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Supplementary information

Monomer diffusion into static and evolving polymer networks during frontal photopolymerisation

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1 Eulerian kinematics and conservation of volume

The diffusion-driven expansion of the polymer network will cause a material element that is originally located at a point Z to be displaced by an amount u to a new position z. In an Eulerian framework, this displacement is written as

$$u(z,t) = z - Z(z,t).$$
 (1)

In physical terms, (1) describes how far the material element that is currently located at point z at time t has moved from its initial position given by Z(z,t). The time dependence of Z reflects the fact that different material points can pass through the same Eulerian coordinate z as t increases. The initial polymer network is assumed to be undeformed, u(z,0) = 0. Due to symmetry considerations, the displacement at the centerline must be equal to zero. Furthermore, the displacement at the surface must be equal to the difference between the current and initial (half) thickness of the layer. Thus, the boundary conditions for u are given by

$$u(0,t) = 0, \quad u(h(t),t) = h(t) - h(0).$$
 (2)

The deformation of the polymer network is conveniently described by the local stretch, λ , which characterises the degree of expansion ($\lambda > 1$) or shrinkage ($\lambda < 1$) that a material element has undergone. In an Eulerian framework, the local stretch is defined as $\lambda \equiv (\partial Z/\partial z)^{-1}$ and, by using (1), can be written as

$$\lambda = \left(1 - \frac{\partial u}{\partial z}\right)^{-1}.$$
(3)

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By inverting (3) for the strain $\partial u/\partial z$, integrating across half of the layer (i.e., from z = 0 to z = h(t)), and imposing the boundary conditions (2), an implicit relationship between the half-thickness of the layer h and the local stretch can be obtained,

$$h(t) - h(0) = \int_0^{h(t)} (1 - \lambda^{-1}) \,\mathrm{d}z.$$
(4)

From a physical standpoint, (4) represents global conservation of volume for the polymer network. Due to the local incompressibility of the monomer and polymer network, the local stretch is linked to the volume fraction of monomer via

$$\lambda = \frac{1}{1 - \phi_m},\tag{5}$$

which represents the local conservation of volume. Using (5) in (4) shows the intuitive result that the net expansion of the polymer network is equal to the total volume of absorbed monomer:

$$h(t) - h(0) = \int_0^{h(t)} \phi_m(z, t) \,\mathrm{d}z.$$
(6)

2 Derivation of the equilibrium monomer fraction

The governing equations for the swelling of a static polymer network can be written as

$$\frac{\partial \phi_m}{\partial t} + \frac{\partial}{\partial z} \left(\phi_m v_m \right) = 0, \tag{7a}$$

$$\phi_m v_m + (1 - \phi_m) v_n = 0, \tag{7b}$$

$$\phi_m (1 - \phi_m)(v_m - v_n) = -\frac{\Omega_m D(\chi)\phi_m}{k_B T} \frac{\partial}{\partial z} \left(\mu_m + p\right), \tag{7c}$$

$$\frac{\partial \sigma_n^e}{\partial z} = \frac{\partial p}{\partial z},\tag{7d}$$

where the chemical potential of monomer, effective stress, and local stretch are given by

$$\mu_m = \mu_m^0 + \frac{k_B T}{\Omega_m} \left[\log \phi_m + (1 - m^{-1})(1 - \phi_m) \right],$$
(8a)

$$\sigma_n^e = G(\chi)(\lambda - \lambda^{-1}), \tag{8b}$$

$$\lambda = (1 - \phi_m)^{-1}.\tag{8c}$$

Boundary conditions at the free surface are given by

$$\sigma_n^e - p = 0, \qquad z = h(t), \tag{9a}$$

$$\mu_m + p = \mu_m^0, \quad z = h(t).$$
 (9b)

The half-thickness of the polymer network satisfies

$$h(t) - h(0) = \int_0^{h(t)} \phi_m(z, t) \,\mathrm{d}z.$$
 (10)

At equilibrium, the monomer and polymer velocities vanish, $v_m = v_n = 0$; the momentum balance for the monomer (7c) implies that the total chemical potential $\mu_m + p$ is constant in space and, from (9b), equal to that of the monomer bath. Thus,

$$\mu_m + p = \mu_m^0 \tag{11}$$

throughout the network. Integration of the momentum balance for the mixture (7d) and imposing the boundary condition (9a) implies that the pressure is given by

$$p = \sigma_n^e = G(\chi) \left[(1 - \phi_m)^{-1} - (1 - \phi_m) \right].$$
(12)

Using the expressions for the chemical potential (8a) and the pressure (12) in (11) yields an equation for the equilibrium monomer fraction ϕ_m^{eq} :

$$\log \phi_m^{\rm eq} + (1 - m^{-1})(1 - \phi_m^{\rm eq}) + \frac{G(\chi)\Omega_m}{k_B T} \left[(1 - \phi_m^{\rm eq})^{-1} - (1 - \phi_m^{\rm eq}) \right] = 0.$$
(13)

The equilibrium film thickness, h^{eq} , can be calculated from (10) and is given by

$$h^{\rm eq} = \frac{h(0)}{1 - \phi_m^{\rm eq}} = \lambda^{\rm eq} h(0).$$
(14)

Equation (13) can also be obtained by minimising the total free energy $\mathcal{E}(\lambda, \phi_m) = \int_0^h \mathcal{F} dz$ under the constraint (8c) and using (14), where \mathcal{F} is the Helmholtz free energy density

$$\mathcal{F}(\lambda,\phi_m) = \frac{1}{2} \frac{G(\chi)}{\lambda} \left(\lambda^2 - 1 - 2\log\lambda\right) + \frac{k_B T}{\Omega_m} \left[\phi_m \log\phi_m + m^{-1}(1 - \phi_m)\log(1 - \phi_m)\right].$$
(15)

To carry out the energy minimisation, we first note that \mathcal{E} can be explicitly evaluated as

$$\mathcal{E}(\lambda,\phi_m) = \lambda h(0)\mathcal{F}(\lambda,\phi_m). \tag{16}$$

By introducing a Lagrange multiplier θ , the minimisers of \mathcal{E} that satisfy the constraint (8c) can be obtained by solving

$$\frac{\partial(\lambda \mathcal{F})}{\partial \lambda} - \theta = 0, \qquad (17a)$$

$$\lambda \frac{\partial \mathcal{F}}{\partial \phi_m} + \frac{\theta}{(1 - \phi_m)^2} = 0, \tag{17b}$$

$$\lambda - \frac{1}{1 - \phi_m} = 0. \tag{17c}$$

Elimination of θ and λ from the system yields (13).

3 Estimates of the diffusion coefficient

The dependence of the diffusion coefficient on the conversion fraction χ and the monomer temperature T has been estimated by fitting the model (7)–(10) (equivalently, the reduced model (18) in the main text) to the data produced from swelling experiments using static polymer networks. Numerical values for the diffusivity D are given in Table 1, which exhibit a strong increase with temperature, as expected. Surprisingly, the diffusivity appears to keep the same order of magnitude as the conversion fraction is increased for fixed temperatures. The calculated values for $\chi = 0.85$ are likely erroneous because the model is unable to capture the linear swelling kinetics associated with case-II diffusion. While an improved model that incorporates case-II diffusion [2, 5] might yield refined estimates for the diffusion coefficients, we leave this as an area of future work.

Table 1: Values for the cooperative diffusion coefficients, D, obtained by fitting the model (7)–(10) to the swelling data for static networks. The units of D are mm^2/min .

	$T=21~^{\circ}\mathrm{C}$	$T=45~^{\circ}\mathrm{C}$	$T=65~^{\circ}\mathrm{C}$
$\chi = 0.12$	4.8×10^{-6}	5.0×10^{-5}	1.9×10^{-4}
$\chi=0.35$	—	—	2.5×10^{-4}
$\chi=0.42$	1.9×10^{-6}	2.8×10^{-5}	_
$\chi=0.85$	2.9×10^{-6}	2.9×10^{-5}	1.5×10^{-4}

4 A simplified FPP-swelling model

The full FPP-swelling model can be written as

$$\frac{\partial \phi_n}{\partial t} + \frac{\partial}{\partial z} \left(\phi_n v_n \right) = K I_0 (1 - \phi_n) \exp(-\bar{\mu} z), \tag{18a}$$

$$\phi_n v_n = \frac{\Omega_m D(\chi)(1 - \phi_n)}{k_B T} \frac{\partial}{\partial z} \left(\mu_m + \sigma_n^e\right), \tag{18b}$$

$$\frac{\partial \lambda}{\partial t} + v_n \frac{\partial \lambda}{\partial z} = \lambda \frac{\partial v_n}{\partial z},\tag{18c}$$

$$\frac{\partial \sigma_n^e}{\partial t} + v_n \frac{\partial \sigma_n^e}{\partial z} = G(\chi)(\lambda + \lambda^{-1}) \frac{\partial v_n}{\partial z} - \frac{\sigma_n^e}{\tau_r},$$
(18d)

where the chemical potential is given by (8a) and the diffusivity is assumed to have the form $D(\chi) = D_0 \exp(-a\chi)$. Initial conditions for (18) are given by $\phi_n = 0$, $\lambda = 1$, and $\sigma_n^e = 0$ for t = 0.

In the absence of monomer diffusion, the network velocity is zero, $v_n = 0$, and the network fraction, position of the polymerisation front (i.e., the unswollen pattern height), and the induction time are given by

$$\phi_n(z,t) = 1 - \exp\left[-KI_0 t \exp(-\bar{\mu}z)\right],$$
(19a)

$$z_f(t) = \bar{\mu}^{-1} \log(t/\tau_i),$$
 (19b)

$$\tau_i = (KI_0)^{-1} \log(1/(1-\phi_c)).$$
(19c)

Furthermore, the network remains unstretched and stress-free, $\lambda = 1$ and $\sigma_n^e = 0$.

A simplified model for the polymerisation front z_f , valid in the limit of slow diffusion relative to conversion, $\delta \equiv D_0 \bar{\mu}^2 / (KI_0) \ll 1$, can be derived from the full system of governing equations using perturbation methods. First, the model is cast into dimensionless form by rescaling the variables as $z = \bar{\mu}^{-1}\tilde{z}$, $t = (KI_0)^{-1}\tilde{t}$ and $v_n = D_0\bar{\mu}\tilde{v}_n$. Due to the assumption of slow diffusion, we expect that the deformation and stress of the polymer network will be small. Therefore, we write $\lambda = 1 + \delta \tilde{\lambda}$ and $\sigma_n^e = \delta G(1)\tilde{\sigma}_n^e$. The diffusivity and elastic modulus are written as $D(\chi) = D_0\tilde{D}(\chi)$ and $G(\chi) = G(1)\tilde{G}(\chi)$. After dropping the tildes, the dimensionless model can be written as

$$\frac{\partial \phi_n}{\partial t} + \delta \frac{\partial}{\partial z} \left(\phi_n v_n \right) = (1 - \phi_n) \exp(-z), \tag{20a}$$

$$\phi_n v_n = -D(\chi) \left[\left(1 - (1 - m^{-1})(1 - \phi_n) \right) \frac{\partial \phi_n}{\partial z} - \beta \delta (1 - \phi_n) \frac{\partial \sigma_n^e}{\partial z} \right], \quad (20b)$$

$$\frac{\partial\lambda}{\partial t} + \delta v_n \frac{\partial\lambda}{\partial z} = (1 + \delta\lambda) \frac{\partial v_n}{\partial z},$$
(20c)

$$\frac{\partial \sigma_n^e}{\partial t} + \delta v_n \frac{\partial \sigma_n^e}{\partial z} = G(\chi) [1 + \delta \lambda + (1 + \delta \lambda)^{-1}] \frac{\partial v_n}{\partial z} - \frac{\sigma_n^e}{\tau_r},$$
(20d)

where $\beta = v_m G(1)/(k_B T) \simeq 13$ for this particular system (optical adhesive NOA81 at a temperature of T = 65 °C). We will assume that δ is sufficiently small that $\beta \delta \ll 1$ as well. Under this condition, the problems for the stress, stretch, and composition decouple and, thus, the network fraction can be obtained from (20a) and (20b). To proceed further, we now pose a perturbative expansion in powers of δ of the form

$$\phi_n(z,t) = \phi_n^{(0)}(z,t) + \delta \phi_n^{(1)}(z,t) + \dots, \qquad (21a)$$

$$v_n(z,t) = v_n^{(0)}(z,t) + \delta v_n^{(1)}(z,t) + \dots,$$
 (21b)

$$z_f(t) = z_f^{(0)}(t) + \delta z_f^{(1)}(t) + \dots, \qquad (21c)$$

$$\tau_i = \tau_i^{(0)} + \delta \tau_i^{(1)} + \dots$$
 (21d)

An expansion in τ_i is required in order to ensure that the approximation for z_f satisfies $z_f(\tau_i) = 0$, at least in an asymptotic sense. The leading-order contributions to the network fraction, polymerisation front, and induction time, $\phi_n^{(0)}$, $z_f^{(0)}$, and $\tau_i^{(0)}$, are the dimensionless versions of (19) given by

$$\phi_n^{(0)}(z,t) = 1 - \exp(-t\exp(-z)), \tag{22a}$$

$$z_f^{(0)}(t) = \log\left(t/\tau_i^{(0)}\right),$$
 (22b)

$$\tau_i^{(0)} = \log(1/(1-\phi_c)). \tag{22c}$$

The correction to the front position, $z_f^{(1)}$, is determined by expanding the condition $\phi_n(z_f(t), t) = \phi_c$ in powers of δ to find that

$$z_f^{(1)}(t) = -\left[\frac{\partial \phi_n^{(0)}(z_f^{(0)}(t), t)}{\partial z}\right]^{-1} \phi_n^{(1)}(z_f^{(0)}(t), t) = \left[\tau_i^{(0)}\right]^{-1} \exp\left(\tau_i^{(0)}\right) \phi_n^{(1)}(z_f^{(0)}(t), t).$$
(23)

Similarly, the correction for the network fraction, $\phi_n^{(1)}$, is governed by

$$\frac{\partial \phi_n^{(1)}}{\partial t} + \frac{\partial}{\partial z} \left(\phi_n^{(0)} v_n^{(0)} \right) = -\phi_n^{(1)} \exp(-z), \tag{24a}$$

$$\phi_n^{(0)} v_n^{(0)} = -D(\phi_n^{(0)}) \left(1 - (1 - m^{-1})(1 - \phi_n^{(0)}) \right) \frac{\partial \phi_n^{(0)}}{\partial z},$$
(24b)

with $\phi_n^{(1)} = 0$ when t = 0, where we have replaced the conversion fraction χ with the leading-order network fraction $\phi_n^{(0)}$. To obtain the solution of this problem, we first carry out a change of variable to write the equations in a frame of reference that travels with $z_f^{(0)}$. This change of variable is given by $\hat{z} = z - z_f^{(0)}(t)$ and $\hat{t} = t$. In addition, we use the ansatz $\phi_n^{(1)}(\hat{z}, \hat{t}) = \hat{t}\Phi_n(\hat{z})$, which, from (23), implies that

$$z_f^{(1)}(t) = \left[\tau_i^{(0)}\right]^{-1} \exp\left(\tau_i^{(0)}\right) t \Phi_n(0).$$
(25)

Therefore, the correction to the front position is a linear function of time. The problem for Φ_n is given by

$$\Phi - \frac{\mathrm{d}\Phi}{\mathrm{d}\hat{z}} + \frac{\mathrm{d}}{\mathrm{d}\hat{z}} \left(\hat{\phi}_n^{(0)} \hat{v}_n^{(0)}\right) = -\tau_i \exp(-\hat{z}) \Phi_n, \tag{26a}$$

$$\hat{\phi}_n^{(0)} \hat{v}_n^{(0)} = -D(\hat{\phi}_n^{(0)}) \left(1 - (1 - m^{-1})(1 - \hat{\phi}_n^{(0)}) \right) \frac{\mathrm{d}\phi_n^{(0)}}{\mathrm{d}\hat{z}},\tag{26b}$$

where $\hat{\phi}_n^{(0)}(\hat{z}) = 1 - \exp(-\tau_i^{(0)} \exp(-\hat{z}))$. By integrating (26a), we find that

$$\Phi_n(0) = -\exp(-\tau_i^{(0)}) \int_0^\infty \frac{\mathrm{d}}{\mathrm{d}\hat{z}} \left(\hat{\phi}_n^{(0)} \hat{v}_n^{(0)}\right) \exp(-\hat{z} + \tau_i^{(0)} \exp(-\hat{z})) \,\mathrm{d}\hat{z}.$$
(27)

Although (27) is cumbersome, it can be significantly simplified by exploiting the smallness of ϕ_c , which implies that $\tau_i^{(0)} = \log(1/(1-\phi_c)) \sim \phi_c$ is also small. Thus, by expanding (27) about $\tau_i^{(0)} \ll 1$, we find that

$$\Phi_n(0) \simeq \frac{1}{2} \frac{\tau_i^{(0)}}{m} - \frac{1}{6} \left(\frac{9 - 4m + 4a}{m} \right) \left(\tau_i^{(0)} \right)^2 + \dots,$$
(28)

Using only the leading contribution of (28), the dimensionless front position can be approximated by

$$z_f(t) = \log\left(t/\tau_i^{(0)}\right) + (1/2)\delta m^{-1}t + \dots$$
(29)

To put (29) into a more physically meaningful form, we impose the condition $z_f(\tau_i) = 0$; using the expansions in (21), we find that the correction to the induction time is $\tau_i^{(1)} = -(1/2)m^{-1}\tau_i^{(0)}$. Thus, by setting $\tau_i^{(0)} = \tau_i - \delta \tau_i^{(1)}$ in (29) and expanding about δ , the front position z_f can be written as

$$z_f(t) = \log(t/\tau_i) + (1/2)\delta m^{-1}(t-\tau_i).$$
(30)

Therefore, in the limit of slow diffusion, the dimensional position of the polymerisation front can be approximated as

$$z_f(t) = \bar{\mu}^{-1} \log \left(t/\tau_i \right) + (1/2)\bar{\mu}D_0 m^{-1} (t - \tau_i).$$
(31)

When ϕ_c is larger, as in the case of acrylate systems ($\phi_c \simeq 0.5$ [4]), the integral in (27) must be evaluated using numerical quadrature. The growth rate of $z_f^{(1)}$, which describes the diffusion-induced departure from the logarithmic kinetics (22b), can then be determined via the relationship (25), i.e.,

$$\frac{\mathrm{d}z_f^{(1)}}{\mathrm{d}t} = \left(\tau_i^{(0)}\right)^{-1} \exp\left(\tau_i^{(0)}\right) \Phi_n(0).$$
(32)

Figure 1 shows the results of numerically calculating the growth rate of $z_f^{(1)}$ using (32) for various values of ϕ_c and the diffusivity exponent *a* in the cases when the chain length is set to m = 5 (Fig. 1 (a)) and m = 50 (Fig. 1 (b)). The figure shows that increasing *m* only leads to small quantitative changes in the results. In all cases, the overall trend is that $dz_f^{(1)}/dt$ decreases with increasing *a*, which is to be expected since this corresponds to more rapidly decreasing diffusivities and restricted monomer transport. Interestingly, for moderate values of the critical conversion fraction ($\phi_c = 0.25$ and 0.5), the growth rate of $z_f^{(1)}$ can become negative for sufficiently large values of *a*, indicating that the overall height of the network, $z_f(t) = z_f^{(0)}(t) + \delta z_f^{(1)}(t)$, grows more slowly than when there is an absence of diffusion ($\delta = 0$). This 'stunted' network growth arises when two conditions are met: (i) ϕ_c is sufficiently large that newly converted material is distributed throughout the mixture by diffusion before it can accumulate and lead to a crossing of the ϕ_c threshold, and (ii) *a* is sufficiently large that monomer is unable to enter or move within the polymer network due to low values of *D* above ϕ_c .

By fitting (31) to the experimental data with m = 5 (see Fig. 2), we find that $D_0 = 0.18 \text{ mm}^2/\text{min}$ and 0.36 mm²/min when $I_0 = 1 \text{ W/m}^2$ and $I_0 = 10 \text{ W/m}^2$, respectively. These values are an order of magnitude larger as those predicted by fitting the full model to the data, which is likely a result of neglecting mechanical effects in the derivation of (31). Using the fitted values of D_0 from the simple



Figure 1: Growth rates of the correction to the polymerisation front $z_f^{(1)}$ as a function of the diffusivity exponent a and the critical network fraction ϕ_c for two chain lengths (a) m = 5 and (b) m = 50. Lines and symbols denote calculations of the growth rate (32) by numerical integration of (27) and using the asymptotic approximation valid for $\phi_c \ll 1$ given by (28), respectively.

model, we find that $\delta = 3.2$ and $\delta = 0.66$ for $I_0 = 1$ and 10 W/m², respectively. In neither of these cases is $\beta \delta \ll 1$.

The simple expression for the front position (31) is still able to capture the reaction-dominated and diffusion-dominated time regimes seen in the experimental data despite the fact that δ is not small. This is possible because the combination δm^{-1} is small. Moreover, as ϕ_n increases, the decrease in the dimensionless diffusivity $\tilde{D}(\phi_n)$ is faster than the growth of $\tilde{M}(\phi_n) \equiv 1 - (1 - m^{-1})(1 - \phi_n)$, implying that $\delta \tilde{D}(\phi_n)\tilde{M}(\phi_n) \leq \delta m^{-1} \ll 1$, i.e., the slow diffusion assumption is indeed valid even though δ itself is not small. In essence, this shows that δm^{-1} is perhaps a more suitable parameter to describe the relative rate of diffusion and the validity of (31).

5 Numerical implementation of the FPP-swelling model

Numerically implementing the FPP-swelling model (18), which is based on a sequential growth-swelling decomposition (See Sec. 4.1.3 of the main text), is straightforward. Our approach uses implicit time stepping of the governing equations with χ replaced by the network fraction ϕ_n computed at the previous time step multiplied by $\chi_{\text{max}} \simeq 0.85$, the maximum conversion fraction for NOA81 [3]. Spatial derivatives are discretised using second-order finite difference formulae. The resulting nonlinear system of algebraic equations is solved at each time step using Newton's method.

6 The role of crosslink-induced stress reduction

Figure 3 compares simulation results when crosslink-induced stress reduction is included in (solid lines) and absent from (dash-dotted lines) the FPP-swelling model (18). The evolution of the polymerisation front z_f is shown in Fig. 3 (a). We see that the inclusion of stress reduction leads to a slightly more rapid propagation of the front. To understand this result, we first note that, from (18b), the volumetric network flux, $q = \phi_n v_n$, can be decomposed into a Fickian component q_F driven by composition gradients



Figure 2: Comparison of the simplified FPP model (31), shown as dashed-dotted lines, with the experimental data (symbols). The leading-order approximation to the front position, $z_f^{(0)}$, given by (19b), is shown as the dashed curves.



Figure 3: Numerical simulations of the FPP-swelling model (18) with (solid lines) and without (dash-dotted lines) crosslink-induced stress reduction showing (a) the polymerisation front, (b) the effective stress, and (c) the Darcy (stress-driven) contribution to the network flux given by (33b). In panels (b) and (c), we use $I_0 = 10$ W/m² and t = 127 s, corresponding to $z_f = 1.5$ mm.

and a Darcy contribution $q_{\rm D}$ driven by gradients in the stress (equivalently, the pressure). Therefore, we can write $q = q_{\rm F} + q_{\rm D}$, where

$$q_{\rm F} = -D(\chi) \left[1 - (1 - m^{-1})(1 - \phi_n) \right] \frac{\partial \phi_n}{\partial z},$$
 (33a)

$$q_{\rm D} = \frac{\Omega_m D(\chi)}{k_B T} (1 - \phi_n) \frac{\partial \sigma_n^e}{\partial z}.$$
(33b)

The effective stresses and the Darcy fluxes are plotted in Fig. 3 (b) and (c), respectively, when $I_0 = 10$ W/m² and t = 127 s, corresponding roughly to $z_f = 1.5$ mm. We see that, in the absence of stress reduction, large gradients in the effective stress give rise to a negative Darcy flux, which drives the network towards the illuminated surface and opposes the expansion of the network due to monomer diffusion. Stress-reduction effects significantly decrease the stress gradients and the backflow due to the negative Darcy flux.

7 Comparison of alternative permeability laws

7.1 Linear and nonlinear laws in the model for a static polymer network

The governing equations for a static polymer network with a nonlinear permeability law can be combined into a single nonlinear diffusion equation given by

$$\frac{\partial \phi_m}{\partial t} = \frac{\partial}{\partial z} \left(\mathcal{D}(\phi_m) \frac{\partial \phi_m}{\partial z} \right), \tag{34a}$$

where the effective diffusivity \mathcal{D} is

$$\mathcal{D}(\phi_m) = D(\chi)(1 - \phi_m)^{1 - \alpha} \left(1 - (1 - m^{-1})\phi_m + \beta\phi_m \left[1 + (1 - \phi_m)^{-2} \right] \right).$$
(34b)

Here, $\beta = \Omega_m G(\chi)/(k_B T)$ is a dimensionless constant representing the relative strength of elasticity. From the form of the effective diffusivity (34b), it is clear that differences between linear ($\alpha = 1$) and nonlinear ($1.5 \le \alpha \le 2$) [1] permeability laws will only be appreciable if the monomer uptake is sufficiently large. If the monomer remains dilute, $\phi_m \ll 1$, then $(1 - \phi_m)^{1-\alpha} \simeq 1$ for all values of α . The associated boundary and initial conditions for the model are

$$\left. \frac{\partial \phi_m}{\partial z} \right|_{z=0} = 0, \quad \phi_m(h(t), t) = \phi_m^{\text{eq}}, \quad \phi_m(z, 0) = 0.$$
(34c)

The half-thickness of the polymer network evolves according to

$$(1 - \phi_m^{\rm eq}) \frac{\mathrm{d}h}{\mathrm{d}t} = \mathcal{D}(\phi_m^{\rm eq}) \left. \frac{\partial \phi_m}{\partial z} \right|_{z=h(t)},\tag{34d}$$

which is supplemented with the initial condition $h(0) = h_i$.

To assess the impact of using different linear permeability laws in this study, we fit the model (34) to swelling data obtained using a bath temperature of T = 65 °C and static networks with conversion fraction $\chi = 0.12$ and $\chi = 0.35$, as these conditions led to the greatest expansion and thus monomer uptake. The diffusivity $D(\chi)$ is taken to be the single fitting parameter and we set $m = \infty$ and $V_m =$ $\Omega_m N_A = 525 \times 10^{-6} \text{ m}^3/\text{mol.}$ Figure 4 compares the fits using linear and nonlinear ($\alpha = 2$) permeability laws. The results are virtually indistinguishable, however, there are minor differences in the values of the diffusivity: we find that $D(0.12) = 1.9 \times 10^{-4} \text{ mm}^2/\text{min} (\alpha = 1), D(0.12) = 1.2 \times 10^{-4} \text{ mm}^2/\text{min}$ $(\alpha = 2), D(0.35) = 2.5 \times 10^{-4} \text{ mm}^2/\text{min} (\alpha = 1), \text{ and } D(0.35) = 1.8 \times 10^{-4} \text{ mm}^2/\text{min} (\alpha = 2).$ For both values of χ , the diffusivity decreases as α is increased. This is because slower diffusion is offset by enhanced monomer transport due to stronger changes in the network geometry (i.e., increasing pore size). Figures 4 (b) and (d) plot the evolution of the strain on logarithmic axes, which clearly show that both permeability laws give rise to $t^{1/2}$ swelling kinetics. These swelling kinetics are the result of the self-similarity of the diffusive process for small times and not due to the choice of permeability law. However, once the monomer reaches the centerline of the network and boundary effects become relevant, this self-similarity will be destroyed and the swelling kinetics will be altered and influenced by the permeability law.



Figure 4: Comparisons of the static swelling model with linear ($\alpha = 1$) and nonlinear ($\alpha = 2$) permeability laws. Lines correspond to numerical simulations of (34) and symbols to experimental data obtained from static swelling experiments with a bath temperature T = 65 °C. The strain is defined as $\varepsilon(t) = h(t)/h(0) - 1$ and shown using linear axes (panels (a) and (c)) and logarithmic axes (panels (b) and (d)).

7.2 Exponenial and algebraic permeability laws in the model for an evolving polymer network

The assumption that the diffusivity varies according to $D_{\exp}(\chi) = D_0 \exp(-a\chi)$ leads to an exponential permeability law of the form (see (8) or (19c) in the paper)

$$k_{\exp} \sim \frac{(1-\phi_n)\exp(-a\phi_n)}{\phi_n},\tag{35}$$

where we have taken $\chi \simeq \phi_n$. Common permeabilities that are used in the literature [1] take the form

$$k_{\rm alg} \sim \frac{1 - \phi_n}{\phi_n^{\alpha}},\tag{36}$$

where $1.5 \leq \alpha \leq 2$, which is equivalent to assuming that the diffusivity varies according to $D_{\text{alg}}(\chi) = D_0 \chi^{1-\alpha}$. Both permeabilities have the same qualitative features; however, the algebraic form (36) has a stronger singularity as $\phi_n \to 0$. Thus, unlike the case of a static network, where the form of the nonlinearity in the permeability law is only relevant for sufficient large monomer uptake, it immediately becomes apparent in the case of an evolving network because the system begins in a monomer-rich $(\phi_n \ll 1)$ state.

We have fitted the model for an evolving polymer network to the experimental data for the network height z_f using both the exponential (35) and algebraic (36) permeability laws, taking a = 5 and $\alpha = 2$, and using D_0 as the fitting parameter. The computed and experimentally measured network heights, along with the unswollen profiles $z_f^{(0)}$, are are shown in Fig. 5 (a)–(b). For each intensity I_0 , the model curves are nearly identical. However, the value of the diffusion coefficient D_0 varies by an order of magnitude: we find $D_0 \simeq 8 \times 10^{-2} \text{ mm}^2/\text{min}$ and $D_0 \simeq 4 \times 10^{-3} \text{ mm}^2/\text{min}$ using the exponential (35) and algebraic (36) laws, respectively. The decrease in D_0 is due to the more singular nature of D_{alg} and hence k_{alg} , which drives a stronger flow of monomer into the polymer network. To compensate for the stronger flow, the value of D_0 must decrease. Figure 5 (c)–(d) compares the network fraction, excess monomer fraction, and the local stretch at a fixed time of t = 680 s with $I = 1 \text{ W/m}^2$ using the different permeability laws. The network fractions are very similar, although the expansion of the network and the positive and negative monomer excesses are more localised when the exponential form of the permeability is used. This is because the diffusivity D_{exp} decreases more rapidly with conversion fraction compared to D_{alg} , leading to restricted monomer transport in highly converted regions of the polymer network.

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Figure 5: Comparisons of models for evolving polymer networks with exponential (35) and algebraic (36) permeability laws. (a)–(b) Evolution of the network height $z_f(t)$ for different incident intensities I_0 . Solid lines correspond to numerical simulations, dashed lines are the unswollen height profile, and symbols are experimental data. (c)–(d) The network fraction ϕ_n (solid line), unswollen network fraction $\phi_n^{(0)}$ (dashed line), excess monomer fraction (dash-dotted line), and local stretch λ (dotted line) at a fixed time of t = 680 s with $I_0 = 1 \text{ W/m}^2$.

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