A viscoelastic study of microemulsion-gels

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Tetraethylorthosilicate was polymerized with acidic water in microemulsions containing formamide, cetyltrimethylammonium bromide, decanol, and decane. The viscoelasticity of the gelled samples was determined, giving the storage and loss moduli against the frequency of the applied oscillations. The resulting data illustrate the relative strengths and elasticity of the condensed networks present in the samples.

1. Introduction
By employing the sol–gel method one can produce non-crystalline solids without elevated sintering temperatures [1–5]. The sol–gel method typically uses a solvent, e.g. ethanol, to which is added an alkoxide, water and a catalyst, generally a mineral acid or base. It has been shown that a microemulsion or a lyotropic liquid crystal can also be used as a gel precursor [6–8]. The microemulsion–gel method differs from the sol–gel method in that the precursor solution consists of colloidally dispersed polar liquids in a non-polar phase, solubilized by a surfactant. One considerable advantage of the microemulsion–gel method is that a wide variety of additives can be solubilized and will be present in the gel after condensation.

Various experimental parameters have been shown directly to influence the hydrolysis and condensation processes and therefore the final oxide network formed [9–15]. However, the precise structure and properties of these networks are still subject to investigation [16–19]. Viscosity measurements are an obvious method of observing a condensing gel [20–26], however, recently dynamic oscillatory measurements have also proven to be a very useful method of studying the viscoelastic properties of polymer networks [27–34].

When a gel is subjected to a low amplitude oscillatory strain, the stress response, τ, is given by

$$\tau = G'\gamma_0 \sin \omega t + G''\gamma_0 \cos \omega t \qquad (1)$$

where G' is the storage modulus, G'' is the loss modulus, γ_0 is the maximum amplitude and ω is the frequency of the oscillations. G' is the elastic response of the gel, while G'' is the viscous response. These moduli are then used to calculate the loss tangent given by

$$\tan \delta = G''/G' \qquad (2)$$

Typically, for gels, G' is greater than G'', indicating elastic behaviour. Also typical for gels is a constant value of G' over the frequency range employed, whereas G'' is constant for low frequencies, but obeys a power law at higher frequencies

$$G'' = \omega^\Delta \qquad (3)$$

The value of the viscoelastic exponent, Δ, is typically between 0.5 and 1 and decreases as the gel network gets stronger.

It has recently been shown that non-aqueous microemulsions can also be used to form gels [8]. These gels are formed in a colloidally dispersed system and the relation between the precursor dispersion and the properties of the final gel are not known. A viscoelastic study of the final gels was chosen as a suitable means to gain further insight into the gels formed by these precursors.

2. Experimental procedure
2.1. Materials
Formamide (Fisher, Certified ACS), cetyltrimethylammonium bromide (Aldrich, 95%), decanol (Aldrich, 99%), decane (Fisher, 99.7%), and tetraethylorthosilicate (Aldrich, 99 + %) were all used as-received.

2.2. Preparation of samples and viscoelastic measurements
Microemulsions of formamide, cetyltrimethylammonium bromide, and 75/25 decanol/decane were prepared, to which was added tetraethoxysilicate (TEOS) and water (pH 1), Table I. The molar ratio of water to TEOS was approximately 2 for each sample. These compositions were mixed on a vortexer until they became transparent, ~ 1 min. After standing for a week the compositions had gelled, whereupon each was sealed.

Both the steady-shear and dynamic tests were carried out on a Rheometrics Systems Four with Fluids Servo and 100 gm-cm sensitive transducer. All tests were conducted at room temperature using parallel plate geometry with a diameter of either 2.5 or 5.0 cm and a 1 mm gap.

3. Results

Figs 1–8 show the storage and loss moduli against the applied frequency for a series of microemulsion gels long after the gel point, approximately four times the gel time. Comparing Figs 1–3 reveals that $G'(\omega)$ and $G''(\omega)$ were greatest for sample RB-5 (Fig. 2) which employed a precursor microemulsion which contained significant amounts of both polar and non-polar phases. This trend is also observed for Figs 4–8, where sample RB-11 (Fig. 5) displayed the greatest values of $G'(\omega)$ and $G''(\omega)$. However, in the latter case the difference displayed is not as pronounced due to the increased SiO_2 content of the system. The values of the loss tangent, $\tan\delta$, and the power law exponent, Δ,

TABLE I Microemulsion–gel compositions

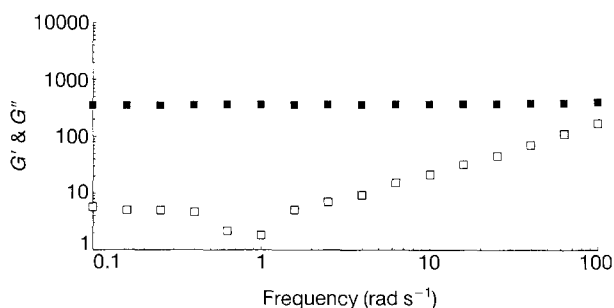| Sample	Formamide	CTAB	Decanol/decane	Water (pH 1)	TEOS
RB-3	1.000	0.300	0.701	0.040	0.201
RB-5	0.503	0.305	1.201	0.045	0.201
RB-6	0.302	0.300	1.401	0.043	0.206
RB-10	1.000	0.300	0.702	0.078	0.402
RB-11	0.699	0.300	1.000	0.076	0.402
RB-12	0.503	0.305	1.201	0.076	0.402
RB-13	0.302	0.300	1.401	0.073	0.403
RB-20	0.302	0.300	1.401	0.156	0.801

Figure 1 Storage and loss moduli against frequency for sample RB-3. ■, G'; □, G''.
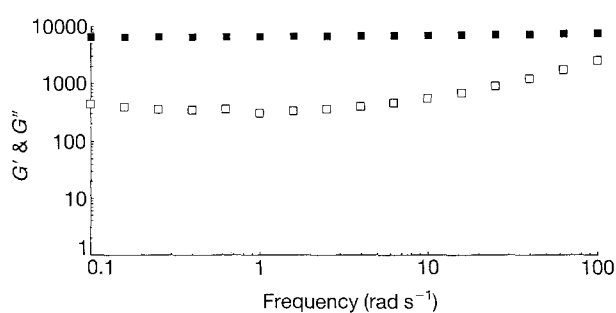

Figure 4 Storage and loss moduli against frequency for sample RB-10. ■, G'; □, G''.
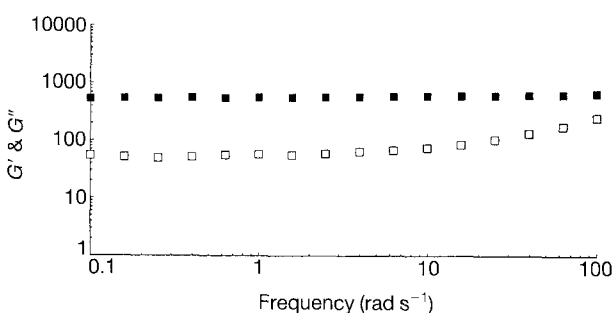

Figure 2 Storage and loss moduli against frequency for sample RB-5. ■, G'; □, G''.
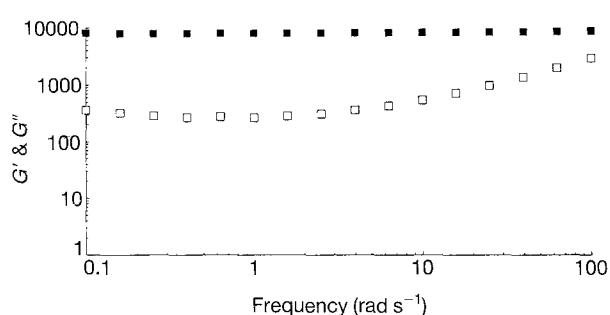

Figure 5 Storage and loss moduli against frequency for sample RB-11. ■, G'; □, G''.
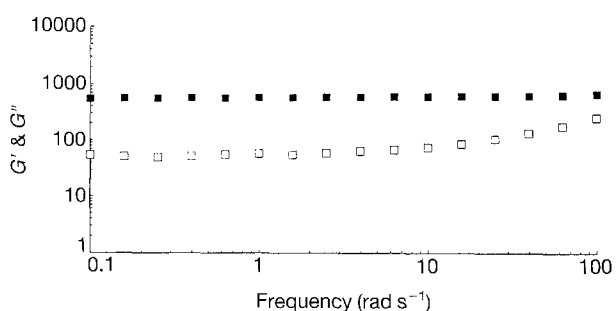

Figure 3 Storage and loss moduli against frequency for sample RB-6. ■, G'; □, G''.
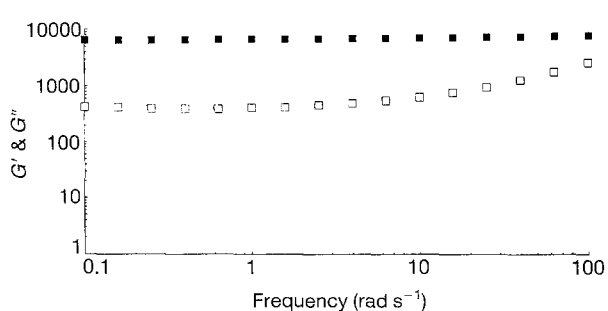

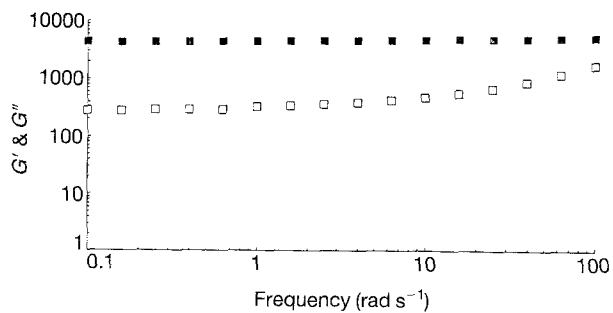*Figure 6* Storage and loss moduli against frequency for sample RB-12. ■, G'; □, G''.

Figure 7 Storage and loss moduli against frequency for sample RB-13. ■, G'; □, G".
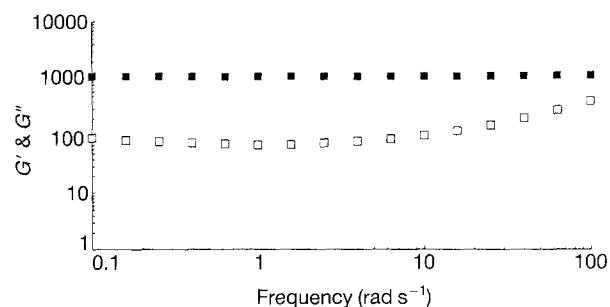

Figure 8 Storage and loss moduli against frequency for sample RB-20. ■, G'; □, G".

TABLE II Viscoelastic values of microemulsion gels

Sample	Δ-viscoelastic exponent	tan δ-loss tangent	Formamide–decanol/decane molar ratio
RB-3	0.962	0.02	4.88
RB-5	0.602	0.08	1.43
RB-6	0.583	0.09	0.78
RB-10	0.663	0.05	4.88
RB-11	0.737	0.03	2.83
RB-12	0.620	0.06	1.43
RB-13	0.531	0.07	0.78
RB-20	0.602	0.08	0.78

given in Table II, also indicate this trend for samples RB-10 through RB-13. Figs 9 and 10 illustrate this trend, as the value of $G''(\omega)$ is greatest for a formamide/(decanol/decane) molar ratio of ~ 2.5.

A comparison of Figs 3, 7 and 8 (samples, RB-6, RB-13, and RB-20, respectively) reveals the resultant change in $G'(\omega)$ and $G''(\omega)$ due to additional silicate present for the same precursor microemulsion. Increasing the TEOS added from 10 to 20% resulted in an order of magnitude increase in $G'(\omega)$ and $G''(\omega)$. However, an increase from 20 to 40% resulted in only doubling the values of $G'(\omega)$ and $G''(\omega)$.

Figs 9–11 show the loss tangent against applied frequency for three groups of samples. The first group of samples, those with the least TEOS, displays the greatest variation of values for a given frequency. The loss tangent for sample RB-3, the most polar solvent
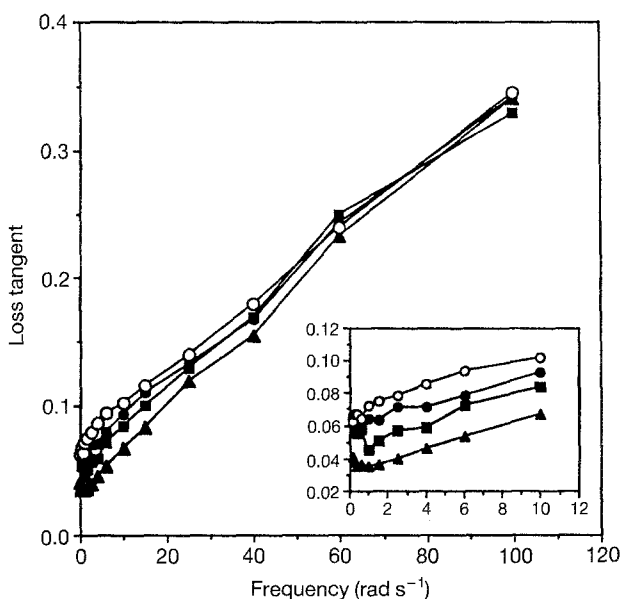

Figure 10 Loss tangent against applied frequency for samples RB-10 —■—, RB-11 —▲—, RB-12 —●—, and RB-13 —○—.
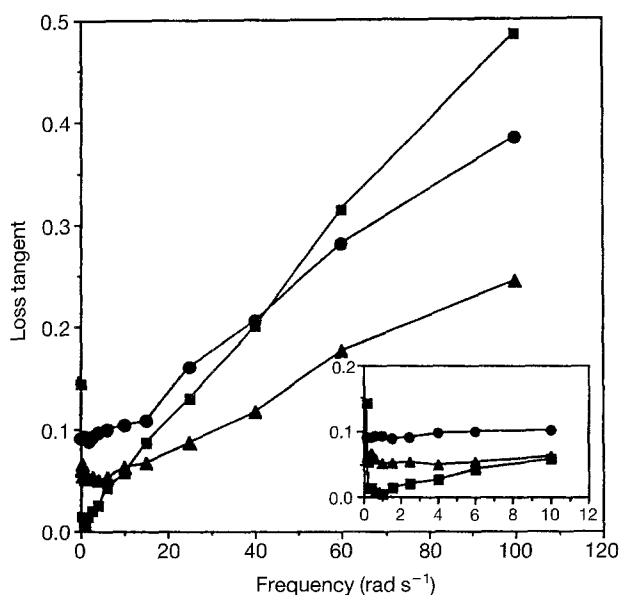

Figure 9 Loss tangent against applied frequency for samples RB-3 —■—, RB-5 —▲—, and RB-6 —●—.
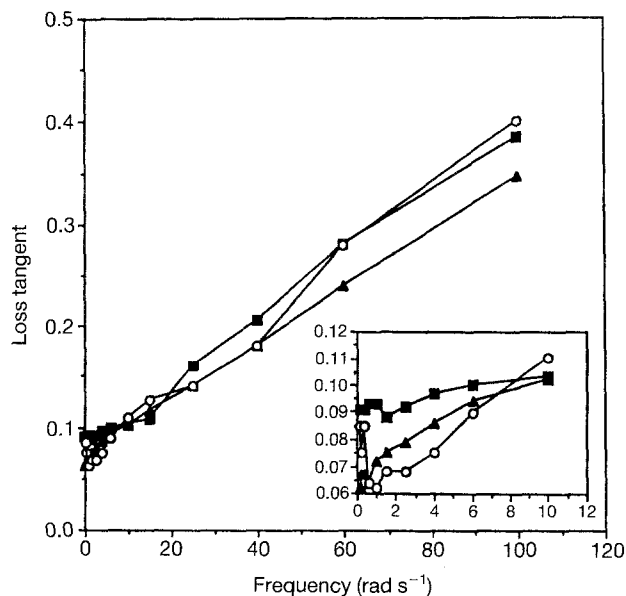

Figure 11 Loss tangent against applied frequency for samples RB-6 —■—, RB-13 —▲—, and RB-20 —○—.

system for 10% added TEOS, underwent the greatest change over the frequency range employed of all the samples tested.

4. Discussion

The results show a rheological behaviour typical of a gel. The microemulsion medium obviously did not cause significant deviation from the solvent gel properties. $G'(\omega)$ was constant over the frequency range, $G''(\omega)$ was constant for low frequencies and increased for higher frequencies, and $G'(\omega) \gg G''(\omega)$, all conditions typical of a gel structure. In addition, the values of Δ were also typical of polymeric networks, for which $0.5 < \Delta < 1$. Values of the loss tangent less than 1 would be expected for gels at times well after the gel point (see Table II).

However, the results show trends in the storage and loss moduli as well as in the loss tangent with changing reaction medium properties. The medium of the solvent system used has earlier been shown to significantly influence the condensation process [35] and a comparison of the influence on the properties of the final gel network may be of interest. The present results show the value of the storage modulus to be greatest for the samples with a precursor formamide/ decanol-decane molar ratio of approximately 2.5 (Figs 12 and 13). At these ratios there are significant amounts of both polar and non-polar compounds present, and this ratio has a direct influence on the gel network formed.

The influence can be estimated from earlier ^{29}Si NMR results of condensing microemulsion gels in non-aqueous systems [35]. The NMR spectra showed a more non-polar environment to advance the incorporation of cyclic tetramers into the silicate network, while the polar environment did so at slower rate. In the former case there was a disproportionate amount of linear polymers present during the latter

stages of gelation, whereas for polar systems the linear moieties are consumed concurrently with the cyclic tetramers. Combining this information with the present viscoelastic response of these gels, it is concluded that gels formed from the microemulsions composed of balanced amounts of both clusters and linear moieties at the gel point, i.e. polar to non-polar solvent molar ratio ~ 2.5–3, consist of networks with the greatest storage modulus, Figs 12 and 13. Hence it seems that a combination of cluster–cluster bonds enhanced by cluster–linear chain–cluster bonds form the most elastic gel network, while gels formed by direct cluster–cluster bonds only (e.g. RB-3 and RB-10) or by cluster–linear chain–cluster bonds only (e.g. RB-6 and RB-13) form more viscous networks. However, for the intermediate case the clusters are directly bonded and secondarily bonded via linear moieties forming a rigid, yet flexible, network.

The gelation of silanols and organic polymers has been modelled as a random process described by percolation and fractal geometry [36–41]. Due to certain shortcomings of percolation theory, kinetic models have been proposed [42, 43]. The presence of a broad distribution of cluster sizes is predicted by both percolation and kinetic theories, and the precise nature of this distribution has a direct bearing on the resultant gel. The Cole–Cole plot of RB-11 (Fig. 14)
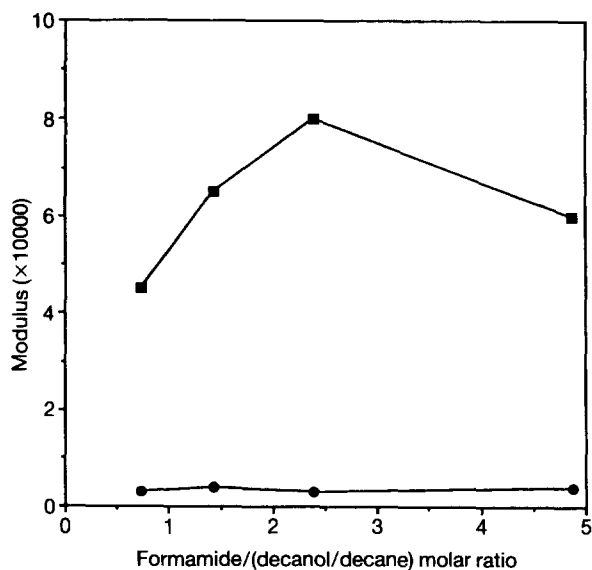

Figure 13 Storage and loss moduli against formamide/ (decanol/decane) molar ratio for samples RB-10 through RB-13 at a frequency of 60 rad s⁻¹, $G'(60\ \text{rad s}^{-1})$—■—, $G''\ (60\ \text{rad s}^{-1})$ —●—.
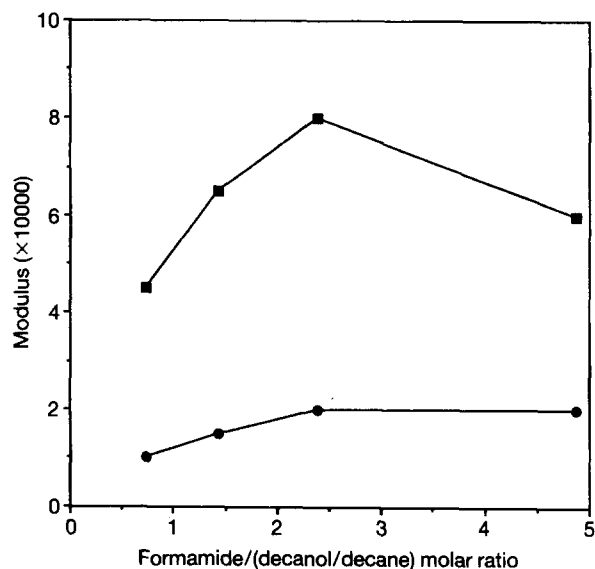

Figure 12 Storage and loss moduli against formamide/ (decanol/decane) molar ratio for samples RB-10 through RB-13 at a frequency of 0.15 rad s⁻¹, G' (0.15 rad s⁻¹) —■—, G'' (0.15 rad s⁻¹) —●—.
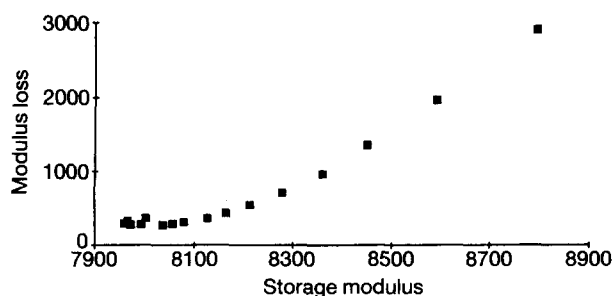

Figure 14 Cole–Cole plot for sample RB-11.

illustrates that there is no single relaxation time. As the relaxation time is different for clusters of different compositions, there is more than one relaxation time for these gels, and thus the Cole–Cole plot is not semi-circular [44].

It has been shown that each cluster contains smaller clusters within its composition [17, 18, 45]. It has also been established that the presence of smaller clusters in the interstitial liquid screen the larger clusters and thus facilitate cluster–cluster aggregation [16, 17]. ^{29}Si NMR has also revealed that larger clusters are rapidly formed in non-polar solvents, whereas polar solvents gradually form smaller aggregates [35, 46]. These smaller aggregates are then able to further condense without significantly depleting the interstitial system of available polymers. From this information, certain conclusions appear to be reasonable. For systems employing a non-polar solvent, the amount of smaller, linear clusters is substantial in the later stages of gelation and thus the spatial correlation length changes relatively late in the gelation process [17], whereas for polar solvent systems, the linear moieties are consumed gradually as the larger aggregates form [35]. From this it can be seen that the concentrations of linear polymers at different stages during the gelation process directly influence the gel formed, and thus its viscoelastic properties. The consequences are evident in Fig. 9. The use of a polar solvent producing larger aggregates composed of smaller aggregates and relatively few interstitial linear polymers showed a low value of the loss tangent for the lowest frequencies of the shear. Obviously, the resultant large aggregates could rearrange themselves at these frequencies over long timescales, adjusting to the shear field without significant loss. This elastic relaxation was not possible for higher frequencies and shorter timescales, at which the large three-dimensional aggregates underwent loss.

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