Role of Double Helices in Carrageenan Gelation: the Domain Model

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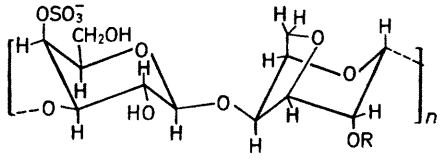
Summary Optical rotation, light scattering, and rheological studies show that intermolecular association of ι-carrageenan through double helices is limited to formation of small soluble clusters of chains (domains), development of an infinite network and hence gelation requires further association of these domains by cation-mediated aggregation of helices

THE previous 'junction zone' model of polysaccharide gel structure[1] is now elaborated to take account of new evidence that different levels of chain association may be involved in crosslinking, and that this can give a microheterogeneous or 'domain' character For the particular case of carrageenan gelation it is still proposed, as previously,[1-3] that chains are linked through double helices terminated by irregularities in covalent structure, but it is now clear that this step leads only to small clusters (domains) which require further association by cation mediated helix–helix aggregation to



R = SO_3^-: ι (**1**), R = H: κ(**2**)

develop a cohesive network This elaboration is outlined schematically in Figure 1 and is based on the following evidence

(i) ι-carrageenan (**1**) in the presence of Li^+, Na^+, or Me_4N^+ as sole counterion shows substantial helix formation as monitored[3,4] by optical rotation (Figure 2), but does not gel However, firm gels are obtained with larger Group 1 metal ions (K^+, Rb^+, Cs^+) and with NH_4^+, under identical conditions of concentration and ionic strength (see Table) and when the extent of helix formation was similar (judged by the optical rotation shift) (ii) Light scattering studies

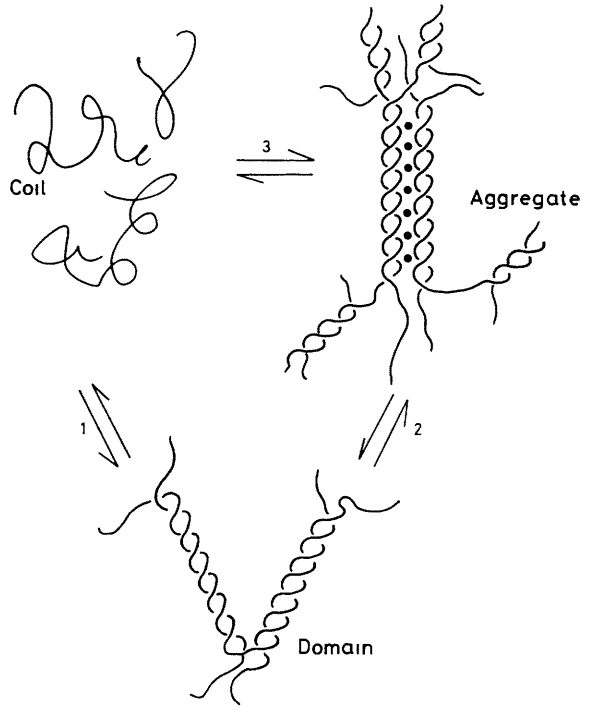


FIGURE 1 The domain model of carrageenan gelation 1 The primary mode of interchain association for ι-carrageenan is the coil–domain transition which is promoted by cooling and reversed on heating In an ionic environment which maintains isolation of the individual helices (*e g* Me_4N^+) the domain is the stable ordered state 2 Below the helix melting point, and in the presence of cations (●) which promote gelation (*e g* K^+, Rb^+, Cs^+, NH_4^+, or high concentrations of Na^+) further association occurs by the domain aggregate transition Only bound counterions relevant to the model are shown 3 An alternative mechanism of association for ι-carrageenan in the presence of gel-promoting cations, and the sole mechanism for κ-carrageenan, appears to be a direct coil–aggregate transition, which occurs at a higher temperature than the coil–domain transition

(Sofica, model 42,000) of ι-carrageenan segments having regular residue sequence, and under conditions of ionic environment (Me_4N^+) which do not promote gelation of the parent polymer, show the expected doubling of molecular weight on helix formation [from $(67 \pm 2) \times 10^3$ to $(140 \pm 5) \times 10^3$]. In the presence of cations (K^+) which do promote gelation of the parent molecule, however, substantially higher molecular weights are observed (6—8 × starting value) showing aggregation levels beyond the double helix. Since spectroscopic studies of these samples[3] show essentially complete conformational ordering with little, if any mismatching of chainlength, we conclude that the aggregation involves helical rather than other chain sequences. (iii) Under non-aggregating conditions (Me_4N^+) the coil–helix transition of intact ι-carrageenan is accompanied by an approximately tenfold increase in molecular weight, which we interpret in the light of the foregoing evidence as association through double helical junction zones to build up the soluble 'domain' structure. (iv) κ-Carrageenan (**2**) shows closely analogous cation specificity in its gelation behaviour, but helix formation (as monitored by optical rotation) is observed only under ionic conditions which would promote helix aggregation in ι-carrageenan, suggesting that the isolated helices and the domain intermediates (Figure 1) may not have separate existences for κ-carrageenan but require further stabilisation by helix aggregation. Indeed, low-angle light scattering studies (Chromatix KMX-6) of segmented κ-carrageenan (K^+) show much greater aggregated (*ca.* 1000 × random coil molecular weight) than for ι (K^+). Thus we attribute the increase in transition midpoint, and development of thermal hysteresis through the series Me_4N^+ ι, K^+ ι, K^+ κ (Figure 2) to progressively greater stabilisation of the ordered conformation by aggregation.

The topological difficulties that would exist in the formation of an infinite network through double helical junctions alone are likely to be diminished by the 'domain' model since side-by-side association of helices does not require free chain ends. The present experimental evidence is confined to carrageenan systems but it seems possible that a similar mechanism of gelation through quaternary association of limited domains may apply to other polysaccharide gels where the primary interchain association is through double or multi-stranded helices.

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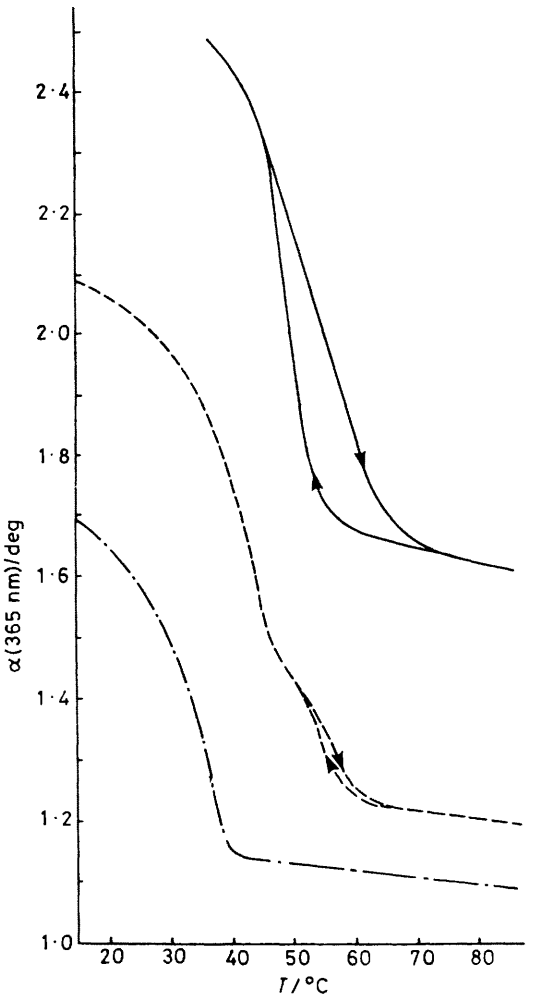

FIGURE 2. Thermally induced order–disorder transitions of ι-carrageenan in the Me_4N^+ (— · —) and K^+ (— — —) salt forms, and of K^+ κ-carrageenan (—). Carrageenan concentration (excluding counterion) 1% w/v; cation concentration 0·12 M. Optical rotation at 365 nm was measured at 25 °C on a Perkin-Elmer 241 polarimeter, using a 10 cm pathlength cell. The carrageenans were commercial samples (X52 and GS 350) from Pierrefitte–Auby. Structural regularity was enhanced by treatment with alkaline borohydride.[5] Segmented iota carrageenan samples prepared by Smith degradation,[6] and used in our light scattering studies, showed conformational behaviour closely similar to that of the intact polymers.

TABLE. Effect of counterion on carrageenan gel strength (yield stress N)[a]

	Li^+	Na^+	K^+	Rb^+	Cs^+	NH_4^+	Me_4N^+
κ	—[b]	—[b]	2·2	2·4	1·4	0·9	—[b]
ι	—[c]	—[c]	0·30	0·30	0·05	0·05	—[b]

[a] Measurements were made at ambient temperature on an Instron Universal Materials Tester, using cylindrical gel samples (12·5 mm diameter, 12 mm height), compressed between parallel plates. Polysaccharide concentration 2% w/v; cation concentration 0·25 M. [b] Mobile solution. [c] Some thickening, but no measurable gel.

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