Supporting Information

Bimetallic aluminum complexes with cyclic β-ketiminato ligands: cooperative effect improves capability in polymerization of lactide and ε-caprolactone

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Table S1. Crystal data and structure refinements of complexes 4a-c

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<th>4a</th>
<th>4b</th>
<th>4c</th>
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<tr>
<td>Empirical formula</td>
<td>C₂₈H₃₄Al₂N₂O₂</td>
<td>C₃₂H₄₀Al₂N₂O₂</td>
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<td>Monoclinic</td>
<td>Triclinic</td>
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<td>Space group</td>
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<td>P2(1)/c</td>
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<td>113(2)</td>
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<td>0.416 and -0.330</td>
<td>0.385 and -0.365</td>
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<td>4b</td>
<td>4c</td>
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The distances between Al(1) and Al(2)

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<th>4b</th>
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Table S3 Ring-opening polymerization of L-LA and \( \varepsilon \)-CL by 4a-c/PrOH system

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<tr>
<th>Run</th>
<th>Complex</th>
<th>Mono.</th>
<th>([\text{Al}]/[\text{OH}]/[\text{M}])</th>
<th>time (min)</th>
<th>Conv. (%)</th>
<th>TOF (h(^{-1}))</th>
<th>( M_n,\text{theo}) (^{c,d} ) (( \times 10^4 ))</th>
<th>( M_n/\sigma^{f} ) (( \times 10^4 ))</th>
<th>( M_n/M_n^{f} )</th>
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<tbody>
<tr>
<td>1</td>
<td>4a</td>
<td>( \varepsilon )-CL</td>
<td>1:1:100</td>
<td>10</td>
<td>97</td>
<td>582</td>
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<td>1.54</td>
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<td>2</td>
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<tr>
<td>4</td>
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<td>( \varepsilon )-CL</td>
<td>1:0:100</td>
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<td>--</td>
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<td>5</td>
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<td>0.53</td>
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<td>1700</td>
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<td>9</td>
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<td>890</td>
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<td>188</td>
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<td>5.53</td>
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<td>69</td>
<td>73</td>
<td>0.79</td>
<td>0.89</td>
<td>1.21</td>
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\(^{a}\) 25 \( \mu \)mol of Al complex in 2 mL toluene, and polymerization at 80 °C; \(^{b}\) Non-optimized turnover frequency calculated over the whole reaction time; \(^{c}\) Calculated \( M_{n,\text{theo}}=[\varepsilon \)-CL]_0/[OH]×conv.(\varepsilon \)-CL)×114.14+\( M_{\text{PrOH}} \); \(^{d}\) Calculated \( M_{n,\text{theo}}=[L-LA]_0/[OH]\times\text{conv.}(L-LA)\times144.13+M_{\text{PrOH}} \); \(^{f}\) Experimental \( M_n \) values were determined by GPC analysis in THF using polystyrene standards and corrected by the equation: \( M_n=0.58\times M_n^{(\text{GPC})} \) for PLA, and \( M_n=0.56\times M_n^{(\text{GPC})} \) for PCL. \( ^{g} \) \( P_m=0.33 \).
Table S4 Synthesis of PLA-b-PCL copolymer by 4c/iPrOH system

<table>
<thead>
<tr>
<th>Entry</th>
<th>Complex</th>
<th>Time&lt;sup&gt;b&lt;/sup&gt;</th>
<th>(M_n,\text{GPC}(\times 10^4))</th>
<th>(M_n(\times 10^4))</th>
<th>(M_w/M_n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA-b-PCL&lt;sup&gt;e&lt;/sup&gt;</td>
<td>4c</td>
<td>1.5h(LA)+1h(CL)</td>
<td>4.0</td>
<td>2.12</td>
<td>1.34</td>
</tr>
</tbody>
</table>

<sup>a</sup> Reaction conditions: 25 μmol complex in toluene, iPrOH 1.0 equiv. to Al, monomer 5.0 mmol, 80 °C; <sup>b</sup> After LA reaction for 1.5 h, CL was added and reacted for the prescribed time; <sup>c</sup> GPC data determined by SEC in THF relative to polystyrene standards; <sup>d</sup> GPC data determined by SEC in THF relative to polystyrene standards corrected by the Mark–Houwink correction factor (\(M_n=M_n,\text{SEC} \times 0.56 \times \text{PCL\%} + M_n,\text{SEC} \times 0.58 \times \text{PLLA\%}\)); <sup>e</sup> the first block PLA with \(M_n,\text{GPC}=1.83 \times 10^4\), \(M_w/M_n=1.21\), conversion > 99%

Table S5. Experimental \(T_g\) of the CL/LA copolymers as a function of the mole fraction of \(\varepsilon\)-CL unit

<table>
<thead>
<tr>
<th>Entry</th>
<th>Time (h)</th>
<th>CL in copolymer&lt;sup&gt;b&lt;/sup&gt; (%)</th>
<th>(T_g) (°C)</th>
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<td>2</td>
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<td>21.8</td>
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<td>4</td>
<td>3</td>
<td>50.0</td>
<td>-2.6</td>
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<sup>a</sup> Reaction conditions: 25 μmol of Al catalyst in 2 mL of toluene, iPrOH/[Al] = 2.0, [CL]/[LA]/[Al]=100:100:1, copolymerization at 80 °C; <sup>b</sup> CL in copolymer measured by \(^1\)H NMR.

Table S6. Calculate reactivity ratios for L-LA and \(\varepsilon\)-CL in Poly(LA-grad-CL) copolymers

<table>
<thead>
<tr>
<th>Entry</th>
<th>Conv. (%)</th>
<th>X&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Y&lt;sup&gt;c&lt;/sup&gt;</th>
<th>G&lt;sup&gt;d&lt;/sup&gt;</th>
<th>F&lt;sup&gt;e&lt;/sup&gt;</th>
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<td>1</td>
<td>3.1</td>
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<td>3.15</td>
<td>0.29</td>
<td>0.059</td>
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<sup>a</sup> Reaction conditions: 25 μmol of Al catalyst in 2 ml of toluene, [iPrOH]/[Al] = 2.0, 80 °C; The reactivity ratios were calculated using the nonlinear least squares (NLLS) method, the monomer composition in the obtained oligomer was examined at a low conversion (≤10%).

<sup>b</sup> X = \(M_{LA}/M_{CL}\), \(M_{LA}\) and \(M_{CL}\) were defined as moles of monomer in the copolymerization reaction system;

<sup>c</sup> Y was defined as the mole ratio of two kinds of monomer;

<sup>d</sup> G = X(\(Y-1\))/Y;

<sup>e</sup> F = X^2/Y^3.
<table>
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<tr>
<th>Run</th>
<th>LA:CL :Al:OH (mol:mol)</th>
<th>Conversion (%)</th>
<th>$M_n^b$/10^4</th>
<th>$M_w/M_n^b$</th>
<th>$L_{CL}^c$</th>
<th>$L_{LA}^c$</th>
<th>CL (mol %)~(^d)</th>
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~\(^a\) Reaction conditions: 25 µmol of Al catalyst and copolymerization at 80 °C for 8 h; ~\(^b\) Determined by GPC in THF using polystyrene as standard; ~\(^c\) Average sequences length of the caproyl unit and lactidyl unit was determined by ~\(^{13}\)C NMR; ~\(^d\) Monomer conversion was determined by ~\(^1\)H NMR. ~\(^d\) CL in the copolymer (mol %)
Fig. S1. Molecular structure of complex 4a with thermal ellipsoids at the 30% probability level. Hydrogen atoms are omitted for clarity.

Fig. S2. Molecular structure of complex 4b with thermal ellipsoids at the 30% probability level. Hydrogen atoms are omitted for clarity.

Fig. S3. $^1$H NMR spectrum of binuclear aluminum complexes 4c in the presence of $^i$PrOH (toluene-d$_8$, 400 MHz)
Fig. S4. Methyne proton of the hydroxyl end group of the PLA-\(\text{b}\)-PCL copolymer (CDCl\(_3\), 25 °C).

Fig. S5. GPC profiles of PLA and PLA-\(\text{b}\)-PCL obtained by the 4c/iPrOH system (in THF at 25 °C).

Fig. S6. \(^{13}\)C NMR spectrum of PLA-\(\text{b}\)-PCL synthesized by 4c/iPrOH system (CDCl\(_3\), 25 °C).

Fig. S7. DSC curve of PLA-\(\text{b}\)-PCL prepared by 4c/iPrOH system.
Fig. S8. $^1$H NMR spectrum of poly(LA-grad-CL) copolymer (run 2, Table 3) (CDCl$_3$, 25°C).

Fig. S9. $^{13}$C NMR spectra (CDCl$_3$, 25°C) of the copolymers obtained at different conversion.

Fig. S10. Experimental $T_g$ of the CL/LA copolymers as a function of the mole fraction of $\varepsilon$-CL unit.
**Fig. S11.** G-F plot for Poly(LA-grad-CL) copolymers by 4c/PrOH system.

**Fig. S12.** $^1$H NMR spectrum of binuclear aluminum complexes 4c (toluene-d$_8$, 400 MHz)

**Fig. S13.** $^1$H NMR spectrum of β-ketiminato ligand 3a (CDCl$_3$, 25 °C).
Fig. S14. $^1$H NMR spectrum of β-ketiminato ligand 3b (CDCl$_3$, 25 °C).

Fig. S15. $^1$H NMR spectrum of β-ketiminato ligand 3c (CDCl$_3$, 25 °C).

Fig. S16. $^1$H NMR spectrum of binuclear aluminum complexes 4a (CDCl$_3$, 25 °C).

Fig. S17. $^1$H NMR spectrum of binuclear aluminum complexes 4b (CDCl$_3$, 25 °C).
Fig. S18. $^1$H NMR spectrum of binuclear aluminum complexes 4c (CDCl$_3$, 25 °C).

Fig. S19. $^1$H NMR spectrum of $\beta$-ketiminato ligand for M1 (CDCl$_3$, 25 °C).

Fig. S20. $^1$H NMR spectrum of mononuclear aluminum complex M1 (CDCl$_3$, 25 °C).

Fig. S21. $^1$H NMR spectrum of mononuclear aluminum complex for M2 (CDCl$_3$, 25 °C).
Synthesis of aluminum complexes M1 and M2

Into a stirred solution of $\text{C}_6\text{H}_{11}\text{N}=\text{CHC}_4\text{H}_4\text{OH}$ (2.0 mmol) in toluene (10 mL), AlMe$_3$ (1 M hexane solution, 2.1 mL) was added drop-wise over 10 min. After stirred for 8 h the solution was concentrated and cooled to -20 °C, yellow solid was isolated by filter and recrystallized from mixture of toluene/hexane and afforded $[\text{C}_6\text{H}_{11}\text{N}=\text{CHC}_4\text{H}_4\text{O}]\text{Al(CH}_3\text{)}_2$ (M1) Yield: 92%. $^1$H NMR (400 MHz, CDCl$_3$) 7.88 (d, 1H, $\text{N} = \text{C-H}$), 7.67 (s, 1H, Ar-H), 7.33 (m, 2H, Ar-H), 7.18 (d, 1H, Ar-H), 3.22 (dd, 1H, CH-(CH$_2$)$_2$), 2.95–2.77 (m, 2H, -CH$_2$-), 2.62–2.47 (m, 2H, -CH$_2$-), 1.92 (t, 4H, -CH$_2$-CH), 1.80–1.02 (m, 6H), -0.71 (s, Al-CH$_3$, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$): 166.33, 139.73, 133.29, 130.76, 127.15, 126.69, 125.93, 104.37, 67.35, 31.08, 28.69, 25.94, 25.56, 25.15, 24.5, -8.45.

Synthesis for $[\text{C(CH}_3)_3\text{CHN}=\text{CHC}_4\text{H}_4\text{O}]\text{Al(CH}_3\text{)}_2$ (M2) was performed according to the same procedure as that of M1 Yield: 88%. $^1$H NMR (400 MHz, CDCl$_3$) 7.95 (d, 1H, N = C-H), 7.51 (s, 1H, Ar-H), 7.42–7.25 (m, 2H, Ar-H), 7.19 (d, 1H, Ar-H), 3.22 (s, 2H -CH$_2$-CH), 2.95–2.78 (m, 2H, -CH$_2$-), 2.66–2.46 (m, 2H, -CH$_2$-), 1.01 (s, 9H, CH$_3$), -0.73 (d, 6H, Al-CH$_3$). $^{13}$C NMR (100 MHz, CDCl$_3$): 166.46, 139.45, 133.18, 130.87, 127.26, 126.75, 125.97, 106.16, 67.57, 33.97, 28.51, 25.84, 25.39, 25.17, -8.65.