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The structure of κ/ι-hybrid carrageenans II. Coil–helix transition as a function of chain composition☆

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Abstract—This paper describes the effect of the κ/ι-ratio on the physical properties of κ/ι-hybrid carrageenans (synonyms: kappa-2, κ-2, weak kappa, weak gelling kappa). To this end, a series of κ/ι-hybrid carrageenans ranging from almost homopolymeric κ-carrageenan (98 mol-% κ-units) to almost homopolymeric-carrageenan (99 mol-% ι-units) have been extracted from selected species of marine red algae (Rhodophyta). The κ/ι-ratio of these κ/ι-hybrids was determined by NMR spectroscopy. Their rheological properties were determined by small deformation oscillatory rheology. The gel strength (storage modulus, G') of the κ/ι-hybrids decreases with decreasing κ-content. On the other hand, the gelation temperature of the κ-rich κ/ι-hybrids is independent of their composition. This allows one to control the gel strength independent of the gelation or melting temperature.

The conformational order–disorder transition of the κ/ι-hybrids was studied using optical rotation and high-sensitivity differential scanning calorimetry. High-sensitivity DSC showed that the total transition enthalpy of the κ/ι-hybrids goes through a minimum at 60 mol-% κ-units, whereas for the mixture of κ- and ι-carrageenan, the total transition enthalpy is a linear function of the composition. With respect to the ordering capability, the κ/ι-hybrid carrageenans seem to behave as random block copolymers with length sequence distributions truncated from the side of the small lengths. Intrinsic thermodynamic properties (e.g., transition temperature and enthalpy) of κ- and ι-sequences in these copolymers are close to those of their parent homopolymers. The critical sequence length for κ-sequences is 2-fold of that for ι-sequences.

Keywords: Carrageenan; κ/ι-Hybrids; Kappa-2; Polysaccharides; Coil-to-helix transition; Structural analysis; Differential scanning calorimetry

1. Introduction

Carrageenans represent one of the major texturising ingredients in the food industry. They are natural ingredients used for decades in food applications and are regarded as safe.[2] The dairy sector accounts for a large part of the carrageenan applications in food products, such as frozen desserts, chocolate milk, cottage cheese and whipped cream.[2–4] In general, carrageenan serves as a gelling, stabilising and viscosity-building agent. Carrageenan is the generic name for a family of polysaccharides, obtained by extraction from certain species of red algae (Rhodophyta). They are mixtures of water-soluble, linear, sulfated galactans. They are composed of alternating 3-linked β-D-galactopyranose (G-units) and 4-linked α-D-galactopyranose (D-units) or 4-linked 3,6-anhydrogalactose (DA-units), forming the 'ideal'

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disaccharide repeating unit of carrageenans (see Fig. 1). These sulfated galactans are classified according to the presence of the 3,6-anhydrogalactose on the 4-linked residue and the position and number of sulfate groups. The most common types of carrageenan are traditionally identified by a Greek prefix. The three commercially most important carrageenans are called κ-, ι- and λ-carrageenan. In addition, two other types, called μ- and ν-carrageenan, are often encountered in carrageenan samples obtained by mild extraction methods. The μ- and ν-carrageenans are the biological precursors of, respectively, κ- and ι-carrageenan. The κ- and ι-carrageenans are gel-forming carrageenans, whereas λ-carrageenan is a thickener/viscosity builder. In general terms, κ-carrageenan gels are hard, strong and brittle, whereas ι-carrageenan forms soft and weak gels that are shear reversible.[2] To describe more complex structures, a letter code based nomenclature for red algae galactans has been developed.[5] The letter codes for κ- and ι-carrageenan are included in Figure 1.

The different types of carrageenan are obtained from different species of the Rhodophyta. κ-Carrageenan is predominantly obtained by extraction of the tropical seaweed, *Kappaphycus alvarezii*, known in the trade as *Eucheuma cottonii* (or simply Cottonii).[6] *Eucheuma denticulatum* (trade name *Eucheuma spinosum* or simply Spinosum) is the main species for the production of ι-carrageenan. The largest commercial source of these tropical species is the Philippines where wild harvesting has been replaced by seaweed farming. The seaweeds are usually extracted with alkali at elevated temperatures to transform the biological precursors, μ- and ν-carrageenan, into κ- and ι-carrageenans. κ/ι-Hybrid carrageenans (synonyms: kappa-2, κ-2, weak kappa, weak gelling kappa) are obtained from different species in the Gigartinaceae family. The gametophytic thalli produce κ/ι-hybrid carrageenans, whereas the sporophytic thalli of these seaweeds produce λ-carrageenan and other related carrageenan types, such as ξ, θ and π-carrageenan.[7,8]

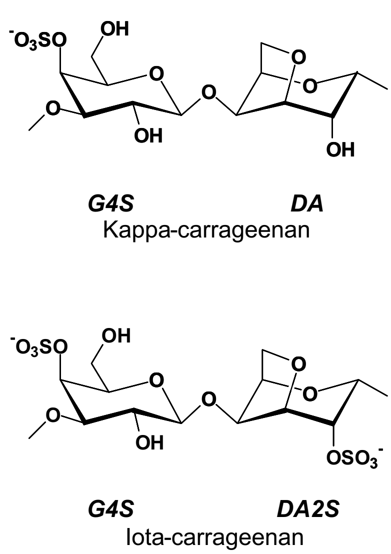

Figure 1. Molecular structure of carrageenan repeating units.

The structure of the κ/ι-hybrid carrageenans has been a major topic for several research groups. Several schemes are conceivable for these κ/ι-hybrids: a mixture of homopolymeric κ- and ι-carrageenan chains or a mixed or heteropolymeric chain comprising both κ- and ι-repeating units. In the later case, the distribution can be either blockwise or random. Small amounts of ι-carrageenan present in *K. alvarezii* extracts are identified to be separated chains.[9] However, κ/ι-hybrids with a more equal distribution of κ- and ι-repeating units are found to be heteropolymeric type of κ/ι-hybrids.[1,10,11] From an industrial point of view, the κ/ι-hybrids are of increasing importance for their specific functionalities in dairy applications.[8,11,12] The term kappa-2 carrageenan has been arbitrarily given to κ/ι-hybrid carrageenans with a κ-content from 80 to 45 mol-% κ-repeating units.[10,12] Within this study the term κ/ι-hybrid carrageenan is preferred as the samples range from homopolymeric κ-carrageenan to homopolymeric ι-carrageenan. The different algal sources producing these κ/ι-hybrids are generally summarised in a so-called Stancioff diagram[10,13] (see also Fig. 3). The original, commercial source of the κ/ι-hybrid carrageenan was *Chondrus crispus* (from Canada), also known as Irish moss. At present, *Sarcothalia crispata*, *Gigartina skottsbergii* and *Chondracanthus chamissoi* (from Chile), known in trade as Luga Negra, Gigartina broad leaf or simply Gigartina are the important species for the commercial production of this carrageenan. The harvesting from natural populations has been and will be restricted by several authorities and, thereby, stimulating the research in seaweed production by aquaculture.[8,14,15] For this reason several red seaweed species were analysed for the presence of κ/ι-hybrid carrageenans in relation to their functional properties. Moreover, a vast amount of literature is available on the analysis of specific carrageenans produced by the different life stages of species belonging to Gigartinales. The list of studied species includes *C. crispus*, *Gigartina alveata*, *G. clavifera*, *G. decipiens*, *G. pistillata*, *G. skottsbergii*, *Gymnogongrus torulosus*, *S. crispata*, *S. atropurpurea* and several commercial and underutilised species collected from the occidental Portuguese coast.[8,10–12,16–24]

Although the functional properties in dairy applications have been studied for κ/ι-hybrids extracted from specific species, no systematic analysis of the κ/ι-hybrids has been reported. Most of the studies mentioned above started from a certain seaweed species and studied the functional properties of the carrageenans extracted. In contrast, we focus on the physical properties of the κ/ι-hybrids, whereby the botanical source is of secondary importance. We focused on purified κ/ι-hybrid