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Communications to the Editor

Criteria for the Point of Gelation in Reversibly Gelling Systems According to Dynamic Light Scattering and Oscillatory Rheology

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According to Ferry[1] a gel is defined as a substantially diluted system which exhibits no flow. In statistical mechanics gelation is understood as a critical phenomenon, and the critical point is defined by divergence of the correlation length ξ or the second moment of the molar mass distribution which implies divergence of the weight-average molar mass M_w.[2–5] Both quantities can be obtained by scattering measurements from covalently bound structures after extrapolation of the data to zero concentration. Such a dilution procedure cannot be applied to reversibly associating systems since dissociation to an individual chain will occur on dilution.

At present there is much discussion[6] as to whether a gel point can be defined dynamically by measurements at finite concentrations of the eventually formed gel. Winter and Chambon[7,8] demonstrated with end-linked poly(dimethylsiloxane) (PDMS) gels that power law behavior is obtained at the gel point for the shear moduli $G(t)$, $G'(\omega)$, and $G''(\omega)$ for permanently cross-linked chains. Loss and storage moduli were found to coincide for a stoichiometric balance of cross-linker to chain end groups, whereas G'' appeared to be larger than G' in systems with a deficiency of cross-linker.

Somewhat later Martin and Wilcoxon[9] realized with inorganic gels of SiO_2 similar power law behavior for the time correlation function of dynamic light scattering at a point of conversion that corresponded to the gel point.

Te Nijenhuis et al.[6,10–12] also proved power law relationships for G' and G'' with a reversibly gelling PVC system, and just recently Lang and Burchard[13] found the same behavior also for the time correlation function (TCF) of dynamic light scattering (LS) with the reversibly gelling Tamarind seeds polysaccharide (TSP) in 1 N Na_2SO_4 aqueous medium. No proof has been given so far as to whether the mentioned power laws occur in rheology and dynamic light scattering under the same conditions.

We now report data from dynamic light scattering and oscillatory rheology measurements performed with the same system. The polymer used is an exopolysaccharide from *Rhizobium leguminosarum*, strain 8002 (*Rhiz. legum.* 8002), with the molecular parameters M_w = 480 000 g/mol, R_g = 100.0 nm, R_h = 28.8 nm, $\rho = R_g/R_h = 3.5$, L_w = 287 nm, and $l_k \gg L_w$ where L_w is the contour length and l_k the Kuhn segment length. Measurements were made in 0.1 N NaCl aqueous solution. A 2.0% (w/v) solution was used. An ALV light scattering goniometer equipped with the ALV 3000 structurator/correlator was used (ALV, Langen in Hessen, Germany). Reversible gelation was observed also with 1.5% and 3.0% solutions which disclosed a weak decrease of the gel temperature when the concentration was increased. Figure 1 shows time correlation functions (TCF) for the 2% solution plotted double logarithmically against the delay time for five different temperatures. Typical solution dynamics is observed at the high temperatures of 50 and 45 °C, whereas at the low temperatures of 16 and 39 °C the dynamics is characteristic of gels. Behavior very close to power law is obtained at 44 °C. With the exception of the curve at 16 °C the TCF's could be fitted by stretched exponentials, with an additional constant term for the gels

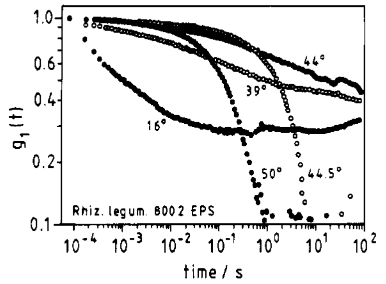

Figure 1. Double-logarithmic plot of time correlation functions for 2% *Rhiz. legum.* 8002 exopolysaccharide in 0.1 N NaCl aqueous medium at five temperatures. M_w = 480 000 g/mol, R_g = 100.0 nm, and R_h = 28.8 nm.

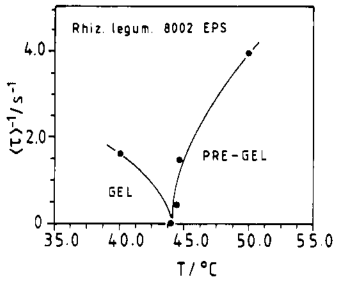

Figure 2. Inverse mean relaxation time as a function of temperature for the aqueous 2% *Rhiz. legum.* 8002 system in 0.1 N NaCl solution. The minimum occurs close to 44 °C.

$$g_1(t) = A \exp[-(t/\tau)^\beta] + C \qquad (1)$$

in which A and C are constants corresponding to the correlation strength and the gel plateau, respectively. The two other parameters β and τ characterize the type and mean relaxation time of the TCF which is given by

$$\langle\tau\rangle = (\tau/\beta)\Gamma(1/\beta) \qquad (2)$$

with Γ being the gamma function. The inverse relaxation time is proportional to the translational diffusion coefficient at temperatures above the gel point, and it is the cooperative diffusion coefficient of the gel mode below the gelling temperature. Divergence of $\langle\tau\rangle$ can be expected at the gel point, i.e., $1/\langle\tau\rangle = 0$. Figure 2 exhibits the dependence of the mean relaxation time as a function of temperature. Apparently close to 44 °C one has $1/\langle\tau\rangle$ = 0. For the TCF at 16 °C a more sophisticated fitting function had to be applied which will be discussed in a separate paper.

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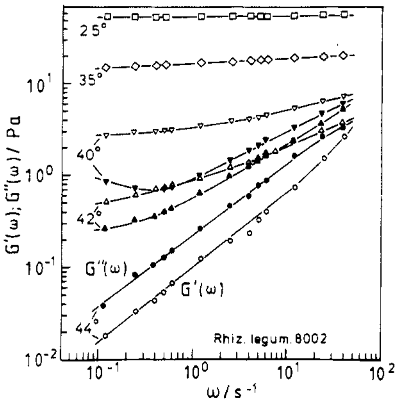

Figure 3. Frequency dependence of storage and loss moduli $G'(\omega)$ (open symbols) and $G''(\omega)$ (filled symbols) for the same polysaccharide as in Figures 1 and 2 at various temperatures. The loss moduli at 25 and 35 °C are very similar to those at 40 °C and are not shown. Nearly parallel lines are obtained at 44 °C with exponents of 0.790 ± 0.02. A Bohlin CS rheometer with CP4/40 geometry was used, i.e., cone–plate geometry, 4° cone angle, 40-mm diameter for the plate and cone. The applied strain was 0.1, i.e., an angular distortion of 0.4°.

Finally oscillatory rheologic measurements were performed with a Bohlin CS rheometer at temperatures in the range from 16 to 44 °C. A cone–plate geometry was used with a 40-mm plate/cone diameter and a cone angle of 4°. The applied strain was 0.1 which corresponds to a deformation angle of 0.4°. The results at some selected temperatures are shown in Figure 3. Clear gel behavior is obtained at temperatures below 42 °C. Up to 40 °C the curves for the loss modulus $G''(\omega)$ are not changing significantly, and for clarity only $G'(\omega)$ is plotted. At 42 °C the loss modulus is still considerably lower than $G'(\omega)$, while only 2° higher at 44 °C; both moduli appear to run parallel to each other with exponents of 0.79 ± 0.02. Now $G'' > G'$ is found which agrees with the findings of te Nijenhuis[6] for the PVC gel. The transition from solution to gel behavior is very sharp, and at the true gel point possibly both moduli coincide completely over the whole frequency domain.

In conclusion we can state that at the presumed gel temperature of 44 °C we find (i) power law behavior for the TCF of dynamic light scattering, (ii) divergence of the mean relaxation time, and (iii) power law behavior for both the storage and loss moduli. To our knowledge this is the first example of a thermoreversibly gelling material where all three criteria for a gel point were measured and found to be consistent with the picture of an onsetting gel. Power law behavior of the time correlation function and indications of divergence of the mean relaxation time were found also with polyurethanes by Adam et al.[14] and by Martin et al.[9] with inorganic silica gels. Recently the same research group[15] also performed mechanical relaxation measurements with the same silica gels and found again power law behavior for $G'(\omega)$ and $G''(\omega)$ at the gel point.

We emphasize, however, as was pointed out earlier,[13] that power law behavior may be only a sufficient but not necessary condition for critical gelation. Gelation may occur with hard globular structures of very large dimensions, and these structures may no longer fulfill the condition that in a system of finite dimension the substructure dimensions are small compared to the critical correlation length at the gel point.

The mechanism of the gelation process is still unknown to us. There is, however, strong evidence that by the addition of salt or nonionic low molar mass compounds the activity of water is reduced. This will probably cause a strong lateral association of the very stiff triple helices of this polysaccharide[16] which eventually leads to gelation. Details of the solution properties for the present microbial polysaccharide will be given in a forthcoming paper.[17]

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