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The Principle of Polysaccharide Gels

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Abstract

For several decades attention has been directed to natural polysaccharide gels and synthesized polymer gels. The structure-function relationships at molecular level in water of polysaccharides, κ-carrageenan, ι-carrageenan, agarose (agar), and gellan family of polysaccharides (gellan, welan, rhamsan, S-657, deacetylated rhamsan and native gellan gum), which are industrially useful polysaccharides extracted from family of red seaweeds and bacteria, in principle are discussed on the view point of rheological aspects. The polysaccharide molecules (0.1% - 1.0%) play a dominant role in the center of the tetrahedral cavities occupied by water molecules (99.0% - 99.9%), and the arrangement is similar to a tetrahedral structure in a gelation process. The cage and hydrophobic effect play thermal dynamically dominant role in gelation process which gives lowest entropy to electrons of sugar residues. Though the chemical structure of these polysaccharides similar each other, their rheological (gelling) characteristics are quite different. Many investigations about the gelling properties of the polysaccharides have been undertaken to elucidate the structure-function relationship, but no other researchers have established mechanism at the molecular level. There is consistency in our investigations. Thus, the rheological analysis is one of significant methods for understanding the structure-function relationship of polysaccharides in aqueous media. The discussion provides many important information not only in academic field, but also in industrial one, such as food, cosmetic, pharmaceutical, drug delivery and tissue industries, and biotechnology.

1. Introduction

Gels are solid, jelly-like materials formed from colloid polysaccharides, proteins and synthesized polymers. Gels

have been applied in the food, cosmetic, paint, pharmaceutical, photographic, petroleum and chemical industries, and have additional potential uses in catalysis, separation of materials, drug delivery, and tissue engineering. Recently, many applications of polysaccharide and synthesized polymer conjugated gels are discovered because of the gel's ability to trap and immobilize functional agents, such as enzymes, pharmaceuticals, tissue engineering and other bioactive agents. Specifically, some polysaccharides are paid attentions to develop in biomedical applications [1]-[3].

Polysaccharides that are produced commercially from seaweeds, plants, animals and micro-organisms have been used in food, cosmetic, paper, textile, oil, pharmaceutical, medical, and other industries as viscous enhancing, water-holding, emulsifying, oil-drilling, coating, encapsulating, protective, gelling and other agents. Specifically, for several decades attention has been directed to polysaccharide gels. Therefore, we previously investigated the structure-function relationship [4] and gelation mechanism of polysaccharides in aqueous solutions at a molecular level using a rheogoniometer, polarimeter and ^{1}H-NMR spectrometer. The polysaccharides, such as κ-carrageenan [5]-[7], ι-carrageenan [8] [9], agarose (agar) [10], gellan gum [11] [12], amylose [13] [14], curdlan [15], alginate [16] [17], and deacetylated rhamsan gum [18], in water changed into an ice-like structure with hydrogen bonding between polymer and water molecules, and between water-water molecules even at a concentration range of 0.1% - 1.0% (W/V) at room temperature, resulting in gelation. Such dramatic changes from liquid into gels have been understood at the molecular level in principle [19]. Amylopectin (rice) [20]-[22] and starch (rice, potato and wheat) gelatinization [23]-[27] and retrogradation [26] [28] processes including water molecules were also discussed at molecular level in principle [29].

We review herein the gelation mechanism of κ-carrageenan [5]-[7], ι-carrageenan [8] [9], agarose(agar) [10] and gellan family of polysaccharides [11] [12] [30]-[33] which are industrial useful polymers and discuss their structure-gelling relationship in principle. Though the chemical structure of these polysaccharides similar each other (**Figure 1**), their rheological (gelling) characteristics are quite different.

2. Gelation Mechanism of Polysaccharides

As metioned above, we proposed gelation mechanism for κ-carrageenan [5]-[7], ι-carrageenan [8] [9], agarose (agar) [10], gellan gum [11] [12], amylose [13] [14], curdlan [15], alginate [16] [17], and deacetylated rhamsan gum [18] at the molecular level. Though xanthan gum which is one of bacterial polysaccharides produced commercially by *Xanthomonas campestris* does no gel alone, but shows curious rheological characteristics [34]-[39] and forms gel in a mixture solution with galactomannan [40]-[46] and glucomannan [47] [48]. We proposed co-gelation mechanism of xanthan and galactomannans (locust-bean gum [40]-[42], guar gum [43], tara-bean gum [44], *Leucaena* gum [45], *Leonix* gum [46], and konjac glucomannan [47] [48]. A little interaction was observed in a mixture of high galactose content guar gum (33%) or *Leucaena* gum (40%). The results indicated that the
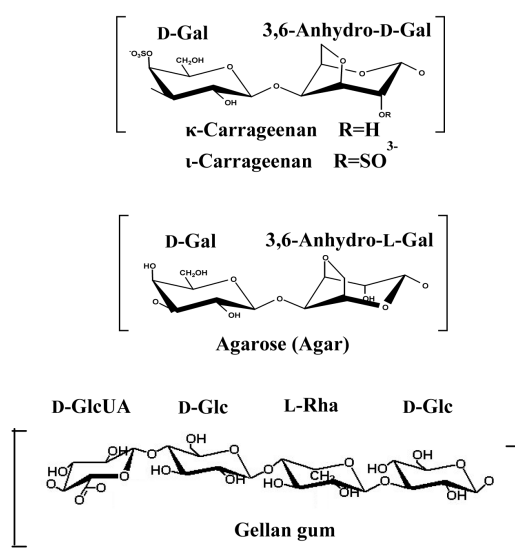
Figure 1. Chemical structure of carrageenans, agarose and gellan gum.

weak interaction was due to the presence of side-chains of the galactomannan molecules. These side-chains prevented the insertion of the charged trisaccharide side-chains of the xanthan molecules into the galactomannan molecules. More strong co-gelation than that of galactomannan (locust-bean gum) occurred in a mixture solution of xanthan and konjac glucomannan [47] [48] due to free from side-chains on the latter molecules. The D-mannose-specific interaction between the extra-cellular bacterial polysaccharide xanthan and typical galactomannan and glucomannan components of the plant cell wall suggest a role in the host-pathogen relationship because *Xanthomonas campestris* is one of the plant pathogen bacteria.

We also discussed the molecular origin for the thermal stability of non-gelling polysaccharides, such as, welan [30], rhamsan [31] [32], S-657 gum [33], S-88 gum [49], schizophyllan [50], and rice amylopectin [20]-[22]. The structures of these polysaccharides are similar to those of the gelling polysaccharides, gellan gum, curdlan and amylose. The thermal stability of the polysaccharides as described above is attributed to intramolecular associations (hydrogen bonding and van der Waals forces of attraction), where methyl and hydroxyl groups, and hemiacetal oxygen atom contributed.

We observed that there are some basic rules in the gel-formation processes of polysaccharides [19] [29]. The gelation occurs because of the formation of intra- and inter-molecular associations, where hemiacetal oxygen, hydroxyl or methyl groups of the sugar residues of the polysaccharides contribute to hydrogen bonding or van der Waals forces of attraction. The sulfuric acid and carboxyl groups of the sugar residues of certain acidic polysaccharides, e.g., κ-carrageenan, ι-carrageenan, gellan gum, alginic acid, and deacetylated rhamsan gum also participated in intra- and/or intermolecular associations through univalent or divalent cations that have ionic bonding or electrostatic forces of attraction.

2.1. Gelation Mechanism of κ-Carrageenan

κ-Carrageenan is well known for its gel-forming property [5] [7] [51]-[56]. The polysaccharide consists of alternating disaccharide units of O-3-linked β-D-galactopyranosyl 4-sulfate and O-4-linked 3,6-anhydro-D-galactopyranosyl residues (**Figure 1**) and used in food, cosmetic and other industries. A very large increase in elastic modulus was observed on addition of 13.5 mM KCl to a 0.2% solution of κ-carrageenan [5]. The tendency of the curve showing the elastic modulus for an increase in temperature up to 10˚C suggested that intra- and inter-molecular association co-involved. However, least elastic modulus was observed on addition of 16.6 mM NaCl. κ-Carrageenan is a cation-selective binding polymer [5] [51]-[56], which gels in the presence of large-site univalent cations, such as K$^+$ (van der Waals rad. 275 pm), Rb$^+$ (303 pm) and Cs$^+$ (343 pm), but does not do so in the presence of small cations, *i.e.*, Na$^+$ (227 pm) and Li$^+$ (182 pm). This characteristic behavior was confirmed for the potassium and sodium salts of κ-carrageenan in our study [5] [7]. The cations having a negative Jones-Dole B coefficient of viscosity are structure disordering and show negative hydration of water molecules, whereas the cation having a positive coefficient are structure ordering and show positive hydration [57] [58]. The K$^+$ ion has a negative B coefficient whereas the Na$^+$ ion has a positive one. Furthermore, the 3,6-anhydro-α-D-galactose residues affect the hydrophobic character of the polymer by controlling its solubility. At low temperature, in the presence of ionic bonding between the sulfate and a large cation, it would be attracted to the adjacent 3,6-anhydro oxygen atom by the electrostatic forces of attraction.

On this basis, we proposed an intramolecular K$^+$-bridge on κ-carrageenan molecule between sulfate oxygen of C-4 which oriented at axial configuration of D-galactopyranosyl residue and 3,6-ring oxygen of 3,6-anhydro-α-D-galactopyranosyl residue, as illustrated in **Figure 2** [5]. The bridge built up at low temperature, owing to the decrease in kinetic energy and Brownian motion of the molecular chains and solvent (water), but dissociation take place at temperature range of 10˚C - 25˚C, which was estimated to be a transition temperature, owing to an increase in kinetic energy and Brownian motion. The intramolecular bridge does not take place in the presence of Na$^+$ ion in spite of the ionic bonding still being present at low temperature, because the radius of the ion is too small for an association with the ring oxygen group and the presence of too much hydration prevents an electrostatic forces of attraction being involved in the bridge. The cation-specific intramolecular bridge, which was preferentially placed to make polysaccharide molecule rigid, was the first demonstration of this effect at a molecular level [5]. The bridge is likely to be established in view point of the flexibility of the α-D-(1→3) linkage between the 3,6-anhydro-D-galactopyranosyl and the D-galactopyranosyl-4-sulfate, the sulfate group of which is oriented at axial configuration and corresponds to a rod-like and less extended structure.

On the basis of the intramolecular cation-bridge proposed, a model of intermolecular association of the κ-carrageenan molecules was developed [6] [7]. As the kinetic energy and Brownian motion of the molecules and
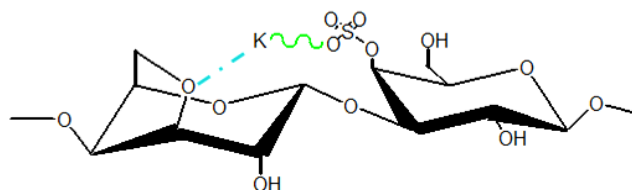
Figure 2. Intramolecular cation selective bridge in κ-carrageenan inaquesou solution at low temperature: ( ) ionic bonding and ( ) electrostatic forces of attraction.

solvent decreases at low temperature, many intramolecular cation-bridges serve to keep rigid the chains, which results in an intermolecular association. This suggests that the ring oxygen groups play the same role in the intermolecular association as do the sulfate groups. Thus, we proposed an intermolecular association between sulfuric acid groups on different molecules with electrostatic forces of attraction, as presented in **Figure 3** [6] [7]. The transition temperature was observed at 25˚C where inter- and intramolecular associations dissociated above the temperature.
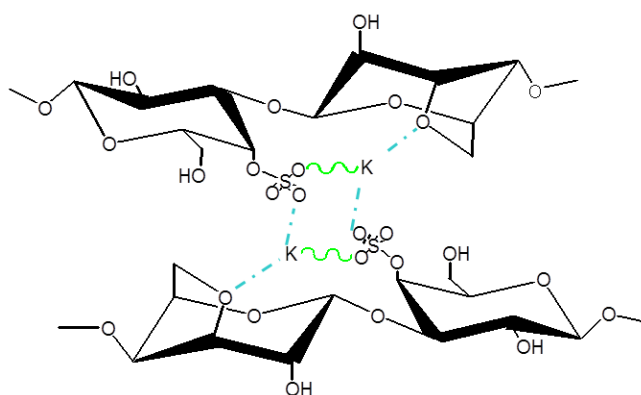
2.2. Gelation Mechanism of ι-Carrageenan

ι-Carrageenan is a more highly sulfated galactan and is also most characterized polysaccharide [59]-[65]. The polymer consist of O-3-linked β-D-galactopyranosyl 4-sulfate and O-4-linked 3,6-anhydro-α-D-galactopyranosyl 2-sulfate residues (**Figure 1**). The polysaccharide is used in food, cosmetic and other industries as in κ-carrageenan. Gelation occurred for Ca-salt of ι-carrageenan on cooling, but did not for K or Na salts [8]. The transition temperature was observed at 45˚C. Furthermore, a little increase in elastic modulus was observed during increasing temperature up to 10˚C as same as in κ-carrageenan solution [5]. We concluded that the Ca salt of ι-carrageenan involves an intramolecular association through Ca cation with ionic bonding between sulfate oxygens, as illustrated in **Figure 4** [8]. Each cation is co-ordinated to two sulfate groups by ionic bonding. Since ionic bonding is stronger than electrostatic forces of attraction, the molecular chain become rigid even at room temperature and, therefore, intermolecular associations take place.

Thus intramolecular Ca-bridge proposed was developed into an intermolecular association mechanism of the Ca salt of ι-carrageenan [8]. The intermolecular Ca-bridges may take place on different molecules having electrostatic forces of attraction (**Figure 5**). The intra- and inter-molecular cation bridges of the Ca-salt of ι-carrageenan differs essentially from that of the K-salt of κ-carrageenan, because the former consists of double ionic forces and electrostatic forces of attractions, whereas the latter consists of single bonding and triple electrostatic forces of attraction. These different mechanism provide an explanation for the conformational transition of ι- and κ-carrageenan in aqueous solution. Since ionic bonding is stronger than electrostatic forces of attraction, the molecular chain can keep rigid even at intermediate temperature (45˚C) which was conformational transition temperature [8]. Intra- and inter-molecular Ca-bridges dissociate above the transition temperature.

2.3. Gelation Mechanism of Agarose (Agar)

Agarose is the major gelling constituent of agar extracted from red seaweeds. The polymer forms strong gelling ability [10] [66] [67] and is used in the separation, purification, and characterization of biomacromolecules in such techniques as gel filtration, affinity chromatography [68], hydrophobic chromatography [69] and electrophoresis. The polymer is currently attempted to use in pharmaceutical [1], drug delivery and tissue engineering [3] as a gelling agent. It consists of a copolymer alternating O-3-linked β-D-galactopyranosyl and O-4-linked 3,6-anhydro-α-L-galactopyranosyl residues, the structure of which is similar to that of κ-carrageenan and ι-carrageenan, except for the sulfate content and L-configuration (**Figure 1**).

Gelation occurred at a concentration of 0.08% at low temperature (0˚C) and stayed constant during increase in temperature up to 60˚C in the presence of 0.1% of salt (NaCl, KCl, CaCl$_2$, or MgCl$_2$), then decreased rapidly with further increase in temperature [10]. This might be caused by salting-out effect which might take place because of the rigidity of the molecular chains of agarose through the formation of intra- and inter-molecular association, resulting from the tetrahedral distribution of anhydro-α-L-galactosyl residues and water molecules. However, the least elastic modulus was observed in the presence of urea (4.0 M). Thus, we proposed an intra-

Figure 3. Gelation mechanism of κ-carrageenan: (〰〰) ionic bonding and (— · —) electrostatic forces of attraction.
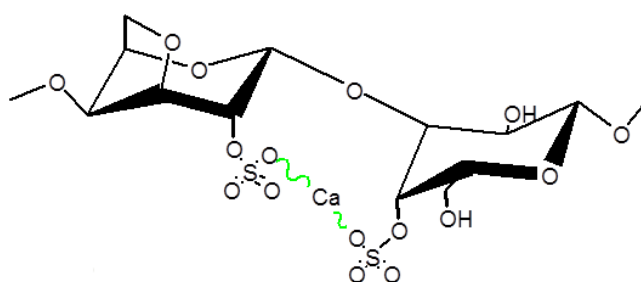

Figure 4. Intramolecular Ca^{2+} bridge with ionic bonding (〰〰) in ι-carrageenan molecule.
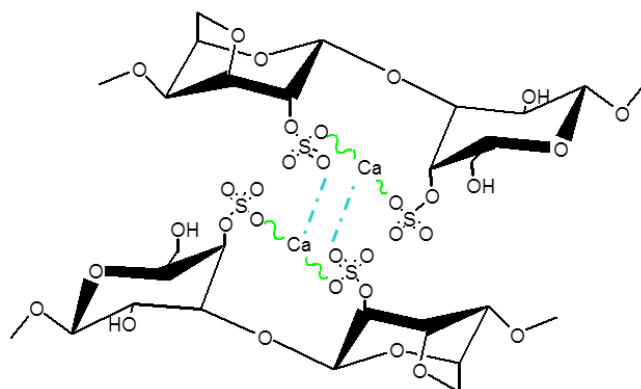
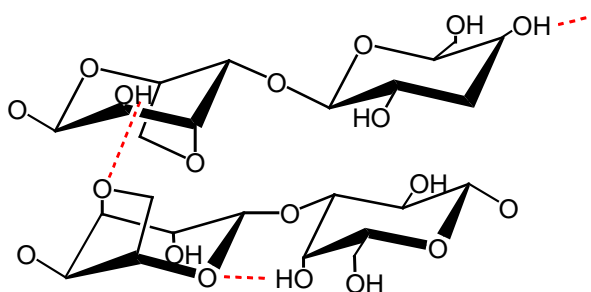**Figure 5.** Gelation mechanism of ι-carrageenan: (〰〰) ionic bonding and (— · —) electrostatic forces of attraction.

molecular hydrogen bonding between OH-4 which oriented at axial configuration of the β-D-galactopyranosyl and the adjacent hemiacetal oxygen atom of the 3,6-anhydro-α-L-galacctopyranosyl residues (**Figure 6**) [9]. The 3,6-anhydro-L-galactopyranosyl residue is a cage-like sugar that contributes by stabilizing the proposed intra-molecular hydrogen bonding, even at high temperature > 60°C. Intermolecular hydrogen bonding was also pro-posed between the ring O-3,6-atom and the OH-2 which oriented at axial configuration of 3,6-anhydro-α-L-ga-lactopyranosyl residues on different molecules (**Figure 7**) [10]. This intermolecular hydrogen bonding results from the cage effect of the 3,6-anhydro-α-L-galactopyranosyl residues which adopt a tetrahedral distribution and therefore attract not only each other, but also water molecules with hydrogen bonding. The mode of intra- and intermolecular hydrogen bonding of agarose molecules has been supported by ^{1}H- and ^{13}C-NMR spectroscopy [70].
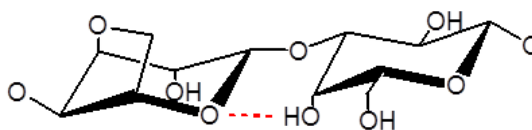
Figure 6. Intramolecular hydrogen bonding (— — —) in agarose molecule.

Figure 7. Gelation mechanism of agarose. (— — —): Hydrogen bonding.

Although agarose is a diastereomeric derivative of κ-carrageenan and ι-carrageenan, it shows an intramolecular association similar to that of the κ- and ι-carrageenan. The role of such polysaccharides in biological tissues seems to be the cohesion, the retention of water and salts, and the physical organization. Thus, the gelation mechanisms for these polysaccharides, proposed may be useful for further developments of not only industrial applications, but also for an understanding of the biological functions.

2.4. Molecular Origin for Rheological Characteristics of Gellan Family of Polysaccharides, Gellan, Welan, Rhamsan, S-657 Gum and Deacetylated Rhamsan Gum

2.4.1. Gelation Mechanism of Gellan Gum

Gellan gum is a bacterial polysaccharide produced by *Sphingomonas elodea* and has potential industrial applications as a gelling agent alternate to agar (agarose) and carrageenans in food industry and biotechnology [71] [72]. The primary structure of the polysaccharide consists of tetrasaccharide repeating units (**Figure 1**), 3)-β-D-Glc$p$-(1→4)-β-D-Glc$p$UA-(1→4)-β-D-Glc$p$-(1→4)-α-L-Rha$p$-(1 [73] [74]. The polysaccharide contains 6% of *O*-acetyl and L-glycerate groups at C-6 and C-2 of →3)-β-D-Glc$p$-(1 [75]. Under suitable condition, the native gellan gum forms weak gels [12], however, it forms stiff, brittle gels on deacylation [11] as in agarose. The physicochemical investigations for deacylated gellan gum were done by many workers [76]-[78]. A tertiary structure of the polymer was reported to consist of two identical left-handed, 3-fold double helices in the solid state [78] similar to that of agarose.

A gelation occurred in gellan gum (K$^+$ salt) concentration at 0.8% upon cooling and transition temperature was observed at 15°C and 20°C at 0.8% and 1.0% [11]. In the presence of CaCl$_2$ (6.8 mM), very large increase in elastic modulus was observed in 0.2% gellan solution and kept a constant value during increase in temperature to 80°C, which was estimated to be a transition temperature, then decreased rapidly. It meant that the thermal stable gelation occurred. However, the polymer showed a little increase in elastic modulus even at 0.4% in the presence of KCl (13.5 mM), but stayed at low value with addition of NaCl (16.6 mM). On the contrary, an increase in elastic modulus occurred in the presence of urea (4.0 M) which was well known as a hydrogen bonding breaker. The result suggested that hydrophobic interaction took place in gel formation process [12].

On the basis of the experimental results, we proposed a gelation mechanism of gellan gum as shown in **Figure 8**. The intramolecular hydrogen bonding might take place between OH-4 of the D-glucopyranosyl residue and the adjacent hemiacetal oxygen atom of the L-rhamnopyranosyl residue and between OH-3 of the D-glucopyranosyl residue and the adjacent hemiacetal oxyten atom of the D-glucuropyranosyl residue, to make gellan gum molecule rigid. The thermal stable gelation might be attributed to contributing methyl group of L-rhamnopyranosyl residue [11] [12]. Thus, we proposed an intermolecular van der Waals interaction between the methyl group which oriented at axial configuration of the L-rhamnopyranosyl residue due to taking $^4C_1$ py-
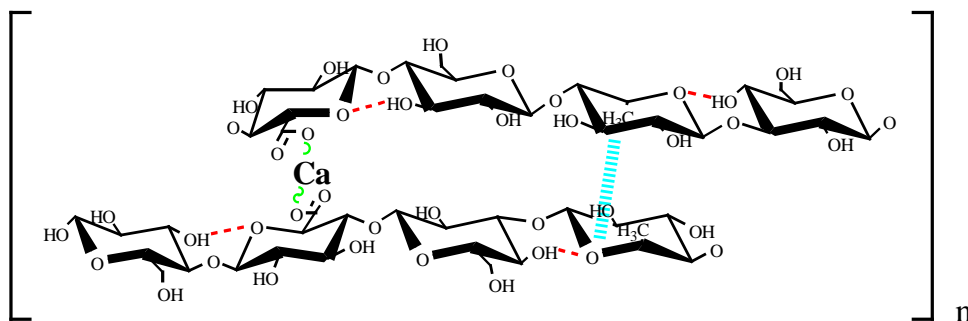
Figure 8. Gelation mechanism of gellan gum in aqueouss solution. Association; ‒ ‒ ‒, Hydrogen bonding; ∿∿∿, ionic bonding; ⁄⁄⁄⁄, van der Waals forces of attraction.

ranose-ring conformation and the hemiacetal oxygen atom of the L-rhamnopyranosyl residue on different molecules. In the presence of Ca^{2+} ions, an intermolecular Ca^{2+} bridge also took place with ionic bonding between carboxyl oxygen atoms of D-glucuropyranosyl residues on different molecules. The intermolecular van der Waals forces of attraction and ionic bonding were stable even at high temperature (80˚C).

2.4.2. Molecular Origin for Thermal Stability of Welan Gum

Welan gum is produced by *Alcaligenes* ATCC 31555, and is non-gel forming, but gives a thermostable highly viscous solutions at a high temperature > 100˚C [71] [72] [79] [80]. The main chain of welan gum consists of tetrasaccharide repeating units as in gellan gum and every D-glucopyranosyl residue next to the D-glucuropyranosyl residue is substituted at *O*-3 by either α-L-rhamnopyranosylot α-L-mannopyranosyl residue in the ratio of 2:1 [81].

The elastic modulus was scarcely changeable with increasing temperature even in 1.0% solution at high temperature (80˚C) [30]. A little decrease of elastic modulus was observed with addition of $CaCl_2$ (6.8 mM), indicating that side-chains of welan gum molecules prevent the formation of intermolecular Ca^{2+} bridges. Thus, intramoleclar associations between the OH-4 of the D-glucopyranosyl residue and the adjacent hemiacetal oxygen atom of the L-rhamnopyranosyl residue with hydrogen bonding, and between the methyl group of the L-rhamnopyranosyl residue which oriented at equatorial configuration because of taking $^1C_4$ pyranose-ring conformation and the adjacent hemiacetal oxygen atom of the D-glucopyranosyl residue with van der Waals forces of attraction were proposed (**Figure 9**) [30]. The intramolecular associations contributed to the thermal stability of the polysaccharide in aqueous solutions.

2.4.3. Molecular Origin for Thermal Stability of Rhamsan Gum

Rhamsan gum is produced by *Alcaligenes* ATCC 31961, and non-gel forming but gives a thermostable, highly viscous solution even at high temperature > 100˚C [71] [72]. The main chain of the rhamsan gum consists of tetrasaccharide repeating units as in gellan gum and every D-glucopyranosyl residue next to the L-rhamnopyranosyl residue is substituted at C-6 by β-D-glucopyranosyl-(1→6)-α-D-glucopyranosyl disaccharide side-chains [82].

A very large elastic modulus was observed at concentration above 0.3% and kept a constant value with increasing temperature [31] [32]. A weak sigmoid curve was shown at 1.0% concentration the phenomenon of which was similar to that of xanthan gum [34] [38] [39]. The elastic modulus of rhamsan gum (0.2%) showed almost the same values with addition of $CaCl_2$ (6.8 mM) during increase in temperature in comparison with polysaccharide alone. Thus, intramoleclar associations between the OH-4 of the D-glucopyranosyl residue and the adjacent hemiacetal oxygen atom of the L-rhamnopyranosyl residue with hydrogen bonding, and between the methyl group of the L-rhamnopyranosyl residue which oriented at equatorial configuration and the adjacent hemiacetal oxygen atom of the D-glucopyranosyl residue with van der Waasl forces of attraction were proposed (**Figure 10**) [31] [32]. The intramolecular association contributed to the thermal stability of the polysaccharide in aqueous solutions.

2.4.4. Molecular Origin for Thermal Stability of S-657 Gum

The S-657 gum produced by *Xanthomonas* ATCC 53159 is non-gelling but gives a thermostable, highly viscous
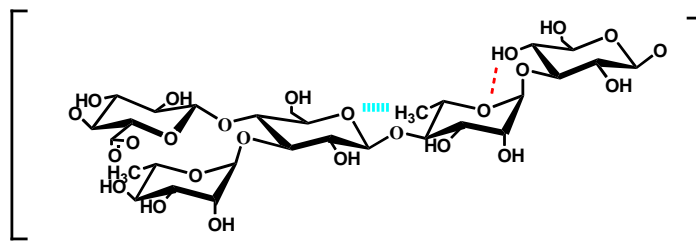
Figure 9. Intramolecular associations in welan gum. Associations: ▬ ▬ ▬, Hydrogen bonding; //// , van der Waals forces of attraction.
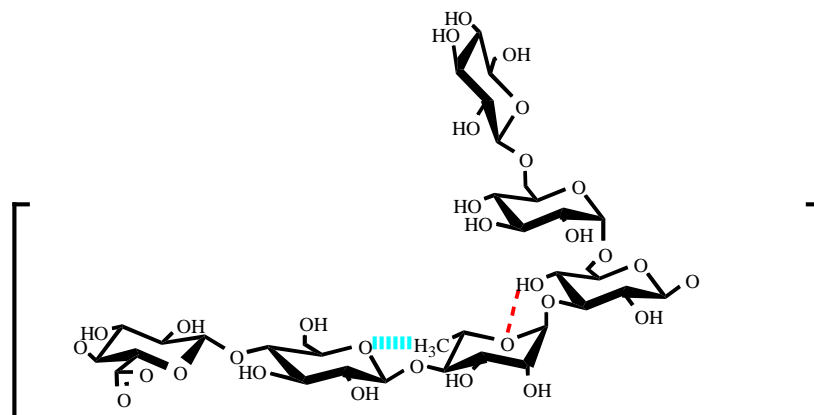
Figure 10. Intramolecular associations in rhamsan gum. Associations: ▬ ▬ ▬, Hydrogen bonding; //// , van der Waals forces of attraction.

solution even at high temperatures [71] [72] [83]. The main chain of the rhamsan gum consists of tetrasaccharide repeating units as in gellan gum and every D-glucopyranosyl residue next to the D-glucuropyranosyl residue is substituted at C-3 by α-L-rhamnopyranosyl-(1→4)-α-L-rhamnopyranosyl disaccharide side-chains [84].

Gelation did not occur even at 1.0% and at low temperature (0˚C). The elastic modulus showed a sigmoid curve with increasing temperature. Almost same elastic modulus was observed during increase in temperature in the presence of $CaCl_2$ (6.8 mM). Thus, intramolecular associations between the OH-4 of the D-glucopyranosyl residue and the adjacent hemiacetal oxygen atom of the L-rhamnopyranosyl residue with hydrogen bonding, and between the methyl group of the L-rhamnopyranosyl residue which oriented at equatorial configuration and the adjacent hemiacetal oxygen atom of the D-glucopyranosyl residue with van der Waals forces of attraction were proposed (**Figure 11**) [33]. The intramolecular associations contributed to the thermal stability of the polysaccharide in aqueous solutions.

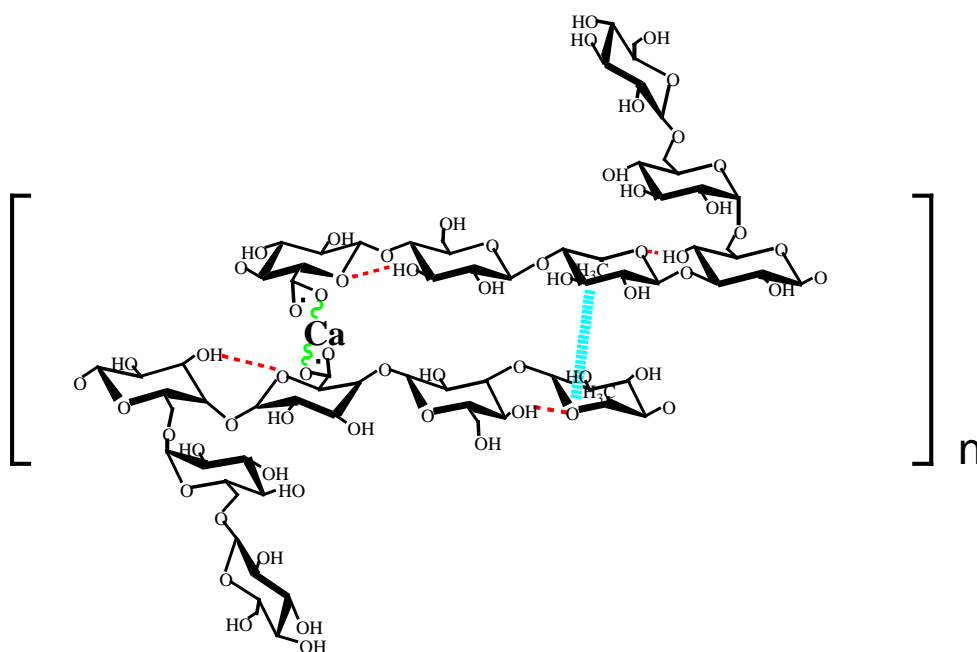### 2.4.5. Gelation Mechanism of Deacetylated Rhamsan Gum

The rhamsan gum contains one *O*-acetyl group per tetrasaccharide repeating units [81], and is non gelling polysaccharide, as mentioned above. However, after deacetylation, the polymer formed gel above 0.3% at low temperature (0˚C) [18]. A gelation occurred in 0.2% deacetylated rhamsan gum solution with addition of $CaCl_2$ (6.8 mM). The elastic modulus kept a constant value during increase in temperature up to 60˚C, which was estimated a transition temperature, then decreased rapidly. The elastic modulus of deacetylated rhamsan gum (0.5%) increased a little with addition of urea (4.0 M) at low temperature and kept constant values during increase in temperature and decreased rapidly when the temperature reached 50˚C, which was estimated transition temperature. As mentioned above, elastic modulus of gellan gum solution also increased on addition of urea (4 M) at low temperature, but it decreased rapidly after temperature reached 15˚C.

Rheological properties of deacetylated rhamsan gum differed from those of native polymer [18], but agreed with those of gellan gum [11] [12]. Thus, we proposed intramolecular and intermolecular associations, as shown in **Figure 12** [18], which was similar to those of gellan gum (**Figure 8**). The intramolecular hydrogen bonding might take place between OH-4 group of the D-glucopyranosyl residue and adjacent hemicetal oxygen atom of
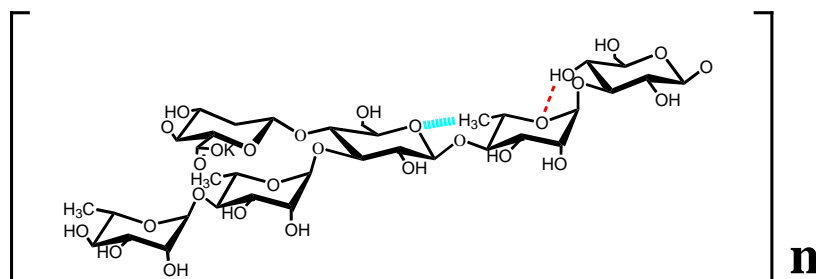
Figure 11. Intramolecular associations in S-657 gum. Associations: ▬ ▬ ▬, Hydrogen bonding; ∕∕∕∕, van der Waals forces of attraction.

Figure 12. Gelation mechanism of deacetylated rhamsan gum. Associations: ▬ ▬ ▬, Hydrogen bonding; ∕∕∕∕, van der Waals forces of attraction; ∿∿∿, ionic bonding.

the L-rhamnopyranosyl residue, and between OH-3 of the D-glucopyranosyl residue and adjacent hemiacetal oxygen atom of the D-glucuropyranosyl residue, to make the polymer rigid. The intermolecular van der Waals forces of attraction might take place between the methyl group and counter hemiacetal oxygen atom of L-rhamnopyranosyl residues on different molecules. In the presence of $CaCl_2$, an intermolecular Ca^{2+} bridge, as in ι-carrageenan [8], gellan gum [11] [12] and alginate [16] [17], might also take place with ionic bonding. Although the L-rhamnopyranosyl residues in part of native rhamsan gum adopt a $^1C_4$ pyranose-ring conformation, they exit in a $^4C_1$ pyuranose-ring conformation in deacetylated rhamsan gum [18]. Such a conformational change of the L-rhamnosyl residue was confirmed by ^{1}H-NMR spectroscopy [18]. The gelation mechanism of deacetylated rhamsan gum was proposed, as shown in **Figure 12** [18].

3. Principle of Polysaccharide Gels

The H_2O molecule can participate in four hydrogen bonds, two of them involving the two hydrogens of the molecule and the lone pair of electrons of the oxygen and hydrogens of two neighboring molecules. This tetrahedrally directed bonding is involved in the crystal structure of ice, which is the same as the arrangement of the gelling waters in polysaccharide solution. At a minimum concentration of 0.1% - 1.0% (W/V) in water (99.9% - 99.0%), the gelling polysaccharides mentioned above changed into an ice-like structure with the formation of hydrogen bonding between the polysaccharides and water, and between water molecules, which subsequently

resulting in gelation even at room temperature. Such dramatic changes from liquid into gels have generally been understood at the molecular level [19] [29].

We discuss herein the role of polysaccharides for an example agarose in gel-formation processes in water. On the basis of the discussions mentioned above, the agarose molecules play a dominant role in the center of tetrahedral cavities (cages) that are occupied by water molecules. This arrangement is similar to a tetrahedral ice-like structure and should lead to a cooperative effect. This effect stabilizes extended regions of the ice-like water that is hydrogen bonding on the surface of the polymer molecules. On the surface of the polymer molecules, ring oxygen and hydroxyl groups participate in hydrogen bonding with water molecules, and more extended ice-like hydrogen bonding with water molecules achieved to form a cluster, as shown in **Figure 13**. Namely, agarose gel
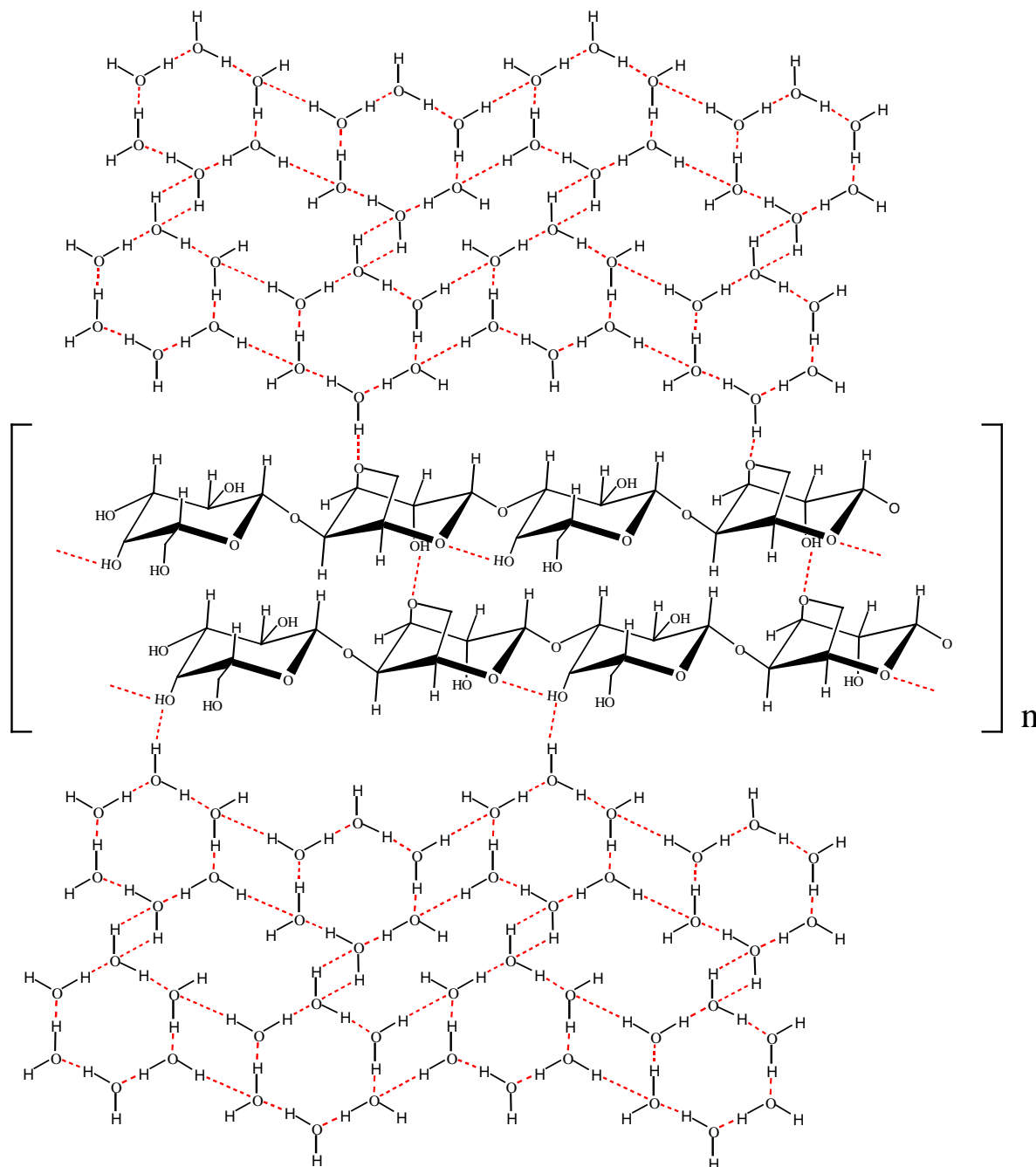
Figure 13. Gelling agarose in water molecules. Red dotted lines represent hydrogen bonding.

formation corresponds to a total of the clusters. The intra- and inter-molecular associations result in cage effect, which lead to the lowest energy state of electrons of the lone pairs of 3,6-anhydro-oxygen and hemiacetal oxygen atoms. The conformation adopts a tetrahedral distribution, and therefore, attracts not only each other but also water molecules due to hydrogen bonding. The intra- and inter-molecular hydrogen bonding of agarose molecules results in gelation up to a high temperature (60˚C), and their periphery is surrounded by hydrophobic carbon and hydrogen atoms, which are required to play a role in the hydrophobic effect. This hydrophobic effect leads to hydrogen bonding that easily occurs within water molecules because of decrease in entropy. Therefore, hydrogen bonding also takes place easily with water molecules on the outside of the polymer helices (**Figure 13**).

Accordingly, the gel-forming polysaccharides molecules, as mentioned above, may adopt single, double, or multi-stranded conformations involving intra- and inter-molecular associations and play a role in the center of the tetrahedral cavities leading and stabilizing the extended regions of ice-like water molecules with hydrogen bonding, and resulting in gelation.

4. Conclusions

In gel-formation processes of biopolymer, polysaccharides, cage and hydrophobic effect play thermal dynamically dominant role. The former effect is observed in daily life: Water molecules at low temperature around 0˚C immediately changed into ice crystals upon the addition of some contaminant such as small dust particles which lead to the lowest energy state of electrons, between water molecules through tetrahedrally directed hydrogen bonding. Furthermore, an amylose solution at a concentration of 1.0% (W/V), changed into a gel immediately under weak mechanical stimulation (cage effect) [13] [14]. The latter effect is also observed: A droplet of water forms a spherical shape where tetrahedrally directed hydrogen bonding takes place, minimizing contact with the hydrophobic plant leaf surface. This hydrophobic effect leads to hydrogen bonding that easily occurs within water molecules because of a decrease in entropy. Such effect, cage and hydrophobic, may also play role in proteins, synthesized polymers and sugar-fatty acid complex gel formation processes. Specifically, hydrophobic effect may play in organo-gel formation in organic solvents with van der Waals forces of attraction.

Though many investigations the gelling properties of the polysaccharides have been undertaken to elucidate the structure-function relationship, no other researchers have established mechanism at the molecular level. There is reasonable consistency in our investigations. Thus, the rheological analysis is one of the significant methods for understanding the structure-function relationship of polysaccharides in aqueous media. We expect that the era of polysaccharides gels will be arriving in the 21st century, being applied not only from the food industry, but also in a variety of products, such as cosmetics, pharmaceuticals, chemicals, drug delivery, tissue engineering, and other industries.

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