Supporting information

for

Ligand-Free Synthesis of Gold Nanoparticles Included Within Block Copolymer Films

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FitGISAXS description[1]:

The FitGISAXS software uses various structural models for the GISAXS analysis. In the case of the analysis of arrays of cylinders perpendicular to a substrate, the analysis is made with the *Paracrystal 2D-hex model*, which uses the 2D-paracrystal theory[2] assuming a hexagonal lattice.

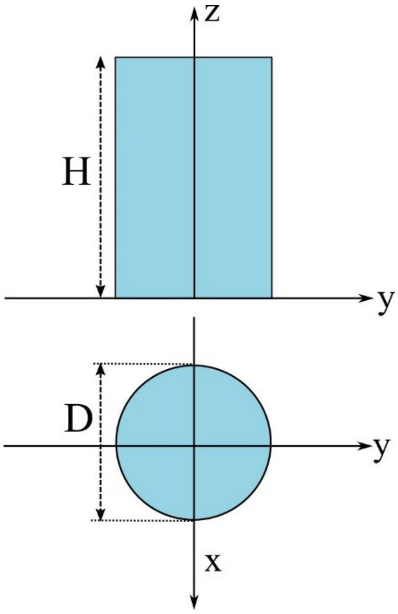

Figure S1. *Cylinder* form factor

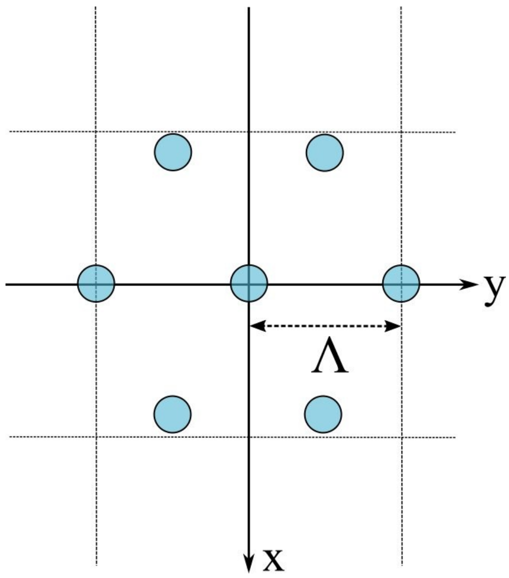

Figure S2. 2D-paracrystal model with hexagonal lattice

The structure factor corresponding to a hexagonal lattice is the following:

$$S(q_{//}) = \prod_{k=x,y} \frac{1 - exp\left(-q_{//}^{2}.\sigma^{2}\right).exp\left(-2.\frac{\Lambda}{\Lambda_0}\right)}{1 - 2.exp\left(-\frac{1}{2}.q_{//}^{2}.\sigma^{2}\right).exp\left(-\frac{\Lambda}{\Lambda_0}\right).\phi_k + exp\left(-q_{//}^{2}.\sigma^{2}\right).exp\left(-2.\frac{\Lambda}{\Lambda_0}\right)}$$

[1] Babonneau, D. FitGISAXS: software package for modelling and anlysis of GISAXS data using IGOR Pro. *Journal of Applied Crystallography* **2010**, 43, 929

[2] Leroy, F.; Lazzari, R.; Renaud, G. Effects of near-neighbor correlations on the diffuse scattering from a one-dimensional paracrystal. *Acta Crystallographica Section A* **2004**, A60, 565

with Λ, the lattice parameter (defined as in the figure S2), assumed to be proportional to D with a constant factor c ($\Lambda = c.D$); Λ_0, the correlation length taking into account the finite size effects; σ, the standard deviation for Λ ; $\phi_x = \cos\left(q_x.\Lambda_y.\frac{\sqrt{3}}{2}\right)$ and $\phi_y = \cos\left(q_y.\Lambda_y\right)$

The fit of GISAXS data for arrays of cylinders perpendicular to a substrate can be achieved by varying the parameters D, H, Λ and σ.

Polydispersity of the cylinder dimensions in the configuration can be simulated with a Gaussian function in order to get a more realistic structural information.

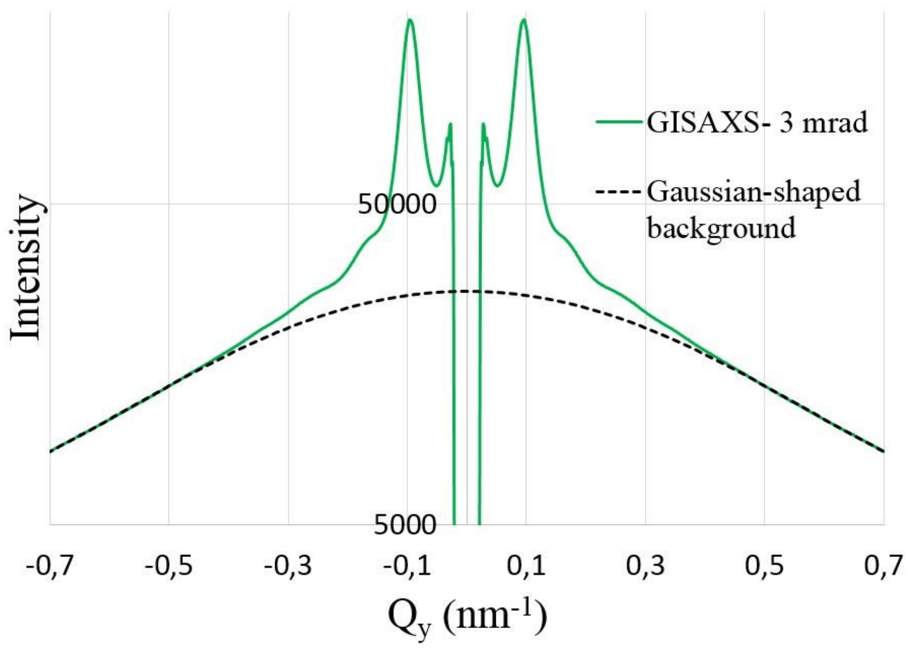

Figure S3. Intensity *versus* Q_y curves for the incidence of 3 mrad (green solid line) and corresponding Gaussian-shaped background curve (black dotted line) used to model the scattering from the polymer matrix.

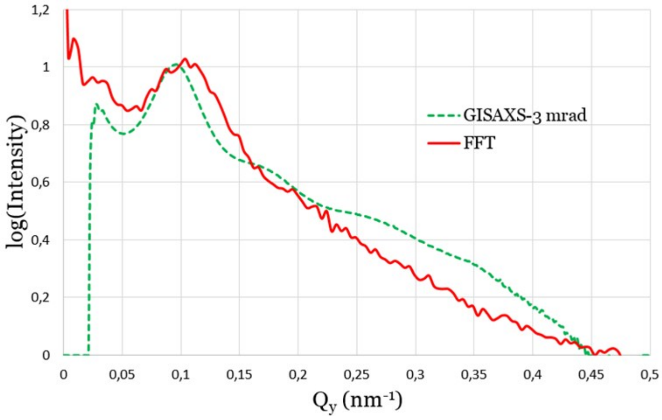

Figure S4. Comparison between the log(Intensity) vs Q_y curves from GISAXS analysis (at an incidence angle of 3 mrad) and FFT of an AFM height image for a PS_{48}-b-$P4VP_{25}$ film. The Q_y position of the first peak is 0.100 nm^{-1} and 0.104 nm^{-1}, respectively. Both curves have been normalized for a better comparison.

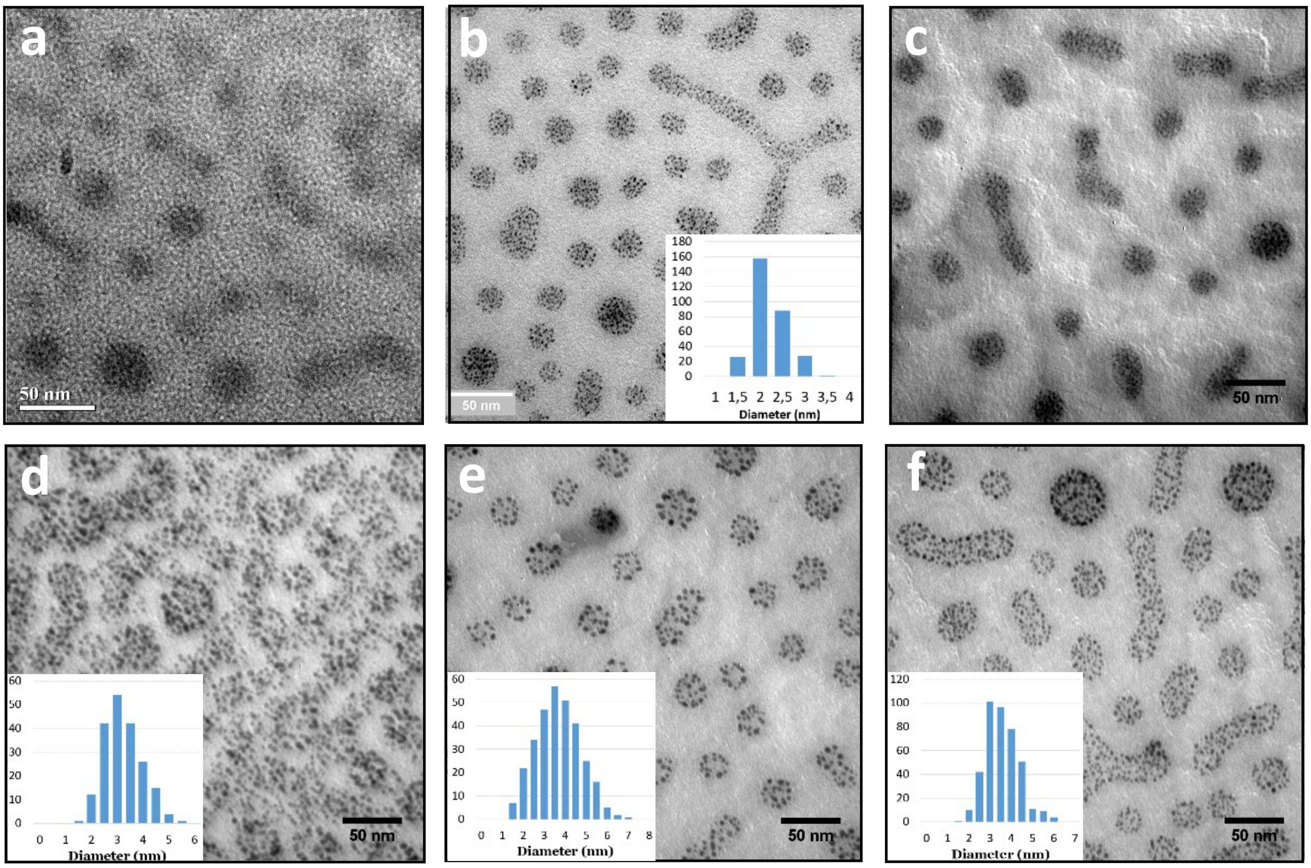

Figure S5. TEM pictures of the cylinders of PS_{27}-b-$P4VP_7$ containing AuNPs formed by sonication for an initial ratio gold/pyridine of (a) 0.2, (b) 0.5, (c) 1, (d) 2, (e) 3.5 and (f) 5.5, with inset the size distribution of the AuNP diameter over 300 particles.

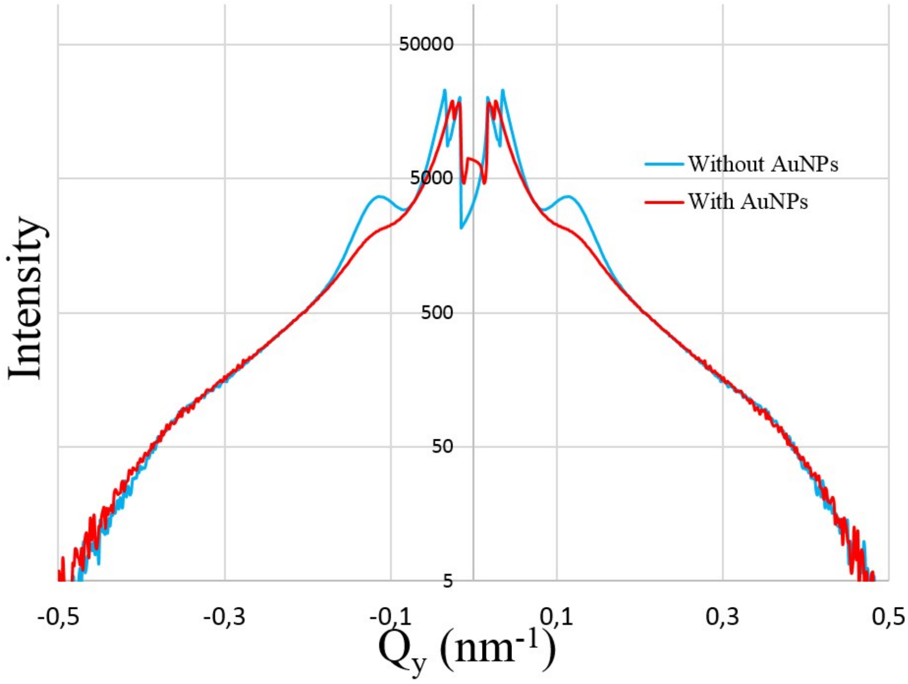

Figure S6. Intensity *versus* Qy curves for the incidence of 4 mrad for a PS27-b-P4VP7 film without (blue line) and with (red line) AuNPs formed by sonication (AuNP diameter = 2 nm). Note that the first peak position does not shift for the gold-containing film from the one without AuNPs, showing the persistence of the hexagonal cylindrical organization in both cases.

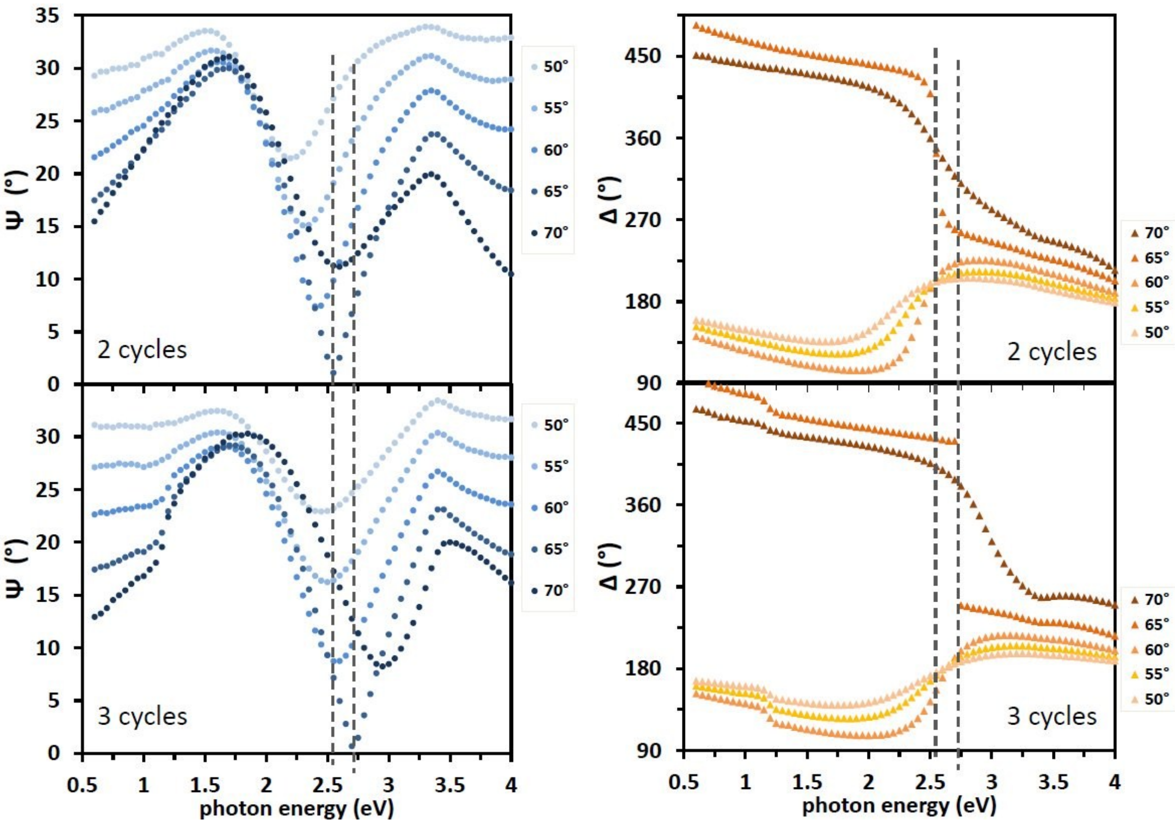

Figure S7. Evolution of the ellipsometric angles Ψ (left, in blue) and Δ (right, orange) for the films loaded with the AuNPs after 2 growth cycles (upper curves) and 3 growth cycles (lower curves). The spectral position at which the extinction of Ψ and the jump of Δ occur shifts from 2.55eV (λ=486nm) to 2.70eV (λ=459nm) from the 2-cycle film to the 3-cycle film.