

Syntheses and Characterization of Disilane Unit Containing Polytitana- and Polyzirconasiloxanes

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Disilane unit containing polytitana- and polyzirconasiloxanes were synthesized by the reaction of 1,1,2,2-tetramethyl-1,2-disilanediol with bis(2,4-pentanedionato)titanium diisopropoxide or bis(2,4-pentanedionato)zirconium diisopropoxide. These polymers consisted of disilane unit and metalloxane bonding as main chain with pendants of methyl and 2,4-pentanedionato groups and terminals of isopropoxy and silanol groups. On the other hand, a cyclotitanasiloxane was prepared by the reaction of 1,1,2,2-tetramethyl-1,2-disilanediol with titanocene dichloride in the presence of triethylamine.

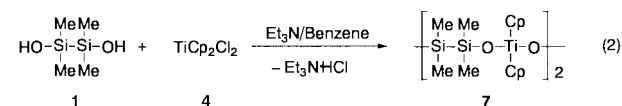
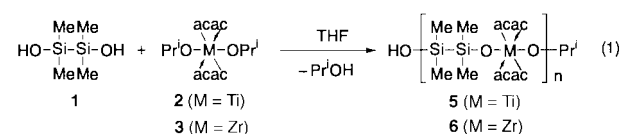
The inorganic polymers, which consist of siloxane and metalloxane bondings in a main chain, are known as polymetallasiloxanes. Polymetallasiloxanes are potential ceramic precursors, since these polymers easily provide ceramic materials in the forms of bulk bodies, fibers, and thin films through molding and pyrolysis procedures. For example, silica-titania fibers are obtained by the dry spinning of polytitanasiloxane and following pyrolysis.

The condensation reaction between silanol and metal alkoxide is one of the desirable process to form metallasiloxane bonding. Since the sequence of the main chain is easily designed and controlled by this process, cyclic,^{1,2} bicyclic,² spiro,³ and cage-type⁴ oligometallasiloxanes have been synthesized. The formation of cyclics, however, provides an obstacle on the isolation and characterization of linear polymetallasiloxanes. The condensation reaction of α,ω -oligosilanediol with metal alkoxide is expected to form a linear alternating copolymer, because a rigid oligosilane backbone may help the formation of linears rather than cyclics. Moreover, this copolymer may be converted to the corresponding linear metallasiloxane by a selective oxidation of silane units.

The backbone structure of Si-Si-O-M-O- is the simplest unit catenation of oligosilane containing metalloxanes. The construction of this sequence has never been reported within the last decade, except for the followings. The first compound was synthesized by a sol-gel reaction of 1,2-dimethoxy-1,1,2,2-tetramethyldisilane or 1,1,2,2-tetramethoxy-1,2-dimethyldisilane, and metal alkoxide to provide a random polymetallasiloxane.⁵ Stannasiloxanes [OSiBu'FSiBu'FOSnBu'₂]₂⁶ and [OSiMePhSiMePhOFe]₂⁷ were synthesized by a controlled reaction.

In this paper, therefore, the preparation of disilane unit containing polytitana- and polyzirconasiloxane will be reported. A condensation reaction between heterofunctional groups was designed as a fundamental reaction to construct a backbone as shown in equations (1) and (2). 1,1,2,2-Tetramethyl-1,2-disilanediol **1** was selected as a disilane unit, while bis(2,4-pentanedionato)titanium(IV) diisopropoxide **2**, bis(2,4-pentane-

dionato)zirconium(IV) diisopropoxide **3**, and titanocene(IV) dichloride **4** were used as a metallasiloxane component. As a result, the backbone structure of Si-Si-O-Ti-O- or Si-Si-O-Zr-O- would be formed by a selective condensation reaction between silanol and isopropoxy or chloro groups.



Disilane containing polytitanasiloxane **5**⁹ was isolated by reprecipitation as yellowish white powder. Compound **5** was decomposed at 154–156 °C without melting and soluble in methanol, acetone, chloroform, THF, and benzene. The ¹H nuclear magnetic resonance (NMR) spectrum showed signals due to silylmethyl (3H, 0.21 ppm) and 2,4-pentanedionato (3H, 1.91 ppm; 3H, 2.02 ppm; 1H, 5.54 ppm), and isopropoxy (0.12H, 1.20 ppm; 0.02H, 4.01 ppm) groups, while no signal due to silanol was observed. Because the signal due to isopropoxy group was so small, a doublet signal was observed as a collapsed broad signal. The ¹³C NMR spectrum showed signals due to silylmethyl (1.9 ppm) and 2,4-pentanedionato (25.4 ppm; 26.9 ppm; 103.0 ppm; 186.6 ppm; 191.5 ppm), and isopropoxy (24.8 ppm; 63.9 ppm) groups. The ²⁹Si NMR spectrum showed a signal due to [Ti(acac)₂OSiMe₂SiMe₂O] unit at -1.9 ppm, which supports a unique environment around a silicon atom. The infrared (IR) spectrum showed absorption peaks ν_{SiOH} , $\nu_{\text{C=O}}$, $\nu_{\text{C=C}}$, δ_{SiCH_3} , and ν_{SiOTi} , that indicate the formation of Si-Si-O-Ti-O- bondings as a main chain with side chain of methyl and 2,4-pentanedionato groups and terminals of silanol and isopropoxy groups. The molecular weight was estimated to be ca. 10000 based on the proton ratio of methyl groups in silylmethyl and isopropyl groups, while ca. 3650 by vapor pressure osmometry. The difference between molecular weights may be due to the production of low molecular weight polymers rather than high molecular weight polymers and a relatively big polydispersity. The metal content of silicon/titanium was 14.3%/12.2%, which agreed with the calculated value 14.2%/12.2%. The ultraviolet absorption in acetonitrile showed a maximum absorption peak at 217 nm, that is due to the disilane unit. These spectral and analytical data support the formation of alternating copolymer of disilane and titanasiloxane bondings.

Disilane containing polyzirconasiloxane **6**¹⁰ precipitated during the reaction as a whitish yellow powder, which decomposed at 179–182 °C. The IR spectrum showed absorption peaks ν_{SiOH} , $\nu_{\text{C=O}}$, $\nu_{\text{C=C}}$, δ_{SiCH_3} , and ν_{SiOZr} , that indicate the formation of Si–Si–O–Zr–O– bonding as a main chain with methyl and 2,4-pentanedionato groups as side chain. The silicon content was 12.7%, which agreed with the calculated value 12.8%. Since **6** was insoluble in common organic solvents such as methanol, acetone, chloroform, THF, benzene, and hexane, the molecular weight of **6** could not be measured.

Cyclotitanasiloxane **7**¹¹ was isolated by reprecipitation as a brown powder, which decomposed at 232–234 °C and soluble in acetone, chloroform, THF, and benzene. The ¹H NMR spectrum showed signals due to silylmethyl (6H, 0.22 ppm) and cyclopentadienyl (5H, 6.29–6.59 ppm) groups, while no signals due to silanol and isopropyl groups were observed. The ¹³C NMR spectrum showed signals due to silylmethyl (1.9 ppm) and cyclopentadienyl (114.3 ppm; 118.8 ppm; 120.1 ppm). The ²⁹Si NMR spectrum showed a signal ascribed to (TiCp₂OSiMe₂SiMe₂O) unit at 3.9 ppm. The IR spectrum showed absorption peaks $\nu_{\text{C=C}}$, δ_{SiCH_3} , and ν_{SiOTi} . The metal content of silicon/titanium was 17.2%/14.7%, which agreed with the calculated value 17.1%/14.7%. The number-average molecular weight was measured by gel permeation chromatography to be 660, which corresponds the molecular weight of [TiCp₂OSiMe₂SiMe₂O]₂ (MW = 653). These spectral and analytical data support the formation of cyclotitanasiloxane which consists of Si–Si–O–Ti–O– catenation. Since this reaction is carried out in benzene, instead of THF, the terminal silanol group of intermediate becomes unstable to promote the cyclization reaction rather than the formation of linear polytitanasiloxanes.

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Dedicated to Prof. Hideki Sakurai on the occasion of his 70th birthday.

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- 9 A tetrahydrofuran (THF, 10 mL) solution of **2** (2.42 g (6.7 mmol)) was added dropwise to a THF (10 mL) solution of **1** (1.00 g (6.7 mmol)) and then heated to 30 °C for 1 h. After the evaporation of solvents under reduced pressure, the resultant was dissolved in THF (10 mL) and then poured into hexane (300 mL) with vigorous stirring. Filtration and drying under reduced pressure provided **5**. Yield: 2.16 g (82%).
- 10 A tetrahydrofuran (THF, 10 mL) solution of **3** (2.71 g (6.7 mmol)) was added dropwise to a THF (10 mL) solution of **1** (1.00 g (6.7 mmol)) and then heated to 30 °C for 1 h. After the evaporation of the solvent under reduced pressure, the resultant was dried under reduced pressure provided **6**. Yield: 2.61 g (90%).
- 11 A benzene (60 mL) solution of **1** (1.00 g (6.7 mmol)), triethylamine (1.35 g (13 mmol)), and **4** (1.66 g (6.7 mmol)) was heated at 40 °C for 3 h. After filtration of triethylamine hydrogen chloride, the solvents were removed under reduced pressure. The resultant was dissolved in benzene (10 mL) and then poured into hexane (300 mL) with vigorous stirring. Filtration and drying under reduced pressure provided **7**. Yield: 0.52 g (24%).