Bull. Chem. Soc. Jpn., ***68***, *123—127(1995)*

The Dependence of the Polarity of Solvents on 1,3 : 2,4-Di-*O*-benzylidene-D-sorbitol Gel

Seiji Yamasaki* **and Hisao Tsutsumi**

Tokyo Research Laboratories, Kao Corporation, 2-1-3 Bunka, Sumida, Tokyo 131

(Received May 17, 1994)

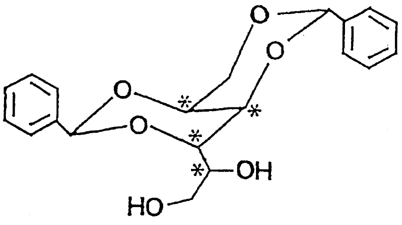
1,3 : 2,4-Di-*O*-benzylidene-D-sorbitol (D-DBS) is known as a chiral oil gelator for a wide variety of organic solvents. The relationship between texture, structure of the gel, and the aggregated structure formed by D-DBS was investigated in various solvents. In the low polar solvents, the gel held a mesh type network structure in which the fiber appeared to be a rope-like helical structure. In the moderately polar solvents, the gel held an isotropic mesophase, but in the polar solvents, a spherulite texture was observed. From the experiments for the critical gel concentration of D-DBS in various solvents, it is assumed that there are three regions that differ in the form of hydrogen bonding, depending upon the polarity of solvents. By IR spectroscopic measurements, we found that, with the increase of solvent polarity, the hydrogen bonding between D-DBS and the solvent became more predominant than the intramolecular hydrogen bonding, and the hydrogen bonding between D-DBS became weaker at the same time. In addition, the intensities of CD spectra in the D-DBS gel decreased according to the increase of the solvent polarity. Here it is considered that textures and structurs observed in the gel are related to the aggregated structure that is mainly formed through hydrogen bonding among D-DBS.

In the studied chiral oil gelators such as 12-hydroxyoctadecanoic acid, *N*-dodecanoyl-L-glutamic acid dibutylamide, cholesteryl 4-(2-anthryloxy)butyrate (CAB), and 1,3 : 2,4-di-*O*-benzylidene-D-sorbitol (D-DBS), only D-DBS can cause gelation of a wide variety of organic solvents (including alkanes, aromatic molecules, halohydrocarbons, esters, ketones, aldehydes, ethers, monohydric and polyhydric alcohols, and sulfoxide).[1—3] In the D-DBS–ethylene glycol system, D-DBS formed two kinds of mesophases in the gel. The gel of D-DBS was a metastable state which changed to the crystalline phase. In the crystal, helical aggregated structure was observed.[4] Lin et al. demonstrated that the structures formed by CAB in the gel state were different from solvent to solvent and they also showed that the helical twist structure was observed in CAB–1-octanol gel.[5] The chiral amphiphile *N*-dodecyl-L-glutamic acid formed lyotropic cholesteric liquid crystals in nonpolar solvents like benzene.[6] On the other hand, it was soluble in an alcoholic solvent. The analysis of CD spectra was attributed to the formation of a chiral aggregate through hydrogen bonds among surfactants in the solution state.[7] In this paper, we discuss the changes of the texture, structure of the gel, and the aggregated structures of D-DBS depending upon the polarity of solvents, using IR and CD spectral measurements, solubility measurements, and microscopic observations.

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 its purity was found to be above 95% by the NMR technique. (Impurity was 1,3 : 2,4 : 5,6-tri-*O*-benzylidene-D-sorbitol.) It was used without further purification. The solvents were obtained from Dohjin-Kagaku Co., Ltd. The polar parameter of solvent (donor number (DN)) in this work means the proton-donating power that was measured by T. Kagiya et al., using an IR method.[8,9] Solvents used in this work were chloroform (DN=7.5), benzene (DN=20), *p*-xylene (DN=27.9), benzonitrile (DN=53), acetonitrile (DN=63.7), 1,4-dioxane (DN=96), THF (DN=116.2), DMF (DN=199.8), DMSO (DN=149.6), and pyridine (DN=119.2), which were dried over molecular sieves.

Methods. Each sample used for phase equilibria was weighed directly into a glass test tube with a Teflon®-sealed screw cap. After they were dissolved at 100—120 °C, the samples were observed for phase equilibria after being kept at 25 °C for 24 h. The difference of phases was visually observed with and without crossed polarizers. The mesophases of the gel states were identified based on the optical texture through microscopic observation in polarized light. A Nikon XF-2 microscope with a polarizer was used. The IR spectra



Scheme 1.

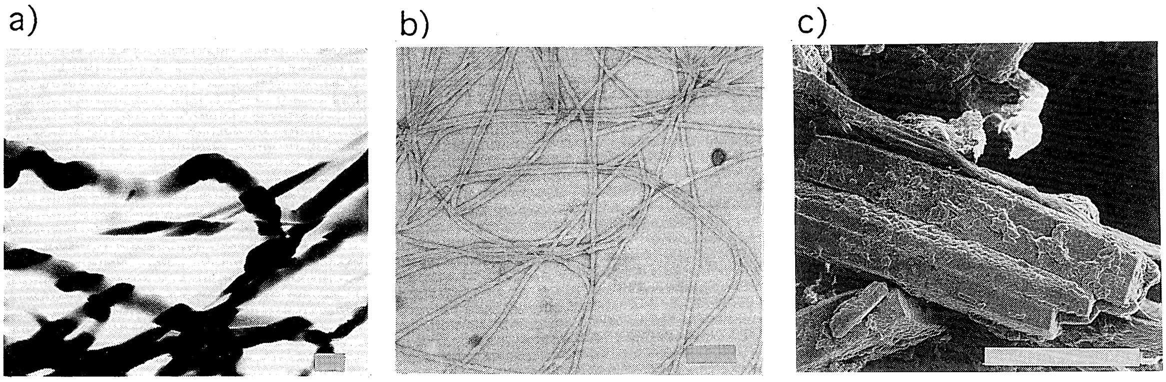


Fig. 1. Electron micrographs of the D-DBS gel. a) *p*-xylene (DN=27.9, bar 100 nm), b) 1,4-dioxane (DN=96, bar 50 nm), c) DMSO (DN=149.6, bar 100 μm).

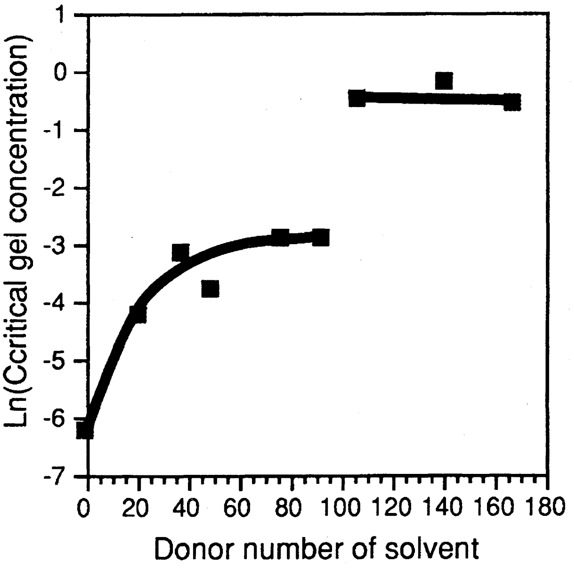


Fig. 2. The plot of the logarithm of the critical gel concentrations against the donor number of solvents.

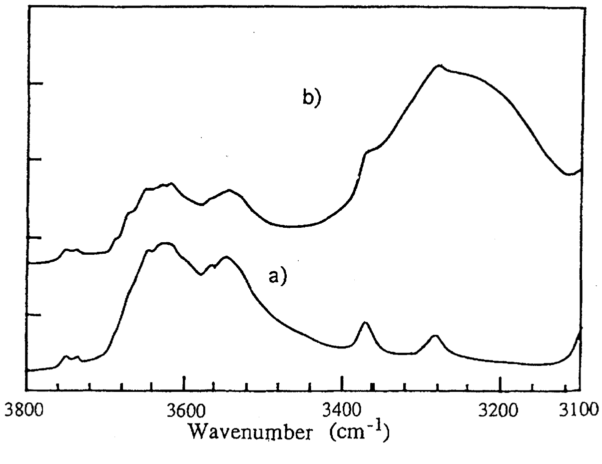


Fig. 3. IR spectra of the solution and gel of D-DBS in acetonitrile. a) solution, b) gel.

were obtained by using a JASCO FT-IR 8000, sandwiching gel and solution between KBr plates. IR measurements were done from 4000 to 1000 cm^{-1}. The CD spectra were obtained using a JASCO type J-600. The path length of the quartz cell was 0.03 mm. The wavelength was scanned from 400 to 200 nm at a speed of 20 nm min^{-1}. The scanning electron microscopic observation was done with a JEOL type JMS-840. The gel of D-DBS was frozen by immersing it in liquid nitrogen, and lyophilized. The dried samples were used for the SEM measurements. Transmission electron microscopic (TEM) observation was done at room temperature on a Hitachi H-7100 electron microscope, operated at 75 kV. For the negative staining method, the dried specimen on a carbon-coated electron microscope grid was negatively stained with 0.7% uranyl acetate solution.

Results and Discussion

The Texture and Structure of D-DBS Gel in Various Solvents. The texture and structure of the gel in various solvents was observed by the optical and electron microscope. Table 1 shows the texture and structure of D-DBS gels in typical solvents. In the low polar solvent like *p*-xylene (DN=27.9), its gel was soft and the solvent easily separated from the gel phase. Needle-like crystals of D-DBS precipitated from the gel. In the moderately polar solvent like 1,4-dioxane (DN=96), the gel was an isotropic mesophase under crossed polarizers. The gel of a highly polar solvent, such as DMF (DN=119.8) or DMSO (DN=149.6) displayed a spherulitic texture. The optical sign of the spherulitic textures, as identified by using a sensitive color plate, was negative. This sign indicates that the crystal of D-DBS grows along the spherulite radius. A similar texture was observed in D-DBS–ethylene glycol gel.[2] The

Table 1. The Texture and Structure of D-DBS Gel in Various Solvents

Solvent	*p*-Xylene	1,4-Dioxane	DMSO
Donar number	27.9	96	149.6
Texture[a)]	Needle	Isotropic	Spherulitic
Structure[b)]	Rope-like	Rope-like	Columnar

a) Microscopic observation in polarized light. b) Electron microscopic observation.

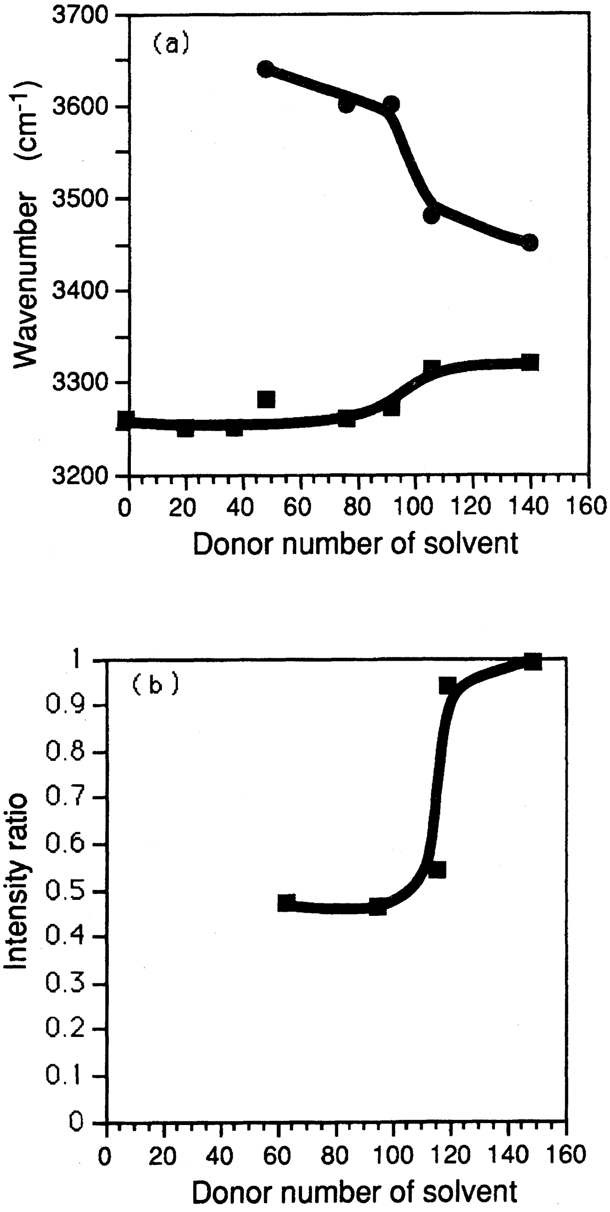


Fig. 4. Wavenumbers of the hydroxy absorption (high wavenumber νOH;●/low wavenumber νOH;■, a) and intensity ratio (high wavenumber νOH/low wavenumber νOH, b) in IR spectra plotted against the donor number of solvents.

gels in highly polar solvent were in a metastable state, which gradually changed to a crystalline phase. The structures of the gels and crystal, which were observed by an electron microscopy, are shown in Fig. 1.

The fibers in the low polar solvent had a rope-like helical structure, in which both the diameter and the helical pitch were about 100 nm (Fig. 1a). In the moderately polar solvent, 1,4-dioxane, it was a rope-like helical structure. The diameter was about 3.8 nm (Fig. 1b). It is considered that the polarized light intensity of the gel in the moderately polar solvent is weak, since the diameter of the fiber in the gel is smaller than the light wavelength. In highly polar solvents the crystals that separated from the gel phase appeared to be columnar (Fig. 1c). These results indicated that the texture and the structure of D-DBS were transformed according to the donor number of the solvents.

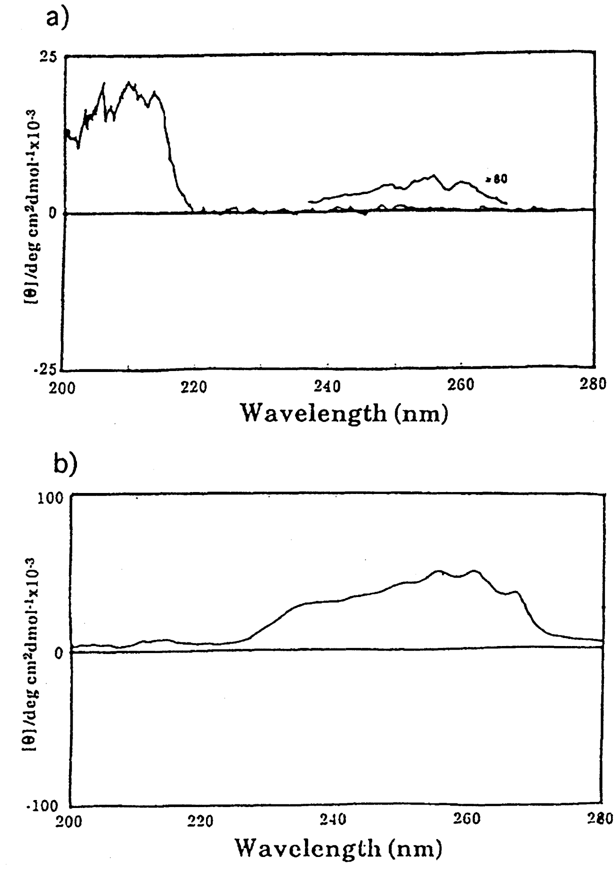


Fig. 5. CD spectra of D-DBS in the solution and gel in acetonitrile. a) solution, b) gel.

The Relation between the Critical Gel Concentration of D-DBS and the Donor Number of Solvents. The critical gel concentration of D-DBS was measured at 25 °C. The proton-donating power of the donors (the donor number) were evaluated by means of the ratios of the O–H shifts of the donors (RO–H) to those of methanol in various proton acceptor solutions.[8,9] Figure 2 shows the relationship between the donor number and logarithm of the critical gel concentration. An inflection point at 39 and a discontinuous point at 107 were observed. The logarithm of the critical gel concentrations in various solvents was proportional to the donor number from 0 to 38 and it was constant from 38 to 93 and from 107 to 168. It is assumed that the aggregation which D-DBS forms, partly dissolves in the highly polar solvents those above 107. From the solubility measurements, we consider that there are three different forms of hydrogen bonding. These results were found to be related to the transformation of the gels observed through the electron microscope.

The Forms of Hydrogen Bonding in Various

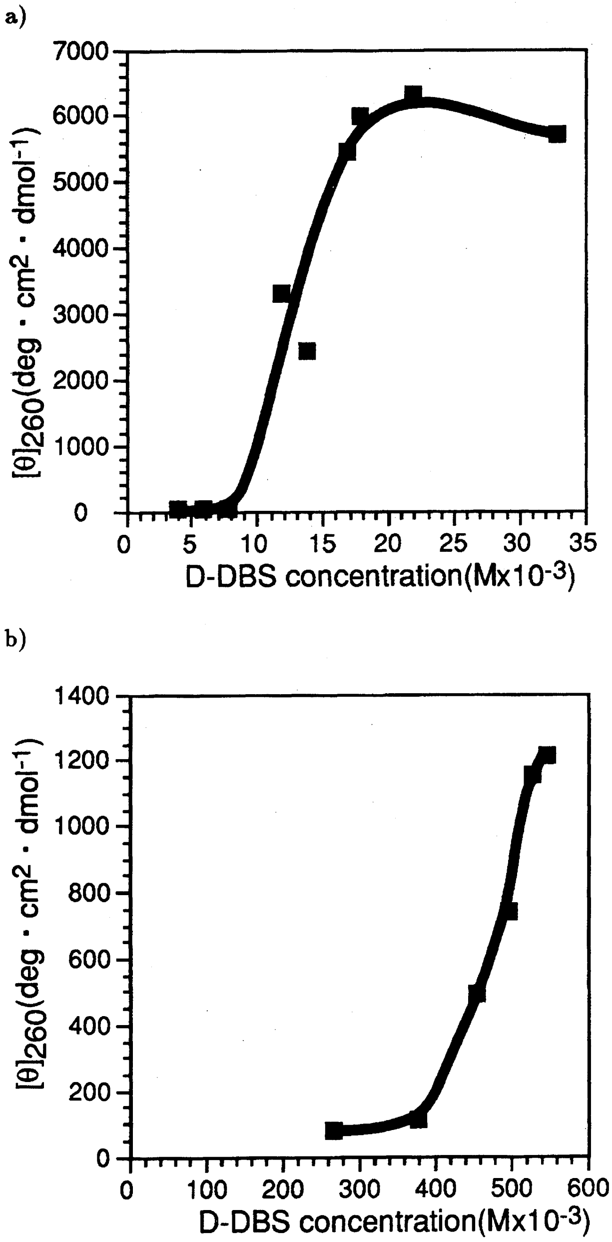


Fig. 6. Plot of the logarithm of the molar ellipticity value [θ] 260 against D-DBS concentrations in acetonitrile (upper) and DMSO (lower).

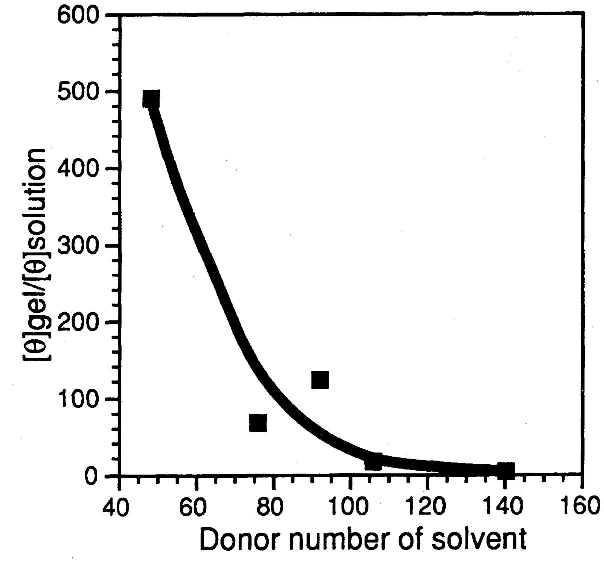


Fig. 7. Plot of the logarithm of the molar ellipticity ratio (gel/solution) against the donor number of solvents.

Solvent Gels. Typical IR spectra of D-DBS in the gel and solution of acetonitrile are shown in Fig. 3. The absorption of the hydroxyl group in the solution state was detected around 3600 cm^{-1} (Fig. 3a), which suggested weak hydrogen bonding between D-DBS and the solvent molecules.$^{10)}$ During gelation, a new absorption band appeared around 3270 cm^{-1} (Fig. 3b). Two kinds of νOH bands were observed in the gel. The absorption band at a higher wavenumber can be assigned to the OH band of hydrogen bonding between D-DBS and the solvent. The IR absorption band at 3270 cm^{-1} is assumed to be assigned to the OH band of hydrogen bonding between D-DBS molecules, because the same band was also observed in the crystalline form. Both the wavenumbers of νOH bands in the gel against the donor number of solvents are shown in Fig. 4a. The absorption band at the higher wavenumber disappeared below 49 and the wavenumber decreased with an increase in the donor number. On the other hand, the absorption bands at 3270 cm^{-1} were constant at 0—77, and the wavenumbers increased above a donor number of 93. The intensity ratio (high wavenumber νOH/low wavenumber νOH) in the gel against the donor number of solvents are shown in Fig. 4b. The intensity ratio increased above 93 of the donor number of solvents. Comparing the gel-forming ability of D-DBS derivatives, 5- or 6-hydroxyl-group-blocked compounds by methyl group, the 5-methoxy derivative could cause gelation of solvents, but the 6-methoxy one couldn't. It is assumed that the 6-hydroxyl group in D-DBS molecule must be essential to form the aggregates of D-DBS, while the 5-hydroxyl group may interact with the solvent molecules or an acetal oxygen atom.$^{11)}$ It is considered that the hydrogen bonding between D-DBS and the solvent became more predominant than the intramolecular hydrogen bonding between the 5-hydroxy group and an acetal oxygen atom, and the hydrogen bonding between D-DBS became weaker at the same time, with the increase of solvent polarity.

CD Spectra of the Solution and Gel in D-DBS–Solvent system. CD spectroscopy is one of the most suitable techniques to analyze gel formation and the phase transition in chiral amphiphile–water system.$^{12,13)}$ The CD spectra in solution and gel of the D-DBS–acetonitrile systems are shown in Fig. 5. A positive Cotton effect was observed in all the spectra. D-DBS had great CD enhancement due to the formation of a gel. The molar ellipticity values $[\theta]_{260}$ in acetonitrile and DMSO against D-DBS concentration are shown in Fig. 6.

In the acetonitrile system, $[\theta]_{260}$ values increased dramatically with the phase transition from the solution to the gel. Whereas, The change of $[\theta]_{260}$ values in the DMSO system was smaller than the one in acetonitrile. The ratio of $[\theta]$gel/$[\theta]$ solution of the 260 nm CD band against the donor number of solvents is shown in Fig. 7. It drastically decreased with increasing donor number. These results indicated that the chiral arrangement of the aggregated structure formed with D-DBS decreased depending upon the increase of the donor number of the solvent.

From the relation between the donor number of solvents and the IR and CD spectra, we assumed that the interaction among D-DBS was weaker with increasing the donor number of the solvent. Here it is considered that the textures and the structures of D-DBS gel are dependent upon the aggregated structure which is mainly formed though hydrogen bonding among D-DBS.

We would like to thank Miss Tomoko Sadahiro and Mr. Hiromitsu Kawada for helpful advice and supports.

References

1) M. Honma, *Gendaikagaku*, **197**, 54 (1987).

2) S. Yamamoto, *Kougyou Kagaku Zasshi*, **45**, 695, (1942).

3) Y-C. Lin and R. Weiss, *Macromolecules*, **20**, 414 (1987).

4) S. Yamasaki and H. Tsutsumi, *Bull. Chem. Soc. Jpn.*, **67**, 906 (1994).

5) Y-C. Lin, B. Kachar, and R. G. Weiss, *J. Am. Chem. Soc.*, **111**, 5542 (1989).

6) K. Sakamoto, R. Yoshida, M. Hatano, and T. Tachibana, *J. Am. Chem. Soc.*, **100**, 6898 (1978).

7) K. Sakamoto and M. Hatano, *Bull. Chem. Soc. Jpn.*, **53**, 339 (1980).

8) T. Kagiya, Y. Sumida, and Y. Tachi, *Bull. Chem. Soc. Jpn.*, **43**, 3716 (1970).

9) T. Kagiya, Y. Sumida, and T. Inoue, *Bull. Chem. Soc. Jpn.*, **41**, 3817 (1968).

10) K. Nakamoto, M. Margoshes, and R. E. Rundle, *J. Am. Chem. Soc.*, **77**, 6480 (1955).

11) S. Yamasaki, Y. Ohashi, H. Tsutsumi, and K. Tsujii, "The Meeting of the Chemical Society of Japan," Sapporo, September 1989, Abstr., 3C10, p. 350.

12) T. Kunitake and N. Yamada, *J. Chem. Soc., Chem. Commun.*, **1986**, 655.

13) T. Kunitake, N. Nakashima, and M. Shimomura, *J. Am. Chem. Soc.*, **102**, 6642 (1980).