Dynamic Light Scattering at the Gel Point

Gelation of macromolecular systems is known as a typical critical phenomenon.[1,2] The critical point of gelation is clearly defined by the condition that the second moment of the cluster size distribution diverges.[3] This definition is equivalent to the divergence of the weight-average molecular mass and of the static correlation length, ζ, i.e., $M_W \rightarrow \infty$ and $\zeta \rightarrow \infty$, where ζ is proportional to the Z-average of the root-mean-square radius of gyration of the formed clusters, $\zeta \sim (\langle S^2 \rangle_Z)^{1/2}$. Thus, no problems of principle arise if static or equilibrium properties of the clusters can be measured.

There is at present much discussion as to whether a gel point can also be defined dynamically. A common check for gelation is the simple tilting test, in which for instance a test tube is turned upside down; if no visible flow occurs within a few seconds the system is considered a gel. Often this simple test coincides within experimental error with the more accurate determination of the point where M_W tends to infinity.

However, in many cases creep flow with little recovery is observed after a longer time of exposure in the gravity field or stronger external forces. Such behavior appears to be the rule for most physical gels where cross-links are formed by reversible physical interactions and not by permanent chemical bonds. Furthermore, the point of gelation in a physical gel is a function of the volume fraction, Φ, of the polymer. Thus extrapolation of measured quantities to zero concentration, needed for the determination of M_W or ζ, cannot be performed, since dissociation into smaller clusters occurs on dilution. Therefore other criteria have to be found to define the point of gelation for such physical gels.

Recently Winter[4] reported power law behavior over a wide range of shear frequencies for the shear modulus of a permanently gelling system. Since the shear modulus $G(t)$ and the time correlation function (TCF) of the electric field $g_1(t)$ in dynamic light scattering (LS) are connected via the longitudinal modulus and the cooperative diffusion coefficient,[5] one might expect $g_1(t)$ also to show power law behavior in the critical region. Such behavior was indeed observed for covalently cross-linked networks,[6] but no data were reported on the development of the TCF in the region *beyond* the gel point.

Shear modulus[7] and time correlation function of dynamic LS[8] can both be expressed as a sum of exponentials, each of them characterized by the relaxation time of a certain molecular process. Consequently, similar behavior of the two quantities can be expected, not only at the critical point but also over the whole range of extent of cross-linking, starting from molecularly dispersed solutions and ending up with the readily formed gel. This statement should hold for permanently cross-linked as well as for physically clustered systems, which would not necessarily imply the above-mentioned power law behavior (see below).

We have performed light scattering measurements on a thermoreversibly gelling system below and beyond the gel point in order to check this expection. Thermoreversible gels were prepared by mixing a solution of 0.18% (w/v) of the so-called Tamarind Gum (Gidley et al.[9]), a kernel polysaccharide of *Tamarindus indica*, with solutions of Na_2SO_4 of different concentrations of 5 mmol of NaN_3. All solutions had been filtered over Millipore filters of 0.45-μm pore size before mixing. They were poured into light scattering cells (after melting the ones that had already gelled). Since we observed an increase of the melting temperatures of the gels for at least 4 weeks, for certainty, the samples were allowed to equilibrate for a period of 3 months before the time correlation functions were measured with an ALV-3000 196-channel correlator/structurator in the multi-τ mode.

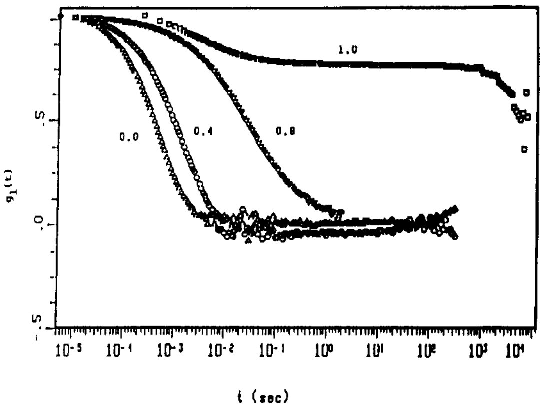

Figure 1. Time correlation functions $g_1(t)$ at a 90° scattering angle for a 0.09% (w/v) polysaccharide sample recorded at 25 °C. The numbers indicate the molar sulfate concentrations.

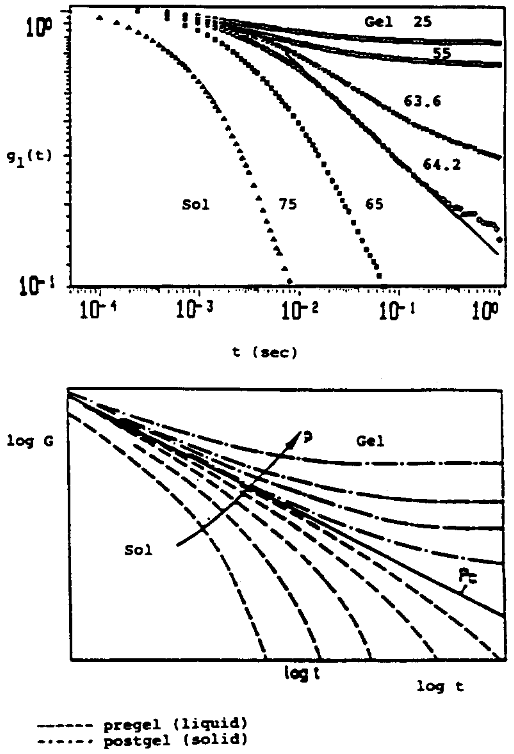

Figure 2. (Top) Time correlation functions at a 90° scattering angle for the sample with 0.09% (w/v) polysaccharide and 1.0 M sodium sulfate recorded at the temperatures indicated by the numbers. (Bottom) Shear modulus of a poly(dimethylsiloxane) as a function of time in dependence on the degree of polymerization.[4,11]

Figure 1 shows time correlation functions for different concentrations of sodium sulfate measured at room temperature and a 90° scattering angle of this 0.09% sample. There is a shift in the relaxation time toward higher values with increasing concentration of SO_4^{2-}, which is much larger than the increase of the solvent viscosity due to the sodium sulfate added. Samples of a sulfate concentration larger than 0.8 mol/L exhibited no flow in the gravity field at room temperature but melted at higher temperatures. Samples with concentrations of SO_4^{2-} higher than 1.2 mol/L could no longer be melted. For this

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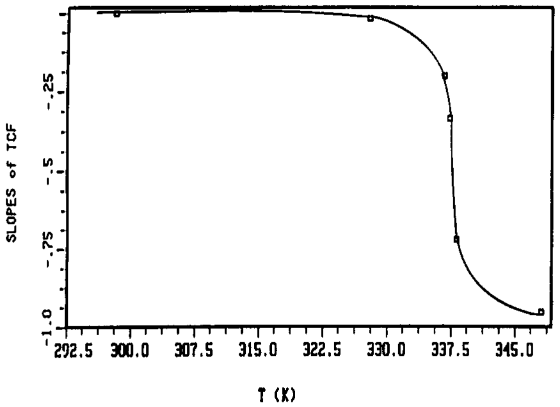

Figure 3. Slopes of the linear parts of the time correlation functions in Figure 2 as a function of temperature. The estimated point of inflection is T = 64.3 ● 0.2 °C.

reason a mixture containing 0.09% (w/v) polysaccharide and 1.0 M SO_4^{2-} was chosen to study the temperature dependence of the time correlation function.

If the results are plotted double logarithmically, as in Figure 2, one recognizes in every function a linear part. In Figure 3 the slopes of these linear parts are shown as a function of temperature. Around a certain temperature there is a very sharp increase in the slopes, resembling a jump from almost zero to nearly unity. In the present stage of our knowledge we cannot yet offer a physically sensible interpretation of these slopes, but it is very tempting to identify the temperature at the point of inflection in Figure 3 as the gel point.

A most striking feature of the TCFs is that they exhibit qualitatively the same change in shape as the elastic modulus of other systems, when passing the critical point of gelation.[4] According to this similarity, there should exist one curve (Figure 2) showing power law behavior over a fairly wide range of relaxation times. The correlation function recorded at 62.4 °C appears to fulfill this requirement best, from which we derive an exponent of $a = -0.34 \pm 0.015$. For the covalently cross-linked system studied by Martin et al.[6] the corresponding exponent was $a = -0.27 \pm 0.03$, and they have shown that such power law behavior of the dynamic structure factor is a critical feature, e.g., may be regarded as a characteristic of the gel point. Therefore, we may say that the critical temperature of the system under consideration lies very close to 62.4 °C, with an estimated error of 0.2 °C. This value is identical with the temperature of the inflection point in Figure 3, which may strengthen our intuitive hypothesis concerning the identification of the inflection point with the critical point.

We emphasize that the reported power law behavior is not a trivial and universal expection for physical gels. There have been reported typical physical and thermoreversible gels that do not show power law behavior but, instead, behave like strongly entangled rodlike, micellar filaments.[10] The simple tilting test clearly indicates gel behavior, but the oscillary rheological measurements demonstrate flow behavior at frequencies below $\omega < 1$ rad/s.

Hence, the observed power law behavior in our thermally reversible system indicates only an aggregation process similar to the random cross-linking in permanently bound clusters. The duration of association and dissociation seems not to play a significant role here, which probably means that the lifetime for a bond is longer than the largest relaxation time that can be reliably detected by light scattering. In typical gels formed by entanglement the lifetime of a cross-link is, by definition of such a transient network, zero or at least very short compared with the fastest relaxation time that can be measured by dynamic LS. Interesting behavior can be expected in the region between these two limits.

Acknowledgment. This work originated from the EEC Science Stimulation Contract No. ST2P/0250/3/I on the properties of Tamarind kernel polysaccharide and its new derivatives.

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Received September 18, 1990
Revised Manuscript Received November 23, 1990