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Supporting Information for

Crack Tip Field of a Double-Network Gel: Visualization of Covalent Bond Scission through Mechanoradical Polymerization

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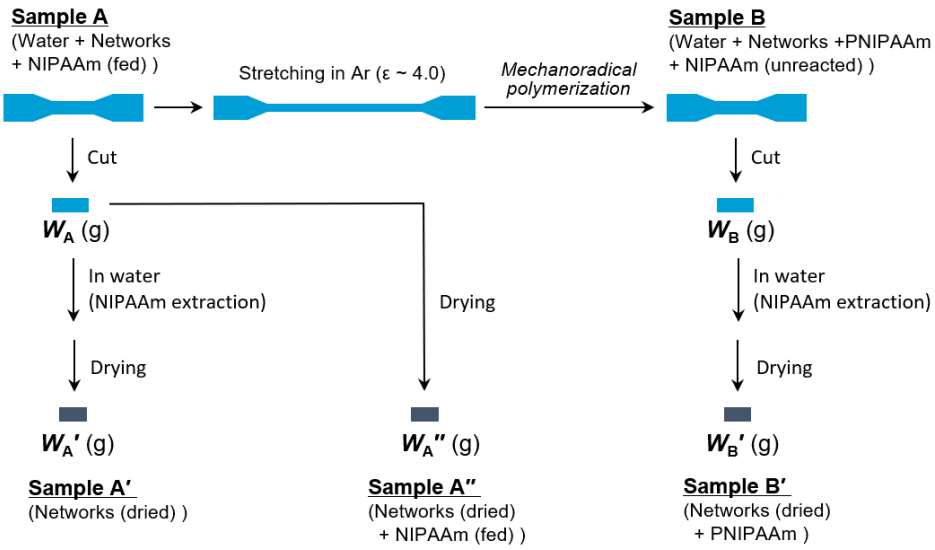
Supporting Methods

Chemicals. 2-Acrylamido-2-methylpropane sulfonic acid sodium salt (NaAMPS, 49.8 wt.% aqueous solution) was provided by Toagosei. *N*,*N*′-Methylenebis(acrylamide) (MBAA), 2-oxoglutaric acid, and *N*-isopropylacrylamide (NIPAAm) were purchased from FUJIFILM Wako Pure Chemical Corporation. Acrylamide (AAm) was purchased from Junsei Chemical. 8-Anilino-1-naphthalenesulfonic acid (ANS) was purchased from Tokyo Chemical Industry. Acetone was purchased from Kanto Chemical. All materials except for AAm were used as received, and AAm was recrystallized from acetone once before use.

Synthesis of DN gels. Double-network hydrogels were synthesized following a previously reported procedure.[S1,S2] First, poly(2-acrylamido-2-methylpropane sulfonic acid sodium salt) (PNaAMPS) single-network gels were synthesized as the first network. An aqueous solution of 1.0 M NaAMPS, 3.0–3.5 mol% MBAA, and 1 mol% 2-oxoglutaric acid was prepared, where the concentration denoted as mol% was the molar percentage with respect to the monomer. For quantitative discussion of the comparison between tearing test and tensile test (Figures 7, 8, S3, and S4), the MBAA concentration was fixed as x_1 = 3.0 mol%. The solution was poured into a glass mold made of two flat glass plates separated using a silicone rubber spacer (1.0 mm thick) in an argon glove box. The solution in the mold was irradiated with UV light (365 nm, 4 mW cm^{-2}) for 8 h in a glove box to allow for radical polymerization, resulting in a PNaAMPS single-network gel sheet. Afterwards, the PNaAMPS gel was immersed in a second network precursor solution for more than 1 day at 10 °C to swell the gel and introduce the second-network monomers to the gel. The second-network precursor aqueous solution comprises 2.0–4.0 AAm, 0.01–0.02 mol% MBAA, and 0.01 mol% 2-oxoglutaric acid. For quantitative discussion of the comparison between tearing test and tensile test (Figures 7, 8, S3, and S4), AAm and MBAA concentrations were fixed at C_2 = 4.0 M and x_2 = 0.02 mol%, respectively. The swollen gel was sandwiched between two flat glass plates, moved to an argon glove box, and then irradiated with UV light for 9 h in a glove box to synthesize the second PAAm network in the presence of the first PNaAMPS network. The synthesized DN gel was immersed in a large volume of deionized water for at least 1 day to remove unreacted reagents and make the gel equilibrium-swollen state in water.

Tensile test for mechanical characterization. To characterize the tensile mechanical properties of a DN gel, we conducted uniaxial and uniaxial cyclic tensile tests in air. In the uniaxial tensile test, dumbbell-shaped DN gels (standardized to JIS-K 6251-7; 12 mm gauge length, 2 mm width, and 3.1 mm thickness) were uniaxially stretched using a tensile tester (INSTRON 5965, Instron Co.) at a cross-head velocity of 100 mm min^{-1} (nominal strain rate of ~0.1 s^{-1}).[S3] The stress σ was characterized as the nominal stress, which is the measured force divided by original cross-sectional area. The strain ε was measured using a non-contacting video extensometer (AVE, Instron Co.). Under the same experimental conditions, cyclic tensile tests with incremental imposed strains were also performed to characterize the dissipated mechanical energy density U_{diss} as a function of strain ε from mechanical hysteresis (see Figure S3).[S3]

Supporting Figures



W_A'/W_A : Weight fraction of the first and second networks in sample A (also in sample B).
W_A''/W_A : Weight fraction of the networks and fed NIPAAm in sample A.
W_B'/W_B : Weight fraction of the networks and synthesized PNIAAm in sample B.

Monomer conversion : (synthesized PNIPAAm fraction) / (fed NIPAAm fraction)
$= (W_B'/W_B - W_A'/W_A) / (W_A''/W_A - W_A'/W_A)$

W_A'/W_A (wt. fr.)	W_A''/W_A (wt. fr.)	W_B'/W_B (wt. fr.)	$W_B'/W_B - W_A'/W_A$ (wt. fr.)	$W_A''/W_A - W_A'/W_A$ (wt. fr.)	**Monomer conversion (%)**
0.177 (±0.003)*	0.236 (±0.002)*	0.201 (±0.004)*	0.024 (±0.005)**	0.059 (±0.004)**	**40.7 (±8.6)****

*Standard deviation from three individual measurements. **Standard deviation obtained by the law of propagation error.

Figure S1. Characterization of monomer conversion of mechanoradical NIPAAm polymerization in a typical case. We characterized the monomer conversion from weight analysis as described in this Figure. First, the weight fraction of the first and second network in an unstretched DN gel fed with NIPAAm (sample A) was characterized as W_A'/W_A. The weight fraction of the networks in the unstretched gel (sample A) was identical to that in a stretched gel (sample B) because of the stretching resulted in no weight change. Second, the weight fraction of the solid (sum of the networks and fed NIPAAm monomer) in the unstretched sample was characterized as W_A''/W_A. Third, the weight fraction of the polymer (sum of the networks and mechanically-synthesized PNIPAAm polymer; excluding residual unreacted NIPAAm monomer that can be washed out by immersing the gel in water) was characterized as W_B'/W_B, assuming that PNIPAAm polymer cannot be extracted from the gel by immersing the gel in water because it should be tethered to the ruptured end of the first network. Based on these three results, the monomer conversion was characterized as the synthesized PNIPAAm polymer weight fraction divided by the fed NIPAAm monomer weight fraction; that is, $(W_B'/W_B - W_A'/W_A) / (W_A''/W_A - W_A'/W_A)$. For a DN sample stretched at a strain of ~4, the NIPAAm monomer conversion was estimated as 40.7±8.6 %. The feed formulation in the synthesis of the DN gel was NaAMPS 1.0 M and MBAA 3.0 mol% for the first network, and AAm 4.0 M and MBAA 0.01 mol% for the second network. To extract NIPAAm monomer from a gel, the gel was immersed in large volume of water for three days. To remove water from a gel, the gel was dried at 120 °C in a vacuum for 6 h.

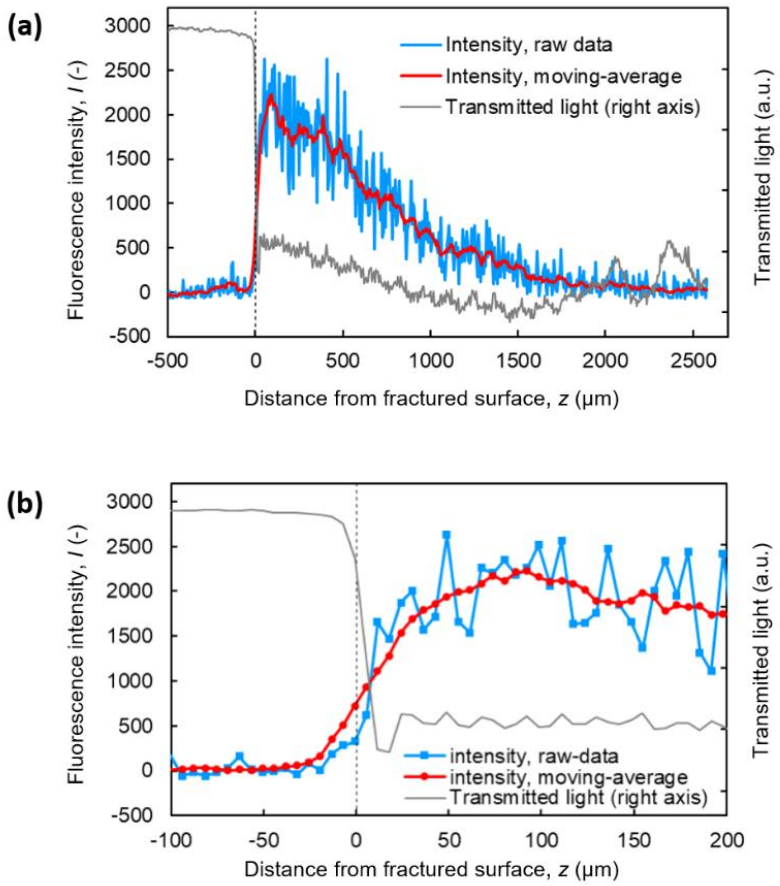
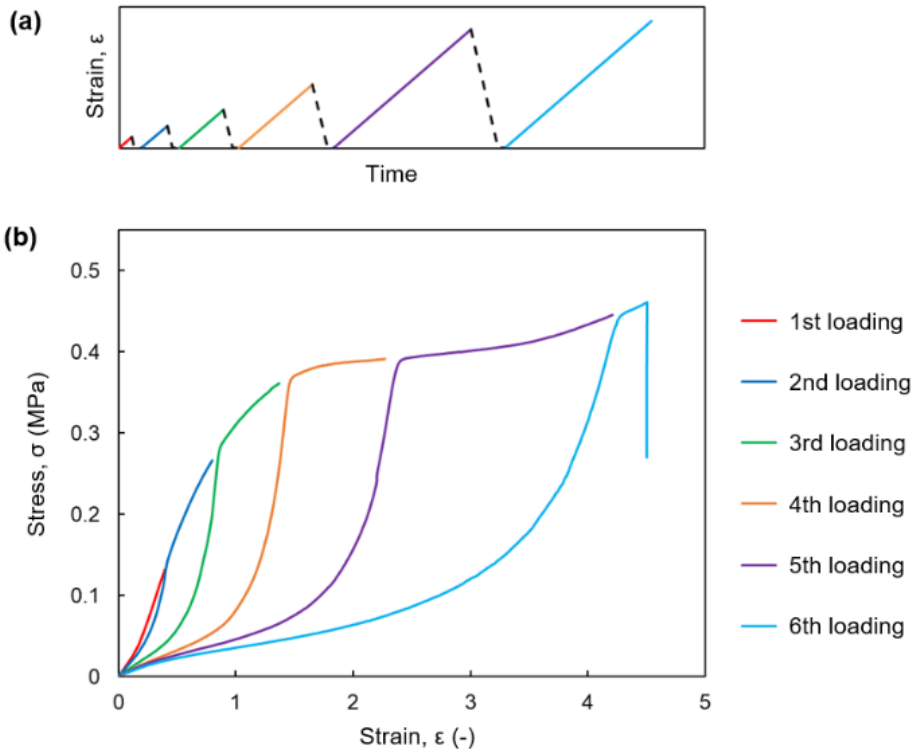


Figure S2. A typical **(a)** full view and **(b)** expanded view of fluorescence intensity profiles and transmitted light profile around the fractured surface of a DN gel. Because the raw fluorescence intensity profile (blue curve) contains relatively strong noise, we used the moving-average over 9 raw-data points in the main text and the moving-average intensity values are plotted against the z-position of the center point of the 9 points (red curve). As the raw data was sampled at a 6.2 μm interval in the z-position, the 9-point moving-average gives an average over ~50 μm. The fluorescence intensity was measured by excitation of the 402.5 nm laser light. To determine the position of the gel, the transmitted light was also observed. The profile of the transmitted light (gray curve) clearly indicates the fractured surface (boundary of air and the gel) so that this profile was used to determine the fractured surface at point $z = 0$. In **(b)**, the fluorescence intensity of raw data steeply increased at the surface, while that of moving-averaged data was blunted due to the moving-averaging processing.



(c)

Cycle number, n (-)	ε_{max} (-)	ΔU_{diss} (MJ/m^3)	U_{diss} (MJ/m^3)
1	0.40	0.004	0.004
2	0.80	0.042	0.046
3	1.37	0.105	0.151
4	2.27	0.200	0.351
5	4.21	0.410	0.761

Figure S3. A typical result of the cyclic tensile test of a DN gel. **(a)** Schematic of the mechanical input of the cyclic tensile test. Only the loading curves were recorded because with respect to DN gels, an unloading curve overlaps with the subsequent loading curve. **(b)** Cyclic stress−strain loading curves of the DN gel. **(c)** Dissipated mechanical energy density U_{diss} as a function of imposed strain ε_{max}. Following the reported procedure,[S3] U_{diss} for each maximum strain ε_{max_n} (corresponding cycle number n) was characterized from the accumulation of the mechanical hysteresis: $U_{diss_n} = \sum_{i=1}^{n} \Delta U_{diss_i}$, where $\Delta U_{diss_n} = \int_0^{\varepsilon_{max_n}} \sigma_n(\varepsilon)\, d\varepsilon - \int_0^{\varepsilon_{max_n}} \sigma_{n+1}(\varepsilon)\, d\varepsilon$ is the hysteresis area of each sequential step (n^{th} and $(n+1)^{th}$ stress–strain curves with the stress $\sigma_n(\varepsilon)$ and $\sigma_{n+1}(\varepsilon)$, respectively) in the strain range $0 < \varepsilon < \varepsilon_{max_n}$. The data of U_{diss}–ε_{max} plot (Figure 7c in the main text) were obtained from four individual tests of this DN gel to collect the multiple data points.

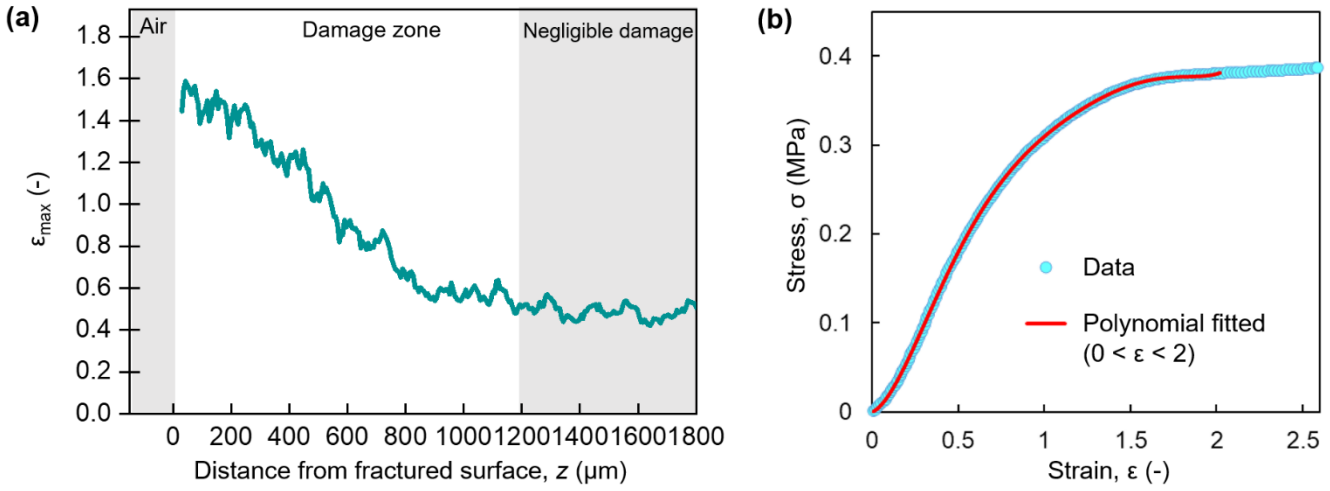


Figure S4. Supporting figure describing the protocol in order to obtain the maximum stress profile $\sigma_{max}(z)$ shown in Figure 8b (main text). The profile of the maximum stress imposed as a function of the distance z from the fractured surface, $\sigma_{max}(z)$, was obtained from the maximum strain profile $\varepsilon_{max}(z)$ (Figure S4a) and the uniaxial stress–strain curve (Figure S4b) which are identical as shown in Figures 8a and 7a in the main text, respectively. To convert each ε_{max} value in the $\varepsilon_{max}(z)$ plot into the corresponding σ_{max} value, we used a polynomial fitting curve for the stress–strain curve in Figure S4b. Because the ε_{max} characterized in Figure S4a is no more than 2.0, we used the fitting curve within the range of $0 < \varepsilon < 2$ ($\sigma = 0.1026\ \varepsilon^6 - 0.7004\ \varepsilon^5 + 1.8683\ \varepsilon^4 - 2.4113\ \varepsilon^3 + 1.3615\ \varepsilon^2 + 0.0888\ \varepsilon$) as shown in Figure S4b. The resulting $\sigma_{max}(z)$ is shown in Figure 8b in the main text.

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