

Titanium complexes supported by bis(aryloxo) ligand: Structure and lactide polymerization activities

Jolanta Ejfler, Michał Kobyłka, Lucjan B. Jerzykiewicz, Piotr Sobota*

Faculty of Chemistry, University of Wrocław, 14 F. Joliot-Curie, 50-383 Wrocław, Poland

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Abstract

Titanium bis(aryloxo) complexes, $[\text{Ti}_2(\mu\text{-OEt})_2(\text{edbp})_2(\text{OEt})_2]$ (**1**) and $[\text{Ti}(\text{edbp})(\text{O}^i\text{Pr})_2]$ (**2**) ($\text{edbp-H}_2 = 2,2'$ -ethylidenebis(4,6-di-*tert*-butylphenol)) have been prepared and characterized. It was shown that compounds **1** and **2** were efficient initiators in a process of ring-opening polymerization (ROP) of cyclic esters. The catalytic behavior of complexes **1** and **2** in the polymerization of L- and rac-lactide (L-LA and rac-LA) was studied in toluene at 70 °C with a monomer to initiator ratio fixed at 100. The dimeric complex **1** initiated polymerization of lactide in 90% conversion within 2.5 h to afford polylactide (PLA) with M_n of 17,500 and PDI of 1.06. The parameters of PLA obtained with the monomeric complex **2** were similar ($M_n = 18,000$, PDI = 1.08). Microstructures of polymers obtained from rac-LA for both initiators were assigned as heterotactic. © 2006 Elsevier B.V. All rights reserved.

Keywords: Bis(aryloxo) complexes; Lactides; Polymerization; Titanium

1. Introduction

The development of biodegradable polymers as resorbable biomaterials and commodity thermoplastics from renewable resources has received significant attention [1]. Synthetic routes to these polyesters generally employ main group alkoxides [2] and recently transition metal compounds to effect the controlled ring-opening polymerization (ROP) of cyclic esters [3]. Enantiomerically pure or racemic chiral metal alkoxide initiators have enabled the preparation of isotactic, stereoblock polylactides (PLA) from rac-LA presumably via enantiomorphic site control (ESC). The ROP of rac-LA using achiral metal alkoxide complexes generally favors heterotactic PLA via chain-end control (CEC). The commercial utility of polyesters and particularly as potential environmentally friendly replacement for bioresistant polymers such as polyolefin indicate that further research in this area is valuable, both for searching new effective initiators and for improving synthetic methods.

Titanium complexes with various chelating bis(aryloxo) ligands have been noticed as highly active catalyst precursors for olefin polymerization as well as initiators for ROP of cyclic esters [4]. Additionally titanium alkoxides are attractive initiators in ROP reactions because its low toxicity minimizes

concerns regarding the presence of these compounds in commercial PLA products. Up to now only few examples of bis(aryloxo) titanium compounds having sulfur-, methylene- or tellurium-bridged chelating bis(aryloxo) ligands have been reported as initiators for living polymerization of lactides [5]. We expected that such effects of the chelating bis(aryloxo) ligands with additionally alkoxo activation groups on the metal site could be also observed in polymerization of the cyclic esters.

We have recently been interested in revealing the catalytic properties of bis(aryloxo) titanium complexes having 2,2'-ethylidenebis(4,6-*tert*-butylphenol) as an ancillary ligand in olefin polymerization and as precursors in the polymerization of the phenylacetylene [6]. Here, we describe syntheses and characterization of new bis(aryloxo) alkoxo titanium complexes $[\text{Ti}_2(\mu\text{-OEt})_2(\text{edbp})_2(\text{OEt})_2]$ (**1**) and $[\text{Ti}(\text{edbp})(\text{O}^i\text{Pr})_2]$ (**2**) which possess structural features that encourage us to explore their catalytic behavior for ROP of lactides.

2. Experimental

2.1. Materials and instrumentation

All the reactions and operations were performed under an inert atmosphere using standard Schlenk techniques. Reagents were purified by standard methods: thf, distilled from CuCl, predried over NaOH, and then distilled from Na/benzophenone;

* Corresponding author. Tel.: +48 71 3757306; fax: +48 71 3282348.
E-mail address: plas@wchuwr.chem.uni.wroc.pl (P. Sobota).

toluene, distilled from Na; CH₂Cl₂, distilled from P₂O₅, *n*-hexane, distilled from Na, methanol distilled from Mg. L-LA (3*S*)-*cis*-3,6-dimethyl-1,4-dioxan-2,5-dione and rac-LA 3,6-dimethyl-1,4-dioxan-2,5-dione (98%) (Aldrich) were sublimed and recrystallized from toluene prior to use. Ti(OR)₄ (R = Et, ^{*i*}Pr) as well as NaOR (R = Et, ^{*i*}Pr) were purchased from Aldrich and were used as received. ¹H and ¹³C NMR spectra were detected at range of temperature from 213 to 333 K using Bruker ESP 300E spectrometer. Chemical shift data are reported in parts per million and referenced to the residual protons in deuterated solvents. The weights and number-average molecular weights of PLAs were determined by gel permeation chromatography (GPC; HPLC-HP 1090 II with DAD-UV/vis and RI detector HP 1047A) using polystyrene calibration. IR spectra were measured on a Perkin-Elmer 180 instrument in Nujol mulls.

2.2. Catalytic polymerization

In a typical experiment the monomer L-LA was placed in a Schlenk flask and titanium complex in toluene was then added. Next the flask was placed in a silicon oil bath. The reaction mixture was stirred at the desired temperature for the prescribed time. Next at certain time intervals about 1 cm³ aliquots were removed and reaction was terminated by adding methanol. After the solvent was evaporated a sample was taken for determination of the conversion using ¹H NMR. The remaining residues were redissolved in CH₂Cl₂ and the polymer was precipitated from an excess of cold methanol. Filtration and drying in vacuo yielded a white polymer.

2.3. NMR tube polymerization

Compounds **1** or **2** and monomer L-LA were placed in Schlenk flask and dissolved in toluene-*d*₈ and the resulting mixture was then placed into NMR tube. The reaction was followed by ¹H NMR spectroscopy until polymerization was about 80% complete. The reactions were followed by integration of lactide methine signal and methine protons of polymer (PLA) as a function of time.

2.4. Complex syntheses

2.4.1. Synthesis of [Ti₂(μ-OEt)₂(edbp)₂(OEt)₂] (**1**)

To a rapidly stirred *n*-hexane solution (70 cm³) of edbp-H₂ (2.13 g, 4.9 mmol), Ti(OEt)₄ (1.12 g, 4.9 mmol) was added. The colour of the reaction mixture gradually changed from light yellow to dark red. The mixture was stirred for 48 h at room temperature, filtered and washed with *n*-hexane. Red solid then precipitated from the CH₂Cl₂ solution. Total yield: 2.59 g (92%). Analysis—found: C, 71.05; H, 9.49; Ti, 8.28. C₆₈H₁₀₈O₈Ti₂ requires: C, 71.06; H, 9.47; Ti, 8.33%. ¹H NMR (major form, 300 MHz, CD₂Cl₂, 25 °C): δ = 1.22 (t_{br}, 12H, CH₃), 1.28 (s, 36H, C(CH₃)₃), 1.43 (s, 36H, C(CH₃)₃), 1.69 (d, 6H, CH(CH₃), J_{H-H} = 7.1 Hz), 3.66 (q_{br}, 4H, CH₂), 4.27 (q, 2H, CH(CH₃), J_{H-H} = 7.1 Hz), 4.65 (q_{br}, 4H, CH₂), 7.07 (d, 4H, Ph, J_{H-H} = 2.3), 7.29 (d, 4H, Ph, J_{H-H} = 2.3). ¹H NMR (minor form, 300 MHz, CD₂Cl₂, 25 °C): δ = 1.22 (t_{br}, 12H,

CH₃), 1.30 (s, 18H, C(CH₃)₃), 1.35 (s, 18H, C(CH₃)₃), 1.37 (s, 18H, C(CH₃)₃), 1.41 (s, 18H, C(CH₃)₃), 1.82 (d, 6H, CH(CH₃), J_{H-H} = 6.4 Hz), 3.66 (q_{br}, 4H, CH₂), 4.65 (q_{br}, 4H, CH₂), 4.78 (q, 2H, CH(CH₃), J_{H-H} = 6.4 Hz), 7.16 (d, 2H, Ph, J_{H-H} = 2.3), 7.19 (d, 2H, Ph, J_{H-H} = 2.3), 7.39 (d, 2H, Ph, J_{H-H} = 2.3), 7.49 (d, 2H, Ph, J_{H-H} = 2.3). IR (cm⁻¹): 1602 (w), 1410 (s), 1360 (s), 1336 (m), 1294 (m), 1232 (vs), 1202 (m), 1158 (m), 1136 (vs), 1112 (vs), 1090 (m), 1076 (vs), 1034 (s), 940 (s), 920 (w), 908 (m), 882 (s), 868 (m), 842 (vs), 648 (w), 636 (s), 582 (vs), 560 (vs), 494 (m), 474 (m).

2.4.2. Synthesis of [Ti₂(μ-OEt)₂(edbp)₂(OEt)₂] (**1-1a**)

Recrystallization of **1** from *n*-hexane/toluene (1:1) at lower temperature (−30 °C) gave dark red cocrystallite (**1-1a**) in 1:1 ratio. Spectroscopic data and elemental analyses were identical to those described above.

2.4.3. Synthesis of [Ti(edbp)(O^{*i*}Pr)₂] (**2**)

To a rapidly stirred *n*-hexane solution (70 mL) of edbp-H₂ (2.13 g, 4.9 mmol), Ti(O^{*i*}Pr)₄ (1.39 g, 4.9 mmol) was added. The colour of the reaction mixture gradually changed from light yellow to red. The mixture was stirred for 48 h at room temperature, filtered and washed with *n*-hexane. Yellow solid then precipitated from the CH₂Cl₂ solution. Total yield: 2.71 g (90%). Analysis—found: C, 71.89; H, 9.76. C₃₆H₅₈O₄Ti requires: C, 71.72; H, 9.71. ¹H NMR (major form, 300 MHz, CD₂Cl₂, 25 °C): δ = 1.21 (d, 6H, CH(CH₃), 1.23 (d, 6H, CH(CH₃)), 1.30 (s, 18H, C(CH₃)₃), 1.36 (s, 36H, C(CH₃)₃), 1.66 (d, 3H, CH(CH₃), J_{H-H} = 7.2 Hz), 4.49 (q, 1H, CH(CH₃), J_{H-H} = 7.2 Hz), 4.52 (s, 1H, CH(CH₃)₂), 4.55 (s, 1H, CH(CH₃)₂), 7.19 (d, 2H, Ph, J_{H-H} = 2.3), 7.26 (d, 2H, Ph, J_{H-H} = 2.3). IR (cm⁻¹): 1596 (m), 1412 (m), 1364 (vs), 1288 (m), 1264 (m), 1224 (s), 1200 (s), 1158 (s), 1136 (m), 1100 (s), 930 (s), 908 (s), 886 (vs), 804 (w), 772 (s), 744 (s), 652 (w), 638 (s), 592 (s), 540 (w), 491 (m), 481 (vs).

2.5. X-ray crystallographic study

Crystal data collection and refinement are summarized in Table 1. Preliminary examination and intensities data collections were carried out on a KUMA CCD KM-4 κ-axis diffractometer with graphite-monochromated Mo Kα. All data were corrected for Lorentz and polarization effects. Data reduction and analysis were carried out with the Kuma Diffraction programs. The structures were solved by direct methods and refined by the full-matrix least-squares method on all F² data using the SHELXTL software [7]. Carbon bonded hydrogen atoms were included in calculated positions and refined in the riding mode. All non-hydrogen atoms were refined with anisotropic displacement parameters. The poor crystal quality and the weak diffracting power (ratio observed/unique reflections = 45%) of crystalline compound **1-1a** allowed only partial structure determination in these cases. In particular, there are voids in the crystal structures that are most likely occupied by highly disordered solvent. All attempts to locate solvent molecules in **1-1a** were unsuccessful. Therefore, the refinements of **1-1a** do not allow detailed

Table 1
X-ray data for **1**

Compound 1	
Formula	C ₆₈ H ₁₀₈ O ₈ Ti ₂
Formula weight	1149.28
<i>T</i> (K)	100(1)
Space group	<i>C2/c</i>
Crystal system	Monoclinic
Unit cell dimensions	
<i>a</i> (Å)	20.021(3)
<i>b</i> (Å)	18.865(3)
<i>c</i> (Å)	22.196(4)
α (°)	90
β (°)	108.60(10)
γ (°)	90
<i>V</i> (Å ³)	7945(2)
<i>Z</i>	4
<i>D_c</i> (Mg/m ³)	0.961
<i>F</i> (000)	2496
Habit	Block
Crystal size (mm)	0.4 × 0.2 × 0.2
μ (mm ⁻¹)	0.243
θ range (°)	3.40–28.46
Number of reflections measured	27011
Number of unique reflections	9338
<i>R</i> _(int)	0.0786
Number of observed reflections	5438 [<i>I</i> > 2 σ (<i>I</i>)]
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0666, <i>wR</i> ₂ = 0.1651
<i>S</i>	1.002

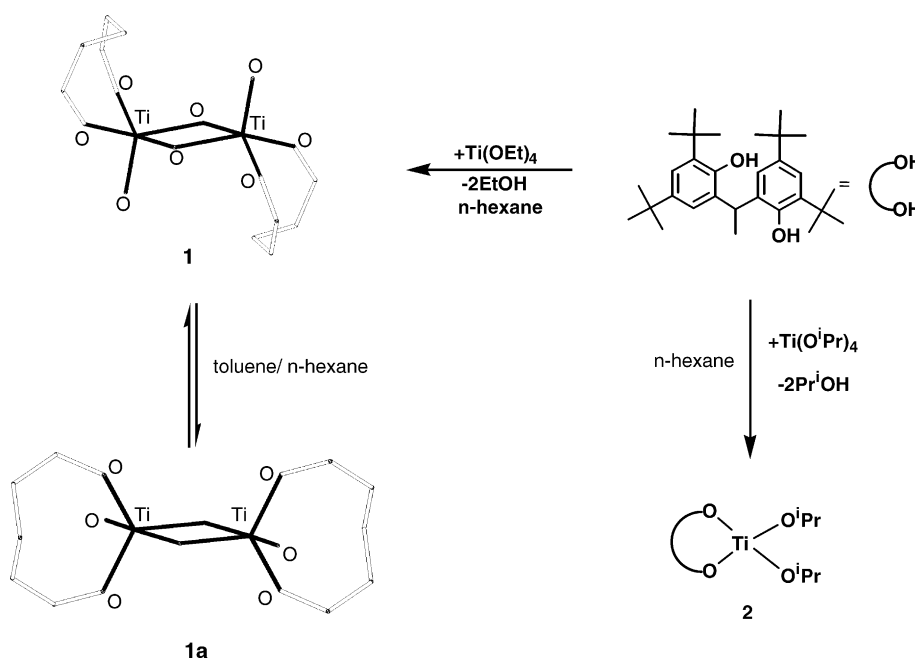
discussion. However, the connectivity and other broad structural features of the main complex are well refined and undoubtedly correct. Crystal structure has been deposited at the Cambridge Crystallographic Data Centre (Deposition No. CCDC 2940).

3. Results and discussions

3.1. Synthesis and ¹H NMR studies of the titanium complexes

The reaction of Ti(OR)₄ (R = Et, ^{*i*}Pr) with 1 equiv. of 2,2'-ethylidenebis(4,6-di-*tert*-butylphenol) (**Scheme 1**) in *n*-hexane at ambient temperature, followed by standard workup, gives [Ti₂(μ-OEt)₂(OEt)₂(edbp)₂] (**1**, 92%) and [Ti(edbp)(O^{*i*}Pr)₂] (**2**, 90%) as red for **1** and yellow for **2** solids. Recrystallization of **1** from *n*-hexane/toluene (1:1) at room temperature gave red crystals **1** and at lower temperature (−30 °C) dark red cocrystallite **1-1a** in 1:1 ratio. All the compounds were conveniently characterized by ¹H NMR spectroscopy. ¹H NMR of complex **1** is consistent with the obtained X-ray structure but the spectra depend on deuterated solvent which is used. For example, when red compound **1** is dissolved in CDCl₃, the colour of solution changes to deep red and all the signals from ligand and OEt groups can be identified (two doublets at phenyl region at 7.22 and 7.17 ppm; quartet from ligand ethylidene group at 4.43 ppm, broaden quartet at 3.66 ppm which was assigned to terminal and bridging group of OEt, doublet from ethylidene group at 1.66 ppm, two singlets from *tert*-butyl groups at 1.34 and 1.28, respectively, and triplets at 1.22 which were assigned to CH₃ from OEt groups). The spectrum is consistent with the dimeric, symmetrical structure as it is shown for **1**. Using the other deuterated solvents changes the spectrum of **1**.

In toluene-*d*₈ and CD₂Cl₂ second set of signals, besides those described earlier, has appeared (with four signals of *tert*-butyl groups, and four doublets in phenyl regions). The difference between spectra is only in molar ratio between moieties: in toluene-*d*₈ it is 1:1 and in CD₂Cl₂, the ratio is 1:2. All the signals in these solvents can be assigned to second form of dimeric com-

Scheme 1. Syntheses of **1**, **1-1a** and **2**.

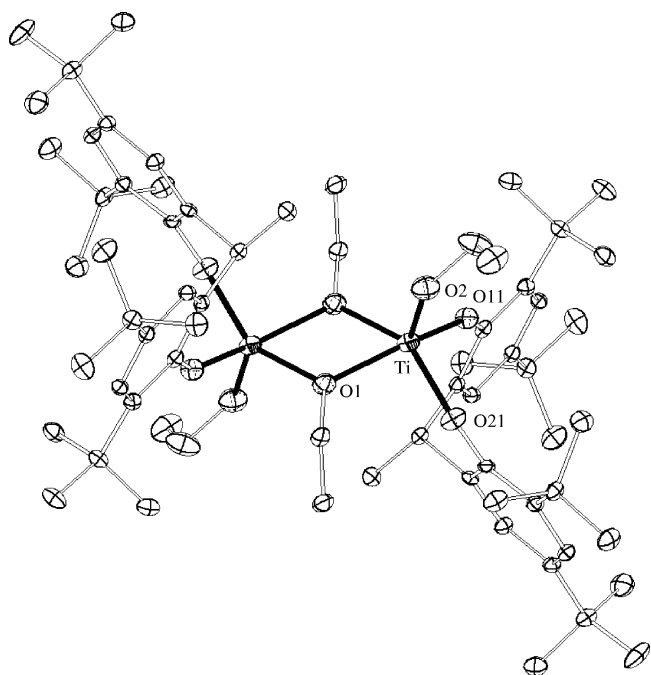


Fig. 1. ORTEP drawing (50% probability) of **1**. Selected bond lengths [Å]: Ti(1)–O(1) 2.008(2), Ti–O(1)ⁱ 2.019(2), Ti–O(2) 1.776(3), Ti–O(21) 1.860(2), Ti–(O11) 1.837(2); symmetry operation: (i) $-x+0.5, 1.5+y, z$.

pond, namely **1a**. The crystal structure of **1·1a** species gives a good proof for such hypotheses.

In the ¹H NMR spectra of compound **2** also all signals are doubled. Two septets and doublets from OⁱPr in each set of signals give a proof for monomeric structure of compound **2**. It is believed that monomeric structure is favored due to the bulkiness of OⁱPr groups in contrast to OEt. Similar monomeric complexes with aryloxo ligands and OⁱPr groups were found in the literature [8].

3.2. Structures of the complexes **1** and **1·1a**

The molecular structure of complex **1** with selected bond lengths and bond angles are shown in Fig. 1. The structure of **1** shows a dimeric feature containing a Ti₂O₂ core bridging through the oxygen atom of the ethoxy group. The bridging oxygen atom distances are roughly equivalent to the two Ti centres, with the Ti(1)–O(1) and Ti–O(1)ⁱ distance of 2.008(2) and 2.019(2) Å, respectively. The terminal Ti–O bond distances from ethoxide ligand are Ti(1)–O(2) 1.776(3) Å, well within the normal range previously reported for titanium alkoxo compound [9,10]. In red crystal of **1** two oxygen atoms from terminal ethoxy groups are located as it is shown in Fig. 1.

Unfortunately, the structure of cocrystallite **1·1a** was not determined completely in view of low-quality crystals. Nonetheless, the structure is clearly visible and can be discussed. An overall view of the molecules is presented in Scheme 1. The structure of the cocrystallite is composed of two independent isomers [Ti₂(μ-OEt)₂(OEt)₂(edbp)₂] molecules which are statistically distributed in the crystal. The structure **1** differs from **1a** in the way of terminal ethoxy groups located in the respect

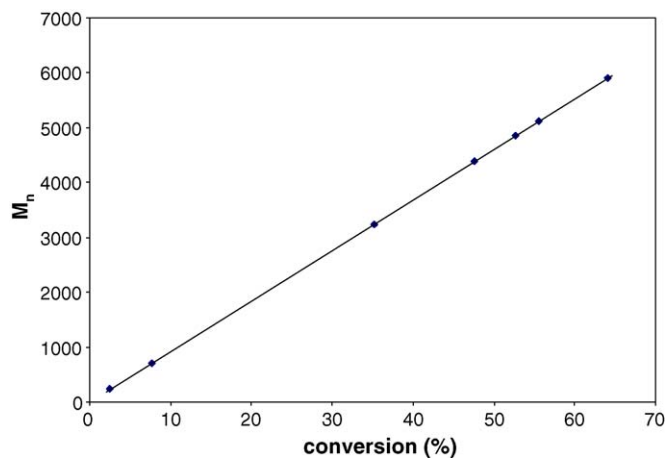


Fig. 2. Plot of M_n vs. conversion for initiator **1·1a**.

of the plane formed by two titanium and two alkoxo-bridging atoms.

3.3. Polymerization of lactide

The catalytic behavior of complexes **1** and **2** in the polymerization of L- and rac-lactide (L-LA and rac-LA) was studied in toluene at 70 °C with a monomer to initiator ratio fixed at 100. The complex **1** initiated polymerization of lactide in 90% conversion within 2.5 h to afford PLA with M_n of 17,500 and PDI of 1.06. It is worth to note that in the polymerization conditions **1** is the mixture of two isomers **1** and **1a** but it does not play significant role in polymerization activity (see Scheme 2). The parameters of PLA obtained with the monomeric complex **2** were similar ($M_n = 18,000$, PDI = 1.08) but the polymerization reaction proceeded faster to reach 98% conversion within 1 h 12 min. The molecular weight of the polymer increased linearly to the conversion of monomer indicating living nature of polymerization systems Fig. 2 (for **1**) and Fig. 3 (for **2**). The polymerization process was monitored by ¹H NMR spectra of the formed PLAs during the polymerization test carried out in NMR tube. It can be seen that with the proceeding ROP the intensities

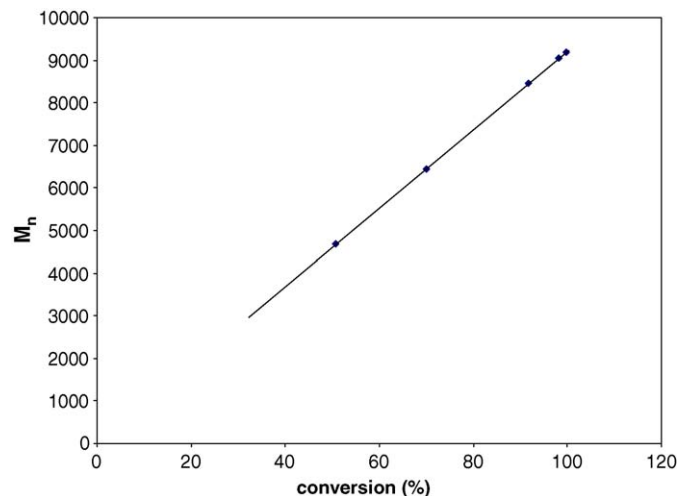
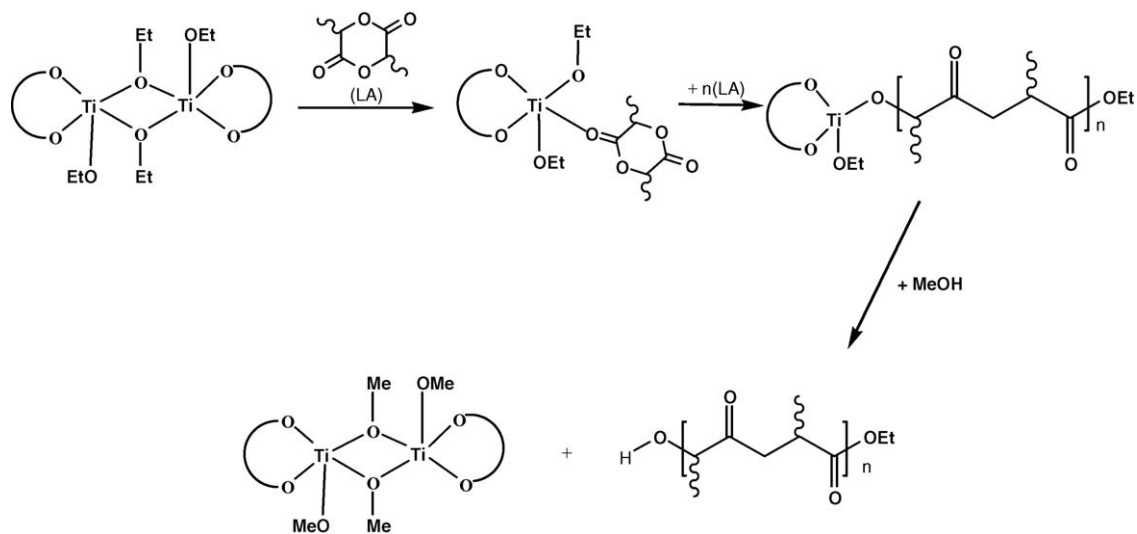


Fig. 3. Plot of M_n vs. conversion for initiator **2**.



Scheme 2. Polymerization mechanism of lactides initiated by **1-1a**.

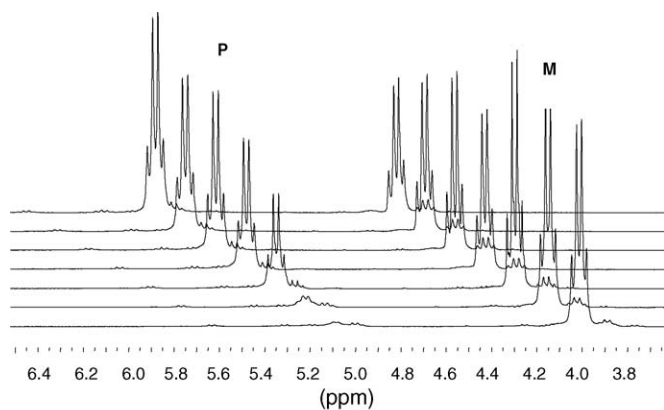


Fig. 4. Overlaid ^1H NMR spectra of synthesized PLA initiated by **1-1a** (polymerization at 70° ; toluene $[\text{LA}] = 1.02 \text{ M}$; $[\text{LA}]/[\text{I}] = 40$; P: polymer; M: monomer).

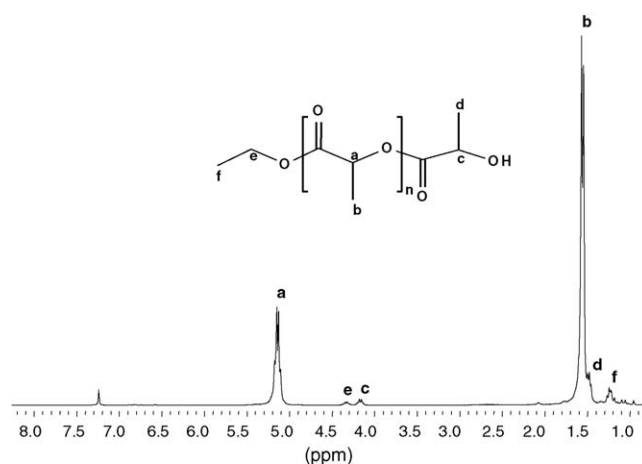


Fig. 6. ^1H NMR spectra of PLA obtained with **1-1a** as an initiator.

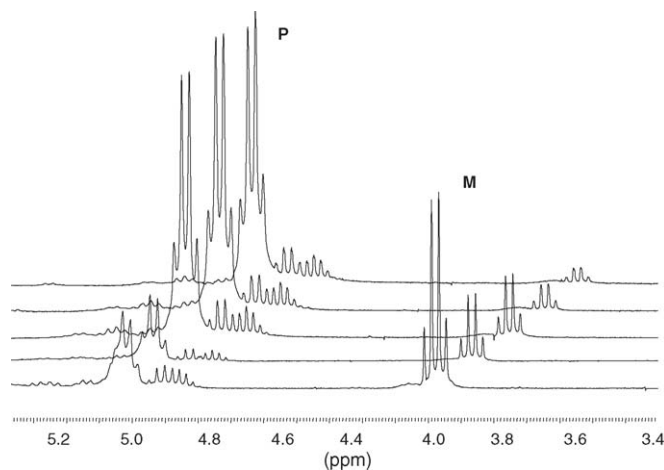


Fig. 5. Overlaid ^1H NMR spectra of synthesized PLA initiated by **2** (polymerization at 70° ; toluene $[\text{LA}] = 0.5 \text{ M}$; $[\text{LA}]/[\text{I}] = 46 \text{ M}$; P: polymer; M: monomer).

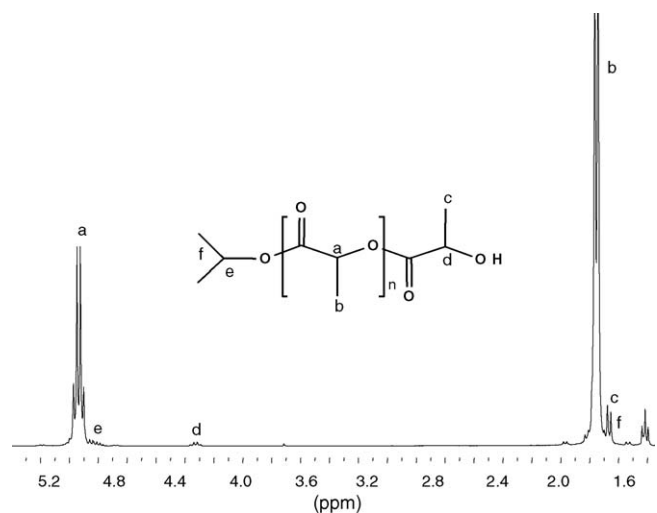


Fig. 7. ^1H NMR spectra of PLA obtained with **2** as an initiator.

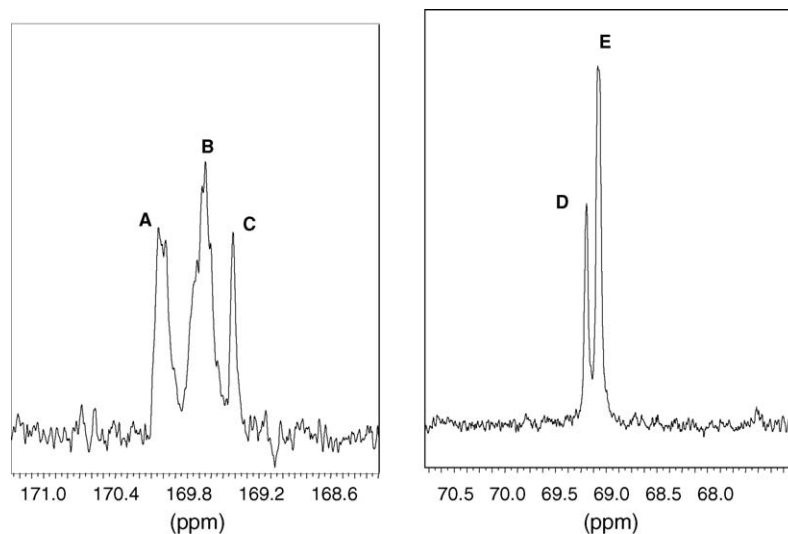


Fig. 8. Expanded region of carbonyl and methine carbon atoms in ^{13}C NMR spectra of poly(*rac*-LA) samples obtained in the presence of **1-1a** as initiators; (A) iiiii + iiiis/siiii + siis, (B) iiii/siiii + iisii + sisii + sisis, (C) isisi, (D) isi and (E) iii + iis/sii + sis.

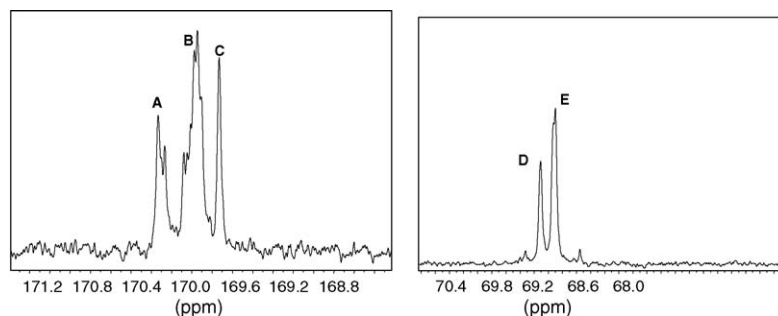


Fig. 9. Expanded region of carbonyl and methine carbon atoms in ^{13}C NMR spectra of poly(*rac*-LA) samples obtained in the presence of **2** as initiators; (A) iiiii + iiiis/siiii + siis, (B) iiii/siiii + iisii + sisii + sisis, (C) isisi, (D) isi and (E) iii + iis/sii + sis.

of peak signals corresponding to the monomer decrease while the intensities of signals assigned to PLA increase which implies the propagation of polymeric species. Figs. 4 and 5 show the relationships between methine protons of monomer and polymer for **1-1a** and **2**, respectively. Additionally as soon as the polymerization starts the signals of corresponding ethyl or isopropyl esters end group appear in the spectrum. The ^1H NMR spectra of methanol quenched PLAs also show that the polymer chains are terminated by corresponding ester and hydroxyl groups (Figs. 6 and 7). These results suggest coordination–insertion mechanism occurring through the insertion of LA into alkoxo titanium group (Scheme 2). The dimeric complex **1** showed a lower conversion in longer time than **2** and the activities of these titanium complexes were higher comparable to similar titanium bis(aryloxo) initiators [4,5].

It has been reported that carbonyl and methine carbon are the stereo-sensitive groups leading to hexad and tetrad sequences, respectively [11]. Figs. 8 and 9 show the ^{13}C NMR spectra of carbonyl and methine groups in PLA prepared using **1** and **2** as initiators, respectively. The intensities of the corresponding hexad and tetrad stereosequences were calculated according to the literature [12]. These values suggest that the ROP of *rac*-LA in the presence of titanium complexes **1** and **2** shows a preference of heterotactic addition.

In conclusion, complexes **1** and **2** are good initiators for controlled polymerization of *rac*-LA providing monodisperse PLA with higher degree of heterotactic addition. The reaction shows a first-order dependence on [LA], consistent with a coordination–insertion mechanism, and the titanium isopropoxide or ethoxide ligands are transferred to the end of the growing polymer chain during initiation. The polymerization reaction proceeded faster for **2** (98% conversion within 1 h 12 min) than for **1** (90% conversion within 2.5 h). This difference is probably attributed to lactide coordination to the dimeric complex **1** with generation of the monomeric species during polymerization process (Scheme 2).

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