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Polymer concentration dependence of the gel point for chemically modified biopolymer networks using small amplitude oscillatory rheometry

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Abstract

Solutions of xanthan gum form a strong gel upon the addition of aluminium ions (Al(III)). We have previously reported on the stoichiometric (ratio of crosslinker to polymer present) dependence of the thermal gel point and final gel strength. The results presented here expand on previous work, presenting the thermal gelation characteristics for a range of xanthan concentrations and different stoichiometries. The limiting stoichiometric ratio, below which gelation does not occur, is found to be independent of polymer concentration. The relaxation exponent is shown to decrease with increasing polymer concentration, whilst the temperature of gelation T_g, is shown to increase. The 'gel strength' measured at the complete extent of gelation is shown to increase with increasing polymer concentration and the previously defined effective stoichiometry, r_e, becomes less pronounced. For systems of constant stoichiometry and varying polymer concentrations, the storage modulus is shown to follow a power law relationship with an exponent of approximately two. All observed trends support the previously proposed mechanism of gelation for xanthan-Al(III) systems and provide new insight into the gelation of xanthan in the presence of metal ions. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Xanthan; Gelation; Rheology

1. Introduction

Xanthan-Al(III) gelling systems offer unique properties in comparison to other metal ions as they gel on the addition of heat. The interest in technical literature into the gelation of xanthan, in the presence of trivalent metal ions, is predominantly due to applications in the drilling industry in the tertiary stage oil recovery [1–5]. A detailed rheological characterisation of xanthan in the presence of chromic and aluminium ions has been provided by Nolte et al. [6]. Nolte et al. suggest that xanthan crosslinks with metal ions via the formation of dimeric or monomeric ionic bridge between a hydrated metal ion and the carboxyl group on the xanthan repeat unit. These researchers suggest possible combinations of chromic and aluminium ions with xanthan to better match the gel requirements in the tertiary stage oil recovery. Previously we have reported on the stoichiometric and thermal dependence of xanthan-Al(III) gels at a constant polymer concentration of 0.5 wt% [7], from which a physical mechanism of gelation was proposed. The results presented here expand on our previous work by investigating the effect of polymer concentration for a range of stoichiometries, the results from which provide further evidence for the proposed gelation mechanism.

In our previous studies, we have identified the applicability of the Winter and Chambon technique [8–10] when investigating the process of gelation and characterising the gel point. It has been found that the Winter–Chambon [8,9] technique adequately describes the fundamental definition of a gel proposed by Flory [11] for a large range of systems, both ideal and non-ideal, and is thus considered suitable for analysis of the linear viscoelastic experiments presented here. Winter and Chambon propose a constitutive equation to describe both stoichiometrically balanced and imbalanced gels.

$$\tau(t) = S \times \int_{-\infty}^{t} (t - t')^{-n} \gamma(t')\, dt' \qquad (1)$$

where, t is time, τ is the excess stress tensor and γ is the rate

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of deformation tensor. Eq. (1) contains two material parameters: S the effective strength of the network at the gel point, and n, the relaxation exponent. Determination of these parameters then enables distinction between a range of gel structures. It follows from the model, that the loss and storage modulus at the gel point are parallel, resulting in a frequency independent value of $\tan(\delta)$, where δ is the phase angle. For xanthan-Al(III) systems, the temperature at which $\tan(\delta)$ is frequency independent represents the temperature of gelation, T_g. From δ the relaxation exponent, n can be calculated directly i.e. $n = 2\delta/\pi$. A gel with n approaching 1 is a purely viscous gel whereas n approaching 0, suggests a purely elastic gel whilst a value of $n = 0.5$ suggests a stoichiometrically balanced, ideal gel [8]. Please note that no solutions exist to Eq. (1) when $n \geq 1$ and a value of $n \leq 0$ would defy principles of thermodynamics [9].

2. Experimental methods

The linear viscoelastic experiments reported here were performed on a Rheologica Stresstech Rheometer fitted with an extended temperature cell (ETU-10). A 40 mm 4° cone was used for polymer concentrations of 0.5 wt% and greater whilst to extend the measurable stress range of the instrument a 25 mm couette geometry with $R_i/R_o > 0.90$ was used for lower polymer concentrations (where R_i and R_o are the inner and outer wall radii respectively). Xanthan samples were prepared by hydrating for 24 h in distilled water following which the crosslinker solution was added at a controlled temperature of 10°C to avoid any gelation prior to experimentation. The crosslinker used in these experiments was aluminium ions from an $Al_2{\cdot}(SO_4)_3{\cdot}18\text{-}H_2O_{(aq)}$ source. Both the sample preparation and the procedure followed for the gelation of xanthan-Al(III) are described in detail elsewhere [7].

3. Results and discussion

A series of small amplitude oscillatory rheometry experiments have been performed to determine T_g, n and G' at $T = 85$°C completely for four xanthan concentrations, 0.1, 0.25, 0.5 and 1.0 wt%. Additionally, the concentration dependence of G' measured at $T = 85$°C has been studied at three constant stoichiometries. The results shall be discussed in light of the recently proposed mechanics of gelation [7].

3.1. Determination of temperature of gelation, T_g

The stoichiometric ratio, r defined as the ratio of xanthan to crosslinker present, is such that below $r = 1$ it was not possible to form a gel over the temperature range investigated [7]. The definition of r has been previously derived to follow [7]:

$$r \approx \left(\frac{[\mathrm{Al}_x(\mathrm{OH})_y^{(3x-y)+}] \times 2}{[\mathrm{xanthan}]} \right) \tag{2}$$

where [xanthan] is the molar concentration of polymer present, and $[\mathrm{Al}_x(\mathrm{OH})_y^{(3x-y)+}]$ is the molar concentration of the various hydrated species present. Previously the pH dependence of gelation investigated [7] together with the pH dependence of the dissociation of Al(III) into its various hydrated species [12] suggests monomeric and dimeric species to be responsible for gelation, as has been previously expected [6].

Here we shall illustrate the determination of the gel point for three polymer concentrations at a constant r of 2.4. Figs. 1–3 illustrate the frequency dependence for gels of 0.1 wt% and 280 ppm Al(III), 0.5 wt% and 1400 ppm Al(III) and 1.0 wt% and 2800 ppm Al(III), respectively. In each figure, α_T represents an arbitrary horizontal shift factor to separate the data at different temperatures. This shift factor has no physical meaning, providing only a convenient method for separating the data. Fig. 1 representing the lowest polymer concentration illustrates clearly the crossover of G' and G'' for low temperature data, followed by the congruency of G' and G'' at higher temperatures. Such a transition in G' and G'' is not observed in Figs. 2 and 3, even at the lowest temperature investigated. Due to the 'weak-gel' characteristics of concentrated solutions of xanthan gum, not observing a crossover is perhaps expected [13]. It is proposed that if much lower values of ω were measured, then we would indeed observe such a crossover,

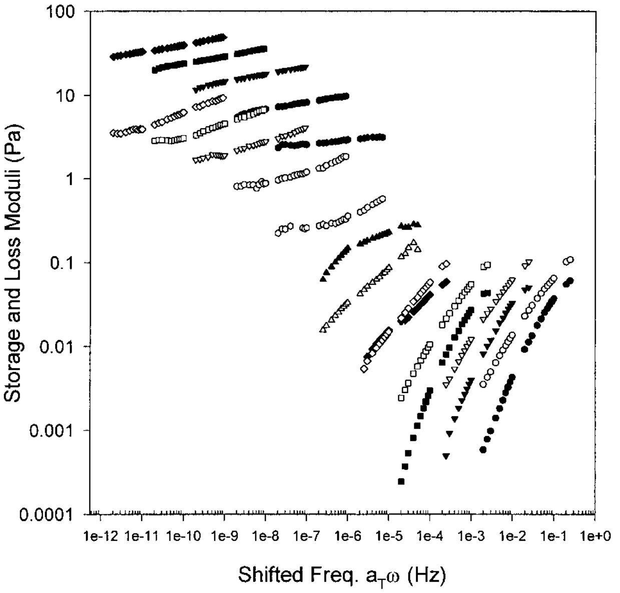

Fig. 1. Frequency dependence of the storage (filled symbols) and loss modulus (empty symbols) for 0.1 wt% xanthan and 280 ppm Al(III) measured at a range of temperatures. A shift factor α_T, has been used to separate the data. Circle, 10°C; inverted triangle, 15°C; square, 20°C; diamond, 25°C; triangle, 27°C; hexagon, 30°C; circle, 35°C; inverted triangle, 40°C; square, 45°C; and diamond, 50°C.

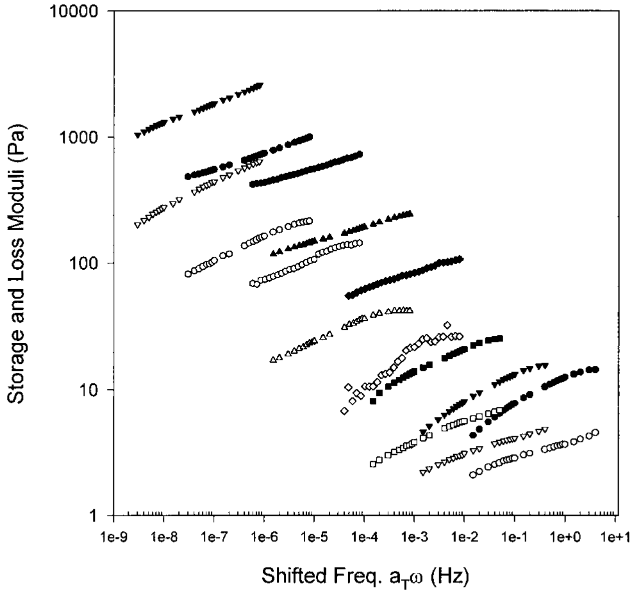

Fig. 2. Frequency dependence of the storage (filled symbols) and loss modulus (empty symbols) for 0.5 wt% xanthan and 1400 ppm Al(III) measured at a range of temperatures. A shift factor α_T, has been used to separate the data. Circle, 10°C; inverted triangle, 20°C; square, 30°C; diamond, 35°C; triangle, 40°C; hexagon, 45°C; circle, 50°C; and inverted triangle, 60°C.

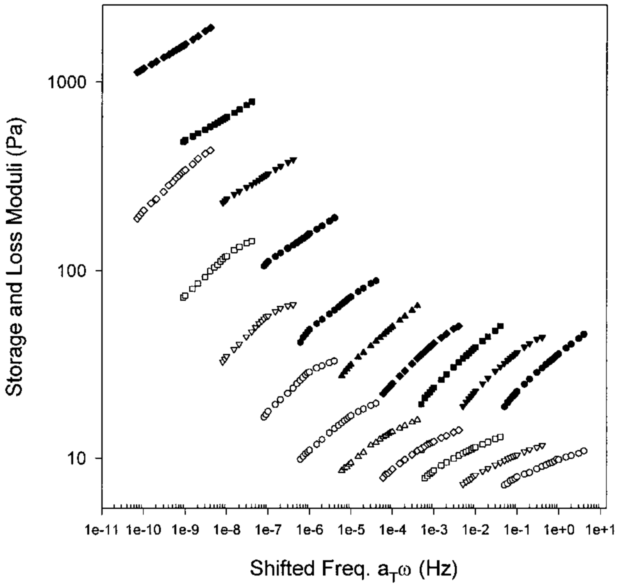

Fig. 3. Frequency dependence of the storage (filled symbols) and loss modulus (empty symbols) for 1.0 wt% xanthan and 2800 ppm Al(III) measured at a range of temperatures. A shift factor α_T, has been used to separate the data. Circle, 10°C; inverted triangle, 15°C; square, 20°C; diamond, 25°C; triangle, 30°C; hexagon, 35°C; circle, 40°C; inverted triangle, 45°C; square, 50°C; and diamond, 60°C.

however the experiments do become unfeasible due to the measurement time, t_{exp} scaling as $t_{\text{exp}} \propto 1/\omega_{\text{min}}$, where ω_{min} is the lowest investigated frequency. To accurately determine T_g it is most appropriate to consider tan(δ) and the point at which tan(δ) exhibits frequency, ω independence or alternatively $\tan(\delta) = K\omega^q$ where $q = 0$ at the gel point and K is a constant from which the relaxation exponent n may be calculated. Fig. 4 illustrates the dependence of q on temperature for the three systems described above. An increase in T_g with increasing polymer concentration is observed. It is important now to determine if the trend observed in Figs. 1–4 holds over a range of stoichiometries and determine if the observed trend is consistent with the proposed model.

3.2. Stoichiometric dependence of the temperature of gelation, T_g

Fig. 5 illustrates the T_g for a range of stoichiometries for four polymer concentrations. Each T_g was determined as discussed above. Previously, the data of 0.5 wt% xanthan has been presented [7] indicating an upper asymptotic limit of T_g at $r = 1$ suggesting gelation will not occur at $r < 1$ and a lower asymptotic limit at large r beyond which no further decrease in T_g is observed. Fig. 5 illustrates similar behaviour for all concentrations investigated. All curves appear to asymptote towards $r = 1$ (within experimental error) suggesting that defined stoichiometry follows a linear dependence on polymer concentration. The temperature to which T_g asymptotes at large r appears to increase with increasing polymer concentration, agreeing with the observed trends for constant stoichiometry (i.e. $r = 2.4$) discussed above.

Previously [7] we have suggested that due to xanthan molecules changing from a semi-flexible molecule to an extended random coil with increasing temperature, and the

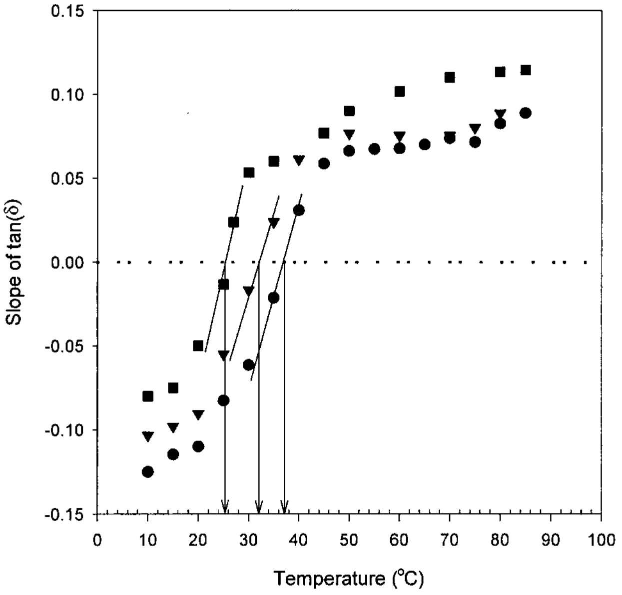

Fig. 4. Power law dependence of $\tan(\delta) = K\omega^q$, where q is reported on the y axis. Intersection of $q = 0$, represents the temperature of gelation as defined by Winter and Chambon. Squares, 0.1 wt% and 280 ppm Al(III); inverted triangles, 0.5 wt% and 1400 ppm; and circles, 1.0 wt% and 2800 ppm Al(III). All values of q were obtained by linear regression with $R^2 > 0.95$.

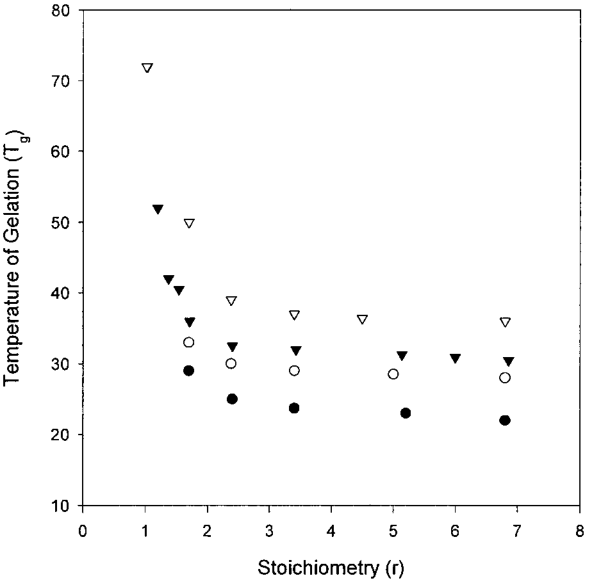

Fig. 5. Temperature of gelation (T_g) as determined by Winter and Chambon, versus stoichiometry for a range of polymer concentrations. Closed circles, 0.1 wt% xanthan; open circles, 0.25 wt% xanthan; closed inverted triangles, 0.5 wt%; and open inverted triangles, 1.0 wt%.

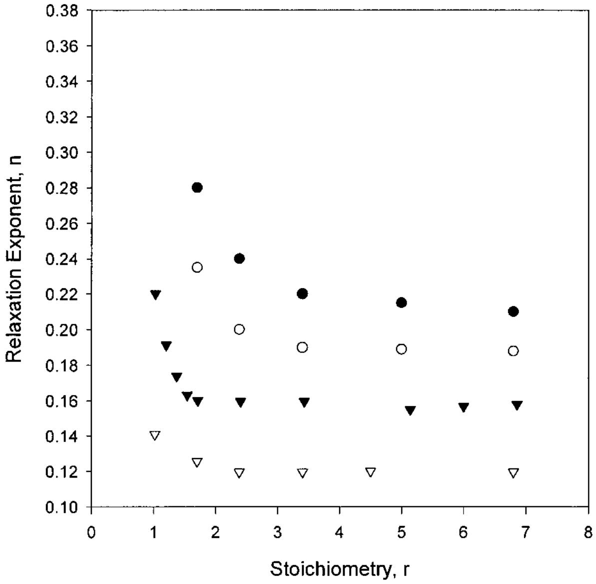

Fig. 6. Relaxation exponent (n) as determined by Winter and Chambon, versus stoichiometry for a range of polymer concentrations. Closed circles, 0.1 wt% xanthan; open circles, 0.25 wt% xanthan; closed inverted triangles, 0.5 wt%; and open inverted triangles, 1.0 wt%.

diffusion of both the polymer and crosslinker increasing with temperature, statistically more crosslinks would be expected as the temperature is increased. However, it is also intuitive that for a higher polymer concentration, more crosslinks will be required per unit volume to achieve percolation. Overall, we expect that the temperature at which percolation is achieved, to increase with increasing concentration. Fig. 5 supports this hypothesis showing that for increased polymer concentration, a higher T_g is observed. The observed trend is consistent with the previously proposed mechanism of gelation [7].

3.3. Stoichiometric dependence of the relaxation exponent, n

In addition to T_g, the technique of Chambon and Winter [9] allows the determination of the relaxation exponent, n. n provides a measure of the degree of elasticity at the gel point with $n = 0$ indicating a purely elastic gel and $n = 1$ suggesting a purely viscous gel. A value of $n = 0.5$ suggests a gel of balanced stoichiometry [8–10]. The relaxation exponent, n follows a similar relationship with r as shown for T_g with r for the xanthan-Al(III) system reported here [7]. As r decreases, n did not reach an asymptotic limit but rather reached a value of 0.22 for 0.5 wt% xanthan and $r = 1.03$. Fig. 6 illustrates the dependence of n on stoichiometry for a range of polymer concentrations showing similar trends to the original 0.5 wt% xanthan data. As polymer concentration decreases the dependence of n on r shifts vertically. This suggests that as polymer concentration decreases, the gel becomes more viscous which is consistent with less crosslinks at the gel point. At the limit of $r = 1$, n appears to vary between 0.14 for 1.0 wt% xanthan up to as high as 0.36 for 0.1 wt%, however this is an extrapolated value as measurements of 0.1 wt% xanthan and $r = 1.03$ was determined to be outside the limits of the equipment used. The observed trend of a vertical shift to higher relaxation exponents with lower polymer concentration is considered consistent with a lower crosslink density at lower polymer concentrations, agreeing with the discussion above.

3.4. Stoichiometric dependence of the storage modulus at full extent of gelation

In addition to T_g and n, we analyse the dependence of the final gel strength on stoichiometry for a range of polymer concentrations. The final gel strength, defined here as the reduced storage modulus measured at $\omega = 1$ Hz and a temperature of 85°C, is reported in Fig. 7. The reduced storage modulus is the value of the storage modulus of the gel without the contribution of the polymer solution in the absence of crosslinker. As has been previously shown for 0.5 wt% xanthan, G' at 85°C approaches zero at $r = 1$. Initially G' increases linearly with r before going through a maximum following which a slight decrease is observed at high values of r. Such a trend is observed in Fig. 7 for all polymer concentrations investigated. The stoichiometry where a maximum in G' is observed has previously been defined as an effective stoichiometry r_e. r_e is the characteristic crosslinker to polymer ratio above which side branching, or closed loop reactions, become significant and the overall gel strength decreases [9]. Fig. 7 illustrates the maximum in G' becomes more pronounced with

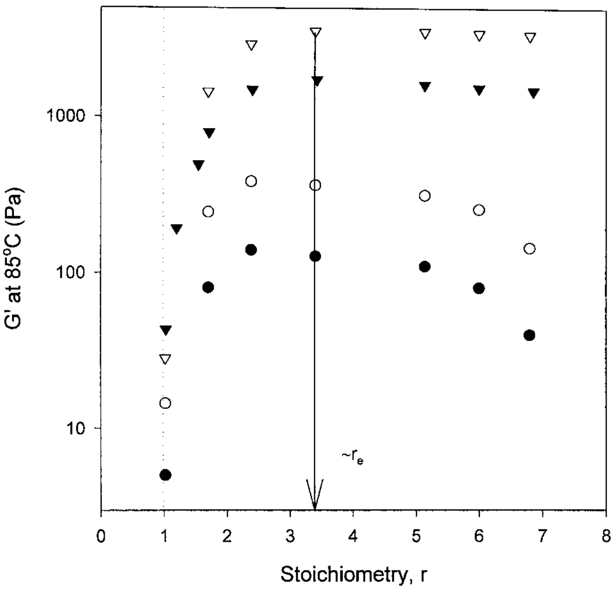

Fig. 7. Storage modulus measured at 85°C and $\omega = 1$ Hz versus stoichiometry for a range of polymer concentrations. Closed circles, 0.1 wt% xanthan; open circles, 0.25 wt% xanthan; closed inverted triangles, 0.5 wt%; and open inverted triangles, 1.0 wt%. Dotted line represents limit of gelation.

decreasing polymer concentrations. Previously the position of the maximum in G' has been related to the stoichiometry above which T_g becomes independent of temperature [7]. It is proposed that presently, the same conclusion may not be drawn between polymer concentrations as it is believed that the value of r_e at the maxima are not significantly separable within experimental error. The approach of G' to zero for all polymer concentrations as r approaches one further supports the definition of stoichiometry [7].

3.5. Dependence of the storage modulus on polymer concentration for constant r

Various investigations have been conducted on the dependence G' has on polymer concentration for gelling systems. For systems where large molecular weight polymers associate to form gels, generally G' is expected, in the limit of high concentration, to follow a power law dependence on concentration of approximately two [14,15]. Fig. 8 illustrates the dependence of G' at $\omega = 1$ Hz and a temperature of 85°C for three stoichiometries $r = 1.03$, 2.4 and 6.8. A power law fit of the form $G' \propto C^{\beta}$ where C is the polymer concentration resulted in $\beta = 1.58$, 1.85 and 2.13 for $r = 1.03$, 2.4 and 6.8, respectively. The basis of all applied theories of polymer gelation stem from the original work of Flory–Stockmayer [16,17]. A review of the application of these theories to the concentration dependence of biopolymer gels is presented by Clark and Ross-Murphy [14]. Clark and Ross-Murphy conclude that in the limit of high concentrations the majority of theories predict, $\beta \rightarrow 2$. Clark and Ross-Murphy [14] report theories that predict both $\beta = 9/4$ and β that asymptote to values less than two. Clark and Ross-Murphy [14] suggest that for any further advances in the interpretation of the concentration dependence of biopolymer gels, it is necessary to include 'trapped entanglements' in the theoretical approach. Trapped entanglements are extra contributions to the shear modulus that are made permanent by surrounding permanent crosslinks [14,18]. It is likely that trapped entanglements will provide a significant contribution to the measurements reported in Fig. 8, due to the high initial molecular weight of the xanthan molecule (ca. 3.5×10^6 g/mol). The values of β measured in this work are seen to increase with stoichiometry, and it is felt that this is a combination of both a contribution from an increasing functionality (number of crosslinking sites per individual molecule) and the contribution of 'trapped entanglements'. It is, however, not possible to separate the two contributions in the results presented here.

Below some polymer concentrations, C_o, it is not possible to form a gel network. Clark and Ross-Murphy stress that C_o is not the same as the overlap concentration, C^* and one would expect $C_o < C^*$, as demonstrated for globular proteins [14]. As C_o is approached from above, β is predicted to approach infinity however data in this region is seldom accessible, due to the low values of storage modulus expected. Fig. 8 illustrates a significant deviation from a power law approximation as C_o is approached, however it is suggested that the actual value of C_o is significantly lower than the lowest polymer concentration measured, of 0.01 wt% ($\approx$ 0.1 mg/ml). Such a low value of

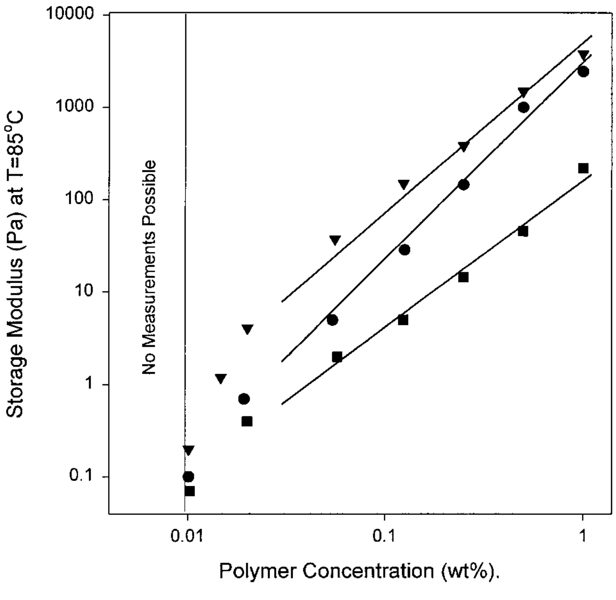

Fig. 8. Storage modulus measured at 85°C and $\omega = 1$ Hz for a range of polymer concentrations at constant stoichiometries. Squares, $r = 1.03$; inverted triangles, $r = 2.4$; and circles, $r = 6.8$. Solid lines represent power law fits $G' = K \times C^{\beta}$ where K is a constant, C is the polymer concentration in wt% and p is the power law coefficient. All fits reported $R^2 > 0.95$ and $\beta = 1.58$, 1.84, 2.13 for stoichiometries $r = 1.03$, 2.4 and 6.8, respectively.

C_o can be explained by the presence of anisotropic aggregates in xanthan solutions, reported to occur at low concentrations [19]. It is proposed that the presence of such anisotropic aggregates together with a crosslinker (Al(III)), would enable the percolation of a network at very low polymer concentrations, facilitated especially by the association of the ends of the anisotropic aggregates, similar to a 'star-branched' network [20]. To confirm such hypothesis and to expand on the understanding of the behaviour of xanthan in the presence of trivalent metal ions, spectroscopic studies (namely static and dynamic light scattering) will be performed on unmodified commercial xanthan samples both in the presence of a non-gel inducing electrolyte (NaCl) and in the presence of a trivalent metal ion (Al(III)).

4. Conclusions

The above results present an interesting expansion on our previous submitted work of the gelation of xanthan in the presence of Al(III) [7]. The trends observed in T_g, n and G' at $T = 85°C$ as a function of r, are in qualitative agreement with the previously proposed mechanism of gelation. T_g is observed to increase with increasing polymer concentration. This is consistent with more crosslinks being required to form a gel with an increase in polymer concentration, independent of stoichiometry. The elasticity of the gel follows a power law relationship at higher polymer concentrations with an exponent of β increasing from 1.58 to 2.13 with an increase in stoichiometry. The dependence of β on stoichiometry is proposed to be a combination of changing polymer functionality and the contribution of 'trapped entanglements'. A limiting polymer concentration required for gelation is proposed to be $C_o < 0.01$ wt%. The low value of C_o is speculated to be due to a possible 'star-branched' structure. Further structural analysis will be obtained through analysis of the xanthan-Al(III) system with dynamic and static light scattering.

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