Supporting information

Experimental section

Material and instrumentation

PS-*b*-P4VP (number average molecular weight M_n^{PS} = 57.5 kg.mol^{-1}, M_n^{P4VP} = 18.5 kg.mol^{-1}, Đ = 1.15), PEG homopolymer (M_n = 10.2 kg.mol^{-1}, Đ = 1.05) and P4VP homopolymer (M_n = 18100, Đ = 1.11) were purchased from Polymer Source. All other chemicals were purchased from Acros or Aldrich and were of highest purity grade. All chemicals were used as received unless otherwise specified. Atomic force microscopy (AFM) was performed on a Digital Instruments Nanoscope V scanning force microscope in tapping mode using NCL cantilevers (Si, 48 N/m, 330 kHz, Nanosensors). To determine the overall thickness of the thin films, the film was scratched with a razor blade and imaged with AFM. Water contact angle measurements were performed with an OCA-20 apparatus (Data-physics Instruments GmbH) in the sessile drop configuration. The results are the average of three values each obtained with a droplet volume of 6 µL. Transmission electron microscopy (TEM) was performed on a LEO 922 microscope, operating at 120 kV accelerating voltage in bright field mode. Samples for TEM experiments were prepared by drop-casting a solution containing the particles onto TEM grid (carbon-copper 200 mesh). The grids were then dried in vacuum for 15 h. The stained samples were exposed to RuO_4 vapors during 15 min. DLS experiments were performed on a Malvern CGS-3 apparatus equipped with a He-Ne laser with a wavelength of 632.8 nm. The measurements were performed at a 90° angle and each sample was measured at least 5 times in order to check the reproducibility. The results were analyzed using a CONTIN algorithm, a method based on a constraint inverse Laplace transformation of the data and which gives access to a size distribution histogram for the objects present in solution. The Stokes–Einstein approximation was used to convert diffusion coefficients into apparent hydrodynamic radii. The polydispersity index (PDI) of the micelles was estimated from the Γ_2/Γ_1 ratio in which Γ_1 and Γ_2 represent the first and second order moments calculated from the Cumulants method. Before measurements the solutions were filtered (0.45 µm PTFE syringe filter) to remove dust.

PS-*b*-P4VP thin film preparation

Silicon substrates were cleaned by a piranha solution (H_2SO_4 98%/H_2O_2 30% 3/1 v:v) during 30 min before being rinsed several times in ultra-pure water. The substrates were then dried with the spin-coater at a velocity of 4000 rpm for 20 s. Filtered solutions (0.45 µm) of polymer in chloroform were then spin-coated onto these substrates at 2000 rpm during 40 s. The thickness of the films was controlled by the solution concentration. The films were then annealed in 1,4-dioxane vapors for 12 h at room temperature in a sealed chamber containing 5 ml of 1,4-dioxane.

Alkyne functionalization of PS-*b*-P4VP films

The alkyne functionalization of the P4VP domains was carried out at room temperature in a desiccator evacuated at 50 mbar containing the PS-*b*-P4VP films and 100 µl of 4-bromo-1-butyne. After 1.5 h the films were removed and dried under vacuum. A thick film of P4VP is functionalized in the same conditions of the PS-*b*-P4VP thin film and then used to estimate, by ^{1}H NMR, the degree of functionalization of P4VP by 4-bromo-1-butyne.

Selective cross-linking of the PS-*b*-P4VP films

The chemical cross-linking of the P4VP domains was carried out at room temperature in a desiccator evacuated at 50 mbar containing the alkyne functionalized PS-*b*-P4VP films and 100 µl of 1,4-diiodobutane. After 24 h the films were removed and dried under vacuum.

PEG grafting onto P4VP in solution

The α-methoxy-ω-azide terminated poly(ethylene glycol) (PEG-N_3) was synthesized from α-methoxy-poly(ethylene glycol) by a procedure described elsewhere.[1] To optimize the reaction, the PEG grafting was firstly carried out in solution using a partially alkyne functionalized P4VP homopolymer (degree of functionalization ≈ 0.25). 2.4 mg (0.000106 mmol) of functionalized P4VP, 37 mg (0.00365 mmol) of PEG-N_3 were dissolved in 1 mL of a mixture methanol-water (1/1 v/v). 1.5 mg (0.0177mmol) of tris(benzyltriazolylmethyl)amine and 4.4 mg (0.0177 mmol) $CuSO_4.5H_2O$ are then dissolved in 1 ml of water and 160 µl of this stock solution were added to the mixture containing the PEG-N_3. The mixture is then degassed by bubbling argon for 15 min before the addition of 56 µl of a 0.1 mol.L^{-1} aqueous solution of sodium ascorbate. After 24 h the PEG-grafted P4VP is precipitated in cold diethyl ether and dried under vacuum. The efficiency of the grafting is verified by GPC and FTIR (Fig. S5).

PEG grafting onto PS-*b*-P4VP thin films.

The procedure used to graft PEG-N_3 onto the PS-*b*-P4VP films was similar to the one described for P4VP in solution. 22 mg of PEG-N_3 were dissolved in 2 mL of a methanol-water mixture (1/1 v/v). 9.4 mg (0.0177mmol) of Tris(benzyltriazolylmethyl)amine and 4.4 mg (0.0177 mmol) $CuSO_4.5H_2O$ are then dissolved in 1 ml of water and 97 µl of this stock solution were added to the mixture containing the PEG-N_3. The mixture is then degassed by bubbling argon for 15 min before the addition of 35 µL of a 0.1 mol.L^{-1} aqueous solution of sodium ascorbate (0.0354 mmol). The solution was stirred for 15 min to ensure a complete dissolution of all reagents and then syringed over the substrates (alkyne functionalized PS-*b*-P4VP films on silicon wafer) in a deoxygenated

vial. After 24 h the films are removed from the solution and thoroughly rinsed with water and methanol before drying under vacuum.

Dissolution of the PEG-grafted PS-*b*-P4VP thin films

The PEG-grafted PS-*b*-P4VP films were immersed into 1 ml of a good solvent of the PS matrix (chloroform, toluene or dimethylformamide) for 12 h in order to dissolve them completely and retrieve the nanoparticles. The solution containing the nanoparticles was filtered with a 1 μm PTFE syringe filter before characterization.

Self-assembly of PEG-grafted nanoparticles in a poor solvent of one face

The film was initially dissolved in 500 μl of DMF and then 500 μl of water was slowly added to the solution in order to promote the assembly of the nanoparticles. The resulting solution was characterized by DLS and TEM.

Results

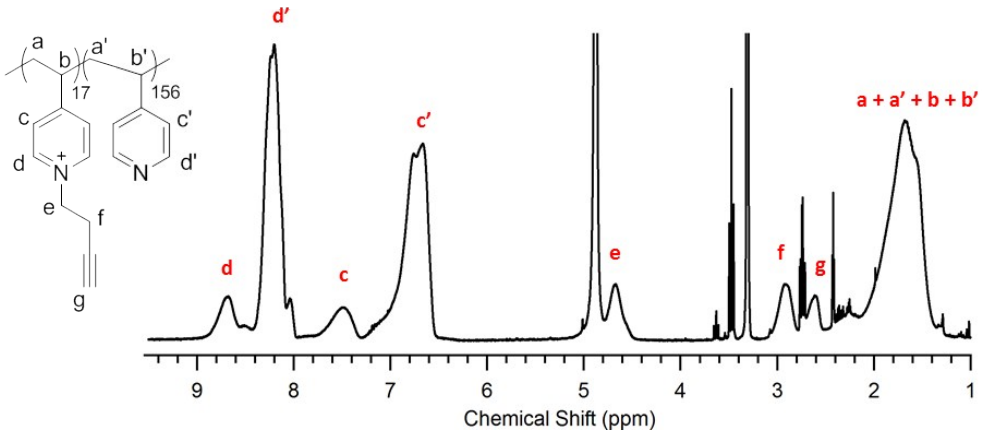

Fig. S1 ^{1}H NMR spectra of a thick P4VP film functionalized during 1h30 with 4-bromo-1-butyne vapor (50 mbar, RT) and dissolved in MeOD.

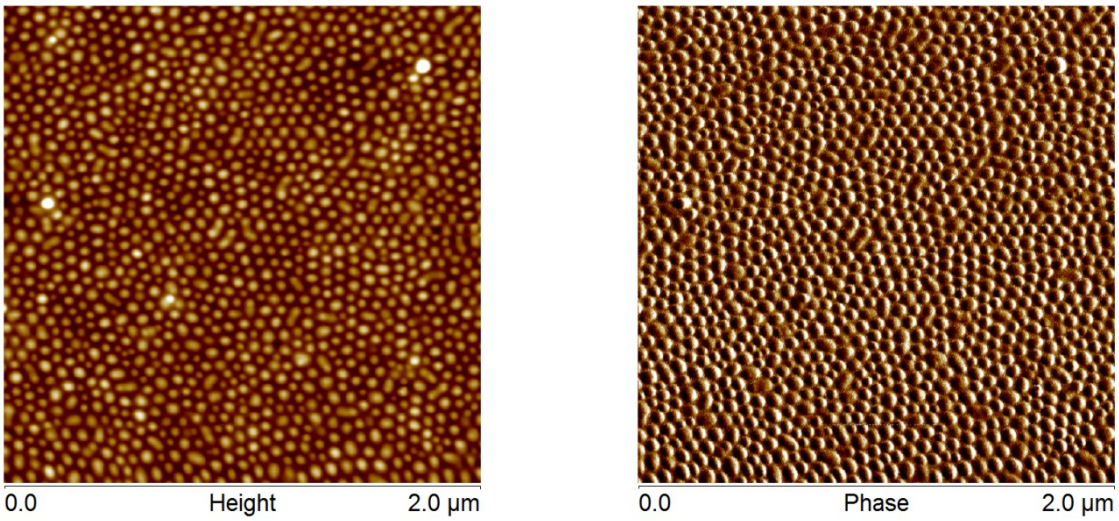

Fig. S2 AFM images (height and phase) of a 30 nm thick PS-*b*-P4VP thin film after functionalization with 4-bromo-1-butyne and cross-linking with 1,4-diiodobutane.

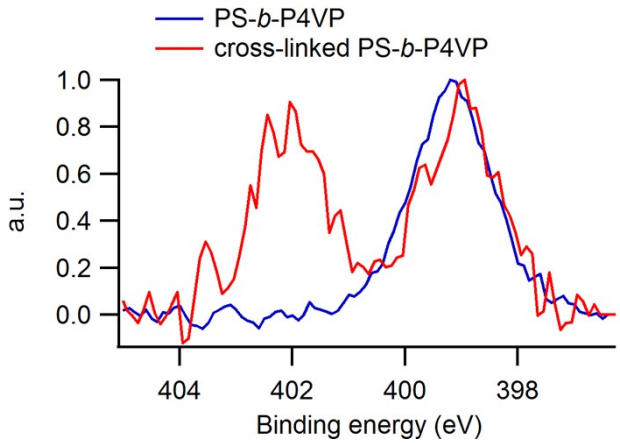

Fig. S3 XPS spectra of the N 1s region of PS-*b*-P4VP thin films before cross-linking and after reaction with 1,4-diiodobutane vapor for 24 h.

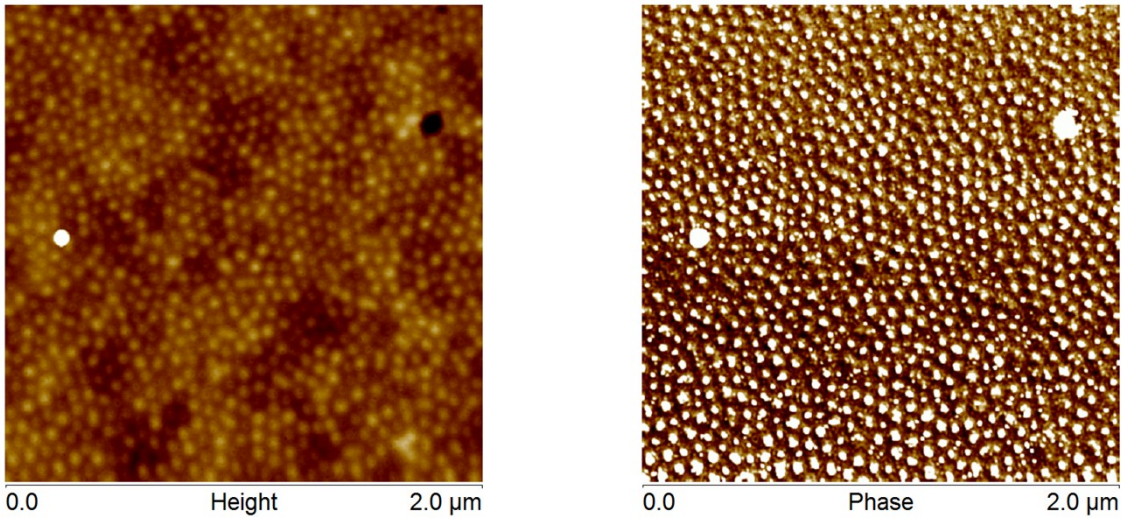

Fig. S4 AFM images (height and phase) of a 30 nm thick cross-linked and alkyne functionnalized PS-*b*-P4VP thin film after 24h of immersion in a methanol-water mixture (1/1 v/v).

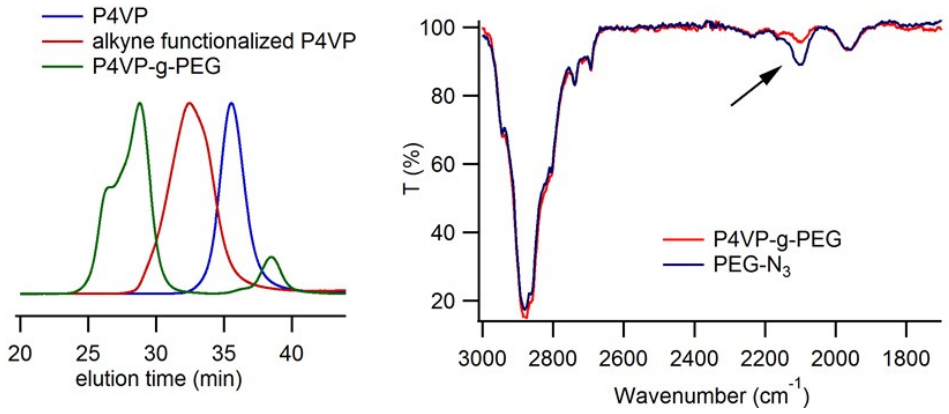

Fig. S5 GPC traces of P4VP before and after alkyne functionalization and of P4VP-*g*-PEG. FTIR spectra of PEG-N_3 and P4VP-g-PEG showing the disappearance of the peak associated to the azide stretching at 2100 cm^{-1} after grafting.

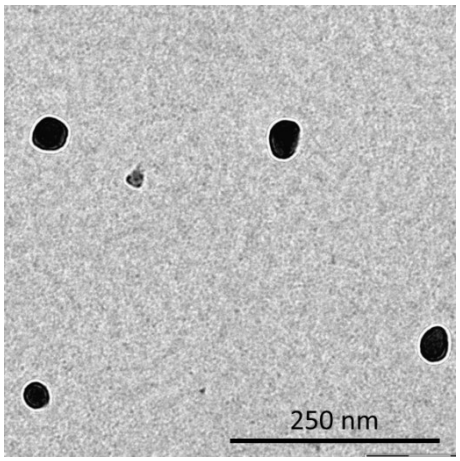

Fig. S6 TEM image of the nanoparticles formed from an ungrafted PS-*b*-P4VP thin film.

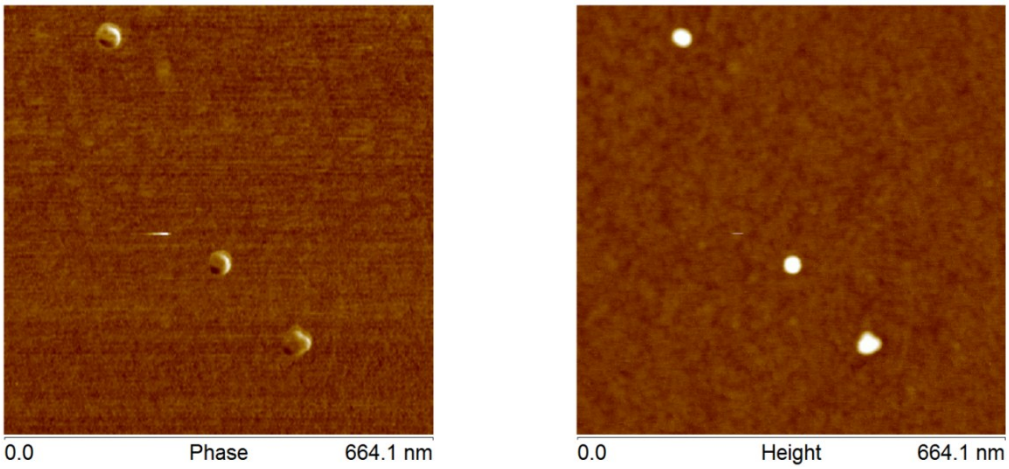

Fig. S7 AFM phase and height images of nanoparticles formed from a PEG-grafted PS-*b*-P4VP thin film deposited onto a silicon wafer by spin-coating.

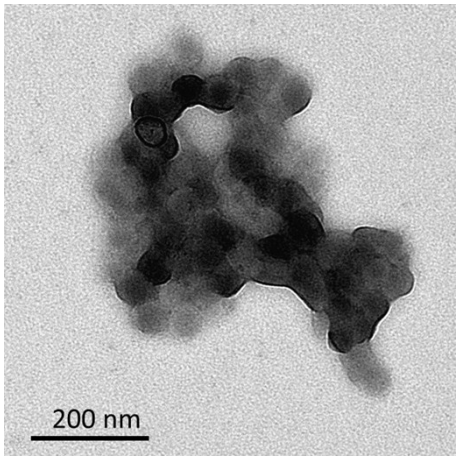

Fig. S8 TEM image of the aggregate formed from particles obtained from a PEG grafted PS-*b*-P4VP thin film in DMF-water (1/1 v/v).

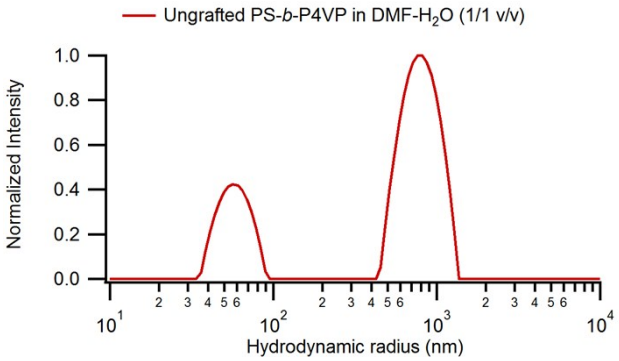

Fig. S9 Size distribution of the particles obtained from ungrafted PS-*b*-P4VP films in solution in a DMF-water mixture (1/1 v/v).

Reference

[1] A. Van Quaethem, P. Lussis, D. A. Leigh, A.-S. Duwez and C.-A. Fustin, *Chem. Sci.*, 2014, **5**, 1449-1452.