Synthesis of Mesoporous Silicate Gel from Tributylstannyl Ester of Polymeric Silicic Acid and Chlorosilane

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ABSTRACT : Tributylstannyl ester of polymeric silicic acid (PTBS) was used for the preparation of a mesoporous organic–inorganic hybrid gel. Reactions of PTBS and polyhalosilane 1 such as methyltrichlorosilane (1a), dichlorodimethylsilane (1b) or bis(chlorodimethylsilyl)alkanes, used as cross-linker, proceeded efficiently with elimination of tributylstannyl chloride to afford silylated gels containing the corresponding organic groups. Specific surface areas of obtained gels measured by BET method were from 510 $m^2 g^{-1}$ to 608 $m^2 g^{-1}$. Maximum pore volume of 0.377 mL g^{-1} and average pore size of 33 Å were recorded on the gel obtained from 1,2-bis(chlorodimethylsilyl)ethane (1c) and PTBS. Plots of pore size distribution of gels obtained from 1a, 1b, and 1c showed sharp single peaks in mesopore range, indicating pore size to be controlled by the steric effects of organic groups of 1. In using 1,6-bis(chlorodimethylsilyl)hexane (1d), the results of BET analysis indicated the formation of nonporous gel.
   KEY WORDS   Polysiloxane / Stannyl Ester of Silicic Acid / Chlorosilane / Mesoporous Gel / Hybrid Material /

Micro- and mesoporous silica gels have been investigated for physical properties and synthetic usages.[1-10] Recently, a new class of highly porous materials consisted of organic and inorganic networks has been presented, in which silsesquioxane derivatives are used as convenient and practical starting compounds.[11-15] One noteworthy characteristic of the procedures to form such silicate-like materials is easy control of morphology at the molecular level of design, i.e., steric effects of organic groups are reflected in specific surface areas and pore size of gels. Hydrosilylation to silsesquioxane derivatives, which can be performed in non-aqueous reaction system, is a sophisticated route to form such mesoporous gels.[16] This procedure is free from problems encountered in sol–gel process such as long reaction times, supercritical drying, and large number of residual hydroxyl groups. We have presented several works on synthetic applications of polymeric tributylstannyl ester of silicic acid (PTBS), proposed as an versatile intermediary compound for the preparation of organofunctionalized polysiloxanes and silica gels.[17-20] In previous investigations, reactions of PTBS and chlorosilanes were found to proceed readily with elimination of tributylstannyl chloride to afford polysiloxanes or silylated gels having organofunctional groups.

The reaction using polyhalosilanes was applicable to the formation of organically modified gels.[20] Such use of PTBS and polyhalosilanes can be carried out in non-aqueous medium under mild conditions. No condensation process for the formation of inorganic matrix is essentially required in the use of PTBS, since it consists of polymeric siloxane units. These characteristics should be favorable for the preparation of a new class of mesoporous hybrid gels mentioned above. The procedure using PTBS and polyhalosilanes was applied to synthesis of hybrid gels involving polyester and polysiloxane components.[21] Reactions of PTBS with polyhalosilanes were found to provide access to new micro- and mesoporous silycate-like materials. Therefore, we investigated the preparation of porous silycate gels, obtained from PTBS and chlorosilanes (1) having alkyl groups as shown in the Scheme.

EXPERIMENTAL

All reactions were carried out under argon atmosphere. Benzene for the reactions was refluxed over sodium metal and distilled. Gravimetric analysis was conducted as reported.[17] 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 G 2500H, G2000H, and G1000H, were connected in series and tetrahydrofuran (THF) was used 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 μs for ^{13}C NMR and 4 μs for ^{29}Si NMR measurement, in which polydimethylsilane was used as standard. Surface area and pore size distribution were measured by nitrogen sorption using the volume technique on a COULTER OMNI SORP 100 CX. Samples were degassed at 80°C, 3 μmHg for 30 min. be-
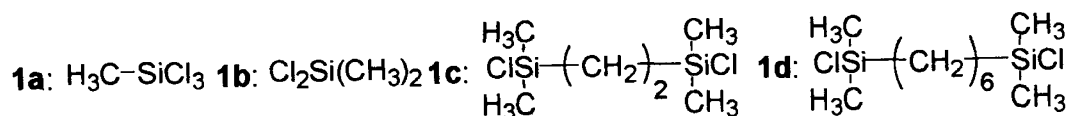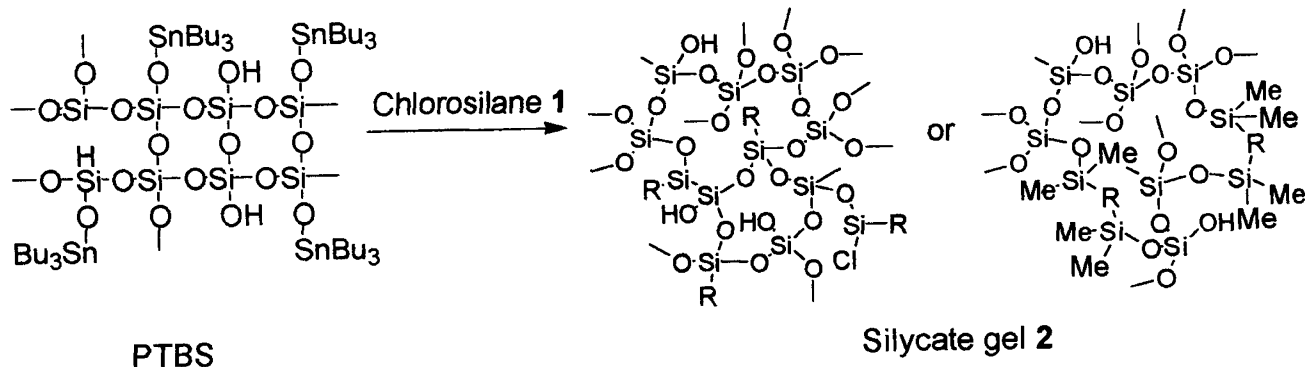
Scheme.

fore analysis. Scanning electron microscope (SEM) photographs were obtained using HITACHI S-2360 N coupled with HORIBA EMAX 2770 energy-dispersive X-ray spectrometer.

Preparation of PTBS

PTBS was prepared from bis(tributyltin)oxide [(Bu$_3$Sn)$_2$O] and water glass as reported before.[18] 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 2.10 mmol g^{-1} and 6.20 mmol g^{-1}, respectively.

Preparation of Silycate Gel (2)

Chlorosilane 1 was added to a solution of PTBS in toluene at room temperature under argon atmosphere. After stirring for 10 h, the mixture, jelly in appearance, was refluxed for 3 h. The precipitated gel was filtered and washed successively with benzene, diemethylformamide (DMF), methanol, water, acetone, and *n*-hexane. The obtained gel 2 was dried at 60°C for 24 h under reduced pressure such as 5 mmHg. 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%. The content of silyl units in 2 was estimated from elemental and gravimetric analysis, in which the number of carbons was assigned to the remaining tributyl group of tin and organic group of the silyl unit.

From PTBS (2.00 g, Si = 12.40 mmol, Sn = 4.20 mmol) and methyltrichlorosilane (1a) (0.21 g, 1.41 mmol), 2a (0.98 g) was obtained (Table I, Run 1): IR (KBr) 2960, 1640, 1260, 1080 cm^{-1}; ^{13}C CP/MAS NMR (67.8 MHz) δ −5.16; ^{29}Si CP/MAS NMR (53.5 MHz) δ −108.1, −100.5, −91.0, −63.7, −53.3, −44.4. *Anal*. Found: C, 6.09%; H, 1.47%.

From PTBS (2.00 g, Si = 12.40 mmol, Sn = 4.20 mmol) and dichlorodimethylsilane (1b) (0.28 g, 2.20 mmol), 2b

(1.07 g) was obtained (Table I, Run 2): IR (KBr) 3500, 3500, 2960, 1640, 1270, 1080 cm^{-1}; ^{13}C CP/M AS NMR (67.8 MHz) δ −0.63; ^{29}Si CP/MAS NMR (53.5 MHz) δ − 110.1, −101.8, −17.2. *Anal*. Found: C, 11.63%; H, 2.48%.

From PTBS (4.00 g, Si = 24.80 mmol, Sn = 8.40 mmol) and 1,2-bis(chlorodimethylsilyl)ethane (1c) (0.93 g, 4.32 mmol), 2c (1.96 g) was obtained (Table I, Run 3): IR (KBr) 3500, 2960, 1640, 1270, 1080 cm^{-1}; ^{13}C CP/MAS NMR (67.8 MHz) δ −1.15, 9.27; ^{29}Si CP/MAS NMR (53.5 MHz) δ −109.4, −100.4, −91.8, 8.2, 13.5. *Anal*. Found: C, 15.79%; H, 3.29%.

From PTBS (3.00 g, Si = 18.60 mmol, Sn = 6.30 mmol) and 1,6-bis(chlorodimethylsilyl)hexane (1d) (0.86 g, 3.20 mmol), 2d (1.78 g) was obtained (Table I, Run 4): IR (KBr) 3500, 2960, 1640, 1270, 1080 cm^{-1}; ^{13}C CP/MAS NMR (67.8 MHz) 0.58, 18.70, 23.76, 27.99, 33.80; ^{29}Si CP/MAS NMR (53.5 MHz) δ −109.4, −100.2, −91.4, 7.3, 13.3. *Anal*. Found: C, 23.21%; H, 4.81%.

RESULTS AND DISCUSSION

Replacement of tributyltin groups in PTBS by silyl groups under mild and neutral conditions has been reported in preceding works, which enables ready preparation of organofunctionalized polysiloxanes and silylated gels.[18,19] In these reactions, polyhalosilanes were effective cross-linking agents to afford silylated gels based on polysiloxane matrix. This procedure should afford porous gels, pore size of which is controlled by alkyl groups contained in polyhalosilanes. Reactions of PTBS and polyhalosilanes with lactones proceeded efficiently to give hybrid gels consisted of inorganic polysiloxane networks and organic polyester components.[21] The results of these experiments suggest that pore size and/or volume affect on the efficiency of encapsulation of polyesters. Accordingly, to obtain information on ability of the encapsulation, preparations of silycate gels 2 by several chlorosilanes 1 were carried out under similar conditions to those in the previous work.[21]

The reaction was carried out by mixing PTBS and 1 in

Table I. Preparation of silycate gel (**2**) from PTBS and chlorosilane (**1**)

Run	Clorosilane 1	Silycate gel 2						
		Content of Si[a] mmol g^{-1}	Content of Sn[a] mmol g^{-1}	Silyl unit[b] mmol g^{-1}	Yield[c] (Product) %	Surface area[d] m^2 g^{-1}	Total pore volumed[d] mL g^{-1}	Average pore diameter[e] Å
1	**1a**	13.4	0.2	2.67	95(**2a**)	510	0.257	27
2	**1b**	13.4	0.3	2.90	99(**2b**)	534	0.318	32
3	**1c**	14.4	0.3	1.64	85(**2c**)	608	0.377	33
4	**1d**	11.8	0.2	1.82	84(**2d**)	—	—	—

[a] Estimated by gravimetric analysis. [b] Estimated from data of elemental analysis. [c] Yield based on content of Si in **2** and PTBS. [d] Surface area and pore size distribution measured by nitrogen sorption and calculated using BET. [e] Calculated from data of total pore volume and surface area.

toluene under argon atmosphere at room temperature. A jelly-like mixture, formed after the reaction continued at room temperature, was successively refluxed in toluene for 3 h to make sure the gelation proceeded adequately. In the reaction using methyltrichlorosilane **1a**, ca. 0.3 equivalent of **1a** to Sn in starting PTBS was used. In other cases using dichlorodimethylsilane **1b**, 1,2-bis-(chlorodimethylsilyl)ethane **1c**, or 1,6-bis(chlorodimethylsilyl)hexane **1d**, 0.5 equivalent of the chlorosilane to Sn was added to a solution of PTBS. The results of reactions are listed in Table I and show silycate gels **2** were obtained in high yields. The use of tri- or di-chlorosilanes **1a** and **1b** led to the formation of gels **2a** and **2b** in almost quantitative yields, respectively (Table I, Run 1 and 2). However, bis-silylchlorides **1c** and **1d** having a methylene spacer gave the corresponding gels **2c** and **2d** in somewhat lower yields such as 85% and 84% (Table I, Run 3 and 4). These results seem reasonable, because the steric effects of methylene spacers of chlorosilanes **1c** and **1d** are thought to be an unfavorable factor for the substitution reaction of tributylstannyl moieties in polymeric silicic acid structure. Bis-silyl derivative, monochlorodialkylsilyl species, should not be so reactive as tri- and di-chlorosilyl ones. The effects of reactivity of **1** were shown presence of silyl units in **2**. The contents of silyl units in **2a** and **2b** were 2.67 mmol g^{-1} and 2.90 mmol g^{-1}, but those in **2c** and **2d** were less than 1.82 mmol g^{-1}.

The incorporation of silyl units into gels **2** was confirmed by spectral data and elemental analysis. IR spectral data demonstrated the presence of siloxane components in **2** by the strong and broad absorption appeared around 1100 cm^{-1} due to Si–O–Si bonds. Absorption assigned to methylene and methyl groups was clearly observed at ca. 2980 cm^{-1} in the spectra of **2c** and **2d**, but was very weak in these of **2a** and **2b**. Solid-state CP/MAS NMR spectra provided more definitive evidence of presence of silyl units in gels **2**. In the ^{13}C NMR of **2a**, signals assigned to carbon of methyl group of silyl unit was observed at −5.16 ppm. In **2b**, **2c**, and **2d**, the corresponding signals of methyl carbons appeared at −0.63, −1.15, and 0.59 ppm, respectively. Signals of carbons of methylene spacer in **2c** were detected at 9.27 ppm and these in **2d** were at 18.70, 23.76, 27.99, and 33.80 ppm. Thus, signals of carbons assigned to the cross-linking silyl groups could be seen clearly, indicating, essentially, no modification in organic fragments. As
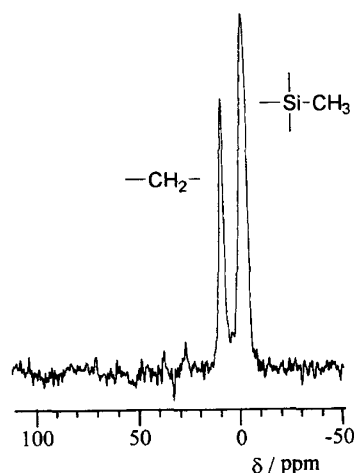
Figure 1. Solid-state ^{13}C CP/MAS NMR spectrum of **2c**.

a representative example, the ^{13}C NMR spectrum of **2c** is shown in Figure 1.

The presence of silyl groups in **2** was confirmed by solid-state ^{29}Si NMR spectra. In the spectrum of **2a** obtained from the trichlorosilane **1a**, the signal assigned to T structure was detected at −53.3 ppm with two shoulder peaks at −63.7 and −44.4 ppm. This suggests that the silyl unit from **1a** formed mainly bi-dendate T^2 structure, surrounded by two Si-O bonds. Accordingly, signals at −44.4 and −63.7 ppm seem assignable to Si surrounded by one Si–O (T^1) and three Si–O bonds (T^3), respectively. Such speculation was supported by reported data, in which methylltrichlorosilane was generally transformed into a bi-dendate structure.[22−24] In the spectrum of **2c**, a shoulder peak at 8.21 ppm was observed besides that at 13.5 ppm. Two signals appeared at 7.3 and 13.3 ppm in the spectrum of **2d** and were assigned to Si of the dimethylsilyl group. The presences of shoulder signals indicated two M structures for **2c** and **2d**.[22] Two chlrorosilyl groups in **1c** and **1d** are thus not consumed completely in the reaction with tributylstannyl groups of PTBS. Namely, some of **1c** and **1d** units are incorporated into the gels **2c** and **2d**, keeping one unreacted chlorosilyl group, which should be hydrolyzed to silanol groups by washing with water. Q structures incorporated from polysiloxane components of PTBS
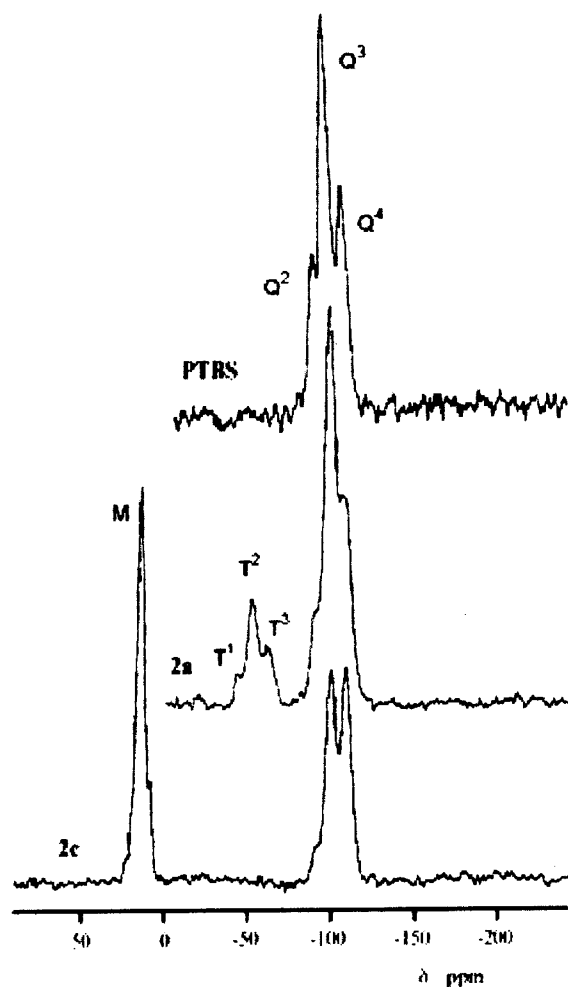
Figure 2. Solid-state ^{29}Si CP/MAS NMR spectra of PTBS, **2a**, and **2c**.

Figure 3. Differential pore distribution curve of **2c**.

were represented by signals appearing at -108.1, -100.5, and -91.0 ppm. These signals are thought assignable to Q^4, Q^3, and Q^2, respectively. The chemical shifts almost coincided with those observed in the spectrum of starting PTBS. However, the change of intensity of the signals due to Q^2 structure was smaller in the spectrum of **2a** compared to spectra of other gels **2b**, **2c**, and **2d**. Considering that the number of tributylstannyl groups contained in all gels **2** was small, polysiloxane components in **2a** seem to possess more silanol groups, formed after elimination of tributylstannyl groups without replacement by silyl groups. This is supported by the data of IR analysis of **2a**, in which the absorption around 3500 cm^{-1} due to hydroxyl group was stronger than for other gels. In ^{29}Si NMR spectra of **2b**, **2c**, and **2d**, remarkable decrease of intensity of signals assigned to Q^2 was observed in comparison with other signals at Q structure. Apparent increase of intensity of the signals at $ca. -109$ ppm was observed, suggesting that the Q^2 structures consisting of Si–O–Sn bonds in PTBS were changed to Q^3 and/or Q^4 structure by substitution of tributylstannyl groups to silyl groups. The spectra of PTBS, **2a**, and **2c** are shown in Figure 2.

Porosity of the obtained gels **2** was evaluated by nitrogen sorption porosimetry. Surface area, pore volume,
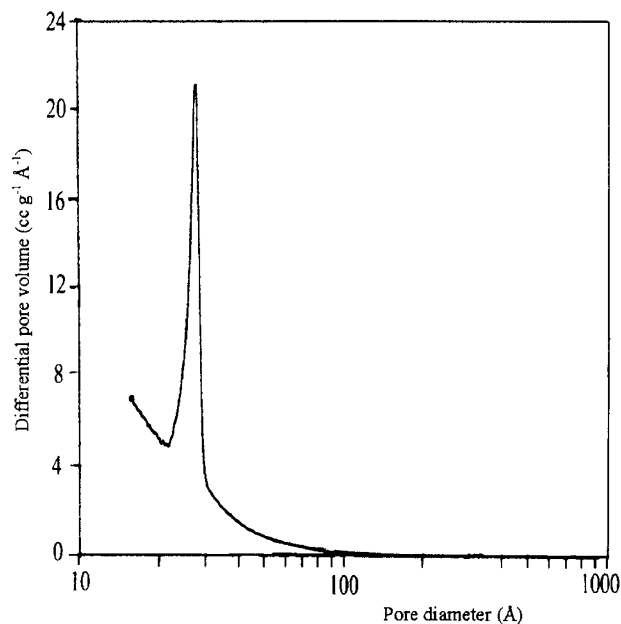
and average pore size are listed in Table I. Surface areas of gels **2a**–**c** obtained by BET method were varied from 510 m^2 g^{-1} to 608 m^2 g^{-1}. Steric effects of organic groups of cross-linkers **1a**–**c** were not found in the data of surface area and total pore volume. Increase of average pore diameters from 27 Å of **2a** to 33 Å of **2c** was observed, attributable to steric factors of organic groups in **1**. The use of **1a** should lead to the formation of **2a** involving only monomethyl substituent at silyl groups. With **1c**, dimethylsilyl groups with two methylene spacer were present in resulting gel **2c**. These observations support previous results of the preparation of polyester modified silica gels starting from ε-caprolactone, in which **1a** is shown the most effective cross-linker among the chlorosilanes **1** for encapsulation of polyester components.[21] This means that the inorganic matrix showing a smaller pore diameter appropriately traps monomeric cyclic esters or olygomeric ester species and polyesters are formed in the matrix, since in the encapsulation starting from polyesters, all cross-linkers **1a**–**c** were effective for the preparation of the hybrid gels. Accordingly, gels **2a**–**c** classified as mesoporous may have appropriate pore size for keeping polymers but monomeric cyclic lactones and the ring-opening polymerization should proceed in the pore formed by PTBS and chlorosilanes **1**.[25,26] Thus, the average pore diameter of **2a**–**c** should reflect the size of organic groups of cross-linkers **1a**–**c**. In gels **2a**–**c**, pore size was controlled well as demonstrated in the pore size distribution curves calculated by BJH.[27] As shown in Figure 3, a single peak at ca. 28 Å was observed for **2c**. The pore size distribution curves of **2a** and **2b** showed single sharp peaks at ca. 10 Å and 25 Å. The use of **1d** having the longest spacer among the chlorosilanes **1** using here led to the formation of nonporous gel **2d**. In measurement of porosity of **2d**, nitrogen sorption using the volume technique was not applicable, as was also observed on gels as bridged polysilsesquioxanes. In a reported work, collapse of porosity occurred when the

methylene spacer was longer than pentamethylene groups.[13] Although the starting materials and procedure were different from ours, the use of **1d** having hexamethylene groups resulted in the formation of analogous nonporous gels.

SEM photographs showed interesting images of porous gel **2** obtained by several different chlorosilanes **1**. **2b** and **2c** essentially consisted of brick-like masses, over 10 μm in length. In the case of **2a**, smaller masses are noted possibly due to porosities of **2a—c**, in which mesopores are built up. The structure of PTBS may contribute to formation of mesopores, but micropores. PTBS was a protected polysiloxanes and the ratio of Si to Sn was ca. 3. PTBS was thus speculated to consist of ladder or plate like structures. Accordingly, the bridged products by bi- or tri-dentate silyl groups might be in layers. Such additional effects caused by the structure of PTBS besides theses of organic groups of silyl cross-linkers may lead to the formation of mesopores. Contrary to these images of **2a—c**, **2d** was formed from aggregates of particles. This is thought compatible with the unsuccessful measurement of nitrogen sorption of gel. A longer methylene spacer of **1d** may block the assembly of polysiloxane components leading to the formation of brick-like masses. The formation of gel proceeded under hydrophobic conditions. This seems to bring methylene spacer to the surface of gel, which is unfavorable for the assembly of inorganic components and sorption of nitrogen in BET method. As representative examples, SEM images of **2b** and **2d** are shown in Figure 4.

CONCLUSION

In the preparation of mesoporous gels **2** from PTBS and chlorosilanes **1** through metal exchange reaction from tributylstannyl groups to silyl groups, the effects of methyl groups and methylene spacers of **1** were clearly observed. Steric factors of methyl and methylene groups of **1** were not reflected in surface areas of **2**, but in average pore diameter. The use of cross-linkers **1a—c** made possible good control of pore diameter, as demonstrated as a sharp peak in pore size distribution curves. The use of **1d** having the longest hexamethylene spacer among **1**, expected to form typically mesoporous gel, resulted in the formation of gel **2d** showing no porosity. Such characteristics were reflected in SEM images, in which differences of shapes from brick-like masses of **2c** to small particles of **2d** were observed. Chlorosilanes involving rigid organic groups such as aromatic or carbon–carbon unsaturated spacer, but a long methylene spacer, may thus be useful for preparation of mesoporous gels from PTBS. Further evaluation of silicate gels **2** such as absorption abilities to a variety of organic compounds is being made.
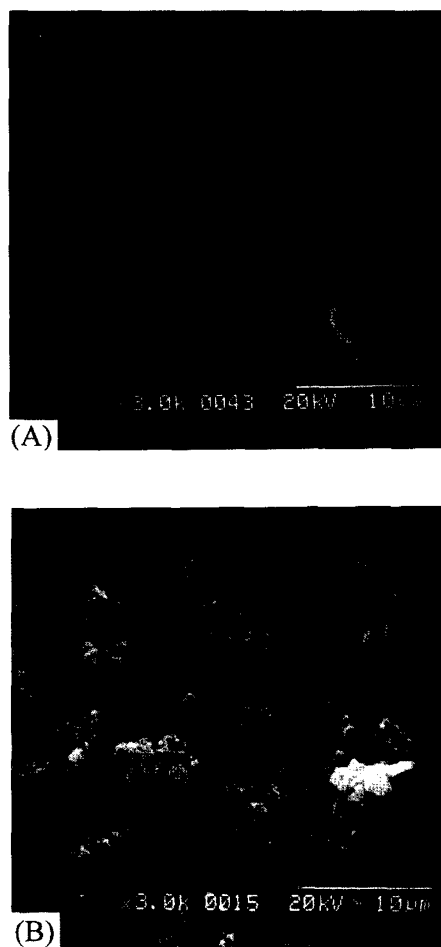

Figure 4. SEM images of 2c(A) and 2d(B).

REFERENCES

1. Y. Tsuruta and K. Wada, *Bull. Chem. Soc. Jpn.*, **70**, 283 (1997).
2. T. Lopez, M. Moran, J. Navarrete, L. Herrera, and R. Gomez, *J. Non-Crys. Solid*, **147 & 148**, 753 (1992).
3. T. Lopez, P. Bosch, J. Naverrete, M. Asomoza, and R. Gomez, *J. Sol-Gel Sci. Technol.*, **1**, 193 (1994).
4. H. W. Oviatt, K. J. Shea, S. Kalluri, Y. Shi, and W. H. Steier, *Chem. Mater.*, **7**, 493 (1995).
5. G.-H. Hsuie, R.-H. Lee, and R.-J. Jeng, *Chem. Mater.*, **9**, 883 (1997).
6. J. W. Aylott, D. J. Richardson, and D. A. Russell, *Analyst*, **122**, 77 (1997).
7. S.-K. Lee and I. Okui, *Analyst*, **122**, 81 (1997).
8. S. Dire, E. Pagani, F. Babonneau, R. Ceccato, and G. J. Carturan, *J. Mater. Chem.*, **7** (1), 67 (1997).
9. T. Okui, Y. Saito, T. Okubo, and M. Sadakata, *J. Sol-Gel Sci. Technol.*, **5**, 127 (1995).
10. A. J. E. Pope, S. Sakka, and L. C. Klein, Ed., "Sol–Gel Science

and Technology", American Chemical Society, Washington, D.C., 1997.

11. K. J. Shea, D. A. Loy, and O. Webster, *J. Am. Chem. Soc.*, **114**, 6700 (1992).

12. C. Sanchez and F. Ribot, *New J. Chem.*, **18**, 1007 (1994).

13. D. A. Loy and K. J. Shea, *Chem. Rev.*, **95**, 1431 (1995).

14. K. M. Choi and K. J. Shea, *J. Am. Chem. Soc.*, **116**, 9052 (1994).

15. G. C. Cerveau, R. J. Corriu, C. Lepeytre, and P. H. Mutin, *J. Mater. Chem.*, **8**, 2707 (1998).

16. 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).

17. T. Iida, T. Kageyama, T. Sugizaki, and O. Moriya, *Polym. J.*, **29**, 867 (1997).

18. T. Iida, T. Sugizaki, T. Kageyama, and O. Moriya, *J. Polym. Sci., Polym. Chem. Ed.*, **36**, 655 (1998).

19. T. Sugizaki, M. Oikawa, O. Moriya, and T. Kageyama, *J. Polym. Sci., Polym. Chem. Ed.*, **37**, 2363 (1999).

20. T. Sugizaki, O. Moriya, Y. Nakamura, T. Endo, M. Oikawa, and T. Kageyama, *Polym. J.*, **31**, 625 (1999).

21. O. Moriya, A. Matsui, M. Oikawa, T. Sugizaki, Y. Nakamura, T. Endo, and T. Kageyama, *Polym. J.*, **32**, 82 (2000).

22. D. Derouet, S. Forgeard, J-C, Brosse, J. Emery, and J-Y. Buzare, *J. Polym. Sci., Polym. Chem. Ed.*, **36**, 437 (1998).

23. A. Gerli, M. Sabat, and L. G. Marzilli, *J. Am. Chem. Soc.*, **114**, 6711 (1992).

24. E. Lippmaa, M. Magi, A. Samoson, G. Engelhardt, and A. R. Grimmer, *J. Am. Chem. Soc.*, **102**, 4889 (1980).

25. C.-G. Wu and T. Bein, *Science*, **264**, 1757 (1994).

26. K. Moller, T. Bein, and R.-X. Fischer, *Chem. Mater.*, **10**, 1841 (1998).

27. E. P. Barrett, L. G. Joyner, and P. P. Halender, *J. Am. Chem. Soc.*, **73**, 373 (1951).