Electronic Supplementary Material (ESI) for Polymer Chemistry.

Anti-protein and anti-bacterial behavior of amphiphilic silicones

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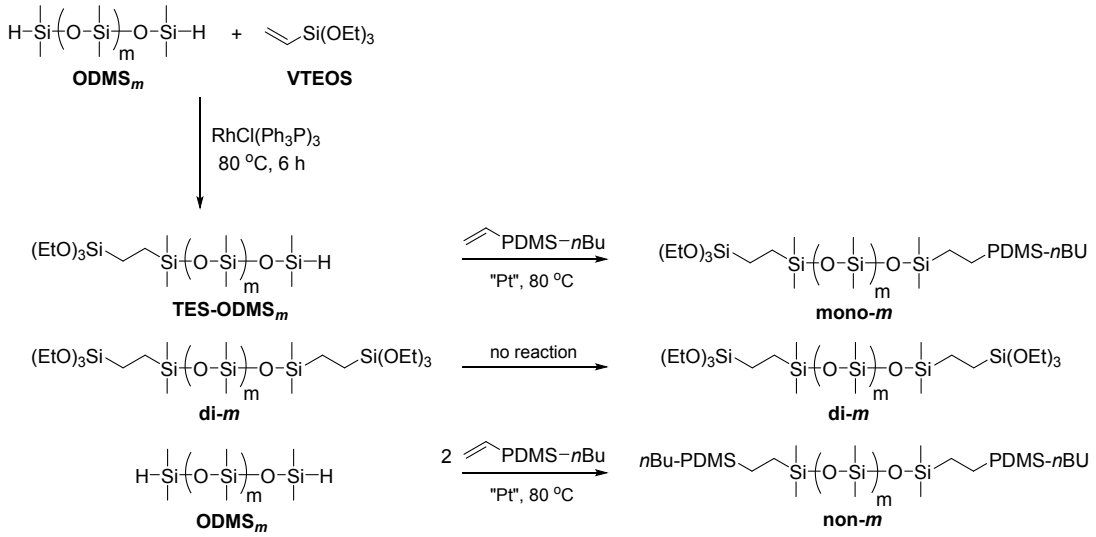

Scheme S1. Synthesis of products used for GPC analysis. If Rh-catalyzed hydrosilylation of **ODMS$_{17}$**, **ODMS$_{24}$**, and **ODMS$_{30}$** each with **VTEOS** (1:1 molar ratio) was non-regioselective, subsequent reaction of the three possible products (monosubstituted, disubstituted, or nonsubstituted) would each react with **CH$_2$=CH–PDMS-*n*-Bu** to produce **mono-*m***, **di-*m***, and **non-*m***, respectively.

Synthesis of mono-17. TES-ODMS$_{17}$ (0.05 g, 0.03 mmol), **CH$_2$=CH–PDMS-*n*-Bu** (2.1 g, 0.03 mmol), and Karstedt's catalyst (50 µL) were combined in toluene in a round-bottom (rb) flask equipped with a rubber septum and heated to 70 °C for 12 h. The reaction was monitored by IR until the disappearance of Si–H was observed. The catalyst was removed by refluxing the reaction mixture with activated charcoal for 12 h. The reaction mixture was filtered and the volatiles were removed under reduced pressure. In this way, **mono-17** (1.66 g, 77% yield) was obtained. IR (ν): no Si–H band.

Synthesis of mono-24. TES-ODMS$_{24}$ (0.08 g, 0.038 mmol), **CH$_2$=CH–PDMS-*n*-Bu** (2.03 g, 0.034 mmol), and Karstedt's catalyst (50 µL) in toluene were reacted as above. In this way, **mono-24** (1.03 g, 49% yield) was obtained. IR (ν): no Si–H band.

Synthesis of mono-30. TES-ODMS$_{30}$ (0.10 g, 0.039 mmol), **CH$_2$=CH–PDMS-*n*-Bu** (2.32 g, 0.039 mmol), and Karstedt's catalyst (50 µL) in toluene were reacted as above. In this way, **mono-30** (1.48 g, 61% yield) was obtained. IR (ν): no Si–H band.

Synthesis of di-17. ODMS$_{17}$ (2.00 g, 1.4 mmol), **VTEOS** (0.54 g, 2.8 mmol), and Wilkinson's catalyst (10 mg) were combined in toluene in a rb flask equipped with a rubber septum and heated to 80 °C for 12 h. Toluene was removed under reduced pressure, the product was purified by flash column chromatography, and volatiles were removed under reduced pressure. In this way, **di-17** (2.32 g, 91% yield) was obtained.

Synthesis of di-24. ODMS$_{24}$ (2.01 g, 0.001 mol), **VTEOS** (0.40 g, 0.002 mol), and Wilkinson's catalyst (10 mg) in toluene were reacted as above. In this way, **di-24** (2.16 g, 90% yield) was obtained.

Synthesis of di-30. ODMS$_{30}$ (1.98 g, 0.84 mmol), **VTEOS** (0.32 g, 1.7 mmol), and Wilkinson's catalyst (10 mg) in toluene were reacted as above. In this way, **di-30** (2.14 g, 93% yield) was obtained.

Synthesis of non-17. ODMS$_{17}$ (0.03 g, 0.022 mmol), **CH$_2$=CH–PDMS-*n*-Bu** (2.32 g, 0.039 mmol), and Karstedt's catalyst (50 µL) were combined in toluene in a round-bottom (rb) flask equipped with a rubber septum and heated to 70 °C for 12 h. The reaction was monitored by IR until the disappearance of Si–H was observed. The catalyst was removed by refluxing the reaction mixture with activated charcoal for 12 h. The reaction mixture was filtered and the volatiles were removed under reduced pressure. In this way, **non-17** (1.80 g, 77% yield) was obtained. IR (ν): no Si–H band.

Synthesis of non-24. ODMS$_{24}$ (0.037 g, 0.019 mmol), **CH$_2$=CH–PDMS-*n*-Bu** (2.13 g, 0.036 mmol), and Karstedt's catalyst (50 µL) in toluene were reacted as above. In this way, **non-24** (0.96 g, 44% yield) was obtained. IR (ν): no Si–H band.

Synthesis of non-30. ODMS$_{30}$ (0.04 g, 0.017 mmol), **CH$_2$=CH–PDMS-*n*-Bu** (2.03 g, 0.034 mmol), and Karstedt's catalyst (50 µL) in toluene were reacted as above. In this way, **non-30** (0.95 g, 46% yield) was obtained. IR (ν): no Si–H band.

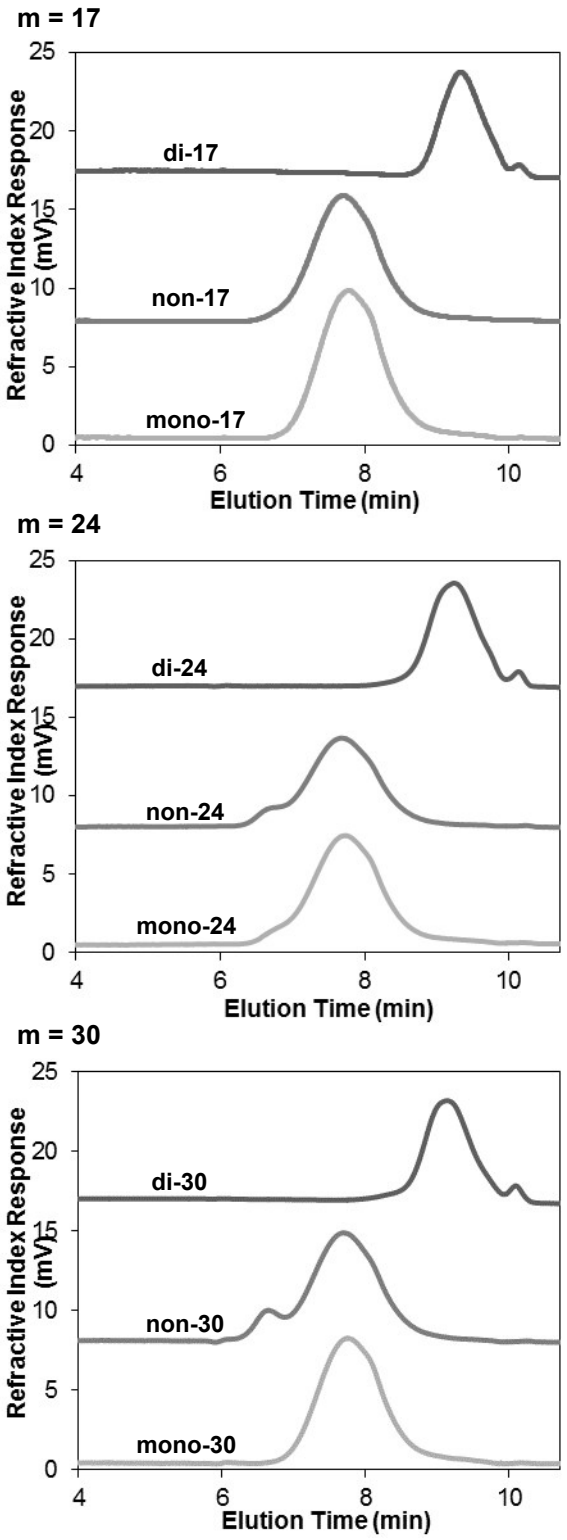

Fig. S1. GPC chromatographs of **di-*m***, **non-*m***, and **mono-*m***. The absence of **di-*m*** (and thus **non-*m***) confirms that **mono-*m*** is the product of monosubstituted **TES-ODMS$_m$** and **CH$_2$=CH–PDMS-*n*-Bu**.

Table S1. Surface atomic % composition by XPS of surface-grafted PEO-silane amphiphiles and a PEO control (*n* = 8).

	C 1s	*C-Si/ C-C*	*C-O*	O 1s	Si 2p
Surface	**Total**	***284.5 eV***	***286.4 eV***		
Oxidized wafer	5	-	-	34	61
PEO control	20	19	81	36	44
m = 0	10	32	68	37	52
m = 4	16	31	69	39	46
m =13	22	54	46	30	48
m =17	23	66	34	34	44
m =24	38	72	28	30	32
m =30	44	68	32	27	30

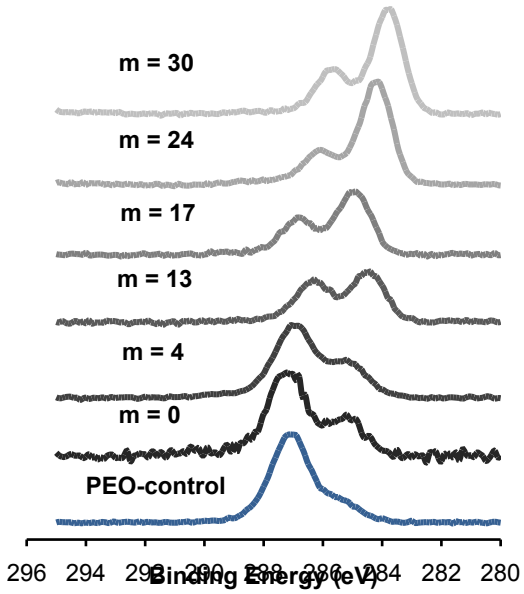

Figure S2. HR C 1s XPS spectra of silicon wafers grafted with PEO-silane amphiphiles and the PEO-control.

Table S2. Static contact angles (θ_{static}) of silica wafers grafted with PEO-silane amphiphiles, the siloxane-control and the PEO-control at 0 sec and 2 min following water droplet placement.

	0 sec	2 min
Siloxane-control	98.7 ± 0.4	97.8 ± 0.4
PEO-control	41.9 ± 4.5	39.9 ± 4.3
m = 0	52.6 ± 4.3	49.6 ± 4.3
m = 4	64.1 ± 4.7	61.6 ± 4.6
m = 13	81.4 ± 2.6	78.6 ± 2.6
m = 17	86.0 ± 1.6	84.0 ± 1.5
m = 24	88.8 ± 2.4	86.7 ± 2.4
m = 30	93.2 ± 0.5	91.1 ± 0.5

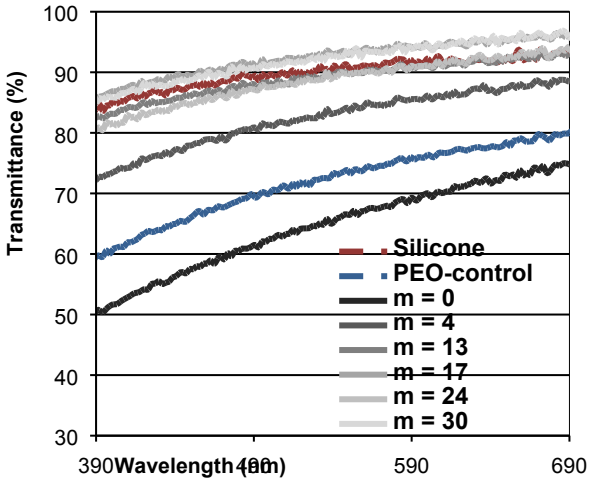

Fig. S3. UV-Vis transmission spectra of unmodified silicone and silicones bulk-modified with PEO-silane amphiphiles and the PEO-control.

Table S3. Static contact angles (θ_{static}) of unmodified silicone and silicones bulk-modified with PEO-silane amphiphiles and the PEO-control at 0 sec, 15 sec, 1 min and 2 min following water droplet placement.

	0 sec	15 sec	1 min	2 min
Silicone	115.1 ± 0.9	114.4 ± 0.4	114.0 ± 0.5	111.8 ± 0.6
PEO-control	113.3 ± 0.5	106.0 ± 5.6	100.5 ± 4.9	98.3 ± 5.6
m = 0	115.9 ± 7.8	71.8 ± 0.9	58.4 ± 0.7	51.9 ± 1.3
m = 4	112.7 ± 1.1	76.3 ± 1.1	51.6 ± 1.6	40.6 ± 1.6
m = 13	112.4 ± 2.3	74.2 ± 2.4	46.0 ± 0.9	35.6 ± 1.2
m = 17	111.6 ± 1.0	76.6 ± 3.7	45.1 ± 1.2	36.2 ± 1.3
m = 24	111.6 ± 1.9	82.7 ± 4.3	52.6 ± 1.7	45.0 ± 1.7
m = 30	114.0 ± 1.7	79.3 ± 4.1	51.8 ± 0.8	45.0 ± 1.1

Table S4. Fibrinogen adsorption measured on unmodified silicone and silicones bulk-modified with PEO-silane amphiphiles and the PEO-control.

	Fibrinogen Adsorption (ng/cm^2)
Silicone	166.9 ± 9.9
PEO-control	131.0 ± 19.5
m = 0	135.9 ± 10.4
m = 4	3.5 ± 2.4
m = 13	2.0 ± 1.3
m = 17	3.3 ± 0.8
m = 24	15.4 ± 1.3
m = 30	3.1 ± 0.9

Table S5. Crystal violet absorbance values of biofilm growth measured on unmodified silicone and silicones bulk-modified with PEO-silane amphiphiles and the PEO-control.

	S. epidermidis	***S. aureus***	***E. coli***	***P. aeruginosa***	***C. albicans***
Silicone	1.462 ± 0.153	0.414 ± 0.093	0.973 ± 0.101	0.859 ± 0.013	0.457 ± 0.212
PEO-control	1.622 ± 0.042	0.197 ± 0.114	0.707 ± 0.148	0.957 ± 0.062	1.389 ± 0.168
m = 0	1.286 ± 0.104	0.007 ± 0.010	0.250 ± 0.083	0.651 ± 0.043	0.187 ± 0.126
m = 4	0.003 ± 0.002	0.013 ± 0.006	0.004 ± 0.003	0.867 ± 0.031	0.004 ± 0.004
m = 13	0.006 ± 0.007	0.014 ± 0.003	0.009 ± 0.004	1.453 ± 0.135	0.001 ± 0.001
m = 17	0.001 ± 0.001	0.002 ± 0.001	0.038 ± 0.021	1.433 ± 0.061	0.003 ± 0.003
m = 24	0.017 ± 0.010	0.052 ± 0.035	0.115 ± 0.022	1.412 ± 0.161	0.006 ± 0.004
m = 30	0.013 ± 0.009	0.014 ± 0.002	0.112 ± 0.040	1.427 ± 0.085	0.003 ± 0.001

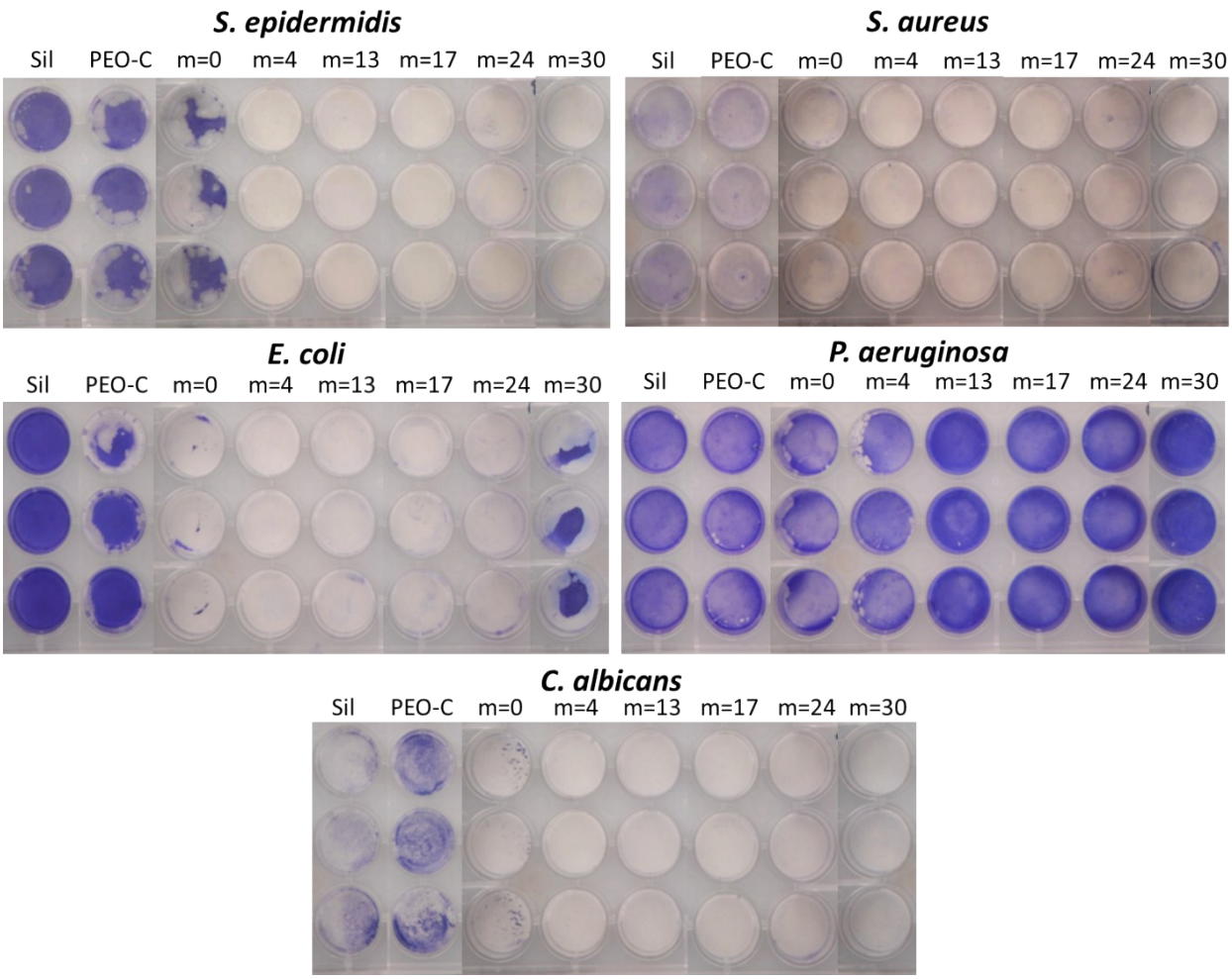

Fig. S4. Images of unmodified silicone and silicones bulk-modified with PEO-silane amphiphiles and the PEO-control after staining biofilm growth with crystal violet. [Sil = Silicone. PEO-C = PEO control.]