Supporting Information

Synthetically Simple, Highly Resilient Hydrogels

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Materials and instruments

Poly(ethylene glycol) (PEG) (M_n = 12 kDa), 5-norbornene-2-carboxylic acid (99% exo), triphenylphosphine, pentaerythritol tetrakis(3-mercaptopropionate) (PETMP), hydroxyl terminated polydimethylsiloxane (PDMS) (M_n = 4.5 - 5.5 kDa, 4.4 kDa according to NMR), diisopropyl azodicarboxylate (DIAD), 2-hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone, 30% acrylamide/N,N'-methylenebisacrylamide (29/1) precursor solution, tetramethylethylenediamine (TEMED), and ammonium peroxydisulfate (APS) were purchased from Alfa Aesar, Sigma Aldrich, Acros Organics, Gelest, or Bio-Rad Laboratories and used without further purification. Knox® gelatin was purchased from Walmart.

^{1}H NMR spectra were recorded on a Bruker DPX 300 spectrometer. Chemical shifts were expressed for deuterated chloroform as the solvent. Gel permeation chromatography (GPC) was conducted with a Polymer Laboratories PC-GPC50 with two 5 μm mixed-D columns, a 5 μm guard column, and a RI detector (HP1047A), with polystyrene standards and THF as the eluent at a flow rate of 1.0 mL/min.

Precursor synthesis

PEG precursor (nor-PEG-nor): PEG (41 g, 3.3 mmol) was dissolved into 200 mL dichloromethane (DCM) upon heating. 5-norbornene-2-carboxylic acid (2.76 g, 20 mmol) and triphenylphosphine (5.24 g, 20 mmol) were added to the PEG solution, which was placed in an ice bath, and DIAD (4 mL, 20 mmol) was added slowly drop-wise. The mixture was stirred at room temperature for 48 hours under nitrogen, then concentrated and precipitated in cold ether three times. The white powder was obtained after drying under vacuum at room temperature, with a yield of 87%. ^{1}H NMR ($CDCl_3$) δ (ppm): 6.17-6.06 (m, 4H), 4.28-4.19 (t, 4H), 3.81-3.48 (m, 1088H), 3.08-3.0 (m, 2H), 2.96-2.86 (m, 2H), 2.31-2.19 (t, 2H), 1.97-1.87 (m, 2H), 1.59-1.47 (m, 2H), 1.44-1.18 (m, 4H). GPC (THF): PDI=1.07.

PDMS precursor (nor-PDMS-nor): Hydroxyl-terminated polydimethylsiloxane (PDMS) (20 g, 4.5

mmol) was dissolved in 100 mL tetrahydrofuran (THF). 5-norbornene-2-carboxylic acid (3.7 g, 0.027 mol) and triphenylphosphine (7.1 g, 0.027 mol) were added to the PDMS solution, which was then placed in an ice bath, followed by the drop-wise addition of 5.5 mL DIAD. The reaction mixture was stirred at room temperature for 48 hours under nitrogen, then concentrated and washed with methanol three times. The transparent viscous liquid was obtained after drying under vacuum at room temperature, with a yield of 80%. ^{1}H NMR ($CDCl_3$) δ (ppm): 6.19-6.08 (m, 4H), 4.29-4.23 (t, 4H), 3.69-3.62 (t, 4H), 3.50-3.40 (t, 4H), 3.09-3.05, (m, 2H), 2.97-2.91 (m, 2H), 2.33-2.25 (m, 2H), 2.00-1.91 (m, 2H), 1.70-1.52 (m, 6H), 1.43-1.33 (m, 4H), 0.60-0.48 (m, 4H), 0.23-0.00 (m, 318H). GPC (THF): PDI=1.9.

Preparation of hydrogels

100:0 PEG hydrogels: the norbornene end-functionalized PEG (nor-PEG-nor, M_n = 12 kDa) precursor (100 mg, 8×10^{-3} mmol), pentaerythritol tetrakis(3-mercaptopropionate) (PETMP) (2 mg, 4×10^{-3} mmol), and 2-hydroxy-4’-(2-hydroxyethoxy)-2-methyl-propiophenone as photoinitiator (1 mg) were dissolved in DMF (0.4 mL).

30:70 PEG/PDMS hydrogels: the nor-PEG-nor precursor (53.3 mg, 4.3×10^{-3} mmol), the norbornene end-functionalized PDMS (nor-PDMS-nor, M_n = 4.4 kDa) precursor (46.7 mg, 10.4×10^{-3} mmol), PETMP (3.6 mg, 7.4×10^{-3} mmol), and photoinitiator (1 mg) were dissolved in THF (1 mL). The precursor solution was put into the desired mold and then exposed to ultraviolet light with a wavelength of 365 nm for 1 hour. The cross-linked gel was removed from the mold and repeatedly washed with excess DMF or THF to remove unreacted materials. Finally, the gel was immersed in excess deionized water, which was replaced daily until equilibrium swelling was reached.

Polyacrylamide (PAAm) hydrogels: A 10 wt% PAAm gel was prepared by redox solution polymerization via mixing a 30% precursor solution (3.3 mL), TEMED (4 μL), and 10% APS (100 μL) in distilled water (6.6 mL). The mixture was stirred for one minute and then dropped into the desired mold, which was then placed into a well-sealed desiccator filled with nitrogen. The gel was formed within thirty minutes and tested in the preparation state.

Gelatin hydrogels: A 10 wt% gelatin gel was made via mixing gelatin powder (0.1 g) in distilled water (0.9 mL). The powder was dissolved upon heating and then the solution was poured into the desired mold and placed in the refrigerator at 4 ºC overnight to form the hydrogel. The hydrogel was tested in the preparation state.

Swelling properties of hydrogels

The equilibrium water content, ϕ_{water}, was calculated by the equation $(W_{swollen} - W_{dry})/W_{swollen}$, where W_{dry} is the weight of the dry network and $W_{swollen}$ is the weight of the corresponding swollen hydrogel. The equilibrium mass swelling ratio, Q, was equal to $1/(1-\phi_{water})$.

Mechanical properties of hydrogels

Tensile testing: Dumbbell-shaped hydrogels were made with a customized Teflon mold, with dimensions of 63.6 mm in length, 2.7 mm in width, and 2.5 mm in thickness. The samples were gripped on an Instron, and Velcro was used to increase the friction between the hydrogels and the grips so that no slipping occurred during the measurements. A 50 N load cell was used, and samples were extended at a rate of 50 mm/min. Raw data were recorded as force versus displacement and converted to stress versus strain with respect to the initial cross-sectional area and gage length, respectively. Linear curve fitting was performed to obtain the Young's modulus, E. Integration of the stress-strain curves yielded the area under the curves, and resilience was calculated as the ratio of the area under the unloading curve to the area under the loading curve. For fracture measurements, samples with the same dimensions were used, and the size of the notch ranged from 0.1 mm to 1 mm. Fracture energy was determined by integrating the area under the stress-strain curve, and was multiplied by the initial length of the sample to calculate the critical strain energy release rate, G_c.

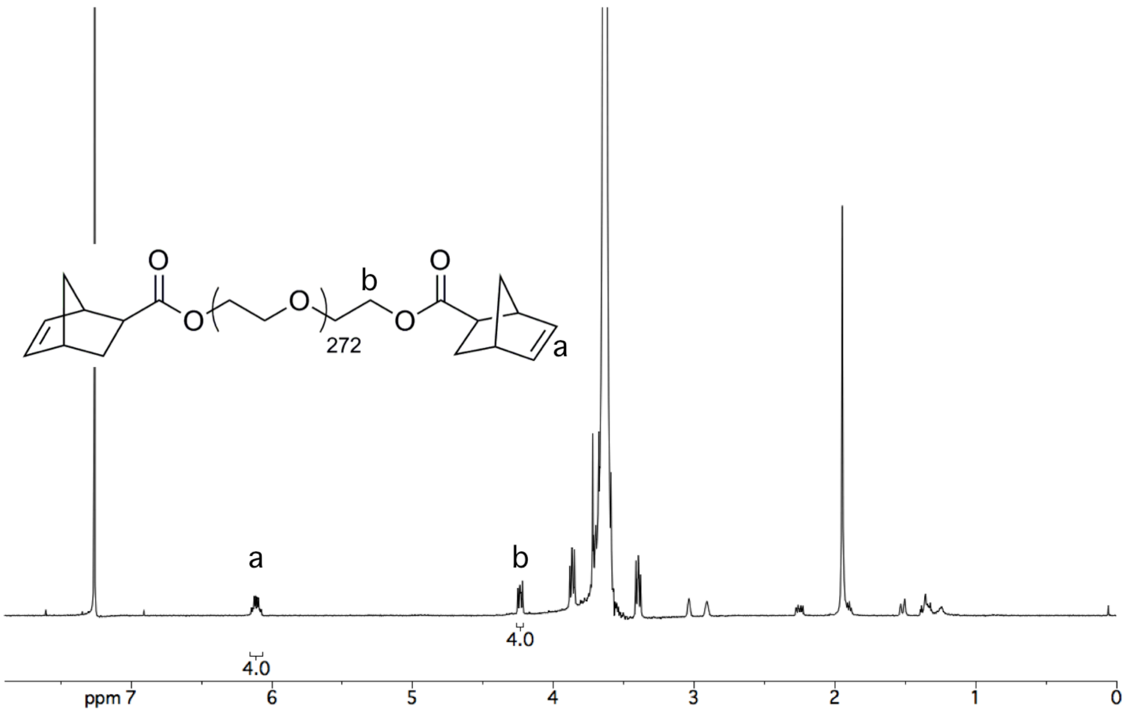
Compression testing: Modified syringes were used as molds to create cylindrical samples. An Instron with two parallel compression platens and either a 50 N or 1 kN load cell were used to measure the mechanical properties by compressing the hydrogels at a rate of 5 mm/min. Raw data, recorded as force versus displacement, were converted to stress versus strain with respect to the initial sample dimensions. Integration of the stress-strain curves yielded the area under the curves, and resilience was calculated as the ratio of the area under the unloading curve to the area under the loading curve for one loading cycle.

SANS Characterization

Samples for small angle neutron scattering (SANS) were prepared as described above for the 100:0 PEG hydrogels, except the final immersion and equilibration steps were performed in D_2O. SANS measurements were conducted on the 30 m SANS instrument at the NG-7 beamline at the National Institute for Standards and Technology (NIST) Center for Neutron Research, Gaithersburg, MD. Spectra were obtained at 25 °C in quartz sample cells with a path length of 2 mm. Spectra were collected for one hour and forty-five minutes per sample. Deuterated water was used to quantify the solvent scattering. The q-range covered in these experiments was $0.003 \text{ Å}^{-1} < q < 0.5 \text{ Å}^{-1}$. The sample-to-detector distance was 1.0 to 15.3 m, continuously variable. Data reduction and normalization were performed using standard techniques.[1]

Polymer precursor functionalization

a.



b.

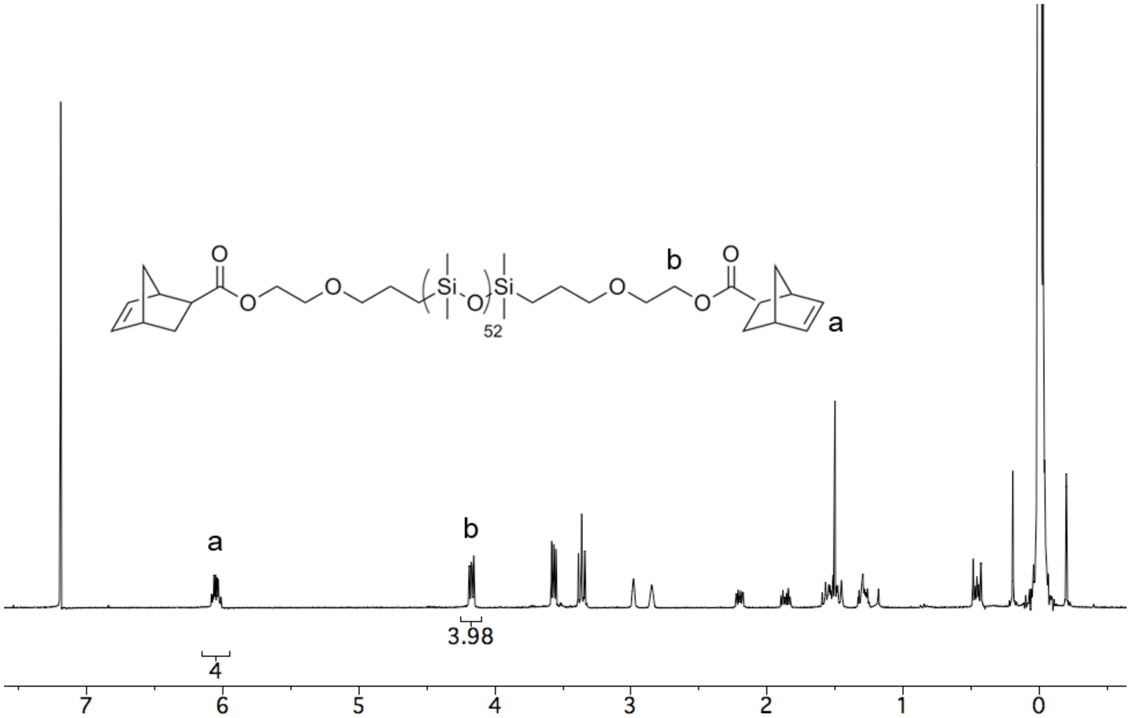


Figure S1. a. ^{1}H NMR of the norbornene end-functionalized PEG precursor (nor-PEG-nor) ($CDCl_3$). b. ^{1}H NMR of the norbornene end-functionalized PDMS precursor (nor-PDMS-nor) ($CDCl_3$).

Hydrogel composition

Table S1. Summary of the hydrogels studied, including the gel fraction, polymer content in the initial and equilibrium-swollen states (ϕ_0 and ϕ, respectively), and equilibrium mass swelling ratio (Q).

Sample[a]	Gel Fraction	ϕ_0	ϕ	Q
100:0 PEG/PDMS	0.92±0.04	0.19±0.01	0.049±0.003	20±1
70:30 PEG/PDMS	0.88±0.04	0.10±0.04	0.05±0.01	20±4
50:50 PEG/PDMS	0.89±0.06	0.10±0.06	0.10±0.02	11±2
30:70 PEG/PDMS	0.89±0.02	0.09±0.01	0.18±0.05	6±1
Gelatin[b]	-	0.087±0.003	0.087±0.003	11.5±0.5
PAAm[b]	0.98±0.01	0.104±0.003	0.104±0.003	9.7±0.3

[a]The PEG/PDMS samples are described by the mol ratio of PEG:PDMS.

[b]The mechanical properties of the gelatin and PAAm hydrogels were measured in the initial state.

Resilience in compression testing

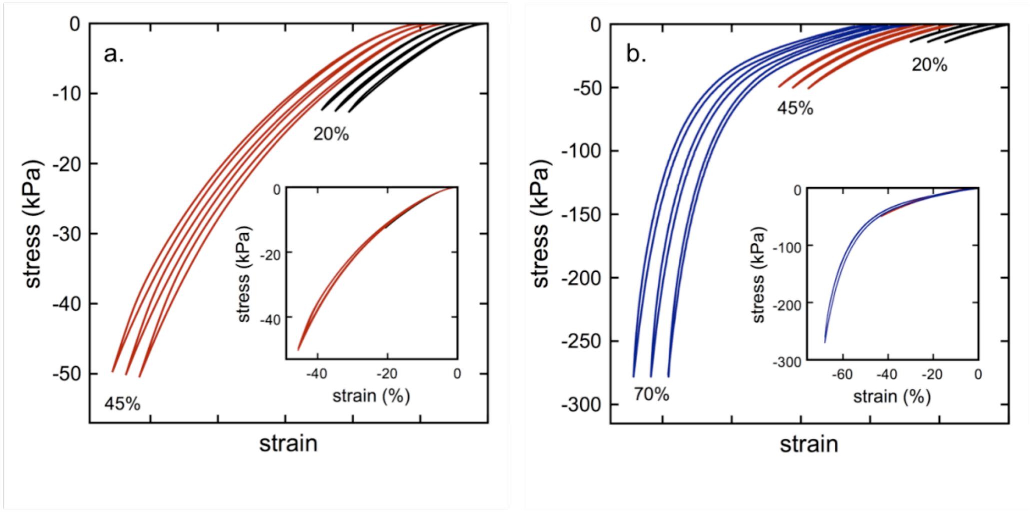


Figure S2. Curves from cyclic loading in compression. a and b. Representative stress-strain curves for the 100:0 and 30:70 PEG/PDMS hydrogels, respectively. For clarity, the curves are shifted on the x-axis, and the final strains are given on the plots. The increment of the tick marks on the x-axis is 10% strain in a and 20% strain in b. The insets show the original stress-strain curves. The strains are not indicative of the maximum compressive strains. (The maximum compressive strains of the 100:0 and 30:70 PEG/PDMS hydrogels are 85% and 77%, respectively.)

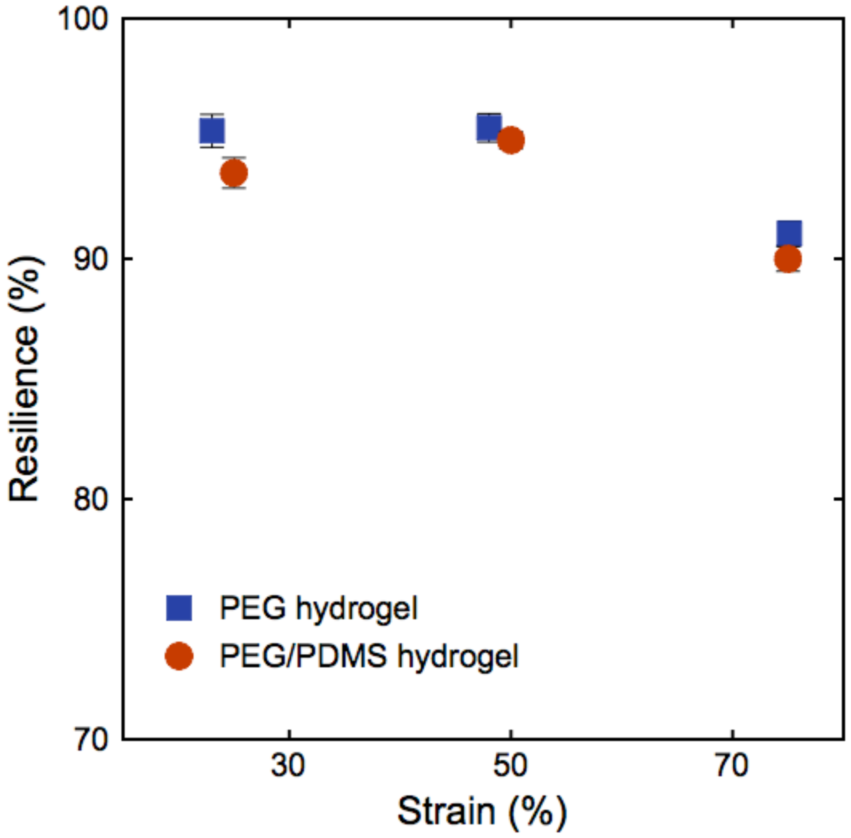


Figure S3. Resilience as a function of strain in compression for the 100:0 and 30:70 PEG/PDMS hydrogels. Error bars indicate one standard deviation, with n≥3.

SANS characterization

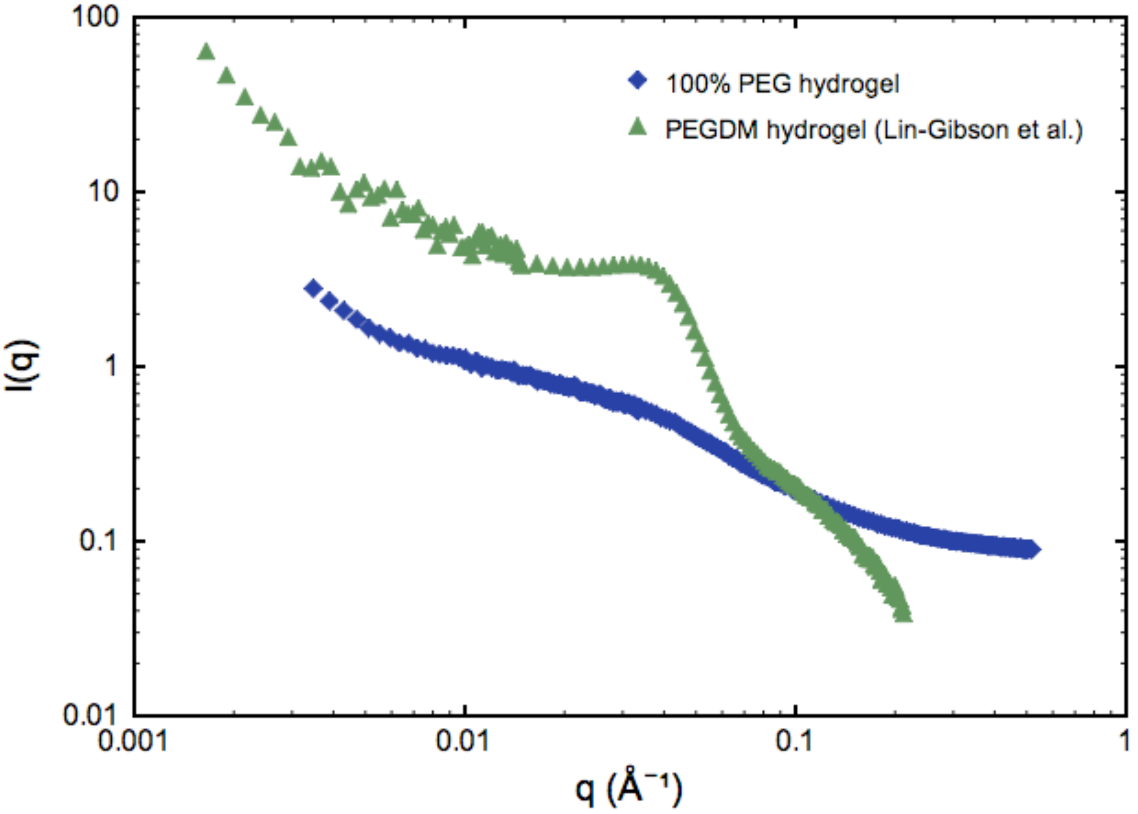


Figure S4. SANS spectra of the tetra-functional 100:0 12 kDa PEG hydrogel and a photopolymerized 8 kDa PEG-dimethacrylate (PEGDM) (mass fraction = 10%) hydrogel (PEGDM data from Lin-Gibson et al.[2]), demonstrating the uniform structure of the tetra-functional PEG gels as compared to randomly cross-linked systems with multifunctional cross-link junctions.

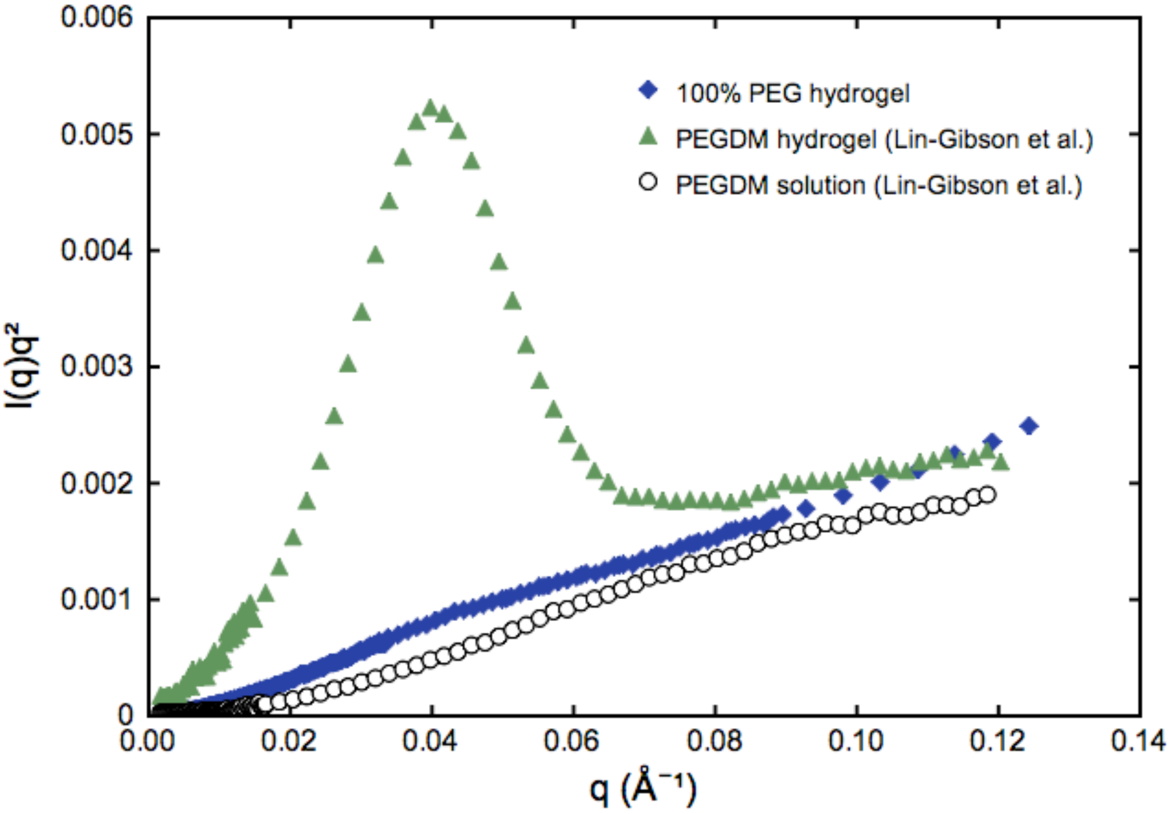


Figure S5. Kratky plot of SANS data from the tetra-functional 100:0 12 kDa PEG hydrogel, as well as a 10 wt% 4 kDa PEGDM solution, and a photopolymerized 10 wt% 8 kDa PEGDM hydrogel (PEGDM data from Lin-Gibson et al.[2]), indicating the homogeneous structure of the tetra-functional 100:0 PEG hydrogel.

G_c calculation

The critical strain energy release rate, G_c, was estimated using the Lake-Thomas theory,[3] which suggests that G_c is not limited by the dissociation energy of a single bond in the backbone, but accounts for the energy stored in all of the bonds between two cross-linking points, so that $G_c \approx nUf$, where n is the degree of polymerization, U is the dissociation energy of a repeating unit, and f is the areal chain density. According to the scaling theory derived by Obukhov et al.,[4] we derived $f \approx \phi / a^2 n^{1/2}$ for a theta solvent. By substituting that scaling relationship, we can obtain that $G_c \approx n^{1/2} U \phi / a^2$. Using that equation, the theoretical G_c was calculated to be approximately 10 J/m^2 for the PEG hydrogels, where n = 273, U = 1.6×10^{-18} J, a = 3.5 Å and $\phi = 0.04$.

Supplementary Movie 1

This video shows one cycle of tensile testing of a 100:0 PEG hydrogel, stretching to 100% strain and returning. The video is 4x faster than the actual speed of the event. (QuickTime .mov; 1.8 MB)

Supplementary Movie 2

This video is of a 30:70 PEG/PDMS hydrogel ball (left) and a gelatin ball (right) bouncing. It can be seen that the PEG/PDMS hydrogel bounces higher and longer than the gelatin hydrogel. The video is 4x slower than the actual speed of the event. (QuickTime .mov; 3.7 MB)

References

(1) Kline, S. R., Reduction and analysis of SANS and USANS data using IGOR Pro. *Journal of Applied Crystallography* **2006,** 39, 895-900.

(2) Lin-Gibson, S.; Jones, R. L.; Washburn, N. R.; Horkay, F., Structure-property relationships of photopolymerizable poly(ethylene glycol) dimethacrylate hydrogels. *Macromolecules* **2005,** 38, (7), 2897-2902.

(3) Lake, G. J.; Thomas, A. G., Strength of Highly Elastic Materials. *Proceedings of the Royal Society of London Series a-Mathematical and Physical Sciences* **1967,** 300, (1460), 108-119.

(4) Obukhov, S. P.; Rubinstein, M.; Colby, R. H., Network Modulus and Superelasticity. *Macromolecules* **1994,** 27, (12), 3191-3198.