Electronic Supplementary Material (ESI) for Polymer Chemistry.

Highly Tunable Polyurethanes: Organocatalyzed Polyaddition and Subsequent Post-polymerization Modification of Pentafluorophenyl Ester Sidechains

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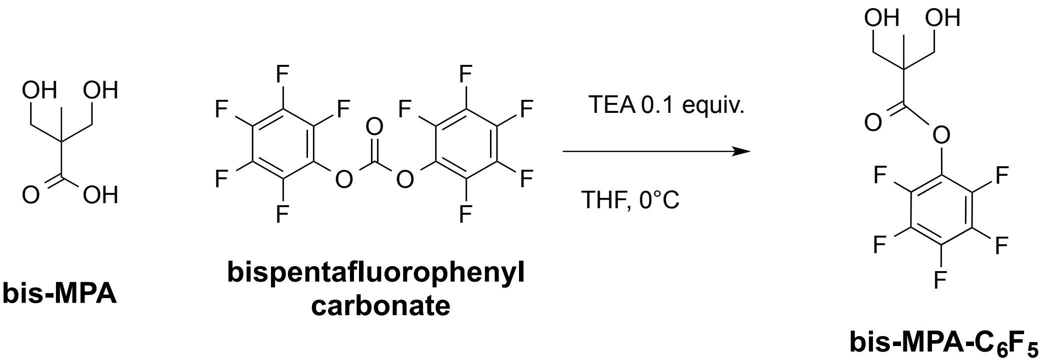
Supplemental Information

Materials. Bis(pentafluorophenyl)carbonate was obtained from Central Glass Co., Ltd. (Japan). Poly(ethylene glycol) end-capped diol (PEG_{1500} , M_n =1500 g mol^{-1}) was dried by azeotropic distillation in benzene. Hexamethylene diisocyanate (HDI) and was dried by stirring with CaH_2 in anhydrous dichloromethane (DCM) followed by filtration and solvent removal *in vacuo*. Anhydrous DCM was obtained by using a solvent drying system from Innovative Technologies. All other materials were purchased from Sigma-Aldrich and used as received.

Methods. ^1H, and ^{19}F NMR spectra were acquired on a Bruker Avance 400 instrument at 400 MHz. Gel permeation chromatography (GPC) was performed in tetrahydrofuran (THF) using a Waters system equipped with four 5 μm Waters columns (300 mm × 7.7 mm) connected in series with an increasing pore size (100, 1000, 105, and 106 Å), a Waters 410 differential refractometer, and a 996 photodiode array detector. The system was calibrated with polystyrene standards.

Preparation of pentafluorophenyl 3-hydroxy-2-(hydroxymethyl)-2-methylpropanoate (bis-MPA-C_6F_5 diol)



Scheme S1. Synthesis of pentafluorophenyl ester-containing diol.

A 100 mL round bottom flask was charged with 2,2-bis(hydroxymethyl)propionic acid (bis-MPA) (3.00 g, 22.0 mmol, 1.0 equiv), bis-(pentafluorophenyl)carbonate (PFC) (9.53 g, 24.0 mmol, 1.1 equiv) and 70 mL of anhydrous THF. It was stirred for 30 minutes, and cooled down to 0° C prior to the addition of triethylamine (TEA) (0.22 g, 2.2 mmol, 0.10 equiv) Initially the reaction was heterogeneous, but after 24 h a homogeneous solution was formed. The solution was concentrated *in vacuo* and loaded onto a silica gel column. The crude product was purified by flash column chromatography using a mixture of ethyl acetate/hexanes (4:1 v/v) as eluent. Concentration of the product-containing fractions by rotary evaporation afforded a white crystalline powder (4.36 g, 65 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.09 (d, J = 11.5 Hz, CH_2, 2H,), 3.9 (d, J = 11.4 Hz, CH_2 , 2H), 2.55 (s, OH, 2H), 1.32 (s, CCH_3, 3H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 171 (s, C=O, 1C), 148-136 (m ,C_{Ar}, 6C), 67 (s, CH_2, 2C), 51 (s, CH, 1C), 17 (s,CH_3, 1C) 19F NMR (400 MHz, $CDCl_3$): δ -154.0 ~ -154.1 (m, 2F), -157.3 (m, 1F), -162.4 ~ -162.5 (m, 2F).

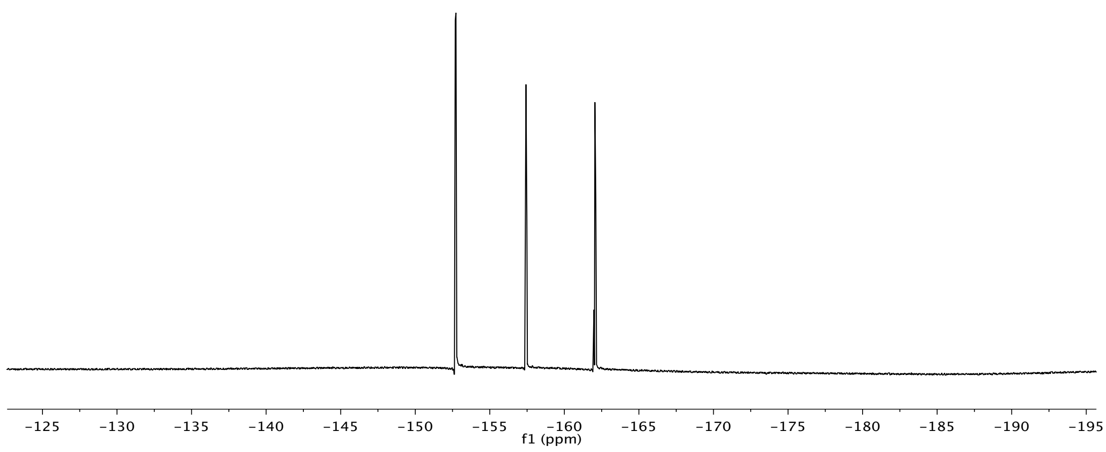


Figure S1. ^{19}F NMR of bis-MPA-C_6F_5 diol.

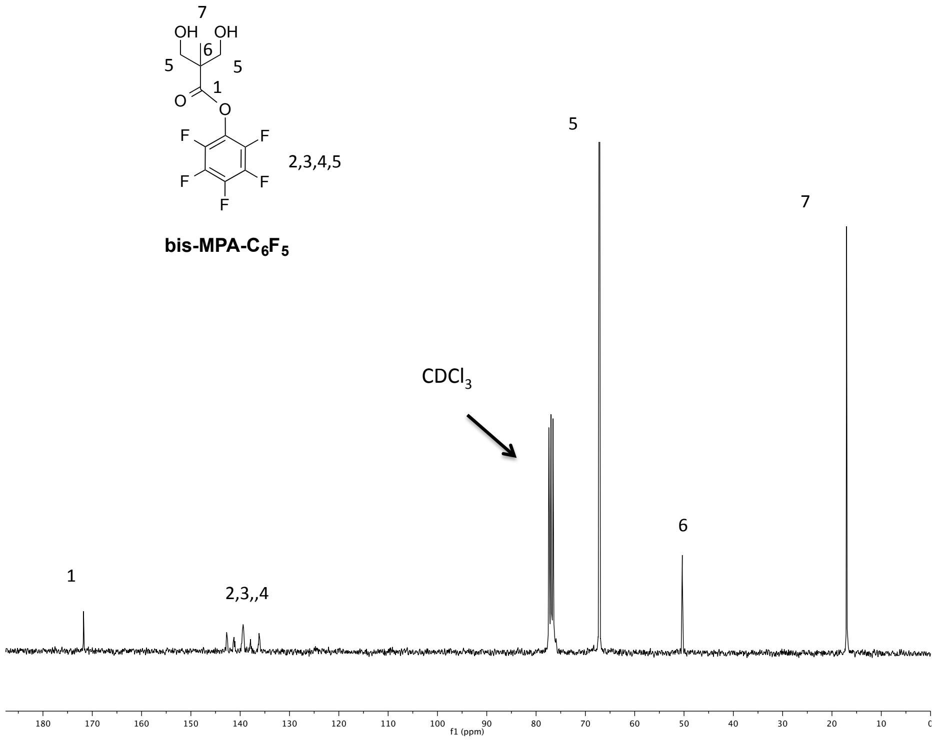
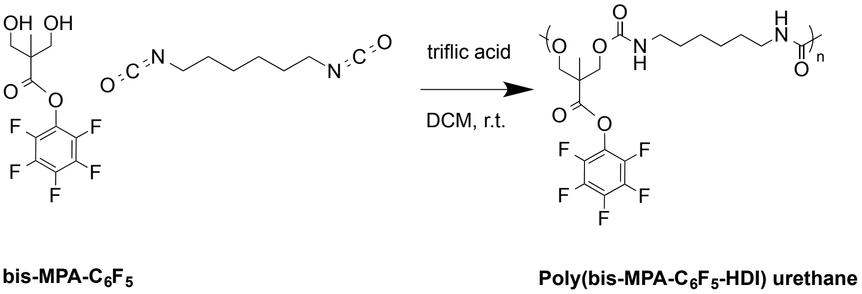


Figure S 2. ^{13}C NMR of bis-MPA-C_6F_5 diol.

Homopolymer : General procedure for the synthesis of poly(MPA-OC_6F_5-HDI) urethane

In a nitrogen-purged glovebox, a 20-mL vial containing a small magnetic stir-bar was charged with bis-MPA-C_6F_5 diol (1.00 g, 3.30 mmol, 1 equiv), hexamethylene diisocyanate (HDI) (0.560 g, 3.30 mmol, 1 equiv) and 15 g of dichloromethane (0.5 M with respect to initial concentration of both monomers). The bis-MPA-C_6F_5 diol only partially dissolves at this concentration. Trifluoromethanesulfonic acid (triflic acid) (0.020 g, 0.15 mmol) was added to the stirred solution. As the reaction proceeded, the undissolved bis-MPA-C_6F_5 diol slowly went into solution. The reaction was monitored by ^{1}H NMR. Once the reaction was complete (ca. 3 h) the polymer was precipitated into hexanes, filtered, and dried to obtain a white solid (1.4 g, 90 % yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 4.40 (m, CH_2, 4H), 3.35 (m, CH_2 , 4H) 1.61-1.30 (s, CH_3, 3H), (s, CH_2, 2H) (s,CH_2, 2H) . GPC (RI): M_n (PDI) = 37200 Da (1.42). ^{19}F NMR (400 MHz, $CDCl_3$): δ -154.0 ~ -154.1 (m, 2F), -157.3 (m, 1F), -162.4 ~ -162.5 (m, 2F).



Scheme S2. Synthesis of pentafluorophenyl ester-containing polyurethane.

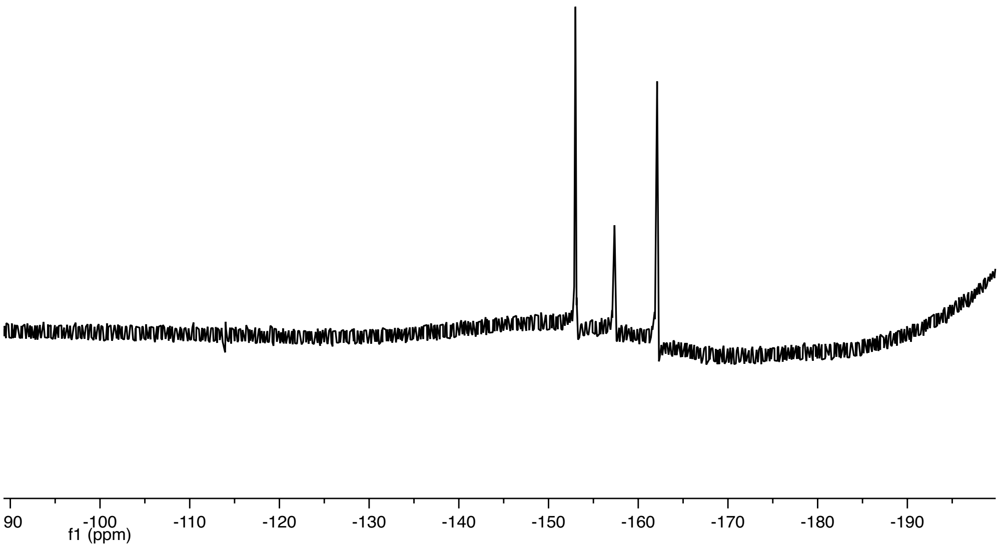


Figure S3. ^{19}F NMR of poly(MPA-OC$_6$F$_5$-HDI) urethane

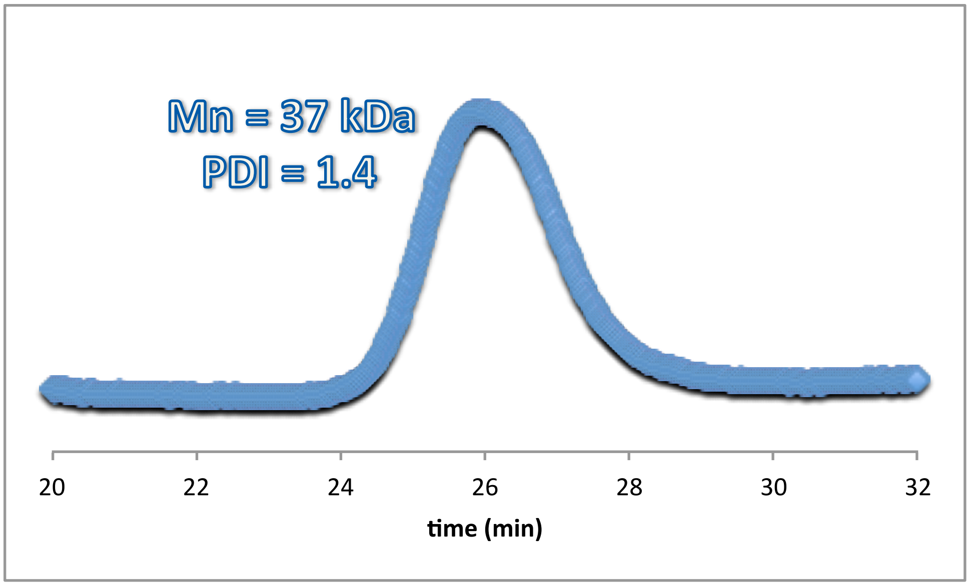
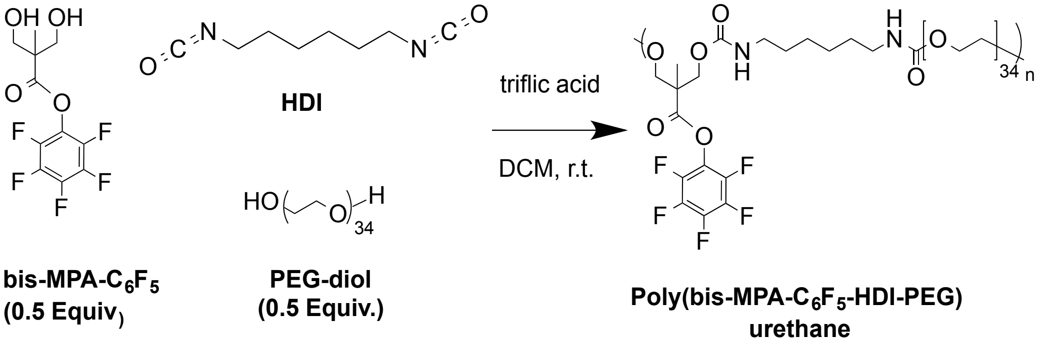


Figure S4. GPC trace of poly(MPA-OC$_6$F$_5$-HDI) urethane

Segmented Polyurethane: General procedure for the synthesis of poly(MPA-OC_6F_5-HDI-PEG) urethane

In a nitrogen-purged glovebox, a 20-mL vial containing a small magnetic stir-bar was charged with PEG_{1500} diol (0.45 g, 0.30 mmol, 1 equiv.), hexamethylene diisocyanate (HDI) (0.1 g, 0.60 mmol, 1 equiv.) and 3 g of dichloromethane (0.5 M with respect to initial concentration of both monomers). Trifluoromethanesulfonic acid (triflic acid) (0.005 g, 0.03 mmol) was added to the stirred solution. The reaction was monitored by ^{1}H NMR. Once the reaction reached 50 % conversion, bis-MPA-C_6F_5 diol (0.090 g, 0.30 mmol, 1 equiv) was added. The polymer was precipitated into hexanes, isolated by filtration, and dried to obtain a white solid (0.50 g, 77 % yield). ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 7.20 (s, NH, CH_2), 4.25 (m, CH_2, 2H), 4.10 (m, CH_2 , 2H) 3.65-3.55 (m, CH_2, 66H) 2.9 (s, CH_2, 4H) 1.50-1.10 (s, CH_3, 4H), (s, CH_2, 4H) (s,CH_2, 1.5H) . GPC (RI): M_n (PDI) = 25000 Da (1.50).



Scheme S3. Synthesis of pentafluorophenyl ester-containing segmented polyurethane.

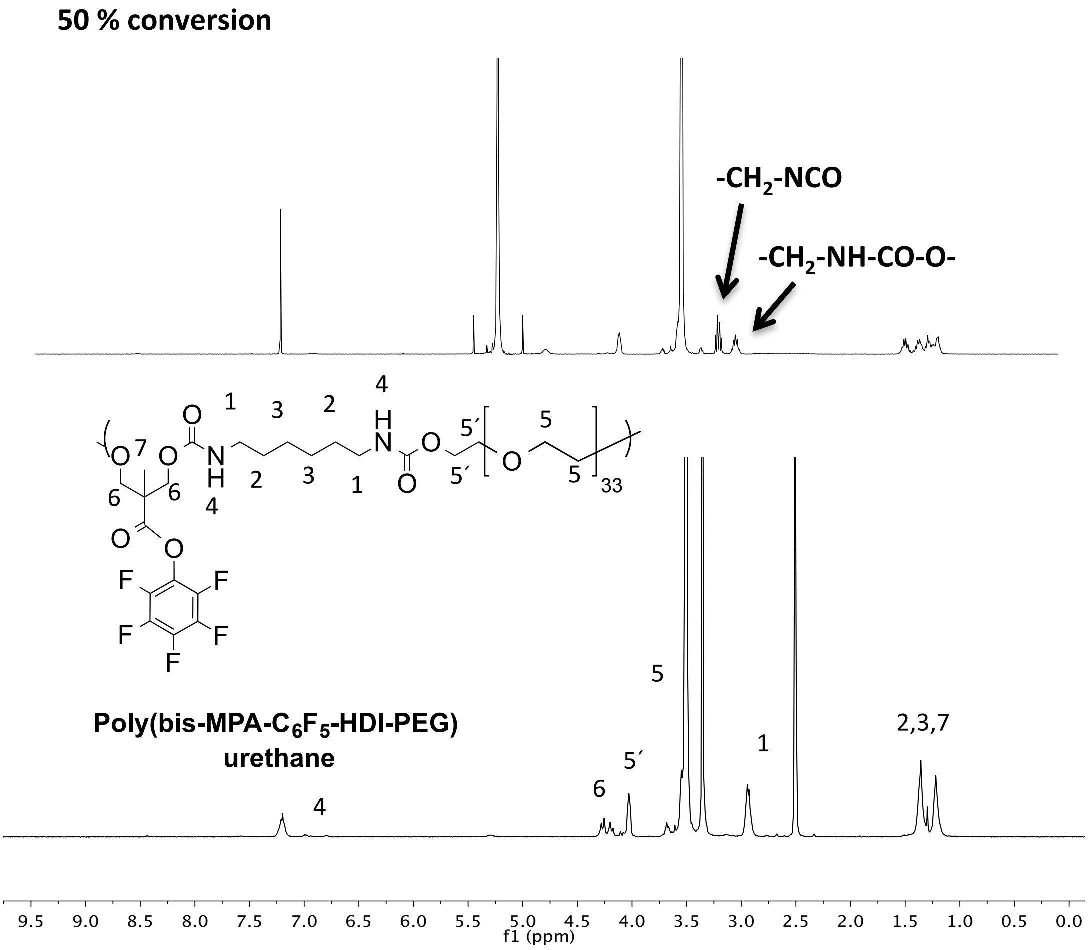


Figure S5. ^{1}H NMR spectra of segmented polyurethane (top) at 50 % conversion prior to the addition of bis-MPA-C_6F_5 and when the reaction was completed (bottom).

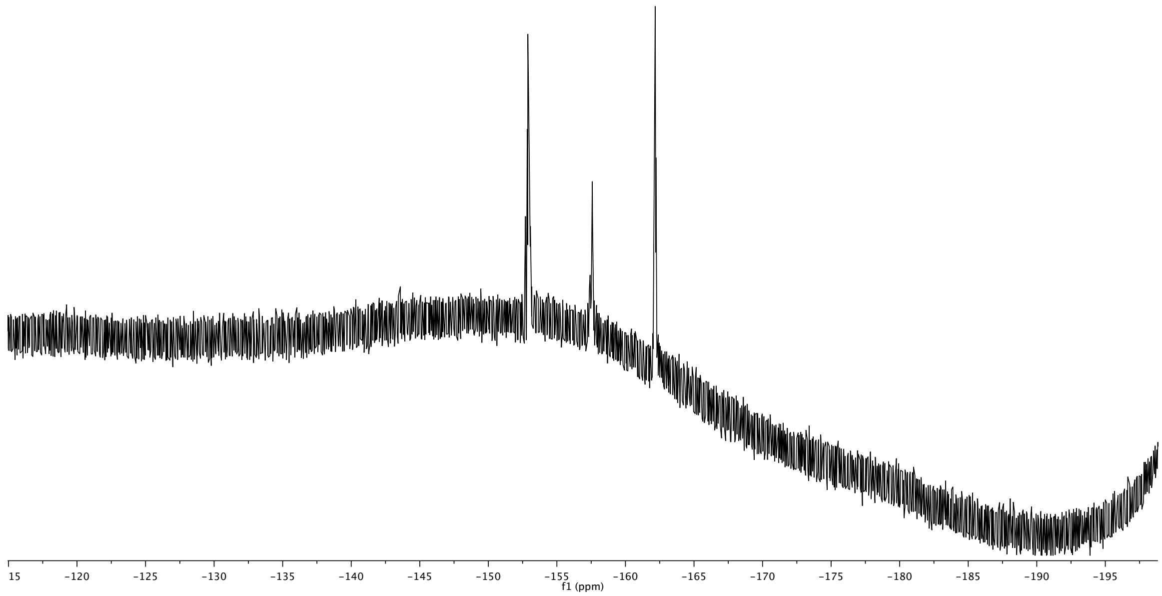


Figure S 6. ^{19}F NMR of poly(MPA-OC$_6$F$_5$-HDI-PEG) urethane

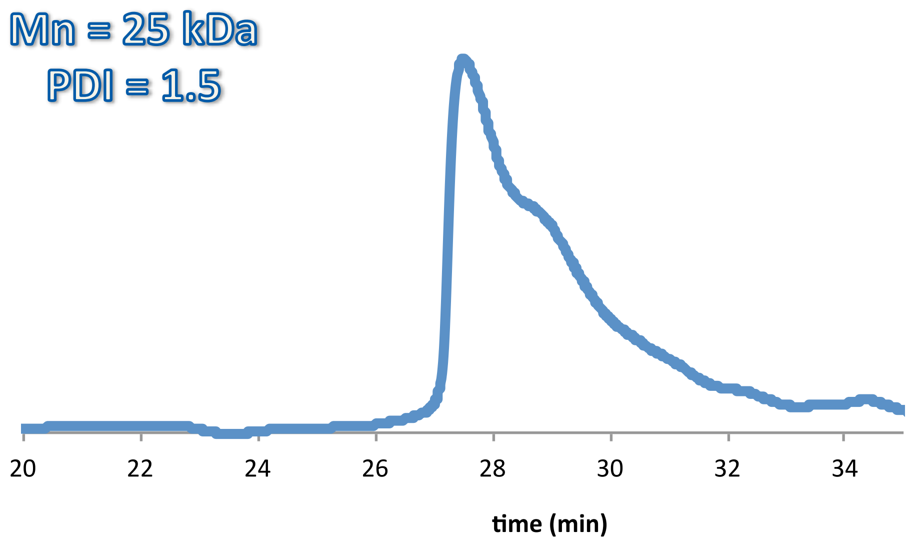
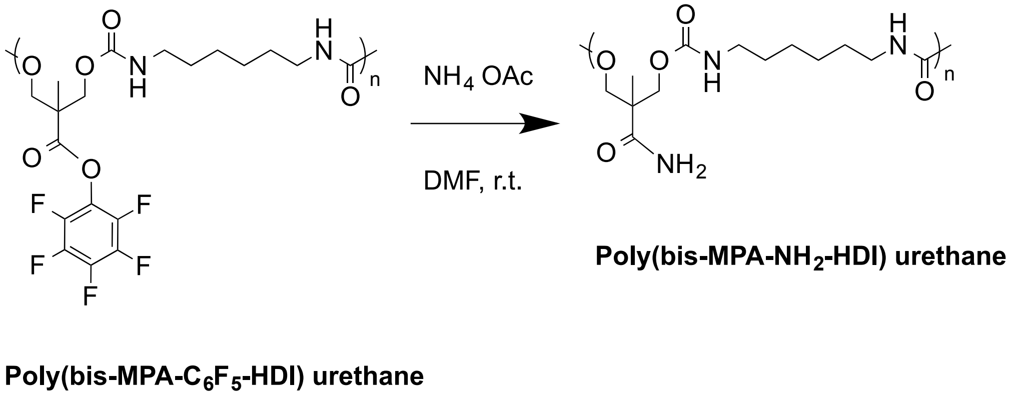


Figure S7. GPC trace of segmented poly(MPA-OC$_6$F$_5$-HDI-PEG) urethane

Post-polymerization modification of poly(MPA-OC$_6$F$_5$-HDI) urethane with ammonium acetate. A 20-mL glass vial containing a magnetic stir-bar was charged with poly(MPA-OC$_6$F$_5$-HDI) (0.0500 g, 0.107 mmol of activated ester) and anhydrous DMF (0.5 mL). Next, ammonium acetate (0.0110 g, 0.143 mmol) was added to the stirred solution. The mixture was allowed to stir at room temperature for 30 minutes, after which the solution was precipitated into excess diethyl ether (16 mL). The flocculent mixture was briefly sonicated and then centrifuged. The mother liquor was decanted and more diethyl ether (20 mL) was added. A second round of sonication, centrifuging, and decanting afforded the polymer as a white solid which was subsequently dried under high vacuum for 24 h. (0.032 g, 99% yield). ^{1}H NMR (DMSO-d$_6$, 400 MHz): δ = 7.40-7.10 (m, NH$_2$, 2H), (m, NH, 2H) 4.10 (s, CH$_2$, 4H), 1.40-1-10 (s, CH$_2$, 2H), (s, CH$_2$, 2H) (s, CCH$_3$, 3H).



Scheme S4. Modification of pentafluorophenyl ester-containing polyurethane using ammonium acetate.

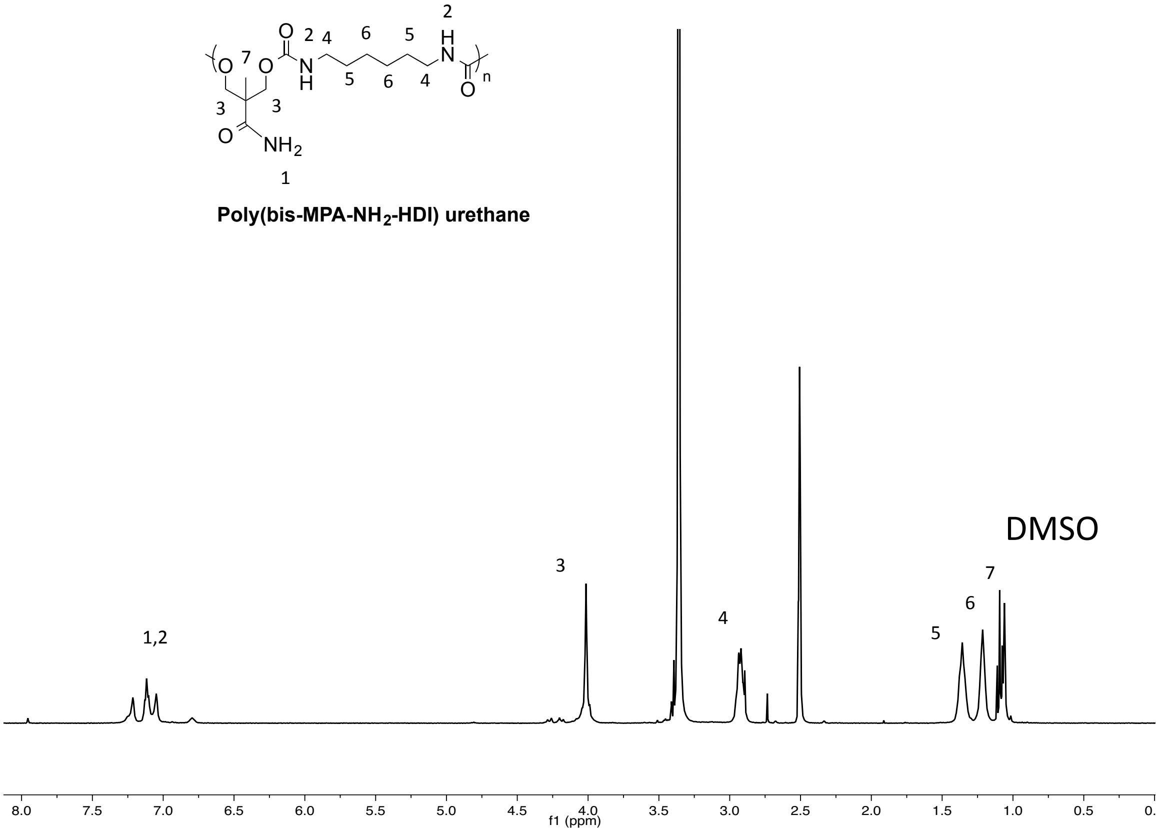


Figure S8. ^{1}H NMR spectrum of poly(bis-MPA-NH$_2$-HDI) urethane in DMSO-d_6

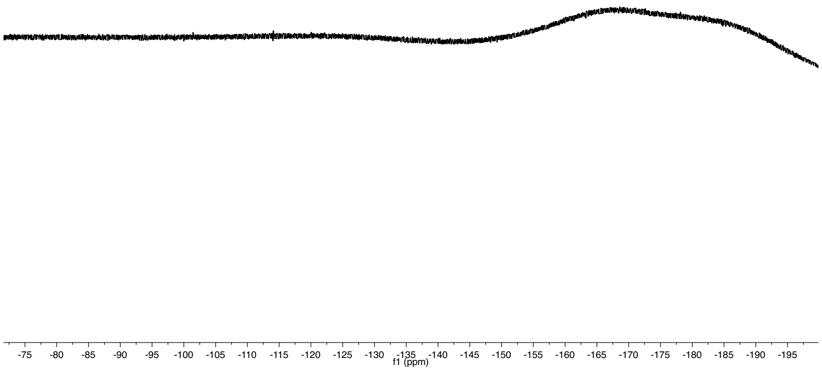
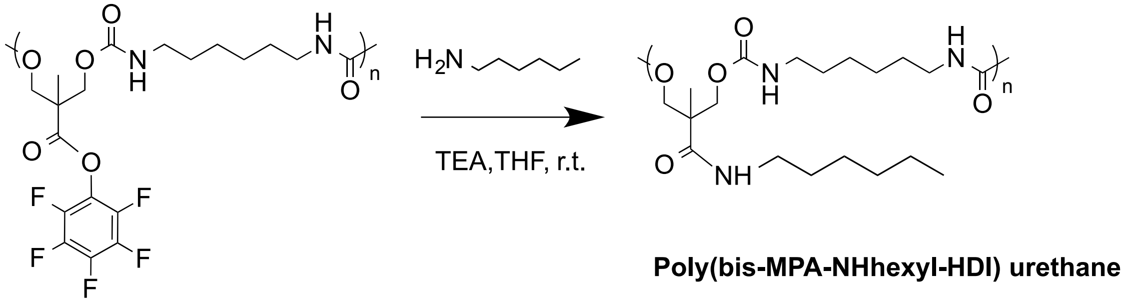


Figure S 9. ^{19}F NMR of isolated poly(bis-MPA-NH$_2$-HDI) urethane[1]

Post-polymerization modification of poly(MPA-OC$_6$F$_5$-HDI) urethane with hexylamine
A 20-mL glass vial containing a magnetic stir-bar was charged with poly(MPA-OC$_6$F$_5$-HDI) (0.0500 g, 0.107 mmol repeat units), anhydrous THF (2.0 mL) and triethylamine (0.0144 g, 0.143 mmol). Next, *n*-hexylamine (0.0132 g, 0.130 mmol) was added to the stirred solution. The mixture was allowed to stir at room temperature for 45 minutes, after which the solution was precipitated into excess diethyl ether (16 mL). The flocculent mixture was briefly sonicated and then centrifuged. The mother liquor was decanted and more diethyl ether (20 mL) was added. A second round of sonication, centrifuging, and decanting afforded the polymer as a white solid which was subsequently dried under high vacuum for 24 h. (0.039 g, 95 % yield). ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 6.60-5.40 (s, NH, 2H) (s, NH, 1H) 4.20 (s, CH$_2$, 4H), 3.20-3.00 (m, CH$_2$, 2H) (m, CH$_2$, 4H) 1.70-0.9 (m, CH$_2$, 2H), (m, CH$_2$, 2H), (m, CH$_2$, 2H), (m, CH$_2$, 2H), (m, CCH$_3$ 3H), (m, CH$_2$, 4H) (m, CH$_2$, 4H) (m, CH$_2$, 6H).



Poly(bis-MPA-NHhexyl-HDI) urethane

Poly(bis-MPA-C$_6$F$_5$-HDI) urethane

Scheme S5. Modification of pentafluorophenyl ester-containing polyurethane using 1-hexylamine.

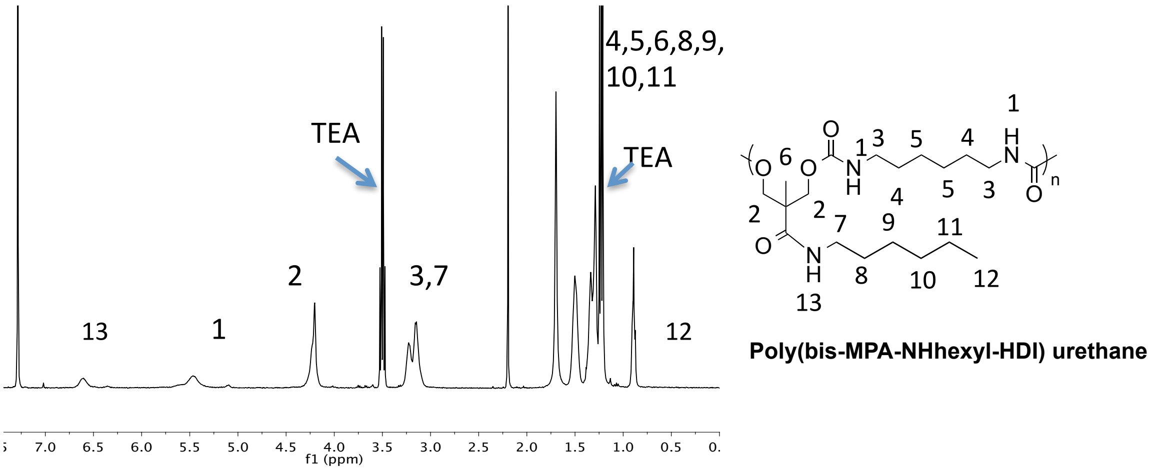


Figure S10. ^{1}H NMR spectrum of poly(bis-MPA-NHhexyl-HDI) urethane in CDCl$_3$.

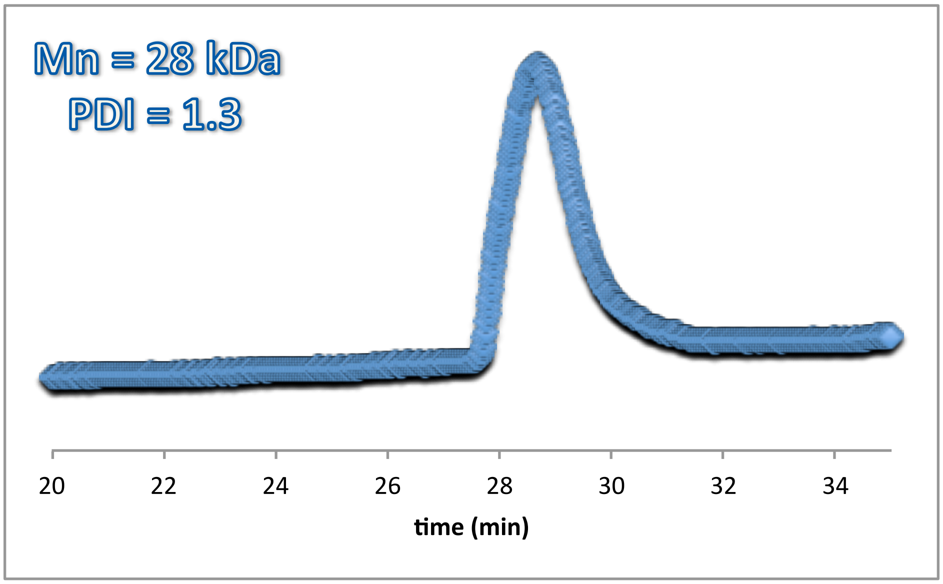
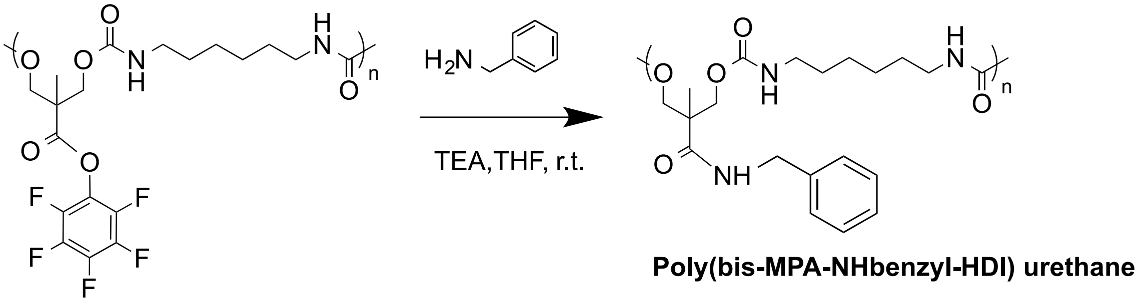


Figure S11. GPC trace of poly(bis-MPA-NHhexyl-HDI) urethane

Post-polymerization modification of poly(MPA-OC_6F_5-HDI) urethane with benzylamine A 20-mL glass vial containing a magnetic stir-bar was charged with poly(MPA-OC_6F_5-HDI) (0.0560 g, 0.120 mmol repeat units), anhydrous THF (0.7 mL), DMF (0.6 mL), and triethylamine (0.0160 g, 0.158 mmol). Next, benzylamine (0.0155 g, 0.145 mmol) was added to the stirred solution. The mixture was allowed to stir at room temperature for 60 minutes, after which the solution was precipitated into excess diethyl ether (16 mL). The flocculent mixture was briefly sonicated and then centrifuged. The mother liquor was decanted and more diethyl ether (20 mL) was added. A second round of sonication, centrifuging, and decanting afforded the polymer as a white solid which was subsequently dried under high vacuum for 24 h (0.043 g, 92 % yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.30 (s, NH, 1H), 7.40-7.00 (m, Ar_H, 5H) (s, NH, 2H), 4.20 (s, CH_2, 2H) 4.10 (s, CH_2, 4H), 3.10 (s, CH_2, 4H), 1.5-1.2 (m, CH_2, 4H), (m, CH_2, 4H) (m, CH_3, 3H).



Poly(bis-MPA-NHbenzyl-HDI) urethane

Poly(bis-MPA-C_6F_5-HDI) urethane

Scheme S6. Modification of pentafluorophenyl ester-containing polyurethane using benzylamine.

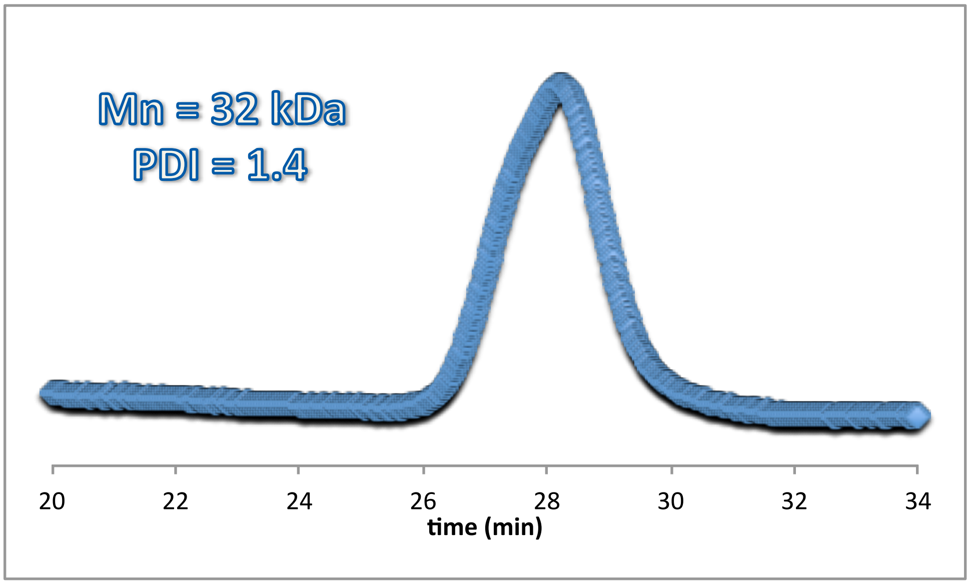
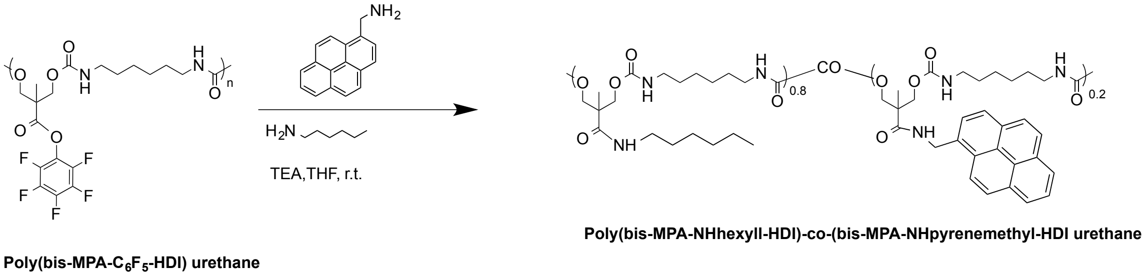


Figure S12. GPC trace of poly(bis-MPA-NHbenzyl-HDI) urethane

Post-polymerization modification of poly(MPA-OC_6F_5-HDI) urethane with 1-aminomethylpyrene and hexylamine. A 20-mL glass vial containing a magnetic stir-bar was charged with poly(MPA-OC_6F_5-HDI) (0.0430 g, 0.0918 mmol repeat units), anhydrous THF (1.0 mL) and triethylamine (0.0226 g, 0.22 mmol). Next, 1-aminomethylpyrene hydrochloride (0.0060 g, 0.022 mmol) and *n*-hexylamine (0.009 g, 0.0892 mmol) were added sequentially (in this order) to the stirred solution. The mixture was allowed to stir at room temperature for 45 minutes, after which the solution was precipitated into excess diethyl ether (16 mL). The flocculent mixture was briefly sonicated and then centrifuged. The mother liquor was decanted and more diethyl ether (20 mL) was added. A second round of sonication, centrifuging, and decanting afforded the polymer as a white solid which was subsequently dried under high vacuum for 24 h. (0.035 g, 89 % yield). ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 6.80-8.80 (m, A_rH, 1.8H), (s, NH, 0.8H) (s, NH, 0.2H) (s, NH, 1.6H) (s, NH, 0.4H) 4.50 (s, CH_2, 0.4H) 4.10 (s, CH_2, 0.8H) 4.00 (s, CH_2, 3.2H) 2.95 (s, CH_2, 1.6H) 2.90 (s, CH_2, 4H) 1.80-0-70 (s, CH_2, 3.2H), (s, CH_2, 0.8H), (s, CH_2, 3.2H), (s, CH_2, 0.8H), (s, CH_2, 1.6H), (s, CH_2, 1.6H), (s, CH_2, 1.6H), (s, CH_2, 1.6H), (s, CH_3, 2.4H), (s, CH_3, 2.4H), (s, CH_3, 0.6H).



Scheme S7. Modification of pentafluorophenyl ester-containing polyurethane using 0.8 equivalents of 1-hexylamine and 0.2 equivalent of 1-aminomethylpyrene.

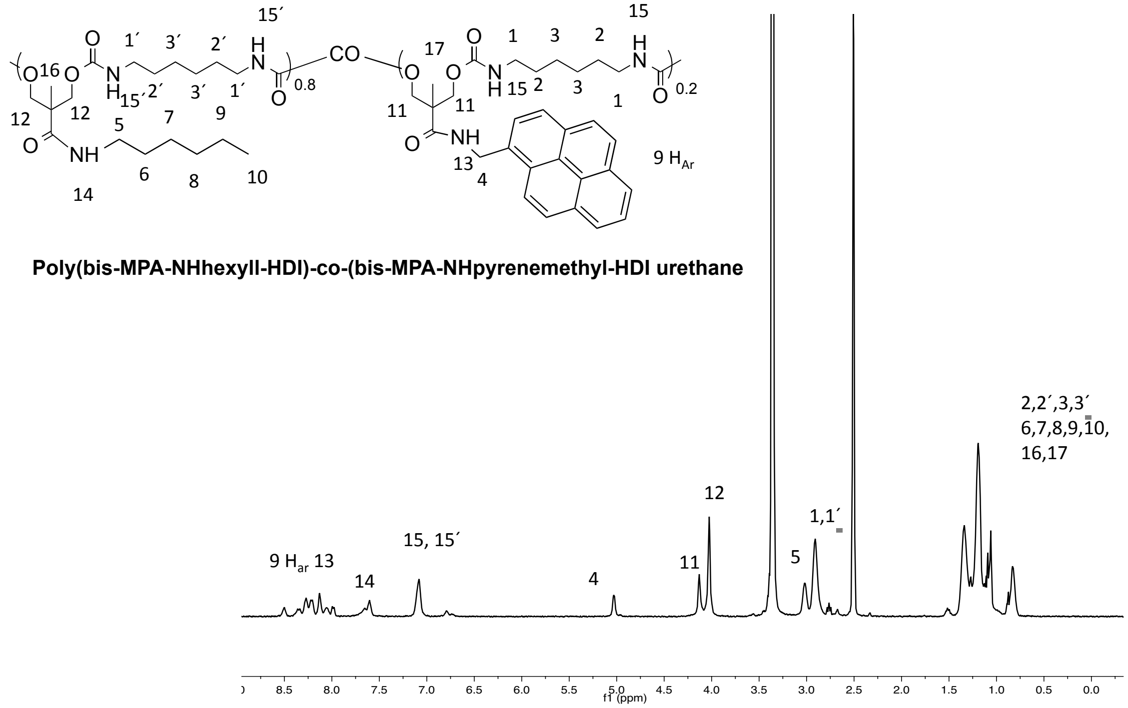


Figure S13. ^{1}H NMR spectrum of poly(bis-MPA-NHhexyl-HDI-co-bisMPA-NHpyrenemethyl) urethane in $CDCl_3$.

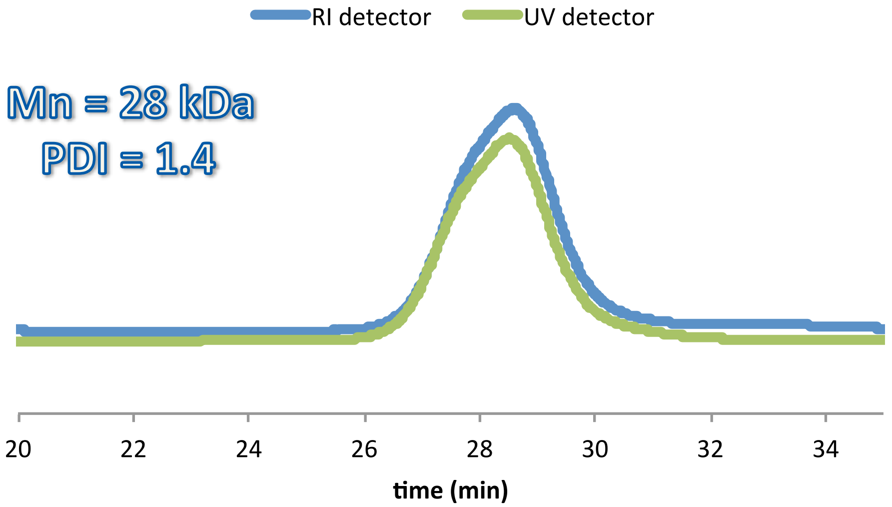
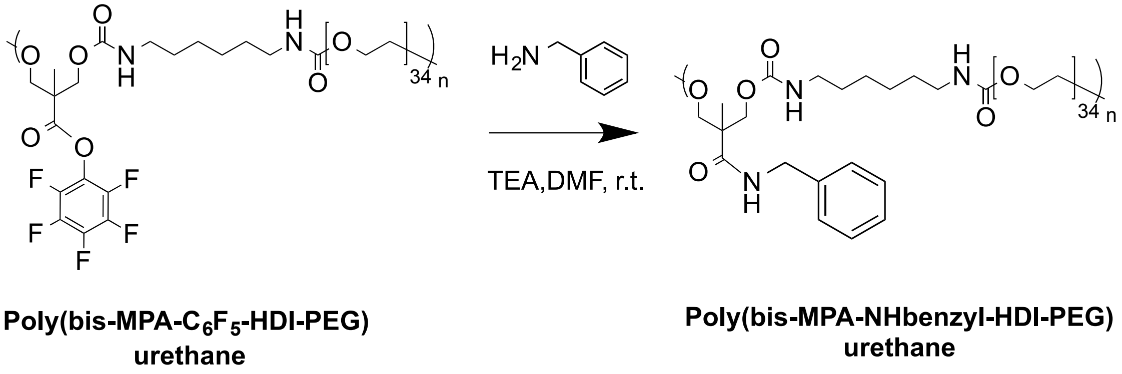


Figure S14. GPC traces using RI (refractive index) detector and UV detector.

Post-polymerization modification of poly(MPA-OC$_6$F$_5$-HDI-PEG) segmented polyurethane with benzylamine

The urethane copolymer (50 mg) was dissolved in ~1 mL of DMF, and benzylamine (0.3 mL of a 10 mg/mL stock solution in DMF; 1.2 equiv relative to the number of pentafluorophenyl esters) was added. 1 drop of TEA was also added, and the reaction mixture was stirred for 2 h at ambient temperature. The reaction mixture was then precipitated into diethyl ether (20 mL). The flocculent mixture was briefly sonicated and then centrifuged. The mother liquor was decanted and more diethyl ether (20 mL) was added. A second round of sonication, centrifuging, and decanting afforded the polymer as a white solid which was subsequently dried under high vacuum for 24 h. ^{1}H NMR (DMSO-d$_6$ 400 MHz): δ = 8.40-7.00 (s, NH, 4H), (s, NH, 2H), (m, Ar$_H$, 5H) 4.25 (s, CH$_2$, 2H) 4.10 (s, CH$_2$, 4H), 4.05 (s, CH$_2$, 4H), 3.65-3.55 (m, CH$_2$, 132H) 2.90 (s, CH$_2$, 8H), 1.5-1.2 (s, CH$_2$, 8H), (s, CH$_2$, 8H) (s, CH$_3$, 3H).



Scheme S8. Modification of pentafluorophenyl ester-containing segmented polyurethane using benzylamine

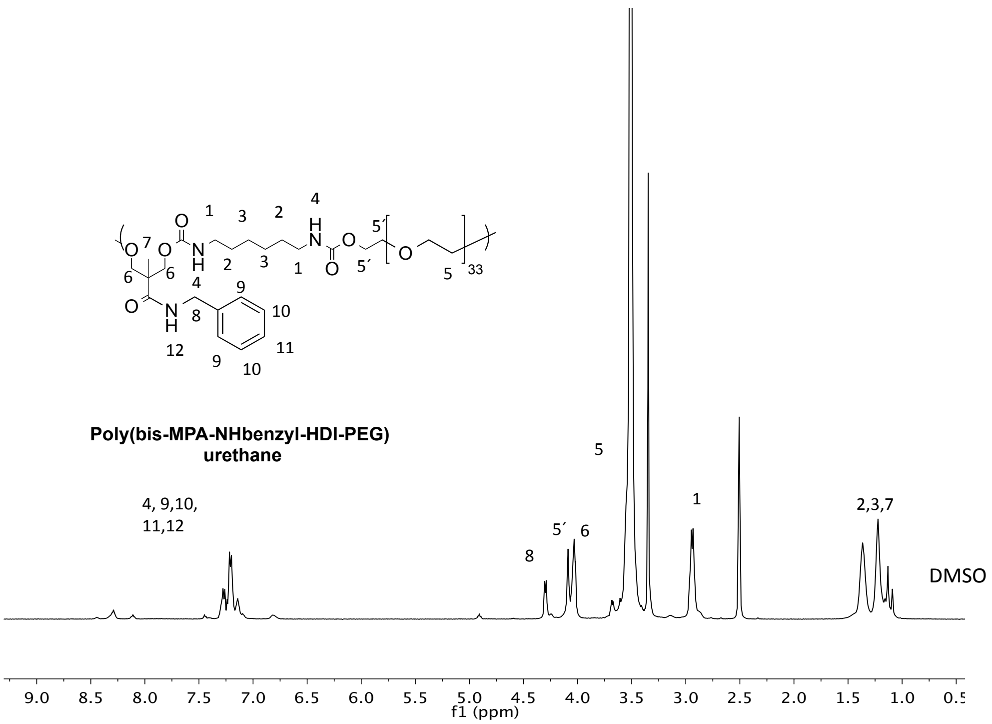


Figure S15. ^{1}H NMR spectrum of poly(bis-MPA-NHbenzyl-HDI-PEG) urethane in DMSO-d_6.

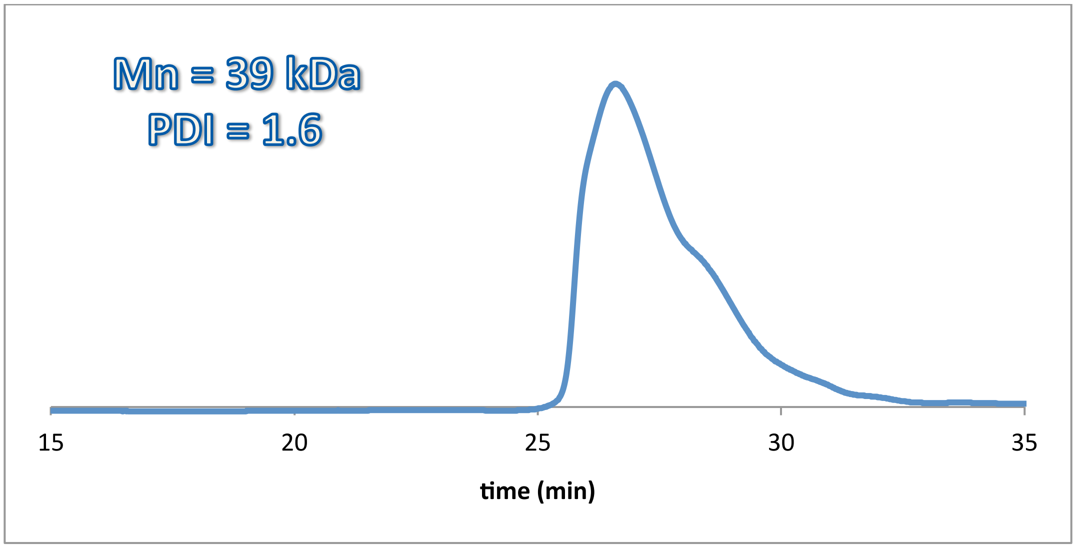


Figure S16. GPC trace of poly(bis-MPA-NHhexyl-HDI-PEG) urethane

1. All the ^{19}F NMR spectra of the postfunctionalized polymers are identical, showing the absence of fluorine signals and indicating that the postpolymerization substitution occurred quantitatively.