# Light Scattering and Viscoelasticity of Aggregating and Gelling κ-Carrageenan

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ABSTRACT: We have studied the evolution in time of the shear modulus and the scattered light intensity of aqueous κ-carrageenan solutions at various concentrations and temperatures. Aggregation was induced by cooling solutions containing 0.01 M KCl. The ionic strength of the solutions was fixed by adding 0.1 M NaCl. The time dependence was found to be similar at all concentrations and temperatures investigated. Equilibrium was not attained even after 12 h maturation. The temperature dependence is mainly kinetic and diverges at a temperature close to the temperature of the coil−helix transition of κ-carrageenan. Varying the concentration influences both the aggregation kinetics and the strength of the gels. No critical minimal concentration for gelation is observed.

## Introduction

The carrageenans are a family of linear sulfated galactans extracted from various species of marine red algae. Different types may be distinguished by their primary structures.[1] κ-Carrageenan is composed of alternating α(1−3)-D-galactose-4sulfated and β(1−4)-3,6-anhydro-D-galactose. This polysaccharide is used in the food industry as a gelling agent.[2,3] It forms a thermoreversible gel on cooling below the temperature ($T_c$) where the conformation changes from a random coil to a helix.[4,5] The temperature, the ionic strength, and the nature of the counterions regulate this conformational change and, consequently, the gelation process.[6,7]

The precise mechanism of the salt-induced gelation of κ-carrageenan continues to be a matter of debate and controversy. Although there is agreement on a two-step mechanism of gelation, i.e., a coil−helix transition followed by aggregation of the helices, the exact nature of these helices and the way the gel is formed are not yet established.[5,8−11]

The local structure of the aggregates and the gel has been studied by X-ray scattering in an attempt to elucidate the helical structure.[12−14] The large-scale structure has been studied recently using microscopy.[15,16] The authors found that in the presence of potassium, a specific counterion, κ-carrageenan forms rigid-rod-like aggregates on cooling below $T_c$. On the other hand, in the presence of iodide, a specific co-ion, helices are formed, but aggregation is inhibited.

The mechanical properties of κ-carrageenan gels have been extensively investigated.[17,18] In these studies it was assumed that the gelation of κ-carrageenan occurs fast enough that measurements can be done in the equilibrium state. The temperature dependence of the storage shear modulus ($G'$) was investigated using simple temperature ramps. For a given frequency $G'$ was found to increase strongly below a characteristic temperature close to $T_c$.[19,20] The concentration ($C$) dependence of $G'$ at a given temperature was observed to follow a power law: $G' = KC^n$, with $n \approx 2$. These experiments were done using concentrations higher than 1 g/L and after a fixed, relatively long cooling time (overnight).

The purpose of the present work is to study the aggregation kinetics and to extend the investigation to lower concentrations. We use both dynamic mechanical measurements and light scattering. Light scattering is very sensitive to the presence of aggregates and is therefore a powerful method for studying the initial stages of aggregation even at very low concentrations. Light scattering has been used in the past to characterize κ-carrageenan[21] but not to study its aggregation.

## Experimental Section

**Materials.** The κ-carrageenan used for this study was an alkali-treated extract from *Eucheuma cottonii* supplied by SKW Biosystems, (Baupte, France). The solutions were prepared by as follows: A freeze-dried sample of κ-carrageenan in the sodium form was dissolved while stirring a few hours in hot Millipore water (70 °C) with 200 ppm sodium azide added as a bacteriostatic agent. The pH was adjusted to 9 to eliminate the risk of hydrolysis during preparation.[22−24] The solution was dialyzed against Millipore water to eliminate excess salt. Hot Millipore water containing 0.2 M NaCl and 0.02 M KCl was added to set the final ionic conditions at 0.1 M NaCl and 0.01 M KCl. We chose a concentration of 0.01 M KCl in order to have a convenient coil−helix transition temperature close to ambient.[25] NaCl was added to screen electrostatic interactions and to make the ionic strength independent of the κ-carrageenan concentration. We found that the temperature ($T_c$) below which optical rotation increases abruptly is 24.5 °C with and without the presence of 0.1 M NaCl. A detailed study of the optical rotation is in progress and will be reported at a later stage. In ref 25 the transition midpoint temperature is used to characterize the transition which is a few degrees lower. However, we found that the initial abrupt rise is a better measure of the critical temperature where aggregation starts (see Figure 9). The solutions always contained a small amount of large aggregates which perturb the light scattering results. These aggregates were removed by filtration through 0.2 μm pore size Anotop filters. The absence of aggregated material and other spurious scatterers was checked by dynamic light scattering. The solutions were stored at 50 °C.

**Experimental Techniques.** Dynamic storage ($G'$) and loss ($G''$) moduli were measured using a stress controlled rheometer (Haake RS100) with a cone and plate geometry (diameter 60 mm, angle 1°, gap 0.049 mm). The sample which was kept at 50 °C for at least 24 h is introduced into the apparatus keeping the temperature above $T_c$ and is covered with paraffin oil to

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prevent evaporation. The temperature is subsequently lowered to a set value below $T_c$ which induces aggregation. The rate of temperature decrease is imposed by the apparatus used but is the same for all experiments. The applied stress is chosen to keep a low strain (<1%), especially in the initial stages of gelation. In fact, if the strain is too high at this stage, the gel structure, and thus the shear modulus, is influenced during the whole experiment. Therefore, we did preliminary experiments to find the optimum stress at different stages of gelation that gave sufficient signal without perturbing the gel structure. At the lowest concentrations and for temperatures close to $T_c$, no stress was applied before the gel modulus reached about 0.1 Pa so as to avoid disrupting the incipient gel. With the geometry used here we were able to avoid the effects of wall slip[20] up to $C = 2$ g/L.

Light scattering measurements were made using an ALV-5000 multibit, multi-τ full digital correlator in combination with a Malvern goniometer and a Spectra-Physics laser emitting vertically polarized light at $\lambda = 488$ nm or $\lambda = 532$ nm. The temperature is controlled by a thermostat bath to within ±0.1 °C. The sample was kept in the scattering cell at 50 °C for at least 24 h before it was introduced into the apparatus which was set at a given temperature below $T_c$. Measurements were done for short periods of time at several angles of observation ($\theta$). This series of measurements was repeated during at least 10 h. The relative excess scattering intensity ($I_r$) was calculated as the total scattered intensity minus the solvent scattering divided by the scattering intensity of toluene at 20 °C.

## Results

**Characterization.** The κ-carrageenan used in this study was characterized in 0.1 M NaCl in the absence of KCl using dynamic (DLS) and static (SLS) light scattering, size exclusion chromatography (SEC), and nuclear magnetic resonance (NMR). In general, the relative excess scattering intensity $I_r$ can be written as[26]

$$I_r = KCM_wS(q) \tag{1}$$

where $S(q)$ is the structure factor and $K$ is a contrast factor:

$$K = \frac{4\pi^2 n_s^2}{\lambda^4 N_a}\left(\frac{\partial n}{\partial C}\right)^2\left(\frac{n_{tol}}{n_s}\right)^2\frac{1}{R_{tol}} \tag{2}$$

Here $N_a$ is Avogadro's number, $(\partial n/\partial C)$ is the refractive index increment, and $R_{tol}$ is the Rayleigh ratio of toluene at 20 °C ($3.96 \times 10^{-5}$ cm$^{-1}$ at $\lambda = 488$ nm and $2.79 \times 10^{-5}$ cm$^{-1}$ at $\lambda = 488$ nm[27]). $(n_{tol}/n_s)^2$ corrects for the difference in scattering volume of the solution with refractive index $n_s$ and the toluene standard with refractive index $n_{tol}$. $S(q)$ expresses the scattering wave vector dependence of the scattering intensity ($q = 4\pi n_s \sin(\theta/2)/\lambda$, with $\theta$ the angle of observation). $S(q)$ depends on the structure of the solute and on the interactions. Using the so-called Zimm approximation, eq 1 can be written in terms of the static correlation length ($\xi$) and the $z$-average second virial coefficient ($A_2$):[26]

$$\frac{KC}{I_r} = \frac{1}{M_w}(1 + 2A_2C)(1 + (q\xi)^2) \tag{3}$$

if higher order terms in $C$ and in $q\xi$ can be neglected. At infinite dilution $\xi$ is proportional to the $z$-average radius of gyration ($R_{gz} = \sqrt{3}\xi$). Figure 1a shows the concentration dependence of $KC/I_r$ extrapolated to $q = 0$ from which we obtain $M_w = 2.2 \times 10^5$ g mol$^{-1}$ and $A_2 = 3.28$ mL mol/g. The concentration dependence of $\xi$ is shown in Figure 1b, from which we obtain $R_{gz} = 52$ nm.

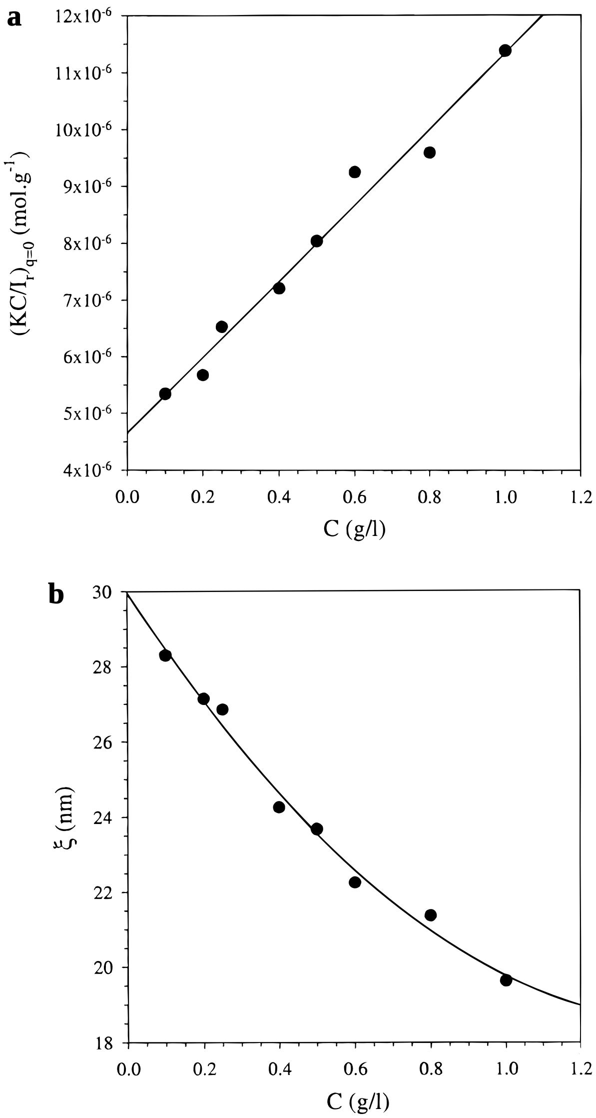

**Figure 1.** (a) Concentration dependence of $KC/I_r$ extrapolated to $q = 0$ of aqueous κ-carragheenan solutions containing 0.1 M NaCl at 20 °C. (b) Concentration dependence of the static correlation length of aqueous κ-carragheenan solutions containing 0.1 M NaCl at 20 °C.

We have used d$n$/d$C$ = 0.145 mL/g. This value was obtained from SEC using an on-line refractive index detector with light at 632 nm and is the same as found by Slootmaekers et al.[21] We measured the temperature dependence of $I_r$ in the range 15−40 °C. The variation of $I_r$ and thus d$n$/d$C$ is negligible in this range.

The size distribution was investigated using SEC. We used the following two columns in series: TSK PW 5000 of 30 cm and TSK PW6000 of 60 cm. The eluent was 0.1 M $NaNO_3$. We injected 300 μL of solution with sufficiently low concentration ($C = 0.5$ g/L) so that interactions are negligible. Figure 2 shows the refractive index signal as a function of the elution volume. The polydispersity index was calculated using pullulan calibration: $M_w/M_n = 2.6$.

With DLS the intensity autocorrelation function is measured which is related to the field autocorrelation function via the so-called Siegert relation.[28] For dilute solutions of monodisperse particles with $qR_g < 1$, the normalized field correlation function ($g_1(t)$) is a single-exponential decay with relaxation time $\tau = (q^2D)^{-1}$, where $D$ is the translational diffusion coefficient. $D$ is

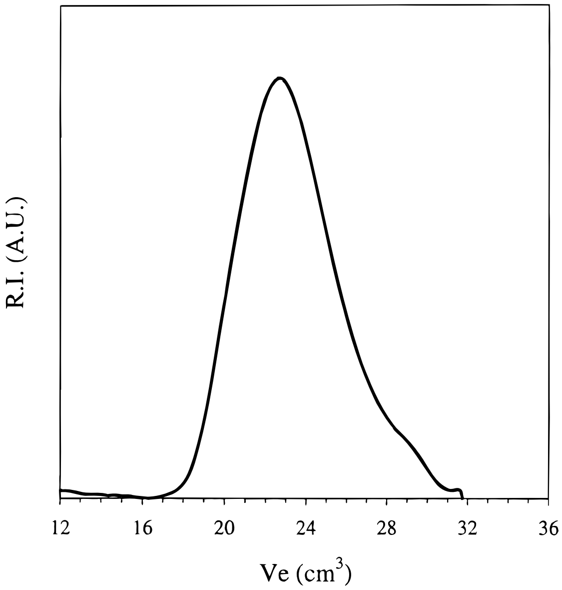

**Figure 2.** Refractive index signal as a function of elution volume of $\kappa$-carragheenan.

related to the hydrodynamic radius $R_h$ via the so-called Stokes–Einstein relation:

$$D = \frac{k_B T}{6\pi\eta R_h} \tag{4}$$

with $k_B$ Boltzmann's constant, $T$ the absolute temperature, and $\eta$ the solvent viscosity. For polydisperse dilute solutions $g_1(t)$ is characterized by a distribution of relaxation times ($A(\tau)$):

$$g_1(t) = \int A(t) \exp(-t/\tau)\, d\tau \tag{5}$$

If interactions are negligible and $qR_{gz} < 1$, the distribution of relaxation times may be expressed as the distribution of hydrodynamic radii ($R_h = \tau q^2 k_B T/6\pi\eta$). An example of $g_1(t)$ measured on a solution with a low concentration and $qR_{gz} < 1$ is shown in Figure 3a. The computer routine REPES[29] was used to obtain the corresponding relaxation time distribution. The relaxation time distribution was transformed to the distribution of $R_h$ shown in Figure 3b. Note that the amplitude is proportional to the scattered light intensity and thus to CM at low concentrations and $qR_{gz} < 1$.

At finite concentration the cooperative diffusion coefficient can be determined using the average relaxation rate ($\Gamma = 1/\tau$) extrapolated to $q = 0$: $D_c = \langle\Gamma\rangle/q^2$. $\langle\Gamma\rangle/q^2$ has a weak $q$ dependence due to polydispersity, rotation, and internal motion. Figure 4 shows the concentration dependence of $D_c$. $D_c$ has a linear concentration dependence over the range investigated:

$$D_c = 8.9 \times 10^{-8}(1 + 0.585C) \quad \text{cm}^2/\text{s} \tag{6}$$

The $z$-average hydrodynamic radius, $R_{hz}$, can be calculated from $D_c$ extrapolated to $C = 0$ via eq 4: $R_{hz} = 24$ nm. Note that $R_{hz}$ represents $1/\langle R_h^{-1}\rangle$, while $R_{gz}$ obtained from SLS represents $\langle R_g^2\rangle^{1/2}$, and gives stronger weight to large particles. Using $\langle\tau\rangle$ in the calculation, we obtained $\langle R_h\rangle = 31$ nm.

NMR measurements were done at 90 °C in order to estimate the amount of $\iota$-carrageenan. We found that the sample used here contains at most a few percent $\iota$-carrageenan.

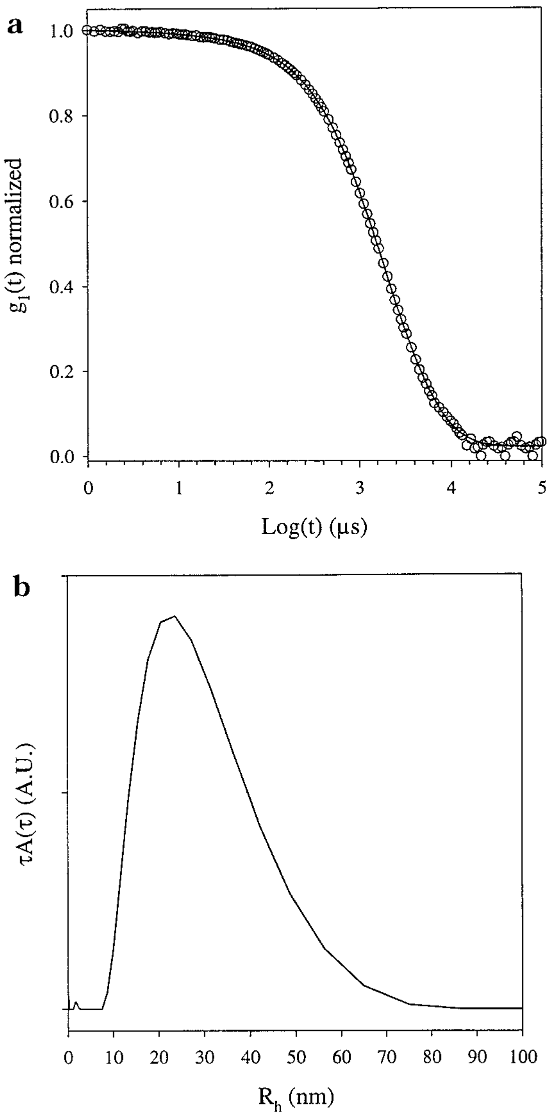

**Figure 3.** (a) Normalized electric field correlation function of an aqueous $\kappa$-carragheenan solution with $C = 0.2$ g/L containing 0.1 M NaCl at 20 °C. The measurement was done at $q = 7.35 \times 10^{-3}$ nm$^{-1}$, which means $qR_{gz} = 0.37$. (b) Distribution of $R_h$ derived from the correlogram shown in (a).

**Mechanical Measurements.** Figure 5a shows the time evolution of the storage modulus at 1 Hz for different concentrations upon cooling from 40 to 15 °C. At the highest concentrations $G'$ increases as soon as the temperature is below $T_c$, which is 24 °C at 0.01 M KCl. There is a lag between the time needed to reach $T_c$ indicated by the dotted line in Figure 5a and the time needed to stabilize at the set temperature. During this lag the kinetics are not well defined. Fortunately, this effect is only significant for the three highest concentrations. Decreasing the concentration both decreases the gel strength and slows the kinetics of the gel formation. However, the shape of the time evolution remains the same. This is shown in Figure 5b where all data at $t > 2 \times 10^4$ s have been superimposed by simple vertical ($a_G$) and horizontal ($a_t$) shifts. The shift factors used to obtain the master curve are plotted in Figure 6. Within the experimental error both shift factors have a power law dependence on the concentration: $a_t = 1.0C^{2.2}$ and $a_G = 0.9C^{-2.1}$, with $C_{ref} = 1.0$ g/L. This time-independent

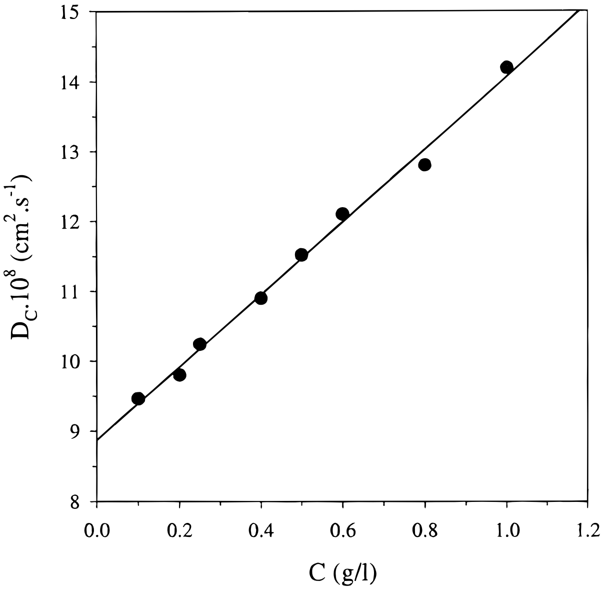

**Figure 4.** Concentration dependence of the cooperative diffusion coefficient of aqueous κ-carragheenan solutions containing 0.1 M NaCl at 20 °C. The solid line represents the result of a linear least-squares fit; see eq 6.

concentration dependence of the shear modulus is close to that reported in the literature.[30] As mentioned in the Introduction, in these studies the concentration dependence of $G'$ was determined after a fixed time. That nearly the same concentration dependence is found in the two cases is a consequence of the fact that at longer times $G'$ has the same weak power law dependence on time (parallel slopes in a log−log representation) at different concentrations. At $C > 1$ g/L the weak power law dependence is reached rather quickly. However, at low concentrations an apparent divergence of $G'$ will be found if it is measured after a given time. This divergence could be erroneously interpreted as a critical concentration for gelation. The master curve clearly shows that after an initial sharp rise $G'$ continues to increase at a lower rate. There is no sign of a stabilization even after 10 h at the highest concentration. At low concentrations even the initial rise takes several hours.

The frequency dependence of $G'$ measured after 10 h at 15 °C is negligible in the range $10^{-3}$−10 Hz. The frequency dependence of $G''/G'$ shows a weak minimum at 0.1 Hz (see Figure 7). The value of the minimum is independent of the concentration except at very low concentrations for which $G'$ has not yet completely reached the lower rate of increase even after 10 h.

The time evolution of $G'$ at different temperatures is shown in Figure 8a for a fixed concentration ($C = 1.0$ g/L). The time dependence of the temperature is similar to that shown in Figure 5a. A master curve can be formed using only horizontal shifts except at 24 and 25 °C for which we also need a vertical shift (see Figure 8b). The horizontal shift factors are plotted versus temperature in Figure 9. It is clear that $a_t$ diverges at about 25 °C, which is close to $T_c$. In fact, at 26 °C there was no evidence of gel formation even after 10 h. The fact that there is no need for vertical shifts means that the effect of temperature is purely kinetic for temperatures more than a few degrees below $T_c$. The frequency dependence of $G'$ measured after 10 h is again negligible, at least in the range $10^{-3}$−10 Hz, while the ratio $G''/G'$ again shows a weak minimum at 0.1 Hz (see Figure 10). The value of the minimum depends on the temperature at temperatures for which $G'$ has not yet completely reached the lower rate of increase after 10 h.

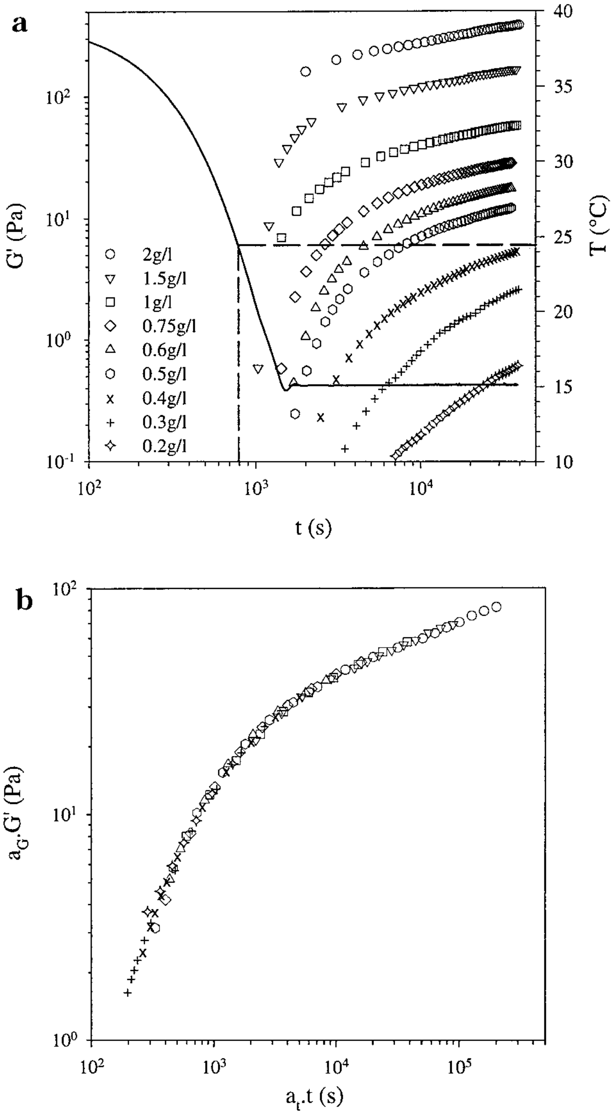

**Figure 5.** (a) Time dependence of the storage shear modulus upon cooling to $T = 15$ °C at different concentrations indicated in the figure. The solid line indicates the time dependence of the temperature which is the same for all concentrations. The dashed lines indicate the position of the temperature where the coil−helix transition occurs. (b) Master curve of the data shown in (a) obtained by vertical and horizontal shifts with $C_{\text{ref}} = 1.0$ g/L.

**Light Scattering Measurements.** With the rheological setup used in this study we were unable to investigate the aggregation process at concentrations lower than about 0.2 g/L. However, light scattering is very sensitive to the formation of aggregates even at lower concentrations. Figure 11 shows the time evolution of the relative excess scattering ($I_r$) at $q = 2.97 \times 10^{-2}$ nm$^{-1}$ for different concentrations after cooling to 15 °C. Again there is a period between the time that the sample reaches $T_c$ and that it stabilizes at 15 °C in which the kinetics are not well defined. For all concentrations the intensity increases, and no stabilization of $I_r$ is observed even after 12 h. It follows from eq 1 that the intensity depends on both $M_w$ and the structure factor, and therefore the increase of $I_r$ is not directly the increase of $M_w$. We will discuss the $q$-dependent

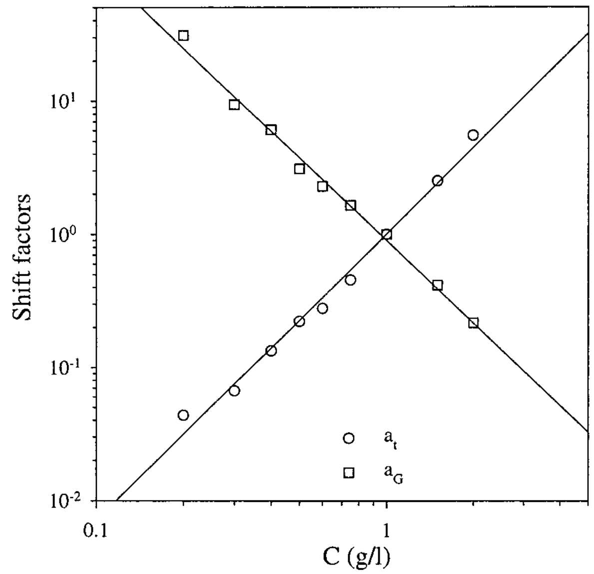

**Figure 6.** Concentration dependence of the horizontal ($a_t$) and vertical ($a_G$) shift factors used to obtain the master curve shown in Figure 5b. The solid lines represent linear least-squares fits: $a_t = 1.0C^{2.2}$ and $a_G = 0.9C^{-2.1}$.

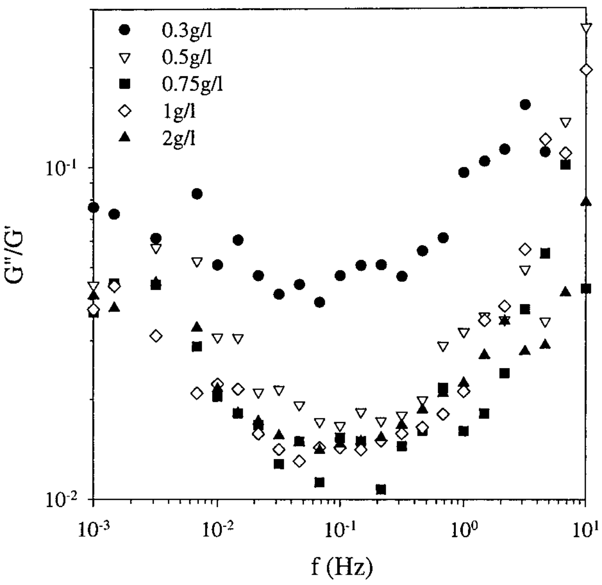

**Figure 7.** Frequency dependence of $G''/G'$ at different concentrations indicated in the figure ($T = 15$ °C).

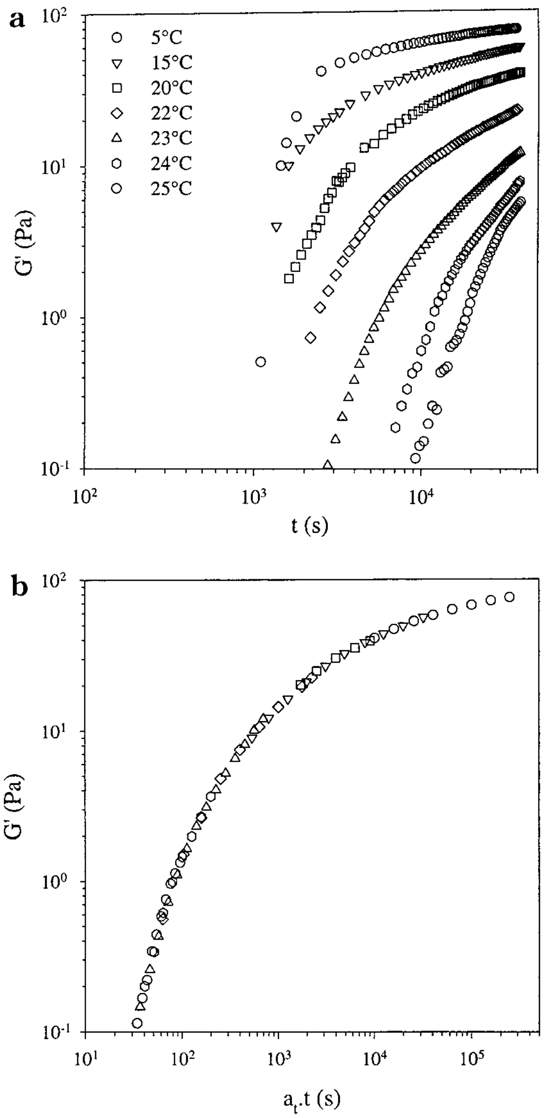

**Figure 8.** (a) Time evolution of the storage shear modulus at $C = 1.0$ g/L upon cooling to different temperatures indicated in the figure. (b) Master curve of the data shown in (a) obtained by horizontal shifts with $T_{\mathrm{ref}} = 15$ °C. Vertical shifts were needed at 24 °C ($G'/2.1$) and 25 °C ($G'/4.2$).

structure factor in detail elsewhere but insist here on the fact that aggregation occurs even at concentrations below which the gel modulus is measurable. There is no indication of a critical concentration below which no aggregation occurs. The scatter of $I_r$ at long times for the sample with the highest concentration is due to the fact that $I_r$ fluctuates very slowly in time. This is a clear sign of slow dynamics of the system. Such a sudden appearance of a slowly fluctuating $I_r$ is typical for gel-forming systems close to the gel point. It is usually accompanied at longer times by nonergotic scattering. Comparison with Figure 5a shows that the very slow intensity fluctuations appear somewhat before $G'$ becomes measurable.

The temperature dependence of the time evolution of $I_r$ is shown in Figure 12a for a fixed concentration (0.1 g/L) at $q = 2.97 \times 10^{-2}$ nm$^{-1}$. The time dependence of the temperature is similar to that shown in Figure 11. Figure 12b shows that a master curve can be obtained by simple horizontal shifts showing that the effect of temperature is mainly kinetic. The shift factors used in Figure 12b are compared in Figure 9 to those obtained from the shear modulus. The temperature dependence of $I_r$ is similar to that of $G'$ even though the concentrations differ by a factor of 10.

We have investigated the dependence of $I_r$ on the angle of observation in the range between 30° and 150° and found that the concentration and temperature dependence of the increase of $I_r$ is the same over this angular range.

## Discussion

The mechanical data alone do not give specific information about the gel structure. Very different systems such as high solutions of soft spheres,[31] gelatin,[32] and clay particles[33] have similar frequency and concentration dependencies of the shear modulus. Also, a similar time evolution of $G'$ is found for very different systems such as gelatin[34] and globular protein gels.[35,36] Long time measurements are needed to establish whether $\kappa$-carrageenan gels finally reach equilibrium.

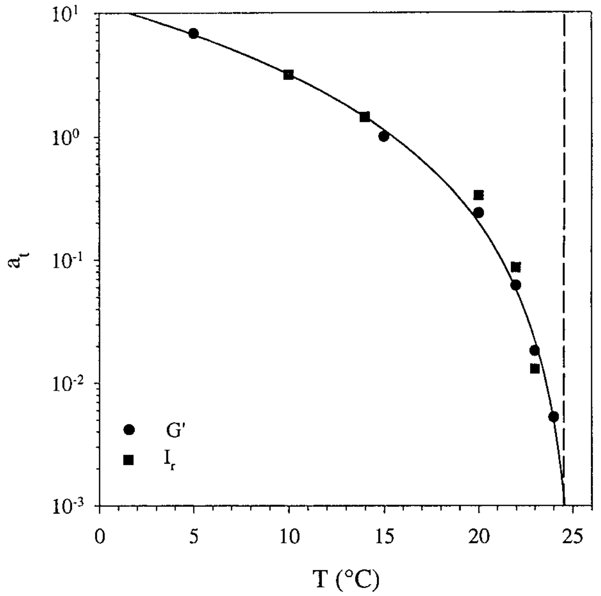

**Figure 9.** Temperature dependence of the horizontal shift factors $a_t$ used to obtain the master curves of $G'$ shown in Figure 8b (circles) and of $I_r$ shown in Figure 12b (squares).

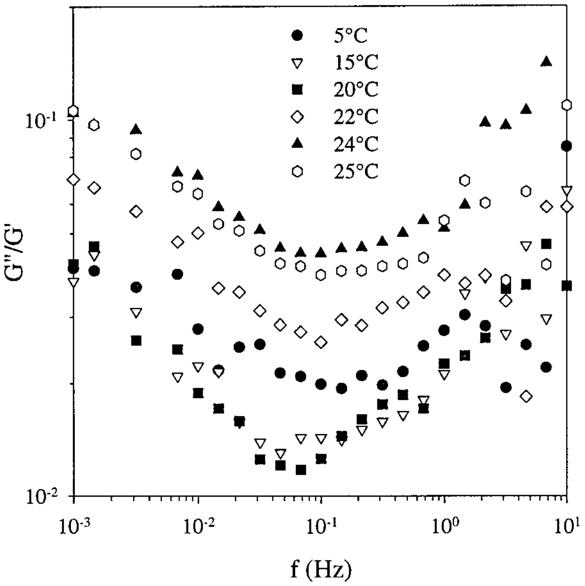

**Figure 10.** Frequency dependence of $G''/G'$ at different temperatures indicated in the figure ($C = 1.0$g/L).

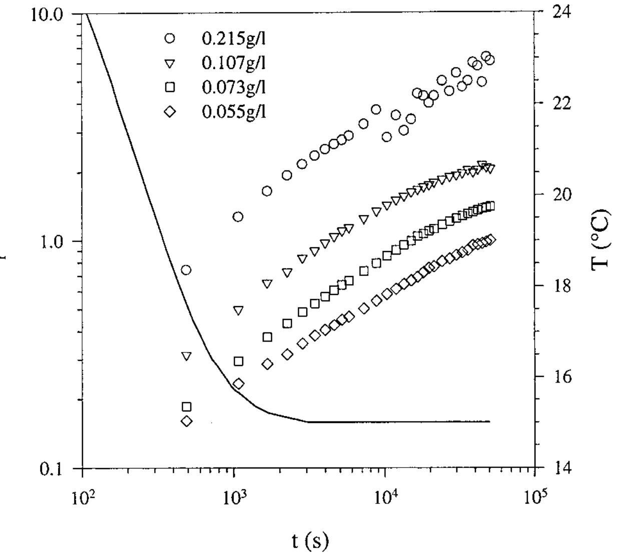

**Figure 11.** Time dependence of the relative excess scattering intensity at different concentrations ($q = 2.97 \times 10^{-2}$ nm$^{-1}$, $T = 15$ °C). The solid line indicates the time dependence of the temperature which is the same for all concentrations.

An important observation is that the time dependence of $G'$ is similar at all concentrations and temperatures investigated. Such a universal time dependence was recently noted for gelatin,[32] but no attempt was made to superimpose the data. The similarity is a strong indication that the development of the gel structure is independent of the concentration and the temperature. The idea is that at a given concentration the same structure is reached after different cooling times depending on the temperature. Mechanical measurements suggest that at different concentrations the same structure is formed but with different densities. If this is the case, then the concentration dependence of the kinetics suggests a second-order process for the aggregation, while the concentration dependence of $G'$ could mean that the strength of the gel is determined by the number of binary interactions.

The invariance of the frequency dependence of $G''/G'$ supports the idea that the development of the gel structure is independent of temperature and concentration in the range investigated here. The minimum in the $G''/G'$ as a function of frequency implies the existence of at least two relaxation processes both outside the window of observation: one at $f > 10$ Hz and one at $f < 10^{-3}$ Hz. The value of the minimum decreases during the first stage of the gelation and then stabilizes at about 0.013 independent of the concentration and the temperature. However, the position of the minimum remains the same even at low concentrations and temperatures close to $T_c$ which could mean that the relaxation processes are the same also in the early stage. The appearance of such a minimum is not specific for a particular gel structure as it is observed for systems with very different structures.[31−33,35,36] Nevertheless, the similarity strongly suggests that the development of the structure of gels is independent of concentration and temperature.

In the present context we use the term “gel” merely to indicate that the system does not flow and that $G'' \ll G'$. We do not want to imply that a three-dimensional network is formed. In fact, we do not eliminate the hypothesis that there are no specific cross-links between the $\kappa$-carrageenan aggregates. In any case, the presence of a slow relaxation process excludes a high density of permanent cross-links. Microscopy shows that long rigid-rod-like aggregates are formed.[15,16] It is possible that it is merely the steric hindrance between these aggregates which causes the observed resistance to mechanical deformation.

We have seen that the effect of temperature on $\kappa$-carrageenan aggregation is purely kinetic except very close to $T_c$. It is possible that in this temperature range the aggregation kinetics are limited by the coil−helix transition and not by the association of the helices.

Interestingly, there is no evidence for the existence of a minimal critical concentration of association followed by gelation. There is just a gradual transition between the system at high concentrations where strong self-supporting gels are observed and the system at low concentrations where the resistance to mechanical deformation is too weak to detect. Light scattering measurements clearly show that the aggregation pro-

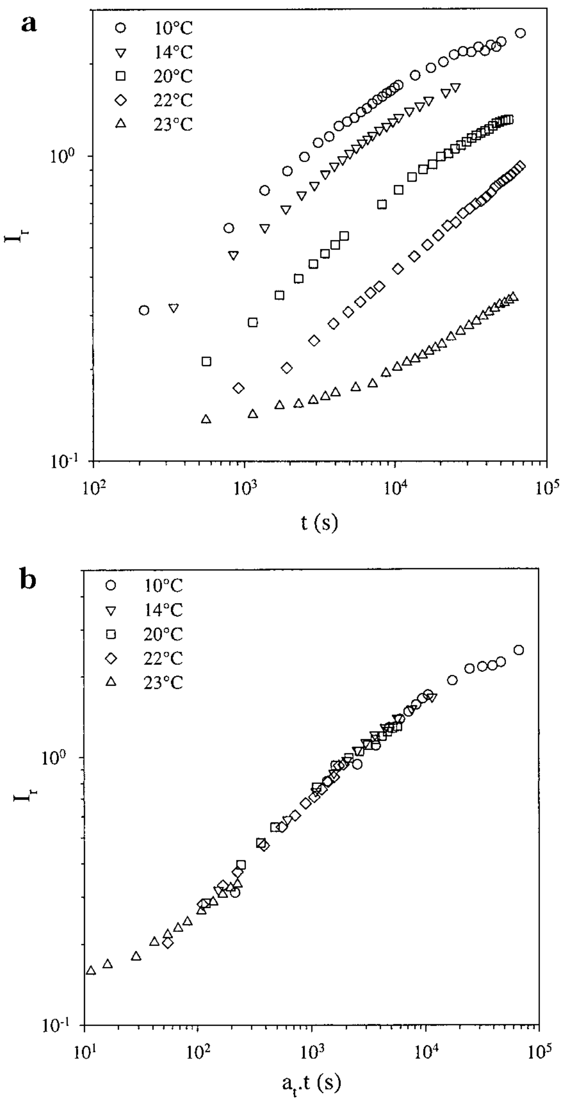

**Figure 12.** (a) Time evolution the relative excess scattering intensity at $C = 0.1$ g/L upon cooling to different temperatures indicated in the figure ($q = 2.97 \times 10^{-2}$ nm$^{-1}$). (b) Master curve of the data shown in (a) obtained by horizontal shifts with $T_{\mathrm{ref}} = 15$ °C.

cess takes place even at very low concentrations. We are conducting a study of dynamics during the aggregation process using DLS to probe the dynamics without imposing a mechanical stress. DLS measurements of aggregating $\kappa$-carrageenan show that the relaxation processes of the system slow down and eventually become slower than the duration of the measurement. This slow-down is observed even at low concentrations for which the system behaves macroscopically as a liquid. Details of the DLS measurements and also of the angular dependence of the static light scattering will be reported elsewhere.

## Conclusions

The aggregation of $\kappa$-carrageenan upon cooling in the presence KCl does not reach equilibrium within a period of at least 12 h. The time dependence of the shear modulus and the scattered light intensity is similar in the range of concentrations (0.05−2 g/L) and temperatures (down to 20 deg below $T_C$) investigated. The frequency dependence of the loss modulus indicates the presence of at least two relaxation modes: one at $f >$ 10 Hz and one at $f < 10^{-3}$ Hz. The experimental results suggest that the structure of $\kappa$-carrageenan gels is not strongly concentration or temperature dependent. The concentration dependence of the kinetics indicates a second-order process for the aggregation while the concentration dependence of the shear modulus indicates that the gel strength is determined by the number of binary contacts.

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