Supporting Information

Experimental Section

Monomer Synthesis

Synthesis of 4-hydroxyphenethyl 2-(4-hydroxyphenyl)acetate (HTy)

A 2 L round bottom flask was attached to an overhead stirrer and a Dean-Stark apparatus with water-cooled condenser and a heating mantle was placed beneath the flask. 4-hydroxyphenylacetic acid (157.4 g, 1.03 mol), Tyrosol (142.9 g, 1.03 mol), phosphoric acid (5.07 g, 51.7 mmol), and 315 mL of toluene were added to the flask. The reaction mixture was stirred and heated at reflux until no more water was collected by azeotropic distillation. The reaction mixture was allowed to cool and phase separate and the upper layer was decanted leaving a thick syrup. The syrup was dissolved in 600 mL of ethyl acetate and washed twice with 150 mL of 5% sodium bicarbonate solution and twice with 150 mL of brine solution. The ethyl acetate solution was dried over magnesium sulfate and concentrated *in vacuo* to obtain a thick syrup. The syrup was concentrated *in vacuo* several times with cold dichloromethane to obtain a white powdered residue. The powder was recrystallized from a dichloromethane:hexane mixture, collected by vacuum filtration, and dried in a vacuum oven at 40 ˚C for 72 h. Yield: 223 g, 79%. Melting Point: 94 ˚C. ^{1}H NMR (500 MHz, DMSO-d_6, δ in ppm): 9.27 (s, 1H), 9.18 (s, 1H), 7.02 - 6.94 (m, 4H), 6.71 - 6.64 (m, 4H), 4.14 (t, J = 6.9 Hz, 2H), 3.48 (s, 2H), 2.74 (t, J = 6.9 Hz, 2H).

Synthesis of dimethyl hex-5-enoylglutamate (Gluhexenamide dimethylester)

L-glutamic acid dimethyl ester hydrochloride (1.0 g, 4.7 mmol) was mixed with triethylamine (0.47 g, 4.7 mmol) in 10 mL of dichloromethane (DCM). Separately, 5-hexenoic acid (0.59 g, 5.2 mmol), 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDCI) (0.99 g, 5.2 mmol), and hydroxybenzotriazole monohydrate (HOBt) (0.80 g, 5.2 mmol) were dissolved in 10 mL DCM. The two solutions were combined and stirred overnight. The solution was washed twice with 20 mL of 10% sodium bicarbonate solution, dried over magnesium sulfate, and concentrated *in vacuo* to obtain an oil that was used without further purification. Yield: 86 %. ^{1}H NMR (500 MHz, DMSO-d_6, δ in ppm): 8.18 (d, J = 7.5 Hz, 1H), 5.77 (ddt, J = 16.9, 10.2, 6.6 Hz, 1H), 5.03 - 4.90 (m, 2H),

4.23 (ddd, *J* = 9.2, 7.5, 5.3 Hz, 1H), 3.60 (s, 3H), 3.57 (s, 3H), 2.42 - 2.31 (m, 2H), 2.10 (t, *J* = 7.6 Hz, 2H), 2.02 - 1.90 (m, 3H), 1.79 (dddd, *J* = 13.8, 9.2, 7.9, 6.6 Hz, 1H), 1.55 (d, *J* = 7.5 Hz, 2H).

Synthesis of hex-5-enoylglutamic acid (Gluhexenamide)

Dimethyl hex-5-enoylglutamate (1.1 g, 4.5 mmol) was combined with sodium hydroxide (0.5 g, 12.5 mmol) in a 3.5:1 tetrahydrofuran:water mixture (7 mL). The resulting solution was stirred overnight and concentrated *in vacuo.* The pH was lowered to ~3 by adding concentrated hydrochloric acid. This solution was extracted with 3 portions of 20 mL ethyl acetate. The ethyl acetate solution was dried over magnesium sulfate and concentrated *in vacuo*. 0.8 g of oily residue was obtained. Yield: 90%. ^{1}H NMR (400 MHz, DMSO-d_6, δ in ppm): 12.40 (s, 2H), 8.02 (d, *J* = 7.8 Hz, 1H), 5.77 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.09 - 4.85 (m, 2H), 4.17 (ddd, *J* = 9.2, 7.9, 5.1 Hz, 1H), 2.28 - 2.20 (m, 2H), 2.14 - 2.07 (m, 2H), 2.03 - 1.87 (m, 3H), 1.79 - 1.66 (m, 1H), 1.61 - 1.49 (m, 2H). ESI-MS m/z: $[M-H]^-$ Calculated for $C_{11}H_{16}NO_5^-$ 242.10, found 242.09. ESI-MS: $[M+Na]^+$: Calculated for $C_{11}H_{17}NNaO_5$ 266.10, found 265.98.

Synthesis of dimethyl pent-4-ynoylglutamate (Glupentynamide dimethylester)

L-glutamic acid dimethyl ester hydrochloride (1.0 g, 4.7 mmol) was mixed with triethylamine (0.47 g, 4.7 mmol) in 10 mL DCM. Separately, 4-pentynoic acid (0.51 g, 5.2 mmol), EDCI (0.99 g, 5.2 mmol), and HOBt (0.80 g, 5.2 mmol) were dissolved in 10 mL DCM. The two solutions were combined and stirred overnight. The solution was washed twice with 20 mL of 10% sodium bicarbonate solution, dried over magnesium sulfate, and concentrated *in vacuo* to obtain an oil that was used without further purification. Yield: 93 %. ^{1}H NMR (400 MHz, DMSO-d_6, δ in ppm): 8.32 (d, *J* = 7.6 Hz, 1H), 4.28 (td, *J* = 8.4, 5.4 Hz, 1H), 3.66 - 3.53 (m, 6H), 2.74 (td, *J* = 2.1, 1.0 Hz, 1H), 2.43 - 2.24 (m, 6H), 1.98 (dtd, *J* = 13.3, 7.8, 5.3 Hz, 1H), 1.90 - 1.71 (m, 1H).

Synthesis of pent-4-ynoylglutamic acid (Glupentynamide)

Dimethyl pent-4-ynoylglutamate (1.1 g, 4.3 mmol) was combined with sodium hydroxide (0.5 g, 12.5 mmol) in a 3.5:1 tetrahydrofuran:water mixture (7 mL). The resulting solution

was stirred overnight and concentrated *in vacuo.* The pH was lowered to ~3 by adding concentrated hydrochloric acid. This solution was extracted with 3 portions of 20 mL ethyl acetate. The ethyl acetate solution was dried over magnesium sulfate and concentrated *in vacuo* to obtain 0.64 g of solid powdered product. Yield: 66 %. Melting Point: 97 ˚C. ^{1}H NMR (400 MHz, DMSO-d_6, δ in ppm): 12.35 (s, 2H), 8.15 (d, J = 7.9 Hz, 1H), 4.20 (ddd, J = 9.2, 7.8, 5.0 Hz, 1H), 2.77 – 2.68 (m, 1H), 2.43 – 2.18 (m, 6H), 2.03 – 1.84 (m, 1H), 1.83 – 1.65 (m, 1H). ESI-MS m/z: $[M+Na]^+$ Calculated for $C_{10}H_{13}NNaO_5$ 250.07, found 250.02; $[M+H]^+$ Calculated for $C_{10}H_{14}NO_5$ 228.09, found 227.94.

Polymer Synthesis

General Synthesis of polyesters

In a round bottom flask, 1 equivalent of diol (HTy), 0.97 combined equivalents of diacids, and 0.33 equivalents of 1,4-dimethylpyridinium p-toluenesulfonate (DPTS) were combined with DCM and magnetically stirred for 15 min. The stirring reaction mixture was cooled for 30 min in an ice bath and then 2.1 equivalents of N,N′-diisopropylcarbodiimide (DIC) were added. The stirring reaction mixture was kept in an ice bath for 1 hour and then allowed to gradually warm to room temperature overnight. After 16 hours, the reaction mixture was precipitated by gradually adding isopropanol (5x DCM volume) while stirring. The precipitate was collected by vacuum filtration, redissolved in DCM, and reprecipitated using isopropanol twice. The final precipitate was collected by vacuum filtration and dried in a vacuum oven at 40 ˚C for 48 hours. The precipitate was analyzed by ^{1}H-NMR, FTIR, GPC, DSC, and TGA.

Synthesis of poly(HTy-co-50%phenylenediacetate ester) (HP)

Yield: 88%. GPC: M_n = 84 kDa, M_w = 143 kDa, PDI = 1.7; DSC: T_g = 50 ˚C, T_{m1} = 131 ˚C, T_{m2}= 147 ˚C; TGA: T_d = 320 ˚C; ^{1}H NMR (500 MHz, DMSO-d_6, δ in ppm): 7.35 (s, 4H), 7.22 - 7.18 (m, 4H), 7.03 – 6.99 (m, 4H), 4.21 (t, J = 6.7 Hz, 2H), 3.92 (d, J = 4.4 Hz, 4H), 3.62 (s, 2H), 2.84 (t, J = 6.7 Hz, 2H), (Figure S1); FTIR (ATR) ν_{max} (cm^{-1}): 2917 (w), 1748 (m), 1728 (m), 1606 (w), 1506 (m), 1468 (w), 1422 (w), 1337 (w), 1218 (m), 1193 (m), 1165 (m), 1119 (s), 1017 (m), 915 (m), 807 (w), 788 (w), 689 (w), 648 (w).

Synthesis of poly(HTy-co-45%phenylenediacetate-co-5%BocGlu ester) (HP5BG)

Yield: 94%. GPC: M_n = 80 kDa, M_w = 141 kDa, PDI = 1.8; DSC: T_g = 46 ˚C, T_{m1} = 125 ˚C, T_{m2} = 141 ˚C; TGA: T_d = 320 °C; ^{1}H NMR (500 MHz, DMSO-d_6, δ in ppm): 7.60 (s, 1H), 7.35 (s, 36H), 7.27 - 7.18 (m, 40H), 7.07 – 6.99 (m, 40H), 4.30 (s, 1H), 4.23 (t, J = 6.6 Hz, 20H), 3.93 (d, J = 4.2 Hz, 36H), 3.64 (s, 20H), 2.86 (t, J = 6.6 Hz, 20H), 2.75 (s, 2H), 2.28 – 2.19 (m, 1H), 2.13 – 2.04 (m, 1H), 1.39 (s, 9H), (Figure S2); FTIR (ATR) v_{max} (cm^{-1}): 3035 (w), 2956 (w), 1749 (m), 1731 (m), 1607 (w), 1506 (m), 1423 (w), 1339 (w), 1300 (w), 1218 (m), 1193 (m), 1164 (m), 1120 (s), 1017 (m), 915 (m), 834 (w), 808 (w), 789 (w), 689 (w), 649 (w).

Synthesis of poly(HTy-co-45%phenylenediacetate-co-5%Gluhexenamide ester) (HP5GH)

Yield: 90%. GPC: M_n = 77 kDa, M_w = 126 kDa, PDI = 1.6; DSC: T_g = 47 ˚C, T_{m1} = 128 ˚C, T_{m2} = 143 ˚C; TGA: T_d = 320 ˚C; ^{1}H NMR (500 MHz, DMSO-d_6, δ in ppm): 8.51 – 8.47 (m, 1H), 7.34 (s, 36H), 7.25 - 7.16 (m, 40H), 7.05 - 6.98 (m, 40H), 5.82 - 5.69 (m, 1H), 5.01 - 4.88 (m, 2H), 4.59 - 4.49 (m, 1H), 4.21 (t, *J* = 6.6 Hz, 20H), 3.92 (d, *J* = 4.3 Hz, 36H), 3.62 (s, 20H), 2.84 (t, *J* = 6.6 Hz, 20H), 2.75 (s, 2H), 2.25 (m, 1H), 2.18 (t, *J* = 7.3 Hz, 2H), 2.13 - 2.05 (m, 1H), 2.05 - 1.99 (m, 2H), 1.64 - 1.56 (m, 2H), (Figure S3); FTIR (ATR) v_{max} (cm^{-1}): 3035 (w), 2955 (w), 1749 (m), 1731 (m), 1674 (w), 1607 (w), 1506 (m), 1423 (w), 1338 (w), 1300 (w), 1218 (m), 1193 (m), 1164 (m), 1120 (s), 1017 (m), 915 (m), 844 (w), 808 (w), 789 (w), 688 (w), 648 (w).

Synthesis of poly(HTy-co-45%phenylenediacetate -co-5%Glupentynamide ester) (HP5GP)

Yield: 84%. GPC: M_n = 78 kDa, M_w = 129 kDa, PDI = 1.6; DSC: T_g = 50 ˚C, T_{m1} = 127 ˚C, T_{m2} = 144 ˚C; TGA: T_d = 320 ˚C; ^{1}H NMR (500 MHz, DMSO-d_6, δ in ppm): 8.62 - 8.58 (m, 1H), 7.34 (s, 36H), 7.25 - 7.17 (m, 40H), 7.06 - 6.98 (m, 40H), 4.59 - 4.52 (m, 1H), 4.21 (t, *J* = 6.7 Hz, 20H), 3.92 (d, *J* = 4.3 Hz, 36H), 3.62 (s, 20H), 2.84 (t, *J* = 6.7 Hz, 20H), 2.80 - 2.70 (m, 3H), 2.41 (s, 4H), 2.30 - 2.22 (m, 1H), 2.13 - 2.04 (m, 1H), (Figure S4); FTIR (ATR) v_{max} (cm^{-1}): 3035 (w), 2956 (w), 1749 (m), 1731 (m), 1679 (w), 1607 (w), 1506

(m), 1423 (w), 1379 (w), 1338 (w), 1300 (m), 1218 (m), 1193 (m), 1164 (m), 1120 (s), 1017 (m), 915 (m), 844 (m), 808 (m), 789 (m), 688 (w), 649 (w), 596 (w), 556 (w).

Functionalization Studies

Bulk reactivity of HP5GH and HP5GP

A solution of HP5GH (0.2 g in 2 mL DCM) was combined with 65 mg (3 equivalents) of 1*H*,1*H*,2*H*,2*H*-perflurodecanethiol and 10 mg of Irgacure-2959 (photoinitiator). The solution was transferred into a quartz cuvette and stirred with a magnetic stirrer. The solution was stirred under UV light (365 nm) for 5 hours. The solution was then added dropwise into a stirring solution of isopropanol to precipitate the polymer. The resulting residue was partially dried and re-dissolved in 2 mL DCM and reprecipitated to wash out the unreacted thiol. The resulting residue was filtered and dried in a vacuum oven at 40 ˚C. The reaction product was analyzed by ^{1}H and ^{19}F NMR.

Surface reactivity of HP5GH with 1*H*,1*H*,2*H*,2*H*-perflurodecanethiol

Compression molded films of polymer HP5GH were cut into 5 mm diameter discs. Each disc was then kept in a Teflon dish and 10 µL solution of Irgacure-2959 in methanol (MeOH) and a 100 µL solution of 1*H*,1*H*,2*H*,2*H*-perflurodecanethiol in MeOH were added. The concentrations of the thiol and Irgacure-2959 are shown in Table S1. Each film was then irradiated with UV for a predetermined time. The film was then flipped and identical amounts of Irgacure-2959 and 1*H*,1*H*,2*H*,2*H*-perflurodecanethiol were added to the other side and irradiated with UV. The UV source was kept at a distance of 14 cm and had a power of 3.6 mW/cm^2. For longer UV exposures, 50 uL of fresh MeOH was added on top to compensate for the loss of solvent due to evaporation. After irradiation of both sides, the film was transferred to a 1 dram vial and washed with 1 mL MeOH by vortexing for 20 seconds. The MeOH was separated and discarded and the washing was repeated 9 more time. Finally, each film was sonicated in 1mL MeOH for 10 min, the MeOH was discarded, and the film was dried in a vacuum oven for 16 hours. The treated films were mounted on XPS instrument platform and data was collected for two distinct spots.

Surface reactivity of HP5GH with bovine serum albumin (BSA)

Two QCM gold plated crystals were spin coated with 2% (w/v) DCM solution of HP5GH and dried overnight under vacuum. A solution of 100 µl BSA (0.25 mg/mL) was placed on top of the crystals. To these crystals, a 50 µl solution of Irgacure-2959 (1mg/mL) was added (Irgacure-2959 was dissolved by stirring in PBS for 1 hour). One crystal was then placed under UV light (365 nm) for 5 min and another was kept in dark. Then the crystals were rinsed by 10 mL PBS. The crystals were then placed in the QCM chamber and the frequency was measured while a flow of PBS was maintained. The frequency data was converted to areal mass using the Sauerbrey equation.

Surface reactivity of HP5GP with Az-Heparin

Synthesis of Az-Heparin

A batch of 376 mg of Heparin (5 kDa) was combined with 25.9 mg of imidazole sulfonyl azide tetrafluoroborate, 30 mg of potassium carbonate, and 7.7 mg of copper sulfate pentahydrate and dissolved in 37.5 mL deionized (DI) water. The reaction was stirred overnight, then dialyzed for 24 hours using D7884 dialysis membrane from Sigma-Aldrich, and lyophilized to obtain a white powdered residue.

QCM Experiment of HP5GP with Az-Heparin and BMP-2.

A QCM gold plated crystal was spin coated with 2% (w/v) DCM solution of HP5GP and dried overnight under vacuum. The polymer coated crystal was then loaded on QSENSE module and flowed over with PBS until a stable baseline was achieved. Then a solution of az-Heparin (1mg/ml) mixed with 0.1 mg copper sulfate pentahydrate and 1 mg of sodium ascorbate was flowed over the polymer coated QCM crystal until an equilibrium was reached, then PBS was flowed over the polymer coated surface to remove the unreacted az-Heparin. Then a solution of BMP-2 (24 µg/ml) was flowed over the coated QCM crystal until an equilibrium was reached. Then PBS solution was flowed over the QCM crystal.

QCM control experiment 1: HP5GP/HP + Az-Heparin. A QCM gold plated crystal was spin coated with 2% (w/v) DCM solution of HP5GP or 2% (w/v) HP and dried overnight

under vacuum. The polymer coated crystal was then loaded on QSENSE module and flowed over with DI water until a stable baseline was achieved. Then a solution of az-Heparin (1mg/ml) mixed with 0.1 mg copper sulfate pentahydrate and 1 mg of sodium ascorbate was flowed over the polymer coated QCM crystal for 6 hours. Then a solution of sodium dodecyl sulfate (2% aqueous) was flowed for 30 min followed by DI water overnight.

QCM control experiment 2: HP5GP + BMP-2. A QCM gold plated crystal was spin coated with 2% (w/v) DCM solution of HP5GP and dried overnight under vacuum. The polymer coated crystal was then loaded on QSENSE module and flowed over with PBS until a stable baseline was achieved. Then a solution of BMP-2 (24 μg/ml) was flowed over the coated QCM crystal until an equilibrium was reached. Then PBS solution was flowed over the QCM crystal.

Table S1. The list of results from reactions between HP5GP and 1*H*,1*H*,2*H*,2*H*-perfluorodecanethiol.

Expt No.	Polymer	Thiol (mg)	Photoinitiator (mg)	UV Exposure Time (min)	%C (Avg)	%O (Avg)	%F (Avg)	%F/%C	Corrected %F/%C	% reaction
1	HP5Gluhexe	1	0.01	5	78.63	18.505	1.935	0.0246	0.0232	55
2	HP5Gluhexe	0.5	0.01	5	81.01	18.075	0.465	0.0057	0.0043	10
3	HP5Gluhexe	0.1	0.01	5	81.125	17.96	0.1	0.0012	-0.0002	0
4	HP5Gluhexe	0.05	0.01	5	81.98	17.385	0.055	0.0007	-0.0008	0
5	HP5Gluhexe	0.01	0.01	5	80.375	18.38	0.11	0.0014	-0.0001	0
6	HP5Gluhexe	0.1	0.01	1	81.9	17.455	0.16	0.0020	0.0005	1
7	HP5Gluhexe	0.1	0.01	0.5	81.53	17.85	0.12	0.0015	0.0000	0
8	HP5Gluhexe	0.1	0.01	30	81.77	17.21	0.27	0.0033	0.0019	4
9	HP	1	0.01	5	80.75	18.435	0.115	0.0014	0.0000	0
10	HP	1	0.01	30	80.99	18.49	0.16	0.0020	0.0000	0
11	HP5Gluhexe	0	0	0	81.54	17.94	0.075	0.0009		
12	HP5Gluhexe	1	0.01	1	80.56	18.63	0.81	0.0100	0.0086	20
13	HP5Gluhexe	1	0.01	5	80.03	18.53	1.44	0.0179	0.0165	39
14	HP5Gluhexe	1	0.5	1	80.71	18.19	1.10	0.0137	0.0122	29
15	HP5Gluhexe	1	0.5	5	79.68	18.18	2.14	0.0268	0.0254	60
16	HP5Gluhexe	0.5	0.5	5	80.75	17.97	1.28	0.0159	0.0144	34
17	HP5Gluhexe	1	0.5	15	80.39	17.76	1.86	0.0231	0.0212	50
18	HP5Gluhexe	1	0.01	15	78.36	18.40	3.25	0.0414	0.0394	94
19	HP5Gluhexe	1	0.1	5	79.88	17.89	2.23	0.0279	0.0265	63

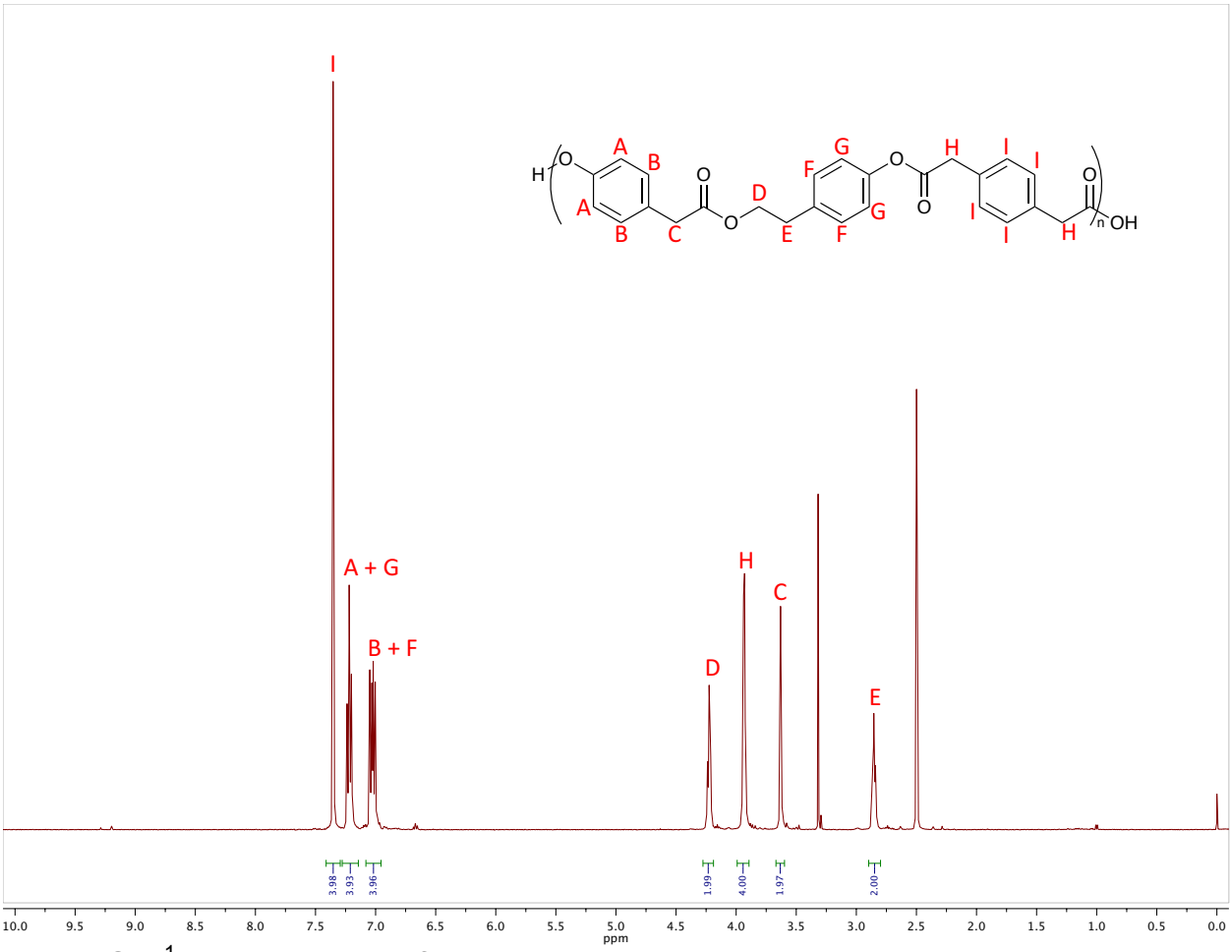

Figure S1. ^{1}H NMR spectra of HP

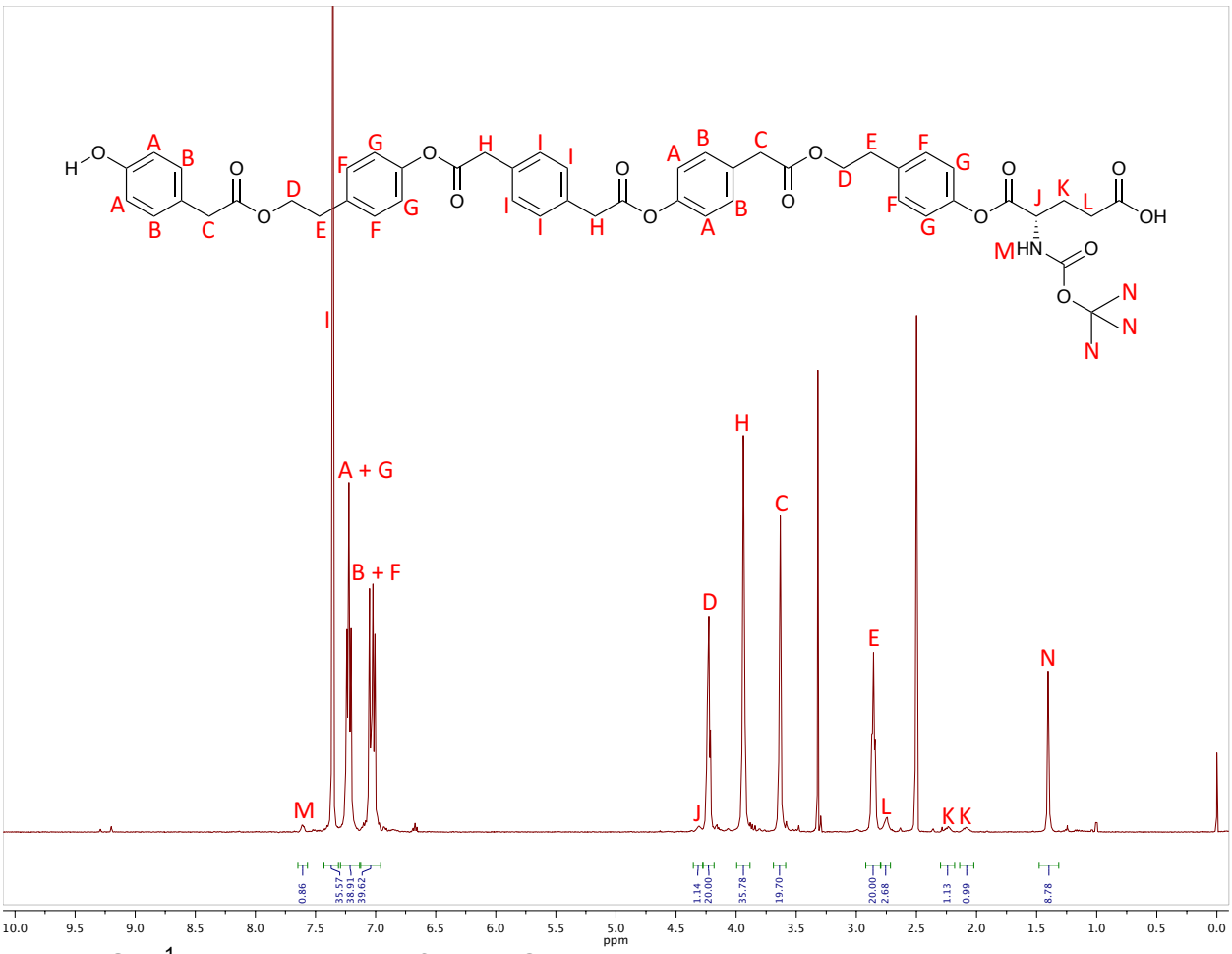

Figure S2. ^{1}H NMR spectra of HP5BG

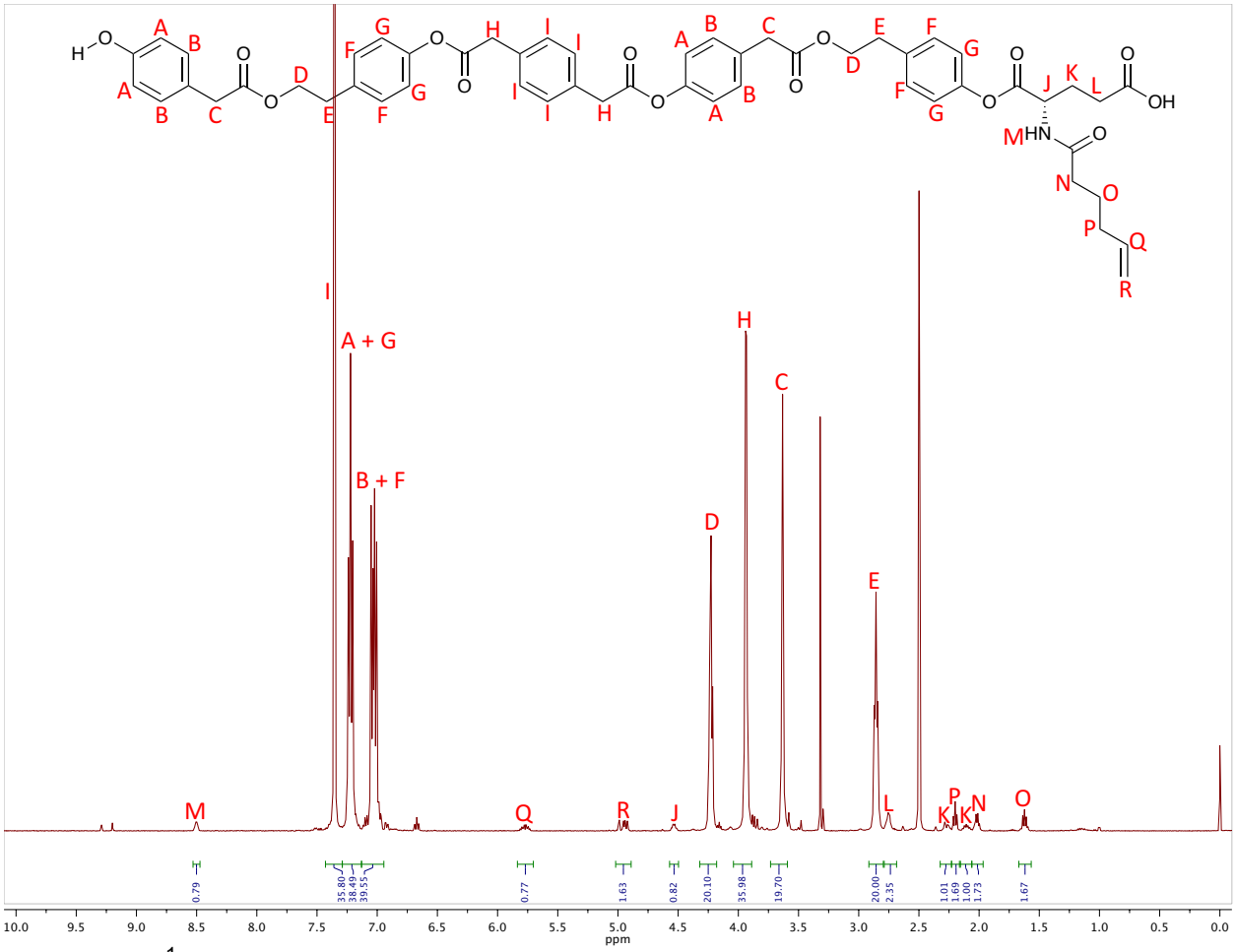

Figure S3. ^{1}H NMR spectra of HP5GH

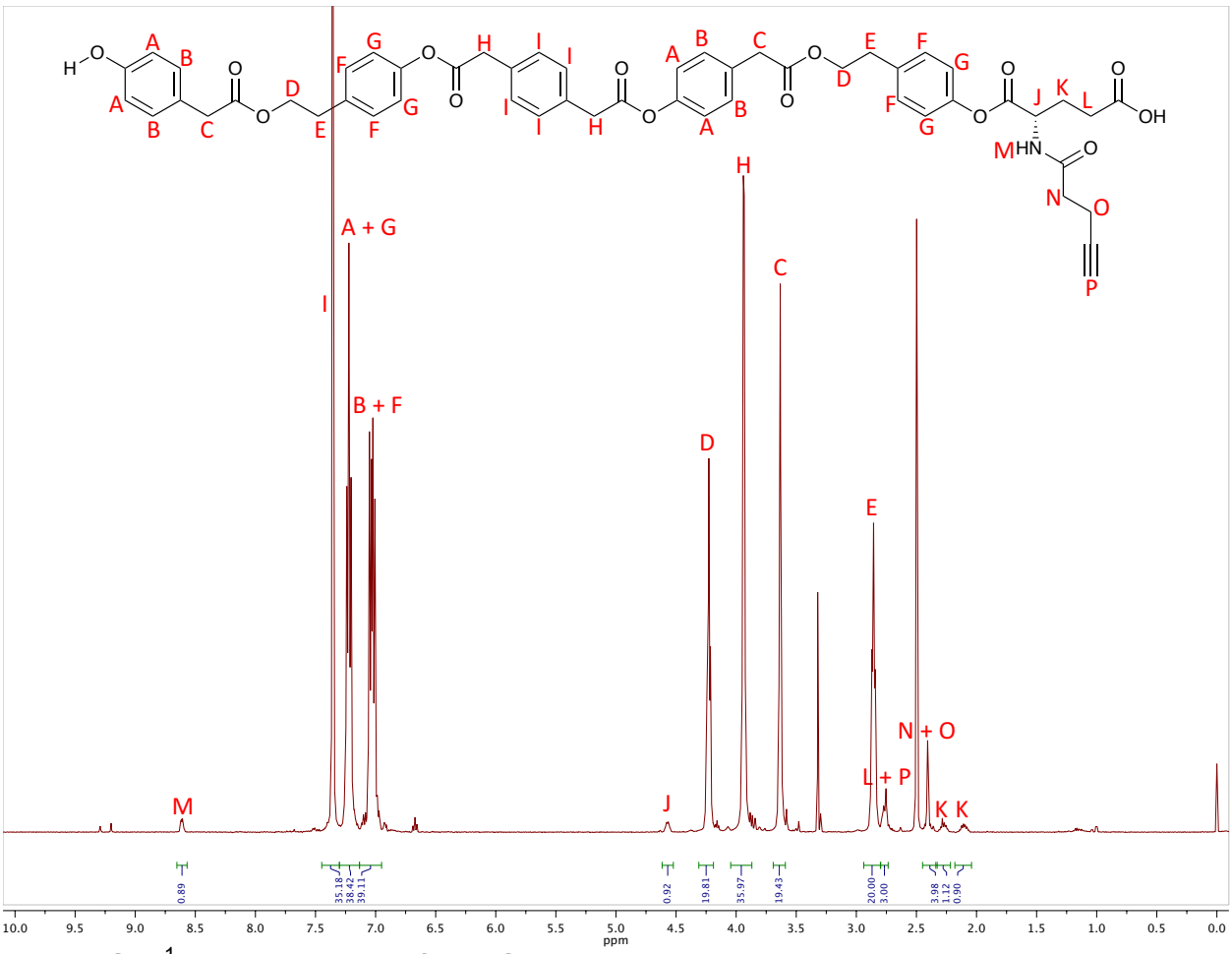

Figure S4. ^{1}H NMR spectra of HP5GP

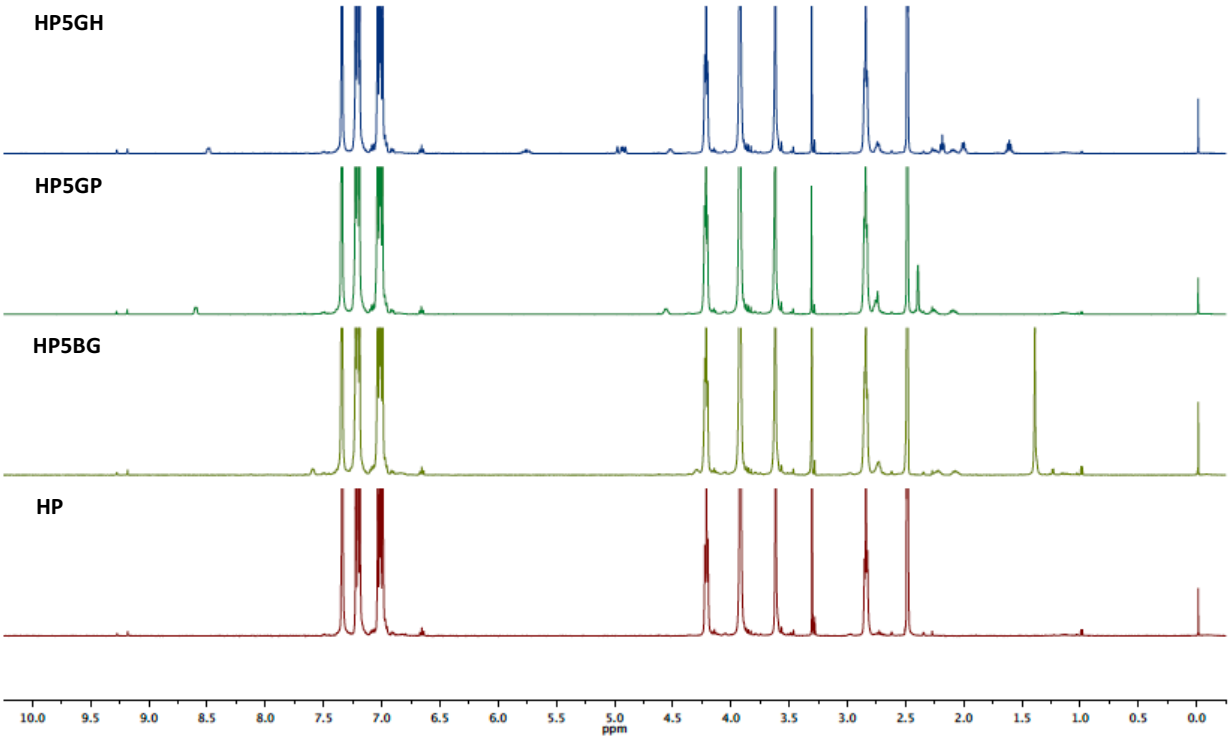

Figure S5. Stacked ^{1}H NMR spectra for the polymers.

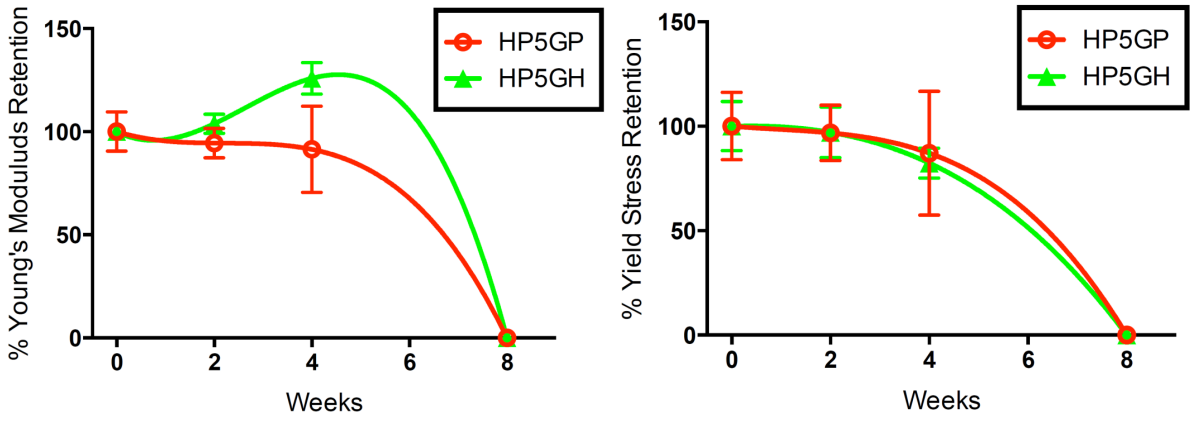

Figure S6. Left: Young's modulus over time at 37 ˚C in PBS; Right: Yield strength over time at 37 ˚C in PBS.

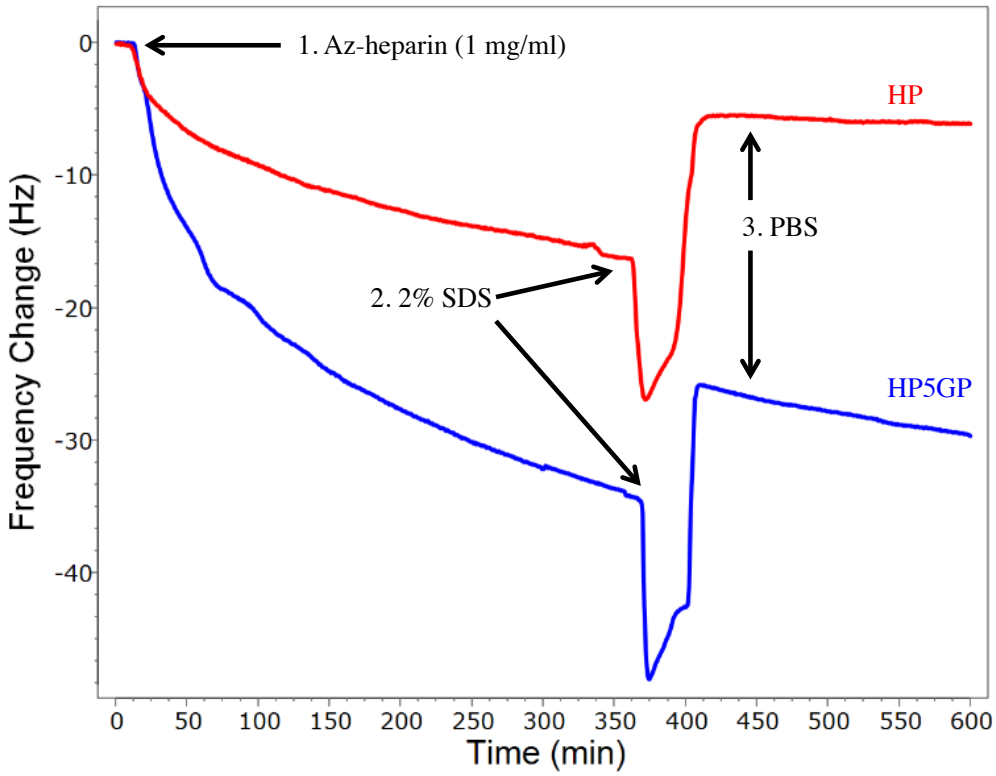

Figure S7. Graph of frequency change over time when az-Heparin, 2% SDS, and PBS were flowed over a QCM crystal coated with HP5GP.

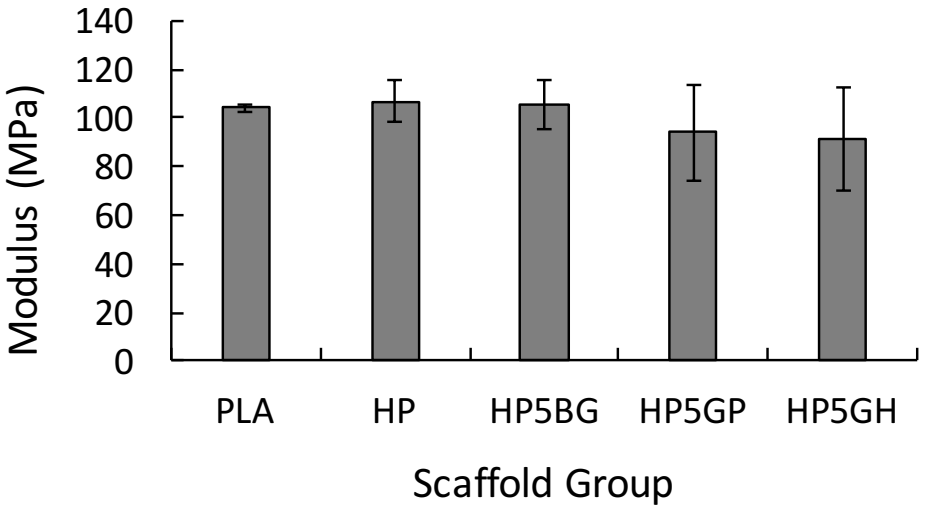

Figure S8. Young's modulus values of the 3D printed scaffolds.