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Supporting Information

A General Strategy for Creating Self-Defending Surfaces for Controlled Drugs Production for Long Periods of Time

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Additional experimental data

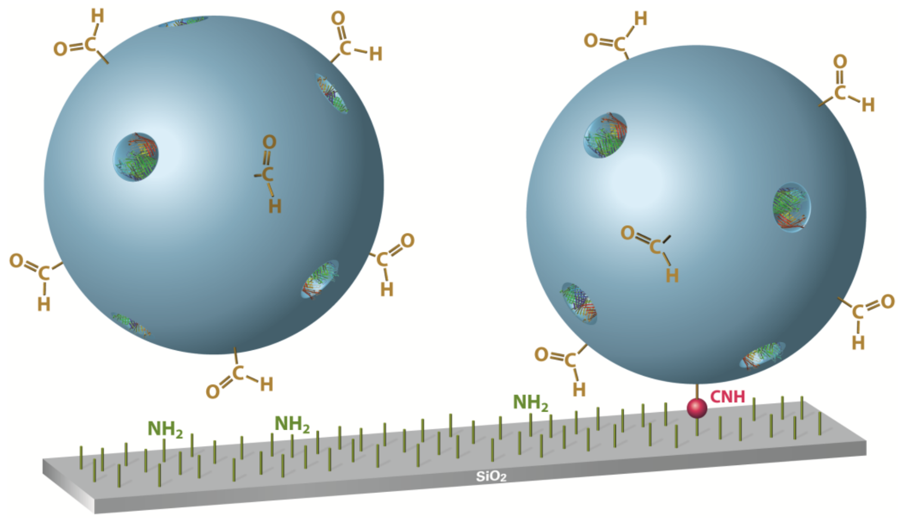


Figure S1. Schematic representation of the chemistry as applied to nanoreactor immobilization *via* an amino bond.

ATR-FTIR measurments

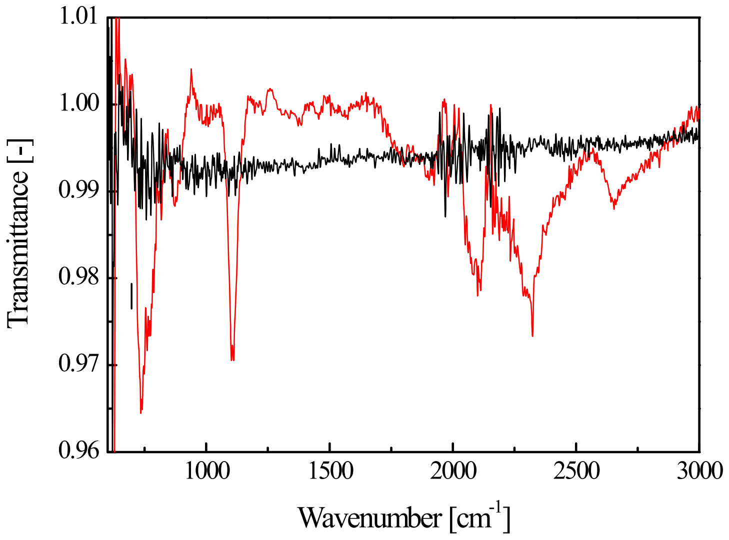


Figure S2. ATR-FTIR spectra of an unmodified silicon wafer (in black) and an amino functionalized silicon wafer (in red).

Atomic force microscopy (AFM)

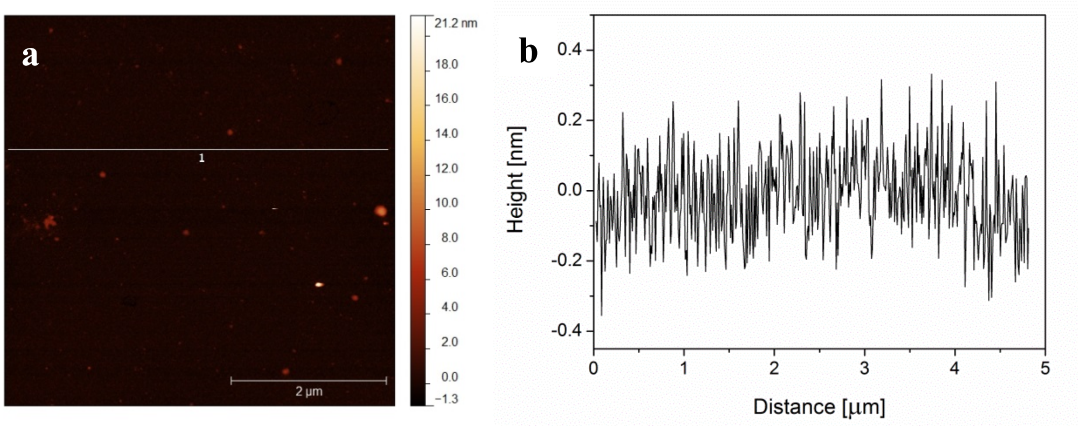
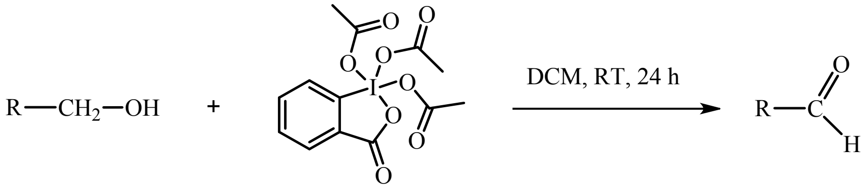


Figure S3. An AFM image of the amino functionalized silicon wafer surface showing homogenous, high uniformity and low roughness (~ 0.22 nm) (a) and the corresponding cross section (b). Scale bar: 2 µm.

Dess-Martin oxidation of the hydroxyl, terminal groups of the polymer



Scheme S1. Scheme of Dess-Martin oxidation of primary alcohols to aldehydes.

Analytical tests employed to confirm the presence of aldehyde groups

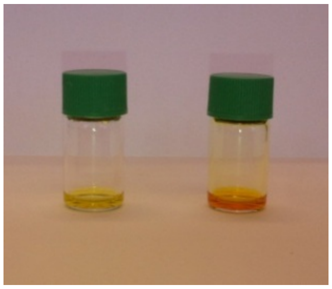


Figure S4. Pictures of aldehyde-terminated (right side) and hydroxyl-terminated copolymer (left side) after Brady's test.

Figure S5. Pictures of aldehyde-terminated (right side) and hydroxyl-terminated (left side) copolymer after the Tollens' test

Dynamic light scattering (DLS)

The observed differences (broadening of the peaks) in DLS results can be attributed to the quality of the polymeric film used for rehydration as well as rehydration itself. Because the polymeric films were not exactly the same, i.e. their homogeneity and thickness, and parameters of rehydration, for example speed of stirring, consequently the self-assembly did not proceed in exactly the same manner. Nevertheless, DLS measurements proved already unchanged self-assembly of oxidized copolymer.

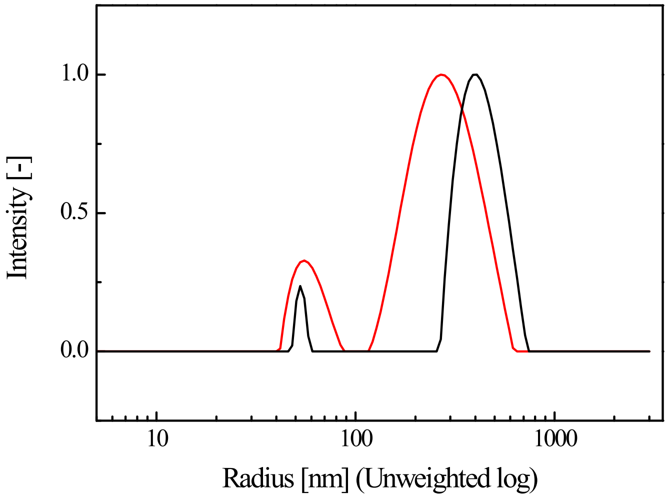


Figure S6. DLS size distribution at 90° for self-assembled nanoreactors made of unmodified block copolymer (in black) and oxidized copolymer (in red).

Transfer Electron Microscopy (TEM)

Transmission electron microscopy (TEM) measurements were performed on a Philips EM 400 (Philips Electronics, Netherlands) operated at 80 kV. The device was equipped with a Megaview III charge-coupled device camera and it was controlled with Morgagni 268D control and image acquisition software. Glow-discharged, parlodion-and carbon-coated, copper grid (200 mesh) were used. The samples were negatively stained with a 2% uranyl acetate solution.

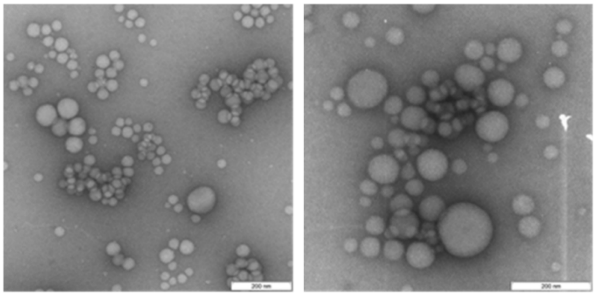


Figure S7. Representative TEM images of nanoreactors made of the hydroxyl-terminated (left image) and aldehyde-terminated (right image) block copolymer. Scale bar: 200 nm.

^{1}H-NMR measurements

Detailed peak assignments for the PDMS pre-polymer:

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 0 ppm (Si-***CH_3***, 6H), 0.5 ppm (Si-***CH_2***-CH_2, 4H), 1.5 – 1.6 ppm (Si-CH_2-***CH_2***-CH_2, 4H), 1.9 – 2.0 ppm (-***OH***), 3.4 ppm (Si-CH_2-CH_2-***CH_2***-O-CH_2, 4H), 3.5 ppm (O-***CH_2***-CH_2-OH, 4H), 3.6 ppm (O-CH_2-***CH_2***-OH, 4H).

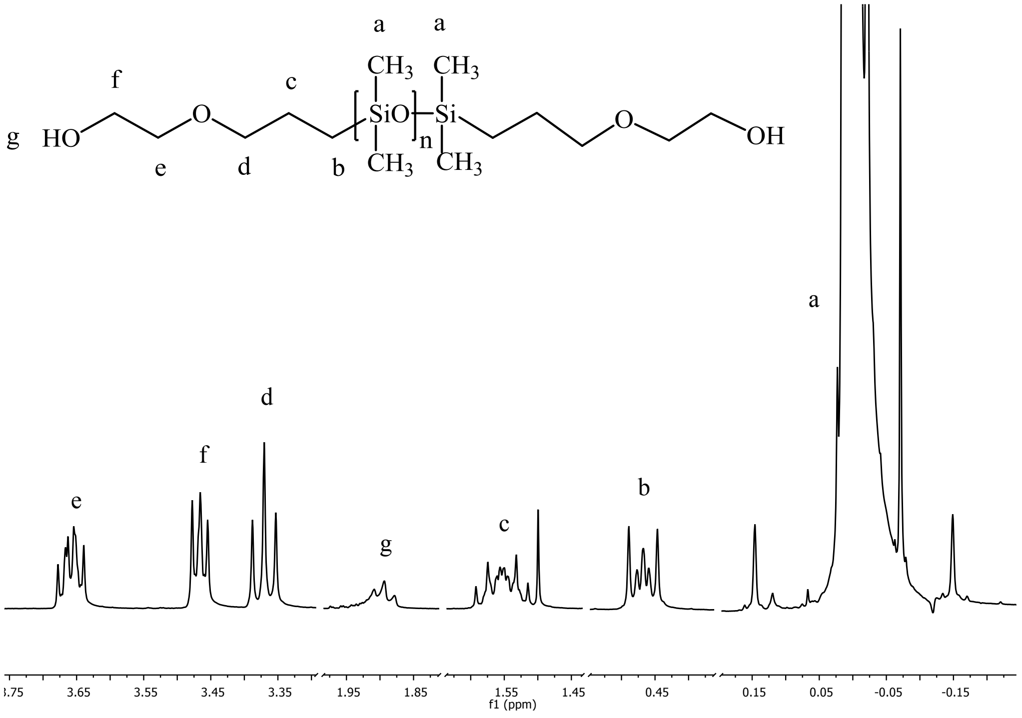


Figure S8. ^{1}H-NMR spectrum of α,ω-bis(3-hydroxypropyl)poly(dimethylsiloxane) (PDMS) pre-polymer in $CDCl_3$.

Detailed peak assignments for the amphiphilic block copolymer poly(2-methyloxazoline)-*block*-poly(dimethylsiloxane)-*block*-poly(2-methyloxazoline) (PMOXA$_{16}$-PDMS$_{72}$-PMOXA$_{16}$):

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 0 ppm (Si-$\boldsymbol{CH_3}$, 6H, a), 0.5 ppm (Si-$\boldsymbol{CH_2}$-CH_2, 4H, a), 2.0 – 2.2 ppm ($\boldsymbol{CH_3}$-CON<, 6H, b), 3.3 – 3.5 ppm (HO-$\boldsymbol{CH_2}$-$\boldsymbol{CH_2}$-N<, 8H, c)

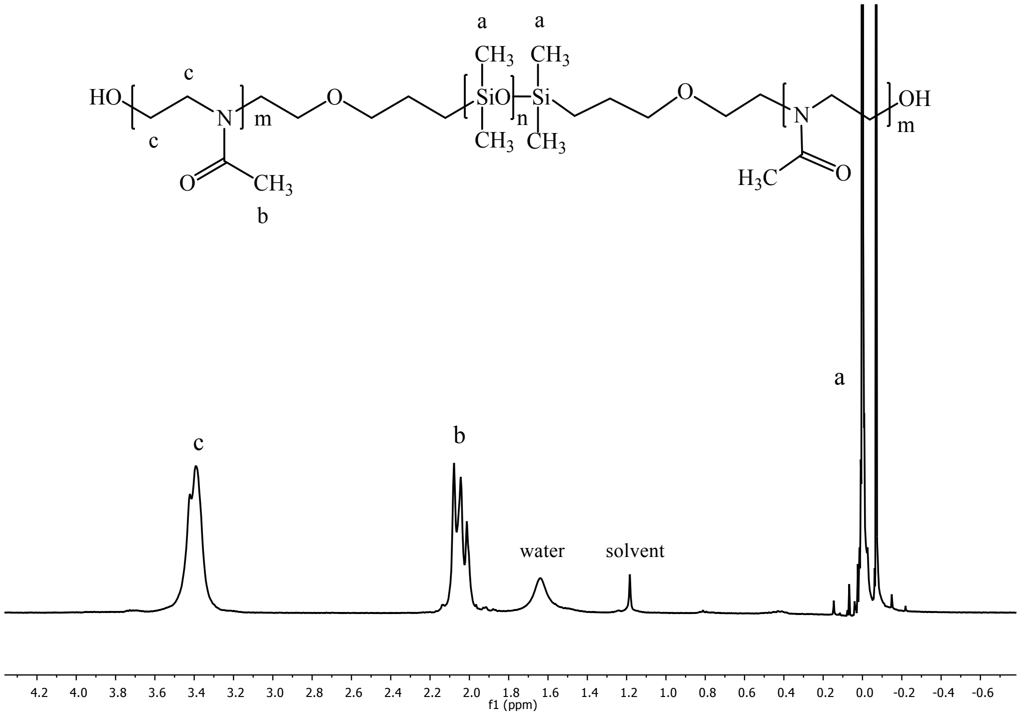
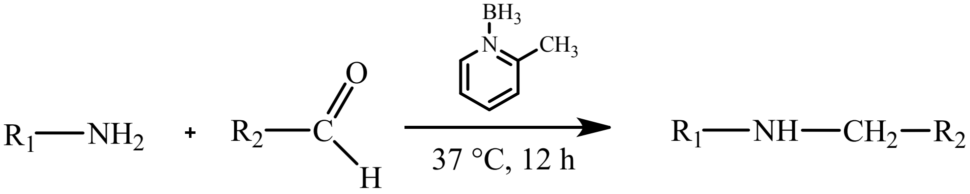


Figure S9. ^{1}H-NMR spectrum of poly(2-methyloxazoline)-*block*-poly(dimethylsiloxane)-*block*-poly(2-methyloxazoline) in $CDCl_3$.

Nanoreactor immobilization *via* amino bond on the silanized silicon wafer



Scheme S2. Schematic representation of the chemistry as applied to nanoreactor immobilization *via* an amino bond.