# The Synthesis of the Polymer Containing the Si-O-phenylene Bond, using Transition Metal Salts as Catalysts[1]

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Various transition metals were found to be effective as catalysts in the dehydrocondensation of phenols and silanes.

$$R_3SiH + PhOH \xrightarrow{\text{metal salt}} R_3SiOPh + H_2$$

The effective species were $PdCl_2$, $H_2PtCl_6 \cdot 6H_2O$, $PtCl_2$, $RhCl_3$, $NiCl_2$, silane-treated $NiCl_2$, $PtI_2$, PtS, Raney Ni, Pd-black, Pt-black, Au-black, $FeCl_3$, $ZnCl_2$, $CuSO_4$, CuCl, Cu-Cr, $Cu(CH_3CO_2) \cdot CuO$, the methyl ethyl ketoxime complex of Pd, $Pt(OX)_3$, and $Pd(OX)_2$. The ineffective species were metal mirrors of Pd, Au, Ag, Pt, and Cu, and the acetylacetonato complex of Ni, Co(II), Co(III), and Cu. The reaction was then extended to the preparation of polymers containing a Si–O–phenylene linkage in the main chain. Dihydricphenols, *e.g.*, bisphenol A, hydroquinone, 4,4′-dihydroxydiphenyl gave high-molecular-weight polymers with an equimolar amount of a dihydrosilane, *e.g.*, diphenylsilane, *p*-toluylmethylsilane and *p*-bisdimethylsilylphenylene, in bulk or in a solvent at temperatures above 150°C. The polymer obtained began to flow above 100°C.

It has been known that Group VIII metals and metal halides catalyze the reaction of an organosilane with compounds containing a hydroxy group:[2–7]

$$R_3SiH + ZOH \xrightarrow{\text{cat.}} R_3SiOZ + H_2$$

$$Z = \text{H, alkyl, aryl, acyl, } etc.$$

Dolgov *et al.*[7] reported that the dehydrocondensation of trialkylsilanes with alcohols and mono- or polyhydric phenols proceeded smoothly at the temperature of 100°C and that gave alkoxy- and phenoxysilanes in almost quantitative yields in the presence of a catalytic amount of colloidal nickel prepared from $NiCl_2$.

We now wish to report in the catalytic activity of various transition metals, especially the salts of Ni, Pd, and Pt, in the reactions of organosilanes and phenols. Among these catalysts, several metal salts, such as $PdCl_2$ and the Pd complex of methyl ethyl ketoxime, initiated the reaction, even at room temperature. Such a reation was used in the preparation of polymers containing siloxane linkage in the main chain from difunctional phenols and difunctional silanes.

Polyaryloxysilanes have been reported to be obtained from difunctional phenols and dianilino- or diphenoxysilanes through a melt-polycondensation reaction procedure at temperatures above 200°C and under reduced pressure.[8,9] Here, a similar polymer was prepared under much milder conditions.

## Experimental

*Materials.* 4,4′-Dihydroxydiphenyl was prepared by the hydrolysis of a diazonium compound derived from commercial 4,4′-benzidine according to the usual method. Recrystallization from dioxane gave pure 4,4′-dihydroxydiphenyl; mp 277—278°C. All the other phenols were commercially available, and they were recrystallized before use. The phenyldimethylsilane, *p*-toluylmethylsilane,[10] diphenylsilane,[11] and *p*-bis(dimethylsilyl)-benzene[12] were prepared by methods previously reported. The purity of the silanes was ascertained by gas chromatography, using dioctyl phthalate (D.O.P.) or thermol-3 as the liquid phase.

*The Reaction of Silane with Phenol.* To a mixture of 3.0 g of phenyldimethylsilane and 2.35 g of phenol, were added 0.02 g of metal salt. In the case of a very active catalyst, $PdCl_2$, for example, a vigorous exothermic reaction occurred, hydrogen gas evolved immediately after the addition of the catalyst at room temperature, and the solution turned dark. In the case of a catalyst with a mild activity, such as $NiCl_2$, an exothermic reaction occurred when the bath temperature was 110°C. After the reaction, the catalyst was removed by filtration and the product was distilled under reduced pressure to give phenoxysilane. The identity of the product was confirmed by infrared spectroscopy and gas chromatographs. The evolved gas was analysed by gas chromatography using a Molecular Sieve 13X column.

*Polycondensation.* The polymerization was carried out by heating a mixture of 5.00 g of bisphenol A and 4.03 g of diphenylsilane with 0.02 g of $PdCl_2$ at 150—160°C for 10 hr. The resulting polymer was purified by reprecipitation from THF-*n*-hexane and dried. The powdery polymer thus obtained was submitted to elemental analysis and other analyses. The other polymers were prepared by a similar method. The viscosity was determined by the use of an Ubellohde viscosimeter at 30°C in a tetrahydrofuran solution and in a concentration of 0.5 g/d*l*.

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1) Presented in part at the meeting of Chemical Society of Japan, Sendai, Oct., 1968.

2) B. N. Dolgov, N. P. Kharitonv, and M. G. Voronkov, *Zh. Obsch. Khim.*, **24**, 1178 (1954).

3) B. N. Dolgov, "Chemistry and Practical Use of Organosilicon Compounds. No. 1," Leningrad (1958), p. 18.

4) A. D. Petrov, V. F. Mironov, V. A. Ponomarenko, and E. A. Chernyshev, "Synthesis of Organosilicon Monomers," Consultant Bureau, New York (1964), pp. 411—413.

5) L. H. Sommer and J. E. Lyons, *J. Amer. Chem. Soc.*, **89**, 1521 (1967).

6) K. Yamamoto, M. Kumada, I. Nakajima, K. Maeda, and N. Imaki, *J. Organometal. Chem.*, **13**, 329 (1968).

7) B. N. Dolgov, Yu. I. Khudobin, and N. P. Kharitonov, *Izvest. Akad. Nauk. SSSR*, **1958**, 113.

8) J. E. Curry and J. D. Byrd, *J. Appl. Polymer Sci.*, **9**, 295 (1965).

9) W. R. Dunnavant, R. A. Markle, P. B. Stickney, J. E. Curry, and J. D. Byrd, *J. Polymer Sci., Part A-1*, **5**, 707 (1967).

10) M. Maienthal, M. Helman, C. P. Haber, L. A. Hymo, S. Carpenter, and A. J. Carr, *J. Amer. Chem. Soc.*, **76**, 6392 (1954).

11) I. E. Baines and C. Eaborn, *J. Chem. Soc.*, **1956**, 1436.

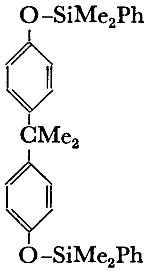
12) R. West and E. G. Rochow, *J. Org. Chem.*, **18**, 303 (1953).

13) Pt complex of 8-hydroxyquinoline.

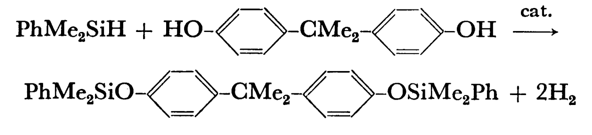
## Results and Discussion

*Activity of Catalyst in the Reaction of Silane and Phenol.* The reaction of phenyldimethylsilane with phenol and bisphenol-A was carried out in the presence of a metal salt as a catalyst. The reaction products were confirmed to be siloxanes by elemental analysis, as is shown in Table 1. The yield of the products was almost quantitative, and the gas evolved was found to be composed of hydrogen and a trace of methane. From these results, therefore, the reaction was considered to proceed as is shown in Eqs. (1) and (2):

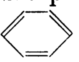
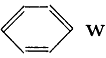
Table 1. Reaction between silane and phenol with $PdCl_2$ as catalyst

| Product | Bp °C/mmHg | Yield % | Elemental analysis Found (Calcd) C% | H% | Si% |
|---|---|---|---|---|---|
| $PhMe_2SiOPh$ | 94—95/0.3 | 93 | 74.19 (74.68) | 7.26 (7.02) | 12.9 (12.3) |
|  | 220—223/0.2 | 92 | 74.63 (74.95) | 7.32 (7.30) | 11.1 (11.3) |

$$PhMe_2SiH + PhOH \xrightarrow{cat.} PhMe_2SiOPh + H_2 \qquad (1)$$



(2)

The infrared spectra of phenyldimethylphenoxysilane, phenyldimethylsilane, and phenol are summarized in Fig. 1. In this figure, the absorptions around 3300, 2100, 920, and 880 cm$^{-1}$ were identified as the absorptions of OH(3300), SiH(2100, 880), and Si-O- (920) respectively. When the reaction proceeded, the absorptions of OH and SiH diminished and the appearance of a new absorption of Si-O- was observed. The rates of the reactions using various kinds of metal derivatives as catalysis were estimated by the volumetry of the hydrogen gas evolved and by infrared spectroscopy. The order of the rates thus obtained may be attributed to the order of the activity of the catalysis used, because all the reactions were carried out under the same conditions. The orders of the activity of catalysts used were as follows:

1) For metal halide:

$PdCl_2 > H_2PtCl_6 \cdot 6H_2O > PtCl_2 > RhCl_3 > NiCl_2$

2) For metal black:

Pd-black > Pt-black ≈ Raney Ni ($W_2$) > Au-black

3) For other metal salts:

$PtI_2$, PtS, $Pt(OX)_3$,[13] $Pd(OX)_2$, methyl ethyl ketoxime of Pd, $CuSO_4$, CuCl, Cu–Cr, $Cu(CH_3CO_2)CuO$, $FeCl_3$, $ZnCl_2$

The metal mirrors of Pd, Au, Ag, Pt, and Cu showed little activity. We tried to use acetylacetonato complexes of Ni, Cu, Co(II), and Co(III) as homogeneous catalysts, but they provoked no reaction. As is shown in Table 2, all the metals which are active as catalysts in the reactions of phenols and silanes were found to be transition metals.

Table 2. The catalytic metals in periodic table of the reaction between phenols and silanes

| VIa | VIIIb | | | Ib | IIb |
|---|---|---|---|---|---|
| Cr | ⬚ Fe | Co | ▣ Ni | ☐ Cu | ⬚ Zn |
| Mo | ☐ Ru | ☐ Rh | ▣ Pd | Ag | |
| W | | | ▣ Pt | ☐ Au | Hg |

▣: highly active; ☐: active; ⬚: slightly active.

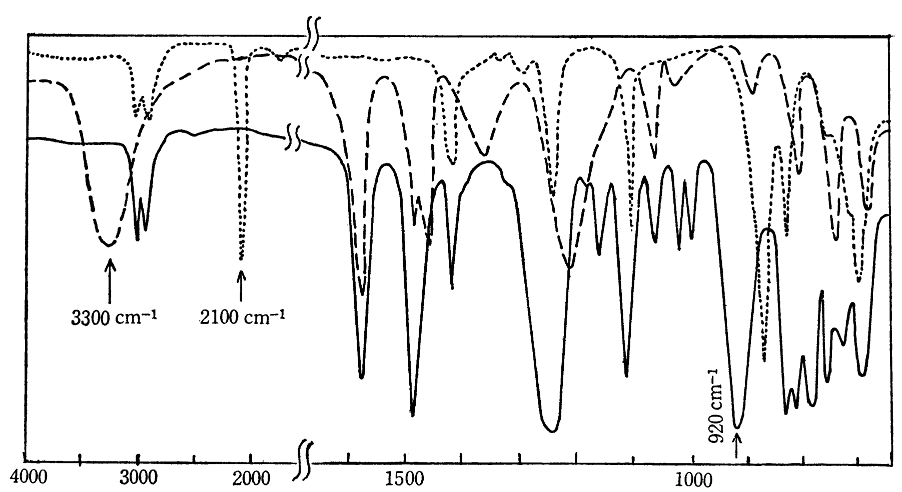


Fig. 1. Infrared spectra of phenyldimethylsilane, phenol, and phenyldimethylphenoxysilane.

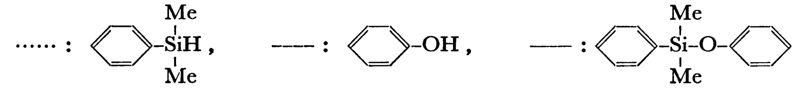


TABLE 3. BULK OR SOLUTION POLYMERIZATION OF DIHYDRIC AND DIHYDROSILANES

| Dihydric phenol | Dihydro silane | Polymerization condition (in $N_2$) cat. $PdCl_2$ | | | $\eta_{inh}$ in THF at 30 °C | Elemental analysis | | |
|---|---|---|---|---|---|---|---|---|
| | | temp (°C) | time (hr) | solvent | | C% Found (Calcd) | H% Found (Calcd) | Si% Found (Calcd) |
| B.P.A. | TMS | 110 | 20 | none | (0.100)[b] | 75.84<br>(76.62) | 6.84<br>(6.71) | 7.77<br>(7.79) |
| B.P.A. | DPS | 150 | 10 | diglyme | 0.122 | 78.41<br>(79.37) | 6.22<br>(5.92) | 6.47<br>(6.88) |
| HQ. | DPS | 150 | 10 | diglyme | 0.079 | 71.55<br>(74.45) | 4.66<br>(4.86) | 9.35<br>(9.67) |
| DHDP. | DPS | 210 | 1.5 | none | 0.079 | 74.77<br>(78.65) | 5.46<br>(4.95) | 7.10<br>(7.65) |
| DHDP. | BDMSP | 210 | 1.5 | none | 0.103 | 68.39<br>(68.02) | 6.22<br>(6.80) | 15.1<br>(15.0) |
| DHDP. | BDMSP | 160[a] | 12 | THF | (0.090)[b] | 67.96<br>(68.02) | 6.44<br>(6.80) | 15.4<br>(15.0) |

B.P.A. bisphenol A　T.M.S. *p*-toluylmethylsilane
HQ. hydroquinone　D.P.S. diphenylsilane
DHDP. 4,4′-dihydroxydiphenyl　BDMSP. *p*-bis-dimethylsilylphenylene
a) cat: $Pt(OX)_3$　b) in toluene

In these reactions, the reaction mixtures turned dark when heated, and the formation of colloidal metal was observed in the reactions, using almost all of the metal salts. The metal salts seemed to be reduced by silane; the colloidal metal black thus formed had a high catalytic activity in the reaction of silane and phenol. The results will be presented in detail in the following paper.

*Polycondensation.* The polycondensation reactions of various phenols and dihydrosilanes were carried out in bulk (or in solution); the results are shown in Table 3. These polymers tend to flow above 100°C as a consequence of the chain mobility of the silicon-oxygen bond.

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