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Extremely Stretchable and Fast Self-Healing Hydrogels

Insu Jeon, Jiaxi Cui, Widusha R. K. Illeperuma, Joanna Aizenberg, and Joost J. Vlassak**

Hydrogels are materials that consist of crosslinked polymer networks dispersed in water.[1] While a number of promising properties, such as biocompatibility and environmental friendliness,[2,3] responsiveness to external stimuli,[4–6] adhesion,[7] antibiofouling behavior,[8–10] and biodegradability[11] have been integrated into hydrogels, the relatively poor mechanical behavior of hydrogels remains a challenge, impeding their use in real-world applications that require mechanical integrity.[12,13] Many attempts have been made to improve the mechanical properties of hydrogels by optimizing their network structure.[14–20] Typical strategies include the use of double networks,[14,17,21,22] diamond-like structures with homogeneous spacers,[15] slide-ring connections,[16] and dynamic crosslinking systems.[18–20] Among these strategies, dynamic crosslinks based on supramolecular associations such as hydrophobic interactions,[18] hydrogen bonding,[19] host–guest interactions,[20] and electrostatic interactions[2,23] supply more diversity and a wider spectrum of properties. Because of their ability to readily break and reform crosslinks, these types of hydrogels are often quite stretchable[18] and even self-healable. Most of these types of hydrogels rely on a single dynamic crosslink mechanism. We report in this study that a hierarchical system of noncovalent crosslinks can lead to superior stretchability and damage recovery. This system of crosslinks allows the hydrogels to stretch up to 100 times their initial length and to completely self-heal within 30 s without external energy input.

The hierarchical system of interactions includes hydrophobic association, multiple hydrogen bonds (H-bonds), and encapsulation. We use a novel crosslinker UPyHCBA that consists of an acrylic head, a hydrophobic alkyl spacer connected by carbamate, and a 2-ureido-4-pyrimidone (UPy) tail (**Figure 1**a) to provide both hydrophobic association and hydrogen bonds. UPyHCBA was synthesized by coupling UPy-based isocyanate with 4-hydroxybutyl acrylate using dibutyltin dilaurate as a catalyst. The UPy unit is a well-studied supramolecular building block originally developed by Meijer et al.[24] It forms self-complementary dimers with quadruple H-bonds and is widely used to prepare supramolecular materials with promising properties, including monomer-like behavior at elevated temperature[25,26] and the ability to self-heal.[27–29] The dimer affinity is very high in hydrophobic environments, but decreases significantly when the environment is hydrophilic.[19] Consequently, hydrophobic microphases often form to maintain the bonds.[30] We used sodium dodecyl sulfate (SDS) micelles to provide a hydrophobic environment for the UPyHCBA, and prepared the hydrogels by micellar polymerization[31,32] of UPyHCBA and acrylamide (Figure 1b–d). SDS emulsions with relatively large micelles were made using an 0.5 M aqueous solution of NaCl.[33] The loading of UPyHCBA increased the stability of the emulsion significantly through a decrease in the Krafft temperature, thus supplying a wider temperature range for in situ copolymerization. The loading of UPyHCBA, the polymerization, and the multiple block structures of UPyHCBA and acrylamide obtained were characterized by a combination of various techniques (for detail, see Figures S1–S5 in the Supporting Information). The resulting hydrogels contained ≈81 wt% water and displayed a well-defined shape (Figure S3, Supporting Information).

As-prepared hydrogels were cut into rectangular shapes for tensile testing (**Figure 2**a–c). Typical nominal stress (S) and stretch (λ) curves are shown in Figure 2d for gels with different amounts of UPyHCBA. The hydrogel with 9.1×10^{-3} M UPyHCBA showed exceptional stretchability (Figure 2b–d) with a stretch of more than 100—it was not possible to fracture this gel due to the limitations of the tensile tester. Unless mentioned otherwise, this hydrogel was used for all measurements and experiments. First yield—clear evidence of crosslinking—was observed in this gel at a stretch of ≈1.25. The elastic modulus was 1.66 ± 0.47 kPa over a stretch range from 1 to 1.25; the maximum nominal stress was 3.92 ± 0.87 kPa. The test results indicate that the gel is quite soft, but does not fracture easily. Both the elastic modulus and the maximum stress increase with increasing UPyHCBA concentration, while the strain to fracture decreases (Figure S6, Supporting Information). Because of the extreme stretch, the cross-sectional areas of the specimens change significantly during testing (Figure 2b,c) and it is informative to evaluate the true stress (σ) in the samples. The true stress is defined as the applied load divided by the actual cross-sectional area of the specimen, and is a better measure of the load bearing capability of a material in case of very large deformation than the nominal stress. Under the assumption that the gel is incompressible, the true stress is calculated from the nominal stress using the expression $\sigma = S \cdot \lambda$. Figure 2e shows the true stress versus stretch curves of the specimens. The maximum true stress is approximately two orders of

Prof. I. Jeon, Dr. J. Cui, Dr. W. R. K. Illeperuma,
Prof. J. Aizenberg, Prof. J. J. Vlassak
School of Engineering and Applied Sciences
Harvard University
Cambridge, MA 02138, USA
E-mail: vlassak@seas.harvard.edu

Prof. I. Jeon
School of Mechanical Engineering
Chonnam National University
77, Yongbong-ro, Buk-gu, Gwangju 61186, South Korea

Dr. J. Cui
INM-Leibniz Institute for New Materials
Campus D2 2, Saarbrücken 66123, Germany
E-mail: jiaxi.cui@leibniz-inm.de

Prof. J. Aizenberg
Wyss Institute for Biologically Inspired Engineering
Harvard University
Cambridge, MA 02138, USA

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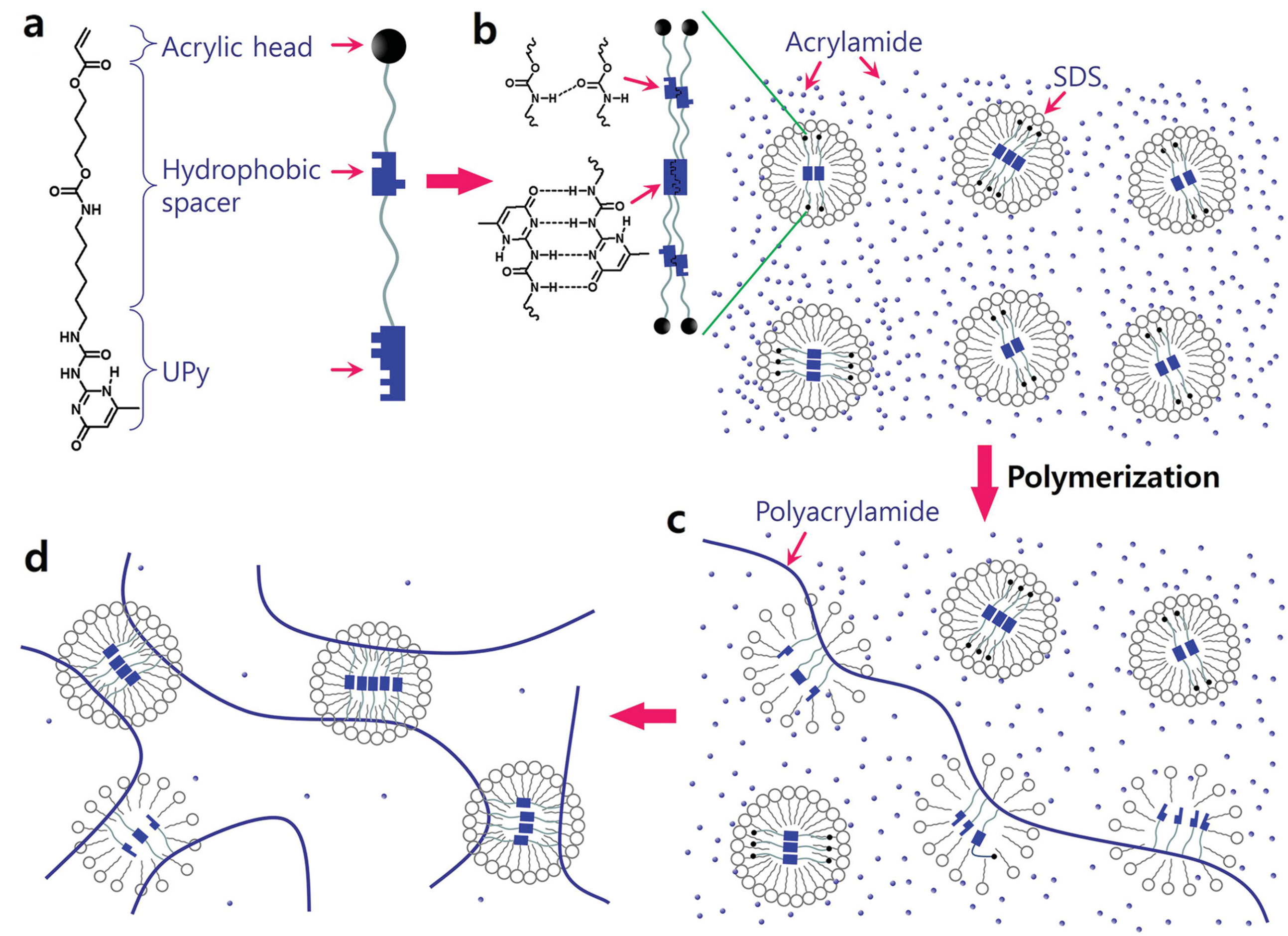

Figure 1. Schematic of the micellar copolymerization of the UPyHCBA and acrylamide. a) The structure of the UPyHCBA monomer, (b) SDS micelles loaded with UPyHCBA in an aqueous acrylamide solution, and (c,d) micellar copolymerization of acrylamide and UPyHCBA loaded in SDS micelles.

magnitude larger than the nominal stress. Evidently, these gels can endure very large true stresses during deformation.

The effect of the deformation rate on the tensile behavior was evaluated for gels crosslinked with 9.1×10^{-3} M UPyHCBA. Tensile experiments were performed at four different extension rates (**Figure 3**a). The figure shows that the stress level increases with deformation rate. This increase in stress is independent of the applied stretch resulting in a set of parallel stress–stretch traces. This behavior is typical for a viscoelastic material. Even at a rate of 960 mm min^{-1}, the samples did not fracture (Movie S1, Supporting Information), suggesting fast reconfiguration of the crosslinks. The intercepts on the y-axis of linear fits to the stress–stretch curves are shown as a function of the extension rate in the Supporting Information section (Figure S7, Supporting Information). The results suggest that the stress has a logarithmic dependence on the stretch rate and show that the tensile curves are reasonably well represented by a large-deformation visco-elastic Zener model using Mooney-Rivlin springs and a logarithmic rate-dependence (Figure S8, Supporting Information).

To probe crosslink dynamics, two types of cyclic tensile tests were carried out. In the time-dependent tests, the sample was cyclically deformed to a stretch of six with 1 or 2 min of recovery time between consecutive cycles (Figure 3b). The loading segment of the first cycle overlaps with the nominal stress–stretch curve, while later cycles show slight hardening; all cycles show significant hysteresis. The hysteresis ratio, i.e., the hysteresis for each deformation cycle was normalized by the hysteresis of the first cycle, as a function of cycle number (Figure S9, Supporting Information). With a hysteresis ratio of ≈93%, recovery for the second cycle is nearly complete after only 1 min; for later cycles, the ratio exceeds 100% because of the slight hardening that occurs. The results suggest fast crosslink dynamics. Results obtained in cyclic tests with increasing maximum stretch and with 2 min of recovery time between individual cycles are presented in Figure 3c. The hysteresis increases with increasing extension and a slight change in the shape of the loop is observed. As the number of cycles increases, the loading curves decrease progressively below the unidirectional tensile curve, revealing that the 2-min recovery time between the cycles is not quite sufficient to fully restore the damage in the sample as the stretch increases.

Stress-relaxation measurements were carried out to further investigate the viscoelastic behavior of the gels. Figure 3d presents the stress-relaxation curves for three different stretch values. Despite the large variation in stretch, similar stress-relaxation curves were observed for all tests: the degree of stress relaxation increases with imposed stretch, but the time

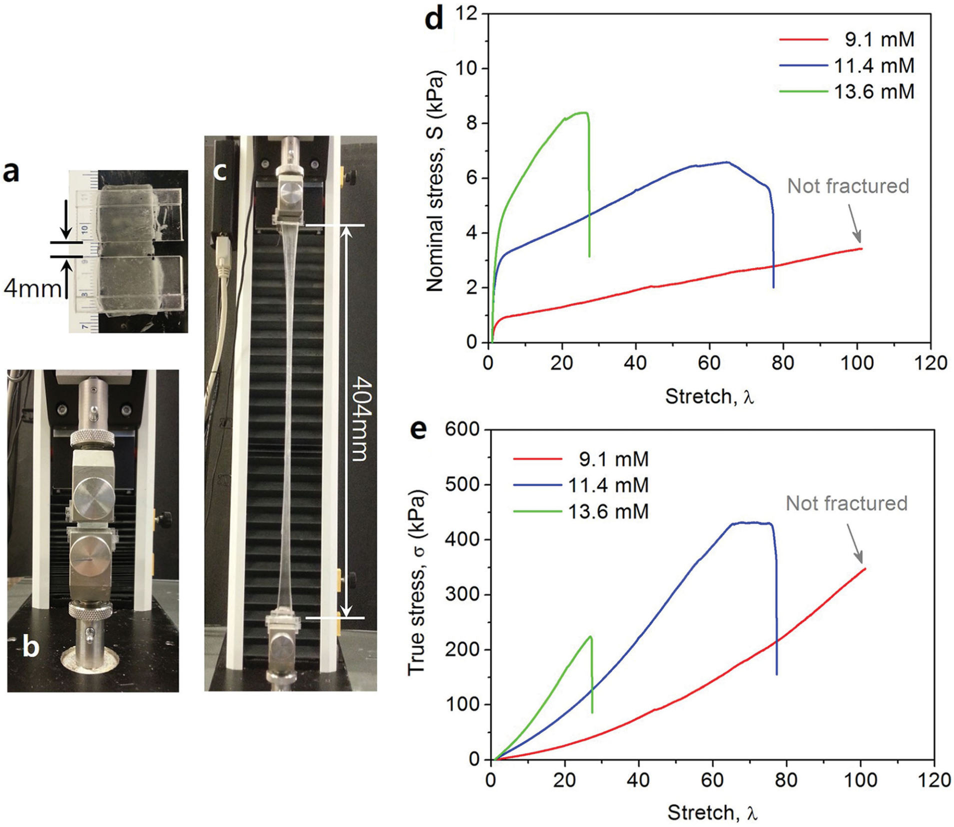

Figure 2. a) Hydrogel specimen for tensile testing. Upper and lower sections of the sample were sandwiched between two polystyrene plates using glue (Krazy Glue, KG585) to produce a 4 mm gauge length. The width and thickness of the specimen were 15.0 and 6.0 mm, respectively. A gel specimen prepared using 9.1×10^{-3} M UPyHCBA (b) before and (c) after stretching. d) Representative nominal stress–stretch curves of gel specimens made using 9.1×10^{-3} M, 11.4×10^{-3} M, and 13.6×10^{-3} M UPyHCBA. e) True stress–stretch curves of the gel specimens.

constant over which the stress relaxes is comparable and is on the order of a few minutes. Normalization of the stress-relaxation curves by the plateau stress collapses all relaxation curves into a single master curve that is well fitted with a generalized Maxwell equation (Figure S10 and Table S1, Supporting Information). The shape of the master curve suggests more than two distinct relaxation mechanisms, one with a characteristic relaxation time of a few seconds, and several with much longer time constants.

To characterize the self-healing behavior of the gels, rectangular tensile specimens were cut in two (**Figure 4**a). After both pieces were held together for 3 min, the samples (Figure 4b) were mounted in the tensile tester. They were then tested after another 2 min under the same conditions as the pristine samples (Figure 4c; Movie S2, Supporting Information). Stress–stretch curves were comparable to those of normal specimens (Figure 4d), although healed specimens showed an elevated stress level at small stretches. Evidently, the hydrogels have the ability to heal quickly and to form bonds that are at least as strong as the pristine gels. Since it took several minutes to mount samples in the test machine, it was not possible to perform quantitative measurements of the maximum healing rate. A qualitative test was conducted on one specimen that was cut in half: holding the cut surfaces together for less than 30 s without any external energy input led to a robust bond between the pieces allowing the sample to be stretched without fracture (Movie S3, Supporting Information). Furthermore, samples were able to heal repeatedly in the same region and usually failed in pristine regions when stretched to fracture.

In a number of semiquantitative experiments, we found that the self-healing ability of hydrogels depends on the time the cut surface is exposed to air. Hydrogel surfaces that were exposed to air for about 2.5 min after cutting showed the best self-healing properties (Figure S11, Supporting Information). During exposure, water evaporation from the cut surfaces locally enhances the concentration of polymer, as well as NaCl and SDS. As the concentration of NaCl increases, SDS tends to form larger aggregates—this was confirmed by the observation that cut surfaces turned opaque after storage in air. The SDS reconfiguration could be observed in the healed region via local changes in transparency: after contact, the region became opaque (Figure S12, Supporting Information) and then shrank slightly, yielding a relatively homogeneous state.[34] The expansion of the opaque region is attributed to the formation of larger SDS aggregates at the interface. Eventually, the opaque region shrinks as water diffuses into the depleted regions and the size of the SDS micelles decreases again. We propose that this reconfiguration in the healed region activates a crosslink exchange between the UPyHCBA

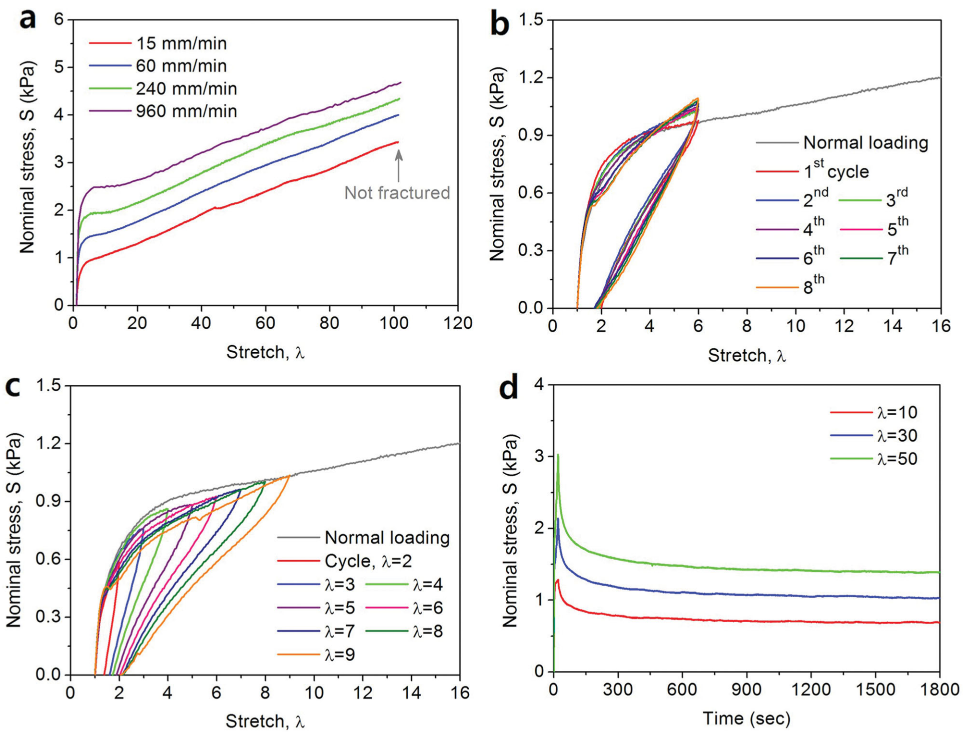

Figure 3. a) Representative nominal stress–stretch curves of gels copolymerized using 9.1 × 10^{-3} M UPyHCBA for several extension rates. b) Hysteresis loops under cyclic loading with a constant stretch, $\lambda = 6$. The recovery time between the first two cycles was 1 min; the time between subsequent cycles was 2 min. c) The hysteresis loops obtained for tests with increasing maximum stretch and 2 min of recovery time between individual cycles. d) Stress-relaxation curves for gels subjected to different stretch values.

units by exposing them to the aqueous environment: the UPyHCBA dimers disassemble when exposed to the aqueous environment and then reassemble when encapsulated in newly formed SDS micelles (Figure 4e). The role of water evaporation in the self-healing mechanism is further supported by a reduction in self-healing under conditions of high humidity (see Supporting Information).[35] When exposed surfaces were allowed to dry out for longer periods of time (>3 min), a white powder began to precipitate on the surfaces, suggesting a drying out of SDS (and NaCl) on the surfaces. In this state, reconfiguration was very difficult and the ability to self-heal decreased.

The presence of the UPy moiety in the hydrogels and its ability to form hydrogen bonds with many substrates makes this class of hydrogels tacky. Tackiness is, however, distinct from self-healing: when two samples are pressed together, they adhere immediately. If the samples are pulled apart right away, they detach along the original surface. If the samples are allowed to heal, on the other hand, new crosslinks form across the interface making it nearly indistinguishable from the rest of the gel and fracture happens elsewhere (Figure S13, Supporting Information). More direct evidence for this behavior was obtained by modifying the SDS concentration in the samples: extraction of SDS using a NaCl solution increased the tackiness of the gel by releasing the UPy units from the micelles (compare Movie S4 and S5, Supporting Information), but significantly decreased its ability to self-heal (samples always failed along the original interface). Without the association effect of the SDS micelles, the UPy units are either solvated or form permanent bonds, neither of which contributed to self-healing. A decrease in crosslink density caused by solvation was observed as a significant increase in swelling (43% by weight) after extraction of the SDS; the formation of a number of permanent bonds was suggested by the low solubility of the hydrogel after complete removal of the SDS.

The effect of the hierarchical system of interactions created by the UPy moiety and the SDS is quite remarkable. A stretch greater than 100 is much larger than that observed for hydrogels crosslinked by hydrophobic association. While the maximum nominal stresses supported by our gels are lower than those of hydrogels based on hydrophobic association,[18] the true stresses are significantly higher. Rapid self-healing has been reported in a hydrogel made from acryloyl-6-aminocaproic acid. The self-healing ability of this gel stems from the formation of intermolecular H-bonds across the damaged interface. While healing of the interface starts within seconds,[36] complete recovery of the fracture stress in this system requires a significantly longer time (≈24 h). UPyHCBA-based gels, by contrast, heal within ≈30 s. The healed region is as stretchable as the pristine material without the need for a lengthy healing time, which has not yet been reported in the literature.

With their fast self-healing ability, along with their remarkable mechanical properties, including extreme stretchabilty, endurance under high true stress, and good fatigue resistance, we believe that these hydrogels show potential for biomedical applications such as artificial soft tissues, wound care materials, or scaffolds for cell cultivation. The system of hierarchical dynamic crosslinks used in this study is fairly general and can be used

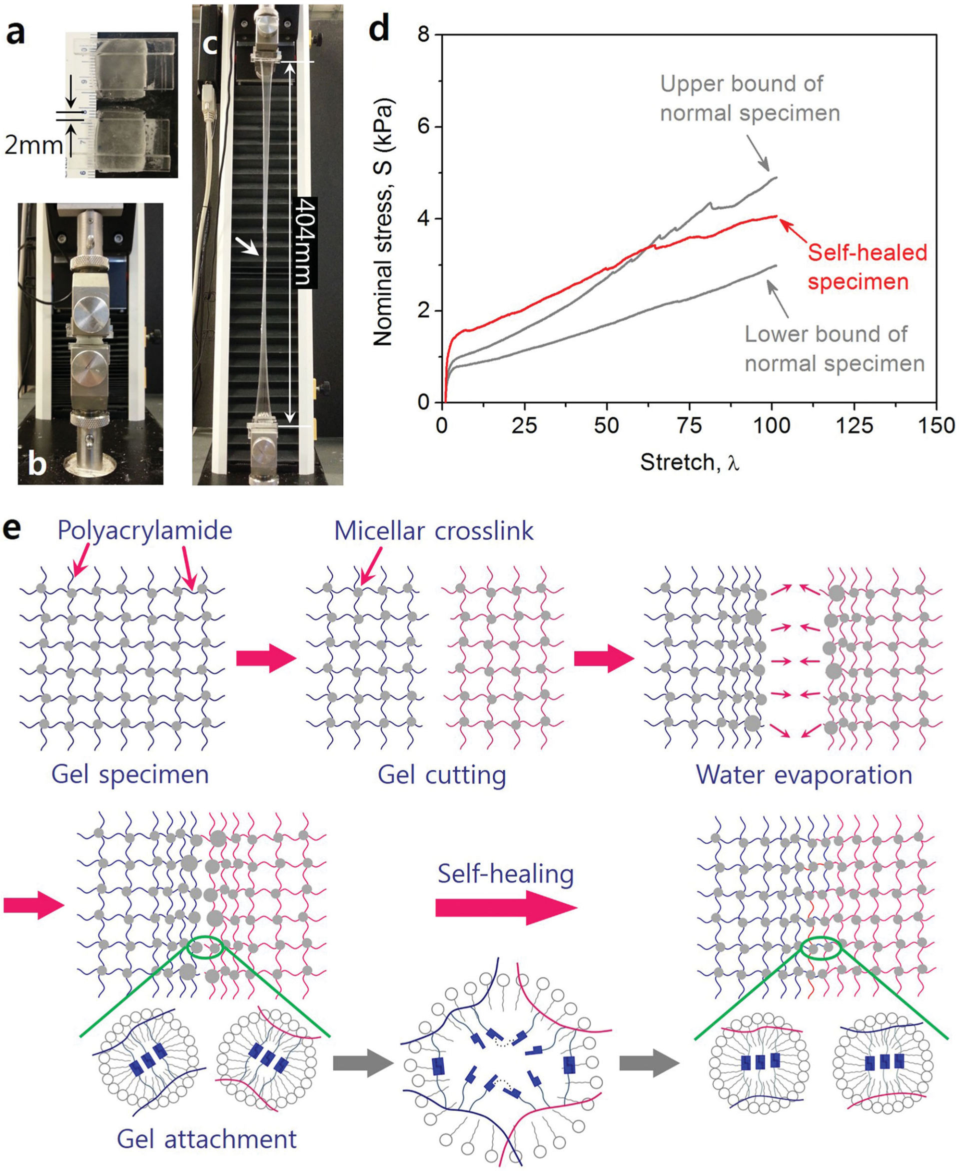

Figure 4. a) The tensile test specimen was cut at a distance of 2 mm from the polystyrene plates. b) Healed specimen installed in test jig. c) Typical stretch behavior of a healed specimen, similar to that of a pristine specimen (arrow points out the healed region), (d) representative nominal stress–stretch curve of a healed specimen together with the curves of two pristine specimens. e) Schematic representation of the self-healing mechanism.

to synthesize a broad range of hydrogels by changing monomer precursors or aqueous solutions to achieve specific functions.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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[34] Cut samples that were exposed to air for 3 min were brought into contact with each other inside a sealed chamber. The region adjacent to the cut surface became cloudy and then shrank to a relative homogeneous state. In these hydrogels, SDS is the only component that can induce cloudiness through dynamic light scattering, and thus we attribute the cloudiness to the temporary formation of larger SDS micelles. We propose that this process contributes to the self-healing behavior. See the Supporting Information section for a more detailed discussion.
[35] The hydrogels also self-heal under conditions of high relative humidity (92%), although the process is significantly slower (≈3 min) and the bond is not as strong—the stretch to failure is reduced by ≈50% for hydrogel samples synthesized with 9.1×10^{-3} M UPyHCBA.
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