Linear Viscoelasticity at the Gel Point of a Crosslinking PDMS with Imbalanced Stoichiometry

FRANCOIS CHAMBON and H. HENNING WINTER,*
University of Massachusetts, Department of Chemical Engineering and Department of Polymer Science and Engineering, Amherst, Massachusetts 01003, U.S.A.

Synopsis

The evolution of linear viscoelasticity during cross-linking of a stoichiometrically imbalanced polydimethylsiloxane (PDMS) was measured by small amplitude oscillatory shear. At the gel point (GP), stress relaxation was found to follow a power law, $S^{(n)}$, as described by the previously suggested gel equation. However, while stoichiometrically balanced gels (PDMS, polyurethanes) gave the specific exponent value of $n = 1/2$, a higher exponent value, $1/2 < n < 1$, was measured on a stoichiometrically imbalanced PDMS sample. Transformation of the data from the frequency to the time domain required the hypothesis that the power law behavior extends over the entire frequency range, $0 < \omega < \infty$. The imbalanced gel exhibited a higher loss than storage modulus, $G''(\omega) > G'(\omega)$, and a higher rate of stress relaxation. GP was found to occur before the crossover point of the loss and storage moduli, $G''(\omega, t)$, and $G'(\omega, t)$, as measured during the cross-linking reaction (reaction time, $t$) at constant frequency, $\omega$. This suggests new methods for localizing GP, for instance by the detection of a loss tangent independent of the frequency. All the experiments were performed with end-linking networks far above the glass transition temperature. The network junctions were assumed to be due to chemical cross-links only and not due to any other association phenomenon such as crystallization or phase separation.

INTRODUCTION

Cross-linking reactions are able to connect macromolecules into a tridimensional polymeric network. During the initial stages of the cross-linking process, branched molecules of widely distributed sizes and of various architectures are formed. Their average molecular weight increases with increasing extent of the cross-

*Author to whom correspondence should be sent.

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linking reaction, \( p \). The system reaches its gel point (GP) at a critical extent of reaction \( (p = p_c) \) at which either the weight-average molecular weight diverges to infinity (infinite sample size) or a first macromolecular cluster extends across the entire sample (finite sample size). Consequently, the system loses its solubility, the steady-shear viscosity diverges to infinity, and the equilibrium modulus starts to rise to a finite value. The newly formed macroscopic network structure starts to coexist with the remaining branched molecules which are not yet attached. Beyond GP, the network stiffness continues to increase steadily with increasing cross-link density until the system reaches completion of the chemical reaction.

This study is concerned with the linear viscoelasticity of model polymers for which gelation is caused by the end-linking reaction of primary chains in the absence of any other physical association, such as crystallization or phase separation. Experimental temperatures are kept far above the glass transition and physical entanglement effects are minimized by choosing a prepolymer molecular weight below the critical limit for entanglements. For such systems the linear viscoelastic behavior at GP is described by the gel equation:\(^1\)

\[
\tau(t) = S \int_{-\infty}^{t} (t - t')^{-1/2} \dot{\gamma}(t') \, dt',
\]

where \( \tau \) is the stress tensor and \( \dot{\gamma} \) is the rate of deformation tensor. The only material parameter is the strength of the network at GP, \( S \). Equation (1) describes the experimentally observed congruency of the loss and storage moduli\(^1\)\(^-\)\(^3\)

\[
G' = S \sqrt{\omega/2} \quad \omega^{1/2} = G'' \quad p = p_c
\]

and predicts a power law relaxation modulus

\[
G(t) = S t^{-1/2} \quad p = p_c
\]

In addition, it predicts an infinite steady-shear viscosity \( (\eta_s \to \infty) \) and a zero equilibrium modulus \( (G_e = 0) \) which are classical attributes of GP\(^4\).

Equation (1) was found to be valid for two cross-linking polymers, a PDMS\(^1\)\(^-\)\(^2\) and a polyurethane\(^3\) (PU), which differed generally in the chemistry of the cross-linking reaction and specifically in the functionality of the cross-linking points. The previous experiments were all performed on samples prepared at effectively
balanced stoichiometric ratio of the reactants.

In this study we repeated the earlier experiments\(^2\) on a PDMS sample, however, with imbalanced stoichiometry. Our objective was to find the range of validity of the gel equation and its possible limitations. The classical definition of GP\(^4\) (\(\eta_\infty \to \infty, G_\infty = 0\)) as well as its commonly accepted classification as a critical phenomenon\(^5-7\) suggest a unique rheological behavior for the gel state independent of the details of the molecular structure. However, it could be expected that the stoichiometric ratio of the reactants will affect the rheology at GP since it strongly influences the number of elastically effective chains and consequently the final properties of the network structure.

**DEFINITION OF BALANCED STOICHIOMETRY**

PDMS networks were prepared by the hydroolysis reaction of tetrakis(dimethylsiloxyl)silane and \(\alpha, \omega\) divinyl-terminated linear PDMS prepolymer in the presence of cis-dichlorobis(diethyl sulfide)-platinum (II) catalyst. The functionality of the crosslinker was measured by Si\(_{29}\) nuclear magnetic resonance (NMR) and was found to be 3.97, which is very close to the ideal value of 4. HNMR was used to determine the vinyl concentration of the prepolymer. It was found to be \(1.58 \times 10^{-4}\) mole vinyl/g PDMS with a precision of \(\pm 3\%\). The number-average molecular weight of the prepolymer was determined by gel permeation chromatography (GPC) and vapor pressure osmometry (VPO) and was found to be \(\bar{M}_n = 12,060\) and \(\bar{M}_n = 10,300\), respectively, with a polydispersity \(\bar{M}_w/\bar{M}_n = 2\). Given the accuracy of these measurements (\(\pm 20\%\)) this indicates a most probable functionality for the prepolymer close to but less than 2. Details of the components' characterization and of the sample preparation are reported elsewhere.\(^2,8\)

The stoichiometric ratio of the system, \(r\), is defined here as the ratio of silane to vinyl groups. For nonstoichiometric systems, most of the structural irregularities obtained at complete conversion of the least abundant functional groups are, in addition to the inner loops, dangling ends. Networks with such imperfections have a lower number of elastically active strands and therefore exhibit a lower modulus.\(^9\) Computer simulations\(^9\) of end-linked elastomers in bulk show that, even when loop formation is accounted for, the most perfect networks are always obtained at
balanced stoichiometry. However, it has often been observed that
the maximum elasticity of the final network does not occur at
balanced stoichiometry but instead at stoichiometric ratios
slightly higher than unity. Among the most credible explana-
tions which can account for such a discrepancy is the fact that
computer simulations fail to include side reactions leading to
an increased number of dangling ends, and reactants with imper-
fected functionality.

The stoichiometric ratio corresponding to the network with the
highest modulus, but not to chemical stoichiometry, has been
called effective stoichiometry, \( r_e \). This definition of stoichiometry
is adopted in the present study. In order to determine \( r_e \) for the
PDMS system, a set of networks with increasing silane concen-
tration was synthesized. The stoichiometric ratios were adjusted
using the results of the functional analysis. After mixing, the
liquid samples were transferred to the rheometer, a Rheometrics
Dynamic Mechanical Spectrometer. Reaction between the 25 mm
diameter parallel disks was allowed to take place overnight at
34°C followed by two additional hours at 130°C. A nitrogen atmo-
sphere was used for the first stage of the curing process. The
dynamic storage modulus, \( G' \), of the fully cured samples was
measured at low frequency, \( \omega_r = 0.5 \) rad/s, and small shear strain
amplitude, \( \gamma = 0.01 \). The frequency was chosen to be sufficiently
low to fall well within the terminal plateau region of the cross-
linked elastomers. As a result, the values of \( G' \) measured are close
to the equilibrium modulus of the networks and are directly rep-
resentative of their elasticity. Results of these measurements are
shown in Figure 1. It is important to mention that during the
measurement of such high moduli a significant error is intro-
duced by the compliance of the rheometer. This error was not corrected
here since only relative values were needed. The maximum of the
storage modulus is observed at \( r \) close to 1.3 instead of the ideal
value of 1; \( r_e \) for this system is therefore concluded to be 1.3. The
same definition of stoichiometry was utilized in our previous
reports. However, since accurate functional analysis data were
not available at that time it had been erroneously stated that
the PDMS sample with balanced stoichiometry was prepared
at \( r = 1 \). Instead, the composition of this sample was \( r = 1.3 \n(not accounting for the uncertainty in the above molecular
weight and functionality data), which is close to \( r_e \).
Fig. 1. Storage modulus, $G'$, of fully cured PDMS samples as a function of the stoichiometric ratio, $r$, at $T = 34^\circ$C and $\omega_o = 0.5$ rad/s.

According to Flory's theory of an ideal cross-linking process,$^4$ the PDMS system should reach the gel state for stoichiometric ratios ranging from $1/3 < r < 3$. Slightly higher values of $r$ are anticipated here to compensate for the nonideal behavior of the reaction. In order to investigate the effect of the stoichiometric ratio on the linear viscoelastic properties at GP, PDMS samples with $r = 0.91$ were synthesized. An intermediate value of $r$, well within the predicted range for gelation to occur, was chosen. However a system with $r < r_c$ was preferred since, as seen in Figure 1 and as predicted by computer simulations,$^{10}$ cross-linker deficiencies are more effective than cross-linker excesses in creating network imperfections. When compared with networks of balanced stoichiometry, systems with $r < r_c$ are therefore expected to exhibit more drastic changes in their rheological properties at intermediate states of network development (i.e., at GP) than systems with $r > r_c$. 
LINEAR VISCOELASTIC EXPERIMENTS

After preparation, the PDMS samples were transferred to the rheometer and reacted at 34°C using a nitrogen atmosphere to prevent moisture absorption. The experimental conditions used to measure the changes in dynamic storage, \( G'(\omega, t) \), and loss, \( G''(\omega, t) \), moduli during isothermal cure were identical to those used for stoichiometrically balanced networks.\(^1\,^2\) Viscous behavior dominates the initial part of the experiment, \( G'' \gg G' \), and elastic behavior dominates the final stages of the reaction, \( G' \gg G'' \). The most interesting part of a typical curing curve is shown in Figure 2. From the previous studies\(^1\,^3\) the instant of gelation was expected to occur at the crossover point of the loss and storage moduli in Figure 2. To verify whether this criterion is still valid for networks with imbalanced stoichiometry, the cross-linking reaction was stopped at different stages in the vicinity of this crossover point. Tetramethylethlenediamine (TMEDA) was used for this purpose. With two electron donor sites

![Diagram](image)

**Fig. 2.** Curing curve of PDMS with imbalanced stoichiometry at \( T = 34°C \) and \( \omega, = 0.5 \text{ rad/s} \). The loss and storage moduli of the poisoned samples are represented by the dark squares.
(i.e., bidentate ligand) TMEDA is extremely efficient at deactivating the catalyst. Also, since it is a liquid at room temperature, it diffuses rapidly through the polymeric material. TMEDA was prepared in the form of a 0.6 M solution in toluene and the molar ratio of TMEDA to platinum employed was about 1000. Introduction of only a small number of foreign molecules into the samples is sufficient to poison the catalyst. This could be done rapidly and without altering the network structure.

As shown by the dark squares in Figure 2, the evolving network was represented by a discrete set of stable samples with increasing extent of reaction. The observed superposition indicates that partially cured samples were homogeneous and representative of intermediate stages of the continuously cross-linking samples. In addition, the temperature stability of the poisoned samples allowed the application of time—temperature superposition from −50°C to +140°C. The PDMS samples crystallize below −50°C and their dynamic moduli were too low to enable accurate measurements above +140°C. The frequency dependence of the reduced storage, $G'(\omega, t_i)$, and loss, $G''(\omega, t_i)$, moduli at different times, $t_i$, on the curing curve are presented in Figure 3. An evolution of the rheological properties comparable to

![Graph](image)

Fig. 3. Reduced storage and loss moduli at intermediate states of conversion for PDMS with imbalanced stoichiometry. $t_i$ is not the instant of intersection (see Fig. 2) of $G'$ and $G''$. The curves were shifted sideways (factor A) to avoid overlap.
that of PDMS\textsuperscript{1,2} and PU\textsuperscript{3} networks with balanced stoichiometry is observed. At \( t_c - 3 \) min and \( t_c - 1.8 \) min, both \( G' \) and \( G'' \) are expected to decrease to zero at low frequency while at \( t_c + 1.2 \) min a low frequency plateau in \( G' \) has appeared.

The \( t_c \) is the instant at which the sample exhibits power law behavior, that is when \( G' \) and \( G'' \) are given by a straight line in the log-log plot. This power law behavior was found to extend over the entire experimental range of nearly five decades of frequency. Solubility tests\textsuperscript{8} confirmed that the samples before \( t_c \) are still liquids while the samples after \( t_c \) are already solids. This suggests that at \( t_c \), the extent of reaction reaches its critical value \( p_c \). Consequently, a sample at GP exhibits power law dynamic moduli. This is a common feature of imbalanced and balanced gels.

A major difference, however, between stoichiometrically imbalanced and balanced gels is that \( G' (\alpha_T \omega) \) and \( G'' (\alpha_T \omega) \) at GP are parallel but no longer congruent. For the imbalanced gel, the loss modulus is still larger than the storage modulus. Consequently, GP does not coincide with the crossover point of \( G' \) and \( G'' \) in Figure 2, but occurs earlier. This is a surprising result which requires reconsideration of the gel equation, Eq. (1).

**ANALYSIS OF LINEAR VISCOELASTICITY AT GP**

The dynamic moduli of balanced and imbalanced PDMS gels are compared in Figure 4. It has to be shown that this behavior is consistent with the known properties\textsuperscript{4} of network polymers at GP. For this purpose, and following a previous analysis,\textsuperscript{1} we transform the data from the frequency to the time domain. The transformation is based on the hypothesis that power law behavior for the dynamic moduli is valid over the entire frequency range. At \( t = t_c \),

\[
G'(\omega) = G'_c \omega^n
\]

\[
G''(\omega) = G''_c \omega^m \quad 0 < \omega < \infty
\]

where \( G'_c \) and \( G''_c \) are two material constants (values of complex moduli at \( \omega = 1 \text{ s}^{-1} \)) and, as known from experiments, the exponents \( m, n \) are about equal in value. Such hypothesis leads, as will be shown here, to predictions which are in agreement with observations. However, it should be emphasized that with this hypothesis we neglect the behavior at the transition to the glass-
like behavior at high frequency. The resulting constitutive equation will not be able to describe the combined effects of gelation and vitrification, in other words, it will not be able to predict the relaxation behavior at extremely short times. This restriction has to be kept in mind when applying the gel equation.

Introducing Eqs. (4) and (5) into the Kramers$^{15}$–Kronig$^{16}$ relation

$$\frac{G'(\omega)}{\omega^2} = \frac{2}{\pi} \int_0^{\infty} \frac{G''(x)/x}{\omega^2 - x^2} \, dx$$  \hspace{1cm} (6)

shows that the two exponents have to be exactly equal, $m = n$, and it gives a relation between $G'_c$, $G''_c$ and $n$

$$G'_c = G''_c / \tan(n\pi/2) \quad n < 1$$  \hspace{1cm} (7)

The complex moduli are then related by

$$G' = \frac{G''}{\tan(n\pi/2)} = G'_c \omega^n, \quad n < 1 \quad \text{and} \quad 0 < \omega < \infty.$$  \hspace{1cm} (8)
The verification of Kramers–Kronig relation indicates that a power law behavior for dynamic moduli over the entire frequency range does not violate the rules of linear viscoelasticity. Equation (8) predicts that $G''$ is greater than $G'$ for $n > 1/2$, $G''$ is less than $G'$ for $n < 1/2$, and $G''$ is equal to $G'$ for $n = 1/2$.

The storage and loss shear moduli for viscoelastic materials are defined with a relaxation modulus $G(t)$$^{14}$

$$G'(\omega) = \omega \int_0^\infty G(t) \sin(\omega t) \, dt$$

$$G''(\omega) = \omega \int_0^\infty G(t) \cos(\omega t) \, dt$$

The unique solution for Eqs. (9) and (10) together with Eq. (8) is found to be a relaxation modulus

$$G(t) = St^{-n} \quad 0 < n < 1 \quad \text{and} \quad 0 < t < \infty,$$

with

$$S = \frac{2\Gamma(n)}{\pi} \sin(n\pi/2) G'_i$$

where $\Gamma(n)$ is the gamma function. Therefore, at $p = p_c$, the relaxation modulus will exhibit a power law behavior with a slope $-n$. The values of $n$ range between 0 and 1. No solution exists for $n \geq 1$, and the relaxation modulus would not decay in time for $n \leq 0$ which would violate thermodynamics principles.

The limits of the gel behavior will be discussed in greater detail separately.$^{17}$ For the analysis of the data, we neglected the glassy behavior at high frequency by hypothesizing gel behavior over the entire frequency range, $0 < \omega < \infty$. As a consequence, we calculated power law relaxation behavior for the entire time domain $0 < t < \infty$. In reality, the gel will exhibit transition to glassy behavior at some very high frequency, the glass frequency $\omega_g$, and correspondingly, the power law relaxation behavior of the real gel is valid only in the time range $t_g < t < \infty$. The very short glass time, $t_g$, corresponds to the glass frequency, $\omega_g$. $\omega_g$ or $t_g$ could not be measured for our samples since they are far outside the experimental frequency window.

It is interesting to note that continuum mechanics arguments led Giesekus and Heindl$^{18}$ to the conclusion that a power law relaxation modulus gives properties intermediate between liquid
and solid behavior. They called such a material an "improper fluid" (German: unechte Flussigkeit) but did not suspect that it might exist in nature. Heindl and Giesekus\textsuperscript{19} and later Larson\textsuperscript{20} suggested a power law relaxation modulus which was modified with the objective to model the power law shear thinning behavior of some polymeric liquids, and they discussed general properties of these liquids.

It remains to be shown that, for any value of the power law exponent $0 < n < 1$, the material defined at $t = t_c$ is at the gel transition. The steady shear viscosity as defined by the theory of linear viscoelasticity\textsuperscript{14} is calculated as

$$\eta_0 = \int_0^\infty G(t) \, dt = \frac{S}{1-n} \lim_{t \to \infty} t^{-n}, \quad 0 < n < 1, \quad p = p_c.$$  \hspace{1cm} (13)

It is seen to diverge to infinity for any value of $n$ below 1.

Linear viscoelastic theory, as applied to Eq. (11), predicts a vanishing equilibrium modulus

$$G_e = \lim_{t \to \infty} G(t) = S \lim_{t \to \infty} t^{-n} \quad 0 < n < 1 \quad p = p_c \quad (14)$$

The relaxation modulus decays to zero for any value of $n$ above 0. Therefore the material at $t = t_c$ as defined above exhibits the classical attributes\textsuperscript{4} of the gel behavior provided that the relaxation exponent has values between 0 and 1.

It is important to note that the short time contribution to the above predicted behavior is very small. This supports the starting hypothesis [Eqs. (2) and (3)] that for describing the gel behavior far away from vitrification, the short time behavior (i.e., vitrification) may be ignored.

In summary, power law dynamic moduli and power law stress relaxation are characteristics of the rheological behavior at GP. The power law exponent is not limited to $n = 1/2$ but rather to a range of values between 0 and 1. This new result is now included in the gel equation.

**GEL EQUATION**

Analysis of the experiments indicates that the relaxation modulus obeys a power law at GP [Eq. (11)]. The exponent, $n$, of the
power law was found to be a function of the stoichiometric ratio of the reactants, \( r \),
\[
    r = \begin{cases} 
        \frac{1}{2} & \text{for } r = r_s \\
        > \frac{1}{2} & \text{for } r < r_s
    \end{cases}
\]  \ (15)

The gel equation [Eq. (1)] has to be modified accordingly. It takes the simple form
\[
    \tau(t) = S \int_{-\infty}^{t} (t - t')^{-n} \tilde{\eta}(t') \, dt' \quad 0 < n < 1 \quad p = p_c.
\]  \ (16)

Two material parameters are needed, the gel "strength," \( S \), and the relaxation exponent, \( n \). These two parameters depend on the molecular structure in a way which is not yet known. An attempt to relate the exponent \( n \) to molecular structure (i.e., fractal dimension at GP) is discussed elsewhere.\(^{21,22}\)

For the PDMS samples, the values of the relaxation exponent are \( n = 0.5 \) and \( n = 0.58 \). The dependence of \( n \) or \( r \) will be studied in a future paper, using PU as model polymer.\(^{22}\) The switch to a new polymer is necessary for that purpose since the molecular parameters of PDMS are not known with sufficient accuracy.

The gel equation may be rewritten with a finite strain measure.\(^1\) Experiments are in progress for justifying a specific choice of strain measure.

**GEL POINT DETERMINATION WITHOUT STOPPING THE CURING REACTION**

Infinite shear viscosity and zero equilibrium modulus are the most often employed criteria\(^{7,20-26}\) to localize GP. However, since they involve limiting properties, GP can only be determined by extrapolation. Instead, with the gel equation [Eq. (16)] we have now a description of the rheological behavior at GP. This result is of direct practical interest since it indicates that any method able to detect the occurrence of the power law behavior will be suitable to determine the instant of gelation, \( t_s \). In the special case of \( n = 1/2 \), Eq. (16) predicts congruency of the dynamic moduli. In this case only, the instant of gelation can be determined from the intersection of the loss and storage moduli on the curing curve.\(^{1-3}\)

However, this method to measure the gel time is of limited interest since it will apply only to specific network polymers.
A more general method to detect GP may be based on the observation that, at \( p = p_c \),

\[
\tan\delta(\omega) = \frac{G''(\omega)}{G'(\omega)} = \tan(n\pi/2) \quad 0 < n < 1.
\] (17)

is independent of frequency. While subjecting a curing sample to a multifrequency deformation, the tangent of the loss angle, \( \tan\delta \), can be recorded as a function of the curing time at different frequencies. The instant of gelation is found by \( \tan\delta \) independent of the frequency, and the value of the power law exponent can be directly deduced from the amplitude of \( \tan\delta \) at that point.\(^{27}\)

**CONCLUSIONS**

The critical gel state is a new material state between liquid and solid. In the special case of a cross-linking PDMS at the gel point (GP), stress relaxation occurs in a power law with a relaxation exponent, \( n \), which may take a value in the range between 0 and 1. The previously found value \( n = 1/2 \) seems to be restricted to stoichiometrically balanced gels\(^1\)-\(^3\) whereas larger values \( 1/2 < n < 1 \) have been found for an imbalanced gel with crosslinker deficiency. The relaxation exponent, therefore, allows to distinguish between different gel structures. A detailed study of the relation between \( n \) value and stoichiometry is in progress.

The power law relaxation modulus is introduced into a linear viscoelastic constitutive equation to give the gel equation. It describes all the currently known rheological phenomena at GP (within the range of linear viscoelasticity) and gives an independent definition of GP.

The commonly accepted rheological criteria for characterizing the critical gel state\(^4\) (\( \eta_0 \to \infty, G_\infty = 0 \)) are too imprecise to accurately determine the instant of gelation, and are inadequate to detect differences in gel behavior. The fact that the steady-shear viscosity cannot be reached at GP, and the experimental difficulties encountered in measuring an actual zero equilibrium modulus imply that these two quantities may not be the pertinent rheological parameters to characterize GP. Instead this study suggests that significant progress in understanding the gelation phenomenon will arise when gelation theories can predict nondivergent rheological functions, such as dynamic moduli, at GP.
Power law relaxation has been observed with some polymeric liquids at intermediate frequencies.\textsuperscript{30,38} They behave gel-like over a limited frequency range. In the case of the critical gel (polymer at GP), the power law region is stretched over a very large frequency range. This results in a shift of the terminal zone of relaxation toward very low frequencies. Based on this observation a Rouse model with infinitely long relaxation time was suggested\textsuperscript{1} to explain the power law exponent, $n = 1/2$, observed with balanced gels. This study clearly indicates that the general rheological behavior at GP cannot be explained in terms of a Rouse spectrum. New molecular theories (such as recently developed fractal theories\textsuperscript{21}) predict an extended power law region and are therefore able to describe the unusual behavior observed at GP. This will be discussed in a follow-up article.\textsuperscript{22}

Finally, we emphasize again that the above results were found for chemical gels which are formed by end-linking reaction in bulk. Similar behavior might be found in critical gels of other crosslinking mechanisms. The power law relaxation only occurs at temperatures far above the glass transition temperature and at frequencies below the high frequency glass transition, $\omega < \omega_g$. The interference of vitrification with gelation would give rise to a much more complex rheological behavior.

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