Studies on the network structure of mixed kappa and iota carrageenan gels by NMR

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博士学位論文内容要旨
Abstract

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論文題目 Title	Studies on the network structure of mixed kappa and iota carrageenan gels by NMR （NMR によるイオターカッパ混合カラギーナンゲルの網目構造に関する研究)		

Carrageenan, a family of linear polysaccharide extracted from red algae seaweed, has been widely used in food, cosmetic and pharmaceutical industries. Kappa- and iota-carrageenans (CR) are two commercially important types since their hot solutions can form gels at the presence of some metallic cations if cooling to a certain temperature. Researches on the mixture enable novel applications in industry. Independent gelation of their mixture has been testified by many macroscopic methods; however, it is still unclear about the gelation mechanism and micro-structure of the mixed gel. Microscopy methods are not practical for studying mixed gels containing different polysaccharide chains but with similar chemical structures, which cannot be separately stained. Nuclear Magnetic Resonance (NMR), providing several methods to obtain microscopic information, is a powerful tool for studying the molecular mobility, which can help a better understanding of the gelation mechanism and the structure of the mixed gel.

Chapter 1 shows the general introduction about κ- and ι-carrageenan in terms of chemical structure, gelling properties, and previous researches based on their mixtures, etc. Gel formation in an aqueous solution is a complex process that depends on polysaccharide structures, temperature, polymer concentrations and also the presence of co- and counter-ions. The gelation of κ- and ι-CR begin from the occurrence of double helix, and then undergo coil-to-helix transition. The molecular mechanism of gelation of the helix-forming carrageenans have not yet been firmly established, although a variety of models have been proposed. κ-CR solution can form a hard and brittle gel with the formation of aggregates and shows thermal hysteresis upon melting, while ι-CR solution can only form a much weaker and softer gel without hysteresis. The helix formation and subsequent helix aggregation of κ-CR is strongly enhanced by alkaline cations except Na^+ and divalent cations. For ι-CR, on the other hand, only weak dependence of the coil-helix transition temperature on the presence of alkaline cation is observed and no thermal hysteresis is present. It is logical to attribute the different gelling properties of κ- and ι-CR to that they may follow respective mechanism of gelation. For κ-CR, all evidence suggests that specific ion binding occurs to the individual helices instead of between aggregating helices. The mechanism of gelation of ι-CR is more controversial. Yuguchi et al. claimed the double helix in ι-CR but little tendency toward further aggregation, but other researchers got opposite conclusion indicating significant aggregation of ι-CR helices even in dilute solutions.

Chapter 2 introduces the mechanisms used in the following studies, including the measurements of T_2 relaxation time, diffusion coefficient by solution NMR and some basic techniques in solid-state NMR. The rate of relaxation is influenced by the physical properties of the molecule, so a study of relaxation phenomena can lead to information on internal motions of macromolecules. The translational diffusion provides information on molecular dynamics. For polymer, it can lead to a series of predictions about polymer length, interactions with solvent or other small molecules, etc. NMR is becoming a suitable and powerful tool to study translational motion of polymer without a distortion or disturbing of the structure. Solid-state NMR, being widely applied in materials chemistry, is especially valuable at probing complex molecular systems, particularly composites and other heterogeneous aggregates. It became a central tool in investigating and understanding the structural and dynamic properties of amorphous solids on the molecular and microscopic levels. For biological and biochemical systems, such as amino acids, proteins, polysaccharide, etc., this method is also used in determination of their conformation, alignment, interaction with binding partners, and their response to changes in the environment.

Chapter 3 is the studies on mixed κ- and ι-carrageenan solution by solution NMR methods. T_2 relaxation time and diffusion coefficients of carrageenans were measured during cooling and reheating to reflect the mobility behavior of carrageenan chains. The movements of probe molecules were also measured to describe

the hindrance from carrageenan gel network. Two-step gelation of κ- and ι-CR were confirmed. Gelation mechanism of the mixed solution in microscopic level and the size of phase separation can be inferred from the results. The temperature dependence of signal intensity for the CR chains in the mixed solution showed a steep decrease at gelling temperatures upon cooling, and a steep increase in G' was observed in rheological measurements, indicating the formation of aggregates. Diffusion coefficients and ^{1}H T_2 for κ-CR and ι-CR chains increased as the signal intensity decreased, indicating that longer CR chains were preferentially involved in forming the aggregates, resulting in a decrease in the average Mw of the solute CRs chains. Diffusion measurements for PEO added as a probe polymer in the mixed solution showed an intermediate behavior between that in pure κ- and ι-CR solutions. The probe molecules showed mono-model diffusion in the mixed solution, indicating two possibilities for the microscopic network structure: an interpenetrating network (IPN) structure, or micro-phase separation.

Chapter 4 introduces the research by Solid State NMR (SSNMR) methods. Solution NMR failed to detect the signals of carrageenan in gel state due to the extremely short T_2 because of the restricted mobility of CR chains in gel network structure. As a result, solid-state NMR was used to study the network structure of mixed kappa- and iota-CR gels or solutions by studying on the chains' mobility. Cross polarization (CP) and 2D ^{13}C-^{1}H correlation measurements provide information on conformation and space proximity between molecules, which give hints for the micro-structure of mixed carrageenan gels. A new peak in A1-C region was observed in mixtures of κ- and ι-CR regardless of status of the samples, and it showed stronger intensity as increasing the portion of κ-CR. This is attributed to the concentration of partial κ-CR chains due to expulsion water to ι-gels, which modifies their conformations of A1-C. CP efficiency measurements shows that the signal intensities of κ-CR were stronger than ι-CR and the mixed CR follows the similar intensities as pure κ-CR. This indicates κ-CR chains have lower molecular mobility, supporting that κ-CR forms more rigid aggregates than ι-CR.

The last chapter gives summary and prospect for the obtained results and evaluates the used methodologies. Diffusion measurements of probe molecule provides important information on microstructure in gels, as well as on the degree of restriction caused by hydrodynamic interaction with the polysaccharide network or by hindrance from the solute polysaccharide. The solid-state NMR is also a novel method to detect the chains mobility of κ- and ι-CR in the mixture at gel states.