

Hydrolysis and Condensation Reactions of Methacrylate-Modified Aluminum Alkoxides*

Ertuğrul ARPAÇ & Efraim AVŞAR†
*Department of Chemistry, Faculty of Arts and Sciences,
Akdeniz University, Antalya-TURKEY*

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The hydrolysis of aluminum tri-sec-butoxide and compounds obtained by substituting the larger functional groups for the present alkyl groups in $\text{Al}(\text{O-sec-Bu})_3$, and the reaction of these products with a polymerizable organic ligand, i.e. methacrylic acid, were studied together with the hydrolysis reactions of the final products. A good method of preparing high-tech materials and new composites uses organo-substituted silicon esters and/or alkoxides of various elements in a polycondensation process. Introducing a suitable organic network into the inorganic backbone gives desirable properties in new coating materials. The preparation of such materials is possible via the hydrolysis of metal alkoxides. Usually, different alkoxides have different hydrolysis rates and mechanisms and thus different condensation and complexation characteristics.

Introduction

Organically modified alkoxides are widely used for preparing new high-technology materials¹⁻⁴. By proper selection of metal alkoxides, a molecular oxide network can be obtained through appropriate inorganic polymerizations. By controlling the whole process accurately, and characterizing all the chemical species formed throughout the reactions, high-tech materials with the desired properties can be synthesized. Obviously, the desired properties of the resulting material essentially depend on the metal alkoxides, various chemical additives, and, as a whole, on the so-called "sol-gel" process.

In this study $\text{Al}(\text{O-sec-Bu})_3$ was chosen as the starting material. Reliable information on the extent of its hydrolysis was first obtained. In order to improve the processing properties of the aluminum alkoxides chosen, chemical modification with methacrylic acid was carried out.

Generally complexing ligands (such as methacrylic acid) are used in order to control hydrolysis and condensation reactions¹. By introducing a polymerizable ligand into the inorganic structure, a molecular scale fixation of metal oxide within the polymeric matrix can be achieved. In general, hydrolysis of the modified precursor results in stable sols with particles size in the nano range.

* Dedicated to professor M. Bahattin Baysal for his 75 th. Birthday

† Author to whom correspondence should be addressed

Experimental

Chemicals, Apparatus and Procedure

Reagent grade $\text{Al}(\text{O-sec-Bu})_3$ (Fluka, 0.01 mole) was hydrolyzed with various quantities of water (1-4 moles per aluminum tri-sec-butoxide) in 15.8 g of 4-methyl-2-pentanone (Merck) at room temperature. The extent of the hydrolysis was measured using a differential NIR-spectrometer (Nicolet 66 SXR) and Karl-Fischer titrator (Mettler 2200). During the hydrolysis reaction aliquots of the reaction mixture were taken at fixed time intervals and the total amount of sec-butanol formed in the hydrolysis and subsequent condensation reaction were determined by gas chromatography (Beckman 2120). The internal standard technique was used. Here, 4-methyl-2-pentanone was chosen as the standard. The hydrolysis-condensation product was separated from the aqueous part in a vacuum. Elemental and TG-DTA analyses were carried out on the water-free samples.

Aluminum tri-2-butoxyethoxide was obtained by treating the pure $\text{Al}(\text{O-sec-Bu})_3$ (0.01 mole) with 2-butoxyethanol (Aldrich, 0.03 moles) in 20 g of 2, 2, 4-trimethylpentane (Aldrich) at room temperature. This mixture was stirred for about 30 minutes. The Sec-butanol formed in the reaction and was separated from the reaction mixture in a vacuum. The reaction between $\text{Al}(\text{O-sec-Bu})_3$ and 2-butoxyethanol was followed by gas chromatography, and it was found that all the (O-sec-Bu) had been completely replaced by 2-butoxyethoxide (BuOEtO). Again the internal technique was used. different amounts of sec/butanol were added to a fixed amount of 2, 3, 4-trimethylpentane (isooctane), chosen as the standard, and the ratios of the sec-BuOH peak area to the iso-octane peak area were plotted against the ratios of the sec-BuOH weight to iso-octane weight.

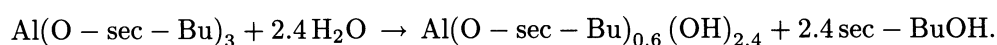
The experimental procedure used in the hydrolysis of $\text{Al}(\text{OEtOBu})_3$ was again essentially the same as that described for $\text{Al}(\text{O-sec-Bu})_3$. When methacrylic acid (MA) is added gradually to a solution of $\text{Al}(\text{OEtOBu})_3$ in 4-methyl-2-pentanone in 1:1 and 2:3 molar ratios, 2-butoxyethanol is eliminated and $\text{Al}(\text{OEtOBu})_2(\text{MA})$ and $\text{Al}(\text{OEtOBu})_{1.5}(\text{MA})_{1.5}$ complexes respectively, are formed.

Hydrolyses of these new precursors were carried out by the addition of 1-4 moles of water per mole of $\text{Al}(\text{OEtOBu})_{3-n}(\text{MA})_n$ at room temperature. The amount of unreacted water was determined through by Karl-Fischer titration. All ^{13}C -NMR spectra were obtained with Bruker AC-200 spectrometer at 50.33 MHz in CDCl_3 solvent. TMS was used as the reference.

Results and Discussion

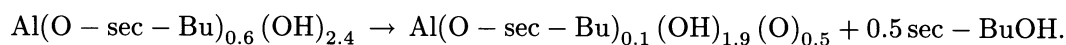
Hydrolysis and condensation of $\text{Al}(\text{O-Sec-Bu})_3$

For a complete hydrolysis of aluminum tri-sec-butoxide, 2.4 moles of water was required. This result was also confirmed by differential NIR-sepectroscopy measurements, Figure 1, in which the area under the free H_2O peak ($5212\text{-}5275\text{ cm}^{-1}$) was calculated. According to the data from the Karl-Fischer titrations and NIR-sepectroscopy, the hydrolysis reaction of $\text{Al}(\text{O-sec-Bu})_3$ proceeds in the form:



In order to determine the total amount of sec-butanol formed in the hydrolysis and in the subsequent spontaneous-condensation reaction, gas chromatography was used. The total amount of sec-butanol formed in the hydrolysis and condensation reactions was found to be 2.9 moles. Therefore, the actual stoichiometry

of the condensation reaction is



Thermogravimetric analysis of the products of the hydrolysis-condensation reactions shows that the total weight loss was 37% up to 700 °C, corresponding to 63% Al₂O₃ (33 % in Al), which concurs excellently with the elemental analysis. Obviously, the 37-percent weight loss was due to the eliminations of H₂O and the organic constituents at high temperatures. The thermal analysis data show two endothermic peaks at 96 and 140 °C, probably due to H₂O attached to the compound, and three exothermic peaks at 226, 271 and 443 °C, due to organic constituents bonded to the Al atom.

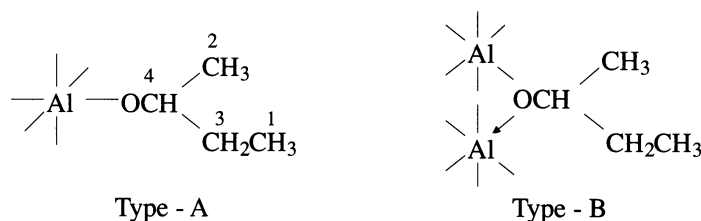
Alcoholysis of Al(O-sec-Bu)₃ with 2-butoxyethanol

The reaction between aluminum tri-sec-butoxide and 2-butoxyethanol (BuOEtOH) in a 1:3 molar ratio was completed at room temperature. Both gas chromatography and the ¹H-NMR spectrum indicate that all the O-sec-Bu groups were completely substituted by the equivalent number of the OEtOBu group. The observed chemical shifts are

$$\begin{array}{c} \begin{array}{c} | \\ \text{---Al---} \\ | \end{array} \begin{array}{cccccc} \text{OCH}_2 & \text{CH}_2 & \text{OCH}_2 & \text{CH}_2 & \text{CH}_2 & \text{CH}_3 \\ 6 & 5 & 4 & 3 & 2 & 1 \end{array} \end{array}$$

Number of atoms	1	2	3	4	5	6
δ(H)/ppm	0.90	1.35	1.55	3.45	3.60	3.85

The ¹³C-NMR spectrum, Figure 2, of Al(O-sec-Bu)₃ shows that sec-butoxy groups were coordinated with Al atoms in two different ways as shown below:



The observed liquid-state ¹³C-NMR chemical shifts for both bonding types are as follows:

Number	δ(C), Chemical shifts/ppm	
	Type - A	Type - B
1	10.3	10.6
2	21.4	21.7
3	31.6	34.1
4	68.6	73.2

Aluminum-27 spectra of Al(O-sec-Bu)₃ in CDCl₃ were obtained with a Bruker AC-200 spectrometer at 52.12 MHz. The ²⁷Al-NMR spectrum has a singlet at 0.16 ppm, which indicates that Al center in a octahedral environment⁶.

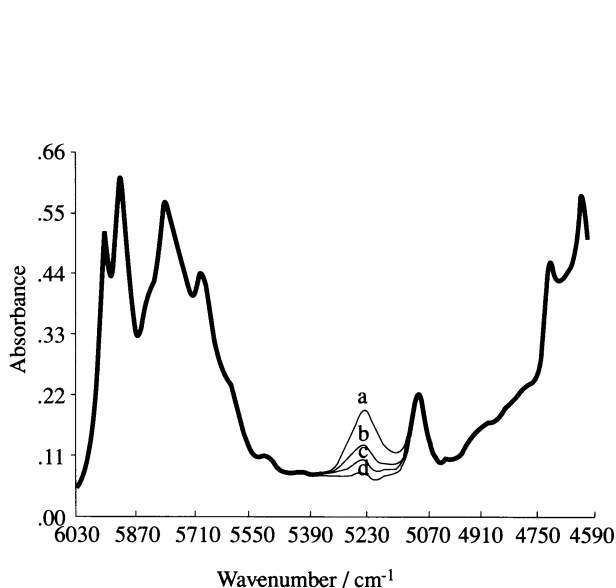


Figure 1. The differential NIR spectra of $\text{Al}(\text{O-sec-Bu})_3$ in ethanol solvent. mole ratios of $\text{Al}(\text{O-sec-Bu})_3/\text{H}_2\text{O}$: a) 1/5, b) 1/4, c) 1/3, d) 1/2

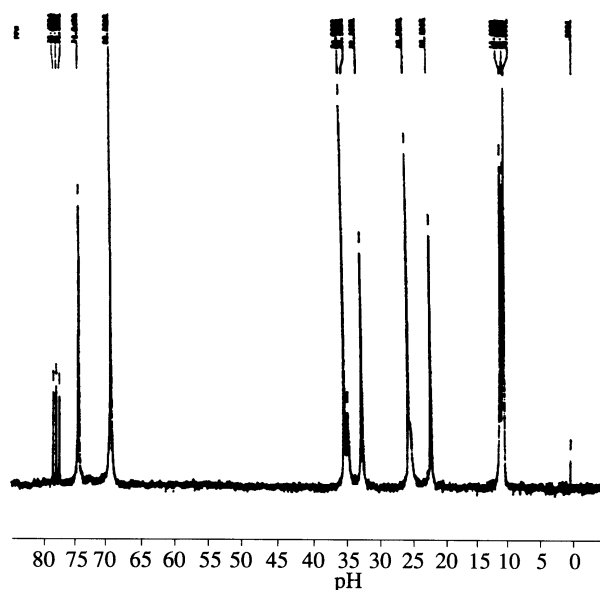
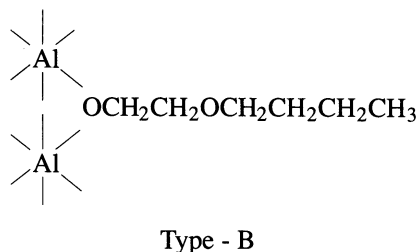
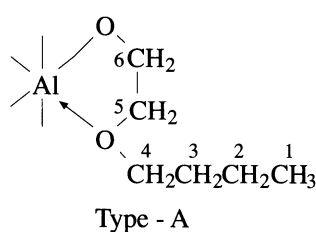


Figure 2. The $^{13}\text{C-NMR}$ spectrum of $\text{Al}(\text{O-sec-Bu})_3$ in CDCl_3 solvent

The $^{13}\text{C-NMR}$ spectrum (Figure 3) of the product resulting from the alcoholysis reaction shows that all the O-sec-Bu groups were completely substituted by 2-butoxyethoxide groups, and the 2-butoxyethoxide groups were coordinated with aluminum in two distinct ways:



The observed liquid-state $^{13}\text{C-NMR}$ chemical shifts of the alcoholysis product are given below:

Number of C - atoms	$\delta(\text{C})/\text{ppm}$	
	A	B
1	14.04	14.04
2	19.33	19.55
3	31.26	32.28
4	60.96	62.26
5	70.02	70.99
6	71.16	74.89

The $^{12}\text{Al-NMR}$ spectrum of this compound has a singlet at 5.7 ppm, which shows that the Al atom is in an octahedral environment⁶. Spectroscopic evidence reveals that the structural model of this compound is the same as that in Figure 4.

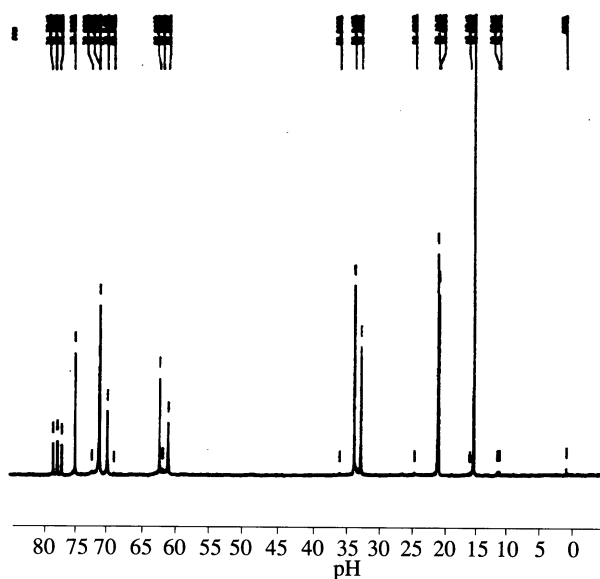


Figure 3. The ^{13}C -NMR spectrum of $\text{Al}(\text{OEtOBu})_3$ in CDCl_3 solvent

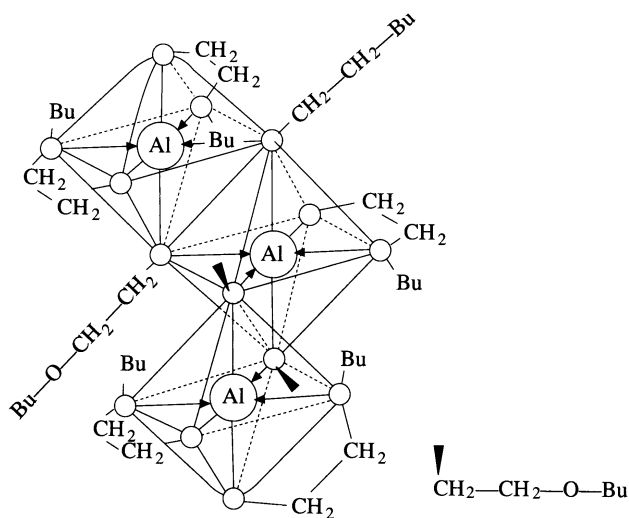
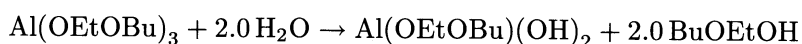


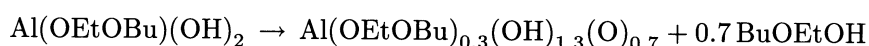
Figure 4. The proposed structure of $\text{Al}(\text{OEtOBu})_3$

Hydrolysis of $\text{Al}(\text{OEtOBu})_3$

Hydrolysis of aluminum tri-2-butoxyethoxide was conducted with 1-4 moles of water/Al. For complete hydrolysis 2 moles of water are required. In order to find the extent of the condensation reaction after the hydrolysis reaction, the amount of total butoxyethanol formed must be measured. It was found by gas chromatography that the total amount of BuOEtOH formed in the reactions was 2.7 moles. Thus, the hydrolysis and condensation reactions proceed in the form:



and



respectively.

Thermogravimetric analysis of the product of the hydrolysis-condensation reaction reveals that the weight loss was 44.7 percent. This result concurs with the structural model proposed, Figure 4, and corresponds to 53.4 % Al_2O_3 . The weight loss (44.7%) was caused by the elimination of H_2O and organic constituents at high temperature.

Complexation $\text{Al}(\text{OEtOBu})_3$

Methacrylic acid (MA) was used as an organic network former. Alkoxides of aluminum, titanium or zirconium which are partly converted by polymerizable methacrylic acid are useful precursors in sol-gel chemistry^{4,5}.

The complexation reaction of $\text{Al}(\text{OEtOBu})_3$ with methacrylic acid was recorded with a IR spectrometer. The observed shift of the carbonyl band indicates that the methacrylic acid reacted with Al maximum in a 3:2 (MA:Al) molar ratio. The complexation reaction was studied with 3:2 and 1:1 molar ratios.

a) Complex $\text{Al}(\text{OEtOBu})_2(\text{MA})$

In the reaction of 1 equivalent of $\text{Al}(\text{OEtOBu})_3$ with 1 equivalent of methacrylic acid at room temperature, the FT-IR spectrum indicates no sign of the free-OC vibration band. Since no band was observed in the carbonyl region, all methacrylate groups must be attached to Al atoms, Figure 5.

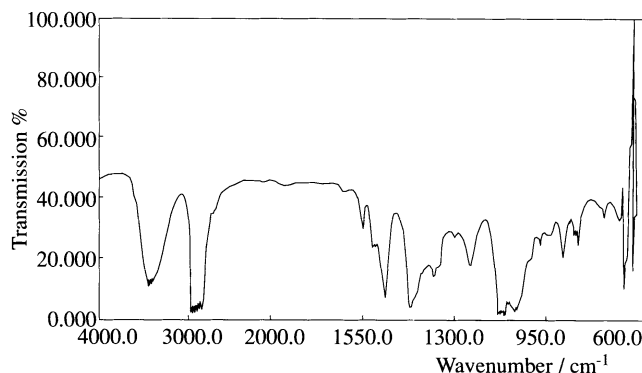
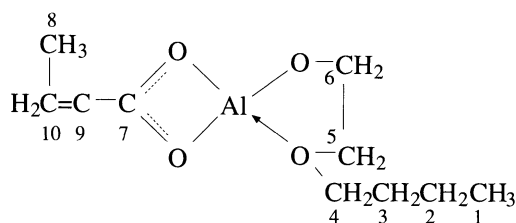


Figure 5. The FT-IR spectrum of the complex $\text{Al}(\text{OEtOBu})_2(\text{MA})$

Infrared bands at 1558 cm^{-1} and 1461 cm^{-1} were assigned to asymmetric and symmetric $-\text{COO}$ vibrations, respectively⁷. A band at 1646 cm^{-1} , due to $\nu(\text{C}=\text{C})$, indicates the presence of unbounded double bonds. All these results show that methacrylic acid is attached to Al by bidentate chelating.

The $^1\text{H-NMR}$ spectrum clearly shows the presence of the methacrylate group beside the 2-butoxyethoxide group. The observed ^1NMR chemical shifts of the complex are:



C-atoms	1	2	3	4	5	6	7	8	9	10
$\delta(\text{H})/\text{ppm}$	0.9	1.4	1.8	3.4	3.4	3.6		1.9		(5.4,6.1)

The $^{13}\text{C-NMR}$ chemical shifts of the same complex were found to be:

C-atoms	1	2	3	4	5	6	7	8	9	10
$\delta(\text{C})/\text{ppm}$	13.9	19.4	31.8	61.7	71.2	72.2	174	19.5	140	125(?)

The $^{27}\text{Al-NMR}$ spectrum shows a broad singlet at 68 ppm which reveals that Al is tetrahedrally coordinated⁶.

b) Complex $\text{Al}(\text{OEtOBu})_{1.5}(\text{MA})_{1.5}$

The addition of methacrylic acid to a solution of $\text{Al}(\text{OEtOBu})_3$ in a 3:2 molar ratio gives $\text{Al}(\text{OEtOBu})_{1.5}(\text{MA})_{1.5}$. The absence of a carbonyl vibration band and the appearance of asymmetric and symmetric stretching bands of a chelating or bridging $-\text{COO}$ group at 1568 cm^{-1} and 1461 cm^{-1} reveal that methacrylic acid is bonded to Al atoms through bidentate coordination⁸. Uncoordinated double bonds of $\nu(\text{C}=\text{C})$ appear at 1651 cm^{-1} .

The $^{13}\text{C-NMR}$, Figure 6, chemical shifts of the complex $\text{Al}(\text{OEtOBu})_{1.5}(\text{MA})_{1.5}$ are as follows:

C-atoms	1	2	3	4	5	6	7	8	9	10
$\delta(C)/\text{ppm}$	13.9	19.4	31.8	61.7	70.8	70.8	174	18.5	140	125

Aluminum-27 spectrum gives a singlet at -3.0 ppm indicating that Al centers in an octahedral environment ⁶.

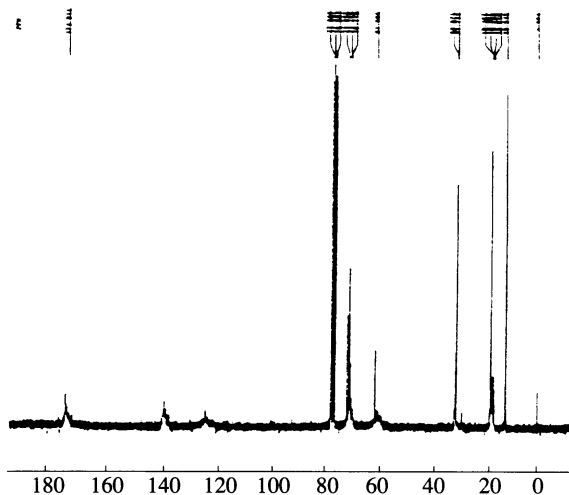


Figure 6. The ¹³C-NMR spectrum of the complex $\text{Al}(\text{OEtOBu})_{1.5}(\text{MA})_{1.5}$ in CDCl_3 solvent

Hydrolysis of Methacrylate Complexes

a) $\text{Al}(\text{OEtOBu})_2(\text{MA})$

The addition of various amounts of water to a fixed quantity of complex $\text{Al}(\text{OEtOBu})_2(\text{MA})$ causes hydrolysis. Karl-Fischer titration measurements show that for a complete hydrolysis 1.3 moles of water/Al were required. The FT-IR spectrum of the hydrolysis product has asymmetric and symmetric bands of a bridging -COO group at 1565 and 1462 cm^{-1} , respectively ^{7,8}. Bands at 1650 cm^{-1} , assigned to $\nu(\text{C}=\text{C})$, and at 3491 cm^{-1} , assigned to $\nu(\text{OH})$, show the presence of carbon double bonds and OH groups, respectively.

b) $\text{Al}(\text{OEtOBu})_{1.5}(\text{MA})_{1.5}$

The experimental procedure used here was the same as described for $\text{Al}(\text{OEtOBu})_2(\text{MA})$. The full amount of water required for complete hydrolysis was found to be 0.9 moles per mole complex.

The FT-IR band at 1652 cm^{-1} is due to $\nu(\text{C}=\text{C})$. The band at 3491 cm^{-1} is due to $\nu(\text{OH})$. The bands at 1567 and 1461 cm^{-1} are asymmetric and symmetric -COO stretching vibrations respectively ⁸.

In summary, modification of $\text{Al}(\text{OEtOBu})_3$ with different amounts of methacrylic acid gives products of different compositions. The hydrolysis of these products results in chemically different starting materials for sol-gel chemistry. Since these building blocks contain double bonds in the ligand, subsequent polymerization reactions are always possible. Polymerization of methacrylate-modified aluminum alkoxides with various unsaturated organic molecules produces new organic-inorganic polymers with unusual properties.

Acknowledgements

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