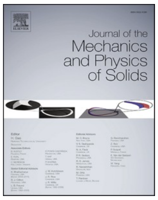
J. Mech. Phys. Solids 168 (2022) 105017

Contents lists available at ScienceDirect

Journal of the Mechanics and Physics of Solids

journal homepage: www.elsevier.com/locate/jmps



Polyacrylamide hydrogels. V. Some strands in a polymer network bear loads, but all strands contribute to swelling

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ARTICLE INFO

Keywords:
Gel
Thermodynamics
Flory-Rehner model
Polyacrylamide
Swelling

ABSTRACT

When a polymer network is stretched, some polymer strands do not bear loads. Examples include looped strands, dangling strands, and extremely long strands. When the polymer network is submerged in a solvent, however, all strands mix with solvent molecules. This distinction between strands that bear loads and strands that do not leads us to modify the Flory-Rehner model. The modified model has three parameters: the density of load-bearing strands, N, the density of all strands, M, and the interaction parameter, χ. For a polymer network submerged in a reservoir of solvent and bearing triaxial stresses, the modified model provides equations of state, relating the stresses to stretches, as well as the chemical potential of solvent molecules and temperature in the reservoir. We synthesize polyacrylamide hydrogels using precursors of various concentrations of monomer, crosslinker, and transfer agent. We determine the three parameters N, M, and χ by fitting the modified model to several experiments, including free swelling, fast tension, and stress relaxation. In all samples tested, M is several times N, whereas χ is nearly constant. This work demonstrates the consequences of the notion that some polymer strands in a polymer network bear loads, but all strands contribute to swelling.

1. Introduction

A polymer network typically consists of looped strands, dangling strands, and extremely long strands (Fig. 1). Such strands bear negligible loads when the network is stretched (Flory, 1953; Gu et al., 2019; Yang et al., 2019). However, when the polymer network is submerged in a solvent, all strands participate in the swelling of the network. This distinction between strands that bear load and strands that do not is absent in existing thermodynamic models of gels. For example, the Flory-Rehner model has two parameters: the interaction parameter, χ, and the density of polymer strands, N (Flory and Rehner, 1943). The same density of polymer strands, N, governs both entropy of stretching and entropy of mixing.

In this paper, we differentiate the density of load-bearing strands, N, from the density of all strands, M. Only the load-bearing strands contribute to the entropy of stretching, but all strands contribute to the entropy of mixing. This distinction leads us to modify the Flory-Rehner model. We express the modified model as three equations of state, which relate the triaxial stresses to the stretches, temperature, and chemical potential of solvent molecules (Section 2). The modified model consists of three parameters, N,

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https://doi.org/10.1016/j.jmps.2022.105017
Received 11 May 2022; Received in revised form 28 July 2022; Accepted 29 July 2022

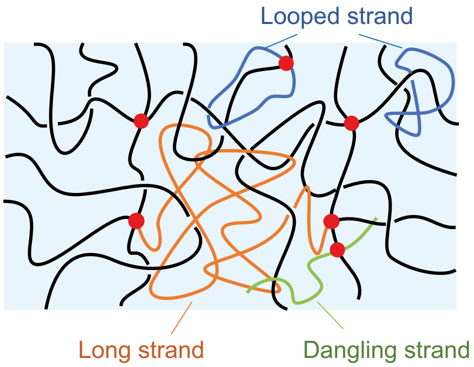

Fig. 1. A polymer network commonly has strands that do not bear loads. Examples include looped strands, dangling strands, and extremely long strands. Red dots represent crosslinks.

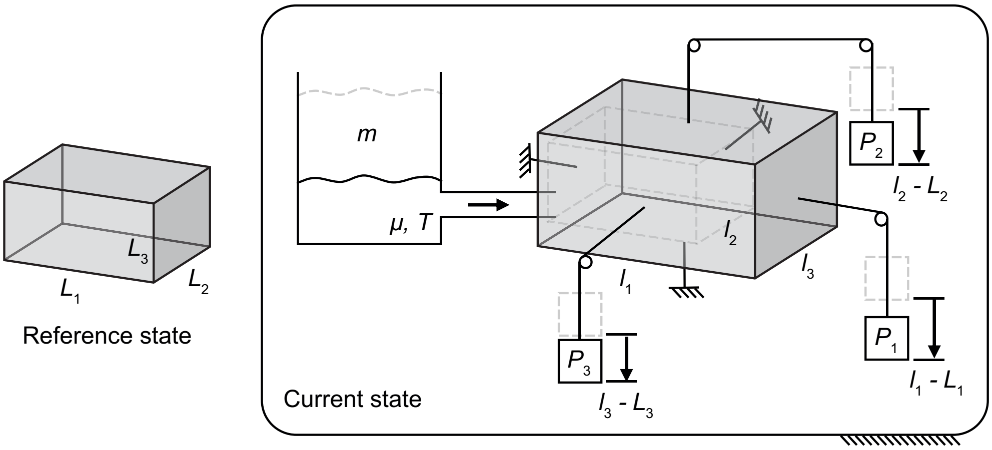

Fig. 2. In the reference state, a polymer network is dry, taken to be a rectangular block of edges L_1, L_2, and L_3. In the current state, the polymer network is in contact with a reservoir of a solvent, in which the temperature is T and the chemical potential of solvent molecules is μ. The gel bears loads represented by weights P_1, P_2, and P_3. In a current state, the edges of the block are l_1, l_2, and l_3. The polymer network imbibes a number m of solvent molecules.

M, and χ, which can be determined by fitting the model to various experiments, including free swelling, fast stretching, and stress relaxation (Section 3). We demonstrate the marked difference in N and M using polyacrylamide hydrogels synthesized from precursors of various concentrations of monomer, crosslinker, and transfer agent (Section 4). In all samples studied, M is several times N, whereas χ is nearly constant.

2. Modified Flory-Rehner model

A polymer network is in contact with a reservoir of a solvent, in which the temperature and chemical potential of solvent molecules are held constant. The polymer network imbibes solvent molecules and forms a gel. The gel bears triaxial forces, represented by three hanging weights. The gel, the reservoir of solvent, and the weights constitute an isolated system. The isolated system has several internal variables, including the number of solvent molecules in the gel and the heights of the weights. The entropy of the isolated system is the sum of the entropies of the parts of the isolated system. As the internal variables change, the isolated system maximizes the entropy to attain equilibrium. The resulting equations of state determine the values of the internal variables in equilibrium.

2.1. *An isolated system of three independent internal variables*

A dry polymer network, a rectangular block of edges L_1, L_2, and L_3, is taken to be the reference state (Fig. 2). In the current state, the polymer network is in contact with a reservoir of a solvent, in which the temperature is T and the chemical potential of solvent molecules is μ. The polymer network imbibes the solvent, resulting in a gel. The gel bears loads, represented by three hanging weights P_1, P_2, and P_3. Under constant T, μ, P_1, P_2, and P_3, the polymer network imbibes a certain number of solvent molecules, m, and the edges of the gel become l_1, l_2, and l_3.

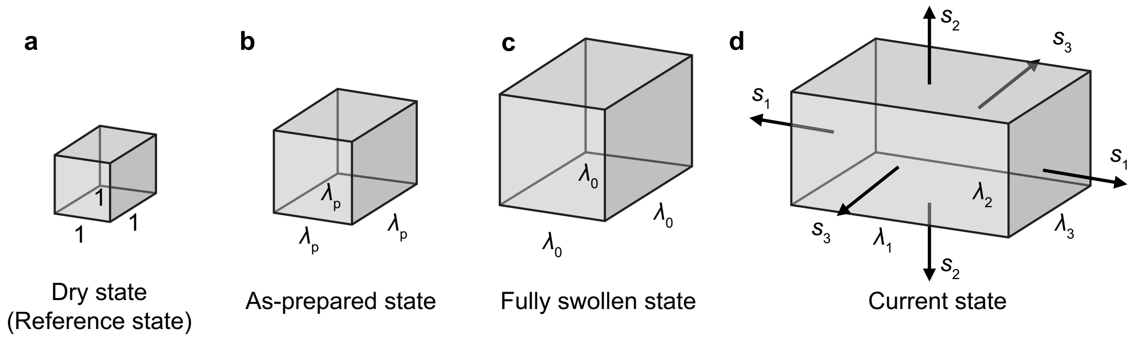

Fig. 3. The stretches and stresses in four states of a gel.

Following a commonly adopted approximation, we assume that the volume of the gel is the sum of the volume of the dry polymer and the volume of the solvent in the gel:

$$L_1L_2L_3 + \Omega m = l_1l_2l_3, \tag{1}$$

where Ω is the volume per solvent molecule.

We regard the gel, weights, and the environment together as an isolated system. Subject to a constant temperature, chemical potential, and weights, the gel imbibes solvent and deforms. Consequently, m, l_1, l_2, and l_3 are the internal variables of the isolated system. The assumption (1) relates m to l_1, l_2, and l_3, so that the system has only three independent internal variables, l_1, l_2, l_3. We consider the macroscopic behavior of the gel, which is independent of the size of the isolated system. Define the stretches by $\lambda_1 = l_1/L_1$, $\lambda_2 = l_2/L_2$, and $\lambda_3 = l_3/L_3$. The three stretches are scale-free and independent internal variables of the isolated system.

2.2. Four states of a gel

We define four states of a gel. When there is no solvent in the gel, the polymer network is in a dry state. As noted above, we chose the dry state as the reference state, in which the stretches are $\lambda_1 = \lambda_2 = \lambda_3 = 1$ (Fig. 3a). In the dry state, many polymers are in a glassy or semicrystalline state. In such cases, the thermodynamic model developed in this paper is not applicable. As will be evident, the physics of the dry polymer does not enter the model. Rather, the dry state is only used here to define the block in which the stretches are $\lambda_1 = \lambda_2 = \lambda_3 = 1$. The thermodynamic model developed here will only be used when the polymers are in a rubbery state.

In preparing a gel, the polymer network is often formed in a mold with a certain amount of solvent. Let λ_p be the stretch in the as-prepared state (Fig. 3b). For a polymer network cured from a monomer precursor, the monomers polymerize into polymer chains, and polymer chains crosslink in the polymer network. Each polymer strand takes approximately a configuration of random walk, which is relaxed. As another example, consider a polymer network cured from a solution of polymer chains. The polymer chains can be in either a relaxed state or an unrelaxed state, depending on the thermomechanical process of the solution before crosslink. After crosslink, the polymer strands in the network can be either relaxed or unrelaxed. To simplify the matter, in this paper we assume that the polymer strands are relaxed in the as-prepared state.

When the as-prepared gel is submerged in the pure solvent, subject to no applied forces, the network imbibes the solvent. Upon equilibrating with the reservoir, the gel reaches a fully swollen state. Let λ_0 be the stretch in the fully swollen state in the absence of applied forces (Fig. 3c).

In the current state, the gel is subject to applied forces P_1, P_2, and P_3. Define the nominal stresses by $s_1 = P_1/(L_2L_3)$, $s_2 = P_2/(L_1L_3)$, and $s_3 = P_3/(L_1L_2)$. This paper defines nominal stress as the force in the current state divided by the area in the dry state. This definition can be modified if any other reference state is used. In a fast tensile test, in which the solvent molecules have no time to migrate, the volume of the gel remains unchanged. However, in a stress-relaxation test, in which the solvent molecules can migrate in or out of the gel, the volume of the gel changes over time. In both cases, denote the stretches in the current state by λ_1, λ_2, and λ_3 (Fig. 3d).

2.3. Entropy of stretching

The deformation of rubber-like materials is an entropic process. When the polymer network is stretched, the entropy of strands decreases, but the energy of strands changes negligibly. Here we limit ourselves to small to modest stretches, where the neo-Hookean model applies. In the as-prepared state, each strand is taken to be in a configuration of random walk and is fully relaxed. Relative to the reference state, the dry network (Fig. 3a), the as-prepared state has an equal-triaxial stretch of λ_p (Fig. 3b). When the network undergoes a three-dimensional affine deformation, each strand is in a state of the triaxial stretch of λ_1, λ_2, and λ_3. The ratio of the end-to-end distance in the current state to that in the as-prepared state is $\lambda_1/\lambda_\mathrm{p}$, $\lambda_2/\lambda_\mathrm{p}$, and $\lambda_3/\lambda_\mathrm{p}$ (Tanaka, 1978). This deformation changes the entropy of the strand by $-1/2k((\lambda_1/\lambda_\mathrm{p})^2 + (\lambda_2/\lambda_\mathrm{p})^2 + (\lambda_3/\lambda_\mathrm{p})^2 - 3)$, where k is the Boltzmann constant (Treloar, 1943). The change in the entropy of the network is the sum of the entropy of all load-bearing strands. Let N be the density of load-bearing strands (i.e., the number of load-bearing strands in the network divided by the volume of the network in the dry state). Consequently, the network has

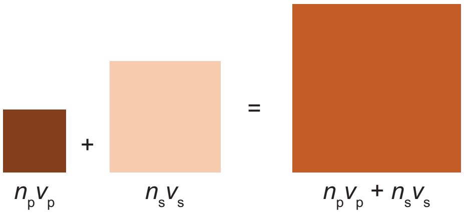

Fig. 4. Mixing polymer and solvent.

the entropy of stretching

$$S_{\text{stretch}} = -\frac{1}{2}NL_1L_2L_3k\left(\left(\frac{\lambda_1}{\lambda_p}\right)^2 + \left(\frac{\lambda_2}{\lambda_p}\right)^2 + \left(\frac{\lambda_3}{\lambda_p}\right)^2 - 3\right) \tag{2}$$

2.4. *Entropy of mixing*

In the Flory-Rehner model, N is also used to calculate the entropy of mixing. As we will show, this practice leads to large errors for a real polymer network, in which many strands do not bear loads but participate in mixing with solvent molecules. Only load-bearing strands contribute to the entropy of stretching, but all strands contribute to the entropy of mixing. Let M be the total number of strands in the network divided by the volume of the network in the dry state. The ratio N/M is the fraction of load-bearing chains in the network.

The entropy of mixing of a polymer solution is computed as follows (Brassart et al., 2016). The result reproduces that of a lattice model (Huggins, 1941). When the polymer chains and solvent molecules are separate, they occupy volumes $n_p v_p$ and $n_s v_s$, respectively (Fig. 4). Here n_p is the number of polymer chains, v_p is the volume per polymer chain, n_s is the number of solvent molecules, v_s is the volume per solvent molecule. In the separated state, each polymer chain can explore the volume $n_p v_p$, and each solvent molecule can explore the volume $n_s v_s$, so that the number of configurations is $(n_p v_p)^{n_p}(n_s v_s)^{n_s}$. When the polymer chains and solvent molecules mix, the volume of the solution is $n_p v_p + n_s v_s$. In the mixed state, each polymer chain can explore the volume $n_p v_p + n_s v_s$, and each solvent molecule can also explore the volume $n_p v_p + n_s v_s$, so that the number of configurations is $(n_p v_p + n_s v_s)^{n_p}(n_p v_p + n_s v_s)^{n_s}$. Consequently, the mixing of the polymer strands and solvent molecules changes the number of configurations by a factor of $[(n_p v_p + n_s v_s)/(n_p v_p)]^{n_p}[(n_p v_p + n_s v_s)/(n_s v_s)]^{n_s}$. Recall that the entropy is defined by Boltzmann constant times the logarithm of the number of configurations. Thus, the entropy of mixing is

$$S_{\text{mix}} = kn_p\log\left(\frac{n_p v_p + n_s v_s}{n_p v_p}\right) + kn_s\log\left(\frac{n_p v_p + n_s v_s}{n_s v_s}\right) \tag{3}$$

Note that the absolute entropy of polymer strands will also include the contributions of internal motions of individual monomer units. Similarly, the absolute entropy of solvent molecules will also include contributions of the internal motions of individual solvent molecules. The Huggins model assumes that these internal motions do not change before and after mixing, so they do not contribute to the entropy of mixing. When its center of mass is fixed, each polymer chain has the same number of quantum states in the pure polymer and in the solution. A similar assumption is made about each solvent molecule. The entropy of mixing is entirely because the solution increases the volume accessible to each polymer chain and each solvent molecule. Furthermore, the model assumes that the volume of the solution is the sum of the volume of pure polymer and that of the pure solvent.

Next, consider the entropy of mixing of a gel, i.e., the entropy of mixing of a polymer network and solvent molecules. In the gel, each polymer strand cannot explore the entire volume of the gel anymore, because the crosslinks inhibit the translational motion of the polymer strands. This inhibition decreases the absolute entropy. However, the entropy of mixing, by definition, is the relative entropy from the dry polymer to the gel. The volume of the gel is larger than that of the dry polymer, so that each polymer strand explores a larger volume in the gel than in the dry polymer. The ratio of the volume of the gel to that of the dry polymer is $(n_p v_p + n_s v_s)/(n_p v_p)$. We assume that this increase in volume is affine, and that by the same ratio each polymer strand explores a larger volume in the gel than in the dry polymer. Therefore, the mixing changes the number of configurations of all strands in the gel by a factor of $[(n_p v_p + n_s v_s)/(n_p v_p)]^{n_p}$. This contribution to the entropy of mixing for a gel is the same as that for a polymer solution. Furthermore, each solvent molecule can still explore the volume of the entire gel. Consequently, the entropy of mixing of a gel is the same as that of a polymer solution. This result reproduces that derived using a lattice model by Flory (1953). We emphasize that n_p is the total number of polymer strands in the network, including both the strands that bear loads and the strands that do not. The two types of strands make the same contribution to mixing.

Rewrite the entropy of mixing as follows:

$$S_{\text{mix}} = -L_1L_2L_3\frac{k}{\Omega}\left[M\Omega\log\left(\frac{1}{J}\right) + (J-1)\log\left(1-\frac{1}{J}\right)\right]. \tag{4}$$

Here we adopt the notation $J = (n_p v_p + n_s v_s)/(n_p v_p)$, $M = v_p^{-1}$, $L_1L_2L_3 = n_p v_p$, and $\Omega = v_s$, where J is the swelling ratio $J = l_1 l_2 l_3/$

$(L_1L_2L_3) = \lambda_1\lambda_2\lambda_3$.

2.5. Energy of mixing

When polymer chains and solvent molecules mix, the energy of mixing takes place at the level of individual monomer units and solvent molecules. Consequently, the energy of mixing of a polymer solution can be computed by modifying the Hilderbrand regular solution model of molecules of similar sizes (Hildebrand and Scott, 1962; Hildebrand and Wood, 1933). Following Flory (1941) and Huggins (1941), we assume that the volumes of each monomer unit and solvent molecule are similar, and that each monomer unit and solvent molecule have the same number of interaction sites z. Denote the total number of monomer units and solvent molecules by n, the number fraction of monomer units by y_m, and the number fraction of solvent molecules by y_s. Note that $y_m + y_s = 1$. The monomer units have zny_m interaction sites, and the solvent molecules have zny_s interaction sites. Denote the energy per monomer-to-monomer interaction by u_{mm}, the energy per solvent-to-solvent interaction by u_{ss}, and energy per monomer-to-solvent interaction by u_{ms}. Before mixing, the pure monomer units form $zny_m/2$ bonds, and have energy $u_{mm}zny_m/2$. Similarly, the pure solvent molecules form $zny_s/2$ bonds, and have energy $u_{ss}zny_s/2$. After mixing, each monomer unit has zy_m monomer neighbors and zy_s solvent molecule neighbors. Similarly, each solvent molecule has zy_m monomer unit neighbors and zy_s solvent neighbors. In the solution, ny_m monomer units form $zny_my_m/2$ monomer-to-monomer interactions, and ny_s solvent molecules form $zny_sy_s/2$ solvent-to-solvent interactions. Furthermore, the ny_m monomer units and ny_s solvent molecules form zny_sy_m monomer-to-solvent interactions. Consequently, the solution has energy $zny_my_mu_{mm}/2 + zny_sy_mu_{ms} + zny_sy_su_{ss}/2$. The difference in the energy before and after mixing gives the energy of mixing:

$$U_{\text{mix}} = z\left(u_{\text{ms}} - \frac{u_{\text{mm}} + u_{\text{ss}}}{2}\right)ny_{\text{m}}y_{\text{s}}. \tag{5}$$

Rewrite the energy of mixing as:

$$U_{\text{mix}} = L_1L_2L_3\frac{kT}{\Omega}\chi\left(1 - \frac{1}{J}\right). \tag{6}$$

This model assumes that the volume per monomer unit is similar to the volume per solvent molecule, Ω. Note that $y_m = J^{-1}$, $y_s = 1$ - J^{-1}, and $n\Omega = L_1L_2L_3J$. We adopt the notation $\chi = z[u_{ms}$ - $(u_{mm} + u_{ss})/2](kT)^{-1}$.

2.6. Isolated system conserves energy

We have adopted a reference state, in which the polymer and solvent are unmixed, $m = 0$, and the weight has not moved $\lambda_1 = \lambda_2 = \lambda_3 = 1$. Thus, the energy of the reference state is the sum of the energy of the pure polymer and the energy of the reservoir before losing any solvent molecule. The potential energy of the weights in the reference state is taken to be zero.

In the current state, the energy of the isolated system is:

$$U_{iso} = U_{mix} + U_{res} - P_1(l_1 - L_1) - P_2(l_2 - L_2) - P_3(l_3 - L_3). \tag{7}$$

The first term comes from the mixing of the polymer and the solvent. The second term results from m molecules leaving the reservoir. The last three terms come from the potential energy of the hanging weights. The isolated system conserves energy, so that $U_{\text{iso}} = \text{constant}$.

2.7. Isolated system maximizes entropy

The reservoir is a system that only exchanges with the rest of the world by energy and solvent molecules, so that the entropy of the reservoir is a function of its energy and its number of molecules, $S_{res}(U_{res}, m_{res})$. Recall the definition of the temperature and chemical potential, $dS_{res} = (1/T)dU_{res}$ - $(\mu/T)dm_{res}$. The reservoir has constant temperature T and chemical potential μ. Upon changing energy by U_{res} and the number of solvent molecules by $m_{res} = -m$, the reservoir changes its entropy by $S_{res} = (U_{res} + \mu m)/T$. Replacing U_{res} using (7), we obtain that

$$S_{res} = [U_{iso} - U_{mix} + P_1(l_1 - L_1) + P_2(l_2 - L_2) + P_3(l_3 - L_3) + \mu m]/T \tag{8}$$

In the current state, the entropy of the isolated system is the sum of the entropies of the parts: $S_{iso} = S_{stretch} + S_{mix} + S_{res}$. The first two terms come from the gel and the third term comes from the solvent reservoir. The weights themselves do not change entropy when they move up or down. The entropy of the isolated system is:

$$S_{\text{iso}} = S_{\text{stretch}} + S_{\text{mix}} + [U_{iso} - U_{\text{mix}} + P_1(l_1 - L_1) + P_2(l_2 - L_2) + P_3(l_3 - L_3) + \mu m]/T \tag{9}$$

Substituted m using (1), the entropy of the isolated system S_{iso} is a function of the independent internal variables λ_1, λ_2, and λ_3.

As the internal variables λ_1, λ_2, and λ_3 change, the isolated system reaches equilibrium by maximizing its entropy, so that

$$\frac{\partial S_{\text{iso}}(\lambda_1, \lambda_2, \lambda_3)}{\partial \lambda_1} = 0$$

$$\frac{\partial S_{\mathrm{iso}}(\lambda_1,\lambda_2,\lambda_3)}{\partial \lambda_2}=0 \tag{10}$$

$$\frac{\partial S_{\mathrm{iso}}(\lambda_1,\lambda_2,\lambda_3)}{\partial \lambda_3}=0.$$

These conditions of equilibrium lead to the equations of state:

$$s_1=\frac{kT}{\Omega}\left[N\Omega\frac{\lambda_1}{\lambda_{\mathrm{p}}^2}+\left[\log\left(1-\frac{1}{\lambda_1\lambda_2\lambda_3}\right)+(1-M\Omega)\frac{1}{\lambda_1\lambda_2\lambda_3}+\frac{\chi}{(\lambda_1\lambda_2\lambda_3)^2}-\frac{\mu}{kT}\right]\lambda_2\lambda_3\right]$$

$$s_2=\frac{kT}{\Omega}\left[N\Omega\frac{\lambda_2}{\lambda_{\mathrm{p}}^2}+\left[\log\left(1-\frac{1}{\lambda_1\lambda_2\lambda_3}\right)+(1-M\Omega)\frac{1}{\lambda_1\lambda_2\lambda_3}+\frac{\chi}{(\lambda_1\lambda_2\lambda_3)^2}-\frac{\mu}{kT}\right]\lambda_1\lambda_3\right] \tag{11}$$

$$s_3=\frac{kT}{\Omega}\left[N\Omega\frac{\lambda_3}{\lambda_{\mathrm{p}}^2}+\left[\log\left(1-\frac{1}{\lambda_1\lambda_2\lambda_3}\right)+(1-M\Omega)\frac{1}{\lambda_1\lambda_2\lambda_3}+\frac{\chi}{(\lambda_1\lambda_2\lambda_3)^2}-\frac{\mu}{kT}\right]\lambda_1\lambda_2\right]$$

Here we write the equations of state in the form of nominal stress as a function of λ_1, λ_2, and λ_3. In deriving (11), both the temperature T and the chemical potential μ referred to those in the reservoir. In equilibrium, T is the temperature of the gel, and μ is the chemical potential of solvent molecules in the gel.

The first term originates from the entropy of stretching (neo-Hookean model), the second and third terms originate from the entropy of mixing, and the forth term originates from the energy of mixing. The third term can also be calculated by using the compressible neo-Hookean model (Hong et al., 2008). However, the compressible neo-Hookean model uses one density of strands and does not distinguish the strands that bear loads and the strands that do not bear loads. Also, in this case, the entropy of mixing should only be calculated for the solvent to avoid double counting the entropy of mixing for the polymers.

True stress is defined as the force divided by the area in the current state. Thus, the true stresses in the three directions are $s_1/(\lambda_2\lambda_3)$, $s_2/(\lambda_1\lambda_3)$, and $s_3/(\lambda_2\lambda_1)$. From (11), we obtain that

$$\frac{s_1}{\lambda_2\lambda_3}-\frac{s_3}{\lambda_2\lambda_1}=\frac{NkT}{\lambda_{\mathrm{p}}^2\lambda_1\lambda_2\lambda_3}\left(\lambda_1^2-\lambda_3^2\right) \tag{12a}$$

$$\frac{s_2}{\lambda_1\lambda_3}-\frac{s_3}{\lambda_2\lambda_1}=\frac{NkT}{\lambda_{\mathrm{p}}^2\lambda_1\lambda_2\lambda_3}\left(\lambda_2^2-\lambda_3^2\right) \tag{12b}$$

3. Experiments

The stretch of the as-prepared gel, λ_{p}, is calculated from the composition of the precursor (Section 3.1). We then determine the three parameters, N, M, and χ, in three tests. First, we submerge the as-prepared hydrogel in pure water to swell to equilibrium and measure λ_0 (Section 3.2). Second, we prepare a pure shear sample and measure the stress-stretch curve at a fast loading rate (Section 3.3). Third, for a sample submerged in pure water, we apply a constant stretch and measure the stress relaxation (Section 3.4). All tests are repeated three times to calculate statistical deviation. Since all mechanical experiments are conducted in series, the three parameters N, M, and χ are determined using one sample.

3.1. Synthesis

We use acrylamide (AAm, A8887), N,N'-methylenebisacrylamide (MBAA, M7279), ammonium persulfate (APS, 215589), N,N,N', N'-Tetramethylethylenediamine (TEMED, T22500), and 3-Mercaptopropionic acid (3-MPA, M5801) as a monomer, crosslinker, initiator, accelerator, and transfer agent, respectively. All chemicals are purchased from Sigma Aldrich and used as received. Deionized water (DI water) is purchased from Poland Spring. Rubber sheets are purchased from McMaster-Carr (3788T21) and are used as a spacer. We dissolve 14 g of AAm and 0.261 g of MBAA in 86 g of DI water. The amount of MBAA varies depending on the crosslinker density. We dissolve APS in DI water to prepare a 0.2 M solution. For every 1 mL solution of monomer and crosslinker, 30 μL of APS solution and 0.5 μL of TEMED are added. After vortexing the final solution for a few seconds, the precursor is poured immediately onto a 15 cm × 15 cm acrylic sheet mold (8560K257) with a 0.5 cm-thick rubber spacer. The precursor is cured at room temperature for 24 h.

After cure, the mass of the sample is measured. Assuming that all monomers in the precursor polymerize during cure, the volume of the polymer network in the dry state, V, is taken to be the same as the volume of monomers in the precursor. Consequently, λ_{p} is calculated by:

$$\lambda_{\mathrm{p}}=\left(\frac{V_{\mathrm{p}}}{V}\right)^{\frac{1}{3}}, \tag{12}$$

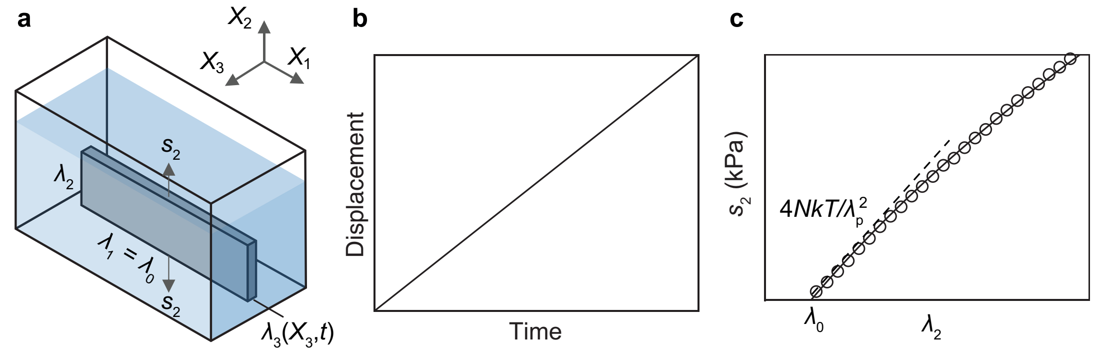

Fig. 5. (a) Schematic of fast loading test under a pure shear condition in the solvent. The grippers fix λ_1 to be λ_0. As the sample is fully swollen and tested in the solvent, the chemical potential of solvent in the gel is zero before deformation, and becomes non-zero when the sample is stretched quickly because the sample has no time to reach equilibrium. (b) The loading profile of the fast loading test. (c) Example of the stress-stretch curve. The x-intercept is λ_0 and the initial slope gives N. We can check if the neo-Hookean model (solid line) works for fully swollen gel at a certain stretch range.

where V_p is the volume of the precursor. When the densities of the monomer and the solvent are similar (e.g. acrylamide: 1.13 g/cm^3, DI water: 1.00 g/cm^3), V_p/V can be estimated by the mass ratio.

3.2. Free swelling

The as-prepared sample is then submerged in a large amount of pure water. After more than 48 h, the sample swells to equilibrium, and the mass is measured. The stretch of the fully swollen state is calculated from:

$$\lambda_0 = \lambda_p \left(\frac{V_0}{V_p} \right)^{\frac{1}{3}}, \tag{13}$$

where V_0 is the volume of the gel in the fully swollen state. The chemical potential of water molecules in pure water is set to zero. The fully swollen state is stress-free. Consequently, the equations of state (11) reduce to a single equation:

$$\frac{N\Omega}{\lambda_p^2 \lambda_0} + \log\left(1 - \frac{1}{\lambda_0^3}\right) + (1 - M\Omega)\frac{1}{\lambda_0^3} + \frac{\chi}{\lambda_0^6} = 0. \tag{14}$$

3.3. Fast tension

The fully swollen gel is cut into 8.9 cm × 3.8 cm. The sample is weighed again to calculate the final thickness. The long edges of the gel are glued onto acrylic sheets using cyanoacrylate (Krazy glue), and then loaded at a tensile machine (Instron 5966). The deforming region of the sample takes the shape of a long rectangle, 8.9 cm × 1.3 cm. All samples are tested in pure water, so that the next stress relaxation test can be done right after the fast tension. Instead, we set the loading rate to be 0.08 s^{-1} which is much faster than the rate of diffusion (Kalcioglu et al., 2012).

We measure the stress-stretch curve of the fully swollen gel (Fig. 5). Let X_1, X_2, and X_3 be the material coordinates in the width, loading, and thickness direction, respectively. Due to the rigid constraint of the acrylic sheets, the contraction in the width direction is negligible $\lambda_1 = \lambda_0$. The traction in the thickness direction is free, $s_3 = 0$. Prior to loading, the gel is in the fully swollen state, and is in equilibrium with the reservoir of pure water. During loading, however, the polymer network is not in equilibrium with the reservoir of pure water, so that the chemical potential of solvent molecules in the gel is unknown. Because the loading is fast, the solvent molecules in the gel migrate negligibly. Consequently, the chemical potential of the solvent in the gel is uniform, and the volume of the gel does not change $\lambda_1\lambda_2\lambda_3 = \lambda_0^3$. (12b) gives:

$$s_2 = \frac{NkT}{\lambda_p^2}\left(\lambda_2 - \frac{\lambda_0^4}{\lambda_2^3}\right), \tag{15}$$

The parameter N can be obtained from the initial slope of the stress-stretch curve as follows:

$$\left.\frac{\partial s_2}{\partial \lambda_2}\right|_{\lambda_2=\lambda_0} = \frac{4NkT}{\lambda_p^2}. \tag{16}$$

We plot one stress-stretch curve as an example (the circles in Fig. 5c). The measured force and the displacement are converted into nominal stress and stretch. The stretch at zero stress is λ_0. From the initial slope, we get N by using (16). We also put the value of N to (15) and plot the stress-stretch curve (the solid line in Fig. 5c). Whether S_{stretch} of the fully swollen sample is valid at the given stretch

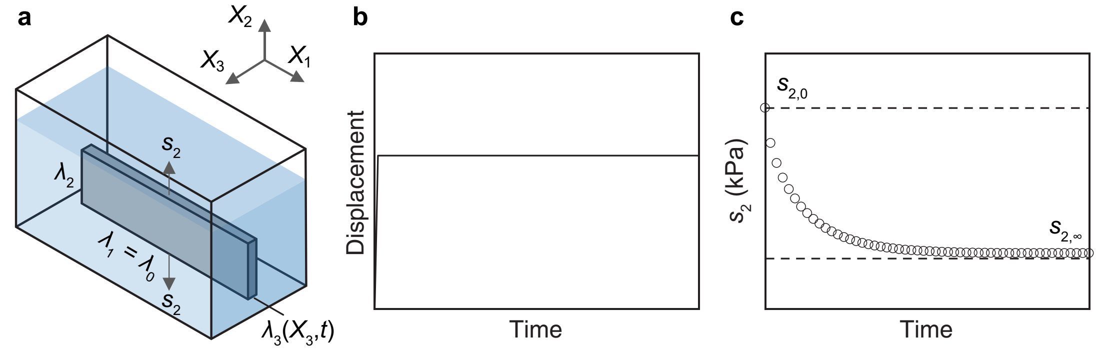

Fig. 6. (a) Schematic of stress relaxation test under a pure shear condition in pure water. By acrylic grippers, the λ_1 is fixed to be λ_0. After equilibrium, the chemical potential of the solvent is zero. (b) The loading profile of the stress relaxation test. (c) Example of stress relaxation. The initial stress $s_{2,0}$ decreases over time and becomes the final stress $s_{2,\infty}$.

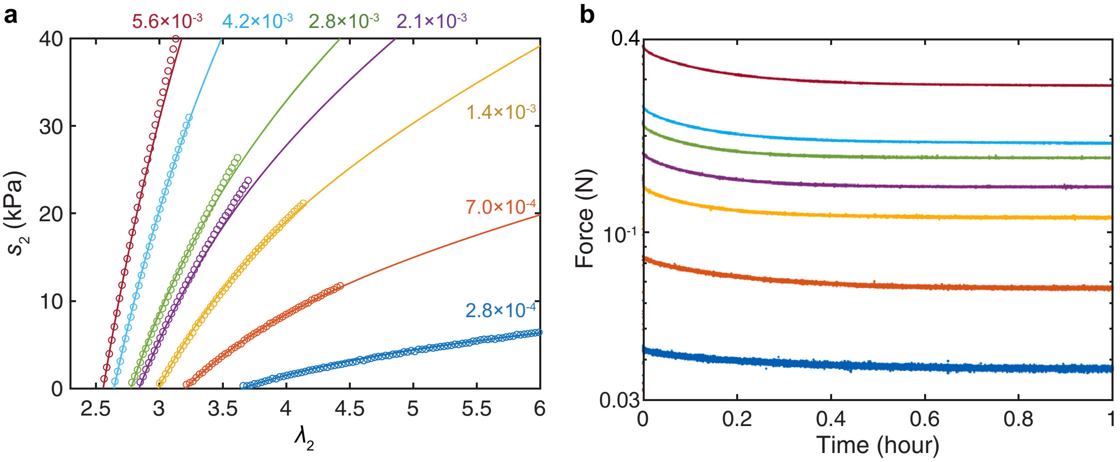

Fig. 7. (a) The stress-stretch curves of samples of various crosslinker densities. (b) The stress relaxations of samples of various crosslinker densities. The crosslinker density is defined as the molar ratio of the crosslinkers to the monomers in the precursor.

range can be confirmed by how the measured data fit well with (15).

3.4. Stress relaxation

We submerge the fully swollen gel in pure water, apply a constant stretch, and measure the stress as a function of time Fig. 6). The displacement is empirically chosen in the range in which the neo-Hookean model works well. In the transient state, the polymer network is not in equilibrium with the pure solvent, so that the equations of state ((11) do not apply. However, after being subjected to a fixed stretch for a long time, the polymer network and the reservoir of pure water reach a new state of equilibrium, where the gel equilibrates with the reservoir. Consequently, the chemical potential of water molecules in the gel becomes zero. In the new equilibrium state, the sample still satisfies the conditions $\lambda_1 = \lambda_0$ and $s_3 = 0$. Thus, the third equation of (11) becomes

$$\frac{N\Omega}{\lambda_p^2}\lambda_{3,\infty} + \left[\log\left(1 - \frac{1}{\lambda_0\lambda_2\lambda_{3,\infty}}\right) + (1 - M\Omega)\frac{1}{\lambda_0\lambda_2\lambda_{3,\infty}} + \frac{\chi}{\left(\lambda_0\lambda_2\lambda_{3,\infty}\right)^2}\right]\lambda_0\lambda_2 = 0, \tag{18}$$

where $\lambda_{3,\infty}$ is the stretch in the thickness direction in the new state of equilibrium.

We call the initial nominal stress $s_{2,0}$ and the equilibrium nominal stress $s_{2,\infty}$. In the initial state, the gel is not in equilibrium with the reservoir, but the time is too short for the solvent molecules to migrate into the gel. Consequently, the chemical potential of the solvent in the gel is nonzero, but uniform. For the initial state, (12b) becomes:

$$s_{2,0} = \frac{NkT}{\lambda_p^2}\left(\lambda_2 - \frac{\lambda_3^2}{\lambda_2}\right), \tag{19}$$

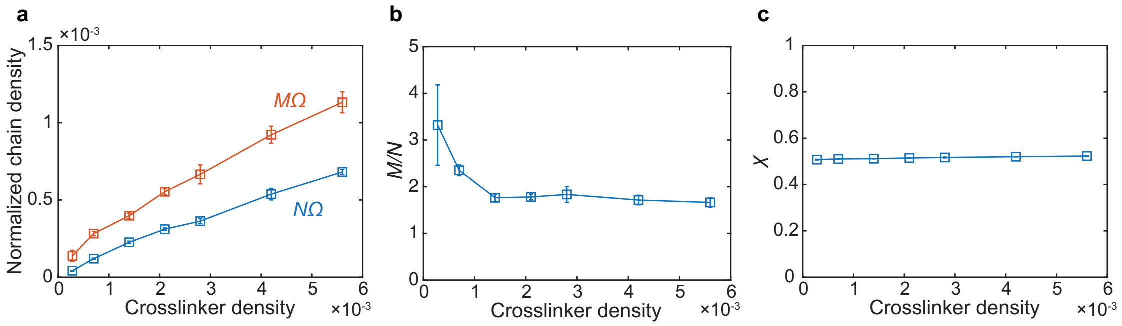

Fig. 8. The effects of crosslinker density on the three parameters of the model. (a) The density of load-bearing strands, N, and the density of all strands, M. (b) The ratio M/N. (c) The interaction parameter, χ.

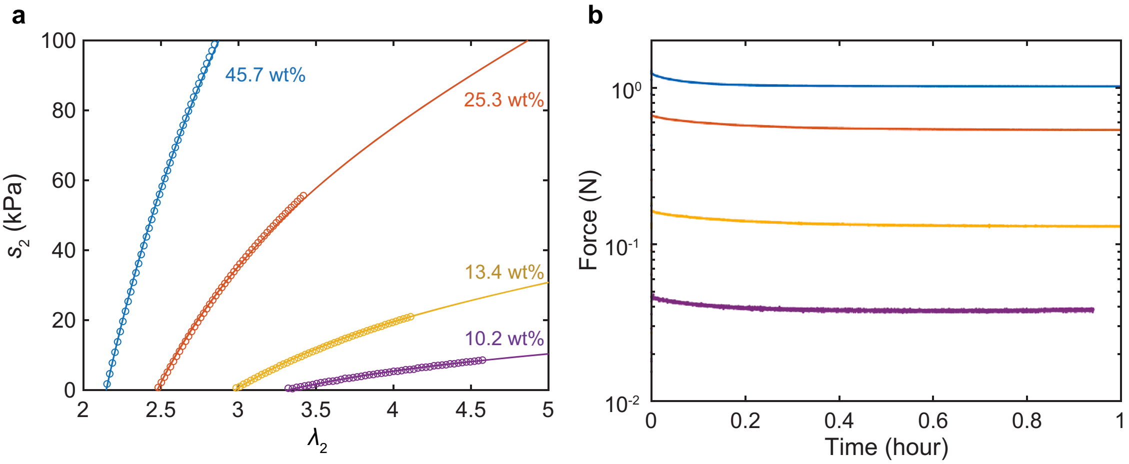

Fig. 9. (a) The stress-stretch curves at various monomer concentrations. (b) The stress relaxations at various monomer concentrations.

where $\lambda_1\lambda_2\lambda_3 = \lambda_0^3$. For the equilibrium state, (12b) becomes

$$s_{2,\infty} = \frac{NkT}{\lambda_p^2}\left(\lambda_2 - \frac{\lambda_{3,\infty}^2}{\lambda_2}\right). \tag{20}$$

The combination of (19) and (20) gives:

$$\lambda_{3,\infty} = \sqrt{\frac{\lambda_0^4}{\lambda_2^2} + R\left(\lambda_2^2 - \frac{\lambda_0^4}{\lambda_2^2}\right)}, \tag{21}$$

where $R = (s_{2,0} - s_{2,\infty})/s_{2,0}$. When we measure the value of R, we can calculate $\lambda_{3,\infty}$ from (21). Plugging $\lambda_{3,\infty}$ in (18), we get one equation that relates N, M, and χ.

4. Results

4.1. Effect of crosslinker

We synthesize polyacrylamide hydrogels with various crosslinker densities (i.e., the molar ratio of the crosslinkers to the monomers in the precursor), and study how crosslinker densities affect the three parameters in the model. The stress-stretch curves of the fast loading tests are plotted in Fig. 7a. As the crosslinker density increases, λ_0 decreases, and the initial slope increases. The measured data fit well with the predictions of the neo-Hookean model. The stress relaxation data are plotted in Fig. 7b. 10–20% of stress relaxation ratios are observed. Following the procedures described in Section 3, we determine all the parameters.

We plot dimensionless numbers, $N\Omega$ and $M\Omega$, as functions of the crosslinker density (Fig. 8a). N and M increase as the crosslinker density increases because additional crosslinkers generate more chains per unit volume. Also, $M > N$ at all crosslinker densities we study, indicating the existence of strands that do not bear loads. It is perhaps surprising that such high fractions of polymer chains

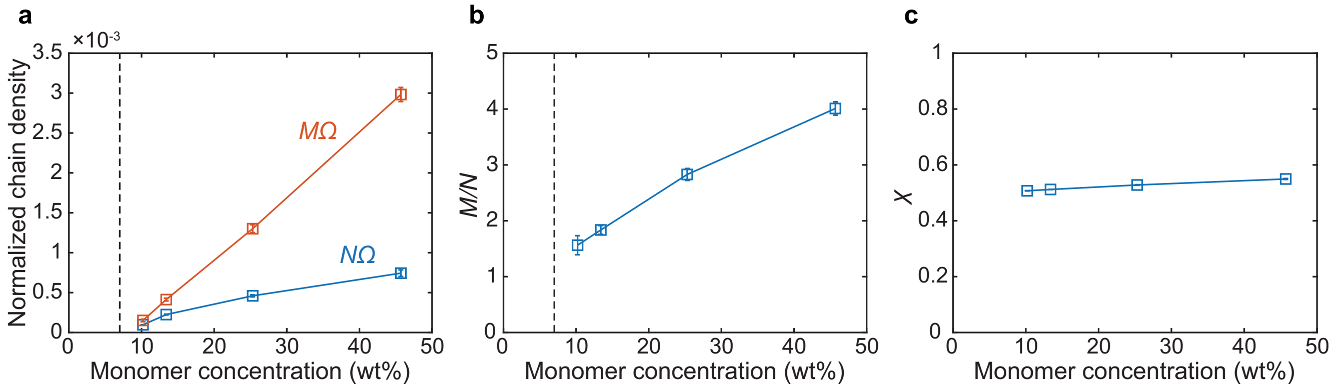

Fig. 10. The effects of monomer concentration on the three parameters of the model. (a) The density of load-bearing strands, N, and the density of all strands, M. The dashed line is the percolation limit. (b) The ratio M/N. (c) The interaction parameter χ.

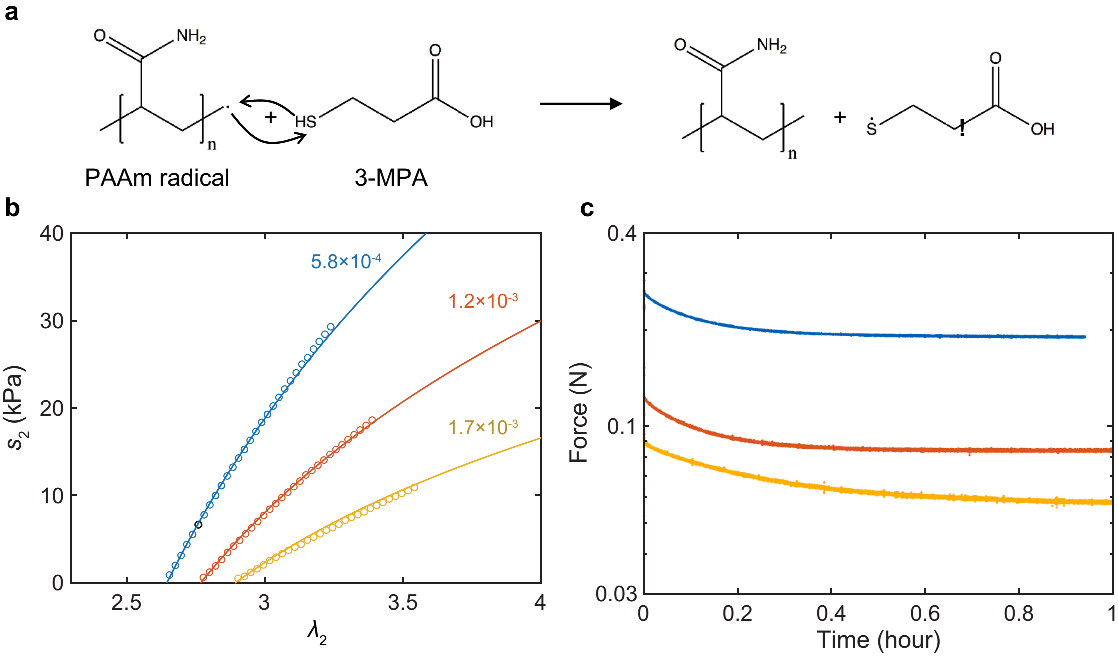

Fig. 11. (a) The transfer process by 3-Mercaptopropionic acid (3-MPA). (b) The stress-stretch curves at various transfer agent densities. (c) The stress relaxations at various transfer agent densities. The transfer agent density is defined as the molar ratio of 3-MPA to the monomers in the precursor.

contribute to swelling but not to bearing load. At this writing, we do not have other independent means to ascertain this conclusion.

Observe that $M/N = 3.3$ at a low crosslinker density, and plateaus at $M/N = 1.7$ as the crosslinker density increases (Fig. 8b). In this experiment, the molar ratio of the initiator to monomer is kept constant ($\sim 10^{-3}$) for all crosslinker densities, so that the average length of polymer chains is constant. At low crosslinker density, the M/N ratio is high, possibly because the fraction of dangling strands at the ends of polymer chains is high. At high crosslinker densities, the fraction of dangling strands at the end of the polymer chains is negligible, but our data still show that $M/N = 1.7$, indicating that a portion of strands that do not bear load comes from strands such as looped strands, excessively long strands, and dangling strands made by routes other than the initiators.

The interaction parameter χ does not change with crosslinker density (Fig. 8c). This result is unsurprising, because χ measures the energy of mixing of monomer units and water molecules, and because the amount of the crosslinkers is negligible compared to that of monomer units and water molecules.

4.2. Effect of monomer concentration

In a polymer network, polymer chains entangle (Fig. 1). During swelling and deforming, the crosslinks keep the polymer chains from detangling. Following common practice, we write $N = N_c + N_e$, where N_c and N_e are contributions from crosslinks and entanglements. To vary the density of entanglements, we synthesize polyacrylamide hydrogels with various monomer concentrations in the precursor, while fixing the crosslinker density (Kim et al., 2021). When the monomers polymerize at a high concentration, the crowded monomers polymerize into densely entangled polymer chains. When the monomers polymerize at a low concentration, the sparse polymer chains barely entangle. The stress-stretch curves of the fast tensile tests are plotted in Fig. 9a. As the monomer concentration increases, λ_0 decreases, and the initial slope increases. The stretch range is small enough to use the neo-Hookean model. The stress relaxation is ~10% (Fig. 9b).

We plot N and M as functions of the monomer concentration in the precursor (Fig. 10a). We vary the monomer concentration from 10.2 to 45.7 wt%. When the monomer concentration is lower than 7 wt%, gelation does not occur. When the monomer concentration is higher than 50 wt%, the precursor precipitates at room temperature. As the monomer concentration increases, the density of entanglements increases, and the effective length of the strands decreases. Consequently, both N and M increase. In all monomer concentrations we study, M is 2–4 times higher than N, suggesting that a large fraction of the effective strands formed by entanglements do not bear load but contribute to swelling (Fig. 10b). The interaction parameter does not change in monomer concentration (Fig. 10c).

4.3. Effect of transfer agent

We increase the fraction of dangling strands by using a transfer agent, 3-Mercaptopropionic acid (3-MPA). The transfer agent has been used to control the length of polymer chains by transferring the radical from one polymer chain to another, terminating the

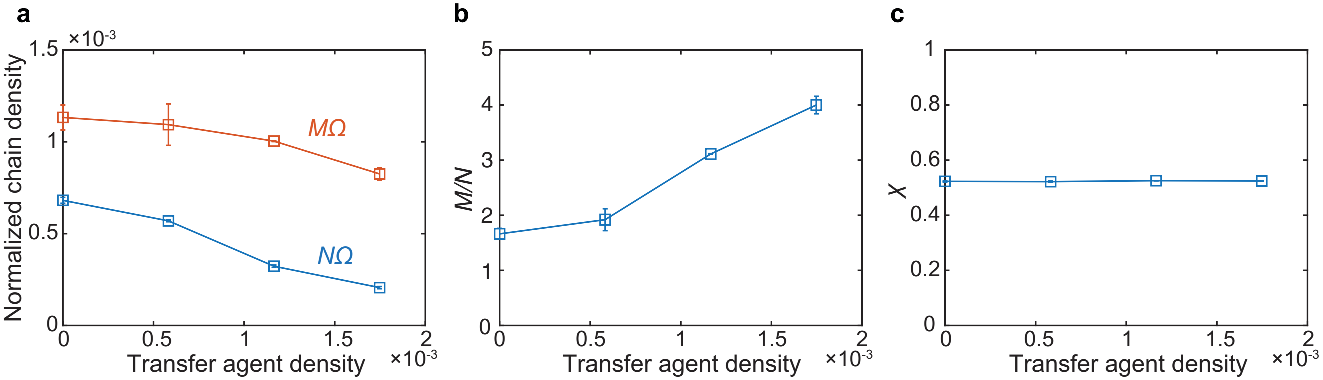

Fig. 12. The effects of the transfer agent on the three parameters of the model. (a) The density of load-bearing strands, N, and the density of all strands, M. (b) The ratio M/N. (c) The interaction parameter χ.

polymerization (Liu et al., 2018; Yao et al., 2019). To be specific, when a free radical on a polyacrylamide chain reacts with a 3-MPA, the radical moves to the agent, and the chain is terminated with the carboxylic functional group of 3-MPA, forming a dangling strand (Fig. 11a). We synthesize polyacrylamide hydrogels by varying the transfer agent density, the molar ratio of the 3-MPA to the monomers, and determine the parameters by following the procedure described in Section 3.

We plot N and M as a function of the transfer agent density (Fig. 12a). N decreases faster than M, and the ratio of M to N increases from 1.7 to 4.0, indicating that the fraction of strands that do not bear load increases by the dangling strands (Fig. 12b). The interaction parameter does not change as the amount of the transfer agent is still negligible compared to that of the polymer and water (Fig. 12c).

5. Conclusion

When a polymer network is submerged in a solvent and bears loads, all polymer strands contribute to swelling, but only a fraction of polymer strands contribute to load-bearing. This difference has motivated us to modify the Flory-Rehner model. We use the density of all strands, M, for the entropy of mixing, and use the density of load-bearing strands, N, for the entropy of stretching. The modified model has three parameters: M, N, and the interaction parameter, χ. We prepare polyacrylamide hydrogels with various amounts of crosslinker, monomer, and transfer agent. We determine the three parameters for the polyacrylamide hydrogels by fitting the modified model to several experiments, including free swelling, fast tension, and stress relaxation. In all cases, $M > N$ and χ is a constant. Our work shows the significance of differentiating strands that bear load and strands to not. Also, this model may provide a measure of strands that do not bear loads, which is important to understanding network topologies.

CRediT authorship contribution statement

Junsoo Kim: Conceptualization, Methodology, Investigation, Formal analysis, Writing – original draft, Writing – review & editing. **Tenghao Yin:** Investigation, Validation. **Zhigang Suo:** Methodology, Funding acquisition, Supervision, Writing – original draft, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

Acknowledgments

This work was supported by MRSEC (DMR-2011754). J. Kim was supported by Kwanjeong Lee Chong Hwan Educational Foundation of Korea (KEF-2017). T. Yin is supported by the China Scholarship Council as a visiting scholar at Harvard University.

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