Electronic Supplementary Material (ESI) for Soft Matter.

Supplemental Information: Swelling Responses of Surface-Attached Bottlebrush Polymer Networks

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A. NMR for Bottlebrush Polymers

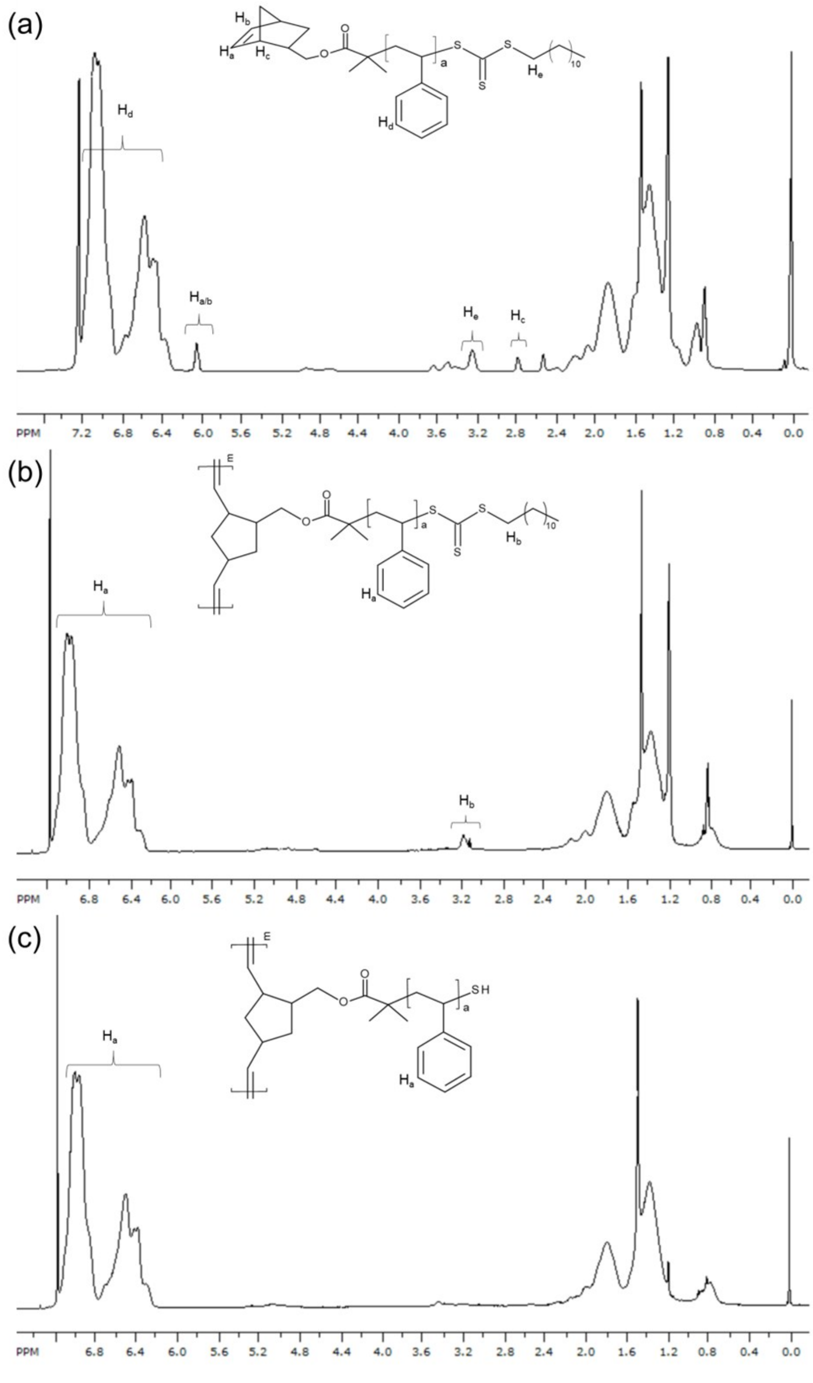

Figure S1. ^{1}H NMR spectra of NB-PS-CTA macromonomer (a), P(NB-PS-CTA) bottlebrush polymer (b) and P(NB-PS-SH) bottlebrush polymer (c) in $CDCl_3$ at a 10mg/mL concentration

Figure S1 illustrates the ^{1}H NMR spectra obtained for a PS macromonomer (Figure S1a) PS bottlebrush before the removal of the chain transfer agent (CTA) and PS-SH bottlebrush after the removal the CTA. The removal of the CTA terminal group is indicated by the disappearance of the peak at 3.25ppm which corresponds to the hydrogen on the dodecyl chain.

B. Gel Permeation Chromatography (GPC)

Figure S2 reports the GPC traces for the respective PS bottlebrush polymers used in this study. The dotted black line represents the linear PS macromonomer, NB-PS-CTA, while the solid green line represents the CTA terminated PS bottlebrush polymers, P(NB-PS-CTA). Finally, the red solid line represents the thiol-terminated PS bottlebrush polymers obtained after aminolysis. After aminolysis, the bottlebrush peaks are shifted to longer retention times which indicates a decrease in overall molecular weight. Note that a small percentage of BB_200 material is slightly crosslinked during aminolysis, so some of the bottlebrushes have $f_2 = 2 \times 65$ branches. However, this has little impact on the analysis by Eq (5) in the manuscript, as the f_2-containing term is already negligible when $f_2 = 65$. The residual macromonomer could be incorporated in the network as a crosslink or dangling chain, or it could be extracted during the soak step (prior to swelling).

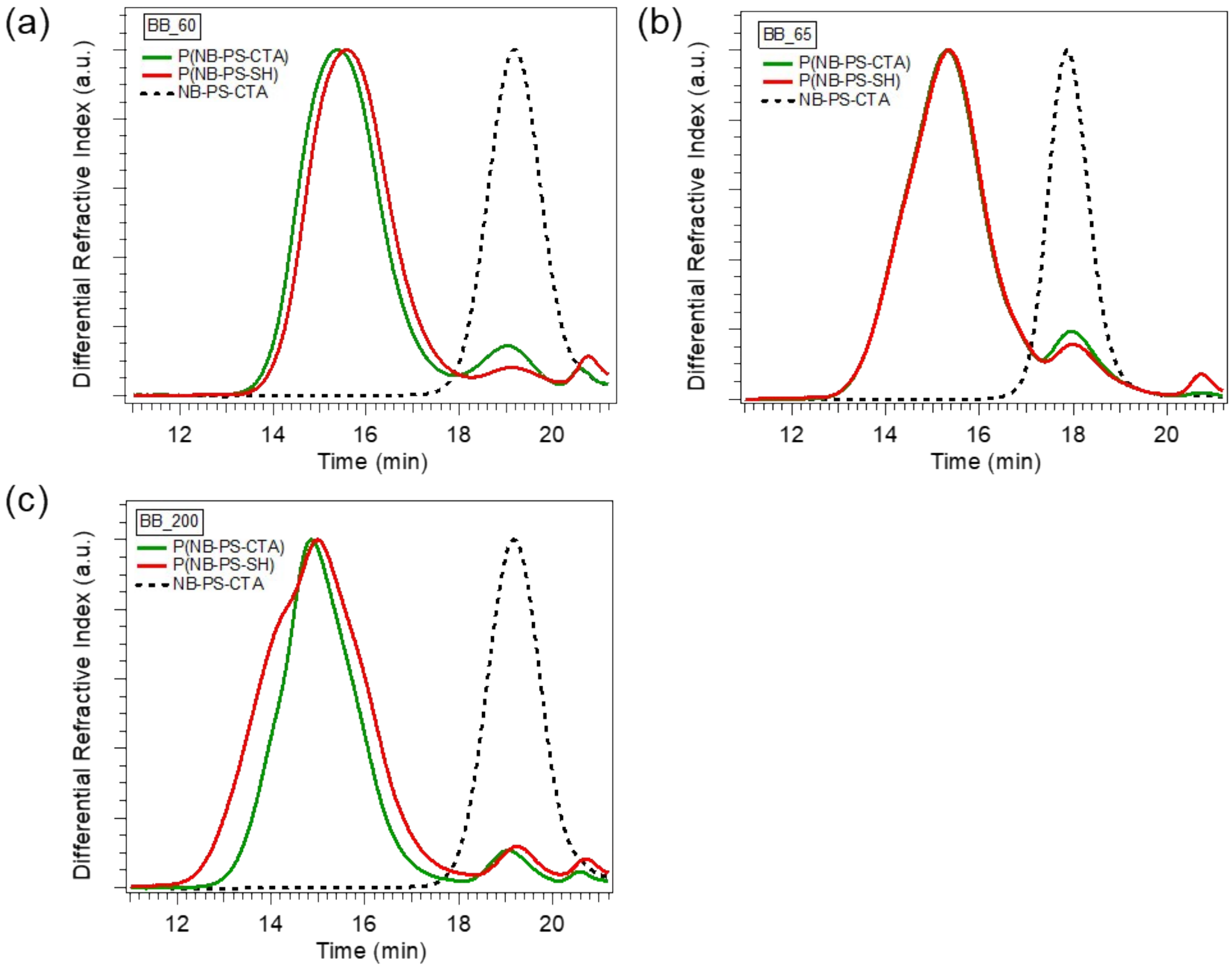

Figure S2. GPC traces of PS bottlebrushes and macromonomers used. (a) BB_60 (b) BB_65 and (c) BB_65. The macromonomers, NB-PS-CTA are represented by the dotted black line, the bottlebrush polymers with the CTA end group, P(NB-PS-CTA) are represented by the solid green line and the bottlebrush polymers with the thiol end group, P(NB-PS-SH) are represented by the solid red line.

C. Optical Microscopy of Polymer Films

Optical microscopy images of the linear and bottlebrush PS polymer thin films crosslinked at 1.8mJ/cm^2 were acquired using a NIKON LV150 reflected light microscope. The images were acquired at 50x magnification for both linear and bottlebrush PS polymers with overall molecular weight of ~60kg/mol (Figure S3) and 200kg/mol (Figure S4). At a crosslinking dose of 1.8mJ/cm^2, these films exhibited the largest extent of swelling and were still optically flat over tens of micrometers after the swelling measurements. The difference in image color before and after swelling is due to differences in illumination, not thickness change.

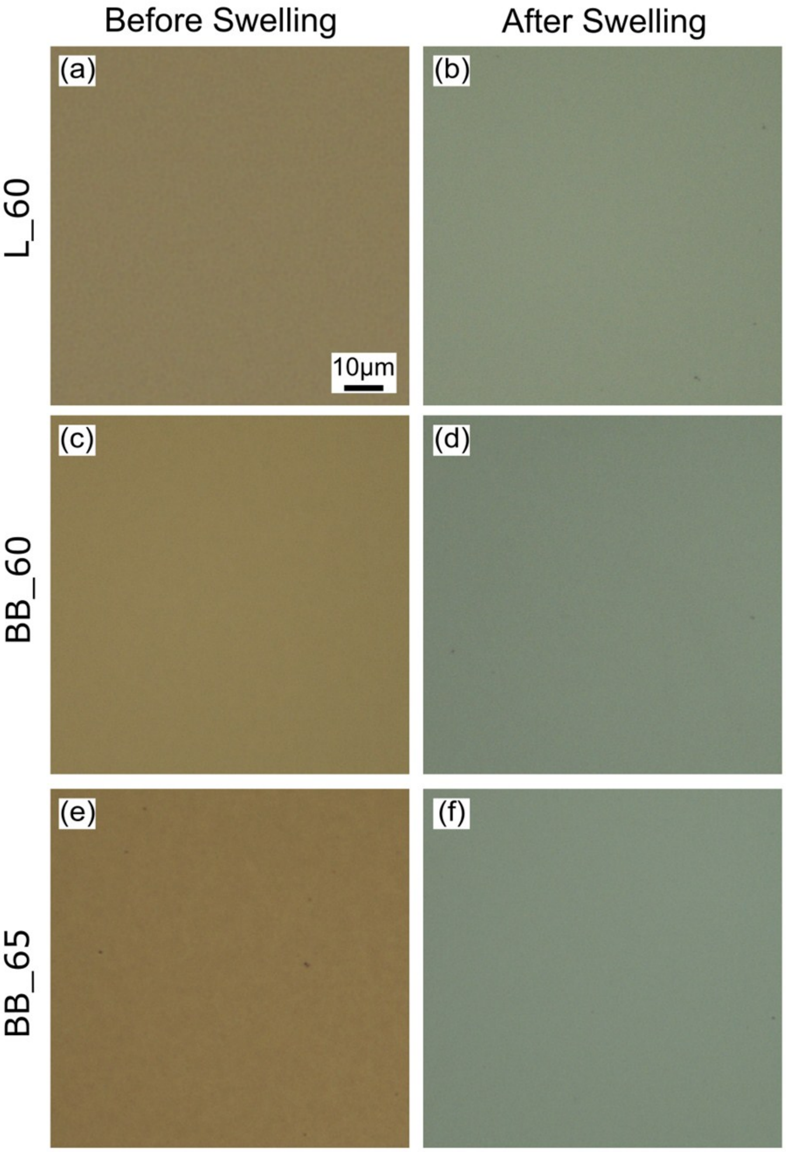

Figure S3. Optical microscopy images (50x) before swelling measurements (left) and after swelling measurements (right) of linear and bottlebrush PS polymer thin films with an overall molecular weight of 60kg/mol that were crosslinked at 1.8mJ/cm^2. The polymers are represented in each row where (a-b) L_60, (c-d) BB_60 and (e-f) BB_60.

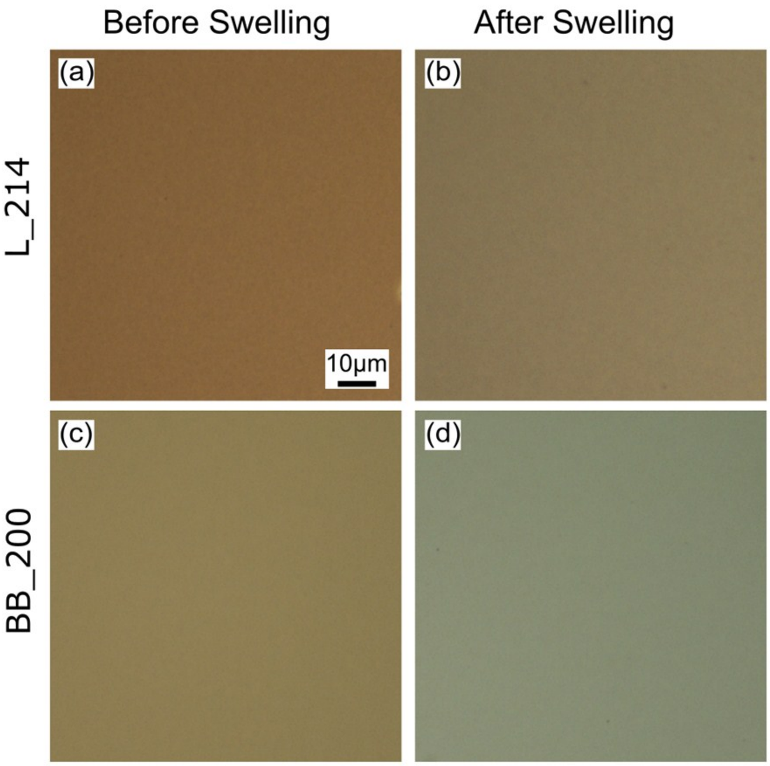

Figure S4. Optical microscopy images (50x) before swelling measurements (left) and after swelling measurements (right) of linear and bottlebrush PS polymer thin films with an overall $M_w \sim 200$ kg/mol that were crosslinked at 1.8mJ/cm^2. The polymers are represented in each row where (a-b) L_214, (c-d) BB_200.

D. Comparison of Swelling in Toluene and THF

The following figures compare trends for swelling in toluene and THF.

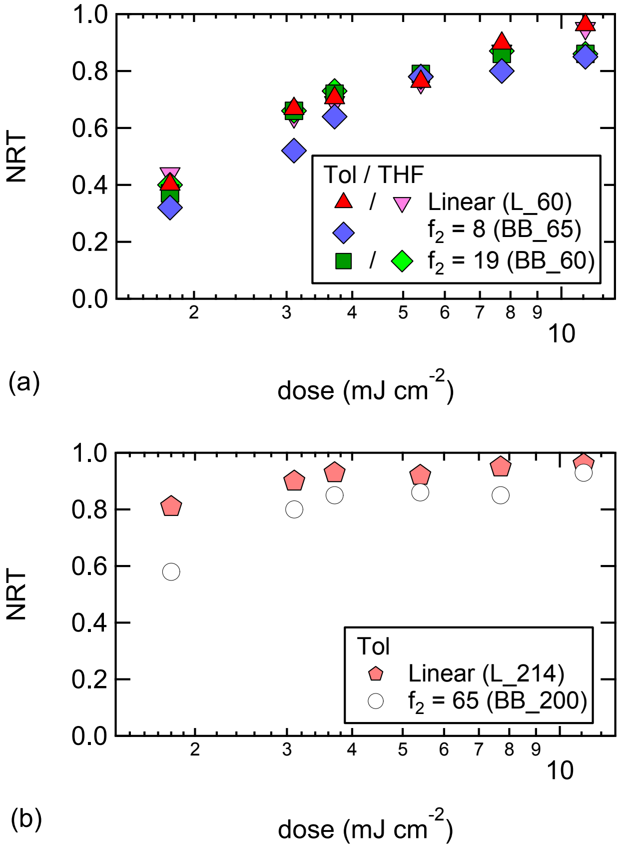

Figure S5. Normalized residual thickness (NRT) of surface-attached polystyrene networks as a function of radiation dose. Overall molecular weights of a) $M_w \approx 60$ kg/mol; and b) $M_w \approx 200$ kg/mol.

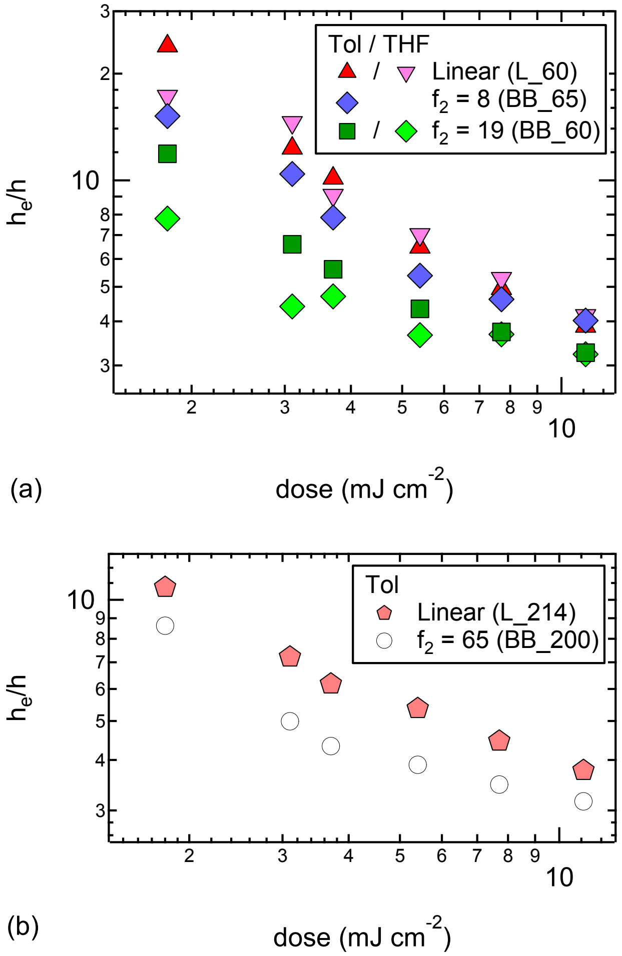

Figure S6. Swelling ratio of surface-attached polystyrene networks as a function of radiation dose. Overall molecular weights of a) $M_w \approx 60$ kg/mol; and b) $M_w \approx 200$ kg/mol.

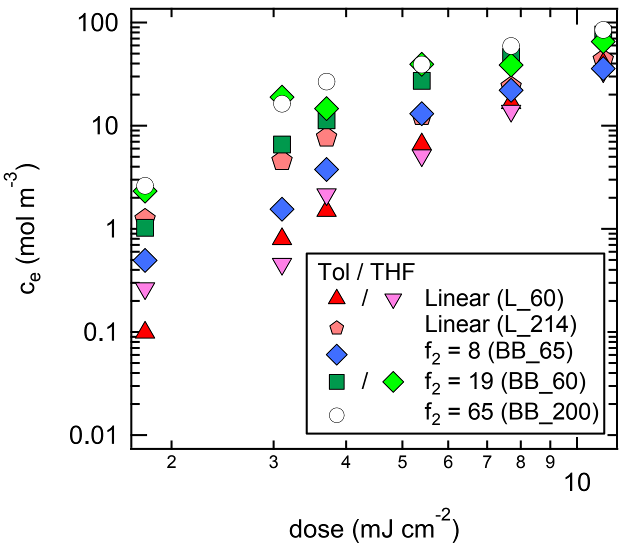

Figure S7. Calculated concentration of elastically effective chains (c_e) as a function of radiation dose.

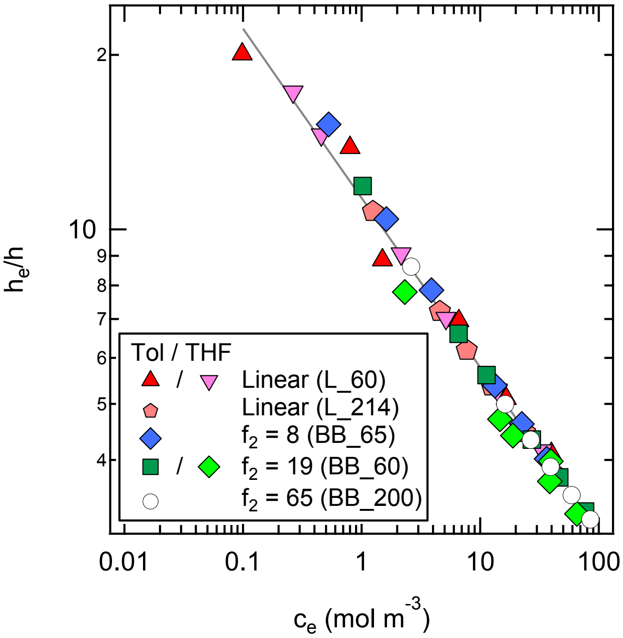

Figure S8. Measured swelling ratio as a function of calculated concentration elastically effective chains. Grey line marks the scaling $h_e/h \sim c_e^{-0.3}$. Note: Data for swelling in THF are scaled to account for the dependence on χ and $\hat{V}_1$ in Eq. 8 of the manuscript.

E. Equilibrium Swelling of Polymer Networks: Corrections for Architecture and Confinement

The following pages summarize the derivation of Flory's free energy model for equilibrium swelling of polymer networks.[1] We include two modifications that account for the thin film geometry and the different polymer architectures: First, the swelling is restricted to one dimension,[2] as the networks are attached to a substrate with covalent bonds. Second, to describe the bottlebrush architecture, we include the formation of intramolecular "crosslinks" with junction functionality N_b, where N_b is the number of branch points.[3]

I. Linear Polymer Precursor

Our aim is to derive a function for the equilibrium volume fraction of polymer ϕ_2, which is related to the equilibrium extension ratio λ. Towards this aim, we develop the change in free energy due to the swelling process:

$$(Eq. 1) \quad \Delta G = \Delta H - T\Delta S$$

We start with the analysis for crosslinking a linear polymer. Following the approach from Flory[1,4], the swelling entropy of a cross-linked polymer network (ΔS_4) is calculated from three changes of state (Figure S9):

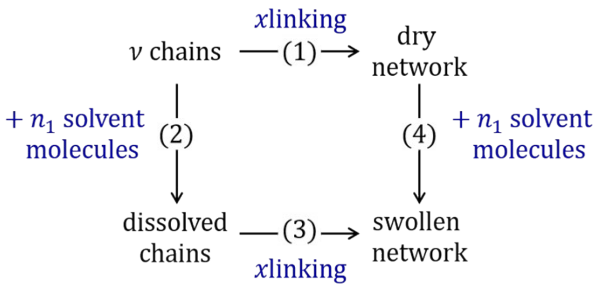

Figure S9. Path to calculate swelling entropy of a crosslinked polymer network.

The entropy change from joining ν linear chains into $2\nu/f$ crosslinks, producing a network, is calculated with Boltzmann's Law and Sterling's approximation from the probability function in Eq. 2:

$$(Eq. 2) \quad \Omega = \left(\frac{f\Delta\tau}{V}\right)^{2\nu(f-1)/f}\left[\left(\frac{2\nu}{f}\right)!\right]^{f-1}$$

f is the junction functionality, $\Delta\tau$ is the volume increment, V is the system volume, and k is Boltzmann's constant. First, for crosslinking in the dry state, we have

$$(Eq. 3) \quad S_1 = \frac{2k(f-1)}{f} ln\left(\frac{2\nu\Delta\tau}{V_0 e}\right)$$

Where V_0 is the dry system volume. Second, the entropy change for dissolution of ν chains in n_1 solvent molecules follows the ideal mixture model, and is

$$(Eq. 4) \quad S_2 = -k\left[n_1\, ln(1-\phi_2) + \nu \ln(\phi_2)\right]$$

where ϕ_2 is the volume fraction of polymer in the polymer/solvent system. Third, the entropy change for crosslinking of ν linear chains in n_1 solvent molecules, thereby forming a swollen network, is

$$(Eq. 5) \quad S_3 = \frac{2k\nu(f-1)}{f} ln\left(\frac{2\nu\Delta\tau}{V_f e}\right) + S_{el}$$

Note that the first term in the entropy defined by Eq. 5 is the same as Eq. 3, except the dry volume V_0 is replaced by the swollen volume V_f. The elastic entropy term in Eq. 5, S_{el}, describes the affine deformation of ν Gaussian chains due to swelling:

$$(Eq.6) \quad S_{el} =- \frac{k\nu}{2}\left[\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3\right] + k\nu \ln\left(\lambda_z\lambda_y\lambda_z\right)$$

The parameters λ_x, λ_y and λ_z capture the extension ratio along each direction. Finally, combining all the individual processes, and noting that $\phi_2 = V_0/V_f$, yields the entropy change for the swelling of a crosslinked network:

$$(Eq. 7) \quad \Delta S_4$$
$$= S_3 + S_2 - S_1 =- \frac{k\nu}{2}\left[\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3\right] + k\nu \ln\left(\lambda_z\lambda_y\lambda_z\right) - kn_1\, ln\left(1 - \phi_2\right) + \left[\frac{2k\nu(f-1}{f}\right.$$

The typical junction functionality for a random crosslinking process is $f = 4$, and this value is used for subsequent derivations in this section.

The enthalpy of mixing captures non-ideal solution behavior through a van Laar function (Flory-Huggins),[5,6]

$$(Eq. 8) \quad \Delta H = kT\chi n_1 \phi_2$$

where χ is the polymer-solvent interaction parameter. We then substitute Eq. 7 and Eq. 8 into Eq. 1, which yields

$$(Eq. 9) \quad \Delta G$$
$$= kT\chi n_1\phi_2 + \frac{kT\nu}{2}\left[\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3\right] - kT\nu\ln\left(\lambda_x\lambda_y\lambda_z\right) + kTn_1\, ln\left(1 - \phi_2\right) - \Big[\frac{2kT\nu(f -}{f}$$
$$ln\left(\phi_2\right)$$

At equilibrium, the solvent's chemical potential is the same both inside and outside the network, i.e.,

$$(Eq. 10) \quad \mu_1 - \mu_1^o = \left.\frac{\partial \Delta G}{\partial n_1}\right|_{T,P} = 0$$

where μ_1 and μ_1^o are the chemical potentials of solvent in the network and pure solvent, respectively. To evaluate the partial derivative in Eq. 10, we make the following substitutions in Eq. 9:

- $\phi_1 = \frac{n_1\hat{V}_1}{n_1\hat{V}_1 + V_0}$
- $\phi_2 = \frac{V_0}{n_1\hat{V}_1 + V_0}$

Note that $\hat{V}_1$ is the solvent molar volume. We use the chain rule to evaluate λ-dependent terms in Eq. 10:

- $\left.\frac{\partial \Delta G}{\partial n_1}\right|_{T,P} = \left.\frac{\partial \Delta G}{\partial \lambda}\right|_{T,P}\left.\frac{\partial \lambda}{\partial n_1}\right|_{T,P}$

The extension ratios are all equal for isotropic swelling, i.e., $\lambda_x = \lambda_y = \lambda_z = \lambda = \phi_2^{-\frac{1}{3}}$. Evaluation of Eq. 10 with $f = 4$ leads to the following expression for equilibrium swelling in three dimensions:

$$(Eq. 11a)\quad \chi\phi_2^2 + \ln\left(1 - \phi_2\right) + \phi_2 = \nu\frac{\hat{V}_1}{V_0}\left[\frac{\phi_2}{2} - \phi_2^{1/3}\right]$$

The swelling of a surface-attached film is constrained to one-dimension, *z*, so $\lambda_x = \lambda_y = 1$ and $\lambda_z = 1/\phi_2$.[2] Therefore, the entropy change due to swelling is modified, and evaluation of Eq. 10 leads to the following expression for equilibrium swelling in one dimension:

$$(Eq. 11b)\quad \chi\phi_2^2 + \ln\left(1 - \phi_2\right) + \phi_2 = \nu\frac{\hat{V}_1}{V_0}\left[\frac{\phi_2}{2} - \phi_2^{-1}\right]$$

Lastly, for an imperfect network that includes some "dangling" chains, we define the number of effective chains as $\nu = \nu_e$,[1,4] with

$$(Eq. 13)\quad \nu_e = \nu_0\left[1 - \frac{M_x\ f}{M\,f - 2}\right] = \frac{V_0\rho}{M_x}\left[1 - \frac{M_x\ f}{M\,f - 2}\right] = \frac{V_0\rho}{M_x}\left[1 - \frac{2M_x}{M}\right]$$

where ν_0 is the number of network chains, M_x is the number-average molecular weight between crosslinks, M is the primary number-average molecular weight of the system (before crosslinking), and ρ is the polymer density. (A perfect network is achieved when $M \rightarrow \infty$, as this eliminates chain ends.) This correction assumes the average length of each dangling end is M_x. Finally, the concentration of elastically effective chains is $c_e = \nu_e/V_0$, the number of effective junctions in the system is $n_x = 2\nu_e/f$, and the molar density of effective crosslinks is $c_x = n_x / V_0$.

II. Bottlebrush Polymer Precursor

The derivation for crosslinking of bottlebrush polymers follows a similar analysis as the preceding section, but we treat the bottlebrush backbone as a pre-formed junction with functionality $f = N_b$, where N_b is the degree of polymerization for the bottlebrush backbone. The entropy change is calculated from a new path that is illustrated in Figure S10, which follows closely to the derivation first reported by Cima and Lopina.[3] The enthalpy of mixing still follows the form of Eq. 8.

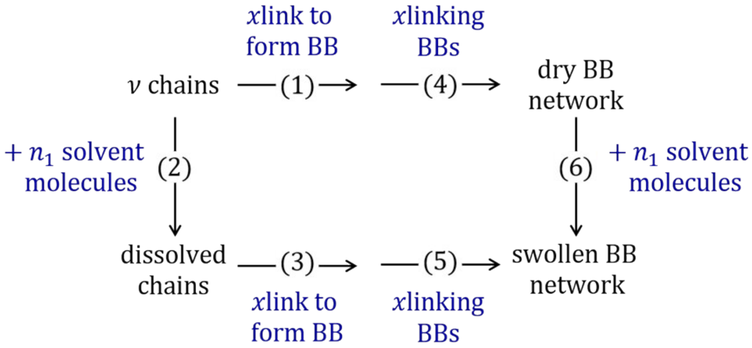

Figure S10. Path to calculate swelling entropy of a crosslinked bottlebrush polymer network.

To calculate the swelling entropy, we now define the probability of forming 1) bottlebrush cores with functionality $f_2 = N_b$; and 2) crosslinks between arms with functionality $f_1 = 4$. The number of chains ends in a radiation junction is ν_0, and the number of chain ends in a bottlebrush junction is ν_b. If we assume that the probability of joining of two bottlebrush side-chain ends at their ends is very low, so the total number of effective chains is $\nu = \nu_0 + \nu_b/2.$ This leads to the following probability function for the bimodal distribution of crosslinks:[3]

$$(Eq. 14) \quad \Omega = \frac{\left[\left(\frac{2\nu}{f_2}\right)!\right]^{f_2 - 1}\left[\left(\frac{2\nu_0}{f_1}\right)!\right]^{f_1 - 1}}{\left[\left(\frac{2\nu_0}{f_2}\right)!\right]^{f_2 - 1}\left[\left(\frac{\nu_b}{f_1}\right)!\right]^{f_1 - 1}}\left(\frac{f_2\Delta\tau}{V}\right)^{2\nu_b(f_2 - 1)/f_2}\left(\frac{f_1\Delta\tau}{V}\right)^{2(\nu_0 - \nu_b/2)(f_1 - 1)/f_1}$$

With application of Sterling's approximation, we derive the entropy of network formation in both the dry ($S_1 + S_4$) and swollen ($S_3 + S_5$) states. The expressions become quite cumbersome, so for brevity, we note that most of the terms will cancel when calculating the full path in Fig 2. As a checkpoint, we have:

$$(Eq. 15)\ S_5 + S_3 - S_4 - S_1 = k\left[-\frac{\nu_b}{f_2} - \frac{2\nu_0 - \nu_b}{f_1} + 2\nu_0\right]ln(\phi_2) + S_{el}$$

S_{el} was previously defined in Eq. 6, but for the bottlebrush system we replace ν by $\nu_0 - \nu_b/2$. The total entropy change for the swelling process is then

$$(Eq. 16)\ \Delta S_6$$

$$= S_5 + S_3 + S_2 - S_4 - S_1 = k\left[-\frac{\nu_b}{f_2} - \frac{2\nu_0 - \nu_b}{f_1} + 2\nu_0\right]ln(\phi_2) - \frac{k}{2}\left(\nu_0 - \frac{\nu_b}{2}\right)\left[\lambda_x^2 + \lambda_y^2 + \lambda_z^2 -\right.$$

$$\ln\left(\lambda_z\lambda_y\lambda_z\right) - k\left[n_1\ ln(1 - \phi_2) + \nu\ln\left(\phi_2\right)\right]$$

And the total free energy change is

$$(Eq. 17)\quad \Delta G$$

$$= kT\chi n_1\phi_2 + \frac{kT}{2}\left(\nu_0 - \frac{\nu_b}{2}\right)\left[\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3\right] - kT\left(\nu_0 - \frac{\nu_b}{2}\right)\ln\left(\lambda_x\lambda_y\lambda_z\right) + kTn_1\ ln(1 - \phi$$

$$ln(\phi_2) + k\nu Tln(\phi_2)$$

Following the same procedures as before, *i.e.*, the application of Eq. 10 and related substitutions, we arrive at the equilibrium swelling relations for bottlebrush networks. The results for isotropic and one-dimensional swelling of bottlebrush polymer networks are reported in Eq. 18a and Eq. 18b, respectively:

$$(Eq.\,18a)\quad \chi\phi_2^2 + \ln(1-\phi_2) + \phi_2 = \left(\nu_0 - \frac{\nu_b}{2}\right)\frac{\hat{V}_1}{V_0}\left[\left(\frac{\nu_b}{f_2(\nu_0-\nu_b/2)} + \frac{2}{f_1}\right)\phi_2 - \phi_2^{1/3}\right]$$

$$(Eq.\,18b)\quad \chi\phi_2^2 + \ln(1-\phi_2) + \phi_2 = \left(\nu_0 - \frac{\nu_b}{2}\right)\frac{\hat{V}_1}{V_0}\left[\left(\frac{\nu_b}{f_2(\nu_0-\nu_b/2)} + \frac{2}{f_1}\right)\phi_2 - \phi_2^{-1}\right]$$

Equations 18a and 18b can be written in terms of the molecular weight between crosslinks by making the substitution[3]

$$(Eq.\,19)\quad \nu_0 - \frac{\nu_b}{2} = \nu_e = \left(\nu_0 + \frac{\nu_b}{2}\right)\left(1 - \frac{M_x}{M_{sc}}\right) = \frac{V_0\rho}{M_x}\left(1 - \frac{M_x}{M_{sc}}\right)$$

The parameter M_{sc} is the molecular weight of a bottlebrush side-chain, and the dangling end correction (one per side-chain) is based on a junction functionality of $f_1 = 4$. Substitution of Eq. 19 into Eq. 18b leads to

$$(Eq.\,20)\quad \chi\phi_2^2 + \ln(1-\phi_2) + \phi_2 = \frac{\hat{V}_1\rho}{M_x}\left(1 - \frac{M_x}{M_{sc}}\right)\left[\left(\frac{1}{f_2(M_{sc}/M_x - 1)} + \frac{1}{2}\right)\phi_2 - \phi_2^{-1}\right]$$

As discussed in the preceding section, this correction assumes the length of a dangling end is M_x.

III. Scaling Law

Both swelling relations for surface-attached films, meaning Eq. 11b and Eq. 20, can be written in a more compact form:

$$(Eq.\,21)\quad \chi\phi_2^2 + \ln(1-\phi_2) + \phi_2 = a\left[b\phi_2 - \phi_2^{-1}\right]$$

Expanding the ln term to second order in ϕ_2 and substituting $\lambda = 1/\phi_2$, we arrive at

$$(Eq.22)\quad \lambda^3 - b\lambda = \left(\frac{1}{2} - \chi\right)\frac{1}{a}$$

When crosslink density is high, meaning M_x is small, we have $b = 0.5$ for both bottlebrush and linear primary polymers, and $a \propto \hat{V}_1 / M_x$. This leads to the scaling

$$(Eq.23)\quad \lambda \propto \left[\left(\frac{1}{2} - \chi\right)\frac{M_x}{\hat{V}_1}\right]^{1/3}$$

As the concentration of elastic chains in this limit is $c_e \propto 1 / M_x$, we can alternatively write

$$(Eq.23)\quad \lambda \propto \left[\left(\frac{1}{2} - \chi\right)\frac{1}{\hat{V}_1}\right]^{1/3} c_e^{-1/3}$$

IV. References

(1) Flory, P. J. Statistical Mechanics of Swelling of Network Structures. *The Journal of Chemical Physics* **1950**, *18* (1), 108–111.
(2) Toomey, R.; Freidank, D.; Rühe, J. Swelling Behavior of Thin, Surface-Attached Polymer Networks. *Macromolecules* **2004**, *37* (3), 882–887.
(3) Cima, L. G.; Lopina, S. T. Network Structures of Radiation-Crosslinked Star Polymer Gels. *Macromolecules* **1995**, *28* (20), 6787–6794.
(4) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press, 1953.
(5) Flory, P. J. Thermodynamics of High Polymer Solutions. *The Journal of Chemical Physics* **1941**, *9* (8), 660–660.
(6) Huggins, M. L. Solutions of Long Chain Compounds. *The Journal of Chemical Physics* **1941**, *9* (5), 440–440.