Supplementary information for

Aluminum alkyl complexes supported by [OSSO] type bisphenolato ligands: synthesis, characterization and living polymerization of *rac*-lactide

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Results and Discussion about Aluminum Complex 1a

The isolation of pure complex [(etbmp)AlMe] (**1**) was accompanied by the precipitation of a white powder **1a** (~5% of the theoretical yield) even under extremely strict exclusion of air and moisture. **1a** showed a complicated resonance pattern in the ^{1}H NMR spectrum including 6 signals for the 4-methyl group and no Al-methyl resonance. Needle-like single crystals of **1a** were obtained from the mother liquor upon standing at room temperature, which immediately lost transparency when taken out of the solution. From the ^{1}H NMR spectrum, we speculated **1a** to be a derivative of "[(etbmp)$_3$Al$_2$]". In order to obtain **1a** on the preparative scale, we attempted the reactions of AlMe$_3$ or complex **1** with excess etbmpH$_2$, but no reaction occurred to produce **1a**. Thus, most likely **1a** was formed by the rearrangement of complex **1** in solution. ^{1}H NMR spectroscopic data of **1a**, δ_H (200 MHz, CDCl$_3$): 7.10 (d, 1H, ^{4}J = 2 Hz, Ar-*H*), 7.01 (d, 1H, ^{4}J = 2 Hz, Ar-*H*), 6.97 (s, 2 H, Ar-*H*), 6.96 (d, 1H, Ar-*H*), 6.94 (s, 2 H, Ar-*H*), 6.91 (d, 1 H, ^{4}J = 2 Hz, Ar-*H*), 6.89 (d, 1 H, ^{4}J = 2 Hz, Ar-*H*), 6.85 (d, 1 H, ^{4}J = 2 Hz, Ar-*H*), 6.62 (d, 1 H, ^{4}J = 2 Hz, Ar-*H*), 3.00-2.80 (m, 12 H, SCH_2), 2.20 (s, 3 H, 4-CH_3), 2.19 (s, 3 H, 4-CH_3), 2.16 (s, 3 H, 4-CH_3), 2.14 (s, 3 H, 4-CH_3), 2.08 (s, 3 H, 4-CH_3), 1.97 (s, 3 H, 4-CH_3), 1.36 [s, 9 H, 6-C(CH_3)], 1.24 [s, 9 H, 6-C(CH_3)], 1.17 [s, 18 H, 6-C(CH_3)], 1.13 [s, 9 H, 6-C(CH_3)], 1.05 [s, 9 H, 6-C(CH_3)].

Ring-Opening Polymerization of *rac*-Lactide

Kinetic analysis

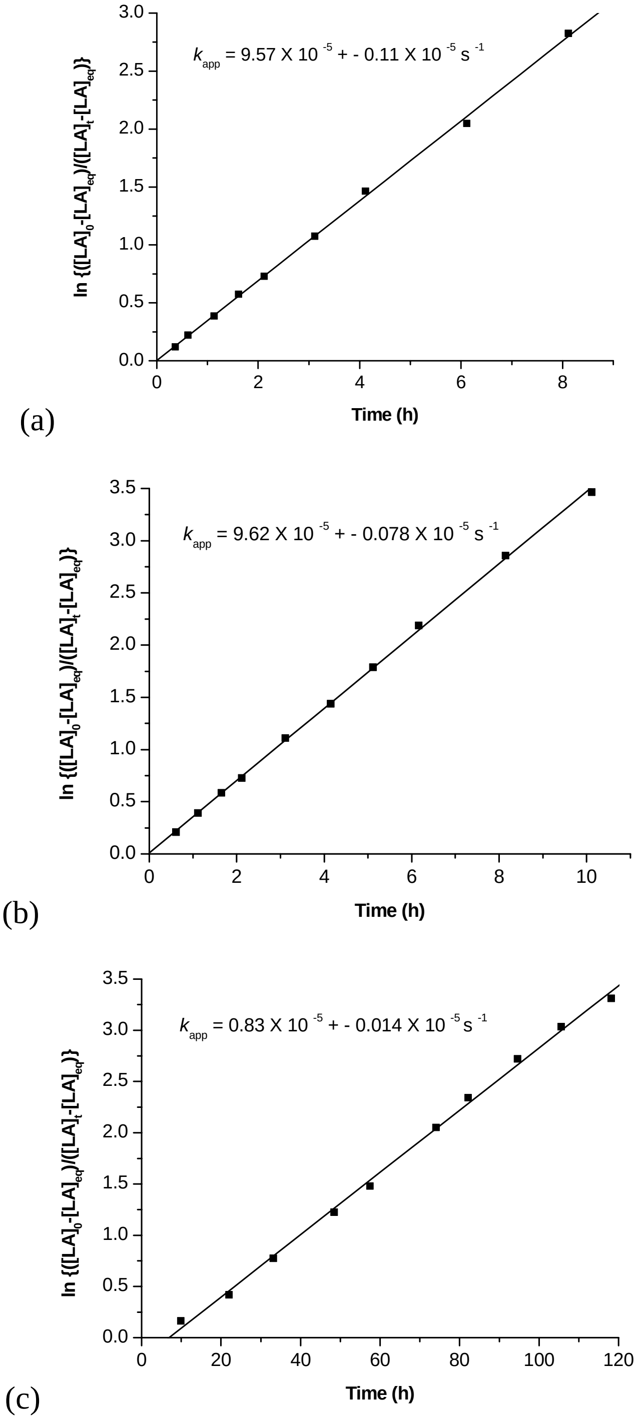
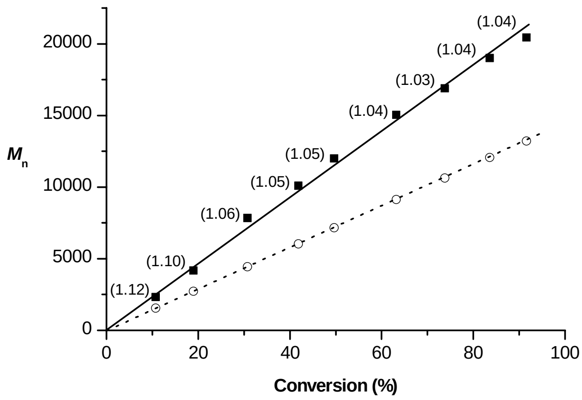
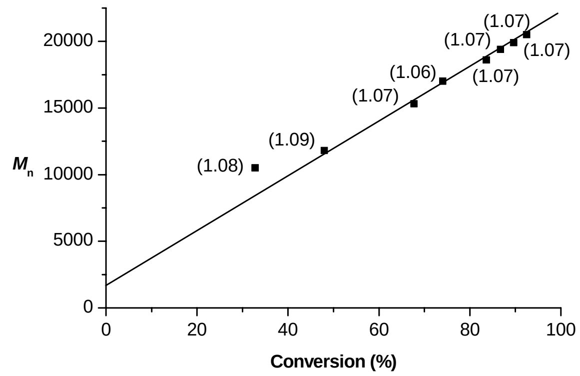


Figure S1. Semilogarithmic plots of *rac*-lactide conversion with time using (a) complex **1**/ ^{i}PrOH; (b) complex **2**/ ^{i}PrOH; (c) complex **3**/ ^{i}PrOH in toluene at 70°C, $[LA]_0$: $[Al]_0$: $[^{i}PrOH]_0$ = 100:1:1; $[LA]_{eq}$ = 0.02 mol L^{-1}



(a)



(b)

Figure S2. Plots of number molecular weight M_n of PLA versus monomer conversion using (a) complex **1** / ^{i}PrOH; (b) complex **3** / ^{i}PrOH in toluene at 70°C, $[LA]_0$:$[Al]_0$:$[^iPrOH]_0$ = 100:1:1.

Microstructure analysis of Polylactides

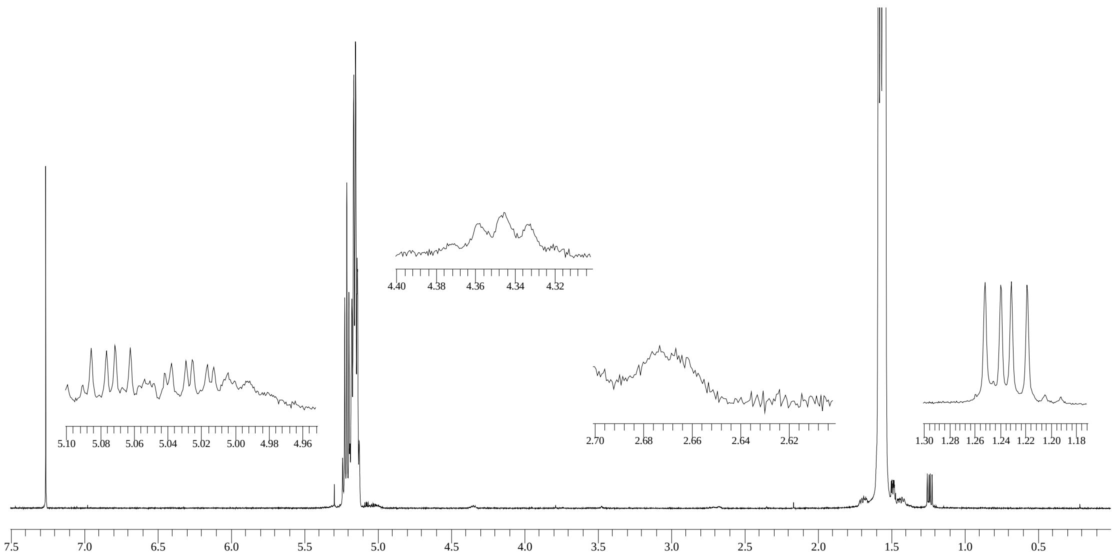
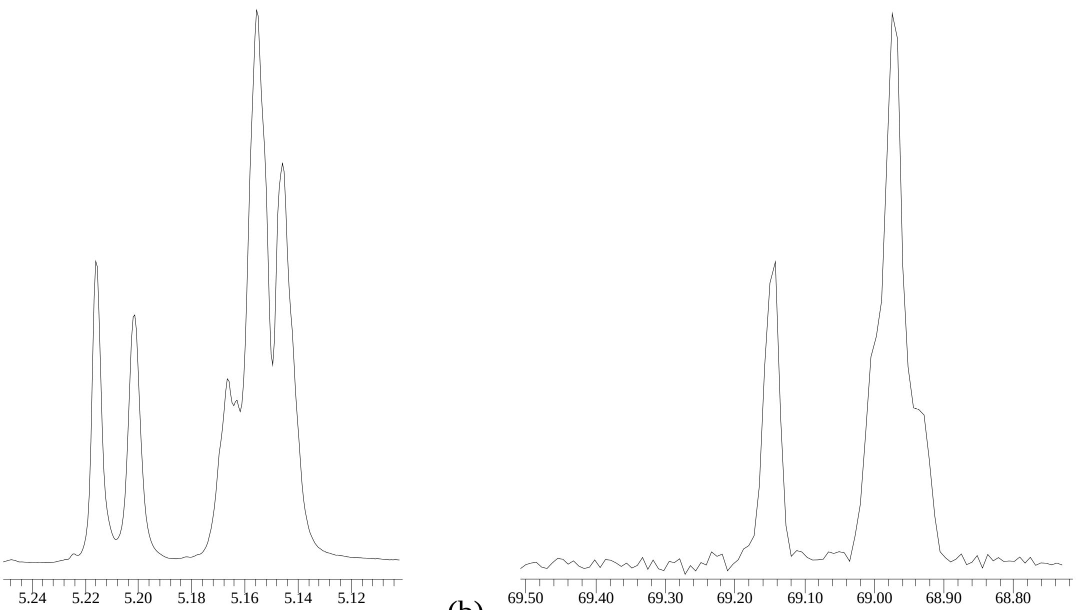


Figure S3. [1]H NMR($CDCl_3$, 500 MHz) spectrum of polylactide using complex **1** / ^{i}PrOH in toluene at 70°C, $[LA]_0$: $[Al]_0$: $[^{i}PrOH]_0$ = 100:1:1, 95% conversion.



(a) (b)

Figure S4. (a) Methine region in homonuclear decoupled ^{1}H NMR; (b) Methine region in ^{13}C NMR ($CDCl_3$, 500 MHz) of polylactide using complex **1**/ ^{i}PrOH in toluene at 70°C, $[LA]_0$: $[Al]_0$: $[^{i}PrOH]_0$ = 100:1:1, 95% conversion. Atactic polymer, no transesterification.

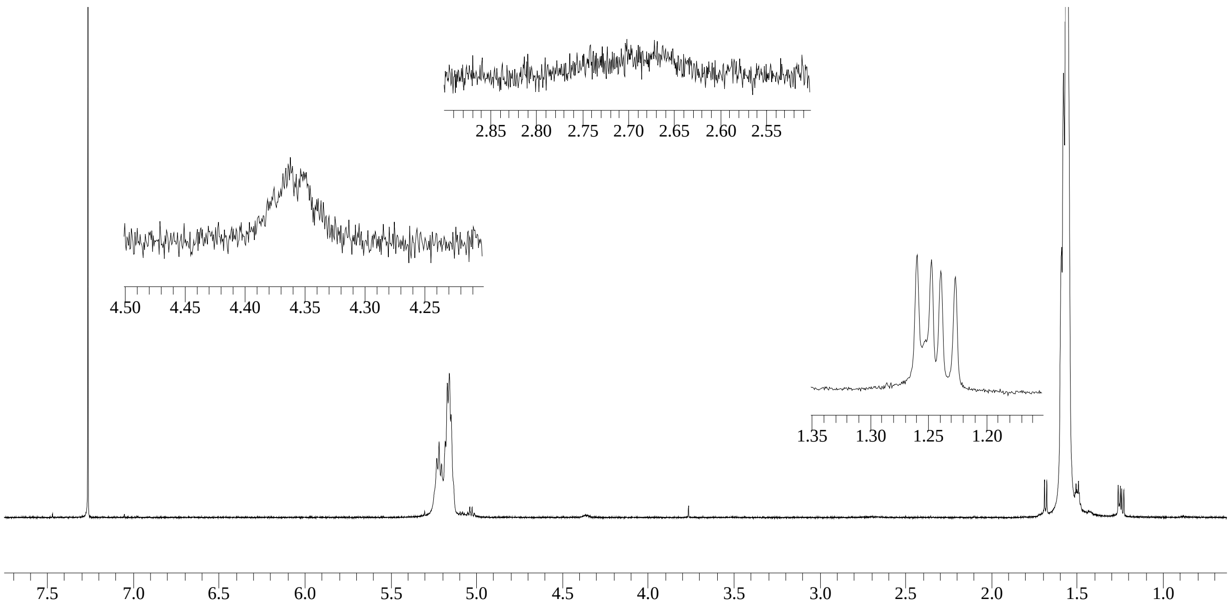


Figure S5. ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of polylactide using complex **3** / ^{i}PrOH in toluene at 70°C, $[LA]_0$: $[Al]_0$: $[^iPrOH]_0$ = 100:1:1, 33% conversion.

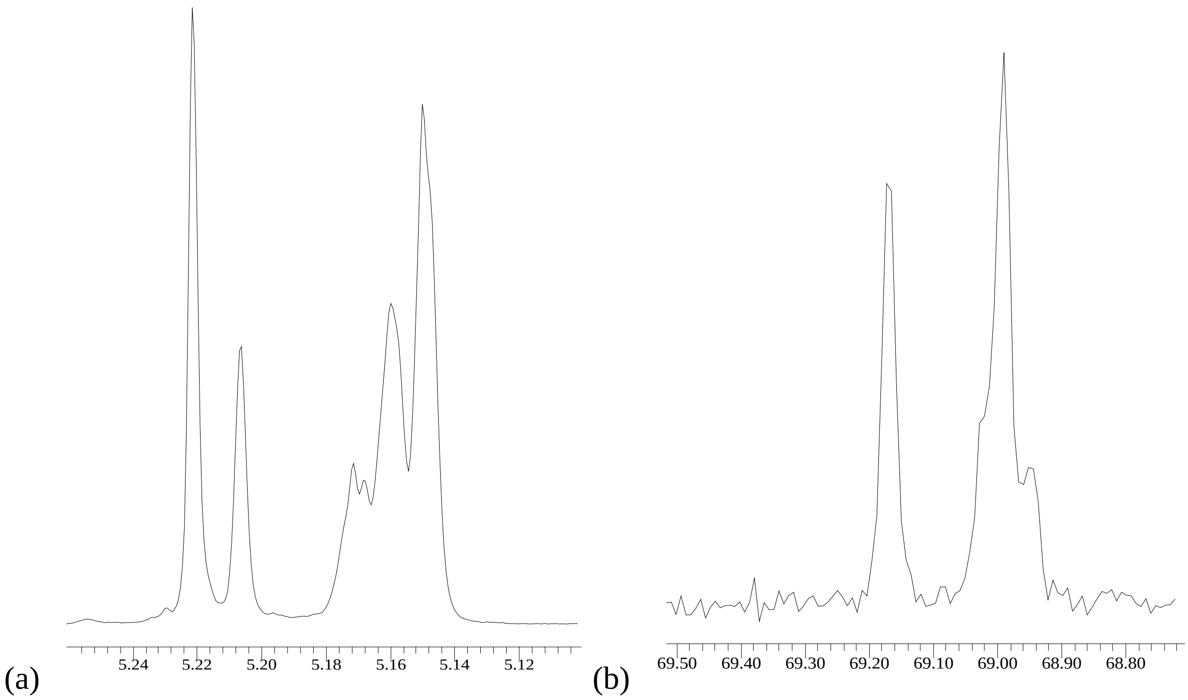


Figure S6. (a) Methine region in homonuclear decoupled ^{1}H NMR; (b) Methine region in ^{13}C NMR ($CDCl_3$, 500 MHz) of polylactide using complex **3**/ ^{i}PrOH in toluene at 70°C, $[LA]_0$: $[Al]_0$: $[^iPrOH]_0$ = 100:1:1, 93% conversion. Heterotactic-enriched polymer, no transesterification.