

# Synthesis of Iron-Containing Polysilazane and Its Antioxidation Effect on Silicone Oil and Rubber

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**ABSTRACT:** A polysilazane containing iron (PSZI) was synthesized by the polycondensation of silazane lithium salts with  $\text{FeCl}_3$ , and the structure of PSZI was characterized by IR, NMR, and elemental analyses. PSZI was used as an antioxidation additive for methylsilicone oil and rubber. The gelling time of silicone oil was increased from 3 to 1000 h at  $300^\circ\text{C}$  in air when 5 wt % of PSZI was added. The elongation at break of heat-vulcanized silicone rubber after ageing at

$300^\circ\text{C}$  for 312 h remained at 130% when 3 wt % of PSZI was added, whereas for the widely used antioxidative stabilizer  $\text{Fe}_2\text{O}_3$ , the elongation after ageing for 240 h was only 65%. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 306–309, 2003

**Key words:** polysiloxanes; antioxidants; additives; polysilazane; iron-containing

## INTRODUCTION

Silicone polymers, including silicone oil and rubber, have been widely used in a number of industries, especially for their resistance to high temperatures. To meet the demand of applications at high temperatures, additional silicones of higher temperature resistance ( $>300^\circ\text{C}$  for extended times or  $350^\circ\text{C}$ ) need to be developed. Two main reactions could lead to degradation of the heat resistance of silicone oil and rubber in air: (1) degradation or reversion of the main chain to give low molecular weight cyclosiloxanes; (2) oxidation scission of the side groups. To improve the heat resistance of silicone rubber, a heat-vulcanized (HTV) silicone rubber containing cyclodisilazane structural units (abbreviated Si–N rubber) was synthesized in our laboratory,<sup>1–3</sup> and it retained an elongation of 100% and tensile strength of  $80\text{ kg/cm}^2$  after being heated at  $350^\circ\text{C}$  in air for 24 h. For the room temperature–vulcanized (RTV) silicone rubber, we proposed the concept of thwarting reversion by using a particular polysilazane as crosslinking agent in the absence of organotin catalyst.<sup>4</sup> The as-prepared silicone rubber had a heat-resistant temperature up to  $350^\circ\text{C}$  and the activation energy of thermal degradation increased to 330 from 70 kJ/mol.

To improve their thermal stability in air, an effective antioxidative stabilizer must be developed. During the past few decades, many kinds of oxidative stabilizers have been investigated.<sup>5–9</sup> Iron compounds, in particular ferric compounds, are widely used as stabilizers for silicones.  $\text{Fe}_2\text{O}_3$  is perhaps the most commonly used stabilizer and believed to be more effective than most other organic or inorganic antioxidants.<sup>8</sup> Iron salts of carboxylic acid are also commonly used as antioxidants, especially for silicone oil.<sup>9</sup>

Here we describe a polysilazane containing iron (PSZI) synthesized by the condensation of silazane lithium salts with  $\text{FeCl}_3$ , and its antioxidation effect on silicone oil and rubber is investigated.  $\text{Fe}[\text{N}(\text{SiMe}_3)_2]_3$ , synthesized by the condensation of  $(\text{Me}_3\text{Si})_2\text{N-Na}$  and  $\text{FeCl}_3$ , was first reported by Burger and Wannagat,<sup>10</sup> and characterized by Alyea et al.<sup>11</sup> and Hursthouse and Rodesiler<sup>12</sup>; later,  $\text{Fe}[\text{N}(\text{SiMe}_3)_2]_2$  and its derivatives were prepared and investigated by Andersen et al.<sup>13</sup> and Olmstead and Power<sup>14</sup>; various formulations of  $\text{Fe}[\text{N}(\text{SiMe}_n\text{Ph}_{3-n})_2]$  ( $n = 0, 1, 2$ ) were studied by Chen et al.<sup>15</sup> However, all these authors mainly focused on low-molecular iron silylamides and their structure; the polymers containing Si–N–Fe bond and their applications described in the present work were not mentioned. In this study, our focus is on the possibility of using these compounds as antioxidants for silicones, so PSZI with higher molecular weight and lower vaporization may be a better choice.

## EXPERIMENTAL

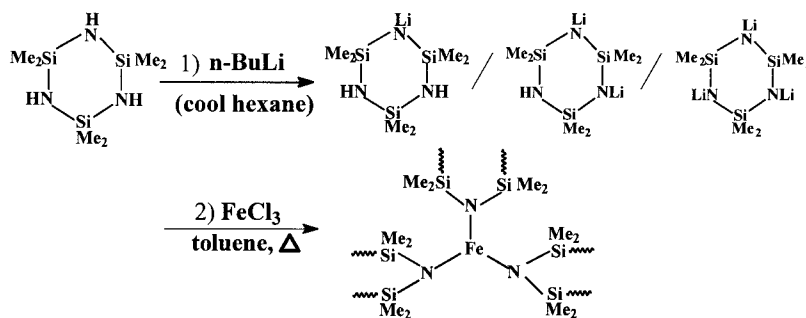
### Materials

Hexamethylcyclotrisilazane ( $\text{D}_3^{\text{N}}$ ) was prepared in our laboratory according to the literature.<sup>1,16</sup> Tetrahy-

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Scheme 1

drofuran (THF), *n*-hexane, and toluene were dried by refluxing over sodium and distilled under nitrogen. *n*-Butyllithium (1.6M in hexane) was purchased from Aldrich (Milwaukee, WI). Methylsilicone oil of 300 cP was purchased from Beijing Second Chemical Factory. Methylvinylsilicone gum (Model 110-2,  $M_w = 490,000$ ) and fumed  $\text{SiO}_2$  (#2) were purchased from Chenguang Second Chemical Factory and Shenyang Chemical Factory, respectively.

### Measurements

Infrared spectra were recorded with a PE 2000 IR spectrometer (Perkin Elmer Cetus Instruments, Norwalk, CT) using a KBr-pressed plate.  $^{29}\text{Si}$ -NMR spectra were recorded on a Unity 200 spectrometer (Varian, Palo Alto, CA) using  $\text{CDCl}_3$  as solvent. Elemental analysis was performed using different apparatus and methods (C, H, and N were determined by the combustion method at Carlo Erba 1106; Cl was titrated by  $\text{HgNO}_3$  solution; Fe and Li were measured by atom emission spectrometry at the Institute of Physics, the Chinese Academy of Sciences).

The ageing test of silicone oil and rubber was conducted as follows: 1.6 mL methylsilicone oil was poured into a glass dish and placed in an air-circulation oven maintained at  $300^\circ\text{C}$ , and the weight change and gelling time were determined. Dumbbell-like vulcanized sheets of 2 mm thickness and 4 mm width were hung on an iron frame and placed into the oven. Their mechanical properties at different ageing times were measured. The formulation of the silicone rubber was as follows: 100 parts by weight silicone gum; 45 parts #2 fumed  $\text{SiO}_2$  pretreated by octamethylcyclotetrasilazane ( $\text{D}_4\text{N}$ ); 3 parts antioxidation additive ( $\text{Fe}_2\text{O}_3$  or PSZI); and 1 part dicumyl peroxide. Conditions of vulcanization were  $160^\circ\text{C}$  for 10 min, 7–8 MPa, and postcuring was conducted at  $160^\circ\text{C}$  for 2 h, at  $180^\circ\text{C}$  for 2 h, and at  $200^\circ\text{C}$  for 20 h.

### Synthesis

Silazane lithium salts were prepared according to the method of Fink.<sup>17,18</sup>  $\text{FeCl}_3$  was added to react directly with the silazane lithium salts, as shown in Scheme 1.

Freshly distilled *n*-hexane (60 mL) and 15.8 g (0.072 mol)  $\text{D}_3\text{N}$  were added to a 250-mL three-neck flask equipped with a dropping funnel and a gas inlet tube; 128 mL (1.6M) *n*-BuLi was charged into the funnel by a syringe in a dropwise manner, while stirring, after air had been replaced by dry nitrogen. As *n*-BuLi was added, a white precipitate formed. The reaction mixture was stirred for 8 h at room temperature, then the solvent was removed by filtration under nitrogen. Under the protection of nitrogen, 160 mL toluene, 2 mL triethylamine, and 11.09 g (0.068 mol)  $\text{FeCl}_3$  were added to the flask while stirring. The bath temperature was increased to  $80^\circ\text{C}$  and maintained for 24 h. The upper black solution was filtered out, and 80 mL toluene was added to the flask to wash the slurry. The procedure of washing and filtration was repeated twice. The incorporated solution was condensed to 100 mL by distillation under vacuum below  $80^\circ\text{C}$ , and 100 mL hexane was added to the solution while stirring. After standing for 24 h, the solution was filtered and the solvent was distilled under vacuum to give 16.6 g black solid. Different degrees of lithiation (mol ratio: *n*-BuLi/ $-\text{NH}$ ) of 0.5–0.98 at  $3\text{BuLi}/\text{FeCl}_3 = 1$  were also applied to the reaction, and the products were found to change from a viscous liquid to a tough solid and brittle solid with the increase of degree of lithiation.

## RESULTS AND DISCUSSION

### Synthesis and characterization of PSZI

#### Spectral characterization of PSZI

Silazane lithium salts can be a silazane monolithium salt, silazane dilithium salt, or silazane trilithium salt by adjusting the degree of lithiation,<sup>17,18</sup> so the molecular weight and the branched degree of PSZI can be controlled. The synthesized PSZIs were characterized by FTIR, NMR spectra, and elemental analyses. From the FTIR in Figure 1, we observe that the IR absorptions of PSZI are similar to that of  $\text{D}_3\text{N}$  at  $2961$ ,  $1403$   $\text{cm}^{-1}$  (C—H);  $1260$ ,  $861$ ,  $801$   $\text{cm}^{-1}$  ( $\text{Si}-\text{CH}_3$ )<sup>19,20</sup>; and  $934$   $\text{cm}^{-1}$  ( $\text{Si}-\text{N}-\text{Si}$ ).<sup>21,22</sup> The new absorption at  $1639$   $\text{cm}^{-1}$  disappeared when IR was recorded by dissolv-

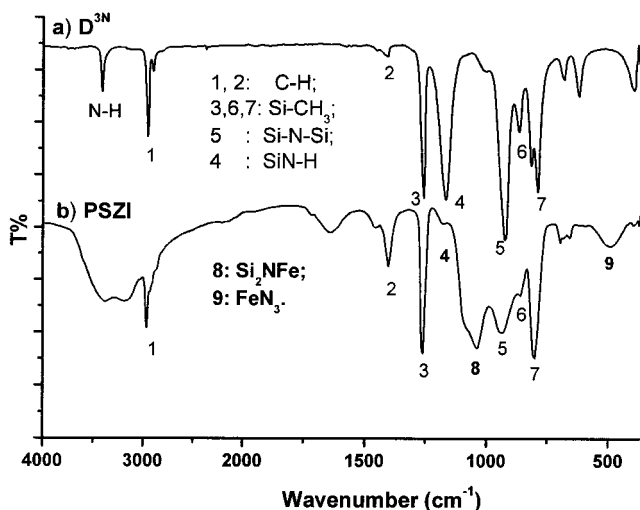


Figure 1 IR spectra of PSZI.

ing PSZI in THF, so it should result from the water absorption of the KBr-pressed plate. However, a new absorption at  $493\text{ cm}^{-1}$  was still evident and can be assigned to the Fe—N<sub>3</sub> bond (analogous to Si—N<sub>3</sub> absorption). That the N—H absorption<sup>21,22</sup> at  $1175\text{ cm}^{-1}$  decreased significantly, and a new peak at  $1036\text{ cm}^{-1}$  appeared, indicate that a substantial proportion of Si<sub>2</sub>NH was replaced by Si<sub>2</sub>NFe, similar to the phenomenon when Si<sub>2</sub>NH was replaced by Si<sub>2</sub>NSi.<sup>18,23–25</sup>

Compared with the <sup>29</sup>Si-NMR of D<sub>3</sub><sup>N</sup>, the signals of PSZI appear as one or more peaks shifted by 4–10 ppm to a lower magnetic field, which varied with different degrees of lithiation. At a degree of lithiation of 0.96, only one major peak appears [Fig. 2(b)]; at 0.55, four major peaks appear [Fig. 2(c)], which means that one, two, or three N—H on the ring of D<sub>3</sub><sup>N</sup> could be replaced by N—Fe. We found that the <sup>29</sup>Si-NMR peak of PSZI would shift downfield relative to that of D<sub>3</sub><sup>N</sup>, and the more NH was replaced by NFe, the more it shifted to a lower magnetic field. In summary, PSZI can be synthesized by this method, but the structure is complicated and more detailed structural characterization and investigation are in progress in our laboratory.

Reaction temperature, solvent, and isolation condition

The reactions in toluene at 60, 80, and 110°C for 24 h were studied. It was shown that 80°C was an optimal reaction temperature. At 110°C, the product was impure, and the Cl content was always higher than 5%. At 60°C, both reaction yields were lower than 30% for 24 h. The mixture of THF and hexane is also an optimal solvent for the condensation reaction, but THF must be extracted out during the isolation because the byproduct LiCl is slightly soluble in THF. Toluene and 20–100 vol % hexane were added to precipitate LiCl

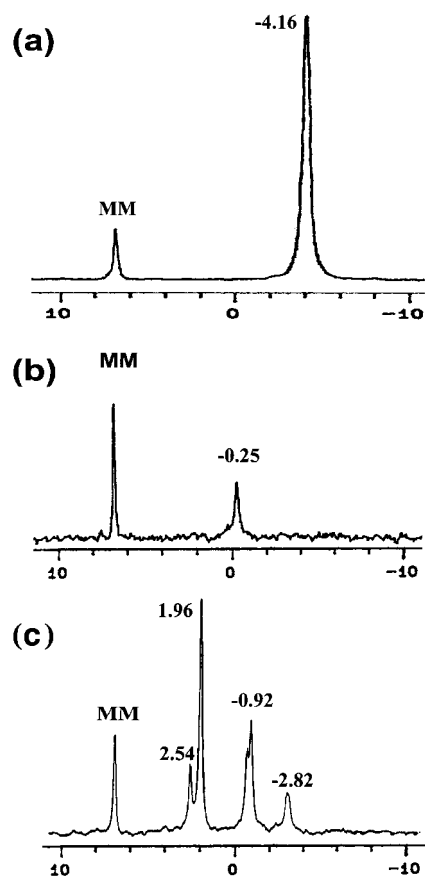


Figure 2 <sup>29</sup>Si-NMR spectra of PSZI: (a) D<sub>3</sub><sup>N</sup>; (b) Li/-NH = 0.96; (c) Li/-NH = 0.55. MM, Me<sub>3</sub>SiOMe<sub>3</sub>; external standard,  $\delta = 6.9\text{ ppm}$ .

and other impurities. When the volume ratio of toluene/hexane is about 1, the Cl and Li content can be reduced to <0.3 and <0.1%, respectively.

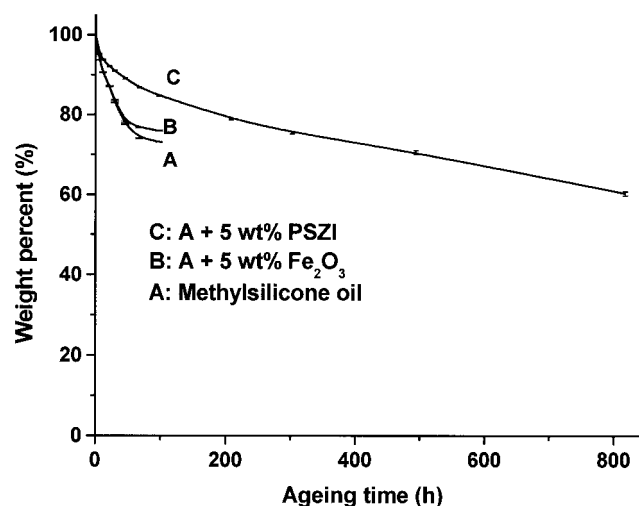


Figure 3 Weight change of methylsilicone oil at 300°C in air.

TABLE I  
Mechanical Properties of Silicone Rubber Ageing for Various Times at 300°C in Air<sup>a</sup>

Additive	$A_T$	$W_t$	H	Ts	El
(none)	0	100	48	64	300
	12	93	77	—	—
$Fe_2O_3$	0	100	43	55	400
	168	78.6	74	42	120
	240	73.8	83	42	65
PSZI	0	100	42	70	480
	168	87.1	52	42	250
	312	73.4	73	43	130

<sup>a</sup>  $A_T$ , ageing time (h);  $W_t$ , weight percent (%); H, Shore A hardness; Ts, tensile strength (kg/cm<sup>2</sup>); El, elongation at break. Additive content: 3 wt % of silicone gum.

### The antioxidation ability of PSZI

The antioxidant for silicone oil

It was shown by a gelling test that PSZI possesses good antioxidation ability. The gelling time ( $G_T$ ) of methylsilicone oil at 300°C in air was only 3 h; the  $G_T$  was 3.5 h when 5 wt % of  $Fe_2O_3$  was added. When 5 wt % PSZI was added, the  $G_T$  could increase to about 1000 h, and the weight loss also decreased (Fig. 3). The improved antioxidation of PSZI may result from its solubility in silicone oil, whereas  $Fe_2O_3$  does not dissolve in silicone oil, resulting in sedimentation at the bottom of the dish. In fact, only the PSZI prepared from the optimal degree of lithiation (0.6–0.95) and containing low Cl content (<4%) had the antioxidation effect.

The antioxidant for HTV silicone rubber

PSZI can also be used as a stabilizer for HTV methylsilicone rubber. It was observed that vulcanized sheets without antioxidative additives lost mechanical strength and elasticity after ageing at 300°C for only 12 h. As seen from Table I, when 3 wt % of  $Fe_2O_3$  or PSZI was added, the vulcanized sheets held an elongation of more than 60% and tensile strength of 42 kg/cm<sup>2</sup> after ageing for over 240 h. In particular, the samples with added PSZI showed an elongation of 130% and hardness of 73 after ageing for 312 h, significantly better than that with  $Fe_2O_3$  ageing for 240 h (elongation of 65% and hardness of 83).

### CONCLUSIONS

A polysilazane containing iron (PSZI) was prepared by polycondensation of  $D_3^N$  lithium salts and  $FeCl_3$  in warm toluene or THF. The ageing test of silicone oil and rubber at 300°C in air indicated that PSZI can improve the antioxidation property of silicone oil and rubber.

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### References

- Xie, Z. M.; Li, Q. S.; Wang, J. T.; Xie, Z. S. *Polym Commun* 1979, 4, 215.
- Li, Q. S.; Xie, Z. M. *Polym Commun* 1986, 3, 208.
- Xie, Z. M.; Wang, J. T.; Li, Q. S. *Acta Polym Sinica* 1989, 1, 46.
- Wang, Q. Z.; Shi, T.; Xie, Z. M.; Sun, X.; Wang, J. T.; Li, G. L. *Acta Polym Sinica* 1994, 5, 573.
- Baker, H. R.; Singleterry, C. R. *J Chem Eng Data* 1961, 6, 146.
- Baney, R. H. In: *Proceedings of Polymer Conference Series*, Wayne State University, Detroit, MI, May 20, 1968.
- Robert, A. R. AD-A137914 (report unclassified); *Thermally Stable Elastomers: A Review*; Naval Weapons Center: China Lake, CA, 1983; p. 10.
- Warrick, E. L.; Pierce, O. R.; Polmanteer, K. E.; Saam, J. C. *Rubber Chem Technol* 1979, 52, 437.
- Nielsen, J. M. *J Polym Sci Polym Symp* 1973, 40, 189.
- Burger, H.; Wannagat, U. M. *Monatsch Chem* 1963, 94, 1007 (1963).
- Alyea, E. C.; Bradeley, D. C.; Copperthwaite, R. G. *J Chem Soc Dalton Trans* 1972, 1580.
- Hursthouse, M. B.; Rodesiler, P. F. *J Chem Soc Dalton Trans* 1972, 2100.
- Andersen, R. A.; Faegri, K., Jr.; Green, J. C.; Haaland, A.; Lappert, M. F.; Leung, W.-P.; Rypdal, K. *Inorg Chem* 1988, 27, 1782.
- Olmstead, M. M.; Power, P. P.; Shoner, S. C. *Inorg Chem* 1991, 30, 2547.
- Chen, H.; Bartlett, R. A.; Rasika, D. H. V.; Olmstead, M. M.; Power, P. P. *J Am Chem Soc* 1989, 111, 4338.
- Brewer, S. D. *J Am Chem Soc* 1948, 70, 3888.
- Fink, W. *Angew Chem* 1961, 73, 467, 736.
- Fink, W. *Helv Chim Acta* 1962, 45, 1081.
- Young, C. W.; Servais, P. C.; Currie, C. C.; Hunter, M. J. *J Am Chem Soc* 1948, 70, 378.
- Smith, A. L. *J Chem Phys* 1953, 21, 1997.
- Kriegsmann, H. *Z Elektrochem* 1957, 61, 1088.
- Grenoble, M. E.; Hanner, P. J. In: *Proceedings of the Tenth Annual Symposium on Spectroscopy*; American Chemical Society, Chicago, IL, 1959.
- Ebsworth, E. A. V.; Hall, J. R.; Mackillop, M. J.; Mckean, D. C.; Sheppard, M.; Woodward, L. A. *Spectrochim Acta* 1958, 13, 202.
- Kriegsmann, H.; Foster, W. *Z Anorg Allg Chem* 1958, 298, 212.
- Robinson, D. W. *J Am Chem Soc* 1958, 80, 5924.