Electronic Supplemental Information

Materials. All chemicals and reagents were purchased from Sigma-Aldrich (Milwaukee, WI). *tert*-Butyl acrylate (*t*BA) and *n*-butyl acrylate (*n*BA) were purified by passing through an inhibitor removal column. The purified monomers were sealed and stored at 4 °C before use. All other reagents were of analytical grade and were used without further purification. Water was deionized and filtered through a NANOpure Diamond water purification system (Barnstead, Thermo Scientific).

Composition and molecular weight analysis. ^{1}H NMR spectra were recorded on a Bruker AV400 NMR spectromenter under standard quantitative conditions and were analyzed with MestRec software. Gel permeation chromatography (GPC) spectra were obtained on a Waters GPC (Milford, MA) system with a 2414 refractive index detector. Tetrahydrofuran (THF) or phosphate buffered saline (PBS) were used as the mobile phase and the flow rate was maintained at 1 mL/min. Molecular weight calibration was based on polystyrene (Polyscience, Warrington, PA) or hyaluronic acid standards (Genzyme, Cambridge, MA and Lifecore, Chaska, MN).

Synthesis of poly(*t*-butyl acrylate)-Br macroinitiator. The macroinitiator was synthesized by atom transfer radical polymerization (ATRP) of *t*BA employing ethyl 2-bromopropionate (EBP) as the initiator, copper (I) bromide (CuBr) as the catalyst and *N*,*N*,*N'*,*N"*,*N"*-pentamethyldiethylenetriamine (PMDETA) as the ligand. To a round bottom flask was added EBP (0.13 mL, 1 mmol), *t*BA (30 mL, 0.2 mol), CuBr (148 mg, 1 mmol) and PMDETA (0.22 mL, 1 mmol) and the reaction mixture was degassed by three freeze-thaw cycles under N_2. After 2 h of polymerization at 70 °C, the flask was opened and allowed to cool to ambient temperature. The reaction mixture was purified by dissolution/precipitation with methylene chloride (methanol/water = 7:3, v/v) three times and was dried under vacuum at 40 ^{o}C for 24 h. A white powder with 95% yield was obtained. GPC: M_n= 13,000 g/mol; M_w/M_n = 1.22. ^{1}H NMR ($CDCl_3$, δ): 1.13 (t, C***H*****$_3$**CH_2O–), 1.45 (m, –C(C***H*****$_3$**$)_3$–), 1.52, 1.78 (m,

–C***H₂***CH–), 2.20 (m, –CH_2C***H***–), 4.05 (m, CH_3C***H₂***O– and –CH_2C***H***Br, overlapping). ^{1}H NMR analysis indicated a polymer composition of P*t*BA_{100}-Br and a M_n of 12,500 g/mol.

Synthesis of poly(*t*-butyl acrylate)-*b*-poly(*n*-butyl acrylate). To a round bottom flask was added P*t*BA_{100}-Br (4 g, 0.33 mmol), *n*BA (15 mL, 0.11 mol), CuBr (22 mg, 0.15 mmol) and PMDETA (32 μL, 0.15 mmol), and the reaction mixture was degassed by three freeze-thaw cycles under N_2. The flask was heated in a thermostated oil bath at 85 ^{o}C for 1 h. The polymerization was terminated by exposing the reaction mixture to the air and cooling the flask to room temperature. The mixture was purified by dissolution/precipitation with methylene chloride/(methanol/water = 7:3, v/v) three times and dried under vacuum at 40 ^{o}C for 24 h. A white powder with 96% yield was obtained. GPC: M_n = 15,000 g/mol; M_w/M_n = 1.09. ^{1}H NMR ($CDCl_3$, δ): 0.95 (t, CH_3***₃***CH_2–), 1.45 (m, –C(CH_3***₃***)***₃***–), 1.42-1.68 (m, –C***H₂***CH–, –C***H₂***CH_2CH_2– and –CH_2C***H₂***CH_2–), 1.78 (m, –C***H₂***CH–), 2.20 (m, –CH_2C***H***–), 4.05 (m, –CH_2C***H₂***O–). ^{1}H NMR analysis indicated a polymer composition of P*t*BA_{100}-*b*-P*n*BA_{16} and a M_n of 14,500 g/mol.

Synthesis of poly(acrylic acid)-*b*-poly(*n*-butyl acrylate). To a round bottom flask was added P*t*BA_{100}-*b*-P*n*BA_{16} (2 g, 0.133 mmol), trifluoroacetic acid (TFA, 5.1 mL, 69 mmol) and 30 mL choloroform. The mixture was stirred for 48 h at room temperature. The final product was obtained after evaporating the solvent and TFA. ^{1}H NMR (DMSO-d_6, δ): 0.95 (t, CH_3***₃***CH_2–), 1.42-1.68 (m, –C***H₂***CH–, –C***H₂***CH_2CH_2– and –CH_2C***H₂***CH_2–), 1.78 (m, –C***H₂***CH–), 2.20 (m, –CH_2C***H***–), 4.05 (m, –CH_2C***H₂***O–). ^{1}H NMR analysis indicated 100% deprotection and a M_n of 8,900 g/mol.

Modification of PAA-*b*-P*n*BA with hydroxyethyl acrylate (HEA) and the assembly of block copolymer micelles (BCMs). PAA_{100}-*b*-P*n*BA_{16} (0.8 g, 0.086 mmol) and HEA (0.90 mL, 8.6 mmol) were dissolved in dimethylformamide (DMF, 10 mL) and the solution was stirred at room temperature for 30 min before the addition of *N*-(3-dimethylaminopropyl)-*N'*-ethylcarbodiimide (EDC). The mixture was stirred at room

temperature in the dark for 4 h. The reaction mixture was then directly dialyzed against de-ionized water for 3 days in the dark to remove any residual impurities and to form micelles simultaneously. To calculate the esterification efficiency and the micelle concentration, a pre-determined amount of the above solution was freeze-dried and the dry powder was weighed before being dissolved in DMSO-d_6 for ^{1}H NMR analysis. ^{1}H NMR (DMSO-d_6, δ): 0.95 (t, C***H*****$_3$**CH$_2$–), 1.42-1.68 (m, –C***H*****$_2$**CH–, –C***H*****$_2$**CH$_2$CH$_2$– and –CH$_2$C***H*****$_2$**CH$_2$–), 1.78 (m, –C***H*****$_2$**CH–), 2.20 (m, –CH$_2$C***H***–), 3.85-4.40 (m, –CH$_2$CH$_2$C***H*****$_2$**O–, –OCH$_2$C***H*****$_2$**O– and –OC***H*****$_2$**CH$_2$O–), 5.80-6.40 (C***H*****$_2$**=CH– and CH$_2$=C***H***–). ^{1}H NMR analysis indicated a 20 mol% acrylation of the PAA block and the final polymer had a composition of P(AA$_{100}$-*g*-HEA$_{20}$)-*b*-P*n*BA$_{16}$ and a M_n of 11,200 g/mol.

Hydrogel synthesis. Hydrogels were prepared by free radical polymerization of AAm in the presenece of varying amounts of crosslinkable BCMs or MBA. Samples are referred to as S-x-BCM and controls were designated as C-x-MBA, where x designates the concentration of the crosslinkers in the gelation solution. For example, to S-7.5-BCM gels, 0.5 mL 7.5 mg/mL BCM solution was mixed with 250 mg AAm in a scintilation vial. To this mixture was added 5 μL of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TEMED) and 10 μL of freshly made ammonia persulfate (APS) solution (64 mg/mL in deionized water). Immediately upon mixing, the solution was rapidly loaded into a square-shaped Teflon mold (0.5″×0.5″). The mold was sealed with a Teflon lid and the reaction was allowed to occur overnight. Hydrogel samples were allowed to reach equilbrium swelling state prior to the mechanical testing.

Critical micelle concentration (CMC). Freshly dialyzed micelle solution was used to prepare a stock solution at a concentration of 1 mg/mL. The polymer stock solution was then subjected to serial dilution with concentrations down to 10^{-5} mg/mL. Each sample was then prepared by carefully dropping 24 μL of a pyrene solution (2.5×10^{-5} mol/L in acetone) into an empty vial, evaporating the acetone under vaccum at 40 ^{o}C for 2 h, adding 1 mL of one of the polymer solutions, and stirring the closed vials 24 h at 50 ^{o}C. The final

concentration of pyrene in water thus reached 6×10^{-7} mol/L, which is below the pyrene saturation concentration in water at 22 ^{o}C. Steady-state fluorescence spectra of the air-equilibrated samples were recorded with a HORIBA Jobin Yvon SPEX FluoroMax-4 spectrafluorometer (90° angle geometry, 1 cm×1 cm quartz cell) using the following conditions: excitation at 333 nm, slit width 3 nm for the excitation, and 1.5 nm for the emission. The intensities of the bands I_1 at 372 nm and I_3 at 383 nm were then evaluated, and their ratio was plotted versus the polymer concentration. I_1/I_3 remains constant (~2.0) at polymer concentrations c < 0.005 mg/mL, below which pyrene was in aqueous environment. When pyrene was sequestered into the hydrophobic core of the micleles, I_1/I_3 decreased. The cmc was determined as the intersection between the plateau at $I_1/I_3 \sim 2.0$ and the tangent of the curve where I_1/I_3 decreased proportionally with an increase of polymer concentration.

Particle size analysis. The average size and size distribution of BCMs were analyzed by dynamic light scattering (DLS) using a Malvern Zetasizer nanoZS apparatus (Malvern Instruments, UK). BCMs were dispersed in deionized water at a concentration of 15 mg/mL. To confirm the presence of micelles in the gelation solutions, BCMs dispersed in an aqeuous medium containing 500 mg/mL AAm were also subjected to the same analysis. The viscosity of BCM solutions were determined using a rheometer (AR2000, TA Instrument, New Castle, DE) with a 60 nmm aluminum parallel plate geometry at ambient temperature with a constant shear rate of 1 rad/s. Five separate injections were analyzed and the z-average particle size and the polydispersity index (PDI) were determined at 25°C using dynamic light scattering combined with Malvern's DTS software (v.6.01).

Micelle morphology. Bright field transmission electron microscopy (TEM) images were acquired using a FEI Tecnai 12 microscope operating at an accelerating voltage of 120 kV. Images were collected on a Gatan CCD. TEM samples were prepared by applying a drop of polymer solution (about 2-4 μL, ~15 mg/mL in deionized water) onto a carbon coated copper TEM grid (300 mesh) and allowing the solvents to evaporate under ambient conditions.

Afterwards, a droplet of freshly prepared saturated uranyl acetate aqueous solution (about 10μL) was deposited onto the dried samples. After about 1 min, the excess solution was wicked away by a piece of filter paper, and the sample was allowed to dry before imaging.

Characterization of vinyl group conversion in S-x-BCM gels. The as-synthesized S-10-BCM gels were thoroughly with water to remove any unreacted AAm monomers. The purified gels were solublized in 12 N HCl at 100 ºC for 24 h. After neutralization with NaOH (3 N in H_2O), the solution was lyophilized. NaCl was removed from the dry product by acetone wash followed by centrifugation (5000 RPM for 5 min). Excess acetone was allowed to evaporate under reduced pressure. The final product was re-solublized in DMSO-d_6 for ^{1}H NMR characterizations. HEA treated under the same condition was included as the control.

Characterization of hydrogel swelling ratio and sol fraction. The as-synthesized hydrogels were cut into five disks, dried at 37 ^{o}C for 2 days. The dehydrated gels were weighed and the initial dry weight (W_i) was recorded. After equilibrating in deionized water at 37 ^{o}C for 2 days, the wet weight of the swollen gels (W_s) was recorded. The swollen gels were dried again at 37 ^{o}C for 3 days. The final dry weight (W_f) was recorded. The equilibrium swelling ratio (SW) was determined by $SW = \frac{W_s}{W_i}$, and the sol fraction (SF) was calculated according to $SF = \frac{W_i - W_f}{W_i} \times 100$.

Mechanical testing. Tensile measurements were performed using a Rheometrics Mechanical Analyzer (RSA III, TA Instruments, New Castle, DE) at 22 °C. Hydrated samples were cut into a dumbbell shape with ASTM D412-06a standardized sizes (length 12 mm, width 2 mm, thickness 1-2 mm). The initial grip separation was 12 mm and the stretching speed was 100 mm/min. The tensile modulus (kPa) was calculated as the slope of the initial linear portion of the stress-strain curve. The ultimate tenisle stress and strain at the breaking point were also recorded. Cyclic loading-unloading experiments were performed in

immediate succession on each sample at maximum strains (ε_{max}) varying from 50% to 350%.

At least five specimens were tested for each composition.

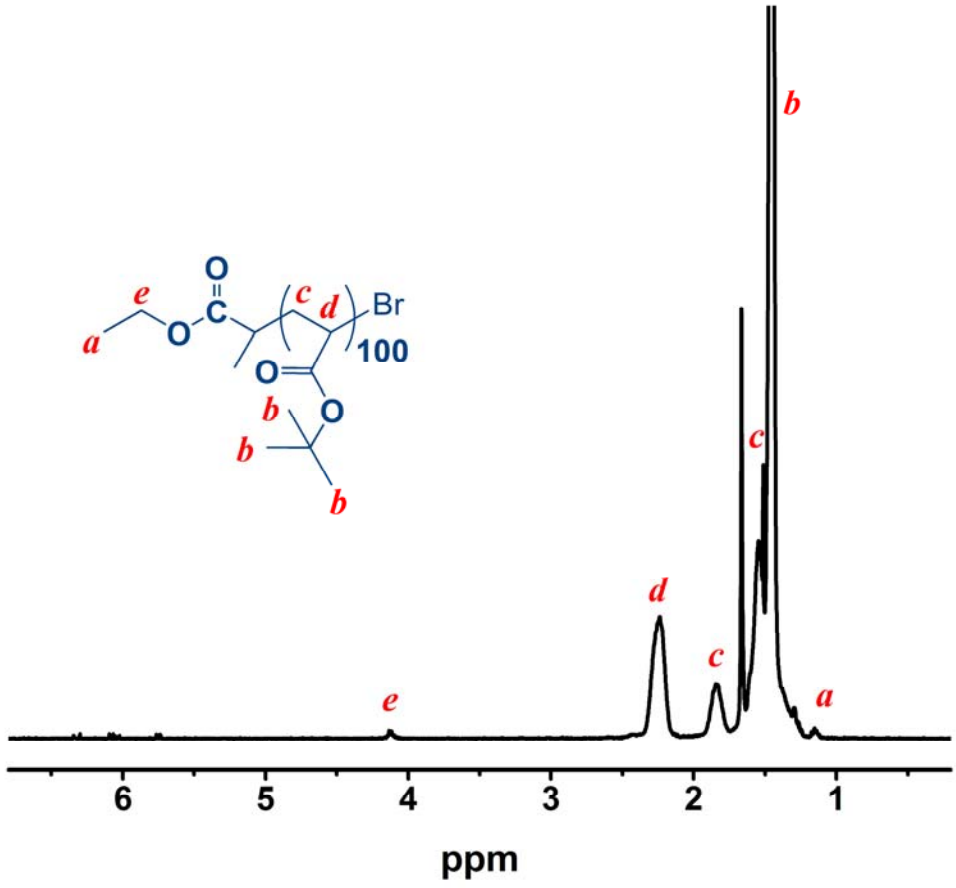

Figure S1. ^{1}H NMR spectrum of P*t*BA$_{100}$-Br ($CDCl_3$).

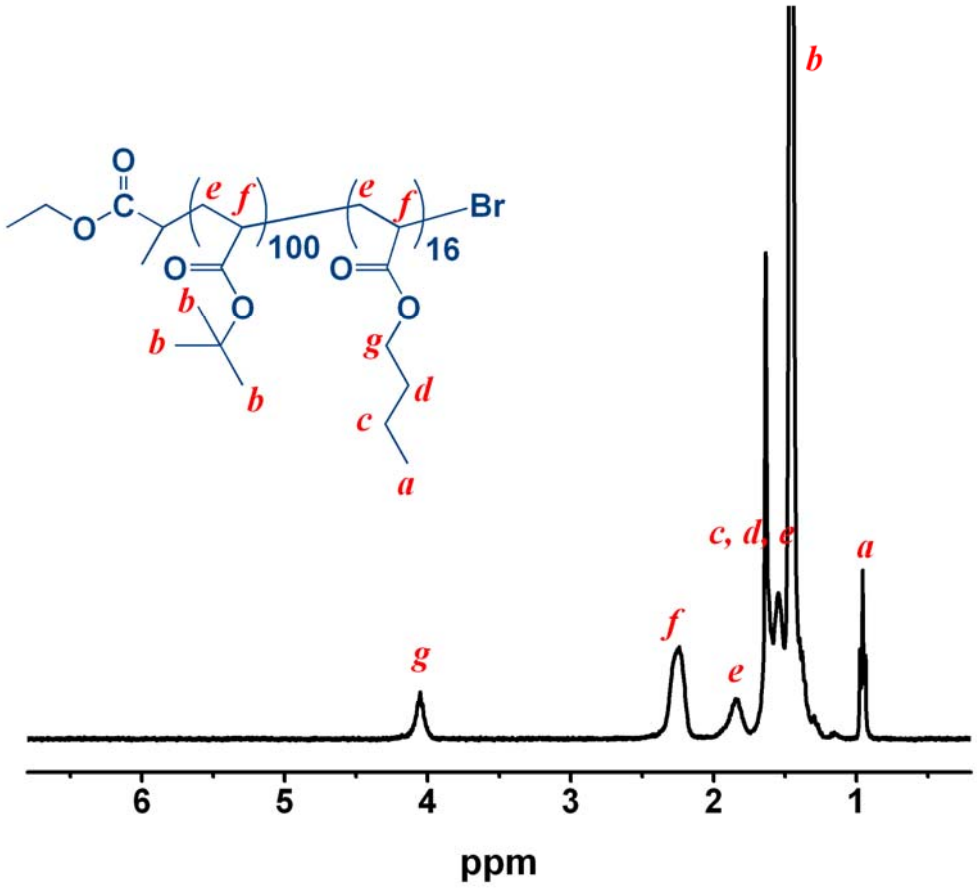

Figure S2. ^{1}H NMR spectrum of P*t*BA$_{100}$-*b*-P*n*BA$_{16}$ ($CDCl_3$).

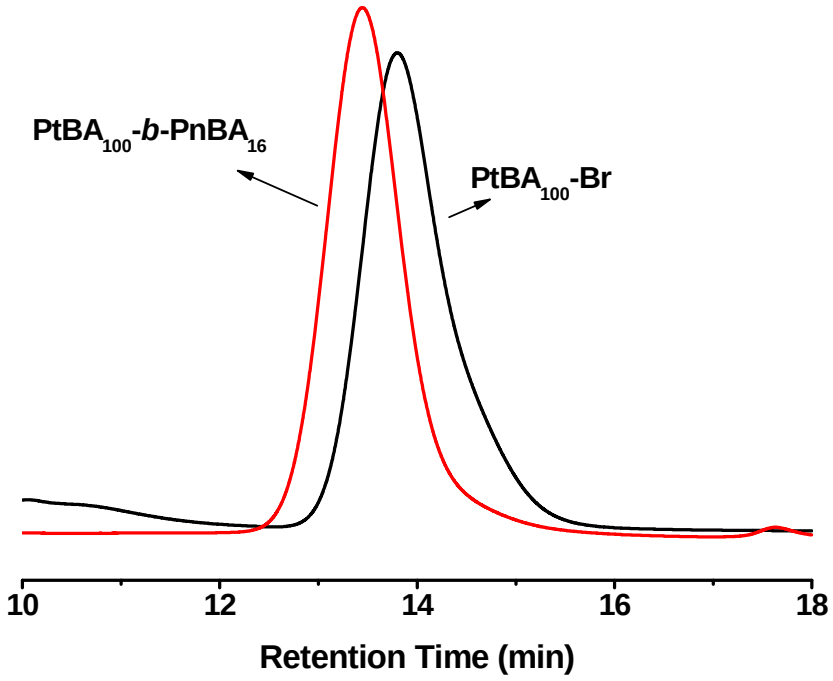

Figure S3. GPC traces of P*t*BA$_{100}$-Br (dotted line, M_n = 13,000 g/mol, M_w/M_n = 1.22) and P*t*BA$_{100}$-*b*-P*n*BA$_{16}$ (solid line, M_n = 15,000 g/mol, M_w/M_n = 1.09). Mobile phase: THF; Detector: refrective index.

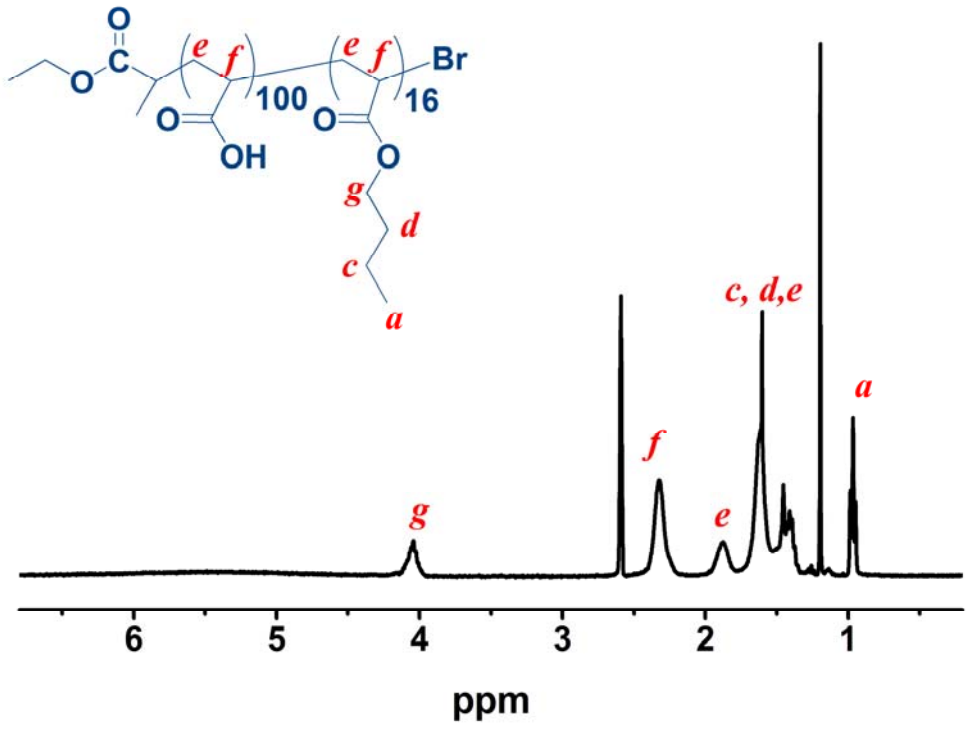

Figure S4. ^{1}H NMR spectrum of PAA_{100}-*b*-P*n*BA_{16} (DMSO-d_6)

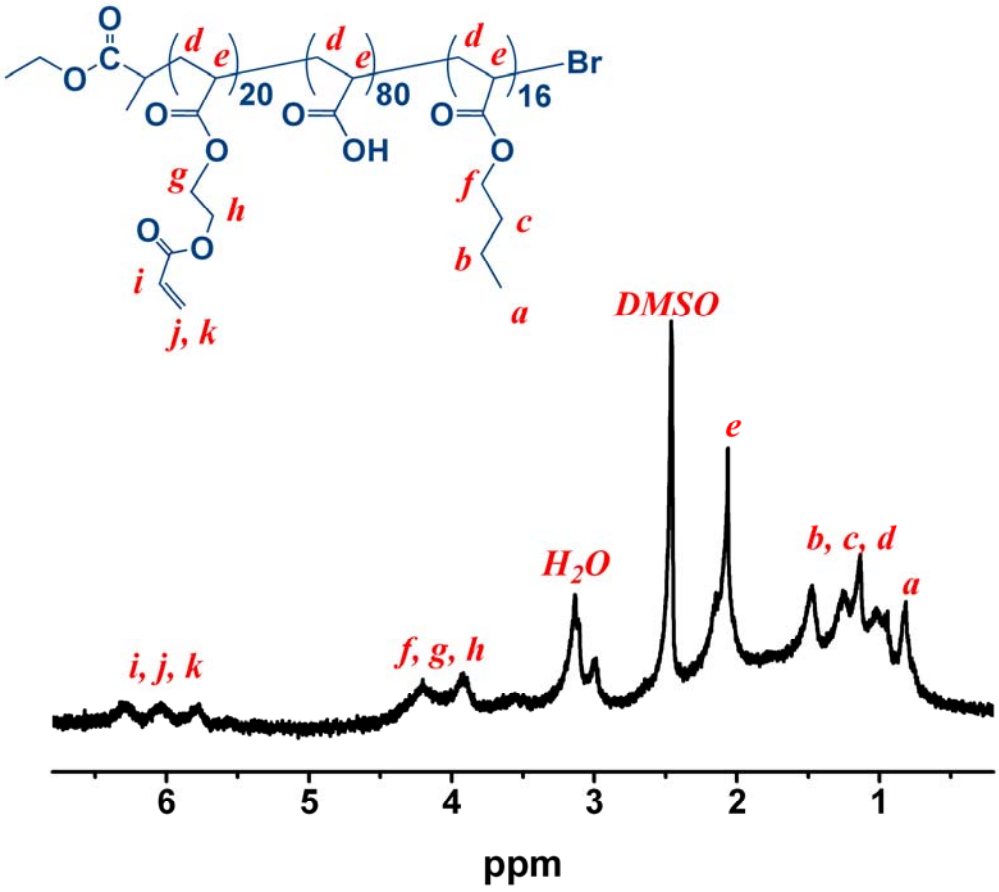

Figure S5. ^{1}H NMR spectrum of P(AA$_{100}$-*g*-HEA$_{20}$)-*b*-P*n*BA$_{16}$ (DMSO-d_6).

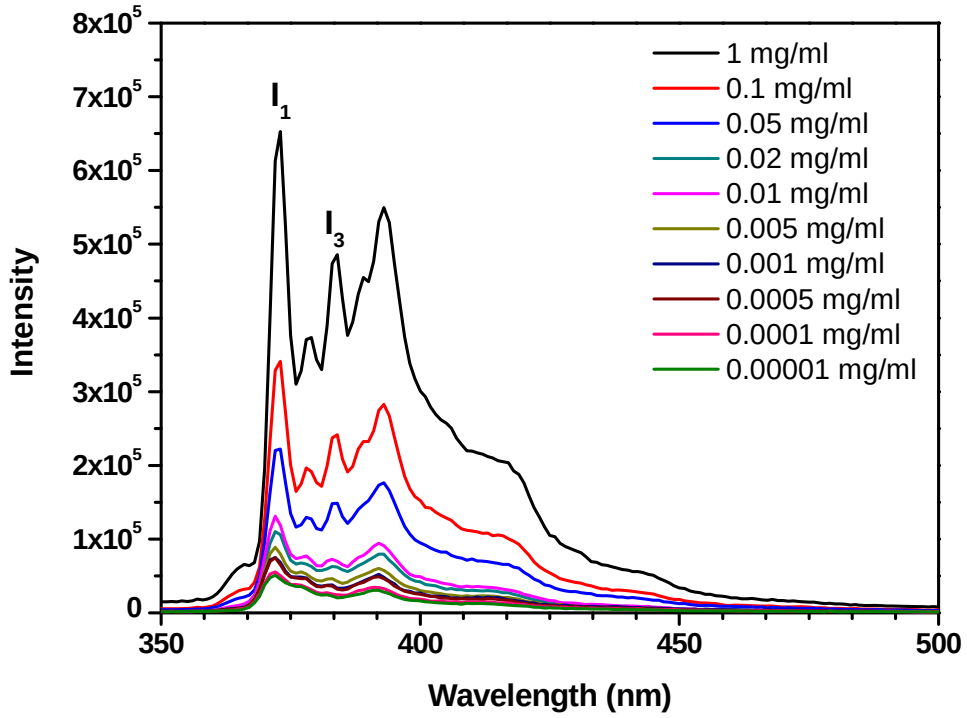

Figure S6. Typical emission spectra of aqueous solutions of pyrene at a concentration of 6.0×10^{-7} M in the presence of various amounts of BCMs (0.00001 to 1 mg/mL).

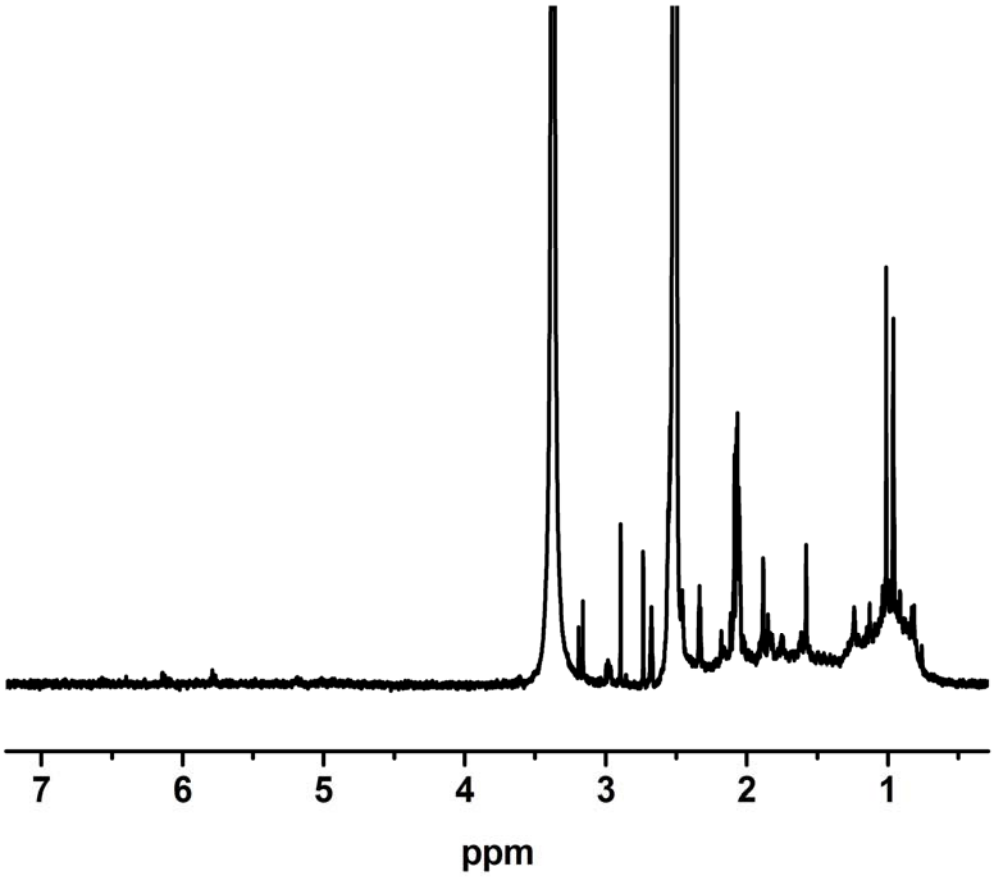

Figure S7. ^{1}H NMR spectrum of acid-hydrolyzed S-10-BCM in DMSO-d_6)

T**able S1.** Hydrogel composition, sol fraction (SF) and equilibrium swelling ratio (SW).[1]

Sample ID[2]	Composition[3]	SF (%)	SW
C-0.2-MBA	1: 12: 1200: 0.48	19.5 ± 3.0	54.6 ± 5.9
C-0.5-MBA	1: 12: 1200: 1.2	12.7 ± 2.5	28.6 ± 1.9
C-2-MBA	1: 12: 1200: 4.8	7.1 ± 0.8	10.6 ± 0.2
S-7.5-BCM	1: 12: 1200: 2.4	21.3 ± 2.0	74.7± 11.7
S-10-BCM	1: 12: 1200: 3.2	14.9 ± 1.7	48.1 ± 5.6
S-15-BCM	1: 12: 1200: 4.8	14.0 ± 1.3	41.5 ± 6.5

[1]Results were reported as an average of 5 repeats ± standard deviation; [2]Gels are identified as control (C-x-MBA) or sample (S-x-BCM) synthesized in the presence of x mg/mL MBA or BCM. [3]Molar ratio of APS, TEMED, AAm and the double bond content in the crosslinker.