Syntheses of Fluoroalkyl and Fluoroaryl Titanates

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Tetrakis(1H,1H-perfluoroethyl) titanate, $Ti(OCH_2CF_3)_4$, tetrakis(1H,1H-perfluoropropyl) titanate, $Ti(OCH_2CF_2CF_3)_4$, tetrakis(2,2,2-trifluoro-1-methylethyl) titanate, $Ti[OCH(CH_3)CF_3]_4$, tetrakis(2,2,2-trifluoro-1,1-dimethylethyl) titanate, $Ti[OC(CH_3)_2CF_3]_4$, tetrakis((1H,1H,3H-perfluoropropyl) titanate, $Ti(OCH_2CF_2CF_2H)_4$, tetrakis(1H,1H,5H-perfluoropentyl) titanate, $Ti[OCH_2(CF_2CF_2)_2H]_4$, tetrakis(1H,1H,7H-perfluoroheptyl) titanate, $Ti[OCH_2(CF_2CF_2)_3H]_4$, and tetrakis(1H,1H,9H-perfluorononyl) titanate, $Ti[OCH_2(CF_2CF_2)_4H]_4$, were prepared by the reaction of titanium tetrachloride with fluoro-substituted alcohols in the presence of ammonia. Tetrakis(pentafluorophenyl) titanate, $Ti(OC_6F_5)_4$ was synthesized by the ester interchange reaction of tetraisopropyl titanate with pentafluorophenyl acetate. These compounds were characterized on the basis of chemical analysis, IR, ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra. Tetrakis(2,2,2-trifluoro-1,1-dimethylethyl) titanate was the monomeric in nitrobenzene, but tetrakis(1H,1H-perfluoroethyl) titanate and tetrakis(1H,1H-perfluoropropyl) titanate were associated in the same solvent, in which the highest association numbers observed were 3.5 and 1.5, respectively. These titanates were very sensitive to moisture and easy to decompose to give titanium oxide and alcohol or phenol.

Metal alkoxides have been the subject of extensive research because of their potential as precursor materials for several applications, such as new-ceramics, adhesives and coupling agents, which are molecular bridges between the interface of an inorganic filler and an organic polymer. Many of alkyl or aryl titanates and their halogenated derivatives were prepared[1] and the reactivities of these titanates towards various types of donors such as amides, amines, ethers, and amino acids have been reported.[2] The number of worldwide commercial applications for coupling agents established using monoalkoxy-type titanates such as titanium isopropoxide tris(2-heptylundecanoyloxide) are now very substantial, as indicated by over one hundred patents.[3–6]

In recent years, dramatic developments have been made in the utilization of organofluoro compounds because of the resulting materials with high performance. However, only a few research reports concerning fluoro-substituted alkoxides of metals have appeared in the literature. Redwood and his co-workers[7,8] have prepared the trifluoromethoxides of heavier alkali metals by the reaction of carbonyl fluoride on a suspension of alkali metal fluoride in acetonitrile. Kapoor et al.[9,10] reported syntheses of 2,2,2-trifluoroethoxides and 2,2,2-trifluoro-1-(trifluoromethyl)ethoxides of metals, such as germanium, titanium, zirconium, niobium, and tantalum, by the reaction of metal chlorides with the appropriate alcohol. Mazdiyasni et al.[11] reported syntheses of 2,2,2-trifluoro-1-(trifluoromethyl)ethoxides of aluminium, silicon, germanium, titanium, zirconium, and hafnium, through reactions of suitable metal chlorides with sodium 2,2,2-trifluoro-1-(trifluoromethyl)ethoxides. In these reports, the fluoro-substituted alkoxides of metals studied have been limited to only one or two species of low molecular weight or simple structural alcohols, as a starting material. However, the chemical and physical properties of fluoro-substituted alkoxides of metals having a longer $-CF_2-$ bonding or a bulky structure in the alkyl moiety should be important for making new type titanate coupling agents, which possess a dispersing capacity of inorganic particles in a fluorinated organic polymer. Especially, these alkoxides are expected to be stable against moisture, because many compounds having the fluorinated carbon structure possess water repellency.

In this paper, the results of the syntheses and characterizations of fluoro-substituted alkoxides of titanium are reported. The characterizations of these compounds were achieved through chemical analysis, IR, ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra. Molecular association of these compounds in nitrobenzene has been also determined.

Experimental

Special precautions were adopted to avoid any hydrolysis of the starting materials and products, and all experiments were carried out under an atmosphere of purified nitrogen to preclude oxygen and moisture.

Materials. 1H,1H-Perfluoroethanol, CF_3CH_2OH (bp 74—75 °C) (**1**), 1H,1H-perfluoro-1-propanol, $CF_3CF_2CH_2OH$ (bp 81 °C) (**2**), 1,1,1-trifluoro-2-propanol, $CF_3CH(CH_3)OH$ (bp 75—76 °C) (**3**), 2-trifluoromethyl-2-propanol, $CF_3C(CH_3)_2OH$ (bp 80—81 °C) (**4**) were commercially available. 1H,1H,3H-Perfluoro-1-propanol, $HCF_2CF_2CH_2OH$ (bp 109—110 °C) (**5**), 1H,1H,5H-perfluoro-1-pentanol, $H(CF_2CF_2)_2CH_2OH$ (bp 139—140 °C) (**6**), 1H,1H,7H-perfluoro-1-heptanol, $H(CF_2CF_2)_3CH_2OH$ (bp 169—170 °C) (**7**), and 1H,1H,9H-perfluoro-1-nonanol, $H(CF_2CF_2)_4CH_2OH$ (bp 63 °C/53 Pa) (**8**) were received as gifts from Daikin Industries, Ltd. Pentafluorophenol, C_6F_5OH (bp 143 °C) (**9**) was obtained from PCR Inc. These alcohols, except **8**, were kept over anhydrous magnesium sulfate for a few days and distilled over a small amount of calcium hydride. **8** and **9** were purified by distillation. Titanium tetrachloride (bp

136 °C) and tetraisopropyl titanate (bp 84 °C/133 Pa) were commercially available and purified by distillation. The solvents used were purified by usual methods.

Measurements. IR spectra were measured in a liquid film or by a KBr method with a Hitachi 215 Grating Spectrophotometer. Pulsed Fourier Transform 100-MHz ^{1}H and 25-MHz ^{13}C NMR were run in THF-d_8 with TMS as an internal standard using a JEOL JNR-PX-100 spectrometer at room temperature: ^{1}H NMR spectra (pulse repetition time, 5 s; number of accumulations, 4) and ^{13}C NMR spectra (pulse repetition time, 5 s; number of accumulations, 18500). The resonance peaks of the ^{13}C NMR spectra were assigned by the peak splitting pattern using the method of off-resonance. The FT mode 90-MHz ^{19}F NMR was recorded at 27 °C on a JEOL JNM-FX-90Q in THF with fluorobenzene (−113.6 ppm[12] from $\mathrm{CFCl_3}$ in $\mathrm{CDCl_3}$) as an external standard: pulse repetition time, 0.5 s; number of accumulations, 20. The assignments of the ^{19}F NMR spectra were referred to in the databook.[12] The molecular association numbers of some fluoro-substituted alkoxides of titanium were measured using the cryoscopic method in nitrobenzene. Gas chromatograms were performed with a Hitachi 063 (PEG-6000 supported Chromosorb A NAW 30/60 mesh 5 m packed column, TCD) or Hitachi G-3000 gas chromatograph (OV-1 25 m Fused capillary column, FID) and these intensities were measured with a Hitachi 834 chromato processor.

Analytical Methods. Titanium was determined gravimetrically as titanium oxide after the hydrolysis of titanium alkoxides. The fluoroalkoxyl group was determined by using gas chromatography after the hydrolysis of titanium alkoxide to alcohol by adding aqueous ammonia.

Synthesis of Tetrakis(1H,1H-perfluoroethyl) Titanate, $\mathbf{Ti(OCH_2CF_3)_4}$ (T1). To a stirred 1H,1H-perfluoroethanol **1** 13.8 g (138 mmol), 5.3 g (28 mmol) of titanium tetrachloride was slowly added using a dropping funnel below 5 °C in a two-necked 200-ml flask connected with a dropping funnel and a reflux condenser. The reaction was exothermic. After 30 min, the mixture was allowed to react at 80 °C. The evolution of hydrogen chloride was observed continuously for about 5—8 h. After an addition of 100-ml benzene, dry ammonia gas was slowly introduced to the system for about 3 h at 10 °C; the mixture was reluxed for 30 min. The completion of the substitution reaction was checked by flame testing a clear solution using copper wire. After removing the ammonium chloride formed by filtration, benzene and excess **1** were evaporated using a vacuum-evaporator. A transparent colorless liquid **T1** was obtained by distillation (yield 10.2 g, 82.9%). **T1** gradually transformed into a white waxy solid: bp 114 °C/133 Pa (lit,[9] bp 94 °C/27 Pa) mp 62 °C; IR 2940, 2870, 1450, 1405, 1365, 1280, 1150, 1080, 960, 827, 695, 670 cm^{-1}; ^{1}H NMR δ=4.60 ($\mathrm{CH_2}$, q, J=8.9 Hz); ^{13}C NMR δ=59.7—70.3 (b, m), 124.3 (a, q, J=279.4 Hz) for $(\mathrm{C^aF_3C^bH_2O})_4\mathrm{Ti}$; ^{19}F NMR δ=36.0 (m (=multiplet)). Found: Ti, 10.7; RfO (fluoroalkoxyl group), 89.3%. Calcd for $\mathrm{C_8H_8F_{12}O_4Ti}$: Ti, 10.8; RfO, 89.2%.

Synthesis of Tetrakis(1H,1H-perfluoropropyl) Titanate, $\mathbf{Ti(OCH_2CF_2CF_3)_4}$ (T2). To a stirred 1H,1H-perfluoro-1-propanol **2** (29.5 g, 0.20 mol), titanium tetrachloride (7.5 g, 0.04 mol) was added below 5 °C. After removing hydrogen chloride formed, 100 ml of THF was added and dry ammonia gas was introduced into the solution. The product was purified by distillation to give **T2** (yield 19.5 g, 75.7%): bp 125 °C/1067 Pa, mp 56 °C; IR 2940, 2875, 1350, 1190, 1090, 1008, 948, 926, 800, 730, 688 cm^{-1}; ^{1}H NMR δ=4.81 ($\mathrm{CH_2}$, q, J=15.1 Hz); ^{13}C NMR δ=70.4 (c, m), 114.7 (b, t(=triplet)(q(=quartet)), J=253.6(36.0) Hz), 120.4 (a, q(t), J=286.0(35.7) Hz) for $(\mathrm{C^aF_3C^bF_2C^cH_2O})_4\mathrm{Ti}$; ^{19}F NMR δ=28.1 (a, m), −13.3 (b, t, J=13.4 Hz) for $(\mathrm{CF_3^aCF_2^bCH_4O_4})\mathrm{Ti}$. Found: Ti, 7.29; RfO, 92.2%. Calcd for $\mathrm{C_{12}H_8F_{20}O_4Ti}$: Ti, 7.44; RfO, 92.6%.

Synthesis of Tetrakis(2,2,2-trifluoro-1-methylethyl) Titanate, $\mathbf{Ti[OCH(CH_3)CF_3]_4}$ (T3). The synthesis of **T3** was carried out in a similar manner to that of **T1**. The colorless liquid product was purified by distillation to give **T3** (yield 45.5%): bp 59 °C/133 Pa; IR 3000, 2920, 1458, 1385, 1282, 1180, 1130, 1108, 1030, 960, 800, 704 cm^{-1}; ^{1}H NMR δ=1.42 ($\mathrm{CH_3}$, d, J=6.4 Hz), 4.62 (CH, septet, J=6.4 Hz); ^{13}C NMR δ=18.0 (b, d, J=1.5 Hz), 79.5 (c, q, J=32.1 Hz), 126.4 (a, q, J=282.3 Hz) for $[\mathrm{C^aF_3(C^bH_3)C^cHO}]_4\mathrm{Ti}$; ^{19}F NMR δ=31.4 (d(=doublet), J=7.3 Hz). Found: Ti, 9.73; RfO, 90.2%. Calcd for $\mathrm{C_{12}H_{16}F_{12}O_4Ti}$: Ti, 9.58; RfO, 90.4%.

Synthesis of Tetrakis(2,2,2-trifluoro-1,1-dimethylethyl) Titanate, $\mathbf{Ti[OC(CH_3)_2CF_3]_4}$ (T4). In a similar manner to that mentioned above, **T4** was synthesized. The white solid product was purified by distillation to give **T4** (yield 79.8%): bp 78 °C/67 Pa, mp 42 °C; IR 2990, 2945, 1460, 1385, 1320, 1155, 1120, 1013, 1000, 900, 775, 670 cm^{-1}; ^{1}H NMR δ=1.44 ($\mathrm{CH_3}$, s); ^{13}C NMR δ=22.8 (b, s(=singlet)), 24.3 (small peak)(b, s), 71.8 (c, q, J=29.3 Hz), 126.5 (small peak)(a, q, J=284.3 Hz), 137.5 (a, q, J=284.3 Hz) for $[\mathrm{C^aF_3(C^bH_3)_2C^cO}]_4\mathrm{Ti}$; ^{19}F NMR δ=29.1(s). Found: Ti, 8.83; RfO, 91.2%. Calcd for $\mathrm{C_{16}H_{24}F_{12}O_4Ti}$: Ti, 8.62; RfO, 91.4%.

Syntheses of Tetrakis(1H,1H,3H-perfluoropropyl) Titanate, $\mathbf{Ti(OCH_2CF_2CF_2H)_4}$ (T5), Tetrakis(1H,1H,5H-perfluoropentyl) Titanate, $\mathbf{Ti[OCH_2(CF_2CF_2)_2H]_4}$ (T6), Tetrakis(1H,1H,7H-perfluoroheptyl) Titanate, $\mathbf{Ti[OCH_2(CF_2CF_2)_3H]_4}$ (T7) and Tetrakis(1H,1H,9H-perfluorononyl) Titanate, $\mathbf{Ti[OCH(CF_2CF_2)_4H]_4}$ (T8). These procedures and purification techniques were almost the same as that for the preparation of **T2**.

T5 was colorless liquid (yield 52.4%): bp 131 °C/27 Pa; IR 2945, 2860, 1455, 1405, 1353, 1285, 1240, 1230, 1200, 1100, 1045, 945, 935, 835, 800, 750, 690 cm^{-1}; ^{1}H NMR δ=4.70 ($\mathrm{CH_2}$, t, J=14.7 Hz), 5.43 ($\mathrm{HCF_2}$, t(t), J=52.7(3.7) Hz); ^{13}C NMR δ=70.6 (c, t, J=24.9 Hz), 109.5 (a, t(t), J=249.0 (37.1) Hz), 115.0 (b, t(t), J=249.0(27.3) Hz) for $(\mathrm{HC^aF_2C^bF_2C^cH_2O})_4\mathrm{Ti}$; ^{19}F NMR δ=−27.5 (a, d, J=53.2 Hz), −27.6 (a, d, J=53.2 Hz), −15.0 (b, m) for $(\mathrm{HCF_2^aCF_2^bCH_2O})_4\mathrm{Ti}$. Found: Ti, 8.31; RfO, 91.4%. Calcd for $\mathrm{C_{12}H_{12}F_{16}O_4Ti}$: Ti, 8.38; RfO, 91.6%.

T6; colorless liquid (yield 69.1%): bp 148 °C/27 Pa; IR 2945, 2870, 1450, 1401, 1359, 1285, 1245, 1160, 1140, 1085, 986, 948, 895, 805, 763, 710 cm^{-1}; ^{1}H NMR δ=4.94 ($\mathrm{CH_2}$, t, J=14.7 Hz), 5.38 ($\mathrm{HCF_2}$, t(t), J=51.4(4.0) Hz); ^{13}C NMR δ=76.7 (e, t, J=24.4 Hz), 112.5 (a, t(t), J=255.6(31.7) Hz), 113.7 (b, t(m), J=253.9 Hz), 115.9 (c, t(m), J=266.0 Hz), 120.0 (d, t(t), J=257.1(31.5) Hz) for $(\mathrm{HC^aF_2C^bF_2C^cF_2C^dF_2C^eH_2O})_4\mathrm{Ti}$; ^{19}F NMR δ=−25.9 (a, d, J=53.1 Hz), −18.2 (b, s), −13.0 (c, m), −9.1 (d, m) for $(\mathrm{HCF_2^aCF_2^bCF_2^cCF_2^dCH_2O})_4\mathrm{Ti}$. Found: Ti, 4.93; RfO, 95.6%. Calcd for $\mathrm{C_{20}H_{12}F_{32}O_4Ti}$: Ti, 4.93; RfO, 95.1%.

T7; slightly brown liquid (yield 73.2%): bp 214 °C/400 Pa; IR 2950, 2885, 1455, 1403, 1365, 1290, 1265, 1195, 1140, 1095, 1000, 955, 860, 802, 763, 740, 720, 655 cm^{-1}; ^{1}H NMR δ=4.88 ($\mathrm{CH_2}$, t, J=13.7 Hz), 6.48 ($\mathrm{HCF_2}$, t(t), J=51.8(5.8) Hz);

^{13}C NMR δ=72.9 (g, t, J=24.0 Hz), 109.5 (a, t(t), J=253.0 (31.5) Hz), 111.6 (b, t(x(=no detectable)), J=274.4 Hz), 112.2 (c, t(x), J=272.2 Hz), 112.9 (d, t(x), J=269.8 Hz), 114.3 (e, t(x), J=270.7 Hz), 117.2 (f, t(t), J=257.9(27.8) Hz) for $\mathrm{(HC^aF_2C^bF_2C^cF_2C^dF_2C^eF_2C^fF_2C^gH_2O)_4Ti}$; ^{19}F NMR δ=−25.9 (a, d, J=53.1 Hz), −17.4 (b, s), −10.9 (c and d, m), −9.7 (e, m), −8.9 (f, m) for $\mathrm{(HCF_2^aCF_2^bCF_2^cCF_2^dCF_2^eCF_2^fCH_2O)_4Ti}$. Found: Ti, 3.45; RfO, 96.6%. Calcd for $\mathrm{C_{28}H_{12}F_{48}O_4Ti}$: Ti, 3.49; RfO, 96.5%.

T8; slightly brown waxy solid (yield 56.8%): bp 210 °C/1.3 Pa; IR 2950, 2870, 1455, 1403, 1370, 1352, 1290, 1200, 1140, 1017, 995, 950, 880, 830, 805, 780, 738, 710, 660 cm^{-1}; ^{1}H NMR δ=4.90 ($\mathrm{CH_2}$, t, J=13.9 Hz), 6.32 ($\mathrm{HCF_2}$, t(t), J=50.5(5.4) Hz); ^{13}C NMR δ=71.8 (i, t, J=24.7 Hz), 109.5 (a, t(t), J=253.3(31.7) Hz), 111.6 (b, t(m), J=264.9 Hz), 112.2 (c, t(x=no detectable), J=258.8 Hz), 112.7 (d, t(x), J=262.5 Hz), 112.7 (e, t(x), J=264.9 Hz), 113.6 (f, t(x), J=266.7 Hz), 113.8 (g, t(x), J=271.0 Hz), 117.6 (h, t(t), J=257.9(29.5) Hz) for $\mathrm{(HC^aF_2C^bF_2C^cF_2C^dF_2C^eF_2C^fF_2C^gF_2C^hF_2C^iH_2O)_4Ti}$; ^{19}F NMR δ=−25.8 (a, d, J=51.3 Hz), −17.2 (b, s), −10.7 (c and d, m), −9.4 (e to g, m), −9.5 (h, m) for $\mathrm{(HCF_2^aCF_2^bCF_2^cCF_2^dCF_2^eCF_2^fCF_2^gCF_2^hCH_2O)_4Ti}$. Found: Ti, 2.59; RfO, 97.6%. Calcd for $\mathrm{C_{36}H_{12}F_{64}O_4Ti}$: Ti, 2.70; RfO, 97.3%.

Synthesis of Tetrakis(pentafluorophenyl) Titanate, Ti($\mathbf{OC_6F_5}$)$_4$ (T9). **T9** was prepared by a method involving an ester interchange. 18.4 g (0.1 mol) of pentafluorophenol **9** was allowed to react with excess potassium carbonate in 15 ml of water at room temperature. After completion of the reaction, potassium pentafluorophenolate was extracted to tetrahydrofuran (THF). A white solid potassium pentafluorophenolate was obtained after evaporating THF at room temperature under vacuum. A colorless liquid pentafluorophenyl acetate, $\mathrm{C_6F_5OCOCH_3}$, (bp 170—172 °C) was obtained by distillation after reacting excess acetyl chloride and potassium pentafluorophenolate at 50 °C. Tetraisopropyl titanate (0.70 g, 2.5 mmol) and pentafluorophenyl acetate (2.88 g, 12.7 mmol) were mixed in a 50-ml distillation flask and heated at 100 °C for 10 h; 0.82 g (yield 42.7% vs. tetraisopropyl titanate) of dark-red solid **T9** (bp 193 °C/0.67 Pa, mp 97—99 °C) was obtained by a fractional distillation i. vac., after removing almost all isopropyl acetate formed and excess pentafluorophenyl acetate by distillation under reduced pressure (2000 Pa) at 80 °C. IR; 1600, 1510, 1487, 1350, 1515, 1190, 1175, 1165, 1090, 1030, 990, 980, 850, 735, 715, 662 cm^{-1}; ^{1}H NMR no proton; ^{13}C NMR δ=140.9 (para, d(t), J=244.7(13.9) Hz), 143.8 (meta, d(m), J=249.1 Hz), 146.1 (ortho, d(m), J=249.1 Hz); ^{19}F NMR δ=120.0 (para, t(m), J=22.0 Hz), 123.6 (meta, t, J=20.2 Hz), 129.8 (ortho, d, J=20.2 Hz). Found: Ti, 6.35%. Calcd for $\mathrm{C_{24}F_{20}O_4Ti}$: Ti, 6.14%.

Results and Discussion

These obtained fluoro-substituted titanates were sensitive to moisture and decomposed to give titanium oxide and alcohol or phenol. Considering the hydrolytic nature of these obtained compounds, metal and fluoro-substituted alkoxyl group analyses were in fair agreement with the calculated values.

The NMR spectra of tetrakis(1H,1H,5H-perfluoropentyl) titanate, $\mathrm{Ti[OCH_2(CF_2CF_2)_2H]_4}$, **T6** as an example are shown in Figs. 1—3. These spectrum patterns resembled that of the starting alcohol, except for an absence of the OH group. The ^{13}C NMR spectrum pattern was relatively complicated (see Fig. 2). The resonance peaks of a carbon atom were coupled magnetically with the geminal and vicinal fluorine atoms. In the case of the ^{13}C NMR spectra having a fluorinated carbon atom, it is well-known that the peak intensities of a carbon bonded to a hydrogen atom, such as $\mathrm{HCF_2}$–, $\mathrm{H_2CF}$–, or –HCF–, are stronger than that of a carbon bonded only to fluorine atoms, such as $\mathrm{CF_3}$– or –$\mathrm{CF_2}$–. A group of peaks of the terminal $\mathrm{HCF_2}$– (triplet(triplet)) was observed with the strongest one at 112.5 ppm from TMS in THF-d_8, and the other –$\mathrm{CF_2}$– peaks were weaker and split in a complicated manner.

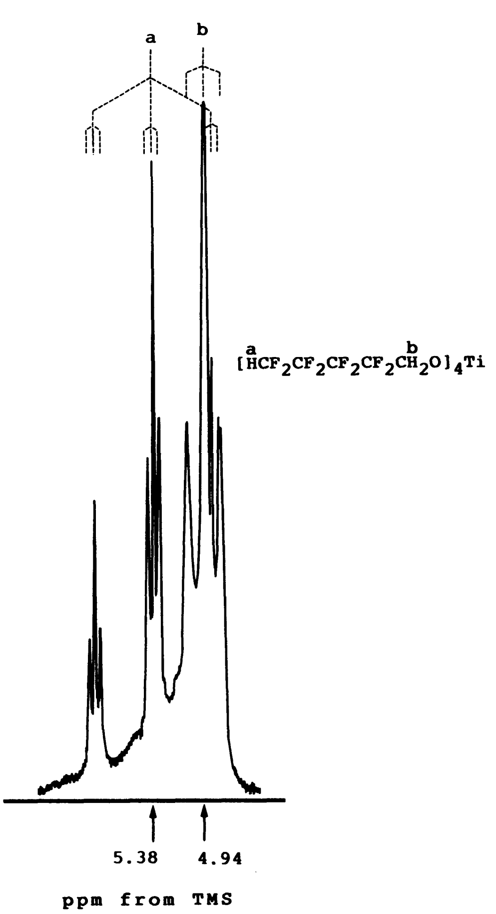

Fig. 1. Pulsed Fourier transform 100 MHz ^{1}H NMR spectrum of [$\mathbf{HCF_2CF_2CF_2CF_2CH_2O}$]$_4$**Ti** in THF-$d_8$ (recorded at r.t.; internal standard, TMS; pulse repetition time, 5 s; number of accumulations, 4).

In ^{19}F NMR, the resonance peaks of –$\mathrm{CF_3}$ of tetrakis(1H,1H-perfluoroethyl) titanate **T1**, were observed as multiplet peaks centered at 36.0 ppm from fluorobenzene in THF. However, the –$\mathrm{CF_3}$ peaks of the starting alcohol, 1H,1H-perfluoroethanol **1**, were triplet at 34.7 ppm. The same difference in the ^{19}F NMR was detected between tetrakis(1H,1H-perfluoropropyl) titanate **T2** and 1H,1H-perfluoro-1-propanol

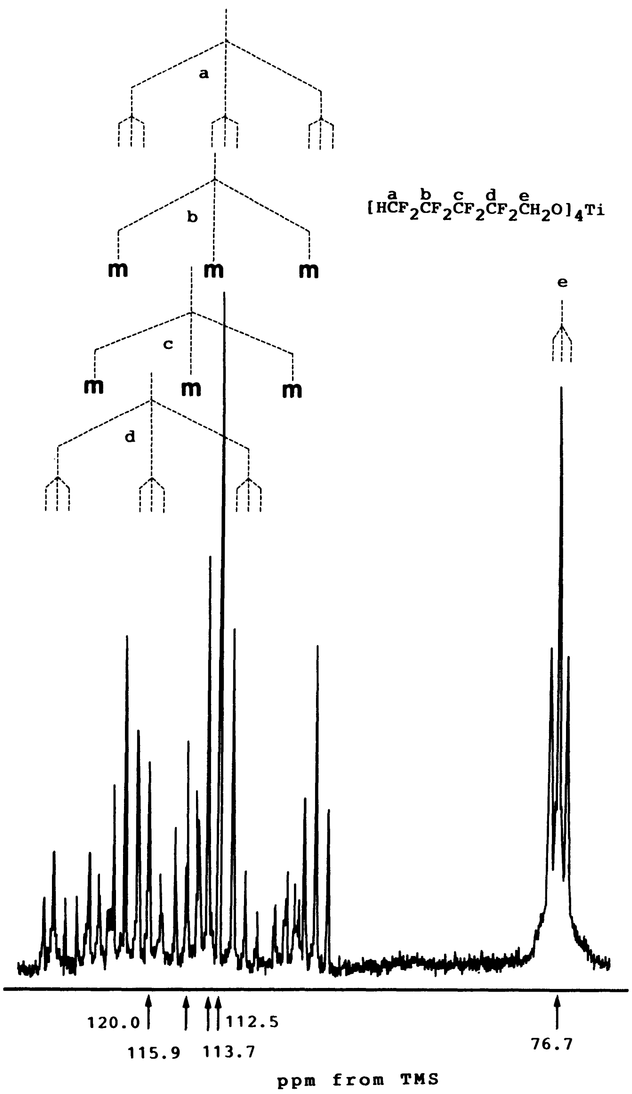

Fig. 2. Pulsed Fourier transform 25 MHz ^{13}C NMR spectrum of [$HCF_2CF_2CF_2CF_2CH_2O$]$_4$Ti in THF-d_8 (recorded at r.t.; internal standard, TMS; pulse repetition time, 5 s; number of accumulations, 18500), "m" shows multiplet.

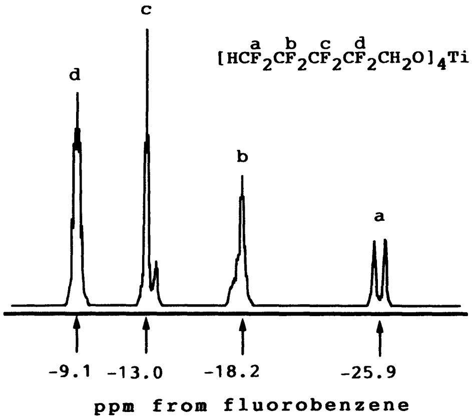

Fig. 3. Pulsed Fourier transform 90 MHz ^{19}F NMR spectrum of [$HCF_2CF_2CF_2CF_2CH_2O$]$_4$Ti in THF (recorded at 27 °C; external standard, fluorobenzene; rocked with benzene-d_6; pulse repetition time, 0.5 s; number of accumulations, 20).

2, though the observation could not differentiate between tetrakis(2,2,2-trifluoro-1,1-dimethylethyl) titanate **T4** and 2-trifluoromethyl-2-propanol **4**. These results suggest that the magnetic circumstances of the fluorine atoms composed of four -CF_3 groups in **T4** are equivalent. On the other hand, the fluorine atoms making four -CF_3 groups in **T1** and **T2** form a more complicated magnetic circumstances by molecular association with the mutual titanate molecules in THF. This suggestion was confirmed by measurements of the molecular association number of these three titanates (see later).

Mazdiyasni et al.[11] again tried to synthesize either aluminium or group-IV metal hexafluoro-substituted isopropoxides by an ammonia method described in the literature.[9,10] They found that the only poor yield product obtained was the fluorinated alkoxides of metal having two molecules of ammonia. They also described that the ammonia was apparently bonded strongly enough to prevent its loss during vacuum sublimation or fractional distillation at relatively high temperatures.

The present authors carried out ammonia analyses for a few products by the Kjeldal method. The ammonia contents (0.0025, 0.0127, 0.0023, and 0.0034%) were obtained from **T1**, **T2**, **T4**, and tetrakis(1H,1H,3H-perfluoropropyl) titanate **T5**, respectively. Analytical data showed that either the ammonia molecule did not form ammonia adducts of pure titanates or it dissociated from the ammonia adducts of titanates during vacuum distillation at relatively high temperatures. From these results the ammonia method for these titanate syntheses has been found to be a suitable method, since these analytical values indicate that ammonia contamination only represented one ammonia molecule per ca. 200—1500 titanate molecules.

Molecular Association Numbers of Some Titanates: The molecular association numbers of three titanates, tetrakis(1H,1H-perfluoroethyl) titanate **T1**, tetrakis-(1H,1H-perfluoropropyl) titanate **T2**, and tetrakis-(2,2,2-trifluoro-1,1-dimethylethyl) titanate **T4**, were measured by the cryoscopic method in nitrobenzene. The results are shown in Fig. 4. The bulky **T4**, which has the most bulky fluoro-substituted alkyl groups among the three titanates, shows a monomeric in nitrobenzene. The association number obtained is unity, an independent concentration in the concentration range 0.2—1.8 wt%, as shown by the open squares. The maximum molecular association numbers of **T2** and **T1** were 1.5 (closed circles) and 3.5 (open circles), respectively, and the numbers became larger as the concentration increased within the same concentration range. Considering the electronegativity of the

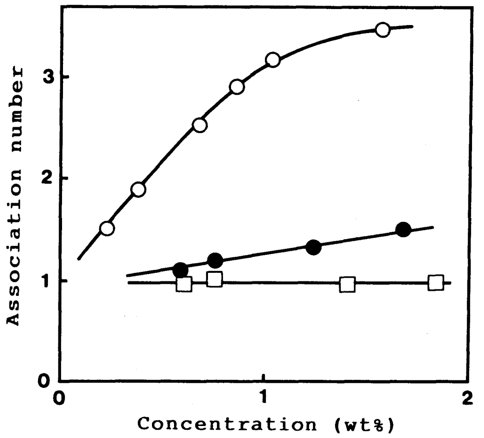

Fig. 4. Association curves of $\mathbf{Ti(OCH_2CF_3)_4}$ (**T1**) (○), $\mathbf{Ti(OCH_2CF_2CF_3)_4}$ (**T2**) (●), and $\mathbf{Ti[(OC(CH_3)_2CF_3)]_4}$ (**T4**) (□): measured by the cryoscopic method in nitrobenzene. The bulky **T4** shows a monomeric in nitrobenzene and the association number is unity being concentration independently in the concentration range 0.2—1.8 wt%. The maximum molecular association numbers of **T2** and **T1** were 1.5 and 3.5, respectively, and the numbers become larger with concentration increase in the same concentration range.

fluorine atom, the partial charge density ($\delta+$) on the titanium atom of these fluoroalkyl titanates should be higher than those of the alkyl titanates. Therefore, the electronegative alkoxyloxygen ($\delta-$) of the fluoroalkyl titanate would be favorable to coordinate to the titanium atom of another fluoroalkyl titanate molecule; in other words, a fluoroalkyl titanate would be subject to form a molecular association. However, the results of the molecular association measurement indicate that the molecular association numbers of these titanates were influenced by a steric effect of the fluoro-substituted alkoxyl groups, rather than their inductive effect. These results also elucidate the difference of the magnetic circumstances of the fluorine atoms in **T1**, **T2**, and **T4** mentioned above, i.e. the magnetic circumstances of the fluorine atoms composed of four $-CF_3$ groups in the monomeric **T4** are equivalent, while the fluorine atoms making four $-CF_3$ groups in the associated **T1** and **T2** form a more complicated magnetic circumstances.

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