

- Comput. Physics. Comm.*, **9**, 31 (1975).
6. (a) Y. S. Lee and A. D. McLean, *J. Chem. Phys.*, **76**, 735 (1982); (b) A. D. McLean and Y. S. Lee, 'Current Aspects of Quantum Chemistry 1991', *Studies Phys. Theor. Chem.*, **2**, 219 (1982).
 7. P. A. Christiansen, W. C. Ermler, and K. S. Pitzer, *Ann. Rev. Phys. Chem.*, **36**, 407 (1985).
 8. (a) J. P. Desclaux and P. Pyykko, *Chem. Phys. Lett.*, **29**, 534 (1974); **39**, 300 (1976); (b) P. Pyykko and J. P. Desclaux, *Nature (London)*, **266**, 336 (1977).
 9. (a) J. G. Snijders, E. J. Baerenda, *Mol. Phys.*, **36**, 1789 (1978); (b) J. G. Snijders, E. J. Baerends, and P. Ros, *Mol. Phys.*, **38**, 1909 (1979).
 10. C. Y. Yang and S. Rabii, *Phys. Rev. A.*, **12**, 362 (1975).
 11. A. Rosen and D. E. Ellis, *J. Chem. Phys.*, **62**, 3039 (1975).
 12. Y. Ishikawa, R. C. Binning, Jr., and K. M. Sando, *Chem. Phys. Lett.*, **101**, 111 (1982).
 13. J. Wood, I. P. Grant, and S. Wilson, *J. Phys. B.*, **18**, 3027 (1985); *ibid.*, **17**, 493 (1984); *ibid.*, **17**, 245 (1984); *ibid.*, **17**, 201 (1984).
 14. W. Kutzelnig, *Int. J. Quant. Chem.*, **25**, 107 (1984).
 15. R. E. Stanton and S. Havriliak, *J. Chem. Phys.*, **81**, 1910 (1984).
 16. S. P. Goldman, *Phys. Rev. A.*, **31**, 3541 (1985).
 17. K. G. Dyall, P. R. Taylor, K. Faegri, Jr., and H. Partridge, *J. Chem. Phys.*, **95**, 2583 (1991).
 18. S. N. Datta and C. S. Ewig, *Chem. Phys. Lett.*, **85**, 443 (1982).
 19. G. Malli and J. Oreg, *Chem. Phys. Lett.*, **69**, 313 (1980).
 20. (a) O. Matsuoka and S. Huzinaga, *Chem. Phys. Lett.*, **140**, 567 (1987); (b) S. Okada and O. Matsuoka, *J. Chem. Phys.*, **91**, 4193 (1989); (c) S. Okada, M. Shinada, and O. Matsuoka, *J. Chem. Phys.*, **93**, 5013 (1990).
 21. Y. K. Kim, *Phys. Rev.*, **154**, 17 (1967).
 22. G. Malli and J. Oreg, *J. Chem. Phys.*, **63**, 830 (1975).
 23. O. Matsuoka, N. Suzuki, T. Aoyama, and G. Malli, *J. Chem. Phys.*, **73**, 1320 (1980).
 24. K. K. Baeck and Y. S. Lee, *Chem. Phys. Lett.*, **147**, 367 (1988).
 25. Y. S. Lee, W. C. Ermler, and K. S. Pitzer, *J. Chem. Phys.*, **73**, 360 (1980).
 26. J. Oreg and G. Malli, *J. Chem. Phys.*, **61**, 4349 (1974); *ibid.*, **65**, 1746 (1976); *ibid.*, **65**, 1755 (1976).
 27. R. E. Powell, *J. Chem. Ed.*, **45**, 558 (1968).
 28. H. A. Bethe and E. E. Salpeter, 'Quantum Mechanics of One- and Two-electron Atoms', Springer-Verlag, Berlin (1957).
 29. R. E. Moss, 'Advanced Molecular Quantum Mechanics', Chapman and Hall (1973).
 30. I. P. Grant, *Phys. Rev. A.*, **25**, 1230 (1982).
 31. (a) Y. S. Lee, K. K. Baeck, and A. D. McLean, *J. Comp. Chem.*, **7**, 112 (1989); (b) C. K. Park, Master Thesis at Kaist (1991).
 32. F. Mark and F. Rosicky, *Chem. Phys. Lett.*, **74**, 562 (1980).
 33. W. H. E. Schwarz and H. Wallmeier, *Mol. Phys.*, **46**, 1045 (1982).
 34. GAUSSIAN82.
 35. O. Matsuoka, *Chem. Phys. Lett.*, **155**, 544 (1987).
 36. K. G. Dyall and K. Faegri Jr., *Chem. Phys. Lett.*, **174**, 25 (1990).
 37. Y. S. Lee and K. K. Baeck, *Bull. Korean Chem. Soc.*, **7**, 428 (1986).
 38. T. Aoyama, H. Yamakawa, and O. Matsuoka, *J. Chem. Phys.*, **73**, 1329 (1980).
 39. Y. S. Lee, W. C. Ermler, K. S. Pitzer, and A. D. McLean, *J. Chem. Phys.*, **70**, 288 (1979).
 40. K. K. Baeck and Y. S. Lee, *J. Chem. Phys.*, **93**, 5775 (1990).

Novel Polysilamethylenosilanes; New Precursors for Silicon Carbide

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Novel polysilamethylenosilanes (PSMS) were prepared by Wurtz type co-condensation of various mixtures of 2,4,4,6-tetrachloro-2,6-dimethyl-2,4,6-trisilaheptane (TSH) and dimethyldichlorosilane (D). When TSH was incorporated more than 25 mole%, PSMS polymers were soluble in common organic solvents probably due to the polycarbosilane linkage brought from TSH. The molecular weights of the polymer were measured by gel permeation chromatography and showed higher molecular weight with high TSH content. The thermal gravimetric residues increased as TSH contents increased. These properties suggested that PSMS polymers could be useful as ceramic precursors for silicon carbide.

Introduction

The polysilane processing route to silicon carbide has re-

ceived an exploratory research interest in industry and in academic sector¹ as well since Yajima *et al.* reported the utilization of dimethylpolysilane as the silicon carbide pre-

cursor in 1975.²⁻³ Yajima process, however, suffers from several shortcomings. The difficult separation of the product from the reaction mixture due to the insolubility of dimethylpolysilanes is the major problem.

West reported soluble polysilanes prepared from methylphenyldichlorosilane instead of dimethyldichlorosilane.⁴⁻⁵ Schilling *et al.* used methylvinylidichlorosilane and methylidichlorosilane in addition to dimethyldichlorosilane as the starting materials to prepare soluble polymer precursors for silicon carbide.⁶⁻⁷ The products obtained from the mixture of these chlorosilanes have polysilane linkages and polycarbosilane linkages as well due to the involvement of vinyl group in the dechlorination reaction giving Si-C-C-Si linkage.

We wish to report new organosilicon polymeric precursors for silicon carbide which are soluble in most of common organic solvents. Mixtures of chlorotrisilaheptanes and dimethyldichlorosilane were dechlorinated with sodium metal in an appropriate solvent to give polysilamethylenosilanes.

Experimental

Reagents and Solvents. 2,4,4,6-Tetrachloro-2,6-dimethyl-2,4,6-trisilaheptane (TSH) was prepared from the direct reaction of α -chloromethyl dimethylchlorosilane with metallic silicon in the presence of copper catalyst⁸. Dimethyldichlorosilane (D) was purchased from Petrarch Co. (USA) and sodium from Jansson Co. (Germany). Toluene was purchased from Dong Yang Chemical Co. (Korea), dried over sodium/benzophenone and distilled before use.

Physical Measurements. Structural characterizations were performed by typical spectroscopic techniques such as NMR (Jeol JNM-PMX 60, 60 MHz; Varian Gemini 300, 300 MHz) and FT-IR (Analect FX-6160). Molecular weights were determined by Gel Permeation Chromatography (Waters 590) with three columns of pore size 10^4 , 10^3 , 500 \AA with 1 ml/min toluene eluent, equipped with a differential refractometer detector. Molecular weights were calculated using a calibration curve obtained from the polystyrene standards. Thermogravimetric analysis (TGA) was performed with a Perkin-Elmer TGS-2 with N_2 flowing. Heating rate was $5^\circ\text{C}/\text{min}$ over the ranges of $50\text{--}950^\circ\text{C}$.

Synthesis of Polysilamethylenosilane. A 500 ml round bottom, three neck flask was equipped with a mechanical stirrer, a pressure equalizing addition funnel and a reflux condenser. The whole system was filled with dried N_2 and maintained N_2 atmosphere during the whole period of reaction.

100 ml of freshly distilled toluene was placed in the flask and 10.0 g (453 mmole) of sodium, cut into small pieces, was added. The content was heated to reflux using heating mantle with vigorous agitation to disperse sodium into a sodium sand in a refluxing toluene. Then right after heating was stopped, the mixture of dimethyldichlorosilane (D, 15.5 g, 120 mmole) and 2,4,4,6-tetrachloro-2,6-dimethyl-2,4,6-trisilaheptane (TSH, 12.6 g, 40 mmole) was added dropwise to the flask with a dropping rate of which the reflux of toluene was maintained without external heating due to exothermic nature of the reaction. During the addition, silvery color of sodium changed to black. After addition, heating was resumed to maintain reflux of toluene for about 8 hrs. The content was allowed to cool down to room temperature and

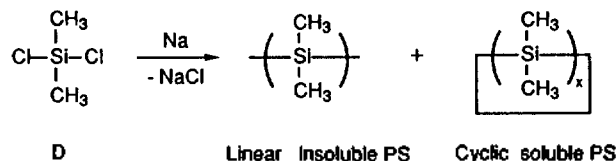
Table 1. Results for the Syntheses of Polysilamethylenosilanes

Exp. #	Soluble Polymer	Reactants (mol%)		Product Yields (%)	
		D	TSH	Soluble	Insoluble
1		100	0	10.8	63.4
2	P-7	92.3	7.7	48.0	52.0
3	P-25	75.0	25.0	95.0	-
4	P-43	56.3	43.7	96.0	-
5	P-100	0	100	93.7	-

the black mixture of the product polysilamethylenosilane was filtered through medium porosity glass filter to separate toluene solution of product from solid such as sodium chloride and unreacted sodium. The residue was washed with dried toluene several times and washing solution was combined with filtrate. Toluene was removed from the filtrate, leaving 13.0 g (yield 94.9%; assuming all the chlorine was eliminated) of the slightly yellow, grease-like polysilamethylenosilane product. The filter residue was treated with excess amount of ethanol and then water to destroy or dissolve unreacted sodium or sodium chloride to recover the insoluble product.

Results and Discussion

Several polysilamethylenosilanes were prepared by Wurtz type co-condensation reaction of various compositions of 2,4,4,6-tetrachloro-2,6-dimethyl-2,4,6-trisilaheptane (TSH) and dimethyldichlorosilane (D). The distribution ratio of the soluble and insoluble products according to the mixing ratio of TSH and D were given in Table 1. In Exp. 1, formation of dimethylpolysilane (DMPS) from the dechlorination of D only, 63.4% was recovered as insoluble powder of linear polysilane and 10.8% as soluble liquid of cyclic polysilane with small molecular weight.

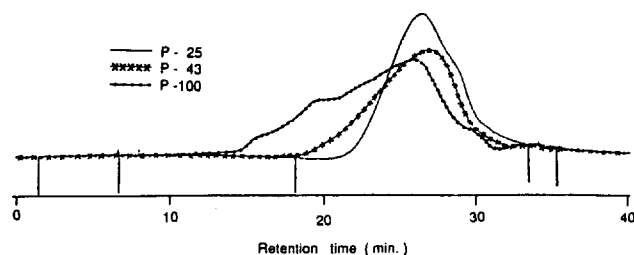
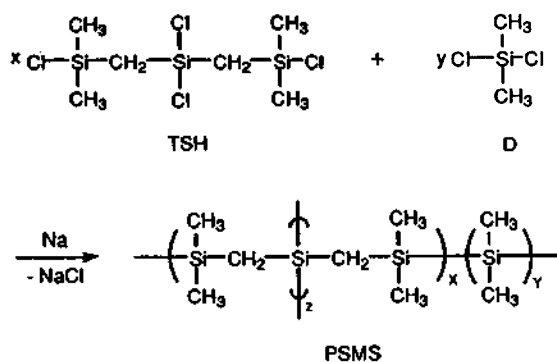


It was known that the yields for the dechlorination of D was about 50% to 80% depending on the solvent, reaction time and alkali metals used.⁹⁻¹³ Those white DMPS were insoluble in common organic solvents and infusible but thermally degraded to volatile, low molecular weight polysilanes at elevated temperature. However, DMPS could be thermally rearranged at high temperature and high pressure to polycarbosilanes which were soluble in common organic solvents. This procedure is known as Yajima's process.² When the mixtures of TSH and D were dechlorinated with sodium, polysilamethylenosilanes (PSMS) were obtained, which contained polycarbosilane linkages in addition to the polysilane linkages resulting from Wurtz type condensation reaction between silicon-chloride bonds, where all four chlorines of TSH and two chlorines of D were expected to react with sodium giving Si-Si bond formation as represented in the following scheme.

Table 2. Properties of Polysilamethylenosilanes

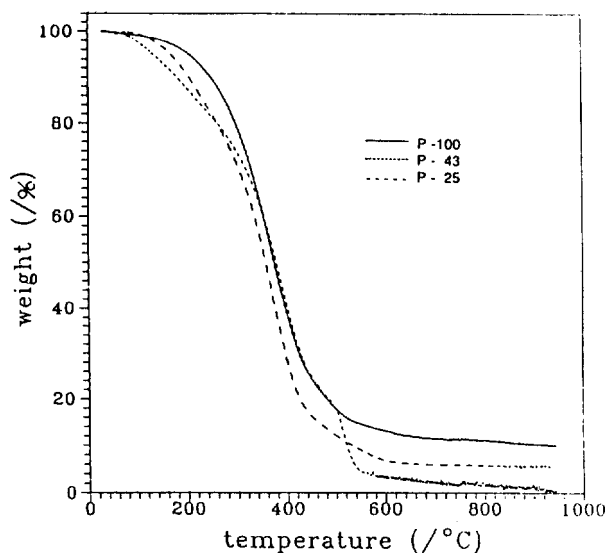
Soluble polymer	\bar{M}_w	TGA residue(%)
P-25	2,030	1.0
P-43	4,450	5.7
P-100	27,300	10.7

TGA was measured up to 950°C.

**Figure 1.** Gel Permeation chromatograph of polysilamethylenosilanes.

Since PSMS already possessed the polycarbosilane linkages in their polymeric backbone, it should have properties similar to polycarbosilanes. In fact, 7.7% TSH addition to D decreased the amount of insoluble product by more than 10% and increased soluble product by about 40%, thereby reducing the loss during the workup to practically zero. It was assumed that the loss was from the formation of volatile, cyclic polysilane with low molecular weights and low boiling points. Therefore, adding TSH, even in small quantity, prevented the formation of small molecules. That could be rationalized from the structural view of TSH which had four silicon-chloride bonds in one molecule. However, polysilane linkages were still dominant in this composition and about a half amount of products were obtained as insoluble products. When TSH content was increased to 25% and above, the PSMS products were all soluble, giving slightly yellow, highly viscous liquids in about 95% yields.

We tried to characterize the materials since these were new and could be used as ceramic precursors. The molecular weights of the polymers were listed in Table 2. Gel permeation chromatograms of PSMS polymers were shown in Figure 1. Weight average molecular weights of PSMS polymers were increasing with high TSH contents probably due to crosslinks. Judging from the trend, it was believed that the molecular weights of polymers could be controlled by adjusting compositions of TSH and D if desirable. In case of P-

**Figure 2.** Thermogravimetric curves for polysilamethylenosilanes.

100, higher molecular weight PSMS polymer was less soluble in organic solvents than P-25 and P-43. In the infrared absorption spectra of the PSMS, absorption at 2950 and 2900 cm^{-1} (C-H stretching), 2100 cm^{-1} (Si-H stretching), 1400 cm^{-1} (C-H deformation in Si-CH₃), 1355 cm^{-1} (CH₂ deformation in Si-CH₂-Si), 1260 cm^{-1} (Si-Me deformation), 1020 cm^{-1} (CH₂ deformation in Si-CH₂-Si) and in the vicinity of 800 cm^{-1} (Si-Me deformation and Si-C stretching) were seen. ¹H-NMR spectra of PSMS polymers showed broad and intense peaks at about δ 0.1 ppm for protons of Si-CH₃ and Si-CH₂-Si and small peak at about δ 4.0 ppm for proton of Si-H which was arrived from the chain-stopping reaction by silylanions¹⁴. ¹³C-NMR spectra of PSMS polymers showed broad and large peaks in Si-C carbon region from -10 to 15 ppm relative to TMS¹⁵ indicating simple structures of Si and C in PSMS. ²⁹Si-NMR spectrum of P-25 polymer showed two other peaks at δ -12 ppm and δ 7 ppm respectively probably due to Si surrounded with carbons beside the peaks at δ -38.5 ppm due to Si connected to Si as in polysilanes.¹⁶ The intensity of the peak due to Si-Si was decreased by increasing TSH giving area % for this peak to overall Si peaks 27.7% for P-25, 14.4% for P-43 and 5.6% for P-100. This result was coincide with the fact that polycarbosilane linkages would be increased when TSH content was increased thereby decreasing polysilane linkages.

When thermal properties of PSMS polymers were investigated with TGA up to 950°C with the rate of 5°C/min, thermal degradation (Figure 2) patterns for those polymers were quite similar each other. However, when TSH content of the polymers increased, initial degradation started at higher temperature and gave higher residue % (Table 2) providing a good prospect as a ceramic precursor. In case of dimethylpolysilanes which did not contained TSH at all, degradation was completed at about 400°C with no residue left¹⁷.

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References

1. W. H. Atwell, Chap. 32, "Silicon-Based Polymer Science", J. M. Zeiger and F. W. G. Fearon eds., Advances in Chemistry Series 224, Am. Chem. Soc., Washington, D. C., 1990.
2. S. Yajima, J. Hayashi, and M. Omori, *Chem. Letters*, 931 (1975).
3. S. Yajima, J. Hayashi, M. Omori, and K. Okamura, *Nature*, **261**, 683 (1976).
4. K. S. Mazdiyasi, R. West, and L. D. David, *J. Am. Ceram. Soc.*, **61**, 504 (1978).
5. R. West, L. D. David, P. I. Djurovich, and H. Yu, *Am. Ceram. Soc. Bull.*, **62**, 899 (1983).
6. C. L. Schilling and J. P. Wesson, *Am. Ceram. Soc. Bull.*, **62**, 912 (1983).
7. C. L. Schilling, *British Polymer J.*, **18**, 355 (1986).
8. I. N. Jung, G. H. Lee, S. H. Yeon, and M. Y. Suk, *Bull. Kor. Chem. Soc.*, **12**, 445 (1991).
9. C. A. Burkhard, *J. Am. Chem. Soc.*, **71**, 963 (1949).
10. L. F. Brough, *J. Chem. Soc., Chem. Comm.*, 1902 (1978).
11. J. P. Wesson, *J. Polym. Soc., Polym. Chem. Ed.*, **17**, 2833 (1979).
12. R. West, *J. Am. Chem. Soc.*, **103**, 3409 (1981).
13. S. Yajima and Y. Hasegawa, *J. Mater. Sci.*, **13**, 2569 (1978).
14. C. L. Schilling, Jr., *Abstracts of Int. Symp. on Organosilicon Chem. Directed Towards Mat. Sci.*, Sendai, Japan, L305, p. 43, 1990.
15. E. A. Williams, Chap. 8, "The Chemistry of Organic Silicon Compounds" P. Saul and Z. Rappoport eds., Part 1, John Wiley and Sons, 1989.
16. Y. Hasegawa and K. Okamura, *J. Mater. Sci.*, **21**, 321 (1986).
17. S. Yajima, *J. Mater. Sci.*, **13**, 2569 (1978).