# THE CRITICAL GEL
*The Universal Material State between Liquid and Solid*

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## 1. Chemical and Physical Gelation

Nature allows polymers to pass through the gel point with striking simplicity and elegance. However, what are the rheological properties at the gel point ? Is the polymer at the gel point, the ‘critical gel’, at a distinct material state which has its own properties? It seems that these questions, until recently, have not been pursued. The questions might have been avoided since it was well known that the established rheological concepts fail altogether at the gel point: the concept of a viscosity is inapplicable since the viscosity diverges to infinity and the concept of an equilibrium modulus is useless since the modulus is still zero at the gel point. The gel point itself had remained mysterious.

The name 'gelation' will be used synonymously with forming of a soft solid from a liquid, as it occurs in chemically crosslinking polymers when passing through their gel point or in crystallizing polymers when sample-spanning connectivity is reached during early states of crystallization. The reversal of this phenomenon will be called anti-gelation: the dissolution of the molecular structure or superstructure of a soft solid and the resulting transition from the solid to the liquid state. For gelation, connectivity may be introduced such that it is practically irreversible (e.g., chemical bond) or reversible (e.g., physical junction, long range self-organization). For anti-gelation the disconnecting process may also be irreversible (e.g., mechanical breaking of chemical bonds, thermal degradation) or reversible (e.g., thermally induced phase transition, melting of crystal). Different time scales and driving mechanisms govern the phenomena of gelation and anti-gelation so that they cannot be considered to be mutually symmetric.

Two main groups of gelation phenomena have been distinguished, chemical and physical. *Chemical* gels are well defined by their covalent junctions which connect molecules into three-dimensional networks. Molecular conformations relax with slower and slower modes as the molecules grow in size. The molecular weight distribution is infinitely broad (Flory, 1941; Stockmayer, 1943; Schosseler et al, 1984; Norisuye et al., 1988). Flory (1941, 1942) and Stockmayer (1943) describe the evolution of structure in their classical theory which has been modified in many ways since. Most advanced structural information is obtained from percolation theory (Stauffer, 1985; de Gennes, 1971). The conversion of the chemical reaction, $0 \leq p < 1$, is the independent variable which defines the progress of the gelation process. The gel point is reached when the largest molecular cluster diverges to infinite size (Flory and Stockmayer). This defines the threshold value $p_c$ of the chemical conversion. A crosslinking or vulcanizing sample before its gel point, $p < p_c$, can be dissolved in a good solvent; because of this propery, it is called a “sol”. Beyond the gel point, $p_c < p$, the polymer can only be swollen in a good solvent, but it does not dissolve in its entirety. The polymer is called a gel, even if it contains substantial ammounts of unattached molecules (sol fraction). In this terminology, the liquid-to-solid transition is often called “sol-gel transition“.

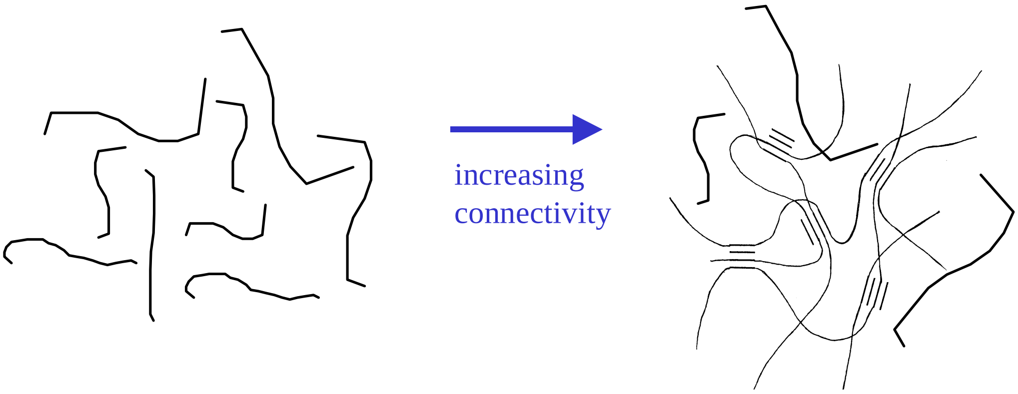

Figure 1. Gelation: Chemical or physical junctions connect molecules into large clusters and, eventually, into a sample spanning network.

*Physical* gels are able to form supermolecular aggregates which connect into a sample spanning network. Connectivity can be achieved by a wide range of mechanisms which have been reviewed extensively by Nijenhuis (1997). In analogy to chemical gelation, where large scale connectivity is achieved by covalent bonds between molecules and the gel point is reached when the largest molecular cluster diverges to infinity size (see Flory and Stockmayer), physical gelation may be defined by the growth of physically connected aggregates: the physical gel point is reached when the correlation length of molecular (or supramolecular) motion diverges to infinity. The rheology during gelation was found to have the exact same features as that of chemical gelation.

The analogy between chemical and physical gelation applies very well to systems with long living bonds. It becomes less defined when renewal of physical bonds occurs on the time scale of observation and the system behaves as a liquid. In this case, a characteristic renewal time of the physical bonds determines long time ordering processes and rheology of a physical gel. The analogy between physical and chemical gelation applies only to time scales shorter than the characteristic reneval time. Physical gels typically have a yield stress beyond which the stucture gets broken and liquid behavior sets in. Below the yield stress, the physical gel is a solid at experimental times shorter than the renewal time and a liquid at experimental times longer than the renewal time.

The polymer at the gel point, the critical gel, is barely connected in the sense that the loss of a few "junctions" will decrease the correlation length in the material below sample size and the material returns to fluid state. Gelation is reversed, i.e. a solid-to-liquid transition is introduced. This anti-gelation is desirable in applications which require molecular mobility: molecules or clusters of molecules become free enough to rearrange and find new equilibrium states which would not be accessible for the solid state.

It should be mentioned that a glass transition is able to also introduce long range connectivity in molecular motion. Here, we are not concerned about the glass transition, at least not at this part of the discussion. All phenomena here are considered to occur far above this glass transition temperature. Dynamically induced glass behavior is also outside our considerations since the glass transition merely dominates the behavior at short times (or high frequencies) while the gelation process governs the long time behavior.

Several phenomena might cause inhomogeneities. The statistical crosslinking proces causes fluctuations in crosslink density. Wall effects might also lead to inhomogeneities on the molecular level. These small scale inhomogeneities would not be visible in rheological experiments since they average out in a macroscopic experiment.

The entire chapter focuses on observations near the gel point and on gelation-associated rheological phenomena. A somewhat more complete review has appeared recently (Winter and Mours, 1997). Here, we will review some basic observations near the gel point, find a mathematical expression for these observations, explore material parameters for the gel point, make some rheological predictions, and give an outlook on applications for soft materials.

## 2. Rheometry Near the Gel Point

### 2.1. RHEOLOGICAL MATERIAL FUNCTIONS FOR SOFT MATERIALS

We will discuss gelation in the classical frame work of linear viscoelasticity (see Ferry, 1980). Without loss of generality, we can limit ourselves to shear flow behavior (shear rate $\dot{\gamma}$, shear strain $\gamma$) since extensional behavior in linear viscoelasticity is determined by the same linear viscoelastic properties as shear. Scalar notation suffices when focusing on shear experiments. Frequently used shear material functions are the zero shear viscosity

$$\eta_o = \lim_{\substack{t \to \infty \\ \dot{\gamma} \to 0}} \eta(\dot{\gamma}, t) \ , \tag{1}$$

which predicts the shear stress in steady shear flow at low shear rates: $\tau = \eta_o \dot{\gamma}$, and the equilibrium modulus

$$G_e = \lim_{t \to \infty} G(t) \ . \qquad (2)$$

The equilibrium modulus is the long-time limiting value of the relaxation modulus $G(t)$. The physical meaning of the relaxation modulus can best be explained by a thought experiment in which an equilibrated test sample gets deformed, at $t = 0$, by a sudden shear strain $\gamma_o$ and, from thereon, is held in the deformed state, $\gamma = \gamma_o = \text{constant}$. The resulting stress $\tau(t)$, divided by the strain, defines the relaxation modulus

$$G(t) = \frac{\tau(t)}{\gamma_o} \ , \qquad (3)$$

which decays to zero for a liquid and to the equilibrium modulus, $G_e$ , for a solid, see sketch in figure 2.

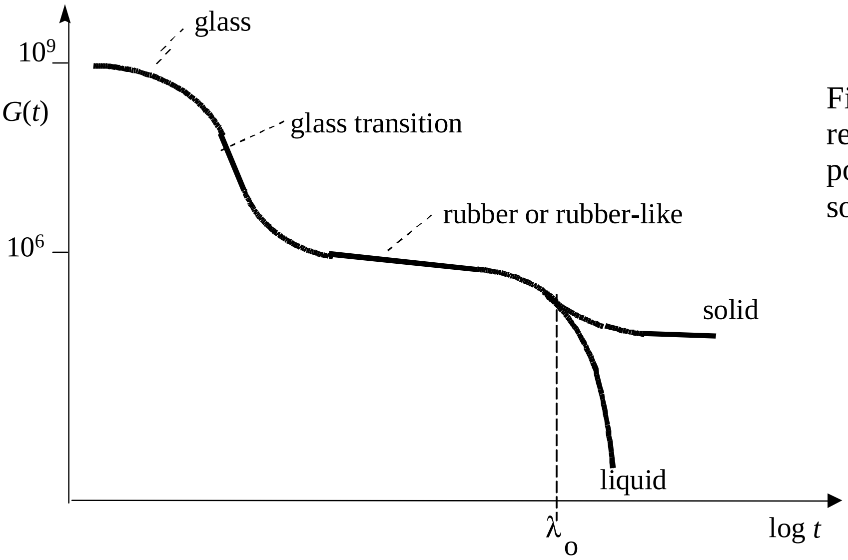

Figure 2. Typical relaxation modulus of polymeric liquids and solids (see Ferry, 1980)

The equilibrium modulus is related to the relaxation time spectrum $H(\lambda)$

$$G(t) = G_e + \int_0^{\lambda_{\max}} \frac{d\lambda}{\lambda} H(\lambda) e^{-t/\lambda} \quad . \qquad (4)$$

by a Laplace transform. Either one by itself, $G(t)$ and $H(\lambda)$ can completely define the viscoelasticity of a material.

The integral over the relaxation modulus of a liquid is the zero shear viscosity

$$\eta_o = \int_o^{\infty} dt \ G(t), \qquad (5)$$

Polymeric liquids and solids relax with a wide distribution of relaxation times which may be expressed as a sum of exponential decay functions (Maxwell modes)

$$G(t) = G_e + \sum_{i=1}^{\infty} g_i \, \mathrm{e}^{-t/\lambda_i} . \tag{6}$$

Parameters $g_i$ and $\lambda_i$ can be determined experimentally. Analytic forms of $G(t)$ have been proposed for selected molecular architectures (see Ferry, 1980; Doi, 1974; Doi and Edwards, 1986). The relaxation modulus $G(t)$ is suitable for the rheological description of liquids and of solids. It, therefore, is well suited for studying the liquid-to-solid transition, as will be shown below.

## 2.2. DIVERGENCE OF EQUILIBRIUM RHEOLOGICAL PROPERTIES

Directly at the gel point, the polymer is not a liquid any more and it is not yet a solid, see figure 3. Its zero shear viscosity diverges

$$\lim_{p \to p_c} \eta_o(p) = \infty \tag{7}$$

and its equilibrium modulus is still zero

$$\lim_{p \to p_c} G_e(p) = 0 . \tag{8}$$

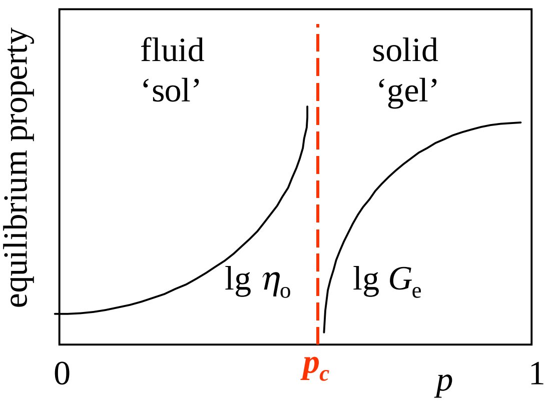

Figure 3. Divergence of equilibrium properties at the gel point, $p \to p_c$: zero shear viscosity and equilibrium modulus

In the close vicinity of the gel point, $|p_c - p| << 1$, the steady shear viscosity and equilibrium modulus grow with power laws (Staufer et al., 1982; de Gennes, 1979)

$$\eta_o(p) \sim (p_c - p)^{-s}, \qquad \text{for sol, } p < p_c \tag{9}$$

$$G_e(p) \sim (p - p_c)^{z}, \qquad \text{for gel, } p_c < p \tag{10}$$

having critical exponents, *s* and *z*. The viscosity of the sol increases due to the diverging cluster size. The equilibrium modulus of the gel gradually builds up since an increasing fraction of the material joins and, thereby, strengthens the sample spanning permanent network.

The longest relaxation time diverges in a power law on both sides of the gel point

$$\lambda_{max}(p) \sim \begin{cases} (p_c - p)^{-\alpha_-} & \text{for } p < p_c \\ (p - p_c)^{-\alpha_+} & \text{for } p_c < p, \end{cases} \qquad (11).$$

$\alpha_-$ and $\alpha_+$ are the critical exponents for the sol and the gel. In the sol, $\lambda_{\max}$ belongs to the largest cluster. The largest cluster reaches infinite size at the gel point, but it still can relax and the corresponding $\lambda_{\max}$ has become infinitely large. Beyond the gel point, the relaxable components (for chemical gelation this would be the sol fraction, unattached chain ends, long loops, etc.) gradually incorporate into the permanent network and $\lambda_{\max}$ decays again (Vilgis et al., 1988).

Associated rheological experiments have been successful in finding the approximate location of the gel point by the divergence of the viscosity, for instance, but they did not reveal any information about the properties of the critical gel itself. Also, the experimental times became longer and longer near the gel point; shear viscosity measurements woul result in large stains which destroy the evolving microstructure (mechanically induced anti-gelation). Obviously, different experiments are needed for characterizing critical gels.

For the study of the vicinity of the gel point, one needs a rheological material function which applies to all three states, the liquid, the solid, and the transition state from one to the other (critical gel). Such material functions are the relaxation modulus, the relaxation time spectrum, and the dynamic moduli, $G'(\omega)$ and $G''(\omega)$, for instance. The dynamic moduli are most accessible to experiment and will be discussed next.

## 2.3. TIME-RESOLVED RHEOMETRY

One such experiment, which does not fail at the gel point, is small amplitude oscillatory shear. This dynamic mechanical experiment is performed by placing the viscoelastic material (test sample) in a mechanical device (rheometer) which allows small amplitude sinusoidal shearing at a strain

$$\gamma(t) = \gamma_o \sin(\omega t) \tag{12}$$

After some start-up time ($\sim 1/\omega$), the stress in the sample responds sinusoidally

$$\begin{aligned}\tau(t) &= \tau_o \sin(\delta + \omega t) \\ &= G'(\omega)\,\gamma_o \sin(\omega t) + G''(\omega)\,\gamma_o \cos(\omega t) \qquad (13)\end{aligned}$$

The frequency of the sinusoidal stress response, $\tau(t)$, is the same as that of the strain, $\gamma(t)$, however, $\tau(t)$ is shifted by a phase angle $\delta(\omega)$. $\tau_o(\omega, \gamma_o)$ is the amplitude of the sinusoidal stress. Storage modulus $G'$ and loss modulus $G''$ are a measure of stored and dissipated energy per cycle, respectively.

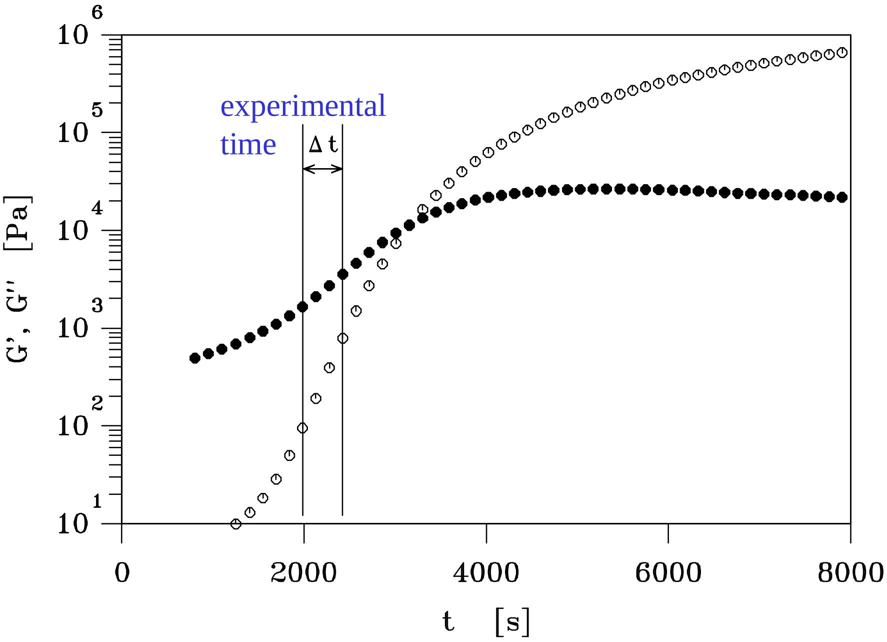

Figure 4. Typical growth of $G'(\omega)$ and $G''(\omega)$ during chemical or physical gelation. The inverse slope is the mutation time which commonly is defined with the physical property which grows fastest; here, this is $G'$. The total change of $G'$ during the experimental time $\Delta t$ needs to be sufficiently small. For practical purposes, a change of 10% can be considered to be small enough.

Small amplitude oscillatory shear is equally applicable to liquids and to solids and, hence, could be expected to give meaningful results near the gel point. No singularity occurs at the transition through the gel point, see figure 4. The measured storage and loss moduli, $G'(\omega)$ and $G''(\omega)$, grow during early stages of gelation. Beyond the gel point, $G''(\omega)$ goes through a maximum and starts to decay.

The dynamic mechanical experiments brought about the problem that the sample changes during the taking of each data point due to the crosslinking reaction. The viscoelastic polymer does not only have the two time scales which rheologists are so familiar with, the longest relaxation time $\lambda_{\max}$ and the experimental time $\Delta t$ (which often are compared in the Deborah number $N_{\mathrm{De}} = \lambda_{\max} / \Delta t$), but also a characteristic time for change in the material, $\lambda_{\mathrm{mu}}$. This characteristic time of change, called mutation time

$$\lambda_{\mathrm{mu}} = \left( \frac{1}{G'} \left| \frac{\partial G'}{\partial t} \right| \right)^{-1} \tag{14}$$

has been defined as the time which is needed for the moduli to grow by factor (e) or decay by factor (1/e) (Mours and Winter, 1994). We chose $G'$ for defining $\lambda_{\mathrm{mu}}$ since changes were larger with $G'$ than with $G''$. The value of $\lambda_{\mathrm{mu}}$ depends not only on the rate of gelling but also on the experimental frequency (Scanlan and Winter, 1991)

$$\lambda_{\mathrm{mu}} \sim \omega^{\kappa} \tag{15}$$

where $\kappa$ is about 0.2 for a wide range of gels.

Individual data points have been considered acceptable if the total change of $G'$ (during its measurement), as expressed in the mutation number

$$N_{\mathrm{mu}} = \Delta t / \lambda_{\mathrm{mu}} \quad << 1, \tag{16}$$

was below 10%. A computer code (GELPRO) has been developed for analyzing the time resolved rheometry experiments in terms of $G'(\omega,t)$ and $G''(\omega,t)$ and mutation number values.

## 3. Properties of the Critical Gel

### 3.1. RELAXATION PATTERN NEAR THE GEL POINT

Our initial difficulties, when starting the study of critical gels, were caused by the fact that we did not know what special features we should expect in the immediate vicinity of the gel point. It was unclear what its characteristic dynamic mechanical properties might be, especially since $G'(\omega)$ and $G''(\omega)$ data were known to proceed smoothly through the gel point, see fig. 4. Dynamic mechanical measurements seemed to be impractical since they did not give any clear indication of where the gel point occured. Tung and Dynes (1982) proposed to define the gel point by the instant of $G' = G''$ ($G' - G''$ crossover). However, Tung and Dynes also realized that this $G' - G''$ crossover depends on frequency and immediately eliminated their proposal: it is obvious that the gel point cannot depend on the frequency of observation. The search was not over yet.

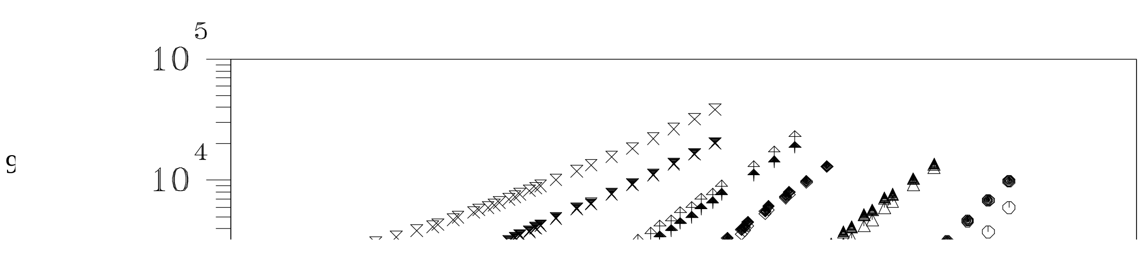

Figure 5. Dynamic mechanical data on endlinked PDMS (Chambon and Winter, 1985). The shift factor A has the only purpose of separating the curves from each other.

The breakthrough came when François Chambon succeeded in stopping the crosslinking reaction by spraying a mist of catalyst poison onto thin samples of endlinking polydimethylsiloxane (PDMS) (Chambon and Winter, 1985). He was able to prepare a discrete set of samples with fixed extent of crosslinking before, near, and beyond the gel point. Dynamic mechanical experiments with these stopped samples (over an extended frequency window, involving time-temperature superposition) suddenly showed the evolving relaxation time spectrum of gelation (Chambon and Winter, 1985). One of our first data sets is shown in figure 5. Both moduli grow with increasing extent of reaction. Most pronounced are the changes at low frequencies where the storage modulus, $G'(\omega)$, slopes downward at initial stages of gelation and slopes to the left at late stages of gelation.

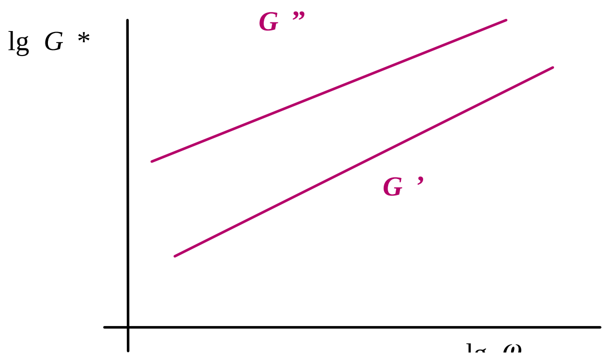

Figure 6. Power law distribution of $G'(\omega) \sim \omega^{n'}$ and $G''(\omega) \sim \omega^{n''}$. Are the slopes perfectly identical or slightly different from each other?

At a distinct intermediate state, $G'(\omega)$ straightens out into a power law $G'(\omega) \sim \omega^n$. *G*" adopts a power law also, and it seemed to have the same slope. Before proceeding we had to find out whether *G*' and *G*" were exactly parallel or whether their slope could be slightly different. The answer came through the famous Kramers-Kronig relation which would be violated by different slopes as sketched in figure 6; *G*' and *G*" have to be perfectly parallel (Winter and Chambon, 1986; Chambon and Winter, 1987). The critical gel state is characterised by both,

$$G'(\omega) \sim \omega^n \text{ and } G''(\omega) \sim \omega^n . \qquad (17)$$

Straight and parallel $G'(\omega)$ and $G''(\omega)$ are an expression of power law distribution of relaxation times.

At first, we called this intermediate state "viscoelastic transition" but further experiments showed that it belonged to the gel point: A chemically crosslinking sample, which was stopped before reaching this transition state, could be readily dissolved in a good solvent while samples beyond the transition point could only swell. These are typical features of a sol-gel transition in chemical gels.

## 3.2. RHEOLOGICAL SIGNATURE OF THE CRITICAL GEL

The *G** data have been converted from the frequency domain to the time domain. The resulting relaxation modulus is schematically shown in figure 7. The puzzle had revealed itself. The critical gel was found to relax with a universal scaling law (Chambon and Winter 1985, Winter and Mours 1997). This expresses itself in a self-similar relaxation modulus

$$G(t) = S_c t^{-n_c} \qquad \text{for } \lambda_o < t \qquad (18)$$

The associated relaxation time spectrum is also self-similar

$$H(\lambda) = \frac{S_c}{\Gamma(n_c)} \lambda^{-n_c} \qquad \text{for } \lambda_o < \lambda \qquad (19)$$

The Gamma function can be approximated with a parabola

$$\Gamma(n_c) = \frac{1}{n_c}\Gamma(1+n_c) \approx \frac{1}{n_c}\left[1 - 0.1138\left(1 - 4(n_c - 0.5)^2\right)\right] \qquad (20),$$

since $1<(1+n_c)<2$.

The regularity in the relaxation modes is startling. Relaxation processes appear to be the same on all length scales. These observations provide us with a second property at the gel point. The self-similar relaxation by itself is not sufficient proof of the gel point, but together with the condition of diverging eta, ge, and la, self-similarity can be used to find the gel point or to model the stress. This will be explored in the following.

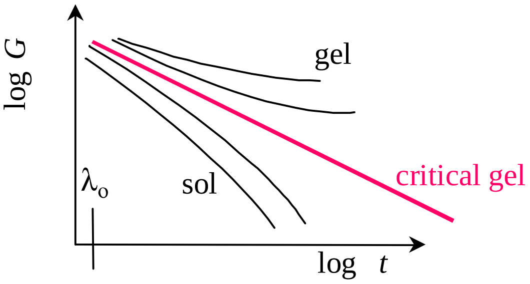

Figure 7. Relaxation modulus of critical gel and its vicinity. Only the long-time behavior of $G(t)$ is sketched.

The main origins of the self-similar relaxation pattern seem to be twofold. First, the broadening of the molecular weight distribution (Schosseler et al., 1984) causes the spectrum to stretch and span over a wider time window. Such polydispersity has been known to straighten the spectrum and to 'smear out' any distinct transition features (Larson, 1985). The second cause is the hyperbranched structure of the crosslinked molecules. At about the same time when we started to understand the rheological expression of gelation, Muthukumar (1985) and Cates (1985) predicted that uniformly sized molecules of self-similar architecture exhibit self-similar relaxation pattern. This branching seems to be the second major origin of the self-similar relaxation of critical gels. Both phenomena, broad distribution of molecular sizes and branched molecular architecture are characteristic for critical gels.

## 3.3. CROSS-OVER TO SHORT-TIME BEHAVIOR OF THE CRITICAL GEL

The self-similar spectrum applies to the long time behavior only. Below some material specific relaxation time $\lambda_o$, crossover occurs to shorter length scale dynamics (entanglements, sequential motion, for instance). Such limit at short time scales occurs with all polymeric materials above $T_g$ (liquids, solids, and critical gels), see schematic in fig. 2. The cross-over becomes evident when probing the critical gel at high frequency, $\omega > 1/\lambda_0$. In critical gels which are crosslinked from large precursor molecules (above entanglement molecular weight), $\lambda_0$ is the largest relaxation time of the precursor (DeRosa and Winter, 1994, Mours and Winter, 1996).

## 3.4. REFERENCE TIME SCALE, DIVERGENCE OF LONGEST RELAXATION TIME, AND DEBORAH NUMBER

Viscoelastic materials, such as polymers, are typically characterized by a longest relaxation time, $\lambda_{\max}$, which belongs to the largest molecular cluster. However, such time scale is unavailable for the critical gel. This lack of characteristic time scale is unique for a viscoelastic material. As a substitute, we might scale relaxation processes with the cross-over time, $\lambda_o$, and redefine the stiffness of the critical gel (Scanlan, Izuka)

$$S_c = G_o \lambda_o^{n_c} \tag{21}$$

by introducing a material specific modulus $G_o$.

The importance of elasticity in a given flow process (of duration $\Delta t$) is commonly judged by the Deborah number (Reiner 1969).

$$N_{De} = \lambda_{\max} / \Delta t \ . \tag{22}$$

$N_{De} \geq 1$ implies that elasticity is important for a polymeric liquid or, where applied to viscoelastic solids, that the transient part of elasticity contributes significantly to the rheological behavior in a specific application of duration $\Delta t$. The longest relaxation time provides the reference time scale for distinguishing viscous from elastic phenomena under transient conditions. The diverging longest relaxation time of the critical gel, $\lambda_{\max} \to \infty$ or $1/\lambda_{\max} \to 0$, results in a diverging Deborah number, $N_{De} \to \infty$, for all rheological experiments $(\Delta t > 0)$. The Deborah number criterion becomes meaningless. It does not provide any help in the classification of flow processes.

## 3.5. MATERIAL PARAMETER VALUES

The critical gel has two material parameters $n_c$ and $S_c$. Their value has not yet been predicted from a theoretical model. $S_c$ is clearly dependent on $n_c$, but the relation is only confirmed by experiment. Values of parameters $n_c$ and $S_c$ can be determined from G', G" data at the gel point (at $p=p_c$) and measured at low frequency $\omega<1/\lambda_o$. The relaxation exponent is, obviously, independent of frequency

$$n_c = \frac{2\delta}{\pi} \quad ; \delta = \tan^{-1} \frac{G''}{G'} \ . \tag{23}$$

The front factor can be calculated from any of the dynamic moduli

$$S_c = \frac{G'(\omega)}{\omega^{n_c} \ \Gamma(1-n_c) \cos \frac{n_c \pi}{2}} \tag{24}$$

The dimensions of $S_c$ already indicate that $S_c$ contains a characteristic modulus $G_o$ and a characteristic time $\lambda_o$, see eq. 21. The physical meaning of $G_o$ and $\lambda_o$ has been explored experimentally by Scanlan et al. (1991) and by Izuka et al. (1995). Experiments on a wider range of materials is needed before a definite answer can be given.

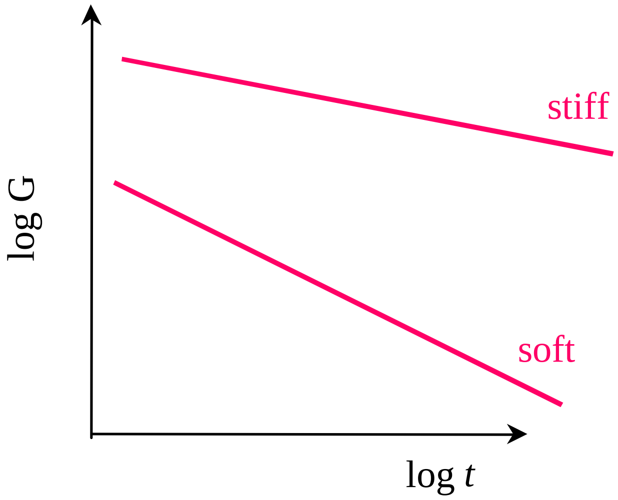

Figure 8. Comparison of soft and hard critical gels. Soft critical gels have large $n_c$, $(n_c \to 1)$, and small $S_c$ while stiff critcal gels have small $n_c$, $(n_c \to 0)$, and large $S_c$.

Experiments have repeatedly shown a connection between $S_c$ and $n_c$. Whenever the relaxation exponent was increased (by adding a plasticiser, or by offsetting the stoichiometry, for instance), the stiffness $S_c$ dropped, and vice versa.

### 3.6. TEMPERATURE DEPENDENCE

Isothermal, rheological experiments on critical gels at temperatures $T_1$ and $T_2$ show the temperature dependence of the two parameters, $n_c$ and $S_c$ (Izuka et al., 1994). Time temperature superposition was found to apply for all the experimentally studied systems at their gel point. $n_c$ and $S_c$, are governed by the monomeric friction coefficient and the temperature dependence of the density. Time-temperature superposition is only possible if the relaxation exponent is constant (Izuka et al., 1994)

$$n_c(T) \equiv n_c(T_0) \qquad \text{with} \qquad 0 < n < 1 . \tag{25}$$

The amount of vertical and horizontal shift is not clear for the self-similar relaxation modulus. However, for finding agreement with the short-time relaxation, a conventional shift has been proposed, just like the well known shift for polymeric liquids or solids (Ferry, 1980). The shifted relaxation modulus may be expressed as (Izuka et al., 1994)

$$G(t,T) = \underbrace{S_c(T_o)\frac{\left(a_T\right)^{n_c}}{b_T}}_{S_c(T)} t^{-n_c} \qquad . \tag{26}$$

Remarkable is the power law exponent for the shift factor $a_T$ : only a fraction of the shift factor becomes effective; the fraction is larger for a soft critical gel (large $n_c$) than for a stiff one (small $n_c$).

Physical gels show distinctly different temperature dependence since not only the chain friction is affected by temperature but also the character of the physical junctions (functionality, characteristic renewal time of bonds).

## 3.7. MOLECULAR WEIGHT DEPENDENCE

We are only beginning to understand molecular weight effects on the material parameters $n_c$ , $S_c$ , and $\lambda_o$. Several experimental observations give guidance for further studies. For instance, experiments with model chemical gels suggest a value of $n_c$ near 0.5 for high molecular weight systems (Mours et al., 1996) and larger values (near 0.7) for critical gels which are made from small precursor molecules (Martin et al., 1987,1988). Imbalanced stoichiometry does also produce softer critical gels (larger $n_c$) because of the increase of imperfections in the network (Chambon et al., 1987).

In the special case of long, linear precursor molecules with a molecular weight above the entanglement limit, $M > M_e$, it is possible to express the cross-over relaxation time $\lambda_o$ as function of molecular weight (De Rosa et al., 1994)

$$\lambda_o = \lambda_e{}^{n_c} (M / M_e)^{3.4} \quad , \tag{27}$$

where $\lambda_e$ is the crossover time to glass transition modes, and $M_e$ is the entanglement molecular weight. Material parameters $\lambda_e$ and $M_e$ belong to the linear viscoelasticity of un-crosslinked polymers with long, linear, flexible molecules of (nearly) uniform molecular weight (Baumgärtel et al., 1990). Further parameters given by the precursor are the slope, $m$, of the loss modulus $G''(\omega)$ in the entanglement region (a typical value is $m$=0.25), and the plateau modulus $G_N^o$ . With these, the molecular weight dependence of the front factor was found to be (De Rosa et al., 1994),

$$S_c = \Gamma(n_c)\, m\, G_N^o\, \lambda_o{}^{n_c} = \Gamma(n_c)\, m\, G_N^o\, \lambda_e{}^{n_c} (M / M_e)^{n_c 3.4} \quad , \tag{28}$$

The stiffness scales with molecular weight to the 3.4$n_c$ -power. With $n_c$ of about 0.5 for high molecular weight precursors, the exponent adopts an value of 1.7. $\Gamma(n_c)$ is the gamma function at $n_c$.

# 4. Stress Predictions for Critical Gels

## 4.1. CONSTITUTIVE EQUATION FOR THE STRESS

The rheological constitutive equation for the stress in critical gels needs to be distinctly different from that of a liquid or a solid. Combining the relaxation modulus, eq.13, with the classical equation of linear viscolelasticity of Boltzmann (see Ferry 1980) leads to such a constitutive equation for the critical gel (Winter and Chambon, 1986)

$$\tau(t) = \int_{-\infty}^{t} dt' \, S_c \, (t - t')^{-n_c} \, \dot{\gamma}(t') \, , \tag{29}$$

The short-time crossover (see section 3.3 ) is neglected here for simplicity, but one may include it for stress applications where short modes contribute significantly. The above equation is written in terms of the shear stress $\boldsymbol{\tau}(t)$ and the shear rate $\dot{\gamma}(t)$ but can be generalized to tensorial form

$$\boldsymbol{\pi}(t) = -P(t)\mathbf{1} + n_c S_c \int_{-\infty}^{t} dt' \, (t - t')^{-(n_c+1)} \, \mathbf{C}^{-1}(t;t') . \tag{30}$$

$\mathbf{C}^{-1}(t;t')$ is the well known Finger strain tensor (see Larson, 1988) between states *t'* and *t*. Large strain behavior and breaking of the structure is not included in this equation. The breaking of critical gels is a topic which needs to be investigated in the future (Venkataraman et al., 1990).

4.2. MODELING CALCULATIONS

The constitutive equation is useful for predicting the stress in critical gels under a wide range of different strains. An example is the stress growth in start-up of uniaxial extension (see Chung and Lodge, 1972) at constant extension rate $\dot{\varepsilon}_o$

$$\tau_{11} - \tau_{22} = \frac{S_c}{\Gamma(n_c)} \int_0^{\infty} \frac{d\lambda}{\lambda} \lambda^{-n_c} \left\{ \frac{1 - 2\dot{\varepsilon}_o \lambda e^{-(1-2\dot{\varepsilon}_o\lambda)t/\lambda}}{1 - 2\dot{\varepsilon}_o \lambda} - \frac{1 + \dot{\varepsilon}_0 \lambda e^{-(1+\dot{\varepsilon}_0\lambda)t/\lambda}}{1 + \dot{\varepsilon}_o \lambda} \right\} \qquad (31).$$

$\tau_{11} - \tau_{22}$ is the difference of tensile stresses in stretching direction and in perpendicular direction. The dynamic mechanical material functions under oscillatory shear (for $0 < \omega < 1/\lambda_o$) are predicted as

$$G'(\omega) = \Gamma(1 - n_c) S_c \, \omega^{n_c} \cos \frac{n_c \pi}{2} \qquad (32),$$

$$G''(\omega) = \Gamma(1 - n_c) S_c \, \omega^{n_c} \sin \frac{n_c \pi}{2} \qquad (33),$$

$$\delta = \frac{n_c \pi}{2} \qquad (34),$$

$$\left| G^*(\omega) \right| = \Gamma(1 - n_c) S_c \omega^{n_c} \qquad (35),$$

$$\left|\eta^*(\omega)\right| = \frac{1}{\omega}\left|G^*(\omega)\right| = \Gamma(1-n_c)\ S_c\ \omega^{n_c-1} \qquad (36),$$

The shear creep compliance $J(t)$ (for start-up of creep at constant shear stress) is found to grow as (Mours and Winter, 1997)

$$J(t) = \frac{t^{n_c}}{S_c}\frac{\sin\pi n_c}{\pi n_c} = \frac{1}{G(t)}\frac{\sin\pi n_c}{\pi n_c} \qquad \text{for } \lambda_0 < t < \infty \qquad (37).$$

The product $J(t)G(t)$ is a constant for the critical gel.

These are some examples. They demonstrate the use of the constitutive equation for stress predictions in critical gels.

## 5. The Critical Gel as Reference State

### 5.1. GEL POINT DETECTION

The distinct rheology of the critical gel can be used in novel methods of detecting the gel point. Fortuitously, the gel point is not only marked by diverging properties (viscosity, longest relaxation times, diverging scattering size) but also by distinct properties at finite length (and time) scale: the power law distribution of relaxation modes (and similar behavior in dynamic light scattering, see Shibayama et al. 1998, 1999). The emerging power law spectrum in the approach of the gel point and its gradual disappearance beyond the gel point can be probed at finite experimental times, by small amplitude oscillatory strain experiments for instance (mechanical spectroscopy). The experiments need to be performed at low frequencies, $\omega < 1/\lambda_o$. High frequency experiments would probe the gel outside the power law region and, hence, would not be able to distinguish liquid from solid behavior.

A frequently used experiment for detecting the gel point is shown in figures 8 and 9. The loss tangent, $\tan\delta = G''/G'$, of the gelling sample is measured at a set of discrete frequencies, all of them chosen below $1/\lambda_o$. The gel point is the instant at which $\tan\delta(\omega)$ vs. time reduces to a single intercept (Holly et al., 1988). The value of $\tan\delta_c$ directly gives the relaxation exponent (Chambon and Winter, 1987), see eq 23.

Instead of $\tan\delta$ one could plot related rheological properties such as dynamic stiffness

$$S(\omega) = \frac{G'(\omega)}{\omega^n\ \Gamma(1-n)\cos\frac{n\pi}{2}} \qquad (38)$$

$$\text{with } n(\omega) = \frac{2}{\pi}\arctan\frac{G''}{G'} \qquad (39)$$

and look for frequency independence at the gel point.

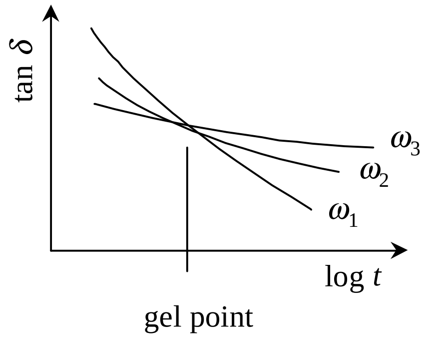

Figure 9. The value of loss tangent tan$\delta(\omega)$ decays during gelation. The intercept of tan$\delta(\omega_i)$ marks the gel point. Experimental parameter is the frequency of the dynamic mechanical experiment.

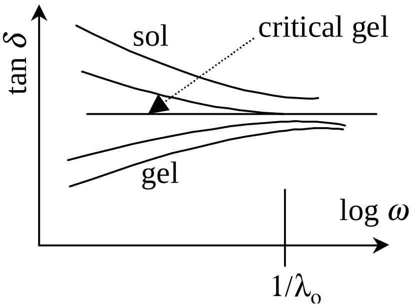

Figure 10. The sample at the gel point has the flat tan$\delta(\omega)$. The value of tan$\delta(\omega)$ decays during gelation.

In gelation studies, we often encounter special situations which do not allow wide range of frequency variation. Then, a *single* frequency method is desirable. This is possible, to a reasonable approximation, if the value of $n_c$ is known for a universality class of samples. For known $n_c$, one may

1) measure the evolving tan$\delta$ and wait until it reaches the value of tan($n_c\pi/2$).
2) one can normalize the evolving dynamic moduli, $G'/\cos(n_c\pi/2)$ and $G''/\sin(n_c\pi/2)$., see figure 11: the instant of liquid-to-solid transition (gel point) is marked by the cross-over of the normalized dynamic moduli, $G'/\cos(n_c\pi/2)$ and $G''/\sin(n_c\pi/2)$.

Applications of these methods are envisioned for rapidly gelling systems or for degrading polymers which do not allow a range of frequency measurements.

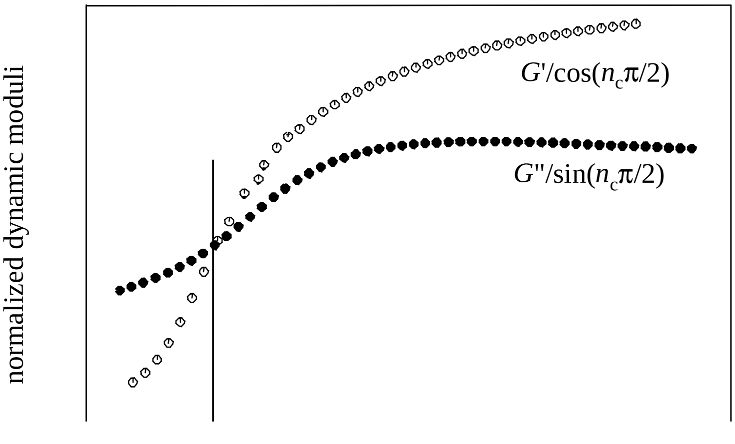

Figure 11. The cross-over of the <u>normalized</u> dynamic moduli, $G'/\cos(n_c\pi/2)$ and $G''/\sin(n_c\pi/2)$ marks the gel point. The method is applicable to gelation of a universality class of polymers for which $n_c$ is known

### 5.2. CONVERSION OF CROSSLINKING REACTION

For chemical gelation, the connectivity at the gel point does not depend on temperature while, obviously, the cross-linking rate and the gel time (time to reach the gel point, $t_c$ ) are strongly affected by heating or cooling of the sample. This temperature invariance of the chemical conversion $p$ is the main reason for favoring the conversion $p$ as reference variable over the gel time, $t_c(T)$.

The rate of reaction determines the extent of reaction $p(t)$. For a first order crosslinking reaction (at constant temperature), for example, the extent of reaction grows as (de Rosa et al., 1997)

$$p(t) = 1 - (1 - p_c)\, e^{-k(t-t_c)} \tag{40}$$

where $k$ is the reaction constant. The instant of gelation and the threshold value $p_c$ provide a reference point, which can be measured for specific systems of interest. Preferably, one would want to use a theoretical value of $p_c$, for instance from the Flory-Stockmayer theory. An example is the endlinking of linear molecules (functionality of $f$=2) with four-functional crosslinker molecules ($g$=4); the threshold value is predicted as

$$p_c = \frac{1}{\sqrt{r(f-1)(g-1)}} \quad . \tag{41}$$

Both equations combined result in a simple relation for $p(t)$

$$p(t) = 1 - \left(1 - \frac{1}{\sqrt{r(f-1)(g-1)}}\right) e^{-k(t-t_c)} \quad . \tag{42}$$

The stoichiometric ratio $r$ has a strong effect on $p_c$.

### 5.3. CRITICAL EXPONENTS OF NEARLY CRITICAL GELS

Polymers in the vicinity of the gel point are called 'nearly critical' gels. They are defined by their distance to the gel point, $p$ - $p_c$, see section 2.2. The dynamic exponent $n_c$ connects the critical exponents $\alpha_-$ and $\alpha_+$ of the longest relaxation time to the critical exponents of the viscosity and the equilibrium modulus, eqs 9 and 10 (Winter, 1987):

$$s = (1 - n)\ \alpha_-, \qquad \text{for sol, } p < p_c \tag{43}$$

$$z = n\alpha_+, \qquad \text{for gel, } p_c < p \tag{44}$$

Only three of the five critical exponents are independent. In all these arguments, the critical gel has served as a reference state. If one assumes symmetry of the diverging $\lambda_{\max}$ around the gel point

$$\alpha_- = \alpha_+ = \alpha \tag{45}$$

then the critical exponents are related as (Winter, 1987; Martin et al., 1989)

$$n = \frac{s}{s + z} \tag{46}$$

or $\alpha = s + z$, $s = (1 - n_c)\alpha$, and $z = n_c\alpha$. Into these relations one may introduce specific values ($s$, $z$) from percolation theory or from branching theory and determine the corresponding values for $n_c$ and $\alpha$. This procedure relies on the symmetry hypothesis (Winter, 1987) which does not seem to be generally valid, at least not for highly entangled polybutadienes which have strongly different values for $\alpha_-$ and $\alpha_-$ (Mours and Winter, 1986). The wide range of values for the relaxation exponent, $0 < n < 1$, lets us expect that the dynamic exponents $s$ and $z$ are non-universal.

### 5.4. RELAXATION TIME SPECTRUM OF THE NEARLY CRITICAL GEL

Steady shear flow properties are sensitive indicators of the approaching gel point for the liquid near gel point, $p<p_C$. The most simple proposal for approximating the relaxation time spectrum is:

$$H(\lambda) = \begin{cases} \dfrac{S}{\Gamma(n)}\lambda^{-n} & \text{for } \lambda_0 < \lambda < \lambda_{\max} \\ 0 & \text{for } \lambda_{\max} < \lambda \end{cases} \tag{47}$$

With this spectrum, we can now calculate material functions of steady shear flow in the limit of low shear rate (linear viscoelastic limit). The above constitutive equation with the simple spectrum can be integrated to obtain the zero shear viscosity $\eta_o$, the first normal stress coefficient $\psi_1$ at vanishing shear rate, and the equilibrium compliance $J_e^o$ :

$$\eta_o(p) = \int_0^{\lambda_{\max}} H(\lambda)\, d\lambda = \frac{S\ \lambda_{\max}{}^{1-n}}{(1-n)\,\Gamma(n)} \tag{48}$$
,

$$\psi_1(p) = 2\int_0^{\lambda_{max}} H(\lambda)\,\lambda d\lambda = \frac{2\,S\,\lambda_{max}{}^{2-n}}{(2-n)\,\Gamma(n)} \qquad (49),$$

$$J_e^o(p) = \frac{\Psi_1}{2\eta_o{}^2} = \frac{\Gamma(n)}{S}\,\frac{(n-1)^2}{2-n}\,\lambda_{max}^{\;n} \qquad (50).$$

As a result, we find that the divergence of the above three linear viscoelastic material functions of sols depends on the divergence of $\lambda_{\max}$

$$\lambda_{\max}(p) \sim \eta_o{}^{1/(1-n)} \sim \psi_1{}^{1/(2-n)} \sim J_e^{o\,1/n} \qquad (51).$$

## 6. Applications to Soft Polymeric Materials

Soft material states near the liquid-to-solid transition are of interest for applications as adhesives (Winter, 1989; Zosel, 1991), sound and vibration dampeners (damping plateau, eq. 34, instead of the usual damping peak), superabsorbers, hydrogels (Nishinari, 1997; Zheng et al., 1998; Cabana et al., 1997), silica gels (Shibayama et al., 1999), crystallizing solutions (te Nijenhuis et al., 1989; Li et al., 1997) cross-linking liquid crystals (Richter et al., 2000), food, pharmaceuticals, and photographic media (to name a few), but also as intermediates for selforganization of molecules or supramolecules into long range order. Many of these soft materials are close to their gel point, i.e. they are liquids just before reaching their gel point or they are solids which have barely passed the gel point.

The solidification process in polymers also samples the critical gel state. Polymers are mostly used in their solid state while they are processed in their liquid state. In between these two states lies the solidification process, which strongly affects the development of the end-use properties (mechanical, barrier, optical, etc.). The liquid-to-solid transition occurs gradually so that the polymer may accumulate large strains while processing near liquid-to-solid transitions. In addition, the molecular and supermolecular motions slow down so that equilibrium states can not be attained and non-equilibrium structures are frozen in.

Physical gelation and ordering are related processes. Ordering into supermolecular structures requires molecular mobility. However, increased order also correlates motion of a longer and longer distances, i. e. it reduces mobility and may cause gelation. This gelation phenomenon will interrupt the ordering process. Higher states of order are inherently excluded by the ordering process itself. The challenge is to find suitable ordering dynamics which give the highest order in the material. Crystallization of polymers sets an example of such interplay between ordering and gelation (Pogodina et al., 1998, 1999; Gelfer et al., 1999; Horst et al., 2000). Microphase separating block copolymers also show the interplay of ordering and gelation. After quenching below the ordering temperature, ordered structures nucleate and grow until they form borders with neighboring grains (Sakamoto et al., 1998; Soenen et al., 1997; Jeong et al., 1999). Shear deformation breaks the solid structure and enhances molecular mobility. Long range order is facilitated by reversing the gelation process temporarily, in this case by mechanically breaking the structure (Keller et al., 1970).

Figure 12 . Schematic of liquid-to-solid transitions in composite liquids: aggregation into a sample filling network, lattice ordering due to repulsion between particles, and jamming of particles at high stress.

Several mechanisms are known to solidify particulate systems, see figure 12. The particles in a continuous matrix might be able to aggregate and form a sample spanning network. Strong repulsion between particles might also reduce mobility (due to increased order). High speed flow can cause jamming of the particles and temporary solidification. Such transitions in particulate systems are difficult to explore since they occur in narrow experimental windows. The most basic experiments are still missing.

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