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Concentration dependence of critical exponents for gelation in gellan gum aqueous solutions upon cooling

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ABSTRACT

The sol–gel transition in aqueous gellan gum solutions induced upon cooling was investigated by rheology measurements. The gelation temperature was determined from the crossover point of storage and loss moduli, i.e., $G' = G''$ (T_c) and from the Winter's criterion (T_{gel}), respectively, which increased with gellan concentration. T_{gel} was higher than T_c and the difference became larger as the gellan concentration got higher. The relaxation critical exponent n was estimated with the Winter's method and the self-similarity was observed from the critical gel. The scaling for the zero-shear viscosity η_0 before the gel point and the equilibrium modulus G_e after the gel point was established against the relative distance ε from the gel point over the gellan concentration C_g of 1.0–2.5 wt%, giving the critical exponents k and z. The critical exponent n calculated from k and z agrees well with n from the Winter's criterion. However, no universal n was found for the gelation in aqueous gellan gum solutions, indicating that this gelation should be classified into the cross-linking category for the physical gelation. The critical exponent n decreased with increasing C_g for the gellan gum solution. The fractal dimension d_f calculated from n with the screened hydrodynamic interaction and the excluded volume effect suggested a denser structure in the critical gel with higher C_g.

1. Introduction

Gellan gum is a microbial polysaccharide produced by fermentation of the organism *Pseudomonas elodea* and composed of tetrasaccharide repeating units: 1,3-β-D-glucose, 1,4-β-D-glucuronic acid, 1,4-β-D-glucose, and 1,4-α-L-rhamnose [1,2] as shown in Fig. 1. Native gellan contains a substitution of an L-glycerate group at C_2 and a partial substitution of an acetate group at C_6 of 1,3-β-D-glucose. The commercial gellan gum product has been completely de-esterified by alkali treatment [3] and the deacetylated gellan gum has lower sol–gel transition temperature and stronger gel strength compared with the native one [4–6]. With the presence of cations, aqueous gellan gum solutions transfer into hydrogels with decreasing temperature at very low concentrations. By comparing with other polysaccharide gels, the gellan gel is resistant to heat and its strength is less pH dependent [5]. Gellan gum hydrogel at very low concentrations can provide an abundant gel textures by carefully controlling the added salts [7]. The gelation temperature and gel strength depend on the polymer concentration, cation species and content. Divalent cations induce the gelation much more effectively than monovalent ones. Therefore, gellan gum has been popularly used in food industry as a thickening agent [8–10]. Moreover, gellan gum is one of the most potential in-situ gelling polymers in human body and widely adapted in the biomedicine technology, such as drug delivery vehicles and protein immobilization media [11–13]. For an example, a commercial deacetylated gellan gum has been granted regulatory approval as a pharmaceutical excipient and in a controlled release glaucoma formulation [11].

Because many applications of the gellan gum concern its gelation in aqueous solutions, the gelation process has been intensively investigated up to now. Rheology

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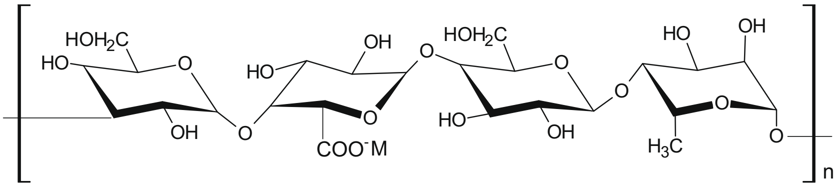

Fig. 1. Chemical structure of gellen gum repeat unit.

method is a convenient way to monitor the gelation process and to determine the gel point for the viscoelastic properties change drastically over the gel point to show the mechanics change from liquid to solid. Some researchers employed the crossover point of the storage modulus G' and loss modulus G'' (i.e., $G' = G''$) to define the gelation point T_c, while the temperature where G' increased steeply was coil-helix transition temperature T_{ch} [14–16]. Circular dichroism (CD) spectrum was used to detect the gellan chain conformation from single coil to double helix during gelation as shown by the molar ellipticity from the peak at about 201 nm ($[\theta]_{201}$) [17–19]. Based on a single coil-double helix equilibrium model [20], the double helix content was estimated from the CD results [19]. The exothermic peak in differential scanning calorimetry (DSC) at the cooling curve and the endothermic peak at the heating curve were observed for the coil to helix and helix to coil transition, respectively, [21–23]. Miyoshi and Nishinari found that the T_{ch} values determined by rheology and DSC were almost identical and proposed a phase diagram for aqueous gellan gum solutions with and without cations [14].

The signal intensity in spin echo and the spin–spin relaxation time T_2 of nuclear magnetic resonance (NMR) were used to monitor the gellan chain mobility during sol–gel transition [24–26]. Matsukawa and Watanabe observed the gelation process in low-acyl (LA) gellan, high-acyl (HA) gellan solutions and the mixed solution of LA and HA gellan (0.5 wt% each) with rheology, CD and NMR methods [26]. They found that the CD spectrum of the mixed gellan solution was a superposition of those for the HA and LA gellan solutions. During cooling, 1 wt% of the HA gellan solution and the mixed gellan solution showed almost the same T_{gel}. They suggested that the double helix only formed with the same kind of gellan chains in the mixed solution.

Besides, fluorescence [27,28], dynamic light scattering (DLS) [29], atomic force microscope (AFM) [30], and small angle X-ray scattering (SAXS) [31,32], etc. were also adopted to study the gelation process of gellan gum in aqueous solutions. Horinaka et al. observed the change in fluorescence anisotropy ratio during the sol–gel transition for a FITC-labeled gellan sample, which reflected the chain mobility change, and discussed the influence of temperature, concentrations of gellan and added salts [28]. Okamoto and Kubota determined the gel point by the quantitative change in the profile of correlation function of DLS and obtained the critical exponents γ and ν corresponding to the cluster mass and correlation length, respectively, [29]. Morris et al. observed the surface structure of gellan gels with an AFM and provided a fibrous model for the gellan gel [30]. Yuguchi et al. tested the temperature dependence of SAXS profile of the gellen gum solution with various concentrations and evaluated the cross-sectional radius of gyration $R_{G,c}$ [32]. At low concentrations where no gelation took place, $R_{G,c}$ increased to a value corresponding to the double helix during cooling. In contrast, a much larger $R_{G,c}$ was estimated at higher concentrations where gel was formed, suggesting the association of the double-helices.

Up to now, however, only a few studies concerned the critical behavior of the sol–gel transition in the aqueous gellan solutions. This gelation process is generally considered to consist of two steps and thermoreversible [18,33]. The first step is the conformation change from random coil to double helix and then the double-helices aggregate together to form junction zones in the second step, eventually resulting in the gelation in concentrated aqueous gellan solutions. The gel point becomes a very important reference state for discussing the structure and behavior of different gellan gum gels. The problem is, however, that making "critical gel" measurements on physically gelling systems is intrinsically very difficult.

The sol–gel transition is a very common phenomenon in the nature and is one of the most important processes in food manufacture, polymer processing. Winter and Chambon [34,35] found experimentally that at the gel point the storage and loss moduli G' and G'' exhibited the same power law dependence on the angular frequency ω as $G' \sim G'' \sim \omega^n$. Thus, the relaxation modulus $G(t)$ became $G(t) = St^{-n}$. Here, S was the gel strength and n the relaxation critical exponent. With the Kramers–Krönig relation, tangent of the loss angle $\tan\delta$ was derived as

$$\tan\delta = \tan\left(\frac{n\pi}{2}\right) \quad (1)$$

This relation suggests an interpolation method to determine the gel point actually, i.e., ω independency of $\tan\delta$ provides the gel point and the relaxation critical exponent n.

Whether the critical exponent n is universal or depending on the structure details of the system is still a problem, which is significant for describing and predicting this kind of phase transition theoretically. It seems that the gelation induced by chemical cross-linkers follows the universal prediction fairly well [36–39]. As for the physical gelation, the universality sometimes is broken because of the transient nature of the physical cross-linkers formed by intermolecular interactions, which makes it difficult either to describe the critical phenomenon in the framework of present gelation theories or to determine the gel point unambiguously.

In this research, the sol–gel transition of deacetylated K-type gellan gum (Gelrite®), which is the most popular product of gellan gum used in the food and biomedical industries, was investigated and the gel point was determined with rheology methods. Moreover, the universality of the critical exponents for this sol–gel transition and the fractal dimension of the critical gel were discussed to further understand the gel structure of gellan gum.

2. Experimental section

2.1. Gellan gum sample

Deacetylated potassium-type gellan gum (Gelrite®) sample was purchased from Sigma and purified as follows: The aqueous solution of ~2.5 wt% gellan gum was first dialyzed against distilled water at 70 °C using a cellulose tubular membrane until conductivity of the water outside became constant before and after refreshing. Then, the solution was filtered and freeze-dried to produce purified dry sample. Metal ion content in the gellan sample was detected by atomic absorption spectrum and the data were listed in Table 1. The aqueous gellan gum solution was prepared in the same way as that described by Matsukawa et al [25]. The powdered gellan gum was mixed with deionized water and stirred at room temperature overnight to homogenize the suspension. Then, the homogeneous suspension was heated to 70 °C and stirred for 2 h and at 90 °C for 1 h for complete dissolution. Finally, completely homogenized gellan gum solution was directly put into an incubator at preset-temperature to achieve equilibrium at the specified temperature.

2.2. Rheology measurements

The rheology measurement was conducted to determine the gel point with a strain-controlled ARES-RFS rheometer with different fixtures, including parallel plates of 25 and 50 mm diameters and a cone-plate of 50 mm diameter with the cone angle of 0.04 rad. Temperature was controlled by a Peltier plate at the accuracy of ±0.05 °C. Strain sweep was conducted first at several temperatures covering solution and gel phases with parallel plates of 1 mm gap to determine the linear viscoelastic region at 1 rad/s. The gellan gum solution at 90 °C was directly poured into the preheated test fixture at 55 °C and then cooled to desired temperatures. For temperature sweep test, the strain was appropriately changed manually in the range from 10% for the solution phase down to 0.1% for the gel phase to ensure the measurement within the linear viscoelasticity region. The cooling rate was 1 °C/min and the angular frequency was 1 rad/s. Frequency sweep at fixed temperature was also carried out within the linear viscoelaticity region to determine the gel point. The dynamic viscoelastic spectra were measured within the linear region over the angular frequency ω from 10^{-2} to 10^{2} rad/s. For the samples before the gel point, the shear rate dependence of viscosity η was measured at desired temperatures to determine the zero-shearing viscosity.

Table 1
Metal ion contents in gellan gum sample.

Metal ion	K	Na	Ca	Mg
Content/wt%	0.22	0.063	0.029	0.0025

3. Results and discussion

3.1. Determination of gel point by rheology methods

We determined the gel point (i.e., gelation temperature) for the sol–gel transition in gellan gum solutions of different concentrations by rheology method proposed by Winter and Chambon [34,35]. Fig. 2 depicts the temperature dependence of the storage modulus G' and loss modulus G'' determined during temperature sweep on cooling at 1 °C/min for the aqueous gellan gum solution at indicated concentrations C_g. These curves demonstrate the sol–gel transition at moderate temperatures varying with the solution concentration. At high temperature, both G' and G'' are almost constant and G' is always lower than G'', indicating a viscoelastic fluid for the solution within this temperature range. At low temperature, on the other hand, the values of G' and G'' are also constant but G' is higher than G'', except for the solution of 0.5 wt%, implying a solid viscoelasticity. Within the transition range, G' and G'' evidently increase with decreasing temperature and G' starts to exceed G''

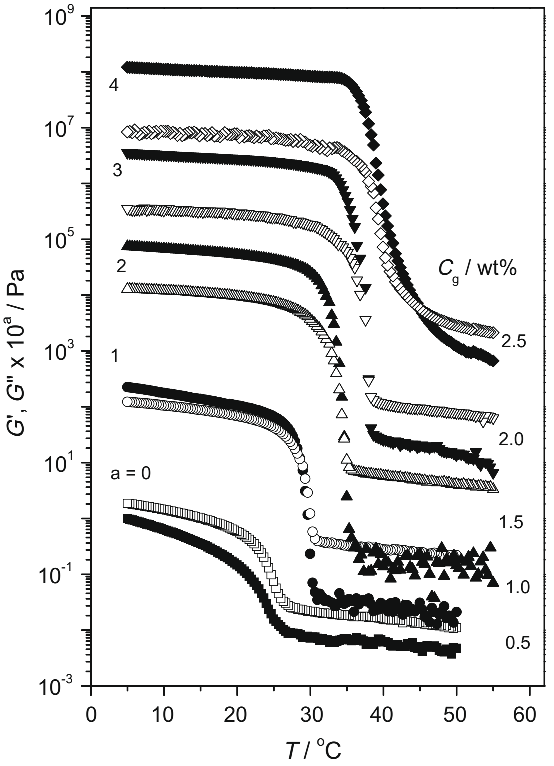

Fig. 2. Temperature dependence of storage modulus G' (solid symbol) and loss modulus G'' (open symbol) for aqueous gellan gum solutions with indicated concentration C_g. The data were vertically shifted by a factor of 10^a with given a value to avoid overlapping.

at a certain temperature. The change in G' during cooling is much larger than that in G'', suggesting that the elasticity would become predominant in the gellan gum solution upon cooing. The above facts mean that the solution changes to an elastic gel with solid-like mechanic properties. As for the solution of 0.5 wt%, though G' is always lower than G'', a steep rise in G' and G'' is still recognized within 5 °C range.

When the temperature where G' equals to G'' is taken as the critical gelation temperature T_c as described in some literature [14–16], T_c values for the gellan gum solution of different C_g are listed in Table 2. For the solutions of $C_g \geqslant 1.0$ wt%, T_c becomes higher with increasing concentration. At the same time, the dynamic modulus at T_c increases slightly with gellan concentration at the magnitude of 0.13 ~ 0.64 Pa. Because the gel network is formed through aggregation of the double-helices of gellan gum chains upon cooling [33] and is easier to spread over the whole solution at higher concentrations. In the solution of 0.5 wt%, the formed helix aggregation is not strong enough to resist the deformation strain with elastic contribution.

Figs. 3–6 show the angular frequency ω dependence of the dynamic moduli for 1.0, 1.5, 2.0 and 2.5 wt% of aqueous gellan gum solutions at indicated temperatures. The data were vertically shifted by a factor of 10^a to avoid overlapping. Some G' values at high temperatures scattered since the torque at low frequency for the sol phase was below the instrument sensitivity. Commonly, at high temperatures, G' and G'' are proportional to $\omega^{1.48-1.69}$ and $\omega^{0.96-0.98}$, respectively, and G'' is always higher than G' in the low frequency range without any plateau appearing in the G' vs ω curve. These are the typical characteristics of a viscoelastic polymer fluid without network structure according to the Rouse–Zimm theory [40]. As temperature is decreased, the storage modulus G' becomes higher than the loss modulus G'' and a plateau in the G' vs ω curve starts to appear in low frequency range, indicating the formation of network. With the increasing gellan gum concentration, the gelation temperature becomes higher. As known from Figs. 3–6, the gelation temperature is about 33 ~ 34 °C for 1.0 wt%, 39 ~ 40 °C for 1.5 wt%, 45 ~ 47 °C for 2.0 wt% and 55 ~ 56 °C for 2.5 wt% of gellan gum solutions, respectively.

From Figs. 3–6 we can see that the crossover point of $G' = G''$ used to determine the critical gelation temperature T_c in the temperature sweep measurement appears at different frequencies. Therefore, we determined the gel point T_{gel} for the gellan gum aqueous solution according to the Winter's criterion of $\tan\delta = \tan(n\pi/2)$ using the interpolation method. Fig. 7, taken the solution of 1.0 wt% as an example, demonstrates this interpolation for the temperature T_{gel} from the data in Fig. 3 where $\tan\delta$ is independent of frequency. In this way, we determined the gel point T_{gel} and critical exponent n of relaxation modulus precisely for the sol–gel transition in the gellan gum solutions. The results are summarized in Table 2. The uncertainty in the n value came from determination of the intersecting point from the $\tan\delta$ vs T curve. Consequently, the Winter's criterion is available for the gelation in aqueous gellan gum solutions during cooling and the self-similarity is found in the gellan gum critical gel structure.

T_{gel} in Table 2, like T_c, increases with increasing gellan gum concentration in consistent with the transition of

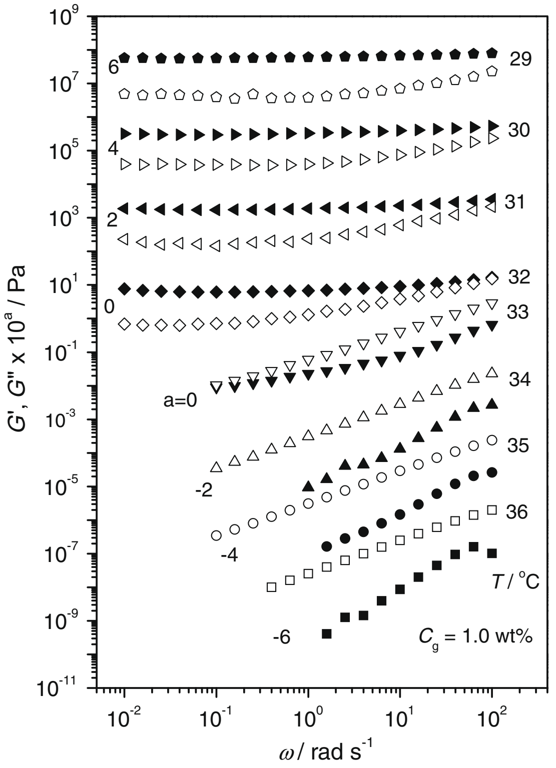

Fig. 3. Angular frequency ω dependence of storage modulus G' (solid symbol) and loss modulus G'' (open symbol) for gellan gum solution of C_g = 1.0 wt% at indicated temperature. The data were vertically shifted by a factor of 10^a with given a value to avoid overlapping.

Table 2
Critical exponents for sol–gel transition in aqueous gellan gum solutions.

Concentration/wt%	T_c/°C	T_{gel}/°C	n^a	k	z	n^b
0.5	<5	–	–	–	–	–
1.0	28.6	33.1	0.77 ± 0.002	0.51 ± 0.06	1.72 ± 0.11	0.76 ± 0.04
1.5	34.6	39.4	0.53 ± 0.001	1.02 ± 0.14	1.24 ± 0.23	0.55 ± 0.07
2.0	38.0	45.6	0.43 ± 0.001	1.74 ± 0.14	1.48 ± 0.12	0.46 ± 0.04
2.5	44.6	55.3	0.38 ± 0.001	2.18 ± 0.04	1.43 ± 0.11	0.40 ± 0.02

[a] The critical exponent according to the Winter's criterion.

[b] The critical exponent calculated from $n = z/(z + k)$.

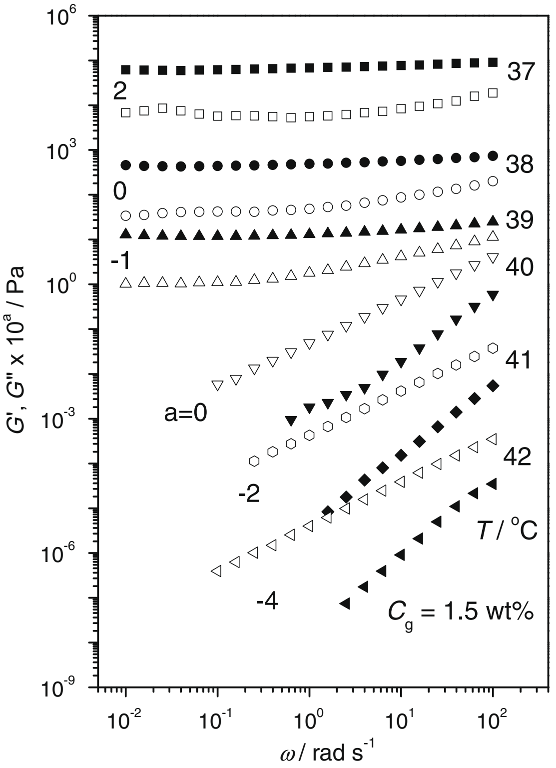

Fig. 4. Angular frequency ω dependence of storage modulus G' (solid symbol) and loss modulus G'' (open symbol) for gellan gum solution of $C_g = 1.5$ wt% at indicated temperature. The data were vertically shifted by a factor of 10^a with given a value to avoid overlapping.

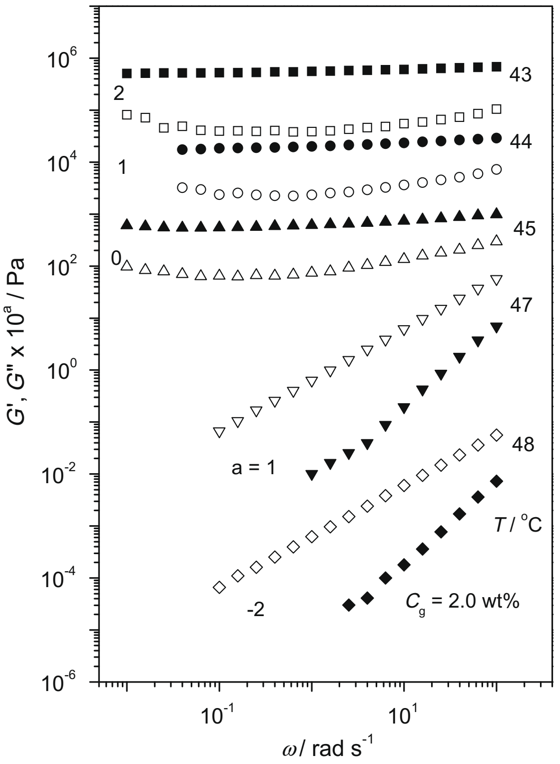

Fig. 5. Angular frequency ω dependence of storage modulus G' (solid symbol) and loss modulus G'' (open symbol) for gellan gum solution of $C_g = 2.0$ wt% at indicated temperature. The data were vertically shifted by a factor of 10^a with given a value to avoid overlapping.

single coil to double helix further to aggregate helices. However, the former is always higher than the latter and this difference becomes larger at higher concentrations. For an example, the difference of T_{gel} from T_c for 1 wt% solution is 4.5 °C, this is enlarged to 10.7 °C for 2.5 wt% solution. This will be discussed later.

3.2. *Concentration Dependence of Critical Exponents and Fractal Dimension*

Fig. 8 illustrates gellan gum concentration dependence of the critical gelation temperature T_c and T_{gel} obtained from different methods. The fact that T_{gel} is always higher than T_c at the same concentration indicates that the $G' \sim G'' \sim \omega^n$ appears at more initial stage (higher temperature) than $G' = G''$. The latter is a special case as mentioned by Winter et al. and $G' = G''$ may be only available at a certain frequency [41]. One can image according to Figs. 3–6 that there should be a temperature where the $G' \sim \omega$ curve crosses over the $G'' \sim \omega$ curve. The cooling rate of 1 °C/min used in the temperature sweep test may be fast and time lag effect on the gelation may exist. It is worth noticing that the Winter's criterion is based on the observation that no characteristic time scale exists for the critical gel; but the intersection of G' and G'' curves will relate to the testing time (i.e., frequency).

Therefore, we adopted T_{gel} as the gel point in the following discussion. From data in Table 2, we found that the critical exponent n decreased with increasing concentration C_g. There is no universal n for the gelation in aqueous gellan gum solutions even at such low concentrations. According to our category for the physical gelation [42], the present gelation should be classified into the cross-linking, in which the network junction occurs on existing macromolecules, not following the random percolation prediction.

In the vicinity of the gel point, the zero-shear viscosity η_0 and the equilibrium shear modulus G_e follow the power laws of the relative distance ε from the critical point as $\eta_0 \sim \varepsilon^{-k}$ and $G_e \sim \varepsilon^z$, where $\varepsilon = |p - p_c|/p_c$ [43]. Here, k and z are the critical exponents for viscosity and modulus, respectively, and p is the actual cross-linking probability and p_c is p at the critical gel point. η_0 is expected to diverge when $\varepsilon \to 0$. If the gelation occurs in a completely random way, the critical exponent n, k, and z are expected to be universal and independent of the system details [39].

The shear viscosity η for the aqueous gellan gum solutions at temperatures slightly beyond the gel point T_{gel} was measured at different shear rates to evaluate the zero-shear viscosity η_0. η_0 was plotted against ε in Fig. 9 for four concentrations of the gellan gum solution, where the relative distance to the critical gel point was approximated with T to replace p as $\varepsilon = |T - T_{gel}|/T_{gel}$ [44]. The equilibrium modulus G_e was estimated from the plateau value of storage modulus G' at temperatures slightly below

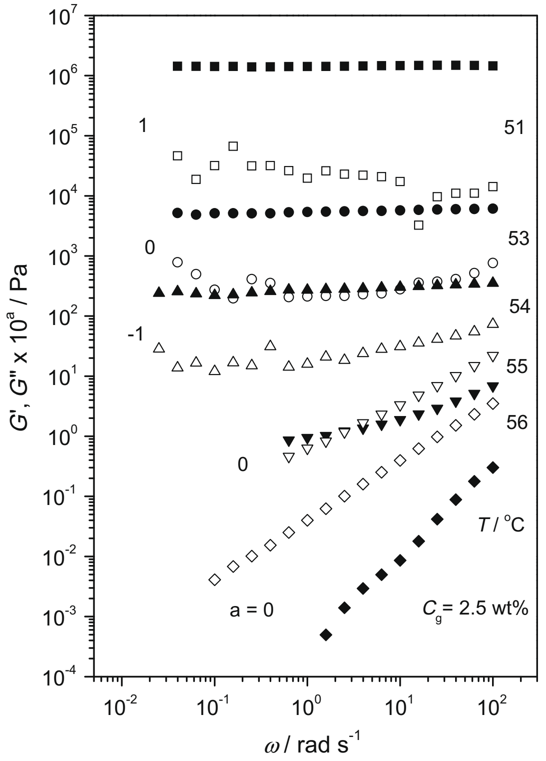

Fig. 6. Angular frequency ω dependence of storage modulus G' (solid symbol) and loss modulus G'' (open symbol) for gellan gum solution of $C_g = 2.5$ wt% at indicated temperature. The data were vertically shifted by a factor of 10^a with given a value to avoid overlapping.

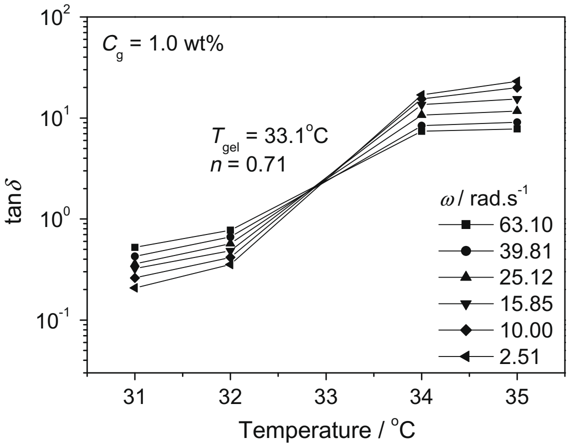

Fig. 7. tanδ at indicated ω plotted against T for gellan gum solution of $C_g = 1.0$ wt% to determine the gel point T_{gel} and critical exponent n according to the Winter's criterion.

T_{gel} and plotted against ε in Fig. 10. Ross-Murphy argued that the critical exponents depended on the ε range and suggested a suitable interval of $0.01 < \varepsilon < 0.1$ [45]. The ε in the present work was restricted in the range of $0.01 < \varepsilon < 0.1$ as seen from Figs. 9 and 10 and the exponents k and z were evaluated from the slope and listed in Table 2.

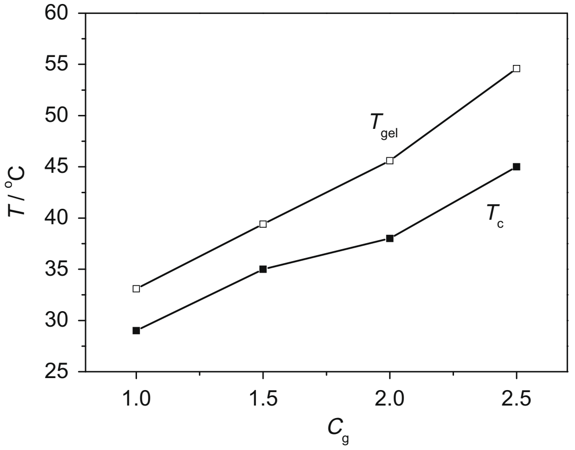

Fig. 8. Concentration dependence of T_c and T_{gel} for the gelation in aqueous gellan gum solutions.

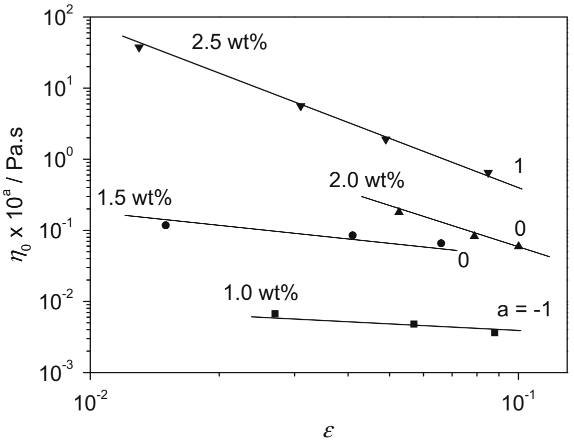

Fig. 9. Zero-shear viscosity η_0 plotted against ε, the relative distance from the gel point for the aqueous gellan gum solutions with indicated C_g. The data were vertically shifted by a factor of 10^a with given a value to avoid overlapping.

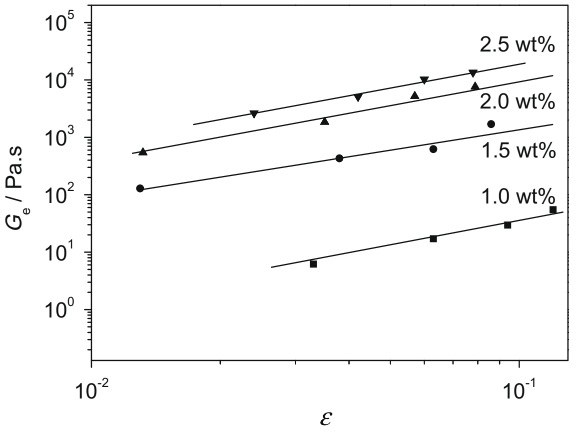

Fig. 10. Equilibrium modulus G_e plotted against ε, the relative distance from the gel point for the aqueous gellan gum solutions with indicated C_g.

The relaxation critical exponent n can be also calculated from the exponents z and k as $n = z/(z + k)$ [46] and the calculated n values are listed in Table 2 for comparison. As expected, the n calculated from k and z agrees fairly well with the corresponding n determined by the Winter's criterion, indicating the self-similar structure existing in the critical gel formed by gellan gum chains in water. However, this calculated n, as well as k and z, also varies with concentration of the gellan gum solutions, no universal exponents are established for the present polysaccharide solution.

There are several theoretical models proposed to describe cross-linked polymers at the gel point. The Rouse limit without hydrodynamic interaction gives $n = 0.66$, $z = 2.7$ and $k = 1.35$, the Zimm limit with hydrodynamic interaction gives $n = 1$, $z = 2.7$, and $k = 0$, and the percolation analogue to the electrical network predicts $n = 0.71$, $z = 1.94$, and $k = 0.75$ [46]. A lot of experiments have been performed on various gelation systems and typically observed value for k is between 0.7 and 1.7 and the z value is $1.8 \sim 3.0$ [38,47–50]. For the physical gelation, n varies from 0.11 to 0.8 [51–53]. The concentration dependence of the relaxation critical exponent n in Table 2 cannot be described by any available theories because all of them lead to constant critical exponents.

In order to reveal further the structure of the critical gel, we related the critical exponents to the fractal dimension. Based on the fractal analysis of the critical gel, several relations between the critical exponent n and the fractal dimension d_f have been proposed. Muthukumar derived a theoretical expression for the frequency dependence of the complex viscosity in terms of the arbitrary fractal dimension of the molecular cluster [54]. Then, Muthukumar and Winter proposed a relation between the critical exponent n and the fractal dimension d_f with complete screen of the excluded volume [55,56]. Muthukumar further investigated the cross-linking process for polydisperse systems using a hyperscaling relation from the percolation theory [57]. When hydrodynamic interaction is completely screened out and the excluded volume effect is dominant in the cluster,

$$n = \frac{d}{d_f + 2} \tag{2}$$

If the hydrodynamic interaction as well as the excluded volume effect can be screened out completely, n is expressed by

$$n = \frac{d}{\bar{d}_f + 2} = \frac{d(d + 2 - 2d_f)}{2(d + 2 - d_f)} \tag{3}$$

where $\bar{d}_f$ is the fractal dimension of the gel network where the excluded volume effect is fully screened and d is the space dimension. If only partial screening exists, the fractal dimension takes a value in between d_f and $\bar{d}_f$. According to this theory, a looser structure will lead to a lower value of d_f and a higher value of n.

We have calculated d_f from n for the present critical gels using Eqs. (2) and (3) and plotted in Fig. 11 as a function of the gellan gum concentration C_g. The unreasonable values of d_f higher than three was obtained from Eq. (2) (Fig. 11) for the gellan gum, because d_f is not larger than d when $d \leqslant 3$. This seems due to a reduction in the excluded volume effect with increasing gellan gum concentration; because the chain excluded volume in dilute polymer solutions decreases gradually to approach the unperturbed state with increasing concentration. Consequently, we rely our further discussion on the d_f values evaluated from Eq. (3). The d_f value for the critical gel of gellan gum is about two and slightly increases with increasing C_g, indicating that the cluster space in the critical gellan gel is still loose and becomes more densely filled at higher C_g. We also reported a similar d_f variation with polysaccharide concentration for the critical gel of high molecular weight alginate induced by calcium cation [58]. This change in the structure of the critical gel can be attributed to the increase in the double helix content at higher concentration. The sol–gel transition in the gellan gum solution is caused by random aggregation of the double-helices, which are formed during the random coil-double helix conformational transition at the gel temperature [33]. Therefore, the double helix content will determine the intermolecular aggregation probability and the fibrous structure for the gellan gum network. Both temperature and gellan gum concentration have been known to influence the helix content in gellan gum solutions [19]. At the same temperature, the solution with higher C_g has more helix content, leading to more intensive aggregation and denser critical gel. Owing to the narrow concentration range available in the present experiments, the change in d_f for the critical gellan gum gel is quite limited.

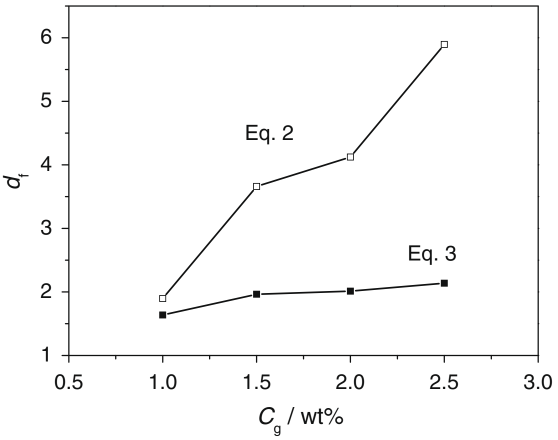

Fig. 11. Concentration dependence of the fractal dimension d_f calculated from n using Eqs. (2) and (3) for the critical gellan gum gel.

4. Concluding remarks

The sol–gel transition in aqueous solutions of gellan gum caused by random aggregation of double-helices was investigated with rheology methods. The gel point T_{gel} and relaxation critical exponent n were determined using the Winter's criterion and the self-similar structure was found in the critical gel. With increasing gellan gum concentration C_g, T_{gel} increased and n decreased. This means that the concept of universal critical exponent fails for this sol–gel transition because this gelation belongs to the cross-linking mechanism, deviating from the original hypothesis of the random percolation. The fractal dimension d_f estimated from n was about two and slightly increased with C_g when hydrodynamic interaction and excluded volume were ignored. The C_g range was restricted by that the solution with lower concentration cannot produce dynamic modulus high enough to be accurately detected while the solution with higher concentration has even high gelation temperature and high viscosity causing difficulty in de-bubble from the sample before rheology measurement.

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References

[1] Jansson P, Lindberg B, Sandford PA. Carbohydr Res 1983;124:135–9.
[2] O' Neill MA, Selvenderan RR, Morris VJ. Carbohydr Res 1983;124:123–33.
[3] Morris VJ. Bacterial polysaccharides. In: Stephen AM, editor. Food polysaccharides and their application. New York: Springer; 1995. p. 41–375.
[4] Chandrasekaran R, Thanilambal VG. Carbohydr Polym 1990;12:431–42.
[5] Mazen F, Milas M, Rinaudo M. Int J Biol Macromol 1999;26:109–18.
[6] Rinaudo M. Food Hydrocolloid 2001;15:433–40.
[7] Sanderson GR. In: Harris P, editor. Food gels. London: Elsevier Applied Science; 1990. p. 201–32.
[8] Omoto T, Uno Y, Asai I. Progr Colloid Polym Sci 1999;114:123–6.
[9] Morrison NA, Sworn G, Clark RC, Chen YL, Talashek T. Progr Colloid Polym Sci 1999;114:127–31.
[10] Bajaj I, Singhal R. Food Chem 2007;104:1472–7.
[11] Nanjawade BK, Manvi FV, Manjappa AS. J Control Release 2007;122: 119–34.
[12] Jerome PF. J Chromatography A 2007;1165:86–92.
[13] Coviello T, Dentini M, Rambone G, Desideri P, Carafa M, Murtas E, et al. J Control Release 1998;55:57–66.
[14] Miyoshi E, Nishinari K. Progr Colloid Polym Sci 1999;114:68–82.
[15] Miyoshi E, Takaya T, Nishinari K. Carbohydr Polym 1996;30:109–19.
[16] Nishinari K, Miyoshi E, Takaya T, Williams P. Carbohydr Polym 1996;30:193–207.
[17] Kanesaka S, Watanabe T, Matsukawa S. Biomacromolecules 2004;5:863–8.
[18] Ogawa E, Takahashi R, Yajima H, Nishinari K. Biopolym 2005;79:207–17.
[19] Ogawa E, Takahashi R, Yajima H, Nishinari K. Food Hydrocolloid 2006;20:378–85.
[20] Nakanishi T, Norisuye T. Biomacromolecules 2003;4:736–42.
[21] Miyoshi E, Nishinari K. Progr Colloid Polym Sci 1999;114:83–93.
[22] Izumi Y, Saito S, Soma K. Progr Colloid Polym Sci 1999;114: 48–55.
[23] Nishinari K. Progr Colloid Polym Sci 1997;275:1093–107.
[24] Matsukawa S, Huang Z, Watanabe T. Progr Colloid Polym Sci 1999;114:92–7.
[25] Matsukawa S, Tang Z, Watanabe T. Progr Colloed Polym Sci 1999;114:15–24.
[26] Matsukawa S, Watanabe T. Food Hydrocolloid 2007;21:1355–61.
[27] Kani K, Horinaka J, Maeda S. Carbohydr Polym 2005;61:168–73.
[28] Horinaka J, Kani K, Honda H, Uesaka Y, Kawamura T. Macromol Biosci 2004;4:714–20.
[29] Okamoto T, Kubota K. Carbohydr Polym 1996;30:149–53.
[30] Morris VJ, Kirby AR, Gunning AP. Progr Colloed Polym Sci 1999;114:102–8.
(31) Yuguchi Y, Urakawa H, Kitamura S, Wataoka I, Kajiwara K. Progr Colloed Polym Sci 1999;114:41–7.
[32] Yuguchi Y, Mimura M, Urakawa H, Kitamura S, Ohno S, Kajiwara K. Carbohydr Polym 1996;30:83–93.
[33] Nijenhuis K. Adv Polym Sci 1997;130:219–35.
[34] Winter HH, Chambon F. J Rheol 1986;30:367–82.
[35] Chambon F, Winter HH. J Rheol 1987;31:683–97.
[36] Takahashi M, Yokoyama K, Masuda T. J Chem Phys 1994;101: 798–804.
[37] Donald FH, Amis EJ. Macromolecules 1990;23:2512–9.
[38] Adam M, Lairez D. Macromolecules 1997;30:5920–9.
[39] Adolf D, Martin JE, Wilcoxon JP. Macromolecules 1990;23: 527–31.
[40] Ferry JD. Viscoelastic properties of polymers. New York: Wiley; 1980. p. 33–55.
[41] Winter HH, Moganelli P, Chambon F. Macromolecules 1988;21: 532–5.
[42] Lu L, Liu X, Tong Z, Gao Q. J Phys Chem B 2006;110:25013–20.
[43] Stauffer D, Coniglio A, Mireille A. Adv Polym Sci 1982;44:103–58.
[44] Takenaka M, Kobayashi T, Hashimoto T, Takahashi M. Phys Rev E 2002;65:041401 [1–7].
[45] Ross-Murphy SB. Polym Bull 2007;58:119–26.
[46] Winter HH, Mours M. Adv Polym Sci 1997;134:165–234.
[47] Adam M, Delsanti M, Durand D, Hild G, Munch J. Pure Appl Chem 1981;53:1489–94.
[48] Fujii T, Yano T, Kumagai H, Miyawaki O. Biosci Biotech Biochem 2000;64:1618–22.
[49] Martin JE, Adolf D, Wilcoxon JP. Phys Rev Lett 1988;61:2620–3.
[50] Mortimer S, Ryan AJ, Stanford JL. Macromolecules 2001;34:2973–80.
[51] Izuka A, Winter HH, Hashimoto T. Macromolecules 1997;30:6158–65.
[52] Horst RH, Winter HH. Macromolecules 2000;33:130–6.
[53] Richtering HW, Gagnon KD, Lenz RW, Fuller RC, Winter HH. Macromolecules 1992;25:2429–33.
[54] Muthukuma M. J Chem Phys 1985;83:3161–8.
[55] Muthukuma M, Winter HH. Macromolecules 1986;19:1284–5.
[56] Hess W, Vilgis TA, Winter HH. Macromolecules 1988;21: 2536–42.
[57] Muthukuma M. Macromolecules 1989;22:4656–8.
[58] Lu L, Liu X, Dai L, Tong Z. Biomacromolecules 2005;6:2150–6.