Supporting Information

Salen complexes of Zirconium and Hafnium: Synthesis, structural characterization and polymerization studies

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Fig. S1 $^1$H NMR (400 MHz, CDCl$_3$) of Compound 1
Fig. S2 $^{13}$C NMR (100 MHz, CDCl$_3$) of Compound 1
Fig. S3 ESI-Mass spectrum of Compound 1
Fig. S4 $^1$H NMR (400 MHz, CDCl$_3$) of Compound 2

Fig. S5 $^{13}$C NMR (100 MHz, CDCl$_3$) of Compound 2
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Fig. S23 $^{13}$C NMR (100 MHz, CDCl$_3$) of Compound 8
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Fig. S25 $^1$H NMR (400 MHz, CDCl$_3$) of Compound 9
Fig. S26 $^{13}$C NMR (100 MHz, CDCl$_3$) of Compound 9
Fig. S27 ESI-Mass Spectrum of Compound 9
**Fig. S28** Molecular structure of 2; thermal ellipsoids were drawn at 30 % probability level. Selected bond lengths (Å) and bond angles (°): Zr(1)-Zr(2) 3.496(2), Zr(1)-N(1) 2.479(15), Zr(2)-N(2) 2.472(13), Zr(1)-O(1) 2.062(9), Zr(1)-O(5) 2.143(9), Zr(2)-O(2) 2.050(8), Zr(2)-O(5) 2.161(8), O(4)-Zr(2)-Zr(1) 102.3(3), O(3)-Zr(2)-Zr(1) 127.8(3), O(2)-Zr(2)-Zr(1) 126.8(3), O(5)-Zr(2)-Zr(1) 35.5(2), N(2)-Zr(2)-Zr(1) 82.8(3), N(1)-Zr(1)-Zr(2) 83.7(3), O(6)-Zr(1)-Zr(2) 101.2(3), O(7)-Zr(1)-Zr(2) 126.7(3).

**Fig. S29** Molecular structure of 3; thermal ellipsoids were drawn at 30 % probability level. Selected bond lengths (Å) and bond angles (°): N(1)-Zr(1) 2.4374(15), N(2)-Zr(1) 2.3928(14),
N(3)-Zr(1) 2.3960(14), N(4)-Zr(1) 2.4170(14), O(1)-Zr(1) 2.1011(12), O(2)-Zr(1) 2.1071(12), O(3)-Zr(1) 2.1082(12), O(4)-Zr(1) 2.0795(12), O(4)-Zr(1)-O(1) 95.61(5), O(4)-Zr(1)-O(3) 143.27(5), N(2)-Zr(1)-N(3) 129.73(5), N(3)-Zr(1)-N(4) 69.24(5).

Fig. S30 Coordination polyhedron of a distorted square antiprism geometry.

Fig. S31 Representative GPC traces for the polymerization of (a) rac-LA (entry 2, Table 1); (b) L-LA (entry 11, Table 1) and (c) ε-CL (entry 14, Table 1) using 2.
Fig. S32 Plot of $M_n$ and $M_w/M_n$ vs. % conversion for $L$-LA, rac-LA and $\varepsilon$-CL polymerization using 2 at 140 °C ($L$-LA and rac-LA) and 80 °C ($\varepsilon$-CL).

Fig. S33 Plot of $M_n$ and $M_w/M_n$ vs. $[M]/[C]$ for rac-LA polymerization using 2, 3, 6 and 9 in the presence of benzyl alcohol at 140 °C.
**Fig. S34** Homonuclear decoupled $^1$H NMR spectra of PLA from rac-LA using 2 in CDCl$_3$.

**Fig. S35** $^1$H NMR spectrum of the crude product obtained from a reaction between rac-LA and 2 in 15: 1 ratio.
Fig. S36 MALDI-TOF of the crude product obtained from a reaction between rac-LA and 6 in 10:1 ratio.

Fig. S37 $^1$H NMR spectrum of the crude product obtained from a reaction between rac-LA and 6 in 10:1 ratio.
**Fig. S38** MALDI-TOF of the crude product obtained from a reaction between \textit{rac}-LA and 2 in the presence of BnOH in 15: 1: 2 ratio.

**Fig. S39** $^1$H NMR spectrum of the crude product obtained from a reaction between \textit{rac}-LA and 2 in the presence of BnOH in ratio 15: 1: 2.
Fig. S40 Representative GPC traces for the copolymerization of cyclohexene oxide and CO$_2$ using 3 (entry 6, Table 2) and 4 (entry 7, Table 2).

Fig. S41 MALDI-TOF mass spectrum of PCHC sample produced by 2 at 50 °C and 35 bar CO$_2$ pressure from CHO and CO$_2$ using TBAB as cocatalyst.
**Fig. S42** $^{13}$C NMR spectrum of poly(cyclohexene carbonate) in the carbonate region produced from cyclohexene oxide and CO$_2$.

**Fig. S43** Representative TGA trace and derivative plot of PCHC produced by 2 (Table 2, entry 2).
**Fig. S44** Representative DSC trace of PCHC produced by 2, 2nd heat cycle (Table 2, entry 2).

**Fig. S45** $^{13}$C NMR spectrum of an aliquot from the reaction mixture of SO/CO$_2$ in CDCl$_3$. 
Fig. S46 $^{13}$C NMR spectrum of an aliquot from the reaction mixture of PO/CO$_2$ in CDCl$_3$.

Fig. S47 Representative GPC traces for the polymerization of (a) CHO (entry 3, Table 4); (b) PO (entry 12, Table 4) and (c) SO (entry 21, Table 4) using 3.
**Fig. S48** $^1$H NMR (500 MHz, CDCl$_3$) of the crude product obtained from a reaction between CHO and 2 in 1000: 1 ratio at 80 °C.

![NMR spectrum](image1.png)

**Fig. S49** $^1$H NMR (500 MHz, CDCl$_3$) of the crude product obtained from a reaction between PO and 2 in 1000: 1 ratio at 40 °C.

![NMR spectrum](image2.png)
**Fig. S50** $^1$H NMR (500 MHz, CDCl$_3$) of the crude product obtained from a reaction between SO and 2 in 1000:1 ratio at 100 °C.

![H NMR spectrum](image)

**Fig. S51** $^{13}$C NMR (125 MHz, CDCl$_3$) Spectrum of the representative PCHO obtained from a reaction between CHO and 2 in 1000:1 ratio at 80 °C.

![C NMR spectrum](image)
Fig. S52 $^{13}$C NMR (125 MHz, CDCl$_3$) Spectrum of the representative PPO obtained from a reaction between PO and 2 in 1000: 1 ratio at 40 °C.

Scheme S1 Polymerization proceeds through the coordination-insertion mechanism for rac-LA.

Table S1 Crystal data for the structures of 1, 2, 3, 5, 6 and 9
Table S2 Polymerization data based on changing ratios in case of rac-LA using 1, 2, 3, 5, 6 and 9 in the presence of benzyl alcohol at 140 °C.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Initiator</th>
<th>[M]/[C]/[BnOH] ratio</th>
<th>′Time/min</th>
<th>Yield (%)</th>
<th>(\bar{M}_n^{obs}) kgmol(^{-1})</th>
<th>(\bar{M}_n^{theo}) kgmol(^{-1})</th>
<th>(M_w/M_n)</th>
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<tr>
<td>1</td>
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<td>28</td>
<td>95</td>
<td>9.52</td>
<td>6.95</td>
<td>1.04</td>
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<tr>
<td>2</td>
<td>1</td>
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<td>94</td>
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<td>13.6</td>
<td>1.07</td>
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<tr>
<td>3</td>
<td>1</td>
<td>400: 1: 2</td>
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<td>99</td>
<td>31.4</td>
<td>28.6</td>
<td>1.09</td>
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<tr>
<td>4</td>
<td>1</td>
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<td>149</td>
<td>98</td>
<td>46.0</td>
<td>42.5</td>
<td>1.10</td>
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<tr>
<td>5</td>
<td>1</td>
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<td>202</td>
<td>99</td>
<td>61.1</td>
<td>57.2</td>
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<tr>
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Table S3 DSC and TGA measurements for the different copolymers obtained in Table 2.

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<tr>
<th>Entry</th>
<th>Initiator</th>
<th>Copolymers</th>
<th>$T_g^a$ (°C)</th>
<th>$T_{d5}^b$ (°C)</th>
<th>$T_{d50}^b$ (°C)</th>
<th>$T_{d95}^b$ (°C)</th>
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<tbody>
<tr>
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<td>2</td>
<td>PCHC</td>
<td>55</td>
<td>92</td>
<td>187</td>
<td>&gt;900</td>
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<tr>
<td>2</td>
<td>3</td>
<td>PCHC</td>
<td>48</td>
<td>85</td>
<td>179</td>
<td>&gt;900</td>
</tr>
<tr>
<td>3</td>
<td>6</td>
<td>PCHC</td>
<td>52</td>
<td>90</td>
<td>185</td>
<td>&gt;900</td>
</tr>
<tr>
<td>4</td>
<td>9</td>
<td>PCHC</td>
<td>50</td>
<td>88</td>
<td>182</td>
<td>&gt;900</td>
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</tbody>
</table>

$^a$Time of polymerization measured by quenching the polymerization reaction when all monomer was found consumed.

$^b$Measured by GPC at 27 °C in THF relative to polystyrene standards after applying a multiplication factor of 0.58 (for rac-LA). $^cM_n$ (theoretical) at actual conversion = [Conversion × $[M]_0/[C]_0$ × mol. Wt. (monomer)] + mol. Wt. (BnOH).