ESRF	**Experiment title:** Coupling rheology and structural measurements to understandthe brittle to ductile transition in self-assembled transient networks	**Experiment number:** SC-2895
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Report:

The ailm of this experiment was to decipher a possible structural signature of the transition from brittle-like to ductile-like behavior of transient networks. We use self-assembled networks made of surfactant micelles linked by tri-block copolymers. Our contrôl parameter is the molar ratio, R, of cosurfactant over surfactant (when R increases, micelles elongate). Experiments couple rheology and SAXS measurements. We used a Couette cell, and SAXS data were taken in the radial configuration.

Experiments were conducted in the following way: for a given sample, we fixed a shear-rate and measured at as function of time the evolution of both the stress and the scattering patterns, taking typically 1 image every 2 sec for about 300 sec. Typically, about 20 different shear rates were imposed to each sample. In order to avoid sample damage, the vertical position of the incident beam on the Couette cell is different for each imposed shear rate.

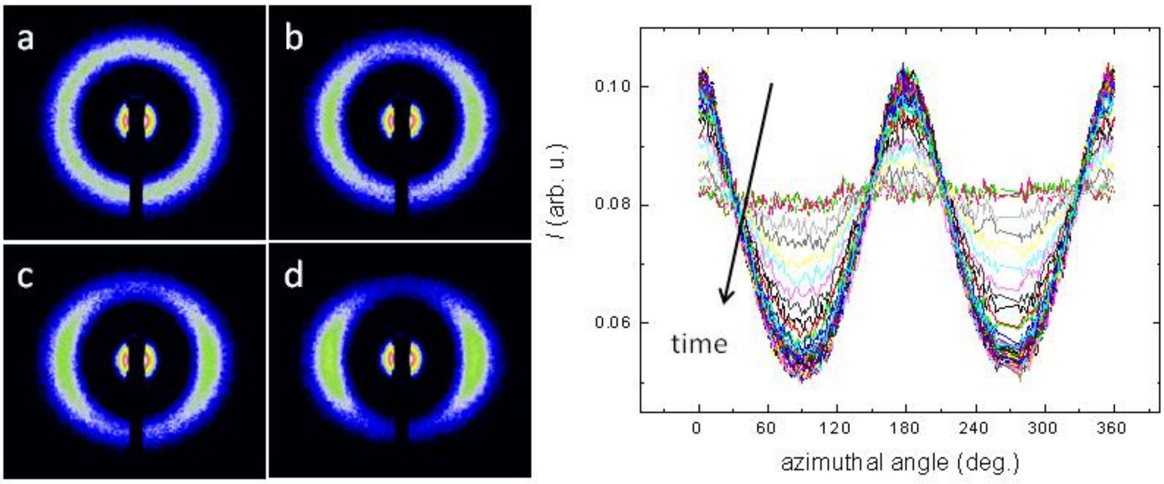

Fig. 1: (left) *typical scattering patterns for a sample with R=0.35 taken at various times under a shear rate of 0.44* s^{-1}. *(right) Evolution with time of the azimuthal profiles taken at the position of the peak.*

For samples with R<0.175, the scattering patterns were all isotropic, as expected for sufficiently short micelles. Anisotropy develops with time unders stress (fig. 1) for networks with longer micelles (R>0.175). We calculate the azimuthal profiles of the scattering patterns at the peak position, and define the contrast of the profile as $A = (I_{\max} - I_{\min}) / (I_{\max} + I_{\min})$, where $I_{\max}$ and $I_{\min}$ are respectively the maximal and minimal intensity along the profile.

In fig. 2, we show that the contrast follows the evolution of the stress as a function of the shear rate. We find that the contrast is higher for more elongated micelles (R larger) and increases with the shear rate (micelles become more and more aligned) when the shear rate/stress increases. Figure 2 also illustrates the two radically different behaviors of our samles: in (A), above a critical shear rate, both the stress and the contrast decrease: this is a signature of a fracture mechanism. By contrast, when the micelles are more elongated, a plateau-like evolution of both the stress and the contrast is observed: this a characteristic feature of shear-banding, before the sample eventually fractures.

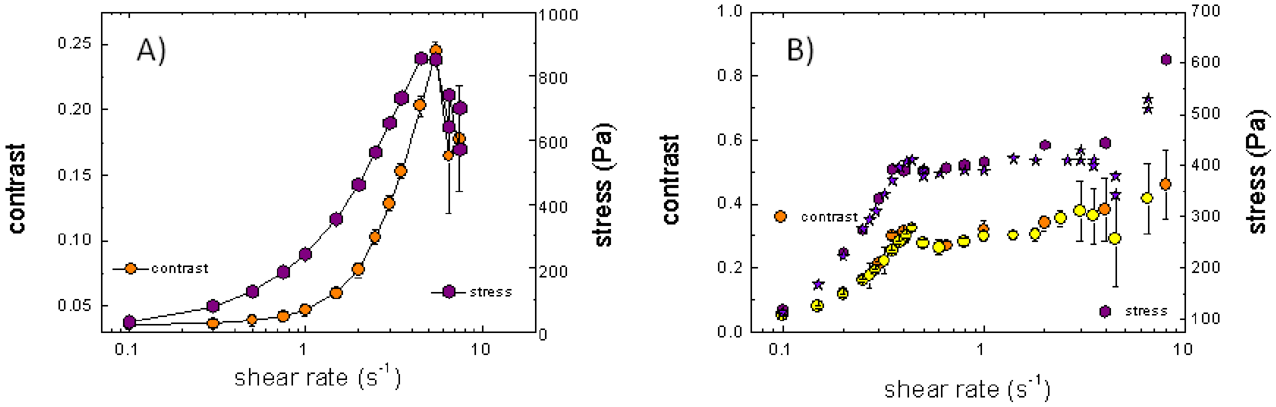

Fig. 2: *Contrast of the scattering pattern and stress as a function of shear rate, for a sample with R= 0.25 (A) and R=0.35 (B). Sample (A) exhibits a brittle-like behavior, and sample (B) exhibits a ductile-like behavior.*

To clearly identify a signature of the transition between the behavior of the various samples, we have analyzed the fluctuations of the contrast. The error bars in figure 2 are in fact the standard deviation of the contrast. In A, one sees that the fluctuations of the contrast are very small, and increases as the sample fractures. In B, the fluctuations are small and increase abruptly at the end of the stress plateau. For all samples, one can define a shear rate, $\dot{\gamma}_{fluct.}$, at which the standard deviation of the fluctuations normalized by their mean values increases abruptly. We believe that $\dot{\gamma}_{fluct.}$ signs the onset of a fracture mechanism. This shear rate can be compared with the shear rate, $\dot{\gamma}_{lin.}$, at which the rheology data departs from a "linear" Newtonian regime and starts to exhibit shear-thinning.

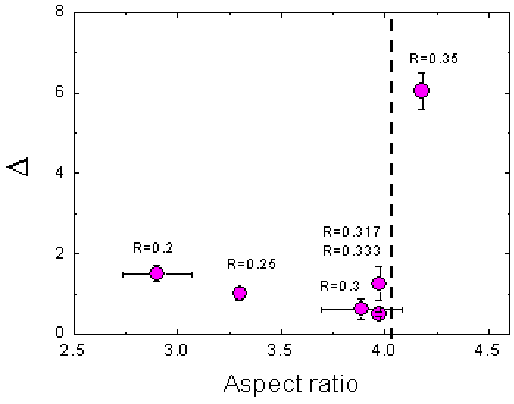

Fig.3: *Δ as a function of the aspect ratio of the micelles. The aspect ratio was evaluated from the position of the SAXS peak, assuming a simple model of micelles located on a cubic lattice.*

We evaluate the "ductility" zone, Δ, as the range of shear rate over which the sample is not Newtonian anymore but has not fractured yet. Δ, defined as $\Delta = (\dot{\gamma}_{fluct.} - \dot{\gamma}_{lin.}) / \dot{\gamma}_{lin.}$ is plotted in figure 3. Δ is the equivalent of the normalized range of strain for which a material departs from its linear elastic behavior before it breaks, and quantifies how ductile is the material. As shown in Figure 3, Δ is small and constant for micelles with an average low aspect ratio and increases abruptly above a critical aspect ratio.

We believe this result provides a clear strutural signature of the brittle-like to ductile-like behavior of transient network.