

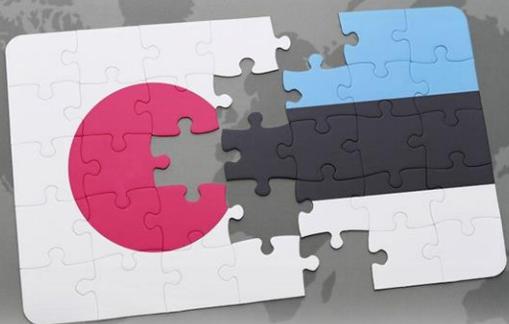
Tallinn University
School of Natural Sciences and Health

STRUCTURE AND FUNCTIONALITY OF SEAWEED-DERIVED POLYSACCHARIDES

Rando Tuvikene

Fostering Japanese-Estonian research cooperation
in the field of Bioengineering and Biotechnology

Tokyo, 2024





25 years of research on algal polysaccharides.

Furcellaran – a specific type
of carrageenan from
Furcellaria lumbricalis.



エストニアにおけるフルセラリア

Furcellaria lumbricalis の資源と利用

Rando Tuvikene

バルト海は、商業的な海藻種の成長に適さない物理的条件が卓越しているため、天然海藻資源の採取という意味ではあまり大きな役割を担っていない。バルト海では約 160 種の海藻が見つまっているが、そのうち、*Furcellaria lumbricalis* (Hudson) J. V. Lamouroux (以前は *F. fastigiata* とされていた) は、この海域で大規模に収穫されている唯一の海藻である。バルト海では、*F. lumbricalis* に 2 つの異なる生態型が見つまっている。本種の付着型はバルト海の花藻生育帯下部の硬い基質でふつうにみられる。一方、海底に付かずに横たわる非付着型の *F. lumbricalis* は非常にユニークである。



Furcellaria lumbricalis, 200 000 t wet weight.

PHYCOCOLLOIDS

Phycocolloids – hydrocolloids deriving from seaweeds.

Agars
E406

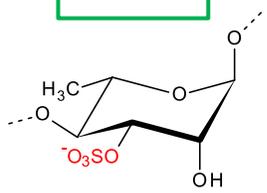
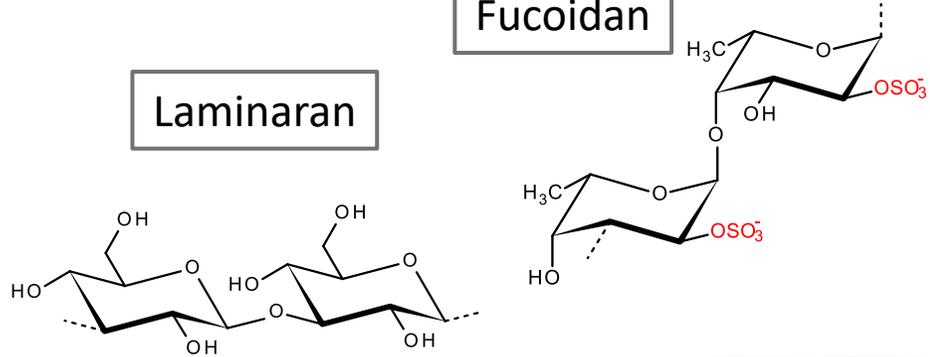
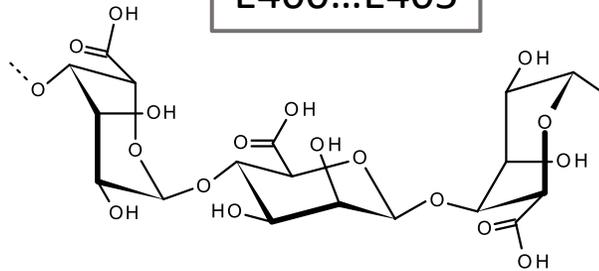
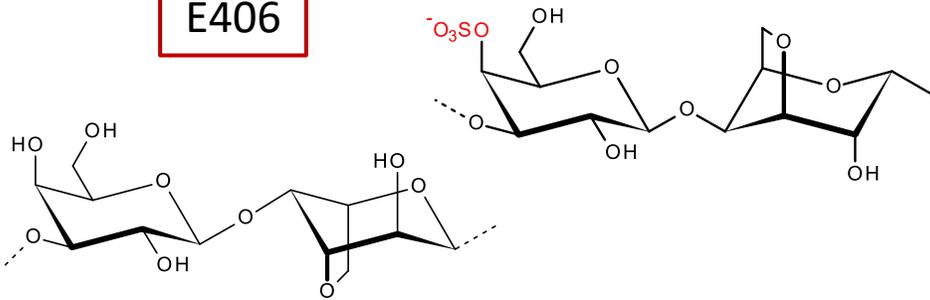
Carrageenans
E407

Alginates
E400...E405

Fucoidan

Laminaran

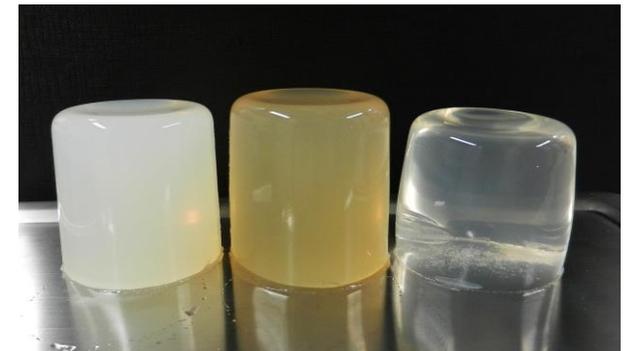
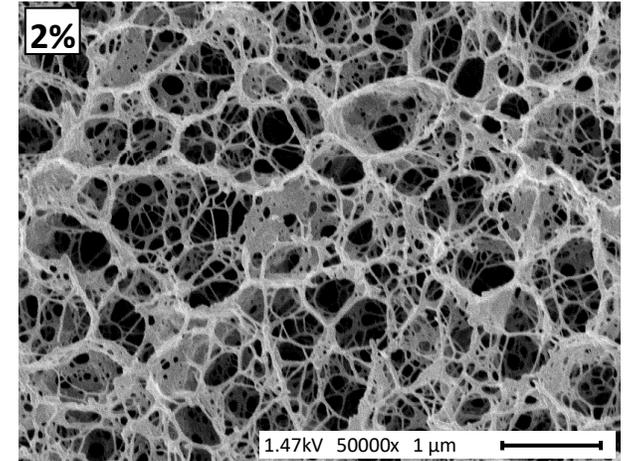
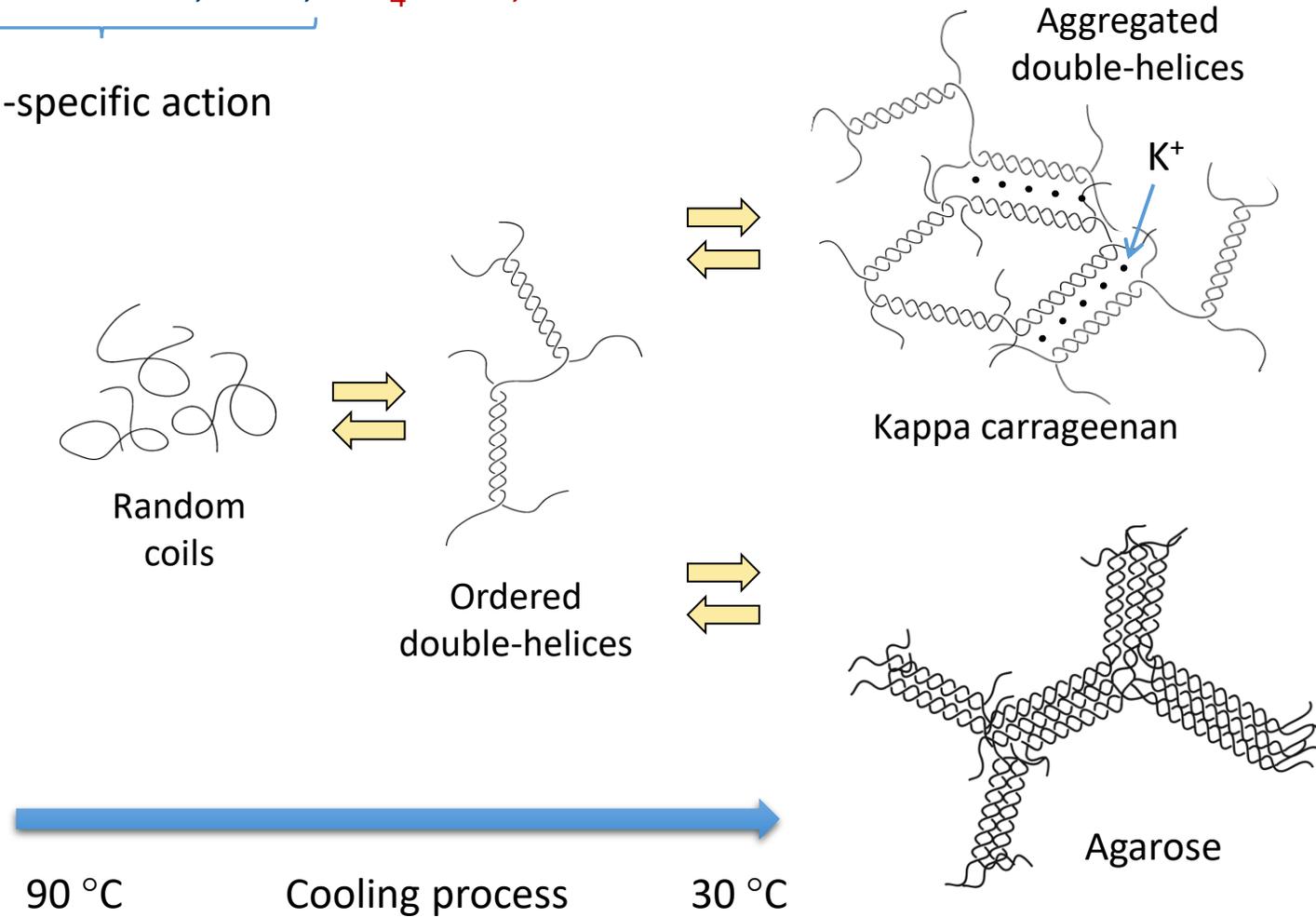
Ulvan



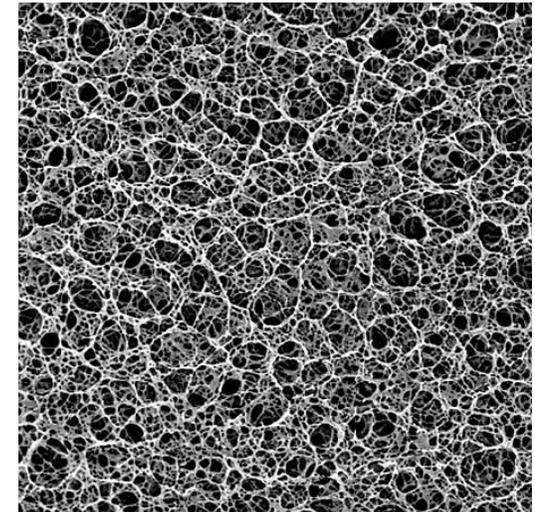
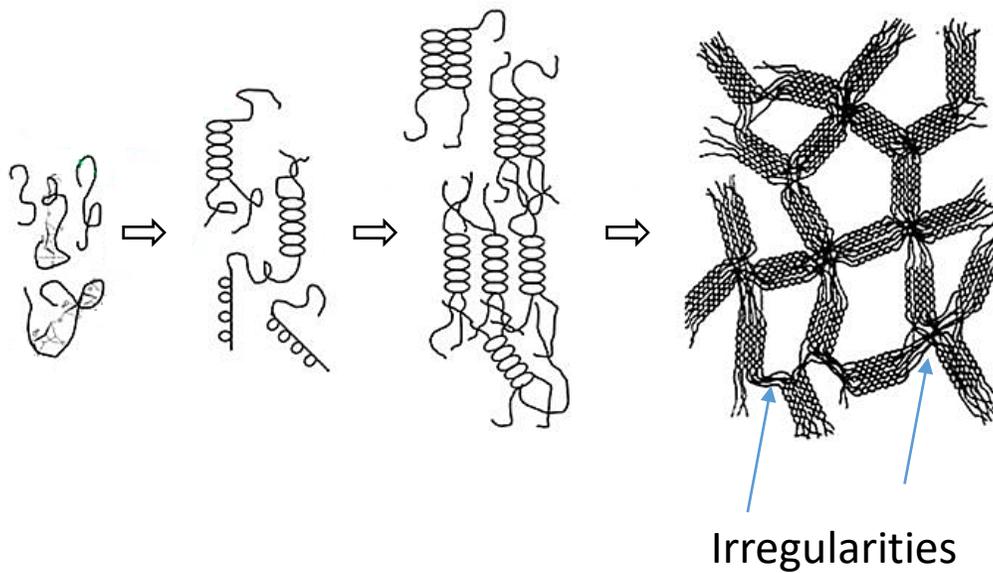
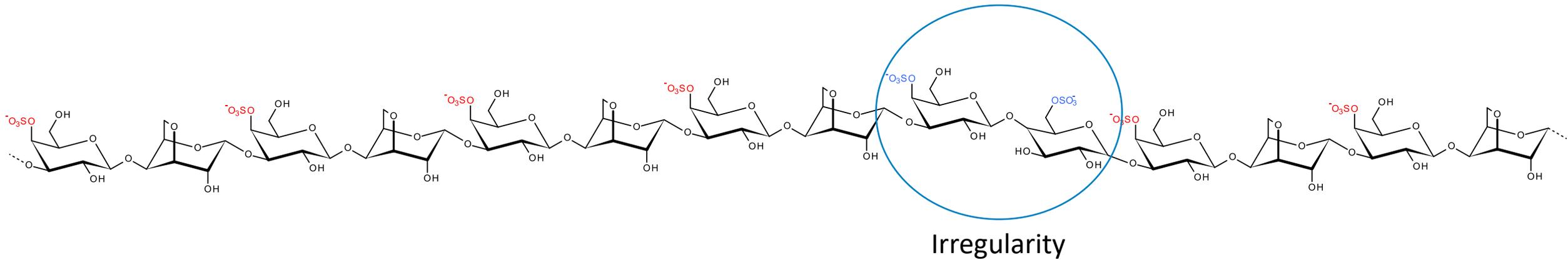
GELATION PROCESS – GALACTANS

$\text{Li}^+, \text{Na}^+ \ll \text{Ca}^{2+}, \text{Cu}^{2+}, \text{NH}_4^+ < \text{K}^+, \text{Cs}^+ < \text{Rb}^+$

Non-specific action

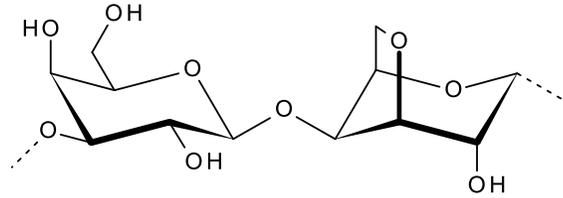


IRREGULARITIES IN THE STRUCTURE

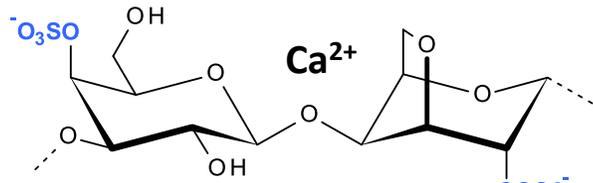


Random irregularities in the structure stabilize the overall gel structure

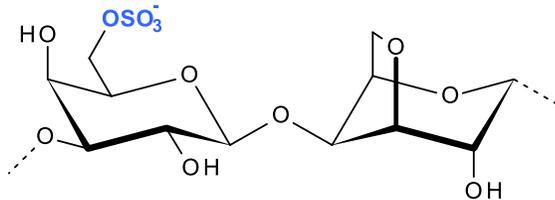
WEAK GELS



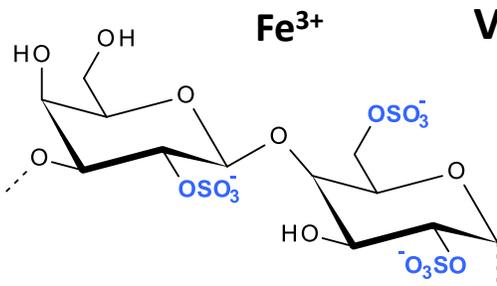
Beta carrageenan



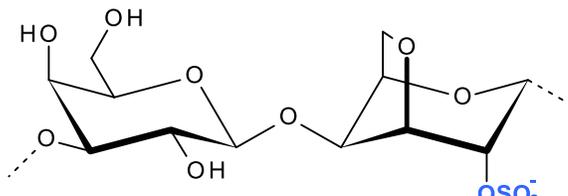
Iota carrageenan



Omega carrageenan

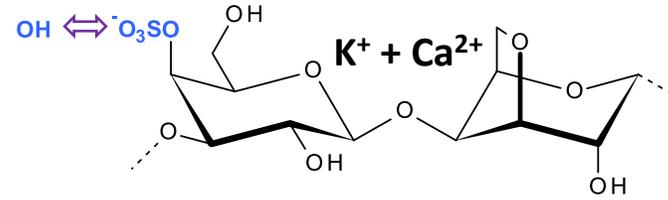


Lambda carrageenan

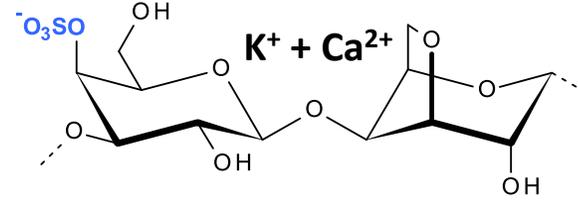


Alpha carrageenan

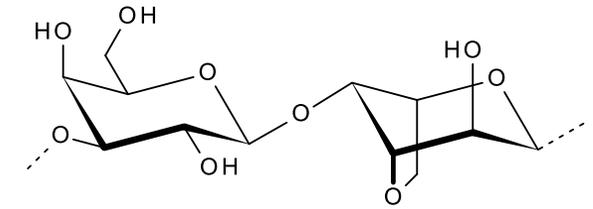
STRONG GELS



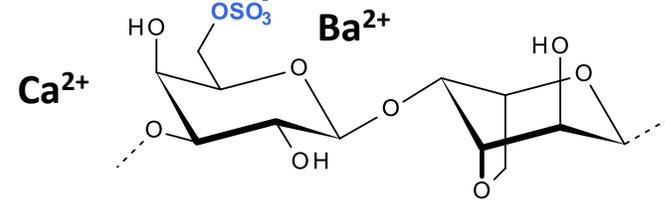
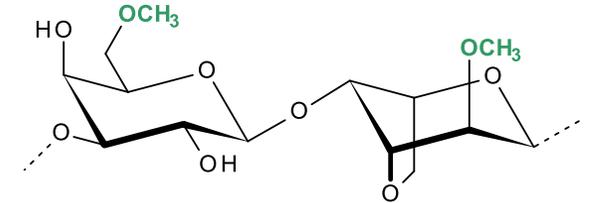
Furcellaran



Kappa carrageenan

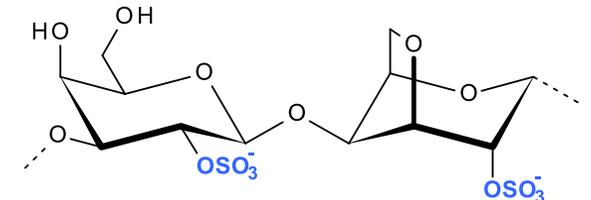


Agarose

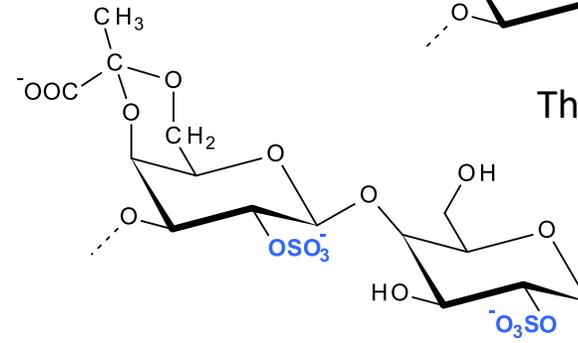


Funoran

LOW-VISCOSITY SOLUTIONS



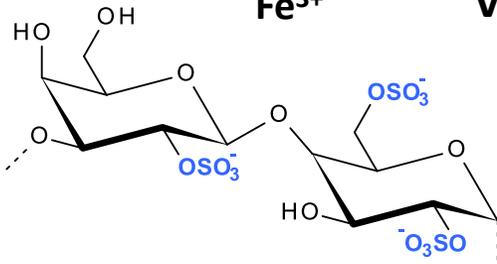
Theta carrageenan



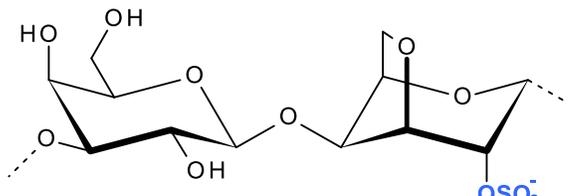
Pi carrageenan

VISCOUS SOLUTIONS

Fe³⁺

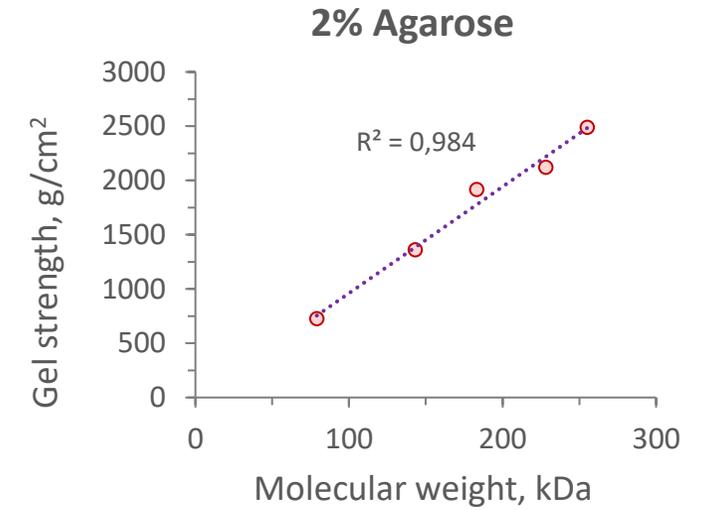
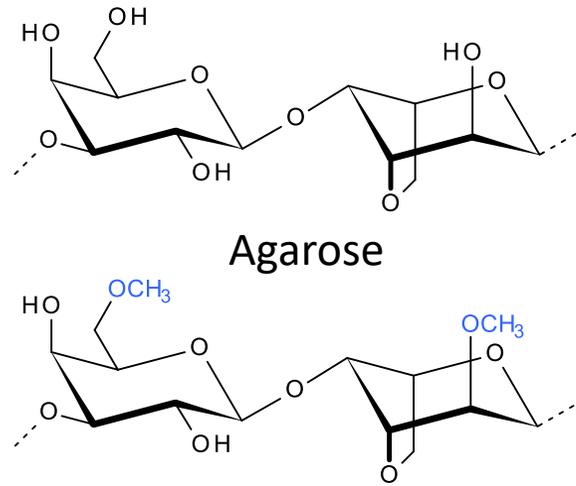
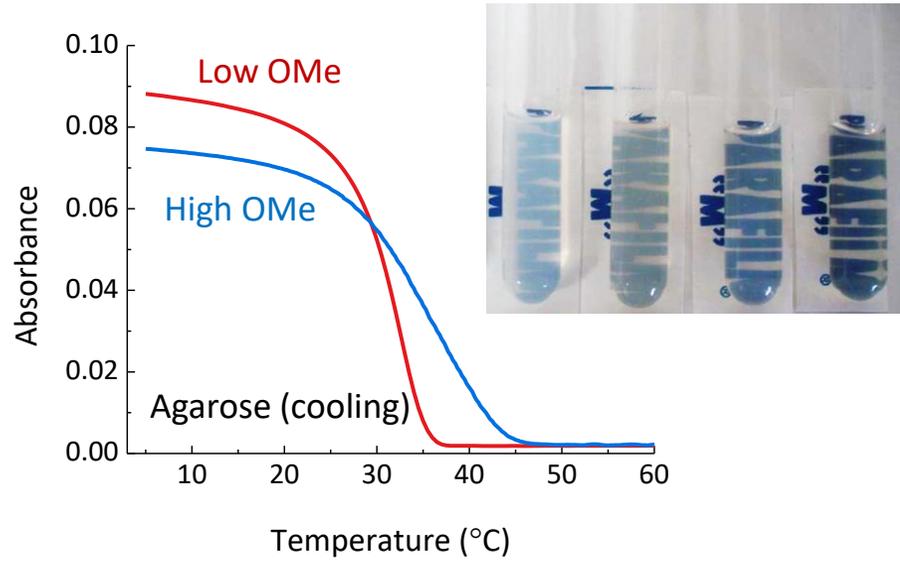


Lambda carrageenan



Alpha carrageenan

GEL PROPERTIES



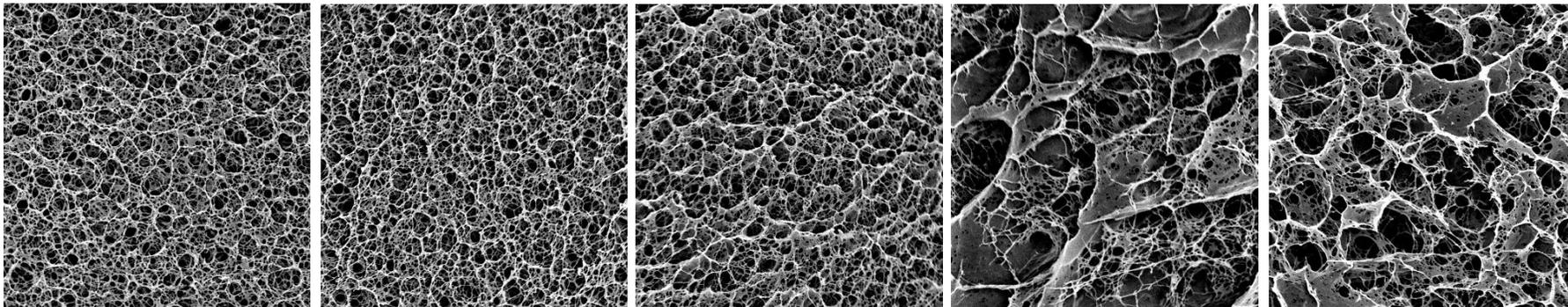
255 kDa

228 kDa

183 kDa

143 kDa

79 kDa



2488 g/cm²

2022g/cm²

1916 g/cm²

1361 g/cm²

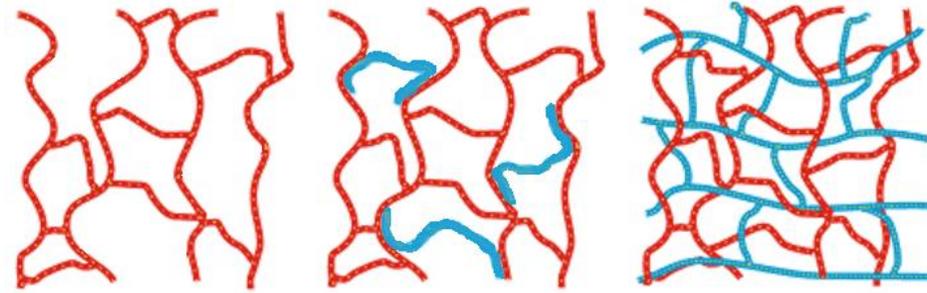
726 g/cm²

2.2% agarose gels, size of the micrographs: 8x8 μm²

SEAWEED CULTIVATION EXPERIMENTS



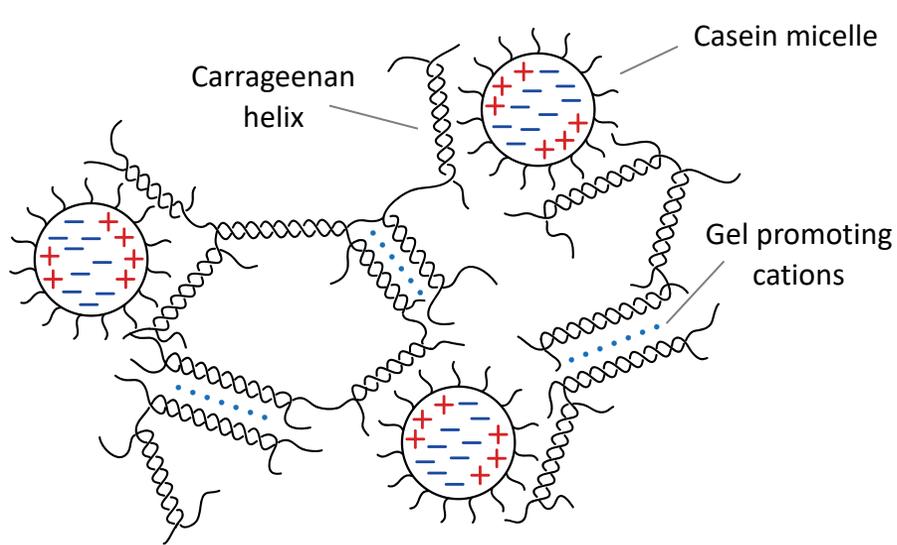
PROTEIN REACTIVITY



Gel network

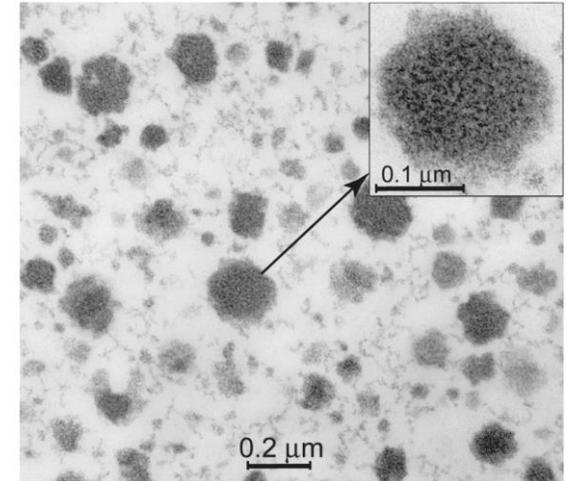
Reinforced structure

Intertwined networks



Protein reactivity against

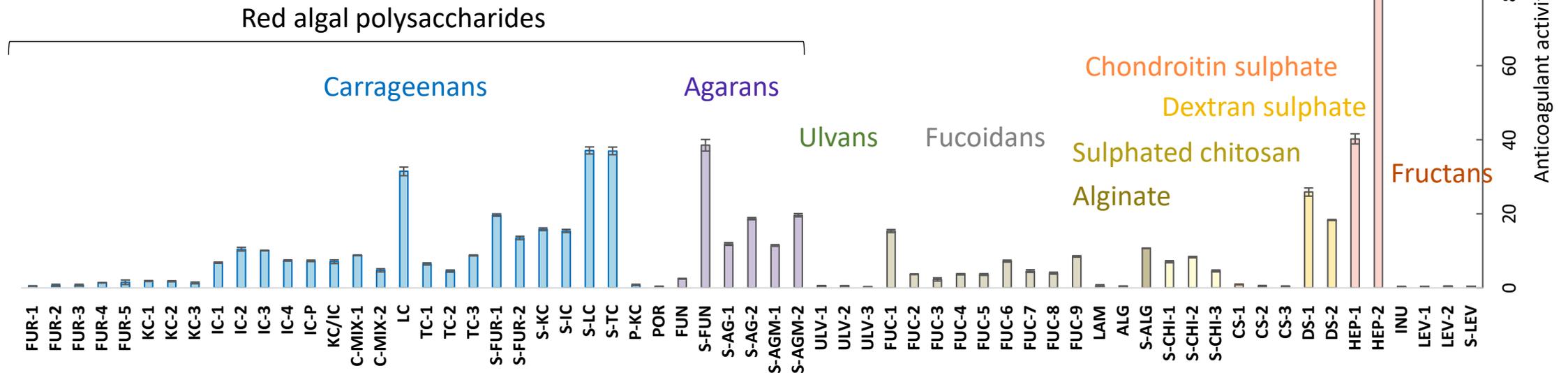
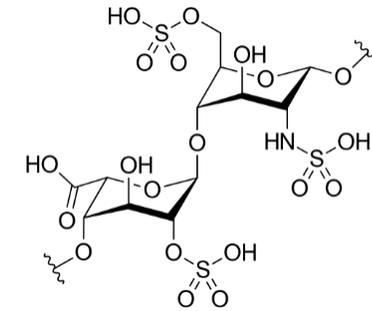
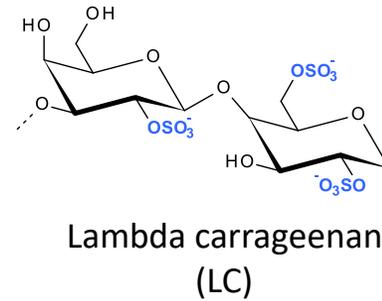
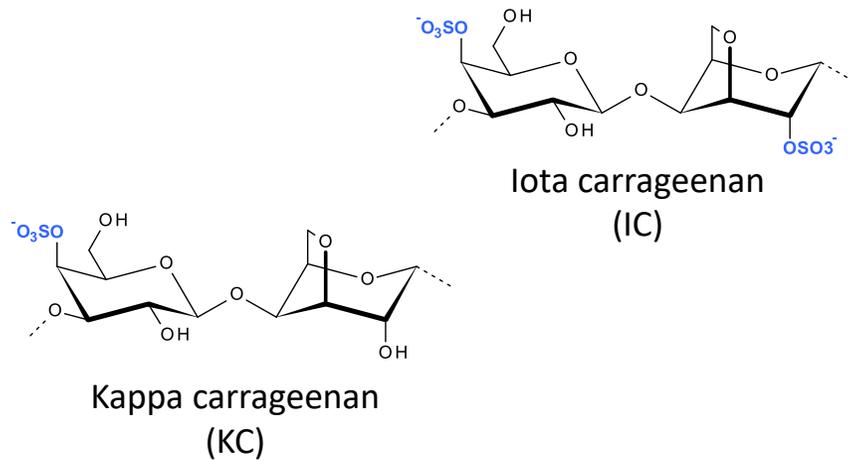
- Casein
- Beta-lactoglobulin
- Gelatin
- Soy protein



Casein micelles
Schmidt, 1982

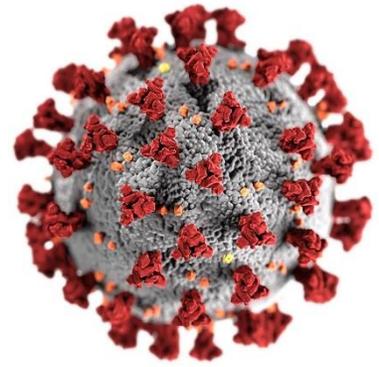
Interaction between casein micelles and kappa carrageenan helices.

ANTICOAGULANT ACTIVITY



ANTIVIRAL PROPERTIES

Bind to the **surface proteins** of the virus.



SARS-CoV-2



Sulphated chitosan

Chondroitin sulphate

Dextran sulphate

Alginate

Heparin

Ulvans

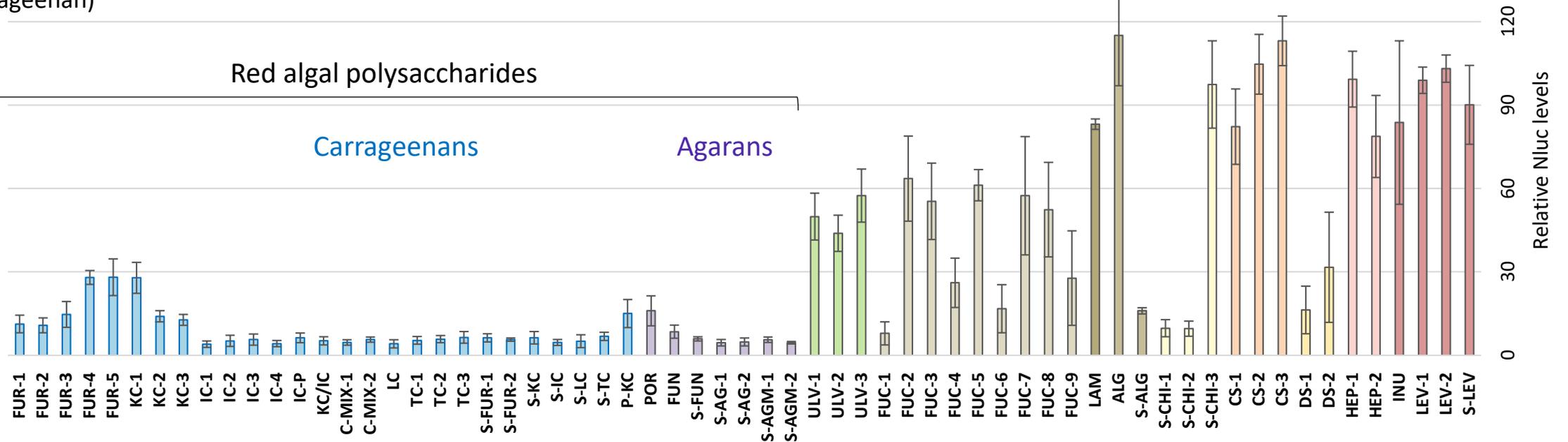
Fucoidans

Fructans

Red algal polysaccharides

Carrageenans

Agarans



CLARIFYING PROPERTIES



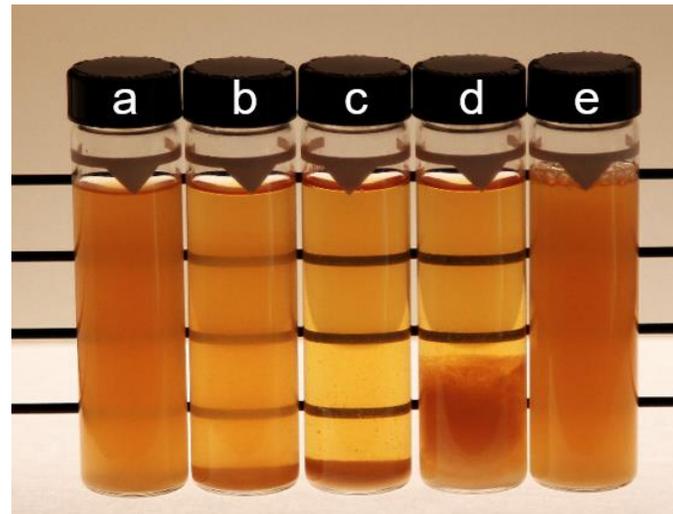
Some carrageenans are effective clarifying agents for beer wort, beer and wine.

Semi-refined *Chondrus crispus* is often used.

Lower Mw \Rightarrow Lower effect



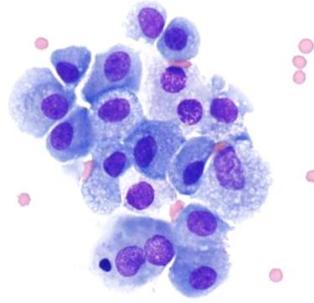
Reduction of protein haze in wines



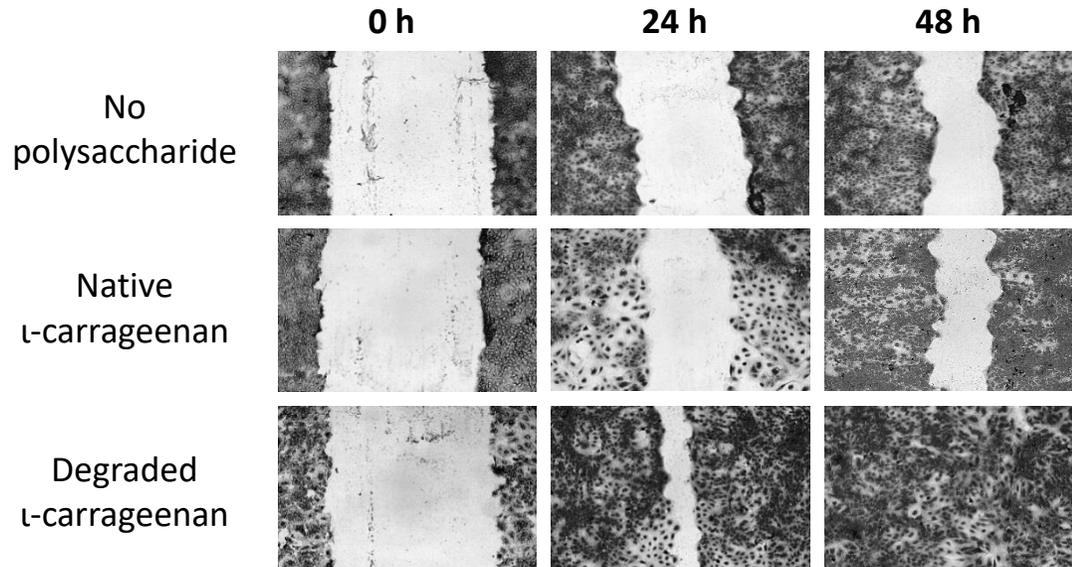
- (a) Blank
- (b) Furcellaran (2.5 ppm)
- (c) Furcellaran (10 ppm)
- (d) Furcellaran (40 ppm)
- (e) Iota carrageenan (20 ppm)

BIOLOGICAL ACTIVITIES

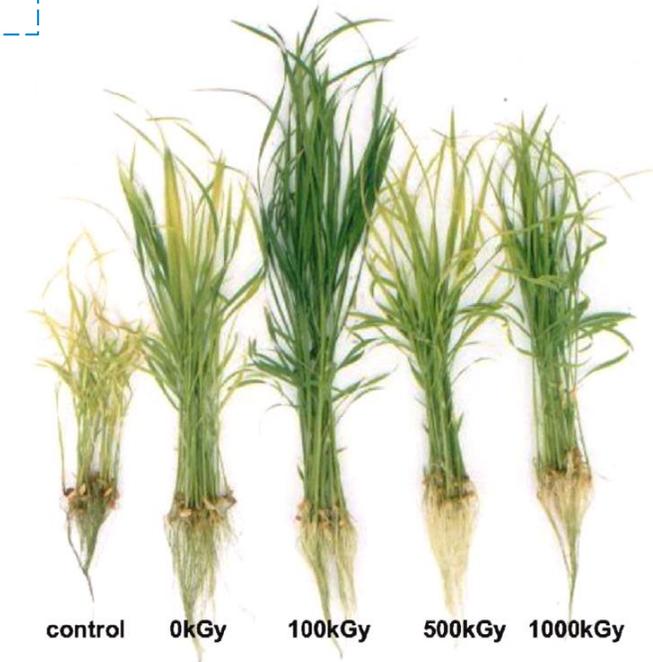
Effect on immune cells
(macrophages)



Sulphated polysaccharides
often show diverse biological
activities.



Effect of carrageenan preparations (125 µg/mL) on HaCaT cell migration.



Rice seedlings treated with native and irradiated ι-carrageenan samples.

L.V. Abad, et al., Nuclear Instruments and Methods in Physics Research B, 2014, 336, 167–172.

POSTDOCTORAL STUDIES



国立大学法人

東京海洋大学

Tokyo University of Marine Science and Technology



JSPS



Eesti Teadusagentuur
Estonian Research Council

2010 – 2012

Postdoctoral studies: „Structure-property relations of red algal galactans of different sulfation levels“ (硫酸基含有量の異なる紅藻類由来多糖の構造と溶液物性の関係).



Shinagawa campus

POLYSACCHARIDES FROM SEAWEED SPECIES OF JAPAN



Gloiopeltis furcata



Meristotheca papulosa



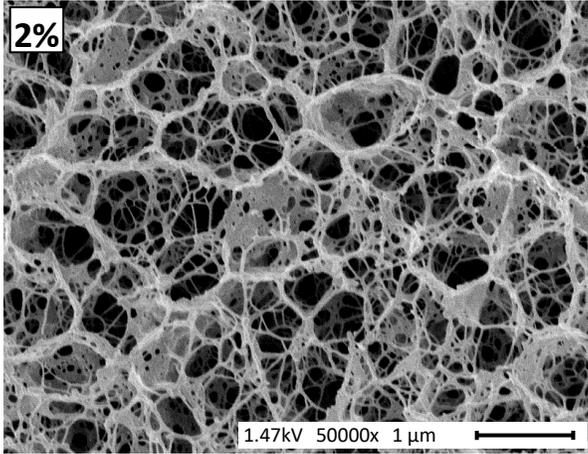
Pyropia yezoensis



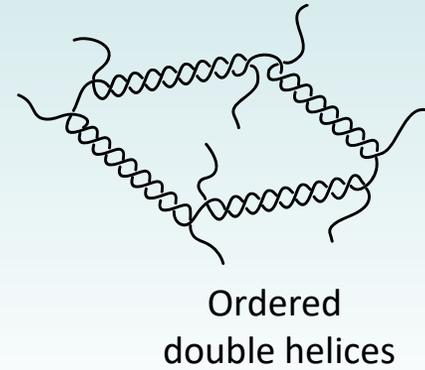
Gelidium elegans



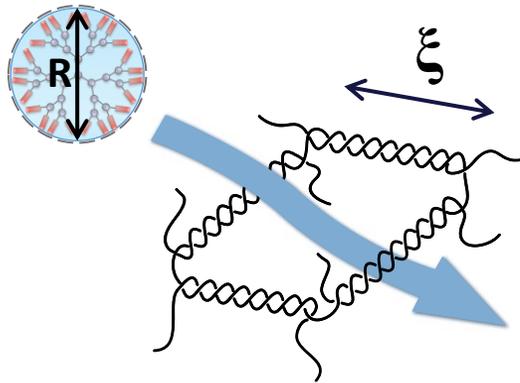
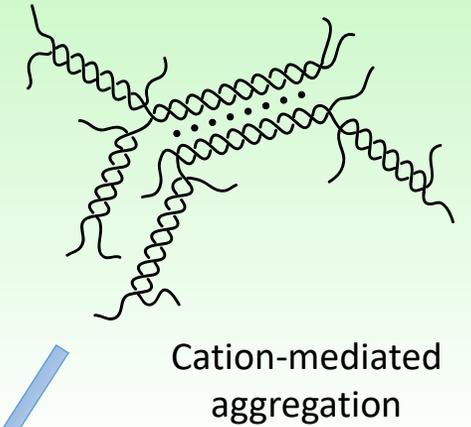
GEL STRUCTURE BY GRADIENT NMR



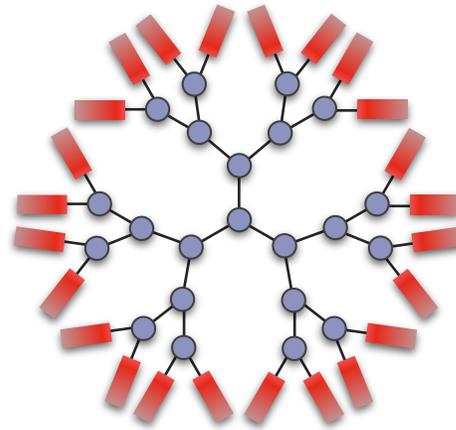
cooling



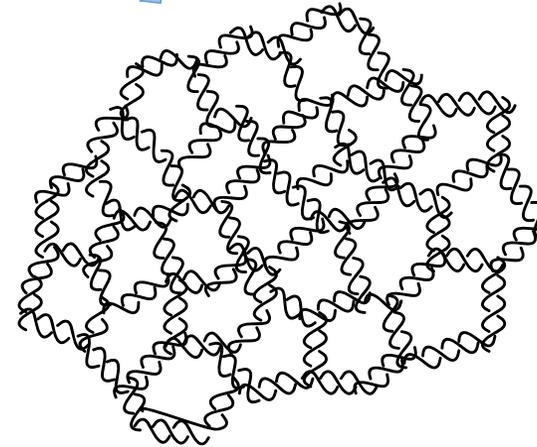
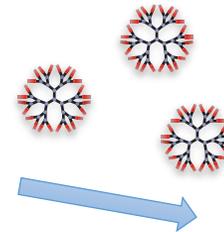
K⁺



$$\frac{D}{D_0} = \exp \frac{-R_H}{\xi}$$



Dendrimer



Ordered gel network

Dendrimers act as probe molecules to determine the mesh size of the network

FUNORAN



Gloiopeltis sp (フノリ)

Funoran – polysaccharides from the red algae of the genus *Gloiopeltis*.

Soluble in **cold water**.

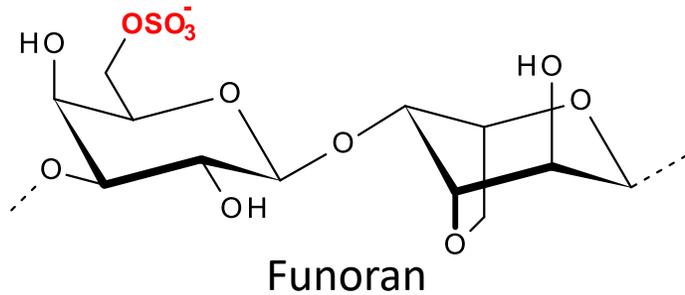
Forms **viscous solutions**.

Glue-like properties at high concentration.



SULPHATED AGAROSES – FUNORAN

6-O-sulfated agaroses from *Gloiopeltis* species.



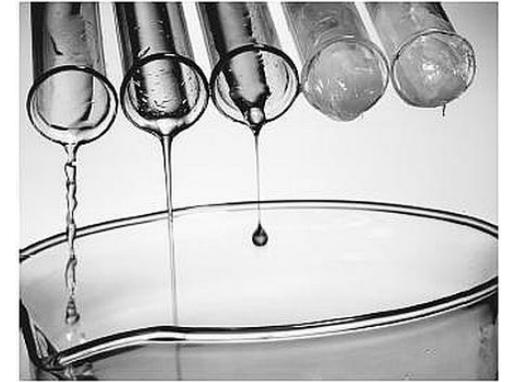
Dissolution at 20 °C (1.5% funoran)

+ CaCl₂ solution

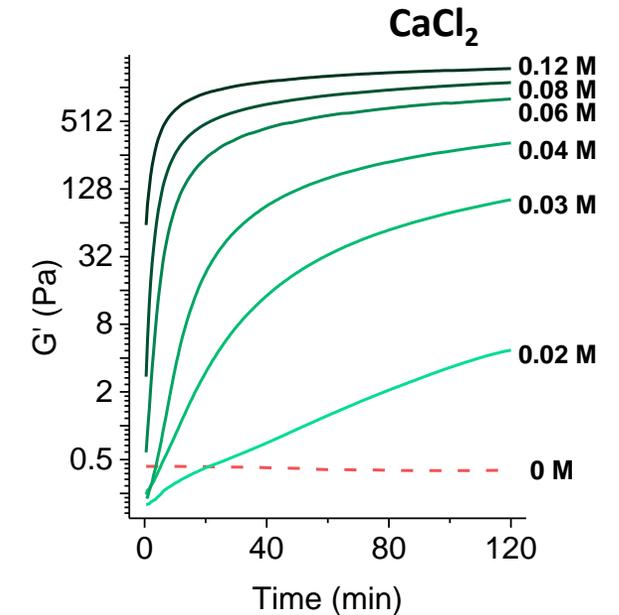
Rapid mixing

Gelation after 2 min

Transparent gels



Demonstrating funoran gelation 10 years after discovering the phenomenon (local media of Estonia).



1.5% funoran solutions at 15.8°C.

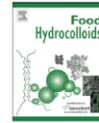
SULPHATED AGAROSES – FUNORAN

Food Hydrocolloids 43 (2015) 481–492

Contents lists available at ScienceDirect

Food Hydrocolloids

journal homepage: www.elsevier.com/locate/foodhyd



ELSEVIER

Funorans from *Gloiopeltis* species. Part I. Extraction and structural characteristics



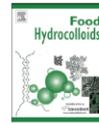
Rando Tuvikene^{a,b,d,*}, Marju Robal^a, Daisuke Fujita^c, Kadri Saluri^a, Kalle Truus^a, Yuri Tashiro^d, Hiroo Ogawa^d, Shingo Matsukawa^d

Food Hydrocolloids 43 (2015) 649–657

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ELSEVIER

Funorans from *Gloiopeltis* species. Part II. Rheology and thermal properties



Rando Tuvikene^{a,b,e,*}, Marju Robal^a, Hugo Mändar^c, Daisuke Fujita^d, Kadri Saluri^a, Kalle Truus^a, Tom Brenner^c, Yuri Tashiro^c, Hiroo Ogawa^c, Shingo Matsukawa^e

Algal Research 76 (2023) 103334

Contents lists available at ScienceDirect

Algal Research

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ELSEVIER

Structural and physicochemical characterization of funoran extracted from *Gloiopeltis furcata* by different methods



Marwa E. Atya^{a,d}, Xi Yang^a, Yuri Tashiro^b, Rando Tuvikene^c, Shingo Matsukawa^{a,*}

^a Department of Food Science and Technology, Tokyo University of Marine Science and Technology, 4-5-7 Konan, Minato-ku, 108-8477 Tokyo, Japan

^b Kyoto Prefectural University, Kyoto 606-8522, Japan

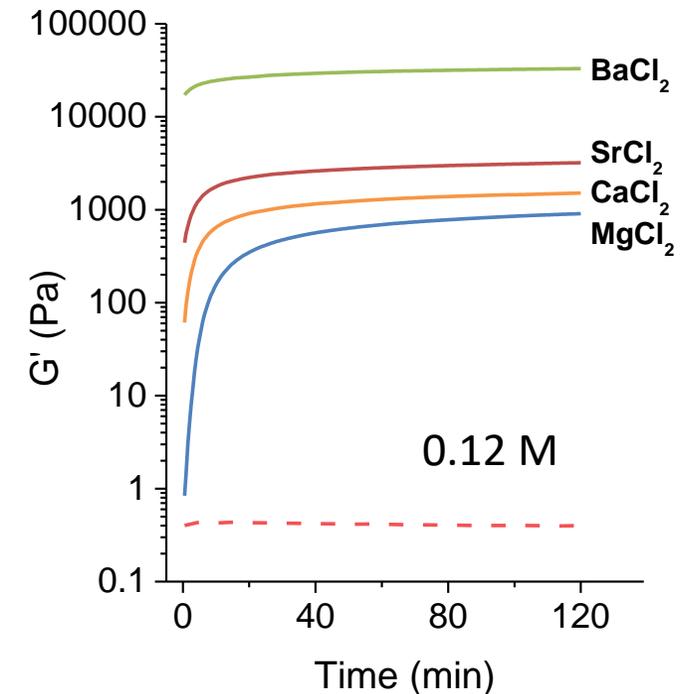
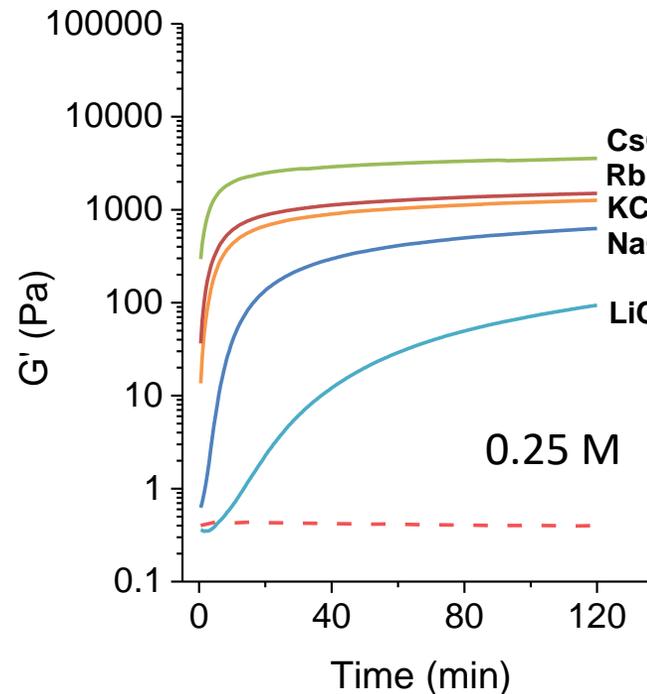
^c School of Natural Sciences and Health, Tallinn University, Narva mnt 29, 10120 Tallinn, Estonia

^d National Institute of Oceanography and Fisheries, Egypt

Cations enhance funoran gel formation in the orders:

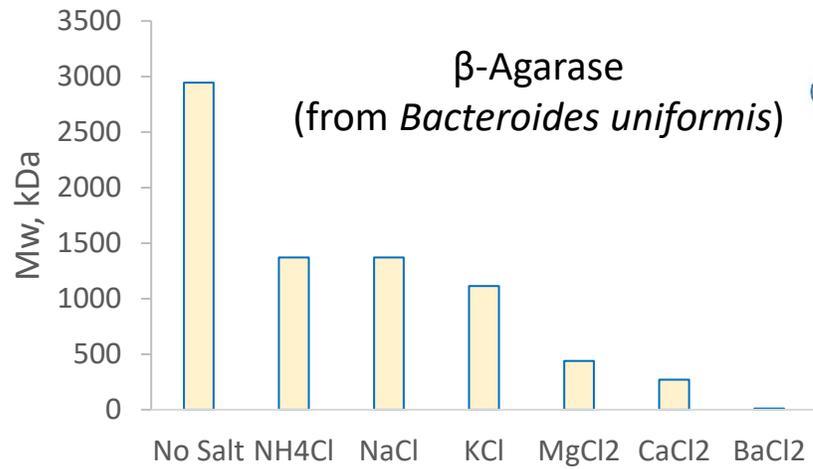
$\text{Ba}^{2+} \gg \text{Sr}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+}$

$\text{Cs}^+ > \text{Rb}^+ > \text{K}^+ > \text{NH}_4^+ > \text{Na}^+ \gg \text{Li}^+$

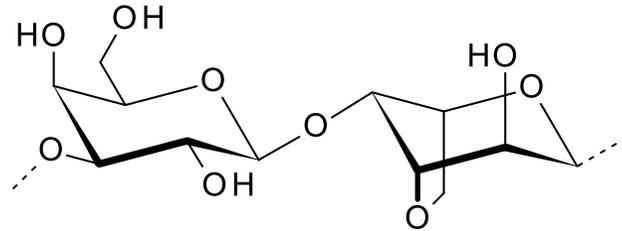
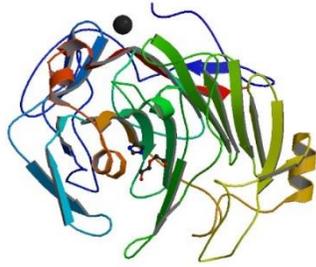


1.5% funoran solutions at 15 °C in the presence of various salts.

SULPHATED AGAROSSES – FUNORAN

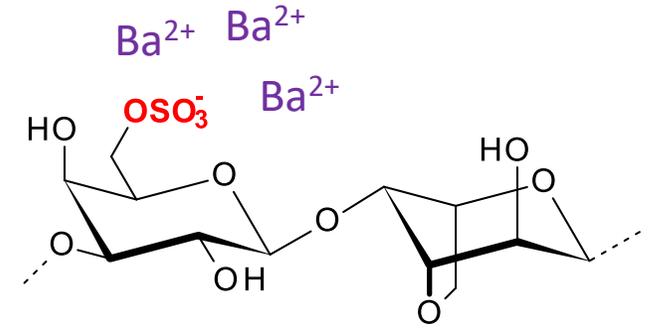


β -Agarase
(from *Bacteroides uniformis*)

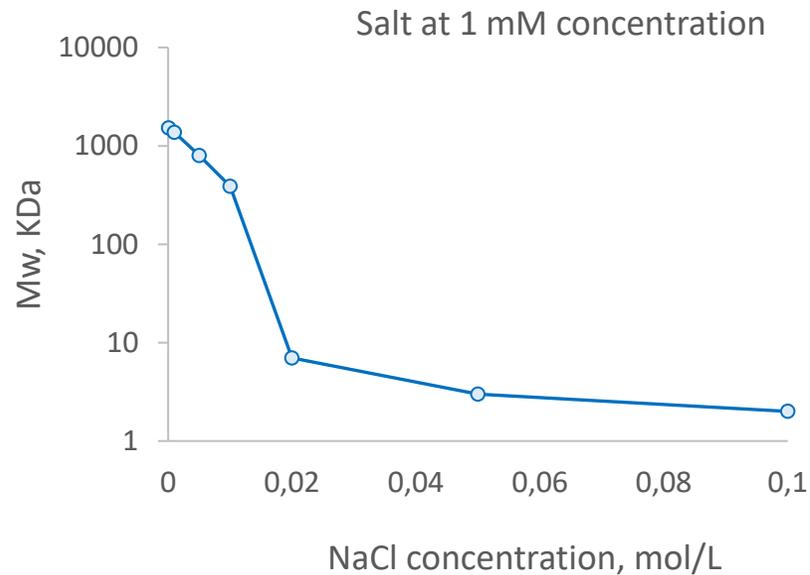


Agarose

Shielding effect



Funoran



Funoran samples degraded by β -agarase

Biocatalysis and Agricultural Biotechnology 43 (2022) 102394

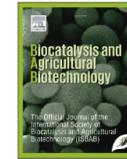


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Fermentation optimization, purification and biochemical characterization of a porphyran degrading enzyme with funoran side-activity from *Zobellia uliginosa*

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RESEARCH AND ITS FOCUS

Bipolymers

Isolation, purification

Characterization

Functionalisation

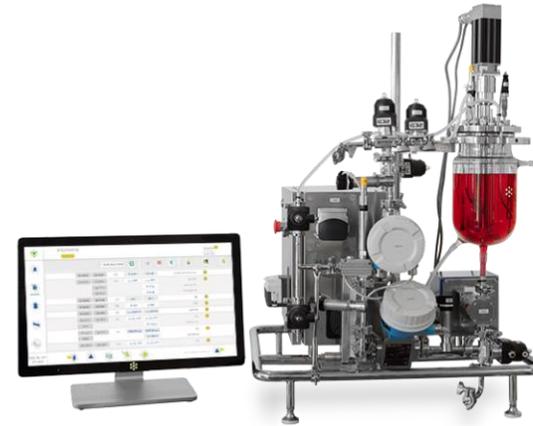
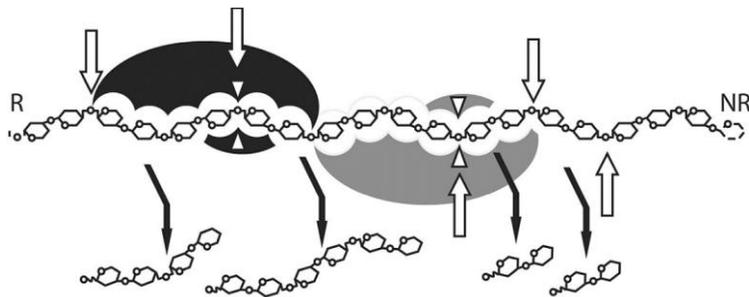
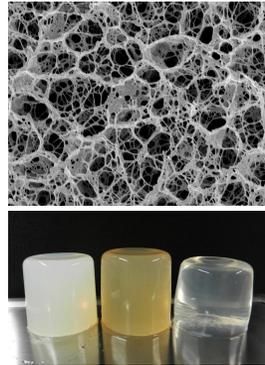
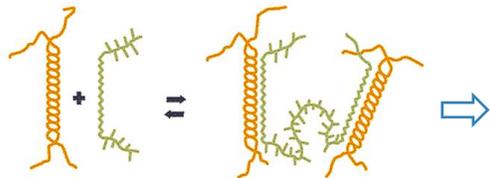
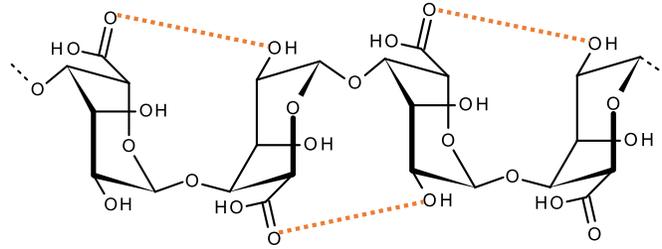
Interactions

Applications

Structure-property relations of polysaccharides

Biopolymers from **marine biomasses**

Polysaccharide degrading **enzymes**



Rheological properties
(texture, viscosity)

Biological
activities



MODIFICATION, STRUCTURAL UPGRADING

**Chemical, physical, enzymatic
modification**

THANK YOU FOR THE ATTENTION!