



Polyacrylamide hydrogels. VI. Synthesis-property relation

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ABSTRACT

Synthesis-property relation is fundamental to materials science, but many aspects of the relation are not well understood for many materials. Impetus for this paper comes from our recent appreciation for the distinct roles of entanglements and crosslinks in a polymer network. Here we study the synthesis-property relation of polyacrylamide hydrogels prepared by free radical polymerization. Some of the as-prepared hydrogels are further submerged in water to swell either to equilibrium or to a certain polymer content. The synthesis parameters include the composition of a precursor, as well as the polymer content of a hydrogel. Series of hydrogels are prepared along several paths in the space of synthesis parameters. For each hydrogel, the stress-stretch curve is measured, giving four properties: modulus, strength, stretchability, and work of fracture. We interpret the experimentally measured synthesis-property relation in terms of entropic polymer networks of covalent bonds. When the precursor has a low crosslinker-to-monomer molar ratio, the resulting polymer network has on average long polymer segments. When the precursor has a low water-to-monomer molar ratio, the resulting polymer network has on average many entanglements per polymer segment. We show that crosslinks lower strength, but entanglements do not. By contrast, both crosslinks and entanglements increase modulus. A network of highly entangled long polymer segments exhibits high swell resistance, modulus, and strength.

1. Introduction

Materials map the space of synthesis parameters to the space of properties (Fig. 1). Both spaces have high dimensions, and the map is nonlinear. Studying the synthesis-property map is a fundamental challenge in materials science. The high dimensionality and nonlinearity make it impossible to study the map by experiments alone. It has been a long tradition to complement experimental studies with mechanistic pictures of microstructural processes. Rarely, however, are the mechanistic pictures detailed enough to make complete predictions. The study of the synthesis-property map of any given material is work in progress.

Here we study the synthesis-property map of polyacrylamide hydrogels prepared by free radical polymerization. A precursor consists of four ingredients: solvent (water), monomer (acrylamide, AAm), crosslinker (*N,N'*-methylenebisacrylamide, MBAA), and photoinitiator (2-hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone, Irgacure-2959) (Fig. 2). The synthesis parameters include the composition of a precursor, characterized by the water-to-monomer molar ratio W , the crosslinker-to-monomer molar ratio C , and the photoinitiator-to-monomer molar ratio I . To reduce the dimension of the space of synthesis parameters, we set $I/C = 0.4$ for all

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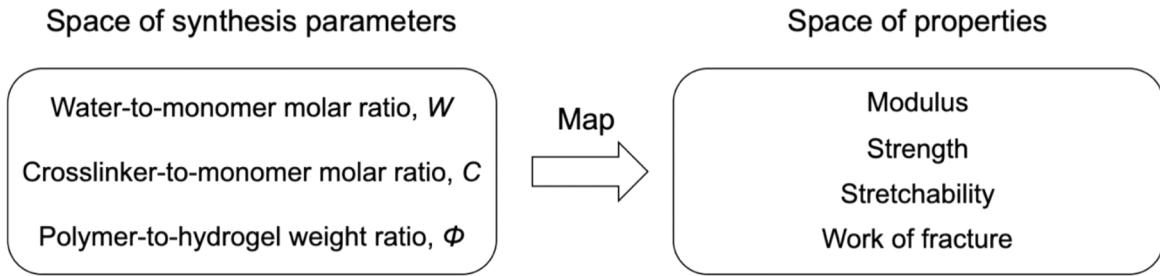


Fig. 1. Materials map the space of synthesis parameters to the space of properties. Listed are the synthesis parameters and the material properties studied in this paper.

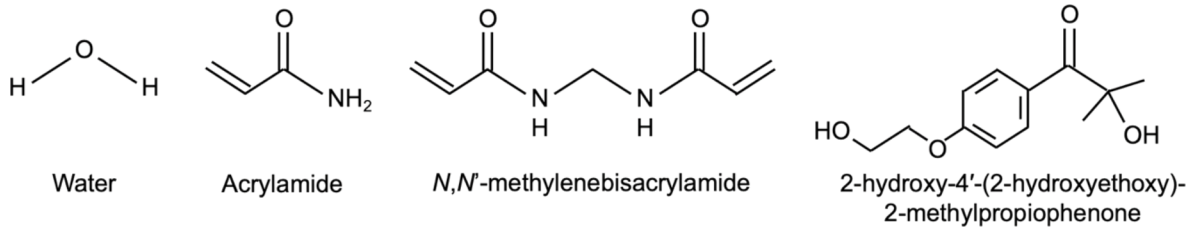


Fig. 2. A precursor consists of four species of molecules: solvent (water), monomer (AAM), crosslinker (MBAA), and photoinitiator (Irgacure-2959).

hydrogels. Some as-prepared hydrogels are submerged in water to swell either to equilibrium or to a certain polymer content. For these hydrogels, the synthesis parameters further include the polymer-to-hydrogel weight ratio ϕ . For each hydrogel, the stress-stretch curve is measured, giving four properties: modulus, strength, stretchability, and work of fracture.

We dissolve monomers, crosslinkers, and photoinitiators in water (Fig. 3a). Under an ultraviolet lamp, the photoinitiator activates the reactions, so that the monomers link into polymer chains, and polymer chains crosslink into a polymer network (Fig. 3b). The resulting aggregate of water and polymer network is called the as-prepared hydrogel. Submerged in water, the as-prepared hydrogel imbibes more water (Fig. 3c).

The parameters of synthesis affect properties of a material through its structure. The structure of a hydrogel is determined by the composition of the precursor, as well as the amount of swelling after polymerization. A hydrogel is prepared using a precursor of various values of crosslinker-to-monomer molar ratio C . The crosslinker MBAA has two functional groups, which are incorporated into two polymer chains, making a crosslink. Each crosslink is assumed to connect four polymer segments, and each polymer segment is assumed to end at two crosslinks. Consequently, each polymer segment on average has $(2C)^{-1}$ monomer units. Polymer segments are long on average for a hydrogel prepared using a precursor of a low C .

A hydrogel is commonly prepared using a precursor of a large water-to-monomer molar ratio W , so that monomers are sparse in precursor (Fig. 3a). The sparse monomers form a sparsely entangled polymer network (Fig. 3b). Submerged in water, the as-prepared hydrogel can imbibe a large quantity of water (Fig. 3c). By contrast, in a hydrogel prepared using a precursor of a small water-to-monomer molar ratio W , the monomers are crowded (Fig. 3d). The crowded monomers form a highly entangled polymer network (Fig. 3e). Submerged in water, the as-prepared hydrogel imbibes a modest quantity of water (Fig. 3f).

When the hydrogel swells, the crosslinks preserve not only the number of monomers per polymer segment, but also the number of entanglements per polymer segment. That is, swelling reduces polymer content of a hydrogel, but preserves the topology of the polymer network. In an as-prepared hydrogel, the polymer content ϕ is determined by the water-to-monomer molar ratio W of the precursor:

$$\phi = M_{\text{AAM}} / (M_{\text{AAM}} + WM_{\text{Water}}), \quad (1)$$

where $M_{\text{AAM}} = 71.08$ g/mol is the molar mass of AAM and $M_{\text{Water}} = 18$ g/mol is the molar mass of water. Submerged in water, the as-prepared hydrogel imbibes more water. In some instances, we take hydrogels out of water after they gain a certain weight, before they swell to equilibrium. These hydrogels are homogenized in a plastic bag at room temperature overnight. Such a sample has a polymer content ϕ not set by W and C of the precursor. In other instances, the hydrogels are left in water to swell to equilibrium. Such a sample has a polymer content ϕ set by W and C of the precursor.

The emphasis in this paper is placed on how the synthesis parameters affect properties determined by the stress-stretch curves, including modulus, strength, stretchability, and work of fracture. We interpret the experimentally measured synthesis-property relation of polyacrylamide hydrogels in terms of entropic polymer networks of covalent bonds. The synthesis parameters, W , C , and ϕ , form a three-dimensional space (Fig. 4). Here we explore this space by preparing hydrogels along four paths. We describe experimental methods of synthesizing the hydrogels and measuring their properties (Section 2). Series i starts with precursors of commonly used compositions: a high value of $W = 22.38$ and various values of C from 3×10^{-4} to 3×10^{-3} (Section 3). The as-

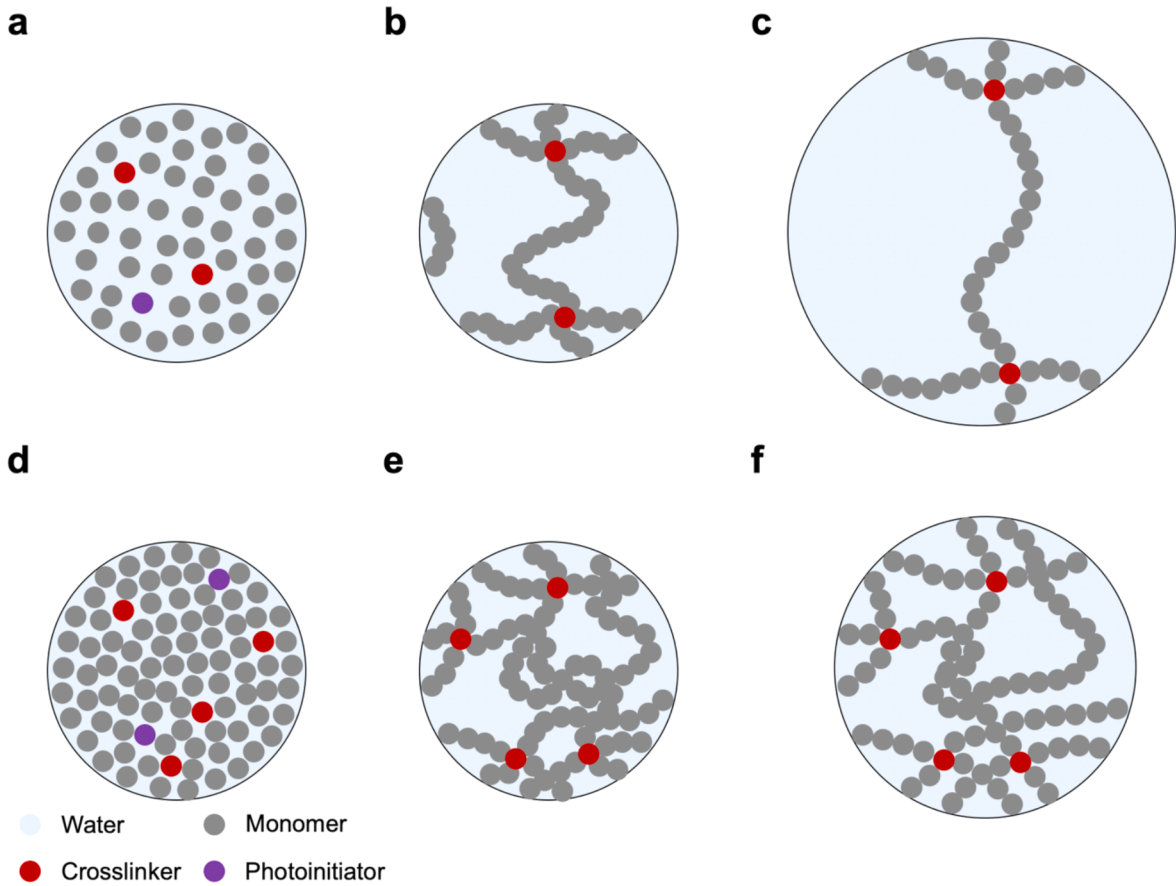


Fig. 3. Synthesis of a hydrogel by free radical polymerization. (a) A precursor of a large water-to-monomer molar ratio. (b) The monomers form a sparsely entangled polymer network. (c) Submerged in water, the sparsely entangled hydrogel imbibes a large quantity of water. (d) A precursor of a small water-to-monomer molar ratio. (e) The monomers form a highly entangled polymer network. (f) Submerged in water, the highly entangled hydrogel imbibes a modest quantity of water.

prepared hydrogels in series i have a polymer content of $\phi = 15$ wt%, and are used to measure stress-stretch curves without further swelling. Series ii starts with precursors of rarely used compositions: an exceptionally low value of $W = 2$ and various values of C from 6×10^{-6} to 1.2×10^{-3} (Section 4). The value of $C = 6 \times 10^{-6}$ is also exceptionally low. The low values of W and C lead to a polymer network of unusually dense entanglements and long polymer segments. The as-prepared hydrogels of series ii are submerged in water to swell to equilibrium. Because of the dense entanglements, such fully swollen hydrogels of various C have a similar polymer content of $\phi = 15$ wt%. To illustrate the effect of entanglements further, series iii are prepared using precursors of $C = 6 \times 10^{-4}$ and various values of W from 2 to 22.38 (Section 5). The as-prepared hydrogels of series iii are submerged in water to swell to equilibrium. Value of W affects the density of entanglement, so that polymer contents ϕ ranges from 4 wt% to 15 wt%. To study the effect of polymer content, series iv starts with precursors of $C = 6 \times 10^{-4}$ and various values of W from 2 to 22.38 (Section 6). The as-prepared hydrogels of series iv are submerged in water to a similar polymer content of $\phi = 15$ wt%.

The impetus of the current paper comes from our recent appreciation for the distinct roles played by entanglements and crosslinks. This paper belongs to a series in which we use polyacrylamide hydrogels as a model system to study the mechanics of highly elastic polymer networks (Hassan et al., 2022; Kim et al., 2022; Liu et al., 2019; Wang et al., 2021a; Yang et al., 2019). Polyacrylamide hydrogels are commonly synthesized in academic and industrial labs, and have found extensive applications in biology, agriculture, and medicine (Caulfield et al., 2002). Whereas the effect of C and ϕ on properties have long been appreciated, the effect of W on properties has only begun to receive attention recently (Kim et al., 2021). A precursor of a lower W leads to a hydrogel of more entanglements per polymer segment. For a hydrogel swollen to equilibrium, modulus is set by entanglements, but the toughness and fatigue threshold are set by crosslinks. A hydrogel prepared by a precursor of low W and low C has dense entanglements and sparse crosslinks, simultaneously achieving high modulus, toughness, and fatigue threshold. This design principle resolves the conflict

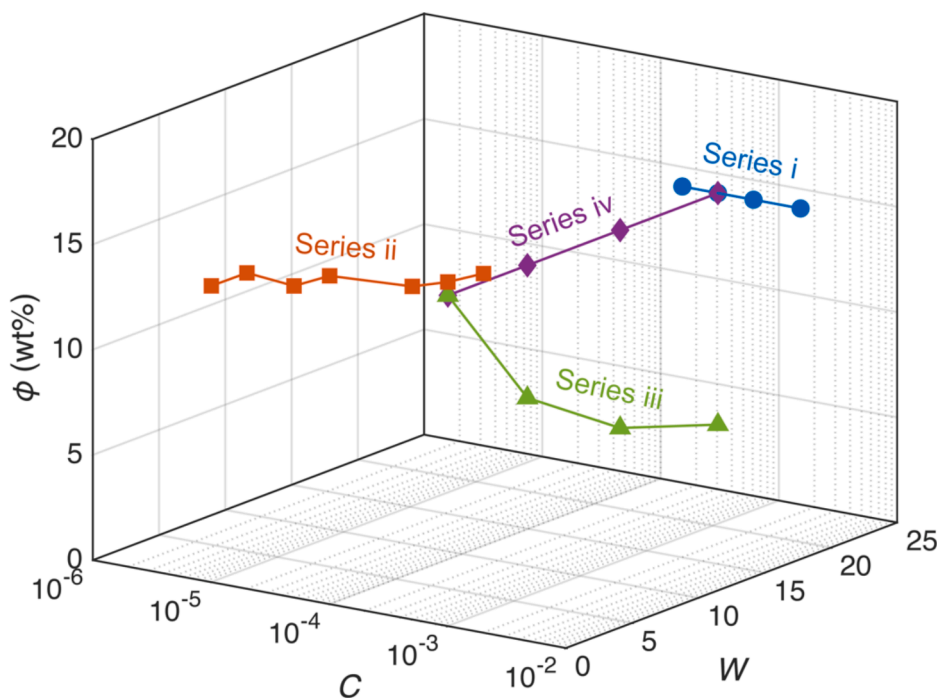


Fig. 4. Space of three synthesis parameters. A composition of a precursor is characterized by the water-to-monomer molar ratio W and the crosslinker-to-monomer molar ratio C . The polymer content of the hydrogel is ϕ . Four series of samples are synthesized.

between modulus and fatigue threshold of polymer networks. It was also noted that a hydrogel of dense entanglements and sparse crosslinks has a high strength (Kim et al., 2021). This effect was not studied in the previous paper and provided an initial focus of the current paper.

A stress-stretch curve measured with a sample without precrack determines modulus, strength, stretchability, and work of fracture. Even a sample without any precrack inevitably contains crack-like flaws. Small flaws do not influence stress-stretch curve, but large flaws do. A material-specific length exists, called the fractocohesive length, below which flaws do not reduce strength (Chen et al., 2017; Wang et al., 2020). A representative value of the fractocohesive length of a polyacrylamide hydrogel is 1 mm (Yang et al., 2019). Given that polyacrylamide hydrogels typically contain flaws smaller than, say, 0.1 mm, stress-stretch curves of polyacrylamide hydrogels are flaw-insensitive. In recent decades, toughness of polymer networks has been extensively studied (Gong et al., 2003; Kim et al., 2021; Long and Hui, 2016; Sun et al., 2012; Wang et al., 2021b), but strength of polymer networks has not. Since the 1950s, strength of elastomers has been studied, including the effects of orientations of chains (Taylor and Darin, 1955), unequal chain lengths (Bueche, 1957), dangling chains (Bueche, 1956), and degree of crosslinks (Bueche and Dudek, 1963; Flory et al., 1949). Strength of elastomers has been extensively measured as a function of temperature and strain rate, showing that viscoelasticity affects strength (Smith, 1978). By contrast, strength of hydrogels have been less studied. A polyacrylamide hydrogel containing high water content exhibits near-perfect elasticity—that is, the stress-stretch curve has negligible hysteresis (Yang et al., 2019), and is insensitive to strain rate (Hassan et al., 2022). This paper studies how synthesis parameters, W , C , and ϕ , affect the strength, as well as modulus, stretchability, and work of fracture, of polyacrylamide hydrogels.

2. Experimental section

2.1. Preparation of hydrogels

All chemicals were used as purchased, including deionized water (Poland Spring), acrylamide (AAM; Sigma-Aldrich, A8887), N,N' -methylenebisacrylamide (MBAA; Sigma-Aldrich, M7279), 2-hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone (Irgacure-2959; Sigma-Aldrich, 410896), and ethanol (Sigma-Aldrich, E7023).

The precursor of the polyacrylamide hydrogel was an aqueous solution of AAM ($W = 2, 8, 15, \text{ or } 22.38$) as the monomer, and MBAA ($C = 6 \times 10^{-6}, 1.2 \times 10^{-5}, 3 \times 10^{-5}, 6 \times 10^{-5}, 3 \times 10^{-4}, 6 \times 10^{-4}, 1.2 \times 10^{-3}, \text{ or } 3 \times 10^{-3}$) as the crosslinker. For hydrogels of low water-to-monomer molar ratios, the aqueous solution of concentrated monomers was heated in a microwave oven for ~ 15 s to fully dissolve the monomers, and then was mixed with the crosslinker. The photoinitiator Irgacure-2959 does not dissolve in water. Instead, Irgacure-2959 was dissolved in ethanol (0.1 M). Each precursor was then prepared by mixing a water-AAM-MBAA solution and the ethanol-Irgacure-2959 solution to ensure a fixed ratio of $I/C = 0.4$. In the resulting precursor, the amount of ethanol is small compared to that of water, and we do not study how the concentration of ethanol affects the mechanical behavior of the hydrogels.

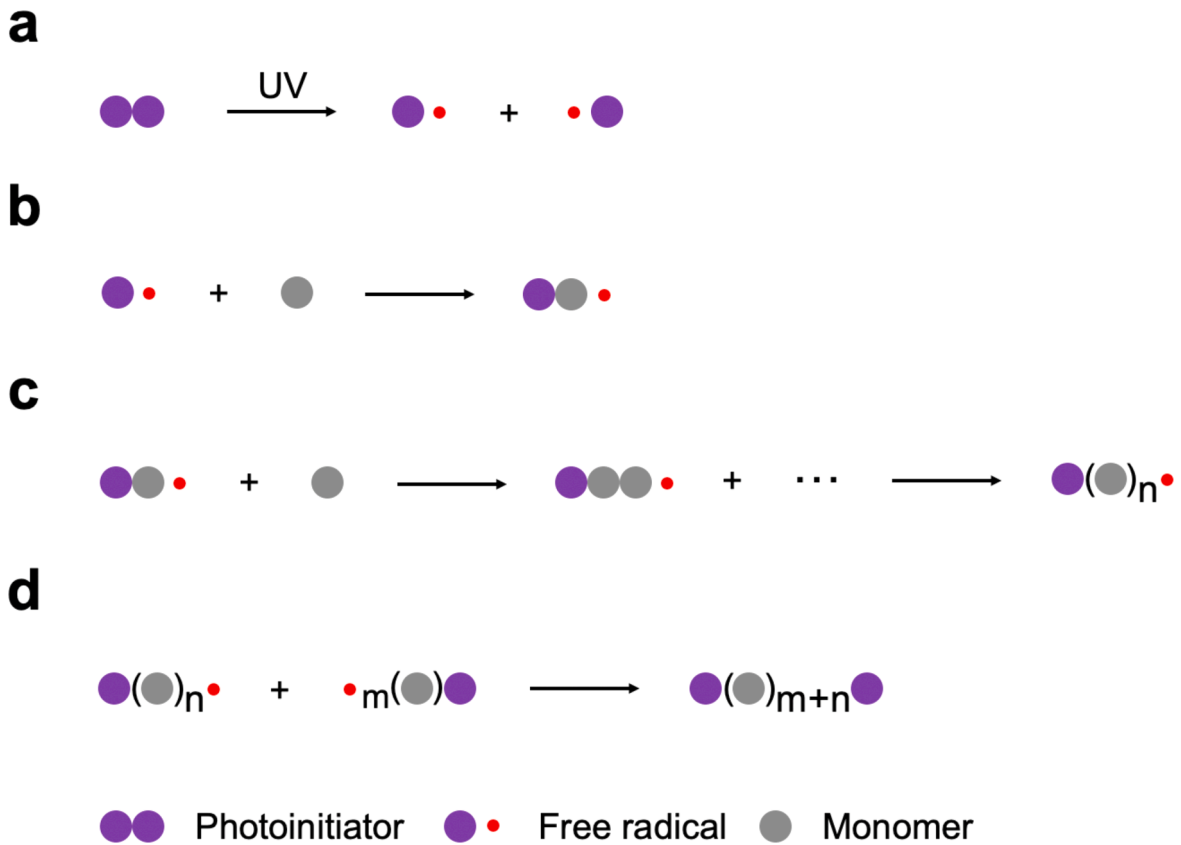


Fig. 5. Steps of free radical polymerization. (a) Formation of free radicals. (b) Radical reaction with a monomer. (c) Propagation. (d) Termination.

The precursor was poured into a 1.5 mm-thick acrylic mold glued on a glass substrate. Another glass sheet was used to seal the mold. The precursor was gelled under a UV lamp (wavelength 365 nm and intensity 1.5 mW/cm²; 10 ea, Sankyo Denki, F8T5BL) for 3 hours.

2.2. Choice of the photoinitiator-to-crosslinker molar ratio

The photoinitiators participate in polymerization as follows (Flory, 1953; Liu et al., 2014). Under an ultraviolet lamp, a photoinitiator decomposes into two free radicals (Fig. 5a). Upon meeting with a monomer, a free radical reacts with the monomer, opens the double bond on the monomer, and transfers the free radical to the monomer (Fig. 5b). The new free radical meets another monomer and repeats the process. This process, called propagation, turns monomers into a growing polymer chain (Fig. 5c). The process of propagation can also incorporate crosslinkers into a growing polymer chain. Each crosslinker is bifunctional, and can be incorporated into two growing polymer chains. When the free radicals of two growing polymer chains meet each other, the two free radicals react to form a single polymer chain, and the growth of the polymer chain terminates (Fig. 5d). When I is too low, a few long polymer chains form, but the rate of polymerization is low. When I is too high, many short polymer chains form. For all hydrogels studied in this paper, we fix the photoinitiator-to-crosslinker molar ratio to $I/C = 0.4$. Under such conditions, each polymer chain likely contains multiple crosslinkers. For hydrogels prepared using precursors of other values of I/C , see (Kim et al., 2021).

2.3. Mechanical test

After curing, some as-prepared hydrogels were subject to tensile test directly, other as-prepared hydrogels were submerged in deionized water for 22 hours to swell to equilibrium before tensile test, and still others were submerged in deionized water to imbibe various amounts of water before being subject to tensile test. The polymer content of each hydrogel after swelling was determined by measuring the mass of the as-prepared and the swollen hydrogels.

Samples of the hydrogels were cut into dumbbell shapes using a metallic cutter. The stress-stretch curve of each sample was measured using a tensile machine (Instron 5966; 100 N load cell). The crosshead velocity was 20 cm/min. For the polyacrylamide hydrogels studied here, the stress-stretch curves are insensitive to stretch rate (Kim et al., 2021). The force and time were recorded by the tensile machine. To obtain the displacement, two points separated by a length of 2 cm in the straight region of the dumbbell sample were marked by a pen and a camera was used to track the displacement of the marks as a function of time by a video. To ensure the

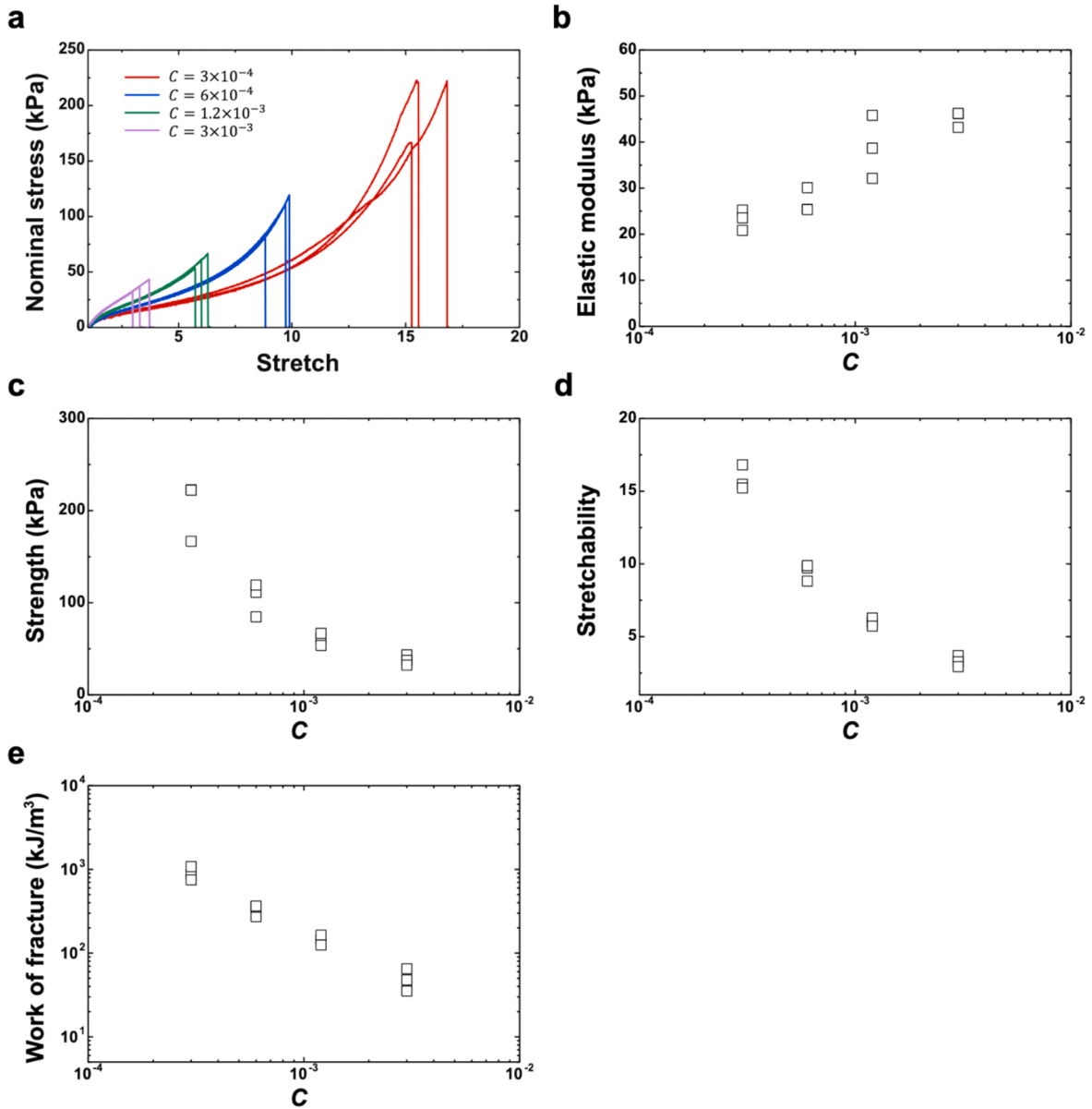


Fig. 6. Effect of crosslink density for hydrogels prepared with a fixed water-to-monomer molar ratio $W = 22.38$ and various crosslinker-to-monomer molar ratios C . The hydrogels are tested as prepared. (a) Stress-stretch curves up to rupture. (b) Elastic modulus. (c) Strength. (d) Stretchability. (e) Work of fracture.

accuracy, for each composition, displacement-time relations of three samples on average were used to determine the force-displacement curve. Nominal stress was defined as the force divided by the cross-sectional area of the undeformed sample. Stretch was defined as the length of the deformed sample divided by the length of the undeformed sample.

3. Effect of crosslinks on as-prepared hydrogel

For hydrogels of series i, we prepare samples using precursors of $W = 22.38$ and various values of C . We cut the samples into dumbbell shapes from the as-prepared hydrogels, uniaxially pull the samples to rupture, and measure the stress-stretch curves (Fig. 6a). As shown in the previous studies, the stress-stretch curves of the hydrogels are insensitive to stretch rate (Hassan et al., 2022). In this work, we fix the stretch rate at 0.17 s^{-1} . Here we report nominal stress, which is the force divided by the cross-sectional area of undeformed hydrogel. In the literature, true stress is also commonly used, which is the force divided by the cross-sectional area of deformed hydrogel. Hydrogels and elastomers are nearly incompressible. Under uniaxial tension, the true stress equals the nominal stress times the stretch.

For each sample, the slope of its stress-stretch curve at small stretch defines elastic modulus, the maximum stress defines strength, the maximum stretch defines stretchability, and the area under the stress-stretch curve defines the work of fracture. As C increases, elastic modulus increases (Fig. 6b), strength decreases (Fig. 6c), stretchability decreases (Fig. 6d), and work of fracture decreases (Fig. 6e). We next discuss our data in terms of a molecular picture.

According to the theory of entropic elasticity, the shear modulus is $\mu = \Phi^{1/3}NkT$ (Treloar, 1975). Here Φ is the volume fraction of polymer, N is the number of polymer segments divided by the volume of dry polymer, and kT is the temperature in the unit of energy. The mass per AAm monomer unit is 1.18×10^{-25} kg, the density per AAm monomer unit is 1.13×10^3 kg/m³, so that the volume per AAm monomer unit is $V = 1.04 \times 10^{-28}$ m³. For the hydrogels tested in the experiment, $\Phi = 0.14$. As noted above, each polymer segment is assumed to have $(2C)^{-1}$ monomer units on average. As an example, when $C = 1.2 \times 10^{-3}$, $N = 2C/V = 2.31 \times 10^{25}$ m⁻³. Taking $k = 1.38 \times 10^{-23}$ J/K and $T = 300$ K, we estimate the elastic modulus $E = 3\mu = 3\Phi^{1/3}NkT = 1.49 \times 10^5$ Pa. This estimated value is higher than the measured value, 3.89×10^4 Pa (Fig. 6b). Such discrepancy has been reported before (e.g., (Yang et al., 2019)). The estimation assumes that all polymer chains in the network carry stress, but not all polymer chains in a real network carry stress. Consequently, the estimated modulus is higher than the measured modulus.

In a polyacrylamide hydrogel, monomer units are linked by covalent bonds to form polymer chains, and polymer chains are crosslinked by covalent bonds to form a polymer network. When the polymer network is stretched to rupture, some covalent bonds must break. By a perfect polymer network we mean that all monomer units are bound into the network, all polymer chains have the same lengths, and all polymer chains are oriented to the same direction near rupture. When such a perfect network is stretched, all polymer chains carry the same stress and rupture simultaneously. Consequently, the strength of the perfect network is comparable to the strength of covalent bonds. The energy per covalent bond is on the order of $eV = 1.6 \times 10^{-19}$ J. The elongation of a covalent bond at rupture is on the order of 10^{-10} m. Consequently, the force to break a covalent bond is on the order of $f = 10^{-9}$ N. This order of magnitude is consistent with both atomic simulation (Beyer, 2000) and experimental measurement using atomic force microscope (Grandbois et al., 1999). The cross-sectional area per monomer unit is on the order of b^2 , where $b \sim 10^{-9}$ m is the length of a monomer unit. Thus, the strength of a perfect polymer network is on the order of $f/b^2 \sim 10^9$ Pa.

A real polymer network, however, is imperfect: not all monomer units are bound into the network, polymer chains have different lengths, and polymer chains are oriented to different directions. When a real network is stretched, some polymer chains carry higher stress than others. Just before the network ruptures into two halves, only a small fraction of the polymer chains across the fracture plane carry the high stress near the covalent bond strength. The majority of the polymer chains carry stresses much below the covalent bond strength. Assume that nearly all monomer units carry the force according to entropic elasticity. The entropic force per monomer unit scales as kT/b , so that the entropic stress scales as kT/b^3 . Considering the polymer volume fraction, Φ , gives the entropic stress in a real network by $\Phi^{1/3}kT/b^3$. Taking $kT \sim 10^{-21}$ J, $b \sim 10^{-9}$ m, and $\Phi \sim 10^{-1}$, we estimate that the strength of a real network is on the order of 10^5 Pa, which is comparable to the measured strength (Fig. 6c). The commonly reported strength of polymer networks are in the range of $10^4 - 10^7$ Pa (Gong et al., 2003; Hua et al., 2021; Sakai et al., 2010, 2008; Yang et al., 2019). To strengthen a polymer network, one must deconcentrate stress, so that more monomer units across the putative fracture plane carry high stress near rupture.

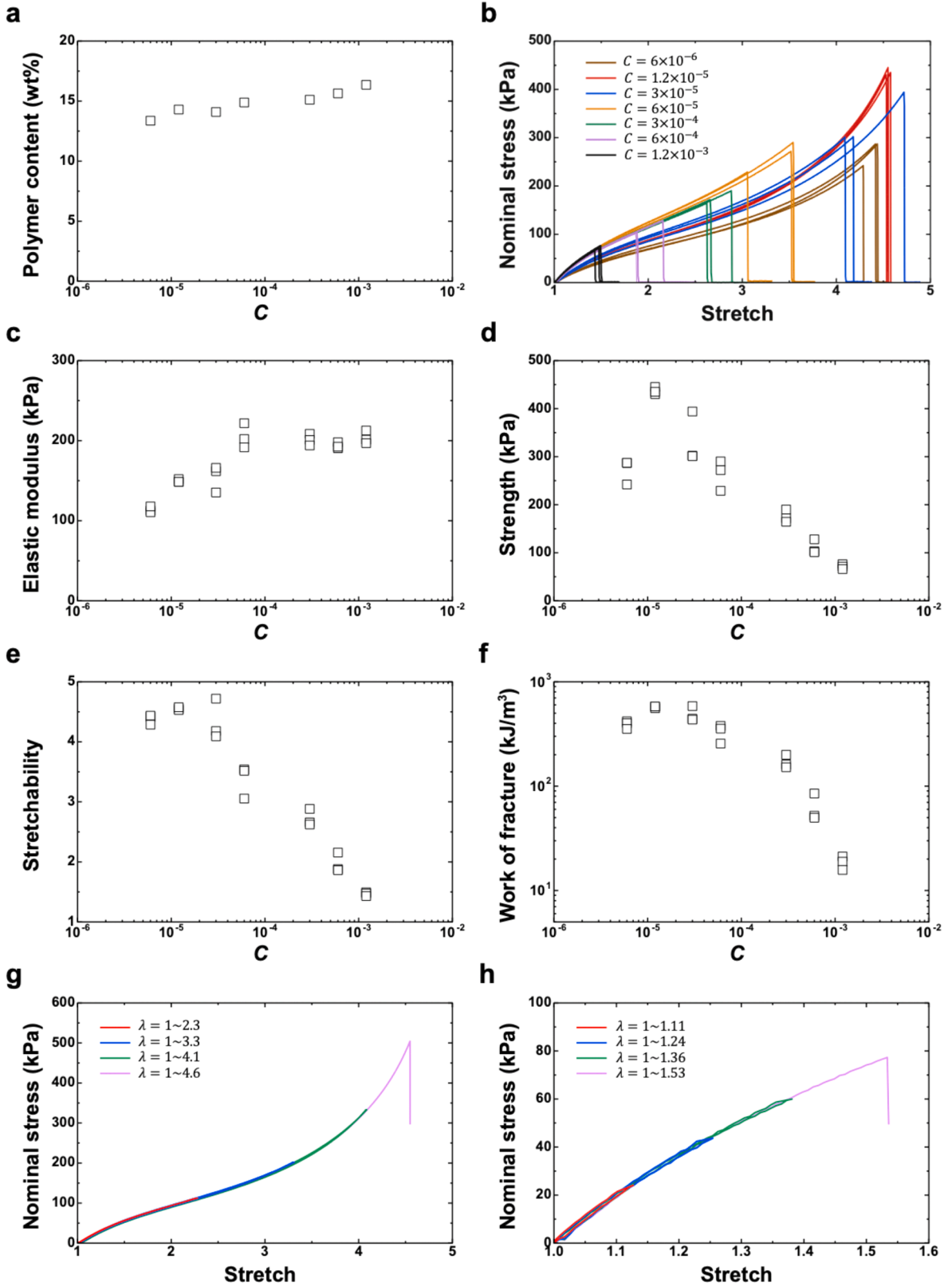
The measured strength is much lower than the strength of covalent bonds. This large difference indicates that most polymer chains are entropic when a few polymer chains break covalent bonds. Our data affirm that the strength of a real network is on the same order of magnitude as that predicted under the assumption that near breaking point most chains are still entropic.

It has long been reported that the strength of a polymer network is not a monotonic function of the crosslink density. When the crosslink density is low, the strength increases as the crosslink density increases. This behavior is caused by the incomplete formation of the network when the crosslinks are too sparse. For a given W , a critical C exists, below which the hydrogel does not form an elastic network and is squishy. Unless otherwise noted, hydrogels in this work are prepared using C above the critical value. For $W = 22.38$, the critical value is $C \sim 10^{-4}$.

When the crosslink density is above the critical value, an elastic network is formed, and the strength of the polymer network decreases as the crosslink density increases. All our reported data are in this regime (Fig. 6c). The molecular origins of this behavior have been speculated by many previous authors. When crosslinks are dense, the polymer segments are short, so that the orientations of stretched chains are restricted by the low mobility of the chains (Flory et al., 1949) and the short segments are under critically high stress due to prestretch (Kothari et al., 2018; Wagner et al., 2022). Also, as the crosslink density increases, the fraction of polymer chain loops increases, which do not bear load (Tonelli, 1974). We understand this trend as follows. As noted before, a low value of C gives a polymer network of longer polymer segments. Also note that water has a low viscosity, so that the friction between polymer segments is low. Consequently, just before a polymer segment ruptures, all monomer units on the segment carry a stress near the covalent bond strength. A long polymer segment deconcentrates stress.

We move on to the observed stretchability. Each polymer segment has $(2C)^{-1}$ monomer units and length of each monomer unit is b . Before a polymer segment is stretched, according to the random-walk model, the end-to-end distance of the polymer segment is $b(2C)^{-1/2}$ (Rubinstein and Colby, 2003). When the polymer segment is fully stretched, the end-to-end distance of the polymer segment is $b(2C)^{-1}$. As a result, the stretchability of a perfect network is $(2C)^{-1/2}$. When $C = 1.2 \times 10^{-3}$, the stretchability of a perfect network is 20.41, which is about three times of the measured stretchability (Fig. 6d). As mentioned above, when a real network is stretched near rupture, only a small fraction of polymer chains are fully stretched. It is unsurprising that the real network has a much reduced stretchability than a perfect network.

For a perfect polymer network, the work of fracture is the density of covalent energy w , which is the covalent energy $eV \sim 10^{-19}$ J divided by the volume per monomer $V \sim 10^{-28}$ m³. Consequently, the work of fracture of a perfect network is $w \sim 10^9$ J/m³, which is three to four orders of magnitude higher than the measured work of fracture (Fig. 6e). This difference is consistent with the much reduced strength and stretchability.



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Fig. 7. Effect of crosslink density for hydrogels prepared with a fixed $W = 2$ and various C . The as-prepared hydrogels are submerged in water to swell to equilibrium. (a) The polymer content in fully swollen hydrogels. The fully swollen hydrogels are subject to the uniaxial tensile test. (b) Stress-stretch curve up to rupture. (c) Elastic modulus. (d) Strength. (e) Stretchability. (f) Work of fracture. Under various amplitudes of stretch, loading-unloading curves of hydrogels prepared with (g) $C = 1.2 \times 10^{-5}$ and with (h) $C = 1.2 \times 10^{-3}$.

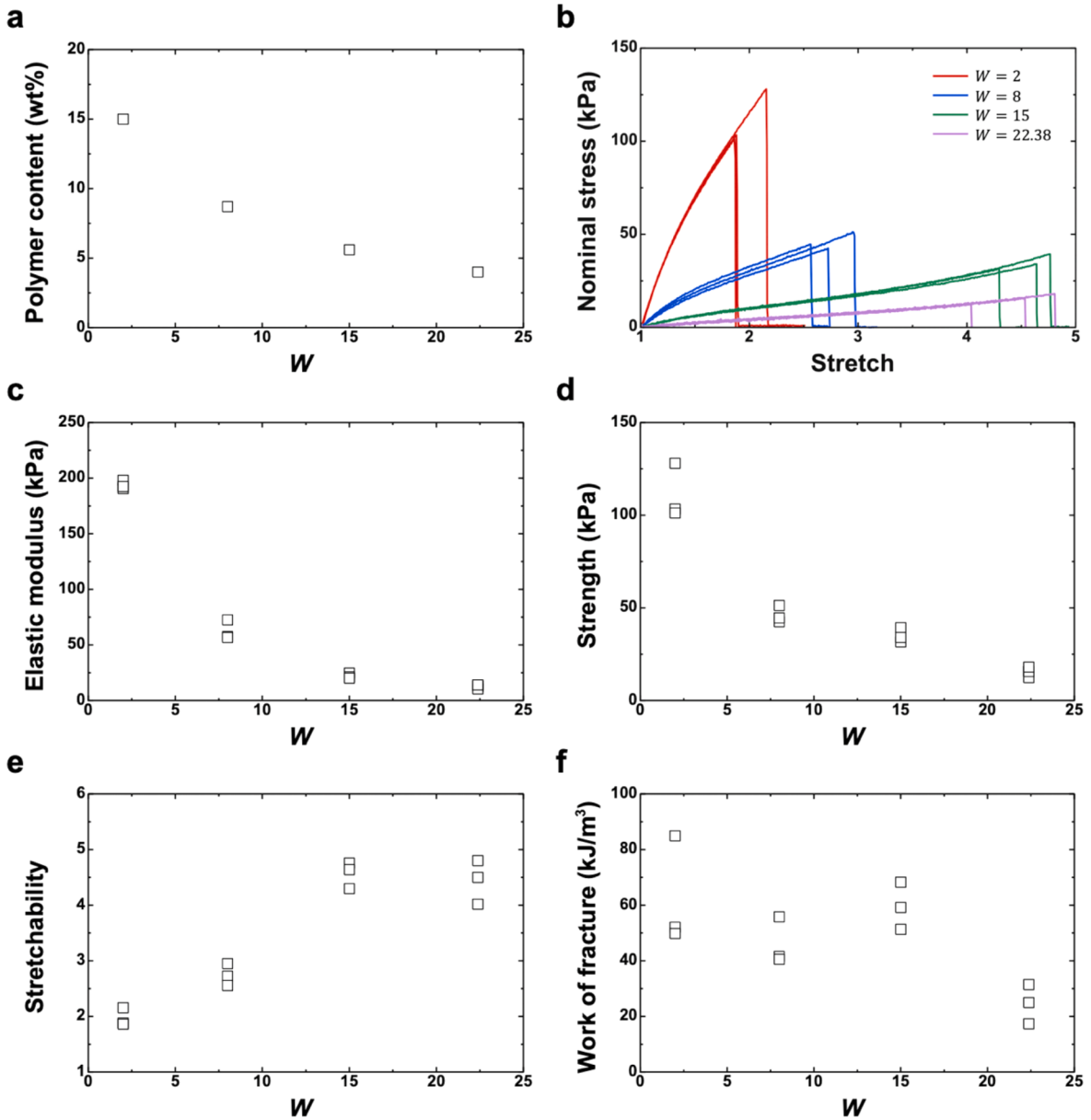


Fig. 8. Effect of water content for hydrogels prepared with fixed $C = 6 \times 10^{-4}$ and various W . The as-prepared hydrogels are submerged in water to swell to equilibrium. The fully swollen hydrogels are characterized by various properties. (a) Polymer content. (b) Stress-stretch curve up to rupture. (c) Elastic modulus. (d) Strength. (e) Stretchability. (f) Work of fracture.

4. Effect of crosslinks on fully swollen hydrogel of dense entanglements

For hydrogels of series ii, we prepare samples using precursors of $W = 2$ and various values of C . As W of the precursors is small, the crowded monomers in the precursor result in polymer networks of dense entanglements (Kim et al., 2021). The as-prepared hydrogels are submerged in water to swell to equilibrium. During swelling, the crosslinks keep the topology of the network invariant, so that the entanglements in the network persist after swelling.

For such fully swollen hydrogels, we first determine the polymer content by measuring the mass of as-prepared and fully swollen hydrogels. In the testing range of C , a plateau of polymer content of ~ 15 wt% is observed (Fig. 7a). These results show that the dense entanglements maintain the polymer content of the fully swollen hydrogels.

Next, we cut the samples into dumbbell shapes from the fully swollen hydrogels, uniaxially pull the samples to rupture, and measure the stress-stretch curves (Fig. 7b). As C increases, the elastic modulus increases and then plateaus (Fig. 7c), the strength increases to a maximum and then decreases (Fig. 7d), the stretchability increases to a maximum and then decreases (Fig. 7e), and the work of fracture increases to a maximum and then decreases (Fig. 7f). We interpret our data as follows.

To ensure the hydrogels are well formed, C needs to be larger than a critical value. For $W = 2$, when $C < 10^{-5}$, the elastic modulus is small, indicating that the formation of the hydrogel is incomplete; when $C > 10^{-5}$, a plateau of elastic modulus is observed (Fig. 7c), indicating that the density of entanglements is much higher than the density of crosslinks in the range of C tested. The density of entanglements, estimated by the plateau of modulus, has recently been reported to be $\sim 10^2$ entanglements per polymer segment (Kim et al., 2021). As a result, the dense entanglements maintain the modulus of the fully swollen hydrogels.

The measured strength is again a non-monotonic function of crosslink density (Fig. 7d). This trend has long been reported in elastomers (Flory et al., 1949; Taylor and Darin, 1955). For the hydrogels tested in our experiment, when $C < 10^{-5}$, the strength is small due to the incomplete network formation of the hydrogel; when $C > 10^{-5}$, the strength decreases as C increases (Fig. 7d).

Observe again that the strength of well-formed hydrogels decreases as the crosslink density increases. We have noted above that a polymer network of low C has long polymer segments, and long polymer segments deconcentrate stress, giving the polymer network a high strength. In a polyacrylamide hydrogel, abundant water molecules lubricate the polymer segments, so that the highly entangled hydrogel has near-perfect elasticity (Kim et al., 2021). Furthermore, the measured toughness of a hydrogel increases with average length of polymer segments (Kim et al., 2021). These observations indicate that the entanglements slip readily, so that high tension is transmitted along the entire length of each polymer segment. Consequently, dense crosslinks lower strength, but dense entanglements do not. By contrast, both dense crosslinks and dense entanglements increase modulus.

The measured stretchability and work of fracture are also non-monotonic functions of crosslink density (Fig. 7e and f). Similar to the measured strength, when $C < 10^{-5}$, the stretchability and work of fracture are small due to the incomplete network formation of the hydrogel; when $C > 10^{-5}$, the stretchability and work of fracture decrease as C increases.

It is noted that the measured strength, stretchability, and work of fracture of the fully swollen hydrogels are much smaller than the theoretical values. It corroborates that when a real polymer network is stretched near rupture, most polymer chains are entropic and only a small fraction of polymer chains are fully stretched.

We also cyclically stretch the hydrogels of $C = 1.2 \times 10^{-5}$ and $C = 1.2 \times 10^{-3}$ to various amplitudes and measure the loading-unloading curves (Fig. 7g and 7h). The fully swollen hydrogels exhibit near-perfect elasticity and have negligible hysteresis.

5. Effect of water content in precursor on fully swollen hydrogel

For hydrogels of series iii, we prepare samples using precursors of $C = 6 \times 10^{-4}$ and various values of W . The as-prepared samples are submerged in water to swell to equilibrium.

The polymer content of the fully swollen hydrogels increases as W decreases (Fig. 8a). The observation is understood as follows. In a precursor of a small water-to-monomer molar ratio W , the monomers are crowded, resulting in an as-prepared hydrogel of a highly entangled polymer network. By contrast, in a precursor of a large water-to-monomer molar ratio W , the monomers are sparse, resulting in an as-prepared hydrogel of a sparsely entangled polymer network. In either case, when the as-prepared hydrogel is submerged in water to swell to equilibrium, the crosslinks prevent polymer chains from disentangling, so that swelling keeps the number of entanglement per polymer segment invariant. Consequently, a precursor of larger value of W results in fewer entanglements in the as-prepared hydrogel, and a lower polymer content in the swollen hydrogel. So far as swelling is concerned, entanglements function as crosslinks. More entanglements restrain the network more, leading to less swelling.

We then cut the samples into dumbbell shapes from the fully swollen hydrogels, uniaxially pull the samples to rupture, and measure the stress-stretch curves (Fig. 8b). As W increases, the elastic modulus decreases (Fig. 8c), the strength decreases (Fig. 8d), and the stretchability increases (Fig. 8e). The work of fracture is not a monotonic function of W (Fig. 8f). So far as modulus is concerned, entanglements also function as crosslinks. More entanglements restrain the network more, stiffening the network.

The effect of W on strength is less straightforward. So far as strength is concerned, entanglements do not exactly function as crosslinks. The as-prepared hydrogels (series i) have shown that, for a fixed polymer content, strength decreases as the crosslink density increases (Fig. 6c). For fully swollen hydrogels (series ii), the polymer content is nearly constant, independent of crosslink density (Fig. 7a), but the strength decreases as the crosslink density increases (Fig. 7d). For fully swollen samples (series iii), the polymer content and strength both decrease as W increases (Fig. 8a and 8d). However, a precursor of larger value of W results in a hydrogel of fewer entanglements. In this case, fewer entanglements does not lead to higher strength. As W increases, the polymer content decreases, so that the strength decreases. As W increases, the number of entanglements per polymer segment decreases, so that the stretchability increases. With the increasing of W , the strength decreases and the stretchability increases. Consequently, the effect of W on the work of fracture is not distinct.

For hydrogels prepared with precursors of sparse monomers, there is a conflict between modulus and strength (Fig. 6b and 6c). By contrast, for hydrogels prepared using precursors of concentrated monomers, modulus and strength can be both increased (Fig. 8c and 8d).

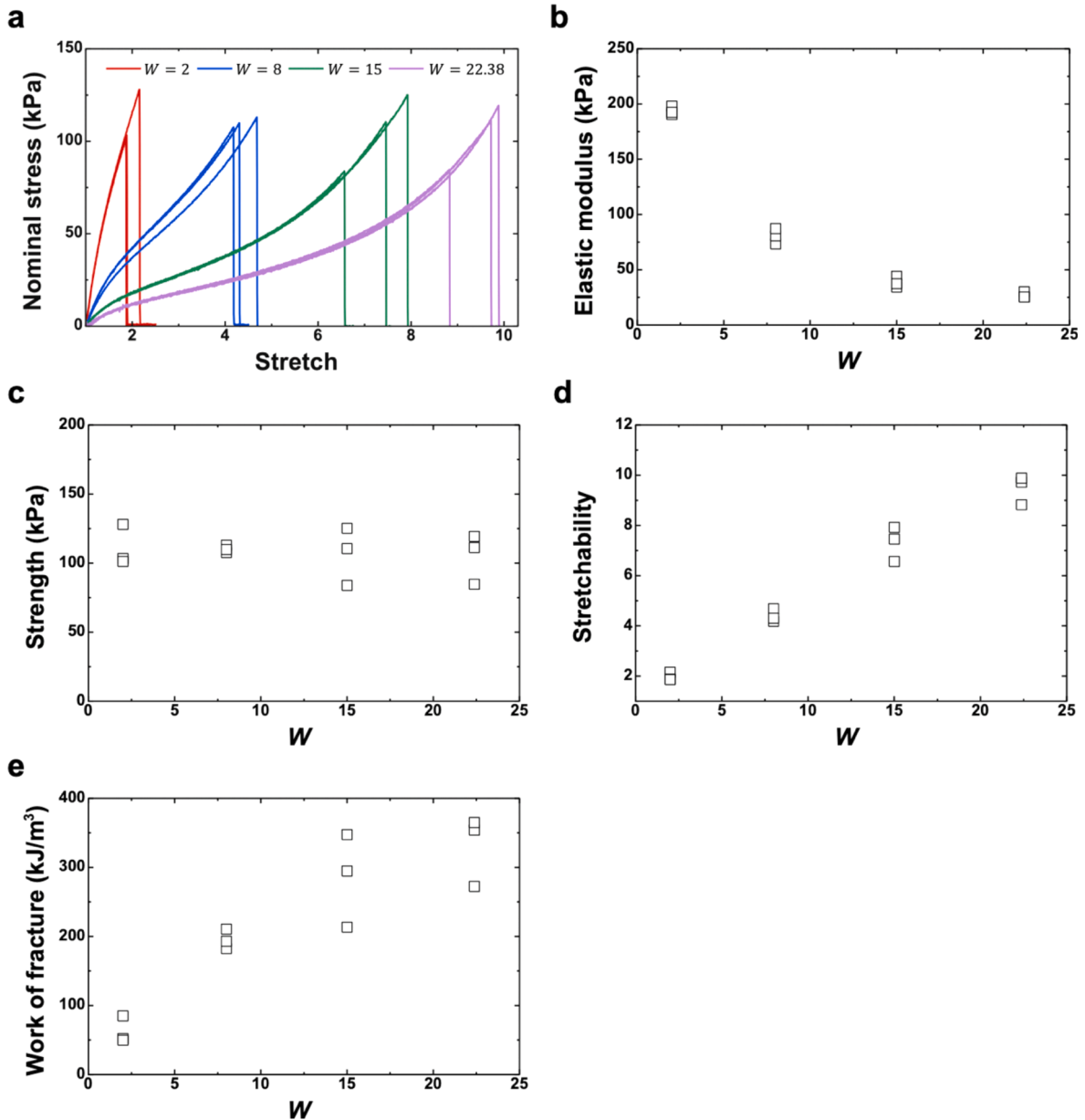


Fig. 9. Effect of water content for hydrogels prepared with fixed $C = 6 \times 10^{-4}$ and various W . The hydrogels are tested after being made to imbibe various amounts of water to have similar polymer content of ~ 15 wt%. (a) Stress-stretch curve up to rupture. (b) Elastic modulus. (c) Strength. (d) Stretchability. (e) Work of fracture.

6. Effect of water content in precursor on hydrogel swollen to certain degree

For hydrogels of series iv, we prepare samples using precursors of $C = 6 \times 10^{-4}$ and various values of W . The as-prepared samples are submerged in water to swell to certain degrees, so that the polymer content of the swollen samples is similar. After imbibing different amounts of water, the swollen hydrogels prepared with various values of W have a similar polymer content of ~ 15 wt%. The samples are homogenized in a plastic bag overnight at room temperature. We choose the value of 15 wt% on the basis of the following considerations. The polymer content of the as-prepared hydrogel of $W = 22.38$ is 15 wt%, and that of the fully swollen hydrogel of $W = 2$ is close to 15 wt% (Fig. 7a). To use samples prepared with precursors of $W = 2$, the polymer content of the swollen hydrogel cannot be below 15 wt%. To use samples prepared with precursors of $W = 22.38$, the polymer content of the swollen hydrogel cannot be beyond 15 wt%. Consequently, the target of 15 wt% can use the entire range of W that can be used in the experiment of series iv.

The stress-stretch curves are measured for samples prepared with precursors of four values of W (Fig. 9a). As W increases, the elastic modulus decreases (Fig. 9b), the strength is nearly constant (Fig. 9c), the stretchability increases (Fig. 9d), and the work of fracture

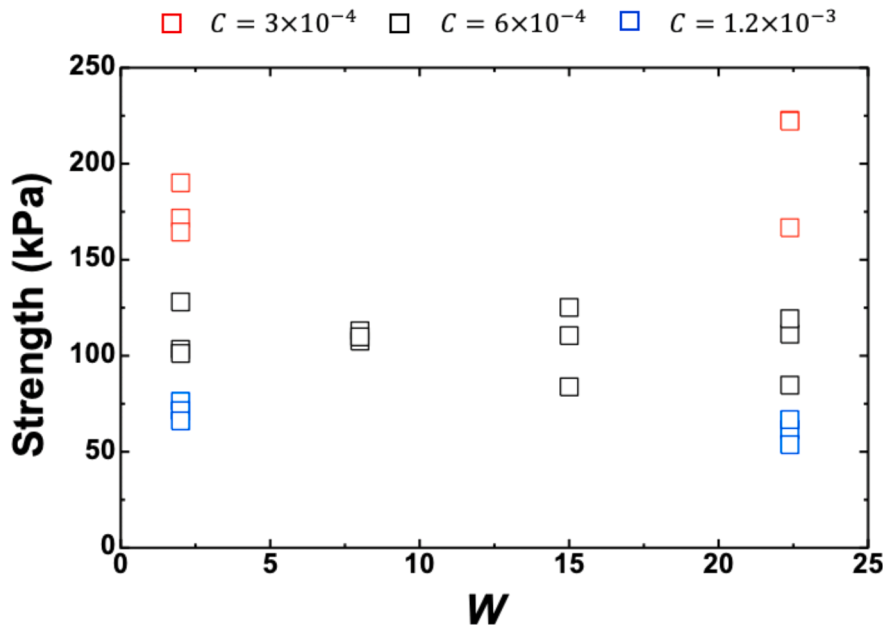


Fig. 10. Hydrogels are prepared under several conditions, but all have similar polymer content of ~ 15 wt% when the strength is measured.

increases (Fig. 9e).

We identify two effects of W on modulus: entanglement and prestretch. We have discussed the effect of entanglement on modulus before. A precursor of a larger value of W results in a hydrogel of fewer entanglements per polymer segment, and therefore a lower modulus. For a hydrogel prepared using a precursor of low W , after imbibing a small amount of water, some entanglements may not carry load when stretch is small. Under these circumstances, it is uncertain how effective entanglements contribute to modulus. The effect of prestretch on modulus is understood as follows. When the precursor has a larger value of W , the as-prepared hydrogel must imbibe less water to become a hydrogel of a polymer content of 15 wt%, so that the polymer chains in the swollen hydrogel are less prestretched before mechanical test. Because the polymer chains are entropic, for the hydrogels of similar polymer content, a hydrogel of less prestretched polymer chains has a lower modulus. Both effects of entanglement and prestretch lead to the observed trend that the modulus of the hydrogel is low when W of a precursor is high. At this writing, we have not found an experimental means to partition the contributions due to these two effects.

A precursor of larger value of W produces a hydrogel of fewer entanglements and smaller prestretch. Both effects increase the stretchability. As W increases, strength is nearly constant, but stretchability increases, so that the work of fracture also increases.

Note that the strength is nearly constant, independent of the value of W of the precursor (Fig. 9c). We next compare hydrogels prepared under various conditions that lead to a similar polymer content, close to 15 wt%. The hydrogels prepared with the precursors of $W = 2$, after being submerged in water to swell to equilibrium, have a similar polymer content of 15 wt% (Fig. 7a). The hydrogels prepared with the precursors of $W = 22.38$ have a polymer content of 15 wt%, and their strengths are measured as prepared. The hydrogels prepared with precursors of intermediate values of W are submerged in water to swell to a polymer content of 15 wt%. These data indicate that, so long as the polymer content is similar, the strength is sensitive to the crosslinker-to-monomer molar ratio C , but is insensitive to the water-to-monomer molar ratio W (Fig. 10). This picture confirms our molecular picture. Long polymer segments deconcentrate stress, leading to a polymer network of high strength. Entanglements do not impede the transmission of high stress along a long polymer segment, and do not lower the strength of the network. Entanglements, however, restrain the polymer network of long polymer segments from excessive swelling.

7. Conclusion

We characterize the stress-stretch curve of a polyacrylamide hydrogel by four properties: modulus, strength, stretchability, and work of fracture. Each property depends on various synthesis parameters, including the crosslinker-to-monomer molar ratio C of the precursor, the water-to-monomer molar ratio W of the precursor, and the polymer content ϕ of the hydrogel. The map from the space of synthesis parameters to the space of properties is complex. We explore this map along a few paths in the space of synthesis parameters. For well-formed hydrogels, when W is fixed, the strength of both as-prepared and fully-swollen hydrogels increases as C decreases; when C is fixed, the strength increases as W decreases; when polymer content is similar, the strength is sensitive to C , but is insensitive to W . We interpret these experimental findings in terms of the molecular picture of an entropic polymer network of covalent bonds. The average length of polymer segments is set by C , and the average number of entanglement per polymer segment is set by W . A network of long polymer segments has high strength because long polymer segments deconcentrate stress. Entanglements do not impede the

transmission of high stress along the long polymer segments, and therefore do not lower the strength of the polymer network. Entanglements, however, do restrain a network of long polymer segments from excessive swelling. These findings call for further study of synthesis-property relations of hydrogels.

Declaration of Competing Interest

The authors declare no competing interest.

Data availability

Data will be made available on request.

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References

- Beyer, M.K., 2000. The mechanical strength of a covalent bond calculated by density functional theory. *J. Chem. Phys.* 112, 7307–7312.
- Bueche, A.M., 1956. The ultimate properties of simple elastomers. *J. Polym. Sci.* 19, 275–284.
- Bueche, F., 1957. Tensile strength of rubbers. *J. Polym. Sci.* 24, 189–200.
- Bueche, F., Dudek, T.J., 1963. Tensile strength of amorphous gum rubbers. *Rubber Chem. Technol.* 36, 1–10.
- Caulfield, M.J., Qiao, G.G., Solomon, D.H., 2002. Some aspects of the properties and degradation of polyacrylamides. *Chem. Rev.* 102, 3067–3084.
- Chen, C., Wang, Z., Suo, Z., 2017. Flaw sensitivity of highly stretchable materials. *Extreme Mech. Lett.* 10, 50–57.
- Flory, P.J., 1953. *Principles of Polymer Chemistry*. Cornell university press.
- Flory, P.J., Rabjohn, N., Shaffer, M.C., 1949. Dependence of tensile strength of vulcanized rubber on degree of cross-linking. *J. Polym. Sci.* 4, 435–455.
- Gong, J.P., Katsuyama, Y., Kurokawa, T., Osada, Y., 2003. Double-network hydrogels with extremely high mechanical strength. *Adv. Mater.* 15, 1155–1158.
- Grandbois, M., Beyer, M., Rief, M., Clausen-Schaumann, H., Gaub, H.E., 1999. How strong is a covalent bond? *Science* 283, 1727–1730.
- Hassan, S., Kim, J., Suo, Z., 2022. Polyacrylamide hydrogels. IV. Near-perfect elasticity and rate-dependent toughness. *J. Mech. Phys. Solids* 158, 104675.
- Hua, M., Wu, S., Ma, Y., Zhao, Y., Chen, Z., Frenkel, I., Strzalka, J., Zhou, H., Zhu, X., He, X., 2021. Strong tough hydrogels via the synergy of freeze-casting and salting out. *Nature* 590, 594–599.
- Kim, J., Yin, T., Suo, Z., 2022. Polyacrylamide hydrogels. V. Some strands in a polymer network bear loads, but all strands contribute to swelling. *J. Mech. Phys. Solids* 168, 105017.
- Kim, J., Zhang, G., Shi, M., Suo, Z., 2021. Fracture, fatigue, and friction of polymers in which entanglements greatly outnumber cross-links. *Science* 374, 212–216.
- Kothari, K., Hu, Y., Gupta, S., Elbanna, A., 2018. Mechanical response of two-dimensional polymer networks: role of topology, rate dependence, and damage accumulation. *J. Appl. Mech.* 85.
- Liu, J., Yang, C., Yin, T., Wang, Z., Qu, S., Suo, Z., 2019. Polyacrylamide hydrogels. II. elastic dissipater. *J. Mech. Phys. Solids* 133, 103737.
- Liu, M., Li, M.-D., Xue, J., Phillips, D.L., 2014. Time-resolved spectroscopic and density functional theory study of the photochemistry of Irgacure-2959 in an aqueous solution. *J. Phys. Chem. A* 118, 8701–8707.
- Long, R., Hui, C.-Y., 2016. Fracture toughness of hydrogels: measurement and interpretation. *Soft Matter* 12, 8069–8086.
- Rubinstein, M., Colby, R.H., 2003. *Polymer physics*. Oxford University Press, New York.
- Sakai, T., Akagi, Y., Matsunaga, T., Kurakazu, M., Chung, U.-I., Shibayama, M., 2010. Highly elastic and deformable hydrogel formed from tetra-arm polymers. *Macromol. Rapid Commun.* 31, 1954–1959.
- Sakai, T., Matsunaga, T., Yamamoto, Y., Ito, C., Yoshida, R., Suzuki, S., Sasaki, N., Shibayama, M., Chung, U.-I., 2008. Design and fabrication of a high-strength hydrogel with ideally homogeneous network structure from tetrahedron-like macromonomers. *Macromolecules* 41, 5379–5384.
- Smith, T.L., 1978. Strength of elastomers. A perspective. *Rubber Chem. Technol.* 51, 225–252.
- Sun, J.-Y., Zhao, X., Illeperuma, W.R.K., Chaudhuri, O., Oh, K.H., Mooney, D.J., Vlassak, J.J., Suo, Z., 2012. Highly stretchable and tough hydrogels. *Nature* 489, 133–136.
- Taylor, G.R., Darin, S.R., 1955. The tensile strength of elastomers. *J. Polym. Sci.* 17, 511–525.
- Tonelli, A.E., 1974. Effects of crosslink density and length on the number of intramolecular crosslinks (defects) introduced into a rubbery network. *Polymer* 15, 194–196.
- Treloar, L.G., 1975. *The physics of rubber elasticity*. Oxford University Press.
- Wagner, R.J., Dai, J., Su, X., Vernerey, F.J., 2022. A mesoscale model for the micromechanical study of gels. *J. Mech. Phys. Solids* 167, 104982.
- Wang, Y., Yang, X., Nian, G., Suo, Z., 2020. Strength and toughness of adhesion of soft materials measured in lap shear. *J. Mech. Phys. Solids* 143, 103988.
- Wang, Y., Yin, T., Suo, Z., 2021a. Polyacrylamide hydrogels. III. Lap shear and peel. *J. Mech. Phys. Solids* 150, 104348.
- Wang, Z., Zheng, X., Ouchi, T., Kouznetsova, T.B., Beech, H.K., Av-Ron, S., Matsuda, T., Bowser, B.H., Wang, S., Johnson, J.A., Kalow, J.A., Olsen, B.D., Gong, J.P., Rubinstein, M., Craig, S.L., 2021b. Toughening hydrogels through force-triggered chemical reactions that lengthen polymer strands. *Science* 374, 193–196.
- Yang, C., Yin, T., Suo, Z., 2019. Polyacrylamide hydrogels. I. Network imperfection. *J. Mech. Phys. Solids* 131, 43–55.