Amphiphilic, thixotropic additives for extrusion-based 3D printing of silica-reinforced silicone

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Electronic Supplementary Information:

Table S1. Properties of PEO-SA SMAs, including PEO content (wt%) in a 5 wt% SMA mixture.

	Architecture	MW (g/mol)	PDMS Repeat Units	PEO Repeat Units	PEO Content (wt%)
PEO Control	Linear	588	-	8	2.99%
TSP_{13}	Linear	1710	13	8	1.03%
TSP_{30}	Linear	2968	30	8	0.59%
HSP_{13}	Linear	1520	13	8	1.16%
HSP_{30}	Linear	2778	30	8	0.63%
Triblock [SP]	Linear	1944	13	16	1.81%
Star [SP]	Star	5872	52	32	1.20%
SGP	Graft	5650	52	4	0.16%
Triblock [SGP]	Graft	6470	52	6	0.20%

Table S2. Per **Figure 2a**, static contact angle (DI water) values for Sylgard 184 formulations with no additional filler added.

	t = 0 min	t = 1 min	t = 2 min
Sylgard 184	113.7° ± 3.5°	111.3° ± 2.0°	110.6° ± 1.9°
PEO Control	112.2° ± 5.7°	103.2° ± 2.6°	99.6° ± 2.9°
TSP_{13}	92.4° ± 3.6°	34.8° ± 5.7°	33.3° ± 5.7°
TSP_{30}	99.0° ± 13.1°	80.4° ± 15.1°	61.7° ± 12.0°
HSP_{13}	99.7° ± 1.8°	74.1° ± 3.4°	45.5° ± 2.9°
HSP_{30}	83.3° ± 1.4°	77.1° ± 0.6°	59.3° ± 1.0°
Triblock [SP]	31.1° ± 4.2°	11.5° ± 1.3°	11.2° ± 1.1°
Star [SP]	95.6° ± 7.6°	15.8° ± 3.2°	13.6° ± 2.4°
SGP	105.6° ± 1.5 °	91.3° ± 2.8°	80.2° ± 2.1°
Triblock [SGP]	102.2° ± 3.1°	89.3° ± 1.6°	82.2° ± 1.8°

Table S3. Per **Figure 2b**, static contact angle (DI water) values for Sylgard 184 formulations with 5 wt% additional HMDS-treated silica filler added.

	t = 0 min	t = 1 min	t = 2 min
Sylgard 184	109.5° ± 4.9°	106.0° ± 2.5°	105.1° ± 2.6°
PEO Control	106.8° ± 2.3°	101.6° ± 1.7°	96.7° ± 0.9°
TSP_{13}	112.8° ± 5.3°	72.7° ± 1.7°	55.6° ± 3.9°
TSP_{30}	118.5° ± 3.7°	93.7° ± 3.7°	76.6° ± 2.7°
HSP_{13}	103.9° ± 1.2°	94.0° ± 1.7°	87.3° ± 1.7°
HSP_{30}	114.9° ± 3.8 °	82.9° ± 4.0°	56.7° ± 1.9°
Triblock [SP]	60.4° ± 27.3°	6.3° ± 5.4°	5.4° ± 4.7°
Star [SP]	94.8° ± 2.0°	11.2° ± 3.2°	3.0° ± 5.2°
SGP	103.2° ± 2.9 °	87.9° ± 3.0°	73.8° ± 1.0°
Triblock [SGP]	107.1° ± 0.9°	97.6° ± 4.1°	89.6° ± 3.6°

Table S4. Per **Figure 3a**, **Figure 3b**, and **Figure 3c**, respectively, yield stress values for uncured Sylgard 184 formulations with 0, 5 wt%, and 17.3 wt% of additional HMDS-treated silica filler added,

	No Filler Added (Pa)	5 wt% HMDS Filler Added (Pa)	17.3 wt% HMDS Filler Added (Pa)
Sylgard 184	n/a	n/a	n/a
Triblock [SP]	141 ± 84	87 ± 55	84 ± 5
Star [SP]	75 ± 18	65 ± 30	194 ± 47
SGP	40 ± 18	31 ± 7	212 ± 14
Triblock [SGP]	40 ± 17	22 ± 6	92 ± 11

Table S5. Yield stress values for uncured Sylgard 184 formulations with 17.3 wt% of additional DiMeDi-treated silica filler added, as shown in **Figure 4**.

	Yield Stress (Pa)
Sylgard 184	539 ± 48
Triblock [SP]	3385 ± 1238
Star [SP]	1405 ± 162
SGP	1727 ± 224
Triblock [SGP]	1307 ± 512

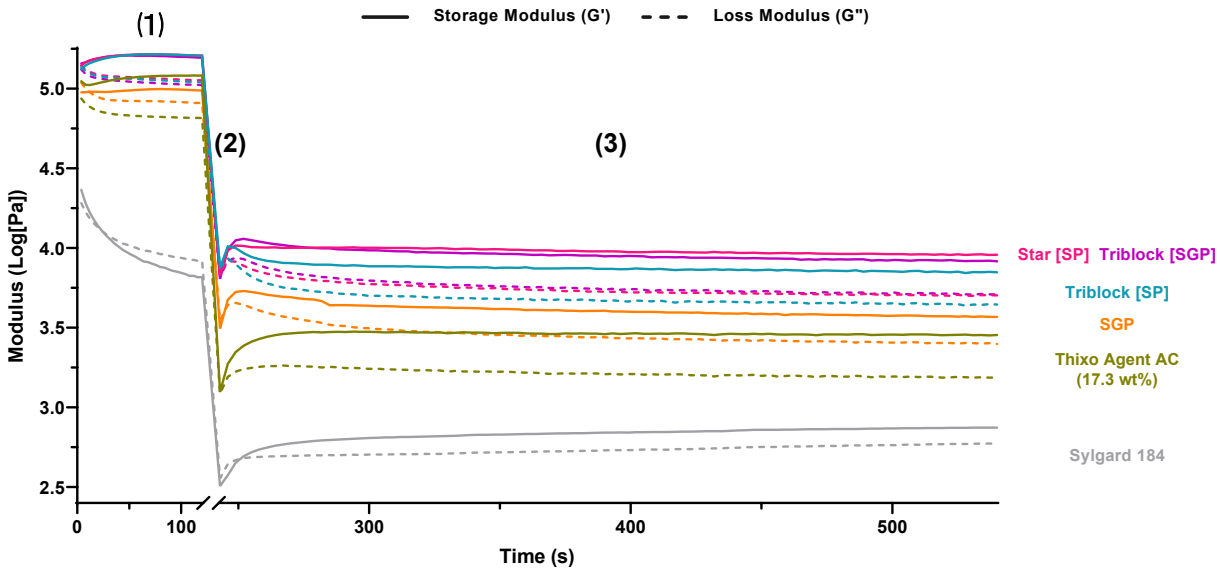

Figure S1. 3 Interval thixotropy test (3ITT) of uncured formulations: unmodified silicone (Sylgard 184) and modified silicones, each containing 17.3 wt% additional DiMeDi silica filler, along with the designated additive: (1) 120 s of oscillation at a constant 1% strain amplitude, (2) 120 s of rotation at a constant shear rate of 1,000 Hz, (3) 300 s of oscillation at a constant 1% strain amplitude (i.e. the recovery period).

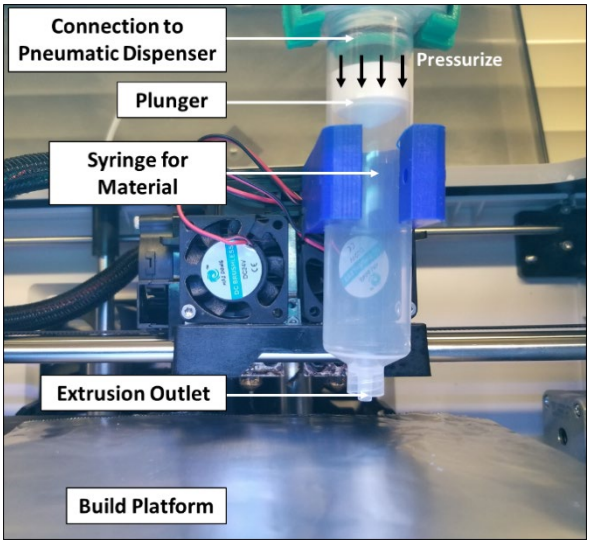

Figure S2. The extrusion-based 3D printing setup using a syringe-type pneumatic material dispenser.

Table S6. Per **Figure 5b**, storage modulus (G') after recovery of uncured formulations: unmodified silicone (Sylgard 184) and modified silicones, each containing 17.3 wt% additional DiMeDi silica filler, along with the designated additive.

	Storage Modulus (Pa)
Sylgard 184	608.4 ± 111.9
Thixo Agent AC (17.3 wt%)	4,272 ± 4,400
Triblock [SP]	8,286 ± 2,607
Star [SP]	11,023 ± 5,014
SGP	5,225 ± 2,225
Triblock [SGP]	102,48 ± 1,239

Table S7. Per **Figure 5c**, loss factor (G"/G') after recovery for uncured formulations: unmodified silicone (Sylgard 184) and modified silicones, each containing 17.3 wt% additional DiMeDi silica filler, along with the designated additive.

	Loss Factor (G"/G')
Sylgard 184	0.80 ± .10
Thixo Agent AC (17.3 wt%)	0.55 ± 0.15
Triblock [SP]	0.63 ± 0.12
Star [SP]	0.56 ± 0.11
SGP	0.68 ± 0.020
Triblock [SGP]	0.62 ± 0.059

Table S8. Per **Figure 6**, extrusion pressure and print speeds for uncured formulations: unmodified silicone (Sylgard 184) and modified silicones, each containing 17.3 wt% additional DiMeDi silica filler, along with the designated additive.

Formulation	Extrusion Pressure (psi)	Print Speed (mm/min)
Unmodified	26	737.7
Thixo Agent AC	32	789.5
Triblock [SP]	62	818.2
Star [SP]	78	692.3
SGP	76	748.2
Triblock [SGP]	74	668.8

Table S9. Per **Figure 7**, static contact angle (DI water) values for uncured formulations: unmodified silicone (Sylgard 184) and modified silicones, each containing 17.3 wt% additional DiMeDi silica filler, along with the designated additive.

	t = 0 min	t = 1 min	t = 2 min	t = 3 min	t = 4 min	t = 5 min
Sylgard 184	116.0° ± 1.5°	112.5° ± 0.8°	111.7° ± 0.7°	109.8° ± 2.8°	107.9° ± 2.7°	107.2° ± 2.5°
Triblock [SP]	124.3° ± 1.4°	81.0° ± 3.1°	61.2° ± 3.1°	52.9° ± 2.8°	47.9° ± 3.0°	43.9° ± 3.0°
Star [SP]	121.2° ± 2.0°	118.2° ± 1.4°	105.0° ± 2.8°	97.0° ± 3.6°	86.6° ± 4.3°	78.0° ± 3.0°

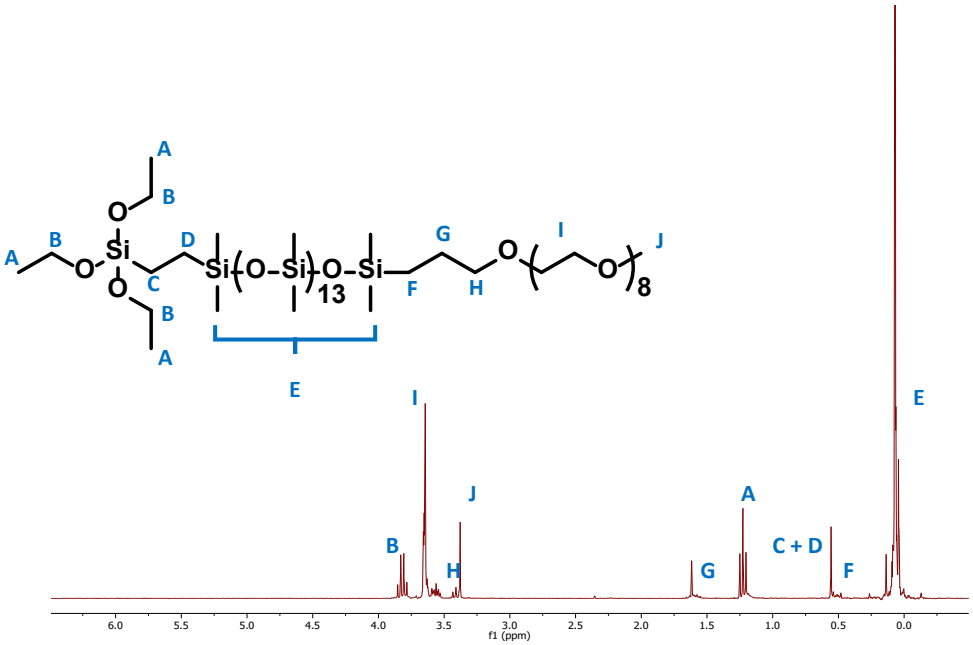

Figure S3. ^{1}H NMR of "***TSP$_{13}$***", (CDCl3; δ, ppm): 0.05-0.10 (m, 90H, SiCH_3), 0.47-0.55 (m, 2H, SiCH_2CH$_2$CH$_2$), 0.55-0.57 (m, 3H, SiCH_2CH_2), 1.15-1.19 (m, 1H, SiCH_2CH_2), 1.19-1.26 (t, J = 7.0 Hz, 9H, [CH_3CH$_2$O]$_3$Si), 1.54-1.66 (m, 2H, SiCH$_2$CH_2CH$_2$), 3.38 (s, 3H, OCH_3), 3.39-3.45 (t, J = 6.9 Hz, 2H, SiCH$_2$CH$_2$CH_2), 3.50-3.70 (m, 32H, CH_2CH_2O) and 3.78-3.86 (q, J = 7.0 Hz, 6H, [CH$_3$CH_2O]$_3$Si).

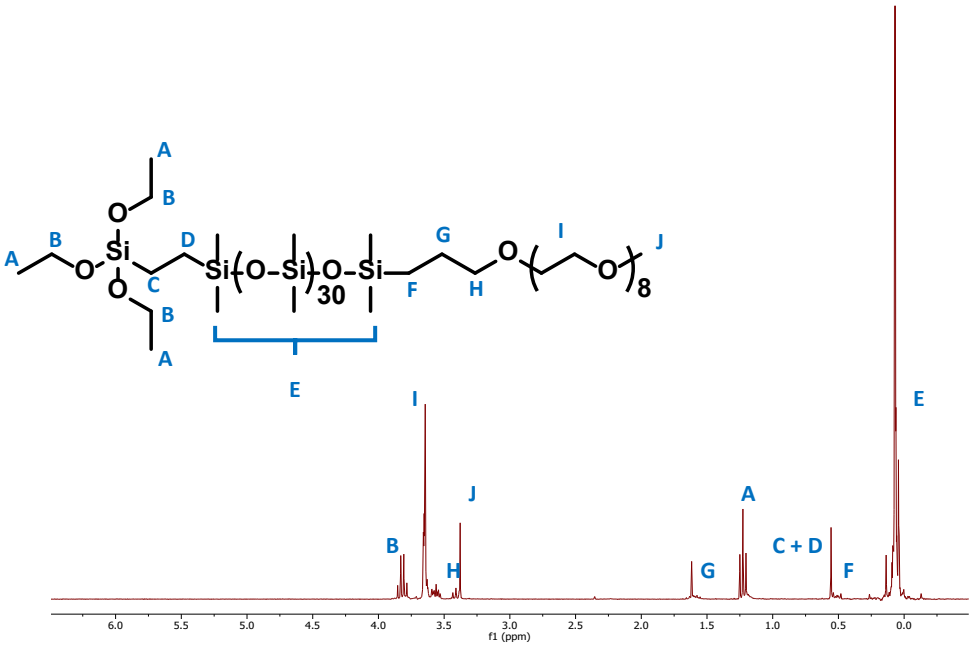

Figure S4. ^{1}H NMR of "***TSP$_{30}$***", (CDCl3; δ, ppm): 0.05-0.10 (m, 192H, SiCH_3), 0.47-0.55 (m, 2H, SiCH_2CH$_2$CH$_2$), 0.55-0.57 (m, H, SiCH_2CH_2), 1.15-1.19 (m, 1H, SiCH_2CH_2), 1.19-1.26 (t, J = 7.0 Hz, 9H, [CH_3CH$_2$O]$_3$Si), 1.54-1.66 (m, 2H, SiCH$_2$CH_2CH$_2$), 3.38 (s, 3H, OCH_3), 3.39-3.45 (t, J = 6.9 Hz, 2H, SiCH$_2$CH$_2$CH_2), 3.50-3.70 (m, 32H, CH_2CH_2O) and 3.78-3.86 (q, J = 7.0 Hz, 6H, [CH$_3$CH_2O]$_3$Si).

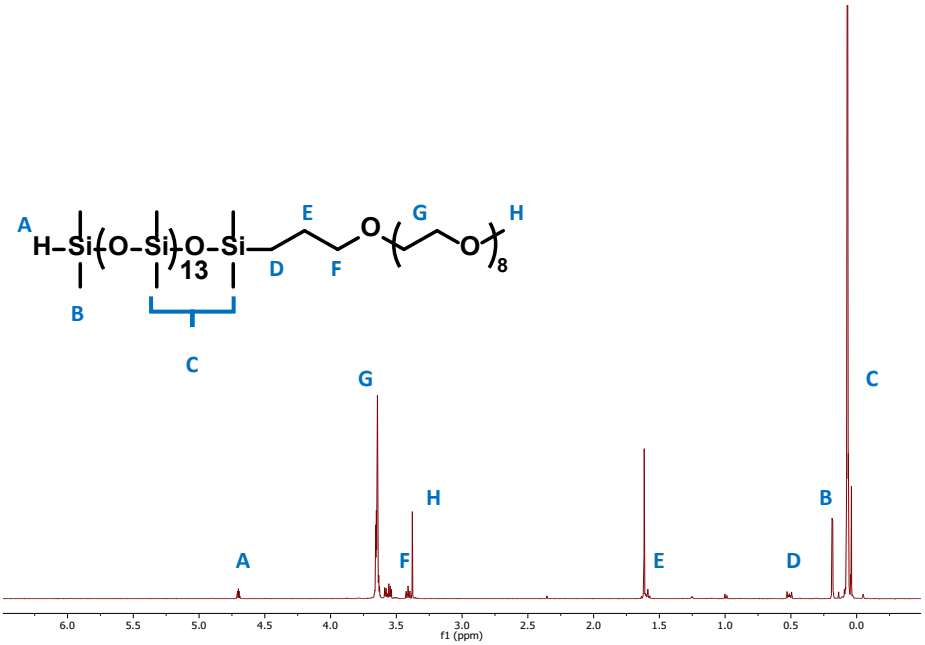

Figure S5. ^{1}H NMR of "***HSP*$_{13}$**", (CDCl3; δ, ppm): 0.05-0.10 (m, 84H, SiCH_3), 0.17-0.19 (d, J = 2.8 Hz, 6H, OSi[CH_3]$_2$H), 0.47-0.55 (m, 2H, SiCH_2CH$_2$CH$_2$), 1.56-1.64 (m, 2H, SiCH$_2$CH_2CH$_2$), 3.38 (s, 3H, OCH_3), 3.39-3.44 (t, J = 6.9 Hz, 2H, SiCH$_2$CH$_2$CH_2), 3.52-3.70 (m, 32H, CH_2CH_2O), 4.65-4.75 (m, 1H, Si*H*).

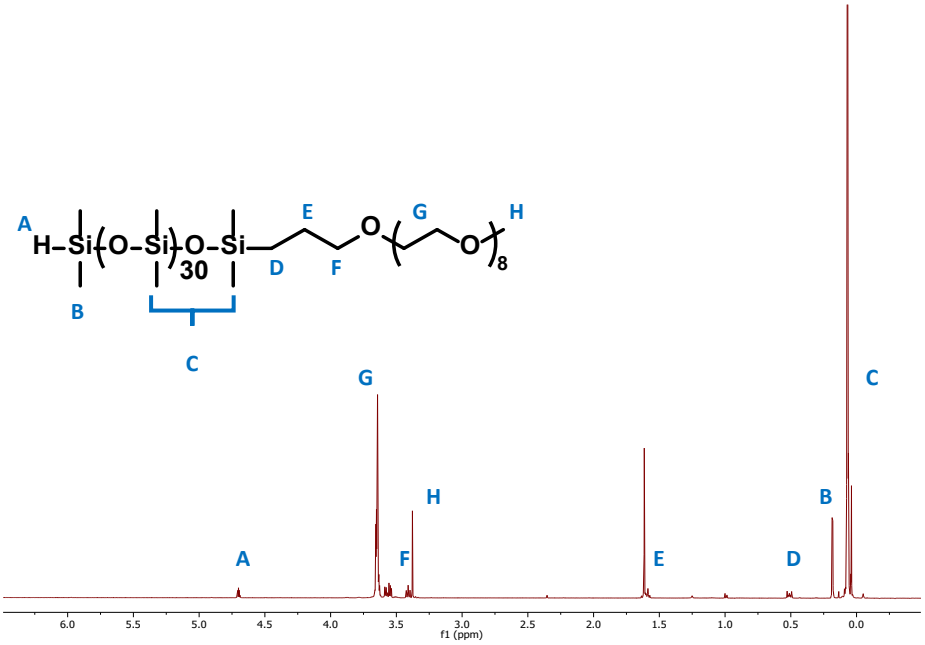

Figure S6. ^{1}H NMR of "***HSP*$_{30}$**", (CDCl3; δ, ppm): 0.05-0.10 (m, 186H, SiCH_3), 0.17-0.19 (d, J = 2.8 Hz, 6H, OSi[CH_3]$_2$H), 0.47-0.55 (m, 2H, SiCH_2CH$_2$CH$_2$), 1.56-1.64 (m, 2H, SiCH$_2$CH_2CH$_2$), 3.38 (s, 3H, OCH_3), 3.39-3.44 (t, J = 6.9 Hz, 2H, SiCH$_2$CH$_2$CH_2), 3.52-3.70 (m, 32H, CH_2CH_2O), 4.65-4.75 (m, 1H, Si*H*).

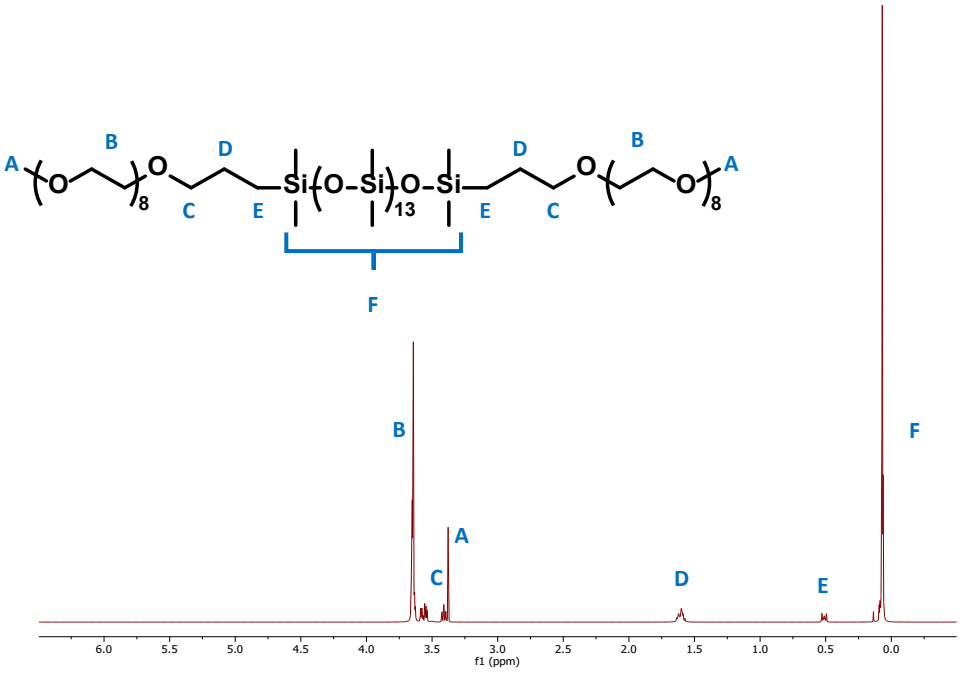

Figure S7. ^{1}H NMR of "***Triblock [SP]***", (CDCl3; δ, ppm): 0.05-0.10 (m, 90H, SiCH_3), 0.47-0.55 (m, 4H, SiCH_2CH$_2$CH$_2$), 1.56-1.64 (m, 4H, SiCH$_2$CH_2CH$_2$), 3.38 (s, 6H, OCH_3), 3.39-3.44 (t, J = 6.9 Hz, 4H, SiCH$_2$CH$_2$CH_2), 3.52-3.70 (m, 64H, CH_2CH_2O).

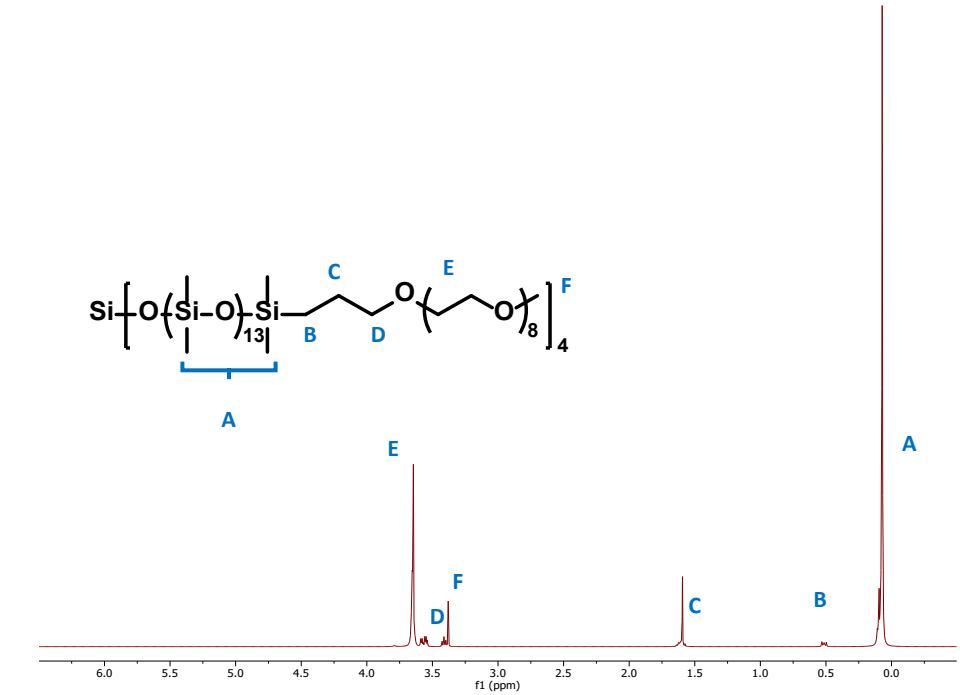

Figure S8. ^{1}H NMR of "***Star [SP]***", (CDCl3; δ, ppm): 0.02-0.13 (m, 336H, SiCH_3), 0.48-0.54 (m, 8H, SiCH_2CH$_2$CH$_2$), 1.54-1.64 (m, 8H, SiCH$_2$CH_2CH$_2$), 3.37 (s, 12H, OCH_3), 3.41 (t, J = 7.12 Hz, 8H, SiCH$_2$CH$_2$CH_2), 3.53-3.70 (m, 128H, CH_2CH_2O).

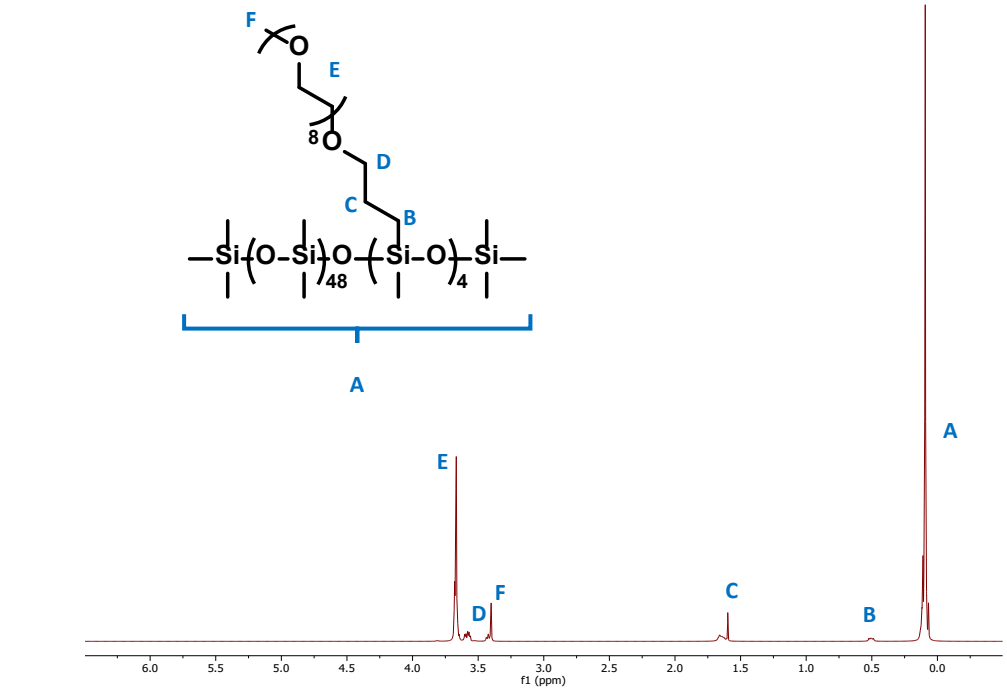

Figure S9. ^{1}H NMR of "***SGP***", (CDCl3; δ, ppm): 0.02-0.18 (m, 318H, SiCH_3), 0.45-0.54 (m, 8H, SiCH_2CH$_2$CH$_2$), 1.57-1.72 (m, 8H, SiCH$_2$CH_2CH$_2$), 3.40 (s, 12H, OCH_3), 3.42 (t, J = 7.08 Hz, 8H, SiCH$_2$CH$_2$CH_2), 3.55-3.69 (m, 128H, CH_2CH_2O).

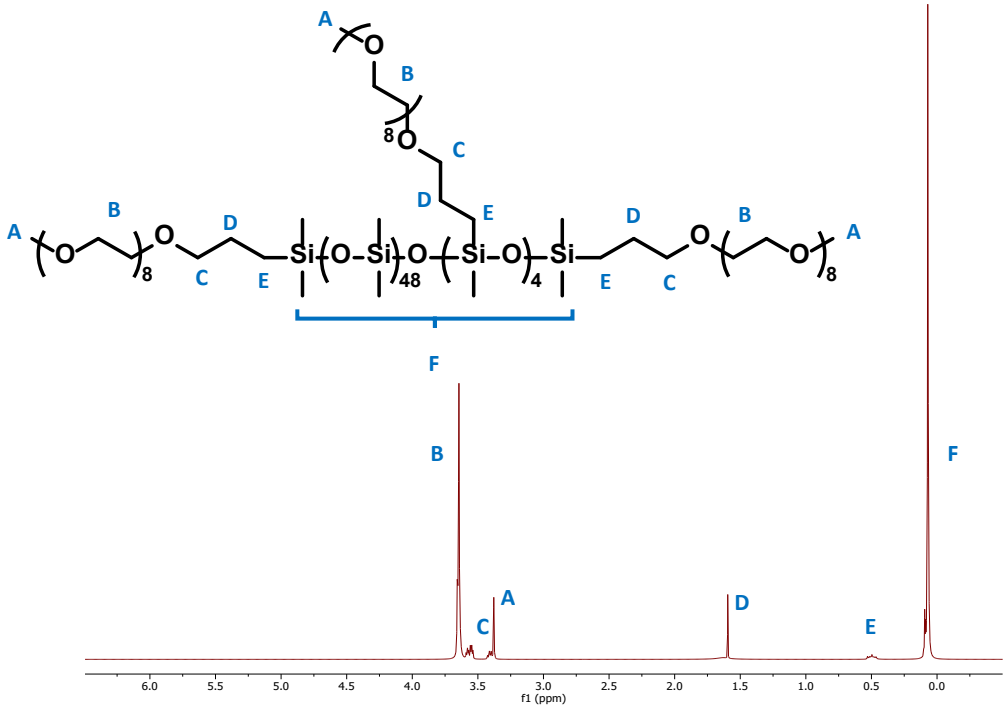

Figure S10. ^{1}H NMR of "***Triblock [SGP]***", (CDCl3; δ, ppm): 0.03-0.26 (m, 312H, SiCH_3), 0.41-0.54 (m, 12H, SiCH_2CH$_2$CH$_2$), 1.51-1.66 (m, 12H, SiCH$_2$CH_2CH$_2$), 3.37 (s, 18H, OCH_3), 3.40 (t, J = 7.12 Hz, 12H, SiCH$_2$CH$_2$CH_2), 3.50-3.70 (m, 192H, CH_2CH_2O).