# Syntheses and Molecular Structures of Titanium Derivatives with Polymerizable Ligands. Toward Extended Arrays

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Dedicated to Professor Michael Veith on the Occasion of his 60th Birthday

Abstract. The reactions between Ti(OR)<sub>4</sub> and allylacetatoacetate (HAAA) in 1:1 or 1:2 stoichiometry at rt gave Ti<sub>2</sub>(OR)<sub>6</sub>(AAA)<sub>2</sub> R = Et (1), iPr (2) and Ti(OR)<sub>2</sub>(AAA)<sub>2</sub> R = Et (3), iPr (4) species. A monosubstituted derivative Ti<sub>2</sub>(OiPr)<sub>6</sub>(AMP)<sub>2</sub> (5) was isolated with allylmethylphenol (AMPH). 1 and 5 were characterized by single crystal X-ray diffraction. Their molecular structures consist of dimers with the polymerizable ligands in terminal positions and-bridging alkoxide ligands assembling five and six-coordinated metal atoms, respectively. The Ti-O bond lengths of 1 are in the range 1.76(1) to 2.11(1) Å with the variation Ti-OEt < Ti- $\mu$ -OEt < Ti- $\eta^2$ -

O (allylacetatoacetate). All compounds were characterized by FT-IR and <sup>1</sup>H NMR.The possibility to accede to more extended arrays either by hydrolysis or by radical initiated homo- or co-polymerization reactions was investigated for the allylacetato derivatives as well as for Ti(OiPr)<sub>2</sub>(AAEMA)<sub>2</sub> AAEMA = [2-(methacryloyloxy)-ethylacetoacetato] for the latter reactions.

Keywords: Titanium; Alkoxides; Polymerizable ligands; X-Ray structure; Sol-gel process

### Synthesen und Strukturen von Titan-Derivaten mit polymerisierbaren Liganden

**Inhaltübersicht**. Ti(O*i*Pr)<sub>4</sub> reagiert mit Allylacetoacetate (HAAA) im Verhältnis 1:1 oder 1:2 bei Raumtemperatur zu Ti<sub>2</sub>(O-R)<sub>6</sub>(AAA)<sub>2</sub> (R = Et (1), *i*Pr (2)) und Ti(OR)<sub>2</sub>(AAA)<sub>2</sub> (R = Et (3), *i*Pr (4)). Mit Allylmethylphenol (AMPH) wurde Ti<sub>2</sub>(O*i*Pr)<sub>6</sub>(AMP)<sub>2</sub> (5) isoliert. 1 und 5 wurden durch Einkristallstrukturanalyse charakterisiert. Ihre Molekülstruktur besteht aus Dimeren mit endständigen, polymerisierbaren Liganden und verbrückenden Alkoxidliganden um fünf- bzw. sechsfach-koordinierten Metallatomen.

Introduction

Hybrid organic-inorganic materials have gained increasingly attention in the last decade. When the metal coordination sphere presents a polymerizable ligand, materials displaying an organic as well as an inorganic network and thus combining the properties of inorganic and organic materials can be obtained. Metal alkoxides bearing polymerizable ligands are often used as a means to accede to hybrid organic-inorganic polymers [1]. Such compounds have been developed for early transition metals mostly titanium andzirconium [2] and to a lower extent, hafnium [3], niobium [4], and lanthanides [5]. Titanium is especially attractive as nuclear diagnostic in Internal Confinement Fusion (ICF) experiments and study of laser-material interactions. Derivatives based on polymerizable OR groups remain scarce

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Die Bindungslängen Ti-O in 1 betragen 1.76(1) bis 2.11(1) Å in der Reihe Ti-OEt < Ti- $\mu$ -OEt < Ti- $\eta^2$ -O (Allylacetoacetat). Alle Verbindungen werden durch FT-IR- und <sup>1</sup>H NMR-Spektroskopie charakterisiert. Die Möglichkeit ausgedehntere Wirkgruppen sowohl durch Hydrolyse oder durch radikalinitiierte Homo- oder Kopolymerisation zu erhalten, wurde für die Allylacetato-Derivate wie für Ti(O*i*Pr)<sub>2</sub>(AAEMA)<sub>2</sub> (AAEMA = 2-(methacryloyloxy)ethylacetoacetato) untersucht.

[6], most of the compounds are thus based on polymerizable ancillary ligands such as diols (for instance cis-2-butene-1,4-diol),  $\beta$ -diketoesters [2-(methacryloyloxy)ethylacetoacetate = HAAEMA] [7] or acids (acrylic, methacrylic) [1, 4]. A large number of structurally characterized oxo or oxohydroxo clusters of group 4 metals based on acrylate or methacrylate (OMc) ligands such as for instance Ti<sub>6</sub>( $\mu$ -O)<sub>2</sub>( $\mu$ <sub>3</sub>-O)<sub>2</sub>(OEt)<sub>8</sub>(OMc)<sub>8</sub>, Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>(OMc)<sub>10</sub>(PrOH), M<sub>4</sub>( $\mu$ <sub>3</sub>.O)<sub>2</sub>(OMc)<sub>12</sub>(M = Zr, Hf) [3] or Ti<sub>4</sub>Y<sub>2</sub>( $\mu$ <sub>3</sub>-O)<sub>4</sub>-( $\mu$ -OMc)<sub>12</sub>( $\mu$ <sub>1</sub>-OMc)<sub>2</sub>(HOC<sub>2</sub>H<sub>4</sub>OMe)<sub>2</sub> [8] have been reported. Functional aryloxides such as 2-methoxy-4-allylphenol, 2-MeO-C<sub>6</sub>H<sub>3</sub>-4-CH=CH<sub>2</sub>Me (isoeugenol) have been used as well with titanium alkoxides but incontrast to the previous heteroleptic species, no structural characterization was achieved [9].

We report here the synthesis and characterization by FT-IR and <sup>1</sup>H NMR of titanium derivatives with allylacetatoacetate (HAAA) or 2-allyl-6-methylphenol (AMPH) as ligands. The molecular structures of  $Ti_2(OEt)_6(n^2-AAA)_2$  (1) and  $Ti_2(OPr^i)_6(AMP)_2$  (5) were established by single crystal X-ray diffraction. The hydrolytic and polymerization behaviour of various Ti species was investigated.

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| Compound  | FT-IR $(cm^{-1})$ |                  |  | <sup>1</sup> H NMR (CDCl <sub>2</sub> , 25 °C, ppm) |                                   |   | OR (R = Et, iPr)   |                                      |   |  |
|---|-------------------|------------------|--|---|-----------------------------------|---|--|--------------------------------------|---|--|
|   | vC=O              | υC=C             | υŤi-OR                                 | MeCO  | COCHCO                            | OCH <sub>2</sub>  | $CH_2 =$   | =CH                                  | Me  | CH or CH <sub>2</sub>                                  |
| HAAA  | 1745<br>1719      | 1649<br>1636     | -                                      | 2.2 (s)   | 3.4 (s)*                          | 4.6 (d)<br>J = 6 Hz                                     | 5.2 (m)  | 5.95 (m)                             | _   | _  |
| $Ti_2(OEt)_6(AAA)_2$<br>1                                       | 1570m<br>1528vs   | 1633vs<br>1610vs | 595s<br>582m<br>500m                   | 1.9 8(s)<br>2.00 (s)<br>6H                          | 5.0 (s)<br>4.98 (s) 2H            | 4.6-4.76  (m)<br>4H<br>$J_{b}= 6 \text{ Hz}$            | 5.24 (td)<br>4H<br>$J_b = 12 \text{ Hz}$<br>$J_c = 1.8 \text{ Hz}$ | 5.76-5.96 (m)<br>2H                  | 1.2 (t) ; 1.23 (t)<br>18H<br>$J_a = 6.6 \text{ Hz}$ | 4.46 (m),<br>4.74 (m (2:1)<br>12H                      |
| $Ti(OEt)_2(AAA)_2$ 3 Ti O(OEt) (AAA)                            | 1525vs            | 1635vs<br>1613vs | 600s<br>595s                           | 2.00 (s)<br>6H                                      | 4.98 (s)<br>2H                    | 4.45 br<br>4H   | 5.12-5.28<br>(m) 4H  | 5.76-5.95<br>(m) 2H                  | 1.20(t), 1.18(t)<br>J = 6.3 Hz, 6H                  | 4.66 (m)<br>4H   |
| 11 <sub>3</sub> O(OEt) <sub>8</sub> (AAA) <sub>2</sub><br>6a    | 15268             | 1633vs<br>1613vs | 575VS<br>527m<br>441vs<br>390m<br>350m | 1.85 (s)<br>3H<br>1.9 (s)<br>3H                     | 4.96 (s)<br>4.80 (s)<br>2H        | 4.3-4.8 (m)<br>4H                                       | 5.1-5.3 (m)<br>4H  | 2H                                   | $J_{a}^{(1)} = 6 \text{ Hz}$                        | 3.8-4.4 (m)<br>16H                                     |
| $\begin{array}{l} Ti_2(O^iPr)_6(AAA)_2\\ \textbf{2}\end{array}$ | 1578m<br>1529vs   | 1637vs<br>1614vs | 633vs<br>465vs<br>448vs<br>362vs       | 1.96 (s)<br>1.92(s)<br>6H                           | 5.0 (s),<br>5.02 (s)<br>2H        | 4.76 (dt)<br>4H<br>$J_b$ = 6.15 Hz                      | 5.24 (td)<br>4H<br>$J_b = 11 \text{ Hz}$<br>$J_c = 1.4 \text{ Hz}$ | 5.76-5.96 (m)<br>2H                  | 1.22 (d) ; 1.26 (d)<br>36H<br>$J_a = 6 Hz$          | 4.76 (sept)<br>4.65 (br)(2:1)<br>6H<br>$J_a = 6 Hz$    |
| $Ti(OiPr)_2(AAA)_2$ 4 $Ti(O(PPr))(AAA)$                         | 1529 s            | 1629vs<br>1610vs | 625 vs<br>575 vs                       | 1.92 s<br>6H  | 5.02 s<br>2H<br>5.05 (a) 5.02 (a) | 4.75 br<br>4H   | 5.28 m<br>4H   | 5.74 - 5.93 m<br>2H<br>5.76 5.06 (m) | 1.24  d, 12H<br>J = 6 Hz                            | 4.67 sept<br>2H, $J = 6 Hz$<br>4.5 (cent) 4.76m        |
| 6b  | 1529vs            | 1628vs           | 582vs<br>534 sh<br>452vs<br>395m       | 1.90 (s)<br>1.88 s<br>6H                            | 2H                                | 4.7-4.82  (m)<br>4H<br>$J_{\text{b}} = 6.15 \text{ Hz}$ | $J_{b} = 13 \text{ Hz}$  | 2H                                   | $J_{a} = 6.2 \text{ Hz}$                            | $_{A.3}$ (sept), 4.76m<br>8H<br>$J_a = 6.2 \text{ Hz}$ |

Table 1 FT-IR and 1H NMR data of the titanium allylacetato derivatives

\*  $CH_2$ , (s) = singlet, (m) = multiplet, (t) = triplet, Italics identify the most intense peaks

#### **Results and Discussion**

## Synthesis and characterization of titanium allylacetato derivatives, molecular structure of $Ti_2(OEt)_6(AAA)_2$

The reactions between Ti(OR)<sub>4</sub> (R = Et, <sup>i</sup>Pr) and allylacetatoacetate (HAAA) were investigated in 1:1 and 1:2 stoichiometry in non-polar media,hexane or toluene. The heteroleptic species were isolated as colourless crystals and shown by elemental analysis and <sup>1</sup>H NMR to have the fomulae  $[Ti(OR)_3(AAA)]_m$  [R = Et (1), R = iPr (2)] and  $Ti(OR)_2(AAA)_2$  [R = Et (3), iPr (4)]. The monosubstituted compounds were extremely moisture sensitive giving yellow, very soluble oxo derivatives.

The various compounds were characterized by FT-IR and NMR (<sup>1</sup>H and <sup>13</sup>C) data (Table 1). The presence of the allylacetatoacetate ligand was identified by several absorption bands between 1640 and 1525 cm<sup>-1</sup> characteristic of the vC=O and vC=C bonds. No free ligand (vCO 1745, 1719 cm<sup>-1</sup>) was detected. The vTi-OR absorption bands (600-400 cm<sup>-1</sup>) were more diagnostic of the various compounds. The NMR spectra showed numerous peaks due to the unsaturated ligands and were further complicated by the fact that dilution experiments indicated the presence of several molecular species, either geometrical isomers or derivatives resulting from redistribution reactions for the monosubstituted derivatives. Comparison of the spectra obtained for [Ti(OR)<sub>3</sub>(AAA)]<sub>2</sub> and Ti(OR)<sub>2</sub>(AAA)<sub>2</sub> species supported redistribution phenomena as observed for  $[Ti(OR)_3(\beta-dik)]_2$  with R = Me, Et, Pr;  $\beta$ -dik = acac, thd [10]. Indeed, the <sup>1</sup>H NMR spectrum of 1 in CDCl<sub>3</sub> at rt showed two singlets at 1.98 and 2.00 ppm for the methyl groups of the unsaturated ligands as well as two singlets for

the CH signal of the chelate (4.98 and 5.00 ppm). Comparison of the spectra of the mono- and di-substituted ethoxide species showed that the minor signals (about 20 %) resonating at 2.00 ppm for the Me groups and at 4.98 ppm for the CH ones correspond actually to Ti(OEt)2(AAA)2. A similar behavior was observed for the isopropoxide derivative 2. Disproportionation of [Ti(OR)3(AAA)]2 was also confirmed by the signal of Ti(OiPr)<sub>4</sub> at 3.9 ppm for instance for 2 according to eq. (1). The region of the Ti-OR signals indicate the presence of magnetically non equivalent OR groups in a 2:1 integration ratio for 1 and 2. The monosubstituted 1 and 2 derivatives were more stable in  $C_6D_6$  than in CDCl<sub>3</sub> but the chemical shift range and structural information were more limited by the overlapping between the signals of the ligand and/or of the homoleptic titaniumalkoxide especially for Ti(OEt)<sub>4</sub>. Disubstituted species were more stable even in CDCl<sub>3</sub> solutions. This observation is in agreement with the use of *t*-butylacetatoacetate (tboac)  $M(OR)_2(tboac)_2$  (M = Ti, Zr) derivatives as precursors for liquid injection CVD [11].

$$Ti_{2}(OR)_{6}(AAA)_{2} \rightarrow Ti(OR)_{4} + Ti(OR)_{2}(AAA)_{2}$$
(1)

X-ray diffraction studies of 1 indicate its dimeric, centrosymmetric structure  $Ti_2(\mu-OEt)_2(OEt)_4(\eta^2-AAA)_2$  based on six-coordinate metal atoms (fig. 1). Selected bond lengths and angles are collected in Table 2. The Ti-O bond lengths spread over the range 1.803(2) to 2.142(2) Å the variation being Ti-OEt < Ti- $\mu$ OEt < Ti-O( $\eta^2$ -AAA). The Ti- $\mu$ OEt distances [1.975(2) and 2.076(2) Å for Ti(1)-O(4) and Ti(1)-O(4a), respectively] indicate a unsymmetrical bridge as a result of the *trans* effect of the terminal OR ligand. The



Fig. 1 Molecular structure of  $Ti_2(\mu$ -OEt)\_2(OEt)\_4(\eta^2-AAA)\_2 showing the atom numbering scheme (thermal ellipsoids at 20 % probability).

bonding of the allylacetatoacetate ligand is asymmetric as well [2.142(2) Å for Ti(1)-O(1) and 1.986(2) Å for Ti(1)-O(2)]. The stereochemistry around the titanium atom is quite distorted [73.51(8)-170.84(10)°] as a result of the acute intrabridge O(4a)-Ti(1)-O(4) angle (73.51(8)°) as well as of the bite angle of the β-ketoesterate ligand. The Ti-O-C angles for the terminal alkoxide ligands [126.6(3)° and 142.6(3)°] are guite small. The Ti…Ti distance [3.246(1) A] as well as all metric parameters are in agreement with the literature [12]. The unsaturated chains are in trans positions suggesting that they will be available for homo- or co-polymerisation. The structure of 1 is similar to that reported for a Ti<sup>IV</sup> glycinate derivative Ti<sub>2</sub>(OEt)<sub>6</sub>(NH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>)<sub>2</sub> [13].

#### Titanium species with functional aryloxide ligands

The reaction between Ti(OiPr)<sub>4</sub> and 2-allyl-6-methylphenol (AMPH) in a 1:1 stoichiometry afforded yellow crystals, 5 (eq (2)). Their IR spectrum indicate strong absorption bands at 373, 363 and  $335 \text{ cm}^{-1}$  whereas the presence of the aryloxide was evidenced by vC=C absorption bands at 1639 and 1590  $\text{cm}^{-1}$ . The unsaturated allyl group was best observed in the NMR spectra at 5.02 ppm for instance for the CH<sub>2</sub> group, these spectra supported a Ti(OiPr)<sub>3</sub>(AMP) formula (yield 64 %), whilst <sup>13</sup>C NMR spectra showed two types of isopropoxide ligands at 25.5 and 26.6 ppm.



The solid state structure of the allylmethylphenoxide derivative 5 confirmed its stoichiometry. It corresponds to a dimer

| Ti(1)-O(5)         | 1.803(2)   | - |  |
|--------------------|------------|---|--|
| Ti(1)-O(6)         | 1.809(2)   |   |  |
| Ti(1)-O(4)         | 1.975(2)   |   |  |
| Ti(1)-O(2)         | 1.986(2)   |   |  |
| Ti(1)-O(4)#1       | 2.076(2)   |   |  |
| Ti(1)-O(1)         | 2.142(2)   |   |  |
| Ti(1)-Ti(1)#1      | 3.2461(10) |   |  |
| O(5)-Ti(1)-O(6)    | 95.92(11)  |   |  |
| O(5)-Ti(1)-O(4)    | 96.92(10)  |   |  |
| O(6)-Ti(1)-O(4)    | 102.22(9)  |   |  |
| O(5)-Ti(1)-O(2)    | 98.62(11)  |   |  |
| O(6)-Ti(1)-O(2)    | 89.84(10)  |   |  |
| O(4)-Ti(1)-O(2)    | 159.21(9)  |   |  |
| O(5)-Ti(1)-O(4)#1  | 166.38(10) |   |  |
| O(6)-Ti(1)-O(4)#1  | 95.60(9)   |   |  |
| O(4)-Ti(1)-O(4)#1  | 73.51(8)   |   |  |
| O(2)-Ti(1)-O(4)#1  | 88.66(8)   |   |  |
| O(5)-Ti(1)-O(1)    | 85.89(10)  |   |  |
| O(6)-Ti(1)-O(1)    | 170.84(10) |   |  |
| O(4)-Ti(1)-O(1)    | 86.43(8)   |   |  |
| O(2)-Ti(1)-O(1)    | 81.00(9)   |   |  |
| O(4)#1-Ti(1)-O(1)  | 83.89(8)   |   |  |
| C(40)-O(4)-Ti(1)   | 125.6(2)   |   |  |
| C(40)-O(4)-Ti(1)#1 | 127.6(2)   |   |  |
| Ti(1)-O(4)-Ti(1)#1 | 106.49(8)  |   |  |
| C(4)-O(1)-Ti(1)    | 130.6(2)   |   |  |
| C(2)-O(2)-Ti(1)    | 135.8(2)   |   |  |
| C(50)-O(5)-Ti(1)   | 142.6(3)   |   |  |
| C(60)-O(6)-Ti(1)   | 126.6(3)   |   |  |
|                    |            |   |  |

Table 2 Selected bond lengths/Å and angles/° for Ti<sub>2</sub>(OEt)<sub>6</sub>(AAA)<sub>2</sub>.

 $Ti_2(\mu - O^iPr)_2(O^iPr)_4(AMP)_2$  (fig. 2). Selected bond lengths and angles were collected intable 3. The Ti-O bond lengths range from 1.767(2) to 2.109(2) Å, with the ranking Ti-OiPr < Ti-O(AMP) < Ti-µOiPr. The metal atom is only five-coordinated and this lower coordination number with respect to that in 1 leads to shorter Ti-O distances. The stereochemistry at the titanium atom corresponds to a distorted trigonal bipyramid with two of theisopropoxide groups being in the apical positions and the angles varying from 72.56(8)° (intrabridge) to 170.14(8)°. The last isoproposide group, in equatorial position, gives raise to a quite long Ti-O linkage of 2.109(2) Å, thus leading to an unsymmetrical bridge [vs 1.932(2) Å]. The shortest bond length, Ti-O(2) is associated to a large Ti-O-C angle [175.9(2)° vs 137.5(2)° for the other terminal ligands). The Ti…Ti distance, 3.2597(8) Å, is similar to that observed for 1 or other polynuclear Ti species [12]. 5 was extremely sensitive to hydrolysis especially in the solid state. Its hydrolysis in solution (h = 1) lead to gels andwas faster in isopropanol than in toluene. No further reactivity studies were undertaken.

#### Reactivity: toward the formation of extended arrays Hydrolysis-polycondensation reactions

The Ti-AAA bond is quite labile: free allylacetatoacetate is detected by NMR for hydrolysis ratio h [h = molar ratiowater/M(OR)<sub>n</sub>] as low as 0.05. The loss of the AAAH ligand (also evidenced by FT-IR) by hydrolysis leads to the formation of yellow, highly soluble oxo species (broad Ti-

Symmetry transformations used to generate equivalent atoms: #1 - x + 1, -y, -z + 1



Fig. 2 Molecular structure of  $Ti_2(O'Pr)_6(AMP)_2$  showing the atom numbering scheme (thermal ellipsoids at 20 % probability).

| Table 3 Selected bo                                      | ond lengths/Å | and angle | es/deg for |
|--|---------------|-----------|------------|
| Ti <sub>2</sub> (OiPr) <sub>6</sub> (AMP) <sub>2</sub> . |               |           |            |

| Ti(1)-O(2)<br>Ti(1)-O(5)<br>Ti(1)-O(4)<br>Ti(1)-O(3)<br>Ti(1)-O(3)#1<br>Ti(1)-Ti(1)#1 | 1.767(2)<br>1.799(2)<br>1.854(2)<br>1.932(2)<br>2.109(2)<br>3.2597(8) |  |
|---|---|--|
| O(2)-Ti(1)-O(5)   | 99.90(9)  |  |
| O(2)-Ti(1)-O(4)   | 97.61(9)  |  |
| O(5)-Ti(1)-O(4)   | 113.31(9)   |  |
| O(2)-Ti(1)-O(3)   | 98.15(8)  |  |
| O(5)-Ti(1)-O(3)   | 118.26(9)   |  |
| O(4)-Ti(1)-O(3)   | 121.92(8)   |  |
| O(2)-Ti(1)-O(3)#1   | 170.14(8)   |  |
| O(5)-Ti(1)-O(3)#1   | 87.69(8)  |  |
| O(4)-Ti(1)-O(3)#1   | 84.98(8)  |  |
| O(3)-Ti(1)-O(3)#1   | 72.56(8)  |  |
| C(20)-O(2)-Ti(1)  | 175.9(2)  |  |
| C(6)-O(3)-Ti(1)   | 134.9(2)  |  |
| C(6)-O(3)-Ti(1)#1   | 117.6(2)  |  |
| Ti(1)-O(3)-Ti(1)#1  | 107.44(8)   |  |
| C(7)-O(4)-Ti(1)   | 138.7(2)  |  |
| C(10)-O(5)-Ti(1)  | 138.9(2)  |  |

Symmetry transformations used to generate equivalent atoms: #1 - x + 2, -y, -z

O-Ti absorption bands between 890 and 700 cm<sup>-1</sup>). Comparison of the hydrolytic behaviour of titanium complexes with various saturated and unsaturated ligands indicate that the Ti-O(AAA) bond is more susceptible to hydrolysis than the Ti-O(acac) one. The bridging 2-butene-1,4-diolate for instance is retained up to h = 1 for  $[Ti_4(OPr^i)_8(\mu,\eta^2-OCH_2CH=CHCH_2O)_2(\mu_3,\eta^2-OCH_2CH=CHCH_2O)_2]$  [7]. The formation of oxo species is favoured for the monosubstituted species 1 and 2 either in the solid state by adventitious hydrolysis or in solution by long reactions times and trace amounts of water in the AAAH ligand. <sup>1</sup>H NMR spectra of the yellow isolated species display an OR/AAA integration ratio of 4/1. Analytical data are in agreement with formula such as  $[Ti_3O(OEt)_6(AAA)_2]_m$  (6) (v Ti-O 786 cm<sup>-1</sup> for instance) or  $[Ti_4O_3(OR)_8(AAA)_2]_m$  for more



Scheme 1 First steps of the hydrolytic condensation of the monosubstituted Ti allylacetato derivatives

extensive hydrolysis. Such formula confirm the partial loss of the  $\beta$ -ketoesterate ligand and can result from hydrolysiscondensation according to eq 3 and 4

$$3 \operatorname{Ti}_{2}(\mathrm{OR})_{6}(\mathrm{AAA})_{2} + 2 \operatorname{H}_{2}\mathrm{O} \rightarrow 2 \operatorname{Ti}_{3}\mathrm{O}(\mathrm{OR})_{8}(\mathrm{AAA})_{2} + 2 \operatorname{HAAA} + \mathrm{R}_{2}\mathrm{O}$$
(3)

$$2 \operatorname{Ti}_{2}(\operatorname{OR})_{6}(\operatorname{AAA})_{2} + 3 \operatorname{H}_{2}\operatorname{O} \to \operatorname{Ti}_{4}\operatorname{O}_{3}(\operatorname{OR})_{8}(\operatorname{AAA})_{2} + 2 \operatorname{HAAA} + 4 \operatorname{ROH}$$
(4)

Unfortunately all attempts to get crystals suitable for X-ray analysis of the yellow species obtained under various hydrolytic conditions of 1 or 2 were unsuccessful. NMR data suggest magnetically non equivalent alkoxide ligands but useful structural information could not be reached due to overlapping between the OR and AAA signals at low temperature. Numerous and diverse polynuclear Ti oxo cores have been reported. Trinuclear titanium oxo species such as for instance  $Ti_3(\mu_3-O)(OiPr)_7(O_3C_9H_{15})$  in which the tridentate ligand results from coupling of acetone [14] or  $Ti_3(\mu_3-O)(\mu OAc_{2}(\mu - ONp)_{2}(ONp)$  [15] (ONp = neopentoxide) are known. Tetranuclear Ti oxo cores are represented for instance by  $Ti_4(\mu_3-O)_2(\mu-OR)_2(OR)_8(acac)_2$  [16] or by  $Ti_4(\mu_3-O)_2(DR)_8(acac)_2$  [16] or by  $Ti_4(\mu_3-O)_2(\mu-OR)_2(OR)_8(acac)_2$  [16] or by  $Ti_4(\mu_3-O)_2(\mu-OR)_2(OR)_8(acac)_2$  [16] or by  $Ti_4(\mu_3-O)_2(\mu-OR)_2(OR)_8(acac)_2$  [16] or by  $Ti_4(\mu_3-O)_2(\mu-OR)_8(acac)_2$  [16] or by  $Ti_4(\mu_3-O)_8(acac$ O)( $\mu$ -O)<sub>2</sub>( $\eta$ <sup>2</sup>-dmae)<sub>2</sub>( $\eta$ <sup>1</sup>-dmae)<sub>4</sub>( $\mu$ , $\eta$ <sup>2</sup>-dmae)<sub>2</sub> (dmae OC<sub>2</sub>H<sub>4</sub>NMe<sub>2</sub>) [17]. The bridging OR ligands of the  $Ti_2(OR)_6(AAA)_2$  species being the most nucleophilic centres for the attack of water [18], condensation is likely to proceed via an hydroxyalkoxide Ti<sub>2</sub>(OR)<sub>5</sub>(OH)(AAA)<sub>2</sub> intermediate. It can react either according to eq. (3), or with a Ti(OR)<sub>4</sub> moiety (resulting from redistribution reactions eq. (1)) or dimerize after loss of a AAAH ligand by intramolecular H transfert. Scheme 1 represents simple possible structural cores based on 6-coordinate titanium for the early hydrolytic products.

Controlled hydrolysis of 1 was also done on 0.2 M solutions in THF by adding water in the same solvent and for various hydrolysis ratios. Colloidal yellow solutions were obtained for h = 0 to 4 for freshly hydrolyzed solutions. Particles size (hydrodynamic diameters) were determined by dynamic light scattering. Particles of 203 and 290 nm



Scheme 2 Homo and co-polymerization reactions of compound 7. For sake of clarity, the modification of only one polymerizable ligand is represented. The growth of the inorganic network (formation of Ti-O-Ti bonds) will result from the subsequent hydrolytic reactions by addition of water.

respectively were observed for instance for h = 1 and h =1.5. As expected, the particle size increases with the hydrolysis ratio (700 nm for h = 2). Reversible gels, which became progressively irreversible, were formed after one week for h = 4. Similar observations were made in 0.2 M toluene but the stability of the sols was higher in polar media, THF or ethanol. Complete hydrolysis with excess of water (h = 50) gave colorless powders analyzing as TiO(OH)<sub>0.5</sub>(AAA)<sub>0.5</sub> thus confirming partial loss of the functional ligand. As a general feature, the yellow color of the sols changed to orange and orange-red by increase of h as well as by aging. This increase of coloration suggests complex reactions as observed for the reaction between acetone and titanium alkoxides [14]. Indeed, allylacetatoacetate can undergo re-esterification or cleavage reactions in the presence of alcohol and under hydrolytic conditions with formation of various organics such as allyl alcohol, 3-oxo butanoic acid and acetone [19]. IR and <sup>1</sup>H NMR data of aged solutions or gels support such features (vCO 1765,  $1735 \text{ cm}^{-1}$  in the FT-IR) but were not fully investigated.

#### Homo and copolymerisation reactions

The feasibility of homo and copolymerisation reactions wasinvestigated for  $Ti(OEt)_{3-x}(AAA)_x$  species (x = 1, 2) and compared to those of other titanium derivatives bearing polymerizable ligands such as  $Ti(OiPr)_2(AAEMA)_2$  7 or  $Ti(OiPr)_3(oleate)$  8 [7]. Thermal activation appeared better than photochemical one due to lower degradation of most complexes (<5 %). Monitoring was achieved by FT-IR or NMR [20]. The coordinated AAA ligands showed a low conversion intocarbon-carbon bond formation. Moreover, the poor hydrolytic stability of the allylacetato species hampered easy differentiation of the inorganic, namely hydrolysis, and organic polymerisation reactions. Better resultswere obtained with 7 with the acrylate functionality and with 8. Homopolymerization of 7was achieved in toluene at 75 °C in the presence of AIBN as initiator. After 4 h, the initial solution was transformed into a glassy gelindicating crosslinking. The M-OR absorption bands at 623, 600, 580,  $525 \text{ cm}^{-1}$  were unchanged with respect to those of 7 indicating that gelation was not due to hydrolysis and formation of the Ti-O-Ti network.

Copolymerization of 7 with styrene was also achieved in toluene in the presence of AIBN. After 2 h at 55 °C, a soft gel was obtained. Scheme 2 is a cartoon of the homo and copolymerization reactions of 7. Formation of the polystyrene (PS) network was evidenced by its characteristic sharp absorption bands at 464 cm<sup>-1</sup> and by the harmonics at 1943, 1858, 1803 cm<sup>-1</sup> for instance. Longer reaction times lead to growth of the organic network with hardening and shrinkage of the gel as a glassy, transparent insoluble polymer whereas the Ti-OR absorption bands remained unaffected. No metallic species was found in the mother liquor nor extracted by washing the polymer with isopropanol indicating that the AAEMA moiety was anchored to the PS backbone. Elemental analysis of the polymeric material obtained after washing with toluene in order to remove non reacted PS confirmed the presence of titanium (2.6 %). Hydrolysis of the Ti-polystyrene copolymer and subsequent washing with ethanol and toluenelead to formation of the Ti-O-Ti network (broad absorptions from 880 to 450  $\text{cm}^{-1}$ in the FT-IR). Besides those absorptions, the spectra displayed those of the acrylate moiety (vCO<sub>2</sub> at 1720 cm<sup>-1</sup>)

| Chemical formula                                | $C_{26}H_{48}O_{12}Ti_2(1)$                 | C <sub>38</sub> H <sub>64</sub> O <sub>8</sub> Ti <sub>2</sub> (5) |
|---|---|--|
| Formula weight                                  | 648.44                                      | 744.68   |
| a/Å   | 9.9670(3)                                   | 9.8690(2)  |
| b/Å   | 10.8730(5)                                  | 9.9530(2)  |
| c/Å   | 15.8520(5)                                  | 12.3110(4)   |
| $\alpha / ^{\circ}$                             |   | 84.564(1)  |
| β/°   | 93.568(2)                                   | 75.066(1)  |
| γ/°   |   | 63.768(2)  |
| V/Å <sup>3</sup>                                | 1714.57(11)                                 | 1047.83(5)   |
| Z   | 2   | 1  |
| Crystal system                                  | monoclinic                                  | triclinic  |
| Space group                                     | $P2_1/c$                                    | PĪ   |
| Absorption coefficient/mm <sup>-1</sup>         | 0.518                                       | 0.425  |
| Wavelength λ/Å                                  | 0.71070                                     | 0.71070  |
| grange for data collection/°                    | 3.11-27.48                                  | 3.24-24.72   |
| Reflections collected                           | 11719                                       | 14777  |
| Independent reflections                         | 3820  | 3534   |
| Refinement method                               | Full-matrix least-squares on F <sup>2</sup> | Full-matrix least-squares on F <sup>2</sup>                        |
| Data / restraints / parameters                  | 3820 / 2 / 181                              | 3534 / 0 / 217   |
| Goodness of fit on F <sup>2</sup>               | 1.022                                       | 1.051  |
| Final R indices $[I > 2\Sigma(I)]$              | R1 = 0.0696, wR2 = 0.1969                   | R1 = 0.0549, wR2 = 0.1492  |
| R indices (all data)                            | R1 = 0.0829, wR2 = 0.2205                   | R1 = 0.0622, wR2 = 0.1550  |
| $\Delta \rho \min - \Delta \rho \max/e. Å^{-3}$ | -0.537 0.665                                | -0.521 0.596   |

Table 4 Crystallographic data of  $Ti_2(OEt)_4(\mu-OEt)_2(\eta^2-AAA)_2$  and of  $Ti_2(O^iPr)_4(\mu-O^iPr)_2(AMP)_2$  (at 123K)

and of the PS backbone at 1603, 1495, 1453, 760, 709.6  $cm^{-1}$  whereas elemental analysis accounted for 2.5 % of Ti. The Ti doped polystyrene was slightly more stable thermally than the non-doped one as shown by TGA [7b].

#### **Experimental Section**

All experiments were performed under dry nitrogen using Schlenk tubes and vacuum line techniques. Solvents were purified by standards methods. Allylacetatoacetate and HAAEMA (Aldrich) were dried over molecular sieves whereas 2-allyl-6-methylphenol (Aldrich) was purified by chromatography over alumina. The titanium alkoxides were distilled under vacuum. Ti(OiPr)<sub>2</sub>(AAEMA)<sub>2</sub> was synthesized as reported [7]. Analyses were obtained from the Centre de microanalyses du CNRS. FT-IR spectra were obtained as Nujol mulls with a Perkin-Elmer Paragon 500 spectrometer or as KBr pellets (for the polymeric materials) whereas NMR data were obtained with a AC-300 Bruker spectrometer. The spectroscopic (FT-IR, NMR) data of the Ti allylacetatoacetate complexes are collected in table 1. Particle sizes were measured in solution with a Coulter N4 Plus submicron particle sizer.

#### Syntheses

**Ti(OR)<sub>3</sub>(AAA) (R = Et (1), iPr (2)).** 1.64 ml (11.5 mmol) of HAAA diluted in 7 ml of hexane were added to 2.64 g of Ti(OEt)<sub>4</sub> (11.5 mmol) in 23 ml of hexane. Concentration after 24 h gave1 at  $-20 \,^{\circ}$ C (2.98 g, 80 %) as colourless crystals. Anal. for C<sub>13</sub>H<sub>24</sub>O<sub>6</sub>Ti, C 47.75 (calc. 48.16), H 7.21 (7.46) %. 1 was soluble in usual solvents including aliphatic hydrocarbons.

<sup>13</sup>C{<sup>1</sup>H} NMR ( $C_6D_6$ , ppm):  $\delta$  S =18.7, 25.5 Me(Et); 65.3 (MeCO); 68.6, 71.2 OCH<sub>2</sub> (Et); 73.4 (OCH<sub>2</sub>CH=); 88.4 (CHCO); 117.2 (=*C*H<sub>2</sub>); 133.5 (*C*H=); 172.4 (MeCO); 185 (*C*O<sub>2</sub>).

The same procedure applied to 2.79 g (9.84 mmol) of  $Ti(O^{i}Pr)_{4}$  and 1.35 ml (9.84 mmol) of HAAA in toluene gavea yellow oil. Colourless crystals of **2** were obtained by adding hexane-isopropanol (4/ 1 ml), filtration and washing with isopropanol (2.9 g, 82%). Anal.  $C_{16}H_{30}O_{6}Ti$ , found C, 52.32 (calc. 52.47), H, 8.15 ( 8.26)% **Ti(OR)**<sub>2</sub>(**AAA**)<sub>2</sub>(**R=Et (3), iPr (4)**). The same procedure as for **1** but applied to 2.64 ml (19.26 mmol) of HAAA and 2.4 ml of Ti-(OEt)<sub>4</sub> (9.63 mmol) gave **3** at -10 °C (2.36 g; 58 %). soluble in usual organic solvents. Anal. for C<sub>18</sub>H<sub>28</sub>O<sub>8</sub>Ti Found C, 51.23 (calc. 51.44); H, 6.65 (6.71) %.

Same procedure for 4, anal. for  $C_{20}H_{32}O_8Ti$  (448.35) found C 53.10 (calc.53.58), H 7.03 (7.19) %

Ti<sub>3</sub>O(OR)<sub>8</sub>(AAA)<sub>2</sub> (R = Et (6a), *i*Pr (6b)). Hydrolysis of 1 as a solid gave a yellow pasty material. Drying under high vacuum gave a yellow solid, 6a very soluble in hydrocarbons, soluble in ethanol. Hydrolysis of 1 in toluene (h = 0.5) gave the same compound after 48 h. Anal. for  $C_{30}H_{58}O_{15}Ti_3$ , found C, 39.96 (39.69), H: 5.07 (5.09) %.

The isopropoxide derivative was best obtained by reacting 0.92 ml (6.73 mmol) of commercial HAAA with 1.91 g of  $Ti(O^{i}Pr)_{4}$  (6.73 mmol) in 23 ml hexane at rt for 70 h (53 %). Anal  $C_{38}H_{74}O_{15}Ti_{3}$  (914.35) found C 49.25 (49.87) H, 7.97 (8.16) %

 $Ti(O'Pr)_3(AMP)$  (5) 2-allylmethylphenol (0.41 g, 2.69 mmol) was added to  $Ti(OPr^i)_4$  (1.15 g, 2.69 mmol) in 10 ml of toluene. The medium became yellow immediately. After 2 h, it was evaporated to dryness. Yellow crystals were obtained by recrystallization in petroleum ether (1.19 g, 64 %). 5 is extremely moisture sensitive giving an orange oil.

IR (cm<sup>-1</sup>): 1638 m, 1590 w (vC=C); 1266 vs, 1214 s, 1196 m, 1128 vs, 1013 s, 1000 sh, 951 m, 912 s, 800 sh, 754 s, 735 s, 680 s; 652 s, 640 sh, 630 s; 545 m (vTi-OR), <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta = 1.27$  d (J = 6 Hz, 18H, Me(Pr); 2.31 s [3H, Me(Ar)]; 3.47d (2H, J=6.6 Hz, CH<sub>2</sub>=CH*CH*<sub>2</sub>)], 4.58 sept br (J = 6 Hz, 3H, CH(Pr)]; 5.02 d (J = 9.1 Hz, 2H, CH<sub>2</sub>=), 6.0 td (J<sub>b</sub> = 6.6 Hz, J<sub>c</sub> = 9.1 Hz, 1 H, CH=), 6.76 t (J = 7.3 Hz, 1 H, CH(Ar)], 6.97 overlapping of d (J = 7.3 Hz, 2H, CH(Ar). <sup>13</sup>C{<sup>1</sup>H} NMR:  $\delta = 17.2$  Me(Ar), 25.1, 26.3 Me-(iPr), 36.0 (*CH*<sub>2</sub>CH=CH<sub>2</sub>); 116.4 (=CH<sub>2</sub>); 121.2 CH(Ar); 127.0, 129.2 C(Ar); 137.4 (CH=); 153.7 OC(Ar).

#### Homo and copolymerization experiments

They were achieved under inert atmosphere in the presence of 2,2'azobis(2-methylpropionitrile) (AIBN) (2 % molar / C = C) at 50 °C in THF or toluene for 1 h or induced by UV-radiation (Heraus lamp TQ 150, 280-360 and 460-510 nm, 150 W) in the presence of benzophenone (3 % M) in toluene. Polymerization reactions were quenched by adding the parent alcohol. Styrene was distilled in order to remove the stabilizing reagent. Typical conditions are as follows:

Copolymerization of styrene:  $Ti(O'Pr)_2(AAEMA)_27$  (0.334 g, 0.53 mmol) was dissolved ina mixture of styrene (0.5 ml, 4.36 mmol) and toluene (0.5 ml). 1 mg of AIBN were added. The medium was heated in a Parr bomb at 75 °C. After quenching, the material was washed 3 times with toluene in order to remove PS. The resulting solid was separated by centrifugation and dried under vacuum.

Homopolymerization of 7: 0.403 g (0.686 mmol) of 7 were dissolved in 0.5 ml of toluene containing 2 mg of AIBN. Heating was achieved at 75 °C in a Parr bomb. The polymeric insoluble material was separated, washed with the parent alcohol orethanol and dried under vacuum.

#### X-Ray structure dermination of 1 and of 5

Suitable crystals of 1 were grown from the reaction medium, those of **5** were obtained by recrystallization in petroleum ether. The crystals were fixed at a glass fibre with paratone. Data collection was doneon a Nonius CCD diffractometer at 123 K. 11 828 reflections of which 3856 were unique were measured for **1** and 14 777 reflections of which 3534 were unique were measured for **5**. Cell parameters were refined using DENZO [21]. Absorption corrections were applied with NUMABS for both compounds [22]. The structures weresolved by Patterson methods and refined by least squares using SHELXTL [23]. All non-H atoms were refined anisotropically giving the values of R listed in table 4. For **1**, C(7) and C(51) display quite high thermal motion and constraints were imposed in order to obtain reasonable C-C distances. C(1) was disordered over two positions (50 % occupation). Hydrogen atoms positions were calculated at theoretical positions and refined isotropically riding on C.

Full details for **1** and **5** have been deposited at the Cambridge Crystallographic Data Centre, CCDC numbers: 175650 for **1** and 175 651 for **5**. Copies of the data can be obtained free of charge on application to The Director CCDC, 12 Union Road, Cambridge CB2 1EZ, UK.

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