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The Phase Transition in the Gel State of the 1,3 : 2,4-Di-*O*-benzylidene-D-sorbitol/Ethylene Glycol System

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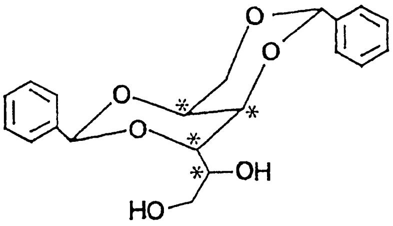
In chiral oil gelators, only 1,3 : 2,4-di-*O*-benzylidene-D-sorbitol (D-DBS) can form gels with alcoholic solvents. The D-DBS concentration dependence of the state in the binary system D-DBS/ethylene glycol, were studied using optical, rheological and spectral measurements. Based on the changes in the transmission and mechanical properties, two phase transition points, which depended upon the D-DBS concentration, were observed at 10 and 30 mM. The low-concentration point was the critical gel concentration. The gel was formed above 10 mM. D-DBS formed spherical domains in the gel between 10—30 mM and made continuous crystals on the entire gel above 30 mM. The aggregated structure of D-DBS in ethylene glycol was studied, utilizing electronic and circular dichroism measurements. According to the gelation, the absorption of the transition moment along the long axis of the benzene ring was red-shifted. The relative orientation changed in 10—30 mM from the hyperchromism and hypochromism of the electronic absorptions, but was fixed above 30 mM. D-DBS exhibited remarkable CD enhancements due to the formation of a gel. The concentration dependence of the molar ellipticities of the CD absorptions was similar to the tendency of the electronic spectra. This indicated that the aggregated structure was changed, depending upon the D-DBS concentration in ethylene glycol; the optical and mechanical properties were related to the aggregated structure which D-DBS formed.

In chiral oil gelators, 12-hydroxyoctadecanoic acid, *N*-dodecanoyl-L-glutamic acid dibutylamide and 1,3 : 2,4-di-*O*-benzylidene-D-sorbitol (D-DBS), only D-DBS can form gels with alcoholic solvents, such as ethanol or ethylene glycol.[1,2] In the D-DBS/ethylene glycol system, D-DBS formed two kinds of mesophases in the gel state. The gel state of D-DBS was metastable below the phase transition temperature from a gel to an isotropic solution, which changed to the crystalline phase. In the crystalline state, a helical aggregated structure was observed using electron microscopy.[3] The phase transition from the gel state to the liquid crystalline state of a chiral surfactant having an amino acid/water system was studied using thermoanalysis as well as the electronic and circular dichroism (CD) spectra.[4] The chiral amphiphiles, *N*-dodecyl-L-glutamic acid, formed a lyotropic cholesteric liquid crystal in a nonpolar solvent, such as benzene. In the liquid crystal phase, absorption in the CD spectra was observed, which originated from a cholesteric liquid crystal.[5] On the other hand, the different absorption maximum in the CD spectra was observed in an alcoholic solution. The analysis of the CD spectrum was attributed to the formation of a chiral aggregate through hydrogen bonds among the surfactants.[6] In the present work, we investigated the relationship between the mechanical and optical properties of D-DBS/ethylene glycol gel as well as the aggregated structure which D-DBS forms, depending upon the D-DBS concentration.

Experimental

Materials. 1,3 : 2,4-di-*O*-benzylidene-D-sorbitol (D-DBS, showed in Scheme 1), was purchased from Shin-Nihon-Rika Co., Ltd., and was determined to be more than 95% pure by the NMR technique. (An impurity was 1,3 : 2,4 : 5,6-tri-*O*-benzylidene-D-sorbitol.) The sample was used without further purification. The solvent, the ethylene glycol used in this work, was obtained from Nacalai-Kagaku Co., Ltd., and dried over Molecular Sieve 3A.



Scheme 1.

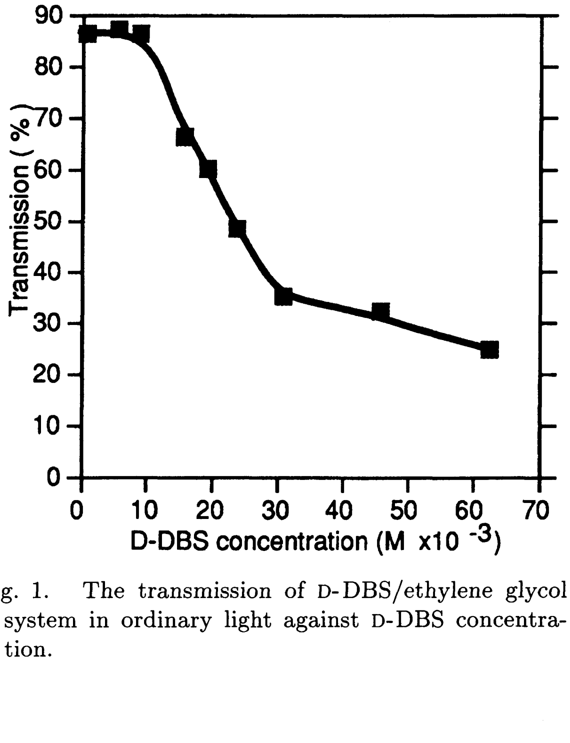


Fig. 1. The transmission of D-DBS/ethylene glycol system in ordinary light against D-DBS concentration.

Methods. The samples used for the phase equilibria were weighted directly into glass test tubes with a Teflon-sealed screw cap. The samples were dissolved at 100 °C and cooled down to room temperature. The units of the D-DBS concentration used were $\mathrm{mM}=1\times10^{-3}\,\mathrm{mol\ dm}^{-3}$. All of the measurements were carried out at 25 °C. The hardnesses were obtained by using a Fudoh Co., Ltd. NRM-2010, and was calculated from the yield stress in a stress–strain curve.[7] The transmission and electronic spectra of the solution and gel states were found using a Shimadzu Co., Ltd. MPS-2000; the transmissions were observed at 530 nm with a 1 cm light length. The electronic spectra were measured with 0.03—5 mm light length quartz cells. Spectra scanning was carried out from 300 to 180 nm at intervals of 2 nm. CD spectra measurements of the solution and gel were carried out using a JASCO J-600 in the 300 to 200 nm region at a speed of 20 $\mathrm{nm\,min}^{-1}$. The path length of the quartz cells was 0.03 mm above 12 mM and 1 mm in the solution state.

Results and Discussion

Macroscopic Characterization of the Gel State. The change in the mechanical and optical properties of D-DBS gel, depending upon the D-DBS concentration, was evaluated by means of the transmission of ordinary light as well as rheological measurements. According to naked-eye and microscopic observations, the gel was formed at a concentration of more than 10 mM. Below the critical concentration, the sample was in the solution states (region A). D-DBS partly formed spherical domain at concentrations

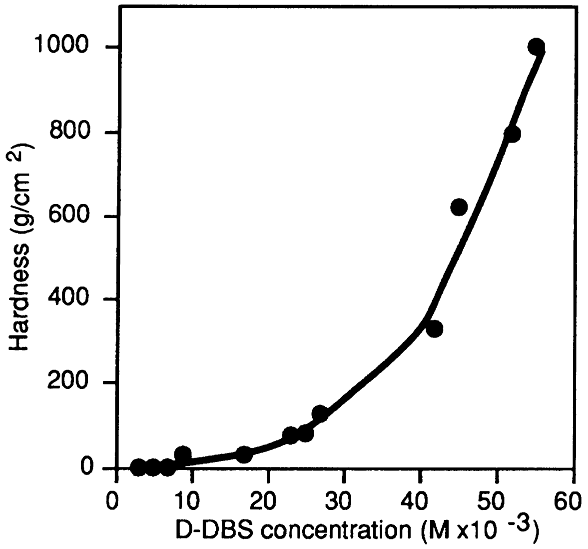


Fig. 2. The hardness curve of D-DBS ethylene glycol system against D-DBS concentration.

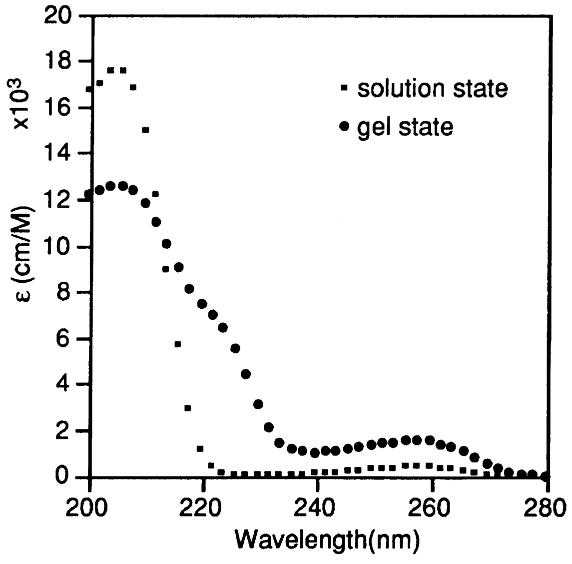


Fig. 3. The electronic spectra of D-DBS in the solution and gel state. ■: The solution state; ●: The gel state.

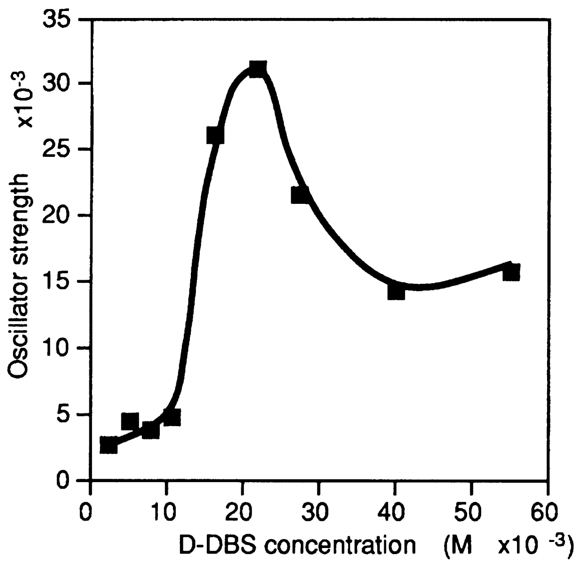


Fig. 4. The oscillator strengths of benzene absorption of D-DBS against D-DBS concentration.

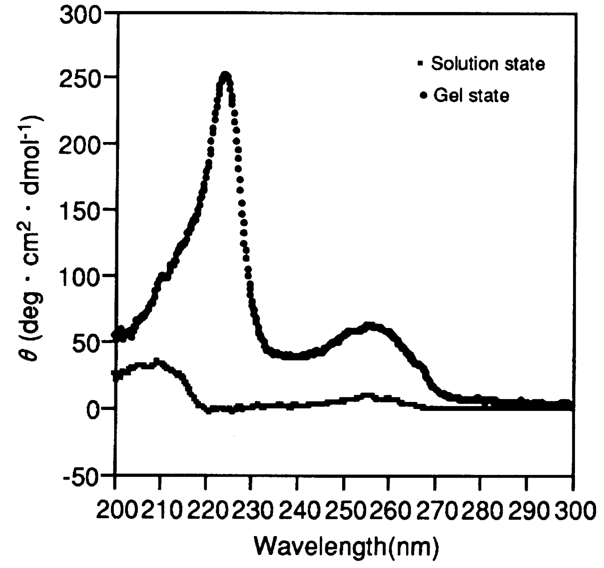


Fig. 5. The CD spectra in the solution and gel state. ■: The solution state; ●: The gel state.

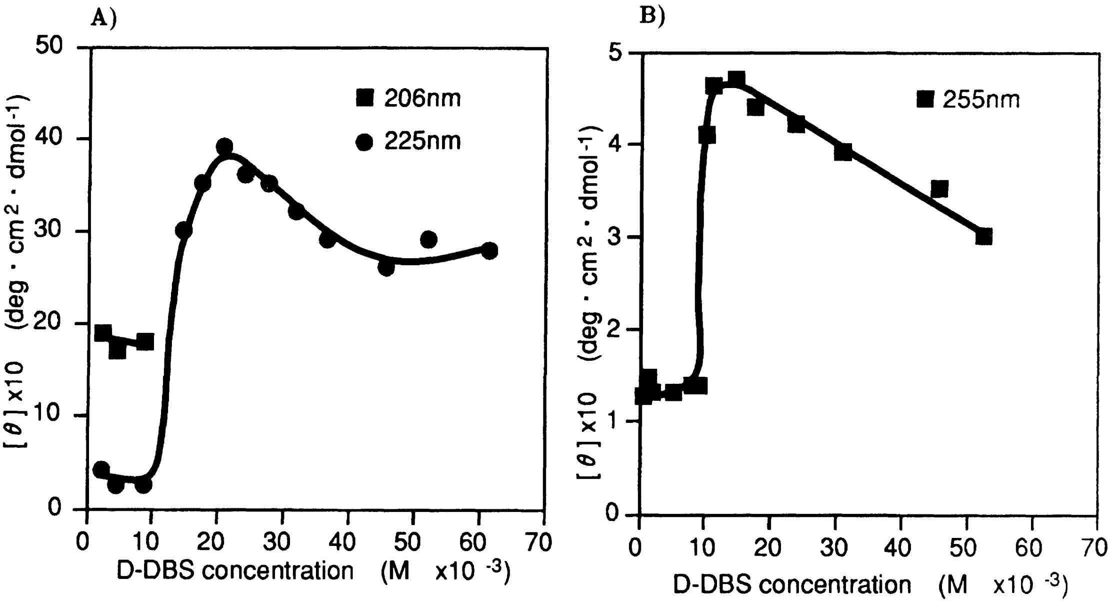


Fig. 6. The molar ellipticities of 206, 225, and 255 nm absorption against D-DBS concentration. A) ■: The 206 nm absorption; ●: The 225 nm absorption. B) The 255 nm absorption.

between 10—30 mM (region B). Above 30 mM (region C), the spherical domains overlapped each other.[3] The degree of the size of the spherical domain was evaluated by means of transmission measurements. The turbidity of the gel states increased, depending upon the D-DBS concentration. The transmission of the D-DBS/ethylene glycol system using ordinary light against the D-DBS concentration is shown in Fig. 1.

Two changing points in the curves for ordinary light were observed at 10 and 30 mM, indicating that the size of the spherical domain changed at 30 mM. The degree of interaction between the spherical domain was studied using the gel hardness. A hardness curve against the D-DBS concentration is shown in Fig. 2.

As is evident in this figure, the hardness curve slowly increased from 10 to 30 mM, after which it drastically did. This indicates that the interaction between the spherical domains is weak in region B, but increases due to an overlap of the domain. Two transitions were observed based on the macroscopic measurements. It is assumed that D-DBS forms two kinds of gels, depending upon the D-DBS concentration.

UV Spectra of the Solution and Gel State of D-DBS in Ethylene Glycol. The relative orientation of the benzene ring in D-DBS was studied using electronic measurements. The typical electronic spectra of D-DBS were measured in the solution and gel states (Fig. 3).

In the solution state, absorptions of the benzene ring were observed at 206 and 255 nm. The absorption near 206 nm is associated with the transition moment along the long axis of the benzene ring; the 255 nm absorption corresponds to the transition moment along the short axis of benzene.[12] Concerning the gelation process, a new absorption appeared at 225 nm, other than that at 206 nm. This is presumed to indicate that the short-wavelength absorption is partly red-shifted from 206 to 225 nm. To evaluate the intensity of the longest wavelength absorption, the oscillator strengths of D-DBS were calculated according to the following equation:[8]

$$f = 4.32 \times 10^{-9} \int \varepsilon(\nu)\mathrm{d}\nu, \qquad (1)$$

where f is the oscillator strength. These value were obtained by dividing the absorption curves into rectangles at intervals of 2 nm. The oscillator strengths of the 225 nm absorption band against the D-DBS concentration are shown in Fig. 4.

According to the gelation, the oscillator strength increased and decreased between 10—30 mM (region B). It was constant above 30 mM (region C). Both hyperchromism and hypochromism were observed in region B. Depending on the relative orientation of the transition moments, hypochromism (parallel stacking) or hyperchromism (linear array) were observed.[8,9] Based on the change in the oscillator strength in the 255 nm absorption band, it is indicated that the relative orientation of the benzene rings in D-DBS are ordered like a linear array after gelation at 10—15 mM, whereas it changes from a linear array to parallel stacking, depending upon the D-DBS concentration.

CD Spectra of Solution and Gel D-DBS in Ethylene Glycol. The CD spectra represent one of the most suitable techniques to analyze the phase transition from the gel state to the solution state in the chiral amphiphiles/water system.[4] Typical CD spectra in the solution and gel states of the D-DBS/ethylene glycol system are shown in Fig. 5. The positive Cotton effect was observed in each spectra. D-DBS exhibited remarkable CD enhancements due to the formation of a gel.

As indicated in this figure, the 206 and 255 nm absorptions were observed in solution. Accompanying the formation of the gel, the 206 nm band disappeared, and only the 225 nm band was observed, which was observed in the electronic spectra of the gel state. The molar ellipticities of each absorption are plotted against the D-DBS concentration in Fig. 6.

The 206 nm values, which were observed only in the solution state, decreased to 10 mM. On the other hand, the curve of the molar ellipticity ($[\theta]_{225}$) increased at 10—20 mM and decreased at 20—30 mM, after which it became a straight line which was almost parallel to the abscissa above 30 mM. The $[\theta]_{255}$ increased rapidly in the 10—15 mM region, and then slowly decreased above 15 mM. The concentration dependence of the CD magnitude of the 225 nm absorptions was correlated with the macroscopic transitions and the results of the electronic absorption. The CD band at 206 nm is attributable to the asymmetric structure of the optical active sorbitol in D-DBS. A change in the magnitude of the CD band was observed during the formation of a helical structure of protein,[10] and the formation of a micelle of the optically active acylamino acid/alcoholic solution.[5,6] It is assumed that the CD absorption at 220 nm, observed in the gel state reflects a D-DBS aggregation which enhanced the chirality of D-DBS.

Conclusion

It was demonstrated that there were three concentration regions, in which D-DBS formed different mesophases, based on optical, mechanical and spectral measurements depending upon the D-DBS concentration. In the concentration region below 10 mM (region A), the mesophase was the solution state. It is assumed that D-DBS was molecularly dispersed in the solution state, based on the low-molar ellipticities of the CD spectra. Regarding the gelation process, the red shift of the band assigned to the electronic absorption of the benzene ring indicates that the surrounding of the benzene ring in the solution is more hydrophilic than in the gel state.[11] D-DBS formed a gel state above 10 mM. In region B, D-DBS formed spherical domains, which did not interact with each other. The aggregated structure which D-DBS formed, changed with the concentration; this was confirmed by a spectral measurement. In region C, the spherical crystals interacted with each other and the aggregated structure was fixed; this was confirmed based on an increase in the hardness and a non-concentration dependency of the spectral results, respectively.

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