(\frac{a}{d_{hkl}}\right)^2 = 2, 4, 5, 6, 8, 9, 10, 12, 13, 14, 16, 17, 18, 20$$

The lattice parameter, a, for the hexagonal (H_1) and the discontinuous cubic phase (I_1) were obtained by plotting the following equations respectively[1, 2]:

L_α $$\left(\frac{1}{d}\right) = \frac{1}{a} \cdot h$$

H_1 $$\left(\frac{1}{d_{hk}}\right)^2 = \left(\frac{4}{3 \cdot a^2}\right) \cdot \left(h^2 + h \cdot k + k^2\right)$$

(I_1) (*Pm3n*) $$\left(\frac{1}{d_{hkl}}\right)^2 = \left(\frac{1}{a^2}\right) \cdot \left(h^2 + k^2 + l^2\right)$$

The linearity of the plot and the (0,0) intercept are indications of a valid space group assignment.

SAXS and WAXS spectra

C_{16}mimCl containing 4.8 wt.% water at 20 ℃ and 80℃

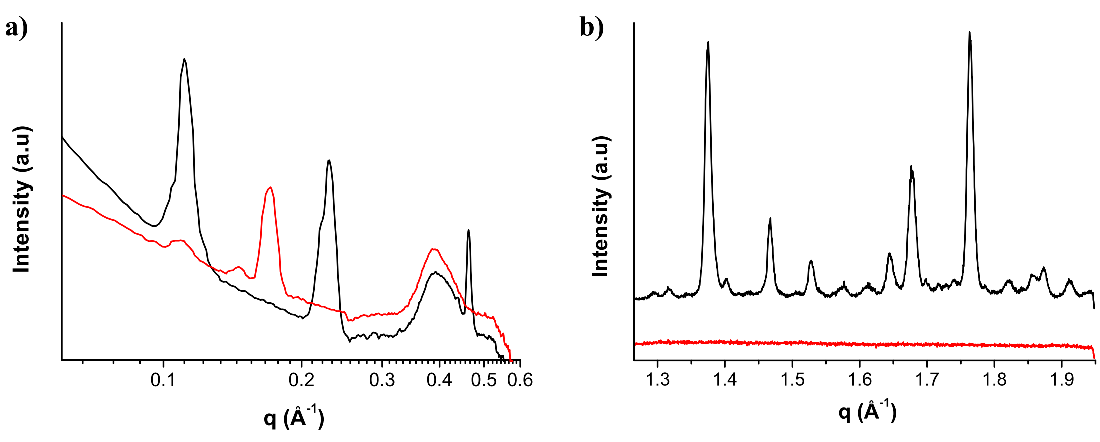

Figure S1: SAXS (a) and WAXS (b) integrated patterns of the C_{16}mimCl containing 4.8 wt.% water at 20°C (black line) and 80°C (red line).

C_{16}mimAcr containing 4.9 wt.% water at 20 ℃ and 80℃

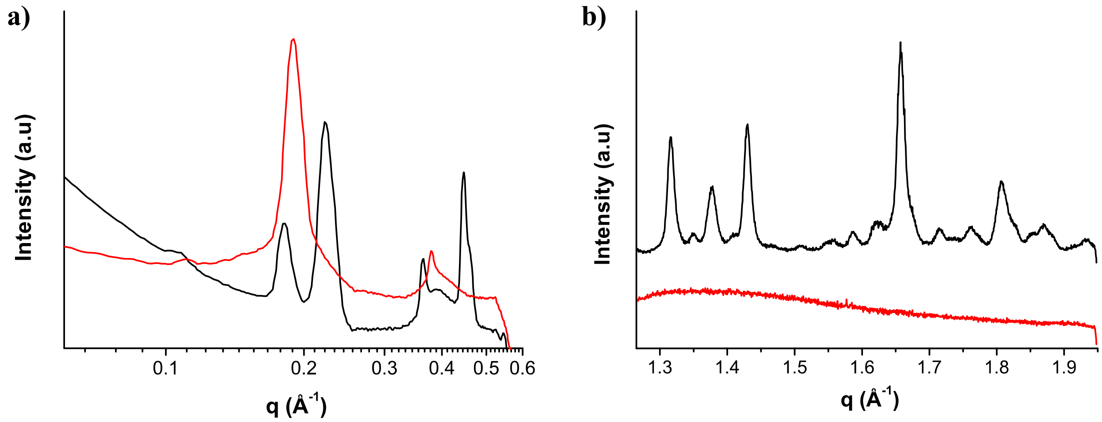

Figure S2: SAXS (a) and WAXS (b) integrated patterns of the C_{16}mimAcr containing 4.9 wt.% water at 20°C (black line) and 80°C (red line).

C_{16}mimCl/water system

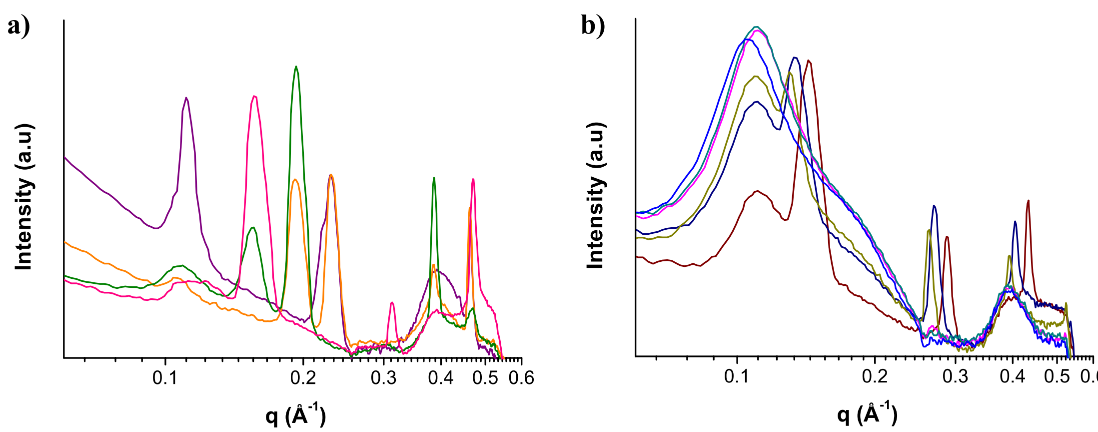

Figure S3: SAXS integrated patterns of the C_{16}mimCl containing 4.8, 10, 20, 30 wt.% water (a) 40, 50, 60 (gel), 60 (liq), 65 and 70 wt.% water (b).

C_{16}mimAcr/water system

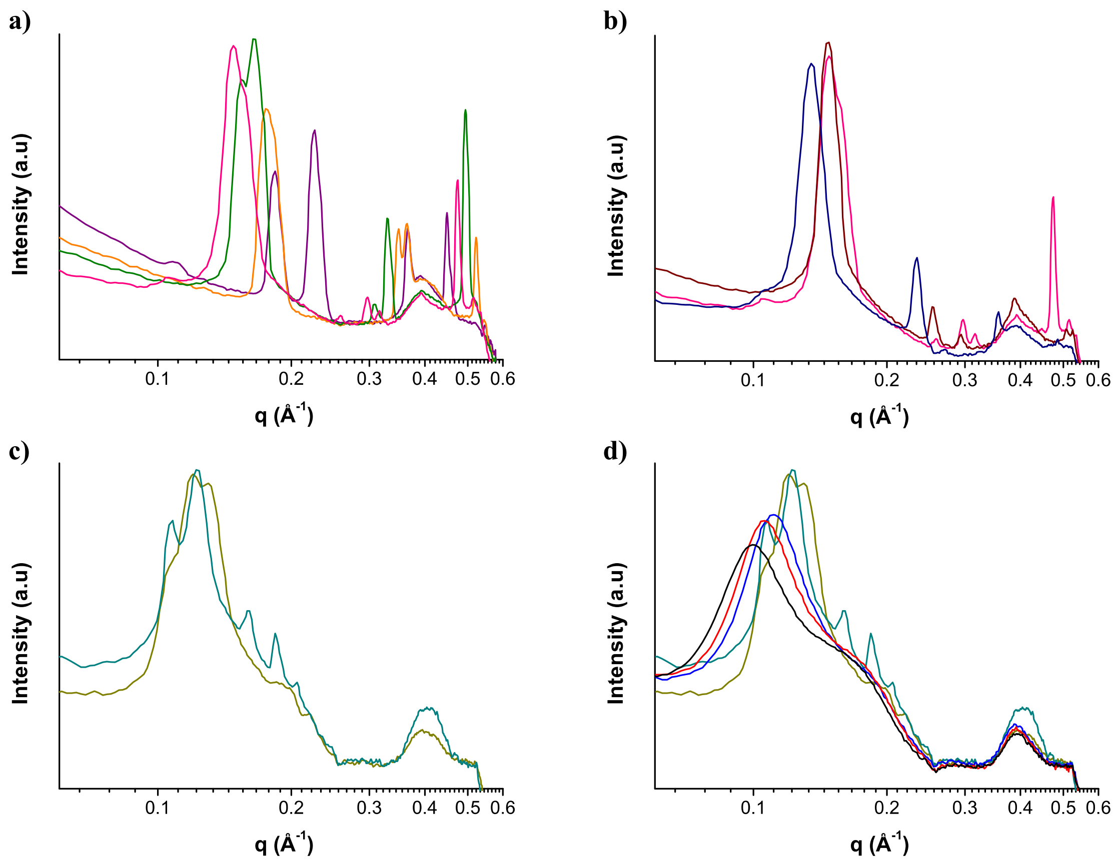

Figure S4: SAXS integrated patterns of the C_{16}mimAcr containing 4.9, 10, 20, 30 wt.% water (a) 30, 40, 50 wt.% water (b) 60, 65 wt.% water (c) 60, 65, 70, 75 and 80 wt.% water (d).

SAXS data and phase assignment

C_{16}mimCl/water system: lamellar phase (L$_\alpha$)

Table S1. Phase assignment and the calculated lattice parameter, a, of the lamellar phase (L_α) of the C_{16}mimCl/water system at 20 °C.

C_{16}mimCl/water system: phase assignment and lattice parameter, a						
Phases	(wt.%)	q_{100} /Å^{-1}	q_{200} /Å^{-1}	q_{300} /Å^{-1}	q_{400} /Å^{-1}	a /Å
Lamellar (L_α)	4.8	0.104	0.221	N/O	N/O	57.4 ± 1.26
		0.111	0.229	N/O	0.463	54.4 ± 0.34
		0.118	0.234	N/O	0.475	53.0 ± 0.22
	10	0.192	0.385	N/O	N/O	32.6 ± 0.02
		0.199	N/O	N/O	N/O	31.5
		0.230	0.462	N/O	N/O	27.2 ± 0.02
		0.239	0.471	N/O	N/O	26.5 ± 0.17
	20	0.163	N/O	0.488	N/O	38.6 ± 0.00
		0.170	N/O	0.499	N/O	37.7 ± 0.28
		0.193	0.385	N/O	N/O	32.5 ± 0.04
	30	0.157	0.314	0.470	N/O	40.1 ± 0.01
		0.166	N/O	N/O	N/O	37.8

N/O: not observed.

C_{16}mimCl/water system: lamellar phase (L_α) and micellar phase (L_1)

Table S2. Phase assignment and the calculated lattice parameter, a, of the lamellar phase (L_α) and the correlation lengths of pair distribution of micelles, ξc, of the micellar phase (L_1) of the C_{16}mimCl/water system at 20 °C.

C_{16}mimCl/water system: phase assignment, correlation lengths of micelles ξc and lattice parameter, a							
Phases	(wt.%)	$q_{\xi c}$ /Å^{-1}	ξ_c / Å	q_{100} /Å^{-1}	q_{200} /Å^{-1}	q_{300} /Å^{-1}	a /Å
Lamellar (L_α) + Micellar (L_1)	40	0.111	56.6	0.143	0.288	0.432	43.6 ± 0.04
	50	0.111	56.7	0.134	0.27	0.405	46.5 ± 0.05
	60 (gel)	0.110	57.0	0.131	0.263	0.393	47.9 ± 0.03
	60 (liq)	0.110	57.1	0.127	N/O	N/O	49.5

N/O: not observed.

C_{16}mimCl/water system: micellar phase (L_1)

Table S3. Phase assignment and the correlation lengths of pair distribution of micelles, ξc, of the micellar phase (L_1) of the C_{16}mimCl/water system at 20 °C.

C_{16}mimCl/water system: phase assignment and correlation lengths of micelles ξc			
Phases	(wt.%)	$q_{\xi c}$ /Å^{-1}	ξ_c / Å
Micellar (L_1)	65	0.110	57.1
	70	0.107	58.4

C_{16}mimAcr/water system: lamellar phase (L$_\alpha$)

Table S4. Phase assignment and the calculated lattice parameter, a, of the lamellar phase (L_α) of the C_{16}mimAcr/water system at 20 °C.

C_{16}mimAcr/water system: phase assignment and lattice parameter, a					
Phases	(wt.%)	q_{100} /Å^{-1}	q_{200} /Å^{-1}	q_{300} /Å^{-1}	a /Å
Lamellar (L_α)	4.9	0.183 0.225 0.234	0.366 0.449 0.457	0.549 N/O N/O	34.3 ± 0.02 28.0 ± 0.03 27.3 ± 0.23
	10	0.174 0.180	0.349 0.364	0.522 0.529	36.1 ± 0.02 35.2 ± 0.37
	20	0.154 0.165 0.173	0.307 0.330 0.347	N/O 0.494 0.502	40.8 ± 0.07 38.1 ± 0.03 37.1 ± 0.45

N/O: not observed.

C_{16}mimAcr/water system: lamellar phase (L$_\alpha$) and hexagonal phase (H$_1$)

Table S5. Phase assignment and the calculated lattice parameter, a, of the lamellar phase (L_α) and hexagonal phase (H_1) of the C_{16}mimAcr/water system at 20 °C.

C_{16}mimAcr/water system: phase assignment and lattice parameter, a								
Phases	(wt.%)	q_{100} /Å^{-1}	q_{110} /Å^{-1}	q_{200} /Å^{-1}	q_{210} /Å^{-1}	q_{300} /Å^{-1}	q_{220} /Å^{-1}	a /Å
Lamellar (L_α) + Hexagonal	30	0.148 0.157	0.258 N/A	0.298 0.316	N/O N/A	N/O 0.474	0.512 N/A	43.8 ± 2.74 39.8 ± 0.05
	40	0.147 0.156	0.254 N/A	0.294 N/O	0.389 N/A	N/O N/O	0.510 N/A	45.5 ± 3.26 40.3

(H$_1$)								

N/O: not observed, N/A: not applicable.

C_{16}mimAcr/water system: hexagonal phase (H$_1$)

Table S6. Phase assignment and the calculated lattice parameter, a, of the hexagonal phase (H$_1$) of the C_{16}mimAcr/water system at 20 °C.

C_{16}mimAcr/water system: phase assignment and lattice parameter, a						
Phases	(wt.%)	q_{100} /Å^{-1}	q_{110} /Å^{-1}	q_{200} /Å^{-1}	q_{210} /Å^{-1}	a /Å
Hexagonal (H$_1$)	50	0.135	0.234	0.268	0.357	53.8 ± 0.13

Figure S5 shows the plot of the square function of the reciprocal spacing ($(1/dhk)^2$) of the reflection peaks indexed in Table S6, plotted versus $m = (h^2 + h*k + k^2)$ as an example of the SAXS data fit for a hexagonal phase. From the slope of the linear fit, the lattice parameter a, could be calculated using the equation described earlier for a hexagonal phase.

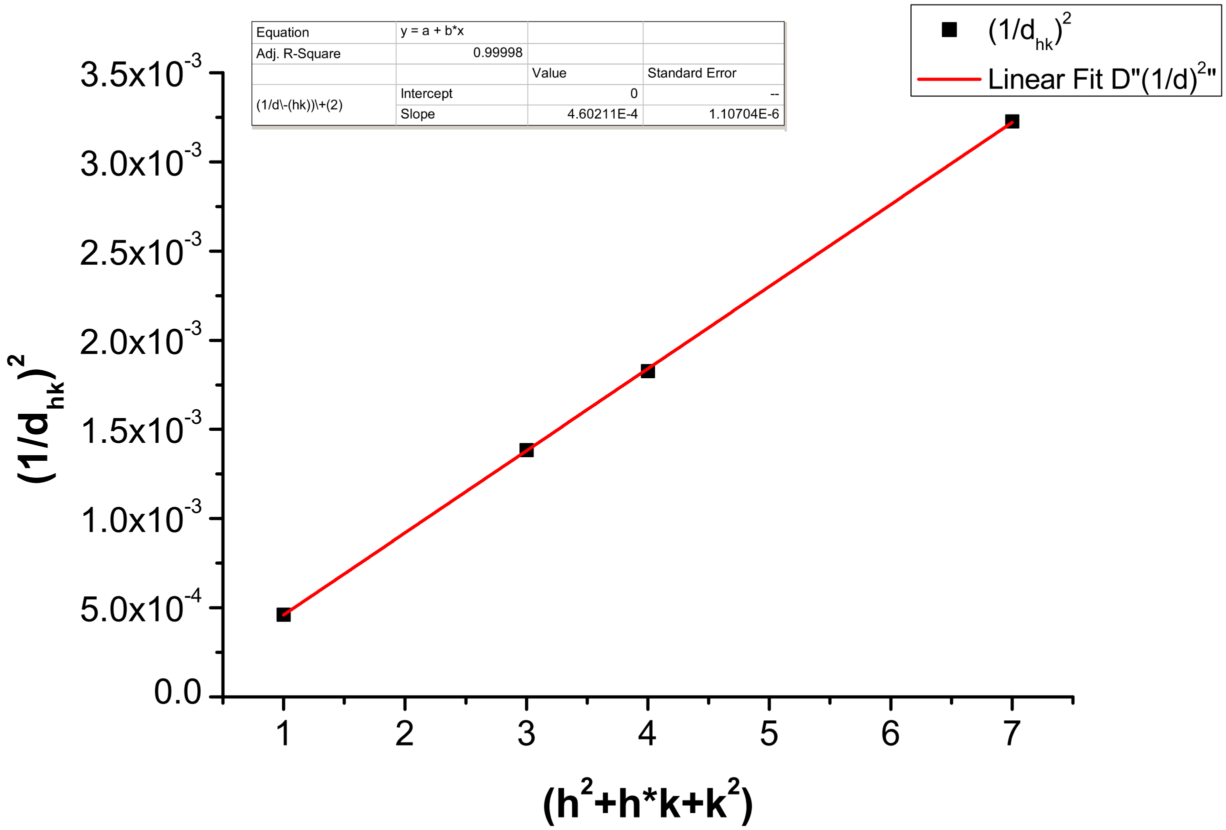

Figure S5: Plot of the square function of the reciprocal spacing ($(1/dhk)^2$) of the reflection peaks indexed in Table S6, plotted versus m = ($h^2 + h*k + k^2$).

C_{16}mimAcr/water system: discontinuous cubic phase (I$_1$)

Table S7. Phase assignment and the calculated lattice parameter, a, of the discontinuous cubic phase (I_1) of the C_{16}mimAcr/water system at 20 °C.

C_{16}mimAcr/water system: phase assignment and lattice parameter, a		
Phases	Discontinuous cubic (I_1)	
(wt.%)	60	65
q_{100} /Å^{-1}	N/O	N/O
q_{110} /Å^{-1}	N/O	N/O
q_{200} /Å^{-1}	0.107	0.107
q_{210} /Å^{-1}	0.119	0.122
q_{211} /Å^{-1}	0.130	0.130
q_{220} /Å^{-1}	0.148	0.147
$q_{300+221}$ /Å^{-1}	0.158	0.160
q_{310} /Å^{-1}	0.168	0.171
q_{222} /Å^{-1}	0.185	0.184
q_{320} /Å^{-1}	N/O	0.190
q_{321} /Å^{-1}	0.198	0.205
q_{400} /Å^{-1}	N/O	0.213
$q_{410+322}$ /Å^{-1}	0.218	0.221
$q_{330+411}$ /Å^{-1}	N/O	0.226
q_{420} /Å^{-1}	N/O	0.240
a /Å	118.4 ± 0.47	117.4 ± 0.73

N/O: not observed.

Figure S6 shows the plot of the square function of the reciprocal spacing ($(1/dhk)^2$) of the reflection peaks indexed in Table S7, plotted versus m = ($h^2 + k^2 + l^2$) as an example of the SAXS data fit for a discontinuous cubic phase. From the slope of the linear fit, the lattice parameter a, could be calculated using the equation described earlier for a discontinuous cubic phase.

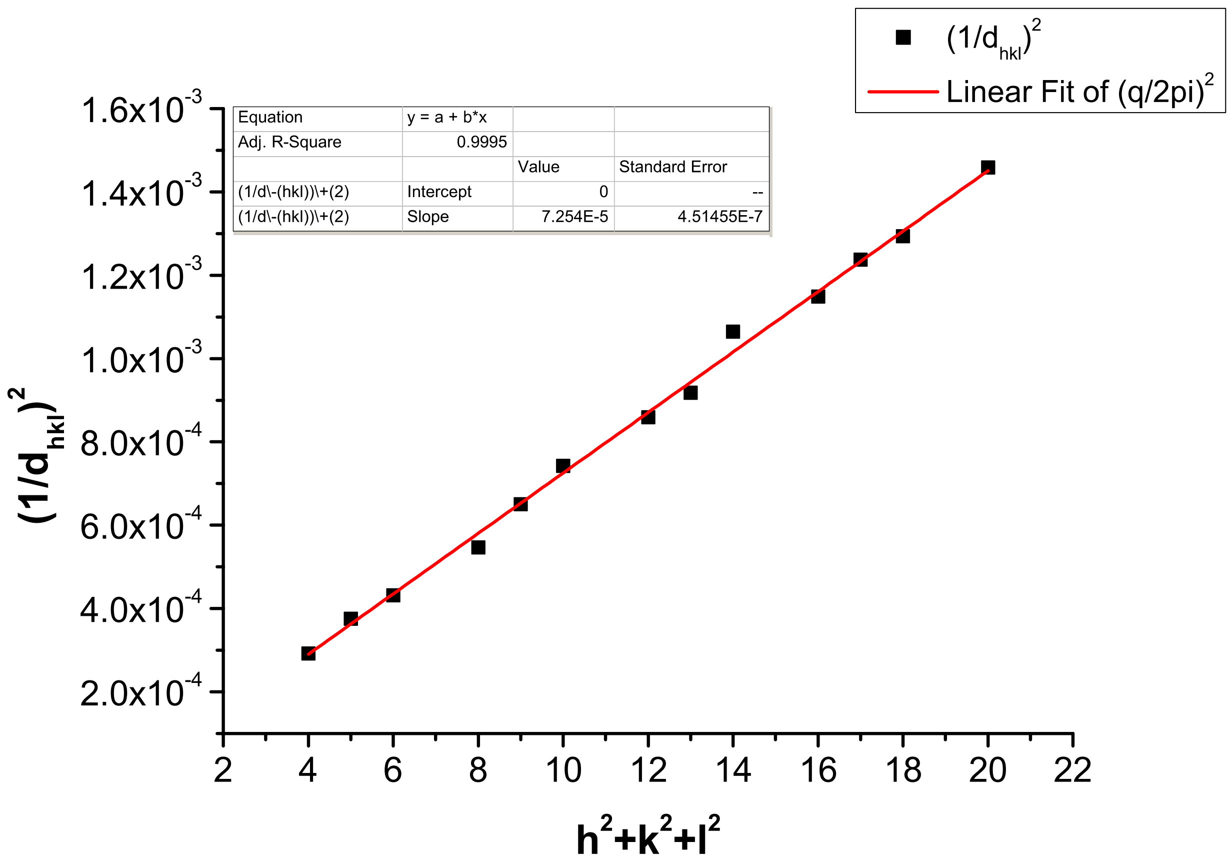

Figure S6: Plot of the square function of the reciprocal spacing ($(1/dhk)^2$) of the reflection peaks indexed in Table S7, plotted versus m = ($h^2 + k^2 + l^2$).

C_{16}mimAcr/water system: micellar phase (L$_1$)

Table S8. Phase assignment as well as the correlation lengths of pair distribution of micelles, ξc, of the micellar phase (L_1) of the C_{16}mimAcr/water system at 20 °C.

C_{16}mimAcr/water system: phase assignment and correlation lengths of micelles ξc			
Phases	(wt.%)	$q_{\xi c}$ /Å^{-1}	ξ_c / Å
Micellar (L_1)	70	0.112	56.1
	75	0.106	59.3
	80	0.099	63.1

1. Yaghmur, A.; de Campo, L.; Salentinig, S.; Sagalowicz, L.; Leser, M. E.; Glatter, O. Oil-Loaded Monolinolein-Based Particles with Confined Inverse Discontinuous Cubic Structure (Fd 3 m). *Langmuir* **2006,** *22* (2), 517-521.
2. Svensson, A.; Topgaard, D.; Piculell, L.; Söderman, O. Molecular self-diffusion in micellar and discrete cubic phases of an ionic surfactant with mixed monovalent/polymeric counterions. *The Journal of Physical Chemistry B* **2003,** *107* (47), 13241-13250.