Supporting Information

Preparation, Characterization, and Protein-Resistance of Films Derived from a Series of α-Oligo(ethylene glycol)-ω-alkenes on H−Si(111) Surfaces

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Content:

1. Synthesis of OEG-Terminated n-Alkenes

General Procedures for the Synthesis of $C_{m+2}EG_n$. All solvents and chemicals of high quality required for the synthesis of $C_{m+2}EG_n$ were purchased from Sigma-Aldrich and Alfa Aesar and were used without purification. Tetrahydrofuran (THF) was freshly distilled from sodium/benzophenone prior to use. All reactions were carried out under N_2. Flash chromatography was carried out on silica gel (230–400 mesh from Natland International Corporation) or prepacked Thomson columns (silica, 32–36 μm) with FlashMaster Personal. ^{1}H- and ^{13}C-NMR spectra were recorded on a GE QE-300 NMR spectrometer operating at 300 MHz using $CDCl_3$ (^{1}H, 7.26 ppm; ^{13}C, 77.00 ppm) as the internal standard. Chemical shifts were reported in ppm, and spin multiplicities were reported as s, d, t, q or m. Mass spectra were collected with a ThermoFinnigan LCQ-DECA XP Plus mass spectrometer. The synthesis of $C_{11}EG_3$, $C_{11}EG_6$, and $C_{11}EG_7$ were previously described.[1, 2] The synthesis of $C_{10}EG_n$ (n = 3–7) and $C_{11}EG_n$ (n = 4, 5) is summarized in Scheme S1 and S2, respectively.

Scheme S1.Synthesis of $C_{10}EG_n$ (n = 3–7)
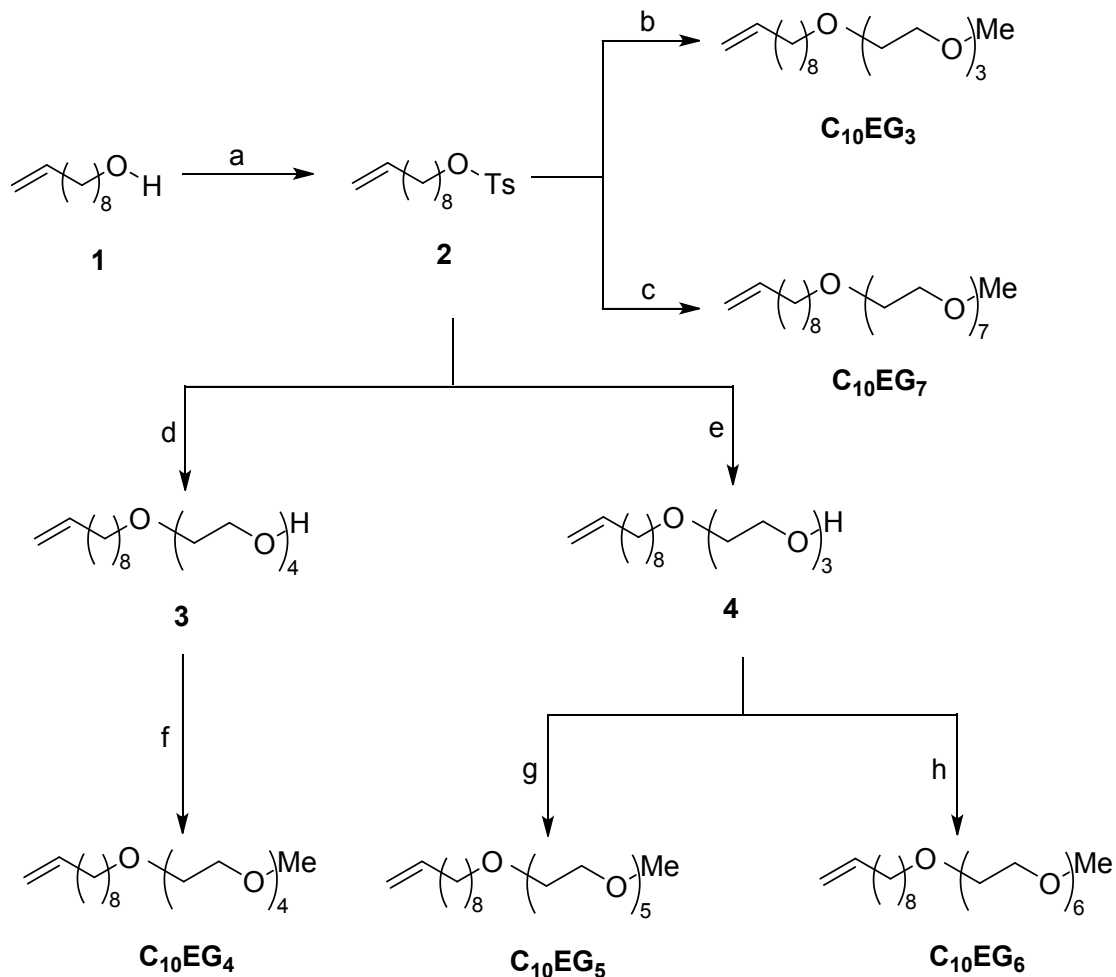
Reagents and conditions: (a) TsCl, $(CH_3)_2N(CH_2)_3N(CH_3)_2$, toluene, 0 °C, 91%; (b) tri(ethylene glycol) monomethyl ether, NaH, THF, reflux, 95%; (c) hepta(ethylene glycol) monomethyl ether, NaH, THF, reflux, 68%; (d) tetra(ethylene glycol), NaH, THF, r.t., 81%; (e) tri(ethylene glycol), NaH, THF, r.t., 87%; (f) CH_3I, NaH, THF, reflux, 99%; (g) **5**, NaH, THF, reflux, 78%; (h) **6**, NaH, THF, reflux, 78%.

Scheme S2.Synthesis of C$_{11}$EG$_n$ (n = 4, 5)
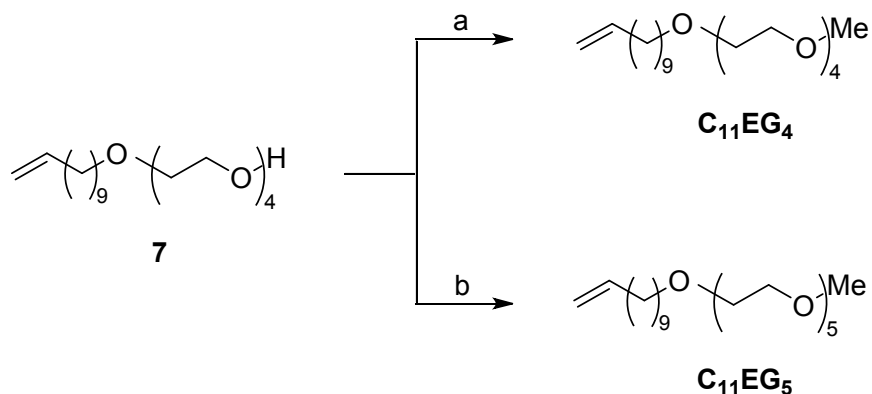
Reagents and conditions: (a) ^{t}BuOK, CH$_3$I, THF, r.t., 91%; (b) ^{t}BuOK, CH$_3$O(CH$_2$)$_2$OTs, THF, r.t., 79%.

Synthesis of Dec-9-enyl-4-Toluenesulfonate (2).[3]p-toluenesulfonyl chloride (9.15 g, 48.0 mmol) in toluene (32 mL) was added to a stirred solution of 9-decen-1-ol (**1**) (5.0 g, 32 mmol) and (CH$_3$)$_2$N(CH$_2$)$_3$N(CH$_3$)$_2$ (6.25 g, 48.0 mmol) in toluene (48 mL) at 0–5 °C, and the mixture was stirred for 1 h. Water was added to the mixture which was extracted with ethyl acetate (EtOAc). The organic phase was washed twice with water and once with brine, dried over anhydrous MgSO$_4$ and then concentrated under reduced pressure. The crude product was purified by flash chromatography (EtOAc/hexane 2:98) to afford **2** (9.0 g, 91%) as a white crystal. MP: 33.0–33.5°C. ^{1}H NMR (CDCl$_3$): δ = 7.77–7.81 (d, 2H, J = 8.40 Hz), 7.25–7.35 (d, 2H, J = 8.70 Hz), 5.72–5.84 (m, 1H), 4.90–5.02 (m, 2H), 3.97–4.03 (t, 2H, J = 6.50 Hz), 2.44 (s, 3H), 1.98–2.05 (q, 2H, J = 7.10 Hz), 1.58–1.67 (m, 2H), 1.10–1.36 (m, 12H). ^{13}C NMR (CDCl$_3$): δ = 144.60, 139.08, 133.14, 129.77, 127.86, 114.18, 70.67, 33.72, 29.18, 28.91, 28.83, 28.80, 28.76, 25.27, 21.63.

Synthesis of 2-{2-[2-(2-Dec-9-enyloxy-ethoxy)-ethoxy]-ethoxy}-ethanol (3). NaH (0.14 g, 5.6 mmol) was added to a solution of tetra(ethylene glycol) (3.65 g, 18.8 mmol) in dry THF (12 mL) while stirring under N$_2$. After the mixture was stirred at r.t. overnight, **2** (1.17 g, 3.75 mmol) in dry THF (3 mL) was added dropwise. The reaction mixture was stirred at r.t. for additional 48 h. The solvent was removed under reduced pressure. CH$_2$Cl$_2$ was added, and the mixture was poured into water. The organic layer was separated, and the aqueous layer was extracted twice with CH$_2$Cl$_2$. The combined organic layers were washed once with saturated aqueous

NaHCO$_3$solution, twice with water, dried with MgSO$_4$, filtered and concentrated under reduced pressure. The crude product was purified by flash chromatography (EtOAc/hexane 40:60) to afford **3** as a colorless oil (1.02 g, 81%). ^{1}H NMR (CDCl$_3$): δ = 5.79–5.81 (m, 1H), 4.90–5.02 (m, 2H), 3.55–3.75 (m, 16H), 3.41–3.46 (t, 2H, J = 6.80 Hz), 3.08 (br s, 1H), 1.99–2.06 (q, 2H, J = 7.00 Hz), 1.55–1.59 (m, 2H), 1.25–1.40 (m, 10H). ^{13}C NMR (CDCl$_3$): δ = 139.20, 114.07, 72.66, 71.53, 70.50, 70.45, 70.16, 69.97, 61.64, 33.75, 29.49, 29.36, 29.03, 25.99.

Synthesis of 2-[2-(2-Dec-9-enyloxy-ethoxy)-ethoxy]-ethanol (4).[4]NaH (0.11 g, 4.6 mmol) was added to a solution of tri(ethylene glycol) (2.32 g, 15.4 mmol) in dry THF (10 mL) while stirring under N$_2$. After the mixture was stirred at r.t. overnight, **2** (0.96 g, 3.0 mmol) in dry THF (3 mL) was added dropwise. The mixture was stirred at r.t. for additional 48 h. The solvent was removed under reduced pressure. CH$_2$Cl$_2$ was added, and the mixture was poured into water. The organic layer was separated, and the aqueous layer was extracted twice with CH$_2$Cl$_2$. The combined organic layers were washed once with saturated aqueous NaHCO$_3$ solution, twice with water, dried with MgSO$_4$, filtered and concentrated under reduced pressure. The crude product was purified by flash chromatography (EtOAc/hexane 40:60) to afford **4** as a colorless oil (0.77 g, 87%). ^{1}H NMR (CDCl$_3$): δ = 5.76–5.85 (m, 1H), 4.91–5.02 (m, 2H), 3.57–3.72 (m, 12H), 3.42–3.47 (t, 2H, J = 6.80 Hz), 2.65 (br s, 1H), 2.00–2.06 (q, 2H, J = 6.50 Hz), 1.53–1.60 (m, 2H), 1.28–1.40 (m, 10H).

Synthesis of Tosyl di(ethylene glycol) monomethyl ether (5).[5] A stirred solution of NaOH (0.75 g, 19.0 mmol) and di(ethylene glycol) monomethyl ether (1.50 g, 12.5 mmol) in water (4 mL) and THF (4 mL) was treated dropwise with a solution of p-toluenesulfonyl chloride (TsCl, 2.38 g, 12.5 mmol) in THF (4 mL) over 10 minutes below 5 ºC. The solution was stirred at 0–5 ºC for additional 2 h, and then poured into ice-water (10 mL). The mixture was extracted twice with CH$_2$Cl$_2$. The combined organic extracts were washed twice with water and once with brine, and dried over MgSO$_4$. Upon evaporation of the solvent, **5** was obtained as a colorless oil (3.25 g, 95%). ^{1}H NMR (CDCl$_3$): δ = 7.78–7.81 (d, 2H, J = 8.10 Hz), 7.32–7.35 (d, 2H, J = 8.40 Hz), 4.15–4.18 (t, 2H, J = 4.80 Hz), 3.68–3.70 (t, 2H, J = 4.80 Hz), 3.47–3.58 (m, 4H), 3.35 (s, 3H), 2.44 (s, 3H).

Synthesis of Tosyl tri(ethylene glycol) monomethyl ether (6).[5]A stirred solution of NaOH (4.80 g, 120 mmol) and tri(ethylene glycol) monomethyl ether (13.80 g, 84.0 mmol) in water (24 mL) and THF (24 mL) was treated dropwise with a solution of TsCl (16.02 g, 84.0 mmol) in

THF (24 mL) over 20 minutes below 5 ℃. The solution was stirred at 0–5 ℃ for additional 2 h, and then poured into ice-water (60 mL). The mixture was extracted twice with CH_2Cl_2. The combined organic extracts were washed twice with water and once with brine, and dried over anhydrous $MgSO_4$. Upon evaporation of the solvent, **6** was obtained as a colorless oil (25.50 g, 95%). ^1H NMR ($CDCl_3$): δ = 7.78–7.81 (d, 2H, J = 9.00 Hz), 7.32–7.35 (d, 2H, J = 7.80 Hz), 4.14–4.17 (t, 3H, J = 5.00 Hz), 3.52–3.70 (m, 10H), 3.37 (s, 3H), 2.44 (s, 3H).

Synthesis of $C_{10}EG_3$. NaH (0.066 g, 2.7 mmol) was added to a solution of tri(ethylene glycol) monomethyl ether (0.30 g, 1.8 mmol) in dry THF (1 mL) while stirring under N_2. The mixture was heated to reflux for 3 h, and then cooled to r.t. A solution of **2** (0.85 g, 2.7 mmol) in dry THF (1 mL) was added dropwise. The reaction mixture was stirred at r.t. overnight. After the reaction was completed, the solvent was removed under reduced pressure. CH_2Cl_2 was added, and the mixture was poured into water. The organic layer was separated, and the aqueous layer was extracted twice with CH_2Cl_2. The combined organic layers were washed once with saturated aqueous $NaHCO_3$ solution, twice with water, dried with $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by flash chromatography (EtOAc/hexane 10:90) to afford $C_{10}EG_3$ as a colorless oil (0.52 g, 95% yield). ^1H NMR ($CDCl_3$): δ = 5.76–5.85 (m, 1H), 4.90–5.01 (m, 2H), 3.53–3.72 (m, 12H), 3.41–3.46 (t, 2H, J = 6.90 Hz), 3.37 (s, 3H), 1.99–2.04 (q, 2H, J = 6.90 Hz), 1.54–1.62 (m, 2H), 1.28–1.40 (m, 10H). ^{13}C NMR ($CDCl_3$): δ = 139.19, 114.08, 71.91, 71.45, 70.55, 70.48, 70.01, 59.02, 33.76, 29.58, 29.39, 29.04, 28.88, 26.03. ESI-MS: 325.2 (100%, M + Na$^+$).

Synthesis of $C_{10}EG_4$. NaH (0.022 g, 0.90 mmol) was added to a stirred solution of **3** (0.15 g, 0.45 mmol) in dry THF (0.2 mL) under N_2. The reaction mixture was heated to reflux for 3 h, and then cooled to r.t. CH_3I (0.19 g, 1.4 mmol) was added dropwise. The reaction mixture was stirred at rt for 48 h. After the reaction was completed, the solvent and the excess CH_3I were removed under reduced pressure. Flash chromatography (methanol/CH_2Cl_2 1: 99) over a short column gave $C_{10}EG_4$ as a colorless oil (0.16 g, 99%). ^1H NMR ($CDCl_3$): δ = 5.75–5.85 (m, 1H), 4.90–5.01 (m, 2H), 3.52–3.65 (m, 16H), 3.41–3.46 (t, 2H, J = 6.90 Hz), 3.37 (s, 3H), 2.01–2.04 (q, 2H, J = 7.20 Hz), 1.52–1.62 (m, 2H), 1.24–1.40 (m, 10H). ^{13}C NMR ($CDCl_3$): δ = 139.19, 114.07, 71.90, 71.51, 70.56, 70.49, 70.02, 59.03, 33.78, 29.59, 29.40, 29.05, 28.88, 26.05. ESI-MS: 369.3 (100%, M + Na$^+$).

Synthesis of C$_{10}$EG$_5$. NaH (0.025 g, 1.0 mmol) was added to a solution of **4** (0.15 g, 0.52 mmol) in dry THF (0.2 mL) under N$_2$. The mixture was refluxed for 3 h, and then cooled to r.t. A solution of **5** (0.43 g, 1.6 mmol) in dry THF (0.2 mL) was added dropwise. The reaction was stirred at r.t. for 60 h. The solvent was removed under reduced pressure. CH$_2$Cl$_2$ was added, and the mixture was poured into water. The organic layer was separated, and the aqueous layer was extracted twice with CH$_2$Cl$_2$. The combined organic layers were washed once with saturated aqueous NaHCO$_3$ solution, twice with water, dried with MgSO$_4$, filtered and concentrated under reduced pressure. The crude product was purified by flash chromatography (methanol/CH$_2$Cl$_2$ 2:98) to afford **C$_{10}$EG$_5$** as a colorless oil (0.17 g, 83% yield). ^{1}H NMR (CDCl$_3$): δ = 5.79–5.82 (m, 1H), 4.90–5.01 (m, 2H), 3.51–3.72 (m, 20H), 3.41–3.46 (t, 2H, J = 6.90 Hz), 3.37 (s, 3H), 2.02–2.06 (q, 2H, J = 6.90 Hz), 1.54–1.67 (m, 2H), 1.28–1.42 (m, 10H). ^{13}C NMR (CDCl$_3$): δ = 139.18, 114.09, 71.91, 71.51, 70.53, 70.50, 70.02, 59.02, 33.77, 29.58, 29.40, 29.05, 26.03. ESI-MS: 413.8 (100%, M + Na$^+$).

Synthesis of C$_{10}$EG$_6$. NaH (0.020 g, 0.84 mmol) was added to a solution of **4** (0.12 g, 0.42 mmol) in dry THF (0.2 mL) under N$_2$. The reaction mixture was heated to reflux for 3 h, and then cooled to r.t. A solution of **6** (0.39 g, 1.2 mmol) in dry THF (0.2 mL) was added dropwise. The reaction mixture was stirred at r.t. for 60 h. After the reaction was completed, the solvent was removed under reduced pressure. CH$_2$Cl$_2$ was added, and the mixture was poured into water. The organic layer was separated, and the aqueous layer was extracted twice with CH$_2$Cl$_2$. The combined organic layers were washed once with saturated aqueous NaHCO$_3$ solution, twice with water, dried with MgSO$_4$, filtered and concentrated under reduced pressure. The crude product was purified by flash chromatography (methanol/CH$_2$Cl$_2$ 2:98) to afford **C$_{10}$EG$_6$** as a colorless oil (0.14 g, 78%). ^{1}H NMR (CDCl$_3$): δ = 5.75–5.85 (m, 1H), 4.90–5.02 (m, 2H), 3.46–3.72 (m, 24H), 3.40–3.44 (t, 2H, J = 6.60 Hz), 3.38 (s, 3H), 2.00–2.05 (q, 2H, J = 6.80 Hz), 1.55–1.61 (m, 2H), 1.28–1.42 (m, 10H). ^{13}C NMR (CDCl$_3$): δ = 139.18, 114.10, 71.90, 71.50, 70.53, 70.50, 70.02, 59.04, 33.78, 29.60, 29.41, 29.05, 28.88, 26.05. ESI-MS: 457.5 (100%, M + Na$^+$).

Synthesis of C$_{10}$EG$_7$. NaH (0.035 g, 1.4 mmol) was added to a solution of hepta(ethylene glycol) monomethyl ether[6] (0.33 g, 0.97 mmol) in dry THF (0.5 mL) while stirring under N$_2$. The reaction mixture was heated to reflux for 3 h, and then cooled to r.t. A solution of **2** (0.60 g, 1.9 mmol) in dry THF (1 mL) was added dropwise. The reaction mixture was stirred at reflux temperature for 48 h. The solvent was removed under reduced pressure. CH$_2$Cl$_2$ was added, and

the mixture was poured into water. The organic layer was separated, and the aqueous layer was extracted twice with CH_2Cl_2. The combined organic layers were washed once with saturated aqueous $NaHCO_3$ solution, twice with water, dried with $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by flash chromatography (methanol/CH_2Cl_2 1:99) to afford **$C_{10}EG_7$** as a colorless oil (0.63 g, 68%). ^{1}H NMR (CDCl$_3$): δ = 5.76–5.85 (m, 1H), 4.90–5.01 (m, 2H), 3.53–3.71 (m, 28H), 3.41–3.46 (t, 2H, J = 6.60 Hz), 3.37 (s, 3H), 1.99–2.04 (q, 2H, J = 6.80 Hz), 1.54–1.58 (m, 2H), 1.28–1.42 (m, 10H). ^{13}C NMR (CDCl$_3$): δ = 139.21, 114.10, 71.90, 71.52, 70.54, 70.49, 70.02, 59.03, 33.79, 29.59, 29.41, 29.05, 28.88, 26.05. ESI-MS: 501.7 (100%, M + Na$^+$).

Synthesis of $C_{11}EG_4$. Potassium *tert*-butoxide (^{t}BuOK, 0.22 g, 2.0 mmol) was added to a stirred solution of **7**^{7} (0.40 g, 1.1 mmol) in dry THF (5 mL) under N$_2$. The mixture was stirred at r.t. for 1 h, and iodomethane (1.0 mL, 15.9 mmol) was added. The reaction mixture was stirred at r.t. for 2 days, and evaporated to give a residue, to which were added EtOAc (15 mL) and water (15 mL). The organic layer was separated, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by flash chromatography (EtOAc/hexane 50:50) to afford **$C_{11}EG_4$** as a colorless oil (0.36 g, 91%). ^{1}H NMR (CDCl$_3$): δ = 5.75–5.85 (m, 1H), 4.85–5.02 (m, 2H), 3.48–3.65 (m, 16H), 3.41 (t, 2H, J = 6.90 Hz), 3.38 (s, 3H), 1.95–2.03 (q, 2H, J = 6.90 Hz), 1.46–1.61 (m, 2H), 1.18–1.38 (m, 12H). ^{13}C NMR (CDCl$_3$): δ = 139.23, 114.09, 71.98, 71.55, 70.63, 70.55, 70.09, 59.02, 33.80, 29.66, 29.53, 29.47, 29.44, 29.12, 28.94, 26.10. ESI-MS: 383.7 (100%, M + Na$^+$).

Synthesis of $C_{11}EG_5$. ^{t}BuOK (1.0 g, 8.9 mmol) was added to a stirred solution of **7** (0.35 g, 1.0 mmol) in dry THF (5 mL) under N$_2$. The mixture was stirred at r.t. for 1 h, and 2-Methoxyethyl tosylate (1.5 g, 6.5 mmol) was added. The reaction mixture was stirred at r.t. for 1 day. NaOH (2 M, 20 mL) was added and the reaction mixture was stirred for additional 2 h. The reaction mixture was extracted with EtOAc/hexane (3:2, 2x30 ml). The organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by flash chromatography (EtOAc/CH_2Cl_2 40:60) to afford **$C_{11}EG_5$** as a colorless oil (0.32 g, 79%). ^{1}H NMR (CDCl$_3$): δ = 5.65–5.80 (m, 1H), 4.80–4.95 (m, 2H), 3.43–3.60 (m, 20H), 3.36 (t, 2H, J = 6.85 Hz), 3.30 (s, 3H), 1.90–2.00 (q, 2H, J = 6.85 Hz), 1.40–1.57 (m, 2H), 1.10–1.36 (m, 12H). ^{13}C NMR (CDCl$_3$): δ = 139.02, 114.02, 71.85, 71.40, 70.51, 70.47, 70.42, 69.97, 58.91, 33.70, 29.54, 29.43, 29.37, 29.31, 29.02, 28.82, 25.99. ESI-MS: 427.9 (100%, M + Na$^+$).

2. Calculation of Packing Density and Protein Adsorption by Ellipsometry

Table S1. Ellipsometric thickness before (T_e) and after (T_e') treatment with fibrinogen, estimated packing density (A_m) and protein adsorption (A) of $C_{11}EG_n$ and $C_{10}EG_n$ films on Si(111) prepared at low vacuum (~1 mbar) and medium vacuum (~0.05 mbar) conditions

fllm	low vacuum (~1 mTorr)					medium vacuum (~0.05 mTorr)				
	T_e (Å)	T_e' (Å)	$A_m{}^a$ (Å^2/molecule)	$N_{chains}/N_{surf, Si}{}^b$ (molecule/Si)	A^c (% ML)	T_e (Å)	T_e' (Å)	$A_m{}^a$ (Å^2/molecule)	$N_{chains}/N_{surf, Si}{}^b$ (molecule/Si)	A^c (% ML)
$C_{10}EG_3$	21	35	23.9(1.1)	0.54(0.026)	23.3(1.4)					
$C_{10}EG_4$	22	31	26.2(1.2)	0.49(0.022)	15.0(0.92)	30	32	19.2(0.64)	0.67(0.022)	3.3(0.16)
$C_{10}EG_5$	25	29	26.0(1.0)	0.49(0.020)	6.7(0.39)	33	35	19.7(0.60)	0.65(0.020)	3.3(0.14)
$C_{10}EG_6$	27	29	26.7(1.0)	0.48(0.018)	3.3(0.18)	34	35	21.2(0.62)	0.60(0.018)	1.7(0.069)
$C_{10}EG_7$	28	29	28.4(1.0)	0.45(0.016)	1.7(0.089)	36	36	22.1(0.61)	0.58(0.016)	0(0)
$C_{11}EG_3$						25	52	21.0(0.84)	0.61(0.024)	45.0(1.9)
$C_{11}EG_4$						28	37	21.4(0.76)	0.60(0.021)	15.0(0.69)
$C_{11}EG_5$						30	32	22.4(0.75)	0.57(0.019)	3.3(0.16)
$C_{11}EG_6$						32	33	23.3(0.73)	0.55(0.017)	1.7(0.075)
$C_{11}EG_7$						34	34	24.1(0.71)	0.53(0.016)	0(0)

a: Packing density calculated from Equations S1:[8]

$$A_m = M_W / \rho \, d_{ML} \, N_A \qquad (S1)$$

where Mw (g/mole) is the molecular weight, ρ (g/cm^3) is the density, $d_{ML \, (cm)}$ is the thickness and N_A is the Avogadro's number (6.023×10^{23} molecules/mole). The value of $\rho = 1$ g/cm^3 has been used for PEG molecules on surfaces.[8] Here, we assume that the density of OEG molecules on surfaces is also 1 g/cm^3. The number in the parentheses represents the errors derived from the errors in ellipsometric measurements.

b: Number of hydrocarbon chains per surface silicon atom is calculated as follows:

$$N_{chains}/N_{surf, \, Si} = 1/(A_m \times N_{surf, \, Si}) \qquad (S2)$$

where N_{chains} is the number of carbon chains per unit area, and $N_{chains} = 1/A_m$; $N_{surf, \, Si}$ is the number of silicon atom per unit area, which is 7.8×10^{14} atom/cm^2.[9] The $N_{chains}/N_{surf, \, Si}$ values have errors of ~±0.02 molecule/silicon atom due to the errors of ellipsometry data. The number in the parentheses represents the errors derived from the errors in ellipsometric measurements.

c: % protein adsorption. Calculation is as follows:

$$A(\% \, ML) = T_p / T_{p0} \times 100\% = (T_e' - T_e) / T_{p0} \times 100\% \qquad (S3)$$

where A is the percentage of protein adsorption of a monolayer; T_p is the ellipsometric thickness of the adsorbed fibrinogen layer; T_{p0} is the ellipsometric thickness of a fibrinogen monolayer on H-Si(111),

which is 60Å.The number in the parentheses represents the errors derived from the errors in ellipsometric measurements.

3. Measurement of the Thickness of $C_{10}EG_7$Monolayer on Si(111) by XPS

The film thickness was also measured by variable angle XPS using the following equation (S4).[10]

$$A_{Si} = S_{Si}^{ML} \Big/ S_{Si}^{H} = \exp[-d/\lambda_{ML}(E_{Si2p})\sin\theta] \tag{S4}$$

where$S_{Si}^{ML}$and S_{Si}^{H} are the measured Si2p signal intensity of the OEG-modified and H-Si surfaces, respectively; d is the monolayer thickness in angstroms; θ is the take-off angle; and $\lambda_{ML}(E_{Si2p})$is the attenuation length of the Si2p photoelectrons in the OEG monolayer expressed in angstroms. The attenuation length (λ_{ML}) of photoelectrons scattering in OEG monolayers has not been reported. Laibinis*et al.* measured the attenuation length (λ) of photoelectrons with kinetic energies in the range of 500–1500 eV in a series of alkylthiolate SAMs on Ag, Cu and Au substrate surfaces, and derived the following empirical formula (S5):

$$\lambda \text{ (Å)} = 9.0 + 0.022 \, KE \tag{S5}$$

where *KE* is the kinetic energyin electronvolts.[11] This formula applies to the attenuation length of Si2p photoelectrons generated with Al Kα in hydrocarbon films on silicon, since the kinetic energy of Si2p photoelectrons$KE_{si2p} = 1487 - E_{Si2p} = 1387.5$eV ($E_{Si2p}$ (~99.5 eV) is the binding energy of Si2p) within the above range. Due to the unavailability of the attenuation length of Si2p signals for OEG-terminated monolayers, the empirical formula above has been used for estimating the attenuation lengths of Si2p signals with OEG or PEG films on various substrates, assuming this value is similar to that of the hydrocarbons.[12, 13] The λ_{ML} value of Si2p photoelectrons in our $C_{10}EG_7$ monolayers is thus estimated to be 39.5 Å using 99.5 eV as the binding energy of Si2p photoelectrons.

To determine the thickness (*d*) of the $C_{10}EG_7$ films on silicon(111) using equation (S4), we measured the Si2p signal intensity of the $C_{10}EG_7$-modified and hydrogen-terminated silicon surfaces at different take-off angels (Table S2). The plot of $-\text{Ln}A_{Si}$ as a function of $1/\sin\theta$ is presented in Figure S1. The linear fitting of the data points with Origin 7.0 resulted in a slope of 1.00. Thus, according to equation (S4),

$$d = \lambda_{ML}(E_{Si2p}) \tag{S6}$$

Therefore, the thickness of 39.5 Å for the **C$_{10}$EG$_7$** monolayer was obtained from equation (S6). This value is consistent with the ellipsometric value (40 Å), although it should be noted that the measurement above of the Si2p signal intensity did not consider the azimuth angle corresponding to the rotation angle around the surface normal, which may vary the Si2p signal intensities by 20%.[10]

Table S2. Intensity of Si2p signals from **C$_{10}$EG$_7$** monolayers and H-Si surfaces at difference take-off angles.

θ	$1/\sin\theta$	S_{Si}^{ML}	S_{Si}^{H}	A_{Si} (S_{Si}^{ML}/S_{Si}^{H})	$-\text{Ln}A_{Si}$
30	2.00	3474.05	18144.76	0.19	1.65
45	1.41	9588.56	27786.74	0.35	1.06
60	1.15	17744.46	39951.89	0.44	0.81
75	1.04	23952.73	47725.58	0.50	0.69
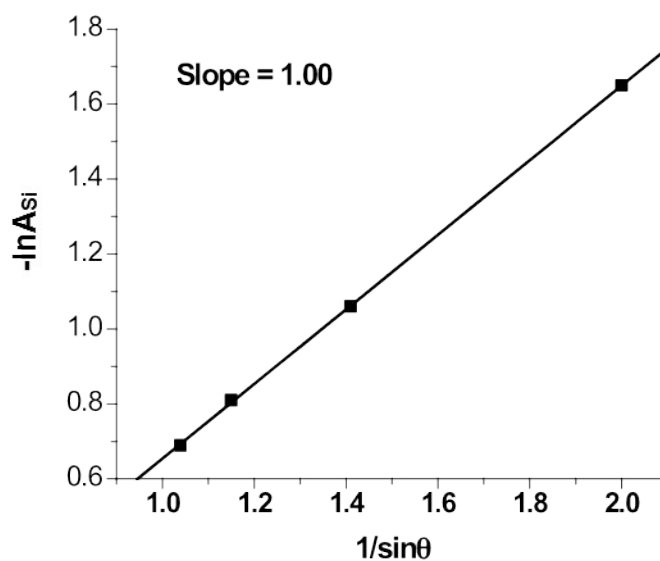
Figure S1. Plot of $-\text{Ln}A_{Si}$ as a function of $1/\sin\theta$.

$$\frac{N_{chains}}{N_{surf, Si}} = \left(\frac{S_{ML}{}^C}{S_{Si}{}^{Si}}\right)\left(\frac{d_{ML}}{L_{carbon}}\right)\left(\frac{\sigma_{Si}\,\lambda_{Si}{}^{Si}\,\rho_{Si}{}^{Si}}{\sigma_c\,\lambda_{ML}{}^C\,N_{surf.\ Si}}\right)\left(\frac{e^{(-d_{ML}/\lambda_{ML}{}^{Si}\sin\theta)}}{1\ -\ e^{(-d_{ML}/\lambda_{ML}{}^{Si}\sin\theta)}}\right) \quad (S7)$$

4. Calculation of Packing Density of C₁₀EG₇Monolayer on Si(111) by XPS

The surfacedensity of the **C₁₀EG₇** monolayer on Si(111) was estimated using equation (S7),[9]

where N_{chains} is the number of chains per unit area; $N_{surf,\ Si}$ is the number of silicon atoms on surfaces per unit area, which is 7.8×10^{14} atoms/cm²; $S_{ML}{}^C$ is the integrated area of C 1s peak from **C₁₀EG₇** monolayer; $S_{Si}{}^{Si}$ is the integrated area of Si2p peak from silicon substrate; d_{ML} is the monolayer thickness; L_{carbon} is the number of carbon atoms per chain; σ_{Si} and σ_C are the sensitivity factors of Si2p and C1s photoelectrons, which are 0.368 and 0.314, respectively; $\lambda_{ML}{}^C$ and $\lambda_{ML}{}^{Si}$ are the attenuation lengths of C1s and Si2p photoelectrons in the OEG monolayer, which are assumed to be the same as that in the alkylmonolayer, 35.4 Å and 39.5 Å,[10] respectively; $\lambda_{Si}{}^{Si}$is the attenuation length of Si2p photoelectrons in hydrogen-terminated silicon surfaces, which is 19 Å;[10]$\rho_{Si}{}^{Si}$ is the density of silicon atoms in bulk silicon, which is 5.0×10 atoms/cm³;[22] and θ is the take-off angle between the surface and analyzer, which is 45° in our experimental setup.

Using the equation above, the surface density of the **C₁₀EG₇** monolayers on Si(111) was estimated to be 4.8×10^{14} molecules/cm², corresponding to 61% coverage of the top layer of silicon atoms on the surface. Accordingly, the average distance between adjacent molecules is 4.6 Å.

Alternatively, the surface density of **C₁₀EG₇** monolayer on Si(111) can be estimated to be5.0 $\times 10^{14}$ molecules/cm² (equivalent to 20.0 Å²/molecule), using the ellipsometric thickness of the **C₁₀EG₇** film of 40 Å and equation (S1). This result is comparable with the surface density derived from XPS, which is 4.8×10^{14}molecules/cm².

Combining all the results, we can conclude that the packing density of the **C₁₀EG₇** monolayers on silicon is comparable(within experimental error) to the packing density (21.4

Å^2/molecule) of the OEG-terminated thiolate monolayers on Au surfaces that equals to 4.7×10^{14} molecules/cm^2.[14]
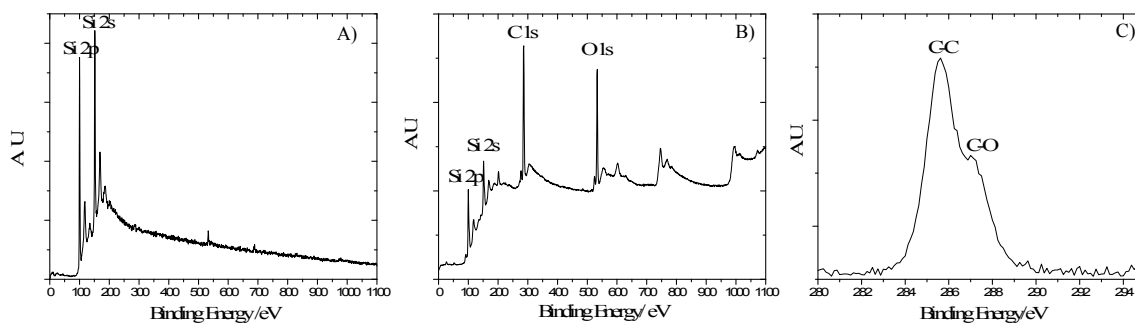
Figure S2. A) XPS survey scan for the pristine H-Si (111) surface B) XPS survey scan for the C$_{10}$EG$_7$ thin film. C) XPS narrow scan for C 1s for the C$_{10}$EG$_7$ film.

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