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| Journal: | *Catalysis Science & Technology* |
| Manuscript ID: | CY-ART-07-2015-001162.R1 |
| Article Type: | Paper |
| Date Submitted by the Author: | 02-Aug-2015 |



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# Uranium Mediated Ring Opening Polymerization of ε-Caprolactone: A Comparative Study

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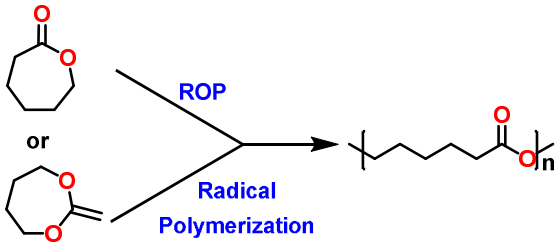
## Abstract

The ring opening polymerization (ROP) of the cyclic ester ε-caprolactone was studied with the uranium (IV) complexes $[(Im^{Dipp}N)_2U(NMeEt)_2]$ (**3**), $[(C_5Me_5)_2U(NMe_2)_2]$ (**4**) and $[(C_5Me_5)_2U(NCMePh)_2]$ (**5**) as initiators. While the bis(imidazolin-2-iminato) complex **3** displayed a surprisingly high catalytic activity of $1.2\cdot10^7$ g(PCL)·mol$^{-1}$·h$^{-1}$ at room temperature, compounds **4** and **5** exhibited lower catalytic activities at high temperatures of 90°C. The activity of the uranium complex **3** was further compared to the imidazolin-2-iminato uranium (IV) complexes $[(Im^{tBu}N)_4U]$ (**1**) and $[(Im^{Mes}N)_3U(NMeEt)]$ (**2**), which display catalytic activities of $7.9\cdot10^3$ g(PCL)·mol$^{-1}$·h$^{-1}$, and $5.3\cdot10^3$ g(PCL)·mol$^{-1}$·h$^{-1}$, respectively at elevated temperatures of 90°C. In order to shed light on the operative mechanisms, kinetic studies were carried out with complexes **3**-**5**.

## Introduction

The history of polycaprolactone (PCL) can be traced back to 1934, when *Carothers et al*. reported the polymerization of ε-caprolactone under heat or by addition of catalytic amounts of potassium carbonate.[1] Since then, two main pathways are used for the synthesis of this polymer, which are based either on the free radical ring-opening polymerization of 2-methylene-1-dioxepane[2] or on the ring opening polymerization (ROP) of ε-caprolactone (Scheme 1), which can be achieved by an anionic,[3] cationic,[3] monomer activated,[4] or coordination-insertion mechanism.[5]

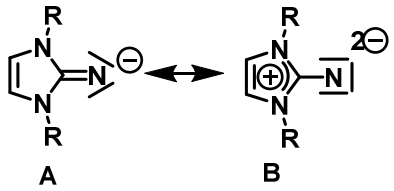



Scheme 1: General synthetic methods for polycaprolactone.

The great interest in this polymer over the last eight decades can be attributed to its low melting point (59 – 64 °C), high solubility in a large variety of organic solvents, exceptional miscibility, and mechanical compatibility with a large number of polymers, as well as its biodegradability and biocompatibility.[6] In addition, the extensive research carried out during the 1970s and 1980s in the field of biodegradable polymers led to interesting correlations between the molecular weight of the polymer, its biodegradation conditions and degradation kinetics.[7] Therefore, the application of PCL in the field of biomedicine is widespread and includes the scaffolds in tissue engineering,[8] long-term drug delivery systems[7b] and contraceptive delivery systems.[9] Additionally, PCL is used as packaging material,[9] in microelectronics[10] and adhesives.[7e] The availability of the monomer, ε-caprolactone, and the wide applicability of the corresponding polyester renders PCL an environmentally friendly, low-cost polymer with an increasing demand over the last two decades.[11]

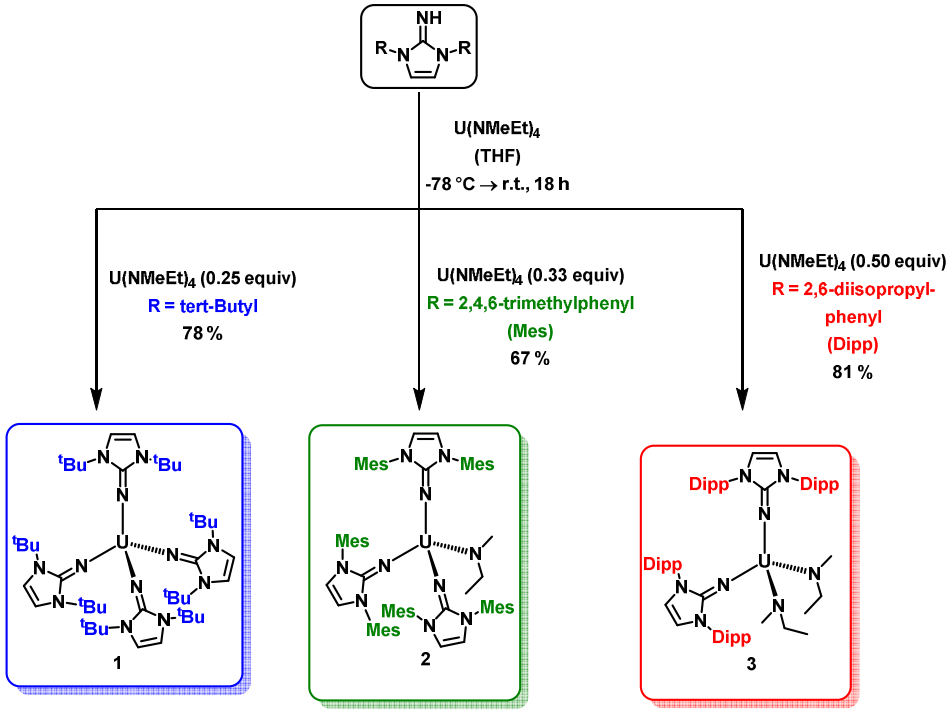
The polymerization of ε-caprolactone has been investigated with a variety of main group[5,12] and transition metals,[5,13] as well as with lanthanide catalysts,[5,14] affording insights into mechanistic details, thermodynamic and kinetic parameters as well as the control of the molecular weight and crystallinity of the resulting PCL. Despite the large variety of metal catalysts examined in the ROP of ε-caprolactone, only a few examples involving actinide-based catalysts can be found in the literature,[15] which can be attributed to the high oxophilicity of these elements. The oxophilic nature should result in a decrease in catalytic activity towards oxygen-containing substrates, since a reaction between the actinide centre and the oxygen atom of the substrate can occur, leading to the formation of thermodynamically stable, catalytically inactive actinide-oxo species as reported by *Marks et al.*[16] Since the low catalytic activity of the early actinides towards oxygen-containing substrates is attributed to their high electrophilicity, decreasing the electrophilic nature of the metal should lead to

an increased reactivity towards oxygen containing molecules such as cyclic esters. Our method of choice for making the actinide centre less electrophilic is based on using highly nucleophilic and strongly electron-donating ligands, *i.e.* the imidazolin-2-iminato motif ($Im^RN^-$), which is obtained by the deprotonation of the respective imidazolin-2-imine ($Im^RNH$). This strongly basic and highly nucleophilic ligand class can be considered as $2\sigma$, $4\pi$ electron donors towards early-transition metals and metals in high oxidation states and therefore as monodentate isolobal analogues to the widely used cyclopentadienyl ligand (Scheme 2).[17] Accordingly, the resulting transition metal and lanthanide metal complexes with Ln (Ln = Sc, Y, Gd, Lu),[18] Ti[19], Zr,[20] V,[21] Mo,[22] W,[23,22] and Re[24] usually exhibit short M-N bonds and large, almost linear M-N-C angles.




Scheme 2: Resonance structure of imidazolin-2-iminato ligands.

Recently, we reported the synthesis and structures of the imidazolin-2-iminato uranium (IV) complexes $[(Im^{tBu}N)_4U]$ (**1**), $[(Im^{Mes}N)_3U(NMeEt)]$ (**2**) and $[(Im^{Dipp}N)_2U(NMeEt)_2]$ (**3**).[25] This series of complexes was obtained by an acid-base reaction between the homoleptic $[U(NMeEt)_4]$ and neutral imidazolin-2-imines $Im^RNH$, which furnished the respective uranium complexes in dependence of the steric demand of the R substituent on the imidazolin-2-imine ligand (Scheme 3). Furthermore, we reported the selective preparation of mono(imidazolin-2-iminato) thorium (IV) and uranium (IV) complexes by a selective protonolysis reaction of actinide metallacycles with neutral imidazolin-2-imines.[26] The uranium complexes **1**-**3** display short U-N bond distances (2.174(11) - 2.177(11) Å) and almost linear U-N-C angles (165.0(4)° - 172.3(4)°), suggesting a higher bond order of the U-N bond.[25]




Scheme 3: Synthesis of imidazolin-2-iminato uranium (IV) complexes.[25]

Herein, we report the reactivity of these complexes in the ROP of ε-caprolactone, giving rise to mechanistic, thermodynamic and kinetic details. Moreover, we compare the reactivity and kinetics of the imidazolin-2-iminato complexes **1**-**3** to two analogous cyclopentadienyl uranium (IV) complexes $Cp^*_2U(NMe_2)_2$ **4**[27] and $Cp^*_2U(NCMePh)_2$ **5** (Figure 1),[28] focussing on the differences in reactivities, mechanisms and rates, despite the isolobal analogy between the respective complexes.

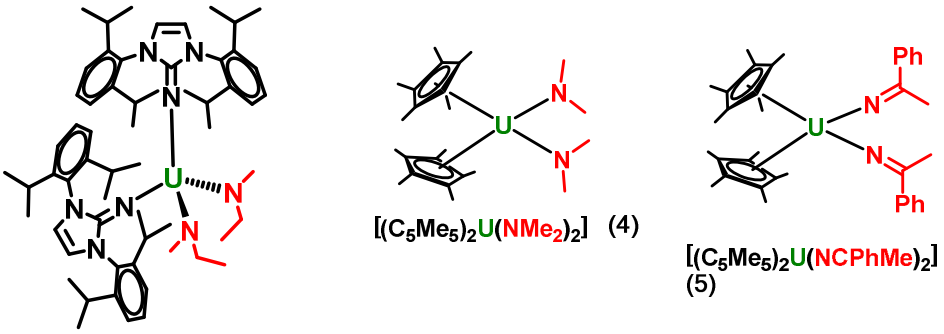



Figure 1: Molecular structures of uranium catalysts **3**-**5**.

## Results and Discussion

Cyclopentadienyl uranium (IV) complexes have been investigated in the catalytic ROP of cyclic esters such as L-lactide and ε-caprolactone, exhibiting high activities.[15a] Due to the high nucleophilicity of imidazolin-2-iminato ligands, we believe that the oxophilicity of the uranium centre should decrease, which should in turn increase the activity of the respective complexes towards oxygen containing substrates. Moreover, in a previous study, a zirconium (IV) imidazolin-2-iminato complex proved suitable for the polymerization of ε-caprolactone.[20] Therefore, we decided to investigate the polymerization of ε-caprolactone with complexes **1**-**3**. Surprisingly, these complexes showed markedly different reactivities towards ε-caprolactone. While complexes **1** and **2** only polymerized the cyclic ester at elevated temperatures of 90 °C with moderate activities of $7.9 \cdot 10^3$ g(PCL)·mol$^{-1}$·h$^{-1}$, and $5.3 \cdot 10^3$ g(PCL)·mol$^{-1}$·h$^{-1}$ for complexes **1** and **2**, respectively, complex **3** polymerizes ε-caprolactone within minutes at room temperature, showing an extraordinary high activity (activity = $1.2 \cdot 10^7$ g(PCL)·mol$^{-1}$h$^{-1}$). The polymerizations using complexes **1** and **2** as initiators were all carried out using 5 mL of toluene as a solvent, and a catalyst to ε-caprolactone ratio of 1/1000. The lower catalytic activity of complexes **1** and **2** as compared to the bis(imidazolin-2-iminato) uranium compound **3**, can probably be attributed to the higher steric encumbrance in complexes **1** and **2**, which make the metal centre less accessible for an incoming substrate molecule. The polymerization results using complex **3** are shown in Table 1.

Table 1 Polymerization results for the ROP of ε-caprolactone mediated by complex **3**.[a]

| Entry | Time (min) | Activity ($g \cdot mol^{-1} \cdot h^{-1}$) | $M_w$[e] (Dalton) | PDI | Yield (%) |
|---|---|---|---|---|---|
| **1**[a] | 10 | $1.2 \cdot 10^7$ | 21 970 | 1.86 | 28 |
| **2**[a] | 30 | $1.1 \cdot 10^7$ | 23 680 | 1.86 | 78 |
| **3**[a] | 60 | $6.8 \cdot 10^6$ | 30 660 | 2.54 | 99 |
| **4**[a] | 120 | $3.4 \cdot 10^6$ | 223 660 | 2.51 | 99 |
| **5**[a] | 300 | $1.4 \cdot 10^6$ | 327 860 | 3.59 | 99 |
| **6**[b] | 30 | $1.3 \cdot 10^7$ | 355 280 | 2.36 | 98 |
| **7**[b] | 720 | $5.6 \cdot 10^5$ | [d] | [d] | 99 |
| **8**[c] | 60 | $2.2 \cdot 10^6$ | 37 890 | 2.03 | 32 |
| **9**[c] | 120 | $3.3 \cdot 10^6$ | 60 110 | 2.29 | 95 |

[a] Polymerization conditions: 5 mL of toluene, r.t., 0.216 μmol of **3**, complex **3**/ε-CL: 1/60 000; [b] conditions as in "a" but at 90°C; [c] carried out in THF; [d] polymer insoluble in THF; no GPC analysis possible. [e] The relative calibration of the $M_n$ values was done using polystyrene standards; The $M_n$ values were multiplied by a factor of 0.56 (Mark-Houwink coefficient) and correlated to the actual PCL values.[31]

The yield of the obtained polymer increases linearly with time until the monomer is fully consumed after ~60 minutes (Figure 2) suggesting a living polymerization (expected PDI = 1.0), however the molecular weight of the polymers is not increasing linearly. In addition, the activity of the catalyst remains constant until all the monomer is polymerized. Additional polymerization time reduces the activity almost linearly since there is no additional monomer. Interestingly, after additional time, the molecular weight of the polymer clearly increases, indicating that the complex is able to continue performing a transesterification, which causes also an increase of the PDI (entry 5, Table 1). Hence, the polydispersity of the obtained polymers at the beginning of the polymerization is close to 2, indicative of a single site polymerization mechanism. These results suggest that the polymerization initiated by complex **3** is in a rapid competition with a chain transfer mechanism (transesterification) between the catalytically active species. Transesterification reactions of this type have been previously observed in the ROP of lactides and lactones, as well as in the co-polymerization of these monomers.[29]

Moreover, the reinsertion of the polymer chain obtained after 720 minutes leads to a polymer with an ultrahigh molecular weight, which is not soluble. When the reaction is carried out at higher temperatures, there is an increase in the activity and in the molecular weight of the polymer. A variation of the solvent to THF resulted in lower activities, suggesting competitive coordination of THF to the active catalytic species, which hampers the coordination of the substrate, ε-caprolactone.

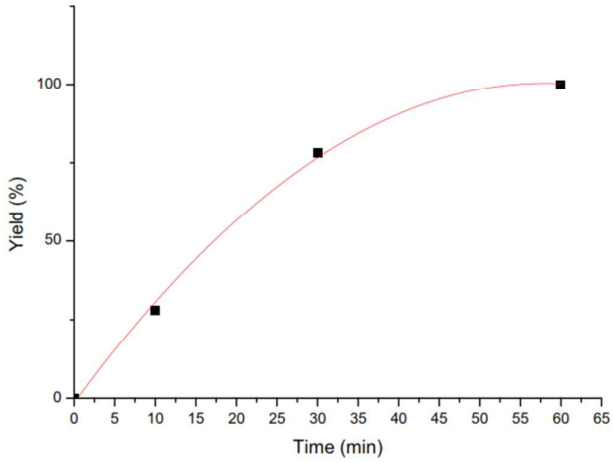



Figure 2: Plot of yield versus time for the polymerization of ε-caprolactone mediated by complex **3**.

For investigating the mechanism of the polymerization reaction mediated by complex **3**, we performed kinetic measurements, which exhibit a first order dependence on ε-caprolactone and catalyst (Equation 1, Figure 3).

$$\frac{\partial \mathrm{p}}{\partial \mathrm{t}} = [\mathrm{complex}\ \mathbf{3}] \cdot [\varepsilon - \mathrm{caprolactone}] \qquad (1)$$

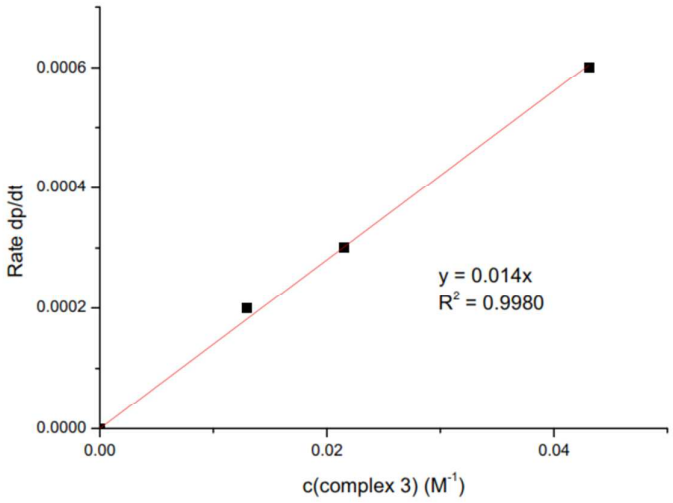



Figure 3: Plot of rate of polymerization $\partial p/\partial t$ versus the concentration of complex **3**.

The thermodynamic parameters were determined from the Arrhenius plot ($E_a$ = 12.8(5) kcal·mol$^{-1}$) and the Eyring plot ($\Delta S^{\ddagger}$ = -33.9(8) cal·mol$^{-1}$·K$^{-1}$, $\Delta H^{\ddagger}$ = 12.2(8) kcal·mol$^{-1}$), which is presented in Figure 4. A plausible mechanism for the polymerization of ε-caprolactone is shown in Scheme 4. In order to determine, whether both amido groups are active in the polymerization, we performed NMR experiments with stoichiometric amounts of the monomer, which lead to the observation that two equivalents of free amine were released per mole of catalyst. After the protonolysis step, the uranium-alkoxo-caprolactonate intermediate **B** undergoes a reaction with an incoming caprolactone monomer, leading to the open chain intermediate **D**, which can insert further monomers into the growing polymer chain, leading to the growing polymer chain **E**. The polymerization is terminated by an additional equivalent of the monomer, ε-caprolactone, leading to the formation of a polymer with caprolactonyl end-group **F** (see SI) and regenerating the active catalyst **A** (Scheme 4).

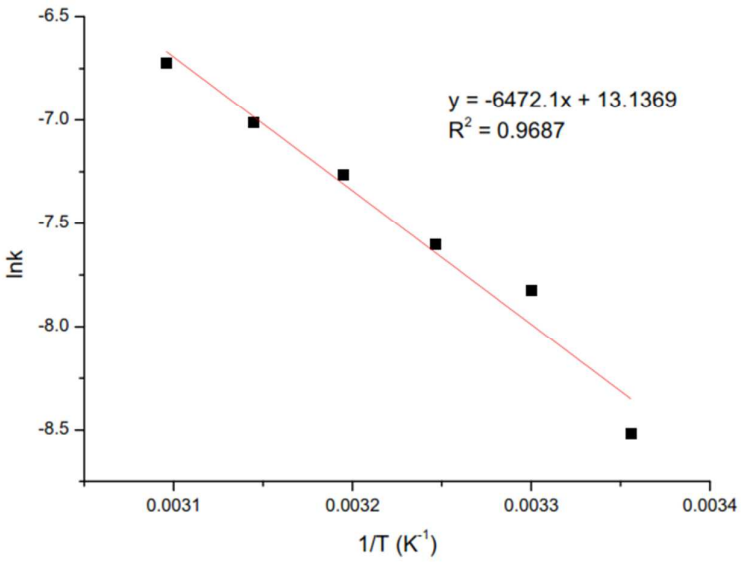
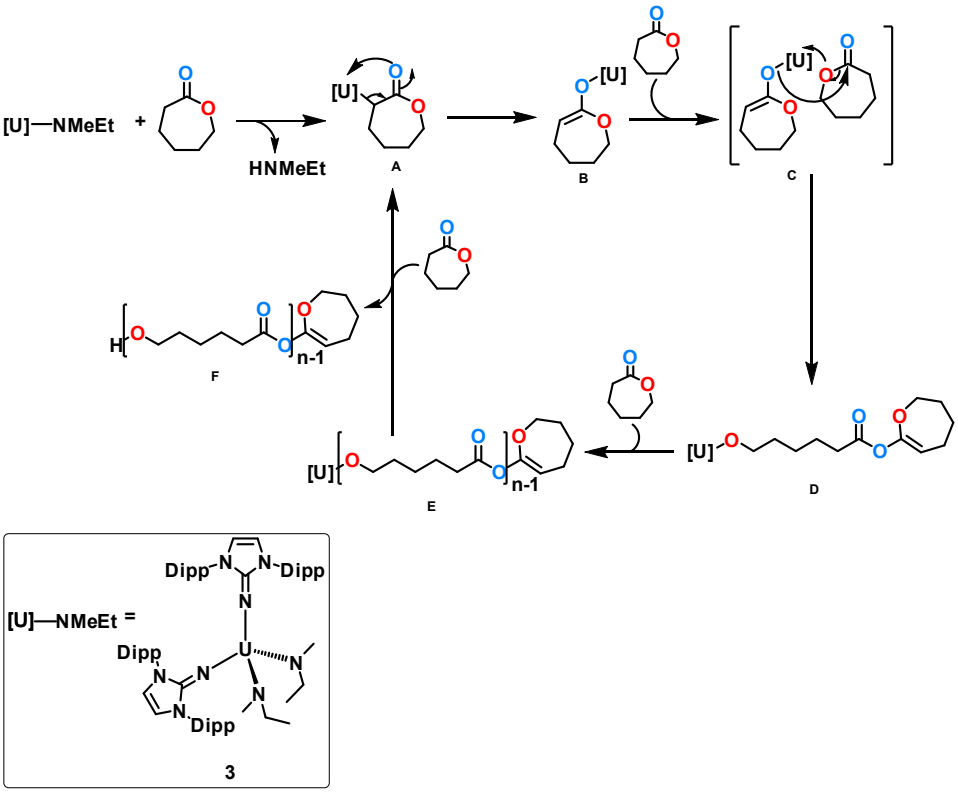



Figure 4: Arrhenius plot for the polymerization of ε-caprolactone mediated by complex **3**.




Scheme 4: Plausible mechanism for the ROP of ε-caprolactone mediated by complex **3**. The second NMeEt unit has been omitted for clarity.

The large discrepancy between the activity of the isolobal cyclopentadienyl uranium (IV) complex $Cp^*_2UMe_2$[15] and complex **3** towards ε-caprolactone raised the question, whether the high activity of **3** could be attributed to the replacement of the cyclopentadienyl moiety by imidazolin-2-iminato ligands or to the replacement of the methyl ligands by amido groups. Therefore, we synthesized the respective isolobal complex $Cp^*_2U(NMe_2)_2$ (**4**)[27], and compared the kinetic data and reactivity with **3**. The polymerization results are shown in Table 2.

Table 2: Polymerization results for the ROP of ε-caprolactone mediated by complex **4**.[a]

| Entry | Time(min) | Activity ($g \cdot mol^{-1} \cdot h^{-1}$) | $M_w$[c] (Dalton) | PDI | Yield (%) |
|---|---|---|---|---|---|
| **1**[a] | 30 | $4.6 \cdot 10^3$ | 41 040 | 2.78 | 2 |
| **2**[a] | 60 | $3.9 \cdot 10^4$ | 58 680 | 1.39 | 34 |
| **3**[a] | 120 | $2.6 \cdot 10^4$ | 73 520 | 2.60 | 45 |
| **4**[a] | 180 | $3.2 \cdot 10^4$ | 97 190 | 1.65 | 85 |
| **5**[a] | 300 | $2.2 \cdot 10^4$ | 99 840 | 1.48 | 98 |
| **6**[a] | 840 | $7.9 \cdot 10^3$ | 148 540 | 1.92 | 98 |
| **7**[b] | 840 | 978 | 9000 | 1.32 | 12 |

[a] Polymerization conditions: 5 mL of toluene, 90°C, 4.08 μmol of complex **4**, complex **4**/ε-CL:1/1000; [b] conditions as in "a" but at r.t. [c] The relative calibration of the $M_n$ values was done using polystyrene standards; The $M_n$ values were multiplied by a factor of 0.56 (Mark-Houwink coefficient) and correlated to the actual PCL values.[31]

In comparison to complex **3**, the cyclopentadienyl analogue **4** displays lower activity at 90 °C and almost no activity at room temperature. The molecular weights of the polymers obtained are lower than those obtained for complex **3**. An increase in the average molecular weight of the polymer can be observed as a function of time (Figure 5), and the polydispersity values indicate a single-site polymerization process. As with complex **3**, when the polymerization is complete, additional times reduces linearly the activity, thus the catalyst is able to perform a transesterification, as indicated by the larger molecular weight and increased PDI.

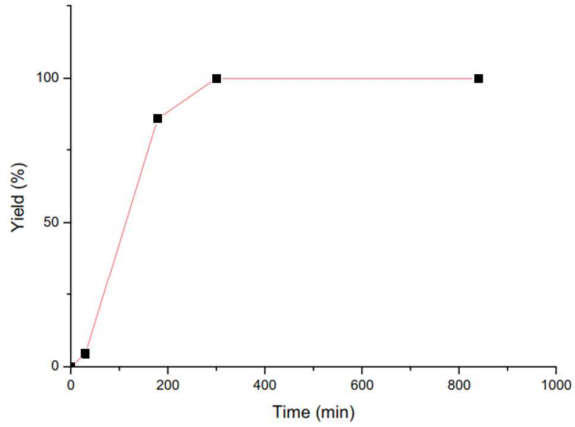



Figure 5: Plot of yield versus time for the polymerization of ε-caprolactone mediated by complex **4**.

The kinetic measurements performed with complex **4** show a first order dependence on monomer and catalyst (equation 2; Figure 6).

$$\frac{\partial \mathrm{p}}{\partial \mathrm{t}} = [\text{complex } \mathbf{4}] \cdot [\varepsilon - \text{caprolactone}] \qquad (2)$$

NMR experiments with stoichiometric amounts of the substrate, confirmed an intermolecular mechanism, initiated by the amido ligands (Scheme 5). However, the metal centre does not react with the acidic hydrogen atom in the α-position to the carbonyl, leading to release of free amine. Instead, the uranium centre reacts with the oxygen atom of the carbonyl group over intermediate **B**, (Scheme 5) and nucleophilic attack at the carbonyl carbon atom leads to an amido end-group in the first polymer chain **F**, generating catalytically active uranium-alkoxocaprolate species **G**. Intermediate **G** can now react with a further equivalent of ε-caprolactone, leading to the formation of the open-chain intermediate **H**. After insertion of additional ε-caprolactone monomers into the growing polymer chain of **H**, the reaction is terminated by an incoming monomer, yielding a polymer with a caprolactonyl end-group (**I**) (see SI) and regenerating the active catalyst **G**.

The energy of activation for the ROP of ε-caprolactone mediated by complex **4** was determined from the Arrhenius plot (Figure 7) with a value of $E_a$ = 19.0(7) kcal·mol$^{-1}$. In comparison to the activation barrier of the polymerization catalysed with complex **3**, compound **4** has a much higher barrier of activation, which explains the high temperature required for the polymerization. The entropy of activation is comparable and just slightly larger than for complex **3** ($\Delta S^{\ddagger}$ = -27.8(8) cal·mol$^{-1}$·K$^{-1}$).

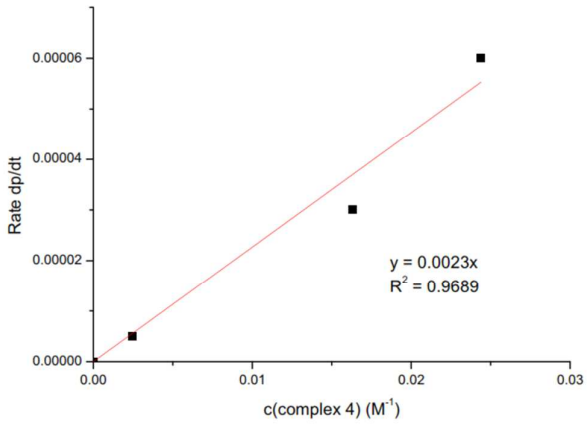



Figure 6: Plot of rate of polymerization $\partial p/\partial t$ versus the concentration of complex **4**.

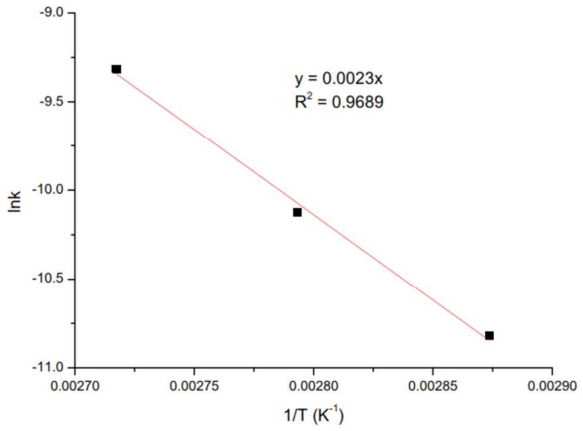
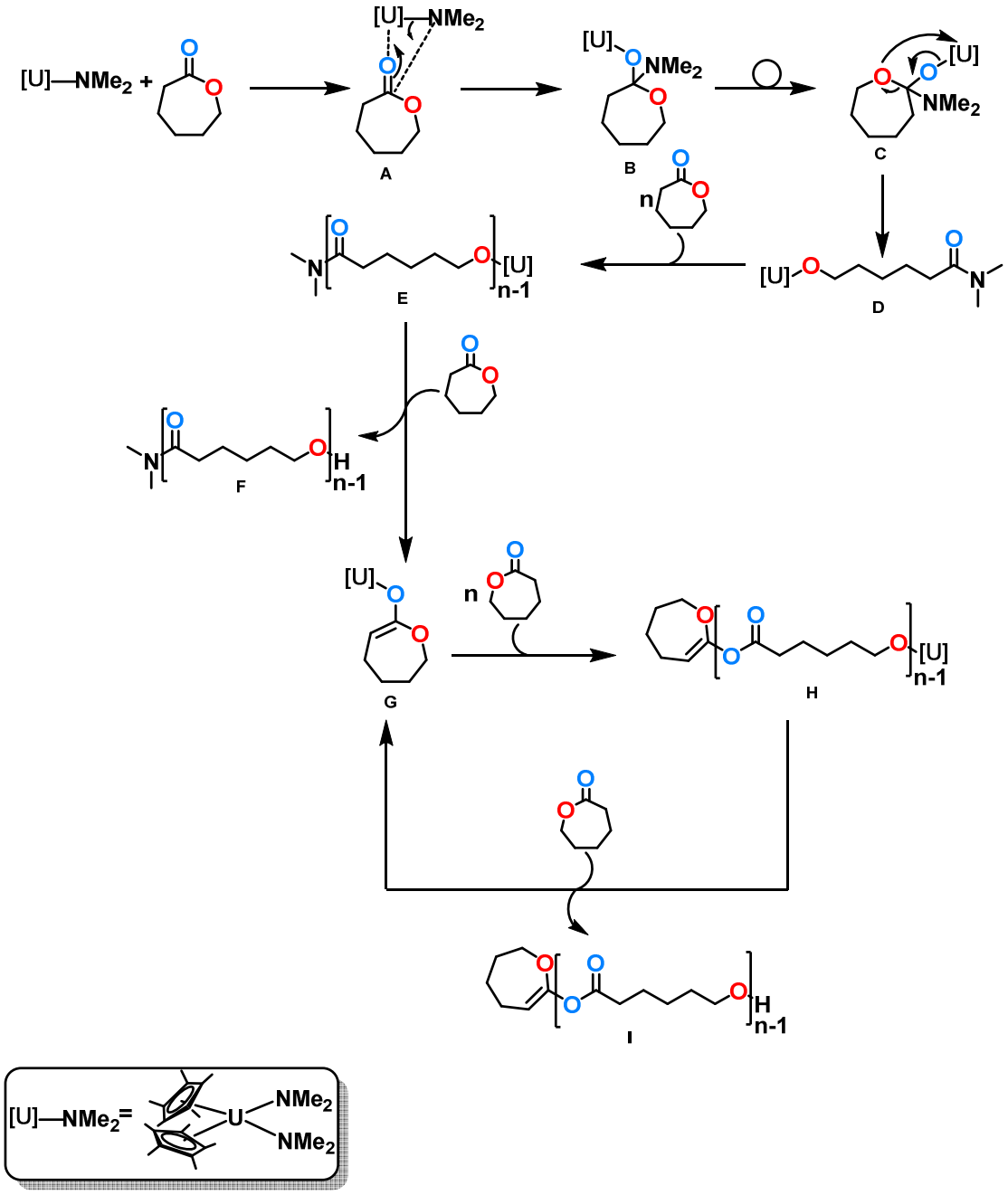



Figure 7: Arrhenius plot for the polymerization of ε-caprolactone mediated by complex **4**.




Scheme 5: Plausible mechanism for the ROP of ε-caprolactone mediated by complex **4**. The second $NMe_2$ unit has been omitted for clarity.

The structural and electronic similarity of the imidazolin-2-iminato ligands to the ketimido ligand reported as ancillary ligands in actinide complexes by *Kiplinger et al.*[28] should also result in a comparable reactivity. Due the π-character attributed to the U-N bond in the latter, the ketimido ligand, similar to imidazolin-2-iminato ligands, should not initiate the polymerization by promoting a nucleophilic attack on the

substrate, in contrast to the amido moieties in **3** and **4**. Therefore, complex **5** should in theory exhibit a very low activity in the ROP of ε-caprolactone, if the U-N bond displays a higher bond order. Therefore, the uranium (IV) bis(ketimido) complex **5** was synthesized and its reactivity towards the ROP of ε-caprolactone was studied. The results are summarized in Table 3. Similar to **4**, complex **5** showed only catalytic activity at higher temperatures. The activities obtained were higher than those of complex **4**, but lower than found for **3**. The isolated polyester exhibits high molecular weights, which increase over time, and narrow polydispersities (~2.0) indicating a single-site catalyst mechanism. When the polymerization was carried out at room temperature or in THF, no product was obtained. For elucidating the mechanism of this reaction, an NMR scale reaction with stoichiometric amounts of ε-caprolactone was carried out. Neither the ketimido ligands nor the cyclopentadienyl ligands could be observed as free ketimine, or cyclopentadiene, respectively, which suggests a Lewis acid catalysed mechanism.

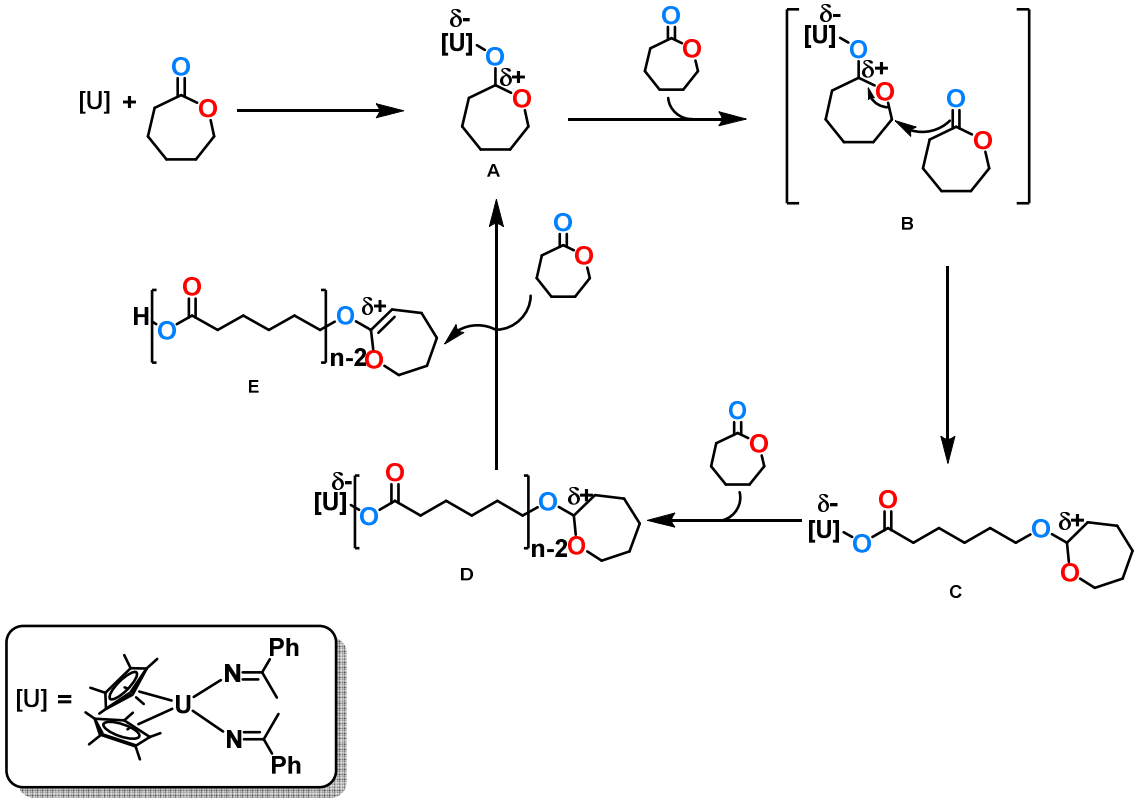
Table 3: Results for the polymerization of ε-caprolactone mediated by complex **5**.[a]

| Entry | Time (min) | Activity ($g \cdot mol^{-1} \cdot h^{-1}$) | $M_w$[d] (Dalton) | PDI | Yield (%) |
|---|---|---|---|---|---|
| **1**[a] | 30 | $4.6 \cdot 10^3$ | [c] | [c] | < 2 |
| **2**[a] | 60 | $6.6 \cdot 10^4$ | 84 140 | 1.87 | 58 |
| **3**[a] | 120 | $5.1 \cdot 10^4$ | 156 580 | 1.80 | 89 |
| **4**[a] | 300 | $2.1 \cdot 10^4$ | 270 050 | 1.72 | 94 |
| **5**[a] | 840 | $7.9 \cdot 10^3$ | 108 700 | 2.54 | 97 |
| **6**[b] | 840 | 0 | [c] | [c] | < 1 |

[a] Polymerization conditions: 5 mL of toluene, 90°C, 3.36 μmol of complex **5**; complex **5**/ε-CL 1/1000. [b] conditions as in "a" but at r.t.; [c] couldn't be determined, due to low conversion. [d] The relative calibration of the $M_n$ values was done using polystyrene standards; The $M_n$ values were multiplied by a factor of 0.56 (Mark-Houwink coefficient) and correlated to the actual PCL values.[31]

The mechanism presented in Scheme 6 involves an activation of the monomer by the Lewis acidic metal complex, which was previously observed with other main group and transition metals, followed by a nucleophilic attack of an incoming monomer unit **B**, leading to the growing polymer chain **D**.[30] The polymerization process is terminated by an additional equivalent of ε-

caprolactone, leading to the formation of a polymer with a caprolactonyl end-group (**E**) (see SI) under regeneration of the active catalyst **A**.




Scheme 6: Plausible mechanism for the ROP of ε-caprolactone mediated by complex **5**.

Kinetic and thermodynamic NMR studies have shown a first order dependence on monomer and catalyst (Equation 3, Figure 8).

$$\frac{\partial \mathrm{p}}{\partial \mathrm{t}} = [\text{complex } \mathbf{5}] \cdot [\varepsilon - \text{caprolactone}] \qquad (3)$$

The energy of activation ($E_a$ = 23.55 kcal·mol$^{-1}$) was determined as described previously from the Arrhenius plot (Figure 9), the enthalpy of activation ($\Delta H^{\ddagger}$ = 22.8(5) kcal·mol$^{-1}$) and the entropy of activation ($\Delta S^{\ddagger}$ = -15.0(9) cal·mol$^{-1}$·K$^{-1}$) were determined from the Eyring plot. The large value for the energy of activation is reflected in the high temperatures required and provides an explanation for the lack of reactivity at room temperature.

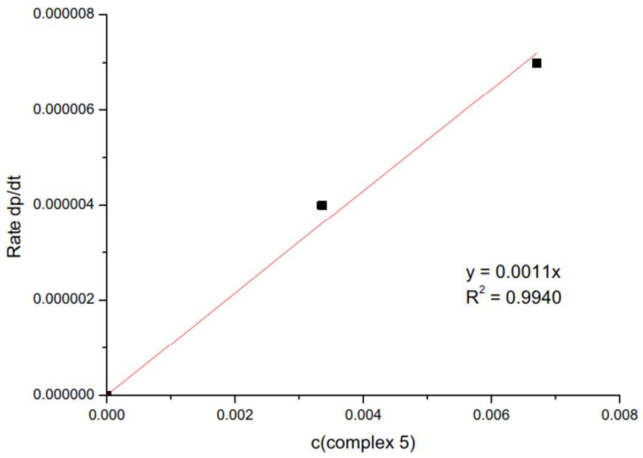



Figure 8: Plot of rate of polymerization $\partial p/\partial t$ versus the concentration of complex **5**.

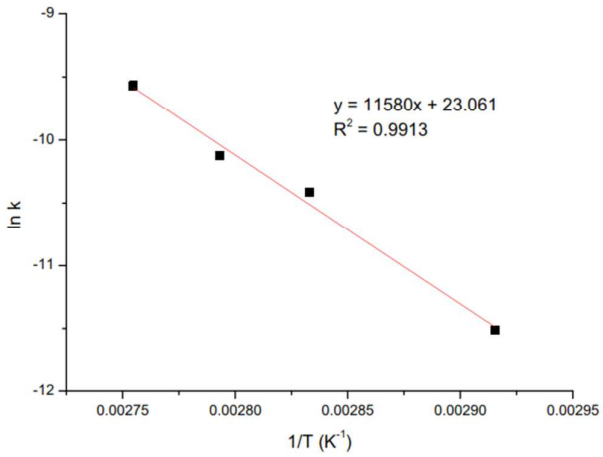



Figure 9: Arrhenius plot for the polymerization of ε-caprolactone mediated by complex **5**.

## Conclusions

A series of imidazolin-2-iminato and pentamethyl)cyclopentadienyl uranium (IV) complexes (**1**-**5**) were studied as initiators in the ring opening polymerization (ROP) of the cyclic ester ε-caprolactone. Due to the high nucleophilicity of the imidazolin-2-iminato ligands, the U-N bond in complexes **1**-**3** displays a higher bond order than one. Hence these complexes should display a slightly decreased oxophilicity and therefore a higher catalytic activity toward oxygen containing molecules. The activity of complex **3** in the ROP of ε-caprolactone was investigated, leading to an extraordinarily high activity.

Mechanistic studies confirmed a coordination-insertion mechanism, in which both amido moieties were found to be active in the polymerization reaction, yielding two equivalents of free amine in the first step of the catalytic cycle. Kinetic NMR studies showed a first order dependence in monomer and catalyst. Because of the isolobal analogy between imidazolin-2-iminato and cyclopentadienyl ligands,[17] the reactivity of complex **4**[27] towards the ROP ε-caprolactone was also investigated. The pentamethylcyclopentadienyl complex **4** was found to be only active at high temperatures, the activity and rates were both lower than that for **3**. Mechanistic studies sustain a coordination-insertion mechanism, which is slightly different from the mechanism for the ROP mediated by complex **3**. Although in both cases, the coordination of the metal centre to the substrate initiates the polymerization reaction, in the case of complex **4**, the amido moieties are not eliminated as free amine, but can be found as an end group in the first polymer chain that is introduced in the first step of the catalytic cycle. Surprisingly, the protonolysis reaction observed for complex **3** was not observed in the activation step for complex **4**, although the resulting *N*-dimethylamine and *N*-ethylmethylamine display very similar p$K_a$ values. However, no dissociation of the pentamethylcyclopentadienyl moiety was observed. Therefore, we synthesized the uranium (IV) ketimido complex **5**[28], in which the two ketimido moieties display similar bonding properties as the imidazolin-2-iminato ligands in **3** and should not dissociate upon addition of the substrate. Owing to the strong bonding of the pentamethylcyclopentadienyl and ketimido ligands in **5**, a coordination-insertion mechanism is not likely, and a lower activity is expected, due to the steric encumbrance of the ligands, rendering the uranium (IV) centre less accessible for an incoming monomer. Mechanistic studies confirmed that all four ligands stay coordinated to the uranium centre upon addition of a stoichiometric amount of ε-caprolactone, suggesting a cationic mechanism, in which the uranium complex **5** acts as a Lewis acid. The ketimido complex **5** exhibits low activity at elevated temperatures (90 °C) and no activity at room temperature, which was further sustained by the low rates of polymerization found by kinetic NMR measurements. Complex **3** displayed the lowest activation barrier, which explains the extremely high activity at low temperatures as compared not just to actinides but to any other reported metal induced polymerization.

## Experimental Section

All manipulations of air sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flamed Schlenk-type glassware on a high vacuum line ($10^{-5}$ torr), or in nitrogen filled Vacuum Atmospheres glovebox with a medium capacity recirculator (1-2 ppm oxygen). Argon and nitrogen were purified by passage through a MnO oxygen removal column and a Davison 4 Å molecular sieve column. Analytically pure solvents were dried and stored with Na/K alloy and degassed by three freeze-pump-thaw cycles prior to use (THF, hexane, toluene, benzene-$d_6$, toluene-$d_8$). $[U(NMeEt)_4]$,[25] $[(Im^{tBu}N)_4]$,[25] $[(Im^{Mes}N)_3U(NMeEt)_2]$,[25] $[(Im^{Dipp}N)_2U(NMeEt)_2]$,[25] $[Cp^*_2U(NMe_2)_2]$[27] $[Cp^*_2U(NCMePh)_2]$,[28] were synthesized according to published procedures. ε-Caprolactone (Sigma Aldrich) was distilled under reduced pressure from $CaH_2$ and stored in the glovebox prior to use. NMR spectra were recorded on DPX 200, Avance 300 and Avance 500 Bruker spectrometers. Chemical shifts for $^1H$ NMR and $^{13}C$ NMR are reported in ppm and referenced using residual proton or carbon signals of the deuterated solvent relative to tetramethylsilane. GPC measurements were carried out on a Waters Breeze system with a styrogel RT column and with THF (HPLC grade, T.G. Baker) as mobile phase at 30 °C. Relative calibration was done with polystyrene standards (Aldrich, 2000 – 1800000 range). $M_n$ values were multiplied by a factor of 0.56 and correlated to actual PCL values.[31]

### Catalytic polymerization of ε-caprolactone

A sealable glass tube, equipped with a magnetic stirring bar, was loaded with the required amount of the uranium complex from a stock solution, the respective amount of ε-caprolactone (in a ratio of catalyst to ε-caprolactone of 1/1000 for complexes **4** and **5**, or 1/ 60 000 for complex **3**, respectively) and 5 mL of dry toluene inside the glove box. The polymerization was carried out under rapid stirring for the required amount of time and at the respective temperature. Then, the reaction was quenched by the addition of methanol. After removing the solvent under reduced pressure, the polymer was precipitated from cold methanol, isolated by filtration, washed with three portions of cold methanol (50 mL each) and dried overnight under vacuum.

The activity was determined as PCL (g) / mol(cat)·time(h). A sample of the isolated PCL (40 mg) was dissolved in THF and used for determination of the $M_n$, $M_w$ and PDI values.

For the kinetic $^1$H NMR studies, a J-Young NMR tube was loaded with the respective amount of catalyst from a stock solution, ε-caprolactone and toluene-$d_8$ inside the glove box, the tube was subsequently sealed, and reaction mixture was frozen at liquid nitrogen temperature until starting the $^1$H NMR measurements. The sample was heated (if required) in the NMR spectrometer.

**ACKNOWLEDGEMENTS**

This work was supported by the German Israel Foundation GIF under Contract I-1264-302.5/2014

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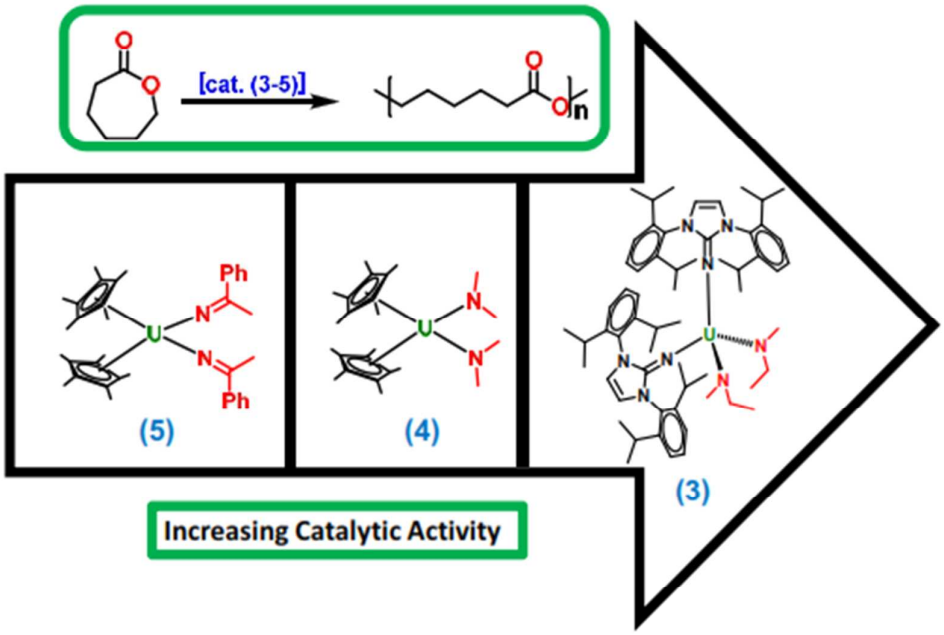


This study shows compares the catalytic activity and the mechanism of the uranium complexes $[(Im^{Dipp}N)_2U(NMeEt)_2]$ (**3**), $[(C_5Me_5)_2U(NMe_2)_2]$ (**4**) and $[(C_5Me_5)_2U(NCMePh)_2]$ (**5**) in the ring opening polymerization of ε-caprolactone, among which the bis(imidazolin-2-iminato) uranium complex **3** displayed the highest catalytic activity.