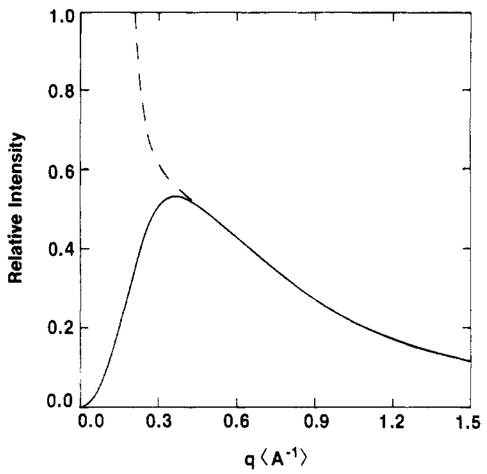

Figure 11. Scattering intensities of Gaussian chains with N = 500, b = 2.7 Å, n_{11} = 33 Å, n_{12} = 6.6 Å, and n_2 = 5.7 Å: (solid line) alternating blocks; (dashed line) random blocks.

of the single-diamine-cured epoxies, i.e., Figures 2 and 3 for D-400- and D-230-cured epoxies, respectively. The initial slope, after neglecting a few data points around the beam stop, is rather close to what is depicted with the fact that the molecular weight of an average epoxy network approaches infinity. The approximation scheme reported earlier by Wu and Bauer[2] also provided a scattering curve with zero slope near q = 0.

Substituting eq 12, 14, and 15 into eq 9 and using the same values for n_{11}, n_{12}, n_2, and b as before in the regular block case gives the resultant curve in Figure 11. No scattering peak can be observed in such a randomly alternating case. This finding is consistent with the diblock results reported earlier by others[4] for the case of high polydispersity.

In summation, the results of both the rigid-rod and the flexible-coil calculations suggest that the network structure of the mixed-diamine-cured epoxies (D-2000/D-400 and D-2000/D-230) could be of the $(-A_1-B-A_2-B-)$ type along the amine linkages. The second peaks at q = 0.35 of both D2K2H411 and D2K4H411 compositions are originated from the correlation of the labeled segments along the epoxy linkages; hence their position is not expected to depend on the arrangement of the amines within the network.

The origination of this regular chemical sequence is rather puzzling. An explanation based on curing kinetics is currently under investigation. If the newtork structure of the epoxies studied herein is indeed kinetics-controlled, the existence of the regularly alternating block will likely be sensitive to the curing conditions.

Conclusions

A pronounced scattering peak has been observed for the epoxies cured with the diamine mixtures containing two diamines with the same repeat unit but different molecular weights. The peak is located at a q value smaller than those observed in any of the single-diamine-cured epoxies. This observation suggests that the two diamines and the epoxy monomer form a regularly alternating lattice. The chemical periodicity of this lattice contains two epoxy monomers, one long-chain diamine and one short-chain diamine.

The linear-chain analogue of the lattice proposed above is of the $(-A_1-B-A_2-B-)_N$ type. The scattering intensity of this regularly alternating chain has been calculated on the basis of a single rigid rod as well as a Gaussian chain. The theoretical results indicate that such an alternating block arrangement will result in a main peak located at a q smaller than that from either $(-A_1-B-)_{2N}$ or $(-A_2-B-)_{2N}$ chains.

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^{39}K and ^{87}Rb NMR Study of Chemical Shift Effects in ι- and κ-Carrageenan Gels

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ABSTRACT: ^{39}K and ^{87}Rb NMR spectra of specific ion forms of ι- and κ-carrageenans in the presence of excess counterions are reported. Chemical shift effects are observed which are attributed to the effects of specific site binding. The effects of temperature, anion type, and urea on the spectra of the potassium form are reported, and it is concluded that the results are consistent with a model in which the primary mechanism for gelation is a change in the solvent property rather than ion binding.

Introduction

The role of metal cations in the gelation of carrageenans has been the subject of considerable interest.[1-5] NMR studies[4,5] have demonstrated that K^+, Rb^+, and Cs^+ can interact strongly with κ-carrageenan and that K^+ and Rb^+ show similar interactions with ι-carrageenan.[3] In the case of Cs^+ interacting with the κ form, strong chemical shift effects were observed,[5] which were interpreted in terms of specific site binding. We now report on a similar study of chemical shift effects using ^{39}K and ^{87}Rb NMR.

Previous work[3] with specific ion forms of ι-carrageenan (2.5% by weight) containing no added salt showed that when a solution of the Rb^+ or K^+ form had its temperature lowered to below the gelation temperature there was a marked apparent loss in signal intensity. For the Rb^+ and K^+ forms of κ-carrageenan[4] this apparent loss was total and no signal was observed. These results were interpreted in terms of changes in ion mobility occurring on gelation. However, no conclusion was made as to the origins of these changes in motional behavior. In order to further investigate these effects we have used different experimental conditions (0.5% polysaccharide and excess concentrations of counterions) that allow observations of a residual signal and chemical shifts.

Experimental Section

Pure ion forms of ι- and κ-carrageenans were prepared, and their purities were checked as described previously.[6,7] Samples were made by heating the appropriate weight of polysaccharide with a volume of salt solution for 2 h at approximately 80 °C in a PTFE-lined digestion vessel. The hot liquid sol was poured into flat-bottom NMR tubes and allowed to gel. Samples were stored for at least 24 h prior to NMR measurements being made.

NMR experiments were carried out with a Bruker CXP 300 NMR spectrometer operating at 13.9 MHz for ^{39}K and 98.1 MHz for ^{87}Rb. The probe used had a Dewared saddle coil arrangement that allowed accurate temperature control. Spectra were obtained with quadrature detection and appropriate phase routing with $\pi/2$ pulse lengths of 20 μs for ^{39}K and 12 μs for ^{87}Rb and spectral widths of 5 and 100 kHz for ^{39}K and ^{87}Rb, respectively. At least 10^4 scans were acquired for each ^{39}K spectrum while the ^{87}Rb spectrum was the result of 5×10^5 transients. The first few points of each free induction decay (FID) were distorted by acoustic ringing within the probe. These points were removed by left-shifting prior to Fourier transformation. Attempts to characterize the broad components of the ^{39}K line(s) were not successful even when the spectral width was increased and a pulse sequence was used that was designed to minimize the effects of ringing within the probe.[8]

Results and Discussion

The ^{39}K spectra of 0.1 mol dm^{-3} KCl solution in water and of 0.5% (by weight) κ-carrageenan gels containing 0.05, 0.1, and 0.2 mol dm^{-3} KCl are shown in Figure 1. Also shown is the spectrum of 2.5% ι-carrageenan gel with no added KCl solution. All spectra were obtained at 303 K. In the case of the three κ-carrageenan gel samples two peaks are clearly visible. One peak has a chemical shift almost identical with that of KCl solution and is sharp. The other is broad but narrows and shifts toward the sharp peak as the salt concentration increases. The spectrum of the ι form is a single broad line showing only a small shift (~1 ppm) from the position of KCl solution.

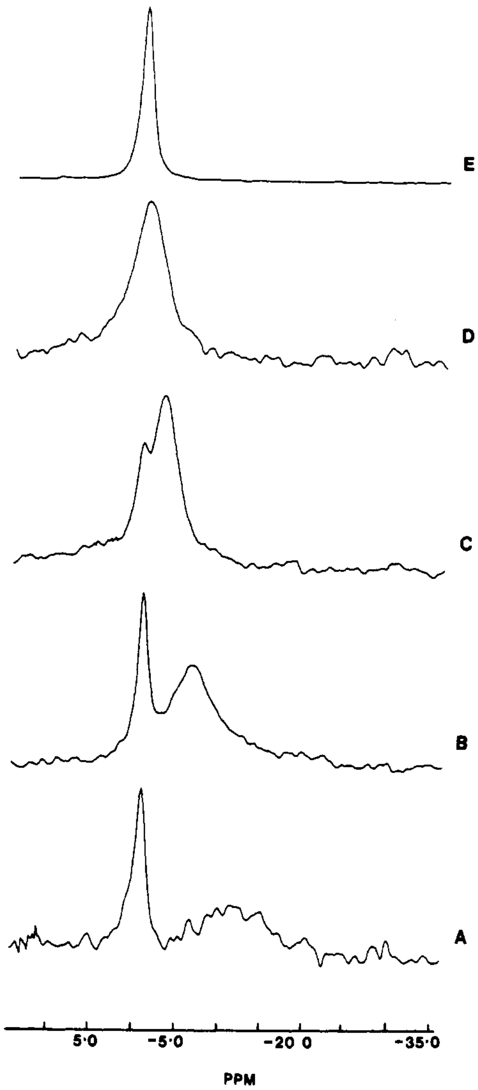

Figure 1. ^{39}K spectra of carrageenans. A, B, and C are the spectra of 0.5% κ-carrageenan solutions containing 0.05, 0.1, and 0.2 mol dm^{-3} added KCl, respectively. D is the spectrum of 2.5% ι-carrageenan with no added salt and E is the spectrum of 0.1 mol dm^{-3} KCl. The spectra were all obtained at 303 K.

When samples of the potassium κ-carrageenan gel were carefully blotted to remove the bulk of the synerised liquid the narrow resonance line decreased significantly in intensity while no change was observed in the position or intensity of the broad line. The narrow line therefore arises from synerised liquid. As the concentration of added salt increases, the chemically shifted line narrows and moves toward the unshifted line. These observations indicate, first, that exchange occurs between some chemically shifted species and free hydrated potassium ions and, second, that the rate of this exchange is greater than the chemical shift difference between the species. The free ions involved in this exchange are not those in the synerised liquid since removal of this liquid has no effect on the position or intensity of the broader line. Measurements of total signal intensity for the gel samples (at 303 K) indicate that it is less than would be expected if all the nuclei were being observed. The loss of signal intensity arises because some part of the spectrum is not observed under the conditions used here. This might result from the presence of broad components lost in the long probe ringdown and or components shifted outside the frequency range of the NMR experiment. Line-shape changes, under conditions of motional narrowing, occur when the spectral density at zero frequency is more intense than at the Larmor frequency (a phenomenon that may have a variety of origins[3,4]). Under these conditions the line shape is a narrow Lorentzian superimposed upon a broader one. The intensity of the latter is often lost.[4] Alternatively, if static quadrupolar interactions are present then the line shape is a triplet and the $\pm^3/_2 \leftrightarrow \pm^1/_2$ transitions are shifted and broadened and may not therefore be characterized. The origin of "signal loss" is revealed when rubidium κ-carrageenan is investigated. Previous work[3,4] has shown that this compound has a spectral behavior similar to that of the potassium ion form. ^{87}Rb has a much higher resonance frequency than ^{39}K and both probe ringdown problems and signal-to-noise ratios are improved. The spectrum of rubidium κ-carrageenan (Figure 2) clearly shows the presence of a broad component underlying the narrower components. This observation indicates that the condition of motional narrowing holds. Figure 2 shows that, as in the potassium form, two chemically shifted resonances are

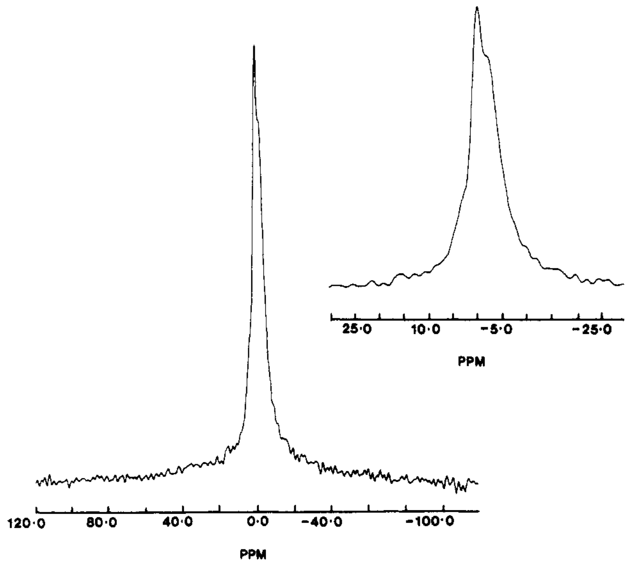

Figure 2. ^{87}Rb spectrum of 0.5% rubidium *κ*-carrageenan in 0.05 mol dm^{-3} RbCl solution. The insert shows an expansion of the central peak. The spectrum was obtained at 303 K.

observed but these are less clearly delineated because of the greater intrinsic width of the ^{87}Rb lines.

We have indicated elsewhere[4] that line broadening can arise either from translational diffusion occurring at an appropriate rate through anisotropic regions or by interactions such as chemical bonding localizing the ion at a specific site on the polymer. The process of specific site binding implies the formation of a true contact ion pair that perturbs the hydration shells. The translational diffusion process includes atmospheric condensation where a hydrated ion species is constrained to diffuse inside a certain volume surrounding the polyelectrolyte. Chemical binding would be expected to cause large NMR chemical shifts whereas the nonspecific interaction implied by diffusion would not. Hence it may be concluded that specific site binding does occur in potassium and rubidium *κ*-carrageenan gels. It is not possible to extract values for the chemical shift and population of the bound ions from the data; however, it is clear that the chemical shift must be large: extrapolation of data to the limit of zero excess counterion gives a limiting chemical shift, relative to ^{39}K ions in solution, of approximtely −21 ppm. This value represents the chemical shift in a 0.5% gel when the ions present are only sufficient to neutralize the polymer. Since the binding constant must be less than infinite it may be assumed that the chemical shift of the bound ions is greater than −21 ppm.

In contrast to the *κ*-carrageenan gels the binding in the *ι*-carrageenan gels is much weaker. The chemical shift in a 2.5% *ι*-carrageenan gel is only −1.2 ppm compared to −10 ppm in 0.5% *κ*-carrageenan gel containing 0.05 mol dm^{-3} KCl. The shifted line is also narrow. These effects must indicate that the degree of specific site binding in the *ι* form is very small compared to the *κ* form. These observations are consistent with those reported previously on the effects of carrageenans on ^{39}K signal intensity and width.[3,4]

In order to examine the relationship between molecular association and ion binding the effects of temperature and urea were examined. The effects of temperature on the spectra of the *κ* form are shown in Figure 3. Three regimes exist: a low-temperature regime where two distinct peaks are observed whose chemical shift difference is independent of temperature, an intermediate regime in which the peaks begin to merge and the apparent signal intensity increases, and a high-temperature regime in which only one line is observed and the apparent signal intensity is much enhanced. These three regions correspond to a stable gel, gel melting, and the sol state, respectively, and demonstrate that ion binding only occurs in the gel state. The experiments were repeated under identical conditions except that the solution also contained 4 mol dm^{-3} urea. Urea has a profound effect on gel rheology; it destabilizes the carrageenan helix, lowering the gel melting point and thus the shear modulus relative to urea-free systems.[11] In our current experiments, however, spectra identical with those obtained for the urea-free system were observed except that the gel-melting spectrum occurs at a lower temperature (328 as opposed to 338 K). Thus although urea changes gel rheology it only affects ion binding inasmuch as it changes the transition temperature. In this system, therefore, the gel rheology is independent of ion binding below the melting temperature. This indicates that for the systems studied here specific ion interactions are not the controlling factor in gel rheology or in gel melting temperatures.

When potassium fluoride was used to make up the *κ*-carrageenan solutions no significant spectral differences were observed when compared to solutions made with KCl. When potassium iodide was used a marked difference in spectral appearance from those with KCl and KF was observed (Figure 4). Other workers have suggested[12,13]

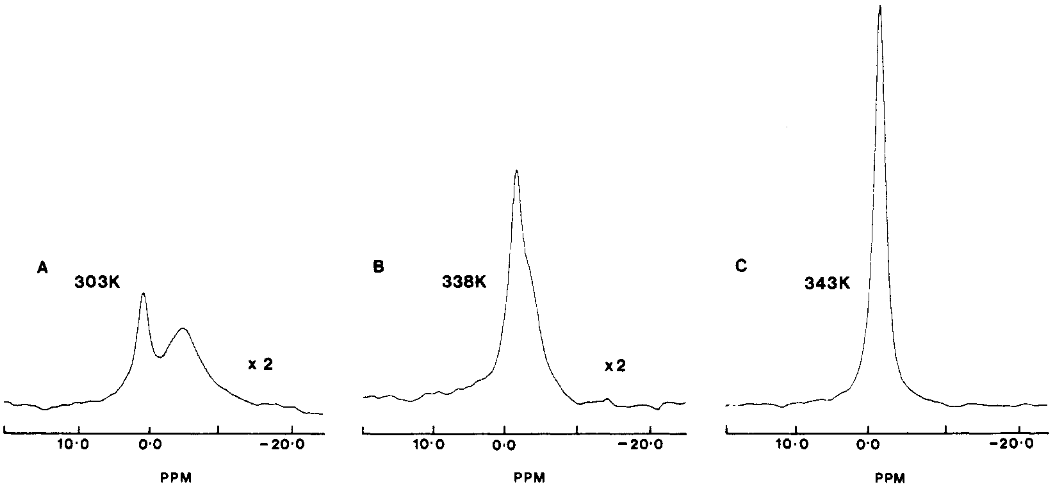

Figure 3. ^{39}K spectra of 0.5% *κ*-carrageenan containing 0.1 M KCl at different temperatures: (A) 303 K; (B) 338 K; (C) 343 K. Spectrum C is half-scale compared to A and B. All spectra are line broadened by 20 Hz.

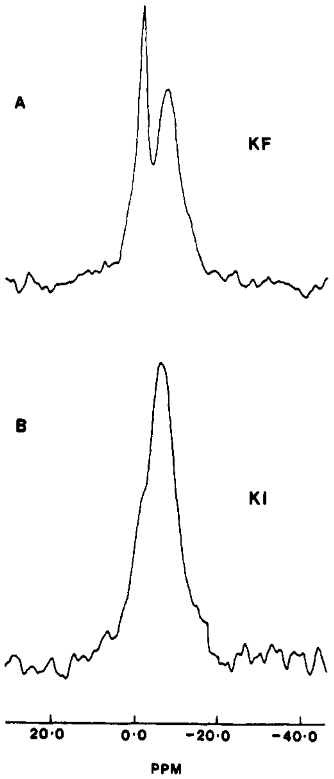

Figure 4. ^{39}K spectra of 0.5% κ-carrageenan with (A) 0.1 mol dm^{-3} KF and (B) 0.1 mol dm^{-3} KI. Both spectra were obtained at 303 K.

that there is an interaction between iodide ions and κ-carrageenan. Grasdalen and Smidsrod[12] have suggested that iodide may prevent aggregation of the polymers. This suggestion is consistent with our observations. The chemical shift of potassium is smaller in the presence of iodide, suggesting a smaller bound fraction of potassium ions. This would be consistent with a decrease in the level of aggregation since the effects of temperature variation on the spectra show that specific ion binding only occurs in the aggregated state below the sol/gel transition temperature.

Conclusions

The results obtained clearly show that specific site binding occurs in the potassium and rubidium forms of κ-carrageenan. This site binding is not, however, a necessary condition for gel formation since sodium and cesium ι-carrageenans gel but do not show site-specific interactions.[3] When urea is added to potassium κ-carrageenan gels the shear modulus of the gels is markedly decreased by destabilizing the helix but no effects on the site binding in the gel state are observed. Effects on ion binding are only observed when iodide is substituted for chloride in the solution. The iodide acts by preventing association of the ordered helical structures. Hence cation binding is probably associated with helix–helix association.

The driving force for gelation must therefore come from some interactions other than specific cation binding. The effects of urea,[11] of a lyotropic series of anions,[13] and of cations[3] are all consistent with a model in which changes in polymer solubility and conformation are induced by means of changes in the local solvent properties. At low concentrations charge effects are likely to concentrate cations close to the polymer[14] and generate sufficiently high local concentrations to affect solvent structure. Similar solvent-modifying effects have also been postulated for anions.[13] In addition urea is well-known for its ability to change water structure.[15] The process of gelation in carrageenans is therefore consistent with a model in which gelation occurs by the change of solvent from a good solvent to a poor solvent, an effect that may be brought about by varying, for example, temperature or salt concentration. When this change occurs the polymer attempts to phase separate. However, at the concentrations at which gelation occurs the polymer entanglement[3] impedes this phase separation and small phase-separated regions appear which form the junction zones of the gel. Cation binding may reflect a subsequent crystallization within the junction zones. Thus cation binding may occur on gelation but may not be essential for gelation.

Acknowledgment. We thank G. R. Chilvers for preparing the samples used in this study.

Registry No. ^{39}K, 14092-91-2; ^{87}Rb, 13982-13-3; ι-carrageenan, 9062-07-1; κ-carrageenan, 11114-20-8.

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