APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. **13**, 495–499 (1999)

An Anhydrous Sol–Gel System Derived from Methyldichlorosilane

Dong Seok Kim,[1] Edwin Kroke,[2] Ralf Riedel,[2] Andreas O. Gabriel[2] and Sang Chul Shim[1]*

[1]Department of Chemistry, Korea Advanced Institute of Science and Technology, 373-1 Kusung-Dong, Yusung-Gu, Taejon 305–701, Korea
[2]Fachgebiet Disperse Feststoffe, Fachbereich Materialwissenschaft, Technische Universität Darmstadt, Petersenstrasse 23, D-64287 Darmstadt, Germany

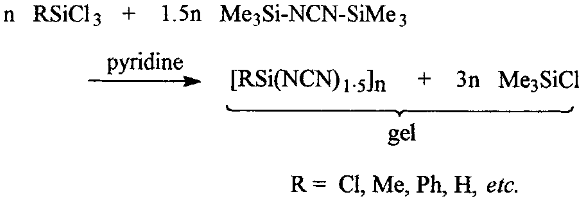
Pyridine-catalyzed reactions of methyldichlorosilane with bis(trimethylsilyl)carbodiimide afford a dichlorosilane-derived anhydrous sol–gel material. Both trimethylchlorosilane formation and Si–H disproportionation act as crosslinking mechanisms. The dried gels form amorphous or crystalline materials, depending on the sample history. The xerogels gave Si/C/N ceramics when pyrolyzed at 1200 °C. Copyright © 1999 John Wiley & Sons, Ltd.

Keywords: methyldichlorosilane; bis(trimethylsilyl)carbodiimide; disproportionation; sol–gel; pyrolysis; ceramic; material

Received 17 July 1998; accepted 6 October 1998

INTRODUCTION

In the last few decades, considerable progress has been made in understanding and developing oxidic sol–gel processes.[1,2] Due to their many advantages, such as product homogeneity, easy processing, and diversity of the compositions available, several applications have been developed.[1] Most of the research in this field, however, has been based on hydrolytic sol–gel routes and few papers on nonhydrolytic[3,4] methods have been reported. Some approaches to oxygen-free sol–gel systems based on thiolysis, aminolysis and related reactions have been published.[5] Riedel *et al.* reported sol–gel systems derived from methyltrichlorosilane,[6] tetrachlorosilane[7] and several other trichlorosilanes[8] (Eqn [1])



$$n\ \mathrm{RSiCl_3} + 1.5n\ \mathrm{Me_3Si\text{-}NCN\text{-}SiMe_3} \xrightarrow{\text{pyridine}} \underbrace{[\mathrm{RSi(NCN)_{1.5}}]_n + 3n\ \mathrm{Me_3SiCl}}_{\text{gel}}$$

$$\mathrm{R} = \mathrm{Cl, Me, Ph, H,}\ etc.$$

[1]

At least trifunctionality is required to form a three-dimensionally crosslinked polymeric gel network. Dichlorosilanes, therefore, are not suitable for the preparation of polymeric gels. We report in this paper that methyldichlorosilane, $\mathrm{MeHSiCl_2}$, can react with bis(trimethylsilyl)carbodiimide to give an anhydrous sol–gel system.

EXPERIMENTAL

All the reactions were carried out in dried glass vessels, in an anhydrous stream of argon. ^{1}H (300 MHz), ^{13}C (75.4 MHz) and ^{29}Si (59.6 MHz) NMR spectra were recorded using pyridine-d_5 solvent on a Bruker AM-300 spectrometer at room temperature. Solid-state ^{29}Si NMR spectra were recorded by the same instrument using the cross-

---

* Correspondence to: Sang Chul Shim, Department of Chemistry, Korea Advanced Institute of Science and Technology, 373-1 Kusung-Dong, Yusung-Gu, Taejon 305–701, Korea.
E-mail: scshim@sorak.kaist.ac.kr

Contract/grant sponsor: Organic Chemistry Research Center—Korea Science and Engineering Foundation.
Contract/grant sponsor: Deutsche Forschungsgemeinschaft, Bonn.
Contract/grant sponsor: Fonds der Chemischen Industrie, Frankfurt.
Contract/grant sponsor: Bayer AG, Leverkusen.

CCC 0268–2605/99/070495–05 $17.50

polarization/magic angle spinning technique with a rotational frequency of 4 kHz, a contact time of 3 ms and a delay time of 3 s. 2D (^{1}H–^{1}H COSY) NMR spectra were recorded on a Bruker AMX 500 spectrometer. X-ray diffractograms were measured by a Rigaku D/MAX-RC 12 kW X-ray diffractometer using Ni-filtered Cu K_α radiation at a scan speed of 4° min^{-1}.

Synthesis of $MeHSiCl_2$-derived gels

Bis(trimethylsilyl)carbodiimide[6] (1.86 g, 10 mmol) was mixed with methyldichlorosilane (1.15 g, 10 mmol) under an argon flow. Pyridine (3.16 g, 40 mmol) was added and the mixture was kept at 45 °C. Solution NMR spectra were taken after a reaction time of 24 h, when the mixture was transparent. ^{1}H NMR: $\delta = 5.21$ (q, $J = 2.2$ Hz, 1.0H), 5.01 (q, $J = 3.1$ Hz, 1.6H), 4.85 (q, 1.4H, 0.61 (t, $J = 3.0$ Hz, 4.2H), 0.56 (d, 2.2H), 0.41 (s, 68H, $(CH_3)_3SiCl$), 0.35 (4.2H), 0.21 (s, 6.3H, $(CH_{33}SiN{=}C{=}N$—), 0.19, 0.18 ppm; ^{29}Si NMR $\delta = 29.22$ (Me_3SiCl), 5.67, 1.13, $-0.31 \sim 2.11$ ($Me_3SiN{=}C{=}N$—, −20.31, −23.42, −38.19, −43.26, −61.52, −62.46, −65.94 ppm. The transparent mixture slowly turned white. Gelatin was detected after 360 h. The gel was further aged at 45 °C for one month. After completion of the aging process, volatile materials were removed by vacuum to obtain a stable xerogel (PMSC-A). ^{29}Si CP/MAS NMR: $\delta = 1.27$, −42.17, −62.16 ppm. Elemental analysis of the xerogel: C, 29.6; N, 38.6; O, 0.51; Si, 27.4%; xerogel pyrolyzed at 1200 °C in Ar: C, 17.8; N, 29.4; O, 0.38; Si, 41.4%.

RESULTS AND DISCUSSION

The pyridine-catalyzed reaction of stoichiometric amounts of methyldichlorosilane with bis(trimethylsilyl)carbodiimide at 45 °C produced a transparent gel (Eqn [2]) through a process similar to that of the methyltrichlorosilane system.[6]

$$MeSiHCl_2 + Me_3Si\text{-}NCN\text{-}SiMe_3 \xrightarrow[45\ ^oC]{pyridine} gel\ (\text{"PMSC"}) \qquad [2]$$

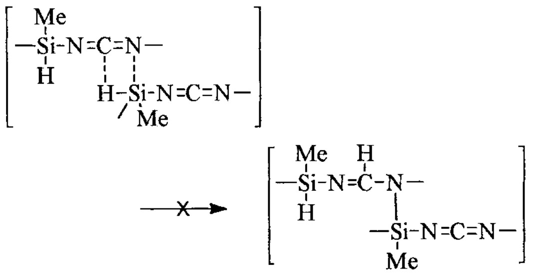
Honey-like high viscosity was observed for a considerable period of time (one to several days) near the gelation point, depending on the experimental conditions. Gelation time and viscosity increase more slowly than those of methyltrichlorosilane system under the similar conditions. As shown in Table 1, the gelation time depends on the pyridine concentration and the reaction temperature. High pyridine content and high reaction temperature accelerated the gelation processes. The long gelation time observed for sample no. 5 Table 1 was due to a large sample volume. The influence of shape and size of the reaction vessels on the gelation process has also been reported for oxidic sol–gel systems.[1]

Table 1 Gelation time of PMSC derived from methyldichlorosilane and bis(trimethylsilyl)carbodiimide

Sample no.	Pyridine content[a]	Temperature (°C)	Gelation time (h)
1	1	45	1320
2	2	45	360
3	4	45	185
4	1	66	213
5	2	66	720
6	4	66	408

[a] Molar equivalent to $MeSiHCl_2$.

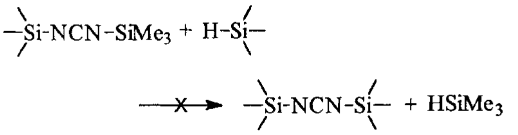
Extensive NMR spectroscopic investigations such as ^{1}H, ^{1}H–^{1}H COSY, ^{13}C and ^{29}Si NMR in pyridine-d_5 solvent were carried out to give an insight into the understanding of crosslinking mechanisms. Kienzle[9] reported that the crosslinking reaction of $MeHSiCl_2$ is due to the hydrosilylation between Si—H and carbodiimide groups as shown in Eqn [3].



[3]

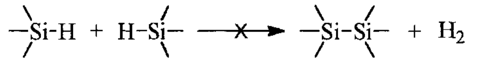
No evidence was found favoring this mechanism in our studies. No vinyl proton was detectable in any NMR experiment.[10] Three different peaks at

5.21, 5.00, and 4.85 ppm arising from Si—H groups were observed in the ^{1}H NMR spectrum and they were assigned to —N=C=N—SiHMeCl, —N=C=N—SiH$_2$Me, and —(N=C=N)$_2$SiHMe by the ^{1}H–^{1}H COSY technique. MeSi(NCN)$_3$ sites[5] were detected at −61 and −62 ppm in the ^{29}Si NMR spectrum of PMSC at the intermediate stage of the sol–gel conversion. These structures assigned by the ^{1}H NMR spectral studies were verified by the ^{29}Si NMR investigations. Formation of trimethylsilane was postulated as a possible crosslinking mechanism, but no evidence supported this hypothesis (Eqn [4]). NMR spectra of trimethylsilane in pyridine-d$_5$ solvent did not match that of poly(methylsilylcarbodiimide)(PMSC) taken during the sol–gel conversion; see also ref. 11



[4]

Crosslinking of MeHSiCl$_2$-derived polymers is also possible by dehydrocoupling of Si–H units as shown in Eqn [5], since this kind of Si–Si bond formation is known to occur catalytically.[12] However, neither significant amounts of hydrogen nor Si–Si bonds were detected in this gel system.



[5]

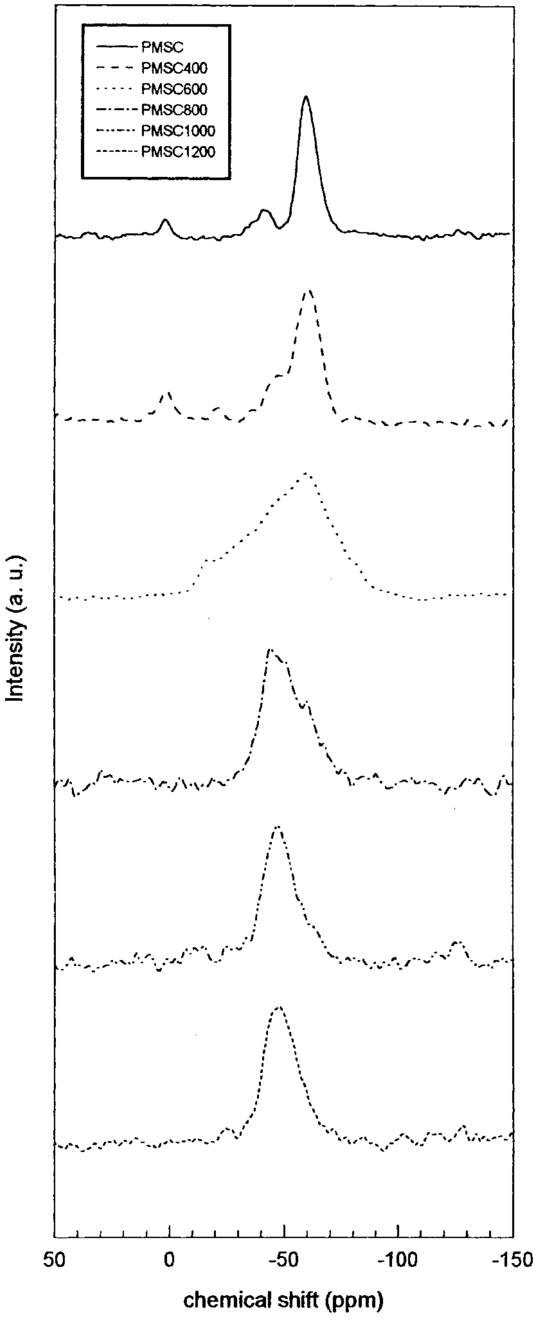
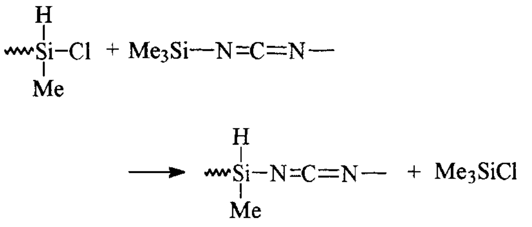
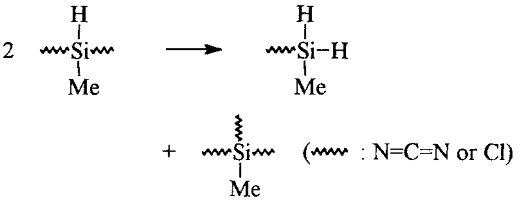


Figure 1 Solid-state ^{29}Si CP/MAS NMR spectra of pyrolyzed PMSC samples. The number after PMSC in the key denotes the pyrolysis temperature.

A plausible alternative route of crosslinking is pyridine-catalyzed disproportionation of difunctional silanes to give mono- and tri-functional silanes.[13] We have now found a similar disproportionation for carbodiimide-substituted silanes resulting in the formation of a crosslinked polymeric gel; Similar results were found independently by J. Schuhmacher, M. Weinmann, J. Bill, F. Aldinger and K. Müller, paper submitted to *Chem. Mater*. This behavior was proved by NMR examination of the reaction mixtures (*vide supra*) combined with a comparison of the reaction behavior of methyldichlorosilane with pyridine in the absence of bis(trimethylsilyl)carbodiimide: a mixture of methyldichlorosilane, methylchlorosilane and methyltrichlorosilane in a ratio of 1:0.3:0.3 was obtained after six days at room temperature by pyridine-catalyzed disproportionation of methyldichlorosilane. The reaction is accelerated with increasing temperature. Therefore, the sol–gel formation of PMSC can be described by Eqns [6] and [7].



$$\sim\!\underset{\mathrm{Me}}{\overset{\mathrm{H}}{\mathrm{Si}}}\!-\mathrm{Cl} + \mathrm{Me_3Si{-}N{=}C{=}N{-}} \longrightarrow \sim\!\underset{\mathrm{Me}}{\overset{\mathrm{H}}{\mathrm{Si}}}\!-\mathrm{N{=}C{=}N{-}} + \mathrm{Me_3SiCl} \qquad [6]$$



$$2\ \sim\!\underset{\mathrm{Me}}{\overset{\mathrm{H}}{\mathrm{Si}}}\!\sim \longrightarrow \sim\!\underset{\mathrm{Me}}{\overset{\mathrm{H}}{\mathrm{Si}}}\!-\mathrm{H} + \sim\!\underset{\mathrm{Me}}{\overset{\wr}{\mathrm{Si}}}\!\sim \quad (\sim : \mathrm{N{=}C{=}N\ or\ Cl}) \qquad [7]$$

Completely aged PMSC gel was dried and pyrolyzed under argon flow at temperatures up to 1200 °C at a heating rate of 4 °C $\mathrm{min^{-1}}$ to prepare Si/C/N ceramics and to investigate the accompanying structural changes. The changes in these PMSC samples were followed by solid-state 29Si CP/MAS NMR (Fig. 1).

Three distinct peaks were clearly detected in the solid-state spectrum of the PMSC sample, whose profile was very similar to that obtained in solution. The peak with the strongest intensity, at −61.5 ppm, is attributed to silicon atoms bonded to three carbodiimide groups. This is in accord with the chemical shift of poly(methylsilysesquicarbodiimide) derived from methyltrichlorosilane and bis(trimethylsilyl)carbodiimide.[6] The peak at −42.2 ppm stems from MeSiH units linked to two carbodiimide groups,[9] while that at 1.3 ppm results from trimethylsilyl end-groups.[14] At 400 °C, a shoulder appeared on the low-field side of the main peak (Fig. 1), suggesting that Si—H-containing environments are being replaced by an Si–N linkage in this temperature range. A very broad peak was observed after annealing at 600 °C, indicating an extensive structural rearrangement. Further increases in the annealing temperature to 800, 1000 and 1200 °C resulted in a single peak at −48.9 ppm (Fig. 1). This chemical shift value coincides with that of β-Si_3N_4 ($\delta = -48.7$ ppm)[7] and corresponds to silicon atoms coordinated by four sp^3-hybridized nitrogen atoms.

The elemental composition [C, H, O, N, Si analysis: Korea Basic Science Institute Seoul Branch, Seoul (Korea) and Mikroanalytisches Labor Pascher, Remagen-Bandorf (Germany)] of as-prepared and dried PMSC was found to be $SiC_{2.52}N_{2.82}H_{3.98}$. This is different from the hypothetical composition of $[MeSiH(N{=}C{=}N)]_n$ and is close to that of $[MeSi(N{=}C{=}N)_{1.5}]_n$ derived from methyltrichlorosilane. A chemical composition of $SiC_{1.01}N_{1.42}O_{0.02}$ was determined after the heat treatment in argon at 1200 °C. Thus, pure silicon carbide will be formed upon crystallization

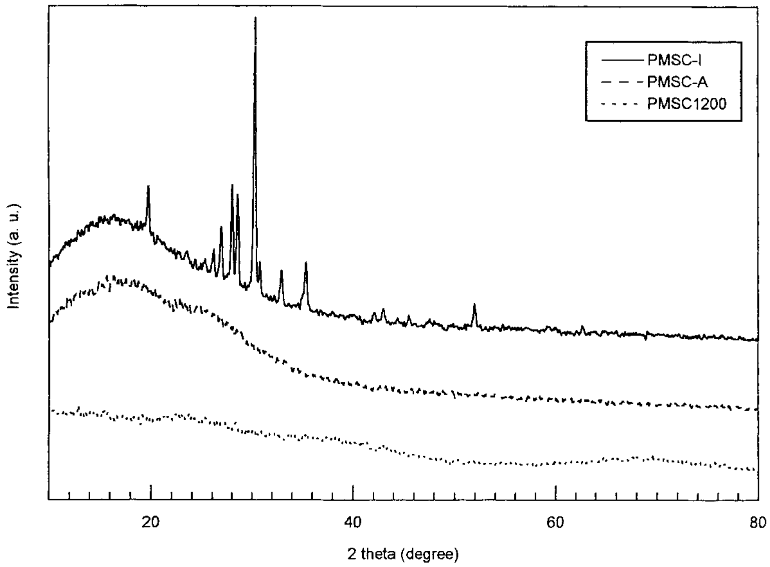


Figure 2 X-ray powder diffraction patterns of PMSC samples.

at 1600 °C in an inert atmosphere, as has been shown previously.[15]

The PMSC xerogel was investigated by X-ray powder diffraction and the results are shown in Fig. 2.

The aged PMSC sample (PMSC-A) was amorphous to X-rays, while an as-synthesized sample (PMSC-I), dried thoroughly in vacuum before the complete aging, showed a distinct XRD pattern. No crystalline phase was found after pyrolysis at 1200 °C, due to the crosslinking behavior described above. Accordingly, the molecular polymeric structures change from crystalline linear polymers to branched amorphous networks.

In conclusion, a novel sol–gel system based on dichlorosilane has been found, the product of which is very similar to the recently discovered carbodiimide gels derived from trifunctional silanes. In a substitution (or carbodiimidolysis)/condensation reaction sequence, oxygen-free gels are formed. Crosslinking is caused by a disproportionation mechanism of the difunctional silane. The gelation behavior depends strongly on temperature and amount of catalyst (pyridine). A crystalline polymeric phase is obtained if the volatile components are removed before the gelation is complete. Aged xerogels are amorphous. Heat treatment of PMSC at 1200 °C provides a Si/C/N ceramic containing amorphous Si_3N_4 and carbon. The molar carbon content of this material is exactly equivalent to the amount of silicon, which makes it an ideal precusor for pure silicon carbide.

Acknowledgements Financial support from the Organic Chemistry Research Center—Korea Science and Engineering Foundation, the Deutsche Forschungsgemeinschaft, Bonn (Germany), the Fonds der Chemischen Industrie, Frankfurt (Germany), and Bayer AG, Leverkusen (Germany) is gratefully acknowledged.

REFERENCES

1. C. J. Brinker and G. W. Scherer, *Sol–Gel Science*, Academic Press, San Diego, CA, 1990.
2. L. L. Hench and J. K. West *Chem. Rev.* **90**, 33 (1990).
3. P. Arnal, R. J. P. Corriu, D. Leclercq, P. Hubert Mutin and A. Vioux, *Chem. Mater.* **9**, 694 (1997).
4. M. Andrianainarivelo, R. J. P. Corriu, D. Leclercq, P. Hubert Mutin and A. Vioux, *Chem. Mater.* **9**, 1098 (1997).
5. E. Kroke, *Proc. 9th CIMTEC—World Ceramics Congress and Forum on New Materials Florence, Italy, June 14–19 1998*, Vincenzini, P. (ed.), in press.
6. (a) A. O. Gabriel and R. Riedel, *Angew. Chem., Int. Ed. Engl.* **36**, 384 (1997); (b) A. O. Gabriel, R. Riedel, S. Storck and W. F. Maier, *Appl. Organomet. Chem.* **11**, 833 (1997).
7. R. Riedel, A. Greiner, G. Miehe, W. Dressler, H. Fuess, J. Bill and F. Aldinger, *Angew. Chem., Int. Ed. Engl.* **36**, 603 (1997).
8. E. Kroke, A. O. Gabriel, D. S. Kim and R. Riedel, in: *From Molecules to Materials*, Auner, N. and Weis, J. (eds), *Organosilicon Chemistry*, VCH, Weinheim, in press 1999.
9. A. Kienzle, Ph. D. Thesis, University of Stuttgart, 1994.
10. I. Ojima and S.-I. Inaba, *J. Organomet. Chem.* **140**, 97 (1977).
11. R. K. Harris and B. J. Kimber, *J. Magn. Reson.* **17**, 174 (1975).
12. (a) J. F. Harrod and E. Samuel, *J. Am. Chem. Soc.* **106**, 1859 (1984); (b) J. F. Harrod, C. T. Aitken and E. Samuel, *J. Organomet. Chem.* **279**, C11 (1985).
13. H. J. Campbell-Ferguson and E. A. V. Ebsworth, *J. Chem. Soc. (A)* 1508 (1966).
14. H. C. Marsmann, *Chem.-Zeit* **96**, 288 (1972).
15. A. O. Gabriel, Ph.D. Thesis, Darmstadt University of Technology, 1998.