Electronic Supplementary Material (ESI) for Soft Matter.

Supporting Information
Controllable Growth of Interpenetrating or Random Copolymer Networks

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S0. List of notations used in the main text

c_0	Dimensionless crosslink density of primary gel
ϕ_0	Volume fraction of polymer in the un-deformed primary gel
$V_0^{(\mathrm{eq})}$	Volume of un-deformed sample of primary gel
ϕ	Volume fraction of the primary monomeric units incorporated into polymer in gel
V_k	Volume of gel sample after the k^{th} stage of growth
λ_k	Relative size (degree of swelling) of gel sample after the k^{th} stage of growth
λ_0	Degree of swelling of the primary gel
$\phi^{(k)}$	Volume fraction of the primary monomeric units incorporated to polymer in gel after the k^{th} stage of growth
ψ	Volume fraction of the secondary monomeric units incorporated into polymer in gel
$\psi^{(k)}$	Volume fraction of the secondary monomeric units incorporated into polymer in gel after the k^{th} stage of growth
$\phi_m^{(\mathrm{g})}$	Volume fraction of the secondary monomers in solution inside gel
ξ_m	Number fraction of the secondary monomers in solution inside gel
$\xi_m^{(k)}$	Number fraction of the secondary monomers in solution inside gel after the k^{th} stage of growth
$\phi_m^{(\mathrm{s})}$	Volume fraction of the secondary monomers in solution outside gel

$S_k^{(IPN)}$	Sol fraction of IPN after the k th stage of growth
$c_k^{(IPN)}$	Dimensionless crosslink density of IPN after the k th stage of growth
$S_k^{(RCN)}$	Sol fraction of RCN after the k th stage of growth
$c_k^{(RCN)}$	Dimensionless crosslink density of RCN after the k th stage of growth
σ_{el}	Elastic stress according to the neo-Hookean model
σ_{tot}	Total elastic stress
π_{FH}	Osmotic pressure of polymer in gel according to the Flory-Huggins theory
χ_{ps}	Flory-Huggins parameter for interactions between the primary monomer and solvent
χ_{pm}	Flory-Huggins parameter for interactions between the primary and secondary monomers
χ_{ms}	Flory-Huggins parameter for interactions between the secondary monomer and solvent
χ_0, χ_1	Interaction parameters for the system NIPA gel in water
T	Temperature
$\mu_m^{(\text{g})}$	Chemical potential of the secondary monomers in solution inside gel
$\mu_m^{(\text{s})}$	Chemical potential of the secondary monomers in solution outside gel
v_0	Volume of one molecular unit

S1. Equilibrium swelling

We consider a polymer network, which encompasses two types of monomeric units, A and B, and is immersed in a solution of the monomer B. The monomers A and B are the respective the primary and secondary units. The dimensionless (in the units of $k_B T$, where k_B is the Boltzmann constant and T is temperature) free energy of the system F_{tot} includes the contributions from the energy of the elastic deformation of the polymer network, $F_{\text{el}}^{(\text{g})}$, and the free energies of the media inside the gel, $F_{\text{FH}}^{(\text{g})}$, and outside the gel, $F_{\text{FH}}^{(\text{s})}$, according to the Flory-Huggins theory:

$$F_{tot} = F_{\text{el}}^{(\text{g})} + F_{\text{FH}}^{(\text{g})} + F_{\text{FH}}^{(\text{s})} \tag{S1.1}$$

The neo-Hookean model is used to calculate the elastic energy. In the most general form, $F_{\text{el}}^{(\text{g})}$ is written as the following function of the strain tensor invariants I_1 and I_3 [1-3]

$$F_{\text{el}}^{(\text{g})} = 2^{-1} c_0 v_0 V_g^{(0)} (I_1 - 3 - \ln I_3^{1/3})$$

Here, c_0 is the crosslink density, v_0 is the volume of one molecular unit (which is taken to be equal for all the species in the gel), and $V_g^{(0)}$ is the dimensionless volume (in the units of v_0) of the gel in the un-deformed state. For uniform swelling, the elastic energy can be written in terms of the ratio $V_g / V_g^{(0)}$, where V_g is the volume of the gel in the swollen state, as $F_{\text{el}}^{(\text{g})} = V_g^{(0)} f_{\text{el}}^{(\text{g})}(c_0, V_g / V_g^{(0)})$, where

$$f_{\text{el}}^{(\text{g})}(c_0, V_g / V_g^{(0)}) = \frac{3c_0v_0}{2}\left[(V_g / V_g^{(0)})^{2/3} - 1\right] - \frac{c_0v_0}{2}\log(V_g / V_g^{(0)}) \qquad \text{(S1.2)}$$

In the main text, we use the dimensionless crosslink density c_0 instead of c_0v_0.

The above equation for $F_{\text{el}}^{(\text{g})}$ is given for a single network. In the case of several interpenetrating networks (IPN), the elastic energy is a sum of a corresponding number of terms with the values of c_0 and $V_g^{(0)}$ specific to each network.

The Flory-Huggins free energy for the gel, $F_{\text{FH}}^{(\text{g})}$, includes the translational entropy of the mobile components in the solution (the solvent and dissolved monomer B), and the energies of interaction between all species present within the gel. The Flory-Huggins free energy $F_{\text{FH}}^{(\text{g})}$ depends on the volume fractions $\phi_\alpha^{(\text{g})} = N_\alpha^{(\text{g})} / V_g$, where $\alpha = a, b, m, s$ labels the respective monomeric units A and B constituting the polymer network, the dissolved secondary monomers, and the solvent particles, and $N_\alpha^{(\text{g})}$ is the number of units α within the gel. The dimensionless free energy density $f_{\text{FH}}^{(\text{g})} = F_{\text{FH}}^{(\text{g})} / V_g$ is given by the following equation:

$$\begin{aligned} f_{\text{FH}}^{(\text{g})} &= \phi_m^{(\text{g})} \ln \phi_m^{(\text{g})} + \phi_s^{(\text{g})} \ln \phi_s^{(\text{g})} \\ &\quad + \chi_{ps}\phi_a^{(\text{g})}\phi_s^{(\text{g})} + \chi_{pm}\phi_a^{(\text{g})}(\phi_m^{(\text{g})} + \phi_b^{(\text{g})}) + \chi_{ms}(\phi_m^{(\text{g})} + \phi_b^{(\text{g})})\phi_s^{(\text{g})} \end{aligned} \qquad \text{(S1.3)}$$

The first two terms on the right-hand side of the above equation correspond to the translational entropy of the solvent and solute. The Flory-Huggins interaction parameters χ_{ps}, χ_{pm}, and χ_{ms} determine the contributions from the interaction energies between the primary monomers and solvent, primary and secondary monomeric units, and secondary monomeric units and solvent, respectively. The secondary monomeric units incorporated into the polymer network (volume fraction $\phi_b^{(\text{g})}$) and present in the solution (volume fraction $\phi_s^{(\text{g})}$) are assumed to contribute equally to the interaction energies.

Taken together, the polymer network and the solution within the network constitute an incompressible system, i.e., $\sum_\alpha \phi_\alpha^{(\text{g})} = 1$. Hence, $\phi_s^{(\text{g})} + \phi_m^{(\text{g})} = 1 - \phi_a^{(\text{g})} - \phi_b^{(\text{g})}$ is the volume fraction of the solution inside the swollen polymer network. It is useful to define the number fraction of secondary monomeric units in the solution inside the gel as $\xi_m = N_m^{(\text{g})}(N_m^{(\text{g})} + N_s^{(\text{g})})^{-1}$ .Then, the volume fractions of the solute and solvent particles within the gel can be represented as $\phi_m^{(\text{g})} = \xi_m(1 - \phi - \psi)$ and $\phi_s^{(\text{g})} = (1 - \xi_m)(1 - \phi - \psi)$, respectively. Here, we introduced the notations $\phi = \phi_a^{(\text{g})}$ and $\psi = \phi_b^{(\text{g})}$ for the respective volume fractions of the primary and secondary monomeric units constituting the polymer network. The free energy density given by eq. (S1.3) can be written in the following final form

$$\begin{aligned} &f_{\mathrm{FH}}^{(\mathrm{g})}(\phi,\psi,\xi_m) = \\ &\qquad (1-\phi-\psi)\log(1-\phi-\psi)+(1-\phi-\psi)[\xi_m\log\xi_m+(1-\xi_m)\log(1-\xi_m)] \\ &\quad +\chi_{ps}\phi(1-\xi_m)(1-\phi-\psi)+\chi_{pm}\phi[\xi_m(1-\phi-\psi)+\psi] \\ &\quad +\chi_{ms}[\xi_m(1-\phi-\psi)+\psi](1-\xi_m)(1-\phi-\psi) \end{aligned}, \qquad \text{(S1.4)}$$

where the free energy of the gel is $F_{\mathrm{FH}}^{(\mathrm{g})} = V_g f_{\mathrm{FH}}^{(\mathrm{g})}(\phi,\psi,\xi_m)$.

The external solution contains only two components: the solvent and the secondary monomer B (solute). Given that $\beta = s,m$ stands for "solvent" and "monomer", the volume fractions of these components in the solution are $\phi_\beta^{(\mathrm{s})} = N_\beta^{(\mathrm{s})}/V_s$. $N_\beta^{(\mathrm{s})}$ is the number of particles β in the external solution, and V_s is the solution volume. Due to the incompressibility of the external solution, $\phi_s^{(\mathrm{s})}+\phi_m^{(\mathrm{s})}=1$. The Flory-Huggins free energy of the external solution can be formulated as a function of $\phi_m^{(\mathrm{s})}$ to obtain $F_{\mathrm{FH}}^{(\mathrm{s})} = V_s f_{\mathrm{FH}}^{(\mathrm{s})}(\phi_m^{(\mathrm{s})})$ with the free energy density of

$$f_{\mathrm{FH}}^{(\mathrm{s})}(\phi_m^{(\mathrm{s})}) = \phi_m^{(\mathrm{s})}\ln\phi_m^{(\mathrm{s})}+(1-\phi_m^{(\mathrm{s})})\ln(1-\phi_m^{(\mathrm{s})})+\chi_{ms}\phi_m^{(\mathrm{s})}(1-\phi_m^{(\mathrm{s})}) \qquad \text{(S1.5)}$$

Thus, the system considered here is described by the following dimensionless free energy F_{tot}

$$F_{tot} = V_g^{(0)} f_{\mathrm{el}}^{(\mathrm{g})}(c_0, V_g/V_g^{(0)}) + V_g f_{\mathrm{FH}}^{(\mathrm{g})}(\phi,\psi,\xi_m) + V_s f_{\mathrm{FH}}^{(\mathrm{s})}(\phi_m^{(\mathrm{s})}) \qquad \text{(S1.6)}$$

where the energy densities $f_{\mathrm{el}}^{(\mathrm{g})}$, $f_{\mathrm{FH}}^{(\mathrm{g})}$, and $f_{\mathrm{FH}}^{(\mathrm{s})}$ are given by the respective equations (S1.2), (S1.4), and (S1.5).

The gel and the external solution are two parts (phases) of the same system, so that $V_g + V_s = V_{tot}$, where $V_{tot} = const$ is the volume of the system. Swelling or de-swelling of the gel results in changing both V_g and $V_s = V_{tot} - V_g$, and redistribution of $N_s^{(g)} + N_s^{(\mathrm{s})} = N_s^{(tot)} = const$ particles of the solvent and $N_m^{(g)} + N_m^{(\mathrm{s})} = N_m^{(tot)} = const$ of the solute between the external solution and gel phases. Correspondingly, the volume fraction of secondary monomer in the outside solution, $\phi_m^{(\mathrm{s})}$, and the monomer content in the solution inside the gel, ξ_m, are related to each other as

$$\phi_m^{(\mathrm{s})} = \frac{N_m^{(tot)} - N_m^{(\mathrm{g})}}{V_{tot} - V_g} = \frac{N_m^{(tot)} - \xi_m[V_g - (N_a^{(\mathrm{g})} + N_b^{(\mathrm{g})})]}{V_{tot} - V_g} \qquad \text{(S1.7)}$$

In equilibrium state of the swollen gel, the free energy F_{tot} of the system exhibits a minimum. Therefore, the equilibrium is determined by the following two equations

$$\left(\frac{\partial F_{tot}}{\partial V_g}\right)_{\xi_m} = 0 \qquad \text{(S1.8)}$$

$$\left(\frac{\partial F_{tot}}{\partial \xi_m}\right)_{V_g} = 0 \tag{S1.9}$$

The partial derivatives in eqs. (S1.8) and (S1.9) are calculated taking into account that $\phi = N_a^{(\mathrm{g})} / V_g$, $\psi = N_a^{(\mathrm{g})} / V_g$, $V_s = V_{tot} - V_g$, and accounting for eq. (S1.7). After calculating the derivatives, it is convenient to take the limit of a large system, where $N_s^{(tot)} \to \infty$, $N_m^{(tot)} \to \infty$, $V_{tot} \to \infty$, but $N_m^{(tot)} / V_{tot} = const = \phi_m^{(\mathrm{s})}$. The latter assumptions allow us to consider $\phi_m^{(\mathrm{s})}$ as a given constant in the resulting equations for the equilibrium state.

Equation (S1.8) provides the condition for mechanical equilibrium given by eq. (1) in the main text, where

$$\sigma_{tot} = V_g^{(0)} \frac{\partial f_{\mathrm{el}}^{(\mathrm{g})}}{\partial V_g} \tag{S1.10}$$

and

$$\pi_{\mathrm{FH}} = -\left(\frac{\partial (F_{\mathrm{FH}}^{(\mathrm{g})} + F_{\mathrm{FH}}^{(\mathrm{s})})}{\partial V_g}\right)_{\xi_m} \tag{S1.11}$$

Calculating the derivative in eq. (S1.10) results in

$$\sigma_{tot} = c_0 v_0 (V_g^{(0)} / V_g)^{1/3} - \frac{c_0 v_0}{2} V_g^{(0)} / V_g \quad ,$$

After noting that $V_g / V_g^{(0)} = \lambda^3$, where λ is the degree of swelling, the above equation is re-written in the following form:

$$\sigma_{tot} = \sigma_{el}(c_0, \lambda) = \frac{c_0}{\lambda^3}\left(\lambda^2 - \frac{1}{2}\right) \tag{S1.12}$$

In the main text, we use the function $\sigma_{el}(c_0, \lambda)$ to denote the elastic stress in a gel, which consists of a single network. In the case of an interpenetrating network, σ_{tot} is a sum of a corresponding number of terms like in eq. (S1.12), and each contribution depends on the corresponding values of crosslink density and degree of swelling in the individual networks.

The derivative with respect of V_g in eq. (S1.11) yields the equation for the Flory-Huggins osmotic pressure:

$$\pi_{\mathrm{FH}} = \phi \frac{\partial f_{\mathrm{FH}}^{(\mathrm{g})}}{\partial \phi} + \psi \frac{\partial f_{\mathrm{FH}}^{(\mathrm{g})}}{\partial \psi} - f_{\mathrm{FH}}^{(\mathrm{g})} - \left((\phi_m^{(\mathrm{s})} - \xi_m) \frac{\partial f_{\mathrm{FH}}^{(\mathrm{s})}}{\partial \phi_m^{(\mathrm{s})}} - f_{\mathrm{FH}}^{(\mathrm{s})} \right)$$

After substituting eqs. (S1.4) and (S1.5) into the above equation, we obtain the Flory-Huggins osmotic pressure in the following form:

$$\begin{aligned}\pi_{\mathrm{FH}}(\phi,\psi,\xi_m,\phi_m^{(\mathrm{s})}) &= -[\phi+\psi+\ln(1-\phi-\psi)] \\ &-[\chi_{ps}+(\chi_{pm}-\chi_{ps}-\chi_{ms})\xi_m+\chi_{ms}\xi_m^2]\phi(\phi+\psi) \\ &-\chi_{ms}(1-\xi_m)^2\psi(\phi+\psi)+\chi_{pm}\phi\psi \\ &+\xi_m\ln\frac{\phi_m^{(\mathrm{s})}}{\xi_m}+(1-\xi_m)\ln\frac{1-\phi_m^{(\mathrm{s})}}{1-\xi_m}+\chi_{ms}(\xi_m-\phi_m^{(\mathrm{s})})^2\end{aligned} \tag{S1.13}$$

Finally, calculating the derivative with respect of ξ_m in eq. (S1.9) leads to the equation for the chemical equilibrium in the system. By utilizing eq. (S1.7), eq. (S1.9) can be transformed to yield the following

$$(1-\phi-\psi)^{-1}\frac{\partial f_{\mathrm{FH}}^{(\mathrm{g})}}{\partial\xi_m}=\frac{\partial f_{\mathrm{FH}}^{(\mathrm{s})}}{\partial\phi_m^{(\mathrm{s})}}$$

The above equation is equivalent to

$$\frac{\partial f_{\mathrm{FH}}^{(\mathrm{g})}}{\partial\phi_m^{(\mathrm{g})}}=\frac{\partial f_{\mathrm{FH}}^{(\mathrm{s})}}{\partial\phi_m^{(\mathrm{s})}} \quad ,$$

which equates the chemical potentials of the secondary monomer in the solutions inside and outside the gel, i.e., to eq. (2) in the main text, where

$$\begin{aligned}\mu_m^{(\mathrm{g})}(\phi,\psi,\xi_m) &= \frac{\partial f_{\mathrm{FH}}^{(\mathrm{g})}}{\partial\phi_m^{(\mathrm{g})}} \\ &= \ln\frac{\xi_m}{1-\xi_m}-2\chi_{ms}[\xi_m(1-\phi)+(1-\xi_m)\psi]-(\chi_{ps}+\chi_{ms}-\chi_{pm})\phi\end{aligned} \tag{S1.14}$$

and

$$\mu_m^{(\mathrm{s})}(\phi_m^{(\mathrm{s})})=\frac{\partial f_{\mathrm{FH}}^{(\mathrm{s})}}{\partial\phi_m^{(\mathrm{s})}}=\ln\frac{\phi_m^{(\mathrm{s})}}{1-\phi_m^{(\mathrm{s})}}-2\chi_{ms}\phi_m^{(\mathrm{s})} \tag{S1.15}$$

S2. Polymerization

The absorbed monomeric units undergo the reversible step 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 by the following system of rate equations for the dimensionless (in the units of v_0^{-1}) concentrations n_k of linear chains containing k monomeric units

$$\frac{dn_k}{dt}=-2\gamma_- n_k-2\gamma_+ n_1 n_k+2\gamma_- n_{k+1}+2\gamma_+ n_1 n_{k-1}, \quad k\geq 2 \tag{S2.1}$$

Note that

$$\sum_{k=1} k n_k(t)=\phi_m^{(\mathrm{g})}=\xi_m(1-\phi-\psi)=const \tag{S2.2}$$

because the total number of monomers does not change during the polymerization reaction. For this reason, eq. (S2.1) is given only for $k\geq 2$.

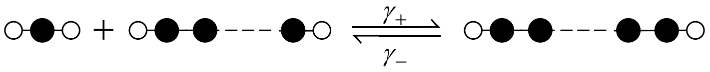

Fig. S1. Schematic representation of the polymerization process.

When the polymerization reaches the state of equilibrium, $dn_k / dt = 0$, $k \geq 1$, the equilibrium concentrations n_k correspond to the Flory MWD

$$n_k = p^{k-1} n_1, \quad k \geq 1 \tag{S2.3}$$

where $p = \gamma_+ n_1 / \gamma_-$ is the distribution parameter. (The Flory MWD $p_k = (1-p)p^{k-1}$ is obtained by normalization of eq. (S2.3), so that $\sum_{k=1} p_k = 1$.) To find the equilibrium value of p (or n_1), we utilize eq. (S2.2) to obtain

$$\frac{p}{(1-p)^2} = \frac{\gamma_+}{\gamma_-} \phi_m^{(\mathrm{g})}$$

The distribution parameter p is found from the above equation to be

$$p = \frac{1 + 2R - \sqrt{1+4R}}{2R} \tag{S2.4}$$

where $R = \gamma_+ \phi_m^{(\mathrm{g})} / \gamma_-$. Correspondingly, the concentration of monomeric units not included in the polymer chains is $n_1 = \gamma_- p / \gamma_+$.

The number and weight averaged degrees of polymerization are given by the following respective equations:

$$\bar{N}_n(p) = \frac{\sum\limits_{k=1} k n_k}{\sum\limits_{k=1} n_k} = \frac{1}{1-p} \tag{S2.5}$$

$$\bar{N}_w(p) = \frac{\sum\limits_{k=1} k^2 n_k}{\sum\limits_{k=1} k n_k} = \frac{1+p}{1-p} \tag{S2.6}$$

Finally, we use the ratio of polymerization rate constants $\gamma_+ / \gamma_- > 2 \times 10^4$ to ensure that the polymers formed during polymerization are relatively long, $\bar{N}_n > 100$.

S3. Crosslink density and sol fraction

The crosslinking 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 crosslinking is characterized by the crosslink density in gel, c_0, and the weight fraction of the sol, S. By definition, the crosslink density is the concentration of the elastically active polymer strands connecting two crosslinks.

We utilize the theory of tree-like branched polymers by Dobson and Gordon to calculate c_0 and S [4,5]. Theories that do not account for the presence of cyclic configurations are in general not applicable to crosslinked polymers. It is, however, argued that the theory of tree-like polymer structures can nevertheless be used to describe densely crossinked systems like vulcanized rubbers, where there are many crosslinks per polymer chain [6]. Here, we use the theory by Dobson and Gordon as outlined in ref. [7].

S3.1 Interpenetrating Polymer Network (IPN)

We assume that the number fraction α of the monomeric units in the polymer chains can form crosslinks. The polymers are obtained through the polymerization process described in Section S2, and exhibit the Flory MWD. Upon crosslinking, the macroscopic network (gel) exits in the system if $\alpha \geq \alpha_{cr}$, where the critical value α_{cr} is [4]

$$\alpha_{cr} = (\bar{N}_w - 1)^{-1} \tag{S3.1}$$

Here, $\bar{N}_w$ is the weight averaged degree of polymerization given by eq. (S2.6). The value of the sol fraction depends on α and on the Flory distribution parameter p [4]

$$S(p,\alpha) = \frac{2(1-p)+(2-p)[\alpha p - (\alpha^2 p^2 - 4\alpha p^2 + 4\alpha p)^{1/2}]}{2\alpha p^2} \tag{S3.2}$$

The number of elastically active chains per a primary polymer chain is closely related to the crosslink density and is determined for the Flory distribution as [5]

$$\xi_{el}(p,\alpha) = \alpha \bar{N}_n(p)(1 - v(p,\alpha)^{1/2})^3(1 + 2v(p,\alpha)^{1/2}) \quad , \tag{S3.3}$$

where the number averaged degree of polymerization $\bar{N}_n$ is given by eq. (S2.5), and $v(p,\alpha)$ is the solution of the following equation

$$v = [1 + \alpha(1-v)(\bar{N}_n(p) - 1)]^{-2} \tag{S3.4}$$

At each stage of the growth, we proceed as follows to characterize the interpenetrating network obtained by crosslinking the polymers inside the swollen gel. First, we use the volume fraction of monomers inside the gel at equilibrium, $\phi_m^{(g)}$, to calculate the Flory distribution parameter p according to eq. (S2.3). The sol fraction $S^{(IPN)}$ is then determined from eq. (S3.2).

Second, we use the calculated p to determine the number of elastically active chains per a primary polymer chain ξ_{el} from eqs. (S3.3) and (S3.4). The crosslink density is calculated by multiplying the obtained ξ_{el} by the concentration of polymer chains $\sum_{k=1} n_k = \phi_m^{(g)} / \bar{N}_n$:

$$c^{(IPN)} = \frac{\xi_{el}\phi_m^{(g)}}{\bar{N}_n} \tag{S3.5}$$

S3.2 Random Copolymer Network (RCN)

The formalism described in the previous section can be adapted to consider the random copolymer networks obtained due to the interchain exchange. For this purpose, we assume that the processes of crosslinking and interchain exchange can be considered 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

$$\Phi^{(k)} = \phi^{(k-1)} + \psi^{(k-1)} + \phi_m^{(\mathrm{g})}$$

and the total concentration of polymer chains

$$C^{(k)} = \frac{\phi^{(k-1)} + \psi^{(k-1)}}{\bar{N}_n^{(k-1)}} + \frac{\phi_m^{(\mathrm{g})}}{\bar{N}_n(p)}$$

do not change for both the direct [8] and end-group [9] inter-chain exchange reactions. In the above equation, k labels the stage of growth, $\bar{N}_n^{(k-1)}$ is the number averaged degree of polymerization of the polymer chains, which make up the RCN at the stage $k-1$, and $\bar{N}_n(p)$ is that of the secondary polymers given by eq. (S2.5). The number averaged degree of polymerization in the entire system is, by definition,

$$\bar{N}_n^{(k)} = \frac{\Phi^{(k)}}{C^{(k)}} = \left(\frac{1-g}{\bar{N}_n^{(k-1)}} + \frac{g}{\bar{N}_n(p)} \right)^{-1} \tag{S3.6}$$

where g is the number fraction of the secondary monomeric units acquired during gel swelling

$$g = \frac{\phi_m^{(\mathrm{g})}}{\phi^{(k-1)} + \psi^{(k-1)} + \phi_m^{(\mathrm{g})}}$$

When the exchange reaction reaches equilibrium, the product of the reaction is a random copolymer, which exhibits the Flory MWD [8,9]. The distribution parameter can be determined according to eq. (S2.5) as

$$p^{(k)} = 1 - 1/\bar{N}_n^{(k)} \tag{S3.7}$$

In this random copolymer system, the number fraction of monomer units capable of forming crosslinks is

$$\alpha^{(k)} = \frac{\alpha_0 \phi^{(k-1)} + \alpha\left(\psi^{(k-1)} + \phi_m^{(\mathrm{g})}\right)}{\phi^{(k-1)} + \psi^{(k-1)} + \phi_m^{(\mathrm{g})}} \tag{S3.8}$$

where α_0 is the fraction of crosslinkers in the primary gel discussed see below.

We assume that the monomer units containing crosslinkers are distributed randomly along the random copolymer chains. Then, the sol fraction and crosslink density in the RCN are determined using the Dobson and Gordon theory by substituting eqs. (S3.7) and (S3.8) into the respective equations (S3.2) and (S3.3), (S3.4) to obtain

$$S_k^{(RCN)} = S(p^{(k)}, \alpha^{(k)}) \tag{S3.9}$$

$$c_k^{(RCN)} = \frac{\xi_{el}(p^{(k)}, \alpha^{(k)})}{\bar{N}_n^{(k)}} \left(\phi^{(k-1)} + \psi^{(k-1)} + \phi_m^{(\mathrm{g})} \right) \tag{S3.10}$$

where $\bar{N}_n^{(k)}$ is given by eq. (S3.6).

To calculate the fraction of monomeric units containing a crosslinker in the primary network, α_0, we assume that there are four elastically active chains connected at each crosslink. Therefore, $\alpha_0 \approx c_0 (2\phi_0)^{-1}$ because removal of one crosslink from the primary network reduces the number of elastically active chains by two. (Recall that c_0 and ϕ_0 are the respective crosslink density and the volume fraction of polymer in the un-deformed primary gel.)

Finally, when considering the first stage of growth, $k=1$, we take $\phi^{(0)}=\phi$, where ϕ is the volume fraction of polymer in the primary gel, and $\psi^{(0)}=0$ (i.e., there are as yet no secondary monomers in the network). For the concentration of polymer chains, we use the concentration of polymer chains connecting two crosslinking points $C=c_0\phi/\phi_0$, which is written under the assumption that there is no dangling chains in the primary gel. Then, at $k=1$, the number averaged degree of polymerization $\bar{N}_n^{(0)}$ in eq. (S3.6) is $\bar{N}_n^{(0)}=\phi_0/c_0$. Thus, all values needed for application of eqs. (S3.6)-(S3.10) at $k=1$ are defined.

S4. Multistage growth of the IPN gel

The following equations must be solved with respect to λ and ξ_m in order to determine the size λ_n of the IPN gel sample and the secondary monomer content $\xi_m^{(n)}$ in the solution within the sample after the n th stage of growth:

$$\sigma_{el}(c_0,\lambda)+\sum_{k=1}^{n}\sigma_{el}(c_k^{(IPN)},\lambda/\lambda_{k-1})=\pi_{\mathrm{FH}}[\phi(\lambda),\psi^{(n)}(\lambda),\xi_m,\phi_m^{(\mathrm{s})}] \tag{S4.1}$$

$$\mu_m^{(\mathrm{g})}[\phi(\lambda),\psi^{(n)}(\lambda),\xi_m]=\mu_m^{(\mathrm{s})}(\phi_m^{(\mathrm{s})}) \tag{S4.2}$$

Here, ϕ and $\psi^{(n)}$ are the volume fractions of the primary monomeric units and secondary monomeric units acquired during n stages of growth, respectively. The volume fractions ϕ and $\psi^{(n)}$ are the following functions of the degree of swelling λ:

$$\phi(\lambda)=\phi_0\lambda^{-3} \tag{S4.3}$$

$$\psi^{(n)}(\lambda)=\psi_0^{(n)}(\lambda_{n-1}/\lambda)^3 \tag{S4.4}$$

The constant $\psi_0^{(n)}$ in eq. (S4.4) is calculated as

$$\psi_0^{(n)}=\psi^{(n-1)}(\lambda_{n-1})+\xi_m^{(n-1)}(1-S_n^{(IPN)})\left[1-\phi(\lambda_{n-1})-\psi^{(n-1)}(\lambda_{n-1})\right] \tag{S4.5}$$

The dimensionless crosslink density of the newly formed network $c_n^{(IPN)}$ in eq. (S4.1), and the sol fraction $S_n^{(IPN)}$ in eq. (S4.5) are calculated using the theory developed by Dobson and Gordon[4,5] as described in the section S3.1 of the SI.

Thus, the stepwise process of growth is described by the iterative procedure, which requires solving the non-linear algebraic equations at each step.

S5. Multistage growth of the RCN gel

Similar to the IPN gel, an iterative procedure can be used to describe the step-by-step growth of the RCN gel. Size of the RCN sample after $n\geq 1$ stages of growth is found from the following equations for the swelling equilibrium (compare with eqs. (S4.1) and (S4.2) for the IPN):

$$\sigma_{el}(c_n^{(RCN)},\lambda/\lambda_{n-1})=\pi_{\mathrm{FH}}[\phi^{(n)}(\lambda),\psi^{(n)}(\lambda),\xi_m,\phi_m^{(\mathrm{s})}] \tag{S5.1}$$

$$\mu_m^{(\mathrm{g})}[\phi^{(n)}(\lambda),\psi^{(n)}(\lambda),\xi_m]=\mu_m^{(\mathrm{s})}(\phi_m^{(\mathrm{s})}) \tag{S5.2}$$

Here, $\phi^{(n)}$ and $\psi^{(n)}$ are the volume fractions of the respective primary and secondary monomers incorporated into the RCN after the n^{th} stage of growth. The function $\phi^{(n)}(\lambda)$ is defined as

$$\phi^{(n)}(\lambda) = \phi_0 \lambda^{-3} \prod_{k=1}^{n} (1 - S_k^{(RCN)}) \tag{S5.3}$$

whereas $\psi^{(n)}(\lambda)$ is given by eq. (S4.4), and the constant $\psi_0^{(n)}$ is calculated as

$$\psi_0^{(n)} = (1 - S_n^{(RCN)}) \left[\psi^{(n-1)}(\lambda_{n-1}) + \xi_m^{(n-1)} (1 - \phi^{(n-1)}(\lambda_{n-1}) - \psi^{(n-1)}(\lambda_{n-1})) \right] \tag{S5.4}$$

In the RCN gel, the values of dimensionless crosslink density $c_k^{(RCN)}$ in eq. (S5.1) and sol fraction $S_k^{(RCN)}$ in eqs. (S5.3) and (S5.4), where the subscript $k = 1, 2, ..., n$ labels the stage of growth, are calculated as described in Section S3.2 of the SI.

It is important to note that due to the interchain exchange, the RCN is in the un-deformed state after each stage of growth as seen from eq. (S5.1). It is also worth noting that the amount of primary monomers in the RCN , eq. (S5.3), decreases from stage to stage because of the sol fraction removal.

S6. Additional calculations

We now discuss the dependence of the gel growth on three parameters: the crosslink density, c_0, the volume fraction of polymer in the undeformed state of the primary gel, ϕ_0, and the ratio of the polymerization rate constants γ_+ / γ_-. These parameters are kept constant throughout of the main text.

S6.1 Effect of crosslink density c_0 on the gel swelling

Stage 0: Figure S2 shows the equilibrium degree of swelling in Stage 0, λ_0, for the Case I system as a function of the polymer-monomer interaction parameter χ_{pm}, for the values of the primary network crosslink density $c_0 = 4 \times 10^{-4}$ (continuous lines), 1.3×10^{-3} (dashed lines) and 5.2×10^{-3} (dotted lines). The calculations for obtaining λ_0 are described in Section 3.1 of the main text. The volume fraction in the undeformed state ϕ_0 of the primary gel is kept constant at 0.139. It is seen that an increase in the crosslink density results in a decrease in the degree of swelling.

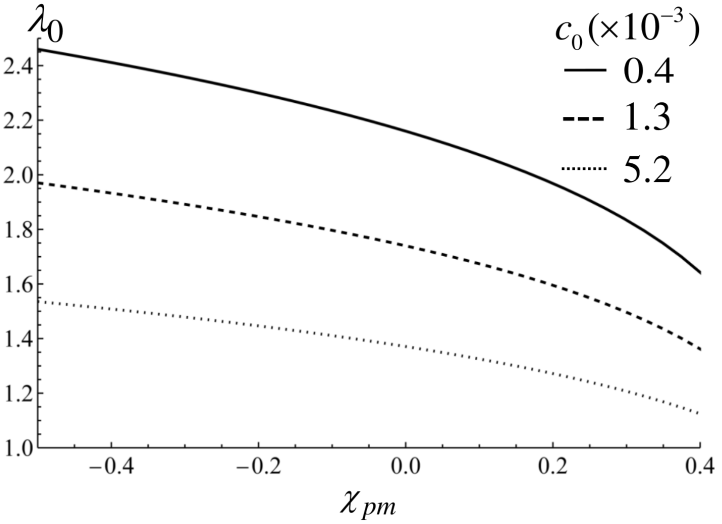

Fig. S2. The equilibrium degree of swelling λ_0 of the primary gel during Stage 0 of the gel growth as a function of the polymer-monomer interaction parameter χ_{pm} in the Case I gel system for the primary network crosslink densities of $c_0 = 4\times10^{-4}$ (solid line), 1.3×10^{-3} (dashed line) and 5.2×10^{-3} (dotted line). The calculations are performed at $\phi_0 = 0.139$.

Stage 1: Figure S3a shows how the equilibrium degree of swelling after the Stage 1 of growth, λ_1, for the IPN (blue lines), and the RCN (red lines) gels at $\chi_{pm} = 0.33$ depends on the fraction of crosslinker-containing monomers in the external solution, α, for the values of c_0 specified above. The procedure for obtaining λ_1 is described in Section 3.2 of the main text. The degree of swelling after the Stage 1 of growth decreases with an increase in c_0, and the latter behavior is consistent with the results for Stage 0. The observed behavior is due to a decrease in the amount of monomers adsorbed by the gel during Stage 0 at the higher values of c_0. After polymerization, if a lower amount of the secondary monomers are incorporated into the network, then the gel exhibits a lower osmotic pressure, which drives the gel swelling.

Figure S3a also shows that the difference between the swelling of the RCN and the IPN, $\lambda_1^{(RCN)} - \lambda_1^{(IPN)}$, increases with an increase in c_0. The latter behavior can be explained as follows. At a higher value of c_0, a decrease in the number of monomers adsorbed during the Stage 0 of growth leads to a decrease in the length of the secondary polymer chains. For the IPN gels, this, in turn, leads to an increase in the sol fraction formed during crosslinking of the secondary chains. For the RCN gels, the sol fraction is even greater as discussed in the main text. In contrast to the RCN, the IPN contains a primary network that is stiffer at a higher c_0. Thus, after the sol removal, although the IPN is left with a loosely crosslinked secondary network, the stronger elastic resistance from the primary network decreases the ability of the gel to swell. The RCN contains a single network, which is less densely crosslinked than that in the IPN, and therefore swells to a greater degree.

Stage 2: Figure S3b shows the degrees of swelling after Stage 1 and Stage 2 of growth, λ_1 and λ_2, respectively, as functions of α for the IPN (cyan lines) and the RCN (magenta lines) gels. After Stage 2 of growth, the difference between the degrees of swelling for the IPN and the RCN, $\lambda_2^{(RCN)} - \lambda_2^{(IPN)}$, is consistently greater than that after Stage 1 for all values of α. The observed behavior is due to the accumulation of the elastic stress from the previous stages of growth in the IPN. The elastic stress is relieved in the RCN as described in Section 3 of the main text.

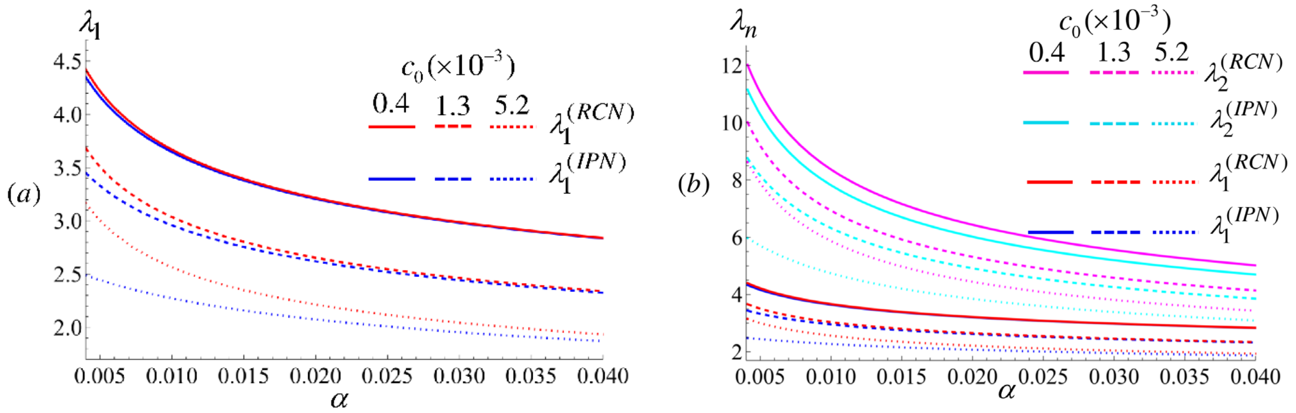

Fig. S3. (a) The equilibrium degree of swelling λ_1 of the IPN (blue) and RCN (red) gels during Stage 1 of the gel growth as functions of the crosslinker content α for the Case I gel system at the primary network crosslink densities of $c_0 = 4\times10^{-4}$ (solid line), 1.3×10^{-3} (dashed line) and 5.2×10^{-3} (dotted line). (b) The equilibrium degree of swelling λ_2 for the Stage 2 of growth of the IPN (magenta) and RCN (cyan) in comparison with the corresponding λ_1 (Fig. S3a) as functions of the crosslinker content α for the Case I gel system at the primary network crosslink densities of $c_0 = 4\times10^{-4}$ (solid line), 1.3×10^{-3} (dashed line) and 5.2×10^{-3} (dotted line). In calculations, $\phi_0 = 0.139$ and $\gamma_+ / \gamma_- = 5\times10^{6}$.

S6.2 Effect of the initial volume fraction of polymer, ϕ_0, on the gel swelling

Stage 0: Figure S4 shows the equilibrium degree of swelling of the primary gel at Stage 0, λ_0, for the Case I system as a function of the polymer-monomer interaction parameter χ_{pm} when the initial volume fractions of the primary network are: $\phi_0 = 0.089$ (dotted lines), 0.139 (dashed lines) and 0.189 (solid lines). The crosslink density of the primary network is kept equal to $c_0 = 1.3\times10^{-3}$. The degree of swelling λ_0 is seen to increase with an increase in ϕ_0 due to an increase in the osmotic pressure of monomeric units (see, eq. (10) in the main text).

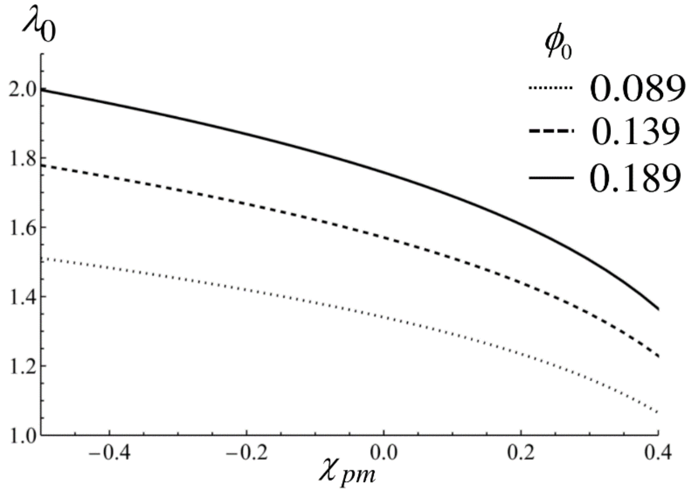

Fig. S4. The equilibrium degree of swelling λ_0 of the primary gel during the Stage 0 of the gel growth as a function of the polymer-monomer interaction parameter χ_{pm} in the Case I gel system when the volume fractions of the undeformed primary network are: $\phi_0 = 0.089$ (dotted lines), 0.139 (dashed lines) and 0.189 (solid lines). The calculations are performed at $c_0 = 1.3 \times 10^{-3}$.

Stage 1: Figure S5a shows how the Stage 1 degree of swelling, λ_1, of the IPN (blue) and the RCN (red) gels at $\chi_{pm} = 0.33$ depends on the fraction of crosslinker-containing monomers in the external solution, α, for the values of ϕ_0 specified above. As ϕ_0 increases, the Stage 1 degree of swelling increases due to an increase in the number of monomeric units adsorbed by the gel in Stage 0, as explained in the previous subsection. For Stage 1, however, the difference $\lambda_1^{(RCN)} - \lambda_1^{(IPN)}$ remains the same for all values of ϕ_0 because the primary network crosslink density is kept constant.

Stage 2: Figure S5b shows the degrees of swelling in Stage 2, λ_2, of the IPN (in cyan) and RCN (in magenta) as functions of α, and reveals the contrast between the latter behavior and the results for the Stage 1, λ_1. The qualitative features of Stage 1 described above also hold true for Stage 2. The difference $\lambda_2^{(RCN)} - \lambda_2^{(IPN)}$ is seen to be consistently higher than in Stage 1 because of the stress accumulation in the IPN, as described above and in Section 3 of the main text.

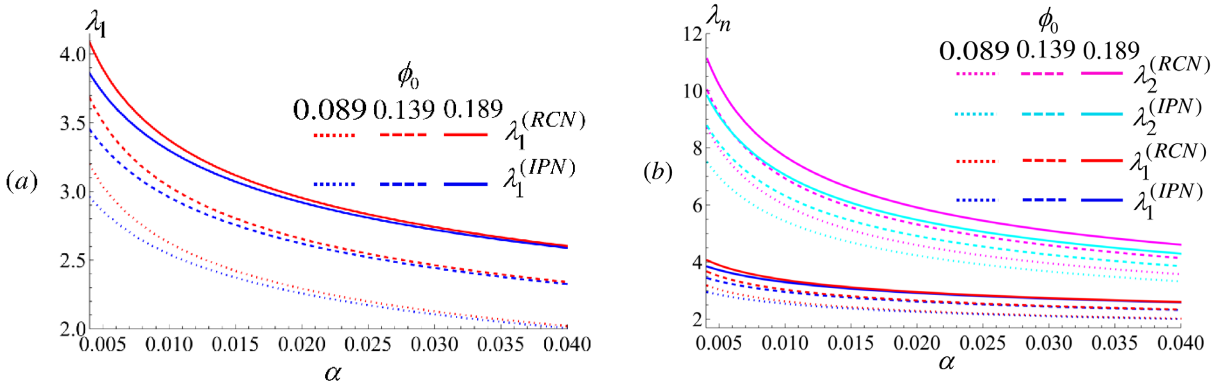

Fig. S5. (a) The equilibrium degree of swelling λ_1 of the IPN (blue) and RCN (red) gels during Stage 1 of the gel growth as functions of the crosslinker content α for the Case I gel system for the initial volume fractions of the primary network $\phi_0 = 0.089$ (dotted lines), 0.139 (dashed lines) and 0.189 (the solid lines). (b) The equilibrium degree of swelling λ_2 for Stage 2 of growth of the IPN (magenta lines) and RCN (cyan lines) and the corresponding λ_1 (Fig. S5a) as functions of the crosslinker content α for the Case I gel system for the initial volume fractions of the primary network $\phi_0 = 0.089$ (dotted lines), 0.139 (dashed lines) and 0.189 (solid lines). Other parameters: $c_0 = 1.3\times 10^{-3}$, $\gamma_+ / \gamma_- = 5\times 10^6$.

S6.3 Effect of polymerization rate constants on the growth of gel

After the polymerization reaction comes to equilibrium, the molecular weight distribution of the secondary chains depends on the parameter γ_+ / γ_- as discussed in Section S2 of the SI. Here, γ_+ and γ_- are the reaction rate constants of the forward and backward reactions, respectively. A higher value of γ_+ / γ_- indicates formation of longer secondary chains.

Figure S6 shows the Stage 1 growth indexes λ_1 / λ_0 for the IPN (blue lines) and RCN (red lines) gels as functions of the crosslinker content α at the two different values of γ_+ / γ_- specified in the figure. The calculations are performed for the Case I system (gel swells in a liquid monomer) at $\chi_{pm} = 0.33$. The gels exhibit a greater growth at the lower value of γ_+ / γ_-, i.e., shorter secondary chains. A decrease in γ_+ / γ_- leads to a reduction in the degree of polymerization of the secondary chains and hence, to an increase in the sol fractions during crosslinking. Formation of a looser polymer network results in an increase in the degree of swelling.

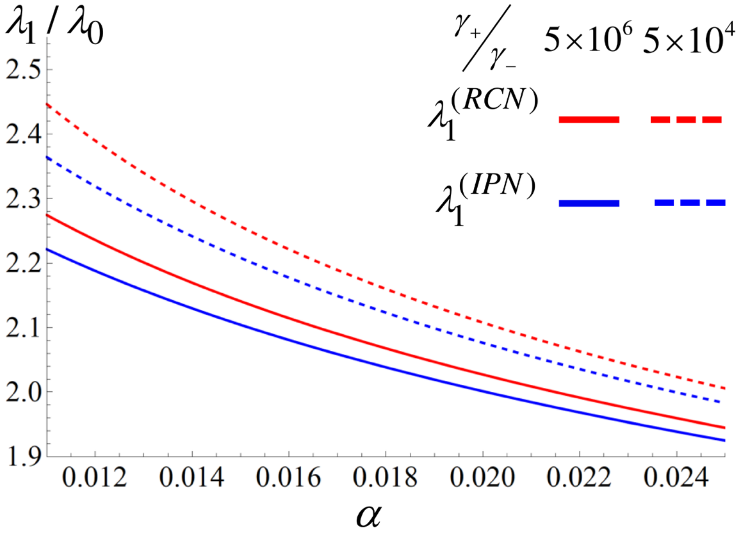

Fig. S6. The growth index λ_1 / λ_0 for Stage 1 of growth of the IPN (blue) and RCN (red) gels as functions of the crosslinker content α for the Case I gel system for the ratio of polymerization rate constants $\gamma_+ / \gamma_- = 5\times10^6$ (solid line) and 5×10^4 (dashed line). In calculations, $c_0 = 1.3\times10^{-3}$ and $\phi_0 = 0.139$.

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