

Supporting Information for:

Nanoscale Rings from Silicon-Containing Triblock Terpolymers

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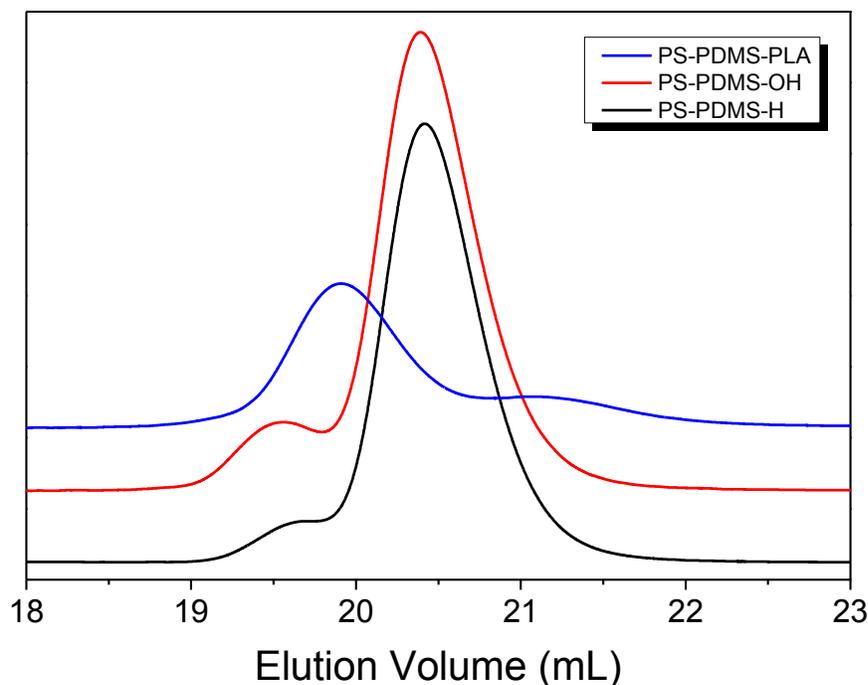


Figure S1. Size exclusion chromatographs for (i) the PS-PDMS precursor diblock polymer prior to end-functionalization with allyl alcohol (black); (ii) the PS-PDMS precursor diblock polymer post end-functionalization with allyl alcohol (red); (iii) the final PS-PDMS-PLA triblock polymer following extraction of coupled product with cold cyclohexane (blue).

Size exclusion chromatography (SEC) was performed on an Agilent 1100 series instrument equipped with an HP 1047A refractive index detector. Three PLgel Mixed C columns as well as a PLgel 5 μm guard from Varian were employed. Chloroform was used as the mobile phase at 35°C flowing at a rate of 1 mL/min. Polymer samples were prepared at a concentration of 0.3% (wt:wt) in chloroform. Molecular weights were determined from calibration curves created from narrow molecular weight PS standards purchased from Polymer Laboratories.

Both PS-PDMS-H and PS-PDMS-OH elute at the same elution volume, indicating no change in the hydrodynamic volume of the polymer, and suggesting no change in the molecular weight upon hydrosilation. After PLA chain growth, the PS-PDMS-PLA triblock polymer elutes at a lower elution volume relative to both the PS-PDMS-H and PS-PDMS-OH, confirming the polymerization of the PLA domains to form the final PS-PDMS-PLA block terpolymer.

The SEC traces of both the PS-PDMS-H and PS-PDMS-OH show a small peak at lower elution volume relative to the major eluting species. We hypothesize that this low eluting species is the ABBA tetrablock polymer that formed as a result of a dichlorodimethylsilane impurity present during the end capping of the PS-PDMS anionic polymerization. This ABBA tetrablock polymer was extracted from the desired ABC triblock terpolymer by washing with cold cyclohexane.

From the final SEC trace of the PS-PDMS-PLA triblock terpolymer an overall PDI of 1.16 was obtained.

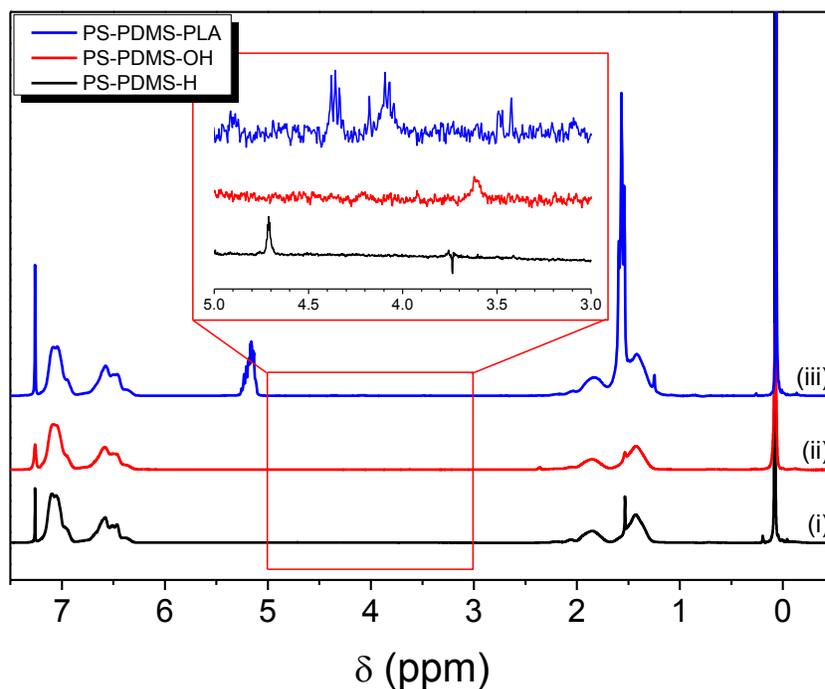


Figure S2: ^1H NMR spectra at each stage in the triblock terpolymer synthesis, for (i) the PS-PDMS precursor diblock polymer prior to end-functionalization with allyl alcohol (black); (ii) the PS-PDMS precursor diblock polymer post end-functionalization with allyl alcohol (red); (iii) the final PS-PDMS-PLA triblock polymer following extraction of coupled product with cold cyclohexane (blue).

^1H NMR spectra were obtained on a Varian INOVA-300, INOVA-500, or VXR-300 spectrometers in CDCl_3 at room temperature. Samples were prepared by dissolving ~ 20 mg of polymer in ~ 0.700 mL deuterated chloroform. Each spectrum was obtained after 32 scans with a 20 second pulse delay.

The number average molecular weight of the PS and PDMS chains were calculated from the integral ratio of the terminal silane proton signal at 4.7 ppm to the aromatic protons of the PS chains between 6.5 – 7.1 ppm or the PDMS main chain protons at 0.07 ppm. From these ratios, the molar mass of the PS and PDMS chains were calculated to be 33.0 kg/mol and 7.0 kg/mol, respectively. The integral of the PLA backbone methylene proton signal at 5.3 ppm was then compared to those of the PS and PDMS backbone protons to calculate a number average molecular weight for the PLA block of 25.0 kg/mol.

Complete removal of the terminal silane signal at 4.7 ppm and appearance of a signal for the methyl protons adjacent to the hydroxyl end group at 3.6 ppm indicate complete conversion of the silane to the hydroxyl functionality. The signal of these methylene protons shifts downfield to 4.1 ppm upon PLA growth. In addition, the emergence of PLA backbone and end group signals occur around 5.3 and 4.4 ppm.

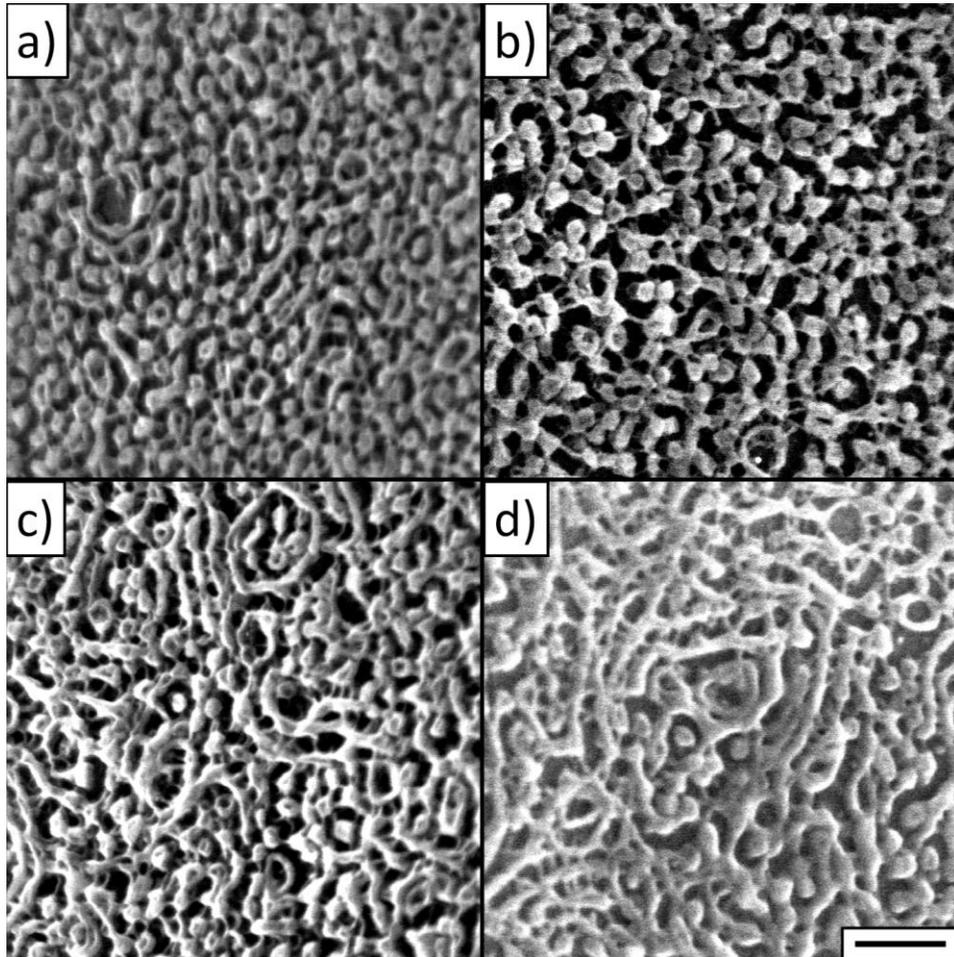


Figure S3: Plan view SEM images of oxygen reactive ion etched PS-PDMS-PLA thin films (52 nm thick), without an initial CF_4 reactive ion etch to remove the PDMS wetting layer. In the top row, a) 30 min toluene anneal followed by a 60 s O_2 RIE, b) 30 min toluene anneal followed by a 120 s O_2 RIE. In the bottom row, c) 60 min toluene anneal followed by a 60 s O_2 RIE, b) 60 min toluene anneal followed by a 120 s O_2 RIE. In all cases, there is clear evidence for linking between the ring features, most likely due to the PDMS wetting layer being converted to SiO_x . Scale bar is 200 nm.

Scanning electron microscopy was performed on a Hitachi S900 FE-SEM using an accelerating voltage between 3.0 and 5.0 kV.

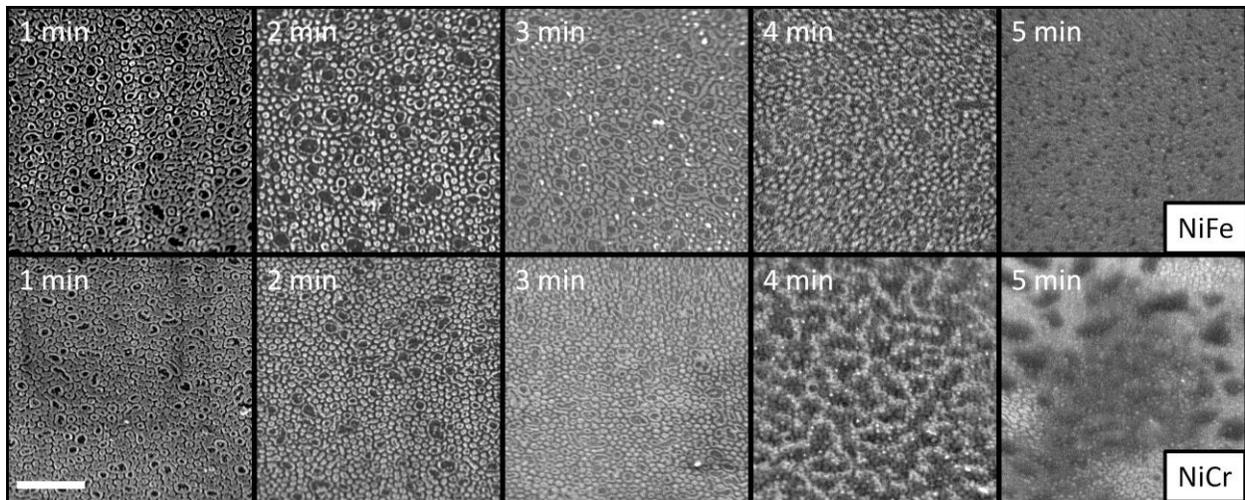


Figure S4: A series of plan view SEM images of nanorings as a function of Ar ion beam mill time. The top row shows images of $\text{Ni}_{80}\text{Fe}_{20}$ and the bottom $\text{Ni}_{80}\text{Cr}_{20}$ films. At 1 min, the images show the initial patterned Au overlayer, while subsequent image shown milling into the underlying alloy film. Scale bar represents 500 nm.

Scanning electron microscopy was performed on a Hitachi S900 FE-SEM using an accelerating voltage between 3.0 and 5.0 kV.

The following is a calculation of expected SiO_x ring height following O₂ RIE of the PS-PDMS-PLA film.

Consider first, post 60 s O₂ RIE, all organic material is removed and the only result is the oxidized Si (SiO₂) within the PDMS block. Initial parameters:

$$t_i = 52 \times 10^{-7} \text{ cm (initial thickness)}$$

Block/ Molecule	Molar mass - M(kg/mol)	Density - ρ(g/cm ³)
PS	33	1.05
PDMS	7	0.98
PLA	25	1.25
SiO ₂	.060	2.65
[SiO(CH ₃) ₂]	.074	0.98

First, consider the volume of initial PDMS (V_i) per unit of lateral area (A)

$$V_i = A \cdot t$$

Then, the initial mass per unit area (m_i) is given by

$$m_i = \rho_{PDMS} \cdot V_i / A = 0.98 \text{ g/cm}^3 \cdot 52 \times 10^{-7} \text{ cm} \cdot A / A = 5.096 \times 10^{-6} \text{ g per unit area}$$

This can be converted to moles per unit area (N_{PDMS}) using M_{PDMS} , and further converted to number of PDMS chains per unit area (n_{PDMS}) with N_A (Avagadro's number)

$$N_{PDMS} = m_i / M_{PDMS} = 5.096 \times 10^{-6} \text{ g} / 7,000 \text{ g/mol} = 7.28 \times 10^{-10} \text{ mol}$$

$$n_{PDMS} = N_{PDMS} \cdot N_A = 7.28 \times 10^{-10} \text{ mol} \cdot 6.022 \times 10^{23} \text{ mol}^{-1} = 4.38 \times 10^{15} \text{ PDMS chains per unit area}$$

To determine the number of Si atoms ($n_{Si/chain}$) per chain

$$n_{Si/chain} = M_{PDMS} / M_{[SiO(CH_3)_2]} = 7000 \text{ g/mol} / 74 \text{ g/mol} = 94.6 \text{ Si atoms / PDMS chain}$$

This results in a total number of Si atoms per unit area (n_{Si}) of

$$n_{Si} = n_{Si/chain} \cdot n_{PDMS} = 94.6 \cdot 4.38 \times 10^{15} = 4.147 \times 10^{17} \text{ Si atoms per unit area}$$

If we assume 100% conversion of Si to SiO₂, then there will now be 4.147×10^{17} SiO₂ molecules per unit area (n_{SiO_2}), which equals 6.886×10^{-8} moles per unit area (N_{SiO_2}).

Since the molar mass (M_{SiO_2}) for SiO₂ is 60 g/mol, we convert N_{SiO_2} to a mass per unit area (m_{SiO_2})

$$m_{SiO_2} = M_{SiO_2} \cdot N_{SiO_2} = 6.886 \times 10^{-8} \text{ mol/unit area} \cdot 60 \text{ g/mol} = 4.132 \times 10^{-6} \text{ g/unit area}$$

Finally, using the density for SiO₂ (ρ_{SiO_2}), we get the final thickness (t_f)

$$t_f = m_{SiO_2} / \rho_{SiO_2} = 4.132 \times 10^{-6} \text{ g/cm}^2 / 2.2 \text{ g/cm}^3 = 1.878 \times 10^{-6} \text{ cm} \approx \mathbf{18.8 \text{ nm}}$$