Supporting Information

Materials. 4-arm PEG amine (Mw 10,000 g/mol) and monofunctional PEG amine (mPEG-NH_2, Mw 5,000 g/mol) were purchased from Laysan Bio Inc. 3-(3,4-dihydroxyphenyl) propionic acid (DHPA; Alfa Aesar, 98%), Triethylamine (Aldrich, 99%), N-hydroxybenzotriazole (HOBt, Advanced ChemTech) and O-Benzotriazole-N,N,N',N'-tetramethyl-uronium-hexafluoro-phosphate (HBTU; Novabiochem) were used as received. 1,3-benzenediboronic acid was purchased from Alfa Aesar with purity of 97% and used without further treatment.

Synthesis of cPEG.[18a]

In a 50 mL Schlenk flask, 4-arm PEG amine (5.0 g, 2.0 mmol of amine groups, Mw 10,000 g/mol) was dissolved in 45 mL of dichloromethane. 0.73 g (4.0 mmol) DHPA, 0.90 g (6.60 mmol) HOBt, 1.53g (4.0 mmol) HBTU and 1.0 mL (6.6 mmol) of triethylamine were added sequentially to the PEG solution. Afterwards, 22.5 mL of DMF was added to dissolve the DHPA and this coupling reaction was carried out at 20 ^oC under N_2 atmosphere with continuous stirring for 2.0 h. The crude product was purified by precipitation in diethyl ether (500 mL) once and in methanol (500 mL) three times at -20 ^oC and in the presence of acetic acid (6.0 mL, 4.0 mmol). The cPEG polymer was vacuum dried after one additional precipitation in diethyl ether. Molecular weight and molecular weight distribution were calculated from MALDI-TOF mass spectrum. (Figure S2). ^1H NMR (CDCl3) δ (ppm): 6.5-7.0 (m, 3H, aromatic), 2.85 (s, 2H, -NHCO-CH_2-), 2.5 (s, 2H, CH_2, adjacent to aromatic), 3.51-3.67 (m, -O-CH_2CH_2O-).

Synthesis of mPEG-cat.

mPEG-cat was synthesized using a similar method as described above. (3.0 g, 0.6 mmol of amine groups, Mw 5,000 g/mol) was dissolved in 10 mL of dichloromethane. 0.22 g (1.2 mmol) DHPA, 0.27 g (1.98 mmol) HOBt, 0.46 g (1.2 mmol) HBTU and 0.28 mL (1.98 mmol) of triethylamine were added sequentially to the PEG solution. Afterwards, 5.0 mL of DMF was added to dissolve the DHPA and this coupling reaction was carried out at 20 ^oC under N_2 atmosphere with continuous stirring for 2.0 h. The crude product was purified by precipitation in diethyl ether (300 mL) once and in methanol (300 mL) three times at -20 ^oC and in the presence of acetic acid (1.8 mL, 1.2 mmol). The PEG polymer was vacuum dried after one additional precipitation in diethyl ether. ^1H NMR (CDCl3) δ (ppm): 6.5-7.0 (m, 3H, aromatic), 2.85 (s, 2H, adjacent to aromatic), 2.5 (s, 2H, -NHCO-CH_2-), 3.51-3.67 (m, -O-CH_2CH_2O-), 3.35(s, 3H, OCH_3).

Formation of Hydrogels.

Hydrogels were prepared by mixing PBS buffer solution of cPEG and BDBA at different molar ratios of catechol to boronic acid. Unless otherwise stated, hydrogels were formed at 15 wt% polymer. A typical procedure used was as follows: In a 1.0 mL vial, 15.0 mg (0.006 mmol catechol) cPEG and 0.05 mL PBS were added to give a clear solution. Then, 0.05mL of BDBA stock solution (0.024 mmol boronic acid, pH = 9.0) was added. The solution mixture was stirred vigourously at 20 ^oC, and a red viscous hydrogel was produced within 30 min.

Characterization

All ^{1}H NMR spectra were recorded on a Varian unity 500 spectrometer in $CDCl_3$ or D_2O. ^{11}B NMR was recorded on a Varian unity 500 spectrometer in D_2O with NaOD or D_2O with DCl and using boron trifluoride as an external standard. UV-vis absorption spectra were obtained on a Perkin-Elmer Lambda 1050 UV-vis spectrometer at room temperature. Rheological measurements were performed in strain-controlled mode on a Paar-Physica MCR 300 rheometer. A cone and plate geometry with a cone diameter of 25 mm and an angle of 2^{o} was employed. The temperature was controlled by the bottom Peltier plate. In each measurement, 0.2 mL of the preformed hydrogel was loaded onto the plate. An evaporation guard was used in combination with damp Kimwipes surrounding the sample to minimize evaporation. Frequency sweeps were performed at 5% constant strain from 0.1 to 100 rad/s at 20 ^{o}C.

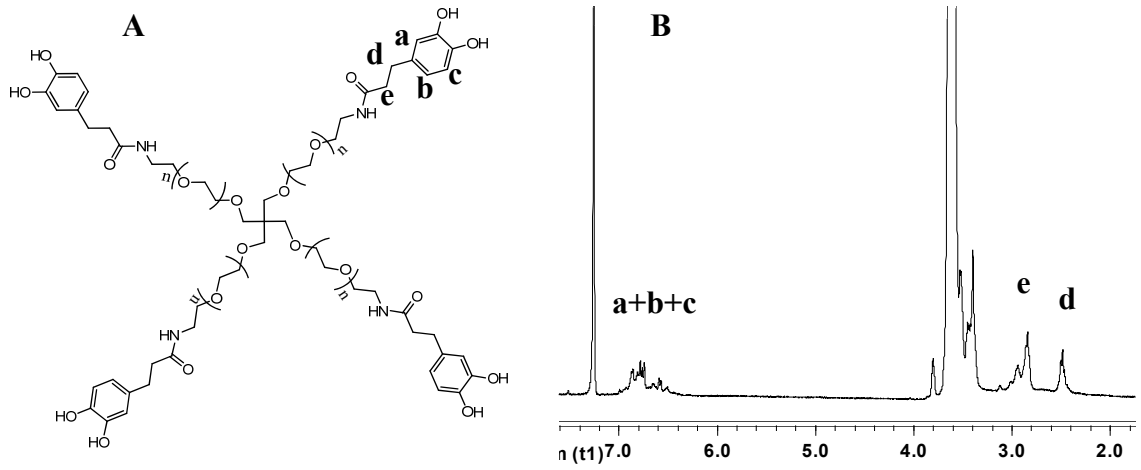

Figure S1. Structure (A) and ^{1}H NMR spectrum of cPEG in $CDCl_3$ (B).

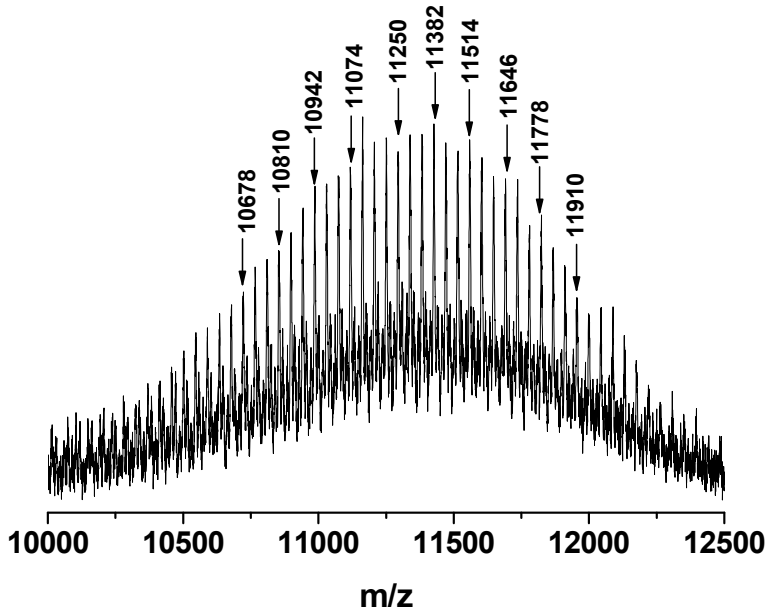

Figure S2. MALDI-TOF spectrum of cPEG. M_n calculated from software (PolyTools, Bruker) was 11200 g/mol.

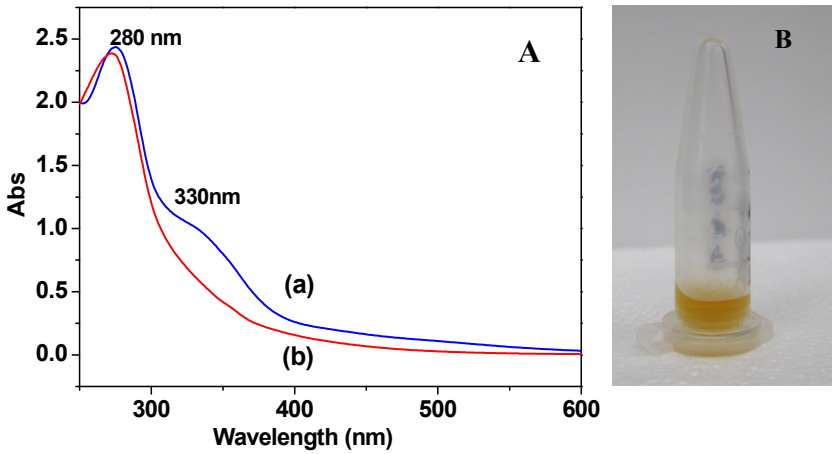

Figure S3. A: UV-vis spectrum of mPEG-cat at (a) pH 9.0 and (b) pH 3.0. B: Photo of aqueous solution of cPEG at pH 9.0 after 30 days.

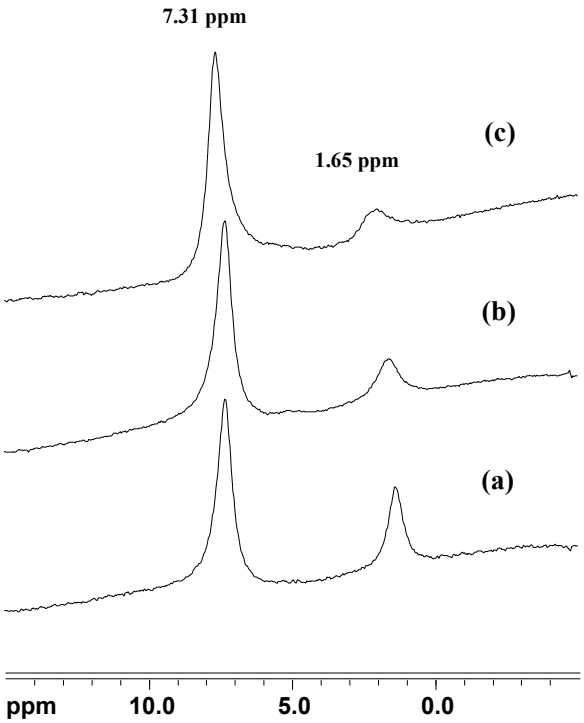

Figure S4. ^{11}B NMR spectra of a 2:1 molar ratio of mPEG-cat and BDBA in D_2O/NaOD at pH 9.0 after (a) 30 min; (b) 24 h and (c) 48 h.

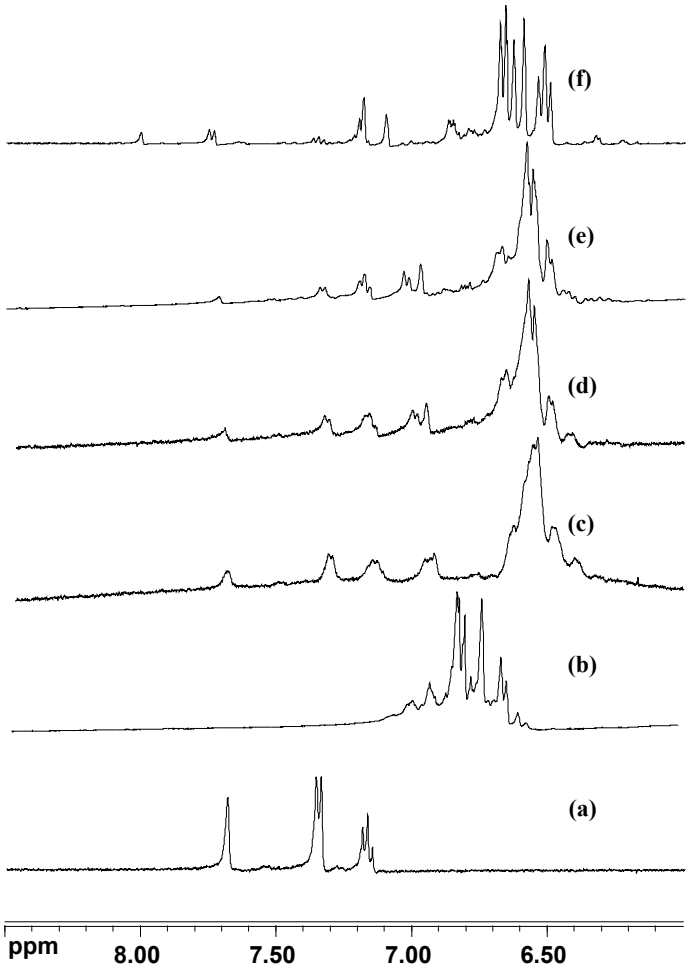

Figure S5. ^{1}H NMR spectra of (a) BDBA in D_2O/NaOD at pH 9.0; (b) mPEG-cat at pH 9.0; (c) mPEG-cat/BDBA in D_2O/NaOD at pH 9.0 after 30 min, (d) 24 h and (e) 48 h; (f) Solution of (e) after addition of DCl to pH 3.0. Experimental conditions: 15 wt% mPEG-cat. The water peak at 4.8 ppm was used as chemical shift standard.

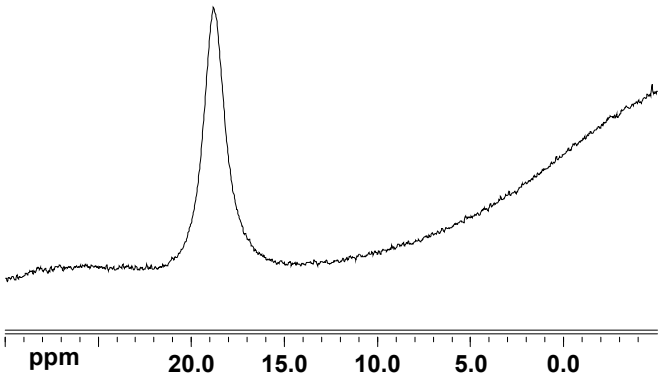

Figure S6. ^{11}B NMR spectrum of mPEG-cat/BDBA mixture at pH 3.0. The solution resulted from acidification of the gel formed from mPEG-cat and BDBA at molar ratio of 2:1 (mPEG-cat:BDBA), pH 9.0 in D_2O/NaOD for 48 h.

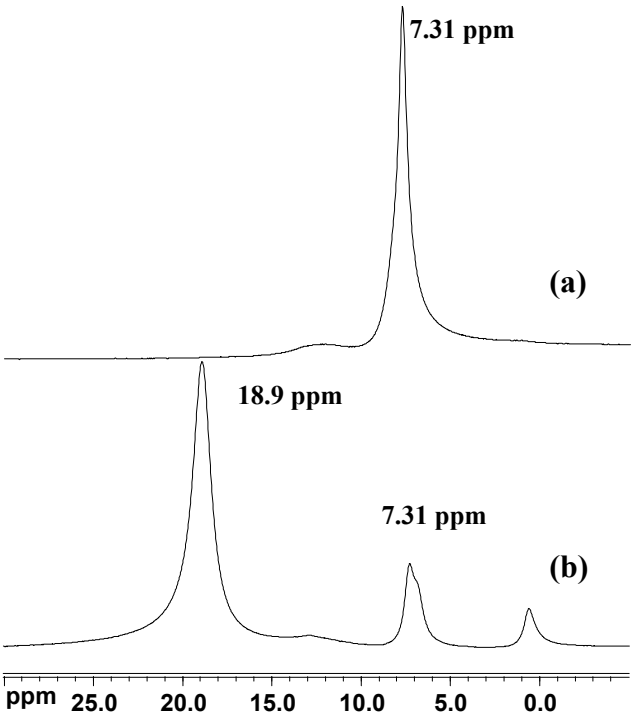

Figure S7. ^{11}B NMR spectrum of borax/dopamine with molar ratio of 1:1 at pH 9.0 (a) and pH 3.0 (b).

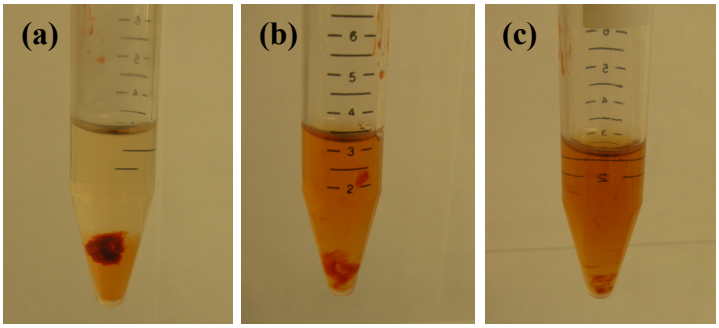

Figure S8. Stability study of hydrogel formed from cPEG with BDBA at 20 min (a), 1.5 h (b) and (c) 17 h. The molar ratio of cPEG to BDBA was 1:8, and stability study was performed in PBS buffer at pH 7.4 and at 37 ^{o}C.

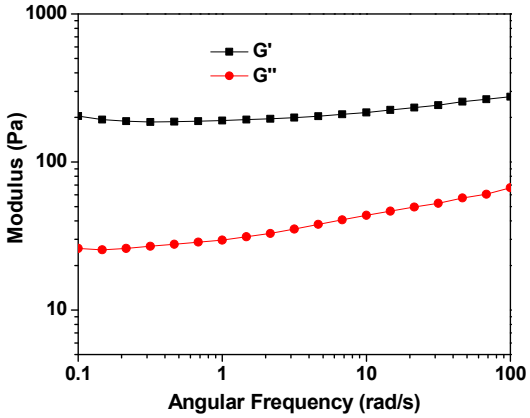

Figure S9. Dynamic frequency sweep of hydrogels formed from BDBA and cPEG with polymer concentration of 15 wt% at 37 ^{o}C. The molar ratio of cPEG to BDBA was 1:8.

Table S1. Effect of stoichiometry on gel formation of a 15 wt% solution of cPEG at pH 9.0.

Molar Ratio[a]	Gelation Time[b]	Physical State
1:2	7 days	Red gel
1:4	2 days	Red gel
1:6	0.5 hour	Red gel
1:8	0.5 hour	Red gel
1:12	0.5 hour	Dark red gel
1:16	7 days	Dark brown solution
1:32	7days	Dark brown solution

[a] cPEG:BDBA.
[b] vial inversion method.