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Kinetics of Swelling of Polyacrylamide Gels

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ABSTRACT: The theory of kinetics of the swelling of a gel previously developed by Tanaka and Fillmore has been generalized to include the effect of nonnegligible shear modulus. The values of the cooperative diffusion coefficient and of the ratio of the shear modulus over the longitudinal osmotic modulus obtained from macroscopic swelling experiments in polyacrylamide gels show good agreement with previous results.

Introduction

The theory of the kinetics of the swelling of a cross-linked polymeric network has been derived by Tanaka and Fillmore.[1] These authors have shown that the characteristic time of swelling is proportional to the square of the linear size of the gel and is also proportional to the cooperative diffusion coefficient of the network, which is defined as $D_c = M_{os}/f$, where M_{os} is the osmotic longitudinal modulus of the gel and f is the coefficient of friction between the network and the gel fluid. In their derivation, Tanaka and Fillmore have assumed that the shear modulus μ of the gel was negligible compared to the osmotic bulk modulus K_{os}. However, most of the gels currently investigated are characterized by a shear modulus of the same order of magnitude as the bulk modulus.[2-4] It is the purpose of the present paper to extend the Tanaka and Fillmore model to the case where the shear modulus cannot be neglected and to compare the theoretical predictions to swelling experiments performed in polyacrylamide gels. Only gels of spherical shape have been considered.

Theory

The equation of motion of a gel network as given by Tanaka, Hocker, and Benedek[5] is

$$\frac{\partial \mathbf{u}}{\partial t} = \frac{K_{os} + \mu/3}{f} \operatorname{grad} (\operatorname{div} \mathbf{u}) + \frac{\mu}{f}\Delta \mathbf{u} \tag{1}$$

where Δ denotes the Laplacian and $\mathbf{u}(\mathbf{r},t)$ is the displacement vector that represents the displacement of a point in the network from its final equilibrium location after the gel is fully swollen. Under this definition $u = 0$ at $t = \infty$.

In the case of a radial deformation (1) becomes

$$\frac{\partial u}{\partial t} = D_c \frac{\partial}{\partial r}\left(\frac{\partial u}{\partial r} + 2\frac{u}{r}\right) \tag{2}$$

with

$$D_c = \frac{M_{os}}{f} = \frac{K_{os} + 4/3\mu}{f} \tag{3}$$

As the center of the sphere is not displaced during the swelling process, one has the condition

$$u(0,t) = 0 \text{ at all } t \tag{4}$$

The boundary condition on the surface of the network is obtained by cancelling the stress normal to the surface at $t \rightarrow \infty$

$$\sigma = M_{os}\left[\frac{\partial u}{\partial r} + (1 - 2\mu/M_{os})\frac{2u}{r}\right] = 0 \quad (t \rightarrow \infty,\ r = a) \tag{5}$$

where a is the final radius of the gel sphere in equilibrium with the surrounding fluid. This condition is assumed to hold at finite time since we are primarily interested in the later stage of the swelling process, that is, the range of large t.

The solution of eq 2, using conditions 4 and 5 is

$$u(r,t) = \sum_n A_n e^{-t/\tau_n} N\left(X_n \frac{r}{a}\right) \tag{6}$$

where $X_n = [a(\tau D_c)^{-1/2}]_n$ is the nth root of the equation

$$\tan X = \frac{(4\mu/M_{os})X}{(4\mu/M_{os}) - X^2} \tag{7}$$

The variation of the two first roots as a function of μ/M_{os} is given in the Appendix.

The function $N(X_n)$ is

$$N(X_n) = \frac{\cos X_n}{X_n} - \frac{\sin X_n}{X_n^2} \tag{8}$$

The A_n are integration constants. The solution given by Tanaka and Fillmore can be generalized by writing the integration constants under the form

$$A_n = AN(X_n)$$

Then eq 6 becomes

$$u(r,t) = \sum_n A_n e^{-t/\tau_n} N(X_n) N\left(X_n \frac{r}{a}\right) \tag{9}$$

The displacement vector is expressed as a decomposition into components, each of them decaying exponentially with a time constant τ_n.

The constant A is given by

$$A = \frac{u(a,0)}{\sum_{n=1}^{\infty} [N(X_n)]^2} \tag{10}$$

By the use of the above relations, the general solution for the displacement is expressed as

$$\frac{u(r,t)}{u(a,0)} = \frac{1}{\sum_{n=1}^{\infty} |N(X_n)|^2} \sum_{n=1}^{\infty} e^{-t/\tau_n} N(X_n) N\left(X_n \frac{r}{a}\right) \tag{11}$$

The series involved in eq 11 are convergent. In the limit of vanishing shear modulus eq 11 reduces to the form given by Tanaka and Fillmore[1]

$$\frac{u(r,t)}{u(a,0)} = 6\sum_{n=1}^{\infty} N(n\pi)N(n\pi r/a)e^{-t/\tau_n'} \tag{12}$$

where

$$\tau_n' = \frac{a^2}{n^2\pi^2 D_c} \tag{13}$$

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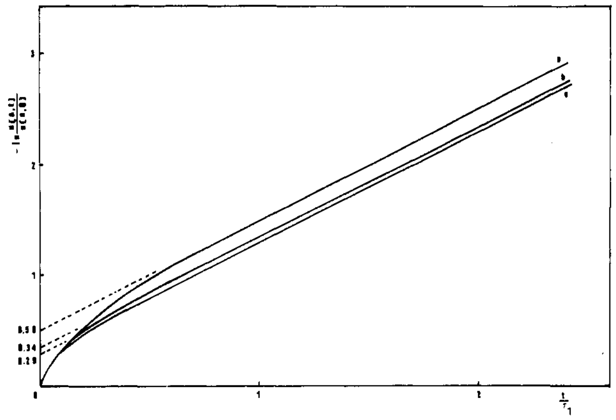

Figure 1. Variations of $-\ln (u(a,t)/u(a,0))$ with the scaled time t/τ_1 calculated from eq 17: (a) $\mu/M_{os} = 0$; (b) $\mu/M_{os} = 0.3$; (c) $\mu/M_{os} = 0.5$.

We consider now the first term of the expansion (11), which becomes dominant over the higher order terms at large t, that is, at the last stage of swelling. This term is given by

$$\left.\frac{u(r,t)}{u(a,0)}\right|_{t\to\infty} \simeq \frac{1}{\sum_{n=1}^{\infty} [N(X_n)]^2} N|X_1|N\left|(X_1)\frac{r}{a}\right| e^{-t/\tau_1} + \ldots \quad (14)$$

with

$$\tau_1 = \frac{a^2}{D_c}\frac{1}{X_1^2} \quad (15)$$

To evaluate the sum at the denominator of the right side of eq 14 we make the approximation $X_n \simeq n\pi$ for $n > 2$ so that we can write

$$\sum_{n=1}^{\infty} |n(X_n)|^2 \simeq |N(X_1)|^2 + \sum_{n=2}^{\infty} |N(n\pi)|^2 \quad (16)$$

From eq 14 and 16 one obtains

$$-\ln \frac{u(a,t)}{u(a,0)} \simeq \frac{t}{\tau_1} - \ln \frac{|N(X_1)|^2}{|N(X_1)|^2 + \sum_{n=2}^{\infty} |N(n\pi)|^2} \quad (17)$$

We have used the above expression for the comparison with the experimental data. It predicts a linear dependence of $-\ln (u(a,t)/u(a,0))$ with time. Both the time constant τ_1 and the intercept depend on the ratio μ/M_{os} through the parameters $X_1, X_2, \ldots X_n$. In the limit case $\mu/M_{os} = 0$ one has

$$X_n = n\pi$$

and

$$-\ln \left.\frac{u(a,t)}{u(a,0)}\right|_{t\to\infty} \simeq \frac{t}{\tau_1'} - \ln \frac{6}{\pi^2} \quad (18)$$

with

$$\tau_1' = \frac{a^2}{\pi^2 D_c} \quad (19)$$

Figure 1 shows the variation of $-\ln (u(a,t)/u(a,0))$ as given by eq 11 and 12 as a function of the scaled time t/τ_1 for different values of the ratio μ/M_{os}. It can be seen that the extrapolation to $t = 0$ of the linear part of the plot increases as μ/M_{os} decreases to reach the value 0.5 for $\mu/M_{os} = 0$. This linear part corresponds to eq 17 and 18, respectively.

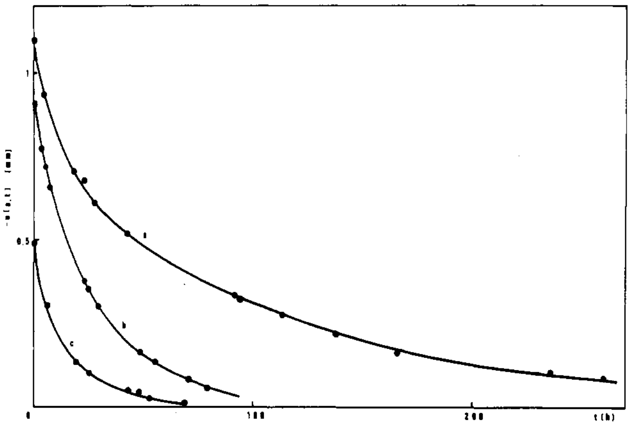

Figure 2. Swelling curves for spherical gels with final radii a = 11.15 mm (a), a = 6.17 mm (b), and a = 4.42 mm (c).

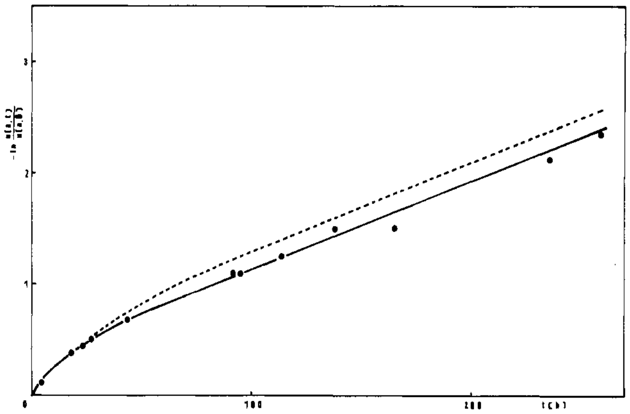

Figure 3. Time dependence of $\ln (u(a,t)/u(a,0))$ for a spherical gel with final radius 11.15 mm. The dashed line represents the variation calculated from eq 18 corresponding to $\mu/M_{os} = 0$. From the slope of the linear part of the experimental curve one obtains τ_1 = 125.8 h.

Experimental Section

Swelling Experiments. The polyacrylamide gels investigated here were prepared by a standard redox reaction employing ammonium persulfate and tetramethylethylenediamine (TEMED). The concentrations used were 5 g of recrystallized acrylamide monomer, 0.133 g of N,N'-methylenebis(acrylamide), 40 mg of ammonium persulfate, and 400 μL of TEMED dissolved in water to make a total volume of 100 μL. After thorough mixing, the preparations are poured through a small aperture in spherical glass molds. Once the gelation is performed, the molds are broken and the gel spheres are transferred into a cell containing an excess of water. This time is taken to be zero (t = 0). The concentration of polymer in the gel is 0.051 g cm^{-3}. At the swelling equilibrium it is 0.033 ± 0.004 g cm^{-3}. The diameter of the gel sphere is measured as a function of time on the screen of a profile projector by using a calibrated scale. Three spheres were investigated with radii at the swelling equilibrium, equal to 4.42, 6.17, and 11.15 mm, respectively. All the experiments were carried out at room temperature.

Quasi-Elastic Light-Scattering Experiments. In order to obtain an independent determination of the cooperative diffusion coefficient D_c, we have measured the average decay rate $\bar{\Gamma} = D_c K^2$ of the autocorrelation function of light scattered from a polyacrylamide gel with the same composition as in the swelling experiments; K is the scattering wavevector. The dynamic light-scattering spectrophotometer operated in a photon-counting mode using a Spectra Physics argon-ion laser (λ = 488 nm) and a Malvern correlator.

Results

Figure 2 shows the swelling curves of the three spheres investigated. In Figure 3 is plotted the time dependence of the quantity $-\ln (u(a,t)/u(a,0))$ for the sphere with final radius 11.15 mm. As expected from the theory and as

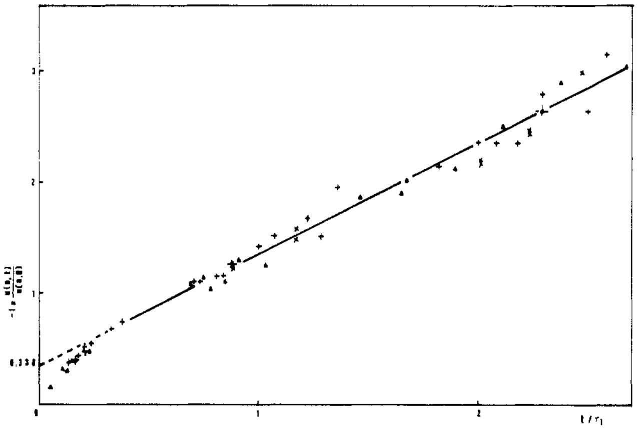

Figure 4. Universal plot of $-\ln (u(a,t)/u(a,0))$ as a function of the scaled time t/τ_1 for three spherical gels with final radii a = 11.15 mm (+), a = 6.17 mm (Δ), and a = 4.42 mm (×).

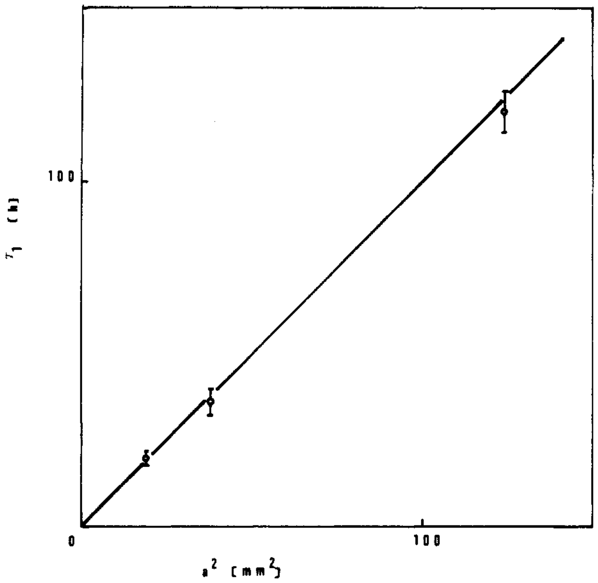

Figure 5. Variation of τ_1 with a^2.

previously observed by Tanaka and Fillmore, the plot becomes linear at large t. The slope of the linear part provides a measurement of τ_1 (τ_1 = 125.8 h). In the same figure is reported the curve calculated under the assumption $\mu/M_{os} = 0$ by using eq 18. It can be seen that the two curves are significantly shifted with respect to one another.

Using the experimental values of τ_1, it is then possible to draw a universal plot of $-\ln (u(a,t)/u(a,0))$ as a function of the scaled time t/τ_1 for the three spheres investigated. The results are reported in Figure 4. For $t/\tau_1 > 0.25$ the data fit a straight line obeying the equation

$$-\ln (u(a,t)/u(a,0)) = 0.998t/\tau_1 + 0.338 \qquad (20)$$

Comparison of the above result with eq 17 leads to

$$-\ln \frac{|N(X)_1|^2}{|N(X_1)|^2 + \sum_{n=2}^{\infty} |N(n\pi)|^2} = 0.338$$

which gives

$$X_1 = 2.624 \text{ rd}$$

By referring to Figure 7, giving from eq 7 μ/M_{os} as a function of X, one obtains

$$\mu/M_{os} = 0.307$$

This value is consistent with the results of Geissler and Hecht who found $\mu/M_{os} \simeq 0.4$, using combined measurements of shear modulus and intensity of scattered light.[2]

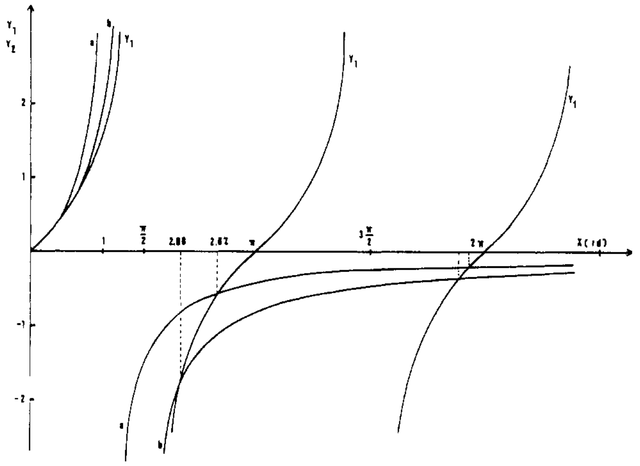

Figure 6. Variation of $Y_1 = \tan X$ and $Y_2 = (4\mu/M_{os})X/(4\mu/M_{os} - X^2)$ for $\mu/M_{os} = 0.3$ (a) and $\mu/M_{os} = 0.5$ (b).

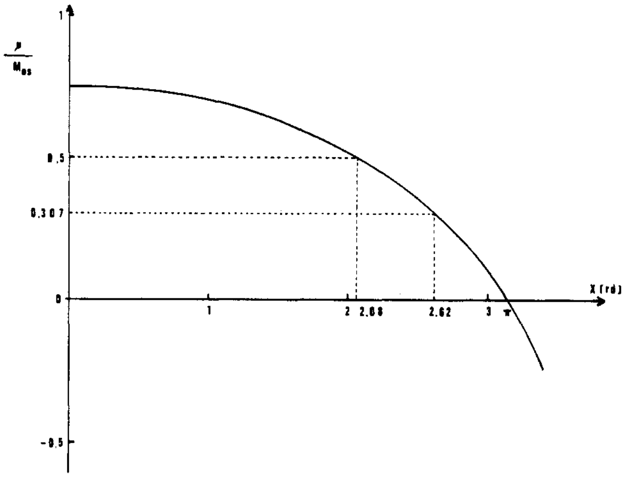

Figure 7. Variations of $\mu/M_{os} = (1/4)\,(X_1^2 \tan X_1)/(\tan X_1 - X_1)$ as a function of X_1.

Figure 5 shows the variation of τ_1 with a^2. Within the experimental accuracy one obtains a straight line the slope of which is equal to $|D_c X_1^2|^{-1}$. Using for X_1 the value 2.624 rd obtained above, one obtains

$$D_c = (4.1 \pm 0.3) \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$$

This value is in good agreement with that measured by quasi-elastic light scattering

$$D_c = (4 \pm 0.1) \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$$

On the other hand, the value of D_c determined from swelling experiments by using eq 19 valid for $\mu_{os}/M = 0$ is $D_c = (3 \pm 0.3) \times 10^{-7}$ cm^2 s^{-1}, that is, significantly lower.

Conclusion

The results presented in this paper show that the kinetics of swelling of spherical polyacrylamide gels is satisfactorily described by the model of Tanaka and Fillmore, generalized to account for the nonnegligible value of the shear modulus. Measurements performed on three gel spheres with different radius led to a value of the cooperative diffusion in good agreement with the results of quasi-elastic light scattering. Finally, the ratio of the shear modulus over the longitudinal osmotic modulus obtained from the kinetics of swelling agrees within the experimental accuracy with previous experiments.

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Appendix

The roots of the relaxation eq 8 are given by the intercepts of the plots of the functions

$$Y_1 = \tan X$$

$$Y_2 = \frac{(4\mu/M_{\text{os}})X}{(4\mu/M_{\text{os}}) - X^2}$$

The solutions of eq 8 have a physical meaning only for $\mu/M_{\text{os}} < 0.5$. Figure 6 shows the curves $Y_1(X)$ and $Y_2(X)$ for μ/M_{os} equal to 0.3 and 0.5, respectively. The abscissa X_n of the successive intercepts are such that $(n\pi - X_n)$ decreases and tends to zero when n increases.

Furthermore, X_1 decreases from the value π for $\mu/M_{\text{os}} = 0$ to 2.08 rd for $\mu/M_{\text{os}} = 0.5$. The variation of μ/M_{os} with X_1 is given in Figure 7.

Registry No. (Acrylamide)·(*N*,*N*′-methylenebis(acrylamide)) (copolymer), 25034-58-6.

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Swelling of Polymer Gels[†]

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ABSTRACT: The swelling of gels in a good solvent is formulated, taking into account different types of gel formation. In agreement with the critical gelation theory, for gels made of polyfunctional units the swelling ratio Q and the gel fraction G obey the scaling relation $Q \sim G^{-3/2}$. In the case of vulcanized gels made of *linear polymers with an average number* Z *of units, the interpenetration of the meshes is accounted for.* The previous result applies then only if the distance to the gelation threshold is smaller than $Z^{-1/3}$. Otherwise, the macroscopic swelling ratio Q depends on the mesh swelling q in the form $Q \sim (G^{1/2}q)^8$. If the sol is washed out prior to swelling, then $Q \sim G^{-5/2}$ in the critical case and $Q \sim G^{-1}Z^{4/5}$ for vulcanized gels. Altogether we present a general theory for the isotropic swelling of cross-linked polymerized material.

I. Introduction

Polymeric gels are materials that are able to absorb an enormous amount of solvent and to swell. The usual way to characterize this swelling is through the ratio $Q \equiv V_f/V_i$, where V_f is the final volume, when the gel cannot assimilate any more solvent, and V_i is the initial volume, before any solvent has been added. Typical values for Q are 10–20, but can be larger for irregular gels near the gelation threshold. In this paper, we evaluate the swelling ratio Q for a gel near its gelation threshold and relate it to other measurable quantities such as the gel fraction, for instance. When one considers this question, one is led to distinguish two cases which, although they seem to be similar, lead to very different conclusions. Thus, we will examine separately the gelation of small polyfunctional units and the vulcanization of long linear polymer chains. Both are described by percolation.[1,3] But whereas the former is related to critical phenomena,[9] the latter follows the classical Flory–Stockmayer theory.[5–7] As a consequence, we shall see that whereas there is only one characteristic distance—the mesh size ξ—in the critical case, this is not true in the classical case (vulcanization[4]). The difference is related to the strong interspersion of the nodes of the network in the latter case. In the critical case swelling is related to the change in this characteristic distance. One may say that swelling is an affine transformation *down* to distances of the order of ξ: there is a homogeneous transformation of the network. If q is the ratio of the final-to-initial distances, after and before swelling, we then expect

$$Q \simeq q^3$$

Such relation seems not to hold for the vulcanized gels studied by the Strasbourg group.[2] Recent neutron-scattering experiments showed indeed that even if the swelling ratio is large, q is of the order of unity for model networks made by cross-linking linear chains by their ends. Thus we will be led to discuss this loss of affinity and relate it to the disinterspersion of the nodes when swelling takes place in a vulcanized gel.

In section II, we will recall within a Flory–de Gennes theory the percolation approach to gelation. This includes the discussion of classical vs. critical gelation and the important concept of the width of the critical region, which is central to the discussion of vulcanization.

Section III deals with the swelling of gels for both cases discussed above, namely those made with small polyfunctional units and those made by vulcanizing linear chains in a melt. We will consider first the swelling of a gel that is initially in its reaction bath. This means that in addition to the gel the finite, eventually large, polymers of the sol are initially present. Crucial to the swelling of a vulcanized gel is the discussion of the "self interpenetration" of the network, which will be explained in this section.

Section IV summarizes our results and gives the extension to the swelling of a dry gel previously washed of its sol.

II. Critical or Classical Gelation

Consider multifunctional units in a vessel as a function of the reaction time. After a short period, branched polymers are formed.[1,5] Above a threshold, an infinite network appears, which is the gel. Whereas below the threshold we have a viscous solution, for large times there is an elastic behavior showing the existence of the gel. The

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