Viscoelastic and SAXS Investigation of Fractal Structure near the Gel Point in Alginate Aqueous Systems

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ABSTRACT: The sol–gel transition and the fractal structure of the gel have been studied for aqueous systems of alginates with different mannuronate/guluronate (M/G) ratios using viscoelastic and small-angle X-ray scattering (SAXS) measurements. The power law for the dynamic moduli, $G'(\omega) \sim G''(\omega) \sim \omega^n$, can be applied near the gel point, and the viscoelastic exponent n depends on the concentration and the M/G ratio of the alginate. The fractal dimension d_f can be obtained from the SAXS data. The value of d_f also depends on the concentration and the M/G ratio. The d_f in the G component-rich system is larger than that in the M component-rich system. That is, the gel structure in the former is denser than that in the latter. The relation between n and d_f is discussed in comparison with the theoretical consideration.

Introduction

Alginate is an anionic polysaccharide which is composed of 1–4-linked α-L-guluronic acid (G) and β-D-mannuronic acid (M) residues. It has been shown that there are three kinds of sequence blocks, GG, MM, and MG, in an alginate molecule and that the unperturbed dimensions of these blocks are in the order of MG block < MM block < GG block.[1,2] We also showed that the mean-square end-to-end distance per uronate residue for the G component is almost twice as long as that for the M component.[3] This suggests that the sequence block of the G residues is stiffer than that of the M residues.

It has also been known that the alginate aqueous system changes to a gel state from a sol state with increasing concentration of the polymer. The alginate concentration at the sol–gel transition point seems to be influenced by the M/G ratio of the system. Here the M/G ratio is the ratio of the mannuronate and the guluronate residue content in an alginate molecule. That is, it is likely that the difference in stiffness between the G block and the M block induces the influence of the M/G ratio on gelation and gel structure in the alginate aqueous systems.

The rheological characterization of gels has been mainly performed in cross-linking polymer systems, and this method is successful to obtain information on gelation and gel properties in the vicinity of the gel point.[4-8] At the gel point, the frequency dependence of the storage modulus G' and the loss modulus G'' can generally be represented by a power law over a wide frequency range, i.e.

$$G'(\omega) \sim G''(\omega) \sim \omega^n \qquad (1)$$

The viscoelastic exponent n can be related to the fractal dimension d_f of the gel systems, and the relation is theoretically discussed for gels which are composed of chemically cross-linked chains.[9,10] However, we can find no articles in which n is experimentally compared with d_f; there are certain difficulties in the measurement of d_f by SAXS during the chemical reaction (cross-linking) process. Since several hours are necessary to obtain d_f by the SAXS measurement, the situation of the system changes as the chemical reaction proceeds during the measurement. On the other hand, the above difficulties can be avoided in the physical gel systems.

Table I
Weight-Average Molecular Weight M_w and the M/G Ratio of the Alginate Systems

sample	M_w	M/G
AG–M1H	1.80×10^5	2.4
AG–G1H	1.85×10^5	0.53

In the present paper, we intend to discuss the relationship between the values of n and d_f near the gel point of the alginate aqueous systems, using viscoelastic and small-angle X-ray scattering (SAXS) measurements.

Experimental Section

Materials. The sodium alginates were purchased from Kimitsu Chemical Industries (Tokyo, Japan). Table I shows the weight-average molecular weight M_w and the M/G ratio of these alginates. The weight-average molecular weight was measured by means of a low-angle laser light scattering photometer (Chromatix, KMX6, λ = 6328 Å) with a 1 M NaCl aqueous solution at a scattering angle of ca. 5°. The specific refractive index increment dn/dc employed was a reported value of 0.163 mL g^{-1} at λ = 5460 Å.[11] The M/G ratio was determined using the method by Haug et al.[12] The alginate samples employed have almost the same molecular weights but different M/G ratios. These alginates were dissolved in 2% acetic acid aqueous solutions.

Measurements. Rheological properties were measured by means of a cone-plate type rheometer (Weissenberg rheogoniometer R18, Sangamo Controls, Ltd.) which was devised to prevent vaporization of water. The diameter and the cone angle were 7.0 cm and 1.77°.

SAXS was measured with a 6-m point-focussing SAXS camera at the High Intensity X-ray Laboratory, Kyoto University. The wavelength of the X-ray was 1.542 Å (Cu Kα radiation). The sample was contained in a cell with mica windows, and the path length of the X-ray in the cell was 1.5 mm.

Results and Discussion

Rheological Characterization near the Gel Point. Figure 1 shows the storage modulus G' and loss modulus G'' at 25 °C plotted logarithmically against angular frequency ω at various concentrations of the alginate AG–G1H aqueous systems. At a low concentration such as 1%, the system shows a viscoelastic liquid behavior, i.e., $G' \sim \omega^2$ and $G'' \sim \omega$. At the gel point, the relation between the dynamic moduli and ω can be expressed by eq 1. This relationship can be applied over 3 decades of ω for the 3% system, and the value of n is 0.55. A plateau region appears in G' at a relatively low frequency region for systems beyond 3%, and simultaneously G' exceeds G''. The slopes

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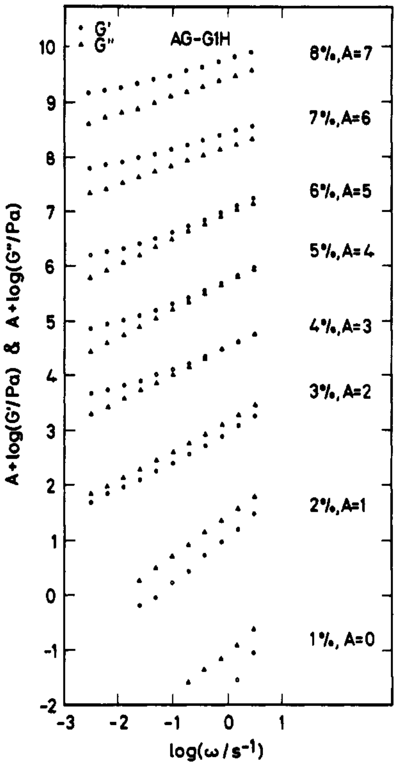

Figure 1. Storage G' and loss G'' moduli at 25 °C, strain amplitude of 0.1, plotted logarithmically against angular frequency ω at various concentrations of the alginate AG–G1H aqueous systems.

of log G'' vs log ω are ca. 0.50 for the 4% and 5% systems. Considering the idea that the storage and loss moduli are congruent $G' = G''$ and proportional to $\omega^{1/2}$ at the gel point,[13] the critical gel concentration range for the systems of AG–G1H can be estimated at 3–5%.

Figure 2 shows the G' and G'' plotted logarithmically against ω at various concentrations of the alginate AG–M1H aqueous systems. Equation 1 can be applied with a certain accuracy for the systems of 3–5% and 9–10%. For the systems of 3–5%, $G'' > G'$, and the values of n range from 0.84 to 0.77. On the other hand, G' is nearly coincident with G'' over a wide range of frequency and the values of n are 0.58 and 0.53 for the 9% and 10% systems. From these results, it is rather difficult to determine the gel point or the critical gel concentration range in the systems of AG–M1H. The above difference in gelation between the systems of AG–G1H and AG–M1H is likely to be attributed to the difference in the content of the G component. However, it should be noted that eq 1 can be applied for the systems of 3 or 5% for both alginate systems, though the values of n are different.

As stated above, the values of the viscoelastic exponent n range between 0.50 and 0.84. According to Scanlan and Winter, the values of n change in a wide range between 0.14 and 0.92 for various systems.[6] On the other hand, the classical theory for the gelation of polymeric systems (Flory,[14] Stockmayer,[15] and Zimm[16]) gives $n = 1$, and the percolation theory gives $n = {}^2/_3$ for the three-dimensional case.[17] Muthukumar showed that it is not so simple to compare the applicability of the classical theory and the percolation theory in the gelation of polymeric systems, because the exponent n depends significantly on the screening extent of the excluded-volume effect in relation with the fractal dimension of the system.[10] Consequently, the direct measurement of the fractal dimension at the gel point is essential for further consideration.

Estimation of the Fractal Dimension with SAXS. The fractal is defined as a homologous (or self-similar) structure in a space or a distribution of mass over a relatively wide range of space size. For a mass fractal, the scattering intensity I in SAXS is given by the power law relation[18–21]

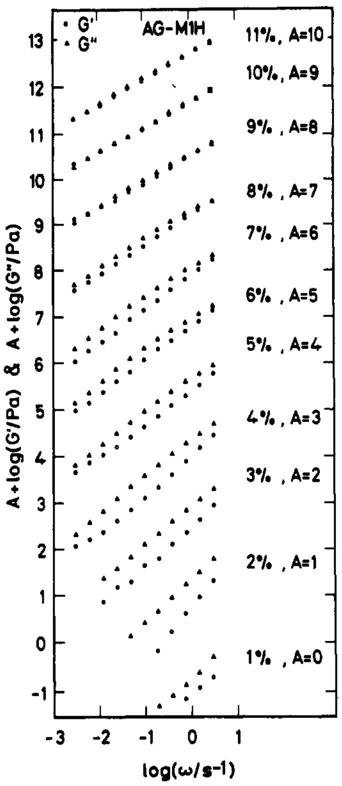

Figure 2. Storage G' and loss G'' moduli at 25 °C, strain amplitude of 0.1, plotted logarithmically against angular frequency ω at various concentrations of the alginate AG–M1H aqueous systems.

$$I \propto q^{-d_f} \quad (\text{for } qR \gg 1) \qquad (2)$$

Here d_f is the fractal dimension, q is the scattering vector given by $(4\pi/\lambda)\sin\theta/2$, where λ is the wavelength of the X-ray and θ is the scattering angle, and R is an average dimension of the structure or material. The allowed range of the fractal dimension is $1 < d_f < 3$ in the three-dimensional space. Figure 3 shows the logarithmic plots between I and q for the 3, 5, and 7% systems of AG–G1H. The relationship can be approximated by a straight line over a certain range of q (ca. 0.01–0.1 Å^{-1}) in each system. As the root-mean-square end-to-end distances of the alginate and other polysaccharides have been estimated at ca. 1000–1500 Å,[3,22] using these values for R, it turns out that the condition of $qR \gg 1$ is approximately satisfied, even if the molecules do not associate at the gel point. According to eq 2, the fractal dimensions can be obtained from the slopes of the straight lines, and they are 2.35 for the 3%, 2.05 for the 5%, and 1.88 for the 7% system. Figure 4 shows similar plots for the 3, 5, and 7% systems of AG–M1H. The fractal dimensions obtained are 1.71 for the 3%, 1.53 for the 5%, and 1.30 for the 7% system. The fractal dimensions for the systems of AG–G1H (G component-rich) are larger than those for the systems of AG–M1H (M component-rich). The fractal dimensions of the systems of AG–G1H increase with decreasing concentration, and the value of d_f is ca. 2.35 in the 3% system, which is near the value of 2.5 for the ordinary diffusion-limiting aggregation (DLA).[23,24] The DLA is an aggregate structure in which the growth probability of the aggregation is controlled only by diffusion. On the other hand, the values of d_f in the systems of AG–M1H are rather small and range from 1.3 to 1.7. Martin and Keefer showed

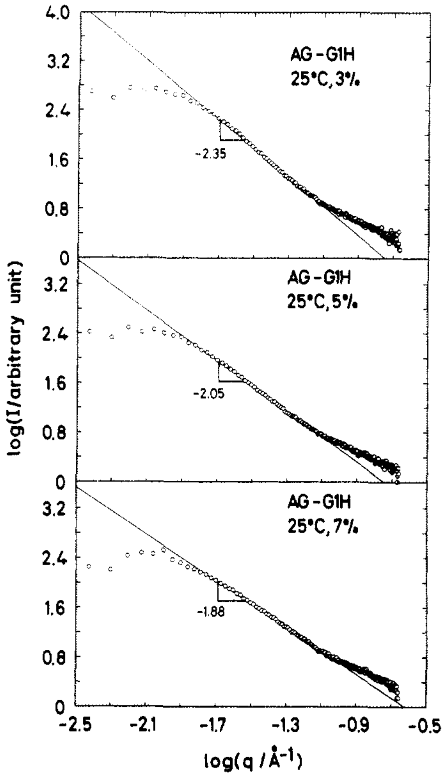

Figure 3. Logarithmic plots between I and q in the SAXS for the 3, 5, and 7% aqueous systems of AG–G1H.

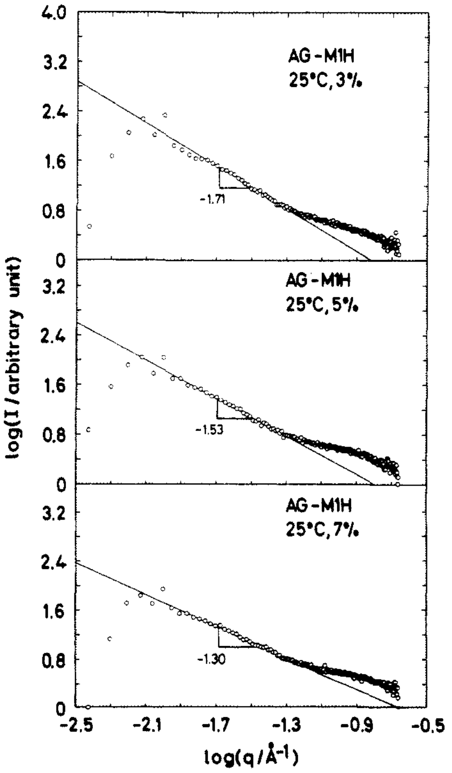

Figure 4. Logarithmic plots between I and q for the 3, 5, and 7% aqueous systems of AG–M1H.

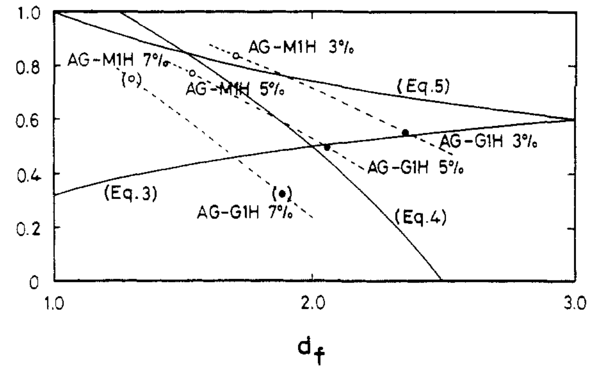

Figure 5. Theoretical relationship between n and d_f according to eqs 3–5 for d = 3. The experimental data for n vs d_f are also plotted. (●) AG–G1H; (○) AG–M1H.

the fractal structure for the d_f of 1.2–1.6 in the two-dimensional space, using a generalized DLA model (η model).[23,25] According to these considerations, the gel structure in the systems of AG–G1H is denser than that in the systems of AG–M1H. This is likely to be reflected in the fact that the alginate concentrations where G' exceeds G'' are 3–4% for the systems of AG–G1H and 9–10% for AG–M1H. The fractal dimension of 1.30 for the 7% system of AG–M1H is very similar to the value for the chitosan system reported in a previous paper.[26]

Relation between n and d_f. According to Muthukumar,[9,10] the relation between n and d_f near the gel point for a monodisperse system in which the excluded-volume effect is completely screened is given by

$$n = d_f/(d_f + 2) \tag{3}$$

With modification for the polydispersity of the cluster at the gel point, the relation becomes

$$n = \frac{d(d + 2 - 2d_f)}{2(d + 2 - d_f)} \tag{4}$$

for the system with a fully screened excluded-volume effect, where d is the space dimension. When the system is polydisperse and the excluded-volume effect is unscreened

$$n = d/(d_f + 2) \tag{5}$$

Figure 5 shows the theoretical relationship between n and d_f according to eqs 3–5 for d = 3. The experimental data for n vs d_f are also plotted in this figure for the systems of AG–G1H and AG–M1H at various concentrations from 3 to 7%. The comparison between the theoretical curves and the experimental data is not simple. From the rheological point of view, it is reasonable to consider that the 3 and 5% systems are near the gel point but the 7 and 9% systems exceed the gel point. When the data for the same concentration in the systems of AG–G1H and AG–M1H are linked as shown by the dotted lines, the relation between n and d_f seems to be approximately along (or parallel to) the theoretical curve using eq 4 and shifts in the direction of the theoretical curve using eq 5. That is, the relation n vs d_f shifts to the behavior of the unscreened excluded-volume effect from the screened excluded-volume effect with decreasing concentration of the alginate.[10,27]

By observing the data in Figure 5 from another point of view, we can see that in the data for the systems of AG–G1H are near the curve according to eq 3 and the data for the systems of AG–M1H are near the curve according to eq 5. Considering that the samples used in this study are natural polymers and are not very simple in structure and also that the theory may not be complete, the correspondence between the theories and the experimental data is rather good. However, at the present time, it appears very difficult to explain the relation in terms of microscopic or molecular parameters.

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