Stress Relaxation of Alginate Gels Crosslinked by Various Divalent Metal Ions

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(Received November 19, 1987)

Rheological properties of Alginate (Alg) gels were studied by measuring tensile stresses under small strains. The Alg gel rods were prepared in $CaCl_2$, $SrCl_2$, $BaCl_2$, and $Pb(NO_3)_2$ solutions in the range of 0.03—1.0 mol dm^{-3}. Their stresses showed long relaxation processes. By curve fitting method, equilibrium elastic moduli G_e, spontaneous elastic moduli G_e+G_r and relaxation times τ were obtained. The results G_e were independent of strains γ, and G_r and τ increased as increasing γ. The effects of Ca ion concentrations C_{Ca} on the elasticities were discussed by taking account of the ratio of Ca ion bindings obtained by dialysis equilibrium and that of junction formation obtained by circular dichroism. The values of G_e were analyzed by the theory of swollen gels. The number of the junctions was found to be constant in the region of $C_{Ca}>0.03$ mol dm^{-3}, and slight increases of G_e to be due to changes of the water content and the density of the Alg gels. The magnitudes of G_e and G_r depended on the kind of counterions, and decreased in the order, Ba- $\gg$ Ca- $>$ Sr- $>$ PbAlg; this was almost the same as that of the ion selectivities.

Alginate (Alg) is a major structural polysaccharide found in intercelluar substances of brown algae. They are gelled by the addition of divalent metal ions except for Mg^{2+} ions. The gelations result from the stackings of alginate chains intermediated by the ions.[1)] The interaction of Alg with them and the rheological properties of the gels such as rigidity and elasticity are dominated by the composition of the Alg, i.e., the ratio of β-D-mannulonate and α-L-guluronate, their block compositions and the kind of metal ions added.[2—4)]

Alginate and its gels are used widely as food additives and pharmaceutically as hemostats. The gels are examined with respect to their application to matrices of drug delivery systems[5)] and to the matrices of immobilized enzymes.[6)] These applications of Alg gels take advantage of the characteristics of the lyotropic gels. However, from the basic point of view, the gel properties have not been elucidated sufficiently. In the previous paper,[7)] effective charge densities of Alg were studied by a membrane potential method and the effects of sol-gel transition on them were reported. In this report, tensile stress relaxations of Alg gels were studied to elucidate their rheological characteristics, and the effects of the kind of metal ions present.

Experimental

Materials. Purified sodium alginate (NaAlg) was prepared from commercial NaAlg (Tokyo Kasei Kogyo Co., Ltd.) by dialyzing against distilled water for 3 d and by filtrating to remove insoluble substances, as described in the previous paper.[7)] The purified NaAlg was stored in a refrigerator after freeze drying. The weight average molar mass of NaAlg was determined to be $\bar{M}_w=1.32\cdot10^5$ g mol^{-1} by using a light scattering photometer LS-8 (Toyo Soda Manufacturing Co., Ltd., Japan). The composition of the NaAlg was analyzed by circular dichroism (CD),[8)] and ^{1}H NMR.[9)] The guluronate fraction F_G and the consecutive guluronate fraction F_{GG} were determined to be 0.37 and 0.28. All other reagents were of special grade. Distilled and deionized water was used for preparation of aqueous solutions.

Dialysis Equilibrium. NaAlg solutions (0.75 w/v%) were put into dialysis tubes (Seamless Cellulose Tubing, Union Carbide Corp.), which were dipped in $CaCl_2$ and $MgCl_2$ solutions in the range of 0.001—0.1 mol dm^{-3} in dialysis cells. They were shaken in a thermostated bath (25 °C) for 48 h which was long enough to attain equilibrium. The concentrations of Ca, Mg, and Cl ions in the outer solutions were determined by chelate titrations and Mohr method, respectively. From these results, amounts of Ca and Mg ions bound to Alg were determined.

Preparation of Alginate Gel Rods for Measuring Stress Relaxations. NaAlg solutions (1.2 w/v%) in straight Teflon tubes (length: 6.0 cm, diameter: 0.4 cm) were gelled by dipping in $CaCl_2$, $SrCl_2$, $BaCl_2$, $Pb(NO_3)_2$, and HCl solutions in the concentration range of 0.03—1.0 mol dm^{-3}. The gels obtained are denoted as Ca-, Sr-, Ba-, Pb-, and HAlg, respectively. To attain an equilibrium swelling state, the gels had to be matured for 7 d in these solutions, renewed once daily. The Alg gel rods were then dipped for not less than 9 d in these solutions which were kept at 4 °C to prevent rotting. Before the measurements of their tensile stress, the Alg gel rods were reequilibrated for 48 h at the experimental temperature (25 °C).

Preparation of Alginate Gel Membranes for Measuring Circular Dichroism. To obtain Alg gel membranes with flat surfaces, a freezing method was developed. NaAlg solutions (1.2 w/v%) were put into Petri dishes with flat bases and were frozen for 20—30 min in a freezing chamber (−3— −5 °C). The frozen samples thus obtained had smooth surfaces. Then, $CaCl_2$ solutions in the concentration range of 0.001—1.0 mol dm^{-3} cooled to about 4—6 °C were poured gently and slowly down the wall of the petri dishes. To obtain equilibrated Alg gel membranes, the $CaCl_2$ solutions were renewed once daily and held at 25 °C for 7 d. By adding HCl solutions instead of $CaCl_2$ solutions, Alg gel (HAlg) membranes were also prepared.

Measurement of Tensile Stress of Alg Gel Rod. The schematic diagram of the apparatus for measuring the tensile stresses of the gels is shown in Fig. 1. The Alg gel rod G was fixed by clamps A and B made of plastic plates with rough surfaces to prevent them slipping. They were suspended in electrolyte solutions in which the gel was equilibrated. The strains were imposed on the gels in steps and the

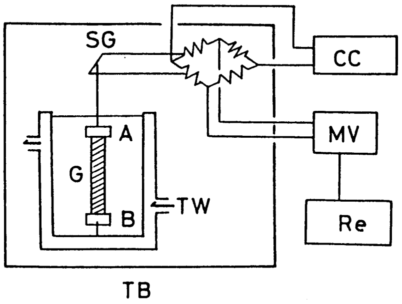

Fig. 1. Apparatus for measurement of gel tensile stress. A and B; clamp, G; Alg gel rod, SG; strain gauge, TW; thermostated water (25 °C), TB; air thermostated bath, CC; constant direct current source, MV; microvolt meter, Re; recorder.

tensile stresses σ were measured at 25 °C by strain gages SG (Shinkoh Communication Industry Co., Ltd.) connected to a constant direct current source CC (Model 691B, Metronix Corp. Tokyo) and a microvolt meter MV (Model AM-1001, Ohkura Electric Co.). The apparatus was set up in an air thermostated bath TB to eliminate temperature effects on the strain gages.

Measurement of Circular Dichroism. Measurements of circular dichroism CD were made on a CD spectropolarimeter (J-40S, NIHON BUNKOU) at 25 °C by using a 1 cm pathlength cell for NaAlg solutions. The CD of the Alg gel membranes were measured by putting them between perforated support film (PARAFILM, AMERICAN CAN COMPANY) and the thermostated 1 cm cell to prevent evaporation of water from the gels as much as possible and to maintain a constant temperature (25 °C).

Measurements of Densities and Water Contents of Alg Gels. The densities of the Alg gels were determined by a floating method, i.e., from the densities of mixed solvents composed of isooctane and carbon tetrachloride in which pieces of Alg gels were floated. The densities of the solvents were measured by densitometer (Anton Paar DMA602). The water content of the Alg gels were measured by the weight change after drying at 70 °C in vacuo for 10 h.

Theory and Method

Determinations of Elastic Modulus. An Alg gel rod elongated under a constant strain γ showes stress relaxation, which is expressed by the following equation as a function of time t,

$$\sigma = (G_e + G_r \exp(-t/\tau))\,\gamma \tag{1}$$

where G_e and (G_e+G_r) are the equilibrium elastic modulus and the spontaneous elastic modulus respectively and τ is the relaxation time. The time courses of the stress of an Alg gel rod elongated under constant strains γ by steps are shown in Fig. 2 as one example. After a first stress of Alg gel σ_1 resulting from the first strain γ_1 attains an equilibrium value, a second strain γ_2 is imposed at time t_2, and the same process is continued consecutively. Imposing the nth strain, the stress σ_n can be expressed by the following equation according to the superimposal principle,

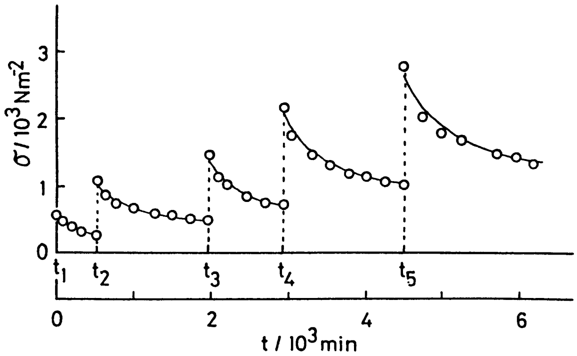

Fig. 2. Stress relaxation curve for CaAlg gel. Solid curves show the values calculated from Eq. 2 by curve fitting method. CaAlg was prepared in 0.3 mol dm^{-3} CaCl$_2$ solution. The value t_k shows time when kth strain is imposed.

$$\sigma_n = \sum_{k=1}^{n} \left\{ G_{ek} + G_{rk} \exp\left(-\frac{t-t_k}{\tau_k} \right) \right\} (\gamma_k - \gamma_{k-1}) \tag{2}$$

where a subscript k denote the values of the gel rod elongated by the kth strain γ_k. The t_1 and γ_0 values are 0. The kth strain γ_k is defined by

$$\gamma_k = (l_k - l_0)/l_0 \tag{3}$$

where l_0 is the initial length of Alg gel rod and l_k is that of the elongated gel by kth strain.

Determination of Counterion Binding Parameters. Under equilibrium conditions, Donnan equilibrium is maintained between the free ions in an alginate phase in a dialysis tube (α phase) and ions in a bulk solution (β phase).[10] Two kinds of counterions occur in both phases, i.e., one was Na ions resulting from original sample NaAlg and the other was metal ions M from added electrolytes. In this report, bounding characteristics of the latter counterions M are discussed. Approximating the activity coefficients of the free counterions and co-ions are unity, the concentration of the free counterion in α phase $C^{\mathrm{f}}_{\mathrm{M}\alpha}$ is obtained by the following equation,

$$C^{\mathrm{f}}_{\mathrm{M}\alpha} = C_{\mathrm{M}\beta}\,(C_{\mathrm{A}\beta}/C_{\mathrm{A}\alpha})^{z_\mathrm{M}} \tag{4}$$

where $C_{\mathrm{M}\beta}$ is the concentration of the added counterion M in the β phase, $C_{\mathrm{A}\alpha}$ and $C_{\mathrm{A}\beta}$ are those of the co-ion (Cl$^-$) in the α and β phases, and z_M is the algebraic charge number of the counterion M. Bounding amounts of the counterions per unit weight of Alg b_M are obtained by

$$b_\mathrm{M} = V_\alpha (C^{\mathrm{T}}_{\mathrm{M}\alpha} - C^{\mathrm{f}}_{\mathrm{M}\alpha})/w \tag{5}$$

where $C^{\mathrm{T}}_{\mathrm{M}\alpha}$ is the total concentration of the counterion in the α phase, and w and V_α are the weight of Alg in the α phase and the volume of the α phase. When the bindings are Langmuir type isotherms, the relation between $1/b_\mathrm{M}$ and $1/C^{\mathrm{f}}_{\mathrm{M}\alpha}$ is linear as expressed by the following equation

$$1/b_\mathrm{M} = 1/b^{\mathrm{s}}_\mathrm{M} + 1/(b^{\mathrm{s}}_\mathrm{M} K\, C^{\mathrm{f}}_{\mathrm{M}\alpha}) \tag{6}$$

and b_M^s and K are the saturated binding amounts and the binding constant.

Results

Counterion Binding Characteristics of Alginate. Binding amounts b_M mol g^{-1} of Ca and Mg ions to Alg at 25 °C were obtained from dialysis equilibria by using Eq. 5 and are shown in Fig. 3 as a function of the free counterion concentrations $C_{M\alpha}^f$. They showed Langmuir type isotherms and linear relations between $1/b_M$ and $1/C_{M\alpha}^f$ held. By Eq. 6, b_M^s/mmol g^{-1} and K/mol dm^{-3} were obtained; for Ca ion, $b_M^s=2.25$ and $K=3.60$, and for Mg ion, $b_M^s=2.27$ and $K=0.584$, respectively. The binding amounts of the Ca ions were saturated in the region of $C_{Ca\alpha}^f>0.008$ mol dm^{-3}. Since the values $C_{Ca\alpha}^f/C_{Ca\beta}$ were almost 1.0 in the region $C_{Ca\alpha}^f>0.008$ mol dm^{-3}, the saturated binding of Ca ions was attained in the region of the concentration of the bulk solutions $C_{Ca\beta}>0.008$ mol dm^{-3}. Hereinafter, the counterion concentrations in the β phase $C_{M\beta}$ are designated by C_M, as well as the concentrations of the bulk solutions used for the preparation of the Alg gels.

CD Spectrum of Alg Gels Different in Ca Ion Concentrations. The characteristic changes in CD accompanied by the gelation of Alg have been reported in the literature and the magnitudes of the changes have been attributed to the formation of junctions between the guluronate blocks (G block) induced by divalent metal ions such as Ca ion.[11,12] To investigate the effects of Ca ion concentrations on the junction formation by the CD method, attempts were made to prepare CaAlg gel membranes in various Ca ion concentrations ($C_{Ca}=0.001$—1.0 mol dm^{-3}). In the region of $C_{Ca}<0.007$ mol dm^{-3}, the gel membranes could not be formed or were too weak to set between the cell and the perforated support film for measuring CD spectrum. The CD spectra of CaAlg gel membranes prepared in the region $C_{Ca}>0.007$ mol dm^{-3} were measured at 25 °C. Figure 4 shows the ellipticities $[\theta]$ of NaAlg (0.6 w/v%) and those of a CaAlg ($C_{Ca}=1.0$ mol dm^{-3}) and a HAlg ($C_H=1.0$ mol dm^{-3}) gels. The CD spectrum of NaAlg showed a negative peak at 215 nm, but that of CaAlg gel showed the negative peak at about 219 nm and a positive one at 203 nm. The spectrum of HAlg gel was a negative broad peak and was found to be different from that of CaAlg.

On increasing the binding ratio of Ca ions to the carboxylic groups of Alg, the junctions, i.e., dimers between the G blocks and its aggregations, were reported to increase and the magnitudes of the peaks at 203 nm $[\theta]_{203}$ to increase.[12] Morris et al. took the difference values between the values $[\theta]$ of NaAlg and Ca-NaAlg as a measures of the formation of the junctions. The relative values of the magnitudes of the peaks at 203 nm and at about 219 nm $[\theta]_{203}/[\theta]_{219}$ can also be taken as this measure. Since the Alg gel mem-

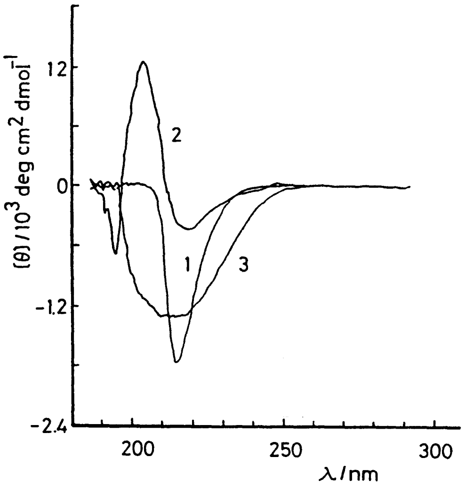

Fig. 4. C.D. spectra of Alg solution (NaAlg) and gels (Ca- and HAlg). 1; NaAlg (0.6 w/v%), 2; CaAlg ($C_{Ca}=1.0$ mol dm^{-3}, $L=0.045$ cm, $W_{H_2O}=0.87$), 3; HAlg ($C_H=1.0$ mol dm^{-3}, $L=0.04$ cm, $W_{H_2O}=0.96$). L is a thickness of a Alg gel membrane.

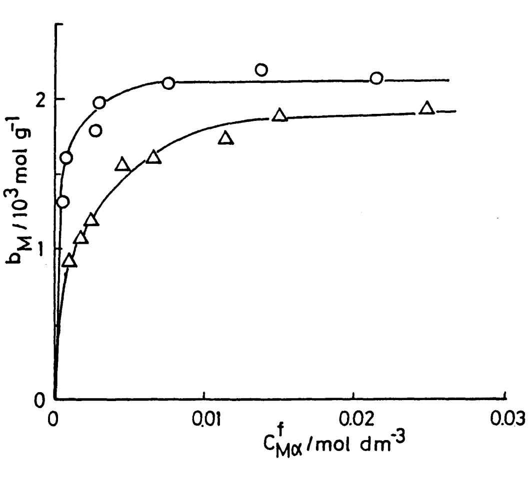

Fig. 3. Counterion binding amounts b_M vs. counterion concentrations $C_{M\alpha}^f$. Ca; ○, Mg; △.

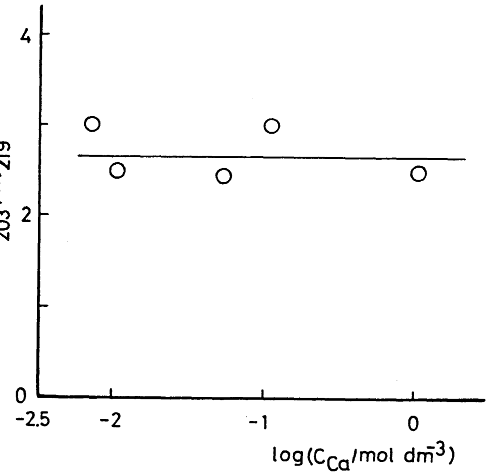

Fig. 5. Relative C.D. values $[\theta]_{203}/[\theta]_{219}$ of CaAlg prepared in various Ca concentrations C_{Ca}.

branes prepared in various Ca concentrations were different in water content and thickness, the relative values are more appropriate values. The values $[\theta]_{203}/[\theta]_{219}$ of CaAlg gel membranes prepared in the region of $0.007<C_{\mathrm{Ca}}/\mathrm{mol\,dm^{-3}}<1.0$ are shown in Fig. 5 as a function of C_{Ca}. They were found to be almost constant above the concentration at which the binding amounts of Ca ions were saturated. Under unsaturated conditions of Ca ion binding, the ratios of the junctions were reported to depend on the binding ratios of the Ca ions.[12] If CD of CaAlg gels prepared in the conditions of the unsaturated Ca ion bindings could be measured, the values $[\theta]_{203}/[\theta]_{219}$ should decrease with decreasing C_{Ca}.

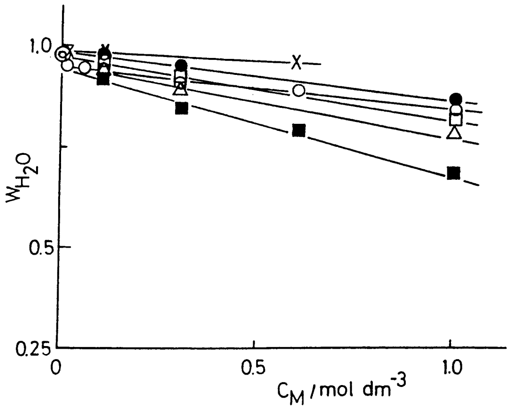

Fig. 6. Effects of counterion concentrations C_M on water contents W_{H_2O} of various Alginate gel and sol. Alginate in sol states: Na; ◎, Mg; ●. Alginate in gel state: Ca; ○, Sr; □, Ba; △, Pb; ■, H; ×.

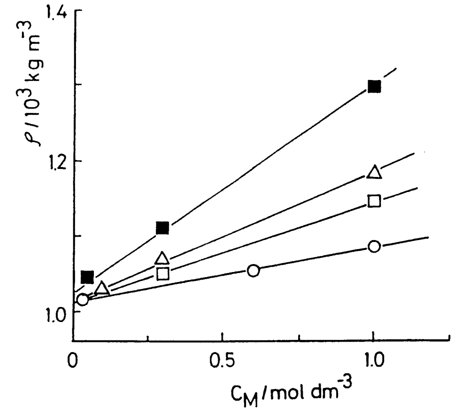

Fig. 7. Effects of counterion concentrations C_M on densities of Alginate gels ρ. Ca; ○, Sr; □, Ba; △, Pb; ■

Water Contents and Densities of Alg Gels. The water contents W_{H_2O} and densities ρ g cm^{-3} of various Alg gels prepared from NaAlg solutions (1.2 w/v%) are shown in Figs. 6 and 7 as a function of the concentration C_M of the solutions. W_{H_2O} decreased and ρ increased linearly with increasing C_M in the experimental range of $C_M<1.0$ mol dm^{-3}, and they depended on the kind of counterions. The order of magnitude of the former was H->Mg->Ca->Sr->Ba->PbAlg, and that of the latter was Pb->Ba->Sr->CaAlg. The smaller the water contents, the bigger became the densities.

Effects of Strains and Ca Ion Concentrations on Stress Relaxation of Alg Gel Rod. The time courses of stress of CaAlg gel rods were measured by imposing strains by steps. Figure 2 shows the results for CaAlg gel prepared in a $CaCl_2$ solution (0.3 mol dm^{-3}). The stress under each strain showed a long relaxation and attained an equilibrium state after above 20 h. From the time courses of the stress under strains, the elastic moduli G_{ek}, G_{rk} and the relaxation time τ_k can be obtained from Eq. 2 by using a curve fitting method. These values obtained by analyzing the time courses of stress measured for more than 20 h were independent of the measuring times. Accordingly we accepted these values as the true ones. The solid curves in Fig. 2 show the results calculated from Eq. 2 by using these elastic parameters. They are in good agreements with the experimental results. The values G_{ek}, G_{rk}, and τ_k obtained under the kth strain γ_k are

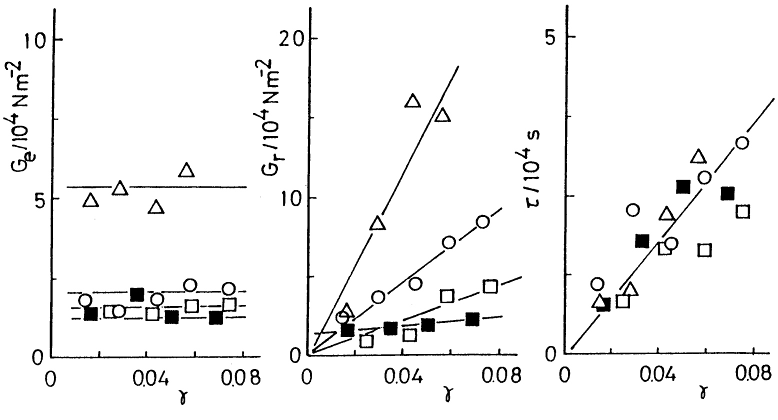

Fig. 8. Effects of strains on elastic moduli G_e, G_r, and relaxation time τ for Alg gels prepared by various divalent counterions. Ca; ○, Sr; □, Ba; △, Pb; ■. Alg gels were prepared in 0.3 mol dm^{-3} solutions.

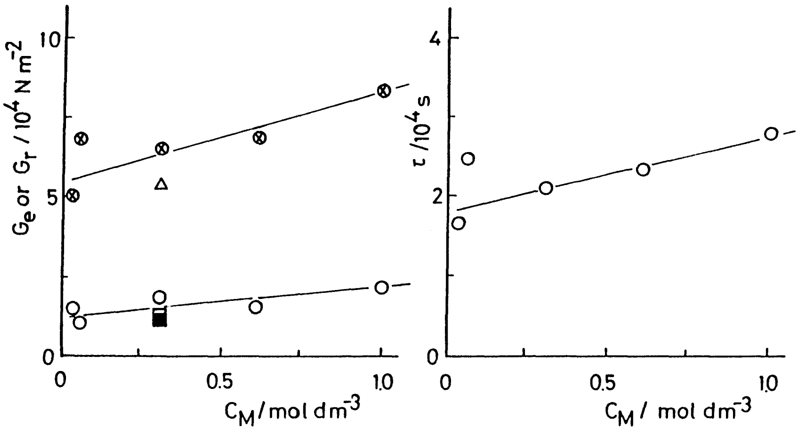

Fig. 9. Effects of counterion concentrations C_M on elastic moduli G_e, G_r, and relaxation time τ at constant strain (γ=0.05). CaAlg: G_e and τ; ○, G_r; ⊗. For Sr-, Ba-, and PbAlg, values G_e (C_M=0.3 mol dm^{-3}) are shown. Sr; □, Ba; △, Pb; ■.

hereinafter designated by G_e, G_r, and τ, i.e., the subscript k is deleted for simplicity. Figure 8 shows the results G_e,G_r, and τ of CaAlg prepared in 0.3 mol dm^{-3} $CaCl_2$ solutions, as a function of strain γ. The values G_e were almost constant in the small strains, but the values G_r and τ increased with increasing γ. The same tendencies were found in the results of CaAlg gels prepared from other $CaCl_2$ solutions at different in concentrations. The diameters and the lengths of the Alg gel rods were measured before and after the stress measurements, and the volume changes were found to be negligible in the experimental region of γ<0.08. Figure 9 shows the values G_e, G_r, and τ of CaAlg gels obtained at γ=0.05 as a function of the concentrations of $CaCl_2$ solutions in which CaAlg gels were prepared. These values were found to increase slightly as increasing C_{Ca} (>0.03 mol dm^{-3}). The increasing rates of G_r and τ were more than those of G_e.

Effects of the Kind of Counterions Used as Crosslinking Agents. The time courses of stress of various Alg gel rods prepared in $BaCl_2$, $SrCl_2$, and $Pb(NO_3)_2$ solutions (C_M=0.3 mol dm^{-3}) were measured. The values G_e, G_r and τ were obtained in the same manner as in the case of CaAlg gels and are shown in Figs. 8 and 9 together with the results for CaAlg. The results G_e of Ba-, Sr-, and PbAlg were independent of γ as well as CaAlg, and their values G_r and τ increased with increasing γ. The values G_e and G_r were found to depend significantly on the kind of counterions, and decreased in the order, Ba-≫Ca->Sr->PbAlg. However, their values for τ did not show significant differences. By adding H ions, Alg was gelled but the gels were too brittle to measure the stress.

Discussion

Estimation of Junction Densities. The stress relaxations of Alg gels are considered to be composed of two components, i.e., (1) a time independent component which is the stress resulting from the permanent junctions, and (2) the time dependent component which is associated with the reorientation of the network from unstable to stable and the rupture of weak junctions. The time independent component in small strains has been reported to be analyzed by the theory of rubber elasticity although the deviations from the ideal rubber elasticity were found at high strains.[13] It is used to give reasonable numbers of junctions per a molecule.[14,15]

Flory developed the theory for the stress of swollen gels by assuming an ideal rubber and a constant volume. The stress σ_e is expressed by the following equation,[16]

$$\sigma_e = RT\, v_p^{-2/3} w_p \left(\frac{1}{\bar{v}_g M_c}\right)\left(1-\frac{2M_c}{\bar{M}}\right)\left(\alpha-\frac{1}{\alpha^2}\right) \qquad (7)$$

where $\bar{M}$ and M_c are number averaged molar mass of polymer and that of the polymer chain interposed by adjacent crosslinks, α is the deformation of the network structure by an elongation ($\alpha=l/l_0=1+\gamma$), v_p and w_p are the volume fraction and the weight fraction of the network polymer in a gel, and $\bar{v}_g$ is a specific volume of the gel. Alg gels showed negligible volume changes due to elongations. The values M_c of Alg gels can be obtained by Eq. 7 from the results σ_e under small strains. The values v_p of Alg gels were obtained by the following equation

$$v_p = 1 - v_w(1-w_p)/\bar{v}_g \qquad (8)$$

where v_w is specific volume of water.

Figure 10 shows the values M_c and the numbers of the junction per alginate molecule $\bar{M}/M_c$ of CaAlg gels as a function of the concentration of Ca ions. They were obtained from the results σ_e of CaAlg gels elongated at γ=0.03 and 0.05, and were found to be independent of the strains (γ<0.05) and the concentrations of Ca ion in the experimental region (0.03<C_{Ca}/

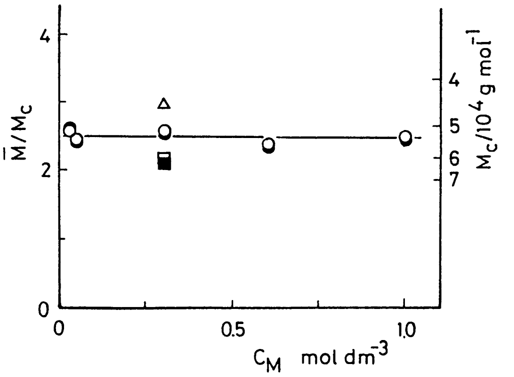

Fig. 10. Effects of counterion concentrations C_M on molar mass per cross-linked unite M_c and number of cross-linked unites per a molecule $\bar{M}/M_c$ under different strains $\gamma=0.03$ and 0.05. CaAlg: ●; $\gamma=0.03$, ○; $\gamma=0.05$. For Sr-, Ba-, and PbAlg, results under $\gamma=0.05$ and $C_M=0.03$ mol dm^{-3} are shown. Sr; □, Ba; △, Pb; ■.

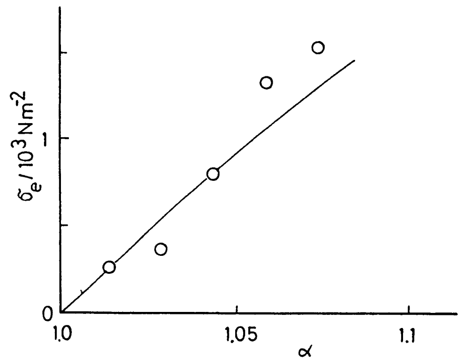

Fig. 11. Equilibrium stress σ_e vs. elongation α for CaAlg (C_M=0.3 mol dm^{-3}). ○; Experimental results. Solid curve shows theoretical values calculated from Eq. 7.

mol dm^{-3}<1.0). In these calculations, the number averaged molar mass of Alg $\bar{M}$ was approximated to be equal to the weight average molar mass obtained by the light scattering method. The mean values M_c and $\bar{M}/M_c$ were $5.2\cdot10^4$ g mol^{-1} and 2.5. From these results, it can be concluded that during stress relaxation, Alg chains deform from unstable elongated network structures to stable ones without altering the numbers of the junctions in small strains. The slight increase of G_e shown in Fig. 9 is not attributable to the change of the numbers of the junction but to that of the water content and the density of the Alg gels shown in Figs. 6 and 7. Figure 11 shows the calculated values σ_e of CaAlg (C_{Ca}=0.3 mol dm^{-3}) from Eq. 7 as a function of α. They are in good agreement with the results in the small α region.

In the concentration region of C_{Ca} $(=C^f_{Ca\alpha})>0.008$ mol dm^{-3}, the binding of Ca ions to Alg and the junction formation were saturated as shown in Figs. 3 and 5. However, in the region of $C_{Ca}<0.03$ mol dm^{-3}, the CaAlg gels were so weak that the elasticities could not be measured. From these results, free Ca ions in the region of $0.008<C_{Ca}/\text{mol dm}^{-3}<0.03$ are considered to strengthen the junctions of the Alg gels, i.e., weaker junctions, such as dimers, aggregate further and grow into strong junctions. The contributions of the former to the elasticities of the gels should be much smaller than those of the latter. The aggregation of the dimers might result from the decrease of electrostatic repulsive force between Alg molecules due to the increase of shielding effects and the decrease of osmotic pressure with the increase of the free Ca ions. These effects also affect the water content W_{H_2O} and the density ρ of CaAlg gels. In the region of $C_{Ca}>0.03$ mol dm^{-3}, although the number of junctions formed by the aggregation is held constant, the values G_e, G_r, and τ are considered to increase with increasing C_{Ca} due to the effects of the changes of W_{H_2O} and ρ.

Segeren et al.[13] reported the value M_c of CaAlg gel to be $1.22\cdot10^4$ g mol^{-1} which is about 1/4 of our result. Comparing their Alg sample with ours, the molecular weight of theirs is almost equal to ouurs, but the fraction of guluronate in their sample is 0.714 which is more than twice as much as ours. The values M_c were found to depend significantly on the fraction of guluronate.

Effects of Counterion Species on the Stresses of Alg Gels. Figure 10 shows also the values M_c and M/M_c of Ba-, Sr- and PbAlg gels prepared in 0.3 mol dm^{-3} solutions. The results of M_c/g mol^{-1} and $\bar{M}/M_c$ were $4.5\cdot10^4$ and 2.9 for BaAlg, $6.0\cdot10^4$ and 2.2 for SrAlg, and $6.0\cdot10^4$ and 2.2 for PbAlg. The values $\bar{M}/M_c$ of Alg gels were found to vary slightly with the counterion species in the range of 2.2—2.9. As shown in Fig. 8, it is interesting that G_e and G_r of Alg gels are dependent on the kinds of counterions but their τ values are almost the same. The differences in these elastic properties of Alg gels formed by various divalent counterions can be explained by the following two reasons: (1) The junctions intermediated by these counterions differ in their strength, i.e., the contributions to the elastic moduli depend on the kind of divalent counterions. (2) All the guluronate blocks (G-blocks) can not be used for the formations of the crosslinks, and the ratios of the G-blocks used for the junctions differ by the kind of divalent counterions.

O. Smidrod et al. showed that on increasing the fraction of guluronate in Alg the selectivities for divalent ions became clear and decreased in the order, $Ba^{2+}>Sr^{2+}>Ca^{2+}\gg Mg^{2+}$.[4] The magnitudes of G_e of Alg gels decreased in the order, Ba->>Ca->Sr->PbAlg as shown in Fig. 8. BaAlg showed the maximum values in both properties. Although the orders of Ca and Sr are different between the elasticity and the selectivity, the difference in elasticities of Ca- and SrAlg was slight. MgAlg did not gell and the elasticity should be 0. Then, it can be summarized that the bigger are the selectivities, the bigger are the elasticities.

Guluronic units in the G-blocks take 1C conformations and form cavities with very hydrophilic inner surface in which the closest distance between the carboxylate groups is 4.7—5.7 A.[17] The junctions of Alg gels are formed by the stackings between the G-blocks intermediated by divalent counterions, which are efficiently coordinated by both carboxylate groups on the inner surface and oxygen atoms of saccharide rings. Taking the hydrophilicity of the cavities in considerations, the stackings between the G-blocks can be intermediated by hydrated counterions. The radii of hydrated ions r_i have been studied by various methods. We discuss qualitatively the relation between G_e of Alg gels and r_i of hydrated ions used for the gelation. The values r_i obtained by Stokes are r_{Mg}=4.4, r_{Ca}=4.2,r_{Sr}=4.2, r_{Ba}=4.1, and r_{Pb}=3.9 Å, respectively.[18] BaAlg possessed the maximum G_e. The size of hydrated Ba ions is considered to be the most suitable for intermediating the stackings of the G blocks and for forming stable junctions. As r_i of counterions are apart from r_{Ba}, weaker junctions are formed. Since r_{Mg} is too large to form stable junctions, Alg can not be gelled by Mg ions.

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