

New acrylic titanium polymers: 1. Synthesis and characterisation of new titanium trialkoxide methacrylate monomers prepared via the esterification of methacrylic acid by titanium tetraalkoxides

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In order to obtain a new family of acrylic organotitanium polymers which could be of major interest in the field of non-toxic, self-polishing, antifouling coatings, five acrylic organotitanium monomers, three of which are new, were synthesised. They were analysed by n.m.r. and FTi.r. spectroscopy as well as by microanalysis. Their main features were studied from a structural point of view. The presence of one to three types of structure was shown. The results were linked to the influence of the steric hindrance of the alkoxy groups attached to the titanium atom.
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INTRODUCTION

Self-polishing coatings, especially those of the organotin family, have been much used in marine applications during the last 15 years^{1,2}. These coatings can protect ships against fouling by the action of biocides included in the formulation and, in particular, organostannic species linked to an acrylic copolymer skeleton. The polymer is hydrolysed by the action of seawater and liberates organostannic species into the sea³. The remaining polymeric backbone becomes appreciably water sensitive and is thus released, as the other biocides. The organotin compounds are very effective against fouling, but their toxicity is so high that they constitute a real menace in the marine environment⁴. They are now partially forbidden, and a substitute for the organostannic polymer family is sought.

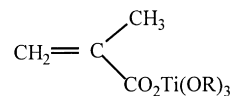
In this context, a major idea consists of preparing self-polishing coatings based on a non-toxic hydrolysable polymer. The prevention of fouling would then be ensured by the self-polishing behaviour of the coating combined with the liberation of biocides included as a filler.

From among many hydrolysable polymers with an acrylic skeleton and an organometallic group easily attacked by water, we selected titanium alkoxide acrylic copolymers. Like a number of transition metal alkoxides, titanium alkoxides (Ti(OR)₄) are very prone to nucleophilic attack. They are therefore extremely reactive towards water⁵. Moreover, their hydrolysis rapidly leads to non-organic species that are non-toxic in the marine environment. Acrylic organotitanium polymers could then have interesting

applications in the field of non-toxic, self-polishing antifouling coatings.

The major aim of this work was to study the feasibility of such a new polymer family. To this end, we first studied the preparation of organotitanium monomers^{6,7}, and then we explored the conditions that led to the polymers.

In this first paper, we wish to report investigations of the synthesis and characterisation of five monomers of general formula where R is *n*-butyl, isopropyl, *t*-butyl, *t*-amyl or 2-ethylhexyl.



These titanium trialkoxide methacrylates are organometallic compounds, among which three are new (in which R is *t*-butyl, *t*-amyl or 2-ethylhexyl)⁷.

The preparation of copolymers based on organotitanium will be reported in a subsequent publication.

EXPERIMENTAL

Monomer synthesis

The reagents were purchased from Aldrich, except titanium tetra-*t*-butoxide, which was obtained from Hüls. Methacrylic acid was dried over CaH₂ and distilled under reduced pressure. The titanium tetraalkoxides were used without further purification.

*Titanium tri-*t*-butoxide methacrylate.* Titanium tetra-*t*-butoxide (25.53 g; 0.075 mol) was placed in a 100 ml, three-necked flask equipped with a funnel for additions, a

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magnetic stirrer, a thermometer and a distillation column. The flask was heated to 55°C, and the pressure was 135 mmHg. Under vigorous stirring, 6.13 g of methacrylic acid (0.075 mol) were added dropwise to the titanium tetra-*t*-butoxide. *t*-Butyl alcohol was fractionated off continuously (b.p., 41°C at 135 mmHg pressure) and the desired product was thus obtained as a pale yellow, non-viscous liquid. The yield of this reaction was 97.5%. The crude product was not purified as it decomposed at higher temperatures.

Titanium tri-*t*-amyloxide methacrylate. In the first step, 14.21 g of titanium tetraisopropoxide (0.050 mol) were placed in a 100 ml, three-necked flask equipped with two funnels for additions, a magnetic stirrer and a distillation column. The flask was heated to 55°C, and the pressure was 150 mmHg. Under vigorous stirring, 13.22 g of *t*-amyl alcohol (0.150 mol) were added dropwise to the titanium tetraisopropoxide, and isopropyl alcohol was fractionated off continuously (b.p., 43°C at 150 mmHg pressure). The intermediate titanium isopropoxide tri-*t*-amyloxide was thus obtained.

The second step was carried out immediately after the first one, at 55°C and under reduced pressure (150 mmHg). Methacrylic acid (4.30 g; 0.050 mol) was added dropwise to the titanium isopropoxide tri-*t*-amyloxide under vigorous stirring. Isopropyl alcohol was fractionated off continuously (b.p., 43°C at 150 mmHg pressure) and the desired product was easily obtained as a pale yellow, non-viscous liquid. The yield of this two-step reaction was 95.8%. The crude product was not purified as it decomposed at higher temperatures.

Titanium tri(2-ethylhexoxide) methacrylate. In the first step, 17.02 g of titanium tetrabutoxide (0.050 mol) were placed in a 100 ml, three-necked flask equipped with two funnels for additions, a magnetic stirrer and a distillation column. The flask was heated to 50°C and the pressure was 110 mmHg. Under vigorous stirring, 4.30 g of methacrylic acid (0.050 mol) were added dropwise to the titanium tetrabutoxide, and butyl alcohol was fractionated off (b.p., 53°C at 110 mmHg pressure). A yellow, viscous product was formed, which was titanium tributoxide methacrylate.

The second step was carried out immediately after the first, at 50°C and under reduced pressure (110 mmHg). Under vigorous stirring, 19.54 g of 2-ethylhexyl alcohol (0.150 mol) were added dropwise to the titanium tributoxide methacrylate. Butyl alcohol was fractionated off continuously (b.p., 53°C at 110 mmHg). A yellow, viscous product was formed with a quantitative yield, which was titanium tri(2-ethylhexoxide) methacrylate. The crude product was not purified as it decomposed at higher temperatures.

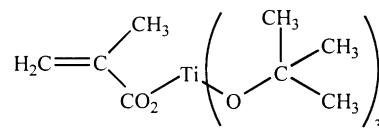
Monomer characterisation

All the monomers were analysed by n.m.r. and FTi.r. spectroscopy, and microanalysis.

The n.m.r. spectra were obtained with use of a Bruker AC-200 spectrometer with C₆D₆ as the deuterated solvent. Chemical shifts were measured with reference to 7.15 ppm (¹H) and 128 ppm (¹³C) for C₆D₆. The following notation is used to characterise the peak multiplicity in the ¹H n.m.r. spectra: s, singlet; sept, septuplet; sh, shoulder; t, triplet; m, multiplet.

FTi.r. spectra were acquired with use of an Ati Unicam spectrophotometer (4000–400 cm⁻¹). Wavenumbers are expressed in reciprocal centimetres.

Titanium tri-*t*-butoxide methacrylate.



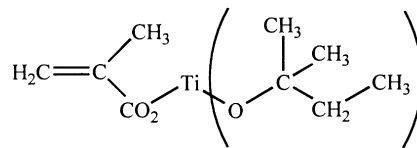
¹H n.m.r. (C₆D₆): 1.4 (s, 27H, 3CH₃ (*t*-Bu)); 1.8 (s, 3H, CH₃); 5.2 and 6.3 [t, 2H, =CH₂].

¹³C n.m.r. (C₆D₆): 17.0 (CH₃); 32.0 (CH₃ (*t*-Bu)); 79.6–86.0 (Ti–O–C); 127.2 (=CH₂); 136.7 (=C); 185.2 (CO₂).

FTi.r. (film). 2972, 2926: ν(CH₃); 1456, 1360: δ(CH₃); 1645: ν(C=C); 1588, 1550, 1525: ν(COO asym); 1425: ν(COO sym); 1005: ν(C–O); 638, 598, 558: ν(Ti–O).

Microanalysis. Calculated for C₁₆H₃₂O₅Ti: C, 54.54%; H, 9.15%; Ti, 13.59%. Found: C, 53.50%; H, 9.39%; Ti, 14.05%.

Titanium tri-*t*-amyloxide methacrylate.



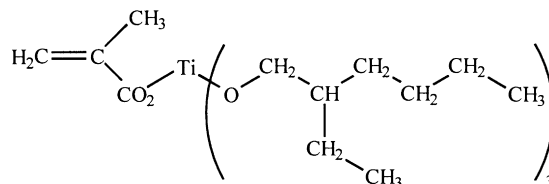
¹H n.m.r. (C₆D₆): 1.0 (t, 9H, CH₃ (*t*-Am)); 1.3 (s, 18H, 2CH₃ (*t*-Am)); 1.5 (m, 6H, CH₂ (*t*-Am)); 1.8 (s, 3H, CH₃); 5.2 and 6.3 (t, 2H, =CH₂).

¹³C n.m.r.: (C₆D₆) 9.1 (CH₃ (*t*-Am)); 17.0 (CH₃); 29.6 (CH₃ (*t*-Am)); 37.2 (CH₂ (*t*-Am)); 80.0 (Ti–O–C); 127.1 (=CH₂); 136.8 (=C); 185.1 (CO₂).

FTi.r. (film). 2970, 2926, 2880: ν(CH₂, CH₃); 1458, 1374, 1359: δ(CH₂, CH₃); 1646: ν(C=C); 1586, 1554, 1517: ν(COO asym); 1423: ν(COO sym); 1005: ν(C–O); 668, 624, 587: ν(Ti–O).

Microanalysis. Calculated for C₁₉H₃₈O₅Ti: C, 57.03%; H, 9.71%; Ti, 12.14%. Found: C, 56.68%; H, 9.74%; Ti, 14.30%.

Titanium tri(2-ethylhexoxide) methacrylate.



¹H n.m.r.: 0.9–1.1 (m, 18H, CH₃ (2-ethylhexyl)); 1.1–1.9 (m, 25H, CH₂ and CH (2-ethylhexyl)); 2.1 (s, 3H, CH₃); 4.6 (t, 6H, Ti–O–CH₂); 5.4 and 6.5 (s, 2H, =CH₂).

¹³C n.m.r.: 11.4 (CH₃ (2-ethylhexyl)); 14.3 (CH₃ (2-ethylhexyl)); 18.5 (CH₃); 23.5 (CH₂ (2-ethylhexyl)); 23.9 (CH₂ (2-ethylhexyl)); 29.6 (CH₂ (2-ethylhexyl)); 30.6 (CH₂ (2-ethylhexyl)); 42.2 (CH (2-ethylhexyl)); 83.1 (Ti–O–CH₂); 125.7 (=CH₂); 138.5 (=C); 173.3 (CO₂).

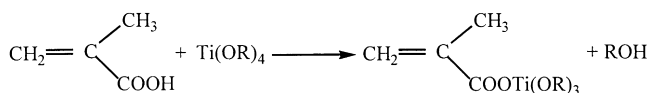
FTi.r. (film). 2958, 2928, 2872 and 2859: ν(CH, CH₂, CH₃); 1456, 1372: δ(CH, CH₂, CH₃); 1644: ν(C=C); 1556, 1519: ν(COO asym); 1423: ν(COO sym); 1088: ν(C–O); 678, 619, 553: ν(Ti–O).

Microanalysis. Calculated for C₂₈H₅₆O₅Ti: C, 64.59%; H, 10.84%; Ti, 9.20%. Found: C, 64.84%; H, 10.59%; Ti, 8.95%.

RESULTS AND DISCUSSION

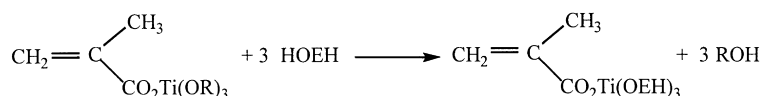
The titanium trialkoxide methacrylate monomers were synthesised via nucleophilic substitution between titanium

tetraalkoxide and methacrylic acid mixed in a stoichiometric molar ratio:



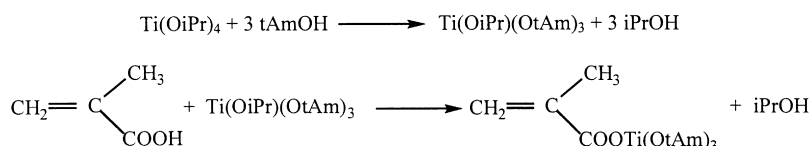
An important factor specific to all our syntheses is that they could be performed without any solvent.

In the present work, the desired product was obtained by continuously fractionating off the alcohol, ROH, under reduced pressure. This was possible only when the titanium tetraalkoxide precursor was available and when the boiling point of the alcohol was lower than that of methacrylic acid, such as for *t*-butanol. When the latter condition was not fulfilled, such as for 2-ethylhexanol (HOEH), a two-step reaction was carried out: the first step was as described previously, with R = *i*Pr or Bu, followed by alcohol exchange:



The ROH was progressively fractionated off and the desired product was easily obtained.

Finally, when the titanium tetraalkoxide precursor was unavailable, such as for *t*-amyl alcohol, another precursor was used and the product was obtained by the two-step reaction:

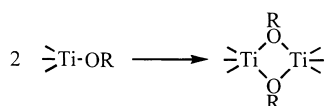


The alcohol *i*PrOH was continuously fractionated off under reduced pressure, and the desired product was thus obtained.

The derivatives with R = *i*Pr and R = Bu were synthesised as described in the literature⁸⁻¹¹. A major aspect of our work was to establish the structural behaviour of the five titanium trialkoxide methacrylates in order to explain the behaviour of copolymers based on these monomers. For this purpose, it was first necessary to clarify the more recent structural data available for titanium tetraalkoxides and for titanium trialkoxide carboxylates.

Titanium tetraalkoxides

In transition metal alkoxides, the oxidation state *n* of the metal is generally less than its normal coordination number *N*. Full coordination of the metal is therefore not satisfied in the monomeric alkoxides $\text{M}(\text{OR})_n$. Consequently, the metal atom tends to increase its coordination number by using its vacant d orbital to accept oxygen or nitrogen lone-pairs from nucleophilic ligands. In non-polar solvents, one finds that coordination expansion of the metal occurs via alkoxy bridging, which leads to the formation of more or less condensed oligomers in which the metal attains a higher coordination number. This oligomerisation is basically nucleophilic addition of a negatively charged OR group to a positively charged metal atom M. It corresponds to an alcoholation reaction which could occur as follows (with M = Ti):



For titanium alkoxides, the oxidation state *n* is equal to 4, whereas its normal coordination number *N* is 6. Therefore, oligomerisation can occur. The molecular complexity depends on the nature of the alkoxy group. It decreases with increasing branching and bulkiness of the OR group because of steric hindrance effects.

Direct evidence for the oligomerisation of titanium alkoxides was recently provided by X-ray absorption experiments^{12,13}. Oligomers are formed in $\text{Ti}(\text{OEt})_4$, $\text{Ti}(\text{OPr})_4$ or $\text{Ti}(\text{OBu})_4$, which are all trimeric species, while bulkier groups lead to monomers, as in $\text{Ti}(\text{O}i\text{Pr})_4$ or $\text{Ti}(\text{O}t\text{-Am})_4$ ¹²⁻¹⁴.

The i.r. spectra of titanium tetraalkoxides exhibit one to three bands due to the Ti–O vibrations around 600 cm^{-1} , and one to two bands due to the C–O(Ti) vibrations around 1000 cm^{-1} ¹⁵.

Two different bands for C–O indicate the presence of an oligomer because of the coexistence of two kinds of alkoxy

group in the molecule: terminal and bridging; one single band is characteristic of a monomer⁵.

It therefore appears that FTi.r. spectroscopy is a good technique for establishing the behaviour of a given titanium tetraalkoxide.

Titanium trialkoxide carboxylates

The preparation of glasses and ceramics by the sol-gel process from titanium tetraalkoxides is rather well known. The reaction of these compounds with chemical additives has been studied in particular, as the resulting products lead to improved materials compared with classical titanium tetraalkoxides¹⁶. With that aim in view, acetic acid has often been used^{17,18}. In order to understand totally its role, several authors have tried to establish the structure of the final product resulting from the reaction between acetic acid and titanium tetraalkoxides in different molar ratios^{13,19-24}. Recently, the structure for the product resulting from the stoichiometric reaction between acetic acid and titanium tetrabutoxide was proposed²². When titanium tetraisopropoxide was used, another structure was found^{23,24}. In these studies, several techniques were used to establish a possible structure for the final product.

By the chemical shifts and by the values of integrations found for the different parts of the final compound, ¹H and ¹³C n.m.r. spectroscopy clearly showed that the reaction occurred in a one-to-one molar ratio, giving rise to a new species in which the acetate ligand was bonded to the titanium atom.

I.r. spectroscopy is a good technique for characterising titanium trialkoxide carboxylates: the i.r. spectra of these compounds exhibit a set of two new bands between 1250 and 1770 cm^{-1} that can be assigned to the ν_a and ν_s vibrations of the carboxylate ligand²⁵. This is evidence that the chemical reaction has occurred. Moreover, it gives the possibility of defining the coordination mode of the carboxylate ligand. This kind of ligand has several coordination modes, as shown in Figure 1, including

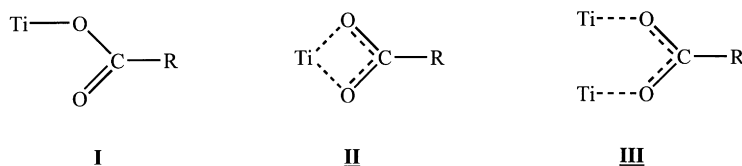


Figure 1 Possible coordination modes for the carboxylate ligands

monodentate **I**, bidentate chelating **II**, and bidentate bridging **III**²⁶ which can be identified by the frequency separation $\Delta\nu = \nu_a - \nu_s$. For the free acetate ion, $\Delta\nu = 164 \text{ cm}^{-1}$. The value of $\Delta\nu$ is much greater in monodentate carboxylates (around 400 cm^{-1}), and is smaller in bidentate ligands ($80\text{--}160 \text{ cm}^{-1}$)²⁶. Bridging carboxylates usually give rise to larger $\Delta\nu$ than chelating ones, *i.e.* between 120 and 160 cm^{-125} .

X-ray absorption experiments performed on the products are very helpful for obtaining structural information. XANES experiments at the Ti K-edge provide information about the coordination around the Ti atom, while EXAFS studies gives the distance of the Ti atom from its neighbours.

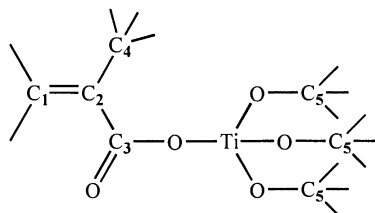
These different techniques allowed possible structures of titanium tributoxide acetate and titanium triisopropoxide acetate to be established^{22–24}. These are shown in Figures 2 and 3.

Titanium trialkoxide methacrylates

The reaction of methacrylic acid with titanium tetraalkoxides has been studied for years^{8–28}. However, recently, this kind of product appeared to be of interest for the sol-gel process, and was then extensively studied^{29–32}. Nevertheless, the structural behaviour of the compounds was never proposed, even though *i.r.* spectroscopy and *n.m.r.* spectroscopy were performed on the final products.

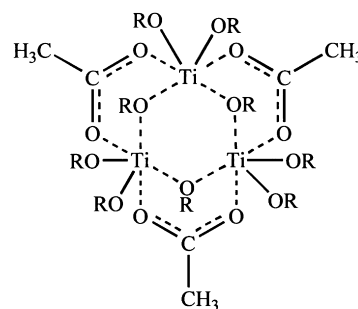
As we saw before, the nature of the alkoxy group has a clear influence on the structure of the titanium tetraalkoxide as well as on the structure of the titanium trialkoxide carboxylate. Therefore, we tried to establish the structural behaviour of the five titanium trialkoxide methacrylates that we prepared. To that end, we analysed these compounds by *i.r.*, and ¹H and ¹³C *n.m.r.* spectroscopy. Our purpose was not to define exactly the structure of these five compounds, but to try to find tendencies in the structural behaviour of our products according to the nature of the alkoxy group.

The atoms comprising the skeleton of our compounds are designated by numbers in order to facilitate this purpose:



R = iPr

Figure 2 A possible structure of acetate titanium triisopropoxide



R = Bu

Figure 3 A possible structure of acetate titanium tributoxide

ligands are in the same configuration. In the case of titanium tributoxide methacrylate, the two kinds of C–O vibrations provide evidence that both bridging and terminal butoxy groups are present, whereas only terminal alkoxy groups are seen for the four other compounds.

Moreover, for the all compounds, one can observe a set of two new bands between 1400 and 1600 cm^{-1} that can be assigned to the $\nu_a(\text{COO})$ (around 1550 cm^{-1}) and $\nu_s(\text{COO})$ (around 1420 cm^{-1}) vibrations of the carboxylate group²⁵. This doublet provides evidence that a chemical reaction has occurred, giving rise to a covalent bond.

A detailed analysis shows that, according to the nature of the alkoxy group, one to three components of the ν_a vibration can be observed, as shown in Table 3. These different components of ν_a lead to different values of the frequency separation $\Delta\nu$ ($\Delta\nu = \nu_a - \nu_s$).

The results in Table 3 show that, according to the values of $\Delta\nu$, and assuming that the observed values for the acetate compounds can be transposed to values for the methacrylate compounds, all the compounds exhibit ligands that are in a bidentate coordination mode, bridging or chelating.

The most important ¹H and ¹³C *n.m.r.* data are given in Table 1, and the *i.r.* data are collected in Table 2.

The *i.r.* spectra of the five titanium trialkoxide methacrylates synthesised as above display the following features. The most characteristic bands of methacrylic acid have disappeared, except that due to the C=C vibration around 1650 cm^{-1} . The Ti–O and C–O vibrations are still present. The titanium trialkoxide methacrylates display the same C–O vibrations as the titanium tetraalkoxide precursors, which allows us to suppose that the Ti–O–C

Table 1 Principal n.m.r. chemical shifts for methacrylic acid (MAOH), titanium tetraalkoxides Ti(OR)₄, and titanium trialkoxides methacrylate MAOTi(OR)₃

Compound	H4 (ppm)	H5 (ppm)	C4 (ppm)	C5 (ppm)
MAOH	1.73(s)	–	17.8	–
Ti(OBu) ₄	–	4.29(t)	–	75.0
MAOTi(OBu) ₃	1.97(s) 2.05(s)	4.51(m) 4.64(t) 4.72(t)	18.7	76.3 74.7 74.2
Ti(OiPr) ₄	–	4.43(sept)	–	76.3
MAOTi(OiPr) ₃	2.01(s) 1.95(sh)	5.07(sept) 4.8–4.9(sh)	18.9	78.1 76.9
Ti(OEH) ₄	–	4.25(sh) 4.55(sh)	–	78.1
MAOTi(OEH) ₃	2.06(s) 2.08(s)	4.59(t) 4.50(sh)	18.5	83.1 81.4
Ti(Or-Bu) ₄	–	–	–	80.0
MAOTi(Or-Bu) ₃	1.76(s) 1.94(s) 2.05(s)	–	17.0	79.6 80.8 85.6 86.0
Ti(Or-Am) ₄	–	–	–	82.5
MAOTi(Or-Am) ₃	1.78(s)	–	17.0	80.0 86.6

Table 2 Principal wavenumbers (cm⁻¹) of bands in the i.r. spectra of methacrylic acid MAOH, titanium tetraalkoxides Ti(OR)₄, and titanium trialkoxide methacrylate MAOTi(OR)₃

Compound	$\nu_{\text{Ti-O}}$	$\nu_{\text{O-C}}$	$\nu_{\text{a(COO)}}$	$\nu_{\text{s(COO)}}$
MAOH	–	–	1698	1299
Ti(OBu) ₄	603 551	1084 terminal 1037 bridging	–	–
MAOTi(OBu) ₃	614 557	1097 terminal 1036 bridging	1556	1424
Ti(OiPr) ₄	620 592	1003 terminal	–	–
MAOTi(OiPr) ₃	629	1009 terminal	1561 1516	1424
Ti(OEH) ₄	661	1068 terminal	–	–
MAOTi(OEH) ₃	678 619 553	1088 terminal	1556 1519	1423
Ti(Or-Bu) ₄	598	1003 terminal	–	–
MAOTi(Or-Bu) ₃	638 598 558	1005 terminal	1588 1550 1525	1425
Ti(Or-Am) ₄	627 588	1006 terminal	–	–
MAOTi(Or-Am) ₃	668 624 587	1005 terminal	1586 1554 1517	1423

When R = Bu, all the methacrylate ligands are equivalent, with a value of $\Delta\nu$ that suggests a bridging coordination mode. When R = iPr or 2-ethylhexyl, there are two values of $\Delta\nu$, which indicates that the methacrylate ligands exist in at least two coordination modes, whereas when R = *t*-Bu or *t*-Am, there are three values of $\Delta\nu$, which indicates that the methacrylate ligands exist in at least three coordination modes. In these four last compounds, both bridging and chelating modes are present.

Table 3 Characteristic bands of methacrylate ligands in CH₂=C(CH₃)-CO₂-Ti(OR)₃ and their frequency separation according to the nature of the alkoxy group R

R	ν_{a} (cm ⁻¹)	ν_{s} (cm ⁻¹)	$\Delta\nu$ (cm ⁻¹)	Coordination mode of the ligand
Bu	1556	1424	132	Bridging
iPr	1561	1424	137	Bridging
	1516		92	Chelating
<i>t</i> -Bu	1588	1425	163	Bridging
	1550		125	Bridging
	1525		100	Chelating
<i>t</i> -Am	1586	1423	163	Bridging
	1554		131	Bridging
	1517		94	Chelating
2-Ethylhexyl	1556	1423	133	Bridging
	1519		96	Chelating

The ¹H and ¹³C n.m.r. spectra provide other interesting details concerning the five compounds. Comparison with spectra recorded for the pure alkoxides shows that new signals have appeared. They can be assigned to CH₂=C(CH₃)-COO groups, and their chemical shifts (see Table 1) clearly show that the methacrylate ligand is bonded to a Ti atom. Moreover, the signals are very often composed of two or three peaks for the methacrylate and the alkoxy groups, showing that the ligands exist in different chemical environments. Therefore, from all this information we can deduce the following main important structural features of the five compounds.

- Titanium tributoxide methacrylate has a carboxylate group in the bridging coordination mode. It is thus necessarily an oligomer, which could be a dimer as shown for titanium tributoxide acetate. The Ti atoms are linked by carboxylate groups as well as by bridging butoxy groups. Finally, it also possesses terminal butoxy groups. Figure 4 illustrates one possible structure of such a compound.
- Titanium trisopropoxide methacrylate and titanium tri(2-ethylhexoxide) methacrylate display the same features. All the alkoxy groups are terminal. Two kinds of methacrylate group are present: a bridging one and a chelating one. Therefore, these two compounds could be a mixture of two different species in equilibrium: an oligomer, perhaps dimer, with the methacrylate group in a bridging coordination, and a monomer, with this group in a chelating position. These two possibilities are shown in Figure 5.
- Titanium tri-*t*-butoxide methacrylate and titanium tri-*t*-amyloxide methacrylate display the same features. Once again, all the alkoxy groups are in the terminal position. Three values of $\Delta\nu$ indicate that three coordination modes are adopted by the methacrylate ligands: two that would be bridging ($\Delta\nu$ around 160 cm⁻¹, and $\Delta\nu$ around 130 cm⁻¹) and one chelating ($\Delta\nu$ around 95 cm⁻¹). The following is considered to justify the choice of a bridging coordination mode for the intermediate value of $\Delta\nu$ (130 cm⁻¹): in a compound where all the alkoxy groups are in the terminal position, chelated structures are necessarily monomers and only one type of such structure can exist, which is shown by the value of $\Delta\nu$ of around 95 cm⁻¹.

Finally, at least three different species are necessary to describe these two compounds. The simplest are:

one monomer, with terminal alkoxy groups and a chelating methacrylate group;

two oligomers, with terminal alkoxy groups and bridging methacrylate groups that would link together the Ti atoms. The variation between the values of $\Delta\nu$ could be explained by the difference in the number of units that would compose the oligomers. For example, we can consider the possibility of dimers and trimers that would coexist. The three possible structures of the two compounds are illustrated in *Figure 6*.

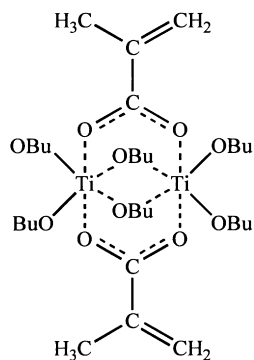
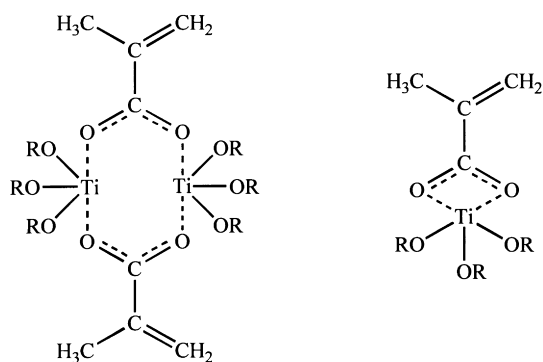
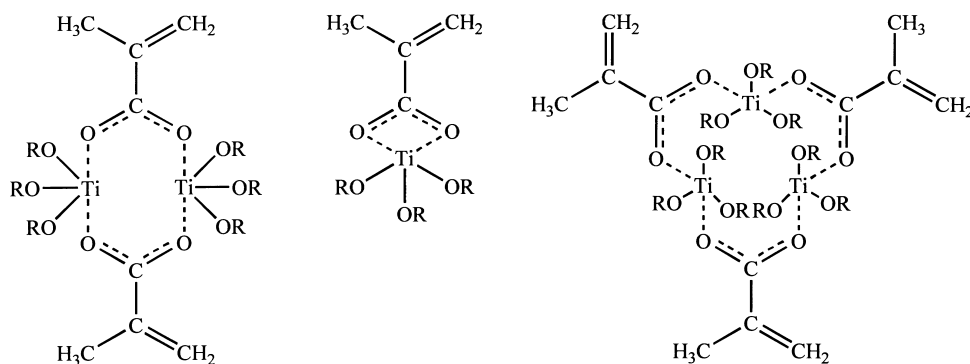


Figure 4 A possible structure of methacrylate titanium tributoxide



R = iPr, EH

Figure 5 Two possible structures in equilibrium of methacrylate titanium triisopropoxide and of methacrylate titanium tri(2-ethylhexoxide)



R = tBu, tAm

Figure 6 Three possible structures in equilibrium of methacrylate titanium tritertibutoxide and of methacrylate titanium tritertioamyloxide

This study shows an important influence of the nature of the alkoxy group on the structural behaviour of the corresponding titanium trialkoxide methacrylates.

When methacrylic acid is added to a titanium tetraalkoxide, the evolution of the reaction, from a structural point of view, is closely linked to the nature of the alkoxy group. The most important parameter seems to be the steric bulkiness.

In all cases, we can see that at least one oligomeric species is formed in which $\Delta\nu$ has a value around 130 cm^{-1} . If the alkoxy groups are not too bulky, they can adopt a terminal as well as a bridging position (R = Bu). However when their bulkiness increases (R = iPr, 2-ethylhexyl), they can only be in a terminal position. Moreover, this increase is also explained by the formation of a new species, which is a monomer with a carboxylate ligand in the chelating coordination mode ($\Delta\nu$ around 95 cm^{-1}). The formation of such a species is logical, as it is typically the kind of reaction outcome that is seen for titanium tetraalkoxides. More surprising is the formation of a third species, with the bulkiest alkoxy groups (R = *t*-Bu, *t*-Am). This species corresponds to an oligomer with a carboxylate ligand in the bridging coordination mode and terminal alkoxy groups. However the value of $\Delta\nu$, close to 160 cm^{-1} , shows that it is really a new species that is different from the first oligomeric species described above. This new oligomer could be the result of the association of a larger number of structural units, and the behaviour could be justified by the highly bulky nature of the alkoxy groups. Whatever the nature of the alkoxy group, the different species are probably in equilibrium. All these observations are grouped in *Table 4*, where the influence of the steric hindrance is clearly shown.

CONCLUSION

In this first part, our purpose was to describe the synthesis and the chemical characterisation of five titanium trialkoxide methacrylate monomers, among which three are new (in which R is *t*-butoxy, *t*-amyloxy or 2-ethylhexoxy).

Due to the particular behaviour of titanium carboxylates, it appeared to us that it was absolutely necessary to study the structures of the compounds we synthesised. To that end, we used i.r. and n.m.r. spectroscopy. From these analyses, we established several structural facts that led us to propose different structures. We showed how the nature of the

Table 4 Influence of steric hindrance on the structures of the titanium trialkoxide methacrylates

Group	<i>t</i> -Butoxy ≈	<i>t</i> -Amyloxy >	Isopropoxy ≈	2-Ethylhexoxy >	Butoxy
Terminal C–O	x	x	x	x	x
Bridging C–O					x
Bridging COO form I	x	x	x	x	x
Chelating COO	x	x	x	x	
Bridging COO form II	x	x			

alkoxy group was essential to the behaviour of the final product, with the coexistence of different species in equilibrium. We explained how new structures appeared with increasing alkoxy group bulkiness. All the compounds contain at least one oligomeric species, and it is very important to remember this fact as we intend to use these different titanium trialkoxide methacrylates in the synthesis of new copolymers.

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