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# Dissertation Summary

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

**Course of Applied Marine Biosciences**

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Carrageenan (CR) is a family of linear polysaccharide which has already been widely used as gelling agent, stabilizer or thickeners in food and pharmaceutical industry. κ- and ι -CR are two important types but have very different gelling behaviors. 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 the hysteresis. The large different gelling properties of κ-and ι-carrageenan provides the basis of industrial use of their mixture to give controllable and desirable characters. However, the gel mechanism of their mixture is still controversial. Therefore we aimed to elucidate the formation and characteristics of network structure in mixed κ- and ι-CR solution in this work.

Many macroscopic methods such as rheology and DSC have already been used in previous studies on mixtures of κ- and ι-CR. However there is still a lack of systematic research from the microscopic level. Nuclear Magnetic Resonance (NMR) is a powerful and non -invasive method that can provide information on the gel mechanism and the mixed network structure. In this study, $^{1}HT_2$ relaxation time and diffusion coefficient (D) of κ- and ι-CR mixed solution were measured by solution NMR. In addition, the diffusion measurement of probe molecules in the mixed CR solution is a novel point since it reflects the obstruction only from the host polymers. Solid State NMR (SSNMR) provides the possibility to research on gel state or powder state of mixed κ- and ι-CR gels, since it is a unique instrument which combines structural and dynamic aspects. Cross polarization (CP) and 2D $^{13}C$-$^{1}H$ correlation measurements provide information on conformation and space proximity between molecules. Therefore, the studies on gel/solid state of mixed κ- and ι-CR were conducted to clarify the individual characteristics of κ- and ι-CR, in terms of chains mobility, compactness of aggregates, etc., to give more hints on the network structure of the mixed gel.

In the solution NMR measurements, temperature dependence of signal intensity for the CR chains in the mixed solution showed a steep decrease at gelling temperatures ($Tc$) upon cooling, indicating the formation of aggregates. The steeper decrease of signal intensity of κ-CR than ι-CR indicated the faster formation of κ-aggregates. Diffusion coefficients and $^1HT_2$ for κ-CR chains increased as the signal intensity decreased, indicating that longer CR chain were preferentially involved in forming the aggregates, resulting in a decrease in the average molecular weight of the solute CRs chains. *Dprobe/Dprobe,0* showed an obvious increase in pure of κ-CR solution and a mono-decrease in pure ι-CR solution during cooling. In mixed CR solution, it showed an intermediate behavior, that is, that is, it increased slightly at around the gelling temperature of κ-CR (*Tc,k*) and plateaued at lower temperatures. 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 with the domain size less than 450 nm.

In Solid state NMR measurements, solution or gel states samples were freeze dried to obtain the solid-state powders. The instantaneous frozen processes by liquid $N_2$ is believed to keep or "photograph" the structures of samples at the states before freezing. A new peak assigned to anomeric carbons' region was observed in the spectra for mixtures of κ-CR and ι-CR regardless of the samples, and it showed stronger intensity as increasing the portion of κ-CR. This was attributed to the concentration of partial κ-CR chains due to expulsion water to ι-gels, which modified their original dominant conformations of the anomeric carbons. The CP efficiency measurements showed that κ-CR had stronger signal intensities than ι-CR and the mixed CR followed the similar intensities as pure κ-CR. This indicates κ-CR aggregates is more rigid than ι-CR since the CP signal intensity is inversely proportional to the molecular motilities. The 2D$^{13}$C-$^1$H correlation measurements failed to directly show the proximity of molecules in gel states, without showing additional correlation peaks in H dimension at different contact times.

Although the diffusion measurements of probe molecules could not determine the network structure in the mixed gel in this study, this method does provide important information on the microscopic structure of gel network in a mixed gelling solution, as well as on the degree of restriction caused by hydrodynamic interaction with the polysaccharide network and by hindrance from the solute polysaccharide chains. Solid-state NMR measurements testified from a molecular level that κ-CR formed a more rigid aggregates than ι-CR. More methods by SSNMR are still needed and possible to study on the mixed polysaccharide systems.