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Controllable growth of interpenetrating or random copolymer networks†

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Interpenetrating and random copolymer networks are vital in a number of industrial applications, including the fabrication of automotive parts, damping materials, and tissue engineering scaffolds. We develop a theoretical model for a process that enables the controlled growth of interpenetrating network (IPNs), or a random copolymer network (RCN) of specified size and mechanical properties. In this process, a primary gel "seed" is immersed into a solution containing the secondary monomer and crosslinkers. After the latter species are absorbed into the primary network, the absorbed monomers are polymerized to form the secondary polymer chains, which then can undergo further crosslinking to form an IPN, or undergo inter-chain exchange with the existing network to form a RCN. The swelling and elastic properties of the IPN and RCN networks can be tailored by modifying the monomer and crosslinker concentrations in the surrounding solution, or by tuning the enthalpic interactions between the primary polymer, secondary monomer and solvent through a proper choice of chemistry. This process can be used repeatedly to fabricate gels with a range of mechanical properties from stiff, rigid materials to soft, flexible networks, allowing the method to meet the materials requirements of a variety of applications.

1. Introduction

Polymer blends combining two or more components allow the properties of polymeric materials to be tailored to meet the requirements of a number of technologies, from formulating stable paints to effective adhesives. The properties of swollen polymer gels can also be adjusted by utilizing two (or more) co-monomers in creating the network. In particular, the gel's behavior can be fine-tuned when the co-monomers form interpenetrating polymer networks (IPNs) or random copolymer networks (RCNs). IPNs involve two (or more) networks that are physically intertwined and cannot be separated without breaking chemical bonds. Random copolymer networks (RCNs) are gels formed from co-monomers that are randomly distributed on the constituent chains. The properties (*e.g.*, mechanical or thermal) of both IPNs and RCNs can be varied by altering a co-monomer or modifying the crosslink density, making these gels useful in a variety of applications. For example, stiff IPNs are used to fabricate items ranging from automotive parts to damping materials, while soft RCNs are valuable in various tissue engineering applications. Herein, we develop a theoretical model to devise a scheme that leads to the formation of either an IPN or a RCN. The model also indicates how the size and properties of a system can be altered allowing each of the networks to exhibit the desired mechanical and thermal behavior.

In our approach, synthetic polymer networks "grow" irreversibly by "consuming" monomer and crosslinker from the surrounding solution and transforming them into a new polymer network. In particular, a "seed" material is placed in a bath of the appropriate chemical components and the system is allowed to increase in mass and size until the material reaches the required characteristics. At that point, it can be removed from the bath to perform the specified function. Additionally, the properties of as-made pieces can be controllably altered by inserting them into a bath of monomer and crosslinker to initiate further growth. Moreover, a damaged material could be put into this "nutrient" bath to repair or replace broken fragments. On a purely metaphorical level, the growth is bio-inspired: allowing a seed to grow by taking in nutrients from the surroundings.[1] To date, there are few general processes for achieving such bio-inspired growth in synthetic systems[2–9] and thus, realizing these advantageous manufacturing processes.

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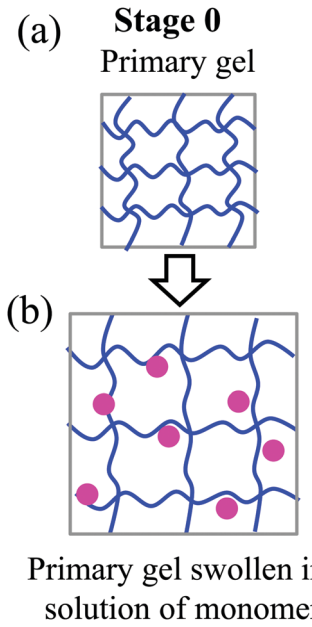

Fig. 1 Schematics of Stage 0 of the gel growth. (a) A primary gel network. (b) The primary gel network swollen in a solution of the secondary monomer depicted by the magenta-colored disks.

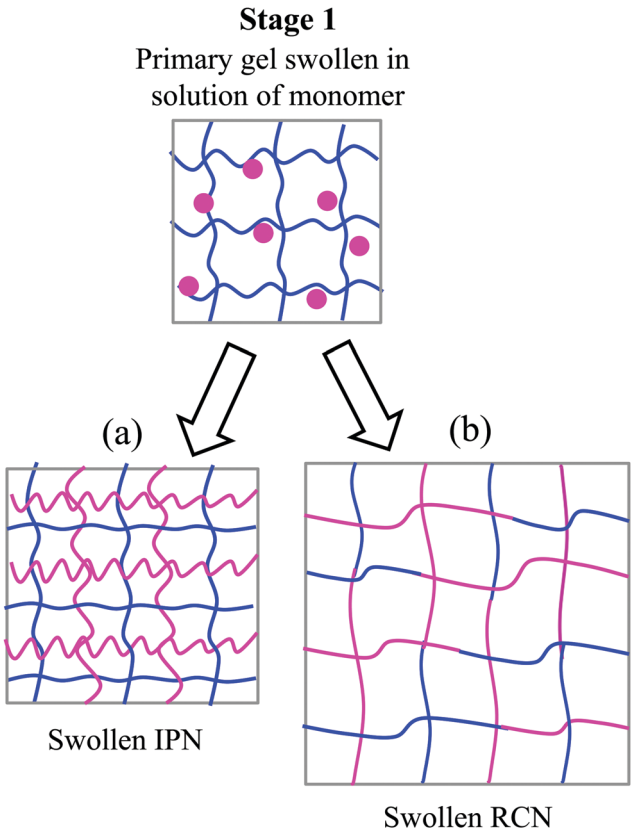

Fig. 2 Schematics of Stage 1 of the gel growth. The secondary monomers absorbed during Stage 0 are polymerized and either (a) crosslinked among themselves to form the interpenetrating network (IPN), or (b) undergo the simultaneous crosslinking among themselves and interchain exchange with the primary gel to form the random copolymer network (RCN). After removal of the sol fraction, the formed gels are swollen in the same monomer solution as in Stage 0 (Fig. 1). The blue- and magenta-colored lines depict the respective primary and secondary polymer chains.

Here, we focus on two different mechanisms for growing the polymer networks. Both mechanisms are initiated by immersing a primary gel (the "seed") into a mixture of solvent and monomer (Fig. 1a). The latter species diffuse into the gel, causing it to swell and expand in size (Fig. 1b). The above steps represent Stage 0 of the gel growth.

At the outset of Stage 1, the absorbed monomers are polymerized to form secondary chains (magenta-colored lines in Fig. 2). These secondary chains are then used to form a new network within the body of the gel. In the first mechanism of growth (Fig. 2a), the secondary chains form crosslinks to create an interpenetrating polymer network (IPN). In the second mechanism, the secondary chains undergo exchange reactions with the primary gel to form a random copolymer network (RCN) (Fig. 2b). After removal of the sol (a mixture of disconnected, small gel-like pieces and uncrosslinked chains), the IPN and RCN are each placed in a bath that is identical to the initial mixture (as in Fig. 1). In the last step of Stage 1, these gels swell ("grow") by incorporating monomeric units from the solution into their network.

Through our theoretical model, we determine how the structures of these IPNs and RCNs affect the uptake of the monomer and solvent and thus, control the gel growth. As discussed below, the chains constituting the primary network in the swollen IPN (Fig. 2a) are relatively stretched. This stretching is entropically unfavorable and hinders uptake of monomer and crosslinker during further stages of growth. In contrast, the chain-exchange reactions between the primary (blue) and secondary (magenta) networks (Fig. 2b) relieves the tension from chain stretching. In addition, the exchange reaction leads to the formation of a considerable quantity of sol and hence, the RCN remains soft. As a result, the RCN provides the distinct advantage that growth in the size of the gel network can be repeated multiple times.

The theoretical model described herein provides the necessary quantitative detail to facilitate experimental realization of such stepwise growth processes. The model reveals how the size and swelling behavior of the network are altered by introduction of a next generation network (*i.e.*, magenta-colored network in Fig. 2). Consequently, the findings can provide valuable guidelines for fine-tuning the growth process to yield gel samples of specified size and mechanical properties.

The biological systems provided inspiration for our studies, not an exact instruction set as pointed out above. The actual biological processes are far more complicated than the scheme described here and thus, our findings cannot be compared to experiments on real, living systems.

It is important to note that researchers[3–9] have developed alternative schemes for creating bio-inspired growing gels and consequently, have synthesized such materials. The latter schemes involve photo-activated processes. For example, Johnson *et al.*[3–6] considered photo-controlled radical polymerization within polymer networks with embedded iniferter groups

("photo-growth"). Absorption of light by the iniferter groups initiates the polymerization process, which inserts monomers and crosslinkers into the network strands. Cui *et al.*[7] used a photo-initiated scheme to promote localized growth and thereby create films with specific surface topologies. Gong *et al.*[2] created mechano-responsive double-network hydrogels that were immersed in a monomer bath and underwent grow and strengthening under repetitive mechanical stress. Moreover, the groups[3–6] have demonstrated the utility of these processes in healing macroscopically damaged networks by re-growing the gels at the site of damage. The mechanisms described here provide an alternative approach for creating growing networks, as well as a mathematical framework for describing and quantifying this process.

2. Theoretical model for the growing networks

We model the stage-wise growth of a polymer gel, starting from the primary network, which is characterized by a crosslink density of c_0; the volume fraction of polymer in the un-deformed state is given by ϕ_0. As noted above, the growth process leads to the formation of either the IPN or RCN structures.

During stages $k = 1, 2, \ldots$ of the growth, the gel sample is immersed in a solution containing the secondary monomer, which has a monomer volume fraction of $\phi_m^{(s)}$. The number fraction of crosslinkers among the secondary monomers is given by α. After the swollen gel reaches equilibrium, the size of the sample is fixed, and the absorbed monomeric units undergo a reversible step-growth polymerization reaction (see the ESI†). The resulting polymer chains exhibit the Flory molecular weight distribution (MWD).[10]

The polymer chains undergo either crosslinking to form the IPN, or simultaneous crosslinking and inter-chain exchange with the existing polymer network to form the RCN (see the ESI†). After removal of the sol fraction, the sample is swollen in the same monomer-containing solution as the previous bath, and the kth stage of growth is considered to be complete.

Growth of the gel after k stages is characterized by the degree of swelling (*i.e.*, relative size), $\lambda_k = (V_k/V_0^{(eq)})^{1/3}$, where V_k is the sample volume after the kth stage of growth, and $V_0^{(eq)}$ is the volume of the un-deformed primary gel. The degree of swelling of the primary gel in the monomer-containing solution before polymerization and crosslinking is denoted λ_0.

For a polymer network composed of the primary and secondary monomers, the equilibrium degree of swelling of the network in the monomer-containing solution is determined by the balance of forces (see eqn (1)) and balance of chemical potentials (see eqn (2)). In the case of force balance, the total elastic stress of the equilibrated sample, σ_{tot}, is balanced by the Flory–Huggins osmotic pressure due to the monomers, $\pi_{FH}(\phi, \psi, \xi_m, \phi_m^{(s)})$. To attain chemical equilibrium, the chemical potential of the secondary monomers in the gel, $\mu_m^{(g)}$, must be equal to the chemical potential of these monomers in the solution, $\mu_m^{(s)}$. The resulting balance equations is written as (see the ESI†)

$$\sigma_{tot} = \pi_{FH}(\phi,\psi,\xi_m,\phi_m^{(s)}) \quad (1)$$

$$\mu_m^{(g)}(\phi,\psi,\xi_m) = \mu_m^{(s)}(\phi_m^{(s)}) \quad (2)$$

here, ϕ and ψ are the respective volume fractions of the primary and secondary monomers that make up the polymer network. The value ξ_m is the number fraction of secondary monomers in the solution lying within the gel (as opposed to the outer bath) and $\phi_m = \xi_m(1 - \phi - \psi)$ is the volume fraction of secondary monomers within the gel. The osmotic pressure and chemical potentials in eqn (1) and (2) depend on the Flory–Huggins interaction parameters χ_{ps}, χ_{pm}, and χ_{ms}. The latter parameters characterize the interactions between the primary monomers and solvent, primary and secondary monomeric units, and secondary monomeric units and solvent, respectively. We refer to eqn (S1.13)–(S1.15) in the ESI† for the explicit formulation of the equations for equilibrium swelling, eqn (1) and (2).

To calculate the elastic stress in the composite gel, σ_{tot} in eqn (1), we employ the neo-Hookean model,[11–13] which describes the elastic stress in a compressible polymer network as a function of deformation, and depends on only one model parameter: the crosslink density c_0 (see the ESI†). For an individual network, the elastic stress is given by the neo-Hookean equation $\sigma_{el}(c_0, \lambda) = c_0\lambda^{-3}(\lambda^2 - 1/2)$. Here, the degree of swelling λ characterizes strain in a swollen gel. Note that the elastic stress σ_{el} is typically formulated[14–16] in terms of the volume fraction $\phi = \phi_0\lambda^{-3}$.

For the IPN, the total stress is a sum of the contributions from the individual networks. In contrast, for the RCN, there is only one contribution to the elastic stress due to the network restructuring in the course of the inter-chain exchange. Below, we briefly outline the calculations for the growth of the IPN and RCN networks, and refer the reader to the SI for further details.

2.1. Growth of the IPN gel

We first discuss the set of equations describing the growth of the IPN. The calculations start with determining the degree of swelling of the primary gel at equilibrium. The primary as-prepared gel does not contain any secondary monomeric units. Since ψ represents the fraction of secondary monomers in the primary network, initially at Stage 0, $\psi = 0$. To determine the degree of swelling, λ_0, and the fraction of the secondary monomeric units in the solution inside the gel, $\xi_m^{(0)}$, we solve the balance equations for forces, eqn (1) and chemical potentials, eqn (2), at $\psi = 0$. We also take into account that the volume fraction of the primary monomeric units depends on the gel size as $\phi = \phi_0\,\lambda^{-3}$.

During the first stage of growth, the gel size is fixed to λ_0, and the secondary monomers are polymerized, crosslinked, and the sol fraction is removed from the system. The newly formed network is un-deformed, and the volume fraction of the secondary monomeric units in this network is $\psi_0^{(1)} = \xi_m^{(0)}(1 - S_1^{(IPN)})(1 - \phi_0\lambda_0^{-3})$, where $S_1^{(IPN)}$ is the sol fraction, and the subscript "0" in $\psi_0^{(1)}$ denotes the un-deformed state. The dimensionless

crosslink density of the newly formed network, $c_1^{(IPN)}$, and the sol fraction, $S_1^{(IPN)}$, are calculated using the theory developed by Dobson and Gordon,[17,18] as described in the ESI.† The equilibrated gel size after the first stage of growth, λ_1, is still determined by the mechanical and chemical balance equations, eqn (1) and (2), but the elastic stress σ_{tot} now includes the contribution of the newly formed network, and $\psi = \psi^{(1)}$:

$$\sigma_{el}(c_0, \lambda) + \sigma_{el}(c_1^{(IPN)}, \lambda/\lambda_0) = \pi_{FH}(\phi, \psi^{(1)}, \xi_m, \phi_m^{(s)}) \quad (3)$$

$$\mu_m^{(g)}(\phi,\psi^{(1)},\xi_m) = \mu_m^{(s)}(\phi_m^{(s)}) \quad (4)$$

The second term on the left-hand side (l.h.s.) of eqn (3) takes into account that the formed network is un-deformed at the sample size of λ_0. The volume fraction of the secondary units, $\psi^{(1)}$, depends on the sample size as $\psi^{(1)} = \psi_0^{(1)}(\lambda_0/\lambda)^3$. Solving eqn (3) and (4) yields the values for λ_1 and $\xi_m^{(1)}$ characterizing the system after the first stage of growth.

This procedure is repeated step-by-step as many times as desired (see Section S4 in the ESI†). After each stage of growth of the IPN, some amount of the secondary monomeric units is incorporated into the sample as another interpenetrating polymer network. Modeling the stepwise process of growth is formulated as an iterative procedure, which requires solving the two non-linear algebraic equations at each step. We refer to the SI for the explicit form of the balance equations, eqn (1) and (2), which determine the size λ_n of the IPN gel after the nth stage of growth.

2.2. Growth of the RCN gel

A similar iterative procedure can be devised to describe the growth of the RCN gel after $n \geq 1$ consecutive stages (see Section S5 in the ESI†). There are, however, two differences between the IPN and RCN gels. These differences are due to the inter-chain exchange reaction, which leads to the formation of copolymers consisting of the primary and secondary monomeric units in the RCN gels. As a result, there is only one contribution to the elastic stress σ_{tot} characterized by a single crosslink density, and the sol fraction (removed from the samples) contains both primary and secondary of monomeric units.

For example, after the first stage of growth, the size of the RCN gel is determined by the following equations for the force and chemical balances (compare with eqn (3) and (4) for the IPN)

$$\sigma_{el}(c_1^{(RCN)}, \lambda/\lambda_0) = \pi_{FH}[\phi^{(1)}(\lambda), \psi^{(1)}(\lambda), \xi_m, \phi_m^{(s)}] \quad (5)$$

$$\mu_m^{(g)}[\phi^{(1)}(\lambda), \psi^{(1)}(\lambda), \xi_m] = \mu_m^{(s)}(\phi_m^{(s)}) \quad (6)$$

here, $c_1^{(RCN)}$ and $S_1^{(RCN)}$ are the respective crosslink density and sol fraction of the RCN gel after the first stage of growth calculated as discussed in the ESI.† Further, $\phi^{(1)}(\lambda) = (1 - S_1^{(RCN)})\phi_0\lambda^{-3}$ is the volume fraction of the primary monomeric units after removal of the sol fraction, and $\psi^{(1)}(\lambda) = \xi_m^{(0)}(1 - S_1^{(RCN)})(1 - \phi_0\lambda_0^{-3})(\lambda_0/\lambda)^3$ is the volume fraction of the secondary monomers incorporated into the RCN during the first stage. (Recall that λ_0 and $\xi_m^{(0)}$ are the solutions of eqn (1) and (2) at $\psi = 0$ for the swelling of the primary network.)

Importantly, in contrast to the IPN, the RCN is in the un-deformed state after each stage of growth due to the interchain exchange. It is also worth noting that the amount of primary monomers in the RCN decreases from stage to stage because of the removal of the sol fraction.

2.3. Sequence of calculations in the model

To analyze the behavior of this "growing" system, we start with the initial stage, Stage 0, which is depicted in Fig. 1a and b and described by eqn (1) and (2) at $\psi = 0$, where a polymer gel consisting of the primary network is immersed in a monomer-containing solution, and calculate the primary degree of swelling λ_0. Then, we proceed to considering Stage 1 of growth for both IPN and RCN gels (see Fig. 2) described by the respective balance equations eqn (3)–(6), and determine the gel size λ_1. Finally, we analyze Stage 2 through calculating the gel size λ_2 for the IPN and RCN as detailed in the respective Sections S4 and S5 of the ESI.† The calculated values λ_1 and λ_2 indicate how size of the primary network increases as a result the stepwise growth processes leading to the irreversible formation of either IPN, or RCN structures.

Below, we determine the factors that control the swelling of the IPN and RCN gels, and thereby, provide routes for tailoring the properties of the networks. First, we demonstrate how we can control the growth of the initial seed; this determines the amount of secondary units that are adsorbed. Next, we show that the RCN is inherently softer than the IPN. We then describe how the degree of swelling for both types of networks can be controlled by tuning the crosslinker fraction, α, and the interaction parameters, χ_{ps}, χ_{ms} and χ_{pm}. We discuss the effectiveness of varying this set of parameters for high ($\phi_m^{(s)} = 1$) and low ($\phi_m^{(s)} = 0.3$) values of the outside monomer concentration. Finally, we show that the growth of the IPN gel in size slows down in successive stages, whereas a substantial growth of the RCN gel can be repeated multiple times. The ESI† contains further discussion of the factors that affect the gel growth (see Section S6 in the ESI†).

3. Results and discussion

As described above, we consider the two mechanisms of gel growth shown schematically in Fig. 2. According to the first mechanism, the absorbed secondary monomers form a new, interpenetrating network (IPN) in the body of the gel (Fig. 2a). The alternative mechanism considers formation of a single random copolymer network (RCN), which incorporates both the primary and secondary monomeric units (Fig. 2b).

For the both IPN and RCN, we focus on two scenarios, which we denote Case I and Case II. The first case corresponds to systems where the gel swells in a liquid composed solely of secondary monomer with no solvent present, *i.e.*, $\phi_m^{(s)} = 1$. The secondary monomer in Case I is considered to be different from the monomeric units comprising the primary gel network, and the interactions between the two types of monomers is described by the Flory–Huggins interaction parameter χ_{pm}.

In Case I, the size of gel is determined solely by balancing the elastic and osmotic forces, eqn (1). The elastic stress σ_{tot} is calculated for the IPNs and RCNs as described in Section 2 above, and the Flory–Huggins osmotic pressure is

$$\pi_{FH}^{(I)}(\phi,\psi) = -[\phi + \psi + \ln(1 - \phi - \psi) + \chi_{pm}\phi^2] \quad (7)$$

where the superscript "I" denotes Case I. The process of gel growth is controlled by the polymer–monomer interaction parameter χ_{pm} and the number fraction of crosslinker-containing monomers, α.

In the second scenario (Case II), the secondary monomers in the outside liquid are identical to the ones in the primary network and, in contrast to Case I, are diluted by a solvent, so that $\phi_m^{(s)} \leq 1$. The interactions in this system are described by the Flory–Huggins interaction parameters $\chi_{pm} = 0$ and $\chi_{ms} = \chi_{ps}$. In the presence of solvent, the gel size is determined by balancing both the forces, eqn (1), and chemical potentials of the secondary monomers inside and outside the gel, eqn (2). In eqn (1), the osmotic pressure is calculated as

$$\pi_{FH}^{(II)}\left(\phi,\psi,\xi_m,\phi_m^{(s)}\right) = -\Big[\phi+\psi+\ln(1-\phi-\psi)+\chi_{ps}(1-\xi_m)^2 \times (\phi+\psi)^2\Big] + \xi_m \ln\frac{\phi_m^{(s)}}{\xi_m} + (1-\xi_m)\ln\frac{1-\phi_m^{(s)}}{1-\xi_m} + \chi_{ps}\left(\xi_m - \phi_m^{(s)}\right)^2 \quad (8)$$

where the subscript "II" denotes Case II, and the elastic stress σ_{tot} is calculated depending on the type of gel growth, *i.e.*, IPN or RCN. The equation of chemical equilibrium, eqn (2), takes the following form in Case II:

$$\ln\frac{\xi_m}{1-\xi_m} - 2\chi_{ps}[\xi_m(1-\phi-\psi)+\phi+\psi] = \ln\frac{\phi_m^{(s)}}{1-\phi_m^{(s)}} - 2\chi_{ps}\phi_m^{(s)} \quad (9)$$

In Case II, the size of the grown gel depend on the polymer–solvent interaction parameter χ_{ps}, the fraction of the crosslinker-containing monomers α, and the volume fraction of the monomer in the outside solution $\phi_m^{(s)}$. We study this system in two limits: the saturated, $\phi_m^{(s)} = 1$, and dilute, $\phi_m^{(s)} = 0.3$, cases.

3.1. Stage 0: growth of the initial seed

The initial seed contains only the primary network. Hence, the equations to determine the gel size at Stage 0, *i.e.*, the equilibrium degree of swelling λ_0, are solved at $\psi = 0$. (Recall that ψ is the volume fraction of the secondary monomers in the polymer network.) Fig. 3 shows the degree of swelling at Stage 0 for various values of the interaction parameters χ_{pm} in Case I (Fig. 3a) and χ_{ps} in Case II (Fig. 3b).

In Case I (where the solution is composedly solely of monomer), the degree of swelling decreases with an increase in the polymer–monomer interaction parameter χ_{pm} (Fig. 3a). The latter finding indicates that a larger repulsion between the primary and secondary monomeric inhibits the absorption of the monomers into the gel.

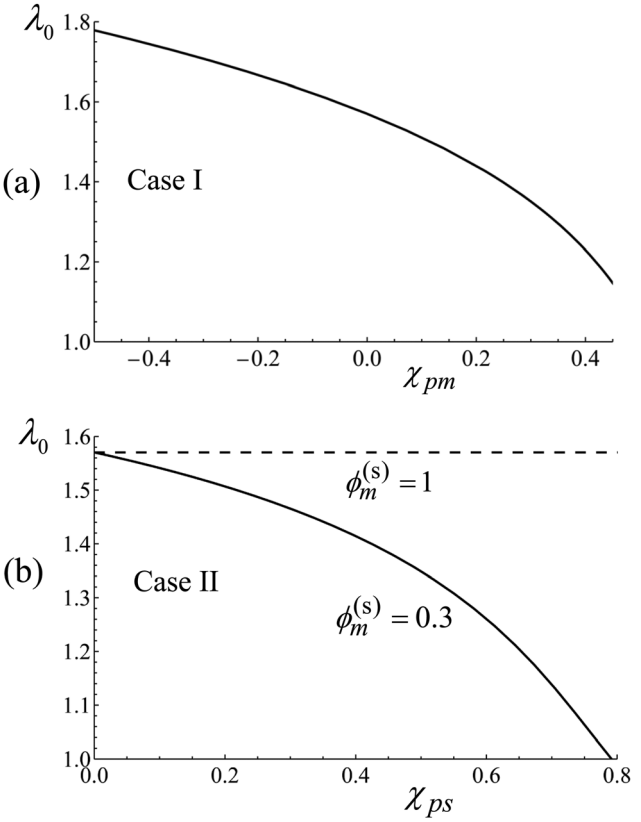

Fig. 3 The equilibrium degree of swelling λ_0 of the primary gel during Stage 0 of the gel growth as a function of (a) the polymer–monomer interaction parameter χ_{pm} in the Case I gel systems, and (b) the polymer–solvent interaction parameter χ_{ps} in the Case II gel systems at the monomer contents in the outside solution of $\phi_m^{(s)} = 0.3$ (solid line) and $\phi_m^{(s)} = 1$ (dashed line). See text for the definitions of Case I and Case II.

A similar dependence on the polymer–solvent interaction parameter, χ_{ps}, is observed in Case II at $\phi_m^{(s)} = 0.3$ (Fig. 3b, the solid line). (As noted above, since the monomers in the solution are the same as those within the primary network in Case II, the Flory–Huggins interaction parameters are $\chi_{pm} = 0$ and $\chi_{ms} = \chi_{ps}$.) Namely, an increase in χ_{ps} (and thus an increase in χ_{ms}) leads to a decrease in the amount of solution absorbed by the gel, and hence a decrease in the degree of the swelling. Note that at $\phi_m^{(s)} = 1$, the degree of swelling does not depend on χ_{ps} because there is no solvent in the system (Fig. 3b, the dashed line).

3.2. Elasticity and swelling of the IPN and RCN gels

The structure of the polymer network formed during gel growth, IPN or RCN, dominates the mechanical properties of the resulting gel. To demonstrate this behavior, we first compare the degrees of swelling for the IPN and RCN gels after Stages 1 and 2 of gel growth for the Case I systems (where growth is controlled by the values of χ_{pm} and α). The calculations are performed at the polymer–monomer interaction parameter of $\chi_{pm} = 0.33$, and the fraction of crosslinker-containing monomers is fixed at $\alpha = 0.004$.

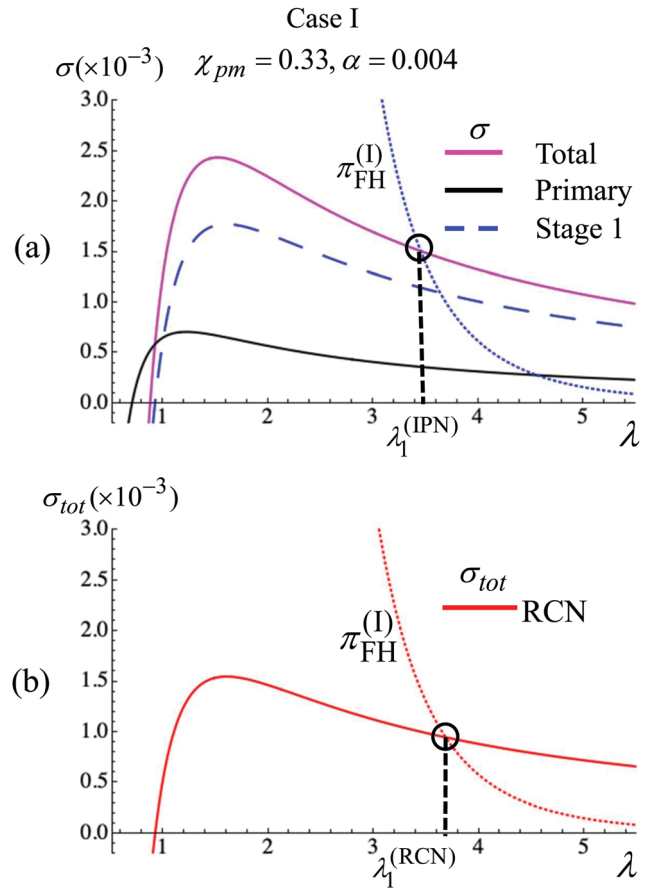

Fig. 4 Illustration of the factors affecting the degree of swelling of the (a) IPN and (b) RCN gels after Stage 1 of the gel growth in the Case I gel systems at the polymer–monomer interaction parameter of χ_{pm} = 0.33 and the crosslinker content of α = 0.004. The equilibrium value of the degree of swelling λ_1 is determined as the intersection of the curves for the total elastic stress σ_{tot} and the Flory–Huggins osmotic pressure $\pi_{FH}^{(I)}$ as functions of the degree of swelling λ. Colors and dashing of curves label various contributions to eqn (1) for (a) IPN and (b) RCN gels as indicated in the figure. Note that there are two contributions to σ_{tot} in (a).

The plot in Fig. 4a shows the solution of eqn (3), where the osmotic pressure is calculated according to eqn (7), that characterizes the IPN gel after Stage 1 of growth (see schematic in Fig. 1a) in the case of no solvent present. The solid, magenta line indicates the total elastic stress σ_{tot} in the IPN as a function of the degree of swelling, λ. According to eqn (3), there are two different contributions to σ_{tot}: the contribution due to the elasticity of the primary network is shown by the black, solid line in Fig. 4a and the contribution due to the interpenetrating network formed during Stage 1 is indicated by the blue, dashed line. Finally, the blue, dotted line in Fig. 4a shows the osmotic pressure $\pi_{FH}^{(I)}$ calculated according to eqn (7). The intersection of the curves for σ_{tot} and $\pi_{FH}^{(I)}$ gives the equilibrium degree of swelling $\lambda_1^{(IPN)}$ after Stage 1 (see Fig. 4a).

Fig. 4b shows σ_{el} and $\pi_{FH}^{(I)}$ for the RCN as obtained from the left-hand-side of eqn (5) and (7), respectively, and the solution $\lambda_1^{(RCN)}$ of eqn (5) given by the intersection of the two curves. In contrast to the IPN, the primary and the secondary units in the RCN form a single network (see schematic in Fig. 1b); hence, there is only one contribution to the elastic stress.

Fig. 4 clearly shows that $\lambda_1^{(RCN)} > \lambda_1^{(IPN)}$. The primary network of the IPN remains stretched after Stage 0, and the extension of the secondary network in the course of further gel swelling increases the elastic stress in the primary network. (For the IPN, only the secondary network is stress-free during crosslinking, as described in the modeling section.) For the RCN, however, the elastic stresses within the primary network after Stage 0 are relieved during the inter-chain exchange during Stage 1. As a result, the RCN is softer than the IPN, and exhibits a greater degree of swelling as seen in Fig. 4.

The difference in size between the IPN and RCN becomes more prominent during further stages of gel growth. Fig. 5a and b show the respective graphical solutions of the force balance equation for the IPN and RCN after Stage 2. (The elastic stresses σ_{tot} for the IPN and RCN after the Stage 2 are calculated according to the equations given in the respective Sections S4 and S5 of the ESI.†) As seen in Fig. 5a, the IPN now consists of three network. Two of these networks, *i.e.*, the primary network

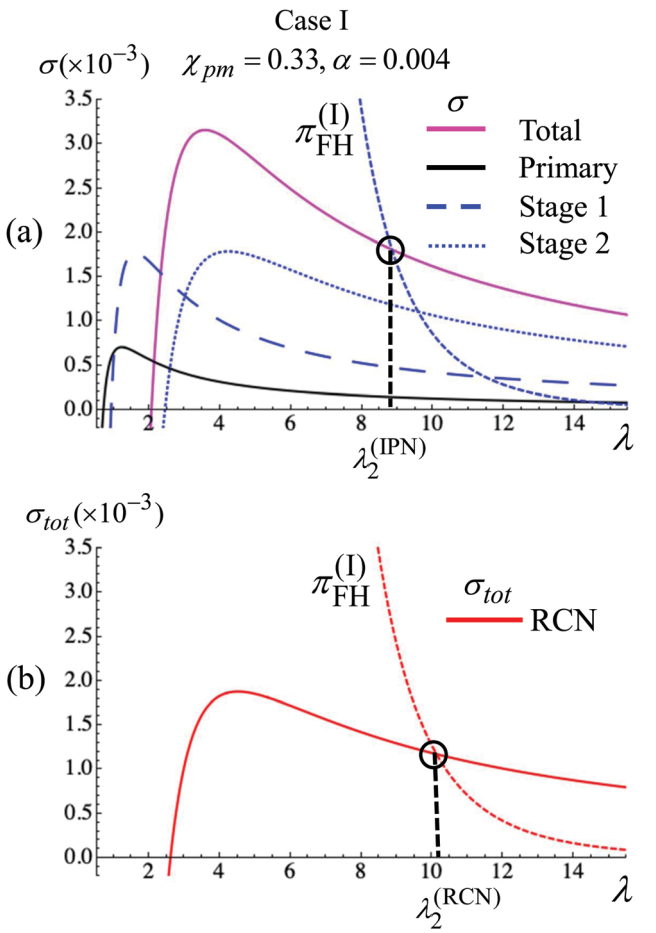

Fig. 5 Illustration of the factors affecting the degree of swelling of the (a) IPN and (b) RCN gels after Stage 2 of the gel growth in the Case I gel systems at the polymer–monomer interaction parameter of χ_{pm} = 0.33 and the crosslinker content of α = 0.004. Notations are the same as in Fig. 4. Note that there are three contributions to σ_{tot} in (a).

and the secondary network formed during Stage 1, are stretched during Stage 2. Due to the inter-chain exchange, RCN does not encompass such cumulative stress. As a result, the difference between the degrees of swelling for IPN and RCN seen in Fig. 5 is greater than that in Fig. 4.

3.3. Stage 1: the effect of crosslinker content

It is convenient to characterize the growth in the size of a gel in terms of the growth index λ_n/λ_0, which is the degree of swelling of the gel after the n-th stage of growth relative to that of the primary gel λ_0 (see Fig. 3). Fig. 6a and b show how the growth index λ_1/λ_0 depends on the fraction of crosslinker-containing monomers in the external solution, α, in the respective Case I and Case II systems for the IPN (the blue lines) and RCN (the red lines) gels. Increases in α lead to the formation of a more densely crosslinked network (see the ESI† for further details) and hence, affect the extent of gel growth. Fig. 6 demonstrates that in all systems, an increase in α reduces the growth index because the more densely crosslinked networks exhibit a smaller degree of swelling. As explained below, however, at a fixed value of α, the growth index can be tuned by varying the volume fraction of monomer in the external solution (Case II).

Recall that in Case I, $\phi_m^{(s)} = 1$ and hence, χ_{pm} is the only interaction parameter in the equation for osmotic pressure, eqn (7); here, we set $\chi_{pm} = 0.33$. In Case II, $\chi_{pm} = 0$ and $\chi_{ms} = \chi_{ps}$ by definition, and we set $\chi_{ps} = 0.33$. Fig. 6a reveals that in Case I, while the growth indices for the IPN and RCN are similar in value, the RCN gel exhibits greater growth (relative swelling) than the IPN. The elasticity of both the networks is dominated by crosslinks between the secondary units. (The total number of crosslinkers in the RCN is the sum of the ones in the primary and the secondary units. Calculations show that there are more secondary than primary units in the regime considered here.) The difference between the growth indices is notable only at sufficiently low values of α. As seen in Fig. 6a, $\lambda_1^{(RCN)}/\lambda_1^{IPN} \approx 1.08$ at $\alpha = 0.004$.

In the Case II systems (where $\chi_{pm} = 0$), the growth index as a function of α shows a pronounced dependence on the volume fraction of monomer in the external solution, $\phi_m^{(s)}$, as seen in Fig. 6b. Specifically, the growth indices of the IPN and RCN gels at $\phi_m^{(s)} = 0.3$ (the solid lines in Fig. 6b) are lower than at $\phi_m^{(s)} = 1$ (the dashed lines in Fig. 6b) at all α. Notably, the RCN gel again exhibits a greater growth than the IPN gel at all values of the crosslinker content α for both values of $\phi_m^{(s)}$ presented in Fig. 6b.

The effect of $\phi_m^{(s)}$ seen in Fig. 6b can be explained by the behavior of the osmotic pressure $\pi_{FH}^{(II)}$, eqn (8), as the value of ξ_m at $\chi_{ps} > 0$ is varied. (Here, $\xi_m = \phi_m/(1-\phi-\psi)$is the volume fraction of secondary monomers within the gel.) Namely, at a sufficiently high degree of swelling, the leading contribution to the osmotic pressure is due to the first two terms of the virial expansion:

$$\pi_{FH}^{(II)}\left(\phi,\psi,\xi_m,\phi_m^{(s)}\right) \approx \left(\frac{1}{2}-\chi_{ps}(1-\xi_m)^2\right)(\phi+\psi)^2+(\phi+\psi)^3/3+\ldots \quad (10)$$

At $\chi_{ps} > 0$, the first term on the right increases with an increase in ξ_m and is maximal at $\xi_m = 1$, which takes place when there is no solvent in the system, *i.e.*, at $\phi_m^{(s)} = 1$. The increase in the osmotic pressure with the change in $\phi_m^{(s)}$ from 0.3 to 1 results in an increase in λ_1/λ_0, as seen in Fig. 6b. At $\phi_m^{(s)} = 1$, the values λ_1/λ_0 for the IPN and RCN gels are close to the values in Fig. 6a for Case I.

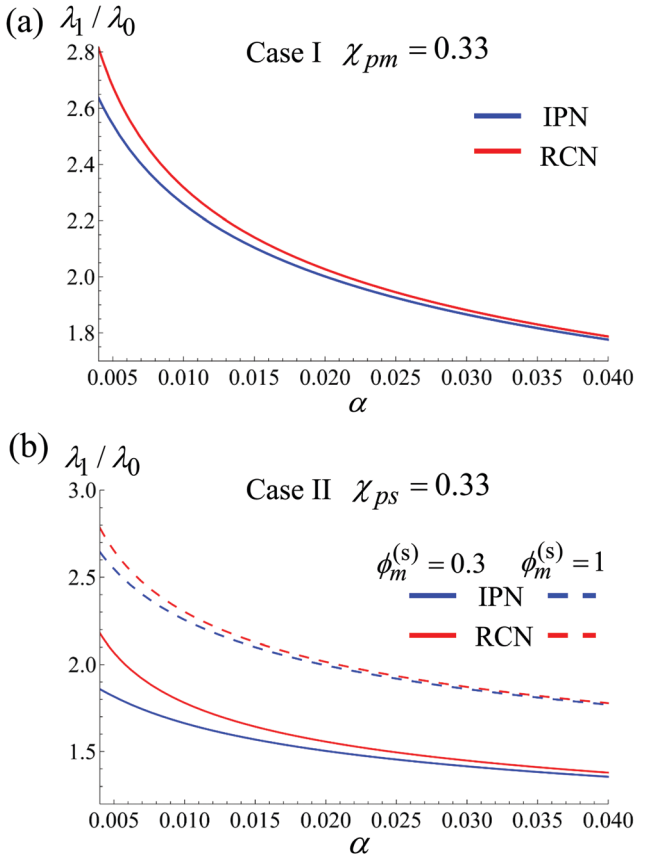

Fig. 6 The growth index λ_1/λ_0 for Stage 1 of growth of the IPN (blue) and RCN (red) gels as functions of the crosslinker content α for (a) the Case I gel systems at $\chi_{pm} = 0.33$, and (b) the Case II gel systems at $\chi_{ps} = 0.33$ and the monomer contents in the outside solution of $\phi_m^{(s)} = 0.3$ (solid line) and $\phi_m^{(s)} = 1$ (dashed line).

The above findings show that the swelling of both the RCN and IPN in the Case I and II systems can be controlled by varying the value of α. Hence, in these scenarios, the elasticity of both types of networks can be tuned to meet specified requirements. For Case II, there remains an alternative approach for tailoring the mechanical properties of this network, as described below.

3.4. Stage 1: the effect of varying the interaction parameters

At a fixed value of α, we anticipate that variations in theχ interaction parameters will affect the swelling of the IPN and the RCN gels. To test this hypothesis, we fixed $\alpha = 0.008$ to obtain the plots in Fig. 7, which show the variation of λ_1/λ_0 (Stage 1 growth index) for the IPN and RCN as a function of χ_{pm} for Case I (Fig. 7a) and as a function of χ_{ps} for Case II (Fig. 7b).

Recall that at Case I, the gel swells in a liquid composed solely of monomer, with no solvent present, *i.e.*, $\phi_m^{(s)} = 1$. For this case (Fig. 7a), the swelling of the IPN is insensitive to the

values of χ_{pm} within the range considered here; however, for the RCN, the value λ_1/λ_0 displays a small increase with an increase inχ_{pm}. The relative insensitivity of the gels to χ_{pm} is due to the saturation of the outside solution with monomers ($\phi_m^{(s)} = 1$). Therefore, a significant number of these monomers are absorbed during the equilibration of the gel (despite the unfavorable χ_{pm}). In this case, incorporation of the secondary monomers into the gel network (described by the volume fraction ψ) affects the Flory–Huggins osmotic pressure $\pi_{FH}^{(I)}(\phi, \psi)$ only through the entropic contribution given by the first three terms on the right-hand side of eqn (7).

The small increase in the growth index of the RCN gel (red line in Fig. 7a) is due to a decrease in the amount of monomers absorbed by the gel during Stage 0 at higher χ_{pm}, where the enthalpic interactions become more repulsive (Fig. 3a). The decrease in monomer absorption leads to a decrease in both the total number and average chain length of the secondary polymers after polymerization. This, in turn, leads to an increase in the sol fraction formed during the simultaneous crosslinking and inter-chain exchange. An increase in the sol fraction is equivalent to having a looser gel network. Therefore, the RCN gel, which is taken to be free of the sol fraction, exhibits an increase in the growth index at higher values of χ_{pm} as seen in Fig. 7a.

As noted above, for Case II, the monomeric units in the solution are the same as the ones in the primary network; therefore, the Flory–Huggins interaction parameters are $\chi_{pm} = 0$ and $\chi_{ms} = \chi_{ps}$. In the case where $\phi_m^{(s)} = 1$ (Fig. 7b), there is no solvent outside of the gel; as a result, the swelling of the gels does not depend on the values of the polymer–solvent interaction χ_{ps}, as also observed in Stage 0 growth. At $\phi_m^{(s)} = 0.3$ (Fig. 7b), however, the enthalpic effects overwhelm the entropic contribution to the osmotic pressure, eqn (8). Hence, the system is more sensitive to variations in the interaction parameter than in Case I (Fig. 7a). Specifically, the polymer–solvent interactions mitigate the increase in osmotic pressure (as discussed in Stage 0). Therefore, as seen in Fig. 7b, λ_1 decreases with increasing χ_{ps}. The greater decrease in the growth index for the RCN than the IPN with an increase in the polymer–solvent repulsion seen in Fig. 7b is likely due to a smaller amount of monomer being incorporated into the RCN gel. The latter behavior leads to a decrease in the osmotic pressure and hence, to a lower degree of swelling.

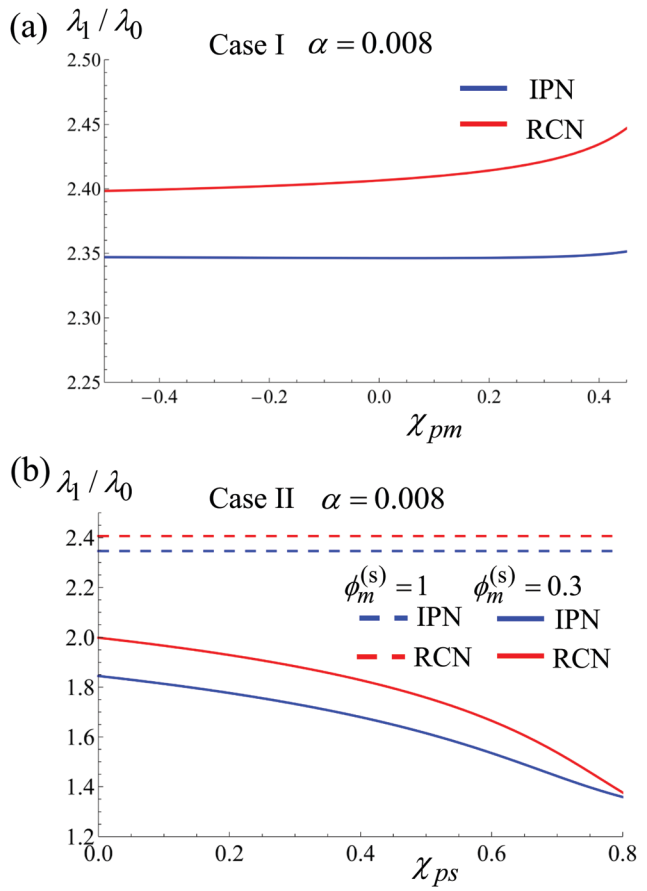

Fig. 7 The growth index λ_1/λ_0 for Stage 1 of growth of the IPN (blue) and RCN (red) gels at the crosslinker content $\alpha = 0.008$ as functions of the Flory–Huggins interaction parameter (a) χ_{pm} in the Case I gel systems, and (b) χ_{ps} in the Case II gel systems at $\phi_m^{(s)} = 0.3$ (solid line) and $\phi_m^{(s)} = 1$ (dashed line).

3.5. Stage 2 of gel growth

The IPN and the RCN gels exhibit distinct differences in their swelling properties between growth Stages 1 and 2. To investigate this behavior, we study their growth in Stage 2 (see Sections S4 and S5 of the ESI† for equations). Focusing on Case I (with $\chi_{pm} = 0.33$), Fig. 8a shows the variation of the Stage 2 growth index λ_2/λ_0 *versus* α, and contrasts it with the behavior in Stage 1. Importantly, the difference in the degrees of swelling of the RCN and IPN gels after Stage 2 of growth, $\lambda_2^{(RCN)} - \lambda_2^{(IPN)}$, is consistently greater than that for Stage 1 for all α. The reason for this behavior is that the elastic stress from the previous stages of growth accumulates in the IPN and is relaxed in the RCN gel (as discussed in the Section 3.2 above).

The inset in Fig. 8a shows the relative growth index, *i.e.*, the differential growth in Stage 2 with respect to Stage 1, $\lambda_R = \lambda_2/\lambda_1 - 1$. For $\lambda_R > 1$, the gel grows more in Stage 2 than in Stage 1. Notably, the relative growth index, λ_R, for both the IPN and the RCN, crosses from less than 1 to greater than 1 at an intermediate value of α (marked by arrows in the inset in Fig. 8a). In other words, below a specific α, an increase in the osmotic pressure (which drives the gel swelling) is greater after Stage 2 than an increase in the elastic stress (which resists the gel growth). Above this α, an increase in the crosslink density after Stage 2 diminishes growth of the gel. It is worth noting that the latter threshold value of α is greater for the RCN than for IPN gel (see inset in Fig. 8a).

Fig. 8a also shows that the Stage 2 growth can be reduced about 50 percent by a 10 fold increase in the crosslinker fraction α. This behavior arises because the amount of the secondary units within Stage 2 gel is sufficiently great that variations in crosslinker content α strongly affect the mechanical properties of the gel.

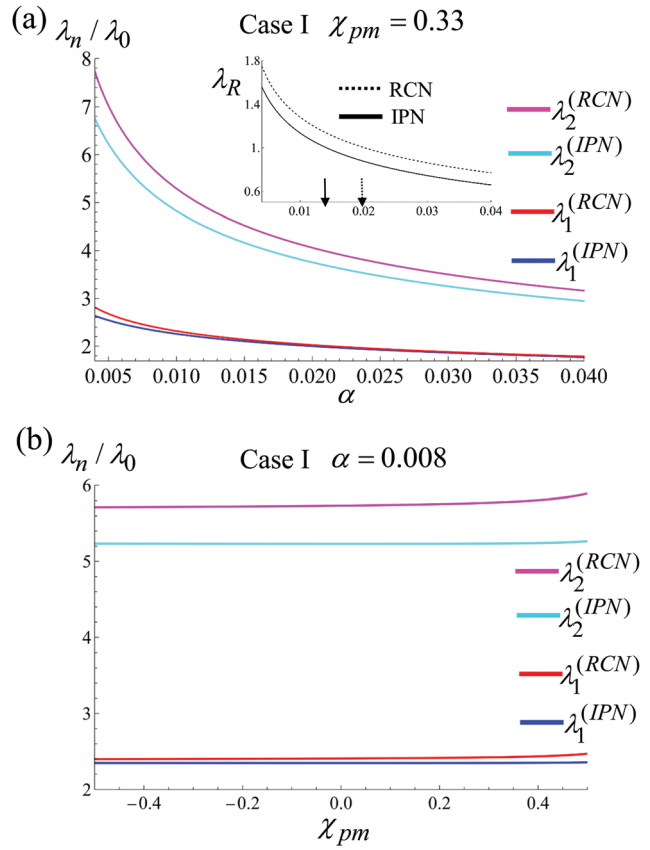

Fig. 8 The growth index λ_2/λ_0 for Stage 2 of growth of the IPN (cyan) and RCN (magenta) gels in contrast with the growth index λ_1/λ_0 for the IPN (blue) and RCN (red) for the Case I gel systems as functions of (a) the crosslinker content α at χ_{pm} = 0.33, and (b) the polymer–monomer interaction parameter χ_{pm} at α = 0.008. In (a), the inset shows the relative growth index $\lambda_R = \lambda_2/\lambda_1 - 1$ as a function of α for the IPN (solid) and RCN (dashed) gels. Note that in (a) and (b), the curves for λ_1/λ_0 are the same as in Fig. 6a and 7a, respectively.

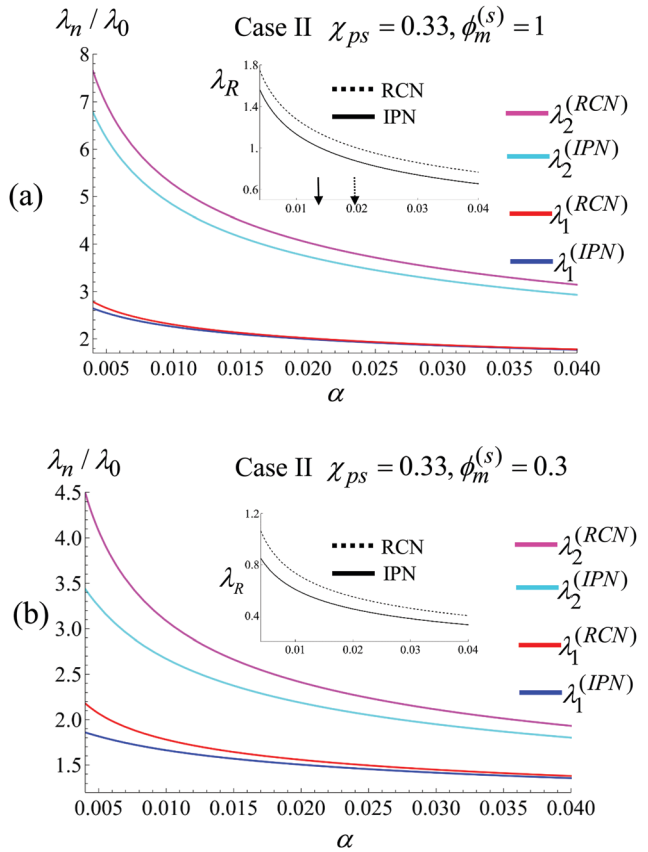

Fig. 9 The growth index λ_2/λ_0 for Stage 2 of growth of the IPN (cyan) and RCN (magenta) gels in contrast with the growth index λ_1/λ_0 for the IPN (blue) and RCN (red) gels for the Case II gel systems as functions of the crosslinker content α at the monomer content in the outside solution of (a) $\phi_m^{(s)}$ = 1 and (b) $\phi_m^{(s)}$ = 0.3. The polymer–solvent interaction parameter is χ_{ps} = 0.33. The insets show the relative growth index $\lambda_R = \lambda_2/\lambda_1 - 1$ as a function of α for the IPN (solid) and RCN (dashed) gels. Note that in (a) and (b), the curves for λ_1/λ_0 are the same as in Fig. 6b.

Fig. 8b shows the dependence of the Stage 2 growth index on χ_{pm} in comparison with that of Stage 1, for α = 0.008. The qualitative features in Stage 2 are the same as Stage 1 (Fig. 7a). The greater difference in the degrees of swelling of the RCN and IPN gels after Stage 2, $\lambda_2^{(RCN)} - \lambda_2^{(IPN)}$, is due to the accumulated elastic stress in the IPN as discussed above, and the insensitivity to χ_{pm} is due to the dominance of entropic contributions to the osmotic pressure over the enthalpic ones, as discussed in Section 3.3 above.

Fig. 9 presents the dependence of the growth index of Case II in Stage 2 on the crosslinker fraction α at high, $\phi_m^{(s)}$ = 1 (Fig. 9a), and low, $\phi_m^{(s)}$ = 0.3 (Fig. 9b); the volume fraction of monomers in the outside solution is χ_{ps} = 0.33. For comparison, the data for Stage 1 growth index are also presented. The relative growth index λ_R is shown in the corresponding insets. It is seen that at $\phi_m^{(s)}$ = 1, the growth behavior of Case II system (Fig. 9a) is quantitatively similar to that of Case I (Fig. 8a) because no solvent is present in both these systems.

After dilution of the outside monomer with solvent to $\phi_m^{(s)}$ = 0.33, the growth index of Case II system as a function of α decreases (Fig. 9b) although the qualitative features are the

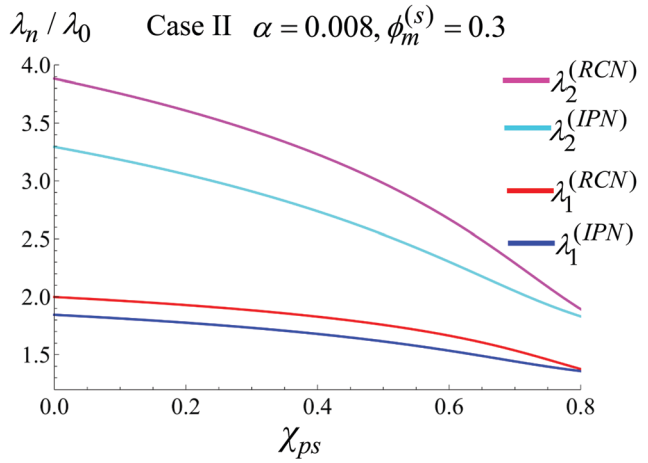

Fig. 10 The growth index λ_2/λ_0 for Stage 2 of growth of the IPN (cyan) and RCN (magenta) gels in contrast with the growth index λ_1/λ_0 for the IPN (blue) and RCN (red) gels for the Case II gel systems as functions of the polymer–solvent interaction parameter χ_{ps}. The monomer content in the outside solution is $\phi_m^{(s)}$ = 0.3, and the crosslinker content is α = 0.008. Note that the curves for λ_1/λ_0 are the same as in Fig. 7b.

same as at $\phi_m^{(s)} = 1$ (Fig. 9a). It is seen, in particular, that $\lambda_R < 1$ for almost all values of α, *i.e.*, Case II gels grow during Stage 2 to a lesser extent than at Stage 1. The outside solution does not contain enough monomer to support as much growth as observed at $\phi_m^{(s)} = 1$.

Finally, Fig. 10 shows the dependence of the growth index of Case II in Stage 1 and Stage 2 of gel growth on the interaction parameter χ_{ps} at the crosslinker content of $\alpha = 0.008$. The decrease in the growth index with an increase in χ_{ps} is more pronounced in Stage 2 than in Stage 1. After Stage 1, the gel already contains some fraction of secondary monomers incorporated to the polymer network. At higher χ_{ps}, adding more secondary monomers during Stage 2 causes a reduction of the osmotic pressure due to the strong enthalpic effects.

4. Conclusions

We developed a model for the growth of a polymer network that absorbs monomer and crosslinker from the surrounding solution to initiate the growth process. The subsequent polymerization of the adsorbed monomers and the crosslinking of the newly formed chains leads to the formation of a secondary network. In this manner, the primary and secondary gels form an interpenetrating network (IPN). Alternatively, the primary and secondary chains can undergo an exchange reaction and thus form a random copolymer network (RCN).

Due to the residual elastic stresses from the stretched primary network, the IPN is always stiffer (*i.e.*, swells less) than the RCN. The swelling of both the IPN and RCN, however, can be tailored to yield the softness required for a variety of applications. Specifically, if the primary networks are immersed in a solution with a high monomer volume fraction (*e.g.* $\phi_m^{(s)} = 1$), the swelling of both the IPN and RCN can be controlled by increasing the crosslinker fraction, α.

If the primary network is placed in a solution with a low monomer volume fraction ($\phi_m^{(s)} = 0.3$), the degree of swelling of both IPN and RCN is low; also the IPN is less sensitive to changes in α. In this scenario, however, the swelling of both the IPN and RCN can be controlled through the appropriate choice of the Flory–Huggins χ-parameters, which characterize interactions between the different components.

These effects and the greater swelling of the RCN over IPN, as well as the sensitivity of the swelling to the various control parameters, are magnified in Stage 2 of growth. Moreover, if the crosslinker fraction is kept sufficiently low, the gel grows more in Stage 2 in comparison with Stage 1, whereas at high crosslinker fraction the growth in Stage 2 is less than in Stage 1. Due to accumulation of stress in the IPN because of the stretching of chains, the repeated growth of this material is hindered. In contrast, the RCN can undergo subsequent interchain exchange reactions and thereby expand in size.

Fundamental aspects of the proposed growth scheme have been experimentally realized[7] in the case where growth emanated from the surface of a gel immersed in solution, and hence, the approach permitted control of the surface topology. In this case, the outer solution contained catalysts and photoinitiators, as well as monomers and crosslinkers. These different species diffused into the gel; when the sample was illuminated through a photomask, the growth process only occurred in the illuminated areas. In this manner, an array of micropillars were grown on a flat sample. These initial experiments indicate the feasibility of achieving the proposed mode of growth.

This growth process can potentially be used to repair damaged gels that encompass voids. The entire damaged sample would now serve as the ''seed'' that is immersed into a bath of monomers and crosslinkers (equivalent to Stage 0). The voids left by the damage are more accessible and permeable than the intact portions and hence the solution would preferentially diffuse to these damaged regions. With these latter regions being preferentially swollen by the monomer solution, polymerization and crosslinking of the absorbed species (Stage 1) can lead to ''regeneration'' of the gel within the voids and a degree of material's repair. (On a qualitative level, similar principles are operative in the regeneration of gels with the introduction of light-sensitive iniferters; illuminated iniferters initiate the polymerization and crosslinking of nearby monomers in solution and thereby fill voids with new gel.[5])

These different processes are controllable and introduce a new method for manufacturing polymeric materials with specified sizes and shapes. The systems, however, are sufficiently complex (with a large number of control parameters) that these calculations can provide valuable guidelines for tailoring the properties of the growing gels.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

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