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Dynamical Critical Behavior during Chemical Gelation and Vulcanization

Walter Hess, Thomas A. Vilgis,* and H. Henning Winter†

Max-Planck-Institut für Polymerforschung, PO 3148, D-6500 Mainz, FRG.

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ABSTRACT: Critical behavior in gelation and vulcanization of polymers is discussed in the context of polymeric fractals. Dynamic mechanical measurements show that in the critical region a power law in the complex viscosity and in the modulus appears. Viscosity and modulus are calculated around the critical point and as functions of the extent of reaction. The power law is interpreted in terms of the fractal dimension of the cluster, and it is shown that this agrees with experiment if one takes swelling phenomena into account.

1. Introduction

A critical gel appears during a random linking process of subunits to larger and larger molecules. The critical gel divides two regimes—the liquid and the solid regime. No matter what type of objects are linked, they always exhibit a gel point if the system is disordered and if all processes are random.[1] At the critical point the system behaves neither as a liquid nor as a solid on any time and length scale: it is believed that it forms a critical object dominated by its large fluctuations in structure. These fluctuations complicate the description of the gel, and an exact solution seems to be impossible. Nevertheless, scaling theory provides a basis for modeling this special type of liquid–solid transition.

Several models for gelation have been proposed[1] and the most well-known are percolation theory[2] and an aggregation approach as reviewed by Herrmann.[3] The resulting cluster has one common feature in all these theoretical models: it is self-similar; i.e., its structure has no dominating length scale, there are holes on all scales, loops on all scales, etc. Consider, for example, the percolation model. Suppose a lattice where the initial bonds are not conducting, and place conducting bonds on the lattice until, at a certain bond concentration p_c, the system becomes conducting. This is then defined as the percolation threshold p_c, and the infinite cluster is formed.

Percolation can be generalized to predict mechanical properties such as shear modulus, viscosity, etc.[1-3] In the Flory–Stockmayer[4,5] theory, for instance, one has a fluid of small f-functional molecules. When they react and link up, the viscosity of the fluid increases until it diverges at the gel point, and a shear modulus is established. Then the solid is formed.

In this paper we discuss properties of end-linking polymers, i.e., flexible polymer chains with reactive end groups and cross-linking molecules. This process, usually called vulcanization,[6] can be treated in the same manner as gelation, with a few differences and exceptions. During the initial period of the reaction, cross-links and chains start to react and form clusters of average size $\bar{S}$, which can be defined[2] by a size distribution function n_s:

$$\bar{S} = \frac{\sum_s n_s s^2}{\sum_s n_s s} \qquad (1.1)$$

Here n_s depends on reaction time t, and a dynamical scaling theory can be applied in gelling and nongelling regimes (see for example ref 3 and references therein).

The typical cluster becomes larger and larger and properties like the viscosity diverge with the diverging cluster size. The linear size of the cluster diverges is given by

$$\xi \sim |p - p_c|^{-\nu} \qquad (1.2)$$

where p is the extent of reaction. Computer simulations in three dimensions predict $\nu = 0.88$ for percolation.[2,3] Other exponents can be defined in analogy to phase transitions (see ref 2). Here we are interested in the exponent for the zero-shear viscosity:

$$\eta_0 \sim (p_c - p)^{-k} \qquad p < p_c \qquad (1.3)$$

and for the static modulus

$$G_\infty \sim (p - p_c)^t \qquad p > p_c \qquad (1.4)$$

Well beyond the gel point, the network becomes strongly linked, i.e., most of the chains are linked together so that single connecting bonds or dangling ends are no longer critical. Then a homogeneous rubber will be formed, and classical theories of rubber elasticity can be applied. The modulus becomes purely entropic:[7,8]

$$G_\infty = NkT \qquad p \rightarrow 1 \qquad (1.5)$$

where N is the number of elastically effective chains and T the temperature.

The infinite cluster is an ill-linked object (compare Figure 5), and the large spatial fluctuations of structural elements will not allow prediction of the elasticity by classical rubber theories. However, the intermediate state between the liquid and the solid is dominated by the self-similar structure. This self-similarity is not only a feature at the gel point but is also present at earlier stages of the reaction at smaller scales. The size of the self-similar regions are measured by a correlation length ξ, which is again a typical cluster size.[1-3]

Consider now the pregel regime, $p < p_c$. For regions $r < \xi$ the system is self-similar within the clusters, while for $r > \xi$ one has a fluid of clusters. Crossover properties around ξ are not studied here in detail. In the postgel regime, $p > p_c$, one has the same situation, i.e., for $r > \xi$ one has already a rubber while for $r < \xi$ the system is still self-similar (compare Figure 5).

One purpose of this paper is to note that ξ can be related to the *dynamic mechanical* behavior, and we suggest this below. Moreover, dynamic mechanic experiments provide a direct method to determine p_c precisely, in contrast to measurements[9] of the static viscosity and shear modulus. Parameters of the fractal nature of the clusters enter into the frequency dependence of the viscosity and the modulus, and one can measure fractal dimensions, dynamical exponents, critical exponents, and swelling properties by this method. The main basis of the following treatment is the polymeric nature of the clusters, i.e., the clusters are made out of flexible chains, so that the cluster loses all its

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† Permanent address: University of Massachusetts, Department of Chemical Engineering, Amherst, MA 01003.

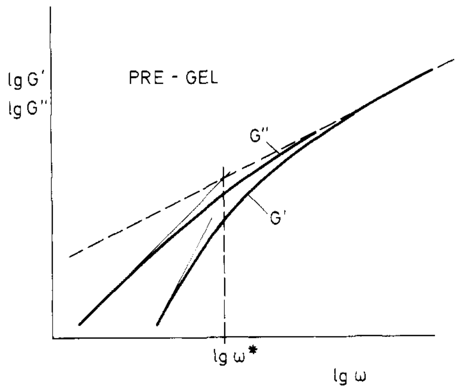

Figure 1. Schematic plot of the frequency dependence of the real and imaginary part of the dynamic modulus in the pregel state. Above the crossover frequency ω^* the typical behavior is a power law (here $\omega^{1/2}$ for a stochiometrically well-balanced system, dashed line), while below ω^* typical liquid behavior is present.

rigidity and behaves in a Brownian fashion.[10,11]

This paper is organized as follows: In section 2 we discuss the main experimental points. Section 3 provides a simple scaling approach to the problem, and a dynamic scaling argument for the frequency dependence of the modulus is given. Section 4 uses a more refined model to describe the viscoelastic properties before and after the gel point. Critical exponents of the zero-shear viscosity and static modulus are predicted, within the limitations of the model.

2. Experimental Motivation

Detection of the gel point by equilibrium quantities such as η_0 and G_∞ seem to be very difficult, since they are based on an extrapolartion $p \rightarrow p_c$. Precise criteria cannot be realized in these experiments. In a series of papers it has been shown[12-16] that dynamic mechanic measurements provide a technique for detecting the gel point precisely. The method has been described in detail in the above references, so we are brief here.

Imagine a polymer melt in which the chains have active groups at the ends. The chain length is below the critical molecular weight, and entanglements are not of importance. In addition, suppose that a cross-linker is added to the melt. This system can be characterized by rheological measurements, and one will obtain the usual liquid behavior at low frequencies, i.e., $G'(\omega) \approx \omega^2$ and $G''(\omega) \approx \omega$. G' and G'' are the real and imaginary part of the complex modulus. Thus one will find a dynamic mechanical behavior that is typical for polymeric fluids.[17]

Now initiate the reaction, and let some of the molecules link up; then stop the reaction at a time t_1 and repeat the rheological measurement. A power law is observed at higher frequencies, while at low frequencies one still has the classical liquid behavior. The crossover frequency ω^*_- separates the two regimes.

If the reaction goes on for some longer time $t_2 > t_1$, more and larger clusters will be formed, and one will still have the dynamic behavior shown schematically in Figure 1. However, the crossover frequency has been shifted to some lower value, and the G' and G'' curves move toward each other in the power law regime. Eventually there comes a point, at a reaction time t_c, where ω^*_- is shifted to zero, and the real part and imaginary parts of the complex modulus follow a power law over the entire range of frequencies:

$$G' \sim G'' \sim \omega^n \qquad (2.1)$$

The corresponding Figure 2 reduces to a straight line with

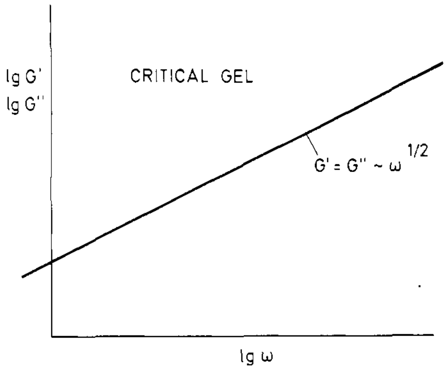

Figure 2. Same as in Figure 1, at the critical extent of reaction. The power law extends throughout the entire frequency range.

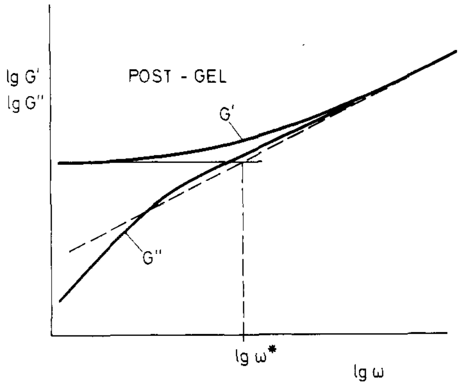

Figure 3. Gel above the gel point exhibiting typical solid behavior at low frequencies. At higher values than the crossover frequency one finds still a power law.

slope n on a log–log plot. For most networks, the rheological exponent n is equal to $^1/_2$, except for those with insufficient cross-linker content;[14] in the latter, larger values occur. An upper bound to the exponent in the dynamic mechanic experiment seems to be $^2/_3$, but more data must be analyzed to confirm these values. Clearly, the frequencies discussed here probe the dynamic behavior on the scale of the self-similar regions, rather than on the scale of a single polymer chain linked in the cluster. Beyond this gel point, at times $t > t_c$, typical solid behavior will be observed at low frequencies, indicated by $G' = G_\infty$ = constant and $G'' \approx \omega$. This is shown schematically in Figure 3. At later stages of the reaction the crossover frequency ω^*_+, separating gel from solid behavior, will be shifted to higher values, and G' and G'' will move apart from each other.

These experimental observations allow the hypothesis that one probes self-similar regions by varying frequencies.[18] There are two main reasons supporting this idea. First, the power law holds over all frequencies of observation. This above would not indicate a self-similar structure, since the Rouse theory also predicts a power law, but we cannot assume the gel to have a linear structure. Second, the crossover frequencies $\omega^*_\pm$ seem to depend on the extent of reaction p. Each frequency ω probes a length scale L. High frequencies correspond to small distances and vice versa. Thus there must be a relationship of the form

$$\omega \sim L^{-z} g(L/\xi) \qquad (2.2)$$

where z is some dynamical scaling exponent that we do not yet know, and g is a generally unknown scaling function. The crossover frequency now divides the power law behavior from the classical liquid or solid behavior. The corresponding length, the correlation length, is a typical

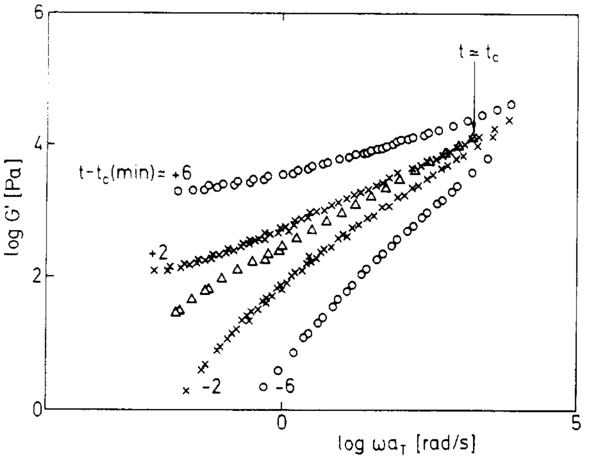

Figure 4. Experimental result.[12] t is the reaction time, before the cross-linking reaction is stopped by poisoning the catalyst. t_c is the gel time, corresponding to the critical extent of reaction p_c.

cluster size. Thus the crossover frequency obeys the scaling law

$$\omega^*_\pm \approx [1/\xi]^{z_\pm} \approx |p - p_c|^{\nu z_\pm} \qquad (2.3)$$

The crossover frequency therefore can be taken as a measure of the correlation length during the gelation process. As ξ diverges at the gel point, $\omega^*_\pm$ becomes zero and the power law for G' and G'' is obtained over the whole range of frequencies.

As an experimental example we show a plot of log G' and log G'' against log ω in Figure 4. We recall that the frequency range is chosen so that one probes only sizes larger than the distance between cross-links. This ensures that the *clusters* are "seen" by the experiment rather than the chains between the cross-links. The intuitive picture one gets is shown symbolically in Figure 5.

3. Polymeric Fractals and Simple Dynamical Scaling

The linkage process can probably be described by percolation, and Figure 5 may be most instructive, but in usual bond-percolation problems the bonds are rigid. Mechanical properties of such rigid percolating networks and fractals have been studied extensively,[19] but we cannot use these results because of the rigidity of the bonds and the non-Brownian nature of these systems. In our case, however, there is no rigidity in the object, and all bonds have to be replaced by long flexible chains.[10] As the simplest model for gelation and vulcanization we may adopt percolation, but bear in mind that the bonds are flexible. This is probably the simplest way to model the properties of the critical gel in the context of the experiments sketched above. The infinite cluster is believed to be a self-similar object since all structural elements, i.e., single connecting bonds, loops, dangling ends, etc., are critical quantities. Their numbers diverge at p_c, so that they appear on all scales of observation.[20] With the replacement of rigid bonds by flexible chains, percolation can be used to describe physical properties during vulcanization, as has been demonstrated previously.[10,18] The main ideas can be summarized as follows.

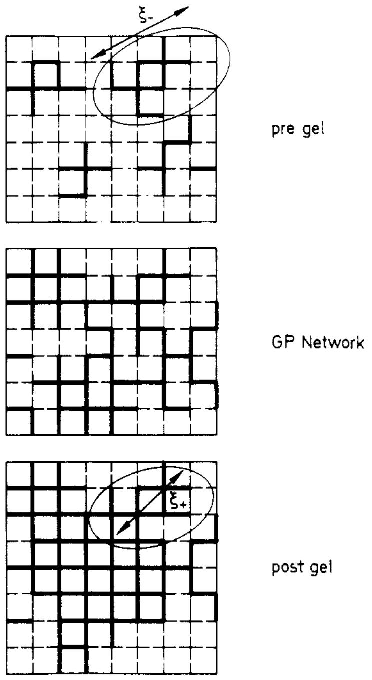

Figure 5. Typical result of bond percolation (schematic). Above the gel point one has only finite clusters, of some typical size ξ. The clusters are supposed to be self-similar on their scale of extension. At the critical point the cluster extents to the whole lattice. Above the gel point the size of the self-similar regions is decreasing again, and the lattice tends to be filled out completely, corresponding to a well-linked network.

First consider phantom chains. Replacement of the rigid bonds by phantom chains does not change the connectivity of the fractal[10] (hence additional contacts between the chains are considered to be fictive), while the size of the object and the dynamical properties are affected drastically. This should be discussed at least in terms of the three basic fractal dimensions.[21] The size of the original fractal (on a lattice) is defined by the fractal or Hausdorff dimension[22] d_{fo} via the mass–radius scaling $m \sim R^{d_{\mathrm{fo}}}$. The index o corresponds to the original fractal, i.e., with rigid bonds.[10] The dynamic properties can be studied via fracton dynamics[21] or equivalently by a random walker placed on the fractal. The latter possibility suggests a scaling law for the root mean square displacement R of the random walker in a time t on the fractal, $R^{d_{\mathrm{wo}}} \sim t$. The case $d_{\mathrm{wo}} = 2$ corresponds to classical Einstein diffusion. R is measured in Euclidian distances. $d_{\mathrm{wo}} > 2$ is usually called slow anomalous diffusion. (Hence in most cases one has from dynamical scaling $z = d_{\mathrm{w}}$.) The density of states is then given by the fracton or spectral dimension d_{s}:

$$d_{\mathrm{s}} = 2d_{\mathrm{fo}}/d_{\mathrm{wo}} \qquad (3.1)$$

d_{s} is an intrinsic parameter of the fractal and is fully determined by the connectivity of the object.[20] By replacing the rigid bonds by flexible chains the connectivity (and so d_{s}) remains unchanged: d_{s} is invariant by this procedure.[10] On the other hand, fractal and walk dimensions are altered to different values d_{f} and d_{w}. Using the "Einstein relation" that connects the fractal-, walk-, and resistivity scaling exponent, one can show[10,23] that for phantom polymers, i.e., for polymers with no exluded volume, d_{w} can be written as $d_{\mathrm{w}} = d_{\mathrm{f}} + 2$, since the resistivity scaling exponent is $\tilde{\zeta} = 2$ for phantom polymers. This special Einstein relation is obvious for a treelike structure (see also ref 32), but it holds also for structures containing loops, as clearly explained by Cates.[10] The reason for this is the phantom nature of the chains so that one can take the analogy between the resistivity, the phantom network, and a network of thermal springs. Thus one can calculate the new fractal dimension d_{f} by the general relation (3.1) to get

$$d_{\mathrm{f}} = \frac{2d_{\mathrm{s}}}{2 - d_{\mathrm{s}}} \qquad (3.2)$$

This is now the fractal dimension of the *ideal polymeric fractal* (i.e., with no excluded volume) with *Gaussian chains* and a connectivity parameter d_s.[10] Hence for d_s = 1 the results for linear chains are correctly reproduced, as they must be. In the percolation problem one has $d_s = {}^4/_3$ independent of the spatial dimensions according to the Alexander/Orbach conjecture. Since $d_s = {}^4/_3$ is the mean-field value for the spectral dimension of all branched objects (lattice animals, Cayley treelike structures, etc.), we use this value for further discussions. Inserting ${}^4/_3$ in (3.2) one obtains $d_f = 4$ in agreement with the Flory-Stockmayer theory[4,5] for Gaussian chains. In three dimensions d_f is larger then the space dimension, and so it is unphysical since the object cannot be packed more densely than the Euclidian dimension. This is clearly due to the phantom nature of the polymer chains; self-interactions, which alter the size of the fractal, should be taken into account.

The fractal dimension in (3.2) is indeed of the same relevance as the phantom fractal dimension of Gaussian chains, and we can use mean-field arguments for the fractal dimension for the same fractal, but now taking excluded volume forces into account.[10]

The crudest treatment in this direction goes back to Flory.[4] The free energy of the object with self-interaction can be written[6] as a sum of two terms:

$$F = (R/R_0)^2 + \upsilon M^2/R^d \tag{3.3}$$

The first term is the elastic or entropic part of the free energy, $R_0^{d_f} \sim M$ is the size of the ideal phantom fractal without excluded volume, and M is the total mass. For correct use of the Flory theory of swelling, R_0 has to be the size of the ideal phantom fractal, given by (3.2). The second term is the mean-field approximation of the excluded volume interaction[4,6] υ is the excluded-volume parameter, and d is the Euclidian dimension of the embedding space. Minimizing the free energy with respect to R, one obtains[6,10] the swollen fractal dimension:

$$D_f = \frac{d_s(d+2)}{d_s+2} \tag{3.4}$$

which gives

$$D_f = 2 \tag{3.5}$$

for $d_s = {}^4/_3$ and three dimensions. This is now the size of the fractal in a solvent. This result should hold in the reacting system even near the gelation threshold p_c, where most properties are controlled by the largest cluster. The size of the largest cluster is diverging, whereas that of finite clusters goes to zero. Thus we may conclude that swelling is due to remaining unreacted chains and smaller clusters. One can show that polymeric fractals in three dimensions are always swollen[24] since the upper critical dimension is that for branched polymers.[6] Even in a melt of clusters, excluded-volume forces remain important,[24] in contrast to linear chains,[25] where the upper critical dimension is 2. Within the framework of the Flory approach one can show that the result $D_f = 2$ is valid as long as the solvent objects do not approach the size of the "infinite" cluster.[6,24,25] Thus one can conclude that (3.5) holds even in the reacting system.[31]

Swelling is due to solvent around the big cluster. The solvent consists of unreacted molecules and of smaller clusters in the experiment described above. This implies that the excluded-volume forces are screened on smaller scales (given by the size of the unreacted chains and the smaller "finite" clusters) but not on scales involving larger parts of the infinite cluster as a typical solvent cluster. Screening of excluded-volume forces on the level of distances between two cross-links is ensured by the presence of unreacted chains and smaller (finite) clusters.

To get a first crude estimate of the frequency dependence of the modulus, we put forward a simple dynamical scaling argument.[26] The modulus of an entropic or Brownian system can be written from dimensional analysis $G \sim kT/V$, where V is the volume and kT the thermal energy. Here V is a fractal volume, $V = \xi^{d_f}$, where ξ is roughly the size of the cluster. The dynamical scaling hypothesis uses the fact that there is only one time in the system, and this is again given by a random walker on the fractal. Consider ideal phantom fractals first. The time t in which the walker explores distances of order ξ is then $t \sim 1/\omega \sim \xi^{d_w}$. Using the expression for d_w for the ideal polymeric phantom fractal, we would find for the frequency dependence of the modulus $G(\omega) \sim \omega^{d_f/(d_f+2)} = \omega^{d_s/2}$, giving the exponents ${}^1/_2$ and ${}^2/_3$ for ideal linear and branched polymers, respectively. These results are in agreement with previous theories.[6,10,11]

In our case we have to consider swollen clusters, as mentioned previously in the paper. Right at the gel transition we assume that the mechanical behavior is dominated by the infinite cluster, since the number of finite clusters is vanishing according to percolation theory.[1,2] Finite clusters and unreacted chains act as swelling agents for the infinite cluster. Therefore, we have to expect a different scaling behavior of the frequency dependence of the modulus. The problem of dynamics including excluded-volume forces is generally unsolved, even for linear chains,[28] and one has to rely on approximate solutions or on crude scaling arguments. To do so, let us take the big cluster to be swollen. The modulus then becomes $G \sim \Delta/\xi^{D_f}$. Hence, D_f is the swollen fractal dimension. To get an estimate for the tiime involved in the system, we assume a scaling relation $\xi^{\hat{z}} \sim t$, where $\hat{z}$ is a scaling exponent for the swollen fractal. At p_c the cluster extends throughout the entire sample. One can get an estimate for the exponent $\hat{z}$ by considering the time for a perturbation starting at one side to arrive at the other side. For a crude approximation we remember that excluded-volume interactions are screened on a length scale of the order of the distance between cross-links and larger but not as large as the biggest cluster itself. If we now model the bonds by long screened chains, i.e., the same as in an ordinary three-dimensional melt of linear chains, and if we assume that the perturbation propagates by a random walk on the connected cluster of screened chains, we estimate $\hat{z} = D_f + 2$. According to the dynamic scaling hypothesis we find

$$G(\omega) \sim \omega^{D_f/(D_f+2)} \tag{3.6}$$

which gives[27] with the swollen fractal dimension, eq 3.5, $G(\omega) \sim \omega^{1/2}$. We will see below how one can justify this very crude scaling argument for the frequency dependence of the modulus by a more advanced model, as also suggested in ref 10. The result (eq 3.6) has been obtained[10,11] by a generalized Rouse theory for these fractals. We summarize the basic equations for later use.

The aim is to calculate the dynamic viscosity and modulus of the gel during various stages of the gelation process. The rheological properties can be derived from an equation of motion of the object[10,11] if all internal modes are known approximately. Because of its polymeric nature, the cluster is dominated by Brownian motion, and one can proceed in close analogy with linear chains. Because of excluded-volume forces the problem cannot be solved exactly, and one may use a crude way of modeling the effect of short-range interactions by using effective powers that do not contradict the Flory result.[10]

Let us first take the ideal Brownian fractal. In analogy to the linear chain, one introduces variables $\mathbf{R}(s)$, where s is defined[10] on the entire fractal with its connectivity d_s. Because of the Brownian nature, one expects an equation of motion of the same type as the Rouse equation for linear chains.[28] The result for the dynamic viscosity is then[10]

$$\eta^*(\omega) \sim \sum_{q>q_0} \frac{1}{i\omega + q^2} \tag{3.7}$$

and the modulus is

$$G^*(\omega) = i\omega\eta^*(\omega) \tag{3.8}$$

q_0 is a lower cutoff due to the largest size L in the system, and it has been shown[10] that $q_0 \sim L^{-d_w/2}$. In contrast to linear chains, for the polymeric fractal one extends the meaning of s to some variable space of d_s dimensions to take the higher dimensional connectivity into account. Then the values of $\mathbf{q}$ are no longer one-dimensional quantities, they are defined as d_s-dimensional vectors. Replacing the sum by an integral (by introducing the density of states according to Alexander and Orbach[21]) we get

$$\sum_{q>q_0} \ldots \rightarrow \int_{q>q_0} \mathrm{d}^{d_s}q \ldots = \int_{q_0} \mathrm{d}q\ q^{d_s-1} \ldots \tag{3.9}$$

There will later be an upper cutoff as well. This upper cutoff is defined by the minimum length where the fractal is no longer self-similar, i.e., at a length scale of the order of the bond length, which here means a few times the distance between cross-links. Below this length l one has still self-similarity—that of a Gaussian chain—accidentally with the same *fractal* dimension but of different *spectral* dimension. One can expect interesting crossover behavior, and this will reported elsewhere. The dynamic viscosity of the ideal fractal is then

$$\eta^*(\omega) \sim \int_{q_0} \mathrm{d}q \frac{q^{d_s-1}}{i\omega + q^2} \tag{3.10}$$

The appearance of q^2 in the viscosity is due to nearest-neighbor interactions, suggesting that there is no further interaction than that of the connected chains.

In the presence of excluded-volume forces the q^2 dependence may be altered in a similar way as for linear chains.[10] There is no exact solution,[28] but one can model the dynamics by a quasi-particle approximation, i.e.

$$\eta^*(\omega) \sim \int_{q_0} \mathrm{d}q \frac{q^{d_s-1}}{i\omega + q^\alpha} \tag{3.11}$$

Here $\alpha = 2$ corresponds to the ideal limit, and α is connected with the fractal dimensions via $D_f = 2d_s/(\alpha - d_s)$ (compare with (3.2)). With the crude Flory argument (3.4)

$$D_f = \frac{2d_s}{\alpha - d_s} \equiv \frac{d_s(d+2)}{d_s + 2} \tag{3.12}$$

giving

$$\alpha = d_s + \frac{2(d_s + 2)}{d + 2} \tag{3.13}$$

which predicts $\alpha = {}^8/_3$ in three dimensions, accidentally the value of 2 times d_s. Thus one immediately recovers for the viscosity the scaling form by taking all modes into account:

$$\eta^*(\omega) \sim \omega^{-2/(D_f+2)} = \omega^{-1/2} \tag{3.14}$$

and for the modulus

$$G^*(\omega) \sim \omega^{D_f/(D_f+2)} = \omega^{1/2} \tag{3.15}$$

as we had earlier from our simple dynamic scaling arguments.

4. Rheological Properties during Gelation

Here we present a simple model for the rheological functions, suited to explain the experimentally observed features in a unified fashion, for the pregel regime, the gel point itself, and the postgel regime. The decisive assumption is that the largest wavelength of the relaxation spectrum is determined by the correlation length of the system. Far beyond the gel point, the length that matters is the distance between the cross-links. This is the rubbery regime. As one approaches the gel point from either side, the correlation length diverges.

Pregel State $p < p_c$. For the time-dependent relaxation modulus we write

$$G(t) = \int_{q_1}^{q_l} g(q)\ e^{-\nu(q)t} \tag{4.1}$$

where $\nu(q)$ is the relaxation frequency of the qth mode, q_l characterizes the largest mode, $q_l = 2\pi/l^{d_w/2}$, and l is the smallest distance on which the cluster is still self-similar. The smallest mode q_1 is related to the characteristic size of the cluster, $q_1 = 2\pi/L^{d_w/2}$, say. According to what was said before, L can be the typical size of the self-similar regions, $L \sim \xi$. Let us assume further that $g(q)$ and $\nu(q)$ are simple scaling functions, i.e.

$$\nu(q) = \nu_l(q/q_l)^\alpha \tag{4.2}$$

$$g(q) = (G_l/Z)(q/q_l)^{d_s-1} \tag{4.3}$$

Here ν_l is the frequency probing roughly a few times the distance between cross-links in the sample. Essentially this is (in terms of frequencies) a higher cutoff in our theory, because at some lower frequencies one probes the dynamics of a cross-linked chain. Also, $G_l = G(t{=}0)$ is the high-frequency modulus, Z is a normalization factor, and from eq 4.1 to 4.3 one finds

$$Z = \int_{q_1}^{q_l} (q/q_l)^{d_s-1} \frac{d_q}{q_l} = \frac{1}{d_s}[1 - (L/l)^{-d_s d_w/2}] \tag{4.4}$$

The scaling form makes sense only as long as $L \gg l$ holds, and therefore $Z = 1/d_s$.

Equation 4.1 then becomes

$$G(t) = d_s G_l \int_{(L/l)^{d_w/2}}^{1} \mathrm{d}x\ x^{d_s-1} \exp(-\nu_l x^\alpha t) \tag{4.5}$$

Despite $L \gg l$, it is not generally allowable to set the lower integration limit to zero, since the spectrum would then become singular at small frequencies, and it is this singularity that we must to treat in detail.

A well-known example for a spectrum like that of (4.5) is given by the Rouse model for monodisperse linear polymers, where one has $\alpha = 2$ and $d_s = 1$. It has been noticed[12] that the observed dynamic moduli could be described by the Rouse model, where the relaxation modulus

$$G(t) \sim t^{-1/2} \tag{4.6}$$

for $\nu_1^{-1} \ll t \ll \nu_l^{-1}$ is in agreement with the experimental findings. But obviously the structure of a cross-linking system cannot be identified with a monodisperse system of linear chains corresponding to the Rouse model, and of course the parameter combination $d_s = 1$ and $\alpha = 2$ is not the only choice that may lead to the observed power law in $G(t)$. Indeed, any combination with

$$\alpha = 2d_s \tag{4.7}$$

leads to a $t^{-1/2}$ scaling law for the relaxation modulus.

In the last section, we saw that for a model of a percolation cluster dissolved in a bath of smaller clusters and unreacted chains, where the spectral dimension is $d_s = {}^4/_3$, the exponent α becomes by swelling ${}^8/_3$ in accord with condition 4.7. We proceed now to work with the complex viscosity, i.e., the Fourier transform of $G(t)$, instead of the modulus directly, simply because experiments are performed (by a rheometer) as functions of the frequency. From eq 4.5 one finds for the dynamic viscosity

$$\eta^*(\omega) = d_s G_l \int_{(L/l)^{d_w/2}}^{1} \mathrm{d}x\ x^{d_s-1} \frac{1}{i\omega + \nu_l x^\alpha} \tag{4.8}$$

The macroscopic steady-flow shear viscosity is obtained as

$$\eta_0 = \int_0^\infty \mathrm{d}t\ G(t) = \eta^*(0) = (G_l/\nu_l)\frac{d_s}{\alpha - d_s}(L/l)^{d_w(\alpha-d_s)/2} \tag{4.9}$$

Close to the gel point, when L becomes very large ($\sim\xi$), we have $\eta_0 \sim \xi^{(\alpha-d_s)dw/2}$. Since $\xi \sim |p - p_c|^{-\nu}$, our approach predicts a divergence for the static viscosity at the gel point:

$$\eta_0 \sim |p - p_c|^{-\nu d_w(\alpha-d_s)/2} \tag{4.10}$$

If we take ν from percolation theory (it is not clear if one can do that, but let us suppose this might be the ν that appears), we get $\eta_0 \sim |p - p_c|^{-k}$, with $k \approx 1.7$. This has to be compared to the experimental values reviewed in Stauffer et al.[9] For frequencies $\nu_1 \ll \omega \ll \nu_l$, the dynamic viscosity is

$$\eta^*(\omega) = \frac{\pi}{\alpha \sin(\pi d_s/2\alpha)}[\sin(\pi d_s/2\alpha) + i\cos(\pi d_s/2\alpha)] d_s G_l \nu_l^{-d_s/\alpha} \omega^{(-d_s/\alpha)-1} \tag{4.11}$$

Thus we find in the power law regime

$$|\eta^*(\omega)| = aS\omega^{(d_s/\alpha)-1} \tag{4.12}$$

The prefactors are given by

$$a = \frac{\pi}{\Gamma(d_s/\alpha)\sin(\pi d_s/\alpha)} \tag{4.13}$$

$$S = d_s/\alpha\Gamma(d_s/\alpha)G_l\nu_l^{-d_s/\alpha} \tag{4.14}$$

The coefficient is independent of the extent of reaction, which influences only the low-frequency behavior.

The coefficient S is chosen so that, following Winter, it characterizes the strength of the corresponding power law of the relaxation modulus:[12-16]

$$G(t) = St^{d_s/\alpha} \tag{4.15}$$

in the appropriate frequency range.

A characteristic relaxation time $\lambda(p)$ can been defined. It is the inverse of the frequency where the intersect of the power law (4.12) meets the low-frequency asymptote η_0, i.e.

$$\eta_0 = aS\lambda(p)^{1-(d_s/\alpha)} \tag{4.16}$$

which yields for $p < p_c$

$$\lambda(p) = (\eta_0/aS)^{\alpha/(\alpha-d_s)} \tag{4.16a}$$

Figure 6 shows a plot of η^* normalized by η_0, as a function of the reduced frequency $\omega\lambda(p)$. The parameters are $d_s = {}^4/_3$ and $\alpha = {}^8/_3$. The ratio L/l was chosen to be 100. Higher values of L/l change the curves only in the high-frequency regime near ν_l. The corresponding Rouse limit $d_s = 1$ and $\alpha = 2$ agrees completely in the entire frequency range. Thus on the basis of the master curve in the representation of the reduced values of the viscosity and frequency, one cannot distinguish between the different cases of linear Rouse chains and a polymeric fractal. Recall the crudeness of the dynamics argument in section 3 when just fractal dimensions were fit to the Flory theory.

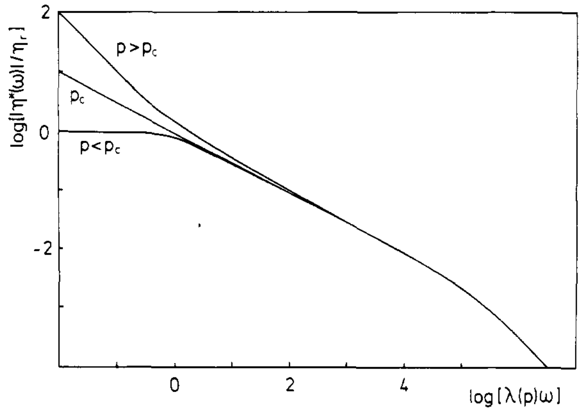

Figure 6. Frequency dependence of the dynamic viscosity as given by eq 4.8 for $p < p_c$ and eq 4.20 for $p > p_c$ in rescaled units. The ratio L/l was chosen to be 100; the spectral dimension d_s is ${}^4/_3$.

On the other hand, cluster size, zero shear viscosity, and characteristic frequencies depend on the actual structure of the system.

At the Gel Point $p = p_c$. If now the cross-linking reaction proceeds, the typical cluster size becomes larger and larger. As a consequence, the lowest frequency in the system tends to zero as the cluster size diverges. The number of relaxation modes therefore increases continuously. Finally at the gel point the correlation length ξ becomes infinite (this means that ξ extents to the sample size), and the smallest frequency ν_1 is essentially zero: the mode characterized by the wavelength ξ freezes in. Physically this makes sense, since this mode describes the rotational diffusion of the cluster as a whole. At the gel point the percolation cluster reaches from one wall of the sample to the other, and such rotation becomes impossible.

Equation 4.10 shows that at the gel point the viscosity diverges as

$$\eta_0 = L^{d_w(\alpha-d_s)/2} \sim |p - p_c|^{-\nu d_w(\alpha-d_s)/2} \tag{4.17}$$

and the characteristic frequency as

$$\lambda(p) \sim \xi^{\alpha d_w/2} \tag{4.18}$$

In the three-dimensional case we now find at the gel point, where the power law is extended to the entire frequency range

$$|\eta^*(\omega)| = (\pi/2)G_l\nu_l^{-1/2}\omega^{-1/2} \tag{4.19}$$

Postgel Regime $p > p_c$. At the gel point only the longest wavelength freezes in, and rotational degrees of freedom cease. Torsional motions are still possible within the cluster. They take place on all length and time scales. As the cross-link reaction proceeds, more and more strands of the cluster link up and connect to the boundary of the sample, and more parts of the cluster become immobile. Of course, the chains between cross-links are still in Brownian motion, but we are interested in the modes on the fractal and not the internal modes of the bonds. Thus the longest wavelength (the largest self-similar part of the cluster) will decrease, and the corresponding modes will successively freeze in. The spectrum thus splits into two parts: frozen-in modes and modes still available for Brownian motion and relaxation of the cluster.

This separation is given by a wavenumber $q_1 = 2\pi/L^{d_w/2}$, where L is again assumed to be of the order of the correlation length. Then we write for the dynamic modulus

$$G(t) = G_\infty + G(t) = G_\infty + d_s \Delta G \int_{(L/l)^{d_w/2}}^{1} \mathrm{d}x \; x^{d_s - 1} \exp(-\nu_l x^\alpha t) \quad (4.20)$$

where $\Delta G = G_0 - G_\infty$, and $G_\infty = \lim_{t\to\infty} G(t)$ is the equilibrium shear modulus, defined here as

$$G_\infty = \int_0^{q_1} g(q) \quad (4.21)$$

where the integral covers all frozen-in modes. Close to the gel point we expect that the spectral density of the frozen-in modes is still the same as at p_c, thus

$$g(q) \sim q^{d_s - 1}, \quad d_s = 4/3 \quad (4.22)$$

$$G_\infty \sim \int_0^{2\pi/\xi^{d_w/2}} \mathrm{d}q \; q^{d_s - 1} \quad (4.23)$$

which yields the prediction

$$G_\infty \sim |p - p_c|^{1.18} \quad (4.24)$$

if we take ν to be that of percolation. The complex viscosity from (4.20) is

$$\eta^*(\omega) = \frac{G_\infty}{i\omega} + G(\omega) = \frac{G_\infty}{i\omega} + d_s G_l \int_{(L/l)^{d_w/2}}^{1} \mathrm{d}x \; x^{d_s - 1} \frac{1}{i\omega + \nu_l x^\alpha} \quad (4.25)$$

For small frequencies we find now elastic behavior, $\eta^*(\omega) \sim G_\infty/i\omega$, or

$$|\eta^*(\omega)| = G_\infty/\omega \quad (4.26)$$

In the intermediate frequency range, $\nu_1 \ll \omega \ll \nu_l$, we obtain the same power law as in the pregel state:

$$|\eta^*(\omega)| = aS\omega^{(d_s/\alpha) - 1} \quad (4.27)$$

and S would be

$$S = (d_s/\alpha)\Gamma(d_s/\alpha)\Delta G \nu_l^{-d_s/\alpha} \quad (4.28)$$

The characteristic relaxation time, defined in a similar way as in the pregel, is now given by

$$\lambda(p) G_\infty = aS\lambda(p)^{\alpha/(\alpha - d_s)} \quad (4.29)$$

which yields

$$\lambda(p) = \left[\frac{aS}{G_\infty}\right]^{\alpha/d_s} = \left[\frac{\pi d_s/\alpha}{\sin(\pi d_s/\alpha)} \frac{G_l}{G_\infty}\right]^{\alpha/d_s} \nu_l^{-1} \quad (4.30)$$

According to eq 4.23 we would expect that λ diverges as one approaches p_c as

$$\lambda \sim |p - p_c|^{-\nu\alpha d_w/2} \quad (4.31)$$

which is symmetric around p_c, since it diverges in the same way as in the pregel case. This is clear, because the correlation exponent and the dynamic scaling exponent are the same below and above the transition in general; this was found in the electrical analogue proposed by de Gennes[6] and considered in ref 29 and 30. In Figure 6 we show the reduced quantities of η and ω for the postgel state with the same parameters as for the pregel state.

Summary

In this paper we considered the problem of gelation by polymeric fractals. In statics similar results are recovered as discussed previously.[31] The extension of the statics to dynamics predicts what is found in the experiments of Winter et al.[12-16] A very crude but simple dynamic scaling argument leads to the same frequency dependence predicted by Cates[10] and Muthukumar[11] by a generalized Rouse theory.

Using the internal modes of the whole fractal, one is able to predict the shape of the curves of the rheological quantities. They agree with experiment quite well, although the theory is very approximate. Modeling of swelling in the dynamics by a crude fitting of fractal dimensions seems to be adequate to describe the large-scale behavior.

The exponents calculated within the limits of this method are mean-field exponents, of course, but they may be treated as first approximations in this complicated excluded volume problem of the gelation cluster. That the magnitude of the exponent of the viscosity and modulus are the same is an artifact in three dimensions; generally this is not the case. The theory may also be applied to predict exponents in surface gelation or two-dimensional gelation.

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