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Analysis of Linear Viscoelasticity of a Crosslinking Polymer at the Gel Point

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Synopsis

We suggest a very simple memory integral constitutive equation for the stress in crosslinking polymers at their transition from liquid to solid state (gel point). The equation allows for only a single (!) material parameter, the strength $S[Pa\ s^{1/2}]$, and it is able to describe every known viscoelastic phenomenon at the gel point. Measurements were performed on polydimethylsiloxane model networks with balanced stoichiometry for which the crosslinking reaction has been stopped at different degrees of conversion. At the gel point, the loss and storage moduli were found to be congruent and proportional to $\omega^{1/2}$ over a wide range of temperature ($-50°C$ to $+180°C$) and five decades of frequency ω. The hypothesis is made that this behavior is valid in the entire range $0 < \omega < \infty$. This congruence hypothesis is consistent with the Kramers-Kronig relation and leads to a constitutive equation which shows that, for our polymer, congruent functions $G'(\omega) - G''(\omega)$ are as much a rheological property at the gel point as are infinite viscosity and zero equilibrium modulus. This makes it now possible to measure exactly the instant of gelation of a crosslinking polymer without having to stop the crosslinking reaction.

INTRODUCTION

Crosslinking polymers undergo phase transition from liquid to solid at a critical extent of reaction. This phenomenon is called gelation . The polymer is said to be at the gel point (GP) if its steady shear viscosity is infinite and its equilibrium modulus is zero. Several processes may contribute to this transition besides the connecting of molecular strands by chemical crosslinking: physical entanglements between the macromolecular strands, vitrification as the glass transition temperature rises with increasing extent of reaction, phase separation of the reaction components or products, and crystallization.

This study is not concerned with gelation in its most general sense but with the phase transition due to chemical crosslinks only. Several theories[1-3] as well as computer simulations[4] predict the critical extent of reaction at which the transition occurs. The transition is understood to occur when at least one of the molecules of the crosslinking polymer has grown very large and its size reaches dimensions of the order of the macroscopic sample.[3] Rheological experiments will be analyzed in which we stayed away from other phase transition such as glass transition, or phase separation. Physical entanglements were avoided, at least initially, by choosing a prepolymer molecular weight below the entanglement limit. The objective of this work is the study of gelation without the interference of other critical phenomena.

Previous experiments during the crosslinking reaction of a network polymer give an indication of the increasing crosslink density without giving sufficient information for formulating constitutive equations. Problems arise from the fact that the stress in a crosslinking polymer is time dependent due to two different phenomena: the viscoelastic behavior in transient deformations and the changing chemical composition as the network is forming with time. Measurement of the viscoelastic behavior, however, requires a sample with stable chemical composition during the entire experiment. For these reasons, Chambon and Winter[5] studied viscoelastic behavior after having stopped the crosslinking reaction.

Presently, there are two accepted methods for the rheological study of crosslinking polymers. In the first method,[6-8] the polymer in its liquid state is subjected to shear flow. The measured viscosity increases with increasing extent of reaction until the stress reaches the limit of the instrument or until the material breaks. For characterization beyond GP, the material is subjected to strain and the steady state modulus is measured during its growth with increasing extent of reaction.[9] Measurements in either the liquid state or the solid state give reliable data away from GP. The transition itself is defined by a singular behavior which is not accessible to these experiments except by extrapolation (see Figure 1). The exact time of GP cannot be determined with this method.

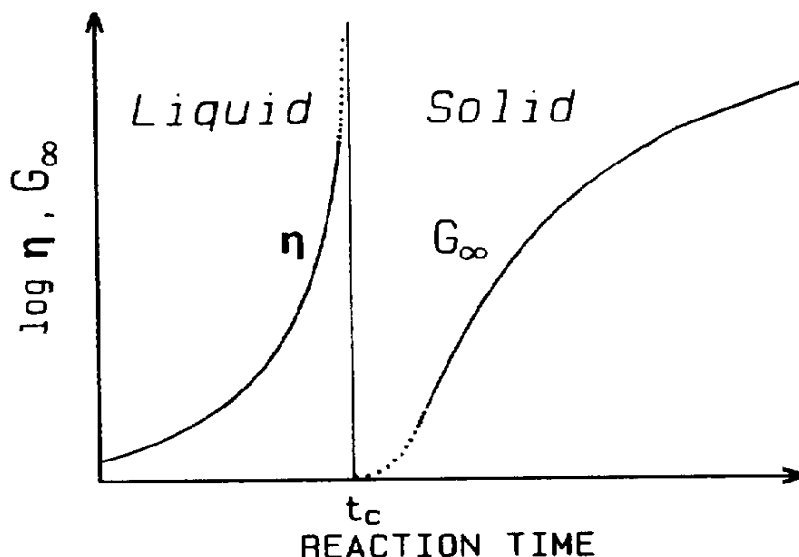In the second method,[10,5] small amplitude oscillatory shear

Fig. 1. Schematic of steady shear viscosity and equilibrium modulus of a crosslinking polymer. No such experiments are possible in the close vicinity of transition from liquid to solid.

gives the components of the complex modulus during the cross-linking process, as shown in Figure 2. The viscous behavior of the oligomeric material dominates the initial part of the experiment. The loss modulus, G'', is large while the storage modulus, G', is still negligible. With increasing molecular weight, the loss modulus increases while the storage modulus rises sharply until it intersects and then exceeds the loss modulus. The storage modulus keeps increasing with increasing crosslink density while the loss modulus goes through a slight maximum. Both moduli level off as the reaction comes to completion.

The oscillatory shear method has the advantage of a *continuous* evolution of the viscoelastic properties as the polymer goes through GP. The data give no indication of the specific instant at which the transition occurs. Earlier experiments[10] suggest that the intersection of G' and G'' marks the time of gelation. However, the time of intersection was found to be a function of frequency of the oscillatory shear experiment. This could indicate that the time of intersection might be close but not identical with the transition time. The instant of gelation is strictly material
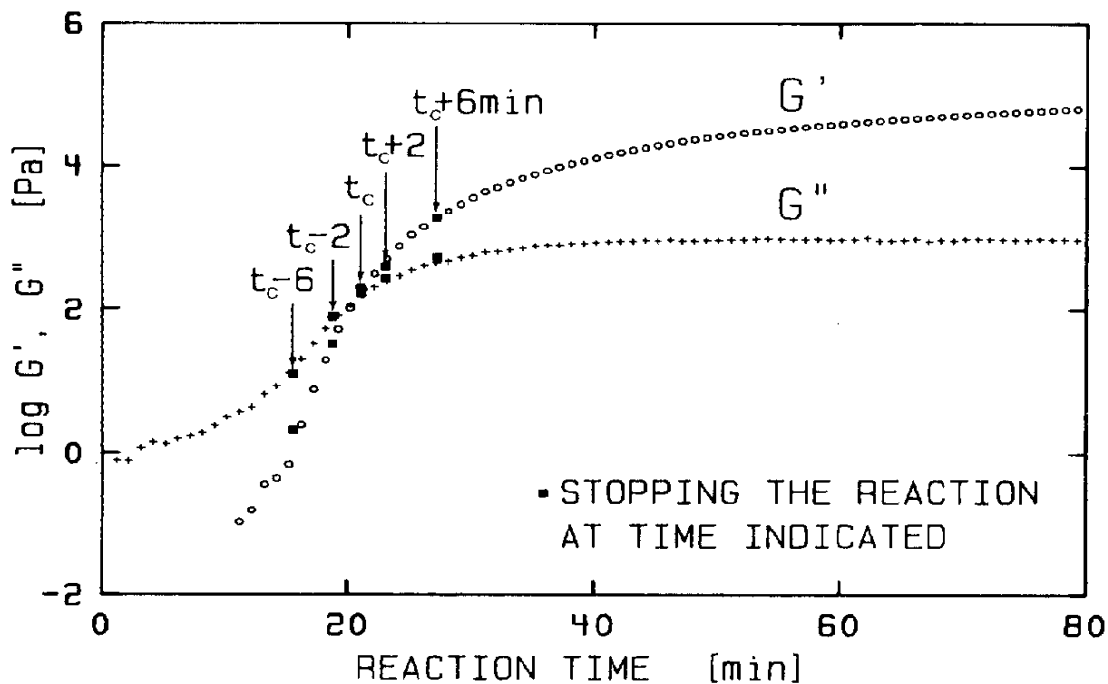
Fig. 2. Evolution of the storage modulus G' and the loss modulus G'' of a crosslinking PDMS in an oscillatory shear experiment at constant frequency ω.

dependent and cannot depend on the frequency of the rheological test (unless there is an influence of the flow on the chemical reaction or there is interference of a second critical phenomenon, such as vitrification).

A complementary result has been reported by Chambon and Winter,[5] who stopped the crosslinking reaction in a PDMS at times near the G', G'' intersection. For one of the samples, the reaction was stopped very near the time of intersection; this sample exhibited congruent $G'(\omega) = G''(\omega)$ over more than five decades of frequency and a wide range of temperature. In this paper we will analyze these experimental data and will suggest a new rheological constitutive equation for network polymers at GP. Based on this constitutive equation we will clearly demonstrate that, in support of the empiricism of Tung and Dynes,[10] GP coincides with the time of intersection of G' and G'' in an oscillatory shear experiment at constant frequency.
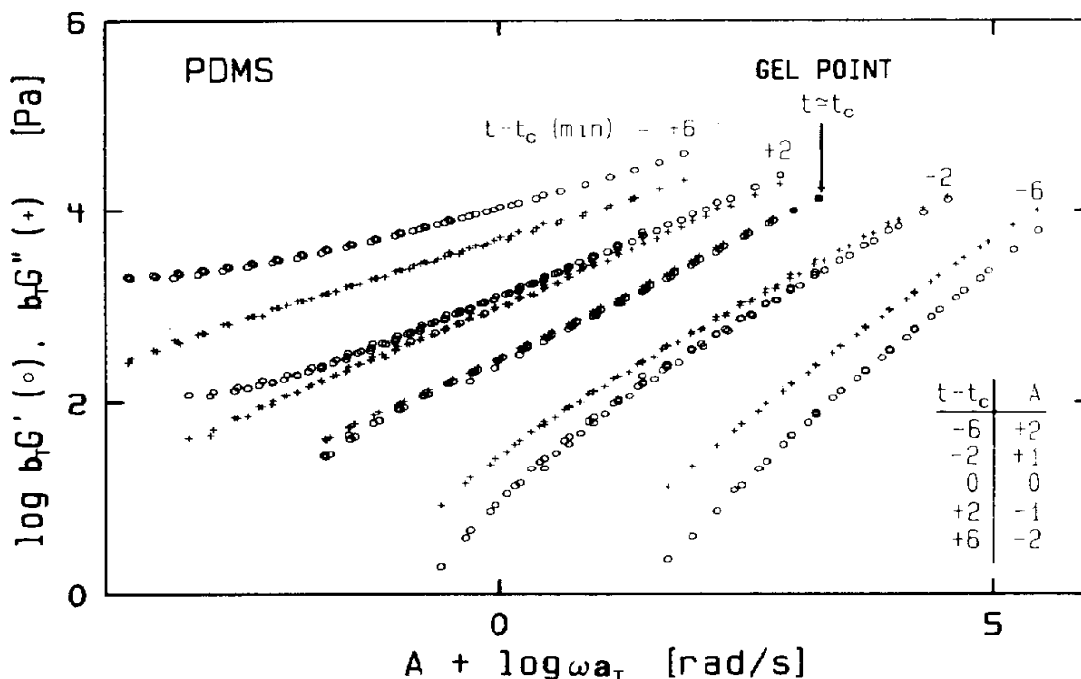
Fig. 3. Reduced storage and loss moduli of PDMS samples for which the reaction has been stopped at intermediate states of conversion. t_c is the instant of intersection (see Figure 2) of G' and G''. The curves were shifted sideways (factor A) to avoid overlap.

EXPERIMENTAL OBSERVATIONS

A polydimethylsiloxane (PDMS) was used for the experiments since it provides good model networks.[11] Divinyl terminated PDMS was endlinked with a tetrasilane crosslinker. The molecular weight of the prepolymers was below the entanglement limit. The samples were prepared at balanced stoichiometry, $r = 1$, and were reacted at rest to avoid any influence of flow history. Details of the sample preparation and the rheological experiments have been reported earlier.[5] Figure 2 shows the evolution of the storage modulus $G'(\omega_0, t)$ and the loss modulus $G''(\omega_0, t)$ during the reaction. The frequency dependence of $G'(\omega, t_i)$ and $G''(\omega, t_i)$ was measured on chemically stable samples which were prepared by stopping the crosslinking reaction at intermediate states, t_i, of conversion (see Figure 3).

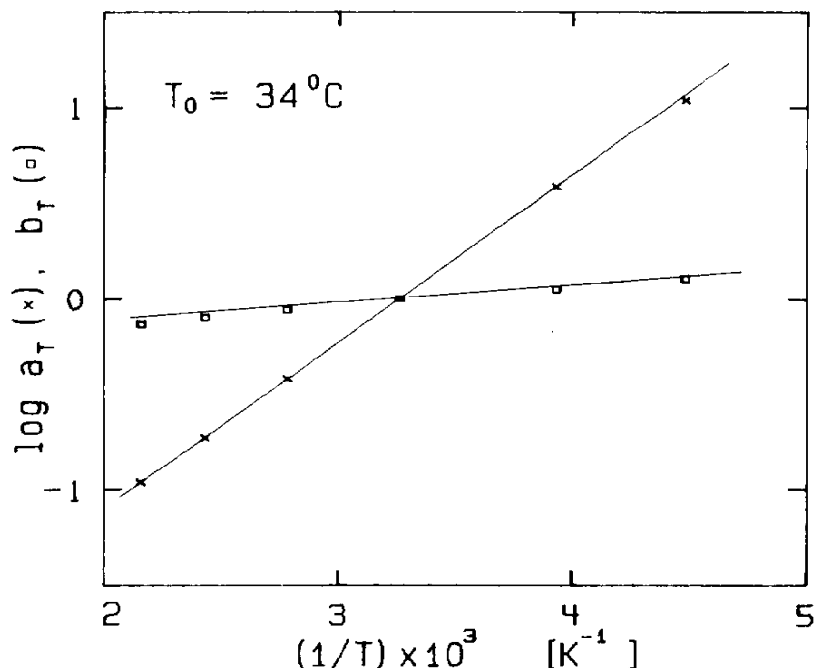Viscoelastic data at temperatures between $-50°C$ and $+180°C$

Fig. 4.   Measured temperature shift factors of PDMS at GP.

could be shifted into single curves. The temperature shift factors (Ferry, 1980) are

$$a_T(T,T_0) = exp\left\{\frac{E}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right\}; \quad b_T = \frac{\rho(T_0)T_0}{\rho(T)T} \qquad (1)$$

The shift factor a_T followed an Arrhenius relation (see Figure 4), i.e., the experiments were performed much above the glass transition temperature. The vertical shift factor was estimated from the changes in sample thickness with temperature. One of the "stopped" samples, with $t = t_c$ in Figure 3, exhibited the congruency of the reduced moduli

$$b_T G_c' = b_T G_c'' = C(a_T\omega)^{1/2} \qquad (2)$$

Subscript c indicates that the material of this sample with congruent $G' = G''$ is, as will be shown below, very close to a critical state. The material constant C is independent of temperature.

For clarification, this condition of $G' = G''$ over the entire range of frequency has to be distinguished from frequency-dependent crossover points which have been observed with most

polymeric liquids.[12] The crossover phenomenon will not be mentioned further. This study is solely concerned with materials which exhibit congruence, $G' = G''$, over a wide frequency range and not just an intersection at a specific frequency value.

Linear viscoelastic theory, as applied to Eq. (2), predicts a steady shear viscosity

$$\eta_0 = \lim_{\omega \to 0} (G''_c/\omega) = C \lim_{\omega \to 0} (\omega^{-1/2}) = \infty \tag{3}$$

and an equilibrium shear modulus

$$G_\infty = \lim_{\omega \to 0} G'_c = C \lim_{\omega \to 0} (\omega^{1/2}) = 0 \tag{4}$$

Infinite viscosity and zero equilibrium modulus are properties of a material at the liquid/solid transition. However, Equations (3) and (4) involve the zero frequency limit, which is outside the experimental range.

It would be interesting to know the range of validity of the power law behavior which was found to occur over more than 5 decades in frequency and which we expect to continue over an even wider range. It is important to note that measurements over a much wider range would not be able to resolve this uncertainty. At *very low* frequency, the sample would exhibit either liquid behavior ($G' \sim \omega^2$; $G'' \sim \omega$) or solid behavior ($G' = $ const.; $G'' \sim \omega$) since we are not able to stop the reaction precisely at the GP. Later on in this paper when discussing the Rouse relaxation time spectrum, we will return to this question and find that the Rouse model would predict a power law behavior at the gel point which actually continues to the limit of $\omega \to 0$. At *very high* frequency, the power law behavior might continue if it would not become masked by the onset of glass transition as a second critical phenomenon. While keeping this upper and lower frequency limit in mind for real materials, it is unimportant for the purpose of analyzing the rubbery behavior at the gel point. We therefore hypothesize that the power law is not restricted in frequency range,

$$G'(T,\omega) = G''(T,\omega) = \sqrt{\pi/2} \, S(T)\omega^n, \qquad 0 < \omega < \infty,$$

with $\qquad S(T) = \sqrt{2/\pi} \, Ca_T^{1/2}/b_T \tag{5}$

and see whether this hypothesis violates the relation of Kramers[13] and Kronig,[14]

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

which involves an integral over the entire frequency range. The factor $\sqrt{\pi/2}$ is introduced for later convenience. Equation (5) is introduced twice into the Kramers-Kronig relation, Eq. (6), without specifying the value of n (which we expect to be about ½ from experiment). The values of the material constant C and of the temperature shift factors have no influence. The resulting equation, after rearrangement,

$$1 = \frac{2}{\pi} \int_0^\infty y^{n-1}(1 - y^2)^{-1} \, dy, \qquad (7)$$

has solutions

$$n = \tfrac{1}{2}, \ -\tfrac{3}{2}, \ -\tfrac{7}{2}, \ -\tfrac{11}{2} \ \ldots \ . \qquad (8)$$

The only valid solution, however, is $n = \tfrac{1}{2}$ since $n < \tfrac{1}{2}$ would predict a relaxation modulus which increases with time and therefore would violate thermodynamic principles. (Note that this proof is restricted to a "power law" (see Eq. (5)). It does not exclude the possible existence of another type of function which satisfies congruency $G' = G''$.)

In summary, the Kramers-Kronig relation 1) confirms the experimentally found value of the exponent ($n = \tfrac{1}{2}$); and 2) shows that $n = \tfrac{1}{2}$ is the only possible value. These results are rather surprising. However, it still has to be shown that congruent $G' = G''$ provides a well-defined experimental method for detecting GP. This can be done through the use of a constitutive equation which will be developed in the following sections.

RELAXATION MODULUS

The extra stress in any viscoelastic liquid or solid at constant density can be described by

$$\underline{\tau}(t) = \int_{-\infty}^t G(t - t')\underline{\dot{\gamma}}(t') \, dt' \qquad (9)$$

The relaxation modulus $G(t - t')$ contains the material properties. Kinematics determines the rate of deformation tensor (where v is velocity),

$$\underset{=}{\dot{\gamma}}(t') = \nabla v(x,t') + (\nabla v(x,t'))^T. \tag{10}$$

Equation (9) is valid as long as the memorized strain is kept within the linear region of the material. The extent of the linear region is hard to define since a nonlinear constitutive equation is required. However, the lack of definition is no real problem since linear behavior can always be confirmed experimentally by repeated tests at increasing strain magnitude.

Equation (9) is suitable for describing the stress in the cross-linking material at its transition from liquid to solid since 1) it is applicable to the liquid state as well as to the solid state; and 2) the relaxation modulus changes smoothly during the transition (as will be shown). The oscillatory shear data can be analyzed through the constitutive equation: the kinematics of oscillatory shear is introduced into Eq. (9) to define the storage and loss moduli,

$$G'(\omega) = \omega \int_0^\infty G(t) \sin (\omega t) \, dt \tag{11}$$

$$G''(\omega) = \omega \int_0^\infty G(t) \cos (\omega t) \, dt. \tag{12}$$

Congruency of $G'(\omega)$ and $G''(\omega)$ requires that Eqs. (11) and (12) are equal and proportional to $\omega^{1/2}$. Fourier transform tables list a solution for this equation. The relaxation modulus is found to have the simple form

$$G(t) = St^{-1/2}. \tag{13}$$

The only material parameter, $S[Pa \ s^{1/2}]$, is called the "strength" of the network at the gel point or the "GP-strength."

This is a result which contradicts several observations which seemed to be generally valid for viscoelastic materials: 1) a *single* material constant is the only adjustable parameter here, while viscoelastic liquids or solids require a relaxation time *spectrum;* 2) the modulus is infinite at the limit of zero time but the limiting modulus of viscoelastic liquids or solids is finite; and 3) the relaxation does *not* occur exponentially in time. Further experiments are required to establish confidence in such unusual behavior.

Equation (13) represents a continuous relaxation spectrum. However, such a spectrum is conventionally defined as[15]

$$G(t) = \int_0^\infty \frac{H(\lambda)}{\lambda} \exp(-t/\lambda)\, d\lambda \tag{14}$$

For comparison, we equate Eqs. (13) and (14) and calculate function $H(\lambda)$

$$H(\lambda) = S(\pi\lambda)^{-1/2} \tag{15}$$

It is interesting to note that at GP, the material behaves like the polymer component of the Rouse model[16] for dilute polymer solutions at the limit of high frequency,

$$1 \ll \lambda_{\max}\omega. \tag{16}$$

For polymer solutions, the Rouse limit is reached by applying high frequencies.[12] However, this limit can also be reached by generating a material of extremely long relaxation time. At the gel point, the relaxation time is infinitely long and the power law behavior can be expected even at the limit of $\omega \to 0$. This coincidence with the Rouse behavior suggests the possibility of expressing the relaxation modulus as a sum of exponential functions as is often done for viscoelastic liquids. The discrete spectrum at GP can then be written as

$$G(t) = St^{-1/2} = \lim_{\lambda_{\max}\to\infty} \frac{2S}{\sqrt{\pi\lambda_{\max}}} \sum_{i=1}^\infty \exp(-ti^2/\lambda_{\max}). \tag{17}$$

The spacing of the relaxation times is the same as in a Rouse spectrum. The spectrum is normalized to obtain the value S at $t = 1s$. No additional material parameter needs to be introduced when defining the discrete spectrum.

For modeling the rheological behavior in the vicinity of GP, we suggest using Eq. (17), however, with a finite maximum relaxation time and an equilibrium modulus (for $t > t_c$).

STRESS AT GEL POINT

The constitutive equation for the extra stress, Eq. (9), with the relaxation modulus, Eq. (13), takes the simple form,

$$\underset{=}{\tau}(t) = S \int_{-\infty}^t (t - t')^{-1/2} \underset{=}{\dot{\gamma}}(t')\, dt'. \tag{18}$$

Density is assumed to be constant. This equation obviously predicts congruent $G'(\omega)$ and $G''(\omega)$ since its derivation is based on

that same condition. It now remains to be shown that Eq. (18) also predicts the behavior at GP. Many experiments can be conceived for defining the viscoelastic phase transition. The predictions of Eq. (18) for transient shear viscosity and transient shear modulus are tested here since these quantities can actually be measured in a shear rheometer.

The *first* experiment gives the transient shear viscosity during start-up of shear flow at constant rate: the material is at GP if the time dependent viscosity grows to infinity without reaching steady state. This is a more precise definition than "infinite viscosity" at steady shear flow which obviously cannot be verified in an experiment.

We model the stress by defining the time dependent shear rate and introducing it into Eq. (18). The sample is kept at rest during times $t < 0$; at time $t = 0$ and thereafter, the sample is sheared at constant rate $\dot{\gamma}_{12}$. The resulting shear viscosity is calculated as

$$\eta(t) = \frac{\tau_{12}(t)}{\dot{\gamma}_{12}} = S \int_0^t (t - t')^{-1/2} \, dt' = 2St^{1/2} \quad \text{for } 0 < t. \quad (19)$$

The shear viscosity grows with time without ever reaching steady state. This satisfies the first condition of GP.

The *second* experiment gives the transient modulus during shear stress relaxation at rest after a rapid strain: the material is at GP if the stress relaxes to zero and hence the equilibrium modulus is zero.

We again model the stress by defining the time-dependent shear rate and by introducing it into Eq. (18). The sample is subjected to a rapid shear experiment with a shear rate,

$$\dot{\gamma}_{12}(t) = \begin{cases} 0 \text{ for } t < 0, \\ \dot{\gamma}_0 \text{ for } 0 < t < t_0, \\ 0 \text{ for } t_0 < t. \end{cases} \quad (20)$$

The total shear strain of this experiment amounts to $\dot{\gamma}_0 t_0$.

With this strain history, the transient modulus is calculated as

$$g(t) = \frac{\tau_{12}(t)}{\dot{\gamma}_0 t_0} = \frac{S}{t_0} \int_0^{t_0} (t - t')^{-1/2} \, dt'; \quad t_0 < t,$$

$$= St^{-1/2} 2/[1 + (1 - t_0/t)^{1/2}]. \quad (21)$$

The duration, t_0, of the shearing motion in a rapid strain experiment is very short compared to that of the relaxation experiment. The equation for the transient shear modulus simplifies to

$$g(t) = St^{-1/2}, \tag{22}$$

as expected from the equation for the relaxation modulus. The transient shear modulus approaches zero at long times. Therefore, the equilibrium modulus is equal to zero. This satisfies the second criterion of GP.

In summary, the constitutive equation, Eq. (18), is able to describe the known rheological phenomena at GP. Analysis of the experiments confirms that congruent G' and G'' is a property of the PDMS polymer at GP.

FINITE STRAIN MEASURE

An infinitesimal strain measure was selected when formulating the constitutive equation. This is permissible for studying material behavior in the limit of very small strain. However, continuum mechanics principles (objectivity) are violated by such an equation when applied to finite strains. The infinitesimal strain measure has to be replaced by a finite strain measure. Possible formulations for the stress are

$$\underset{\approx}{\tau}(t) = -S \int_{-\infty}^{t} (t - t')^{-1/2} \frac{\partial}{\partial t'} (\underset{\approx}{C}_t^{-1}(t')) \, dt' \tag{23}$$

or

$$\underset{\approx}{\tau}(t) = \frac{S}{2} \int_{-\infty}^{t} (t - t')^{-3/2} [\underset{\approx}{C}_t^{-1}(t') - \underset{\approx}{1}] \, dt' \tag{24}$$

with a Finger strain tensor $\underset{\approx}{C}_t^{-1}(t')$ and a unit tensor $\underset{\approx}{1}$, definitions of which are given in standard continuum mechanics texts. Volume changes are assumed to be negligibly small ($\rho = $ const.). The two equations are identical; transformation is possible by partial integration. The very few available experimental data were taken at small strain and therefore do not give any indication of a suitable choice of finite strain measure. Behavior at finite strain will be investigated in a later study.

STRENGTH OF THE NETWORK AT THE GEL POINT

The only material parameter in the constitutive equation, the strength S, can be measured in an oscillatory shear experiment without stopping the crosslinking reaction. The value of S is determined by G' at the time of its intersection with G'', as shown in Figure 2.

$$S = G_c' \, [\pi\omega_0/2]^{-1/2}, \tag{25}$$

where ω_0 is the frequency of the experiment. The PDMS has a strength of 226 $Pa \, s^{1/2}$ at $T = 34°C$. The temperature dependence is found to be

$$S(T) = S(T_0)a_T^{1/2}/b_T \tag{26}$$

S decreases with temperature.

CONCLUSIONS

An extremely simple relation between stress and strain, Eqs. (18) or (23), describes the known rheological phenomena in a polydimethylsiloxane at its gel point (GP). The clarity and simplicity of this relation (one material parameter only) implies that it might be universally valid for endlinking polymers of balanced stoichiometry. However, experiments on other polymer systems are needed for support of such a far-reaching conclusion.

The constitutive equation, Eq. (18), is based on the congruence hypothesis Eq. (5), which says that there exists an intermediate state of the material at which $G'(\omega)$ and $G''(\omega)$ are congruent functions in the entire range $0 < \omega < \infty$.

A new material property has been defined: the strength S with a dimension of $Pa \, s^{1/2}$. It is easily measured in a single oscillatory shear experiment during the crosslinking reaction. S depends, in some general way which is yet unknown, on molecular structure. For engineering applications, one would like to know how S depends on reaction conditions and whether there exists a relation between S and final network properties after complete conversion.

The transition from viscoelastic liquid to viscoelastic solid is a gradual one. There is no discontinuity in the rheological behavior. The rheological constitutive equation of the GP-network, Eq.
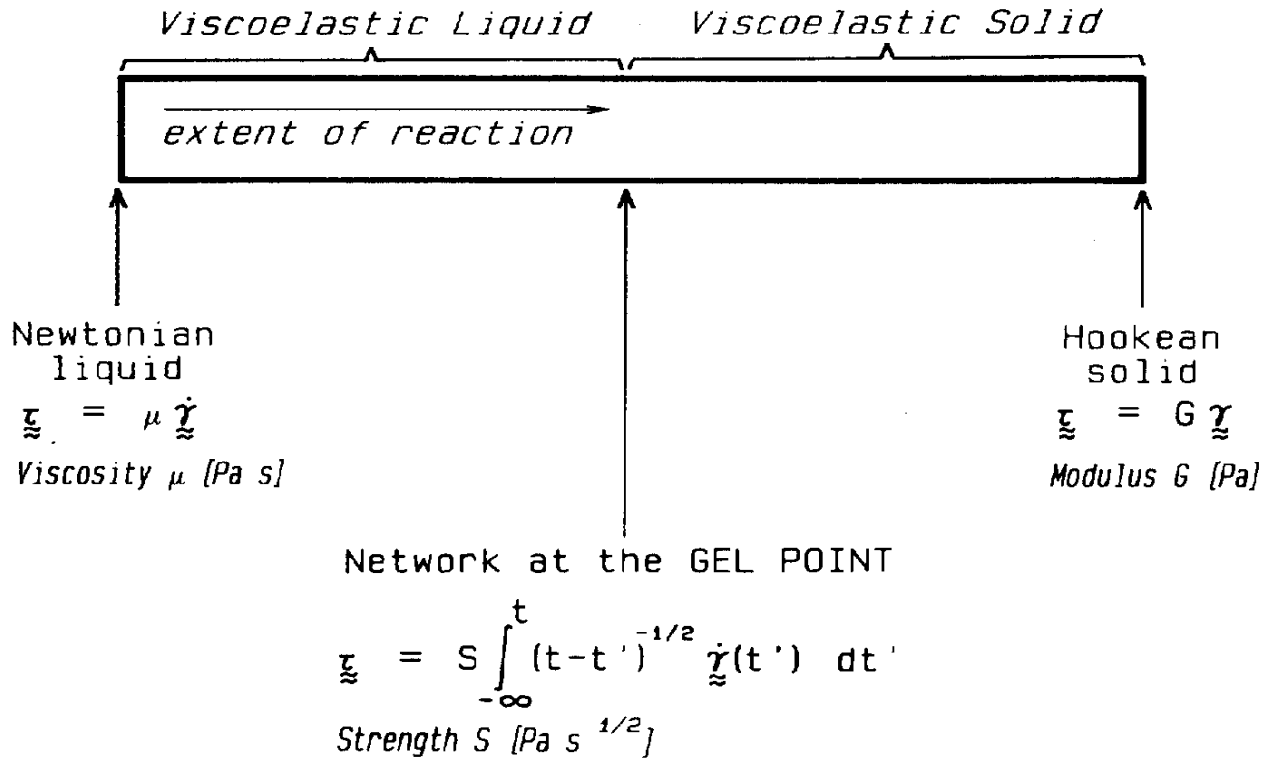
Viscoelastic Liquid   *Viscoelastic Solid*

extent of reaction

**Newtonian
liquid**

$$\underset{\approx}{\tau} = \mu\, \underset{\approx}{\dot{\gamma}}$$

Viscosity μ [Pa s]

**Hookean
solid**

$$\underset{\approx}{\tau} = G\, \underset{\approx}{\gamma}$$

Modulus G [Pa]

Network at the GEL POINT

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

Strength S [Pa s $^{1/2}$]

Fig. 5. Evolution of rheological behavior of a crosslinking polymer (at con-
stant density) with three idealized states: the Newtonian liquid at the beginning
of the reaction, the viscoelastic transition network at a critical conversion, and the
Hookean solid at completion of reaction. Each of the three idealized states is
described by a constitutive equation with a single material parameter. The equa-
tions of the Hookean solid and the GP-network are written in a form which is
limited to infinitesimal strain.

(18), describes a limiting behavior as shown in Figure 5: The
viscoelastic liquid is bounded by the purely viscous limit (Newto-
nian liquid) and by the viscoelastic transition limit (GP-network);
the viscoelastic solid is bounded by the viscoelastic transition
limit (GP-network) and the purely elastic limit (Hookean solid).
Each of the limiting behaviors is characterized by an extremely
simple constitutive equation which contains only one material
parameter even though constitutive equations for intermediate
materials (viscoelastic liquid and viscoelastic solid) are very com-
plex. This is a highly significant result in several respects: 1)
viscoelastic liquids and solids can now be classified by their
closeness to either one of the rheological limiting behaviors; 2)

the existence of the limiting behavior at GP restricts the formulation of constitutive equations for viscoelastic liquids and solids; and 3) molecular theory for GP, if it were available, would help to formulate molecular theories of the liquid and the solid state. The simplicity of this rheology gives rise to the hope that a molecular theory for GP can be derived.

For chemically crosslinking polymers, there is an interesting difference between GP and other transitions such as the glass transition or the melting transition. A chemically crosslinked polymer at GP, such as the "stopped" PDMS samples of Chambon and Winter, *cannot* be moved in or out of this transition by changing the temperature or the frequency of the shearing experiment. In comparison, physically crosslinked networks undergo reversible GP at critical temperature and pressure. Even so, a change in frequency should not shift GP. One might speculate that physically and chemically crosslinked networks at GP follow the same rheological law.

This study demonstrates that rheology is sufficient to measure the instant of GP. It is expected that the rheologically-measured GP coincides with the transition of other properties such as cessation of large scale molecular motion[17] and appearance of an insoluble component in the material. Measured conversion at GP will have to be compared with the theoretical values.[1-3] A comparison of these different properties is planned.

References

1. P. J. Flory, *J. Am. Chem. Soc.*, **63**, 3083, 3091, 3096 (1941); "Principles of Polymer Chemistry," Cornell Univ. Press, Ithaca, NY, (1953).
2. W. H. Stockmayer, *J. Chem. Phys.*, **11**, 45 (1943); **12**, 125 (1944).
3. D. Stauffer, A. Coniglio, and M. Adam, *Adv. Pol. Sci.*, **44**, 74 (1982).
4. Y. K. Leung and B. E. Eichinger, *J. Chem. Phys.*, **80**, 3877, 3885 (1984).
5. F. Chambon and H. H. Winter, *Polym. Bull.*, **13**, 499 (1985).
6. S. Lipshitz and C. W. Macosko, *Polym. Eng. Sci.*, **16**, 803 (1976).
7. J. M. Castro, C. W. Macosko, and S. J. Perry, *Polym. Com.*, **25**, 82 (1984).
8. A. Apicella, P. Masi, and L. Nicolais, *Rheol. Acta*, **23**, 291 (1984).
9. R. J. Farris and C. Lee, *Polym. Eng. Sci.*, **23**, 586 (1983).

10. C. Y. M. Tung and P. J. Dynes, *J. Appl. Pol. Sci.*, **27**, 569 (1982).

11. E. M. Valles and C. W. Macosko, *Macromolecules*, **12**, 521 (1979).

12. J. D. Ferry, "Viscoelastic Properties of Polymers," J. Wiley, New York, 1980.

13. H. A. Kramers, *Atti. Congr. Int. Ficici*, Como, **2**, 545 (1927).

14. R. de L. Kronig, *J. Opt. Soc. Amer.*, **12**, 547 (1926).

15. R. B. Bird, R. Armstrong and O. Hassager, "Dynamics of Polymeric Liquids," J. Wiley, New York, (1977).

16. P. E. Rouse, *J. Chem. Phys.*, **21**, 1272 (1953).

17. M. Schmidt and W. Burchard, *Macromolecules*, **14**, 370 (1981).