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Osmotic Deswelling of Gels by Polymer Solutions

J. Bastide,[†,§] S. Candau,[‡] and L. Leibler*[,†]

Centre de Recherches sur les Macromolécules, 67083 Strasbourg Cedex, France, Laboratoire d'Acoustique Moléculaire, ERA au CNRS, Université Louis Pasteur, 67070 Strasbourg Cedex, France, and Faculté des Sciences, Ile de Saulcy, 57000 Metz, France.
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ABSTRACT: Thermodynamic properties of swelling equilibria of polymer networks immersed in solutions of linear polymers are studied. Measurements of the swelling degree of a series of styrene gels in semidilute solutions of high-molecular-weight polystyrene in benzene have been performed. A considerable deswelling with respect to gels swollen in a pure solvent is observed. Within the experimental accuracy no chains permeated into the gel phase. A new scaling approach is developed to describe the swelling of gels in polymer solutions. This method permits calculation of both the swelling degree and partition coefficient (proportion of free linear chains permeating into the gel). Good agreement with experimental data for both semidilute and dilute regimes is found. Some new quantitative predictions are made concerning the swelling by lower molecular weight semidilute solutions. Measurements of elastic moduli of osmotically deswollen gels and their dependence on gel monomer concentrations are reported.

I. Introduction

Polymer networks swollen in a good-quality diluent deswell when transferred to a solution of a high-molecular-weight linear polymer in the same solvent.[1-5] The extent of deswelling depends essentially on the osmotic pressure of the solution in which the gel is immersed. It was long ago proposed to use this property to measure the solvent–polymer interaction parameter or the linear polymer molecular weight.[3,4] Studies hitherto reported have mainly dealt with the case of gels in dilute polymer solutions. The aim of the present work is to study the thermodynamic properties of gels in the presence of more concentrated (semidilute) polymer solutions.

We have performed deswelling experiments on a series of polystyrene networks of different structure immersed in polystyrene–benzene solutions of concentration ranging from 5% to 30%. A spectacular deswelling degree (1.5–6 times) has been observed. This offers new possibilities of studying the equilibrium properties of gels under strong isotropic compression. In particular, important information about local conformation and dynamics of chains in the compressed state of the gel may be obtained by inelastic light scattering and by small-angle neutron scattering from deswollen gels.[6]

The theoretical discussion presented in this paper gives a phenomenological, thermodynamic interpretation of the experimental results we have obtained. The essential difficulty encountered in theoretical studies of swelling of gels is to find an appropriate form of the free energy and in particular to relate its elastic part to some microscopic parameters characterizing the network (e.g., the radius of gyration of network chains).[7-12] The scaling approach proposed here does not require the detailed knowledge of the variation of these microscopic parameters during the swelling (deswelling) process. It permits us to calculate the deswelling degree and the proportion of linear chains permeating into the gel phase (the partition coefficient). The results are compared with available experimental data for both the semidilute regime (reported in this work) and dilute solutions.[5] Good agreement is found.

To get additional information about the scaling form of the elastic energy, we have also performed stress–strain measurements and determined the elastic moduli of swollen gels. The results are presented in the next section, in which the deswelling experiments are also described.

Table I

Anionic Gels

sample	mol wt of precursor	[DVB]/[LE]	C_p PS concn prior to cross-linking	swelling degree in pure benzene
54	34 000	5	0.091	20.5
64	12 500	3	0.109	9.8
65	12 500	3	0.146	8.5

Radicalar Gels

sample	concn of St prior to cross-linking	concn of DVB prior to cross-linking	swelling degree in pure benzene
B7	0.3	0.010	16
B12	0.3	0.013	8.5

II. Experimental Section

Samples and Techniques. In Table I are listed the principal characteristics of the polystyrene networks and their swelling equilibrium in benzene. Samples 54, 64, and 65 were prepared by a synthesis previously described, using anionic block copolymerization of styrene and divinylbenzene (DVB).[13] In the first step, bifunctional living polystyrene is prepared at low

[†] Centre de Recherches sur les Macromolécules.
[‡] Université Louis Pasteur.
[§] Faculté des Sciences, Ile de Saulcy.

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Table II

sample	ϕ_e	q_{exptl}	q_{theor}
54	0	20.5	
	0.047	13.7	14.6
	0.094	9.4	9.3
	0.14	6.5	6.6
	0.187	5.2	5.1
B7	0	16.0	
	0.047	11.3	12.7
	0.094	9.2	8.7
	0.14	6.4	6.4
	0.187	4.6	5.0
B12	0	8.5	
	0.047	7.9	7.9
	0.234	3.6	3.8
	0.3	2.8	3.1
64	0	9.8	
	0.094	6.0	7.1
	0.14	5.0	5.7
65	0	8.5	
	0.094	5.7	6.6
	0.14	4.9	5.4

temperature (−70 °C) in an aprotic solvent (equal volumes of tetrahydrofuran and toluene) with a bifunctional initiator (α-methylstyrene tetramer). When a little DVB is added to the "living" polystyrene solution, the polymerization of DVB is initiated only by the living ends of the polystyrene molecules. In a cross-linked network obtained in this way, each linear chain element is connected to two different branch points consisting of poly(vinylbenzene) nodules. Prior to the reaction, a small aliquot of the living precursor polystyrene was removed for characterization. The average molecular weight of the precursor was determined by gel permeation chromatography (GPC). The structural characteristics of the gels obtained depend mainly on three parameters: (i) the molecular weight of the precursor; (ii) the number of DVB molecules per living end (DVB/LE) (this parameter is closely related to the functionality of the cross-link points); and (iii) the concentration C_p of the polymer in the reactor prior to cross-linking. The concentration range in which the cross-linking reaction can be achieved is rather limited (typically 5–15% for a precursor molecular weight of ~20 000).

For concentrations C_p higher than ~15% very inhomogeneous gels are obtained because of the high viscosity of the polymer solution. On the other hand, at low concentrations, a deactivation of living extremities occurs, producing a high ratio of pendent chains. The intermediate range is optimal for making gels with the minimal number of defects. However, it should be stressed that the number of trapped entanglements strongly depends on the C_p value.

Samples B7 and B15 were prepared by radical copolymerization of styrene with a small amount of DVB in toluene solution and in the presence of 2,2′-azobis(isobutyronitrile) as initiator.[14] The swelling solutions were made from a polystyrene of molecular weight 765 000, prepared by the anionic process ($M_w/M_n < 1.2$).

Swelling Measurements. The usual weighing methods for swelling measurements are unsuitable for osmotic deswelling studies because of the high viscosity of the polymer solutions; therefore, we applied an optical technique using a profile projector (Nikon Model 6C). Thin gel cylinders (diameter ≈5 mm, thickness ≈2 mm in the dried state) were studied. The swelling degree q is given by

$$q = (A_s/A_d)^{3/2}$$

where A_s and A_d are circular surface areas of the gel in the swollen and dry states, respectively.

Swelling equlibrium is reached after a time of about 1–3 days, depending on the sample. No further volume change is observed even if the sample is maintained in the solution for a few months. The surrounding solution volume was much larger than the immersed gel volume (about 20 times) so that during the deswelling process the concentration of the surrounding solution was practically unchanged. To determine the amount of linear polymer penetrating into the network, the following method was used. After measurement of the deswelling degree, the gel was rapidly and superficially washed and dried. Then its mass was compared with that of a dry sample measured before the deswelling experiment.

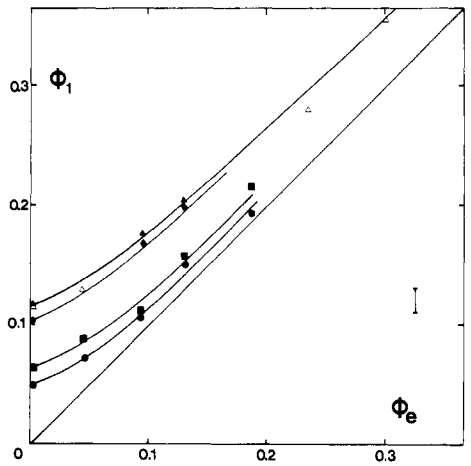

Figure 1. Experimental values of the monomer volume fraction $\phi_1 = 1/q$ of polystyrene gels immersed in benzene solutions of high-molecular-weight polystyrene ($M_w = 7.65 \times 10^5$). ϕ_e denotes the monomer volume fraction in the surrounding solution. (●) 54; (♦) 64; (▲) 65; (■) B7; (△) B12.

Table III

ϕ_1 monomer vol fraction in gel phase (sample 54)	elastic modulus $10^{-3}E$, dyn/cm²
0.049	38.3
0.086	56.0
0.179	69.7
0.208	80.0

Stress–Strain Measurements. Stress–strain measurements were performed on gel 54 swollen at equilibrium in polymer solutions of different concentrations. The apparatus for uniaxial compression measurements and the related experimental procedure have been described elsewhere.[14] All measurements were carried out at deformation ratios $0.75 < \lambda < 1$.

Experimental Results

A. Osmotic Deswelling. In Table II are reported the experimental swelling degrees q of the samples described before, measured for various volume fractions ϕ_e of surrounding polystyrene solutions. As already mentioned in the Introduction, the most striking observation is the very large deswelling obtained for high-concentration solutions of linear polymers. The other important result is that the free polymer chains do not penetrate into the deswollen network. Actually, no chains could be detected (by the weighing method described above, which gives an accuracy better than 5%) even when gels were immersed in the polymer solutions for 2 weeks.

Figure 1 shows the variation of the volume fraction $\phi_1 = 1/q$ of the network as a function of the volume fraction ϕ_e of the surrounding solution. The different curves tend to converge to an asymptote at high values of ϕ_e. It should be stressed that the volume fraction of polymer in the gel always exceeds that of the surrounding solution.

B. Elastic Moduli. In Table III are reported the values of the elastic modulus E of gel 54 for different volume fractions of polymer chains in the surrounding solution. The stress–strain relation for an incompressible rubber is given by the Mooney–Rivlin equation[15]

$$\sigma = 2C_1(\lambda - 1/\lambda^2) + 2C_2(1 - 1/\lambda^3)$$

where σ is the stress per unit undeformed area of swollen gel and C_1 and C_2 are constants independent of λ. As in previous studies on swollen gels at small deformation, C_2 is found to be zero. The elastic modulus E is defined by

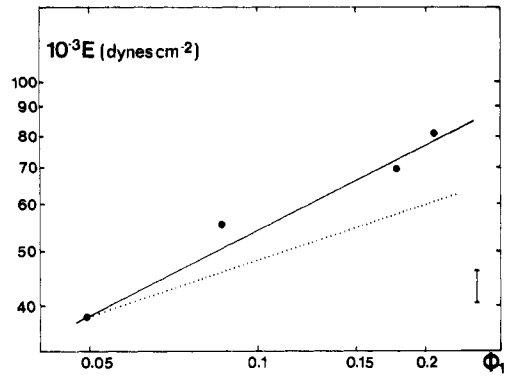

Figure 2. Variation of the elastic modulus E as a function of the monomer volume fraction ϕ_1 inside gel 54. The continuous line corresponds to the relation $E \sim \phi_1^l$ with $l = 0.5$; the dotted line corresponds to $l = {}^1/_3$.

the slope of the linear dependence $\sigma = E(\lambda - 1/\lambda^2)$. Figure 2 shows a log–log plot of E versus ϕ_1.

III. Discussion

The first part of this section presents a phenomenological scaling approach which describes the deswelling of networks by polymer solutions. Both semidilute and dilute solution cases are considered, and particular attention is paid to the variation of deswelling degree and of the partition coefficient (the proportion of free linear polymer permeating the gel from the solution) with the molecular mass of the linear polymers. In the second part, a detailed comparison is made with available experimental data and some predictions are drawn which will need to be confirmed by future experiments.

A. Theory. The scaling approach presented here applies to the problem of swelling equilibrium in solvents of varying quality, and it can be naturally extended to treat the problem of osmotic deswelling. We introduce and illustrate the method by considering, first of all, the simple case of the swelling equilibrium of a calibrated gel immersed in a *pure good solvent*.

The classical theory of this swelling process is based on a lattice model.[8] The free-energy density (per site) of the gel phase is given by[8]

$$G/kT = (1 - \phi_1) \ln (1 - \phi_1) + \chi\phi_1(1 - \phi_1) + G_{el}/kT \approx u\phi_1^2 + G_{el}/kT \quad (1)$$

where ϕ_1 denotes the volume fraction of network monomers in the gel, χ is the Flory–Huggins interaction parameter, $u = {}^1/_2 - \chi$, k and T are the Boltzmann constant and the temperature, respectively, and G_{el} represents the elastic energy contribution.

It is important to remark that in swelling equilibrium the concentration of monomers in the gel corresponds to the semidilute rather than to the dilute regime and it is necessary to take the effect of monomer correlations into account. Then[11]

$$G/kT = u^*\phi_1^{2.25} + G_{el}/kT \quad (2)$$

The effective interaction coefficient u^* may be determined, for instance, from osmotic pressure studies; for a detailed discussion see part B of this section.

There is no fully satisfactory microscopic statistical theory relating the elastic energy term G_{el} to the molecular parameters of the network. The expressions used by various authors have given rise to much controversy.[7-12,16] The essential question underlying all the microscopic approaches is the description of the local conformation of the chains during the deformation of the network. Recent neutron scattering experiments on osmotically deswollen polystyrene gels indicate a very small variation of radius of gyration of the labeled elementary chains (smaller than 10%), even for rather large deswelling degrees (of the order of 4.5).[6] This result is not compatible with any microscopic theory hitherto proposed; these existing theories would predict a change of radius of gyration of the order of at least 25% for a deswelling degree $Q/Q_0 = 4.5$.[17] It should be stressed that the affine deformation hypothesis gives an even larger variation of the chain dimensions and thus seems to be a very poor approximation. Previous interpretations of osmotic deswelling were based on the classical affine hypothesis.[1-5,18,19] For this reason, we here propose an extremely simple although completely phenomenological approach. No hypothesis is made on the variation of chain dimensions during the deswelling process. Instead we postulate a scaling form of the macroscopic elastic energy contribution G_{el}. We will show that this approach can explain the experimental results of thermodynamic equilibrium of gels in both dilute and semidilute solutions.

The following form for the elastic energy contribution is proposed:

$$G_{el}/kT = \frac{\phi_1}{N} F(\phi_1/\phi^*) \quad (3)$$

where N denotes the number of monomers between cross-links and $\phi^* \simeq N^{-4/5}$ the overlap volume fraction in a good solvent. Here F is a dimensionless function which may depend on the gel functionality. In writing (3) we have supposed that G_{el} is proportional to the concentration of elastic chains, ϕ_1/N, and that it depends on the degree of interpenetration and deformation of chains, ϕ_1/ϕ^*. Actually, it may be argued that both the chain distortion energy and confinement energy in the semidilute regime depend on N solely through ϕ_1/ϕ^*. Taking only a dominant term we may write G_{el} as

$$G_{el}/kT \simeq A\phi_1^l \quad (4)$$

where A depends on the functionality of the network and on N. If it is supposed that G_{el} obeys eq 3, one finds

$$A \propto N^{-(9-4l)/5} \quad (5)$$

We discuss the value of the exponent l in part B. Here we only observe that if the elastic energy G_{el} is taken to be that of chain deformation,[10] $(\phi_1/N)/(R^2/R_F^2)$, where R is given by a packing condition $\phi_1 R^3/Na^3 = 1$ and R_F is the Flory radius of gyration, $R_F = aN^{3/5}$, the exponent l is equal to ${}^1/_3$. The free-energy density being known from eq 2, 4, and 5, the equilibrium concentration ψ may be found. It is given by the condition (cf. Appendix A)

$$\mu_s(\psi) = 0$$

with μ_s denoting the chemical potential of the solvent equal to

$$\mu_s = \phi_1^2 \frac{\partial(G/\phi_1)}{\partial\phi_1} = kT[1.25u^*\phi_1^{2.25} - (1 - l)A\phi_1^l] \quad (6)$$

Thus, the equilibrium monomer volume fraction ψ is given by

$$\psi = [(1 - l)A/1.25u^*]^{1/(2.25-l)} \quad (7)$$

This is a fundamental result for gel swollen by good solvents. In fact, if G_{el} scales as in eq 5 we get for *any* value of the exponent l

$$\psi \propto N^{-4/5} \simeq \phi^* \quad (8)$$

Therefore, in this general way we have found the same

dependence of the equilibrium concentration ψ on N as predicted by de Gennes,[11] the so-called "c^* theorem". Very similar reasoning may be applied to the case of a gel swollen in a Θ solvent. In Appendix B we show that, again, independently of the value of l, the standard "c^* theorem" result is obtained.

The very approach we have introduced for a gel swollen in a pure solvent may be easily applied to the problem of deswelling by a polymer solution. When the gel swollen in a good solvent is transferred into the solution of linear polymer in the same solvent a new equilibrium is established: the gel deswells. In principle, equilibrium may be reached by two processes: the extraction of the solvent from the network and the permeation of linear free polymer chains into the network. The free-energy density of the gel phase may be written as

$$G'/kT = \frac{\phi_2}{n} \ln \frac{\phi_2}{n} + u^*(\phi_1 + \phi_2)^{2.25} + G_{el}/kT \quad (9)$$

where ϕ_1 denotes the volume fraction of monomers of the network, ϕ_2 is the monomer volume fraction of the free linear polymer chains in the gel, and n is the polymerization index of these chains. The first term in (9) represents the entropy of mixing of linear chains which have permeated into the network. The second term reflects the similarity of the gel and a semidilute solution with the volume fraction $\phi_1 + \phi_2$. Actually, the "osmotic" contribution to the free-energy density (9) (first two terms) may be obtained by treating the solution as a melt of nonoverlapping blobs of size ξ equal to the correlation length associated with the overall monomer concentration $\phi_1 + \phi_2$; i.e., ξ scales[11] like $(\phi_1 + \phi_2)^{-3/4}$. The last term in eq 9 reflecting the network elasticity will be supposed to scale exactly as in eq 3 and consequently it will be written as in eq 4, i.e.

$$G_{el}/kT \simeq A\phi_1^{\,l} \quad (10)$$

At this point it is very important to stress some limits of the applicability of expression 9. The essential point is that the "osmotic" part of the free-energy density (9) (first two terms) is incorrect if the free linear chains are very short. In such a case the gel phase would be better described as a network swollen by a mixture of two solvents (short polymer chains plus solvent) rather than as a semidilute solution of two polymers in a good solvent. The free-energy density may be used[20] in the form (9) for chains with $n > dN^{1/2}$. The constant d depends slightly on the concentration of the polymer chains ϕ_2 and will be of the order of 2–3 for situations of interest in this paper. (In fact, the constant d may be evaluated by using the blob model:[20] $d \simeq \phi_2^{-5/8} \lesssim \phi_e^{-5/8}$; ϕ_e is the volume fraction of monomers in the solution surrounding the gel.) Another important assumption in writing eq 9 is that the overall monomer volume fraction $\phi_1 + \phi_2 \ll 1$, i.e.; the deswelling degree ϕ_1^{-1} is not so high that neither the network chains nor the free chains obey ideal chain statistics.

As already mentioned, when the gel is immersed in a polymer solution, the gel phase is composed a priori of three components, among which only two are free to move to the surrounding two-component solution. Therefore in equilibrium the chemical potential of the solvent in the gel phase is equal to that in the surrounding solution. Moreover, the chemical potentials of linear chains inside and outside the gel phase are equal. These two conditions are equivalent to the following ones (cf. Appendix A):

$$\mu_s' = G' - \mu_1'\phi_1 - \mu_2'\phi_2 = G'' - \mu_2''\phi_e = \mu_s'' \quad (11)$$

$$\mu_2' = \mu_2'' \quad (12)$$

where the single and double primes refer to the gel phase and solution phase, respectively, μ_s denotes the chemical potential of the solvent, ϕ_1 and ϕ_2 are the equilibrium volume fractions of network and linear polymer monomers, respectively, and ϕ_e denotes the volume fraction of monomers in the surrounding solution. Also, $G'(\phi_1,\phi_2)$, the free-energy density of the gel phase, is given by eq 9 and 10, and $G''(\phi_e)$ denotes the free-energy density (per site) of the polymer solution. Further, μ_1' and μ_2'' denote the so-called exchange potentials

$$\mu_1' = \partial G'/\partial\phi_1 \quad (13)$$

$$\mu_2' = \partial G'/\partial\phi_2 \quad (14)$$

and

$$\mu_2'' = \partial G''/\partial\phi_e \quad (15)$$

The equilibrium conditions (11) and (12) enable us to calculate the swelling degree of the gel

$$q = \phi_1^{-1} \quad (16)$$

and the partition coefficient defined by

$$K = \phi_2/\phi_e \quad (17)$$

as a function of the external concentration ϕ_e and of the polymerization index n. It is interesting to point out that it is not necessary to know the detailed form of the elastic energy G_{el} (10) to predict q and K. We show below that, without knowing the value of the constant A, the swelling degree and partition coefficient may be expressed in terms of the equilibrium volume fraction ψ of the gel swollen in a pure good solvent, which is a quantity directly accessible from experiment.

Two principal regimes of solution concentration will be considered, first the semidilute regime, $\phi_e > n^{-4/5}$, and second the dilute regime. In these regimes the dependence of G'' on ϕ_e is different.

1. Gel Immersed in a Semidilute Solution ($\phi_e > n^{-4/5}$). In a semidilute solution regime the free energy of the surrounding polymer solution with a monomer volume fraction $\phi_e > n^{-4/5}$ is given by

$$G''/kT = u^*\phi_e^{2.25} + \frac{\phi_e}{n} \ln \frac{\phi_e}{n} \quad (18)$$

Actually this formula may be obtained with the blob picture: the solution behaves like a melt of chains composed on incompressible blobs wiih dimensions given by the correlation length $\xi \simeq a\phi_e^{-3/4}$. With the help of eq 18, 9, 10, and 13–15, the equilibrium conditions (11) and (12) give

$$(\phi_1 + \phi_2)^{2.25} - [(1 - l)A/1.25u^*]\phi_1^{\,l} = \phi_e^{2.25} + (\phi_e - \phi_2)/1.25u^*n \quad (19)$$

$$(\phi_1 + \phi_2)^{1.25} + (1/2.25u^*n) \ln (\phi_2/\phi_e) = \phi_e^{1.25} \quad (20)$$

As already stressed above, it is convenient to express A in terms of ψ, the equilibrium volume fraction in the absence of linear polymer (i.e., $\phi_e = 0$ and, of course, $\phi_2 = 0$). From (19) (or (7)) the equilibrium conditions now take an extremely simple form:

$$(\phi_1 + \phi_2)^{2.25} - \psi^{2.25-l}\phi_1^{\,l} = \phi_e^{2.25} + (\phi_e - \phi_2)/1.25u^*n \quad (19a)$$

$$(\phi_1 + \phi_2)^{1.25} = \phi_e^{1.25} - \ln (\phi_2/\phi_e)/2.25u^*n \quad (20a)$$

From (19a) and (20a) the equations for the partition coefficient K and for the swelling coefficient $q = \phi_1^{-1}$ are obtained

$$(1 - a \ln K)^{1.8} - 1.8a(1 - K) - 1 - b[(1 - a \ln K)^{0.8} - K]^l = 0 \quad (21)$$

$$\phi_1 = \phi_e[1 - a \ln K]^{0.8} - K \quad (22)$$

where

$$a = (2.25u^* n \phi_e^{1.25})^{-1} \quad (23)$$

$$b = (\psi/\phi_e)^{2.25-l} \quad (24)$$

We start the discussion of the dependence of the partition coefficient K and of ϕ_1 on both the concentration ϕ_e and the chain length n by the interesting limiting case of linear polymer chains with high molecular mass, i.e., with $n \gg N$. This case is of particular interest since it corresponds to the situation studied experimentally in the present work. In such a case the following assumption may be made:

$$K \ll 1 \quad (25)$$

and

$$|a \ln K| \ll 1 \quad (26)$$

Then, using (25) and (26), we get from (21) and (22), respectively

$$K = \exp[-1.25u^* n \phi_e^{-(1-l)} \psi^{2.25-l}] \quad (27)$$

$$\phi_1 = \phi_e\{1 + (\psi/\phi_e)^{2.25-l}/[1.8 - 0.8l(\psi/\phi_e)^{2.25-l}]\} \quad (28)$$

In deriving (27) and (28) we have assumed that ϕ_e is well beyond $\phi_e^* \simeq n^{-4/5}$ and consequently the coefficient a is negligibly small so that the osmotic pressure is equal to $1.25u^*\phi_e^{2.25}$.

Before discussing the results (27) and (28), we examine the internal self-consistency of these results and of the assumptions (25) and (26). The condition (26) requires that $0.56(\psi/\phi_e)^{2.25-l} \ll 1$ and is fulfilled when the solution is more dense that the gel swollen by a pure good solvent, e.g., if $\phi_e > 1.5\psi$. The second condition (25) requires

$$n \gg 5(\phi_e/\psi)^{1-l}\psi^{-1.25} \quad (29)$$

(Here u^* has been put equal to 0.16 and $l = 0.5$; cf. part B of this section.) For typical calibrated gels, ψ is of the order of 0.05 for loose gels and up to 0.2 for tight ones. For such values of ψ, result 27 is valid for $n \gg 500$ for loose gels and $n \gg 50$ for tight gels. Also, ϕ_e is taken to be 0.3 (upper limit of concentrations of interest in this paper).

It is very interesting to compare the obtained conditions for n with the polymerization index N of chains forming the network: for loose gels with $\psi = 0.05$, N may be estimated to be about 350 whereas for tight gels with $\psi = 0.2$, N is about 60. (These estimates correspond to the precursor length for end-linked gels, and, on the other hand, to c^* values obtained from light scattering experiments.[21,22])

To sum up, when the gel immersed in a semidilute solution of a high polymer (of (29)), only an extremely small proportion of free chains permeates into the gel. Equation 21 shows that the partition coefficient decreases exponentially with the molecular mass of linear chains. It is important to note that tight gels (with $\psi \sim 0.2$) are practically impermeable; i.e., even the chains of very small molecular mass $n \sim 50$ cannot permeate inside the gel unless the gel is transferred into a very concentrated solution, $\phi_e > 0.3$. From (28) we get an approximate expression for the swelling degree q

$$q = \phi_e^{-1}[1 - 0.56(\psi/\phi_e)^{2.25-l}] < \psi^{-1} \quad (30)$$

i.e., we predict a very considerable deswelling of gel. Actually, the equilibrium volume fraction ϕ_1 is of the order of $\phi_e > \psi$. Of particular interest is the fact that in the limit of high molecular mass, the deswelling does not depend on the free-chain molecular mass. It should be also observed that ϕ_1 is always higher than ϕ_e.

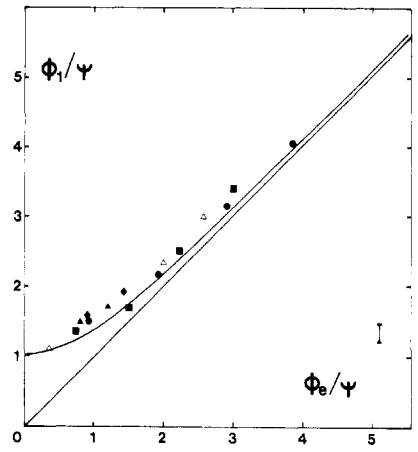

Figure 3. Calculated variation of the deswelling degree $\alpha = \phi_1/\psi$ as a function of the concentration of the surrounding solution measured by the ratio ϕ_e/ψ. Equation 31 has been used with the value of the exponent $l = 0.5$. In the scale of the figure there will be no difference if the value $l = 1/3$ is taken. Comparison with experimental data (cf. Figure 1). All gels should follow the continuous line obtained from eq 31.

As far as the variation of K and q with the concentration of surrounding solution is concerned, the following phenomena have to be stressed. First, as might be expected, the concentration of chains permeating into a gel increases when the external concentration ϕ_e increases. Second, the ratio ϕ_1/ψ characterizing the deswelling depends only on ψ/ϕ_e. These two facts are of crucial importance: for small concentrations, $\phi_e < \psi$, the partition coefficient is very small, $K \ll 1$, and although formula 28 is not valid, ϕ_1/ψ still depends solely on the ratio ϕ_e/ψ. In fact, since for high n the volume fraction ϕ_2 is small compared with both ϕ_1 and ϕ_e, ϕ_2 may be neglected in (19a) (but not in (20a)), from which we get the following equation for ϕ_1/ψ:

$$(\phi_1/\psi)^{2.25} - (\phi_1/\psi)^l - (\phi_e/\psi)^{2.25} = 0 \quad (31)$$

Hence, for semidilute solutions of long chains the *deswelling degree*

$$\alpha = \frac{q(\text{pure solvent})}{q(\text{solution})} = \frac{\phi_1}{\psi} \quad (32)$$

is a universal function of the ratio ϕ_e/ψ; i.e., it is independent of the cross-linking degree of the gel. Figure 3 shows the variation of α with ϕ_e/ψ for $l = 0.5$. It should be stressed that the predicted deswelling depends only very weakly on the value of the exponent l.

We now turn our attention to the more general case of smaller free linear chains with $n \sim N$. We suppose, however, that the chain molecular weight is still sufficiently high so that the free-energy density is still given by eq 9 (cf. the remarks below eq 9 and 10). For $n \sim N$ the chains can permeate into the gel, when the gel is an especially loose one. The partition coefficient can be computed by solving eq 21. In Figure 4 we show the variation of both the partition coefficient and deswelling degree as a function of the molecular weight of linear polymer for a typical gel ($\psi = 0.06$) and for the concentration of the surrounding solution $\phi_e \simeq 0.2$. An interesting phenomenon can be observed: when chains permeate the gel, it swells. It should be also pointed out that a significant number of chains do permeate the network even when their polym-

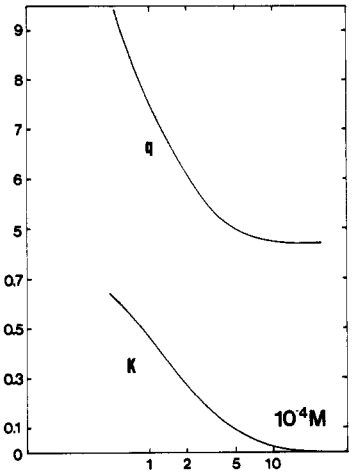

Figure 4. Calculated values of the partition coefficient $K = \phi_2/\phi_e$ and the swelling degree q as a function of the molecular weight M of the linear polymer for a typical gel with $\psi = 0.067$ (corresponding $q = 15$). $N \sim 200$ and $\phi_e = 0.2$.

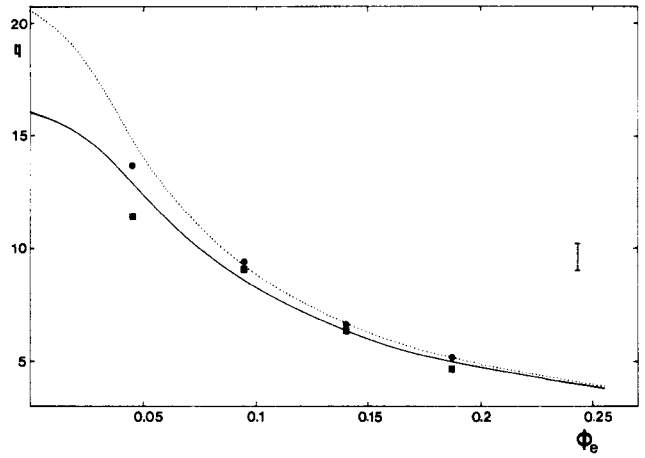

Figure 5. Calculated variations of the swelling degree q as a function of the monomer volume fraction ϕ_e of the semidilute surrounding solution. Molecular mass of chains $M = 7.65 \times 10^5$. The values of $\psi_1 = 1/q$ are, respectively, $\psi = 0.06$ ($q = 16$; gel B7) (continuous line) and $\psi = 0.05$ ($q = 20.5$; gel 54) (dotted line). The partition coefficient is always smaller than $K \simeq 5 \times 10^{-9}$ (for $\phi_e \lesssim 0.2$). Experimental values of q for different ϕ_e are also presented.

erization index n is larger than N characterizing the network. For instance, N associated with the gel considered in Figure 4 is about 200. Ten percent of linear polymer with $n \sim 450$ is expected to penetrate from the solution to the gel.

Eventually to complete the analysis of the semidilute regime we study the variation of the swelling degree with the volume fraction of the surrounding solution with $n \gg N$ fixed. This variation, directly measurable experimentally, is shown on Figure 5.

2. Gel Immersed in a Dilute Solution ($\phi_e < \phi_e^* \sim n^{-4/5}$). In a dilute solution regime the free energy of the surrounding solution is given by

$$G''/kT = u\phi_e^2 + \frac{\phi_e}{n} \ln \frac{\phi_e}{n} \tag{33}$$

The excluded-volume coefficient u in the Flory–Huggins lattice model is given by $u = {}^1/_2 - \chi$. However, for comparison with experimental results and in order to get the correct crossover with the semidilute regime it is necessary to take into account the dependence of the parameter u on the molecular mass of polymer chains. In part B of this section we use for u the experimental values obtained from osmotic pressure measurements.

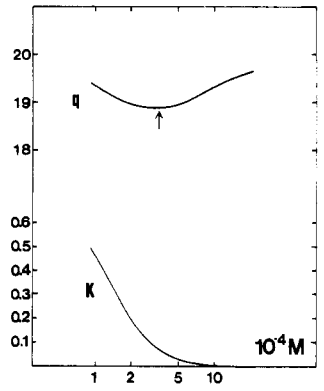

Figure 6. Variation of the partition coefficient K and the swelling degree q for a typical gel $\psi = 0.05$ ($q = 20$) as a function of the molecular mass M of linear chains. $\phi_e = 0.01$ corresponds to a dilute regime. The arrow indicates the molecular weight corresponding to N, the polymerization index of network chains, estimated from the empirical formula for the overlap concentration c^* of ref 22.

The equilibrium conditions (11) and (12) yield the following equations for the partition coefficient K and the equilibrium concentration ϕ_1:

$$\zeta^{1.8} - \psi^{(2.25-l)}(\zeta^{0.8} - K\phi_e)^l - \phi_e^2 u/1.25u^* - \phi_e(1 - K)/1.25nu^* = 0 \tag{34}$$

$$\phi_1 = \zeta^{0.8} - K\phi_e \tag{35}$$

where

$$\zeta = 2u\phi_e/2.25u^* - (1/2.25u^*n) \ln K \tag{36}$$

The discussion of the dependence of K and q on both polymerization index n and the concentration ϕ_e is quite similar to that for the semidilute regime. For high polymers the gel is impermeable, and when n is decreased, the partition coefficient increases; i.e., chains can permeate into the network. This is illustrated in Figure 6, where K for a typical network is plotted as a function of molecular weight of the linear polymer. In the same figure the variation of swelling degree q with n is presented. It can be remarked that the predicted deswelling degree is much smaller than that of the semidilute regime.

B. Comparison with Experiments. 1. Stress–Strain Measurements. Figure 2, in which the results of the elastic moduli of osmotically deswollen gels are plotted as a function of equilibrium concentration ϕ_1, indicates that E is approximately proportional to $\phi_1^{0.5}$. In the framework of Flory–Huggins lattice theory a variation like $\phi_1^{1/3}$ rather than $\phi_1^{0.5}$ should be expected. The above result gives some hint concerning the value of the exponent l in expression 10 for the elastic term of the free-energy density. Actually for the small uniaxial deformations of the gel the free-energy density may written in the form

$$G'/kT = G_0 + \frac{\phi_1}{N} F_1\left(\frac{\phi_1}{\phi^*}, \lambda\right) \simeq G_0 + \frac{\phi_1}{N} F_1\left(\frac{\phi_1}{\phi_1^*}, \lambda = 1\right) + \frac{\phi_1}{N} \left.\frac{\partial F_1}{\partial \lambda}\right|_{\lambda=1} (\lambda - 1) + \ldots \tag{37}$$

where G_0 is the osmotic contribution (cf. (9)) and λ denotes the deformation ratio along the axis of the deformation. For the deformed gels the function F_1 depends both on ϕ_1/ϕ^* and on λ. If we assume that F_1 can be factorized, i.e., $F_1 = h(\lambda)F(\phi_1/\phi^*) \approx h(\lambda)A\phi_1^{-(1-l)}$, we obtain the elastic modulus E defined in section IIB

$$E \propto \phi_1^{l} \tag{38}$$

Thus stress–strain measurements seem to indicate that the value of the exponent l is about 0.5.

It is important to stress that the interpretation of the deswelling experiments for both semidilute and dilute regimes does not depend strongly on the value of the exponent l. The comparisons of the predictions of section IIIA and of the experimental results confirm this point. Slightly better agreement is obtained when $l = 0.5$.

2. Deswelling by Semidilute Solutions. In the experiments we have performed, gels were immersed in benzene solutions of polystyrene with molecular weight $M_w = 765\,000$. The polymerization index of these chains n is much larger than N even for very loose gels. For the whole concentration range ϕ_e investigated here, condition 29 is fulfilled. Hence the theory predicts that (i) free chains practically do not penetrate into the gel (calculated K is always smaller than 10^{-7}), (ii) considerable deswelling is induced by high external concentrations, and (iii) the network volume fraction ϕ_1 always exceeds that of the surrounding solution. All these phenomena are confirmed by experiments described in section II and Figure 1.

To make quantitative comparisons, an estimation of the coefficient u^* in expression 9 for the free-energy density is necessary. We have calculated u^* from the osmotic pressure measurements on semidilute solutions of polystyrene in benzene.[23] Using the relation

$$\pi v_1/kT \simeq 1.25u^*\phi^{2.25}$$

with v_1 denoting molar volume of the benzene, we find $u^* \approx 0.16$. This value of u^* has been used for the calculation of the theoretical curves plotted in Figure 5 relative to the gels 54 and B7. There is good agreement with the experimental results shown on the same figure. In Table II the calculated values of q are compared with those measured for all gels studied and for all concentrations of surrounding solution.

Much more interesting is the verification of the predictions of eq 31. In Figure 3 we have plotted experimental values of the deswelling degree $\alpha = \phi_1/\psi$ (eq 32) for different values of the ratio ϕ_e/ψ. The full curve has been calculated from eq 31, with $l = 0.5$. It is remarkable that all data relative to gels of very different structure gather around the theoretical curve. It should be noted that this theoretical curve does not depend on u^*.

3. Osmotic Deswelling by Dilute Solutions. For the sake of completeness we compare the predictions of the theory with the data concerning the polystyrene networks in dilute benzene solutions reported in ref 5. Basic predictions of section IIIA (cf. Figure 6) qualitatively agree with the experimental results: (i) small chains permeate into the gel; (ii) for fixed ϕ_e, when n decreases the swelling degree increases; (iii) the observed deswelling degree is small compared with that observed for high ϕ_e. In order to make quantitative comparisons we have used eq 34–36. The excluded-volume parameter $u(n)$ (eq 33) has been estimated from osmotic pressure measurements

$$u = v_1A_2/v_2^2$$

where A_2 denotes the second virial coefficient and v_2 is the specific volume of polystyrene. The following dependence of A_2 on molecular weight M has been supposed:[24]

$$A_2 = CM^{-d}$$

with $C = 7.76 \times 10^{-3}$ and $d = 0.24$.

In Table IV we show experimental values of the partition coefficient K and of the swelling degree q for a gel with $\psi \approx 0.035$ and compare them with theoretical predictions.

Table IV
Comparison of Theoretical Predictions and Experimental Results of Ref 5 (Gel 1878)

mol wt of linear chains in surrounding polymer soln	K_{exptl}	K_{theor}	q_{exptl}	q_{theor}
9 400	0.64	0.62	26.6	27.7
19 000	0.39	0.37	26.1	26.4
33 000	0.13	0.18	25.1	25.7
95 000	0.001	0.007	24.5	25.9
185 000		8×10^{-5}	26.5	24.9
570 000		10^{-12}	25.1	26.7
1 000 000		10^{-21}	25.1	26.8
3 500 000			26.2	26.8

In view of the experimental difficulties in measuring K and q values, rather satisfactory agreement is found. Moreover, the following points should be stressed. First, we do not have detailed information about the structure of the gel. The gel was a rather loose one. Such gels contain in general a considerable fraction of pendant chains. The presence of these chains strongly influences the osmotic deswelling.[25] The second point concerns the result obtained for the chains with small molecular mass $M = 9400$. These chains are probably near the limit of applicability of expression 9 for the free-energy density: N corresponding to $\psi \approx 0.035$ is about 500. Finally, for the highest molecular masses, $\phi_e = 0.01 > \phi_e^*$ lies in a semidilute rather than in a dilute concentration range.

IV. Conclusion

The principal experimental result of this work is that calibrated networks immersed in semidilute solutions of high polymers exhibit strong deswelling with respect to the equilibrium state in pure good solvent (Figures 1, 3, and 5 and Table II). Within the accuracy of experiment no high-molecular-weight chains could be detected inside the gel phase. From a thermodynamic standpoint these results may be explained qualitatively by the following picture. The equality of the solvent chemical potential in the gel phase and in the surrounding solution leads to the conclusion that $\phi_1 + \phi_2$, the overall concentration inside the gel, is higher than ϕ_e, the concentration in the solution. This is due to the very fact that the gel elasticity opposes osmotic pressure effects in the gel phase. The partition coefficient ϕ_2/ϕ_e is essentially determined by the second equilibrium condition, namely, the equality of the chemical potential of the free chains inside and outside the gel. In this respect the "translational" term $(kT/n) \ln \phi_2$ originating from the entropy of mixing of free chains in the gel phase plays an important role (cf. eq 20).

As we have already stressed, $\phi_1 + \phi_2 > \phi_e$ and, therefore, the term $(1/n) \ln (\phi_2/\phi_e)$ has to be roughly of the order of $\phi_e - (\phi_1 + \phi_2)$. For large n this is fulfilled only for very small values of ϕ_2; i.e., only an exponentially small fraction of long chains can permeate into the gel phase. Moreover, the swelling degree $q = \phi_1^{-1}$ is of the order of ϕ_e^{-1}, much smaller than the swelling degree in the pure solvent ψ^{-1} (since $\phi_e > \psi$).

A detailed quantitative analysis has been presented in section IIIA-1 and good agreement with experimental results has been found. One of the most interesting theoretical predictions concerns dependence of the equilibrium concentration on the ratio ϕ_e/ψ (cf. Figure 3). As predicted, gels with very different structures follow the same universal theoretical law.

The scaling approach of this paper predicts that smaller chains will penetrate into the gel phase even if their polymerization index n is larger than that of network chains

N (cf. sections IIIA-1 and IIIA-2 and Figures 4 and 6). However, it should be pointed out that even for rather concentrated solutions ($\phi_e \sim 0.3$) for $n \gtrsim N$, the partition coefficient is significant but not very high (e.g., for $n \sim N$ for rather loose gel, $\psi \approx 0.05$, $\phi_e = 0.2$, one gets $K = \phi_2/\phi_e \approx 0.1$). When n decreases ($n < N$) the proportion of free chains permeating into the gel increases rapidly and the gel swells. In the dilute regime of ϕ_e these phenomena have been already observed experimentally[5] and we have found satisfactory agreement with the scaling approach (section IIIB-2). It will be extremely interesting to perform experiments in the semidilute regime with chains of length $n \lesssim N$. In this regime the swelling of the gel when the chains enter inside the gel phase is expected to be very large.

Finally, it is important to realize that the impermeability of the gels to the high-molecular-weight polymer chains is a thermodynamic effect and not solely a kinetic effect as has been sometimes postulated.

Note: During the preparation of the manuscript, we received a preprint by F. Brochard dealing with some theoretical aspects of the problem of gels immersed in homopolymer solutions and melts. Our approach, although different, leads for gels immersed in dilute polymer solutions to qualitatively similar results.

Acknowledgment. We are indebted to F. Brochard, H. Benoît, and P. G. de Gennes for interesting and stimulating discussions. We also thank F. Brochard for sending a preprint of her paper prior to publication.

Appendix A. Equilibrium Conditions

When a gel is immersed in a linear polymer solution, thermodynamic equilibrium is reached when (i) the solvent chemical potentials μ_s in the gel phase and in the surrounding polymer solution are equal or (ii) the chemical potential μ_p of linear polymers inside and outside the gel are equal.

The chemical potential μ_s' of the solvent in the gel phase is equal to

$$\mu_s' = \left.\frac{\partial G_{tot}'}{\partial n_s}\right|_{n_1,n_2} = \left.\frac{\partial}{\partial n_s}[(n_1 + n_2 + n_s)G']\right|_{n_1,n_2} \quad \text{(A-1)}$$

where n_s, n_1, n_2 denote the number of sites occupied by the solvent, monomers of the network, and the monomers of free polymer chains. $n_1 + n_2 + n_s$ is equal to the number of sites. The volume fractions ϕ_1 and ϕ_2 are defined by

$$\begin{aligned} \phi_1 &= n_1/(n_1 + n_2 + n_s) \\ \phi_2 &= n_2/(n_1 + n_2 + n_s) \end{aligned} \quad \text{(A-2)}$$

From (A-1) and (A-2) one gets

$$\mu_s' = G' - \phi_1\mu_1' - \phi_2\mu_2' \quad \text{(A-3)}$$

where the exchange potentials μ_i' are defined by

$$\mu_i' = \partial G'/\partial\phi_i \qquad i = 1, 2 \quad \text{(A-4)}$$

It is interesting to note that $\mu_s' = -\pi' v_1$, where π' denotes the osmotic pressure (v_1 denotes the molar volume of the solvent).

Similarly, the chemical potential of the solvent in the solution equals

$$\mu_s'' = G'' - \mu_2''\phi_e \quad \text{(A-5)}$$

where $\mu_2'' = \partial G''/\partial\phi_e$ is the exchange potential. Condition (i) reads

$$\mu_s' = \mu_s'' \quad \text{(A-6)}$$

The second equilibrium condition (ii) requires

$$\mu_p' = \partial G_{tot}'/\partial(n_2/n) = \mu_p'' = \partial G_{tot}''/\partial(n_e/n) \quad \text{(A-7)}$$

where n is the polymerization index of the linear chains. Making use of the condition (A-6) and of (A-4) one gets the condition

$$\mu_2' = \mu_2'' \quad \text{(A-8)}$$

(A-6) and (A-8) give a set of two equations determining the phase equilibrium of a gel immersed in a solution.

When a gel is immersed in a pure solvent, $\phi_e = 0$ and the only equilibrium condition is (A-6) which reduces to

$$\mu_s' = G' - \phi_1\mu_1' = 0 \quad \text{(A-9)}$$

Appendix B. Gel Swollen in a Θ Solvent

In a Θ solvent the free-energy density of the gel may be written (in analogy to (1) and (4)) as

$$G'/kT = \omega\phi_1^3 + G_{el}/kT = \omega\phi_1^3 + \zeta\frac{\phi_1}{N}\left(\frac{\phi_1}{\phi_\Theta^*}\right)^{-(1+l')}$$

with the overlap concentration scaling like

$$\phi_\Theta^* \simeq N^{-1/2}$$

The equilibrium condition

$$\mu_s' = (G' - \mu_1'\phi_1)|_{\phi_1=\psi_\Theta} = 0$$

gives independently of l'

$$\psi_\Theta \simeq N^{-1/2}$$

i.e., the equilibrium concentration in a Θ solvent is proportional to ϕ_Θ^*. This is the so-called "c^* theorem" result.

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