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COMMUNICATION

High activity of an indium alkoxide complex toward the ring opening polymerization of cyclic esters

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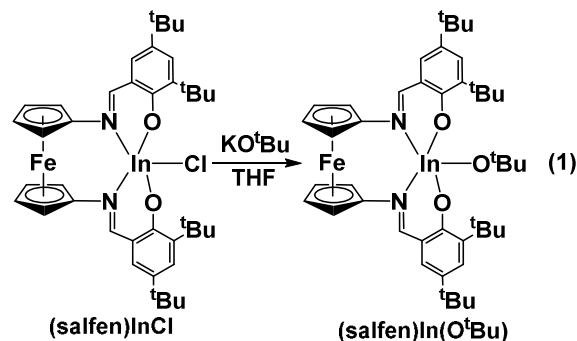
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Abstract. An indium complex supported by a ferrocene-derived Schiff base ligand has an unprecedented high activity toward ϵ -caprolactone, δ -valerolactone, and β -butyrolactone. L-lactide, D,L-lactide, and trimethylene carbonate polymerizations also showed moderate to high activity.

Over the past two decades, the ring-opening polymerization of cyclic esters has been increasingly studied because of the promise to produce biodegradable polymers from biomass.¹ Industrial applications for these polymers range from disposable plastic utensils to 3D printing and biomedical tissue scaffolding.² Of the numerous pre-catalysts developed toward this end, indium complexes have demonstrated high activity and stereoselectivity for a number of monomers.³⁻¹³ Lactide polymerizations have been particularly well examined, but many of the precatalysts¹⁴⁻²⁰ often require initiators. β -butyrolactone,^{8, 21} ϵ -caprolactone,²⁰ and trimethylene carbonate²² polymerizations have also been achieved by indium catalysts. Although less studied, low catalyst loadings²¹ and the potential range of lactone and carbonate monomers²³ make their polymerization a promising area toward finding new biodegradable polymers.

In our recent studies, a cerium complex supported by a Schiff base ligand with a ferrocene backbone polymerized L-lactide in a controlled fashion.²⁴ Phosphinimine analogues with yttrium and indium also demonstrated good activity in lactide and trimethylene carbonate polymerizations.²² Therefore, we decided to combine indium's activity with the Schiff base, ferrocene-derived ligand in order to study the activity of the resulting complexes toward a broad range of cyclic ester polymerizations. Additional motivation was found from recent studies that point to the biocompatibility, robustness, and high activity of indium catalysts in the ring opening polymerization of cyclic esters.^{10, 25}

Herein, we report a ferrocene-derived Schiff base indium complex that possesses a remarkable range of activity toward cyclic esters and exceptionally fast polymerization rates with lactones. Compound (salfen)In(O^tBu) (salfen = 1,1'-di(2,4-di-*tert*-butyl-6-iminephenoxy)ferrocene) represents the first indium precatalyst capable of δ -valerolactone polymerization and the most active indium catalyst to date in the polymerization of β -butyrolactone and ϵ -caprolactone. The polymerization rates of ϵ -caprolactone are even competitive with those of current industrial catalysts.



Compound (salfen)In(O^tBu) was synthesized from the reaction of (salfen)InCl and freshly sublimed KO^tBu. In turn, (salfen)InCl was synthesized by combining InCl₃ with K₂(salfen), which was generated from H₂(salfen) and two equivalents of KH (Eq 1). Needle crystals of (salfen)InCl were isolated from a diethyl ether solution. The solid state molecular structure (Figure 1) shows a distorted octahedral indium center and a THF molecule coordinated trans to the chloride ligand. Similarly to the phosphinimine indium chloride analogue previously reported by us,²² a long In-Fe distance (3.98 Å) and a staggered configuration of the Cp rings were apparent. Elongation of the In-heteroatom distances compared to other compounds, such as (salen)InCl (salen = N,N-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamine (*rac*- or (R,R)-

$\text{H}_2(\text{ONNO}))^9$ and (phosfen)In(OPh) (phosfen = 1,1'-di(2-*tert*-butyl-6-diphenylphosphiniminophenoxy)ferrocene),²² by about 0.25 Å possibly compensates for the distortion caused by the staggered Cp rings.

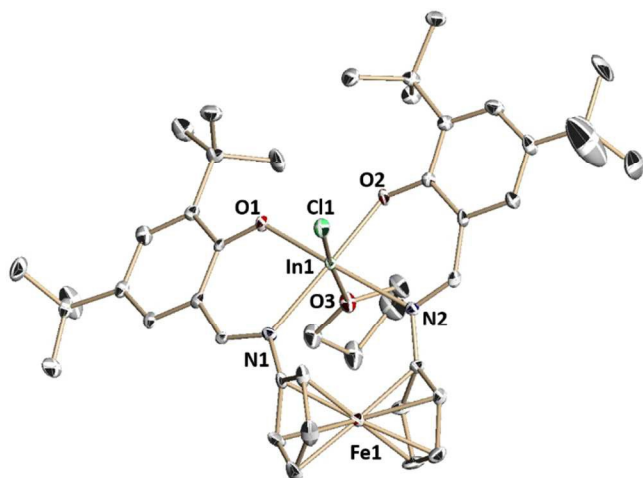
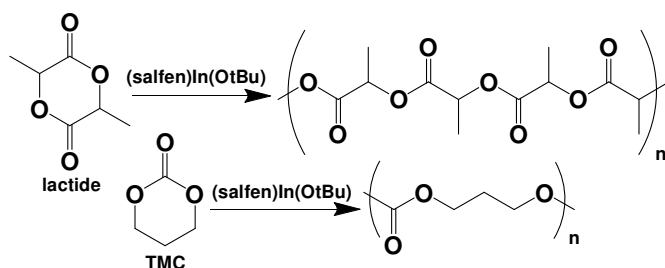


Figure 1. Thermal-ellipsoid (50% probability) representation of (salfen)In(OtBu); hydrogen, disordered counterparts, and solvent atoms were removed for clarity.

Compound (salfen)In(OtBu) was evaluated for polymerization activity toward L-lactide, D,L-lactide, trimethylene carbonate, ϵ -caprolactone, δ -valerolactone, and β -butyrolactone. Reacting (salfen)In(OtBu) with 100 equivalents of L-lactide led to 95% conversion of the monomer in 270 min (Table 1, entry 2); PDI values ranged from 1.06 - 1.16. D,L-lactide showed a similar activity attaining 98% conversion in 280 minutes (Table 1, entry 4). A selectivity of $P_m = 0.52$ was determined using homodecoupled ^1H NMR spectroscopy and Bernoullian statistics (see the Supporting Information for details) that is higher than that obtained for our previously reported (phosfen)Y(OtBu) complex.²²

Table 1. Polymerization of L-lactide (LLA), rac-lactide (DLLA), and trimethylene carbonate (TMC) by (salfen)In(OtBu).^a



| Entry | Monomer | [M]/[I] | Time (min) | Conversion ^b (%) | $M_{n,theo}$ ^c | $M_n^{c,d}$ | PDI ^e |
|-------|---------|---------|------------|-----------------------------|---------------------------|-------------|------------------|
| 1 | LLA | 50 | 120 | 97 | 8.4 | 15.9 | 1.12 |
| 2 | LLA | 100 | 270 | 95 | 15.1 | 32.8 | 1.16 |
| 3 | DLLA | 50 | 150 | 96 | 8.7 | 15.4 | 1.07 |
| 4 | DLLA | 100 | 280 | 98 | 17.5 | 32.2 | 1.06 |
| 5 | TMC | 50 | 5 | 95 | 4.0 | 28.1 | 1.75 |
| 6 | TMC | 100 | 10 | 94 | 6.8 | 39.7 | 1.70 |

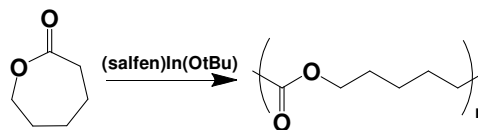
^aConditions: [I] = 0.005 M, room temperature, 1,3,5-trimethoxybenzene as the internal standard, toluene as the solvent. ^bConversion determined by ^1H NMR spectroscopy. ^c M_n reported in 10^3 g/mol. ^dDetermined by GPC in chloroform calibrated versus polystyrene standards. ^ePDI = M_w/M_n .

10^3 g/mol. ^dDetermined by GPC in chloroform and calibrated versus polystyrene standards. See note in SI about TMC. ^ePDI = M_w/M_n .

Trimethylene carbonate was polymerized rapidly, reaching full conversion of 100 equivalents in less than 10 minutes (Table 1, entry 6), although higher PDI values (1.70 – 1.75) were observed. Compared with our previous indium complex,²² which reached 49% conversion in one day, the present results represent a considerable improvement. Aluminum catalysts have achieved similar activity²⁶⁻²⁹ albeit with raised temperatures. The highest conversions, however, have been obtained with lanthanide complexes³⁰ and organocatalysts.²⁹

The polymerization of ϵ -caprolactone was particularly impressive. Compound (salfen)In(OtBu) polymerized 1500 equivalents in 5 minutes (Table 2, entry 4), trapping the stir bar in a matrix of polymer. However, at higher monomer:catalyst ratios, a plateauing of the polymer molecular weight was observed (Table 2, entries 4-7). Also, the polymerization of 2000 equivalents of ϵ -caprolactone took 20 minutes to reach completion. PDI values ranged from 1.15 to 1.28 (Table 2). The activity of (salfen)In(OtBu), which is capable to polymerize 1500 equivalents in 5 minutes is much faster than that of industrially used Sn(oct)₂.^{31, 32}

Table 2. Polymerization of ϵ -caprolactone by (salfen)In(OtBu).



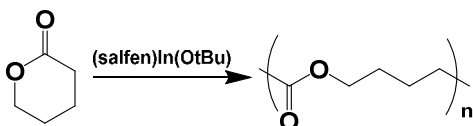
| Entry | [M]/[I] | Time (min) | Conversion ^b (%) | $M_{n,theo}$ ^c | $M_n^{c,d}$ | PDI ^e |
|-------|---------|------------|-----------------------------|---------------------------|-------------|------------------|
| 1 | 100 | 2 | 99 | 13.0 | 109.7 | 1.28 |
| 2 | 250 | 2 | 99 | 25.7 | 148.1 | 1.25 |
| 3 | 500 | 5 | 99 | 76.0 | 232.7 | 1.19 |
| 4 | 750 | 5 | 99 | 95.8 | 266.3 | 1.22 |
| 5 | 1000 | 5 | 99 | 106.3 | 298.1 | 1.16 |
| 6 | 1500 | 5 | 99 | 184.8 | 310.0 | 1.18 |
| 7 | 2000 | 20 | 99 | 233.6 | 322.5 | 1.15 |

^aConditions: [I] = 0.005 M, room temperature, 1,3,5-trimethoxybenzene as the internal standard, toluene as the solvent. ^bConversion determined by ^1H NMR spectroscopy. ^c M_n reported in 10^3 g/mol. ^dDetermined by GPC in chloroform calibrated versus polystyrene standards. ^ePDI = M_w/M_n .

Encouraged by the ϵ -caprolactone polymerizations results, (salfen)In(OtBu) was tested for activity toward other lactone monomers. The polymerization of 100 equivalents of δ -valerolactone at room temperature in toluene reached over 90% conversion in a few minutes (Table 3, entry 1). Lowering the catalyst loading to 0.1 mol% did not decrease the polymerization time (Table 3, entry 5). Like in the case of ϵ -caprolactone, the newly generated polymer locked the stir bar in a gel-like substance. PDI values ranged from 1.38 to 1.46. Although aluminum alkoxide,^{33, 34} thiolate,³⁵ and porphyrin³⁶ complexes have been known to polymerize δ -valerolactone since the 1990s, monomer equivalents above 200 or conversions under several hours were rarely achieved. A recent aluminum complex has shown great promise, polymerizing up to 1250 equivalents in 30 minutes, albeit with PDI values ranging between 1.93 and 4.89.³⁷ Organocatalysts have also demonstrated good activity with moderate control.³⁸ Our current catalyst is the first indium complex capable of δ -valerolactone polymerization that

achieves faster activity and greater control than many current catalysts. It should be noted that while the polymerizations of other monomers proceed under greater control, it is not necessarily a detriment to have slightly broad molecular weight distributions. Less controlled polymer mixtures exhibit elastic mechanical properties that can make them easier to produce and process.^{39, 40}

Table 3. Polymerization of δ -valerolactone (VL) by (salfen)In(O^tBu).



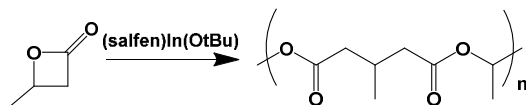
| Entry | [M]/[I] | Time (min) | Conversion (%) ^b | M _{n,theo} ^c | M _n ^{c,d} | PDI ^e |
|-------|---------|------------|-----------------------------|----------------------------------|-------------------------------|------------------|
| 1 | 100 | 5 | 99 | 11.9 | 31.8 | 1.46 |
| 2 | 250 | 5 | 99 | 27.7 | 77.5 | 1.46 |
| 3 | 500 | 5 | 99 | 46.7 | 112.6 | 1.38 |
| 4 | 750 | 5 | 99 | 64.4 | 218.5 | 1.43 |
| 5 | 1000 | 5 | 99 | 87.7 | 190.3 | 1.43 |

^aConditions: [I] = 0.005 M, room temperature, 1,3,5-trimethoxybenzene as the internal standard, toluene as the solvent. ^bConversion determined by ¹H NMR spectroscopy. ^cM_n reported in 10³ g/mol. ^dDetermined by GPC in chloroform calibrated versus polystyrene standards. ^ePDI = M_w/M_n.

On the other hand, γ -butyrolactone showed no signs of polymerization after 4 days. Calculations by the Houk group have demonstrated that despite γ -butyrolactone's 8 kcal strain energy, the smaller geometric distortion in the ester group and the unusual stability of coiled polyhydroxybutyrate often renders γ -butyrolactone less likely to polymerize than δ -valerolactone.⁴¹

Furthermore, (salfen)In(O^tBu) showed an excellent polymerization activity with β -butyrolactone: 100 equivalents were polymerized in 30 minutes (Table 4, entry 1). Increasing the monomer amount to 500 equivalents resulted in a slower reaction, taking 60 minutes to reach full conversion. A similar decrease in activity has been observed with yttrium catalysts.⁴² Most promising, these results indicate that (salfen)In(O^tBu) is the fastest among group 13 precatalysts for the polymerization of β -butyrolactone.⁴³⁻⁴⁶ Bernoullian statistics and NMR techniques were used to determine the selectivity of the process. The P_m value was found to be 0.47, comparable to the value reported for other indium catalysts.²¹ Low PDI values ranging from 1.07 to 1.12 were found.

Table 4. Polymerization of β -butyrolactone by (salfen)In(O^tBu).



| Entry | [M]/[I] | Time (min) | Conversion (%) ^b | M _{n,theo} ^c | M _{n,GPC} ^{c,d} | PDI |
|-------|---------|------------|-----------------------------|----------------------------------|-----------------------------------|------|
| 1 | 100 | 30 | 99 | 10.4 | 15.1 | 1.08 |
| 2 | 200 | 45 | 99 | 17.3 | 27.8 | 1.07 |
| 3 | 300 | 45 | 99 | 27.2 | 31.2 | 1.10 |
| 4 | 400 | 60 | 99 | 34.4 | 43.9 | 1.08 |

| | | | | | | |
|---|-----|----|----|------|------|------|
| 5 | 500 | 60 | 99 | 42.8 | 47.2 | 1.12 |
|---|-----|----|----|------|------|------|

^aConditions: [I] = 0.005 M, room temperature, 1,3,5-trimethoxybenzene as the internal standard, toluene as the solvent. ^bConversion determined by ¹H NMR spectroscopy. ^cM_n reported in 10³ g/mol. ^dDetermined by GPC in chloroform calibrated versus polystyrene standards. ^ePDI = M_w/M_n.

Although the PDI values were low for all investigated monomers, there is a substantial difference between theoretical and experimental M_n values, although this difference diminishes at high monomer / precatalyst ratios. It is possible that this difference is a consequence of using a standard that is a different polymer (polystyrene) than the sample being tested.^{37, 47-50} However, the large disparities between the theoretical and experimental molecular weights in the ϵ -caprolactone and δ -valerolactone polymerizations prompted further examination. Consequently, the polymerizations of ϵ -caprolactone and δ -valerolactone were carried out at low temperatures. The resulting polymers yielded even larger molecular weights and PDI values (Table 5). This indicated to us that a relatively slower initiation rate compared to the propagation rate had led to the polymerization of just a few chains of very long polymers. Lowering the temperature likely prolonged the initiation period, initiating fewer chains, amplifying the effect. A kinetic study of rac-lactide polymerization further confirmed a lengthy initiation period relative to the propagation phase (Figures S36-37).

Table 5. Polymerization of ϵ -caprolactone (CL) and δ -valerolactone (VL) by (salfen)In(O^tBu) at different temperatures.

| Entry | M | [M]/[I] | Temp. (°C) | Time (min) | Conversion (%) ^b | M _{n,theo} ^c | M _n ^{c,d} | PDI ^e |
|-------|----|---------|------------|------------|-----------------------------|----------------------------------|-------------------------------|------------------|
| 1 | CL | 100 | 22 | 2 | 99 | 13.0 | 109.7 | 1.28 |
| 2 | CL | 100 | 0 | 2 | 99 | 12.9 | 116.2 | 1.38 |
| 3 | VL | 100 | 22 | 5 | 99 | 11.9 | 31.8 | 1.46 |
| 4 | VL | 100 | 0 | 10 | 99 | 10.0 | 124.5 | 1.65 |

^aConditions: [I] = 0.005 M, 1,3,5-trimethoxybenzene as the internal standard, toluene as the solvent. ^bConversion determined by ¹H NMR spectroscopy. ^cM_n reported in 10³ g/mol. ^dDetermined by GPC in chloroform calibrated versus polystyrene standards. ^ePDI = M_w/M_n.

In conclusion, two ferrocene-derived Schiff base indium complexes, (salfen)InCl and (salfen)In(O^tBu), were synthesized and characterized. Compound (salfen)In(O^tBu) was particularly impressive with lactone polymerizations in addition to being highly active toward lactide and carbonate polymerizations. Our results indicate that (salfen)In(O^tBu) showed unprecedented activity toward ϵ -caprolactone, δ -valerolactone, and β -butyrolactone leading to extremely high molecular weight polymers in minutes. To our knowledge, (salfen)In(O^tBu) is the fastest indium catalyst for ϵ -caprolactone, δ -valerolactone, and β -butyrolactone and the first indium catalyst for δ -valerolactone polymerization.

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Notes and references

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Electronic Supplementary Information (ESI) available for synthesis, characterization, NMR spectra, X-ray crystallography (CCDC 1047483), and polymer characterization. See DOI: 10.1039/c000000/x/

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