Figure A. TGA Experiment for a hybrid PS-b-(P4VP/HAuCl₄)₁₀ quantifying the weight loss of side products after the reduction process. A temperature ramp is applied from 20°C to 170°C at a heating rate of 1°C/min. Second, once 170°C is reached, temperature is held constant for four hours.

From the TGA experiment we observe: the experimental total weight loss is 6%, arising from the reduction of gold precursor. The reduction process mainly occurs in a time window of 90 min, starting at the minute 120 (T=125°C) after which there is a steep weight loss, and finishing at the minute 210. After four hours at 170°C, the weight loss is within 0.8% of remnant side products. The reduction process under oxygen and argon atmosphere occurs essentially with the same path.

We have a set of conclusions arising from this experiment: the experimental 6% weight loss arising from the reduction process agrees to the predicted weight loss. The predicted weight loss is calculated by adding only the mass of Au that would be present in the system to the mass of neat BCP (without H and 4Cl).

The polymer used was

PS(120,400 g/mol)-b-P4VP(5,000 g/mol)

4VP = 105 g/mol; H AuCl₄.H₂O = 339.8 + (1.5)18 g/mol

100 mg of BCP require 13.8 mg of H AuCl₄ so that P4VP:H AuCl₄ is 1:1

-. The new weight of BCP plus precursor is 113.7 mg

Under 100% reduction, 13.8 mg of H AuCl₄ provide with 7.4 mg of Au.
Weight of BCP after 100% reduction of precursor is 107.4 mg

\[
\text{The predicted weight loss} = 100 - \frac{107.4 \text{mg}}{113.8 \text{mg}} \times 100\% = 5.6\%
\]

This means that most of the remnant molecules of gold precursor are released from the material during the tablet pressing process. This implies that the chlorine molecules detected in XPS correspond to small traces of side products of the reduction process and these traces are not significant compared to the total weight of the material.

![Figure B. Wide angle x-ray scattering (WAXS) diffraction pattern for a tablet of the material tested ex-situ, after tablet pressing. The reflections identified indicate the corresponding lattice spacings of crystalline gold. This result confirms that the process of reduction takes place within the P4VP-rich regions during tablet pressing.](image-url)
Figure C. High resolution TEM micrograph of the material. The fringes demonstrate characteristic crystalline structure of the gold nanoparticles within the P4VP domain.

Figure D. Photograph of the bulk hybrid material: solution in THF, after solvent evaporation (i) and, after tablet pressing (ii). Notice the change in colour of the material, from yellow (non-reduced gold precursor) to brown (metallic gold nanoparticles.)
Figure E. Particle size distribution for the hybrid material PS$_{327}$-b-(P4VP/HAuCl$_4$)$_{27}$ after mechanical shear.

Figure F. a) 2D scattering map of a hybrid PS-b-(P4VP/Au) di-block-copolymer system sheared with large amplitude oscillating shear at 120°C. b) 2D scattering map of a hybrid PS-b-(P4VP/HAuCl$_4$) di-block-copolymer system after solvent evaporation (not heated-not sheared). c) Azimuthal intensity distribution of the 2D pattern (q-range: integrated over the 1$^{st}$ layer reflection).
CALCULATION OF THE VOLUME FRACTION OF METALLIC GOLD

The total volume \( V \) in the system PS-b-P4VP/Au is:

\[
V = V_{Au} + V_{PS} + V_{P4VP}
\]

\( V_{Au} \): Total Volume of metallic gold

\( V_{PS} \): Total volume of PS domains

\( V_{P4VP} \): Total volume of P4VP domains

\[
V = \frac{m}{\rho} = \frac{\text{weighted mass}[g]}{\text{density}[g/cm^3]}
\]

\[
V_{Au} = \frac{N_{P4VP} \cdot \text{molecules of P4VP CHAINS} \cdot (\text{molec. weight Au})}{\rho_{Au}} = \frac{N_{P4VP} \cdot (\text{weighted mass of BCP}) \cdot \frac{1}{M_n} \cdot m_{Au}}{\rho_{Au}}
\]

\[
V_{P4VP} = \frac{N_{P4VP} \cdot (\text{weighted mass of BCP}) \cdot \frac{1}{M_n} \cdot (\text{molec. weight 4VP segments})}{\rho_{P4VP}}
\]

\[
V_{PS} = \frac{N_{PS} \cdot (\text{weighted mass of BCP}) \cdot \frac{1}{M_n} \cdot (\text{molec. weight S segments})}{\rho_{PS}}
\]

\[
\phi_p = \frac{V_{Au}}{V_{Au} + V_{P4VP} + V_{PS}}
\]

\[
\phi_{Au} = \frac{N_{P4VP} \cdot w_{BCP} \cdot \frac{1}{M_n} \cdot m_{Au}}{\rho_{Au}} + \frac{N_{P4VP} \cdot w_{BCP} \cdot \frac{1}{M_n} \cdot m_{Au}}{\rho_{P4VP}} + \frac{N_{PS} \cdot w_{BCP} \cdot \frac{1}{M_n} \cdot m_{S}}{\rho_{PS}}
\]

The weighted mass of BCP (\( w_{BCP} \)) and the number average molecular weight of the polymer cancels out and the volume fraction of gold results a function of the number of pyridines (\( N_{P4VP} \)) and the densities:
\[
\phi_{Au} = \frac{\frac{N_{P4VP} \cdot m_{Au}}{\rho_{Au}}}{\frac{N_{P4VP} \cdot m_{Au}}{\rho_{Au}} + \frac{N_{P4VP} \cdot m_{4VP}}{\rho_{P4VP}} + \frac{N_{PS} \cdot m_{S}}{\rho_{PS}}}
\]

\[m_{Au} = 197.0 \text{ [g/mol]} \]
\[m_{PS} = 104.0 \text{ [g/mol]} \]
\[m_{P4VP} = 105.0 \text{ [g/mol]} \]
\[N_{PS} = 327 \]
\[N_{P4VP} = 27 \]
\[\rho_{Au} = 19.3 \text{ g/cm}^3 \]
\[\rho_{PS} = 1.05 \text{ g/cm}^3 \]
\[\rho_{P4VP} = 1.11 \text{ g/cm}^3 \]

References.