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SYNTHESIS AND REACTIONS OF UNSATURATED LIGANDS CONTAINING Al AND Zr ALKOXIDE PRECURSORS

D. Hoebbel, T. Reinert, K. Endres, H. Schmidt
Institut für Neue Materialien, Im Stadtwald, 66123 SAARBRÜCKEN-GERMANY
A. Kayan, and E. Arpac
Akadeniz Üniversitesi, 07200 ANTALYA-TURKEY

Abstract. - The Al and Zr alkoxides $Al(OBu^s)_3$ and $Zr(OPr^i)_4$ were complexed by allyl acetoacetate (AAA) nearly completely in molar ratios 1:1 and 1:2, proved by IR and ^{13}C NMR spectroscopy. The hydrolysis reaction of these complexes releases remarkable amounts of AAA at molar ratios $H_2O/OR > 1$. The Al/AAA complexes are accessible to additive reactions with HSi groups containing silicic acids and polysiloxanes leading to a reactive Al alkoxide precursor or polymer attached to a silicic acid or polysiloxane backbone. The hydrosilylation reaction of the Zr/AAA complexes causes side reactions of the silicic acid component. A pathway is described to overcome this difficulty.

I. INTRODUCTION

Sol-gel derived inorganic organic polymers are playing an increasing role in the preparation of new materials with tailor-made properties [1-3]. Starting compounds for such polymers include not only the commonly used functional silicon alkoxides but also reactive Al, Ti, and Zr alkoxides or their complexes with organic acids and diketones [4-6]. The organic complex ligands influence the reactivity and the condensation degree of the metal alkoxides due to the diminished ratio of alkoxide to metal. In case of a reactive organic ligand with functional groups (e.g. double bonds, epoxide groups) the ligand can take part in building up a polymeric inorganic organic network. From the literature [5] a series of functional organic ligands with unsaturated double bonds are known for the complexation of Al-, Ti- or Zr-alkoxides e.g.: methacrylic acid, cinnamic acid or aceto acetoxy ethylmethacrylate. For the vast majority of these metal alkoxide complexes a remarkable lack of knowledge exists about the degree of complexation, stability of the complex ligand against hydrolysis, hydrolysis and condensation reactions of the metal alkoxide complexes and the reactivity of the double bond in the complex against polymerization and additive reactions.

The aim of this work is to obtain more insight in these areas for allyl acetoacetate complexed Al- and Zr-alkoxides. The results of this study shall contribute to new routes in the preparation of precursors and to improve the control of their reactions.

II. EXPERIMENTAL

A. Synthesis and Hydrolysis of Aluminium- and Zirconium-Alkoxides Complexed by AAA

Allyl acetoacetat (AAA, ALDRICH) was slowly added to $Al(OBu^s)_3$ (FLUKA) or $Zr(OPr^i)_4$ (ABCR, 75.3% in n-propanol) under dry nitrogen atmosphere a) without solvent and b) in dioxane or toluene in the molar ratios AAA/metal = 1, 1.5 and 2. The mixture was stirred for 1h at room temperature. The solvent was removed in vacuo (room temperature, 1 mbar) giving compounds of oily consistence. The hydrolysis of the dioxane solved complexes (1.5 mM/g, AAA/metal = 1) were performed by dioxane, containing 3.6 % H_2O , in molar ratios $H_2O/OR = 0.5, 1, 1.5$ and 2 at room temperature. The transparent liquid products are stable in closed bottles over more than 10 days, except the Zr-hydrolyzate ($H_2O/OR = 2$), which gels after 4 hours.

B. Additive Reaction

The additive reactions of the Al/AAA and the Zr/AAA complexes were carried out with a silicic acid derivative $[(CH_3)_2HSi]_8Si_8O_{20}$ ($Q_8M_8^H$) [7] and the polymethylhydro-dimethylsiloxane ($MD_{19}D_{11}^H$) (ABCR) in ratios double bond to HSi = 1:1. The same procedure was always carried out, and is described as follows:

$Q_8M_8^H$ (0.363 mM) was dissolved in 3 ml of dried toluene followed by the addition of $Al(OBu^s)_2AAA$ (2.91 mM) solved in 3 ml toluene containing 1×10^{-4} mol Pt /mol double bond. After stirring the mixture for 4 h at 90-95° C the solvent was removed (50°C, 1 mbar), giving a transparent resin, soluble in toluene.

C. Methods

The NMR spectra were obtained on BRUKER AC200 (liquid state) and MSL200 (solid state) spectrometers operating at a field of 4.7 Tesla. Aquisition parameters: Liquid state: $^{13}C\{^1H\}$ experiment: inverse gated, standard (st.):

SiMe₄, pulse width (p.w.): 6.4 μs (60°), repetition time (r.t.): 10s, 200-3000 scans; ²⁹Si{¹H}: inverse gated, st. SiMe₄ or D₄ (19.07ppm), p.w. 11.7 μs (60°), r.t. 10s with Cr(acac)₃, 300-3000 scans; ²⁷Al: single pulse, external st. 1 M aqueous AlCl₃·6H₂O, p.w. 22.6 μs (60°), r.t. 200ms, 500-5000 scans. Solid state: ²⁹Si{¹H}: single pulse-MAS-experiment (rotation frequency: 3 kHz), external st. Q₈Mg, p.w. 3.3 μs (60°), r.t. 60s, 400-1000 scans.

IR spectra were recorded on BRUKER IFS25 with the attenuated total reflectance (ATR) technique (45°, ZnSe-crystal), the water content in the hydrolyzates was determined by Karl-Fischer-titration method (KYOTO ELECTR, MKA210).

III. RESULTS AND DISCUSSION

A. Characterization of Allyl Acetoacetate (AAA) Complexed Al Alkoxides

The reaction of Al(OBu^s)₃ and allyl acetoacetate CH₂=CH-CH₂-O-C(O)-CH₂-C(O)-CH₃ (AAA) in a molar ratio Al:AAA = 1:1 and 1:2 at room temperature leads to transparent liquids, the constitution of which were characterized by IR, ¹³C and ²⁷Al NMR spectroscopy. In the IR spectra of both compounds the typical C=O vibration bands of the uncomplexed AAA (keto type) at 1740 and 1715 cm⁻¹ disappears and new bands of the C=C and C=O vibrations occur at lower wave numbers (1610 and 1520 cm⁻¹), characteristic for metal acetoacetate complexes[8]. The ¹³C NMR spectra of both complexes do not show resonance signals of C-atoms in C=O and O-C=O groups of the AAA (keto type) at δ = 200.7 and 167 ppm but high and low field shifted signals at δ = 174.4 and 186.8 ppm, typical of the enolic form of AAA bonded to a metal atom. Both methods confirm a complete complexation for the molar ratio Al:AAA = 1:1 and 1:2. The ²⁷Al NMR spectra of the series Al(OBu^s)₃ - Al(OBu^s)₂AAA - Al(OBu^s)(AAA)₂ are shown in Fig. 1, I-III.

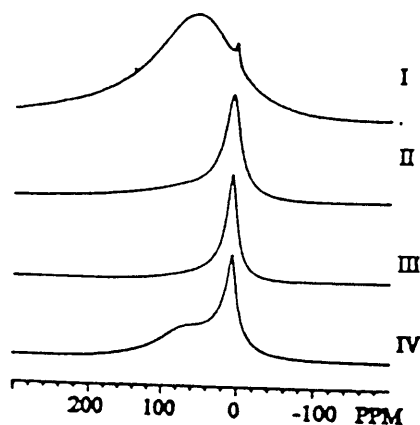


Fig. 1. ²⁷Al NMR spectra of I: Al(OBu^s)₃, II: Al(OBu^s)₂AAA, III: Al(OBu^s)(AAA)₂ and IV: additive product of MD₁₉D^H₁₁M and Al(OBu^s)₂AAA.

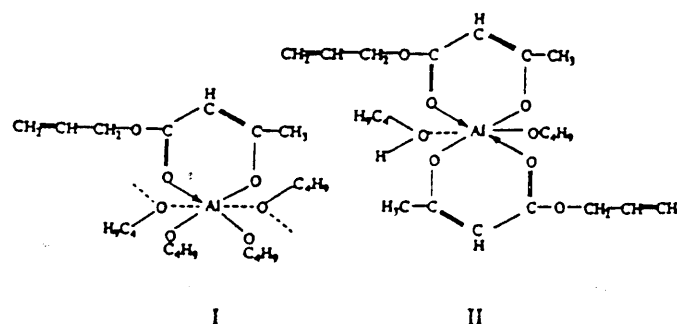


Fig. 2. Structural scheme of I: Al(OBu^s)₂AAA and II: Al(OBu^s)(AAA)₂

The Al-atoms in Al(OBu^s)₃ are mainly coordinated by four oxygen atoms (δ = 54 ppm) according to the results of previous studies [9]. In the 1:1 and the 1:2 complexes the coordination number six (δ = 5 ppm) prevails. The octahedral Al coordination can be formed by solvation with alcohol molecules, by M-O(R)-M bridges of metal alkoxide groups and by bridging through AAA-ligands. A significant shift of the Al/O coordination number from 4 towards 6 with increasing degree of complexation is observed in the ²⁷Al NMR spectra. More detailed studies of the complexity of the Al/AAA compounds are in progress, so that Fig. 2 shows only a simplified structural scheme of the monomeric complexes in their main coordination state.

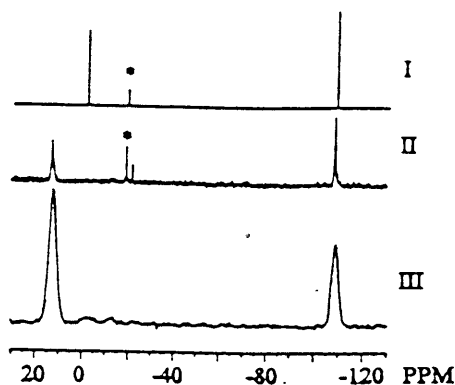
B. Allyl Acetoacetate (AAA) Complexed Zr Alkoxides

By mixing of Zr(OPrⁿ)₄ with AAA in molar ratios Zr/AAA = 1:1, 1:1.5 and 1:2 at room temperature, transparent liquid reaction products were obtained. The IR and ¹³C NMR spectroscopic examination confirmed a complete complexation in the 1:1 product after 1h reaction time. The small signals at δ = 50 ppm (-C(O)-CH₂-C(O)-, keto type) in the ¹³C NMR spectra from the 1:1.5 and 1:2 reaction products suggest that approximately 5% of the AAA remained unreacted. A comparable amount of AAA was detected in both reaction products after longer reaction times (2 days). It is assumed that the unreacted AAA could be an equilibrium concentration from higher complexed Zr/AAA compounds.

C. Additive Reactions of $Al(OBu^s)_2AAA$ and $Al(OBu^s)(AAA)_2$

Generally, the double bonds in the Al and Zr/AAA complexes should be suitable for additive reactions with HSi groups containing compounds. For the hydrosilylation of the complexes two compounds were used: the monomolecular H-dimethylsilylated double four-ring silicic acid $[(CH_3)_2HSi]_8Si_8O_{20}$ ($Q_8M_8^H$) of a cage-like structure (Fig. 4) and a polyhydromethyl dimethylsiloxane with alternating $(CH_3)_2Si$ and CH_3HSi groups and the following formula derived from ^{29}Si NMR measurements: $(CH_3)_3Si-O-[Si(CH_3)_2-O]_{19}-[SiHCH_3-O]_{11}-Si(CH_3)_3$ ($MD_{19}D_{11}M$). The abbreviations M, D and Q are adopted from the literature [10]. $Q_8M_8^H$ represents an eight-fold functional rigid silicic acid framework and the polysiloxane a more flexible chainlike structure with an average molecular mass of 2200 g per mole. The hydrosilylation of $Al(OBu^s)_2AAA$ with the silicic acid derivative $Q_8M_8^H$ in a molar ratio of double bond to HSi-groups = 1:1 leads to a transparent resin, soluble in organic solvents. The additive reaction of the complex $Al(OBu^s)(AAA)_2$, containing two unsaturated organic groups per molecule, in a molar ratio of double bond to HSi groups = 1:1 yields a gel insoluble in organic solvents. The liquid and solid state ^{29}Si NMR spectra of the starting silicic acid derivative $Q_8M_8^H$ and of the reaction products are shown in Fig. 3.

Fig. 3. ^{29}Si NMR spectra of I: $Q_8M_8^H$, additive products of $Q_8M_8^H$ and $Al(OBu^s)_2AAA$ (II) and $Al(OBu^s)(AAA)_2$ (III) (* standard)



The resonance signal of the HSi-groups ($\delta = -1.5$ ppm) caused by $Q_8M_8^H$ (Fig. 3, I) is not detectable in the spectra of the additive products, rather a new signal at $\delta = 13$ ppm appears assigned to $OSi(CH_3)_2CH_2$ groups. From the absence of C-atoms in double bonds ($\delta = 117$ and 132 ppm) proved by ^{13}C NMR, and from the results of the ^{29}Si NMR, a complete additive reaction occurs. The symmetrical single signals at $\delta = -108.6$ ppm in the ^{29}Si NMR spectra (Fig. 3, II, III) show an identical chemical shift compared with the starting $Q_8M_8^H$ proving a preserved double four-ring silicic acid structure in both additive products. A structural scheme of the additive products is shown in Fig. 4.

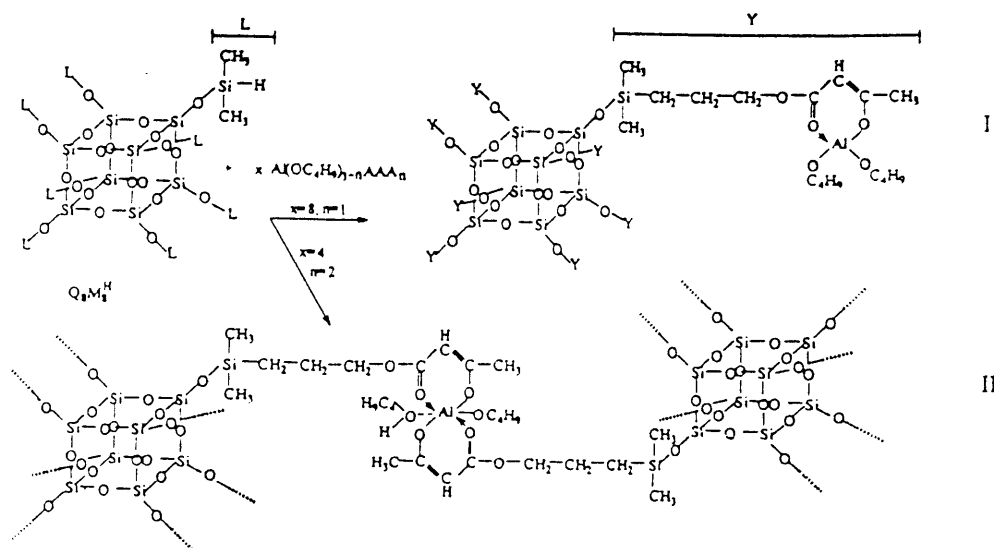


Fig. 4. Structural scheme of additive reactions of $Q_8M_8^H$ and $Al(OBu^s)_2AAA$ (I) and $Al(OBu^s)(AAA)_2$ (II)

Due to the two unsaturated groups per Al atom the complex $Al(OBu^s)(AAA)_2$ is able to link the silicic acid units to a three dimensional network structure (Fig 4, II). The additive reaction of the $Al(OBu^s)_2AAA$ and $Al(OBu^s)(AAA)_2$ with the polysiloxane $MD_{19}D_{11}M$ in molar ratios of double bond : HSi = 1:1 leads to similar result compared with the $Q_8M_8^H$ reaction: the additive reaction of $Al(OBu^s)_2AAA$ with the polysiloxane yields a so-

luble transparent resinous product of high elasticity, the $\text{Al}(\text{OBU}^s)(\text{AAA})_2$ complex reacts to an insoluble gel. This gel shows a considerably higher elasticity than the gel derived from the silicic acid cage. The ^{29}Si NMR and ^{13}C NMR spectra of the additive products do not reveal unreacted HSi groups ($\delta = -35$ to -37 ppm) from the starting polysiloxane or double bonds ($\delta = 117.1$ ppm) from the Al/AAA complex. The NMR studies confirm a complete additive reaction, the preservation of the polysiloxane structure, as well as the AAA complex. The ^{27}Al NMR spectrum of the soluble reaction product (Fig. 1, IV) shows two overlapping broad signals with maxima at 51 ppm and 6 ppm corresponding to a tetrahedral and octahedral Al/O coordination. A rough quantitative estimation of the tetrahedral to octahedral coordinated Al atoms leads to a ratio of 2:1 in the additive product. Fig. 5 gives a structural scheme of both additive products:

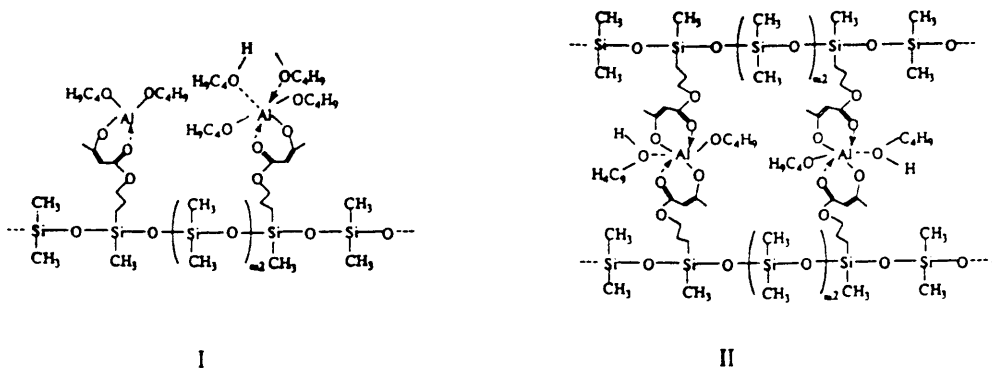


Fig. 5. Structural scheme of additive products of $\text{MD}_{19}\text{D}_{11}^{\text{H}}$ and $\text{Al}(\text{OBU}^s)_2\text{AAA}$ (I) and $\text{Al}(\text{OBU}^s)(\text{AAA})_2$ (II)

The NMR studies suggest the bridged ladder structure for the insoluble polymer in Fig. 5, II carrying one reactive alkoxide group per Al atom.

D. Additive Reactions of $\text{Zr}(\text{OPr}^n)_3\text{AAA}$ and $\text{Q}_8\text{Mg}^{\text{H}}$

The additive reaction of the $\text{Zr}(\text{OPr}^n)_3\text{AAA}$ complex with the silicic acid derivative $\text{Q}_8\text{Mg}^{\text{H}}$ in the molar ratio $\text{AAA} : \text{HSi} = 1:1$ yields a transparent product of oily consistence. Surprisingly, the ^{29}Si NMR spectrum of the reaction product do not show the characteristic single signal of the Q^4 Si atoms in the double four-ring structure. Repeated syntheses confirmed an extensive degradation of the silicic acid structure during the additive reaction with the Zr/AAA complex. To avoid such extreme side reactions, a different reaction pathway was followed. In the first step the silicic acid cage of $\text{Q}_8\text{Mg}^{\text{H}}$ was protected by additive reaction with AAA. The two signals at $\delta = 12.4$ and -109.7 ppm in the ^{29}Si NMR spectrum of the reaction product reveals a complete addition with preservation of the silicic acid structure according the formula $[\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{C}(\text{O})\text{OCH}_2]_3\text{Si}(\text{CH}_3)_2]_8\text{Si}_8\text{O}_{20}$ ($\text{Q}_8\text{Mg}^{\text{AAA}}$). In the second step the eight ketoester groups containing silicic acid derivative was reacted with $\text{Zr}(\text{OPr}^n)_4$ in a molar ratio ligand : $\text{Zr} = 1:1$. The ^{29}Si NMR spectrum shows a signal group in the M region of Si atoms at $\delta = 9$ to 13 ppm and the typical single signal at $\delta = -108.7$ ppm assigned to the Si atoms of the silicic acid cage. Beside these signals only two unknown minor signals at $\delta = -5$ and -11 ppm with an intensity $< 5\%$ appears. From the NMR spectrum it can be concluded, that using the described reaction pathway a successful synthesis of a Zr-alkoxide precursor attached to a double four-ring silicic acid backbone is possible.

E. Hydrolysis and Condensation Reactions of $\text{Al}(\text{OBU}^s)_2\text{AAA}$ and $\text{Zr}(\text{OPr}^n)_3\text{AAA}$

The objective of these experiments was to obtain more information on the stability of the AAA ligand in the $\text{Al}/\text{Zr}/\text{AAA}$ complexes against hydrolysis. The results of the hydrolysis experiments are summarized in Table 1. From these results it follows that for the AAA ligand in the $\text{Al}(\text{OBU}^s)_2\text{AAA}$ complex a reasonable stability against hydrolysis at low $\text{H}_2\text{O}/\text{OR}$ ratios occurs. Higher ratios (1.5 and 2) release about 15-40% of the AAA from the complex already after a short time. This amount of AAA remains practically unchanged over a few days. The Zr/AAA complex releases up to 30% of the AAA already at low $\text{H}_2\text{O}/\text{OR}$ ratios of 0.5 and 1. At ratios ≥ 1.5 the amount of uncomplexed AAA prevails in the hydrolyzate. A fast gelation appears to be due to the extensive degradation of the Zr/AAA complex in connection with the higher functionality of the Zr. The low amount of water used in the early stage of $\text{Al}(\text{OBU}^s)_2\text{AAA}$ hydrolysis and the increasing consumption of water with time points to a slow hydrolysis rate. The Zr complex immediately needs a higher amount of water. Possibly, the fast degradation of the complex is responsible for the higher water consumption. Further work regarding the hydrolytic stability of Al and Zr /AAA complexes attached to silicic acids and polysiloxane is under progress.

Tab. 1 Results of hydrolysis reactions of the $\text{Al}(\text{OBU}^{\text{S}})_2\text{AAA}$ and $\text{Zr}(\text{OPr}^{\text{D}})_3\text{AAA}$ complexes

Molar Ratio	Degree of Complexation AAA : Zr/Al		Consumption of Water H ₂ O/OR	
	Zr(OPr) ₃ AAA	Al(OBU) ₂ AAA	Zr(OPr) ₃ AAA	Al(OBU) ₂ AAA
0.5	0.85:1 (4h)	1:1 (2h)	0.30 (0.5h)	0.15 (0.4h)
	0.85:1 (96h)	1:1 (72h)	0.40 (24h)	0.20 (0.6h)
				0.40 (98h)
1.0	0.70:1 (22h)	0.95:1 (5h)	0.40 (0.2h)	0.40 (0.5h)
	0.70:1 (120h)	0.95:1 (36h)	0.50 (0.5h)	0.65 (27h)
			0.55 (22h)	
1.5	0.40:1 (10h)	0.85:1 (1.5h)	0.75 (0.5h)	0.50 (1h)
		0.85:1 (24h)	0.80 (20h)	0.80 (24h)
			gel (44h)	
2.0	gelation	0.60:1 (18h)	~0.60 (1h)	0.90 (22h)
			gel (4h)	0.90 (26h)

IV. CONCLUSIONS AND SUMMARY

1. $\text{Al}(\text{OBU}^{\text{S}})_3$ and $\text{Zr}(\text{OPr}^{\text{D}})_4$ were complexed by AAA nearly completely in molar ratios metal/AAA = 1:1 and 1:2 leading to precursors with reactive alkoxide and unsaturated groups.
2. The hydrolysis of the $\text{Al}(\text{OBU}^{\text{S}})_2\text{AAA}$ and $\text{Zr}(\text{OPr}^{\text{D}})_3\text{AAA}$ complexes in molar ratio $\text{H}_2\text{O}/\text{OR} = 0.5$ and 1 yields transparent sols, stable against gelation over weeks, higher ratios of 1.5 and 2 likewise produce sols from the Al complex but the Zr complex reacts to gels after a short time.
3. Under the described conditions of hydrolysis an increasing amount of AAA (60 %) is released from the complexes with higher $\text{H}_2\text{O}/\text{OR}$ ratios. The Al complex shows a higher stability against degradation than the Zr complex.
4. The Al/AAA complexes are accessible to additive reactions with HSi groups containing silicic acid and polysiloxane. As a result, novel Al alkoxide precursors and polymeric compounds with a silicic acid or polysiloxane backbone were synthesized.
5. The additive reaction of the Zr/AAA complex with HSi groups containing silicic acid derivative causes a strong degradation of the silicic acid structure. By changing the order in the reaction steps, the synthesis of a Zr alkoxide precursor with a defined silicic acid backbone is possible.
6. The novel silicic acid or polysiloxane attached Al or Zr alkoxide precursors can be used as a source for the preparation of homogeneous and highly stoichiometric Al/Si and Zr/Si containing inorganic organic polymers.

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