GEL POINT

1. Introduction

The gel point (GP) marks the transition of an amorphous material from liquid to solid due to gelation. The transition is caused by the growth of connected structure in the material, a structure that correlates molecular or supramolecular motion over large distances. The internal size distribution broadens in the approach of GP, as shown for chemical gelation (1,2), and the maximum correlation length diverges to infinite size at GP. This appearance of long-range connectivity greatly affects physical properties in general but is most easily seen in rheological experiments (3). Before reaching the GP connectivity, the material is able to flow and to relax while, beyond GP, stress and/or strain invariants need to exceed a yield value to allow flow. Depending on connectivity mechanism, the wide variety of gels are often grouped into two classes (4,5), chemical gels and physical gels.

This article is dedicated to chemical and physical GP phenomena. Not covered are other liquid-to-solid transitions of amorphous materials such as the glass transition (6–9) or the stress-induced solidification by jamming (10). Gelation and the glass transition are similar rheologically. For both classes of amorphous materials, the relaxation time spectrum broadens and adopts power law format near the transition (11), but the power law exponent is positive for the glass transition and negative for gelation, that is the relaxation patterns of gelling fluids and glass formers are inverse near the transition. This provides a decisive criterion that distinguishes gelation from the glass transition.

A polymer at its GP is in a critical state (12–17) and commonly is called a *critical gel* (18) to distinguish it from the various materials that are called *gel*. It is interesting to explore the properties of the critical gel and use these as reference for describing the properties in the vicinity of the GP. The critical gel affords universal rheological properties that are intermediate between liquid and solid, including the temperature shift factors, which also adopt in-between values (19). The critical gel combines extreme ductility and fragility when subjected to large strain. Its high adhesion strength (tackiness) is also an expression of the intermediate state; the critical gel still maintains the wetting properties of the liquid (low molecular weight polymer) while starting to gain the cohesive strength of the solid. The adhesion behavior must be accounted for when designing experiments with gels. It also suggests future applications of gels as adhesives.

The molecular structure at GP is mobile and fragile since large-scale molecular connectivity is barely established while the majority of the constituents are of smaller size. Materials at or near GP are typically far from thermal equilibrium

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due to the diverging internal length scales, which cause structural rearrangements to be very slow (“critical slowdown” at GP). The slow structural dynamics becomes apparent in rheological experiments that probe the long-time behavior. The evolution of viscoelastic properties near GP varies greatly from material to material due to the rich variety of molecular and supramolecular bonding mechanisms. However, as will be discussed below, an exception is the “critical gel,” the material directly at the GP, for which the rich rheological diversity converges to a universal dynamical state of reduced rheological complexity. Typical linear viscoelastic features of critical gels are (1) the stress requires an infinite time to relax, (2) relaxation occurs in a broad distribution of modes, and (3) the long-time tail of the relaxation time spectrum is self-similar, which expresses itself in a power law with strength S and exponent values ($-n_c$) between –1 and 0, depending on material details. Chemically gelling materials share many of their properties with physically gelling materials, but the two material classes are sufficiently different to warrant their own discussion.

It is quite common to use $G'(\omega)$, $G''(\omega)$ data to detect the GP. Often misunderstood is the property $G'(\omega) \neq G''(\omega)$ at GP. GP may occur before or after a possible intersect of $G'(\omega)$ and $G''(\omega)$. Useful for GP detection, however, is the phenomenon that $G'(\omega)$ and $G''(\omega)$ are parallel to each other at GP, which causes $\tan\delta$ to be independent of frequency (at low frequencies). This GP property will be discussed below.

The information most needed when working near the GP can be summed up in the following questions:

- When does GP occur?
- How soft or stiff is the material at GP?
- How fast does the material pass through GP?
- How fragile is the material near GP (reversible or irreversible structuring at large stress or strain)?

These questions can be answered with the knowledge of the properties at GP. The simplicity and universality of the GP behavior, as shown below, suggests the use of the critical gel as a reference state for developing soft matter and for materials processing near GP.

2. Rheological Properties of the Critical Gel

The evolution of equilibrium mechanical properties during gelation is schematically shown in Figure 1 (using the example of chemical gelation). The steady shear viscosity of the liquid state grows as the connectivity increases. In the approach to GP, the steady shear viscosity diverges (ie, an infinite time would be necessary for the flow to reach steady state). Beyond GP, the equilibrium modulus starts to grow. At GP, the viscosity is infinite whereas the equilibrium modulus is still zero because the stress in a deformed critical gel can still relax completely. This shows that the conventional equations for a liquid (characterized by a steady shear viscosity) or for a solid (characterized by an equilibrium modulus) do not apply at GP. The critical gel has its own rheological behavior.

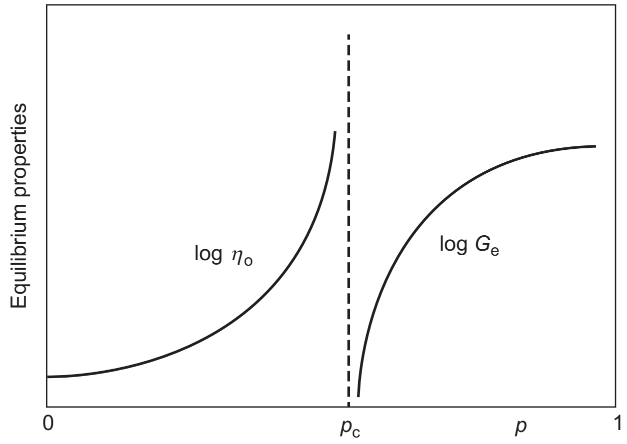

Fig. 1. Evolution of mechanical properties during the gelation of a cross-linking polymer. Parameter is the bond probability or extent of cross-linking p (schematic). Representative properties are the *steady shear viscosity* for the liquid state (sol) and the so-called *equilibrium modulus* for the solid state (gel). Viscoelastic liquid states are in between the Newtonian liquid ($p = 0$) and the critical gel ($p = p_c$). Equivalently, viscoelastic solids are in between the critical gel and the Hookean solid ($p = 1$).

The GP expresses itself in slow power law dynamics for both the linear relaxation modulus $G(t)$ and the relaxation time spectrum $H(\tau)$ (20–22)

$$G(t) = St^{-n_c} \quad \text{for } \tau_0 < t < \infty; \quad H(\tau) = S\tau^{-n_c}/\Gamma(n_c) \quad \text{for } \tau_0 < \tau < \infty \tag{1}$$

This rheological pattern seems to be a universal rheological property, since experiments with a large variety of chemically or physically gelling materials show this self-similar behavior without exception. The gamma function, $\Gamma(n_c)$, arises naturally in the conversion of $G(t)$ into $H(\tau)$. The two material parameters are the stiffness S and the relaxation exponent n_c. Subscript c is used here to identify the critical state at the GP. The lower time limit, τ_0, marks the crossover to material-specific small-scale dynamics of the building blocks of the critical gel. Unresolved is the situation with the physical dimension of the strength, $S[Pa\ s^{n_c}]$, which indicates that S is a composite property $S = G_0\ \tau_0{}^{n_c}$ of some sort (19).

In comparison, a power law behavior has been predicted for molecules of self-similar (fractal) structure (23,24), suggesting that the critical gel is self-similar over a wide range of length scales (18,25). It also has been shown, without use of an analogy, that the onset of rigidity in a randomly cross-linked system is a continuous phase transition (26); at the transition, the correlation length diverges and the system necessarily became self-similar. The scaling behavior is then an automatic consequence of statistical thermodynamics. Several theories have been proposed for the critical gel behavior (2,27,28).

The relaxation exponent n_c may assume values in the range $0 < n_c < 1$ (21,28). Its value cannot be predicted at current state of knowledge. A systematic study of the effect of molecular architecture on the value of the relaxation exponent is still missing. Typical experimental values are as follows:

$n_c \cong 0.5$ for end-linking networks with balanced stoichiometry (20,22,29)
$n_c \cong 0.5$–0.7 for end-linking networks with imbalanced stoichiometry (20,22, 30)
$n_c \cong 0.7$ for epoxies (31)
$n_c \cong 0.8$ for PVC plastisol (32)
$n_c \cong 0.3$ for radiation cross-linked polyethylene (33)
$n_c \cong 0.5$ for micellar block polyelectrolytes (34)

The gel strength S depends on the value of n_c. A large value of S is always associated with a small value of n_c (35). Very little information is available about this relation between S and n_c.

The low-frequency modulus of the critical gel, as described by equation 1, is a power law:

$$G^*(\omega, p_c) = \Gamma(1 - n_c)\ S\omega^{n_c} \quad \text{at GP} \tag{2}$$

The real (the storage modulus G') and imaginary (loss modulus G'') parts are parallel to each other

$$G'(\omega, p_c) = G''(\omega, p_c) / \tan(n_c\pi/2) = \Gamma(1 - n_c)\ S\omega^n \cos(n_c\pi/2) \tag{3}$$

As a consequence, the phase shift δ, defined by the loss tangent $\tan\delta = G''/G'$, does not depend on frequency and is proportional to the ω slope of the dynamic moduli at GP (21):

$$\delta_c = n_c\pi/2 \tag{4}$$

In this way, small amplitude oscillatory shear data provide the two material parameters for GP, the strength $S = G'(\omega, p_c)/[\Gamma(1 - n_c)\ \omega^n \cos(n_c\pi/2)] = G''(\omega, p_c)/[\Gamma(1 - n_c)\ \omega^n \sin(n_c\pi/2)]$ and the relaxation exponent $n_c = 2\delta_c/\pi$. Inserting their values into the general constitutive equation of linear viscoelasticity (36,37) results in a constitutive equation for critical gels, the Winter–Chambon gel equation: (20,21)

$$\sigma(t) = S\int_{-\infty}^{t} \mathrm{d}t'\,\left(t - t'\right)^{-n_c} \dot{\gamma}\left(t'\right) \quad \text{at GP} \tag{5}$$

where $\sigma(t)$ and $\dot{\gamma}(t')$ are the stress and rate of strain tensor. The gel equation predicts all known rheological properties of critical gels, such as infinite viscosity and zero equilibrium modulus, as long as the applied strain is small. For large strains, a suitable strain measure must be introduced (20). Large strain behavior and breaking of the structure (reverse gelation by mechanical field) is not included in this equation. The breaking of critical gels (38) is a topic which needs to be investigated more closely in the future.

Since its discovery in 1985, the power law spectrum at the GP has been found for a wide range and diverse chemical and physical gels. Recent examples are studies by Morris and co-workers (39), Ghiringhelli and co-workers (40), Aliaghaie and co-workers (41), Aoki (42), Bonino and co-workers (43), Ng and co-workers (44), and Eberle and co-workers (45).

3. Chemical Gel Point

Chemically cross-linking polymers belong to the group of network gels. Molecules cross-link into large clusters through covalent bonds. The independent variable of the cross-linking process is the extent of reaction, p, which can be understood as bond probability. The polymer reaches the GP at a critical extent of the cross-linking reaction, $p \to p_c$. At GP, the second moment of the cluster size distribution diverges (15) and the molecular weight distribution is infinitely broad ($M_w/M_n \to \infty$) as molecules range from the smallest unreacted oligomer to the infinite cluster. The molecular motions are correlated over large distances but the critical gel has no intrinsic size scale. The liquid polymer before the GP, $p < p_c$, is called a *sol* because it is soluble in good solvents. The solid polymer beyond the GP, $p_c < p$, called a *gel* is not soluble any more, even in a good solvent. However, unattached molecules (sol fraction) are still extractable from the gel.

3.1. Prediction of the Chemical Gel Point.

Classical mean field theories (46–48) are able to predict the critical conversion p_c quite accurately (49,50). The predictions are mainly based on the assumptions that all functional groups of the same type are equally reactive, all groups react independently of one another, and no intramolecular reactions occur in finite species. The threshold p_c depends on the geometry of the network-forming species. Special cases follow.

Case 1. Homopolymerization of similar f-functional molecules:

$$p_c = 1/(f - 1) \tag{6}$$

The same relation is found for the end-linking of molecules of low functionality ($f = 3$ or 4) and for the vulcanization of long molecular chains. The average number of cross-linking sites along the chain is defined as

$$f = \sum_i f_i^2 n_f \Big/ \sum_i f_i n_f \tag{7}$$

with n_f being the number of molecules of functionality f_i.

Case 2. Cross-linking of f-functional molecules A_f with g-functional molecules B_g, which are mixed at a molar ratio $r = f(A_f)/g(B_g)$ reach their GP at a conversion

$$p_{A,c} = [r(f - 1)(g - 1)]^{-1/2} \tag{8}$$

with $p_B = r\,p_A$. For the formation of a gel, the stoichiometric ratio must be chosen between a lower and upper critical value:

$$r_l = [(f - 1)(g - 1)]^{-1} \quad \text{and} \quad r_u = 1/r_l \tag{9}$$

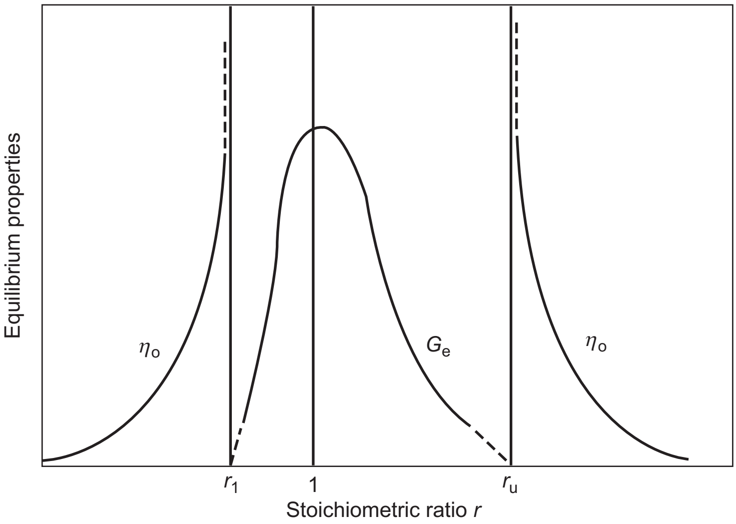

Fig. 2. Steady-state mechanical properties (schematic) of cross-linking polymers with different stoichiometric ratios r, defined as ratio of cross-linking sites of two reacting polymers. The reaction is presumably brought to completion. Steady critical gel behavior is found at the lower and the upper critical values, r_l and r_u.

Otherwise the reaction stops before reaching the GP. The relations in equation 9 follow from equation 8 when considering species A_f or species B_g fully reacted, respectively.

The *stoichiometric ratio* is often chosen as an independent variable of a chemical gelation experiment. Consider a system that consists of cross-linker A (average functionality $f = 3$ or $f = 4$, and so on) and chain extender B (functionality $g = 2$). Assuming that the reaction is always brought to completion, the degree of cross-linking would depend on the stoichiometric ratio r (ratio of cross-linker sites to chain extender sites). The stoichiometry dependence of equilibrium mechanical properties is sketched in Figure 2. The cross-link density is maximum for balanced stoichiometry, r_{st}. The viscosity diverges at a lower and an upper critical ratio r_l and r_u of equation 9. Solid behavior is found everywhere at intermediate stoichiometry $r_l < r < r_u$. It should be noted that the supramolecular cluster formation is not symmetric around $r = r_{st}$. This reflects in the rheology, which is very different for negative or positive $\Delta r = r - r_{st}$ (21,51). Critical gels are formed at $r = r_l$ and $r = r_u$.

4. Physical Gel Point

Physical gels are able to form sample-spanning, supramolecular structures. Connectivity has been found with a wide range of mechanisms, see reviews by te Nijenhuis (52), Larson (53), and Nishinari (54). Physical gels come as both, network materials (associative networks) and repulsive gels. Such repulsive gels can energetically associate into a sample-spanning structure by repulsion instead of attraction, leading to nonequilibrium gel states (5,34). In analogy to chemical gelation, the physical gelation is defined by the growth of physically connected aggregates and the physical GP is reached when the correlation length of molecular (or supramolecular) motion diverges to infinity. Physical gels connect in a rich variety of bonds, which vary with pH value, concentration of connecting component, charge density, crystalline junctions, or stress level. Gels with temperature-dependent connectivity are called *thermo-reversible* (55).

The principal differences between chemical and physical gels lie in the lifetime and the functionality of the junctions. Chemical bonds are considered to be permanent (gels with significant reverse reactions are exceptions (56)), whereas the physical junctions have finite lifetimes (but also might be long lived (57)). Physical junctions are constantly created and destroyed, however, at very low rates so that the network appears to be permanently connected if the time of observation is shorter than the lifetime of the physical network. The constant renewal of bonds is attractive for many applications, which require the healing of broken structure (self-healing property of physical gels).

Different from chemical gelation, physical junctions are typically held together by multiple bonds, possibly of higher functionality, which all have to open eventually before flow or stress relaxation may happen. Even if bond fluctuations occur frequently, they might not manifest themselves in rapid macroscopic events. The finite lifetime of bonds, however, allows new conformations of the material's constituents with time. These have been observed as aging (59), self-healing (60), and slow creep at low stress levels (61). Creeping flow occurs even at low stress when bond openings release stress locally and cause infinitesimal strain events. Over time, many such infinitesimal strain event accumulate into a macroscopic strain and the material can be viewed as viscoelastic liquid (62,63).

The characteristic renewal time,$\tau_{\rm pg}$, of the physical junctions determines long-time ordering processes and rheology of a physical gel. Physical gels behave as liquids for applications that last longer than the renewal of entire junctions. The analogy between physical and chemical gelation applies only to timescales shorter than the characteristic renewal time. Equation 1 changes into

$$G(t) = S_c t^{-n_c} \quad \text{for} \quad \tau_0 < t < \tau_{\rm pg} \tag{10}$$

Physical gels typically have a yield stress or strain beyond which the structure gets broken and liquid behavior sets in (64). Yielding criteria involve invariants of stress, strain, or strain rate as appropriate for shear, extension, or a combination thereof. Below yielding, a physical gel is a solid at experimental times shorter than the bond renewal time and it is a liquid at experimental times longer than the renewal time.

5. Range of the Power Law

The power law of the critical gel of a cross-linking polydimethylsiloxane (PDMS) was found for G' and G'' to extend over a frequency range of more than five decades (21,22), the entire experimental range. A lower frequency limit is given by the correlation length, which is the linear size of a typical cluster of the self-similar structure. This correlation length diverges at GP, and the lower frequency limit of the power law could theoretically be extended to zero. However, a practical lower frequency limit is given by the finite sample size, that is at a scale of observation that exceeds the size of the sample in the rheometer. The upper frequency limit of the power law behavior very much depends on the dynamics of the small-scale structure of the critical gel.

For chemical gelation, the upper frequency limit (and the corresponding lower time limit, τ_0, of eqs. 1 and 10 typically depends on the following two molecular sizes:

1. *Size of the chains between cross-links*: The randomly coiled chains exhibit self-similar behavior, and the transition from the self-similar critical gel to the self-similar chain (between network junctions) is difficult to detect experimentally.
2. *Glass length*: At very high frequency, the scale of observation decreases below the lower scaling length of the polymer called the *glass length*. The *glass length* is given by the size of the network element that determines the transition to glassy behavior at high frequency. This smallest network element depends on the specific molecular structure. It could be the distance between cross-links or the length of a chain unit. At this small-length scale, vitrification dynamics becomes important and deviation from equilibrium self-similar behavior is expected. In this description of chemical gelation, it is tacitly assumed that the scale of observation is sufficiently larger than the glass length. The details of the molecular structure are neglected by neglecting the high frequency transition to the glass behavior of the chemical networks.

Physical critical gels often have a very limited power law region. The slow dynamics is governed by the transition to flow behavior as an expression of the finite lifetime of the physical junctions. The faster dynamics undergoes transition to the dynamics of the structural building blocks. These building blocks are typically quite large in physical gels so that their dynamics can be seen at low frequency. Between these two phenomena, little may remain of the self-similar dynamics of the critical gel. General relations are difficult to find because of the large variety of physical connectivity mechanisms. Nonequilibrium states make the power law parameters path-dependent, that is they depend on the history of the gel formation.

6. Vicinity of the Gel Point

For a material, which passes through its GP, the power law region seems to stretch out and then contract again, having its widest range at GP. The slope gradually decreases during gelation. This phenomenon is visible on cross-linking of PDMS (21,22), and it is very pronounced for radiation cross-linking of polyethylene (33). It is found in physical gels (32,34,52,54,55,57,58,65,67) as well as in chemical gels.

The longest relaxation time $\tau_{\max}$ first grows to infinity and then decays again. In the vicinity of GP, this may be expressed in power laws (68):

$$\tau_{\max} \sim \begin{cases} (p - p_c)^{-s/(1-n_c)} & \text{for} \quad p < p_c \\ (p_c - p)^{-z/n_c} & \text{for} \quad p_c < p \end{cases} \tau_{\max} \tag{11}$$

These equations hold for small values $|p - p_{\mathrm{c}}|$, that is in the vicinity of GP. Materials near GP are often called *nearly critical gels*. The exponents depend not only on the dynamic critical exponent (relaxation exponent n_{c}) but also on the dynamic exponents s and z for the viscosity $\eta \sim (p_{\mathrm{c}} - p)^{-s}$ and the equilibrium modulus $G_{\mathrm{e}} \sim (p - p_{\mathrm{c}})^{z}$. If one, in addition, assumes symmetry of the diverging $\tau_{\max}$near the GP

$$\frac{s}{1 - n_c} = \frac{z}{n_c} \tag{12}$$

then the critical exponents are related as (68)

$$n_c = \frac{s}{s + z} \tag{13}$$

Into these relations, one may introduce specific values (s, z) from percolation theory or from branching theory and determine the corresponding values for n_{c}. The wide range of values for the relaxation exponent $0 < n_{\mathrm{c}} < 1$ lets us expect that the dynamic exponents s and z are nonuniversal. Since s and z can be predicted from theory (14–17,69), n_{c} values can be calculated from equation 13. This result, however, relies on the symmetry hypothesis, which does not seem to be generally valid, at least not for highly entangled polybutadienes (70).

The slow dynamics of a system, for which the relaxation time goes through a singularity, can be described with a discrete relaxation time spectrum with a longest relaxation time $\tau_{\max}(p)$ that diverges at GP:

$$G(t, p) = G_e + \frac{S}{n\,\Gamma(n)\ \tau_{\max}^{n}} \sum_{i=1}^{\infty} \exp\left(-\frac{t i^{1/n}}{\tau_{\max}}\right) \tag{14}$$

Its four parameters G_{e}, S, $\tau_{\max}$, and n all depend on the bond probability p. In the liquid below GP and at GP, the equilibrium modulus is equal to zero, $G_{\mathrm{e}} = 0$. For $n = 0.5$ and $G_{\mathrm{e}} = 0$, this spectrum reduces to the well-known Rouse spectrum. It is remarkable that depending on the value of $\tau_{\max}$, the Rouse spectrum describes a viscoelastic liquid that includes the Newtonian liquid ($\tau_{\max} \to 0$) and the critical gel ($\tau_{\max} \to \infty$) as limiting cases.

Alternatively to equation 14, a cutoff function $F(t, \tau_{\max})$ may be applied to the equation of the critical gel, equation 1:

$$G(t, p) = G_e + S t^{-n} F(t, \tau_{\max}) \tag{15}$$

The model reduces to the power law at the GP $F(t, \tau_{\max}) \to 1$ for $\tau_{\max} \to \infty$. The stretched exponential cutoff function (71)

$$F(t, \tau_{\max}) = e^{-(t/\tau_{\max})^{\beta}} \text{ with } 0 < \beta < 1 \tag{16}$$

was found to give good results with a curing epoxy polymer (72).

7. Measurements of Instant of Gelation

7.1. Equilibrium and Steady-State Rheological Measurements. The appearance of an equilibrium modulus or the divergence of the steady shear viscosity might be used to estimate the position of the GP by extrapolation. Extrapolation is necessary because these measurements fail in the close vicinity of GP. Measurement of the equilibrium modulus (73,74) is extremely difficult because its value remains below the detection limit for a considerable time, and it, theoretically, requires an infinite time to perform the measurement. It should be noted that a nonequilibrium state might get trapped near GP so that the equilibrium state is not attainable, even after long experimental times.

The diverging steady shear viscosity (75–77) helps to find the location of GP. The seeming simplicity of the viscosity measurement, however, is deceiving. It has severe shortcomings:

1. GP is found by extrapolation of an experiment which only asymptotically reaches steady state since the longest relaxation time diverges at GP.
2. The network structure near GP is very fragile, and most likely gets broken during the viscosity measurement, causing an apparent delay in gelation or may induce reverse gelation.
3. Near GP, liquid behavior is shear thinning in some unknown way.
4. Infinite viscosity is not an unambiguous indicator of GP. It may be caused by other phenomena such as vitrification or phase separation.

For these reasons, steady-state measurements give only an apparent GP. The real and the apparent GP might be close together, but additional experiments will be needed to confirm such an assumption.

7.2. Transient Rheological Measurement. The nature of the critical gel suggests GP detection with transient measurements at small strain, which are possible even if the longest relaxation time diverges. A typical evolution of the linear relaxation modulus is shown in Figure 3. The GP power law is distinguished from the other states by being a straight line. It shows that the entire relaxation time spectrum is affected by the gel transition, but that none of the samples is exactly at GP. It was surprising to find that intermediate relaxation modes, which are accessible to experiment, already show the transition through GP even if the diverging longest relaxation time is not accessible to experiment. This GP property opens up the possibility of using low frequency rheology to distinguish between a sol and a gel (3,21,22). It is not necessary to measure the diverging longest relaxation time; measurement of intermediate relaxation

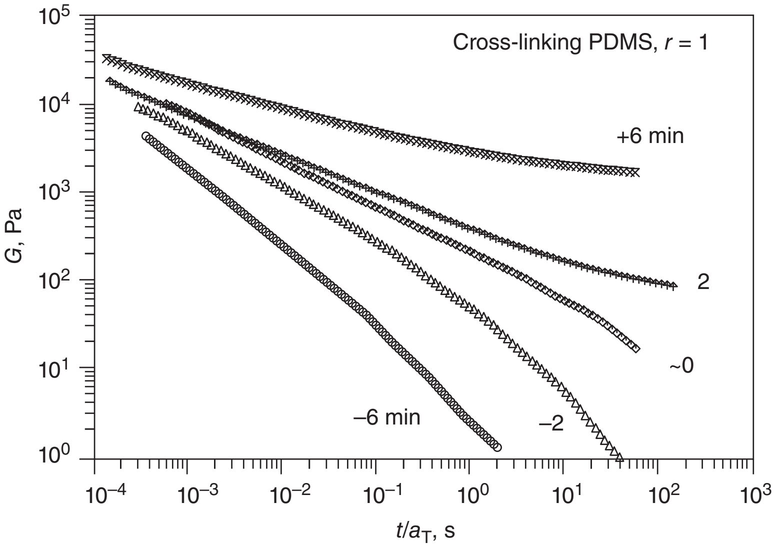

Fig. 3. Evolution of relaxation modulus of a cross-linking polymer as shown with five samples of increased cross-link density. Parameter is the reaction time distance from the GP ($t - t_c$). The values are calculated from dynamic mechanical data (20). The power law relaxation is limiting behavior for the liquid and the solid. One of the samples is very close to the critical gel. However, at very long times it deviates from the power law behavior. It is still a fluid.

modes suffice for detecting the GP in many different ways. Three examples are as follows:

1. At low frequencies, because of the GP powerlaw spectrum, eq.1, the loss angle δ becomes frequency independent at GP. Several GP detection methods find GP by sensing the instance, at which the loss angle δ becomes frequency-independent. Used for this purpose are the normalized loss angle $2\delta/\pi$, the loss tangent $\tan\delta = G''/G'$, the normalized storage modulus $G'/G^* = \cos\delta$, or the normalized loss modulus $G'/G^* = \sin\delta$. Figure 4 shows an example where GP is detected by the intersect of $\tan\delta$ curves (see Fig. 4). A multifrequency experiment has been designed for detecting the GP based on this approach (78). In this way, small amplitude oscillatory shear is especially powerful to show when a soft matter sample has reached its GP.
2. For start-up of shear flow at constant rate, the transient viscosity grows in a power law with time. This might be utilized for detecting GP. The total strain must be kept small because, near GP, stress relaxation is infinitely slow and shear modification cannot be avoided even at extremely low rates of deformation.
3. It is especially simple to detect the instant of gelation of a material whose critical relaxation exponent n_c is known. For any frequency (within the power law region) and any temperature, in a small amplitude oscillatory

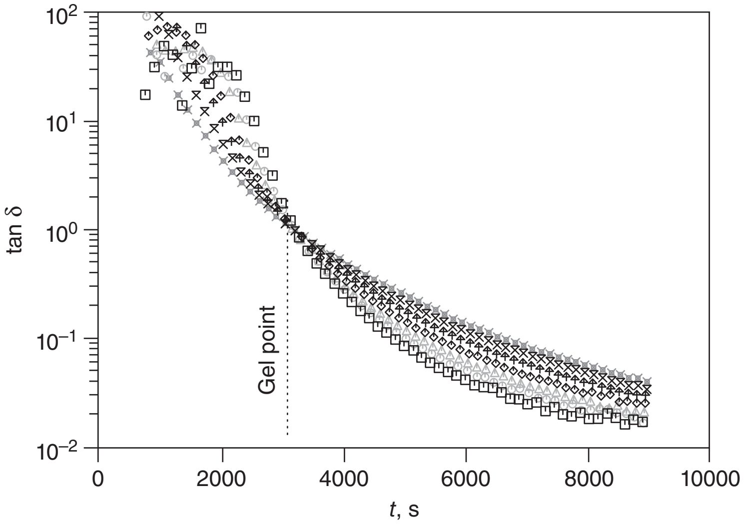

Fig. 4. Loss tangent of a chemically cross-linking polybutadiene as function of reaction time (70). Data were taken at several frequencies. The GP is marked by the instant at which the loss tangent is independent of frequency. All data are taken at low frequencies where the self-similar behavior prevails.

> shear experiment at constant ω_0, GP is reached at the instant at which functions $G'(\omega_0, t)/\cos(n_c\pi/2)$ and $G''(\omega_0, t)/\sin(n_c\pi/2)$ intersect (see eq. 3). In the special case of $n_c = 0.5$, this relation simplifies even further.

It should be noted that an intersect of G' and G'' does not indicate a GP in spite of many published claims to the contrary. The condition $G' = G$" does not occur at GP (79). The only exception is for $n_c = 0.5$.

With dynamic mechanical experiments, the instant of gelation can be measured as precisely as the accuracy of the rheometer permits, a significant advantage over extrapolation methods. An additional advantage is that the strain is kept small, and shear modification of the molecular structure is avoided. The main limitation is the finite experimental time, which tends to get long for data points at low frequencies. Rheological data points are only valid for low mutation number values (80). Rapidly gelling materials do not give sufficient time to the experimentalist to perform mechanical spectroscopy near the GP.

7.3. Nonrheological Methods. Dynamic light scattering has been developed as nondestructive and real-time determination of GP for both chemical and physical systems (81–83). Time-resolved dynamic light scattering not only allows one to determine the gelation threshold but also to investigate critical dynamics near the gelation threshold. At GP, a power law appears in the intensity–time correlation function. Specific features originate from unique aspects of gels such as nonergodicity and frozen inhomogeneities in addition to the divergence of the connectivity correlation.

7.3.1. Experimental Methods Specifically for Chemical Gelation. The predictability of the threshold value p_c suggests that GP can be found by monitoring the degree of cross-linking until it has reached the theoretical p_c value. However, the degree of cross-linking is difficult to measure accurately. Side reactions that parallel the cross-linking reaction (84,85) might interfere with the measurement. For practical purposes, these difficulties are avoided by saying that the polymer is before the GP (sol state) if it completely dissolves in a good solvent and beyond the GP (gel state) if it does not dissolve completely. Numerous solution swelling experiments have confirmed that the rheologically observed GP coincides with the transition from a completely soluble state to an insoluble state (21,22,29).

8. Applications

For many applications, in polymer processing for instance, it is sufficient to know when the liquid-solid transition occurs for the purpose of including it in an application process. In some cases, knowledge of GP might allow to avoid the GP all together. However, many manufacturing processes or other applications proceed while gelation is in progress and the transition from liquid to solid state traps non-equilibrium structural states. Polymers around the GP are used in a broad spectrum of applications such as gel processing, reactive processing (gel as intermediate state), and the development of new polymeric materials (adhesives, absorbents, porous catalysts, vibration dampers, membranes, colloidal glasses). Gelation is also important for soft matter outside the polymer field such as food technology, biological materials, pharmacology, soft electronics processing, and many consumer products.

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H. HENNING WINTER
University of Massachusetts Amherst, MA, USA