Report on Run SC3869

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Insertion of gold nanoparticules in lyotropic membranes

Hydrophobically-coated gold nanoparticles can be successfully inserted in the hydrophobic regions of oil swollen lamellar phases. We have recently shown using small gold nanoparticules (2nm gold core diameter) that confinement in the hydrophobic regions promotes a new repulsive interaction whose range varies as the lamellar period d[1]. The aim of the proposal is to insert larger gold nanoparticles (gold core from 3 to 5 nm) inside lyotropic membranes. On this purpose, lyotropic lamellar phases with various oil swelling have been used. In bulk these nanoparticles interact mainly via an attractive van der Waals interaction and, as for small nanoparticles, confinement is expected to induce original interaction. Since the NPs are larger, the lamellae will be much disturbed and 3D interaction could occur. As for smaller nanoparticles, 2D clusters are expected at higher NP concentrations. The condition of formation of 2D clusters will be analysed. The optical properties of these clusters will then be compared with the bulk resonance plasmon band.

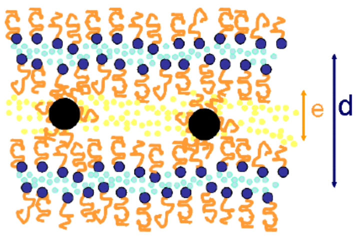


Figure 1 : Schematic drawing of the mixed system

1- Samples

Different nanoparticules with various diameters (3 nm, 4 nm, 5 nm) have been used. The initial lamellar phase was composed of water (47.4w%), SDS (30.6w%), pentanol (22w%). This lamellar phase has been doped with suspensions of nanoparticules in oil. For each nanoparticule size, three different swelling have been used. Previous experiments have shown that the pertinent parameter to take into account is the ratio $R=e_h/D_{app}$ where e_h is the total hydrophobic thickness (oil + surfactant chains) and D_{app} is the total particule diameter (core +ligands). This apparent diameter can be deduced from X-ray scattering on suspensions through the structure factor. Three different swellings (Table 1) have been studied :

R_1=1.1 (A), R_2=1.4 (B), R_3=1.7 (C).

Suspensions in a mixture of dodecane (91w%)+ pentanol(9w%) with four different concentrations in dodecane have been used: 1w%, 10w%, 20w%, 30w%. The samples are described in Table 2.

Lamellar period for	Swelling A	Swelling B	Swelling C
3C12 Nanoparticules	3.4 nm	5.2 nm	6.8 nm
4C12 Nanoparticules	4.0 nm	5.9 nm	7.6 nm
5C12 Nanoparticules	5.0 nm	7.3 nm	9.3 nm

Table 1: Different swellings for the different type of nanoparticules

[1] Pansu, B; Lecchi, A; Constantin, D; Impéror-Clerc, M; Veber, M; Dozov, I. Insertion of Gold Nanoparticles in Fluid Mesophases: Size Filtering and Control of Interactions; *J. Phys. Chem. C,* 2011, 115 (36), pp 17682–17687 DOI: 10.1021/jp2046189

2- Experiments

Each sample was carefully homogenized and sucked into 4 different capillaries: 2 0.1mm*2 mm capillaries, two 0.05mm*1 mm capillaries. Most of the capillaries have been prepared few months before the experiment to promote the best orientation.

The X-ray energy has been fixed to 11keV, high enough to limit absorption but lower than the nearest gold absorption band. The distance between the sample and the CCD detector was fixed to 47 cm. The beamstop diameter was 2.5 mm.

Each capillary has been carefully scanned horizontally and vertically in order to find large enough monodomains with the proper orientation. The pictures show that even large nanoparticules can be successfully inserted in swollen lamellar phases since the diffusion signal due to the particules is anisotropic. The structure factor in the direction perpendicular to the lamellar period give information on the interaction between the particules mainly in the lamellae. As for smaller nanoparticules, at low enough concentration, the particules repell each other with a repulsion length linked to the lamellar period (Table 3). A detailed analysis of this table is required. The diffusion patterns are also more complex and have to be more deeply studied in order to understand in what conditions planar aggregates appear.

Sample	Nanoparticule	Batch	NP w% in dodecane suspension
PLAL212 PA3 1w%	3C12	AL212	1
PLAL212 PA3 10w%	3C12	AL212	10
PLAL212 PA3 20w%	3C12	AL212	20
PLAL212 PA3 30w%	3C12	AL212	30
PLAL212 PB3 1w%	3C12	AL212	1
PLAL212 PB3 10w%	3C12	AL212	10
PLAL212 PB3 20w%	3C12	AL212	20
PLAL212 PB3 30w%	3C12	AL212	30
PLAL269 PC3 1w%	3C12	AL269	1
PLAL269 PC3 10w%	3C12	AL269	10
PLAL269 PC3 20w%	3C12	AL269	20
PLAL269 PC3 30w%	3C12	AL269	30
PLVR27 PA4 1w%	4C12	VR27	1
PLVR27 PA4 10w%	4C12	VR27	10
PLVR27 PA4 20w%	4C12	VR27	20
PLVR27 PA4 30w%	4C12	VR27	30
PLVR27 PB4 1w%	4C12	VR27	1
PLVR27 PB4 10w%	4C12	VR27	10
PLVR27 PB4 20w%	4C12	VR27	20
PLVR27 PB4 30w%	4C12	VR27	30
PLVR27 PC4 1w%	4C12	VR27	1
PLVR27 PC4 10w%	4C12	VR27	10
PLVR27 PC4 20w%	4C12	VR27	20
PLVR27 PC4 30w%	4C12	VR27	30
PLAL256 PA5 1w%	5C12	AL256	1
PLAL256 PA5 10w%	5C12	AL256	10
PLAL256 PA5 20w%	5C12	AL256	20
PLAL256 PA5 30w%	5C12	AL256	30
PLAL256 PB5 10w%	5C12	AL256	10
PLAL256 PB5 20w%	5C12	AL256	20
PLAL256 PB5 30w%	5C12	AL256	30
PLAL265 PC5 1w%	5C12	AL265	1
PLAL265 PC5 10w%	5C12	AL265	10
PLAL265PC5 20w%	5C12	AL265	20
PLAL265 PC5 30w%	5C12	AL265	30

Table 1: Samples used in the experiment SC3869

3C12 Nanoparticules

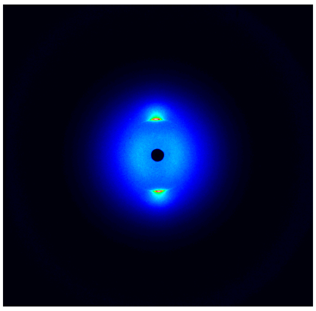
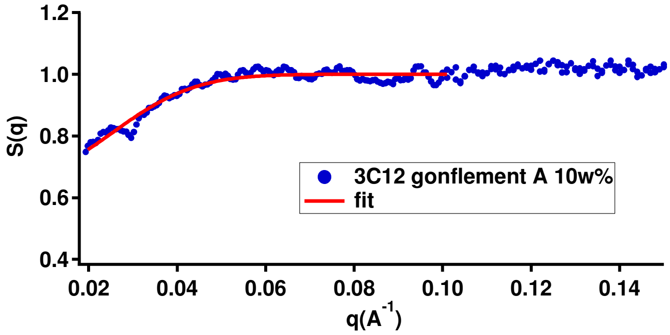


Figure 1: Image 2070 PA3 10w%



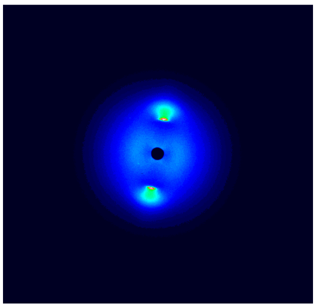
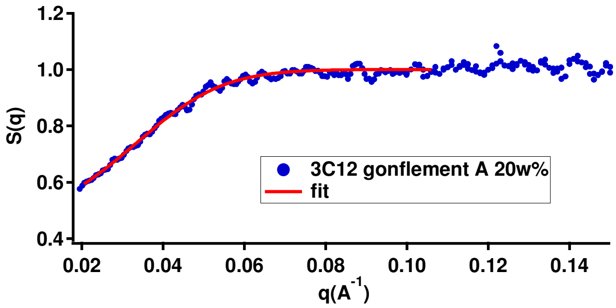


Figure 2 : Image 4694 PA3 20w%



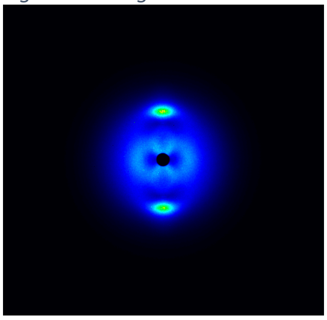


Figure 3 : Image 2415 PA3 30w%

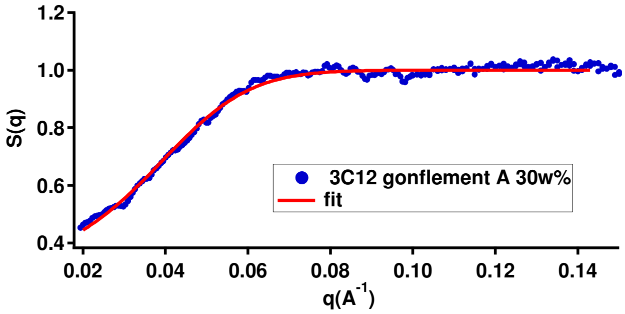
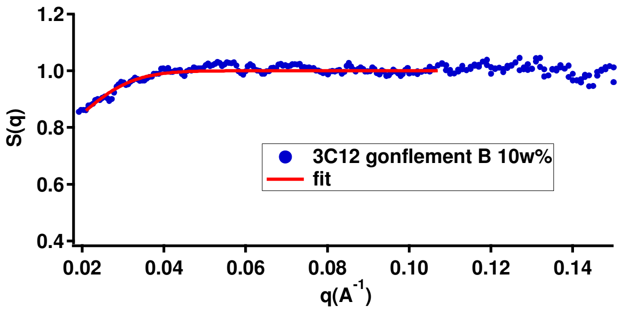


Figure 4 : Image 2534 PB3 10w%



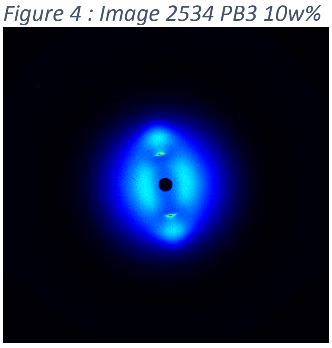
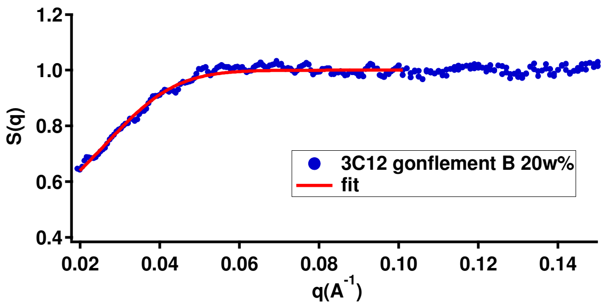


Figure 5 : Image 4714 PB3 20w%



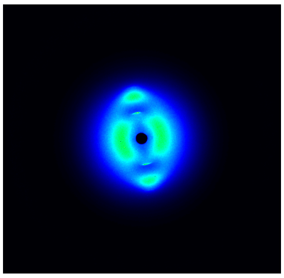
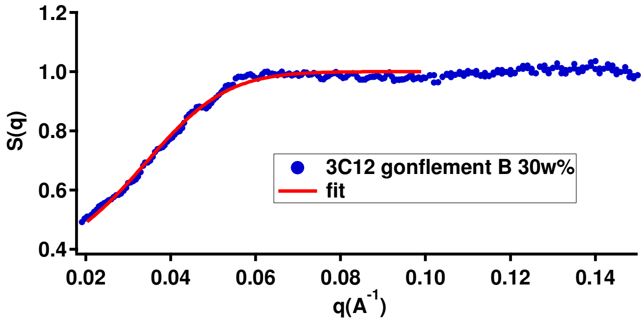


Figure 6 : Image 2597 PB3 30w%



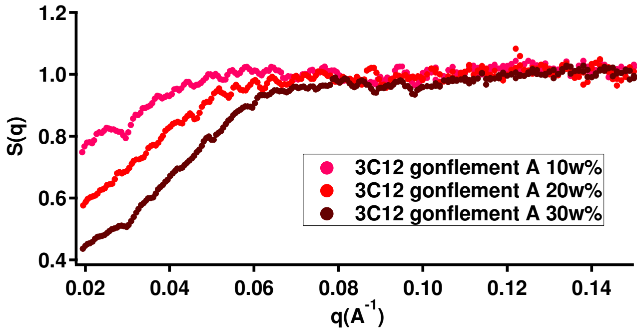


Figure 7 : Effect of nanoparticule concentration on their structure factor perpendicular to the lamellar period (Swelling A)

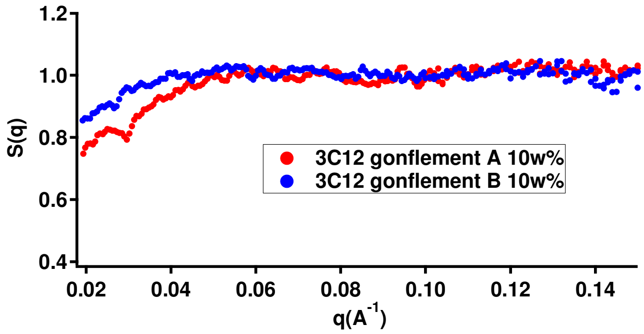


Figure 8 : Effect of swelling on the nanoparticule structure factor perpendicular to the lamellar period (concentration 10w%)

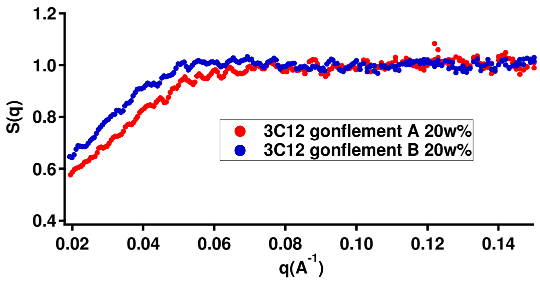


Figure 9 : Effect of swelling on the nanoparticule structure factor perpendicular to the lamellar period (concentration 20w%.

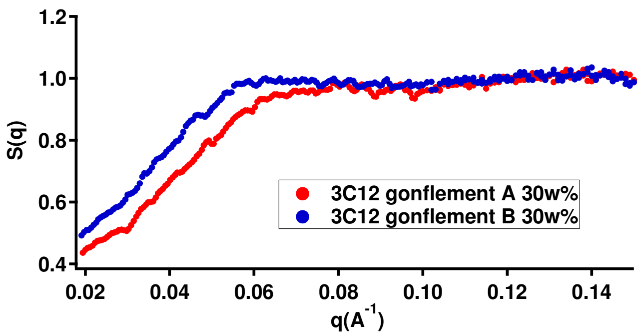


Figure 10 :   Effect of swelling on the nanoparticule structure factor perpendicular to the lamellar period (concentration 30w%)

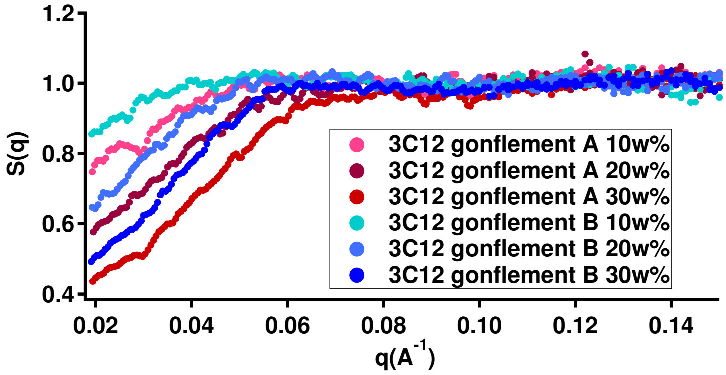


Figure 11 : 3C12 nanoparticule structure factor perpendicular to the lamellar period for different concentrations and swellings.

4C12 Nanoparticules

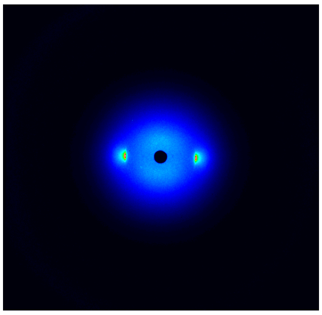
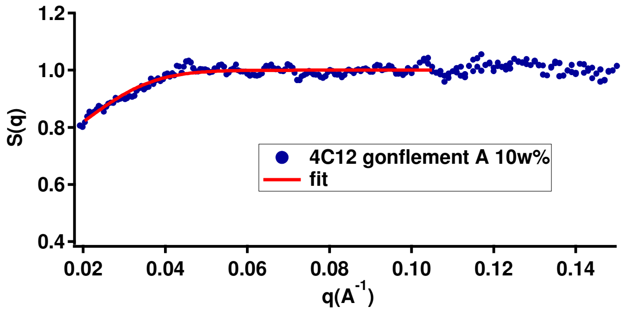


Figure 12 : Image 2383 PA4 10w%



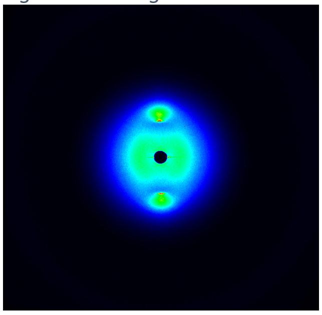
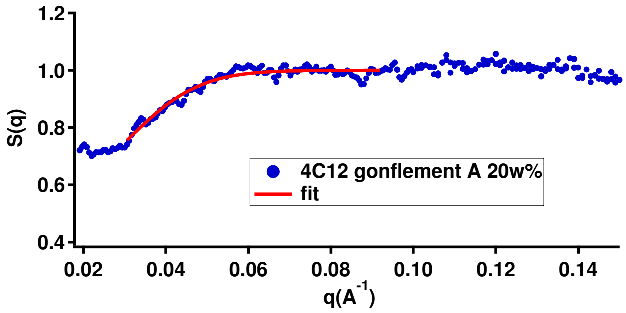


Figure 13 : Image 4655 PA4 20w%



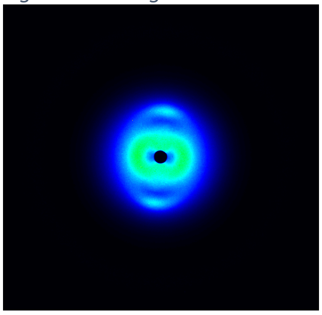
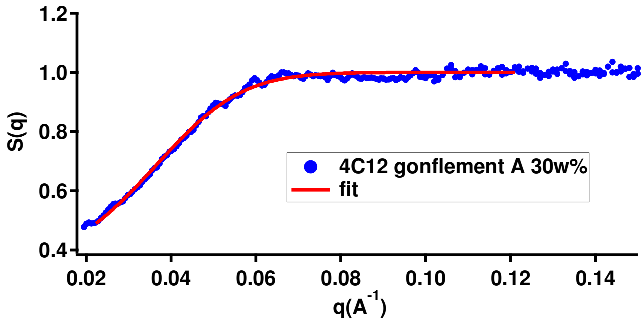


Figure 14 : Image 2257 PA4 30w%



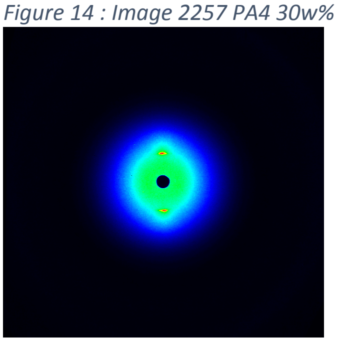
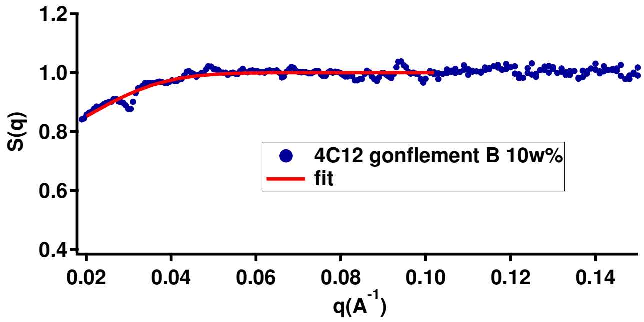


Figure 15 : Image 2649 PB4 10w%



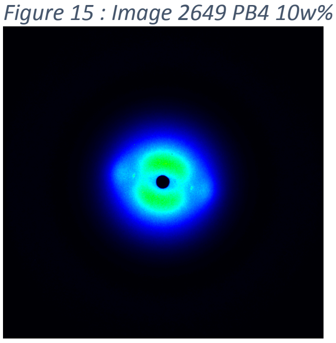
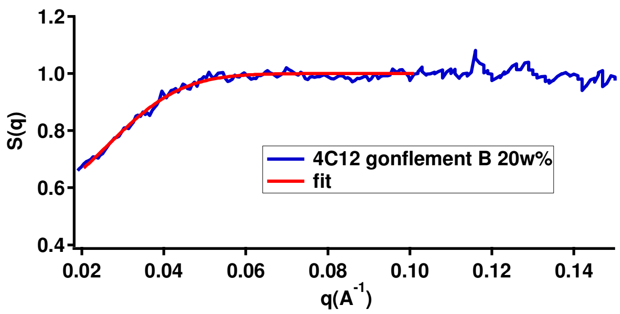
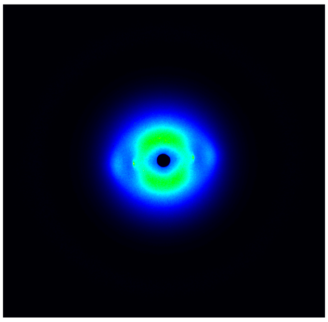


Figure 16 : Image 3083 PB4 20w%





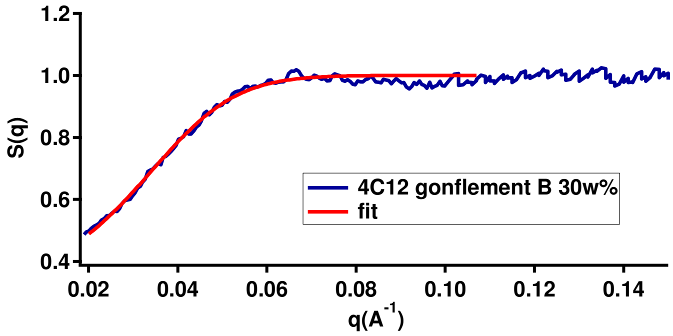
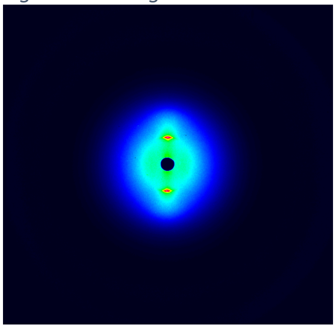


Figure 17 : Image 3106 PB4 30w%



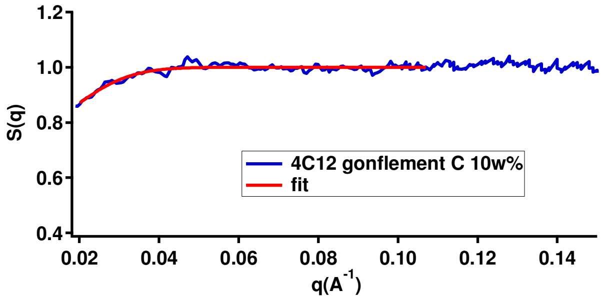
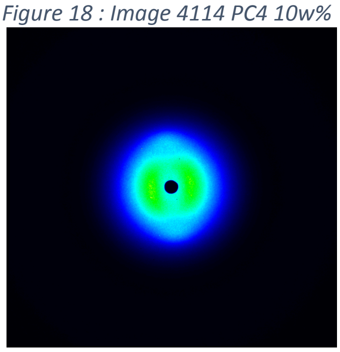


Figure 18 : Image 4114 PC4 10w%



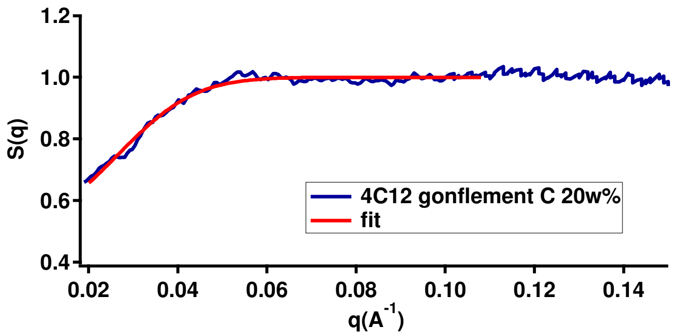
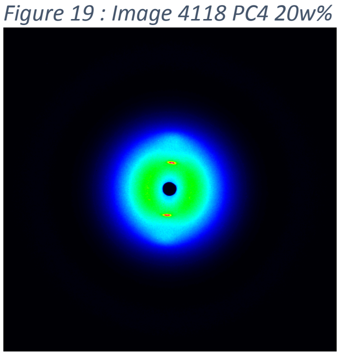


Figure 19 : Image 4118 PC4 20w%



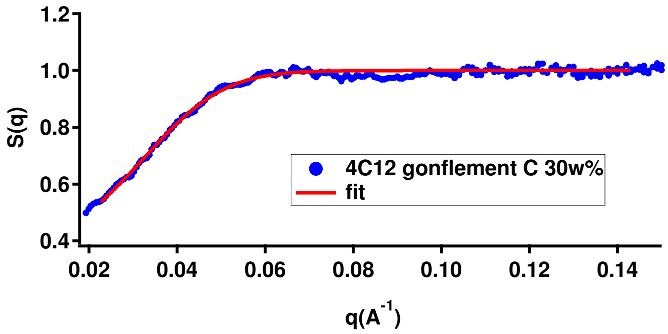


Figure 20 : Image 4182 PC4 30w%

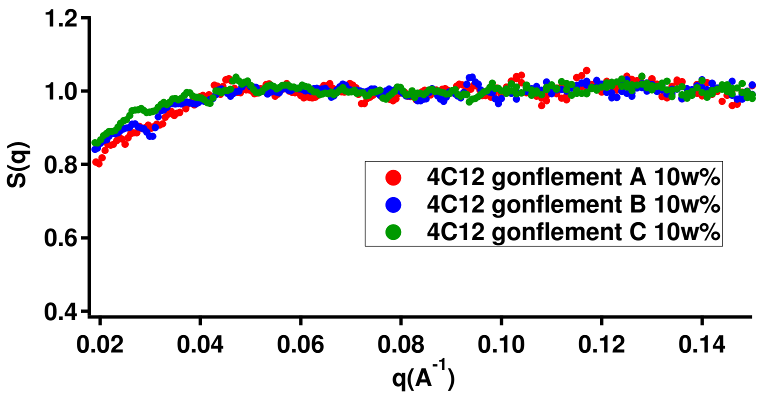


Figure 21 : 4C12 nanoparticule structure factor for different swellings (10w% concentration).

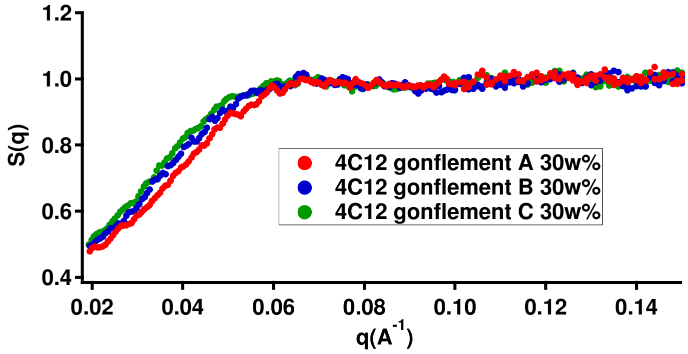


Figure 22 : 4C12 nanoparticule structure factor for different swellings (30w% concentration).

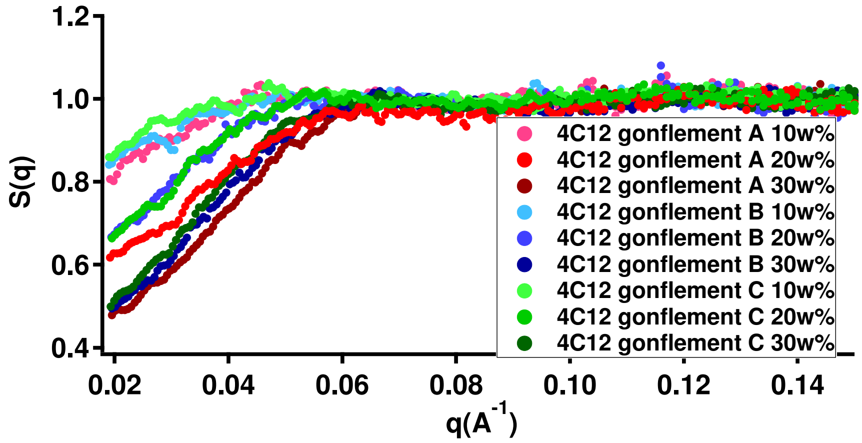


Figure 23 : 3C12 nanoparticule structure factor perpendicular to the lamellar period for different concentrations and swellings.

5C12 Nanoparticules

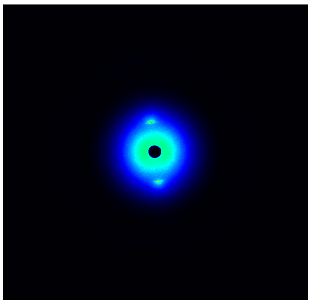
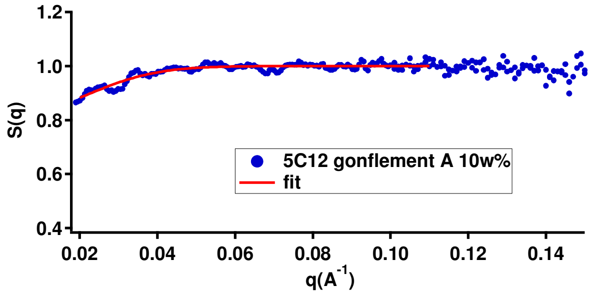


Figure 24 : Image 2207 PA5 10w%



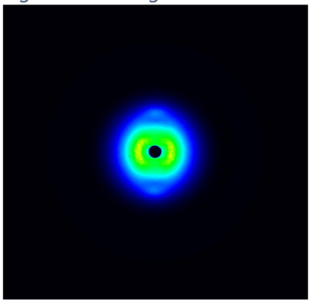
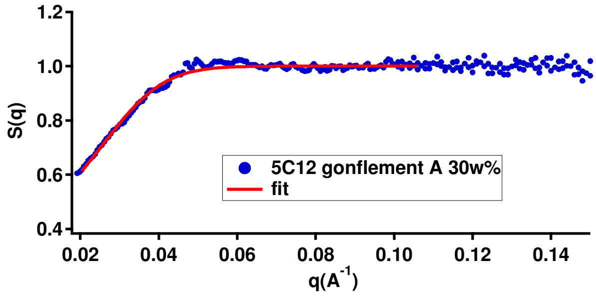


Figure 25 : Image 2150 PA5 30w%



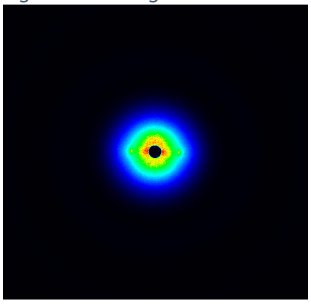
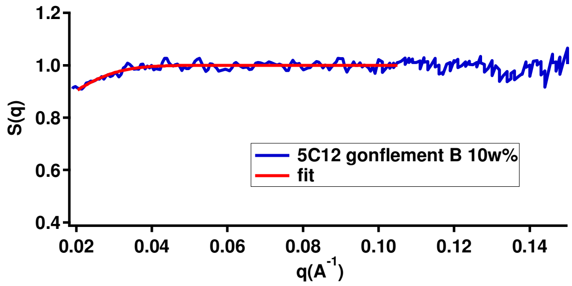


Figure 26 : 3183 PB5 10w%



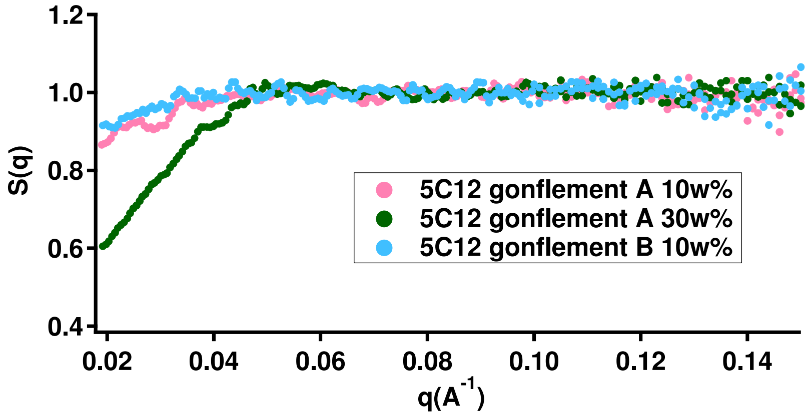


Figure 27 : 5C12 nanoparticule structure factor perpendicular to the lamellar period for different concentrations and swellings.

3- Interaction model

The in plane structure behavior has been modelized using:

$$U(q_r) = 2\pi U_0 \xi^2 exp(-\frac{{q_r}^2 \xi^2}{2})$$

The Gaussian function can then easily be computed:

$$S(q) = \frac{1}{1 + 2\pi c_s \xi^2 U_0 \exp\left(-\frac{q^2 \xi^2}{2}\right)}$$

Particules	Swelling	ϕ_w(%)	R_{app}(nm)	e (nm)	d_{lam}(nm)	c_s(nm^{-2})	$2\pi U_0 \xi^2 c_s$	U_0($k_B T$)	ξ(nm)	L(nm)
3C12	**A**	**10**	**2.4**	**3.2**	**7.1**	**0.0006**	**0.5**	**5.3**	**5.1**	**40**
3C12	**A**	**20**	**2.4**	**3.4**	**7.2**	**0.0016**	**1.0**	**5.5**	**4.4**	**25**
3C12	**A**	**30**	**2.4**	**3.1**	**7.0**	**0.0022**	**1.8**	**7.4**	**4.2**	**21**
3C12	**B**	**10**	**2.4**	**4.8**	**8.6**	**0.0014**	**0.5**	**1.1**	**7.0**	**27**
3C12	**B**	**20**	**2.4**	**4.8**	**8.6**	**0.0031**	**1.0**	**1.8**	**5.4**	**18**
3C12	**B**	**30**	**2.4**	**4.8**	**8.6**	**0.0052**	**1.6**	**2.2**	**4.7**	**14**
4C12	**A**	**10**	**2.6**	**3.5**	**7.3**	**0.0005**	**0.4**	**3.8**	**5.9**	**44**
4C12	**A**	**20**	**2.6**	**3.2**	**7.1**	**0.0010**	**0.9**	**8.3**	**4.2**	**32**
4C12	**A**	**30**	**2.6**	**3.6**	**7.5**	**0.0021**	**1.7**	**6.7**	**4.5**	**22**
4C12	**B**	**10**	**2.6**	**5.4**	**9.2**	**0.0012**	**0.3**	**1.4**	**5.6**	**28**
4C12	**B**	**20**	**2.6**	**5.0**	**8.8**	**0.0023**	**0.9**	**2.1**	**5.3**	**21**
4C12	**B**	**30**	**2.6**	**4.9**	**8.7**	**0.0038**	**1.6**	**3.1**	**4.7**	**16**
4C12	**C**	**10**	**2.6**	**6.1**	**10.0**	**0.0016**	**0.4**	**0.8**	**6.8**	**25**
4C12	**C**	**20**	**2.6**	**7.1**	**10.9**	**0.0047**	**0.9**	**1.1**	**5.4**	**15**
4C12	**C**	**30**	**2.6**	**6.6**	**10.5**	**0.0069**	**1.6**	**4.9**	**7.2**	**12**
5C12	**A**	**10**	**3.2**	**4.7**	**8.5**	**0.0003**	**0.3**	**4.2**	**5.4**	**55**
5C12	**A**	**30**	**3.2**	**4.4**	**8.2**	**0.0011**	**1.3**	**5.5**	**5.9**	**31**
5C12	**B**	**10**	**3.2**	**6.6**	**10.5**	**0.0006**	**0.3**	**1.5**	**7.2**	**39**

Tableau 3 : Fit parameters. with
ϕ_w =nanoparticule weight fraction in oil
R_{app}= their apparent diameter
e= the oil thickness in the lamellar phase leur rayon apparent,
c_s = the particule number per unit area in a lamellae
L = the mean distance between the particules in each hydrophobic layer