Supporting Information

**Dinuclear vs. Mononuclear Complexes: Accelerated, Metal-dependent Ring-Opening Polymerization of Lactide**

Mickael Normand, Thierry Roisnel, Jean-François Carpentier, and Evgeny Kirillov

1. Synthetic procedures and analytical data

2. NMR spectra

**Figure S1.** $^1$H NMR spectrum (500 MHz, C$_6$D$_6$, 298 K) of [ON$_{pipe}$$^1$H]$_2$ (II).

**Figure S2.** $^{13}$C{$_1^H$} NMR spectrum (125 MHz, C$_6$D$_6$, 298 K) of [ON$_{pipe}$$^1$H]$_2$ (II).

**Figure S3.** $^1$H NMR spectrum (500 MHz, C$_6$D$_6$, 298 K) of [ON$_{pipe}$$^1$H]$_2$AlMe$_2$ (II–Al$_2$).

**Figure S4.** $^{13}$C{$_1^H$} NMR spectrum (125 MHz, C$_6$D$_6$, 298 K) of [ON$_{pipe}$$^1$H]$_2$AlMe$_2$ (II–Al$_2$).

**Figure S5.** $^1$H NMR spectrum (500 MHz, C$_6$D$_6$, 298 K) of [ON$_{pipe}$$^1$H]$_2$In(CH$_2$SiMe$_3$)$_2$ (II–In$_2$).

**Figure S6.** $^{13}$C{$_1^H$} NMR spectrum (125 MHz, C$_6$D$_6$, 298 K) of [ON$_{pipe}$$^1$H]$_2$In(CH$_2$SiMe$_3$)$_2$ (II–In$_2$).

**Figure S7.** $^1$H NMR spectrum (400 MHz, C$_6$D$_6$, 298 K) of ON$_{pipe}Ph$H (IPh).

**Figure S8.** $^{13}$C{$_1^H$} NMR spectrum (100 MHz, C$_6$D$_6$, 298 K) of ON$_{pipe}Ph$H (IPh).

**Figure S9.** $^1$H NMR spectrum (400 MHz, C$_6$D$_6$, 298 K) of ON$_{pipe}Ph$AlMe$_2$ (IPh–Al).

**Figure S10.** $^{13}$C{$_1^H$} NMR spectrum (100 MHz, C$_6$D$_6$, 298 K) of ON$_{pipe}Ph$AlMe$_2$ (IPh–Al).

3. Crystallographic data

**Figure S11.** Molecular structure of the bimetallic complex II-In$_2$.

**Table S1.** Summary of Crystal and Refinement Data for Complexes II-Al$_2$ and II-In$_2$.
4. Kinetic data

**Figure S12.** Plot of rac-LA conversion (%) vs. time (s) for the binary system [Al]/iPrOH at different temperatures.

**Figure S13.** Plot of rac-LA conversion (%) vs. time (s) for the binary system II–Al$_2$/iPrOH at different temperatures.

**Figure S14.** Plot of rac-LA conversion (%) vs. time (s) at 110 °C, at different concentrations of catalyst/initiator, with the binary system II–Al$_2$/iPrOH.

**Figure S15.** Plot of ln($k_{app}$) vs. ln([Al]) for ROP of rac-LA by the binary system II–Al$_2$/iPrOH at 110 °C.

**Figure S16.** Plot of ln($k_{app}/T$) vs. 1/T for ROP of rac-LA by the binary systems I$_{SiPh3}$–Al and II–Al$_2$/iPrOH, [rac-LA]$_0$ = 2.0 M in toluene.

**Figure S17.** Semi-logarithmic plots for ROP of rac-LA at 110 °C with [rac-LA]$_0$ = 2.0 M in toluene for the binary systems [In]/iPrOH.

**Figure S18.** Plot of $M_n$ vs. Conversion (%) for ROP with the binary systems I$_{SiPh3}$–Al and II–Al$_2$/iPrOH.

5. References and notes
Experimental Part

General Considerations. All manipulations were performed under a purified argon atmosphere using standard Schlenk techniques or in a glove box. Solvents were distilled from Na/benzophenone (THF, Et₂O) or Na/K alloy (toluene, hexane and pentane) under argon, degassed thoroughly and stored under argon prior to use. Deuterated solvents were stored over Na/K alloy (benzene-d₆, toluene-d₈, THF-d₈; >99.5% D, Eurisotop) or CaH₂ (CD₂Cl₂) and vacuum-transferred just before use. CDCl₃ was dried over a mixture of 3 and 4 Å molecular sieves. 2,9-Dicarboxyaldehyde-1,8-bisphenol,¹ 2-hydroxybiphenyl-3-carbaldehyde² and precursors T²SiPh₃⁻M (M = Al, In)³ were prepared using literature procedures. Racemic lactide (rac-LA) was received from Acros. Purification of rac-LA required a three-step procedure involving first a recrystallization from a hot, concentrated iPrOH solution (80 °C), followed by two subsequent recrystallizations in hot toluene (100 °C). After purification, rac-LA was stored at a temperature of −30 °C in the glove-box. Other starting materials were purchased from Acros, Strem and Alfa and used as received.

Instrumentation and Measurements. NMR spectra of complexes were recorded on Bruker Avance DRX 400 and AM-500 spectrometers in Teflon-valved NMR tubes at 25 °C unless otherwise indicated. ¹H and ¹³C NMR chemical shifts are reported in ppm vs. SiMe₄ and were determined by reference to the residual solvent peaks. Assignment of resonances for organometallic complexes was made from 2D ¹H–¹³C HMQC and HMBC NMR experiments.

Elemental analyses (C, H, N) were performed using a Flash EA1112 CHNS Thermo Electron apparatus and are the average of two independent determinations.

Size exclusion chromatography (SEC) analyses of PLAs were performed in THF (1.0 mL.min⁻¹) at 20 °C using a Polymer Laboratories PL-GPC 50 plus apparatus equipped with two ResiPore 300 × 7.5 mm columns, and RI and Dual angle LS (PL-LS 45/90) detectors. The number-average molecular masses (Mₙ) and polydispersity index (Mₘ/Mₙ) of the polymers were
calculated with reference to a universal calibration vs. polystyrene standards. Reported experimental SEC molar mass values ($M_{n,SEC}$) for PLA samples were corrected by a factor of 0.58, as previously established. Unless otherwise stated, the SEC traces of the polymers all exhibited a unimodal, and usually symmetrical, peak. The microstructure of PLAs was determined by homodecoupling $^1$H NMR spectroscopy at 20 °C in CDCl$_3$ on a Bruker AC-500 spectrometer.

**Crystal Structures Determination.** Diffraction data were collected at 100(2) K using a Bruker APEX CCD diffractometer with graphite-monochromatized MoK$_\alpha$ radiation ($\lambda = 0.71073$ Å). A combination of $\omega$ and $\phi$ scans was carried out to obtain at least a unique data set. The crystal structures were solved by direct methods, remaining atoms were located from difference Fourier synthesis followed by full-matrix least-squares refinement based on F2 (programs SIR97 and SHELXL-97)$^5$ with the aid of the WINGX program.$^6$ In most cases, many hydrogen atoms could be found from the Fourier difference analysis. Other hydrogen atoms were placed at calculated positions and forced to ride on the attached atom. The hydrogen atom contributions were calculated but not refined. All non-hydrogen atoms were refined with anisotropic displacement parameters. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities were of no chemical significance. Crystal data and details of data collection and structure refinement for the different compounds are given in Annexes.

$\left[\{\text{ON}^{\text{pippe}}\text{bn}\}\right]_2$ (II). A solution of 2,9-dicarboxyaldehyde-1,8-bisphenol (1.00 g, 4.13 mmol), 4-amino-1-benzylpiperidine (2.30 g, 12.4 mmol) and PTSA (cat., ca. 2 mg) in benzene (20 mL) was stirred under reflux with a Dean-Stark apparatus at 120 °C for 48 h. Volatiles were removed under vacuum and the resulting solid recrystallized in methanol (ca. 20 mL). The resulting material was filtered, washed with cold methanol (30 mL) and dried in vacuo to give II as a yellow solid (2.03 g, 84%). $^1$H NMR (500 MHz, C$_6$D$_6$, 298 K): $\delta$ 1.49 (m, 4H, CH$_2$ pip), 1.53-1.60 (m, 4H, CH$_2$ pip), 1.95 (m, 4H, CH$_2$ pip), 2.59 (m, 4H, CH$_2$ pip), 2.75 (m, 2H, CH
pip), 3.28 (s, 4H, NCH2Ph), 6.87 (t, \( J_{HH} = 7.6 \text{ Hz} \), 2H, Haro), 6.96-6.97 (dd, \( J_{HH} = 1.7 \text{ and } 5.7 \text{ Hz} \), 2H, Haro), 7.10-7.13 (m, 2H, Haro), 7.21 (t, \( J_{HH} = 7.6 \text{ Hz} \), 4H, Haro), 7.33-7.34 (m, 4H, Haro), 7.70-7.71 (dd, \( J_{HH} = 1.75 \) and 5.7 Hz, 2H, Haro), 14.10 (s, 2H, ArOH).  13C{1H} NMR (125 MHz, C6D6, 298 K): δ 33.33 (CH2 pip), 51.28 (CH2 pip), 62.97 (NCH2Ph), 64.93 (CH pip), 117.60, 119.14, 126.54, 126.84, 128.15, 128.75, 130.58, 134.70, 139.32 (Caro), 159.56 (ipso-C phenol), 163.03 (ArCH=N).  Anal. calcd. for C38H42N4O2: C, 77.78; H, 7.21; N, 9.55; found: C, 77.16; H, 7.26; N, 9.87.  Mp: 253 °C.

\[\{\text{ONpipeBn}\}_{2}\text{AlMe}_2\] (II−Al2).  A solution of \([\{\text{ONpipeBn}\}_{2}H]\)2 (II) (1.00 g, 1.70 mmol) in toluene (ca. 10 mL) was added to a solution of AlMe3 (0.341 mL of a 1.0 M solution in n-heptane, 3.41 mmol) in toluene (ca. 10 mL).  The reaction mixture was stirred at room temperature for 24 h.  Then, volatiles were removed under vacuum and the resulting material washed with n-hexane (ca. 10 mL), and dried in vacuo to give II−Al2 as a yellow solid (1.15 g, 96%).  1H NMR (500 MHz, C6D6, 298 K): δ –0.29 (s, 12H, Al(CH3)2), 1.39 (m, 4H, CH2 pip), 1.57 (td, \( J_{HH} = 1.9 \text{ and } 9.9 \text{ Hz} \), 4H, CH2 pip), 1.74-1.81 (qd, \( J_{HH} = 3.5 \) and 3.75 Hz, 4H, CH2 pip), 2.62-2.64 (m, 4H, CH2 pip), 2.74 (tt, \( J_{HH} = 4.1 \) and 12 Hz, 2H, CH pip), 3.25 (s, 4H, NCH2Ph), 6.66-6.72 (m, 4H, Haro), 7.10-7.13 (tt, \( J_{HH} = 1.3 \) and 7.3 Hz, 2H, Haro), 7.18-7.21 (m, 4H, Haro), 7.30-7.31 (m, 4H, Haro), 7.36 (s, 2H, ArCH=N), 7.87 (dd, \( J_{HH} = 2.1 \) and 5 Hz, 2H, Haro).  13C{1H} NMR (125 MHz, C6D6, 298 K):δ –7.91 (Al(CH3)2), 32.51 (CH2 pip), 52.19 (CH2 pip), 62.57 (NCH2Ph), 65.11 (CH pip), 116.55, 119.54, 127.09, 128.29, 128.73, 130.16, 134.10, 138.70, 139.30 (Caro), 162.18 (ArC−O−Al), 169.34 (ArCH=N).  Anal. calcd. for C42H52Al2N4O2: C, 72.18; H, 7.50; N, 8.02; found: C, 72.52; H, 7.12; N, 8.22.

\[\{\text{ONpipeBn}\}_{2}\text{In(CH}_2\text{SiMe}_3\}_{2}\] (II−In2).  A solution of \([\{\text{ONpipeBn}\}_{2}H]\)2 (II) (0.083 g, 0.142 mmol) in toluene (5 mL) and In(CH2SiMe3)3 (0.117 g, 0.283 mmol) in toluene (2 mL) was stirred at 90 °C for 18 h.  Then, volatiles were removed in vacuo, n-hexane (ca. 10 mL) was vacuum-condensed in and the resulting solution was filtered off.  The filtrate was concentrated under vacuum to give II−In2 as a bright yellow solid (0.092 g, 56%).  1H NMR (500 MHz,
C₆D₆, 298 K): δ –0.19 (d, ²J_H-H = 12.5 Hz, 4H, CHH/Me₃), –0.12 (d, ²J_H-H = 12.5 Hz, 4H, CHH/Me₃), 0.20 (s, 36H, Si(CH₃)₃), 1.43 (m, 4H, CH₂ pip), 1.65 (td, J_H-H = 1.3 and 10.2 Hz, 4H, CH₂ pip), 1.77 (qd, J_H-H = 3.5 and 12 Hz, 4H, CH₂ pip), 2.56 (tt, J_H-H = 3.9 and 11.6 Hz, 2H, CH pip), 2.70 (m, 4 H, CH₂ pip), 3.28 (s, 4 H, NCH₂Ph), 6.78 (t, J_H-H = 7.8 Hz, 2H, Haro), 6.86-6.88 (dd, J_H-H = 2.0 and 8.0 Hz, 2H, Haro), 7.09 (tt, J_H-H = 1.8 and 7.3 Hz, 2H, Haro), 7.16-7.19 (m, 4H, Haro), 7.30 (m, 4H, Haro), 7.54 (s, 2H, CH=N), 7.91 (dd, J_H-H = 2.0 and 7.2 Hz, 2H, Haro). ¹³C{¹H} NMR (125 MHz, C₆D₆, 298 K): δ 2.24 (CH₂Si(CH₃)₃), 2.70 (Si(CH₃)₃), 34.07 (CH₂ pip), 52.05 (CH₂ pip), 54.72 (NCH₂Ph), 68.92 (CH pip), 114.00, 118.74 127.12, 128.32, 128.80, 132.55, 135.31, 138.52, 138.61 (Caro), 167.84 (ArC−O−In), 169.86 (ArCH=N).

Anal. calcd. for C₅₄H₸₄In₂N₄O₂Si₄: C, 55.76; H, 7.28; N, 4.82; found: C, 56.19 ; H, 7.37; N, 5.04.

Scheme 1. Synthetic route toward the phenol-imine pro-ligand (ON₄p₄p₄b₄b₄)H (I₄b₄).

{ON₄p₄p₄b₄b₄}H (I₄b₄). A solution of 2-hydroxybiphenyl-3-carbaldehyde (2.30 g, 11.7 mmol), N-benzyl-4-aminopiperidine (2.60 g, 13.9 mmol) in methanol (30 mL) was stirred [without catalyst] under reflux for 3 h. The reaction mixture was allowed to cool to room temperature, and volatiles were removed under vacuum till the apparition of a precipitate. The suspension was then stored at –30 °C for 24 h. The precipitate was filtered off, washed with cold methanol (3 × 20 mL) and dried in vacuo to give I₄b₄ as a yellow solid (0.303 g, 20%). ¹H NMR
(400 MHz, C₆D₆, 298 K): δ 1.44-1.50 (m, 2H, CH₂ pip), 1.57-1.62 (m, 2H, CH₂ pip), 1.96 (t, J_H−H = 9.2 Hz, 2H, CH₂ pip), 2.61-2.63 (m, 2H, CH₂ pip), 2.76 (m, 1H, CH pip), 3.31 (s, 2H, NCH₂Ph), 6.80 (t, J_H−H = 7.5 Hz, 1H, Haro), 6.91-6.93 (dd, J_H−H = 1.6, 7.6 Hz, 1H, Haro), 7.21 (t, J_H−H = 7.6 Hz, 2H, Haro), 7.28 (t, J_H−H = 7.8 Hz, 2H, Haro), 7.33-7.37 (m, 3H, Haro), 7.80-7.81 (m, 3H, Haro and ArCH=)=N), 14.31 (s, 1H, ArOH). 13C{¹H} NMR (100 MHz, C₆D₆, 298 K): δ 33.33 (CH₂ pip), 51.29 (CH₂ pip), 62.99 (NCH₂Ph), 64.97 (CH pip), 118.24, 119.23, 128.77, 129.64, 130.51, 133.14, 138.21, 139.19 (Caro), 159.10 (ipso-C phenol), 163.00 (ArCH=N). Anal. calcd. C₂₅H₂₆N₂O: C, 81.05; H, 7.07; N, 7.56; found: C, 80.88; H, 7.10; N, 7.49.

{ONpipeBn}PhAlMe₂ (I⁻⁻⁻⁻Al). A solution of {ONpipeBn}PhH (I⁻⁻⁻⁻) (0.053 g, 0.140 mmol) in toluene (ca. 3 mL) was added to a solution of AlMe₃ (0.140 mL of a 1.0 M solution in n-heptane, 0.140 mmol) in toluene (ca. 3 mL). The reaction mixture was stirred at room temperature for 18 h. Then, volatiles were removed under vacuum and the resulting material washed with n-hexane (ca. 5 mL), and dried in vacuo to give I⁻⁻⁻Al as a yellow solid (0.042 g, 70%). ¹H NMR (400 MHz, C₆D₆, 298 K): δ –0.47 (s, 6H, Al(CH₃)_2), 1.22 (m, 2H, CH₂pip), 1.43 (t, J_H−H = 10.8 Hz, 2H, CH₂ pip), 1.62 (m, 2H, CH₂ pip), 2.47 (m, 2H, CH₂ pip), 2.61 (m, 1H, CH pip), 3.11 (s, 2H, NCH₂Ph), 6.49 (t, J_H−H = 7.6 Hz, 1H, Haro), 6.57 (m, 1H, Haro), 6.64 (m, 2H, Haro), 7.04-7.16 (m, 6H, Haro), 7.26 (s, 1H, Haro), 7.28 (s, 1H, ArCH=)=N), 7.60 (s, 1H, Haro), 7.62 (s, 1H, Haro). 13C{¹H} NMR (100 MHz, C₆D₆, 298 K): δ –9.17 (Al(CH₃)_2), 31.47 (CH₂ pip), 51.10 (CH₂ pip), 61.51 (NCH₂Ph), 64.31 (NCH pip), 116.05, 118.51, 127.27, 128.39, 132.74, 132.91, 136.45, 137.37, 137.57 (Caro), 160.76 (ArC–O=–Al), 168.20 (ArCH=N). Anal. calcd. C₂₇H₃₁AlN₂O: C, 76.03; H, 7.33; N, 6.57; found: C, 76.35; H, 7.49; N, 6.51.

**General Procedure for Kinetic Studies of ROP of racemic Lactide.** Each polymerization experiment was conducted in a Teflon valve-sealed Schlenk flask as previously described. After a given time period, the reaction was quenched with H₂O (ca. 0.5 mL of a 10
wt% H₂O solution in THF). The monomer (LA) conversion was calculated from ¹H NMR spectra of the crude reaction mixture in CDCl₃, from the integration (Int.) ratio \( \text{Int}_{\text{polymer}} / (\text{Int}_{\text{polymer}} + \text{Int}_{\text{monomer}}) \), using the methyl hydrogen resonances for PLA at δ 1.49 ppm and for LA at δ 1.16 ppm. Then, the polymer was separated from the crude reaction mixture by filtration and was re-precipitated 3 times with excess pentane (ca. 15 mL). The polymer was then dried under vacuum till constant weight.

The microstructure of PLAs was determined by homodecoupling ¹H NMR spectroscopy (methine region) at 20 °C in CDCl₃ on a Bruker AC-500 spectrometer.
Figure S1. $^1$H NMR spectrum (500 MHz, C$_6$D$_6$, 298 K) of [{ON$_{pipeBn}$H}$_2$ (II). * stands for grease.
Figure S2. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (125 MHz, C$_6$D$_6$, 298 K) of [ON$_{\text{pipeBr}}$]$_2$ (II). * stands for residual signal of C$_6$D$_6$. 

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Figure S3. $^1$H NMR spectrum (500 MHz, C$_6$D$_6$, 298 K) of [ON$^{\text{pipeBn}}$AlMe$_2$]$_2$ (II–Al$_2$). * stands for grease.
**Figure S4.** $^{13}$C{$^1$H} NMR spectrum (125 MHz, C$_6$D$_6$, 298 K) of [{ONpipeBn}AlMe$_2$]$_2$ (II–Al$_2$). * stands for residual signal of C$_6$D$_6$. 
Figure S5. $^1$H NMR spectrum (500 MHz, C$_6$D$_6$, 298 K) of $\left[\text{ON}^\text{pipeBn}\right]\text{In(CH}_2\text{SiMe}_3)_2$ (II−In$_2$). * stands for signal of residual C$_6$D$_6$. 
Figure S6. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (125 MHz, C$_6$D$_6$, 298 K) of $[\{\text{ONpipeBn}\} \text{In(Ch}_2\text{SiMe}_3\}_2]_2$ (II–In$_2$). * stands for residual signal of C$_6$D$_6$. 
Figure S7. $^1$H NMR spectrum (400 MHz, C$_6$D$_6$, 298 K) of $\{\text{ON}^{\text{pipeBn}}\}_1\text{Ph}^\text{H}$ ($\text{I}^\text{Ph}$). * and ** stand for signals of residual C$_6$D$_6$ and grease, respectively.
Figure S8. $^{13}\text{C}^{1}\text{H}$ NMR spectrum (100 MHz, C$_6$D$_6$, 298 K) of ON$^{\text{piper}}$Br$_2$Ph (I$^{\text{Ph}}$). * and ** stand for signals of residual C$_6$D$_6$ and grease, respectively.
Figure S9. $^1$H NMR spectrum (400 MHz, C$_6$D$_6$, 298 K) of \{ON$_{\text{pipe}}$Bn$^{\text{Ph}}$\}$_{\text{Ph}}$AlMe$_2$ (I$^{\text{Ph}}$-Al). * stands for signal of C$_6$D$_6$. 
**Figure S10.** $^{13}$C-$^1$H NMR spectrum (100 MHz, C$_6$D$_6$, 298 K) of {ON$_{\text{pipeBn}}$}$^{\text{Ph}}$AlMe$_2$ (1$^{\text{Ph}}$Al). * stands for signal of C$_6$D$_6$. 

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**Figure S11.** Molecular structure of the dinuclear complex \( \text{II-In}_2 \) (all hydrogen atoms are omitted for clarity; ellipsoids drawn at 50% level).
**Table S1. Summary of Crystal and Refinement Data for Complexes II-Al\textsubscript{2} and II-In\textsubscript{2}.**

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</tbody>
</table>
Figure S12. Plot of rac-LA conversion (%) vs. time (s) for the binary system [Al]/iPrOH at different temperatures: (a) mononuclear systems; conditions: toluene, [rac-LA]₀/[Al]/[iPrOH]₀ = 500:1:5 ([rac-LA]₀ = 2.0 M; [Al]₀ = 4.0 mM; [iPrOH]₀ = 20 mM). ISiPh₃-Al: ♦ — 90 °C, $k_{app} = 3.4 \pm 0.2 \cdot 10^{-4} \text{s}^{-1}$, $R^2 = 0.964$; ● — 100 °C, $k_{app} = 5.9 \pm 0.4 \cdot 10^{-4} \text{s}^{-1}$, $R^2 = 0.976$; ▲ — 110 °C, $k_{app} = 1.1 \pm 0.2 \cdot 10^{-3} \text{s}^{-1}$, $R^2 = 0.965$; ◀ — 120 °C, $k_{app} = 2.1 \pm 0.2 \cdot 10^{-3} \text{s}^{-1}$, $R^2 = 0.975$. IPh-Al: ■ — 110 °C, $k_{app} = 2.5 \pm 0.1 \cdot 10^{-3} \text{s}^{-1}$, $R^2 = 0.996$; (b) dinuclear system; conditions: toluene, [rac-LA]₀/[Al]/[iPrOH]₀ = 1000:2:10 ([rac-LA]₀ = 2.0 M; [Al]₀ = 4.0 mM; [iPrOH]₀ = 20 mM). II–Al₂: ► — 90 °C, $k_{app} = 4.7 \pm 0.4 \cdot 10^{-3} \text{s}^{-1}$, $R^2 = 0.985$; ★ — 100 °C, $k_{app} = 8.3 \pm 0.6 \cdot 10^{-3} \text{s}^{-1}$, $R^2 = 0.989$; + — 110 °C, $k_{app} = 1.2 \pm 0.1 \cdot 10^{-2} \text{s}^{-1}$, $R^2 = 0.985$; * — 120 °C, $k_{app} = 2.2 \pm 0.2 \cdot 10^{-2} \text{s}^{-1}$, $R^2 = 0.987$. 
Figure S13. Plot of rac-LA conversion (%) vs. time (s) for the binary system II−Al$_2$/iPrOH at different temperatures: conditions: toluene, $[rac-LA]_0/[Al]/[iPrOH]_0 = 1000:4:10$ ($[rac-LA]_0 = 2.0$ M; $[Al]_0 = 8.0$ mM; $[iPrOH]_0 = 20$ mM). ♦ — 90 °C, $k_{app} = 6.0 \pm 0.6 \cdot 10^{-3}$ s$^{-1}$, $R^2 = 0.979$; • — 100 °C, $k_{app} = 9.3 \pm 0.7 \cdot 10^{-3}$ s$^{-1}$, $R^2 = 0.985$; ▲ — 110 °C, $k_{app} = 1.8 \pm 0.1 \cdot 10^{-2}$ s$^{-1}$, $R^2 = 0.989$; ◄ — 120 °C, $k_{app} = 3.0 \pm 0.2 \cdot 10^{-2}$ s$^{-1}$, $R^2 = 0.988$. 
Figure S14. Plot of rac-LA conversion (%) vs. time (s) at 110 °C, at different concentrations of catalyst/initiator, with the binary system II–Al₂/iPrOH. Conditions: toluene, [rac-LA]₀/[Al]/[iPrOH]₀ = 1000:n:50 ([rac-LA]₀ = 2.0 M; [iPrOH]₀ = 100 mM). ♦ — n = 4 ([Al]₀ = 8.0 mM), $k_{app} = 3.0 \pm 0.2 \cdot 10^{-2}$ s⁻¹, $R^2 = 0.991$; • — n = 8 ([Al]₀ = 16.0 mM), $k_{app} = 6.0 \pm 0.1 \cdot 10^{-2}$ s⁻¹, $R^2 = 0.999$; ▲ — n = 20 ([Al]₀ = 40.0 mM), $k_{app} = 1.1 \pm 0.1 \cdot 10^{-1}$ s⁻¹, $R^2 = 0.973$.

Figure S15. Plot of ln($k_{app}$) vs. ln([Al]) for ROP of rac-LA by the binary system II–Al₂/iPrOH at 110 °C, [rac-LA]₀ = 2.0 M, [iPrOH]₀ = 100 mM in toluene and [Al]₀ = 4.0 mM, 8.0 mM, 16.0 mM and 40.0 mM.
Figure S16. Plot of ln($k_{app}/T$) vs. 1/T for ROP of rac-LA by the binary systems $\text{I}^{\text{SiPh}_3}-\text{Al}$ and $\text{II}-\text{Al}_2$/$\text{iPrOH}$, [rac-LA]$_0$ = 2.0 M in toluene. ♦ — $\text{I}^{\text{SiPh}_3}-\text{Al}$; $\Delta H^\circ$ = 16.4(1) kcal·mol$^{-1}$, $\Delta S^\circ$ = -29(4) cal·mol$^{-1}$·K$^{-1}$, $\Delta G^\circ_{298}$ = 25.2(1) kcal·mol$^{-1}$, $R^2$ = 0.996. ● — $\text{II}-\text{Al}_2$ (1000:2:10); $\Delta H^\circ$ = 13.5(1) kcal·mol$^{-1}$, $\Delta S^\circ$ = -32(5) cal·mol$^{-1}$·K$^{-1}$, $\Delta G^\circ_{298}$ = 23.1(1) kcal·mol$^{-1}$, $R^2$ = 0.990. ▲ — $\text{II}-\text{Al}_2$ (1000:4:10); $\Delta H^\circ$ = 14.8(1) kcal·mol$^{-1}$, $\Delta S^\circ$ = -29(5) cal·mol$^{-1}$·K$^{-1}$, $\Delta G^\circ_{298}$ = 23.2(1) kcal·mol$^{-1}$, $R^2$ = 0.993.
Figure S17. Semi-logarithmic plots for ROP of rac-LA at 110 °C with $[rac\text{-}LA]_0 = 2.0 \text{ M}$ in toluene for the binary systems: • — $^1\text{ISiPh}_3\rightarrow\text{In}$, $[\text{rac}\text{-}LA]_0/[\text{In}]/[\text{iPrOH}]_0 = 500:1:10$, $k_{\text{app}} = 0.70 \pm 0.05 \cdot 10^{-3} \text{ M}^{-1}\cdot\text{s}^{-1}$, $R^2 = 0.983$; ♦ — $^2\text{In}_2$, $[\text{rac}\text{-}LA]_0/[\text{In}]/[\text{iPrOH}]_0 = 1000:2:20$, $k_{\text{app}} = 0.8 \pm 0.1 \cdot 10^{-3} \text{ M}^{-1}\cdot\text{s}^{-1}$, $R^2 = 0.996$. 

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Figure S18. Plot of $M_n$ vs. conversion (%) for ROP with the binary systems $1^\text{SiPh3-Al}$ and $2^\text{Al_2/iPrOH}$, $[\text{rac-LA}]_0 = 2.0 \text{ M in toluene at 110 °C}$: • $1^\text{SiPh3-Al}$, $[\text{rac-LA}]_0/\text{[Al]}/[\text{iPrOH}]_0 = 500:1:5$; ■ $2^\text{Al_2}$, $[\text{rac-LA}]_0/\text{[Al]}/[\text{iPrOH}]_0 = 1000:2:10$.

References and notes

2 T. V. Hansen, L. Skattebol, Organic Syntheses, 2005, 82, 20, 64-68.