Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information

Repeatable mechanochemical activation of dynamic covalent bonds in thermoplastic elastomers

Keiichi Imato,[1,2] Takeshi Kanehara,[2] Shiki Nojima,[2] Tomoyuki Ohishi,[3] Yuji Higaki,[3] Atsushi Takahara,[2,3]* Hideyuki Otsuka[1]*

[1] *Department of Chemical Science and Engineering, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo 152-8550, Japan*

[2] *Graduate School of Engineering, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan*

[3] *Institute for Materials Chemistry and Engineering, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan*

*E-mail: otsuka@polymer.titech.ac.jp

General methods. All solvents and reagents used for synthesis were purchased from Sigma-Aldrich, Wako Pure Chemical Industries, Tokyo Chemical Industry, or Kishida Chemical and used as received, unless otherwise noted. Dihydroxy diarylbibenzofuranone (DABBF) monomer was synthesized according to our previously published methods.[40] 1,4-Butanediol (BDO) was purified by dehydration over anhydrous magnesium sulfate and by distillation under reduced pressure over calcium hydride. ^{1}H NMR spectroscopic measurements were carried out at 25 °C using a 400 MHz Bruker spectrometer in dimethylsulfoxide-d_6. Differential scanning calorimetric (DSC) measurements were carried out using a SII Nanotechnology DSC6220 with a heating rate of 10 °C/min. Tensile tests were carried out at 25 °C on a SHIMADZU EZ Graph instrument equipped with a 50 N load cell using a strain rate of 833 %/min and dumbbell-shaped specimens (ISO 37-4, 12 mm × 2 mm × 0.3–0.5 mm) or strip specimens (50 mm × 3 mm × 0.3–0.5 mm).

Synthesis of segmented polyurethane elastomer P1. In a typical run, poly(tetramethylene ether glycol) (PTMG) (M_n = 1400) (3.82 g, 2.73 mmol) was added to a sample tube and dried in vacuo for 12 h at 70 °C. Then, dihydroxy DABBF (2.16 g, 2.73 mmol), *N*,*N*-dimethylacetamide (DMAc) (46 mL), and 4,4′-methylenebis(phenyl isocyanate) (MDI) (2.76 g, 11.0 mmol) were added to the tube. After N_2 purge, di-*n*-butyltin dilaurate (1 drop) was added to the mixture with stirring. After stirring for 3 h at room temperature, BDO (0.492 g, 5.46 mmol) was added to the mixture under N_2, and the mixture was stirred for 48 h at room temperature. The reaction was stopped by adding excess methanol. The crude product was purified by precipitation in water, washing with hexane and diethylether, and drying in vacuo. The product was dissolved in DMAc and the solution was cast to give a yellowish transparent film (94% yield).

Synthesis of segmented polyurethane elastomer P2. In a typical run, PTMG (M_n = 2900) (3.10 g, 1.07 mmol) was added to a sample tube and dried in vacuo for 12 h at 80 °C. Then, dihydroxy DABBF (0.845 g, 1.07 mmol), DMAc (24 mL), and MDI (2.02 g, 8.05 mmol) were added to the tube. After N_2 purge, di-*n*-butyltin dilaurate (1 drop) was added to the mixture with stirring. After stirring for 3 h at room temperature, BDO (0.532 mL, 5.92 mmol) was added to the mixture under N_2, and the mixture was stirred for 48 h at room temperature. The reaction was stopped by adding excess methanol. The crude product was purified by precipitation in water, washing with hexane and diethylether, and drying in vacuo. The product was dissolved in DMAc and the solution was cast to give a yellowish transparent film (94% yield).

Estimation of dissociated DABBF in segmented polyurethane elastomers. Electron paramagnetic resonance (EPR) measurements of the segmented polyurethane elastomers during tensile deformation were carried out on a JEOL JES-F A200 EPR X-band spectrometer equipped with a BALDWIN tensile tester using strip specimens (110 mm × 3–4 mm × 0.3–0.5 mm). The effective measuring range is 43.5 mm height. The specimens were stretched and contracted under a strain rate of 91 %/min. The spectra were measured at each strain at room temperature using a microwave power of 1 mW and a field modulation of 0.2 mT with a time constant of 0.03 s and a rate of 0.75 mT/s. The radical concentration was determined by comparing the area of the observed integral spectrum with that of 0.001 mM 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPOL) solution in anisole (0.1 mL), which was placed in a 3 mm glass capillary, degassed, and measured under the same experimental conditions as the samples, with the assumptions that the proportion of the elastomers was the feed ratio, that the density of the elastomers was 1 g/cm^3, and that the Poisson's ratio of the films was 0.5. The Mn^{2+} signal was used as an auxiliary standard. The g value was calculated by using the equation: $g = h\nu/\beta H$, where h is Planck's constant, ν is the microwave frequency, β is the Bohr magneton, and H is the magnetic field.

SAXS and WAXD measurements. Small angle X-ray scattering (SAXS) measurements were carried out using a Nanostar (Bruker AXS) at room temperature. The wavelength of the X-ray beam was set at 0.154 nm for CuKα radiation. The camera length was set at 1070 mm. Two-dimensional (2D) scattering data were recorded with a VÅNTEC-2000 detector (2048 × 2014 pixels). The pixel resolutions of the detectors were 68 μm. Wide angle X-ray diffraction (WAXD) measurements were carried out using a Smartlab (Rigaku) at room temperature. The wavelength of the X-ray beam was set at 0.154 nm for CuKα radiation. The camera length was set at 175.5 mm. Two-dimensional (2D) diffraction data were recorded with a PILATUS 100 K (487 × 195 pixels). The pixel resolutions of the detectors were 172 μm. *In-situ* WAXD measurements were carried out at the BL40B2 beam line of SPring-8 (Japan Synchrotron Radiation Research Institute). Two-dimensional (2D) scattering data were recorded with a 1032 × 1032 pixel CMOS flat panel (FP) detector (C9728DK, Hamamatsu

Photonics). The pixel resolutions of the detector was 50 μm. The scattering vector, q (= $4\pi\sin\theta/\lambda$), where λ and θ are the wavelength of the X-ray beam and scattering angle, respectively; was calibrated using the peak positions of celium oxide. The wavelength of the X-ray beam was set at 0.1 nm. The camera lengths were set at 72.8 mm. The elastomer film of **P1** was clamped at both ends with a homemade tensile testing apparatus model OZ501 (Sentech) equipped with a 20 N load cell with gauge length of 10 mm, which was installed on the beam-line. The film was symmetrically stretched stepwise to 0%, 100%, 200% strain at room temperature. WAXD data were accumulated at each nominal strain. The stretching rate in each step was 10 mm/min (100% strain/min). Data processing was carried out with FIT2D software.

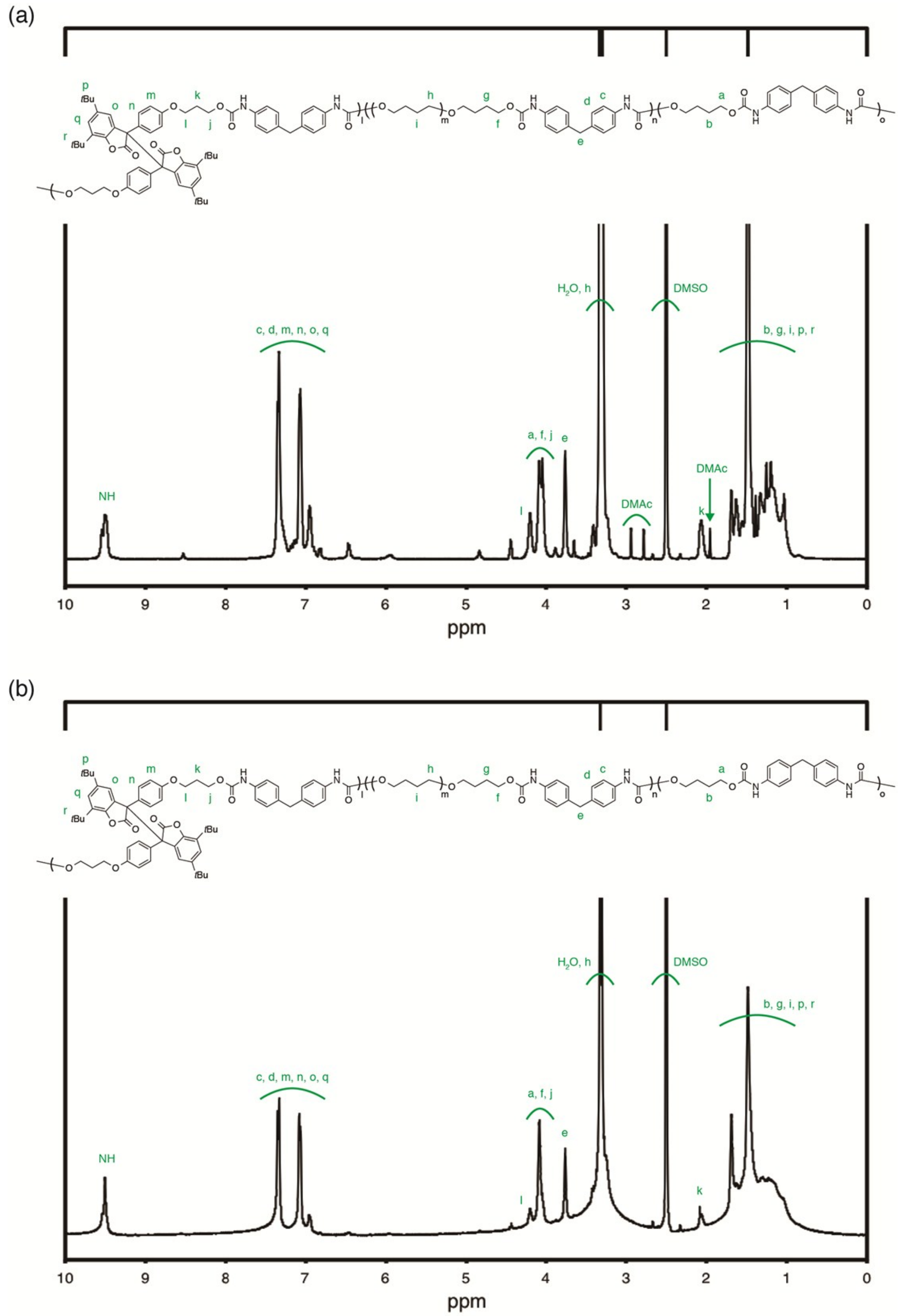

Figure S1. Chemical structures and ^{1}H NMR spectra of segmented polyurethane elastomers of (a) **P1** and (b) **P2**.

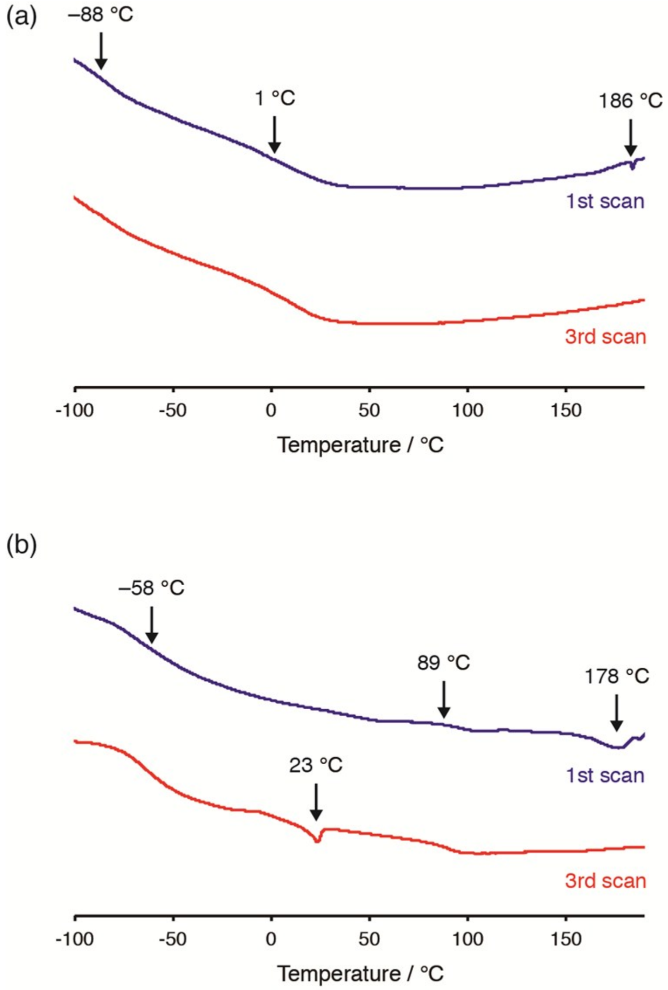

Figure S2. DSC curves of segmented polyurethane elastomers of (a) **P1** and (b) **P2** (blue: 1st scan, red: 3rd scan).

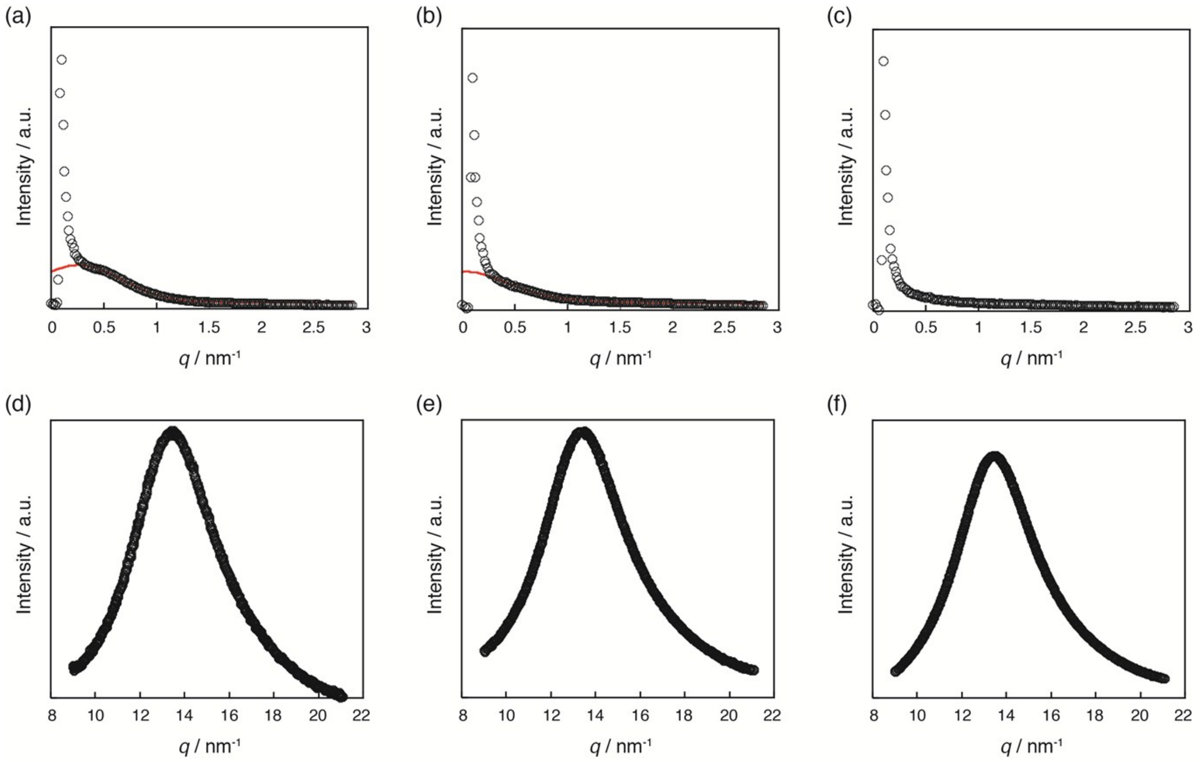

Figure S3. Circular averaged SAXS intensity profiles for elastomer **P1** (a) as-cast, (b) annealed at 100 °C, and (c) annealed at 200 °C for 10 min. Circular averaged WAXD intensity profiles for the elastomer (d) as-cast, (e) annealed at 100 °C, and (f) annealed at 200 °C for 10 min. A weak scattering peak was observed in the SAXS profile before annealing, and the scattering shoulder peak was disappeared completely after thermal annealing. The disappearance may be attributed to the less electron density contrast in the hard segment domains and soft segment matrix as well as the disordering of weakly ordered PTMG aggregates, because the rubbery elasticity was remained in the annealed samples. No crystalline diffraction was observed in the WAXD profile.

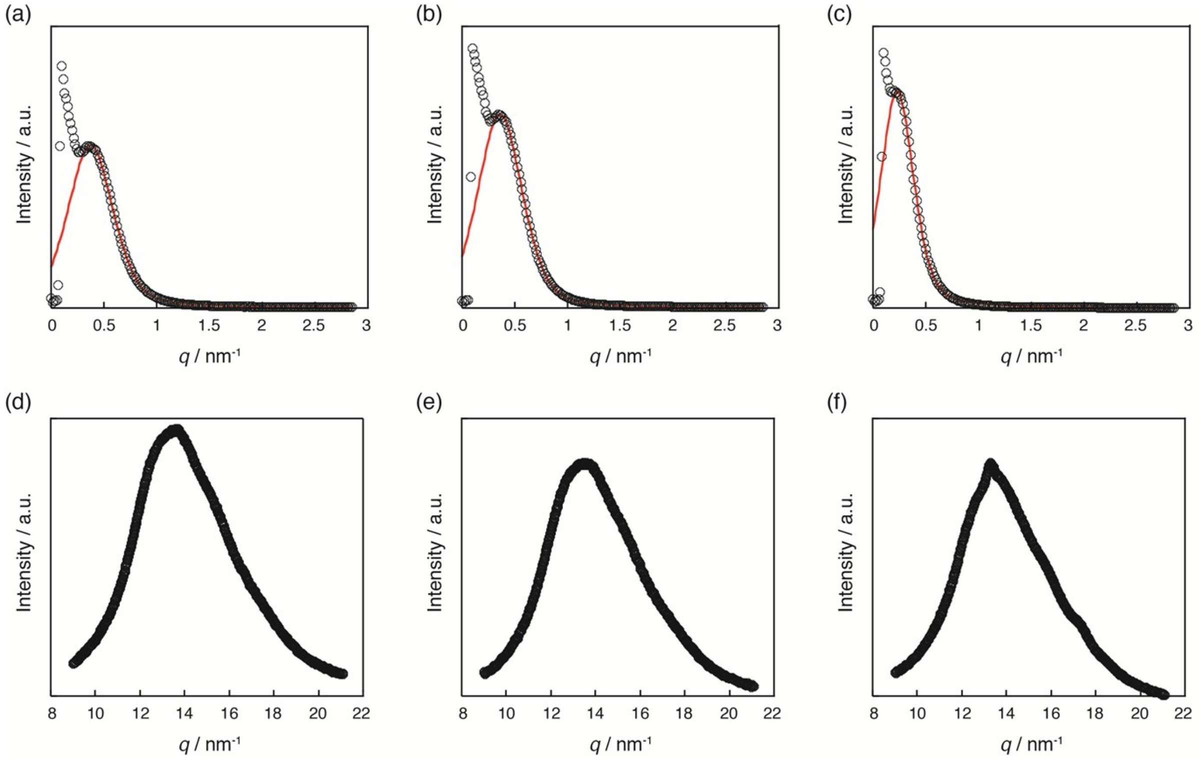

Figure S4. Circular averaged SAXS intensity profiles for elastomer **P2** (a) as-cast, (b) annealed at 100 °C, and (c) annealed at 200 °C for 10 min. Circular averaged WAXD intensity profiles for the elastomer (d) as-cast, (e) annealed at 100 °C, and (f) annealed at 200 °C for 10 min. The SAXS pattern includes a broad scattering peak indicating that domain structure exists in the elastomer. The long-period was estimated from the scattering vector of the scattering peak to be 16.8 nm in the as-cast film, while it grows up to 17.4 nm and 27.3 nm after thermal annealing at 100 °C and 200 °C, respectively. The phase separation of the hard segment domains and soft segment matrix progressed by thermal annealing. Sharp diffraction peaks were observed in the WAXD profiles over the amorphous halo. The weak intensity of the crystalline diffractions indicates the low crystallinity, while the crystallinity increased through thermal annealing. Therefore, the PTMG chains are supposed to crystallize in the well-segregated soft segment matrix.

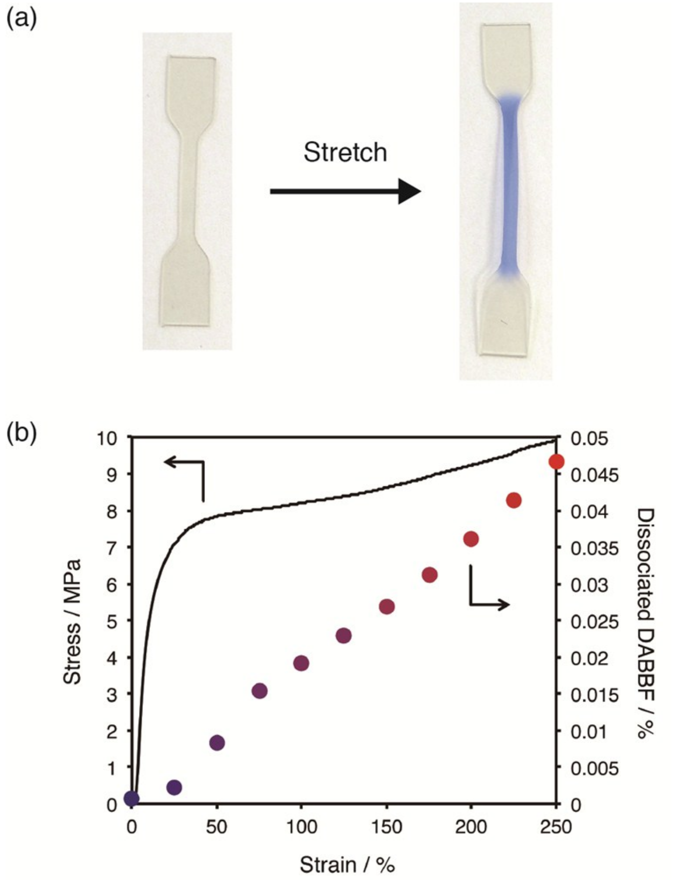

Figure S5. (a) Photographs of manual stretching of a dumbbell-shaped DABBF-containing elastomer **P2**. (b) A part of the typical stress–strain curve of the elastomer and ratio of dissociated DABBF mechanophores in the elastomer vs. strain.

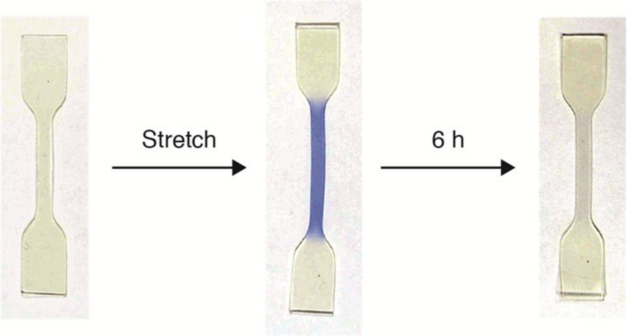

Figure S6. Photographs of a dumbbell-shaped segmented polyurethane elastomer **P1** before and after manual elongation and 6 h after the release.

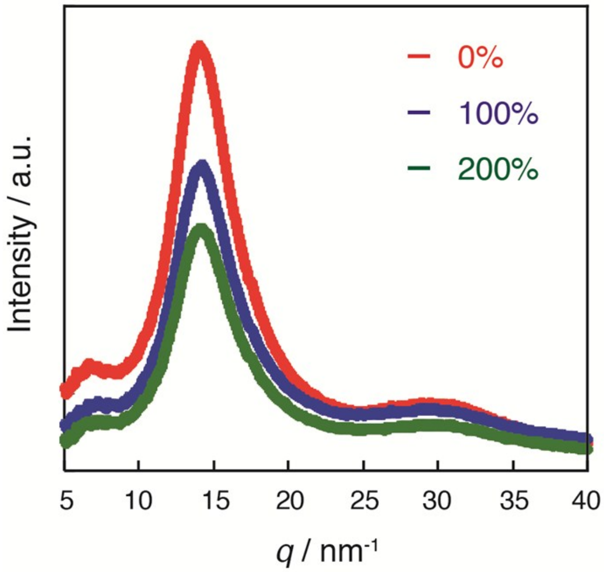

Figure S7. Circular averaged WAXD intensity profiles for elastomer **P1** at 0% (red), 100% (blue), or 200% (green) strain. Diffraction peaks of strain-induced crystals were not observed.

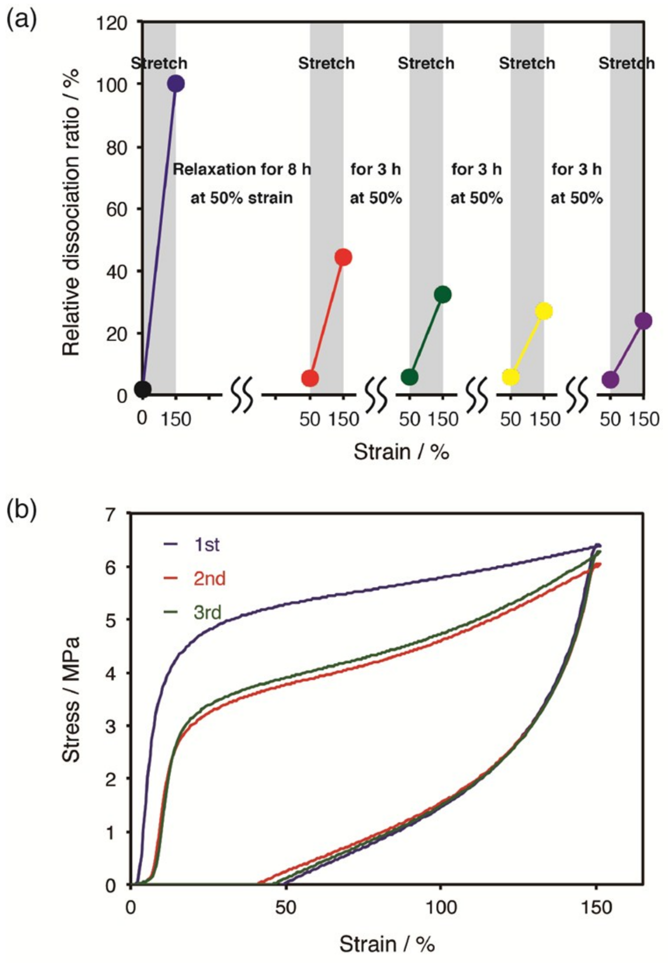

Figure S8. (a) Ratio of dissociated DABBF mechanophores in repeated activation of elastomer **P2**. The sample was elongated to 50% and 150% strains and relaxed for 2 or 8 h at 50% strain. (b) Cyclic stress-strain curves of the elastomer from 0% to 150% strain.