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Alkoxysilanes. II. Preparation of Tributoxysiloxychlorosilanes, Silanols, and Their Polymeric Substances

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Tributoxysiloxychlorosilanes $[(BuO)_3SiO]_xSiCl_{4-x}$ (Bu=*t*: $x=1, 2$; Bu=*s*: $x=1, 2, 3$ or 4) were prepared by the reaction of silicon tetrachloride with tributoxysilanol in the presence of pyridine. The hydrolysis of these compounds led to the formation of tributoxysiloxysilanols $[(BuO)_3SiO]_xSi(OH)_{4-x}$ (Bu=*t*: $x=2$; Bu=*s*: $x=2$ or 3). Tri-*t*-butoxysiloxysilanetriol was obtained from the corresponding trichlorosilane under mild hydrolytic conditions by using aniline as an hydrogen-chloride acceptor. On the other hand, the hydrolysis of the trichlorosilane with excess water in the presence of pyridine gave a resinous product. The fractional precipitation of this product gave a white powder soluble in such organic solvents as benzene, *n*-hexane, ether, and carbon tetrachloride; the powder had a molecular weight between 2500 and 4300. This resin turned into glassy solids upon being heated at 200 or 300°C under reduced pressure; these solids had molecular weights between 5500 and 12500. The possible structures for these polymeric substances were discussed on the basis of the results of the elemental analysis, the IR spectra, and the gas chromatography of volatile substances produced in the course of polymerization.

Although alkoxysilanes with functional groups have been prepared, the isolation of alkoxysilanes $(RO)_xSiX_{4-x}$ (R=Me, Et, Pr, Bu; X=OH, NH_2; $x=1, 2$ or 3) containing hydroxy or amino1) groups as functional groups is very difficult because of the easy condensation. Tiralkoxysilanols with *s*-2) or *t*-3)alkoxy groups, however, are obtained, and in the latter case di-*t*-butoxysilanediol4) is also isolated. The above facts show that the steric hindrance of alkyl groups protects the functional group from condensation. Therefore, we tried to prepare tributoxysiloxychlorosilanes in which the alkoxy group on an alkoxysilane is replaced by the tributoxysiloxy group and tried to isolate the stable silanediol and silanetriol by the hydrolysis of the corresponding chlorosilanes:

$$SiCl_4 + x(BuO)_3SiOH + xC_5H_5N$$
$$= [(BuO)_3SiO]_xSiCl_{4-x} + xC_5H_5NHCl$$

$$[(BuO)_3]_xSiCl_{4-x} + xH_2O$$
$$= [(BuO)_3SiO]_xSi(OH)_{4-x} + xHCl$$

In the course of our investigation into the hydrolysis of alkoxysiloxychlorosilane, our attention was called to polymeric substances produced because the structures of the polyalkyl(aryl)silsesquioxanes formed by the hydrolysis of alkyl(aryl)trichloro-

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silane[5] or alkyltrialkoxysilanes[6,7] were discussed, but the structures of substances formed by the hydrolysis of alkoxysiloxytrichlorosilane were not. Therefore, it seemed necessary that the structures of the polymers were considered since it was thought that the polymeric substances formed by the hydrolysis of tri-*t*-butoxysiloxytrichlorosilane do not have such a simple structure constructed of silsesquioxane units as have the hydrolysis products of alkyltrichlorosilanes.

Experimental

The boilling points and melting points are uncorrected. The experiments were carried out under a dry atmosphere.

Materials. The amines and the solvents were dehydrated, and the silicon tetrachloride was purified by distillation. Tri-*s*-butoxysilanol was obtained by the method of Wright[2]; bp 89.5°C/1 mmHg, n_D^{20} 1.4135.

Tri-*t*-butoxysilanol was first prepared by Backer and Klasens[8] by the hydrolysis of sodium tri-*t*-butoxysilanolate. Wright *et al.* had described how silanol was obtained by the hydrolysis of tri-*t*-butoxychlorosilane in boilling water, but its details had not been documented. In the present work, the silanol was prepared in good yields by a modification of the procedure of Wright.

To a solution of 72.7 g of pyridine and 280 g of water, 200 g of tri-*t*-butoxychlorosilane[9] were added. Then the mixture was stirred at 70—80°C for 1 hr and left standing overnight. After the white solid thus formed was filtered and washed with water, the solid was dissolved in petroleum ether and dehydrated with anhydrous sodium sulfate. The solvent was removed, and the residue gave 130 g (70%) of a white crystalline solid, mp 65—66°C (lit. 65.5°C). Found: C, 54.67; H, 11.64; Si, 10.60%; mol wt, 268. Calcd for $C_{12}H_{28}O_4Si$: C, 54.51; H, 10.67; Si, 10.60%; mol wt, 264.

Preparation of Tri-*s*- and -*t*-butoxysiloxychlorosilanes. Into a solution of tri-*t*-butoxysilanol and pyridine in *n*-hexane, silicon tetrachloride in *n*-hexane was stirred, drop by drop, at 0—−5°C. (In the preparation of *s*-derivatives the addition of the silanol was reversed, and for tris or tetrakis derivatives toluene was used as the solvent.) The mixture was refluxed for one (trichloro-derivatives) or two (the other derivatives) hours. After the filtration of pyridine hydrochloride and the removal of the solvent, the filtrate gave products by fractional distillation *in vacuo* with a 20 cm Widmer column. The results are shown in Table 1.

Preparation of Tri-*s*- and -*t*-butoxysiloxysilanols. Into a mixture of pyridine, water, and petroleum ether, tributoxysiloxychlorosilane in dry petroleum ether was vigorously stirred, drop by drop, at 0—−5°C. Then the oil layer was separated and dried over anhydrous sodium sulfate. The evaporation of the solvent gave silanols by fractional distillation *in vacuo*. The results are given in Table 2.

Preparation of Tri-*t*-butoxysiloxysilanetriol. A mixture of 2.5 g of water, 13.2 g of aniline, and 300 m*l* of ether was made homogeneous by the addition of 30 m*l* of acetone.[10] To the solution, 18.7 g of tri-*t*-butoxysiloxytrichlorosilane in 200 m*l* of ether were then stirred in, drop by drop, at −10—−20°C for 2 hr. Then the mixture was allowed to come to room temperature, and the aniline hydrochloride was filtered out. The white solid formed by evporation of the ether *in vacuo* was dissolved in 60 m*l* of benzene without heating. The needle crystals which formed when the solution stood for several hours were filtered out, washed with benzene, and dried *in vacuo*; yield 3 g (18.8%); mp 114—117°C. The results of the elemental analysis are given in Table 2.

Hydrolytic Polycondensation of Tri-*t*-butoxysiloxytrichlorosilane. Into a mixture of 29.8 g of pyridine, 198 g of water, and 50 m*l* of petroleum ether, a 50 g portion of the trichlorosilane in 50 m*l* of petroleum ether was stirred at 0°C. The oil layer was then separated, washed fully with water, and dried over anhydrous sodium sulfate. The evaporation of the solvent *in vacuo* gave a colorless residue (39 g). The purification of this product was carried out by fractional precipitation. Into 50 m*l* of vigorously stirred methanol there were added, drop by drop, 6 g of the product dissolved in 10 m*l* of benzene. A white precipitate was formed and separated by decantation. The precipitate was again submitted to the same treatment, giving 1.0 g (No. 1-a) of a white solid when dried *in vacuo*. The solvent was evaporated from the mother liquor under reduced pressure, and the residue was treated with 5 m*l* or 3 m*l* of benzene through the same method to give 1.2 g (No. 1-b) and 1.3 g (No. 1-c) respectively of a white solid. The results of the elemental analysis are given in Table 4.

Heat Polymerization of the Hydrolysis Product. The unpurified hydrolysis product (9.5 g) obtained in the above experiment was heated at 200 or 300°C for 2 hr under reduced pressure (1—2 mmHg). The volatile and sublimable products formed in the procedure were trapped into a vessel cooled with dry ice and acetone. The total weight loss was 1.9 g at 200°C and 4.1 g at 300°C, including 1.7 and 1.9 g, respectively, of tri-*t*-butoxysilanol as the sublimate. The colorless glassy solid (4.5 g) at 200°C was treated by the same procedure to give 1.3 g (No. 2-a; 10 m*l* of benzene), 0.6 g (No. 2-b; 5 m*l*), and 0.4 g (No. 2-c; 3 m*l*) of a white powder. The residue (1.5 g) at 300°C was extracted with 100 m*l* of benzene for 3 hr to give 1.2 g of a soluble solid and 0.3 g (20 wt%) of an insoluble one. The former (2 g) was further treated with benzene to give 1.4 g (No. 3-a; 10 m*l* of benzene) and 0.5 g (No. 3-b; 5 m*l*) of a white powder.

It was confirmed by means of gas chromatography that the volatile substance obtained in the course of

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[6] M. M. Sprung and F. O. Guenther, *ibid.*, **77**, 3990, 3996 (1955).

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[8] H. J. Backer and H. A. Klasens, *Rec. Trav. Chim.*, **61**, 500 (1942).

[9] M. G. Voronkov, A. N. Razarev and A. K. Baigojii, *Zh. Obs. Chim.*, **26**, 3072 (1956).

[10] T. Takiguchi, *J. Am. Chem. Soc.*, **81**, 2359 (1959).

the heat polymerization, which was dissolved in benzene, contained water and *t*-butyl alcohol. The results are given in Table 4.

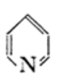
Heat Polymerization of Tri-*t*-butoxysiloxysilanetriol. The silanetriol (2.6 g) was heated at 145—155°C for 30 min under reduced pressure (2 mmHg). The same treatment of the product with 5, 3, and 1 m*l* of benzene gave 0.3 g (No. 4-a), 0.7 g (No. 4-b), and 0.8 g (No. 4-c) of a white powder. The results are given in Table 4.

Instruments. The IR spectra were measured in a KBr disk or a liquid film with a Hitadhi EPI-S2 spectrometer. The NMR spectra were measured with a Varian A-60 spectrometer in a carbon tetrachloride solution or in dueterated chloroform, with tetramethylsilane as the internal standard. The molecular weight was determined by the cryoscopic method or the vapor-pressure method in benzene. The gas chromatography was measured under these conditions: carbowax 6000, 1-m, 136°C, 46 m*l*/min. The thermal property of the products was determined by thermogravimetric analysis and by differential thermal analysis.

Results and Discussion

Monomers. The chlorosilanes and the silanols obtained are shown in Tables 1 and 2. As is shown in Table 1, the number of the replaced chlorine atoms indicates that the tri-*t*-butoxysiloxy group has a greater steric hindrance than the tri-*s*-butoxysiloxy one. Under these experimental conditions, further substituion did not occur even when excess tri-*t*-butoxysilanol was used. The difference in this steric hindrance between the two groups greatly contributes to the stabilization of the functional group. Table 2 shows that bis(tri-*s*-

TABLE 1. TRI-*s*- AND -*t*-BUTOXYSILOXYCHLOROSILANES $[(BuO)_3SiO]_xSiCl_{4-x}$

Reactants (g)			Products						
$SiCl_4$	$(BuO)_3SiOH$		*x*	Yield %	Bp °C/mmHg	n_D^{20}	Mol wt Found (Calcd)	Anal, Found (Calcd) % Cl	Si
			Bu=*s*						
51.0	79.2	23.7	1	62.0	81—82/1	1.4134	402 (398)	26.86 (26.73)	13.89 (14.12)
15.0	47.0	14.0	2	67.0	165.5—166/1.5	1.4159	643 (625)	11.28 (11.34)	13.65 (13.46)
15.0	70.0	21.0	3	50.0	196—199/2	1.4196	850 (854)	4.37 (4.15)	13.29 (13.17)
6.4	40.0	15.5	4	44.1	215—217/1	n_D^{50} 1.4095	1081 (1081)	—	13.16 (12.99)
			Bu=*t*						
55.4	86.0	25.7	1	65.2	80—82/1 solid	1.4065	412 (398)	*26.62 (26.73)	14.02 (14.12)
32.2	100.0	29.9	2	82.5	151—152/2.5 Mp 47—49	n_D^{50} 1.3962	639 (625)	**11.26 (11.32)	13.47 (13.46)

* Found: C, 34.84; H, 7.37%. Calcd: C, 36.21; H, 6.84%.
** Found: C, 45.59; H, 9.16%. Calcd: C, 46.06; H, 8.70%.

TABLE 2. TRI-*s*- AND -*t*-BUTOXYSILOXYSILANOLS $[(BuO)_3SiO]_xSi(OH)_{x-4}$

Reactants (g)			Products					
*1 $(RO)_xSiCl_{4-x}$	H_2O		*x*	Yield %	Bp °C/mmHg	n_D^{20}	Mol wt Found (Calcd)	Anal. Found (Calcd) % Si
			Bu=*s*					
11.4	21.2	1.3	3	67.0	221—222/1	1.4171	857 (835)	13.51 (13.45)
37.4	47.6	12.3	2	25.2	199—201/2	1.4161	630 (589)	14.25 (14.31)
			Bu=*t*					
25.0	42.0	7.1	2	84.9	155/1.5 Mp 49—51	n_D^{60} 1.3915	604 (589)	*3 14.35 (14.31)
18.7	2.5	13.15*2	1	18.8	Mp 114—117	—	—	*4 16.23 (16.40)

*1 R=$(BuO)_3Si$ (Chlorosilanes in Table 1). *2 Aniline
*3 Found: C, 48.58; H, 9.89%. Calcd: C, 48.95; H, 9.58%.
*4 Found: C, 44.22; H, 9.04%. Calcd: C, 42.07; H, 8.82%.

TABLE 3. NMR AND IR SPECTRA OF TRI-*s*- AND -*t*-BUTOXYSILOXYSILANOLS

Compound	NMR Spectra : Chemical shift (τ)			IR Spectra (cm^{-1})
	t-Bu, *s*-Bu(CH$_3$-, -CH$_2$-) (s) (m)	-CH- (sept)	-OH (s)	ν_{OH}
$(\overset{t}{Bu}O)_3SiOH$	8.67 (27.1H)	—	6.08 (1H)	3400
$(\overset{t}{Bu}O)_3SiOSi(OH)_3$	8.67	—	5.85	3430
$[(\overset{t}{Bu}O)_3SiO]_2Si(OH)_2$	8.68 (27.5H)	—	6.09 (1H)	3450
$(\overset{s}{Bu}O)_3SiOH$	9.20—9.24 (22.1H)	6.00 (3.1H)	5.40 (1H)	3350
$[(\overset{s}{Bu}O)_3SiO]_2Si(OH)_2$	8.40—9.20 (5.2H)	5.75—6.20 (1H)		3360
$[(\overset{s}{Bu}O)_3SiO]_3Si(OH)$	8.40—9.25 (27.5H)	6.00 (9.3H)	6.90 (1H)	3450

butoxysiloxy)silanediol polymerizes partially during prolonged distillation at a high temperature (yield 28%), whereas bis(tri-*t*-butoxysiloxy)silanediol can be distilled quantitatively (yield 80%) without condensation. On the other hand, tri-*t*-butoxysiloxysilanetriol is unstable and easily polymerizes, like other silanetriols.

The silanetriol is slightly soluble in benzene and chloroform. The other products obtained as solids are very soluble in organic solvents and have low melting points.

The silanols were confirmed by the IR and NMR spectra given in Table 3. The IR spectra are essentially identical and exhibited characteristic peaks at 3425—3460 (OH), 1365 and 1387 (branching of the alkyl groups), and 1060—1070 (Si–O–Si) cm^{-1}. A little shift toward the lower wave numbers for the hydroxy group of going from *t*- to *s*-derivatives was observed, probably because of an increace in the hydrogen bond with a decrease in the steric effect. The relative ratio of the protons of the hydroxy to those of the alkyl group is in good accordance with each of the structures. The NMR spectra of tri-*t*-butoxysiloxysilanetriol were measured in deuterated chloroform, but an exact ratio was not given because of its low solubility. The proton signal for the hydroxy group of bis(tri-*s*-butoxysiloxy)silanediol was not detected as a singlet. Since proton signals of the *t*-derivatives have a tendency toward an up-field shift as the number of substituent increases, in this case the signal seems to overlap with that of the methine proton. The ratio of the sum of methine and hydroxy protons to that of methyl and methylene protons is in good agreement with the structure.

The signal for the hydroxy proton of the silanols has a tendency to shift up-field with a larger steric hindrance; this is parallel to that tendency observed in the IR spectra.

Polymers. The results of the hydrolytic polycondensation and the heat polymerization are given in Table 4. Although No. 3-c was insoluble and infusible, the polymers were white powders, soluble in such organic sovents as benzene, *n*-hexane, ether, and carbon tetrachloride, and insoluble in methanol and ethanol.

The structures of these polymers are thought to be similar to those of polyalkyl(aryl)silsesquioxanes.

TABLE 4. POLYALKOXYSILSESQUIOXANE

Product	Fused point °C	Mol wt	Analysis (Found %)			Atom ratio		
			C	H	Si	C	H	Si
No. 1-a	183—188	3180	39.03	8.31	20.89	4.4	11.2	1
No. 1-b	137—142	4300	39.31	8.36	20.05	4.6	11.7	1
No. 1-c	78—83	2550	40.68	8.48	19.20	5.0	11.8	1
No. 2-a	175—185	5500	33.86	7.05	22.50	3.5	8.7	1
No. 2-b	235—245	—	38.92	8.36	20.04	4.5	11.7	1
No. 3-a	290	12500	31.80	6.49	25.21	3.0	7.2	1
No. 3-c	infusible	—	10.50	8.99	28.51	0.9	8.9	1
No. 4-a	150—155	—	40.16	8.35	18.79	5.0	12.4	1
No. 4-b	82—87	2930	41.92	8.84	18.44	5.3	13.6	1

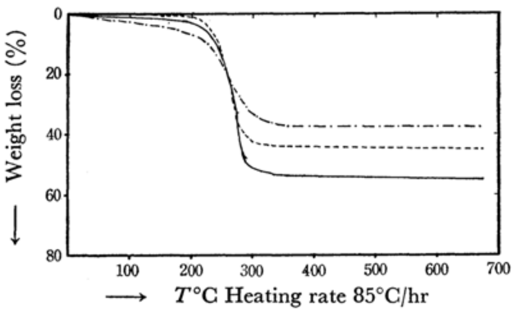


Fig. 1. Thermogravimetric analysis curve of polymer.

——— No. 1-a
------------ No. 3-a
–·–·–· No. 3-c

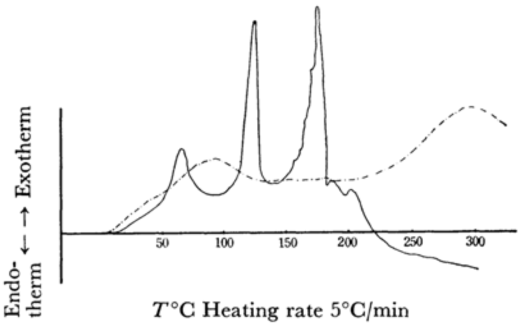
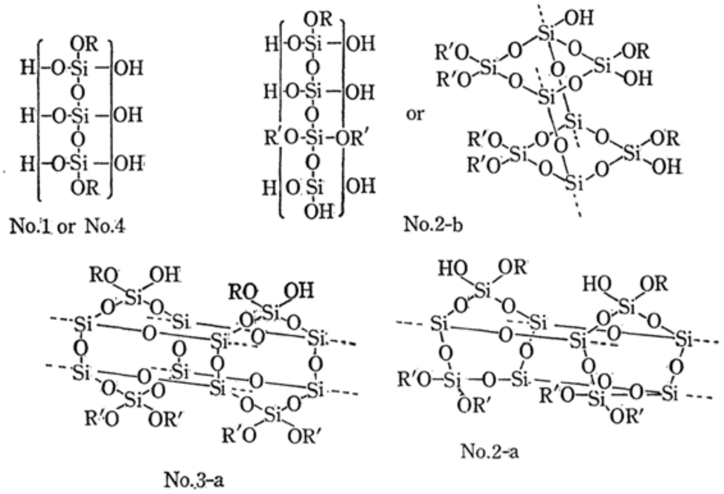


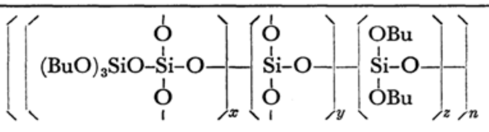
Fig. 2. Differential thermal analysis curve of tri-*t*-butoxysiloxysilanetriol (——) and No. 2-a (–·–·–).



where R=Si(OBu)$_3$ and R′=Bu

Fig. 3. The possible structures of polymers.

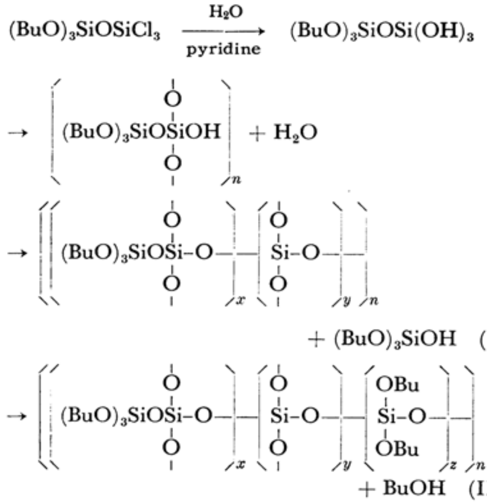
TABLE 5. EMPIRICAL FORMULAS DERIVED FROM THE UNIT STRUCTURE



$$\left[\left((BuO)_3SiO-\overset{\overset{|}{O}}{\underset{\underset{|}{O}}{Si}}-O-\right)_x\left(\overset{\overset{|}{O}}{\underset{\underset{|}{O}}{Si}}-O-\right)_y\left(\overset{OBu}{\underset{OBu}{Si}}-O-\right)_z\right]_n$$

x	y	z	Atom ratio			Mol wt Obs	n	Corresponding polymer No. Formula	Mol wt Calcd	Anal. % (Calcd)		
			C	H	Si					C	H	Si
1	0	0	6	13.5	1							
1	0.4	0	5	11.3	1	4300	12.4	No. 1, No. 4 $C_{144}H_{330}O_{81}Si_{31}$	4199	41.2	7.9	20.0
1	1	0	4	9.0	1							
1	1	1	5	11.2	1							
1	2	1	4	9.0	1	5500	8.7	No. 2-b $C_{160}H_{374}O_{107}Si_{40}$	5133	37.4	7.3	21.4
1	3	1	3.3	9.5	1	5500	7.9	No. 2-a $C_{160}H_{376}O_{124}Si_{48}$	5632	34.1	6.7	23.5
1	4	1	2.9	6.4	1	12500	16.5	No. 3-a $C_{320}H_{746}O_{277}Si_{112}$	12171	31.6	6.2	25.8

It has been known that alkyl(aryl)silsesquioxanes are obtained from the corresponding trichlorosilanes or silanetriols and are composed of a ladder-type linear chain[11] or a cage-like[7,12] structure repeating a cyclosiloxane ring. In the present work, however, it is evident from the results of the elemental analysis (Table 5) that none of the polymers are constructred of a simple silsesquioxane, a so-called "T" unit. The unit structures of these polymers are the Q (tetrafunctional silicon atom: SiO_2) and the D (difunctional silicon atom $(Bu^tO)_2$-$SiO_{0.5}$), along with the T (trifunctional silicon atom $(Bu^tO)_3SiOSiO_{1.5}$). This is confirmed from the following facts: 1. Tri-*t*-butoxysilanol was obtained as a component of the fractional precipitation and as a sublimate in the course of the heat polymerization *in vacuo*. 2. *t*-Butyl alcohol was detected as a volatile substance at from 200 to 300°C. Additional pieces of evidence are the remarkable weight loss at the temperature shown by thermogravimetric analysis curve (Fig. 1) and the three exothermic peaks at 65, 125, and 175°C observed in the differential thermal analysis of tri-*t*-butoxysiloxysilanetriol (Fig. 2). The two peaks at 90 and 295°C were also found for the No. 2-a polymer. These facts result from three different condensations in the course of the polymerization:



$$(BuO)_3SiOSiCl_3 \xrightarrow[\text{pyridine}]{H_2O} (BuO)_3SiOSi(OH)_3$$

$$\rightarrow \left((BuO)_3SiO\overset{\overset{|}{O}}{\underset{\underset{|}{O}}{Si}}OH \right)_n + H_2O \qquad (I)$$

$$\rightarrow \left((BuO)_3SiO\overset{\overset{|}{O}}{\underset{\underset{|}{O}}{Si}}{-}O{-} \left(\overset{\overset{|}{O}}{\underset{\underset{|}{O}}{Si}}{-}O{-} \right)_x \right)_y\Bigg)_n + (BuO)_3SiOH \qquad (II)$$

$$\rightarrow \left((BuO)_3SiO\overset{\overset{|}{O}}{\underset{\underset{|}{O}}{Si}}{-}O{-} \left(\overset{\overset{|}{O}}{\underset{\underset{|}{O}}{Si}}{-}O{-} \right)_x \left(\overset{OBu}{\underset{OBu}{Si}}{-}O{-} \right)_y \right)_z\Bigg)_n + BuOH \qquad (III)$$

The empirical formulas cited in Table 5 have been deduced by comparison with the atom ratio calculated from the experimental data (Table 4) and that obtained from the structural units, x, y, and z, in (II) and (III); the calculated values are also shown. The results of the elemental analysis (Tables 4 and 5) show that the polymers of No. 1 and No. 4 have no significant difference in structure except for the molecular weight and are in agreement with a (II) structure; on the other hand, the polymers of No. 2 and No. 3 are constructured of (III).

The probable structures of these polymers are shown in Fig. 3. In view of the fact that each of the polymers except for No. 3-c is very soluble in organic solvents, there appears to be no significant cross-linking. The polymers of No. 1 and No. 4 seem to have a linear sheet-like structure formed by the condensation of the three molecules of the silanetriol. As to the polymers of No. 2 and No. 3, however, it seems reasonable to assume three-dimensional polymers like a prism or cube (Fig. 4) rather than sheet-like ladder types. In this case the structural units might be eight, ten or twelve member-rings, since two or three functional silane monomers containing larger steric groups are apt to give cyclic or cage-like structures and since the stretching vibration of Si–O–Si in the cyclosiloxanes with more than eight member-rings is in the region of wave number higher than 1045 cm^{-1} (in these cases, at 1060—1070 cm^{-1}).[12,13] Besides the fact that the polymers of No. 3 contain an insoluble gel (20%) indirectly shows a three-dimensional structure in No. 2 and No. 3. The polymer of No. 3-c seems to be a network polymer.

The IR spectra of all polymers are essentially identical and show absorption peaks at 3400—3450, 2960, 1389, 1364, 1240, 1190, and 1060—1070 cm^{-1}.

The X-ray powdery diffraction pattern of No. 2-a indicates no crystallinity.

The authors wish to thank Mr. Isao Orita for his assistance in the experiments.

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