

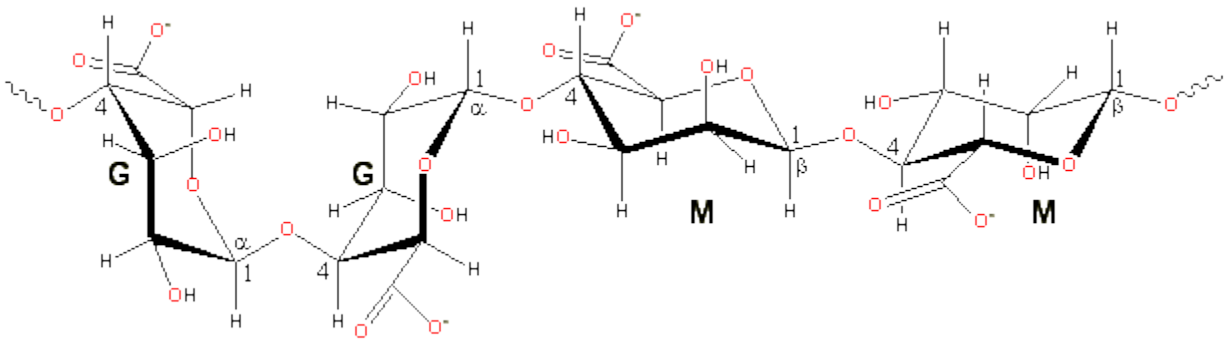
# Alginate

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## Source

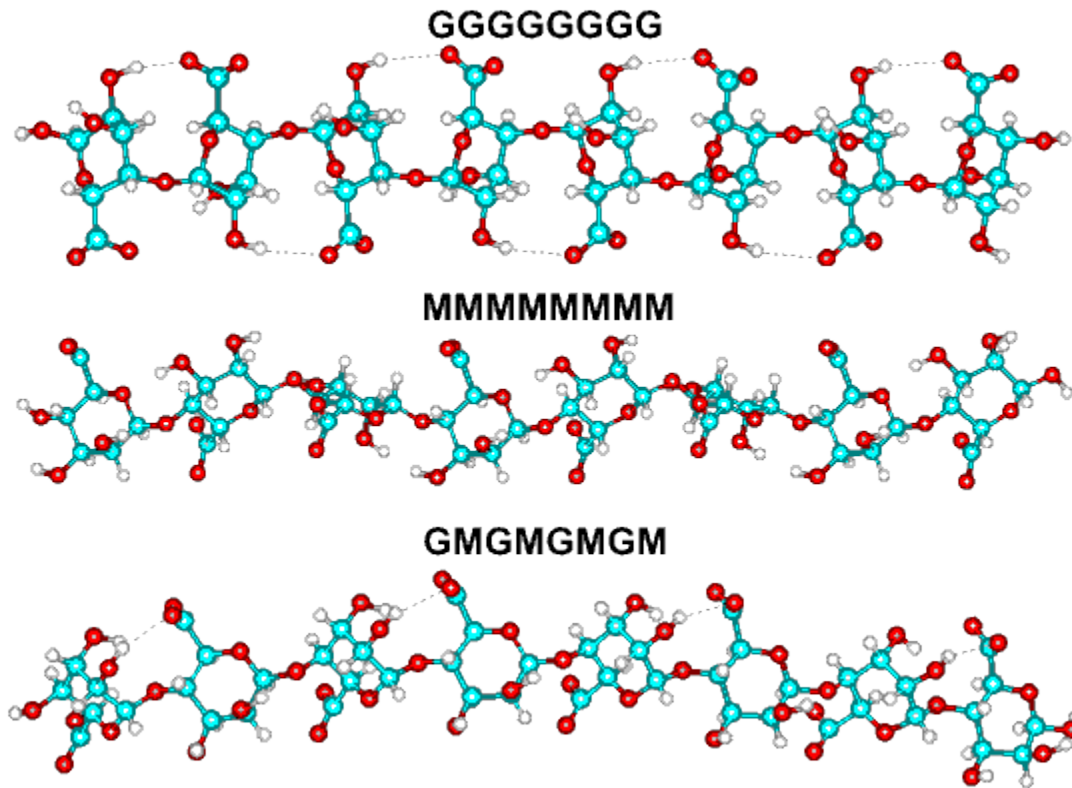
Alginates ([E400-E404](#)) are produced by brown seaweeds (*Phaeophyceae*, mainly *Laminaria*).

## Structural unit



Alginates are linear unbranched polymers containing  $\beta$ -(1 $\rightarrow$ 4)-linked D-mannuronic acid (**M**) and  $\alpha$ -(1 $\rightarrow$ 4)-linked L-guluronic acid (**G**) residues. Although these residues are epimers (D-mannuronic acid residues being enzymatically converted to L-guluronic after polymerization<sup>a</sup>) and only differ at C5, they possess very different conformations; D-mannuronic acid being  ${}^4C_1$  with diequatorial links between them and L-guluronic acid being  ${}^1C_4$  with diaxial links between them. Bacterial alginates are additionally O-acetylated on the 2 and/or 3 positions of the D-mannuronic acid residues. The bacterial O-acetylase may be used to O-acetylate the algal alginates, so increasing their water binding.

## Molecular structure :



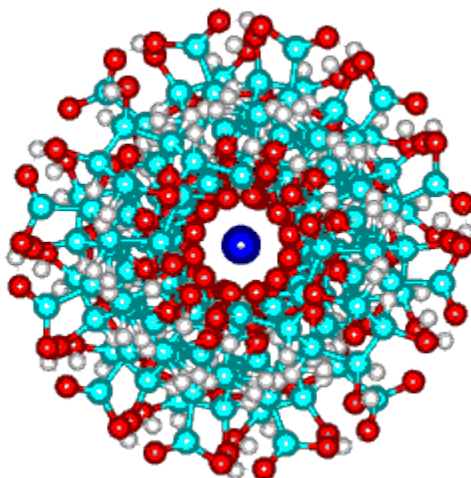
Alginates are not random copolymers but, according to the source algae, consist of blocks of similar and strictly alternating residues (that is, **MMMMMMMM**, **GGGGGG** and **GMGMGMGM**), each of which have different conformational preferences and behavior. As examples, the **M/G** ratio of alginate from *Macrocystis pyrifera* is about 1.6 whereas that from *Laminaria hyperborealis* about 0.45. Alginates may be prepared with a wide range of average molecular weights (50 - 100000 residues) to suit the application.

Poly  $\beta$ -(1 $\rightarrow$ 4)-linked D-mannuronate prefers forming a 3-fold left-handed helix with (weak) intra-molecular hydrogen bonding between the hydroxyl group in the 3 position and the subsequent ring oxygen (that is, O3-H $\rightarrow$ O'). Poly  $\alpha$ -(1 $\rightarrow$ 4)-linked L-guluronate forms stiffer (and more acid-stable) 2-fold screw helical chains, preferring intra-molecular hydrogen bonding between the carboxyl group and the 2-OH group of the prior residues and (weaker) the 3-OH group of the subsequent residues. The diaxial links also inherently allow less flexibility. Alternating poly  $\alpha$ -(1 $\rightarrow$ 4)-linked L-guluronate- $\beta$ -(1 $\rightarrow$ 4)-linked D-mannuronate contains both equatorial-axial and axial-equatorial links and take up dissimilar rather disorderly conformations. They have hydrogen bonds between the carboxyl group on the mannuronate and the 2-OH and 3-OH groups of the subsequent guluronate but the differing degrees of freedom of the two residues gives greater overall flexibility than the poly  $\beta$ -(1 $\rightarrow$ 4)-linked D-mannuronate chains. The free carboxylic acids (without counter

ion) have a water molecule  $\text{H}_3\text{O}^+$  firmly hydrogen bound to carboxylate ( $\text{pK}_a$  **M** 3.38,  $\text{pK}_a$  **G** 3.65).  $\text{Ca}^{2+}$  ions can replace this hydrogen bonding, zipping guluronate, but not mannuronate, chains together stoichiometrically in a supposedly egg-box like conformation (the ions being the eggs in the puckered box formed by sequential saccharides; the box possibly consists of six oxygen ligands from the 2-OH and 3-OH plus a carboxylate oxygen of the subsequent residue, supplied by each poly-guluronate chain) with 7<sup>th</sup> and 8<sup>th</sup> ligands from the (1 $\rightarrow$ 4)-O-linkages slightly further away. The chains are stabilized by hydrogen bonding between the other carboxylate oxygen and 2-OH groups on the subsequent residues. Poly-guluronate has specific binding sites for calcium consisting of five oxygen ligands from the 2-OH and 3-OH, (1 $\rightarrow$ 4)-O-linkage and carboxylate and ring oxygen of the subsequent residue, so holding the calcium ready for this junction zone formation. Initially dimers are formed [1379].

This junction zone optimally requires 10-12 residues (depending on parameterization) to form half a complete revolution (as optimized using the AMBER-96 force field [313]) of the parallel left-handed double helix (see below) and consequent permanent junction zone formation. Interactions with further poly-guluronate segments favor an unwound sheet-like structure; the winding -unwinding only requiring changes in the [anomeric linkage angles](#) ( $\phi$  and  $\psi$ ) of about  $10^\circ$  whilst retaining the hydrogen bonding and ionic linkages. A possibly-related two-stage junction zone formation has been recently proposed to occur in alginic acid gels, based on X-ray scattering and rheological characterization [603]. Curiously, calcium poly-guluronate also forms a (only slightly less) stable parallel right-handed helix ( $\phi$  and  $\psi$  further changing by about  $10^\circ$ ) of about the same number of residues per helix where the calcium ions sit in a pocket approximately equispaced from 10 oxygen ligands (from the 2-OH and 3-OH, (1 $\rightarrow$ 4)-O-linkage and a carboxylate and ring oxygen of the subsequent residue from both chains) and where hydrogen bonds are found from alternative carboxyl groups and both the prior 2-OH group and the 3-OH group of the prior residues on the parallel strand. Under similar conditions, poly-mannuronic acid blocks take up a less-gelling ribbon conformation, where carboxylate groups on sequential residues may bind calcium intra- or inter-molecularly.

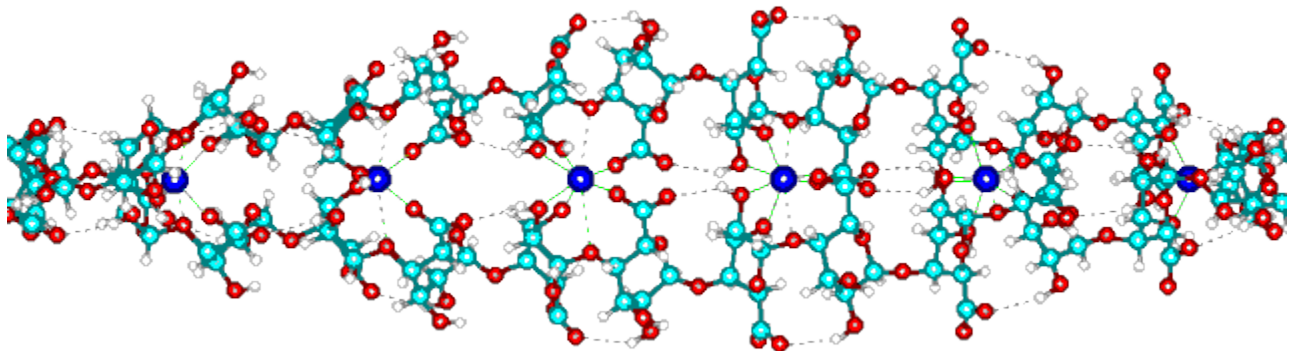
### Calcium poly- $\alpha$ -L-guluronate left-handed helix



Possible helix formation from egg-box dimers.

view down axis ➤

▼ view along axis, showing the hydrogen bonding and calcium binding sites.



'Designer' alginates may be available in the future by the 5-epimerization of  $\beta$ -(1 $\rightarrow$ 4)-linked D-mannuronic acid residues to  $\alpha$ -(1 $\rightarrow$ 4)-linked L-guluronic acid residues in algal alginates using bacterial epimerases. An available natural alternative is to harvest the seaweed from exposed seaboards (more **G** giving the kelp strength) or sheltered bays (more **M**).

## Functionality

The primary function of the alginates are as thermally stable cold setting gelling agents in the presence of calcium ions; gelling at far lower concentrations than [gelatin](#). Such gels can be heat treated without melting, although they may eventually degrade. Gelling depends on the ion binding ( $\text{Mg}^{2+} \ll \text{Ca}^{2+} < \text{Sr}^{2+} < \text{Ba}^{2+}$ ) with the control of the di-cation addition being important for the production of homogeneous gels (for example, by ionic diffusion or controlled acidification of  $\text{CaCO}_3$ ). High **G** content produces strong brittle gels with good heat stability (except if present in low molecular weight molecules) but prone to water weepage (syneresis) on freeze-thaw, whereas high **M** content produces weaker more-elastic gels with good freeze-thaw behavior and high **MGMG** content zips with  $\text{Ca}^{2+}$  ions to reduce shear [760]. However, at low or very high  $\text{Ca}^{2+}$  concentrations high **M** alginates produce the stronger gels. So long as the average chain lengths are not particularly short, the gelling properties correlate with average **G** block length (optimum block size  $\sim 12$ ; see also the similarity to [pectin](#) gelling) and not necessarily with the **M/G** ratio which may be primarily due to alternating **MGMG** chains. The future prospects are

excellent as recombinant epimerases with different specificities may be used to produce novel designer alginates.

Alginate's solubility and water-holding capacity depend on pH (precipitating below about pH 3.5), molecular weight (lower molecular weight calcium alginate chains with less than 500 residues showing increasing water binding with increasing size), ionic strength (low ionic strength increasing the extended nature of the chains) and the nature of the ions present. Generally alginates show high water absorption and may be used as low viscosity emulsifiers and shear-thinning thickeners. They can be used to stabilize phase separation in low fat fat-substitutes for example, as alginate/caseinate blends in [starch](#) three-phase systems. Alginate is used in a wide variety of foodstuff such as pet food chunks, onion rings, stuffed olives, low fat spreads, sauces and pie fillings. The health roles of alginates have been reviewed [[1679](#)].

Propylene glycol alginates have widespread use as acid-stable stabilizers for uses such as preserving the head on beers.

Interactive structures are available ([Jmol](#)).

Source : <http://www1.lsbu.ac.uk/water/hyalg.html>