**DSC and TMA Studies of Polysaccharide Physical Hydrogels**

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Various kinds of polysaccharides found in a wide variety of plants, bacteria, crustaceans and insects form hydrogels via physical aggregation in aqueous media. The major mass of hydrogels is water filled, ca. 95 - 99.5%, in a network structure, although the solid shape of the gel is maintained. In this paper, firstly the wide range of gelation mechanisms are briefly described, and then the thermal analysis of representative gel-forming polysaccharides, such as carrageenan, alginate, galactomannan, and pectin, is introduced. By differential scanning calorimetry (DSC), gel-sol and the sol-gel transition temperature of thermoreversible hydrogels are measured and phase diagram is established. It is suggested that binary systems showing sinusoidal gel-sol-gel transition are capable of being assembled. By thermomechanical analysis (TMA), the dynamic modulus (E') at around 1 × 10⁴ Pa of thermo-irreversible hydrogels was obtained using a sample holder designed to measure the viscoelastic properties in water. Reliable coordination is shown between the results obtained by DSC and TMA. In this review, the current research and several topics on concerning the thermal properties of polysaccharide physical hydrogels are introduced.

**Keywords** Polysaccharide, water, hydrogel, DSC, TMA

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1 Introduction

Polysaccharide is the most abundant organic material on Earth. In nature, polysaccharides are found in a wide variety of plants, bacteria, shellfishes and also in insects.¹² Polysaccharides with a large amount of water form a complex matrix system in living organs. Ordinarily, it is considered that polysaccharides exhibit functional properties in a multifaceted form, such as carbohydrate-protein, carbohydrate-lignin complex, etc. in a living body. Accordingly, it is appropriate to accept that the original conformational structure is reorganized when each...
polysaccharide is extracted or isolated from the natural state. Polysaccharide hydrogel is composed of a three-dimensional network of saccharide molecular chains whose volume is filled with water and expanded throughout its whole volume. The major mass of hydrogels is water filled in a network structure, ordinarily more than 90%, although the solid shape of the gel is maintained. Cross-linking is established through the physical aggregation of polysaccharide molecular chains. Various types of aggregation, such as hydrogen bonds, crystallization, helix formation, complexation, etc., are recognized. Molecular order is locally established and is referred to as the network junction zone. In this review, the thermal properties of various kinds of polysaccharide hydrogels which are organized via specific molecular aggregation will be introduced.

The gelation mechanism and functional properties of polysaccharide hydrogels have been investigated by a wide range of analytical means. In the initial stage of nuclear magnetic relaxation studies, the molecular mobility of water molecules restrained by polysaccharide network has received special attention. A static mechanical test is also used in order to calculate the cross-linking density of the network for hydrogels, although this method has been utilized for synthetic polymer hydrogels. Viscoelastic measurement using a dynamic viscometer has widely and most frequently been applied by DSC and TMA. The water-polysaccharide interaction will be reviewed based on results mainly obtained via specific thermal stimulation.

2 Hydrogelation of Polysaccharides

When polysaccharides are treated in a large-scale industrial process, chemical and structural modification take place. Accordingly, the physicochemical properties of obtained polysaccharides are not equal to the original ones. However, even though the structure of natural polysaccharides is artificially damaged, it can be said that each polysaccharide maintains the specific character attained via a long evolution process. The characteristic feature of each polysaccharide is markedly observed when they form hydrogels, i.e., the mechanism of hydrogelation is different from each other, especially when gelation is stimulated via an environmental situation, such as temperature, presence of ion, thermal loading, etc.

Large numbers of polysaccharides are found in nature, and many of them have the potential to form hydrogels. Table 1 shows representative polysaccharides having a gel-forming ability. The gelation mechanism of each polysaccharide depends mainly on the chemical structure; however, some polysaccharides which were classified into non-gelling ones are found to organize cross-linking points via a specific thermal stimulation. The gelation mechanism of polysaccharide hydrogels has been investigated by many researchers, and polysaccharide hydrogels are generally classified into several categories according to the mechanism of molecular aggregation.

(1) Molecular chains randomly dispersed in solution form helices by cooling and the junction zone is organized via co-aggregation of helices. This type of gel is named cold set gels. Agarose,\(^{43,45}\) carrageenan family,\(^{46,47}\) κ-carrageenan\(^{4,20,25,35,36}\) and curdian,\(^{42,46,47,69,70}\) whose chemical structures are shown in Table 1, are representative polysaccharides of heat set gels. It is thought that when molecular motion of MC is enhanced by heating, water molecules restrained by MC, molecular chains are liberated and the MC chains contact with each other to form a co-aggregated domain which acts as a junction zone.

(2) Among several kinds of polysaccharide, gelation occurs when sol is heated instead of cooled. This type of gel is categorized as heat set gels.\(^{46}\) Methylcellulose (MC)\(^{21,22,26,27,39,60,66,68}\) and curdian,\(^{42,46,47,69,70}\) whose chemical structures are shown in Table 1, are representative polysaccharides of heat set gels. In this article, the thermal properties of a wide variety of polysaccharide hydrogels, formed via various types of molecular aggregations, will be reviewed based on results mainly obtained by DSC and TMA. The water-polysaccharide interaction will receive special attention for discussing of molecular aggregation.
### Table 1  Chemical structure and gelation mechanism of representative polysaccharides

| Polysaccharide      | Chemical structure | Gelation mechanism | Ref. No.        |
|---------------------|--------------------|--------------------|-----------------|
| Agarose             | ![Chemical structure](image1.png) | (1)                | 43 - 45         |
| Alginate            | ![Chemical structure](image2.png) | (3) | 14, 71 - 74 |
| Carrageenan         | ![Chemical structure](image3.png) | (1) | 7, 20, 25, 35, 36, 45, 48 - 60 |
| -κ-Carrageenan      | ![Chemical structure](image4.png) | (1) | 7, 20, 25, 35, 36, 45, 48 - 60 |
| -ι-Carrageenan      | ![Chemical structure](image5.png) | (1) | 49, 59         |
| -λ-Carrageenan      | ![Chemical structure](image6.png) | No gelation | 65             |
| Curdlan             | ![Chemical structure](image7.png) | (2)                | 19, 37, 66, 69, 70 |
| Galactomannan       | ![Chemical structure](image8.png) | (5)                | 81, 82          |
| Fenugreek gum       | ![Chemical structure](image9.png) |                   |                 |
| Guar gum            | ![Chemical structure](image10.png) |                   |                 |
| Tara gum            | ![Chemical structure](image11.png) |                   |                 |
| Locust bean gum     | ![Chemical structure](image12.png) | (4)                | 15, 17, 72, 74 - 78 |
| Cassia gum          | ![Chemical structure](image13.png) | (4)                | 24              |
| Gellan gum          | ![Chemical structure](image14.png) | (1)                | 29, 61 - 64     |
| Hyaluronan          | ![Chemical structure](image15.png) | (6)                | 42, 83, 84      |
| Pectin              | ![Chemical structure](image16.png) | (4)                | 15, 17, 72, 74 - 78 |
| Xanthan gum         | ![Chemical structure](image17.png) | (6)                | 85 - 89         |
| Methyl celluloseb   | ![Chemical structure](image18.png) | (2)                | 21, 22, 26, 27, 39, 60, 66 - 68 |

*a. Numerals show gelation mechanism described in the text. b. Prepared by substitution of the hydroxyl groups of cellulose with methoxyl groups.*
properties of hydrogels are affected by annealing at sol-state as a function of the temperature and time.41

Besides the gelation mechanism, hydrogels are classified in two categories, i.e. thermo-reversible and thermo-irreversible gel. Heat-set gels and cold-set gels are thermo-reversible; in contrast, gels formed by ionic bridges are thermo-irreversible.

3 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) is a useful tool for investigating the thermo-reversible transition of hydrogels. Among various types of calorimeters, either a power compensate type or a heat-flux type DSC are ordinarily used for sol-gel transition measurements.16,30 Sample cells of sensitive calorimeters for biomaterials, such as Privalov type, are not appropriate for highly viscous samples, like hydrogels.30

Ordinarily, gel-sol or sol-gel transition of aqueous solution of polysaccharides is observed in a temperature range from 300 to 360 K, depending on the kinds of polysaccharide. The temperature range of the gel-sol transition is broader than the gel-sol transition of hydrogels with various κC and methylcellulose (MC) mixed hydrogels with various mixing ratios. The polymer concentration is 2%. The polymer concentration is 2%. (a) MC, (b) κC:MC = 1:9, (c) 2:8, (d) 3:7, (e) 4:6, (f) 5:5, (g) 6:4, (h) 7:3, (i) 8:2, (j) 9:1, (k) κC.

Figure 1 shows stacked DSC heating curves of κ-carrageenan (κC) and methylcellulose (MC) with various mixing ratios. The polymer concentration is 2%. The polymer concentration is 2%. (a) MC, (b) κC:MC = 1:9, (c) 2:8, (d) 3:7, (e) 4:6, (f) 5:5, (g) 6:4, (h) 7:3, (i) 8:2, (j) 9:1, (k) κC.

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Stacked DSC heating curves of κ-carrageenan (κC) and methylcellulose (MC) binary hydrogels with various mixing ratios. The polymer concentration is 2%. The polymer concentration is 2%. (a) MC, (b) κC:MC = 1:9, (c) 2:8, (d) 3:7, (e) 4:6, (f) 5:5, (g) 6:4, (h) 7:3, (i) 8:2, (j) 9:1, (k) κC.

Figure 1 shows stacked DSC heating curves of κ-carrageenan (κC) and methylcellulose (MC) mixed hydrogels with various mixing ratios. The patterns of the DSC curves were reproducible by repeated runs, although the gel-sol transition is affected by the thermal history.20 In DSC heating curves, DSC baseline gradually shifted to the endothermic direction at around 300 K and an endothermic peak due to gel-sol transition is observed.

The endothermic peak of the gel-sol transition of κC shifts to a high temperature with an increasing mixing ratio. In DSC cooling curves, although not shown here, an exothermic peak due to sol-gel transition was clearly observed. In DSC heating curves, the high temperature side endothermic peak is attributed to a sol-gel transition of MC. The peak temperature of the endothermic peak is observed at 335 K, regardless of the mixing ratio.

Figure 2 shows the relationship between the gel-sol and sol-gel transition temperature and the κC concentration (Fig. 2a) or the MC concentration (Fig. 2b). As shown in Fig. 2(a), the low-temperature side peak, attributed to gel-sol transition of κC, increases with the increasing κC concentration. In contrast, the high-temperature side peak attributed to the sol-gel transition of MC maintains a constant value, regardless κC concentration.

The above results indicate that polysaccharide systems, which show a sinusoidal change of the gel-sol-gel as a function of
temperature, can be designed when an appropriate combination is chosen.

3-2 Structural change of hydrogels

As described in the previous sections, the junction zone of κC gel is formed via conformational changes of molecules from the coil to the helix. Although various factors, such as the concentration, kind of alkali metal ions, pH and concentration, are concerned with hydrogelation, the effect of the thermal history on the gel-sol or sol-gel transition behavior is difficult to be ignored when a thermal investigation is carried out. The change of the molecular conformation associated with the dissociation of entangled chains in the sol state via annealing has been investigated. DSC is a useful method among various experimental techniques, when molecular relaxation in the sol state is concerned with the gelation, since the thermal history of the sol state can be easily and precisely controlled.

The effect of the thermal history of hydrosol is clearly observed in the following results obtained by DSC, i.e. κC gels with a concentration 5.0% were cooled from 370 to 280 K at various cooling rate, from 0.1 to 0.5 K min⁻¹. The sol-gel transition temperature decreases from ca. 322 to 313 K with increasing cooling rate. Furthermore, a sub-exothermic peak was observed at around 313 K in a cooling rate from 0.1 to 2.0 K min⁻¹. The enthalpy of the sol-gel transition linearly decreases from 2.2 to 1.7 J g⁻¹ as a function of the cooling rate. In order to confirm the effect of annealing, κC sol was maintained at 323 to 343 K for 60 min, and the sol-gel transition was measured at the same cooling rate. The remarkable change of the enthalpy of the sol-gel transition was observed, i.e. the enthalpy of the sol-gel transition increased from 0.2 to 1.7 J g⁻¹ with increasing annealing temperature. It was clearly shown that the thermal histories, such as the cooling rate from the sol to the gel, or annealing at around gel-sol transition temperature, markedly affect the junction zone formation.

The above facts strongly suggest that molecular helices having various sizes and different kinds of defects are organized in the junction zone, depending on the temperature and time where hydrosol is located. Polysaccharide hydrosol is in the non-equilibrium state and molecular equilibration takes place as functions of the temperature and time. The molecular equilibration of polysaccharide in a concentrated aqueous solution has mainly been investigated in weak gel forming polysaccharides, shown in Table 1. By DSC, the molecular equilibration of hydrosol has been investigated via a quantitative evaluation of bound water restrained by polysaccharide molecules.

In general, water restrained by hydrophilic polymers can be categorized into three groups: non-freezing, freezing bound and free water. The first-order phase transition is not found in non-freezing water, which is restrained by the hydrophilic groups via hydrogen bonding. The amount of non-freezing water (Wₐ) is calculated as

\[ W_\text{ad} = W_c - W_b - W_r \]  

where \( W_c \) is the total amount of water in the system measured directly by weighing (\( W_c = \text{mass of water/mass of dry polysaccharide} \)) and \( W_b \) is the amount of free water calculated from the enthalpy of melting (\( \Delta H_m \)) of ice in the system. In the water-biopolymer system, ordinarily freezing bound (\( W_b \)) water coexists with free water. Freezing bound water is defined as water whose phase transition temperature is observed at a temperature lower than that of free water. On this account, the total bound water is a summation of \( W_\text{ad} \) and \( W_b \).

In order to follow the molecular equilibration of polysaccharide in the sol state, \( W_\text{ad} \) was calculated from \( \Delta H_m \) of ice formed in polysaccharide hydrosol as a function of time. The \( \Delta H_m \) of ice formed in polysaccharide hydrosol is smaller than that calculated from added water. It is thought that non-freezing water cooperatively moves with matrix polysaccharide molecules in water. Based on NMR relaxation studies, it is known that the molecular mobility of non-freezing water is far slower than that of free water, i.e. the correlation time (\( \tau_c \)) calculated from spin-lattice and the spin-spin relaxation time is ca. 10⁻⁵ to 10⁻⁶ s, while \( \tau_c \) of free water is 10⁻⁹ s. Water molecules restrained via hydrogen bonding with the hydroxyl group polysaccharide are hardly involved in crystallization with the surrounding free water molecules. Ordinarily, each hydrophilic group attached to
polymers restrains ca. 1 water molecule as non-freezing water. Although the amount of non-freezing water depends on the thermal history and molecular conformation of the polymers matrix. The major factor determining the amount of non-freezing water is the chemical structure of the polymer matrix, i.e., the number of hydrophilic and ionic groups in the repeating unit of polymers. The non-freezing water content restrained by various kinds of polysaccharides is found elsewhere.

In sol state, the amount of non-freezing water restrained by polysaccharide varies in a complex manner until the thermal history of the system is attained. Takahashi and his associates showed that oscillatory changes of non-freezing water are restrained by hyaluronan, which is observed until conformational equilibration is achieved. The hyaluronan sol (3%) is annealed at 333 K for various time intervals from 0 to 50 h, and \( W_{nf} \) was calculated from the enthalpy of melting. When the \( W_{nf} \) values are correlated with the annealing time, \( W_{nf} \) decreases in an oscillatory manner as a function of the annealing time and approaches a constant value (ca. 0.125 g g\(^{-1}\)).

The behavior of non-freezing water in the structure formation process of polysaccharide hydrogels is simply explained by the phenomenological theory, assuming the change of the number of sorption and desorption sites;

\[
\begin{align*}
n &= C \exp(-\gamma t) \cos(\omega t + \delta),
\end{align*}
\]

where \( \omega = (\omega_0^2 - \gamma^2)^{1/2} \), \( n \) represents the averaged rate constant for adsorption and desorption of water, \( \gamma \) represents the averaged rate constant for adsorption and desorption of water molecules and \( \omega_0 \) is a constant representing the effect of the change in the number of adsorption sites on the time.

4 Thermomechanometry (TMA)

4.1 Dynamic viscoelastic properties of polysaccharide hydrogels

Thermomechanometry (thermomechanical analysis, TMA) is a branch of thermal analysis by which the deformation of materials under constant stress or strain is detected as a function of temperature or time under controlled conditions. With modern apparatus, it is possible to vary the applied stress or strain from static to the dynamic mode. The atmospheric condition can be changed, such as inert gas, air or humid atmosphere, according to the experimental plan.

TMA has generally been used for measuring of the glass transition temperature or softening temperature of synthetic polymers in the dry state. In our previous studies, a sample probe was designed to measure the hydrogels in water. A laboratory-made sample holder of TMA is schematically shown in Fig. 3. The dynamic modulus \( (E') \) and dynamic loss modulus \( (E'') \) of hydrogels can be measured using this TMA. The hydrogel sample is dipped in water using the sample probe shown in Fig. 3. Stress is applied sinusoidally and the response signal is detected. From a Lissajous diagram, \( E' \) and tan \( \delta = E''/E' \) were calculated.

When \( \kappa \) CG hydrogels with concentration of 2% was measured in water using a the sample probe of TMA shown in Fig. 3, the \( E' \) values were obtained in a range from 1 × 10\(^4\) to 2 × 10\(^5\) Pa. \( E' \) of pectin hydrogel was also measured as a function the cross-linking density. \( E' \) increased from 1.5 × 10\(^4\) to 3.0 × 10\(^5\) Pa with increasing degree of Ca substitution from 0.29 to 0.43. \( E'' \) of gellan gum was not calculated since \( E' \) was smaller than 10\(^4\) Pa.

As shown in Table 1, among galactomannan polysaccharides, locust bean gum (LBG) and cassia gum (CG) form hydrogels by freezing and thawing. Dynamic modulus and tan \( \delta \) of LBG and CG hydrogels were formed by freezing and thawing were measured by TMA using the sample probe shown in Fig. 3. LBG hydrogels are thermo-irreversible and no gel-sol transition is observed. Once a rigid gel is organized via freezing and thawing, the effect of the number of freezing and thawing (n) is scarcely detected, when the concentration is constant (1%). As shown in Fig. 4(a), a significant difference in dynamic modulus \( (E') \) was not observed. It is seen that \( E' \) of LBG and CG hydrogels maintains a constant value when \( n \) exceeds 2. Figure 4(a) indicates the effect of the side chain frequency (see Table 1) is apparent, although the effect of \( n \) is not large. LBG and CG hydrogels were prepared at various cooling rates. Figure 4(b) shows the relationship between \( E' \) of LBG and CG hydrogel and cooling rate. It is seen that \( E' \) increases with increasing cooling rate. \( E' \) is affected by the crystallization rate of water in the sol. The above fact suggests that a densely crosslinked hydrogel is formed, when a small amount of ice is formed by rapid cooling.

The gel-sol transition for hydrogels can be measured as an abrupt change of the sample length under applied stress. The temperature of the sample holder shown in Fig. 3 can be controlled from 273 to 363 K by the circulation of water from a constant-temperature bath. Accordingly, the temperature increases stepwise. The gel-sol transition temperature \( (T_{gs}) \) of \( \kappa \)-carrageenan hydrogels with concentrations from 0.5 - 5% was measured using TMA in water. At the same time, \( T_{gs} \) of the same samples with various concentrations was measured by DSC at a heating rate of 0.5 K min\(^{-1}\). As already reported, it is known that \( T_{gs} \), of \( \kappa \)-carrageenan hydrogel increases with increasing concentration. Figure 5 shows the relationship...
between $T_{g-s}$ measured by DSC and that of TMA. It is clearly seen that there is a coincidence between $T_{g-s}$ values obtained by TMA and DSC, especially on a low concentration range.

The most advantageous point of TMA measurable in water is that dynamic modulus of hydrogels can be detected in the range of $10^3$ to $10^4$ Pa. In this range, $E'$ of hydrogel can be measured by neither dynamic mechanical analysis nor rheometry. It is considered that this measuring method can be utilized for evaluating various physical properties of hydrogels, such as dynamic viscoelastic properties, static stress relaxation in water, gel-sol transition temperature and creep and swelling behavior.

### 4.2 Swelling dynamics of polysaccharide gel films

A laboratory-made TMA sample holder was constructed to follow the swelling procedure of dry gel film. The schematic design of the sample holder is shown in Fig. 6. The dry gel film was placed on a quartz plate and a predetermined stress applied. Water is supplied from the bottom via a flexible tube. Deformation is detected as a function of time. Figure 7 shows the relationships between swelling ratio ($\varepsilon = l_t/l_0$, where $l_0$ is sample thickness at room temperature, $l_t$ is that at time $t$) of gel film of Ca-alginate and swelling time. As shown in Fig. 7, swelling ratio increases with increasing swelling time and decreases with increasing load. From these results, a master curve can be constructed. 

![Diagram](image1.png)

Fig. 4 (a) Relationships between the dynamic modulus ($E'$) measured by TMA and the number of freezing and thawing cycles ($n$). Closed diamonds, LBG; open circles, CG. Sample preparation: LBG or CG sol concentration, 1%; freezing temperature, 253 K; cooling rate, <0.5 K min$^{-1}$; thawing temperature, 298 K; thawing time, 6 h. (b) Relationships between the dynamic modulus ($E'$) measured by TMA and the cooling rate. Number of freezing and thawing ($n$) is 1.

![Diagram](image2.png)

Fig. 5 Relationship between the gel-sol transition temperature by DSC ($T_{g-s, DSC}$) and those by DSC ($T_{g-s, TMA}$) of $\kappa$-carrageenan hydrogels with various concentrations. Concentration, 0.5 - 5%.

![Diagram](image3.png)

Fig. 6 Schematic diagram of a self-designed sample cell of TMA.

![Diagram](image4.png)

Fig. 7 Swelling curves under various loads. The solid line shows a swelling curve without a load. The dotted line shows the static value. $\varepsilon$, swelling ratio ($= l_t/l_0$, where $l_0$ is sample thickness at room temperature; $l_t$, that at time $t$). Sample: Alginate gel films cross-linked via Ca ion$^{12}$. Numerals in the figure show the applied load in grams.
drawn with a swelling curve without a load as shown by the solid line in the Fig. 7. The degree of swelling at 120 min which corresponds to the saturation point agrees well with the equilibrium value of swelling measured by the static method. The above results indicate that dynamic swelling can be investigated using a TMA equipped with a newly designed apparatus.

5 Conclusions

A wide variety of polysaccharides in the gel form are utilized, especially as base matrices for medicine and food in which unique viscoelastic properties play an important role. Thermal analysis is a traditional technique having a long historical background and is useful in current research in order to establish phase diagrams of complex systems and also to investigate the molecular motion accompanying the phase transition behavior of polysaccharide-water systems. For a general survey of the novel function of polysaccharides, which are representative nature-friendly compounds, TA is necessarily required. In this nature, and that TA will be utilized in future research.

features of each gel, new results are obtainable. It is considered presented. By using simple devices which fit the characteristic representative polysaccharide hydrogels have been introduced. In particular, simple examples of modifications to TMA

Thermal especially as base matrices for medicine and food in which novel function of polysaccharides, which are representative

unique viscoelastic properties play an important role. Thermal analysis is a traditional technique having a long historical unique viscoelastic properties play an important role. Thermal analysis is a traditional technique having a long historical

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