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Aluminum and titanium complexes bearing 2,6-Bis(2-hydroxyphenyl)pyridines for ring-opening polymerization of lactide, ε -caprolactone and their copolymerization: Effect of a ligand on coordination chemistry and reactivity

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ABSTRACT

In ring-opening polymerization (ROP) of cyclic esters, the rational design of the catalyst is generally applied to solve the task of providing polyester biocompatibility (non-toxicity) and the problem of copolymer homogeneity when using comonomers of different nature (e. g. lactones and lactides). In the present work, we report the synthesis of aluminum and titanium complexes, based on substituted 2,6-bis(2-hydroxyphenyl)pyridine proligands 1 and 2. It was found that the structure of the pro-ligand drastically affect the structure of the reaction product. Pro-ligand 2 with a bulky *tert*-butyl group leads to the monomeric complexes 6 (LAIMe) and 7 (LTI $(O^{i}Pr)_{2})$, while the ligands with less bulky groups lead to the oligomeric Al-containing compounds 3 and 4, and in the case of Ti bis-ligand complex 5 is formed. Complexes 6 (in presence of BnOH) and 7 turned out to be active in the ROP of ε -caprolactone and ι -lactide and gave PCL and PLA with high molecular masses. Compound 6 was an effective initiator of copolymerization of ε -caprolactone and ι -lactide which led to statistical copolymer poly(LA-stat-CL) with comonomer subunits ratio of 1:1.

1. Introduction

One of the main and still completely unresolved problems of modern technologically advanced world is environmental pollution with commodity plastics waste [1]. It should be noted that a significant part of the produced commodity polymers is used for packaging. Two classes of biodegradable polymers are usually distinguished: natural polymers, such as polysaccharides, polypeptides and polyhydroxyalkanoates etc. as well as synthetic polymers, among which aliphatic polyesters, such as poly-*L*-lactide (PLA) and poly- ε -caprolactone (PCL), attract special attention due to their relative synthetic availability and properties suitable for the manufacture of products from them. The most commonly used approach to the synthesis of PLA and PCL is a ring-opening polymerization (ROP) of the corresponding cyclic esters, respectively lactide (LA) and ε -caprolactone (ε -CL), in the presence of a

metal complex as an initiator [2–9]. In industry, tin(II) bis-2-ethylhexanoate (tin octoate) in the presence of alcohol is a preferred catalytic system for the bulk polymerization due to its high stability during polymerization process and adequate activity at high temperature, which makes it possible to obtain target polymers with the required molecular weight in a controlled manner [10,11]. However, conventional drawbacks of tin octoate are caused by potential toxicity of tin compounds (although it is known that toxic tin compounds are mainly alkyl derivatives of Sn(IV) [12]), as well as relatively low activity of tin octoate, which requires a high temperature of the polymerization process. In addition to being used in packaging, biodegradable polymers also find biomedical applications as a materials for controlled drug delivery, slow-release medication administration, tissue engineering scaffolds, bone surgery and orthopedics, formation of artificial organs, nerve regeneration and wound healing [13,14]. Due to higher requirements of

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biomedical materials, the development of new initiators based on non-toxic metals, which produce high-molecular PLA and PCL in a controlled manner, narrow molecular weight distribution due to the absence of side reactions like transesterification, remains relevant. Another important task in ROP is a search for new initiators that are active in the synthesis of copolymers and allow to obtain copolymers with a statistical distribution of comonomer subunits. The one of the most important copolymers of LA is poly(lactide-co-caprolactone), poly (LA-CL). Two these homopolymers have contrasting physical and thermal properties: PCL exhibits good elasticity and permeability but poor mechanical characteristics (toughness), which is the opposite to PLA [15]. The preparation of a statistical copolymer poly(LA-stat-CL) may lead to biodegradable materials with improved properties. At the same time the copolymerization of LA and ε -CL, in most cases, results in the formation of block- or gradient copolymers due to the different chain propagation rates for these monomers on the most of studied initiators. It is noteworthy that ε -CL reacts typically faster than LA in their respective homopolymerizations, while copolymerization of both monomers often leads to the preferential consumption of LA over ϵ -CL [2,15–18].

The ligand design has a decisive influence on the activity of the complex in the ROP of cyclic esters and on the properties of the resulting polymers, provided that the metal is in principle active in such processes [19–23]. During this work, we focused our attention on aluminum and titanium complexes, whose compounds had previously demonstrated activity in ROP, and the metals themselves are traditionally considered as low-toxic. In search of a ligand system for Al and Ti that is suitable for ROP, we turned our attention to polydentate ligands based on pyridine containing two aromatic hydroxyl groups (1, 2, Fig. 1). We believed that this ligand forms sufficiently strong metal-phenolic oxygen bonds, which should increase the stability of the complex under the ROP conditions, and the structure of the ligand on the one hand should allow to preserve the monomeric structure of the complex, and on the other hand- to leave enough space for the attack of the metal atom by the monomer during polymerization. According to the literature data this type ligands has been used for the preparation of Ti [24–26], Zr [24–26], Hf [25,26], V [26,27], Ta [28], Mo [29,30], W [29], Ir [31], Cu [32], Zn [32], Al [33,35], Y [34,35], Sc [34], La [34], Ge [36], Sn [36] derivatives, however, these complexes were not used as initiators in the ROP, except Y [34,35], Sc [34], La [34] and Al complexes [33,35]

(Fig. 1).

As a part of our program [36–39] to prepare novel initiators for ROP based on different type ligands and to study the influence of ligand structure on complexes geometry, in the present work we report the synthesis of Al and Ti complexes based on 2,6-bis(2-hydroxyphenyl)pyr-idines and the study of their activity in ROP.

2. Results and discussion

Two pro-ligands 1 and 2 which differ in the steric volume of substituents (H and t-Bu, respectively) in the ortho-positions to the hydroxyl group, that is, in the immediate vicinity of the metal atom, were used for preparation of the complexes. It has recently been shown in the chemistry of tetrylenes, based on these ligands, that the steric volume of the ortho-substituent has a fundamental effect on the structure of the resulting product [34]. Reaction of pro-ligand 1 with AlMe₃ (1:1 stoichiometry) afforded a mixture of Al-containing compounds, among which, the complexes containing three and four aluminum atoms (3 =Al₂L₃, L – dianion of ligand 1, $m/z = 1149 (3 + H^+)$; 4 (MeAl₃L₄, L – dianion of ligand 1, $m/z = 1542 (4 + H^{+})$ were detected by mass-spectrometry. The expected heteroleptic titanium complex containing two isopropoxy groups was also not formed. In the reaction of pro-ligand 1 with titanium (IV) isopropoxide in a ratio of 1:1, only the homoleptic bis-ligand complex 5 was isolated. On the contrary, the reaction of pro-ligand 2 containing a bulky tert-butyl substituent in the ortho-positions to OH groups with AlMe3 or Ti(OⁱPr)4 produced the expected heteroleptic complexes 6 and 7 with good yields (Scheme 1).

The formation of the complexes 5–7 was unambiguously proven by ¹H, ¹³C NMR spectroscopy as well as by elemental analysis. The compounds 5–7 possess a symmetrical structure, since the phenolic rings in the ligands are spectrally identical. The crystal structures of 5 and 6 were determined by single-crystal X-ray diffraction. The molecular structure of 5 is shown in Fig. 2. Selected bond lengths and angles of 5 are listed in Fig. 2 caption.

The coordination polyhedron of titanium atom in 5 represents a distorted octahedron. The compound 5 exhibits *trans*-disposition of two nitrogen atoms at Ti atom. This is one from two possible *trans*-isomers, where two oxygen atoms of one ligand also occupy the *trans*-positions in octahedral environment of Ti atom. A similar arrangement of atoms in the octahedron was found in the previously studied derivatives of



Fig. 1. Pyridine-containing metal complexes known to date.



Scheme 1. Synthesis of complexes 3-7.



Fig. 2. Molecular structure of 5. Hydrogen atoms and solvate molecule of chloroform omitted for clarity. Selected bond lengths (Å) and angles (deg) for 5: Ti(1)-O(2) 1.8868(16), Ti(1)-O(2A) 1.8868(16), Ti(1)-O(1) 1.8894(16), Ti(1)-O(1A) 1.8895(16); Ti(1)-N(1) 2.2096(19), Ti(1)-N(1A) 2.2097(19); O(2)-Ti(1)-O(2A) 95.12(10), O(2)-Ti(1)-O(1) 163.98(7), O(2)-Ti(1)-O(1A) 88.96(7), O(1A)-Ti(1)-O(1) 91.34(10), O(2)-Ti(1)-N(1) 81.99(7), O(2)-Ti(1)-N(1A) 95.09(7), O(1)-Ti(1)-N(1A) 100.82 (7), O(1)-Ti(1)-N(1A) 175.69(9).

aminobis(phenols) $[Pr^{n}N(CH_{2}-o-Ar-O)_{2}]Ti[(O-o-Ar'-CH_{2})_{2}NR]$ [39]. Notably, in related bis-ligand complexes based on dialkanolamines, two nitrogen atoms usually occupy *cis*-positions in the octahedral environment of the titanium atom [40]. The Ti–N distances in 5 are slightly shorter than those previously found in $[Pr^{n}N(CH_{2}-o-Ar-O)_{2}]Ti$ $[(O-o-Ar'-CH_{2})_{2}NR]$ [2.248(2)–2.308(4) Å] [40] and considerably shorter than those, previously found in bis-ligand complexes based on dialkanolamines which vary in the range 2.310(2)–2.471(3) Å [41]. This difference is probably explained by higher polarity of Ti–O bonds in phenolic species which leads to depletion of electron density at titanium center. The Ti–O distances in 5 are very close to those previously found in [PrⁿN(CH₂–o-Ar–O)₂]Ti[(O–o-Ar'–CH₂)₂NR] [1.865(2)– 1.913(3) Å] [40].

The molecular structure of 6 is shown in Fig. 3. Selected bond lengths



Fig. 3. Molecular structure of 6. Hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (deg) for 6: Al(1)-O(2) 1.747(2); Al(1)-O(1) 1.743(2); Al (1)-N(1) 1.910(2); Al(1)-C(35) 1.930(3); O(2)-Al(1)-N(1) 95.71(9); O(2)-Al(1)-C(35) 116.60(11); O(2)-Al(1)-O(1) 111.17(9); O(1)-Al(1)-N(1) 96.53(9); O(1)-Al(1)-C (35) 117.51(11); N(1)-Al(1)-C(35) 115.53(11).

and angles of 6 are listed in Fig. 3 caption.

Compounds 6 and 7 were tested as catalysts towards the ROP of ε -CL and ι -LA as well as in copolymerization of these cyclic esters. The polymerizations of ε -CL in the presence of 6 (with BnOH, ratio 6: BnOH=1:1) were conducted in bulk and in toluene solution both at 100 °C; and in the presence of 7 (without BnOH) under solvent-free conditions at 100 °C. Polymerizations of ι -LA in the presence of 6 (with BnOH used as a co-initiator, ratio 6:BnOH=1:1) were conducted in bulk and in toluene solution both at 100 °C; and in the presence of 7 (without BnOH) used as a co-initiator, ratio 6:BnOH=1:1) were conducted in bulk and in toluene solution both at 100 °C; and in the presence of 7 (without BnOH) in toluene solution at 100 °C. The copolymerization was

Table 1

Polymerization	results	for	cataly	vsts	6	and	7.
2							

investigated in the presence of 6 in bulk at 150 °C and in toluene solution at 100 °C in the presence of BnOH. The polymerizations were monitored by taking aliquots at regular time intervals, which were analysed using ¹H NMR spectroscopy to determine the cyclic ester conversion, and by GPC (gel permeation chromatography) to determine the number average molecular weight (M_n) and molecular weight distribution (M_w/M_n). The polymerization results are summarized in Table 1.

The Al atom in 6 is four-coordinated by the tridentate ligand (dianion of 2) and the methyl group in a distorted-tetrahedral geometry (angles around Al $95.71(9)-117.51(11)^{\circ}$). The Al–O(phenolate) bond lengths

Entry	Catalyst, [cat]	[M] ₀ /[<i>cat</i>]/[B <i>n</i> OH] ₀	t, (h)	Conversion ^d , [%]	M_n^{e} (theor), [g/mol]	$M_{n (exp)}^{f}$, [g/mol]	$M_{\rm w}/M_{\rm n}$
1	6 ^a	300(e-CL):1:1	0.25	96	-	_	-
2			0.75	98	-	-	-
3			2	>99	34,000	36,670	1.60
4	6 ^b	300(e-CL):1:1	0.25	69		-	-
5			0.75	84		-	-
6			2	>99	34,000	35,939	1.45
7	6 ^a	300(L-LA):1:1	1	10		-	-
8			6	24		-	-
9			24	63	27,347	27,308	1.11
10	6 ^b	300(L-LA):1:1	1	26		-	-
11			6	65		-	-
12			24	>99	42,973	68,848	1.16
13	6 ^b	100(ε-CL):100(L-LA):1:1	1	ε-CL 2 %, ι-LA 9 %		-	-
14			3	ε-CL 3 %, ι-LA 21 %		-	-
15			24	ε-CL 20 %, l-LA 76 %	11,280	13,800,	1.25
						copolymer composition: 22 % CL, 78 % LA	
16	6 ^c	100(e-CL):100(L-LA):1:1	120	52 % (ε-Cl), 60 % (L-LA)	14,676	20,300,	1.49
						copolymer composition: 50 % CL, 50 % LA	
17	7 ^a	300(e-CL):1	0.25	17		-	-
18			0.5	45		-	-
19			1	62		-	-
20			2	78		-	-
21			22	>99	33,900	25,938	1.58
22	7 ^b	300(L-LA):1	1	11		-	-
23			2	24		-	-
24			6	38		-	-
25			24	74	31,970	19,001	1.40

^a Polymerization in bulk: 100 °C.

^b Polymerization in toluene solution (5 ml), 100° C, [M] = 1 mol/l.

^c Polymerization in bulk: 150°C.

 $\label{eq:conversion} \stackrel{d}{\to} According to \\ ^{1}H NMR data. \\ ^{e}M_{n(theor)} = M_w(LA) \times [LA] o \times (conversion) \mbox{ and } M_{n \ (theor)} = M_w(LA) \times [LA] o / [BnOH] \times (conversion) + M_w(BnOH) \mbox{ with addition of alcohol}; \\ M_{n(theor)} = M_w(CL) \times [CL] o \times (conversion) \mbox{ and } M_{n(theor)} = M_w(CL) \times [CL] o \times (conversion) + M_w(BnOH) \mbox{ with addition of alcohol}.$

 $^{\rm e}$ The molecular weights and the M_w/M_n of the polymers were determined by GPC relative to PMMA standards and multiplied by a correction factor of 0.58 for polylactide and 0.56 polycaprolactone.

in 6 are similar to those observed for related tetracoordinated Al aminobis(phenolate) complexes (1.714(4)–1.7493(7) Å) [39–41] and pyridinebis(naphtholate) complex (1.745(1) and 1.759(1) Å) [33]. The distances Al–C and Al–N in 6 are also close to those found previously in closely related compounds: Al–C aminobis(phenolate) complexes (1.919 (3)–1.9465(11) Å) [42–44], pyridinebis(naphtholate) complex (1.922 (2) Å) [33]; Al–N aminobis(phenolate) complexes (1.985(4)–2.0101(8) Å) [42–44], pyridinebis(naphtholate) complex (1.9394(15) Å) [33]. It should be noted that some shortening of the length of the Al–N bond in 6 in comparison with the aminobis(phenolate) complexes is apparently associated with a more rigid structure of the pyridine-containing ligand.

Aluminum complex 6 is active for the polymerization of ε -caprolactone both in bulck and in solution. Compound 6 produces PCL in presence of BnOH (1:1) with high molecular mass in controlling manner. The activity and the characteristics of the isolated polymer are close to those previously found for aluminum aminobis(phenolate) complexes [43,44]. The titanium complex 7 proved to be less active, but also producing PCL with a high molecular weight. In this case, the reaction occurs without the addition of benzyl alcohol, since the isoproxide group bound with the titanium atom in compound 7 has a good migrating ability, unlike the alkyl group in 6. Both prepared complexes were also tested in ROP of *L*-LA and demonstrated slightly lower activity compared to that for ε -CL (Table 1). Previously it was found that ε -CL usually has a higher polymerization rate in its respective homopolymerizations than *L*-LA [15].

The effectiveness of the compound 6 as a catalyst in copolymerization of *L*-LA and ε -CL has been also demonstrated. It was found that the initiator 6 has an excellent ability to produce a statistical copolymer poly (LA-stat-CL) in bulk at 150°C with high molecular mass and low dispersity, which is comparable to the best initiators described in the literature [15]. It should be noted that at 100 °C in toluene solution the conversion of *L*-LA becomes noticeably higher than the conversion of ε -CL. The microstructure of prepared poly(LA-stat-CL) has been analyzed by ¹³C NMR spectroscopy. The ¹³C NMR spectrum of the carbonyl region from 169 to 174 ppm is shown in Fig. 4. Eight resonances of triads were found, which were assigned according to the literature data [45], with the same integral intensity, which indicates the statistical nature of the copolymer. The average block lengths ($L_{LA}^e = 1.49$ and $L_{CL}^e = 1.65$) were calculated following the method reported previously [46]. It should be noted that the signal at 171 ppm, indicating transesterification reactions during polymerization, was not detected [47,48]. Thus, the mechanism of formation of a random copolymer differs from that found for tin octoate (transesterification leads to a redistribution of monomer sequences [47]), and represents the sequential addition of monomers to one polymer chain, which is consistent with recent mechanistic studies of the copolymerization of LA and ϵ -CL [49,50]

3. Materials and methods

All reactions with air- and/or water-sensitive compounds 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 and benzene were refluxed over Na and distilled; benzyl alcohol was distilled under vacuum. Starting materials were synthesized according to the literature procedures: 6,6'-(pyridine-2,6-diyl)bis(5-methylphenol) (1) [36], 6,6'-(4-phenylpyridine-2,6-diyl)bis(2,4-di-tert-butylphenol) (2) [51]. AlMe₃ (2.0 M solution in toluene) and Ti(OⁱPr)₄ (Sigma-Aldrich, St. Louis, MO, USA) were used as purchased. *L*-Lactide was recrystallized from toluene and sublimed in a vacuum, *ɛ*-caprolactone was distilled over CaH₂. CDCl₃ (dried with CaH₂) was obtained from Deutero GmbH (Kastellaun, Germany). ¹H (400.13 MHz) and ¹³C (100.61 MHz) NMR spectra were recorded on a Bruker Avance 400 (Bruker Corporation, Billerica, MS, USA) or Agilent 400-MR (Agilent Technologies, Santa Clara, CA, USA) spectrometers at room temperature (if otherwise stated). ¹H and ¹³C



Fig. 4. ¹³C NMR spectrum of carbonyl region of copolymer poly(LA-stat-CL) (Table 1, № 16).

chemical shifts are reported in ppm relative to Me₄Si as internal standard. Elemental analysis was performed using EuroEA-3000 instrument (EuroVector, Pavia, Italy). Gel permeation chromatography (GPC) was carried out on an HPLC chromatograph (column phenogel 10^4 Å, refractive index detector), solvent - THF, flow rate - 1 ml/min, sample concentration - 1 %, sample volume - 200 µL. Calibration of the system was carried out by PMMA standards. The study of substances by mass spectrometry with MALDI-TOF ionization was performed on a Bruker Autoflex instrument (Bruker Corporation, Billerica, MS, USA).

Synthesis of complexes **3** and **4**. 2 M solution of AlMe₃ in toluene (0.64 mL, 1.27 mmol) was added dropwise to the solution of ligand **1** (0.4673 g, 1.27 mmol) in toluene (20 mL) at -30 °C in an argon atmosphere. The reaction mixture was slowly warmed-up to room temperature and stirred for 1 day. Then the solvent was removed *in vacuo*, diethyl ether was added and the mixture was stirred for 30 min. The residue was filtered off, washed with ether and dried *in vacuo*. MALDI-TOF-MS **3** Al₂L₃, where L – ligand dianion **1** *m*/*z* = 1149 and **4** (Al₃L₄, where L – ligand dianion **4**, *m*/*z* = 1542).

Synthesis of complex **5**. The solution of $Ti(O^{i}Pr)_{4}$ (0.49 g, 1.73 mmol) in toluene (10 mL) was added dropwise to the solution of ligand **1** (0.55 g, 1.73 mmol) in toluene (10 mL) at 20 °C in an argon atmosphere. The solution was stirred for 15 h. A yellow precipitate was formed 30 min after the start of the reaction. Then the solvent was removed *in vacuo*. The solid residue was recrystallized from the *n*-hexane/toluene mixture. Compound **5** (0.41 g, 76 %) was obtained as a white powder.

¹H NMR (CDCl₃), δ : 8.10 (s, 4H, Ar), 7.81 (d, J = 7.8 Hz, 4H, Ar), 7.59 (m, 10H, Ar), 6.66 (d, J = 8.3 Hz, 4H, Ar), 5.71 (d, J = 8.3 Hz, 4H, Ar), 2.39 (s, 12H, CH₃).

¹³C NMR (CDCl₃), δ: 159.34, 154.61, 151.55, 138.14, 131.44, 129.91, 129.50, 129.18, 128.28, 127.53, 124.65, 121.30, 116.45 (Ar), 21.08 (*C*H₃).

Found (%): C 77.28, H 5.01, N 3.75. $\rm C_{50}H_{38}TiN_2O_4.$ Calculated (%): C 77.12, H 4.92, N 3.60.

Synthesis of complex **6**. 2 M solution of AlMe₃ in toluene (0.5 mL, 1 mmol) was added dropwise to the solution of ligand **2** (0.49 g, 1 mmol) in toluene (10 mL) at -30 °C in an argon atmosphere. The reaction mixture was slowly warmed-up to room temperature and stirred for 1 day. Then the solvent was removed *in vacuo*. The solid residue was recrystallized from the *n*-hexane/toluene mixture. Compound **6** (0.40 g, 72 %) was obtained as a white powder.

¹H NMR (CDCl₃), δ : 8.03 (t, J = 8.1 Hz, 1H, Ar). 7.65 (d, J = 7.8 Hz, 2H, Ar), 7.50 (d, J = 2.3 Hz, 2H, Ar), 7.45 (d, J = 2.3 Hz, 2H, Ar), 1.51 (s, 18H, C(*CH*₃)₃), 1.37 (s, 18H, C(*CH*₃)₃), -0.94 (s, 3H, AlC*H*₃).

¹³C NMR (CDCl₃), δ: 155.91, 155.42, 141.44, 141.29, 140.82, 128.14, 123.33, 122.19, 121.48 (Ar), 35.77 (C(CH₃)₃), 34.52 (C(CH₃)₃), 31.74 (C(CH₃)₃), 29.95 (C(CH₃)₃),

Found (%): C 77.38, H 8.79, N 2.65. $\rm C_{34}H_{46}AlNO_2.$ Calculated (%): C 77.48, H 8.87, N 2.73.

Synthesis of complex **7**. The solution of $Ti(O^{i}Pr)_{4}$ (0.30 r, 1.06 mmol) in toluene (10 mL) was added dropwise to the solution of ligand **2** (0.52 r, 1.06 mmol) in toluene (10 mL) at 20 °C in an argon atmosphere. The solution was stirred for 15 h. Then the solvent was removed *in vacuo*. The solid residue was recrystallized from the *n*-hexane/toluene mixture. Compound **7** (0.37 g, 56 %) was obtained as a white powder.

¹H NMR (CDCl₃), δ : 7.91 (t, J = 7.8 Hz, 1H, Ar), 7.62 (d, J = 7.8 Hz, 2H, Ar), 7.45 (d, J = 2.3 Hz, 2H, Ar), 7.38 (d, J = 2.3 Hz, 2H, Ar), 4.74 (m, 2H, CH(CH₃)₂), 1.54 (s, 18H, C(CH₃)₃), 1.34 (s, 18H, C(CH₃)₃), 0.98 (br. s, 12H, CH(CH₃)₂).

¹³C NMR (CDCl3), δ: 158.11, 156.44, 140.74, 138.89, 136.67, 126.23, 125.25, 123.60, 122.31 (Ar), 80.07 (*C*H(CH₃)₂), 35.49 (*C* (CH₃)₃), 34.52(*C*(CH₃)₃), 31.80 (C(*C*H₃)₃), 30.21 (C(CH₃)₃), 25.40 (CH (CH₃)₂).

Found (%): C 72.02, H 8.95, N 2.22. C₃₉H₅₇TiNO₄. Calculated (%): C 71.87, H 8.82, N 2.15.

Typical Polymerization Procedure in Bulk

All manipulations were performed under inert atmosphere. To the

initiator 6 (0.0518 g, 0.098 mmol) ε -caprolactone (3.3557 g, 29.40 mmol) was added. Then BnOH (10.0 μ l, 0.48 mmol) was added with stirring and the reaction mixture was heated at 100 °C for 2 h. The reaction was terminated by the addition of MeOH (1.0 mL), evaporated, and purified by reprecipitation using CH_2Cl_2 as a solvent and methanol as a non-solvent. The polymer obtained was dried in vacuum.

Typical Polymerization Procedure in Solution

All manipulations were performed under an inert atmosphere. To the solution of initiator 7 (0.0236 g, 0.036 mmol) in toluene (10 ml) *L*-lactide (1.5624 g, 10.84 mmol) was added. The reaction mixture was heated at 100 °C for 6 h. The reaction was terminated by the addition of MeOH (1.0 ml), evaporated and purified by reprecipitation using CH₂Cl₂ as a solvent and methanol as a non-solvent. The polymer obtained was dried in a vacuum.

4. Conclusions

During this work two prospective Al- an Ti-contained initiators of the ROP of *L*-lactide and ε -caprolactone, based on 2,6-bis(2-hydroxy-3,5-di (*tert*-butyl)phenyl)pyridine, have been prepared and fully characterized. We have demonstrated that these complexes can be effective initiators for the production of PCL and PLA with relatively narrow dispersities and controllable molecular weights as homopolymers, as well as can produce a statistical copolymer poly(LA-stat-CL) in bulk at 150 °C with high molecular mass and low dispersity.

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CRediT authorship contribution statement

Badma N. Mankaev: Investigation, Methodology, Software, Writing – original draft. Valeriia A. Serova: Investigation. Milana U. Agaeva: Investigation. Konstantin A. Lyssenko: Investigation. Artem N. Fakhrutdinov: Investigation. Andrei V. Churakov: Investigation. Elena V. Chernikova: Investigation. Mikhail P. Egorov: Conceptualization, Funding acquisition. Sergey S. Karlov: Conceptualization, Data curation, Writing – original draft, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The authors are unable or have chosen not to specify which data has been used.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2023.122973.

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