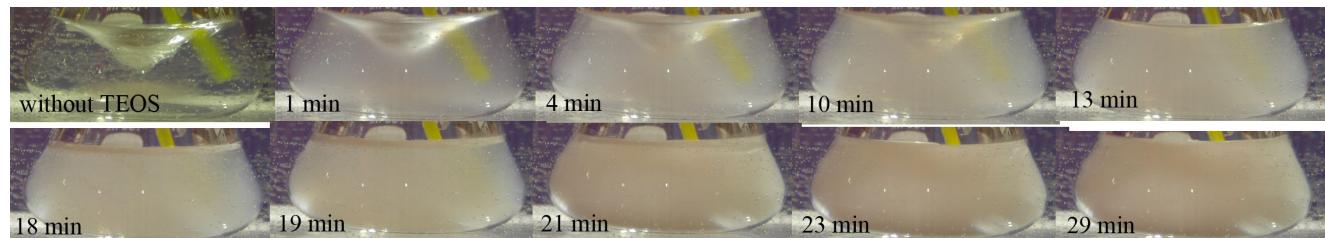


## SUPPORTING INFORMATION

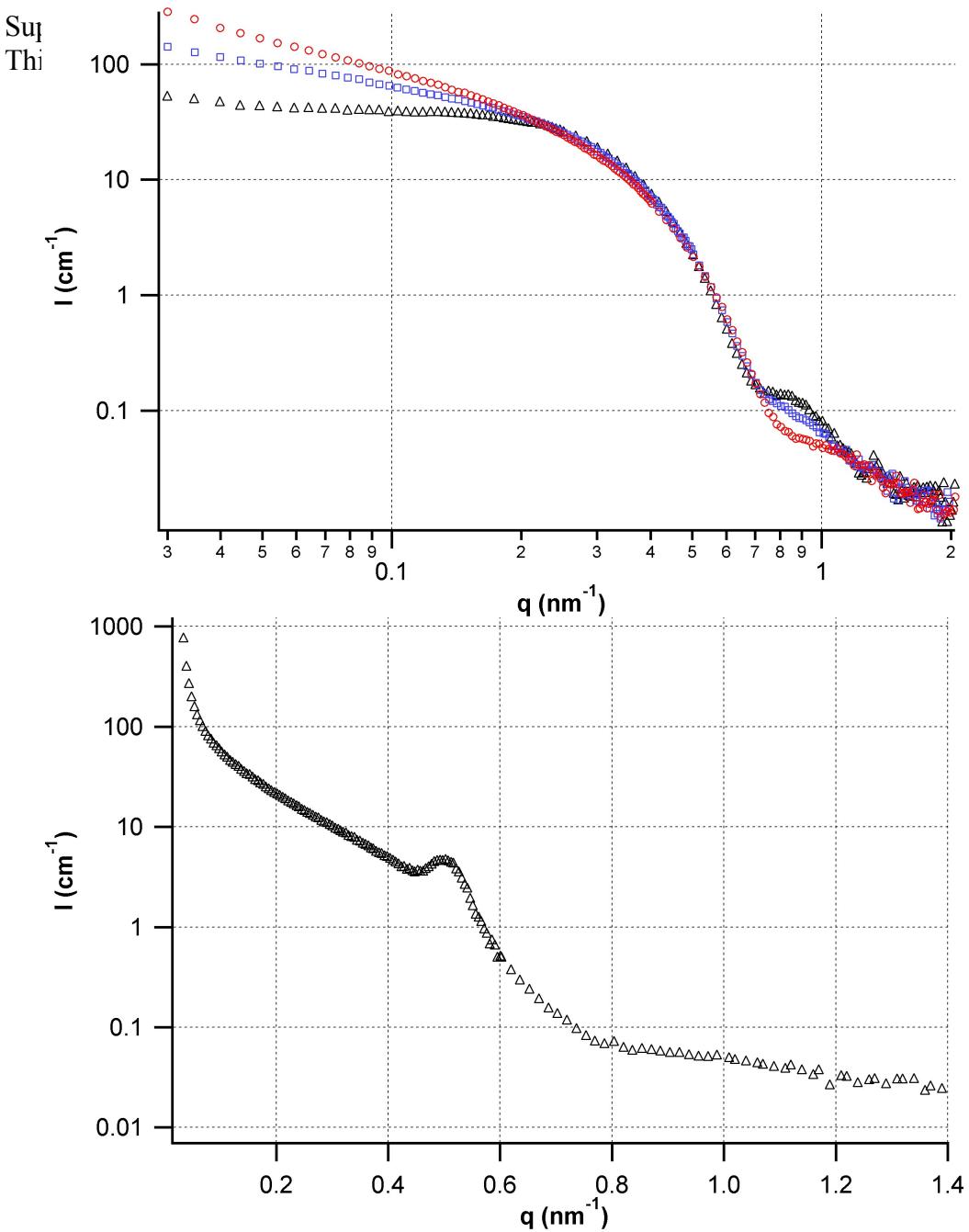


**Figure SI-1**

Pictures of the synthesis flask taken in real time simultaneously to the SANS measurements.

Prior to the addition of TEOS, the acidic Pluronic solution appeared transparent. After the addition of TEOS, the solution became immediately turbid and has become increasingly opaque until a thick white precipitate has formed after about 23 minutes of the reaction time.

The fact that the solution is turbid means that it is not homogeneous at large scales (comparable to visible wavelength) and that the reaction system is a multi-phase medium. For example, until TEOS hydrolysis is not completed (probably after about 5 minutes), TEOS could form an emulsion of droplets within the water phase because it is not soluble in water. Condensation reactions involving the silica species lead to the formation of hybrid micelles (even long cylindrical micelles have been shown in the following), which density is certainly fluctuating throughout the synthesis mixture and give another contribution to the turbidity. Finally, before the visual observation of the precipitation, small grains of hybrid material could scatter light before the detection of their internal structure by SANS.



**Figure SI-2**

(a) Evolution of the scattering curves between 5 and 20 minutes. Between 5 and 23 minutes, the SANS data show a continuous evolution, mainly characterised by the increase of the intensity at low  $q$  and a  $q^{-1}$  slope in a log-log (see figure SI-2) that is the signature of 1D objects.

(b) Beginning of the precipitation at 23 minutes. Only the (10) 2D-hexagonal peak is detected within the 1 minute data acquisition time. Long-range order is already observed because the width of this peak is fixed by the experimental resolution.

### **Ex-situ analysis of the precipitate and of the calcined material**

SAXS analysis of the obtained powder were made after the *in-situ* experiment.

This analysis confirmed the 2D hexagonal structure, with the observation of three diffraction peaks ((10), (11) and (20)) and a parameter of 10.72 nm of the uncalcined powder.

Calcination of this powder was made as follows : it was heated up under nitrogen from room temperature to 400°C at 2°C/min and then kept 30 min at 400°C

The calcination was carried out in the following way : the powder was heated up under nitrogen from room temperature to 400°C at 2°C/min and kept 30 minutes at 400°C. After, it was cooled down to 300°C and then kept 30 minutes at this temperature. During this period, nitrogen was turned off and oxygen turned on. Last, it was heated up under oxygen from 300°C to 500°C at 1°C/min and kept at 500°C for 240 minutes.

After calcination, a contraction of the overall structure is observed by SAXS and the final parameter value is 9.16 nm.

**Nitrogen adsorption/desorption** experiments were made on the calcined material and are given in the following table :

BET Surface Area	603 m <sup>2</sup> /g
Total Pore Volume	0.43 cm <sup>3</sup> /g
Micropore Volume	0.12 cm <sup>3</sup> /g
Average Pore Diameter (4V/A by BET):	2.86 nm
BJH Desorption Average Pore Diameter (4V/A):	3.42 nm

### SANS data modelling

The scattered intensity is the product of the form factor  $[F(q)]^2$  by the structure factor  $S(q)$ .

$$I(q) = [F(q)]^2 S(q)$$

In case of dilute suspension of object without interaction,  $S(q)$  equals one and the previous equation is reduced to :

$$I(q) = [F(q)]^2$$

Except for a few data points at very low  $q$ -values ( $q < 0.06 \text{ nm}^{-1}$ ), the SANS data are well modeled by suspension of objects without interactions and  $S(q)$  equals one.

### Form factors

Pluronic micelles made of an hydrophobic core of PPO of radius  $R_2$  and an hydrophilic shell of PEO of radius  $R_1$  are better described using a core-shell models. The three equations used in the present study describe the scattered intensity of core-shell spheres, ellipsoids and cylinders [i,ii].

In the following,  $\phi$  is the volume fraction occupied by the micelles and  $V_1$  is the volume of one micelle.  $\rho_0$ ,  $\rho_1$  and  $\rho_2$  are respectively the scattering length densities of the solvent, the shell region and the core region. For the acidic deuterated water solution,  $\rho_0 = 54.9 \cdot 10^9 \text{ cm}^{-2}$ .

The absolute intensity scattered by core-shell spherical micelles is given by:

$$I(q)(\text{cm}^{-1}) = \frac{\phi}{V_s} (\rho_1 - \rho_0)^2 [V_1 F_s(q, R_1) + \beta V_2 F_s(q, R_2)]^2 \text{ where } \beta = \frac{\rho_2 - \rho_1}{\rho_1 - \rho_0}.$$

We define the constant contrast as:  $K_c = \frac{\phi}{V_s} (\rho_1 - \rho_0)^2$  and  $F_s(q, R)$  is the form factor of a

sphere:

$$F_s(q, R) = \left[ 3 \frac{\sin(qR) - (qR)\cos(qR)}{(qR)^3} \right]$$

The form factor of a core-shell ellipsoid reads as:

$$I(q)(\text{cm}^{-1}) = K_c \int_0^{\pi/2} [F_s(q, r(R_1, \varepsilon, \alpha)) + \beta F_s(q, r(R_2, \varepsilon, \alpha))]^2 \sin \alpha d\alpha$$

$$\text{Where } r(R, \varepsilon, \alpha) = R \sqrt{\sin^2 \alpha + \varepsilon^2 \cos^2 \alpha}$$

A slightly different aspect ratio  $\varepsilon_c$  is taken for the core, in order to keep a constant thickness for the shell.  $\varepsilon$  is the anisotropy factor for the shell.

The form factor of a core-shell cylinder of length  $2L$  is:

$$I(q)(cm^{-1}) = K_c \int_0^{\pi/2} [F_c(q, R_1, L) + \beta F_c(q, R_2, L)]^2 \sin \alpha d\alpha$$

$$\text{With } F_c(q, r, L) = \frac{\sin(qL \cos \alpha)}{(qL \cos \alpha)} \frac{2J_1(qr \sin \alpha)}{(qr \sin \alpha)}$$

$\alpha$  is the angle between the normal to the particle and the scattering vector  $q$ .  $J_1$  is the first order Bessel function.

The smearing effects of the size distribution of the scatters and of the instrumental resolution are taken into account as follows. :

### Polydispersity in size

The polydispersity on the radius  $G(r_{ext}, \sigma, r')$  is represented by a log-normal distribution.

$$G_{LN}(r_0, \sigma, r) = \frac{1}{r \sigma \sqrt{2\pi}} \exp\left(-\frac{1}{2\sigma^2} \left(\ln \frac{r_0}{r}\right)^2\right)$$

$\sigma$  is the standard mean deviation, related to the FWHM by  $\Delta r_0 = \sigma r_0$ . The mean radius of the particle obtained by this function is  $\langle r \rangle = r_0 \exp(\sigma^2/2)$ .

### Instrument resolution

The shape of the direct beam is well described using a gaussian function  $R(q, \Delta q, q')$  where  $\Delta q$  is the FWHM. All details of calculation can be found somewhere else [iii].

$$R(q, \Delta q, q') = \frac{1}{\Delta q \sqrt{2\pi}} \exp\left(-\frac{(q' - q)^2}{2(\Delta q)^2}\right) \text{ with } (\Delta q)^2 = q^2 \left[ \left( \frac{1}{2\sqrt{2 \ln 2}} \frac{\Delta \lambda}{\lambda} \right)^2 \right] + \left[ \left( \frac{4\pi}{\lambda} \right)^2 - q^2 \right] \Delta \theta^2$$

$(\Delta \lambda / \lambda)$  is the FWHM (full width at half maximum) of the triangle function describing the wavelength spread.  $(\Delta \lambda / \lambda) = 10\%$  for the Dornier velocity selector used on the D22 instrument.

The final equation for modelling can be written as

$$I_{\text{model}}(q) = \int_0^{\infty} R(q, \Delta q, q') \int_0^{\infty} K_c G(r_{ext}, \sigma, r') F^2(r', q') dr' dq' . \quad (1)$$

Agreement between the model and the experimental points can be estimated from a  $\chi^2$  test:

$$\chi^2 = \sum_{N=2} \left[ (I_{\text{model}}(q) - I_{\text{exp}}(q)) / E(q) \right]^2 / (N - 2) . \quad (2)$$

Where  $N$  is the number of points in the experimental curve (*ca* 80 points per instrumental setting on the D22 detector) and  $E(q)$  the statistic error of the intensity.

Except for the spheres where the curves reach a plateau, the 6 first experimental points are not taken into account during the fitting procedure. The upturn at low  $q$  indicates a biphasic sample and the presence of attractive interactions. The structure factor hides the form factor.

The scattering curves are fitted using an in-house Fortran program.

The level of the intensity  $Kc$  is adjusted to the experimental points.

The unknown parameters are  $R_1$ ,  $R_2$ ,  $\varepsilon$  or  $L$ ,  $\beta$ , and  $\sigma$ .

The accurate determination of the length of cylinders requires to reach the Guinier regime when  $qR < 1$ . The experimental minimum  $q$  value is  $0.03 \text{ nm}^{-1}$ , which correspond in the real space to *ca.* 100 nm ( $q=\pi/L$ ). Nevertheless, at  $q < 0.06 \text{ nm}^{-1}$ , the scattering at low  $q$  suffers from the attractive structure factor. Consequently, above  $L = 50 \text{ nm}$ , the convergence of the program is poor and yields to an error of 10% on the length.

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i Lord Rayleigh, proc. Royal . Soc. London, Ser. A, 84 (1911) 25-38

ii J. S. Pedersen, *Adv. Colloid Interface Sci.* **1997**, 70, 171-210

iii I. Grillo; *Effect of instrumental resolution and polydispersity on ideal form factor in Small Angle Neutron Scattering* **2000**, ILL Technical Report n° ILL01GR08T