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The Thermal Behavior of 1,3 : 2,4-Di-*O*-benzylidene- D-sorbitol/Ethylene Glycol Gel

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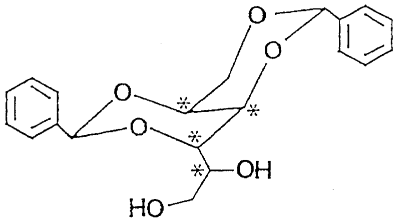
The so-called 1,3 : 2,4-di-*O*-benzylidene-D-sorbitol (D-DBS) can cause the gelation of alcoholic solvents. The thermal behavior of a 1 wt% D-DBS/ethylene glycol gel was studied using thermal, optical, mechanical, and spectroscopic measurements. Changes in the optical and mechanical properties were observed at around 45 and 80 °C. Upon heating, the diameter of the spherulitic texture in the gel decreased above around 45 °C and disappeared at around 80 °C. In a thermal analysis, an endothermic peak was observed at around 80 °C, which agreed with the gel state-isotropic solution phase-transition point. The aggregated structure of D-DBS in ethylene glycol was studied, using UV absorption and circular dichroism (CD) measurements. The relative orientation of the benzene rings changed above 45 °C, due to the hypochromism of the UV absorptions. The gel showed a temperature dependence of the CD spectra. With increasing temperature, the value of the molar ellipticities increased at 27—82 °C, and drastically decreased at 82—93 °C, indicating that the aggregated structure underwent a change at between 45—80 °C and disappeared above 80 °C. The macroscopic level, as well as the optical and mechanical properties were related to the change in the aggregated structure formed by D-DBS.

1,3 : 2,4-Di-*O*-benzylidene-D-sorbitol (D-DBS; where D-sorbitol is an erroneous, but common name for D-glucitol) can cause gelation of alcoholic solvents, such as ethanol or ethylene glycol.[1,2] The aggregated structure of D-DBS in the gel state was studied, mainly by IR, UV, and CD spectroscopy as well as electron microscopy.[3] In the D-DBS/ethylene glycol system, D-DBS formed two kinds of mesophases in the gel state. The gel state–crystalline state and the gel state–isotropic solution phase transitions are clearly shown in the phase diagram of the D-DBS/ethylene glycol binary system. Electron-microscopic pictures of the crystalline state show a helically aggregated structure.[4] The phase transition from a gel state to a liquid-crystalline state of the azobenzene-containing chiral amphiphile/water system was studied using a thermal analysis, as well as UV and CD spectroscopy.[5] Chiral amphiphiles containing two fluorocarbon chains and one flexible hydrocarbon chain resulted in a bilayer molecular structure in an organic solvent. The CD data indicated that the component molecules in the aggregate were highly organized in organic media.[5,7] In the present work, we investigated the relationship between the mechanical and optical properties of D-DBS/ethylene glycol as well as the temperature dependence of the aggregated structure formed by D-DBS.

Experimental

Materials. 1,3 : 2,4-Di-*O*-benzylidene-D-sorbitol (D-DBS, shown in Scheme 1) was purchased from Shin-Nihon-Rika Co., Ltd., and was determined to be more than 95% pure by the NMR technique. (One impurity was 1,3 : 2,4 : 5,6-tri-*O*-benzylidene-D-sorbitol.) The sample was used without further purification. The solvent, an ethylene glycol, was obtained from Nacalai Tesque, Inc., and dried over molecular sieves.



Scheme 1. The chemical structure of 1,3 : 2,4-di-*O*-benzylidene-D-sorbitol (D-DBS).

Methods. The D-DBS concentration in ethylene glycol was 1 wt% in all measurements. The samples were dissolved at 100 °C and cooled down to room temperature. Observations of the gel state were carried out under polarized light using a Nikkon XF-2 microscope equipped with a Mettler Co., Ltd. FP-800 thermoregulator. Differential scanning calorimetry (DSC) was carried out with a Seiko Instrument & Electronics Co., Ltd. heat-flux type DSC-200. The gel was put into a 15 μl silver capsule cell and heated at a rate of 5 °C min^{-1}. The heat capacity was evaluated by comparing the DSC heating curves of the samples to that of sapphire.[8,9] The gel hardness was obtained by using a Fudoh Co., Ltd. NRM-2010 rheometer, and was determined from the yield stress obtained from stress–strain curves.[10] The transmission under polarized light and the UV spectra of the gel state were obtained by using a Shimadzu type MPS-2000 spectrometer equipped with a thermoregulator; the transmissions were observed at 530 nm with a 1 cm cell. The UV spectra were measured with a 0.03 mm light-length quartz cell in a wavelength range of 300 to 190 nm in 2 nm increment. The CD absorption measurements of the gel were conducted with a JASCO type J-600 spectrometer equipped with a thermoregulator. The CD spectra were obtained from 300 to 180 nm at a scanning speed of 20 nm min^{-1}. The light path-length of the quartz cell was 0.03 mm. Spectral measurements were carried out after keeping the sample at each respective temperature for 20 min.

Results and Discussion

Thermal Behavior of the Gel. The temperature-dependent optical and mechanical behaviors of the D-DBS/ethylene glycol gel were examined by means of transmission under polarized light as well as by a rheological method. According to macroscopic and microscopic observations under polarized light, a gel structure prevails between 23—80 °C. Above 80 °C, the sample was in a solution state. The gel has a spherulitic texture, as displayed between cross polarizers.[4] The diameter of the spherulites decreased at temperatures above around 45 °C and disappeared at 80 °C. The quantity of the spherulitic domain was evaluated based on the transmission measurements between crossed polarizers. The transmission of D-DBS/ethylene glycol gel under polarized light plotted against the temperature, is shown in Fig. 1.

Changing points in the curve were observed at around 45 and 80 °C, indicating that the quantity of the spherulitic structure changed above 45 °C.

As a next step, the relationship between the optical and mechanical behavior was investigated.

The hardness-temperature curve is shown in Fig. 2.

As is evident from this figure, the hardness curve decreased at around 45 °C and the gel hardness values appeared to be zero above 80 °C. In the temperature dependence of the macroscopic properties, the mechanical property was related to the quantity of the spherulitic texture in the gel.

In a DSC measurement, the D-DBS/ethylene glycol gel exhibits an endothermic peak at around 80 °C (78—100 °C), which is a first-order phase transition, since the heat capacity of the gel was divergent at this phase-transition point. It agreed with the gel state–isotropic solution phase transition by a macroscopic observation. Two changing points were observed based on macroscopic measurements. It is assumed that the structure of the gel became loose at between 45—80 °C and disappeared above 80 °C.

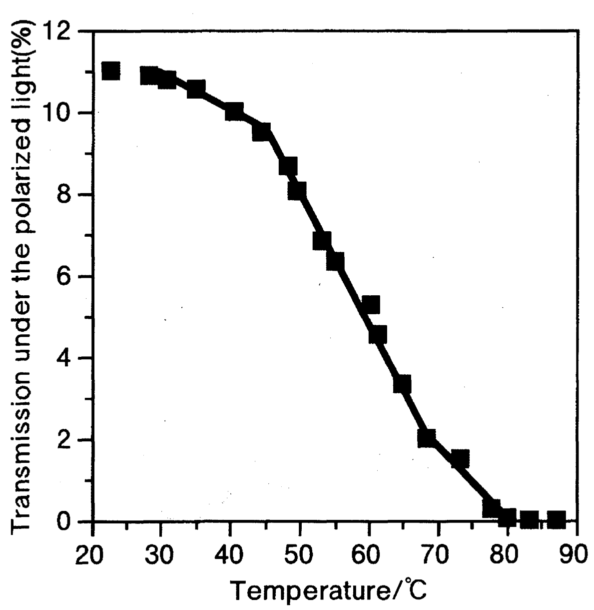


Fig. 1. Transmission under polarized light against temperature.

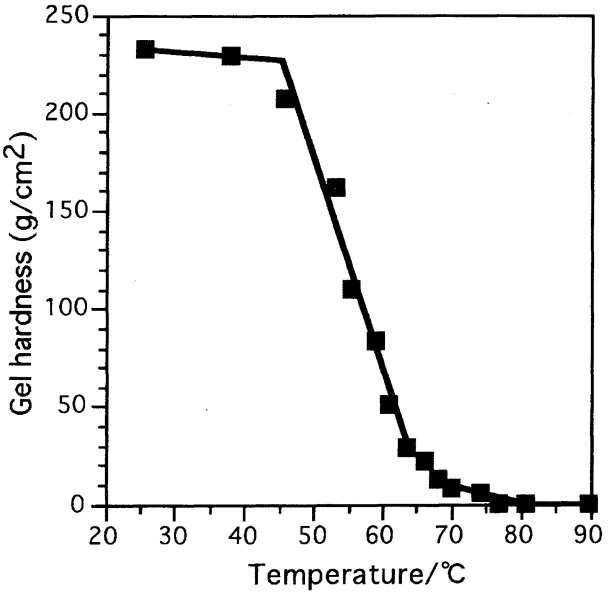


Fig. 2. Gel hardness of D-DBS/ethylene glycol gel against temperature.

The Temperature Dependence of the UV Spectra of D-DBS/Ethylene Glycol Gel. The relative orientation of the benzene rings in D-DBS was studied by measuring the UV absorption. In the gel state, the absorptions due to the benzene-ring structure were observed at 206, 220, and 255 nm. The absorption near to 255 nm is associated with the transition moment along the short axis of the benzene moiety.[12] Typical UV spectra around the 255 nm absorption peak at a temperature of between 27—93 °C are shown in Fig. 3. The molar extinction coefficient of the 255 nm absorption band increases along with increasing temperature. The oscillator strength (f) was calculated from the extinction coefficient using

$$f = 4.32 \times 10^{-9} \int \varepsilon(\nu)\mathrm{d}\nu,\text{[13,14]} \qquad (1)$$

where f is the oscillator strength. These values were obtained by dividing the absorption curves into rectangles of 2 nm-wavelength increments. The temperature dependence of the oscillator strength of the 255 nm band is shown in Fig. 4.

A change in the oscillator strength was observed at 45 °C; this temperature agreed with the optical and mechanical changes of the gel. Hyperchromism was observed with increasing temperatures. Depending on the relative orientation of the transition moments, hypochromism (parallel stacking) or hyperchromism (linear array) is observed.[13,14] Concerning the process from solution to the gel state, depending upon the D-DBS concentration, hypochromism was observed in the benzene absorption band.[3] The regularity along the short axis of benzene ring became loose above 45 °C.

The Temperature Dependence of CD Spectra of D-DBS/Ethylene Glycol Gel. CD spectroscopy is one

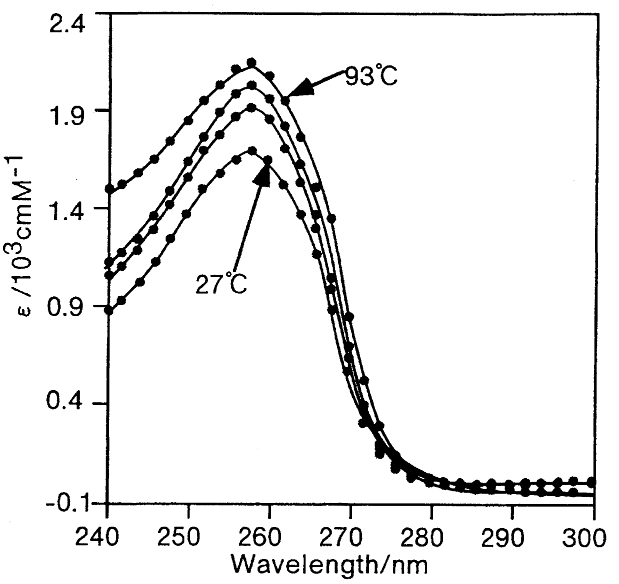


Fig. 3. UV spectra of D-DBS/ethylene glycol gel between 27—87 °C.

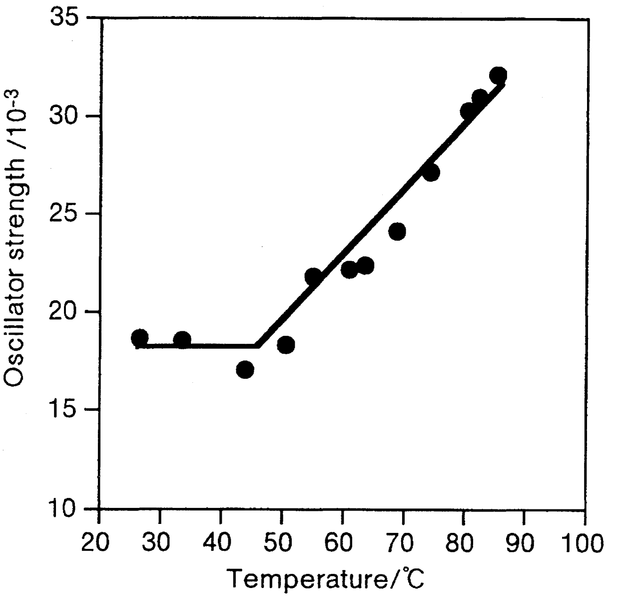


Fig. 4. Oscillator strengths of the benzene absorption of D-DBS against temperature.

of the most suitable techniques used to analyze the phase transition of chiral amphiphile/water systems.[5] Typical CD spectra over temperature ranges of 25—80 °C and 80—93 °C are shown in Fig. 5. A positive Cotton effect was observed in each spectrum. In the gel state, absorptions of the benzene rings were observed at 220 and 255 nm. D-DBS exhibited CD enhancements due to the formation of a gel.[13]

The molar ellipticities $[\theta]$ at 220 and 255 nm are plotted against temperature in Fig. 6. The $[\theta]_{220}$ value increased at 27—82 °C and decreased between 82—93 °C. The $[\theta]_{255}$ value slightly decreased between 27—75 °C. However, the decrease was much pronounced above 82 °C.

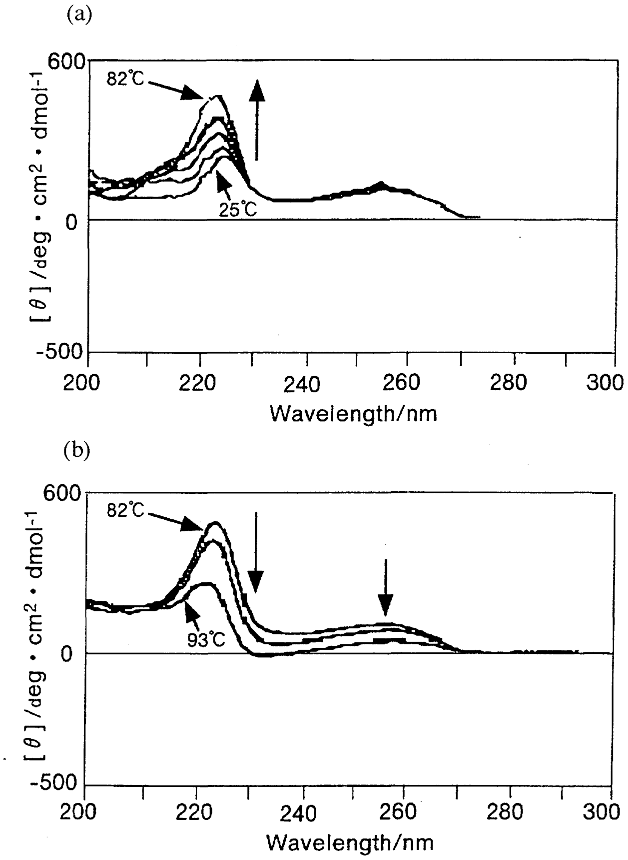


Fig. 5. CD spectra of D-DBS/ethylene glycol gel between 25—93 °C.

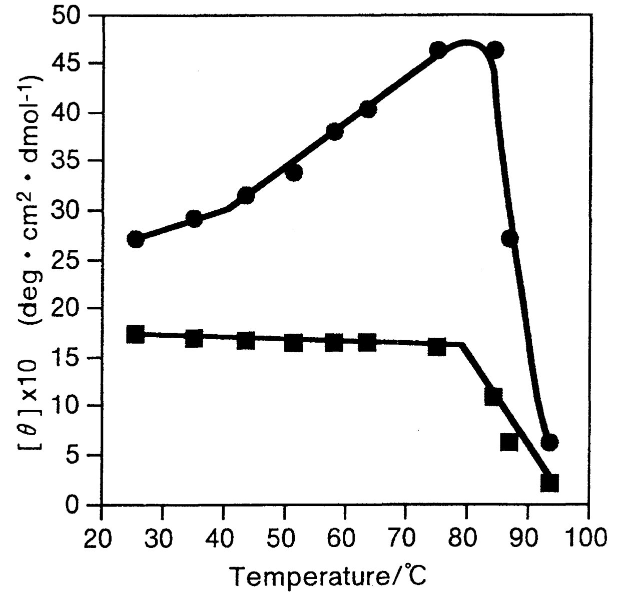


Fig. 6. Molar ellipticities at 220 and 255 nm absorption against temperature. ●: 220 nm absorption; ■: 255 nm absorption.

The temperature dependence of the $[\theta]_{220}$ value correlated with the results of the optical, mechanical, and UV spectroscopic measurements.

The DSC behavior of the D-DBS/ethylene glycol gel was consistent with the 220 and 255 nm absorptions.

From the change in the value of the CD spectra, it was proven that the chirality of D-DBS was enhanced between around 45—80 °C and the aggregated structure which D-DBS formed, disappeared above 80 °C.

Conclusion

In the temperature-dependent experiments, structural changes were observed at 45 and 80 °C. Both of the following changes occurred as the temperature was increased from 45 to 80 °C: 1) The gel hardness and transmission under polarized light decreased. 2) The UV spectra showed hyperchromism. 3) The $[\theta]_{220}$ value increased and the $[\theta]_{255}$ value decreased. The D-DBS aggregated structure is assumed to be a fibrous micelle in an isotropic gel.[3] The formation of a twist-like aggregated structure was observed in the spherulitic crystal.[4] The fibrous micelle may further assemble to a twist-like structure in the crystalline phase. We thought that the aggregated axis of the fibrous micelle in the crystal phase distorts rather than in the isotropic phase, owing to a hindrance of the phenyl groups, based on the CD spectra.[11] The hydrogen bonding seems to play an important role for the formation of the D-DBS aggregate on the basis of the IR spectrum. The enhancement of $[\theta]_{220}$ at between 45—80 °C may be dependent upon the change of the D-DBS aggregated structure, since the hydrogen bonding is weaker with increasing temperature. Although the relative orientation of the short axis in the benzene ring becomes loose, that of the long axis is more organized with increasing temperature between 45—82 °C, based on the UV and CD spectra. It is concluded that the D-DBS aggregated structure in a spherulitic crystal changes to the fibrous micelle form between 45—82 °C.

The following macroscopic and spectral property changes occur at 80 °C: 1) The gel hardness and transmission under polarized light approached zero. 2) The $[\theta]_{220}$ and the $[\theta]_{255}$ value disappeared. And 3) The sample was a solution state.

D-DBS may be molecularly dispersed above 80 °C, based on the low-molar ellipticities of the CD spectra. It was demonstrated that the change in the mechanical property was related to the quantity of the spherulitic texture and the aggregated structure which D-DBS formed, based on the macroscopic and spectroscopic measurements.

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