Abstract
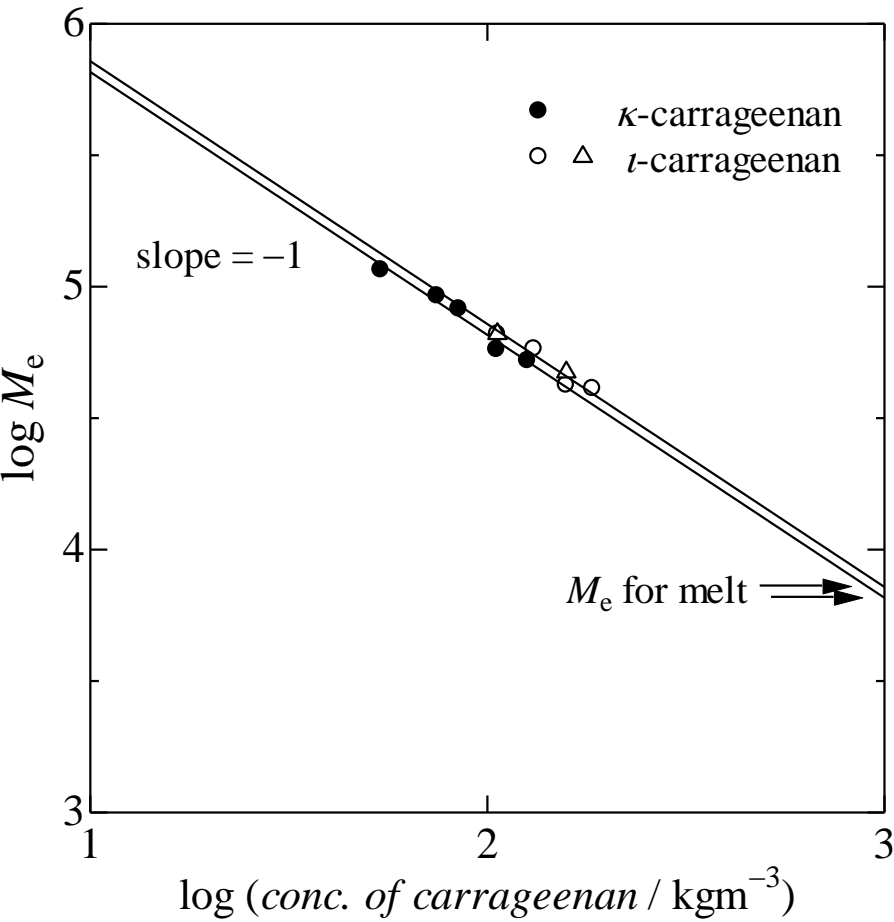
The molecular weight between entanglements (M_e) for κ- and ι-carrageenans, sulfated galactans, was examined in concentrated solutions using an ionic liquid 1-butyl-3-methylimidazolium acetate as a solvent. The dynamic viscoelasticity data for the solutions measured at different temperatures were overlapped according to the time-temperature superposition principle, and the obtained master curves exhibited the flow and rubbery plateau zones, being typical of concentrated polymer solutions having entanglement coupling. The values of M_e for κ- and ι-carrageenans in the solutions were determined from the plateau moduli. Then the values of M_e in the molten state ($M_{e,melt}$) estimated as a material constant to be 6.6×10^3 and 7.2×10^3, respectively. The close values of $M_{e,melt}$ for κ- and ι-carrageenans indicate that 4-sulfate group of ι-carrageenan are not so influential for the entanglement network. Compared with agarose, a non-sulfate galactan, carrageenans have larger values of average spacing between entanglements.

κ-carrageenan
ι-carrageenan

slope $= -1$

M_e for melt

$\log M_e$

$\log (\textit{conc. of carrageenan} / \text{kgm}^{-3})$

Molecular Weight between Entanglements for κ- and ι-Carrageenans in an Ionic Liquid

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1. Introduction

Sulfated polysaccharides have attracted a great deal of attention because of their desirable bioactivities, and many of the natural as well as synthetic sulfated polysaccharides have been obtained and tested until now [1-6]. In industry, many of sulfated polysaccharides are utilized as thickening or gelling agents, but there are few studies on the fundamental aspect of the polysaccharides [7,8]. The chain properties are fundamental characteristics of the polymers which affect the bioactivities as well as the gelling ability, and therefore become indispensable for the further application of the polysaccharides.

Carrageenan is one of the familiar sulfated polysaccharides used as a thickening (gelling) agent, and can be classified into several types: κ- and ι-carrageenans have a common chemical structure of alternating α-(1-3)-D-galactose-4-sulfate (S) and β-(1-4)-3,6-anhydro-D-galactose (A) units; the difference is that ι-carrageenan has an additional sulfate group in A unit to be 2-sulfate [9]. Examining chain properties of the two types of carrageenans (κ- and ι-carrageenans) reveals, of course, the characters of respective sulfate polysaccharides, but also gives the information on the effect of the number of sulfate groups. By computer simulation, the chain properties such as the characteristic ratio (C_∞) for the polysaccharides have been obtained to show a flexible nature for both the carrageenans [9,10]. Characterization of κ- and ι-carrageenans has been performed by several research groups, and their results lead to a stiffer

chain nature compared with the simulation using the dimer model [11-13].

The molecular weight between entanglements (M_e) in the molten state ($M_{e,melt}$) is also a fundamental parameter [14,15] reflecting polymer chain properties, and can be estimated by examining the concentration dependence of the plateau modulus of solutions although the molten states of κ- and ι-carrageenans cannot be realized [16]. However, to our knowledge, there have been no reports on M_e for the carrageenans even in concentrated solutions, partly because aqueous solutions of κ- and ι-carrageenans form gels with increasing polymer concentration owing to the aggregation of helical part of polymer chains [11]. This means that preparation of concentrated solutions of κ- and ι-carrageenans is almost impossible using water as the solvent. Now, it is well known that ionic liquids work as good solvents for several polysaccharides insoluble to conventional solvents [17-19]. For some polysaccharides we have actually obtained concentrated solutions with ionic liquids, and have estimated the values of M_e successfully from the rheological properties of the solutions [18-22]. In this study, the idea that using an ionic liquid to determine M_e in solutions has been applied to κ- and ι-carrageenans. The values of $M_{e,melt}$ have been estimated from the concentration dependence of M_e.

2. Experimental

2.1 Materials

Powdery κ-carrageenan (lot #: 108301, MRC-Polysaccharide, Japan) (κ-M) and

ι-carrageenan (lot #: 105204, MRC-Polysaccharide, Japan) (ι-M) were used in this study. The

manufacturer characterized the samples as follows: The viscosity for 1.5% aqueous solutions of

κ-M and ι-M at 75 °C were 35 and 56 mPas, respectively; the metal content (%) regarding Ca^{2+},

Na^+, and K^+ species were respectively 0.9, 0.3, and 5.1 for κ-M and 3.3, 2.3, and 3.0 for ι-M.

For ι-carrageenan another sample purchased from Funakoshi, Japan (sample-coded as ι-F) was

also employed. All samples were used without further purification, although ι-M and ι-F were

dried in a vacuum oven at 80 °C for more than 12 h just before use. The solvent,

1-butyl-3-methylimidazolium acetate (BmimAc; BASF, Germany), was used as received. The

melting point of BmimAc has been reported to be below −20 °C [23], and thus the solutions

have remained in the liquid state over a temperature range examined. Concentrated solutions of

the carrageenans were prepared in the following way. Each carrageenan sample was added into

the solvent (BmimAc) in a dry glass vessel on a hot plate at 80 °C and the mixture was quickly

stirred with a stainless spatula at 80 °C. Then the glass vessel was sealed and the mixture was

further stirred overnight on a hot plate at 80 °C. The concentration of carrageenan (c) ranged

from 5.4×10^1 to 1.3×10^2 kgm^{-3} (ca. 5 to 12 wt%) for κ-M, from 1.0×10^2 to 1.8×10^2 kgm^{-3} (ca. 10

to 18 wt%) for ι-M, and from 1.0×10^2 to 1.6×10^2 kgm^{-3} (ca. 10 to 15 wt%) for ι-F. In the

calculation of c, the reported value of the density of 1.055×10^3 kgm^{-3} at room temperature was

used for BmimAc; while a common value of 1.0×10^3 kgm^{-3} was assumed for the densities for

the carrageenans [18], since the molten states of carrageenans cannot be attained.

2.2 Measurements

Dynamic viscoelasticity was measured for the concentrated solutions using an ARES

rheometer (now TA Instruments, USA) under a nitrogen atmosphere. A cone-plate geometry

with the diameter of 25 mm and the cone angle of 0.1 rad was used. The storage modulus (G') as

well as the loss modulus (G'') was measured as a function of angular frequency (ω) with an

amplitude of oscillatory strain (γ) of 0.1 which ensures the linear viscoelasticity. The measured

temperature (T) ranged from 20 to 80 °C for κ-M, and from 0 to 100 °C for ι-M and ι-F.

3. Results and Discussion

Fig. 1 shows the master curves of G' and G'' for the κ-M solutions, where the ω

dependence of G' and G'' measured at different temperatures have been superposed at the

reference temperature (T_r) of 80 ^{o}C only by using a horizontal shift factor a_T. The curves for the

different solutions are shifted upwards by a factor of A to avoid overlapping. As seen in the

figure, the time-temperature superposition principle holds well for all the κ-M solutions

measured, meaning that no conformational change such as coil-helix transition occurs in

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BmimAc over the T-range examined. The master curves for all solutions have two zones typical of polymer liquids: First one is the flow zone observed in the low ωa_T region where the G'' curve holds the relation $G'' \propto \omega$, and the second one is the zone at high ωa_T where the G' curve shows a plateau called the rubbery plateau. Every plateau in the figure tilts because of the polydispersity of the carrageenan sample. The plateau, originating from the entanglement coupling between polymer chains, becomes higher with increasing c, although the vertical shift may make it difficult to notice the change. The T-dependence of a_T used for the master curves in Fig. 1 is shown in Fig. 2. The values of a_T at a given T are almost independent of c and all data points fall on a single line, indicating that the T-dependence of a_T obeys an Arrhenius-type equation.

Fig. 3 shows the similar curves of G' and G'' for the ι-M solutions. It is seen that the time-temperature superposition principle also holds for the ι-M solutions. The flow zone as well as the rubbery plateau exists for all solutions. The ι-F solutions showed the similar curves to those of the ι-M solutions if the comparison was made at the same c. The T-dependence of a_T at $T_r = 80\ ^{o}C$ is shown in Fig. 4. The data can also be represented by an Arrhenius-type equation. It should be noted that the data for the ι-F solutions are also consistent with those for the ι-M solutions shown here.

For a tilted rubbery plateau, as observed in this study, there exist several definitions for the

plateau modulus (G_N^0). Among them we adopt here a definition that the G' value at ω where the

loss tangent ($\tan\delta$; $\tan\delta = G''/G'$) vs. ω curve shows a minimum should be taken as G_N^0 [18-22].

Then the value of M_e for a polymer in concentrated solution can be calculated by eq 1 as

$$M_e = \frac{10^3 cRT}{G_N^0} \tag{1}$$

where R is the gas constant [14,15,24]. Since G_N^0 for the κ-M solution at $c = 1.3\times10^2$ kgm^{-3} is

estimated to be 7.1×10^3 Pa (Fig. 1), we have $M_e = 5.2\times10^4$. The values of M_e for the other

solutions were determined in a similar manner. Fig. 5 shows double logarithmic plots of M_e vs. c.

Straight lines in the figure commonly have a of -1, which is based on the well-known relation

$M_e \propto c^{-1}$ for concentrated polymer solutions [14,16], and a line is drawn to be the best fit for

each type of carrageenans. The data points for each sample appear to fall on the line, recalling

that the $M_e \propto c^{-1}$ relation also holds for the carrageenan solutions. Therefore, $M_{e,melt}$ for κ- and

ι-carrageenans can be estimated as the value of M_e at $c = 1.0\times10^3$ kgm^{-3}, the density assumed for

carrageenans (in the molten state) in this study. This leads to the values of $M_{e,melt}$ for κ- and

ι-carrageenans of 6.6×10^3 and 7.2×10^3, respectively, and these can be considered as the material

constants. For comparing the chain properties of various saccharides, we used the number of

monosaccharide units between entanglements in the molten state N_{unit} instead of M_e. The values

of N_{unit} for κ- and ι-carrageenans are calculated to be 34 and 31, respectively, if each

polysaccharide is assumed to be composed of uniform repeating units stated in the introduction.

It is revealed that κ- and ι-carrageenans have similar chain properties regarding entanglement coupling; from the point of chemical structure, this result suggests that 2-sulfate group of A unit does not affect the chain property significantly.

It has been shown by several research groups [25-27] that $M_{e,melt}$ is related to the characteristic ratio (C_∞), a measure of chain stiffness. The explicit expression has not been established yet, and therefore, we cannot estimate C_∞ from $M_{e,melt}$. However, we can say at least that closer values of $M_{e,melt}$ for κ- and ι-carrageenans imply closer values of C_∞ for these polysaccharides. This is actually consistent with the simulation results described in the introduction that both types of carrageenans are flexible.

We now compare N_{unit} for carrageenan, represented here by κ-carrageenan, with that for agarose. Agarose is a non-sulfated galactan composed of α-(1-3)-D-galactose and β-(1-4)-3,6-anhydro-L-galactose units. Although A unit of κ-carrageenan is replaced with the corresponding L-galactose unit, the chemical structure of agarose is quite similar to that of κ-carrageenan except for the sulfate group. In our previous study, N_{unit} for agarose has been determined to be 15 [20], which is appreciably smaller than that for κ-carrageenan. This may suggest that 4-sulfate group of S unit of κ-carrageenan is influential in N_{unit}.

4. Conclusions

The values of M_e for κ- and ι-carrageenans in concentrated solutions were determined by dynamic viscoelasticity measurements using BmimAc as a solvent. It was assured that rheological behavior of the carrageenan solutions is typical of concentrated polymer solutions with entanglement coupling. From the c-dependence of M_e, the material constants $M_{e,melt}$ for κ- and ι-carrageenans was determined to be 6.6×10^3 and 7.2×10^3, respectively. The close values of $M_{e,melt}$ or N_{unit} mean that 2-sulfate group of A unit does not affect the chain properties significantly, while 4-sulfate group of S unit might be influential.

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Figure Captions

Fig. 1   Master curves of ω dependence of G' and G'' for κ-M solutions at $T_r = 80$ °C. The

curves are shifted upwards by A.

Fig. 2   Shift factor for κ-M solutions plotted against the reciprocal of T. All data points fall on

a single line.

Fig. 3   Master curves of ω dependence of G' and G'' for ι-M solutions at $T_r = 80$ °C. The

curves are shifted upwards by A.

Fig. 4   Shift factor for ι-M solutions plotted against the reciprocal of T. All data points fall on a

single line.

Fig. 5   Double-logarithmic plot of M_e vs. c for κ- and ι-carrageenans in solution. Each line is

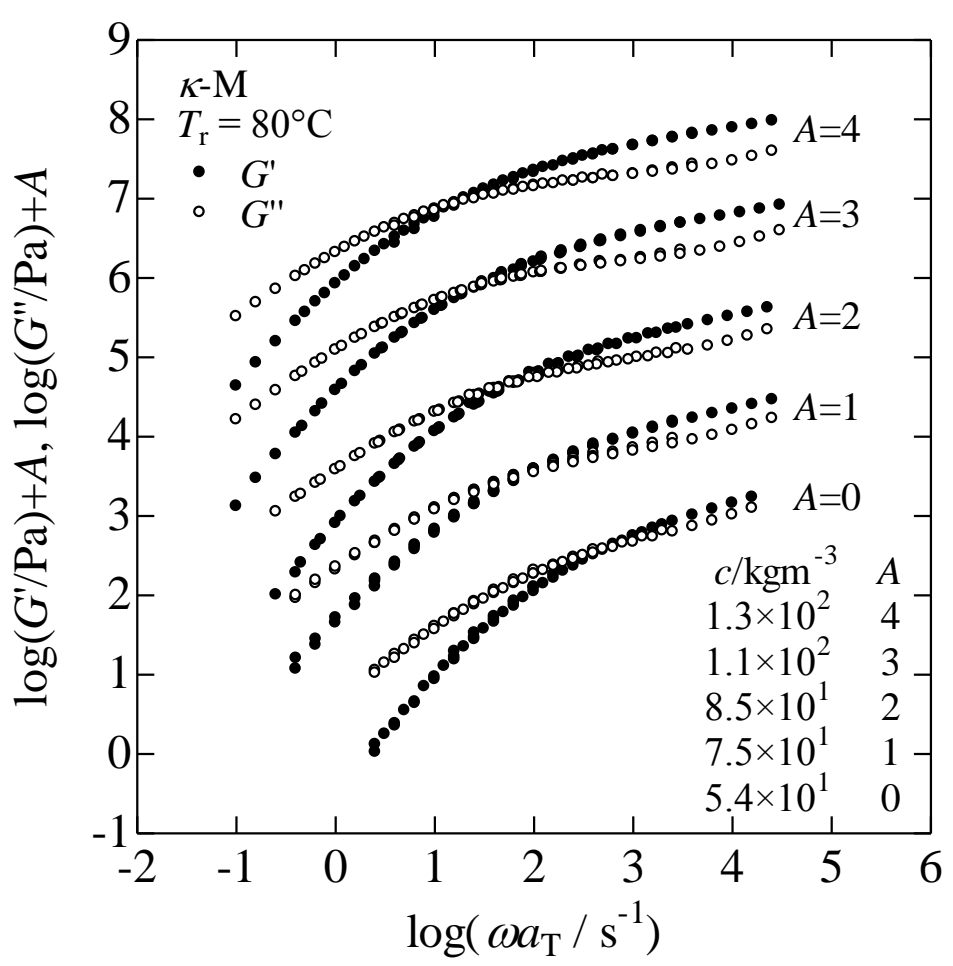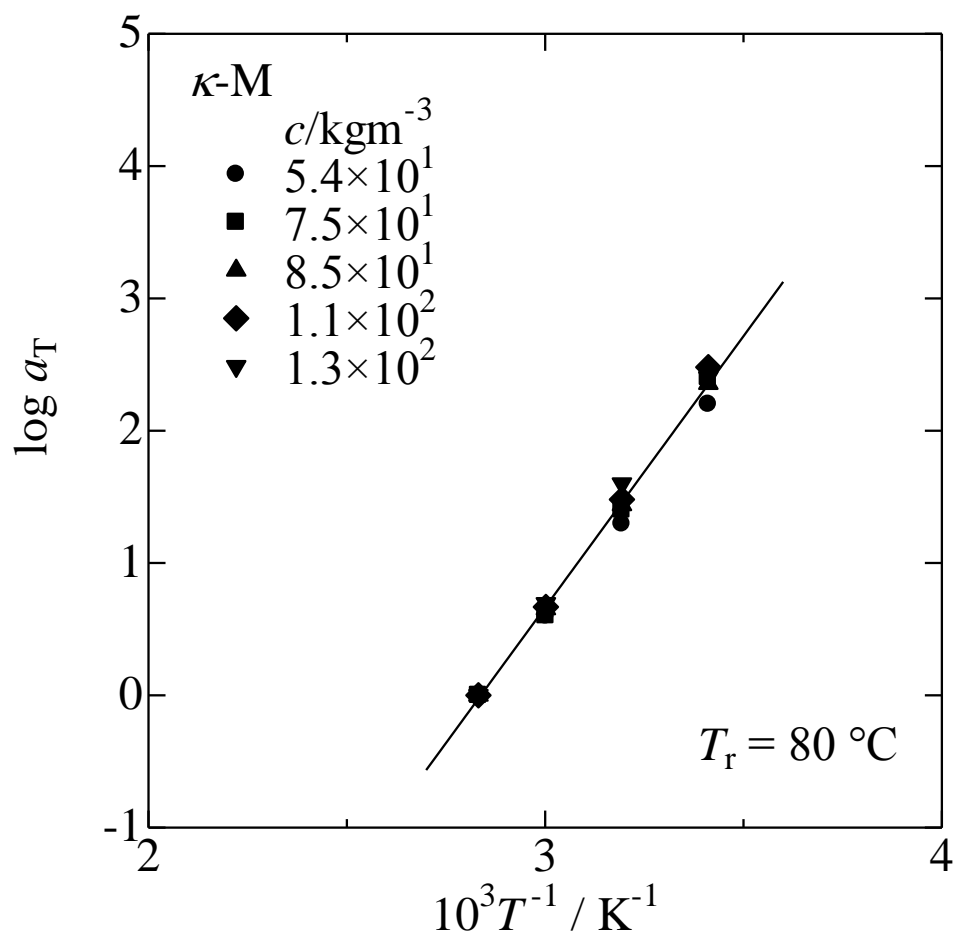the best fit one with a slope of -1. $M_{e,melt}$ is determined as M_e at $c = 10^3$ kgm^{-3}.
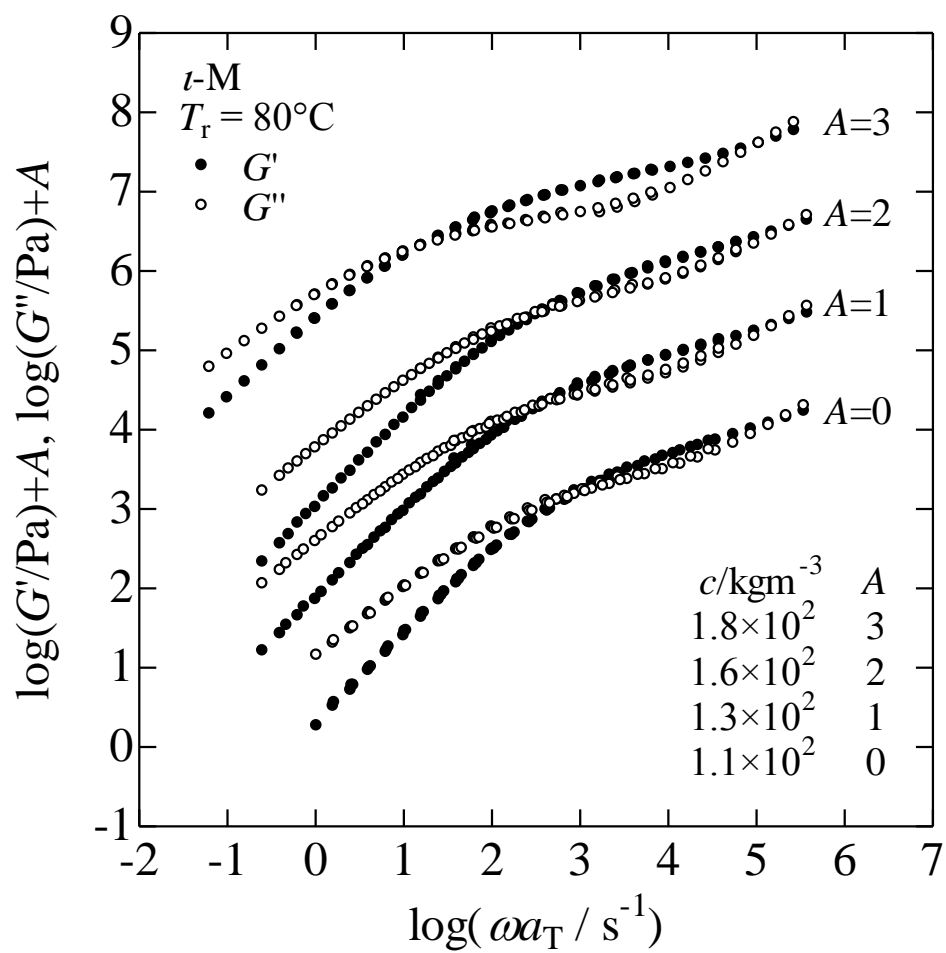
Figure(s)

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