Can the Gel Point of a Cross-linking Polymer Be Detected by the G' — G'' Crossover?

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Dynamic mechanical measurements allow direct determination of the instant at which a network polymer gels. In such an experiment, the evolution of $G'(t,\omega_0)$ and $G''(t,\omega_0)$ is measured in small amplitude oscillatory shear as a function of cross-linking time t. The frequency ω_0 is kept constant throughout. At the beginning of the experiment, G'' is orders of magnitude larger than G', and at completion of reaction, this order is reversed. It recently has been suggested by Tung and Dynes that the gel point (GP) might occur at the time at which G' and G'' cross each other. However, there is much dispute whether GP occurs exactly at the crossover or just somewhere in its vicinity. This study resolves the dispute by modeling the rheological behavior at GP: There is only one class of network polymers for which GP coincides with the crossover. This class of polymers exhibits, when reaching GP, power law relaxation $G(t) \sim t^{-n}$ with a specific exponent value $n = \frac{1}{2}$. Examples are stoichiometrically balanced network polymers and networks with excess cross-linker, however, only at temperatures much above the glass transition. Otherwise, the power law behavior would be masked by vitrification. Power law relaxation seems to be property of polymers at GP in general. However, some polymers have a different exponent value, $n \neq \frac{1}{2}$, in which case the crossover occurs before GP (for $n < \frac{1}{2}$) or after GP (for $n > \frac{1}{2}$); i.e., the crossover cannot be used for detecting GP. While there are no networks known to us with $n < \frac{1}{2}$, recent experiments showed that network polymers that are lean on cross-linker exhibit power law relaxation with $n > \frac{1}{2}$. A new method is suggested for measuring GP of these imbalanced networks.

INTRODUCTION

A widely believed myth states that the *gel point* (GP) of a cross-linking polymer occurs the instant at which the complex moduli, G' and G'', cross each other [1]. It refers to an experiment in which the evolution of the complex moduli of a cross-linking sample is measured in small amplitude oscillatory shear at constant frequency (see *Fig. 1*). Confusion arises from the fact that the above statement is true for some network polymers and wrong for others. The purpose of this study is to define clearly the specific class of network polymers for which GP occurs at the crossover point. For other classes of network polymers, less restrictive rheological methods of detecting GP can be suggested.

The gel point of a chemically cross-linking system is defined unambiguously by the instant at which the weight average molecular weight diverges to infinity. As a consequence, the cross-linking polymer undergoes a transition from liquid to solid state. This phenomenon is called *chemical gelation* to distinguish it from physical gelation in which the network is formed by reversible association mechanisms. This study is solely concerned with chemical gelation at temperatures much above the glass-transition temperature.

Knowing GP is important in polymer processing for several reasons: Shaping has to occur before GP while the polymer is still able to flow and stress can relax to zero. Exact knowledge of GP may allow for processing in the critical
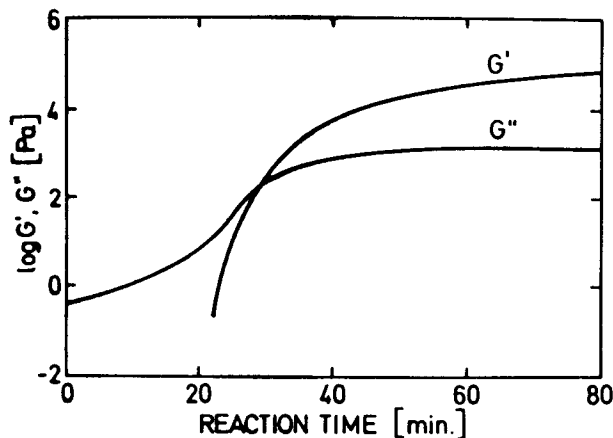
Fig. 1. *Evolution of loss modulus, G'', and of storage modulus, G', as a function of reaction time. The dynamic moduli are measured in small amplitude oscillatory shear.*

gel state (near GP), and novel techniques of gel processing can be developed.

This liquid/solid transition occurs at a critical reaction time, t_c, or at a critical extent of cross-linking, p_c, which depends on molecular structure. For model networks, Flory (2, 3) and Stockmayer (4) and later Gordon (5) and Macosko and Miller (6) predicted p_c as a function of cross-link functionality and stoichiometric ratio. The predictions have been found in close agreement with experiment despite differences between molecules of ideal networks and real polymer samples (7). This suggests that GP can be detected by monitoring the degree of cross-linking and waiting until it has reached the theoretical p_c value. However, the degree of cross-linking is difficult to measure with sufficient accuracy. Instead, one commonly measures the extent of reaction, which is not the same in case of side reactions that parallel the cross-linking reaction (8).

This paper is solely concerned with determining GP by rheological methods and does not mention other important physical methods that are based on extrapolation (examples: sol fraction, light scattering in dilute solution, self-diffusion) or on direct measurement (examples: nuclear magnetic resonance (NMR), sound absorption, dielectric properties). However, numerous solution swelling experiments confirmed that the rheologically observed GP coincides with the transition from a completely soluble state to an insoluble state (9).

The most common rheological tests for detecting GP measure the appearance of an equilibrium modulus (10, 11) or the divergence of the steady shear viscosity (7, 11–14). Measurement of the equilibrium modulus is extremely difficult since its value is zero at GP and it remains below detection limit for considerable time.

Measuring the diverging steady shear viscosity for approximately locating GP has the advantage that the experiment is extremely sim-

ple. It has, however, severe disadvantages that do not seem to be discussed in the literature:

1. GP is found by extrapolation. The actual experiment ends some time before GP when the stress causes overload of the instrument or sample breakage.
2. Near GP, the relaxation times become very long and steady shear flow cannot be reached in the transient experiment.
3. Near GP, the liquid behaves shear thinning in some unknown fashion.
4. The network structure near GP is very fragile. It most probably gets broken by the shear flow experiment, causing an apparent delay in gelation.
5. Infinite viscosity is not an unambiguous indicator of GP. It can be equally caused by other phenomena such as glass transition or phase separation.

Rheology can give a much more precise definition of GP. This will be discussed in the following, starting with rheology during gelation and then suggesting possible measures of GP.

EVOLUTION OF LINEAR VISCOELASTICITY AT INCREASING DEGREE OF CROSS-LINKING

The evolution of rheological properties during cross-linking can be best described with the frequency-dependent dynamic viscosity $\eta^*(\omega,p)$ or the time-dependent relaxation modulus $G(t,p)$, using the conversion of reaction, p, as parameter. The following discussion is based on the experimental studies of Chambon, Winter, et al. (15–19) on end-linking networks at temperatures much above the glass-transition temperature. Details of the experiments can be found in these publications and shall not be repeated here.

The dynamic viscosity evolves gradually as the cross-linking reaction proceeds. This is schematically shown in Fig. 2. The components (in this example) are initially of low molecular weight. This results in a low viscosity, independent of frequency, and no elasticity. With increasing conversion p, the viscosity increases (and some elasticity sets in). At low frequency, the viscosity is constant (slope 0). Shear thinning (frequency dependence) is observed at high frequencies, with an onset frequency that shifts to lower and lower values as GP is approached $(p \rightarrow p_c)$.

At GP, the magnitude of the dynamic viscosity follows a power law

$$\eta^*(\omega,p_c) = \frac{\pi}{\Gamma(n) \sin (n\pi)} S\omega^{n-1}. \qquad (1)$$

S is a material constant and n is the network specific relaxation exponent. The onset of shear thinning has shifted to the zero frequency limit, $\omega \rightarrow 0$; i.e., the material behaves shear thinning at all frequencies. Beyond GP, the dynamic viscosity grows further, with a dramatic increase

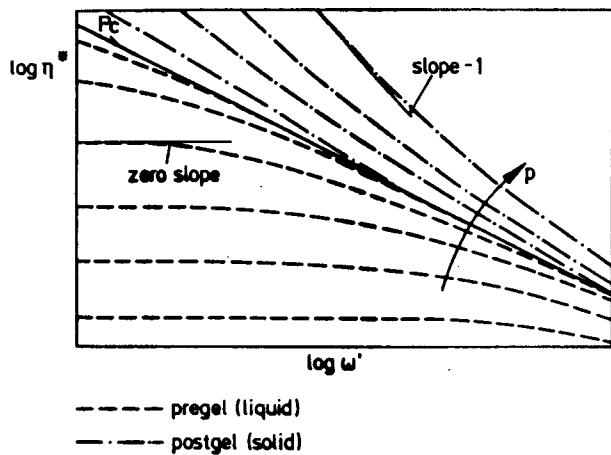— — — — pregel (liquid)

— · — — postgel (solid)

Fig. 2. Frequency dependence of dynamic viscosity as measured in a small amplitude oscillatory shear experiment (schematic drawing in accordance with data of Chambon and Winter, 1985). Parameter is the degree of cross-linking, p.

(slope of −1) at low frequencies as expected from a solid.

The gel transition can be detected just by the curvature of the viscosity curve in the log-log plot. The curvature is negative before GP, zero at GP (power law), and positive beyond GP.

The linear viscoelastic behavior alternatively can be expressed through the relaxation modulus $G(t,p)$ (see Fig. 3). The initial material of low molecular weight relaxes rapidly, beyond detection limit of our rheometer. With increasing conversion, the relaxation modulus grows, the relaxation times become noticeably longer, and the time-dependent modulus approaches a straight line in the log-log plot. It was a surprising discovery (15, 16) that the relaxation modulus of the critical gel follows a power law. The stress can still relax to zero even if it requires infinite time. Just beyond GP, the short time relaxation is not affected immediately. However, at long times the modulus approaches a finite value which is called equilibrium modulus. This equilibrium modulus grows further as the cross-linking reaction is driven to completion.

The maximum relaxation time of the cross-linking system undergoes an interesting evolution. The initial relaxation time is very short since the molecular weight of the reaction components is low. Near GP, the relaxation time rises sharply. At GP, it diverges to infinity and the relaxation spectrum does not contain a characteristic time any more. Beyond GP, the relaxation time decreases. The maximum relaxation time of the final network is again very short, provided that the network has reached a high degree of perfection. The final relaxation time is expected to be of the same order as the initial one.

It has not yet been possible to model the entire evolution of linear viscoelasticity in a constitutive equation. However, knowledge of the me-

— — — — — pregel (liquid)
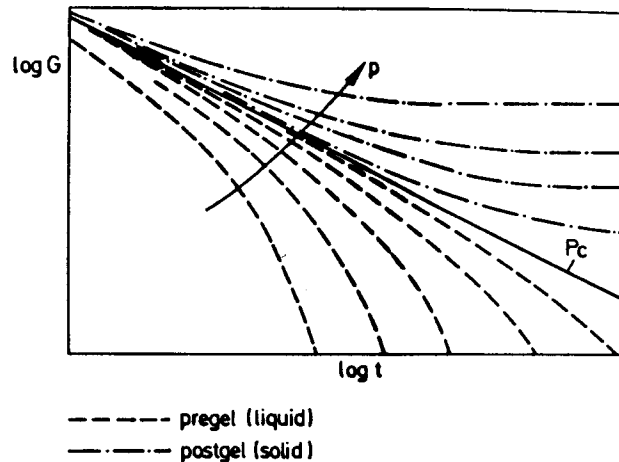
— · — — — postgel (solid)

Fig. 3. Linear viscoelastic relaxation modulus as determined from oscillatory shear data.

chanical behavior directly at GP is sufficient to determine GP experimentally. This will be discussed in greater detail.

LINEAR VISCOELASTICITY AT THE GEL POINT

The polymer "at GP" is characterized by a limiting behavior for both the viscoelastic liquid in the pregel region and the viscoelastic solid in the postgel region. However, a real sample cannot be directly at GP. The sample might be arbitrarily close to GP, but it is either still a liquid or already a solid. Such a sample very close to GP will in the following be called a critical gel or a network polymer at GP.

Stress relaxation at GP was found to occur in a power law:

$$G(t) = St^{-n}; \qquad p = p_c \qquad (2)$$

where the strength S depends on the flexibility of molecular chains and cross-links, and on the cross-link density at GP. The relaxation exponent may have values

$$0 < n < 1.$$

Stoichiometrically balanced end-linking networks were found (16) to relax with $n = \frac{1}{2}$ while stoichiometrically imbalanced networks follow (18, 19)

$n = \frac{1}{2}$ for excess of cross-linker and

$n > \frac{1}{2}$ for lack of cross-linker.

The relaxation modulus can be introduced into the general constitutive equation for the linear viscoelastic region (20) and thus obtain the gel equation (16):

$$\tau(t) = S \int_{-\infty}^{t} (t - t')^{-n} \dot{\gamma}(t') \, dt', \qquad p = p_c. \qquad (3)$$

With the gel equation, many new rheological experiments may be invented for detecting GP.

DETECTION OF GEL POINT BY RHEOLOGICAL EXPERIMENT

It is especially simple to detect the instant of gelation of a network that relaxes with $n = \frac{1}{2}$. A relaxation modulus $G(t) = St^{-\frac{1}{2}}$ gives congruent moduli:

$$G'(T,\omega) = G''(T,\omega) = \sqrt{\pi/2}\ S(T)\ \omega^{\frac{1}{2}}, \quad p = p_c \quad (4)$$

and a loss tangent:

$$\tan \delta = G''/G' = 1. \quad (5)$$

For any frequency or temperature, the storage modulus has the same value as the loss modulus. This confirms small amplitude oscillatory shear as an experiment in which GP is reached when G' and G'' cross each other and, hence, tan δ is equal to 1. This is the only class of network polymers for which GP can be detected by the crossover.

Detection of GP is more complicated when the relaxation exponent is not equal to $\frac{1}{2}$. The dynamic moduli of the system at GP follow the same power law, however with different front factor. They do not coincide at GP, but they are parallel:

$$G' = \frac{G''}{\tan (n\pi/2)} = \frac{\pi}{2\ \Gamma(n)\ \sin (n\pi/2)} S\omega^n. \quad (6)$$

The gel point has to be found through the power law relaxation behavior, which can be detected in many different ways. Two examples come to mind immediately:

1. The loss tangent of GP,

$$\tan \delta = G''/G',$$

is independent of the frequency of the dynamic experiment. A multifrequency experiment might be designed for detecting GP (21).

2. The transient viscosity during the start-up of shear flow follows a power law. This might be utilized for detecting GP. The total strain has to be kept small since, near GP, stress relaxation occurs infinitely slow and shear modification cannot be avoided even at extremely low rate of deformation.

With dynamic mechanical experiments, the instant of gelation can be measured as precisely as the accuracy of the rheometer permits. This is a major advantage over the extrapolation methods that were discussed in the introduction. The strain is kept small, and any shear modification of the molecular structure is avoided. This is a specific advantage over the method that detects GP by diverging viscosity.

CONCLUSIONS

The critical gel must have the property $G'(\omega) = G''(\omega)$ for any frequency ω; then the $G' - G''$ crossover coincides with the gel point (GP). This condition is only satisfied if stress relaxation in the critical gel follows a power law $t^{-\frac{1}{2}}$. The exponent must be exactly $-\frac{1}{2}$ (16). Stoichiometrically balanced network polymers far away from their glass-transition temperature exhibit such behavior (16, 17).

For other network systems at GP, stress relaxation also occurs in a power law; however, the relaxation exponent has a different value, $n \neq \frac{1}{2}$. GP clearly does not coincide with the $G' - G''$ crossover. GP occurs earlier than the crossover for $n > \frac{1}{2}$. Such behavior has been found with stoichiometrically imbalanced systems that are lean on cross-linker (18, 19).

In general, the instant of gelation can be measured by rheology. For that purpose, we suggest dynamic mechanical measurements that evolve monotonously without exhibiting a singularity at GP. The dynamic rheological properties would not immediately indicate GP. However, detection of GP is made relatively easy by the fact that stress relaxation in a critical gel (network polymer at GP) occurs in a power law. Equivalently, the dynamic moduli and the dynamic viscosities follow a power law in frequency. This power law behavior can be detected in a rheological experiment, and it may be used to measure GP. The characteristic dynamic behavior during chemical gelation allows one even to distinguish between the fluid state before GP and the solid state beyond GP.

It should be emphasized again that power law behavior at GP is restricted to temperatures much above the glass transition. The dynamic mechanical behavior would be considerably more complicated if vitrification would interfere with the chemical gelation (22). Furthermore, the power law relaxation behavior has been only observed with end-linking systems. It might also occur with other systems and the range of validity will have to be studied in further experiments.

ACKNOWLEDGMENT

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