Controlled Ring-Opening Homo- and Copolymerization of ε-Caprolactone and D,L-Lactide by Iminophenolate Aluminum Complexes: An Efficient Approach toward Well-Defined Macromonomers

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ABSTRACT: The aluminum complexes containing two iminophenolate ligands of the type (p-$XC_6H_4NCHC_6H_4O$-o)$_2$AlR′ (R′=Me (**3, 4**) or R′=$O(CH_2)_4OCH{=}CH_2$ (**5, 6**), X=H (**3, 5**), F(**4, 6**)) were synthesized and characterized by ^{1}H, ^{13}C NMR spectroscopy, and X-ray crystallography. The reaction of $AlMe_3$ with two equivalents of substituted iminophenols gave five-coordinated {ONR}$_2$AlMe (**3, 4**) complexes. Subsequent reaction of these methyl complexes with unsaturated alcohol, $HO(CH_2)_4OCH{=}CH_2$, resulted in target compounds **5** and **6** in a good yield. It was shown that the complexes (**3**-**6**) are monomeric in solution (NMR) and in solid state (X-ray analysis). The catalytic activity of the complexes **5** and **6** towards ring-opening polymerization (ROP) of ε-caprolactone and D,L-lactide was assessed. Complex **5** showed higher activity as compared with **6**, while both of these catalysts induced controlled homo- and copolymerization to afford the macromonomers with high content of vinyl ether end groups ($F_n > 80\%$) in a broad range of molecular weights (M_n = 4000–30,000 g mol^{-1}) with relatively narrow MWD (M_w/M_n = 1.1–1.5). © 2014 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2014**, *52*, 1237–1250

KEYWORDS: biomaterials; block copolymers; diblock copolymers; living polymerization; metal-organic catalysts; macromonomers; polyesters; ring-opening polymerization; X-ray

INTRODUCTION Biodegradable and biocompatible polyesters such as polycaprolactone (PCL), polylactide (PLA), or polyglycolide (PGA) have attracted much attention due to the wide range of their applications, including medicine (implants, orthopedic fixation devices, tissue engineering), pharmacology (drug delivery systems), and in the production of environmentally friendly polymer materials.[i] Homopolyesters, however, are characterized by a number of disadvantages, for example, PLA and PGA possess good mechanical properties but poor elasticity and brittleness, while PCL along with excellent drug permeability and elasticity exhibits poor mechanical strength.[1(g),2] Therefore, block or random copolymerization of lactide (LA), ε-caprolactone (CL), and glycolide (GA) are particularly of keen interest due to the possibility to tune the properties of biomaterials obtained via control the composition, monomer sequencing and molecular weight.[3,4] For the further expansion of the application of biodegradable polyesters in biomedical field, block copolymers such as PCL (or PLA)-block-polyethylene glycol, polydimethylsiloxane-block-PCL and others have been synthesized and successfully used for encapsulation and delivery of drugs, as scaffolds in tissue engineering etc.[5] Recently, the synthesis of biodegradable polyesters containing functional groups (halogen, amino, silane, and especially double bond)[6–8] has attracted significant attention due to the possibility of their use as the building blocks/macromonomers for constructing the advanced structures such as terpolymers,[7] graft,[9] comb-like,[10] brush-like,[11] star-shaped[12] copolymers, or cross-linked biodegradable networks.[8] The particular interest represents the synthesis of PCL macromonomers possessing vinyl ether end group,[7,8,13] since they easily copolymerize with maleic anhydride,[14,15] or terpolymerize with maleic anhydride and third monomer[7] giving the access to a series of amphiphilic graft copolymers containing hydrophilic backbone and hydrophobic PCL side chains, which can be used for drug delivery.[7,16] These graft copolymers (especially those contained short rigid backbone and long PCL chain as branch[16(c)]) showed quite different behavior during their

Additional Supporting Information may be found in the online version of this article.

self-assembly in comparison with PCL-based amphiphilic block copolymers.[16]

The PCL macromonomers end-capped with vinyl ether end group were synthesized by the polymerization of CL using the simple catalytic systems based on aluminum alkoxide generating *in situ* via reaction of triethylaluminum and 1,4-butanediol vinyl ether[7,13] or titanium alkoxide ($Ti(OR)_4$, $R = O(CH_2)_4OCH{=}CH_2$).[8] Both of these Lewis acid alkoxides allowed to synthesize only oligomers of CL with $M_n \leq 1200$ g mol^{-1}. Furthermore, in the case of using aluminum alkoxide as catalyst the formation of saturated acetal from 1,4-butanediol vinyl ether was reported as side reaction,[7] while for titanium alkoxide as catalyst the functionality (content of vinyl ether end groups) was less than unity.[8] Other problems associated with using nonligated metal complexes such as metal alkoxides or related tin compounds are racemization (for lactide polymerization) and transesterification, which led to polymers with unpredictable molecular weight, broad molecular weight distribution and formation of macrocycles or low molecular weight oligomers.[17] Therefore, during the last decade many efforts, made by different research groups, have focused on the developments of single-site metal initiators with multidentate ligands for ring-opening polymerization (ROP) of ε-caprolactone and lactide. Well-designed ligands provide the ability to tune electronic and steric properties of the metal centers changing their acidity and reactivity. Thus, a large number of metal complexes including Mg,[18,19] Zn,[19,20] Fe,[21] Ti,[22] rare-earth elements,[23] Al[24–29] and others has been used as initiators/catalysts for ROP of cyclic esters. Among them, aluminum complexes with different multidentate ligands such as salen,[24] salan,[1(g),25] dialkoxy-diimino,[26] and others[1(c,g),27,28] have attracted much attention due to their high activity, effectiveness in controlling the molecular weight, and polymer tacticity (for ROP of lactide) as well as biocompatibility. Although substituted iminophenols are synthetically easily available in a cost-effective approach, aluminum complexes with bidentate iminophenolate {ON}– or related ligands are considerably less studied in the polymerization of CL and D,L-lactide.[4,29]

In continuation of our research program on the synthesis of metal complexes with multidentate ligands,[30] in this article we report the synthesis, characterization, and investigation of catalytic activity in ROP of functionalized with unsaturated alcohol ($HO(CH_2)_4OCH{=}CH_2$) aluminum complexes based on easily accessible iminophenolate ligands. In contrast to well-known complexes of iminophenolate ligands of general structure $LAlMe_2$,[29] our synthetic strategy was to synthesize the complexes containing two iminophenolate ligands per metal center, L_2AlMe (L_2AlOR). This approach would allow creating a sterically hindered environment around the metal center on the one hand, and simplifying the synthetic pathway towards catalytic complexes, on the other hand. The aim of this study is to develop a practical, cost-effective approach toward macromonomers of CL and LA and their copolymers in a broad range of molecular weights under bulk polymerization conditions. We are also interested in evaluating the activity and stereoselectivity (for D,L-lactide) of these L_2AlOR catalysts in ring-opening homo- and copolymerization of ε-caprolactone and D,L-lactide.

EXPERIMENTAL

General Procedures and Materials

All manipulations were carried out using standard Schlenk techniques under an atmosphere of argon. Solvents were purified using standard procedures. Diethyl ether ("Aldrich") was stored under solid KOH and then distilled under sodium/benzophenone. Dichloromethane ("Aldrich") was distilled under CaH_2. Benzene, toluene, hexane (all from "Aldrich") were refluxed over sodium and distilled. ε-Caprolactone ("Aldrich", 97%) was dried over CaH_2, distilled from CaH_2 under reduced pressure and stored under argon. D,L-lactide ("Aldrich", 98%) was twice recrystallized from toluene and dried in vacuum at 55 °C. Deuterated solvent ($CDCl_3$) from Carl Roth GmbH +Co. KG (Ruth, 99.8%) was dried over CaH_2, distilled and stored under argon. Solution of $AlMe_3$ (2.0 M in toluene, "Aldrich") was used as received. Salicylaldehyde (Aldrich), aniline ("Aldrich"), 4-fluoroaniline ("Aldrich"), $HO(CH_2)_4OCH{=}CH_2$ ("Aldrich") were distilled before use. 2-[(E)-(phenylimino)methyl]phenol (**1**) was obtained according to published procedure.[31]

Instrumentation and Measurements

^{1}H NMR (400.130 MHz), ^{13}C NMR (100.613 MHz), ^{19}F (376.498 MHz) spectra were recorded with a Bruker 400 or Agilent 400MR spectrometers at 295 K. For ^{1}H homonuclear decoupled NMR spectra were acquired in $CDCl_3$ with methyl protons decoupled from the methine protons during the acquisition time. Chemical shifts are given in ppm relative to internal Me_4Si (^{1}H and ^{13}C NMR spectra), internal $CFCl_3$ (^{19}F spectra). Elemental analyses were carried out by the Microanalytical Laboratory of the Chemistry Department of the Moscow State University. Size exclusion chromatography (SEC) was performed on a Agilent 1200 apparatus with Nucleogel GPC LM-5, 300/7,7 column and one precolumn (PL gel 5 μm guard) thermostated at 30 °C. The detection was achieved by differential refractometer. Tetrahydrofuran (THF) was eluted at a flow rate of 1.0 mL/min. The calculation of molar mass and polydispersity was based on polystyrene standards (Polymer Labs, Germany).

Synthesis of Ligands and Complexes

Synthesis of 2-((E)-[(4-fluorophenyl)imino]-methyl)phenol (2)

Initially 4-fluoroaniline (1.82 mL, 18.95 mmol) was added to solution of salicylaldehyde (2.00 mL, 18.99 mmol) in EtOH (30 mL) at room temperature. Reaction mixture was stirred overnight, the solid obtained was filtered off, washed with cold EtOH, and dried in vacuum to give **2** as a yellow solid (3.88 g, 95%).

^{1}H NMR (400.130 MHz, $CDCl_3$, δ, ppm) 13.11 (s, 1H, OH), 8.55 (s, 1H, CH=N), 7.39-7.33 (m, 2H, ArH), 7.26-7.20 (m,2H, ArH), 7.13-7.05 (m, 2H, ArH), 7.03-6.99 (m, 1H, ArH), 6.95-6.89 (m, 2H, ArH). ^{13}C{^{1}H} NMR (100.613 MHz, $CDCl_3$, δ, ppm) 162.36 (CH=N), 161.60 (d, $^1J_{C\text{-}F}$ = 246.6 Hz, ArCH), 161.00 (ArCH), 144.59 (d, $^4J_{C\text{-}F}$ = 2.9 Hz, ArCH),

133.15 (ArCH), 132.23 (ArCH), 122.54 (d, $^{3}J^{C\text{-}F}$ = 8.1 Hz, ArCH), 119.07 (ArCH), 118.96 (ArCH), 117.20 (ArCH), 116.13 (d, $^{2}J_{C\text{-}F}$ = 22.7 Hz, ArCH). ^{19}F NMR (376.498 MHz, $CDCl_3$, δ, ppm) -115.34 (1F, s).

Synthesis of Complex 3

At −60 °C the solution of $AlMe_3$ in toluene (0.89 mL, 2.0 M, 1.78 mmol) was added to solution of ligand **1** (0.70 g, 3.55 mmol) in toluene (20 mL). The reaction mixture was slowly warmed to ambient temperature and then was heated under reflux for 4 h. The volatiles were removed under reduced pressure, hexane and ether (approximately 20:1) was added to residue and the solution obtained was stored at −30 °C overnight. The solid formed was filtered off and dried under vacuum. The compound **3** was obtained as a white solid (1.34 g, 87%).

^{1}H NMR (400.130 MHz, $CDCl_3$, δ, ppm) 8.21 (s, 2H, 2CH=N), 7.56-7.50 (m, 4H, ArH), 7.46-7.41 (m, 4H, ArH), 7.39-7.36 (m, 2H, ArH), 7.34-7.26 (m, 4H, ArH), 6.84-6.77 (m, 4H, ArH), -1.02 (s, 3H, AlMe). ^{13}C{^{1}H} NMR (100.613 MHz, $CDCl_3$, δ, ppm) 166.97 (CH=N), 163.65 (ArCH), 151.17 (ArCH), 135.27 (ArCH), 134.02 (ArCH), 128.73 (ArCH), 126.51 (ArCH), 123.63 (ArCH), 121.34 (ArCH), 120.13 (ArCH), 117.27 (ArCH), -6.61 (AlMe).

Synthesis of Complex 4

At −60 °C the solution of $AlMe_3$ in toluene (1.16 mL, 2.0 M, 2.32 mmol) was added to solution of ligand **2** (1.00 g, 4.65 mmol) in toluene (20 mL). The reaction mixture was slowly warmed to ambient temperature and then was heated under reflux for 4 h. The volatiles were removed under reduced pressure, hexane (10 mL) was added to residue and the solution obtained was stored at −20 °C overnight. The solid formed was filtered off and dried under vacuum. The compound **4** was obtained as a yellowish solid (0.89 g, 82%).

^{1}H NMR (400.130 MHz, $CDCl_3$, δ, ppm) 8.19 (s, 2H, CH=N), 7.53-7.48 (m, 4H, ArH), 7.42-7.35 (m, 2H, ArH), 7.32-7.28 (m, 2H, ArH), 7.14-7.08 (m, 4H, ArH), 6.82-6.78 (m, 4H, ArH), -1.08 (s, 3H, AlMe). ^{13}C{^{1}H} NMR (100.613 MHz, $CDCl_3$, δ, ppm) 167.21 (CH=N), 163.55 (ArCH), 161.39 (d, $^{1}J_{C\text{-}F}$ = 245.2 Hz, ArCH), 147.17 (d, $^{4}J_{C\text{-}F}$ = 2.9 Hz, ArCH), 135.53 (ArCH), 134.12 (ArCH), 125.06 (d, $^{3}J_{C\text{-}F}$ = 8.1 Hz, ArCH), 121.26 (ArCH), 119.97 (ArCH), 117.47 (ArCH), 115.52 (d, $^{2}J_{C\text{-}F}$ = 22.7 Hz, ArCH), -7.04 (AlMe). Anal. Calcd. for $C_{27}H_{21}AlF_2N_2O_2$: C 68.93, H 4.50, N 5.95; found: C 68.56, H 4.34, N 5.63.

Synthesis of Complex 5

At −60 °C the vinyl ether of 1,4-butanediol (0.22 mL, 1.84 mmol) was added dropwise to solution of complex **3** (0.80 g, 1.84 mmol) in toluene (20 mL). The reaction mixture was slowly warmed to ambient temperature and stirred for 3 days. The mixture was concentrated under reduced pressure and hexane (20 mL) was added to residue, the solution obtained was stored at −20 °C overnight. The solid formed was filtered off and dried under vacuum. The compound **5** was obtained as a yellowish solid (0.81 g, 82%).

^{1}H NMR (400.130 MHz, $CDCl_3$, δ, ppm) 8.34 (s, 2H, 2CH=N), 7.65-7.60 (m, 4H, ArH), 7.46-7.40 (m, 4H, ArH), 7.36-7.27 (m, 5H, ArH), 7.15-7.11 (m, 1H, ArH), 6.82-6.76 (m, 2H, ArH), 6.65-6.60 (m, 2H, ArH), 6.39-6.32 (m, 1H, OCH=), 4.07-4.01 (m, 1H, =C(H)H), 3.93-3.88 (m,1H, =C(H)H), 3.30 (br s, 4H, 2OCH_2), 1.20 (br s, 2H, 2CH2), 1.06 (br s, 2H, 2CH_2). ^{13}C{^{1}H} NMR (100.613 MHz, $CDCl_3$, δ, ppm) 167.69 (CH=N), 163.71 (ArCH), 150.97 (ArCH), 135.35 (ArCH), 133.80 (ArCH), 128.61 (ArCH), 126.54 (ArCH), 123.71 (ArCH), 121.14 (ArCH), 119.71 (ArCH), 117.50 (ArCH), 151.91 (OCH=), 85.91 (=CH_2), 68.07 (OCH_2), 62.22 (OCH_2), 25.35 (CH_2), 25.33 (CH_2). Anal. calcd. for $C_{32}H_{31}AlN_2O_4$: C 71.90, H 5.84, N 5.24; found: C 71.42, H 5.65, N 5.04.

Synthesis of Complex 6

At −60 °C the vinyl ether of 1,4-butanediol (0.21 mL, 1.17 mmol) was added dropwise to solution of complex **4** (0.80 g, 1.70 mmol) in toluene (20 mL). The reaction mixture was slowly warmed to ambient temperature and stirred for 3 days. The mixture was concentrated under reduced pressure and hexane (20 mL) was added to residue, the solution obtained was stored at −20 °C overnight. The solid formed was filtered off and dried under vacuum. The compound **6** was obtained as a yellowish solid (0.85 g, 88%).

^{1}H NMR (400.130 MHz, $CDCl_3$, δ, ppm) 8.31 (s, 2H, 2CH=N), 7.61-7.56 (m, 4H, ArH), 7.39-7.29 (m, 4H, ArH), 7.15-7.07 (m, 4H, ArH), 6.83-6.75 (m, 2H, ArH), 6.63-6.57 (m, 2H, ArH), 6.41-6.34 (m, 1H, OCH=), 4.01-4.06 (m, 1H, =C(H)H), 3.92-3.87 (m, 1H, =C(H)H), 3.34-3.25 (m, 4H, 2OCH_2), 1.26-1.17 (m, 2H, 2CH_2), 1.09-1.03 (m, 2H, 2CH_2). ^{13}C{^{1}H} NMR (100.613 MHz, $CDCl_3$, δ, ppm) 167.89 (CH=N), 163.69 (ArCH), 161.36 (d, $^{1}J_{C\text{-}F}$ = 245.5 Hz, ArCH), 147.01 (d, $^{4}J_{C\text{-}F}$ = 2.5 Hz, ArCH), 135.65 (ArCH), 133.92 (ArCH), 125.21 (d, $^{3}J_{C\text{-}F}$ = 8.3 Hz, ArCH), 121.11 (ArCH), 119.57 (ArCH), 117.74 (ArCH), 115.39 (d, $^{2}J_{C\text{-}F}$ = 22.4 Hz, ArCH), 151.89 (OCH=), 85.95 (=CH_2), 67.95 (OCH_2), 62.30 (OCH_2), 24.40 (CH_2), 25.30 (CH_2). Anal. Calcd. for $C_{32}H_{29}AlF_2N_2O_4$: C 67.36, H 5.12, N 4.91; found: C 67.03, H 4.85, N 4.64.

Ring-Opening Polymerization

The ring-opening polymerization of ε-caprolactone in bulk was carried out as follows ([monomer]/[initiator] = 300): 10 mL Schlenk tube equipped with a magnetic stirrer bar was charged by the initiator solution in dichloromethane 1.57 mL (1.57 × 10^{-4} mol of a 0.1 mol L^{-1} solution). After removing the solvent under vacuum ε-caprolactone (5 mL) was added to the reactor. Then, the reaction vessel was immersed into an oil bath preheated to 100°C. The ring-opening polymerization of D,L-lactide in bulk was carried out as follows ([monomer]/[initiator] = 100): 10 mL Schlenk tube equipped with a magnetic stirrer bar was charged by D,L-lactide (5.00 g) and the initiator solution in dichloromethane 3.47 mL (3.47 × 10^{-4} mol of a 0.1 mol L^{-1} solution) was added to the reactor. After removing the solvent under vacuum the reaction vessel was immersed into an oil bath

TABLE 1 Summary of Crystal Data for Compounds **4a, 4b, 4′**, and **6**

Compound	**4a**	**4b**	**6**	**4′**
Formula	$C_{27}H_{21}AlF_2N_2O_2$	$C_{27}H_{21}AlF_2N_2O_2$	$C_{32}H_{29}AlF_2N_2O_4$	$C_{78}H_{60}Al_4F_6N_6O_{12}$* 2$CHCl_3$
Formula weight	470.44	470.44	570.55	1733.98
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	P-1	P-1	$P2_1/n$	$P2_1/n$
a/Å	10.179(2)	9.9199(19)	16.248(5)	14.540(2)
b/Å	10.850(3)	10.973(2)	7.802(2)	25.262(4)
c/Å	11.388(3)	12.495(2)	22.784(7)	22.497(3)
α/°	71.836(3)	64.835(3)		
β/°	77.199(3)	66.905(3)	100.271(5)	95.814(2)
γ/°	71.192(3)	77.541(3)		
V/Å^3	1,120.9(4)	1130.5(4)	2,841.8(15)	8,221(2)
Z	2	2	4	4
D_c/g cm^{-3}	1.394	1.382	1.334	1.401
F(000)	488	488	1,192	3,552
Total reflections	11,617	8,895	19,881	68,215
Unique reflections	5,386 (R_{int} = 0.0204)	4,360 (R_{int} = 0.0246)	5,141 (R_{int} = 0.0668)	15,296 (R_{int} = 0.0453)
R_1 [$I > 2\sigma(I)$]	0.0366	0.0380	0.0660	0.1140
wR_2 (all data)	0.1105	0.0964	0.1678	0.3559
GOF	1.096	1.045	1.055	2.665

preheated to 130 °C. The block copolymerization of ε-caprolactone and D,L-lactide in bulk ([ε-caprolactone]/[initiator] = [D,L-lactide]/[initiator] = 50, was carried out as follows: 10 mL Schlenk tube equipped with a magnetic stirrer bar was charged by initiator solution in dichloromethane 9.45 mL (9.45×10^{-4} mol of a 0.1 mol L^{-1} solution). After removing the solvent under vacuum ε-caprolactone (5 mL) was added to the reactor. Then, the reaction vessel was immersed into an oil bath preheated to 130 °C. After 5 min from the beginning of polymerization D,L-lactide (5.00 g) was added to the reactor. After a predetermined time, ~0.3 mL aliquots were withdrawn from the flask and subjected to ^{1}H NMR spectroscopy and SEC to determine monomer conversion and molecular weight of the produced polymers, respectively. For the chain end analysis, the crude polymers were purified by re-precipitation from petroleum ether. The precipitated polymers were separated from the solution by centrifugation and dried in vacuum.

Single Crystal X-ray Diffraction Studies

Crystal data and details of X-ray analyses are given in Table 1. Experimental datasets were collected on Bruker SMART APEX II diffractometer using graphite monochromatized Mo-Kα radiation (λ = 0.71073 Å) at 173 K. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 (Ref. 32 with anisotropic thermal parameters for all nonhydrogen atoms (except disordered phenyl ring in **6** and disordered solvent chloroform molecules in **4′**). In the structure **4a** all hydrogen atoms were found from different Fourier synthesis and refined isotropically. In other three structures all hydrogen atoms were placed in calculated positions and refined using a riding model. Poor crystallinity of compound **4′** (very diffuse reflection peaks) resulted in high final *R* values.

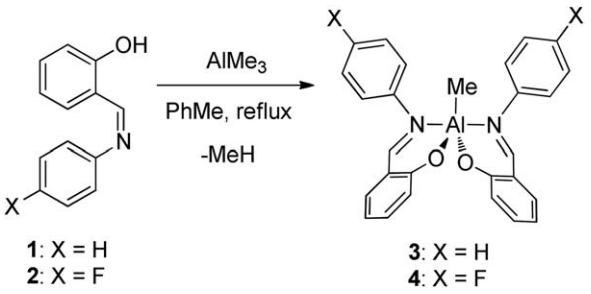
The crystallographic data for **4a, 4b, 4′**, and **6** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications (Supporting Information) under the CCDC numbers 970011-970014. They can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

RESULTS AND DISCUSSION

Synthesis and Solid State Structures

In this work we used the easily accessible iminophenols as ligands for synthesis of aluminum complexes. These compounds (**1, 2**) were obtained in reaction of salicylic aldehyde with corresponding amine in ethanol (for more detail see Experimental part, Supporting Information, Figs. S1 and S2). The introduction of fluorine substituent into imine group of ligand have been explained by the known from the literature higher catalytic activity in ROP of cyclic esters of the aluminum complexes containing electron withdrawing groups.[4,33]

The reaction of iminophenol ligands with $AlMe_3$ (2:1) results in corresponding methylaluminum complexes L_2AlMe (**3, 4**) in high yields. The gaseous methane is a sole byproduct in this reaction (Scheme 1). It should be noted that the complexes of above mentioned type are very rare in literature.[29(b)] The structure of complexes **3, 4** was established using ^{1}H and ^{13}C NMR spectroscopy (see Supporting Information, Figs. S3–S6). Both compounds have only one set of



SCHEME 1 Synthesis of aluminum complexes **3, 4**.

signals so in solution **3, 4** may be characterized as C_2 symmetric monomeric compounds.

Two crystal modifications of compound **4** (namely **4a** and **4b**) were investigated by X-ray diffraction analysis [Fig. 1(a)]. In both polymorphs, Al complexes are monomeric and have very similar geometric parameters [Fig. 1(b)].

In **4a**, aluminum atom has a slightly distorted trigonal bipyrimidal coordination ($\tau = 0.82$)[34] where oxygen atoms and methyl group occupy equatorial sites while nitrogen atoms are in axial positions. The aluminum atom is displaced by 0.0199(7) Å from the plane formed by equatorial atoms. Analysis of Cambridge Structural Database (CSD, version 5.34[35]) showed that Al-O distances in **4** are close to the average value found for salicylideneaminato-N,O compounds of five-coordinated aluminum (1.801 Å, 88 ref codes). However, Al-N bond lengths in **4** are significantly longer than the average value from CSD—2.015 Å. The latter may be caused by the fact that almost all salicylideneaminato complexes of Al with CN = 5 in CSD represent salen-type molecules with *cis* arrangement of nitrogen atoms. Complex **4b** is isostructural with unsubstituted compound **3**.[36]

It is known that aluminum complexes especially containing Al-C bonds are very sensitive to the traces of water. For example, solution of compound **4** ($CDCl_3$) is partially hydrolyzed under action of moisture at prolonged storage giving complex **4′** in a low yield (Scheme 2, Fig. 2). So in general for storage purposes organometallic aluminum compounds

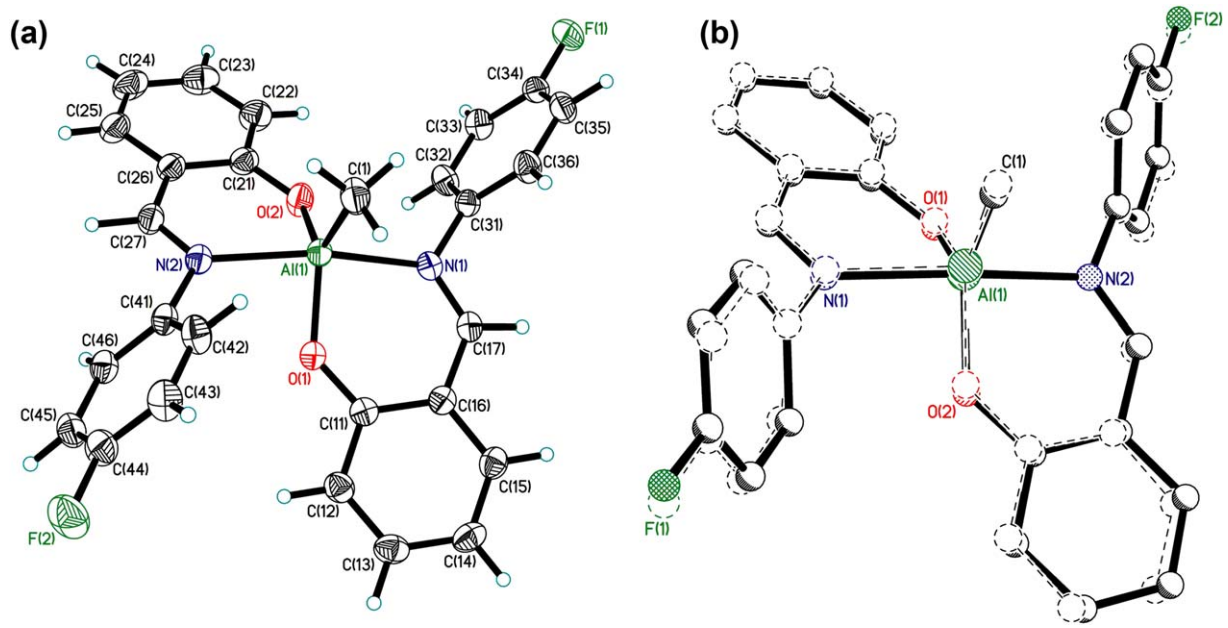
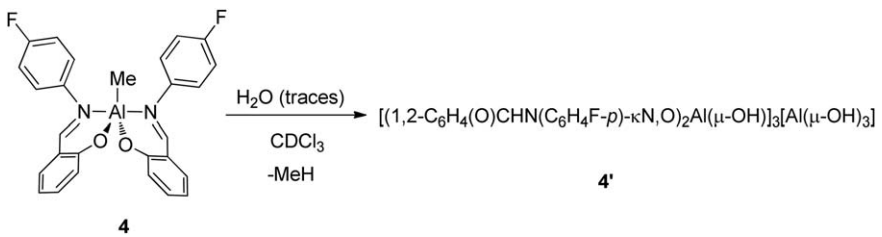


FIGURE 1 a. Molecular structure of complex **4a**. Displacement ellipsoids are drawn at 50% probability level. Selected bond lengths (Å) and angles (deg): Al(1)-O(2) 1.7724(11), Al(1)-O(1) 1.7808(10), Al(1)-C(1) 1.9580(15), Al(1)-N(1) 2.1085(12), Al(1)-N(2) 2.1098(12); N(1)-Al(1)-N(2) 164.98(5), O(2)-Al(1)-O(1) 121.36(5), O(2)-Al(1)-C(1) 118.54(6), O(1)-Al(1)-C(1) 120.06(6). b. Orthogonal least-squares fit of the molecules **4a** and **4b**. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



SCHEME 2 Synthesis of complex **4′**.

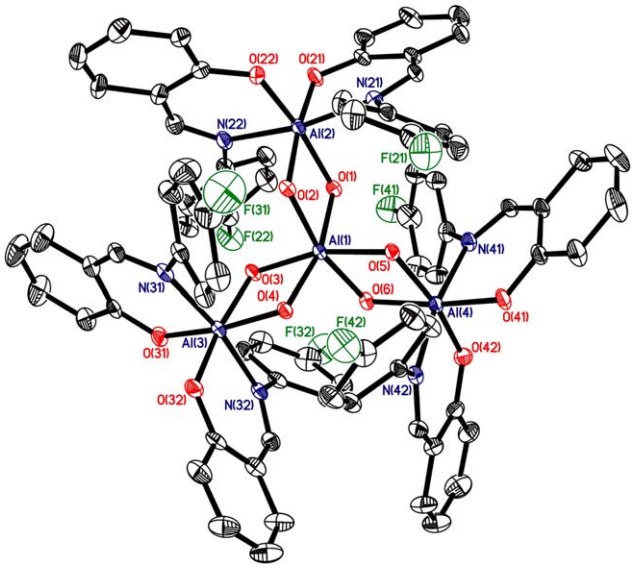


FIGURE 2 Molecular structure of complex **4′**. Hydrogen atoms and solvated chloroform molecule are omitted for clarity. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

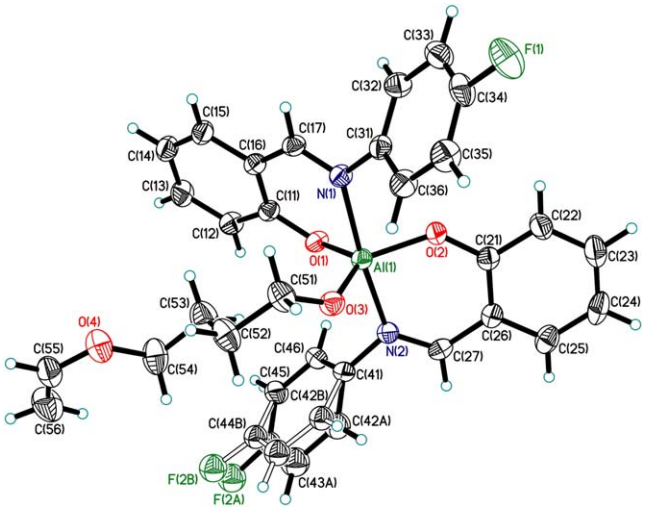


FIGURE 3 Molecular structure of complex **6**. Selected bond lengths (Å) and angles (deg): Al(1)-O(3) 1.724(3) Å, Al(1)-O(2) 1.770(3), Al(1)-O(1) 1.775(3), Al(1)-N(2) 2.043(3), Al(1)-N(1) 2.068(3); O(3)-Al(1)-O(2) 123.15(13), O(3)-Al(1)-O(1) 118.71(13), O(2)-Al(1)-O(1) 118.12(13), O(3)-Al(1)-N(2) 89.69(13), O(2)-Al(1)-N(2) 89.20(12), O(1)-Al(1)-N(2) 89.82(12), O(3)-Al(1)-N(1) 96.07(12), O(2)-Al(1)-N(1) 85.85(12), O(1)-Al(1)-N(1) 89.29(11), N(2)-Al(1)-N(1) 173.86(13). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

should be converted to alkoxides (see below) which are more stable to hydrolysis.

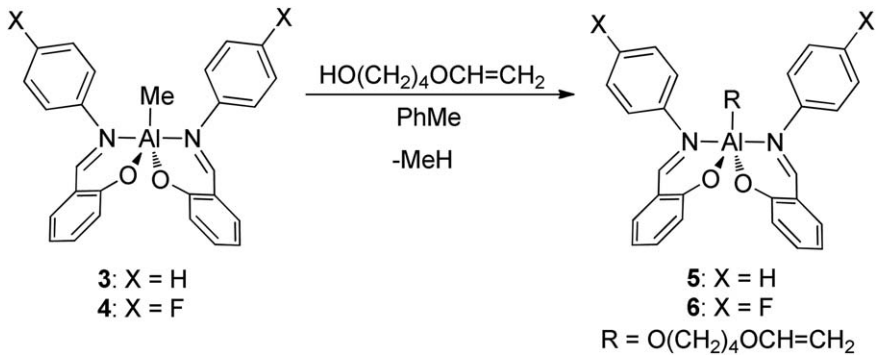
Complex **4′** contains four aluminum atoms and all of them have octahedral coordination ("Mitsubishi" like structure). The central atom is coordinated only by OH- groups with average Al-O bond length Al(1)-O(μ) = 1.888(4) Å. Each peripheral aluminum atom is coordinated by two bridging OH-groups and two salicylaldiminate ligands with trans arrangement of N atoms (average value of angle N-Al-N is 171.0(2)°, average value of bond length Al-N is 2.137(4) Å).

The complexes **5, 6** modified with unsaturated alcohol were prepared by reaction of corresponding methyl complexes (**3, 4**) with one equivalent of $HO(CH_2)_4OCH{=}CH_2$ (Scheme 3). The gaseous methane is a sole byproduct in this reaction, so the target compounds were isolated in high yields.

The structures of the complexes **5, 6** were established using ^1H and ^{13}C NMR spectroscopy (see Experimental part; Supporting Information, Figs. S7–S10). In solution these complexes, similarly to compounds **3, 4**, have one set of signals and, therefore, may be characterized as C_2-symmetric compounds. The molecular structure of **6** in solid state was investigated by X-ray analysis (Fig. 3).

It is established that complex **6** is monomeric in solid state. The aluminum atom has a distorted trigonal bipyramidal coordination (τ = 0.85). The oxygen atoms of iminophenol ligand and unsaturated alkyloxo ligand are situated in equatorial plane. Of interest, Al-O(3) bond length with alkyloxo substituent is noticeably shorter than Al-O distances associated with iminophenol ligands.

On the other hand, the Al-O(3)-C(51) angle is quite large with 134.0(2)°. These facts indicate the noticeable degree of π-donation from the equatorial alkyloxo ligand towards the



SCHEME 3 Synthesis of aluminum complexes **5, 6**.

TABLE 2 Ring-Opening Polymerization of ε-Caprolactone Initiated by **5** and **6** at Different Temperatures in Bulk[a]

Initiator	T (°C)	Time (min)	Conv. (%)	$M_{n,\ theor}$[b] (g mol^{-1})	$M_{n,\ NMR}$[c] (g mol^{-1})	$M_{n,\ SEC}$[d] (g mol^{-1})	M_w/M_n	F_n[e] (%)	N[f]
5	80	60	48	16,530	19,500	17,200	1.11	86	1.0
		100	85	29,190	34,750	29,300	1.31	92	1.0
	100	15	28	9,690	13,600	12,550	1.11	90	0.8
		60	91	31,240	39,600	32,700	1.55	100	1.0
	130	15	45	15,500	20,100	17,400	1.08	50	0.9
		30	100	34,300	30,700	23,000	1.81	62	1.5
6	80	30	19	6,610	8,200	7,350	1.16	64	0.9
		120	64	22,000	–	24,600	1.41	–	0.9
	100	15	39	13,450	18,300	17,700	1.21	82	0.8
		60	78	26,790	–	27,500	1.52	–	1.0
	130	15	51	17,560	13,110	12,600	1.15	65	1.4
		60	89	30,550	22,000	19,400	1.45	56	1.6

[a] Conditions: Initiator:[**5**] = [**6**] = 31.5 mM; [CL]/[initiator] =300.
[b] M_n(theor) = [CL]/[initiator] × 114 × Conv.+115.
[c] Determined from ^{1}H NMR data as follows: M_n = I(**j**)/I(**k**) ×114+115, see Figure 6 for assignments.
[d] Experimental molecular weight determined by SEC versus polystyrene standards and corrected by a factor 0.52.[22(c)]
[e] Calculated from ^{1}H NMR spectra as follows: F_n = 2I(**c**)/I(**k**) ×100, see Figure 6 for assignments.
[f] Number of polymer chains per catalyst molecule, calculated as N = M_n(theor)/M_n(exp).

aluminum centre. The same features were previously reported for some closely related monomeric salen Al compounds.[37] In general, the structures **4** and **6** are very similar and their main geometrical parameters differ insufficiently. In **6**, one phenyl ring is rotationally disordered over two positions with occupancy ratio 0.53/0.47.

Ring-Opening Polymerization

The complexes **5** and **6** were tested in the homopolymerization of CL and LA as well as in their block copolymerization in bulk at different monomer to initiator ratios and temperatures.

Polymerization of ε-Caprolactone

In a preliminary series of experiments, the effect of temperature on ROP of ε-caprolactone with complexes **5** and **6** on the reaction rate and the properties of obtained polymers at monomer to initiator ratio of 300/1 mol/mol was briefly investigated. Both the catalysts studied showed high activity toward ROP of CL, while the catalysts activity increased upon temperature increase (Table 2). The catalytic activity depends on the substituent on the imine nitrogen: initiator containing unsubstituted phenyl group on imine nitrogen (**5**) showed much higher activity in comparison with complex **6** possessing electron acceptor *p*-F-C_6H_4 substituent (Table 2, Fig. 4). In contrast, an opposite effect of electron withdrawing substituents in aryl group of imine nitrogen on catalysts activity in ROP of CL and LA was observed for $LAlMe_2$ complexes activated by corresponding alcohol.[4,29(d,e)]

The molecular weight distribution (MWD) of the polyesters obtained was relatively narrow ($M_w/M_n \leq 1.2$) up to 60 to 80% of monomer conversion but broadening at higher monomer conversions up to values 1.3 to 1.8 (see Table 2, Supporting Information Fig. S11). The number-average molecular weight (M_n) increased with increasing monomer conversion and good correlation between experimental and theoretical values (calculated assuming that each initiator molecule gives one polymer chain) of M_n were observed for polymerizations performed at 80 °C and 100 °C, respectively [Table 2, Fig. 5(b) and Supporting Information Fig. S11]. In addition, the number of chains per initiator molecule (N) for polymerization ran at 80 °C and 100 °C is close to 1 (Table 2) indicating that ROP of CL proceeded with near

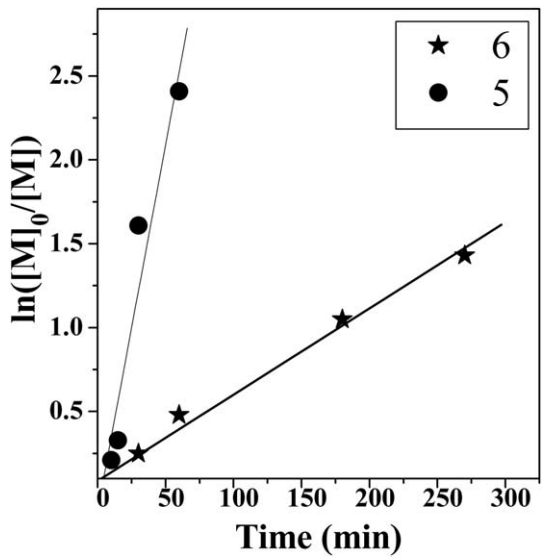


FIGURE 4 Ln($[M]_0/[M]$) versus time plots for the bulk polymerization of ε-caprolactone in the presence of catalytic complexes **5** and **6** at 100 °C; Initiator: [**5**]= [**6**]= 31.5 mM; [CL]/[initiator] = 300 mol/mol.

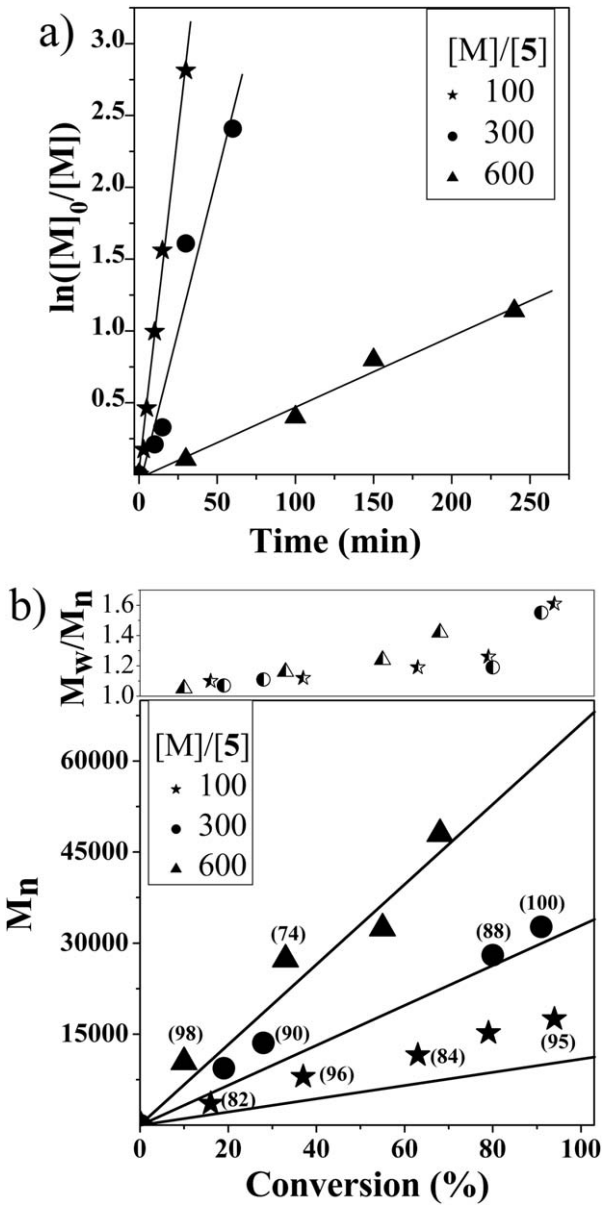


FIGURE 5 (a) Ln($[M]_0/[M]$) versus time and (b) M_n versus conversion plots for the bulk polymerization of ε-caprolactone initiated by complex **5** at different $[M]/[\mathbf{5}]$ ratios at 100 °C. Initiator concentrations: $[\mathbf{5}]$ = 94.5 mM ($[M]/[\mathbf{5}]$ = 100), 31.5 mM ($[M]/[\mathbf{5}]$ = 300), and 15.7 ($[M]/[\mathbf{5}]$ = 600). The values in parentheses are the content of vinyl ether end groups (F_n).

quantitative initiator efficiency as well as that monomeric catalytic complexes acted as initiators under bulk polymerization conditions. The monomeric structure for complexes **5** and **6** both in solution and solid state was established by ^{1}H, ^{13}C NMR and crystallographic analysis, respectively (see above). At higher polymerization temperature (130 °C), the considerable deviation of experimental values of M_n from calculated ones (Table 1, Supporting Information Fig. S11) as well as significant broadening of MWD were observed for both of catalysts suggesting that inter- and/or intramolecular transesterification of the polymer chain operated under these conditions. The considerably higher than 1 values of N for polymerization ran at 130 °C also confirmed that side reactions took place at such conditions. Taking into account these results, we can conclude that optimal reaction temperature to conduct bulk controlled ROP of CL lies between 80 °C and 100 °C.

To confirm the controlled nature of polymerization, we further investigated the ROP of ε-caprolactone initiated by complex **5** at different $[CL]/[\mathbf{5}]$ ratios. The first-order plots $\ln([M]_0/[M])$ versus time shown in Figure 5(a) were linear and started at the origin for all $[CL]/[\mathbf{5}]$ ratios. The number-average molecular weights of the polymers increased with monomer conversion and were inversely proportional to initiator concentration [Fig. 5(b)]. The experimental M_n values were very close to the calculated ones assuming that each catalyst molecule generates one polymer chain [Fig. 5(b)] excepts the ratio $[M]/[\mathbf{5}]$ = 100, where the experimentally determined M_ns were slightly exceed theoretical line that may be associated with aggregation of catalyst at its high concentrations. In addition, MWD of obtained polymers was quite narrow ($M_w/M_n \leq 1.2$) up to high conversions of monomer and broadened up to 1.6 at complete conversion, where the transesterification reactions became predominant [Fig. 5(b)]. These results confirm that **5** initiates the controlled ROP of ε-caprolactone in bulk to afford well-defined poly(ε-caprolactone)s with controlled molecular weight ($M_n \leq$ 50,000 g mol^{-1}) and relatively narrow MWD ($M_w/M_n \leq$1.2 up to 80% of monomer conversion).

The effectiveness of catalysts **5** and **6** in the synthesis of poly(ε-caprolactone) macromonomers was then estimated. As shown in Table 2, catalytic complex **5** afforded polyesters with higher functionality at the chain end in comparison with catalyst **6**. For both of the catalysts, the higher content of vinyl ether end groups was observed for polymerization experiments performed at 100 °C (F_n = 80–100%), whereas at 130 °C the functionality decreased up to 50% (Table 2). The applicability of catalyst **5** for the synthesis of macromonomers with predictable molecular weight was further investigated. As shown in Table 2, Figure 5, and Supporting Information Figure S12, poly(ε-caprolactone)s with controlled molecular weight in a range between 4500 g mol^{-1} and 30,000 g mol^{-1} with high content of vinyl ether end groups were successfully synthesized via ROP of CL with catalyst **5** by varying $[CL]/[\mathbf{5}]$ ratios from 25:1 to 300:1.

The presence of vinyl ether end groups was confirmed by ^{1}H NMR spectroscopy (Fig. 6), where the well resolved characteristic peaks of protons of vinyl group appeared at 6.47 ppm (CH_2=C<u>H</u>–O–, **c**) and 3.75 ppm (CH_2=CH-O-C<u>H_2</u>-, **d**), respectively, while the resonance of hydroxymethylene end group (**k**) appeared at 3.65 ppm. The signals of CH_2 protons of vinyl ether end group (<u>CH_2</u>=CH-O-CH_2-, **a, b**) and –C<u>H_2</u>–OC(O)– (**e**) are located in a region between 3.9 and 4.2 ppm[7] and overlapped with the signals of main chain protons (**j**). No signals of other end groups were detected in ^{1}H NMR spectrum.

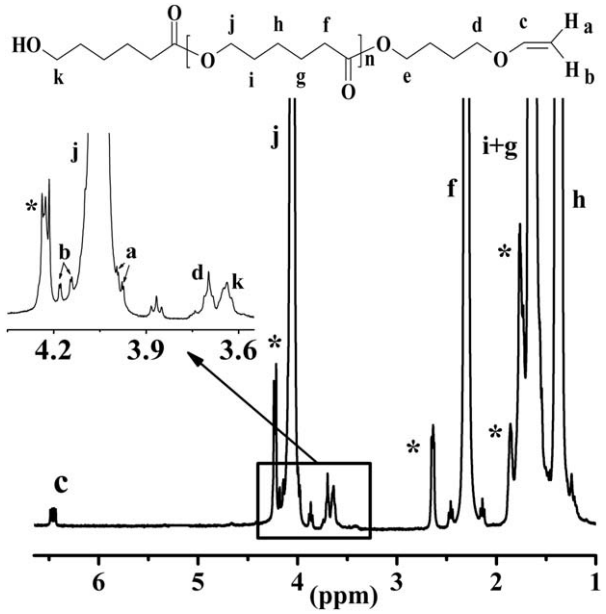


FIGURE 6 ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of poly(ε-caprolactone) synthesized with initiator **5** at 100 °C and at [CL]/[**5**] = 300, [**5**] = 31.5 mM. The signals labeled by asterisks correspond to ε-caprolactone residue.

In summary, ROP of ε-caprolactone using complex **5** as initiator represents an efficient approach towards synthesis of macromonomers with high content of vinyl ether end groups (F_n > 80–100%) in a broad range of molecular weight (M_n = 1000–30,000 g mol^{-1}) with relatively narrow MWD (M_w/M_n = 1.1–1.5).

Polymerization of D,L-Lactide

The activity of catalysts **5** and **6** in ROP of D,L-lactide in bulk at 130 °C was then explored (Table 3). Similarly to polymerization of ε-caprolactone (see Fig. 4), catalyst **5** induced faster polymerization of D,L-lactide as compared with **6**: the rate constants ($k_{p\ app}$s) under the same polymerization conditions were 10.8 × 10^{-2} s^{-1} and 5.0 × 10^{-2} s^{-1}, respectively (Supporting Information Fig. S13).

Interestingly, much higher difference (ca. 1 order of magnitude) in the activity of these catalytic complexes was observed in the case of ROP of CL: $k_{p\ app}$s were 4.4 × 10^{-2} s^{-1} and 5.1 × 10^{-3} s^{-1} for catalysts **5** and **6**, respectively (Fig. 4). This observation indicates that the monomer nature has a significant influence on the relative activity of catalysts.[29(c)] According to Table 3, both of the catalysts initiated controlled ROP of D,L-lactide affording polymers with controlled molecular weight and relatively narrow MWD and high content of vinyl ether end groups (F_n = 87–100%). In contrast to polymerization of CL, the number of polymer chains (N) for polymerization of LA is close to 1 only at moderate monomer conversions indicating that initiation (or the insertion of the first monomer unit) is relatively slow in comparison with the propagation (Table 3).

The ROP of D,L-lactide with **5** as initiator was investigated at three different monomer/initiator ratios ([M]/[**5**] = 100, 300, 600) in order to examine the livingness of the process as well as the possibility to synthesize the macromonomers with high molecular weight. As shown in Figure 7(a), the first-order plots were linear, but the reaction was accompanied by induction period, which was decreased with increasing of complex concentration. Since the corresponding catalytic complex is monomeric in solution and in solid state, the observed induction period can be explained by slow coordination of the first monomer molecule or with structural rearrangement of the catalyst giving the "true" active species.[23(c,e),38] The number-average molecular weight of the obtained polymers increased in direct proportion to monomer conversion for all [M]/[**5**] ratios studied and experimental values of M_n were in good agreement with calculated

TABLE 3 Ring-Opening Polymerization of D,L-Lactide Initiated by **5** and **6** in Bulk at 130 °C[a]

Initiator	Time (min)	Conv. (%)	$M_{n,\ theor}$[b] (g mol^{-1})	$M_{n,\ NMR}$[c] (g mol^{-1})	$M_{n,\ SEC}$[d] (g mol^{-1})	M_w/M_n	F_n[e]	N[f]
5	3	6	980	6,400	4,800	1.12	100	0.2
	5	51	7,460	10,100	7,420	1.12	98	1.0
	10	78	11,350	14,400	10,270	1.34	94	1.1
	15	87	12,640	16,300	13,500	1.30	92	1.0
	30	97	14,080	21,620	16,200	1.61	99	0.9
6	1	9	1,410	1,700	2,200	1.02	95	0.7
	5	27	4,000	6,500	7,400	1.10	93	0.6
	30	84	12,200	14,850	10,790	1.32	87	1.1
	60	95	13,800	15,750	12,990	1.39	89	1.1

[a] Conditions: [D,L-LA]/[initiator] = 100; [**5**] = [**6**] = 90 mM.
[b] M_n(theor) = [D,L-LA]/[initiator] ×144×Conv.+115.
[c] Determined using ^{1}H NMR spectroscopy as M_n = I(**g**)/I(**h**) × 72 + 115, see Figure 8 for assignments.
[d] Experimental molecular weight determined by SEC versus polystyrene standards and corrected by a factor 0.58.
[e] Calculated from ^{1}H NMR spectra as follows: F_n = I(**c**)/I(**h**) × 100, see Figure 8 for assignments.
[f] Number of polymer chains per catalyst molecule, calculated as N = M_n(theor)/M_n(exp).

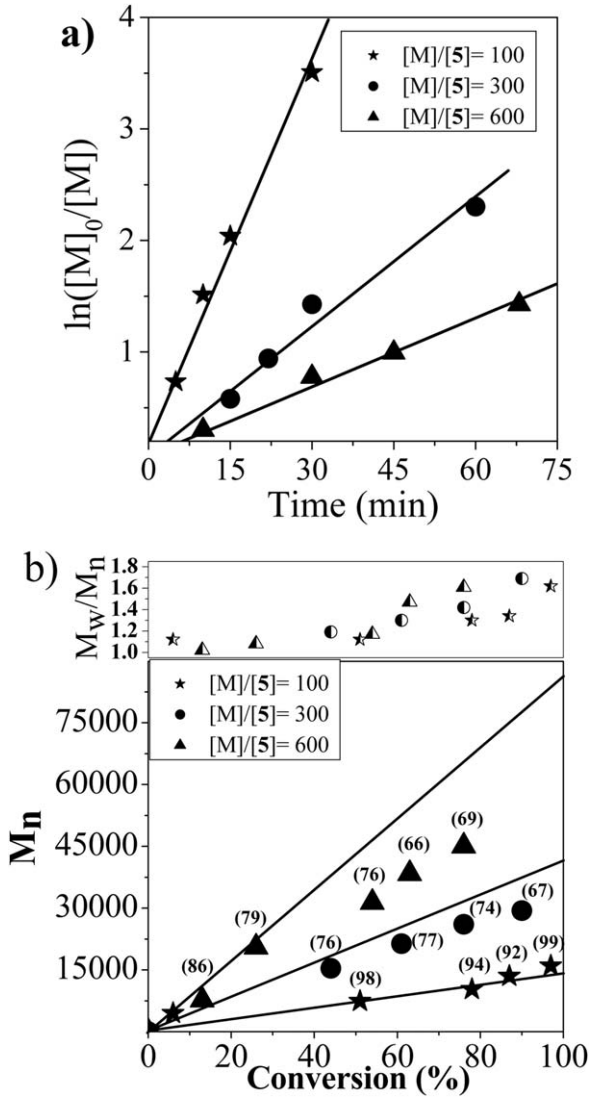


FIGURE 7 (a) Ln([*M*]$_0$/[*M*]) versus time and (b) M_n versus conversion plots for the bulk polymerization of D,L-lactide initiated by complex **5** at different [*M*]/[**5**] ratios at 130 °C. Initiator concentrations: [**5**] = 90 mM ([*M*]/[**5**] = 100), 30 mM ([*M*]/[**5**] = 300) and 15 mM ([*M*]/[**5**] = 600). The values in parentheses are the content of vinyl ether end groups (F_n).

ones for [*M*]/[**5**] ratios of 100/1 and 300/1 [Fig. 7(b)]. However, for higher [*M*]/[**5**] ratio the experimental M_ns deviated from theoretical line, while MWD broadened even at moderate monomer conversions indicating that inter- and/or intramolecular transesterification were significant for this particular monomer to initiator ratio. MWD values were relatively narrow ($M_w/M_n \leq 1.2$) up to high monomer conversions only for ROP of LA at low [*M*]/[**5**] ratios [Fig. 7(b)]. The high functionality (content of vinyl ether end groups) was also observed only for [*M*]/[**5**] ratio of 100/1 [Fig. 7(b)], while for ROP of CL F_n was high (90–100%) up to [*M*]/[**5**] ratio of 300/1 [Fig. 5(b)]. The poorer control over functionality, molecular weight, and molecular weight distribution at high [*M*]/[**5**] ratios in ROP of LA as compared with CL can be explained by the necessity to conduct the polymerizations at higher temperature for the former monomer.

The high content of vinyl ether end groups for poly(D,L-lactide)s synthesized using **5** as initiator at [*M*]/[**5**] = 100 in bulk at 130 °C is also confirmed by ^{1}H NMR spectroscopy (Fig. 8). As it is evidenced from ^{1}H NMR spectrum, almost all macromolecules possessed vinyl ether (signals **d, b, a, e** and **c** at 3.71, 4.0, 4.17, 4.20, and 6.47 ppm, respectively) and hydroxymethine (resonance at 4.36 ppm, **h**) end groups, respectively.

In order to estimate stereospecificity of catalyst **5** in ROP of D,L-lactide, the homonuclear decoupled ^{1}H NMR spectra of representative samples of poly(D,L-lactide) were recorded (Supporting Information Fig. S14). The peaks were assigned to appropriate tetrads in accordance with the literature data.[39]

According to Supporting Information Figure S14, almost no dependence of the microstructure of synthesized polymers on the substituents in the imine nitrogen was observed: slightly prevailing isotactic poly(lactide)s were obtained with both of catalysts studied here. We supposed that conducting the polymerization at lower temperature can improve the stereoregulation during the ROP of D,L-lactide.[22(g),24(e),28(c)] However, no significant differences were observed in homonuclear decoupled ^{1}H NMR spectra of poly(lactide)s synthesized at 130 °C in bulk and at 70 °C in toluene (Supporting Information Fig. S14). These data are consistent with known low efficiency of aluminium complexes with bidentate ligands towards stereocontrolled ROP of D,L-lactide.[4,28(c),29(e)]

Thus, ROP of D,L-lactide with **5** as initiator allowed to synthesize well-defined macromonomers ($M_n \leq 15{,}000$ g mol^{-1}) with high content of vinyl ether end groups (F_n = 90–100%)

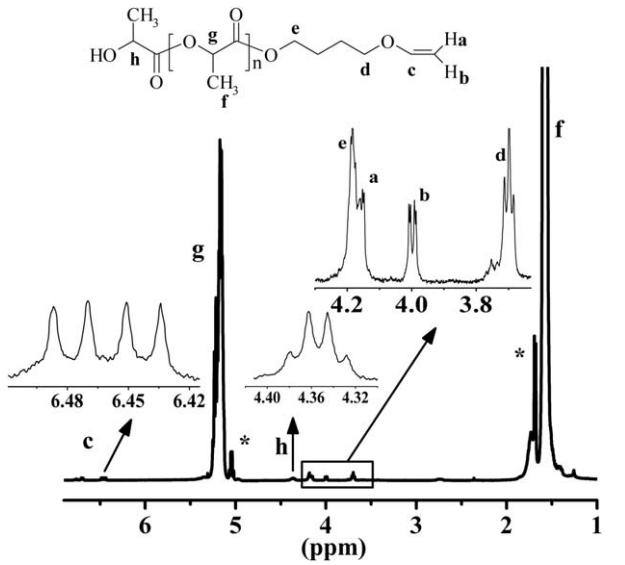


FIGURE 8 ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of poly(D,L-lactide) synthesized with initiator **5** at 130 °C and at [LA]/[**5**] = 100, [**5**] = 90 mM. The signals labeled by asterisks correspond to D,L-lactide residue.

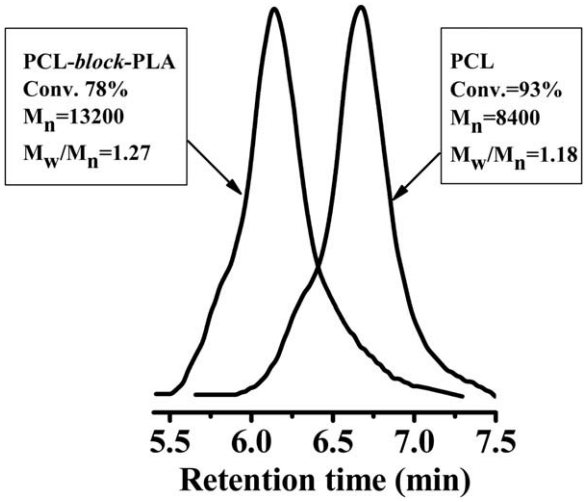


FIGURE 9 SEC traces for (a) poly(ε-caprolactone) prepolymer and (b) poly(ε-caprolactone)–block–poly(D,L-lactide) synthesized with **6** as initiator in bulk at 130 °C: [**6**] = 189 mM; [CL]/[**6**] = [LA]/[**6**] = 50/1 mol/mol.

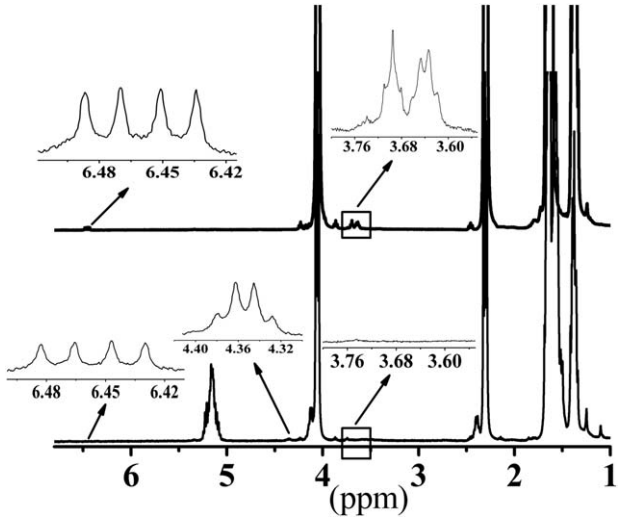


FIGURE 10 ^{1}H NMR spectrum of poly(ε-caprolactone)–*block*–poly(D,L-lactide) synthesized with **6** in bulk at 130 °C: [**6**] = 189 mM; [CL]/[**6**] = [LA]/[**6**] = 50/1 mol/mol.

and relatively narrow MWD ($M_w/M_n \leq 1.2$ up to 80% of monomer conversion).

Synthesis of Block Copolymers

We have also briefly investigated the efficiency of iminophenolate aluminum complexes **5** and **6** in the synthesis of macromonomers based on copolymers of CL and LA. Block copolymer of PCL and PLA was synthesized via sequential ROP of CL and LA in bulk at 130 °C. To retain the high functionality at such high polymerization temperature, the low monomer to initiator ratios were used [CL]/[initiator] = [LA]/[initiator] = 50/1. In a first series of experiments we used complex **5** as initiator in the synthesis of block copolymer. However, both the poly(ε-caprolactone) prepolymer as well as the resulting block copolymer had considerably higher molecular weight than theoretical one and relatively broad MWD (Supporting Information Fig. S15). These results can be explained by the possible partial aggregation of catalytic complex **5** at such high its concentration (189 mM) that leads to relatively low initiator efficiency. In addition, the polymerization is considerably faster with complex **5** as compared with **6** resulting in almost instantaneous consumption of CL. As we showed above, the side reactions become important under monomer starved conditions that leads to observed broadening of MWD (Supporting Information Fig. S15).

Taking into account that **6** induced slower polymerization of CL and LA and allowed to synthesize polyesters with narrower MWD (see Table 3), we therefore tested this catalytic complex in the synthesis of block copolymer of PCL and PLA. As shown in Figure 9, the poly(ε-caprolactone) prepolymer with M_n slightly higher than theoretical one (M_n(theor) = 5400 g mol^{-1}) and narrow MWD (M_w/M_n = 1.18) was successfully formed. According to ^{1}H NMR spectroscopy the content of vinyl ether end group was 94% (Fig. 10).

Upon the addition of LA the molecular weight increased to 13,200 g mol^{-1}, the SEC curves shifted to high molecular weight region, while MWD remained relatively narrow (M_w/M_n = 1.27) (Fig. 9). In addition, on the ^{1}H NMR spectrum the signal of hydroxymethylene protons (–CH_2–OH) of PCL prepolymer at 3.65 ppm disappeared completely and a new signal at 4.36 ppm corresponding to methine protons of –CH(CH_3)OH end group was appeared (Fig. 10). The content of vinyl ether end groups for block copolymer (under nonoptimized experimental conditions for the synthesis of block copolymers) was however relatively low (F_n = 54%). In other words, chain extension experiments as well as ^{1}H NMR spectroscopy confirm the formation of true block copolymer PCL-block-PLA containing vinyl ether end groups. It should be noted, however, that SEC traces of both the poly(ε-caprolactone) prepolymer as well as the resulting block copolymer are not symmetrical and displayed shoulders in the high molecular weight (both PCL and PCL-block-PLA) and low molecular weight regions (PCL-block-PLA) (Fig. 9). The shoulder in low molecular weight region for block copolymer probably corresponds to the fraction of "dead" cyclic macromolecules formed predominantly under monomer starved conditions (*vide supra*). The appearance of shoulder in high molecular weight region can be explained by the possible dimerization or trimerization of synthesized macromonomers (*vide infra*).

As shown above, iminophenolate aluminum complexes **5** and **6** allowed to synthesize macromonomers of CL and LA as well as their copolymers with controlled molecular weight up to M_n = 30,000 g mol^{-1}, relatively narrow molecular weight distribution and high content of vinyl ether end groups (>85%) under bulk polymerization conditions. However, to estimate the real efficiency of these catalysts towards synthesis of well-defined macromonomers, the several points should be clarified. First of all, as it is evident from Tables 2 and 3, the molecular weight determined by NMR ($M_{n,\ NMR}$) is

higher (especially for high [*M*]/[initiator] ratios) than one determined by SEC ($M_{n,\ SEC}$). This difference, according to Deivasagayam and Peruch,[22(g)] is consistent with the occurrence of intermolecular transesterification side reaction leading to the formation of cyclic oligomers. Indeed, the calculation of $M_{n,\ NMR}$ is based on the signals of terminal –CH_2–OH and –CH(CH_3)–OH groups for PCL and PLA, respectively (see Figs 6 and 8 for details), but these end groups are absent in cyclic oligomers that leads to observed overestimation of molecular weight. The second question is the lower than quantitative content of vinyl ether end groups (Tables 2 and 3, Figs. 5 and 7), which was also reported for the ε-caprolactone oligomerization with Ti[OCH_2(-CH_2)$_4$OCH=CH_2]$_4$ as initiator.[8] Based on the coordination-insertion mechanism, theoretically all macromolecules synthesized via ROP of CL and LA with L_2AlOCH_2(-CH_2)$_4$OCH=CH_2 as initiator should contain one hydroxyl group and one vinyl ether end group even if transesterification side reactions accompanied the polymerization. The formation of cyclic acetals from hydroxyvinyl ether[40] or probably from synthesized macromonomers as possible side reaction leading to consumption of vinyl ether end groups was reported by Iojoiu et al.[7] However, this reaction would also lead to disappearance of one vinyl ether end group and simultaneously one hydroxyl end group,[7,38] that is, the functionality calculated from ^{1}H NMR spectra based on the chain end signals should be theoretically 100%. In our opinion the decrease of the content of vinyl ether end groups can be explain by the partial hydrolysis of L_2Al–OR by adventitious water with the formation of L_2Al–OH/[L_2Al]$_2$O[22(c)] or species related to above presented **4′**, which will give α-hydroxyl-ω-(carboxyl acid) instead of α-hydroxyl-ω-(vinyl ether) polyesters after monomers insertion. The hydrolysis would be more pronounced at higher temperatures that is consistent with the experimental data: the content of vinyl ether end groups decreased with increasing the temperature (Table 2). In addition, the decrease the initiator concentration would also facilitate the hydrolysis. Indeed, ^{1}H NMR spectrum of poly(D,L-lactide) synthesized at high [LA]/[initiator] ratio showed a broad signal at 13.1 ppm, which can correspond to carboxyl acid terminal group (Supporting Information Fig. S16). Another process leading to consumption of vinyl ether end groups can be dimerization or trimerization of synthesized macromonomers due to the extremely high reactivity of vinyl ethers in the cationic polymerization even in the presence of weak Lewis acids or protic impurities.[41] An indirect proof of occurrence of such side reaction can be the appearance of shoulder in SEC curves in high molecular weight region (see for example Fig. 9).

CONCLUSIONS

Here we reported the comprehensive investigation of the synthesis and structure of the aluminum complexes containing two iminophenolate ligands (L_2AlMe and L_2AlOCH_2 (CH_2)$_4$OCH=CH_2) and their reactivity in ring-opening homo- and copolymerization of ε-caprolactone and D,L-lactide in bulk. The corresponding methyl complexes **3** and **4** were synthesized by the reaction of $AlMe_3$ with two equivalents of substituted (both previously reported and new) iminophenols. These complexes reacted with high yields with HO(CH_2)$_4$OCH=CH_2 giving the catalysts **5, 6**. It was established by ^{1}H, ^{13}C NMR, and X-ray that these complexes are monomeric in solution and in solid state. The catalytic activity of these complexes in ROP of CL and LA depends on the substituent on the imine nitrogen: initiator containing unsubstituted phenyl group on imine nitrogen (**5**) showed much higher activity in comparison with complex **6** possessing electron acceptor *p*-F-C_6H_4 substituent. Both of these compounds (**5** and **6**) initiated controlled ROP of CL and LA affording poly(ester)s with high content of vinyl ether end groups (F_n > 80–100%) in a broad range of molecular weight (M_n = 4500–30,000 g mol^{-1}) with relatively narrow MWD (M_w/M_n = 1.1–1.5). The complex **6** was also used for the synthesis of macromonomers based on block copolymers of CL and LA. The synthesized macromonomers can be copolymerized with maleic anhydride and other monomers to give a series of new graft copolymers with hydrophilic backbone and hydrophobic PCL side chains for drug delivery.

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