

Electronic Supplementary Information

Surface cleaning of artworks: structure and dynamics of nanostructured fluids confined in polymeric hydrogel networks

Rosangela Mastrangelo, Costanza Montis, Nicole Bonelli, Paolo Tempesti, and Piero Baglioni

| | |
|---|---|
| Fitting model for PVA FT1 and PVA FT3 SAXS curves | 2 |
| PolyCore-Shell Ratio Model for the fitting of Microemulsion's SAXS Profile | 3 |
| SAXS curves of PVA FT1 and PVA FT3 with and without microemulsion | 4 |
| Dynamic Light Scattering (DLS) theoretical notions and Cumulant method analysis . | 5 |

Fitting model for PVA FT1 and PVA FT3 SAXS curves

PVA FT1 and PVA FT3 SAXS curves have been fitted according to the following equation:

$$I(Q) = \frac{A}{(1 + \xi Q)^m} + \frac{B}{Q^n} + Bkg \quad (S1)$$

where A and B are scale factors, ξ is the polymer's correlation length, m is the Porod exponent, which is related to the local polymer structure²³ and describes the polymer/solvent interactions,²⁴ n is the exponent associated to the power law regime in the low-Q region ($Q < 0.2 \text{ nm}^{-1}$), Bkg is a parameter accounting for background correction. When $1 \leq n \leq 3$, n represents the mass fractal dimension (d_m) that is 3 for full solid materials.²⁵ On the other hand, when $3 \leq n \leq 4$, one can obtain the surface fractal dimension (d_s) from the equation:

$$d_s = 6 - n \quad (S2)$$

d_s is 2 for smooth surfaces and goes towards 3 as the roughness increases.²⁶

PolyCore-Shell Ratio Model for the fitting of Microemulsion's

SAXS Profile

The SAXS profile of the o/w microemulsion was fitted using the PolyCoreShellRatio model of the NCNR Igor Pro data analysis package.[Hayter JB. Physics of amphiphiles-micelles, vescicles and microemulsions. In: DeGiorgio V., Corti M., editors. Proceeding of the International School of Physics; 1983, pp. 59-93.] This model calculates the form factor for a polydisperse spherical particle with a core-shell structure. In this model, the ratio $R(\text{core})/R(\text{core+shell})$ is held constant. The form factor is normalized by the mean particle volume such that:

$$P(Q) = \frac{A}{Vol} \langle f^2 \rangle + Bkg \quad (\text{SS3})$$

where f is the single particle scattering amplitude and the average $\langle \rangle$ is over a Schulz distribution of radii.

SAXS curves of PVA FT1 and PVA FT3 with and without microemulsion

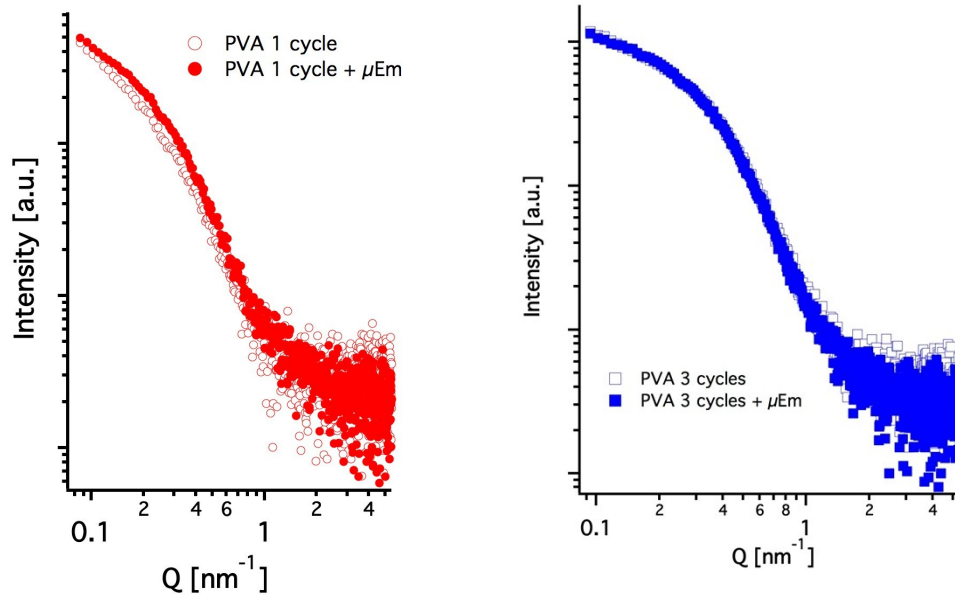


Figure S1. Comparison between the SAXS curves of PVA FT1 (left) and PVA FT3 (right) as prepared and when loaded with the microemulsion. No significant differences are evidenced, especially in the case of PVA FT3 where the two curves are perfectly superimposable.

Dynamic Light Scattering (DLS) theoretical notions and Cumulant method analysis

In DLS experiments the time correlation functions $G_2(\tau)$ of the scattered light were measured at different angles and the normalized intensity autocorrelation function ($g_2(q, \tau)$) are obtained directly from the software during the measurement. $g_2(q, \tau)$ is connected to the normalized electric field autocorrelation function $g_1(q, \tau)$, by the Siegert relation

$$g_2(q, \tau) = 1 + \beta^2 |g_1(q, \tau)|^2 \quad (\text{S4})$$

with $\beta^2 \leq 1$ a coherence factor that depends on the experimental conditions.

For a suspension of polydisperse Brownian spheres, $g_1(q, \tau)$ decays exponentially

$$g_1(q, \tau) = \int_0^{\infty} P(q, D) \exp(-q^2 D \tau) dD \quad (\text{S5})$$

where D is the diffusion coefficient and $P(q, D)$ is the intensity-weighted probability distribution function of the diffusion coefficient.

Particle sizing is performed by extracting D from $g_2(q, \tau)$ fitting and applying the Stokes-Einstein equation

$$D = \frac{k_B T}{6\pi\eta R_h} \quad (\text{S6})$$

where k_B is the Boltzmann constant, T is the absolute temperature, η is the viscosity of the solvent, and R_h is the hydrodynamic radius of the spheres.

In the classic cumulant method analysis, we have that $\ln[g_1(q,\tau)]$ is written as a Taylor series in the correlation time

$$\ln[g_1(q,\tau)] = \ln\beta^2 + 2[-\Gamma_1\tau + \frac{\Gamma_2\tau^2}{2!} + \dots + \frac{(-1)\Gamma_n\tau^n}{n!}] \quad (\text{S7})$$

and by stopping to the second order we have

$$\Gamma_1 = Dq^2 \quad (\text{S8})$$

and

$$\Gamma_2 = \frac{\bar{D}^2 - D^2}{D^2} \Gamma_1^2 \quad (\text{S9})$$

where

$$\bar{D}^n = \int_0^\infty D^n P(D) dD \quad (\text{S10})$$

is the n th order of the intensity-weighted probability distribution function of D ($P(D)$).

The polydispersity index (PDI) is defined as

$$\sigma^2 = \frac{\Gamma_2}{\Gamma_1^2} \quad (\text{S11})$$

