A Variable-Temperature Fourier Transform Infrared Study of Gelation in ι- and κ-Carrageenans

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ABSTRACT: Variable-temperature Fourier transform infrared (VT FTIR) spectra for different ion forms of ι- and κ-carrageenans are reported. By the use of Fourier self-deconvolution (FSD) to improve spectral resolution, it was possible to identify changes that occurred in the spectra of both ι- and κ-carrageenans with temperature. By the use of these improved spectra, previous assignments have been reassessed, and it is concluded that although the assignment of the sulfate symmetric stretch is probably correct it is not sensitive to ion binding. Other intensity changes in the spectra on gelation may be readily quantified and used to follow the helix-to-coil transition on gel melting. The results are compared to optical rotation measurements and shown to be similar. The effects of iodide on the FTIR spectra are compared with the effects on NMR spectra, and it is concluded that, while NMR is sensitive to aggregation processes, FTIR is insensitive to these but is sensitive to helix-coil transitions.

Introduction

Red marine algae (*Rhodophycae*) produce three familiar and commercially important polysaccharide extracts: furcelleran, agar/agarose, and carrageenan. They all consist of alternate α (1,3) and β (1,4) linked residues. The differences between them arise in the degree of sulfation of the polysaccharide repeat unit and the amount of 3,6-anhydro-D-galactose or 3,6-anhydro-L-galactose they contain.

Carrageenans can be subdivided according to their degree of sulfation. Thus, ι-carrageenan has two sulfate residues per repeat unit while κ-carrageenan has one (Figure 1). Under appropriate conditions, ι- and κ-carrageenans yield thermoreversible gels.[1] It is this property which has enabled them to be widely employed in the food industry as, amongst other things, gelling and stabilizing agents in suspensions and dispersions. Considerable investigation has been carried out on the mechanism of gelation. Most of the work has concentrated on the conformational changes occurring on gelation, but more recently the role of the counterions in this process has been attracting attention.[2-9]

Spectroscopic methods such as multinuclear nuclear magnetic resonance (NMR) and infrared spectroscopy (IR) have been applied to the problem of ion binding in the carrageenans.[3-9] Consideration of NMR line shapes indicates that the strongest interactions in ι-carrageenan are with K^+ and Rb^+; Na^+ gives no evidence of any strong interaction, and Cs^+ only weakly interacts. In the κ-carrageenans, strong interactions are seen with K^+, Rb^+, and Cs^+ forms, and no interaction at all is observed in the Na^+ form. However, this type of NMR experiment only monitors the mobility of the counterion and does not give any direct evidence as to the origin of the mobility changes. NMR chemical shift studies[7] have suggested, however, that there is site-specific interaction with the polymer, i.e., direct binding to the sulfate groups rather than some nonspecific condensation mechanism.

IR spectroscopy has been used to investigate the sulfate groups in carrageenan gels.[8,9] This work has identified the S-O symmetric stretch at 1090 cm^{-1} as sensitive to ion interaction; its presence has been related to ion binding. Thus, a band was seen in K^+ and Cs^+ κ- and ι-carrageenans but not in the Na^+ forms. More recently, techniques such as Fourier self-deconvolution[10] (FSD) have been applied by us in order to improve the resolution of the spectra. When combined with variable-temperature (VT) methods, it has been possible to study the effects of different ions on the sol-gel transition.

In this paper we present an extended Fourier transform infrared study of κ- and ι-carrageenans in specific ion forms using VT methods in order to thoroughly investigate the changes occurring in the IR spectrum during gelation. The effects of varying ionic strength are also reported.

Experimental Section

The κ- and ι-carrageenans, from *Euchema cottonii* (Sigma Chemical Co.), were ion exchanged into pure ion forms by using a method described previously.[11,12] The purity was checked by using a Phillips PSEM 501B scanning electron microscope fitted with an ion probe (Link 868 series2 EDS) and by using atomic absorption spectroscopy. Contaminants (especially K^+ in κ-carrageenan and Ca^{2+} in ι-carrageenan) were absent or present in insignificant amounts.

Carrageenan solutions were prepared by adding the solvent (D_2O, H_2O) to the dry pure ion form in a PTFE-lined digestion vessel, which was then heated at 353 K for 2 h. Carrageenan gels with differing ion concentrations were prepared in the same way except that the dry pure ion form was added to the appropriate volume of an ionic solution. This method of preparation has been used previously in NMR and IR experiments. Except where otherwise stated, 2% w/v concentrations of carrageenan were used.

FTIR measurements were carried out on a Digilab FTS60, operating at 4-cm^{-1} resolution with a TGS detector; 500 interferograms were coadded before Fourier transformation, and triangular apodisation was employed. Spectra were run at 5 K intervals from 298 to 353 K and then reduced in 5 K steps back down to 298 K. A modified Specac VT unit coupled to an automated temperature controller (Control and Readout Model 452) was used, allowing the cell temperature to be controlled from the console of the spectrometer. A 20-min temperature equilibration delay when the desired temperature had been reached was used, and the temperature of the cell was checked before and after every measurement.

The samples were run in a transmission cell with ZnSe windows and a 25-μm spacer. Single-beam background water spectra were recorded first at the specified temperatures. To avoid gelation problems when loading the carrageenan samples into the cell, the hot samples were injected into a preheated cell at 353 K and then allowed to cool to the minimum temperature used. The spectra obtained were baseline corrected by using a multipoint fitting routine. FSD was carried out by using methods described by Cameron and Moffat[10] and modified for use on the Digilab FTS60.

Spectra were recorded in D_2O at 298 K by using a Spectra-Tech continuously variable-angle attenuated total reflectance (ATR) attachment with a ZnSe crystal (45°, 50- × 20- × 3-mm parallelogram). The angle of incidence was set at 45°. The spectra were run at 4-cm^{-1} resolution, and 256 scans were coadded. The

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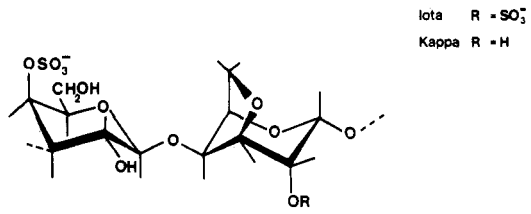

Figure 1. Repeat unit of ι- and κ-carrageenans.

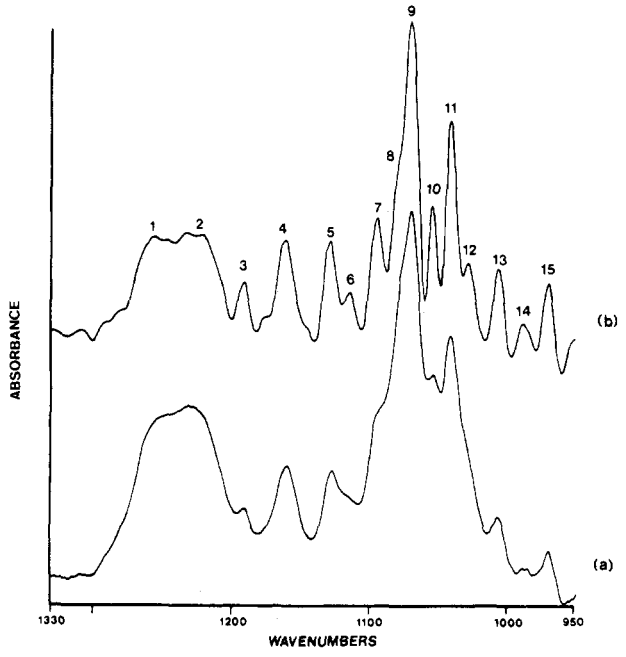

Figure 2. FTIR spectra of K^+ κ-carrageenan at 298 K, (b) deconvoluted and (a) nondeconvoluted.

gel samples were applied cold to the ATR crystal, and the mounting plate was screwed down to ensure even coverage. The empty cell was used as the background and the spectrum of D_2O digitally subtracted from the gel spectra.

Optical rotation studies were carried out on a 1% (w/v) κ-carrageenan sample in 0.67 M KCl (filtered hot through a 0.22-μm filter). The measurements were made at 405 nm on a JASCO DIP-360 digital polarimeter. A 100-mm VT cell and a 15-min temperature equilibration time were used and measurements taken at 5-K intervals from 299 to 351 K.

Results and Discussion

At the concentration (2% w/v) used in these experiments, Na^+, K^+, Rb^+, and Cs^+ ι-carrageenan were gels at room temperature (298 K), as were K^+, Rb^+, and Cs^+ κ-carrageenan, whereas Na^+ κ-carrageenan was a sol. All the gelling ion forms of κ-carrageenan gave similar spectra at 298 K in the region 1330–950 cm^{-1}; that for the K^+ form is shown in Figure 2a. FSD was used to improve peak resolution, and the result is shown in Figure 2b. The FSD process used relies on the input of a peak half-width and a line narrowing factor (*k* value). A Lorentzian line shape is assumed. A 15-cm^{-1} half-width and a *k* value of 1.5 were used; however, all the peaks in the region 1330–950 cm^{-1} do not have the same half-width, so the application of this blanket deconvolution may not be valid for all bands, but comparison of the spectra showed no peaks in the deconvoluted spectra that were not present as peaks or shoulders in the nondeconvoluted spectra. Hereafter all spectra referred to will be deconvoluted.

In the spectrum of K^+ κ-carrageenan (Figure 2b), 15 major bands between 1330 and 950 cm^{-1} are resolved; the results are summarized in Table I. Precise assignment of the peaks in this region is difficult, as most of the vibrations arise from highly coupled C–O, C–OH, and S–O modes; however, some assignments have been made previously.[9] Peaks 1 and 2 have been assigned to S–O asymmetric stretch, peak 7 to S–O symmetric stretch, peak 9 to a combination of C–O and C–OH modes, and peak 8 to C–OH modes. The spectra of κ-carrageenans in D_2O at 298 K were also obtained in order to further identify modes with a high C–OH contribution. In previous work,[9] D_2O studies were limited to the region 1100–900 cm^{-1} due to interference above 1100 cm^{-1} from D_2O. However, the use of ATR and digital subtraction allowed the removal of the interfering bands and extended the observable region to 1170 cm^{-1} so that the effects of deuterium exchange on peak 7, the peak believed to arise from S–O symmetric stretch, could be studied. The spectra of K^+ κ-carrageenan in D_2O and H_2O are shown in parts a and b of Figure 3, respectively. Peaks 8, 13, and 14 are lost and peaks 4,5, and 6 are reduced in intensity and/or shifted, indicating a contribution from C–OH modes. Peaks 7, 9, 10, 11, 12, and 15, however, are unaffected. These peaks may have

Table I
Comparison of Peak Positions for K^+ ι- and K^+ κ-Carrageenans in H_2O and D_2O

	frequency of absorption maxima, cm^{-1}			
	in H_2O		in D_2O	
peak	κ	ι	κ	ι
1	1256	1254		
2	1225	1222		
3	1190	1187		
4	1160	1154	1164	1168
5	1127	1125	1133	1038
6	1113	1116	1108	1108
7	1094	1098	1096	1099
8	1076	1083[a]		
9	1069	1072	1072	1072
10	1053	1055	1058	1055
11	1040	1040	1044	1043
12	1027	1028	1031	1029
13	1006	1003		1005
14	988	989		992
15	969	965	968	964

[a] Appears above gel melting temperature.

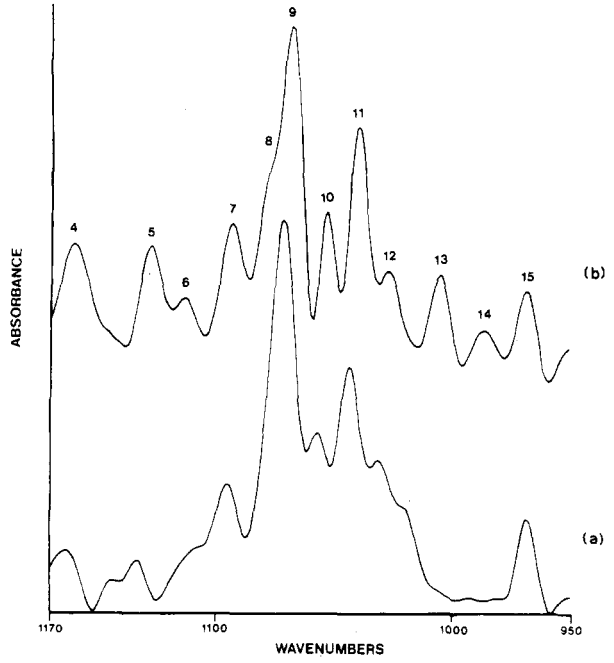

Figure 3. FTIR spectra of K^+ κ-carrageenan in (a) D_2O and (b) H_2O at 298 K.

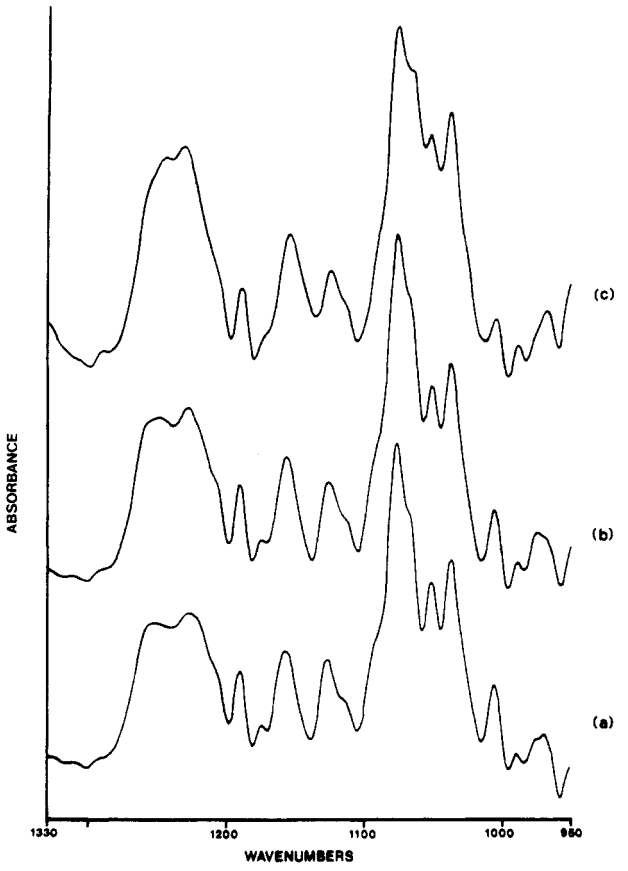

Figure 4. FTIR spectra of Na^+ κ-carrageenan at (a) 303 K, (b) 318 K, and (c) 353 K.

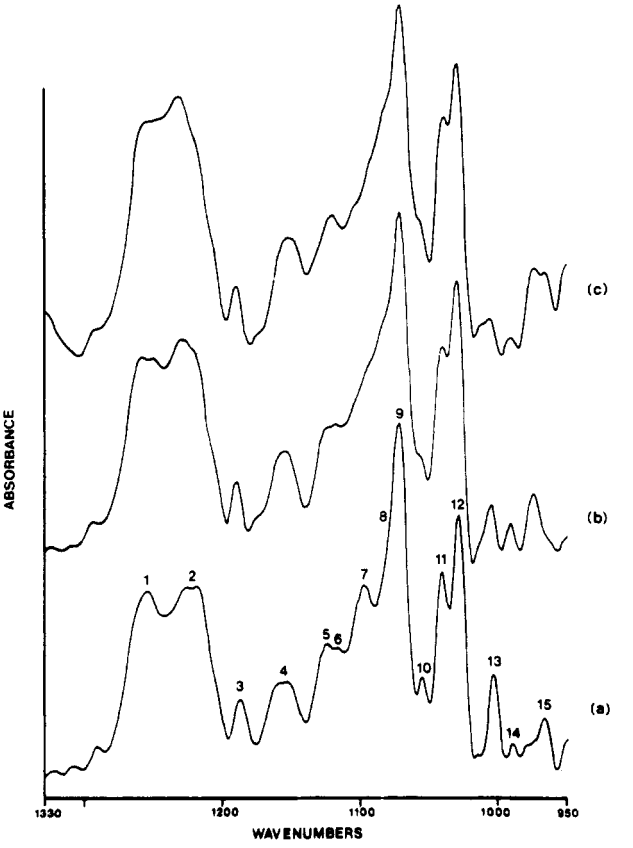

Figure 5. FTIR spectra of K^+ ι-carrageenan at (a) 303 K, (b) 318 K, and (c) 353 K.

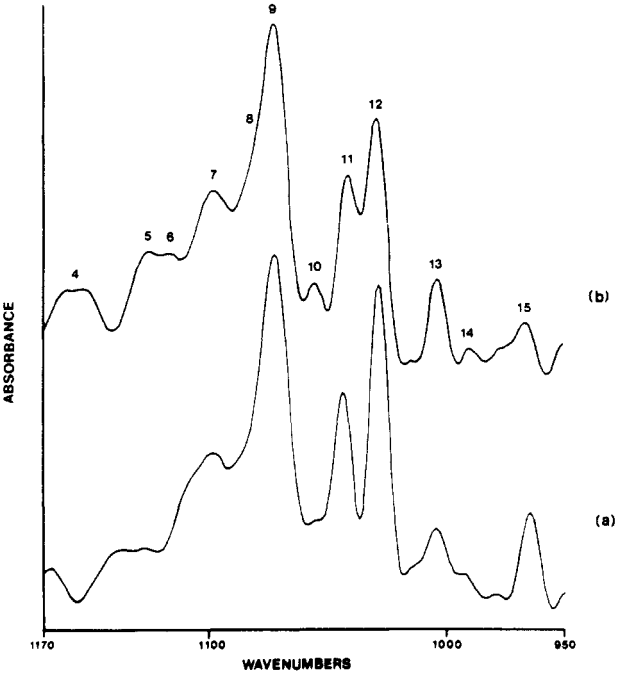

Figure 6. FTIR spectra of K^+ ι-carrageenan in (a) D_2O and (b) H_2O at 298 K.

little or no contribution from C–OH modes, but the observation of no shift after deuteration is not a positive identification of a non-C–OH mode since it is known that such modes may shift to higher or lower frequency or remain unchanged in certain circumstances.[13-15] The room-temperature spectrum of Na^+ κ-carrageenan is shown in Figure 4a. The main differences between the 298 K spectrum of a sol (Na^+ form) and a gel (K^+, Rb^+, Cs^+ forms), for κ-carrageenan, are the absence of peak 12, the reduction of peaks 6, 7, and 9 to shoulders, and the more intense peak 8. The spectrum of K^+ ι-carrageenan, at 298 K, is displayed in Figure 5a and shows, like κ-carrageenan, 15 peaks. However, all ion forms including Na^+ produce similar spectra. Table I shows a comparison between the peaks for K^+ ι-carrageenan and K^+ κ-carrageenan. Generally those for ι-carrageenan appear at slightly different wavenumber than those for the corresponding κ-carrageenan. This is not surprising since the extra sulfate per residue of the ι-carrageenan leads to a change in the coupling of the vibrations. However, the spectra are sufficiently similar so that the assignments made for κ-carrageenan apply to ι-carrageenan as well. K^+ ι-carrageenan in D_2O and H_2O is displayed in parts a and b of Figure 6, respectively, and shows a reduction in intensity for peaks 5, 6, 10, and 13 and a shift for peak 4 and 14 compared to the spectrum in H_2O. Peaks 9, 11, 12, and 15 remain unchanged as does peak 7.

A comparison of peak intensities between K^+ κ-carrageenan and K^+ κ-carrageenan was also made. The most intense peak in each spectrum was used as a reference (peak 9 in both cases), and all others were ratioed to that peak. The results are shown in Table II. Most of the main peaks in the spectra (excluding peaks 6, 14, and 15 which are of low intensity and difficult to measure) have similar relative intensities, apart from peaks 1, 2, 3, 7, and 12. Peaks 1 and 2, the S–O asymmetric stretch, are roughly doubled in relative intensity in ι-carrageenan compared to κ-carrageenan. This is as expected due to the two sulfate groups per repeat unit of ι-carrageenan compared to one in κ-carrageenan. The reasons for the differences for peaks 3, 7, and 12 will be discussed later. In the variable-temperature study, spectra were run at 5-K intervals from 298 to 353 K and back down to 298 K. In the interests of clarity, only three temperatures (from the heating cycle)

Table II
Comparison of Internally Ratioed Peaks in K^+ κ- and K^+ ι-Carrageenan at 298 K

	K^+ κ in H_2O		K^+ ι in H_2O	
peak	freq of absorptn max, cm^{-1}	ratio	freq of absorptn max, cm^{-1}	ratio
1	1256	0.27	1254	0.52
2	1231	0.29	1226	0.53
3	1189	0.11	1187	0.21
4	1159	0.26	1156	0.25
5	1127	0.25	1125	0.36
6	1112	0.09	1116	0.35
7	1093	0.34	1097	0.54
8	1076	0.55	1083	0.58
9	1068	1.00[a]	1071	1.00*
10	1052	0.36	1054	0.27
11	1039	0.67	1040	0.57
12	1026	0.18	1028	0.74
13	1005	0.17	1003	0.27
14	987	0.02	989	0.08
15	968	0.11	965	0.15

[a] Internal reference peak.

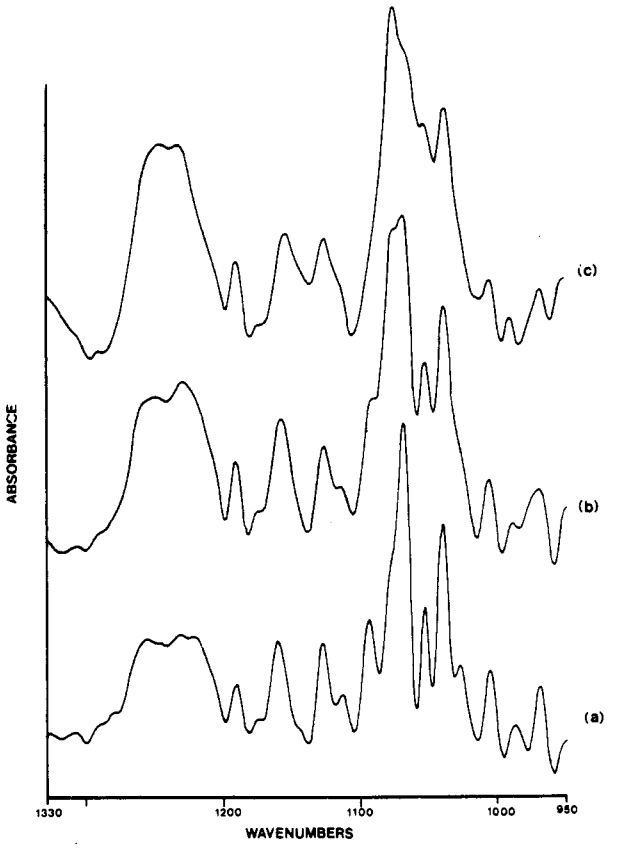

Figure 7. FTIR spectra of K^+ κ-carrageenan at (a) 303 K, (b) 318 K, and (c) 353 K.

are illustrated; 303, 318, and 353 K corresponding to (in gelling ion forms) the gel state, approximate gel–sol transition temperature, and the sol state. The spectra for Na^+ and K^+ κ-carrageenan are shown in Figures 4 and 7, respectively. The series of spectra for the K^+ form show that, as the temperature is increased, peak 12 is lost, peaks 6, 7, and 9 become shoulders, and peak 8 undergoes a large increase in intensity. Generally the peaks are broader at higher temperatures. The Na^+ κ form does not show the changes observed in other ion forms, only a general broadening of the lines at higher temperatures. It can be seen that the high-temperature spectra of K^+ κ is almost identical with that of the room-temperature Na^+ form. This might be expected as the Na^+ form at room temperature is a sol and is likely to be in the random coil conformation, as is the K^+ form at high temperatures. The structure apparent in the 298 K spectra for the gelling ion forms must result from helix formation. Aggregation is unlikely to affect the spectra since it has been shown that the spectra of polysaccharides tend to be sensitive to shorter range order.[16]

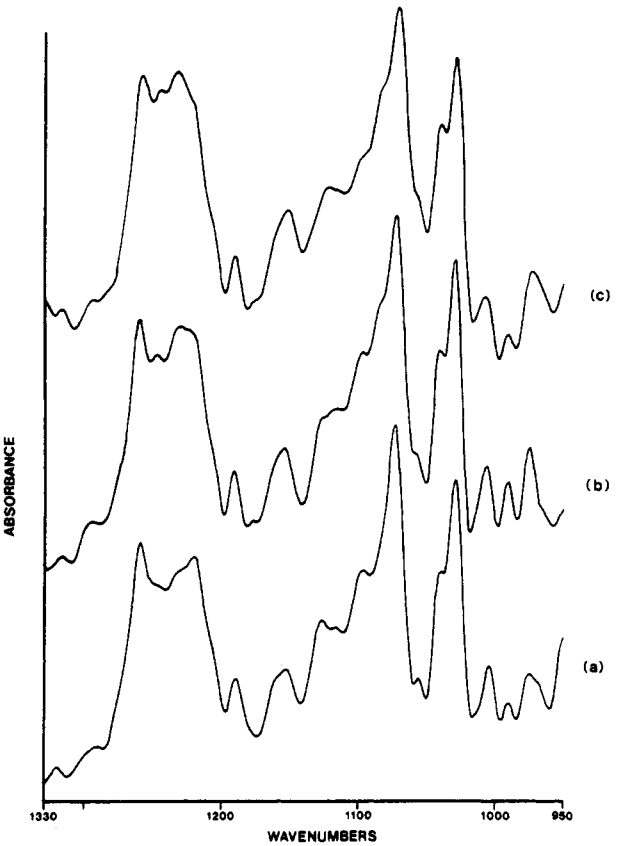

Figure 8. FTIR spectra of Na^+ ι-carrageenan at (a) 303 K, (b) 318 K, and (c) 353 K.

The other ion forms of κ-carrageenan (Rb^+ and Cs^+) show identical changes to the K^+ form, the only differences arising in the temperature at which the changes take place. The high-temperature spectra for all the ion forms of κ-carrageenan are very similar.

The variable-temperature spectra for Na^+ and K^+ ι-carrageenans are shown in Figures 8 and 5, respectively. The changes that occur in both sets of spectra are similar to each other and involve the apparent loss of peak 7 and growth of peak 8. All the ion forms of ι-carrageenan show this apparent change with the intensity of peak 7 following the trend $Na^+ < K^+ < Rb^+ \simeq Cs^+$. Again the high-temperature spectra of all the ion forms are very similar.

Careful study of the VT spectra, for the gelling ion forms of both ι- and κ-carrageenan, shows the major change on going from gel to sol to be the growth of peak 8, although this effect is not so marked for the ι-carrageenans. The growth of peak 8 causes the valley between peaks 7 and 9 to become filled in, leading to the apparent loss of peak 7.

In previous work,[9] attention was focused on peak 7 which was seen in the K^+ and Cs^+ but not the Na^+ ion forms of ι- and κ-carrageenan. The fact that Na^+ ι-carrageenan exhibited no peak 7 was a significant result in that it was a gel under the conditions of the experiment. This meant that the presence of peak 7 could not be correlated to gelation. Therefore, the conclusion was that peak 7 was associated with ion binding and was only seen in those carrageenans for which the NMR results indicated ion

interaction. The appearance of peak 7 in the IR, it was argued, was due to ion binding perturbing the symmetry of the sulfate group, resulting in the weakly allowed symmetric stretch becoming more allowed and consequently more intense. However, the earlier results were obtained without the benefit of FSD. In fact, FSD and improved data handling shows that peak 7 is present in Na^+ ι-carrageenan, thus invalidating the previous argument. Furthermore, peak 7 can be seen as a shoulder in the deconvoluted spectra in all forms at high temperature. Therefore, the presence of peak 7 is not related to ion binding since NMR shows that this does not occur in any high-temperature form. As peak 7 is apparently unaffected by ion binding, it throws doubt on the assignment of the S–O symmetric stretch.

Recently Malfait et al.[17] reported a Raman study of Na^+ κ-carrageenan and some related compounds where they attempt to identify the S–O symmetric stretch which is intense in the Raman. Malfait et al. report two very strong bands at 1086 and 1038 cm^{-1}. They assign the band at 1038 cm^{-1} to the S–O symmetric stretch and state that deuteration does not decrease the intensity of this band as confirmation. However, examination of their table of band frequencies and intensities for solutions in D_2O shows no 1038 cm^{-1} band present for Na^+ κ-carrageenan, although the band at 1086 cm^{-1} is still relatively intense. We suggest therefore that the band at 1086 cm^{-1} is a more suitable candidate for the S–O symmetric stretch and not the 1038 cm^{-1} band as Malfait et al. suggest. The FTIR spectrum of Na^+ κ-carrageenan at 298 K shows a weak shoulder at 1092 cm^{-1}, peak 7 having been swamped by peak 8. In order to compare peaks, not shoulders, we can consider K^+ κ-carrageenan which has peak 7 at 1093 cm^{-1}. The Raman spectra[17] were run at 5-cm^{-1} resolution and the FTIR at 4 cm^{-1}; the FTIR and Raman peaks, although apparently 7-cm^{-1} apart, could thus arise from the same vibrational mode.

Consideration of peak intensities can also be used to try and confirm the assignment of peak 7. ι-Carrageenan has an extra sulfate per repeat unit, so any sulfate bands in the carrageenan spectrum should be doubled in the case of ι-carrageenan compared to κ-carrageenan. As stated earlier, peaks 3, 7, and 12 are all increased in ι-carrageenan to κ-carrageenan making them candidates for the S–O symmetric stretch. The increases in relative intensity are 2 for peak 3, 1.6 for peak 7, and 4 for peak 12. Cabassi et al.[18] give Raman frequencies for the S–O symmetric stretch in some sulfated carbohydrates which range from 1070 to 1040 cm^{-1}. These results suggest that peak 3 (1190 cm^{-1}), although doubled in relative intensity in ι-carrageenan, is too high in frequency to be considered as the S–O symmetric stretch. This leaves peaks 7 and 12. Peak 12 at 1028 cm^{-1} is rather low in frequency to be considered as the symmetric stretch. Cabassi et al. report that the lower frequency S–O symmetric stretches occur in sulfamino compounds and most of the other carbohydrate S–O stretches occur at frequencies greater than 1060 cm^{-1}. The relative intensity increase for peak 12 may also be too large for it to be considered. This leaves peak 7 as the most suitable candidate for the S–O symmetric stretch. We must, however, point out that as yet there is no definite evidence to prove that the assignment of peak 7 is correct.

By varying gel concentration or ion concentration, it is possible to gel any carrageenan ion form. If Na^+ κ-carrageenan is therefore made to gel by adding excess salt, the relationship between peak 8 and gelation can be tested. A Na^+ κ gel (3% w/v in 0.5 M NaCl) was run, and the VT spectra indicated that peak 7 is present, although much weaker than in the other gelling ion forms at 298 K. As the temperature is increased, peak 8 grows and peak 7 apparently disappears. Thus, we can confirm that peak 8 is reduced in intensity and peak 7 is observed when gelation occurs.

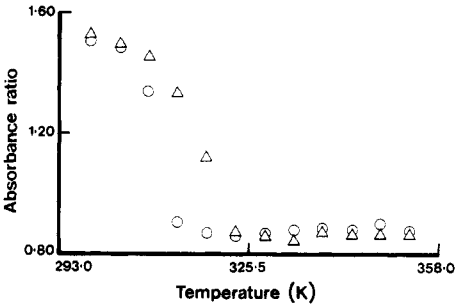

Figure 9. Absorbance ratio versus temperature plot for Rb^+ κ-carrageenan: (△) temperature increasing and (○) temperature decreasing.

Table III
Transition Temperature Midpoints for Different Ion Forms of κ-Carrageenan

ion	T_u, K	T_d, K
Na^+		
K^+	308	304
Rb^+	314	308
Cs^+	308	303
K^+ (0.05 M KCl)	319	314
K^+ (0.1 M KCl)	328	324
K^+ (0.1 M KI)	336	332
K^+ (0.1 M NaCl)	313	308

If the observed changes in the spectra are not related to ion binding, then they must arise from conformational effects. It is clear, however, that even though direct ion binding is not observed by FTIR the spectra are certainly affected by the differing counterions so that a VT FTIR study can still provide a great deal of information. Carrageenans are charged polysaccharides with a helical conformation in the gel state. Helix formation produces an increased charge density around the polymer[19] which is stabilized by the presence of the counterion. An increase in the ionic strength of the solvent will thus result in increased stabilization of the helix, producing a gel with a higher melting temperature. Further studies were therefore carried out with varying ion concentration.

K^+ κ-carrageenans (2% w/v) in 0.05 and 0.1 M KCl were compared. The two sets of spectra and those for K^+ κ in H_2O show no differences in the position of the peaks; however, peak 8 appears slightly weaker in intensity at the higher ion concentrations. It is possible to quantify the changes that occur for peak 8 by measuring the intensity ratio at 1076 to 1068 cm^{-1} (peak 9). The result, for Rb^+ κ, temperature increasing and decreasing, is shown in Figure 9. A hysteresis curve is seen similar to those observed in optical rotation measurements. From the curve it is possible to define a transition temperature midpoint for the heating cycle (the midpoint between the end and start of the flat portions of the heating and cooling curves), T_u, and one for the cooling cycle, T_d. By defining transition temperatures, a table can be drawn up which displays T_u and T_d for all the ion forms of κ-carrageenan. Table III shows the results. The Na^+ form of κ-carrageenan at 2% w/v shows no transition; the gelling ion forms, however, show transitions with hysteresis, the higher ion concentration gels having higher T_u values. As they are stronger gels with higher melting temperatures, we suggest the transitions observed must relate to the gel melting process. Gel melting temperatures usually correspond to the tem-

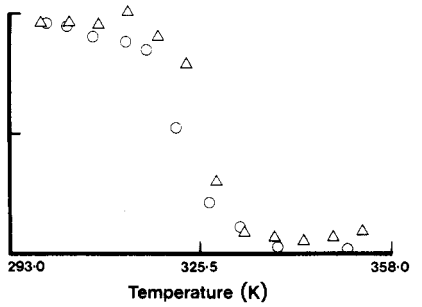

Figure 10. Comparison between VT FTIR (△) and optical rotation (○) measurements for K^+ κ-carrageenan. For this experiment, a 1% (w/v) concentration of carrageenan was used. One unit on Y axis = 0.55 deg for optical rotation and 0.4 absorbance ratio for VT FTIR.

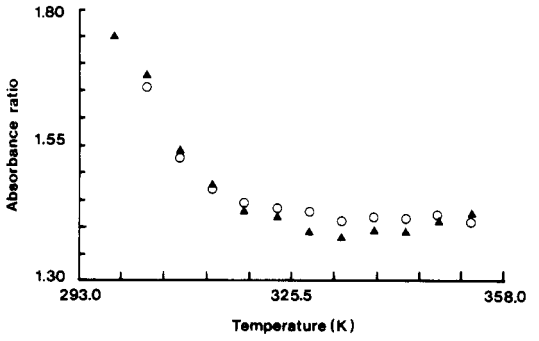

Figure 11. Absorbance ratio versus temperature plot for K^+ ι-carrageenan: (▲) temperature increasing and (○) temperature decreasing.

perature at which the helix-to-coil transition occurs. These results therefore indicate that FTIR ratio measurements may be used to monitor the helix-to-coil transition in the κ-carrageenan system. To test this, a K^+ κ-carrageenan sample (1% w/v in 0.67 M KCl) was studied by optical rotation and FTIR. The results are displayed in Figure 10. These curves gave T_u values of 323 K from FTIR and 327 K from optical rotation, indicating that FTIR ratio measurements do in fact correspond to the helix-to-coil transition in the κ-carrageenan system.

In general the changes that occurred, especially for peaks 7 and 8, for the ι-carrageenans were less pronounced than for the κ-carrageenans; however, ratio measurements (peak 9/peak 8) can also be carried out on ι-carrageenans; the results for K^+ ι-carrageenan are shown in Figure 11. The initial ratio is similar to that in the K^+ κ-carrageenan; however, the ratio never falls below 1, indicating that peak 8 never becomes more intense than peak 9, unlike in the κ-carrageenan spectra. No hysteresis occurs in the ι-carrageenan spectra.

Investigation into the effect of iodide was also carried out. A K^+ κ-carrageenan gel was prepared in 0.1 M KI. The spectra show similar changes to those for the K^+ form in 0.1 M KCl. However, ratio measurements indicate that the sample in KI has higher T_u and T_d values than in KCl.

Norton et al.[20] studied the effect of a lyotropic series of anions on κ-carrageenan and concluded that the ordered conformation of κ-carrageenan was stabilized by anions of high Hofmeister number such as iodide and thiocyanate. Previous workers have also suggested a possible interaction between iodide and κ-carrageenan, more specifically that iodide prevents aggregation of the polysaccharide polymer.[6] These observations are consistent with our IR results if we envisage a model with ion binding occurring only on aggregation of the polymer helicies. We have shown that IR spectra are not sensitive to aggregation,[16] thus, we only observe the stabilizing effect of iodide on the polymer helix and the resulting change in transition temperature. NMR, however, monitors ion binding and will be sensitive to aggregation not helix formation, due to ion binding only occurring in this state, and when iodide is present, a reduced chemical shift effect for ^{39}K is observed,[7] indicating that iodide does in fact reduce the level of aggregation.

We therefore find that IR and NMR are complementary techniques, IR being sensitive to the helix-to-coil transition and NMR sensitive to ion binding which occurs in the aggregated state after helix formation.

Conclusion

The results obtained in this study show that the major changes occurring in the IR spectra of ι- and κ-carrageenans with temperature are a result of conformational changes taking place during the gel-to-sol transition and not a result of ion binding effects as reported previously. The conformational changes give rise to an increase in peak 8, causing the apparent loss of peak 7. The assignment of the S–O symmetric stretch in the IR is still open to question, although peak 7 still appears to be the best candidate. The most interesting information comes from other vibrations which arise from the polymer backbone. By measuring these changes using ratios, it is possible to follow the helix-to-coil transition in κ-carrageenans. Whereas most optical rotation work needs long path lengths (10 cm) and dilute solutions (1%) to obtain good results, FTIR can be used with higher concentrations where optical rotation was previously impractical.

One of the most interesting features of the work is the confirmation of the highly specific effects of counterions on polymer structure. This is particularly noticeable in the κ-carrangeenans where K^+ and Rb^+ have very strong effects on structure, but structural effects with Na^+ can only be induced at high salt concentrations. It is tempting to argue that some specific ion binding mechanism is involved, and indeed NMR results do show that K^+ and Rb^+ will bind to κ-carrageenans. However, there is no evidence of Na^+ binding at any concentration and the addition of iodide decreases the K^+ binding observed by NMR but makes no significant difference to the changes observed in the IR spectra. In order to account for such phenomenon and the effects of counterions in the ι-carrageenans, a two-stage model of gelation is proposed, consistent with previous deductions from NMR results.[7] In this, the charge density at the polymer solvent interface is assumed to cause locally high concentrations of counterions;[21] these in turn modify the local solvent structure and thus solvent quality. When the change in the solvent structure is such that solvent–polymer interactions become unfavorable, coil–helix transitions occur. The point at which the transitions occur will thus depend upon the nature of the counterion and its solvent modifying properties, but will also depend on the presence of other variables such as temperature, counterion concentration, polymer concentration, and the presence of other solutes.

The second stage of the gelation process is the aggregation of the polymers to form junction zones. It is at this point that specific ion binding has a role to play. If the ion can be accommodated easily into the aggregate structure, strong aggregates will be formed. If, however, the inclusion of the ions into the structure is not energetically favorable or aggregation inhibitors are present, then weak structures will be formed.

The specificity of K^+ and Rb^+ arises from their efficiacy in both stages of gelation. Their solvent-mediated nonspecific interactions with the polymer readily cause coil–helix transitions which then form strong aggregates because of the highly specific interactions of these ions.

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Registry No. K^+ κ-carrageenan, 62362-84-9; Na^+ κ-carrageenan, 37359-47-0; K^+ ι-carrageenan, 62362-83-8; Na^+ ι-carrageenan, 60616-95-7; Rb^+ κ-carrageenan, 116977-52-7.

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Preliminary Kinetic Investigation on Syndiotactic Polymerization of Styrene

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ABSTRACT: This paper reports preliminary kinetic data on syndiotactic polymerization of styrene, in the presence of $Ti(OC_4H_9)_4$–methylalumoxane. The temperature coefficient of the kinetic rate constant is 8 kcal/mol. The distribution of the molecular weights is bimodal. The polymerization rate increases more than linearly with increasing monomer concentration.

Introduction

As reported in the literature,[1-3] syndiotactic polymerization of styrene can be promoted by homogeneous catalytic systems consisting of methylalumoxane (MAO) and soluble compounds of titanium or zirconium, such as tetrabenzyltitanium, tetrabenzylzirconium, cyclopentadienyltitanium trichloride, titanium(IV) alkoxides, titanium(III) acetylacetonate, etc. In this paper we report the results of a preliminary kinetic investigation concerning the title polymerization in the presence of the catalytic system titanium tetrabutoxide (TTB)–MAO in toluene. In addition, some results obtained in the presence of other syndiotactic specific catalytic systems are reported for comparison.

Experimental Section

TTB was purchased from Aldrich. MAO was prepared as previously reported[4] by reaction of $Al(CH_3)_3$ and $CuSO_4 \cdot 5H_2O$ in toluene; the solvent and the unreacted $Al(CH_3)_3$ were removed by distillation under reduced pressure and the oligomeric MAO was isolated. Toluene was distilled under nitrogen atmosphere after refluxing over potassium for 48 h. Styrene was distilled in vacuo over CaH_2 before using.

All polymerization runs were carried out by introducing sequentially the proper amounts of toluene, MAO, and styrene in 100-mL glass flasks. The flasks were immersed in an oscillating thermostatic bath and the polymerizations were initiated by injecting the required amount of TTB. Polymerization runs were stopped by injecting methanol and the polymers were coagulated with acidified methanol, recovered by filtration, washed with fresh methanol, and dried under vacuum. Polymerization conditions and results are reported in Tables I–VI. Polymer samples were fractionated by exhaustive extraction with boiling acetone. Molecular weights of the raw polymers or, where specified, of the extraction residues, were determined by GPC in 1,2-dichlorobenzene at 135 °C by using a Waters 150-C apparatus.

Table I
Yields and Molecular Weights of Polystyrenes Obtained at Increasing Times[a]

run	temp, °C	time, min	yield, mg	$\bar{M}_w$	$\bar{M}_n$
1	50	20	42	224000	11000
2	50	30	56	251000	13000
3	50	40	95	281000	16000
4	50	60	143	308000	12000
5	50	80	148	344000	29000
6	87	15	115	76000	16000
7	87	30	255	75000	8000
8	87	45	340	78000	15000
9	87	60	543	75000	8000

[a] Polymerization conditions: toluene, 25 mL; styrene, 15 mL; MAO, 4.0 mmol (based on Al); TTB, 4.5×10^{-5} mol.

Results and Discussion

In Table I (runs 1–5) are reported the amounts of polymer produced in a series of low-conversion polymerization runs performed at 50 °C. Under these conditions, the yield of polymer increases linearly with increasing reaction time, showing that the activity of the catalyst is

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