

## Coordination Behavior of Acetoacetate Ligands with Attached Methacrylate Groups Containing Alkyl-Spacers of Different Length to Titanium and Zirconium Alkoxides

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Received February 20, 2007; accepted (revised) February 24, 2007; published online May 2, 2007  
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**Summary.** Metal-alkoxides containing polymerizable groups are regularly used as precursors for inorganic–organic hybrid materials applying the combination of the sol–gel process and organic polymerizations. Here we report the synthesis of acetoacetoxy derivatives that are linked to methacrylate groups *via* alkyl chains of different chain length. The coordination of the resulting molecules to titanium- and zirconium-alkoxides ( $M(OR)_4$ ;  $M = \text{Ti, Zr}$ ;  $R = \text{ethyl, butyl, isopropyl}$ ) was investigated applying NMR and FT-IR measurements. The results were related to structural data of the dinuclear complex  $[\text{Ti}(\text{O}^i\text{Pr})_3(\text{EAA})]_2$  (HEAA: ethyl acetoacetate) which was obtained by single crystal X-ray diffraction. The study revealed that the  $\beta$ -keto ester groups acted as chelating ligands in all cases and thus polymerizable coordination compounds were formed. However, NMR analyses in solution showed that transesterification of the methacrylic-type monomers occurred even at mild conditions as a side reaction in a ratio which was found to be dependent on the type of metal alkoxide used.

**Keywords.** Coordination chemistry; NMR spectroscopy; Organic–inorganic hybrid composites; Transition metals compounds; Transesterification.

### Introduction

Hybrid inorganic–organic materials are promising systems for a variety of applications because of their unique properties arising from both inorganic and organic components [1]. It is desirable to use well-defined molecular building blocks in their synthesis

which are tailored for the specific requirements of the final material [2, 3]. One important pathway in the preparation of the inorganic component in hybrid inorganic–organic materials is the sol–gel process because of its mild reaction conditions and its solvent based chemistry that opens many possibilities for the compositional and structural design of hybrid materials [4]. Typical molecular precursors of this process are silicon and metal alkoxides. Contrary to the silicon-based sol–gel process, where reaction parameters are well understood and tailoring of the structure and composition of the resulting materials is state of the art, the transition metal-based sol–gel process is much more difficult to control. The electropositive character of the metals and the higher number of coordination sites result in a much higher reactivity of the precursors and the control over material formation is reduced [5, 6]. In addition, if stable inorganic–organic materials should be prepared it is often necessary to attach the organic groups to the metal alkoxides by strong chemical bonds that endure the conditions of the hydrolysis and condensation reactions. Bidentate ligands are typically used in transition metal alkoxides to reduce their reactivity by blocking coordination sites and thus decreasing their reactivity as well as to incorporate additional organic functionalizations [7]. When the metal alkoxides are bearing polymerizable groups, such as methacrylates, hybrid inorganic–organic composites can be synthesized consisting of a metal oxide

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network and an organic polymer by copolymerization of the functionalized complexes followed by a sol-gel process. In the resulting materials a strong interaction between the organic polymer and the inorganic oxide network is formed *via* a metal-ligand coordination [8, 9]. Metal alkoxides regularly used in the formation of such materials are the oxophilic early transition metals such as titanium and zirconium [10–12]. Coordinating groups used to introduce polymerizable functions in metal alkoxides derivatives or clusters are based on acids [13, 14], diols [15], or isoeugenol-type compounds [16].  $\beta$ -Keto esters with attached polymerizable bonds such as 2-(methacryloyloxy)ethyl acetoacetate (HAAEMA) have only rarely been employed in the modification of metal alkoxides [15, 17–19]. *Devi et al.* showed in various papers the coordination of the bulky *tert*-butyl acetoacetate to Hf-, Ti-, and Zr-alkoxides and their thermal decomposition targeting them as precursors for MOCVD [20–22]. In these studies bulky alkyl esters without further chemical functionalization were used. The formation of monomeric or dinuclear species was observed in dependence of the type of ligand and metal center and the ratio between metal alkoxides and acetoacetate. The studies revealed that the decomposition of the coordinating ligands under thermolytic conditions results in the formation of a variety of products.

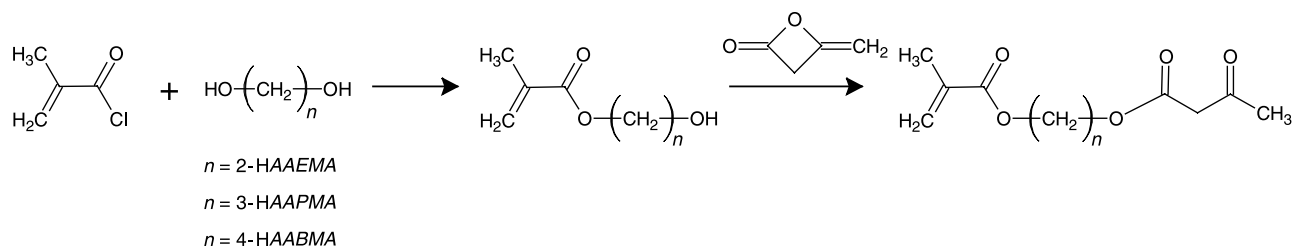
Here we present a study on the synthesis and coordination behavior of  $\beta$ -keto esters, such as 2-(methacryloyloxy)ethyl acetoacetate (HAAEMA), ethyl acetoacetate (EAA), 3-(methacryloyloxy)propyl acetoacetate (HAAPMA), and 4-(methacryloyloxy)butyl acetoacetate (HAABMA) and their coordination behavior to titanium and zirconium alkoxides. Beside the additional polymerizable functionality the ligands also contain further *Lewis*-basic sites that allow potential interactions with the metal centers. Their molecular structure was investigated in solution by FT-IR and 2D NMR and compared with

solid state results of the binuclear model compound  $[\text{Ti}(\text{O}^i\text{Pr})_3(\text{EAA})]_2$  by single crystal X-ray diffraction. In this study we reveal that even at mild conditions transesterification reactions that have an influence on the chemical composition of the final material occur.

## Results and Discussions

### *Synthesis and Characterization of $\beta$ -Keto Ester Containing a Methacrylate Group with Different Alkyl Chain Lengths*

HAAEMA is a commercially available monomer that is regularly used in the formation of metal containing polymers by either coordinating the metal first to the acetoacetate group followed by polymerization or by free radical polymerization of the methacrylate functions followed by the coordination of the metal [23, 24]. In both cases insoluble crosslinked polymers are often obtained due to several reasons: (i) the precursors contain several polymerizable groups and therefore they act as inherent cross linking agents, (ii) an equilibrium between compounds with different coordination patterns exists in solution, or (iii) exchange reactions occur in the final materials. Increasing the length of the alkyl spacer can have some influences on the coordination behaviour, for example by inter- or intramolecular interaction of the ester functionalities of the methacrylate group after coordination of the acetoacetate group to a metal centre. We therefore synthesized molecules with increased alkyl chain lengths between the two functional groups, namely the molecules 3-(methacryloyloxy)propyl acetoacetate (HAAPMA) and 4-(methacryloyloxy)butyl acetoacetate (HAABMA). Several synthetic strategies were used for the controlled formation of these molecules. The method with the highest selectivity relating to the targeted products as well as the highest yield was the reaction



Scheme 1

of diols with methacrylic acid chlorides in a first step to form the 3-hydroxypropyl 2-methacrylate and the 3-hydroxybutyl 2-methacrylate. These compounds were reacted with diketene, which opens to form the appropriate products in yields around 60% (Scheme 1).

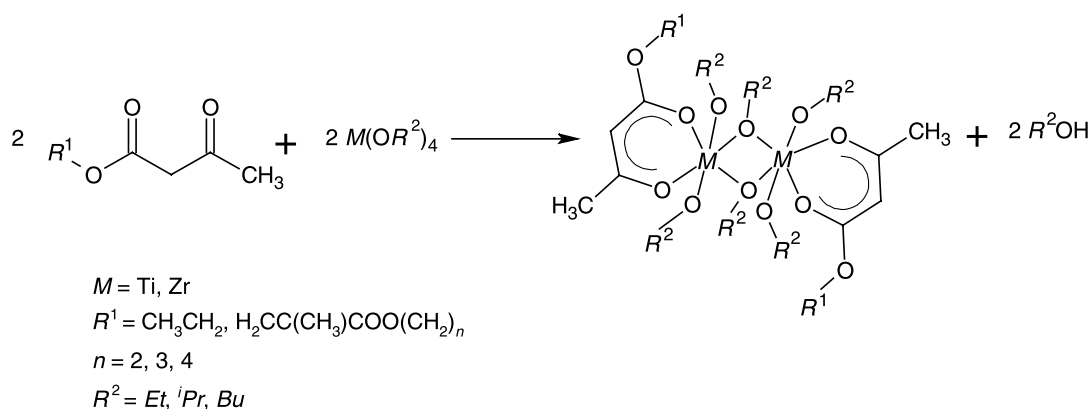
#### Coordination of the Ligands to Titanium Alkoxides

The reactions between  $Ti(OR)_4$  ( $R = Et, iPr$ ) and different  $\beta$ -keto esters (HEAA, HAAEMA, HAAPMA, HAABMA) were carried out in the stoichiometric ratios 1:1 and 1:2 under variation of the solvent (toluene, *n*-heptane, dichloromethane, chloroform) to investigate the coordination behavior of the alkoxides and the utilized ligands. HEAA was used in our studies as a model compound since it is known as a good chelating ligand [25] and the NMR spectro-

scopic analysis of its coordination compounds with the alkoxides are much simpler than that of the larger  $\beta$ -keto esters. Contrary to the ligands with longer alkyl chains we were able to receive a crystalline product reacting HEAA with  $Ti(OR)_4$  ( $R = Et, iPr$ ) in *n*-heptane in a 1:1 ratio (Scheme 2), while no crystalline product suitable for analysis was obtained under the same conditions in a 2:1 ratio.

The structure obtained from suitable crystals in the single crystal X-ray diffraction analysis revealed a binuclear centrosymmetric dimer consisting of two Ti atoms each coordinated by one chelating EAA, two terminal alkoxide ligands, and two bridging alkoxides (Fig. 1). Selected bond lengths and angles are presented in Table 1.

Each Ti atom has a distorted octahedral environment where the Ti–O bond distances of the terminal alkoxides revealing similar values (180.90(12)



Scheme 2

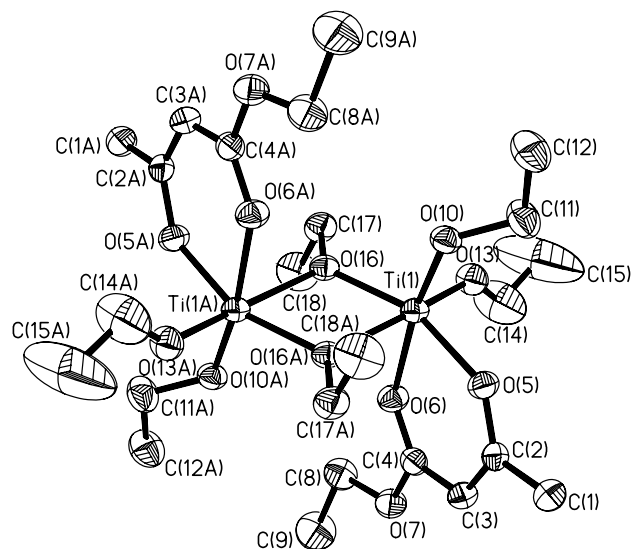
Table 1. Selected bond lengths/pm and angles/ $^\circ$  for **1**

Ti(1)–O(5)	197.24(11)	O(13)–Ti(1)–O(16)	96.96(5)
Ti(1)–O(6)	213.59(11)	O(10)–Ti(1)–O(16)	102.07(5)
Ti(1)–O(10)	181.09(11)	O(5)–Ti(1)–O(16)	159.23(5)
Ti(1)–O(13)	180.90(12)	O(13)–Ti(1)–O(16) <sup>#1</sup>	166.24(5)
Ti(1)–O(16)	197.27(11)	O(10)–Ti(1)–O(16) <sup>#1</sup>	96.47(5)
Ti(1)–O(16) <sup>#1</sup>	207.59(11)	O(5)–Ti(1)–O(16) <sup>#1</sup>	88.62(5)
Ti(1)–Ti(1) <sup>#1</sup>	324.96(6)	O(16)–Ti(1)–O(16) <sup>#1</sup>	73.26(5)
C(2)–O(5)	129.65(19)	O(13)–Ti(1)–O(6)	85.25(5)
C(4)–O(6)	124.14(19)	O(10)–Ti(1)–O(6)	171.16(5)
C(4)–O(7)	134.13(19)	O(5)–Ti(1)–O(6)	81.48(5)
O(7)–C(8)	144.8(2)	O(16)–Ti(1)–O(6)	86.65(4)
		O(16) <sup>#1</sup> –Ti(1)–O(6)	84.54(4)
O(13)–Ti(1)–O(10)	95.04(6)	C(2)–O(5)–Ti(1)	35.93(11)
O(13)–Ti(1)–O(5)	98.96(6)	C(4)–O(6)–Ti(1)	130.41(11)
O(10)–Ti(1)–O(5)	89.75(5)	C(4)–O(7)–C(8)	116.30(13)

Symmetry transformations used to generate equivalent atoms: <sup>#1</sup>  $-x, -y + 1, -$

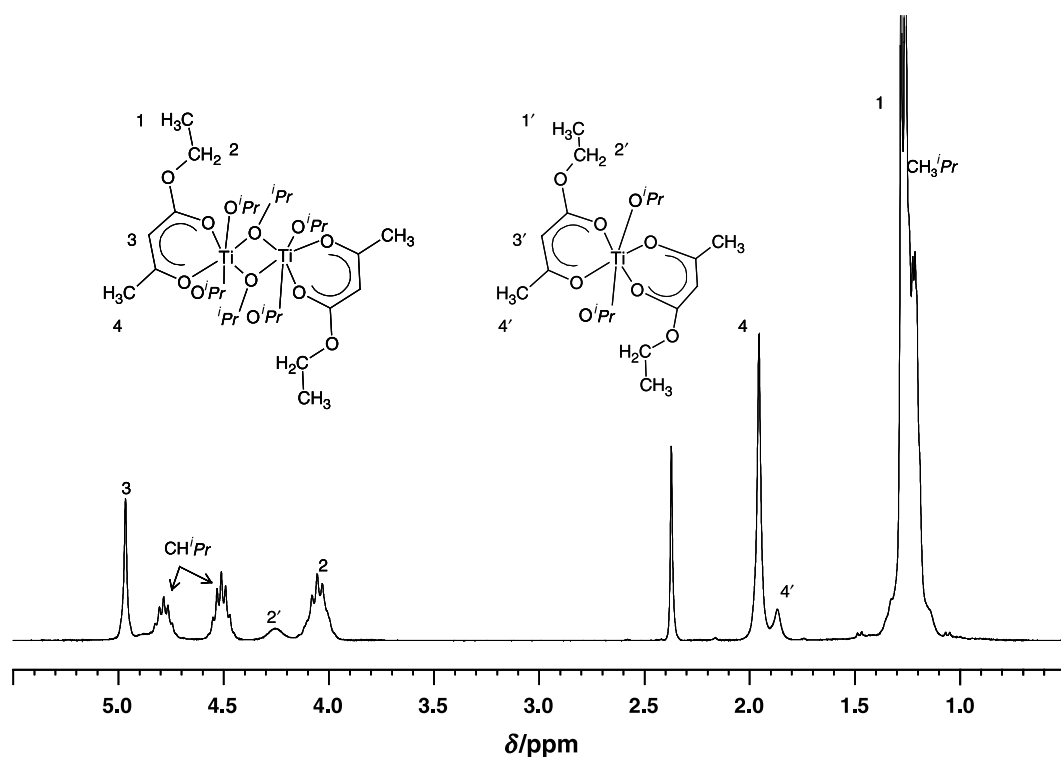
and 181.09(11) pm) while the bridging alkoxides display longer Ti–O bonds (197.27(11) and 207.59(11) pm), as expected. These values show that the alkoxide bridge is not symmetric. The Ti–O bonds of the chelating *EAA* display two distinctly different values with Ti(1)–O(5) 197.24(11) pm and Ti(1)–O(6) 213.59(11) pm leading to an asymmetrical bridging situation, which most likely is based on the stronger trans influence of the terminal alkoxide compared to the  $\beta$ -diketonate. The structures are similar to various  $\beta$ -diketonate derivatives described by *Errington et al.* [26]. However, the previously described structures with acetylacetonate ligands do not show a distinct difference in the Ti–O distances of the bidentate ligand. An asymmetric bonding was also observed by *Hubert-Pfalzgraf et al.* who reacted allylacetoacetate with  $\text{Ti}(\text{OEt})_4$  and obtained a similar structure [27].

The crystalline products were characterized in solution by FT-IR and NMR spectroscopy. The IR results of all coordination compounds showed the presence of the specific bands for the chelating acetoacetate ligands ( $\bar{\nu}(\text{C}=\text{C})$  and  $\bar{\nu}(\text{C}=\text{O})$ ) between 1650 and 1520  $\text{cm}^{-1}$ . In all cases complete coordination of the ligands was observed and no free ligands in



**Fig. 1.** ORTEP plot of the structure of  $\text{Ti}_2(\mu_2\text{-OEt})(\text{OEt})_2(\text{EAA})_2$ . Thermal ellipsoids are at a 50% probability level. H-atoms were omitted due to clarity

solution could be detected (Table 2).  $^1\text{H}$  NMR of  $[\text{Ti}(\text{O}^i\text{Pr})_3\text{EAA}]_2$  (Fig. 2) reveals clearly that coordination occurred by the disappearance of the methylene signal at 3.42 ppm corresponding to the keto form of the ethyl acetoacetate and the appearance



**Fig. 2.**  $^1\text{H}$  NMR spectra of  $\text{Ti}(\text{O}^i\text{Pr})_6(\text{EAA})_2$

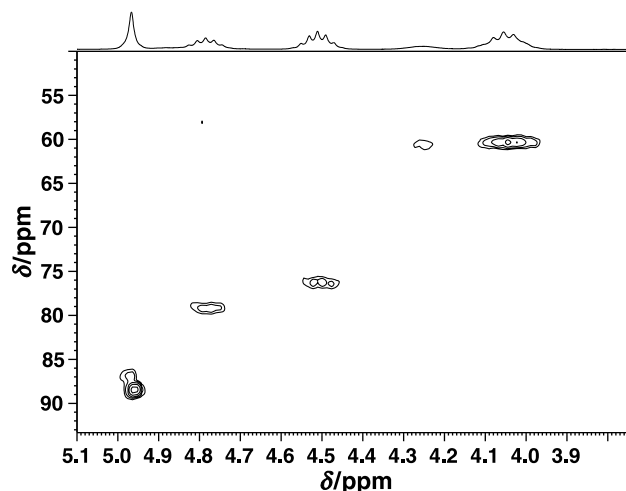


Fig. 3. HSQC spectra of  $[\text{Ti}(\text{O}^i\text{Pr})_3\text{EAA}]_2$  in  $\text{CDCl}_3$

of the methine signal of the chelating form at 4.98 ppm (Scheme 1). NMR spectroscopy also confirmed that no uncoordinated free ligand was present. The  $^{13}\text{C}$ -signals of the carbonyl carbons of ethyl acetoacetate showed also shifts from 200.5 to 167.0 ppm in the uncoordinated form, to 184.6 and 172.6 ppm in the coordinated species. No correlation could be made concerning either an intramolecular or intermolecular coordination type.

$^{13}\text{C}$ -HSQC analysis (Fig. 3) of the compound shows two correlations for CH (methine) protons of coordinated ligands at 4.91/88.64 ppm respective 4.97/87.15 ppm. In addition two sets of signals corresponding to two non-equivalent isopropoxy ligands at 4.77/79.2 and 4.5/76.2 ppm and one broad signal at 4.25/60.6 ppm are visible. The broad signal can be an indication of ligand exchange reactions which are known to take place in these types of complexes [26, 28]. We considered that these different signals are due to the different non-equivalent isopropoxy species. The two sets of signals derived from two non-equivalent isopropoxy species in a relative ratio of 2:1 are supported by the molecular structure obtained by the X-ray analysis. The signal at 4.04/60.4 could be assigned to the  $\text{CH}_2\text{-O}$  of the ester residue. Changing the ratio of HEAA to  $\text{Ti}(\text{O}^i\text{Pr})_4$  to 2:1 provides a similar NMR spectrum with identical chemical shifts as in case of the 1:1 ratio. This shows that in solution equilibrium of similar species is reached in both samples. The presence of the different signals in both cases can be explained by ligand exchange reactions that occur in the solution. This is

also supported by the appearance of the broad peak in the  $^1\text{H}$  NMR and HSQC spectra at 4.25/60.6 ppm which can be assigned to the monomeric disubstituted form of the EAA-Ti complex that resulted from redistribution reactions. This is also confirmed by the peak from 1.9 ppm attributed to the  $\text{CH}_3$  protons of the EAA ligand for the monomeric form of the Ti complex, which is in agreement with previous studies where redistribution of  $[\text{Ti}(\text{OR})_3(\text{L}_b)]_2$  with  $R = \text{Me}$ ,  $\text{Et}$ ,  $^i\text{Pr}$ ,  $\text{L}_b =$  bidentate ligand (e.g. *acac*, *thd*, or allyl acetoacetate) in  $\text{Ti}(\text{OR})_4$  and  $\text{Ti}(\text{OR})_2(\beta\text{-dik})_2$  was observed. Depending on the alkoxides and the ligand it was shown that a complete or partial reaction occurs. In the case of  $R = ^i\text{Pr}$  and  $\text{L}_b = \text{acac}$  the equilibrium was completely shifted to the mentioned compounds while for other alkoxides or bidentate ligands both species were observed in solution [26, 27].

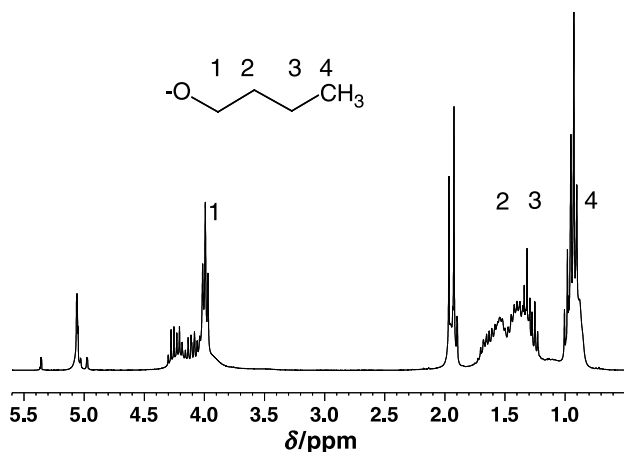
The spectra of the coordination compounds obtained from reactions of HAAEMA and  $\text{Ti}(\text{O}^i\text{Pr})_4$  in 1:1 and 1:2 ratios are much more complicated in the alkyl regions of the chemical shifts due to the overlapping of many different signals. However, the spectra resemble those of the ethyl acetoacetate coordinated titanium alkoxides with regard to the coordination of the acetoacetoxy group. All NMR analyses showed a complete coordination of the ligands and no free acetoacetoxy derivatives were detected. Both the monomeric and dimeric species resulting from redistribution reactions in solution could be observed similar to the case of ethyl acetoacetate ligands. Other systems which were analyzed, such as  $[\text{Ti}(\text{OEt})_3\text{EAA}]_2$  and  $[\text{Ti}(\text{OEt})_3\text{AAEMA}]_2$ ,  $\text{Ti}(\text{O}Bu)_3\text{EAA}$  and  $\text{Ti}(\text{O}Bu)_3\text{AAEMA}$  also showed analogous results proving complete coordination of the acetoacetoxy group.

As mentioned above the length of the alkyl chain between the polymerizable methacrylate and the coordinating acetoacetoxy group can have an influence on the coordinating behavior. For example the two oxygen atoms of the ester groups can form a reasonably unstrained intramolecular ring and thus one ligand would be able to coordinate to free coordination sites of the metal or intermolecular stabilization can occur. Thus, we investigated systematically the influence of the length of the alkyl chain on the coordination and the ligand exchange reaction. 3-(Methacryloyloxy)propyl acetoacetate (HAAPMA) and 4-(methacryloyloxy)butyl acetoacetate (HAABMA) were synthesized by the above men-

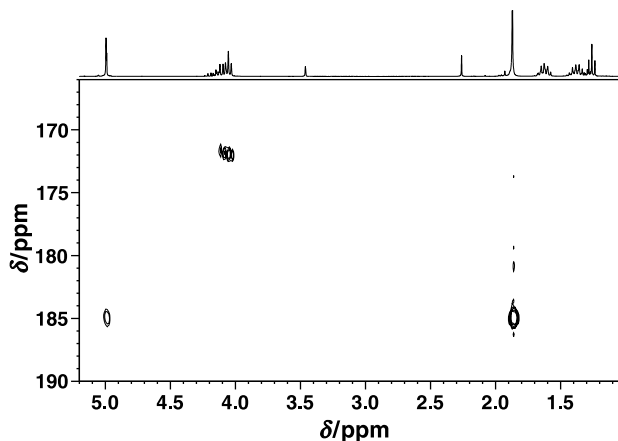
tioned reactions. The coordination with  $Ti(O^iPr)_4$  was carried out applying the same conditions as for HAAEMA in a 1:1 ratio. The  $^1H$  NMR spectra revealed in both cases the complete coordination of the ligands. In addition two sets of signals for the ligand and two different isopropoxy species were observed, confirming the dynamic equilibrium between different coordinated species. No indication for coordination of the methacrylic part of the molecule to the titanium atom was detected in solution analyses (NMR, FT-IR). This leads to the conclusion that stabilizing influences of the methacrylic group on the coordination by inter- or intramolecular coordination of the oxygen atoms can be neglected.

#### Coordination of the Ligands to Zr Alkoxides

Contrary to the preferentially six coordinated Ti, Zr as its larger homologue offers an expandable coordination sphere with potential coordination numbers between 6 and 9. Therefore we investigated the coordination of the mentioned ligands to Zr alkoxides which changes the coordination behavior of the bidentate ligands drastically. The FT-IR spectra of the reaction product between  $Zr(OBu)_4$  and HEAA in a 1:1 ratio showed the typical presence of the chelating ligand bands between  $1650$  and  $1520\text{ cm}^{-1}$ .  $^1H$  NMR (Fig. 4) of the same reaction supported the FT-IR results as coordination was observed from the appearance of the proton of the coordinating ligand at  $5.05\text{ ppm}$ . However, all spectra showed broad and unresolved peaks from which further assignments were not possible.



**Fig. 4.**  $^1H$  NMR spectra of the reaction product between  $Zr(OBu)_4$  and HEAA in 1:1 ratio



**Fig. 5.** HMBC spectra of the reaction product between  $Zr(OBu)_4$  and HEAA in 1:4 ratio

Contrary the analyses of a 1:4 mixture of  $Zr(OBu)_4$  and HEAA gave well resolved spectra and all signals could be assigned by 2D NMR spectra. The interesting fact which could be observed from the  $^{13}C$  HMBC is that the methylene protons of a butoxy ligand ( $-CH_2O-$ ) at  $4.05\text{ ppm}$  gave a long range correlation to a carbonyl carbon at  $171.9\text{ ppm}$  (Fig. 5), which provides evidence that the butyl group is linked to a carboxylate group of the ligand. This means that even under these mild conditions transesterification occurs in which a butyl acetoacetate is formed from ethyl acetoacetate under participation of the metal alkoxide (Scheme 3). In these reactions  $Zr(OBu)_4$  acts as a *Lewis* acid. The transesterification reactions were observed at all ratios investigated (from 1:1 to 1:4) between the alkoxides and the  $\beta$ -keto ester ligands.

The resulting ester is still coordinated to the metal center as proven by NMR which reveals only the presence of the chelating form of the ligand. Transesterification ratio could not be deduced due to signal overlapping in the  $^1H$  NMR spectra which made the integration not possible. However this reaction cannot be ignored in the formation of sol-gel materials, especially when the ligand is carrying a second functionality. Some examples of transesterification reactions in presence of metal alkoxides were already shown in literature. *Seebach et al.* used, for example,  $Ti(OEt)_4$  as catalyst in the transesterification between  $MeC(O)CH_2COOR^1$  and  $R^2OH$  at elevated temperatures [29]. *Pajot et al.* synthesized  $Ti_5(O^iPr)_{10}(OCH_2CH_2O)_5$  by the reaction between  $Ti(O^iPr)_4$  with 2-hydroxyethyl methacrylate [30].

In this reaction the glycolate ligands were formed due to the transesterification of the 2-hydroxyethyl methacrylate mediated by the Ti alkoxide. Neither in the case of HEAA nor HAAEMA a transesterification was previously reported but considering especially the fact that HAAEMA is a diester this reaction seems to be quite probable. No transesterification was observed in the cases of the Ti alkoxides under the same conditions. This behavior of the Zr butoxides can be either due to the metal center or can be specific for the alkoxide type.

Reacting  $Zr(OBu)_4$  and HAAEMA in a 1:1 ratio the  $^1H$  NMR reveals broad bands in the region of the methine, methylene, and methylic protons from which the assignments were difficult to make but no signal from uncoordinated ligand was observed. Again, a sharp triplet of a  $-CH_2O-$  signal of a butoxy group at 4.15 ppm could be observed, giving a long range correlation in the  $^{13}C$  HMBC (Fig. 6) to a carbonyl carbon at 167.6 ppm.

The protons of a methacrylic moiety at 6.09/5.56 ( $=CH_2$ ) and 1.94 ( $CH_3$ ) showed long range correlation to the same carbon. This means that transesterification of HAAEMA has occurred and butyl methacrylate was formed (Scheme 3).

Since the signals in the  $-CH_2O-$  region are overlapping we were not able to identify signals cor-

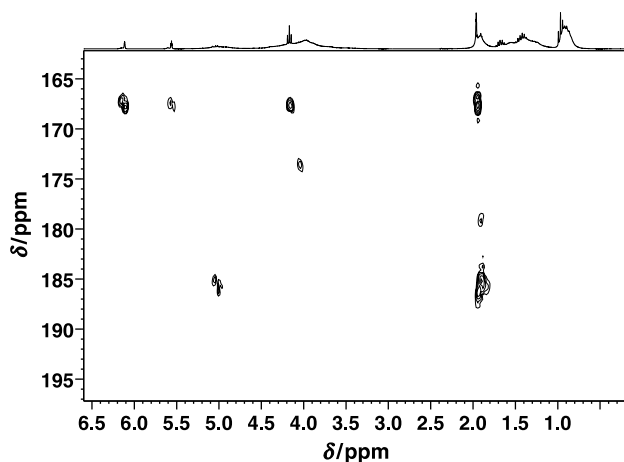
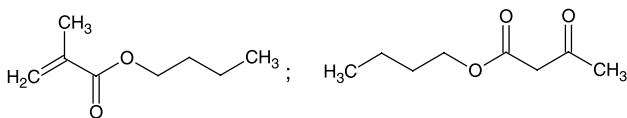


Fig. 6. HMBC spectra of the products of the reaction between  $Zr(OBu)_4$  and HAAEMA in 1:1 ratio



Scheme 3

responding to the glycol part ( $-O-CH_2-CH_2-O-$ ) of the AAEMA ligand which is the linkage between the coordinative and polymerizable functionalities. This is a strong indication that the ligand is quantitatively decomposed and the only present species are butyl methacrylate and coordinated butyl acetoacetate, resulting from transesterification reactions. Transesterification was also found from the analysis of the products of the reaction between  $Zr(OBu)_4$  and HAAEMA in 1:2 and 1:4 ratios. These facts cannot be neglected particularly in the case of a 1:1 ratio when most of the ligand is decomposed.

Implications for materials obtained by the sol-gel process are that one should be able to form similar materials by mixtures of butyl keto ester and butyl methacrylate.

The ligands showed no decomposition in the cases of Ti alkoxides so we wanted to know if the transesterification is due to the metal center or it is directly related to the alkoxide type. Because the  $Zr(OBu)_4$  is a solvated species (commercially available as 80% weight solution in *n*-butanol), we could not accurately compare it with  $Ti(O^iPr)_4$ . Therefore  $Ti(O^iPr)_4$  was compared with  $Zr(O^iPr)_4$ . In the case of  $Ti(O^iPr)_4$  no decomposition was detected under the same conditions. Similar results were obtained in the reaction between  $Zr(O^iPr)_4$  and HEAA as well as HAAEMA in 1:1 and 1:2 ratios. Both reactions showed that full coordination occurred and no transesterification was detected, which leads to the conclusion that transesterification of HAAEMA with the alkoxides does not occur in the case with  $Zr(O^iPr)_4$  but only in the case of reacting HAAEMA with  $Zr(OBu)_4$ . So the transesterification is primarily based on the nature of the metal alkoxide type. This means that for the solvated alkoxides the ligand is totally decomposed while in the cases of the alkoxides with an isopropoxy frame the decomposition is not visible. Instead the system is very complex, with ligand exchange reactions occurring in solution.

## Conclusions

Coordination between Ti and Zr alkoxides and  $\beta$ -keto esters was investigated in the solid state as well as in the liquid state. From X-ray single crystal diffraction analysis coordination compounds obtained from Ti ethoxides or isopropoxides and HEAA in 1:1 ratio appear as alkoxide-bridged dimers with chelating ethyl acetoacetate ligands, presenting a cen-

triosymmetric structure. In these structures the metal center is six-fold coordinated. In solution the picture is different because simple  $^1\text{H}$  NMR analysis does not allow a complete analysis of the structure due to ligand exchange reactions which do not allow clear assignments. However, 2D-NMR analyses supported a full coordination of  $\beta$ -keto esters in the case of Ti alkoxides. Investigation of the spacer length between coordinating part and polymerizable group shows that this parameter does not have an influence on the coordination.  $\text{Zr}(\text{O}i\text{Bu})_4$  can mediate the transesterification reaction of  $\beta$ -keto esters, which is probably based on the presence of free butanol in the commercially available systems. Similar reactions cannot be observed with  $\text{Zr}(\text{O}^i\text{Pr})_4$ . These facts make Zr butoxides not a suitable candidate for the coordination with difunctional  $\beta$ -keto esters if well defined materials are targeted.

## Experimental

### Materials

All chemicals were obtained from Aldrich, Fluka, or ABCR and used as received. All solvents were dried with standard procedures and stored under argon atmosphere [31]. All operations using metal alkoxides were carried out under argon atmosphere applying *Schlenk* technique.

### Measurements

Solution NMR spectra were recorded on a Bruker Avance 300 ( $^1\text{H}$  at 300.13 MHz,  $^{13}\text{C}$  at 75.47 MHz) equipped with a 5 mm inverse-broadband probe head with a  $z$ -gradient unit. 2D-Experiments were measured with Bruker standard pulse sequences (COSY (Correlated Spectroscopy), TOCSY (Total Correlation Spectroscopy), HSQC (Heteronuclear Single Quantum Correlation), HSQC-TOCSY, HMBC (Heteronuclear Multi Bond Correlation)). Solid State NMR spectra were recorded on a Bruker DPX 300 ( $^{13}\text{C}$  at 75.40 MHz) equipped with a 4 mm broadband MAS probe head.  $^{13}\text{C}$  spectra were recorded with ramped CP/MAS spectra (Cross Polarization and Magic angle spinning). Rotor spinning speed was usually 6–8 kHz. FT-IR spectra were recorded on a Bruker Tensor 27 instrument working in ATR MicroFocusing MVP-QL with a ZnSe crystal. The software used for analysis was OPUS<sup>TM</sup> version 4.0.

### X-Ray Diffraction

A selected crystal was mounted on a Bruker-AXS SMART diffractometer with an APEX CCD area detector. Graphite-monochromated  $\text{Mo-K}\alpha$  radiation (71.073 pm) was used for all measurements. The nominal crystal-to-detector distance was 5.00 cm. A hemisphere of data was collected by a combination of three sets of exposures at 173 K. Each set had a different  $\phi$  angle for the crystal, and each exposure took 20 s

**Table 2.** Crystal data and structure refinement for **1**

Empirical formula	$\text{C}_{30}\text{H}_{60}\text{O}_{12}\text{Ti}_2$	
Formula weight	708.58	
Crystal system,	triclinic, $P-1$	
space group		
Unit cell	$a = 997.04(19)$	$\alpha = 91.290(4)$
dimensions [pm, °]	$b = 1042.6(2)$	$\beta = 114.835(3)$
	$c = 1175.2(2)$	$\gamma = 115.749(3)$
Volume [ $\times 10^6$ pm <sup>3</sup> ]	966.6(3)	
Z, Calculated density	1, 1.217	
[g · cm <sup>-3</sup> ]		
Absorption coefficient	0.465	
[mm <sup>-1</sup> ]		
$F(000)$	380	
Crystal size [mm <sup>3</sup> ]	0.30 × 0.30 × 0.30	
Theta range for data	1.97–25.00	
collection [°]		
Limiting indices	–11 ≤ $h$ ≤ 11, –12 ≤ $k$ ≤ 9, –13 ≤ $l$ ≤ 13	
Reflections	5079/3284 [ $R(\text{int}) = 0.0193$ ]	
collected/unique		
Completeness to	96.8%	
$\theta = 28.30^\circ$		
Max. and min.	0.8732 and 0.8732	
transmission		
Data/restraints/	3284/0/199	
parameters		
Goodness-of-fit on $F^2$	1.055	
Final $R$ indices	$R1 = 0.0705$ , $wR2 = 0.2077$	
[ $I > 2\sigma(I)$ ] <sup>a</sup>		
$R$ indices (all data) <sup>a</sup>	$R1 = 0.0774$ , $wR2 = 0.2121$	
Largest diff. peak and	0.824 and –0.669	
hole [ $\text{e} \cdot \text{\AA}^3$ ]		

<sup>a</sup> Weight =  $1/[\sigma^2(F_0^2) + (0.0651 \cdot P)^2 + 0.61 \cdot P]$  where  $P = (\text{Max}(F_0^2, 0) + 2 \cdot F_c^2)/3$

and covered  $0.3^\circ$  in  $\omega$ . The data were corrected for polarization and *Lorentz* effects, and an empirical absorption correction (SADABS) was applied [32]. The cell dimensions were refined with all unique reflections. The structure was solved by direct methods (SHELXS97) [33]. Refinement was carried out with the full-matrix least-squares method based on  $F^2$  (SHELXL97) [33] with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were inserted in calculated positions and refined riding with the corresponding atom. Crystal structure and refinement data are shown in Table 2.

CCDC 611043 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

### Synthesis of Hydroxypropyl Methacrylate and Hydroxybutyl Methacrylate

Hydroxypropyl methacrylate and hydroxybutyl methacrylate were synthesized following published procedures [34].



*Synthesis of 3-(Methacryloyloxy)propyl Acetoacetate (HAAPMA) and 4-(Methacryloyloxy)butyl Acetoacetate (HAABMA)*

The synthesis was based on known literature procedures [35]. Diketene (0.075 moles, 6.43 g) was added under Ar to a solution of 7 g 3-hydroxypropyl methacrylate (0.05 moles) (or 4-hydroxybutyl methacrylate) and 0.502 cm<sup>3</sup> triethylamine (0.0036 mol) in 30 cm<sup>3</sup> dichloromethane keeping the temperature between 0 and 5°C. The mixture was allowed to warm up at room temperature overnight under vigorous stirring. The reaction mixture was extracted several times with water. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel using hexane/ethyl acetate. HAAPMA: Yellowish liquid, 6.65 g, yield 60%; FT-IR (ATR):  $\bar{\nu}$  = 1637 (C=C), 1716 (C=O) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25°C):  $\delta$  = 1.93 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 2.03 (s, 3H, CH<sub>3</sub>C=), 2.26 (s, 3H, CH<sub>3</sub>CO), 3.46 (s, 2H, (CO)<sub>2</sub>CH<sub>2</sub>), 4.22 (t, 2H, *J* = 6.20 Hz, OCH<sub>2</sub>), 4.24 (t, 2H, *J* = 6.27 Hz, CH<sub>2</sub>O), 5.57 (s, 1H, CH<sub>2</sub>=C(CH<sub>3</sub>)), 6.09 (s, 1H, CH<sub>2</sub>=C(CH<sub>3</sub>)) ppm; <sup>13</sup>C NMR (CDCl<sub>3</sub>, 25°C):  $\delta$  = 16.7 (CH<sub>3</sub>C=), 28.1 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 28.7 (COCH<sub>3</sub>), 48.0 (COCH<sub>2</sub>CO), 61.4 (CH<sub>2</sub>O), 62.9 (C OCH<sub>2</sub>), 123.5 (CH<sub>2</sub>=C), 134.3 (CH<sub>2</sub>=C), 165.4 (=C(CH<sub>3</sub>)COO), 170.8 (OCO), 198.7 (H<sub>2</sub>CO) ppm. HAABMA: Yellowish liquid, 7.17 g, yield: 61%. FT-IR (ATR):  $\bar{\nu}$  = 1636 (C=C), 1718 (C=O) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25°C):  $\delta$  = 1.63–1.72 (m, overlapped, 4H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.63–1.72 (m, overlapped, 4H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.89 (s, 3H, CH<sub>3</sub>C=), 2.3 (s, 3H, CH<sub>3</sub>CO), 3.62 (s, 2H, (CO)<sub>2</sub>CH<sub>2</sub>), 4.12 (broad, overlapped, 2H, OCH<sub>2</sub>) 4.13 (broad, overlapped, 2H, CH<sub>2</sub>O), 5.51 (s, 1H, CH<sub>2</sub>=C(CH<sub>3</sub>)), 6.05 (s, 1H, CH<sub>2</sub>=C(CH<sub>3</sub>)) ppm; <sup>13</sup>C NMR (CDCl<sub>3</sub>, 25°C):  $\delta$  = 16.2 (CH<sub>3</sub>C=), 25.2 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 25.3 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 28.3 (COCH<sub>3</sub>), 50.1 (COCH<sub>2</sub>CO), 60.3 (CH<sub>2</sub>O), 62.8 (OCH<sub>2</sub>), 123.4 (CH<sub>2</sub>=C), 136.1 (CH<sub>2</sub>=C), 165.2 (=C(CH<sub>3</sub>)COO), 168.1 (OCO), 198.6 (CH<sub>2</sub>CO).

*Synthesis of  $\beta$ -Keto Esters Modified Metal Alkoxides*

The  $\beta$ -keto ester ligand was added dropwise to a solution of a metal alkoxide in an absolute solvent (*n*-heptane, dichloromethane, toluene, alcohol) in ratios between 1:1 and 4:1 under stirring. The reaction was carried out overnight and the solvent was evaporated afterwards under reduced pressure. The resulting product was either an oily liquid (Ti compounds) or a solid (Zr compounds) soluble in most organic solvents (dichloromethane, *n*-heptane, toluene). Elemental analyses were carried out only in the cases of the well-defined Ti-ethyl acetoacetate for which also X-ray structures were obtained. Due to the fact that many of the compounds have been previously synthesized and the spectroscopic analyses were fitting well with previous data, we did not carry out further elemental analyses, the compounds being very moisture sensitive.

*Synthesis of [Ti(O<sup>i</sup>Pr)<sub>3</sub>(EAA)]<sub>2</sub> Crystals*

Ethyl acetoacetate (10 mmol, 1.26 cm<sup>3</sup>) in 5 cm<sup>3</sup> *n*-heptane was added dropwise to a solution of Ti(O<sup>i</sup>Pr)<sub>4</sub> (10 mmol) in 20 cm<sup>3</sup> *n*-heptane in a 1:1 ratio and the mixture was stirred overnight. The solution was concentrated under reduced pressure and colorless crystals were obtained by cooling the

solution at –20°C overnight. C<sub>30</sub>H<sub>60</sub>O<sub>12</sub>Ti<sub>2</sub>, yield 2.68 g (76%) colorless crystals; elemental anal.: calc. C 50.85, H 7.94, found C 49.63, H 6.54% (the differences are due to the fact that the compounds are highly moisture sensitive, leading to small decomposition when exposed to air).

*Ti<sub>2</sub>(O<sup>i</sup>Pr)<sub>6</sub>(EAA)<sub>2</sub> (1)*

FT-IR (ATR):  $\bar{\nu}$  = 1633, 1610 (C=C), 1520 (C=O) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25°C):  $\delta$  = 1.21 (m, overlapped, CH<sub>3</sub>CH<sub>2</sub>O), 1.21 (m, overlapped, 36H, CH<sub>3</sub><sup>OiPr</sup>), 1.81 (s, 2H, CH<sub>3</sub>CO), 1.95 (s, 6H, CH<sub>3</sub>CO), 4.04 (q, *J* = 6.75, 13.40 Hz, 4H, CH<sub>2</sub>O) 4.23 (br, 1H, CH<sub>2</sub>O), 4.50 (sept, 4H, *J* = 5.91, 12.05 Hz, CH<sup>OiPr</sup>), 4.77 (sept, 2H, *J* = 6.07, 11.97 Hz, CH<sup>OiPr</sup>), 4.97 (s, 2H, COCHCO) ppm; <sup>13</sup>C NMR (CDCl<sub>3</sub>, 25°C):  $\delta$  = 14.4 (CH<sub>3</sub>CH<sub>2</sub>), 25.0 (CH<sub>3</sub>CO), 60.4 (CH<sub>2</sub>O), 87.2, 88.6 ((CO)<sub>2</sub>CH), 172.4 (COO), 184.7 (CH<sub>3</sub>CO); O<sup>i</sup>Pr: 26.6 (CH<sub>3</sub>), 76.2, 79.3 (CH) ppm.

*Ti(O<sup>i</sup>Pr)<sub>2</sub>(EAA)<sub>2</sub> (2)*

FT-IR (ATR):  $\bar{\nu}$  = 1637, 1614 (C=C), 1525 (C=O) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25°C):  $\delta$  = 1.21 (br, overlapped, 6H, CH<sub>3</sub>CH<sub>2</sub>O) 1.21 (br, overlapped, 36H, CH<sub>3</sub><sup>OiPr</sup>), 1.93 (s, 6H, 1.81, 2H, CH<sub>3</sub>CO), 4.02 (br, 4H, CH<sub>2</sub>O), 4.23 (br, 1H, CH<sub>2</sub>O) 4.48 (sept, 2H, *J* = 5.37 Hz, CH<sup>OiPr</sup>) 4.76 (sept, 4H, *J* = 5.96, 11.68 Hz, CH<sup>OiPr</sup>) 4.93 (s, 2H(s), COCHCO) ppm; <sup>13</sup>C NMR (CDCl<sub>3</sub>, 25°C):  $\delta$  = 14.1 (CH<sub>3</sub>CH<sub>2</sub>), 25.0, 25.6 (CH<sub>3</sub>CO), 60.2 (CH<sub>2</sub>O), 88.1, 86.6 ((CO)<sub>2</sub>CH), 172.3 (COO), 184.6 (CH<sub>3</sub>CO); O<sup>i</sup>Pr: 24.8 (CH<sub>3</sub>), 77.1, 78.8 (CH) ppm.

*Ti<sub>2</sub>(O<sup>i</sup>Pr)<sub>6</sub>(AAEMA)<sub>2</sub> (3)*

FT-IR (ATR):  $\bar{\nu}$  = 1634, 1609 (C=C), 1519 (C=O) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25°C):  $\delta$  = 1.22 (d, 24H, *J* = 6.05 Hz, CH<sub>3</sub><sup>OiPr</sup>), 1.91, 1.97 (br, CH<sub>3</sub>CO), 1.95 (br, overlapped, 6H, CH<sub>3</sub>C=), 4.23 (m, br, OCH<sub>2</sub>), 4.29 (m, br, CH<sub>2</sub>O), 4.51 (br, CH<sup>OiPr</sup>), 4.77 (br, overlapped region, 8H, CH<sup>OiPr</sup>), 5.02 (s, 1H, (CO)<sub>2</sub>CH), 5.59 (1H, CH<sub>2</sub>=C(CH<sub>3</sub>)–), 6.12 (s, 1H, CH<sub>2</sub>=C(CH<sub>3</sub>)–) ppm; <sup>13</sup>C NMR (CDCl<sub>3</sub>, 25°C):  $\delta$  = 18.2 (CH<sub>3</sub>C), 25.2 (CH<sub>3</sub>CO), 62.1 (OCH<sub>2</sub>CH<sub>2</sub>O), 62.3 (OCH<sub>2</sub>CH<sub>2</sub>O), 86.5, 87.9 ((CO)<sub>2</sub>CH), 172.2 (OCOCHCO), 167.0 (COO), 125.9 (CH<sub>2</sub>=), 136.9 (CH<sub>3</sub>C=), 185.8 (CH<sub>3</sub>CO); O<sup>i</sup>Pr: 25.0 (CH<sub>3</sub>), 76.2, 79.3 (CH) ppm.

*Ti(O<sup>i</sup>Pr)<sub>2</sub>(AAEMA)<sub>2</sub> (4)*

FT-IR (ATR):  $\bar{\nu}$  = 1637, 1615 (C=C), 1525 (C=O) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25°C):  $\delta$  = 1.22 (br, 18H, CH<sub>3</sub><sup>OiPr</sup>), 1.80 (s, br, CH<sub>3</sub>CO), 1.87 (s, br, overlapped, CH<sub>3</sub>CO), 1.88 (s, overlapped, CH<sub>3</sub>C=), 4.17 (m, OCH<sub>2</sub>), 4.20 (m, CH<sub>2</sub>O), 4.71 (m, br, overlapped region, CH<sup>OiPr</sup>), 4.95, 4.98 (s, 1H, (CO)<sub>2</sub>CH), 5.52 (s, 1H, CH<sub>2</sub>=C(CH<sub>3</sub>)–), 6.05 (s, 1H, CH<sub>2</sub>=C(CH<sub>3</sub>)–) ppm; <sup>13</sup>C NMR (CDCl<sub>3</sub>, 25°C):  $\delta$  = 18.2 (CH<sub>3</sub>C), 25.2 (CH<sub>3</sub>CO), 87.7, 86.3 ((CO)<sub>2</sub>CH), 62.2 (OCH<sub>2</sub>CH<sub>2</sub>O), 65.3 (OCH<sub>2</sub>CH<sub>2</sub>O), 166.8 (COO), 125.6 (CH<sub>2</sub>=), 135.6 (CH<sub>3</sub>C=), 173.4 (OCOCHCO), 185.7 (CH<sub>3</sub>CO); O<sup>i</sup>Pr: 24.9 (CH<sub>3</sub>), 77.5, 79.3 (CH) ppm.

*Ti<sub>2</sub>(O<sup>i</sup>Pr)<sub>6</sub>(AAPMA)<sub>2</sub> (5)*

FT-IR (ATR):  $\bar{\nu}$  = 1629, 1610 (C=C) 1525 (C=O) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25°C):  $\delta$  = 1.3 (d, 18H, *J* = 5.89 Hz, CH<sub>3</sub><sup>OiPr</sup>), 1.25 (m, 2H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O), 1.92, 1.97 (s, CH<sub>3</sub>CO), 1.96

(s,  $CH_3C=$ ), 4.01 (m,  $CH_2O$ ), 4.17 (t,  $J = 5.93$  Hz,  $OCH_2$ ), 4.48 (m,  $OCH^{O^iPr}$ ), 4.75 ( $J = 5.78$ , 11.40 Hz, overlapped region,  $OCH^{O^iPr}$ ), 4.94, 4.96 (s, 1H,  $(CO)_2CH$ ), 5.56, 6.08 (s, 1H,  $CH_2=C(CH_3)$ ) ppm.

#### $Ti_2(O^iPr)_6(AABMA)_2$ (6)

FT-IR (ATR):  $\bar{\nu} = 1630$ , 1609 (C=C), 1524 (C=O)  $cm^{-1}$ ;  $^1H$  NMR ( $CDCl_3$ , 25°C):  $\delta = 1.21$  (m, 18H,  $CH_3^{O^iPr}$ ), 1.35 (m, 2H,  $(CH_2)_2CH_2CH_2$ ), 1.65 (m, 2H,  $CH_2CH_2(CH_2)_2$ ), 1.93 (br,  $CH_3CO$ ), 1.93 (m,  $CH_3C=$ ), 4.02 (t,  $CH_2O$ ); 4.12 (t,  $J = 5.68$  Hz,  $OCH_2$ ), 4.48 (sept, 2H,  $J = 6.04$ , 11.96 Hz,  $OCH^{O^iPr}$ ), 4.75 (sept, 1H,  $J = 6.04$ , 12.06 Hz,  $OCH^{O^iPr}$ ), 4.95 (s, 1H,  $(CO)_2CH$ ), 6.08, 5.55 (s, 1H,  $CH_2=C(CH_3)$ ) ppm.

#### $Ti_2(OEt)_6(EAA)_2$ (7)

FT-IR (ATR):  $\bar{\nu} = 1630$ , 1613 (C=C), 1523 (C=O)  $cm^{-1}$ ;  $^1H$  NMR ( $CDCl_3$ , 25°C):  $\delta = 1.22$  (m, br,  $CH_3^{OEt}$ ), 1.22 (m, br, overlapped signals, 12H,  $CH_3CH_2$ ), 1.89 (s,  $CH_3CO$ ), 1.96 (s, 3H,  $CH_3CO$ ), 4.05 (m,  $CH_2O$ ), 4.43 (m, overlapped signals, 8H,  $OCH_2^{OEt}$ ), 4.97 (s, 1H,  $(CO)_2CH$ ) ppm;  $^{13}C$  NMR ( $CDCl_3$ , 25°C):  $\delta = 14.9$  ( $CH_3CH_2$ ), 24.7 ( $CH_3CO$ ), 60.4 ( $CH_2O$ ), 86.3, 88.7 ( $(CO)_2CH$ ), 172.4 ( $COO$ ), 184.7 ( $CH_3CO$ );  $O^iPr$ : 24.7 ( $CH_3$ ), 77.1, 78.8 (CH) ppm.

#### $Ti_2(OEt)_6(AAEMA)_2$ (8)

FT-IR (ATR):  $\bar{\nu} = 1634$ , 1609 (C=C), 1519 (C=O)  $cm^{-1}$ ;  $^1H$  NMR ( $CDCl_3$ , 25°C):  $\delta = 1.23$  (t, 9H,  $J = 6.84$  Hz,  $CH_3^{OEt}$ ), 1.91 (s,  $CH_3CO$ ), 1.98 (s, 3H,  $CH_3CO$ ), 1.94 (s, 3H,  $CH_3C=$ ), 4.23 (br,  $OCH_2$ ); 4.27 (br,  $CH_2O$ ), 4.36 (br,  $OCH_2^{OEt}$ ), 4.45 (br, overlapped region, 10H,  $OCH_2^{OEt}$ ), 5.02 (s,  $(CO)_2CH$ ), 5.04 (s, 1H,  $(CO)_2CH$ ), 5.58 (s, 1H,  $CH_2=C(CH_3)$ ), 6.12 (s, 1H,  $CH_2=C(CH_3)$ ) ppm;  $^{13}C$  NMR ( $CDCl_3$ , 25°C):  $\delta = 18.2$  ( $CH_3C=$ ), 25.4 ( $CH_3CO$ ), 62.3 ( $OCH_2CH_2O$ ), 62.7 ( $OCH_2CH_2O$ ), 87.0, 88.2 ( $(CO)_2CH$ ), 125.0 ( $CH_2=$ ), 135.8 ( $CH_3C=$ ), 167.1 ( $COO$ ), 171.5 ( $OCOCHCO$ ), 185.7 ( $CH_3CO$ );  $OEt$ : 18.4 ( $CH_3$ ), 71.1, 73.2 (CH) ppm.

#### $Ti(OBu)_6(AAEMA)_2$ (9)

FT-IR (ATR):  $\bar{\nu} = 1631$ , 1608 (C=C), 1523 (C=O)  $cm^{-1}$ ;  $^1H$  NMR ( $CDCl_3$ , 25°C):  $\delta = 1.88$  (s,  $CH_3CO$ ), 1.97 (s, 3H,  $CH_3CO$ ), 1.93 (s, 3H,  $OCH_3C=$ ), 4.44 (m, overlapped,  $CH_2CH_2O$ ), 5 (s,  $(CO)_2CH$ ), 5.03 (s, 1H,  $(CO)_2CH$ ), 5.53, 5.58 (s, 1H,  $CH_2=C(CH_3)$ ), 6.1, 6.13 (s, 1H,  $CH_2=C(CH_3)$ ), Butoxy: 0.89 (t, 9H,  $CH_3$ ), 1.36 (m,  $CH_2CH_3$ ), 1.54 (m, overlapped signals, 10H,  $OCH_2CH_2$ ), 4.46 (m, overlapped, 10H,  $OCH_2$ ) ppm;  $^{13}C$  NMR ( $CDCl_3$ , 25°C):  $\delta = 18.2$  ( $CH_3C=$ ), 25.5 ( $CH_3CO$ ), 62.3 ( $OCH_2CH_2O$ ), 62.7 ( $OCH_2CH_2O$ ), 88.3, 88.8 ( $(CO)_2CH$ ), 126.0 ( $CH_2=$ ), 136.0 ( $CH_3C=$ ), 167.2 ( $COO$ ), 170.5 ( $OCOCHCO$ ), 186.1 ( $CH_3CO$ );  $OBu$ : 14.1 ( $CH_3$ ), 19.1 ( $CH_2CH_3$ ), 34.5 ( $OCH_2CH_2$ ), 75.6, 77.7 ( $OCH_2$ ) ppm.

#### $Zr_2(O^iPr)_6(AAEMA)_2$ (10)

FT-IR (ATR):  $\bar{\nu} = 1615$  (C=C), 1521 (C=O)  $cm^{-1}$ ;  $^1H$  NMR ( $CDCl_3$ , 25°C):  $\delta = 1.24$  (m, br,  $CH_3^{O^iPr}$ ), 1.91, 1.96 (br,  $CH_3CO$ ), 1.93 (br,  $CH_3C=$ ), 4.06 (m, br,  $OCH^{O^iPr}$ ); 4.30 (br,  $OCH_2$ ); 4.33 (br,  $CH_2O$ ), 5.06 (m, br,  $(CO)_2CH$ ), 5.54, 5.59 (s,  $CH_2=C(CH_3)$ ), 6.09, 6.14 (s, overlapping signals, no integration possible,  $CH_2=C(CH_3)$ ) ppm;  $^{13}C$  NMR ( $CDCl_3$ ,

25°C):  $\delta = 18.5$  ( $CH_3C=$ ), 25.7 ( $CH_3CO$ ), 60.4 ( $OCH_2CH_2O$ ), 62.3 ( $OCH_2CH_2O$ ), 88.1 ( $(CO)_2CH$ ), 167.1 ( $COO$ ), 125.8 ( $CH_2=$ ), 135.8 ( $CH_3C=$ ), 173.0 ( $OCOCHCO$ ), 187.5 ( $CH_3CO$ );  $O^iPr$ : 21.9 ( $CH_3$ ), 71.0, 71.1 (CH) ppm.

#### $Zr_2(OBu)_6(EAA)_2$ (11)

FT-IR (ATR):  $\bar{\nu} = 1609$  (C=C), 1573, 1520 (C=O)  $cm^{-1}$ ;  $^1H$  NMR ( $CDCl_3$ , 25°C):  $\delta = 1.14$ –1.28 (m,  $CH_3CH_2$ ), 1.89, 1.92, 1.96 (s,  $CH_3CO$ ), 4.33–4.04 (m,  $CH_2O$ ), 5.05, 5.06 (s,  $(CO)_2CH$ ), Butoxy: 0.89 (m, 9H,  $CH_3$ ), 1.41 (m,  $CH_2CH_3$ ), 1.60 (m,  $OCH_2CH_2$ ), 3.99 (t, overlapping signals, no integration possible,  $J = 6.63$  Hz,  $OCH_2$ ) ppm;  $^{13}C$  NMR ( $CDCl_3$ , 25°C):  $\delta = 14.2$  ( $CH_3CH_2$ ), 25.4 ( $CH_3CO$ ), 60.4 ( $CH_2O$ ), 88.2, 86.7 ( $(CO)_2CH$ ), 171.9 ( $COO$ ), 185.7 ( $CH_3CO$ );  $OBu$ : 14.0 ( $CH_3$ ), 19.1 ( $CH_2$ ), 36.3 ( $CH_2$ ), 69.4 ( $OCH_2$ ) ppm.

#### $Zr_2(OBu)_6(AAEMA)_2$ (12)

FT-IR (ATR):  $\bar{\nu} = 1615$  (C=C), 1571, 1519 (C=O)  $cm^{-1}$ ;  $^1H$  NMR ( $CDCl_3$ , 25°C):  $\delta = 1.90$ , 1.96 (s,  $CH_3CO$ ), 1.94 (s,  $CH_3C=$ ), 3.98 (m, broad,  $OCH_2CH_2O$ ), 5.01, 5.04 (br,  $(CO)_2CH$ ), 5.56 (s,  $CH_2=C$ ), 6.11 (s, 1H,  $CH_2=C$ ), Butoxy: 0.89 (m,  $CH_3$ ), 1.37 (br, overlapped,  $CH_2CH_3$ ), 1.67 (m, br, overlapped,  $OCH_2CH_2$ ), 4.17 (t, overlapping signals, no integration possible,  $J = 6.59$  Hz,  $OCH_2$ ) ppm;  $^{13}C$  NMR ( $CDCl_3$ , 25°C):  $\delta = 18.4$  ( $CH_3C=$ ), 25.9 ( $CH_3CO$ ), 89.4, 88.2 ( $(CO)_2CH$ ), 62.4 ( $OCH_2CH_2O$ ), 64.4 ( $OCH_2CH_2O$ ), 125.1, 126.0 ( $CH_2=$ ), 136.9 ( $CH_3C=$ ), 167.6 ( $COO$ ), 173.4 ( $OCOCHCO$ ), 185.9 ( $CH_3CO$ );  $OBu$ : 14.2 ( $CH_3$ ), 19.4 ( $CH_2CH_3$ ), 36.5 ( $OCH_2CH_2$ ), 69.7 ( $OCH_2$ ) ppm.

## Acknowledgements

Financial support of this work by the Austrian Fonds zur Förderung der wissenschaftlichen Forschung (FWF, project nr. P17424) is gratefully acknowledged.

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