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Primary Hydrolysis Products of Methacrylate-Modified Titanium and Zirconium Alkoxides

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$Ti(OEt)_4$ reacts at room temperature with a maximum of 1.33 mol equiv of methacrylic acid. This ratio is retained in the primary hydrolysis product $Ti_6O_4(OEt)_8(OMc)_8$ (OMc = OOC—C(Me)=CH$_2$), which was characterized by an X-ray structure analysis. The monoclinic lattice parameters (space group $P2_1/c$) are $a = 1412.0$ (3), $b = 1710.1$ (1), $c = 1501.9$ (2) pm, $\beta = 107.458$ (7)°, and $V = 3479 \times 10^6$ pm^3. $Zr(OPr^n)_4$ reacts at room temperature with a maximum of about 2 equiv of methacrylic acid, and both $[Zr(OPr^n)_3(OMc)]_n$ and $[Zr(OPr^n)_2(OMc)_2]_n$ were isolated. While the bismethacrylate compound is hydrolyzed to give $[ZrO(OMc)_2]_n$, the monomethacrylate only reacts with 1.33 equiv of water to yield a compound of the composition $[Zr_3O_3(OH)(OPr^n)_2(OMc)_3]_n$.

Introduction

Advanced materials synthesized by sol–gel processing are increasingly derived from organically modified alkoxides. By proper choice of the organic moieties, novel materials are obtained which contain an organic polymeric network in addition to the inorganic (oxidic) network and, partially, combine the properties of inorganic and organic materials.

In siloxane chemistry polymerizable organic substituents can be linked to silicon via a Si–C bond. Organically modified alkoxysilanes, such as $X_3SiCH{=}CH_2$, $X_3Si(CH_2)_3OC(O)C(Me){=}CH_2$ or $X_3Si(CH_2)_3OCH_2\overline{CHCH_2O}$ are successfully used for this purpose (e.g., ref 2). A different mode of linking the hydrolyzable alkoxide moiety and the polymerizable organic group is necessary for aluminum, titanium, or zirconium alkoxides, because Al–C, Ti–C, or Zr–C bonds are cleaved by water. The polymerizable organic group can be introduced via an unsaturated carboxylic acid, such as methacrylic acid. Zirconium methacrylates were already used to prepare polymers.[2b,3]

Alkoxides of titanium, zirconium, or aluminum in which part of the alkoxy groups is substituted by bidentate carboxylate or β-dicarbonylate ligands are interesting precursors in sol–gel chemistry.[4]

The effect of acetic acid on $Ti(OR)_4$ was particularly well studied.[5–8] On addition of 1 equiv of acetic acid to $Ti(OBu^n)_4$, 1 equiv of butanol is eliminated and $[Ti(OBu^n)_3(OAc)]_n$ (Ac = $CH_3C(O)$–) is formed. Hydrolysis of this new precursor proceeds by initial removal of butanol, while the acetate ligand remains bonded to titanium until a later stage of the polycondensation process. Precipitation of TiO_2 is thus prevented and gelation time is considerably increased. On addition of 2 mol of acetic acid to 1 mol of $Ti(OBu^n)_4$, crystals of $Ti_6O_4(OBu^n)_8(OAc)_8$ are obtained, in which the OAc/Ti ratio is 1.33.[9] The oxo ligand stems from an esterification reaction between the excess of acetic acid and the liberated alcohol. The stoichiometry of the primary hydrolysis products depends to some extent on the nature of the alkoxy group. While $Ti(OEt)_4$ gives a product, $Ti_6O_4(OEt)_8(OAc)_8$, having the same composition and structure as the *n*-butoxy derivative,[10] crystals of both $Ti_6O_4(OPr^i)_{12}(OAc)_4$[11] and $Ti_6O_4(OPr^i)_8(OAc)_8$[12] were obtained from the reaction of the secondary alkoxide $Ti(OPr^i)_4$ with acetic acid. In all compounds the acetate groups are exclusively in a bridging mode.

Mixed alkoxy carboxylates are also formed in the reaction of $Zr(OPr^i)_4{\cdot}Pr^iOH$ with fatty acids.[13] While $Zr(OPr^i)_3(OOCR)$ is prepared at room temperature, the di- and tricarboxylates $Zr(OPr^i)_{4-n}(OOCR)_n$ ($n = 2, 3$) are obtained by refluxing zirconium tetrapropoxide with the corresponding amount of acid in benzene. Substitution of the fourth alkoxy group is not possible; instead, the oxy species $Zr_2O(OOCR)_6$ is formed. As above, the oxygen atom stems from an esterification reaction.[13] $Zr_4O_6(OAc)_4$ is obtained by addition of a stoichiometric amount of aqueous acetic acid to $Zr(OPr^i)_4$ in isopropyl alcohol.[14] The chemistry of oxy carboxylates of zirconium is rather complicated, and several compounds of the stoichiometry $Zr_aO_b(OH)_c(OOCR)_d{\cdot}xH_2O$ are known.[15]

In this article we address two questions: (i) How does the presence of an olefinic group in the carboxylic acid influence composition and structure of the primary hydrolysis products, i.e., is the effect of methacrylic acid on

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$Ti(OEt)_4$ different from that of acetic acid? This question is particularly important with respect to the availability of the double bonds for polymerization after the inorganic network has been formed. (ii) Are there differences between methacrylate-modified titanium and zirconium alkoxides with respect to their composition and their primary hydrolysis products?

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer infrared spectrometer 283, and ^1H NMR spectra on Bruker AC200 and AW80 spectrometers.

Preparation of $Ti_6O_4(OEt)_8(OMc)_8$ (1) (OMc = OC(O)C(Me)=CH_2). Methacrylic acid (0.2 mol) was slowly added to $Ti(OEt)_4$ (0.1 mol). The mixture was allowed to stand for a week in a closed vessel while colorless crystals separate from the reaction mixture, which were then filtered off and dried in vacuo. Anal. Calcd for $C_{48}H_{80}O_{28}Ti_6$: C, 41.40; H, 5.79; Ti, 20.64. Found: C, 41.86; H, 5.71; Ti, 20.86. IR (KBr) 3425 (vw), 2970 (w), 2927 (w), 2866 (w), 2363 (vw), 1643 (w), 1558 (s), 1539 (s, sh), 1456 (m), 1427 (s), 1413 (s), 1373 (m), 1246 (m), 1120 (m, br), 1067 (m, br), 1007 (w), 827 (m), 797 (m), 688 (m), 616 cm^{-1} (s, br). ^1H NMR ($CDCl_3$) δ = 1.10–1.45 (m, 12 H, $CH_2C\mathit{H}_3$), 1.84 (s, 6 H, $=CC\mathit{H}_3$), 1.94 (s, 3 H, $=CC\mathit{H}_3$), 2.00 (s, 3 H, $=CC\mathit{H}_3$), 4.24–4.76 (m, 8 H, $C\mathit{H}_2CH_3$), 5.36, 5.39, 5.49, 5.52, 6.06, 6.11, 6.16, 6.26 (eight s, 1 H, $=C\mathit{H}_2$).

X-ray Structure Analysis of 1. Crystals of 1 were separated from the reaction mixture and sealed in a glass capillary without drying. Unit-cell parameters: monoclinic, a = 1412.0 (3), b = 1710.1 (1), c = 1501.9 (2) pm, β = 107.458 (7)°, $V = 3479 \times 10^6$ pm^3; space group $P2_1/c$ (Z = 2), d_{calc} = 1.33 g/cm^3. The cell constants were determined by least-squares refinement of 25 reflections with high-θ-angles from different parts of the reciprocal space.

Data collection: Reflection intensities were measured in the range 2° $\leq 2\theta \leq$ 48° on an Enraf-Nonius CAD4 diffractometer by the $\omega/2\theta$ scan method using Mo Kα radiation (λ = 71.069 pm, graphite monochromator). After Lorentz, polarization, and an empirical absorption correction (μ = 7.2 cm^{-1}), 5685 independent structure factors were obtained. A decay correction was also employed, because the intensity of two check reflections decreased during the measurements by 28%.

Solution of the structure: The structure was solved by MULTAN. The ethyl groups attached to the oxygen atoms O(3), O(9), and O(11) are disordered, and therefore more than one position (with different weights) was assigned to most of the carbon atoms. Only one position per carbon atom was refined for C(130) and C(131), but the high-temperature factors also indicate some degree of disorder. The bond lengths C(61)–C(62) and C(61)–C(63) are nearly the same, and therefore the methyl and methylene groups of this methacrylate ligand is also disordered. Positions of the hydrogen atoms were calculated according to an ideal geometry except the hydrogen atoms attached to disordered carbon atoms. The atomic parameters were refined by full-matrix least-squares analysis with anisotropic thermal parameters for the Ti, O, and some C atoms and isotropic thermal parameters for the disordered carbon atoms. Hydrogen parameters were not refined (Enraf-Nonius SDP). The highest residual electron density (0.57×10^{-6} e/pm^3) was located close to the OEt groups, because of the extensive disorder. R = 0.067, R_w = 0.070 ($1/w = \sigma^2$) for 4447 reflections with $I \geq 2\sigma(I)$. Atomic coordinates are given in Table I, and selected bond distances and angles in Table II.

$[Zr(OPr^n)_3(OMc)]_n$ (2). Methacrylic acid (20 mmol) was slowly added to a solution of $Zr(OPr^n)_4$ (Dynamit Nobel) (20 mmol) in 100 mL of n-propyl alcohol (exothermic reaction). The solution was stirred for 30 min at ambient temperature and then the solvent was removed in vacuo. $C_{13}H_{26}O_5Zr$: C, 44.16; H, 7.41; Zr, 25.8. Found: C, 44.07; H, 7.22; Zr, 26.1. ^1H NMR (C_6D_6) δ = 0.9 (t, 9 H, $CH_2C\mathit{H}_3$), 1.7 (tq, 6 H, $C\mathit{H}_2CH_3$), 1.9 (s, 3 H, $=CC\mathit{H}_3$), 4.0 (t, 6 H, OCH_2), 5.4 (s, 1 H, $=CH_2$), 6.3 (s, 1 H, $=CH_2$).

$[Zr(OPr^n)_2(OMc)_2]_n$ (3). Methacrylic acid (40 mmol) was slowly added to a solution of $Zr(OPr^n)_4$ (Dynamit Nobel) (20 mmol) in 100 mL of n-propyl alcohol (exothermic reaction until the first 20 mmol of methacrylic acid was added). The solution was stirred for 30 min at ambient temperature and then the solvent was removed in vacuo. $C_{14}H_{24}O_6Zr$: C, 44.30; H, 6.37; Zr, 24.0. Found: C, 43.83; H, 6.70; Zr, 23.9. ^1H NMR (C_6D_6) δ = 0.9 (m, 6 H, $CH_2C\mathit{H}_3$), 1.9 (m, 4 H, $C\mathit{H}_2CH_3$), 2.0 (s, 6 H, $=CC\mathit{H}_3$), 4.0 (m, 4 H, OCH_2), 5.5 (s, 2 H, $=CH_2$), 6.5 (s, 2 H, $=CH_2$).

Table I. Atomic Coordinates in 1

atom	x	y	z	B(equ)
Ti1	0.83316 (9)	0.01873 (7)	0.51995 (8)	4.94 (3)
Ti2	0.93066 (9)	−0.04511 (7)	0.35012 (7)	4.55 (3)
Ti3	0.7025 (1)	−0.03034 (9)	0.28269 (9)	6.18 (3)
O1	0.8268 (3)	−0.0198 (2)	0.4000 (3)	4.5 (1)
O2	0.9635 (3)	0.0538 (2)	0.5534 (3)	4.34 (9)
O3	0.7787 (4)	0.1113 (3)	0.4896 (3)	6.8 (1)
O4	0.8899 (3)	−0.0899 (3)	0.5743 (3)	5.5 (1)
O5	0.8365 (3)	0.0382 (3)	0.6580 (3)	6.7 (1)
O6	0.7056 (3)	−0.0368 (3)	0.5171 (3)	6.9 (1)
O7	0.8968 (3)	−0.1591 (2)	0.3474 (3)	5.6 (1)
O8	1.0423 (3)	−0.0677 (2)	0.6689 (3)	5.2 (1)
O9	0.8121 (3)	−0.0335 (3)	0.2295 (3)	5.6 (1)
O10	0.9912 (3)	0.0683 (3)	0.7422 (3)	5.6 (1)
O11	0.6063 (4)	−0.0631 (4)	0.1824 (4)	8.4 (2)
O12	0.6185 (4)	−0.0477 (4)	0.3688 (4)	8.1 (2)
O13	0.6756 (4)	0.0714 (4)	0.2685 (4)	8.2 (2)
O14	0.7327 (4)	−0.1519 (3)	0.3135 (3)	6.9 (1)
C30	0.779 (2)	0.196 (1)	0.539 (2)	16.8 (7)
C31	0.844 (2)	0.227 (2)	0.506 (2)	13.2 (7)
C32	0.787 (2)	0.195 (2)	0.468 (2)	13.0 (8)
C33	0.764 (3)	0.239 (2)	0.516 (2)	12 (1)
C40	0.9685 (5)	−0.1114 (4)	0.6323 (4)	4.8 (1)
C41	0.9768 (6)	−0.1949 (4)	0.6632 (5)	6.2 (2)
C42	1.0620 (8)	−0.2199 (5)	0.7234 (7)	10.2 (3)
C43	0.8879 (8)	−0.2420 (5)	0.6283 (6)	9.2 (3)
C50	0.9008 (5)	0.0573 (4)	0.7328 (4)	5.6 (2)
C51	0.8673 (5)	0.0674 (5)	0.8179 (5)	6.4 (2)
C52	0.9340 (7)	0.0777 (6)	0.9020 (5)	8.6 (3)
C53	0.7639 (7)	0.0638 (8)	0.8040 (6)	11.0 (3)
C60	0.6311 (6)	−0.0582 (5)	0.4535 (5)	6.6 (2)
C61	0.5514 (6)	−0.0971 (6)	0.4838 (7)	9.5 (3)
C62	0.4644 (8)	−0.1137 (8)	0.415 (1)	14.6 (5)
C63	0.5709 (8)	−0.115 (1)	0.5786 (8)	16.6 (4)
C70	0.8113 (6)	−0.1896 (4)	0.3367 (4)	6.2 (2)
C71	0.8104 (7)	−0.2755 (4)	0.3546 (6)	8.0 (2)
C72	0.8938 (8)	−0.3182 (5)	0.3772 (7)	9.7 (3)
C73	0.715 (1)	−0.3076 (6)	0.3472 (9)	14.3 (5)
C90	0.817 (1)	0.0089 (9)	0.139 (1)	8.2 (4)
C91	0.769 (1)	−0.045 (1)	0.062 (1)	10.5 (5)
C92	0.800 (1)	−0.041 (1)	0.134 (1)	6.2 (4)
C93	0.797 (2)	0.046 (2)	0.100 (2)	11.6 (8)
C110	0.548 (1)	−0.1363 (9)	0.139 (1)	16.2 (5)
C111	0.546 (3)	−0.155 (3)	0.064 (3)	15 (1)
C112	0.463 (3)	−0.118 (2)	0.126 (2)	15 (1)
C113	0.461 (3)	−0.097 (2)	0.070 (3)	12 (1)
C130	0.579 (1)	0.119 (1)	0.230 (1)	17.8 (6)
C131	0.613 (2)	0.182 (1)	0.206 (1)	23.0 (8)

$[Zr_3O_3(OH)(OPr^n)_2(OMc)_3]_n$ (4). A solution of 20 mmol of $Zr(OPr^n)_4$ and 20 mmol of methacrylic acid (equivalent to 20 mmol of 2) in 100 mL of n-propyl alcohol was stirred for 30 min. After addition of 20, 40, 60, or 80 mmol of water the solution was stirred for an additional 48 h (the solution remains clear) and then the amount of unreacted water was determined by Karl Fischer titration.[16] While all water was consumed if 20 mmol of H_2O were added, only 27 mmol of water was consumed in the other experiments, independent of the amount of added water. For elemental analysis, the solvent was removed in vacuo from the reaction mixture after 48 h. $C_{18}H_{30}O_{12}Zr_3$: C, 30.36; H, 4.25; Zr, 38.4. Found: C, 29.45; H, 3.74; Zr, 38.6. ^1H NMR ($CDCl_3$) δ = 0.9 (m, br, 6 H, $CH_2C\mathit{H}_3$), 1.9 (m, br, 13 H, $C\mathit{H}_2CH_3$ and $=CC\mathit{H}_3$), 3.8 (m, br, 5 H, OCH_2 and OH), 52. (s, br, 3 H, $=CH_2$), 6.1 (s, 3 H, $=CH_2$).

The same compound (4) was obtained by the following procedure: 0.5 equiv of methacrylic acid was added to a 72% solution of $Zr(OPr^n)_4$ in n-propyl alcohol. The solution was cooled to 0 °C. Then a mixture of the second 0.5 equiv of methacrylic acid and 1.3 equiv of water was added during 30 min at 10 °C. The reaction mixture was stirred for 1 h, and then the solvent was removed in vacuo.

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Table II. Selected Bond Distances (pm) and Angles (deg) in 1

Ti(1)–O(1)	189.5 (4)	C(40)–O(4)	124.7 (7)
Ti(1)–O(2)	186.5 (4)	C(40)–O(8)	127.0 (7)
Ti(1)–O(3)	176.0 (5)	C(50)–O(5)	125.9 (7)
Ti(1)–O(4)	209.0 (4)	C(50)–O(10)	126.3 (9)
Ti(1)–O(5)	208.8 (5)	C(60)–O(6)	124.7 (8)
Ti(1)–O(6)	203.4 (5)	C(60)–O(12)	124.3 (9)
Ti(2)–O(1)	189.5 (5)	C(70)–O(7)	128.7 (9)
Ti(2)–O(2)	175.2 (3)	C(70)–O(14)	124.3 (9)
Ti(2)–O(7)	200.5 (4)	C(40)–C(41)	149.3 (9)
Ti(2)–O(8)	200.4 (4)	C(41)–C(42)	134 (1)
Ti(2)–O(9)	207.9 (4)	C(41)–C(43)	146 (1)
Ti(2)–O(10)	205.8 (5)	C(50)–C(51)	150 (1)
Ti(3)–O(1)	209.3 (3)	C(51)–C(52)	134.3 (9)
Ti(3)–O(9)	195.2 (5)	C(51)–C(53)	142 (1)
Ti(3)–O(11)	179.3 (5)	C(60)–C(61)	150 (1)
Ti(3)–O(12)	202.9 (6)	C(61)–C(62)	138 (1)
Ti(3)–O(13)	178.0 (6)	C(61)–C(63)	140 (2)
Ti(3)–O(14)	214.5 (5)	C(70)–C(71)	149 (1)
		C(71)–C(72)	134 (1)
		C(71)–C(73)	144 (2)
O(1)–Ti(1)–O(2)	97.4 (2)	O(8)–Ti(2)–O(9)	85.6 (2)
O(1)–Ti(1)–O(3)	100.0 (2)	O(8)–Ti(2)–O(10)	85.7 (2)
O(1)–Ti(1)–O(4)	88.0 (2)	O(9)–Ti(2)–O(10)	83.7 (2)
O(1)–Ti(1)–O(5)	168.8 (2)	O(1)–Ti(3)–O(9)	76.9 (2)
O(1)–Ti(1)–O(6)	91.7 (2)	O(1)–Ti(3)–O(11)	166.2 (2)
O(2)–Ti(1)–O(3)	96.0 (2)	O(1)–Ti(3)–O(12)	89.1 (2)
O(2)–Ti(1)-O(4)	86.9 (2)	O(1)–Ti(3)–O(13)	96.5 (2)
O(2)–Ti(1)–O(5)	87.5 (2)	O(1)–Ti(3)–O(14)	80.7 (2)
O(2)–Ti(1)–O(6)	163.9 (2)	O(9)–Ti(3)–O(11)	98.4 (2)
O(3)–Ti(1)–O(4)	171.0 (2)	O(9)–Ti(3)–O(12)	162.0 (2)
O(3)–Ti(1)–O(5)	89.5 (2)	O(9)–Ti(3)–O(13)	98.5 (3)
O(3)–Ti(1)–O(6)	95.4 (2)	O(9)–Ti(3)–O(14)	86.0 (2)
O(4)–Ti(1)–O(5)	82.1 (2)	O(11)–Ti(3)–O(12)	92.6 (3)
O(4)–Ti(1)–O(6)	80.2 (2)	O(11)–Ti(3)–O(13)	97.0 (3)
O(5)–Ti(1)–O(6)	81.3 (2)	O(11)–Ti(3)–O(14)	86.0 (2)
O(1)–Ti(2)–O(2)	105.6 (2)	O(12)–Ti(3)–O(13)	94.2 (3)
O(1)–Ti(2)–O(7)	91.2 (2)	O(12)–Ti(3)–O(14)	80.6 (2)
O(1)–Ti(2)–O(8)	92.4 (2)	O(13)–Ti(3)–O(14)	174.1 (3)
O(1)–Ti(2)–O(9)	78.5 (2)	Ti(1)–O(1)–Ti(2)	129.4 (2)
O(1)–Ti(2)–O(10)	162.2 (2)	Ti(1)–O(1)–Ti(3)	128.2 (2)
O(2)–Ti(2)–O(7)	94.3 (2)	Ti(2)–O(1)–Ti(3)	101.9 (2)
O(2)–Ti(2)–O(8)	92.6 (2)	Ti(1)–O(2)–Ti(2)	136.9 (2)
O(2)–Ti(2)–O(9)	175.7 (2)	Ti(2)–O(9)–Ti(3)	100.5 (2)
O(2)–Ti(2)–O(10)	92.2 (2)	O(4)–C(40)–O(8)	125.2 (6)
O(7)–Ti(2)–O(8)	171.1 (2)	O(5)–C(50)–O(10)	125.3 (6)
O(7)–Ti(2)–O(9)	87.0 (2)	O(6)–C(60)–O(12)	124.7 (8)
O(7)–Ti(2)–O(10)	88.5 (2)	O(7)–C(70)–O(14)	124.0 (6)

[ZrO(OMc)$_2$] (5). The experiment was performed as for 4, starting with a solution of 20 mmol of Zr(OPr^n)$_4$ and 40 mmol of methacrylic acid (equivalent to 20 mmol of 3) in 100 mL of n-propyl alcohol.

Alternative procedure: A mixture of 1 equiv of methacrylic acid and 1 equiv of water was slowly added to a 72% solution of Zr(OPr^n)$_4$ in *n*-propyl alcohol at 0 °C. Then a second equivalent of methacrylic acid was added dropwise at 0 °C. After addition of methacrylic acid the solvent was quickly removed in vacuo. $C_8H_{10}O_5Zr$: C, 34.64; H, 3.63; Zr, 32.9. Found: C, 34.59; H, 3.85; Zr, 31.2. ^{1}H NMR (CDCl$_3$) δ = 1.8 (m, 3 H, =CCH$_3$), 5.4 (s, br, 1 H, =CH$_2$), 6.1 (s, 1 H, =CH$_2$).

Results and Discussion

Ti(OEt)$_4$/Methacrylic Acid. Reaction of 1 equiv of methacrylic acid with Ti(OEt)$_4$ at room temperature is exactly the same as has been described for acetic acid.[6] For this reason, details are not repeated here. If the amount of methacrylic acid is gradually increased while the reaction is monitored by IR spectroscopy, the ν(CO) band of uncoordinated methacrylic acid appears after addition of about 1.3 equiv (Figure 1).

From the reaction mixture between methacrylic acid and Ti(OEt)$_4$ in a 2:1 molar ratio, colorless crystals separate within a week. Elemental analysis and ^{1}H NMR data are consistent with the composition $Ti_6O_4(OEt)_8(OMc)_8$ (1) (OMc = OC(O)C(Me)=CH$_2$). As with acetic acid, only 1.33 equiv of acid is consumed for coordination, while the remainder generates water by esterification. Since this Ti:OMc ratio corresponds to what is observed on titration of Ti(OEt)$_4$ with methacrylic acid, we assume that species of the composition [Ti$_3$(OEt)$_8$(OMc)$_4$]$_n$ are initially formed, which are subsequently hydrolyzed (generation of water by esterification is much slower than substitution of OEt by OMc). In the infrared spectrum of 1 (KBr pellet, see Experimental Section) the bands at 1558, 1539 and 1456, 1413 cm^{-1} are assigned to asymmetric and symmetric COO stretching vibrations.[17] Since no band is seen in the carbonyl region, all methacrylate groups must be in a chelating or bridging coordination mode. A band at 1644 cm^{-1}, assigned to ν(C=C), shows the presence of uncoordinated double bonds (for comparison: ν(C=C) in methacrylic acid at 1636 cm^{-1}). The IR spectrum of 1 between 4000 and 1200 cm^{-1} is very similar to that of [Ti(OEt)$_3$(OMc)]$_n$, formed by reaction of Ti(OEt)$_4$ and methacrylic acid in a 1:1 molar ratio. Two additional strong bands at 798 and 687 cm^{-1} in the spectrum of 1 are tentatively assigned to Ti–O–Ti vibrations.

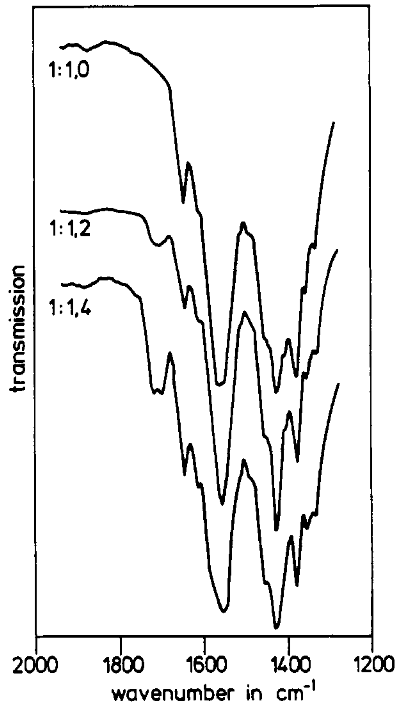

Figure 1. Infrared spectra of Ti(OPr^n)$_4$ reacted with 1.0, 1.2, or 1.4 mol equiv of methacrylic acid.

Integration of the signals in the ^{1}H NMR spectrum of 1 (see Experimental Section) shows that OEt and OMc groups are present in a 1:1 ratio. According to the solid-state structure of 1 (vide infra) there are four pairs of stereochemically inequivalent methacrylate ligands, i.e., there are four signals for each of both =CH$_2$ protons (the geminal HCH couplings are not resolved). Two of the methacrylate methyl signals coincide and therefore only three signals (2:1:1 ratio) are observed. The signals of the diastereotopic ethyl CH$_2$ groups are split to an ABX$_3$ spin system. A quantitative assignment was not undertaken, because the signals of the four inequivalent CH$_2$ groups partially overlap. For the same reason, the ethyl CH$_3$ signals are also unresolved.

The result of the X-ray structure analysis of 1 is shown in Figures 2 and 3. Important bond distances and angles

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[17] von Thiele, K. H.; Pause, M. *Z. Anorg. Allg. Chem.* **1978**, *441*, 23.

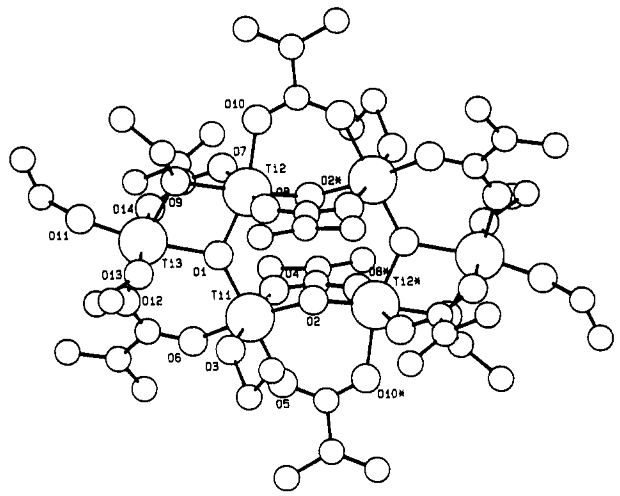


Figure 2. Molecular structure of $Ti_6O_4(OEt)_8(OMc)_8$ (1). Only one position of the disordered ethyl groups is drawn.

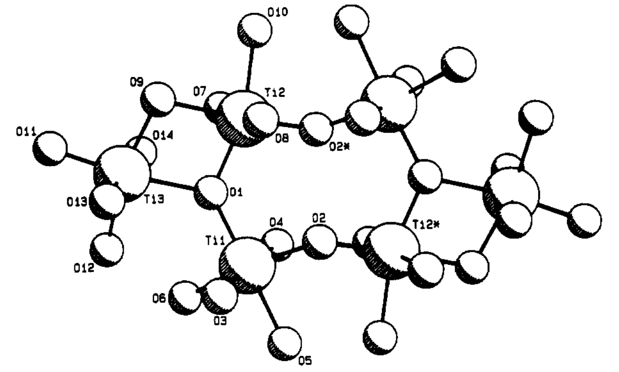


Figure 3. Inner core of the structure of 1 showing the linkage of the $[TiO_6]$ octahedra.

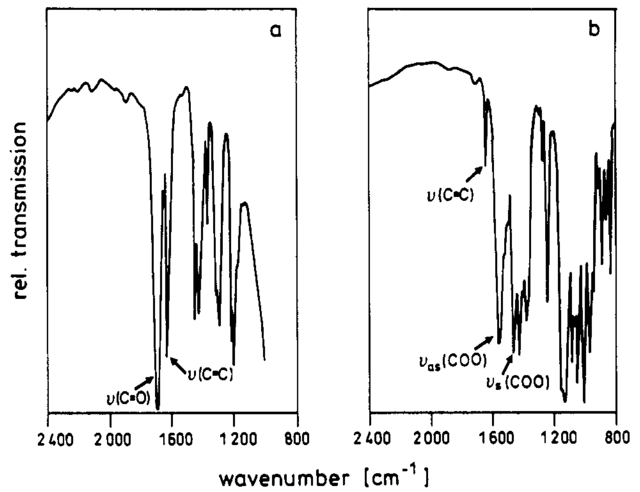
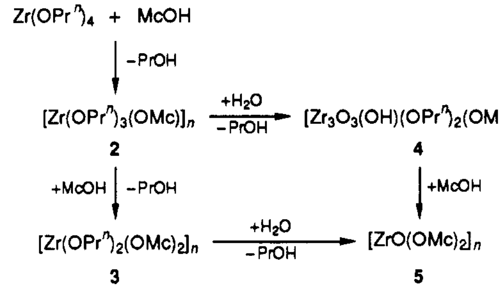


Figure 4. Infrared spectra of $[Zr(OPr^n)_3(OMc)]_n$ (2) (b), compared with uncoordinated methacrylic acid (a).

Scheme I[a]



[a] Mc = $H_2C{=}C(Me){-}C(O){-}$.

are given in Table II. The overall structure is crystallographically centrosymmetric and consists of six connected $[TiO_6]$ octahedra, sharing both edges and corners (Figure 3). The oxygen atoms bonded to the metal atoms originate from five different types of ligands: μ_2- and μ_3-oxo bridges (O(2) and O(1), respectively), terminal (O(3), O(11), and O(13)) and bridging (O(9)) ethoxy ligands, and bridging methacrylate ligands (O(4)–O(8), O(10), O(12), and O(14)). The three crystallographically independent titanium atoms have different ligand environments: both Ti(1) and Ti(2) are coordinated by three methacrylate ligands, a μ_2- and a μ_3-oxygen, but they differ by the bonding mode of an OEt ligand (terminal at Ti(1) and bridging at Ti(2)) and by the position of the methacrylate oxygen atoms (Ti(1), fac; Ti(2), mer); Ti(3) is coordinated by two methacrylate ligands, the μ^3-oxygen, two terminal and one bridging OEt ligand.

The Ti–O bond lengths are in the range 176–215 pm. This considerably large variation is due to the different kind of oxygen donors but is also influenced to a high degree by the nature of the trans ligand. The longest Ti–O distances are generally found trans to a terminal OEt ligand. For instance, the distance of the μ_3-oxygen atom O(1) to Ti(3) (209.3 (3) pm) is significantly longer than to Ti(1) and Ti(2) (both 189.5 (4) pm, because of the different trans ligands (OEt at Ti(3), methacrylate at Ti(1) and Ti(2)).

The linkage of the $[TiO_6]$ octahedra and the coordination of the individual titanium atoms in 1 is the same as in the acetate derivatives $Ti_6O_4(OR)_8(OAc)_8$ (R = Bu^n, Et, Pr). The $Ti_6O_4(OR)_8(OOCR')_8$ building block therefore seems to be rather general for carboxylate-modified titanium alkoxides. The important conclusion of this work is that the double bonds of the methacrylate ligands do not interfere with the formation of the primary hydrolysis product. The methacrylate ligands are at the envelopment of the hexanuclear unit and their double bonds are fully accessible for a polymerization reaction.

$Zr(OPr^n)_4$/Methacrylic Acid. Addition of an equimolar amount of methacrylic acid to a solution of $Zr(OPr^n)_4$ in propyl alcohol results in an exothermic reaction and formation of a clear, yellowish solution. Both IR (Figure 4) and ^1H NMR spectra indicate that the total amount of methacrylic acid is consumed. The C=O vibration of uncoordinated methacrylic acid disappears, and the asymmetric stretching vibration of a bridging or chelating COO group at 1550 cm^{-1} is observed instead. Assignment of the symmetric stretching vibration is less obvious, because there are two bands at 1460 and 1425 cm^{-1}. The ^1H NMR spectrum and elemental analysis correspond to the composition $[Zr(OPr^n)_3(OMc)]_n$ (**2**, Scheme I). The propyl groups must be stereochemically equivalent or highly dynamic, because all NMR signals are sharp and well resolved.

Potentiometric titration of $Zr(OPr^n)_4$ (or **2**) with methacrylic acid at ambient temperature results in saturation at an uptake of about 1.8 mol of methacrylic acid/mol zirconium. The same result is obtained by IR spectroscopically monitoring the reaction (Figure 5): the ν(CO) band of uncoordinated methacrylic acid appears after addition of 1.8 equiv of methacrylic acid.

Both elemental analysis of the compound, isolated after addition of 2 equiv of methacrylic acid to $Zr(OPr^n)_4$, and integration of the signals in its ^1H NMR spectrum approximately correspond to the composition $[Zr(OPr^n)_2(OMc)_2]_n$ (**3**, Scheme I). However, both methods are too

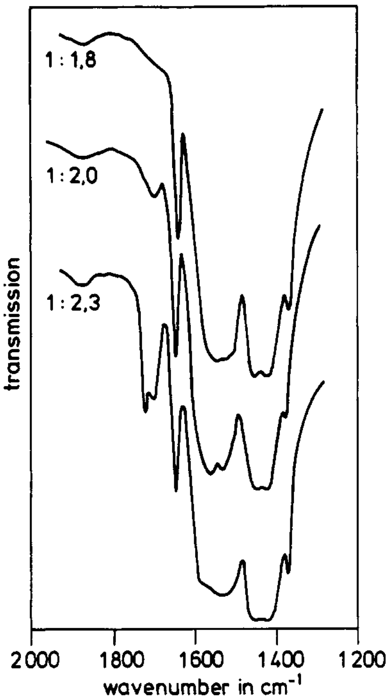


Figure 5. Infrared spectra of $Zr(OPr^n)_4$ reacted with 1.8, 2.0, or 2.3 mol equiv of methacrylic acid, respectively.

crude to recognize smaller deviations from this stoichiometry. The isolated compounds 2 and 3 have similar ^1H NMR spectra. While in 3 the methacrylate signals are well resolved, the signals of the propyl groups appear as rather broad multiplets, indicating the presence of stereochemically inequivalent OPr groups.

There are two possible explanations for the apparently contradicting spectroscopic and analytic results: (i) Addition of the second equivalent of methacrylic acid results in an equilibrium mixture of about 20% $[Zr(OPr^n)_3(OMc)]_n$ and 80% $[Zr(OPr^n)_2(OMc)_2]_n$. Workup of the reaction mixture (removal of propyl alcohol) could result in the isolation of pure $[Zr(OPr^n)_2(OMc)_2]_n$. (ii) A compound with the approximate composition $[Zr_5(OPr^n)_{11}(OMc)_9]_n$ is formed. We cannot distinguish between both possibilities; for simplicity we will refer to 3 as $[Zr(OPr^n)_2(OMc)_2]_n$ in the remainder of this article.

Alcoholic solutions of 2 and 3 are not stable for an extended period. We assume that part of the methacrylate ligands dissociate and are esterified with the propanol solvent. The thus-generated water converts 2 and 3 to mixed oxy/alkoxy carboxylates.

To study the hydrolysis reaction of 2 and 3 (Scheme I), various amounts of water (between 1 and 4 mol equiv) were added to propyl alcohol solutions of 2 or 3. Contrary to the hydrolysis of unmodified $Zr(OR)_4$, no precipitate is formed. After 48 h at room temperature, the amount of unreacted water was determined by Karl–Fischer (KF) titration,[16] and the products isolated from the clear solutions were analyzed by elemental analysis. The hydrolysis products of both 2 and 3 are still soluble in organic solvents, such as CH_2Cl_2 or $CHCl_3$. If the monomethacrylate 2 is reacted with water, both KF titration and elemental analysis show that only up to 1.33 equiv of water is consumed (Scheme I). Thermogravimetric analysis of the resulting compound 4 results in a weight loss of 46.9 up to 600 °C. Assuming that all the organic parts are removed at this temperature, 4 contains 53.1% ZrO_2 (39.3% Zr), which agrees well with the elemental analysis. The ^1H NMR spectrum is also consistent with the composition $Zr_3O_3(OH)(OPr^n)_2(OMc)_3$ or an oligomer thereof. Contrary to 2, the hydrolysis product 4 is stable is propyl alcohol solution (the IR spectrum did not change during 7 months) and does not dissociate methacrylic acid.

During Karl–Fischer titration of 3, 1 equiv of water is consumed, the full amount of water needed for complete hydrolysis and condensation (Scheme I). Starting from $[Zr(OPr^n)_2(OMc)_2]_n$ (3), it appears reasonable that the hydrolysis product 5 is the known compound $ZrO(OMc)_2$. Thermogravimetric analysis of 5 results in a weight loss of 56.8% up to 600 °C, corresponding to 43.2% ZrO_2 (32.0% Zr), which agrees well with the elemental analysis. Compound 5 is also obtained by addition of 1 equiv of methacrylic acid to isolated 4.

If the hydrolysis reactions are repeated several times, the elemental analyses of both 4 and 5 from different runs deviate from the values given in the Experimental Section by higher oxygen and hydrogen contents. However, the Zr:C ratio remains constant. This is probably due to adsorption of water or to formation of hydrolyzed species such as $Zr_3O_2(OH)_3(OPr^n)_2(OMc)_3$ and $Zr(OH)_2(OMc)_2$.

In conclusion, our investigations show that the modifications of $Ti(OEt)_4$ and $Zr(OPr^n)_4$ by methacrylic acid results in products of a different composition, if more than 1 equiv methacrylic acid is employed. Hydrolysis of the derived alkoxycarboxylates therefore provides structurally and chemically different building blocks for sol–gel-derived materials, in which the double bond of the methacrylate group is still available for polymerization reactions. Copolymerization of methacrylate-modified zirconium alkoxides with other unsaturated molecules was already shown to give new organic–inorganic copolymers with interesting properties.[2b,c,3] The results presented in this work allow a more deliberate synthesis of such materials and provide a better understanding of their microstructure.

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Supplementary Material Available: Tables of all atomic coordinates and thermal parameters and a complete list of bond distances and angles (10 pages); list of observed and calculated structure factors (21 pages). Ordering information is given on any current masthead page.