SUPPORTING INFORMATION

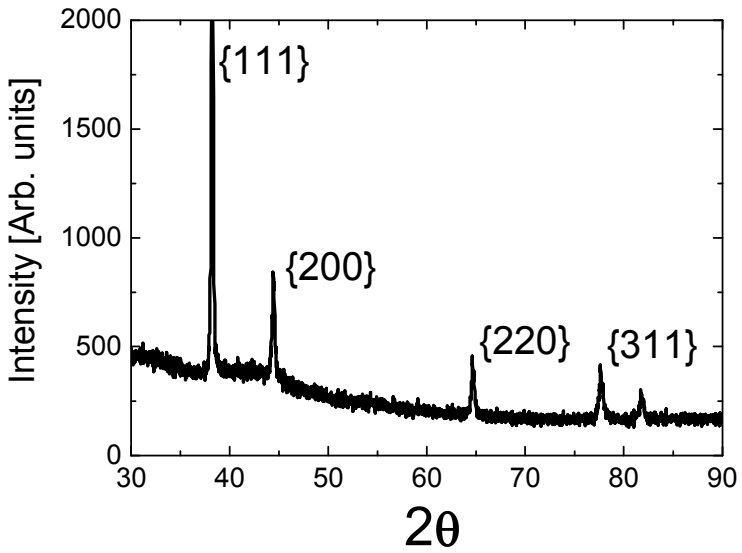

Figure A. Wide angle x-ray scattering (WAXS) diffraction pattern for a tablet of the material tested ex-situ, after tablet pressing. The reflections identified indicate the corresponding lattice spacings of crystalline gold. This result confirms that the process of reduction takes place within the P4VP-rich regions during tablet pressing.

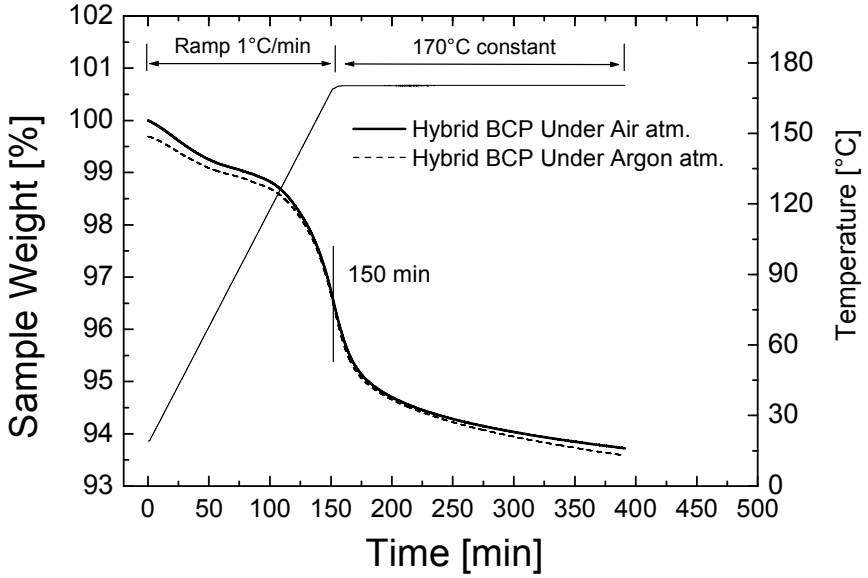

Figure B. TGA Experiment for a hybrid PS-b-(P4VP/HAuCl4)1.0 quantifying the weight loss of side products after the reduction process. A temperature ramp is applied from 20°C to 170°C at a heating rate of 1°C/min. Second, once 170°C is reached, temperature is held constant for four hours.

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; $HAuCl_4.H20$ = 339.8 + (1.5)18 g/mol

100 mg of BCP require 13.8 mg of $HAuCl_4$ so that P4VP:$HAuCl_4$ is 1:1

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

Under 100% reduction, 13.8 mg of $HAuCl_4$ provide with 7.4 mg of Au.

-.Weight of BCP after 100% reduction of precursor is 107.4 mg

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

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. For this reason, we can rule out the influence of side products on Tg of both PS and P4VP blocks. This behaviour can be scaled to the system under consideration in the manuscript. For this reason, we demonstrate that the Tg shift is produced only by the presence of nanoparticles.0

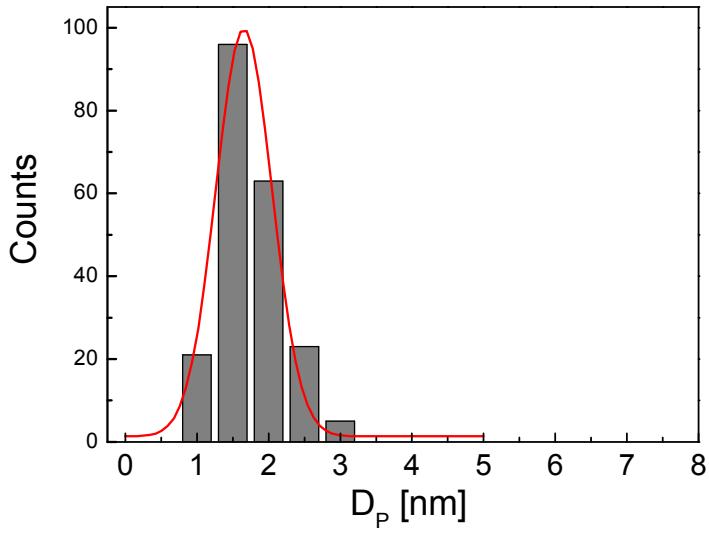

Figure C. Histogram of particle sizes from the TEM micrograph presented in figure 4b. A Gaussian fit to the data yields a mean particle size of 1.7 nm

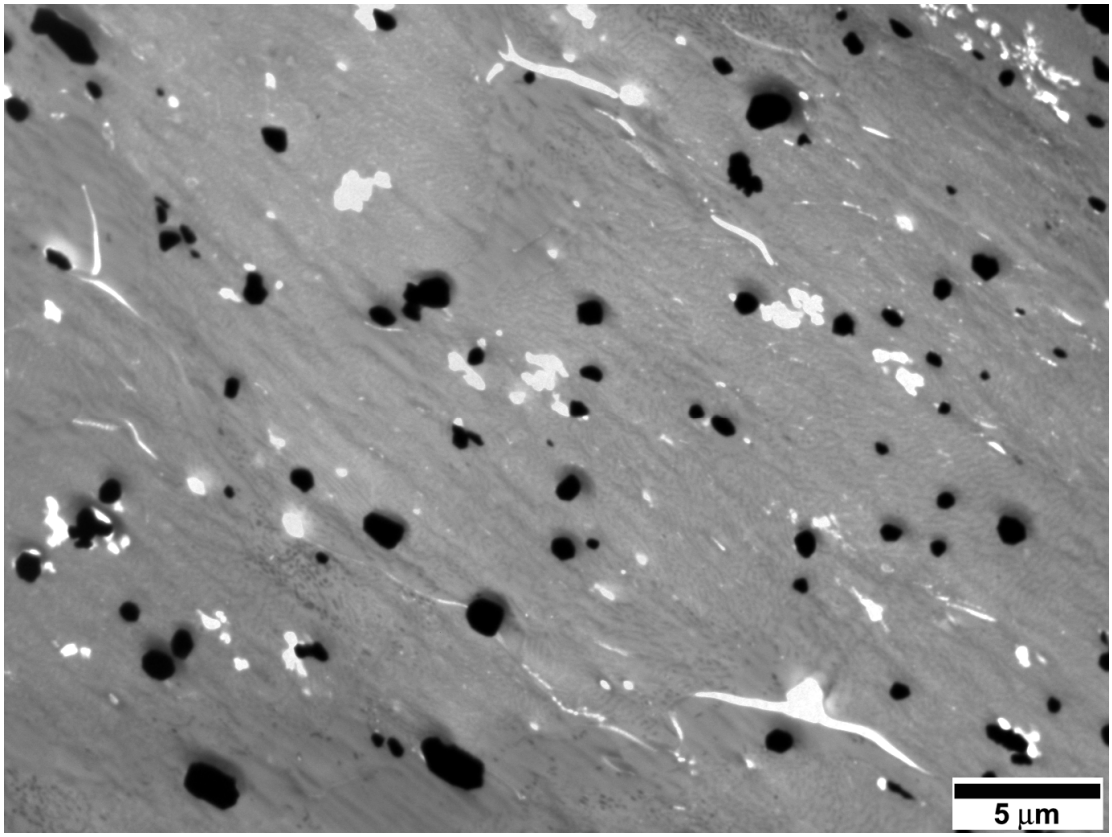

Figure D. Transmission electron micrograph of non-stained microtomed sections of the hybrid material PS-b-(P4VP/Au)$_{1.0}$ after the orientation process. The starting solution was prepared in THF and the gold precursor was reduced to metallic gold using sodium borohydride ($NaBH_4$) as reduction agent. Since THF is a non-selective solvent, the P4VP block is relatively extended at room temperature. When the gold precursor is reduced, gold nanoparticles can freely aggregate in big clusters and are rejected from the polymer matrix upon solvent evaporation

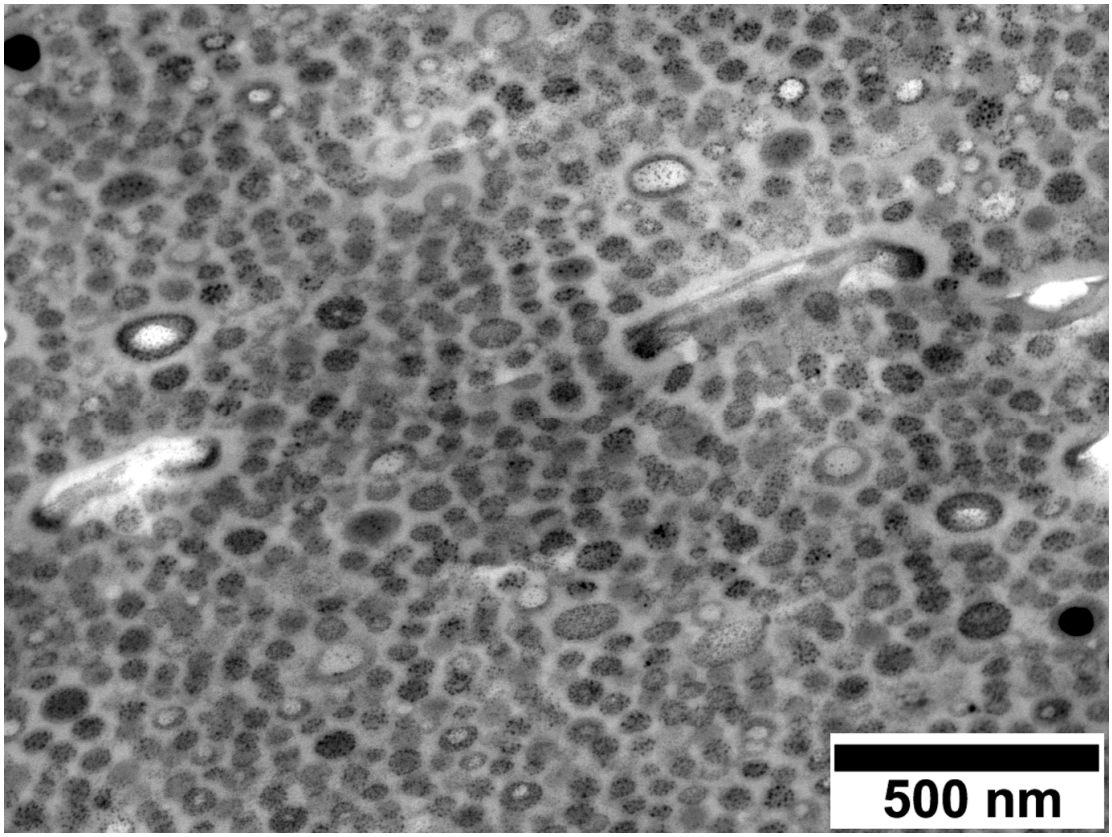

Figure E. Transmission electron micrograph of non-stained microtomed sections of the hybrid material PS-b-(P4VP/Au)$_{1.0}$ after the orientation process. The starting solution was prepared in toluene and the gold precursor was reduced to metallic gold using sodium borohydride ($NaBH_4$) as reduction agent. In contrast to the case in figure D, toluene is a selective solvent for the PS block. The polar P4VP block coils reducing segmental contacts with toluene, leading to a micellar solution. Upon addition of $NaBH_4$, the micelle core (P4VP) protects the generation of small nanoparticles, surrounded by a PS corona. (As previously demonstrated by Moller, Spatz. Et al.- Ref 17 and 18 main article) After solvent evaporation and tablet pressing, the polymer can not rearrange into the known morphologies.

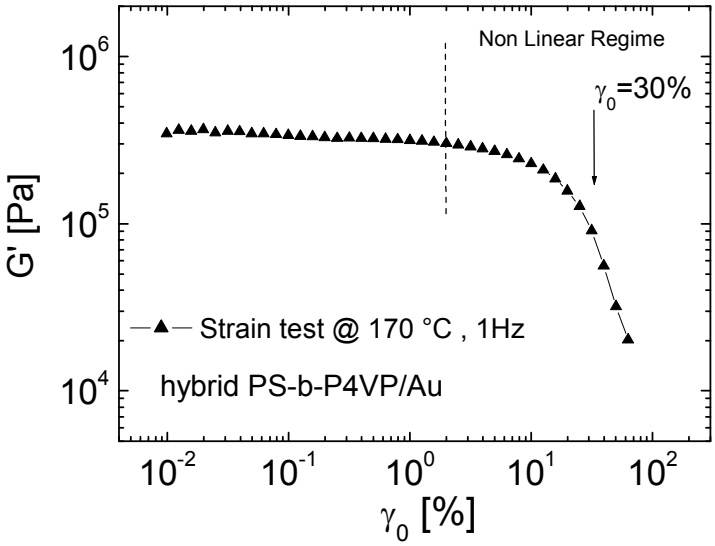

Figure F. Dynamic strain tests for hybrid diblock-copolymer systems. The strain amplitude was varied from 0.01% to 60% at a frequency of 1Hz and temperature of 170 °C.