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# Rheological Gel-Point Determination for a Polysaccharide System Undergoing Chemical Cross-Linking

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Dynamic viscoelastic properties of polymer solutions have been thoroughly investigated, and the underlying principles appear well established.<sup>1</sup> Recently, the more complicated problem of understanding the dynamic viscoelastic changes occurring during chemical or physicochemical processes involving polymers has been addressed.

In particular, attention is being focused on the gel-point (GP) determination in polymer cross-linking systems, one important topic of discussion being whether or not a GP can indeed be defined dynamically for such systems.

Winter and Chambon<sup>2,3</sup> demonstrated using end-linked poly(dimethylsiloxane) (PDMS) chemical gels formed *in situ* (i.e., in the rheometer) that GP can be precisely identified and located by monitoring the dynamic viscoelastic parameters throughout the reticulation process. At the GP, power law behavior is observed 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  $G''$  larger than  $G'$  resulted in systems with a deficiency of cross-linking agent.

Muller et al.<sup>4</sup> established the dependence of the exponents of the power law at GP on the stoichiometric conditions for poly(ethylene oxide)/pluriscyanate chemical cross-linking reactions.

In addition, the possibility of extending the Winter and Chambon criterion also to physical reversible gelation of poly(vinyl chloride) (PVC) has been explored.<sup>5,6</sup>

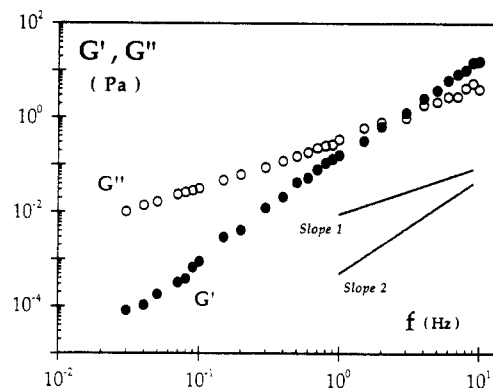
A few similar experimental data are available also for the physical gelation of some biopolymers. For instance, Cuvelier and Launay<sup>7</sup> followed the moduli frequency dependence evolution at different temperatures for gelatin,  $\iota$ -carrageenan, and xanthan/carob gum aqueous systems and found a power law behavior at a critical, characteristic temperature for each biopolymer system.

Recently, for a physically gelling polysaccharide system a power law behavior was found by Coviello and Burchard<sup>8</sup> using dynamic light scattering techniques, in agreement with rheological evidences.

Finally, physical gelation in pectic acid/Ca(II) aqueous systems has been recently investigated,<sup>9,10</sup> and the critical exponents have been determined according to percolation theory.<sup>11,12</sup>

However, as far as we know, there are no examples of chemical gelation of polysaccharides monitored and characterized according to the criteria originally proposed by Winter and Chambon. One likely reason is that polysaccharide cross-linking reactions normally employed are rather harsh, can lead to chain degradation, and are difficult to carry out in a rheometer.

In our laboratory we have developed a process for the partial esterification of glycuronans (tetrabutylammonium salt form) with alkyl or arylalkyl halides which can be performed in homogeneous solution (e.g., in dimethyl sulfoxide) at room temperature and which brings about only moderate, if any, chain degradation.<sup>13,14</sup> Reticulation



**Figure 1.** Frequency dependence of storage and loss moduli for PGA/TBA 6% (w/v) in DMSO at 20 °C. Lines with slopes 1 and 2 are reported for comparison with experimental curves.

processes can then be achieved simply by using, e.g., dihaloalkanes, the degree of cross-linking being controlled by the stoichiometric ratio of reactants.

The results reported here concern the rheological study of a pectic acid sample, a linear homopolymer of  $\alpha$  (1 $\rightarrow$ 4)-linked D-galacturonic acid residues (PGA; Sigma product no. P-1879;  $M_w$  70 000, polymerization degree = ca. 350; galacturonic acid content 98%; 2% rhamnose content as backbone irregularity), undergoing controlled chemical gelation.

In practice, the polymer obtained in the tetrabutylammonium (TBA) salt form (equivalent weight = 419), utilizing a Dowex "50  $\times$  8" ion exchange resin, was dissolved (6% w/v;  $c[\eta] = 4$ ) in dimethyl sulfoxide (DMSO) and added, at 20 °C, to a suitable volume of dibromohexane (Fluka no. 34191) to obtain the desired stoichiometric ratio (0.15–1.0 mol of Br/equiv of PGA).

The mixture was then transferred in the cylindrical cell of a Bohlin CS rheometer kept at 20 °C (coaxial cylinder geometry; Bohlin "C14"; R1/R2 = 0.909).

To avoid moisture contamination, the entire measuring system was protected with a homemade drybox and fluxed with pure, dry nitrogen.

The applied strain was 0.05 (a function named "auto-stress" for the simulation of a constant strain deformation experiment has been used; data obtained confirm the required deformation).

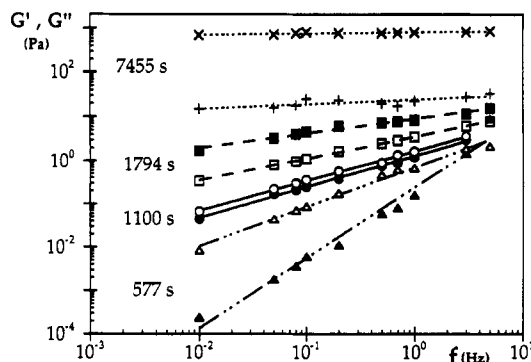
During the cross-linking reaction oscillatory sweep measurements were done in the 0.01–5-Hz frequency range.

Before running a cross-linking experiment, an oscillation measurement in the 0.01–10-Hz frequency range was performed on the polymer solution (obviously in the absence of the dibromoalkane) to control its homogeneity. Typical results of such an experiment are reported in Figure 1.

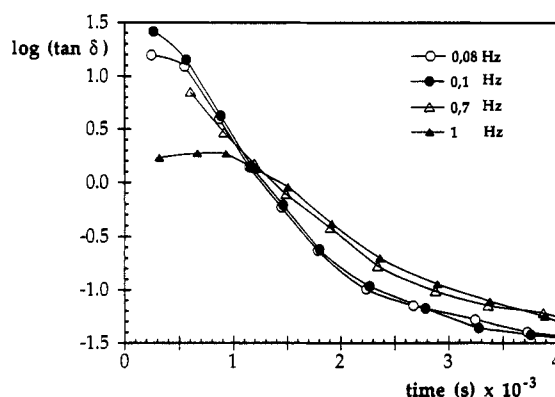
Thereafter, the dibromoalkane was added; the dynamic viscoelastic data collected during the course of the cross-linking reaction clearly revealed, as shown in Figure 2, the evolution of the system into a viscoelastic solid with moduli parallel to each other and independent of frequency.

A set of data on moduli and phase evolution are summarized in Figures 2 and 3.

The plot of  $\log(\tan \delta)$  against time (Figure 3) exhibits a quite sharp crossing point for all frequencies considered at around 1100 s after the start of the reaction: at the same time, the two moduli  $G'$  and  $G''$  show the characteristic power law behavior. The frequency range explored is quite limited, mainly because of the relatively high reaction speed.



**Figure 2.** Storage and loss moduli evolution of the PGA/TBA sample during cross-linking with dibromohexane in DMSO at different aging times.  $G'$  and  $G''$ : at 577 s ( $\blacktriangle$  and  $\triangle$ ); at 1100 s (GP) ( $\bullet$  and  $\circ$ ); at 1794 s ( $\blacksquare$  and  $\square$ ); at 7455 s ( $\times$  and  $+$ ). Experimental equivalent ratio between the polymer and cross-linker is 1.



**Figure 3.** Time dependence of the  $\log(\tan \delta)$  in the earlier stages of the reticulation reaction. GP occurs at 1100 s.

On the other hand, no experimentally facile procedure to slow down or to stop the reaction at a given extent of cross-linking without introducing excessive perturbation in the system has been found.

Data were corrected for the extent of reaction occurring during the oscillatory sweep experiments according to the procedure of Lairez et al.<sup>15</sup>

The example reported here refers to a cross-linking reaction under balanced stoichiometry of reactants conditions: in this case, a 0.70 value for the average power law exponent of the moduli in the vicinity of the gel point was calculated.

Our estimated value is not too different from that reported in the literature for other polymeric systems (see ref 7 for a review).

Preliminary results obtained in our laboratory suggest that for reactions with unbalanced stoichiometry the system considered follows the same power law behavior (same exponent) while the gel point is shifted toward longer times.

In conclusion, we emphasize that the new cross-linking system described here provides an additional example of the Winter and Chambon criterion and that the critical exponent found is in agreement with predictions based on percolation theory.<sup>16-18</sup>

It is also noteworthy that the reaction products recovered and purified at the end of the rheological experiments are, as expected, insoluble in common solvents, can be swollen in aqueous media, and exhibit a characteristic, spongelike spatial connectivity.

Our rheological studies of polygalacturonate systems undergoing chemical gelation are currently being extended to include the case of other glycuronans and cross-linking agents of different chain length under both balanced and unbalanced reaction conditions.

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