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Synthesis of Oligosilanes by Electrolysis of Hydrosilanes

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The novel electrochemical reaction of hydrosilane compounds was investigated for the synthesis of polysilanes. The product obtained by electrolysis of Methylphenylsilane**1a** was an oligosilane of Mn=454 (GPC) in 60% yield, which consisted of Si-Si bonds for the main chain. When diphenylsilane was electrolyzed in a similar manner as **1a**, the major product was a dimer in 23% yield.

Polysilanes are polymers consisting of Si-Si bonds, and the most general method for their synthesis is the Wurtz coupling reaction of chlorosilanes with alkali metals. However, because of the obvious defects such as a low yield of obtained polymers, and the difficulty in polymerization of monomers possessing functional groups, novel synthetic pathways have been investigated. For example, the electroreductive method of chlorosilanes using magnesium, aluminum or copper as sacrificial anodes,1-2) dehydrogenative polymerization of hydrosilanes using a transition metal catalyst,3-4) and anionic polymerization of masked disilenes5) were recently reported.

We found a new method for synthesizing oligosilanes by electrolysis of hydrosilane compounds. Methylphenylsilane(**1a**) was electrolyzed as shown in the following equation;

$$\underset{\mathbf{1a},\ \mathbf{1b}}{R^1R^2SiH_2} \xrightarrow[\substack{0.2\ \mathrm{M}\ {}^{n}Bu_4NBF_4/DME \\ \text{Pt-Pt electrodes, passed 2 F/mol}}]{\qquad\qquad\qquad\qquad} \underset{\mathbf{2a},\ \mathbf{2b}}{H\!\left(R^1R^2Si\right)_{n}\!H} \qquad (1)$$

1a, **2a** ; R^1=Me, R^2=Ph
1b, **2b** ; R^1=Ph, R^2=Ph

In a 10 ml undivided cell, 2 ml of 0.2 M ${}^{n}Bu_4NBF_4$/DME (1M = 1mol dm^{-3}) solution was prepared under argon, and 0.12 g (1 mmol) of **1a** was added to the solution. The electrolysis was carried out using platinum plates(1 cm*2 cm*0.05 mm) as the anode and cathode until 2 F/mol were passed through the cell with controlled current (10 mA) for 5.3 h. The monomer conversion reached 80%. The reaction mixture was then concentrated and passed through a silica-gel column with toluene to remove electrolytes. A transparent liquid was obtained in 60% yield (ratio of the weight versus **1a**) after evaporation of the resulting solution in vacuo.

A characterization of the product (**2a**) was performed by GPC, HPLC and GC/MS. The number-average molecular weight of **2a** was Mn=454 (Mw/Mn=1.05), and the GPC profile (figure 1) shows that there were at least five components in the obtained oligomers. The IR spectrum of **2a** indicates that the oligomer has Si-CH_3(1260 cm^{-1}), Si-Ph(1430 cm^{-1}), and Si-H(2130 cm^{-1}) groups. Since the strength of the absorption band between 1000-1100 cm^{-1} was very weak, few siloxane bonds were formed in the main chain of the oligomer, which implied the formation of silicon catenation.

On the other hand, every component of the product could be completely separated as the same profile as GPC by HPLC using an ODS column (20.0 mmID*25.0 cmL) with acetonitrile as the eluent. The yield, molecular weight, and UV absorption maximum(λ_{max}) of the isolated oligomers are summarized in Table 1. The λ_{max} ranged from 230 to 260 nm and a remarkable red shift was observed with increasing molecular weight, which indicates an extension of Si-Si catenation.

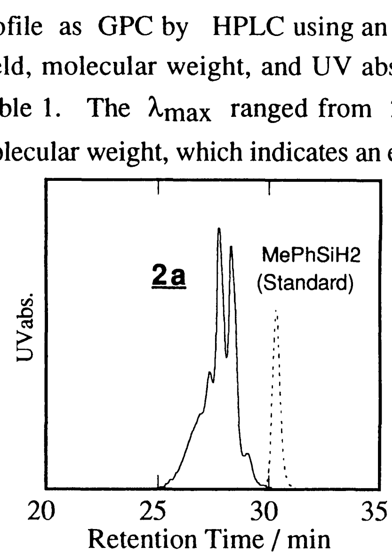

Fig. 1. GPC profile of Oligomer **2a**.

Furthermore, the GC/MS analysis of **2a** revealed that there were mostly two volatile oligomers, and they were identified as 1,2-diphenyl-1,2-dimethyldisilane (m/z=242), 1,2,3-triphenyl-1,2,3-trimethyltrisilane(m/z=362), respectively corresponding to the fraction No.1 and 2. These results are distinct evidence that the products of Eq.(1) are oligosilanes(**2a**).

Diphenylsilane(**1b**) was also electrolyzed using the same conditions as **1a**. In this case, the conversion was 38% and 1,1,2,2-tetraphenyldisilane(**2b**, n=2), was chiefly produced in 23% yield.[6]

Table 1. Characterization of the Oligomers**2a** fractionated by HPLC[a]

Fraction No.	UV abs.[b] λ_{max}/nm	Mole. GPC[c]	Wt. Mass	Degree of Polymerization	Yield[d] /%
1	230	219	242	2	10
2	243	304	362	3	14
3	251	378	-	4	16
4	257	427	-	5	6

a)Eluent acetonitrile, Detector UV 254 nm. b)Measured on flow of HPLC. c)Polystyrene standards, peak top. d)Based on the weight of isolated fraction by HPLC.

Generally, hydrosilanes are active on the anode. It is considered that reactive species, probably silylradical cations, are first formed, then they should attack other monomers to form Si-Si bond. Further investigations of the raction mechanism and the electrochemical polymerization of other hydrosilane compounds are now in progress.

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6) Spectrum data of **2b**: ^{1}H-NMR($CDCl_3$): δ 5.17(s, 2H, Si-Si-H), 7.26-7.57(m, 20H, C_6H_5); IR(KBr); 3069m, 3051m, 3011m, 1428s, 1116s, 790s, 733s, 721s, 698s (phenyl ring), 2112s(Si-H) cm^{-1}.; UV(CH_3CN): λ_{max} 236 nm.

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