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Comparison of Critical Exponents Determined by Rheology and Dynamic Light Scattering on Irreversible and Reversible Gelling Systems

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Summary: The sol-gel transition of a radical chain cross-linking copoly-merization system [*N*-vinylcaprolactam/2-hydroxylethyl methacrylate/allyl-methacrylate] and various thermoreversible gelling systems (mixtures made of xanthan gum and locust bean gum as well as gelatin) have been studied using in-situ time-resolved dynamic light scattering (DLS) and in-situ rheology. A critical dynamical behavior was observed near the sol-gel transition, which is characterized by the presence of a power-law spectra in the time-intensity correlation function $g_2(t)-1 \propto t^{-\mu}$ and in the low-amplitude oscillatory shear experiment $G'(\omega) \propto G''(\omega) \propto \omega^{n}$. A comparison of the obtained critical dynamical exponents μ and n were made according to the theory by Doi and Onuki. This theory predicts a relation between these exponents, but up to now no detailed experimental comparison was done in the past. It was found that for all investigated systems $n > \mu$.

Keywords: critical exponents; dynamic light scattering; gelation; rheology

Introduction

Gelation[1,2] is still a very important branch of critical phenomena. The sol-gel transition point is of primary importance in characterizing the mechanical properties of a gelling system in a wide variety of industrial applications. At the gel point, the largest cluster extends through the whole sample. Beyond this point, an elastic network with an equilibrium modulus is formed. There is a difference between chemical and physical gels. Chemical gels are irreversible and their cross-links have an infinite lifetime. In physical gels,[3] various forces, such as van der Waals, electrostatic attraction, hydrogen bonding, can be employed to bind polymer chains together to form a reversible gel network, in which the cross-links have a finite lifetime. Most of such reversible gels consist of double-or triple-helical sections where the chain length of the macromolecule is much larger than these ordered sections.[4] During gelation the sample changes from liquid-to-solid like behavior, which can be studied with dynamic-mechanical experiments.

Winter and coworkers reported a power law behavior for the shear moduli over a wide range of shear frequencies and later generalized it to

$$G'(\omega) \propto G''(\omega) \propto \omega^{n} \quad \text{with} \quad 0 < n < 1 \tag{1}$$

or

$$\frac{G''(\omega)}{G'(\omega)} = \tan\delta = \tan\left(\frac{n\pi}{2}\right) \tag{2}$$

for all gelling systems.[5] The frequency independence of the loss tangent in the vicinity of the gel point has been widely examined for chemical and physical gels and has also been employed to determine the gel point.

There are also some counterarguments[6,7] that the method introduced by

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Winter and coworkers is an assumption, neglecting entanglements and is not always useful. Many other gelling systems have a rather low gelation concentration and obtaining good shear data below the gel point should be difficult.[7] For other systems, including heat set globular proteins, G' appears to be $>G''$ well before gelation and no cross-over or power law is observed due to the highly ordered structure before gelation.[7,8]

A power law relaxation in rheology cannot be a sure indication for a gelation threshold. Self-similar relaxations has been associated with self-similar structures on the molecular and supermolecular level.[5] According to Winter and Mours,[5] a liquid-solid transition requires additional characteristics such as no upper time limit for the self-similar region, stretching out of the spectrum at the approach of the gel point and shrinking beyond the gel point and different curvature of the storage modulus before and after the gel point.

The light scattering technique is very suitable to study the gelation process without disturbing the gelling system. Shibayama and Norisuye[9] pointed out, that four methods in DLS for the determination of the gelation threshold are applicable: (i) the change in the scattered intensity (occurrence of speckle patterns), (ii) the power-law behavior in the time-intensity correlation function (TCF), (iii) a characteristic broadening of the decay time distribution function and (iv) the suppression of the initial amplitude of the TCF. These methods are non-destructive and no dilution of the sample is required. Each of these methods is a phenomenon based on the characteristic features of gels, i.e. (i) inhomogeneity, (ii,iii) connectivity divergence and (iv) nonergodicity.

In DLS, at the gelation threshold, a power law behavior[10] for the TCF is revealed,

$$g_2(t) - 1 = \frac{\langle I(0) \cdot I(t) \rangle}{\langle I \rangle^2} - 1 \propto t^{-\mu} \qquad (3)$$

with $0.21 \le \mu \le 0.9$,[10–12] here $\langle I(t) \rangle$ is the scattering intensity at time t with respect to $t = 0$ and $\langle \ldots \rangle$ denotes a time average.

The power-law behavior, which possesses no characteristic relaxation time, is self-similar. The incipient gel is a self-similar (fractal) distribution of fractal clusters of all sizes, from monomers to the infinite cluster. For many gelling systems a clear power-law behavior in the time-intensity correlation function at the gelation threshold was reported.[9,13,14]

Doi and Onuki[15] have discussed dynamic coupling between stress and composition in polymer solutions and blends. They obtained a power-law decay for the dynamic structure factor, $S(q,t)$, and the time-dependent shear modulus, $G(t)$, where both quantities follow the same power-law exponent (see eq. (5.35) in ref.[15]), that is in our notations

$$g_1(q,t) \propto S(q,t) \propto G(t) \propto t^{-\beta} \qquad (4)$$

with β in the range from 0.2 to 0.4. Since by Laplace and Fourier transformations the shear relaxation modulus $G(t)$ and the storage $[G'(\omega)]$ and loss parts $[G''(\omega)]$ of the complex modulus are connected it can be concluded that

$$G(t) \propto t^{-\beta} \Leftrightarrow G'(\omega) \propto G''(\omega) \propto \omega^{\mathrm{n}} \qquad (5)$$

That implies, that the critical exponents β and n have the same value at the gel point, $n = \beta$. The quantity $g_1(q,t)$ is the normalized first-order electric field TCF (see Equation (6)).

Since the shear modulus $G(t)$ and the TCF in the dynamic light scattering are connected via the longitudinal modulus and the cooperative diffusion coefficient,[10,16,17] it was concluded that both physical quantities show a power law behavior in the critical region.[16] As a first example, Coviello and Burchard[18] observed a power law in DLS and oscillatory rheology during gelation on a thermoreversible gelling system of *Rhizobium leguminosarum* at the same temperature. Shibayama and Norisuye[9] pointed out, that this problem of comparison of the exponents μ and n is not settled at all.

Here the results on the radical irreversible cross-linking system will be shown as an example which is representative for all the other studies.

Experimental Part

Sample Preparation

For the radical cross-linking gelation study, a mixture of 5.11 g of freshly under vaccum (20 Pa, 139 °C) distilled *N*-vinylcaprolactam (VCl, Aldrich), 2.10 g of 2-hydroxylethyl methacrylate (HEMA) and 0.025 g of allyl methacrylate (AMA) as a cross-linker were dissolved in 14 ml ethanol. The amount of the initiator was 60 mg of azobisisobutyronitrile (AIBN, Acros). HEMA and AMA were taken as received from Aldrich. The ratio of the components (VCl/HEMA/AMA) in the initial state in mol-% was 80/20/0.36. The cross-linking reaction itself and all the experiments pursuing the gelation process were done at 60 °C and always on a new prepared mixture.

Rheology

For rheology measurements a Fluids Spectrometer RFS 2 from Rheometric Scientific with a couette system (cup diameter: 34 mm, bob diameter: 32 mm, bob length: 33.3 mm) was used. Strains were applied in the range from 500% (in the liquid state, at the beginning of the measurement to provide an accurate torque response) up to 20% (around the gelation threshold to avoid a break down of the formed gel structure). The material was shown to behave linearly at these levels. 17 ml of the solution were taken here for the measurement.

Dynamic Light Scattering

An ALV DLS/SLS-5000 light scattering system was used equipped with an ALV-5000/EPP multiple digital time correlator. An Uniphase 1145P 22 mW He-Ne laser ($\lambda = 632.8$ nm) served as the light source. The online DLS experiments were carried out at an angle of $\theta = 90^\circ$ as a function of cross-linking time. The solution was filtered using a 0.2 μm nylon membrane filter. Typically, the sample in a test tube (diameter 10 mm, 3 ml reaction solution) was immersed and thermostated within an error of ± 0.1 °C in a toluene bath. This point was taken as the start of the reaction. The acquisition time of each run was 5 min to obtain enough data points especially at longer delay times. In dynamic LS, the TCF $g_2(q,t)$ in the homodyne mode was measured. It can be expressed by the Siegert relation

$$g_2(q,t) = A(1 + \mathrm{B}|g_1(q,t)|^2) \tag{6}$$

where t is the decay time, A is a measured baseline, B is the coherence factor (which is close to 1, when using fiber optics like in this given case) and $g_1(q,t)$ is the normalized first-order electric field TCF.

Results and Discussion

Figure 1 shows the storage ($G'(\omega)$) and loss ($G''(\omega)$) moduli as a function of angular frequency ω for three reaction times of the radical cross-linking system. At 143 min the solution before the gel point tends to behave classically as a Newtonian liquid ($G' \propto \omega^{1.65}$, $G'' \propto \omega^{0.97}$).

After 157 min, both moduli appear to run parallel to each other over two decades, indicating that the gel point was reached.

The loss tangent (*tan δ)* values were of course also constant over the frequency axis and were found to be around $\tan\delta \approx 2.7$ (not shown here) and in a plot tan δ versus reaction time all points intersect at the gel point, resulting in $\tan\delta \neq \mathrm{f}\ (\omega)$ (see Figure 2).

The following relations were calculated with a linear fit in a double-log plot:

$$G'(\omega) \propto \omega^{0.773\pm0.011} \text{ and } G''(\omega) \propto \omega^{0.736\pm0.002} \tag{7}$$

After the gel point, the storage modulus G' became larger than G'', the elastic portion became evident. The system now behaved as a visco-elastic solid.

Dynamic scaling based on percolation theory[13] does not yield unique results for the dynamic exponents as it does for the static exponents.[5,20] Several models can be

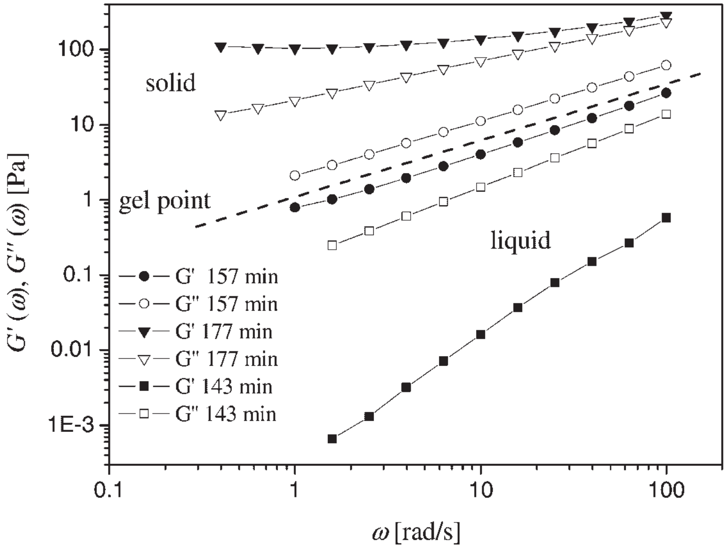

Figure 1.
Double-logarithmic plot of the storage $G'(\omega)$ and loss $G''(\omega)$ moduli as a function of angular frequency ω at three selected reaction times at 60 °C; Adapted with permission from ref.,[19] copyright (2004) by WILEY-VCH.

found that result in different values for n, s and z. These models use either Rouse and Zimm limits of hydrodynamic interactions or Electrical Network analogies. De Gennes proposed an analogy between the divergence of the viscosity and the divergence in the conductivity in a random superconductor-resistor network.[21] If the de Gennes values of the exponents z ($z = 1.94$; $G_e \propto \varepsilon^z$) and s ($s = 0.75$; $\eta_0 \propto \varepsilon^{-s}$), obtained from simulations are substituted into $n = z/(z+s)$, one obtaines $n = 0.72 \pm 0.02$.[13] The obtained dynamic exponent (average value $n \approx 0.75$) differs in this case only slightly from this prediction. This means, that this gelation process is described by percolation and supports de Gennes' analogy between the viscosity of the gelation bath and percolating superconductivity. De Gennes[22] predicted that percolation theory should hold for cross-linking of small-molecule precursors. However, he argued that for vulcanizing polymers (high M_w) only a very narrow regime near the gel point exists for which percolation is valid, i. e. these polymers should exhibit more mean-field-like behavior.

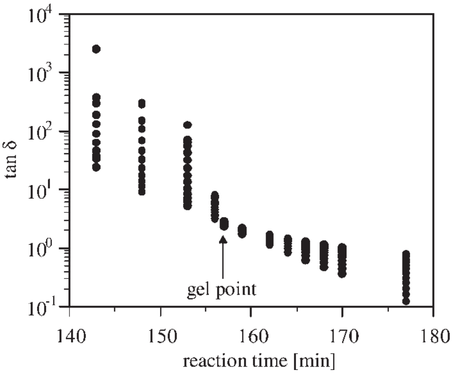

Figure 2.
Plot of tan δ at various angular frequencies versus reaction time.

In Figure 3 the scattered intensity profile during the cross-linking process is to be seen.

At the beginning of the reaction, the scattered intensity of about 25 kHz up to 25 min of the sample is due to the induction period of the reaction. After that, the intensity increased as a result of a growth of PVCL clusters. If the polymer concentration in the reaction bath reaches the so-called chain overlap concentration c^*, the intensity rise was abrupt, followed by a

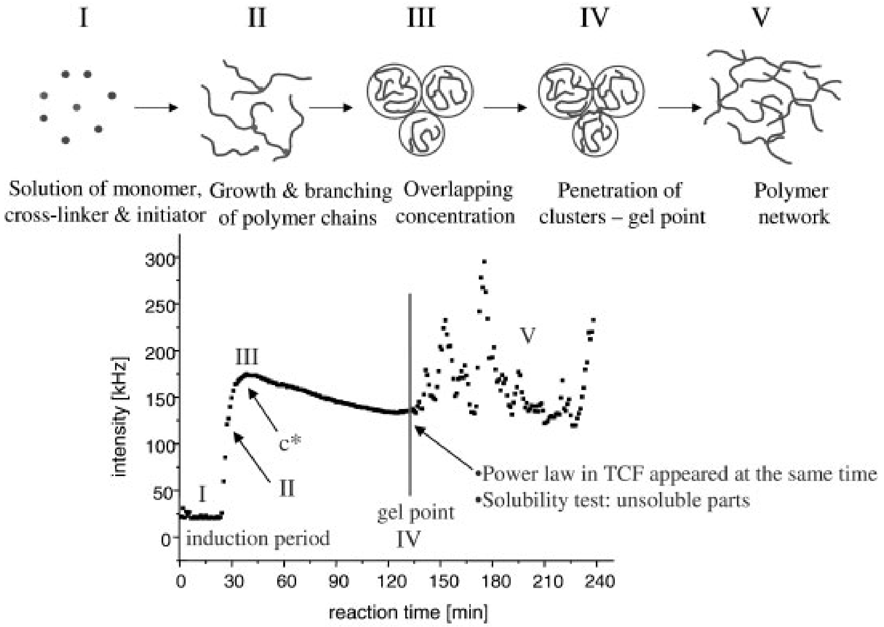

Figure 3.
Light scattered intensity profile and the presentation of the different stages during gelation process of the system [VCl/HEMA/AMA] at a scattering angle of $\theta = 90^\circ$.

gradual decrease to a plateau value. When an infinite network is formed, the polymer chains in the network lose their freedom to move freely and they are confined to a limited space. This results in non-cancellation of concentration fluctuations and an emergence of position-dependent concentration fluctuation (i.e. frozen inhomogeneities). These types of frozen inhomogeneities are observed as speckle patterns.[9]

At a certain time (specially emphasized in the Figure 3), the intensity shows strong fluctuations, which means an appearance of frozen inhomogeneities by cross-links. This point corresponds to the gelation threshold. At this point, finite clusters start to connect each other. The same time (140 min) at which the speckles where observed, a power law in the TCF can be found, see Figure 4.

Typical polymer solution dynamics in the time-correlation function is observed from the beginning of the reaction up to 135 min reaction time. The decrease in the time correlation function in the region of 0.1 ms can be interpreted as a superposition from the collective diffusion mode (caused by slightly cross-linked clusters and sol molecules) and the cluster mode[19] (caused by formed larger connected gel clusters). After 140 min, a power law behavior was found over three decades in frequency. At this time, slight deviations from the power law behavior of the time correlation function at longer delay times ($t > 10^3$ ms) showed, that the current measurement is just beyond the gel point. Therefore, the real exponent can be slightly smaller, but cannot be measured in a more exact way due to the rather fast reaction rate. A linear fit (solid line, regression coefficient = 0.99) was applied to the data at 140 min in a range between 5…1000 ms, resulting in an exponent of

$$\mu = 0.62 \pm 0.001 \tag{8}$$

After this time, the dynamics is more characteristic for gels. The value of the exponent supports the assumption of a high degree of branching of the critical gel clusters. The higher the value of μ, the higher

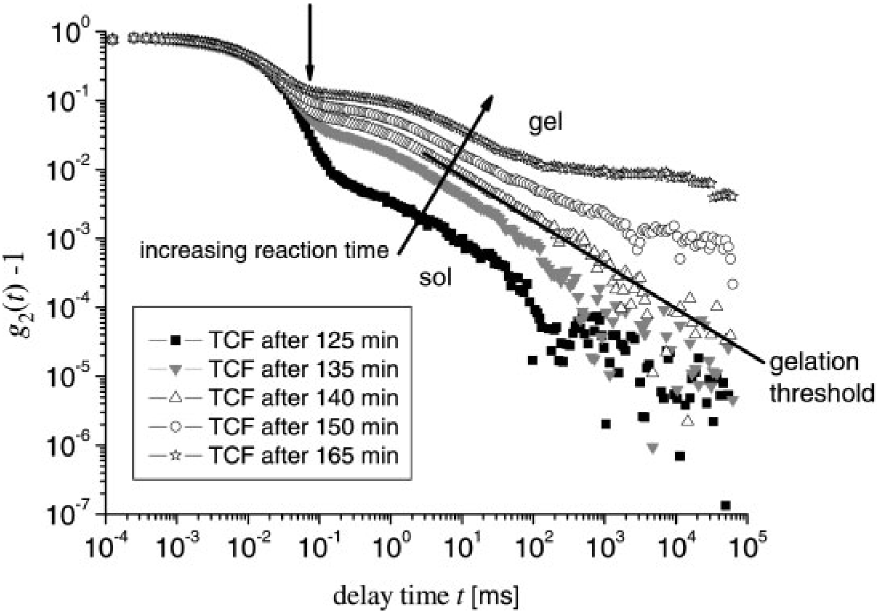

Figure 4.
TCFs $g_2(t)-1$ versus the delay time t at a scattering angle of $\theta = 90^\circ$ and at several reaction times at 60 °C. The arrow around 0.1 ms shows the crossover between collective mode and cluster mode; Adapted with permission from ref.,[19] copyright (2004) by WILEY-VCH.

the amount of branching.[11] Calculating $g_1(t)$ from $g_2(t)-1$-values according to the Siegert relation (Equation (6)), one obtaines a value of $\beta = 0.31$.

If we compare the upper and lower limits of the relaxation time scales in rheology and DLS (at $\theta = 90^\circ$) where the power law is present then we find, that there is a good overlap for about two decades: rheology (0.01...1 s) and DLS (0.005...1 s).

The difference in the reaction times between DLS and rheology, which were necessary to reach the gel-point, can be attributed to the different reaction volumes. A system with a larger reaction volume needs longer reaction times to reach the gelation threshold. Another reason therefore can be the variation in the induction periods: In the rheology experiment, the sample is in contact with oxygen, which cannot be avoided. A solubility test of 3 ml solution of the reaction mixture (like in the present DLS experiments) showed the occurrence of gelation after 145 min. Insoluble amounts of the formed gel were consequently observed. On the other hand, no gelation was detected at 135 min.

Similar extended DLS and rheology studies were done on other thermoreversible systems (three mixtures made of xanthan gum and locust bean gum[23,24] (XG/LBG) and gelatin[12]). The following critical exponents were observed: (XG/LBG): $n_1 = 0.62$, $\mu_1 = 0.36$; $n_2 = 0.67$, $\mu_2 = 0.32$; $n_3 = 0.59$, $\mu_3 = 0.41$; gelatin: $n_4 = 0.68$, $\mu_4 = 0.21$.

It must be mentioned, that the difference in the estimated gelation temperature (power laws in the oscillatory shear experiment and in the TCFs in the DLS) on all mixtures made of xanthan gum and locust bean gum was 5–7 K.[23,24] On the other hand, on gelatin[12] the same gelation threshold temperature was found in rheology, DLS and NMR diffusion experiments. A detailed explanation for the unusual behavior has been given,[24] which can be of importance for other gelation studies using different methods as well.

Conclusion

On irreversible and reversible gelling systems rheology and DLS studies have been done. The occurrence of a power law behavior observed on both methods was mostly assigned to the gel point. The physical meaning of μ and, as a consequence, the physical origin of the power law behavior in DLS seems to be not completely understood in detail and is therefore different from that of the rheological exponent n. It was shown, that up to now in each investigated case the relation $n > \mu$ $(n \neq \beta)$ at the gel point is valid and no fixed mathematical relation exists between them. A reconsideration, new derivation and modification of the results of Doi and Onuki is necessary.

It could be also of interest to carry out DLS and diffusing wave spectroscopy (DWS) investigations on model gelling systems and to convert these data into elastic and viscous moduli. A recent example of that procedure was given by Dasgupta and Weitz.[25] The direct comparison of such data with directly measured rheological results considering Doi and Onuki seems relevant.

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