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Microscopic Studies of 1,3 : 2,4-Di-*O*-benzylidene-D-sorbitol in Ethylene Glycol

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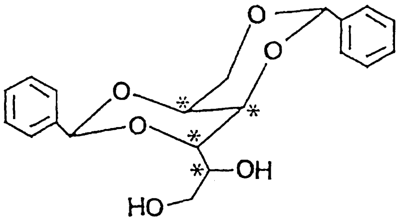
1,3 : 2,4-Di-*O*-benzylidene-D-sorbitol (D-DBS) is known to be a chiral oil gelator which forms the gel state with organic solvents having a wide range of polarities. Microscopic and thermoanalytical studies on the binary system, D-DBS/ethylene glycol, were carried out. The gel of the D-DBS/ethylene glycol system showed optical anisotropy under crossed polarizers. Two kinds of mesophases have been identified in the gel state. One was the crystalline phase, by means of observing the spherulitic texture. The other was an isotropic mesophase between spherulitic textures. In the crystalline phase the supramolecular helicoidal strucrture was observed by polarized and electron microscopy. The isotropic mesophase comprized of a network-like structure. It changed to the crystalline phase below the phase transition temperature from a gel to an isotropic solution (T_i), and the crystal of D-DBS was precipitated out from ethylene glycol. It is thus concluded that the gel state of D-DBS/ethylene glycol is a metastable state and that the chirality of D-DBS affects the shape which D-DBS forms in the crystalline state.

The chiral oil gelators known so far are 12-hydroxyoctadecanoic acid, *N*-dodecanoyl-L-glutamic acid dibutyl amide and 1,3 : 2,4-di-*O*-benzylidene-D-sorbitol (D-DBS). In those 3 gelators, only D-DBS can form gels with alcoholic solvents, such as ethanol or ethylene glycol.3) Tachibana carried out pioneering studies on the mesophases and supramolecular helicoidal aggregates of 12-hydroxyoctadecanoic acid and its salt. The mesophase of the solid and gel state of 12-hydroxyoctadecanoic acid is a chiral smectic structure; the helicoidal structure was associated with the lamellar structure.1) The helicoidal structure was found to exist locally as small domains within mesomorphic solids base on the measurements of the circular dichroism and X-ray diffraction.2) The gel of the *N*-dodecanoyl-L-glutamic acid dibutyl amide/ hexadecane system displayed a spherulitic texture under crossed polarizers, and the gelator formed a fibrous structure in the gel state.4) In chiral surfactants/water systems the amphiphiles having an amino acid residue,5) gluconamide6) and DNA derivatives,7) formed a helical aggregated-type structure below the phase transition temperature from the gel to liquid crystalline (T_c). In the present work we investigated the relationship between the structure and the thermodynamical stability of the mesophases in the D-DBS/ethylene glycol system by means of microscopic and thermoanalytical examinations.

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 Dohjin-Kagaku Co., Ltd., and dried over molecular sieves (3A).



Scheme 1.

Methods. The samples used for phase equilibria were weighed directly into glass test tubes with a Teflon-sealed screw cap. The samples were dissolved at 100—250 °C and cooled down to room temperature. The nonannealed samples were observed for phase equilibria after keeping them at each temperature for 30 min. Observations of the annealed samples were carried out after 24—48 h. The structure of the gel state was identified based on the optical texture through a microscopic observation in polarized light.9) The phase transition temperatures were determined using a microscope (Nikkon XF-2 equipped with a thermoregulator a Mettler Co., Ltd. FP-800) and differential scanning calorimetry (DSC). The DSC was carried out with Seiko Instrument & Electronics Co., Ltd. DSC-10. The gels were put into 75 μl silver capsule cells and heated at a rate of 1 °C min^{-1}. The shape of the gel state was examined by electron microscopy. Scanning electron microscopy (SEM) was carried out by using a JSM-840 (JEOL Co., Ltd.). The crystals which separated out from the solvent were lyophilized and employed as SEM samples. The structure of the gel state was observed by the cryo-SEM method, after the gel had been frozen in liquid nitrogen. A structural change due to the evaporation of ethylene glycol was observed by scanning electron microscopy (an Akashi Co., Ltd. WT-250). The ^{13}C NMR spectra were measured at 35 °C with a JEOL JNM-GX-270 spectrometer. The measurement methods were CP/MAS (cross polarization magic angle spinning) and PST/MAS (pulse saturation magic angle spinning) in the solid state. The solid of D-DBS and the gel of 30 g% D-DBS/ethylene glycol were measured. The following are the magnetic data of D-DBS : (5 g% D-DBS/DMSO-d_6) $\delta=$ 62.5, 67.6, 68.3, 69.2, 70.0, 77.5, 99.2, 126.0, 127.8, 128.8, 128.4, 128.5, 138.4, 138.

Results and Discussion

Phase Diagram of the D-DBS/Ethylene Glycol System. The dependence of the thermal behavior of the phase transition on the ethylene glycol content was examined by means of measurements of DSC and microscopic observations with a thermoregulator. As shown in the heating DSC curve in Fig. 1, the D-DBS/ethylene glycol system exhibits a primary endothermic peak due to the melting points of ethylene glycol at about −33 °C. After further heating, another endothermic peak corresponding to the phase transition from the gel state to isotropic liquid ($T_{\rm i}$) appears at about 130 °C.

The $T_{\rm i}$ transition temperatures and the melting points of the solvent for samples of different solvent contents are shown in Fig. 2. The transition temperatures are plotted against the D-DBS content.

As is evident in this figure, the $T_{\rm i}$ transition temperature curve decreases rapidly with increasing solvent content to $\phi_{\rm DBS}$ 0.82, after which it is a straight line that is nearly parallel to the abscissa to $\phi_{\rm DBS}$ 0.10. Furthermore, the curve decreases rapidly to $\phi_{\rm DBS}$ 0.01. The samples below $\phi_{\rm DBS}$ 0.005 were solutions at 0—30 °C. This $T_{\rm i}$ transition temperature curve is similar to the solubility curve of a surfactant–water system.[8] When the D-DBS content of the sample reaches a specified value at $\phi_{\rm DBS}$ 0.63, the endothermic peak due to a melting of the solvent first appears. This result indicates that about 3.5 ethylene glycol molecules solvate the D-DBS molecule. Since the depression of the freezing point of ethylene glycol is observed between $\phi_{\rm DBS}$ 0.01—0.05, D-DBS partly dissolves in ethylene glycol. We studied the stability of this gel phase below the $T_{\rm i}$ phase transition temperature. The gel was clear at $\phi_{\rm DBS}$ 0.01 under the nonaneal condition at 25 °C. The transmission of the D-DBS gels decreased from $\phi_{\rm DBS}$ 0.01 to 0.15, and were opaque above $\phi_{\rm DBS}$ 0.15. In the case that the gel was kept at the phase transition temperature from the gel to crystalline state, the clear gels increased their opacity and the crystal separated out from the ethylene glycol phase. The phase transition curve from the gel to the crystalline phase is shown in Fig. 2. This point was defined by a naked eye observation.[10] The transition from the gel to crystalline phase was observed below $\phi_{\rm DBS}$ 0.15. These results suggest that the clear gel state is a metastable state and transforms into the thermodynamic stable crystalline phase below the phase-transition temperature from a gel to an isotropic solution.

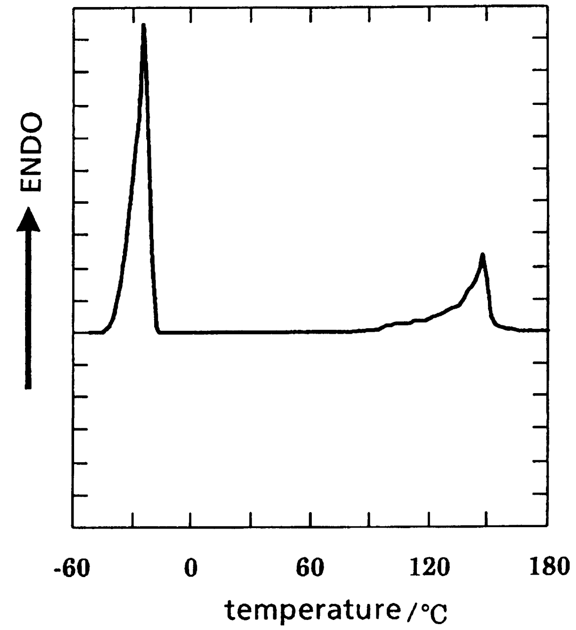


Fig. 1. DSC curve of the D-DBS/ethylene glycol system ($\phi_{\rm DBS}$=0.30) in heating direction.

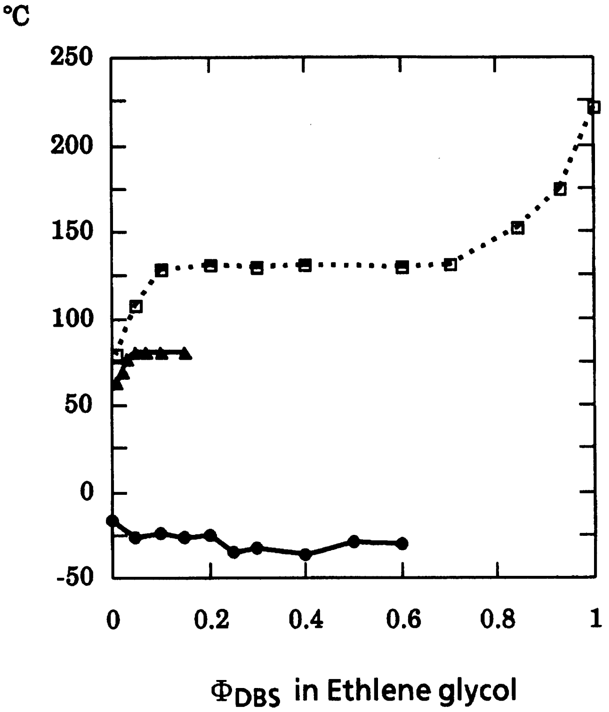
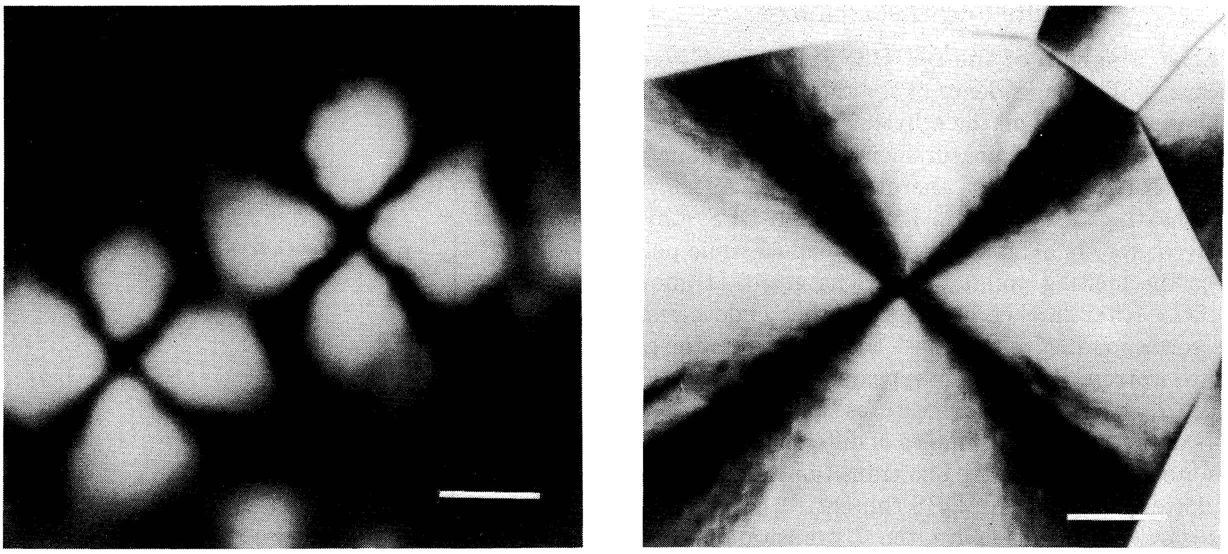


Fig. 2. Phase diagram of the D-DBS/ethylene glycol system. Temperature of the phase transition from the gel state to isotropic solution(□); melting point of ethylene glycol(●); temperature of the phase transition from the gel state to crystalline state(▲).

Microscopic Observation of Gel. The microscopic texture of D-DBS gel is shown in Fig. 3. The gel displayed a spherulitic texture between cross polarizers. In the texture of the gel state of low concentration ($\phi_{\rm DBS}$=0.01, Fig. 3a) the texture consists of two kinds of mesophase. One is spherulitic domains; the other is an isotropic mesophase between the spherulitic textures. In high concentrations above $\phi_{\rm DBS}$ 0.15 ($\phi_{\rm DBS}$=0.30, Fig. 3b), however, the texture was only a spherulitic texture. It is assumed that the increase in the opacity of the gel state is related to an increase in the crystalline ratio in the gel phase. These textures are similar



(a) (b)

Fig. 3. Microscopic textures of gel of D-DBS/ethylene glycol between crossed polarizers. (a) $\phi_{\mathrm{DBS}}=0.01$; (b) $\phi_{\mathrm{DBS}}=0.30$ (scale bars 20 μm).

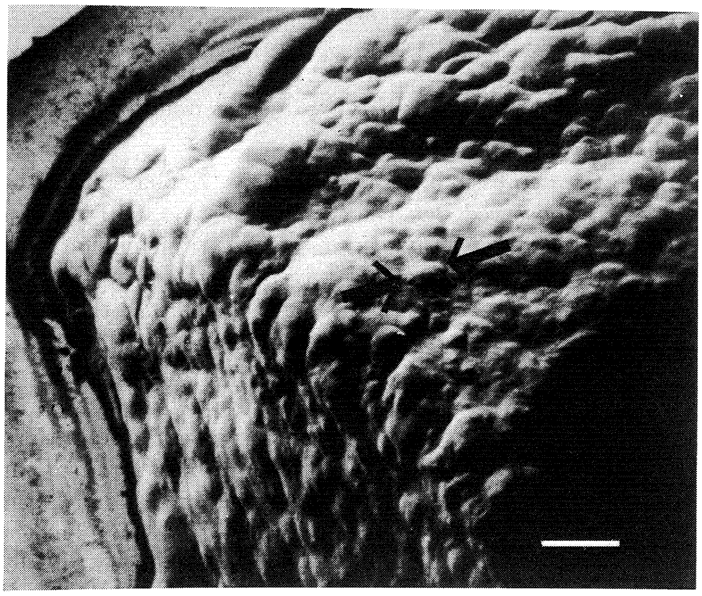


Fig. 4. Electron micrograph of the structural change of D-DBS/ethylene glycol gel owing to evaporation of ethylene glycol (scale bar 200 μm).

to the pattern observed in the gel and solid states of 12-hydroxyoctadecanoic acid[1,2] and the liquid crystals of the cesium decylsulfate/methylammonium decylsulfate/decanol/water system.[9]

Thus, the microscopic observation indicates that the gels have local orders with a mesomorphic structure. The spherulic domains showed an extinction cross, which was unchanged upon rotation of the stage of the polarizing microscope. The optical sign of the spherulitic textures, as determined by using a sensitive color plate, was negative. In a texture of high concentration, dark concentric rings were observed (Fig. 3b). The pitch of these rings was about 6—8 μm. An analysis of such rings in the texture was reported for a spherulitic crystal in a polymer.[11] Their appearance depends on the helicoidal arrangement of the biaxial index ellipsoid along a sperulite radius parallel to the microscope stage.[11] The pitchs of the rings have been shown to have a half helical pitch of the helicoidal arrangement of the index ellipsoid.[11] The appearance of such

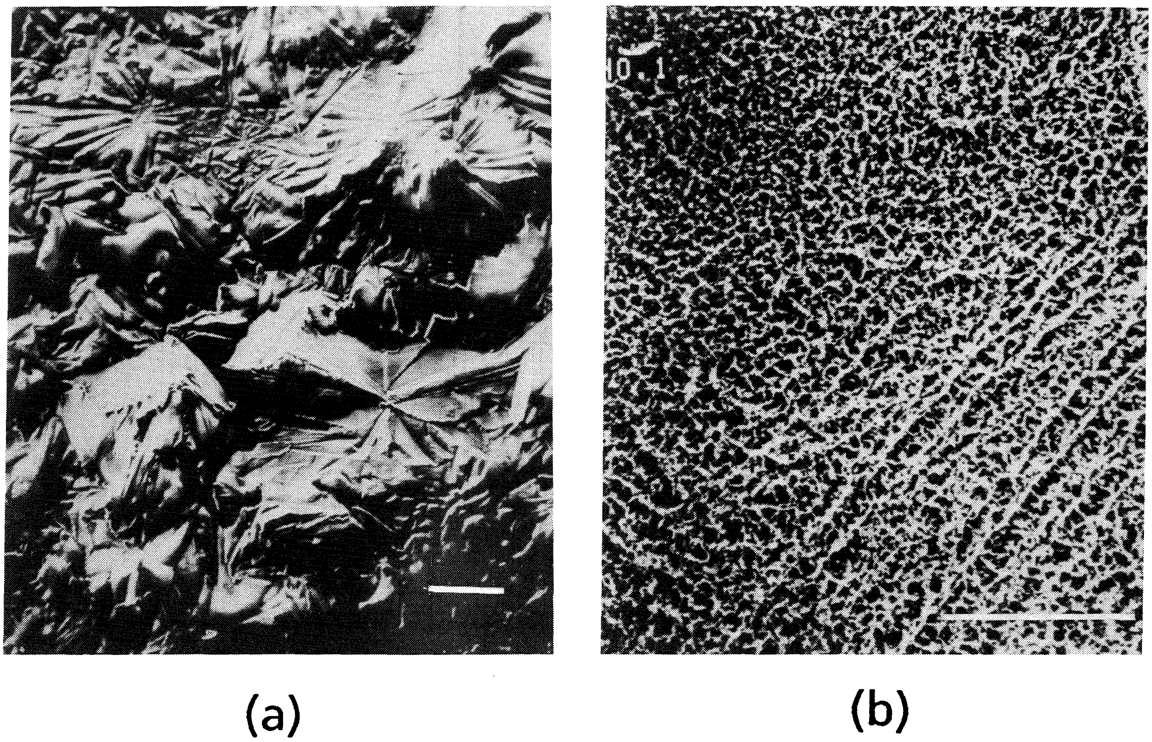


Fig. 5. Electron micrograph accoding to the cryo-SEM method. a) Sectional view of the spherulitic crystal (scale bar 200 μm), b) Structure between the spherulitic crystal (scale bar 15 μm).

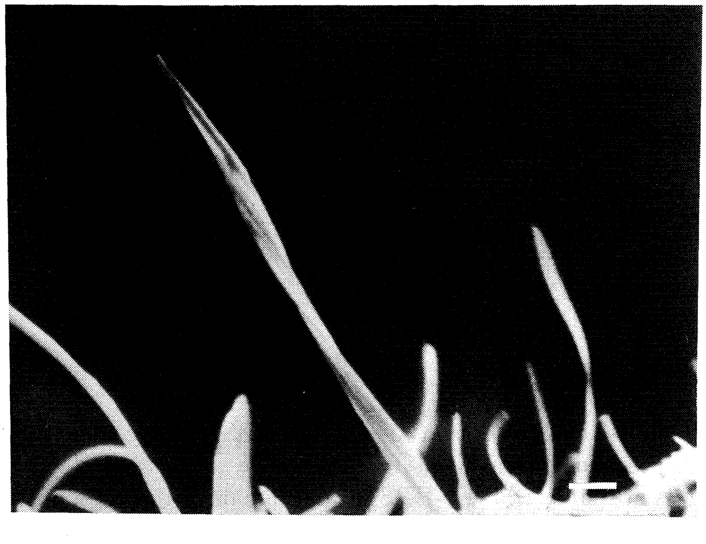


Fig. 6. Electron micrograph of anneal gel of D-DBS/ethylene glycol (scale bar 1 μm).

rings in the texture indicates that D-DBS forms a helicoidal structure in the D-DBS/ethylene glycol system, in agreement with 12-hydroxyocadecanoic acid, which T. Tachibana reported.[12,13)]

Electron Microscopic Observation of the Gel. We investigated whether the structural change in the gel state was influenced by the evaporation of ethylene glycol. After 3 min, the surface of the gel was plane. After 10 min, a spherulitic shape was observed (Fig. 4).

The structure between spherulitic shapes was contracted by evaporation of the solvent, whereas the spherulitic shapes hardly changed. It is assumed that the structure between spherulitic shapes plays a role in holding ethylene glycol in the gel state. The cryo-SEM photographs of each structure are shown in Fig. 5.

In a low-magnification picture, the sectional view of the spherulitic crystal indicates that the structure which D-DBS formed, grows along a spherulite radius. This result agrees with the optical sigh of the spherulitic texture. In a high-magnification picture a network structure was observed. It is considered that the network structure is a structure between spherulitic textures.

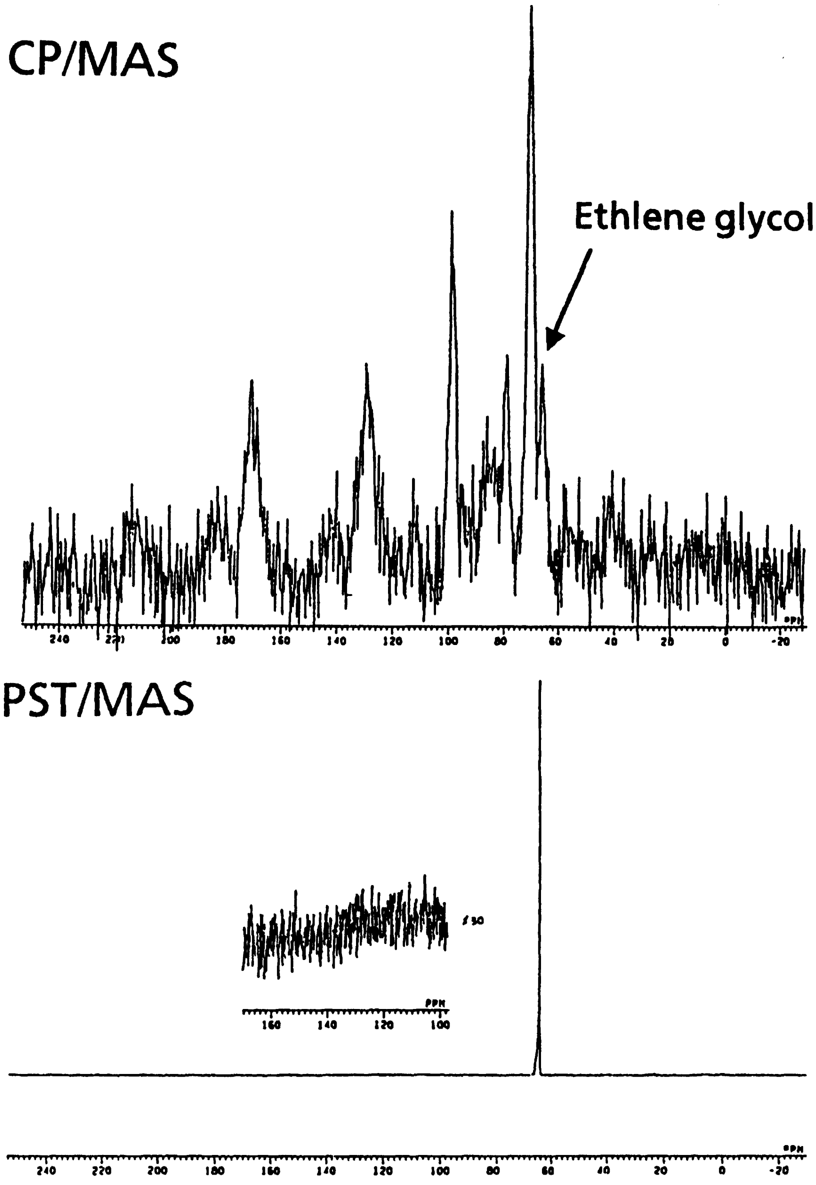


Fig. 7. Solid state NMR of the gel (ϕ_{DBS}=0.30); a) CP/MAS, b) PST/MAS.

From the microscopic results it is concluded that D-DBS/ethylene glycol gel in low concentration (ϕ_{DBS}= 0.01—0.1) consists of two kinds of shapes which D-DBS forms.

Electron Microscopic Observation of the Crystal. Under an electron microscope a crystal of D-DBS separated out from the solvent. Figure 6 shows the formation of a helical aggregated structure. This structure is twist like, which is similar to the 12-hydroxyoctadecanoic acid and its salts.[12—14)] It has a diameter of about 0.8 μm and a half helical pitch of about 6—8 μm. The helical sense is right handled. The helical pitch is approximately equal to the result of the dark concentric rings in the spherulitic texture. It is assumed that the chirality of D-DBS affects the shape in the crystalline state.

^{13}C-Solid State NMR of Gel. The mobility of D-DBS and ethylene glycol in D-DBS gel was evaluated by solid state NMR studies. In CP/MAS NMR, the signals of the crystalline component were enhanced by the CP effect, whereas those of the mobile component were observed by the PST/MAS method, which detected the molecular mobility range between the solution and liquid crystalline components. The CP/MAS and PST/MAS spactra of 30 g% D-DBS/ethylene glycol gel is shown in Fig. 7.

In the CP/MAS spectrum, D-DBS and a little ethylene glycol (63 ppm) were observed. In the PST/MAS spectrum, however, only ethylene glycol (63 ppm) was detected. The CP/MAS NMR suggests that D-DBS is the crystalline state in the gel state. The mobility of D-DBS in the gel state is similar to that of a surfactant in the gel state.[8,10)] It is considered that ethylene glycol in the CP/MAS spectrum of D-DBS gel is a bound solvent, but that in PST/MAS is a bulk free solvent and ethylene glycol solvates to D-DBS. The state of ethylene glycol agrees with the results of DSC. It is demonstrated that there are two kinds of states of ethylene glycol in D-DBS gel. In conclusion, it is indicated that the clear gel in low concentration of D-DBS consists of two kinds of mesophases. The crystalline state, as the spherulitic state in the spherulitic texture, is a thermodynamicaly stable phase and the isotropic mesophase between the spherulitic textures is a metastable phase. D-DBS formed a helically aggregated structure in the crystalline phase. It is assumed that the chirality of D-DBS affects the shape of the crystalline state.

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