

# Optical, Viscoelastic, and Electric Properties On Gelation Of Carrageenan Gels

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Viscoelasticity, strain-optical coefficient, optical transmission, DC conductivity, and dielectric properties of  $\kappa$ - and  $\iota$ -carrageenan aqueous solutions on sol-gel transition were measured to investigate the structure of cross-link point, gel network structure and the effect of counter ions and added salts. The results suggest that potassium ions are trapped around helical molecules in the early stage of gelation. It is also suggested that the branching number increases with decreasing temperature in the case of 2.0wt% K-form  $\kappa$ -carrageenan, in spite of same ionic concentration. The number hardly changes on formation process of gel network in the case of 1.0wt% K-form  $\kappa$ -carrageenan with added 20mM KCl.

Key Words: carrageenan, sol-gel transition, viscoelasticity, conductivity, permittivity, strain optical coefficient

## 1. INTRODUCTION

Carrageenans are polysaccharides extracted from marine red algae. The backbone is based on an alternating disaccharide-repeating unit of 1,3-linked  $\beta$ -D-galactose and 1,4-linked 3,6-anhydro- $\alpha$ -D-galactose. Its solution with specific counter ions forms physically cross-linked polyelectrolyte thermo-reversible gels. One of the most interesting features is that macroscopic properties of the gel are affected by amount and species of counter ions.

We are particularly interested in the structure of crosslink points and the formation process of the gel network structure. More experimental work is needed to obtain the information about cross-link point and gel network structure, which should be highly relevant for the molecular understanding of the gelation mechanisms and the macroscopic properties of the gels. In this study, temperature dependence of dynamic shear modulus, strain optical coefficient, optical transmission, DC conductivity, and dielectric property for  $\kappa$  and  $\iota$ -carrageenan aqueous solutions with various cation species and amount of cations was studied. The correlation between the shear modulus and the strain optical coefficient was studied in order to investigate the structure of gel network and crosslink point. The cation effect on these structures was also studied. Optical measurements give important information about the orientation of polymer chain and the optical anisotropy of segment. From the measurements of DC conductivity and dielectric constant, we can obtain the information about the mobility of cations passing through gel network structure and the trapping to the helical molecules.

## 2. EXPERIMENTAL

### 2.1 SAMPLES

	Na	K	Ca	Cs
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%

Table I. The ratio of each cation to sulfur in purified  $\kappa$ -carrageenan

$\kappa$  and  $\iota$ -carrageenan was purchased from Sigma Chemical Co. Ltd. The solutions were prepared by dissolving for two weeks. We refined the potassium, sodium, and cesium-form  $\kappa$  and  $\iota$ -carrageenan by the following method. Its aqueous solution was purified by dialysis, de-ionized by passage through Amberlite IR-120 (H+) cation exchange resin, and neutralized with KOH, NaOH, and CsOH aqueous solution for each cation-form, and then freeze-dried.

Each cation content in the purified sample was determined by inductively coupled plasma spectrometry, and the sulfur content was determined by ion chromatography. The ratio of Cs was calculated by subtraction of the other ratios for Na, K, and Ca from total. The ratio of each cation to sulfur was listed in Table I.

### 2.2 APPARATUS

The optical measurements were performed with the apparatus described elsewhere[1]. The transmitted intensity  $I$  reflects retardation, azimuth and transparency of the sample. Transparency  $I/I_0$  abruptly decreases on sol-gel transition, and depends on sample and temperature. We can obtain each term individually, and the strain optical coefficient was estimated by retardation and compensated strain[1].

We modified Rheograph GSA (Toyoseiki-Seisakusyo co. ltd.) in order to shift the range of modulus to lower[1]. Wide range of modulus (more than 6 to 7 decades) can be measured with concentric cylinder geometry cell.

DC conductivity and dielectric measurements were carried out with parallel plate cell over the frequency range from 0.01Hz to 1MHz.

In low frequency range of 0.01Hz~100kHz, the apparatus optimized for the condition of  $\tan\delta \gg 1$  was used. In high frequency range of 1k~1MHz, HP4284A impedance analyzer was used.

### 3. RESULTS AND DISCUSSION

Fig. 1 shows the temperature dependence of the optical transmission  $I/I_0$ , the strain optical coefficient  $\Delta n/\Delta\gamma$ , and the dynamic shear modulus  $G'$ ,  $G''$  for 2.0wt% Cs-form  $\kappa$ -carrageenan aqueous solution.

The temperature at which remarkable change

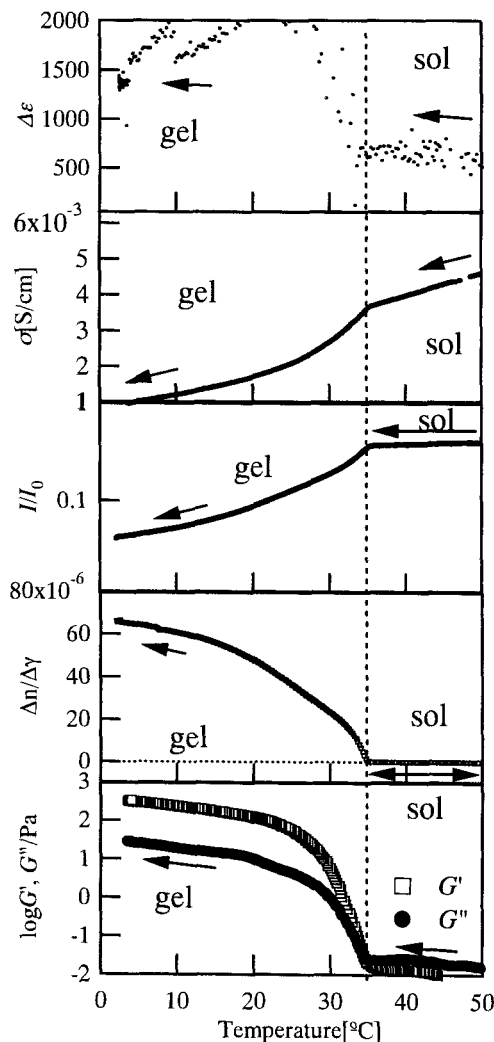


Fig. 1. Temperature dependence of conductivity  $\sigma$ , dielectric relaxation strength  $\Delta\epsilon$ , optical transmission  $I/I_0$ , strain-optical coefficient  $\Delta n/\Delta\gamma$ , and shear modulus  $G'$ ,  $G''$  of 2.0wt% Cs-form  $\kappa$ -carrageenan in sol-gel transition process.

occurs in each experiment is consistent with each other. We call this temperature as onset temperature  $T_0$ . It is reasonable to consider that  $T_0$  relates the onset temperature of coil-helix transition.

In the temperature region higher than 34°C ( $T_0$ ), the value of  $\Delta n/\Delta\gamma$  is nearly zero (lower than  $10^{-7}$ ), which reflects that the orientation of the polymer chain due to the deformation hardly occurs. Above  $T_0$ , the loss modulus  $G''$  is larger than the storage modulus  $G'$ , which reflects that the sample is in sol state. On the other hand, below  $T_0$ , the value of  $\Delta n/\Delta\gamma$  increases with decreasing temperature, and gradually reaches constant value. The remarkable decrease of  $I/I_0$  also starts at  $T_0$ . The change in  $I/I_0$  indicates the change in the density fluctuation of the order of the wavelength of He-Ne Laser due to the formation of gel network. The increase of  $\Delta n/\Delta\gamma$  reflects the increase in the orientation of polymer chain due to the increment of number of crosslink point. DC conductivity abruptly decreases at  $T_0$ , which can be interpreted as the trapping of counterion to helical molecules. Huge dielectric relaxation strength was observed below the  $T_0$ . It is reasonable to consider that this phenomenon is caused by the binding of cations to helical molecules.

The investigation on response to mechanical deformation gives very important knowledge of gel network. From the experiments on temperature and frequency dependence of viscoelasticity, we can obtain the information including the number of the crosslink point, the structure of the crosslink region, and the gel network structure. However, it is difficult to obtain each term individually.

On the other hand, the investigation on the strain optical coefficient offer the information about the orientation of polymer chains in the gel network due to the mechanical deformation and the anisotropy of refractive index around a polymer chain.

By taking correlation between strain optical coefficient and storage modulus, we can obtain the information about the formation process of gel network in more detail.

The correlations between  $G'$  and  $\Delta n/\Delta\gamma$  for K, Cs, Ca-form  $\kappa$ -carrageenan without added salt, and K-form  $\kappa$ -carrageenan 1.0wt% with added KCl are shown in Fig.2.

In the low temperature region (upper right region in the figure), a linear relationship was observed for all the experimental results, in the double logarithmic plot of  $\log G'$  and  $\log \Delta n/\Delta\gamma$ , which is represented as equation Eq. (1).

$$G' = \left( \frac{d\tau}{d\gamma} \right) = \left( \alpha \frac{d\Delta n}{d\gamma} \right)^\beta, \quad (1)$$

where  $\tau$  is stress,  $\gamma$  is strain, and  $\Delta n (= n_{\perp} - n_{\parallel})$  is birefringence.

The  $\alpha$  in Eq. (1) strongly depends on cation species (Ca, Cs and K-form  $\kappa$ -carrageenan) and also depends on the type of carrageenan ( $\kappa$  and  $\iota$ ). However,  $\alpha$  does not depend on the amount of added KCl. The  $\alpha$  is

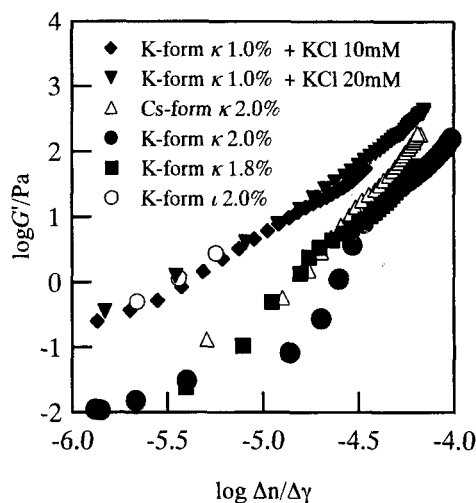


Fig.2 Correlation between strain optical coefficient  $\Delta n/\Delta\gamma$  and storage shear modulus  $G'$ .

quite different for each sample, even though little difference of polymer concentration exists. It is reasonable to consider that the difference of  $\alpha$  reflects the optical anisotropy of segment. Thus the difference of  $\alpha$  indicate that optical anisotropy around a helical molecule depends on cation species, but does not depend on the amount of added salt and polymer concentration.

In the case of Ca-, Cs-, and K-form  $\kappa$ -carrageenan, the exponent  $\beta$  is much larger than unity. This phenomenon indicates that the structure inside the crosslink region itself and the molecular structure connecting between crosslink regions change continuously in the low temperature region.

We have pointed out[1] that there exist three origins of the increment of stress for inducing orientation of helical molecules. The first, increment of the number of the helical carrageenan included in a crosslink region, the second, decrement of flexibility of polymer chain connecting crosslink points, and the third, the changes in the gel network structure. The third is based on the change in structure in aggregation, for example, the change in branching number of crosslink region.

In the case of K-form  $\kappa$ -carrageenan, the abrupt increase of  $\Delta n/\Delta\gamma$  was observed in the narrow temperature region in the early stage of gelation, which indicates that the optical anisotropy around helical molecules increases abruptly in this temperature region. This suggests that the potassium ions are bound to helical region concentratedly in early stage of gelation.

It has been reported that the aggregation of the helical region is essential to form a gel in the case of  $\kappa$ -carrageenan, but the aggregation may not be unexpendable for crosslinks in the case of  $\iota$ -carrageenan[2]. The structure of the crosslink point of  $\iota$ -carrageenan is quite different from that of  $\kappa$ -carrageenan, but not clear. In our experiments, the exponent  $\beta$  for K-form  $\iota$ -carrageenan is relatively

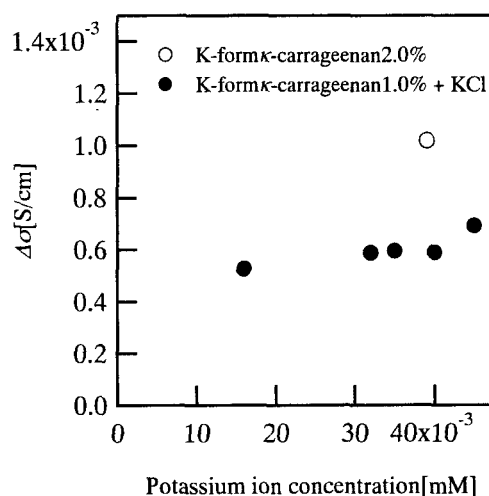


Fig.3 Potassium concentration dependence of decrement at the gelation temperature.

close to unity, which is much smaller than that of K-form  $\kappa$ -carrageenan. This indicates that the formation process of gel network is also different from each other.

It is reasonable to consider that the polymer chain connecting between crosslink regions consists of the coil and helical molecules, and the influence of cation species on the conformation of the polymer chain connecting between crosslink regions is only the change in the content of helical molecules. The other possibility to enlarge the stress inducing unit orientation is the change in the network structure and structure inside the crosslink region. The change in the network structure is based on branching number at crosslink point. Consequently, the cation species will affect the structure in the crosslink region.

In the case of 1.0wt% K-form  $\kappa$ -carrageenan solution with added 10 and 20mM KCl, the exponent  $\beta$  in Eq. (1) is much smaller than that of salt free and higher concentration samples (K-form  $\kappa$ -carrageenan 1.8, 2.0wt%), which is rather close to unity. These results suggest that the structure of the crosslink region hardly changes with increasing number of crosslink points.

Potassium ion concentration dependence of the decrement of DC conductivity at gel point is shown in Fig.3. In the case of 1.0wt% K-form  $\kappa$ -carrageenan, no significant concentration dependence of added KCl was observed in this concentration region. On the other hand, the decrease in the  $\Delta\sigma$  for 2.0wt% K-form  $\kappa$ -carrageenan without KCl is much larger than that of 1.0wt% K-form  $\kappa$ -carrageenan with added KCl. These results basically support that  $\alpha$  in Eq.(1) reflects the magnitude of optical anisotropy of segment.

However, the difference of  $\alpha$  for each cations can not be explained by only the amount of trapped cations estimated from DC conductivity. Optical anisotropy of segment may be affected by state of aggregation which depends on cation species and

amount of cations.

Frequency dependence of  $G'$  and  $G''$  of K-form  $\kappa$ -carrageenan 2.0wt% at 20, 36, and 45°C, which corresponds to far below, near, and far above the sol-gel transition temperature, is shown in Fig. 4.

The shear modulus  $G'$  and  $G''$  near the sol-gel transition temperature shows a power law dependence with the same relaxation exponent  $n$ . This indicates that the sample is in a critical gel state [3-4]. And the structure is based on self similarity over a wide length scale. The relaxation exponent  $n$  is related to fractal dimension.

According to Muthukumar[5-6], in the case of complete screening of excluded volume effects of polymer chain in concentrated solution, the relationship between the relaxation exponent  $n$  and fractal dimension is given by,

$$n = \frac{D(D+2-2D_f)}{2(D+2-D_f)} \quad (2)$$

where  $D$  is the space dimension and  $D_f$  is the fractal dimension.

$D_f$  estimated from equation (2) using the relaxation exponent  $n$  which is shown in Fig.5 is 2.32 for 2.0wt% K-form  $\kappa$ -carrageenan, 2.30 for 2.2wt% Cs-form  $\kappa$ -carrageenan, and 2.10 for 1.0wt% K-form  $\kappa$ -carrageenan with added 20mM KCl.

It is suggested that self-similarity structure forms in the early stage of gelation affect the change in the branching number of crosslink. Total ionic concentrations of both sample are almost the same. Therefore the formation process of crosslink region is mainly affected by polymer concentration.

In the case of 2.0wt% K-form  $\kappa$ -carrageenan, the fractal dimension of gel network structure is high in the early stage of gelation. The branching number in

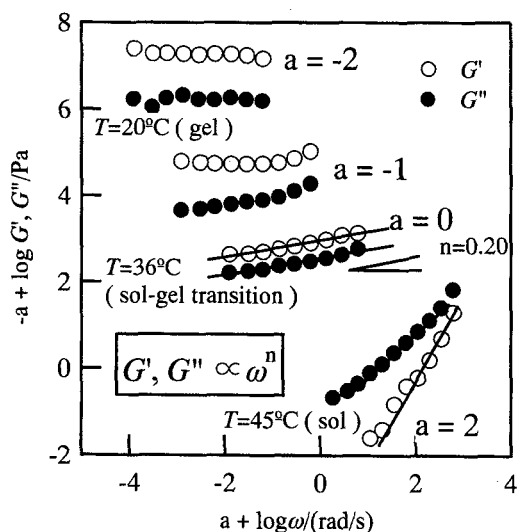


Fig.4 Frequency dependence of storage shear modulus  $G'$  and loss shear modulus  $G''$  of K-form  $\kappa$ -carrageenan 2.0%. The data are shifted along both axes to avoid overlap.

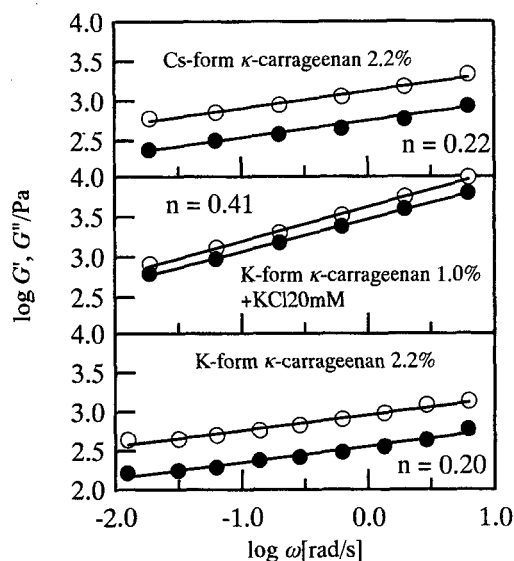


Fig.5 Frequency dependence of storage shear modulus  $G'$  (  $\circ$  ) and loss shear modulus  $G''$  (  $\bullet$  ) near the sol-gel transition temperature.

the crosslink region increases with decreasing temperature. On the other hand, in the case of K-form  $\kappa$ -carrageenan 1.0wt% with added KCl, the fractal dimension of gel network structure is low in the early stage of gelation.

#### 4. CONCLUSION

Gelation mechanism of  $\kappa$ -carrageenan gels was studied. From the analysis of taking correlation between shear storage modulus and strain optical coefficient, it is suggested that the branching number in a crosslink region increases with decreasing temperature.

K-form  $\kappa$ -carrageenan 1.0wt% with added KCl 20mM solution exhibits low (2.10) fractal dimensional structure in early stage of gelation, and only a little change of branch number occurs during gelation. On the other hand, 2.0wt%  $\kappa$ -carrageenan without KCl exhibits the high (2.32) fractal dimension, and the branching number increases with decreasing temperature. These differences of structure seem to be affected by polymer concentration.

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