

# Silylation of Water Glass. IV. Synthesis and Characterization of Silylated Silicic Acids

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## Synopsis

Trimethylsilylated (TMSS) and dimethylphenylsilylated silicic acids (DMPS) were prepared via extraction with tetrahydrofuran, started from aqueous sodium silicate. Characterization of these silylates based on the  $^{13}\text{C}$  and  $^{29}\text{Si}$  NMR spectra, X-ray diffraction, gel permeation chromatography, and solution viscosity were conducted to study their molecular structures. It was found that the GPC elution volume was significantly deviated from the calibration curve and also the exponents in solution viscosity vs. molecular weight ( $\bar{M}_n$ ) relationship were very low, almost 0.3. These solution properties suggest that such silylates have compact spherical structures with a high degree of branching, also supported from the other data.

## INTRODUCTION

The trimethylsilylated silicic acid (TMSS) was readily prepared by homogeneous reaction of trimethylchlorosilane with the silicic acid in organic media, as was reported in the previous papers.<sup>1-3</sup> It was found that the silylates exhibited some excellent properties, particularly, surface properties and thermal stability. However, a serious problem still remained without solution to utilize as plastics, coatings, and/or fibers, that is, very poor film- and fiber-forming properties. This is mainly attributed to the following reasons: low molecular weight, low cohesive force, and structural factor.

Recently, Bechtold et al. intensively studied the polymerization and silylation of silicic acid generated from not only sodium silicate but also tetraethylsilicate.<sup>4</sup> They suggested coiled or globular nature of the polymers to explain their limited propensity for film and fiber formation.

In this work, the TMSS and the dimethylphenylsilylated silicic acid (DMPS) derived from aqueous sodium silicate were carefully characterized to obtain their structural information.

## EXPERIMENTAL

### Preparation of Silylated Silicic Acids

Homogeneous silylation of silicic acid was described elsewhere.<sup>1,3</sup>

To 220 mL of 0.64 mol/L  $\text{H}_2\text{SO}_4$  aqueous solution, 100 mL of 0.80 mol/L aqueous sodium silicate solution ( $\text{Na}_2\text{O}\cdot 3,32\text{SiO}_2$ , Nippon Chemical Ind., JIS third class) was added with stirring. The solution was mixed with 160 mL of tetrahydrofuran (THF) and allowed to stand for 3 h. Then the solution was separated to two layers on addition of sodium chloride. The THF layer was dried over anhydrous sodium sulfate.

The silicic acid-THF solution was mixed with trimethylchlorosilane or dimethylphenylchlorosilane in a 500-mL three-necked flask. To the solution, excess triethylamine was added as an acid acceptor. After the reaction for given hours, the volatile liquid was evaporated from the solution, followed by addition of water to separate the silylate. The benzene solution of the silylate was filtered through a filter paper to remove the gel, and poured into a methanol-water mixture (85:15 in vol) to precipitate the polymer. The silylate thus obtained was found to still contain silanol group as detected from its IR spectra, and therefore subjected to repeated silylation under the conditions similar to the first run. The silylate was further purified by means of column chromatography using silica gel (Wakogel Q-22) in a column of 2.0 cm diameter and 30 cm length, eluted with *n*-hexane-benzene mixture (9:1 in vol).

Successive solution fractionation of the silylate was conducted as follows: The TMSS and DMPS with molecular weights of 11,900 and 17,200, respectively, were added into the methanol-methyl ethyl ketone mixture at 30°C and allowed to stir magnetically for more than 30 min to equilibrate. Then the turbid solution was filtered through a sintered glass disk. The filtrate was evaporated to obtain the first fraction. The fractionation was further continued by putting the silylate solid into the methanol-methyl ethyl ketone mixture with an increased volume of the latter solvent. Thus, the TMSS and DMPS were divided into 9 and 15 fractions, respectively. The polydispersity factor ( $\overline{M}_w/\overline{M}_n$ ) was almost 1.6 or less by gel permeation chromatography (GPC).

High molecular weight polyphenylsilsesquioxane (PPSQ) was prepared by hydrolysis of phenyltrichlorosilane, followed by polymerization with KOH in diphenylether.<sup>5</sup>

### Characterization of Silylates

Analysis of silicon in these silylates was made by the wet oxidation method with a sulfuric acid-ammonium nitrate oxidant.

<sup>13</sup>C and <sup>29</sup>Si NMR spectra were taken in DCCl<sub>3</sub> with a JEOL PFT-100 Fourier transform NMR spectrometer at room temperature (25 MHz for <sup>13</sup>C and 20 MHz for <sup>29</sup>Si).

To measure the number-average molecular weight ( $\overline{M}_n$ ), a Hewlett-Packard 302 Vapor Pressure Osmometer was used at 37°C with toluene. Also the higher  $\overline{M}_n$  was determined with a Knauer Membrane Osmometer at 40°C in toluene.

The gel permeation chromatography (GPC) was done with a Shimadzu Liquid Chromatograph 830 having a differential refractive index detector. The columns used here were polystyrene gel (HSG 60, 50, 40, and 30) with THF at 45°C. The elution counts of the chromatograms were calibrated with six monodisperse polystyrenes (Pressure Chemicals Co.).

Limiting viscosity number was measured using a Ubbelohde type viscometer (Fica Viscomatic) with negligible kinetic energy correction at 25°C.

X-ray powder diffraction was measured with a Rigaku D-3C diffractometer (Cu K $\alpha$  radiation) and a Rigaku goniometer SG-7.

## RESULTS AND DISCUSSION

The silicic acid-THF solution thus prepared was usually stable to gelation

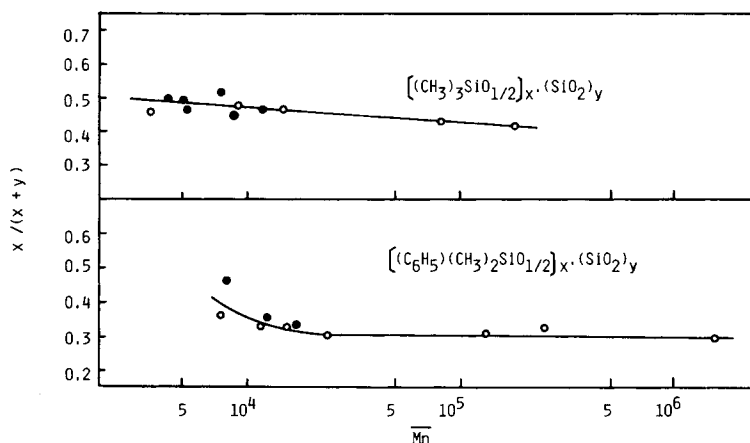


Fig. 1. Silylate composition,  $x/(x + y)$  vs. number-average molecular weight ( $\overline{M}_n$ ): (O) fractionates; (●) unfractionates.

at room temperature even after standing for a week. However, the molecular weight of silicic acid gradually increased with the elapse of time, finally, to form gel. In this experiment, the silicic acid solution was subjected to silylation after storage for 1 day at ca. 5°C.

The silylation results for the silicic acid are summarized in Table I.

The yield of the silylates was almost quantitative based on the silicic acid used. The number-average molecular weights ( $\overline{M}_n$ ) ranged from 4000 to 17,000, depending on, mainly, the concentration of reactants and reaction temperature.

The chemical composition of the silylates was determined by means of silicon analysis after repeated silylation. Apparent composition formula of these silylates is assumed to be  $[R(\text{CH}_3)_2\text{SiO}_{1/2}]_x \cdot (\text{SiO}_2)_y$ , where R is the  $\text{CH}_3$  or  $\text{C}_6\text{H}_5$  group.

Figure 1 shows a relationship of composition and molecular weight ( $\overline{M}_n$ ) in these silylates.

The fraction of the organic portion, i.e.,  $\text{R}(\text{CH}_3)_2\text{SiO}_{1/2}$ , denoted as  $x/(x + y)$ , was 0.5 or less, and slightly decreased with  $\overline{M}_n$ . A similar tendency was observed even for the fractionated samples.

IR spectra were measured to obtain structural information of these silylates. However, strong Si—O—Si asymmetric stretching vibration did not afford it in detail, different from the case of poly(phenylsilsesquioxane) (PPSQ).<sup>5,6</sup>

Proton-decoupled  $^{13}\text{C}$  and  $^{29}\text{Si}$  NMR spectra of two silylates and PPSQ are shown in Figures 2(A) and 2(B). Two  $^{29}\text{Si}$  peaks in the silylates were attributed to the organosilyloxy Si at lower field and the silica Si derived from silicate at higher field. The silica  $^{29}\text{Si}$  peaks around -110 ppm were evidently superimposed on the background  $^{29}\text{Si}$  due to the tube. Furthermore, resolution of the silica  $^{29}\text{Si}$  peaks were not sufficient to assume the chemical structure of the silica backbone. The half height width of the silica  $^{29}\text{Si}$  peaks was much larger than those of PPSQ, trimethylsilyloxy, and dimethylphenylsilyloxy  $^{29}\text{Si}$  by almost twice. This indicates that these silylates contain rigid silica backbones with a high degree of branching.

Figure 3 shows X-ray powder diffraction patterns of PPSQ, TMS, DMPS, and amorphous silica. The amorphous silica used here was made from the silicic

TABLE I  
Silylation of Silicic Acid in THF

No.	Reactants		THF (mL)	Triethyl- amine (mL)	Temp (°C)	Time (h)	Yield (g)	Silylate Time of silyln.	$\overline{M}_n$ (VPO)
	Silicic acid [SiO <sub>2</sub> : g (mmol)]	Chlorosilane (mmol)							
77	2.7 (45)	320	50	35	RT	20	7.0	1	4320
103	12.0 (200)	240	140	30	RT	0.5	17.6	2	5260
13-16	12.0 (200)	160	140	0	70	6	21.3	2	7620
101-102	12.0 (200)	160	140	12	70	10	17.9	2	8650
58 <sup>a</sup>	10.3 (170)	240	120	15	70	10	21.5	2	11,900
35	5.6 (91)	115	65	10	70	2	15.4	2	8160
36	5.6 (91)	91	65	10	70	2	11.8	2	12,700
57 <sup>a</sup>	10.3 (171)	150	120	15	70	10	24.5	2	17,200

<sup>a</sup> These silylates were fractionated by successive solution method.

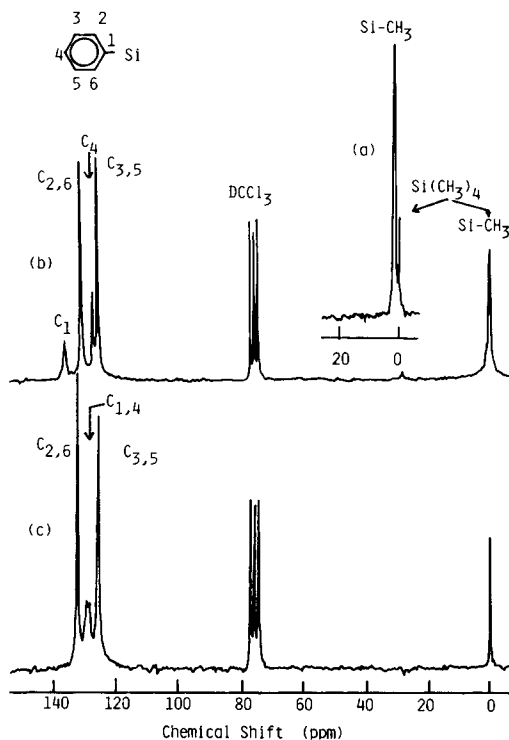


Fig. 2(A).  $^{13}\text{C}$  NMR spectra of TMSS, DMPS, and PPSQ, 25 MHz, in  $\text{DCCl}_3$ , 300 mg/mL: (a) TMSS; (b) DMPS; (c) PPSQ.

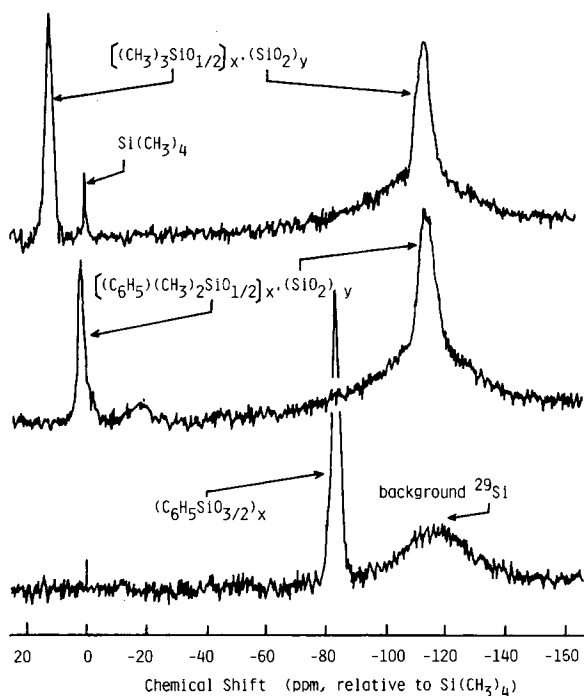


Fig. 2(B).  $^{29}\text{Si}$  NMR spectra of TMSS, DMPS, and PPSQ, 20 MHz, in  $\text{DCCl}_3$ , 450 mg/mL, doped with  $\text{Cr}(\text{acac})_3$ .

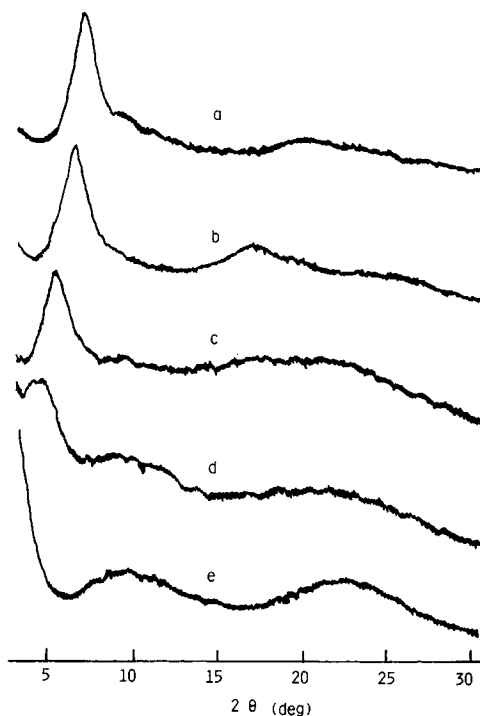


Fig. 3. X-ray diffraction patterns of PPSQ, TMSS, DMPS, and amorphous silica, 30 kV, 10 mA: (a) PPSQ ( $\overline{M}_w = 170,000$ ); (b) TMSS ( $\overline{M}_n = 4320$ ); (c) DMPS ( $\overline{M}_n = 12,700$ ); (d) DMPS ( $\overline{M}_n = 1,570,000$ ); (e) amorphous  $\text{SiO}_2$ .

acid-THF solution by evaporating, washing with methanol and water, and heating at  $110^\circ\text{C}$ . As can be seen from this figure, the degree of crystallinity in these silylates was very low. However, their diffraction patterns were similar to those of PPSQ.<sup>7,8</sup> The  $d_1$  spacings of the silylates estimated from the first narrower and intenser reflections were observed to lengthen in the following order: PPSQ < TMSS < DMPS. This was probably because of bulkiness of these substituents, i.e., phenyl, trimethylsiloxy, and dimethylphenylsiloxy groups. It was also noted that, as the molecular weight increased, the diffraction patterns became similar to that of the amorphous silica, as shown in Figure 3.

The spacing vs. molecular weight relationship is shown in Figure 4. The  $d_1$  spacing for both TMSS and DMPS increased with the molecular weight to reach almost constant values. Also, the  $d_1$  spacing for the DMPS was found to be slightly larger than that for the TMSS over a wide range of molecular weights. On the contrary, the  $d_2$  spacing for the TMSS was almost constant, regardless of the molecular weight. It was difficult to illustrate the molecular structures for the silylates from the X-ray diffraction data, although it was found that their structural regularity decreased and the silica backbones became larger with an increase of the molecular weight. Accordingly, 3-dimensional structures can be assigned for these silylates.

Figure 5 shows gel permeation chromatograms of the DMPS. All the chromatograms exhibited single, broad, and distorted peaks, similar to those of the TMSS.<sup>1</sup>

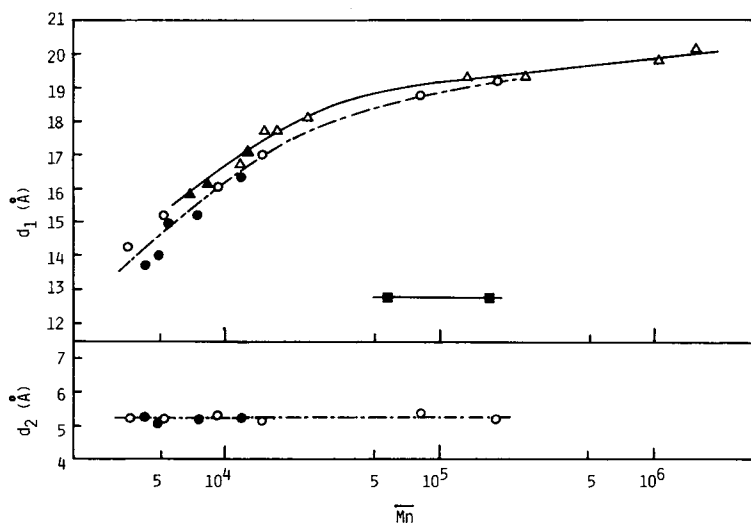


Fig. 4. Spacings ( $d_1$  and  $d_2$ ) vs. molecular weight ( $\overline{M}_n$ ): (O, ●) TMSS; ( $\Delta$ ,  $\blacktriangle$ ) DMPS; (■) PPSQ; (●,  $\blacktriangle$ , ■) unfractionates; (O,  $\Delta$ ) fractionates.

The  $\overline{M}_n$  determined by vapor pressure osmometry (VPO) were about 2.5 times higher than those by the GPC method, which was calibrated by monodisperse polystyrenes. Also, the  $\overline{M}_n$  of the fractionated silylates were found to be always over the calibration curve, as revealed in Figure 6. This apparent discrepancy comes from structural characteristics of the silylates being of high random branching in the silica backbones.

It is well known that viscosity-molecular weight relationship,  $[\eta] = KM^\alpha$ , is

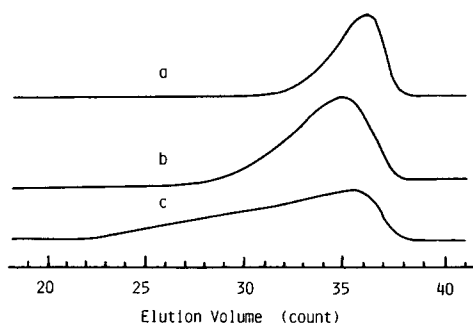


Fig. 5. Gel permeation chromatograms of unfractionated DMPS THF, concn 10 mg/mL, elution rate 1 mL/min:

	$\overline{M}_n$ (VPO)	GPC		
		$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$
a	8186	3190	4140	1.31
b	12,700	5320	9430	1.77
c	17,200	6830	32,500	4.76

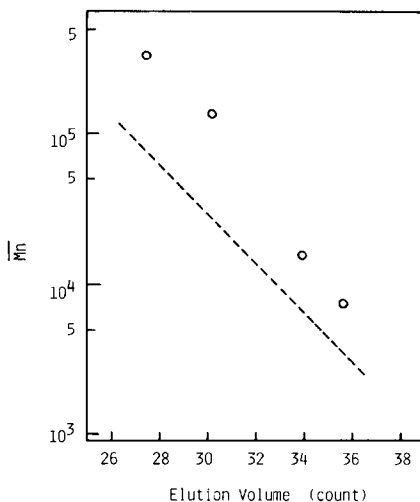


Fig. 6. Deviation of GPC elution volume in fractionated DMPS from polystyrene calibration curve.

an effective criterion to assume molecular structure in dilute solutions. Figure 7 shows Mark-Houwink-Sakurada plots of both the silylates in a good solvent, benzene. The limiting viscosity number  $[\eta]$  was extremely low over the measured molecular weight ranges. Both the curves for conventional double logarithmic plots were adequately approximated by straight lines, except for the lower molecular weight ranges, less than ca. 5000. The following relationships between  $[\eta]$  and  $\overline{M}_n$  were established by least squares method: for TMSS

$$[\eta] = 1.24 \times 10^{-1} \overline{M}_n^{0.31} \quad (\text{cm}^3/\text{g})$$

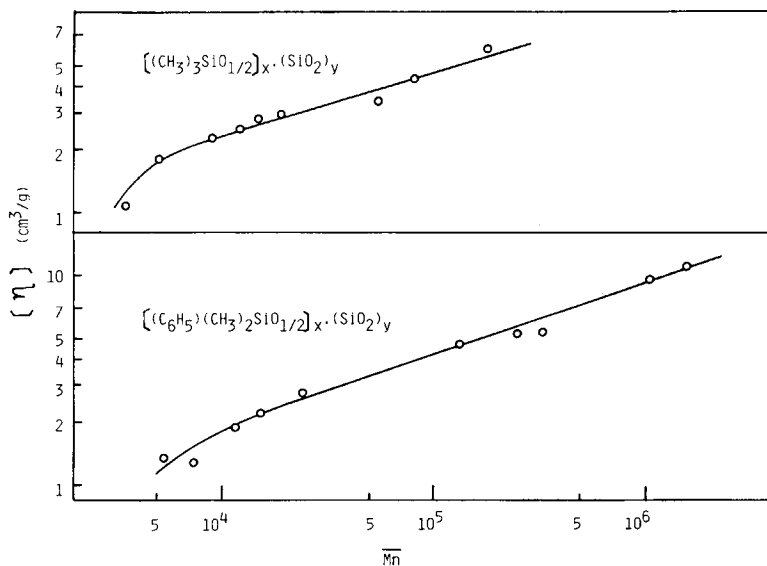


Fig. 7. Mark-Houwink-Sakurada plots of TMSS and DMPS, 25°C, in benzene.



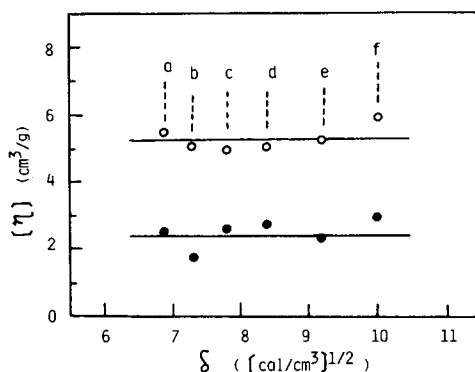


Fig. 8. Limiting viscosity number of DMPS vs. solubility parameter of solvent, 25°C: (a) diisopropylether; (b) *n*-hexane; (c) isoamyl acetate; (d) methyl isobutyl ketone; (e) benzene; (f) *o*-dichlorobenzene.

for DMPS

$$[\eta] = 7.9 \times 10^{-2} \overline{M}_n^{0.34} \quad (\text{cm}^3/\text{g})$$

at 25°C, in benzene

The exponents were almost 0.3, very low compared with those of flexible vinyl polymers (0.5–0.8)<sup>9</sup> and syndiotactic PPSQ having rigid rod structure (0.9).<sup>10</sup> This suggests that these silylates exist as compact spheres even in a good solvent. However, it appears that the silylates with molecular weights of lower than 5000 can be considered to be of linear structure to some extent.

The viscosity measurement was further conducted with some solvents having different solubility parameters. Figure 8 represents the plots of viscosity vs. solubility parameter in the DMPS. No significant variation in the viscosity was

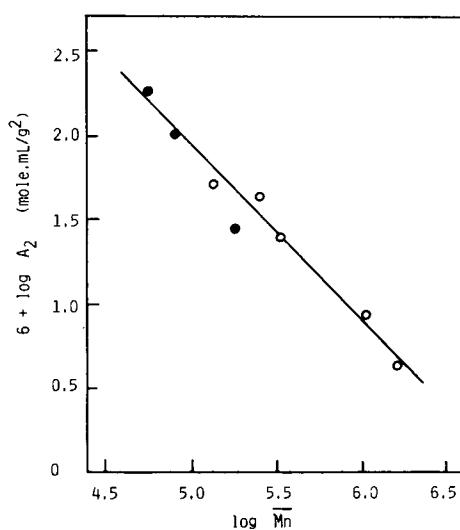


Fig. 9. Second virial coefficient ( $A_2$ ) vs. molecular weight ( $\overline{M}_n$ ), 40°C, in toluene.

observed over the measured range of solubility parameters (6.9–10.0). These solution viscosity behaviors look similar to these of polymethylsiloxanes,<sup>11,12</sup> although the degree of branching in the silylates might be much higher than that of crosslinked polymethylsiloxanes.

The second virial coefficients ( $A_2$ ) were estimated from membrane osmometry. The  $A_2$  values were relatively low compared with those of PPSQ<sup>10</sup> and polystyrene<sup>13</sup> within the molecular weight ranges (56,000–1,570,000). The molecular weight dependence of the  $A_2$  is shown in Figure 9. For both the TMSS and DMPS, the plots fell on a same straight line, roughly expressed in the following equation, having a high negative exponent:

$$A_2 = 10.3 \overline{M}_n^{-1.0} \quad (\text{cm}^3 \cdot \text{mol/g}^2) \quad \text{at } 40^\circ\text{C, in toluene}$$

It was already reported by Audsley and Aveston<sup>14</sup> and Greenberg and Sinclair<sup>15</sup> based on light scattering study that silicic acid in aqueous solution had compact spherical structure. Therefore, it is rather reasonable to presume that the silicic acid molecule in nonaqueous media is also regarded as spherical.

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