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ARTICLE TYPE

Aluminum complexes based on pyridine substituted alcohols: synthesis, structure, catalytic application in ROP

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A series of substituted pyridine dialcohols (2,6-bis(hydroxyalkyl)pyridines), **1**-**4**, was used for the synthesis of various types of aluminum complexes. Aluminum methyl derivatives, **2**-**4a**, were obtained by reaction of $AlMe_3$ with corresponding ligand or transmetallation reactions of germylenes. Aluminum chloride complexes, **3**-**4b**, were obtained by substitution of Me group under action of chlorinating agents. Methoxy-, **2**-**4c**, or benzyloxy-, **2d**, aluminum complexes were synthesized in transalkoxylation reaction of $Me_2Al(OX)$ (X = Me, Bn) by corresponding ligand. All complexes obtained were thoroughly investigated by multinuclear NMR and X-ray analysis. It is established that the structure of ligand (number of carbon atoms) determines the nature of the complexes formed. Compounds were used as initiators of ring-opening polymerization of *L*-lactide and ε-caprolactone and showed moderate activity with controlled or immortal character.

Introduction

In recent years compounds derived from renewable resources have been involved in industry priority processes.[1] Creation of materials that are readily degradable in the environment is another important trend.[2] Classic examples of such materials are biodegradable polymers of cyclic esters such as polylactide (PL), polyglycolide (PG), poly-ε-caprolactone (PCL) and their copolymers. Synthesis of biodegradable polymers of this type is performed via ring-opening polymerization (ROP) of cyclic esters. Polymerization, initiated by organic compounds[3] or metal complexes, allows process to be high-controlled, leading to materials with the desired structure, stereochemistry, molecular weight distribution. The properties of the polymer strongly depend on the initiator that is used. There are a lot of metals (alkali earth, Al, Zn, Ti, Zr, Sn, lanthanides) that have been employed in ROP as well as ligands.[4-7] Aluminum complexes (in general, phenoxide type) attract researcher's attention due to low cost, high control of ROP and possibility to investigate the polymerization process.[8-21]

It is established that ligand strongly influences the catalytic activity of the complex. Thus it is important for systematic investigation of "structure of complex : catalytic activity" correlation to use ligands closely related in structure because the small changes in structure can cause crucial changes in catalytic activity. Pyridine-containing dialcohols (ONO type ligands) are of great interest because of their special steric and electronic properties. This promising ligand platform was used to stabilize low-valent species such as Sn (II) and Ge (II)[22] as well as for synthesis of complexes of Sn (IV),[23] Cr,[24] V,[24, 25] Si,[26] Ti,[27, 28] Zr,[29] Mo[30] and some others. Yet, to the best of our knowledge, there are neither reports concerning the use of pyridine-containing dialcohols in ROP nor aluminum complexes based on such ligands in the literature. According to the literature aluminum complexes based on other ONO-type ligands are limited by few examples.[31-35] Such complexes based on tridentate ligands have found their application in catalysis in the number of processes. As far as pyridine-diols are concerned, the main attention was paid to the ligands containing bulky substituents at carbon atoms of the alkoxy group. It is obvious that the presence of such substituents in the complex molecule can stabilize nonpolymeric or nonoligomeric structure which is important if the "single-site catalyst" concept is considered. Herein we report the synthesis, structural characterization of series of novel aluminum complexes based on 2,6-bis(hydroxyalkyl)pyridines and their application in the ring-opening polymerization of *L*-lactide and ε-caprolactone. We managed to reveal the dependence of the structure of the aluminum complexes on the structure of the pyridine-containing dialcohols.

Results and Discussion

Ligands. In the course of this work the ligands of three types containing 0, 1 or 2 carbon atoms between pyridine and C(OH) parts of the ligand were used for synthesis of aluminum complexes. Compounds **1**,[23] **2**,[36] **3**[37] (Chart 1) have been synthesized previously and unsymmetrical compound **4** is a novel substance (Scheme 1).

Compound **4** was prepared through the monolithiation of Me group by the treatment with 2 equivalents of *n*-BuLi with subsequent reaction with 2,2-diphenyloxirane (Scheme 1).

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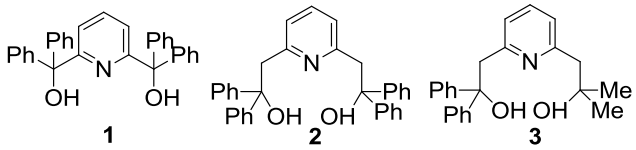
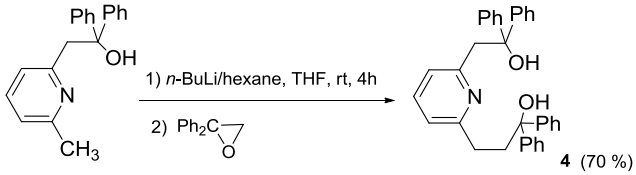


Chart 1. Ligands **1**, **2**, **3**.



Scheme 1. Synthesis of ligand **4**.

In addition, single crystals of ligand **4** were grown from a saturated solution in toluene and the structure was investigated by X-ray analysis (Fig. 1, Table 1). It should be noted that to date there are only three other molecular structures of pyridine dialcohols derived from 2,6-lutidine which have been investigated by X-ray crystallography.[38-40] The solid state structure clearly shows the intramolecular H-bond interactions between the pyridine *N*-atom and hydroxylic hydrogen. This H-bond may be regarded as mostly electrostatic and "moderate" in terms of strength.[41] It should be noted that **4** represents the rare example of the molecule without chiral centers crystallizing in Sohncke space group *P*1.

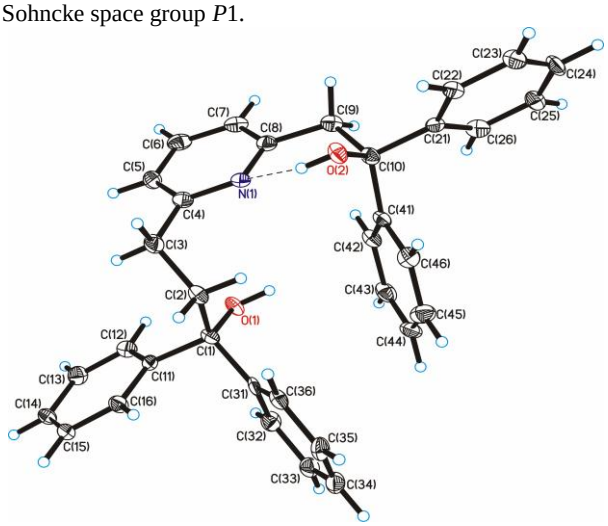
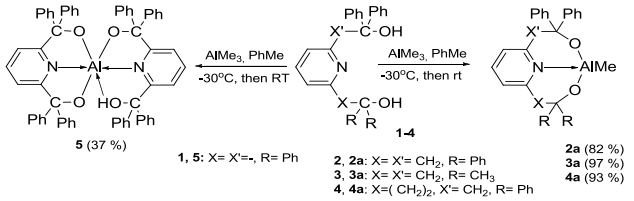


Fig. 1 Molecular structure of **4**. Displacement ellipsoids are shown at 50 % probability level. Selected interatomic distances [Å] and angles [°]: O(1)-H(1) 0.88(5), O(2)-H(2) 0.85(5), H(2)...N(1) 1.94(5), O(2)...N(1) 2.715(4), O(2)-H(2)...N(1) 151(4).

Methyl aluminum complexes based on 2,6-bis(hydroxyalkyl)pyridines. The methyl aluminum complexes **2a**, **3a**, **4a** were obtained by the treatment of the ligands **2**-**4** with one molar equivalent of $AlMe_3$ at -30°C (Scheme 2) in order to avoid undesirable side-reactions (such as fast reaction of $AlMe_3$ with several ligand molecules). The yields of the target compounds are high (82 - 97 %). In contrast to the abovementioned ligands, reaction of ligand **1** in similar conditions (one or two equivalents of $AlMe_3$) afforded the mixture of compounds from which the unusual complex **5** was isolated. All the aluminum complexes discussed herein have been characterized by elemental analysis, ^{1}H and ^{13}C NMR spectroscopy.



Scheme 2. Synthesis of **2a**, **3a**, **4a** and **5**.

The complexes under discussion were isolated as white powders soluble in THF, toluene, chlorinated solvents and insoluble in hexane and ether. Compounds **2a**, **3a**, **4a** are moisture- and air-sensitive.

In ^{1}H NMR spectra the protons of CH_2-groups became diastereotopic because of strong N→Al interaction. The corresponding phenyl and/or methyl groups (according to ^{13}C NMR) at each hydroxyalkyl group are diastereotopic, too.

It should be noted that the ^{13}C NMR spectra of **2a**, **3a**, **4a** contain only one set of signals corresponding to ligand framework ($CDCl_3$ solution). This fact may be related to both the monomer structure of aluminum complexes and possible equilibrium between monomeric and dimeric structures. In the case of equilibrium it's rapid in the NMR time scale. We recorded the NMR spectrum of **3a** in $CDCl_3$-DMSO-d6 mixture (dropwise addition of DMSO-d6 to the solution of **3a** in $CDCl_3$; see Supporting Information) and two species were found in the solution. It may be attributed as the complex of **3a** with DMSO-d6 formed. The nature of second species (monomeric and dimeric) is still in question. In order to clarify the structure we carried out DOSY NMR experiment[42-44] for **3a** to determine the molecular mass of **3a** in DMSO-d6 solution. Two species were detected in this spectrum (see Supplementary materials), too. Further calculations according to the equation that relates the molecular weight and the diffusion coefficient (see for details Supplementary materials) gave the molecular weights for these species: M= 820 Da (D= $1.74*10^{-10}$ m^2/s), M= 497.1 Da (D= $2.19*10^{-10} m^2/s$) which is in good correlation with molecular weight for dimeric **3a** (774.9 Da) and monomeric complex **3a** with additional DMSO-d6 ligand (**3a***DMSO-d6, 465.6 Da). Thus, one can conclude that there is monomer-dimer equilibrium in the solution (both DMSO and chloroform) of the methyl derivative **3a**.

Furthermore, based on this fact it may be proposed that **3a**, **4a** have the similar behavior in solution (C_S symmetric structure at room temperature on the NMR time scale).

For structure investigation of the aluminum complexes in solution one of the most useful tools is the ^{27}Al NMR spectroscopy. Due to technical reasons, it is not always possible to register spectra of complexes, so every result is very important. The ^{27}Al NMR ($CDCl_3$) spectra were obtained for compounds **2a** (δ= 40 ppm) and **4a** (δ= 90 ppm). According to these data it may be confirmed that methylaluminum complexes based on pyridine containing dialcohols are dimeric or at least take part in the equilibrium process monomer-dimer in solution (for four-coordinate Al alkoxides δ= ~70 ppm; for five-coordinate Al alkoxides δ= ~40 ppm; for six-coordinate Al alkoxides δ= ~0 ppm).[45-53] It should be noted, that crystal structure (X-ray data; see below) of **3a** was studied; this derivative formed dimer with five-coordinate Al atoms due to bridging CH_2CZ_2O-groups, what is in correlation with NMR data.

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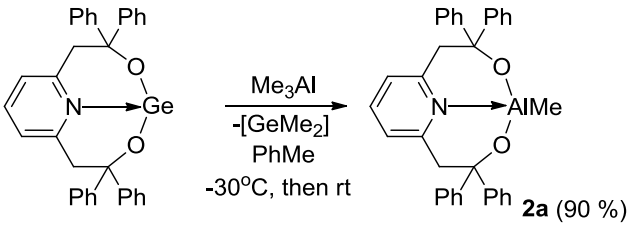
Table 1 Crystallographic and data collection parameters for **4, 3a**, **4c** and **5**

Compound	**4**	**3a**	**4c**	**5**
Formula	$C_{34}H_{31}NO_2$	$C_{48}H_{52}Al_2N_2O_4$•C_7H_8	$C_{70}H_{64}Al_2N_2O_6$•2(C_7H_8)	$C_{62}H_{47}AlN_2O_4$•2($CHCl_3$)
Formula weight	485.60	867.01	1267.46	1149.73
Crystal size /mm^3	0.21×0.20×0.11	0.24×0.04×0.02	0.25×0.20×0.15	0.13×0.10×0.08
Crystal system	triclinic	monoclinic	monoclinic	triclinic
Space group	*P*1	*C*2/c	$P2_1$/c	*P*-1
Z	1	4	2	2
a /Å	5.8707(13)	21.108(7)	10.4452(19)	13.2405(6)
b /Å	9.289(2)	14.946(5)	18.143(3)	13.2544(6)
c /Å	11.820(3)	19.243(6)	18.099(3)	16.8269(8)
α /°	103.040(3)	90	90	98.855(4)
β /°	92.480(3)	130.425(4)	97.931(3)	106.372(4)
γ /°	99.805(3)	90	90	95.552(4)
Volume /Å^3	616.5(2)	4621(3)	3397.0(11)	2768.8(2)
$D_{calcd.}$ /mg m^{-3}	1.308	1.246	1.239	1.379
T /K	120(2)	173(2)	150(2)	296(2)
μ /mm^{-1}	0.080	0.112	0.101	3.396
Total reflections	5649	14589	21052	9770
Unique data (R_{int})	2673 (0.0507)	4166 (0.0727)	5959 (0.0752)	8457 (0.0808)
Data/restraints/parameters	2673/3/340	4166/0/285	5959/7/396	8457/72/684
θ (^{0})	2.29 to 27.00	2.24 to 25.25	2.25 to 25.05	2.79 to 62.49
GoF on F^2	1.051	0.968	1.035	1.045
final *R* indices	R_1 = 0.0483,	R_1 = 0.0474,	R_1 = 0.0817,	R_1 = 0.0901,
($I > 2\sigma(I)$)	wR_2 = 0.0962	wR_2 = 0.0915	wR_2 = 0.2206	wR_2 = 0.1927
R indices (all data)	R_1 = 0.0759,	R_1 = 0.0972,	R_1 = 0.1266,	R_1 = 0.2187,
	wR_2 = 0.1068	wR_2 = 0.1028	wR_2 = 0.2494	wR_2 = 0.2522
largest diff. peak hole (e/Å^3)	0.224 / -0.286	0.260 / -0.280	0.482/ -0.375	0.581 / -0.722

It should be noted that methylaluminum complexes of this type may be obtained in high yields by transmetallation reaction[54-56] from corresponding germylenes. For the compound **2a** this method is preferable not only because of the higher yield of the product (90 *vs.* 82 %) but also because of the higher purity of the product (Scheme 3).



Scheme 3. Synthesis of **2a** from germylene.

To date there are no aluminum complexes based on pyridine containing alcohols investigated by X-ray analysis. Several related structures presented on Chart 2.[57-60]

At the same time it should be noted that alkyl Al complexes based on aminobis(phenolate) ONO ligands (Chart 3) are monomeric with tetrahedral aluminum atom.[32, 61] Furthermore, under comparison of structural features of four-coordinate (Chart 3) and five-coordinate Al complexes (for example, **3a**, Fig. 2) it may be concluded that increasing the coordination number results in elongation of bond lengths[31, 32, 62] (compare *d*(Al-C) 1.977 *vs.* 1.91-1.96 Å, *d*(Al-N) 2.185 *vs.* 1.98- 2.10 Å, *d*(Al-O) 1.759 *vs.* 1.71- 1.75 Å).

The molecular structures of complexes **3a** and **5** were investigated in the solid state by X-ray analysis (Figs. 2, 3; Table 1).

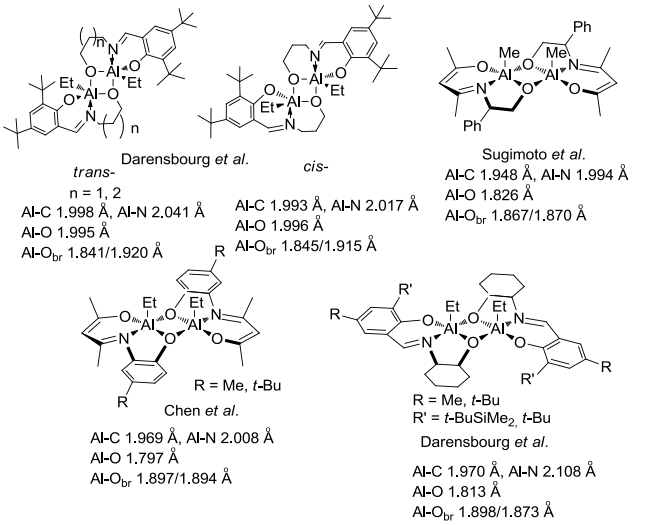
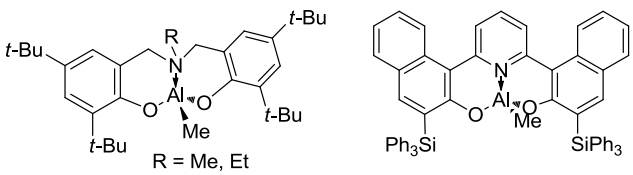


Chart 2. Molecular structures of dimeric alkyl aluminum complexes



containing ONO ligands.

Chart 3. Molecular structures of monomeric alkyl aluminum complexes containing ONO ligands.

In crystal, the molecule **3a** lies on 2-fold axis. The aluminum atom in **3a** is five-coordinate, this compound in solid state is dimeric where the almost planar Al_2O_2 cycle was formed. The dimerization is caused by bridging $OCMe_2$ group (the least

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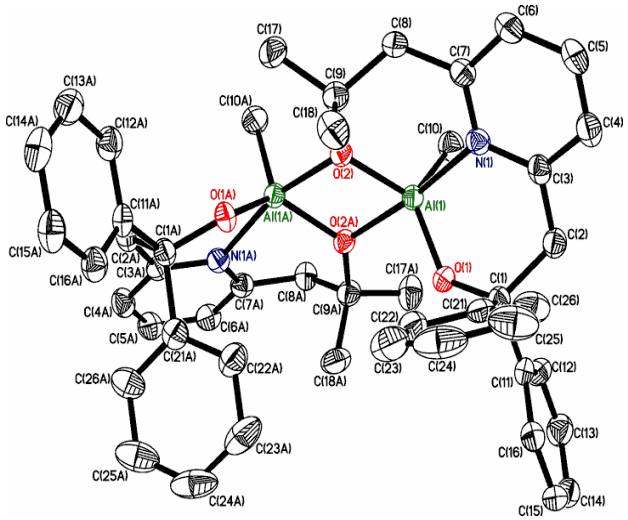
sterically hindered near oxygen atom) from another unit. In this compound the two methyl groups at the neighboring aluminum atoms are situated in *cis* position in relation to Al_2O_2 cycle and the possible diastereomeric complex (*trans*-isomer) was not formed even in solution (according to NMR spectroscopy data). The ligands in **3a** are arranged in a distorted trigonal bipyramidal geometry (trigonal index (τ) 0.69) around the aluminum centre with nitrogen and coordinating oxygen atoms in axial positions (O(2A)-Al(1)-N(1) 166.13(8)°). The equatorial positions are occupied by two oxygen atoms of the 2,6-bis(alkyloxy)pyridine ligand and the bridging alkoxide oxygen atom from the neighboring ligand. The length of N→Al bond (2.1850(19) Å) is expectedly longer than in related dimeric phenolic compounds (compare with Chart 2 with imine N) because of the strong intermolecular O(2A)→Al(1) interaction in **3a**. The covalent bond length Al-O(1) in **3a** (based on alkyl alcohol) is somewhat



shorter than the related one in phenolic derivatives (Chart 2).

Fig. 2 Molecular structure of complex **3a**. Displacement ellipsoids are shown at 50 % probability level. Hydrogen atoms and solvated toluene molecule are omitted for clarity. Selected interatomic distances [Å] and angles [°]: Al(1)-O(1) 1.7594(16), Al(1)-O(2) 1.8272(17), Al(1)-O(2A) 1.9413(15), Al(1)-C(10) 1.977(2), Al(1)-N(1) 2.1850(19); O(1)-Al(1)-O(2) 124.67(8), O(1)-Al(1)-C(10) 121.94(10), O(2)-Al(1)-C(10) 113.39(9).

Other parameters are very similar. The both chelate six-membered Al-O-C-C-C-N rings are in half-chair conformation with C (CH_2 group) and N atoms as flaps.

The coordination number of aluminum atom in **5** is six and aluminum atom has distorted octahedral geometry with *trans*-disposition of two nitrogens of different ligand frameworks and oxygen atoms of one ligand (*mer*-disposition). It should be noted that the coordination bond Al←OH is the longest aluminum-oxygen bond in this compound, and in solution it dissociates (according to ^{13}C NMR spectra). The *d*(Al-O(2)) situated *trans* to the bond mentioned above is the shortest. Besides, the bonds Al-N in **5** are shorter than the similar in **3a**, due to a greater number of acceptor substituents in **5**.

It should be noted that the hexacoordinated aluminum complexes based on ONO ligands are very rare. To date there is only one structure based on pyridine-2,6-dicarboxylic acid.[63]

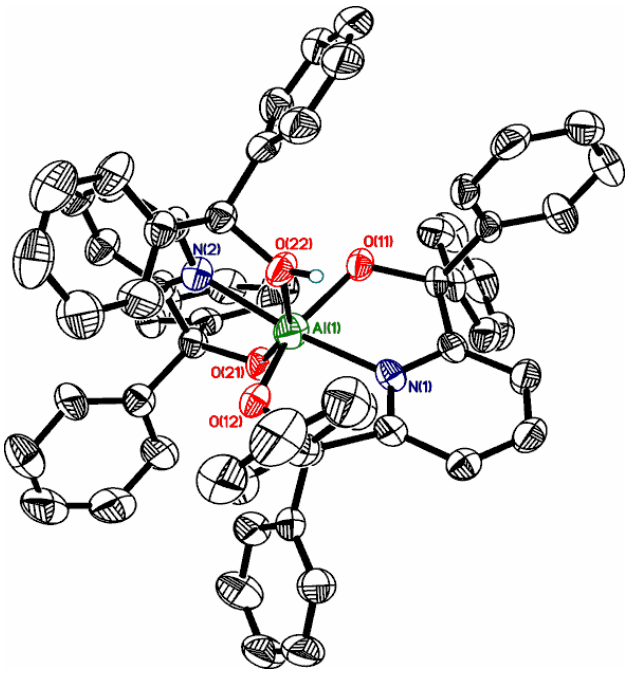
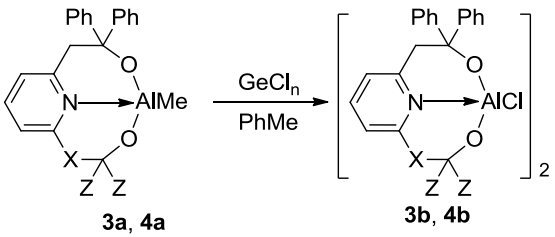


Fig. 3 Molecular structure of complex **5**. Displacement ellipsoids are shown at 30 % probability level. Hydrogen atoms (except hydroxyl H1) are omitted for clarity. Selected interatomic distances [Å] and angles [°]: Al(1)-O(21) 1.754(5), Al(1)-O(12) 1.920(6), Al(1)-O(11) 1.929(6), Al(1)-O(22) 2.177(5), Al(1)-N(1) 1.983(6), Al(1)-N(2) 2.013(6); O(12)-Al(1)-O(11) 155.5(2), O(12)-Al(1)-N(1) 79.5(2), O(11)-Al(1)-N(1) 80.7(2), N(1)-Al(1)-N(2) 169.3(3), O(21)-Al(1)-O(22) 155.4(2).

Chemical properties of methyl aluminum complexes based on 2,6-bis(hydroxyalkyl)pyridines. The aluminum complexes based on 2,6-bis(hydroxyalkyl)pyridines containing chlorine atoms were obtained by treatment of corresponding methyl aluminum derivatives with germanium chlorides, $GeCl_4$ and $GeCl_2$·dioxane (Scheme 4). It is more effective when germylene compound is used in this reaction, possibly due to lower acidity.

The complexes **3b**, **4b** were isolated as white moisture-sensitive powders soluble in chlorinated solvents and toluene. The structures of compounds **3b**, **4b** were investigated by NMR spectroscopy and composition was established based on elemental analysis. There are only one set of signals in spectra and the dimeric structure with bridge $OCPh_2$ group may be proposed for these compounds.[52]



3a, **4a** **3b**, **4b**

3a, **3b**: X= CH_2, Z= CH_3, $GeCl_n$= $GeCl_4$ (41 %)

3a, **3b**: X= CH_2, Z= CH_3, $GeCl_n$= $GeCl_2{\cdot}C_4H_8O_2$ (89 %)

4a, **4b**: X= $(CH_2)_2$, Z= Ph, $GeCl_n$= $GeCl_2{\cdot}C_4H_8O_2$ (91 %)

Scheme 4. Synthesis of aluminum complexes containing chlorine.

Alkoxy aluminum complexes based on 2,6-

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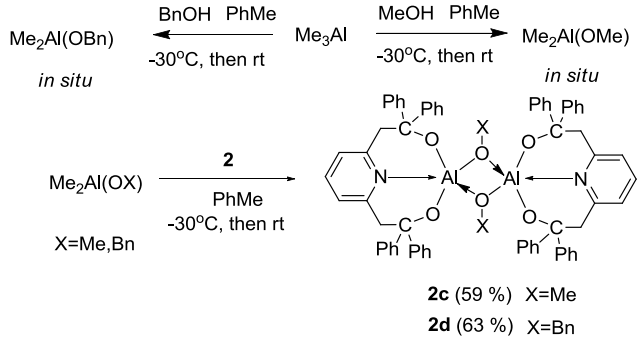
bis(hydroxyalkyl)pyridines. Synthesis of aluminum alkoxides stabilized by polydentate ligands is an actual synthetic problem. So in the course of this work we investigated the approaches to the methoxy aluminum complexes based on 2,6-bis(hydroxyalkyl)pyridines. We performed reactions of formed *in situ* $Me_2Al(OMe)$ with the ligand **2**. It was proposed that substitution of methyl groups at Al atom when treating with alcohols is more preferable. At the same time it should be noted that numerous attempts to substitute the methyl groups in complexes **2a**, **3a**, **4a** under action of various alcohols (MeOH, BnOH, $HO(CH_2)_4OCH=CH_2$) resulted in a mixture of compounds including formation of free ligand. Apparently the same situation is observed under polymerization in the presence of added co-initiator (see below).

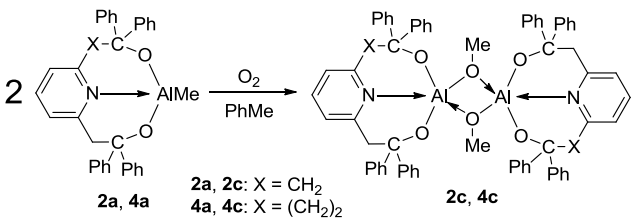
It was established that methoxy aluminum complex **2c** was formed in reaction of **2** with $Me_2Al(OMe)$ (Scheme 5). Reaction between $Me_2Al(OBn)$ and **2** allowed us to obtain aluminum complex bearing benzyloxy group at the aluminum atom (Scheme 5).



Scheme 5. Synthesis of aluminum complexes **2c**, **2d** from $Me_2Al(OAlk)$.

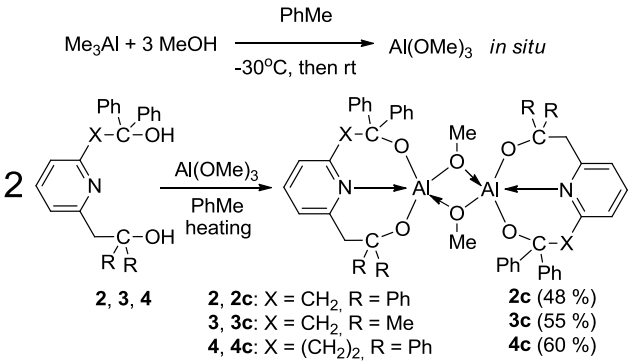
The formation of these two compounds was unambiguously proven by elemental analysis, ^1H and ^{13}C NMR spectroscopy and by the parallel synthesis (for **2c**).

Methoxy aluminum complexes based on 2,6-bis(hydroxyalkyl)pyridines were obtained by exposing corresponding methyl derivatives to dried air (oxidation) (Scheme 6). At the same time treatment of methyl derivative **4a** with methanol does not lead to methoxy derivative but yields the mixture of products (according to NMR) including the free ligand **4**.



Scheme 6. Synthesis of methoxy complexes **2c**, **4c** by action of air on methyl aluminum complexes.

The methoxy derivatives of aluminum based on 2,6-bis(hydroxyalkyl)pyridines were synthesized using free ligand and $(MeO)_3Al$ formed *in situ* (Scheme 7). It should be noted that in this case the transesterification reaction proceeds under more severe conditions than reactions mentioned above.



Scheme 7. Synthesis of methoxy aluminum complexes **2c**, **3c**, **4c** using $Al(OMe)_3$.

The alkoxy complexes were isolated as moisture-sensitive white solids soluble in $CHCl_3$, CH_2Cl_2, THF, PhMe. The structures of the obtained compounds were established by ^1H and ^{13}C NMR spectroscopy, elemental analysis, and in the case of compounds **2c** and **4c** by X-ray study (Figure 4 and Figure S4, Supporting Information). In the case of compound **2c** the quality of the crystals is not sufficient for precise X-ray experiment, but the connectivity of atoms has clearly been determined.

In the NMR spectra of the alkoxy complexes **2c**, **3c**, **2d** there is only one set of signals. The protons in CH_2 groups are diastereotopic. So we may conclude that in solution these derivatives exist as dimers with C_i symmetry similar to X-ray structures.

Unfortunately, the DOSY spectra of methoxy and chloro derivatives were not recorded due to bad solubility, but we believe that these derivatives are also dimeric due to additional bond formation between Al atom and methoxy (chloro) group of the second monomer unit.

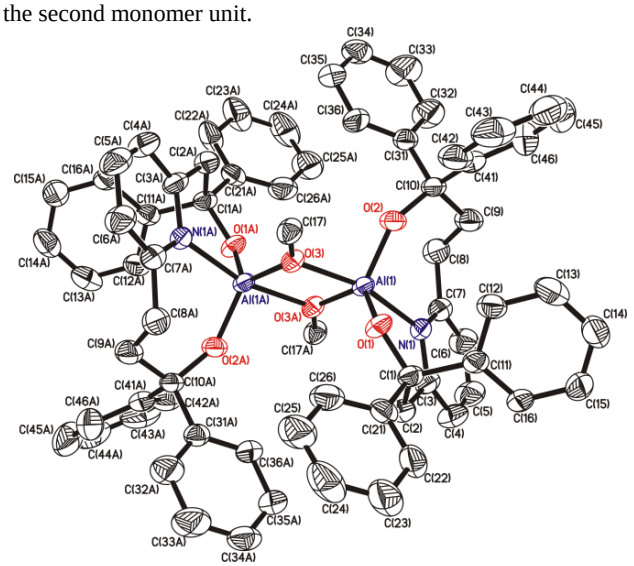


Fig. 4 Molecular structure of complex **4c**. Displacement ellipsoids are shown at 50 % probability level. Hydrogen atoms are omitted for clarity. Selected interatomic distances [Å] and angles [°]: Al(1)-O(1) 1.739(3), Al(1)-O(2) 1.732(3), Al(1)-O(3A) 1.823(3), Al(1)-O(3) 1.915(3), Al(1)-N(1) 2.100(3); O(1)-Al(1)-O(2) 113.24(16), O(1)-Al(1)-O(3A) 122.99(14), O(2)-Al(1)-O(3) 94.00(13), O(3A)-Al(1)-O(3) 75.69(13).

It should be noted that unlike the previously studied Al structures based on ONO ligands[58, 64] (Chart 4) the main feature

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of the aluminum alkoxides presented in this work is a dimerization through the methoxy groups (not through polydentate ligand).

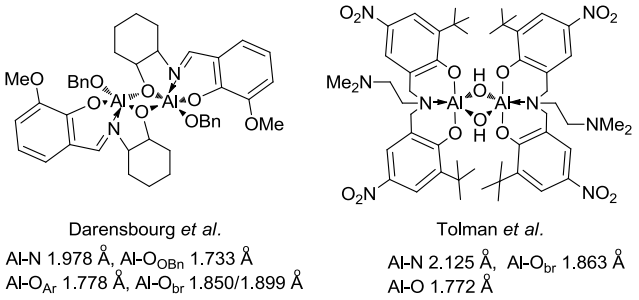


Chart 4. The molecular structures of dimeric alkoxide aluminum complexes based on ONO ligands investigated to date.

According to the X-ray diffraction analysis coordination number of aluminum atoms in **2c** and **4c** is five, the compounds being dimeric in the solid state. Dimerization occurs due to the formation of additional bond between the aluminum atom and the oxygen atom of the OMe group of the second monomeric unit (least sterically hindered oxygen atom), which results in the formation of flat Al_2O_2 cycle. The two Al–OMe distances within the ring are significantly different (Al–O_{eq} 1.823(3) and Al–O_{ax} 1.915(3) Å). This is a typical feature of five-coordinate dimeric aluminum alkoxides.[65, 66] The coordination polyhedron of the central atom in **4c** is distorted trigonal bipyramid (trigonal index (τ) is 0.82), with the coordinating nitrogen and oxygen atom of the MeO being in axial positions (O(3)-Al(1)-N(1) 161.76(13) °). The equatorial positions are occupied by two oxygen atoms of the 2,6-bis(dialkylalkoxy)pyridine ligand and the methoxide oxygen atom. Coordinating Al-N bond length in **4c** is 2.100(3) Å which is shorter than that in **3a** (2.1850(19) Å), due to the absence of the donor methyl group connected with aluminum atom. It should be noted that Al-N bond (2.100(3) Å) is somewhat longer than in related five-coordinate Al complexes containing Py→Al coordination (2.01-2.03 Å),[35, 61] based on phenolate ligands. Moreover, the Al(1)-O(1) and Al(1)-O(2) bonds formed by six- and seven-membered rings are almost equal. In general, the Al-O bond lengths in **4c** formed by alkyl alcohols (1.72-1.75 Å) are similar to found earlier for phenolate (1.72-1.82 Å)[17, 31, 61, 67-69] or alkylalkoxy derivatives (1.71-1.74 Å).[58, 70] The six-membered chelate ring Al-O(2)-C(10)-C(9)-C(8)-N is in half-chair conformation with C(9) and N atoms as flaps and seven-membered ring Al-O(1)-C(1)-C(2)-C(3)-C(4)-N is in twist-chair conformation with C(3) and N atoms as flaps.

It should be noted that molecule **4c** lies on crystallographic inversion centre, *i.e.* coordinating atoms of each of the two ligands are located in the *trans*-positions in relation to Al_2O_2 cycle (*trans*-isomer). However, according to the NMR data there are two sets of signals in solution which do not change their intensity if the solution is heated ($CDCl_3$, 50°C), that indicates the presence of two diastereomeric complexes: the abovementioned *trans*- and *cis*- isomer (Chart 5) which are stable and do not pass into the each other or into the monomer. Numerous attempts to crystallize the *cis*-isomer do not lead to the desired result.

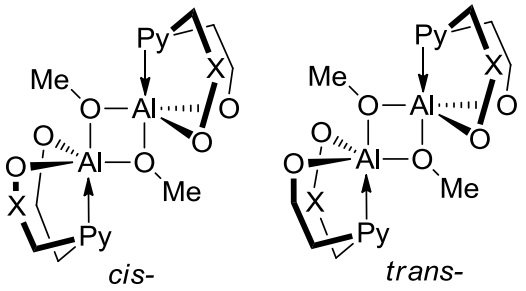
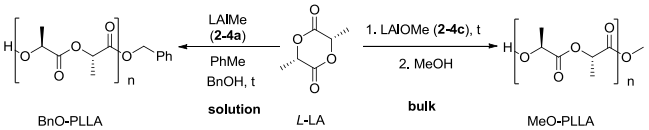
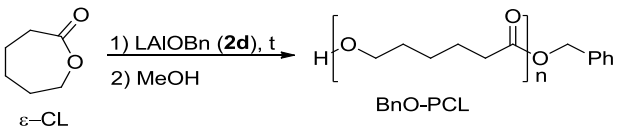


Chart 5. Schematic representation of *trans*- and *cis*- isomers for Al complex (**4c**) based on unsymmetrically substituted pyridine dialcohol.

Ring-opening polymerization. The aluminum complexes obtained were tested as initiators in the *L*-lactide polymerization under two different conditions: in toluene solution at 80 °C (for **2-4a**) in the presence of BnOH as an external nucleophile[71] and in bulk of the molten lactide at 100°C (for **2-4c**) (Scheme 8). Furthermore, polymerization of ε-caprolactone was studied in bulk, too (Scheme 9). The results of the catalytic tests are presented in Table 2.



Scheme 8. ROP of *L*-lactide promoted by complexes **2-4a** and **2-4c**.



Scheme 9. Polymerization of ε-caprolactone.

All substances under investigation turned out to be moderately active in polymerization. Practically full conversion of *L*-lactide is observed within 1-5 hours when polymerization was carried out in bulk molten lactide and 87-99% of conversion was observed within 27 h in toluene solution. Besides, the rate of polymerization increases with the decrease of the [cat]/[BnOH] ratio from 1:2 to 1:1 (full conversion for less than 7 h). This tuning of conditions is accompanied by increase in polydispersity (for example, entries 1 and 2, 4 and 5) and in molecular weight (entries 1 and 2, 6 and 7). It should be noted that all polymers have narrow polydispersity indexes (M_w/M_n= 1.1-1.4) what indicates that the process is controllable. In similar conditions the methyl and methoxy derivatives exhibit almost similar catalytic behavior in polymerization (compare M_n and PDIs).

Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry of PLAs at maximum conversion was conducted in order to define structure and composition of polymers at low monomer/initiator ratio. According to MALDI-TOF-MS data the sample obtained with **2a** as initiator (see Supporting Information, Fig. S5) is monodispersed which is in agreement with ^{1}H NMR spectrometry where the polymer is H- and BnO- end-capped (Fig. S6).

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Table 2. Ring-opening polymerization with **2-4a**, **2-4c** and **2d**.

entry	initiator	$[M]_0/[cat]_0/[BnOH]_0$	t, [h]	conversion, [%][g]	M_n[d] (theor), [g mol^{-1}]	M_n[e] (NMR), [g mol^{-1}]	M_n[f] (GPC), [g mol^{-1}]	M_w/M_n	N[h]
1[a]	**2a**	50/1/2	27	98	3640	4068	3100	1.25	1.2
2	**2a**	50/1/1	4	>99	7240	2572	4112	1.37	1.8
3	**2a**	100/1/10	20	>99	1540	2376	1856	1.19	0.8
4	**3a**	50/1/2	27	95	3530	3276	2300	1.11	1.5
5	**3a**	50/1/1	5	>99	7240	2703	4320	1.33	1.7
6	**4a**	50/1/2	27	87	3240	3276	2400	1.11	1.4
7	**4a**	50/1/1	7	>99	7240	5806	4373	1.35	1.7
8	**4a**	100/1/1	4	>99	14370	5272	4576	1.23	3.1
9[b]	**2c**	50/1/-	1	>99	7160	6296	4400	1.18	1.6
10	**2c**	200/1/-	4	>99	28550	7116	7930	1.22	3.6
11	**3c**	200/1/-	2	>99	28550	6038	8157	1.48	3.5
12	**4c**	50/1/-	1	>99	7160	5653	4698	1.38	1.5
13	**4c**	100/1/-	2	95	13710	5884	7070	1.34	1.9
14[c]	**2d**	300:1	0.5	>99	33960	16530	21168	3.24	1.6

[a]Polymerization of *L*-lactide in toluene solution, 80 °C, [cat]= 0.02 M. [b]Polymerization of *L*-lactide in bulk, 100 °C. [c]Polymerization of ε-caprolactone in bulk, 130 °C. [d]For solution polymerization: M_n(theor)= M_w(LA)×$[LA]_o/[BnOH]$×(conversion) + M_w(BnOH); for bulk polymerization: M_n(theor)= M_w(LA)×$[LA]_o/[cat]$×(conversion) + M_w(ROH) or M_n(theor)= M_w(CL)×$[CL]_o/[cat]$×(conversion) + M_w(ROH), R= Me or Bn. [e]Calculated using ^{1}H NMR spectra: M_n= $I(CH)_{PLLA}$×M_w(LA) + M_w(MeOH), M_n= $I(CH)_{PLLA}$×M_w(LA) + M_w(BnOH) or M_n= $I(\underline{CH_2}Ph)_{PCL}$×$M_w$(CL) + M_w(BnOH). [f]Calculated according to the equation M_n= 0.58×M_n(GPC) for polylactide and M_n= 0.56×M_n(GPC) for polycaprolactone. [g]Obtained from ^{1}H NMR spectroscopy of the crude reaction mixture. [h] Number of polymer chains per catalyst molecule, calculated as $N=M_n$(theor)/M_n(exp).

Thus, these results indicate the absence of side-reactions, which is intermolecular esterification. Analogous results are obtained with **3a** as initiator. In the case of initiation with complex **4a** side process of intermolecular esterification can be observed but at small extent. Polymerization in bulk with **2c** as initiator led to PLAs end-capped by MeO- (Fig. S7). MALDI-TOF-MS data was also consistent with ^{1}H NMR spectrometry data. There is also slight flow of transesterification reactions in this case.

It should be noted that no epimerization processes are observed. Homodecoupled ^{1}H NMR analyses[72] revealed that all PLAs are isotactic (Fig. S8).

At comparing the results obtained for polymerization in solution and in bulk it is established that at low monomer content (50:1:1 and 50:1) the polymer characteristics are similar (up to 4000 Da). The increasing the monomer content (to 100:1) results in molecular weight increasing only in the bulk polymerization.

By analyzing these data one can range initiators in accordance with their activity: **2a>3a>4a** (Fig.S9) and this row of activity is independent on the quantity of BnOH (1 or 2 equivalents).

Polymerization with **3a** and **4a** is linear (first-order dependence) (Figs. S10, S11). There is no induction polymerization period is observed which indicates the direct catalytic activity of the complexes. So the high control of polymerization is observed for low monomer content. Increasing the monomer content results in loss of control and intensive side reactions.

For methoxy derivatives the activity for all complexes studied is almost similar and there is no dependence on ligand structure. At the same time it is evident that increasing the monomer content results in increasing the PDI that is typical for intensive side reactions (intra- and intermolecular transesterification reaction) in these cases.

In the case of methyl aluminum complexes **2a**, **3a** the catalytic behavior is almost similar, but more sterically voluminous ligand in **4a** results in some decreasing of the polymerization rate (see entries 1, 4, 6). Increasing the monomer content results apparently in side processes.

The increasing of quantity of coinitiator added (alcohol) results in immortal character[73] of polymerization with proportional increasing of polymer chains (compare entries 1-3) and the molecular weight of the polymer decreases with the amount of BnOH. However, the molecular weight distribution remains narrow. In this case the type of polymerization is also highly controllable.

From Table 2 it is evident that at low monomer content alkoxy complexes **2-4c** initiate one polymer chain per initiator molecule (Table 2, lines 9, 12). On the basis of MALDI and NMR in this case the polymerization performed using only OMe group according to coordination-insertion mechanism of ROP.[5] Increasing the monomer content results in additional growth of chains (up to 3) what may be explained by using the ligand group of 2,6-bis(hydroxyalkyl)pyridine as initiators,[74] and such polymers (containing ligand fragments) may be identified by NMR (Figure S12, Supporting Information), but isolation of them

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is problematic possibly due to better solubility under isolation conditions. For methyl complexes the situation is similar (Table 2, lines 7, 8). Furthermore, in this case at equimolar quantity of coinitiator ([cat]/[BnOH]= 1/1) there are two polymer chains per initiator (Table 2, lines 2, 5, 7). It should be noted that increasing the quantity of added coinitiator results in decreasing the number of polymer chains (Table 2, lines 1, 3).

The ε-caprolactone polymerization proceeds in a rather harsh conditions very quickly (full conversion over 0.5 h; only one polymer chain per initiator molecule) but with poor controllable character (PDI is 3). These results are suggestive of intensive transesterification occurring during the polymerization process.

At the end it is necessary to compare the catalytic behavior of various aluminum compounds. Aluminum isopropoxide has low activity in polymerization of lactide (in case of *rac*-lactide conversion is 60%, PDI= 2.4).[75] It seems that aluminum complexes based on substituted pyridine dialcohols are more active and provide polymer with better characteristics. At the same time the phenolic ligands (related to presented on Chart 3) provide the more controllable character of lactones polymerization.

So it may be concluded that application of aluminum complexes based on substituted pyridine containing dialcohols results in moderately active *L*-lactide ROP (PDI is up to 1.48) with controlled or immortal polymerization type.

Experimental part

Experimental Details. All manipulations were performed under a dry, oxygen-free argon atmosphere using standard Schlenk techniques. Solvents were dried by standard methods and distilled prior to use: toluene, *n*-hexane were refluxed under Na and distilled; ether, THF were stored under KOH, refluxed under Na/benzophenone and then distilled; methanol was refluxed under Mg and then distilled off; benzyl alcohol was distilled under vacuum. *L*-Lactide was recrystallized from toluene and sublimed in vacuum, ε-caprolactone was distilled over CaH_2. Starting materials were synthesized according to the literature procedures: 2,2-diphenyloxirane,[76, 77] Py[2-(CH_3)-6-(CH_2CPh_2OH)],[36] Py[2,6-(CPh_2OH)$_2$] (**1**),[23] Py[2,6-(CH_2CPh_2OH)$_2$] (**2**),[36] Py[2-(CH_2CMe_2OH)-6-(CH_2CPh_2OH)] (**3**),[37] $GeCl_2{\cdot}C_4H_8O_2$,[78] Py(CH_2CPh_2O)$_2$Ge.[22] *n*-BuLi (2.5 M solution in hexane) (Aldrich), $AlMe_3$ (2.0 M solution in toluene) (Aldrich), $GeCl_4$ (Aldrich) were used as supplied. C_6D_6 (dried over sodium) and $CDCl_3$ (dried with CaH_2) obtained from Deutero GmbH. ^{1}H (400.13 MHz), ^{13}C (100.61 MHz) and ^{27}Al (104.26 MHz) NMR spectra were recorded on a Bruker Avance 400 or Agilent 400-MR spectrometers at room temperature (if otherwise stated). ^{1}H and ^{13}C chemical shifts are reported in ppm relative to Me_4Si as external standard; in ^{27}Al NMR experiments $Al(D_2O)_6^{3+}$ ($Al_2(SO_4)_3$ in D_2O) was used as an external standard. Elemental analyses were carried out by the Microanalytical Laboratory of the Chemistry Department of the Moscow State University. Gel permeation chromatography (GPC) was performed on high pressure liquid chromatograph equipped with a column system Styrogel HR 5E, HR 4E, 300h7, 8mm and refractometric detector. Tetrahydrofuran was used as the eluent, flow rate 1 ml/min. The concentration of the sample solutions was 1 mg/ml, injected sample volume of 100 μl. Calibration of the system was carried out on polystyrene standards. Study of PLA by mass spectrometry with ionization MALDI (Bruker Autoflex) performed at the Chemistry Department of Moscow State University.

Synthesis of ligands. 3-[6-(2-Hydroxy-2,2-diphenylethyl)pyridine-2-yl]-1,1-diphenylpropan-1-ol, Py[2–($CH_2CH_2CPh_2OH$)-6-(CH_2CPh_2OH)] (4). Solution of *n*-BuLi (2.5 M in hexane, 11.60 ml, 29.00 mmol) was added dropwise to solution of Py[2-(CH_3)-6-(CH_2CPh_2OH)] (4.00 g, 13.80 mmol) in THF (80 ml) at 0°C. The reaction mixture was slowly warmed to room temperature and stirred for 4 h. Then solution of 2,2'-diphenyloxirane (2.71 g, 13.80 mmol) in THF (10 ml) was added dropwise at room temperature to the reaction mixture. The mixture was stirred overnight. Then 2 N solution of NH_4Cl was added, organic phase was separated and water phase was extracted with CH_2Cl_2 (3x40 ml). The combined organic phases were washed with saturated solution of NaCl and dried over Na_2SO_4. All volatiles were removed under reduced pressure and the residue was recrystallized from CH_2Cl_2. Compound **4** (4.70 g, 70%) was isolated as a white powder, m.p. 123°C. ^{1}H NMR ($CDCl_3$, 25°C): δ = 2.51-2.58 (m, 2H, $CH_2CH_2CPh_2OH$); 2.62-2.67 (m, 2H, $CH_2CH_2CPh_2OH$); 3.69 (s, 2H, CH_2CPh_2OH); 6.72-6.77, 6.83-6.87, 7.06-7.12, 7.15-7.23, 7.27-7.32, 7.34-7.39, 7.44-7.48 (7m, 23H, Py and Ph) ppm. ^{13}C NMR ($CDCl_3$, 25°C): δ = 32.23 ($CH_2CH_2CPh_2OH$); 40.93 ($CH_2CH_2CPh_2OH$); 47.00 (CH_2CPh_2OH); 77.95, 78.55 ($2CPh_2$); 120.90, 121.73, 126.10, 126.21, 126.47, 126.85, 127.97, 128.19, 137.18, 146.84, 147.33, 158.54, 160.58 (Py and Ph) ppm. Anal. Calcd. for $C_{34}H_{31}NO_2$ (485.6155): C 84.09; H 6.43; N 2.88. Found: C 83.94, H 6.41, N 2.95%. Crystals suitable for X-ray analysis were obtained from concentrated toluene solution at –18°C.

Synthesis of complexes. Reaction of Py[2,6-(CPh_2OH)$_2$] (1) with Me_3Al. Synthesis of {Py[2,6-(CPh_2O)$_2$]}{Py[2-(CPh_2O)-6-(CPh_2OH)]}Al (5). At –30°C solution of trimethylaluminum (2.0 M in toluene, 0.25 ml, 0.50 mmol) was added dropwise to solution of Py(CPh_2OH)$_2$ (**1**) (0.22 g, 0.50 mmol) in toluene (15 ml). Reaction mixture was slowly warmed to room temperature and stirred overnight. Volatile materials were removed under reduced pressure and residue was recrystallized from toluene. Compound **5** (0.09 g, 37%) was isolated as a colorless crystals. ^{1}H NMR ($CDCl_3$, 25°C): δ = 6.56-6.65, 6.72-6.77, 6.79-6.85, 7.10-7.16, 7.20-7.27, 7.30-7.36, 7.40-7.43, 7.59-7.62, 7.79-7.81 (9m, 23H, Py and Ph); 7.86 (br s, 1H, OH) ppm. ^{13}C NMR ($CDCl_3$, 25°C): δ = 78.17, 78.22, 78.36 ($3CPh_2$); 122.21, 122.41, 122.71, 126.90, 127.04, 127.13, 127.22, 127.52, 127.68, 127.78, 127.95, 128.50, 128.80, 130.05, 131.47, 138.80, 139.09, 141.95, 143.74, 146.92, 148.38, 161.42, 164.34, 165.19 (Py and Ph) ppm. Anal. Calcd. for $C_{62}H_{47}AlN_2O_4$ (911.0292): C 81.74; H 5.20; N 3.07. Found: C 81.24, H 5.04, N 2.96%. Crystals suitable for X-ray analysis were obtained from concentrated toluene/chloroform solution at –18°C.

Py[2,6-(CH_2CPh_2O)$_2$]AlMe (2a). Method 1. At –30°C solution of trimethylaluminum (2.0 M in toluene, 1.15 ml, 2.29 mmol) was added dropwise to solution of Py[2,6-(CH_2CPh_2OH)$_2$] (**2**) (1.08 g, 2.29 mmol) in toluene (20 ml). Reaction mixture was slowly warmed to room temperature and stirred overnight. Volatile materials were removed under reduced pressure, residue washed with ether (3x5 ml) and dried in vacuum. Compound **2a**

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(0.96 g, 82%) was isolated as a white powder. **Method 2.** At –30°C solution of Py[2,6-(CH_2CPh_2OH)$_2$] (**2**) (0.24 g, 0.50 mmol) in toluene (20 ml) was added dropwise to solution of trimethylaluminum (2.0 M in toluene, 0.25 ml, 0.50 mmol) in toluene (20 ml). Reaction mixture was slowly warmed to room temperature and stirred overnight. Volatile materials were removed under reduced pressure, residue washed with ether (3x5 ml) and dried in vacuum. Compound **2a** (0.15 g, 59%) was isolated as a white powder. ^{1}H NMR ($CDCl_3$, 25°C): δ = -0.52 (s, 3H, $AlCH_3$); 3.60, 3.86 (2d, each 2H, ^2J = 14.4 Hz, CH_2); 6.93 (d, 2H, ^3J = 7.8 Hz, β-Py); 7.47 (t, 1H, ^3J = 7.8 Hz, γ-Py); 6.96–7.00, 7.27–7.33, 7.56–7.61 (3m, 20H, Ph) ppm. ^{13}C NMR ($CDCl_3$, 25°C): δ = -10.96 (br, AlMe); 48.60 (CH_2); 78.11 (CPh_2); 124.47, 125.81, 125.84, 126.39, 126.40, 127.49, 128.00, 140.80, 146.96, 150.40, 157.40 (Py and Ph) ppm. Anal. Calcd. for $C_{34}H_{30}AlNO_2$ (511.5891): C 81.74; H 5.20; N 3.07. Found: C 81.24, H 5.04, N 2.96%.

Reaction of Py(CH_2CPh_2O)$_2$Ge with Me_3Al, synthesis of Py(CH_2CPh_2O)$_2$AlMe (2a). At –30°C solution of $AlMe_3$ (2.0 M in toluene, 0.25 ml, 0.50 mmol) was added dropwise to solution of Py(CH_2CPh_2O)$_2$Ge (0.27 g, 0.50 mmol) in toluene (10 ml). Reaction mixture was slowly warmed to room temperature and stirred for 1 d. Volatile materials were removed under reduced pressure, residue was recrystallized from toluene. Compound **2a** (0.23 g, 90%) was isolated as a white crystals. Analytic characteristics are identical to the presented above.

Reaction of Py(CH_2CPh_2OH)$_2$ (2) with $Me_2Al(OMe)$, synthesis of Py[2,6-(CH_2CPh_2O)$_2$]AlOMe (2c). *a) Synthesis of $Me_2Al(OMe)$:* At –30°C MeOH (0.0875 ml, 1.70 mmol) was added to solution of trimethylaluminum (2.0 M in toluene, 0.85 ml, 1.70 mmol) in toluene (10 ml). Reaction mixture was slowly warmed to room temperature and stirred overnight. The obtained solution of $Me_2Al(OMe)$ was used further without additional purification.

b) Synthesis of Py[2,6-(CH_2CPh_2O)$_2$]AlOMe (2c): At –30°C solution of Py(CH_2CPh_2OH)$_2$ (**2**) (0.80 g, 1.70 mmol) in toluene (20 ml) was added dropwise to abovementioned solution of $Me_2Al(OMe)$ in toluene, the reaction mixture was gradually warmed to room temperature and then heated at 80°C for 20 h. Volatile materials were removed under reduced pressure to give **2c** (0.53 g, 59%) as a white powder. ^{1}H NMR ($CDCl_3$, 25°C): δ = 3.45 (s, 3H, OCH_3); 3.37, 3.91 (2d, 4H, ^2J= 14.1 Hz, AM system of CH_2); 6.76-6.79, 6.84-6.88, 7.04-7.08, 7.15-7.18, 7.20-7.24, 7.44-7.55 (6m, 23H, Py and Ph) ppm. ^{13}C NMR ($CDCl_3$, 25°C): δ = 47.77 (CH_2); 49.62 (OCH_3); 77.46 (CPh_2); 124.56, 124.84, 125.15, 125.22, 125.99, 127.34, 127.42, 138.88, 148.74, 151.45, 157.79 (Py and Ph) ppm. Anal. Calcd. for $C_{34}H_{30}AlNO_3$ (527.5885): C 77.40; H 5.73; N 2.65. Found: C 76.94, H 5.90, N 2.57%.

Reaction of Py(CH_2CPh_2OH)$_2$ (2) with $Me_2Al(OBn)$, synthesis of Py[2,6-(CH_2CPh_2O)$_2$]AlOBn (2d). *a) Synthesis of $Me_2Al(OBn)$:* At –30°C BnOH (0.1102 ml, 1.00 mmol) in 5 ml of toluene was added to solution of $AlMe_3$ (2.0 M in toluene, 0.5 ml, 1.00 mmol) in toluene (10 ml). Reaction mixture was slowly warmed to room temperature and stirred overnight. The obtained solution of $Me_2Al(OBn)$ was used further without additional purification.

b) Synthesis of Py[2,6-(CH_2CPh_2O)$_2$]AlOBn (2d): At –30°C solution of Py(CH_2CPh_2OH)$_2$ (**2**) (0.43 g, 0.92 mmol) was added dropwise to abovementioned solution of $Me_2Al(OBn)$ in toluene, the reaction mixture was gradually warmed to room temperature and then heated at 90°C for 21 h. Volatile materials were removed under reduced pressure, residue was washed with ether (2x5 ml) and dried in vacuum to give **2d** (0.35 g, 63%) as a white powder. ^{1}H NMR (C_6D_6, 25°C): δ = 2.10 (s, 2H, OCH_2Ph); 3.02, 3.37 (2d, 4H, ^2J= 14.4 Hz, AM system of CH_2); 6.22-6.26, 6.52-6.57, 6.73-6.78, 6.93-6.98, 6.99-7.03, 7.17-7.21, 7.53-7.57, 7.59-7.64 (8m, 28H, Py and Ph) ppm. ^{13}C NMR (C_6D_6, 25°C): δ = 47.09 (CH_2); 67.08 (OCH_2Ph); 78.69 (CPh_2); 124.58, 125.28, 125.64, 126.65, 126.71, 127.30, 128.11, 128.51, 129.19, 129.27, 138.52, 141.99, 149.40, 152.50, 158.83 (Py and Ph) ppm. Anal. Calcd. for $C_{40}H_{34}AlNO_3$ (603.6844): C 79.58; H 5.68; N 2.32. Found: C 79.70, H 5.93, N 2.13%.

Reaction of Py(CH_2CPh_2OH)$_2$ (2) with Al(OMe)$_3$, synthesis of [2,6-Py(CH_2CPh_2O)$_2$]AlOMe (2c). *a) Synthesis of Al(OMe)$_3$:* At –30°C MeOH (0.2530 ml, 5.10 ml) was added dropwise to solution of $AlMe_3$ (2.0 M in toluene, 0.85 ml, 1.70 mmol) in toluene (10 ml). Reaction mixture was slowly warmed to room temperature and stirred overnight, the volatiles were removed under vacuum to give white powder of Al(OMe)$_3$, which was used without further purification.

b) Synthesis of Py[2,6-(CH_2CPh_2O)$_2$]AlOMe (2c): Toluene (20 ml) was added to abovementioned Al(OMe)$_3$, then at –30°C solution of Py(CH_2CPh_2OH)$_2$ (**2**) (0.80 g, 1.70 mmol) in toluene (20 ml) was added dropwise, the reaction mixture was gradually warmed to room temperature and then heated at 80°C for 40 h. The volatile materials were removed under reduced pressure, residue was washed with ether to give **2c** (0.43 g, 48%) as a white powder. Analytical data correspond to the abovementioned.

Py[2-(CH_2CMe_2O)-6-(CH_2CPh_2O)]AlMe (3a). Method 1. The procedure was analogous to that for **2a** (Method 1): reaction of 2,6-Py(CH_2CMe_2OH)(CH_2CPh_2OH) (**3**) (0.69 g, 2.00 mmol) and Me_3Al (2.0 M in toluene, 1.00 ml, 2.00 mmol) in toluene (30 ml) gave **3a** (0.75 g, 97%) as a white powder. **Method 2.** The procedure was analogous to that for **2a** (Method 2): reaction of Me_3Al (2.0 M in toluene, 0.25 ml, 0.50 mmol) and **3** (0.17 g, 0.50 mmol) in toluene (30 ml) gave **3a** (0.18 g, 96%) as a white powder. ^{1}H NMR ($CDCl_3$, 25°C): δ = -0.85 (s, 3H, $AlCH_3$); 0.66, 1.37 (2s, 6H, CH_3); 2.48, 3.31 (2d, 2H, ^2J = 14.9 Hz, CH_2CMe$_2$); 3.82, 3.99 (2d, 2H, ^2J = 13.9 Hz, CH_2CPh$_2$); 6.75-6.79, 6.90-6.97, 7.10-7.19, 7.21-7.27, 7.38-7.44, 7.46-7.50, 7.63-7.67 (7m, 13H, Py and Ph) ppm. ^{13}C NMR ($CDCl_3$, 25°C): δ = 26.52, 30.90 (CH_3); 47.05 (*C*H$_2$CMe$_2$); 49.90 (*C*H$_2$CPh$_2$); 73.05 (*C*Me$_2$); 77.35 (CPh_2); 122.60, 123.65, 125.41, 125.77, 126.93, 127.26, 127.27, 127.45, 137.88, 149.16, 151.32, 158.00, 158.47 (Py and Ph) ppm. The signal of Al*Me* group was not found in ^{13}C NMR. Anal. Calcd. for $C_{24}H_{26}AlNO_2$ (387.4503): C 74.40; H 6.76; N 3.62. Found: C 74.03, H 6.69, N 3.84%. Crystals suitable for X-ray analysis were obtained from concentrated toluene solution at –18°C.

Py[2-(CH_2CMe_2O)-6-(CH_2CPh_2O)]AlOMe (3c). The procedure was analogous to that for **2c** (reaction of Py(CH_2CPh_2OH)$_2$ (**2**) with Al(OMe)$_3$): reaction of Me_3Al (2.0 M in toluene, 0.55 ml, 1.10 mmol), MeOH (0.1336 ml, 3.30 mmol) and Py(CH_2CMe_2OH)(CH_2CPh_2OH) (**3**) (0.38 g, 1.08 mmol) in toluene (20 ml) at 90 °C for 60 h gave **3c** (0.24 g, 55%) as a white

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powder. ^{1}H NMR ($CDCl_3$, 25°C): δ = 0.58 (s, 3H, CH_3); 0.87 (s, 3H, CH_3); 2.58, 2.81 (2d, 2H, ^2J= 13.6 Hz, AM system of CH_2), 3.42, 3.89 (2d, 2H, ^2J= 13.6 Hz, AM system of CH_2); 3.17 (s, 3H, OCH_3); 6.85-6.92, 6.98-7.05, 7.10-7.15, 7.21-7.29, 7.46-7.50, 7.75-7.81 (6m, 13H, Ph and Py) ppm. ^{13}C NMR ($CDCl_3$, 25°C): δ = 28.64, 33.19 (CH_3); 49.03, 49.16 (CH_2); 49.38 (OCH_3); 68.77 (CMe_2); 77.14 (CPh_2); 122.93, 123.58, 124.91, 125.39, 125.58, 126.30, 126.77, 127.28, 138.48, 148.16, 151.88, 157.45, 158.84 (Py and Ph) ppm. Anal. Calcd. for $C_{24}H_{26}AlNO_3$ (403.4497): C 71.45; H 6.50; N 3.47. Found: C 71.23, H 6.62, N 3.24%.

[Py-2-($CH_2CH_2CPh_2O$)-6-(CH_2CPh_2O)]AlMe (4a). The procedure was analogous to that for **2a** (Method 1): reaction of Py($CH_2CH_2CPh_2OH$)(CH_2CPh_2OH) (**4**) (0.24 g, 0.50 mmol) and Me_3Al (2.0 M in toluene, 0.25 ml, 0.50 mmol) in toluene (20 ml) gave **4a** (0.24 g, 93%) as a beige powder. ^{1}H NMR ($CDCl_3$, 25°C): δ = -0.79 (s, 3H, $AlCH_3$); 1.67-1.74, 2.83-2.88, 3.03-3.13 (3m, 4H, $CH_2CH_2CPh_2$); 3.62, 3.83 (2d, 2H, ^2J= 14.9 Hz, CH_2CPh_2); 6.87-6.91, 6.94-7.03, 7.06-7.12, 7.14-7.24, 7.27-7.33, 7.45-7.52, 7.57-7.67 (7m, 23H, Py and Ph) ppm. ^{13}C NMR ($CDCl_3$, 25°C): δ = -10.77 ($AlCH_3$); 31.71 ($CH_2CH_2CPh_2$); 41.66 (CH_2CPh_2); 49.45 ($CH_2CH_2CPh_2$); 77.44, 79.35 ($2CPh_2$); 123.08, 124.78, 125.60, 125.63, 125.87, 125.92, 126.40, 126.86, 126.94, 127.41, 127.50, 127.76, 127.98, 128.16, 141.52, 146.88, 148.57, 150.23, 151.48, 158.96, 162.19 (Ph and Py) ppm. ^{27}Al NMR ($CDCl_3$, 25°C): δ = 90 ($\omega_{1/2}$= 5000 Hz) ppm. Anal. Calcd. for $C_{35}H_{32}AlNO_2$ (525.6157): C 79.98; H 6.14; N 2.66. Found: C 79.63, H 6.07, N 2.50%.

Py[2-($CH_2CH_2CPh_2O$)-6-(CH_2CPh_2O)AlOMe (4c). Method 1. The procedure was analogous to that for **2b** (reaction of Py($CH_2CPh_2OH)_2$ (**2**) with $Al(OMe)_3$): reaction of Me_3Al (2.0 M in toluene, 0.42 ml, 0.84 mmol), MeOH (34.0 µl, 2.55 mmol) and Py(CH_2CPh_2OH)($CH_2CH_2CPh_2OH$) (**4**) (0.40 g, 0.84 mmol) in toluene (20 ml) at 110 ºC for 12 h gave **4c** (0.26 g, 60%) as a white powder. The compound was isolated as a mixture of two diastereomers (1.1:1). **Method 2.** Under storage of solution of complex **4a** for a long time under dry air the compound **4c** may be obtained. Anal. calcd. for $C_{35}H_{32}AlNO_2$ (541.6151): C 77.61; H 5.96; N 2.59. Found: C 77.30, H 6.10, N 2.27%. *Diastereomer **I**:* ^{1}H NMR ($CDCl_3$, 25°C): δ = 1.74-1.86, 2.51-2.59, 2.60-2.68, 3.25-3.34 (4m, each 1H, CH_2); 3.13 (s, 3H, OMe); 3.60, 3.95 (2d, each 1H, ^2J= 15.3 Hz, CH_2Ph_2); 6.54-7.66 (m, 23H, Py and Ph) ppm. ^{13}C NMR ($CDCl_3$, 55°C): δ = 31.25 ($CH_2CH_2CPh_2$); 40.94 (CH_2CPh_2); 48.25 ($CH_2CH_2CPh_2$); 50.01 (OMe); 77.20, 78.03 ($2CPh_2$); 122.54, 124.44, 125.02, 125.20, 125.50, 125.84, 126.33, 126.86, 127.22, 127.50, 127.70, 128.25, 138.94, 147.02, 149.35, 151.93, 152.08, 152.28, 152.64, 160.80, 163.36 (Ph and Py) ppm. *Diastereomer **II**:* ^{1}H NMR ($CDCl_3$, 25°C): δ = 1.91-2.01, 2.69-2.79, 3.01-3.10, 3.39-3.47 (4m, each 1H, CH_2); 3.14 (s, 3H, OMe); 3.20, 3.69 (2d, each 1H, ^2J= 14.9 Hz); 6.54-7.66 (m, 23H, Py and Ph) ppm. ^{13}C NMR ($CDCl_3$, 55°C): δ = 31.30 ($CH_2CH_2CPh_2$); 40.56 (CH_2CPh_2); 48.95 ($CH_2CH_2CPh_2$); 50.08 (OMe); 77.95, 78.13 ($2CPh_2$); 122.46, 124.33, 124.99, 125.18, 125.28, 125.79, 126.29, 126.43, 127.14, 127.42, 127.70, 128.19, 138.79, 147.05, 149.38, 151.81, 152.00, 152.14, 152.78, 160.40, 163.21 (Ph and Py) ppm. Crystals suitable for X-ray analysis were obtained from concentrated toluene solution at –18°C.

Synthesis of 2,6-Py(CH_2CPh_2O)(CH_2CMe_2O)AlCl (3b). Method 1: Solid $GeCl_2{\cdot}C_4H_8O_2$ (0.11 g, 0.47 mmol) was added to solution of 2,6-Py(CH_2CPh_2O)(CH_2CMe_2O)AlMe (**3a**) (0.18 g, 0.47 mmol) in toluene (10 ml). Reaction mixture was stirred at room temperature overnight, and then the volatile materials were removed under reduced pressure. The residue was recrystallized from toluene at –18°C to give compound **3b** (0.17 g, 89%) as a yellowish solid. **Method 2:** $GeCl_4$ (0.07 ml, 0.62 mmol) was added slowly to solution of 2,6-Py(CH_2CPh_2O)(CH_2CMe_2O)AlMe (**3a**) (0.24 g, 0.62 mmol) in toluene (20 ml). Reaction mixture was stirred at room temperature overnight, and then the volatile materials were removed under reduced pressure. The residue was recrystallized from toluene at –18°C to give compound **3b** (0.10 g, 41%) as a yellowish solid. ^{1}H NMR ($CDCl_3$, 25°C): δ = 0.72, 1.59 (2s, 6H, CH_3); 2.48, 3.67 (2d, 2H, ^2J= 15.3 Hz, CH_2CMe_2); 3.84, 4.24 (2d, 2H, J = 14.3 Hz, CH_2CPh_2); 6.83-6.87, 6.98-7.03, 7.12-7.19, 7.22-7.29, 7.45-7.52, 7.57-7.60 (6m, 13H, Py and Ph) ppm. ^{13}C NMR ($CDCl_3$, 25°C): δ = 26.64, 30.81 (CH_3); 46.82 (CH_2CMe_2); 49.18 (CH_2CPh_2); 75.92 (CMe_2); 77.56 (CPh_2); 123.52, 124.64, 125.92, 126.30, 126.80, 126.83, 127.57, 127.68, 139.26, 148.12, 149.77, 158.06, 158.60 (Py and Ph) ppm. Anal. Calcd. for $C_{23}H_{23}AlClNO_2$ (407.8685): C 67.73; H 5.68; N 3.43. Found: C 67.65, H 5.69, N 3.80%.

Synthesis of 2,6-Py($CH_2CH_2CPh_2O$)(CH_2CPh_2O)AlCl (4b). Solid $GeCl_2{\cdot}C_4H_8O_2$ (0.08 g, 0.34 mmol) was added portionwise to solution of 2,6-Py($CH_2CH_2CPh_2O$)(CH_2CPh_2O)AlMe (**4a**) (0.18 g, 0.34 mmol) in toluene (20 ml). Reaction mixture was stirred at room temperature overnight. The volatile materials were removed under reduced pressure to give compound **4b** (0.17 g, 91%) as a beige solid. ^{1}H NMR ($CDCl_3$, 25°C): δ = 1.72-1.81, 2.85-2.96, 3.14-3.22 (3m, 4H, $CH_2CH_2CPh_2$); 3.94 (br s, 2H, CH_2CPh_2); 6.98-7.02, 7.15-7.28, 7.30-7.35, 7.47-7.51, 7.54-7.58, 7.60-7.62, 7.66-7.68, 7.70-7.76 (8m, 23H, Py and Ph) ppm. ^{13}C NMR ($CDCl_3$, 25°C): δ = 31.29 ($CH_2CH_2CPh_2$); 42.06 (CH_2CPh_2); 49.28 ($CH_2CH_2CPh_2$); 78.53, 79.14 ($2CPh_2$); 123.70, 125.28, 125.31, 125.56, 125.91, 126.08, 126.29, 126.72, 126.77, 127.75, 127.95, 128.13, 128.21, 129.02, 142.70, 145.95, 147.36, 148.96, 150.25, 159.93, 162.77 (Ph and Py) ppm. Anal. Calcd. for $C_{34}H_{29}AlClNO_2$ (546.0338): C 74.79; H 5.35; N 2.57. Found: C 74.54, H 5.90, N 2.50%.

Typical polymerization procedure in solution. All manipulations were performed under inert atmosphere. To the solution of initiator **2a** (0.1213 g, 0.24 mmol) in toluene (12 ml) *L*-lactide (1.7086 g, 11.85 mmol) was added. Then BnOH (52.0 µl, 0.48 mmol) was added at stirring and the reaction mixture was heated at 80°C for 27 h. The reaction was terminated by addition of MeOH (1.0 ml), evaporated and purified by reprecipitation using CH_2Cl_2 as solvent and methanol as a non-solvent. The polymer obtained was dried in vacuum.

Typical polymerization procedure in bulk. All manipulations were performed under inert atmosphere. To the initiator **2c** (0.10538 g, 0.10 mmol) *L*-lactide (0.7343 g, 5.09 mmol) was added. The reaction mixture was heated at 100 °C for 4.5 h. The reaction was terminated by addition of MeOH (1.0 ml), evaporated and purified by reprecipitation using CH_2Cl_2 as solvent and methanol as a non-solvent. The polymer obtained was dried in vacuum.

Polymerization procedure for ε-CL. All manipulations were performed under inert atmosphere. To the initiator **2d** (0.0363 g,

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0.06 mmol) ε-caprolactone (2.0580 g, 18.03 mmol) was added. The reaction mixture was heated at 130 °C for 0.5 h. The reaction was terminated by addition of MeOH (1.0 ml), evaporated and purified by reprecipitation using CH_2Cl_2 as solvent and methanol as a non-solvent. The polymer obtained was dried in vacuum.

X-Ray crystallography. Crystal data and details of X-ray analyses are given in Table 1. Experimental datasets were collected on a Stoe IPDS 2T (for **5**) machine using Cu-Kα radiation (λ = 1.54186 Å) and Bruker SMART APEX II (for **4**, **3a** and **4c**) diffractometer using graphite monochromatized Mo-Kα radiation (λ = 0.71073 Å). The structures were solved by direct methods and refined by full-matrix least-squares on F^2 with anisotropic thermal parameters for all non-hydrogen atoms[79] except disordered solvent toluene molecule in **4c** and disordered solvent $CHCl_3$ molecules in **5**. All hydrogen atoms were placed in calculated positions and refined using a riding model. High final R-values for **5** were the result of poor quality of obtained single crystals.

The crystallographic data for **4**, **3a**, **4c** and **5** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications under the CCDC numbers 1046664-1046667. They can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Conclusions

In this work we have prepared and fully characterized a number of novel aluminum complexes based on substituted 2,6-bis(hydroxyalkyl)pyridines with aluminum atom bearing methyl, methoxy, benzyloxy group or chlorine. It was found that the structure of the ligand determines the nature of the complex formed. If there is one carbon atom in the side chain of the ligand (ligand **1**), only octahedral aluminum complex **5** was isolated. If the side chain of the ligand is increased by one or two carbon atoms (ligands **2**, **3**, **4**) it results in dimeric in solid state complexes with five-coordinate Al atoms. Studies of these complexes in the ring-opening polymerization of *L*-lactide have demonstrated that all complexes are active in polymerization with controlled or immortal character. Further work is underway to optimize polymerization conditions and employ aluminum complexes in both polymerization of *L*-lactide and stereoselective polymerization of *rac*-lactide.

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Notes and references

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† Electronic Supplementary Information (ESI) available: cif files of compounds **4**, **3a**, **4b** and **5**; polymer characteristics; NMR spectra for compounds obtained. See DOI: 10.1039/b000000x/

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