

Thermal and Rheological Properties of Physical Gels Formed from Benzylidene- D-sorbitol Derivatives

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The thermal and rheological properties of gels formed from 2,4-(mono)-*O*-benzylidene-D-sorbitol (MBS), 1,3:2,4-di-*O*-benzylidene-D-sorbitol (DBS), and 1,3:2,4:5,6-tri-*O*-benzylidene-D-sorbitol (TBS) in ethylene glycol (EG) and from DBS in glycerol (GL) were investigated. In all the gels studied, the values of the enthalpy of melting for the gel obtained from the Eldridge–Ferry plot agreed well with those obtained from the peak area of the DSC curves. This agreement has not been demonstrated clearly for biopolymeric systems thus far but can now be successfully shown by first using small molecule systems. In conclusion, the transitions of the gel formation and gel melting proceed via a second order or higher order process. The experimental results show that the ease by which formation and stabilization of gels takes place for the sorbitol derivatives in EG is in the following order: DBS > TBS > MBS. Accordingly, the main reason for the stabilization of sorbitol gels in alcoholic solvents is concluded to be not simply due to hydrogen bonding or hydrophobic interactions among benzylidene groups but rather it is due to a delicate balance of chemical structure that facilitates the formation of crystals. In particular, the symmetric structure of a DBS molecule, which has a rigid and chiral ten-member ring symmetrically connected with two benzylidene groups in equatorial positions, is considered to be the most crucial reason to form most stable gels studied in this work.

Many systems where thermoreversible physical gelation takes place have been reported on intensively and extensively.^{1,2)} We have previously studied thermoreversible gels formed from biopolymers such as polysaccharides^{3–9)} and cellulose derivatives.^{10,11)} However, the structure of the junction points and/or the gelation mechanism are still unclear in many systems of biopolymeric physical gels, since biopolymer systems have inherent complicated properties such as molecular weight, conformational change, high-order structure, and intramolecular interaction among nonadjacent units. We then started with studies of thermoreversible gelation of small molecules such as sugar alcohol to investigate the essential features of physical gelation.

Gelation induced by the addition of small molecules to organic solvents has also come to be a major topic. The reported gelator molecules are of a wide structural diversity; 12-hydroxystearic acid,^{12,13)} semifluorinated *n*-alkanes,¹⁴⁾ steroids,^{15,16)} aromatic linked steroids (ALS),^{17–19)} compounds with long alkyl chains,^{20–24)} lecithin,²⁵⁾ calixarenes,²⁶⁾ cyclodextrin,²⁷⁾ depsipeptides,²⁸⁾ and dipeptides.^{29–31)} However, the main reason for the induction of gelation has not been identified. For example, a long-chain alkylamide of *N*-benzyloxycarbonyl-L-valyl-L-valine can cause physical gelation,³²⁾ but, it is not obvious whether the main cause of gel formation is the long alkyl chain or the steric structure of the dipeptides.

1,3:2,4-di-*O*-benzylidene-D-sorbitol (DBS)³³⁾ is a derivative of the natural sugar alcohol D-glucitol and is known as a chiral oil gelator since Yamamoto discovered the gelation

of DBS in alcoholic solvents in 1942.³⁴⁾ Recently Yamasaki et al. reported the gel properties of DBS, using several measurements such as circular dichroism, microscopy, ¹³C-solid state NMR and so on.^{35–39)} According to Yamasaki et al., the DBS–EG gel state is metastable, having two kinds of mesophases: One is the crystalline phase consisting of the spherulitic texture, and the other is the isotropic mesophase comprising a network-like structure between spherulitic textures.³⁵⁾

In this paper, our aim is to clarify the main cause of formation and stabilization of the gels of D-sorbitol derivatives with different numbers of benzylidene groups (1, 2, and 3) by thermal and viscoelastic measurements. The results would be useful for the clarification of the gelation mechanism of not only the DBS system as an oil gelator, but also polysaccharide systems.

Experimental

Materials. Figure 1 shows the chemical structure of 2,4-(mono)-*O*-benzylidene-D-sorbitol (MBS),⁴⁰⁾ 1,3:2,4-di-*O*-benzylidene-D-sorbitol (DBS), and 1,3:2,4:5,6-tri-*O*-benzylidene-D-sorbitol (TBS).⁴¹⁾

MBS, DBS, and TBS were synthesized according to the method by Uchiyama.⁴²⁾ MBS was prepared from 1 mol benzaldehyde and 1 mol D-sorbitol with 50–60% sulfuric acid as catalyst. The mixed solution turned to be very viscous during the stirring for 20 min. After it was kept at 5 °C in the refrigerator for 1 d, ice-water was poured into the solution, which was then neutralized with an aqueous solution of sodium hydroxide. The precipitate was filtered and washed with ice-water. The crude MBS was recrystallized from

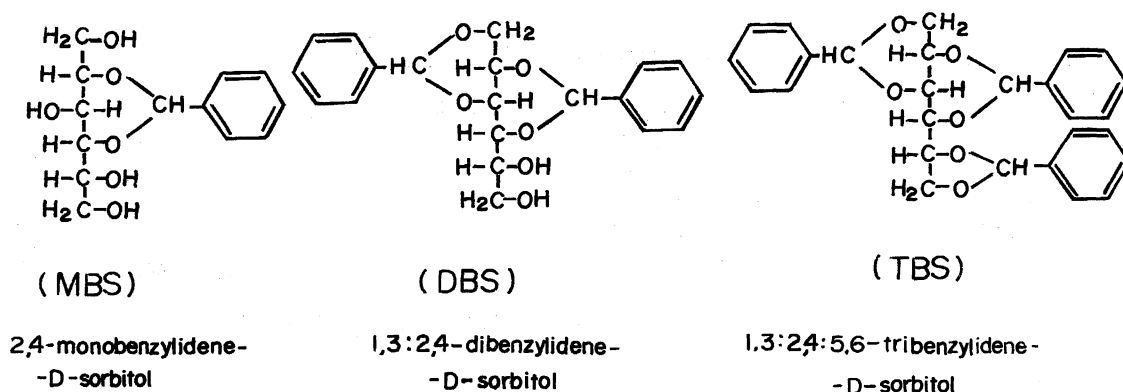


Fig. 1. Chemical structures of MBS, DBS, and TBS.

water. The average yield was 70% of the theoretical value.

DBS and TBS were prepared from 1 mol D-sorbitol with 2 and 3 mol benzaldehyde, respectively, by the same method as follows. The mixture of benzaldehyde and D-sorbitol was dissolved in cyclohexane with *p*-toluenesulfonic acid as catalyst and heated under reflux at 80 °C until the reaction was finished. The cyclohexane solution was washed with an alkaline aqueous solution and extracted repeatedly with water. Then the solution was evaporated and dried. The crude materials were repeatedly washed with 90% ethanol, filtered, and dried under vacuum. The average yields were 60% of the theoretical values for DBS and TBS.

Ethylene glycol (EG) and glycerol (GL) (Wako Co., special grade) were used as solvents without further purification.

Differential Scanning Calorimetry (DSC) Measurements. DSC measurements of gels were done with a Sensitive DSC SSC 5200 (Seiko Instruments & Electronics, Ltd.). 45 ± 0.1 mg each of the gels was sealed into silver pans of 70 μ l. Samples were weighed to within 0.01 mg using an M₁-20 analytical balance (Chou Keiryoku Co.). The pans were dried thoroughly at 300 °C for 30 min before the measurements. We must emphasize that this treatment is quite important, because steep exothermic peaks due to silver appear at about 150 °C unless the pans are first heated at 300 °C. Distilled water was used as a reference material and the weight was made equal (within ± 0.1 mg) to that of the sample gel to obtain a flat baseline. To decide on the scanning conditions, we tried different heating and cooling rates, 0.5, 1, 2, and 4 °C min⁻¹, and measured the DSC curves of a DBS-EG gel. Except for the scanning rate of 4 °C min⁻¹, no large difference was observed. The DSC curves obtained by using a rate of 0.5 °C min⁻¹ were so broad that it was not easy to identify a peak temperature. Thus, the following conditions were chosen. For heating, the temperature was raised from 5 °C at a rate of 2 °C min⁻¹ to observe an endothermic peak accompanying the transition. For cooling, the temperature of the sample was raised to a temperature higher than the peak temperature of gel melting, T_m , by 10 to 15 °C, was kept there for 15 min, and then was lowered at the rate of 2 °C min⁻¹.

Rheological Measurements. Dynamic Young's modulus E' and mechanical loss $\tan \delta$ were measured by observing forced longitudinal vibrations at 2.5 Hz of cylindrically molded gels (15 mm diameter and 10 mm length) with a DDE-V4 Reospectra mechanical spectrometer (Reorogi Co.). The temperature was raised from room temperature to 150 °C at a heating rate of 2 °C min⁻¹.

Results and Discussion

The Properties of DBS-EG Gels. Figure 2 shows the

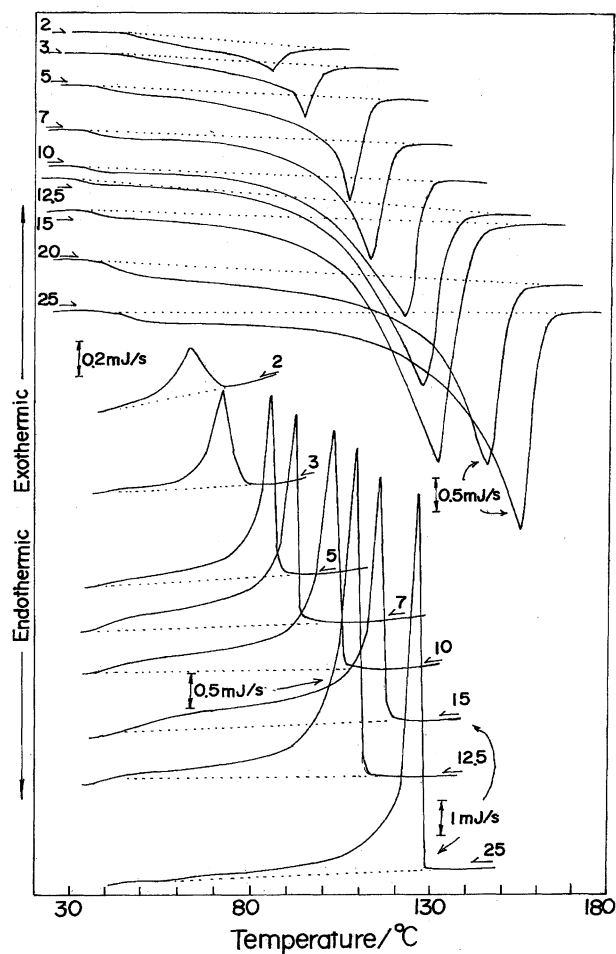


Fig. 2. Heating and cooling DSC curves of DBS-EG gels of various concentrations. The figures beside the curves represent the concentration in percentage (w/w). The broken lines are baselines used for the calculation of enthalpies.

heating and cooling DSC curves of DBS-EG gels at different concentrations. In the heating process, an endothermic peak was observed according to the gel melting. The peak temperature and the peak area gave the melting temperature of the gel, T_m , and the enthalpy of gel melting, ΔH_m , respectively. With an increase in concentration of DBS, c_{DBS} , T_m became higher, with an increase in ΔH_m . In the cooling process,

there was a sharper exothermic peak at the transition from sol to gel. The peak temperature and the peak area gave the setting temperature of the gel, T_s , and the enthalpy of gel forming, ΔH_s , respectively. We tried heating and cooling rates at 0.5, 1, 2, and 4 °C min⁻¹ and measured the DSC curves of a DBS-EG gel. Although T_s slightly decreased and T_m slightly increased with an increase in a rate between 0.5 and 2 °C min⁻¹, the difference was a few degrees at most. The values of ΔH_m and ΔH_s were almost constant, rates between 0.5 and 4 °C min⁻¹. Thus, we decided to compare the DSC data obtained for a heating and cooling rate of 2 °C min⁻¹. With increasing c_{DBS} , T_s became higher and ΔH_s larger.

Figure 3A shows the Eldridge-Ferry plot⁴³⁾ for DBS-EG gels. The relationship between $1/T_m$ and $\log_e c_{\text{DBS}}$ (w/w) yields a straight line, thus they were found to follow to the

Eldridge-Ferry equation:

$$\log_e c = \frac{\Delta H_m^{\text{EF}}}{RT_m} + \text{constant}, \quad (1)$$

where ΔH_m^{EF} is the heat absorbed on forming a mole of junction points that stabilize the network structure of the gel. This relation indicates that the gel melting does not proceed via a first-order transition but rather a second or higher order one, where the system is believed to transform continuously from the sol to the gel state. The plot gives a value of $\Delta H_m^{\text{EF}} = 48.2$ kJ mol⁻¹ by using the least squares method.

Originally, the Eldridge-Ferry equation⁴³⁾ was concerned with gel melting, however, we tried to obtain the relationship between $1/T_s$ and $\log_e c_{\text{DBS}}$. A plot of $1/T_s$ vs. $\log_e c_{\text{DBS}}$, as shown in Fig. 3B, gives essentially a straight line with a value of $\Delta H_s^{\text{EF}} = 44.2$ kJ mol⁻¹, which is almost identical

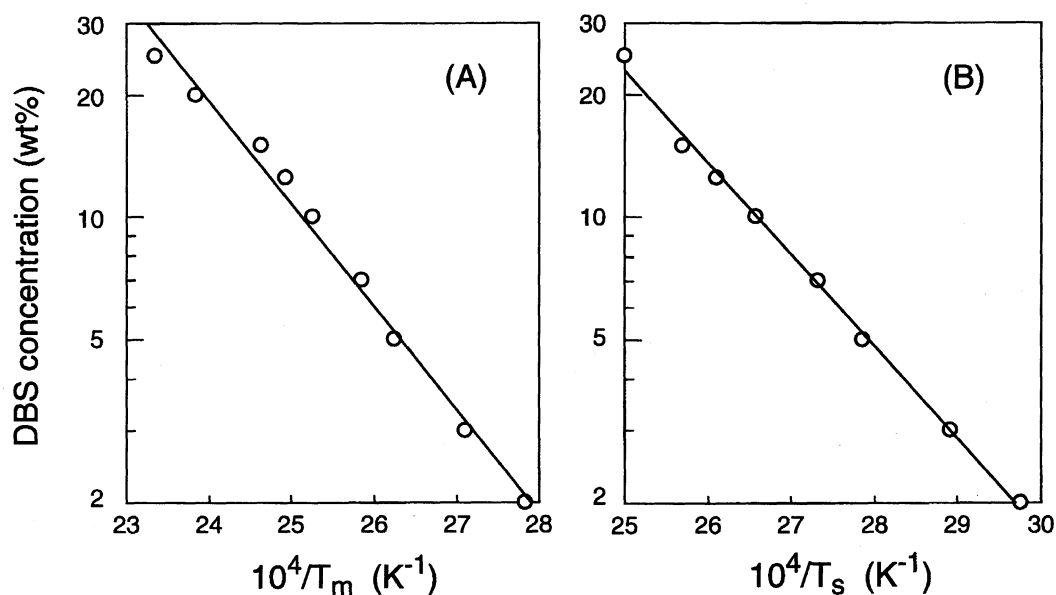


Fig. 3. (A) Eldridge-Ferry plot for DBS-EG gels: (B) a plot of $1/T_s$ versus $\log_{10}$ (concentration of DBS (wt%)).

Table 1. Thermal Properties of DBS-EG Gels at Various Concentrations

The temperature of gel melting, T_m , temperature of gel setting, T_s , enthalpies obtained from the peak area of the DSC curves for gel melting, ΔH_m , and for gel formation, ΔH_s , and enthalpies obtained from the Eldridge-Ferry plot for gel melting, ΔH_m^{EF} , and for gel formation, ΔH_s^{EF} .

Concentration (% (w/w))	T_m K	T_s K	ΔH_m kJ mol ⁻¹	ΔH_m^{EF} kJ mol ⁻¹	ΔH_s kJ mol ⁻¹	ΔH_s^{EF} kJ mol ⁻¹
2	359.4	336.0	44.8		44.6	
3	369.0	345.9	51.3		46.1	
5	381.0	359.0	48.7		44.1	
7	386.8	366.0	46.5		43.2	
10	396.0	376.4	46.6		43.1	
12.5	401.1	383.0	46.1		42.6	
15	406.0	389.1	50.6		45.2	
20	419.5	—	58.7		—	
25	428.3	400.0	61.7		49.4	
Average			47.8 (2—15%)	48.2	44.1 (2—15%)	44.2

with ΔH_m^{EF} . Table 1 summarizes the values of T_m , T_s , ΔH_m , ΔH_s , ΔH_m^{EF} , and ΔH_s^{EF} obtained from the DSC measurements for DBS-EG gels. Note that ΔH_m , ΔH_s , ΔH_m^{EF} , and ΔH_s^{EF} agree with one another, especially at lower concentration than 20%. We have to emphasize that we can first present their good correspondence, because they cannot be compared in polymer systems where ΔH_m and ΔH_s per a mole of polymer can never be measured.

ΔH_m reflects all the interactions in a gel, including the interaction among DBS molecules, between a DBS molecule and an EG molecule, among DBS aggregates (or microcrystals), and among DBS aggregate and EG molecules, while ΔH_m^{EF} reflects the interaction at junction points. We cannot specify the structure of the junction points, since we have not done X-ray investigations of this gel system. However, the junction points are assumed to be formed by the interaction among DBS aggregates including EG molecules or the interaction among DBS crystals through EG solvents. The close agreement between ΔH_m^{EF} and ΔH_m at concentrations below 15% suggests that the structure of junction points is homogeneous in DBS-EG gel; ΔH_m is still equal to ΔH_m^{EF} , although a greater number of DBS and solvent molecules are probably taking part in junction points at higher concentrations. In the case of a macromolecular gel system, junction points should be influenced by molecular weight, conformational change, high order structure, intramolecular interaction among non-adjacent units, fraction of tacticity and so on, thus, the linearity of Eq. 1 was lost at lower concentrations of polymer molecules and at lower molecular weight of polymer.⁴³⁾ In this sense, the good correspondence between ΔH_m and ΔH_m^{EF} would be characteristic of gel system formed by small molecules.

By the way, the values of ΔH_m at higher concentrations of DBS were found to deviate from ΔH_m^{EF} . Two reasons are probable to explain this deviation. First, a greater number of

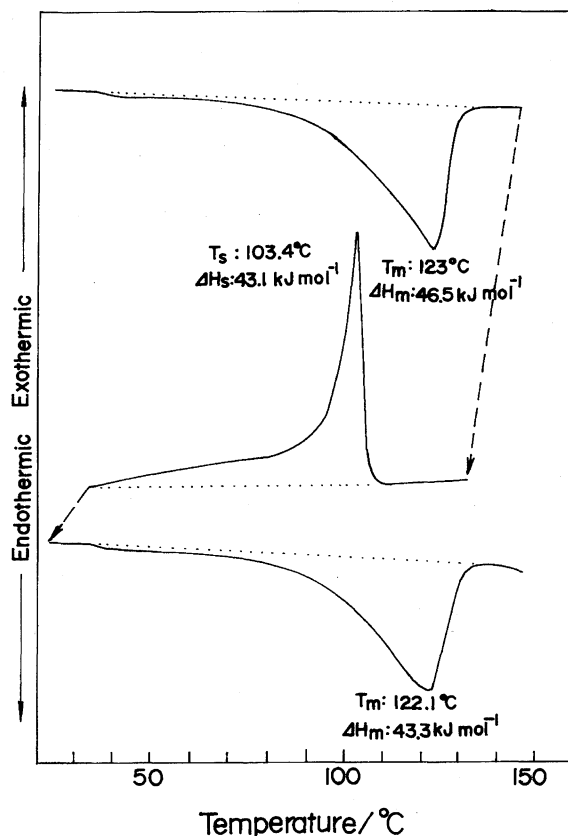


Fig. 4. DSC curves of 10% DBS-EG gel obtained for repeated heating and cooling processes: (i) heating from 5 to 150 °C, (ii) cooling from 150 to 5 °C after keeping at 150 °C for 15 min, and (iii) heating from 5 to 150 °C after keeping at 5 °C for 10 min.

microcrystals, which require more energy to melt, of DBS are formed at higher concentrations; this nucleation is also effective to urge the growth of network fibers. Second, the

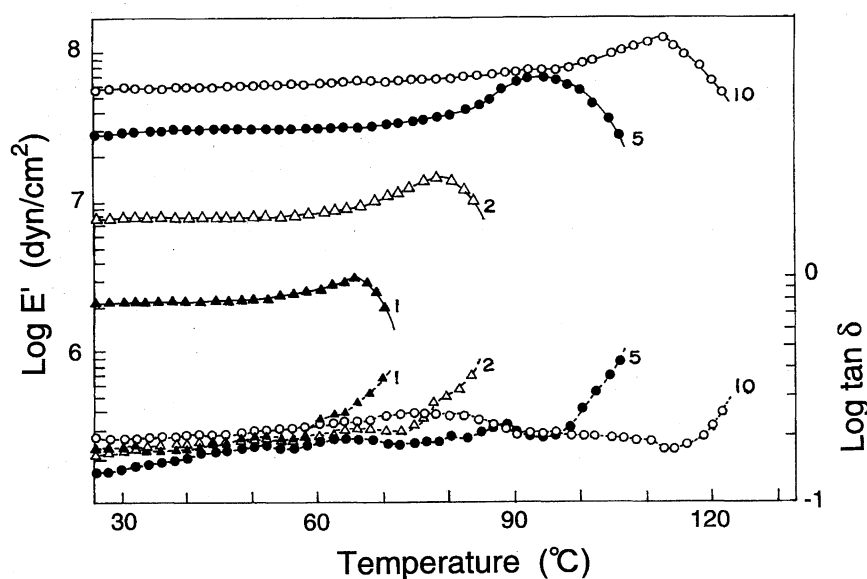


Fig. 5. Dynamic Young's modulus, E' (upper line), and mechanical loss tangent, $\text{tan } \delta$ (lower line), of DBS-EG gels at various concentrations. The figures beside the curves represent the concentration in percentage (w/w).

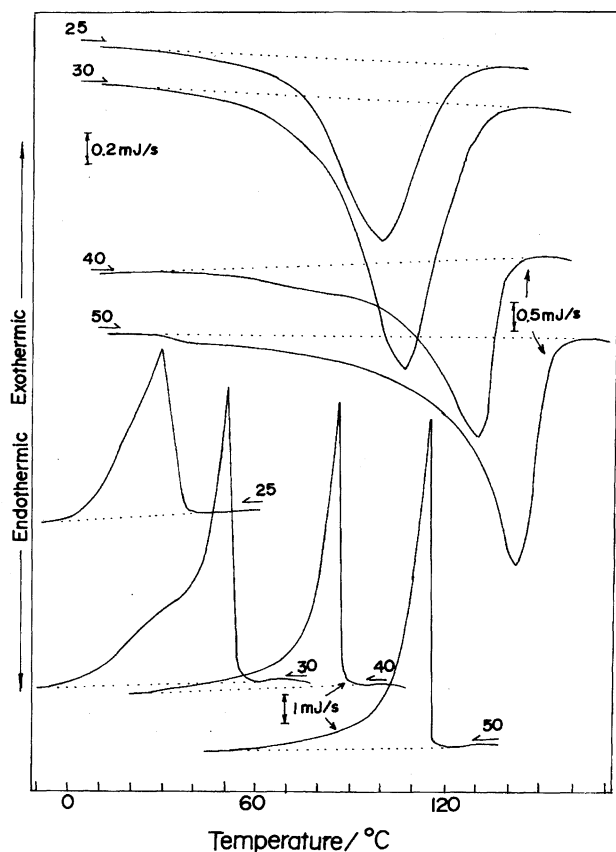


Fig. 6. Heating and cooling DSC curves of MBS-EG gels of various concentrations. The figures beside the curves represent the concentration in percentage (w/w). The broken lines are baselines used for the calculation of enthalpies.

interaction between the network fibers comes to contribute to ΔH_m at higher concentrations of DBS. Anyway, we conclude that the value of 47.8 kJ mol^{-1} (average value of ΔH_m with c_{DBS} of 2 to 15%) or 48.2 kJ mol^{-1} (ΔH_m^{EF}) is the energy required for releasing the junction points of DBS-EG gels, and that the higher energy observed for the gels with higher c_{DBS} is due to the additional interaction.

We repeatedly measured the DSC curves for 10% DBS-EG: (i) heating from 5 to 150 °C, (ii) cooling from 150 to 5 °C after keeping at 150 °C for 15 min, and (iii) heating from 5 to 150 °C after keeping at 5 °C for 10 min (Fig. 4). In the case of polysaccharide gels such as carrageenan gels³⁾ and agarose gels,⁴⁾ the exothermic peak in the heating DSC curve was shifted to higher temperatures by the repeated heating and cooling. The repetition of heating and cooling promotes syneresis and the aggregation of helical rods of polysaccharide molecules. However, the values of T_m and ΔH_m did not change much in DBS-EG gels. This indicates that the gel structure of DBS-EG was not changed by the change in temperature: This behavior agrees with the Eldridge-Ferry relation being valid, since it assumes that the ratio between the number of actual junctions and the number of potential junctions is constant at each temperature and that it can be described as a function of temperature.

Figure 5 shows the temperature dependence of the dy-

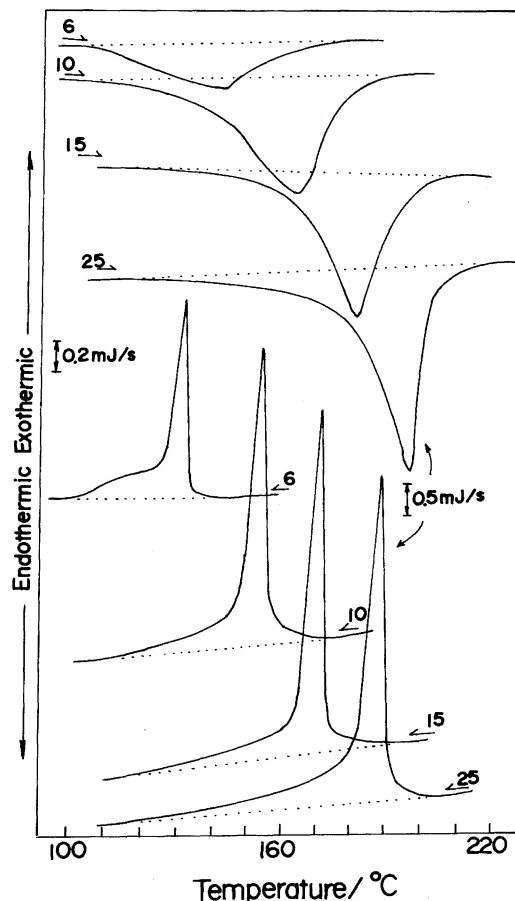


Fig. 7. Heating and cooling DSC curves of TBS-EG gels of various concentrations. The figures beside the curves represent the concentration in percentage (w/w). The broken lines are baselines used for the calculation of enthalpies.

namic modulus E' and the mechanical loss $\tan \delta$ for DBS-EG gels of various concentrations. The value of E' at each DBS concentration remained constant at lower temperatures, and began to increase gradually beyond a certain temperature. This increase is due to the appearance of the entropy elasticity, meaning that the interaction between fibers of DBS and solvents is strong enough to expand the fibers in the sol area. The value of E' increased with an increase in DBS concentration at the same temperature. The temperature at which E' began to decrease and $\tan \delta$ began to increase shifted to higher temperatures with increasing DBS concentrations. This corresponds with the fact that T_m shifted to higher temperatures with an increase in DBS concentration, shown as Fig. 2. As expected, the temperature at which E' begins to be undetectable (right end of curves) is nearly equal to T_m as measured by the DSC measurements. For example, in the 2% DBS-EG gel ($T_m=86^\circ\text{C}$), E' became undetectable at ca. 85°C ; in the 5% gel ($T_m=108^\circ\text{C}$), E' became undetectable at ca. 110°C ; in the 10% gel ($T_m=123^\circ\text{C}$), E' became undetectable at ca. 125°C .

In summary, the thermal and rheological properties of DBS-EG gels suggest that (1) the number of the junction points is constant at the same temperature and is a function

Table 2. Thermal Properties of MBS-EG Gels at Various Concentrations

The temperature of gel melting, T_m , temperature of gel setting, T_s , enthalpies obtained from the peak area of the DSC curves for gel melting, ΔH_m , and for gel formation, ΔH_s , and enthalpies obtained from the Eldridge-Ferry plot for gel melting, ΔH_m^{EF} , and for gel formation, ΔH_s^{EF} .

Concentration (% (w/w))	T_m K	T_m K	ΔH_m kJ mol ⁻¹	ΔH_m^{EF} kJ mol ⁻¹	ΔH_s kJ mol ⁻¹	ΔH_s^{EF} kJ mol ⁻¹
25	372.5	302.1	18.9		13.6	
30	379.9	323.5	21.1		16.8	
40	403.2	358.8	21.7		18.4	
50	415.2	387.9	22.5		18.7	
Average			21.1	22.6	16.9	8.8

Table 3. Thermal Properties of TBS-EG Gels at Various Concentrations

The temperature of gel melting, T_m , temperature of gel setting, T_s , enthalpies obtained from the peak area of the DSC curves for gel melting, ΔH_m , and for gel formation, ΔH_s , and enthalpies obtained from the Eldridge-Ferry plot for gel melting, ΔH_m^{EF} , and for gel formation, ΔH_s^{EF} .

Concentration (% (w/w))	T_m K	T_m K	ΔH_m kJ mol ⁻¹	ΔH_m^{EF} kJ mol ⁻¹	ΔH_s kJ mol ⁻¹	ΔH_s^{EF} kJ mol ⁻¹
6	412.2	405.7	37.1		32.4	
10	437.9	428.2	40.1		32.5	
15	454.0	445.4	46.9		31.5	
25	469.1	462.0	46.7		31.5	
Average			42.7	27.5	32.0	24.1

of concentration, (2) the transition of gel formation and gel melting proceeds via a second-order or higher-order reaction, (3) the values of the enthalpy of gel formation and gel melting obtained by the Eldridge-Ferry plot agree well with those obtained from the peak area of the DSC curves corresponding to the transition from gel to sol and from sol to gel, and (4) the increase in elasticity of the gel due to the increase in entropy is observed, indicating a strong interaction between

the fibers of DBS crystals and EG solvents.

The Properties of MBS-EG and TBS-EG Gels. We have examined the thermal and rheological properties of MBS-EG and TBS-EG gels to investigate the main cause of stabilization of these gels from the standpoint of the chemical structure. MBS-EG does not form gels at concentrations below 10%, while TBS-EG can form gels at concentrations higher than 0.5%. The order of the concentration when the

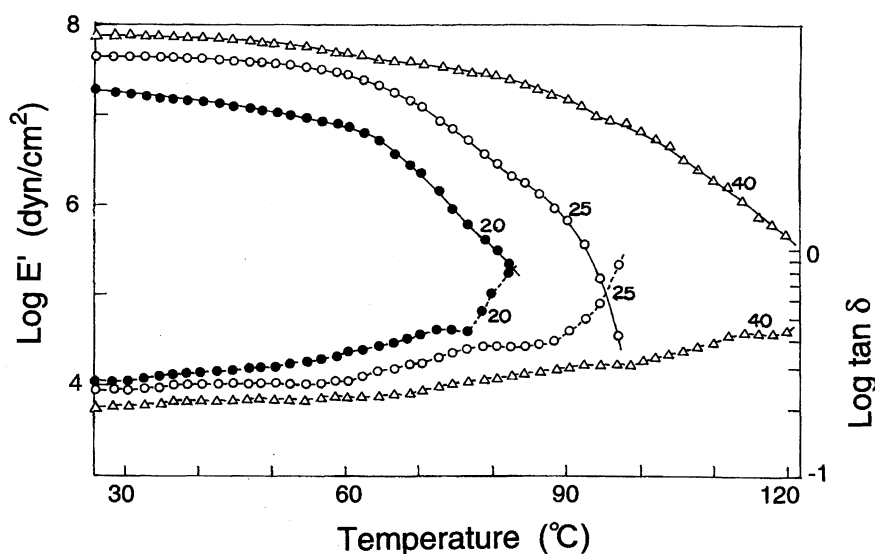


Fig. 8. Dynamic Young's modulus, E' (upper line), and mechanical loss tangent, $\tan \delta$ (lower line), of MBS-EG gels at various concentrations. The figures beside the curves represent the concentration in percentage (w/w).

Table 4. Thermal Properties of DBS-EG Gels at various Concentrations
 The temperature of gel melting, T_m , temperature of gel setting, T_s , enthalpies obtained from the peak area of the DSC curves for gel melting, ΔH_m , and for gel formation, ΔH_s , and enthalpies obtained from the Eldridge-Ferry plot for gel melting, ΔH_m^{EF} , and for gel formation, ΔH_s^{EF} .

Concentration (% (w/w))	T_m K	T_m K	ΔH_m kJ mol ⁻¹	ΔH_m^{EF} kJ mol ⁻¹	ΔH_s kJ mol ⁻¹	ΔH_s^{EF} kJ mol ⁻¹
0.5	384.2	349.4	57.3		43.0	
1	397.2	362.5	60.8		46.5	
2	412.0	382.2	64.4		48.3	
3	421.5	392.6	64.4		44.1	
4	429.1	402.3	64.4		46.5	
5	435.8	408.6	68.7		49.4	
Average			63.3	62.4	46.3	45.8

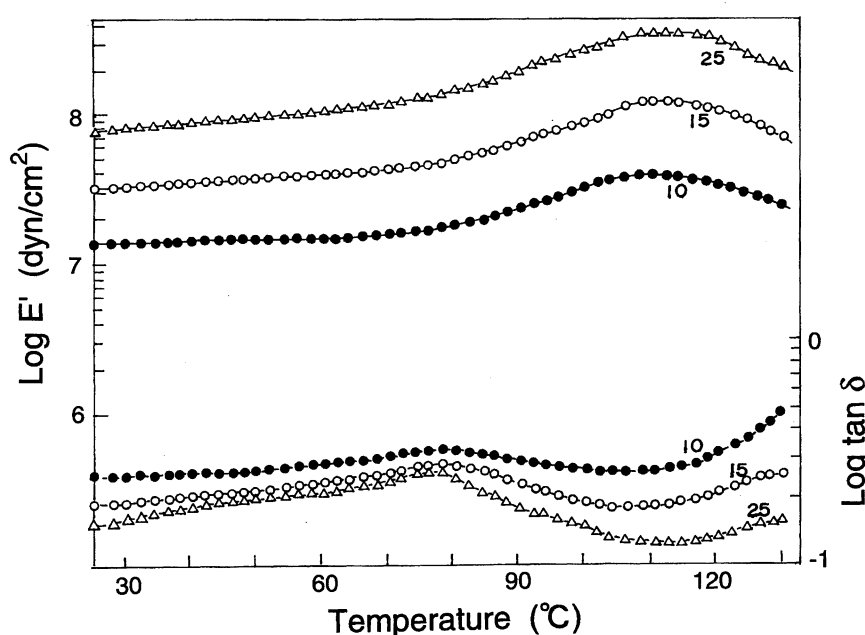


Fig. 9. Dynamic Young's modulus, E' (upper line), and mechanical loss tangent, $\tan \delta$ (lower line), of TBS-EG gels at various concentrations. The figures beside the curves represent the concentration in percentage (w/w).

gelation takes place and the gels are stabilized so much is MBS $\gg$ TBS>DBS when the solvent is EG. DBS-EG gel was found to be formed above 10 mM.³⁶⁾

Figures 6 and 7 show the heating and cooling DSC curves of MBS-EG gels and TBS-EG gels at different concentrations, respectively. The thermal behavior of each gel is basically identical with that of DBS-EG gel. The endothermic and exothermic peaks of DBS-EG are the sharpest among all the gels with the same concentration of 25% studied in this paper. It suggests that the structure of junction points in DBS-EG is most distinct, probably due to the stable conformation of crystal. In other words, the chemical structures of junction points of MBS-EG and TBS-EG are not perfectly stabilized.

We applied the Eldridge-Ferry equation to the MBS-EG and TBS-EG gel systems, since a plot of $\log_e$ (concentration) vs. $1/T_m$ and a plot of $\log_e$ (concentration) vs. $1/T_s$ give essentially straight lines with values of ΔH_m^{EF} and ΔH_s^{EF} , re-

spectively, by the least squares method. Tables 2 and 3 summarize the values of T_m , T_s , ΔH_m , ΔH_s , ΔH_m^{EF} , and ΔH_s^{EF} obtained from the DSC measurements for MBS-EG and TBS-EG gels, respectively.

Roughly speaking, ΔH_m , ΔH_s , ΔH_m^{EF} , and ΔH_s^{EF} agree almost completely with one another, however, they are not exactly the same as the values for DBS-EG gels. ΔH_m and ΔH_m^{EF} for MBS-EG gels agree well with each other, while ΔH_m of TBS-EG is 1.5 times as large as ΔH_m^{EF} . What we should emphasize here is that ΔH_s and ΔH_s^{EF} are smaller than ΔH_m and ΔH_m^{EF} in the case of MBS-EG and TBS-EG gels.

The order of the enthalpy values is of DBS>TBS $\gg$ MBS (Tables 1, 2, and 3). The values of enthalpies are considered to show how much the gel structure, i.e., the junction point, is stabilized. In this sense, DBS-EG gels are most stabilized of all, while the structure of MBS-EG gel is weakest.

Next we measured the temperature dependence of E' and $\tan \delta$ for MBS-EG gels of various concentrations (Fig. 8).

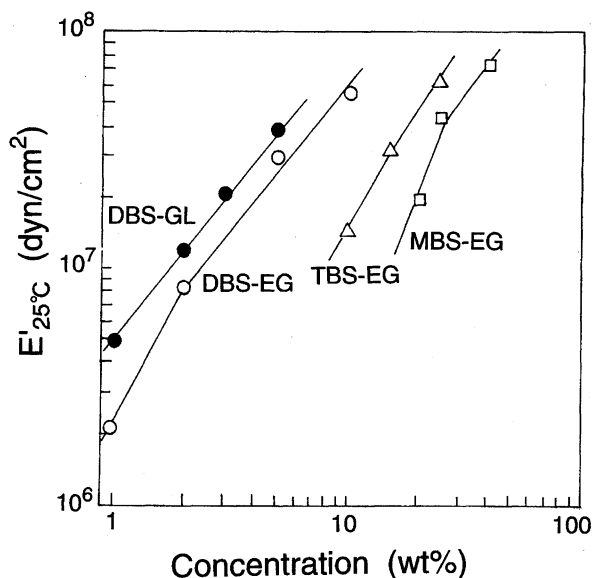


Fig. 10. Concentration dependence of E' at 25 °C.

The behavior is different from that of DBS-EG gels. E' decreased gradually, and beyond a certain temperature, it began to decrease rapidly. This means that entropy elasticity was not observed. On the other hand, the viscoelastic properties of TBS-EG gels have quite similar tendencies to those of DBS-EG gels, as is shown in Fig. 9. The change in E' of TBS-EG gels accompanying the increase in entropy is less drastic than with DBS-EG gels. In any cases, E' was observed to be higher at higher concentrations. When the E' values of the three gels are compared at the same concentration, the order should be DBS > TBS > MBS (DBS > TBS at 10% and TBS > MBS at 25%).

In conclusion, (1) the stability of MBS-EG gels is the weakest of the three gels studied in the present work, while the stability of DBS-EG gels is best of all, and (2) the enthalpy for the gel formation is smaller than that for the gel melting in the case of MBS-EG and TBS-EG gels.

The Properties of DBS-GL (Glycerol) Gels. In order to get information on the role of solvent molecules, we studied the physical properties of DBS-GL since GL has one more hydroxy group than EG. The Eldridge-Ferry plots for both the gel melting and gel forming give essentially straight lines. The thermal parameters obtained from the DSC measurements are summarized in Table 4. The ΔH_m calculated from the endothermic peak area of the heating DSC curve is identical with the ΔH_m^{EF} calculated from the Eldridge-Ferry plot, while the ΔH_s calculated from the exothermic peak area of the cooling DSC curve is identical with the ΔH_s^{EF} from the Eldridge-Ferry plot. However, the value of ΔH_m is 1.4 times as large as ΔH_s .

Figure 10 shows the concentration dependence of E' at 25 °C. The value of E' for DBS-GL is higher than that for DBS-EG, when the concentration of DBS is the same. The thermal and rheological behavior of DBS gels suggest that the gel structure of DBS is stabilized more in GL solution than in EG solution. Thus, it is clear that the hydrogen bond

between DBS molecules and solvent molecules is important in the stabilization of gels.

The Reaction for the Stability of MBS, DBS, and TBS Gels in EG. In this section we discuss two issues related to the stabilization of the gels formed from the sorbitol derivatives: (i) why ΔH_m is larger than ΔH_s and (ii) the main driving force for the formation and stabilization of the gels.

The ratio of the average value of ΔH_s to that of ΔH_m is 1.08 for DBS-EG, 1.25 for MBS-EG, 1.33 for TBS-EG, and 1.37 for DBS-GL. The gel state, once kept at low temperatures, includes various interactions among many different groups, for example, even an oxygen atom with low electron density could participate in hydrogen bonding at low temperatures where the molecular motion of functional groups is so restricted that a functional group can form hydrogen bonding with another group situated nearby. Once hydrogen bonds are formed, they will be kept up to a high temperature.⁴⁴⁾ Thus, it is quite natural that the heat required for the gel melting, ΔH_m , should be larger than that released by the stabilization due to the gel formation, ΔH_s . Needless to say, ΔH_s definitely includes the contribution of hydrogen bond interaction, however, since gels are urged to form much more hydrogen bonding at 5 °C, which is the starting temperature in DSC measurements, ΔH_m becomes larger than ΔH_s . In this sense, the value of ΔH_s is supposed to demonstrate the net energy based on the gel structure. Note that ΔH_s of DBS-GL (46.3 kJ mol⁻¹) is nearly the same as ΔH_s of DBS-EG (44.1 kJ mol⁻¹), while ΔH_m of DBS-GL (63.3 kJ mol⁻¹) is 1.3 times as much as ΔH_s of DBS-EG (47.8 kJ mol⁻¹). This clearly shows that the main structure of junction points in DBS-GL gels is almost identical with that in DBS-EG gels, but that the junction points or networks of DBS-GL gels can be more easily stabilized by additional hydrogen bonding with solvent GL, which has one more hydroxy group. On the other hand, we would like to emphasize that the ΔH_s value of MBS-EG is quite low compared to the ΔH_s values of the other gels. Accordingly, the stabilization of the gels is in the order DBS-EG > TBS-EG > MBS-EG in this work.

Let us consider the main cause of formation and stabilization of the gels of these sorbitol derivatives in alcoholic solvents. The gel structure is considered to be stabilized in the case where (1) ΔH_m (or ΔH_m^{EF}) and ΔH_s (or ΔH_s^{EF}) are larger and (2) E' is higher, when the concentration of sorbitol derivatives is the same. Thus, the sorbitol derivatives in EG to efficiently form and stabilize gels in the order DBS-EG > TBS-EG > MBS-EG.

With regard to solvent, molecules having more hydroxy groups can form and stabilize gels of DBS more effectively, although the values of ΔH_s 's are nearly the same. As is pointed out above, the junction points or networks of DBS-GL gels can be more stabilized by hydrogen bonding with the solvent GL: The number of hydroxy groups is 3 (GL) and 2 (EG).

From the thermal and rheological measurements of MBS-EG, DBS-EG, and TBS-EG gels, the number of hydroxy groups in a sorbitol derivative is found to be not an

important factor to stabilize and form gels efficiently, because the properties of MBS-EG gels are shown to be most unstable in spite of four hydroxy groups: the number of hydroxy groups is 4 for MBS, 2 for DBS, and 0 for TBS.

Yamasaki et al. studied the influence of hydrogen bonding on gelation by comparing the gel properties of some DBS derivatives.³⁸⁾ They reported that the 6-position hydroxy group of DBS seems to be important in the formation of the gel. It is quite reasonable because this is a primary hydroxy and the farthest group from the rigid closed ring. Moreover, when we studied the gelation mechanism of some regioselective cellulose derivatives, the hydrogen bond engaged in the hydroxy group at the 6-position of the repeating unit of cellulose is the major interaction site, forming a crosslinking point of the cellulose gel network.^{10,11)} However, our present results have clearly shown that neither the 6-position hydroxy group nor other hydroxy groups of the sorbitol derivatives contribute to the gelation very much. The formation of MBS-EG gels requires the greatest amount of sorbitol derivatives, while TBS, which has no hydroxy group, can form gels at low concentrations. Since the number of oxygen atoms taking part in an ether group is 6 for TBS, 4 for DBS, and 2 for MBS, the hydrogen bond with an ether oxygen is not the main factor, either.

Another possibility is that the hydrophobic interaction among benzyldene groups keeps sorbitol derivatives associated with one another. However, the number of benzyldene groups is not so crucial to stabilize the gels, because it is 3 for TBS, 2 for DBS, and 1 for MBS: DBS forms more stable gels than TBS and MBS.

All these facts suggest that the main cause for the formation and stabilization of gels in this work on sorbitol derivatives is not due to simple interactions between the sorbitol derivatives and solvents. According to Yamasaki et al., the DBS-EG gel state is a metastable state having two kinds of mesophases: One is the crystalline phase consisting of the spherulitic texture, and the other is the isotropic mesophase comprising a network-like structure between spherulitic textures.³⁵⁾ These observations suggest that the formation of crystals could be an important factor in the DBS-EG gel system.

Webber et al. identified the absolute stereochemical configuration of the benzyldene group of 2,4:5,6-di-*O*-benzyldene-3-*O*-methyl-D-glucitol in dioxane by means of ¹H NMR spectra.^{46,47)} The benzyldene groups are found to be situated not in the axial positions against the D-glucitol ring, but rather in the equatorial positions. This structure should be stabilized due to a small repulsion energy without large steric hindrance. Thus, the benzyldene groups of MBS, DBS, and TBS in EG are assumed to be in equatorial positions as shown in Fig. 11. It is difficult to assume which derivative of sorbitol is most readily crystallized, however, it is possible to assume which crystal is most stable. Since the chemical structure of DBS has the best symmetry of these three derivatives, the crystal that DBS molecules form must be stabilized best of all. In other words, the balance of chemical structures is considered to be the most crucial factor for the formation

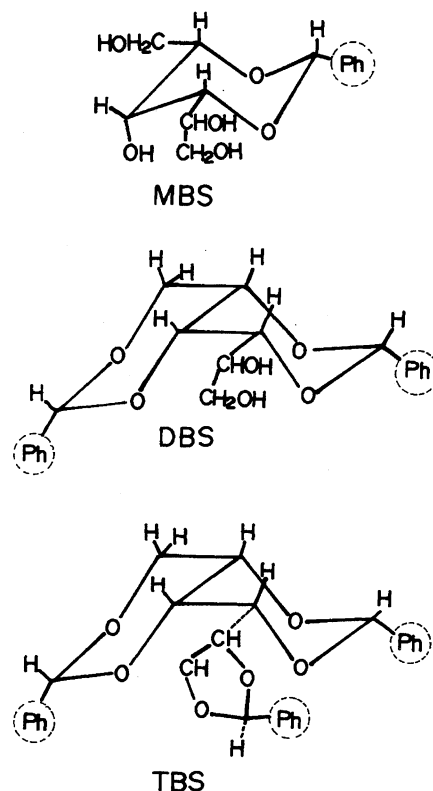


Fig. 11. Most probable conformations of MBS, DBS, and TBS molecules.

and stabilization of gels in this sorbitol derivative's system.

It is needless to say that hydrogen bonding and van der Waals interaction are important in both the kinetic process of the gelation, i.e., nucleation, and the stability of the DBS fibers in the equilibrium state. However, the most important factor can be specified to the structure itself of a six-member ring and/or a ten-member ring formed in MBS, DBS, and TBS together with the connection of benzyldene groups in equatorial positions. If a compound does not have such a rigid and chiral structure, a fiber network would not be formed and gelation would not take place. In particular, the symmetric structure of a DBS molecule is considered to form the most stable gels of all the compounds studied in the present work. Importance of the molecular architecture is already suggested in the formation of stable physical gels of low molecular weight compounds.¹⁶⁾ In order to test this conclusion, we will report on the gelation behavior of DBS derivatives in the near future.

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