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Supporting Information for
Tough and Fatigue-Resistant Polymer Networks by Crack Tip Softening

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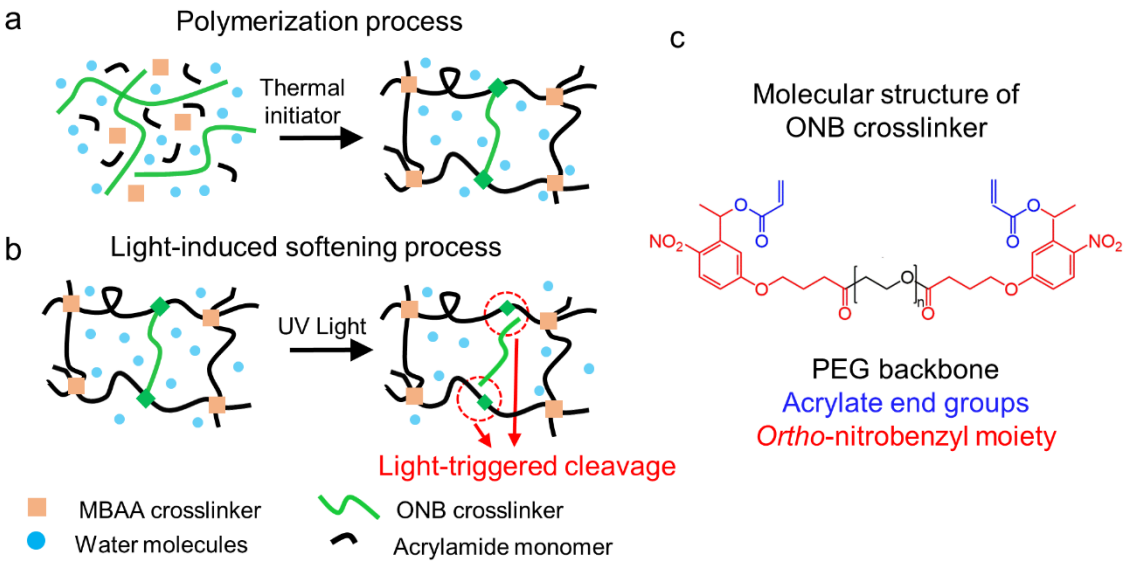

Figure S1. Chemistry of polymerization and light-induced softening of the hydrogels. (a) Polymerization process of hydrogels. (b) Light-induced softening process of hydrogels. (c) Molecular structure of the ONB crosslinker.

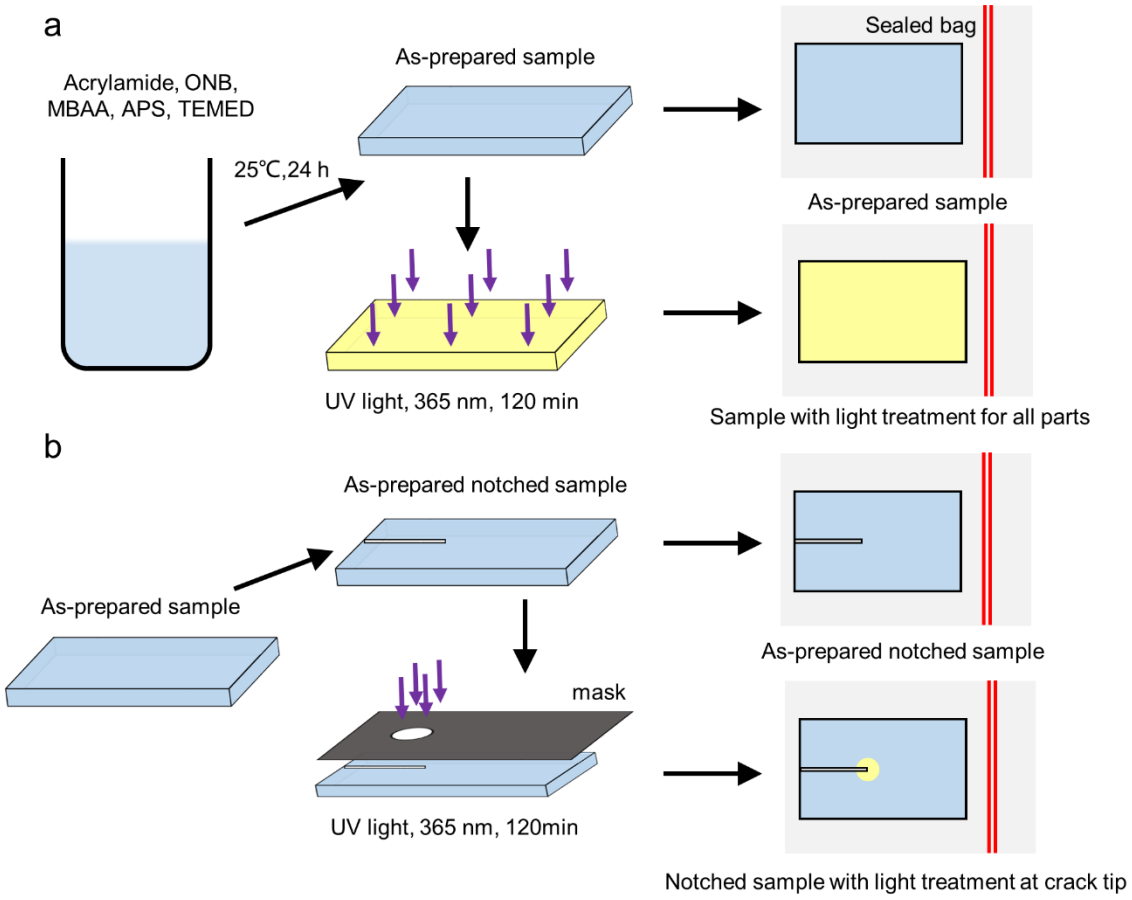

Figure S2. Fabrication of light-softened polyacrylamide hydrogels. (a) Unnotched samples and (b) Notched samples.

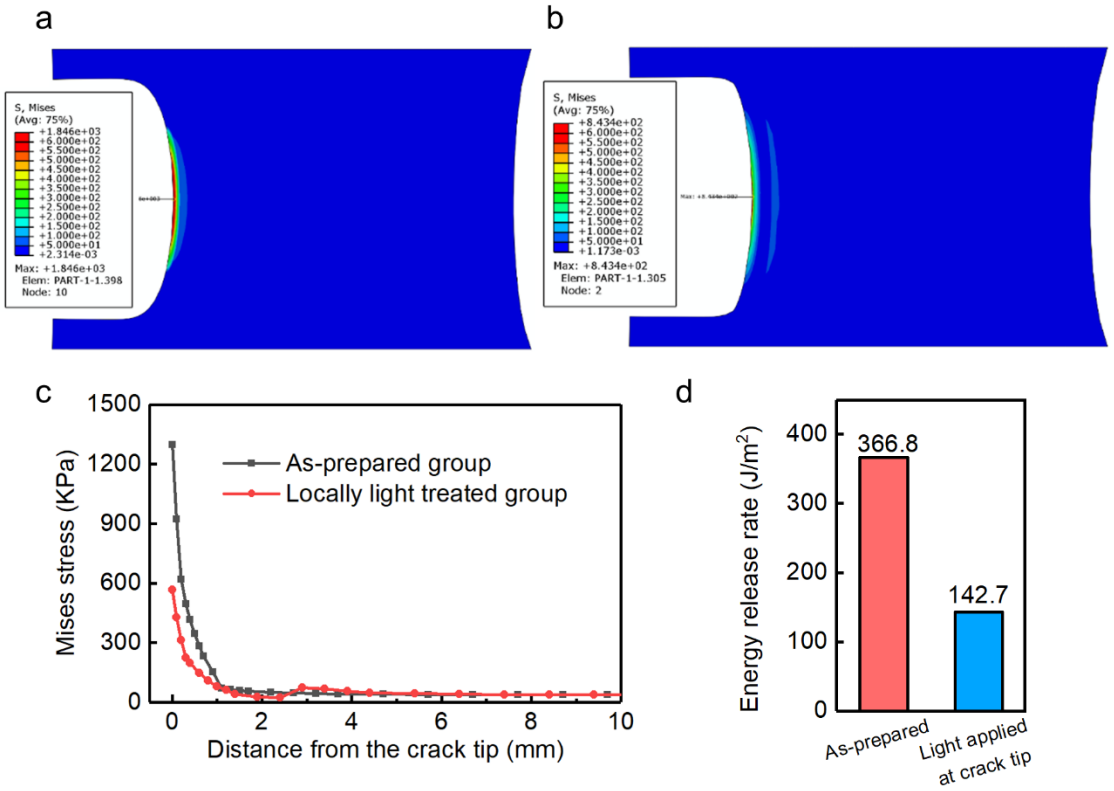

Figure S3. FEM simulation of the stress fields in two kinds of samples. (a) as-prepared samples. (b) CTS samples. (c) Mises stress calculated as a function of distance from the crack tip. The points were picked on the x-axis along the crack tip. (d) Energy release rate for the two groups of samples was calculated by J-integral in Abaqus software.

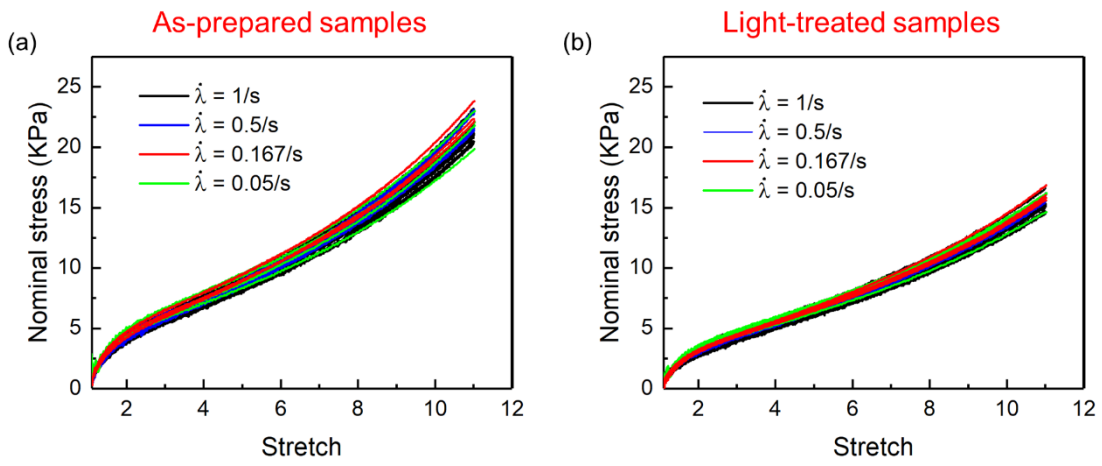

Figure S4. Stress-stretch curves of polyacrylamide hydrogels at various loading rates. (a) As-prepared samples (b) Light-treated samples.

We prepare polyacrylamide hydrogel samples with a MBAA concentration of 5 μL/mL and an ONB concentration of 10 μL/mL. The samples are stretched from λ= 1 to λ= 11 and no samples suffered fracture. Four rates of stretch are used: 0.05/s, 0.167/s, 0.5/s, and 1/s. For each loading rate, at least 3 samples are tested. All stress-stretch curves are plotted in Figure S4. The light-treated sample has a lower stress-stretch curve than the as-prepared one. For both kinds of hydrogels, curves measured by stretching rates ranging about two orders of magnitudes are nearly consistent. Small scattering indicates that dangling chains do not slide much with each other during stretching (1-3). Polyacrylamide hydrogels are stretch-rate-independent.

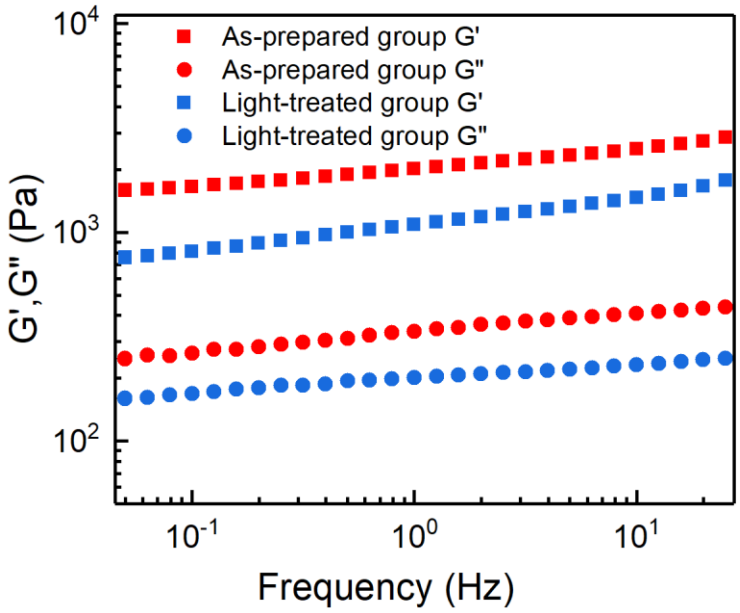

Figure S5. Rheological properties of polyacrylamide hydrogel samples.

It has been confirmed that storage modulus of a polymer network can change ~10 times when substantial entanglement exists (2, 3). We prepare polyacrylamide hydrogel samples with a MBAA concentration of 5 μL/mL and an ONB concentration of 10 μL/mL. Rheological tests are performed to characterize the entanglement effect on the modulus. Hydrogel samples are cut into disk-shaped with diameter of 10 mm and thickness of 2 mm. The maximum oscillatory shear strain is controlled as 5% to measure the rheological properties (e.g., storage modulus, loss modulus) at small deformations. As shown in Figure S5, the storage modulus ranges from 1.6 KPa to 2.7 KPa for as-prepared samples and from 0.7 KPa to 1.6 KPa for light-treated samples at a frequency from 0.05 to 20 rad/s. These changes are far less than one order of magnitude. As a result, dangling chains do not slide much with each other during shearing. Polyacrylamide hydrogels are shear-rate-independent.

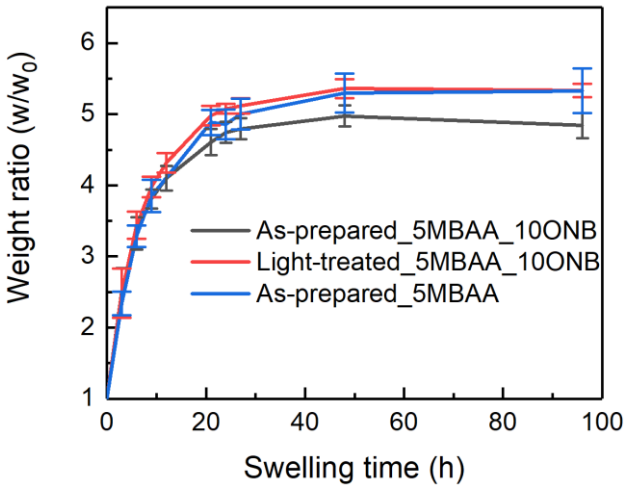

Figure S6. Swelling properties of hydrogel samples. The weight ratio of hydrogel samples as a function of swelling time.

Entanglements affect the swelling ratio of a hydrogel (4-6). In a polymer network, the entropy of mixing drives swelling, and the entropy of elasticity drives de-swelling. When monomers polymerized at a high concentration, the crowded monomers polymerized into densely entangled polymer chains. In this case, crosslinks are outnumbered enormously by entanglements. The entanglements function as additional crosslinks and drive de-swelling. When the monomers polymerized at a low concentration, the sparse polymer chains barely entangle. In this sense, crosslinks prevail over entanglements. The entanglement among the sparse polymer chains are not strong, which could be disassociated by mechanical loads or swelling. The dangling chains act as a network defect, which does not bear the load but contributes to the swelling.

We prepare three groups of samples to study the swelling of hydrogels (Figure S6). For the black and red curves, hydrogels are made from a MBAA concentration of 5 μL/mL and an ONB concentration of 10 μL/mL. For the blue curve, the hydrogels are made only from a MBAA concentration of 5 μL/mL. The mass ratio of a fully swollen hydrogel to an as-prepared hydrogel defines the swelling ratio. Table S1 gives the equilibrium value of the polymer-to-hydrogel mass ratio, ϕ.

In our experiments, the polymer mass content of all the hydrogels is about 12% in the as-prepared state, which is much lower than that of the highly entangled hydrogels. The concentrations of both the MBAA and ONB crosslinkers are kept at least 5 μL/mL for all the precursors, which is not low enough to produce certain entanglements. Comparison between the black and the blue curves indicates that more crosslinks yield a smaller swelling ratio. After light treatment, ONB crosslink degrades, resulting in dangling chains and possible entanglement among these chains. However, the swelling ratio after degradation of ONB (red curve) is almost consistent with that of an ONB free sample (blue curve). These findings show that ONB degradation does not cause much entanglements in the polymer network.

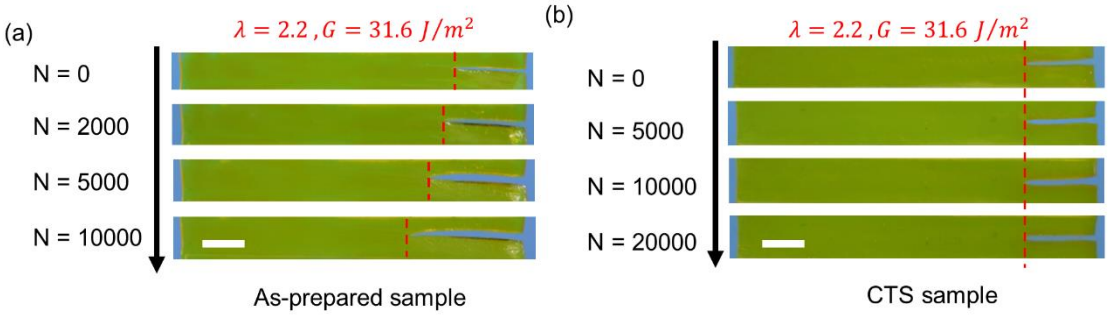

Figure S7. Fatigue resistance of an as-prepared sample and a CTS sample. (a) photos of an as-prepared sample before and after 10000 cycles at energy release rate G =31.6 J/m^2. The scale bar is 10 mm. The crack propagated several milometers after 10000 cycles. The hydrogel is highly transparent, and is paint yellow to show the crack clearly. (b) photos of a CTS sample before and after 20000 cycles at energy release rate G =31.6 J/m^2. The crack advance is not observed.

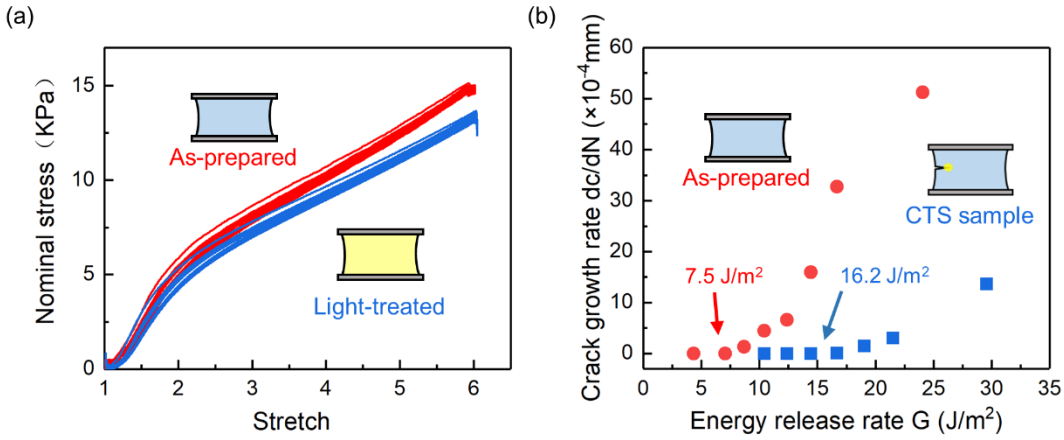

Figure S8. Fatigue cycle test of the hydrogel with another recipe. For every 1 mL precursor, 10 μL MBAA and ONB solutions were added. (a) Nominal stress as a function of stretch for the hydrogels before and after UV light treatment. The unnotched sample is stretched from λ= 1 to λ= 6 and applied repeatedly for the calculation of the energy release rate G. The hydrogel samples possessed a high crosslink content and is more rigid, easier to fracture, so the maximum stretch is set as 6, and not 11. (b) G-dc/dN curves for the as-prepared samples and the CTS samples. The fatigue threshold is 7.5 J/m^2 for the as-prepared group and 16.2 J/m^2 for the CTS samples.

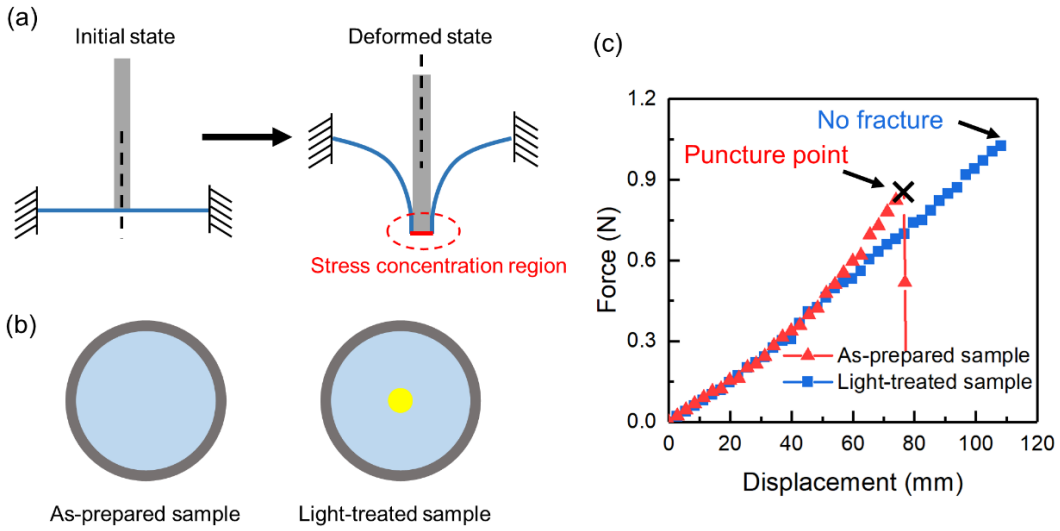

Figure S9. Punctuation of hydrogel membranes. (a) Schematic of initial and deformed states of a hydrogel membrane indented by a metal bar (7-9). (b) Schematic of as-prepared samples and light-treated samples. The light-treated sample is softened over the central of the membranes. (c) Forces as a function of the indentation displacement.

	As-prepared state	Fully-swollen state
As-prepared_5MBAA _10ONB	12.1%	2.50±0.09 %
Light-treated_5MBAA _10ONB	12.1%	2.26±0.04 %
As-prepared_5MBAA	12.2%	2.27±0.07 %

Table S1. Polymer content of hydrogel samples at as-prepared state and fully-swollen state.

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