Carbohydrate Polymers 2 (1982) 270–272

SOME PHYSICAL PROPERTIES OF CARRAGEENAN IN SOLUTION AND GEL STATE

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The carrageenans are sulphated D-galactans from certain red algae and have alternating $\alpha(1\rightarrow3)$ and $\beta(1\rightarrow4)$ linked structures. A fraction named κ-carrageenan has the four-linked unit in the 3,6-anhydro form and a sulphate group on position 4 of the three-linked unit. It forms the strongest of the thermo-reversible gels given by different carrageenan fractions. The gel strength increases with increasing ionic strength and is enhanced by Cs^+, Rb^+ and K^+ ions, while Na^+, Li^+ and $N(CH_3)_4^+$ ions have comparatively little effect.

There is controversy regarding the gelling mechanism of carrageenan. According to Bayley (1955), Smidsrød (1980) and Smidrød *et al.* (1980) the junctions in the κ-carrageenan networks consist of cation-specific salt bridges between ordered chain segments. According to the first model of Rees and coworkers (McKinnon *et al.*, 1969) the junctions are double helices, whereas in the second (the domain model) (Rees, 1981), they are cation-mediated aggregates of double helices.

In this work, ^{133}Cs NMR was used to study the selective binding of monovalent ions to κ-carrageenan (Grasdalen & Smidsrød, 1981). Above the temperature at which the gel melts, the ^{133}Cs NMR line from the Cs salt of κ-carrageenan was typical of isotropic solutions with rapid molecular motion (Lindman & Forsén, 1976). Upon cooling, an abrupt change, both in line shape and line shift took place simultaneously with gelation, indicating changes in the mode of counter-ion binding. The changes were in full agreement with the theoretical predictions of Bull *et al.* (1979) for Cs^+ ions involved in site binding with a correlation time for bound ions greater than 10^{-8} s. Studies of competitive binding of the type shown in Fig. 1 showed selectivities consistent with *inter*molecular binding sites in the junction zones. It was estimated that a maximum of 30% of the sulphate groups contributed to the selective binding sites in 3% (w/v) Cs κ-carrageenate gels at 25°C. In these gels, most of the carrageenan chains were probably in an ordered (non-random coil) conformation.

Carbohydrate Polymers 0144-8617/82/0002-0270/$02.75 –

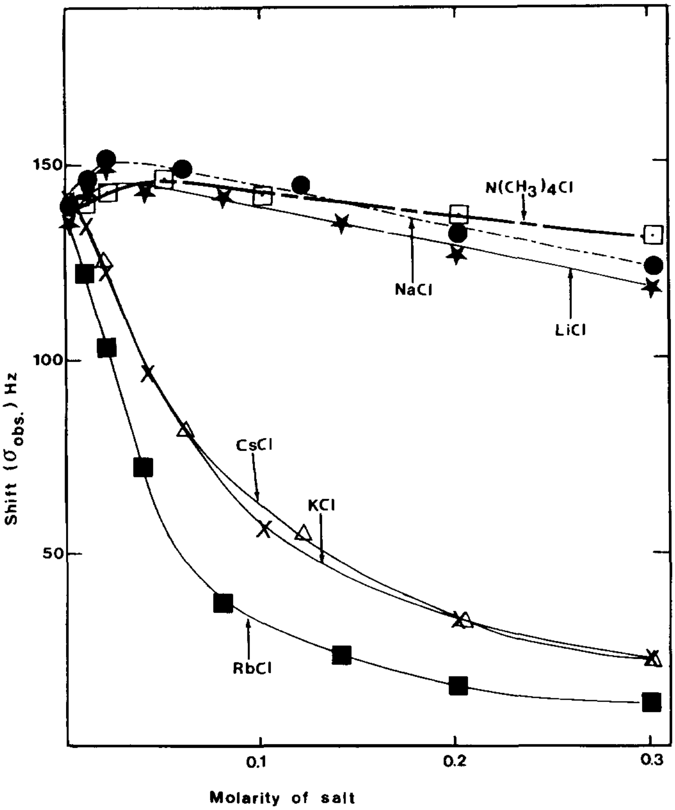

Fig. 1. ^{133}Cs NMR line shift as a function of the concentration of salt added to a 3% (w/v) salt-free Cs κ-carrageenate gel in D_2O at 25°C.

The gels could be dissolved by adding iodides of monovalent cations to them. The resulting solutions had the same high optical rotation as the gels, suggesting that the chains were kept in the same ordered conformation in solution. By comparing the addition of tetramethylammonium iodide and tetramethylammonium chloride to solutions of κ-carrageenan at 20°C, it was found that the iodide induced an ordered conformation of the chains at concentrations above 20 mM whereas, in 150 mM chloride, the chains were still in the random coil conformation as judged by measurements of optical rotation. This ordering of the chains was associated with binding of iodide ions as judged by ^{127}I NMR (Grasdalen & Smidsrφd, 1982). Both optical rotation and ^{127}I NMR showed that formation of the ordered conformation was independent of the concentration of carrageenan between 0·1 and 3·0% (w/v). Osmometry and light-scattering experiments showed that formation of the ordered conformation was not associated with any increase in molecular weight, but the intrinsic viscosity increased, suggesting a stiffening of the chains. The ordering therefore probably occurred within single carrageenan chains, resulting in the formation of single helices.

The present results, taken together, lend support to our gel model proposed earlier (Smidsrød, 1980; Smidsrød *et al.*, 1980). This 'cation-specific, nested, single-helix model' is shown schematically in Fig. 2.

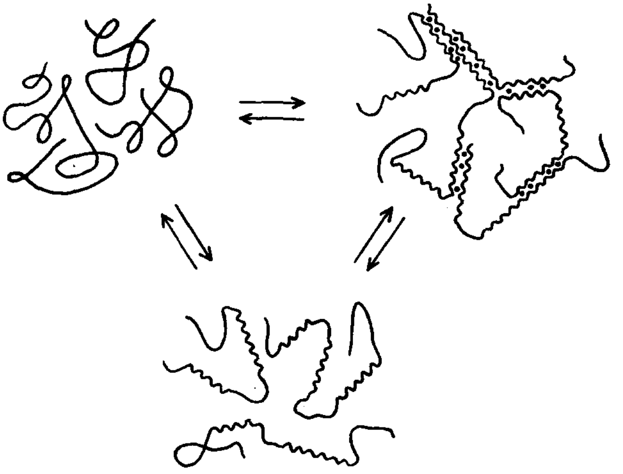

Fig. 2. Proposed model for conformational transition and gelation in κ-carrageenan systems. (Cation-specific, nested, single-helix model.)

REFERENCES

Bayley, S. T. (1955). *Biochim. Biophys. Acta*, **17**, 194.

Bull, T. E., Forsén, S. & Turner, D. L. (1979). *J. Chem. Phys.*, **70**, 3106.

Grasdalen, H. & Smidsrød, O. (1981). *Macromolecules*, **14**, 229.

Grasdalen, H. & Smidsrød, O. (1982). *Macromolecules*, in press.

Lindman, B. & Forsén, S. (1976). In: *Chlorine, Bromine and Iodine NMR, Physicochemical and Biological Applications*, Springer-Verlag, Heidelberg.

McKinnon, A. A., Rees, D. A. & Williamson, F. B. (1969). *Chem. Comm.*, 701.

Rees, D. A. (1981). *Pure & Appl. Chem.*, **53**, 1.

Smidsrød, O. (1980). In: *IUPAC International Congress of Pure and Applied Chemistry*, ed. A. Varmavuori, Pergamon, Oxford and New York, p. 315.

Smidsrød, O., Andresen, I. L., Grasdalen, H., Larsen, B. & Painter, T. (1980). *Carbohydr. Res.*, **80**, C11.