

Synthesis of Polyester Modified Silica Gel from Polymeric Tributylstannyl Ester of Silicic Acid and ϵ -Caprolactone

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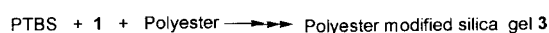
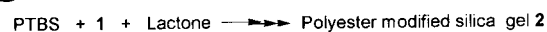
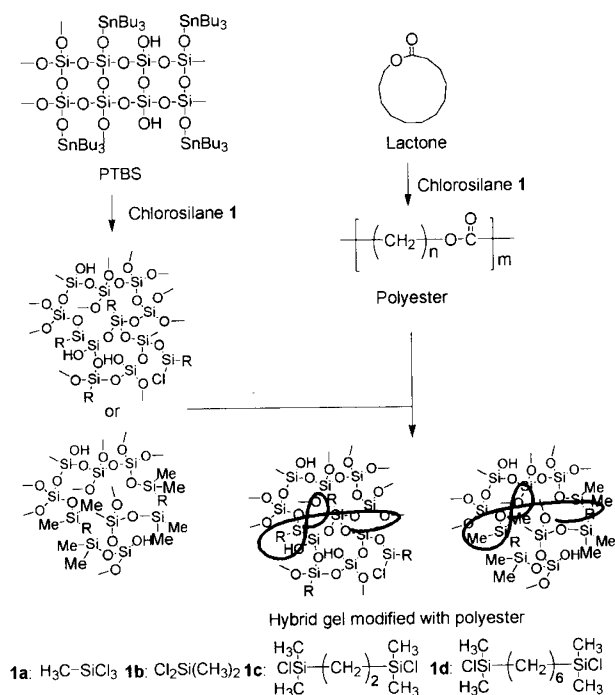
In preceding reports, polymeric tributylstannyl ester of silicic acid (PTBS) was found an effective intermediary compound for the preparation of organofunctionalized polysiloxanes and silica gels.^{1,2} Reactions of PTBS with chlorosilanes proceed under mild and neutral conditions as a new approach for the incorporation of various organofunctional groups into inorganic components.^{3–5} As one of such synthetic applications of PTBS, polyhalosilane such as dimethyldichlorosilane is employed for reactions with PTBS as cross-linking agents to afford gels consisted of silica matrix and organofunctional groups.⁵ The synthetic route is expected to be a possible access to new micro- and meso-porous materials. Reactions of PTBS with several polyhalosilanes such as dimethyldichlorosilane and bis(dimethylchlorosilyl)alkane gave porous gels, the specific surface areas of which were *ca.* 500 m² g⁻¹, in good yields.⁶ Such porous gels seem favorable for encapsulation of organic compounds, which lead to organically modified silica gel as micro- and/or nano-composite.^{7–9} Polyhalosilane is regarded as a Lewis acid. Accordingly, it should initiate a cationic polymerization when a suitable monomer exists in the reaction system. This means that the reaction for the preparation of the porous gel enables simultaneous formation of organic components. The procedure to build a polymer network and inorganic matrix at the same time seems to be usable for the preparation of interpenetrating polymer networks.^{10–12}

In sol-gel process using tetraalkoxysilane, the preparation of hybrid materials by simultaneous formation of inorganic and organic matrix through polymerization of organic monomer is known. Most examples are carried out under radical conditions except for a few, because the presence of water in sol-gel process should be unfavorable for ionic polymerization.^{13–15} However, the use of PTBS and polyhalosilanes can be carried out in non-aqueous medium under mild conditions to give silica matrix. Therefore, the use of PTBS and polyhalosilane is profitable for the polymerization under ionic conditions. Based on the above, we have investigated the procedure to prepare nanocomposite gels through simultaneous formation of inorganic and organic component. In this report, a new access to in-

organic-organic hybrid material, in which lactones are chosen as monomers to form organic component *via* ring-opening polymerization, is described.

EXPERIMENTAL

All reactions were carried out under argon atmosphere. Benzene for the reactions was refluxed over sodium metal and distilled. Lactones were distilled before use. Other reagents were used as supplied. Gravimetric analysis was conducted as reported.¹ IR spectra were recorded on a JASCO FT/IR 230. Gel permeation chromatographic (GPC) analysis was carried out on a TOSOH HLC 8020 chromatograph equipped with a refractive index detector. TSK gel G2500H, G2000H, and G1000H, were connected in series and tetrahydrofuran (THF) was used



Scheme

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as eluent. Calibration was performed using standard polystyrene. Solid-state CP/MAS NMR measurements were carried out with samples in double air bearing 6 mm rotor of zirconia on a JEOL JNM GX-270 spectrometer operating at 67.8 MHz for ^{13}C and 53.5 MHz for ^{29}Si . Magic Angle Spinning was performed at 5.6 kHz spinning rate. The proton 90° pulse was $5\ \mu\text{s}$ for ^{13}C NMR and $4\ \mu\text{s}$ for ^{29}Si NMR measurements, in which polydimethylsilane was used as a standard.

Preparation of PTBS

PTBS was prepared from bis(tributyltin) oxide $[(\text{Bu}_3\text{Sn})_2\text{O}]$ and water glass as reported before.² The number-average molecular weight (M_n) of PTBS was estimated as 11300 and M_w/M_n as 1.18 by GPC measurement (polystyrene standard). Sn and Si determined by gravimetric analysis were $2.45\ \text{mmol g}^{-1}$ and $6.35\ \text{mmol g}^{-1}$, respectively.

Ring-Opening Polymerization of Lactone by Chlorosilane Catalyst

To a solution of ϵ -caprolactone (**CL**) (1.00 g, 12.6 mmol) in toluene (1.5 mL), methyltrichlorosilane (**1a**) (0.07 g, 0.47 mmol) was added at room temperature under argon atmosphere. After stirring for 10 h, the solution was concentrated by a rotary evaporator under reduced pressure. The residue was poured into *n*-hexane and the solid precipitated was collected. The solid was dissolved in THF and reprecipitated from methanol. The resulting solid was dried at room temperature under reduced pressure (5 mmHg) for 24 h to obtain polyester (**PCL-1**, 0.76 g, 76%): $M_n=4300$, $M_w/M_n=2.44$; IR (KBr) 2870, 1720 (C=O), 1370, 1240, 1180, 1040 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.30–1.40 (m, 2H), 1.50–1.60 (m, 4H), 2.20–2.30 (m, 2H), 4.00–4.10 (m, 2H); ^{13}C NMR (CDCl_3) δ 24.20, 25.14, 27.96, 33.85, 63.76, 173.31.

In a similar manner, from **CL** (1.00 g, 12.6 mmol) and bis(chlorodimethylsilyl)hexane (**1d**) (0.11 g, 0.41 mmol), the polyester (**PCL-2**, 0.86 g, 86%) was obtained; $M_n=3600$, $M_w/M_n=2.27$.

In a similar manner, from δ -valerolactone (**VL**) (1.00 g, 10.0 mmol) and **1a** (0.07 g, 0.47 mmol), the polyester (**PVL**, 0.36 g, 36%) was obtained; $M_n=5600$, $M_w/M_n=1.15$; IR (KBr) 2870, 1720 (C=O), 1370, 1240, 1180, 1040 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.50 (m, 4H), 2.20 (m, 2H), 3.95 (m, 2H); ^{13}C NMR (CDCl_3) δ 21.77, 28.41, 33.84, 64.28, 174.08.

General Procedure for Preparation of Polyester Modified Silica Gel (**2**)

Method A. Chlorosilane **1** was added to a solution of PTBS and the lactone in toluene at room temperature under argon atmosphere. After stirring for 10 h, the product, which looked like a jelly, was filtered and washed successively with benzene, diethylformamide (DMF), methanol, water, acetone, and *n*-hexane. The obtained gel **2** was dried at room temperature for 24 h under reduced pressure such as 5 mmHg.

Method B. the mixture of PTBS, lactone, and chlorosilane **1** in toluene was refluxed for 3 h after stirring for 10 h at room temperature. The precipitated gel was treated as in Method A.

The results of the reactions are listed in Table I.

Yield was calculated from Si determined by gravimetric analysis in starting PTBS and **2**. With all tributyltin groups in PTBS assumed to be substituted to silyl groups, the yield was regarded as 100%. Lactone unit in **2** was estimated from elemental and gravimetric analysis, in which the number of carbons was assigned to the lactone unit, remaining tributyl group of tin and organic group of the silyl unit. In the calculation, an equimolar amount of silyl unit to tin in PTBS was considered to be incorporated.

From PTBS (0.20 g, Si: 1.27 mmol, Sn: 0.49 mmol), **CL** (0.50 g, 4.38 mmol), and methyltrichlorosilane (**1a**) (0.04 g, 0.27 mmol) in toluene (2 mL), **2a-CL** (0.13 g) was obtained by Method A (Table I, Run 1): IR (KBr) 3340, 2950, 1730, 1090 cm^{-1} . Anal. Found: C, 17.22%; H, 3.25%.

In a similar manner, **2a-CL** (0.20 g) was obtained by Method B (Table I, Run 2): IR (KBr) 3340, 2950, 1720, 1090 cm^{-1} ; ^{13}C CP/MAS NMR (67.8 MHz) δ 25.50, 30.10, 33.73, 64.08, 173.33; ^{29}Si CP/MAS NMR (53.5 MHz) δ -110.60, -106.23, -103.32, -101.59, -67.57, -64.75. Anal. Found: C, 35.49%; H, 5.20%.

From PTBS (0.20 g, Si: 1.27 mmol, Sn: 0.49 mmol), **VL** (0.44 g, 4.39 mmol), and **1a** (0.04 g, 0.27 mmol) in toluene (2 mL), **2a-VL** (0.12 g) was obtained by Method A (Table I, Run 3): IR (KBr) 3440, 2960, 1735, 1080 cm^{-1} . Anal. Found: C, 17.24%; H, 3.32%.

In a similar manner, **2a-VL** (0.14 g) was obtained by Method B (Table I, Run 4): IR (KBr) 3440, 2960, 1735, 1090 cm^{-1} . Anal. Found: C, 29.73%; H, 4.81%.

From PTBS (0.20 g, Si: 1.27 mmol, Sn: 0.49 mmol), γ -butyrolactone (**BL**) (0.38 g, 4.41 mmol), and **1a** (0.04 g, 0.27 mmol) in toluene (2 mL), **2a-BL** (0.10 g) was obtained by Method B (Table I, Run 5): IR (KBr) 3440, 1080 cm^{-1} . Anal. Found: C, 9.44%; H, 2.56%.

From PTBS (0.20 g, Si: 1.27 mmol, Sn: 0.49 mmol), **CL** (0.50 g, 4.38 mmol), and dimethyldichlorosilane (**1b**) (0.03 g, 0.23 mmol) in toluene (2 mL), **2b-CL** (0.10 g) was obtained by Method A (Table I, Run 6): IR (KBr) 3440, 1090 cm^{-1} . Anal. Found: C, 10.80%; H, 3.32%.

In a similar manner, **2b-CL** (0.16 g) was obtained by Method B (Table I, Run 7): IR (KBr) 3440, 2860, 1740, 1090, 805 cm^{-1} . Anal. Found: C, 31.82%; H, 4.64%.

From PTBS (0.20 g, Si: 1.27 mmol, Sn: 0.49 mmol), **CL** (0.50 g, 4.38 mmol), and 1,2-bis(chlorodimethylsilyl)ethane (**1c**) (0.06 g, 0.28 mmol) in toluene (2 mL), **2c-CL** (0.13 g) was obtained by Method B (Table I, Run 8): IR (KBr) 3450, 2960, 1740, 1090, 835, 790 cm^{-1} . Anal. Found: C, 29.20%; H, 4.42%.

From PTBS (0.20 g, Si: 1.27 mmol, Sn: 0.49 mmol), **CL** (0.50 g, 4.38 mmol), and 1,6-bis(chlorodimethylsilyl)hexane (**1d**) (0.07 g, 0.26 mmol) in toluene (2 mL), **2d-CL** (0.14 g) was obtained by Method A (Table I, Run 9): IR (KBr) 2920, 1720, 1080 cm^{-1} . Anal. Found: C, 25.14%; H, 4.75%.

In a similar manner, **2d-CL** (0.18 g) was obtained by Method B (Table I, Run 10): IR (KBr) 2920, 1730, 1180, 1090 cm^{-1} . Anal. Found: C, 37.84%; H, 5.71%.

General Procedure for Preparation of Polyester Modified Silica Gel (**3**)

The reaction was carried out as in the preparation of gel **2** (Method A and B), using the polyester **PCL-1**

Table I. Preparation of polyester modified silica gel **2** from **PTBS** and lactone with methyltrichlorosilane (**1a**)

Reaction conditions				Polyester modified silica gel 2			
Run	Chlorosilane 1	Lactone ^a	Method ^b	Content of Si	Content of Sn	Lactone unit	Yield ^c (Product)
				mmol g ⁻¹	mmol g ⁻¹	mmol g ⁻¹	%
1	1a	CL	A	12.00	0	2.14	89 (2a-CL)
2	1a	CL	B	6.30	0	4.76	72 (2a-CL)
3	1a	VL	A	13.40	0.09	1.91	91 (2a-VL)
4	1a	VL	B	8.77	0.09	4.45	70 (2a-VL)
5	1a	BL	B	12.30	0.10	1.17	70 (2a-BL)
6	1b	CL	A	13.00	0	0.68	74 (2b-CL)
7	1b	CL	B	8.90	0.15	3.48	81 (2b-CL)
8	1c	CL	B	9.40	0.17	1.25	69 (2c-CL)
9	1d	CL	A	10.36	0.25	0.34	82 (2d-CL)
10	1d	CL	B	7.90	0	2.20	81 (2d-CL)

^a ϵ -Caprolactone (**CL**); δ -Valerolactone (**VL**); γ -Butyrolactone (**BL**). ^b Method A: The reaction was conducted at room temperature for 10 h (Method A). After the reaction conducted at room temperature, the mixture was refluxed for 3 h (Method B). ^c Yield was based on Si (see EXPERIMENTAL section).

instead of lactone.

From **PTBS** (0.20 g, Si: 1.27 mmol, Sn: 0.49 mmol), **PCL-1** (0.50 g), and **1a** (0.03 g, 0.28 mmol) in toluene (2 mL), **3a-CL** (0.16 g) was obtained by Method A (Table II, Run 1): IR (KBr) 3440, 2950, 1735, 1090 cm⁻¹. *Anal.* Found: C, 23.26%; H, 3.72%.

In a similar manner, **3a-CL** (0.22 g) was obtained by Method B (Table II, Run 2): IR (KBr) 3440, 2960, 1730, 1180, 1090 cm⁻¹. *Anal.* Found: C, 34.79%; H, 5.21%.

From **PTBS** (0.20 g, Si: 1.27 mmol, Sn: 0.49 mmol), **PCL-1** (0.50 g), and **1b** (0.03 g, 0.23 mmol) in toluene (2 mL), **3b-CL** (0.10 g) was obtained by Method A (Table II, Run 3): IR (KBr) 3440, 2950, 1090 cm⁻¹. *Anal.* Found: C, 13.50%; H, 2.77%.

In a similar manner, **3b-CL** (0.15 g) was obtained by Method B (Table II, Run 4): IR (KBr) 3440, 2950, 1740, 1170, 1090 cm⁻¹. *Anal.* Found: C, 39.20%; H, 5.90%.

From **PTBS** (0.20 g, Si: 1.27 mmol, Sn: 0.49 mmol), **PCL-1** (0.50 g), and **1d** (0.07 g, 0.26 mmol) in toluene (2 mL), **3d-CL** (0.11 g) was obtained by Method A (Table II, Run 5): IR (KBr) 3440, 1090 cm⁻¹. *Anal.* Found: C, 22.73%; H, 3.83%.

In a similar manner, **3d-CL** (0.28 g) was obtained by Method B (Table II, Run 6): IR (KBr) 3440, 2960, 1740, 1180, 1090 cm⁻¹. *Anal.* Found: C, 47.82%; H, 6.62%.

RESULTS AND DISCUSSION

Lactones having five and seven cyclic members are known to afford polyesters readily *via* cationic ring-opening polymerization.¹⁶ Chlorosilane, as a Lewis acid, should initiate the polymerization of the cyclic esters. Accordingly, the polymerization of lactones such as γ -butyrolactone (**BL**), δ -valerolactone (**VL**), and ϵ -caprolactone (**CL**) under conditions same as for the preparation of polyester modified silica gel **2** in the presence of a small amount of chlorosilane **1a** or **1d** was examined. From the polymerization of **CL** at room temperature using **1a**, polyester (**PCL-1**), with number average molecular weight (M_n) of 4300, was obtained in 76% yield. The use of **1d** as a catalyst led to the formation of polyester (**PCL-2**) with M_n of 3800, in 86% yield. **VL** was polymerized in the presence of **1a** to give the

corresponding polyester (**PVL**) with M_n of 5600, in 36% yield. No ring-opening polymerization of **BL** using chlorosilane **1a** or **1d** was observed.¹⁶ Thus, chlorosilanes **1** initiate the ring-opening polymerization of **CL** and **VL** at room temperature. A one-pot reaction using **1a** as a cross-linking and an initiator, in which polymerization of lactones and gelation of **PTBS** seemed to proceed simultaneously, was tried.

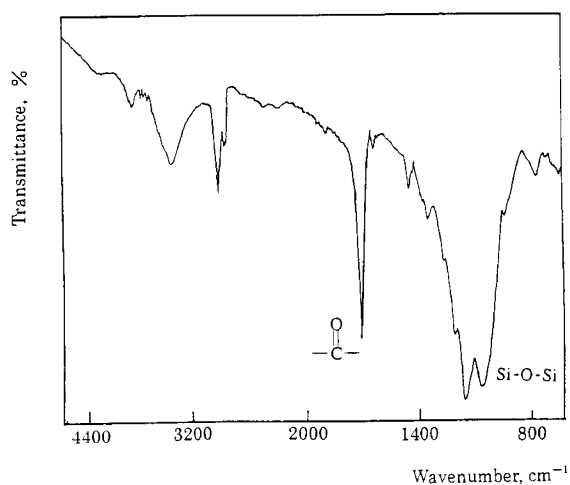
The simultaneous formation of hybrid gel **2** from **PTBS**, **1a**, and lactones was carried out by mixing these reagents under argon atmosphere at room temperature in Method A. In Method B, a jelly-like mixture, formed after the reaction continued at room temperature, was refluxed in toluene for 3 h to reach to more complete gelation. Slightly excess of **1a** to Sn in **PTBS** was used in the reaction. This means that a catalytic amount **1a** must be left and initiate ring-opening polymerization of lactone after most is compensated for the reaction with tributyltin. The results of the reactions are listed in Table I. Lactone unit in gel **2** obtained by Method A was lower than in gel **2** by Method B. In **2a-CL** and **2a-VL** obtained by Method B, lactone unit was 4.76 mmol g⁻¹ and 4.45 mmol g⁻¹, respectively (Table I, Run 2 and 4). Lactone unit in the products obtained by Method A was less than half that mentioned above (Table I, Run 1 and 3). This suggests that silica network of gel **2** obtained at room temperature is too loose to encapsulate the polyester effectively. In using **BL**, which gave no polymeric product, lactone unit was estimated as 1.17 mmol g⁻¹ (Table I, Run 5). From the results of polymerization of lactones and one-pot synthesis of modified gel **2**, the encapsulation of polymeric ester with M_n of several thousand, in silica component may be possible, but monomeric lactone difficult. Other chlorosilanes such as **1b**, **1c**, and **1d** were used as cross-linking agents for the preparation of hybrid gel. Lactone unit in gels **2b-CL**, **2c-CL**, and **2d-CL** obtained by Method B was lower than in **2a-CL** (Table I, Run 2, 7, 8, and 10).

The encapsulation of polymeric lactone **PCL-1** was examined by chlorosilanes **1**. As shown in Table II, trimethylchlorosilane **1a** as a cross-linking reagent enabled the effective preparation of hybrid gel **3a**. **PCL-1**

Table II. Preparation of polyester modified silica gel **3** from PTBS and polyester (PCL-1) with chlorosilane **1**

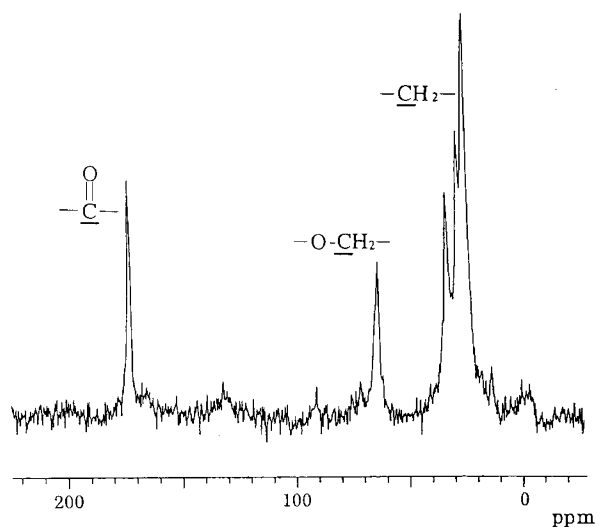
Reaction conditions			Polyester modified silica gel 3			
Run	Chlorosilane 1	Method ^a	Content of Si	Content of Sn	Lactone unit	Yield ^b (Product)
			mmol g ⁻¹	mmol g ⁻¹	mmol g ⁻¹	%
1	1a	A	9.40	0.33	3.06	85 (3a)
2	1a	B	6.16	0	4.68	77 (3a)
3	1b	A	12.30	0	1.04	70 (3b)
4	1b	B	7.95	0.33	4.70	68 (3b)
5	1d	A	11.77	0.16	0	74 (3d)
6	1d	B	4.08	0.13	4.84	65 (3d)

^a The reaction was conducted at room temperature for 10 h (Method A). The mixture was then refluxed for 3 h (Method B). ^b Yield was based on Si (see EXPERIMENTAL section).

**Figure 1.** IR spectra of polyester modified silica gel **2a-CL**.

was incorporated into gel **3** efficiently even by Method A. Lactone unit in **3a** prepared by Method A and B was 3.06 and 4.68 mmol g⁻¹, respectively (Table II, Run 1 and 2). Lactone unit in **3a** obtained by Method A was not so inferior to that by Method B. However, in using cross-linking reagents **1b** and **1d**, thought to make a loose silica matrix by the presence of alkyl groups, lactone unit in gel **3** was changed remarkably according to the method. The use of **1d** resulted in the formation of gel containing no lactone unit by Method A, although 4.84 mmol g⁻¹ of lactone unit was incorporated in **3d** by Method B (Table II, Run 5 and 6). Lactone unit in **3a** and **3b** obtained by Method B was almost the same as in **2a-CL** and **2b-CL**, obtained by one-pot synthesis using **1a** and **1b** (Table II, Run 2 and 3). Silica networks formed by the reactions of PTBS with **1a**, **1b**, or **1d** by Method B are thus sufficiently tight to encapsulate polyester. However, the gel formed by Method A, using **1b** or **1d**, seemed to possess spaces too wide to fix polyester.

The incorporation of polyester into gels **2** and **3** was confirmed by spectral data and elemental analysis. IR spectral data demonstrated the presence of polyester component in gel **2** and **3**, in which the absorption assigned to carbonyl group appeared from 1720 cm⁻¹ to 1740 cm⁻¹ and was observed as a broad peak in some cases. Absorption due to methylene and methyl groups was at ca. 2980 cm⁻¹. Strong and broad absorption at 1100 cm⁻¹ indicated the Si-O-Si unit. The IR spectrum

**Figure 2.** Solid-state ¹³C CP/MAS NMR spectrum of **2a-CL**.

of **2a-CL** is shown in Figure 1. The spectral data of solid-state CP/MAS NMR exhibited the efficient incorporation of polyester and provided information on the structure of gel **2**, although the measurement was made about only **2a-CL** (Table I, Run 2). In the ¹³C NMR (Figure 2), signals assigned to the carbon of methylene group of polyester unit were observed from 25.5 to 33.7 ppm. The signal of carbon attached to oxygen of ester group appeared at 64.1 ppm. The characteristic signal due to the carbon of ester carbonyl group was observed at 173.3 ppm. The signal of carbon of methyl group bonded to Si, attributed to the cross-linking silyl group, could not be seen clearly around 0 ppm. Silyl groups from **1a** thus appear low compared to the polyester component.

The presence of silyl groups in **2a-CL** was confirmed by the solid-state ²⁹Si NMR spectrum (Figure 3). In the spectrum, signals assigned to Si were found from -110 ppm to -101 ppm. The chemical shifts of the signals are in the same region as those reported as Q³ and Q⁴.^{17,18} Q² signals at -93.5 and -95.0 ppm observed in PTBS disappeared in the spectrum. This suggests that two stannyloxy groups bonded to one Si in PTBS are completely substituted to silyloxy groups. Two signals at -67.6 and -64.7 ppm were assigned to Si of methylsilyl group. The former signal seems to indicate the presence of T₃ units which form a tight

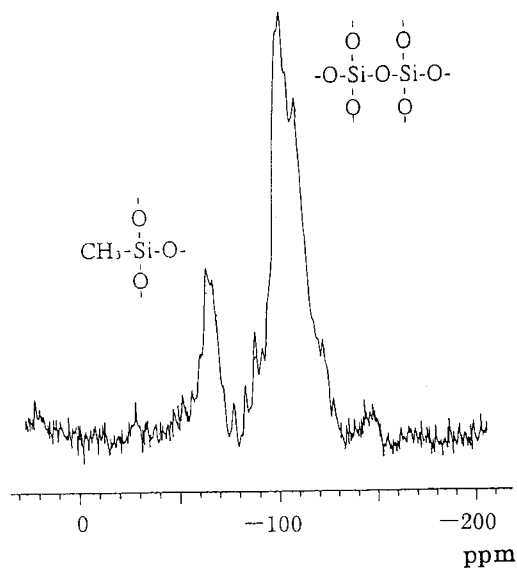


Figure 3. Solid-state ^{29}Si CP/MAS NMR spectrum of **2a-CL**.

inorganic network, *i.e.*, all bonds of methylsilyloxy group are connected to Si.^{19,20} The later signal appeared at higher magnetic field is regarded as that due to T_2 units. In this case, two bonds of methylsilyloxy group bind to Si of siloxane unit but the residual one may exist as Si–OH or end group of polyester. The later bond consisting of Si–O–C=O may be formed during refluxing in toluene solution through the reaction of Si–OH group with lactone components.

Hybrid gel consisting of silica and polyester was obtained from PTBS, chlorosilane **1**, and lactone. The effects of methyl and methylene spacers of **1** were clearly observed in the preparations of gels **2** and **3**. It was difficult to encapsulate monomeric compound effectively as shown when using **BL**. The size of molecule is thought too small for silica network obtained from PTBS and chlorosilane **1**. Method A at room temperature should lead to the formation of gels having loose inorganic networks and is inefficient for the formation of polyester modified gel. Polyester could be encapsulated in any combination of chlorosilane **1** with PTBS by Method B, which should enable the formation of a tight inorganic network. Monomeric lactone or oligomeric polyester may thus be captured in the network at first stage and polymerization may proceed inside and/or outside with shrinkage of the network. Therefore, in one-pot synthesis of gel as shown in Table I, **1a**, a small cross-linking reagent, is effective for the encapsulation, but the use of **1d** having hexamethylene spacer gave unsatisfactory

results. These speculations are supported by the following experimental results obtained from the gelation of PTBS with **1**, in which the average pore sizes of gels observed in Method B are generally smaller than those in Method A.⁶ The average pore sizes of gels obtained from PTBS with **1a**, **1b**, **1c**, or **1d** by Method A were 31, 46, 50, 45 Å. In Method B, they were 27, 32, 33, and 0 Å, respectively. In such encapsulation of polyester, the formation of covalent bonds of Si–O–C=O as an end group of polyester could not be excluded. However, the formation of bonds is not thought related to the efficiency of the encapsulation directly, since this would not lead to explanation for the difference of content of lactone units, which depends on the spacers of **1**.

Thus, the procedure using PTBS with polyhalosilane **1** is a new preparation of organic–inorganic hybrid gel, in which ionic ring-opening polymerization and formation of silica network proceed at the same time.

REFERENCES AND NOTES

1. T. Iida, T. Kageyama, T. Sugizaki, and O. Moriya, *Polym. J.*, **29**, 867 (1997).
2. T. Iida, T. Sugizaki, T. Kageyama, and O. Moriya, *J. Polym. Sci., Polym. Chem. Ed.*, **36**, 655 (1998).
3. T. Sugizaki, T. Kageyama, and O. Moriya, *J. Ceram. Soc. Jpn.*, **106**, 727 (1998).
4. T. Sugizaki, M. Oikawa, O. Moriya, and T. Kageyama, *J. Polym. Sci., Polym. Chem. Ed.*, **37**, 2363 (1999).
5. T. Sugizaki, O. Moriya, Y. Nakamura, T. Endo, M. Oikawa, and T. Kageyama, *Polym. J.*, **31**, 625 (1999).
6. Unpublished data.
7. J. F. Brown, Jr. and L. H. Vogt, Jr., *J. Am. Chem. Soc.*, **87**, 4313 (1965).
8. K. J. Shea, D. A. Loy, and O. Webster, *J. Am. Chem. Soc.*, **114**, 6700 (1992).
9. C. Zhang, F. Babonneau, C. Bonhomme, R. M. Laine, C. L. Soles, H. A. Hristov, and A. F. Yee, *J. Am. Chem. Soc.*, **120**, 8380 (1998).
10. C. Sanchez and F. Ribot, *New J. Chem.*, **18**, 1007 (1994).
11. B. M. Novak, *Adv. Mater.*, **5**, 422 (1993).
12. Ph. Espiard and A. Guyot, *Polymer*, **36**, 4391 (1995).
13. Y. Imai, K. Naka, and Y. Chujo, *Polym. J.*, **30**, 990 (1998).
14. B. M. Novak, M. W. Ellsworth, and C. Verrier, *Polym. Mater. Sci. Eng.*, **70**, 266 (1993).
15. M. W. Ellsworth and B. M. Novak, *J. Am. Chem. Soc.*, **113**, 2756 (1991).
16. H. K. Hall, Jr. and A. K. Schneider, *J. Am. Chem. Soc.*, **80**, 6409 (1956).
17. E. Lippmaa, M. Magi, A. Samoson, G. Engelhardt, and A. R. Grimmer, *J. Am. Chem. Soc.*, **102**, 4889 (1980).
18. H. A. Frank, J. D. Bolt, S. M. de B. Costa, and K. Sauer, *J. Am. Chem. Soc.*, **102**, 4893 (1980).
19. D. Derouet, S. Forgeard, J.-C. Brosse, J. Emery, and J.-Y. Buzare, *J. Polym. Sci., Polym. Chem. Ed.*, **36**, 437 (1998).
20. E.-C. Lee and Y. Kimura, *Polym. J.*, **30**, 730 (1998).