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SUPPORTING INFORMATION

Star Block-Copolymers: Enzyme-Inspired Catalysts for Oxidation of Alcohols in Water

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1. Nomenclature and Abbreviations

Table S1. Nomenclature and abbreviations

Abbreviation	Description
AFM	Atomic Force Microscopy
Cryo-TEM	Cryogenic Transmission Electron Microscopy
DLS	Dynamic Light Scattering
DMF	Dimethylformamide
ESI	Electrospray Ionization
FBA	2,2,3,3,4,4,4-heptafluorobutyl acrylate
FDA	1H,1H,2H,2H-perfluorodecyl acrylate
FS	2,3,4,5,6-pentafluorostyrene
GC-MS	Gas Chomatography - Mass Spectrometry
HR-MS	High resolution Mass Spectrometry
M_n	Number-average molecular weight
M_w	Weight-average molecular weight
NMP	Nitroxide-Mediated Polymerization
NMR	Nuclear Magnetic Resonance Spectroscopy
OEGMa	Oligo(Ethylene Glycol) Methacrylate
OEGSt	Oligo(Ethylene Glycol) Styrene
PDI	Polydispersity Index
PS	Polystyrene
RID	Refractive Index Detector
SEC	Size Exclusion Chromatography
SPM	Scanning Probe Microscopy
TBTA	Tris(benzyltriazolylmethyl)amine
TEMPO	2,2,6,6-tetramethylpiperidinyloxyl
THF	Tetrahydrofuran
UV-Vis	Ultraviolet Visible

2. Materials and Methods

Materials

Commercial reagents were purchased from Sigma Aldrich or VWR and used without any further purification, unless indicated otherwise. Monomers including styrene, 2,3,4,5,6-pentafluorostyrene, 2,2,3,3,4,4,4-heptafluorobutyl acrylate, and 1H,1H,2H,2H-perfluorodecyl acrylate were purchased from Aldrich and purified over Al_2O_3 (Basic) before use. Poly(ethylene glycol) monomethyl ether (M_n 500) purchased from Aldrich was purified by azeotropic distillation in toluene before use. O-(1-(4-(azidomethyl)phenyl)ethyl)-N-(tert-butyl)-N-(2-methyl-1-phenylpropyl)hydroxylamine was synthesized by a published technique.[1] The synthesis of fluorinated macro-initiators as well as diblock copolymers were adapted from works of Schubert[2] and Boutevin[3], respectively.

Nuclear Magnetic Resonance Spectroscopy (NMR):

^{1}H, ^{13}C, ^{19}F NMR analyses were performed on a Bruker AVQ 400 MHz instrument at 298K. Chemical shifts are reported as δ (ppm) values, and coupling constants (*J*) in Hz. TMS or residual solvent signals such as $CDCl_3$ (δ: 7.23), were used as reference peaks.

Gas Chromatography - Mass Spectrometry (GC-MS):

GC-MS analyses were performed on an Agilent 7820A gas chromatograph equipped with a 30m x 0.25mm HP-5MS capillary column (25μ film thickness) and an Agilent 5975C mass-selective detector.

Size Exclusion Chromatography (SEC):

The molecular weight and the molecular weight distribution of polymers were determined from SEC using an Agilent liquid chromatography system fitted with refractive index (RID) and UV-Vis detectors, using two identical PLgel columns (5 μm, MIXED-C) in connected series with THF as the mobile phase (1 mL/min). The column and flow path were temperature controlled at 25°C. Data analysis was performed using GPC-Addon for ChemStation software from Agilent.

High-Resolution Mass Spectrometry (HR-MS):

Measurements were performed on an Orbitrap mass analyzer and the sample was ionized using ESI ion source operating in positive mode.

Dissolved Oxygen Measurements:

Dissolved oxygen was measured using a Mettler Toledo SG6 SevenGO Pro instrument with an Inlab 605 dissolved oxygen probe.

Dynamic Light Scattering (DLS):

DLS measurements were performed to determine the size distribution of monomer aggregates in solution or bulk using a Malvern Zetasizer Nano ZS instrument equipped with a 632.8 nm He-Ne laser. The measurement angle was 173°. The cells were temperature-controlled at 25 ± 0.1 °C.

Atomic Force Microscopy (AFM):

AFM images were obtained on an Agilent 5400 SPM instrument in tapping mode, using Pico View software. Silicon cantilevers were obtained from Bruker (k = 42 N/m; fo = 320 kHz; T: 4um; L: 125 um; W: 40 um). The samples were prepared by spin coating the polymer onto a silicon wafer at 4000 rpm for 30 seconds from a 1 mg/mL micellar solution. P(FBA_{20}-*b*-$OEGSt_4)_3$ sample containing vesicles was prepared by dip-coating the Si-wafer in solution, and then drying the substrate overnight under vacuum. Gwyddion 2.33 was used for data analysis and visualization of AFM images.

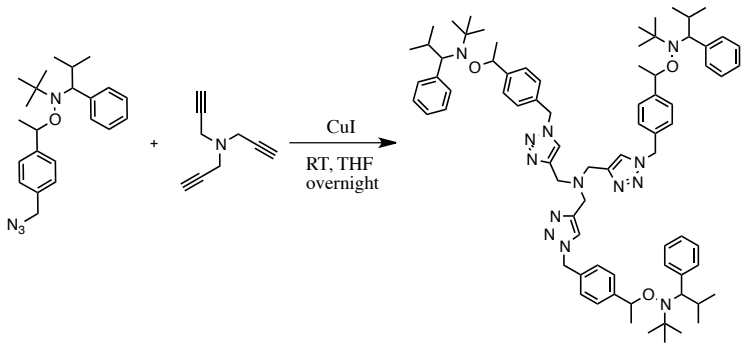
Transmission Electron Microscopy (TEM):

Imaging was performed on a Titan G2 80–300 kV transmission electron microscope (FEI Inc.) equipped with a 4 k×4 k CCD camera (US4000, Gatan, Inc.). Cryo-TEM: Imaging was performed with a low dose on a Titan Krios operating at 300 kV. Images were recorded in zero loss imaging mode using an energy filter (GIF Tridiem, Gatan, Inc) with a slit width of 20 eV.

Copper loaded vesicles were prepared by adding 1 mL of a 1 g/L $CuSO_4$ solution to 1 mL of a 3.3 g/L ($PFBA_{20}$-*b*-$OEGSt_4)_3$ of concentration, followed by dialysis against water overnight using 8K cut-off membranes. The samples were stained using a 4% *w/v* OsO_4 solution.

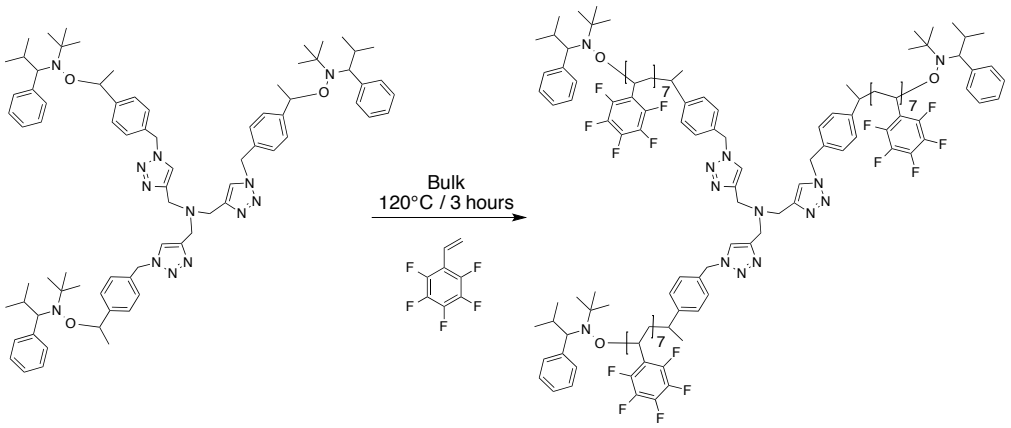
3. SYNTHESIS OF STAR BLOCK COPOLYMERS

1) Tris((1-(4-(1-((*tert*-butyl(2-methyl-1-phenylpropyl)amino)oxy) ethyl)benzyl)-1*H*-1,2,3-triazol-4-yl)methyl)amine



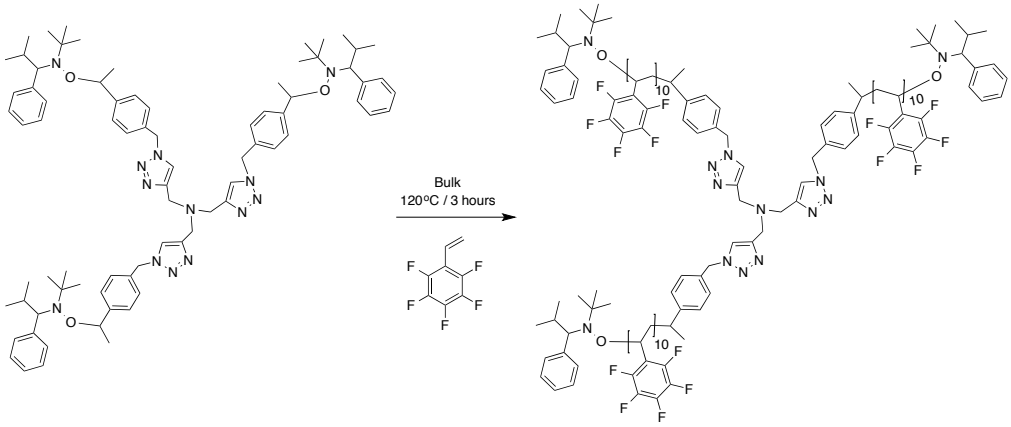
O-(1-(4-(azidomethyl)phenyl)ethyl)-*N*-(*tert*-butyl)-*N*-(2-methyl-1-phenylpropyl) hydroxylamine (1.79 g, 4.7 mmol, 1 eq.) and tripropargylamine (0.2 g, 1.52 mmol, 0.32 eq.) were dissolved in THF (20 mL). Copper iodide (0.09 g, 0.47 mmol, 0.1 eq.) was added and then the reaction mixture was stirred at room temperature under nitrogen. The mixture was analyzed by TLC (hexane/ethyl acetate 19:1) after 16 hours to confirm the reaction was at completion. QuadraSil® MP (0.5 g) was added and the resulting mixture was stirred for 1 hour to remove copper. The mixture was filtered off, and the filtrate was concentrated under vacuum. The resulting solid residue was then purified by column chromatography, using hexane/ethyl acetate (1:1) as the eluent and giving 1.54 g (78%) of a solid white powder. ^{1}H NMR of diastereomers (400 MHz; $CDCl_3$): δ 7.74 (br s, 3 H), 7.45-7.16 (m, 27 H), 5.50 (d, *J* = 15.2 Hz, 6 H), 4.93 (dd, *J* = 6.5, 2.4 Hz, 3 H), 3.74 (br s, 6 H), 3.37 (dd, *J* = 47.3, 10.7 Hz, 3 H), 2.21-2.36 (m, 3 H), 1.62 (d, *J* = 6.6 Hz, 3 H), 1.54 (d, *J* = 6.6 Hz, 3 H), 1.31 (d, *J* = 6.4 Hz, 3 H), 1.05 (s, 9 H), 0.91 (d, *J* = 6.3 Hz, 3 H), 0.78 (s, 9 H), 0.55 (d, *J* = 6.6 Hz, 3 H), 0.22 (t, *J* = 5.6 Hz, 3 H). ^{13}C NMR (101 MHz; $CDCl_3$): δ 146.4, 145.7, 142.4, 142.1, 133.6, 133.0, 131.0, 130.9, 128.0, 127.9, 127.8, 127.7, 127.5, 127.3, 126.9, 126.9, 126.4, 126.3, 83.1, 82.2, 72.2, 72.1, 60.6, 60.5, 54.1, 54.0, 32.1, 31.8, 28.5, 28.3, 24.8, 23.2, 22.2, 22.0, 21.2, 21.3. MS (ESI+) calculated for $[C_{78}H_{106}N_{13}O_3]$+: 1272.85361, found: 1272.85432.

2) Poly(2,3,4,5,6-pentafluorostyrene) three-arm star polymer $(PFS_7)_3$



The TBTA-based NMP initiator (0.090 g, 0.070 mmol, 1 eq.) was introduced into a Schlenk tube and dissolved in 2,3,4,5,6-pentafluorostyrene (1.068 mL, 8.440 mmol, 120 eq.). The solution underwent 5 freeze-pump thaw cycles to remove oxygen, then the flask was filled with argon and immersed in an oil bath heated at 120°C for 3 hours. The Schlenk tube was then removed from the oil bath and the polymer was precipitated twice from dichloromethane in cold methanol, collected and dried under vacuum for 24 hours. M_n: 3843 g/mol; M_w: 4260 g/mol (Calibration of linear PS) PDI: 1.10 ^{1}H NMR: (400 MHz, $CDCl_3$) δ (ppm) 7.73 (m, 3 H, CH); 6.70 - 7.50 (m, 27 H, CH); 5.45 (d, 6 H, CH); 3.74 (m, 6 H, CH); 3.27 (m, 3 H, CH_{NO}); 1.75-3.00 (m, 96 H, CH); 0.19 – 1.50 (s, 54 H, CH) ^{13}C NMR: (101 MHz, $CDCl_3$) δ (ppm) 146.49, 142.14, 144.04, 139.06, 136.49, 128.3, 114.51, 72.35, 59.44, 32.08, 31.76, 28.46, 28.31, 24.75, 23.18, 22.20, 22.0, 21.20, 21.13 ^{19}F NMR: (377 MHz, $CDCl_3$) δ (ppm) -142.96, -154.00, -161.09.

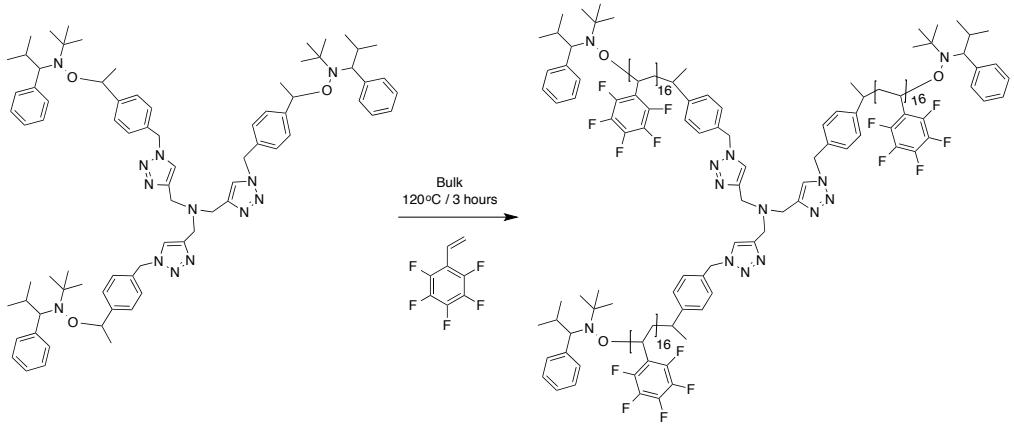
3) Poly(2,3,4,5,6-pentafluorostyrene) three-arm star polymer $(PFS_{10})_3$



The TBTA-based NMP initiator (0.150 g, 0.117 mmol, 1 eq.) was introduced into a Schlenk tube and dissolved in 2,3,4,5,6-pentafluorostyrene (1.948 mL, 0.014 mol, 120 eq.). The solution underwent 5 freeze-pump thaw cycles to remove oxygen, then

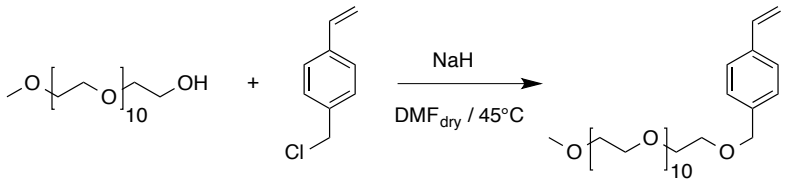
the flask was then filled with argon and immersed in an oil bath heated at 120°C for 3 hours. The polymer was precipitated twice from dichloromethane into cold methanol, then collected and dried for 24 hours under vacuum. M_n: 5550 g/mol; M_w: 6380 g/mol (Calibration of linear PS) PDI: 1.16 ^{1}H NMR: (400 MHz, $CDCl_3$) δ (ppm) 8.30 (m, 3 H, CH); 6.70 - 7.50 (m, 27 H, CH); 5.45 (d, 6 H, CH); 3.74 (m, 6 H, CH); 3.27 (m, 3 H, CH_{NO}); 1.75-3.00 (m, 66 H, CH); 0.19 – 1.50 (s, 54 H, CH) ^{13}C NMR: (101 MHz, $CDCl_3$) δ (ppm) 146.49, 142.14, 144.04, 139.06, 136.49, 128.3, 114.51, 72.35, 59.44, 32.08, 31.76, 28.46, 28.31, 24.75, 23.18, 22.20, 22.0, 21.20, 21.13 ^{19}F NMR: (377 MHz, $CDCl_3$) δ (ppm) -142.86, -154.00, -161.12

4) Poly(2,3,4,5,6-pentafluorostyrene) three-arm star polymer $(PFS_{16})_3$



The TBTA-based NMP initiator (0.090 g, 0.07 mmol, 1 eq.) was introduced into a Schlenk tube and dissolved in 2,3,4,5,6-pentafluorostyrene (2.435 mL, 0.017 mol, 250 eq.). The solution underwent 5 freeze-pump thaw cycles to remove oxygen. The flask was then filled with argon and immersed in an oil bath heated at 120°C for 3 hours. The polymer was precipitated twice from dichloromethane into cold methanol, then collected and dried for 24 hours under vacuum. M_n: 7950 g/mol; M_w: 9650 g/mol (Calibration of linear PS) PDI: 1.20 ^{1}H NMR: (400 MHz, $CDCl_3$) δ (ppm) 8.30 (m, 3 H, CH); 6.70 - 7.50 (m, 27 H, CH); 5.45 (d, 6 H, CH); 3.74 (m, 6 H, CH); 3.27 (m, 3 H, CH_{NO}); 1.75-3.00 (m, 152 H, CH); 0.19 – 1.50 (s, 68 H, CH) ^{13}C NMR: (101 MHz, $CDCl_3$) 146.00, 143.85, 140.78, 139.36, 138.06, 136.78, 130.55, 127.70, 127.33, 126.20, 114.22, 77.02, 61.45, 53.98, 46.02, 38.63, 37.17, 32.06, 27.90, 21.16 ^{19}F NMR: (377 MHz, $CDCl_3$) δ (ppm) -142.96, -154.00, -161.09

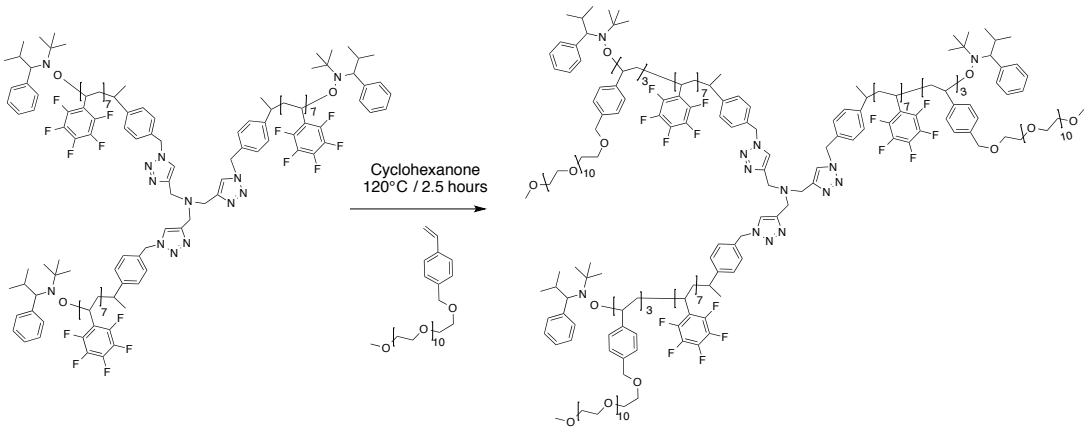
5) 4-polyethylene glycol methylstyrene (Mw: 500 g/mol) OEGSt



Polyethylene glycol mono-methoxy (11.97 g, 23 mmol, 1.2 eq.) was dried by azeotropic distillation in toluene and introduced into a 500 mL three-necks-flask containing 20 mL of dried DMF. The solution was then heated at 45°C under argon. NaH (6.28 g, 157 mmol, 8 eq.) was added, and the mixture was allowed to stir. After 2 hours, 4 chloro-methyl styrene (2.770 mL,

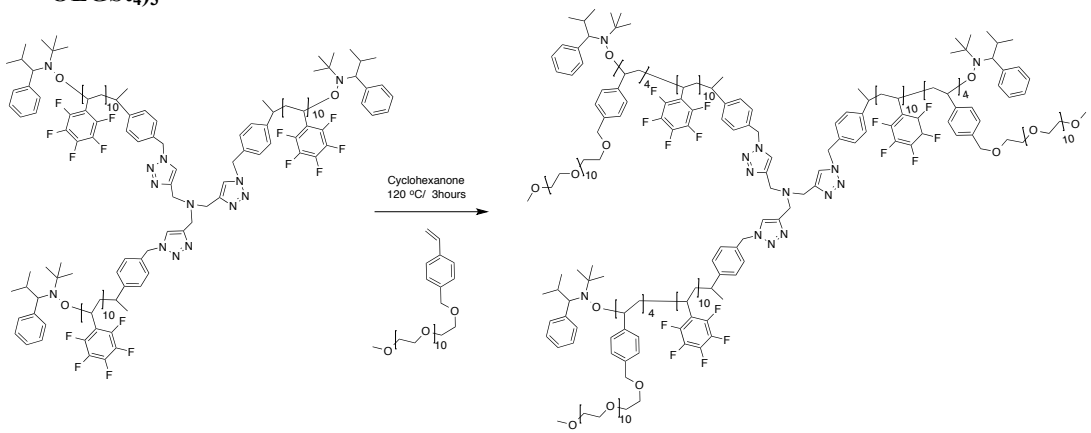
19 mmol, 1 eq.) purified by passing through an Al_2O_3 column was added dropwise to the reaction mixture. The reaction was run for 24 hours under argon. After the reaction, 20 mL of methanol was added, and the mixture was then extracted in dichloromethane. The organic phases were combined, dried in the presence of $MgSO_4$, filtered and then concentrated using a rotary evaporator. The resulting red-yellowish oil was dried under high vacuum to give 11.5 g (Yield: 79%) of the product. ^{1}H NMR: (400 MHz, $CDCl_3$) δ (ppm) 7.38-7.32 (m, 4 H), 6.71 (m, 1 H, H), 5.77 (d, J=17.3 Hz, 1H); 5.22 (d, J= 8Hz, 1H); 4.56 (s, 2H); 3.45-3.85 (s, 58H) 3.39 (s, 3.6H). ^{13}C NMR: (101 MHz, $CDCl_3$) δ (ppm) 137.32, 136.15, 128.84, 125.67, 113.24, 72.48, 71.52; 70.09; 69.02, 61.20, 58.55

6) Poly(2,3,4,5,6-pentafluorostyrene)-*b*-poly(oligo ethylene glycol styrene) three-arm star block copolymer (PFS_7-*b*-$OEGSt_3)_3$



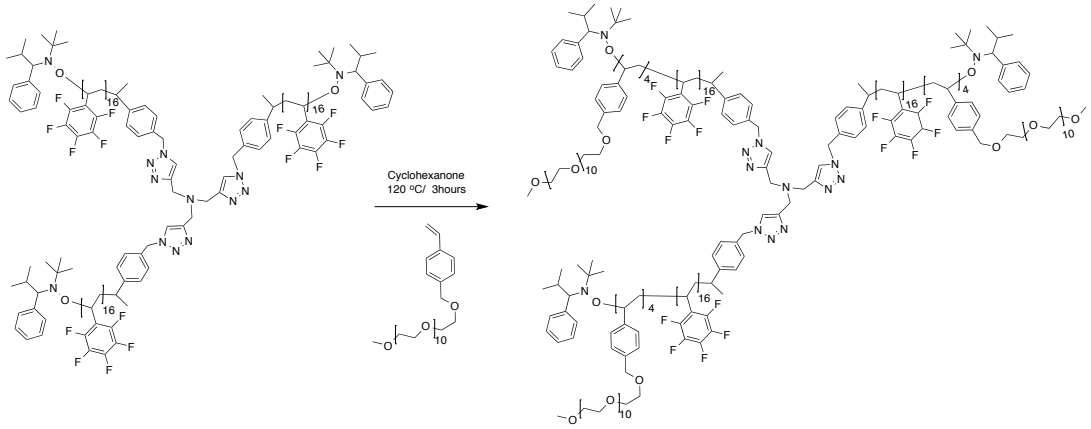
The macro-initiator poly(2,3,4,5,6-pentafluorostyrene) was introduced into a Schlenk tube (0.060 g, 0.013 mmoles, 1 eq.) and dissolved in 3.6 mL of cyclohexanone. 4-polyethylene glycol methyl styrene (0.481 g, 0.780 mmol, 60 eq.) was subsequently added, and the solution underwent 5 freeze-pump-thaws cycles to remove oxygen. The Schlenk tube was filled with argon and introduced into an oil bath heated at 120°C. After 2.5 hours, the Schlenk tube was then transferred to an ice water bath to cool down the reaction mixture, and then the mixture was concentrated using a rotary evaporator. THF was added to the resulting viscous residue, and the solution was dialyzed for two days against water using 1K cut-off dialysis membrane to remove excess of monomer. The dialysis bag was transferred into a beaker with THF for two hours, and the solution was dried to give a yellowish solid residue. M_n: 5900 g/mol; M_w: 6600 g/mol (Calibration of linear PS) PDI: 1.12; ^{1}H NMR: (400 MHz, $CDCl_3$) δ (ppm) 6.70 - 7.50 (m, 62 H, CH); 5.45 (d, 6 H, CH); 4.54 (s, 16 H); 3.5 -3.75 (s, 375 H, CH_2) 3.37 (s, 23 H, CH_3) 1.5-3.00 (m, 96 H, CH); ^{13}C NMR: (101 MHz, $CDCl_3$) δ (ppm) 146.49, 142.14, 144.04, 139.06, 136.49, 128.32, 114.51, 72.35, 71.02, 70.92, 59.44, 38.26, 32.50, 30.12, 23.11, ^{19}F NMR: (377 MHz, $CDCl_3$) δ (ppm) -142.96, -154.00, -161.09

7) Poly(2,3,4,5,6-pentafluorostyrene)-*b*-poly(oligo ethylene glycol styrene) three-arm star block copolymer (PFS_{10}-*b*-$OEGSt_4)_3$



The macro-initiator poly(2,3,4,5,6-pentafluorostyrene) was introduced into a Schlenk tube (0.100 g, 0.014 mmoles, 1 eq.) and dissolved in 2 mL of cyclohexanone. 4-polyethylene glycol methyl styrene (0.594 g, 0.780 mmol, 70 eq.) was subsequently added, and the solution underwent 5 freeze-pump-thaws cycles to remove oxygen. The Schlenk tube was filled with argon and introduced into an oil bath heated at 120°C. After 3 hours, the Schlenk tube was transferred to an ice water bath to stop the polymerization. The solvent was removed on a rotary evaporator to give a viscous residue, which was then diluted in THF. The solution was dialyzed against water for two days using a 1K cut-off dialysis membrane to remove excess of monomer. The dialysis bag was then dialyzed against THF for 2 hours, and the solution was dried to give a yellowish solid residue. M_n: 11200 g/mol; M_w: 13216 g/mol (Calibration of linear PS) PDI: 1.18; ^{1}H NMR: (400 MHz, $CDCl_3$) δ (ppm) 6.70 - 7.50 (m, 74 H, CH); 5.45 (d, 6 H, CH); 4.54 (s, 20 H); 3.5 -3.75 (s, 554 H, CH_2); 3.37 (s, 37 H, CH_3); 1.5-3.00 (m, 214 H, CH); 0.5-1.24 (m, 59 H, CH) ^{13}C NMR: (101 MHz, $CDCl_3$) δ (ppm) 146.49, 142.14, 144.04, 139.06, 136.49, 128.32, 114.51, 72.35, 71.02, 70.92, 59.44, 38.26, 32.50, 30.12, 23.11, ^{19}F NMR: (377 MHz, $CDCl_3$) δ (ppm) -142.86, -154.00, -161.12

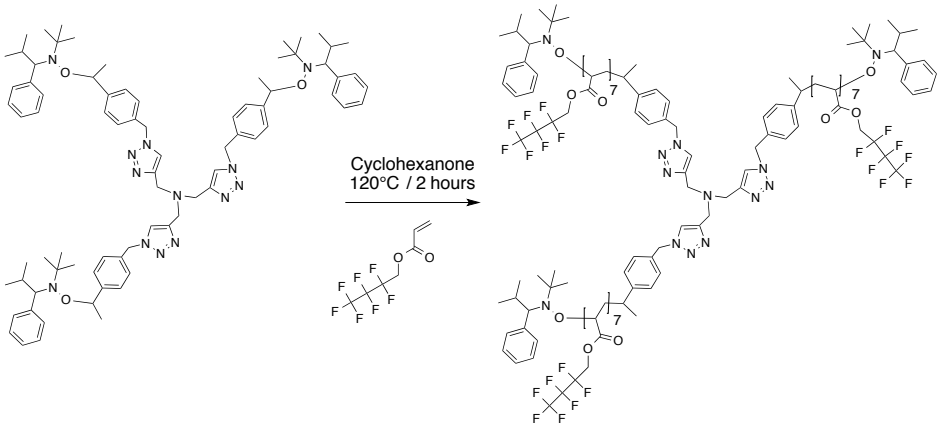
8) Poly(2,3,4,5,6-pentafluorostyrene)-*b*-poly(oligo ethylene glycol styrene) three-arm star block copolymer (PFS_{16}-*b*-$OEGSt_4)_3$



The macro-initiator poly(2,3,4,5,6-pentafluorostyrene) was introduced into a Schlenk tube (0.100 g, 0.009 mmoles, 1 eq.) and dissolved in 3 mL of cyclohexanone. 4-polyethylene glycol methyl styrene (0.572 g, 0.928 mmol, 100 eq.) was subsequently added, and the solution underwent 5 freeze-pump-thaws cycles to remove oxygen. The Schlenk tube was filled with argon and

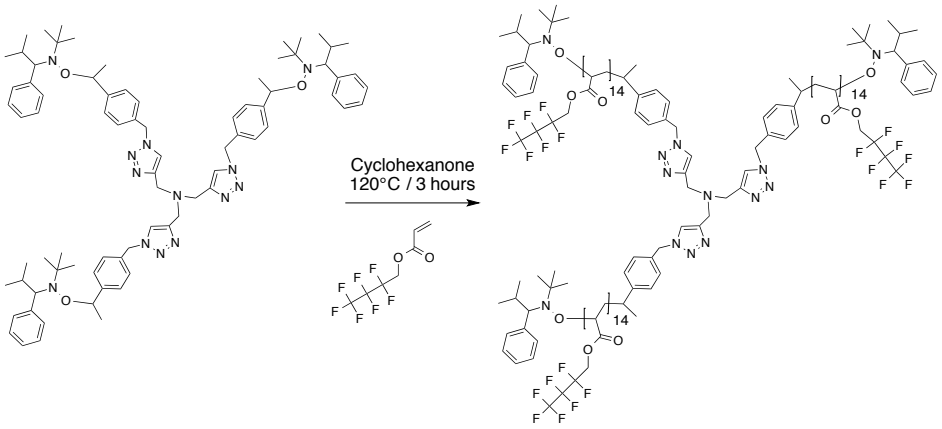
introduced into an oil bath heated at 120°C. After 3 hours, the Schlenk tube was transferred to an ice water bath to stop the polymerization. The solvent was removed using a rotary evaporator to give a viscous residue which was then diluted in THF. The solution was dialyzed against water for two days using 1K cut off dialysis membrane to remove excess of monomer. The dialysis bag was then dialyzed against THF for 2 hours, and the solution was dried to give a yellowish solid residue. M_n: 12400 g/mol; M_w: 15130 g/mol (Calibration of linear PS) PDI: 1.22; ^{1}H NMR: (400 MHz, $CDCl_3$) δ (ppm) 8.34 (m, 3H, CH); 6.70 - 7.50 (m, 84 H, CH); 5.45 (d, 6 H, CH); 4.54 (s, 20 H); 3.5 -3.75 (s, 508 H, CH_2); 3.37 (s, 40 H, CH_3); 1.5-3.00 (m, 182 H, CH); 0.5-1.24 (m, 80 H, CH) ^{13}C NMR: (101 MHz, $CDCl_3$) δ (ppm) 146.49, 142.14, 144.04, 139.06, 136.49, 128.32, 114.51, 72.35, 71.02, 70.92, 59.44, 38.26, 32.50, 30.12, 23.11, ^{19}F NMR: (377 MHz, $CDCl_3$) δ (ppm) -142.86, -154.00, -161.12

9) Poly(2,2,3,3,4,4,4-heptafluorobutyl acrylate) three-arm star polymer $(PFBA_7)_3$



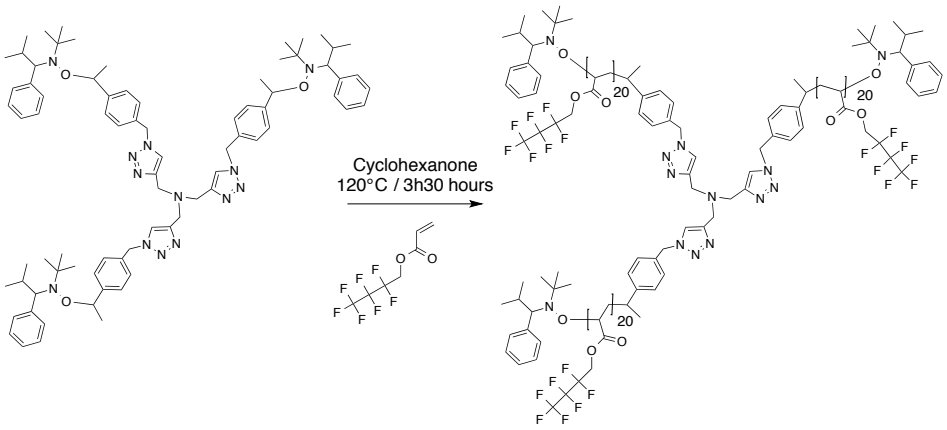
The 2,2,3,3,4,4,4-heptafluorobutyl acrylate monomer (0.700 mL, 3.910 mmol, 100 eq.) was purified through a basic Al_2O_3 column to remove the inhibitor before use. The monomer was then transferred into a Schlenk tube containing NMP initiator (0.050 g, 0.039 mmoles, 1 eq.). 0.7 mL of cyclohexanone was then added to the mixture. The solution underwent 5 freeze-pump-thaw cycles to remove oxygen, the Shlenk tube was then filled with argon, and placed in an oil bath heated at 120°C. After two hours, the polymerization was stopped by placing the Schlenk tube in an ice water bath. Cyclohexane was removed on a rotary evaporator, and the polymer was precipitated in hexane, filtered and then dried under vacuum. M_n: 4154 g/mol; M_w: 4710 g/mol (Calibration of linear PS) PDI: 1.13 ^{1}H NMR: (400 MHz, $CDCl_3$) δ (ppm) 7.73 (m, 3 H, CH); 6.70 - 7.50 (m, 27 H, CH); 5.46 (d, 6 H, CH); 4.55 (s, 46 H, CH_2) 3.81 (m, 6 H); 3.27 (m, 3 H, CH); 1.50-3.00 (m, 66H, CH); 0.19 – 1.50 (s, 44H, CH) ^{13}C NMR: (101 MHz, $CDCl_3$) δ (ppm) 172.75, 141.29; 132.97, 131.18, 130.57, 128.43; 127.78; 126.72, 121.18-105.85, 82.58, 72.25, 61.56, 59.64, 41.15, 34.47, 28.46, 21.46. ^{19}F NMR: (377 MHz, $CDCl_3$) δ (ppm) -81.45, -121.29, -128.28

10) Poly(2,2,3,3,4,4,4-heptafluorobutyl acrylate) three-arm star polymer $(PFBA_{14})_3$



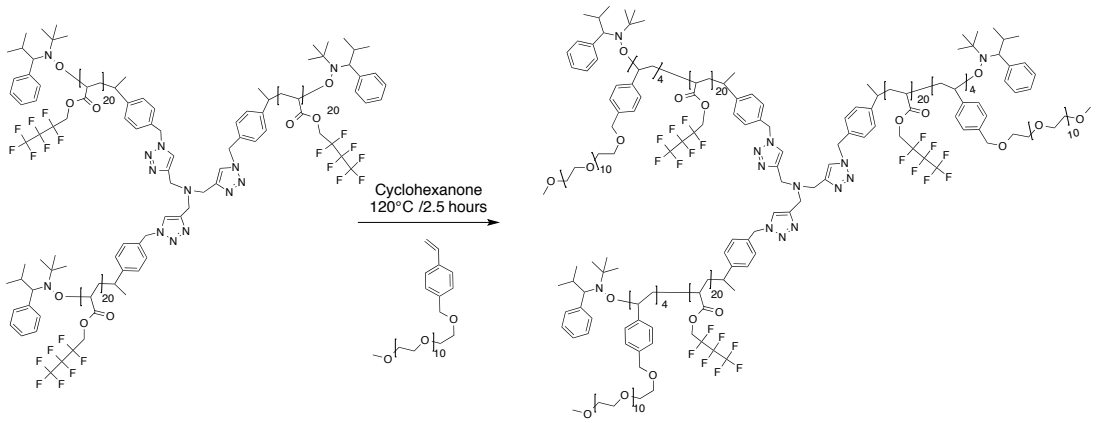
The 2,2,3,3,4,4,4-heptafluorobutyl acrylate monomer (0.700 mL, 3.91 mmol, 100 eq.) was purified through a basic Al_2O_3 column to remove the inhibitor before use. The monomer was then transferred into a Schlenk tube containing NMP initiator (0.050 g, 0.039 mmoles, 1 eq.). The mixture was dissolved in 0.7 mL of cyclohexanone and then the solution underwent 5 freeze-pump-thaw cycles to remove oxygen. The Schlenk tube was then filled with argon, and then placed in an oil bath heated at 120°C to polymerize. After 3 hours, the solution was concentrated on a rotary evaporator to remove the solvent, and the polymer was precipitated into hexane, filtered off and then the precipitate was dried under vacuum. M_n: 7782 g/mol; M_w: 9100 g/mol (Calibration of linear PS) PDI: 1.17 ^{1}H NMR: (400 MHz, CDCl3) δ (ppm) 7.73 (m, 3 H, CH); 6.70 - 7.50 (m, 27 H, CH); 5.46 (d, 6 H, CH); 4.55 (s, 78 H, CH2) 3.81 (m, 3 H); 3.27 (m, 3 H, CH); 1.50-3.00 (m, 174H, CH); 0.19 – 1.50 (s, 48H, CH) ^{13}C NMR: (101 MHz, CDCl3) δ (ppm) 172.75, 141.29; 132.97, 131.18, 130.57, 128.43; 127.78; 126.72, 121.18-105.85, 82.58, 72.25, 61.56, 59.64, 41.15, 34.47, 28.46, 21.46. ^{19}F NMR: (377 MHz, $CDCl_3$) δ (ppm) -81.45, -121.29, -128.28

11) Poly(2,2,3,3,4,4,4-heptafluorobutyl acrylate) three-arm star polymer $(PFBA_{20})_3$



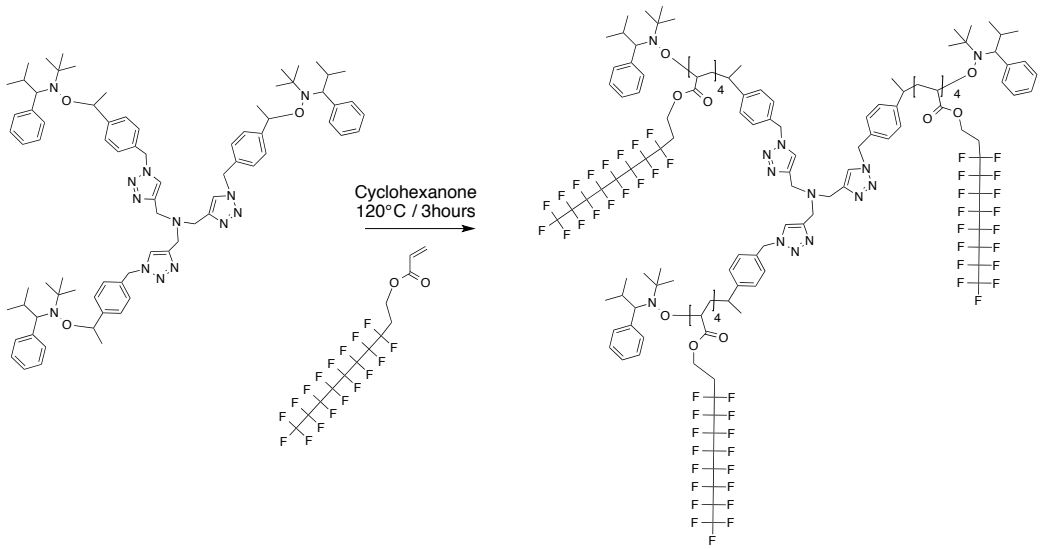
The 2,2,3,3,4,4,4-heptafluorobutyl acrylate (0.700 mL, 3.91 mmol, 200 eq.) was purified through a basic Al_2O_3 column to remove the inhibitor before use. The monomer was then transferred to a Schlenk tube containing NMP initiator (0.025 g, 0.020 mmoles, 1 eq.). The mixture was dissolved in 0.7 mL of cyclohexanone and the solution underwent 5 freeze-pump-thaw cycles to remove oxygen. The Shlenk tube was then filled with argon, and placed in an oil bath heated at 120°C for 3.5 hours. After polymerization, the solvent was removed on a rotary evaporator and the polymer was precipitated into hexane, the solvent was filtered off and then the precipitate was dried under vacuum. M_n: 9206 g/mol; M_w: 10126 g/mol (Calibration of linear PS) PDI: 1.11 ^{1}H NMR: (400 MHz, $CDCl_3$) δ (ppm) 7.73 (m, 3 H, CH); 6.70 - 7.50 (m, 27 H, CH); 5.46 (d, 6 H, CH); 4.55 (s, 120 H, CH_2) 3.81 (m, 6 H); 3.27 (m, 3 H, CH); 1.50-3.00 (m, 188H, CH); 0.19 – 1.50 (s, 54H, CH) ^{13}C NMR: (101 MHz, $CDCl_3$) δ (ppm) 172.75, 141.29; 132.97, 131.18, 130.57, 128.43; 127.78; 126.72, 121.18-105.85, 82.58, 72.25, 61.56, 59.64, 41.15, 34.47, 28.46, 21.46. ^{19}F NMR: (377 MHz, $CDCl_3$) δ (ppm) -81.45, -121.29, -128.28

12) Poly(2,2,3,3,4,4,4-heptafluorobutyl acrylate)-*b*-poly(oligo ethylene glycol styrene) three-arm star block copolymer ($PFBA_{20}$-*b*-$OEGSt_4)_3$



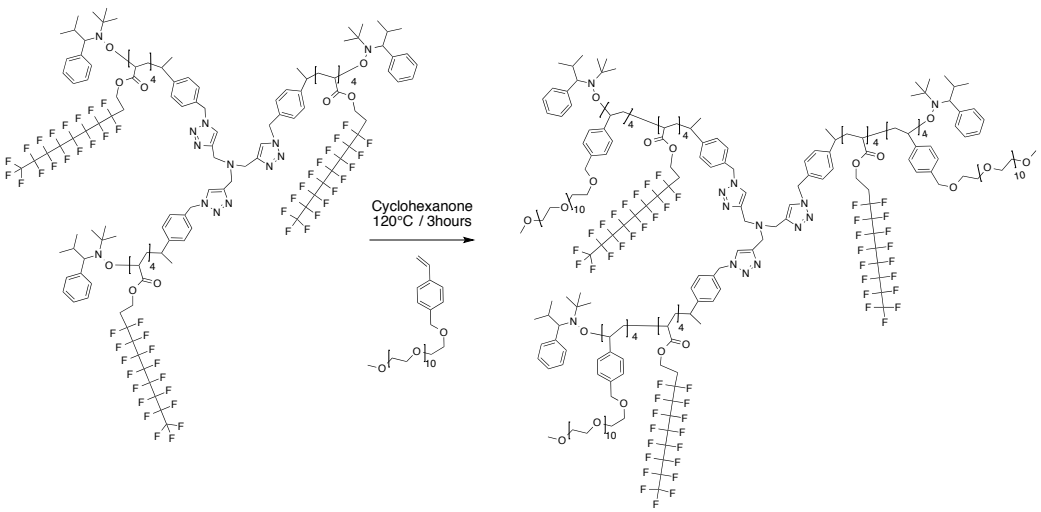
Poly(2,2,3,3,4,4,4-heptafluorobutyl acrylate) macro-initiator (0.100 g, 0.006 mmol, 1 eq.) and 4-polyethylene glycol methylstyrene monomer (0.518 g, 0.840 mmol, 140 eq.) were introduced into a Schlenk tube containing 2 mL of cyclohexanone. The solution underwent 5 freeze-pump thaws cycles, the Schlenk tube was filled with Argon and then introduced into an oil bath heated at 120°C. After 2.5 hours, the Schlenk tube was transferred to an ice water bath to stop the polymerization and the viscous solution was dried using a rotary evaporator to remove cyclohexane. The resulting residues were dissolved in THF and dialyzed against water for two days using a 1K cut-off dialysis membrane. The dialysis bag was transferred in THF for 2 hours, and the solution was dried to give a yellowish solid residue. M_n: 12800 g/mol; M_w: 16400 g/mol (Calibration of linear PS) PDI: 1.28 ^{1}H NMR: (400 MHz, $CDCl_3$) δ (ppm) 7.73 (m, 3 H, CH); 6.70 - 7.50 (m, 102 H, CH); 5.46 (d, 6 H, CH); 4.55 (s, 120 H, CH_2) 3.80-3.45 (m, 776 H, CH); 3.45-3.35 (s, 48 H, CH) 1.00-3.00 (m, 230 H, CH); ^{13}C NMR: (101 MHz, $CDCl_3$) δ (ppm) 172.75, 141.29, 132.97, 131.18; 130.57, 128.43, 127.78, 126.72, 121.18, 105.85, 82.58, 72.25, 72.36, 70.98, 61.56, 59.64, 59.46, 41.15, 34.47, 28.46, 21.46. ^{19}F NMR: (377 MHz, $CDCl_3$) δ (ppm) -81.45, -121.29, 128.28.

13) Poly(1*H*,1*H*,2*H*,2*H*-perfluorodecyl acrylate) three-arm star polymer $(PFDA_4)_3$



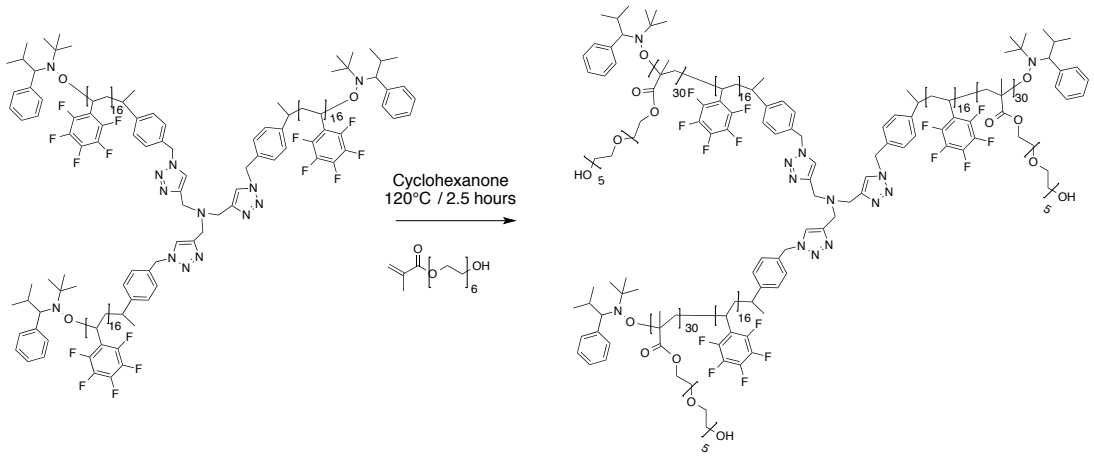
1H,1H,2H,2H perfluorodecyl acrylate monomer (1.230 mL, 3.910 mmol, 100 eq.) was first purified using a basic Al_2O_3 column, and transferred into a Schlenk tube containing NMP initiator (0.050 g, 0.039 mmol, 1 eq.) and 1.23 mL of cyclohexanone. The solution underwent 5 freeze-pump-thaw cycles. The Schlenk tube was filled with argon and placed in an oil bath heated at 120°C. After 3 hours of polymerization, the viscous solution was concentrated on a rotary evaporator and the polymer was then precipitated in hexane, the solvent was filtered off and the precipitate was dried under vacuum. M_n: 7125 g/mol; M_w: 7650 g/mol (Calibration of linear PS) PDI: 1.08 ^{1}H NMR: (400 MHz, $CDCl_3$) δ (ppm) 7.96 (m, 1.5 H); 6.70 - 7.50 (m, 34 H, CH); 5.46 (d, 6 H, CH); 4.55 (s, 25 H, CH) 3.81 (m, 5 H, CH); 3.27 (m, 2.5 H, CH); 1.80-2.80 (m, 42 H, CH); 1.3-2.79 (m, 24 H, CH); 0.19 – 1.25 (s, 54 H, CH) ^{13}C NMR: (101 MHz, $CDCl_3$) δ (ppm) 174.77, 147.21, 144.40, 142.00, 133.25, 131.52, 128.43, 127.78, 126.72, 121.18-108.48, 83.12, 72.25, 61.70, 54.94, 41.72, 34.47, 30.78, 28.46, 21.46. ^{19}F NMR: (377 MHz, $CDCl_3$) δ (ppm) -80.95, -113.93, -122.21, -123.06, -123.79, -126.49

14) Poly(1*H*,1*H*,2*H*,2*H*-perfluorodecyl acrylate)-*b*-poly(oligo ethylene glycol styrene) three-arm star block copolymer ($PFDA_4$-*b*-$OEGSt_4)_3$



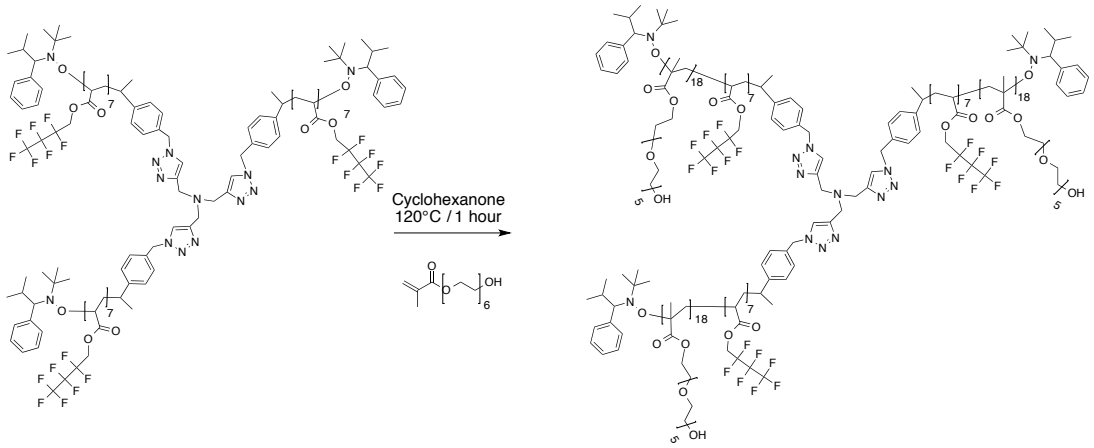
Poly(1*H*,1*H*,2*H*,2*H*-perfluorodecyl acrylate) macro-initiator (0.050 g, 0.06 mmol, 1 eq.) and 4-polyethylene glycol methyl styrene (0.45 g, 0.719 mmol, 110 eq.) were dissolved in 2 mL of cyclohexanone in a Schlenk tube. The solution underwent 5 freeze-pump thaws cycles, the tube was then filled with argon and introduced in an oil bath heated at 120°C. After 2.5 hours, the Schlenk tube was transferred to an ice water bath to stop the polymerization. The viscous solution was dried on a rotary evaporator to remove cyclohexanone, diluted in THF and subsequently dialyzed against water over 2 days using 1K cut-off dialysis membranes. The dialysis bag was then transferred into a beaker filled with THF for 2 hours, and the solution was dried under vacuum to give a yellowish solid residue. M_n: 11500 g/mol; M_w: 14720 g/mol (Calibration of linear PS) PDI: 1.28 ^{1}H NMR: (400 MHz, $CDCl_3$) δ (ppm) 7.96 (m, 1.5 H, CH); 6.70 - 7.50 (m, 147 H, CH); 5.46 (d, 6 H, CH); 4.55 -4.00 (m, 60 H, CH) 3.50-3.75 (s, 549H, CH); 3.37 (s, 3H, CH); 0.50-2.50 (m, 180H + H_2O, CH); ^{13}C NMR: (101 MHz, $CDCl_3$) δ (ppm) 174.77, 147.21, 144.40, 142.00, 133.25, 131.52, 128.43, 127.78, 126.72, 121.18, 108.48, 83.12, 72.25, 71.02, 70.92, 61.70, 54.94, 59.44, 41.72, 34.47, 30.78, 28.46, 21.46 ^{19}F NMR: (377 MHz, $CDCl_3$) δ (ppm) -80.95, -113.93, -122.21, -123.06, -123.79, -126.49 ppm.

15) Poly(2,3,4,5,6-pentafluorostyrene)-*b*-poly(oligo ethylene glycol methacrylate) three-arm star block copolymers ($PFSA_{16}$-*b*-$OEGSt_{30}$)$_3$



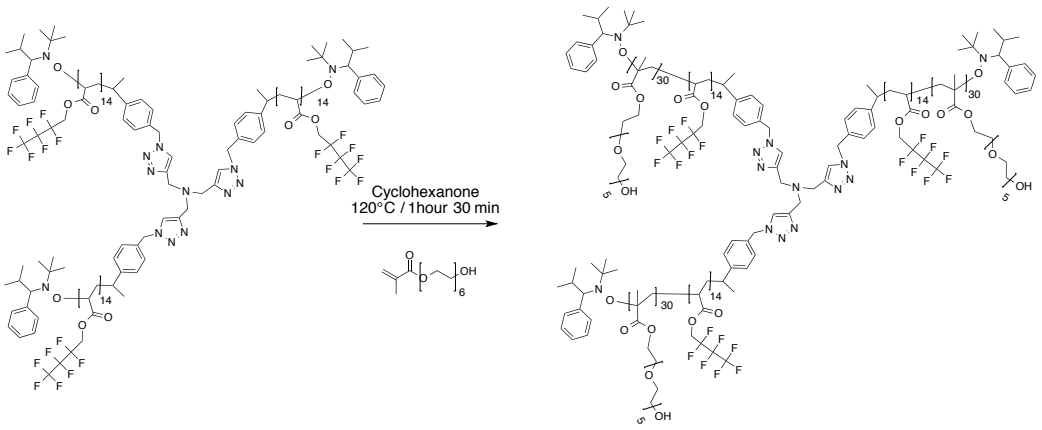
Poly(ethylene glycol) methacrylate was diluted in cyclohexanone (1:1) before purification through a basic Al_2O_3 column. The monomer (0.900 mL, 1.392 mmol, 300 eq.) was then introduced into a Schlenk tube containing poly(2,3,4,5,6-pentafluorostyrene) macroinitiator (0.050 g, 0.004 mmol, 1 eq.) and 0.5 mL of cyclohexanone. The colorless viscous solution underwent 5 freeze-pump thaws cycles and then the Schlenk tube was filled with argon and transferred to an oil bath heated at 120°C. After 2.5 hours of polymerization, the resulting viscous solution was concentrated using a rotary evaporator and further diluted in THF. The solution was dialyzed against water for 2 days using 8K cut-off dialysis membranes to remove any excess of monomer. Afterward, the dialysis bag was transferred to a beaker filled with THF for 2 hours to remove water, and the resulting solution was dried to yield a white solid residue. M_n: 13500 g/mol; M_w: 16470 g/mol (Calibration of linear PS) PDI: 1.22 ^{1}H NMR: (400 MHz, $CDCl_3$) δ (ppm) 7.63 (m, 3 H, CH); 6.70 - 7.50 (m, 25 H, CH); 6.20 and 5.54 (s, 7 H, CH) 5.41 (d, 6 H, CH_2); 4.75 (s, 6 H, CH_2); 4.01 (m, 185 H, CH_2); 3.4-3.8 (s, 2160 H, CH_2); 1.75-3.00 (m, 65 H, $CH_{aliphatic}$); 1.5-2.0 (s, 280 H, CH_3); 0.5 – 1.50 (m, 269 H, CH) ^{13}C NMR: (101 MHz, $CDCl_3$) δ (ppm) 146.49, 141.81, 144.04, 139.06, 136.49, 128.55, 114.68, 32.08, 28.57 ^{19}F NMR: (377 MHz, $CDCl_3$) δ (ppm) -142.86, -154.00, -161.12

16) Poly(2,2,3,3,4,4,4-heptafluorobutyl acrylate)-*b*-poly(oligo ethylene glycol methacrylate) three-arm star block copolymer ($PFBA_7$-*b*-$OEGMA_{18})_3$



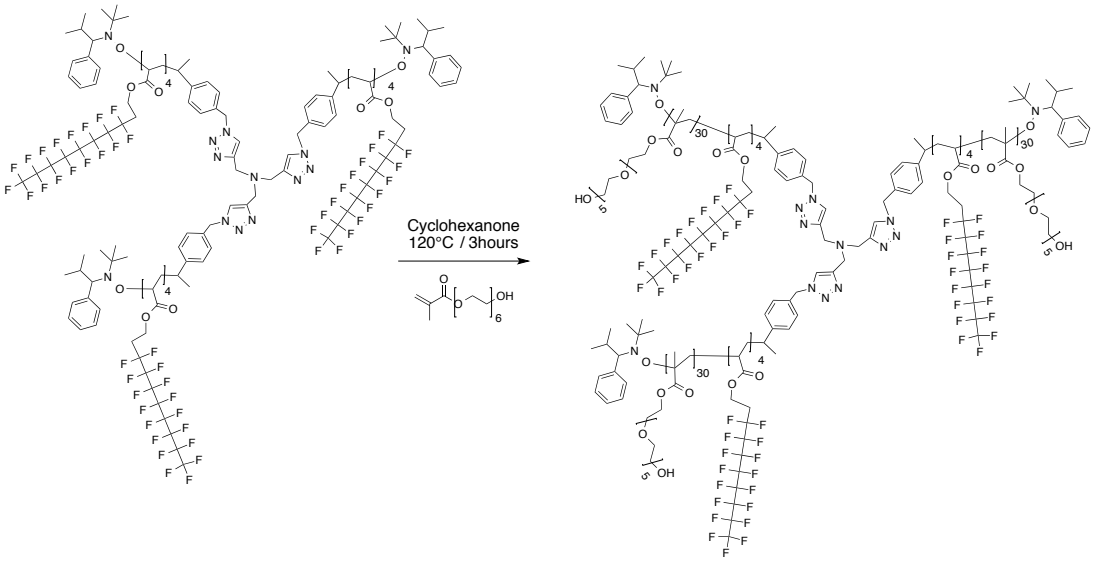
Poly(2,3,3,3,4,4,4 heptafluorobutyl acrylate) macro-initiator was introduced into a Schlenk tube (0.050 g, 0.0025 mmol, 1 eq.) and dissolved in 0.5 mL of cyclohexanone. Poly(ethylene glycol) methacrylate monomer was diluted in cyclohexanone to reach 1:1 volume ratio and further purified using a basic Al_2O_3 column. Poly(ethylene glycol) methacrylate (0.580 mL, 0.75 mmol, 300 eq.) was added to the Schlenk tube and the mixture underwent 5 freeze-pump-thaws cycles to remove oxygen. The Schlenk tube was then filled with argon and placed in an oil bath heated at 120°C. After 1 hour, the viscous solution was dried using a rotary evaporator to remove the solvent and the resulting solid residue was dissolved in THF. The solution was dialyzed against water for two days using 8K cut-off dialysis membranes to remove the excess of monomer. The dialysis bag was then transferred into a beaker filled with THF for 2 hours to remove water, and the solution was dried to yield a white solid residue. M_n: 11230 g/mol; M_w: 13360 g/mol (Calibration of linear PS) PDI: 1.19 ^{1}H NMR: (400 MHz, $CDCl_3$) δ (ppm) 7.63 (m, 3 H, CH); 6.70 - 7.50 (m, 25 H, CH); 6.20 and 5.54 (s, 7 H, CH) 5.41 (m, 6 H, CH); 4.75 (m, 6 H, CH); 4.56 (m, 50 H, CH_2); 4.09 (m, 108 H, CH_2); 3.4-3.8 (s, 1390 H, CH_2); 1.5-3.00 (m, 277 H, CH); 0.5 – 1.50 (m, 220 H, CH); ^{13}C NMR: (101 MHz, $CDCl_3$) δ (ppm) 126.21, 119.70, 73.14, 73.14, 64.35, 62.04, 45.19, 18.76.^{19}F NMR: (377 MHz, $CDCl_3$) δ (ppm) -81.45, -121.29, -128.28.

17) Poly(2,2,3,3,4,4,4-heptafluorobutyl acrylate)-*b*-poly(oligo ethylene glycol methacrylate) three-arm star block copolymer ($PFBA_{14}$-*b*-$OEGMA_{30})_3$



Poly(2,3,3,3,4,4,4 heptafluorobutyl acrylate) macro-initiator was introduced into a Schlenk tube (0.050 g, 0005 mmol, 1 eq.) and dissolved in 0.5 mL of cyclohexanone. Poly(ethylene glycol) methacrylate monomer was diluted in cyclohexanone to reach a 1:1 volume ratio and further purified using a basic Al_2O_3 column to remove the inhibitor. Poly(ethylene glycol) methacrylate (1.080 mL, 1.637 mmol, 300 eq.) was added to the Schlenk tube and the resulting homogenous solution underwent 5 freeze-pump-thaws cycles to remove oxygen. The Schlenk tube was filled with argon and introduced in an oil bath heated at 120°C. After 1 hour, the Schlenk tube was transferred to a cold water bath to stop the polymerization. The viscous solution was dried on a rotary evaporator to remove the solvent and the resulting solid residue was dissolved in THF. The solution was dialyzed against water for two days using 8K cut-off dialysis membranes to remove the excess of monomer. The dialysis bag was then transferred to a beaker filled with THF for 2 hours and the solution was dried under vacuum to yield a white solid residue. M_n: 13200 g/mol; M_w: 15970 g/mol (Calibration of linear PS) PDI: 1.21 ^{1}H NMR: (400 MHz, $CDCl_3$) δ (ppm) 7.63 (m, 3 H, CH); 6.70 - 7.50 (m, 34 H, CH); 6.20 and 5.54 (s, 7 H, CH) 5.41 (m, 6 H, CH); 4.75 (m, 6 H, CH); 4.56 (m, 80 H, CH_2); 4.09 (m, 178 H, CH_2); 3.4-3.8 (s, 2541 H, CH_2); 1.5-3.00 (m, 250 H, CH); 0.5 – 1.50 (m, 370 H, CH); ^{13}C NMR: (101 MHz, $CDCl_3$) δ (ppm) 126.21, 119.70, 73.14, 73.14, 64.35, 62.04, 45.19, 18.76.^{19}F NMR: (377 MHz, $CDCl_3$) δ (ppm) -81.45, -121.29, -128.28.

18) Poly(1*H*,1*H*,2*H*,2*H*-Perfluorodecyl acrylate)-*b*-poly(oligo ethylene glycol methacrylate) three-arm star block copolymer ($PFDA_4$-*b*-$OEGMA_{30}$)$_3$



Poly(*1H,1H,2H,2H* perfluorodecyl acrylate) macro-initiator was introduced into a Schlenk tube (0.050 g, 0.006 mmol, 1 eq.) containing 0.5 mL of cyclohexanone. Poly(ethylene glycol) methacrylate monomer was diluted in cyclohexane to reach a 1:1 volume ratio, and further purified using a basic Al_2O_3 column to remove the inhibitor. Poly(ethylene glycol) methacrylate diluted in cyclohexane (1.280 mL, 1.961 mmol, 300 eq.) was added to the mixture, and the resulting homogenous solution underwent 5 freeze-pump thaws cycles. The Schlenk tube was then transferred to an oil bath heated at 120°C for 3 hours. The resulting viscous solution was concentrated on a rotary evaporator by removing the solvent. The resulting solid residue was then dissolved in THF and dialyzed against water for two days using 8K cut-off dialysis membranes. The dialysis bag was then transferred in THF for 2 hours to remove water, and the solution was dried under vacuum to yield a white solid residue. M_n: 11000 g/mol; M_w: 12320 g/mol (Calibration linear PS) PDI: 1.12 ^{1}H NMR: (400 MHz, $CDCl_3$) δ (ppm) 7.63 (m, 3 H, CH); 6.70 - 7.50 (m, 34 H, CH); 6.20 and 5.54 (s, 6 H, CH) 5.41 (m, 6 H, CH_2); 4.74 (m, 6 H, CH_{2-}); 4.00-4.56(m, 257 H, CH_2); 4.09 (m, 108 H, CH_2); 3.4-3.8 (s, 2354 H, CH_2); 1.5-3.00 (m, 245 H, CH); 0.5 – 1.50 (m, 346 H, CH) ^{13}C NMR: (101 MHz, $CDCl_3$) δ (ppm) 178.11; 167.69, 136.49, 129.38, 128.55, 126.09, 111.05, 108.18, 72.99, 68.30, 61.95, 53.92, 45.14, 29.55, 16.92 ^{19}F NMR: (377 MHz, $CDCl_3$) δ (ppm) -80.95, -113.93, -122.21, -123.06, -123.79, -126.49

4. Characterization

1) ^{1}H NMR Spectra

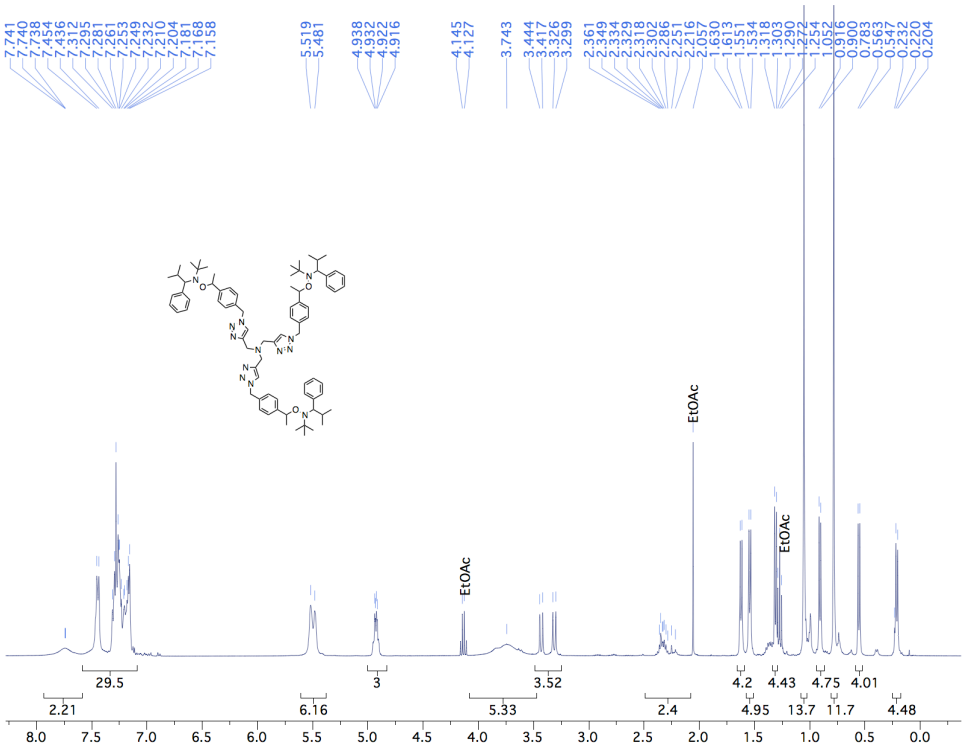


Figure S1. ^{1}H NMR spectrum of tris((1-(4-(1-((*tert*-butyl(2-methyl-1-phenylpropyl)amino)oxy) ethyl)benzyl)-1*H*-1,2,3-triazol-4-yl)methyl)amine in $CDCl_3$.

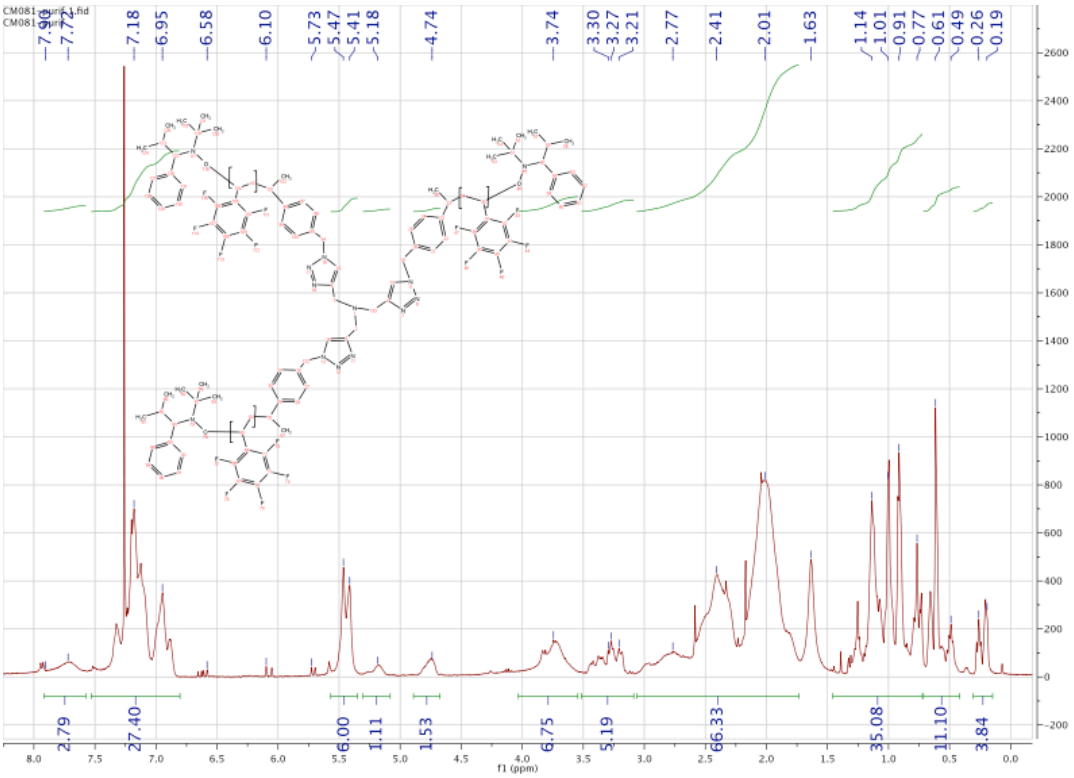


Figure S2. ^{1}H NMR spectrum of $(PFS_7)_3$ three-arm star polymer in $CDCl_3$.

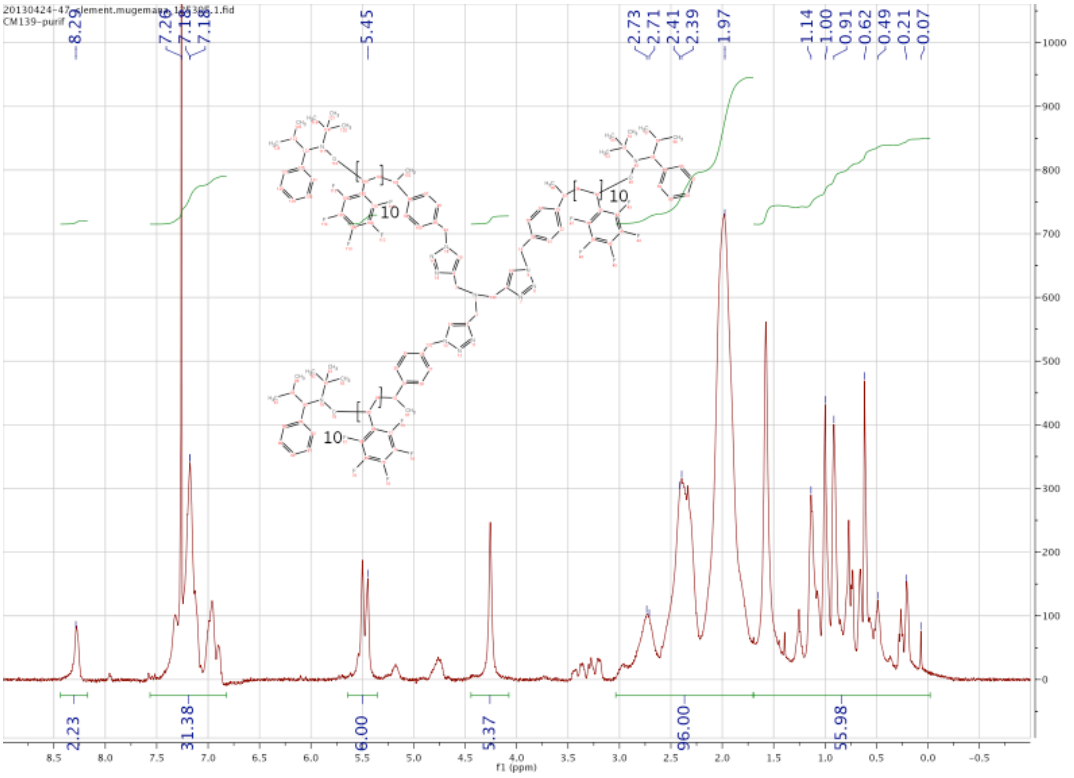


Figure S3. ^{1}H NMR spectrum of $(PFS_{10})_3$ three-arm star polymer in $CDCl_3$.

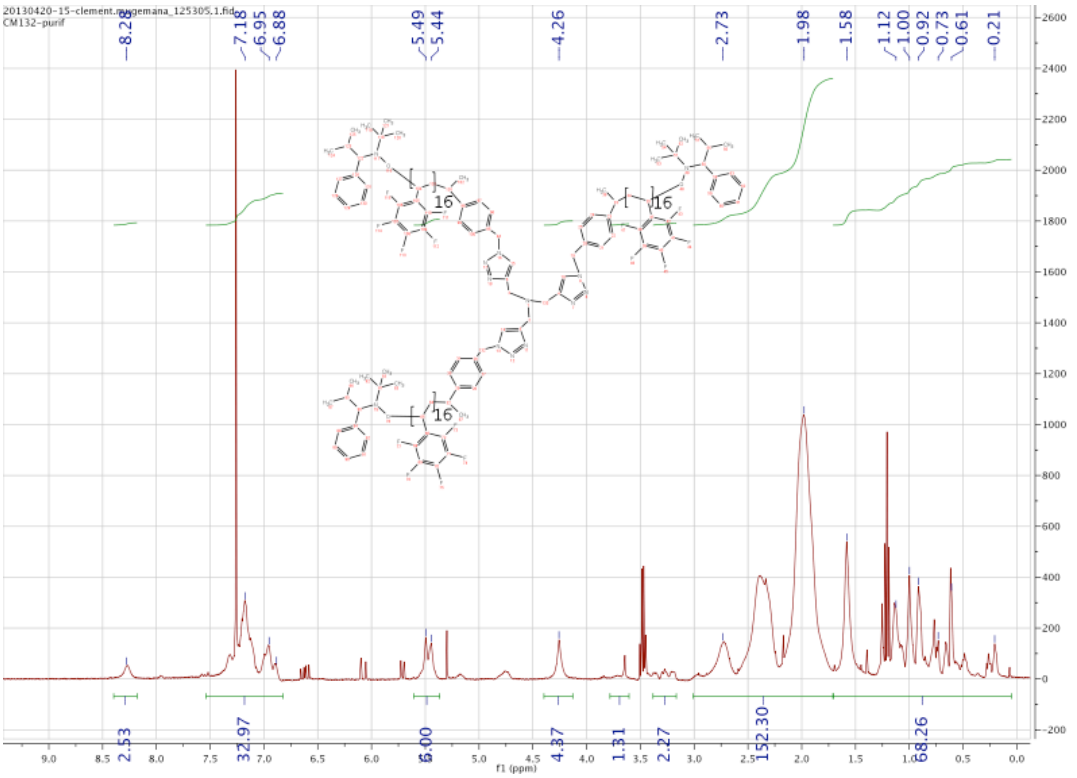


Figure S4. ^{1}H NMR spectrum of $(PFS_{16})_3$ three-arm star polymer in $CDCl_3$.

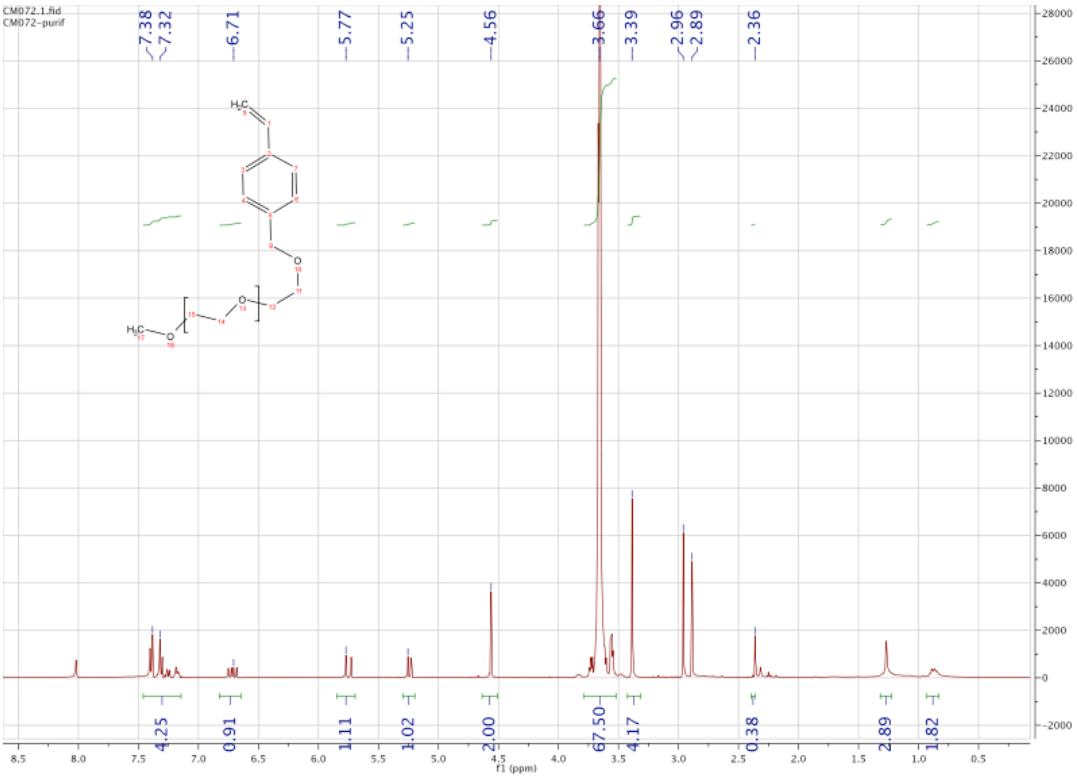


Figure S5. ^{1}H NMR spectrum of polyethylene glycol (Mw: 500 g/mol) methyl styrene in $CDCl_3$.

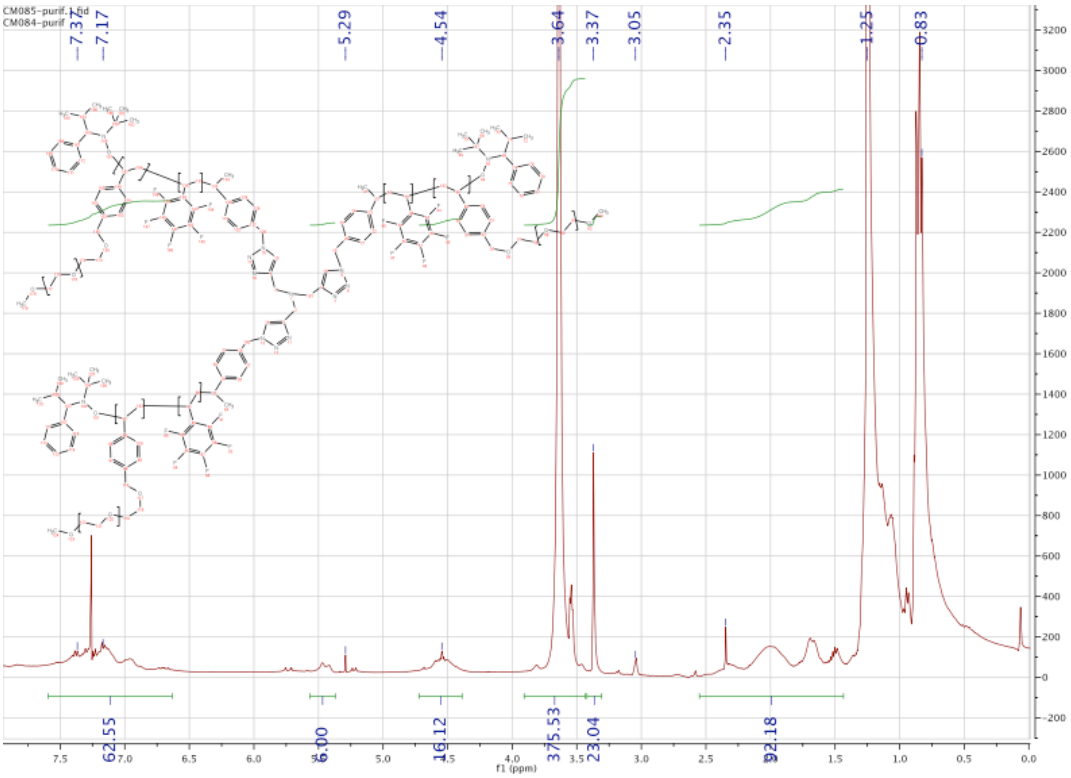


Figure S6. ^{1}H NMR spectrum of $(PFS_{7}$-*b*-$OEGSt_{3})_{3}$ three-arm star block copolymer in $CDCl_{3}$.

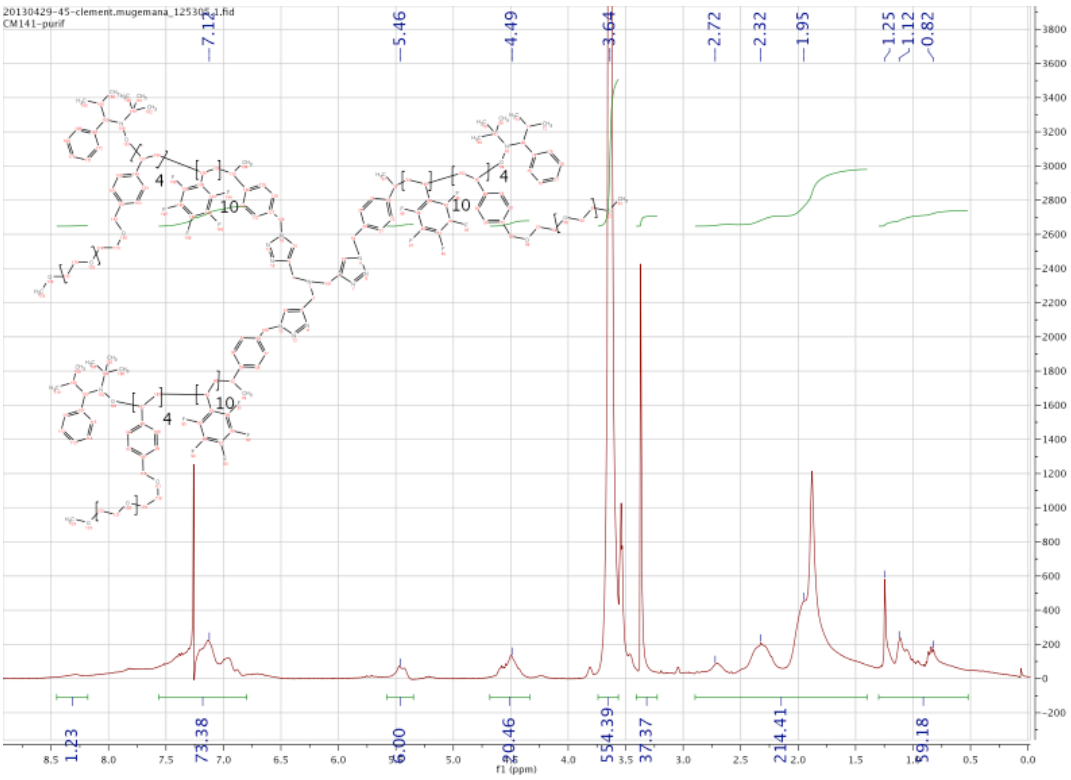


Figure S7. ^{1}H NMR spectrum of $(PFS_{10}$-*b*-$OEGSt_{4})_{3}$ three-arm star block copolymer in $CDCl_{3}$.

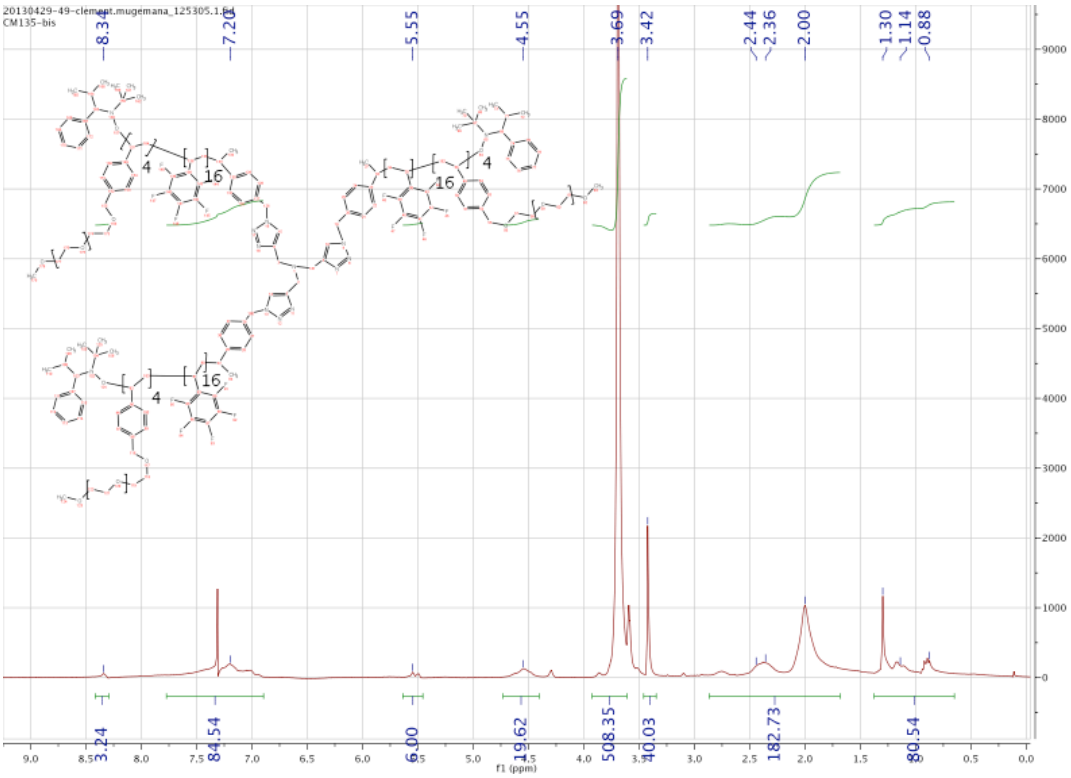


Figure S8. ^{1}H NMR spectrum of $(PFS_{16}$-*b*-$OEGSt_4)_3$ three-arm star block copolymer in $CDCl_3$.

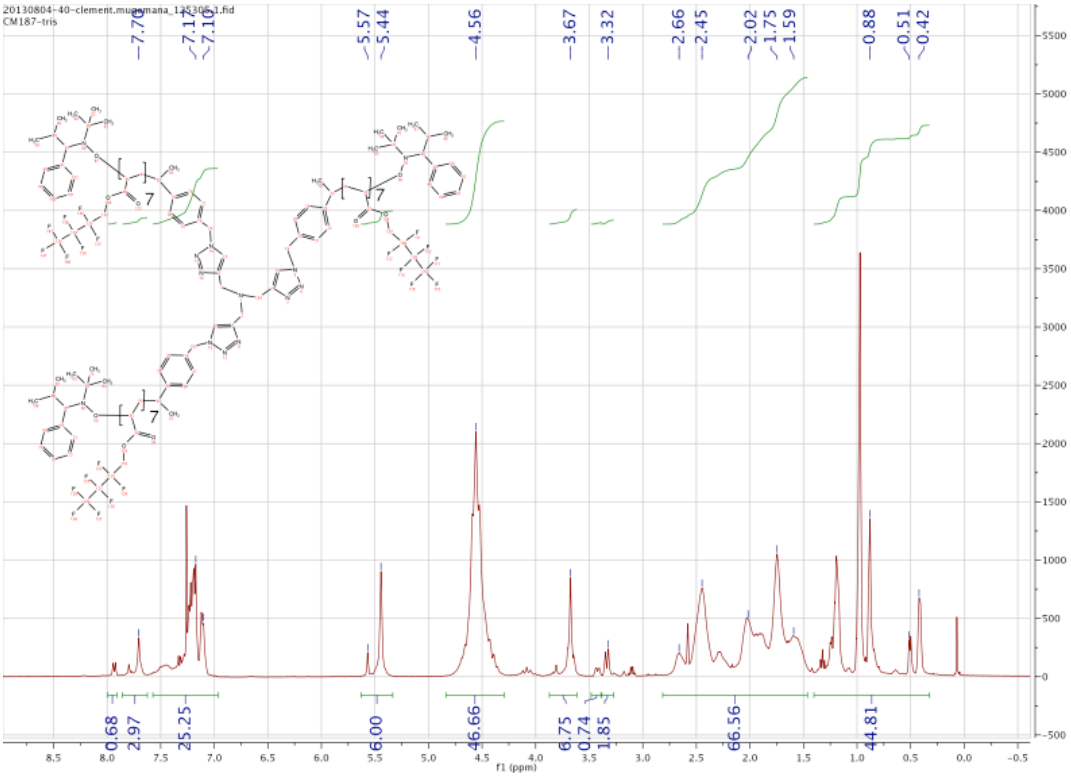


Figure S9. ^{1}H NMR spectrum of $(PFBA_7)_3$ three-arm star polymer in $CDCl_3$.

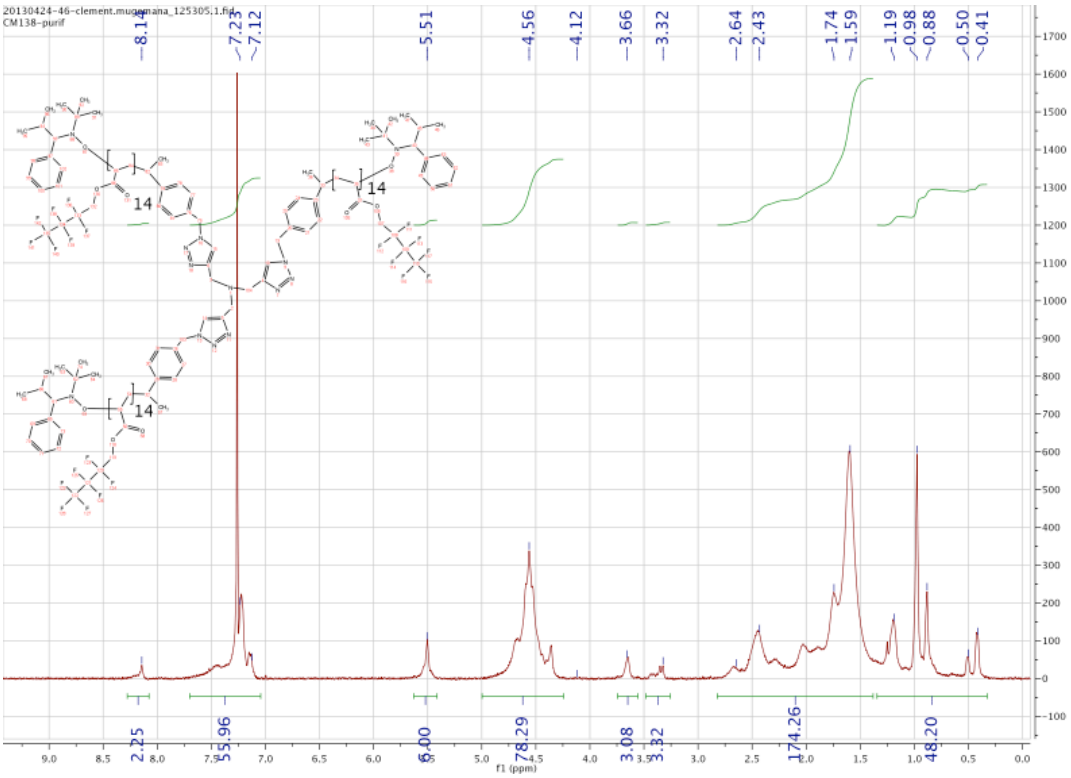


Figure S10. ^{1}H NMR spectrum of $(PFBA_{14})_3$ three-arm star polymer in $CDCl_3$.

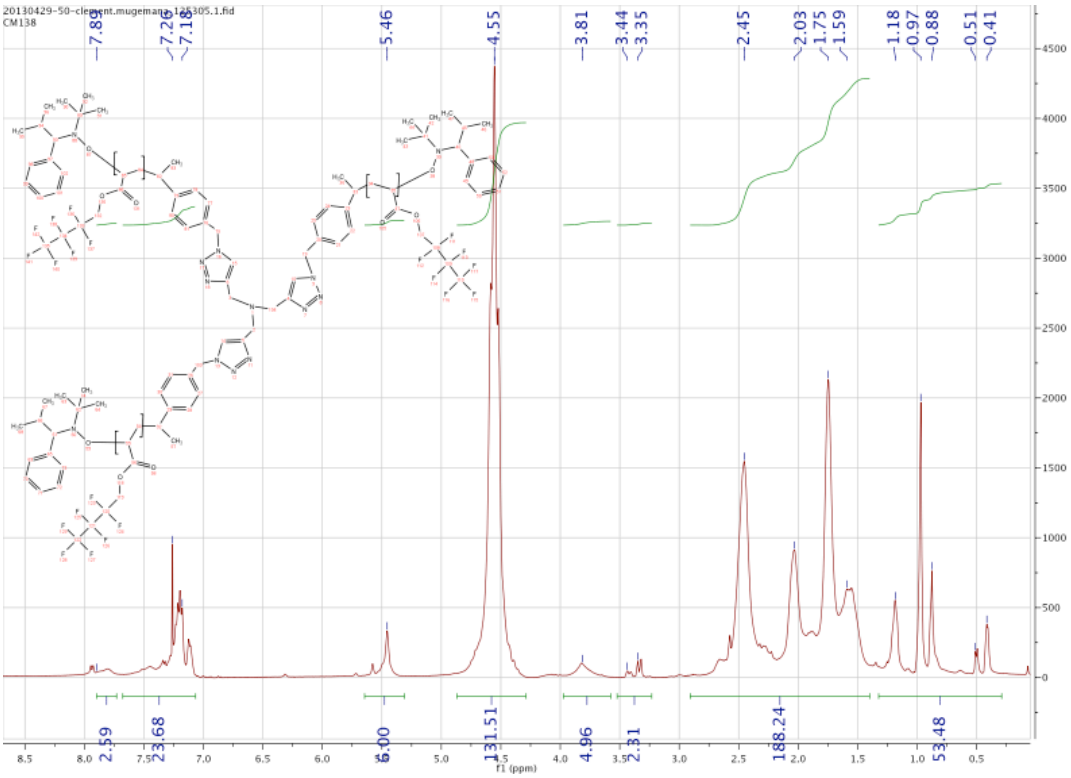


Figure S11. ^{1}H NMR spectrum of $(PFBA_{20})_3$ three-arm star polymer in $CDCl_3$.

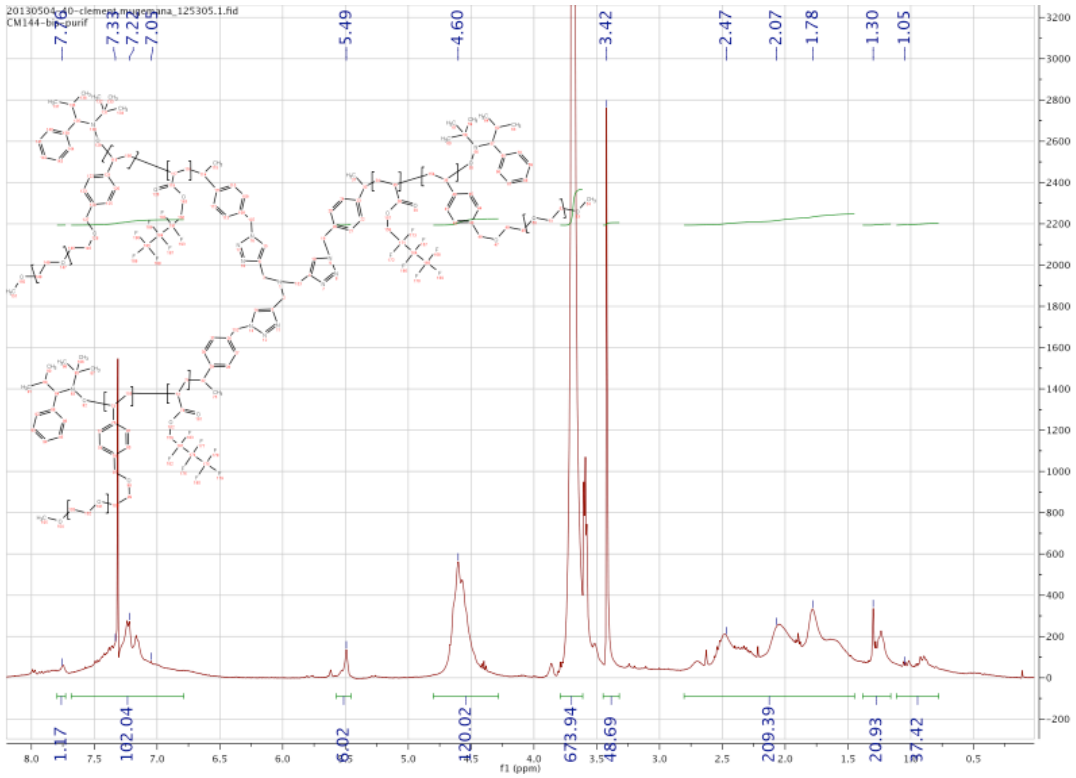


Figure S12. ^{1}H NMR spectrum of $(PFBA_{20}$-*b*-$OGSt_4)_3$ three-arm star block copolymer in $CDCl_3$.

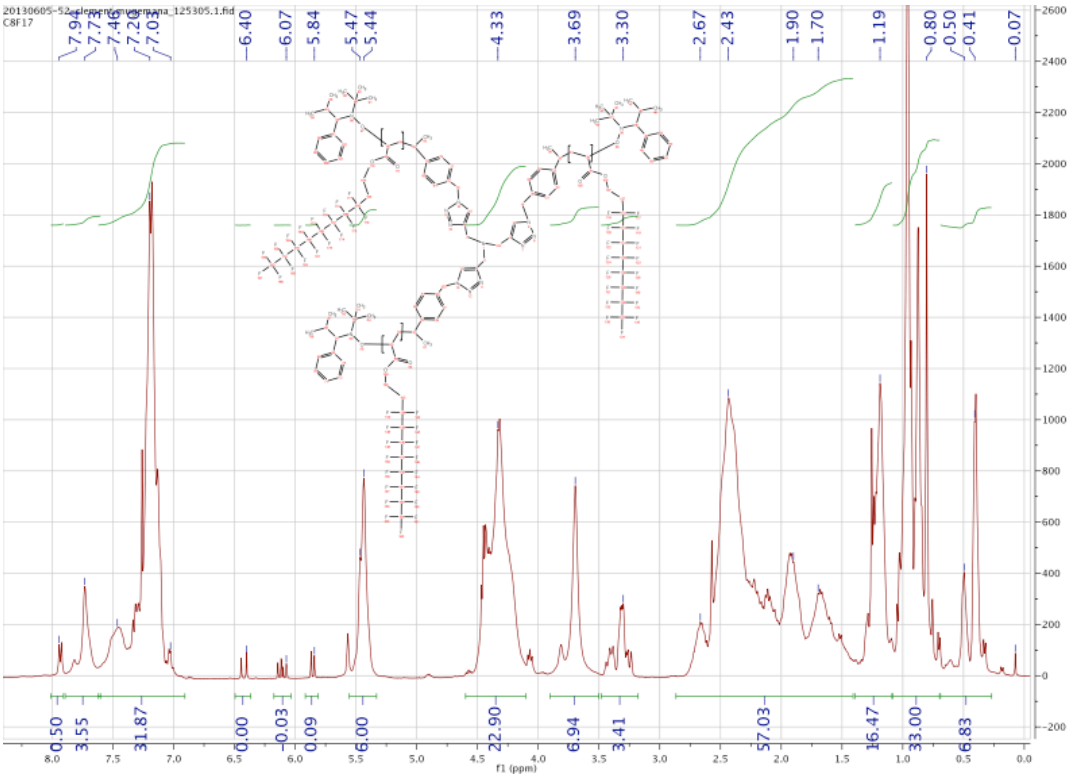


Figure S13. ^{1}H NMR spectrum of $(PFDA_4)_3$ three-arm star polymer in $CDCl_3$.

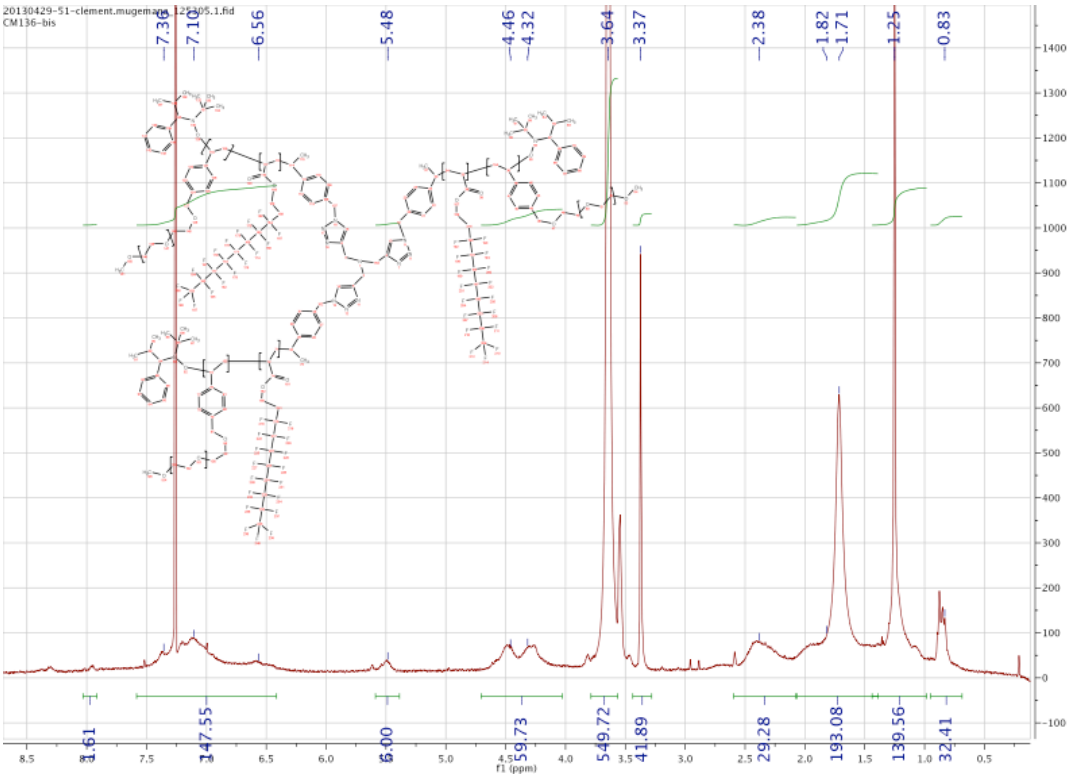


Figure S14. ^{1}H NMR spectrum of (PFDA$_4$-*b*-OEGSt$_4$)$_3$ three-arm star block copolymer in CDCl$_3$.

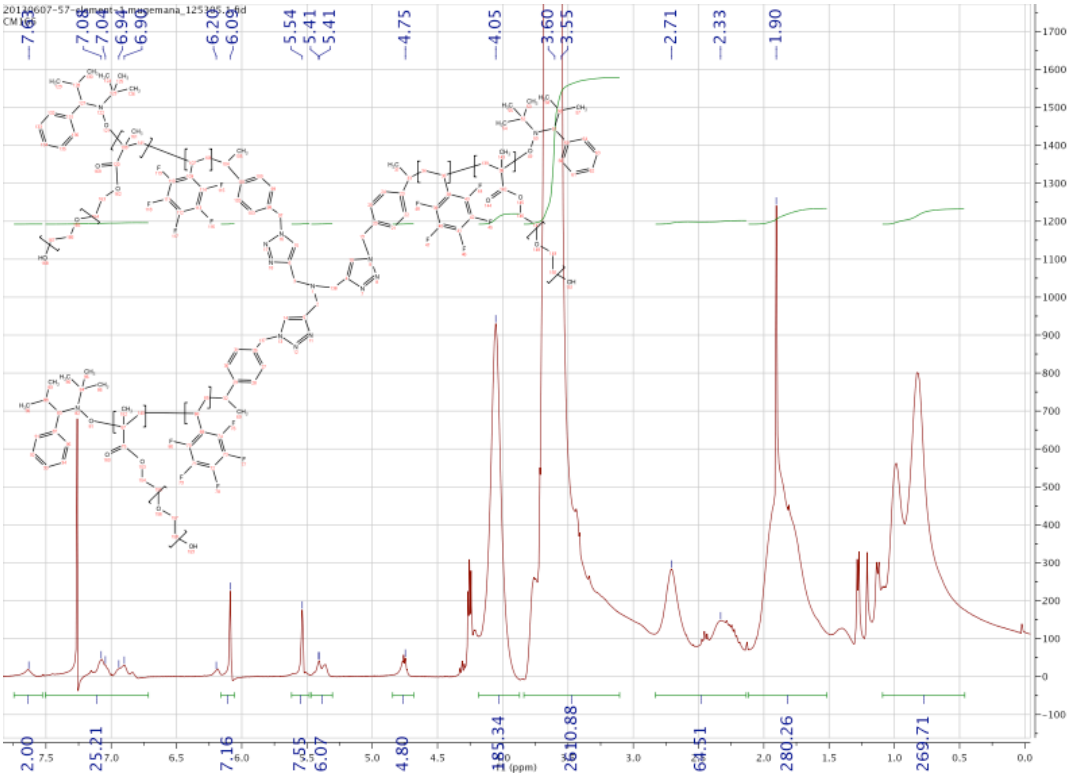


Figure S15. ^{1}H NMR spectrum of (PFS$_{16}$-*b*-OEGMa$_{30}$)$_3$ three-arm star block copolymer in CDCl$_3$.

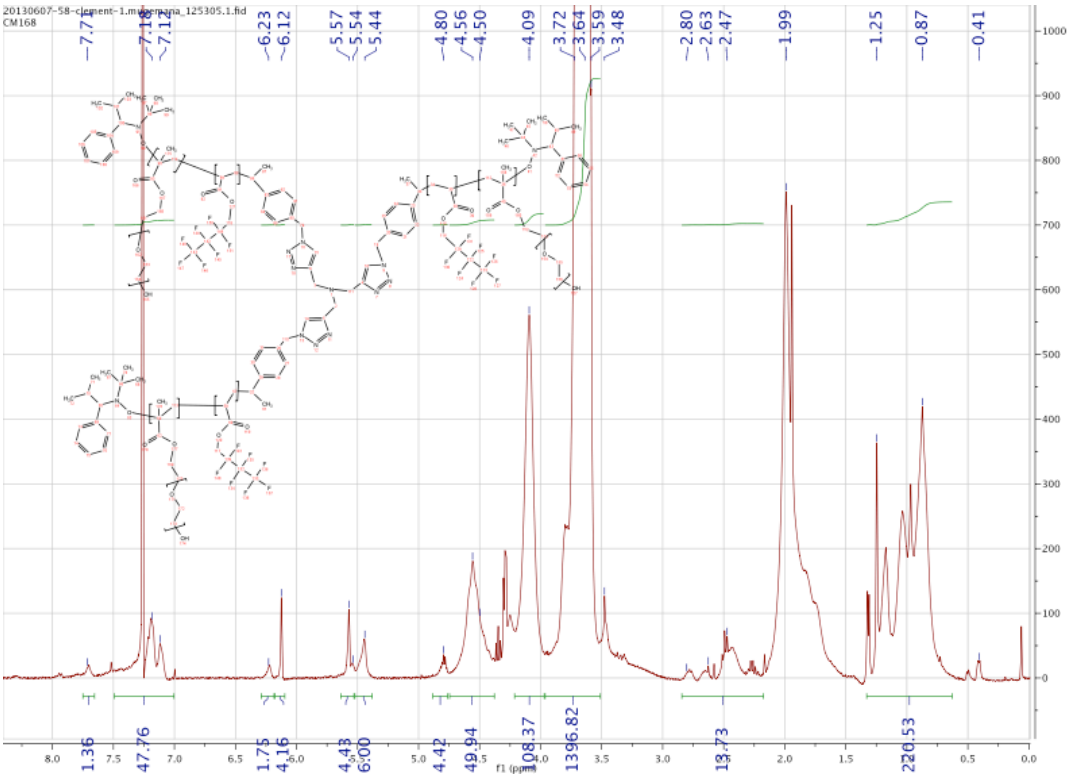


Figure S16. ^{1}H NMR spectrum of (PFBA$_{7}$-*b*-OEGMa$_{18}$)$_{3}$ three-arm star block copolymer in CDCl$_{3}$.

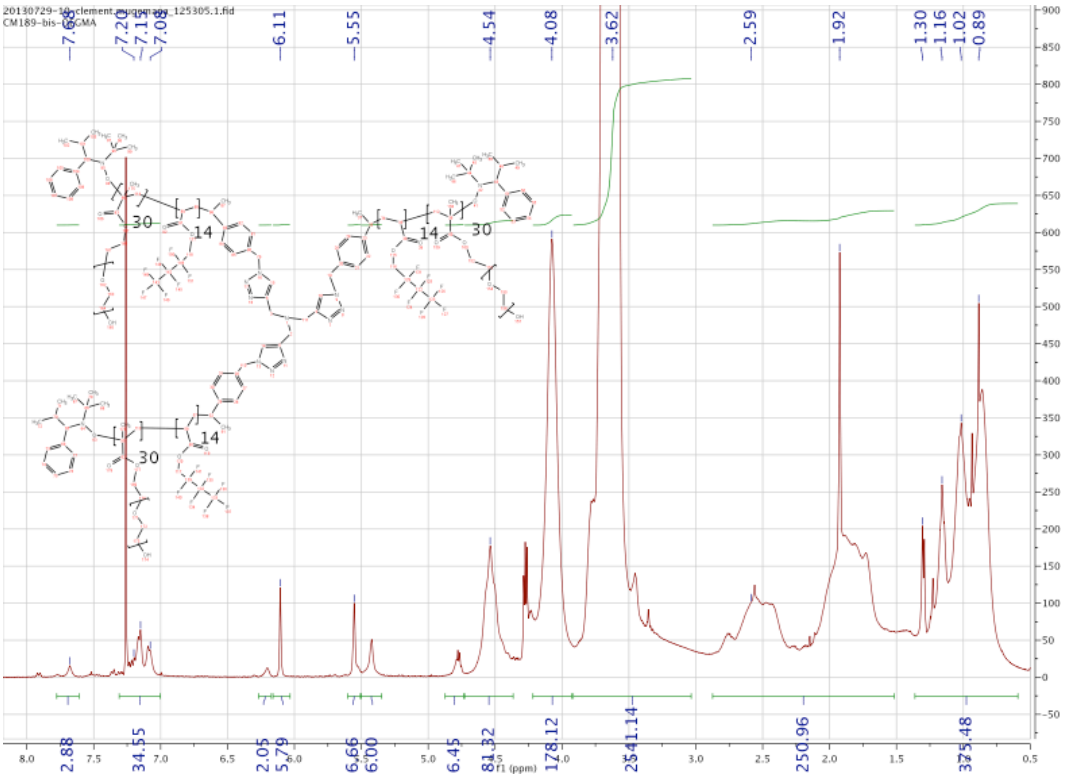


Figure S17. ^{1}H NMR spectrum of (PFBA$_{14}$-*b*-OEGMa$_{30}$)$_{3}$ three-arm star block copolymer in CDCl$_{3}$.

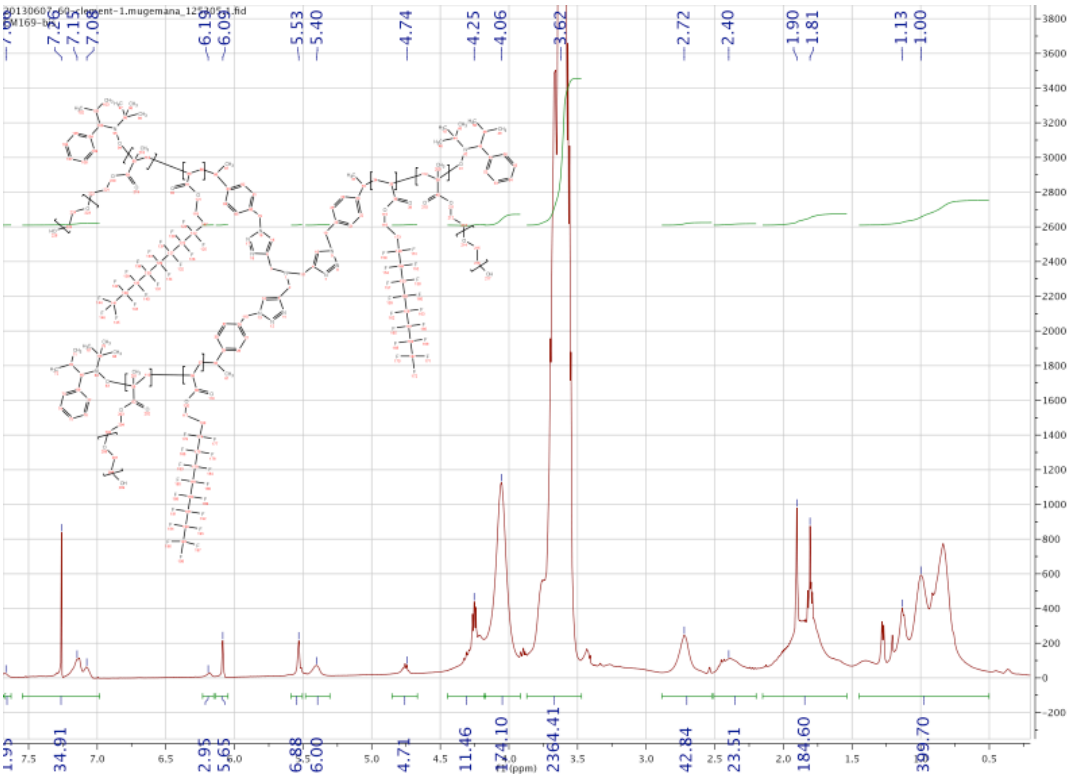


Figure S18. ^{1}H NMR spectrum of (PFDA$_4$-*b*-OEGMa$_{30}$)$_3$ three-arm star block copolymer in $CDCl_3$.

2) ^{13}C NMR spectra

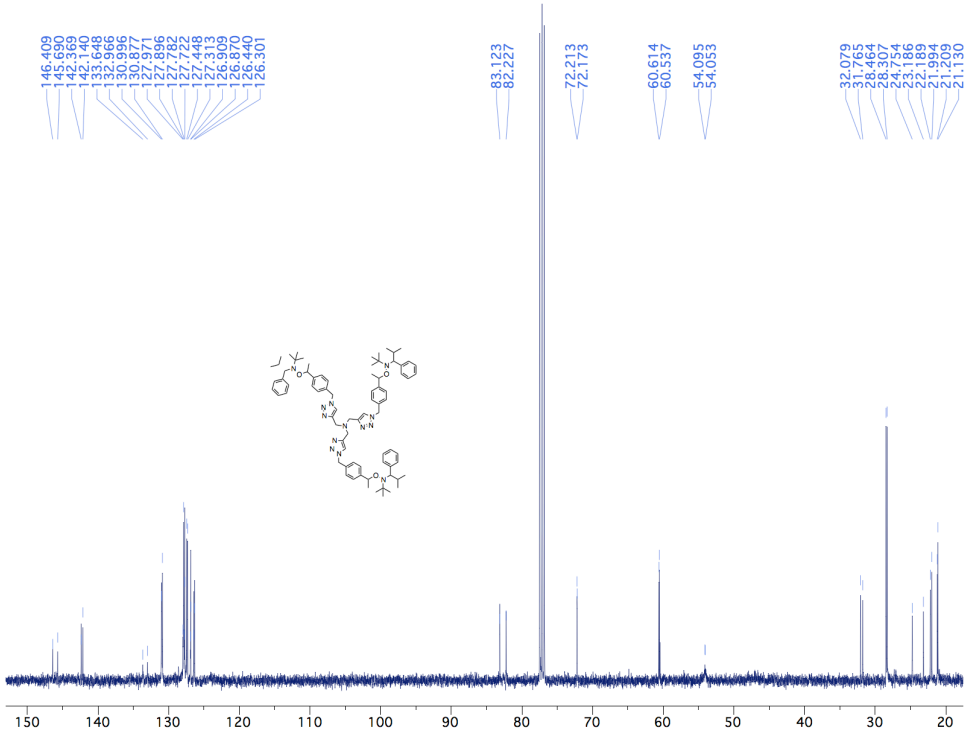


Figure S19. ^{13}C NMR spectrum of tris((1-(4-(1-((*tert*-butyl(2-methyl-1-phenylpropyl)amino)oxy) ethyl)benzyl)-1*H*-1,2,3-triazol-4-yl)methyl)amine in $CDCl_3$.

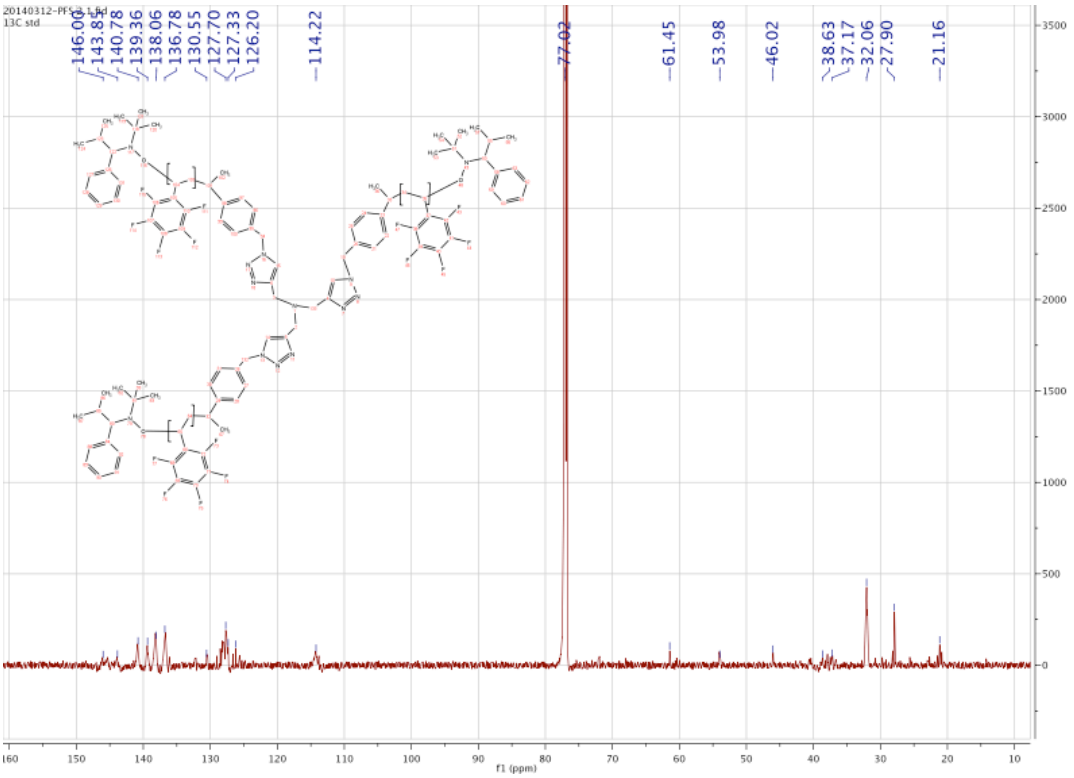


Figure S20. ^{13}C NMR spectrum of $(PFS_7)_3$ three-arm star polymer in $CDCl_3$.

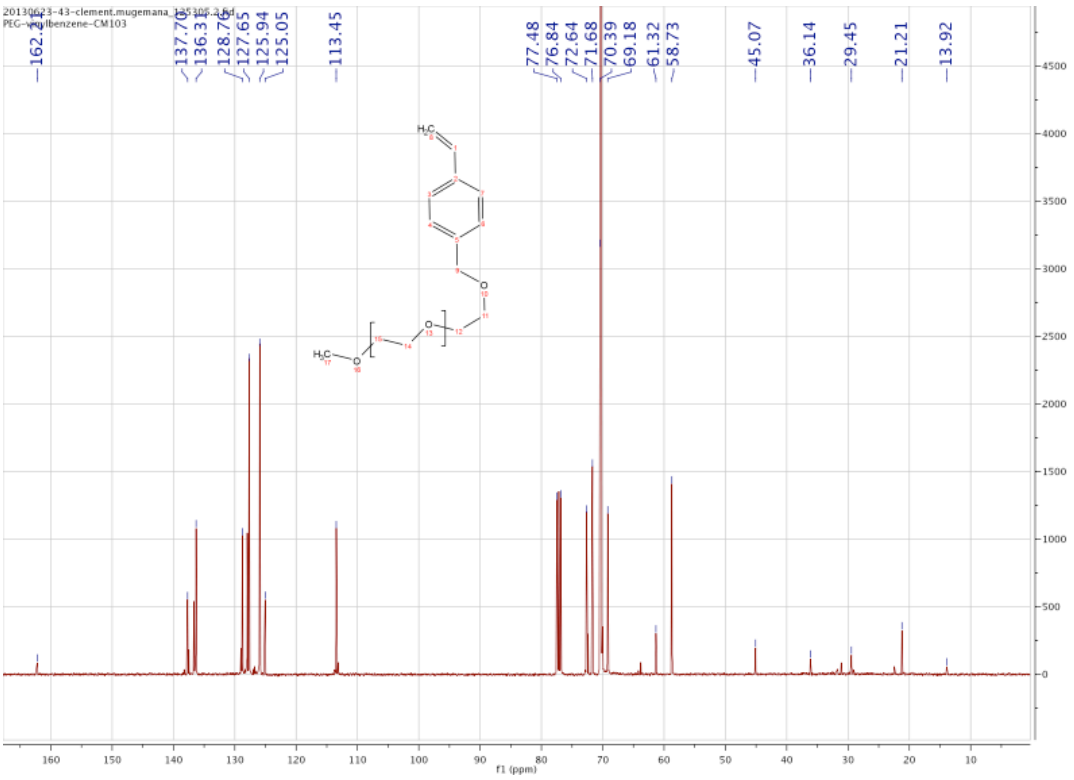


Figure S21. ^{13}C NMR spectrum of 4-polyethylene glycol (Mw: 500 g/mol) methyl styrene in $CDCl_3$.

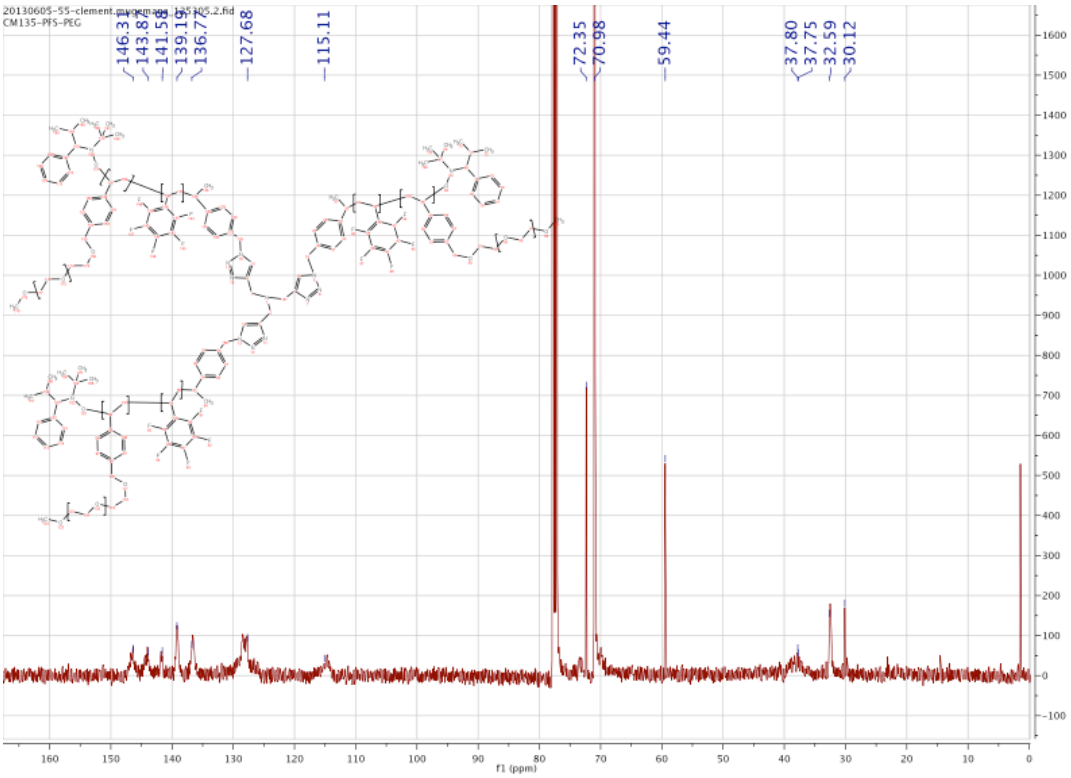


Figure S22. ^{13}C NMR spectrum of $(PFS_7$-*b*-$OEGSt_3)_3$ three-arm star block copolymer in $CDCl_3$.

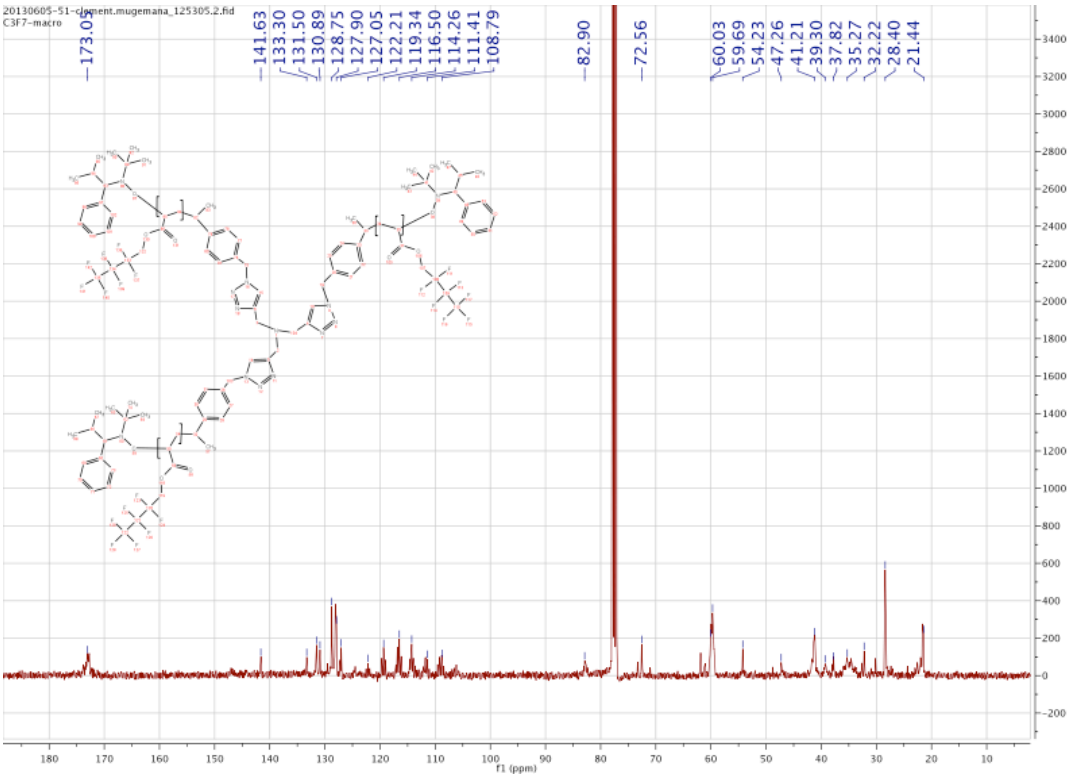


Figure S23. ^{13}C NMR spectrum of $(PFDA_{20})_3$ three-arm star polymer in $CDCl_3$.

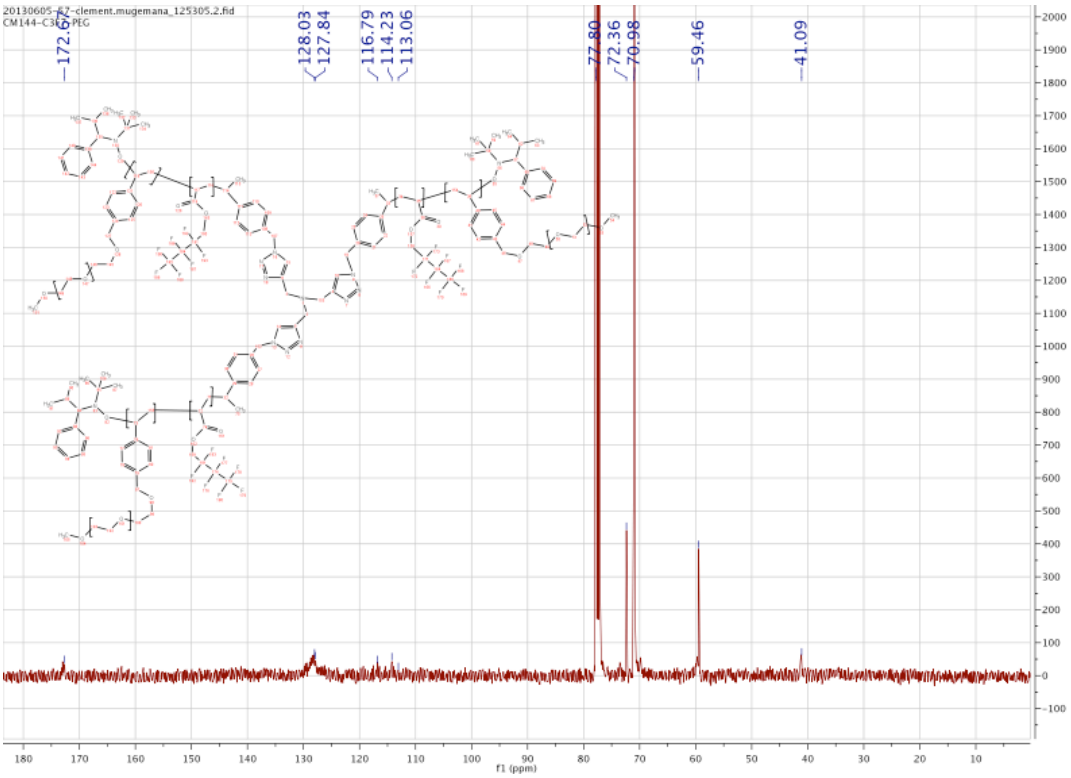


Figure S24. ^{13}C NMR spectrum of $(PFBA_{20}$-*b*-$OEGSt_4)_3$ three-arm star block copolymer in $CDCl_3$.

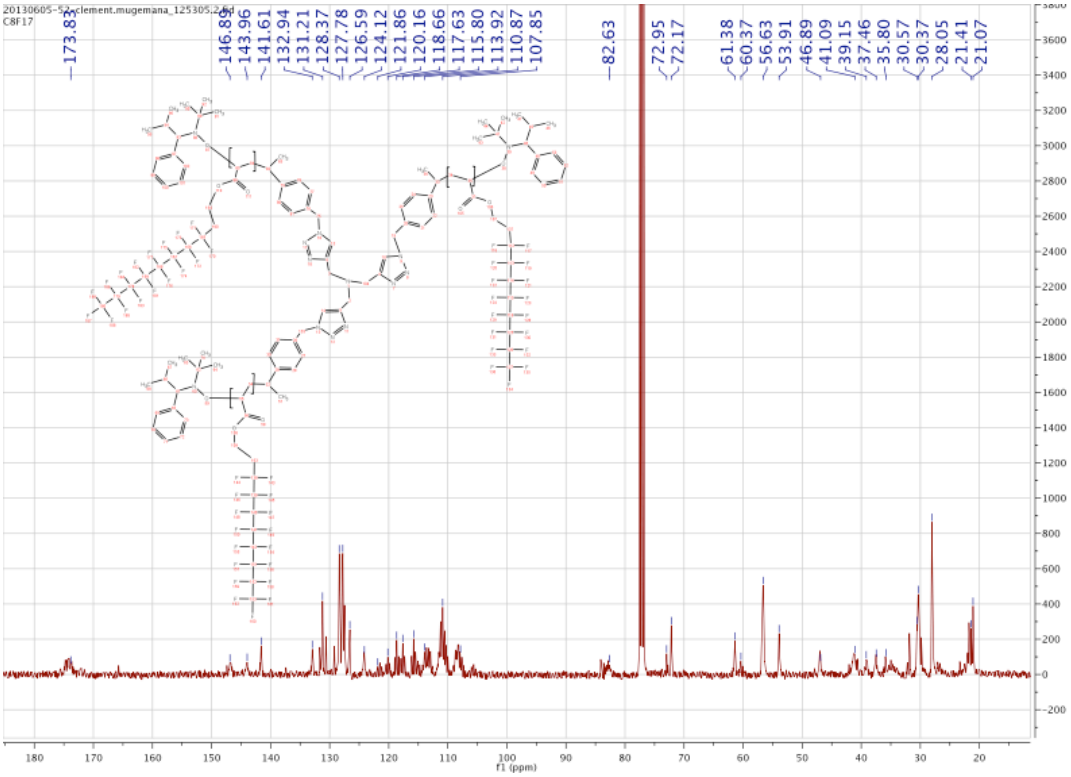


Figure S25. ^{13}C NMR spectrum of $(PFDA_4)_3$ three-arm star polymer in $CDCl_3$.

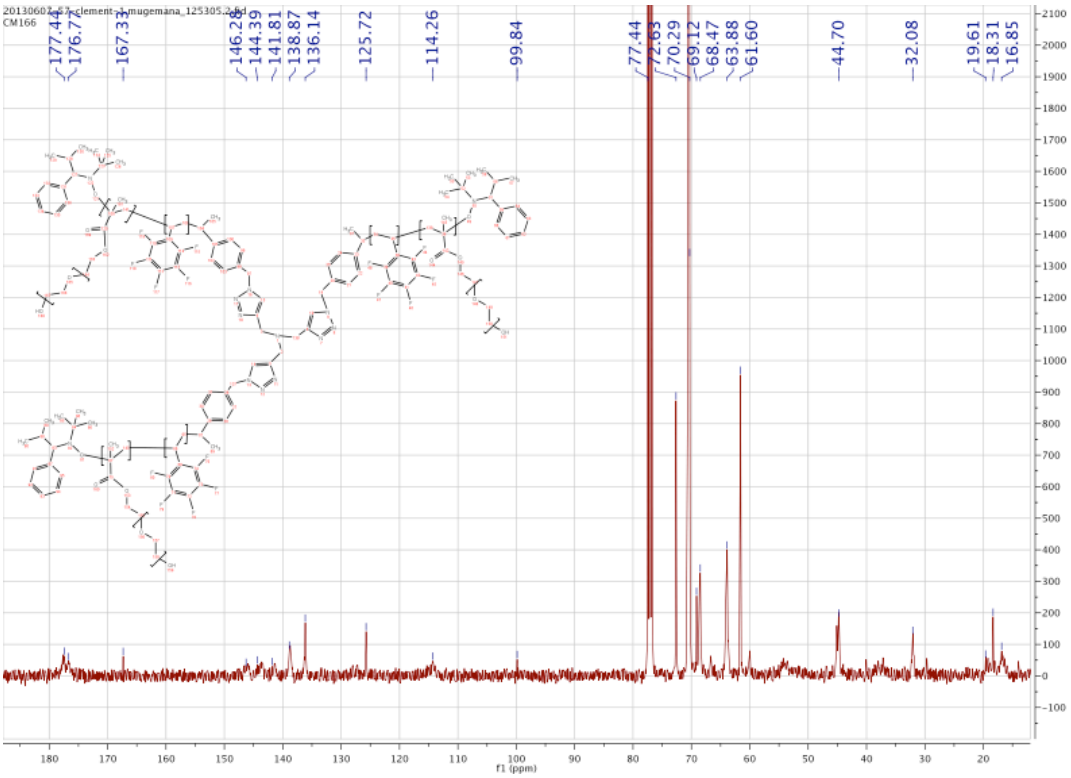


Figure S26. ^{13}C NMR spectrum of $(PFS_{16}$-*b*-$OEGMa_{30})_3$ three-arm star block copolymer in $CDCl_3$.

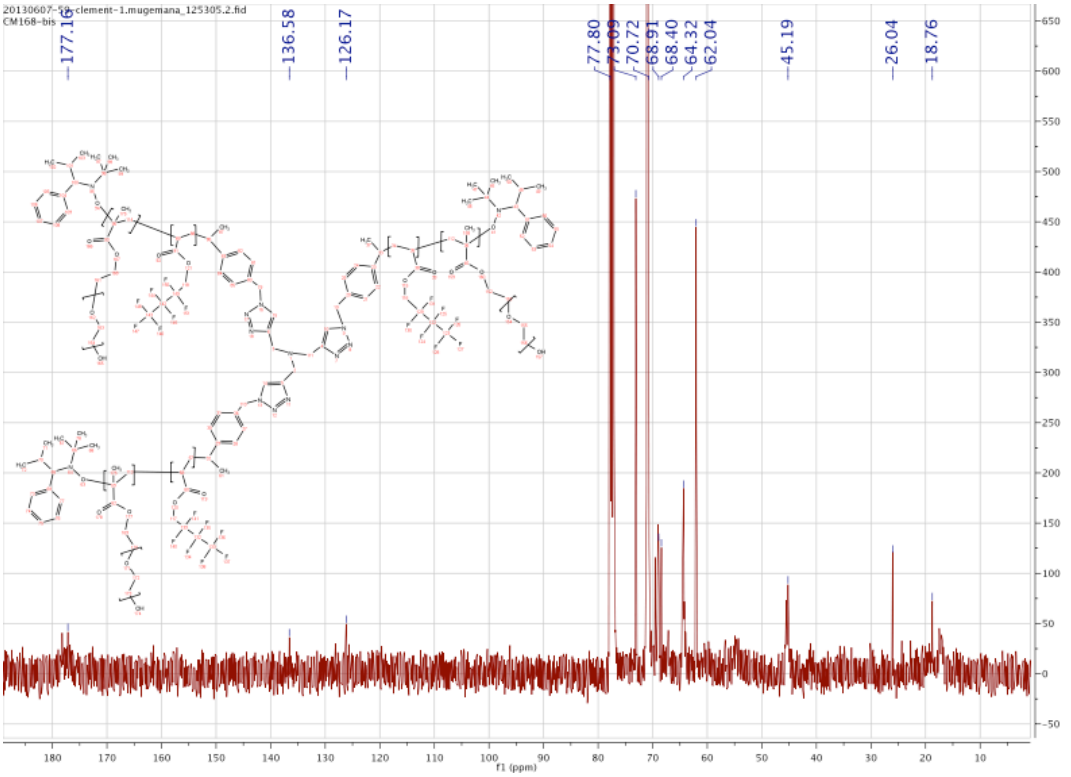


Figure S27. ^{13}C NMR spectrum of $(PFBA_7$-*b*-$OEGMa_{18})_3$ three-arm star block copolymer in $CDCl_3$.

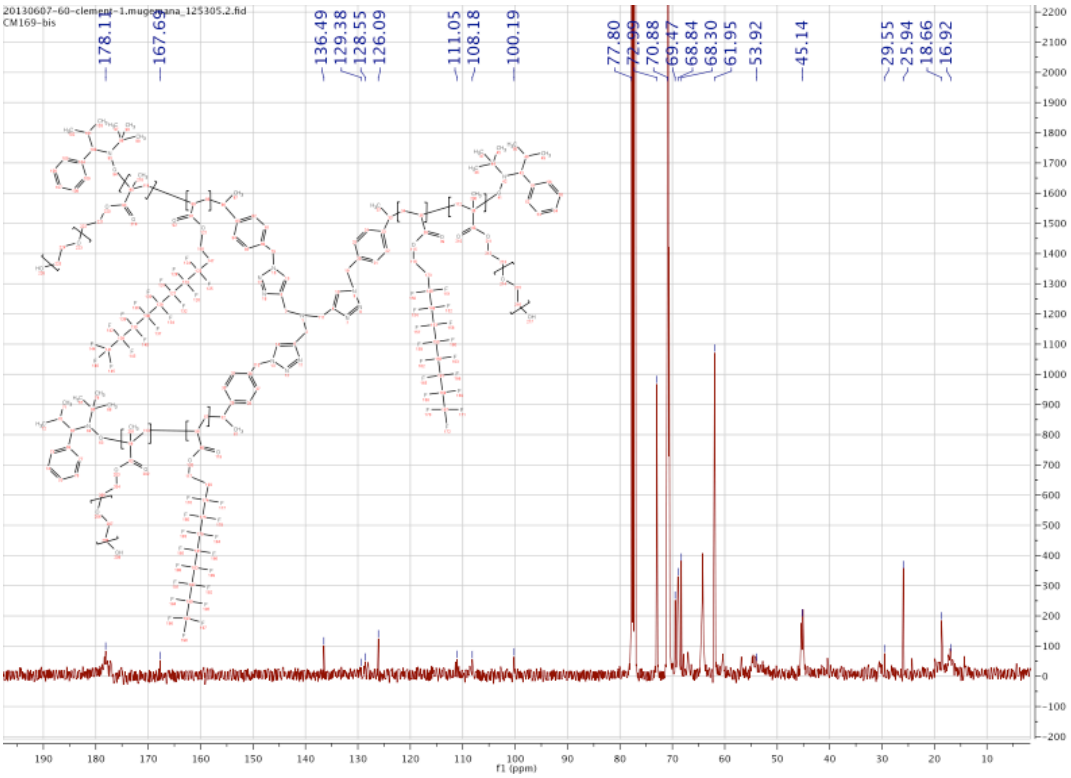


Figure S28. ^{13}C NMR spectrum of (PFDA$_4$-*b*-OEGMa$_{30}$)$_3$ three-arm star block copolymer in $CDCl_3$.

3) ^{19}F NMR Spectra

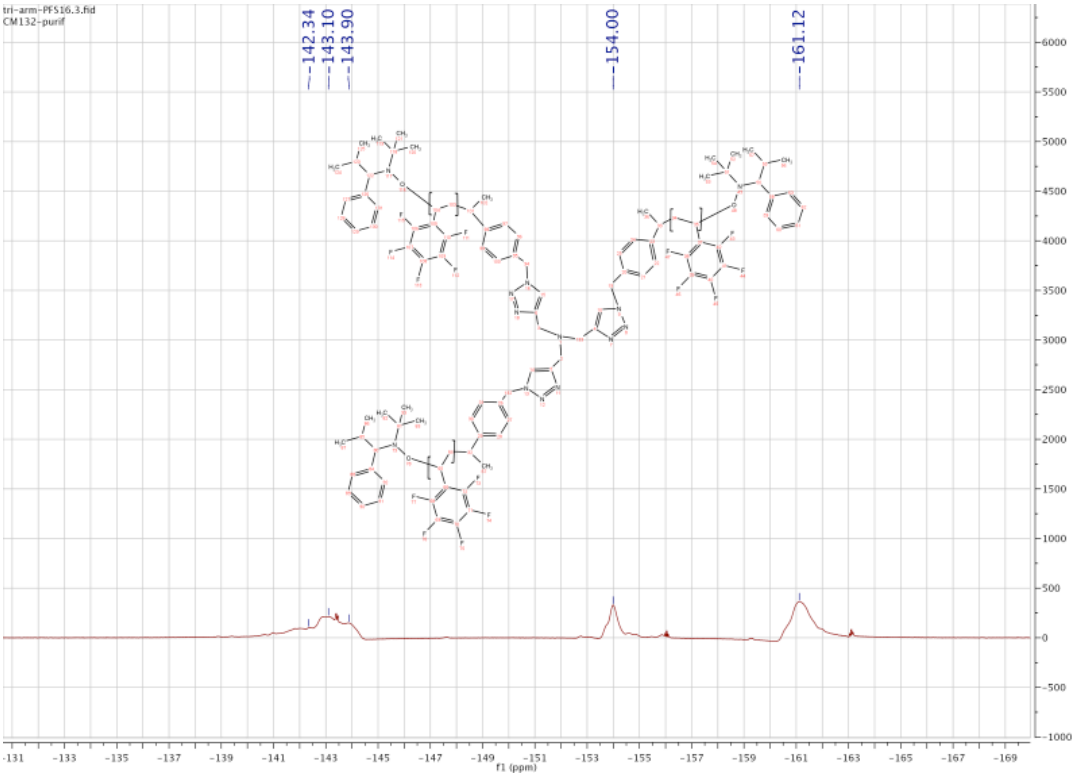


Figure S29. ^{19}F NMR spectrum of (PFS$_{16}$)$_3$ three-arm star block copolymer in $CDCl_3$.

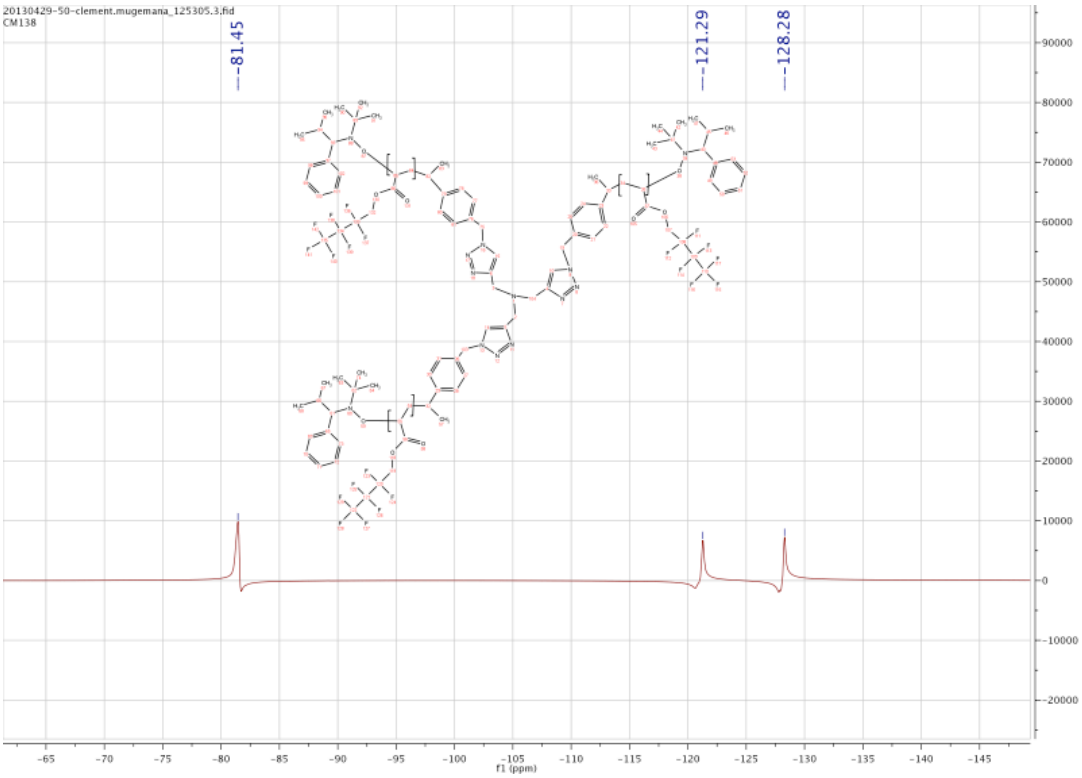


Figure S30. ^{19}F NMR spectrum of $(PFBA_{20})_3$ three-arm star block copolymer in $CDCl_3$.

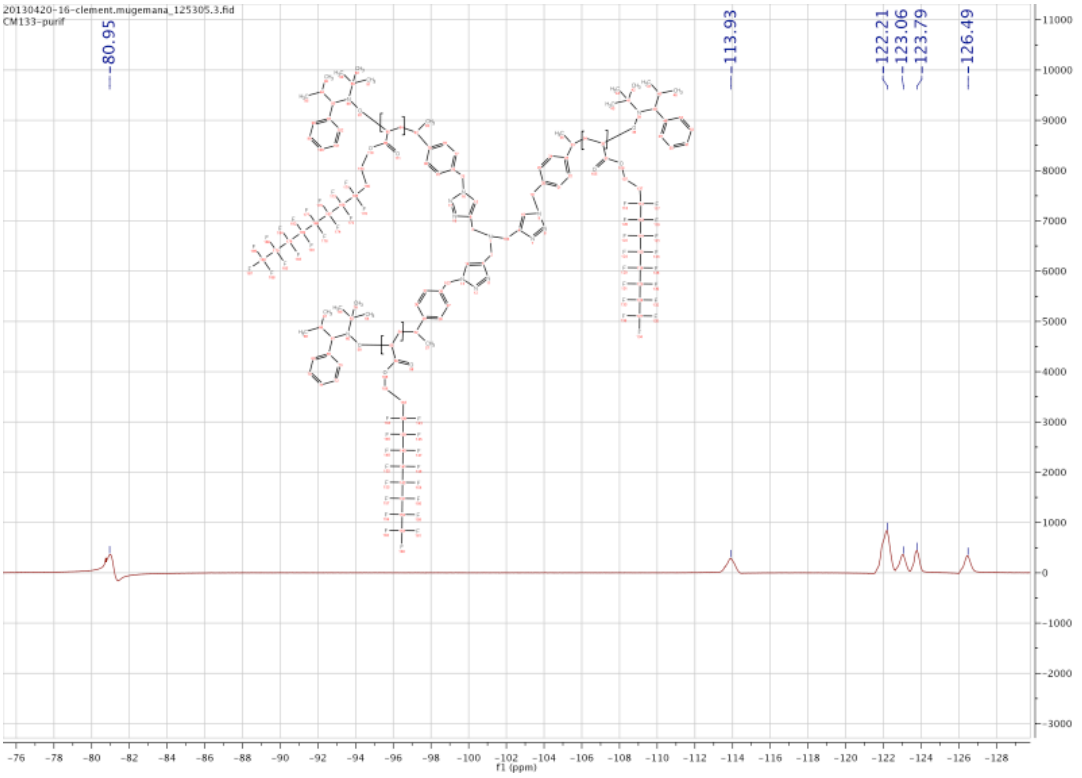


Figure S31. ^{19}F NMR spectrum of $(PFDA_4)_3$ three-arm star block copolymer in $CDCl_3$.

4) Size Exclusion Chromatography

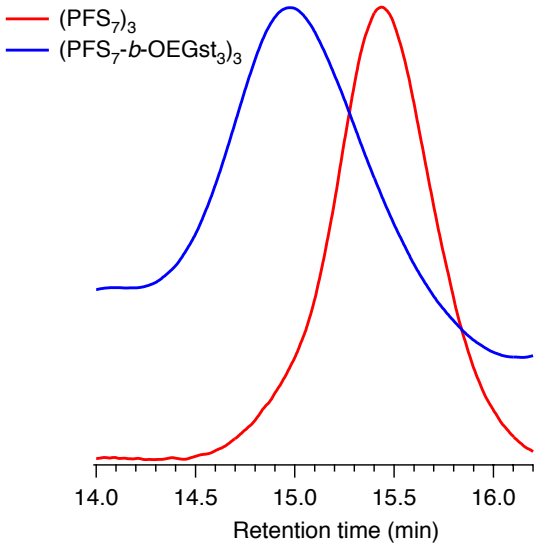


Figure S32. SEC curve (RID) of $(PFS_7)_3$ star macro-initiator and $(PFS_7$-*b*-$OEGSt_3)_3$ three-arm star block copolymer.

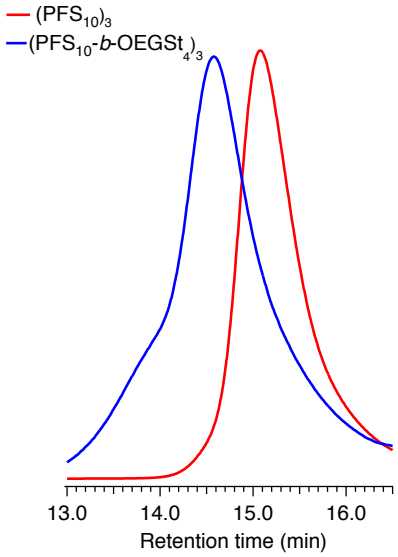


Figure S33. SEC curve (RID) of $(PFS_{10})_3$ star macro-initiator and $(PFS_{10}$-*b*-$OEGSt_4)_3$ three-arm star block copolymer.

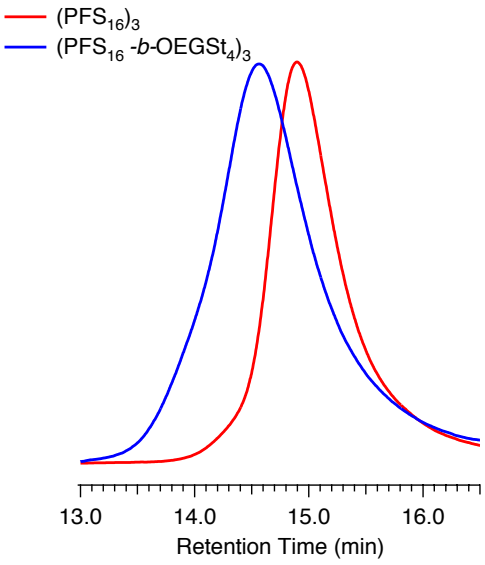


Figure S34. SEC curve (RDI) of $(PFS_{16})_3$ star macro-initiator and $(PFS_{16}$-*b*-$OEGSt_4)_3$ three-arm star block copolymer.

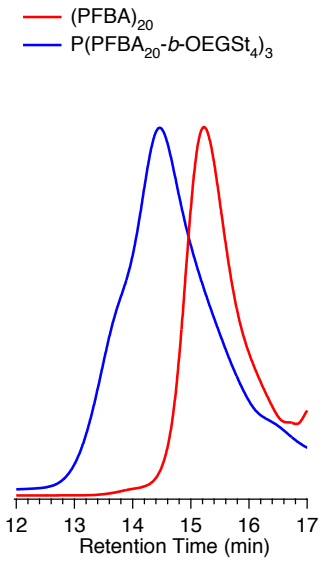


Figure S35. SEC curve (UV) of $(PFBA_{20})_3$ star macro-initiator and $PFBA_{20}$-*b*-$OGSt_4)_3$ three-arm star block copolymer.

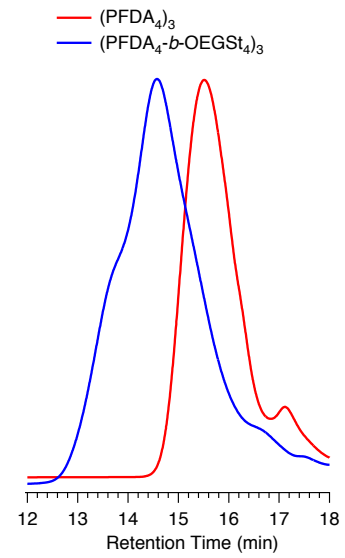


Figure S36. SEC curve (UV) of $(PFDA_4)_3$ star macro-initiator and $(PFDA_4$-*b*-$PEGSt_4)_3$ three-arm star block copolymer.

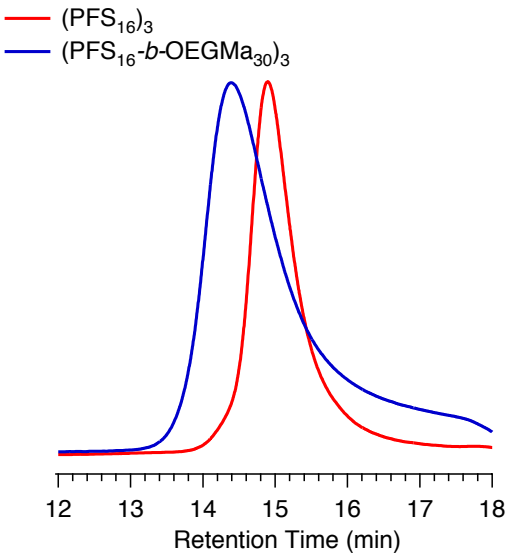


Figure S37. SEC curve (RID) of $(PFS_{16})_3$ star macro-initiator and $(PFS_{16}$-*b*-$OEGMa_{30})_3$ three-arm star block copolymer.

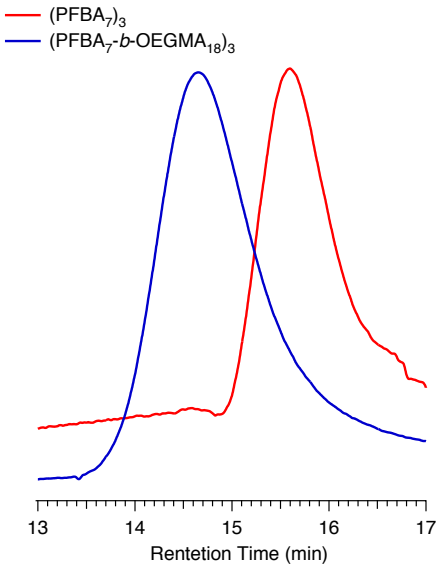


Figure S38. SEC curve (RID) of $(PFBA_7)_3$ star macro-initiator and $(PFBA_7$-*b*-$OEGMa_{18})_3$ three-arm star block copolymer.

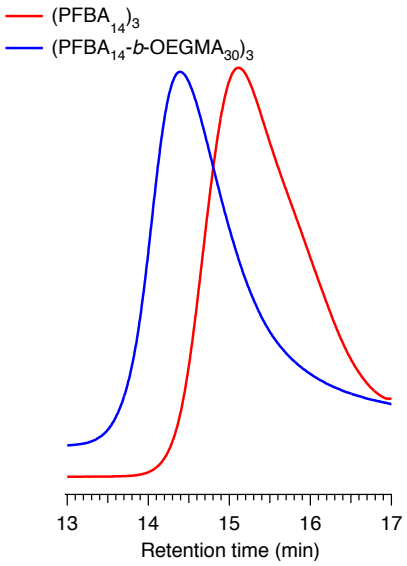


Figure S39. SEC curve (RID) of $(PFBA_{14})_3$ star macro-initiator and $(PFBA_{14}$-*b*-$OEGMa_{30})_3$ three-arm star block copolymer.

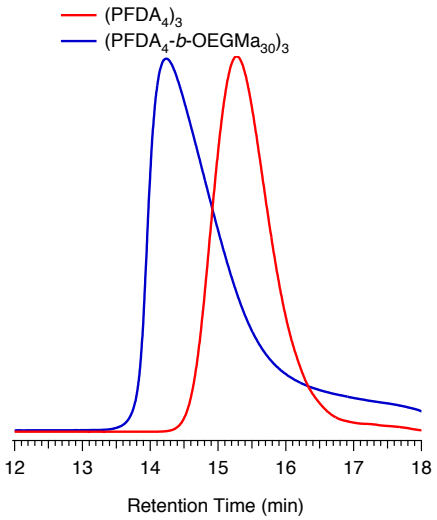


Figure S40. SEC curve (RID) of SEC curve (DRI) of $(PFDA_4)_3$ star macro-initiator and $(PFDA_4$-*b*-$OEGMa_{30})_3$ three-arm star block copolymer.

5) Dynamic Light Scattering

To prepare solutions of $(PFS_7\text{-}b\text{-}OEGSt_3)_3$, $(PFS_{16}\text{-}b\text{-}OEGSt_4)_3$ and $(PFDA_4\text{-}b\text{-}OEGSt_4)_3$, 3 mg of polymers were dissolved in 1.5 mL of DMF, then 0.75 mL of water (deionized water) were added dropwise to induce micellization, and another volume (0.75 mL) of water was added in one portion. The DMF-water solution was then dialyzed overnight against water using an 8K cut-off membrane to give a micellar solution of 1 g/L concentration. The solution was filtered through a 1 μm glass fiber membrane prior to analysis.

Vesicles of $(PFBA_{20}\text{-}b\text{-}OEGSt_4)_3$ copolymer were prepared by dissolving 10 mg of polymer in 1.5 mL of DMF, followed by the addition 1.5 mL of deionized water was added using a syringe pump at 0.5 mL/ hour. The DMF-water solution was then dialyzed overnight against water using an 8K cut-off membrane to give a 1 g/L concentration of the micellar solution. The solution was filtered through a 1 μm glass fiber membrane prior to analysis.

Micelles from $(PFS_{16}\text{-}b\text{-}OEGMa_{30})_3$, $(PFBA_7\text{-}b\text{-}OEGMa_{18})_3$ and $(PFDA_4\text{-}b\text{-}OEGMa_{30})_3$ star block copolymer samples were prepared by vigorously stirring the star polymers in water for 5 days to reach 1 g/L concentration, then filtered through a 1 μm glass fiber membrane prior to analysis.

For each sample, intensity size distribution was measured, and converted to volume size distribution (using standard parameters for polystyrene latex). The conversion of an intensity distribution to a volume distribution relies on several assumptions: Furthermore, knowledge of the refractive index of the material is assumed. However, the volume distributions thus obtained are useful for comparative purposes, and for estimating relative sizes of particle populations.

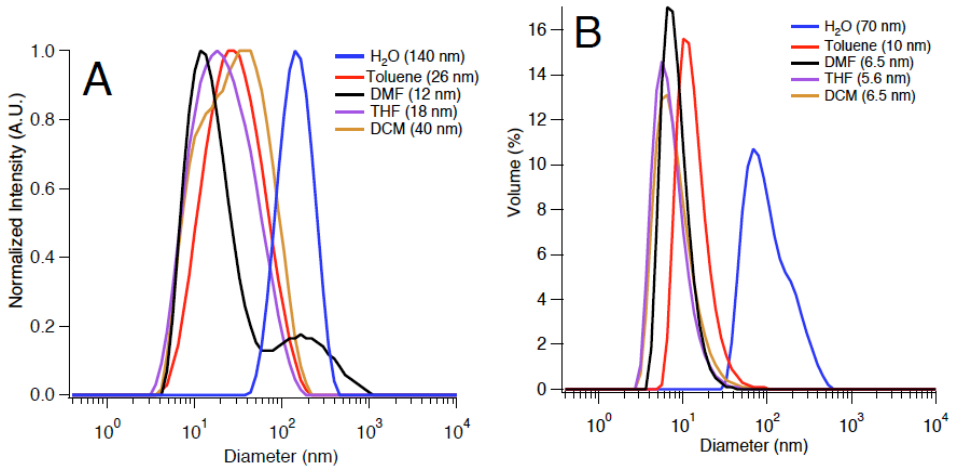


Figure S41. Size distribution by intensity (A) and by volume (B) of $(PFS_{16}\text{-}b\text{-}OEGSt_4)_3$ star polymer in organic solvent and water at 1 g/L concentration.

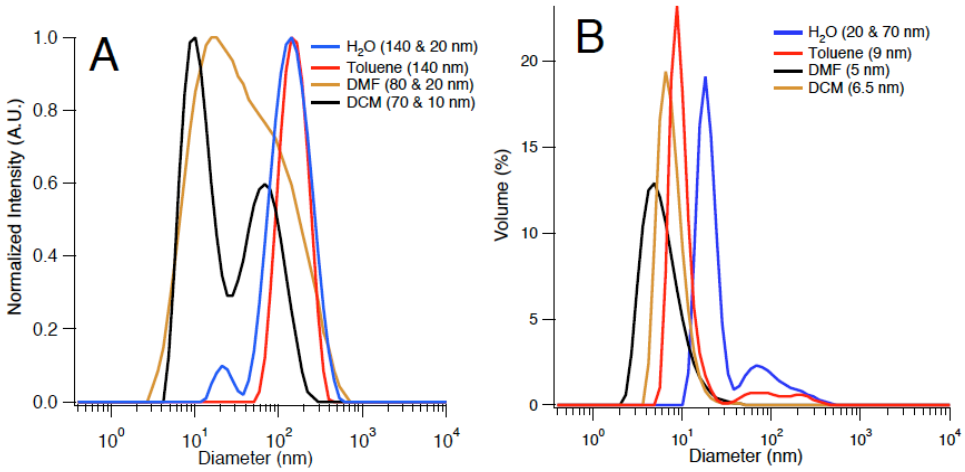


Figure S42. Size distribution by intensity (A) and by volume (B) of ($PFDA_4$-*b*-$OEGSt_4)_3$ star polymer in organic solvent and water at 1 g/L concentration.

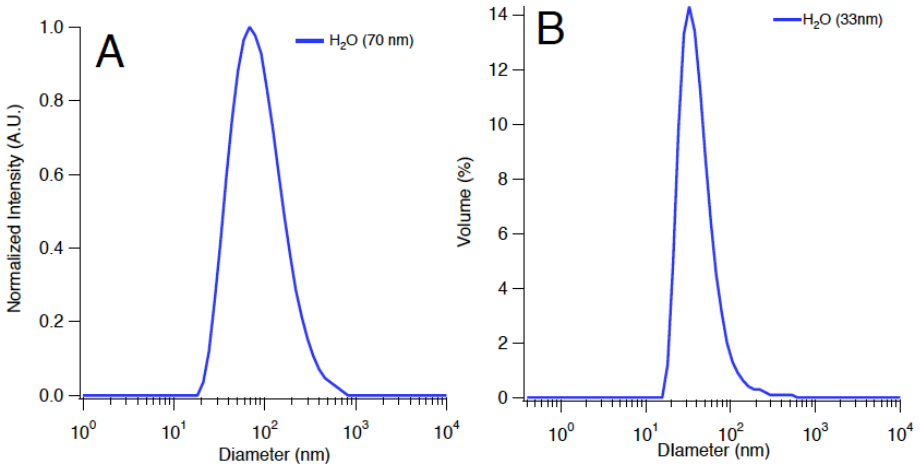


Figure S43. Size distribution by intensity (A) and by volume (B) of ($PFBA_{20}$-*b*-$OEGSt_4)_3$ star polymer in water at 3.3 g/L concentration.

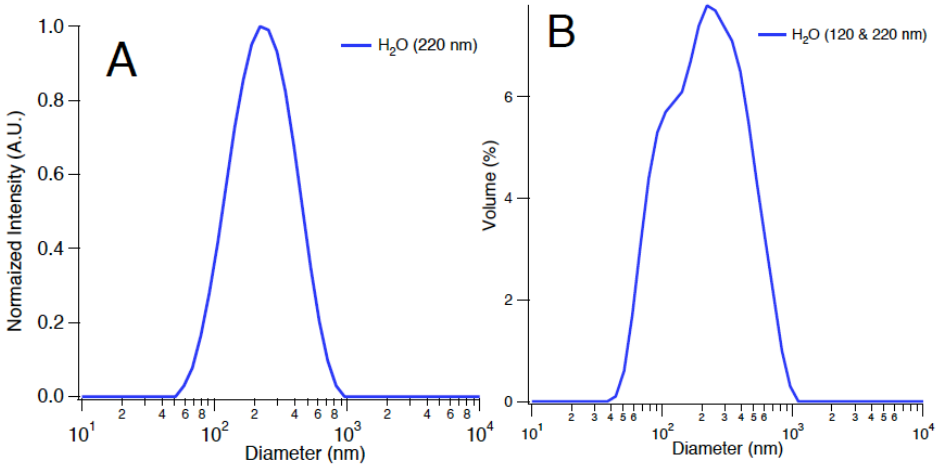


Figure S44. Size distribution by intensity (A) and by volume (B) of (PFS_{16}-*b*-$OEGMa_{30}$)$_3$ star polymer micelles in water at 1 g/L concentration.

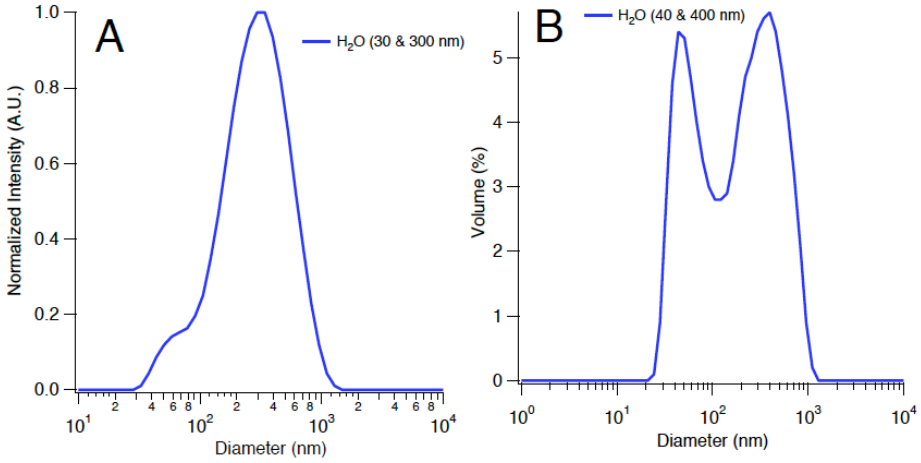


Figure S45. Size distribution by intensity (A) and by volume (B) of ($PFBA_7$-*b*-$OEGMa_{18}$)$_3$ star polymer micelles in water at 1 g/L concentration

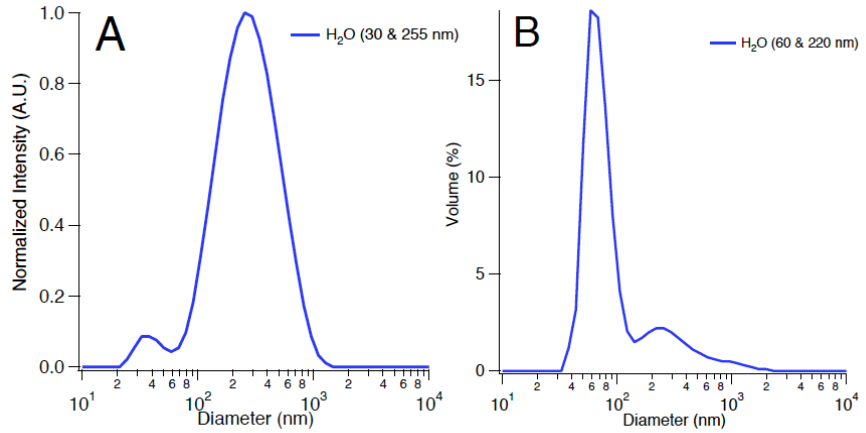


Figure S46. Size distribution by intensity (A) and by volume (B) of (PFBA$_{14}$-*b*-OEGMa$_{30}$)$_3$ star polymer micelles in water at 1 g/L concentration.

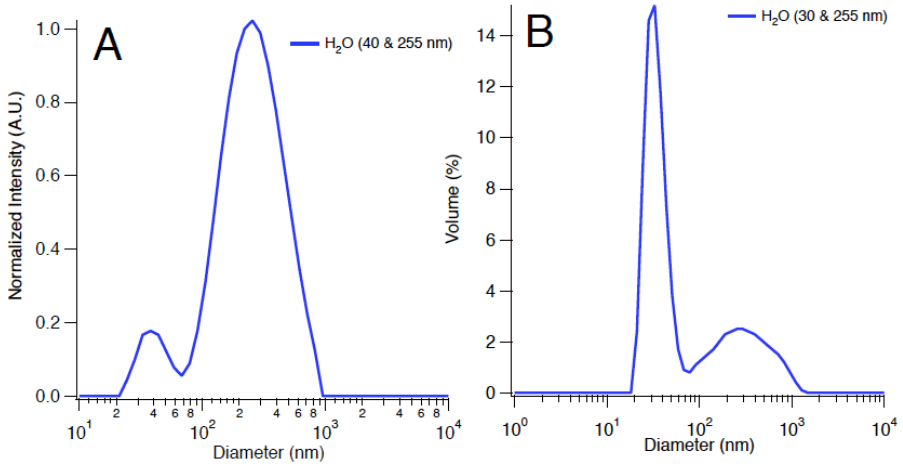


Figure S47. Size distribution by intensity (A) and by volume (B) of (PFDA$_4$-*b*-OEGMa$_{30}$)$_3$ star polymer micelles in water at 1 g/L concentration.

6) Atomic Force Microscopy

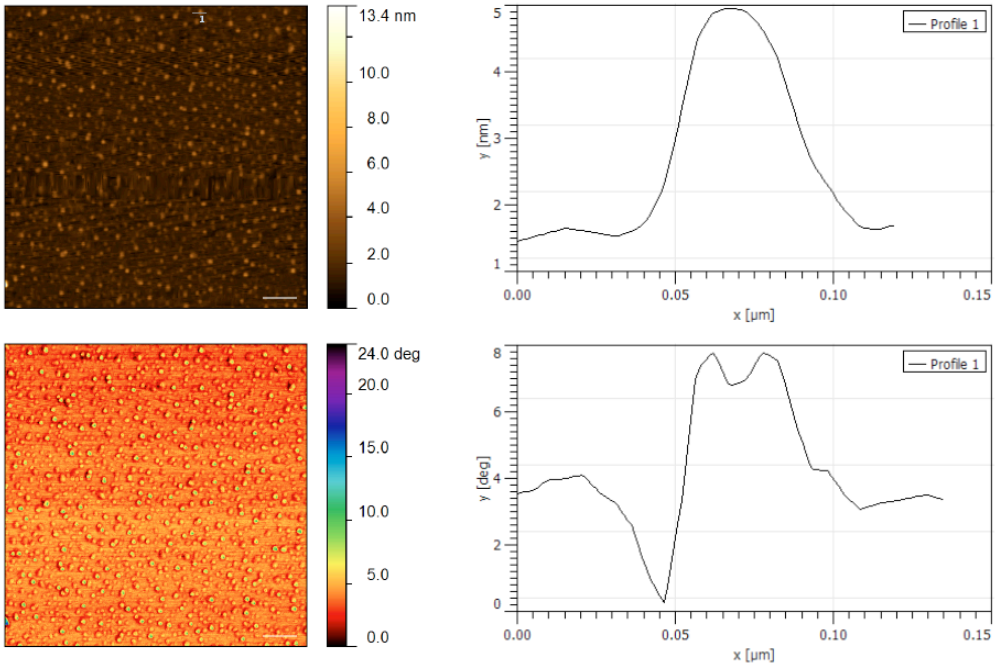


Figure S48. AFM height (top) and phase (down) images of $(PFS_7$-*b*-$OEGSt_3)_3$ star block copolymer with the graphs showing the diameter and the height of aggregates. (Scale bar: 300 nm)

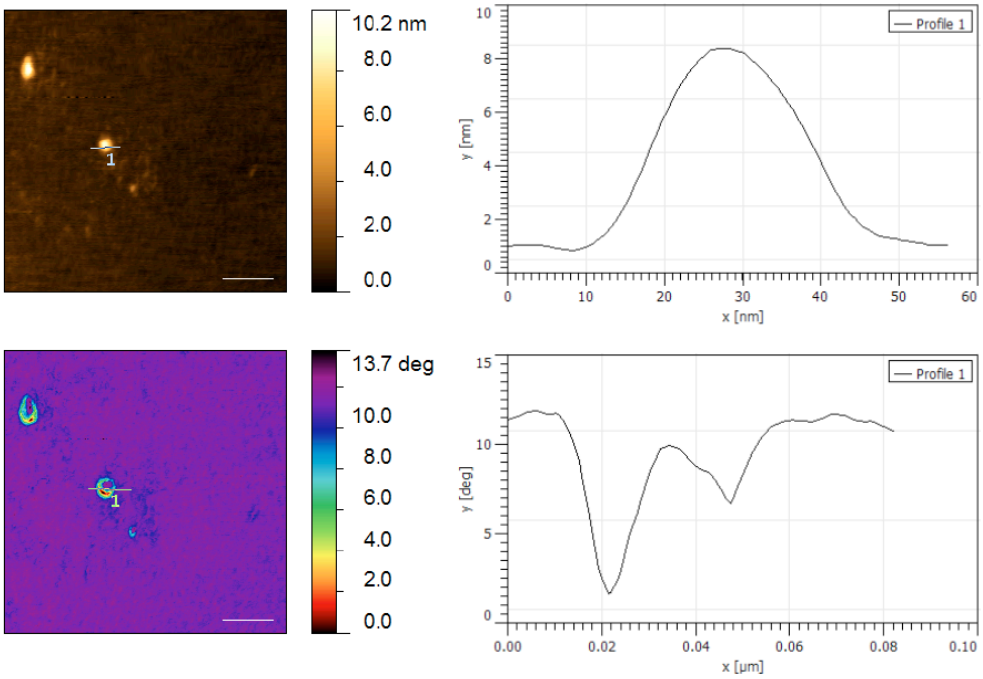


Figure S49. AFM height (top) and phase (down) images of $(PFS_{10}$-*b*-$OEGSt_4)_3$ star block copolymer with the graphs showing the diameter and the height of aggregates. (Scale bar: 200 nm)

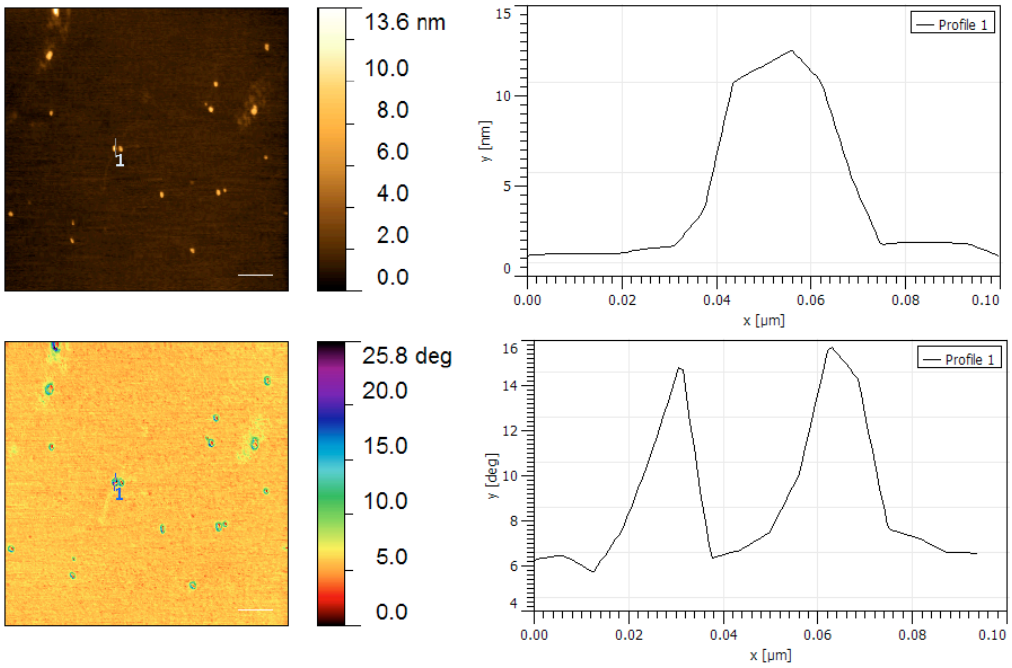


Figure S50. AFM height (top) and phase (down) images of $(PFS_{16}$-*b*-$OEGSt_4)_3$ star block copolymer with the graphs showing the diameter and the height of aggregates. (Scale bar: 200 nm)

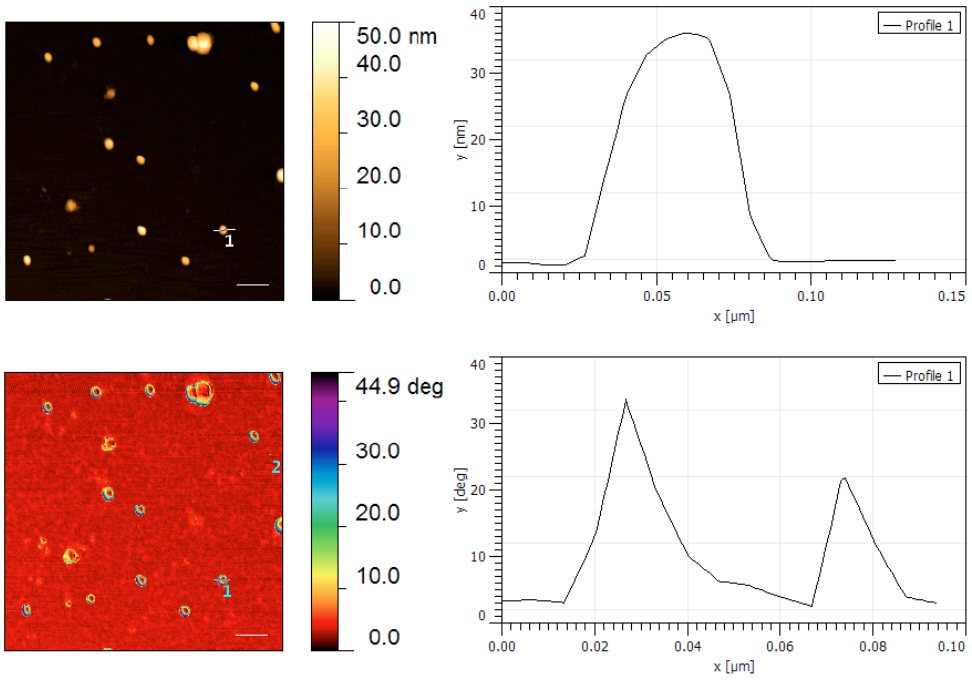


Figure S51. AFM height (top) and phase (down) images of $(PFDA_4$-*b*-$OEGSt_4)_3$ star block copolymer with the graphs showing the diameter and the height of aggregates. (Scale bar: 200 nm)

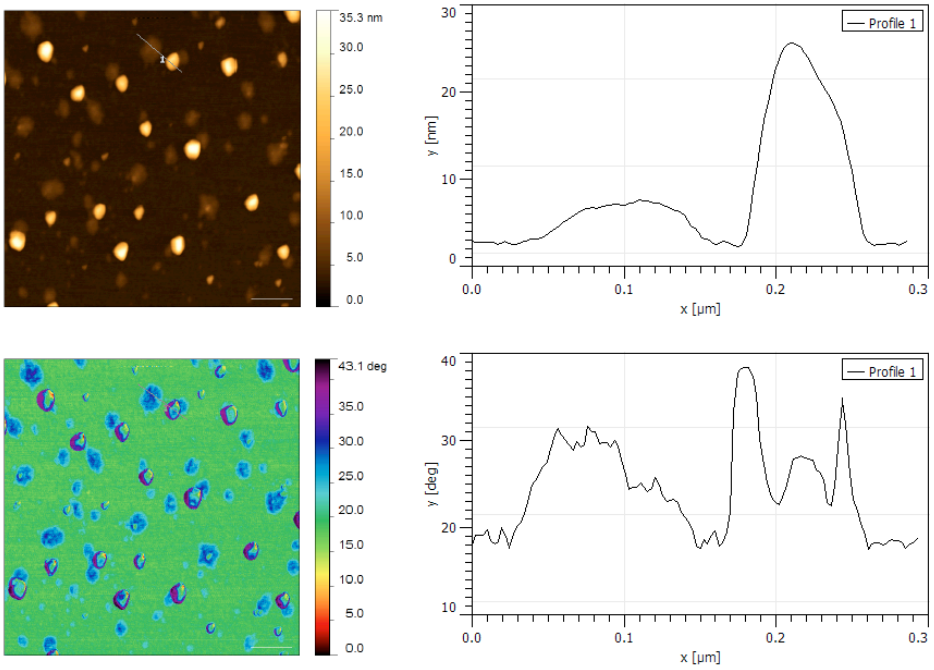


Figure S52. AFM height and phase images of $(PFBA_{20}$-*b*-$OEGSt_4)_3$ star block copolymer with the graphs showing the diameter and the height of aggregates. (Scale bar: 200 nm)

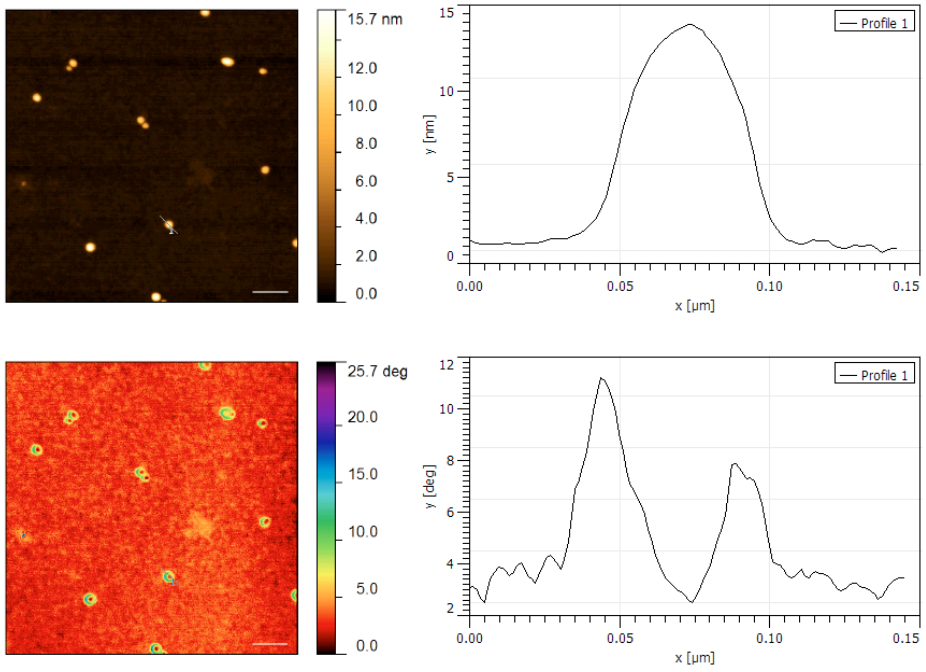


Figure S53. AFM height (top) and phase (down) images of $(PFS_{16}$-*b*-$OEGMA_{30})_3$ star block copolymer with graphs showing the diameter and the height of aggregates. (Scale bar: 200 nm)

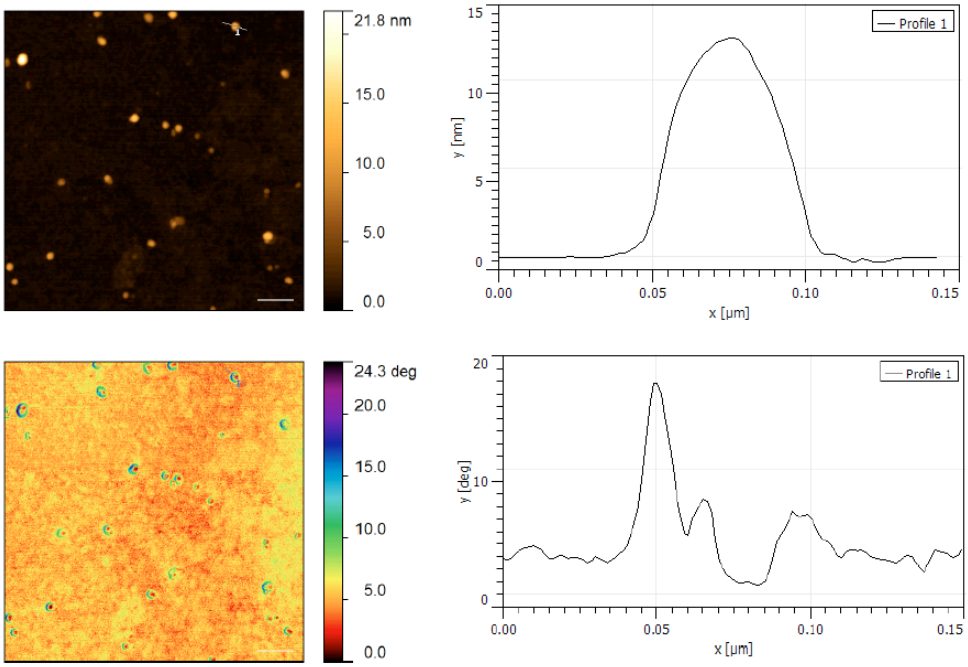


Figure S54: AFM height (top) and phase (down) images of $(PFBA_{7}$-*b*-$OEGMA_{18})_3$ star block copolymer with graphs showing the diameter and the height of aggregates. (Scale bar: 200 nm)

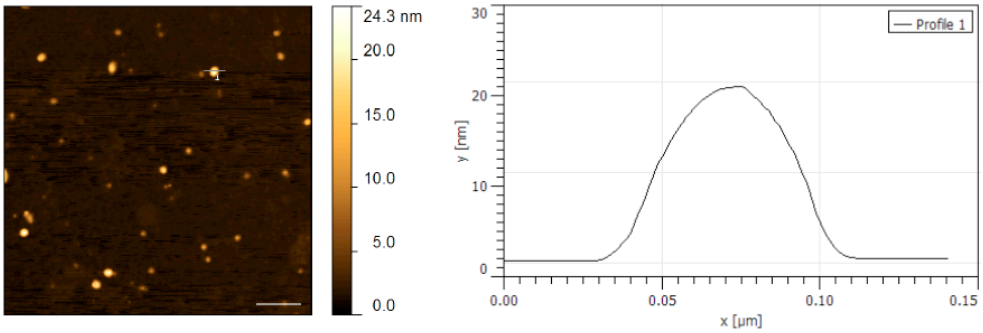


Figure S55: AFM height (top) and phase (down) images of $(PFBA_{14}$-*b*-$OEGMA_{30})_3$ star block copolymer with graphs showing the diameter and the height of aggregates. (Scale bar: 300 nm)

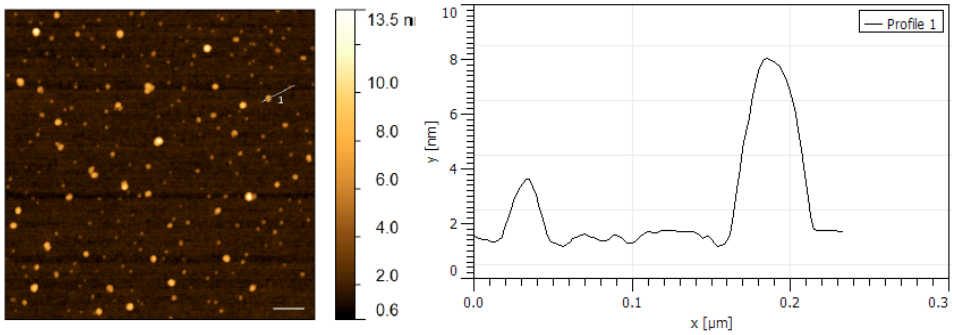


Figure S56: AFM height image of $(PFDA_{4}$-*b*-$OEGMA_{30})_3$ star block copolymer with the graph showing the diameter and the height of aggregates. (Scale bar: 200 nm)

Table S2 summarizes the sizes corresponding to the height and the diameters measured by AFM height and phase images for each of the star block copolymers. The phase images offer the advantage to precisely determine the diameter of the fluorinated core. The diameter of $(PFS_7\text{-}b\text{-}OEGSt_3)_3$, $(PFS_{10}\text{-}b\text{-}OEGSt_4)_3$ and $(PFS_{16}\text{-}b\text{-}OEGSt_4)_3$ star block copolymers obtained by AFM were found to be smaller than those obtained by DLS. In solution, micelles can easily interact through hydrogen bonding of the OEGSt corona chains leading to micellar aggregates. However, since micelles were spin-coated onto a silicon wafer prior AFM analysis, well-defined and isolated micelles were observed. Nevertheless, the measured height were found to be very small than diameter, meaning that the micelles are flattened due to low surface tension of the fluorinated core.

Two populations of different sizes were observed for the $(PFBA_{20}\text{-}b\text{-}OEGSt_4)_3$ and $(PFDA_4\text{-}b\text{-}OEGMA_{30})_3$ star block copolymers. $(PFBA_{20}\text{-}b\text{-}OEGSt_4)_3$, gave larger aggregates with the 30 nm height corresponding to multilayer vesicles, while aggregates of the 4 nm height were considered as bilayers vesicles, this was confirmed by cryo-TEM images. For the $(PFDA_4\text{-}b\text{-}OEGMA_{30})_3$ star block copolymer, the larger population was attributed to micellar aggregates.

Larger aggregates were observed for OEGMa containing star polymers. DLS analysis revealed a larger population with a hydrodynamic diameter ranging from 180 to 240 nm. By increasing the number of the OEGMA repeating units, larger micelles are formed. Larger aggregates might result from a larger overlap between corona chains through hydrogen bonding. AFM analysis revealed isolated micelles with a radius ranging from 35 to 44 nm. The height determined by AFM height image was found to be shorter (12-18 nm) due to the flattening of fluorinated micelles onto the silicon wafer. In this case of $(PFDA_4\text{-}b\text{-}OEGM_{30})_3$, 2 types of aggregates were observed for the same reason as the $(PFDA_4\text{-}b\text{-}OEGSt_4)_3$ star polymer.

Table S2. Height, diameter and core diameter of aggregates determined by AFM

Entry	Polymer	Diameter[a]	Height[b]	Core diameter[c]
1	$(PFS_7\text{-}b\text{-}OEGSt_3)_3$	76 ± 10	6 ±2	54 ±2
2	$(PFS_{10}\text{-}b\text{-}OEGSt_4)_3$	44 ± 6	8 ±1	24 ±2
3	$(PFS_{16}\text{-}b\text{-}OEGSt_4)_3$	46 ± 4	12 ±1	24 ± 4
4[d]	$(PFBA_{20}\text{-}b\text{-}OEGSt_4)_3$	100 ± 14	30 ± 4	-
		120 ± 24	4 ± 1	
5	$(PFDA_4\text{-}b\text{-}OEGSt_4)_3$	74 ± 6	32 ± 3	54 ± 6
6	$(PFS_{16}\text{-}b\text{-}OEGMA_{30})_3$	70 ± 8	9 ± 2	46 ± 6
7	$(PFBA_7\text{-}b\text{-}OEGMA_{18})_3$	70 ± 8	13 ± 3	48 ± 2
8	$(PFBA_{14}\text{-}b\text{-}OEGMA_{30})_3$	88 ± 4	18 ± 2	-
9[e]	$(PFDA_4\text{-}b\text{-}OEGMA_{30})_3$	74 ± 10	12 ± 2	-
		50 ± 4	4 ± 1	

[a] Diameter of micelles determined from the height AFM images. [b] Height of micelles determined from the height AFM images.

[c] Core of micelles determined from the phase AFM images. [d] Two populations of vesicles.

[e] Two populations of micellar aggregates.

7) Transmission electron microscopy

Cryo-TEM images of $(PFS_7\text{-}b\text{-}OEGSt_3)_3$ and $(PFS_{10}\text{-}b\text{-}OEGSt_4)_3$ star block copolymer revealed spherical micelles of 20 ± 2 nm and 24 ± 4 nm diameter, respectively (**Figure S57 and S58**). TEM image of $(PFS_{16}\text{-}b\text{-}OEGSt_4)_3$ sample stained with OsO_4 vapors revealed micelles of 42 ± 4 nm corresponding to diameter of the micelle in agreement with AFM data collected (**Figure S59**). Cryo-TEM image of $(PFDA_4\text{-}b\text{-}OEGSt_4)_3$ revealed spherical micelles of 20 ± 2 nm of diameter (**Figure S61**). Interestingly, $(PFBA_{20}\text{-}b\text{-}OEGSt_4)_3$ sample revealed bilayer vesicles with a diameter ranging from 120 - 350 nm. The thickness of each layer was estimated to be 9 ± 1 nm. Multilayer vesicles of 350 nm of diameter were also observed (**Figure S60**). Addition of $CuSO_4$ led to vesicles containing Cu(II)-TBTA complex exhibiting higher contrast compared to the initial vesicles (**Figure S66**). Finally, (Cryo)-TEM images of micelles prepared from $(PFBA_7\text{-}b\text{-}OEGMa_{18})_3$, $(PFBA_{14}\text{-}b\text{-}OEGMa_{30})_3$, $(PFS_{16}\text{-}b\text{-}OEGMa_{30})_3$ and $(PFDA_4\text{-}b\text{-}OEGMa_{30})_3$ show spherical micelles with a diameter of 44 nm ± 8; 52 nm ± 6; 58 nm ± 10 and 24 nm ± 4 nm, respectively (**Figure S62**, **S63**, **S64 and S65**).

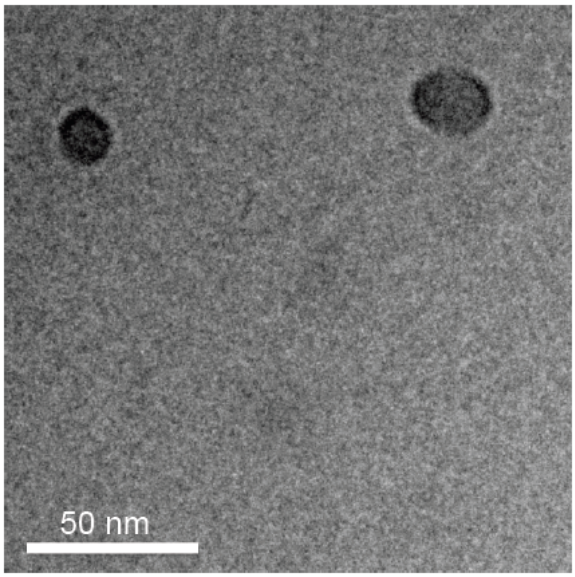


Figure S57. Cryo-TEM image of $(PFS_7\text{-}b\text{-}OEGSt_3)_3$ star block copolymer.

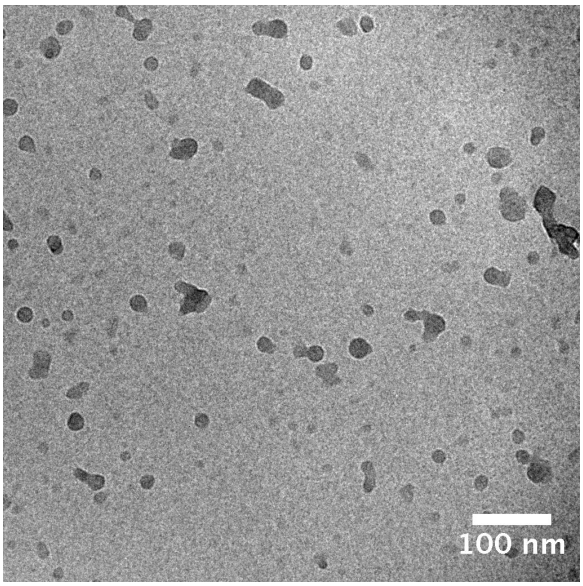


Figure S58. Cryo-TEM image of (PFS_{10}-*b*-$OEGSt_4)_3$ star block copolymer.

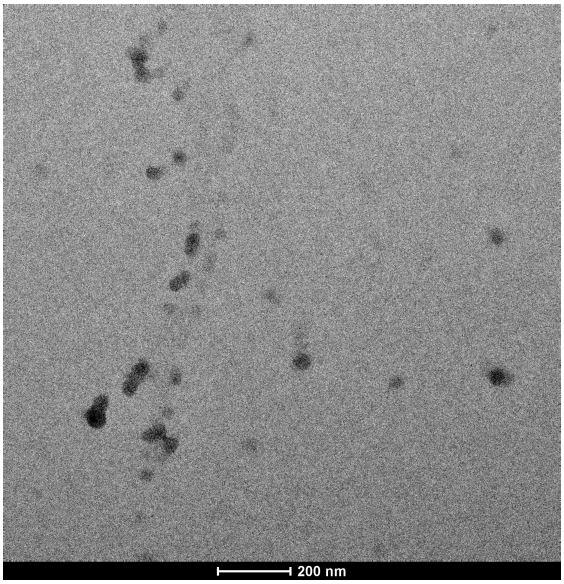


Figure S59. TEM image of (PFS_{16}-*b*-$OEGSt_4)_3$ star block copolymer. (Stained with OsO_4 vapors from 4% concentrated solution)

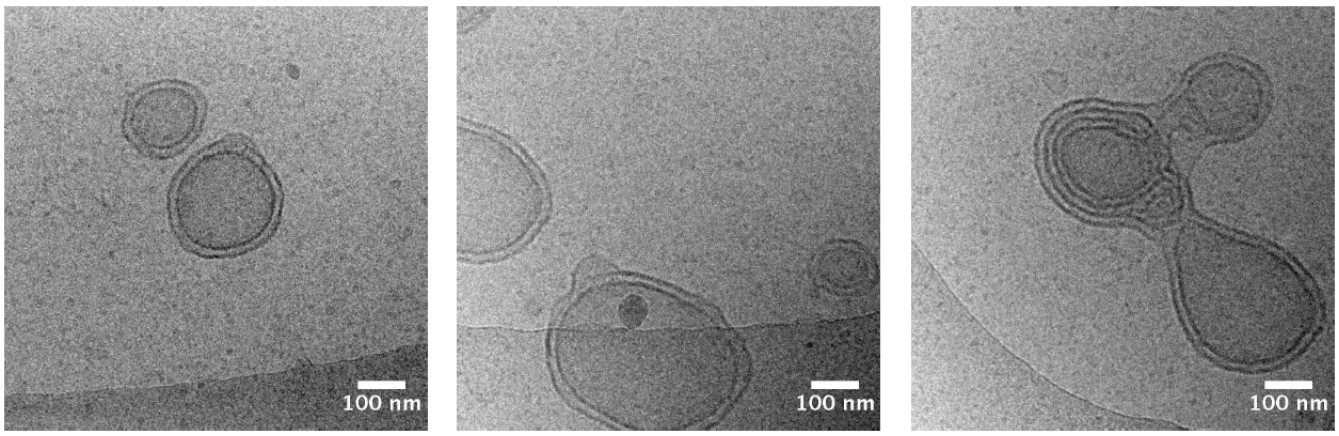


Figure S60. Cryo-TEM image of ($PFBA_{20}$-*b*-$OEGSt_4)_3$ star block copolymer.

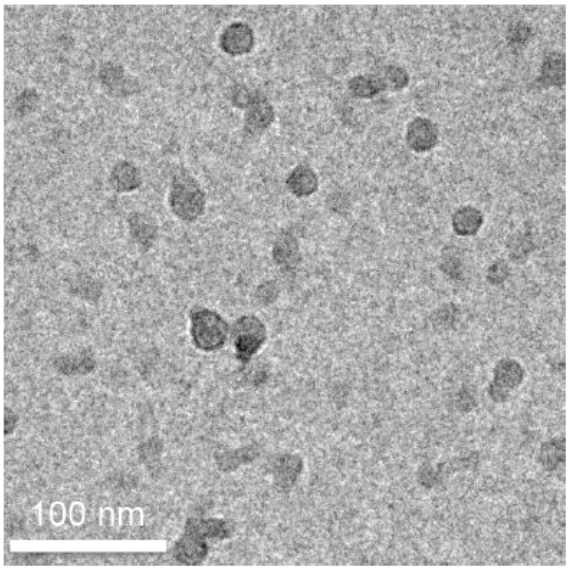


Figure S61. Cryo-TEM image of ($PFDA_4$-*b*-$OEGSt_4)_3$ star block copolymer.

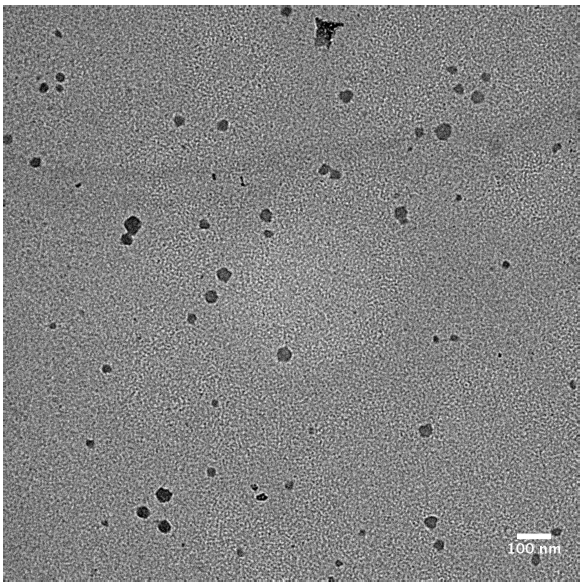


Figure S62. TEM image of ($PFBA_7$-*b*-$OEGMa_{18}$)$_3$ star block copolymer. (Stained with OSO_4 vapors from 4% concentrated solution)

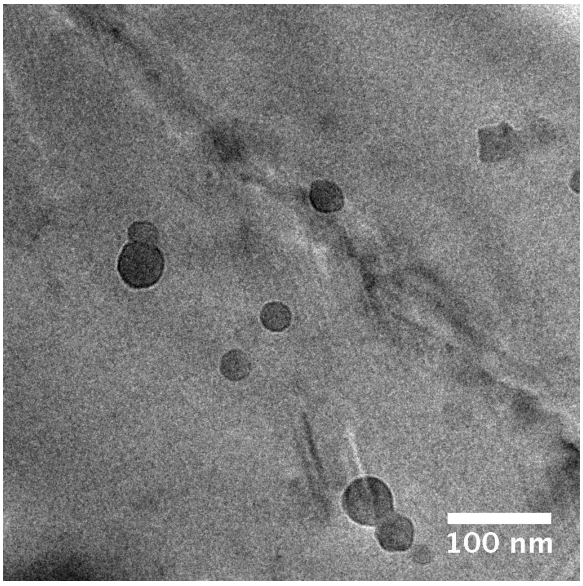


Figure S63. Cryo-TEM image of (PFS_{16}-*b*-$OEGMa_{30}$)$_3$ star block copolymer.

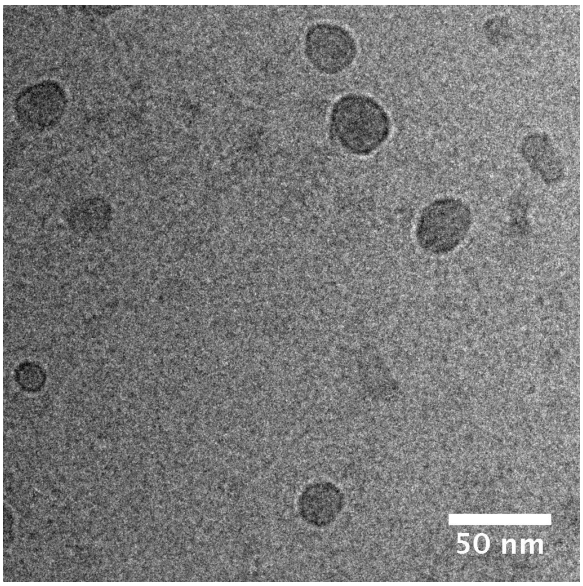


Figure S64. Cryo-TEM image of ($PFDA_4$-*b*-$OEGMa_{30}$)$_3$ star block copolymer.

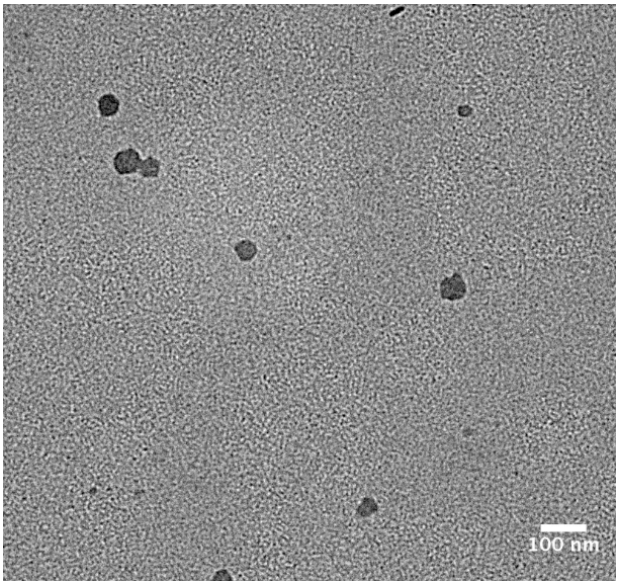


Figure S65. TEM image of ($PFBA_{14}$-*b*-$OEGMa_{30}$)$_3$ star block copolymer. (Stained with OSO_4 vapors from 4% concentrated solution)

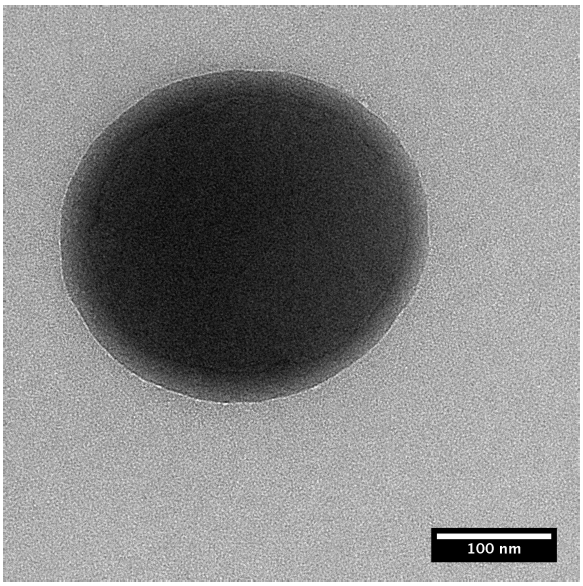


Figure S66. Cryo-TEM image of ($PFBA_{20}$-*b*-$OEGSt_4)_3$ star block copolymer loaded with copper (II).

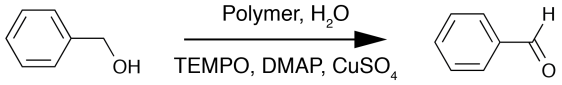
8) Characterization data of macroinitiators and amphiphilic star block copolymers (SEC, DLS, AFM and TEM)

Table S3 Characterization of hydrophobic macroinitiators and amphiphilic star block copolymers

Entry	Polymer	M_n[a]	M_w[a]	PDI_{SEC}	DLS (nm)[b]	PDI_{DLS}
1	$(PFS_7)_3$	3843	4260	1.10	-	-
2	$(PFS_{10})_3$	5550	6380	1.16	-	-
3	$(PFS_{16})_3$	7950	9650	1.20	40	0.5
4	$(PFBA_7)_3$	4154	4710	1.13	-	-
5	$(PFBA_{14})_3$	7782	9100	1.17	50	0.8
6	$(PFBA_{20})_3$	9209	10126	1.11	90[c]	0.4
7	$(PFDA_4)_3$	7125	7651	1.08	30	0.5

[a] Determined by SEC (calibration against linear polystyrene). [b] Hydrodynamic diameters determined by DLS in DMF at 1 $g{\cdot}L^{-1}$. [c] Hydrodynamic diameters determined by DLS in trifluorotoluene at 1 $g{\cdot}L^{-1}$.

5. Catalysis



Entries 1 and 3 through 8: 4-Dimethylaminopyridine (6 mg, 0.05 mmol), the polymer (2 mg), 0.8 mL of a TEMPO stock solution (2 mM), and 4 mL of deionized water were introduced in a 20 mL vial. The solution was then sonicated using a Branson digital sonifier (65% power, 4 min, 5 sec pulse on, 5 sec pulse off). During sonication the vial was placed in an ice bath. After sonication, benzyl alcohol (100 µL, 1 mmol) and 0.2 mL of 0.4 mM $CuSO_4$ solution in H_2O were added. The reaction mixture was stirred at room temperature in air. The conversion and selectivity were monitored by GC-MS and ^1H NMR.

Entries 2 and 9 through 12: To prepare a 28 g/L ($PFBA_{14}$-*b*-$OEGMA_{30})_3$ solution, star polymer (170 mg, 2 µmol) was dissolved in 3 mL of DMF, then 3 mL of water was added dropwise. The solution was dialyzed against water overnight using a

8K cutoff dialysis membrane. 4-dimethylaminopyridine (6 mg, 0.05 mmol), 0.5 mL of star block copolymer micellar solution, and 0.2 mL of TEMPO (2.77 mM) were introduced in 3 mL and stirred at RT under air (balloon). Benzyl alcohol (10 µL, 0.1 mmol) and 0.2 mL of $CuSO_4$ (2.22 mM) in H_2O were added. The reaction mixture was stirred at room temperature under air (a balloon full of air was used in this case). The conversion and selectivity were monitored by ^{1}H NMR (**Figure S67**). After the reaction, 0.05 mL of reaction mixture was added to 0.6 mL of $CDCl_3$. The organic phase was transferred in NMR tube for ^{1}H NMR analysis.

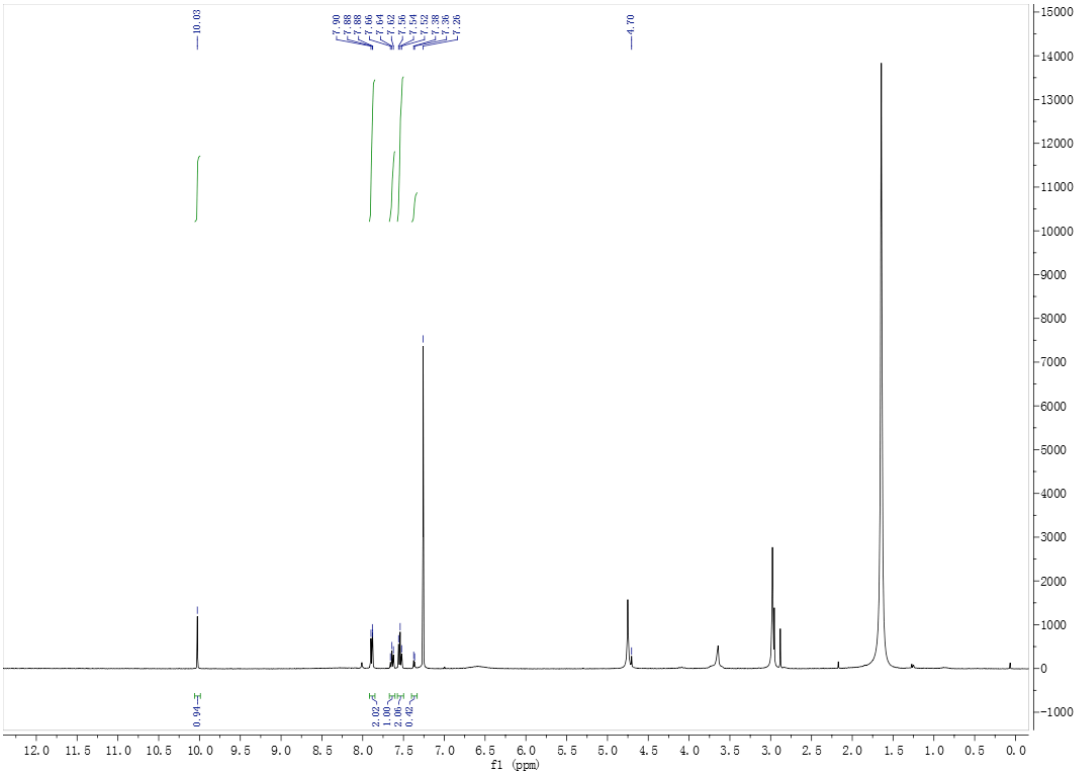


Figure S67. ^{1}H NMR spectrum of the product at 90% conversion after 44 hours. (entry 12- Table S5)

6. Dissolved Oxygen Measurements

5 mL of deionized water and 5 mL of 20 g/L solutions of $(PFBA_{14}$-*b*-$OEGMA_{30})_3$, $(PFS_{16}$-*b*-$OEGSt_4)_3$ and Pluronic P-123 were dispensed into 40 mL vials. The samples were stirred at 300 rpm and 25°C for ~10 min, and then continually flushed with a steady flow of pure oxygen for 1 min, then capped and vigorously shaken. The caps were removed and dissolved O_2 concentrations were recorded every 5 min using Mettler Toledo SG6 SevenGo Pro with an Inlab 605 dissolved oxygen probe (**Figure S68**). For each sample, the measurement was repeated three times idependently (**Figure S69**).

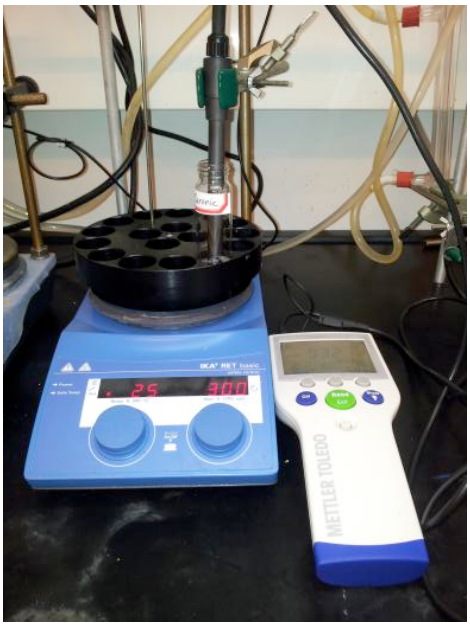


Figure S68. The experimental setup for dissolved oxygen measurements.

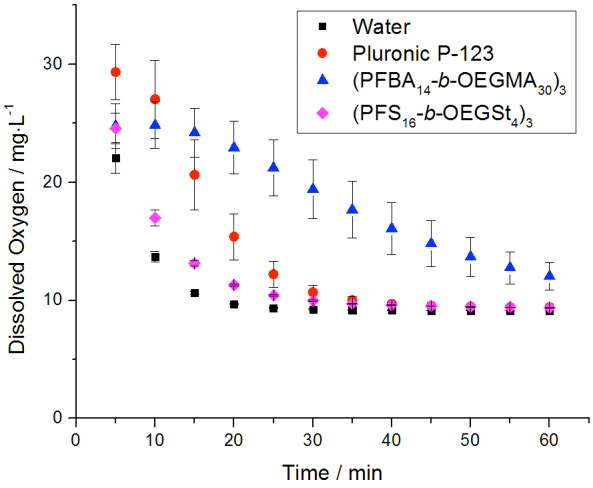


Figure S69. Oxygen release kinetics from O_2-saturated solutions.

7. References

1. A. W. Bosman, R. Vestberg, A. Heumann, J. M. J. Frechet and C. J. Hawker, *J. Am. Chem. Soc.*, **2003,** 125, 715-728.
2. C. Ott, R. Hoogenboom and U. S. Schubert, *Chem. Commun.*, **2008**, 3516-3518.
3. P. Lacroix-Desmazes, P. Andre, J. M. Desimone, A. V. Ruzette and B. Boutevin, *J. Polym. Sci. Polym. Chem.*, **2004**, 42, 3537-3552.