Viscoelastic behaviour at the thermal sol–gel transition of gelatin

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Rheological studies of gelatin solutions in the concentration range 4–14% were performed through the sol–gel transition as a function of concentration, pH and ionic strength. At the gel point, a power-law frequency dependence of the viscoelastic functions $G'(\omega)$, $G''(\omega)$ and $\eta^*(\omega)$ was observed. The power-law exponents n obtained from these dynamic measurements were confirmed by creep experiments and are in agreement with a previous study in a lower concentration range, 1–5%. Under all conditions, the n values fall between 0.64 and 0.72, a range consistent with theoretical treatments of Martin *et al.* and Muthukumar *et al.* The critical gel strength, S, increases with concentration approximately as $S \propto C^{1.33}$ in the concentration range 4–14%. Within experimental error, S is approximately consistent with an empirical relation suggested in the recent literature, $S = G_e^{1-n}\eta_0^n$, where G_e and η_0 are, respectively, the equilibrium modulus of the fully developed gel and the shear viscosity of the initial sol. The implications of these observations with respect to the structure of the critical gel are discussed.

(Keywords: viscoelasticity; gelatin; sol–gel transition; critical gel)

BACKGROUND

Measurements of the oscillatory shear moduli are frequently used to monitor continuously the viscoelastic properties of crosslinking systems from the sol through the transition to the gel state. According to a traditional suggestion[1], the gel point corresponds to the intersection of the storage and loss moduli, $G'(\omega)$ and $G''(\omega)$, i.e. the point at which $\tan\delta = G''/G' = 1$. More recently, experiment[2–7] and theory[6,8,9] indicate that, at the gel point, G' and G'' exhibit a power-law dependence on the oscillation frequency, and gelation may occur before or after the crossover of G' and G'' at a specified frequency.

Several theoretical analyses have developed expressions for the frequency dependence of G', G'' and the complex viscosity, $\eta^*(\omega)$, at the gel point[2–9], using the fractal scaling concept to define the gel network structure. The results of these investigations indicate that at the sol–gel transition point:

$$G' = A\omega^n \tag{1}$$

$$G'' = B\omega^n \tag{2}$$

and

$$\tan\delta = G''/G' = B/A = \tan(n\pi/2) \tag{3}$$

where A and B are related to the material strength factor of the gel, S, by[2]:

$$S = G'\omega^{-n}\Gamma(1-n)^{-1}\cos(n\pi/2) \tag{4}$$

$$S = (A^2 + B^2)^{1/2}\Gamma(n)\sin(n\pi/2) \tag{5}$$

The exponent n is determined by the fractal dimension of the network, the stoichiometry of the gel[5,7] and the strength of the hydrodynamic interaction between the polymer chain segments[6,9,10].

Previous experimental studies include those by Winter *et al.*[2–4,7,8], Muller *et al.*[5] and Martin *et al.*[6] on gels formed from covalent polymeric networks. In such systems, G' and G'' exhibit a power-law dependence with an exponent that depends on the gel stoichiometry[2–5,7,8]. Values ranging between 0.3 and 0.9 have been reported[7]. Lin *et al.*[11] investigated crystallization-induced gelation in the thermoplastic elastomer polypropylene and observed power-law scaling of G' and G'' with an exponent $n = 0.13$. In another recent study, Amis *et al.*[12,13] investigated changes in dynamic viscoelasticity during the thermo-reversible gelation of gelatin at concentrations ranging from 0.90 to 5.10% (w/w) and at five different frequencies over a range from 272 to 9450 Hz using the multiple lumped resonator (m.l.r.) technique. They found a power-law frequency dependence of G' and G''. At the gel point, G' and G'' exhibited power-law frequency dependence with frequency exponents statistically distributed over a range of values from 0.58 to 0.77 under a variety of experimental conditions (temperatures and pH). The corresponding frequency-independent values of $\tan\delta$ range from 1.3 to 2.5. The values of n and $\tan\delta$ are numerically similar to those obtained for chemically crosslinked gels in non-stoichiometric systems. The authors note[12,13] that the viscoelastic behaviour of gelatin at the gel point can be described by the percolation model of Martin *et al.*[6], $2/3 \leqslant n \leqslant 1$ in the Rouse limit.

An interesting feature of systems that gel via a percolation mechanism is that they have $\tan\delta = 1.732$ at the gel point. Thus, they are not physically gel-like and exhibit macroscopic flow at and for a considerable

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distance beyond the gel point. It is therefore of interest to investigate quantitatively the deformation behaviour during gel formation, i.e. to study the creep compliance function through the sol–gel transition. Here, we explore further the viscoelastic behaviour of gelatin during gelation. We observed the previously reported power-law behaviour of G' and G'' at the gel point using the Rheometrics controlled-strain fluids rheometer. We also describe creep compliance measurements using the Carri-Med controlled-stress rheometer. The existence of a sol–gel transition is confirmed by the disappearance of the permanent deformation and a power-law time dependence of creep with an exponent identical to that for the dynamic moduli. Our results extend the range of the previous work[12,13] to higher gelatin concentrations and lower deformation frequencies and provide a more comprehensive picture of the change in viscoelastic properties at the gel point of gelatin.

EXPERIMENTAL

Bovine gelatin (Fisher Chemicals) of bloom strength 100 was used. This is an alkali-precursor gelatin with isoionic point in the pH range 4.7–5.1, and average molecular weight around 80 000. The gelatin was completely dissolved at 50–60°C in doubly distilled, deionized water to the desired concentrations. The pH of these solutions was 5.5 with only small variations in the concentration range 4–14% (w/v). The pH of gelatin solution was adjusted to either 3 or 9 by addition of small amounts of HCl or NaOH. In some experiments, gelatin was dissolved either in phosphate-buffered saline (PBS) to pH = 7 or in 1 M NaCl or 1 M guanidinium chloride (Gdn·HCl) solution at pH 5.5.

A Rheometrics fluids spectrometer utilizing cone-and-plate geometry was used to determine $G'(\omega)$, $G''(\omega)$ *and* $\eta^*(\omega)$. This instrument can perform dynamic frequency scans of the storage and loss moduli from 0.01 to 100 rad s^{-1}. However, in order to confine the measurements to approximately 1 min duration, 10 frequencies from 1 to 63.1 rad s^{-1} (or 0.16 to 10.04 Hz) were selected. This range represents about two decades of lower frequency compared to those monitored by Amis *et al.*[12,13]. Owing to the sensitivity limit of the transducer on the fluids rheometer, our studies were confined to comparatively high gelatin concentrations (4 to 14% (w/v)). In addition, the creep compliance function $J(t)$ was measured with a Carri-Med controlled-stress rheometer. Standard viscoelastic theory[2–4] indicates that, by Fourier transform, if $G' \propto G'' \propto \omega^n$, the stress relaxation modulus behaves as $G(t) \propto t^{-n}$. Also, since tan δ is constant at the gel point, we have $J' \propto J'' \propto \omega^{-n}$, and hence the creep compliance has a power-law time dependence $J(t) \propto t^n$. Thus the creep function provides a complementary test of the dynamic scaling at the gel point. Further, we expect to observe the appearance of 100% recoverable strain when gelation occurs.

The solutions were maintained at 27–30°C prior to measurement of viscoelastic properties. For the latter, 670 μl of solution was rapidly quenched to the measurement temperature in the Rheometrics fluids spectrometer using a 50 mm diameter cone with 0.02 radian angle. Temperature control was achieved by a circulating fluid bath of ethylene glycol and water. Because of its crucial effect on the thermally reversible gelation process, the temperature must be strictly controlled to within ±0.05°C. The instrument was set in the dynamic frequency sweep mode using the 10 g cm transducer and with 5% strain as input. For each time point, measurement of a set of 10 frequencies from 1 to 63.1 rad s^{-1} takes about 1 min. The frequency dependence of the storage and loss moduli at each time point as well as the time dependence of moduli for each of the 10 frequencies were thus obtained. Determination of the gel point was made, following the procedures of Amis *et al.*[12,13], either by plotting tan δ as a function of time for each frequency, and observing the frequency-independent crossover points, or, alternatively, by plotting viscoelastic exponents n' and n'' ($G' \propto \omega^{n'}$, $G'' \propto \omega^{n''}$) obtained from the frequency dependence of G' and G'' at each time point, and observing a crossover where $n' = n'' = n$.

For the creep measurements, 60 μl aliquots of 8% gelatin solution were quenched from 40°C to the desired temperature in the Carri-Med rheometer, using a 20 mm diameter cone with 1 degree angle. The temperature is controlled by a Peltier system, located in the lower plate; thus a small temperature gradient exists across the sample. In our experimental data, two portions may be distinguished following application of a small constant stress for 10 s: initially, creep retardation occurs (0–10 s), followed by creep recovery (10–20 s) on removal of the applied stress. The apparent permanent deformation is defined as the strain at 20 s, $\gamma_{t=20\text{s}}$. Of course, this may not be the true permanent deformation if the relaxation times are substantially longer than the observation time (10 s). The creep retardation curves were fitted by power-law functions with exponent n, that is, $\gamma(t) \propto t^n$ or $J(t) = \gamma(t)/\sigma_0 \propto t^n$. Comparisons can thus be made between the values of exponents deduced from creep and those obtained from the dynamic moduli measurements.

RESULTS AND DISCUSSION

Twenty-nine distinct combinations of experimental conditions were utilized for analyses using the Rheometrics fluids rheometer. Typical results for one set of experiments, performed on a 10% gelatin sol at pH 5.5 and $T = 23.0$°C, are shown in *Figure 1*. In *Figure 1a*, the gel point is determined by observation of a frequency-independent value of tan δ obtained from a multi-frequency plot of tan δ vs. gelling time. In *Figure 1b*, we show that a unique power-law exponent ($n = 0.68$) is found at the gel point, from linear regression log–log fits of G' and G'' vs. ω (frequency) plots. In *Figure 1c*, we show that exponents n' and n'' determined from G' and G'' through the sol–gel transition show a monotonic evolution with gelling time and have a crossover at $n = 0.68$ at the gel point. Clearly, the gelation time t_{gel} can be estimated quite accurately either from *Figure 1a* or from *Figure 1c*.

In *Table 1*, we summarize the results for tan δ and the power-law exponent n, determined at the gel point by the above methodology. All solutions were subjected to a single quench to the gelling temperature from 27–30°C. Two specimens experienced a two-stage quench with a 30 min stay at an intermediate temperature, during which little change in viscoelastic properties was observed. The results were demonstrated to be very reproducible when the sample temperature is strictly controlled to within ±0.05°C. The tan δ and n values generated in this way were found to be numerically self-consistent according to the relation $\delta = n\pi/2$ (equation (3)), with a small

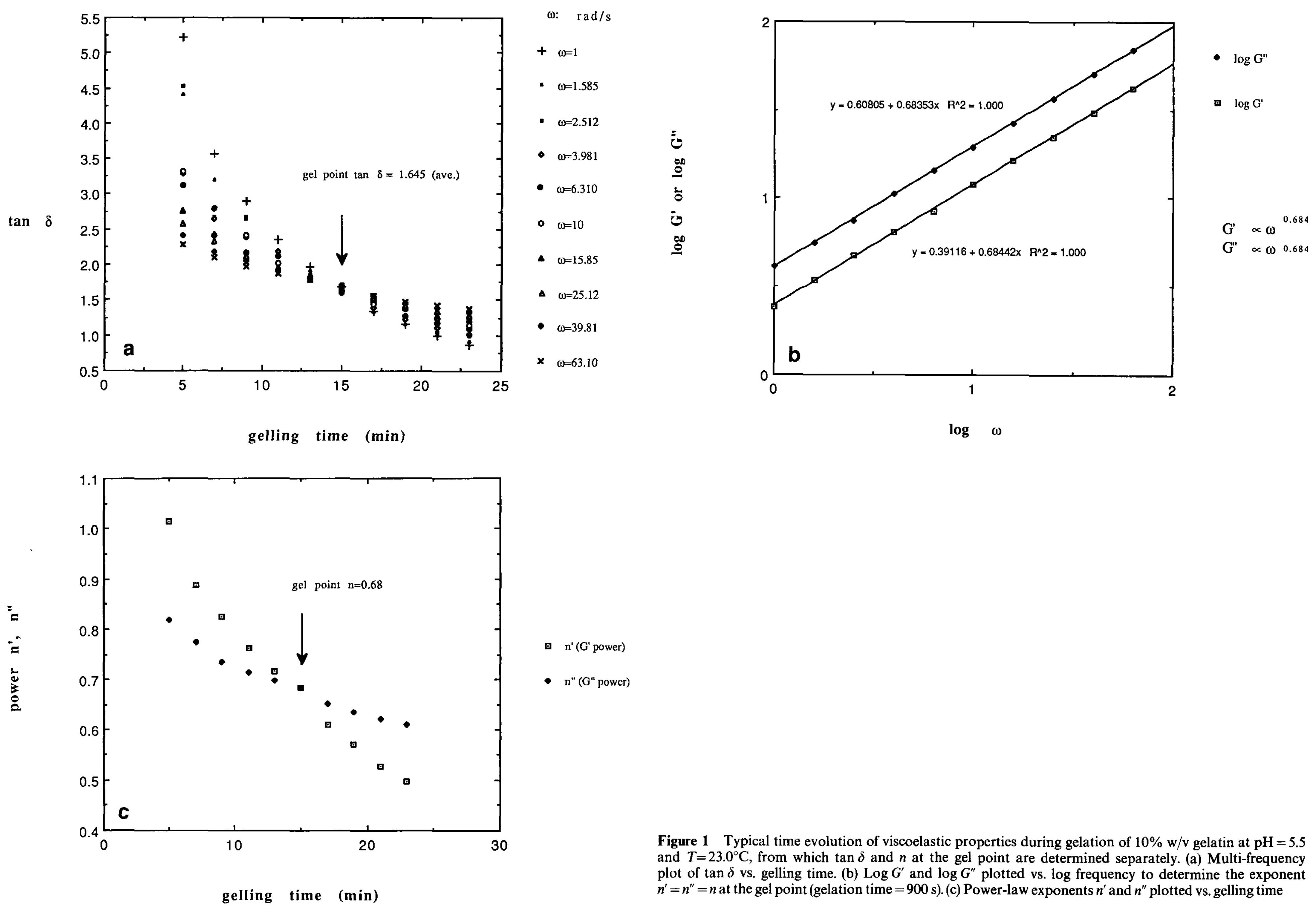

Figure 1 Typical time evolution of viscoelastic properties during gelation of 10% w/v gelatin at pH = 5.5 and $T = 23.0°\mathrm{C}$, from which tan δ and n at the gel point are determined separately. (a) Multi-frequency plot of tan δ vs. gelling time. (b) Log G' and log G'' plotted vs. log frequency to determine the exponent $n' = n'' = n$ at the gel point (gelation time = 900 s). (c) Power-law exponents n' and n'' plotted vs. gelling time

Table 1 Viscoelastic properties at the sol–gel transition of gelatin

Conc. (w/v %)	Other salt	pH ± 0.3	Temp. (°C)	t_{gel} (s)	$\tan\delta$	n	n by eqn (3), $n=2\delta/\pi$	B/A (intercepts)	S by eqn (5)
12		5.5	24.7	960	1.76	0.70	0.67	4.52/2.53	1.85
12		5.5	24.7	930	1.74	0.69	0.67	5.15/2.97	2.20
12		5.5	24.7	960	1.76	0.70	0.67	5.00/2.83	2.12
12		5.5	24.7	930	1.78	0.70	0.67	4.96/2.80	2.10
12		5.5	24.3	600	1.66	0.68	0.65	5.53/3.36	2.54
12	PBS	7.0	24.3	5500	1.84	0.71	0.68	4.45/2.36	1.74
12	1 M NaCl	5.5	21.1	3900[a]	1.98	0.72	0.70	3.84/1.95	1.44
12	1 M NaCl	5.5	20.4	2640	1.87	0.70	0.69	4.65/2.62	1.97
12	1 M NaCl	5.5	20.4	2940	1.71	0.70	0.66	5.19/2.96	2.21
12		3	19.0	2880	1.72	0.69	0.67	4.85/2.82	2.07
12		3	18.3	1170	1.56	0.69	0.64	4.62/3.06	2.31
12	1 M NaCl	3	16.0	3480	1.61	0.64	0.65	4.85/3.01	2.24
12	1 M NaCl	3	15.6	2280	1.64	0.66	0.65	4.52/2.72	2.01
12	1 M NaCl	3	15.2	1200	1.60	0.66	0.64	4.55/2.76	2.09
12		9	22.3	2040	1.69	0.70	0.66	4.89/2.99	2.25
12		9	22.3	2100	1.78	0.71	0.67	4.35/2.63	2.00
12	1 M NaCl	9	19.6	2040	1.70	0.70	0.66	4.94/2.94	2.19
12	1 M NaCl	9	19.5	1830	1.73	0.71	0.67	4.73/2.71	2.01
12	1 M Gdn·HCl	5.5	10.9	2460	1.79	0.72	0.68	4.85/2.70	1.99
12	1 M Gdn·HCl	5.5	10.5	1860	1.71	0.69	0.66	5.50/3.30	2.44
10		5.5	23.6	2220	1.68	0.68	0.66	5.17/2.97	2.20
10		5.5	23.3	1040	1.70	0.69	0.66	5.52/3.25	2.44
10		5.5	23.3	940[a]	1.69	0.67	0.66	4.71/2.91	2.17
10		5.5	23.0	900	1.65	0.68	0.65	4.06/2.46	1.86
10	PBS	7.0	23.0	4680	1.75	0.69	0.67	4.50/2.44	1.83
10	PBS	7.0	22.0	1250	1.73	0.69	0.67	4.50/2.55	1.91
10	PBS	7.0	21.3	720	1.61	0.68	0.65	4.79/2.91	2.20
8		5.5	21.7	2430	1.72	0.69	0.66	2.78/1.63	1.23
8		5.5	21.4	1545	1.70	0.69	0.66	2.60/1.51	1.11
8		5.5	21.0	1380	1.56	0.66	0.64	3.31/2.07	1.58
8	PBS	7.0	21.4	3720	1.77	0.69	0.67	2.51/1.36	1.02
8	PBS	7.0	20.3	1725	1.71	0.68	0.66	3.10/1.81	1.37
4		5.6	17.5	2700	1.63	0.67	0.65	1.18/0.73	0.54
14		5.5	25.0	1260	1.67	0.68	0.66	7.31/4.42	2.95
14		5.5	25.0	1560	1.76	0.70	0.67	6.69/3.88	2.85
Ave.					1.71 ± 0.08	0.69 ± 0.02	0.66 ± 0.01		

[a] Specimens subjected to a two-stage quench (see text)

systematic variation giving an average experimental result $\delta = n\pi/(2)(1.038)$. This small deviation is caused by the finite times required for measurement. The time taken to scan from low to high frequency has the effect of shifting $\tan\delta$ downward more rapidly than shifting n downward by a factor that is of the order 1.038.

As a further check of the self-consistency of the data and the accuracy of the linear regression analysis, a set of $\tan\delta$ and n values were generated from the regression intercepts A and B at the gel point via equations (1)–(3). It was found that values of $\tan\delta$ and exponents computed from this method are very close to those determined from the multi-frequency plots in *Figure 1*. It is concluded that the linear regression fits based on 10 frequencies do not induce significant errors, and thus the experimental power-law exponents n are very reliable.

From *Table 1*, we note that, if the gelling kinetics are comparatively fast, such that each frequency scan requires a substantial fraction of the gelation time (as e.g. in the case of 12% gelatin at 24.3°C or 10% gelatin in PBS at 21.3°C), $\tan\delta$ exhibits small but significant shifts to smaller values. The same situation is evident for n. From the experience gained in our experiments, it was determined that gelation times longer than 900 s are required for optimal measurement of $\tan\delta$ and n (i.e. a single measurement should take less than 7% of the total gelation time).

Our results, together with those of Amis *et al.*[2–4], show that the gelatin concentration does not have a significant effect on the power-law exponent over a rather wide range (1–14%). Higher concentrations result only in a higher range of gelling temperatures and a higher gel strength factor. Increase of temperature acts to accelerate the gelling rate. The effect of temperature and concentration on the power-law frequency exponent appears to be negligible.

It is further evident that a change in pH and/or ionic strength has no influence on the power-law exponent or on the gel strength. However, a change of pH from pH = 5.5 (close to the isoionic point) to a lower or higher value and/or the addition of 1 M NaCl in gelatin causes a considerable delay of gelation. In PBS buffered (pH = 7) gels, this may be caused both by the presence of 0.14 M NaCl in the PBS buffer as well as the pH effect. The addition of the denaturant 1 M Gdn·HCl decreases the gelling rate even more dramatically. These kinetic changes are presumably caused by a decrease in the strength of the intermolecular interactions (hydrogen bonding, dipolar, electrostatic or hydrophobic interactions), which drive collagen fold formation between two segments of gelatin coils.

All of the variables discussed here, including concentration, temperature, pH, ionic strength and the addition of a denaturing agent, apparently do not modify the basic gelation mechanism, in spite of their remarkable influence on the gelation kinetics. Under all conditions we have used, the experimental n values fall between 0.64 and 0.72 (with an average $n = 0.69 \pm 0.02$), and are numerically consistent with the results of Amis *et al.*[12,13]. Such exponent values are similar to previous experimental results for gelation of epoxy resins ($n = 0.70 \pm 0.05$)[6], polyester ($n = 0.69 \pm 0.02$)[14], polyurethanes ($n = 0.69 \pm 0.02$)[15] and tetraethoxysilane ($n = 0.71 \pm 0.05$)[16,17].

From *Table 1*, it is evident that the gel strength parameter, S, defined by equation (4) shows a significant increase with gelatin concentration C in the range 4–14%. A least-squares fit of the data for all concentrations to a power-law relation yields:

$$S = 0.085C^{1.33} \qquad (r^2 = 0.98) \qquad (6)$$

Following the discussion of Winter and Chambon[2–4], S is the only material property at the gel point, and should be related to the structure of the critical gel. Although no formal theoretical interpretation of S appears to exist, recent studies suggest[7] that a numerical relation can be made between S and the viscosity, η_0, of the initial sol and the equilibrium modulus, G_e, of the fully cured gel. Specifically:

$$S = G_e^{1-n}\eta_0^n \qquad (7)$$

where n is the frequency-law exponent. A comparison of our measured S values with prediction of equation (7) is given in *Table 2*. Within the rather large margin of experimental error, including that defined by the experimental accuracy of $n = 0.69 \pm 0.02$, there is reasonable agreement.

For reasons noted earlier, it is of interest to contrast the above studies performed using a controlled-strain rheometer with creep measurements in the sol–gel transition region using a controlled-stress rheometer. The creep experiments were performed on 8% gelatin using a 1°, 2 cm cone at an applied stress $\sigma_0 = 10\,\mathrm{dyn\,cm^{-2}}$ at 23°C in order to minimize the temperature gradient across the sample between cone and plate. The results are shown in *Figure 2*. A gradual evolution of the creep compliance curves from Newtonian viscous behaviour at gelling time 1 min, to mostly elastic behaviour at gelling time 74 min is observed. Initially, the compliance retardation curves can be fitted by a power-law time dependence with exponent n: $\gamma(t) \propto t^n$. It is found that, as gelation proceeds, n decreases uniformly from $n = 1.118$ at gelling time 1 min to $n = 0.563$ at gelling time 43 min. At 43 min as evident in *Figure 2b*, a plateau or equilibrium compliance appears in the curves, together with a very small instantaneous recoverable strain, indicative of the presence of a gel network, i.e. we are beyond the gel point. Observation of an equilibrium compliance makes a power-law description no longer accurate. During the overall transformation from sol to gel, the permanent deformation decreases and becomes zero within experimental error at gelling time 35 min, corresponding to $n = 0.70$. Subsequently, as shown in *Figure 2c*, between 35 and 40 min, the magnitude of the permanent deformation tends to vary irregularly, and so does n. The non-systematic variation in the permanent deformation presumably occurs because the comparatively large strains reached during creep ($\approx 10\%$) disrupt the fragile gel network clusters. Finally, as shown in *Figure 2d*, the equilibrium compliance systematically decreases after 46 min, with a marked instantaneous recoverable strain $\gamma_{t=0\mathrm{s}}$ and $\gamma_{t=10\mathrm{s}}$ appearing. At $t = 35$ min we observe that the permanent deformation approaches zero, and also that the dynamical exponent $n = 0.70$, which is in good agreement with the mean value $n = 0.69 \pm 0.02$ from *Table 1*. We conclude, therefore, that the gel point is at $t = 35$ min.

Note that the applied stress level of $10\,\mathrm{dyn\,cm^{-2}}$ is significantly above the yield stress of the critical gel as evident from *Figure 2c* at the gel point. The yield stress for the critical gel is very small ($< 0.2\,\mathrm{dyn\,cm^{-2}}$) and cannot be measured by the Carri-Med rheometer due to the requirement of having to overcome the cone inertia. (For example, for a pure gelatin sol, we still observe a small apparent yield stress of around $0.2\,\mathrm{dyn\,cm^{-2}}$.)

The mean value observed for the dynamical exponent, $n = 0.69 \pm 0.02$, falls numerically within the ranges predicted by various theories. In principle, therefore, it is possible to deduce the apparent fractal dimension, d_f, of the critical gel from n. However, as noted in the discussions of Muthukumar[10], a wide range of n is

Table 2 Calculated and experimental values of the critical gel strength

Conc. (w/v %)	Temp. (°C)	G_e (dyn cm^{-2})	η_0 (P)	$S = G_e^{0.31}\eta_0^{0.69}$	S (average from our measurements)
4	17.5	160 ± 20	0.08 ± 0.02	0.84 ± 0.20	0.54 ± 0.20
8	21.4	220 ± 20	0.1 ± 0.03	1.08 ± 0.20	1.26 ± 0.22
10	23.3	240 ± 20	0.2 ± 0.03	1.80 ± 0.25	2.09 ± 0.22
12	24.7	200 ± 30	0.3 ± 0.04	2.25 ± 0.30	2.09 ± 0.24
14	25.0	400 ± 70	0.5 ± 0.1	3.97 ± 0.50	2.90 ± 0.20

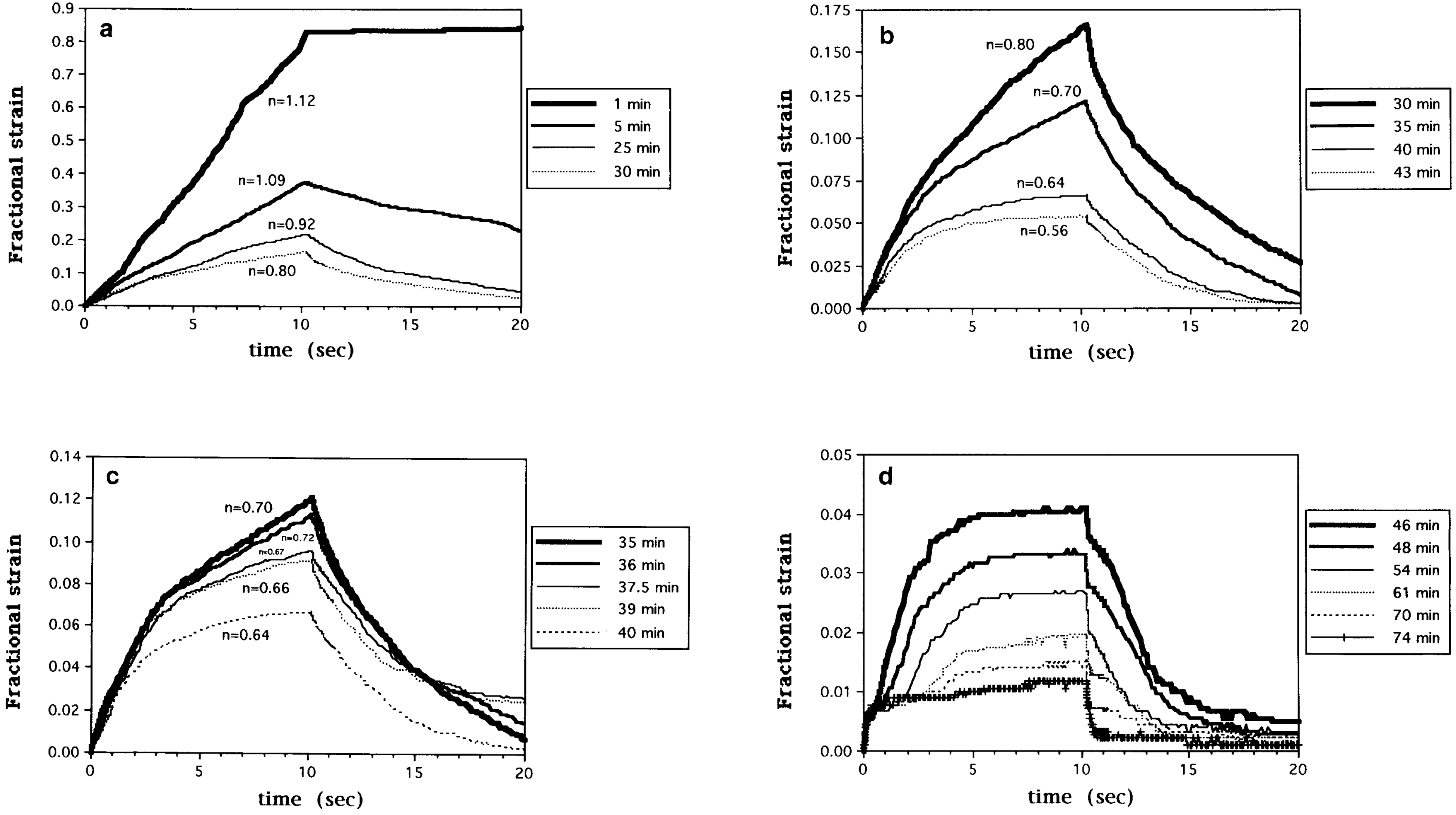

Figure 2 Creep experiments on 8% gelatin at pH = 5.5 and $T = 23.0^\circ$C. Series of curves represent a transition from predominantly viscous to predominantly elastic response: (a) $t = 1$ to $t = 30$ min; (b) $t = 30$ to $t = 43$ min; (c) $t = 35$ to $t = 40$ min; (d) $t = 46$ to $t = 74$ min. Experimental values, n, characterize the apparent power-law time dependence of creep

possible, depending on the strength of the excluded-volume interaction and the hydrodynamic interaction. At least two possibilities can therefore be considered. With regard to the percolation model of Martin[6], as noted by Amis *et al.*[13,16,17]; this n value corresponds closely to that predicted at the Rouse limit ($n = 0.667$) and is quite different from the Zimm limit ($n = 1$). Alternatively, we may consider the interpretation, offered by Muller *et al.*[5], that one is dealing with a non-stoichiometric gel with a deficit of crosslinker. In such a circumstance, the viscoelastic behaviour is determined by the preponderance of linear chains at the gel point. If these exhibit Zimm-like behaviour then, again, $n = 0.667$. Without independent evidence on the structure of the critical gel, we cannot unambiguously choose between these alternatives. However, we note that the remarkable uniformity of the dynamical exponent over a wide range of concentration and solvent conditions suggests that an interpretation based on full screening of hydrodynamic interactions is more appropriate.

CONCLUSIONS

We have extended the viscoelastic studies of Amis *et al.*[12,13] of the sol–gel transition of gelatin to higher concentrations. Self-consistent measurements of both dynamic shear modulus and creep compliance were obtained. Together, these observations indicate that the dynamical exponent has a unique value $n = 0.69 \pm 0.02$ over a wide concentration range, 1–14% w/v, and is independent of ionic strength, pH and denaturant. We conclude that the dynamical behaviour of the critical gelatin gel cluster is not affected by variations in either hydrodynamic interactions or excluded volume. Comparison of these results with theory[6,10] suggests that the critical cluster is a percolation network of dimension $d_f = 2.5$.

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