Supporting Information

Metal Coordination Induces Phase Segregation in Amphipolar Arborescent Copolymers with a Core–Shell–Corona Architecture

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1 Additional Details on Computer Simulations

1.1 Method

The non-bonded forces in eq. (1) are given by the following expressions:

\[
F_{ij}^C = \begin{cases} 
  a_{ij} (1 - r_{ij}), & r_{ij} < 1 \\
  0, & r_{ij} \geq 1 
\end{cases} \tag{S1}
\]

\[
F_{ij}^D = -\lambda [\omega(r_{ij})]^{2} (v_{ij} \cdot \mathbf{r}_{ij}) \mathbf{r}_{ij} \tag{S2}
\]

\[
F_{ij}^R = \sigma \omega(r_{ij}) \xi_{ij} \Delta t^{-1/2} \mathbf{r}_{ij} \tag{S3}
\]

Here \( \mathbf{r}_{ij} = (r_i - r_j)/r_{ij} \) is the unit vector pointing from the \( j \)th to the \( i \)th bead, \( \omega(r_{ij}) = (1 - r_{ij}) \) is a weight function which turns to zero when \( r_{ij} \geq 1 \), \( v_{ij} = v_i - v_j \) is the relative velocity of the beads \( i \) and \( j \), \( \xi_{ij} \) is a zero-mean normally distributed random variable and \( \Delta t \) is a simulation timestep.

The bond \( F_{ij}^B \) force is described by the harmonic potential:

\[
E^B = \frac{1}{2} k_s (r - r_{ij})^2 \tag{S4}
\]

In the classic DPD approach, the momentum for each pair of beads is preserved. To satisfy the fluctuation-dissipation theorem, a relation \( \sigma^2 = 2 k_B T \lambda \) must be provided\(^1\) while the value of \( \lambda \) is set to 4.5 for the decent rate of equilibration of the temperature. The evolution of the system is described by \( N \) equations of motion expressed through the second Newton’s law, \( m \frac{dv_i}{dt} = F_i \). All quantities are measured in units of the mass of the bead, \( m \), thermal energy, \( k_B T \), and the cutoff radius of the interaction potential, \( r_c \). For convenience, the quantities are fixed as \( m = k_B T = r_c = 1 \), so that the characteristic timescale is defined as \( \tau = r_c (m/k_B T)^{1/2} \) and also equals 1.\(^2\)
1.2 Coarse-graining

Table S1. Hansen solubility parameters used in the DPD simulations.

| Substance       | $\delta^d$ | $\delta^p$ | $\delta^h$ |
|-----------------|------------|------------|------------|
| PS$^a$          | 18.5       | 4.5        | 2.9        |
| P2VP$^b$        | 16.3       | 7.1        | 11.6       |
| THF$^a$         | 16.8       | 5.7        | 8          |
| Toluene$^a$     | 18         | 1.4        | 2          |
| CHCl$_3$$^a$    | 17.8       | 3.1        | 5.7        |

$^a$From reference 3; $^b$from reference 4.

1.3 Models

Table S2. Characteristics of simulated coarse-grained models for arborescent polystyrene substrates and CSC copolymers.

| Description     | $M_w^{\text{sim}}$ | $M_w^{\text{exp}}$ | $f_w^{\text{sim}}$ | $f_w^{\text{exp}}$ | $N_w$ $^a$ | $L$ $^b$ | % 2VP |
|-----------------|--------------------|--------------------|--------------------|--------------------|------------|----------|-------|
| Linear substrate| 5720               | 6120               | -                  | -                  | -          | -        | -     |
| G0PS            | 1.04 x 10$^5$      | 1.1 x 10$^5$      | 19                 | 19                 | 19         | -        | -     |
| G1PS-1          | 8.16 x 10$^5$      | 9.3 x 10$^5$      | 137                | 136                | 7.2        | -        | -     |
| G1PS-2          | 9.93 x 10$^5$      | 9.3 x 10$^5$      | 171                | 170                | 9          | -        | -     |
| G2PS            | 1.07 x 10$^7$      | 1.2 x 10$^7$      | 1.2 x 10$^7$       | 1900               | 13.9       | -        | -     |
| G3PS            | 2.59 x 10$^7$      | 2.2 x 10$^7$      | 2926               | 2930               | 1.54       | -        | -     |
| PS-$g$-(P2VP16-b-PS12) | 3.42 x 10$^5$ | 3.4 x 10$^5$ | 12 | 12 | 12 | 54 | 57.5 |
| G0PS-$g$-(P2VP11-b-PS8) | 3.12 x 10$^6$ | 3.1 x 10$^6$ | 161 | 160 | 8.5 | 36 | 57.9 |
| G1PS-$g$-(P2VP7-b-PS7) | 8.26 x 10$^6$ | 8.3 x 10$^6$ | 530 | 529 | 3.87 | 27 | 53 |
| G1PS-$g$-(P2VP15-b-PS11) | 1.94 x 10$^7$ | 1.9 x 10$^7$ | 709 | 708 | 4.15 | 50 | 58 |
| G1PS-$g$-(P2VP30-b-PS20) | 1.70 x 10$^7$ | 1.7 x 10$^7$ | 321 | 319 | 1.88 | 96 | 60.6 |
| G2PS-$g$-(P2VP7-b-PS13) | 3.07 x 10$^7$ | 3.1 x 10$^7$ | 986 | 985 | 0.519 | 38 | 36.4 |
| G2PS-$g$-(P2VP14-b-PS12) | 3.76 x 10$^7$ | 3.9 x 10$^7$ | 1035 | 1040 | 0.545 | 50 | 54 |
| G2PS-$g$-(P2VP12-b-PS22) | 3.64 x 10$^7$ | 3.7 x 10$^7$ | 750 | 750 | 0.395 | 66 | 36.4 |
| G3PS-$g$-(P2VP14-b-PS12) | 7.40 x 10$^7$ | 6.9 x 10$^7$ | 1852 | 1850 | 0.633 | 50 | 54 |

$^a$Mean number of grafts per branch in the last generation; $^b$Length of AB copolymer grafts added in the last grafting cycle.
2 Additional Results & Discussion

2.1 Block Copolymer Side-chain Characteristics

The characteristics of the PS-b-P2VP block copolymers grafted onto polystyrene substrates to yield the arborescent CSC copolymers are provided in Table S3.

Table S3. Block copolymer side-chain characterization.

| Graft Copolymer                      | Block Copolymer Side-chains | PS | P2VP | Copolymer |
|--------------------------------------|----------------------------|----|------|-----------|
| PS-g-(P2VP16-b-PS12)                 |                            |    |      |           |
|                                      | M_w^a M_w/M_n               | 11600 | 1.04 | 15800 27400 55 | 1.11 |
| G0PS-g-(P2VP11-b-PS8)                |                            | 8200 | 1.04 | 10500 18700 50 | 1.19 |
| G1PS-g-(P2VP7-b-PS7)                 |                            | 7000 | 1.06 | 6900 13900 46 | 1.14 |
| G1PS-g-(P2VP15-b-PS11)               |                            | 11200 | 1.02 | 14800 26000 52 | 1.14 |
| G1PS-g-(P2VP30-b-PS20)               |                            | 20400 | 1.02 | 29900 50300 55 | 1.13 |
| G2PS-g-(P2VP7-b-PS13)                |                            | 13500 | 1.17 | 6500 20000 41 | 1.02 |
| G2PS-g-(P2VP14-b-PS12)               |                            | 11700 | 1.06 | 14400 26100 57 | 1.01 |
| G2PS-g-(P2VP12-b-PS22)               |                            | 22300 | 1.12 | 11900 34200 39 | 1.05 |
| G3PS-g-(P2VP14-b-PS12)               |                            | 11700 | 1.03 | 13700 25400 55 | 1.01 |

^a Absolute values from SEC analysis with DRI detector and PS calibration; ^b Determined from difference between PS and copolymer M_n; ^c Absolute values from 1H NMR analysis; ^d From 1H NMR analysis (mol %).

2.2 Additional Arborescent Copolymer Characteristics

Representative SEC traces depicting the progression of the grafting reaction for sample G1PS-g-(P2VP15-b-PS11) are provided in Figure S1. Also included for comparison is the trace for an analogous G2 copolymer of lower overall molecular weight, G1PS-g-(P2VP7-b-PS7), as a result of grafting lower molecular weight side-chains.
Figure S1. SEC traces for the synthesis of G1PS-g-(P2VP15-b-PS11): (a) PS-b-P2VP side chains, (b) G1PS substrate, (c) crude product, (d) fractionated G2 copolymer; (e) lower molecular weight analogue G1PS-g-(P2VP7-b-PS7).

Arborescent copolymers of generations 1 and above displayed a single, narrowly dispersed size population in toluene based on CONTIN analysis. Provided in Figure S2 are examples of size distributions observed for G0 and G3 arborescent copolymers in toluene, and the corresponding G2PS substrate from which the G3 copolymer was derived. Evidence for aggregation was seen for PS-g-(P2VP16-b-PS12) in CONTIN analysis as a broad distribution (Figure S2a) distinct from G2PS and G2PS-g-(P2VP14-b-PS12), seen in Figure S2b and Figure S2c, respectively.
As expected, the radius of the G2PS substrate was smaller than for the G3 copolymer, and both were larger than the G0 copolymer.

![Image of bar charts showing size distribution in toluene from CONTIN analysis](image)

**Figure S2.** Size distributions in toluene from CONTIN analysis of (a) PS-\(g\)-(P2VP16-\(b\)-PS12), and (b) the G2PS substrate and (c) G2PS-\(g\)-(P2VP14-\(b\)-PS12).

The results of computer simulations for an ensemble of identical PS-\(g\)-(P2VP16-\(b\)-PS12) copolymer molecules dissolved in toluene are presented in Figure S3. The simulation snapshot for the equilibrated system (Figure S3a) demonstrates the presence of aggregates with a spherical P2VP core and PS shell. The corresponding relative number (fraction) diagram (Figure S3b), plotted as a function of the number of molecules in the aggregates (aggregation number),\(^5\) indicates the formation clusters containing up to five CSC copolymers. In turn, the scaling
exponent obtained for the hydrodynamic radius of the clusters with molecular weight of 0.225 (Figure S3c) indicates that the size of the cluster grows weakly with the addition of new molecules. Consequently, the aggregation tendency may be considered relatively weak in comparison with linear diblock copolymers. Overall, the simulation results are in agreement with the results shown in Figure S2a.

![Simulation snapshot](image)

**Figure S3.** (a) Simulation snapshot for a PS-\(g\)-(P2VP16-\(b\)-PS12) solution (the solvent beads are not shown); the solvent is poor for the green beads and good for the blue beads; (b) fraction of the aggregates as a function of the number of macromolecules; (c) hydrodynamic radius (nm) as a function of the molecular weight of the aggregates.

DLS analysis was also performed in THF and in chloroform, which are better solvents for both the PS and P2VP components of the copolymers. The hydrodynamic radii of the arborescent copolymers in all three solvents are compared in Table S5. The hydrodynamic radii were slightly larger in these solvents than in toluene for the majority of the samples. One notable exception to this is sample PS-\(g\)-(P2VP16-\(b\)-PS12), for which a decrease was observed in chloroform and THF, as well as better agreement between the first- and the second-order analysis results, due to the suppression of aggregation.
| PS Substrate | Graft Copolymer | $r_{h1}$ | $r_{h2}$ | $r_{DPD}$ | Description | $r_{h1}$ | $r_{h2}$ | PDI | $r_{DPD}$ | $r_{SFM}$ |
|--------------|----------------|----------|----------|----------|-------------|----------|----------|-----|----------|--------|
| 1.7 ± 0.3    | 1.2 ± 0.4      | 1.1 ± 0.2|          |          | PS-g-(P2VP16-b-PS12) | 16 ± 1   | 11 ± 1   | 0.27| 8.5 ± 0.2| 10     |
| 8.2 ± 0.1    | 7.3 ± 0.1      | 5.5 ± 0.5|          |          | G0PS-g-(P2VP11-b-PS8) | 24 ± 1   | 23 ± 1   | 0.11| 12 ± 0.1 | 22     |
| 12.2 ± 0.1   | 11.9 ± 0.3     | 10.3 ± 0.2|          |          | G1PS-g-(P2VP7-b-PS7) | 25 ± 1   | 25 ± 1   | 0.020| 17 ± 0.1 |        |
| 14.1 ± 0.1   | 13.3 ± 0.1     | 10.9 ± 0.3|          |          | G1PS-g-(P2VP15-b-PS11) | 25 ± 1   | 24 ± 1   | 0.062| 21.6 ± 0.1|        |
| 14.1 ± 0.1   | 13.3 ± 0.1     | 10.9 ± 0.3|          |          | G1PS-g-(P2VP30-b-PS20) | 34 ± 1   | 31 ± 1   | 0.15| 21.2 ± 0.1| 20     |
| 30 ± 1       | 28 ± 1         | 23.3 ± 0.2|          |          | G2PS-g-(P2VP7-b-PS13) | 49 ± 1   | 48 ± 1   | 0.065| 30.5 ± 0.1|        |
| 30 ± 1       | 28 ± 1         | 23.3 ± 0.2|          |          | G2PS-g-(P2VP14-b-PS12) | 54 ± 1   | 51 ± 1   | 0.10| 30.6 ± 0.1| 33     |
| 30 ± 1       | 28 ± 1         | 23.3 ± 0.2|          |          | G2PS-g-(P2VP12-b-PS22) | 66 ± 1   | 63 ± 1   | 0.049| 31.5 ± 0.1|        |
| 30 ± 1       | 29 ± 1         | 31.7 ± 0.2|          |          | G3PS-g-(P2VP14-b-PS12) | 82 ± 1   | 75 ± 1   | 0.18| 40 ± 0.1 | 43     |

*Hydrodynamic radii (nm) from first-order analysis of the correlation function; b Hydrodynamic radii (nm) from second-order analysis of the correlation function; c Polydispersity determined from cumulants analysis of DLS correlation function; d Hydrodynamic radii (nm) from DPD simulations; e Characteristic dimension (nm) inferred from the 2D Fast Fourier Transform of SFM images
Table S5. Hydrodynamic radii of arborescent copolymers in different solvents.

| Sample                          | Toluene | THF | CHCl3 |
|---------------------------------|---------|-----|-------|
|                                 | \( r_{h1} \) | \( r_{h2} \) | \( r_{DPD} \) | \( r_{h1} \) | \( r_{h2} \) | \( r_{DPD} \) | \( r_{h1} \) | \( r_{h2} \) | \( r_{DPD} \) |
| PS-\(g\)-(P2VP16-\(b\)-PS12)  | 16 ± 1  | 11 ± 1 | 8.5 ± 0.2 | 10 ± 1 | 9 ± 1 | 11.1 ± 0.5 | 15 ± 1 | 14 ± 1 | 8 ± 0.3 |
| G0PS-\(g\)-(P2VP11-\(b\)-PS8) | 24 ± 1  | 23 ± 1 | 12 ± 0.1  | 35 ± 1 | 32 ± 1 | 16.7 ± 0.2 | 23 ± 1 | 22 ± 1 | 14.6 ± 0.2 |
| G1PS-\(g\)-(P2VP7-\(b\)-PS7)  | 25 ± 1  | 25 ± 1 | 17 ± 0.1  | 28 ± 1 | 28 ± 1 | 22.3 ± 0.2 | 28 ± 1 | 28 ± 1 | 20.2 ± 0.2 |
| G1PS-\(g\)-(P2VP15-\(b\)-PS11) | 25 ± 1  | 24 ± 1 | 21.6 ± 0.1 | 28 ± 1 | 28 ± 1 | 28.6 ± 0.2 | 35 ± 1 | 34 ± 1 | 21.4 ± 0.2 |
| G1PS-\(g\)-(P2VP30-\(b\)-PS20) | 34 ± 1  | 31 ± 1 | 21.2 ± 0.1 | 34 ± 1 | 33 ± 1 | 29.0 ± 0.2 | 42 ± 1 | 41 ± 1 | 22.8 ± 0.1 |
| G2PS-\(g\)-(P2VP7-\(b\)-PS13) | 49 ± 1  | 48 ± 1 | 30.5 ± 0.1 | 56 ± 1 | 55 ± 1 | 29.9 ± 0.1 | 60 ± 1 | 58 ± 1 | 33.9 ± 0.2 |
| G2PS-\(g\)-(P2VP14-\(b\)-PS12) | 54 ± 1  | 51 ± 1 | 30.6 ± 0.1 | 60 ± 1 | 56 ± 1 | 34.1 ± 0.2 | 67 ± 1 | 65 ± 1 | 33.5 ± 0.1 |
| G2PS-\(g\)-(P2VP12-\(b\)-PS22) | 53 ± 1  | 52 ± 1 | 31.5 ± 0.1 | 59 ± 1 | 57 ± 1 | 31.1 ± 0.1 | 66 ± 1 | 63 ± 1 | 34.9 ± 0.2 |
| G3PS-\(g\)-(P2VP14-\(b\)-PS12) | 82 ± 1  | 75 ± 1 | 40 ± 0.1  | 72 ± 1 | 67 ± 1 | 42 ± 0.2  | 79 ± 1 | 76 ± 1 | 42.8 ± 0.2 |

\( a \) Hydrodynamic radii (nm) from first-order analysis of the correlation function; \( b \) Hydrodynamic radii (nm) from second-order analysis of the correlation function; \( c \) Hydrodynamic radii (nm) from DPD simulations
For comparison purposes, the bulk radius ($r_b$) calculated from Equation S5 is also provided in Table S6. The average density ($\rho$) of each copolymer was estimated from its composition determined by $^1$H NMR spectroscopy ($\rho = 1.09$ g/cm$^3$ for P2VP and 1.01 g/cm$^3$ for PS). As expected, all the arborescent copolymers have dimensions ($r_b$) significantly larger in solution than their respective bulk radii due to swelling of the molecules.

$$r_b = \left( \frac{M_w}{\rho N_A \frac{4}{3} \pi} \right)^{\frac{1}{3}}$$

(S5)

Table S6. Hydrodynamic and bulk radii comparison for arborescent copolymers.

| PS Substrate | Graft Copolymer | Description | $r_h^a$ | $r_h^b$ | $r_h^c$ |
|--------------|-----------------|-------------|---------|---------|---------|
| 1.7 ± 0.3    | 1.2 ± 0.4       | 1           | PS-g-(P2VP16-b-PS12) | 16 ± 1 | 11 ± 1 | 5 |
| 8.2 ± 0.1    | 7.3 ± 0.1       | 3           | G0PS-g-(P2VP11-b-PS8) | 24 ± 1 | 23 ± 1 | 10 |
| 12.2 ± 0.1   | 11.9 ± 0.3      | 7           | G1PS-g-(P2VP7-b-PS7) | 25 ± 1 | 25 ± 1 | 15 |
| 14.1 ± 0.1   | 13.3 ± 0.1      | 7           | G1PS-g-(P2VP15-b-PS11) | 25 ± 1 | 24 ± 1 | 19 |
| 14.1 ± 0.1   | 13.3 ± 0.1      | 7           | G1PS-g-(P2VP30-b-PS20) | 34 ± 1 | 31 ± 1 | 18 |
| 30 ± 1       | 28 ± 1          | 16          | G2PS-g-(P2VP7-b-PS13) | 49 ± 1 | 48 ± 1 | 23 |
| 30 ± 1       | 28 ± 1          | 16          | G2PS-g-(P2VP14-b-PS12) | 54 ± 1 | 51 ± 1 | 24 |
| 30 ± 1       | 28 ± 1          | 16          | G2PS-g-(P2VP12-b-PS22) | 66 ± 1 | 63 ± 1 | 24 |
| 30 ± 1       | 29 ± 1          | 20          | G3PS-g-(P2VP14-b-PS12) | 82 ± 1 | 75 ± 1 | 29 |

$^a$ Hydrodynamic radii (nm) from first-order analysis of the correlation function; $^b$ Hydrodynamic radii (nm) from second-order analysis of the correlation function; $^c$ Bulk radii (nm) calculated from Equation S10
Figure S4. SFM height images with the corresponding height profiles along the horizontal lines (a-e) for arborescent copolymers cast from toluene solutions, and simulation snapshots of single macromolecules swollen in a selective solvent (f-j): (a, f) PS-g-(P2VP16-b-PS12), (b, g) G0PS-g-(P2VP8-b-PS8), (c, h) G1PS-g-(P2VP30-b-PS20), (d, i) G2PS-g-(P2VP14-b-PS12) and (e, j) G3PS-g-(P2VP14-b-PS12). The scale bar of all the SFM images is 200 nm. In the snapshots, the green beads represent the P2VP segments while the blue beads represent PS segments. The upper row of smaller (“superscript”) images depict only the P2VP phase of the corresponding larger images, while the lower row of superscript images are for cross-sections through the center of mass.
Figure S5. Simulation snapshots for isolated arborescent copolymer molecules in different solvents: (a) toluene; (b) THF; (c) CHCl₃. The green beads represent the P2VP segments, while the blue beads represent the PS segments. The upper rows of smaller (“superscript”) images (a, c) depict only the P2VP phase of the corresponding larger images.
2.3 HAuCl₄-loaded Arborescent Copolymers of Zeroth and First Generations

**Figure S6.** TEM micrographs (upper row), SFM height images (middle row) and DPD simulation snapshots (lower row) for arborescent CSC templates loaded with 0.5 equiv HAuCl₄/2VP unit in toluene: (a) PS-₉-(P2VP1₆-b-PS1₂), (b) GₐPS-₉-(P2VP8-b-PS8). The SFM images are presented with the respective height profiles along the lines, as shown. For all the simulation snapshots the smaller (“superscript”) images depict only the HAuCl₄ phase.
2.4 Influence of Loading Level

The influence of the concentration of metallic ions in the templates (i.e. the loading level) was examined, since the degree of metal coordination should affect the dynamics of phase segregation. Different morphologies may thus result at different loading levels, due to the steric effects of metallic species housed within the P2VP phase. Initial tests performed with the G0 and G2 templates showed interesting parallels to the intermolecular micelle systems: At increased loading levels, the intermicellar separation increased and a more uniform dispersion of the templates was achieved. Lower loading levels often led to clustering, or to the formation of ‘islands’ of closely packed metal-loaded templates. Similar phenomena have been reported in the literature for PS-\(b\)-P2VP micelles. Provided in Figure S7 are examples of unimolecular micelle distributions and separation for varying HAuCl₄ loading levels (equivalents per 2VP unit) for the G0 template and two G2 templates.
Figure S7. Examples of micelle distributions and separation as a function of loading level: TEM micrographs for HAuCl₄-loaded PS-g-(P2VP16-b-PS12) at (a) 0.125 equiv and (b) 1.0 equiv, G1PS-g-(P2VP15-b-PS11) at (c) 0.25 equiv and (d) 1.0 equiv, and G1PS-g-(P2VP30-b-PS20) at (e) 0.125 equiv, and (f) 1.0 equiv.
Stemming from these experiments, metal uptake was quantified for a G2 copolymer, G1PS-g-(P2VP7-b-PS7), as it was available in larger amounts and thus the experiment could be performed on a larger scale (50 mg template) for improved accuracy. The template was coordinated with varying amounts of HAuCl₄, at loading ratios (Au/2VP) from 0.1 to 1.25. The Au/polymer solutions were subjected to centrifugation (1300 × g, 10 min) to allow settling of unbound HAuCl₄. Sediment was only visible at loading levels of 1.0 and greater. The sediment was collected and extracted with dry toluene three times, to remove any residual polymer (HAuCl₄ is insoluble in toluene). The initial mass of HAuCl₄ added to the polymer solution was compared with the isolated gold residue and the effective loading level was calculated. It was determined that HAuCl₄ could be loaded up to near equivalency (ca. 0.96) to the 2VP units, in agreement with a literature report for analogous intermolecular micelle systems of PS-b-P4VP.⁷

For a more in-depth look at the relationship between morphology and loading level, copolymers G2PS-g-(P2VP14-b-PS12) and G3PS-g-(P2VP14-b-PS12) were used as they produced well-defined phase segregation that was easily captured by microscopic analysis, as seen previously. Further, the formation of intramolecular nanodomains upon metal coordination in these copolymers may arise by two different nucleation mechanisms: one at a time (sequential) or all at once (simultaneous). Even at loading levels as low as 0.05 equiv, phase segregation resembling the higher loading levels was observed. The morphologies, raspberry for G3 and worm-in-sphere for G4, were less defined at low loading levels, especially for the G4 copolymer. However, this also shows that the entire template undergoes phase segregation at once: All the domains emerge at low loading levels, suggesting that a simultaneous nucleation mechanism is operative, with increased phase segregation (definition) at higher loading levels. Higher metal contents should enhance polymer phase incompatibility, resulting in better defined nanodomains. Provided in Figure S8 are AFM images depicting the raspberry and worm-in-sphere phase segregation observed for the G3 and G4 copolymers at 0.05 equiv loading with HAuCl₄ in toluene. Height scans are provided on the left, while the phase scans are seen on the right of each image.
Figure S8. Phase segregation observed by AFM imaging for 0.05 equiv HAuCl₄ loading in toluene of (a) G2PS-g-(P2VP14-b-PS12) and (b) G3PS-g-(P2VP14-b-PS12).

Loading levels of 0.2, 0.5, and 1.0 equiv per 2VP unit were also examined and yielded similar features. While nanodomain definition cannot be accurately quantified, visual analysis of the AFM scans leads to the conclusion that nanodomain morphology does not change over the whole range, and that the domains are no further enhanced at loading levels above 0.5 equiv. It should be noted that this may also be due to a limitation of the AFM instrument being unable to provide adequate resolution to distinguish morphology changes within the segregated domains. A similar trend was observed for a G2 copolymer, G1PS-g-(P2VP30-b-PS20), displaying better-defined toroidal phase segregation for increasing loading levels.

Time-dependent loading experiments were also performed, to examine potential morphology transitions occurring over time. It was determined that loading times significantly shorter than the ones normally used in the experiments are adequate for the coordination of metals, in contrast with what established techniques suggest.⁶ For copolymers displaying intramolecular phase segregation, loading time variations could provide important information with regards to the domain nucleation mechanism. For the G0 template, PS-g-(P2VP16-b-PS12), metal coordination was evident after 30 min by TEM analysis, as revealed by a gold distribution identical to that shown
in Figure 9a. The G2PS-g-(P2VP14-b-PS12) and G3PS-g-(P2VP14-b-PS12) copolymers were loaded with 0.5 equiv of HAuCl₄ in CHCl₃, and films were cast after different time intervals (5 min, 15 min, 30 min, 1 h, 2 h, 6 h, and 24 h). The gold organization observed after 30 min of loading time for the G3 and G4 copolymers, depicted in Figure S9, closely resembles the results obtained after longer equilibration times (24 h). Phase segregation had obviously already occurred after 30 min, producing morphologies similar to the ones seen previously. The deposition of gold salt within the templates appears to be fast, phase segregation being observed after as little as 5 min, and minimal changes up to 24 h.

Figure S9. TEM images after 30 min of equilibration with HAuCl₄ (0.5 equiv) in CHCl₃: (a) G2PS-g-(P2VP14-b-PS12) and (b) G3PS-g-(P2VP14-b-PS12).

2.5 Influence of Side-chain Length

In an attempt to establish structure-property relationships and understand the phase segregation processes, the PS-b-P2VP side-chain length (overall and relative block length) was varied for a series of G2 and G3 copolymers. An identical block ratio was maintained while increasing the overall molecular weight for the G2 copolymers, and the relative length of the PS and the P2VP segments was varied for the G3 copolymers.

In the G2 copolymer series, the total molecular weight of the block copolymer side-chains was roughly doubled for each sample. The resulting arborescent copolymer samples are G1PS-g-(P2VP7-b-PS7), G1PS-g-(P2VP15-b-PS11), and G1PS-g-(P2VP30-b-PS20). The G2 copolymer G1PS-g-(P2VP30-b-PS20), previously discussed herein
and in Reference 11 of the main manuscript, produced ring-like organization of gold within the template due to toroidal phase segregation.

The G2 copolymer with the shortest side-chains, G1PS-\textit{g}-(P2VP7-b-PS7), yielded a spherical distribution of HAuCl\textsubscript{4} in TEM analysis for loading in both toluene and chloroform. Unfortunately, the topology and morphology of the metal-loaded templates could not be clearly visualized in toluene by SFM due to extensive aggregation, which was also observed in TEM analysis. In chloroform the spherical distribution of the metal was better resolved, although aggregation was still prevalent. On the basis of these results, we believe that the molecular weight of the side-chains in G1PS-\textit{g}-(P2VP7-b-PS7) was not large enough to trigger phase segregation of the type observed for G1PS-\textit{g}-(P2VP30-b-PS20).

The G2 copolymer with side-chains of intermediate length, G1PS-\textit{g}-(P2VP15-b-PS11), also did not display definite signs of phase segregation but rather yielded a spherical topology. Aggregation was much less prevalent in this sample however, due to the longer PS coronal segments providing adequate charge shielding between the molecules. A number of species also displayed non-uniform circular organization of gold in TEM analysis, and phase differences across individual templates in SFM analysis. While this is not as prevalent nor as defined as for G1PS-\textit{g}-(P2VP30-b-PS20) in Figure 3 of the main manuscript, the similarities between the two systems are obvious. Considering the absence of phase segregation for the arborescent copolymer with the shortest side-chains, G1PS-\textit{g}-(P2VP7-b-PS7), and faint signs of non-uniform gold distribution for copolymer G1PS-\textit{g}-(P2VP15-b-PS11), it appears that a minimum P2VP molecular weight, and/or a total block copolymer length is required to induce phase segregation, the threshold value laying somewhere between P2VP15-b-PS11 and P2VP30-b-PS20.

For the G3 copolymer series, the overall side-chain length and respective lengths of the PS and P2VP blocks were varied to determine the impact on morphology. Three different copolymers were prepared: G2PS-\textit{g}-(P2VP7-b-PS13), G2PS-\textit{g}-(P2VP14-b-PS12), and G2PS-\textit{g}-(P2VP12-b-PS22). The results show that raspberry-type morphologies are observed independently of the length of the P2VP segments, at least within the range tested, and also independently of the length of the PS segments in the corona. Interpenetration of the PS chains from the substrate and the P2VP in the inner shell apparently affects the extent of phase segregation similarly for all the G3
copolymers. The retention of a raspberry-like morphology for two HAuCl₄-loaded G3 copolymers in toluene and CHCl₃ is illustrated in Figure S10.

**Figure S10.** TEM images of raspberry-like morphology for HAuCl₄-loaded G2PS-g-(P2VP7-b-PS13) in (a) toluene and (b) CHCl₃, and G2PS-g-(P2VP12-b-PS22) in (c) toluene and (d) CHCl₃. (e-h) corresponding snapshots of HAuCl₄ phases obtained from computer simulations.
2.6 Impact of Solvent on Morphology

2.6.1 CHCl₃

**Figure S11.** SFM phase images for arborescent copolymer templates loaded with 0.5 equiv of HAuCl₄/2VP unit in chloroform: (a) G1PS-\(g\)-(P2VP30-\(b\)-PS20), (b) G2PS-\(g\)-(P2VP14-\(b\)-PS12), and (c) G3PS-\(g\)-(P2VP14-\(b\)-PS12).
2.6.2 Methanol

The following figures depict the influence of methanol on the morphology and metal organization within the copolymer templates. The spherical topology is illustrated in Figure S12, with support from a cross-section to demonstrate the smooth contour of the surface when G1PS-g-(P2VP30-b-PS20) is loaded with HAuCl₄ in toluene with 2 % methanol, while Figure S12b confirms that phase segregation is still present, although not to the extent where ring-like organization of the metal can be observed by TEM (Figure inset), as is the case for loading in pure toluene. The more uniform and spherical topology in the presence of metallic ions is therefore a direct result of P2VP phase swelling by methanol.

Figure S12. G1PS-g-(P2VP30-b-PS20) loaded with HAuCl₄ in toluene with 2 % methanol: (a) AFM height image with surface cross-section and (b) AFM phase image with TEM inset.
2.6.3 **THF/Cyclohexane**

G2, G3, and G4 templates were loaded with HAuCl₄ in THF and cyclohexane at various ratios. As can be seen in Figures S13-S15, a loss of nanodomain and an increased trend toward a spherical morphology were observed for increasing cyclohexane contents.

![Figure S13](image)

**Figure S13.** AFM height (left), phase (center), and TEM (right) images for G1PS-g-(P2VP30-b-PS20) loaded with HAuCl₄ in THF/cyclohexane: (a) 75:25, THF:CH and (b) 25:75, THF:CH.
Figure S14. AFM and TEM images for G2PS-g-(P2VP14-b-PS12) loaded with HAuCl₄ in THF/cyclohexane: (a) 75:25 THF:CH and (b) 25:75 THF:CH.
Figure S15. AFM and TEM images for G3PS-g-(P2VP14-b-PS12) loaded with HAuCl₄ in THF/cyclohexane: (a) 75:25 THF:CH and (b) 25:75 THF:CH.
2.7 Influence of Metal Counterion

It was postulated that perhaps the ionization of P2VP was the dominant factor controlling phase segregation, with no dependency on the counterion type used. Copolymers ionized with HCl by the same procedure to a 1.0 equiv loading regime (1:1 HCl:2VP) were cast into thin films and analyzed by SFM to probe phase segregation. Copolymers G1PS-g-(P2VP30-b-PS20), G2PS-g-(P2VP14-b-PS12), and G3PS-g-(P2VP14-b-PS12) did not display significant phase segregation under these conditions. The structures observed had little, if any resemblance to their phase-segregated metal-loaded analogues; toroidal, raspberry, and worm-in-sphere morphologies were definitely not observed for the ionized species without metallic counterions. In fact, the G2 copolymer even lost its spherical shape due to strong adsorption on the mica substrate and consequent flattening of the structure. These findings confirm that phase segregation was induced by the metallic counterions and not solely by the ionic charges. The question then arose as to whether the morphology obtained depended on the type of coordinating metal used.

Again, the three copolymers displaying well-defined intramolecular nanostructures were used to investigate the effect of the metal ion type. Coordination with palladium (II) acetate, Pd(OAc)$_2$, was investigated, as this metal can coordinate without protonation (ionization) of the 2VP units. In HAuCl$_4$ coordination, the charged 2VP adduct formed clearly decreases the compatibility between the PS and P2VP phases, inducing phase segregation to minimize unfavorable interactions. Shown in Figure S16 are TEM images depicting the organization of Pd(OAc)$_2$ within copolymers G1PS-g-(P2VP30-b-PS20), G2PS-g-(P2VP14-b-PS12), and G3PS-g-(P2VP14-b-PS12).

It can be seen clearly that the G2 and G3 copolymers displayed metal organization similar to the HAuCl$_4$-loaded systems, with ring-like and nodular or raspberry-like morphologies, respectively. The G4 copolymer had a significantly different morphology from the worm-in-sphere organization seen previously for HAuCl$_4$ coordination in toluene, however, and encroached on the raspberry morphology seen for the G3 copolymer. This transition to a raspberry morphology could be related to the extent of PS interpenetration from the core within the P2VP shell. Since Pd(OAc)$_2$ and the Pd(OAc)$_2$-2VP complex are more soluble in toluene as compared to HAuCl$_4$ and the 2VPH$^+$AuCl$_4^-$ complex, chain mobility and compatibility with the PS chains from the PS substrate should be increased. This enhanced compatibility should allow the PS chains from the G3PS substrate to interpenetrate the
Pd(OAc)$_2$-2VP phase to a greater extent as compared to the 2VPH$^+$AuCl$_4^-$ complex. The presence of the interpenetrating chains thus led to nodular phase segregation, in analogy to the template derived from the G2PS substrate. A similar morphology transition from cylindrical to nodular species was reported for PS-$b$-P2VP copolymers, but this was accomplished by templating the block copolymers within cylindrical aluminum oxide nanopores and subjecting the system to solvency and temperature variations.\(^8\)

\[\text{Figure S16. TEM images after loading with 0.5 equiv of Pd(OAc)$_2$-2VP unit in toluene: (a) G1PS-$g$-(P2VP30-$b$-PS20), (b) G2PS-$g$-(P2VP14-$b$-PS12), and (c) G3PS-$g$-(P2VP14-$b$-PS12).}\]

The next step was the examination of bimetallic loading. This type of loading or multi-component loading in general, is attractive due to the interesting properties which may result and the potentially broadened application spectrum for the particles, especially if some domains can be loaded selectively with specific metals. Systems such as this have potential for use as multifunctional nanoreactors, or in the release of multiple agents in drug delivery applications.\(^9\) The G4 copolymer was loaded with both HAuCl$_4$ and Pd(OAc)$_2$, in analogy to a previous investigation of PS-$b$-P4VP block copolymers.\(^10\) The raspberry morphology resulting when the G4 copolymer was loaded with HAuCl$_4$ and Pd(OAc)$_2$ in toluene (0.25 equiv each) is depicted in Figure S17.
Figure S17. Bimetallic loading of G3PS-g-(P2VP14-b-PS12) with HAuCl₄ and Pd(OAc)₂: (a) AFM height (left) and phase (right), and (b) TEM images.

The metals were added simultaneously to the copolymer as a solution in toluene containing 0.75% of THF, to also solubilize HAuCl₄. Unfortunately, instrumentation which could provide mapping of the metal over the templates, such as energy-specific transmission electron microscopy,¹¹ was not available. Bimetallic loading was also performed in chloroform for both the G3 and G4 model copolymers, the same result (nodular phase segregation) being observed in both cases by TEM and AFM analysis. In a final bimetallic loading experiment using G3 and G4 copolymer templates, sequential loading of 0.05 equiv HAuCl₄ followed by hexachloroplatinic (IV) acid (H₂PtCl₆, 0.05 equiv),¹² was performed. The HAuCl₄ was added as a toluene solution with 0.75 % of THF for metal solubilization, while H₂PtCl₆ was added as received. The coordination of H₂PtCl₆ with 2VP occurred in a similar fashion to HAuCl₄, by protonation of the nitrogen atom and metallic counterion association. This resulted in phase-segregated morphologies identical to HAuCl₄ loading in toluene, raspberry and worm-in-sphere structures being observed by TEM and AFM analysis for the G3 and G4 copolymers, respectively (Figure S18).
Figure S18. Bimetallic loading of H₂PtCl₆ (0.05 equiv) and HAuCl₄ (0.05 equiv) in toluene: (a) G2PS-g-(P2VP14-b-PS12) and (b) G3PS-g-(P2VP14-b-PS12).

2.8 Influence of Loading Protocol on Phase Segregation

Further investigation into the intramolecular phase segregation process was performed using a film loading procedure, whereby a drop of HAuCl₄ solution was placed on a thin film of the template polymer. Film stability was a concern in this procedure, as subjecting the film to a solvent could result in debonding from the substrate. Consequently, film quality was monitored by optical microscopy to ensure that adhesion to the substrate was maintained. In a control experiment, a film prepared from G1PS-g-(P2VP15-b-PS11) in its neutral state was observed to debond from a silicon AFM substrate upon loading (Figure S19a). The gold-loaded portion of the pre-ionized polymer film is clearly seen in Figure S19b, with no indication of debonding from the surface. Ionization of the copolymer before film casting provided stronger binding to the substrate and prevented debonding, presumably due to stronger interactions with the oxide layer present on the surface.
Figure S19. Optical microscopy images of film adherence to AFM silicon substrates following HAuCl₄ film loading of (a) neutral and (b) ionized arborescent copolymer films of G1PS-\textit{g}-(P2VP15-\textit{b}-PS11).

Film loading for PS-\textit{g}-(P2VP16-\textit{b}-PS12), G1PS-\textit{g}-(P2VP30-\textit{b}-PS20), G2PS-\textit{g}-(P2VP14-\textit{b}-PS12), and G3PS-\textit{g}-(P2VP14-\textit{b}-PS12) produced similar results when viewed by optical microscopy: The previously ionized polymer films did not debond from the substrate during film loading. Consequently, all the polymers were ionized prior to film casting and metal loading in these experiments. Film loading with aqueous HAuCl₄ solution also resulted in interesting phase segregation in the template molecules, even when the polymer was bound to the substrate. Contact of the AFM polymer films with the aqueous HAuCl₄ solution for up to 5 min, or 1 min for the TEM samples, provided enough chain mobility to the partly protonated P2VP chain segments to induce phase segregation. While spherical or toroidal phase segregation are not very evident for the G2 species by AFM imaging (Figure S20a), the morphology is very different from the ionized species without metal, which displayed no phase segregation. This point will be discussed further. TEM analysis nevertheless shows signs of ring-like metal organization, albeit not very well-defined.

The G3 and G4 copolymers (Figures S20b, c) also exhibited significant morphological transitions after HAuCl₄ film loading as compared to the neutral and the ionized metal-free polymer samples. Distinct phase segregation confined by a circular boundary is visible in both cases. While the phase segregation observed by AFM does not closely resemble the raspberry or worm-in-sphere morphologies, TEM imaging does provide very similar results (nodular for the G3 template and cylindrical for G4). The AFM and TEM images obtained for the G2, G3, and G4
copolymers investigated in film loading (G1PS-g-(P2VP30-b-PS20), G2PS-g-(P2VP14-b-PS12), and G3PS-g-(P2VP14-b-PS12), respectively) are compared in Figure S20.

Figure S20. HAuCl4 film-loaded arborescent copolymer films. AFM height scan on the left, AFM phase scan in the middle, and TEM on the right: (a) G1PS-g-(P2VP30-b-PS20), (b) G2PS-g-(P2VP14-b-PS12), and (c) G3PS-g-(P2VP14-b-PS12).
While establishing the film loading procedures, it was postulated that perhaps the ionization of P2VP was the dominant factor controlling phase segregation with no dependency on the counterion type used. Copolymers ionized with HCl by the same procedure to a 1.0 equiv loading regime (1:1 HCl:2VP) were cast into thin films and analyzed by AFM to probe phase segregation. As seen in Figure S21, copolymers G1PS-g-(P2VP30-b-PS20), G2PS-g-(P2VP14-b-PS12), and G3PS-g-(P2VP14-b-PS12) did not display significant phase segregation under these conditions.

The structures observed show little if any resemblance to their phase-segregated metal-loaded analogues shown previously; toroidal, raspberry, and worm-in-sphere morphologies clearly were not observed for the ionized species without metallic counterions. In fact, the G2 copolymer even lost its spherical shape due to strong adsorption on the mica substrate and consequent flattening of the structure. These findings show that phase segregation is induced by the metal counterion and not solely by the polymer charge.

![Figure S21. AFM images for ionized arborescent copolymer films with height scans shown on the left and phase scans on the right: (a) G1PS-g-(P2VP30-b-PS20), (b) G2PS-g-(P2VP14-b-PS12), and (c) G3PS-g-(P2VP14-b-PS12).](image)

### 2.9 Intermolecular Effects

Thickness measurements were performed by ellipsometry for arborescent copolymer films, before and after loading with gold, to determine the average thickness of the material deposited on the substrate. This method is somewhat crude in that the film thickness cannot be directly correlated with the molecular dimensions, since areas
devoid of polymer are unaccounted for in the calculation. This technique was only applied to provide further evidence for monolayer formation. Phase segregation could potentially be induced by orthogonal polymer interactions, however if only a monolayer is present these interactions can be excluded. On the basis of the molecular dimensions determined from DLS, TEM, and AFM analysis, one would expect that for a monolayer, ellipsometry will provide a lower film thickness due to less than 100% surface coverage as well as molecular flattening. The thickness of some of the films cast for AFM analysis was measured by ellipsometry and compared with the film thickness determined by AFM analysis (Table S7).

**Table S7.** Film thickness measurements of native and HAuCl₄-loaded copolymers in toluene using ellipsometry and AFM.

| Sample                   | Ellipsometryᵃ | AFMᵇ          |
|--------------------------|---------------|---------------|
|                          | Nativeᶜ 0.5 Auᵈ | Nativeᶜ 0.5 Auᵈ |
| PS-g-(P2VP16-b-PS12)     | 8.3 ± 0.2 25 ± 1 | -e 22 ± 2      |
| G1PS-g-(P2VP30-b-PS20)   | 12.6 ± 0.6 23 ± 1 | 13 ± 2 31 ± 4 |
| G2PS-g-(P2VP14-b-PS12)   | 12.9 ± 0.8 28 ± 1 | 19 ± 3 51 ± 3 |
| G3PS-g-(P2VP14-b-PS12)   | 13.9 ± 0.2 31 ± 1 | 22 ± 4 60 ± 3 |

ᵃ Average film thickness, nm;ᵇ Height measured at substrate-polymer boundary, nm;ᶜ Native polymer film thickness;ᵈ Thickness of polymer film containing 0.5 equiv HAuCl₄, loaded in toluene;ᵉ Unable to measure, no polymer-substrate boundary present

For the measurement of film thickness by ellipsometry, aside from the G0 species which have been shown to aggregate, the film thickness increases with the generation number of the templates. The variations observed are insignificant within error limits for the G2–G4 templates, however it is necessary to assume similar coverage for each film sample in making the comparison. AFM also offers the ability to quantify film thickness, provided that a bare substrate area is available as baseline. An example of such a measurement is shown in Figure S22 for G3PS-g-(P2VP14-b-PS12) loaded with 0.5 equiv of HAuCl₄ in toluene.
Figure S22. Film thickness measurement from AFM cross-section analysis for HAuCl₄-loaded G3PS-g-(P2VP14- b-PS12).

The film thickness determined from cross-section analysis provides a height difference between the substrate and the arborescent molecules of ca. 60 nm for the G3PS-g-(P2VP14-b-PS12) species, which is indicative of a monomolecular layer. Height measurements were performed at the substrate-polymer boundary for the copolymers listed in Table S8 and led to similar findings: Monolayer films were adsorbed on the substrates, but multilayered sections were also apparent. The only exception to this was again the G0 species, which contained mainly multilayered areas with an average height of 20 nm. These results are in agreement with the conclusions drawn previously from the ellipsometry measurements, concerning the lack of influence of intermolecular interaction from orthogonal species to phase segregation. Additionally, similar intramolecular phase segregation is apparent for species within both mono- and multilayered areas, again in agreement with phase segregation being independent of orthogonal intermolecular or substrate interactions.

Thickness and diameter measurements from AFM analysis on both native and gold-loaded copolymers are provided in Table S8. The AFM height measurements, much like ellipsometry, show a height increase upon metal coordination. Further, molecular flattening is reduced upon coordination with HAuCl₄, as indicated by the larger height to diameter ratio; the gold-loaded copolymers conform to a more spherical topology.
The native G0 and G1 copolymers formed continuous polymer films with no voids exposing the substrate, thus height measurements could not be performed. Further, well-defined unimolecular features were not observed in the film, and thus the radii could not be measured accurately.

Table S8. Analysis of molecular dimensions by AFM.

| Template                  | Nativea | 0.5 Au5 |                  |                  |
|---------------------------|---------|---------|------------------|------------------|
|                           | h5      | d5      | h/d              |                  |
| PS-g-(P2VP16-b-PS12)      | −5      | −5      | −                |                  |
|                           | 22 ± 2  | 28 ± 1  | 0.8              |                  |
| G0PS-g-(P2VP11-b-PS18)    | −5      | −5      | −                |                  |
|                           | 19 ± 2  | 35 ± 2  | 0.5              |                  |
| G1PS-g-(P2VP30-b-PS20)    | 13 ± 2  | 43 ± 1  | 0.3              |                  |
|                           | 31 ± 4  | 45 ± 4  | 0.7              |                  |
| G2PS-g-(P2VP14-b-PS12)    | 19 ± 3  | 90 ± 1  | 0.2              |                  |
|                           | 51 ± 3  | 69 ± 2  | 0.7              |                  |
| G3PS-g-(P2VP14-b-PS12)    | 22 ± 4  | 105 ± 2 | 0.2              |                  |
|                           | 60 ± 3  | 69 ± 2  | 0.8              |                  |

a Native polymer in toluene; b Polymer containing 0.5 equiv HAuCl4, loaded in toluene; c Height of polymer film measured at substrate-polymer boundary, nm; d Diameter of template molecule, nm; e Unable to measure, no polymer-substrate boundary present

2.10 Reduction to Gold Nanoparticles by Various Methods

2.10.1 Reduction with Anhydrous Hydrazine or NaBH4

The yellow-colored pyridinium tetrachloroaurate complex (2VPH+AuCl4−) solutions formed by the different arborescent CSC copolymers had an absorption band at 325 nm, also observed for the unbound gold salt (Figure S23). The spectra, acquired at a concentration of ca. 0.002 % w/v copolymer (0.0024 % w/v HAuCl4), were vertically shifted for improved clarity, and no significant dependence of the absorption spectra on the polymer characteristics (molecular weight, generation) was observed. This implies that coordination did not change the electronic environment of the gold ions significantly, which makes sense since gold was only part of the AuCl4− counterion and not directly coordinated with the pyridine moieties.
Figure S23. UV-Vis absorption of AuCl₄⁻ (a) in solution, and after coordination with the vinylpyridine moieties in arborescent copolymers (b) G1PS-g-(P2VP30-b-PS20), (c) G1PS-g-(P2VP7-b-PS7), (d) G2PS-g-(P2VP14-b-PS12) and (e) G3PS-g-(P2VP14-b-PS12).

After reduction the yellow solutions turned dark purple irrespective of the reduction protocol used. The resulting elemental gold nanoparticles had an absorption maximum near 525 nm, characteristic for the surface plasmon resonance of small Au nanocrystals. Shifts in the absorption maximum, or the appearance of shoulders are indicative of particle size variations, aggregation, or pairing. An example of a red shift due to a gold nanoparticle size increase is provided in Figure S24, which depicts the absorbance spectra for elemental gold nanoparticles obtained by hydrazine reduction in toluene leading to different nanoparticle sizes. The larger and more dispersed nanoparticles obtained in the near equivalency regime (1.2:1 hydrazine:Au) have a higher absorption wavelength maximum (535 nm), while particles obtained in the excess hydrazine regime (10:1 hydrazine:Au) have an absorption maximum shifted to 522 nm, characteristic for smaller nanoparticles.
Figure S24. UV-Vis characterization of Au nanoparticles templated with G1PS-g-(P2VP30-b-PS20): (a) 522 nm maximum, 8 ± 2 nm diameter for excess hydrazine; and (b) 532 nm maximum, 17 ± 9 nm diameter for hydrazine reduction near equivalency.

2.10.2 Film Reduction with NaBH₄

Film reduction was also performed on the HAuCl₄-loaded templates for comparison, to monitor the mobility of the reduced gold and whether metal nanoparticle reorganization would take place under these conditions. The templates were loaded in THF and cyclohexane (25:75, THF:CH) with 0.5 equiv of HAuCl₄, cast onto a substrate, and then subjected to NaBH₄. As seen in Figure S25, when compared to the non-reduced precursor, gold nanoparticle organization exists for the G2 template and noticeably more ring-like assemblies are observed than for the salt-loaded template. The gold nanoparticles within the G3 and G4 templates display organization similar to the salt, with an even distribution of particles for G3 and cylindrical patterns for G4.
Figure S25. TEM images for NaBH₄ film reduction of HAuCl₄-loaded templates: (a) G1PS-g-(P2VP30-b-PS20), (b) G2PS-g-(P2VP14-b-PS12), and (c) G3PS-g-(P2VP14-b-PS12).

The corresponding salt-loaded templates loaded and cast from toluene can be found within the main publication (Figure 3). Even though the NaBH₄ solution can provide solvency for the ionized P2VP phase, the reduced nanoparticles within the film apparently have a low enough mobility to remain confined to the domains defined by the polymer phase.

2.10.3 Solvent-free Solid State Reduction

The reduction of HAuCl₄-loaded arborescent copolymer templates was also performed in the solid state, as polymer films or in the powder form, in the absence of solvent for the reducing agents, in contrast to the reduction procedures previously discussed. The methods used to perform solvent-free reductions involved hydrazine vapor,¹³ UV light irradiation¹⁴,¹⁵ and hydrogen plasma etching,¹⁵,¹⁶ all of which have been applied previously to intermolecular micellar systems. Particular attention focused on the same templates for which well-defined intramolecular phase segregation was observed, namely G1PS-g-(P2VP30-b-PS20), G2PS-g-(P2VP14-b-PS12), and G3PS-g-(P2VP14-b-PS12). The G0 copolymer was also investigated for comparison. Provided in Figure S26 are the gold nanoparticle size distributions resulting from the reduction of HAuCl₄-loaded G2PS-g-(P2VP14-b-PS12) films with hydrazine vapor and UV light.
Figure S26. Size distribution of gold nanoparticles obtained by film reduction of G2PS-g-(P2VP14-b-PS12) with hydrazine vapor and UV light.

Similar trends were observed for the PS-g-(P2VP16-b-PS12), G1PS-g-(P2VP30-b-PS20), and G3PS-g-(P2VP14-b-PS12) templates: Hydrazine vapor reduction led to broad size distributions, with a higher population of smaller radius species. TEM images for the nanoparticles resulting from the two solid state reduction methods, corresponding to the distributions shown in Figure S26, are provided in Figure S27.
Figure S27. TEM images for gold nanoparticles obtained from (a) hydrazine vapor and (b) UV reduction of HAuCl₄-loaded G2PS-g-(P2VP14-b-PS12) films.

Additional TEM images for the PS-g-(P2VP16-b-PS12), G1PS-g-(P2VP30-b-PS20), and G3PS-g-(P2VP14-b-PS12) templates, depicting very similar nanoparticle size distributions, can be found in Appendix S2. The corresponding size distribution charts are provided in Appendix 3. Hydrazine vapor reduction of G1PS-g-(P2VP30-b-PS20) loaded with 0.5 equiv HAuCl₄ was also performed on material in the powdered (freeze-dried) state and resulted in gold nanoparticles with a diameter of 14 ± 8 nm, nearly identical to the nanoparticles formed via vapor reduction in the film. UV-Vis absorption measurements yielded a strong surface plasmon resonance with a maximum at 535 nm, identical with the 17 ± 8 nm nanoparticles obtained by solution reduction with 1.2 equiv of hydrazine.

Plasma reduction was also performed on the same gold-loaded copolymer films and the gold nanoparticles were viewed by scanning electron microscopy (SEM), as shown in Figure S28.
Figure S28. Gold nanoparticles formed by plasma reduction of copolymer films viewed by SEM: (a) PS-g-(P2VP16-b-PS12), (b) G1PS-g-(P2VP30-b-PS20), (c) G2PS-g-(P2VP14-b-PS12), and (d) G3PS-g-(P2VP14-b-PS12).

It can be concluded that, within error limits, all three solid state reduction methods produced very similar nanoparticle sizes, as summarized in Table S9. It is nevertheless clear that hydrazine vapor produced much less defined nanoparticles, with a higher size dispersity. As reported for the other solution reduction protocols, no correlation was found between the nanoparticle size and the template characteristics.
Table S9. Gold nanoparticle diameters by different solid state reduction methods.

| Template                  | Diameter (nm) | N$_2$H$_4$ Vapor | UV  | Plasma |
|---------------------------|---------------|-------------------|-----|--------|
| PS-g-(P2VP16-b-PS12)      | 15 ± 7        | 16 ± 3            | 13 ± 1 |
| G1PS-g-(P2VP30-b-PS20)    | 14 ± 10       | 13 ± 2            | 16 ± 2 |
| G2PS-g-(P2VP14-b-PS12)    | 14 ± 7        | 14 ± 4            | 17 ± 5 |
| G3PS-g-(P2VP14-b-PS12)    | 15 ± 9        | 18 ± 3            | 15 ± 3 |

The broadly dispersed gold nanoparticles obtained in hydrazine vapor reduction may be due to hindered diffusion of the reducing agent to the metal. To reach the metallic salt, hydrazine must diffuse through the PS corona of the template, thus inducing a non-homogeneous reduction process. A high local concentration also exists at the film surface. As the 2VP phase is swollen by hydrazine vapor, chain mobility increases and allows the aggregation of the small nanoparticles.

Hydrogen plasma can easily penetrate the polymer and react with the metal salt in a much more consistent and simultaneous manner, resulting in a more uniform size distribution. It has been shown that the plasma treatment can also degrade and remove all the organic components (such as the polymeric scaffolds), thus providing nanoparticle mobility and a uniform particle size distribution.$^{16,17}$ In a similar fashion, UV irradiation can efficiently reduce the metallic salt with little local concentration differentials, due to uniform penetration of the beam.

UV irradiation for 12 h under ambient conditions in air provides an adequate and consistent concentration of ozone, as evidenced by its distinct smell upon sample removal. The UV/ozone combination is likewise known to remove organic components, including the polymeric templates.$^{18}$ While the films obtained under these conditions were not explicitly tested for residual polymer, the films looked very clean and devoid of any shaded areas indicative of polymer film remnants. Removal of the polymeric template enhances metallic particle mobility, allowing for the formation of uniform particles within a localized area.

In further support of polymer scaffold removal, ellipsometry measurements performed on UV/ozone treated films displayed a dramatic thickness reduction as compared to the salt-loaded copolymers. Provided in Table S10 are film
thickness measurements by ellipsometry for 0.5 equiv HAuCl₄-loaded copolymers before and after treatment with UV/ozone. The large reduction in film thickness following UV/ozone treatment is attributed to removal of the copolymer scaffold, which amounts to the majority of material, leaving only the gold nanoparticles.

**Table S10.** Film thickness measurements by ellipsometry for HAuCl₄-loaded copolymers, before and after UV/ozone treatment.

| Sample⁹ | Thickness (nm) |
|---------|----------------|
|         | AuCl₄⁻ | Au⁺ |
| PS-­⁴⁻-(P2VP16-b-PS12) | 25 ± 1 | 0.9 ± 0.5 |
| G1PS-­⁴⁻-(P2VP15-b-PS11) | 23 ± 1 | 1.3 ± 0.1 |
| G1PS-­⁴⁻-(P2VP30-b-PS20) | 23 ± 1 | 1.6 ± 0.1 |
| G2PS-­⁴⁻-(P2VP14-b-PS12) | 28 ± 1 | 1.1 ± 0.6 |
| G3PS-­⁴⁻-(P2VP14-b-PS12) | 31 ± 1 | 2.3 ± 0.1 |

⁹ Copolymers loaded with 0.5 equiv HAuCl₄; ¹⁰ Thickness of residual film following UV/ozone treatment
3 Appendices

Appendix S1. Synthesis of anhydrous hydrazine and experimental apparatus
Appendix S2. TEM images for gold nanoparticles obtained by reduction with hydrazine vapor (left) and UV light (right) from various templates: (a) PS-g-(P2VP16-b-PS12), (b) G1PS-g-(P2VP30-b-PS20), and (c) G3PS-g-(P2VP14-b-PS12)
Appendix S3. Gold nanoparticle size distributions obtained by hydrazine vapor and UV light reduction of various arborescent copolymer films
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