Mechanical Strength Enhancement by Grain Size Reduction in a Soft Colloidal Polycrystal

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Supplementary information

Optical microscopy. For a given NP concentration inside the micellar samples, the grains start to form at the onset of fluid-crystal transition temperature and the equilibrium size is very rapidly reached as it is shown on the images in figure 1-SI. These images were taken near the transition temperature point between 29 and 31 °C. The number of micellar polycrystalline grains first increases and rapidly stabilizes when the transition point is exceeded, as it is shown on the figure 2-SI (a-h). The average size does not evolve with temperature nor with time above 29 °C. Once the temperature of 42 °C was reached, there was no noticeable texture evolution with time in the course of 3 hours. At this measuring temperature, several images were taken in different sample locations and statistical analysis was performed in order to measure the size distribution of the grains. Average size and error bars, which are the standard deviation of the size distributions, are drawn according to the procedure reported in the reference: G. Cumming, F. Fidler and D. Vaux, *J. Cell Biol.* 2007, **177**, 7-11.

Figure 3-SI below shows 3 optical microscopy images recorded at 42 °C, at a micellar concentration = 15.2 vol. % and NP concentration = 0.42 vol. %, having each an area of 290ß390 μm^2, a number of grains per image of 44, 40 and 37 from left to right respectively. The average grain size is 60 µm.

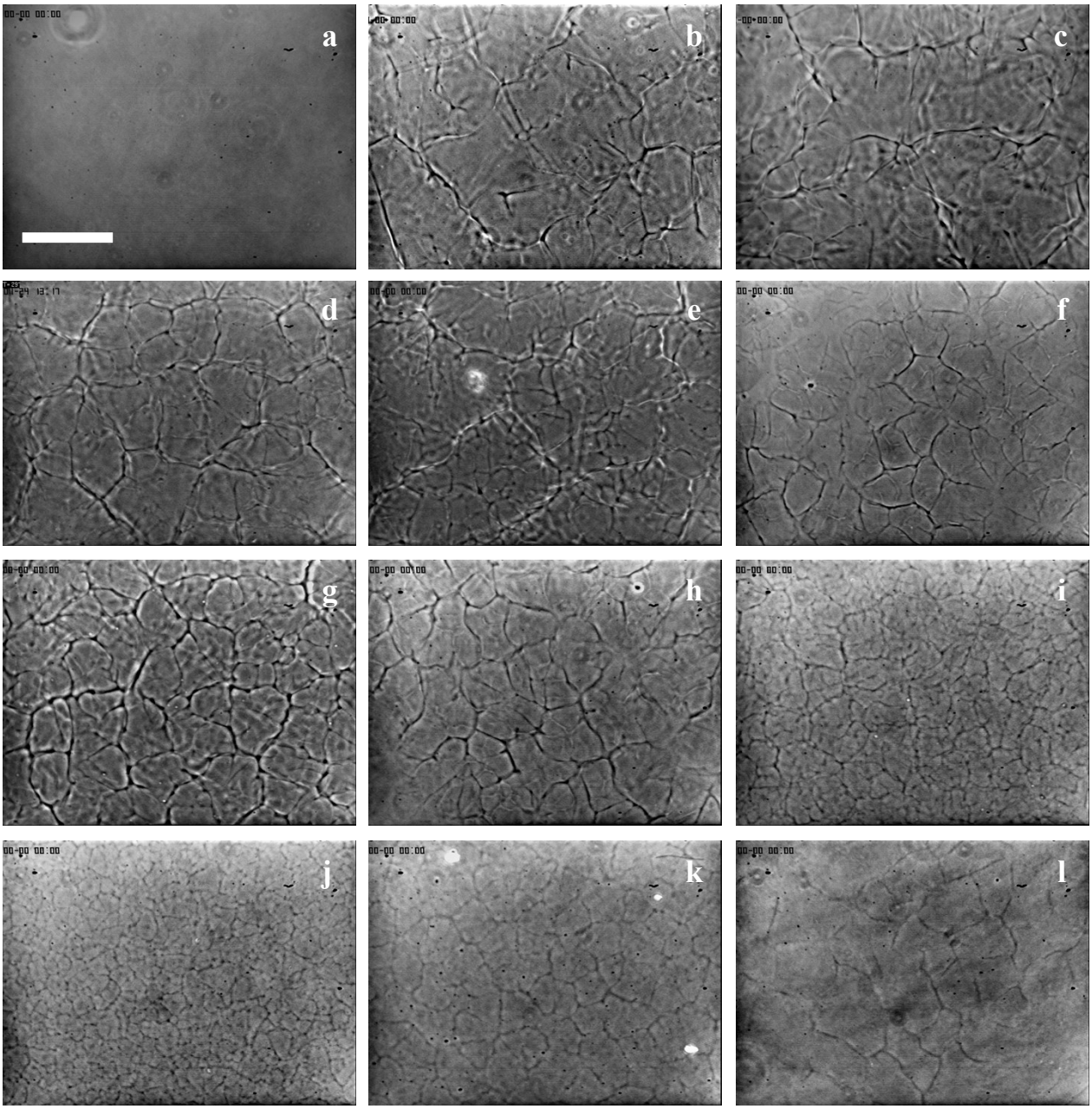

Figure 1-SI. Observation by optical microscopy of samples slightly above the fluid-crystal transition temperature point (29 < T< 31 °C) at constant micellar concentration (15.2 vol. %) and

NP concentration of 0 (a), 0.125 (b), 0.25 (c), 0.417 (d), 0.542 (e), 0.708 (f), 0.833 (g), 1.042 (h), 1.250 (i), 1.67 (j), 2.08 (k) and 2.92 (l) vol. %. The scale bar is 100 µm and holds for all images.

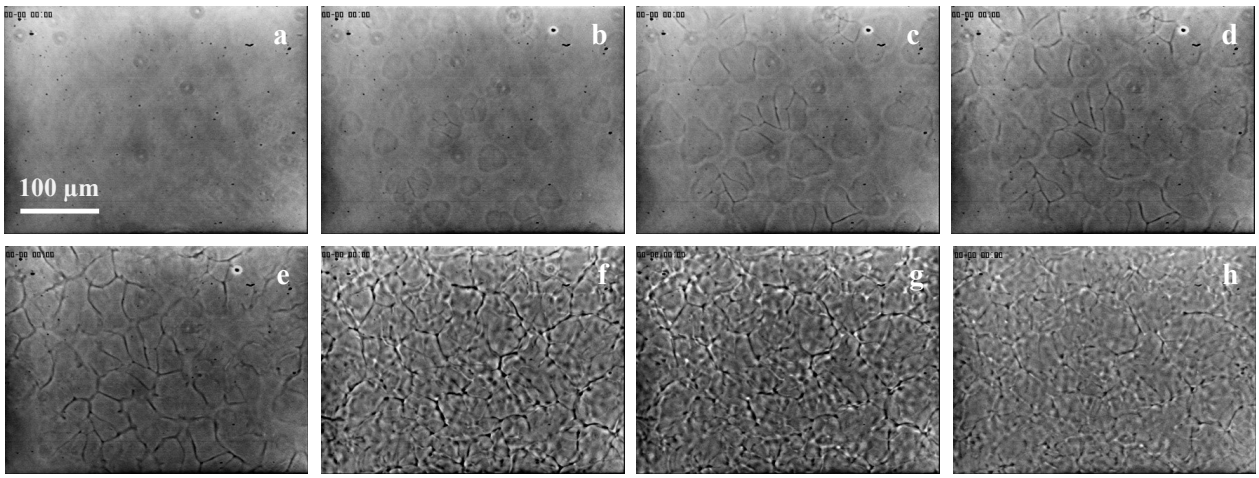

Figure 2-SI. Observation by optical microscopy of a sample at a micellar concentration of 15.2 vol. % and NP concentration of 1.042 vol. % recorded at T = 15, 28.56, 28.85, 29, 29.35, 32.9, 35.25 and 42 °C (a, b, c, d, e, f, g and h respectively). The scale bar is 100 µm and holds for all images.

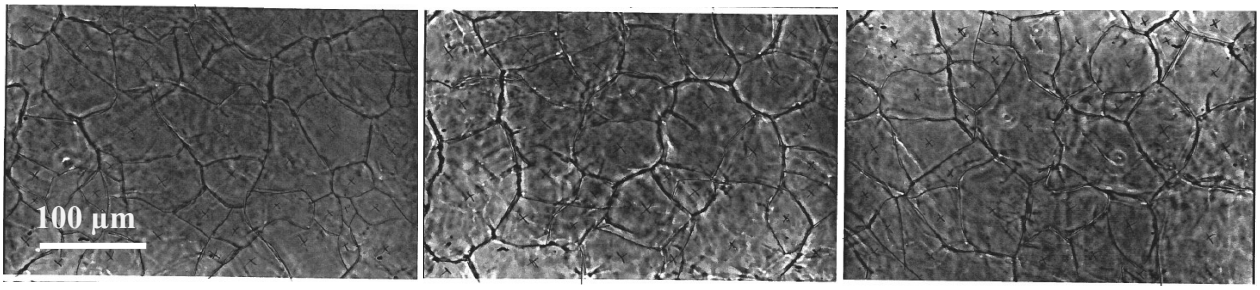

Figure 3-SI. Observation by optical microscopy of a sample at a micellar concentration of 15.2 vol. % and NP concentration of 0.42 vol. % recorded at T = 42 °C. The scale bar is 100 µm and holds for all images.

Small angle X-ray scattering. As a precaution, SAXS data at 25 °C were modelled by using iterative least squares procedure methods to minimize χ^2, by considering that the nanoparticles only contribute to the scattering intensity in the two-component system due to their high scattering length density. The scattering intensity is the product of the contrast factor of NP by their spherical

form factor only, because at this temperature and NP concentration, the structure factor is 1. The fit is shown as a solid black line on figure 4-SI on the left along with the scattering intensity for the sample with the micellar concentration = 15.2 vol. % and NP concentration = 1.25 vol. %. The fit curve accounts for NP size polydispersity using a log-normal distribution with a mean diameter of 26 nm and a standard deviation of 0.1. On this figure, we also represent the scattering intensity of a sample with the micellar concentration = 15.2 vol. % and NP concentration = 0 vol. %. The data shown at 42 °C on figure 4-SI (right) are for comparison purposes.

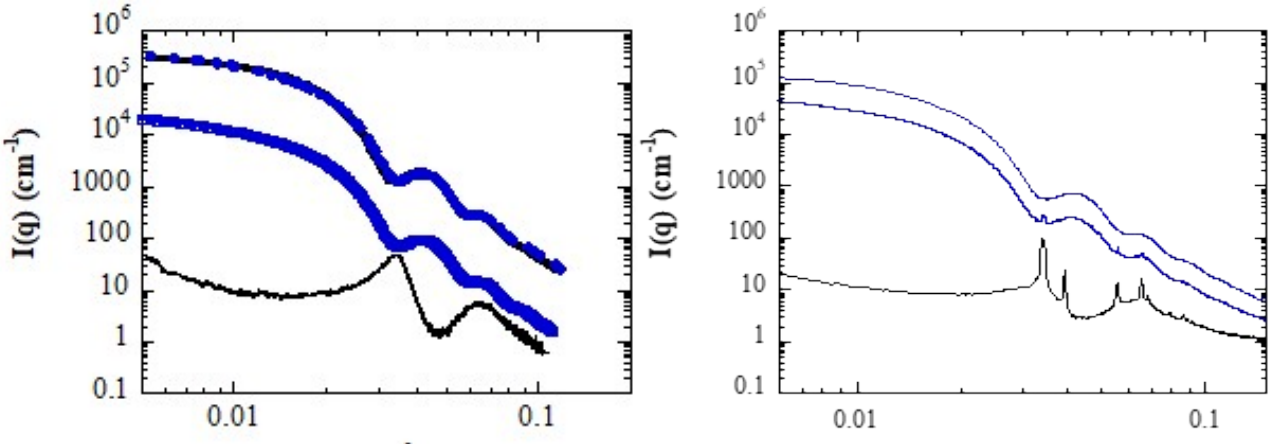

Figure 4-SI. Scattering intensities at 25 °C for NP volume fraction of 0, 0.42 and 1.25 vol % (from down to top, left graph). The solid black line is a fit to the form factor of spherical nanoparticles at NP concentration of 1.25 vol. %. Data at 42 °C for NP volume fraction of 0, 0.42 and 1.25 vol % (from down to top, right graph)

Rheology. The detailed variation of both elastic and viscous moduli of the mixtures as a function of temperature and NP concentration are shown below (figure 5-SI). We notice on this figure that when the temperature increases above 27 °C, both G' and G" sharply increase, and show the expected crossover from viscous liquidlike behavior, defined by a weak G" and G' < G", to viscoelastic solidlike behavior. The viscoelastic modulus increases within a very narrow temperature range around the transition temperature of 29 °C. Upon addition of NPs, G' and G''

curves show two important features. First, the transition temperature does not shift, which indicates a fixed copolymer volume fraction involved in micellization in all solutions. Second, the increase of NP concentration indeed leads to an increase, respectively a decrease, of the plateau elastic modulus, respectively viscous modulus, up to a concentration of 1.67 vol. %. Above this concentration, G' starts decreasing, following the trend displayed by the yield stress while G" only show a decrease (figure 5-SI), in agreement with data reported by Louhichi et al., *Phys. Rev. E* 2015, **92**, 032307. These authors have found that dissipation is strongly influenced by the amount of defect in the polycrystal which is directly related to the increase of heating rate (up to 0.1 °C/min) or NP concentration (up to a NP volume fraction of 1.67 in our case). In both cases the decrease of G'' when more defects are present is probably consistent with the yield stress enhancement which is shown in figure 5. We should however emphasis that we do not observe a regime change in G'' as the NP concentration goes above 1.67 % which is consistent with the previous reports.

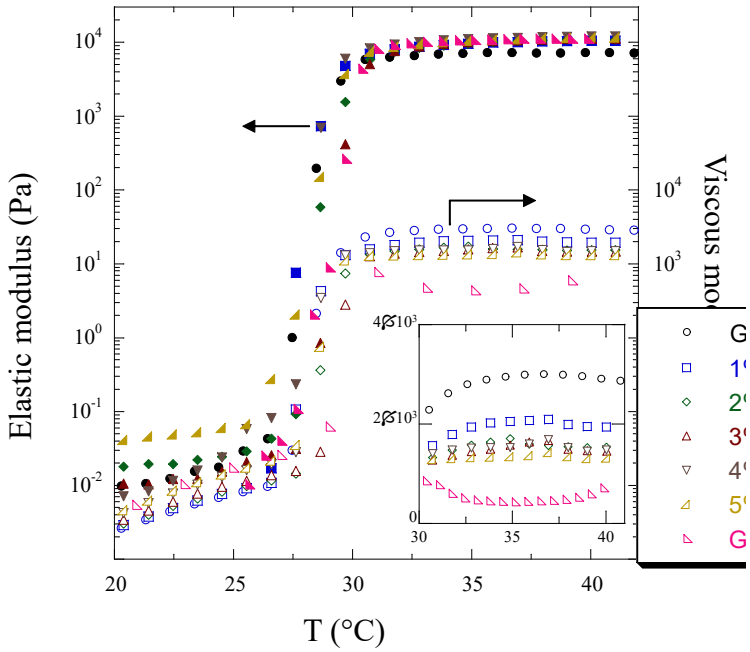

Figure 5-SI. Evolution of elastic and viscous moduli (solid and empty symbols respectively) as a function of temperature at the micellar concentration of 15.2 vol. % and NP concentration of 0, 0.42, 0.83, 1.25, 1.67, 2.08 and 2.70 vol. % (full and empty ●, ■, ◆, ▲, ▼, ◢ and ◣ colored symbols respectively). Inset: zoom on the plateau viscous modulus (Pa) as a function of temperature (°C).

The protocol of shear-rate controlled flow experiments and the fit to Herschel-Bulkley model follow the procedure recently described in reference [40]. The model accurately describes the data and provides the yield stress: *shear stress= yield stress +k[shear rate]*^{n}, where k and n are the consistency index and the flow index respectively. Table 1 below summarize the values deduced from the fits for the curves shown in the manuscript (figure 4) and figure 6-SI below.

Table 1-SI. Fitting parameters from Herschel-Bulkley model as a function of NP concentration: average yield stress, n = 0.37 and average k values.

C (vol. %)	yield stress (Pa)	n	k (Pa s^n)
0.00	94	0.37	10.1
0.42	137	0.37	12.1
0.83	151	0.37	14.5
1.25	169	0.37	8.1
1.67	180	0.37	14.4
2.08	147	0.37	11.2
2.92	127	0.37	4.0

The figure 6-SI below represents both experimental data points and Herschel-Bulkley model fits with n = 0.37 for NP concentration of 0, 0.42, 0.83, 1.25, 1.67, 2.08 and 2.92 vol. % at 42 °C and heating rate of 0.1 °C/min. Each experiment was performed on a fresh sample. The displayed fitting curves gives the yield stress values for each sample, whose average is plotted in figure 5.

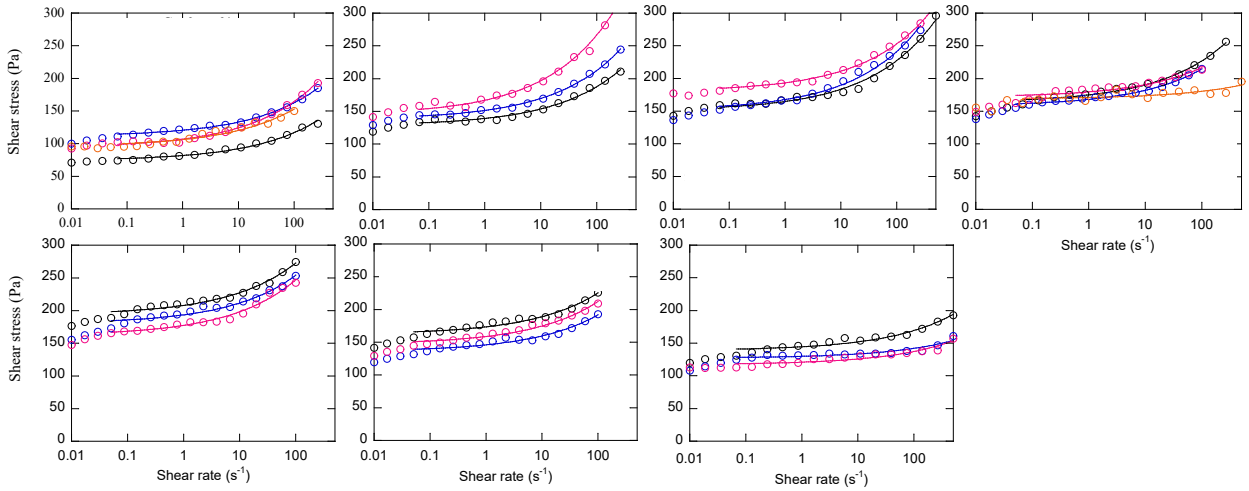

Figure 6-SI. Experimental flow curves at 42 °C (empty circles) with Herschel-Bulkley fits (solid lines) at a micellar concentration of 15.2 vol. % and NP concentration of 0, 0.42, 0.83, 1.25, 1.67, 2.08 and 2.92 vol. % (left to right and top to down) The average yield stress, average consistency index and the flow index for each NP concentration are shown on **Table 1-SI**.