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Application of the ^{27}Al NMR spectroscopy to studies of mechanisms of cyclic esters polymerization

Summary — On account of a vast use of the aluminum-containing initiators and catalysts for the polymer synthesis the applications of the ^{27}Al NMR spectroscopy to studies of the polymerization mechanisms is described. In the extensive introduction the specific features of Al atom, important with regard to the ^{27}Al NMR spectroscopy, are discussed. The latter include strong tendency of the organoaluminum compounds to aggregation and quadrupolar character of the ^{27}Al nucleus. Attention is also drawn to some pitfalls in the quantitative analysis of the ^{27}Al NMR spectra which result from an extraneous multinuclear probe head signal, base-line rolling, and the absorption bands broadening at lower temperatures. Finally, examples of application of the ^{27}Al NMR to determining the active centers structure in the ring-opening polymerization of ϵ -caprolactone (CL) and L,L-lactide (LA) initiated with dialkylaluminum alkoxides, aluminum *tris*-alkoxides or dialkylaluminum alkoxide/(S)-(+)-2,2'-[1,1'-binaphthyl-2,2'-diylbis-(nitrylmethylidene)diphenol] [SB(OH)₂] system are reported in more detail.

Key words: ^{27}Al NMR spectroscopy, ring-opening polymerization, active centers, ϵ -caprolactone, L,L-lactide, aluminum alkoxides, dialkylaluminum alkoxide/(S)-(+)-2,2'-[1,1'-binaphthyl-2,2'-diylbis-(nitrylmethylidene)diphenol].

ZASTOSOWANIE SPEKTROSKOPII ^{27}Al NMR DO BADAŃ MECHANIZMÓW POLIMERYZACJI CYKLICZNYCH ETERÓW

Streszczenie — W związku z szerokim wykorzystaniem w syntezie polimerów inicjatorów i katalizatorów na podstawie związków glinoorganicznych w obszernej części wstępnej przedyskutowano szczególne cechy atomu glinu, ważne w odniesieniu do spektroskopii ^{27}Al NMR. Są to przede wszystkim silna skłonność związków glinoorganicznych do agregacji oraz kwadrupolowy charakter jądra ^{27}Al . Zwrócono również uwagę na pewne trudności w ilościowej analizie widm ^{27}Al NMR wynikające z występowania „aparaturowego” sygnału sondy wielojądrowej, falowania linii podstawowej oraz poszerzania pasm absorbcyjnych w niższej temperaturze (rys. 1—4, równ. 1—4). Szczegółowo omówiona w artykule praca własna dotyczyła zastosowań metody ^{27}Al NMR do oznaczania struktury centrów aktywnych polimeryzacji z otwarciem pierścienia ϵ -kaprolaktonu (CL) i L,L-laktydu (LA) inicjowanej dialkiloalkoksyalkoholanami glinu, *tris*-alkoholanami glinu, bądź układem Et₂AlOEt/(S)-(+)-2,2'-[1,1'-binaftylo-2,2'-diylbis(nitrylometylidyno)difenolem] [SB(OH)₂] (rys. 5—7, równ. 1—9).

Słowa kluczowe: ^{27}Al NMR, polimeryzacja z otwarciem pierścienia, centra aktywne, ϵ -kaprolakton, L,L-laktyd, alkoholany glinu, układ dietyloalkoholan glinu/(S)-(+)-2,2'-[1,1'-binaftylo-2,2'-diylbis(nitrylometylidyno)difenol].

Aluminum-containing compounds ($\text{R}_n\text{AlX}_{3-n}$, where R denotes H or alkyl group, X — the alkoxide, carboxylate, amino group, or halogen atom) belong to the most versatile initiators or catalysts applied in polymerization of α -olefins or heterocyclic monomers (see *e.g.* Ref. [1—6]). $\text{R}_n\text{AlX}_{3-n}$ found also some applications in the controlled vinylic or acrylic monomers polymerization

(see *e.g.* Ref. [7, 8]). Heterogeneous Ziegler-Natta and homogeneous metallocene initiators, in which aluminum trialkyls (R_3Al) and/or aluminoxanes $\{-[\text{Al}(\text{R})\text{O}]_n\}$ play a role of an effective catalysts, have to be mentioned first [1, 2]. In the ring-opening polymerization (ROP) of cyclic ethers and esters the $\text{R}_3\text{Al}/\text{H}_2\text{O}/\text{acetylacetone}$ (AcacH) mixtures originally introduced by Vandenberg [9] were then developed [3, 4, 7]. Later on, it was revealed that the well-defined dialkylaluminum alkoxides ($\text{R}_2\text{AlOR}'$) and aluminum *tris*-alkoxides $[\text{Al}(\text{OR})_3]$ ini-

^{*)} Szkoła Spektroskopii NMR.

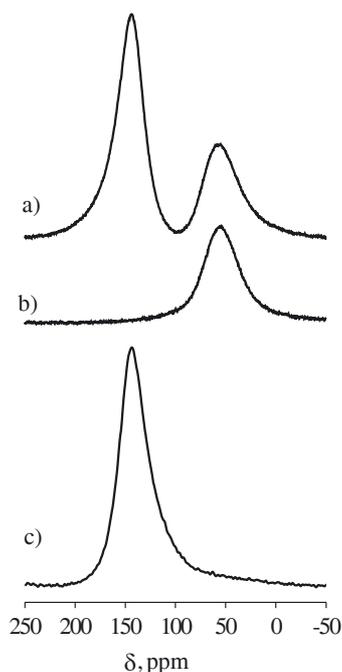


Fig. 2. ^{27}Al NMR spectra of $(\text{Et}_2\text{AlOEt})_3$: a) "virgin" spectrum, b) multinuclear probe head signal, c) spectrum of $(\text{Et}_2\text{AlOEt})_3$ with subtracted multinuclear probe head signal; $[\text{Et}_2\text{AlOEt}]_0 = 0.1 \text{ mol} \cdot \text{L}^{-1}$, 70°C (own results)

Moreover, there are sometimes overlooked phenomena that complicate analysis of the spectra, namely the quadrupolar character of the ^{27}Al nuclei, the base-line rolling, and the artificial multinuclear probe head signal [20].

The latter problem is illustrated in Fig. 2 on the example of the spectrum of trimeric, cyclic aggregate of $\text{Et}_2\text{AlOEt}[(\text{Et}_2\text{AlOEt})_3]$. The "virgin" spectrum shows two absorption bands: at $\delta = 60$ and 146 ppm (Fig. 2a). However, the 60 ppm band is also observed in the absence of the Al-containing compound purposely introduced into the NMR tube, under the otherwise identical measurement conditions (Fig. 2b). The multinuclear probe head signal, becomes particularly important for the diluted samples ($[\text{Al}]_0 < 10^{-1} \text{ mol} \cdot \text{L}^{-1}$). This is a typical concentration range of the initiator (or active species) applied in polymerization, and it requires substantially longer acquisition time. This, in turn, leads to the high intensity of the extraneous probe signal. This difficulty can be removed for example by subtracting the free induction decay signals (FID's) of the Al-containing sample and of the blank sample — the result is shown in Fig. 2c, in which only signal at $\delta = 146$ ppm, coming from the tetracoordinate ($cn = 4$) Al atoms [Al(4)] in $(\text{Et}_2\text{AlOEt})_3$, is present.

The ^{27}Al nucleus composed of 13 protons and 14 neutrons has no spherical shape and the positive charge density shows anisotropy; its spin number (I) is equal to $5/2$. These features result in a quadrupolar character of the ^{27}Al nucleus. Therefore, ^{27}Al NMR spectra typically show the broad diffuse signals, with the half-height

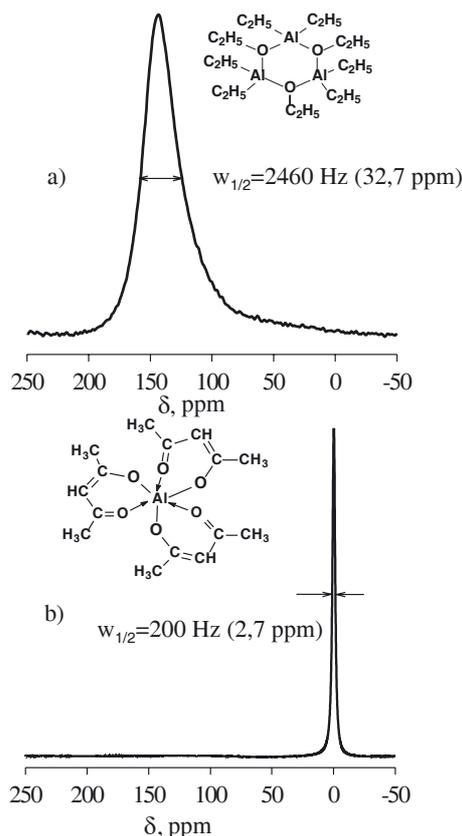


Fig. 3. Comparison of the half-height widths ($w_{1/2}$'s) of signals that come from tetrahedral ($cn = 4$) (a) and octahedral ($cn = 6$) (b) Al atoms; $[\text{Al}]_0 = 0.1 \text{ mol} \cdot \text{L}^{-1}$, 70°C (own results)

width ($w_{1/2}$) that exceeds 10^3 Hz. Only hexacoordinate ($cn = 6$) Al atoms [Al(6)] give narrow peaks ($w_{1/2} \approx 10^2$ Hz), like in aluminum *tris*-acetylacetonate used as the standard in ^{27}Al NMR measurements (Fig. 1 and 3).

Since the NMR correlation time (τ_c) increases with decreasing temperature, the absorption bands tend to broaden at lower temperatures:

$$w_{1/2} = \frac{3}{10} \pi^4 Q^2 \frac{2I+3}{I^2(2I-1)} \frac{e^4}{h^2} q_{zz}^2 \tau_c \quad (3)$$

where: Q — quadrupolar moment, q_{zz} — the electric field gradient, e — elementary charge, h — Planck's constant.

High $w_{1/2}$'s lead to the neighboring bands overlap, which together with the base-line rolling make the accurate integration difficult. Indeed, even within a given compound the ratio of intensities of various Al atoms could be not equal to the expected one. At higher recording temperatures (e.g. 70°C) the resolution is significantly enhanced [due to lower τ_c , Eq. (3)] but first it has to be ensured, that the position of the equilibria between various coexisting species is not altered. For example, it is known that aluminum *tris*-isopropoxide [Al(OⁱPr)₃] exists in a form of trimeric (A₃) and/or tetrameric (A₄) aggregates, which even at the elevated temperatures interexchange very slowly [25, 33, 34] (eq. 4).

The A₄ aggregate contains three Al(4) and one Al(6) atoms and in the corresponding ^{27}Al NMR spectrum the

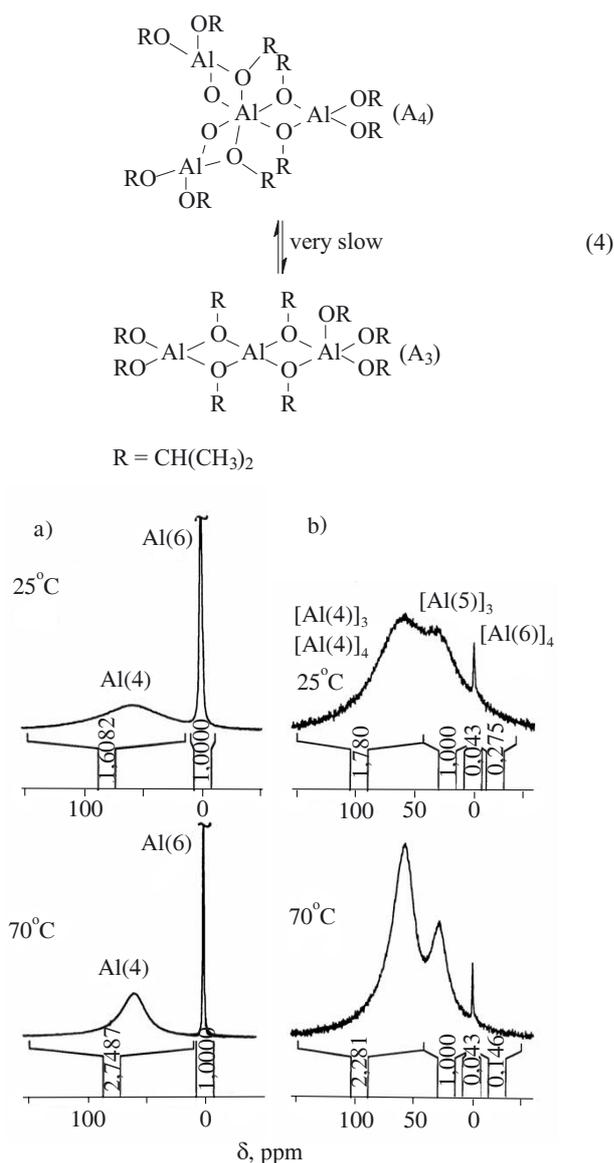


Fig. 4. Comparison of ²⁷Al NMR spectra of Al(OⁱPr)₃ tetramer (A₄) (a) and trimer (A₃) [small Al(6) peak comes from ≈2 mol-% admixture of A₄], (b) recorded at 25 and 70 °C; [Al]₀ = 0.1 mol · L⁻¹ (own results)

[Al(4)]/ [Al(6)] intensities ratio equal to 3 should be expected. Actually, this ratio measured at 25 °C is equal to ≈ 1.6. When temperature increases to 70 °C the absorption bands become narrower and [Al(4)]/[Al(6)] ≈ 2.75, which is not far from the expected value (Fig. 4a). Similarly, for the A₃ aggregate, which contains two Al(4) and one pentacoordinate [Al(5)] metal atoms, [Al(4)]/[Al(5)] equal to ≈ 1.4 and 2 was measured at 25 and 70 °C, respectively (please note that A₃ is contaminated by a minute amount of A₄ — see small peak at 1.5 ppm). Again, measurement carried out at the elevated temperature gave the [Al(4)]/[Al(5)] ratio expected for the A₃ structure.

In the next part of the present paper, some selected applications of the ²⁷Al NMR spectroscopy in studies of

aliphatic cyclic esters polymerization carried out in our laboratory are described.

EXPERIMENTAL

Materials

Monomers and solvents

ε-Caprolactone (CL) (99 %, Aldrich), (*L,L*)-Lactide [(*S,S*)-Lactide in terms of the absolute configuration] (LA) (99 %, Boehringer Ingelheim, Germany), THF (99 %, POCh, Gliwice, Poland), and C₆D₆ (99 %, Dr Glaser AG, Basel, Switzerland) were purified according to the commonly known procedures that employ high vacuum technique (see, *e.g.* Ref. [25, 35–41]).

Initiators and model compounds

Et₂AlOEt (97 %, Aldrich) was distilled under reduced pressure (≈10⁻² mbar, 80 °C), distributed into thin-walled glass phials, and sealed off. Al(OⁱPr)₃ trimer (A₃) and tetramer (A₄) were prepared from the commercially available Al(OⁱPr)₃ (98 %, Aldrich) as already reported [38]. (*S*)-(+)-2,2'-[1,1'-binaphthyl-2,2'-diylbis-(nitrylmethylidene)diphenol] [SB(OH)₂] was synthesized as already described [42]. Aluminum *tris*-acetylacetonate [aluminum pentane-2,4-dionate — Al(acac)₃] (99 %, Aldrich) was used as received. Aluminum *tris*-(ethyl hexanoate-6-alkoxy) was prepared from A₃ and ethyl 6-hydroxycaproate (97 %, Aldrich) by refluxing both reagents in dry benzene (80 °C) and removing the isopropanol formed azeotropically in the inert gas atmosphere.

Measurements

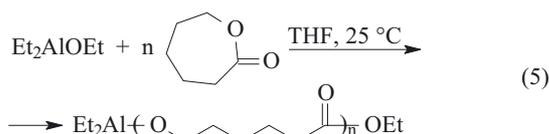
Reacting mixtures were prepared using standard high vacuum technique and kept eventually in the sealed NMR tubes. ²⁷Al NMR spectra were recorded in C₆D₆ (10 vol-%)/THF (90 vol-%) mixtures on a "Bruker DSX 300" operating at 78.17 MHz with regard to ²⁷Al nuclei. Al(acac)₃ was used as an external standard (δ = 0 ppm).

RESULTS AND DISCUSSION

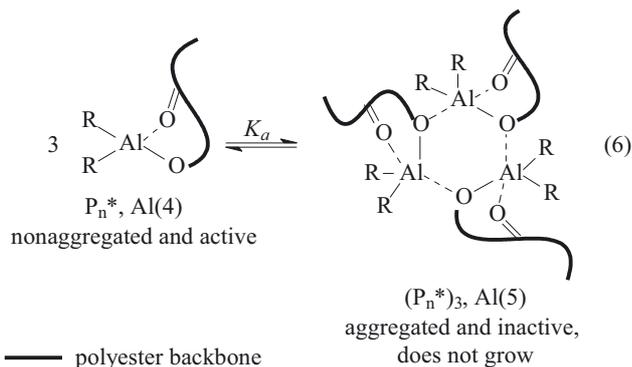
R₂AlOR'/ε-Caprolactone (CL) system

Dialkylaluminum alkoxide/CL system provides one of the first examples of the fully controlled, living ROP polymerization of cyclic esters [35, 43]. This process, in the properly chosen conditions, is devoid of termination and transfer. Polymerization degree of the resulting polyester (*DP*_n) is controlled by the [monomer]₀/[initiator]₀ ratio and the tail end-group is directly derived from the initiator alkoxide ligand, for example — eq. 5.

Another characteristic feature of the R₂AlOR'/CL polymerization is aggregation of initiators and active species [36, 37]. For example, Et₂AlOEt assumes a form



of the cyclic trimer $(\text{Et}_2\text{AlOEt})_3$ containing exclusively Al(4) atoms (Fig. 5a). On the other hand, kinetic studies of CL polymerization, suggested that propagation proceeds on the unimeric (P_n^*) species, being in equilibrium with the otherwise unreactive trimers $[(\text{P}_n^*)_3]$:



^{27}Al NMR spectrum of the corresponding reaction mixture (Fig. 5b) shows presence of the Al(4) atoms in P_n^* and the Al(5) atoms in $(\text{P}_n^*)_3$. In both P_n^* and $(\text{P}_n^*)_3$

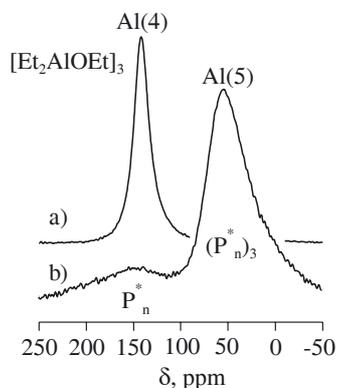


Fig. 5. ^{27}Al NMR spectra of $(\text{Et}_2\text{AlOEt})_3$ initiator (a) and polymerizing mixture $(\text{Et}_2\text{AlOEt})_3/\epsilon\text{-caprolactone}$ (CL) (b); $[\text{CL}]_0 = 2 \text{ mol} \cdot \text{L}^{-1}$, $[\text{Al}]_0 = 0.1 \text{ mol} \cdot \text{L}^{-1}$, 70°C

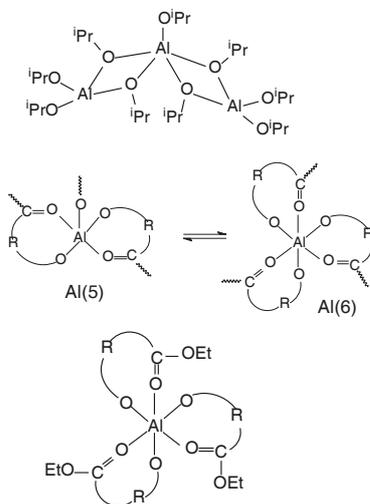
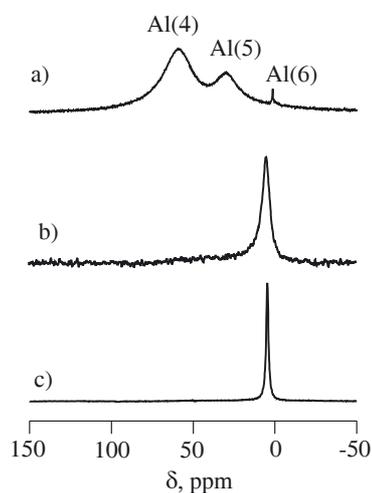
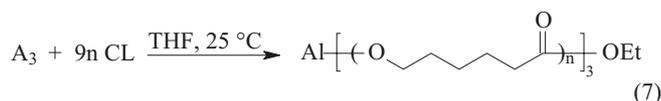


Fig. 6. ^{27}Al NMR spectra of A_3 initiator [small Al(6) peak comes from $\approx 2 \text{ mol}\%$ admixture of A_4] (a), polymerizing mixture A_3/CL (b), and aluminum tris(ethyl hexanoate-6-alkoxylate) (c); $R = (\text{CH}_2)_5$ (c), $[\text{CL}]_0 = 2 \text{ mol} \cdot \text{L}^{-1}$, $[\text{Al}]_0 = 0.1 \text{ mol} \cdot \text{L}^{-1}$, 70°C

species additional coordination by the acyl oxygen atoms is assumed (Eq. 6) in order to account the observed cn 's. The concentration of the Al(4) propagating species, determined from the spectrum in Fig. 5b, is equal to $\approx 10 \text{ mol}\%$ of the total (i.e. of $[\text{P}_n^* + 3(\text{P}_n^*)_3]$) and is close to that determined from kinetic measurements [36].

$\text{Al}(\text{O}^i\text{Pr})_3/\text{CL}$ system

In the ROP of cyclic esters initiated with $\text{Al}(\text{O}^i\text{Pr})_3$ a difference of reactivities between the $\text{Al}(\text{O}^i\text{Pr})_3$ trimer (A_3) and tetramer (A_4) has to be taken into account [25, 38, 39]. For example, A_3 has been shown to be 10^3 times more reactive in CL polymerization comparing to A_4 . Moreover, initiation with A_4 results in a minute A_4 consumption (0.1 mol-%) before the CL monomer is quantitatively consumed. Therefore, only the A_3 initiated polymerization can be considered as the fully controlled process:



Initially, presence of Al(4) and Al(6)- type growing Al-alkoxide species has been assumed on the basis of the ^{27}Al NMR spectra analysis of the reaction mixtures containing the unreacted A_4 [24, 25]. More recent measurements, under the polymerization conditions that allow complete consumption of the much less reactive A_4 , revealed absence of the Al(4) species. Fig. 6 shows that during CL polymerization A_3 transforms quantitatively into the unimeric Al tris-poly(CL) macroalkoxide species. In a majority of the resulting species Al atoms assume the hexacoordinate form [Al(6)], but the presence of a lower field tail absorption suggests that a certain fraction of the alkoxide species assume the Al(5) form (Fig. 6b). Sharp single peak in the spectrum of aluminum tris(ethyl hexanoate-6-alkoxylate), that serves as a

model of the Al-trialkoxide species, points to its perfectly hexacoordinate structure (Fig. 6c).

Most probably, the Al(6)-alkoxides are the dormant, temporary not growing species, whereas propagation proceeds on the much more reactive Al(5)-alkoxides (cf. comparison of A₃ and A₄ reactivities above).

Et₂AlOEt/(S)-(+)-2,2'-[1,1'-binaphthyl-2,2'-diylbis-(nitrilmethylidene)diphenol [SB(OH)₂]/(S,S)-lactide (LA) system

Recently, application of the Al(OⁱPr)₃/SB(OH)₂ mixtures for the stereocontrolled polymerization of racemic LA allowed synthesis of the poly[(S,S)-LA-grad-(R,R)-LA] stereocopolymer [40] (*grad* = gradient). In the present paper we report results obtained for the Et₂AlOEt/SB(OH)₂/LA polymerization — eq. 8.

There are no systematic ²⁷Al NMR data available for SBO₂Al-OR species allowing to correlate chemical shift and Al atom coordination number. Benn and Rufinska

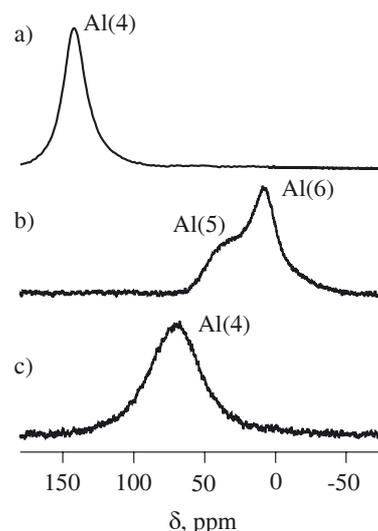
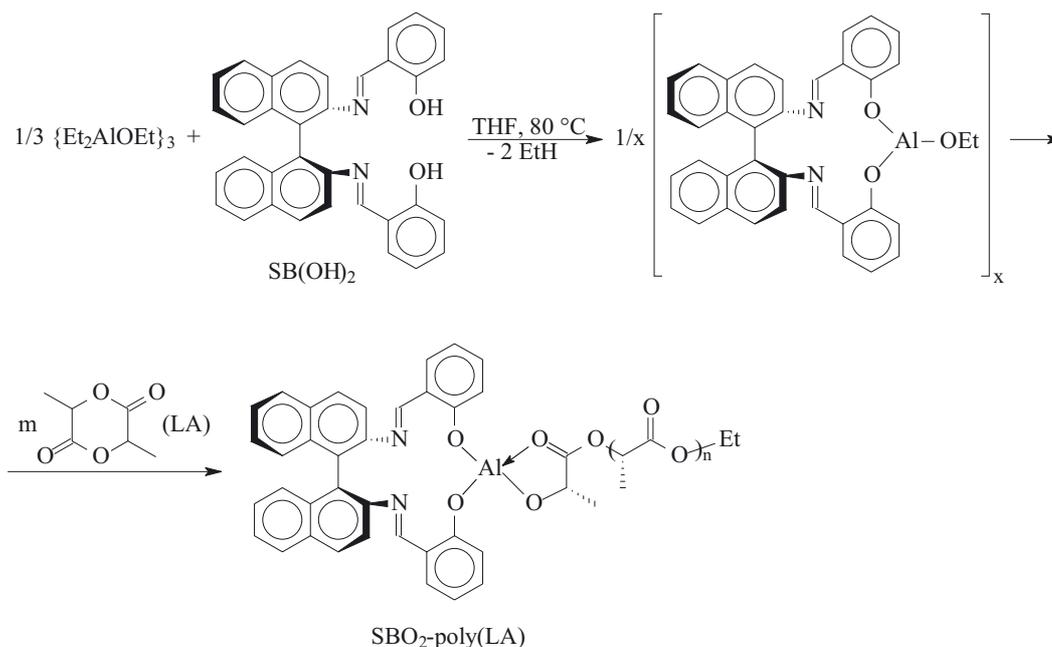


Fig. 7. ²⁷Al NMR spectra of: a) — (Et₂AlOEt)₃, b) — (Et₂AlOEt)₃/SB(OH)₂ mixture reacted 24 h at 80 °C, c) — SBO₂AlOEt/(S,S)-lactide (LA) polymerizing mixture; [Al]₀ = [SB(OH)₂]₀ = 0.1 mol · L⁻¹, [LA]₀ = 1.8 mol · L⁻¹, 70 °C



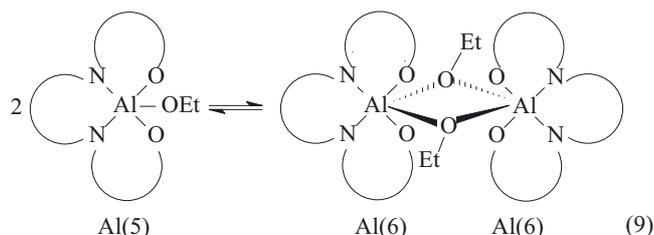
(8)

reported chemical shifts only for AlR₃, R₂AlOR, and Al(acac)₃ [20]. Atwood and Harvey completed chemical shifts for pentacoordinate salen Al complexes (δ = 40–57 ppm) [44]. More recently, Zhong *et al.* reported δ = 35.45 ppm for the Jacobsen ligand-Al-OR derivative [45]. ²⁷Al NMR chemical shifts for Al(OR)₃ can be found in Ref. [33, 44]. Since SBO₂Al-OR species are structurally closer to Al(OR)₃ than to R₂AlOR', these data suggest the following correlation: tetracoordinate aluminum *tris*-alkoxides absorb at δ ≈ 60–70 ppm, pentacoordinate at δ ≈ 40 ppm, and hexacoordinate at δ ≈ 0 ppm. Thus, δ = 35.45 for the pentacoordinate Jacobsen ligand-Al-OR derivative reported by Zhong *et al.* [45] is in agreement with this correlation.

Finally, on the basis of our measurements (Fig. 7) and the existing spectroscopic data we propose that Al atoms in SBO₂Al-poly(LA) active centers are tetracoordinate due to an intramolecular coordination by the oxygen atom from the acyl group of the poly(LA) chain.

However, in the (Et₂AlOEt)₃/SB(OH)₂ mixture (in the absence of the LA monomer) Al(5) and Al(6) species prevail. This observation can, perhaps, be explained by a dynamic equilibrium between unimeric and dimeric structures shifted slightly into the dimer side, schematically — eq. 9.

With the polymerization progress ethoxide substituent is transformed into the high molar mass poly(LA) chain and the equilibrium (9) shifts into the unimer side.



Eventually, intramolecular coordination by the oxygen atom from the acyl group from the ultimate repeating unit of the poly(LA) chain destabilizes the Al(5) structure.

Similar series of measurements carried out for the Al(OⁱPr)₃/SB(OH)₂/LA system revealed identical structure of active species bearing exclusively Al(4) atoms [40].

CONCLUSIONS

The major applications of ²⁷Al NMR spectroscopy in the area of polymer chemistry are related to the studies of the ring-opening polymerization mechanisms [12, 23–28]. Some limitations of this analytical tool are related to: quadrupolar character of the ²⁷Al nucleus that results in NMR lines broadening, extraneous probe head signal, and base-line rolling. These adverse effects can at least partially be eliminated by recording the spectra at higher concentrations of the organoaluminum species ($\geq 0.1 \text{ mol} \cdot \text{L}^{-1}$) and at elevated temperatures ($\geq 50 \text{ }^\circ\text{C}$). There are almost no reports on studies of the unsaturated monomers studies by ²⁷Al NMR, most probably because of the above mentioned limitations. However, the solid-state ²⁷Al NMR measurements allowed determination of the methylaluminumoxanes (MAO) structures [29], which is important for the development of new generation catalysts for polyolefin synthesis. In the present paper particularly rewording were the direct observations of active centers structure in cyclic aliphatic esters polymerizations, obtained by ²⁷Al NMR spectroscopy.

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