Electronic supplementary information

Diblock Copolymer Pattern Protection by Silver

Cluster Reinforcement

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Figure S1: a) GISAXS scattering image of pristine PS-b-P4VP with a schmeaticlly drawn displaying the performed horizontal line cut and in b) is the horizontal line cut displayed and the corresponding fit.



Figure S2: (a) Distribution of Ag_{dcMS}:PS-b-P4VP Ag cluster to Ag cluster distance derived from the AFM Phase image (Figure S4d) together with a gaussian fit. b) Distribution of Ag_{dcMS}:PS-b-P4VP of Ag diameter derived from the AFM image (Figure S4d) together with a gaussian fit. (c) Distribution of Ag_{HiPIMS}:PS-b-P4VP Ag cluster to Ag cluster distance derived from the AFM image (Figure S4f) together with a gaussian fit. (d) Distribution of Ag_{dcMS}:PS-b-P4VP of Ag diameter derived from the AFM image (Figure S4f) together with a gaussian fit.



Figure S3: (a) Distribution of pristine PS-b-P4VP micelles to micelles distance derived from the FESEM image (Figure 1a) together with a gaussian fit. (b) Distribution of pristine PS-b-P4VP micelle diameter derived from the FESEM image (Figure 1a) together with a gaussian fit. (c) Distribution of pristine PS-b-P4VP micelles to micelles distance derived from the AFM image (Figure S4a) together with a gaussian fit. (d) Distribution of pristine PS-b-P4VP micelle diameter derived from the AFM image (Figure S4a) together with a gaussian fit.



Figure S4: AFM images of a) pristine PS-b-P4VP height, b) pristine PS-b-P4VP phase, c) Ag_{dcMS}:PS-b-P4VP height, d) Ag_{dcMS}:PS-b-P4VP phase, e) Ag_{HiPIMS}:PS-b-P4VP height and f) Ag_{HiPIMS}:PS-b-P4VP phase

Calculation of surface energy derived from the contat angle:

The surface energy is estimated from the measured contact angle using following equation:¹

$$\gamma_s = \frac{\gamma_l}{4} (1 + \cos \theta_c)^2$$

 γ_1 is denoted to the surfaces energy of ultrapure water being tabulated at 72.75*10⁻³ mN/m at 20°C and θ_c is the measured contact angle.^{1–3}



Figure S5: XRR of pristine PS-b-P4VP (pink) with corresponding fit (black).

Calculation of the cluster density:

The cluster density can be calculated assuming the geometrical model described by Schwartzkopf et. Al. using following equation being depanded on the correlated distance:⁴

$$\rho = \frac{2}{\sqrt{3}D^2}$$



Figure S6: In-situ evolution of Ag_{dcMS}:PS-b-P4VP (black) and Ag_{HiPIMS}:PS-b-P4VP (blue) in (a) distance, (b) cluster density. In between the vertical blue and black lines is a regime in which the data could not be fitted due to strong overlap between Ag cluster peak and micelle peak being in superposition. Violet bar indicates $\delta_{Ag} = 2 \text{ nm}$ of Ag_{dcMS}:PS-b-P4VP and Ag_{HiPIMS}:PS-b-P4VP showing same structural rearrangement.



Figure S7: (a) XPS spectra of the C1s edge of pristine, (b) Ag_{dcMS}:PS-b-P4VP and (c) Ag_{HiPIMS}:PSb-P4VP. (d) XPS spectra of the N1s edge of pristine, (e) Ag_{dcMS}:PS-b-P4VP and (f) Ag_{HiPIMS}:PSb-P4VP. (g) XPS spectra of O1s edge of Ag_{dcMS}:PS-b-P4VP and (h) Ag_{HiPIMS}:PS-b-P4VP.

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