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Critical exponents for sol–gel transition in aqueous alginate solutions induced by cupric cations

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Abstract

The sol–gel transition in aqueous alginate solutions of four alginate samples having different molecular weights (M_W) and M/G ratios induced by cupric cations was monitored by rheology measurements. The gel point f_{gel} and the relaxation critical exponent n were determined using the Winter's criterion over the alginate concentration C_{Alg} of 1–4 wt%. 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 at the concentration of $C_{Alg} = 1$ wt%, giving the critical exponents k and z. The results indicated that f_{gel} was almost independent of the alginate concentration and became higher for the sample with lower molecular weight. The critical exponent n decreased with the increase in C_{Alg} for these four Cu-alginate samples and the fractal dimension d_f estimated from n suggested a denser structure in the critical gel with high G content. The critical exponent n evaluated from k and z agreed well with n determined from the Winter's criterion.

Keywords: Alginate; Sol–gel transition; Critical exponent and cupric cation

1. Introduction

Alginate is a natural biomacromolecule isolated from seaweed and bacteria consisting of (1 → 4) linked β-D-mannuronate (M) and its C-5 epimer α-L-guluronate (G) residues arranged in blocks of M fragments, G fragments, and alternating G and M fragments (Moe, Dragel, & Smidsrød, 1995). The amount and distribution of each monomer depends on the species, location, and age of seaweed from which the alginate has been isolated. It is an important naturally produced material that forms well-characterized hydrogels by adding divalent cations (except Mg^{2+}) (Ji, 1997). Important properties of alginate include viscosity enhancement, gel-forming ability and stabilization of aqueous mixtures, dispersions and emulsions (Moe et al., 1995). Because the alginate gels formed under gentle conditions, possess little toxicity and readily available, it has found many applications. In bio-sorption, alginate used to absorb heavy metals from wastewater (Jang, Nguyen, & Geesey, 1999; Jang, Nguyen, Kolostyak, & Geesey, 1999). In food and pharmaceutical industry, alginate is used as an additive to improve, modify and stabilize the texture. Other significant applications of alginate were also found in dental impressions, wound dressings, drug delivery vehicles, and cell transplantation matrices.

The sol–gel transition is a critical phenomenon that occurs during the formation of physical and chemical gels. At the critical point, various thermodynamic quantities diverge, which could be expressed in the power law form scaled by the relative distance from the critical point with the corresponding critical exponents (Stauffer, Coniglio, & Mireille, 1982). In the vicinity of the gel point, the zero shear viscosity (η_0), weight-average molecular weight (M_w), typical cluster size (R_{char}), and equilibrium shear modulus (G_e) follow the power laws similarly to the relative distance from the gel point ε. In the term of cross-link proportion, the actual fraction of sites that have been already

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joined in the cross-link to the total sites that can be joined in the cross-link is p, while the critical value of p at the gel point is p_c. The relative distance from the gel point is $\varepsilon = (|p - p_c|)/p_c$, then

$$\eta_0 \sim \varepsilon^{-k} \quad p < p_c, \tag{1}$$

$$M_w \sim \varepsilon^{-\gamma} \quad p < p_c, \tag{2}$$

$$R_{char} \sim \varepsilon^{-\nu} \quad p < p_c, \tag{3}$$

$$G_e \sim \varepsilon^{z} \quad p > p_c. \tag{4}$$

Winter and Chambon found experimentally that the storage and loss moduli G' and G'' exhibited a power-law dependence on the angular frequency ω at the critical gel point (Chambon & Winter, 1987; Winter & Chambon, 1986)

$$G'(\omega) \sim G''(\omega) \sim \omega^n. \tag{5}$$

So that the relaxation modulus $G(t)$ becomes

$$G(t) = S\, t^{-n}. \tag{6}$$

The tangent of the loss angle δ can be derived from Eq. (5) as

$$\tan\delta = G''/G' = \tan(n\pi/2) \tag{7}$$

Thus, ω independence of $\tan\delta$ provides a convenient and accurate interpolation method to determine the gel point and the relaxation critical exponent n.

Recently, we have determined the gel point and critical exponents of aqueous alginate solutions induced by Ca^{2+} cations in situ released using the rheology method at different alginate concentrations (Lu, Liu, Dai, & Tong, 2005). The results indicated the availability of the power law for the gelation and existence of the self-similarity in structure of the critical gel. The alginate concentration dependence of the critical exponent n implicated two gelation processes of the growth and cross-linking according to the molecular weight of alginates before gelation. Owing to the important industrial usage of alginate as a gelation and fluid thickening reagent, the well-characterized gelation for various alginates from different sources with various divalent cations encountered in the solutions are significant for designing and improving the formula and process. However, few study has concerned the critical gelation behavior in aqueous alginate solutions induced by divalent cations except ours (Liu, Qian, Shu, & Tong, 2003; Lu et al., 2005; Lu, Liu, Qian, & Tong, 2003). In the present work, we focused on the sol–gel transition in aqueous alginate solutions induced by Cu^{2+} cations to investigate the difference in critical behavior from that induced by Ca^{2+} cations for the physical gelation process. The another significance of using alginate is to experience different critical gelation processes on the same polymer sample only by changing cross-linking cations, which allows us to reveal the scaling law for the critical gelation further (Colby, Rubinstein, Gillmor, & Mourey, 1992; Stauffer, 1985).

2. Experimental

2.1. Alginate samples

Four sodium alginate samples provided by Kimitsu Chemical Industry Co. Japan were purified as follows: the aqueous solution of alginate about 3 wt% was first dialyzed against distilled water using cellulose tubular membranes (cut-off molecular weight is ~14,000) until the conductivity of water outside became constant before and after refreshing. Then, the solution was filtered and freeze-dried to produce purified dry sample. Molecular weight M_w of the samples was determined by gel permeation chromatography (GPC) with a Waters apparatus, using 0.1 M Na_2SO_4 aqueous solution as the elution and narrowly distributed PEO as the standard. The mole ratio (M/G) of mannuronate (M) to guluronate (G) residues, the mole fraction F_G and F_M of G and M, and the mole fraction of GG, MM, and GM (MG) dyad sequences F_{GG}, F_{MM}, and F_{GM} were determined by ^1H NMR according to Grasdalen's procedure in D_2O of 14 mg/mL at 70 °C (Grasdalen, 1983; Grasdalen, Larsen, & Smidsrød, 1979). The characterization results are summarized in Table 1.

2.2. Rheology measurements

We define the stoichiometric mole ratio $f = [Cu^{2+}]/[COO^-$ in alginate] as a factor which controls the gelation process in alginate solutions with the assumption that the ratio f is proportional to the cross-link density formed inter- and intra-molecularly. An alginate stock solution was prepared by dissolving one sample in pure water, and then 2 g of this solution was mixed with 2 mL cupric chloride solution of proper concentration to make an aqueous Cu-alginate system with a required alginate concentration C_{Alg} and f value. All samples were homogeneous after magnetic stirring for 15 min at room temperature and incubated at 12 °C for 48 h prior to the rheology measurement.

In order to observe the sol–gel transition in aqueous alginate solutions induced by cupric cations, the dynamic moduli and steady shear viscosity were measured with a Rheometrics RFS-II rheometer with different fixtures, including a 25-mm diameter cone plate and a 50-mm diameter cone plate. The angle of the cones was 0.04 rad. All measurements were carried out at 25 ± 0.1 °C.

Table 1
Characterization of alginate samples

Sample	$M_w \times 10^{-4}$	M/G	F_G	F_M	F_{GG}	F_{MM}	F_{GM}
MHGH	330	0.91	0.52	0.48	0.44	0.40	0.08
MLGH	62	0.60	0.63	0.38	0.45	0.20	0.18
MHGL	323	1.85	0.35	0.65	0.10	0.26	0.40
MLGL	122	1.85	0.35	0.65	0.18	0.47	0.18

3. Results and discussion

3.1. Viscoelasticity of aqueous Cu-alginate during sol–gel transition

The shear strain γ dependence of complex modulus G^* for the Cu-MHGH sample of $C_{Alg} = 1$ wt% is shown in Fig. 1 with various f values below and above the gelation threshold at 25 °C as an example for exploring the linear viscoelastic range. The absolute value of G^* is independent of strain γ over the range from 1% to 100% and increases with f. The other alginate samples with different molecular weights, different M/G ratios and at different alginate concentrations show the similar strain and f dependence of G^* during the sol–gel transition. All of the viscoelastic measurements were carried out within the linear range.

Fig. 2 depicts the angular frequency ω dependence of storage and loss moduli G' and G'' for the Cu-MHGH sample of $C_{Alg} = 1$ wt% at various f values. The data are vertically shifted by a factor of 10^a to avoid overlapping. Some G' values at low frequency with low f were too small to be measured accurately. At low f values, G' and G'' are proportional to $\omega^{1.5-1.6}$ and $\omega^{0.9-1}$, respectively and G'' is always higher than G' in the whole frequency range without any plateau appearing in G' vs. ω curves. These correspond to the dynamic characteristics of a viscoelastic polymer fluid without entanglements. At high f values, G' becomes higher than G'' with a plateau appearing in the G' vs. ω curve in low frequency range. This indicates the formation of viscoelastic gels. At a moderate value of f, there is a transition region from solution to gel, where ω dependent curve of G' becomes parallel to or even coincides with that of G'' on the logarithmic coordinate over a wide frequency range, such as the curve of $f = 0.03$ in Fig. 2. This power law behavior suggests that the critical gel possesses the self-similar fractal structure over a wide spatial scale. In the present study, we focused on the sol–gel transition induced by changing the Cu^{2+} relative concentration f at a constant alginate concentration. Therefore, the limiting behavior of $G' \propto \omega^2$ and $G'' \propto \omega^1$ for a dilute solution of monodispersed polymer and $G' \propto \omega^0$ for a completely cross-linked gel was not observed due to the f values used.

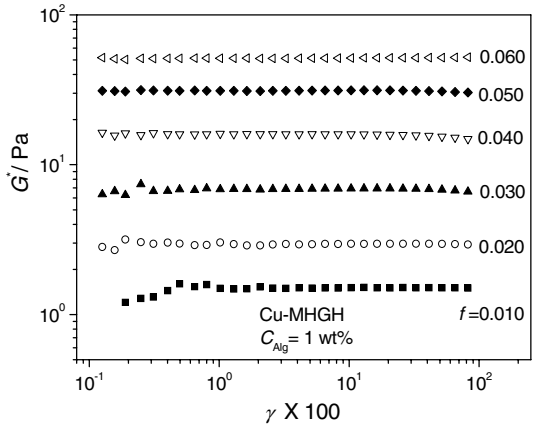

Fig. 1. Shear strain γ dependence of absolute value of complex modulus G^* for Cu-MHGH of $C_{Alg} = 1$ wt% with indicated f values at 25 °C and $\omega = 10$ rad/s.

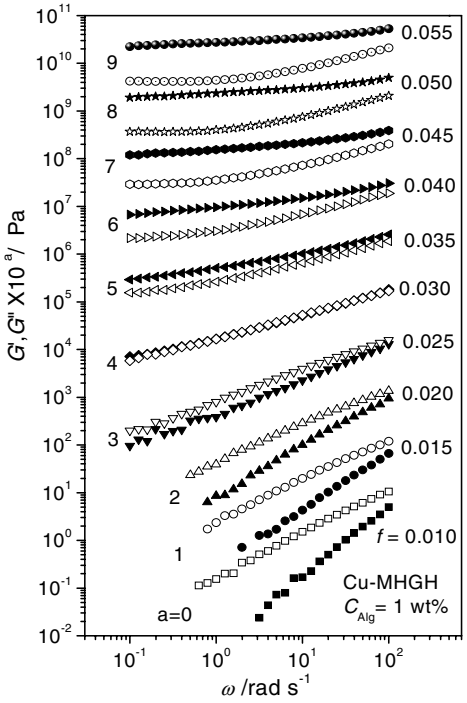

Fig. 2. Angular frequency ω dependence of storage modulus G' (solid symbol) and loss modulus G'' (open symbol) for Cu-MHGH of $C_{Alg} = 1$ wt% with indicated f. The data have been vertically shifted by a factor of 10^a with given a to avoid overlapping.

3.2. Critical exponents for sol–gel transition

In this work, the gel point is assigned as a definite f value f_{gel}, at which the viscosity approaches infinite and a network spreading whole sampling space begins to appear in the system. The values of f_{gel} and n for the sol–gel transition in aqueous alginate solutions induced by adding Cu^{2+} have been determined using the Winter's criterion of Eq. (7). Fig. 3 demonstrates the f dependence of $\tan\delta$ obtained from the data in Fig. 2 at several frequencies. The f_{gel} and $\tan\delta$ values were evaluated from the intersecting point, where $\tan\delta$ became independent of ω, giving the value of the critical exponent n using Eq. (7). The f_{gel} and n values similarly determined for the four alginate systems with $C_{alg} = 1$ wt% are listed in Table 2. The uncertainty in the n value came from determination of the intersecting point from the $\tan\delta$ vs. f plots.

The most obvious manifestation of the sol–gel transition appears in mechanical properties. The zero shear viscosity η_0 diverges as the system approaching the gel point due to the formation of infinite networks over the whole sample. Immediately beyond the gel point, the equilibrium modulus G_e emerges because of the appearance of this infinite

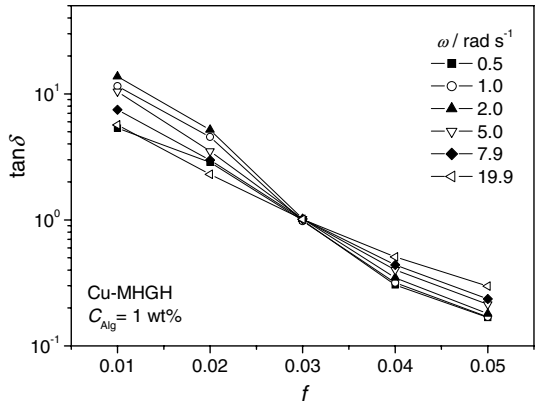

Fig. 3. Tan δ at indicated ω plotted against f for Cu-MHGH of $C_{Alg} = 1$ wt% to determine the gel point f_{gel} and critical exponent n.

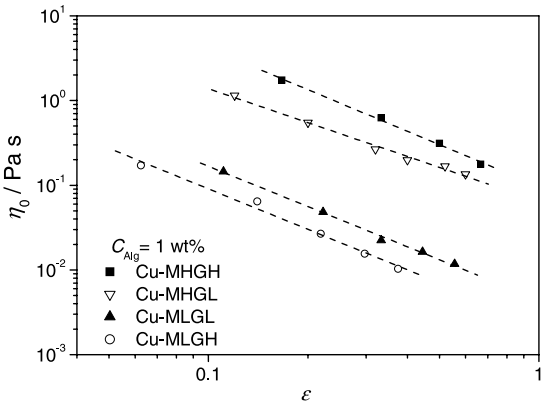

Fig. 5. Zero shear viscosity η_0 plotted against ε, the relative distance from the gel point for the four Cu-alginate samples of $C_{Alg} = 1$ wt%.

Table 2
Critical exponents for Cu-alginate samples of $C_{Alg} = 1$ wt%

Samples	f_{gel} [a]	n[a]	k	z	n[b]
Cu-MHGH	0.03	0.50 ± 0.01	1.63 ± 0.07	1.53 ± 0.05	0.48 ± 0.02
Cu-MLGH	0.064	0.60 ± 0.02	1.59 ± 0.09	2.74 ± 0.19	0.63 ± 0.03
Cu-MHGL	0.025	0.66 ± 0.02	1.33 ± 0.07	2.47 ± 0.17	0.65 ± 0.03
Cu-MLGL	0.045	0.65 ± 0.01	1.58 ± 0.06	2.54 ± 0.18	0.62 ± 0.03

[a] The critical exponent from dynamic moduli using Winter's criterion.
[b] The critical exponent calculated by Eq. (8).

network. For the solution below the gel point, the steady viscosity η was measured at different shear rates as plotted in Fig. 4. The zero shear viscosity η_0 was estimated by extrapolation along the low shear rate plateau and the η_0 values so determined for the four alginate samples at $C_{Alg} = 1$ wt% were plotted double logarithmically against ε in Fig. 5. Here, f is assumed to be proportional to the actual cross-linking proportion p and hence ε is rewritten as $\varepsilon = (|f - f_{gel}|)/f_{gel}$. The zero shear viscosity is higher for the alginate samples with higher molecular weight (Cu-MHGH and Cu-MHGL). Because the observed f_{gel} values (Table 2) were very low, the narrow range of ε led to an extremely small variation in f. Actually, such a small change in the Cu^{2+} concentration was too difficult to be controlled accurately during experiments. The linear fits to the data in Fig. 5 illustrate the possible availability of the power laws of Eq. (1) within the present ε range. There are also several reported examples successfully using the power laws within a wider range of ε (Adolf & Martin, 1990; Takahashi, Yokoyama, Masuda, & Takigawa, 1994; Takenaka, Kobayashi, Hashimoto, & Takahashi, 2002), even extended to $\varepsilon = 2$ (Tixier, Tordjeman, Cohen-Solal, & Mutin, 2004; Tordjeman, Fargette, & Mutin, 2001). From the slope of straight lines in Fig. 5, we estimated the critical exponent k for the zero shear viscosity.

The equilibrium modulus begins to appear and becomes clearly observable after the gel point as seen from the frequency dependence of storage modulus in Fig. 2. The equilibrium modulus G_e was estimated from G' at the low ω plateau and the G_e values for the four alginate samples at $C_{Alg} = 1$ wt% were plotted double-logarithmically against ε in Fig. 6. The equilibrium modulus is higher for the alginate samples with higher G content (Cu-MHGH and Cu-MLGH). From the slope of the linear lines in Fig. 6, we determined the critical exponent z for the equilibrium modulus following Eq. (4). The values of k from η_0 and z from

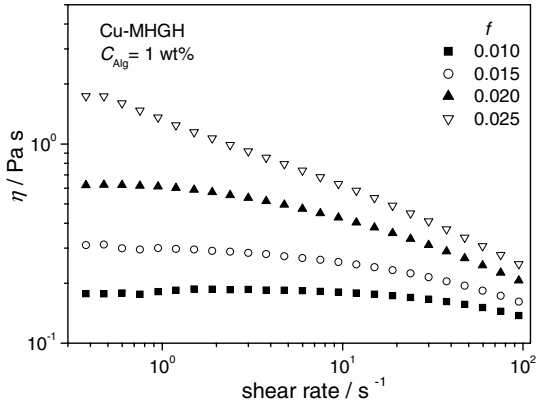

Fig. 4. Shear rate dependence of viscosity η for Cu-MHGH of $C_{Alg} = 1$ wt% before the gelation.

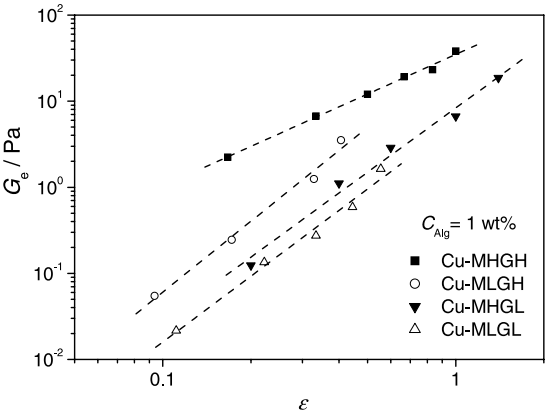

Fig. 6. Equilibrium modulus G_e plotted against ε, the relative distance from the gel point for the four Cu-Alginate samples of $C_{Alg} = 1$ wt%.

G_e for the four Cu-alginate samples at $C_{Alg} = 1$ wt% are summarized in Table 2.

A general expression for the relaxation critical exponent n derived from postulating symmetry of the divergence on both sides of the gel point reads (Winter & Mours, 1997)

$$n = \frac{z}{k+z}. \quad (8)$$

The critical exponent n calculated from k and z using Eq. (8) is listed in Table 2. As expected, the critical exponent n calculated from k and z for the four Cu-alginate samples agrees well with the corresponding n determined by Winter's criterion.

Many theoretical models have been proposed to describe cross-linking polymers at the gel point (Flory, 1953; Flory, 1941; Stauffer, 1974; Stauffer, 1981; Stockmayer, 1943, 1944; Zimm & Stockmayer, 1949). 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 $k = 0.75$ (Winter & Mours, 1997). A lot of experiments have been performed on various gelation systems and typical observed value of k is between 0.7 and 1.7 and the z value is 1.8–3.0 (Adam, Delsanti, Durand, Hild, & Munch, 1981; Adam, Lairez, Karpasas, & Gottlieb, 1997; Fujii, Yano, Kumagai, & Miyawaki, 2000; Martin, Adolf, & Wilcoxon, 1988; Mortimer, Ryan, & Stanford, 2001). For the physical gelation, n varies from 0.11 to 0.8 (Izuka, Winter, & Hashimoto, 1997; Horst & Winter, 2000; Richtering, Gagnon, Lenz, Fuller, & Winter, 1992). The present critical exponent values in Table 2 are relatively close to the Rouse limit for all the samples except Cu-MHGH. It is usually demonstrated that the critical gelation of chemical gels cross-linked by covalent bonds is in fair agreement with the theoretical prediction (Martin, Adolf, & Wilcoxon, 1989). In contrast, the transient nature of the physical gelation cross-linked by intermolecular physical interactions makes it difficult both to describe the critical phenomenon and to determine the gel point with mechanical methods unambiguously (Nijenhuis, 1997).

3.3. Comparison of concentration dependence for Cu^{2+} and Ca^{2+} induced gelation

The alginate concentration C_{Alg} dependence of the gel point f_{gel} and the critical exponent$n$ for our four Cu-alginate samples is depicted in Figs. 7 and 8, respectively. Fig. 7 manifests that f_{gel} is almost independent of the alginate concentration and the f_{gel} value becomes higher for the sample with lower molecular weight without significant M/G dependence. This means that the Cu^{2+} number corresponding to one carboxyl group required to form the critical gel is almost invariable for a given alginate sample. More Cu^{2+} cations are required to connect shorter alginate chains to form an infinite cluster having the structure similar to that formed with longer chains. This finding also suggests that the bounding of Cu^{2+} cations to alginate has no preferential selection to the either M or G residue in alginate chains. This is in contrary to the alginate gelation induced by Ca^{2+} cations, where more calcium cations are chelated by the alginate containing more G residues to reach the similar critical gel (Liu et al., 2003). For the Ca^{2+} induced gelation, with increasing C_{Alg}, f_{gel} for the alginate with lower M_W decreases dramatically while that for the alginate with higher M_W becomes almost a constant (Lu et al., 2005). This discrepancy is due to the difference in gelation mechanism of Cu^{2+} and Ca^{2+} bound to the alginate chains. In the former, four oxygen atoms, two from negatively charged carboxyl groups and other two from uncharged carboxyl groups, coordinate with one central Cu^{2+} ion to form the Cu-alginate complex (Cheng, Guan, & Su, 2000; Wang, Zhang, Konno, & Saito, 1993). While, in the latter, the G residues in alginate are in the alternate $^1C_4$ conformation and paired G-sequences build a buckled 2-fold structure as the shape of 'egg-box' forming cavities to accommodate calcium cations (Grant, Morris, Rees, Smith, & Thom, 1973; Morris, Rees, Thom, & Boyd, 1978). For the same alginate sample at the same

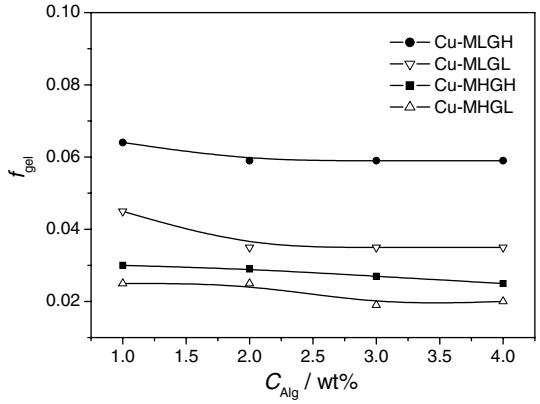

Fig. 7. Alginate concentration dependence of the gel point f_{gel} for the indicated samples.

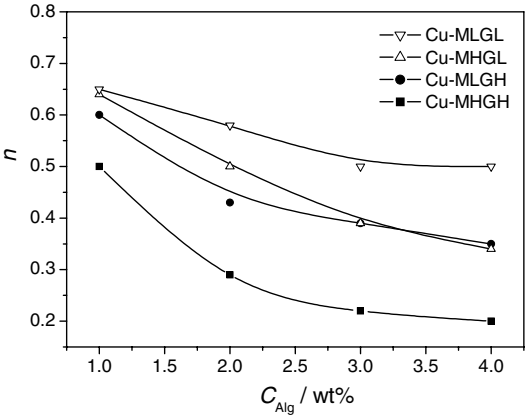

Fig. 8. Alginate concentration dependence of the relaxation critical exponent n for the indicated samples.

concentration, the f_{gel} value is lower for Cu^{2+} induced gelation than for Ca^{2+} induced gelation, indicating the higher binding ability of cupric cations to the alginate uronate units. This is equivalent to increasing the alginate chain length relative to the chain length between two possible cross-linkers at the sol–gel transition due to the non-selection to the specified uronate groups of Cu^{2+} cross-linkers. By using alginate as the gelation polymer, we can tune its effective molecular length to monitor different gelation mechanisms.

On the other hand, the relaxation critical exponent*n* for the four Cu-alginate samples in Fig. 8 decreases with increasing alginate concentration and appears somewhat to depend on the alginate concentration and M/G ratio. The *n* values for the alginate samples with higher G content (Cu-MHGH and Cu-MLGH) are lower than that for the samples with lower G content (Cu-MHGL and Cu-MLGL). The concentration dependence of f_{gel} and *n* may be understood with the concept of alginate relative concentration C_{Alg}/C^*_{Alg}, where C^*_{Alg} is the overlap concentration. The coordination with a Cu^{2+} cation from different chains to form cross-linking requires $C_{Alg}/C^*_{Alg} > 1$ for the chains to contact to each other. f_{gel} invariant with C_{Alg} means that the C_{Alg}/C^*_{Alg} is higher enough to make every Cu^{2+} cation effective in cross-linking at the gel point. If f_{gel} decreases with C_{Alg}, more cross-linking cations are needed at lower C_{Alg}/C^*_{Alg} to form a critical gel.

Based on the fractal analysis of the critical gel, several relationships between the critical exponent *n* and the fractal dimension d_f have been proposed (Hess, Vilgis, & Winter, 1988; Muthukumar & Winter, 1986; Muthukumar, 1985). When the hydrodynamic interaction is completely screened out and the excluded volume effect is dominant in the cluster

$$n = \frac{d}{d_f + 2}. \tag{9}$$

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

$$n = \frac{d}{\bar{d}_f + 2} = \frac{d(d + 2 - 2d_f)}{2(d + 2 - d_f)}. \tag{10}$$

where $\bar{d}_f$ is the fractal dimension of the polymer 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 $\bar{d}_f$ (Muthukumar, 1989).

Following the framework of fractal, we have calculated d_f from *n* for our critical gels using Eqs. (9) and (10), respectively. Unreasonable values of d_f beyond three were obtained from Eq. (9) at high alginate concentrations because at these alginate concentrations the excluded volume was screened within the correlation length (Rubinstein & Colby, 2003). Consequently, we rely the further discussion on the d_f values evaluated from Eq. (10). As depicted in Fig. 9, the alginate with higher G content leads to a higher d_f value for the critical gel when compared with that with higher M content at the same C_{Alg}. This finding indicates that the cluster space in the former critical gel is more densely filled than that in the latter, especially for the Cu-MHGH with the lowest *n* and *z* values. This may be due to the high chain stiffness of alginate samples containing more G residues.

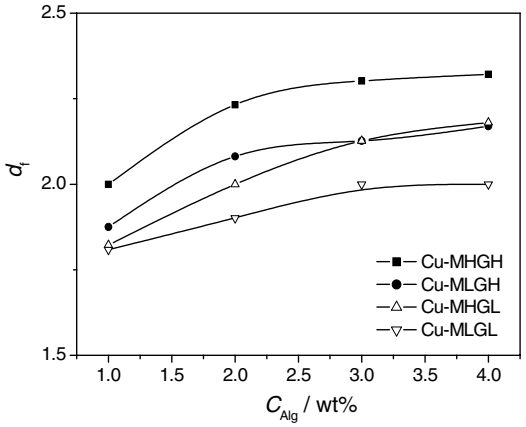

Fig. 9. Alginate concentration dependence of d_f for the indicated samples calculated from *n* using Eq. (10).

In Ca-alginate gelation systems, we have found that if the molecular weight of alginate is low, the critical exponent *n* is about 0.71, independent of the alginate concentration (Lu et al., 2005). While for the alginate samples with high molecular weight the critical exponent *n* decreases with the increase in alginate concentration Thus, we have supposed that the gelation would be classified into two categories referred to as growth and cross-linking according to the effective molecular size before the gelation. In the growth gelation, the gelation occurs from small molecules or precursors which ensure the completely independent cross-linking. Therefore, the critical behavior can be described universally with the percolation model for the model is based on a random connecting or occupying available sites to form clusters in a *d*-dimensional space. In the cross-linking gelation, however, the gelation starts from already existing macromolecular precursors and the cross-link will be correlated with the previously formed junctions, losing the randomicity, in spite of that the junctions are of chemical or physical. This effective molecular size should depend on the individual cross-linking mechanism. In this way, the critical behavior of the sol–gel transition of alginate solutions induced by both cations of Ca^{2+} and Cu^{2+} can be understood comprehensively and consistently.

For the sol–gel transition in the Cu-alginate solution, the critical exponent *n* shows a decrease with increasing C_{Alg} for the same four alginate samples as used in the Ca^{2+} induced gelation. This can be ascribed to the stronger binding ability of Cu^{2+} cations to both G and M units. Therefore, the same alginate chain will be effectively longer relative to the sub-chain length between the cross-linking junctions formed by Cu^{2+} cations. This makes the Cu^{2+} induced alginate gelation belong to the cross-link category,

deviating from the random cross-linking process. In contrast, the Ca^{2+} induced sol–gel transition occurs only due to the chelation of 20 GG residue blocks (Draget, Skjak-Bræk, & Smidsrød, 1997), which makes the alginate chains relatively shorter and leads to the random growth gelation.

We have found a very interesting phenomenon from both the Ca^{2+} (Figs. 5 and 6 in Lu et al., 2005) and Cu^{2+} (Figs. 7 and 8) induced alginate gelation. If the f_{gel} for a specified alginate sample is almost independent of its concentration, the critical exponent n for this sample will decrease with increasing its concentration. Vice versa, if the f_{gel} for a specified alginate sample decreases with increasing its concentration, the critical exponent n for the same sample will be almost independent of its concentration. All the cases of n decrease can be attributed to the cross-linking gelation with effectively longer alginate chains and increasing C_{Alg} at constant f_{gel} will increase the filling density of the critical gel. In contrast, all the cases of constant n can be regarded as the growth gelation with effectively shorter alginate chains and increasing C_{Alg} will reduce the requirement to the divalent cations to form the critical gel, leading to a decrease in f_{gel}.

4. Conclusion

The rheology study on the sol–gel transition in aqueous alginate solutions induced by cupric ions revealed that the gel point f_{gel} was almost independent of the alginate concentration and higher for the sample with lower molecular weight. The relaxation critical exponent n decreased with the increase in C_{Alg} for the four Cu-alginate systems and was lower for the alginate samples with high G content. The change of the critical exponent n indicates that the sol–gel transition of alginate induced by Cu^{2+} cations belongs to the cross-linking gelation, different from the growth gelation induced by Ca^{2+} cations for effectively lower molecular weight alginates.

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