“Weak Gel”-Type Rheological Properties of Aqueous Dispersions of Nonaggregated κ-Carrageenan Helices

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The rheological properties of κ-carrageenan helices dispersed in an aqueous medium, which prevents aggregation of helices, were investigated. A dispersion of 1.5% w/w nonaggregated κ-carrageenan helices exhibited gel-like dynamic mechanical spectra at 20 °C; that is, the storage modulus G' predominated over the loss modulus G'' in the entire frequency range examined (0.5−100 rad/s). However, the observed slight frequency dependence of the moduli and the relatively large value of $\tan \delta$ ($= G''/G' > 0.1$) were typical of so-called weak gels. The magnitude of G' of the κ-carrageenan weak gels was less than that of conventional gels formed by 0.15% w/w κ-carrageenan in an aggregating condition at 20 °C. Under large deformation, enough for the conventional gels to rupture, the weak gel systems flowed but never ruptured, suggesting that the weak gel-type rheological properties of the κ-carrageenan dispersions were due to a sufficiently long relaxation time of topological entanglements among double-helical conformers but not due to the formation of a three-dimensionally percolated permanent network.

Keywords: *Weak gel; κ-carrageenan; viscoelasticity; coil−helix transition; sol−gel transition*

INTRODUCTION

A gel can be defined topologically as a network system that is three-dimensionally percolated into the entire space (*1*). Mechanically, a gel is a soft material, having both solid- and liquid-like characteristics (*2*, *3*). An ideally elastic solid body can deform on application of force and return to its original shape instantaneously on removal of the force. Such a solid body can be identified mechanically as the existence of an equilibrium modulus. Gels are, however, viscoelastic in nature and, theoretically, it could take infinite time for a gel under investigation to reach equilibrium so that we can determine the equilibrium modulus. Alternatively, we often distinguish gels from sols on the basis of the time-scale dependence of the dynamic moduli. The application of oscillating small strains to a material allows us to obtain two dynamic moduli, namely, the storage modulus, G', a measure of the elasticity, and the loss modulus, G'', representing viscous components, at a given frequency ω of oscillation (*4*, *5*). A gel should exhibit a solid-like mechanical spectrum; that is, $G' > G''$ throughout the experimentally accessible frequency range and there is little frequency dependence of the moduli (*2*, *3*).

This mechanical definition of a gel, however, seems to expand the categories of materials that are judged as a gel on the basis of their mechanical spectra and thus, in a practical situation, it could be challenging to mechanically determine whether a material is a gel or a liquid. An example is a semidilute polymer solution, a polymer solution at a sufficiently high concentration, in which entanglements among polymer chains exist. Mechanical spectra for such a system are similar to those of dilute solutions ($G'' > G'$) at low frequencies, because there is sufficient time for the polymer chains to disentangle and flow during a single oscillation (*5*). At high frequencies, on the other hand, interchain entanglements do not have sufficient time to come apart within the period of single oscillation, and thus the system responds as if it were a solid ($G' > G''$) (*5*). It is, therefore, the lifetime or the relaxation time of the entanglements that determines whether the system appears a solid or a liquid in the mechanical spectrum in the available frequency range. In the case that the lifetime of the interchain entanglements is sufficiently longer than the time scale of observation ($\sim 1/\omega$), we gain a gel-like mechanical spectrum. An aqueous solution of xanthan, a microbial exopolysaccharide produced by *Xanthomonas campestris*, is known to exhibit gel-like mechanical spectra, being referred to as a “weak gel” (*6*−*8*). By human perception, a weak gel may look like a gel, not a liquid, whereas the mechanical spectra of weak gels are slightly different from those of conventional gels in two respects: the moduli are a little frequency dependent, and the magnitude of G' is often <10 times that of G'' (*6*, *9*). Additionally, due to the absence of permanent cross-links, such a system should flow but never rupture under large deformations (*8*). It is known that some sorts of colloidal dispersions, such as polystyrene latices (*10*), globular proteins (*11*, *12*), and water-insoluble particles of polysaccharides (*13 14*), also exhibit weak gel-type mechanical spectra even when they do not look like solids to the eye.

κ-Carrageenan, composed ideally of an alternating $\beta(1\rightarrow3)$-D-galactose-4-sulfate and $\alpha(1\rightarrow4)$-3,6-anhydro-D-galactose repeating unit, is a particularly important polysaccharide in the food industry, due to its thermoreversible gel-forming ability, so that extensive studies on its gelation phenomena have been carried out by a number of researchers (*15*). When a dispersion of

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κ-carrageenan is cooled, the random coil forms of κ-carrageenan molecules transfer into double-helical conformers (*16*). It is widely accepted that the helices associate into rigid rods in the presence of specific gel-promoting salts such as KCl, leading eventually to the formation of a gel in an appropriate condition (*17*). Such interhelical association is usually evident from thermal hysteresis between transitions from coil to helix and from helix to coil (*15*, *18*, *19*). The coil-to-helix transition occurring on cooling is considered to reflect the equilibrium between coil and helical conformers, whereas the helix-to-coil transition occurring on heating at higher temperatures reflects the increased thermal stability of the associated helices in the presence of specific salts. These mechanisms are appealing and seem to explain the formation of cross-linking regions, or junction zones, in a gel. However, they are not relevant to the formation of branching that is essential for the formation of a network. Viebke et al. (*17*) have reached a conclusion based on theoretical considerations: κ-carrageenan gel networks are formed at superhelical levels, that is, by fibrously aggregated helices, which was also supported by carefully conducted experimental results. They first prepared a stable dispersion of κ-carrageenan helices in an aqueous medium that prevents the aggregation of helices. Such a nongelling dispersion was reversibly transformed into a gel only by dialyzing against an aggregation-promoting salt solution. Later, a cryotransmission electron microscopic study revealed that microfibers (∼300 nm in length) were actually formed in an aggregating condition (*20*).

The formation of helices and subsequent association of the helices are essential features in common among the gelation schemes of many biopolymers such as agarose, gellan gum, or κ-carrageenan (*21*). To gain insight into the gelation mechanisms of these polysaccharides, it is desirable to investigate the helix formation and the aggregation of the helices independently. Because specific anions, such as the iodide ion, are known to bind to and stabilize κ-carrageenan helices but prevent aggregation of the helices (*22*), a nonaggregating dispersion of κ-carrageenan helices stabilized in the presence of such specific anions is expected to be a good model system. Recently, Piculell and colleagues have shown that a dispersion of κ-carrageenan helices under nonaggregating conditions (e.g., in a 0.1 mol/dm^3 NaI aqueous solution) can exhibit weak gel-type rheological properties (*9*, *20*, *23*), suggesting that aggregation of helices is not necessarily required for a κ-carrageenan helical system to exhibit an elastic nature. The goal of this study was to elucidate whether κ-carrageenan weak gels, formed under nonaggregating conditions, are actually gels or not, in terms of rheology. We have analyzed mechanical responses of κ-carrageenan weak gels under linearly small and destructively large deformations and compared them with those of conventional κ-carrageenan gels, formed in the presence of a gelation-promoting potassium salt.

MATERIALS AND METHODS

Materials. κ-Carrageenan (C-1263, lot 39H1211) was purchased from Sigma Chemical Co. (St. Louis, MO) and used without further purification. Other chemicals were of reagent grade quality. Sample solutions were prepared by dissolving the κ-carrageenan into distilled water, containing either 0.2 mol/dm^3 NaI or 0.2 mol/dm^3 KCl, under stirring for 30 min at 90−95 °C. The ionic concentration of the added salts in the test samples was intended to be high enough to mask the effects of pre-existing ions in the κ-carrageenan as impurities (several percent by weight at most). It has also been shown that the modulus of 1.5% w/w κ-carrageenan aqueous dispersions, containing NaI, increases with increasing concentration of NaI up to a maximum at 0.2 mol/dm^3 (*9*).

Rheological Measurements. Dynamic viscoelastic and steady flow properties of κ-carrageenan dispersions were measured using a stress-controlled rheometer (RheoStress 1, Haake, Germany), equipped with a double-gap cylinder test fixture (DG41; inner gap = 0.25 mm; outer gap = 0.3 mm; height = 55 mm; Haake, Germany). A sample solution was loaded into the test cup of the instrument, which was pre-set at 80 or 90 °C, and then immediately covered with silicone oil to prevent water loss. Because this instrument allows users to select either a controlled-stress or controlled-strain mode for measurements, a controlled-strain mode (set strain = 0.01; 1 rad/s) was chosen for monitoring the storage molulus, G', and the loss modulus, G'', as a function of temperature on cooling or heating at a rate of 1 °C/min. Gel samples were formed by cooling hot sample solutions (80 or 90 °C) to 20 °C at a rate of 1 °C/min, and the following measurements were made. Frequency sweep measurements of G' and G'' were performed at 20 °C in a controlled-strain mode (set strain = 0.01). Dynamic stress sweep measurements were done at 20 °C to determine the strain dependence of G' and G'' by applying oscillating controlled-shear stresses τ, ranging from 0.1 to 100 Pa, at 1 rad/s. Steady stress sweep measurements were done at 20 °C to determine the steady shear viscosity η at steady shear stresses from 1 to 100 Pa. All experiments were performed at least in triplicate. Determined values of G', G'', and η were reproducible with an estimated error of ±10%.

RESULTS AND DISCUSSION

The potassium cation is known to possess a strong gel-promoting ability for κ-carrageenan, whereas the iodide anion prevents gelation even in the presence of an equal amount of potassium ions (*22*). It was presumed at first that iodide ions bind to and stabilize single-helical conformers (*22*), but double helices appeared to be involved because the molecular weight doubled approximately when the coil-to-helix transition took place in the presence of the iodide ion (*16*). The iodide ion prevents helices from aggregating, so network formation on the helical level (a flexible polymer chain connecting two double-helices), if it exists, is insignificant (*17*). Chronakis et al. (*9*) have shown that κ-carrageenan forms gels at relatively high concentrations (∼ >0.9% w/w) even in the absence of aggregates of helices in an aqueous medium containing NaI. However, these gels are different from conventional κ-carrageenan gels in two respects: the low magnitude of the storage modulus and the absence of thermal hysteresis in the sol−gel transition.

Figure 1a shows the temperature dependence of the dynamic moduli on cooling and subsequent heating of 1.5% w/w κ-carrageenan in 0.2 mol/dm^3 NaI, which is a nonaggregating condition. On cooling, both moduli started increasing rapidly at ∼60 °C, which was considered to be due to the coil-to-helix transition of κ-carrageenan. The transition temperature is known to increase with increasing ionic concentration, and the observed value here appears to be consistent with the literature (*9*, *15*). Only slight increases in the moduli were observed below 50 °C, whereas the magnitude of G' was significantly larger than that of G'' at 20 °C, indicating that a gel was formed. On heating, we observed almost identical temperature dependences of the moduli, but a slight (less than a few degrees

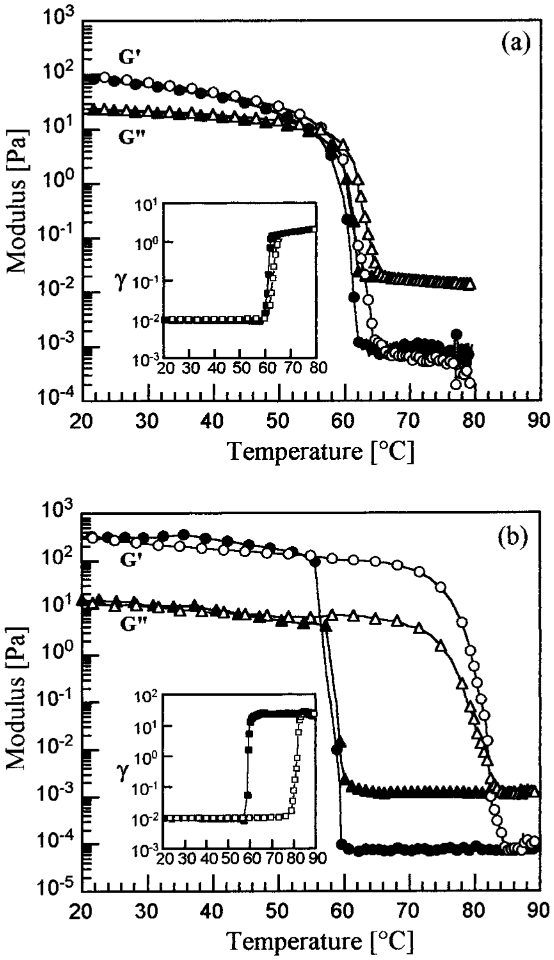

Figure 1. Temperature dependence of G' (circles) and G'' (triangles) on cooling (solid symbols) and heating (open symbols) 1.5% w/w κ-carrageenan in 0.2 mol/dm^3 NaI (a) or 0.15% w/w κ-carrageenan in 0.2 mol/dm^3 KCl (b) (frequency = 1 rad/s; cooling and heating rates = 1 °C/min). (Insets) Applied strain values (solid, cooling; open, heating).

centigrade) thermal hysteresis was recognized. This is unlikely to be due to the existence of impurities such as potassium ions, because thermal hysteresis has not been observed in a mixture of a gel-promoting and a gel-impeding salt as long as the mole fraction of the gel-promoting species is <0.4 (*9*). The estimated content of the potassium ion, in the present study, does not exceed 0.2 times that of the iodide ion at most. Although we cannot exclude the possibility that a small amount of helical aggregates was formed, the observed thermal hysteresis may be due to changes in the magnitude of the applied strain during measurements. The inset in Figure 1a represents the absolute values of strains that were actually applied. We have selected a controlled-strain mode and set the strain value of 0.01 for the measurements. Nevertheless, the apparatus was not able to control the applied strain within the restricted range when the sample was very thin at above ~60 °C. Therefore, it can be speculated that the very large deformation (strain of ~1) at high temperatures might have delayed the coil-to-helix transition on cooling to some extent. Figure 1b shows the temperature dependence of the dynamic moduli of 0.15% w/w κ-carrageenan dispersed in 0.2 mol/dm^3 KCl, which is an aggregating condition. There was strong thermal hysteresis (i.e., ~20 °C difference in the two transition temperatures), which is typical thermal behavior of a conventional κ-carrageenan gel. It is also worth noting that this conventional gel possessed an even higher value of the storage modulus at 20 °C, despite the only $^1/_{10}$ concentration, compared with that shown in Figure 1a. When the dynamic moduli were monitored for 30 min at 20 °C after cooling, no substantial change was observed for the weak gel (Figure 2). The moduli of the conventional gel with KCl slightly decreased with time (Figure 2), indicating that the gel network was gradually shrinking and releasing water (syneresis) in the presence of the aggregation-promoting potassium salt.

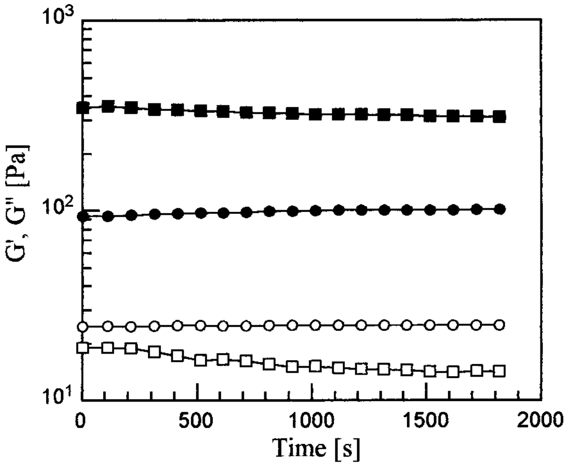

Figure 2. Time dependence of G' (solid symbols) and G'' (open symbols) of 1.5% w/w κ-carrageenan in 0.2 mol/dm^3 NaI (circles) and 0.15% w/w κ-carrageenan in 0.2 mol/dm^3 KCl (squares) at 20 °C (frequency = 1 rad/s; strain = 0.01).

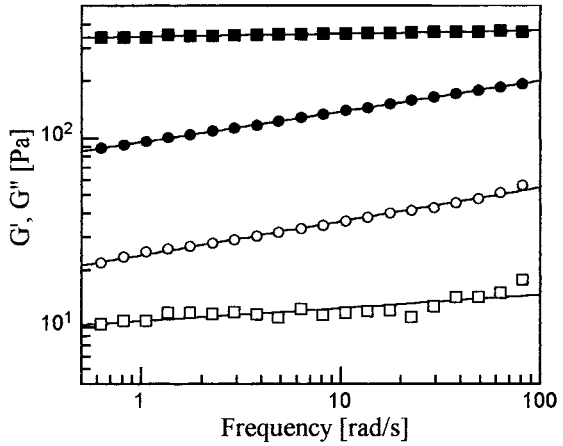

Figure 3. Frequency dependence of G' (solid symbols) and G'' (open symbols) of 1.5% w/w κ-carrageenan in 0.2 mol/dm^3 NaI (circles) and 0.15% w/w κ-carrageenan in 0.2 mol/dm^3 KCl (squares) at 20 °C (strain = 0.01).

Figure 3 represents the frequency dependence of the moduli of two types of κ-carrageenan gels at 20 °C. Both samples exhibited typical gel-type mechanical spectra; i.e., $G' > G''$ in the entire frequency range examined. The moduli of the conventional gel were almost frequency independent. The moduli of the 1.5% w/w κ-carrageenan gel in 0.2 mol/dm^3 NaI were dependent on the frequency, but only slightly in comparison with dilute or semidilute polymer solutions, which show $G'' \propto \omega^1$ and $G' \propto \omega^2$ at low frequencies. The value of tan δ ($= G''/G'$), which is a measure of the relative contribution of viscous components to the mechanical properties of the material, was <0.1 for the conventional gel, suggesting that the gel was predominantly elastic, whereas that of the 1.5% w/w κ-carrageenan gel in 0.2

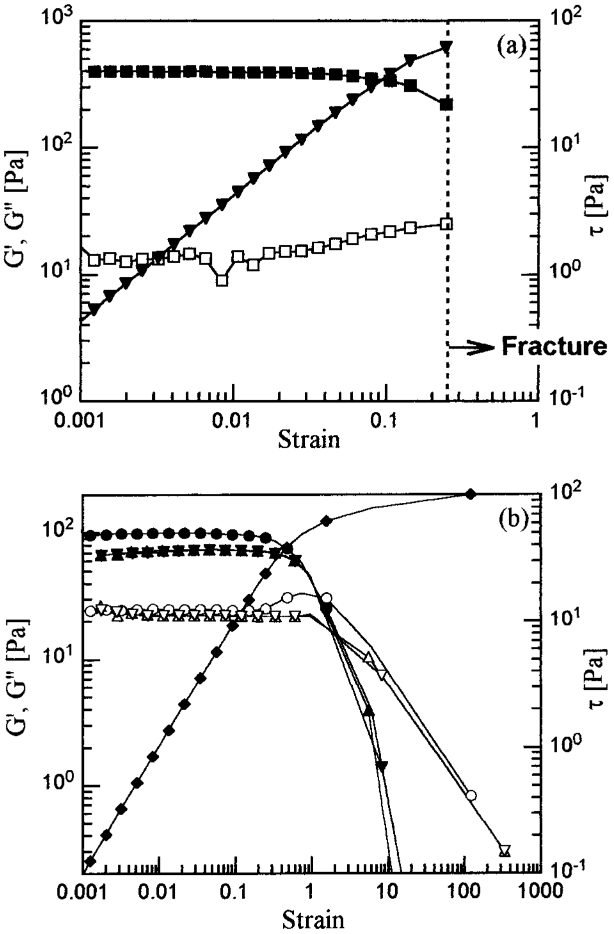

Figure 4. (a) Strain dependence of G' (solid squares) and G'' (open squares) determined by shear stress τ (triangles) sweep measurements for 0.15% w/w κ-carrageenan in 0.2 mol/dm^3 KCl at 20 °C (frequency = 1 rad/s). (b) Strain dependence of G' (solid circles) and G'' (open circles) determined by shear stress τ (diamonds) sweep measurements for 1.5% w/w κ-carrageenan in 0.2 mol/dm^3 NaI at 20 °C (frequency = 1 rad/s). Results of the second- and third-run measurements of the moduli are represented by upright and inverted triangles, respectively.

mol/dm^3 NaI was ~0.4 at all frequencies examined. A relatively large frequency dependence of the moduli, accompanied by a tan δ value >0.1, is a typical feature of a so-called weak gel (*6*, *9*).

There seems to be a consensus that the linear viscoelastic strain region of a weak gel is narrow compared with a true strong gel (*8*). However, this was not the case with the κ-carrageenan weak gel examined. Because the extent of the linear strain region is concentration dependent (*8*), it is considered that gels with similar values of the moduli should be examined for purposes of comparison. With increasing magnitude of the shear stress applied to the conventional gel, the linear viscoelastic strain region was observed up to strain of ~0.1 (Figure 4a). The linear strain region of the weak gel also extended up to ~0.1 (Figure 4b). A remarkable difference between these two types of gels appeared when the measurements were repeated. The conventional gel fractured at strain of ~0.2 (Figure 4a), and therefore it was impossible to gain useful information by repeating the same measurement (data not shown). The weak gel, on the other hand, never fractured even when a very large deformation was applied under the dynamic shear stress of 100 Pa (Figure 4b), when we visually observed that the measuring device rotated very rapidly for many revolutions. The values of the moduli determined at the second-run measurements were slightly less than those at the initial (first-run) measurements (Figure 4b). We have not reached a reasonable explanation for the decrements of the moduli at this point, but it may be suspected that (1) the friction at the interface between the sample and the measuring device was somehow reduced by intensive stirring, (2) entangled helices were oriented in the direction of the flow, or (3) some structural breakdown took place. In any case, no further change in the spectrum was noticeable between the second- and third-run measurements (Figure 4b), confirming that gel-like mechanical characteristics [$G'(\omega) > G''(\omega)$] were not lost when extremely large deformations were applied.

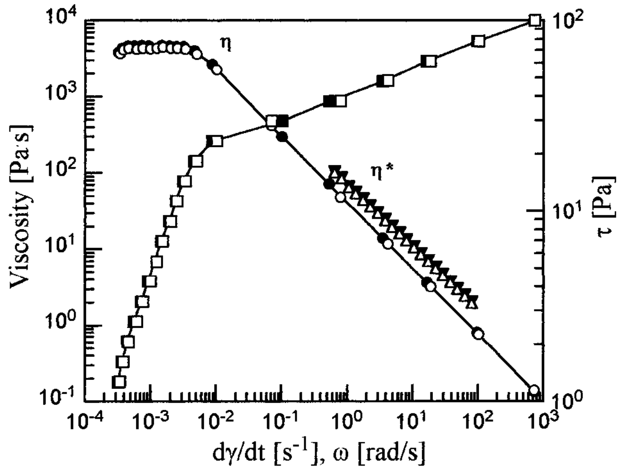

Figure 5. Shear strain rate dependence of the steady shear viscosity (circles) and the shear stress (squares) and frequency dependence of the dynamic viscosity (triangles) of 1.5% w/w κ-carrageenan in 0.2 mol/dm^3 NaI at 20 °C. Solid and open symbols represent the first- and second-run measurements, respectively.

Steady and dynamic rheological properties of the κ-carrageenan weak gel are compared in Figure 5. Under the steady shear flow, a Newtonian flow region was observed at the low limiting shear rate and a strong shear thinning at a higher shear rate. Values of the dynamic viscosity, η^*, were larger than those of the steady shear viscosity, η, at a comparable angular frequency and shear rate. These results are similar to steady and dynamic properties of xanthan, a typical weak gel (*6*−*8*). The empirical Cox−Merz rule (*24*) states that values of η^* and η should be identical at a comparable time scale of observation, as long as the structure that determines the mechanical properties of the material remains intact under steady flow. Therefore, the failure of the rule shown in Figure 5 suggests that rheological properties of the weak gel systems stem from some deformation susceptible structures. However, this does not necessarily mean that such structure is permanently lost when a large deformation is applied: reproducible results were obtained by repeating the steady shear viscosity measurement (Figure 5).

We have checked whether gel-like mechanical properties of the κ-carrageenan weak gel survive the application of destructively large deformations. Figure 6 shows dynamic mechanical spectra of the κ-carrageenan weak gel after severe shear treatments. The first-run measurement was done after the sample had been sheared

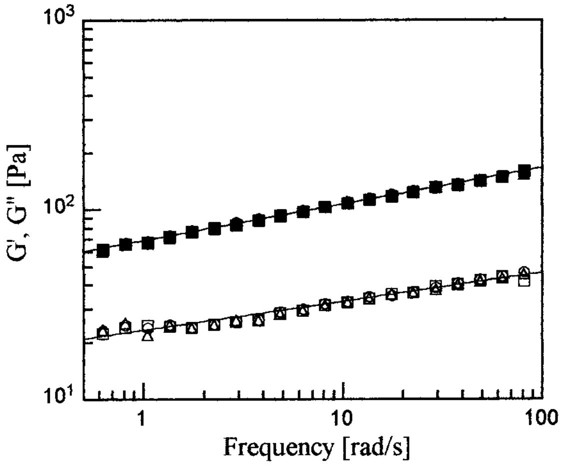

Figure 6. Frequency dependence of *G*′ (solid symbols) and *G*″ (open symbols) of 1.5% w/w *κ*-carrageenan in 0.2 mol/dm^3 NaI at 20 °C. Circles, triangles, and squares represent the first-, second-, and third-run measurements, respectively. Each measurement was done after the application of an extremely large strain (at the shear rate of ~1000 s^{-1} for at least 30 s) to the sample.

at the shear rate of ~1000 s^{-1} for at least 30 s, followed by the same shear treatment and the second-run measurement, likewise the third-run. Compared with the results shown in Figure 3, which are for the sample that had not experienced a large deformation, values of the moduli slightly decreased at all frequencies. However, subsequent applications of extremely large deformations did not influence the gel-like dynamic spectra at all. It is now safely concluded that the dispersion of rigid helical conformers of *κ*-carrageenan exhibited gel-like rheological behavior, under dynamic small strains in an ordinary available frequency range, whereas it was able to flow without fracture under extremely large strains. In our opinion, such a dispersion should be classified as a concentrated polymer solution rather than a gel, due to its essential nature as a liquid. At least, the usage of the term “gel” should be always accompanied by its definition with regard to time and length scales of observation especially.

It should be possible, if the elastic nature of the weak gel is due to temporary entanglements of rigid polymer chains, to make the relaxation time of entanglements come within the observable frequency window by dilution. Figure 7 shows dynamic mechanical spectra of 0.5, 0.7, and 1.0% w/w *κ*-carrageenan dispersed in 0.2 mol/dm^3 NaI at 20 °C. The 1.0% w/w *κ*-carrageenan dispersion exhibited a gel-like spectrum, similar to that of the 1.5% w/w *κ*-carrageenan dispersion (Figure 6), whereas the 0.5% w/w dispersion appeared as a semidilute polymer solution; that is, *G*″ predominated over *G*′ at low frequencies, and there was a crossover between *G*′ and *G*″ in the highest frequency range examined. When the concentration was increased to 0.7% w/w, the crossover frequency, which corresponds to the average relaxation time of entanglements, was lowered close to the lowest end of the accessible frequency (Figure 7). These results are in line with the results of Chronakis et al. (*9*), in the sense that they observed gel-like behavior of *κ*-carrageenan aqueous dispersions containing NaI only at relatively high concentrations of *κ*-carrageenan >0.9% w/w.

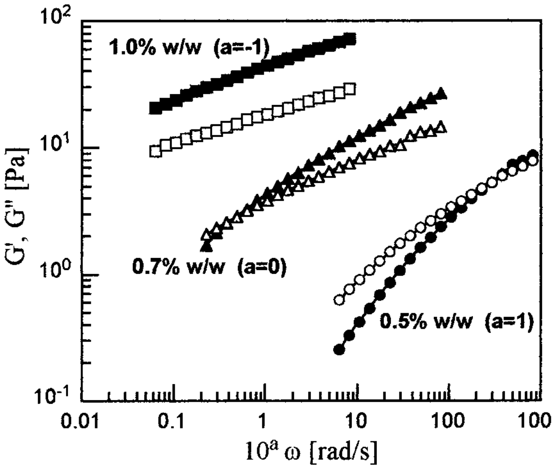

Figure 7. Frequency dependence of *G*′ (solid symbols) and *G*″ (open symbols) of 0.5% w/w (circles), 0.7% w/w (triangles), and 1% w/w (squares) *κ*-carrageenan in 0.2 mol/dm^3 NaI at 20 °C (strain = 0.01). Data were shifted horizontally to avoid overlapping.

It has been believed traditionally that a polysaccharide gel network consists of disordered flexible polymer chains linking ordered junction zones (*21*). Recently, Morris et al. (*25*) have proposed a fibrous model based on atomic force microscopic (AFM) observations of gellan gum gels, suggesting that the network structure is formed at the superhelical level by fibrously aggregated helices, similar to the gelation mechanism proposed for *κ*-carrageenan (*17, 20*). Although the coil-to-helix transition of *κ*-carrageenan is sufficiently cooperative, it is still possible, in an actual gelling situation, that a single polymer chain is involved in two distinct junction zones formed by aggregation of helices so that a network structure at the helical level is frozen in (*17*). It is therefore likely that not only superhelical networks made up of fibrously aggregated helices but also networks composed of ordered junction zones connected by disordered flexible polymer chains, which cannot be observed even by AFM due to their Brownian motions, exist in a real polysaccharide gel. However, as shown in this study, even nonaggregated helical conformers of *κ*-carrageenan are rigid enough for their entanglements to exhibit gel-like viscoelasticity even without the formation of a permanent network structure. It seems to be reasonable to assume that elastic properties of conventional *κ*-carrageenan gels are dominated by contributions from fibrous aggregates of helices.

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