

Supporting Information

Tough self-healing elastomers by molecular enforced integration of covalent and reversible networks

Jinrong Wu^{a, b}, Li-Heng Cai^{b, *}, and David A. Weitz^{b, *}

^aState Key Laboratory of Polymer Materials Engineering, College of Polymer Science and Engineering, Sichuan University, Chengdu 610065, China.

^bSchool of Engineering and Applied Sciences, Harvard University, Cambridge, MA 02138, USA.

*Correspondence and requests for materials should be addressed to: L.-H.C., lhcai@seas.harvard.edu or D.A.W., weitz@seas.harvard.edu

Supporting Information

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SI Materials and Methods

S1. Materials. Acrylic acid (AA, 99%, stabilized with 200ppm 4-methoxyphenol), 1, 12-diaminododecane (DADD, 99+%) and chloroform (99.8+%, stabilized with ethanol) were purchased from Alfa Aesar; 1, 6-hexamethylenediamine (HMDA, 98%) and N, N-dimethylformamide (DMF, 99.8%) were purchased from Sigma Aldrich. All the chemicals were used as received without further purification.

S2. Synthesis of hybrid elastomers. The elastomers were synthesized by two steps, including pre-polymerization and crosslinking. During the pre-polymerization, 0.125 mole AA was added dropwise into 100 mL chloroform solution of DADD and HMDA under agitation at 50 °C in a three-neck flask. The molar ratio of -COOH in AA to -NH₂ in diamine was fixed at 1.25:1, and the molar ratio of HMDA/DADD was varied between 0.3/0.7 and 0.5/0.5. After the addition of AA, the solution was stirred at 50 °C for 16 hours. During this process the vinyl groups of AA react with primary amine groups of diamines through Michael addition, forming secondary amine groups; these secondary amine groups are still reactive and can react with vinyl groups to form tertiary amine groups. After the completion of Michael addition, all the vinyl groups of AA are consumed, producing a mixture that contains five types of amidoamine oligomers carrying both carboxyl and amine groups, as shown in Step 1 in **Figure S1**. The mixture was then heated up to 80 °C and maintained for about 3 hours under nitrogen flow to remove chloroform. Subsequently, the temperature was raised up to 150 °C to enable the condensation reaction between carboxyl groups and amine groups of the oligomers and unreacted diamines, as shown in Step 2 in **Figure S1**. As the reaction proceeds to a certain extent (about 4 hours), the mixture becomes viscoelastic yet without solidifying. Before the mixture starts to rise up the stirring stem, the temperature was lowered to 140 °C. 50 ml DMF was charged into the flask to dissolve the pre-polymer. The pre-polymer is a hyper-branched polymer with tertiary amines serving as branching points and reactive end groups of carboxyl groups and primary amine groups, as shown in **Figure S1**.

During the crosslinking step, an aliquot of the pre-polymer solution was casted in a Teflon mold. This mold was placed in a glass reactor with nitrogen inlet and outlet. The glass reactor was heated at 110 °C for overnight to slowly evaporate DMF. Then the temperature was raised by 10 °C increment every hour to 160 °C to allow condensation reaction between carboxyl groups and amine groups of the hyper-branched polymer. The reaction was maintained at 160 °C for 32 hours to form a covalently crosslinked elastomer sheet with a thickness around 1mm.

S3. FTIR characterization. To confirm the Michael addition between double bonds and amine groups and the condensation reaction between carboxyl and amine groups, Fourier transform infrared

spectroscopy (FTIR) spectra were collected on a Perkin Elmer FTIR spectrometer fitted with an attenuated total reflectance cell. The FTIR spectra of AA, HMDA, DADD and hybrid network elastomer are shown in **Figure S2**. AA exhibits characteristic peaks at 1700, 1635, 1298 and 1241 cm^{-1} , corresponding to C=O stretching, C=C stretching, C-O stretching coupled with O-H in plane bending, and O-H in plane bending coupled with C-O stretching, respectively. HMDA and DADD have characteristic peaks at 3329, 3256, 3166 and 1607 cm^{-1} , corresponding to N-H stretching of carbamate formed by amine capturing CO_2 , asymmetric N-H stretching, symmetric N-H stretching, and N-H in plane bending, respectively. These characteristic peaks of both reactants disappear in the hybrid network, suggesting that the Michael addition and condensation reaction nearly consume all the vinyl groups, carboxyl groups and primary amine groups. The condensation between carboxyl groups and amine groups forms amide groups, as confirmed by the appearance of the characteristic amide I band at 1650 cm^{-1} and amide II band at 1553 cm^{-1} of the hybrid network.

S4. NMR characterization. To investigate the molecular structure of the hyper-branched pre-polymer, its ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were obtained using a Bruke Avance 400 spectrometer, as shown in **Figure S3**. The pre-polymer was dissolved in D_2O and tested at room temperature. The NMR results further confirm the Michael addition and condensation reaction, and the formation of the hyper-branched pre-polymer. In particular, the branching point is a tertiary amine formed by reacting two double bonds with a primary amine or by reacting a carboxyl group with a secondary amine; while the terminal groups consist of primary amines and carboxyl groups.

^1H NMR (400 MHz, D_2O) δ (ppm) 1.25-1.62 (m, $-\text{CH}_2-\text{CH}_2-\text{CH}_2-$), 2.37-2.40 (t, $-\text{CH}_2-\text{CH}_2-\text{COOH}$, $-\text{CH}_2-\text{CH}_2-\text{N}(\text{CH}_2)-\text{CH}_2-$), 2.49-2.51 (m, $-\text{CH}_2-\text{CH}_2-\text{NH}-\text{CH}_2-$, $-\text{NH}-\text{CO}-\text{CH}_2-\text{CH}_2-\text{N}(\text{CH}_2)-\text{CO}-$), 2.71 (m, $-\text{CO}-\text{CH}_2-\text{CH}_2-\text{N}(\text{CH}_2)-\text{CH}_2-$, $-\text{CH}_2-\text{CH}_2-\text{NH}_2$), 2.83 (m, $-\text{NH}-\text{CH}_2-\text{CH}_2-\text{COOH}$), 2.92-2.96 (m, $-\text{NH}-\text{CH}_2-\text{CH}_2-\text{CO}-\text{NH}-$), 3.12 (m, $-\text{CH}_2-\text{CH}_2-\text{NH}-\text{CO}-\text{CH}_2-$), 3.73-3.78 (t, $-\text{CH}_2-\text{CH}_2-\text{N}(\text{CO})-\text{CH}_2-$).

^{13}C NMR (400 MHz, D_2O) δ (ppm) 176.65-180.48 ($-\text{CO}-\text{NH}-$, $-\text{COOH}$), 58.84 ($-\text{CH}_2-\text{CH}_2-\text{N}(\text{CH}_2-\text{CH}_2-\text{CO})-\text{CH}_2-\text{CH}_2-\text{CO}-$), 47.73 ($-\text{CH}_2-\text{N}(\text{CH}_2-\text{CH}_2-\text{CO})-\text{CH}_2-\text{CH}_2-\text{CO}-$, $-\text{CH}_2-\text{CH}_2-\text{N}(\text{CO}-\text{CH}_2)-\text{CH}_2-$), 44.31 ($-\text{CH}_2-\text{CH}_2-\text{NH}-\text{CO}-$, $-\text{CH}_2-\text{NH}-\text{CH}_2-\text{CH}_2-\text{CO}-$, $-\text{CH}_2-\text{NH}_2$), 38.55-39.94 ($-\text{CH}_2-\text{CH}_2-\text{CO}-\text{NH}-$, $-\text{CH}_2-\text{CH}_2-\text{COOH}$), 32.94 ($-\text{CH}_2-\text{CH}_2-\text{NH}_2$, $-\text{CH}_2-\text{CH}_2-\text{NH}-$), 25.02-28.63 ($-\text{CH}_2-\text{CH}_2-\text{CH}_2-$).

S5. Rheological measurements. *Melt of randomly branched polymers.* Rheological experiments were carried out on a stress controlled rheometer (MCR501, Anton Paar) with 25 mm plate–plate geometry at a gap of 750 μm . Frequency sweeps were performed from 10^2 to 10^{-2} Hz at 0.5% strain at temperatures

ranging from 40 °C to 100 °C. Changes in normal force due to a gap contraction with temperature were alleviated by adjusting the gap height.

Hybrid elastomers. To measure the equilibrium modulus of the hybrid elastomer, we quantify its stress relaxation at elevated temperature, 100 °C; this allows the hybrid elastomer to relax relatively fast such that it can reach equilibrium relaxation during experimental time scale. In particular, we laser cut a hybrid elastomer sheet into a disk with diameter of 25mm, and mount the sample between a plate-plate geometry using a thin layer of glue. After the glue is solidified, we raise the temperature to 100 °C. Then we apply a step strain of 1.0%, and monitor how the stress decays with time, as shown by the dots in **Figure S6**. We fit the data using an empirical equation, $G(t) = G_0 \left[1 + \left(\frac{t}{\tau}\right)^{-\alpha}\right]$, in which G_0 is the network equilibrium modulus, τ is the characteristic relaxation time of the network, and α is the exponent that describes how fast the network relaxes. The best fit is shown by the line in **Figure S6**, which gives the equilibrium shear modulus of 2.35 MPa.

S6. SAXS measurement. To test the phase morphology of the hybrid network elastomer, small angle X-ray scattering (SAXS) measurement was performed on XEUSS 2.0 with a wavelength of 0.154nm under vacuum. Two-dimensional SAXS pattern was acquired using a Pilatus SAXS detector. The exposure time was 300s. A silver behenate (AgC₂₂H₄₃O₂) standard was used to calibrate the scattering angle. The sample-to-detector distance was 2479 mm. The diffraction and scattering signals were corrected for beam fluctuation and background scattering. X-ray data analysis was performed using the Fit2D software to acquire SAXS intensity vs. scattering vector curve, as shown in **Figure S5**. The absence of scattering maximums suggests that there is no phase separation in the hybrid network elastomer.

S7. Differential scanning calorimetry (DSC) measurements. To determine the glass transition temperature of the hybrid network elastomers, differential scanning calorimetry (DSC) was performed using Q200 (TA Instruments). The mass of the sample was about 8 mg. The samples were first cooled from room temperature to -60 °C at a cooling rate of 10 °C/min. Afterwards the heat flow of the samples was recorded at a heating rate of 10 °C/min. The glass transition temperature (T_g) was determined as the temperature at the inflexion point of the heat flow curve. The T_g values of the elastomers with HMDA/DADD ratios of 0.3/0.7 and 0.5/0.5 are 4 °C and 14 °C respectively.

S8. Mechanical tests. We characterized the mechanical properties of hybrid elastomers using Instron® 3342 with a 1000N load cell. Dumbbell shaped samples were cut from the sheets formed in the Teflon mold using a normalized cutter. The dumbbell shaped samples have a central part of 10mm in length, 4 mm in width and 0.8-1.2 mm in thickness. Uniaxial tensile measurements were conducted at room

temperature in air using different strain rates, including 0.0014, 0.014, 0.14, 0.41 and 0.68 /sec. Engineering stress is defined as the tensile force per unit of initial cross-section area of the central part. Strain was recorded by a camera, which monitored the displacement of two markers in the central part of a dumbbell shaped sample. Each measurement was repeated at least three times.

Cyclic extension tests with incremental elongation were performed on the same tensile machine at a strain rate of 0.014/sec. The maximum strains of the cyclic extension tests included 0.3, 0.5, 0.8, 1.1 and 1.4. The strain was also recorded and measured using a camera. The efficiency of energy dissipation during each cyclic extension test is defined as the ratio of the integrated area in the hysteresis loop to that under the loading curve. The efficiency is remarkably high with the value of ~75%, as shown in **Figure S7**. Moreover, it is nearly independent of elongation.

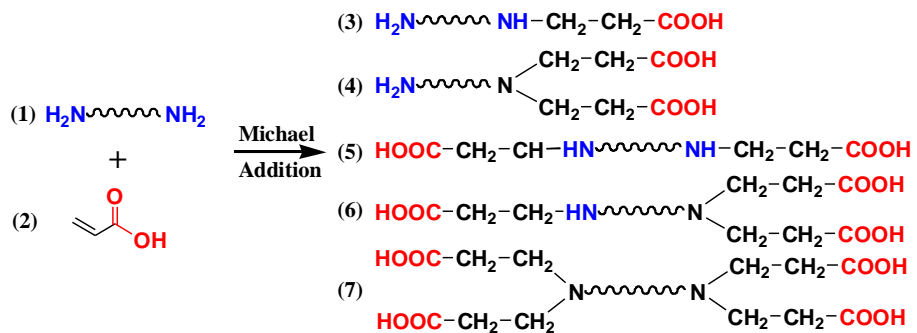
S9. Fracture toughness. Fracture tests were conducted using the classical single edge notch test on the Instron® 3342 with a 1000N load cell. A notch of 1 mm in length was made in the middle of a rectangular specimen of about 1 mm in thickness and 5 mm in width. The specimen was fixed in the two clamps with a pre-set distance of 10 mm. Then, the specimen was subjected to uniaxial tension with a crosshead velocity of 3 mm/min, corresponding to a nominal strain rate of 0.005 s⁻¹. The strain at break (λ_c) of the notched specimen was recorded with the camera. The fracture energy (G_c) was calculated by a method developed by Greensmith:^[24]

$$G_c = \frac{6WC}{\sqrt{\lambda_c}}$$

where c is the notch length. W is the strain energy calculated by integration of the stress-strain curve of an un-notched specimen until λ_c ; the un-notched specimen underwent a tension process with the same strain rate as the notched sample.

SI Figures

Step 1: Michael addition



Step 2: Polycondensation

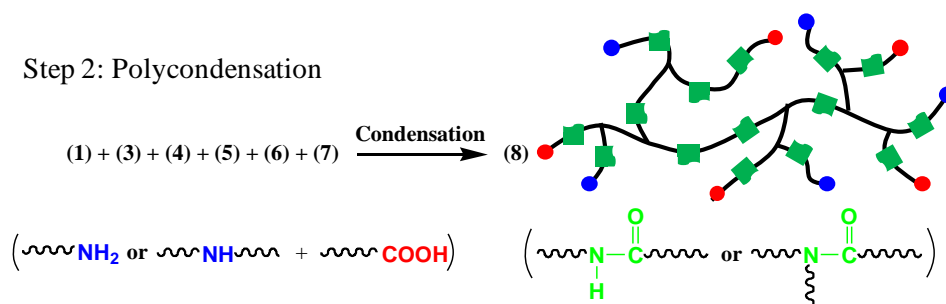


Figure S1. Synthesis of randomly branched polymer. Step 1: Reaction between diamine and acrylic acid produces five types of oligomers by Michael addition at 50°C. Step 2: Polycondensation reaction between amine and carboxyl groups 150 °C gives rise to a randomly branched polymer.

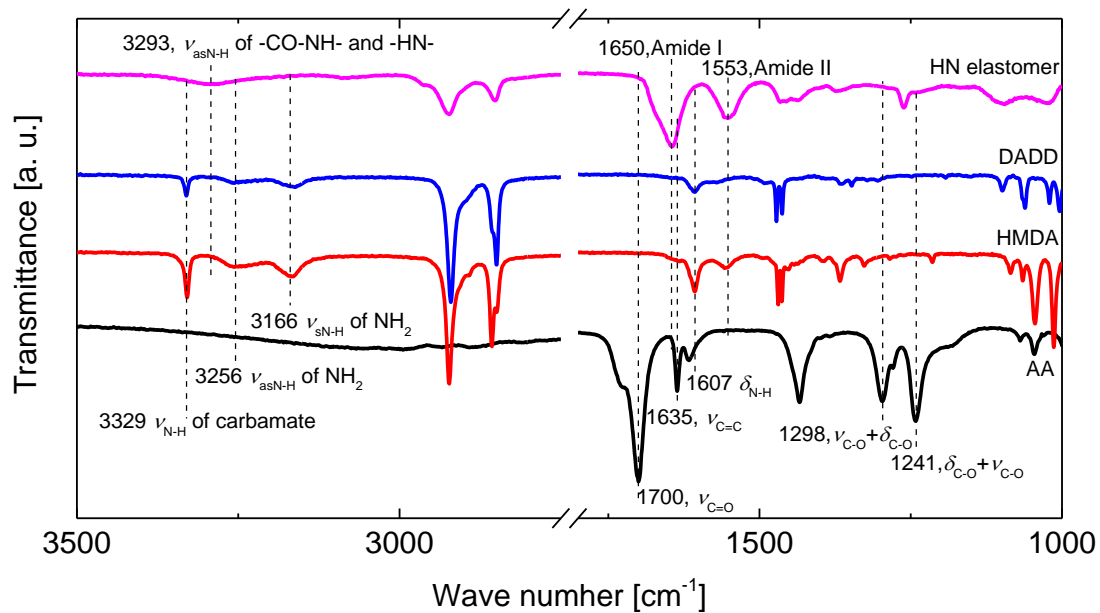


Figure S2. FTIR spectra of AA, HMDA, DADD and hybrid network.

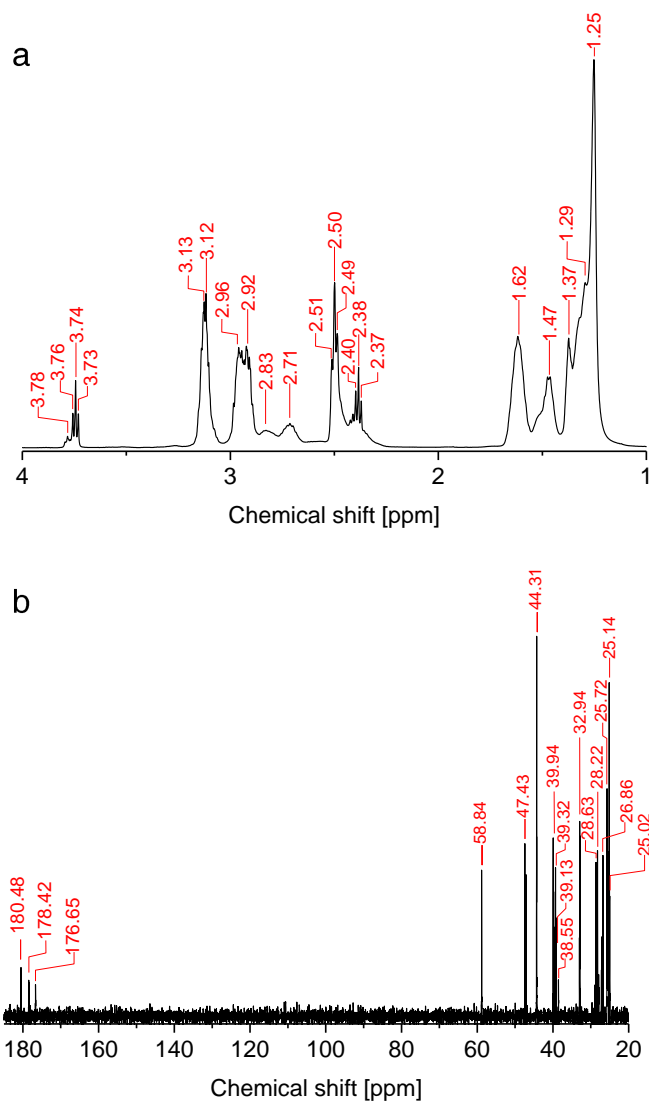


Figure S3. (a) ^1H NMR and (b) ^{13}C NMR spectra of the pre-polymer.

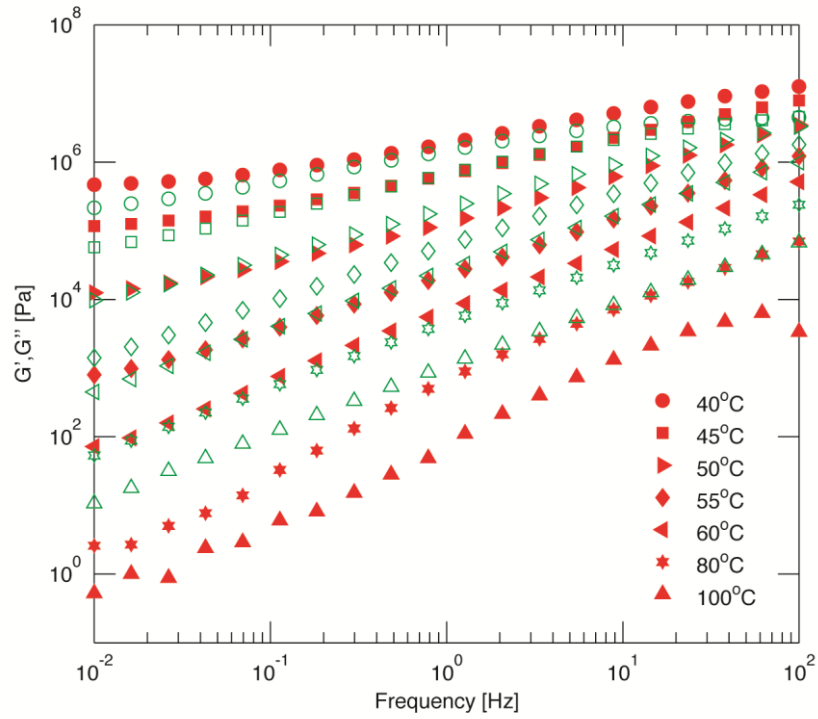


Figure S4. Dependence of storage modulus G' (filled symbols), and loss modulus G'' (empty symbols) on frequency for the melt of pre-polymer with a HMDA/DADD ratio of 0.7/0.3 under different temperatures.

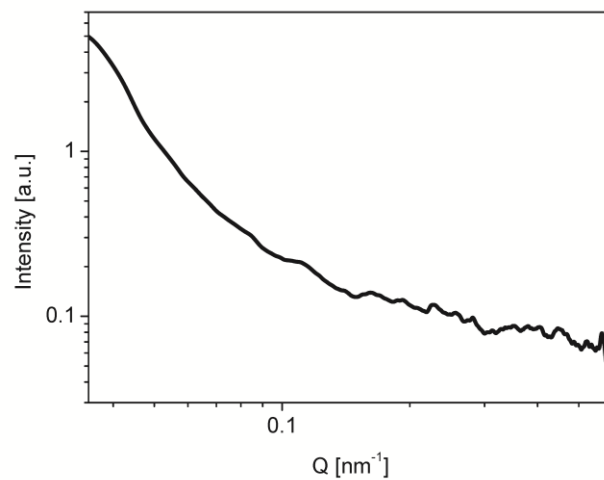


Figure S5. SAXS intensity as a function of scattering vector (Q) based on 360° azimuthally integration of 2D images.

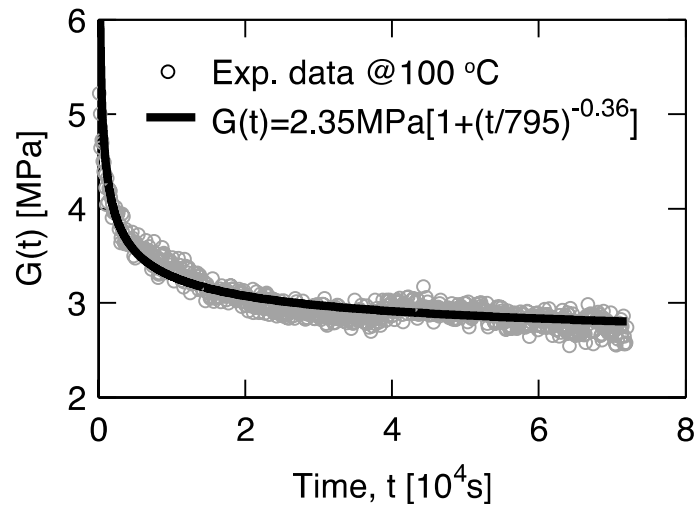


Figure S6. Stress relaxation of the hybrid network at 100°C. Dots are experimental data, and the solid line represents power law fit to the experimental data.

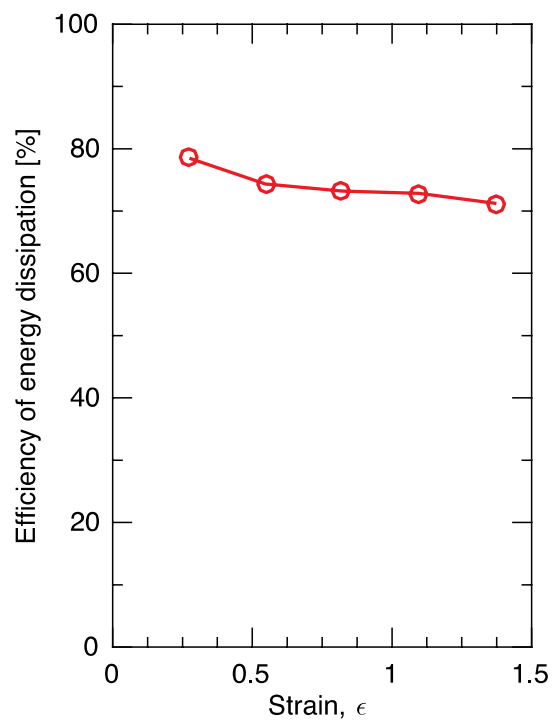


Figure S7. Dependence of energy dissipation efficiency on extents of strain.

SI Movies

SI movie 1. Uniaxial tensile test of a hybrid elastomer sample at strain rate of 0.014/sec. The movie is sped up by 5 times.