Supporting Information

Synthesis of Thermally Stable Au-core/Pt-shell Nanoparticles and Their Segregation Behavior in Diblock Copolymer Mixtures

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Supporting Information 1.

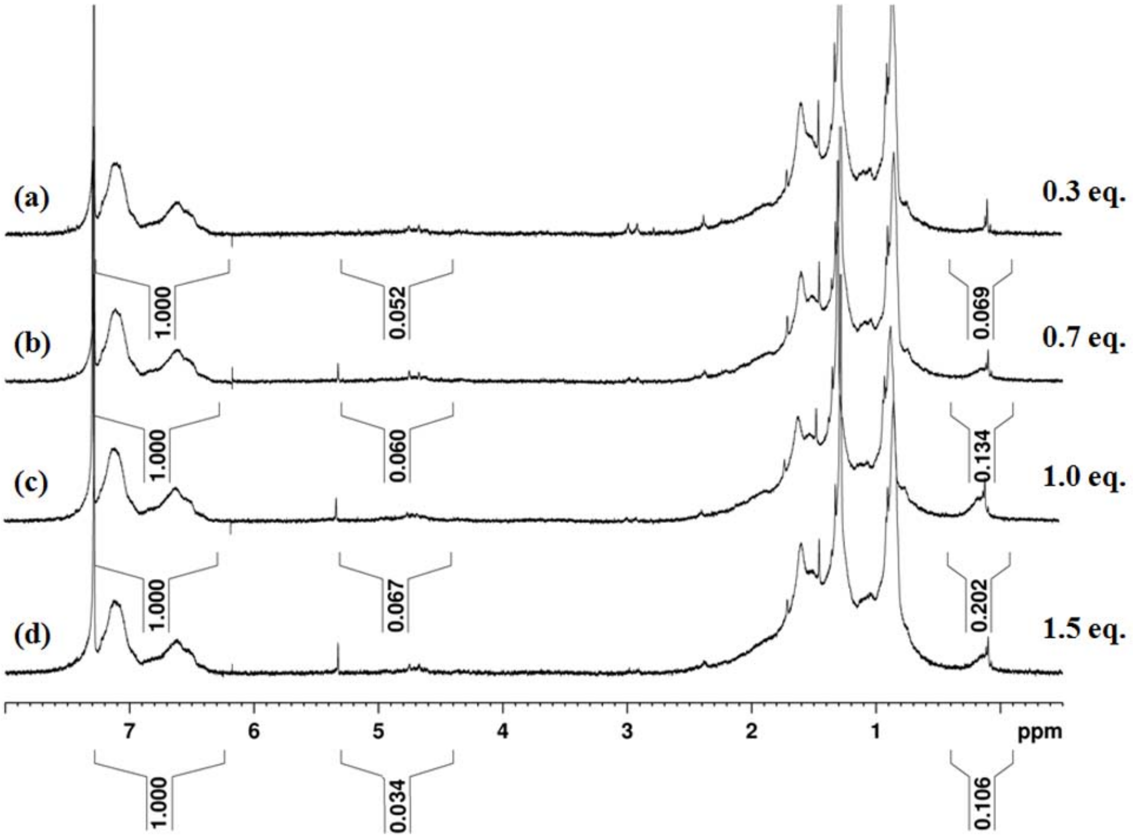

Figure SF1. ^{1}H-NMR spectra of PS_{29}-*b*-I_{21}SAu_3 hydrosilylated with various mole fractions of cross-linker (1,1,3,3-tetramethyldisiloxane) relative to vinyl groups: (a) 0.3 eq., (b) 0.7 eq., (c) 1.0 eq., and (d) 1.5 equivalents. The $\alpha_{C=C}$ values, the integration ratio of the sum of vinyl peaks centered at 4.7 and 5.7 ppm to the aromatic peaks of PS at 6.3-7.4 ppm, are lower than 0.07. The peak at 0.17 ppm originating from the methyl groups of cross-linker ($\alpha_{Si\text{-}CH}$) is a maximum when 1 equivalent is used.

Supporting Information 2.

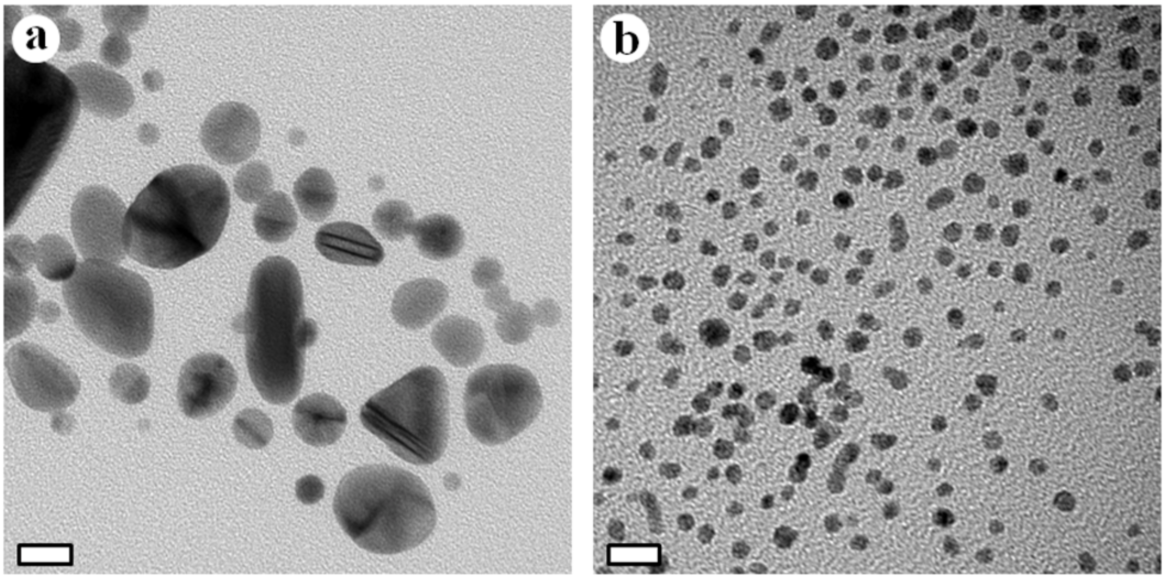

Figure SF2. TEM micrographs of Au nanoparticles after thermal stability test was carried out. (a) PS_{29}-*b*-I_{21}SAu_3 without hydrosilylation. The size of nanoparticles has increased significantly. Most of nanoparticles are precipitated as very large particles, which are not soluble in toluene. (b) PS_{26}-*b*-I_{12}SAu_2 after thermal stability test at 130°C for 1day. Some rod-like particles are observed. ΔD_{core} measured by image analysis was about 0.9 nm. Scale bars are 10 nm.

Supporting Information 3.

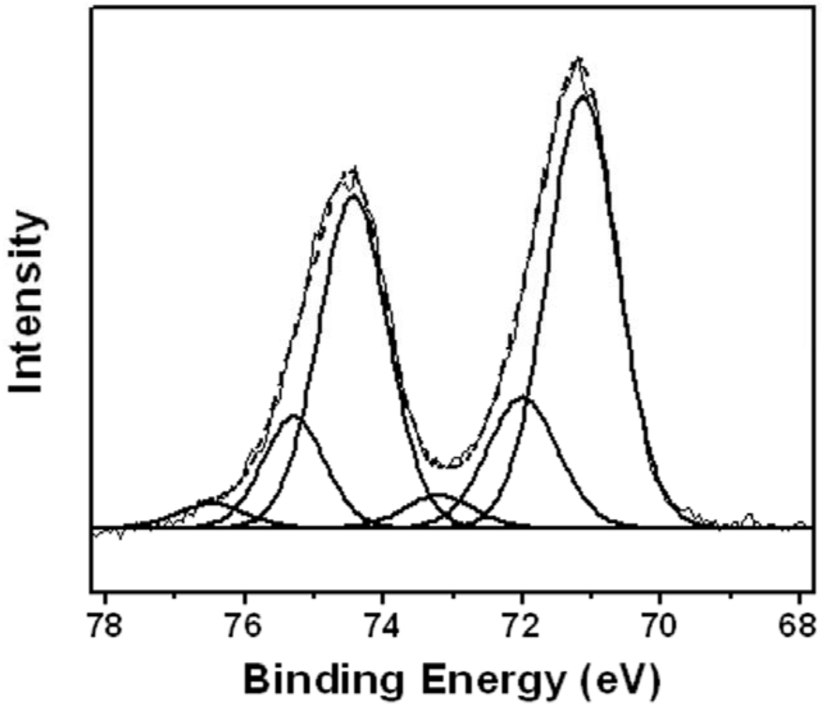

Figure SF3. XPS spectra of Pt peaks deconvoluted using Gaussians with FWHM = 1.2 eV into two metallic Pt doublets ($4f_{7/2}$ and $4f_{5/2}$) at binding energies of 71.1 and 74.4 eV and two additional pairs of less intense peaks at 72.1/75.4 eV and 73.2/76.5 eV.

A pair of peaks at binding energies of 72.1 and 75.4 eV can be assigned based on the energy shift due to both the charge transfer from Pt to sulfur and the formation of a Pt-vinyl complex. It is reasonable that the sulfur from the surrounding ligand on the Pt-shell results in some charge transfer, which has been reported by others.[1-3] In addition, the energy shift due to formation of the Pt-vinyl complex with the remaining vinyl groups on the PI ligand after cross-linking is similar to the Pt-sulfur energy transfer, thus the peaks are superposed.[4,5] Meanwhile, the binding energy of Pt $4f_{7/2}$ and $4f_{5/2}$ at 73.2 and 76.5 eV can be assigned to the energy shift due to formation of the Pt-Si bond. Note that our hydrosilylation reaction was conducted under an excess of hydrosilane that corresponds to 2 equivalents relative to vinyl groups, thus resulting in the formation of Pt-Si rich Pt nanoparticles after hydrosilylation as previously reported.[4,5] The Pt-Si bond can be formed on the Pt-shell of the core-shell nanoparticle as well as on the dihydrosilane cross-linker that has reacted with only a single vinyl group. Therefore, the presence of peaks at higher binding energy reveals that there was residual Pt catalyst in the form of Pt-vinyl and Pt-Si on the cross-linked shell of the Au-Pt nanoparticles.

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(2) Tu, W. X.; Takai, K.; Fukui, K.; Miyazaki, A.; Enoki, T. *J. Phys. Chem. B* **2003,** *107*, 10134.
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(4) Stein, J.; Lewis, L. N.; Gao, Y.; Scott, R. A. *J. Am. Chem. Soc.* **1999,** *121*, 3693.
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Supporting Information 4.

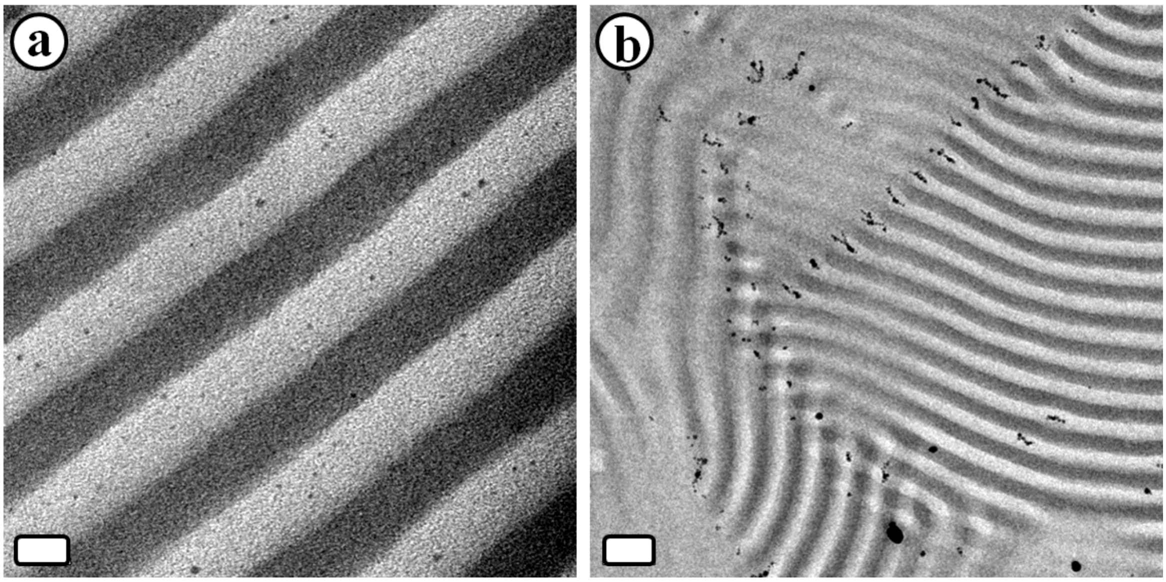

Figure SF4. Cross-sectional TEM micrographs of lamellar forming PS_{547}-*b*-$P2VP_{542}$ block copolymer (114 kg/mol) containing PS_{29}-*b*-I_{21}SAu_4 nanoparticles whose ligands are not crosslinked. The composite sample in (a) was annealed by dichloromethane vapor. The sample in (b) was annealed with dichloromethane followed by thermal annealing at 190°C for three days. Volume fractions of nanoparticles (ϕ_p) were the same for both samples as 3.2%. Scale bars in (a) and (b) are 20nm and 100nm, respectively.