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Preparation of New Types of Organosilicon Polymers. Effective Utilization of Disilane Fraction Produced in the Direct Synthesis of Methylchlorosilanes

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Two types of new organosilicon polymers, $\text{-(}\mathrm{PhMeSiMe_2Si}\text{)-}_n$ and $\text{-(}\mathrm{[PhMe_2Si]MeSi}\text{)-}_n$, were prepared starting from the disilane fractions produced in the Direct Synthesis, via phenylations giving 1,2- and 1,1-dichlorophenyltrimethyldisilane followed by sodium mediated condensations.

In view of the effective utilization of disilane resources formed as the by-products in the Direct Synthesis of methylchlorosilanes, it is of quite interest to convert the disilane pot-residue, in which 1,1,2,2-tetrachlorodimethyldisilane and 1,1,2-trichlorotrimethyldisilane constitute main components, into more usable forms.$^{1)}$ Although there have been known several organosilicon polymers,$^{2)}$ some of which have versatile properties useful for composite materials such as photoresists, organic semi-conductors, ceramic precursors, etc., they are only in limited variety of structures. We now should like to report here the preparation of new types of organosilicon polymers, which showed some useful properties for such materials, starting from the pot-residue via phenylations of 1,1,2-trichloro-1,2,2-trimethyldisilane (**1**) giving dichlorophenyldisilanes and their reductive couplings.

In typical examples, phenylations of **1**$^{3)}$ (Eq. 1) to give 1,2-dichloro-1-phenyl-1,2,2-trimethyldisilane (**2**) (Table 1, Run 7) (bp 118 °C/19 Torr (Torr, 133.32 Pa); 64%; n_D^{25} 1.5287) and 1,1-dichloro-2-phenyl-1,2,2-trimethyldisilane (**3**) (Run 3) (bp 131 °C/20 Torr; 60%; n_D^{25} 1.5331) were readily carried out using phenyllithium in 85% selectivity and phenylmagnesium bromide in the presence of CuI (10%) in 99% selectivity,$^{4)}$ respectively.$^{5,6)}$

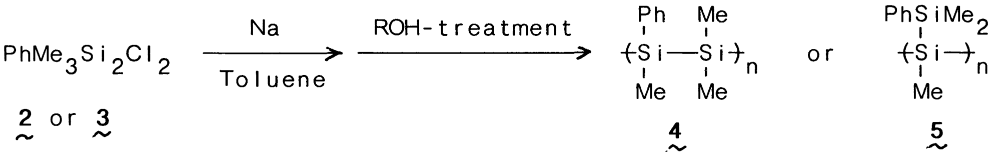
$$\underset{\mathbf{1}}{\mathrm{Cl_2MeSiSiMe_2Cl}} \xrightarrow{\mathrm{PhM}} \underset{\mathbf{2}}{\mathrm{ClPhMeSiSiMe_2Cl}} + \underset{\mathbf{3}}{\mathrm{Cl_2MeSiSiMe_2Ph}} \qquad (1)$$

In the next, dichlorodisilanes **2** and **3** were subjected to a sodium mediated condensation to give polymers **4** and **5**, respectively (Table 2). Typically, **3** was allowed to react with sodium (sand) in toluene with vigorous stirring at 20 °C for 30 h in the dark. After the reaction, cyclohexane, methanol (a small amount), and

Table 1. Preparation of 1,2- (**2**) and 1,1-dichlorophenyldisilane (**3**)

Run[a)]	PhM	Cat. / %	Product distribution / % **2**	 **3**
1	M = MgBr	None	40	60
2	"	CuCl (10)	20	80
3	"	CuI (10)	1	99
4	"	" (5)	20	80
5	"	$CoCl_2$ (10)	70	30
6	"	$NiCl_2(PPh_3)_2$ (10)	40	60
7[b)]	Li	None	85	15
8	"	CuI (10)	60	40

a) Si_2Cl_3, 20 mmol; reaction time, 12 h; ether, 120 ml; all the reactions were carried out at 0 °C—room temperature. b) PhLi in pet. ether was added to **1** in the same solvent.



$$\underset{\mathbf{2}\text{ or }\mathbf{3}}{PhMe_3Si_2Cl_2} \xrightarrow[\text{Toluene}]{\text{Na}} \xrightarrow{\text{ROH-treatment}} \underset{\mathbf{4}}{\left(\overset{Ph}{\underset{Me}{Si}}-\overset{Me}{\underset{Me}{Si}}\right)_n} \text{ or } \underset{\mathbf{5}}{\left(\overset{PhSiMe_2}{\underset{Me}{Si}}\right)_n} \qquad (2)$$

then water was added with stirring to the resulting mixture. The organic layer gave on work-up a solid material which was dissolved in a small amount of purified THF. The solution of the product was poured onto a large amount of warm (50—60 °C) ethanol with stirring to precipitate solid material which was collected on a filter, washed with ethanol, and then dried in vacuo in the dark to yield poly(dimethylphenylsilylmethylsilylene) **5** as white or pale yellow powder.

Table 2. Preparation of poly(1-phenyl-1,2,2-trimethyldisilene) **4** and poly(dimethylphenylsilylmethylsilylene) **5** from dichlorophenyldisilanes (**2** and **3**)[a)]

Run	Si_2Cl_2	Mol.ratio[b)] (Si_2: Na)	Method[c)]	Temp / °C	ROH	Yield[d,e)] / %	Appear-ance[d)]	Polymer[d)]
1	**2**[f)]	1 : 2.1	(I)	50	MeOH	36(56)	Vis.liq.	**4a**
2	"	1 : 2.0	(II)	reflux	EtOH	68(32)	Solid	**4b**
3	**3**	1 : 2.1	"	20	"	10(90)	Powder	**5a**
4	"	"	(I)	"	"	8(90)	"	**5b**
5	$\begin{bmatrix} PhMeSiCl_2 \\ Me_2SiCl_2 \end{bmatrix}$[g)]	"	"	50	"	5(67)	Solid	**6a**

a) **2**: 1,2-isomer; **3**: 1,1-isomer. b) Si_2:Na=20-40:40-90 (mmol); time, 15-30 h; Na-dispersion; solvent, toluene. c) (I): addition of metal to Si_2; (II): addition of Si_2 to metal. d) ROH-insoluble part. e) ( ): ROH-soluble part. f) **2**:**3** = 7:3. g) $PhMeSiCl_2$:Me_2SiCl_2 = 5:5.

Similarly, polymer **4** obtained from **2** (85% pure) usually appears in the form of light yellow liquid with a Me_2Si/PhMeSi ratio near 1, and therefore it should

Table 3. Molecular weights by GPC for polymers[a)]

Polymer	$\overline{Mn}$ x10^{-3}	$\overline{Mw}$ x10^{-3}	$\overline{Mw}/\overline{Mn}$	H ratio[b)] (Me/Ph)	Mp[c)] °C
4a	2.8	3.6	1.3	9/4.6	..
5a	3.2	13.2	4.1	9/4.7	75—105
6a	3.8	36.9	9.7	9/6.3	90—130
6b[d)]	2.7	20.7	7.7	9/5.3	80—120

a) Polystyrene standard. b) By ^{1}HNMR. c) In sealed tube. d) Commercially available "polysilastyrene".

have a repetitive -(Me_2Si-PhMeSi)- unit in the chain backbone. Thus, the polymer is very similar to the polysilastyrene of West et al.[2b)] in that both have the same composition, $PhMe_3Si_2$, but are quite different each other in that the polymer of West et al. is formulated as $-(Me_2Si)_x-(PhMeSi)_{1-x}-$, while polymer **4** is as $-(Me_2SiPhMeSi)_n-$. Further study of our literal polysilastyrene **4** arising from compound **2** of higher purity is necessary. Polymer **5**, which is a silicon-pendant type structure consisting of -([$PhMe_2Si$]MeSi)- unit, is very different from those of the other polysilanes so far reported.[2)]

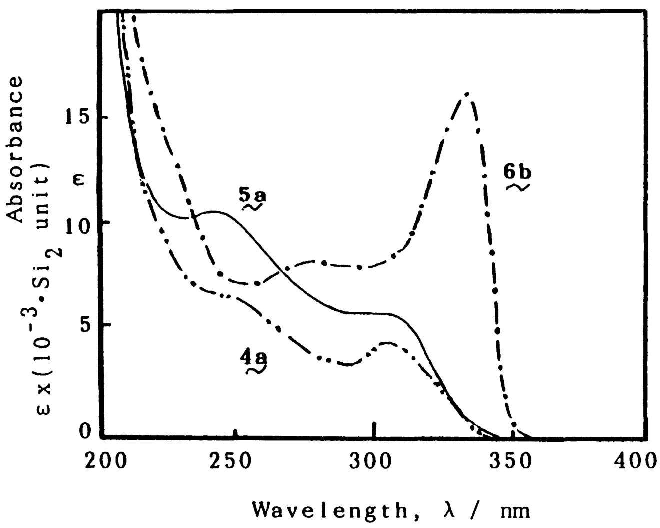


Fig. 1. UV spectra for polymers.

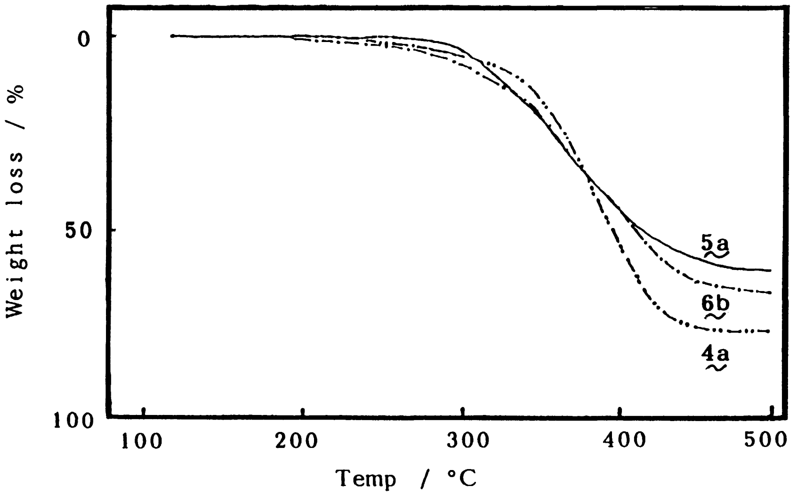


Fig. 2. TGA curves for polymers.

It is worthwhile to note some properties of polymers **4** and **5**, and to compare them with those of commercially available West's polysilastyrene. Molecular weights by GPC were almost comparable to the West's polysilastyrene. The IR spectra for **4** and **5** showed that they are essentially free of undesirable linkages such as Si-H, Si-OH, and Si-O-Si bonds. Also, like other polysilanes,[2a-2c)] **4** and **5** exhibit strong UV absorptions in the region between 250—330 nm, with ε=3000—12000/Si_2 unit (Fig. 1). It is also found that a wide range absorption spectrum for **5** is essentailly transparent from the visible to the infra-red light region and might behave as an organic glass. Thermogravimetric analysis (TGA) (100—500 °C; heating rate, 5 °C/min; in N_2) for polymers **4**, **5**, and **6** (commercially available

West's polysilastyrene) were performed and the weight loss was 75% for **4**, and 59% for **5**, and 65% for **6**, respectively, under the conditions employed (Fig. 2). The lowest weight loss observed for polymer **5** might be attractive in ceramic chemistry.

Finally, it should be emphasized that the present study opened up a way for the conversion of the disilane pot-residue into much valuable forms, in which two types of new organosilicon polymers having versatile properties as useful materials for technologies were produced. Further studies including more selective preparation of monomer **2**, polymerization leading to the formation in higher yields and molecular weights of the polymers, etc. are currently in progress.

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4) The reason why such a high selectivity can be achieved by the addition of the catalyst is not clear at the present time.

5) The isomer distribution of compounds **2** and **3** was determined, after $LiAlH_4$-reduction, in the form of the corresponding hydrodisilanes, $PhMeHSi-SiHMe_2$ (**A**) and $(PhMe_2Si)MeSiH_2$ (**B**), respectively. Thus, the ^{1}HNMR spectrum showed clear differences between **A** and **B** in both the SiH chemical shifts and multiplicities of the signals, and therefore made possible to estimate unequivocally the isomer distribution of **A** and **B**. Analysis for the mixture of **A**:**B** = 99:1, Found; C, 59.59%; H, 8.86%. Calcd for $C_9H_{16}Si_2$: C, 59.92%; H, 8.94%.

6) When a different halogen combination in the substrate halides (disilane **1** and halobenzene for phenylating reagent) is used, **2** and **3** are usually obtained as a mixture consisting of halogen-exchanged compounds associated with Cl, Br, and I.

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