Complexation of Titanium Alkoxides with Pentenoic Acid and Allylacetoacetate and Their Hydrolysis and Addition Reactions with H-Silanes

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Received 8 March 2004; accepted 19 July 2004
DOI 10.1002/app.21315
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Complexation reactions of titanium tetraethoxide [$Ti(OEt)_4$] and titanium tetra-*n*-butoxide [$Ti(OBu^n)_4$] with 3-pentenoic acid (PA) and allylacetoacetate (AAA), in a 1 : 1*M* ratio, were studied in ethanol solution at room temperature. ^{13}C-NMR and FTIR spectra showed that all PA and AAA completely reacted with both titanium alkoxides. Hydridosilane compounds such as triethoxysilane and triethylsilane were added to titanium chelate complexes in a 1 : 1*M* ratio. The investigation of products by ^{13}C- and ^{29}Si-NMR and FTIR showed additions of –SiH to the C═C double bond. The hydrolysis of titanium–PA and AAA complexes, by water in 1 : 4 ratios, resulted in released PA in an amount of 10% and AAA of 20%. The stability of hydrolyzed products was investigated by ^{13}C-NMR, ^{29}Si-NMR, and FTIR. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 95: 790–796, 2005

Key words: NMR; FTIR; silicones; 3-pentenoic acid; inorganic materials

INTRODUCTION

Metal alkoxides have been used in the synthesis of glasses, ceramics, and organic–inorganic materials.[1–3] Metal alkoxides are more sensitive toward hydrolysis–condensation reactions, which lead to precipitation of the metal oxo polymer network. The control of reactivity of metal alkoxides can be made with organic chelate ligands.[4] The organic additives such as organic acids, β-ketoesters, and diketones influence the functionality of precursors and control the degree of polycondensation of the reaction products.[4–6] Unsaturated complexing ligands are of interest for polymerization and addition reactions of metal alkoxide precursors in the course of sol–gel processes.

The most commonly used complexing ligands containing unsaturated bonds are carboxylic acids such as acrylic and methacrylic acid (McOH)[5,7]:

$$Zr(OPr^n)_4 + 2McOH \rightarrow [Zr(OPr^n)_2(OMc)_2]_n + 2Pr^nOH \quad (1)$$

The other commonly used complexing organic compounds with unsaturated bonds are β-ketoesters such as allylacetoacetate (AAA)[6,8,9] and methacryloxyethylacetoacetate[9,10]:

$$Zr(OBu^n)_4 + AAA \rightarrow Zr(OBu^n)_3(AAA) + Bu^nOH \quad (2)$$

When these two organic groups were added to a solution of metal alkoxides, some of the alkoxy groups from the starting material were replaced with these chelate–organic groups.[4,5,9,10] Addition of water to these organically modified metal alkoxide complexes leads to hydrolysis of alkoxy groups and condensation reactions resulting in inorganic networks,[5] as follows:

$$[Zr(OPr^n)_2(OMc)_2]_n + H_2O \rightarrow [ZrO(OMc)_2]_n + 2Pr^nOH \quad (3)$$

This is a result of both chelate effect and steric hindrance effect. In this connection the hydrolytic stability of the unsaturated organic complex ligands is essential for the formation of organic–inorganic network structures. A hydrolysis of the complex would decompose the bonds between metal and unsaturated ligands and consequently it would disturb the formation of a homogeneous organic–inorganic polymer structure. Previous works showed a restricted hydrolytic stability of some metal alkoxide complexes.[9] Depending on the complexation ratio (organic additives/M) and the hydrolysis ratio (H_2O/M), sols, gels, or precipitates are obtained. From the sols and gels, thin films, fibers, and transparent monoliths can be obtained.[4,11]

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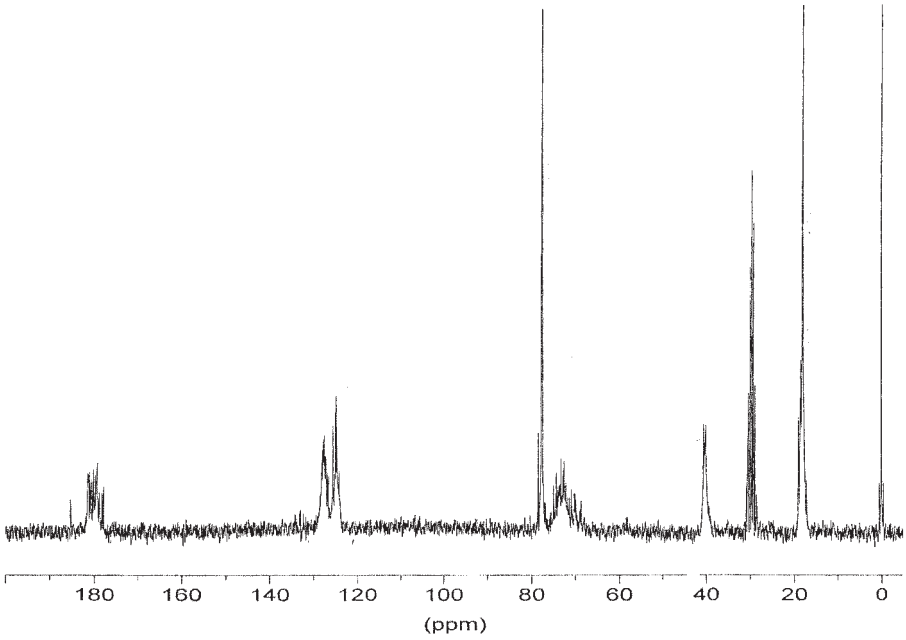


Figure 1 ^{13}C-NMR spectrum of $[Ti(OEt)_3(PA)]_n$.

The diversity of applications of inorganic–organic hybride materials prepared from metal alkoxides and alkoxysilane has motivated increasing interest in silicon materials. These applications are for scratch- and abrasion-resistant coating on organic polymers, photochromic, antireflective, catalysis (or enzyme-like properties), for photographic films and ink-receiving layers, for membranes, and contact lens materials in the optical industry.[11,12] The addition reaction of –SiH containing silanes with unsaturated metal alkoxide complexes is a way to introduce siloxane bonds to metal alkoxide precursors and to modify and to extend their reactions.[13] The concern of this work was to broaden the synthesis and hydrolytic stability of titanium alkoxide complexes with 3-pentenoic acid and allylacetoacetate. Furthermore, the activity of the C═C double bonds toward addition reactions in the complexes and in the free unsaturated compounds constitutes a major focus of this study.

EXPERIMENTAL

The ^{13}C- and ^{29}Si-NMR spectra were recorded on a Bruker AC200 spectrometer (Bruker, Darmstadt, Germany) at fields of 4.7 T [^{29}Si-NMR: inverse gated sequence; external reference: tetramethylsilane (TMS); pulse repetition time (r.t.): 40 s; pulse angle (p.a.): 63°; number of scans (n.s.): 48. ^{13}C-NMR: inverse gated sequence; r.t.: 10 s; p.a.: 60°; n.s: 80–400]. Infrared spectra of products were recorded on a Bruker IFS-25 spectrometer. Chemicals such as titanium tetraethoxide [$Ti(OEt)_4$, 95%, Merck, Darmstadt, Germany], titanium tetra-*n*-butoxide [$Ti(OBu^n)_4$, 99%, Aldrich, Milwaukee, WI], allylacetoacetate (AAA, 98%, Aldrich), 3-pentenoic acid (PA, 97%, Fluka, Buchs, Switzerland), triethylsilane [$(C_2H_5)_3SiH$, ABCR GmbH & Co. KG, Karlsruhe, Germany], triethoxysilane [$(C_2H_5O)_3SiH$, ABCR], platinium–divinyltetramethyl disiloxane complex, ethanol, and butanol were used in the experiments without further purification. To prevent molecular complexity, metal alkoxides were dissolved in their parent alcohol. Therefore, ethanol and butanol were used as solvents for metal ethoxide and metal butoxide studies, respectively.

Preparation of $[Ti(OEt)_3(PA)]_n$ (1)

$Ti(OEt)_4$ (0.01 mol) was stirred in 10 g of ethanol for 2 min and 0.01 mol 3-pentenoic acid (*trans*-form > 90%) was added dropwise to the solution. The color changed to light yellow within 1 min. The mixture was vigorously stirred for 2 h at room temperature. The solvent and liberated ethanol were removed from the mixture under reduced pressure (0 mbar) at around 60°C and an orange viscous liquid (gel) was obtained. ^{13}C-NMR ($CHCl_3$) δ ppm: 18.0 (CH_3, PA_c), 19.0 (CH_3, OEt), 40.3 (CH_2, PA_c), 73.2 (OCH_2, OEt), 124.8 (CH_3—CH═, PA_c), 127.7 (═CH—CH_2, PA_c), 181.4 (COO—Ti, PA_c) (Fig. 1). FTIR (in $CHCl_3$): $\nu_{COOasym}$: 1571 cm^{-1} (broad singlet, strong intensity), ν_{COOsym}: 1434 cm^{-1} (singlet, strong intensity). PA: free acid, PA_c: complexed acid.

$$Ti(OEt)_4 + CH_3CH{=}CHCH_2COOH \rightarrow [Ti(OEt)_3(OOCCH_2CH{=}CHCH_3)]_n + EtOH \quad (4)$$

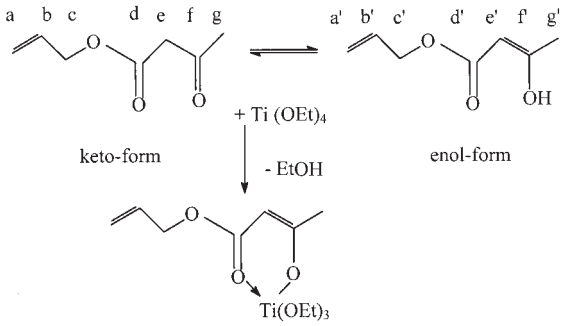


Figure 2 Scheme for the complexation of $Ti(OEt)_4$ with AAA.

Preparation of $[Ti(OBu^n)_3(PA)]_n$ (2)

A preparative procedure analogous to that used above for compound 1 was performed.
^{13}C-NMR ($CHCl_3$) δ ppm: 14.3 ($^4CH_3$, OBu^n), 18.2 (CH_3, PA_c), 19.7 ($^3CH_2$, OBu^n), 35.7 ($^2CH_2$, OBu^n), 40.4 (CH_2, PA_c), 74.0 (O^1CH_2, OBu^n), 125.4 (CH_3—CH═, PA_c), 127.3 (═CH—CH_2, PA_c), 179.0 (COO—Ti, PA_c). About 3% 3-pentenoic acid was uncomplexed by titanium-*n*-butoxide. Signals characteristic for PA appear at δ ppm = 124.1 (CH_3—CH═, PA), 128.5 (═CH—CH_2, PA). FTIR (in $CHCl_3$): $\nu_{COOasym}$: 1571 cm^{-1} (broad singlet, strong intensity), ν_{COOsym}: 1461 cm^{-1} (singlet, strong intensity) (Ti—$O^1CH_2^2CH_2^3CH_2^4CH_3$).

$$Ti(OBu^n)_4 + PA \rightarrow [Ti(OBu^n)_3(PA_c)]_n + Bu^nOH \qquad (5)$$

Preparation of $[Ti(OEt)_3(AAA)]_n$ (3)

$Ti(OEt)_4$ (0.01 mol) was stirred in 10 g of ethanol for 2 min and 0.01 mol allyl acetoacetate was added dropwise to the solution. The solution changed from cloudy to a light yellow color within 1 min. The mixture was vigorously stirred for 2 h at room temperature. The solvent and liberated ethanol were removed from the mixture under reduced pressure (5 mbar) at 60°C and an orange viscous liquid was obtained.
^{13}C-NMR ($CHCl_3$) δ ppm: 18.7 (CH_3, OEt), 25.7 (CH_3, AAA_c, g′), 65.3 [C(O)OCH_2, c′], 73.2 (OCH_2, OEt), 88.4 [C(O)CH C(O), e′], 117.5–118.3 (CH_2═, doublet, a′), 133.9–133.2 (CH═, doublet, b′), 172.4–172.9 (C═C—O—Ti, doublet, f′), 184.5–185.7 (CH_2O—C═O—Ti, doublet, d′). FTIR (in $CHCl_3$): $\nu_{Cdbond]C}$: 1628 cm^{-1} (from enolic form, strong intensity), $\nu_{C—O}$: 1530 cm^{-1} (from enolic form, strong intensity) (Fig. 2).

Hydrolysis of $[Ti(OEt)_3(PA)]_n$ (4)

Compound 1 was prepared as mentioned in the above procedure. Before removal of ethanol, 4 mol water per mole $Ti(OEt)_4$ was added dropwise to the solution and stirred for an additional hour at room temperature. Then, solvent and total liberated ethanol were removed from the mixture under reduced pressure (5 mbar) at 60°C and a beige solid was obtained.
^{13}C-NMR ($CHCl_3$) δ, ppm: 17.9 (CH_3, PA_c), 18.7 (CH_3, OEt), 39.9 (CH_2, PA_c), 71.4 (OCH_2, OEt), 124.3 (CH_3—CH═, PA_c), 127.5 (═CH—CH_2, PA_c), 181.0 (COO—Ti, PA_c). FTIR (in $CHCl_3$): $\nu_{COOasym}$: 1565 cm^{-1} (broad singlet, strong intensity), ν_{COOsym}: 1441 cm^{-1} (singlet, strong intensity). Signals characteristic for 3-pentenoic acid in an amount of 10% (calculated from signal intensity) appear at δ = 122.8 (CH_3—CH═, PA), 129.3 ppm (═CH—CH_2, PA).

Hydrolysis of $[Ti(OBu^n)_3(PA)]_n$ (5)

A preparative procedure analogous to that used above for compound 4 was performed. The solvent used for this hydrolysis reaction was butanol.
^{13}C-NMR ($CHCl_3$) δ, ppm: 14.1 ($^4CH_3$, OBu^n), 18.1 (CH_3, PA_c), 19.3 ($^3CH_2$, OBu^n), 34.5 ($^2CH_2$, OBu^n), 40.0 (CH_2, PA_c), 64.6 (O^1CH_2, OBu^n), 124.6 (CH_3—CH═, PA_c), 127.5 (═CH—CH_2, PA_c), 180.5 (broad signal, COO—Ti, PA_c) (Fig. 3). Signals characteristic for 3-pentenoic acid appear at δ: 124.1 (CH_3—CH═, PA), 128.5 ppm (═CH—CH_2, PA). About 7% 3-pentenoic acid was released from complex by hydrolysis. FTIR (in $CHCl_3$): $\nu_{COOasym}$: 1540 cm^{-1} (broad singlet, strong intensity), ν_{COOsym}: 1435 cm^{-1} (singlet, strong intensity).

Hydrolysis of $[Ti(OEt)_3(AAA)]_n$ (6)

A preparative procedure analogous to that used above for compound 4 was performed.
^{13}C-NMR ($CHCl_3$) δ, ppm: 18.4 (CH_3, OEt), 25.7 (CH_3, AAA_c), 65.3 [C(O)OCH_2, c′], 71.4 (OCH_2, OEt), 88.4 [C(O)CH C(O), e′], 117.5–118.3 (CH_2═, doublet, a′), 133.9–133.2 (CH═, doublet, b′), 172.4–172.9 (C═C—O—Ti, doublet, f′), 184.5–185.7 (CH_2O—C═O—Ti, doublet, d′). FTIR (in $CHCl_3$): $\nu_{C=C}$: 1628 cm^{-1} (from enolic form, strong intensity), $\nu_{C—O}$: 1530 cm^{-1} (from enolic form, strong intensity). Signals characteristic for AAA (keto-form) appear at: 25.4 (CH_3, g), 50.1 [C(O)CH_2C(O), e], 66.1 (OCH_2, c), 119.0 (CH_2═, a), 131.8 (CH═, b), 167.0 (COO, d), 202.8 ppm (C═O, f); 20% AAA was released from complex by hydrolysis.

Reaction of $[Ti(OEt)_3(PA)]_n$ with TREOS (7)

Triethoxysilane (0.01 mol) was added dropwise to a solution of $Ti(OEt)_3(PA)$ (0.01 mol) in 10 g heptane (the ratio of TREOS : PA was kept at 1 : 1). Then, 19.5 mg Pt–divinyltetramethyl disiloxane as catalyst was added. The mixture was refluxed at 80°C for 4 h. After 4 h, the solvent was removed under reduced pressure (~ 10 mbar) at 60°C. The viscous liquid product was brown.
^{29}Si-NMR ($CHCl_3$) δ, ppm: −46.7 [$(EtO)_3$Si—$CH(CH_3)$—, T^0], −49.1 [$(EtO)_3$Si—$CH(CH_2CH_3)$–, T^0], −82.5 [$(EtO)_3$SiO(H), or R (R: organic ligand, Q^0], −89.2 [$(EtO)_3$Si—O—Si–, Q^1].

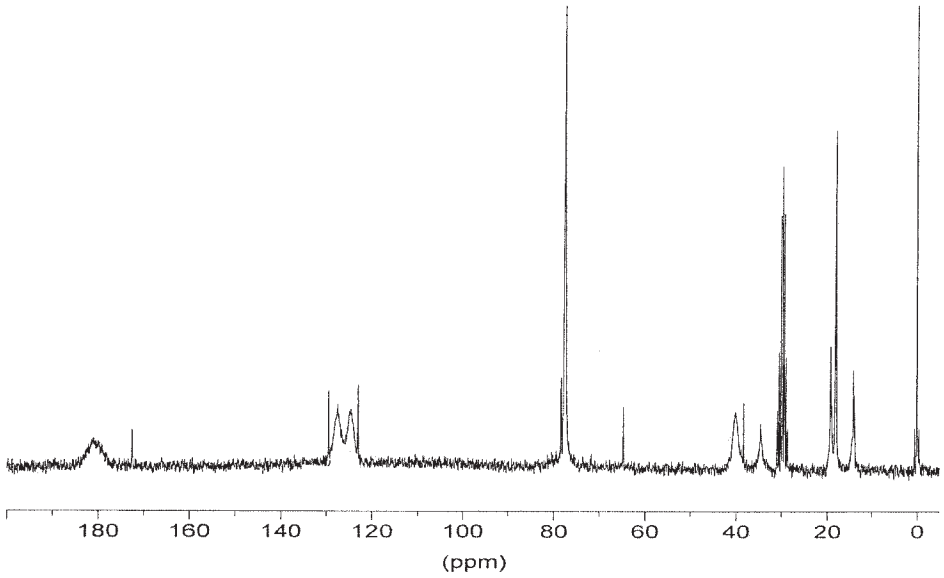


Figure 3 ^{13}C-NMR spectrum of hydrolysis of $[Ti(OBu^n)_3(PA)]_n$.

$$[Ti(OEt)_3(PA)]_n + (EtO)_3SiH \rightarrow [(EtO)_3TiOOCCH_2CH_2CH(-Si(OEt)_3)CH_3]_n + [(EtO)_3TiOOCCH_2CH(-Si(OEt)_3)CH_2CH_3]_n \quad (6)$$

Reaction of $[Ti(OBu^n)_3(PA)]_n$ with TREOS (8)

A preparative procedure analogous to that used above for compound 7 was performed.
^{29}Si-NMR ($CHCl_3$) δ, ppm: −46.6 [$(EtO)_3Si$—$CH(CH_3)$–, T^0], −48.5 [$(EtO)_3Si$—$CH(CH_2CH_3)$–, T^0], −54.2 (T^1), −82.6 [$(EtO)_3SiO(H)$, or (R), Q^0], −89.2 [$(EtO)_3Si$—O—Si–, Q^1], −96.7 (Q^2).

Reaction of $[Ti(OEt)_3(AAA)]_n$ with TREOS (9)

A preparative procedure analogous to that used above for compound 7 was performed.
^{29}Si-NMR ($CHCl_3$) δ, ppm: −46.7 [$(EtO)_3Si$—$CH(CH_3)$–, T^0], −46.9 [$(EtO)_3Si$—$CH(CH_2CH_3)$–, T^0], −53.9 (T^1), −82.4 [$(EtO)_3SiO(H)$ or (R), Q^0], −89.2 [$(EtO)_3Si$—O—Si–, Q^1].

Reaction of $[Ti(OEt)_3(PA)]_n$ with TRES (10)

Triethylsilane (0.01 mol) was added dropwise to a solution of $Ti(OEt)_3(PA)$ (0.01 mol) in 10 g heptane (the ratio of TRES to PA was 1 : 1). Then, 19.5 mg Pt–divinyltetramethyl disiloxane as catalyst was added. The mixture was refluxed at 80°C for 4 h. After 4 h, the solvent was removed under reduced pressure (~ 10 mbar) at 60°C. The viscous liquid product was brown.
^{29}Si-NMR ($CHCl_3$) δ, ppm: 6.3 [Et_3Si—$CH(CH_2CH_3)$–], 8.6 [Et_3Si—$CH(CH_3)$–], 17.6 [Et_3SiOC–].

Reaction of $[Ti(OBu^n)_3(PA)]_n$ with TRES (11)

A preparative procedure similar to that used above for compound 10 was performed.
^{29}Si-NMR ($CHCl_3$) δ, ppm: 6.3 [Et_3Si—$CH(CH_2CH_3)$–], 8.6 [Et_3Si—$CH(CH_3)$–], 16.3 (Et_3SiOC–) (Fig. 4).

$$[Ti(OBu^n)_3(PA)]_n + Et_3SiH \rightarrow [(Bu^nO)_3TiOOCCH_2CH(-SiEt_3)CH_2CH_3]_n + [(Bu^nO)_3TiOOCCH_2CH_2CH(-SiEt_3)CH_3]_n \quad (7)$$

Reaction of $[Ti(OEt)_3(AAA)]_n$ with TRES (12)

A preparative procedure similar to that used above for compound 10 was performed.
^{29}Si-NMR ($CHCl_3$) δ ppm: 6.7 (Et_3Si—CH_2CH_2–), 16.2 (Et_3SiOC–).

Reaction of 3-pentenoic acid with TREOS (13)

3-Pentenoic acid (0.01 mol) was added dropwise to a solution of triethoxysilane (0.01 mol) in 10 g heptane. Then, 19.5 mg Pt–divinyltetramethyl disiloxane as catalyst was added. The mixture was refluxed at 80°C for 4 h. After 4 h, the solvent was removed under reduced pressure (~ 10 mbar) at 50°C. The viscous liquid product was brown.
^{29}Si-NMR ($CHCl_3$) δ, ppm: −36.2 [$(EtO)_3Si$—$CH(CH_2CH_3)$–, T^0], −49.5 (T^1), −56.2 (T^2), −82.6 [$(EtO)_3Si$—O(H), or (R), Q^0], −86.7 (Q^1), −89.6 (Q^2).

Reaction of 3-pentenoic acid with TRES (14)

A preparative procedure similar to that used above for compound **13** was performed.

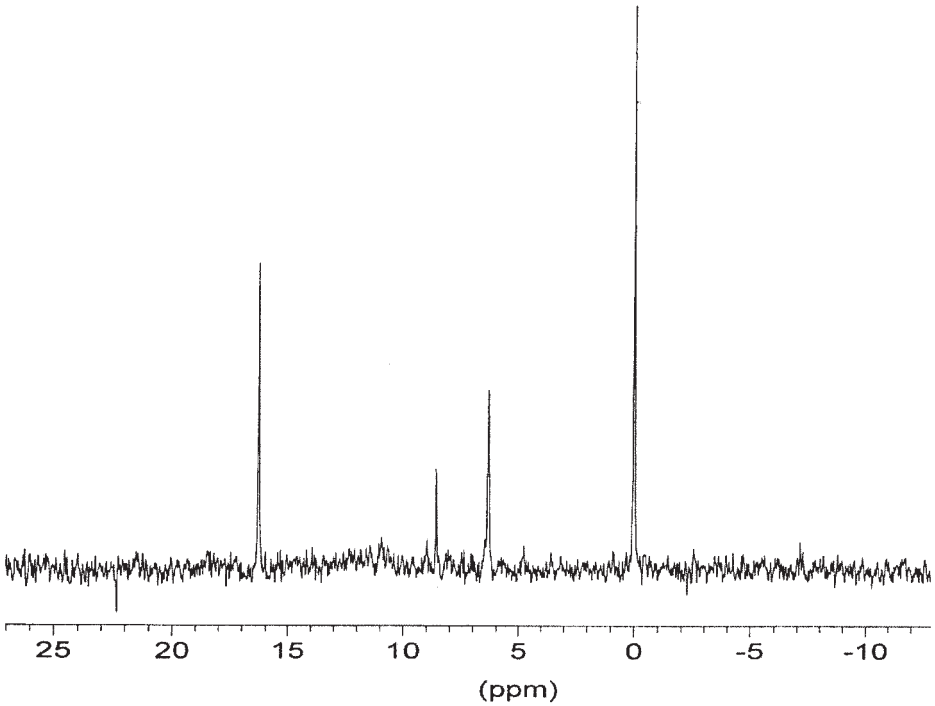


Figure 4 ^{29}Si-NMR spectrum of ([Ti(OBu^n)$_3$(PA)]$_n$ + TRES).

^{29}Si-NMR ($CHCl_3$) δ, ppm: 6.2 [Et_3Si—$CH(CH_2CH_3)$–], 8.4 [Et_3Si—$CH(CH_3)$–], 23.2, 23.9 (Et_3SiOC–).

RESULTS AND DISCUSSION

The ^{13}C-NMR spectrum of free 3-pentenoic acid shows characteristic signals at δ = 17.7 (CH_3), 37.8 (CH_2), 122.8 (CH_3CH═), 129.6 (═$CHCH_2$), and 179 ppm (COOH). When 3-pentenoic acid [PA/M(OR)$_4$ 1 : 1*M* ratio] was added to metal alkoxides compounds, the alkoxy group substituted with PA. The ^{13}C-NMR spectra of new complexes indicate that carbon groups of coordinated PA shift to a different region in the ^{13}C-NMR spectra. For example, the characteristic peaks for coordinated PA of compound [Ti(OEt)$_3$(PA)]$_n$ appeared at δ = 18.0 (CH_3, PA_c) 40.3 (CH_2, PA_c), 124.8 (CH_3—CH═, PA_c), 127.7 (═CH—CH_2, PA_c), and 181.4 ppm (COO—Ti, PA_c) (see Fig. 1). Reaction of Ti(OBu^n)$_4$ with PA gave similar ^{13}C-NMR data. These data are summarized at Table I. The FTIR spectrum of free PA gives a strong band at 1706 cm^{-1} that corresponds to the carboxyl group. The spectrum does not contain a band for a C═C double bond because the expected band of a *trans* C═C (~ 1640 cm^{-1}) is generally extremely weak. After coordination to metal alkoxides the band at 1706 cm^{-1} disappears from this region. The results indicate a complete complexation of PA with Ti-alkoxides. After PA coordinates to metal alkoxides, the carboxyl band appears at 1571 cm^{-1} for νCOO_{asym} and 1434 cm^{-1} for νCOO_{sym} (Table II). For example, the frequency difference between νCOO_{asym} and νCOO_{sym} (137 cm^{-1}) for **1** indicates that PA is bonded to titanium as a bidentate ligand.

The ^{13}C-NMR spectrum of free AAA shows that AAA has a keto (K)-enol (E) form in the ratio of 9 : 1.[9,14] The carbon atom signals that belong to AAA appear at 21.1 (g′), 30.0 (g), 49.9 (e), 64.5 (c′), 65.7 (c), 89.5 (e′), 118.0 (a′), 118.5 (a), 132.0 (b), 132.4 (b′), 166.9 (d), 172.3 (f′), 176.0 (d′), and 200.5 (f) ppm. The letters representing the carbon atoms are shown in Figure 2. In the FTIR spectrum four bands at 1740 cm^{-1} for $\nu_{C—O\,(K)}$, 1715 cm^{-1} for $\nu_{C═O\,(K)}$, 1650 cm^{-1} for $\nu_{C—O,\,C═C\,(E)}$, and 1633 cm^{-1} for $\nu_{C═C}$ of allyl group of AAA were observed.

When allylacetoacetate is coordinated to titanium ethoxide, the carbonyl carbons of AAA shift to a different region in the ^{13}C-NMR spectrum. The carbonyl carbons of [Ti(OEt)$_3$(AAA)]$_n$ appear at 172.4–172.9 ppm (C═C—O—Ti, double, f′, E), 184.5–185.7 ppm (CH_2O—C═O—Ti, double, d′, E). These values indicate the complexation with the enolic form of AAA.

In the FTIR spectrum of compound **3** (prepared in a 1 : 1 ratio), because no band was seen in the carbonyl region at 1740–1715 cm^{-1}, two carbonyl groups of allylacetoacetate must be in a chelating coordination mode. In other words, AAA coordinates to titanium ethoxide in the enolic form. A band at around 1628 cm^{-1} shows the presence of an uncoordinated double bond of the allyl group.

When ^{13}C-NMR spectrum of hydrolyzed product of [Ti(OEt)$_3$(PA)]$_n$ is taken, it shows that almost 10% 3-pentenoic acid is released from the titanium complex. The

TABLE I
^{13}C and ^{29}Si NMR Results

Compound number	NMR	% Complexation	% Free ligand after hydrolysis	% SiH addition to double bond	% SiH addition to C-O	% Condensed T-units	% Condensed Q-units	T:Q
$Ti(OEt)_3PA$ (**1**)	^{13}C	100						
$Ti(OEt)_3PA + 4H_2O$ (**4**)	^{13}C		10					
$Ti(OEt)_3PA + (EtO)_3SiH$ (**7**)	^{29}Si			70	30	6	36	70 : 30
$Ti(OEt)_3PA + Et_3SiH$ (**10**)	^{13}C			25				
$Ti(OEt)_3PA + Et_3SiH$ (**10**)	^{29}Si			49	39			
$Ti(OBu^a)_3PA$ (**2**)	^{13}C	97						
$Ti(OBu^n)_3PA + 4H_2O$ (**5**)	^{13}C		7					
$Ti(OBu^n)_3PA + (EtO)_3SiH$ (**8**)	^{29}Si			57	43	40	68	57 : 43
$Ti(OBu^n)_3PA + Et_3SiH$ (**11**)	^{13}C			30				
$Ti(OBu^n)_3PA + Et_3SiH$ (**11**)	^{29}Si			57	43			
$Ti(OEt)_3AAA$ (**3**)	^{13}C	100						
$Ti(OEt)_3AAA + 4H_2O$ (**6**)	^{13}C		20					
$Ti(OEt)_3AAA + (EtO)_3SiH$ (**9**)	^{29}Si			79	21	38	73	79 : 21
$Ti(OEt)_3AAA + Et_3SiH$ (**12**)	^{13}C			90				
$Ti(OEt)_3AAA + Et_3SiH$ (**12**)	^{29}Si			86	10			
$PA + (EtO)_3SiH$ (**13**)	^{13}C			67	30			
$PA + (EtO)_3$ SiH (**13**)	^{29}Si			63	37	>90%	30	63 : 37
$PA + Et_3SiH$ (**14**)	^{13}C			50				
$PA + Et_3SiH$ (**14**)	^{29}Si			20	80			

intensity ratio of COOH carbon of released PA to COO carbon of PA that is bonded to titanium (product) indicated that 10% PA released from the starting complex **1**. The ^{13}C-NMR spectrum of the $[Ti(OEt)_3(PA)]_n$-hydrolysate shows characteristic signals for released (10%) PA at 122.8 (CH_3—*C*H═, PA), 129.3 ppm (═*C*H—CH_2, PA). This shows that the PA–Ti product is stable to hydrolysis. The data for another hydrolysis reaction are also summarized in Table I. The ^{13}C-NMR spectrum of the $[Ti(OBu^n)_3(PA)]_n$-hydrolysate shows characteristic signals for released (10%) PA at 124.1 (CH_3—*C*H═, PA), 128.5 (═*C*H—CH_2, PA), and complexed PA_c at 18.1 (CH_3, PA_c), 40.0 (CH_2, PA_c), 124.6 (CH_3—*C*H═, PA_c), 127.5 (═*C*H—CH_2, PA_c), and 180.5 ppm (broad signal, COO—Ti, PA_c) (see Fig. 3). As seen Figure 3, hydrolyzed product includes both PA and butoxy groups. ^{13}C-NMR peaks of Ti—$O^1CH_2^2CH_2^3CH_2^4CH_3$ moiety appear at 14.1 ($^4CH_3$, OBu^n), 19.3 ($^3CH_2$, OBu^n), 34.5 ($^2CH_2$, OBu^n), and 64.6 ppm (O^1CH_2, OBu^n). The $[Ti(OEt)_3(PA)]_n$ or $[Ti(OBu^n)_3(PA)]_n$ complexes are more stable to hydrolysis than $[Ti(OEt)_3(AAA)]_n$ and other metal–AAA complexes.[9] This shows that PA is more strongly coordinated to metal alkoxides than AAA in the presence of water.

TABLE II
FTIR (cm^{-1}) Spectra of Compounds 1 and 4[a]

Compound **1**	Compound **4**
2959 (–CH_3, asym str, s)	3401 (O=H, str, br, small)
2932 (–CH_2, asym str, s)	2971 (–CH_3, asym str, w)
2871 (–CH_3, sym str, s)	2936 (–CH_2, asym str, w)
1571 (–COO, asym str, s)	2917 (–CH_3, sym str, w)
1434 (COO, sym str, s)	1565 (COO, asym str, s)
1340 (–CH_3, asym bend, m)	1441 (COO, sym str, s)
1377 (–CH_3, sym bend, m)	1399 (–CH_3, asym bend, s)
1258 (–CH_2, out-of-plane bend, w)	1321 (O-H, in-plane bend, m)
1095 (C-O str, s)	1258 (–CH_2, out-of-plane bend, m)
1037 (C-C str, m)	1115–1070 (C-O and C-C str, w)
998 (CH=CH, C–H out-of-plane bend, m)	966 (CH=CH, C–H out-of-plane bend, s)
866 (CH_3-C, str, m)	947 (CH_3-C, str, m)
731–679 (chelate Ti=O, str, sh, w)	730–606 (chelate Ti-O, str, and Ti-O, br, m)
517 (Ti-O, str, br, m)	459 (Ti=O; str, m)

[a] Ref. 15. Spectra recorded in $CHCl_3$; s, strong; m, medium; w, weak; br, broad; sh, shoulder; asym, asymmetric; bend, bending; str, stretching; sym, symmetric.

When the FTIR spectrum of hydrolyzed product of $[Ti(OR)_3(PA)]_n$ (OR: OEt, OBu^n) is taken, the O—H stretching band appears at around 3401 cm^{-1}. The presence of an OH band indicates that some of the alkoxy groups from starting material are replaced with OH groups by hydrolysis reaction. The hydrolyzed product of $[Ti(OR)_3(PA)]_n$ can be formulated as $[Ti(OR)_{3-x}(OH)_{x+y}(PA)_{1-y}]_n$. When the condensation reaction is considered, the formula of hydrolyzed product may include the oxo-ligand because of the condensation reaction between alkoxy and hydroxy groups. The FTIR data of $[Ti(OEt)_3(PA)]$-hydrolysate are summarized in Table II.

Addition of triethoxysilane and triethylsilane to unsaturated metal alkoxide complexes was investigated by ^{13}C- and ^{29}Si-NMR. ^{29}Si-NMR data for compound **11** show these signals: 6.3 [Et_3Si—$CH(CH_2CH_3)$–], 8.6 [Et_3Si—$CH(CH_3)$–], and 16.3 ppm (Et_3SiOC–) (Fig. 4). Because both ends of the double bond have the same degree of substitution, a mixture of products results at 6.3 and 8.6 ppm. The detection of Et_3Si—OC groups shows that addition reactions occur not only with C═C double bonds (57%) but also with the carboxyl group of the PA ligand (43%), in substantial amounts. Examination of the unreacted double bonds by ^{13}C-NMR shows a degree of addition of only 30%. Regardless of the remarkable differences in the NMR results, both methods show that addition of –SiH to the double bond is in the order of only 30–60%.

FTIR spectra of free triethoxysilane and triethylsilane show strong bands at 2195 and 2102 cm^{-1}. After coordination to unsaturated metal alkoxides, these bands disappear from this region. The results indicate a complete addition of –SiH to the double bond and other groups forming Et_3Si—OC and $(EtO)_3Si$—OC.

The reaction of Et_3SiH with free, uncomplexed PA shows similar low yields of C═C addition products (20–50%) and very high amounts of C—O—Si products. Possibly, the free C(═O)OH groups of PA promotes a much easier reaction with –SiH than that in the complexed state because of lower sterical hindrance. The spectroscopic data of ($[Ti(OBu^n)_3(PA)]_n$ + Et_3SiH) are similar to those of ($[Ti(OEt)_3(PA)]_n$ + Et_3SiH). Addition of Et_3SiH to the double bond is between 30 and 60%. ^{29}Si-NMR spectra of addition products $[Ti(OEt)_3(PA)]_n/[Ti(OBu^n)_3(PA)]_n$ + $(EtO)_3SiH$ show a slightly higher yield of C═C addition product between 60 and 70%. Higher yields of C═C addition are detected in products of the samples $[Ti(OEt)_3(AAA)]_n$ + $Et_3SiH/(EtO)_3SiH$ between 80 and 90%, which is a result of the end-standing C═C group without sterical hindrance compared to that of C—O– group in complexes. The remaining H-silane groups in the mixture are condensed to T + Q units. This kind of condensation is common in the presence of a –COO group in the mixture. The data for other addition reactions with –SiH are summarized in Table I.

CONCLUSIONS

New inorganic–organic compounds were synthesized by a sol–gel process. The complexation reaction (1 : 1) between metal alkoxides and 3-pentenoic acid or allylacetoacetate was almost complete. The H-silane addition to C═C double bond in complexes changes based on silane group between 30 and 90%. Because there is a –COO group in the reaction medium, side reactions occur. In other words, the presence of the C—O– group causes condensation reactions (T or Q) after H-silane addition. Hydrolysis of PA ligands from complexes takes place (10%) under the adopted reaction conditions. New compounds are suitable for sol–gel applications.

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