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Gelation Mechanism of *κ*- and *ι*-Carrageenan Investigated by Correlation between the Strain−Optical Coefficient and the Dynamic Shear Modulus

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ABSTRACT: The temperature and frequency dependence of the dynamic shear modulus, strain−optical coefficient, and the optical transmission of *κ*- and *ι*-carrageenan aqueous solutions were measured in order to clarify the gelation mechanism. The growing of the gel network and the effect of cation species (K, Cs, and Ca) and the amount of added KCl are discussed on the basis of the correlation between the shear modulus and strain−optical coefficient. For all samples, these correlations can be described by a power function in the low-temperature region in the gel state. The exponent can be interpreted as a characteristic parameter reflecting the growing process of the gel network. We found two groups in terms of the value of the exponent. In the case of 2.0 wt % (high polymer concentration) K-form and Cs-form *κ*-carrageenan, the exponent is much higher than unity, but in the case of 1.0 wt % K-form (low polymer concentration) *κ*-carrageenan with added KCl and 2.0 wt % K-form *ι*-carrageenan, it is close to unity. For the former group, the stress required to induce the unit orientation increases, while for the latter group it does not increase much with decreasing temperature. In other words, the structure inside cross-link region changes markedly during the growing process of gel network only for the former group. We concluded that increasing schemes of the number of aggregated helical molecules during the gel growing process strongly depends on the cation species and carrageenan type.

1. Introduction

Carrageenans are natural polysaccharide extracted from agar. Their primary structures are based on an alternating disaccharide repeating unit of 1,3-linked *β*-D-galactose and 1,4-linked 3,6-anhydro-α-D-galactose. They are well-known as gelling agent in food industries. These aqueous solutions with specific cations form physically cross-linked thermoreversible polyelectrolyte gels.

One of the most interesting features that has attracted many researchers is that macroscopic properties of carrageenan gel are affected by the concentration and species of cations. Numerous experimental studies on the cation effects on macroscopic properties of the gels have been presented.[1−3] In terms of the effect on gelation, monovalent alkali metal ions are classified into two groups.[4] One group includes cations such as potassium, rubidium, and cesium, which strongly promote the gelation of *κ*-carrageenan. The other group includes cations such as sodium and lithium, which scarcely promote the gelation. The strength of the promoting effects of divalent cations such as calcium, magnesium, and strontium is intermediate between that of the two groups.[4]

Many studies on gelation mechanism have been performed over the past 30 years using various methods.[5−11] A commonly accepted model of the gelation mechanism is as follows. In the first step, temperature-induced coil−helix conformational transition occurs. Next, the helices aggregate. This aggregation forms a physical cross-link, leading to a macroscopic three-dimensional network. There is still a matter of controversy on the detailed mechanism of the gelation and the structure of the cross-link and the branching of carrageenan systems. Especially, the coil−helix transition has been studied in most detail. Optical rotation studies showed the temperature-induced coil−helix transition and the effect of cations.[4,12−14] X-ray diffraction studies showed that in concentrated solution 3-fold right-handed double helices are formed.[15,16] In contrast, a single helix model was proposed by Smidsrød et al.[17−19] The single- or double-helical molecules aggregate at high ionic strength, as found by using light scattering[20−23] and osmometry.[24]

The question of whether carrageenan forms single or double helices led also to debates on the structure of branching and cross-link points. The structure of the branching and the cross-link points are essential for the macroscopic properties of carrageenan gels. In this study, we focus particularly on the formation of gel network by lowering temperature below the gelation temperature, because this gives physical insight into the cross-linking mechanism as we show in the section 4. In this study, we have developed the apparatus for the measurement of dynamic viscoelasticity and strain−optical coefficient on the growing process of gel network. The temperature dependence of the dynamic shear modulus, the strain−optical coefficient, and the optical transmission for *κ*- and *ι*-carrageenan aqueous solutions were measured. We obtained detailed information on the gelation mechanism, especially the gel network structure, structure of the cross-link, and the optical anisotropy of polymer chain, and the cross-link by using the correlation between the shear modulus and the strain−optical coefficient.

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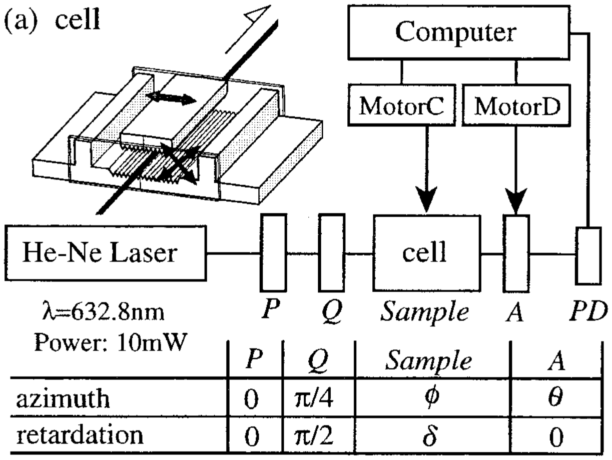
Table 1. Molar Ratio of Cation Content in the Purified Samples to the Sulfur Content (in %)[a]

	sodium	potassium	calcium	cesium
K-form	<0.01	94.46	0.50	5.03
Cs-form	<0.01	4.23	0.10	95.67
Na-form	99.41	<0.01	0.43	0.15
Ca-form	2.23	0.77	86.68	10.32

[a] The ratio for Cs is calculated by subtraction of the other ratios for Na, K, and Ca estimated by ion chromatography from total.



	P	Q	Sample	A
azimuth	0	π/4	φ	θ
retardation	0	π/2	δ	0

Figure 1. Schematic diagram of the apparatus for the strain−optical coefficient and the optical transparency. P is the polarizer, Q the quarter wave plate, A the analyzer, and PD the photodiode. The sinusoidal oscillatory shear deformation is controlled by motor C. The azimuth of the analyzer is controlled by motor D, and the intensity is detected by the photodiode PD.

2. Experiments

2.1. Samples. κ- and ι-carrageenan from Eucheuma cottonii (lot no. 54H0504) were purchased from Sigma Chemical Co. Ltd. The aqueous solutions were prepared by dissolving for 2 weeks. We refined the potassium, sodium, calcium, and cesium-form κ- and ι-carrageenan. Its aqueous solution was purified by dialysis, deionized by passage through Amberlite IR-120 (H^+) cation-exchange resin, and neutralized with KOH, NaOH, CsOH, and $Ca(OH)_2$ aqueous solutions for each cation-form solution and then freeze-dried. The ratio of each cation content in the purified samples to sulfur content is listed in Table 1. The cation content was estimated by ion chromatography, and the sulfur content was estimated by inductively coupled plasma spectrometry.

2.2. Apparatus. The schematic diagram of the apparatus for optical measurement is shown in Figure 1. The light source was linearly polarized He−Ne laser working at 632.8 nm and delivering a power of 10 mW. After passing through the sample, the circularly polarized light becomes elliptically polarized. If the azimuth of analyzer A is perpendicular to that of the polarizer P, transmitted light intensity I through this system is given by

$$I = I_0 \sin^2\left(\frac{\Gamma}{2}\right), \quad \left(\Gamma = \frac{\Delta n d \pi}{\lambda}\right) \tag{1}$$

where Δn is birefringence, I_0 the transmitted intensity when retardation Γ is equal to π, d the optical path length, and λ wavelength. When there is no deformation, Γ should be zero, because the polymer chain orientation is random and isotropic. In this case, according to eq 1, I is expected to be zero. However, in this study, we found that I without deformation is not zero and varies during gelation.

It is important to note that there are three possible origins that induce the change in the transmitted light intensity I during the sol−gel transition. The first is the change in retardation of the sample due to the deformation, the second is the change in azimuth of the sample which is strongly affected by the deformation of the sample, and the third is the change in turbidity of the sample. The two former origins are induced by deformation, but the latter one is not related to deformation. Therefore, it is not possible to obtain the actual retardation of the sample from eq 1.

To obtain the actual retardation of the sample, we used the continuously rotating analyzer method to distinguish the three origins described above, as shown in Figure 1. By using this system, the total transimitted intensity $I(\theta)$ is given by the following equations: where θ is azimuth of analyzer, δ_s is

$$I(\theta) = I_a\left(\frac{1}{2} + \alpha \sin(2\theta + \beta)\right), \quad \alpha = \frac{1}{2}\sin \delta_s, \quad \beta = 2\phi_s, \quad \delta_s = \frac{2\pi d}{\lambda}\Delta n \tag{2}$$

retardation of the sample, ϕ_s is the azimuth of the sample, and I_a is the average transmitted light intensity. I_a is inversely proportional to the optical path length d and is proportional to absorbance coefficient and scattering. We define the normalized transmission intensity I_T as

$$I_T \equiv \frac{I_a}{I_{a,water}} \tag{3}$$

where $I_{a,water}$ is average transmitted intensity when water is used as a reference sample. Finally, we can determine δ_s, ϕ_s, and I_T individually using eqs 2 and 3 with the measurement of angular dependence of transmitted intensity $I(\theta)$.

The depolarization effect due to scattering is much smaller than the birefringent effect, which was confirmed by the experiment with no deformation.

We used the cell with ridges on the surface in order to prevent the sample from slipping (Figure 1a). The optical path length was 40 mm. The change in the intensity due to the optical rotation during conformational transition was much smaller than the change in the intensity due to the birefringence.

It was found that Δn is not constant but depends on position in the cell. This indicates that the strain $\Delta\gamma$ is not constant in the cell, depending on position, because it is reasonable to consider that the value of $\Delta n/\Delta\gamma$ of the same gel structure is constant at any place in the cell. To obtain the actual retardation, we used the following method. First, the distribution of the Δn in the cell was measured, and the distribution of the relative value of strain was obtained. The absolute amplitude of the strain in each location was calculated by the displacement of the upper plate of the cell. Finally, $\Delta n/\Delta\gamma$ was obtained. The strain−optical coefficient with sinusoidal deformation is calculated from the ratio of the amplitudes and phase angles. The amplitude of the strain was 0.0125, which is small enough to keep linearity as shown in Figure 2.

Viscoelastic measurements were made using a custom-built apparatus to investigate the phenomena with exponential changes in modulus. We modified Rheolograph GSA (Toyoseiki-Seisakusyo Co. Ltd.) in order to shift the range of modulus to lower. The schematic diagram of the apparatus for viscoelastic measurements is shown in Figure 3. This apparatus can cover a wide modulus range of 6−7 decades with a concentric cylindrical cell. The outer diameter of the cell is 20 mm, and the gap is 1 mm. The amplitude of strain is 0.025 for the viscoelastic measurement.

All the measurements were performed under the same thermal conditions. The sample was cooled from 60 to 2 °C at a rate of 0.5 °C/min, and kept at 2 °C for 120 min, and then heated from 2 °C at a rate of 0.5 °C/min.

3. Results

The temperature dependence of the dynamic shear modulus, G' and G'', the optical transmission, I_T, and the strain−optical coefficient, $\Delta n/\Delta\gamma$, for 2.0 wt % Cs, K, Na, Ca-form κ- and ι-carrageenan solutions without

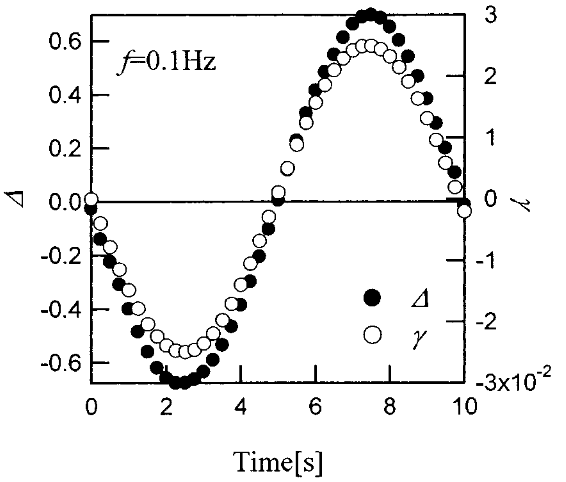


Figure 2. Time dependence of the retardation Δ and the strain γ on the sinusoidal deformation.

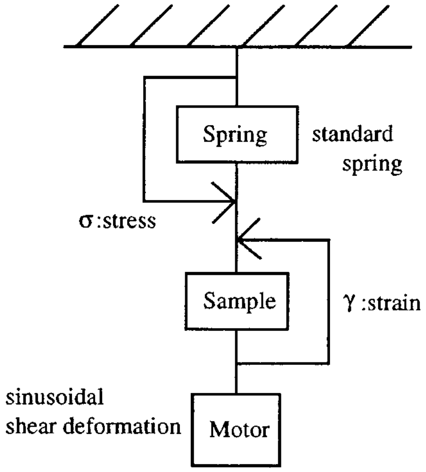


Figure 3. Schematic diagram of the apparatus for the dynamic shear modulus.

added salt and K-form κ-carrageenan with added 10 and 20 mM KCl were measured in the temperature region of 1−50 °C. The frequency dependence of G', G'', and $\Delta n/\Delta\gamma$ were measured for all the samples in the frequency range 0.01−1 Hz. The frequency dependence of the shear modulus for 2.0 wt % Cs-form κ-carrageenan during the cooling process at 45, 36, 34, and 20 °C corresponding to far above, just above, just below, and far below the sol−gel transition temperature is shown in Figure 4. The frequency dependence of $\Delta n/\Delta\gamma$ for 2.0 wt % Cs-form κ-carrageenan at 20 and 34 °C is shown in Figure 5. $\Delta n/\Delta\gamma$ in the sol state is too small to measure accurately. It was observed that the shear modulus depends on frequency except in the case far below the sol−gel transition temperature. At 36 and 45 °C, G' and G'' show typical power law behavior.[25,26] On the contrary, at 20 °C, far below the sol−gel transition temperature, the values of G' and $\Delta n/\Delta\gamma$ do not depend on frequency. The solutions with the other cations show a similar frequency dependence far below the gelation temperature, T_{gel}.

It is well-known that power law behavior is observed near the gelation point for both chemically and physically linked gels.[25,26] At the gelation point, G' and G'' obey the power law with the same relaxation exponent n, reflecting the cross-link and network structure, and also $\tan\delta = n\pi/2$ was satisfied. However, the estimation of the relaxation exponent n for κ-carrageenan is quite difficult, because the gelation of κ-carrageenan proceeds rapidly and the gelation cannot be stopped.

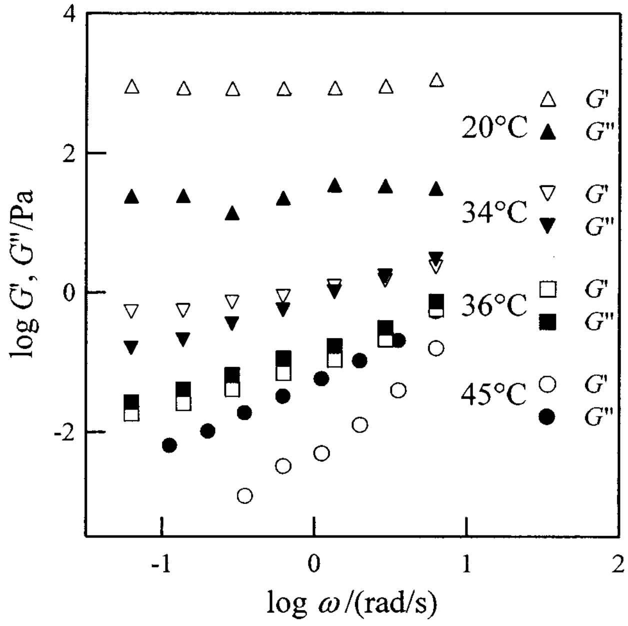


Figure 4. Frequency dependence of G' and G'' of 2.0 wt % Cs-form κ-carrageenan 20, 34, 36, and 45 °C corresponding to far below, just below, just above, and far above the sol-to-gel transition temperature.

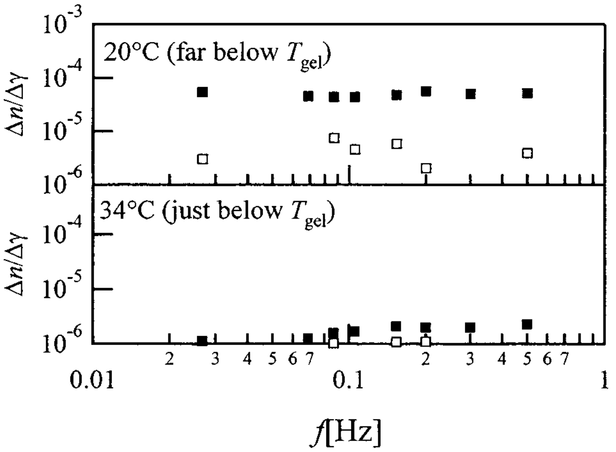


Figure 5. Frequency dependence of the complex strain−optical coefficient of 2.0 wt % Cs-form κ-carrageenan at 20 and 34 °C (■, real part; □, imaginary part).

In this study, our interest is focused on the growing of gel network in the temperature region far below T_{gel}. The analysis with constant frequency should be valid for an investigation of the growth of gel network structure far below the T_{gel}, since neither G' nor $\Delta n/\Delta\gamma$ depends on frequency in this temperature region. We discuss the growing process of the gel network using the data at a constant frequency of 0.5 Hz.

According to Ross-Murphy, the amplitude of the strain applied to the sample affects the modulus and the gel network structure, especially near the gelation temperature.[27] We checked the amplitude dependence of $\Delta n/\Delta\gamma$ at 20 and 34 °C, as shown in Figure 6. We confirmed that almost no amplitude dependence is shown far below the gelation temperature in the amplitude range between 1.25 and 2.5%.

Temperature Dependence. Figure 7 shows the temperature dependence of the optical transmission I_{T},

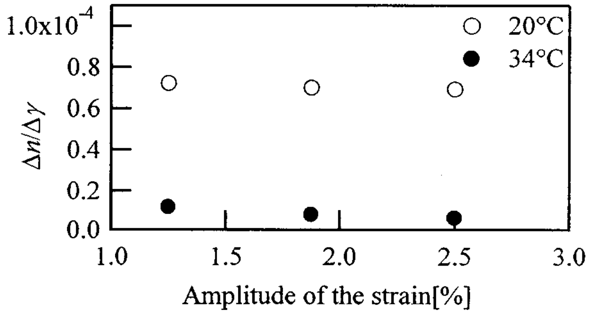


Figure 6. Amplitude dependence of strain−optical coefficient of 2.0 wt % Cs-form κ-carrageenan at 20 and 34 °C.

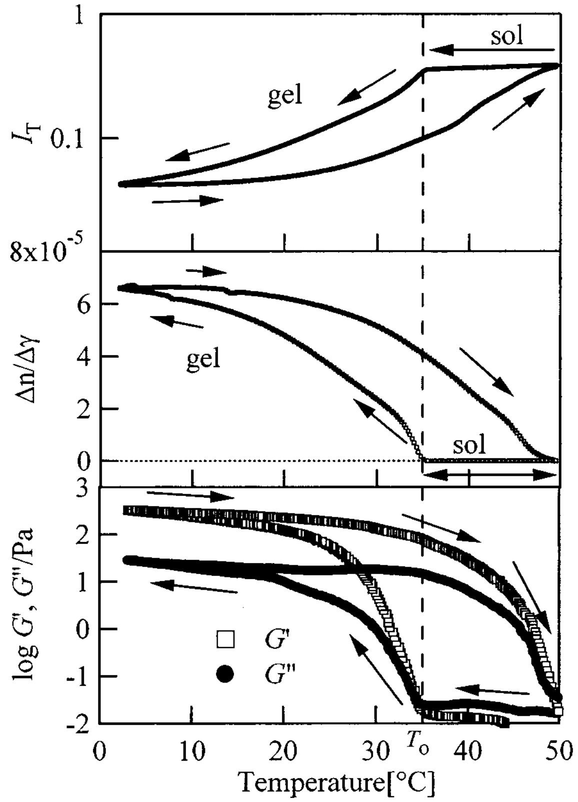


Figure 7. Temperature dependence of the optical transparency, I_T, the strain−optical coefficient $\Delta n/\Delta\gamma$ and the shear modulus G' and G'' of 2.0 wt % Cs-form κ-carrageenan.

the strain−optical coefficient $\Delta n/\Delta\gamma$, and the dynamic shear modulus G', G'' for 2.0 wt % Cs-form κ-carrageenan aqueous solution. The onset temperature T_o at which marked changes occur in the temperature dependence of I_T, $\Delta n/\Delta\gamma$, and G', G'' coincide with each other. In the cooling process, the value of $\Delta n/\Delta\gamma$ is nearly zero (lower than 10^{-7}) at temperatures higher than 34 °C (T_o). This means that there is hardly any orientation of the polymer chains. Above T_o, the loss modulus G'' is larger than the storage modulus G', which means that the sample is in sol state. On the other hand, below T_o, the sign of $\Delta n/\Delta\gamma$ is positive, and the value of $\Delta n/\Delta\gamma$ increases with decreasing temperature and gradually reaches a constant value. At about T_o, G' becomes lager than G''. The remarkable decrement of I_T starts at T_o. In the heating process, $\Delta n/\Delta\gamma$ decreases with increasing temperature and becomes nearly zero at 47 °C. I_T increases with increasing temperature and reaches the initial value of the sol state.

The temperature at which G' crosses with G'' depends on frequency and does not agree with the gelation temperature estimated by the method proposed by Winter and Chambon.[25,26] We consider that T_o does not correspond to the sol-to-gel transition temperature but corresponds to conformational transition temperature.

Effect of Cation Species and Type of Carrageenan (κ and ι) on Thermal Hysteresis. In the case of K-, Cs-, and Ca-form κ-carrageenan solutions, thermal hysteresis was observed for $\Delta n/\Delta\gamma$ and I_T as shown in Figure 8a. But in the case of ι-carrageenan, almost no thermal hysteresis was observed, as shown in Figure 8b. Below the onset temperature T_o, $\Delta n/\Delta\gamma$ increases, and I_T decreases with decreasing temperature for the K-form and Cs-form κ-carrageenan aqueous solutions. K and Cs are cations promoting gelation. The Na-form κ-carrageenan solution does not form gels at low ionic concentration and shows no marked change in $\Delta n/\Delta\gamma$ and I_T.

For the divalent cation Ca-form κ-carrageenan, below T_o, both $\Delta n/\Delta\gamma$ and G', G'' abruptly increase, and I_T decreases, with decreasing temperature. This phenomenon is similar to the case of specific monovalent cations K- and Cs-form. For example, 2.0 wt % Ca-form κ-carrageenan solution forms gel below 10 °C (T_o). The particular feature of this gel is relatively high modulus, although polymer concentration is relatively low.

It is interesting to note that, except for the K-form, for all cation-forms the temperature regions, where $\Delta n/\Delta\gamma$ and I_T exhibit thermal hysteresis, coincide with each other. In the case of the K-form, the thermal hysteresis of $\Delta n/\Delta\gamma$ and I_T appears in a different temperature region.

Concentration Dependence of K-Form κ-Carrageenan. The concentration dependence of $\Delta n/\Delta\gamma$ and I_T for K-form κ-carrageenan solution is shown in Figure 9. The values of $\Delta n/\Delta\gamma$ increase with increasing concentration. For 2.0 wt % K-form κ-carrageenan solution, thermal hysteresis of I_T was observed in the narrow temperature region, and the temperature region in which thermal hysteresis of I_T appears does not coincide with that of $\Delta n/\Delta\gamma$. In the case of 1.5 and 1.8 wt % solutions, near the critical concentration for gelation, the temperature region in which the thermal hysteresis of I_T appears coincides with that of $\Delta n/\Delta\gamma$. As the concentrations become lower, the thermal hysteresis temperature regions of I_T and $\Delta n/\Delta\gamma$ more exactly coincide with each other.

Effect of Added KCl on 1.0 wt % K-Form κ-Carrageenan. The K-form κ-carrageenan solution at 1.0 wt % concentration did not form gel. However, the solutions with 10 and 20 mM added KCl formed gels. $\Delta n/\Delta\gamma$ and G' increase with increasing the concentration of the added KCl. The temperature dependence of $\Delta n/\Delta\gamma$ and I_T for K-form κ-carrageenan with added KCl is shown in Figure 10. The optical properties of the gel with added KCl are quite different from those without added salt. In the case of K-form κ-carrageenan solution with added KCl, a transparent gel was formed, and no marked decrease in I_T was observed. Moreover, $\Delta n/\Delta\gamma$ of K-form κ-carrageenan solutions with added KCl, if normalized by polymer concentration, are relatively higher than those of same polymer concentration solutions without added salt. These results indicate that the gel network structure is strongly influenced by added KCl.

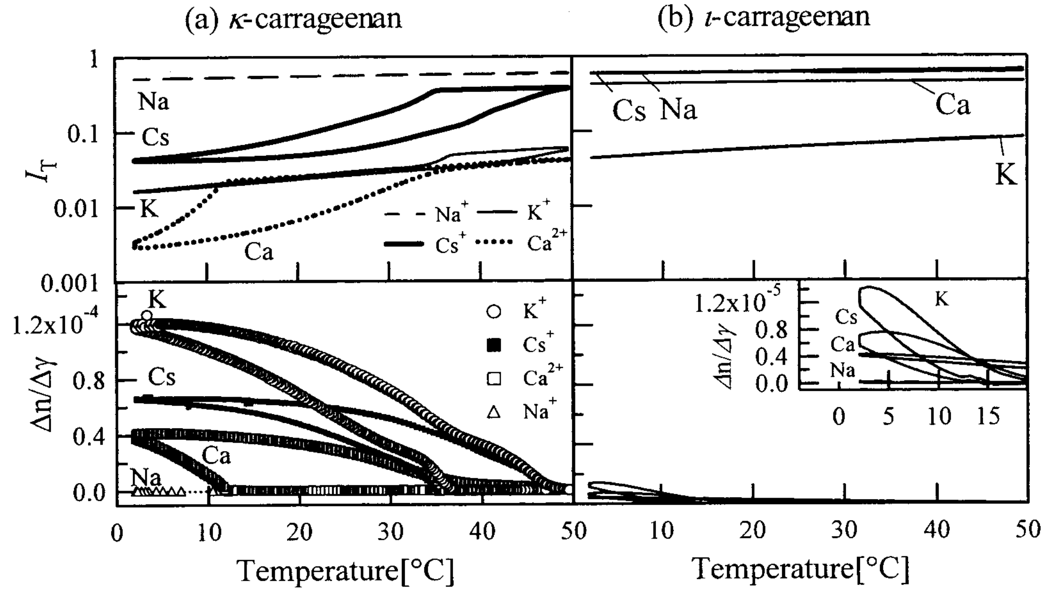


Figure 8. Temperature dependence of the strain–optical coefficient and the optical transparency of K-, Cs-, Ca-, and Na-form κ- and ι-carrageenan solutions. The concentration for all the samples is 2.0 wt %.

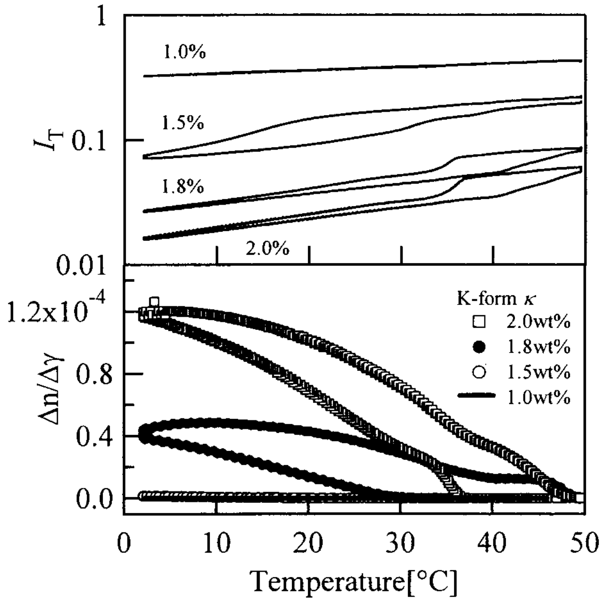


Figure 9. Temperature dependence of the strain–optical coefficient and the optical transparency of K-form κ-carrageenan at various concentrations of 1.0, 1.5, 1.8, and 2.0 wt %.

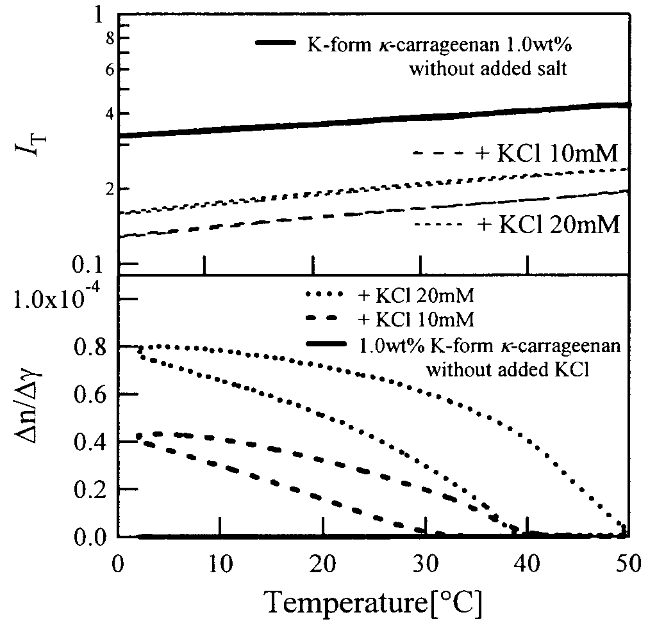


Figure 10. Temperature dependence of the strain–optical coefficient and the optical transparency of 1.0 wt % K-form κ-carrageenan solutions with and without added KCl.

4. Discussion

The investigation on response to mechanical deformation gives very important knowledge of cross-link structure and connection between polymer chains, which are characteristics of the gel. From the temperature and frequency dependence of viscoelasticity, we can obtain the information about the formation of the gel network, including the number of the cross-link points, the structure inside the cross-link region, and the gel network structure. However, it is difficult to obtain separately the contribution of each effect from only the viscoelastic experiments. Moreover, the viscoelasticity of the κ-carrageenan solutions does not exhibit a significant frequency dependence far below the gelation temperature. On the other hand, the investitagation on the strain–optical coefficient offers information about the anisotropy of refractive index of polymer chain and the polymer chain orientation caused by mechanical deformation of gel network. By taking the correlation between the storage modulus and the strain–optical coefficient, we can obtain information about the growing process of gel network through the change in the orientation of the polymer chain and the optical anisotropy of molecule during gelation.

The temperature dependence of G' and $\Delta n/\Delta\gamma$ for 2.0 wt % K-, Cs-, and Ca-form κ- and ι-carrageenan solutions without added salt and for 1.0 wt % K-form κ-carrageenan solutions with added KCl are shown in Figure 11. The correlation between log G' and log $\Delta n/\Delta\gamma$ is deduced from the data in Figure 11 after elimination of temperature as shown in Figure 12. Far below the gelation temperature corresponding to upper right region in Figure 12, the linear relationship between log G' and log $\Delta n/\Delta\gamma$ was observed for all the samples,

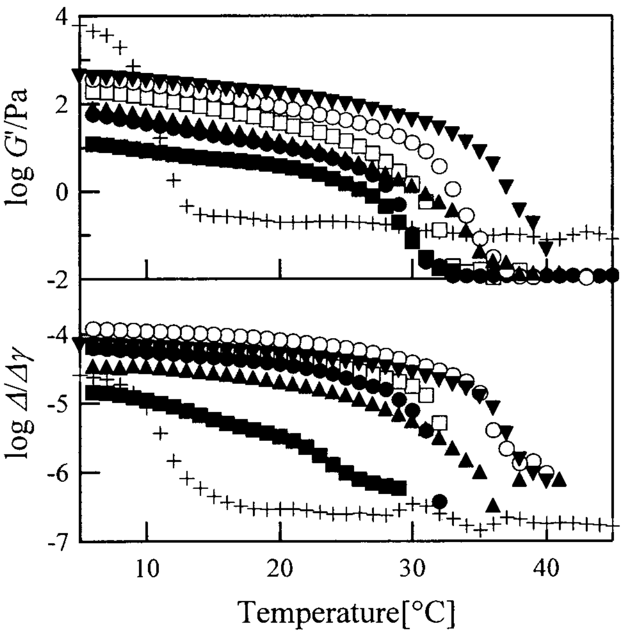


Figure 11. Temperature dependence of the storage modulus and the strain−optical coefficient (+, Ca-form κ 2.0 wt %; □, Cs-κ 2.0 wt %; ■, K-κ 1.5 wt %; ●, K-κ 1.8 wt %; ○, K-κ 2.0 wt %; ▲, K-κ 1.0 wt % + KCl 10 mM; ▼, K-κ 1.0 wt % + KCl20 mM).

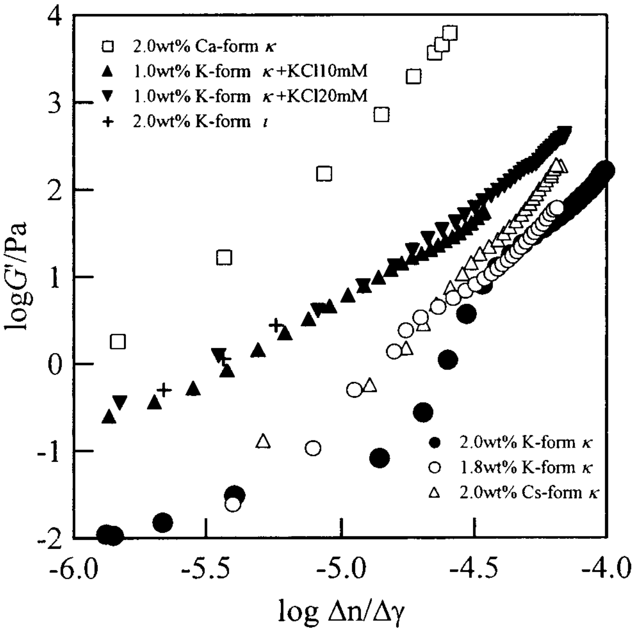


Figure 12. Correlation between the strain−optical coefficient and the storage modulus. Upper right region corresponds to lower temperature.

which is formulated as

$$G' = \frac{d\sigma}{d\gamma} = \alpha\left(\frac{d\Delta n}{d\gamma}\right)^{\beta} \tag{4}$$

Let us consider the physical meaning of the parameter α and β in relation to the growing process of gel network. For example, if $\Delta n/\Delta\gamma$ increases without increasing G', the value of β is equal to zero. This means that only the optical anisotropy of polymer segment increases, since a constant G' means that both the mechanical structure inside the cross-link region and the topological structure of gel network remain unchanged.

We discuss the physical meaning of parameter α with the model of a simple gel structure. We assume that the gel structure obeys the stress−optical law; i.e., the gel network consists of the flexible cross-link points connected by flexible polymer chains. If only the number of the cross-link points increases during the growing of the gel network, G' and $\Delta n/\Delta\gamma$ should increase by the same ratio. In this case, the growth of the gel should be represented by a linear relation with a slope β of unity in the double-logarithmic plot. Therefore, the relationship between storage shear modulus and strain−optical coefficient is written as

$$G' = \frac{d\sigma}{d\gamma} = \frac{1}{C}\left(\frac{d\Delta n}{d\gamma}\right), \quad C \equiv \frac{d\Delta n}{d\sigma} \tag{5}$$

where C is stress−optical coefficient. Birefringence Δn is given by

$$\Delta n = \frac{c\xi}{n} f_{\Delta}(\gamma), \quad \xi = n_{\parallel} - n_{\perp} \tag{6}$$

where ξ is optical anisotropy of segment, $n_{\parallel}$ and $n_{\perp}$ are refractive index of parallel and perpendicular to the axis of helical chain, $f_{\Delta}(\gamma)$ is orientation function, n is mean refractive index of solution, and c is volume concentration.

On the basis of this consideration and by analogy between eq 4 and eq 5, we conclude that the value of α is mainly dominated by the optical anisotropy of the polymer segments. Log α represents the offset of vertical axis at $\log(\Delta n/\Delta\gamma) = 0$ and strongly depends on the value of β. Since the values of $\Delta n/\Delta\gamma$ becomes 10^{-6}−10^{-4} as shown in Figure 12, which is much smaller than 10°, the value of α reflects the optical anisotropy expanded by the value of β. For the more adequate evaluation of optical anisotropy in eq 4, we use the value of the horizontal offset α′ defined as

$$\log G' = \beta\left(\frac{d\Delta n}{d\gamma} - \alpha'\right), \quad \alpha' = \frac{\log \alpha}{\beta} \tag{7}$$

Next, we discuss the physical meaning of β and why the value of β depends on cation species. Far below the gelation temperature, β becomes constant as a result of the fitting procedure. Using eqs 4 and 6, a constant β means that with decreasing temperature the term $(df_{\Delta}/d\gamma)$, reflecting the gel network structure, increases exponentially with the exponent β. That is, β is a characteristic parameter of the growing process of gel network. We found that the value of β is larger than unity for all the samples, which indicates that the stress required to induce a unit orientation increases with decreasing temperature over a wide temperature range.

There are two possibilities for the enlargement of β: (1) a decrease in flexibility of polymer chains connecting cross-link points and (2) changes in the topological structure of the gel network, e.g., an increase of the number of the chains, which bear the shear loads as a brace.

In the first case, the polymer chains connecting cross-link points consist of coil and helix parts. The helical content increases with decreasing temperature for all the carrageenan solutions with any gelation promoting cation.[4,12−14] The increase helical content induces the decrease in flexibility of polymer chains. The increasing helical content during gelation depends on the cation species. However, the increase of the helical content is

Table 2. Correlation Exponents α and β in Eq 4 Estimated from the Data in Figure 12 by a Least-Squares Fitting Procedure

	sample	polymer concn (wt %)	log α	β	$-(\log \alpha)/\beta$
κ	K-form + KCl 10 mM	1.0	8.8	1.63	−5.42
κ	K-form + KCl 20 mM	1.0	9.0	1.63	−5.51
ι	K-form	2.0	8.5	1.54	−5.50
κ	K-form	1.8	12.1	2.48	−4.88
κ	K-form	2.0	12.8	2.65	−4.82
κ	Ca-form	2.0	16.6	2.83	−5.89
κ	Cs-form	2.0	16.7	3.46	−4.84

not the dominant origin of the cation dependence of β, because rheological properties of the gels depend on cation species at low temperatures, where the helical fraction is close to unity.[4,28] It is important to note that the polymer chains connecting cross-link points are semirigid due to the high helical content. Semirigid polymer chain can act as an effective brace for the gel network.

In the second case, the change in the topological structure of gel network is caused by the increase of the branching number in a cross-link region. New branching in a cross-link region is required to set the polymer chain as a brace. According to the commonly accepted model of a branching for κ-carrageenan gel, the branching is an interhelical association.[14] The simplest situation for the increase of the branching number is an increase of the number of helical molecules bundled in a parallel arrangement. However, this model conflicts with the results of the light scattering study, which showed that the molecular weight in an associated region increases sharply just below the coil−helix transition temperature, and hardly increases successively with decreasing temperature.[29]

The values of α' with different cation species (Cs-, K-, and Ca-form κ-carrageenan) are quite different even if the polymer concentrations of the solutions are almost the same and conformational transition occurs for all the gelling samples in Figure 12. For example, the $\Delta n/\Delta\gamma$ of K-form κ-carrageenan is about 10 times higher than that of Ca-form κ-carrageenan. α' does not depend on the amount of added KCl and polymer concentration as listed in Table 2. We conclude from these results that the difference of the α' is dominated by the effects of cations bound to helical molecules, rather than the change in the optical anisotropy during conformational transition of the polymer chain.

In the case of K-form κ-carrageenan, the sharp increase in $\Delta n/\Delta\gamma$ was observed in the narrow temperature range of about 5 deg just below the gelation temperature, which is represented by β lower than unity if eq 4 is used for this temperature range. It is suggested that this phenomenon is caused by the increase of the optical anisotropy of segment, i.e., a sharp increase of α' with a constant exponent β, because it is unlikely that β is lower than unity, corresponding to an increase in orientation at an almost constant modulus. The change in the optical anisotropy depending on temperature in initial stage of gelation is caused not only by the conformational transition but also by the binding of cations due to the increase in the charge density of the polymer chain during the coil-to-helix transition. It is found that this phenomenon occurs sharply in the initial stage of gelation. In carrageenan gels, it is known that cations included in the solution are bound to helical molecules during the coil−helix transition.[30−32] The sharp increase in $\Delta n/\Delta\gamma$ in the initial stage of gelation occurs for both the 2.0% and 1.8% solutions. Despite the small difference of concentration, the behavior appears more clearly in the case of the 2.0% solution. Since the minimum polymer concentration to form gel without added salt is about 1.5 wt % as shown in Figure 9, the effect of these difference of concentration is not small. The gelation proceeds more rapidly in the case of the 2.0% solution. Except for K-form κ-carrageenan, the sharp increase in α' was not observed clearly during the initial stage of gelation. We assume that the increase in α' occurs at the lower side of our measurable range of $\Delta n/\Delta\gamma$ in the case of the other cation forms.

In the case of Cs-, K-, and Ca-form κ-carrageenan without added salt, the exponent β is much larger than unity as listed in Table 2. This indicates that the structure inside the cross-link region and the conformation of chain connecting cross-link regions change successively in the low-temperature region. On the other hand, in the case of 1.0 wt % K-form κ-carrageenan solutions with added KCl 10 and 20 mM, the values of exponent β in eq 4 are also rather close to unity, which are much smaller than those of higher polymer concentration solutions (K-form κ-carrageenan 1.8 and 2.0 wt %) without added salt. The helical fractions of 1.0 wt % κ-carrageenan with added KCl 20 mM and 2.0 wt % κ-carrageenan without added KCl solutions are expected to be comparable, because the total potassium ion concentrations of the two samples estimated from Table 1 are almost the same. The value of the exponent β of a high polymer concentration gel is higher than that for low concentrations. A greater increase of the branching number can be expected in the case of the solution with the higher polymer concentration. These results suggest that the structure inside the cross-link region hardly changes with an increasing number of cross-link points.

We found that, in the case of K-form ι-carrageenan, the value of the exponent β is much smaller than that for K-form κ-carrageenan and without added salt rather close to unity. Thus, these growing mechanisms of them are quite different. According to Piculell et al., aggregation is essential for gelation of κ-carrageenan but is not essential for that of ι-carrageenan.[7,33] We conclude that the difference of the values of β for κ- and ι-carrageenan is caused by the difference of the cross-linking mechanism; i.e., the branching number in the cross-link region increases during gelation in the case of κ-carrageenan gel but hardly increases in the case of ι-carrageenan gel.

5. Conclusion

The temperature and frequency dependence of dynamic shear modulus, strain−optical coefficient, and optical transmission of Cs-, K-, Na-, and Ca-form κ- and ι-carrageenan aqueous solutions were measured in order to clarify the gelation mechanism. The formation of the carrageenan gel network is studied by using the correlation between the shear modulus and strain−optical coefficient. For all the samples, G' is a power function of $\Delta n/\Delta\gamma$ in the low-temperature region in the gel state. The values of α and β in eq 4 depend strongly on the cation species. We conclude that α and β reflect mainly the optical anisotropy of the helical molecule including the effect of bound cations and the growing process of structure inside the cross-link region, respectively. For all samples, $\beta > 1$. This indicates that polymer chains connecting cross-link points are not flexible but semirigid, and the number of polymer chain acting as a brace of the gel network increases with decreasing temperature. We propose that the branching number in a cross-link region increases with decreasing temperature, and the increasing process of the branching number depends strongly on the carrageenan type and cation species. The increasing scheme in the stress inducing the unit orientation is still not clear from only this study. A study of fractal dimension of the gel network should be useful. The rheological and scattering study may clarify the increasing scheme of the branching number in a cross-link region during gelation.

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