## Appendix

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

$$Y_1 = \tan X$$

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

The solutions of eq 8 have a physical meaning only for $\mu/M_{os} < 0.5$. Figure 6 shows the curves $Y_1(X)$ and $Y_2(X)$ for $\mu/M_{os}$ 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 $\pi$ for $\mu/M_{os} = 0$ to 2.08 rd for $\mu/M_{os} = 0.5$. The variation of $\mu/M_{os}$ 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 $\xi$—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 $\xi$: 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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first attempt to describe this sol–gel transition was made some time ago in terms of percolation. Flory, Stockmayer, Gordon, and others provided the basis of this theory and defined all the important quantities. Their approach, however, was on the level of the Curie–Weiss theory for the ferromagnetic transition in magnetism.[8] It was realized recently that it has some shortcomings. In particular, all the exponents appearing in the different quantities turn out to be dependent on space dimension;[8] they are not constants as originally believed. The difference was attributed to the fact that loop formation[1,3] is not allowed in this theory. This is equivalent to considering a Bethe lattice. As we know that the latter cannot be embedded in any space with finite dimension, we expect the Flory–Stockmayer results to hold only for large space dimensions, whereas critical exponents should be valid for lower dimensions, below $d_c = 6$. However, we also know from other critical phenomena that these exponents are found only in a limited critical region: if one goes too far from the threshold, then classical exponents should be observable again. The width of the critical region is usually given by the Ginzburg criterion. It may be calculated more directly in our case within a Flory approach. What is interesting here, as we shall show, is that one may continuously vary this width in the case of vulcanized gels. By increasing either $Z$ or the concentration of the solution, the size of the critical region may be changed continuously. Before we come to this discussion, in section II-c below, let us briefly recall some definitions and the Flory theory in the simpler polycondensation case.

**a. Relevant Quantities.** Let us model on a lattice the reaction of polyfunctional units in a vessel. Every site is occupied. Bonds are present at random with probability $p$. We assume that all the functionalities have the same reactivity, whatever the size of the polymer to which they belong and their location in the macromolecule and that the polymer configurations are stationary.

This is the percolation model. The Flory–Stockmayer[5,6] theory corresponds to the case when the lattice is a Cayley tree. The probability $p$ may be related to time or to the extent of reaction. When $p$ increases, one gets a distribution of polymers with larger and larger sizes. This is the sol "phase". Above a threshold $p_c$ in addition to the sol there appears a gel. Let $\epsilon \equiv p - p_c$ be the distance to the threshold, $P(N,\epsilon)$ the probability of finding a polymer made of $N$ monomers, in the sol and at a distance from the threshold, and $G$ the gel fraction. This is the probability for a monomer of belonging to the infinite network. We assume[1,3]

$$G \sim \epsilon^{\beta} \tag{1}$$

$$P(N,\epsilon) \sim N^{-\tau} f(\epsilon N^{\sigma}) \tag{2}$$

where $\beta$, $\tau$, and $\sigma$ are exponents that depend on the dimension of space and $f(x)$ is an exponentially decreasing function which cuts off the slowly decaying distribution above a typical size

$$N_t \sim \epsilon^{-1/\sigma} \tag{3}$$

As mentioned above, as the reaction proceeds, one gets in the vicinity of the gelation threshold larger and larger polymers. These may be characterized by the weight-average molecular weight $N_w$, which is the second moment of the distribution.[2]

$$N_w \equiv \frac{\int N^2 P(N,\epsilon)\,\mathrm{d}N}{\int N P(N,\epsilon)\,\mathrm{d}N} \sim |\epsilon|^{-\gamma} \tag{4}$$

Note that when one increases $\epsilon$ above the threshold, $N_w$ decreases; this corresponds to the gradual incorporation of the largest finite polymers in the gel fraction.

A final quantity of interest to us is the characteristic distance:

$$\xi \sim |\epsilon|^{-\nu} \tag{5}$$

This distance may be interpreted in two equivalent ways, using either the sol or the gel phase. For the former, it may be considered as the $z$-average radius of the polymers in the sol:

$$\xi^2 \sim \langle R^2 \rangle_z \equiv \frac{\int_0^{\infty} R^2(n) n^2 P(n,\epsilon)\,\mathrm{d}n}{\int n^2 P(n,\epsilon)\,\mathrm{d}n} \tag{6}$$

When the gel above the threshold is used, $\xi$ may be seen as the average mesh size of the incipient network, or node-to-node distance. A node here is an effective (or elastically active) junction connected to infinity, as opposed to a cross-link leading to a dangling end, for instance.

All the exponents defined above were calculated some time ago in the mean-field regime.[5] It was found

$$2\nu = \beta = \gamma = 1; \quad \tau = 5/2; \quad \sigma = 1/2 \text{ (mean field)} \tag{7}$$

The critical exponents were also calculated for space dimensions ranging from 2 to 6.[3,9] They are not independent of each other but are related through scaling relations.[1,8,9] Only two, for instance $\tau$ and $\sigma$, are needed to know all of them. In the next section, we use the Flory approximation to evaluate the fractal dimension[17] of the gel.

**b. Flory Theory of Percolation.** In what follows we will always assume that monomers are a good solvent of larger molecules. We now calculate the variation of the radius of gyration $R$ of a branched polymer as a function of its size $N$, *in the reaction bath.* The polymers we consider are typical large macromolecules whose size is given by relation 3. Because we know that their structure is similar to that of the gel, we expect the same behavior for any finite part of the latter. This was calculated some time ago by Zimm and Stockmayer[10] in the absence of interactions between monomers. Their result is

$$R_0 \sim N^{1/4} l \tag{8}$$

where $R_0$ is the ideal radius and $l$ the unit length.

In order to take into account the interactions, we write down a Flory free energy

$$F = \frac{R^2}{R_0^{\,2}} + \frac{v}{N_w}\frac{N^2}{R^3} \tag{9}$$

where the first term is an elastic contribution and the second one the interaction. $v$ is the excluded volume parameter and will always be assumed to be positive (good solvent). The presence of $N_w$ in the second term is due to the screening of the interaction due to the presence of other polymers. This was introduced by Edwards[11] and is valid as long as the polymers overlap. Relation 9 was used first independently by de Gennes[12] and by Isaacson and Lubensky.[13] Because we are considering large typical macromolecules, there is a relation between $N_w$ and $N$: using relations 3 and 4, we get

$$N_w \sim N^{\gamma\sigma}$$

Within the Flory approximation, classical values are given to the exponents in the preceding relation:

$$N_w \sim N^{1/2} \tag{10}$$

Minimizing the free energy, relation 9, with respect to $R$ and taking (10) into account, leads to

$$R \sim N^{2/5} \qquad (11a)$$

or

$$N \sim R^{5/2} \qquad (11b)$$

Relation 11b gives the fractal dimension $D_p = {}^5/_2$ of the gel in the reaction bath, that is, in the presence of the finite polymers of the sol. It is important to stress that due to the presence of the latter, screening effects are present and lead to this fractal dimension. We will argue in section III below that upon dilution the sol is washed out of the gel. As a result, screening disappears and the gel swells.

**c. Vulcanization. 1. The Melt.** Let us now turn to the more complicated case of vulcanization and analyze the differences with usual percolation discussed above. The basic process is the same here as above. However, the basic unit is a large linear macromolecule made of $Z$ monomers instead of being a small multifunctional unit. Here we consider the case of a melt. The experimental situation is the following: One starts with a melt of amorphous linear polymer chains. Cross-linking of these polymers is subsequently assumed to occur at random. This may be either chemical or physical.[14] Let $p$ be the probability for a monomer being cross-linked. It was shown that there is a threshold $p_c \sim Z^{-1}$ above which a gel appears in the loopless approximation.[5] In what follows, we will consider only the vicinity of this threshold. Then, on the average, every chain is reacted by one of its monomers. As mentioned above, this leads us to take a linear polymer as a basic unit. Because it has $Z$ monomers, we will assume that it is a $Z$-functional unit. Performing this change, namely assuming a linear chain is the basic polyfunctional unit, leads back to the former percolation problem. Two important points have to be stressed: (1) the molecular weight of the basic element is $Z$; and (2) the elementary distance is the radius of a linear polymer, $Z^{1/2}l$, where $l$ is the monomer length.

With these points in mind, we redefine relations 3–5. The quantities $N_w$, $N_t$, and $R$ are now related to the number of true monomers:

$$N_t \sim \epsilon^{-1/\sigma} Z \qquad (3a)$$

$$N_w \sim \epsilon^{-\gamma} Z \qquad (4a)$$

$$\xi \sim \epsilon^{-\nu} Z^{1/2} l \qquad (5a)$$

However, because it is a fraction, $G$ remains unchanged.

$$G \sim \epsilon^{\beta}$$

Note that in the mean field approximation, $\nu = {}^1/_2$ and $\sigma = {}^1/_2$. This implies a slight change in the Zimm–Stockmayer radius: from (3a) and (4a) we get

$$R_0 \sim (N/Z)^{1/4} Z^{1/2} l \qquad (8a)$$

It is now possible to discuss the behavior of the vulcanizate. The Flory free energy is the same as eq 9 above.

$$F = \frac{R^2}{R_0^{\,2}} + \frac{v}{N_w} \frac{N^2}{R^3}$$

In this analysis, the difference between the classical and critical behaviors originates from the interaction term in the free energy. Should it be small compared to unity ($F$ is expressed in terms of $k_BT$, where $k_B$ is Bolzmann's constant and $T$ the temperature), we would have a mean field behavior. Thus depending on the value of this term, one may observe critical or classical behavior. In order to evaluate the width of the critical region, we are going to evaluate this interaction energy. We will assume mean field behavior for all the variables. This is consistent as long as the resulting contribution remains small. When it becomes larger than unity, the assumptions are no longer valid, and thus there is a crossover to the critical behavior. Using (3a)–(5a) and (8a) for the radius, we get

$$F_{\text{int}} \sim (N/Z)^{3/4} Z^{-1/2} \sim \epsilon^{-3/2} Z^{-1/2} \qquad (12)$$

As discussed above, the size of the critical region corresponds to $F_{\text{int}} \sim 1$. This leads to

$$\epsilon^* \sim Z^{-1/3} \qquad (13)$$

When the distance to the threshold is larger than $\epsilon^*$, the interaction energy becomes irrelevant and a mean field behavior is expected. Because $Z$ is large, we realize that this will always be the case practically. On the other hand, for $\epsilon < \epsilon^*$ the critical behavior should be observed. Equation 13 was derived by de Gennes,[15] who considered the fluctuations in connectivity rather than the interactions to evaluate the width of the critical region.

We summarize this discussion by saying that for vulcanization of a melt of linear polymers the critical region is very narrow. As a consequence only classical exponents are practically observable. Further, we shall see in section III.b that the corresponding structure is characterized by a strong overlap of the meshes.

**2. Semidilute Solutions.** The generalization to vulcanization of a semidilute solution of linear polymers in a good solvent is readily made. One has first to note that in such solutions there is one contact per blob between chains, instead of one per monomer as in the case of a melt. Only those contacts may be transformed into permanent cross-links. Each of these blobs is made of $g$ monomers and has a length $\xi_B$, with

$$g \sim C^{-5/4} \qquad (14a)$$

$$\xi_B \sim C^{-3/4} \qquad (14b)$$

where $C$ is the monomer concentration of the solution.

Vulcanization may then be mapped on percolation of $(Z/g)$ functional units. Each unit has a "step" length $(Z/g)^{1/2}\xi_B$. The previous discussion needs only these changes, namely

$$Z \rightarrow Z/g \qquad \text{for functionality}$$

$$Z^{1/2} l \rightarrow (Z/g)^{1/2} \xi_B \qquad \text{for distances}$$

in the definitions (3a)–(5a). Note that the ideal radius, relations 8 and 8a, becomes now

$$R_0 \sim N^{1/4} (Z/g)^{1/4} \xi_B \qquad (8b)$$

The rest of the discussion follows unchanged. As a result, the width of the critical region becomes[16]

$$\epsilon^* \sim \left(\frac{Z}{g}\right)^{-1/3} \sim \left(\frac{C}{C^*}\right)^{-5/12} \qquad (C > C^*) \qquad (13a)$$

where $C^* \sim Z^{-4/5}$ is the so-called overlap concentration of the linear polymer solution. For a melt $C \approx 1$, we recover relation 13 as expected. What is interesting here is that when $C$ decreases, the width of the critical region increases. Therefore in the vicinity of $C^*$ critical exponents should be observable again. Below $C^*$ there is no contact between the polymers, and the whole approach breaks down.

We conclude this part by recalling our results on the fractal dimension of a gel in its reaction bath for both cases:

If the monomers are small multifunctional units, the fractal[17] dimension is ${}^5/_2$, $N \sim R^{5/2}$. This result holds at least in a limited $\epsilon$ range when one considers vulcanization of a rather dilute solution of linear polymers.

For vulcanization of a melt or of a concentrated solution of linear chains, one should rather observe the classical fractal dimension $D_0 = 4$, $N \sim R^4$.

These results are due either to the screening of the interactions by the other polymers or to the irrelevance of the excluded volume interaction. Although the result $D_0 = 4$ may seem to be surprising in a three-dimensional space, we will see below that it is reasonable.

When solvent is added in order to swell the gels, we expect the repulsive interactions to become more and more important because of dilution.

## III. Swelling

It was shown in last section that screening effects are essential for the determination of the fractal dimension of a gel in its reaction bath and thus of its volume. Upon addition of solvent in excess, the finite polymers of the sol are washed out of the gel, except possibly the largest ones. The concentration of the latter is exponentially small. Because of this, the screening effects disappear, and the gel swells. Let us consider first the case of small polyfunctional units.

**a. Critical Gel.** In the following we will consider the maximum swelling of a gel in the critical case. As mentioned above, this corresponds to the replacement of the sol polymers in the gel by solvent molecules. As a result, there is no more screening. In other words, the gel behaves locally as a branched polymer in a good solvent. One may write down a free energy similar to relation 9 above without $N_w$ in the interaction term. As a result, the fractal dimension is $D_A = 2$

$$R_f \sim N^{1/2} \qquad (15)$$

where $R_f$ is the characteristic distance of the gel after the swelling has reached its maximum value. As in section 2a above, this is the mesh size, or node-to-node distance, and corresponds to the swollen value of $\xi$.

In order to evaluate the swelling, one has to realize that in the critical region there is only one node per volume $\xi^3$. This is equivalent to saying that the gel is in a $C^*$ condition even when it is in the reaction bath. One way of checking this is to calculate the concentration inside a sphere with volume $\xi^3$

$$\begin{aligned} \rho &\sim N/\xi^3 \sim \epsilon^{-1/\sigma}\epsilon^{3\nu} \sim \epsilon^{\beta} \\ &\sim G \end{aligned} \qquad (16)$$

where we have used relations 3, 5, and hyperscaling[8]

$$3\nu = 2\beta + \gamma \qquad (17)$$

for space dimension $d = 3$. We find that $\rho$ is of the order of the gel fraction, and thus the gel is in a $C^*$ situation. Let us mention at this level that this will not hold for vulcanization. In the mean field case, relation 17 is not valid, and this has important consequences, to be discussed in section III.b.

When solvent is added, the gel remains in the $C^*$ configuration, but the characteristic distance increases from the initial value $\xi$ to its final value $R_f$. Thus the swelling ratio is

$$Q \sim (R_f/\xi)^3 \qquad (18)$$

Note that this implies that the swelling is affine down to scales of the order of the mesh size, as one might expect.

One may relate $R_f$ to $\xi$ by noting that the total mass in a volume $\xi^3$ is conserved during swelling: from (11b) and (15) we get

$$N \sim \xi^{5/2} \sim {R_f}^2 \qquad (19)$$

and thus

$$Q \sim \xi^{3/4} \qquad (20)$$

Because $\xi$ is not easily measurable, we may relate it to the more directly observable quantities $G$ or $N_w$: from relations 16 and 11a we have

$$G \sim \xi^{-1/2} \qquad (21)$$

leading to

$$Q \sim G^{-3/2} \qquad (22)$$

From relations 4, 16, 17, and 21

$$N_w \sim \xi^2 \qquad (23)$$

and

$$Q \sim {N_w}^{3/8} \qquad (24)$$

Equations 22 and 24 may be checked by weighing the gel fraction or by measuring $N_w$ on the diluted sol. Thus we find that the swelling ratio diverges as one approaches the gelation threshold: the looser the gel, the more it swells. However, swelling is affine at least down to distances of the order of the mesh size. As we will see, this last property will not hold for vulcanization, and this will make swelling even more dramatic.

**b. Gel Vulcanized in a Melt.** As we have seen for vulcanization of a melt of linear polymer chains, mean field rather than critical exponents should generally be observable. An important consequence when we consider the initial state of a vulcanized gel in its reaction bath is that it is no longer in a $C^*$ situation. Instead, we will show that we have many nodes per volume $\xi^3$, or equivalently, that there are several interpenetrating networks. This implies that swelling, in addition to the process we discussed in section 2a above, also includes a disinterpenetration of the networks.

In order to show the interpenetration effect, we evaluate the contribution of a single node to the gel fraction, following the same steps as for eq 16: using (3a) and (5a) with the mean field values $\sigma = \nu = {}^1/_2$, we get

$$\begin{aligned} \rho &\sim N/\xi^3 \sim (\epsilon^{-2}Z)(\epsilon^{3/2}Z^{-3/2}) \qquad (\epsilon > \epsilon^*) \\ &\sim \epsilon^{-1/2}Z^{-1/2} \end{aligned} \qquad (16a)$$

which is much smaller than the gel fraction

$$G \sim \epsilon$$

Thus in order to recover the total density $G$, one needs several nodes per characteristic volume. Let $n$ be this number:

$$n \sim G/\rho \sim \epsilon^{3/2}Z^{1/2} \qquad (25)$$

Again, if we decrease to the crossover value $\epsilon^* \sim Z^{-1/3}$, the number of nodes goes back to unity, and below $\epsilon^*$ one recovers the critical behavior discussed in section III.a. We will focus only on the mean field region $\epsilon > \epsilon^*$ and discuss this large number of nodes per volume $\xi^3$ and its consequences.

The basic reason why there are several nodes per elementary volume is in fact related to the elementary unit, which is here a linear chain. When one analyzes relations 16a or 25, one realizes that $\rho$ being small (or $n$ being large) is not due to the vicinity of the threshold but to the $Z$ prefactors: the $\epsilon$ dependence alone would lead to conclusions opposite to what we found. However, what is crucial here *is the fact that each linear chain has a vanishingly* small contribution to the density. This is why such objects can be packed in a very dense way and thus allow for the $N^{1/4}$ dependence for the radius. This leads to a competition between a very close packing (implying a diverging density) and the "elementary" density for a chain (which is very small). As long as $\epsilon > \epsilon^*$, the "chain effect" is dominant, and mean field behavior can be observed. On the other hand, when one goes too close to the threshold, packing becomes too dense for getting a realistic density.

Let us note that eq 25 is the generalization to three-dimensional space of a similar situation holding for large space dimensions ($d > 6$) recently discussed by Coniglio.[18] The main difference between eq 25 and his results is that here $n$ is large because of the presence of the $Z$ term, whereas in Coniglio's discussion the exponent for $\epsilon$ is negative (for $d > 6$). But the basic reason for this large number of interpenetrating networks is the same and is related to the breakdown of hyperscaling[19] relation 17, in our case for classical exponents in $d = 3$ and in Coniglio's discussion for $d > 6$.

Finally, we note that disinterpenetration was already discussed by Bastide, Candau, and Picot.[2,19]

Starting from the vulcanized gel in its reaction bath, if we add solvent in excess, swelling includes both the change in dimensions of the characteristic distance and the disinterpenetration of the different nodes. The last point implies that starting with a volume element $\xi^3$ we end up with many volume elements $R_f^3$ instead of one in the critical case. The final swollen radius is

$$R_f \sim (N/Z)^{1/2} Z^{3/5} \qquad (26)$$

where we have assumed that the solvent is good for linear chains and that interactions become relevant upon dilution, as in section III.a. The initial radius is from (8a)

$$\xi \sim (N/Z)^{1/4} Z^{1/2}$$

Using (3a) with the classical value $\sigma = {}^1/_2$, we get the ratio of the radii

$$q = R_f/\xi \sim (N/Z)^{1/4} Z^{1/10} \qquad (27)$$

This result differs from the equivalent one in the critical case by the value of the exponents, which are classical here. In addition to this difference, the swelling ratio, which is the ratio of the final-to-initial volumes, also includes the disinterpenetration term

$$Q = V_f/V_i \sim n(R_f/\xi)^3 \qquad (18a)$$

There is, however, an important assumption in relation 18a. We neglect the possible hindrance of swelling by entanglements. The assumption is certainly valid for molecular weights $Z$ smaller than the critical entanglement mass $Z_c$.[19] For higher values of $Z$ this assumption is correct only if the number of trapped entanglements is independent of the extent of reaction or of $\epsilon$. It should certainly be interesting to compare the swelling properties of gels made with small ($Z < Z_c$) or with large ($Z > Z_c$) precursor chains to check this assumption.

Using (1), (3a), (25), and (27) with $\sigma = {}^1/_2$ and $\beta = 1$, we get the following expressions for the swelling ratio:

$$Q \sim (qG^{1/2})^8 \qquad (G > G^* \sim \epsilon^* \sim Z^{-1/3}) \qquad (28)$$

$$Q \sim q^3(\epsilon Z^{1/3})^{3/2} \qquad (29)$$

$$Q \sim Z^{4/5} \qquad (30)$$

which exhibits a stronger dependence than the affine $q^3$ behavior. This is mainly due to the disinterpenetration of the nodes. Equation 30 is rather surprising because it implies that swelling is independent of the extent of cross-linking for $\epsilon > \epsilon^*$: the dependence of $q^3$ corresponding to the swelling of the elementary distance is exactly compensated by the contribution coming from disinterspersion of the nodes. Of course it would be very interesting to check if this holds. In case it does not, two different reasons may be invoked: (1) entanglements hinder swelling in a nontrivial way; and (2) crossover effects, discussed below, alter our analysis.

Equation 28 may be extrapolated to $G = 1$, i.e., to total reaction, in one special case, namely when one cross-links linear chains by their ends. Then our assumption of approximately one reaction per chain is still valid, and we may use the transformation (3a) to (5a) even for complete reaction, $G = 1$. In that special case, we have a perfect network of linear chains which are reacted by all their ends. Let $Z$ be the molecular weight of the precursor chains. We know that there are

$$n \sim Z^{1/2}$$

chains per volume element $R_0^3 \sim Z^{3/2}$. Swelling this network, as above, implies, in addition to the swelling of the individual chains, the disinterpenetration of the nodes until a $C^*$ situation is reached, where the radius of a chain is

$$R_f \sim Z^{3/5}$$

It is easy to evaluate the swelling ratio

$$Q = n(R_f/R_i)^3$$

and to relate it to

$$q = R_f/R_i$$

One finds

$$Q \sim q^8$$

in agreement with (28).

A possible weakness appears in eq 30

$$Q \sim Z^{4/5} \qquad (\epsilon > \epsilon^*) \qquad (30)$$

independent of the distance $\epsilon$ to the gelation threshold. For vulcanization of long chains in a melt, we guess that this result should hold as long as the distance $\epsilon$, where the reaction has been stopped, is sufficiently large. However for shorter chains, or for smaller values of $\epsilon$, crossover effects should alter this result. We have assumed that the different exponents have either critical or mean field values. This is correct as long as $\epsilon$ is very different from $\epsilon^*$. But when $\epsilon$ is not too different from $\epsilon^*$, then one should start rather with effective exponents in between the asymptotic values we used in the previous discussion. This would lead to an $\epsilon$ dependence for $Q$. As we do not know the effective exponents, however, we will not go further in this discussion. Similarly, we will not discuss the case of vulcanization of a semidilute solution. One has just to make the transformation given in section II.c. This leads to

$$Q \sim (Z/g)^{4/5} \qquad (30a)$$

instead of to relation 30 above. For the reasons we just discussed, this result, however, should hold for rather concentrated solutions, well above $C^*$.

## IV. Conclusions

We have discussed the swelling properties of polymeric gels. The basic assumption was that percolation should provide an adequate model for the gelation process. Depending on the system, either critical or classical exponents should be valid. For small polyfunctional monomers or for vulcanization of a rather dilute linear polymer solution ($C \gtrsim C^*$), the critical domain should be rather wide. In the opposite limit of vulcanization of a melt the classical domain only should be observable, and hyperscaling breaks down. Because of this, the swelling is not described by exactly the same process in both cases.

(1) In the critical case, swelling is affine down to distance scales of the order of the mesh size $\xi$. We find the swelling ratio $Q = (V_f/V_i)$ of the final-to-initial volumes diverges as the distance $\epsilon = p - p_c$ to the gelation threshold goes to zero. Swelling in this case corresponds to the gradual disappearance of the screening of the interactions initially present in the reaction bath. This is shown, for instance, by the fractal dimension of the gel, which goes from 2.5 in the reaction bath to 2 in the swollen state. Within the Flory approximation, we find as a function of the gel fraction

$$Q = q^3 \sim G^{-3/2}$$

(2) Because hyperscaling breaks down in the classical case, there are several nodes per volume $\xi^3$ instead of one in the critical region. Thus swelling includes, in addition to the local swelling described above, the disinterpenetration of the different nodes. If $n$ is the number of nodes in a volume $\xi^3$, then after swelling is complete a single volume element is replaced by $n$ volume elements. Each of these has swollen as in (1). Here, because classical exponents are initially valid, the fractal dimension is 4 and goes to 2 in the swollen state, where the interactions are very important. As a result of this combination of two processes, we find that the swelling ratio $Q$ varies as a function of the ratio $q$ of the radii and the gel fraction

$$Q \sim (qG^{1/2})^8$$

rather than $Q \sim q^3$ in the critical "affine" case.

$Q$ may also be expressed in terms of the molecular weight $Z$ of the initial linear chains. We find

$$Q \sim Z^{4/5} \qquad (\epsilon > \epsilon^*)$$

independent of the extent of reaction as long as the distance $\epsilon$ to the threshold is larger than a crossover value $\epsilon^* \sim Z^{-1/3}$ separating the classical ($\epsilon > \epsilon^*$) from the critical ($\epsilon < \epsilon^*$) regimes.

A weakness in our discussion comes from the fact that we suppose, for vulcanization, that the exponents crossover abruptly from their classical to their critical values at $\epsilon = \epsilon^*$. We know that the crossover is in fact smooth and that one should define effective exponents around $\epsilon^*$. Because of this, we expect relation 30 to be valid only if one starts with a system synthesized at $\epsilon \gg \epsilon^*$. For intermediate values of $\epsilon$, effective exponents should be introduced and an $\epsilon$ dependence for $Q$ would result.

A second weakness is that we neglect trapped entanglements. We assume that their presence does not change the $\epsilon$ dependences. In other words, we assume that the probability for getting a trapped entanglement is not singular.

Our final conclusion concerns swelling of a dry gel. Let us consider a gel that has been first synthesized at a distance $\epsilon$ from the threshold, then swollen or washed out of the remaining sol, and finally dried, so that its concentration is of order unity. It is straightforward to calculate the swelling ratio for such gel: the final swollen state is the same as described in sections II and III above, depending on the type of gel we consider. This swelling ratio is simply the inverse of the ratio of the concentrations in the dry and swollen states

$$Q = \frac{V_s}{V_d} \simeq \frac{C_d}{C_s} \sim C_s^{-1}$$

where $V_s$, $V_d$, $C_s$, and $C_d$ are respectively the volumes and concentrations in the dry and swollen states, with $C_d \sim 1$ for the dry gel.

Using (1), (3), and (15), we get for the critical gel

$$Q \sim R_s \sim G^{-5/2} \sim N_w^{5/8}$$

whereas for a vulcanized gel synthesized at $\epsilon > \epsilon^*$ (so that mean field behavior is expected), we have, using (1), (3a), and (26)

$$\begin{aligned} Q &\sim R_s^3/N \sim (N/Z)^{1/2}Z^{4/5} \\ &\sim G^{-1}Z^{4/5} \\ &\sim N_w Z^{-1/5} \qquad (\epsilon > \epsilon^*) \end{aligned}$$

The latter result is generalized, for vulcanization of a semidilute solution, by replacing $Z$ with $(Z/g \sim ZC^{5/4})$, where $C$ is the concentration of the solution where vulcanization has been performed.

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