Preparation and Properties of Novel Titanio- and Zirconiosiloxane Compounds

Takahiro Gunji,* Tsutomu Kitakatsu, and Yoshimoto Abe

Department of Industrial Chemistry, Faculty of Science and Technology, Science University of Tokyo,
2641 Yamazaki, Noda, Chiba 278

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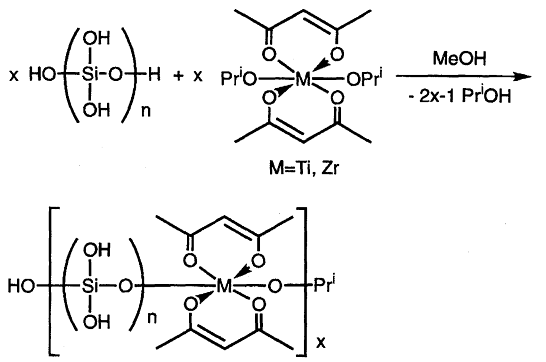
Syntheses and characterization of titaniosiloxane and zirconiosiloxane compounds were investigated. Titaniosiloxane and zirconiosiloxane compounds were prepared by the reaction of di-*t*-butoxymethoxysilanol [DBMS] with titanium or zirconium alkoxides.

DBMS was subjected to the reaction with bis(acetylacetonato)titanium diisopropoxide and titanium tetraisopropoxide to give titaniosiloxane compounds TS12 and TS14, respectively. Titaniosiloxane compounds were isolated by distillation or sublimation. TS12 was estimated to be *cis*-form from its ^{13}C NMR spectrum in $CDCl_3$. TS14 was stable in solution, but apt to decompose after isolation.

ZS12 and ZS14 were prepared by the reaction of DBMS with bis(acetylacetonato)zirconium diisopropoxide and zirconium tetraisopropoxide, respectively. The isolation of ZS12 and ZS14 by distillation or recrystallization was difficult because of decomposition and high solubility, and the formation of ZS12 and ZS14 was confirmed by ^{1}H, ^{13}C, and ^{29}Si NMR and IR spectra.

The precursor method has been examined as a new method for the preparation of oxide ceramics. In this method, ceramics are prepared by formation and pyrolysis of the inorganic precursor polymers. Consequently, ceramics having various properties can be prepared by controlling the structures of precursor polymers, because the characteristics of the inorganic precursor polymers would affect the properties of the ceramics. Metallosiloxane compounds are one of the best precursor candidates for the preparation of SiO_2–M_xO_y oxide ceramics by precursor method. SiO_2–TiO_2 and SiO_2–ZrO_2 ceramics have been prepared by the pyrolysis of polytitaniosiloxane or polyzirconiosiloxane, which were synthesized by the reaction of silicic acid with acetylacetonato chelate compounds of titanium(IV) and zirconium(IV) in methanol, respectively, according to the Eq. 1. The polytitaniosiloxane and polyzirconiosiloxane were random block copolymers.[1] On the other hand, the reaction of silanediol with acetylacetonato chelate compound of titanium or zirconium was investigated according to Eq. 2, with the aim of controlling the sequence of silicon and titanium or zirconium atoms at the atomic level.[2] As a result, cyclic titaniosiloxane or zirconiosiloxane compounds were obtained selectively in high yield, and neither polytitaniosiloxane nor polyzirconiosiloxane were formed. In this work, therefore, preparation of titaniosiloxane or zirconiosiloxane compounds was investigated according to Eqs. 3 and 4 to obtain new titaniosiloxane or zirconiosiloxane compounds with well defined molecular sequence with the aim of the formation of polymetallosiloxane by selective hydrolysis of methoxy group, which is more hydrolyzable than *t*-butoxy group.



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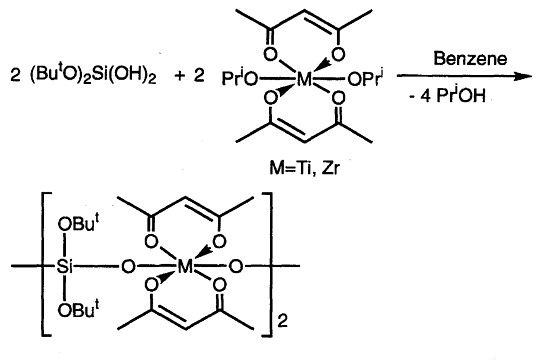

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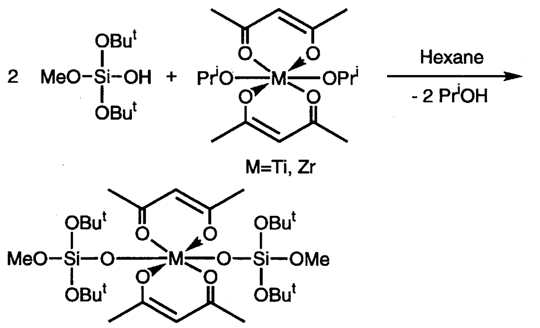

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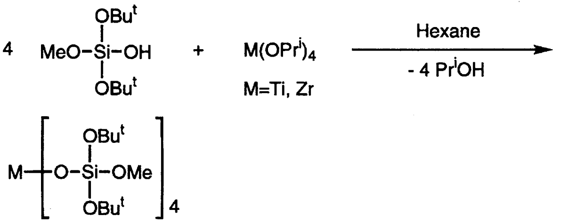

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Results and Discussion

Titaniosiloxane compounds, TS12 and TS14, were purified by distillation or sublimation in a reasonable yield. TS14 was liquefied by decomposition after purification, but it was stable in a common organic solvent except for water. However, the zirconiosiloxane compounds such as ZS12 and ZS14 were not purified.

Progress of the reactions was followed by NMR and IR spectra of products. In the ^{29}Si NMR spectra, a signal due to DBMS at −86.0 ppm disappeared and another signal appeared at higher magnetic field. ^{1}H NMR also indicated the disappearance of the signal due to the silanol group of DBMS. The IR spectrum showed the disappearance of the absorption peak at 3400 cm^{-1} ascribed to v_{SiOH} and an appearance of a new peak due to $v_{\mathrm{Si-O-Ti}}$ or $v_{\mathrm{Si-O-Zr}}$ bond at around 1000 cm^{-1}. These spectral data clearly indicate that the reaction takes place.

The reactions were also monitored by GC analysis of the reaction mixture. In every reaction, isopropyl alcohol was formed in quantitative yield, while t-butyl alcohol was not detected. The GC analysis shows that the silanol group in DBMS attacks the metal atom of the alkoxide or chelate compound to form a titaniosiloxane or zirconiosiloxane bond. On the other hand, DBMS was stable versus self-condensation or degradation. As a result, DBMS reacts selectively with titanium or zirconium alkoxides.

Synthesis of Titaniosiloxane Compounds: TS12 and TS14. TS12 was isolated as an orange viscous liquid in 96% yield by distillation under reduced pressure. The IR spectrum of TS12 indicates the disappearance of the absorption peak due to silanol at ca. 3400 cm^{-1} and the appearance of the absorption peak due to the Si–O–Ti linkage at 920 cm^{-1}. The ^{1}H NMR spectrum shows signals due to t-BuO, MeO, and acac groups at reasonable chemical shifts with the expected integral ratio. In addition, eight signals were observed in the ^{13}C NMR spectrum of TS12, which were ascribed to t-BuO, MeO, and acac groups, and the ^{29}Si NMR spectrum indicated a signal at $\delta=-97.0$. The metal analysis data were also in good agreement with the calculated value for TS12.

Figure 1 shows the ^{13}C NMR spectrum of TS12. The signals at $\delta=24.9$ and 26.6 and those at $\delta=185.7$ and 191.7 indicate that two kinds of methyl and carbonyl groups exist in different spatial positions. Since our recent research revealed that the acac groups in a bis(acetylacetonato)titanium diisopropoxide mainly exist in *cis* form and they are perpendicular to one another,[3] those in TS12 are considered to be perpendicular to one another so that two kinds of NMR signals appear as shown in Fig. 2.

TS14 was isolated as a colorless solid by sublimation at the temperatures of 135—160 °C (0.05 mmHg, 1 mmHg=133.322 Pa) in 85% yield. TS14 was soluble in many common organic solvents and it was stable in such a solution. TS14, however, turned to a transparent pasty solid when isolated and stored in a sealed glass tube, even under reduced pressure. TS14, therefore, was confirmed by ^{1}H, ^{13}C, and ^{29}Si NMR spectra, IR spectrum, mass spectrum and metal analysis for the crude material. In the ^{1}H NMR spectrum, two signals were observed at $\delta=1.3$ and 3.3, which were ascribed to t-BuO group and MeO group, respectively, with the

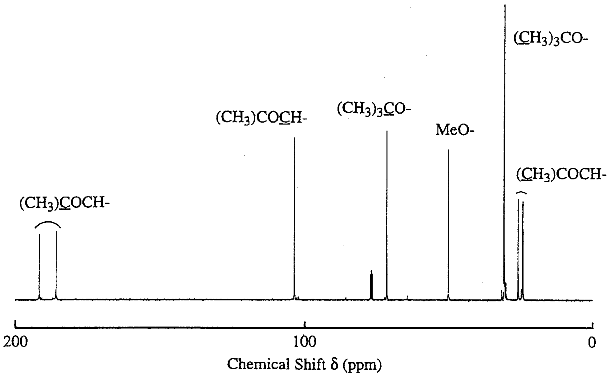

Fig. 1. ^{13}C NMR spectrum of TS12 in CDCl$_3$ with complete decoupling.

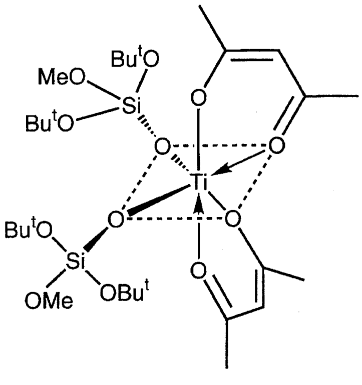

Fig. 2. Estimated structure for TS12.

disappearance of the signal due to silanol at δ=4.3.

Figure 3 shows the GPC traces of TS14 before (a) and after (b) aging. TS14 was stored at room temperature in a sealed bottle under reduced pressure for one week after isolation. Figure 3(a) was measured just after isolation, which exhibits a large peak at the elution volume of 19 ml with a small peak at 25.5 ml. Figure 3(b), however, shows a broad peak at 17 ml with a peak at 25.5 ml. Figure 3(b) clearly shows the decomposition of TS14. In addition, Fig. 4 shows the IR spectra of TS14 before (a) and after (b) aging. The IR spectrum shown in Fig. 4(a) supports the structure of TS14 with a large absorption peak at 920 cm^{-1}. On the other hand, Fig. 4(b) shows an increase of the absorption peak due to the Si–O–Si bond with a decrease of the absorption peak due to the Si–O–Ti bond. The spectral change shown in Fig. 4 supports the decomposition of TS14 and formation of polysiloxane.

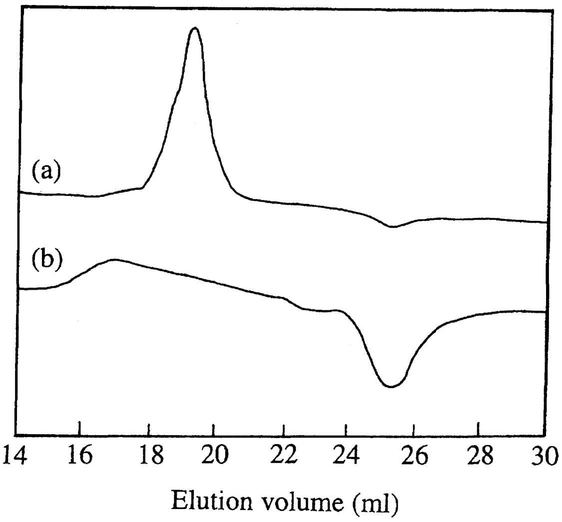

Fig. 3. GPC traces of TS14 before (a) and after (b) storage at room temperatures for one week.

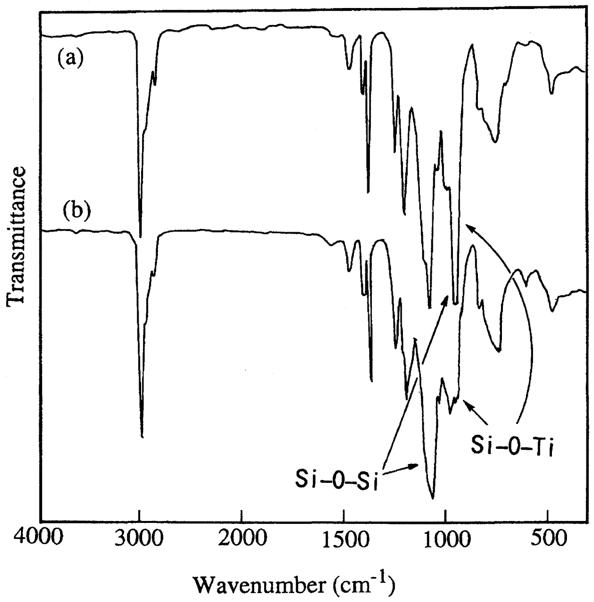

Fig. 4. IR spectra of TS14 before (a) and after (b) storage at room temperatures for one week.

Synthesis of Zirconiosiloxane Compounds: ZS12 and ZS14. ZS12 was obtained as an orange viscous liquid, which was difficult to purify by reprecipitation, recrystallization, or distillation. The DTA-TG analysis under nitrogen atmosphere showed two endothermic peaks at 117 and 400 °C. Total weight loss showed fairly good agreement with the theoretical zirconia content of ZS12. In addition, no sublimation was observed at temperatures below 117 °C, even under reduced pressure (below 0.05 mmHg). As a result, ZS12 was characterized as a crude product without further purification. The results of ^{1}H, ^{13}C, and ^{29}Si NMR spectra, IR spectrum and metal analysis supported the formation of ZS12.

The ^{13}C NMR spectrum of ZS12 showed six signals due to *t*-butoxy and acac groups. In contrast to TS12, methyl and carbonyl groups in acac groups gave a unique signal, respectively, which indicates that acac groups are in the same spatial positions.

ZS14 was obtained as colorless solid. ZS14 decomposed at temperatures of 90 °C under nitrogen atmosphere, and no sublimation was observed below the decomposition temperatures. The IR spectrum of ZS14 showed the absorption peaks due to hydroxy group and Si–O–Zr linkage. The ^{1}H NMR spectrum showed the signals due to *t*-BuO and MeO groups at δ=1.3 and 3.3, respectively, together with the signals due to *i*-PrOH at δ=4.5 and 6.0. In addition, the metal analysis showed good agreement with the structure of ZS14 with one added isopropyl alcohol. As a result, the formation of an isopropyl alcohol adduct of ZS14 was proposed: Zr[OSi(OBu^{t})$_2$(OMe)]$_4$(Pr^{i}OH).

Experimental

Materials. Tetrachlorosilane (Shin-Etsu Chemical Co., Ltd.) and the materials (Wako Pure Chemical Co., Ltd.) *t*-butyl alcohol, isopropyl alcohol, methanol, pyridine, ether, benzene, acetone, hexane, and acetylacetone were dried and purified by conventional methods.

Titanium tetraisopropoxide (TPT) (Matsumoto Pharmaceutical Company Co., Ltd.) was purified by distillation under reduced pressure.

Zirconium tetraisopropoxide (TPZ)–isopropyl alcohol (1/1) (Zr(OPr^{i})$_4$·Pr^{i}OH) and alcohol free TPZ were prepared by the reaction of zirconium tetrachloride (Japan Energy Co., Ltd.) with isopropyl alcohol.[4)]

Bis(acetylacetonato)titanium diisopropoxide (PTP) and bis(acetylacetonato)zirconium diisopropoxide (PZP) were prepared by the reaction of TPT or TPZ with acetylacetone.[5)]

Preparation of Di-*t*-butoxymethoxysilanol (DBMS). All reactions were carried out under nitrogen atmosphere. To a solution of tetrachlorosilane (SiCl$_4$, 112 ml (1.0 mol)) in 190 ml of benzene was added dropwise a solution of *t*-butyl alcohol (188 ml (2.0 mol)), pyridine (161 ml (2.0 mol)), and 500 ml of benzene at 0 °C followed by reflux for 1

h. After filtration of salts and evaporation of solvents, di-*t*-butoxydichlorosilane was distilled under reduced pressures. Yield 211 g (86%), bp 74.5—75.5 °C (17 mmHg).

To a solution of di-*t*-butoxydichlorosilane (205 g (0.85 mol)) in 500 ml of benzene was added dropwise a solution of methanol (26.4 g (0.85 mol)), pyridine (68.4 g (0.85 mol)), and 150 ml of benzene at 0 °C, then refluxed for 1 h. After filtration of salts and the evaporation of solvents, di-*t*-butoxymethoxychlorosilane was distilled under reduced pressures. Yield 176 g (86%), bp 75.5—77.4 °C (21 mmHg).

Finally, to a solution of di-*t*-butoxymethoxychlorosilane (167 g (0.75 mol)) and 500 ml of benzene was added dropwize a solution of water (13.5 g (0.75 mol)), pyridine (59.3 g (0.75 mol)), and 150 ml of ether at −5 °C followed by reflux for 30 min. (Water, pyridine, and ether were well mixed by addition of acetone to the mixture.) After filtration of salts and evaporation of solvents, di-*t*-butoxymethoxysilanol (DBMS) was distilled under reduced pressures. Yield 127 g (76%), bp 48.2 °C (0.5 mmHg).

Synthesis of TS12. Under nitrogen atmosphere, to a solution of bis(acetylacetonato)titanium diisopropoxide (PTP, 1.4 g (0.005 mol)) in 15 ml of hexane was added dropwise a solution of DBMS (2.2 g (0.01 mol)) in 15 ml of hexane at room temperature. Solvents were removed under reduced pressure to give a orange viscous solution of TS12, $(acac)_2Ti[OSi(OBu^t)_2(OMe)]_2$. TS12 was purified by distillation under reduced pressure. Bp 151.0—152.0 °C (0.075 mmHg). ^{1}H NMR δ=1.3 (9H, s, $-\mathbf{OBu}^t$), 1.9 (6H, s, C–$\mathbf{CH_3}$), 3.3 (1H, s, –**OMe**), 5.0 (1H, s, –**CH**=). ^{13}C NMR δ=24.9 ($\mathbf{C}H_3CO$–), 26.6 ($\mathbf{C}H_3CO$–), 31.2 (($\mathbf{C}H_3)_3CO$–), 50.5 ($\mathbf{C}H_3O$–), 72.0 ($(CH_3)_3\mathbf{C}O$–), 103.9 (–**C**H=), 185.7 ($CH_3\mathbf{C}O$–), 191.7 ($CH_3\mathbf{C}O$–). ^{29}Si NMR δ=−97.0. IR 1600 ($\nu_{C=O}$), 1520 ($\nu_{C=C}$), 1380 (ν_{C-C}), 1070 (ν_{Si-O-C}), 920 cm^{-1} ($\nu_{Si-O-Ti}$). Found: C, 48.8; H, 8.0; Si, 8.04; Ti, 7.17%. Calcd for $C_{28}H_{56}O_{12}Si_2Ti$: C, 48.8; H, 8.19; Si, 8.15; Ti, 6.95%.

Synthesis of TS14. Under nitrogen atmosphere, to a solution of titanium tetraisopropoxide ($Ti(OPr^i)_4$, 0.71 g (0.0025 mol)) in 15 ml of hexane, was added dropwise a solution of DBMS (2.2 g (0.01 mol)) in 15 ml of hexane at 0 °C. Solvents were removed under reduced pressures to give a transparent viscous solution of TS14, $Ti[OSi(OBu^t)_2(OMe)]_4$. TS14 was purified by sublimation. Bp (sublimation) 135—160 °C (0.05 mmHg). ^{1}H NMR δ=1.3 (6H, s, $-\mathbf{OBu}^t$), 3.3 (1H, s, –**OMe**). ^{13}C NMR δ=31.6 (($\mathbf{C}H_3)_3CO$–), 50.8 ($\mathbf{C}H_3O$–), 72.8 ($(CH_3)_3\mathbf{C}O$–). ^{29}Si NMR δ=−97.5. IR 1380 (ν_{C-C}), 1070 (ν_{Si-O-C}), 950 cm^{-1} ($\nu_{Si-O-Ti}$). Mass spectrum found 859 (M^+-73), 710 (M^+-222). Found: Si, 12.06; Ti, 5.21%. Calcd for $C_{36}H_{84}O_{16}Si_4Ti$: Si, 12.04; Ti, 5.13%.

Synthesis of ZS12. Under nitrogen atmosphere, to a solution of bis(acetylacetonato)zirconium diisopropoxide (PZP, 0.71 g (0.005 mol)) in 15 ml of hexane was added dropwise a solution of DBMS (2.2 g (0.01 mol)) in 15 ml of hexane at room temperatures. Solvents were removed under reduced pressures to give a orange viscous solution of ZS12, $(acac)_2Zr[OSi(OBu^t)_2(OMe)]_2$. Mp 117 °C (Decomposition). ^{1}H NMR δ=1.3 (9H, s, $-\mathbf{OBu}^t$), 1.9 (6H, s, C–$\mathbf{CH_3}$), 3.3 (1H, s, –**OMe**), 5.4 (1H, s, –**CH**=). ^{13}C NMR δ=26.4 ($\mathbf{C}H_3CO$–), 31.4 (($\mathbf{C}H_3)_3CO$–), 50.5 ($\mathbf{C}H_3O$–), 71.7 ($(CH_3)_3\mathbf{C}O$–), 104.4 (–**C**H=), 191.1 ($CH_3\mathbf{C}O$–). ^{29}Si NMR δ=−94.4. IR 1580 ($\nu_{C=O}$), 1520 ($\nu_{C=C}$), 1370 (ν_{C-C}), 1060 (ν_{Si-O-C}), 960 cm^{-1} ($\nu_{Si-O-Zr}$). Found: Si, 7.82; Zr, 12.82%. Calcd for $C_{28}H_{56}O_{12}Si_2Zr$: Si, 7.67; Zr, 12.46%.

Synthesis of ZS14. Under nitrogen atmosphere, to a solution of zirconium tetraisopropoxide ($Zr(OPr^i)_4\ Pr^iOH$, 0.97 g (0.0025 mol)) in 15 ml of hexane, was added dropwise a solution of DBMS (2.2 g (0.01 mol)) in 15 ml of hexane at room temperature. Solvents were removed under reduced pressure to give a transparent viscous solution of ZS14. Mp 90 °C (Decomposition). ^{1}H NMR δ=1.3 (72H, s, $-\mathbf{OBu}^t$), 1.3 (6H, d, $OCH(\mathbf{CH_3})_2$), 3.3 (12H, s, –**OMe**), 4.5 (1H, m, $OC\mathbf{H}(CH_3)_2$), 6.0 (1H, b, –**OH**). ^{13}C NMR δ=24.8 (($\mathbf{C}H_3)_2CHO$–), 31.6 (($\mathbf{C}H_3)_3CO$–), 50.8 ($\mathbf{C}H_3O$–), 67.8 ($(CH_3)_2\mathbf{C}HO$–), 72.8 ($(CH_3)_3\mathbf{C}O$–). ^{29}Si NMR δ= −94.4. IR 3300 (ν_{OH}), 1380 (ν_{C-C}), 1070 (ν_{Si-O-C}), 950 cm^{-1} ($\nu_{Si-O-Zr}$). Found: Si, 10.81; Zr, 9.10%. Calcd for $C_{39}H_{92}O_{17}Si_4Zr$: Si, 10.84; Zr, 8.80%.

Measurements and Analysis. ^{1}H NMR spectra were measured by using JEOL PMX-60SI spectrometer in carbon tetrachloride. ^{13}C NMR spectra were measured by using JEOL FX-90Q spectrometer at the resonance frequency of 22.43 MHz with complete decoupling in chloroform-*d*. ^{29}Si NMR spectra were measured by using JEOL FX-90Q spectrometer at the resonance frequency of 17.80 MHz in chloroform-*d*. Chromium trisacetylacetonato was added in 3 mol% concentration as a ^{29}Si spin-lattice relaxation agent. IR spectra were measured by using Hitachi 260-50 IR spectrophotometer with the CCl_4 solution method. Mass spectroscopy was measured by using a Shimadzu GCMS-QP2000A gas chromatograph mass spectrometer. Ionization: EI (70 eV). Gas Chromatography (GC) was performed by using an Ohkura GC-103. Gel Permeation Chromatography (GPC) was performed by using HPLC system (Nihon Seimitsu Kagaku CO., Ltd.). Column: Tosoh H2500HXL and Shodex A-801; Detector: Reflective index detector RI-3H type (Nihon Bunseki Kogyo Co., Ltd.); Eluent: THF. DTA-TG analysis was carried out by using a Rigaku TAS-100 Thermoflex (high temperature type) under nitrogen atmosphere. Silicon, titanium, and zirconium contents were determined by the wet method described in our previous paper.[1)]

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