Mechanical selfsimilarity of polymers during chemical gelation

T. A. Vilgis and H. H. Winter

Max-Planck-Institut für Polymerforschung, Mainz, F.R.G.
') Department of Chemical Engineering, University of Massachusetts, Amherst, U.S.A.

Abstract: Network polymers near their gel point exhibit selfsimilar mechanical behavior, as expressed by power law relaxations. The range of selfsimilarity is defined by two limiting length scales. The upper limit is the correlation length, defined by the linear size of the typical cluster, and a lower limit, roughly given by the size of one preformed linear chain, i.e., the mean distance between crosslinks. The correlation length increases with the approach to the gel point, and diverges at the critical extent of reaction, i.e., the gel point where the infinite cluster is formed. Above the gel point, it decreases again with further crosslinking. Dynamic mechanical measurements of the complex modulus at the gel point show a power law in the frequency dependence over the entire frequency range, monitoring selfsimilarity. Swelling effects reduce the fractal dimension of the percolation cluster form 2.5 to 2. It is shown how the power law $G(\omega) \sim \omega^{\nu}$, found by experiment, is connected to the structure of the polymeric cluster.

Key words: Chemical gelation, critical gel state, polymeric cluster, mechanical selfsimilarity.

Introduction

The gel point (GP) of a chemically crosslinked systems is defined as the instant at which the weight average molecular weight diverges to infinity (infinite sample size) or at which the largest molecular cluster extends across the sample (finite sample size). The crosslinking polymer at the GP undergoes a transition from liquid to solid state. This phenomenon is called chemical gelation [1]. It will be shown that in the range of observation, the transition through the GP occurs gradually and that a common limiting behavior exists for both the liquid and the solid near the GP. This limiting behavior is a property of the "critical gel" or the "polymer at GP". It should be noted that no independent state of matter exists directly at the GP. The polymer is either still before the GP (viscoelastic liquid) or it is already beyond the GP (viscoelastic solid). Thus at the GP the material is at its "viscoelastic liquid-solid transition".

This study is solely concerned with the rheological expression of chemical gelation, not including the effect of gelation on other properties of the polymer. The rheological behavior during gelation is very complex. However, it is well understood for the critical gel, where it is given by power law relaxation over a wide frequency range or, equivalently, over a wide time domain [2-5]. The critical gel state can, therefore, be used as a reference state for describing the evolution of rheology during gelation. This approach will be taken in the following.

Experimental observation of mechanical selfsimilarity

Dynamic mechanical experiments in small amplitude oscillatory shear have been performed to measure the relaxation behavior of endlinking polydimethylsiloxane and polyurethane. Experiments near the gel point are difficult to conduct, since any large strain (during sample preparation or transfer, during mechanical measurements) breaks the molecular structure irreversibly. For this reason, the sample in this

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study were prepared directly in the rheometer (no transfer) and any large strain was avoided during the mechanical measurements. Details of the sample preparation are given in Ref. [6]. A simple power law was found to govern the dynamic mechanical behavior of the critical gel, described by a complex modulus [4, 7]

$$G^*(\omega, p_c) = \alpha S (i\omega)^n$$ (1)

with

$$\alpha = \Gamma(1 - n) .$$

The "gel strength" $S$ depends on the mobility of the chain segments (depending on persistency length and crosslink density, for instance). $\Gamma(n)$ is the usual gamma function. The relaxation exponent $n$ may adopt values between 0 and 1. However, for stoichiometrically balanced gels the specific value $n = 1/2$ has been found.

The evolution of rheology can be observed continuously during the entire gelation process. Just before GP, the polymer is still a viscoelastic liquid. However, the approach of the critical gel state is already visible, depending on the frequency of the dynamic experiment. This is shown in Fig. 1, using the dynamic viscosity [8]

$$\eta^* = (G'^2 + G'^2)^{1/2}/\omega$$ (2)

as the representative rheological property. At high frequency (but below the high frequency glass transition), power law behavior is exhibited. The sample appears to be at the gel point in this frequency window. However, deviations from the power law behavior are seen as the frequency is lowered and the finite size of the largest cluster is recognizable. The low frequency behavior is still that of a typical viscoelastic liquid ($G' \sim \omega$, $G'' \sim \omega$ in the limit of $\omega \to 0$). We can define a characteristic frequency, $\omega^*$, by the intersect of the zero frequency viscosity

$$\eta_0 = \lim_{\omega \to 0} |\eta^*(\omega)|$$ (3)

with the power law of the critical gel. $\omega^*$ divides between the gel behavior and the liquid behavior. The value of $\omega^*$ decreases with the approach of GP.

In the post-gel region, $p > p_c$, the polymer exhibits a finite equilibrium modulus $g_\infty$. A characteristic frequency $\tilde{\omega}^*$, can be defined again, given by the intersect of $g_\infty/\omega$ with the power law of the critical gel. Typical dynamic viscosities are shown in Fig. 1. At frequencies above some crossover $\tilde{\omega}^*$, the sample exhibits gel behavior (power law) and at frequencies below it, the sample behaves like a typical viscoelastic solid ($G' = g_\infty, G'' = \omega$ at $\omega \to 0$). The value of the characteristic frequency increases with increasing extent of crosslinking.

In the evolution of viscoelastic properties, the most interesting part of the rheological behavior shifts to lower and lower frequencies as the transition through the gel point becomes imminent. The shift to lower frequencies is so pronounced that the actual transition through the gel point cannot be observed in an experiment, since the characteristic frequency has shifted below the lower limiting frequency of the rheometer. Only far beyond the GP in the post-gel region, does the characteristic frequency becomes large again and the solid behavior becomes measurable within the frequency range of our instrument.

Selfsimilarity seems to be the dominating property of the gel near the GP. Cates [9] and Muthukumar [10] showed that a material with a selfsimilar structure has dynamic mechanical properties which follow a power law. Vice versa, it might be concluded that the critical gel has a selfsimilar structure.
Frequency and scale of observation

As explained above, the mechanical experiment is sensitive to various frequency scales. However, there is the basic frequency-length relationship, in the sense that high frequency probes smaller length scales, and, vice versa (low frequency probes large length scales). This is normally ruled by a dispersion relation between the frequency of the experiment, $\omega$, relaxation time, $t$, and scale of observation, $L$

$$\frac{1}{\omega} \sim t \sim L^a.$$  \hspace{1cm} (4)

Small frequencies probe molecular times in connection with the whole polymer or even larger parts of the material (flow properties) while extremely high frequencies are sensitive to relaxation within one chain or even to local jumps of side groups, etc. ($\alpha$ is an exponent, specific to the model considered).

The power law behavior of the critical gel correlates to a length scale range. Beyond the fifty decades of power law, which were the entire experimental range [7], a lower frequency limit is expected to be given by the sample size and an upper frequency limit is given by the transition single chain behavior, i.e. if the frequency is large enough, length scales much smaller than selfsimilar regions are probed, e.g. finding the range of a single chain between two crosslinks. Power law behavior is found when $L$ has a value in the range between this lower and the upper boundaries of lengths in the material. This will be discussed in the following.

Selfsimilarity hypothesis

The experimentally observed characteristic frequency $\omega^*$ corresponds to a correlation length (apart from model specific constants)

$$\omega^* \sim \xi^{-\alpha}$$  \hspace{1cm} (5)

which is characteristic for the network structure. Relation (5) is quite general. The structure is hypothesized to be selfsimilar at scales below $\xi$, as supported by mechanical selfsimilarity (see Fig. 1, 2). Here we see that at higher frequencies the power law is already established, while at lower frequencies one still has ordinary liquid behavior. This supports the hypothesis given in Eq. (5). We will now give a brief description of a possible model. The critical gel is treated as a polymeric fractal, i.e. a selfsimilar object, in the spirit of Refs. [9, 10]. $\xi$ has to be identified by the size of the selfsimilar regions, i.e. the critical correlation length, as gelation is a critical phenomenon [1, 11], i.e. $\xi \sim |p - p_c|^{-\alpha}$. This implies $\omega^* \rightarrow 0$ if $p \rightarrow p_c$.

The evolution of $\xi$ with the extent of reaction is a direct expression of the evolution of the network structure. The final state, if most of the chains have reacted, is a rubber which is formed by a very large number of crosslinks and has a finite modulus $g_m$ for zero frequency. In this study we are not concerned about the short distance behavior which is probed only at extremely high frequencies far above the frequency window given here, but we are more interested in the large scale elasticity of a size larger than a single polymeric bond, i.e. a chain between two crosslinks or a dangling chain.

In the pre-gel state, we crosslink molecules into clusters which are weak solids of small spatial dimension. The size of the finite clusters can be obtained by light scattering after a crosslinking reaction has been stopped by poisoning the catalyst [7]. The cluster itself is an ill-linked piece of macromolecule, which can, according to Cates [9], be defined as a polymeric fractal, with a distribution of "defects" studied in the percolation problem [11, 12], such as loose ends, loops, and unreacted crosslink sites. With increased reaction time, one gets larger and larger clusters. Assuming there are large clusters in the melt of smaller clusters and uncrosslinked chains, the mechanical experiment is sensitive to the size of a typical cluster. At longer reaction times this size becomes larger and larger until it extends across the entire sample. The size of the typical cluster becomes infinite at the gel point where the critical gel is formed. There is strong evidence, as pointed out in the first section, that the network structure of the critical gel is selfsimilar and so only a very large length matters. Generally one calls such selfsimilar objects "fractals" [11, 12, 15]. The straight line in $G'(\omega)$, $G''(\omega)$ over all $\omega$ considered indicates that there is no dominant length scale in the problem, i.e. the correlation length is infinite and on each scale of observation a similar structure can be found.

The post gel state shows, for the first time, a finite equilibrium modulus $g_m$ indicating a certain amount of elastic active chains. The system is no longer selfsimilar at the whole size. The correlation length decreases again (see Fig. 1, $p > p_c$). Thus, we again have a power law at larger frequencies, measuring the correlation length, while at lower frequencies typical solid behavior is present. The interpretation is very simple: as more and more chains are linked, one loses the "fractal information" of the infinite cluster, and highly
cross-linked regions appear with a characteristic length equal to the distance between two crosslinks.

This can be summarized intuitively in Fig. 2, which suggests a close analogy with the percolation problem [1,11–13]. We want to examine the percolation idea in more detail. The rigid bonds on the lattice have to be replaced by flexible polymer chains [9]. This is the main difference from the application of the usual percolation problem [14].

Modelling of mechanical behavior near the gel transition

1. Polymer at the gel point (critical gel)

Directly at the percolation threshold, when the power law in $G$ and $G'$ is observed, no length scale matters, in contrast to the regimes $t < t_{pol}$, where the size of the typical cluster is the characteristic length scale and $t > t_{pol}$ where the size of the weakly linked

regions dominate. The structure is believed to be self-similar (fractal), which means that the same properties are found at each length scale, and a power law for the mass-size scaling exists [15], $m \sim R^{d_{f}}$, where $d_{f}$ defines the fractal dimension of the object. Looking at the very intuitive picture in Fig. 3b we see that there can be loops within loops on all scales as well as single connecting bonds [12] and the structure is, on average, self-similar on every scale of observation. The elasticity of such rigid networks, i.e., where the bonds are considered to be rigid, has been studied recently by Bergman [16] and Webman and Kantor [17] but we applied their results for describing the critical gel, because they assumed that the bonds were rigid.

In our case there is no rigidity in the object, since the bonds are highly flexible Gaussian chains. This affects the properties of the system and in general we can expect a different fractal dimension $d_{f}$. This problem was solved by Cates [9].

The spectral dimension $d_{w}$, introduced by Alexander and Orbach [18], is an intrinsic exponent and is only sensitive to the connectivity of the fractal. It is defined via the density of states of excitations (fractions), $N$, which scales like $N(\omega) \sim \omega^{d_{f}-1}$ in close analogy to the usual scaling of $N$ in $d$ Euclidian dimensions where $d_{s} = d_{f} = d$.

The relation (Alexander/Orbach relation) between the three basic fractal exponents [18] is $d_{s} = 2d_{f}/d_{w}$.

The physical meaning of $d_{w}$ is as follows: Suppose there is a random walker on the fractal. Measuring the mean displacement of the random walker, $R_{s}$, as a function of time $t$, it is found to be $R_{s} \sim t^{d_{w}}$; hence, $d_{w} = 2$ gives the Einstein result for classical diffusion. For $d_{w}$ greater than 2, one obtains slow anomalous diffusion. In general the exponent $d_{w}$ can be expressed as [9]:

$$d_{w} = d_{f} + \zeta$$  \hspace{1cm} (6)

where $\zeta$ is the resistance scaling exponent on the fractal. If we now replace the bonds of the arbitrary “lattice” fractal by flexible chains, the spectral dimension is not changed because it is only determined by connectivity, which remains constant.

Combining Eq. (6) and the Alexander/Orbach relation, the new $d_{f}$ of the polymeric fractal is $d_{f} = \frac{\zeta}{2 - d_{s}}$ [9]. In ideal phantom polymer chains, it can be shown that for the polymeric case $\zeta = 2$, the final answer is [9]

$$d_{f} = \frac{2d_{s}}{2 - d_{s}}.$$  \hspace{1cm} (7)
In a polymer chain itself, when all the segments are replaced by polymer chains, we get a huge polymer chain and the new $d_f$ should be the same as the old one, which is true for $d_s = 1$, the spectral dimension of a linear polymer chain, so $d_f = 2$, as expected.

Since we are interested in the percolating network, the Alexander-Orbach conjecture [18] suggests $d_s = 4/3$ for all Euclidean dimensions $d$ (within an error of 2%). Thus we would obtain $d_f = 4$, which is meaningless since the largest value of $d_f$ is $d$ when all the material is closely packed. Nevertheless, this agrees with the result of the classical Flory-Stockmayer theory, i.e. the solution of the percolation problem in the mean field limit.

The conclusion is that Eq. (7) is of relevance if the chains are phantoms and excluded volume interaction, etc. has been neglected. The theory should be extended to allow for interactions of the polymeric fractal with itself and a Flory theory will provide a crude estimate [9,13,19]. This can be done by minimizing the free energy

$$ F = \left( \frac{R}{R_0} \right)^2 + v \frac{M^2}{R^d} $$

(8)

where $v$ is the excluded volume parameter, and $R_0 = M$. The first part of the free energy accounts for the elastic contribution, while the second term is the mean-field interaction energy [9,13]. $M$ is the total mass in the fractal. This defines a new fractal dimension of the self-interacting polymeric fractal [9]

$$ d_f = d_s \frac{d + 2}{d_s + 2} $$

(9)

Again, if we assume $d_s = 1$ for a self-interacting polymer chain, we recover the Flory result $d_f = 5/3$ in $d = 3$ [19].

If we now assume that the critical gel is a percolating network, we find for $d_s = 4/3$

$$ d_f = 2 $$

(10)

which is in agreement with the results for percolation clusters and lattice animals [20]. This result can be established since the critical gel is solved in a sea of smaller macromolecules, so that excluded volume forces are screened (at least) on a length scale of the chain itself, but not on the scale of the critical gel, so that the polymers remain within Gaussian statistics, but not the selfsimilar macromolecule.

The last point in this section concerns dynamics. In the measurements of Chambon and Winter [7], the dynamic modulus had the dependence $G(\omega) \sim (\omega \xi)^{1/2}$. This can be derived very simply by employing dynamic scaling [21] near $T_c$. In general, the modulus is given by $G \sim k_B T/V$, where $V$ is the volume of the system. This can generally be written as

$$ G \sim \frac{k_B T}{\xi^{d_f}} $$

(11)

According to the dynamic scaling hypothesis, there is only one time in the system given in terms of frequencies

$$ \omega \sim k^a g(k \xi) $$

(12)

$k$ is the corresponding wave vector in the system; $g(x)$ an unknown scaling function. Using $k = \xi^{-1}, d_w = d_f + 1, g(\xi) \propto \xi^{-1}$ and, since we have still ideal Gaussian chains, $x$ has to be equal to 2, giving

$$ G \sim \omega^{d_f/2} \sim \omega^2 $$

(13)

The value $d_f = 2$ has been found previously by Muthukumar and Winter [22] by comparing theory to experiment. They have not been able to explain the discrepancy with the fractal dimension of the percolation cluster ($\approx 2.5$). Here it is shown that $d_f = 2$ can be understood in terms of swelling, due to the reaction bath (see also [20]). Moreover, it enters directly into the scaling of the dynamic modulus and appears in the dynamic experiment, carried out in the reaction bath, too.

2. Pre-gel and post-gel state

A few remarks should be made about the pre-gel state. In the initial part of the experiment, we expect that chains are starting to link and small clusters of different size are formed. The reaction process might be a mixture of chemically limited and diffusion limited growth, as well as cluster-cluster growth. There is no simple way of predicting the cluster size distribution as a function of reaction time, but various approaches are described in the literature [23]. A scaling approach might be possible for describing the diffusion limited growth [24] and we refer the reader to the original literature.
The most important fact for us is that the correlation length is increasing with ongoing reaction. Thus the size of the selfsimilar regions is increasing. This explains why the power law in the modulus is already established below the critical extent of reaction, for higher frequencies probing shorter distances.

Not too far below \( t_{gel} \), one is left with larger clusters in the solution of smaller clusters and linear chains. If the clusters are interacting as fractals, one may apply the transparency and opacity argument [24] which states that the sum of fractal dimensions of the single clusters is larger than the space dimension; one can approximate the clusters by "hard" balls of a radius \( \xi \). The long-term behavior then becomes similar to that of a suspension of balls in a fluid. Here the clusters are always opaque, since \( 2D_f > d \), and \( D_f > 1.5 \) in all our situations. One may then think of a polydisperse melt of fractal microgels [25, 26].

The post-gel regime \( t > t_{gel} \) may be crudely represented by Fig. 2c, where the gel is already described by a rubber on some scale. The rubber is a well-linked polymer macromolecule. It is clear that the correlation length \( \xi = \left( \frac{1}{(p_c - p)} \right)^{\frac{1}{d}} \), \( (p > p_c) \), decreases for values of \( p > p_c \) while the structure leaves selfsimilarity and tends to a "lattice structure", as represented in Fig. 2c. Clearly, in the crosslinked rubber no lattice exists, but this will be equivalent to a well-linked gel. If more and more crosslinks are added, the zero frequency shear modulus will become proportional to the number of crosslinks (if all react and no wasted loops are formed [27]).

Conclusions

This paper supports the idea of mechanical selfsimilarity, as proposed earlier [2, 22]. The most striking result of the experiment is that it is sensitive to the structure of the material and the result is that right at the percolation threshold, the dynamic modulus exhibits a power law \( G(\omega) \sim \omega^{1/2} \) over the entire frequency range. The question is whether this result can be justified by structural properties of the resulting gel.

We have found from mechanical experiments that the structure is dominated by the polymeric nature of the network, as proposed by Cates [9]. If we assume percolation as the process for the formation of the GP network, the fractal dimension of the network is \( D_f = 4 \), if the excluded volume is neglected. This \( D_f \) value is far too high, since the material cannot packed more densely than the space. Thus the upper limit for the fractal dimension is the Euclidian dimension \( d \).

A more realistic picture is provided if self interactions of the polymeric fractal are taken into account. Swelling of the fractal gives a decreased fractal dimension, as in the case of single polymer chains, where the Gaussian chain has a fractal dimension of 2, while \( d_f \) of a swollen chain is approximately 5/3.

The swelling in our case is much more complicated. Since we have the huge network as a fractal itself, excluded volume is important. On the other hand, at the gel point only a small amount of linear chains have reacted to form the fractal. The rest (a large amount) act as a solvent for the fractal. The solvent molecules are of least of the same length scale as the distance between crosslinks. There are only a few small clusters left close to the percolation threshold. From this assumption we expect that excluded volume interactions are screened on distances between the crosslinks, but are present on larger scales up to the size of the fractal (typically).

On the level of a Flory argument, this can be confirmed in the same way as Daoud and Family [25, 28] did in the case of a solution of a long polymer in small macromolecules, by using the free energy

\[
F = \left( \frac{R}{R_s} \right)^2 + v \frac{N^2}{R d} \frac{1}{N_s} \quad (14)
\]

where \( N \) is the mass of the fractal as before and \( N_s \) the mass of the solvent molecule. The appearance of \( N_s \) in the denominator of Eq. (14) is due to screening of the excluded volume forces in dense systems. As long as \( N_s \ll N \), the Flory argument in Eq. (9) holds.

However, if \( N_s \) is comparable to \( N \), then the interaction term changes to

\[
U = \frac{N}{R d} \quad (15)
\]

and a new fractal dimension occurs [26]

\[
D_f = (d + 2) \frac{d_s}{2} \quad (16)
\]

For linear chains (\( d_s = 1 \), this relation reduces to the fractal dimension of the true self avoiding walk in the mean field approximation [25, 29]. In our case, \( N_s \) is of the order of the distance between the crosslinks and larger, but not comparable to the infinite cluster.

The dynamic scaling argument in the gel regime seems to be general and is in full agreement with the
dynamic scaling hypothesis of de Gennes [13], see also [30].

The behavior below the gel point is more complicate-
ed than at the gel point itself. The approximations pre-
sented here are very crude and should be confirmed by
future experiments. There are various assumptions in
the model which require further clarification. The
most important one is the problem of entanglements as
a possible interaction between clusters. The presence
of entanglements might invalidate the transparency-
city argument and may cause changes in the
dynamics of the system and the thermodynamic prop-
erties. We assumed that entanglements are not a seri-
ous factor in samples with an initial molecular weight
below the critical one.

In the post gel regime, selfsimilarity decreases as the
correlation length decreases. Theory becomes extreme-
dly difficult for the polymer between the gel point
and the rubber. Most of the rubber is formed far above
the gel point, and rubber elasticity theory can be
applied.

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Authors' address:
T. A. Vilgis
Max-Planck-Institut für Polymerforschung
P. O. Box 3148
D-6500 Mainz, F.R.G.