

Phase Transitions of κ -Carrageenan Gels in Various Types of Salts

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ABSTRACT: Sol–gel and gel–sol phase transitions of κ -carrageenan in various types of salts were studied using photon transmission technique. Here, LiCl, NaCl, KCl, MgCl₂, CaCl₂, and SrCl₂ were chosen as the proper salts for the κ -carrageenan–water system. Photon transmission intensity, I_{tr} was monitored against temperature to determine the sol–gel and gel–sol temperatures (T_{sg} and T_{gs}) and activation energies (ΔE_{sg} and ΔE_{gs}). It was observed

that T_{gs} temperatures were notably higher than T_{sg} due to the hysteresis on the phase transition loops. It was observed that stronger carrageenan gels are formed in the presence of KCl compared to the others. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 3008–3016, 2006

Key words: activation energy; gelation; phase separation; polysaccharides

INTRODUCTION

Polymer gels are created from polymer networks and solvents, i.e., the polymer network envelopes the liquid and prevents it from flowing out. In other words, the gel polymer network acts as a container that keeps a large amount of liquid. Gels are classified by the strength of the crosslinkages. Some gels are crosslinked chemically by covalent bonds, whereas others are crosslinked physically by hydrogen or ionic bonds and by the physical entanglement of polymer chain.^{1,2} In general, gels formed by chemical bonding are irreversible gels, since they cannot be dissolved again. However, moderate heating can reversibly dissolve a physically crosslinked gel. Many of the natural polymer gels fall into the class of physical gels. The process of gelation upon cooling can be named as sol–gel phase transition and the reversible gelation process is called a gel–sol phase transition. Phase transitions of gels can be effected by solvent composition, pH changes, ion composition changes in the gel and electric field.

Red algae produce a wide range of galactose-based polysaccharides, one of which (carrageenan) has achieved great interest because of its food and industrial applications. κ -, ι -, and λ -carrageenans are three major types, which differ in number and position of sulfate ester substituents they contain. Carrageenans

are linear, sulfated polysaccharides of the type (AB)_n, consisting of β -1,3-linked D-galactose and α -1,4-linked 3,6-anhydro-D-galactose. In ι -carrageenan both rings are sulfated, while in κ -carrageenan only one-ring is sulfated (Fig. 1). κ -carrageenan is readily available as a food additive.³ In general, the carrageenan family is known to form thermally-reversible gels as a function of temperature and gel-inducing agents. The gelation process of carrageenan solutions has been described by two mechanisms.⁴ According to the first mechanism, suggested by Morris et al.,⁵ crosslinks are formed by segments of a double helix. These segments are then aggregated by ions as K⁺. In the other mechanism, proposed by Smidsrod and Grasdalen,⁴ monohelices are formed, which are subsequently aggregated by K⁺ ions to dimers, trimers, etc. The sol–gel phase transition of κ -carrageenan solutions occurs as a result of coil-to-helix conformational transition upon cooling. Further decrease in temperature results in aggregation between ordered helices. This cooperative process has been generally explained as a “domain model” based on the presence of double helices in the functional zones of carrageenan gel network.⁵ The addition of cation solutions at an adequate concentration appears to improve the gel strength or the elastic modulus of κ -carrageenan gels via enhancing conformational ordering and subsequent aggregation.⁶ Detailed information on molecular structures of carrageenan determined by X-ray fiber diffraction analysis may be found in a review by Millane et al.⁷ As an important characteristic of these systems, the decrease in the degree of sulfation from ι -carrageenan to κ -carrageenan makes the gels more rigid, less elastic, and

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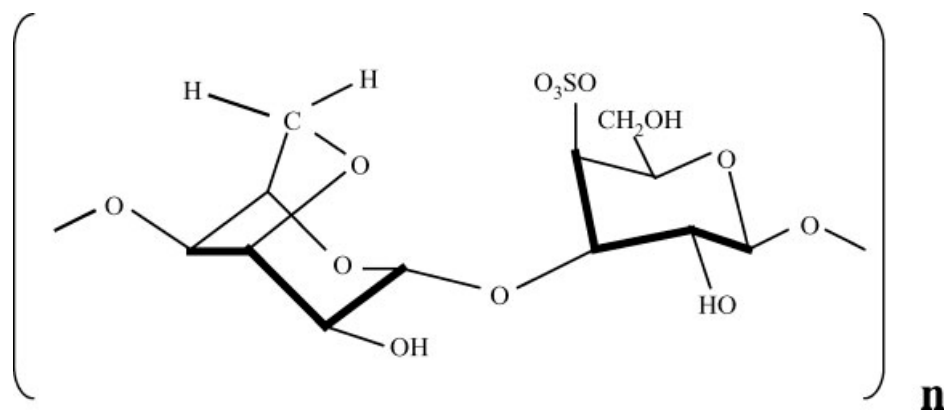


Figure 1 Repetition unit of κ -carrageenan (polysaccharide).

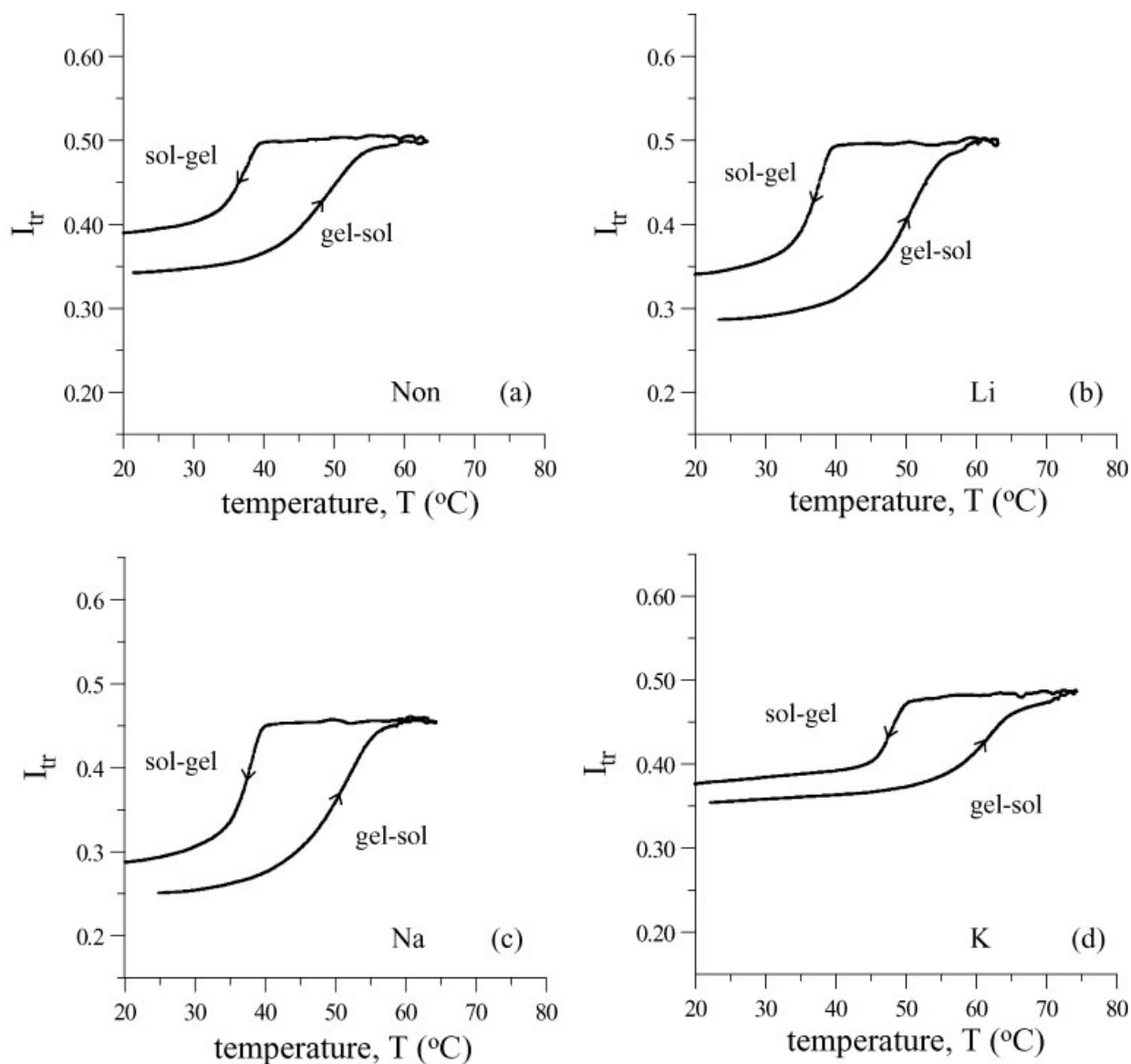


Figure 2 The temperature, T , variation of I_{tr} during gel-sol and sol-gel transitions for the monovalent samples of (a) Non, (b) Li, (c) Na, and (d) K.

brittle, and they require lower concentration of polysaccharides for their formation. In addition, a decrease in anhydrogalactose content increases both the potassium ion sensitivity and the gelling capacity.

The microviscosity of the hydrophobic microdomains, the dynamic rheology, and molecular conformation in the melting process of κ -carrageenan systems were studied by means of fluorescence intramolecular excimer forming probe, by dynamic viscometry, and by optical rotation, respectively.⁸ Helical conformation was considered necessary for aggregation and gelation to occur, and the formation of a helical structure was promoted by adding an appropriate electrolyte to a sufficient ionic strength and by lower-

ing the temperature.⁸ Phase transition temperatures, rheological properties, and gel-network characteristics during sol-gel and gel-sol transitions of κ -carrageenan-salt solution were studied by several groups.⁹⁻¹³ The effectiveness of increasing T_{sg} and T_{gs} at various salt concentrations were examined by following the sequence of $K^+ > Ca^{2+} > Na^+$ in KCl, $CaCl_2$, and NaCl solutions, respectively.

In this work, sol-gel and gel-sol transitions of carrageenan in various types of cation solutions were studied using a photon transmission technique. This technique has previously been used to monitor formation of acrylamide gels in various crosslinker contents,¹⁴ where transmitted photon intensity, I_{tr} , decreased

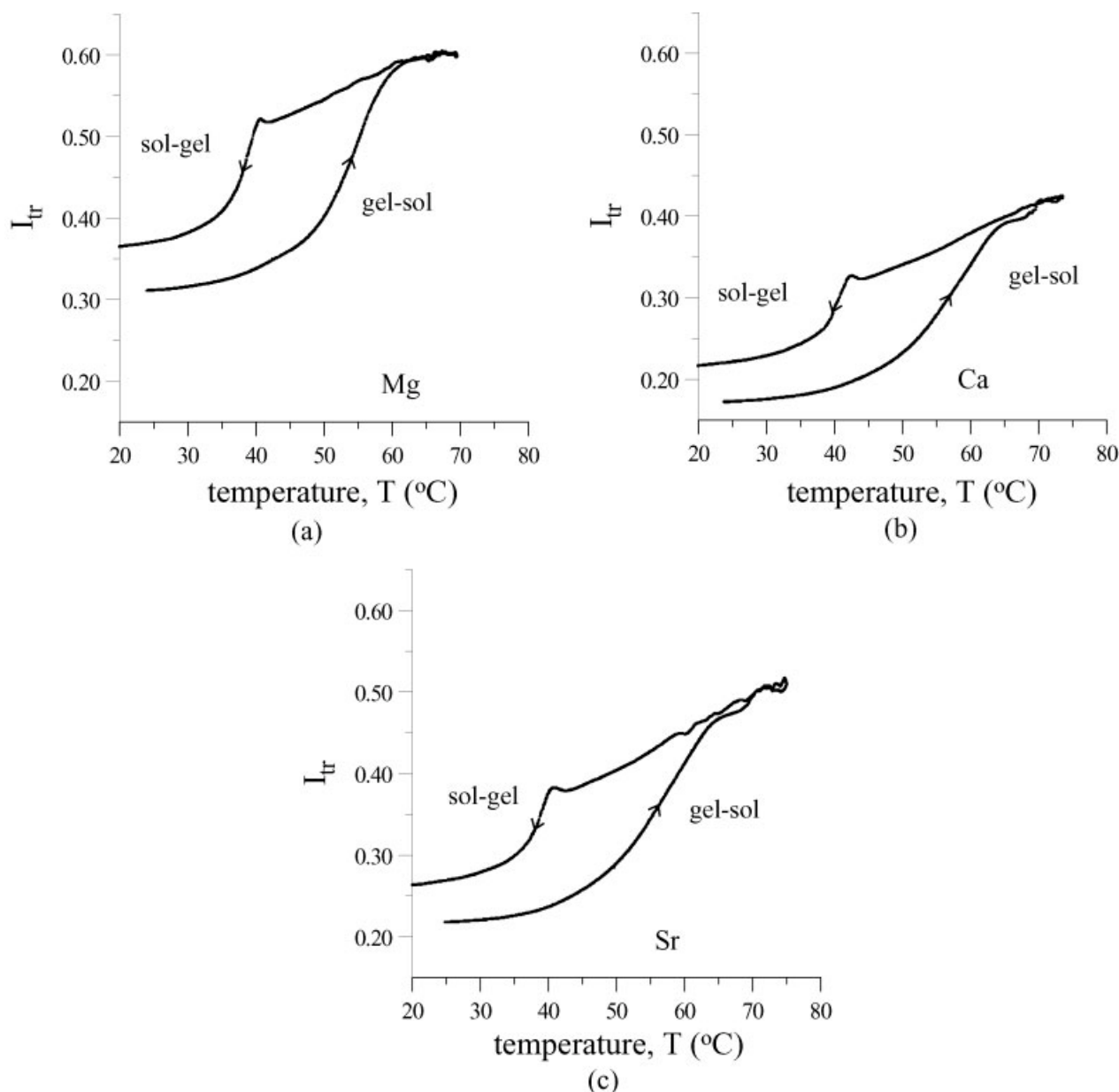


Figure 3 The temperature, T , variation of I_{tr} during gel-sol and sol-gel transitions for the bivalent samples of (a) Mg, (b) Ca, and (c) Sr.

dramatically at a certain reaction time, which is attributed to the formation of microgels in the system. Recently, cation (K^+) effect on sol-gel and gel-sol phase transitions of κ -carrageenan-water system,¹⁵ hysteresis phenomenon in similar systems,¹⁶ and molecular recognition mechanism of κ and ι carrageenan mixtures¹⁷ have been investigated by us using the same technique. Here, it was observed that during the sol-gel transition of carrageenan in both monovalent and bivalent cation solutions, I_{tr} presented a sigmoidal decrease. However, on reheating during the gel-sol transition, I_{tr} intensity increased by following another sigmoidal path back to its initial position, forming a hysteresis loop. T_{sg} and T_{gs} transition temperatures were determined for each hysteresis loop in various carrageenan-cation systems. Sol-gel and gel-sol activation energies (ΔE_{sg} and ΔE_{gs}) were measured. The observed temperatures and activation energies suggest that KCl- κ -carrageenan gel network is much stronger than the others; as a result, the energy need for this system is much lower.

EXPERIMENTAL

Two weight percent of κ -carrageenan (C-1013 Sigma, Stein Heim, Germany) powder was dissolved in vari-

ous salts (Merck, Darmstadt, Germany) (0.5 mmol) without any purification (for practical use) in distilled water (pH 6.5). The monovalent LiCl, NaCl, KCl, and bivalent $MgCl_2$, $CaCl_2$, $SrCl_2$ cations were used to prepare gel samples. The pure (does not contain additional salts) κ -carrageenan-distilled water sample was prepared to use as a standard. These seven samples were marked as Li, Na, K, Mg, Ca, Sr, and Non, respectively. During preparation, the heated carrageenan solutions were held at $90^\circ C$ and were continuously stirred by a magnetic stirrer. Sol-gel and gel-sol transitions were performed in a $3.5 \times 1.5 \times 1.0 \text{ cm}^3$ glass cell equipped with a heat reservoir. Temperature was monitored and *in situ*, photon transmission measurements were performed simultaneously using Perkin-Elmer $\lambda 2$ UV-visible (UVV) spectrometer at 450 nm wavelength. The carrageenan sol at $90^\circ C$ was transferred into the glass cell and was allowed to cool to room temperature before the UVV measurements were started. Then the carrageenan gel was reheated up to $80^\circ C$ at the rate of $(2 \pm 0.2)^\circ C/\text{min}$ to observe the gel-sol transition. Cooling of the carrageenan sol from 80 to $20^\circ C$ was then performed at the same rate to detect the sol-gel transition. Photon transmission intensities, I_{tr} , were monitored against temperature by using the time drive mode of the spectrometer during both transitions. Here the errors on the measured tem-

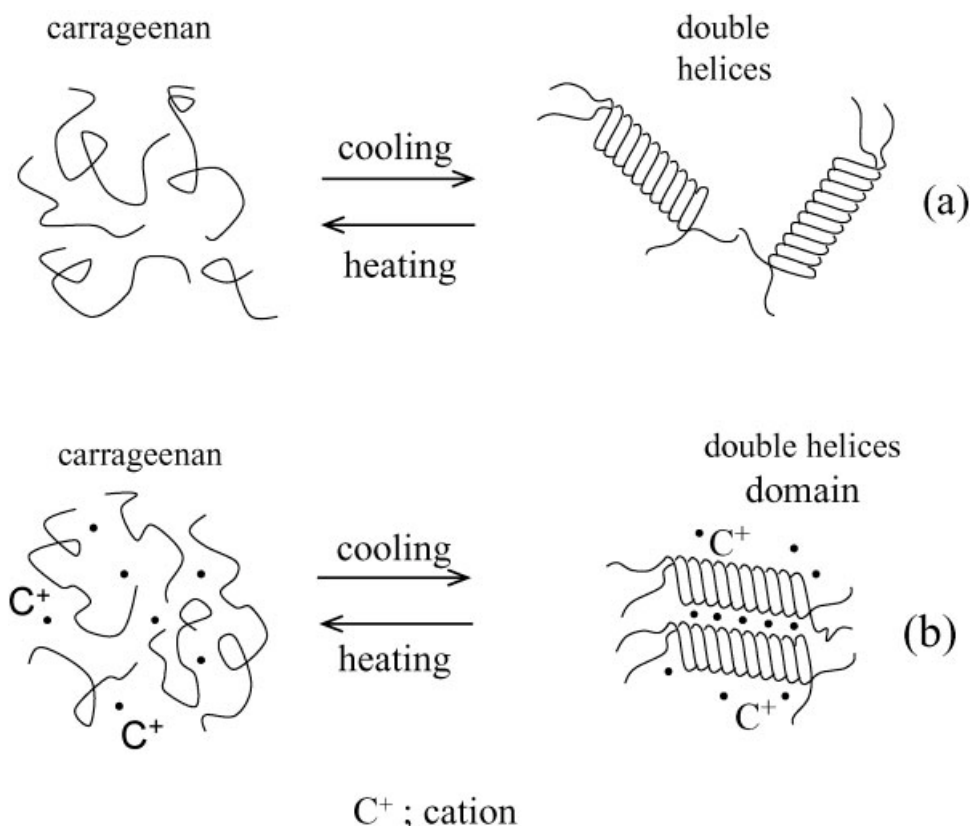


Figure 4 Formation and destruction of double helices and double helix domains in carrageenan gel (a) in pure water, (b) in cationic solution.

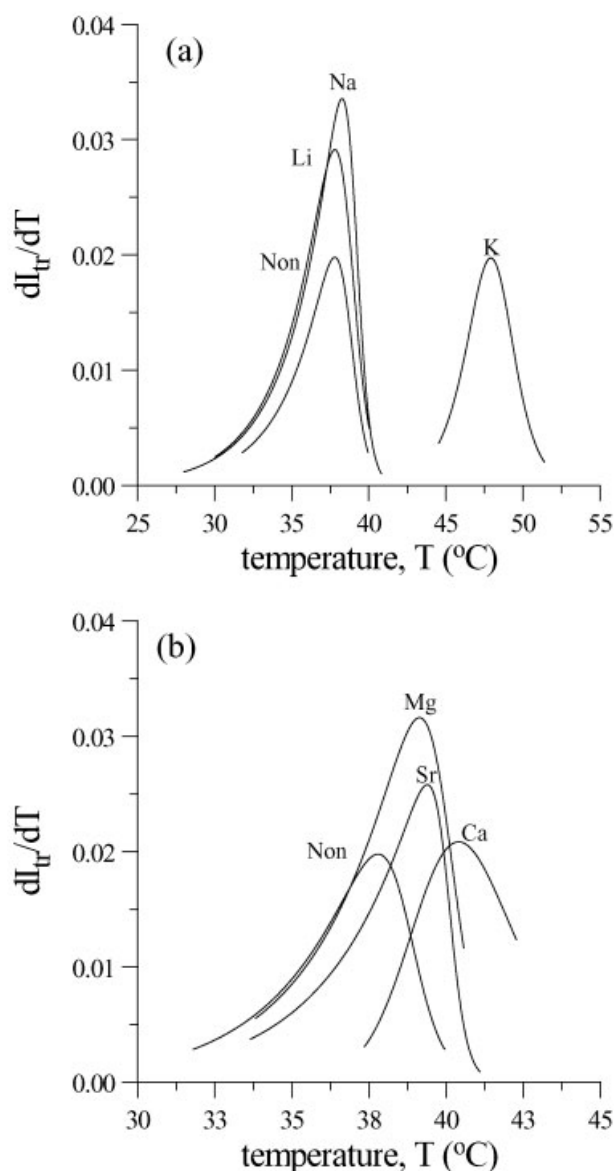


Figure 5 The determination of sol-gel (T_{sg}) temperatures from the peak positions of the first derivatives of sigmoidal curves in Figures 2 and 3 for (a) monovalent and (b) bivalent samples.

peratures and activation energies are mostly originated from the temperature controller device and the transmitted light intensity, I_{tr} . The maximum error on temperature measurement was found to be around $0.5^{\circ}C$. On the other hand, 1–3% error was detected in intensity during I_{tr} measurements.

RESULTS AND DISCUSSION

Figures 2 and 3 show the temperature variation of I_{tr} between 20 and $80^{\circ}C$ for Non, Li, Na, K, and Mg, Ca, Sr gel samples, respectively. It can be seen that transmitted photon intensities, I_{tr} , for all samples increased

upon heating the carrageenan gel samples by indicating that gel-sol transition takes place. However, I_{tr} decreased dramatically upon cooling the carrageenan gels in all cases demonstrating that the sol-gel transitions occurred. It can be postulated that during cooling, double helices are formed through the association of carrageenan molecules and then the double helices are aggregated to higher order assemblies to create a three dimensional network.¹⁸ During gelation; carrageenan-water system starts to decompose into two phases with different network concentrations, which creates concentration fluctuations. In other words, double helix aggregates form a separate phase by excluding water from their domains. As a result, the contrast between carrageenan and water phases can scatter light and dramatically reduce the transmitted light intensity, I_{tr} . On reheating, initially the double

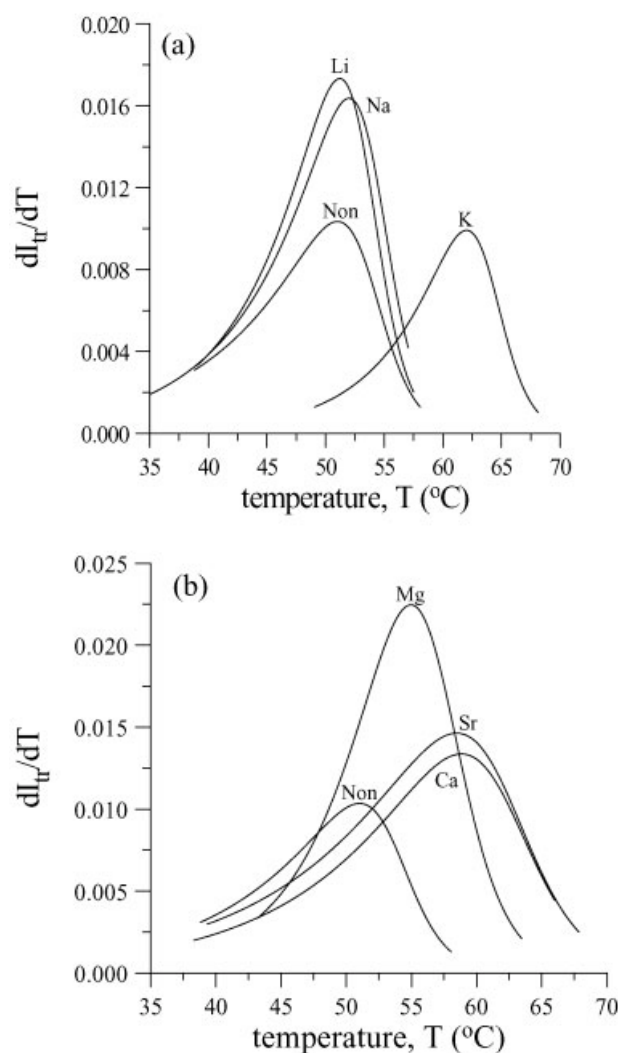


Figure 6 The determination of gel-sol (T_{gs}) temperatures from the peak positions of the first derivatives of sigmoidal curves in Figures 2 and 3 for (a) monovalent and (b) bivalent samples.

TABLE I
Gel-Sol and Sol-Gel Transition Temperatures (T_{gs} and T_{sg}) and Activation Energies (ΔE_{gs} and ΔE_{sg})
for the Various Types of Cations

Samples	Electronegativity	T_{gs} ($^{\circ}\text{C}$)	T_{sg} ($^{\circ}\text{C}$)	ΔE_{gs} (kJ/mol)	ΔE_{sg} (kJ/mol)
Non	–	49.3 ± 1	37.5 ± 0.5	21.4	29.8
Li^+	0.98	51.2 ± 1	37.8 ± 0.5	36.4	50.0
Na^+	0.93	52.0 ± 1	38.3 ± 0.5	35.7	63.8
K^+	0.82	62.0 ± 1	47.9 ± 0.5	21.6	36.1
Mg^{++}	1.31	55.0 ± 1	39.1 ± 0.5	39.5	49.8
Ca^{++}	1.00	58.8 ± 1	40.4 ± 0.5	36.5	56.3
Sr^{++}	0.95	58.5 ± 1	39.4 ± 0.5	33.2	55.1

helix aggregates are destroyed and then double helices are decomposed to carrageenan molecules, which results in the destruction of the gel structure. As the carrageenan–water system becomes homogeneous, the transmitted light intensity increases. Figure 4(a, b) present the formation and destruction of double helices and double helix domains in pure water and in cationic solution, respectively. It is expected that cations play an important role in formation of the double helix domains.

Sol–gel and gel–sol transition curves in Figures 2 and 3 present a clear sigmoidal behavior as expected. The peak positions of the first derivatives (dI_{tr}/dt) of these sigmoidal curves can produce the sol–gel and gel–sol transition temperatures (T_{sg} and T_{gs}), which are shown in Figures 5 and 6 for the monovalent and bivalent cations, respectively. These temperatures are listed in Table I for all gel samples. It is seen that T_{sg} values are much lower than T_{gs} values for all carrageenan samples i.e., during reheating, the gel does not liquefy at gelation temperature, T_{sg} . This hysteresis behavior can be explained as follows; to destroy the double helices aggregates and double helix, system requires much higher temperature than it needs to form gel. Upon cooling, temperature has to be lowered to form double helices and their aggregates. In the case of cation content, both T_{gs} and T_{sg} values are found to be much higher than the gel containing no external cation (Non). Thus, in the presence of cations, stronger gels can be formed, which require higher temperatures to become sol upon heating. These sols can be gelled at higher temperatures due to the cation attraction. Here K^+ presents a unique behavior compared to others; i.e., in the presence of K^+ , carrageenan molecules can form double helix domains much easier than sols without or with other cations. The order of the transition temperatures for ions are in accordance with the literature.⁴ To understand the response of carrageenan gel to the salts introduced into the system, T_{gs} and T_{sg} values are plotted versus electronegativity of cations in Figure 7. It appears that mono and bivalent cations group into two regions. Figure 7 shows that as the electronegativity is

increased, both T_{gs} and T_{sg} values decrease in both groups. This behavior will be explained at the end of the article after producing the sol–gel and gel–sol activation energies.

I_{tr} versus temperature curves in Figures 2 and 3 can be treated using Arrhenius relation as written below,

$$I_{tr}/I_{\infty} = \exp(-\Delta E/kT) \quad (1)$$

where I_{∞} is the transmitted photon intensity at the highest temperature (80°C) where all carrageenan molecules are free in the sol phase. Naturally, at the lowest temperature (20°C), I_{tr} approaches to zero, which means all carrageenan molecules are used to form double helix aggregates to form a gel. ΔE is the sol–gel and gel–sol activation energy depending on the path of the hysteresis loop it follows. In other words, if ΔE is produced from the cooling curve, it can be named as sol–gel activation energy, ΔE_{sg} , while heating curve can provide the gel–sol activating

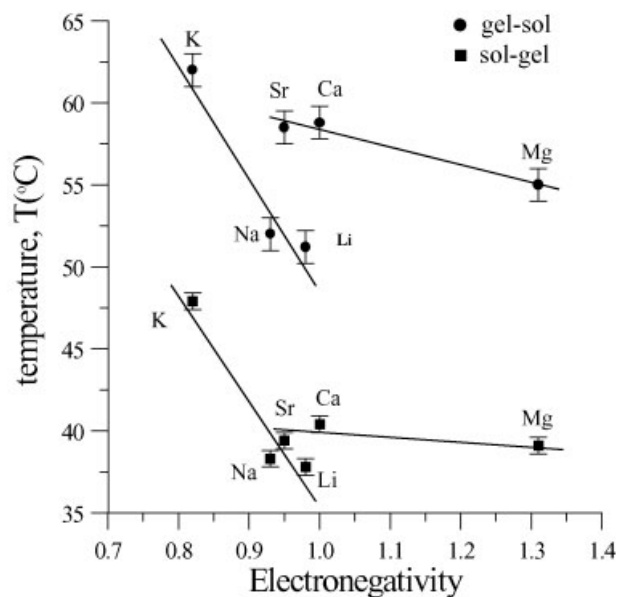


Figure 7 Plots of T_{gs} and T_{sg} values versus electronegativity of the corresponding salts.

energy, ΔE_{gs} , during liquefaction process. Figures 8 and 9 present the Arrhenius plots for Non, Li, Na, K, and Mg, Ca, Sr gel samples, respectively. The slopes of the curves in Figures 8 and 9 produce ΔE_{sg} and ΔE_{gs} activation energies, which are listed in Table I for all gel samples. It is understood that sol-gel transitions need much higher energy than the gel-sol transitions, because to form double helix aggregates, system has to spend more energy than to destroy itself i.e., much less energy is needed for gel-sol transition (liquefaction) process than sol-gel transition. It is interesting to note that carrageenans in KCl solutions need much lower energy for both sol-gel (ΔE_{sg}) and gel-sol (ΔE_{gs}) processes than the others except Non. ΔE_{gs} and ΔE_{sg} values versus electronegativity are plotted in Figure 10, where two distinct groups can be seen for monovalent and bivalent cations and as the electronegativity is increased, both ΔE_{gs} and ΔE_{sg} values present increase. These results are understandable, because system needs higher energy for gel-sol transition when the electron attraction is higher. Similar argument can be hold for the sol-gel transition. To explain the behavior of T_{gs} and T_{sg} against electronegativity, T_{gs} and T_{sg} values are plotted versus ΔE_{gs} and ΔE_{sg} activation energies in Figure 11, where increase correlation between critical temperatures and activation energies explain the behavior of temperatures against electronegativity i.e., at higher electronegativity system needs lower temperature to execute gel-sol and sol-gel transitions.

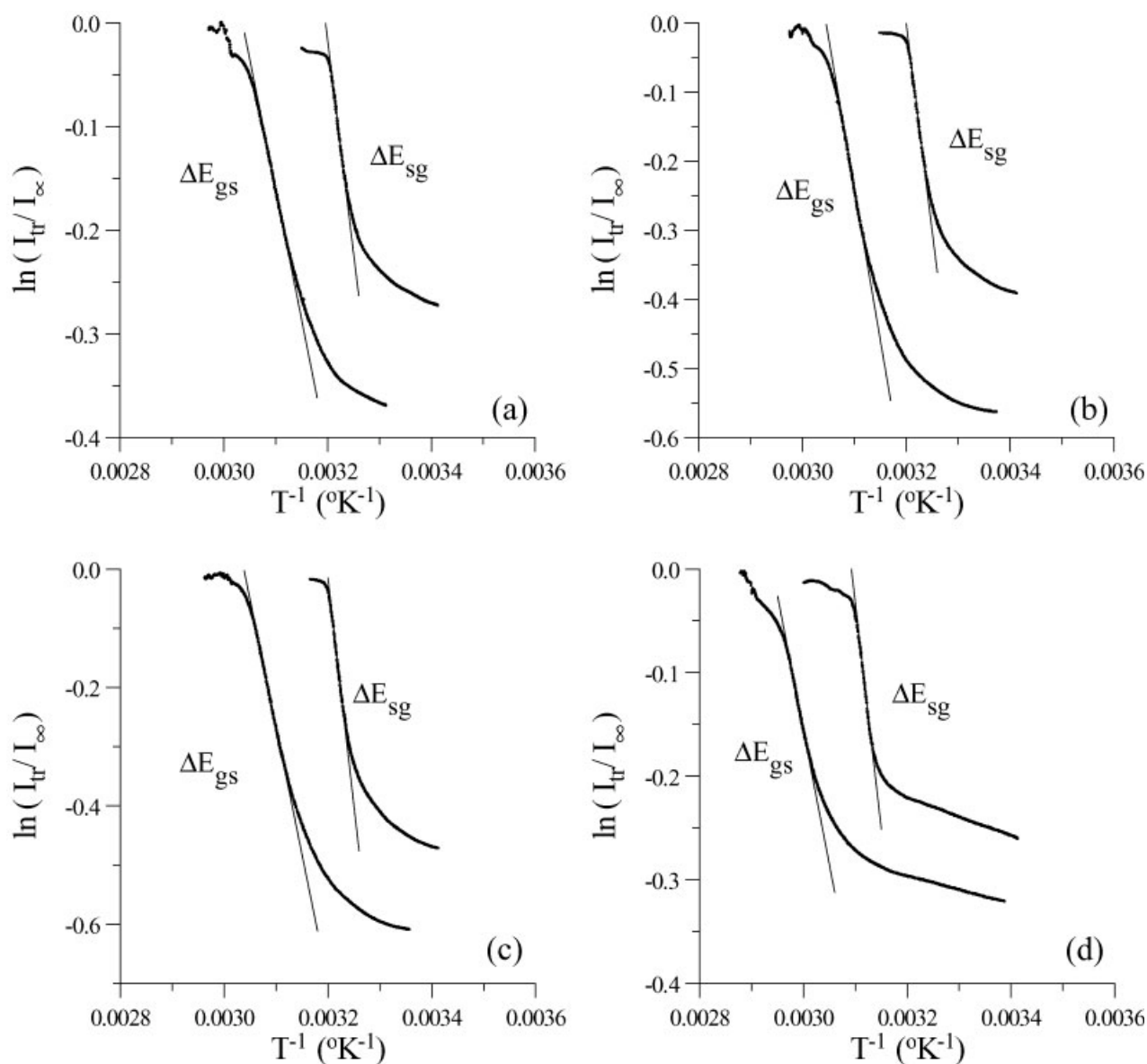


Figure 8 The plots of $\ln I_{tr}$ versus T^{-1} for the samples of (a) Non, (b) Li, (c) Na, and (d) K. The slopes of the curves produce the gel-sol (ΔE_{gs}) and sol-gel (ΔE_{sg}) activation energies, which are listed in Table I.

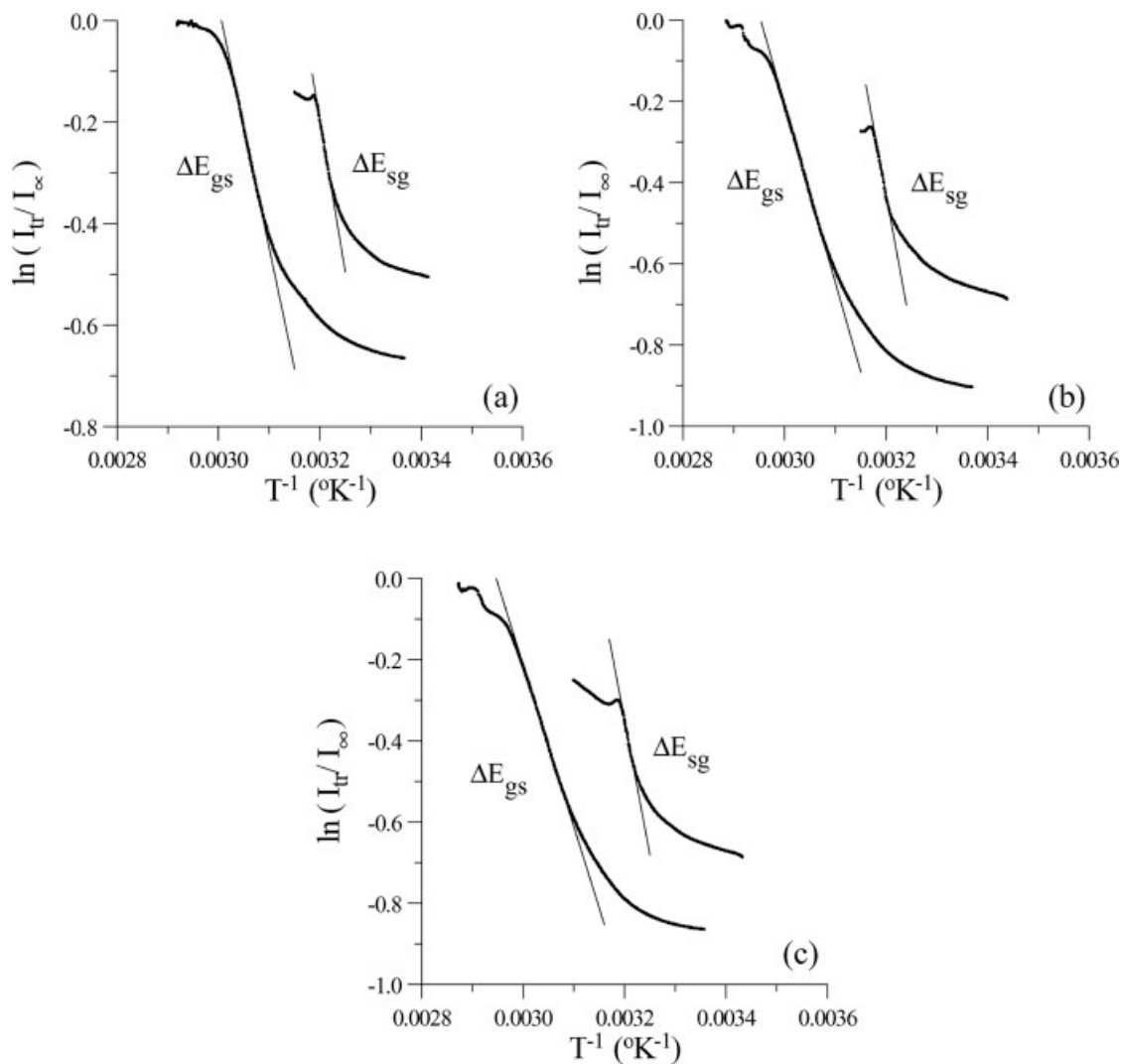


Figure 9 The plots of $\ln I_{tr}$ versus T^{-1} for the samples of (a) Mg, (b) Ca, and (c) Sr. The slopes of the curves produce the gel-sol (ΔE_{gs}) and sol-gel (ΔE_{sg}) activation energies, which are listed in Table I.

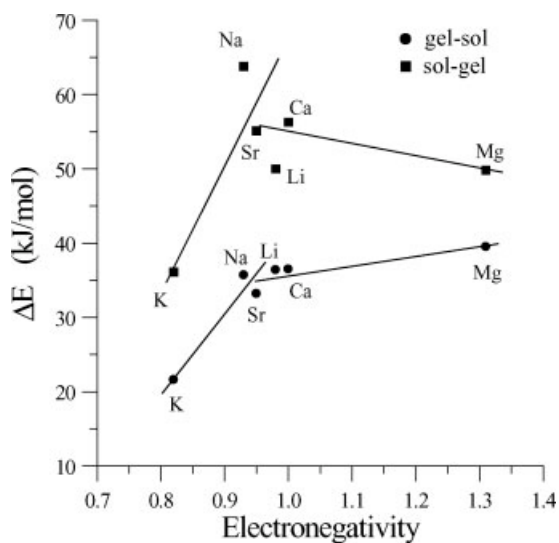


Figure 10 Plots of ΔE_{gs} and ΔE_{sg} values against electronegativity of the corresponding salts.

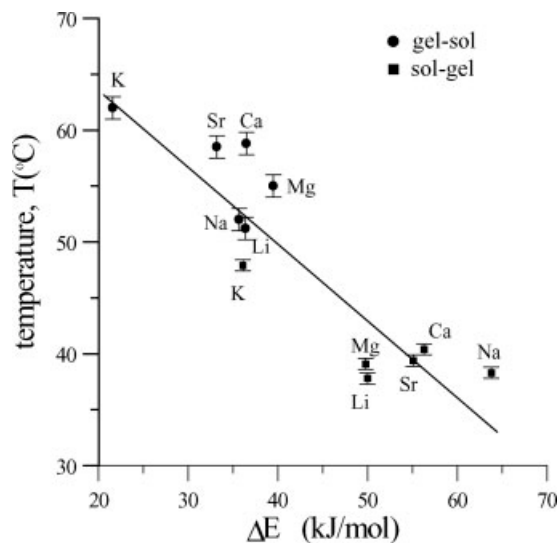


Figure 11 Plots of T_{gs} and T_{sg} values versus ΔE_{gs} and ΔE_{sg} energies.

CONCLUSIONS

In conclusion, this work presented a novel method to study cation effects on sol-gel and gel-sol transition mechanisms in κ -carrageenan-water system with monovalent and bivalent cations. It is understood that I_{tr} can monitor the phase separation of double helix domains during sol-gel transition in carrageenan-water system. Sol-gel and gel-sol transition temperatures and activation energies were easily determined from the hysteresis loops of the photon transmission intensities, I_{tr} . It is observed that both T_{gs} and T_{sg} and ΔE_{gs} and ΔE_{sg} values were found to be grouped into two distinct regions and it is seen that high electronegativity produce lower critical temperatures in these groups.

References

1. de Gennes, P. G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.
2. de Rossi, D.; Kajiwara, K.; Osada, Y.; Yamauchi, A. *Polymer Gels*; Plenum: New York, 1991.
3. Webb, C.; Black, G. M.; Atkinson, B. *Process Engineering Aspects of Immobilized Cell Systems*, 1st ed.; Institution of Chemical Engineers: Rugby, UK, 1986.
4. Te Nijenhuis, K. *Adv Polym Sci* 1997, 130, 1.
5. Morris, E. R.; Rees, D. A.; Robinson, C. *J Mol Biol* 1980, 138, 349.
6. Rochas, C.; Landry, S. *Carbohydr Polym* 1987, 7, 435.
7. Millane, R. P.; Nzewi, E. U.; Arnott, S. In *Frontiers in Carbohydrate Research-1*; Millane, R. P., BeMiller, J. N., Chandrasekaran, R., Eds.; Elsevier Applied Sciences: London, 1989.
8. Hugerth, A.; Nilsson, S.; Sundelof, L. O. *Int J Biol Macromol* 1999, 26, 69.
9. Kusakawa, N.; Ostrovsky, M. V.; Garner, M. M. *Electrophoresis* 1999, 20, 1455.
10. Lai, V. M. F.; Huang, A. L.; Lii, C. Y. *Food Hydrocolloids* 1999, 13, 409.
11. Norton, I. T.; Jarvis, D. A.; Foster, T. *J Int J Biol Macromol* 1999, 26, 255.
12. Mohammed, Z. H.; Hember, M. W. N.; Richardson, R. K.; Morris, E. R. *Carbohydr Polym* 1998, 36, 15.
13. Lai, V. M. F.; Wong, P. A. L.; Lii, C. Y. *J Food Sci* 2000, 65, 1332.
14. Kara, S.; Pekcan, O. *Polymer* 2000, 41, 3093.
15. Kara, S.; Tamerler, C.; Bermek, H.; Pekcan, O. *Int J Biol Macromol* 2003, 31, 177.
16. Kara, S.; Tamerler, C.; Bermek, H.; Pekcan, O. *J Bioact Compat Polym* 2003, 18, 33.
17. Kara, S.; Arda, E.; Pekcan, O. *Phase Transitions* 2005, 78, 915.
18. Mangione, M. R.; Giacomazza, D.; Bulone, D.; Martorana, V.; San Biagio, P. L. *Biophys Chem* 2003, 104, 95.