

Precursor Structure and Hydrolysis-Gelation Process of $\text{Al}(\text{O-sec-Bu})_3$ Modified with Ethylacetoacetate

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Abstract. The precursor structure and hydrolysis-gelation process of aluminum-sec-butoxide, $\text{Al}(\text{O-sec-Bu})_3$, modified with ethylacetoacetate (EAcAc) were investigated using IR, UV and high magnetic field (11.7 T) ^{27}Al NMR spectra. ^{27}Al NMR showed that the reaction of EAcAc with $\text{Al}(\text{O-sec-Bu})_3$ led to the formation of six-coordinated structural units and most of the precursors were assumed to be present as linear trimer containing a four- and two six-coordinated Al atoms. It was found that EAcAc formed the strong chelating bonds with $\text{Al}(\text{O-sec-Bu})_3$, which were hardly hydrolyzed by the attack of water molecules in the gelation process.

Keywords: chemical modification, ^{27}Al NMR, hydrolysis, gelation, structure of precursor

1. Introduction

Chemical modification of metal alkoxides with chelating agents like β -diketones is known to be very effective for the control of reactivities and condensation process of reactive metal alkoxides, such as Al-, Zr-, and Ti-alkoxides which form precipitates easily by hydrolysis [1–3]. The structure of modified metal alkoxides affects the character and structure of gels formed by their hydrolysis. Therefore, it is very important to investigate the structure of modified alkoxides and the influence of their structure on the process of gel formation. As to Al-alkoxides, it has already been reported that alumina thin films [3, 4], fibers [5] and aerogels [6, 7], and mullite [8] and cordierite powders [9] can be prepared from Al-alkoxides modified with β -diketones. The structure of precursors has been studied using IR [3, 7] and ^{27}Al NMR [5, 9], and the size of primary particles that are formed during the hydrolysis and condensation process has been examined by dynamic light scattering [4] and SAXS [7, 8] measurements. However, few systematic studies have been reported about the effects of the structure of modified alkoxides on the hydrolysis and gelation process.

In this study, the structure and the hydrolysis-gelation processes of Al-sec-butoxide modified with

different amounts of ethylacetoacetate are investigated. The structure of modified Al-alkoxide was examined using high magnetic field ^{27}Al NMR (11.7 T) spectroscopy, where the line width of peaks can be reduced. The hydrolysis and condensation processes were examined by IR and UV spectra. From the results obtained, the effect of modification of the starting Al-alkoxide on the gelation process is discussed.

2. Experimental

Aluminum-sec-butoxide, $\text{Al}(\text{O-sec-Bu})_3$, were used as a starting material. Sec-butyl alcohol, sec-BuOH, were used as a solvent to avoid the influence of trans-esterification. $\text{Al}(\text{O-sec-Bu})_3$ and sec-BuOH was mixed and stirred at room temperature for 1 h. Ethylacetoacetate, EAcAc, was added to the solution as a chelating agent, and stirred for 3 h. Water diluted with sec-BuOH was then carefully added to the solution for hydrolysis. The sols thus prepared were kept in closed containers for gelation at 50°C. The molar ratios of sec-BuOH and H_2O to $\text{Al}(\text{O-sec-Bu})_3$ were kept to be 10 and 4, respectively, whereas those of EAcAc to $\text{Al}(\text{O-sec-Bu})_3$ were varied from 0.5 to 2.0. The gelation time was defined as the time at which the solutions showed no fluidity when tilted.

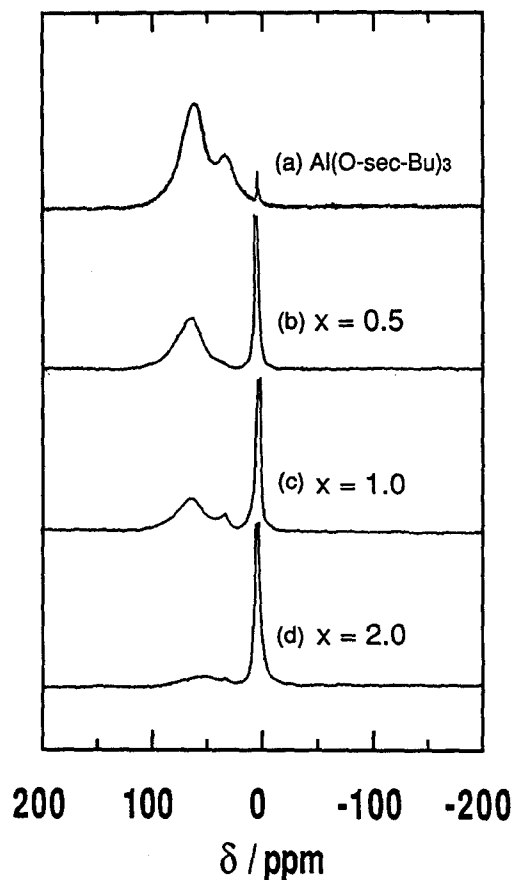


Fig. 1. ^{27}Al NMR spectra of (a) $\text{Al}(\text{O-sec-Bu})_3$, and modified $\text{Al}(\text{O-sec-Bu})_3$ with several molar ratios of $x = \text{EAcAc}/\text{Al}(\text{O-sec-Bu})_3$; (b) $x = 0.5$, (c) $x = 1.0$, (d) $x = 2.0$.

The reaction of $\text{Al}(\text{O-sec-Bu})_3$ with EAcAc and the process of hydrolysis were examined using high magnetic field ^{27}Al NMR, IR and UV-visible spectra. ^{27}Al NMR spectra were measured at 130.3 MHz (11.7 T) using a JEOL JNM-GX500 spectrometer with pulse width of 14 μs and delay time of 1 s between pulses. CDCl_3 was used as a solvent for the measurement and the concentration of samples was about 5–10 wt%. The solution of 0.2 M $\text{AlCl}_3/\text{D}_2\text{O}$ was used as an external standard. UV-visible spectra were measured using a Shimadzu UV240 spectrophotometer with a handmade quartz cell. IR spectra were measured with a Hitachi 260–50 infrared spectrophotometer using two KBr discs with a spacer of 0.1 mm thick for sandwiching the samples, in which the thickness of samples was kept to be 0.1 mm.

3. Results and Discussion

3.1. The Structure of $\text{Al}(\text{O-sec-Bu})_3$ Modified with EAcAc

In order to investigate the coordination state of $\text{Al}(\text{O-sec-Bu})_3$ modified with EAcAc, ^{27}Al NMR spectra were measured. Figure 1 shows the ^{27}Al NMR spectra of (a) $\text{Al}(\text{O-sec-Bu})_3$, and modified $\text{Al}(\text{O-sec-Bu})_3$ with several EAcAc/ $\text{Al}(\text{O-sec-Bu})_3$ molar ratios of (b) 0.5, (c) 1.0 and (d) 2.0. In the ^{27}Al NMR spectra, the peaks at about 0–10, 30–40, 60–70 ppm are assigned to the six-, five- and four-coordinated Al atoms, respectively [10]. In the references [10, 11], the ^{27}Al NMR spectra of Al-alkoxides or modified Al-alkoxides were measured at high temperature (70°C to 120°C) to reduce the line width of peaks, especially the peak due to the four-coordinated Al atoms. However, in this study, the measurement can reduce the line width of peaks with the high magnetic field (11.7 T) and different coordination states can easily be distinguished at room temperature.

In the ^{27}Al NMR spectrum of $\text{Al}(\text{O-sec-Bu})_3$, Fig. 1(a), the peaks due to four-, five- and six-coordinated structural units are observed, consistent with the previously reported reference [10]. With the addition of EAcAc, ^{27}Al NMR spectra of $\text{Al}(\text{O-sec-Bu})_3$ modified with EAcAc show different features from those of $\text{Al}(\text{O-sec-Bu})_3$ itself. In the spectrum Fig. 1(b) for $\text{EAcAc}/\text{Al}(\text{O-sec-Bu})_3 = 0.5$, a broad peak at 65 ppm, assigned to the four-coordinated Al atoms, and a sharp and strong peak at 5 ppm, assigned to the six-coordinated Al atoms, are observed. A peak at around 35 ppm, assigned to the five-coordinated Al atoms, which has been observed in the spectrum of $\text{Al}(\text{O-sec-Bu})_3$, is very weak and observed only as a shoulder. In the spectrum Fig. 1(c) for $\text{EAcAc}/\text{Al}(\text{O-sec-Bu})_3 = 1.0$, however, the peak at 36 ppm appears clearly. In the spectrum Fig. 1(d) for $\text{EAcAc}/\text{Al}(\text{O-sec-Bu})_3 = 2.0$, the strong peak due to the six-coordinated Al atoms and the very weak peak due to the four- and five-coordinated Al atoms are observed.

Figure 2 shows some examples of the structure units present in (a) $\text{Al}(\text{O-sec-Bu})_3$ itself and modified $\text{Al}(\text{O-sec-Bu})_3$ with several EAcAc/ $\text{Al}(\text{O-sec-Bu})_3$ molar ratios of (b) $x = 0.5$ and (c) $x = 1.0$ to discuss the precursor structures in the present study. These models are derived from the previously reported structures of $\text{Al}(\text{O-sec-Bu})_3$ [10] and modified $\text{Al}(\text{O-sec-Bu})_3$ with

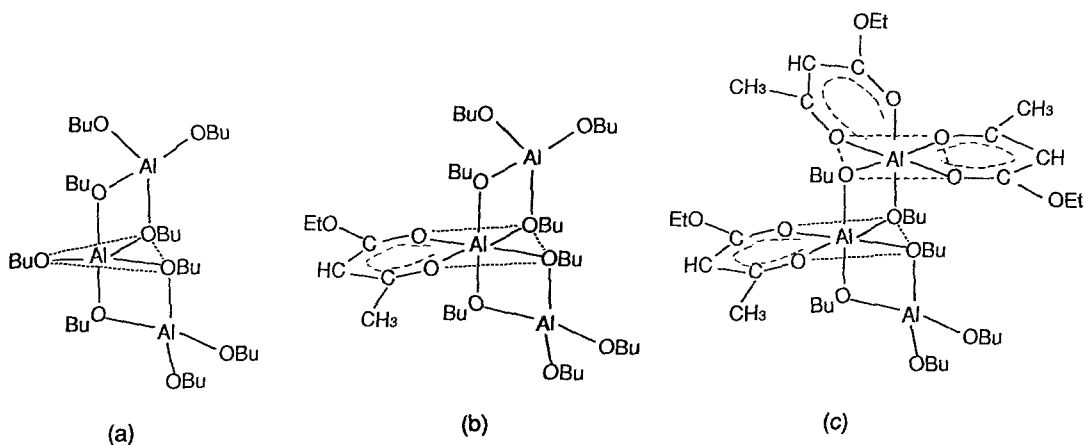


Fig. 2. Structure models of (a) $\text{Al}(\text{O-sec-Bu})_3$, and modified $\text{Al}(\text{O-sec-Bu})_3$ with several molar ratios of $x = \text{EAcAc}/\text{Al}(\text{O-sec-Bu})_3$; (b) $x = 0.5$, (c) $x = 1.0$.

acetylacetone [11], and also the present results. The details of derivation of these proposed models are described in the following discussion.

It is known that the Al-alkoxides are present in solution as oligomeric species and the structure of the species depends on the size of alkoxy groups. Kriz et al. reported that $\text{Al}(\text{O-sec-Bu})_3$ was present mainly as linear trimer which consists of five-coordinated Al atoms between two four-coordinated Al atoms, and/or as tetramer which consists of one central six-coordinated Al atoms surrounded by three four-coordinated Al atoms [10]. As shown in Fig. 1(a), the intensity of the peak due to the six-coordinated Al atoms is very weak. Therefore, it is assumed that the linear trimeric structure as shown in Fig. 2(a) is present as a major species.

With increasing $\text{EAcAc}/\text{Al}(\text{O-sec-Bu})_3$ molar ratio, the intensity of the peaks assigned to the four- and five-coordinated Al atoms decreases and the intensity of the peak assigned to the six-coordinated Al atoms increases. This means that the reaction of EAcAc with $\text{Al}(\text{O-sec-Bu})_3$ leads to the formation of six-coordinated structural units. IR and UV-visible spectra of these solutions showed that all of the added EAcAc had chelated to $\text{Al}(\text{O-sec-Bu})_3$.

When the molar ratio $\text{EAcAc}/\text{Al}(\text{O-sec-Bu})_3$ is smaller than unity, $\text{Al}(\text{O-sec-Bu})_3$ is not fully chelated with EAcAc stoichiometrically. It means that the solution of $\text{EAcAc}/\text{Al}(\text{O-sec-Bu})_3 = 0.5$ consists of chelated $\text{Al}(\text{O-sec-Bu})_3$ and non-chelated $\text{Al}(\text{O-sec-Bu})_3$. In Fig. 1(b), only a weak shoulder is observed at around 30–40 ppm, which corresponds to the five-coordinated Al atoms. Since $\text{Al}(\text{O-sec-Bu})_3$ has originally five-coordinated Al atoms in the linear trimer, it is

assumed that one butoxy group of the five-coordinated structural units in the linear trimer in the $\text{Al}(\text{O-sec-Bu})_3$ solution was substituted by EAcAc to yield the six-coordinated structural units as shown in Fig. 2(b). In addition, some of the four-coordinated Al atoms may form the six-coordinated atoms.

In the case of $\text{EAcAc}/\text{Al}(\text{O-sec-Bu})_3 = 1$, Fig. 1(c), the peak at 35 ppm assigned to the five-coordinated Al atoms is observed. It is then assumed that a part of four-coordinated Al atoms form the five-coordinated structural units by reacting with EAcAc. In the most cases, two terminal butoxy groups of the four-coordinated structural units and one butoxy group of the five-coordinated structural units in the linear trimer as shown in Fig. 2(a) were substituted by EAcAc to yield the linear trimer as shown in Fig. 2(c), which contains two six-coordinated Al-atoms, one being coordinated by two EAcAc and the other being coordinated by one EAcAc, and one four-coordinated Al atom. This structure is the same one as $[\text{Al}(\text{O-}i\text{-Pr})_2(\text{AcAc})]_3$ reported in Ref. [11].

Further addition of EAcAc leads to the formation of six-coordinated structural units.

3.2. Gelation Process of Modified $\text{Al}(\text{O-sec-Bu})_3$

Figure 3 shows the dependence of gelation time at 50°C on water content for several $\text{EAcAc}/\text{Al}(\text{O-sec-Bu})_3$ ratios. All gels obtained under these conditions were homogeneous and transparent. The gelation time decreases remarkably with an increase in the amount of water as well as a decrease in the amount of EAcAc.

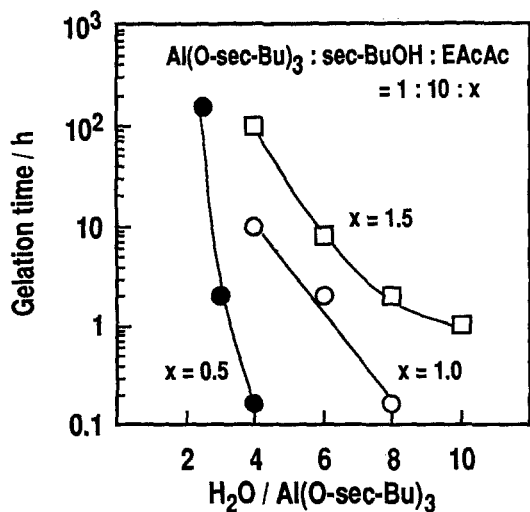


Fig. 3. Change of gelation time as a function of the amount of H₂O with several molar ratios of $x = \text{EAcAc}/\text{Al}(\text{O-sec-Bu})_3$.

When the ratio of water/ $\text{Al}(\text{O-sec-Bu})_3$ was less than 3 and that of $\text{EAcAc}/\text{Al}(\text{O-sec-Bu})_3$ was more than 1.0, the sols did not form gels during aging for 1000 h in the closed containers.

Figure 4 shows the IR spectra of (a) before and (b) after hydrolysis of $\text{Al}(\text{O-sec-Bu})_3$ modified with EAcAc ($\text{EAcAc}/\text{Al}(\text{O-sec-Bu})_3 = 1$) in the wavenumber range between 1800 and 1500 cm^{-1} . Before hydrolysis, a peak at 1650 cm^{-1} , which can be assigned to the C=O stretching vibrations of enolic form of EAcAc or chelated EAcAc, are observed, and there is no apparent peak at about 1720 cm^{-1} . However, after hydrolysis, a peak at about 1720 cm^{-1} which can be assigned to the stretching vibration of non-chelated or the ketonic form of EAcAc is observed due to the partial hydrolysis of coordinated EAcAc with the addition of water.

Figure 5 shows the UV-visible absorption spectra of (a) before and (b) after hydrolysis of $\text{Al}(\text{O-sec-Bu})_3$ modified with EAcAc ($\text{EAcAc}/\text{Al}(\text{O-sec-Bu})_3 = 1$). The concentration of Al was normalized in these measurements. The absorption peak at about 270 nm is attributed to the $\pi-\pi^*$ transition of the chelating bonds of complex formed between $\text{Al}(\text{O-sec-Bu})_3$ and EAcAc. After hydrolysis, the intensity of the peak at 270 nm decreased because of the partial hydrolysis of coordinated EAcAc.

Figure 6 shows the dissociation behavior of EAcAc coordinated to $\text{Al}(\text{O-sec-Bu})_3$ during the gelation process. The ratio of coordinated EAcAc was estimated from the changes of absorption coefficient at 270 nm due to chelated EAcAc in the UV spectra (solid

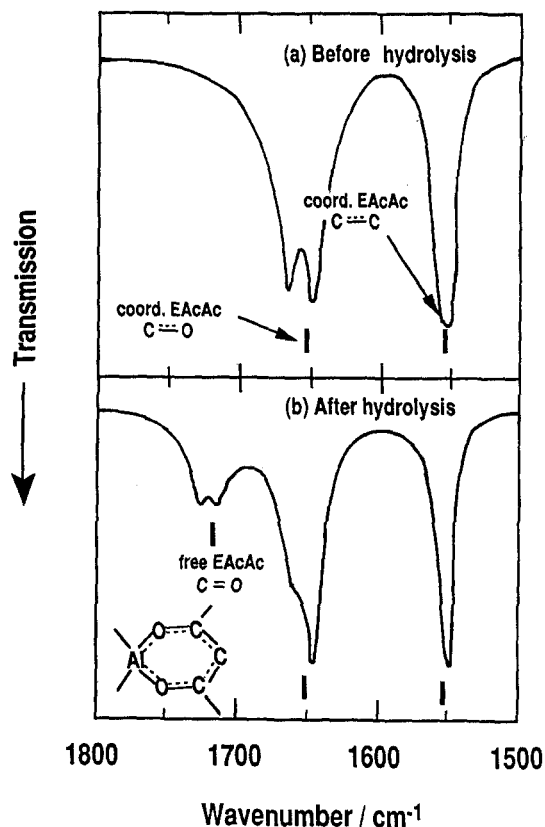


Fig. 4. Infrared absorption spectra of (a) before and (b) after hydrolysis of $\text{Al}(\text{O-sec-Bu})_3$ modified with EAcAc ($\text{EAcAc}/\text{Al}(\text{O-sec-Bu})_3 = 1$).

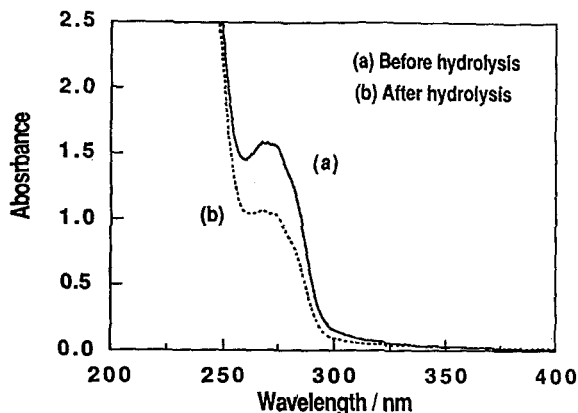


Fig. 5. Ultraviolet absorption spectra of (a) before and (b) after hydrolysis of $\text{Al}(\text{O-sec-Bu})_3$ modified with EAcAc ($\text{EAcAc}/\text{Al}(\text{O-sec-Bu})_3 = 1$).

squares) and of the IR absorption coefficient at about 1720 cm^{-1} (open circles). UV spectra were deconvoluted into two peaks (at about 200 nm and at 270 nm) by the least-squares fitting to calculate the absorption

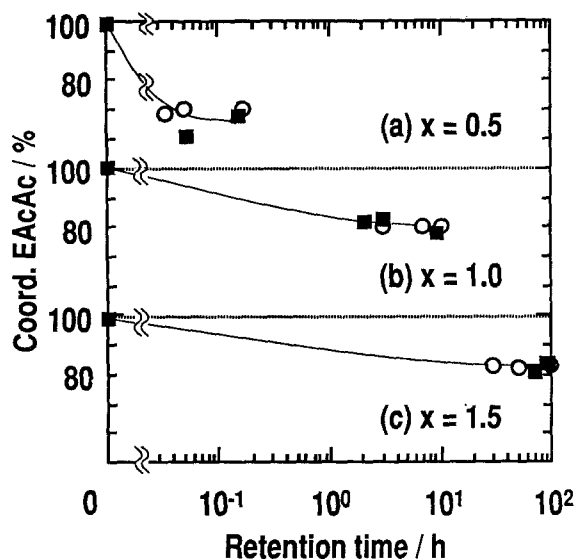


Fig. 6. Dissociation behavior of EAcAc coordinated to $\text{Al}(\text{O-sec-Bu})_3$ during gelation process for the sec-BuOH-EAcAc system. Solid squares are determined from the UV spectra and open circles from the IR spectra. The solutions were prepared in the molar ratios of $\text{Al}(\text{O-sec-Bu})_3:\text{sec-BuOH}:\text{EAcAc}:\text{H}_2\text{O} = 1:10:x:4$.

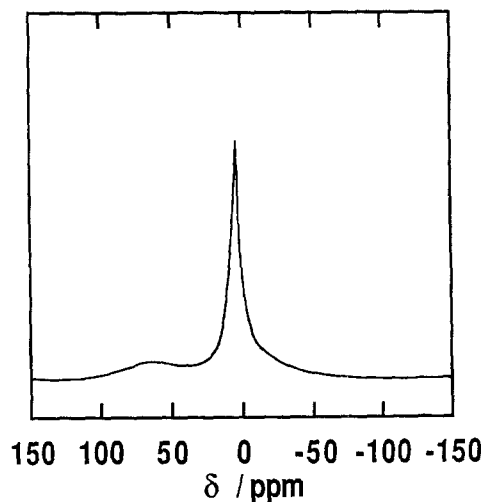


Fig. 7. ^{27}Al NMR spectrum of $\text{Al}(\text{O-sec-Bu})_3$ modified with EAcAc after hydrolysis ($\text{EAcAc}/\text{Al}(\text{O-sec-Bu})_3 = 1$).

coefficient of the peak at 270 nm. In the case of IR spectra, the solution containing the same EAcAc concentration as hydrolyzed solution was used as reference. The curves in the figure are guide to eye and the end points indicate the gelation point. Time scale is represented in log scale, since the gelation time changes remarkably with different $\text{EAcAc}/\text{Al}(\text{O-sec-Bu})_3$ molar ratios; the time becomes longer with an increase in the molar ratios.

In the case of $\text{EAcAc}/\text{Al}(\text{O-sec-Bu})_3 = 0.5$, gels were formed soon and only about 30% of the chelated ligands are hydrolyzed at the gelation point. In the case of $\text{EAcAc}/\text{Al}(\text{O-sec-Bu})_3 = 1.0$ and 1.5, about 15% of the chelated ligands are hydrolyzed in about 1 h after the addition of water. However, the rest of the chelated ligands are not hydrolyzed further and about 80% of them remain even at the gelation point. In spite of a large difference in the gelation time with different $\text{EAcAc}/\text{Al}(\text{O-sec-Bu})_3$ ratios, about 70–80% of the chelating bonds were not hydrolyzed in all the cases when the gels were formed. These results show that EAcAc reacts with Al-alkoxides to form strong chelating bonds and these bonds are hardly hydrolyzed by the attack of water molecules in the gelation process.

As pointed out by Nass and Schmidt [4], EAcAc modifies the alkoxides by occupying a site for condensation and acts as a surfactant, which prevents agglomeration. The remaining of strong chelating bonds through the gelation process means that a part of the condensation sites are always occupied by EAcAc and agglomeration is prevented. Therefore, as the molar ratio $\text{EAcAc}/\text{Al}(\text{O-sec-Bu})_3$ increases, the possibility of condensation reaction decreases, and the gelation time becomes longer.

Figure 7 shows the ^{27}Al NMR spectrum of $\text{Al}(\text{O-sec-Bu})_3$ modified with EAcAc after hydrolysis. Two broad peaks due to four- and six-coordinated Al atoms are observed and the half width of these peaks is broader than that of the peaks observed before hydrolysis. This indicates that many kinds of structural units are formed by the hydrolysis and condensation.

As shown in Fig. 1(b), (c) and (d), ^{27}Al NMR spectra have revealed that most of the modified Al-alkoxides are six-coordinated. The fact that 70–80% of chelated EAcAc was not hydrolyzed in all the cases shows that a certain type of six-coordinated structural units is easily hydrolyzed and others are hardly hydrolyzed. As shown in Fig. 7, ^{27}Al NMR spectrum of $\text{Al}(\text{O-sec-Bu})_3$ after hydrolysis shows the very broad peak at around 5 ppm. This means that many kinds of condensed six-coordinated structural units, most of which are chelated with EAcAc, are present in the sols after hydrolysis.

4. Conclusion

The structure and the hydrolysis and condensation processes of $\text{Al}(\text{O-sec-Bu})_3$ modified with ethylacetate were investigated using IR, UV and ^{27}Al NMR

spectra. ^{27}Al NMR showed that the reaction of EAcAc with $\text{Al}(\text{O-sec-Bu})_3$ led to the formation of six-coordinated structural units and most of precursors were assumed to be present as linear trimer containing both four- and six-coordinated Al atoms. It was found that EAcAc formed the strong chelating bonds with $\text{Al}(\text{O-sec-Bu})_3$, which were hardly hydrolyzed by the attack of water molecules in the gelation process.

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