Preparation of Substituted Network Polysilanes and Their Electrical Conductivities

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Summary: The introduction of various substituents, such as alkyl and aryl groups, into the MeO-functionalized network polysilane, $[MeSi(OMe)_l]_m$ ***(2)*** *via a substitution reaction using Grignard reagents gave the substituted polysilanes* $[MeSi(OMe)_x(R)_y]_n$ ***(3)***, *which are soluble in common organic solvents. Films of polysilanes bearing the (dialkylamino)phenyl side chain p-*$R'_2NC_6H_4$ *(R′ = Me, Et, and Pr) exhibited electrical conductivities on the order of* 10^{-3} $S{\cdot}cm^{-1}$ *when doped with iodine. The electronic absorption bands for the network polysilanes were correlated to their CT complexes associated with the conductivity.*

In recent years, polysilanes have been of interest due to their properties, which are useful for functional materials such as photoresists, ceramic precursors, photoconductors, nonlinear optical materials, etc. Although there are many reports of the chemical and physical properties of linear polysilanes with various substituents on their silicon chains, few studies have focused on network polysilanes because of their limited availability.[1] We have previously reported a convenient and simple method for the preparation of the network polysilanes with methoxy and methyl substituents, which are abbreviated as $[MeSi(OMe)_l]_m$, by the catalytic polymerization of methoxymethyldisilanes, $Me_{6-n}Si_2(OMe)_n$ ($n = 3$, 4, and mixtures 3 + 4), via the silyl anion mechanism.[2]

The MeO-functionalized network polysilane may be useful as a functional material in high technology applications, and we report here the substitution of a part of the methoxy groups by organic substituents (R) to give functionalized polysilanes of the type $[MeSi(OMe)_x(R)_y]_n$. Their properties, including electrical conductivity, are also described. The introduction of the new organic groups proceeded readily using the corresponding Grignard reagent (RMgX). The starting network polysilane (**2**) was obtained using 1,2-dimethyl-1,1,2,2-tetramethoxydisilane (**1**) as the monomer by the method reported previously.[2] A typical Grignard reaction of polysilane **2**, $[MeSi(OMe)_l]_m$, to give polysilane **3**, $[MeSi(OMe)_x(R)_y]_n$, is described in detail in ref 3.[3]

$Me(MeO)_2SiSi(OMe)_2Me$

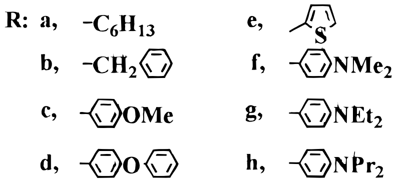
1

$[MeSi(OMe)_l]_m$

2

$[MeSi(OMe)_x(R)_y]_n$

3



Although another type of substituted network polysilane was prepared recently by other workers, by our method using ethoxymethyldisilanes in the presence of an organolithium catalyst,[4] the resulting polysilanes are substantially different from the polysilanes that we report here.

Polysilane **3** was identified and characterized by methods similar to those used in the characterization of linear polysilanes. The degree of substitution achieved was determined by ^1H NMR spectrometry using the hydrogen ratio for the R, MeO, and Me groups (Table 1).[5,6] All polysilanes (**3**) were soluble in common organic solvents, such as benzene, toluene, dichloromethane, and THF, and depending on the substituents present, were quite stable in air. They were much more stable than the starting polysilane **2**.

Since there have been only limited reports describing the properties related to the electrical conductivity of polysilanes,[7] it was of interest to investigate the con-

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(1) (a) Baney, R. H.; Gaul, J. H., Jr.; Kilty, T. K. *Organometallics* **1983**, *2*, 859. (b) Bianconi, R. D. A.; Shilling, F. C.; Weidman, T. W. *Macromolecules* **1989**, *22*, 1697. (c) Kalchauer, W.; Pachaly, B.; Geisberger, G.; Rosch, L. Z. *Anorg. Allg. Chem.* **1992**, *618*, 148. (d) Kabeta, K.; Wakamatsu, S. W.; Sugi, S.; Imai, T. *Synth. Met.* **1996**, *82*, 201.

(2) Watanabe, H.; Abe, M.; Sonoda, K.; Uchida, M.; Ishikawa, Y.; Inomiya, M. *J. Mater. Chem.* **1991**, *1*, 483 and the references cited therein.

(3) Preparation of **3a** from **2** by the Grignard alkylation as a typical example (see Table 1): A $C_6H_{13}MgCl$ (12.3 mmol) solution was prepared from magnesium and hexyl chloride in THF (10 mL). The Grignard reagent was added with stirring to a solution containing polysilane **2**, $[MeSi(OMe)_{0.41}]_n$ (M_w 24 000; M_n 4400) (0.50 g), in THF (10 mL). After a weakly exothermic reaction, the mixture was heated at 40 °C for 20 h with stirring and then dry methanol (2−3 mL) was added to quench the active species. From the resulting mixture, the solvent was removed completely to give a solid material, which was extracted with toluene (ca. 50 mL). The toluene extracts were concentrated under reduced pressure and added with warm methanol (15 mL) to precipitate a solid material, which, in turn, was collected on a filter, washed with methanol, and then dried under reduced pressure. The obtained polysilane **3a** was a pale yellow powder, $[MeSi(OMe)_{0.18}(Hex)_{0.23}]_n$ (M_w 20 100; M_n 4300; 0.54 g, 108% yield based on **2**).

(4) (a) Kabeta, K.; Wakamatsu, S.; Imai, T. *J. Polym. Sci., Part A: Polym. Chem.* **1996**, *34*, 2991. (b) Kabeta, K.; Wakamatsu, S.; Imai, T. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 456.

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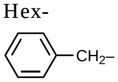
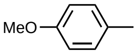
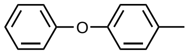
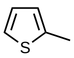
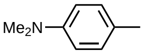
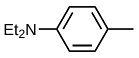
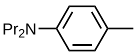
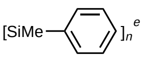
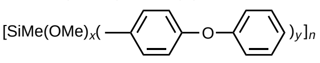
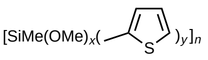
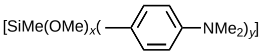
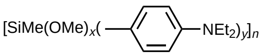
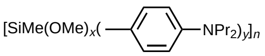
Table 1. Substitution Reactions of Polysilane 2 with Grignard Reagents and Results

	polysilane **2**		RMgBr		polysilane **3**			
run	M_w[a] (×10^{-3})	x[b]	R	equiv[c]	M_w[a] (×10^{-3})	y/x (%)[d]	yield[e] (%)	appearance
1	24.0	0.41	Hex-	2.0	21.0	55	108	pale yellow powder
2	78.0	0.36		3.0	29.0	65	111	
3	7.5	0.37		1.6	8.3	54	111	
4	14.2	0.34		1.9	13.0	44	181	
5	8.4	0.38		1.1	8.9	42	101	yellow powder
6	7.8	0.36		1.5	15.0	61	132	pale yellow powder
7	8.4	0.38		1.4	9.3	55	167	
8	12.0	0.39		1.8	11.5	56	161	

[a] GPC method and polystyrene standards. [b] Ratio, OMe/Me in **2**. [c] Ratio, RM/OMe. [d] Conversion of OMe in R. [e] Based on **2** used.

Table 2. Electrical Conductivities of Network Polysilanes

		σ (S/cm)	
polysilane[a]	M_w[b] (×10^{-3})	*c*	*d*
	24.0	4 × 10^{-8}	1 × 10^{-6}
[SiMe(OMe)$_{0.38}$]$_n$ (**2**)[f]	10.8	7 × 10^{-6}	1 × 10^{-5}
 (**3d**) (x = 0.16; y = 0.18)	15.0	2 × 10^{-7}	6 × 10^{-7}
 (**3e**) (x = 0.17; y = 0.11)	19.5	2 × 10^{-7}	3 x 10^{-7}
 (**3f**) (x = 0.12; y = 0.21)	18.5	2 × 10^{-7}	1 × 10^{-3}
 (**3g**) (x = 0.19; y = 0.22)	10.8	8 × 10^{-8}	1 × 10^{-3}
 (**3h**) (x = 0.27; y = 0.24)	11.7	7 × 10^{-8}	1 × 10^{-3}

[a] Film thickness, 12–17 μm. [b] GPC method; polystyrene standards. [c] Before doping. [d] After doping. [e] Obtained by Wurtz-type coupling reaction of MePhSiCl$_2$ with sodium. [f] Film thickness, 3 μm.

ductivity of **3** and to elucidate their spectral behavior by comparison with other polysilanes. No reports on charge transfer (CT) interactions of network polysilanes were available. First, samples of films of selected polysilanes (**3c**–**h**), polysilane **2**, and linear poly(methylphenylsilane) were prepared on glass plates, and their conductivities were measured by the four-probe method using iodine as a dopant. Before doping, the values for all polysilanes were on the order of 10^{-8}–10^{-6} S·cm^{-1}. The values for polysilanes **3f**–**h** bearing (*N*,*N*-dialkylamino)phenyl groups (p-R$'_2$NC$_6$H$_4$; R$'$= Me, Et, and Pr) increased greatly upon doping to around 10^{-3} and then leveled off. This is comparable to the conductivity of poly(methylphenylsilane) doped with SbF$_5$.[7] In contrast, the conductivities of polysilanes **3c**–**e** having p-MeO, p-C$_6$H$_5$OC$_6$H$_4$, and 2-C$_4$H$_3$S groups, respectively, and for **2** and poly(methylphenylsilane) remained almost unchanged or increased only slightly on doping (Table 2). The remarkable increase in conductivities of **3f**–**h** may be attributed to the stabilizing effect of the strong electron-donating nature of the p-R$'_2$NC$_6$H$_4$ groups[8] on the positively charged silicon network sites generated by doping, as demonstrated in the case of linear polysilane.[7a] In other words, the increased concentration of positive carriers which were stabilized by the strong electron-donating nature of these groups accounts for the high and stable conductivities.

The spectral behavior in CH$_2$Cl$_2$ solution of undoped and doped samples of **3** was investigated. Polysilanes **3f**–**h**, which gave the higher conductivities, are pale yellow in solution and have a strong peak at λ 276 nm tailing into the visible region (ca. 450 nm). After doping, they were light brown in color and a wide band covering the whole UV–vis range and two bands in the λ 294 and 370 nm regions (together with 570(sh) and the 615 nm regions in **3f** (Figure 1)) were observed. On the other hand, **3c**–**e** exhibited similar spectra before and after doping (orange or light brown color). Previously, the absorption band at λ 400 or 420 nm produced by

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(5) ^{1}H NMR (δ, CDCl$_3$; TMS) data of the polysilanes: **2** −0.4–1.4 (SiCH$_3$, 3.0H), 3.0–3.9 (SiOCH$_3$, 1.2H); **3a** −0.5–0.7 (SiCH$_3$, 3.0H and SiCH$_2$–C$_5$, 0.2H), 0.8–1.0 (–C$_4$–CH$_3$, 0.7H), 1.1–1.6 (–C–(CH$_2$)$_4$–C, 1.8H), 3.2–3.8 (SiOCH$_3$, 0.6H); **3b** −0.5–1.0 (SiCH$_3$, 3.0H), 2.0–2.7 (CH$_2$, 0.3H), 3.2–3.7 (SiOCH$_3$, 0.4H), 6.6–7.6 (C$_6$H$_5$, 1.2H); **3c** −0.2–1.0 (SiCH$_3$, 3.0H), 3.0–3.1 (SiOCH$_3$, 0.6H), 3.6–4.1 (OCH$_3$, 0.8H), 6.7–7.0 and 7.2–7.8 (C$_6$H$_4$, 1.0H); **3d** −0.5–1.0 (SiCH$_3$, 3.0H), 3.0–3.7 (SiOCH$_3$, 0.5H), 6.7–7.7 (C$_6$H$_5$ and C$_6$H$_4$, 1.2H); **3e** −0.3–1.2 (SiCH$_3$, 3.0H), 3.1–3.9 (SiOCH$_3$, 0.7H), 6.9–7.9 (C$_4$H$_3$S, 0.5H); **3f** −0.3–1.1 (SiCH$_3$, 3.0H), 2.97 (N–CH$_3$, 1.8H), 3.1–3.7 (SiOCH$_3$, 0.6H), 6.5–6.9 and 7.1–7.7 (C$_6$H$_4$, 1.4H); **3g** −0.2–0.9 (SiCH$_3$, 3.0H), 1.0–1.4 (N–C–CH$_3$, 1.8H), 3.1–3.7 (N–CH$_2$–C, 1.2H and SiOCH$_3$, 0.7H), 6.4–6.8 and 7.1–7.7 (C$_6$H$_4$, 1.2H); **3h** −0.2–0.8 (SiCH$_3$, 3.0H), 0.8–1.0 (N–C–C–CH$_3$, 1.6H), 1.3–1.8 (N–C–CH$_2$–C, 1.6H), 2.9–3.7 (N–CH$_2$–C–C, 1.4H and SiOCH$_3$, 0.6H), 6.2–6.9 and 6.9–7.6 (C$_6$H$_4$, 1.0H); IR data will be described elsewhere.

(6) Part of this work has been presented in the 42nd Symposium on Organometallic Chemistry, Hiroshima, Japan, Oct. 1995; Abstract A215. pp 133–134.

(7) (a) Kakimoto, M.; Ueno, H.; Kojima, H.; Yamaguchi, Y.; Nishimura, A. *J. Polym. Sci., Part A: Polym. Chem.* **1996**, *34*, 2753. (b) Tabei, E.; Fukushima, E.; Mori, S. *Synth. Met.* **1995**, *73*, 113.

(8) The σ^+ substituent parameters for the *para*-Me$_2$N, C$_6$H$_5$O, and MeO groups are −1.7, −0.899, and −0.648, respectively: Gordon, A. J.; Ford, R. A., Ed. *The Chemist's Companion*; John Wiley & Sons: New York, 1972; p 152.

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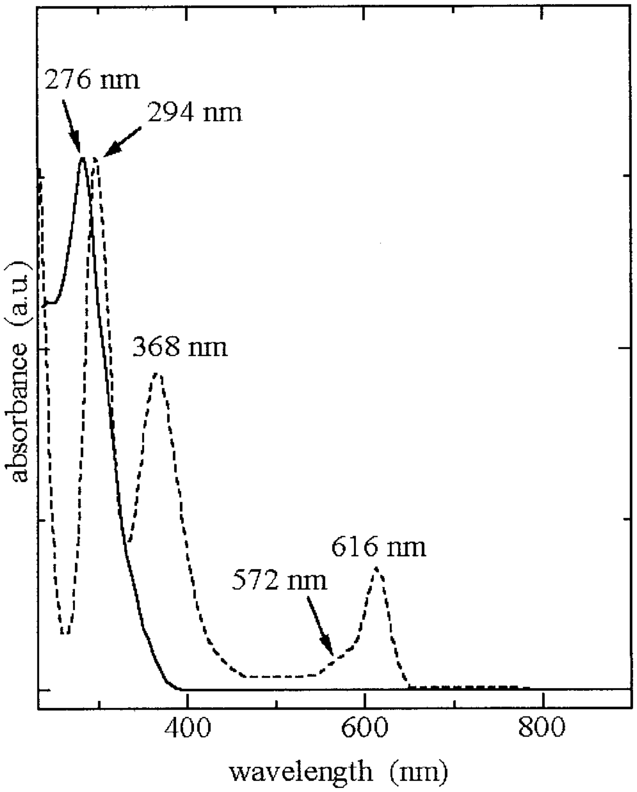

Figure 1. Electronic spectra for polysilane **3f** containing a *p*-(dimethylamino)phenyl group on the network system: before doping (—) and after doping (- - -).

iodine doping in the electronic spectra of certain linear polysilanes has been correlated with their CT complexes.[7] The above results for **3f**−**h** after doping probably indicate that the new, fairly strong bands in the λ 370 nm region, along with the band at 615 nm in **3f**, are due to the CT complexes formed in the network system. Interestingly, the band in the 615 nm region of **3f** was quite labile, and its intensity decreased gradually or on occasion disappeared. These changes were accompanied by a reduction in the iodine peak in the λ 500 nm region when the films were left to stand for several hours or subjected to dedoping in vacuo.

To obtain further information on the CT-complex formation, the selected polysilanes in **3** were examined spectroscopically in CH_2Cl_2 solution. The spectra produced from mixing solutions of **3f**−**h** with iodine gave bands very similar to those described above: the wide band and 370 nm band (CT complex), in addition to the 294 nm band and the light brown color, and no peak at λ 615 nm, were observed in all cases. The spectral differences between the two results may be explained by the different procedures used. The former experiment was carried out by doping with iodine vapor at a high concentration, and hence, the particular species responsible for the labile band (615 nm region) would possibly be formed in these films. The latter procedure, however, was carried out by mixing both substrate solutions at much lower concentrations, and such species were either not formed or could not survive under these conditions. Moreover, the solution prepared by dissolving a sample of **3f** and iodine, which had been ground together under N_2 with a mortar, was pale yellow and showed similar absorption bands in the λ 294 and 370 nm regions in addition to the wide band and 500 nm band, with no band observed at λ 615 nm. With respect to the other polysilanes, such as **3c**−**e**, which had a lower conductivity, in all cases, no new bands were produced on mixing these solutions with iodine, indicating again that these polysilanes did not form their CT complexes. No linear polysilane has been reported to produce the particular labile band described above in either film or solution. Consequently, from the above results and observations, it is likely that the absorption bands in the λ 370 and 615 nm regions in the **3f**−**h** network structures are attributable to the CT complex and the latter band, in particular, to species such as I_3^-, I_5^-, etc. associated with the CT complex are related to the conductivity in the systems. The reason **3g** and **3h** gave no such labile absorption bands remains to be clarified.

Finally, it should be noted that, as expected, all samples of the network system are capable of forming stable films after doping, and polysilanes **3f**−**h** bearing the strong electron-donating groups showed almost constant conductivity, as high as 10^{-3} ($S\cdot cm^{-1}$), after standing for a period of time (at least 15 h) or after repeated cycles of doping and dedoping. The linear polysilanes have been shown to decompose occasionally when left to stand after doping with I_2 or SbF_5.[7a,9] Thus, when compared with the linear polysilanes, the higher stability under oxidative conditions of the network polysilanes is expected to be of practical value.[2]

Supporting Information Available: ^{1}H NMR spectra of polymers **2** and **3a**−**h** (9 pages). Ordering information is given on any current masthead page.

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(9) We observed similar behavior when using a sample produced with an iodine dope for the linear polysilane, poly(methylphenylsilane).