Supplementary Information

Biomimetic growth in polymer gels

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S1. Polymerization

This section is reproduced from ref [1] for a reader's convenience.

We assume that the primary gel swells in a liquid composed solely of secondary monomer with no solvent present. (This scenario was denoted Case I in ref [1].) The absorbed monomeric units undergo the reversible chain-growth polymerization reaction schematically shown in Fig. S1; the reaction proceeds until the equilibrium molecular weight distribution (MWD) is established. We assume that the volume of the gel does not change during the polymerization process. The kinetics of polymerization is described in terms of the dimensionless (in the units of v_0^{-1} with v_0 being volume of one molecular unit) concentrations n_k of linear chains containing $k \geq 1$ monomeric units. When the polymerization reaches the state of equilibrium, the equilibrium concentrations n_k correspond to the Flory MWD

$$n_k = p^{k-1} n_1 , \quad k \geq 1 \tag{S1.1}$$

Here, p is the distribution parameter, which depends on the polymerization rate constants γ_+ and γ_- (see Fig. S1), and on the volume fraction of polymer in the swollen primary gel, ϕ:

$$p \equiv \gamma_+ n_1 / \gamma_- = \frac{1+2R-\sqrt{1+4R}}{2R} \tag{S1.2}$$

where $R = \gamma_+ \gamma_-^{-1}(1-\phi)$.

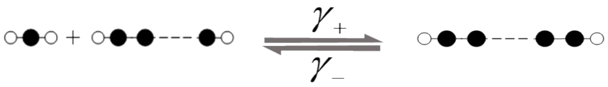


Figure S1. Schematic representation of the polymerization

For the Flory MWD, the number and weight averaged degrees of polymerization are given by the following respective equations:

$$\bar{N}_n(p) = \frac{\sum\limits_{k=1} k n_k}{\sum\limits_{k=1} n_k} = \frac{1}{1-p} \tag{S1.3}$$

$$\bar{N}_w(p) = \frac{\sum\limits_{k=1} k^2 n_k}{\sum\limits_{k=1} k n_k} = \frac{1+p}{1-p} \tag{S1.4}$$

We use the ratio of polymerization rate constants $\gamma_+ / \gamma_- > 2\times10^4$ to ensure that the polymers formed during polymerization are relatively long, $\bar{N}_n > 100$.

S2. Cross-link density and sol fraction

This section is reproduced from ref [1] for a reader's convenience.

The cross-linking of the polymer chains results in the formation of a polymer network that encompasses the gel and sol. The gel spans the entire system and exhibits macroscopic elasticity, and the sol is a collection of network-like polymer structures, which are not attached to the macroscopic gel and could be removed from the sample. Correspondingly, the result of cross-linking is characterized by the cross-link density in gel, c_0, and the weight fraction of the sol, S. By definition, the cross-link density is the concentration of the elastically active polymer strands connecting two cross-links.

We utilize the theory of tree-like branched polymers by Dobson and Gordon to calculate c_0 and S.[2,3] Theories that do not account for the presence of cyclic configurations are in general not applicable to cross-linked polymers. It is, however, argued that the theory of tree-like polymer structures can nevertheless be used to describe densely cross-linked systems like vulcanized rubbers, where there are many cross-links per polymer chain[4]. Here, we use the theory by Dobson and Gordon as outlined in ref.[5]

The theory by Dobson and Gordon is formulated for polymer chains with the Flory MWD. The cross-link density c_0 and sol fraction S are calculated as functions of the Flory distribution parameter p and fraction of monomeric units forming cross-links α. Upon cross-linking, the macroscopic network (gel) exists in the system if $\alpha \ge \alpha_{cr}$, where the critical value α_{cr} is[3]

$$\alpha_{cr} = (\bar{N}_w - 1)^{-1} \qquad \text{(S2.1)}$$

Here, $\bar{N}_w$ is the weight averaged degree of polymerization given by eq. (S1.4). The value of the sol fraction depends on α and on the Flory distribution parameter[3] p

$$S(p,\alpha) = \frac{2(1-p) + (2-p)[\alpha p - (\alpha^2 p^2 - 4\alpha p^2 + 4\alpha p)^{1/2}]}{2\alpha p^2} \qquad \text{(S2.2)}$$

The number of elastically active chains per a primary polymer chain is closely related to the cross-link density and is determined for the Flory distribution as[2]

$$\xi_{el}(p,\alpha) = \alpha \bar{N}_n(p)(1 - v(p,\alpha)^{1/2})^3 (1 + 2v(p,\alpha)^{1/2}) \quad , \qquad \text{(S2.3)}$$

where the number averaged degree of polymerization $\bar{N}_n$ is given by eq. (S1.3), and $v(p,\alpha)$ is the solution of the following equation

$$v = [1 + \alpha(1-v)(\bar{N}_n(p) - 1)]^{-2} \qquad \text{(S2.4)}$$

The cross-link density is calculated using eq. (S1.3) and (S2.3) as

$$c_0 = \frac{\xi_{el}(p,\alpha)}{\bar{N}_n(p)} \Phi \qquad \text{(S2.5)}$$

where Φ is the total volume fraction of polymer in gel. In the case of random copolymer network (RCN), the gel network encompasses the primary and secondary monomeric units.

We consider the random copolymer networks obtained due to the processes of cross-linking and inter-chain exchange as independent. Further, it is assumed that the reaction rate constants are the same for all configurations of the inter-chain exchange that are possible in polymers consisting of two types of monomeric units.

At a fixed system size, the total volume fraction of monomeric units at equilibrium degree of swelling of Stage 0 primary network is

$$\Phi^{(1)} = \phi + \phi_m^{(g)} = 1$$

Here, ϕ is the volume fraction of polymer in the swollen Stage 0 primary gel, and $\phi_m^{(g)}$ is volume fraction of the secondary monomers inside the Stage 0 gel. Superscript "(1)" denotes that the corresponding value characterizes Stage 1 of the gel growth. After polymerization (and cross-linking) of the secondary monomers, the total concentration of polymer chains in the gel is

$$C^{(1)} = c_0 \frac{\phi}{\phi_0} + \frac{1-\phi}{\bar{N}_n(p)}$$

Here, c_0 in the cross-link density of the primary network, and $\bar{N}_n(p)$ is the number averaged degree of polymerization of the secondary polymers given by eq. (S1.3). We calculate the concentration of primary polymer chains connecting two cross-linking points as $c_0 \phi / \phi_0$ under the assumption that there is no dangling chains in the primary gel. The number averaged degree of polymerization in the entire system is, by definition,

$$\bar{N}_n^{(1)} = \frac{\Phi^{(1)}}{C^{(1)}} = \left(c_0 \frac{\phi}{\phi_0} + \frac{1-\phi}{\bar{N}_n(p)} \right)^{-1} \tag{S2.6}$$

It is important to note that inter-chain exchange reactions do not change the total number of polymer chains and the product of the reactions exhibit the Flory MWD, eq. (S1.1).[6,7] The distribution parameter can be determined according to eq. (S1.3) as

$$p^{(1)} = 1 - 1 / \bar{N}_n^{(1)} \tag{S2.7}$$

In this random copolymer system, the number fraction of monomer units forming cross-links is

$$\alpha^{(1)} = \alpha_0 \phi + \alpha (1-\phi) \tag{S2.8}$$

where $\alpha_0 \approx c_0 (2\phi_0)^{-1}$ is the fraction of cross-linkers in the primary network assuming that each cross-link connects four elastically active chains.

We assume that the monomer units containing cross-linkers are distributed randomly along the random copolymer chains. Then, the sol fraction and cross-link density in the RCN are determined using the Dobson and Gordon theory as described above by substituting eqs. (S2.6)-(S2.8) into the respective eq. (S2.2) and (S2.5) to obtain

$$S_1^{(RCN)} = S(p^{(1)}, \alpha^{(1)}) \tag{S2.9}$$

$$c_1^{(RCN)} = \frac{\xi_{el}(p^{(1)}, \alpha^{(1)})}{\bar{N}_n^{(1)}} \tag{S2.10}$$

where $\bar{N}_n^{(1)}$ is given by eq. (S2.6) and we take into the account that $\Phi^{(1)} = 1$.

S3. Gel Lattice Spring Model (gLSM)

The analytical equations[1] used to model the stage-wise growth of a gel were incorporated into our gel lattice spring model (gLSM) computational technique briefly outlined below. The 3D gLSM[8–11] is a finite element approximation and allows us to numerically solve the dynamic equations that describe swelling of gels in the process of growth.

The gLSM is based on the two-fluid model for polymer networks.[12–14] It is assumed that the dynamics of the polymer network is purely relaxational, and the gel motion occurs solely due to the polymer-solvent interdiffusion. The frictional drag force due to the motion of the solvent is balanced by the forces acting on the swollen, deformed gel. Hence, the velocity of the polymer, $\mathbf{v}^{(p)}$, can be calculated as [9]

$$\mathbf{v}^{(p)} = \Lambda_0 (\phi/\phi_0)^{-3/2} (1-\phi) \nabla \cdot \hat{\boldsymbol{\sigma}} \tag{S3.1}$$

Here, the kinetic coefficient Λ_0 is dimensionless and calculated as [9] $\Lambda_0 = k_B T (v_0 \eta_0 l_0^2 t_0^{-1})^{-1}$, and is inversely proportional to the polymer-solvent friction coefficient η_0. Further, l_0 and t_0 denote the units of length and time respectively, and stress is measured in units of $k_B T / v_0$, where v_0 is the volume of a monomeric unit within a polymer chain.

Within the framework of the gLSM, a 3D gel sample is represented by a set of general linear hexahedral elements.[15,16] Initially, the sample is un-deformed and consists of $L_x \times L_y \times L_z$ identical cubic elements; here L_i is the number of elements in the i-direction, $i = x, y, z$. In the un-deformed state, each element is characterized by the volume fraction ϕ_0 and cross-link density c_0. Upon deformation, the elements move together with the polymer network so that the amount of polymer and number of cross-links within each hexahedral element remain equal to their initial values. Correspondingly, the volume fraction of polymer in the element $\mathbf{m} \equiv (i, j, k)$ is determined as $\phi(\mathbf{m}) = \phi_0 \Delta^3 / V(\mathbf{m})$, where Δ and $V(\mathbf{m})$ are the un-deformed element size and volume of the deformed element, respectively.

The gel energy per unit volume in the un-deformed state, $u(I_1, I_3)$, is expressed as a function of the first, I_1, and third, I_3, invariants of the strain tensor $\hat{\mathbf{B}}$:[8–10]

$$u(I_1, I_3) = u_{el}(I_1, I_3) + u_{\mathrm{FH}}(I_3) \tag{S3.2}$$

Here, $u_{el}(I_1, I_3) = \frac{c_0 v_0}{2}(I_1 - 3 - \ln I_3^{1/2})$ represents the free energy density of the neo-Hookean model for the elasticity of a polymer network with Gaussian chains. The second term on the right hand side of eq. (S3.2) describes free energy density due to the polymer-solvent interaction according to the Flory-Huggins model:

$$u_{\mathrm{FH}}(I_3) \equiv u_{\mathrm{FH}}(\phi) = I_3^{1/2} \left[(1-\phi)\ln(1-\phi) + \chi_{pm}\phi(1-\phi) \right] \tag{S3.3}$$

In eq. (S3.3), the volume fraction of polymer ϕ itself depends on I_3 as $\phi = \phi_0 I_3^{-1/2}$, where ϕ_0 is the volume fraction of polymer in the un-deformed state. In the simulations, we use χ_{pm} as the interaction between the monomers of the parent network (p) and the secondary monomer (m).

The gel dynamics is described through motion of the nodes of the elements caused by the forces acting on these nodes. In order to determine the nodal forces, we use the finite element approximation to calculate total energy of the gel as

$$U_{tot} = \Delta^3 \sum_{\mathbf{m}} u(\mathbf{m}) \tag{S3.4}$$

where the contribution from the element $\mathbf{m}$, $u(\mathbf{m})$, depends only on the coordinates of the nodes of this element denoted as $\mathbf{r}_n(\mathbf{m})$, $n = 1,2,\ldots,8$. (Note that $u(\mathbf{m})$ is the gel energy per unit volume of the un-deformed element as given in eq. (S3.2)) As a result, the force acting on node n within element $\mathbf{m}$ is given by the equation

$$\mathbf{F}_n(\mathbf{m}) = -\frac{\partial U_{tot}}{\partial \mathbf{r}_n(\mathbf{m})} \tag{S3.5}$$

The same node can belong to several elements, so the right hand side of the above equation contains contributions from all elements adjacent to a given node. Each node in the lattice can be labeled globally by assigning digits in $\mathbf{n} = (n_x, n_y, n_z)$. Finally, recall our assumption of purely relaxational dynamics, the velocity of the node $\mathbf{n}$ is proportional to the force and is determined from an equation similar to eq. (S3.1)

$$\frac{d\mathbf{r_n}}{dt} = M_\mathbf{n} \mathbf{F_n} \tag{S3.6}$$

where $M_\mathbf{n}$ is the mobility of the node proportional to the kinetic coefficient Λ_0. The details on the derivation and functional forms of $\mathbf{F_n}$ are provided in[8,10,11]. Our method of calculating the mobility $M_\mathbf{n}$ is described below.

The total force consists of the spring and pressure contributions, which are calculated separately within each element and then summed up at each of the nodes. We approximate the un-deformed material with the tri-linear cubical elements of size Δ, so that within each element, the deformation and velocity fields are

$$\mathbf{x}(t) = \sum_{n=1}^{8} N_n(\mathbf{X})\,\mathbf{x}_n(t) \tag{S3.7}$$

$$\mathbf{v}(t) = \sum_{n=1}^{8} N_n(\mathbf{X})\,\mathbf{v}_n(t) \tag{S3.8}$$

where $N_n(\mathbf{X})$, $n = 1,2,\ldots,8$, are the element (local) shape functions, which depend on the coordinate $\mathbf{X}$ in the undeform state. The element shape functions have the property

$$\sum_{n=1}^{8} N_n(\mathbf{X}) = 1 \tag{S3.9}$$

The strain tensor invariants I_1 and $J = I_3^{1/2}$ are calculated through the base vectors as

$$I_1 = \sum_{i=1}^{3} \mathbf{g}_i^2 \tag{S3.10}$$

$$J \equiv I_3^{1/2} = \mathbf{g}_1 \cdot (\mathbf{g}_2 \times \mathbf{g}_3) \tag{S3.11}$$

The base vectors $\mathbf{g}_i(t)$ is given by,

$$\mathbf{g}_i(t) = \frac{\partial \mathbf{x}(\mathbf{X},t)}{\partial X_i}, \quad i = 1,2,3 \tag{S3.12}$$

Within the finite element approximation, the base vectors are functions of the element nodal coordinates:

$$\mathbf{g}_i = \sum_{n=1}^{8} \frac{\partial N_n(\mathbf{X})}{\partial X_i}\mathbf{x}_n \tag{S3.13}$$

Since, the gel dynamics is considered to be in the overdamped limit, the velocity at the given node n of the gel element $\mathbf{m}$ is thus proportional to the force acting at that node

$$\Gamma_{\mathbf{n}} \mathbf{v}_{\mathbf{n}} = \mathbf{F}_{\mathbf{n}} \tag{S3.14}$$

Where $\Gamma_{\mathbf{n}}$ is the nodal friction coefficient. The nodal force is determined by using the global shape function $\Phi_{\mathbf{n}}$

$$\mathbf{F}_{\mathbf{n}} = \int_{V_0} \Phi_{\mathbf{n}}(\mathbf{X}) J \,\hat{\mathbf{F}}^{-1} \cdot \nabla_{\mathbf{X}} \cdot \hat{\boldsymbol{\sigma}} \, dV_0 \,,$$

where $\hat{\mathbf{F}}$ is the deformation-gradient tensor. It can be shown that the above equation provides the same result for the elemental nodal forces as eq. (S3.5). From the force balance equation (S3.1), we obtain

$$\mathbf{F}_{\mathbf{n}} = \Gamma_{\mathbf{n}} \mathbf{v}_{\mathbf{n}} \approx \left(\Lambda_0^{-1} \int_{V_0} (\phi_0^{-1}\phi)^{1/2} (1-\phi)^{-1} \Phi_{\mathbf{n}}(\mathbf{X}) \, dV_0 \right) \mathbf{v}_{\mathbf{n}}$$

Thus, the velocity at the nodes are obtained as

$$\mathbf{v}_{\mathbf{n}} = \mathbf{F}_{\mathbf{n}} / \Gamma_{\mathbf{n}} \tag{S3.15}$$

Here, $\Gamma_{\mathbf{n}}$ is a sum over all the elemental contribution to mobility of global node $\mathbf{n}$. Correspondingly, the elemental contribution to mobility of local node $l = 1, 2, \ldots, 8$ belonging to element $\mathbf{m}$ is calculated as

$$\Gamma_l(\mathbf{m}) = \Lambda_0^{-1} \int_{V_0(\mathbf{m})} (\phi_0^{-1}\phi)^{1/2} (1-\phi)^{-1} N_l(\mathbf{X}) \, dV_0 \,,$$

where N_l is the shape-function at node l and $\phi = \phi_0 J^{-1}$. The numerical integration in the above equation is performed using the 8-point Gaussian numerical integration scheme.

After all nodal velocities are obtained at a given time-step, the nodal coordinates are updated according to the simple Euler integration scheme.

gLSM for Stage 1 growing random copolymer (RCN)

Force calculations

The free energy for the RCN Stage 1 gel is given by:

$$U = \int u_{el}[c_1^{(RCN)}, I_1(t,\tau), I_3(t,\tau)] I_3^{1/2}(\tau) \, dV_0$$
$$+ \int u_{FH}[\phi_0 I_3^{-1/2}(t,\tau), \psi_0 I_3^{-1/2}(t,\tau)] I_3^{1/2}(t) \, dV_0$$

Here, the elastic contribution to the free energy density is given by:

$$u_{el}(t,\tau) = \frac{1}{2} c_1^{(RCN)} \left(I_1(t,\tau) - 3 - \frac{1}{2} \log\left[I_3(t,\tau) \right] \right), \tag{S3.16}$$

and the Flory-Huggins free energy density is

$$u_{\mathrm{FH}}(\phi,\psi) = (1-\phi-\psi)\ln(1-\phi-\psi) + \chi_{pm}\,\phi(1-\phi), \tag{S3.17}$$

where ϕ and ψ are the volume fractions of primary and secondary monomeric units in the polymer network, respectively. Note that the free energy depends on the history of deformation as I_1 and I_3 depends on the swollen Stage 0 gel at time τ. At Stage 0, the primary gel network swells in a liquid consisting of the secondary monomer to a degree of swelling λ_0 .The entrapped monomer undergoes polymerization and cross-linking according to ref [1]. The dimensionless cross-link density of after Stage 1 of growth is given by $c_1^{(RCN)}$. The volume fraction of the secondary monomeric units incorporated into polymer in gel after the stage 1 of growth is given by $\psi^{(1)}$ calculated as describe in the main text.

The main step in the gLSM formulation is the finite element approximation of the invariant $I_1(t,\tau)$ of the relative strain tensor $\hat{\mathbf{b}}(t,\tau)$. The relative strain tensor can be determined using the following decomposition:

$$\hat{\mathbf{b}}(t,\tau) = \hat{\mathbf{F}}(t)\cdot\hat{\mathbf{C}}^{-1}(\tau)\cdot\hat{\mathbf{F}}^{\mathrm{T}}(t)$$

Here, $\hat{\mathbf{F}}(t)$ is the deformation-gradient tensor associated with the deformation $\boldsymbol{X} \to \boldsymbol{x}(\boldsymbol{X},t)$

$$[\hat{\mathbf{F}}(t)]_{ij} = \frac{dx_i(\boldsymbol{X},t)}{dX_j}, \quad i,j = 1,2,3$$

and $\hat{\mathbf{C}}(t)$ is the left Cauchy-Green strain tensor

$$\hat{\mathbf{C}}(t) = \hat{\mathbf{F}}^{\mathrm{T}}(t)\cdot\hat{\mathbf{F}}(t)$$

The superscript "T" stands for the transposition operation. The first relative strain invariant is defined as $I_1(t,\tau) = \mathrm{tr}\,\hat{\mathbf{b}}(t,\tau)$, so it can be equivalently written in the following way

$$I_1(t,\tau)) = \mathrm{tr}[\hat{\mathbf{C}}^{-1}(\tau)\cdot\hat{\mathbf{C}}(t)]$$

The components of the Cauchy-Green strain tensor can be calculated as

$$[\hat{\mathbf{C}}(t)]_{ij} = \mathbf{g}_i(t)\cdot\mathbf{g}_j(t)$$

where $\mathbf{g}_i(t)$ are the base vectors

$$\mathbf{g}_i(t) = \frac{\partial \boldsymbol{x}(\boldsymbol{X},t)}{\partial X_i}, \quad i = 1,2,3$$

In order to calculate the coordinate derivatives of $I_1(t,\tau)$, we represent the latter in the component form

$$I_1(t,\tau) = \mathrm{tr}[\hat{\mathbf{F}}(t)\cdot\hat{\mathbf{C}}^{-1}(\tau)\cdot\hat{\mathbf{F}}^{\mathrm{T}}(t)] = \sum_{i,j,k=1}^{3}\left[\hat{\mathbf{F}}(t)\right]_{ij}\left[\hat{\mathbf{C}}^{-1}(\tau)\right]_{jk}\left[\hat{\mathbf{F}}^{\mathrm{T}}(t)\right]_{ki}$$

Thus, we have

$$\frac{\partial I_1(t,\tau)}{\partial x_n^{\alpha}(t)} = 2\sum_{i,j=1}^{3}\frac{\partial N_n(\mathbf{X})}{\partial X^i}\left[\hat{\mathbf{C}}^{-1}(\tau)\right]_{ij} g_j^{\alpha}(t) \tag{S3.18}$$

The matrix elements of $\hat{\mathbf{C}}^{-1}$ can be calculated analytically as

$$[\hat{\mathbf{C}}^{-1}]_{ij} = \varepsilon_{ikl}\varepsilon_{jmn}\frac{(\mathbf{g}_k\times\mathbf{g}_l)\cdot(\mathbf{g}_m\times\mathbf{g}_n)}{(\mathbf{g}_1\cdot(\mathbf{g}_2\times\mathbf{g}_3))^2}$$

In the above equation, ε_{ijk} is the Levi-Civita symbol, so the sets of indexes (i,k,l) and (j,m,n) are the cyclic permutations of $(1,2,3)$. No summation over the repeated indexes is performed. Thus,

$$\mathbf{F}_n^{(s)} = -\frac{c_1^{(RCN)} v_0}{2} \int\limits_{V_0} \frac{\partial I_1(t,\tau)}{\partial x_n^{\alpha}(t)} d\mathbf{X} \qquad \text{(S3.19)}$$

The final equation (S3.19) is used to calculate the elastic force for the stage 1 (RCN) . The last term in the eq. (S3.16) is calculated as

$$\frac{\partial \log[I_3(t,\tau)]}{\partial x_n} = \frac{1}{J(t)} \frac{\partial J(t)}{\partial x_n} \qquad \text{(S3.20)}$$

Here, we utilize the third invariant of the relative Finger strain tensor, $\hat{\mathbf{b}}(t,\tau)$, $I_3(t,\tau) = \det[\hat{\mathbf{b}}(t,\tau)] = I_3(t)/I_3(\tau)$.

Finally, the pressure force acting on the node n within an element is calculated as:

$$\mathbf{F}_n^{(P)} = \int\limits_{V_0} \mathbf{f}_n^{(P)}(\mathbf{X}) d\mathbf{X}, \qquad \text{(S3.21)}$$

where

$$\mathbf{f}_n^{(P)}(\mathbf{X}) = P(\mathbf{X}) \frac{\partial J(\mathbf{X})}{\partial \mathbf{x}_n} \qquad \text{(S3.22)}$$

and

$$P(\mathbf{X}) = \phi \frac{\partial u_{FH}(\phi,\psi)}{\partial \phi} - u_{FH}(\phi,\psi) + \psi \frac{\partial u_{FH}(\phi,\psi)}{\partial \psi} - u_{FH}(\phi,\psi) + \frac{1}{2} \frac{c_1^{(RCN)}}{J}.$$

Calculation of mobility for grown random copolymer network

Calculation of the mobility for the swelling primary network described above is generalized straightforwardly to the case of grown RCN. In the latter case the volume fraction of polymer in the random copolymer network, ϕ_{tot}, is calculated as (see the main text)

$$\phi_{tot}(t) = \phi^{(1)}[\lambda(t)] + \psi^{(1)}[\lambda(t)],$$

where $\phi^{(1)}(\lambda) = (1 - S_1^{(RCN)})\phi_0 \lambda^{-3}$ is the volume fraction of the primary monomeric units after removal of the sol fraction, and $\psi^{(1)}(\lambda) = (1 - S_1^{(RCN)})(1 - \phi_0 \lambda_0^{-3})(\lambda_0 / \lambda)^3$ is the volume fraction of the secondary monomers incorporated into the stage 1 RCN. Here, λ_0 is the equilibrium degree of swelling of the primary network in the solution containing the secondary monomer before polymerization followed by the simultaneous inter-chain exchange and cross-linking, i.e., at the end of stage 0.

The elemental contribution to mobility of local node $l = 1,2,\ldots,8$ belonging to element $\mathbf{m}$ is calculated as

$$\Gamma_l(\mathbf{m}) = \Lambda_0^{-1} \int\limits_{V_0(\mathbf{m})} (\phi_0^{-1}\phi_{tot})^{3/2} (1 - \phi_{tot})^{-1} N_l(\mathbf{X}) J \, dV_0 \qquad \text{(S3.23)}$$

where N_l is a nodal shape-function. We take into account that $\lambda(t) = J^{1/3}(t)$ in the equation for ϕ_{tot}. In the above equation for $\Gamma_l(\mathbf{m})$, the numerical integration over the reference element volume $V_0(\mathbf{m})$ is performed using the 8-point Gaussian numerical integration scheme.

Calculation of the Elastic Moduli

We use the neo-Hookean model to describe elasticity of a swollen gel - see eqs. (S3.2) and (S3.3) in the SI. Within this model, the shear modulus of a swollen gel depends only on the crosslink density c_0 and the equilibrium degree of swelling λ, $G_0 = c_0 / \lambda$, whereas the osmotic pressure contributes to the bulk modulus.

We utilize the method proposed in our earlier paper[11] to calculate the modulus of the gels. Below we briefly describe the calculation steps.

Linearization of the stress tensor $\hat{\boldsymbol{\sigma}}$ around a state of swelling equilibrium results in

$$\delta\hat{\boldsymbol{\sigma}}(t) = \lambda^{(L)}\,\mathrm{tr}[\hat{\boldsymbol{\varepsilon}}(t)]\hat{\mathbf{I}} + 2\mu^{(L)}\,\hat{\boldsymbol{\varepsilon}}(t)$$

where $\lambda^{(L)}$ and $\mu^{(L)}$ are the first and second Lame parameters, respectively, and $\hat{\mathbf{I}}$ is the unit tensor. The shear modulus G is equal to the second Lame parameter. After Stage 0 of growth, the shear modulus G_0 is

$$G_0 = c_0 / \lambda_0 ,$$

where c_0 is cross-link density in the as-prepared gel, and λ_0 is the degree of swelling of primary gel after Stage 0. For the RCN Stage 1 gel, the shear modulus G_1 is calculated as

$$G_1 = c_1^{(RCN)} \lambda_0 / \lambda_1$$

where $c_1^{(RCN)}$ is cross-link density of the random-copolymer network, and λ_1 is the degree of swelling of Stage 1 gel. The degree of swelling of gel characterizes the linear dimension of gel relative to its size in the un-deformed state. The size of swollen primary gel is denoted λ_0. As, $\lambda_0 = (V_0 / V_{ini})^{1/3}$, where V_0 is the volume of swollen primary gel and V_{ini} is the volume of the as-prepared (un-deformed) primary gel." We assume that the processes of polymerization and crosslinking of secondary chains followed by the inter-chain exchange take place within fixed volume V_0. The newly formed random copolymer network is un-deformed and has the volume V_0. After swelling, the RCN gel acquires the volume V_1, and we use $\lambda_1 = (V_1 / V_{ini})^{1/3}$ to characterize its size relative to the un-deformed size of the primary network. The size of swollen RCN relative its own un-deformed size, i.e., the actual degree of swelling, is λ_1 / λ_0 and hence, $G_1 = c_1^{(RCN)} \lambda_0 / \lambda_1$.

Determining the bulk modulus K requires calculation of the both Lame parameters because $K = \lambda + 2\mu / 3$. For Stage 0 gel, the first Lame parameter $\lambda_0^{(L)}$ is found equal to

$$\lambda_0^{(L)} = \left(\phi \frac{\partial \pi_{\mathrm{FH}}(\phi)}{\partial \phi} - \pi_{\mathrm{FH}}(\phi) \right)_{\mathrm{eq}}$$

where the Flory-Huggins osmotic pressure is given by eq (2) in the main text, the subscript "eq" means that the expression on the left-hand side is calculated under swelling equilibrium. For Stage 1 gel, the first Lame parameter $\lambda_1^{(L)}$ is calculated as

$$\lambda_1^{(L)} = \left(\phi \frac{\partial \pi_{\mathrm{FH}}(\phi,\psi)}{\partial \phi} + \psi \frac{\partial \pi_{\mathrm{FH}}(\phi,\psi)}{\partial \psi} - \pi_{\mathrm{FH}}(\phi,\psi) \right)_{\mathrm{eq}}$$

where the Flory-Huggins osmotic pressure is given by eq (4) in the main text, the subscript "eq" has the same meaning as above.

Finally, Young's modulus E for each stage of growth is calculated as [17]:

$$E = \frac{9KG}{3K + G}$$

Calculation of the average strain $\bar{\lambda}$

We define the average strain $\bar{\lambda}$ as $\bar{\lambda} = \sqrt{I_1 / 3}$, where I_1 is the first invariant of the Finger strain tensor. We calculate the value of I_1 using eq. (S3.10).

Calculation of the repulsion from a wall

We utilize the formalism of node-to-node contact as suggested in[18] to introduce repulsion between the freely moving gel nodes approaching the boundary constraints (walls). We calculate the distance $r_\perp$ of a freely moving node in a gel boundary element from the wall. For a node of a given element represented by the coordinates (x, y, z) , we calculate the normal distance of this node point (x, y, z) from the wall coordinates. For the case, where wall is chosen to be at $y = 0$, we assume that the point $(x, 0, z)$ on the wall will repel the approaching node point. Similarly, if the wall is along the line $x = 0$, we calculate the distance choosing the wall coordinate to be $(0, y, z)$. The repulsion forces are considered to be due to the short-ranged Morse potential as was utilized in[19], and are non-zero only if $r_\perp \le r_c$, where r_c is the cutoff distance. In this case, the force applied to the node X is given by $\mathbf{F}_X^1 = F_\mathrm{M}(r_\perp)\mathbf{n}$ due to normal distance between the sample node point and the wall coordinate, where $F_\mathrm{M}(r) = \frac{a_\mathrm{M} D_\mathrm{M}}{2}\left[\mathrm{e}^{a_\mathrm{M}(r_c - r)} - 1 \right]^2$ is the value of force. Here a_M and D_M are the interaction parameters. In simulations, we assign $r_c = 0.25$, $a_\mathrm{M} = 50$, and $D_\mathrm{M} = 10^{-1}$ which prevent the gel nodes from intersecting with the walls.

S4. Additional Figures

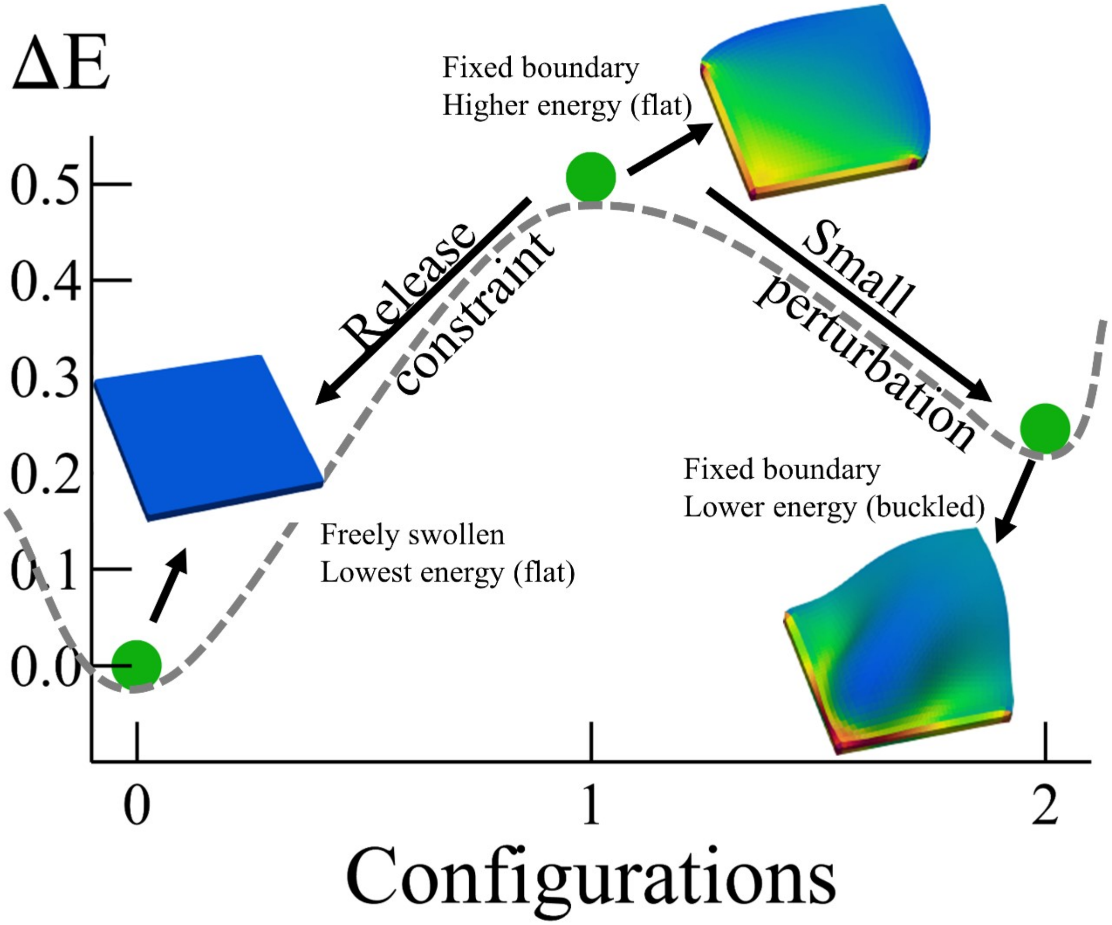


Figure S2 shows the difference in free energy (green disks) of the equilibrium swollen configurations of the Stage 0 primary gel compared with the free energy of the freely swollen equilibrium primary gel. Configuration 0 depicts the equilibrium configuration of the freely swollen Stage 0 gel. When the Stage 0 gel is bound by walls on the two sides $x = 0, y = 0$ and then swollen, the gel reaches a flat steady state depicted by Configuration 1. This is an unstable steady state. Upon addition of an isotropic noise to the gel nodes in Configuration 1, the gel attains a final buckled equilibrium structure. The point (green disk) at ‘2’ shows that the free energy of the buckled Configuration 2 is lower than the constrained flat state at Configuration 1. The gray dashed line is drawn to guide the eye.

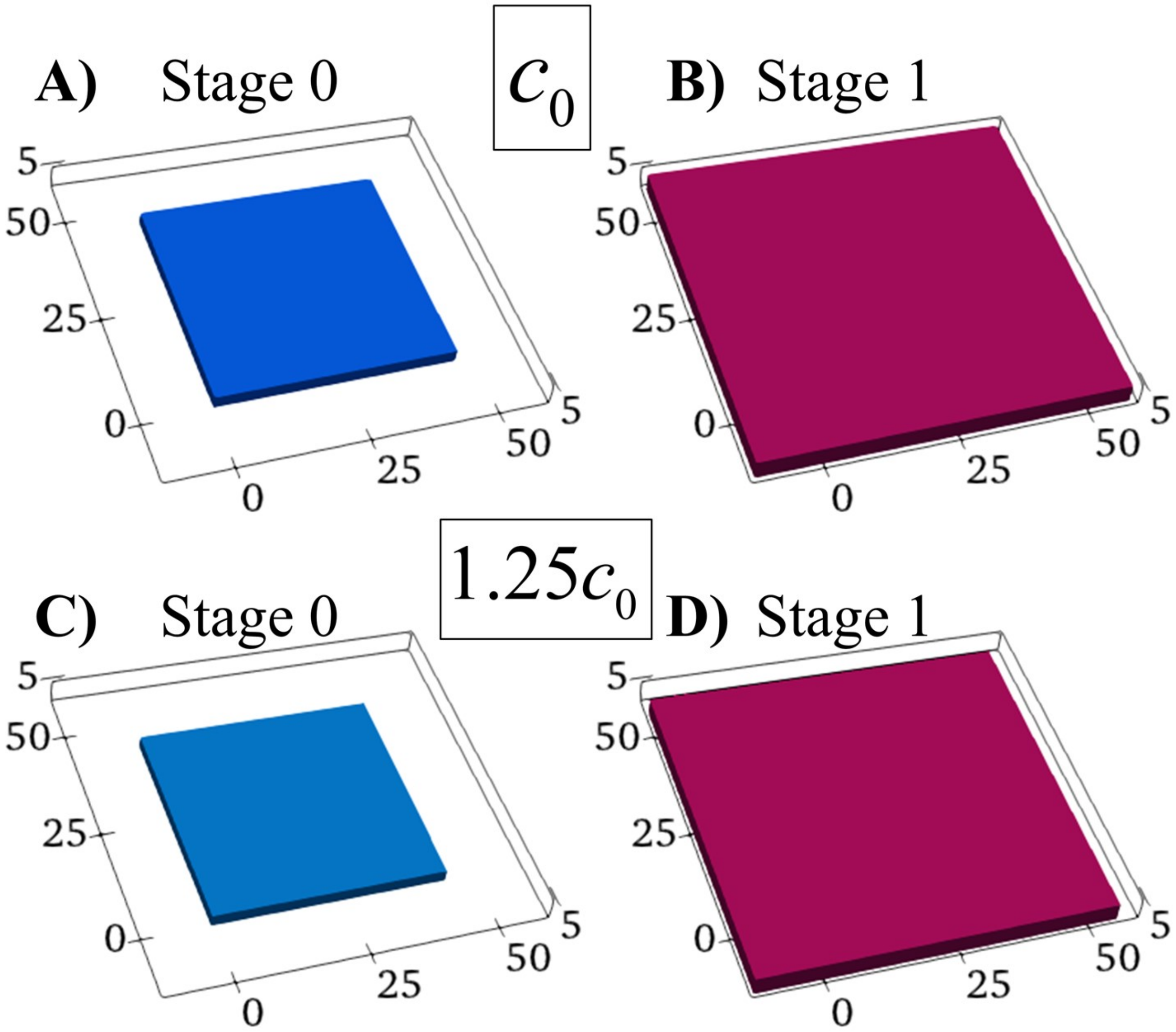


Figure S3 shows the final equilibrium configuration of the Stage 0 primary gels, (A) and (C), and the grown Stage 1 RCN gels, (B) and (D), for two different cross-link density of the parent gel. Cross-link density in (A) is $c_0 = 0.0013$ and in (B) $1.25c_0$ The cross-linker fraction for the grown Stage 1 RCN gels in (B) and (D) is $\alpha = 0.1$.

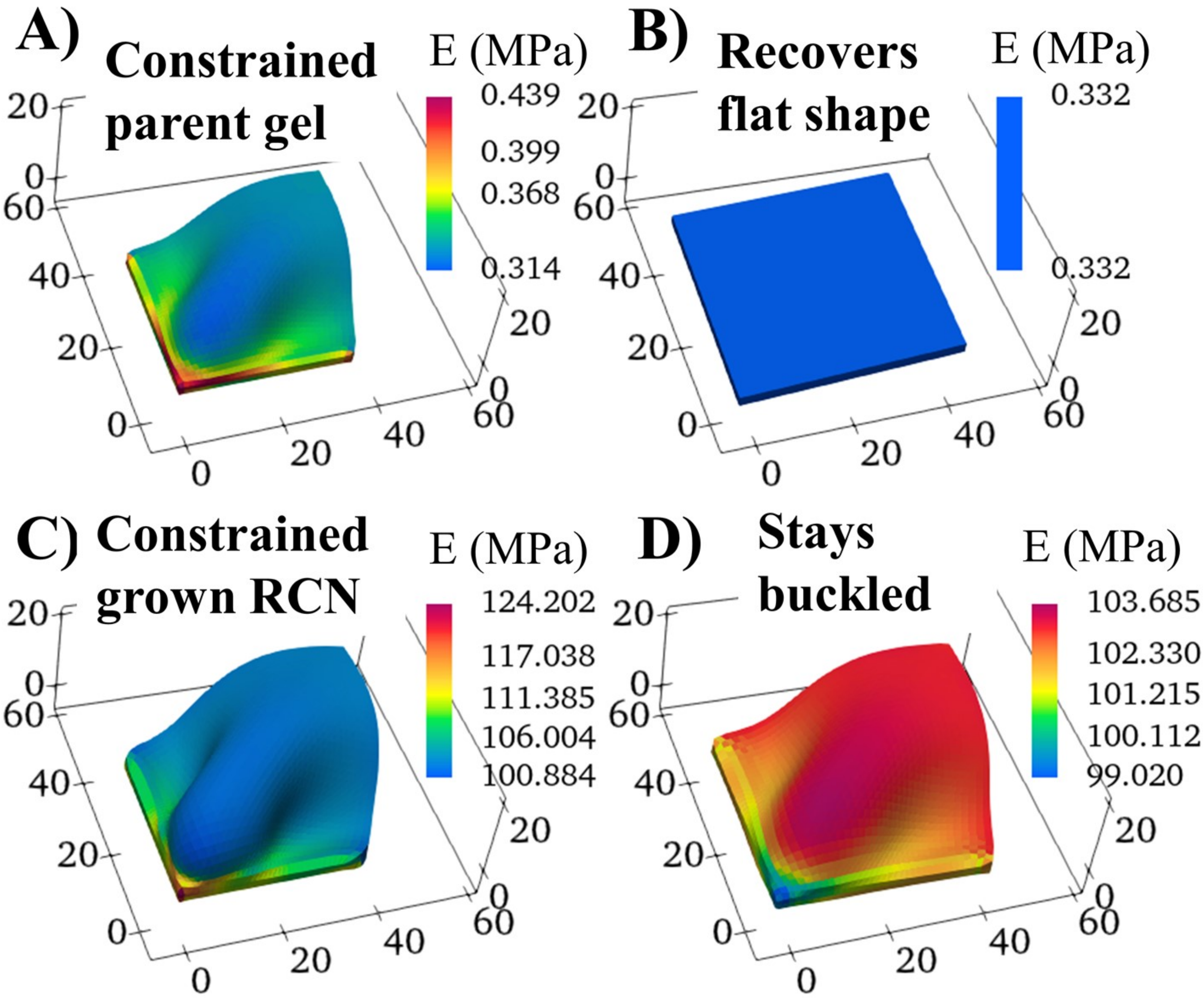


Figure S4 Shape changes due to gel swelling in square shaped gels of size $35 \times 35 \times 2$ due to confining boundaries at the left and bottom surfaces. Figure (A) shows the swollen "buckled" configuration of the Stage 0 gel. Upon release of the boundary constraints, the Stage 0 gel goes from the buckled (A) to the flat (B) configuration. Figure (C) shows the final swollen configuration of the grown Stage 1 RCN gel at $\alpha = 0.4$ where growth of Stage 1 started from the buckled configuration of Stage 0 gel shown in (A). Upon release of boundary constraints, the Stage 1 RCN gel does not relax back to a flat state but stays buckled (D). The color bars represent the Young's modulus, E.

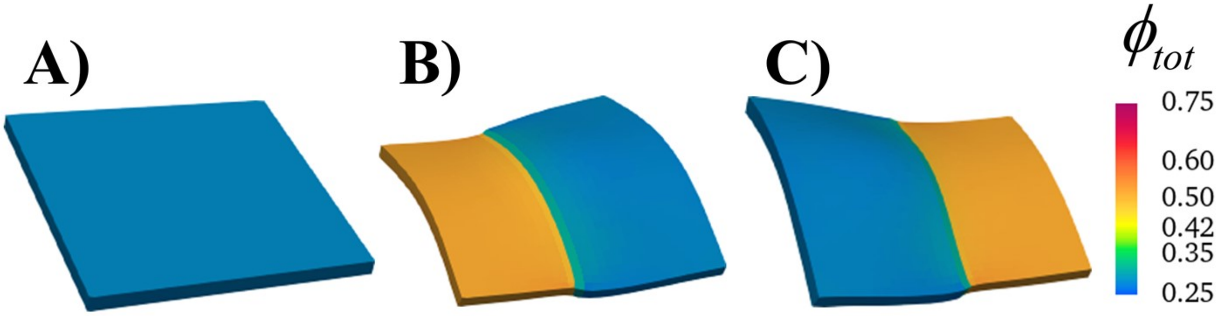


Figure S5 The final equilibrium configuration attained upon release of bounding walls in the patterned gel sample in Figure 5 in the main text. The gel samples were bound by walls at $X = 0$ and $Y = 0$. (A) The gel has uniform distribution of the secondary cross-links at $\alpha = 0.1$ and upon release relaxes to a flat state. (B) The left half of the gel has $\alpha = 0.4$ whereas the right half has $\alpha = 0.1$. Upon release of the boundary constraints, the gel takes the double roll shape. (C) The left half of the gel has $\alpha = 0.1$ and the right half has $\alpha = 0.4$. Upon release of the boundary constraints, the gel takes a similar double roll shape. The colors indicate the spatial distribution of the total volume fraction of polymer in the gel ϕ_{tot}.

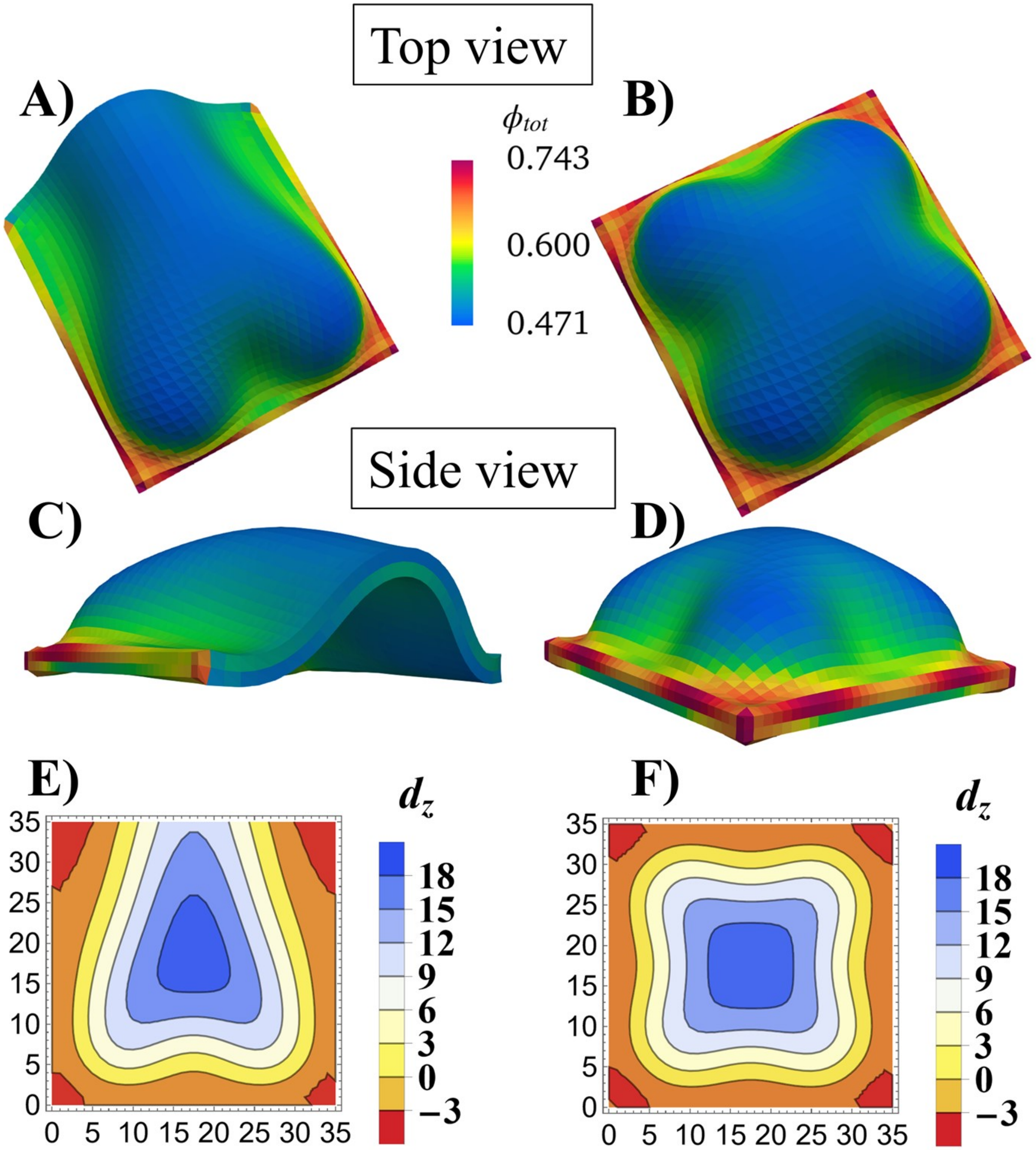
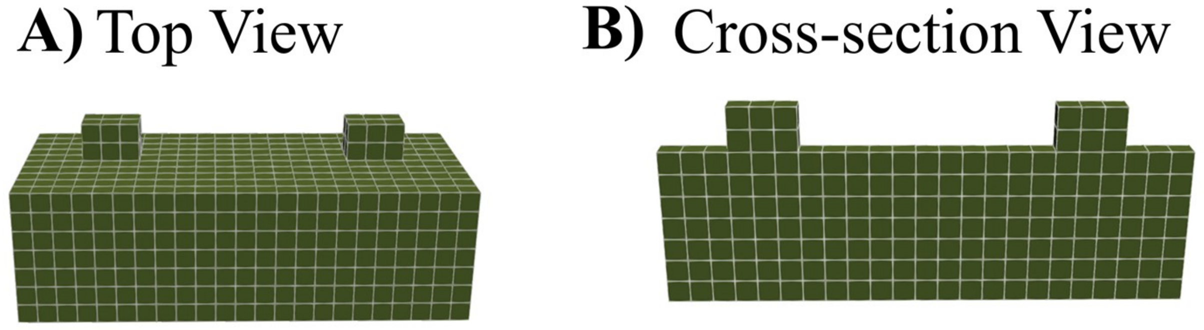


Figure S6 (A-B) Top view and (C-D) Side view of the equilibrium swollen state of the grown Stage 1 RCN gels where the samples of size $\alpha = 0.1$ are bound by walls at three sides, (A) and (C), and four sides, (B) and (D). The colors in (A) - (D) indicate the spatial distribution of the total volume fraction of polymer in the gel ϕ_{tot}. Figures (E)-(F) show a heat-map of the displacement d_z in the vertical direction of the middle layer of the gel elements with respect to a flat reference state where the mid-layer has the value of $Z = 1.3187$ for the Stage 1 gel as a function of the index of the gel nodes along the X and Y direction.



A) Top View

B) Cross-section View

Figure S7 (A) Top view and (B) Side view of the final swollen Stage 0 gel, which was prepared in the shape of the grown RCN Stage 1 gel shown in Fig. 7 in the main text. All the gel elements have the same volume fraction ϕ_0 and cross-link density c_0. The equilibrium degree of swelling of the swollen primary stage 0 gel is 1.3178.

Supplementary Movie 1

Release of boundary constraint of an equilibrated ‘buckled’ grown Stage 1 (RCN) gel prepared from a freely swollen ‘flat’ Stage 0 gel. Grown RCN gel relaxes to a flat state.

Supplementary Movie 2

Release of boundary constraint of an equilibrated ‘buckled’ grown Stage 1 (RCN) gel prepared from an equilibrated ‘buckled’ Stage 0 gel. Grown RCN gel stays buckled.

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