Supporting Information

Functional Nanoparticles-driven Self-assembled Diblock Copolymer Hybrid Nano-Patterns

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This supporting information contains

-Total number of pages: **6 pages**

-Total number of figures: **5 figures**

> SEM, TGA, UV-visible spectra and SAXS pattern of the block copolymers and NPs used in this work

-Total number of schemes: **7 Tables**

> XPS data of the block copolymers and NPs used in this work

> Values of the dispersion, polar and hydrogen bonding parameters for the calcul of the interaction parameter χ_{12}
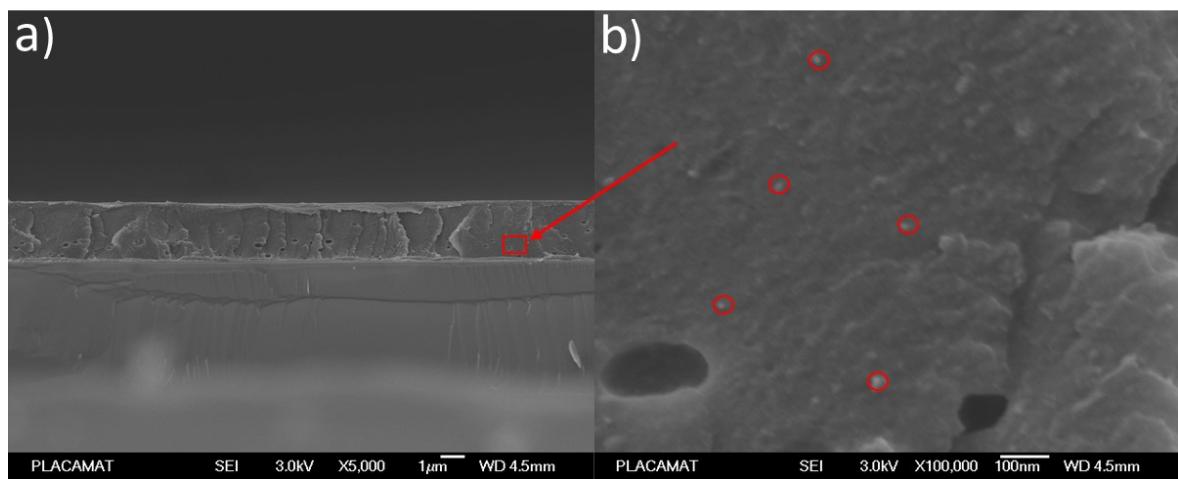
Figure SI1. a) SEM images of the section of the hybrid film with GNPs@PS 31 v%. b) is a magnification image of a)
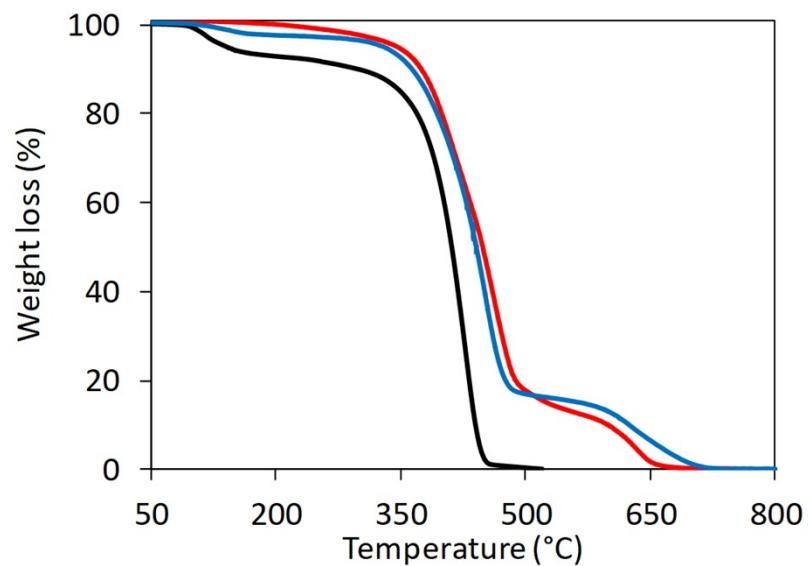

Figure SI2. TGA thermograms of PS macro-initiator (black curve), PS-*b*-PVBN$_3$ (blue curve) and PS-*b*-PVBEG (red curve).
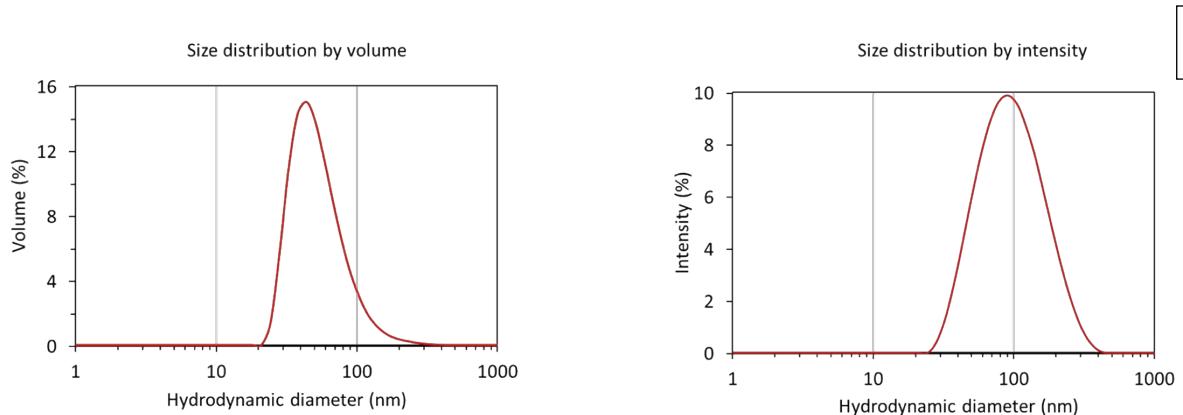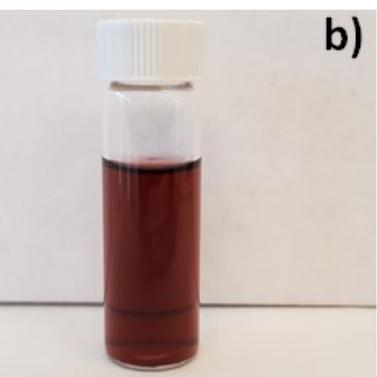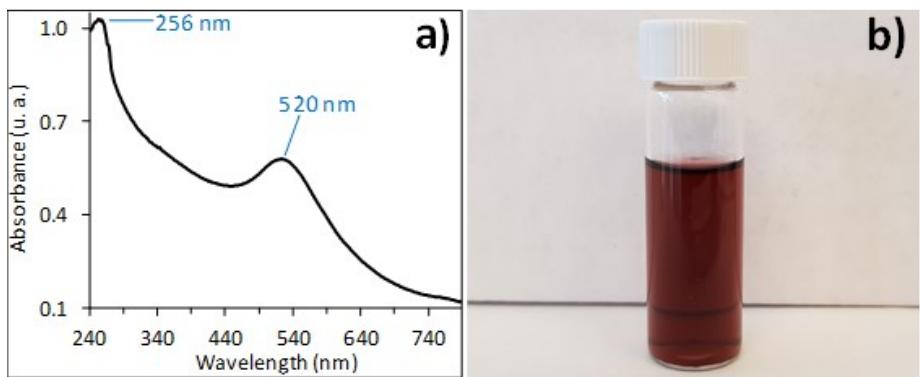
Figure SI3. (a) UV-vis spectrum, (b) photo of a suspension and (c) size distributions by Dynamic Light Scattering of polystyrene-thiol-capped gold nanoparticles.

$$Grafting\ density = \left[\frac{\left(\dfrac{W_{\%shell}}{100 - W_{\%shell}}\right) \times 100 - W_{\%core}}{M_{Ligand} \times S \times 100}\right] 10^6 \left[\mu mol/m^2\right]$$

Equation SI1

Where M_{Ligand} is the molar mass of polystyrene thiol PS-thiol (6000 g.mol^{-1}), S is the specific surface area of gold nanoparticles (62 m^2.g^{-1}, calculated from the hypothesis of a non-porous smooth spherical nanoparticle), and $W\ \%$ the weight loss percentage of the gold core and PS shell, due to its degradation ($_{shell}$) and to the NPs ($W\%_{core}$), *i.e.* before grafting ($\approx$3%). The specific surface area required for this equation, if not calculated by Brunauer–Emmett–Teller (BET) analysis, can also be calculated from Gao equation described below:

$$Surface\ area\ (S) = \frac{\sigma}{d\rho}$$

Equation SI2

where σ is the shape factor of the nanoparticles, equals to 6 for spherical nanoparticles; d is the diameter of the nanoparticles ($\approx$5 nm) and ρ is the density of the material (NP) and is equal to 19.32 g/cm^3.

Table SI1. XPS data of PS-*b*-PVBC film

Orbitals	Components	BE (eV)	FWHM (eV)	At. Conc. (%)
	C=C	284.5	0.9	67.1
C 1s	C−C/C−H	285.0	0.9	22.3
	C-Cl	286.6	0.9	1.9
	π-π*	291	0.9	3.5
Cl 2p	Cl 2p$_{3/2\text{-}1/2}$	200/202	1.1	1.7

BE: Binding Energy   FWHM: Full Width at Half Maximum
At. Conc.: Atomic Concentration

Table SI2. XPS data of PS-*b*-PVBN$_3$ film

Orbitals	Components	BE (eV)	FWHM (eV)	At. Conc. (%)
C 1s	C=C (cycle)	284.5	0.9	67.5
	C−C/C−H	285.0	0.9	24.2
	C−N	286.2	1.1	2.6
	π-π*	291	1.3	3.7
N 1s	N$^-$/N−R	400.5	1.1	1.4
	N$^+$	404.3	1.1	0.7

Table SI3. XPS data of PS-*b*-PVBEG film

Orbitals	Components	BE (eV)	FWHM (eV)	At. Conc. (%)
C 1s	C=C	284.5	1	51.1
	C−C/C−H	285.0	1.0	17.2
	C−N/C−O	286.6	1.0	14.6
	π-π*	291	1.6	1.8
N 1s	N (Triazole)	399.6/401.7	1.2-1.2	2.9
O 1s	O−C	532.8	1.7	12.4

Table SI4. Values of the dispersion, polar and hydrogen bonding parameters.

Polymer	δ_d(MPa$^{1/2}$)	δ_p(MPa$^{1/2}$)	δ_h(MPa$^{1/2}$)	δ_{tot}(MPa$^{1/2}$)
PS	17.6	18.5	19.1	17.7
PVBC	2.3	5	11	7
PVBN$_3$	3	3.7	9.5	5.5
PVBEG	18	19.5	23.9	19.8

Since Flory Huggins interaction parameters (χ_{12}) between PS and PVBN$_3$ or PVBEG are not available, they were calculated from pure component data. First, Hansen Solubility Parameters (HSPs) were determined using HSPiP software (5th edition 4.2.02). Then the relation described by Lindvig et al.[63] was used (Equation 2). This formula gives the Flory-Huggins interaction parameters using HSPs that combine the contribution due to dispersion (van der Waals, δ_d), the contribution due to polar forces (δ_p) and the contribution due to hydrogen-bonding forces (δ_h). The values of the dispersion, polar and hydrogen bonding parameters are reported in Table SI4. Using $\alpha = 1$ in equation 2 and HSP parameters reported in Table SI4, the Fluory-Huggins parameters (χ_{12}) in PS-*b*-PVBC, PS-*b*-PVBN$_3$ and PS-*b*-PVBEG were calculated and were equal to 0.11, 1.27 and 0.28, respectively.

$$\chi_{12} = \alpha \frac{V_1}{RT}\left[(\delta_{d1} - \delta_{d2})^2 + 0.25(\delta_{p1} - \delta_{p2})^2 + 0.25(\delta_{h1} - \delta_{h2})^2\right]$$: Equation 2

V_1 is the molar volume, R the gas constant, T the absolute temperature, δ_d van der Waals contribution, δ_p the contribution due to polar forces and δ_h the contribution due to hydrogen-bonding forces, α is a constant equal to 1.

Table SI5. XPS data of PS-*b*-PVBEG film containing 8 v% of polystyrene-capped gold nanoparticles

Orbitals	Components	BE (eV)	FWHM (eV)	At. Conc. (%)
Au 4f	Au 4f$_{7/2\text{-}5/2}$	83.8−87.7	1.1	0.3
	C=C	284.5	1.0	55.9
	C−C/C−H	285.0	1.0	21.0
C 1s	C−N/C−O	286.2	1.2	8.4
	π-π*	291.0	1.7	2.4
N 1s	N Triazole	399.5/401.8	2.2	1.4
O 1s	O−C	532.7	1.5	7.0

Table SI6. XPS data of PS-*b*-PVBEG film containing 19 v% of polystyrene-capped gold nanoparticles

Orbitals	Components	BE (eV)	FWHM (eV)	At. Conc. (%)
Au 4f	Au 4f$_{7/2-5/2}$	84−87.5	1.1	0.8
	C=C	284.5	0.9	61.9
C 1s	C−C/C−H	285.0	0.9	21.6
	C−N/C−O	286.2	1.3	5.5
	π-π*	291	1.3	4.3
N 1s	N (Triazole)	399.5/401.8	1.1	1.1
O 1s	O−C	532.9	1.7	4.7

Table SI7. XPS data of PS-*b*- PVBEG film containing 31 v% of polystyrene-capped gold nanoparticles

| Orbitals	Components	BE (eV)	FWHM (eV)	At. Conc. (%)
Au 4f	Au 4f$_{7/2-5/2}$	83.8−87.7	1.38	1.1
	C=C	284.5	1	65.6
C 1s	C−C/C−H	285.0	1	19.8
	C−N/C−O	286.4	1.4	2.3
	π-π*	291	1.5	5.1
N 1s	N (Triazole)	399.5/401.7	1.3	0.8
O 1s	O−C	532.6	1.5	2.8
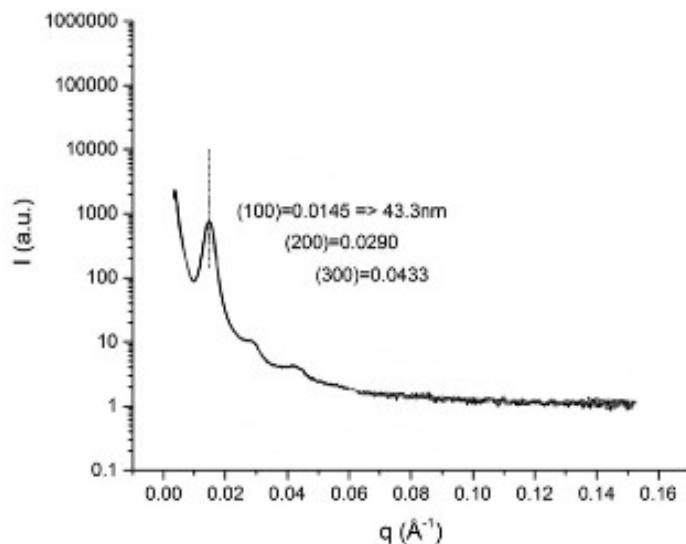
Figure SI4. SAXS pattern of the PS-*b*-PVBEG.
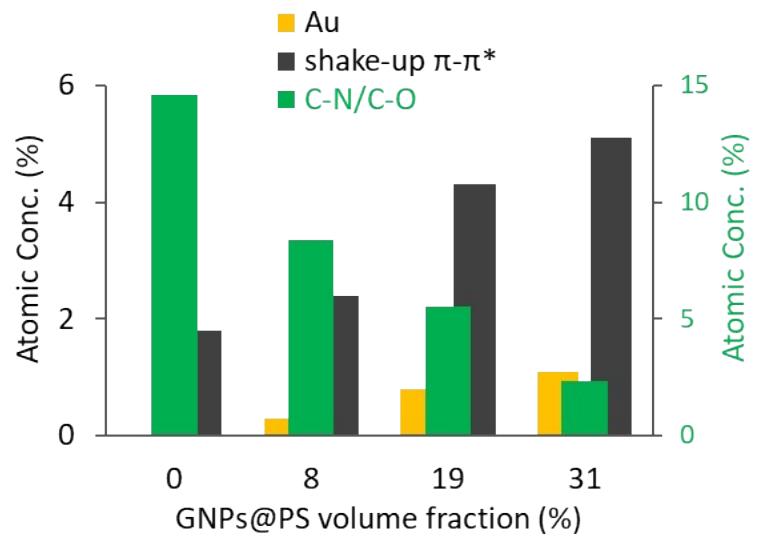
Figure SI5. An overview of the evolution of atomic composition the constituents of the hybrid film with the addition of GNPs@PS