

Notes

Swelling of Constrained Polymer Gels

Y. Rabin*

Department of Physics, Bar-Ilan University,
Ramat-Gan 52900, Israel

E. T. Samulski

Department of Chemistry, University of North Carolina,
Chapel Hill, North Carolina 27599-3290

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Recently there has been some progress in our understanding of osmotic and elastic effects in semidilute solutions of stretched polymers in good solvents.¹⁻³ The emerging physical picture is as follows: In the semidilute regime, each macromolecule can be represented by a Gaussian chain of blobs such that within each blob there are excluded-volume correlations due to repulsive short-range interactions between monomers that belong to the same chain. The intramolecular interactions are screened on length scales larger than the blob size since on these scales each chain interacts mainly with the monomers of other chains.⁴ When the polymers are deformed, as long as the Gaussian chains of blobs are less than fully stretched, the deformation results in a mere rearrangement of the blobs; the blobs remain close-packed and their size, hence the total volume occupied by the chains, and the osmotic pressure are unaffected. The resulting restoring forces due to entropic elasticity of the chains of blobs remain Hookean, i.e., linear in the imposed extension. When the applied force exceeds that needed to produce full extension of the chains of blobs, the stretching begins to affect the probability of finding two monomers that belong to the same chain close to one another in space and the intramolecular excluded-volume correlations become progressively screened. This can be interpreted as a reduction in the blob size, and consequently the semidilute solution of stretched polymers can no longer be represented by a close-packed set of blobs. If the total volume of the solution is kept fixed, the osmotic pressure Π increases with chain elongation,¹ and in the limit of large deformations, Π crosses over from the usual good-solvent dependence on the polymer concentration c , $\Pi \propto c^{9/4}$, to the mean field result, $\Pi \propto c^2$. In this regime, previously considered (for the single polymer case) by Pincus,⁵ the force opposing the deformation becomes inelastic and scales with the $3/2$ power of the chain elongation.

The above results were first applied to grafted polymer layers ("brushes") under combined compression and shear,¹ where it was predicted that when a certain critical shear force is exceeded, the brushes will move apart to a new steady-state separation, a result that has been confirmed by experimental observations.⁶ Subsequently, Alexander and Rabin applied these ideas to the uniaxial stretching of swollen polymer gels in good solvents² and extended the analysis of the transient state of constant-volume deformation⁷ of gels by calculating the volume change in the long-time limit. They found that in steady state the gel swells beyond its equilibrium dimensions, as the result of the increased osmotic pressure due to the stretching.

Although the deformation-induced swelling has apparently been observed,⁸ a detailed experimental study of the above phenomenon may be rather difficult since large stretching ratios are difficult to achieve in practice.

In this work we analyze a different physical situation which may be more attractive from an experimental point of view, namely, the swelling of uniaxially constrained polymer gels. Consider a c^* gel⁴ formed by dissolving monodisperse polymers of N monomers of size b each in a good solvent and cross-linking the chains by reacting all the chain ends with z -functional molecules ($z \geq 3$). In the absence of external constraints the gel reaches a swelling equilibrium in which the repulsive osmotic forces due to excluded-volume interactions between the monomers are balanced by the elastic restoring forces. According to the c^* theorem⁴ the polymer concentration in this state is of the order of the overlap concentration c^* in a solution of disconnected chains of the same contour length N , where c^* scales like $N^{-4/5}$. At this concentration the gel can be represented as a collection of closely packed (and cross-linked) blobs of size $l_0 = bN^\nu$, where $\nu \simeq 3/5$ is the excluded-volume exponent. Each such blob contains a single chain of N monomers, and consequently excluded-volume interactions within a blob are mainly between monomers that belong to the same chain. Denoting the total number of chain monomers in the gel as M and the equilibrium dimension of the swollen gel as L_0 and noticing that the total number of blobs is $(L_0/l_0)^3$, we obtain $M = N(L_0/l_0)^3$ and therefore the gel swells to size

$$L_0 = bM^{1/3}N^{-1/3} \quad (1)$$

As intuitively expected, eq 1 implies that the swelling is enhanced as the quality of solvent is improved (the exponent ν increases going from θ to good solvents).

Let us now consider the swelling of a uniaxially constrained gel. This physical situation can be achieved, for example, by introducing a cylindrical specimen of dry gel of diameter $\leq D$ into a cylinder of diameter $D < L_0$ and of length that is much larger than the equilibrium dimensions of the gel. The gel is then swollen *inside* the cylinder by the addition of solvent. Because of the confining effect of the boundaries, the gel swells until it reaches a diameter D and a length L where L is, in general, greater than L_0 .

Consider a weakly confined gel where D is smaller but of the order of L_0 . Assuming that the deformation is affine, each chain between cross-links is stretched by a factor L/L_0 and compressed by a factor L_0/D parallel and perpendicular to the axis of the cylinder, respectively. Following the classical approach of Flory and Rehner,⁹ the dominant contribution to the free energy is written as a sum of an elastic and an osmotic term, the former following from linear elasticity and the latter determined by excluded-volume correlations:¹⁰

$$\frac{F}{k_B T} = \frac{L_0^3}{LD^2} \left(\frac{L}{L_0} \right)^2 + \left(\frac{L_0^3}{LD^2} \right)^{9/4} \quad (2)$$

where L_0^3/LD^2 is proportional to the volume fraction of the deformed chains, k_B is Boltzmann's constant, and T

Table I
Swelling Dimensions of PDMS Gels

confinement diameters, D (=3.12 initial; dry), mm	3.250	3.825	3.980	4.125	4.220	4.880	5.1 ^a (=D ₀)
lengths L (=7.51 initial; dry), ^b mm	17.3	16.3	15.4	14.2	14.8	13.9	12.8 ^a (=L ₀)
quadrupolar splittings, ^c Hz	22.0		6.5			<4	0

^a No confinement. ^b In toluene at ~25 °C. ^c Deuterated benzene.

is the temperature. Minimizing the free energy with respect to L yields

$$L/L_0 = (L_0/D)^{10/13} \quad (3)$$

In the limit of strong confinement when the radius of the cylinder is much smaller than the equilibrium dimensions of the gel, $D/L_0 \ll 1$, a polymer segment between cross-links can be modeled as a stretched chain of blobs. Assuming again that the deformation is affine, the size of each blob is given by $\xi = l_0 D/L_0 \ll l_0$. Notice that because the stretching along the symmetry axis is produced by confinement in the plane normal to this axis, the deformed gel can still be viewed as a close-packed set of blobs. This differs from the cases discussed in refs 1 and 2, where the deformation was produced by forces directed along the direction of stretching, resulting in a dilute set of blobs. The gel dimension along the axis of the cylinder L can be obtained by balancing the osmotic forces against the tension in the deformed chains, where, for the latter part, we use the nonlinear Pincus elasticity^{1-3,5}

$$\frac{F}{k_B T} = \frac{L_0^3}{LD^2} \left(\frac{L}{L_0} \right)^{5/2} + \left(\frac{L_0^3}{LD^2} \right)^{9/4} \quad (4)$$

The elongation L/L_0 can be obtained by minimizing the above free energy with respect to L . Alternatively, we can calculate the uniaxial deformation via the following blob argument: since excluded-volume correlations are maintained within the blobs, the number of monomers in a blob is $n_\xi = (\xi/b)^{5/3} = N(D/L_0)^{5/3}$. Consequently, each chain of blobs is elongated to size l , given by the product of the blob size ξ and the number of blobs per chain, N/n_ξ :

$$l = bN^{1/2}(L_0/D)^{2/3} \quad (5)$$

Making use of the affine assumption yields the macroscopic elongation ratio

$$L/L_0 = l/l_0 = (L_0/D)^{2/3} \quad (6)$$

The experimental study reported below was conducted to demonstrate the feasibility of confined swelling experiments and show the existence of motionally averaged anisotropy via deuterium nuclear magnetic resonance (NMR). The gel sample we examine is a poly(dimethylsiloxane) network (PDMS MW = 40 000, cross-linked with 4% ethyltriacetoxysilane described and prepared by Geissler et al.¹¹); it does not conform to the c^* gel treated theoretically in the previous section. Nevertheless, its behavior is illustrative of the predicted trends.

A cylindrical sample of the PDMS network (initial diameter $D_i = 3.12$ mm and length $L_i = 7.51$ mm) was swollen in toluene (mixed with 10% deuterated benzene, C₆D₆, for NMR) while confined in a series of glass capillaries of varying inner diameters ($D = 3.25$ – 4.88 mm). After equilibration (at ambient temperature 22 °C; $D_i \rightarrow D$ and $L_i \rightarrow L$), the observed value of L is reported in

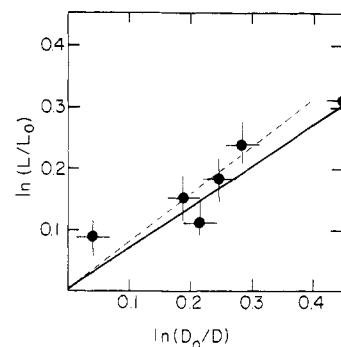


Figure 1. Plot of eq 3 which has been modified to account for initial sample dimensions, $\ln(L/L_0)$ versus $\ln(D_0/D)$, for cylindrical PDMS networks swollen in benzene. The confinement diameters (D), equilibrium swollen lengths (L), and the corresponding unconfined equilibrium dimensions are from Table I; the dashed line has slope $^{10/13}$ and the solid line has slope $^{2/3}$.

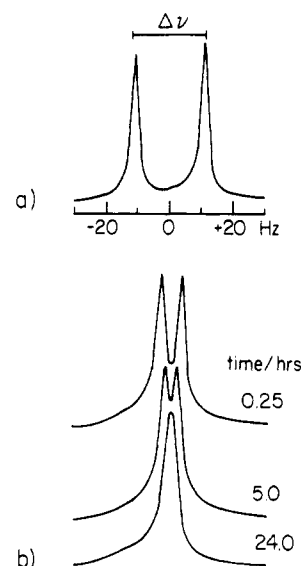


Figure 2. Deuterium NMR spectra of deuterated benzene in confined, swollen PDMS gels: (a) equilibrium quadrupolar splitting for confinement $D = 3.25$ mm ($L = 17.3$ mm); (b) time dependence of NMR spectra after changing confinement in (a) to $D = 4.125$ mm and allowing network to swell to new equilibrium deformation ($L = 14.2$ mm).

Table I along with the unconfined dimensions of the swollen network, D_0 and L_0 (last entry in Table I). In the case of this good solvent for PDMS, modified versions of eqs 3 and 6 that account for the asymmetry of the equilibrium-swollen gel ($D_0 \neq L_0$), $L/L_0 = (D_0/D)^{10/13}$ and $L/L_0 = (D_0/D)^{2/3}$, respectively, are applicable. While there is considerable scatter in the plot of L/L_0 versus D_0/D , the results appear to be consistent with the above predictions (Figure 1). The quality of the data and the small range of elongations achieved do not allow us to determine whether the linear (eq 3) or the nonlinear (eq 6) elasticity gives a better fit to the data. Further experiments on nonentangled gels over a larger range of deformations are clearly needed.

Table I also shows the magnitudes of the residual quadrupolar splittings $\Delta\nu$ of the deuterated benzene swelling agent. The appearance of a discrete $\Delta\nu$ in the deuterium NMR spectrum of the swollen network indicates that the liquid-like diffusional motion of the benzene molecule is anisotropic. The anisotropy is very small ($\Delta\nu \sim 20$ Hz compared to the static quadrupolar interaction ~ 200 kHz), reflecting both a low degree of network chain segmental ordering (imposed by the confined swelling-induced deformation) and the severely attenuated transfer of this

segmental ordering to the mobile solvent molecules (via "collision complexes" with chain segments in the swollen network). The magnitude and behavior of $\Delta\nu$ with benzene content are reminiscent of those originally reported by Deloche and Samulski for labeled swelling agents in mechanically deformed networks.¹² It would appear that NMR may be conveniently used to monitor the change in anisotropy on relieving the confinement constraint and its temporal development as equilibrium is approached in a less restricted confinement (Figure 2). Direct observation of (labeled) chain segmental order with NMR in conjunction with the description of the deformation anticipated for the confined swelling experiment may allow further tests of the osmotic pressure and entropic elasticity in semidilute systems.

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