Transient Networks

Evolution of rheology during chemical gelation

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Abstract: Rheology is a sensitive measure of the evolving molecular structure in a crosslinking polymer. Dynamic mechanical experiments in small amplitude oscillatory shear give the storage modulus $G'(\omega,p)$ and the loss modulus $G''(\omega,p)$ as a function of frequency ω. The extent of crosslinking, $p(t)$, changes with reaction time. Dynamic mechanical experiments allow detection of the gel point (GP) and give a macroscopic description of the *critical gel* state (network polymer at GP). This critical gel state is used as a reference for describing the entire evolution of rheology. The most surprising discovery of these experiments was that critical gels exhibit stress relaxation in a power law, i. e. the relaxation modulus is given as $G(t) = St^{-n}$. The relaxation exponent, n, depends on network structure. The power law behavior is an expression of mechanical self similarity (fractal behavior). The range of self similarity is defined between an upper and a lower frequency limit. The lower frequency limit (reciprocal of characteristic relaxation time) corresponds to an upper scaling length, the *correlation length*, which is of the order of the linear size of the largest molecular cluster (of pre-gel) or of the largest remaining percolation cluster (of post-gel). High frequencies probe relaxation within single chains. The upper frequency limit corresponds to a lower scaling length, the *glass length*, which is given by the dimension of the molecular network units responsible for glassy behavior. The correlation length and, hence, the characteristic relaxation time increase in the approach of the gel point, diverge to infinity at the gel point, and then decrease again with increasing extent of crosslinking. The critical gel has no characteristic length or time scale. All observations are restricted to polymers at a temperature above the glass transition temperature and at frequencies much below the glass frequency.

Key words: Network polymers, gel point, polyurethane, fractal, critical phenomenon.

Introduction

Chemical gelation of polymers has been studied extensively, for applied and for basic scientific reasons. Applications are governed by the change of properties as a function of reaction extent. Basic interest comes from the fact that gelation is a critical phenomenon [26] and that very simple properties are expected at the critical point (gel point).

This study is mostly concerned with the rheological expression of chemical gelation. The initial material is, in our case, of low molecular weight and, therefore, behaves as a Newtonian liquid. The molecular weight grows with the proceeding crosslinking reaction, consequently the viscosity increases, and elasticity sets in after reaching a critical molecular weight. The cross-linking polymer is still a liquid and it exhibits viscoelastic behavior similar to that of a polymer melt or solution. The molecular weight increases further and most dramatic changes of properties occur close to the gel point. The gel point (GP) is defined as the instant at which the weight average molecular weight diverges to infinity (infinite sample size) or at which the largest molecular cluster extends across the sample (finite sample size). At GP, phase transition occurs to a viscoelastic solid. The equilibrium modulus of the solid grows with higher and higher crosslink density until the reaction stops.

The process may be called chemical gelation to distinguish it from physical gelation, in which the network is formed by reversible association mechanisms

between macromolecules. For model networks at GP, the critical extent of crosslinking, p_c, was predicted by Flory [17,18], and Stockmayer [28] and later Gordon [19] and Macosko and Miller [22] as a function of crosslink functionality and stoichiometric ratio. The predictions have been found to be in close agreement with experiment [5] in spite of differences between model networks and real polymer samples. This suggests that GP can be detected by monitoring the degree of crosslinking and waiting until it has reached the theoretical p_c-value. However, the degree of crosslinking is difficult to measure with sufficient accuracy. Difficulties arise from side reactions which parallel the crosslinking reaction [16,23]. The critical reaction time, t_c, for reaching GP can be measured directly. However, t_c is not a material parameter. It depends on both molecular properties and processing history.

Knowing the instant of chemical gelation is important for processing of crosslinking polymers, since shaping has to occur before GP while the polymer is still able to flow and stress can relax to zero. The most common rheological tests for detecting GP measure the appearance of an equilibrium modulus [14,1] or the divergence of the steady state shear viscosity [1,2,6,21]. Measurement of the equilibrium modulus is extremely difficult since its value is zero at GP and it remains below the detection limit for a considerable time. Measuring the diverging steady state shear viscosity has the advantage that the experiment is extremely simple. This method, however, has servere disadvantages which make it less suitable for characterizing gels [31]:

1. Near GP the relaxation time becomes very large and steady shear flow can no longer be reached.

2. The network structure near GP is very fragile. It gets broken by the large deformation of the 'steady' shear flow, causing an apparent delay of GP.

3. In the approach of GP, the gel is a viscoelastic liquid which behaves in a shear thinning way.

4. GP is found by extrapolation. The actual experiment ends some time before GP when the stress increases beyond the limit of the instrument or the strain exceeds the deformability of the sample.

Dynamic mechanical experiments in small amplitude osciallatory shear are better suited, not only for detecting GP but for measuring the entire evolution of rheology.

The following discussion is based on the experimental studies of Chambon and Winter [9], Chambon, Petrovic, MacKnight, and Winter [10], Chambon and Winter [11], and Winter, Chambon, and Morganelli

[30] on endlinking polydimethylsiloxane and polyurethane samples near the gel point and at temperatures much above the glass transition temperature. Details of the experiments can be found in these publications and will not be repeated here. Experimental difficulties arise from the fact that any large strain (during sample preparation or transfer, during mechanical measurements) breaks the molecular structure of chemical gels irreversibly. The samples of this study have therefore been prepared directly in the rheometer (no transfer). Large strain has been avoided during the mechanical measurements. Numerous solution swelling experiments [12] confirmed that the rheologically observed GP (by dynamic mechanical measurement) coincides with the transition from a completely soluble state to an insoluble state.

Linear viscoelasticity at the gel point

The transition through GP occurs gradually. A limiting behavior at GP exists jointly for the liquid and the solid. This limiting behavior is the property of the 'critical gel' or the 'polymer at GP'. It should, however, be emphasized that no independent state of matter exists directly at GP and it is impossible to make a polymer directly at GP. A real polymer sample is either still before GP (viscoelastic liquid) or it is already beyond GP (viscoelastic solid).

The rheological behavior of the critical gel is well understood. A simple power law was found to govern the dynamic mechanical behavior. The storage modulus, G', and the loss modulus, G'', are related as

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

where $\Gamma(n)$ is the Legendre Gamma Function. The 'gel strength' S depends on the mobility of the chain segements (given by persistency length and crosslink density, for instance). The relaxation exponent n may have values in the range

$$0 < n < 1.$$

Stoichiometrically balanced endlinking networks were found to relax with $n = 1/2$ [10,29] while stoichiometrically imbalanced networks follow

$n = 1/2$ for excess of crosslinker and
$n > 1/2$ for lack of crosslinker

[11,30].

It is interesting to note that, independently of these experiments, power law relaxation was predicted for the critical gel [7, 8]. These predictions are based on the assumption that an analogy exists between dielectric and mechanical properties of percolating systems [13].

The power law behavior is an expression of self similar structure [24, 25]. For the critical gel it was found to extend over a frequency range of more than five decades [9] which was the entire experimental range. A *lower* frequency limit is given by the correlation length of the self similar structure. This correlation length diverges at GP and the lower frequency limit could theoretically be equal to zero. However, a practical lower frequency limit is given by the finite sample size, i.e. at a scale of observation which exceeds the size of the sample in the rheometer. The *upper* frequency limit of the dynamic mechanical behavior is given by the molecular structure. At high frequency the scale of observation decreases below the lower scaling length first of the network (distance between junctions points) and then of the polymer chain, which one might call the 'glass length'. The glass length is given by the size of the network element which determines the glassy behavior at low temperature. At this small length scale, vitrification becomes important and deviation from the self similar behavior is expected. This transition is not the subject of the immediate study. For the following, we will tacitly assume that the scale of observation is sufficiently larger than the glass length. We obviously neglect the details of the

molecular structure by neglecting the high frequency glass behavior.

Analysis of the dynamic mechanical data shows that stress relaxation at GP occurs in a power law [11, 30]

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

The relaxation modulus can be introduced into a general constitutive equation for linear viscoelasticity [4, 15]. This results in the 'Gel Equation' [29]

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

which describes every known linear viscoelastic phenomenon at GP. With the gel equation, many new rheological experiments may be invented for detecting GP.

Evolution of linear viscoelasticity at increasing degree of crosslinking

The evolution of rheological properties during crosslinking may be observed through the dynamic viscosity

$$|\eta^*(\omega, p)| = \sqrt{G'^2 + G''^2}/\omega$$

using the extent of crosslinking, p, as parameter. The dynamic viscosity evolves gradually at the crosslinking reaction proceeds, see Figures 1 and 2. Each of the
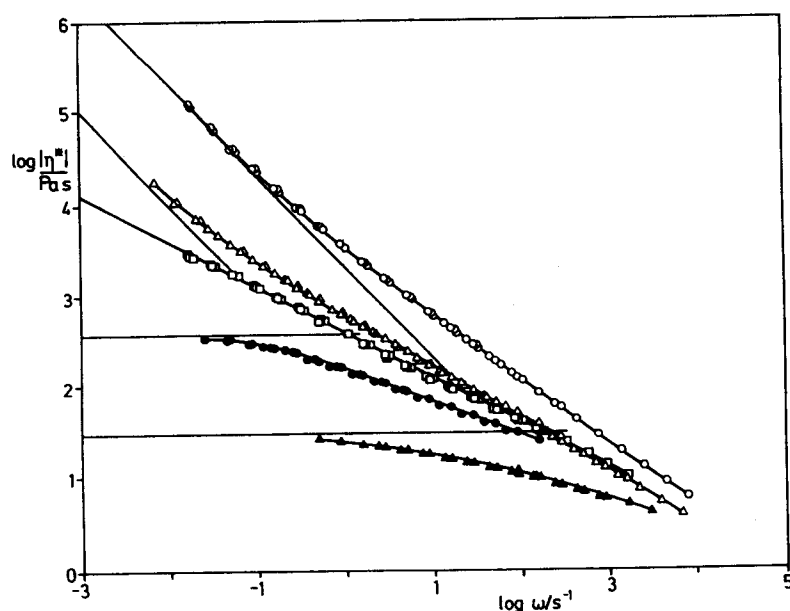
Fig. 1. Dynamic viscosity, as measured in a small amplitude oscillatory shear experiment (data of Chambon and Winter, [9]). Parameter is the degree of crosslinking, p. The power law exponent of the critical gels is $n = 1/2$. Parameter is the distance from the gel point $-260, -120, 0, 120, 260$ s (starting from lowest curve)
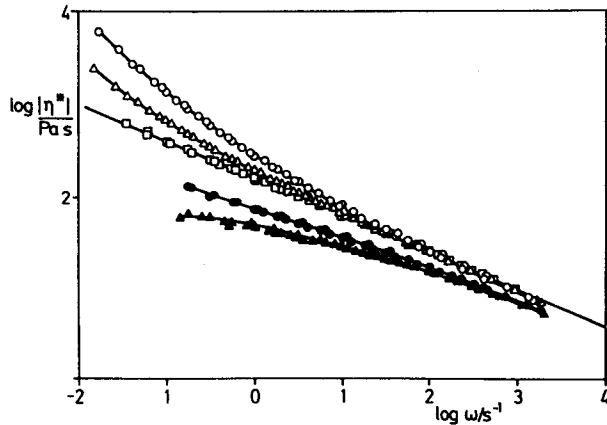
Fig. 2. Dynamic viscosity as measured in a small amplitude oscillatory shear experiment (data of Chambon and Winter [11]). Parameter is the degree of crosslinking, p. The power law exponent of the critical gel is $n = 0.58$. Parameter is distance from GP $-180, -108, 0, 12, 150$ s

samples has stable molecular structure since the reaction was stopped by poisoning the catalyst after predetermined reaction times.

The components of our samples 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 (zero slope as expected by a viscoelastic liquid) and equal to the zero shear viscosity $\eta_o(p)$. Shear thinning (frequency dependence) is observed at high frequencies, with an onset frequency which shifts to lower and lower values as GP is approached ($p \to p_c$). At GP, the dynamic viscosity follows a power law

$$\eta^*(\omega, p_c)| = aS(i\omega)^{n-1},$$

with

$$a = \pi/(\Gamma(n) \sin(n\pi)).$$

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, $\omega \to 0$, i. e. the material behaves as shear thinning at all frequencies. Beyond GP, the dynamic viscosity grows further, with a dramatic increase at low frequencies (slope of -1, as expected from a solid) which is associated with the appearance of an equilibrium modulus $g_\infty(p)$.

Near GP, typical asymptotic behavior for the dynamic viscosity at low and at high frequency is found:

$$\text{low } \omega \text{ asymptote: } |\eta^*| = \begin{cases} \eta_o(p) & \text{for pre-gel} \\ g_\infty(p)/\omega & \text{for post-gel} \end{cases}$$

$$\text{high } \omega \text{ asymptote: } |\eta^*| = aS\omega^{n-1}.$$

The high ω asymptote is the same for the pre-gel and the post-gel. These asymptotes are drawn in Figures 1 and 2 and values are given in Table 1.

Intersects of the asymptotes with the power law of the critical gel define characteristic relaxation times of the crosslinking polymer, see Figure 3. The characteristic relaxation time of the pre-gel is defined as the reciprocal of the frequency at which the zero viscosity asymptote intersects with the power law of the critical gel:

$$\lambda(p) = [\eta_o(p)/(aS)]^{1/(1-n)}; \quad p < p_c.$$

Equivalently, the characteristic relaxation time of the post-gel is defined by the reciprocal of the frequency at which the low frequency asymptote g_∞/ω intersects with the power law of the critical gel:

$$\lambda(p) = [aS/g_\infty(p)]^{1/n}, \quad p_c < p.$$

The characteristic relaxation time of the crosslinking system undergoes an interesting evolution. The initial relaxation time is very short, since the molecular weight of the reaction components is low. Near GP,

Table 1. Asymptotic values of dynamic mechanical data of crosslinking samples of Figures 1 and 2

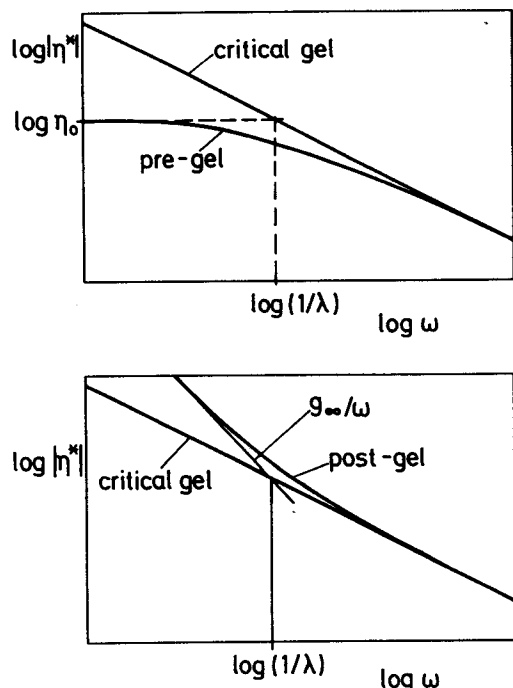| n	$t - t_c$ (s)	η_o (Pa s)	g_∞ (Pa)	S (Pa s^n)	λ (s)
1/2	-260	35	$-$	$-$	$7.4 \cdot 10^{-3}$
	-120	370	$-$	$-$	0.83
	0	$-$	$-$	226	$-$
	120	$-$	100	$-$	16.0
	260	$-$	2000	$-$	0.042
0.58	-180	71	$-$	$-$	0.15
	-108	156	$-$	$-$	1.0
	0	$-$	$-$	73	$-$
	72	$-$	28	$-$	19.0
	150	$-$	89	$-$	2.6

Fig. 3. Definition of the characteristic relaxation time of the pre-gel and the post-gel

the relaxation time rises sharply. The evolution is so dramatic that it could not yet be measured in detail. 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.

With these reference parameters, the viscosity curves are shifted to a form which allows comparison of the shape of the curves, (see Figs. 4 and 5). The high frequency slope is nicely seen in Figure 4, while data do not agree as perfectly in Figure 5. The viscosity curves of the pre-gel and the post-gel seem to curve much more sharply near GP then away from GP. A universal shape of the entire viscosity curve near GP does *not* seem to exist.

Scaling approximation near gel point

Gelation is a critical phenomenon and the evolution of properties near GP has been described by power laws [27] with critical exponents s and z

$$\text{pre-gel:} \quad \eta_0(p) \sim (p_c - p)^{-s}$$

$$\text{post-gel:} \quad g_\infty(p) \sim (p - p_c)^z .$$

Combination with the preceeding equations gives power law relations for the characteristic relaxation times in the pre-gel and the post-gel, however, within the critical range ($|p - p_c| \ll 1$):

$$\text{pre-gel:} \quad \lambda(p) \sim (p_c - p)^{-s/(1-n)}$$

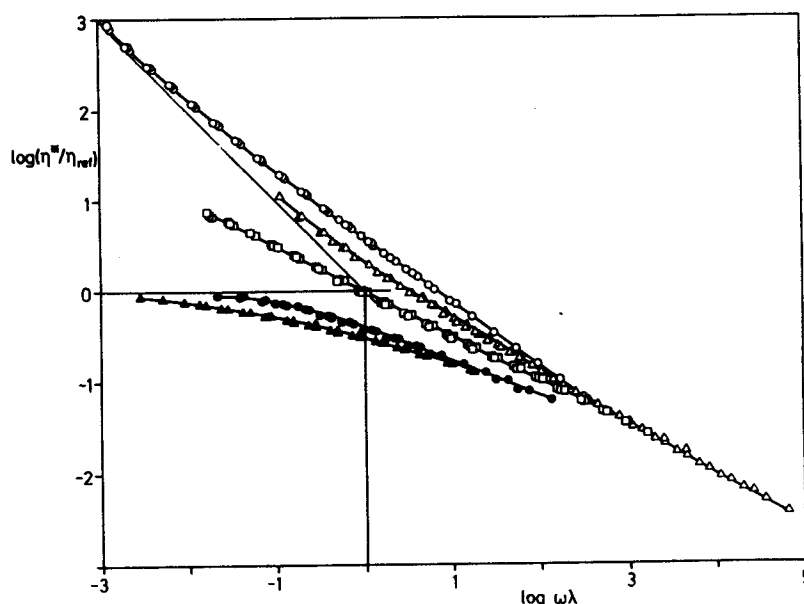$$\text{post-gel:} \quad \lambda(p) \sim (p - p_c)^{-z/n} .$$

Fig. 4. Shifted viscosity curves of Figure 1 for gel with $n = 1/2$. Parameters for the shift are given in Table 1. The reference viscosity η_{ref} was chosen as η_0 in the pre-gel and $g_\infty \lambda$ in the post-gel
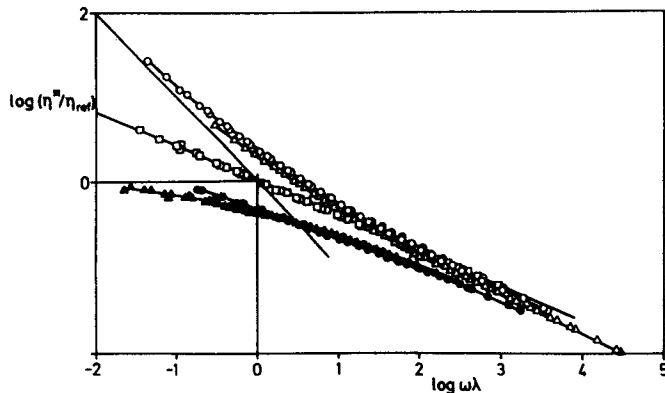
Fig. 5. Shifted viscosity curves of Figure 2 for gel with $n = 0.6$. Parameters for the shift are given in Table 1. The reference viscosity η_{ref} was chosen as n_o in the pre-gel and $g_\infty \lambda$ in the post-gel

The available experimental data is insufficient for determining the exponents. Adam et al. [1] found for polyurethane gels that z is about four times larger than s. Their values seem to depend on network structure. The gel was broken during the flow experiment and it is not yet clear whether it is possible to identify the power laws of broken gels with critical exponents.

It is interesting to consider a special case in which the characteristic relaxation time of the pre-gel and the post-gel follow the same power law (symmetry at $p = p_c$). This is the case if the exponents in the two equations above are set equal and a relation between s and z is calculated

$$ n = \frac{z}{z + s} . $$

Such a relation has already been proposed from theoretical arguments by Clerc et al. [7, 8] for precolating systems. With $n = 1/2$, this relation would predict that the critical exponents are equal, $s = z$.

Conclusions

Gelation is a continuous process with a limiting relaxation behavior at the gel point (GP). The limiting behavior is valid for both the liquid and the solid in the approach of GP ($p \rightarrow p_c$). Singular behavior is only expected in the limit of zero frequency or zero time, i. e. outside the experimentally accessible range. The measured linear viscoelastic behavior of a network polymer at GP (*critical gel*) is simple, as expected for a critical state: stress relaxes in a power law, t^{-n}.

This power law behavior of the critical gel is useful as a reference state for describing the evolution of rheology during gelation and, especially, during the transition through the gel point.

A characteristic relaxation time is defined by the intersecting asymptotes of the viscosity curves. This relaxation time increases in the approach of GP, diverges at GP, and then decreases again. There does not exist a characteristic time for the critical gel.

Detection of GP is made relatively easy by the fact that stress relaxation in a critical gel occurs in a power law. Equivalently, the dynamic moduli and the dynamic viscosities follow a power law in frequency which can be detected in a dynamic mechanical experiment.

It should be emphasized again that the entire study is restricted to polymers at temperatures much above the glass transition. The dynamic mechanic behavior would be considerably more complicated if vitrification interfered with the chemical gelation [20]. Physical entanglements are assumed to be of no importance in this study, since the molecular weights of the prepolymers were chosen as below the entanglement limit. Furthermore, the power law relaxation behavior has only been observed with endlinking systems. It might also occur with other systems and the range of validity will have to be studied in further experiments.

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Discussion

D. RICHTER:

First question: I am surprised that you said that your fractal dimension is equal to 2 (for the stoichiometrically balanced network). This is just the fractal dimension of a Gaussian chain.

WINTER:

That is indeed an amazing result. The linear chain has the same fractal dimension as the stoichiometrically balanced network at the gel point. If the stoichiometry is not balanced, we can produce critical gels with any dimension between 2 and 3. We have not yet found critical gels with a dimension below 2.

D. RICHTER:

Second question: You introduced just the Hausdorff dimension or the geometrical dimension of the fractals into the equation for the dynamic viscosity. I think it should be the spectral dimension of the fractals.

WINTER:

One might expect that all three fractal dimensions should be considered: the Hausdorff dimension, the spectral dimension and the walk dimension. This situation is simplified by the Alexander-Orbach conjecture, which states that for percolating systems, such as critical gels, the spectral dimension is equal to 4/3, independent of the geometric dimension of the problem. We therefore cannot use the spectral dimension for describing the range of relaxation exponents. The remaining fractal dimensions are interconnected, so that we are only free to use one of them for describing our experiments. For convenience, we related the relaxation exponent n to the Hausdorff dimension. You could equally well rearrange the result and express it in terms of the walk dimension.

ILAVSKY:

You mentioned that the structure dimension is equal to 2 and so is, as you will recall, the dimension of the Gaussian chain.

WINTER:

This does not mean that the critical gel has the structure of a Gaussian chain. It forms a highly imperfect network out of interconnected Gaussian chains, swollen in other Gaussian chains, but it certainly is not a Gaussian chain itself. The value of 2 might be just a coincidence. We actually expect to find critical gels with fractal dimensions between 1 and 3. This would correspond to relaxation exponents between 1/3 and 3/5.

REINECKER:

Can you directly verify the relation between the mass and the radius of the gel so that you have an independent verification of this fractal structure?

WINTER:

Such data would be good to have. As a first step, we are planning to measure the linear size of the largest clusters by light scattering. Major difficulties arise from the lack of contrast in our samples and from impurities in the sample. We do not know how to measure the mass of these largest clusters. However, even if we knew the mass-volume relation of the largest cluster, our information would still be insufficient, since the selfsimilar behaviour of the critical gels seems to originate from the entire distribution of macromolecular clusters and not only from the largest one.