

# Critical Exponents and Self-Similarity for Sol-Gel Transition in Aqueous Alginate Systems Induced by in Situ Release of Calcium Cations

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The sol–gel transition in aqueous alginate systems induced by in situ released calcium cations was monitored with rheology methods. Four alginate samples with different molecular weights and M/G ratios were used over the concentration  $C_{\text{Alg}}$  of 2 ~ 6 wt % with different mole ratios  $f$  of  $\text{Ca}^{2+}$  to the alginate repeat unit. The scaling for the zero shear viscosity  $\eta_0$  before the gel point and the equilibrium modulus  $G_e$  after the gel point was described as  $\eta_0 \sim \epsilon^{-k}$  and  $G_e \sim \epsilon^z$ , respectively, where the relative distance to the gel point  $f_{\text{gel}}$  was  $\epsilon = (|f - f_{\text{gel}}|)/f_{\text{gel}}$ . The relaxation critical exponent  $n$  was determined with Winter's criterion, and the critical exponents  $k$  and  $z$  estimated respectively from independent measurements of  $\eta_0$  and  $G_e$  gave  $n$  from  $z/(k + z)$ . Before the gel point, the storage and loss moduli  $G'$  and  $G''$  obtained at various  $\epsilon$  can be superposed fairly well to form the master curve. The critical exponents  $n$ ,  $k$ , and  $z$  were also evaluated from the shift factors and the structure self-similarity was found in the critical gel. The critical exponents evaluated with different methods agreed well with each other, suggesting two categories of the gelation as growth and cross-link. For the alginate with lower molecular weight, the critical exponents were almost independent of alginate concentration and close to the percolation prediction. For the alginate with higher molecular weight, the critical exponents, however, changed with alginate sample and concentration. The relative alginate concentration  $C_{\text{Alg}}/C_{\text{Alg}}^*$  was found to serve as a criterion to divide these two transitions.

## Introduction

Alginate is a naturally derived linear polysaccharide consisting of  $\beta$ -D-mannuronate (M) and its C-5 epimer  $\alpha$ -L-guluronate (G) units arranged in blocks rich in G units or M units, separated by blocks of alternating G and M units.<sup>1,2</sup> The unit sequence endows alginate chains with different stiffness; consequently, the mean square end-to-end distance per uronate residue for the G component is 2.2 times larger than that for the M component.<sup>3</sup> The amount and distribution of each dyad depend on the species, location, and age of seaweed from which the alginate is produced.<sup>4</sup> Alginate is considered as biocompatible and easy to form a hydrogel by divalent cations (except  $\text{Mg}^{2+}$ ). Alginate hydrogel has been intensively studied for cell encapsulation, cell transplantation, tissue engineering, etc.<sup>5,6</sup> Up to now, however, only a few investigations concerned the critical phenomenon of the sol–gel transition in aqueous alginate solutions.

The sol–gel transition is a phase transition accompanying a cross-link process to form at least an infinite network over the whole sample, which is one of most important processes in polymer processing, food manufacture, protein folding and denaturation, and other fields. The analytical solution for the sol–gel transition was derived by Flory and Stockmayer from the mean field theory on the space lattice, ignoring closed loops.<sup>7</sup> Percolation theory described the structural evolution of branched molecules connected intermolecularly in a completely random way, whether chemical or physical.<sup>8</sup> The sol–gel transition is usually formulated by bond percolation analogous to electric circuit conductivity.<sup>9–11</sup> From the definition of the critical gel, the actual ratio of bonds that have been already formed in the

cross-link to the total bonds that can be formed in the cross-link is  $p$ , while the critical value of  $p$  at the gel point is  $p_c$ .

At the gel point, a macroscopic molecule network coexists with remaining finite molecules, and the system changes from a liquid to a solid. Therefore, the solution viscosity, average molecular weight, and correlation length all diverge, and the equilibrium modulus begins to appear larger than zero. Analogous to many physical functions at the phase transition, the zero shear viscosity  $\eta_0$  and the equilibrium modulus  $G_e$  can be expressed in power law forms of the relative distance  $\epsilon$  from the gel point in the vicinity of the gel point, and their exponents characterize the critical phenomena.<sup>12–14</sup> If the relative distance from the gel point is  $\epsilon = (|p - p_c|)/p_c$ , then the zero shear viscosity  $\eta_0$  at  $p < p_c$  is expressed as

$$\eta_0 \sim \epsilon^{-k} \quad (1)$$

and the equilibrium modulus  $G_e$  at  $p > p_c$  as

$$G_e \sim \epsilon^z \quad (2)$$

Here,  $k$  and  $z$  are the critical exponents for viscosity and modulus, respectively.  $\eta_0$  is expected to diverge when  $\epsilon \rightarrow 0$ . If a gel was formed in a random way, the critical exponents  $k$  and  $z$  were said to be universal and independent of the structural details.<sup>15</sup> However, several models including mean field and various percolations predicted different  $k$  and  $z$  values according to different gelation mechanisms.

Experimentally the chemical gelation cross-linked by covalent bonds has been extensively investigated and the critical exponents have been found in a good agreement with the theoretical predictions.<sup>16–18</sup> Winter and Chambon found the critical gel equation for the relaxation modulus  $G(t) = S t^{-n}$  and  $n = 0.5$

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TABLE 1: Characterization of Alginate Samples

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

for the critical gel of cross-linked poly(dimethyl siloxane), where  $S$  was the gel strength and  $n$  the relaxation critical exponent.<sup>19</sup> They generalized this equation with  $0 < n < 1$  from rheology of cross-linking polymers.<sup>20</sup> In contrast, the understanding of the physical gelation is not as good as the chemical gelation. The transient nature of the physical gelation cross-linked by intermolecular physical interactions makes it difficult for both to describe the critical phenomenon and to determine the gel point with mechanical methods unambiguously.

Recently, we have found from the sol–gel transition of aqueous alginate solutions induced by calcium cations that the relaxation critical exponent  $n$  decreased with increasing alginate concentration when the alginate molecular weight was high, indicating the failure of the percolation prediction of universal value for  $n$ .<sup>21</sup> Thus, we suggested two categories for the gelation referred to as growth and cross-link according to the size of molecules or precursors in the solution just before the gelation. In the former, the gelation occurred from small molecules or precursors via completely random cross-links; thus, the critical behavior can be described with the present percolation model, producing universal critical exponents. In the latter, however, the gelation starts from already existing macromolecular precursors, and the cross-linking will be correlated with the previously formed junctions, in spite of that these junctions are of chemical or physical. Nevertheless, our previous finding was based merely on one critical exponent of  $n$  determined on two alginate samples with Winter's criterion.

Therefore, in the present study, we determined experimentally the critical exponents for the zero shear viscosity, equilibrium modulus, and compliance in addition to the relaxation for the sol–gel transition induced by in situ release of calcium cations in aqueous alginate solutions of different concentrations and molecular weights. The self-similar critical structure, the universality of the critical exponents, and the scaling law of these exponents were discussed to verify our preceding suggestion on the two gelation categories.

## Experimental Section

**Alginate Samples.** Alginate samples (Kimitsu Chemical Industry Co., Japan) were purified as follows: the aqueous solution of ~3 wt % alginate was first dialyzed in distilled water using a cellulose tubular membrane (the cutoff molecular weight was about 14000) until the conductivity of water outside became constant before and after refreshing. Then, the solution was filtered and freeze-dried to produce purified dry samples. Molecular weight  $M_w$  of the samples was determined by gel permeation chromatography (GPC) with a Waters apparatus using 0.1 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution as the elution and narrowly distributed PEO as the standard. The mole ratio of mannuronate (M) to guluronate (G) residues (M/G) and the mole fractions of GG, MM, and GM (MG) dyad sequences  $F_{GG}$ ,  $F_{MM}$ , and  $F_{GM}$  were determined by <sup>1</sup>H NMR (nuclear magnetic resonance) according to Grasdalen's procedure<sup>22,23</sup> in D<sub>2</sub>O of 14 mg/mL at 70 °C. The characterization results are summarized in Table 1. The main difference among the four samples was in the molecular weight and M/G ratio.

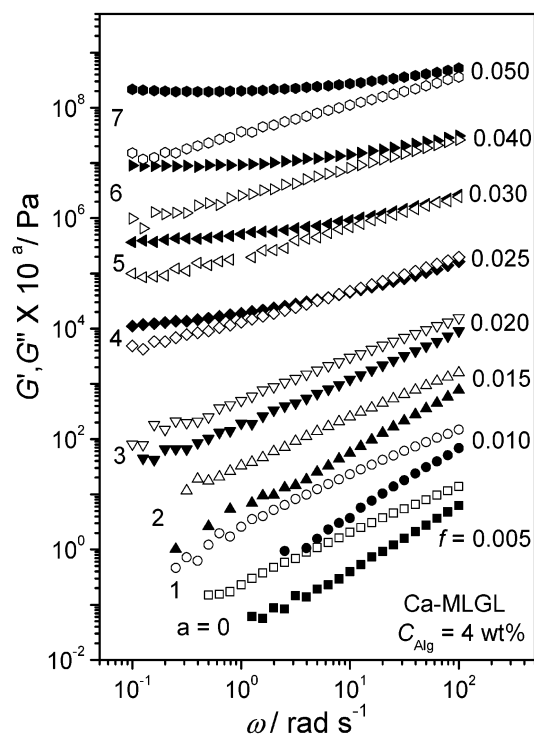
**Preparation of Ca-Alginate Gels by in Situ Release of Ca<sup>2+</sup>.** We define the stoichiometric mole ratio  $f = [\text{Ca}^{2+}]/[\text{COO}^- \text{ in alginate}]$  as a structure parameter which controls the gelation process with the assumption that the ratio  $f$  is proportional to the fraction of inter- and intramolecular cross-links formed. In order to prepare homogeneous Ca-alginate gels at room temperature, the method of in situ release of calcium cations from ethylene diamine tetraacetic acid (EDTA, standard reagent, Tianjin Institute for Chemicals) chelate was adopted through lowering pH with slow hydrolysis of D-glucono-δ-lactone (GDL, Sigma) as described in the literature.<sup>24,25</sup> Ca-alginate gels were prepared by blending 3 mL of concentrated alginate stock solution with 0.8 mL of Ca-EDTA solution of different concentrations at pH = 7, followed by adding required amount of GDL freshly dissolved in 0.2 mL of H<sub>2</sub>O. The total system achieved the desired alginate concentration  $C_{\text{Alg}}$  and  $f$  according to the calibration curve for the concentration relation of added GDL and released Ca<sup>2+</sup>. All samples were homogeneous and transparent after magnetically stirring for 15 min at room temperature and incubated at 12 °C for 48 h prior to the rheology measurement. The  $f$  value was affected only by the concentrations of both alginate and Ca-EDTA solutions because at low pH Ca<sup>2+</sup> was completely released. Therefore, the  $f$  value in our experiments was controlled more accurate than  $\pm 0.001$ .

**Rheology Measurement.** The rheology measurement was conducted in four steps. First, the shear strain  $\gamma$  dependence of the complex modulus  $G^*$  was measured at 10 rad/s to determine the linear viscoelasticity region. Second, the dynamic viscoelastic spectra were measured in the linear region over the angular frequency  $\omega$  of  $10^{-1}$ – $10^2$  rad/s. Third, for the samples below the gel point, the shear rate dependence of steady viscosity was measured in order to obtain the zero viscosity. Fourth, the stress relaxation modulus  $G(t)$  was measured on the samples very close to the sol–gel transition threshold by applying a constant shear strain within the linear viscoelasticity region.

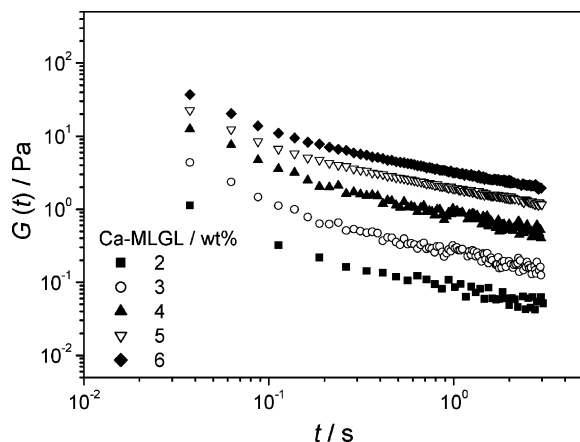
The measurements were performed on a RFS-II rheometer (Rheometrics Ltd) at  $25 \pm 0.1$  °C with different fixtures, including cone plates and parallel plates of 25 and 50 mm diameters with the cone's angle of 0.04 rad.

## Results and Discussion

**Critical Exponents.** Figure 1 shows the angular frequency  $\omega$  dependence of storage and loss moduli  $G'$  and  $G''$  for the Ca-MLGL aqueous system of concentration  $C_{\text{Alg}} = 4$  wt % at various  $f$  values before and after the sol–gel transition. The data were 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 detected accurately. At low  $f$  values,  $G''$  is always higher than  $G'$  in whole frequency range without any plateau appearing at  $G'$  vs  $\omega$  curves. At high  $f$  values,  $G'$  becomes higher than  $G''$  with a plateau appearing at the  $G'$  vs  $\omega$  curve in low-frequency range. At a moderate value of  $f$ , there is the transition region from fluid to gel, where  $\omega$  dependent curve of  $G'$  becomes parallel to  $G''$  on the logarithmic coordinate over a wide frequency range, such as the curves of  $f = 0.02$  in Figure 1. This indicates occurrence of the sol–gel transition in the Ca-MLGL aqueous system, and the gel point is described with the threshold  $f$  value as  $f_{\text{gel}}$ . The values of  $f_{\text{gel}}$  and the relaxation critical exponent  $n$  at the critical gel point were determined using the Winter's criterion, where  $G'(\omega) \sim G''(\omega) \sim \omega^n$ , the relaxation modulus  $G(t) \sim t^{-n}$ , and the loss tangent  $\tan \delta = G'/G''$  was independent of frequency  $\omega$ .<sup>26,27</sup> The value of the quasical critical exponent  $n$  was also determined from the relaxation modulus  $G(t)$  (Figure 2) for the samples very close to the gel



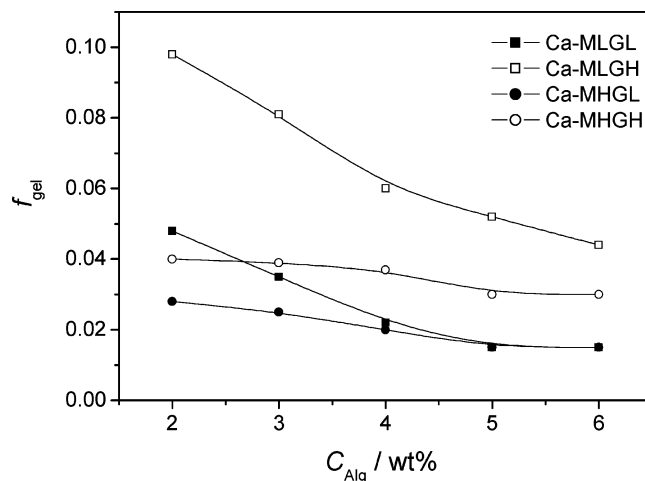
**Figure 1.** Angular frequency  $\omega$  dependence of storage modulus  $G'$  (solid symbol) and loss modulus  $G''$  (open symbol) for Ca-MLGL sample of  $C_{\text{Alg}} = 4$  wt % with indicated  $f$ . The data have been vertically shifted by  $10^a$  with the given  $a$  to avoid overlapping.



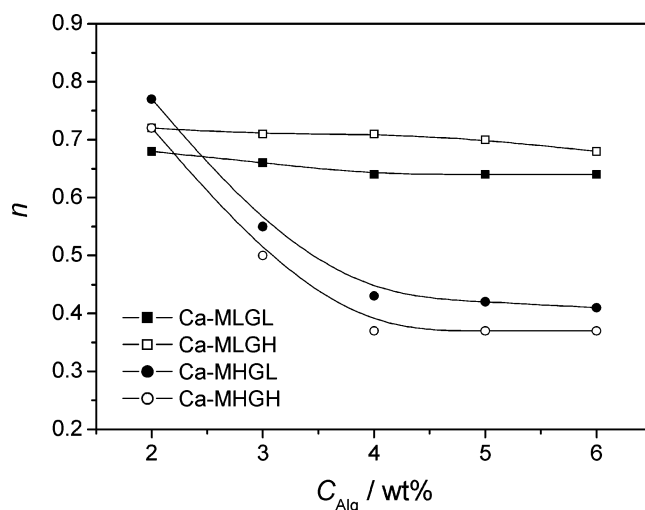
**Figure 2.** Time dependence of the relaxation modulus  $G(t)$  for Ca-MLGL sample at different concentrations with the  $f$  values where  $\log G'$  is almost parallel to  $\log G''$ .

point as described in our previous paper.<sup>21</sup> Similar plots for frequency dependence of the dynamic moduli as well as time dependence of the relaxation modulus have been obtained from all the alginate samples in aqueous system at different concentrations. The  $n$  values so determined are summarized in Table 2 together with other critical exponents. The  $n$  value determined with the Winter's criterion agrees fairly well with that obtained from the relaxation modulus.

The alginate concentration dependence of the gel point  $f_{\text{gel}}$  and  $n$  for the four Ca-alginate samples are compared in Figures 3 and 4, respectively. For the samples Ca-MLGH and Ca-MLGL with lower molecular weight,  $f_{\text{gel}}$  decreases dramatically with increasing alginate concentration. In contrast,  $f_{\text{gel}}$  only slightly declines with the alginate concentration for the samples Ca-MHGL and Ca-MHGH with higher molecular weight. This means that more  $\text{Ca}^{2+}$  cations are needed to cross-link short



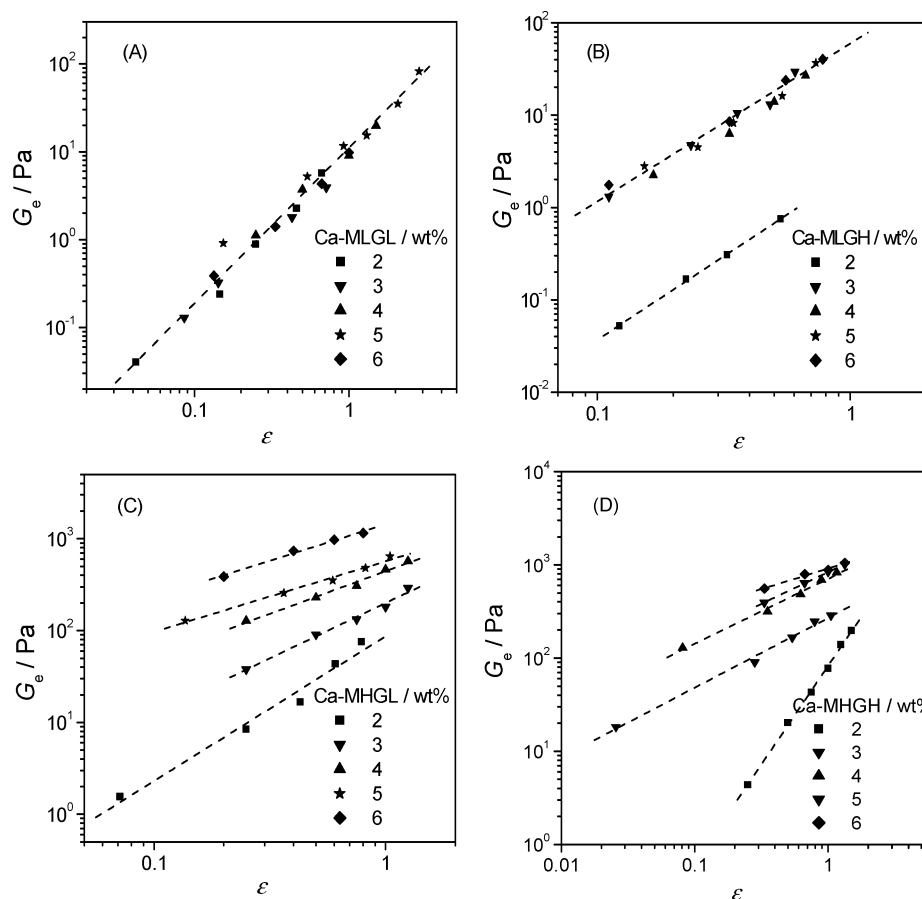
**Figure 3.** Alginate concentration dependence of the gel point  $f_{\text{gel}}$  for the indicated samples.



**Figure 4.** Alginate concentration dependence of the relaxation critical exponent  $n$  for the indicated samples.

alginate chains into an infinite network at lower concentrations. When  $C_{\text{Alg}}$  is higher than 4 wt %, this molecular weight effect on  $f_{\text{gel}}$  becomes weak for there are enough chains to be cross-linked in the solution. On the other hand, we can recognize from Figure 3 the dependence of  $f_{\text{gel}}$  on the alginate M/G ratio. When comparing the sample in pairs of Ca-MHGH and Ca-MHGL, Ca-MLGH and Ca-MLGL having comparable molecular weight for each pair, the  $f_{\text{gel}}$  value for the sample with lower M/G ratio is always higher than that with the higher M/G ratio over the observed concentrations. This finding suggests that more  $\text{Ca}^{2+}$  cations are required to form the critical gel for the alginate chains with more G residues. The cross-linker formed by the fold G sequence of an egg-box shape can accommodate more  $\text{Ca}^{2+}$  cations for one intermolecular junction.<sup>28,29</sup> Therefore, more  $\text{Ca}^{2+}$  cations are chelated into the alginate network with higher G content at the same cross-linking degree of the gel point.

Figure 4 depicts that the relaxation critical exponent  $n$  varies with the alginate concentration in two manners significantly different. For the samples Ca-MLGH and Ca-MLGL with lower molecular weight, the  $n$  is about 0.7, almost independent of alginate concentration. On the other hand, the  $n$  for samples Ca-MHGL and Ca-MHGH with higher molecular weight decreases and then levels off at about a half of the beginning  $n$  value with increasing alginate concentration. This illustrates that



**Figure 5.** Equilibrium modulus  $G_e$  plotted against  $\epsilon$ , the relative distance from the gel point for the four Ca-Alginate samples.

**TABLE 2: Critical Exponents for Ca-Alginate Samples**

sample	$C_{Alg}$ (wt %)	$n^a$	$n^b$	$z^c$	$k^c$	$n^c$	$z^d$	$k^d$	$n^d$
Ca-ML GL	2	$0.68 \pm 0.02$	$0.67 \pm 0.02$	$1.74 \pm 0.04$	$0.76 \pm 0.03$	$0.70 \pm 0.02$	$1.69 \pm 0.07$	$0.78 \pm 0.13$	$0.68 \pm 0.04$
	3	$0.69 \pm 0.01$	$0.66 \pm 0.02$	$1.74 \pm 0.04$	$0.68 \pm 0.03$	$0.72 \pm 0.02$	$1.68 \pm 0.06$	$0.75 \pm 0.12$	$0.69 \pm 0.04$
	4	$0.64 \pm 0.01$	$0.64 \pm 0.02$	$1.74 \pm 0.04$	$0.73 \pm 0.06$	$0.70 \pm 0.03$	$1.66 \pm 0.04$	$0.78 \pm 0.09$	$0.68 \pm 0.03$
	5	$0.64 \pm 0.01$	$0.63 \pm 0.02$	$1.74 \pm 0.04$	-	-	-	-	-
	6	$0.64 \pm 0.01$	$0.63 \pm 0.02$	$1.74 \pm 0.04$	-	-	-	-	-
Ca-ML GH	2	$0.72 \pm 0.01$	$0.63 \pm 0.09$	$1.80 \pm 0.03$	$0.66 \pm 0.05$	$0.73 \pm 0.02$	$1.81 \pm 0.06$	$0.63 \pm 0.15$	$0.74 \pm 0.05$
	3	$0.71 \pm 0.02$	$0.69 \pm 0.04$	$1.68 \pm 0.06$	$0.71 \pm 0.06$	$0.70 \pm 0.03$	$1.78 \pm 0.08$	$0.70 \pm 0.16$	$0.72 \pm 0.06$
	4	$0.71 \pm 0.02$	$0.75 \pm 0.04$	$1.68 \pm 0.06$	$0.71 \pm 0.04$	$0.70 \pm 0.02$	$1.79 \pm 0.09$	$0.63 \pm 0.12$	$0.74 \pm 0.05$
	5	$0.70 \pm 0.02$	$0.72 \pm 0.02$	$1.68 \pm 0.06$	-	-	$1.69 \pm 0.06$	$0.69 \pm 0.08$	$0.71 \pm 0.03$
	6	$0.68 \pm 0.01$	$0.71 \pm 0.05$	$1.68 \pm 0.06$	-	-	$1.70 \pm 0.07$	$0.67 \pm 0.14$	$0.72 \pm 0.05$
Ca-MH GL	2	$0.77 \pm 0.02$	$0.68 \pm 0.06$	$1.58 \pm 0.13$	$0.56 \pm 0.03$	$0.74 \pm 0.03$	$1.60 \pm 0.07$	$0.47 \pm 0.13$	$0.77 \pm 0.05$
	3	$0.55 \pm 0.02$	$0.49 \pm 0.08$	$1.20 \pm 0.07$	$0.69 \pm 0.08$	$0.63 \pm 0.04$	$1.11 \pm 0.05$	$0.95 \pm 0.08$	$0.54 \pm 0.04$
	4	$0.43 \pm 0.01$	$0.44 \pm 0.02$	$0.93 \pm 0.06$	$1.00 \pm 0.10$	$0.48 \pm 0.04$	$1.03 \pm 0.03$	$1.07 \pm 0.03$	$0.49 \pm 0.01$
	5	$0.42 \pm 0.01$	$0.44 \pm 0.02$	$0.77 \pm 0.05$	-	-	-	-	-
	6	$0.41 \pm 0.01$	$0.42 \pm 0.01$	$0.79 \pm 0.06$	-	-	-	-	-
Ca-MH GH	2	$0.72 \pm 0.01$	$0.78 \pm 0.06$	$2.11 \pm 0.04$	$1.38 \pm 0.12$	$0.60 \pm 0.03$	$1.94 \pm 0.18$	$0.92 \pm 0.24$	$0.68 \pm 0.08$
	3	$0.50 \pm 0.01$	$0.45 \pm 0.05$	$0.75 \pm 0.04$	$0.59 \pm 0.05$	$0.56 \pm 0.03$	$0.81 \pm 0.15$	$0.73 \pm 0.24$	$0.53 \pm 0.13$
	4	$0.37 \pm 0.01$	$0.31 \pm 0.06$	$0.70 \pm 0.03$	$1.08 \pm 0.05$	$0.39 \pm 0.02$	$0.76 \pm 0.13$	$0.96 \pm 0.25$	$0.44 \pm 0.11$
	5	$0.37 \pm 0.01$	$0.34 \pm 0.03$	$0.68 \pm 0.02$	-	-	-	-	-
	6	$0.37 \pm 0.01$	$0.37 \pm 0.01$	$0.44 \pm 0.03$	-	-	-	-	-

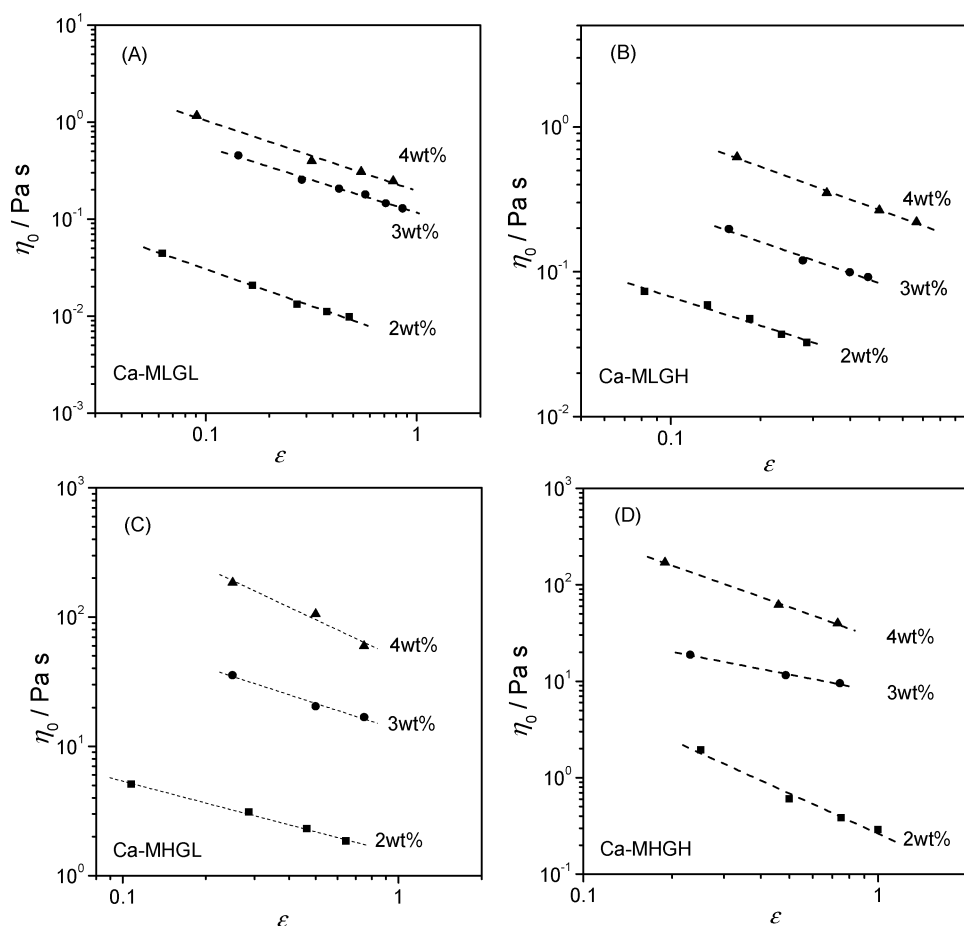
<sup>a</sup> From Winter's criterion. <sup>b</sup> The quasi-critical exponent from relaxation. <sup>c</sup> From equilibrium modulus and zero shear viscosity. <sup>d</sup> From the superposition.

for the alginate with low molecular weight there exists a universal  $n$  value at the sol–gel transition as the percolation prediction of an electric circuit. For the alginate samples with high molecular weight, however, no universal  $n$  value can be observed at this transition.

The equilibrium modulus  $G_e$  was evaluated from the  $G'$  plateau at low  $\omega$  as depicted in Figure 1 for all samples at all tested alginate concentrations after the gel point and plotted against  $\epsilon$  in Figure 5. Here, we used  $f$  to replace  $p$  as  $\epsilon = (|f - f_{gel}|)/f_{gel}$  because  $f$  is proportional to  $p$  according to the cross-

link mechanism. In Figure 5A and 5B, the  $G_e$  values at different concentrations for either of the alginate samples with lower molecular weight can be fit with a single line except that for Ca-MLGH at 2 wt %, which is due to the lowest molecular weight of this sample leading to a much weak gel at this low concentration. In contrast, the change in  $G_e$  with  $\epsilon$  in Figure 5C and 5D manifests a decrease in the slope with increasing alginate concentration. The critical exponent  $z$  values estimated from the slope are listed in Table 2. For two alginate samples of Ca-MLGL and Ca-MLGH with low molecular weight,  $z$  is





**Figure 6.** Zero shear viscosity  $\eta_0$  plotted against  $\epsilon$ , the relative distance from the gel point for the indicated samples.

almost a constant of about 1.7, but for the other two samples of Ca-MHGL and Ca-MHGH with high molecular weight,  $z$  changes with samples and decreases with an increase in alginate concentration. These facts also confirm that the universal critical exponents only exist for the low molecular weight alginates.

The shear rate dependence of the steady viscosity (not dynamic viscosity) was measured for all the samples using a rate sweep process before the gel point; and the zero shear viscosity  $\eta_0$  was estimated by the extrapolation to zero shear rate and plotted against  $\epsilon$  in Figure 6. From the slope of straight lines in Figure 6, we obtained the value of the critical exponent  $k$  as listed in Table 2. Lack of the  $k$  data for the solutions with higher alginate concentration (above 4 wt %) is due to the difficulty in determining  $\eta_0$  accurately within a very narrow gap between measurable  $f$  and  $f_{\text{gel}}$ . For the samples with lower molecular weight (Ca-MLGL and Ca-MLGH), the critical exponent  $k$  is almost a constant of about 0.7, independent of the alginate molecular weight and concentration. On the other hand, the  $k$  for the samples with higher molecular weight (Ca-MHGL and Ca-MHGH) changes obviously with the alginate sample and concentration.

From the values of the critical exponents  $n$ ,  $z$ , and  $k$ , one can recognize that when the molecular weight of alginate is low, the critical exponents are universal, independent of alginate sample and solution concentration. The experimentally determined values of the critical exponents are close to the prediction of  $n = 0.71$ ,  $z = 1.94$ , and  $k = 0.75$  based on the analogy to a random electrical network.<sup>30,31</sup> However, when the molecular weight of alginate is high, the critical exponents are different for different samples and vary with the solution concentration, losing their universality. This behavior will be discussed later.

Many theoretical models have been proposed to describe cross-linking polymers at the gel point. Different values for  $n$ ,  $z$ , and  $k$  have been reported with the models using either the Rouse and Zimm limits for hydrodynamic interaction or the electrical network analogy.<sup>32</sup> 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 of an electrical network produces  $n = 0.71$ ,  $z = 1.94$ , and  $k = 0.75$ . The typical observed value of  $k$  is between 0.7 and 1.7, and the  $z$  value is normally reported to be 1.8–3.0.<sup>33–35</sup> Martin et al. found  $k = 1.4 \pm 0.2$  for epoxy resins and suggested a Rouse melt.<sup>33</sup> Adam et al. obtained  $k = 0.78 \pm 0.05$  from both radical copolymerization with solvent (polystyrene/divinylbenzene/benzene) and polycondensation without solvent (diisocyanate/triol), which was close to the de Gennes prediction.<sup>30,34</sup> They also reported  $z = 2.1 \pm 0.3$  for the radical copolymerization and  $3.2 \pm 0.6$  for the polycondensation.<sup>30,34</sup> Kawabata et al. reported the critical exponent  $z$  of 4.2 for corn starch and 1.8 for cassava starch, respectively.<sup>36</sup> Adam et al. indicated that when the gel was made from end linking high-molecular-weight precursors, no clear scaling was observed from the modulus near the gel point.<sup>30</sup>

**Scaling Relation.** When a system approaching to the gel point from either side of sol or gel, the relaxation becomes slower and the longest relaxation time  $\lambda_{\text{max}}$  will diverge at the gel point. This is attributed to the appearance of an infinite network spanning the whole sample. The divergence of the zero shear viscosity  $\eta_0$  and the equilibrium modulus  $G_e$  is considered to be related with the divergence of the longest relaxation time  $\lambda_{\text{max}}$ , and the longest relaxation time diverges following a power law from both sides of the gel point

$$\lambda_{\max} \begin{cases} (p_c - p)^{-\alpha_-} & \text{for } p < p_c \\ (p - p_c)^{-\alpha_+} & \text{for } p > p_c \end{cases} \quad (3)$$

where  $\alpha_-$  and  $\alpha_+$  are the critical exponents of sol and gel phases, respectively. Postulating symmetry of the divergence on both sides of the gel point leads to an interesting relation between the critical exponents  $n$ ,  $k$ , and  $z$ <sup>37</sup>

$$n = \frac{z}{k + z} \quad (4)$$

Using eq 4 the relaxation critical exponent  $n$  was calculated from  $k$  and  $z$  and also listed in Table 2. The  $n$  determined on Winter's criterion agrees well with the  $n$  evaluated from eq 4 for all of the samples and concentrations. Therefore, the scaling law described by eq 4 is held for the critical exponents of the sol–gel transition in our alginate systems induced by  $\text{Ca}^{2+}$  cations.

**Self-Similarity.** Hodgson and Amis evaluated the static scaling exponents using the predictions of dynamics at the gel point and the viscoelasticity theory.<sup>17</sup> The zero shear viscosity is determined by the arithmetic average of relaxation time  $\langle \lambda \rangle$ , which is calculated from the time integral of the shear relaxation modulus

$$\langle \lambda \rangle \equiv \int_0^\infty G(t) dt \sim \left( \frac{|p - p_c|}{p_c} \right)^{-k} \quad (5)$$

The longest relaxation time  $\lambda_{\max}$  at the neighborhood of the gel point is given by

$$\lambda_{\max} \equiv \frac{\int_0^\infty t G(t) dt}{\int_0^\infty G(t) dt} \sim \left( \frac{|p - p_c|}{p_c} \right)^{-k-z} \quad (6)$$

which has been shown to diverge at the gel point. It is noted that  $\lambda_{\max} \sim \eta_0 J_e^0$ , the product of the zero shear viscosity and the steady-state creep compliance. Since  $\langle \lambda \rangle \sim \eta_0$ , eqs 5 and 6 lead to

$$\frac{1}{J_e^0} \sim \frac{\langle \lambda \rangle}{\lambda_{\max}} \sim \left( \frac{|p - p_c|}{p_c} \right)^z \quad (7)$$

On the basis of these relations, they proposed a working hypothesis for superposition of viscoelastic functions, considering that self-similarity in polymer fractal network growth would induce the mechanical self-similarity before the gel point. According to this hypothesis, we can superpose the frequency dependence curves of  $G'$  and  $G''$  at various  $\epsilon$  of  $p < p_c$  to give master curves of

$$G'(\omega)\alpha_v \text{ vs } \omega\alpha_h \text{ and } G''(\omega)\alpha_v \text{ vs } \omega\alpha_h$$

provided that the self-similarity holds. Here,  $\alpha_h$  and  $\alpha_v$  are horizontal and vertical shift factors, respectively, and defined by

$$\alpha_v = \frac{J_e^0(p)}{J_e^0(p_r)} \sim \left[ \frac{\epsilon(p)}{\epsilon(p_r)} \right]^{-z} \quad (p < p_c) \quad (8)$$

$$\alpha_h = \frac{\langle \lambda(p) \rangle}{\langle \lambda(p_r) \rangle} \sim \left[ \frac{\epsilon(p)}{\epsilon(p_r)} \right]^{-(k+z)} \quad (p < p_c) \quad (9)$$

where  $\epsilon(p_r)$  is the  $\epsilon$  value at the reference reaction extent  $p_r$ .

From eqs 8 and 9, we obtain

$$\frac{\log \alpha_v}{\log \alpha_h} = \frac{z}{k + z} \quad (p < p_c) \quad (10)$$

This equation suggests that one can estimate the  $z/(k + z)$  value from superposed modulus data and shift factors.

We have tested the mechanical self-similarity in our Ca-alginate systems by superposing the  $G'$  and  $G''$  vs  $\omega$  curves obtained at various  $f$  to produce the master curve and Figure 7 depicts the master curves for the Ca-MLGH with various alginate concentrations before the gel point as examples. In order to do this, we shifted  $G'$  and  $G''$  at each  $\epsilon$  by the shift factors  $\alpha_v$  and  $\alpha_h$  with the constraint of eqs 8 and 9. The other systems of different alginate samples also show the similar master curves. These master curves confirm the structure self-similarity in the network of our Ca-alginate systems.

In Figure 8, the shift factors  $\alpha_v$  and  $\alpha_h$  are plotted as functions of  $\epsilon(p)/\epsilon(p_r)$  for the sample Ca-MLGH at different concentrations, and the slope of the straight lines gives the value of  $z$  from  $\alpha_v$  and  $(z + k)$  from  $\alpha_h$ . Thus, the relaxation critical exponent  $n$  can be evaluated with eq 4, and the values of  $z$ ,  $k$ , and  $n$  for all samples determined in this way are summarized in Table 2. The critical exponents so evaluated from the shift factors have a somewhat large error due to the double differential during evaluation. But we can still recognize that the critical exponents change with alginate concentration for the two alginate samples with higher molecular weight and become constants for the other two alginate samples with lower molecular weight.

Following the same method, Takenaka et al. evaluated  $k = 1.4 \pm 0.1$  and  $z = 3.1 \pm 0.1$  for the physical gelation of 1,3:2,4-bis-*O*-(*p*-methylbenzylidene)-D-sorbitol in polystyrene melt.<sup>38</sup> Takahashi et al. reported  $z = 2.0$ – $2.2$  from  $G_e$  and  $z = 2.7$ – $2.8$  from  $J_e^0$  for the end-linking gelation of prepolymers with  $M_n = 2000$  and  $7500$ .<sup>18</sup> They considered that this discrepancy came from that the links of the backbone structure determined the critical exponent from  $G_e$ , while the blobs and dangling chains besides the links incorporated into the network contributed to  $J_e^0$ .

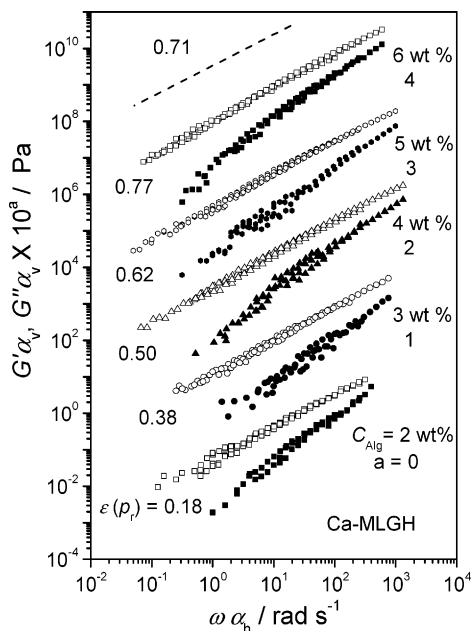
According to the data in Table 2, we can conclude that the critical exponents determined with different methods manifest similar alginate concentration dependence: For the alginate with low molecular weight, the critical exponents are almost independent of the concentration and close to the theoretical predication of electrical network percolation. On the other hand, for the alginate with high molecular weight the concept of universal critical exponents fails. The critical exponents  $n$  and  $z$  decrease with an increase in alginate concentration for these samples.

#### Overlap Concentration in the Vicinity of the Gel Point.

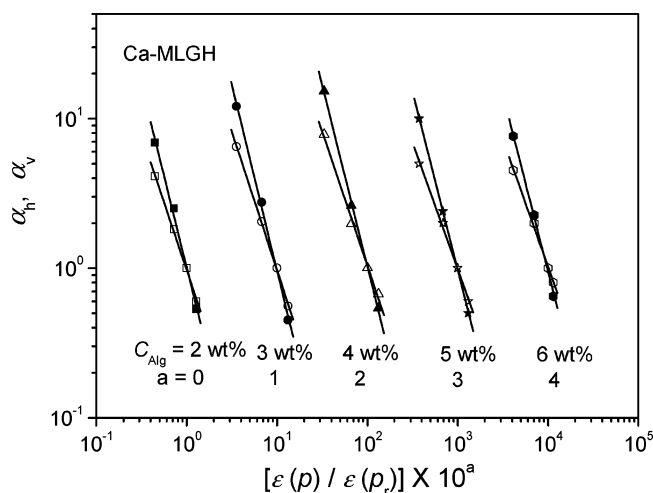
The overlap concentration  $C_{\text{Alg}}^*$  of alginate may be a significant measure for understanding the concentration dependence of  $f_{\text{gel}}$  and  $n$  because the gelation induced by chelating  $\text{Ca}^{2+}$  cations requires the alginate chains to contact each other at  $C_{\text{Alg}}/C_{\text{Alg}}^* > 1$ . We evaluated  $C_{\text{Alg}}^*$  from the reciprocal of the intrinsic viscosity  $[\eta]$  as  $C_{\text{Alg}}^* = 1/[\eta]$ <sup>39</sup> and determined  $[\eta]$  with the Fedors equation<sup>40,41</sup>

$$\frac{1}{2(\eta_r^{1/2} - 1)} = \frac{1}{[\eta]C} - \frac{1}{[\eta]C_m} \quad (11)$$

where  $\eta_r$  is the solution viscosity relative to the solvent and  $C_m$  is a polymer concentration parameter. The viscosity of alginate



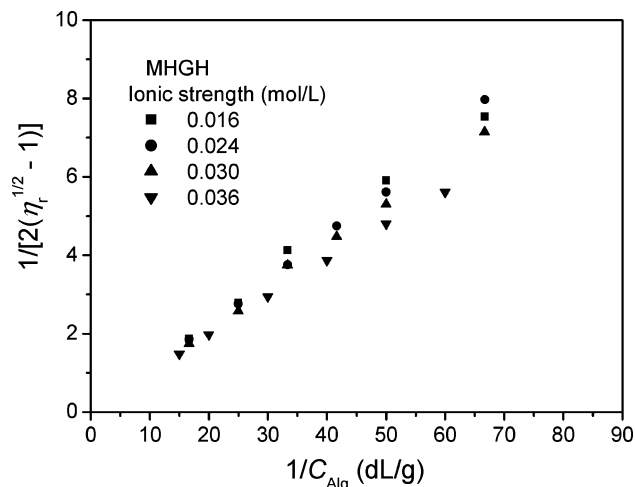
**Figure 7.** Superposition of frequency dependence of  $G'$  (solid symbol) and  $G''$  (open symbol) for Ca-MLGH obtained at various  $\epsilon$  before gel point along a straight line with the slope of  $n$ . The data for different alginate concentrations have been vertically shifted by a factor of  $10^4$  with the given  $a$  to avoid overlapping.



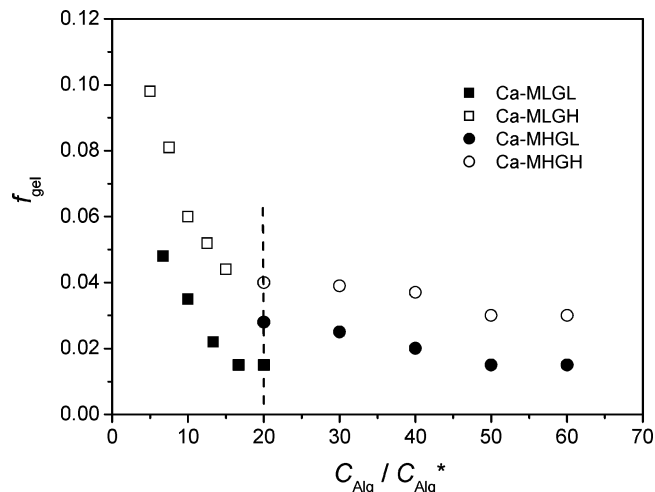
**Figure 8.** Shift factors  $\alpha_h$  (solid symbol) and  $\alpha_v$  (open symbol) for superposition of Ca-MLGH are plotted against  $\epsilon(p)/\epsilon(p_r)$  with indicated concentrations.

solutions was measured with an Ubbelohde viscometer at 25 °C. Because alginate is a polyelectrolyte and the gelation occurs in salt solutions, the ionic strength of the solution was adjusted to cover the vicinity of the corresponding gel point  $f_{gel}$  by adding NaCl into the solvent. Figure 9 illustrates the plots of the Fedors equation for the sample MHGH at several NaCl concentrations, and the estimated  $C_{Alg}^*$  value from the slopes is almost independent of the ionic strength within the experimental error. This appears to be due to the narrow range of the ionic strength tested for a given alginate sample, for we are only interested in the  $C_{Alg}^*$  value at the vicinity of the corresponding  $f_{gel}$ . The  $C_{Alg}^*$  values for the alginate samples so determined are listed in Table 3.

Therefore, all of the alginate concentrations used in the present study are beyond the corresponding  $C_{Alg}^*$  to ensure the chains contact in the solution. The  $f_{gel}$  data in Figure 3 were



**Figure 9.** Illustration of the Fedors equation for sample MHGH in NaCl solution with indicated ionic strength in the vicinity of the gel point.



**Figure 10.**  $C_{Alg}/C_{Alg}^*$  dependence of the gel point  $f_{gel}$  for indicated alginate samples.

**TABLE 3: Overlap Concentration for Alginate Samples at Certain Ionic Strength Range**

sample	ionic strength (mol/L)	$C_{Alg}^*$ (wt %)
MLGL	0.015–0.021	$0.29 \pm 0.01$
MHGL	0.039–0.053	$0.41 \pm 0.01$
MLGH	0.013–0.018	$0.10 \pm 0.01$
MHGH	0.016–0.036	$0.11 \pm 0.01$

replotted against  $C_{Alg}/C_{Alg}^*$  in Figure 10. We find that  $C_{Alg}/C_{Alg}^* = 20$  may be used as a criterion, below which the  $f_{gel}$  decreases dramatically with increasing  $C_{Alg}$  and beyond which the  $f_{gel}$  is almost a constant. Considering the essential meaning of  $C_{Alg}^*$  for the effective spatial volume of macromolecular chains, the present results support our suggestion that the gelation could be classified into two categories of growth and cross-link according to the molecular size in the starting solution. In the former, the cross-linking junctions are formed among small molecules, and relative alginate concentration  $C_{Alg}/C_{Alg}^*$  is lower, leading to higher  $f_{gel}$  values. In the latter, however, the gelation starts from larger alginate macromolecules with higher relative alginate concentration  $C_{Alg}/C_{Alg}^*$ , leading to an invariant  $f_{gel}$ . Apparently, the difference appears in the alginate

concentration dependence of  $f_{\text{gel}}$  and  $n$ . It is actually the behavior of molecular size dependence of the sol–gel transition.

## Conclusion

The present research on the sol–gel transition of aqueous alginate systems induced by in situ release of calcium cations illustrates that the critical exponents evaluated with Winter's criterion, the equilibrium modulus and zero shear viscosity, and the superposition curve agree with each other consistently. The critical exponents characterize the sol–gel transition into two categories as growth and cross-link according to the alginate molecular weight. For the alginate with low molecular weight, the critical exponents were almost universal, independent of its concentration, and close to the percolation prediction. For the alginate with high molecular weight, the critical exponents, however, changed with alginate samples and concentration, losing the universality. The relative alginate concentration  $C_{\text{Alg}}^*/C_{\text{Alg}}^*$  was found to serve as a criterion to divide these two transition mechanisms. We can image that this threshold value should vary with polymer species and cross-link mechanisms.

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