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Network Modulus and Superelasticity

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ABSTRACT: We discuss the elastic modulus G and swelling/deswelling behavior of networks as a function of their concentration ϕ and their preparation state. Simple scaling ideas reproduce the prediction of James and Guth for the modulus of networks swollen in a Θ solvent ($G \sim \phi^{1/3}$) but lead to a new prediction in a good solvent ($G \sim \phi^{7/12}$). We also suggest that both fully swollen modulus and dry modulus are related to swelling in ways that are independent of the network preparation details. By cross-linking long chains at low concentration and removing the solvent, many temporary entanglements are formed that force each network strand into a double-folded treelike compact configuration. These deswollen networks are capable of stretching by enormous amounts (~100×) without breaking (superelastic) and have a much lower modulus than melt-cross-linked networks. The energy stored in temporary entanglements during deswelling is released upon stretching, leading to a weaker-than-linear dependence of stress σ on elongation λ in tension ($\sigma \sim \lambda^{1/3}$).

1. Introduction

It has long been known that the properties of a cross-linked network depend on the preparation conditions (solvent class and concentration at cross-linking). We consider networks that are far beyond the gel point (with essentially zero sol fraction) prepared either by end-linking or random cross-linking of long flexible chains with many cross-links per primary chain, so that there is a well-defined average degree of polymerization N for a network strand.

We first develop scaling predictions for the modulus as a function of preparation conditions and final testing conditions, including the dry and fully swollen states, and predictions for the equilibrium swelling (section 2). By correlating swelling with preparation concentration, we demonstrate that most networks have more trapped entanglements than cross-links. Using a correlation of dry modulus and equilibrium swelling, we show that the affine assumption is valid for swelling. Assuming deswelling is also an affine transformation, we derive the modulus of deswollen networks in section 3.

Then we discuss the possible exploitation of these ideas to prepare networks at low concentration (in semidilute solution) which will have very few trapped entanglements. On deswelling, the strands of these networks form temporary entanglements that change the configurations of the strands, but deswelling does not introduce any permanent entanglements. Thus the modulus of these deswollen networks is considerably lower than melt-cross-linked networks. They also can stretch extremely far in their dry state, because the temporary entanglements can be pulled out. We finish with the stress-elongation behavior of these superelastic networks in tension.

2. Swelling and Modulus of Swollen Networks

Panyukov[1] has developed a blob picture for the equilibrium swelling of networks in a good solvent as a function of preparation conditions. The derivation starts with Flory and Rehner's original idea[2,3] that swelling equilibrium is dictated by a balance between the osmotic part of the free energy, F_{os}, acting to swell the network and the elastic part of the free energy, F_{el}, restricting the swelling. At a polymer volume fraction ϕ, a network, like a solution of linear chains, distributes itself into space-filling de Gennes blobs[4] of size ξ, each of which stores kT of osmotic energy.

$$\frac{F_{\text{os}}}{kT} \cong \left(\frac{b}{\xi}\right)^3 \cong \begin{cases} \phi^{9/4} & T \gg \Theta \\ \phi^3 & T = \Theta \end{cases} \qquad (1)$$

Here, b is the monomer size (Kuhn length) and Θ is the Θ temperature. The second results of eq 1 were obtained from the blob size[4] $\xi \cong b\phi^{-3/4}$ in good solvent ($T \gg \Theta$) and $\xi \cong b\phi^{-1}$ in Θ solvent ($T = \Theta$).

Following Panyukov,[1] the elastic part of the free energy is kT per strand times the Gaussian perturbation from the chains' preferred state at that concentration.

$$\frac{F_{\text{el}}}{kT} \cong b^3\nu\left(\frac{\lambda R_0}{R}\right)^2 \qquad (2)$$

Here, ν is the number density of network strands with average degree of polymerization N ($\nu \cong \phi b^{-3}N^{-1}$), λ is the linear expansion factor, R_0 is the root-mean-square end-to-end distance of a network strand in the preparation state, and R is the end-to-end distance the strand would have if it were a free chain of N monomers in solution at a volume fraction ϕ. Thus the term in the brackets in eq 2 is the actual end-to-end distance of the strand (λR_0, assuming affine displacement of cross-links) relative to its preferred end-to-end distance (both at concentration ϕ). Equation 2 is simply Hooke's law, applied to each network strand, with the spring constant determined by the fact that thermal noise (of energy kT) creates fluctuations of the end-to-end distance of order R. The scaling theory for semidilute solutions[4] provides the prediction for the size of unattached network strands.

$$R \cong \begin{cases} bN^{1/2}\phi^{-1/8} & T \gg \Theta \\ bN^{1/2} & T = \Theta \end{cases} \qquad (3)$$

We assume that swelling causes network junctions (cross-links) to move affinely—on average, junctions move apart on swelling by the same linear expansion λ as the macroscopic network.

$$\lambda \cong \left(\frac{\phi}{\phi_0}\right)^{-1/3} \qquad (4)$$

The affine assumption effectively requires no disinterpenetration of strands on swelling, because the number of

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strands in the volume of size λR_0 in the swollen state ($n = \phi\lambda^3R_0{}^3N^{-1}b^{-3}$) is the same as in the volume of size R_0 in the preparation state ($\phi_0R_0{}^3N^{-1}b^{-3}$) according to eq 4. This is distinct from the c^* theorem[4] which assumes complete disinterpenetration of network strands in the fully swollen state. For the c^* theorem to be valid, there would have to be a length scale where the deformation becomes affine that is *larger* than the strand size. Recent scattering experiments[5] may provide some evidence for such a length scale. Simple scaling cannot discriminate between these two conjectures, and without data to guide us we would anticipate that real networks could swell to some state between the affine and c^* theorem limits. Below we will show that experiments indicate swelling is quite close to affine, and we thus make predictions based on the affine assumption.

Combining eqs 2–4 gives the elastic contribution to the free energy, F_{el} and the elastic modulus G.

$$\frac{F_{\mathrm{el}}}{kT} \cong \frac{Gb^3}{kT} \cong N^{-1}\begin{cases} {\phi_0}^{5/12}\phi^{7/12} & T \gg \Theta \\ {\phi_0}^{2/3}\phi^{1/3} & T = \Theta \end{cases} \tag{5}$$

The Θ solvent result ($G \sim \phi_0{}^{2/3}\phi^{1/3}$) is identical to the prediction of James and Guth[3,6] but the good solvent result is a new prediction. Ilavsky et al.[7] have determined an exponent of 0.56 for the concentration dependence of the modulus for deswollen polyurethane networks prepared in xylene (a good solvent), in excellent agreement with our prediction of $^7/_{12}$. Bastide et al.[8] have determined this exponent to be 0.5 for polystyrene gels in the good solvent benzene.

The equilibrium swelling ratio Q is defined as the ratio of volumes of the gel in the fully swollen and dry states, which is simply the reciprocal of the volume fraction in the fully swollen state. Equilibrium swelling is determined by minimizing the total free energy ($F_{\mathrm{os}} + F_{\mathrm{el}}$) with respect to concentration.

$$Q \cong \begin{cases} N^{3/5}{\phi_0}^{-1/4} & T \gg \Theta \\ N^{3/8}\phi^{-1/4} & T = \Theta \end{cases} \tag{6}$$

Note that eq 6 predicts that the equilibrium swelling depends on the concentration of preparation. The good solvent prediction of $Q \sim N^{3/5}$ is identical to that of Flory and Rehner[2,3] and reasonably consistent with experimental data.[3] As in the case of swelling a linear polymer in good solvent, Flory arrived at the proper scaling by overestimating both the elastic and the osmotic parts of the free energy.[4] The Θ solvent prediction $Q \sim N^{3/8}$ has been suggested previously by Rempp and co-workers,[9] and they have reported some experimental evidence for that scaling in Θ solvent as well.[10] The predicted dependence on ϕ_0 is new for both Θ and good solvent (the Flory-style ideas lead to $Q \sim N^{3/5}\phi_0{}^{-2/5}$ in good solvent[11]).

The physics of equilibrium swelling is the original postulate of Flory and Rehner:[2] *networks swell until the osmotic and elastic contributions to the free energy are equal.* We therefore expect a simple relation between equilibrium swelling and modulus of the fully swollen gel (obtained from eqs 5 and 6).

$$G|_{\phi=1/Q} \cong b^{-3}kT\begin{cases} Q^{-9/4} & T \gg \Theta \\ Q^{-3} & T = \Theta \end{cases} \tag{7}$$

This familiar prediction[4,12] has been reasonably confirmed by recent experiments.[13–15] One study of the effect of temperature and solvent concluded that the exponent x ($G \sim Q^{-x}$) is $x = 2.3$ for good solvent and $x = 3.0$ for Θ solvent.[13] Others find x in the range $2.3 < x < 2.8$ for a variety of solvents,[14] and $x = 2.4$ in good solvent[15] and $x = 3.7$ in Θ solvent.[15]

Experimentally, the dependence of modulus and equilibrium swelling on preparation concentration predicted in eqs 5 and 6 has not yet been properly tested. Attempts have been made by cross-linking monodisperse starting chains (with the same degree of polymerization) at different concentrations. However, it has been clearly shown[7,16,17] that such networks do not have a constant effective strand length N. It has been previously suggested[7,18] that the strand length increases as ϕ_0 decreases because of fewer entanglements being trapped at low concentration. We present below a quantitative description of this effect.

The scaling predictions of eqs 5–7 were developed for networks having no permanent (trapped) entanglements. We call such networks *strongly cross-linked*, because the only way to have a negligible effect of trapped entanglements is to have a higher density of cross-links than trapped entanglements. These strongly cross-linked networks have strand lengths N that are shorter than the length of an entanglement strand at the preparation concentration $N_{\mathrm{e}}(\phi_0)$. The entanglement strand is a random walk of blobs.[4,19]

$$N_{\mathrm{e}}(\phi_0) \cong g\left(\frac{a}{\xi}\right)^2 \cong \left(\frac{a_1}{b}\right)^2\begin{cases} {\phi_0}^{-5/4} & T \gg \Theta \\ {\phi_0}^{-4/3} & T = \Theta \end{cases} \tag{8}$$

The number of monomers in a blob g is determined from scaling[4] ($g \cong \phi_0{}^{-5/4}$ in good solvent and $g \cong \phi_0{}^{-2}$ in Θ solvent), and the tube diameter a is also known from scaling ($a \cong a_1\phi_0{}^{-3/4}$ in good solvent[4] and $a \cong a_1\phi_0{}^{-2/3}$ in Θ solvent,[19] where a_1 is the tube diameter in the melt).

Strongly cross-linked networks have $N < N_{\mathrm{e}}(\phi_0)$ and thus have negligible contributions of permanent entanglements to their modulus (at any concentration ϕ). Lightly cross-linked networks (with $N > N_{\mathrm{e}}(\phi_0)$) are more typical, and the modulus and swelling behavior of these networks are given by eqs 5 and 6, with N replaced by $N_{\mathrm{e}}(\phi_0)$.

$$\frac{Gb^3}{kT} \cong \left(\frac{b}{a_1}\right)^2\begin{cases} {\phi_0}^{5/3}\phi^{7/12} & T \gg \Theta \\ {\phi_0}^{2}\phi^{1/3} & T = \Theta \end{cases} \tag{9}$$

$$Q \cong \begin{cases} (a_1/b)^{6/5}{\phi_0}^{-1} & T \gg \Theta \\ (a_1/b)^{3/4}{\phi_0}^{-3/4} & T = \Theta \end{cases} \tag{10}$$

In practice, most networks have modulus and swelling dominated by trapped entanglements, so the modulus and equilibrium swelling are given by eqs 9 and 10. This statement is supported by the fact that the stronger dependence on preparation concentration of both modulus and swelling predicted by eqs 9 and 10 (compared to eqs 5 and 6) is generally observed in experiments. The exponent for the equilibrium swelling ($Q \sim \phi_0{}^{-y}$) from the data in Figure 1 of ref 10 yields $y = 0.72$. Similar data for other networks in good solvent[18] conclude that $y = 0.71$ and 0.75. These are all in good agreement with the Θ solvent results of eq 10. Although the swelling was done in good solvents, the concentrations in the fully swollen state were greater than ~10% polymer, which is known experimentally to correspond to fully screened excluded volume.[20]

Modulus as a function of preparation concentration has been reported in one study[16] where the modulus was measured in the preparation state ($\phi = \phi_0$), with the result $G \sim \phi_0{}^{1.8-1.9}$. This exponent is certainly higher than predicted by eq 5 (with $\phi = \phi_0$, eq 5 predicts $G \sim \phi_0$), indicating that entanglements are important. However, the exponent is somewhat less than that predicted by eq 9 (with $\phi = \phi_0$, eq 9 predicts $G \sim \phi_0{}^{2.3}$), possibly indicating that at the lowest concentration ($\phi_0 = 0.05$) the chains are not entangled. This seems consistent with the experimental observation of the exponent increasing with precursor chain molecular weight (see Table II of ref 16).

Equations 9 and 10 predict the fully swollen modulus in both good and Θ solvent to scale as $G|_{\phi=1/Q} \sim \phi_0^{-z}$ with $z = {}^9/_4$. On the other hand, eqs 5 and 6 predict $z = {}^9/_{16}$ in good solvent. Experimentally,[18] $z = 1.8$, possibly indicating a crossover between the entanglement-dominated case and the strongly cross-linked case, but closer to entanglement domination.

Combining eq 4 with eqs 6 and 10 (and using $N_e(\phi_0)$ in eq 8 for N in the entangled cases) yields the fully swollen strand size λR_0.

$$\lambda R_0 \cong \begin{cases} bN^{7/10}\phi_0^{1/8} & T \gg \Theta,\ N < N_e(\phi_0) \\ a_1^{2/5}b^{3/5}N^{1/2}\phi_0^{-1/8} & T \gg \Theta,\ N > N_e(\phi_0) \\ bN^{5/8}\phi_0^{1/4} & T = \Theta,\ N < N_e(\phi_0) \\ a_1^{1/4}b^{3/4}N^{1/2}\phi_0^{1/12} & T = \Theta,\ N > N_e(\phi_0) \end{cases} \tag{11}$$

In the entangled cases, the affine assumption leads to an expansion λ that is independent of N, and in the unentangled cases only a very weak dependence on N is predicted ($\lambda \sim N^{1/5}$ in good solvent and $\lambda \sim N^{1/8}$ in Θ solvent). These predictions are in reasonable agreement with SANS experiments[21-23] which indicate a very weak dependence of strand size on swelling.

Since it is independent of N, eq 7 is still valid for lightly cross-linked networks with trapped entanglements. Thus eq 7 is more general than eqs 5, 6, 9, and 10. In fact, eq 7 does not rely on the affine assumption, as the c^* theorem predicts eq 7 as well. Equation 7 only relies on the Flory–Rehner hypothesis[2] that osmotic and elastic contributions to the free energy just balance and the standard scaling for the osmotic pressure[4] provides the fully swollen modulus. Thus it is not surprising that correlations between swollen modulus and equilibrium swelling have been experimentally found long ago.[24] The fact that eq 7 agrees so well with experimental data (see discussion following eq 7) demonstrates the validity of the Flory–Rehner hypothesis.

Another general equation is obtained for the relation between the modulus of the dry network (at $\phi = 1$) and the equilibrium swelling.

$$G|_{\phi=1} \cong b^{-3}kT\begin{cases} Q^{-5/3} & T \gg \Theta \\ Q^{-8/3} & T = \Theta \end{cases} \tag{12}$$

Like eq 7, this relation is independent of the strand length and the preparation concentration and true for both strongly cross-linked networks and entanglement-dominated networks, provided deswelling to the dry state is not so severe that temporary entanglements form (see section 3). For networks that are dominated by entanglements, this restriction requires $\phi_0 \cong 1$. However, unlike eq 7, eq 12 relies strongly on the affine assumption. For networks made in the absence of solvent, the c^* theorem predicts the equilibrium swelling in a good solvent to be $Q \cong N^{4/5}$, and because the modulus of the solvent-free network is $G|_{\phi=1} \cong b^{-3}kTN^{-1}$, the c^* theorem predicts $G|_{\phi=1} \cong b^{-3}kT\,Q^{-5/4}$. Thus a fundamental test of whether either the c^* theorem or the affine assumption is correct is to correlate the dry modulus of networks prepared without solvent with equilibrium swelling in a good solvent. This test has the great advantage of not relying on determining the effective N, which is complicated by imprecise control of reaction chemistry and entanglement effects.

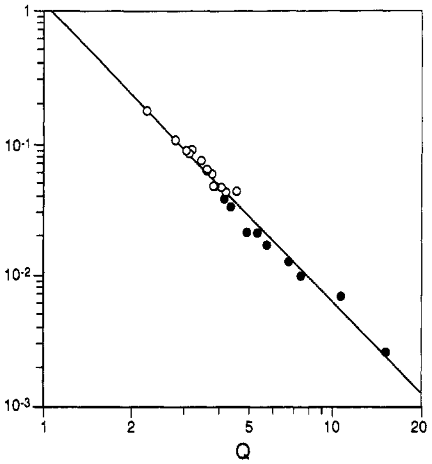

Figure 1. Dry modulus as a function of equilibrium swelling for PDMS networks (data of ref 26). Open symbols are model networks formed by end-linking chains with two reactive ends. Filled symbols are imperfect networks made from mixtures of chains with one and two reactive ends. The line is a least-squares regression fit with a slope of −2.3.

Equation 12 has been tested[25,26] with networks prepared by cross-linking chains in bulk ($\phi_0 = 1$), and the modulus (at $\phi = 1$) was correlated with the equilibrium swelling in good solvent as a power law ($G \sim Q^{-a}$). The exponent values are $1.4 \leq a \leq 1.6$ from one group[25] and $a = 2.3$ from another.[26] The ref 25 results are in reasonable agreement with the expectation of ${}^5/_3$ (and not agreeing well with the c^* theorem prediction of ${}^5/_4$), and the results of ref 26 are discussed in detail below. We should point out that there is a prefactor in eq 12 that depends on solvent choice,[25] and the theory for this prefactor has been discussed recently.[27]

In one study,[26] the predicted insensitivity to network structure of the relation between dry modulus and equilibrium swelling was tested. Two sets of networks were prepared by end-linking chains in ref 26. One set had defects intentionally introduced by incorporation of chains that can only attach to the network at one end, and the other had only bifunctional chains with the intention of minimizing defects. There is indeed a unique relation between dry modulus and equilibrium swelling, which is independent of N and the degree of network imperfection, as shown in Figure 1. A good solvent ($T \gg \Theta$) was used, and the data are reasonably represented by a power law, with $G \sim Q^{-2.3}$, consistent with a crossover from Θ-like behavior for the tightly cross-linked networks (which swelled very little) to $T \gg \Theta$ behavior for the networks capable of swelling a great deal. This crossover occurs for the same reason as it does for solutions of linear polymers—in practice the "good" solvents are never quite good enough ($T > \Theta$, but not $\gg \Theta$). Experimentally,[20] the crossover in linear polymer solutions occurs near $\phi = 0.1$, and this seems consistent with the data in Figure 1. From the data on dry modulus as a function of swelling for networks prepared in the absence of solvent,[25,26] we conclude that swelling in real networks is quite close to affine.

However, the generality of eq 12 for networks prepared at various concentrations has been tested[16] and found to fail. Equation 12 is based on the assumption of no new entanglements being introduced when deswollen from the preparation state to the dry state. This assumption breaks down for networks prepared at low concentration, as temporary entanglements form on deswelling that change the configurations of network strands, as discussed next.

3. Deswelling and Modulus of Deswollen Networks

The case of deswelling (preparing a network in solution and removing solvent) is slightly more complicated but uses the same basic equations for the osmotic and mechanical moduli (eqs 1 and 2). We shall see that eq 2 leads to the remarkable result that the modulus of deswollen networks can be much lower than that of melt-cross-linked networks. The physics is very simple. When strongly deswollen, the average gyration radius of a network strand is much larger than its average end-to-end distance.[23] Under the assumption of affine transformation, any macroscopic perturbation of the network will result in the same relative perturbation in the end-to-end distance of network strands (the cross-links move affinely). However, the gyration radius of network strands is much less perturbed by the deswelling.

Any trapped entanglements are introduced during network formation (at ϕ_0) and no additional entanglements are introduced when the network is swollen. However, the case of deswelling can be more complex, because even if the networks have no trapped entanglements, temporary entanglements may form at some concentration as solvent is removed. We shall see below that the presence of these temporary entanglements decreases the phase space that a strand can sample and thereby alters the concentration dependence of the modulus.

We first consider the case of strongly cross-linked networks with $N < N_e(\phi_0)$. During deswelling, at some concentration ϕ_e such unentangled networks will start to form temporary entanglements. Using standard scaling arguments, we calculate the concentration where entanglements become important.

$$\phi_e \cong \left[\frac{N}{N_e(1)}\right]^{-1/(\alpha-1)} \tag{13}$$

N is the (average) number of monomers between cross-links, $N_e(1)$ is the number of monomers in an entanglement strand in the melt (at $\phi = 1$), and α is the exponent describing the concentration dependence of the plateau modulus in solutions of linear polymers ($G_0 \sim \phi^\alpha$). In good solvents[4] $\alpha = {}^9/_4$ and we use the notation ϕ_e^{good} for the entanglement concentration. In Θ solvents[19] we use the notation ϕ_e^Θ and $\alpha = {}^7/_3$.

For deswelling to concentrations below ϕ_e, no new entanglements are introduced, and the modulus is predicted by eq 5. Above ϕ_e the network strands form temporary entanglements with one another that greatly restrict the allowed configurations of the strands. The end-to-end distance of a strand is determined by the contraction of the gel upon deswelling and can be much smaller than the Gaussian size of the strand. As for swelling, we make the affine assumption: on length scales larger than the distance between junction points, the network is a regular three-dimensional object that deswells (or swells) uniformly and the junction points move affinely (on average) during deswelling.

The effect of temporary entanglements on the configurational statistics of strands is analogous to melts (or concentrated solutions) of ring polymers.[28] We therefore summarize the configurational properties of a melt of rings before proceeding with the configuration of network strands.

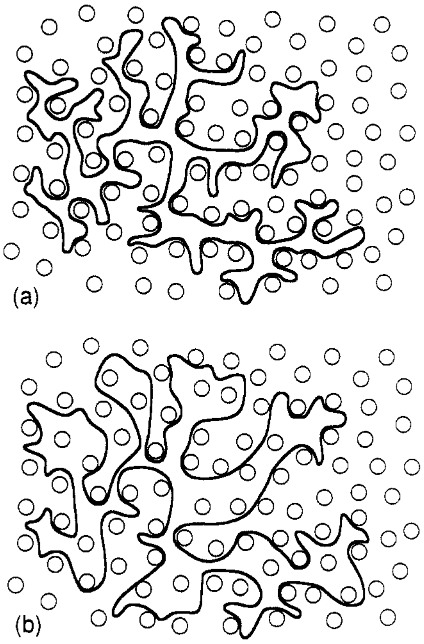

Figure 2. Schematic of a concentrated ring polymer in a Θ solvent. Open circles denote topological constraints caused by double-folded loops of neighboring ring polymers. (a) Ring with no interpenetrating loops. (b) Ring with interpenetrating loops.

The easiest way for nonconcatenated rings to interpenetrate (while preserving their topology) is by forming double-folded loops.[29] In an array of permanent obstacles, ring polymers form the double-folded treelike structure[29,30] shown in Figure 2a. The obstacles in Figure 2a are double-folded loops of neighboring rings. The distance between these obstacles is the entanglement distance $bN_e^{1/2}$. The gyration radius of each random tree of N monomers (of size b) is determined by the statistics of a Gaussian tree.[31]

$$R_{\mathrm{ring}} \cong bN_e^{1/2}\left(\frac{N}{N_e}\right)^{1/4} \cong b(N_eN)^{1/4} \tag{14}$$

The volume fraction of a single ring polymer inside the volume R_{ring}^3 is $(b/R_{\mathrm{ring}})^3N \cong N^{1/4}N_e^{-3/4}$. For $N < N_e^3$ the volume fraction is less than unity and thus rings are not space-filling and strongly overlap each other. The case of extremely high molecular weight ($N > N_e^3$) has been considered previously,[28] where each strand forms a compact globule of size roughly $N^{1/3}$ without overlapping. For flexible polymers $20 \le N_e \le 40$ usually and thus N_e^3 is of order 30 000. For polystyrene this corresponds to a molecular weight between cross-links of 10^7. We therefore only consider the case of $N < N_e^3$ here.

The system shown in Figure 2a can actually gain entropy without introducing any topological problems by having some of the double-folded loops open to allow penetration by other (smaller) loops, shown in Figure 2b. The fact that only smaller loops can penetrate an open loop of a given size leads to a hyperscaling condition: loops of a given size are just at their overlap concentration. The interpenetration is not crucial for the modulus and stress-elongation properties of deswollen networks, derived below. The full details of the loop interpenetration are needed for viscoelastic response and structure factor of deswollen networks, and these will appear in a future publication. The energy required to form the crumpled interpenetrating structures of Figure 2b turns out to be slightly less than that for the structure without loops (Figure 2a) but still of order kT per temporary entanglement.

The end-to-end distance of our network strands in the collapsed state is nonzero, so the analogy with rings is not the complete picture. Below we develop a description of the configuration of deswollen network strands that incorporates this analogy with rings. We divide the contour length L of a strand into two parts: a backbone of length L_{bb} and a collection of double-folded loops of total contour length $L - L_{\mathrm{bb}}$. The length of backbone is determined from minimization of the free energy. There is an entropic free energy penalty of $\sim kT$ per entanglement to form double-folded loops, thereby favoring partitioning of as

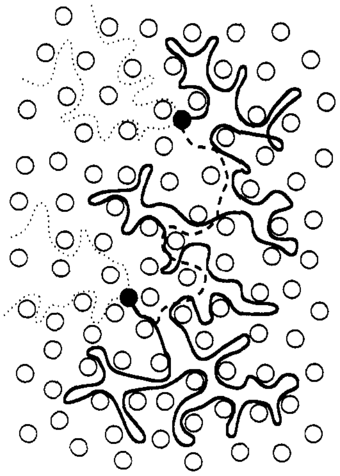

Figure 3. Schematic of a deswollen network strand in a Θ solvent. The strand (solid curve) is divided into a random-walk backbone (dashed curve) and a series of double-folded loops. Network junctions are shown as filled circles (with other network strands attached to these junctions shown as dotted curves). The open circles denote topological constraints due to double-folded loops of neighboring strands.

much of the strands into backbones as possible. However, if the backbones become entangled with each other, they are forced to have many strands sharing the same tube. This tube sharing costs an additional $\sim kT$ per entanglement, so the partitioning of the strand occurs such that backbones are always just at the concentration where they start to entangle. The remainder of the strand (with total contour length $L - L_{\rm bb}$) must form double-folded loops, as depicted in Figure 3. Since there is one backbone per strand, the number density of backbones is the same as the number density of strands.

$$\frac{N_{\rm bb}}{\phi_{\rm bb}} = \frac{N}{\phi} \tag{15}$$

$N_{\rm bb}$ is the number of monomers in the backbone and $\phi_{\rm bb}$ is the volume fraction of backbones. The splitting into backbone and loops is determined by entanglement constraints, the details of which depend on whether we are in Θ solvent or good solvent, and we consider each case in turn.

3.1. $\phi > \phi_{\rm e}^{\Theta}$ in Θ Solvent. For deswelling in a Θ solvent, the standard Θ solvent entanglement criterion[19] (see eq 8) determines the backbone size.

$$N_{\rm bb} \cong N_{\rm e}(1)\phi_{\rm bb}^{-4/3} \cong N_{\rm e}(1)\left(\frac{\phi N_{\rm bb}}{N}\right)^{-4/3} \tag{16}$$

The second result was obtained using eq 15. We now solve for the number of monomers in a backbone.

$$N_{\rm bb} \cong (N_{\rm e}(1))^{3/7}\left(\frac{\phi}{N}\right)^{-4/7} \tag{17}$$

The backbone length effectively defines the configurations that the strand can explore, thereby controlling the fluctuations of the end-to-end distance of the strand and setting the effective spring constant for stretching or compressing the strand. The backbone is a random walk, so the effective fluctuations of the end-to-end distance R in eq 2 are determined by Gaussian statistics.

$$R \cong bN_{\rm bb}^{1/2} \cong b(N_{\rm e}(1))^{3/14}\left(\frac{\phi}{N}\right)^{-2/7} \tag{18}$$

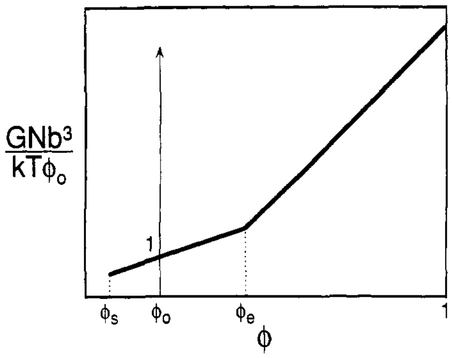

Figure 4. Concentration dependence of modulus for networks prepared in a Θ solvent. Note logarithmic scales.

We now combine eq 13 (with $\alpha = {}^7/_3$) and eq 18.

$$R \cong bN^{1/2}\left(\frac{\phi}{\phi_{\rm e}^{\Theta}}\right)^{-2/7} \tag{19}$$

Substituting into eq 2 allows us to calculate the modulus of a deswollen network prepared in a Θ solvent.

$$\frac{G}{kT} \cong \frac{\phi}{Nb^3}\left(\frac{\phi}{\phi_0}\right)^{-2/3}\left(\frac{\phi}{\phi_{\rm e}^{\Theta}}\right)^{4/7} \sim \phi^{19/21} \tag{20}$$

Other scaling predictions for α (see eq 13) in a Θ solvent all yield nearly the same value of the final exponent in eq 20, namely, quite close to but not greater than unity. The exponent α is believed to be bounded:[32] $2 \le \alpha \le 3$. With $\alpha = 2$,[33] then $G \sim \phi^{5/6}$, and if $\alpha = 3$,[34] then $G \sim \phi$. Note that in each case the modulus has a nearly linear dependence on concentration, as one might naively expect from the simple idea of kT per strand (eq 2 with $\lambda R_0 \cong R$).

The full concentration dependence of modulus for networks made in a Θ solvent and either swollen or deswollen is shown in Figure 4. For strongly cross-linked networks (treated above) the crossover from the unentangled result (eq 5) to the entangled result (eq 20) occurs at $\phi_{\rm e}^{\Theta} > \phi_0$. For lightly cross-linked (entangled) networks (i.e., with $N > N_{\rm e}(\phi_0)$) the effective strand length just becomes $N_{\rm e}(\phi_0)$ and, therefore, $\phi_{\rm e}^{\Theta} = \phi_0$. In this case all deswelling follows the entangled deswelling result (eq 20).

3.2. $\phi > \phi_{\rm e}^{\rm good}$ in Good Solvent. The difference for the good solvent case arises from the strong correlations caused by excluded volume. These correlations force the chain into a string of space-filling blobs of size ξ (see eq 1). When the chains are entangled, these blobs effectively play the role of the renormalized monomer (since Gaussian statistics applies for the backbone on length scales larger than ξ). It is important to note that the blobs are still space-filling, but some blobs are associated with backbones while others are parts of loops, as depicted in Figure 5.

The number of blobs in the backbone is determined from an entanglement criterion, because the backbones are just at the entanglement threshold, as discussed above. Equation 16 applies with a renormalized monomer and the Θ solvent value of α, because entanglement occurs on scales larger than ξ, where excluded volume is screened.

$$\frac{N_{\rm bb}}{g} \cong N_{\rm e}(1)\left(\frac{\phi_{\rm bb}}{\phi}\right)^{-4/3} \tag{21}$$

Here, g is the number of monomers per blob (and thus $N_{\rm bb}/g$ is the number of blobs per backbone) and $\phi_{\rm bb}/\phi$ is the volume fraction of blobs in the backbone (because blobs are space-filling). We use the standard good solvent scaling result that $g \cong \phi^{-5/4}$ along with eq 15 to obtain the

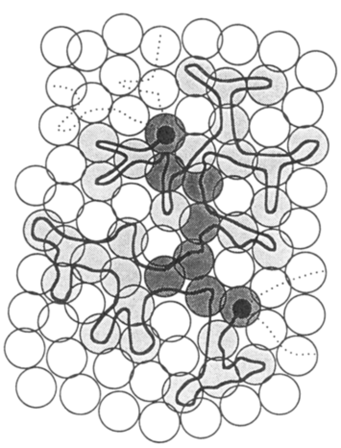

Figure 5. Schematic of a deswollen network strand in a good solvent. The strand (solid curve) is a collection of swollen blobs (circles), some of which are part of the random-walk backbone (darkly-shaded circles) and others which are part of double-folded loops (lightly-shaded circles). The unshaded circles denote blobs from neighboring strands. The small filled circles are network junctions, and the strands attached to these junctions are shown as dotted curves.

number of monomers in a backbone.

$$N_{\mathrm{bb}} \cong (N_{\mathrm{e}}(1))^{3/7} N^{4/7} \phi^{-15/28} \qquad (22)$$

Some blobs of size ξ are parts of backbones, while others are parts of loops that effectively act as a Θ solvent for the backbones. The effective fluctuation size R is given by Gaussian statistics for this backbone strand of blobs.

$$R \cong \xi\left(\frac{N_{\mathrm{bb}}}{g}\right)^{1/2} \cong b\phi^{-1/8} {N_{\mathrm{bb}}}^{1/2} \qquad (23)$$

We now combine eq 13 (with $\alpha = {}^{9}/_{4}$) with eqs 22 and 23.

$$R \cong b\phi^{-1/8} N^{1/2}\left(\frac{\phi}{\phi_{\mathrm{e}}^{\mathrm{good}}}\right)^{-15/56} \qquad (24)$$

Using eq 2, we calculate the modulus of a deswollen network prepared in a good solvent.

$$\frac{G}{kT} \cong \frac{\phi}{Nb^3}\left(\frac{\phi}{\phi_0}\right)^{-5/12}\left(\frac{\phi}{\phi_{\mathrm{e}}^{\mathrm{good}}}\right)^{15/28} \sim \phi^{47/42} \qquad (25)$$

where $\phi_{\mathrm{e}}^{\mathrm{good}}$ is the good solvent value for the entanglement crossover (eq 13 with $\alpha = {}^{9}/_{4}$). The exponent describing the concentration dependence of modulus in eq 25 is close to, but not less than, unity for all scaling conjectures for the Θ solvent value of α: $G \sim \phi^{29/24}$ for $\alpha = 2$ and $G \sim \phi$ for $\alpha = 3$.

The overall situation is quite analogous to the Θ solvent (Figure 4) with the exponents slightly larger. When fully deswollen to the melt ($\phi = 1$), the modulus of the network prepared in good solvent is larger than the one prepared in Θ solvent at the same concentration by a factor $\phi_0^{-1/4}$. In the melt the effective R in eq 2 is independent of preparation solvent, but R_0 is larger in good solvent by a factor $\phi_0^{-1/8}$ (see eq 3).

While the full concentration dependence of modulus during deswelling has not been measured yet, there are some data on the deswollen modulus that imply support for the above ideas.[16,35,36] For networks prepared at low concentration ($\phi_0 \cong 0.03$–0.12) and only slightly deswollen[35] ($\phi < 3\phi_0$), the modulus in both good and Θ solvent exhibits a weak concentration dependence, $G \sim \phi^{0.3-0.4}$, consistent with a regime of concentration near ϕ_0 where temporary entanglements are not important (eq 5).

Rogovina et al.[36] made networks at various concentrations and measured the modulus in the fully swollen and dry states. The modulus of the dried gels decreases as ϕ_0 decreases. We crudely estimate an exponent for the concentration dependence of modulus from their two-point determinations as $G \sim \phi^{0.5-1.0}$. Since the determination involves the swollen modulus, there is a considerable range of swelling included as well as deswelling, but there is some indication of the exponent near unity (as predicted by eq 25) for the networks prepared at roughly $\phi_0 \cong 0.5$. Better evidence comes from the same group's later work[16,37] where they report the modulus in the preparation state and the dry state. For networks prepared at $\phi_0 = 0.05$, the dry modulus is a factor of 50–60 higher than the modulus in the preparation state, suggesting an apparent power law of $G \sim \phi^{1.3}$. This is convincing evidence for deswelling having a much stronger concentration dependence of modulus (eq 25 predicts $G \sim \phi^{1.1}$) than swelling does (eq 5 predicts $G \sim \phi^{7/12}$).

In summary, networks prepared by cross-linking at low concentration (in either good or Θ solvent) and deswelling are predicted to have a high-concentration region where their modulus is roughly proportional to concentration. The departure from the weaker concentration dependences of swelling ($G \sim \phi^{1/3}$ in Θ solvent and $G \sim \phi^{7/12}$ in good solvent) is due to the formation of temporary entanglements. There is reasonable agreement with experiment for the modulus of fully deswollen (dry) gels, but more experimental data on the concentration dependence of the modulus for deswollen networks are needed to test our theory. This can probably best be done by osmotic deswelling[8] via addition of long linear chains to the solvent in equilibrium with a swollen network.

4. Preparation of Superelastic Networks

When networks are made in the absence of solvent, a lower bound on the modulus exists due to the presence of trapped entanglements ($G \geq kTb^{-3}N_{\mathrm{e}}^{-1}$). A way to make new materials with lower modulus is as follows. First prepare the network from very long linear chains at low concentration. The effect we seek is maximized at lower concentration, but the chains should be strongly overlapped to avoid inhomogeneities in the network caused by concentration fluctuations, so it is best to choose a concentration a few times the overlap concentration ϕ^*. The reaction must be performed rapidly (i.e., instantaneous cross-linking by γ irradiation) to avoid phase separation encountered during slow cross-linking at low concentrations.[4] One should note that this preparation concentration ϕ_0 can, in principle, be made as low as one wants by choosing very high molecular weight precursor chains. Very few entanglements will be trapped in the cross-linking process (as compared to cross-linking in the melt). In principle, this can be done in either good or Θ solvent, but good solvent has a lower ϕ^*, so the effect would be larger there. Next remove the solvent, bringing $\phi = 1$, with many temporary entanglements being introduced in the process. The modulus of such networks is predicted in section 3.

Interestingly, the modulus predicted by eqs 20 and 25 for the fully deswollen network (at $\phi = 1$) can be quite low. The simple physics is that the end-to-end distance of the chains in the final state (λR_0 in eq 2) is now smaller by a factor $\phi_0^{1/3}$. Notice that the modulus can be much lower than the kT per entanglement strand obtained by cross-linking in the melt state.

The stress-elongation behavior of such networks should be quite remarkable. Ordinary networks can elongate by roughly a factor of 4 before failing. This is because of the finite extensibility of strands between trapped entanglements. The maximum extension ratio[38] $\lambda_{\max}$ is the ratio of the fully stretched length, of order bN_{e}, and the

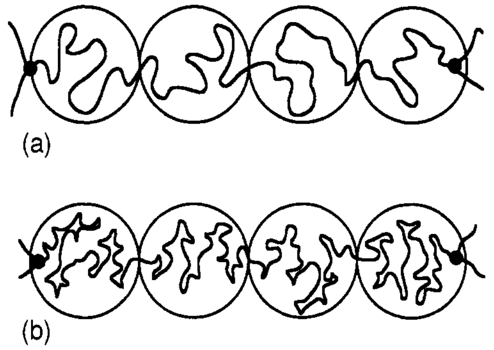

Figure 6. Network strands in tension are stretched into a series of Pincus blobs of size ξ (denoted by circles). (a) A melt-cross-linked network strand in tension is a stretched random walk. (b) A deswollen superelastic network strand in tension is a stretched double-folded fractal.

unstretched (Gaussian) end-to-end distance of the strand $bN_e^{1/2}$.

$$\lambda_{\max} \cong N_e^{1/2} \tag{26}$$

This implies $\lambda_{\max} \cong$ 4–6 for normal flexible polymers (because such polymers have 20–40 Kuhn segments in an entanglement strand).

Networks cross-linked at low concentration (with entanglements dominant, $N_e(\phi_0) < N$) and stretched at the concentration of preparation should be able to elongate much further because of the lower entanglement density.

$$\lambda_{\max}(\phi_0) \cong \frac{bN_e(\phi_0)}{R_0} \cong (N_e(\phi_0))^{1/2} \cong (N_e(1))^{1/2}\phi_0^{(1-\alpha)/2} \tag{27}$$

The exponent $\alpha = {}^9/_4$ in good solvent,[4] and $\alpha = {}^7/_3$ in Θ solvent.[19]

When the solvent is subsequently removed, the maximum extension ratio increases by an additional multiplicative factor of $\phi_0^{-1/3}$, due to the end-to-end distance of a trapped entanglement strand decreasing as concentration increases.

$$\lambda_{\max}(1) \cong \frac{bN_e(\phi_0)}{\phi_0^{1/3}R_0} \cong (N_e(1))^{1/2}\begin{cases}\phi_0^{-23/24} & T \gg \Theta\\ \phi_0^{-1} & T = \Theta\end{cases} \tag{28}$$

This means that networks cross-linked in solution will be able to extend much farther before breaking. For example, a network cross-linked at ϕ_0 = 0.03 should have an elongation at break of $(0.03)^{-23/24} \times 4 \cong 100$. We must note, however, that the deswollen network must be stretched slowly to ensure equilibrium is reached, as the temporary entanglements introduced during deswelling will also cause time-dependent viscoelastic effects. When deformed rapidly, temporary entanglements do not have time to relax and the modulus is of order kT per temporary entanglement strand. The dynamics of these deswollen networks is very interesting and will be discussed in a future publication.

The stress-elongation behavior in extension of superelastic networks is qualitatively different from oridinary melt-cross-linked networks. We illustrate this with a simple scaling argument. First consider a melt-cross-linked network, with ν the number density of network strands (between cross-links for strongly cross-linked networks and between entanglements for weakly cross-linked networks) of N monomers and initial (unstretched) size $R_0 \cong bN^{1/2}$. Each strand stretches into a linear string of Pincus blobs,[39] as shown in Figure 6a. On length scales smaller than the Pincus blob size ξ, the chain is a random walk (with g monomers in a blob, $\xi \cong bg^{1/2}$). The number of blobs in each strand (N/g) is determined by the affine displacement of the strand ends.

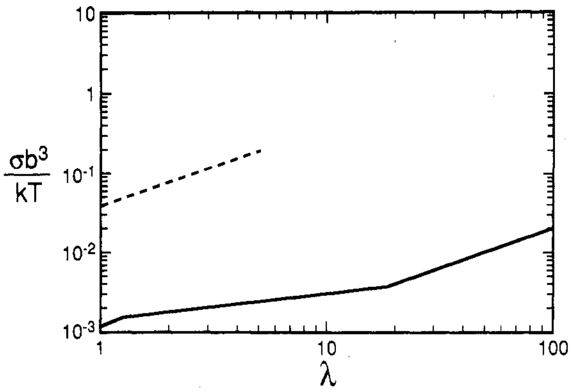

Figure 7. Schematic comparison of the stress-elongation behavior of a superelastic network (solid curve, cross-linked at ϕ_0 = 0.03 and fully deswollen) and a melt-cross-linked network (dashed line). Both have N = 1000 and $N_e(1)$ = 25.

$$\frac{N}{g} \cong \frac{\lambda R_0}{\xi} \cong \lambda\left(\frac{N}{g}\right)^{1/2} \cong \lambda^2 \tag{29}$$

The stored elastic energy is simply kT per blob, $E \cong \nu kT\lambda^2$. The derivative of this energy with respect to elongation gives the stress,

$$\sigma \cong \nu kT\lambda \tag{30}$$

which is the familiar result (Hooke's law) for a network.[3]

On the other hand, the strands of superelastic networks (of end-to-end distance $\phi_0^{1/3}R_0$ and size $b(N_eN)^{1/4}$ have fractal dimension $D = 4$, because they have been deswollen into the interpenetrating random tree state depicted in Figure 3 (see eq 14). Initial extension by elongation λ will follow linear response (with the modulus predicted in section 3) as long as the end-to-end distance of the strand is less than the strand size (i.e., $\lambda\phi_0^{1/3}R_0 < b(N_eN)^{1/4}$). For larger elongations, the strand is pulled into a string of Pincus blobs,[39] where the double-folded treelike structure is preserved inside the blob of g monomers (see Figure 6b). The size of these Pincus blobs is $\xi \cong bN_e^{1/4}g^{1/4}$. The number of blobs in each strand (N/g) is determined by the affine deformation of the ends (analogous to eq 29).

$$\frac{N}{g} \cong \frac{\lambda\phi_0^{1/3}R_0}{\xi} \cong \frac{\lambda\phi_0^{1/3}R_0}{b(N_eg)^{1/4}} \cong \left(\frac{\lambda\phi_0^{1/3}R_0}{b(N_eN)^{1/4}}\right)^{4/3} \tag{31}$$

The stored elastic energy is kT per Pincus blob.

$$E \cong \nu kT\left(\frac{N}{g}\right) \cong \nu kT\left(\frac{R_0}{b}\right)^{4/3}(N_eN)^{-1/3}\phi_0^{4/9}\lambda^{4/3} \tag{32}$$

Differentiating as before leads to a nonlinear stress-elongation relation for superelastic networks.

$$\sigma \sim \lambda^{1/3} \tag{33}$$

This relation should be valid as long as there are more than N_e monomers in a Pincus blob (i.e., for $\lambda < bNR_0^{-1}N_e^{-1/2}\phi_0^{-1/3}$). For larger elongations, the Pincus blobs contain less than N_e monomers, so the double-folded loops have all been pulled out, and one recovers linear elasticity, with $\sigma \cong \nu kT\phi_0^{5/12}\lambda$. This second linear regime eventually ends because of failure at the maximum extension discussed above (eq 28). This stress-elongation behavior in tension is summarized in Figure 7, where we compare the superelastic network with the melt-cross-linked network. The scaling applies for large deformations where small-elongation corrections[40] due to lateral compression $(1 - \lambda^{-3})$ and Mooney–Rivlin corrections $(1 + C\lambda^{-1})$ can be safely neglected. Figure 7 should therefore be interpreted as a qualitative sketch of the stress-elongation behavior, being more correct at large deformations. Unfortunately, the only stress-elongation data on deswollen networks[17,41] that we are aware of were obtained for networks with low degrees of polymerization between cross-links, which were either unentangled or barely entangled in the dry state.

Note that the source of the weaker-than-linear stress-elongation behavior of eq 33 is the energy that is stored in the double-folded loops on deswelling. This energy is released on stretching (as the loops are pulled out), making the network easier to stretch.

5. Conclusions

We derive scaling predictions for the elastic modulus of flexible polymer networks as functions of their concentration and preparation conditions based on the assumption of an affine displacement of cross-links when concentration is changed. We find that some of the predictions are familiar, others are new, and all are in reasonable agreement with literature data. We find that swelling in a Θ solvent obeys the prediction of James and Guth ($G \sim \phi^{1/3}$), swelling in a good solvent obeys our theory ($G \sim \phi^{7/12}$), and deswelling can have a much stronger concentration dependence (we predict $G \sim \phi^{1.1}$ in a good solvent).

On the basis of the relation between the dry modulus and equilibrium swelling (eq 12 and Figure 1), we are able to conclude that during swelling the network strands do not disinterpenetrate, and undergo an affine transformation as opposed to the complete disinterpenetration presumed by the c^* theorem. The strands of deswollen networks, on the other hand, interpenetrate strongly. We assumed that the cross-link points themselves behave affinely during deswelling, but it is not at all obvious that this must be true. The only tests made here are through comparison of the moduli of solution-cross-linked networks in their preparation state and their fully deswollen state. The agreement with our prediction was reasonable, but clearly more data on the concentration dependence of the modulus during deswelling are needed to test the theory, possibly using osmotic deswelling[8] to get stable gels at intermediate concentrations.

Deswollen network strands have a random double-folded treelike configuration caused by the temporary entanglements formed on removal of solvent. Thus another test of our model will involve comparison with scattering data on deswollen networks, which we will address in a future publication. The temporary entanglements give rise to the superelastic properties of deswollen networks. They have lower modulus than melt-cross-linked networks (where all entanglements are permanently trapped and act as effective cross-links) and can stretch extensively (~100×) before failing, because temporary entanglements can be pulled out in tension. Much of the stress-elongation behavior of deswollen networks should obey a weaker-than-linear power law: $\sigma \sim \lambda^{1/3}$.

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