Rheological Properties and Scaling Laws of κ-Carrageenan in Aqueous Solution

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Rheological Properties and Scaling Laws of κ-Carrageenan in Aqueous Solution

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S *Supporting Information*

Critical gel concentration c_g
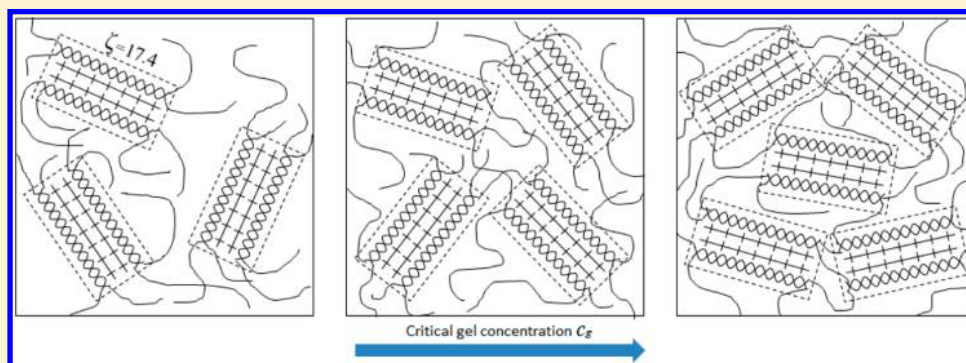
ABSTRACT: Rheological properties, gel network structures, and scaling laws for κ-carrageenan in aqueous solution were studied by rheology and field emission scanning electron microscopy (FESEM). The FESEM micrographs verified that the κ-carrageenan gels were formed by the formation of fibrils. The critical gel concentration, c_g, obtained using the Winter−Chambon criterion, was found to be proportional to temperature as expressed by $c_g \sim T^{0.85}$ where T is the temperature in °C. At the gel point, the critical relaxation exponent n obtained was a constant ($n = 0.62$) and independent of temperature. The critical gel strength S_g increased with increasing c_g. A constant gel strength S_g/c_g was obtained by normalizing S_g with c_g to eliminate the effect of temperature, showing a unique character of κ-carrageenan in aqueous solution during gelation. The molecular structure of the junctions at the gel point was analyzed using the modified Eldridge−Ferry model, which supported the similarity of the fractal structure in the κ-carrageenan gels. Before the gel point, the zero shear viscosity η_0 of κ-carrageenan solutions diverged as the gelling system approached to the gel point, and a scaling law, $\eta_0 \sim \varepsilon^{-\gamma}$, was established, where ε is the relative distance of κ-carrageenan concentration c from c_g and γ is the scaling exponent that was found to be 1.6. Beyond the gel point, the plateau modulus G_e of κ-carrageenan gels depended on the polymer concentration according to a power law, $G_e \sim \varepsilon^z$, where z was found to be 2.7. The critical gel exponent n evaluated from γ and z agreed well with the value of n determined from the Winter−Chambon criterion, further indicating that the characteristic relaxation time of the pregel and the postgel follows the same power law (symmetry at $c = c_g$) for κ-carrageenan in aqueous solution.

■ INTRODUCTION

κ-Carrageenan comes from a family of linear water-soluble polysaccharides extracted from different species of marine red algae and is composed of an alternating disaccharide repeating unit of α-(1−3)-D-galactose-4-sulfate and β-(1−4) 3,6-anydro-D-galactose. The $^1C_4$ conformation of the 3,6-anhydro-D-galactose units allows a helicoidal secondary structure, which is essential for the formation of gels.[1,2] It is widely used as a thickening, gelling agent, or texture enhancer or stabilizer in food, cosmetic, and pharmaceutical industries.[3−9]

The gelation of κ-carrageenan in aqueous solution has been extensively studied by many researchers, which is generally accepted as a two-step model involving a conformational transition of coils to helices followed by aggregation of double helices.[10,11] The physical cross-linking in the κ-carrageenan gels is associated with the formation of double helices and their aggregates. The gelation in this case can be thought of as a process partially driven by microcrystallization, and the formation of double helices constrains the propagation of further aggregation during the gel evolution. On the other hand, because κ-carrageenan is a polyion, the presence of counterions also affects the gelation of κ-carrageenan in aqueous solution. It is well-known that in the presence of specific cations such as K⁺, Cs⁺, and Rb⁺, the formation of double-helical aggregates is strongly favored due to the interaction between the cations and the sulfate ester groups. Hermansson[12] systematically studied the microstructure and rheological properties of κ-carrageenan gels with different monovalent cations and found that the alkali metal ions (Li⁺, Na⁺, K⁺, Rb⁺, and Cs⁺) are all capable of inducing gelation, but

K^+ and Rb^+ are considerably more effective than other cations in inducing gelation. Recently, Nguyen et al.[13] found that the addition of divalent cations such as Ca^{2+} and Mg^{2+} had a weak influence on the gelation of κ-carrageenan. But, addition of a mixture of Na^+ and Ca^{2+} showed a strong synergistic effect. All of these works indicated that the gelation of κ-carrageenan in water is a complicated process.

The junction structure of a physical gel is important in reflecting information about the gel formation and in controlling the entire structure of a gel network. Since the most physical gels are composed of complex junctions, however, it is not easy to elucidate the junction structure by experiments. For κ-carrageenan gels, it is generally accepted that a three-dimensional network is composed of double-helical aggregates as the junctions and flexible chains connecting the junction zones. However, the details in the junction structure of a κ-carrageenan gel have not been completely clarified so far.

Rheology as a sensitive tool has been widely applied to study the evolution of microstructure during the sol−gel transition and viscoelastic properties of gels.[14−16] In this work, we systematically investigated the gelation mechanism of κ-carrageenan in aqueous solution, the junction structure at the gel point, and the relationship between viscoelastic properties and microstructure of κ-carrageenan gels using rheology and field emission scanning electron microscopy (FESEM). The rheological scaling laws were examined and discussed for understanding of the gelation. A schematic diagram was proposed, and the junction structure at the gel point was calculated by the modified Eldridge−Ferry model. This report here provides readers for the first time with the information about the double-helical aggregates of κ-carrageenan during gelation.

■ EXPERIMENTAL SECTION

Materials and Solution Preparation. κ-Carrageenan in the powder form was obtained from Sigma-Aldrich (Singapore). According to the supplier, the molecular weight (M_w) of κ-carrageenan is about 3.0×10^5 g/mol. Before use, the κ-carrageenan powder was dried and kept in a desiccator to avoid the absorption of moisture at room temperature. Aqueous solutions with various concentrations of κ-carrageenan were prepared by dissolving the powder in an appropriate volume of deionized water with continuous magnetic stirring at 80 °C for 2 h. The resulting aqueous solutions were stored at room temperature. The weight percentage (wt %) is used in this study to represent κ-carrageenan concentrations in aqueous solutions for convenience.

Rheological Measurement. The rheological measurement was performed on a rotational rheometer (DHR, TA Instruments, USA) with a parallel plate geometry of 40 mm in diameter and a gap of 0.55 mm and a Peltier temperature control. The sample for rheological measurement was transferred directly from a glass bottle to the bottom plate of the rheometer using a pipet for liquid-like sols and a spoon for solid-like gels. The samples were heated up to 70 °C and kept at this temperature for 30 min to destroy all helix content. Strain sweeps in the range of 0.1−100% at frequencies of 0.1−2 Hz were carried out to determine the linear viscoelastic range of the κ-carrageenan solutions in both sol and gel states. A low-viscosity silicone oil was used to cover the perimeter of the sample held between two plates of the rheometer to prevent water evaporation at long measurement times. The stability of the sample was checked through the measurement of G' and G'' at 0.1 Hz in the linear viscoelastic region. Little changes in G' and G'' were observed over a long period (120 min) at 70 °C with a strain amplitude of 1.0%, which indicated that the effects of water loss could be ignored. Frequency sweeps for κ-carrageenan solutions with various polymer concentrations were performed at different temperatures (10,

20, 30, and 40 °C). A constant strain of 1.0% was applied during frequency sweep.

Morphological Characterization. The morphology of κ-carrageenan gels was observed using field emission scanning electron microscopy (FESEM, JSM-7600F, JEOL, Japan). The sample for FESEM was prepared by freeze-drying as follows. The κ-carrageenan gel with a thickness of about 0.2 mm was deposited on the surface of aluminum foil and frozen under a refrigerator of −20 °C for about 24 h. After then, the frozen sample was quickly transferred into the vacuum freeze-dryer (Telstar cryodos-80, Telstar industrial, Spain) and dried at −80 °C for about 1 week. The final dried sample was sputtered in a vacuum with gold on its surface and observed by FESEM with an accelerating voltage of 5 kV.

■ RESULTS AND DISCUSSION

κ-Carrageenan is able to form a strong gel at a high concentration. Figure 1 displays the dependence of storage
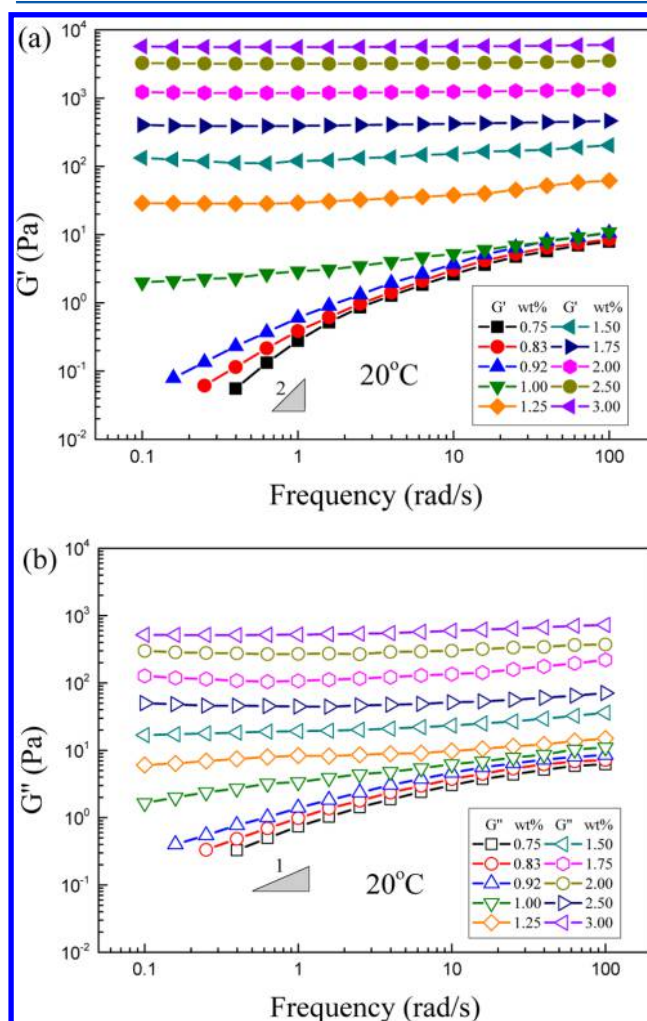

Figure 1. Dependence of storage modulus G' and loss modulus G'' on angular frequency ω for the solutions of various κ-carrageenan concentrations at a fixed temperature 20 °C and a shear strain amplitude 1%.

modulus G' and loss modules G'' on the angular frequency ω for aqueous solutions of various κ-carrageenan concentrations at a fixed temperature of 20 °C. A frequency dependence of G' and G'' was observed for the low κ-carrageenan concentrations such as 0.75, 0.83, and 0.92 wt %. The solution of the lowest κ-carrageenan concentration (0.75 wt %) shows a liquid-like

terminal behavior at low frequencies, $G' \sim \omega^2$ and $G'' \sim \omega^1$ (at $\omega \to 0$). When κ-carrageenan concentration increases to 1 wt %, both G' and G'' are higher than those at 0.92 wt % in the whole frequency region, and the slope of G' tends to 0, indicating the formation of a gel network from the solution. With further increasing κ-carrageenan concentration, G' and G'' become independent of frequency, showing the characteristic of a solid-like gel. The large decrease in slope from the G' curve at 0.92 wt % to that at 1 wt % at low frequencies implies that the sol–gel transition of κ-carrageenan should take place at a κ-carrageenan concentration between 0.92 and 1 wt %. The frequency dependences of G' and G'' at 10, 30, and 40 °C are similar to that observed in Figure 1 (data not shown here). The difference is that the κ-carrageenan concentration at the sol–gel transition increases as the temperature increases.

It is well-known that the aqueous solution of κ-carrageenan is transformed into a gel state at a high concentration due to the formation of a three-dimensional network structure induced by the aggregation of double helices. Figure 2 shows the FESEM
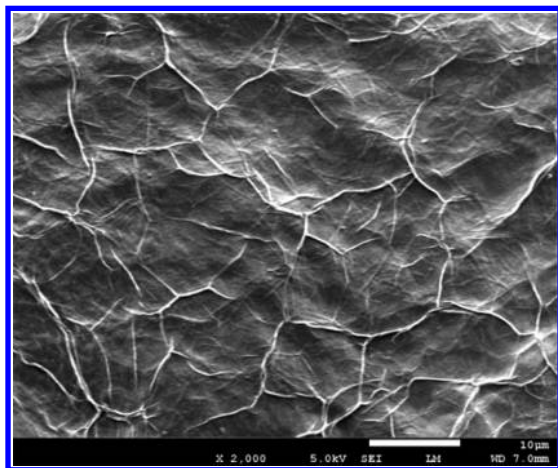

Figure 2. FESEM image for the surface fibril morphology of 3 wt % κ-carrageenan gel obtained by freeze-drying.

image for the surface micrograph of 3 wt % κ-carrageenan. The sample for FESEM was prepared by the freeze-drying method in order to restrict the movement of polymer chains during drying. The FESEM image suggests the formation of fibrils to result in the gelation of κ-carrageenan. Hermansson[12] studied the microstructure of κ-carrageenan at different temperatures and found a fine and regular network structure formed during gelation. The similar microstructure of κ-carrageenan has also been reported by Sokolova et al.,[17] who systematically studied the morphology of various types of carrageenan including hybrid polysaccharides using atomic force microscopy (AFM) and found that κ-carrageenan formed both single- and two-stranded structures at low concentrations. At high concentrations, however, κ-carrageenan formed fibrillar network structures by a side-by-side association.

From Figure 1, it is apparent that the sol–gel transition takes place between 0.92 and 1 wt % κ-carrageenan at 20 °C. To determine the exact critical gel concentration, we follow a procedure defined by the Winter–Chambon criterion.[18] This method was first found experimentally in chemical gels with a scaling law of $G'(\omega) = G''(\omega) \sim \omega^{1/2}$ at the gel point and then generalized to satisfy $G'(\omega) \sim G''(\omega) \sim \omega^n$ ($0 < n < 1$) for other gel systems under a sufficient low frequency, ω. This implies that the phase angle becomes frequency independent at

the gel point. Many researchers have shown that this method is reliable and valid on determination of the gel point for various polymeric gels with different gelation mechanisms, such as poly(vinyl chloride)/bis(2-ethylhexyl) phthalate (PVC/DOP) gel by microcrystalline,[19,20] poly(ethylene oxide)–poly-(propylene oxide)–poly(ethylene oxide) (PEO–PPO–PEO) hydrogel by the arrangement of micelles,[21] alginate hydrogel by ionic association,[22] and dibenzylidene sorbitol gel by self-assembly.[23] However, it has not been reported whether the gel point can be determined by this method for a κ-carrageenan gel formed through the aggregation of double helices.

Figures 3a to 3d show the application of such a criterion to κ-carrageenan solutions within the sol–gel transition range at 10, 20, 30, and 40 °C, respectively. The gel points were determined through the multifrequency plots of loss tangent versus κ-carrageenan concentration. At each given temperature, all tangent delta curves pass through the common point at a certain κ-carrageenan concentration, which is defined as the critical gel point, c_g. In this way, we obtained the critical gel concentrations of 0.55, 0.97, 1.25, and 1.87 wt % of κ-carrageenan at 10, 20, 30, and 40 °C, respectively.

The critical gel concentration c_g obtained from Figure 3 is plotted against temperature in Figure 4. Through a linear fitting to the data, we obtained an approximate power law for the temperature dependence of the critical gel concentration:

$$c_g \sim T^{0.85} \tag{1}$$

where T is the temperature in °C. It is apparent that c_g increases with increasing temperature, which means that at a higher temperature more κ-carrageenan contents are required to participate in the conformational transition of coils to helices and then the double helices aggregate into an infinite network. We consider that the formation of double helical aggregates is a necessary prerequisite of sol–gel transition. The sol–gel transition corresponds to a percolation of polymer chains when the aggregates are first connected across the solution volume. Increasing temperature leads to the increase in c_g. However, it is unclear whether a higher c_g means a larger density of aggregates while the average size of aggregates remains the same, or vice versa. Since the molecular structure of the κ-carrageenan aggregates during gelation has not been fully elucidated in the literature, further works are needed.

As is well-known, a polymeric gel is a three-dimensional network formed from flexible chains through ionic interaction, hydrogen bonding, van der Waals forces, hydrophobic association, self-assembly, or cross-linking by crystalline segments. The complexity in the formation of junctions leads to various gel structures. For an aqueous solution of κ-carrageenan, it is well accepted that the double-helical aggregates induced by the conformational transition of random coils to double helices act as the junction zones to result in a gel. The critical change from a liquid state to a solid state is known as the sol–gel transition at which the zero shear viscosity and relaxation time of the system diverge. Even though a number of gels have been extensively studied and various theoretical models have been proposed to explain the formation and properties of gels, the gelation and formation of microstructures at the gel point have not been satisfactorily described by any single theory.

The well-used experimental and theoretical methods for description of the gelation are based on the scaling laws. To examine and explain rheological properties in the vicinity of the
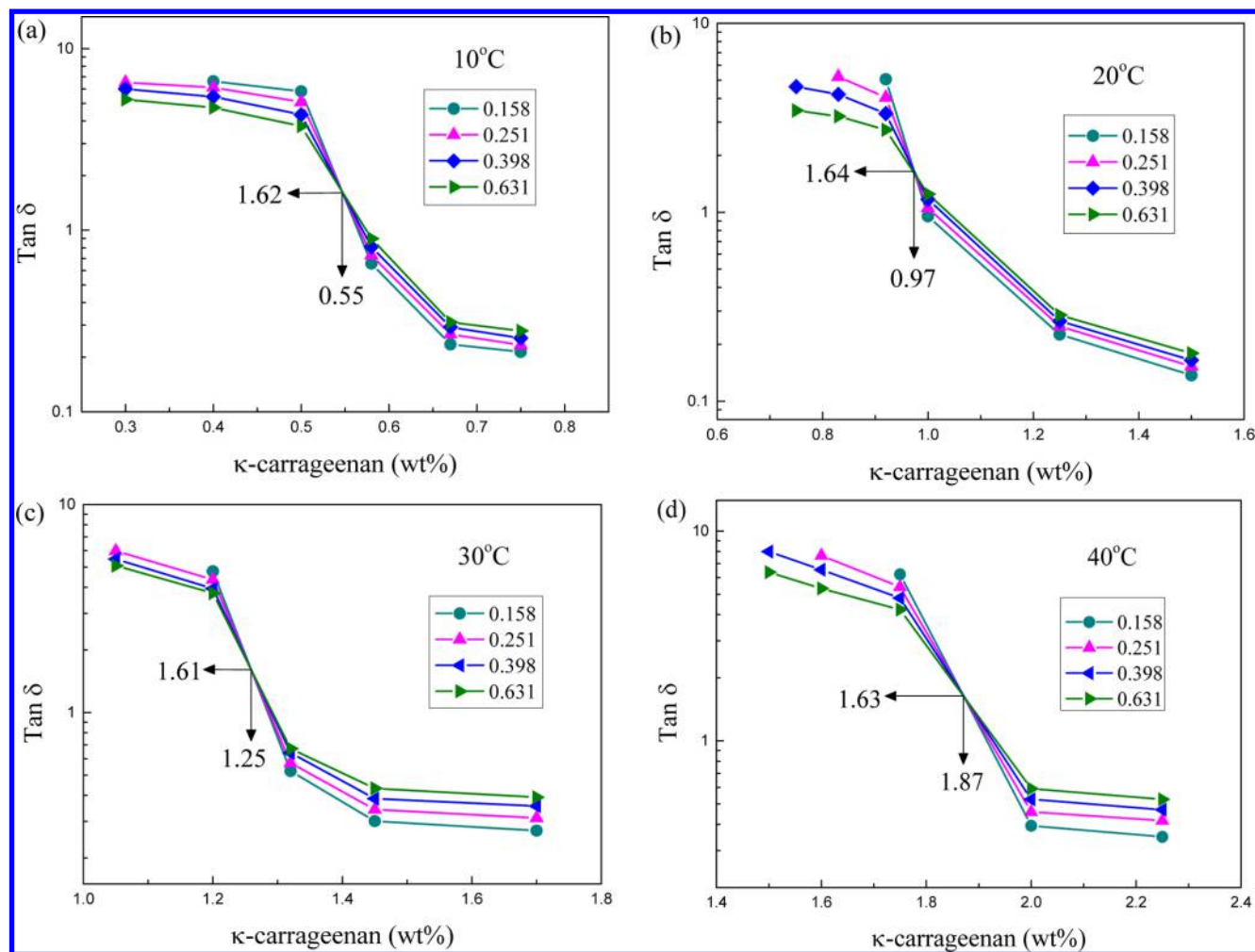
Figure 3. Dependence of loss tangent, tan δ, on κ-carrageenan concentration at different temperatures (a) 10, (b) 20, (c) 30, and (d) 40 °C. The angular frequencies (rad/s) are indicated in the inset in each figure.
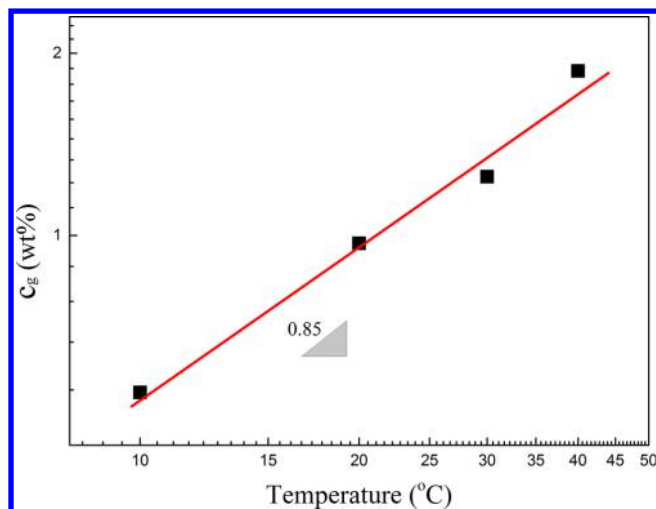

Figure 4. Change of critical gel concentration c_g with temperature.

gel point, the following rheological scaling law has been widely used[24]

$$G''(\omega)/G'(\omega) = \tan \delta = \tan(n\pi/2) \tag{2}$$

which is based on the power law behavior of the shear relaxation modulus $G(t)$ at the gel point

$$G(t) = S_g t^{-n} \tag{3}$$

where n is named as the critical relaxation exponent, which determines the stress relaxation rate at the gel point. S_g is denoted as the critical gel strength. A similar expression can also be applied for G' and G'' at the critical gel point

$$G'(\omega) = G''(\omega)/\tan(n\pi/2) = S_g\omega^n\Gamma(1-n)\cos(n\pi/2) \tag{4}$$

Here $\Gamma(1-n)$ is the Gamma function. By knowing n, one can calculate S_g from $G'(\omega)$ or $G''(\omega)$ at the critical gel point using eq 4.

Using eq 2, we obtained n values at different temperatures as shown in Figure 5. From a rheological point of view, the meaning of n can be understood from the original relation of eq 2. n takes a value between 0 and 1 since the phase angle δ varies from 0 to $\pi/2$. In general, a lower value of n implies the formation of a more elastic gel, and the same value of n means an equivalent viscoelasticity. A number of researches have indicated that n is not universal and varies with the gelling systems.[24] Figure 5 shows the dependence of n on temperature. It is apparent that n is independent of temperature. The universal value of n means that the sol−gel transition takes place at the same viscoelastic distance from a completely viscous liquid ($n = 1$) or from a completely elastic solid ($n = 0$).
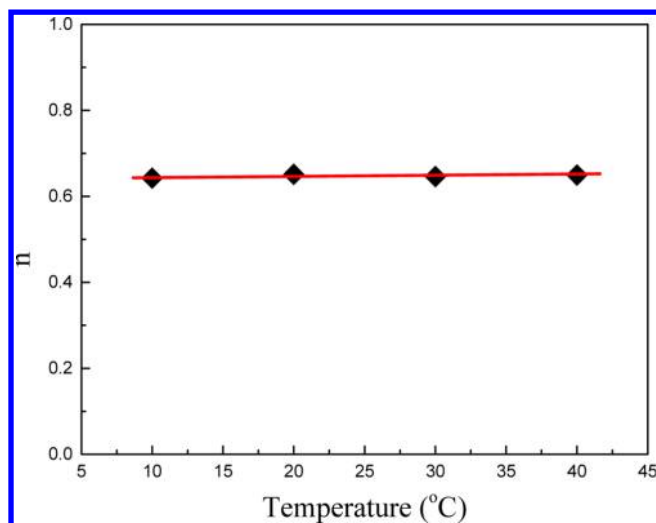
Figure 5. Dependence of the critical gel exponent n on temperature.

From Figure 4, we know that c_g increases with increasing temperature. Therefore, it can be inferred that more junctions were formed during gelation at a higher temperature in order to keep the same viscoelastic distance at the gel point. On the other hand, the transition from a state where the system consists of a set of finite size aggregates to a state where an infinite spanning cluster connects the edges of the system is usually described by percolation. At the percolation, the aggregates of double helices are first connected across the solution volume, which takes place at a higher temperature with increasing c_g.

The physical nature of a gelling system at the gel point can also be described by the critical gel strength S_g defined by eq 3. The studies in the chemical gels have shown that the decrease in n leads to the increase in S_g because of the increase in the cross-linking density, which implies that S_g is related to the physical strength of the gel network at the gel point. According to eq 4, we obtained S_g by means of the existence of a crossover point of G' and $G''/\tan(n\pi/2)$ at the gel point when n is known for a fixed temperature. Using the value of G' at any crossover point and eq 4, we obtained the values of S_g. S_g was plotted against temperature in Figure 6a. Although n is the same, S_g varies with the system to exhibit a temperature dependence of the sol−gel transition. That is, S_g increases as temperature increases, and a linear relationship between S_g and temperature was obtained. This result indicates that S_g is related to the total mass of κ-carrageenan during gelation. For a constant n, increasing the cross-link density of a chemical gel usually leads to an increase in the gel strength, as reported by many scientists.[25] The increase of S_g with increasing temperature may be considered to be due to the increase of the junction density at the gel point. It is surprising to find that the slope 0.85 in the relationship of c_g with temperature in Figure 4 is very close to the slope 0.87 in Figure 6a. That is, S_g is only related to c_g in the system, and thus the gel strength per unit of mass of κ-carrageenan should be the same. Here, we normalized S_g by the corresponding c_g to obtain the result in Figure 6b. As expected, S_g/c_g is almost constant and independent of temperature. Hence, it can be concluded that the increase in c_g with increasing temperature just induces the increase in the junction density, but it has a weak influence on the junction size. This result also suggests that the critical κ-carrageenan gels have the similarity in their fractal structures.
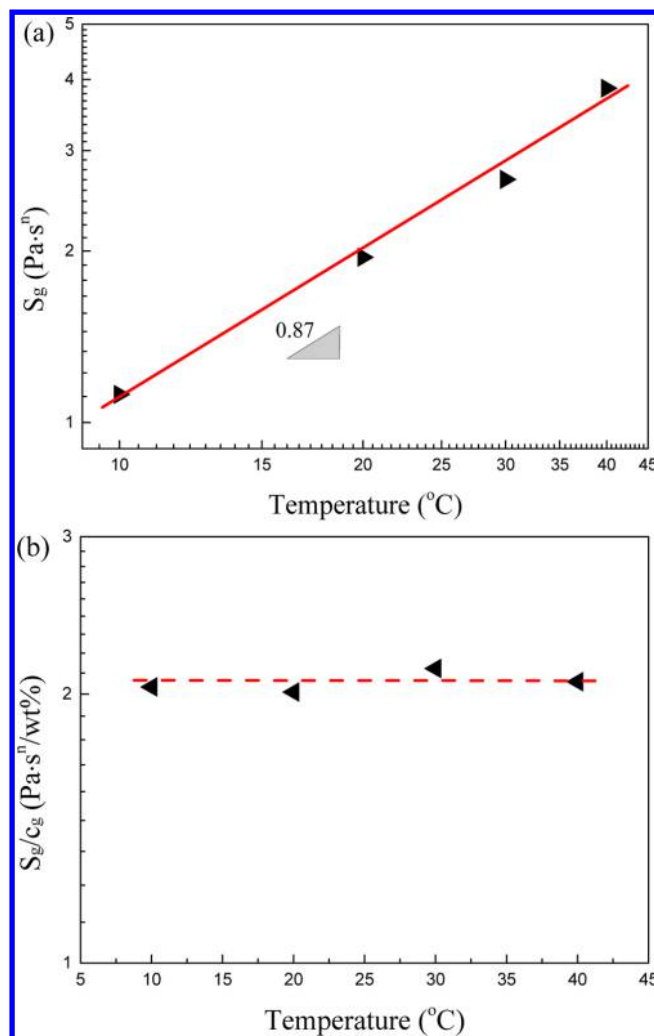

Figure 6. Relationships of (a) the critical gel strength S_g and (b) the normalized critical gel strength S_g/c_g with temperature.

It is of interest to know the junction structure at the gel point because the junction structure may be linked with the gelation mechanism and also has a relationship of viscoelastic properties. Experimentally, it is quite technically difficult to measure the junction structure because of the complexities in gel networks. A theoretical model based on the junction multiplicity has been proposed to analyze the junction structure in thermoreversible gels.[26] A modified Eldridge−Ferry model has been developed and used to describe a multiple junction structure that is composed of s chains and ζ monomers (repeat units) of each chain,[27] where s is called the junction multiplicity and ζ is the junction length, as follows:

$$\ln c_g = \zeta \Delta h / (k_B T) + \ln M / (s - 1) + \text{constant} \qquad (5a)$$

Here Δh is the enthalpy of bonding per mole of the repeat units taking part in the junction, k_B is the Boltzmann constant, T is the absolute temperature, and M is the molecular weight of the given gelling polymer. Although a real junction structure may not be as simple as that described by this model, the relation derived from the model is still of value as a measure for estimation of the junction structure, especially for the case where the junction structure is invariable with concentration, temperature, and molecular weight. In the present study, because the molecular weight of κ-carrageenan is constant, it is

hard to evaluate s by the dependence of c_g on M at a given temperature. The modified Eldridge−Ferry model can be rewritten as follows:

$$\ln c_g = \zeta \Delta h / k_B T + \text{constant} \tag{5b}$$

Now, c_g is just a function of temperature. Using eq 5b, the temperature dependence of a gel with a constant molecular weight M allows us to calculate the junction length ζ. Using the values of c_g in Figure 4, c_g is plotted against $10^3/T$ in Figure 7. It
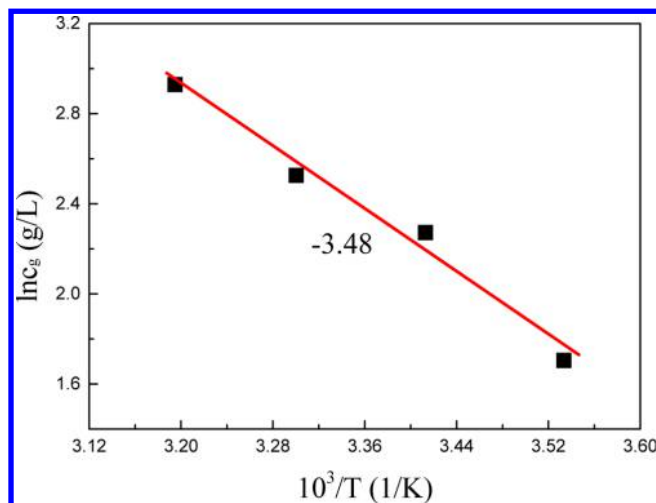

Figure 7. Plot of ln c_g against $10^3/T$ for the κ-carrageenan gels.

should be noted that the units of c_g and T were converted from wt % and °C to g/L and K, respectively, for the use of eq 5b. The solid straight line was given by a linear fitting to the data, and then we directly obtained the slope of −3.48. According to eq 5b, the slope is related with ζ by $\zeta = |\text{slope}|10^3 R/\Delta h$, where R is the gas constant $[10^3 R = 8.31 \text{ kJ/(mol K)}]$ and Δh has units of kJ/mol. To calculate ζ, one needs to know Δh. In this work, we use microdifferential scanning calorimetry to determine the heat of gel melting, which is shown in Figure S1 (Supporting Information). The results show that ζ is equivalent to 17.4, which means that the junction structure comprises 17.4 repeat units or monomers of each polymer chain. On the other hand, since the presence of potassium ion promotes the aggregation of double helices, it is believed that addition of potassium increases the value of ζ, which leads to the increase of the normalized critical gel strength S_g/c_g.

On the basis of our experimental results and the modified Eldridge−Ferry model, a schematic mechanism is proposed in Figure 8 for κ-carrageenan gelation with increasing c_g. At a high temperature, κ-carrageenan molecules exist as random coils in aqueous solution. As temperature decreases, κ-carrageenan molecules at low concentrations are still present as coils, and the solutions show a Newtonian fluid behavior. For the aqueous solutions of κ-carrageenan with high concentrations, however, temperature induced the conformational transition of coils to helices, followed by the aggregation of double helices. The aggregation of double helices leads to the formation of small domains containing a limited number of double helices, which then become physical cross-links of a three-dimensional gel network. With increasing temperature, more κ-carrageenan molecules are required to form a denser gel network while the junction size is independent of c_g. Based on the modified Eldridge−Ferry model, the junction structure calculated contains 17.4 repeat units in each polymer chain. Hermansson[12] found using electron microscopy that the junction zones are formed by the alignment of densely packed superstrands. The likely nature of this kind of association is also suggested by the light scattering to be an extensive helix−helix aggregation in the presence of potassium ions.[28] From Figure 2, we can also find that a further aggregation of double helices beyond the critical gel concentration leads to the formation of fibrils.

Like many physical properties of polymers, critical rheological properties of a gelling polymeric system can be also approximately described by power laws. Various power laws have been proposed to explain or predict rheological features of gelling systems. For example, in the vicinity of the sol−gel transition, the zero shear viscosity η_0 obeys a scaling law[29]

$$\eta_0 \sim \varepsilon^{-\gamma} \quad \text{for } p < p_g \tag{6}$$

Here $\varepsilon = |p - p_g|/p_g$ is the relative distance of a variable p departing from the sol−gel transition point p_g. In this study, p is the κ-carrageenan concentration and p_g is the critical gel concentration. γ is the critical exponent determining the critical characteristics in the vicinity of the sol−gel transition.
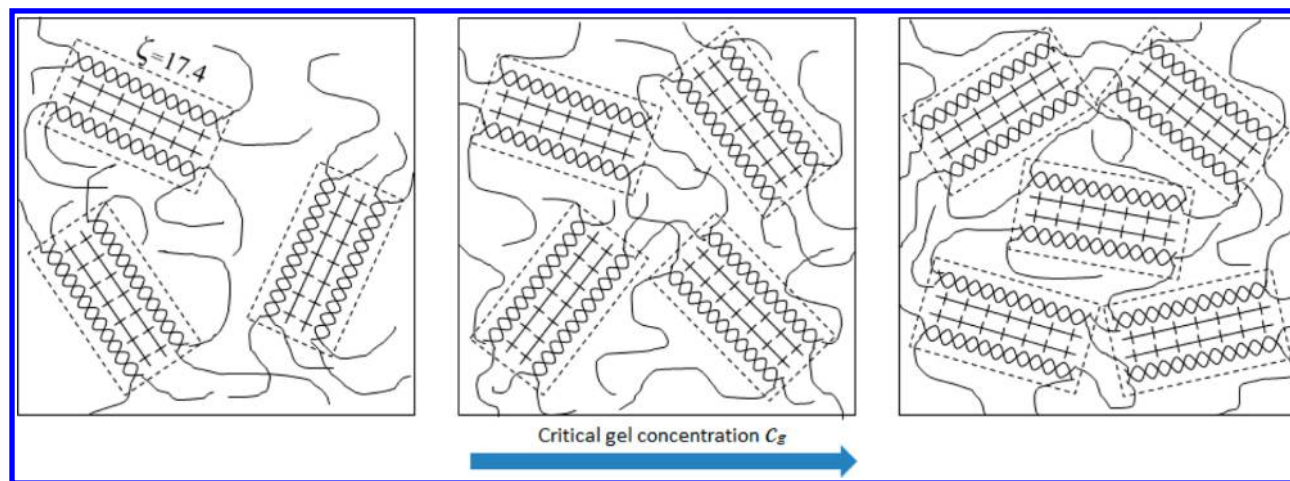

Figure 8. Schematic diagram describing the sol−gel transition mechanism of κ-carrageenan in aqueous solution with increasing the critical gel concentration.

From Figure 1, we know that the dynamic mechanical behavior of the samples before the sol−gel transition follows the liquid-like terminal behavior at low frequencies, which implies the existence of zero shear viscosity. Figure 9 shows the
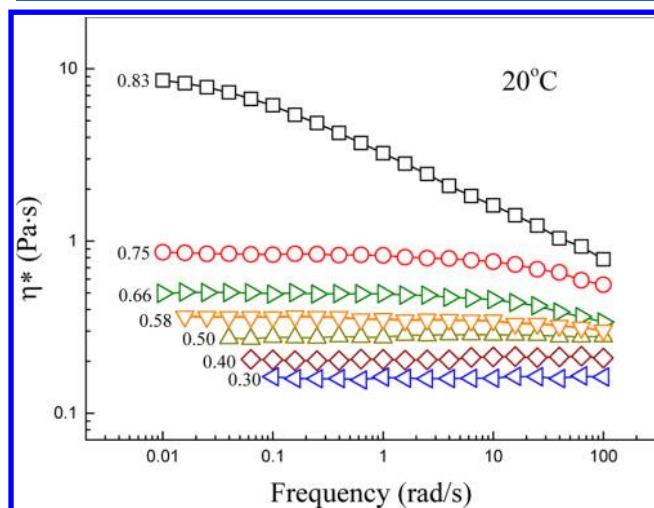

Figure 9. Complex viscosity η^* as a function of angular frequency at 20 °C. κ-Carrageenan concentration ranges from 0.3 to 0.83 wt % as indicated.

complex viscosity η^* as a function of angular frequency at 20 °C, where κ-carrageenan concentrations are indicated in the figure. The frequency-independent behavior of η^* is observed at low frequencies, and the range of the frequency independence of η^* shifts to lower frequencies as the κ-carrageenan concentration increases. If η^* at $\omega \rightarrow 0$ is defined as the zero shear viscosity η_0, it is apparent that η_0 increases with increasing κ-carrageenan concentration. When the κ-carrageenan concentration approaches the critical gel concentration c_g, the sample (0.83 wt %) does not show the frequency independence in the measuring range of frequency and tends to have a much higher η_0 at low frequencies than the others. When the κ-carrageenan concentration is increased to reach to the gel point, η_0 becomes infinite and immeasurable. The similar experimental results have also been observed at 10, 30, and 40 °C, and the corresponding values of η_0 were listed in Table 1.

Based on the Winter−Chambon criterion, the critical gel concentrations at different temperatures have been obtained as shown in Figure 4. Therefore, it is convenient to plot directly the zero shear viscosity η_0 against the relative distance ε for κ-carrageenan pregels, as shown in Figure 10. In a double-logarithmic scale, the data were well fitted by the straight lines. To our surprise, each straight line has the same slope of −1.6. Then one can directly obtain the value of γ, 1.6, which is
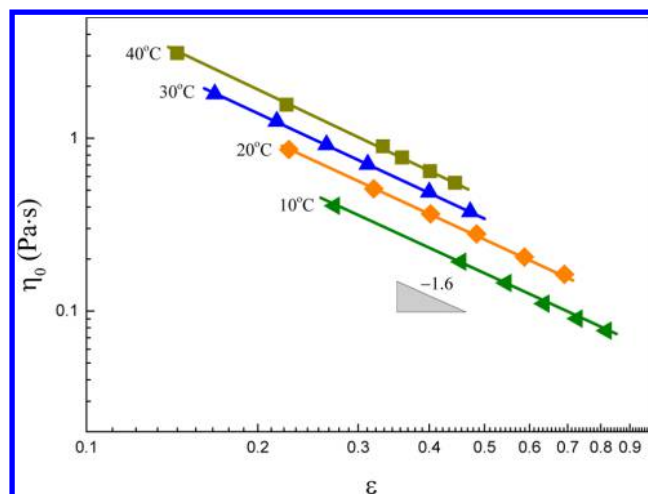

Figure 10. Dependence of the zero shear viscosity η_0 on the relative distance ε at different temperatures.

independent of temperature. The definition of γ by eq 6 clearly gives the meaning of γ that it is a parameter governing the gelation rate. That is, the larger the γ, the faster the gelation rate. On the other hand, the gelation rate is defined as the increment of η_0 per unit relative distance. The constant γ implies the same increment of η_0 against ε even if η_0 increases with increasing κ-carrageenan concentration.

Theoretically, the value of the critical exponent γ in eq 6 has been predicted by many models. The Bethe lattice gives $\gamma = 0$.[30] The percolation theory predicts $\gamma = 4/3$.[31] On the other hand, the value of γ has been obtained by the experiments. For example, $\gamma = 1.67$ was obtained for the poly(vinyl alcohol) gels,[32] $\gamma = 0.9−1.9$ for the end cross-linking hydroxyl-terminated polybutadienes,[33] and $\gamma = 1.3−1.5$ for the silica gels.[34] It seems that γ takes a value between 1 and 2. In this study, we obtained $\gamma = 1.6$, which locates in the expected range and is close to the value of γ predicted by the percolation theory.

From the rheological frequency sweep results in Figure 1 and the surface micrographs of κ-carrageenan gel in Figure 2, we know that the increase in G' and G'' with increasing κ-carrageenan concentration should be attributed to the formation of fibrillar network. Meanwhile, G' is greater than G'' and nearly independent of frequency in the terminal frequency range, which is a characteristic of a solid-like gel. The plateau value of G' is usually denoted as the plateau modulus G_e. Thus, a power law

$$G_e \sim \varepsilon^z \quad \text{for } p > p_g \tag{7}$$

Table 1. Zero Shear Viscosity η_0 as a Function of κ-Carrageenan Concentration c or the Relative Distance ε at Different Temperatures

10 °C			20 °C			30 °C			40 °C		
c (wt %)	ε	η_0 (Pa·s)	c (wt %)	ε	η_0 (Pa·s)	c (wt %)	ε	η_0 (Pa·s)	c (wt %)	ε	η_0 (Pa·s)
0.40	0.272	0.406	0.75	0.227	0.861	1.04	0.168	1.806	1.6	0.144	3.110
0.30	0.455	0.193	0.66	0.320	0.509	0.98	0.216	1.253	1.45	0.224	1.561
0.25	0.545	0.145	0.58	0.402	0.364	0.92	0.264	0.916	1.25	0.332	0.898
0.20	0.637	0.110	0.50	0.485	0.279	0.86	0.312	0.706	1.2	0.358	0.774
0.15	0.727	0.091	0.40	0.588	0.205	0.75	0.400	0.487	1.12	0.401	0.645
0.10	0.818	0.077	0.30	0.691	0.163	0.66	0.472	0.375	1.04	0.444	0.552

has been established to describe the relationship of G_e with ε beyond the sol−gel transition.

The dependence of G_e on ε at different temperatures is shown in Figure 11. It is observed that G_e increases with
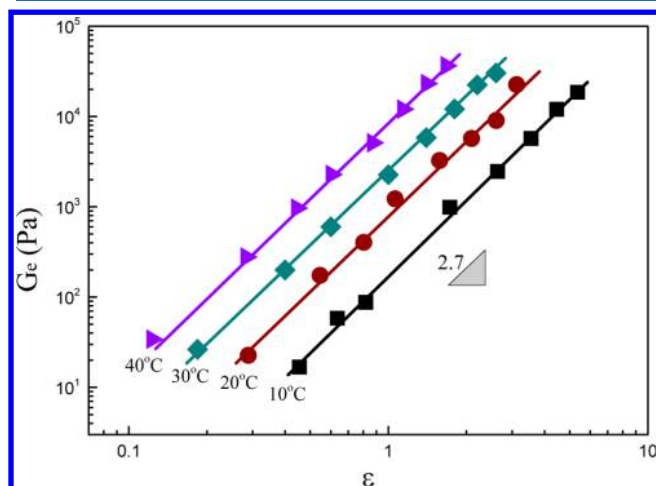

Figure 11. Dependence of plateau modulus G_e on the relative distance ε at different temperatures. The line fitting gives the solid straight lines.

increasing κ-carrageenan concentration at a fixed temperature. On the other hand, G_e decreases with increasing temperature at a given κ-carrageenan concentration due to the decrease of the relative distance induced by increasing the critical gel concentration. To examine the validity of the scaling law for G_e beyond the gel point, a linear fitting to the data was performed. The correlation coefficient, which was used to evaluate the goodness of each fitting, was higher than 0.98. It is surprising that the slopes of each fitting are almost the same: z equals to 2.7, which is independent of temperature. The theories based on the different assumptions have predicted different values of z. For example, using the percolation model, Martin et al.[34] predicted $z = 2.9$. According to the entanglement theory, Liu et al.[23] predicted $z = 2.0$. Based on the Bethe lattice, the mean-field theory predicted $z = 3.0$.[35] Different values of z also were experimentally obtained from various gel systems. For example, Li et al.[36] reported $z = 2.6$ for poly(vinyl chloride) gels induced by the microcrystalline. We obtained $z = 3.0$ for Pluronic PEO−PPO−PEO triblock copolymer hydrogels induced by the stacking of micelles.[21] For gels formed by the hydrogen bonding, Kjoniksen et al.[37] obtained $z = 4.7$ for poly(vinyl alcohol) gel and Hsu et al.[38] obtained $z = 1.9$ for

gelatin gel. However, for the methylcellulose gels induced by hydrophobic association, we previously found that a single power law could not be used to express the entire G_e.[39] The variation of z values for various gel systems suggests that z should be related to the different gel mechanisms and structures. In this study, for the first time we found $z = 2.7$ for the κ-carrageenan gel, which is very close to what is predicted by the percolation model and is the typical characteristic for the gels formed by the aggregation of double helices.

Winter et al. applied an assumption that the longest relaxation time τ_m in the vicinity of the sol−gel transition point p_g takes the same scaling exponent α as $\tau_m \sim \varepsilon^{-\alpha}$ before $(p < p_g)$ and beyond $(p > p_g)$ the gel point to describe the relaxation behavior of critical gels.[40] If this is true, τ_m diverges symmetrically on both sides of the gel point, and the symmetry of τ_m results in the relation $n = z/(z + \gamma)$. Here n is the scaling exponent at the critical gel point. The application of the relation to the κ-carrageenan gels in this work gives a prediction of $n = 0.63$, where $\gamma = 1.6$ and $z = 2.7$ were used. It is apparent that the value of prediction 0.63 agrees well with the corresponding value of n (0.62) obtained using the Winter−Chambon criterion. For the gelation behavior of gullan gum in aqueous solution, Dai et al.[41] found that n calculated from γ and z is consistent with that obtained by the Winter−Chambon criterion. However, n is not constant and decreases with increasing gullan gum concentration when temperature is used as a gelling variable. However, n is constant and independent of temperature for κ-carrageenan hydrogel. Using $\alpha = \gamma/(1 - n)$ for $p < p_g$ and $\alpha = z/n$ for $p > p_g$ to calculate the exponent α, we obtained $\alpha = 4.57$ before the gel point, which is close to $\alpha = 4.15$ beyond the gel point for κ-carrageenan gel. The above results indicate that the approach to the gel point from the side of $p < p_g$ is similar to the other side of $p > p_g$. This further proves that the characteristic relaxation times of the pregel and the postgel follow the same power law (symmetry at $c = c_g$) for κ-carrageenan gel.

◼ CONCLUSIONS

The rheological and morphological properties as well as the scaling laws for κ-carrageenan in aqueous solution have been investigated as a function of κ-carrageenan concentration and temperature by means of rheology and FESEM. The experimental results indicated that the formation of a fibril network induced by the aggregation of double helices leads to a κ-carrageenan gel. The critical gel concentration c_g at a fixed temperature was obtained by the Winter−Chambon criterion and was found to be proportional to temperature T as $c_g \sim$

Table 2. Plateau Modulus G_e as a Function of κ-Carrageenan Concentration c or the Relative Distance ε at Different Temperatures

10 °C			20 °C			30 °C			40 °C		
c (wt %)	ε	G_e (Pa)	c (wt %)	ε	G_e (Pa)	c (wt %)	ε	G_e (Pa)	c (wt %)	ε	G_e (Pa)
3.5	5.36	1.86×10^4	4	3.12	2.25×10^4	4.5	2.60	3.03×10^4	5	1.67	3.65×10^4
3	4.45	1.20×10^4	3.5	2.61	9.05×10^3	4	2.20	2.24×10^4	4.5	1.41	2.31×10^4
2.5	3.55	5.72×10^3	3	2.09	5.72×10^3	3.5	1.80	1.21×10^4	4	1.14	1.21×10^4
2	2.64	2.46×10^3	2.5	1.58	3.26×10^3	3	1.40	5.84×10^3	3.5	0.87	5.12×10^3
1.5	1.73	9.88×10^2	2	1.06	1.22×10^3	2.5	1.00	2.27×10^3	3	0.60	2.28×10^3
1	0.82	8.75×10	1.75	0.80	4.04×10^2	2	0.60	6.01×10^2	2.7	0.44	9.69×10^2
0.9	0.64	5.84×10	1.5	0.55	1.74×10^2	1.75	0.40	2.00×10^2	2.4	0.28	2.78×10^2
0.8	0.45	1.68×10	1.25	0.29	2.27×10	1.48	0.19	2.64×10	2.1	0.12	3.42×10

$T^{0.85}$. At the gel point, the critical relaxation exponent n almost kept constant and independent of temperature, whereas the critical gel strength S_g increased with increasing temperature. A constant gel strength S_g/c_g was obtained by normalizing S_g with c_g to eliminate the effect of temperature, indicating a unique character of κ-carrageenan gelation in aqueous solution. The junction length at the gel point was calculated using the modified Eldridge–Ferry model and found to be 17.4, supporting the similarity of the fractal structure in the κ-carrageenan gels. Two scaling laws, $\eta_0 \sim \varepsilon^{-1.6}$ before the gel point and $G_e \sim \varepsilon^{2.7}$ beyond the gel point, were obtained for κ-carrageenan solutions and gels, respectively. The critical relaxation exponent n determined from the relation $n = z/(z + \gamma)$ is very close to that obtained from the Winter–Chambon criterion, which further indicated that the pregel and postgel obey the similar relaxation behavior when approaching to the gel point.

◼ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.5b01922.

    Figure S1 (DOC)

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Notes

The authors declare no competing financial interest.

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