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Effects of Polymer Concentration and Cross-Linking Density on Rheology of Chemically Cross-Linked Poly(vinyl alcohol) near the Gelation Threshold

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ABSTRACT: The evolution of viscoelasticity during the gelation reactions of semidilute solutions of poly(vinyl alcohol) (PVA) in the presence of cross-linker (glutaraldehyde) has been monitored through the sol−gel transition with dynamic mechanical experiments. The gelation time of the system decreased with increasing PVA and cross-linker concentrations. At the gel point, a power law frequency dependence of the dynamic storage modulus ($G' \propto \omega^{n'}$) and loss modulus ($G'' \propto \omega^{n''}$) was observed with $n' = n'' = n$. The power law exponent is lower than that predicted (0.7) from the percolation model. The value of n decreases with increasing polymer and cross-linker concentrations. The critical gel strength parameter (S) rises with increasing polymer and cross-linker concentrations. Some stress relaxation measurements on gelling PVA systems were also carried out. At the gel point, a power law time dependence of the relaxation modulus was detected, but the relaxation exponent was lower than the corresponding one obtained from oscillatory shear measurements. The fractal dimension (d_f) was determined for the incipient PVA gels. The value of d_f increased with increasing polymer concentration and cross-linking density. This trend of d_f suggests a more "tight" structure of the network at higher polymer concentrations and cross-linking densities.

Introduction

The linear viscoelastic behavior in dynamic experiments of gelling polymer systems near the sol−gel transition has attracted a great deal of attention in recent years. Measurements of the oscillatory shear moduli have frequently been used to monitor continuously the viscoelastic properties in chemically[1−21] and physically[22−23] cross-linked networks during the gel evolution. The structure of the network and the cross-linking density are important factors for the rheological characteristics of the incipient gel. The network structure and the connectivity issue are usually addressed in the framework of percolation and fractal models.[16,34−42]

Poly(vinyl alcohol) (PVA) in semidilute aqueous solutions can form chemical[43] (e.g., by using glutaraldehyde[44] as a cross-linking agent) or physical[45−49] gels due to hydrogen bonding and/or chemical reaction of hydroxy groups. It is also well known that aqueous solutions of PVA may undergo gelation due to complexation with several inorganic ions, e.g., borate ions[50−58] and antimonates.[59] In this case, the ions react with the hydroxy groups of PVA and form cross-links. Several investigations have been reported recently on the thermodynamic,[60−63] structural,[48,56,60,64,65] and dynamic[61,62,66] features of cross-linked PVA hydrogels and the corresponding semidilute polymer solutions. However, there is a lack of studies on rheological properties of PVA systems during the chemical gelation process. For instance, the effects of polymer concentration and cross-linking density on the rheological features of gelling PVA systems have not been addressed.

In this work, oscillatory shear measurements and a few stress relaxation experiments were carried out on chemically gelling systems of PVA. The structure of the network and the gel strength will depend on factors such as the molecular weight of the polymer, PVA concentration, and concentration of the cross-linking agent. The present rheological measurements have been performed on semidilute PVA solutions of different concentration and in the presence of various amounts of cross-linking agent (glutaraldehyde, GA). We will examine how the cross-linker and polymer concentrations affect the rheological characteristics, such as the gelation time, the gel strength, and the value of the scaling exponent for the frequency dependence of dynamic modulus. The aim of this paper is to gain a deeper insight into the factors that govern the evolution of viscoelasticity during the chemical gelation of PVA.

Theoretical Background

The linear viscoelastic behavior at the gel point may be described by the gel equation,[2]

$$\sigma(t) = S\int_{-\infty}^{t}(t - t')^{-n}\dot{\gamma}(t')\,\mathrm{d}t' \qquad (1)$$

where σ is the shear stress; $\dot{\gamma}(t)$, $-\infty < t' < t$, is the rate of deformation of the sample at the gel point; t is the present time; S is the gel strength parameter, depending on the cross-linking density and the molecular chain flexibility; and n is the relaxation exponent. The material parameters S (Pa s^n) and n are characteristic parameters for each incipient gel, and n must be greater than 0 and less than 1. Equation 1 relates the instantaneous stress tensor $\sigma(t)$ to the strain history given by the rate of deformation $\dot{\gamma}(t)$. This gel equation is valid only at the gel point and is restricted to small strains only. A general version of this gel equation has been elaborated,[67] where the model proposed by Winter and Chambon was included as a special case.

It was shown that the shear relaxation modulus, which describes the relaxation of stress after a constant shear strain, exhibits a power law relaxation at the gel point:

$$G(t) = St^{-n} \qquad (0 < n < 1) \qquad (2)$$

This fractal time behavior[68] is a characteristic feature

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of processes that do not have a characteristic time scale. The storage, G', and loss, G'', parts of the complex shear modulus ($G^* = G' + iG''$), which describes storage and dissipation in an oscillating strain field of constant amplitude, are related to the time-dependent modulus via the following Fourier transform:

$$G^* = i\omega\int_0^\infty \exp(-i\omega t)G(t)\,\mathrm{d}t \qquad (3)$$

As a consequence, the dynamic mechanical behavior for the incipient gel is characterized by an analogous power law between dynamic moduli and frequency,[19]

$$G' = G''/\tan\delta = S\omega^n\Gamma(1-n)\cos\delta \qquad (4)$$

where $\Gamma(1-n)$ is the Legendre Γ function. This relationship has been utilized in this work to calculate the values of the S parameter. The phase angle (δ) between stress and strain is independent of frequency (ω) but proportional to the relaxation exponent:[3]

$$\delta = n\pi/2 \quad \text{or} \quad \tan\delta = G''/G' = \tan(n\pi/2) \qquad (5)$$

These results suggest that the incipient gel is described by the following scaling relation:

$$G'(\omega) \propto G''(\omega) \propto \omega^n \qquad (6)$$

A number of theoretical models[7,16,34,35,38−42] have been developed to predict the value of the relaxation exponent. The present understanding of the phenomenology of gelation is essentially based on concepts such as dynamic scaling, fractal analysis, and percolation of clusters. The growing clusters, which appear as the connectivity increases near the gelation threshold, may be described in terms of the fractal geometry in the length scales between the monomer size and the correlation length of connectivity. Let us assume that the structure of the incipient gel can be described by a fractal dimension, d_f, which is defined by $R^{d_f} \sim M$, where R is the radius of gyration and M is the mass of a molecular cluster. A dynamical scaling analysis of flexible fractals in the Rouse limit (no hydrodynamic interaction), taking into account the effect of screening of excluded-volume and hydrodynamic interactions but ignoring entanglement effects, yields for a *monodisperse* solution of polymers of fractal dimension d_f a viscoelastic exponent of[38,39]

$$n = d_f/(2 + d_f) \qquad (7)$$

If we assume that the fractal dimension is located in the range $1 \le d_f \le 3$, then eq 7 predicts that the relaxation exponent is restricted for $^1/_3 \le n \le {}^3/_5$. When *polydisperse* clusters near the gelation threshold are considered and Rouse dynamics prevails, we arrive at the following relationship[6,7] for nonentangled systems:

$$n = d_f(r - 1)/(d_f + 2) \qquad (8)$$

where the hyperscaling function r is a scaling exponent describing the cluster size distribution function near the gel point. This polydispersity exponent is related to the fractal dimension through the expression $r = 1 + d/d_f$, where d ($d = 3$) is the space dimension. From *percolation* statistics ($d_f = 2.5$ and $r \cong 2.2$), it follows that $n = {}^2/_3$. On the other hand, based upon a suggested[34,35] isomorphism between the complex modulus and the electrical conductivity of a percolation network with randomly distributed resistors and capacitors, a value of $n = 0.72$ has been predicted. Since these values are close to each other, dynamic rheological experiments do not allow distinguishing between these predictions. In a recent study,[42] an off-lattice simulation model for associative polymer gels was utilized to describe the decay of the relaxation modulus, $G(t)$. The early-time decay of the relaxation mode was observed to follow a power law, with $n = 0.67$. It should be noted that this model was developed without the incorporation of hydrodynamic interactions and entanglement effects.

In a number of oscillatory shear studies on incipient gels of various natures, values of n in the whole range $0 < n < 1$ have been reported.[9] To rationalize these values, Muthukumar developed a theoretical model[40] in which it is assumed that variations in the strand length between cross-linking points of the incipient gel network give rise to changes of the excluded volume interactions. It is anticipated that increasing strand length should enhance the excluded volume effect. To account for this effect, Muthukumar suggested that, if the excluded volume interaction is *fully screened*, the relaxation exponent for a polydisperse system can be expressed as

$$n = \frac{d(d + 2 - 2d_f)}{2(d + 2 - d_f)} \qquad (9)$$

In the framework of eq 9, all values of the scaling exponent $0 < n < 1$ are possible for a fractal in the physically realizable domain $1 \le d_f \le 3$. In the case of *unscreened* excluded volume interactions, eq 8 is recovered, and n changes from 1 to $^3/_5$ as d_f varies from 1 to 3. Thus, the model is capable of rationalizing values of n in the whole physically accessible range ($0 < n < 1$).

A different theoretical model[41] has recently been elaborated in which the relation between viscoelastic and structural properties of systems of cross-linking polymers near the gel point was considered in the framework of a mechanical ladder model, consisting of springs and dashpots which mimic the rheological features. This phenomenological approach provides a mesoscopic description of the incipient gel. For ladder-like structures, this model predicts a power law in frequency for the complex shear modulus, with an exponent $n = {}^1/_2$. The dependence of n on structural and connectivity properties of the incipient gel could be described in the framework of models based on fractal networks. By the implementation of the fractal concept, it was shown[41] that the parameter n is related to the spectral dimension, d_s, of the fractal through the relationship

$$n = 1 - d_s/2 \qquad (10)$$

For all fractal networks, one has $d_s \ge 1$, and hence n varies between 0 and $^1/_2$. It was pointed out that the role of additional cross-links is to decrease the exponent n.

Experimental Section

Materials and Solution Preparation. A commercial poly(vinyl alcohol) sample, having a molecular weight of M_v = 53 000 (determined from viscosity measurements), was supplied by Hoechst AG. The degree of saponification was 99 mol %, and the sample was used without further purification. Semidilute PVA solutions in the range 4−12 wt % were prepared by dissolving PVA in distilled water (samples were prepared by weighing the components) at about 90 °C, followed by stirring for some hours. The pH of the solutions was

Table 1. Characteristic Molar Ratios of Monomer Units to the Molecules of Cross-Linker for the Investigated Systems

	PVA monomer units: GA molecules		
c(PVA) (wt %)	9 mM GA	13 mM GA	22 mM GA
4	107	72	43
5	134		
6	161	107	64
8	215		
10	268	179	107
12	322		

adjusted to 2.4 by adding small amounts of HCl(aq) to the solutions. Prior to the rheological measurements, prescribed amounts of glutaraldehyde (GA) were added by a BIOHIT micropipet of high precision to the solutions under vigorous stirring. The concentrations of the cross-linking agent were 9, 13, and 22 mM. This yields fairly low cross-linking densities, and only lightly cross-linked gels were formed. The sample compositions, in terms of molar ratios of monomer units to the molecules of the cross-linking agent, are summarized in Table 1. The values of these ratios are of the same magnitude as those reported in previous studies[60,62,64] on PVA systems. Depending on the polymer concentration and the concentration of the cross-linking agent, the gelation time was in the range 2–13 h.

Oscillatory Shear and Stress Relaxation Experiments. Oscillatory shear and a few stress relaxation measurements were carried out in a Bohlin VOR rheometer system with a cone-and-plate geometry, with a cone angle of 5° and a diameter of 30 mm, at a strain less than 0.02. The values of the strain amplitude were checked to ensure that all measurements were conducted within the linear viscoelastic regime, where the dynamic moduli are independent of the strain amplitude. At different times during the gelation process, a frequency sweep extending from about 0.015 to 6 Hz was performed.

In a stress relaxation experiment, the sample is subjected to a rapid applied small strain, which is held constant for the remainder of the experiment, and the decay of stress in the viscoelastic material is monitored as a function of time. From this type of measurement, the stress relaxation modulus $G(t) = \sigma(t)/\gamma_0$, the ratio of stress to the constant strain, can be determined.

Special devices were used to avoid evaporation of solvent in the sample cell. The rheometer is equipped with a temperature control unit that was calibrated to give a temperature in the sample chamber within 0.1 °C of the set value. All measurements were carried out at 25 °C. The sample was allowed to rest for some minutes between measurements.

Results and Discussion

The gel point (t_g) for chemically gelling systems can be determined by observation of a frequency-independent value of tan δ obtained from a multifrequency plot of tan δ versus gelation time. This type of plot is shown in Figure 1 for a typical gelling solution of PVA. The general trend is the same for all the investigated systems: a steady decrease in the loss tangent, with the decrease most pronounced for the lowest measurement frequency. This results in values of tan δ becoming frequency independent at a particular gelation time, which is dependent on the polymer concentration and cross-linking density of the system. An alternative method[27] to determine gel points is by plotting the "apparent" viscoelastic exponents n' and n'' ($G' \propto \omega^{n'}$, $G'' \propto \omega^{n''}$), obtained from the approximate scaling laws of the frequency dependence of G' and G'' at times removed from the gel point, and observing a crossover where $n' = n'' = n$ (the criterion for the gel point, see Figure 2). The values of the apparent viscoelastic exponent for both $G'(\omega)$ and $G''(\omega)$ decrease monotonically and smoothly, and the points of intersection (t_g) are the same as those observed with the other method (cf. Figures 1 and 2).

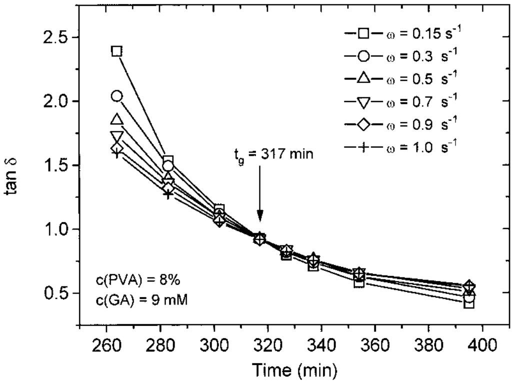

Figure 1. Viscoelastic loss tangent as a function of time for the system and frequencies indicated. The notion t_g marks the gel point.

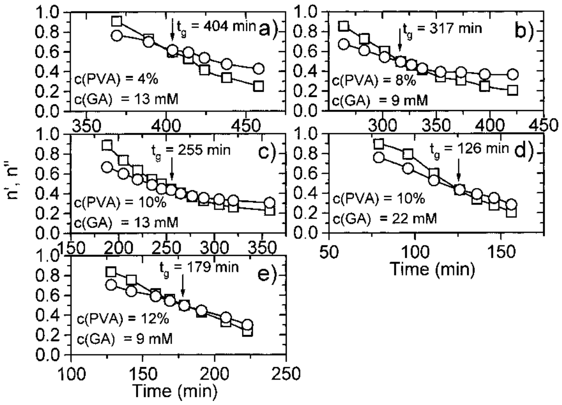

Figure 2. Changes of the apparent exponents n' (□) for the storage and n'' (○) for the loss shear moduli during the course of gelation for the systems indicated. The notion t_g marks the gel point.

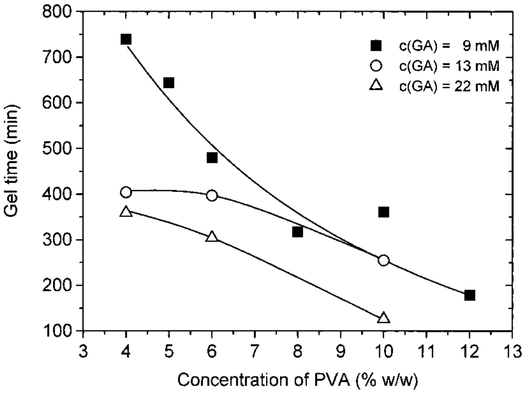

Figure 3. Plot of the gelation time as a function of PVA concentration for the cross-linker concentrations indicated. The solid curves are drawn to show the trends.

The effects of polymer concentration and cross-linking density on the gelation time are illustrated in Figure 3. It is evident that the value of t_g decreases with increasing concentrations of PVA and cross-linking agent (GA). The polymer concentration dependence of t_g is more severe in the presence of a low concentration of GA. This indicates that, at high polymer concentrations, the time-dependent gel evolution is less sensitive to the amount of cross-linking agent, because the number of "active sites" for cross-linking of the polymer network is high. The general picture that emerges is that the kinetics of

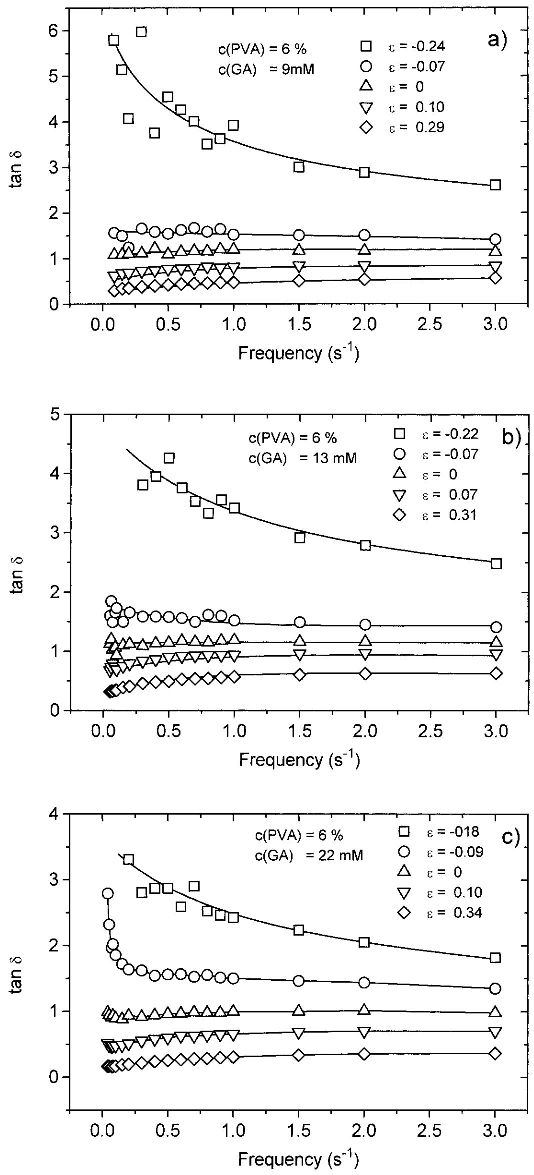

Figure 4. Frequency dependence of the loss tangent during the gel evolution for the systems indicated. The lines are only guides for the eye.

gel formation is controlled by the probability of forming cross-links in the system.

The frequency dependence of the loss tangent during the gelation process (where $\epsilon = (t - t_g)/t_g$ is the relative distance from the gel point) is depicted in Figure 4 at a PVA concentration of 6 wt % and at three different GA concentrations. The general pattern of behavior is the same for all systems. As expected, tan δ at the gel point ($\epsilon = 0$) is practically independent of frequency for all systems. In the pregel regime, tan δ decreases as the frequency increases, as is typical for a viscoelastic liquid. The rather large scatter in the experiment points in the low-frequency domain at early times, announcing that the viscoelastic response is weak at this stage of the gelation process. In the postgel regime, we can observe a moderate increase in tan δ with frequency, indicating that the elastic response of the sample is dominating.

In Figure 5, the frequency dependences of G' and G'' at various stages during the gel evolution are shown for systems of different concentrations of PVA and GA. The curves have been shifted horizontally by a factor B (see the insets in Figure 5) to avoid overlap. Before the gel point, G' is always smaller than G'', and the frequency dependence curves show liquid behavior. After the gel point, G' increases rapidly and becomes larger than G'', which is a characteristic feature of the elastic state that prevails in the postgel regime. At the gel point, G' and G'' curves become parallel to each other, and the power law behavior is observed over an extended frequency domain (see Figure 6). For some incipient gels (GA concentrations of 9 and 13 mM and polymer concentrations in the range 4−6 wt %), $G' < G''$, whereas for other systems (polymer concentrations of 8−12 wt % in the presence of GA concentrations in the range 9−22 mM), $G' > G''$. At the gel point, it is frequently found[6,7,14,18,20,21,27] for chemical (irreversible) gels ("strong" gels) that $G' < G''$, while for physical (reversible) gels ("weak" gels), it has been observed[33,69] that $G' > G''$. In the light of these findings, the incipient PVA gels with $G' < G''$ may be characterized as "strong" gels, while PVA gels with $G' > G''$ may be called "weak". An intermediate state, where the dynamic moduli become congruent and the power law exponent is close to 0.5, is observed at PVA concentrations of 4 and 6 wt % in the presence of a 22 mM concentration of the cross-linker agent. The observation that the storage and the loss moduli are congruent functions with a power law exponent of 0.5 has also been reported previously for

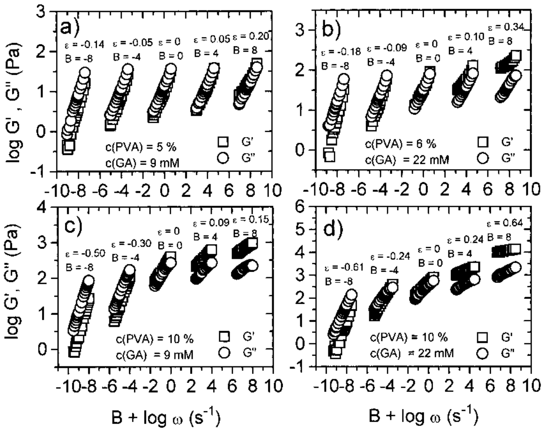

Figure 5. Frequency dependences of the storage modulus G' and the loss modulus G'' at different stages of the gel-forming process for the systems indicated. The curves have been shifted horizontally by a factor B of the value listed in the inset.

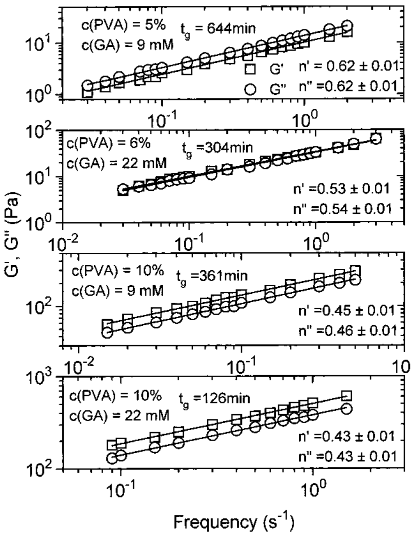

Figure 6. Plot of G' (□) and G'' (○) versus frequency for the indicated systems at the gel point, showing the power law behavior.

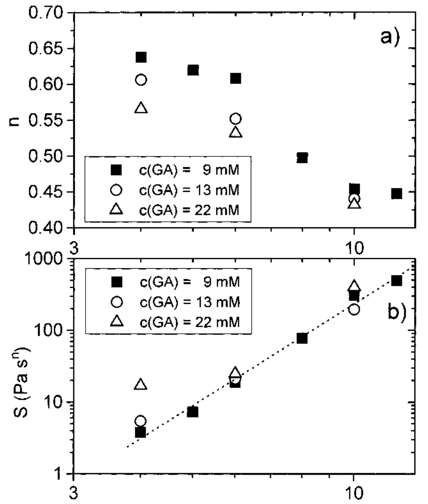

Figure 7. Plot of the viscoelastic exponent n and the gel strength parameter S (calculated from eq 4) at the gel point as a function of PVA concentration at the cross-linker concentrations indicated. The dotted line represents a least-squares fit of the data.

stoichiometrically balanced incipient gels of poly(dimethylsiloxane),[1,2] polyurethane,[4] and poly(ethylene oxide)[10] with hydroxyl functions at both chain ends.

Effects of polymer concentration and concentration of GA on the relaxation exponent, n, and the gel strength parameter, S (see eq 4), for incipient PVA gels are shown in Figure 7. The value of the viscoelastic exponent decreases monotonically with increasing polymer concentration, and we observe, especially at a low polymer concentration, that n falls off with increasing cross-linking density at a given PVA concentration. The values of n are located in the approximate range 0.45–0.65. This trend may indicate that the percolation value ($n = 0.7$) can be reached for a polymer concentration in the incipient semidilute regime at a sufficiently low cross-linking density. At higher polymer and/or cross-linker concentrations, the entanglement effects will probably reduce the value of n. Furthermore, the results in Figure 7a seem to suggest that, at high polymer concentrations, the amount of cross-linker agent has only a minor impact on the value of n. At this stage, several entanglement couplings are probably formed due to the high polymer concentration, and an excess of cross-linker agent will have an insignificant influence on the entanglement situation. A reduction of the value of the viscoelastic exponent with increasing polymer concentration in the semidilute regime was reported by Scanlan and Winter[11] in their rheological study of incipient gels of end-linked poly(dimethylsiloxane) polymers. Furthermore, in recent studies on chemical gelation of end-linking α,ω-dimethylsilylpoly(propylene oxide)[20] and α,ω-dihydroxypolybutadiene[70] solutions, the value of n was reported to decrease with increasing entanglement density, whereas in unentangled prepolymer solutions, the value of n was found to be independent of polymer concentration. In this context, we should also note the model of Schiessel and Blumen, where it was argued that additional cross-links should decrease the value of n. However, no effect of concentration on the power law frequency exponent was revealed[27,28,31] from oscillatory shear measurements on incipient gelatin gels. This finding may indicate that these gelatin systems are unentangled.

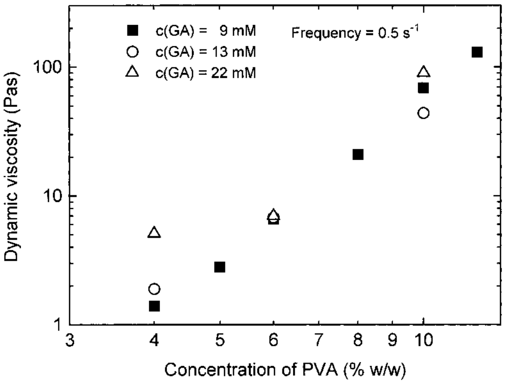

Figure 8. Polymer concentration dependence of the dynamic viscosity (at the gel point) at a constant frequency of 0.5 Hz and at the cross-linker concentrations indicated.

The effects of polymer and cross-linker concentrations on the gel strength parameter are illustrated in Figure 7b. It is evident that the gel strength increases with polymer concentration at all levels of cross-linker addition. The parameter S rises also with increasing cross-linker concentration at a given polymer concentration. This trend seems to be especially pronounced at low polymer concentrations. These features are consistent with the intuitive picture that the concentration of cross-linking agent plays a more prominent role at low than at high polymer concentrations, because at low polymer concentrations the gel network is fragile and sensitive to additional cross-links. At higher polymer concentrations, the polymer entanglements contribute to the strength of the network, and the additional cross-links do not have the same impact on the gel strength parameter as at low polymer concentrations.

The present finding, that S rises with increasing PVA concentration, is parallel with that reported for incipient gels of both chemical[11] and physical[31,33] natures. These investigations have shown that the parameter S is sensitive to changes of the strand length between cross-links. When the strand length shrinks (e.g., increasing polymer concentration), the cross-linking density is increased, thus resulting in a "harder" gel characterized by a higher value of S. The data in Figure 7b seem to follow a power law ($S \propto c^{4.7}$, see the dotted line). This concentration dependence of S is much stronger than that ($S \propto c^{1.33}$) reported[31] for critical gelatin gels. This probably suggests that the growth of cross-links and entanglement couplings is much stronger in the PVA gels.

Another illustration of the viscoelasticity at the gel point is depicted in Figure 8. The dynamic viscosity (measured at a fixed frequency of 0.5 Hz) increases strongly with increasing polymer concentration. Furthermore, the value of η' rises significantly with increasing amount of GA at low polymer concentrations. These results suggest an enhanced viscoelastic response and a stronger gel network as the polymer concentration increases. The network, at low polymer concentrations, seems to be strengthened with increasing addition of GA.

Figure 9 shows a plot of the gel strength as a function of the relaxation exponent. The result from this plot reveals that the gel strength parameter and the relaxation exponent are coupled, and this type of behavior is in accordance with the expectation from eq 2. The complicated dimensions of S, Pa s^n, suggest that it is composed of a material characteristic modulus and a time.[1,2] The gel strength parameter may be expressed[11] as $S = G_0\lambda_0{}^n$, where λ_0 and G_0 are material-specific constants. A least-squares fit of the data (the dotted

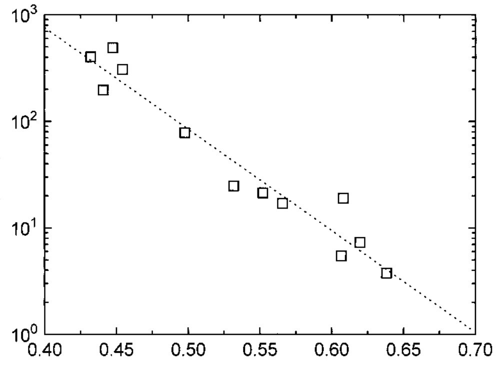

Figure 9. Plot of the gel strength parameter S against the relaxation exponent n. The dotted line shows a linear regression of the data points.

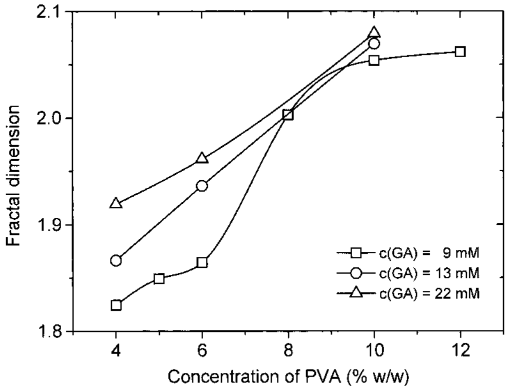

Figure 10. Plot of the fractal dimension d_f (calculated from eq 9) as a function of PVA concentration for the cross-linker concentrations indicated.

line in Figure 9) yields $G_0 = 5.0 \times 10^6$ Pa and $\lambda_0 = 2.9 \times 10^{-10}$ s, and $G_0\lambda_0$ is calculated as 1.4×10^{-3} Pa s.

The relation between the relaxation exponent and the fractal dimension was discussed above in the framework of the model of Muthukumar (see eq 9). The effects of the polymer concentration and the addition of GA on the fractal dimension, calculated with the aid of eq 9, of incipient gels of PVA are depicted in Figure 10. The results show that the fractal dimension increases with increasing polymer concentration and increasing cross-linker density. The effect of cross-linker addition is especially marked at moderate polymer concentrations. It has been argued[11,19,40] that an increase in the value of the fractal dimension leads to a critical gel with a more "tight" network structure. These findings are consistent with the intuitive picture that increasing concentrations of cross-linking agent and/or polymer should produce networks with a more "tight" structure.

The present values of d_f (1.8−2.1) are smaller than the values of 2.6 and 2.8 reported[56] from a small-angle neutron scattering (SANS) study on PVA−borate gels of PVA concentrations of 12.5 and 16.7 wt %, respectively. However, the trend in d_f is the same as in this work: d_f increases with increasing polymer concentration. It was argued[56] that the high values of d_f in the cited paper may be due to the presence of hydrogen bonding in addition to borate-aided cross-links, making the chains of the PVA clusters more densely packed than the chains of percolation clusters. In the sol state, both systems could be described as an ensemble of polydisperse clusters with $d_f \approx 2.2$. In view of the results presented above, it is possible that the cross-linking densities of these gels are higher than those considered in this study. We should also note that a recent SANS study[54] on hydrogels of PVA at different temperatures indicated fractal dimensions around 2. The general conception[16,71] is that the fractal dimension for chemically cross-linked gels is around 2.5 (the percolation value) for incipient gels in a reaction bath and 2.0 for the cross-linked clusters in swelling equilibrium. Experimental light scattering and SANS studies[16,72−76] on gels of various natures have yielded values of d_f in the range 2−2.5. The somewhat low values of d_f observed in the present work probably suggest that we have loosely cross-linked gels composed of swollen clusters.

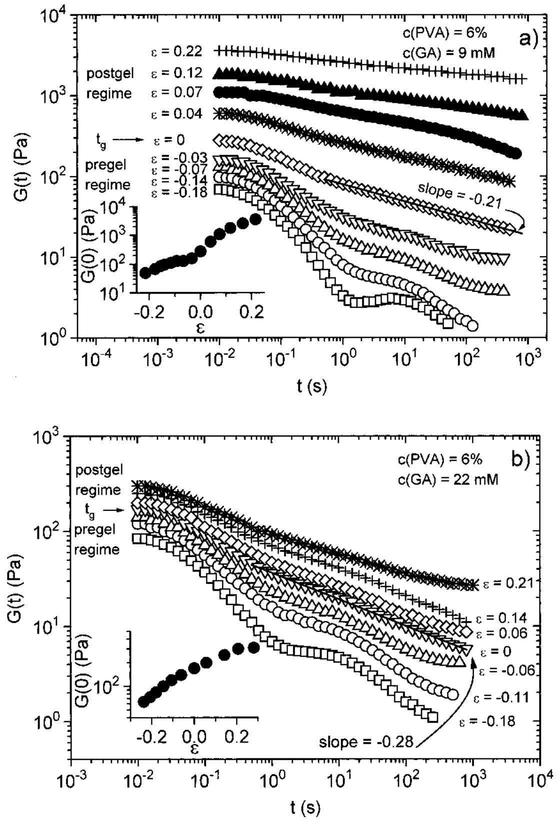

Figure 11. Plot of the shear relaxation modulus versus time at different stages of gelation for the systems indicated. The inset plots show changes of the initial shear relaxation modulus during the gel evolution.

The decay of the linear relaxation modulus (determined from stress relaxation measurements) during the gel formation process is shown in Figure 11 for two different systems. The relaxation modulus, $G(t)$, stretches with increasing reaction time until it shows power law behavior at the gel point ($\epsilon = 0$). At this stage, the relaxation modulus exhibits an exponential profile at short times, and the power law domain observed at longer times covers approximately 3 decades of time. The extension of this power law regime encompasses the time window that was probed in the corresponding dynamic moduli measurements ($\omega = 1/t$). The power law feature of the decay of the relaxation modulus at the gel point is in accordance with the theoretical surmise (cf. eq 2). However, the values (0.21 and 0.28) of the relaxation exponent are significantly lower than the corresponding ones obtained from the present oscillatory shear experiments. The reason for this discrepancy is not yet understood. It is possible that the theoretical description of the rheological features at the gel point for the present systems is more intricate than that predicted by current theoretical models. In the light of this surprising result, a reconsideration of the gel equation may be necessary. However, experimental artifacts, such as the occurrence of slippage during measurement, cannot be rejected as the cause of the low values of the relaxation exponent.

It is well established[77] that the shear relaxation modulus and the time correlation function in dynamic light scattering are connected via the longitudinal bulk modulus and the cooperative diffusion coefficient. In view of this, it is interesting to note that recent dynamic light scattering measurements[78] on PVA/GA systems at the gel point revealed that the decay of the correlation function exhibited a profile similar to the relaxation modulus, i.e., a single exponential at short times, followed by a power law at longer times. However, the time window for power law behavior (3 decades) was shifted toward shorter times, and also in this case the values of the power law exponent was much lower than the relaxation exponents determined from oscillatory shear measurements.

The inset plots of Figure 11 show the change of the initial relaxation modulus, $G(0)$, during the gelation process. These results demonstrate that the viscoelastic response increases as the gel evolves.

Conclusions

The time-dependent growth of viscoelasticity during the chemical gelation of semidilute PVA solutions of various polymer and cross-linker concentrations has been studied by rheological experiments. The main results can be summarized in the following way: (1) The time of gelation decreases with increasing concentrations of polymer and cross-linker agent. (2) At the gel point, the storage and loss moduli show a power law behavior, $G' \propto G'' \propto \omega^n$, with frequency ω. The values of n are lower than that (0.7) predicted from the percolation theory, and n decreases with increasing PVA concentration. Furthermore, the value of n falls off with increasing cross-linking density at moderate polymer concentrations. The decrease of n is attributed to entanglement effects. (3) A few stress relaxation measurements on PVA/GA systems yielded values of the shear relaxation modulus $G(t)$, and this parameter was found at longer times to exhibit a power law dependence on time at the gel point. However, the values of the relaxation exponent are significantly lower than the corresponding ones obtained from the oscillatory shear measurements. The reason for this anomaly is not clear, but it may indicate that the rheological situation for the incipient gels of PVA is intricate. (4) The gel strength parameter S increases with polymer concentration, and the enhancement of S with cross-linker concentration is especially pronounced at low PVA concentrations. This finding, as well as the dynamic viscosity results, suggests that the viscoelastic response is strengthened under these conditions. (5) The value of the fractal dimension d_f, calculated from the model of Muthukumar, increases with increasing polymer concentration and cross-linking density, indicating that the network structure of the incipient gel becomes more "tight".

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