Surprising Activity of Organoactinide Complexes in the Polymerization of Cyclic Mono- and Diesters

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Summary: The use of the neutral organoactinide complexes $Cp*_2AnMe_2$ (An = Th, U) and the cationic complex $[(Et_2N)_3U]$-$[BPh_4]$ for the ROMP of ϵ-caprolactone and L-lactide is presented. Despite their high oxophilic nature, these complexes show high activity for polymerization, yielding high-molecular-weight polymers with a low molecular weight distribution. In several cases the polymerization proceeds in a living fashion.

During the last three decades, organoactinide chemistry has been flourishing, reaching a high level of sophistication. The use of organoactinide complexes under stoichiometric or catalytic conditions to promote synthetically important organic transformation such as terminal alkyne dimerization, oligomerization, hydrosilylation, and hydroamination has grown due to the rich, complex, and highly unique chemistry of actinides.[1] In many instances the regio- and chemoselectivities displayed by organoactinide complexes have been shown to be complementary to those observed with other transition-metal or lanthanide complexes.[1]

Despite the large variety of reactions catalyzed by organoactinides, the common belief was that if oxygen-containing substrates were introduced, a decrease in catalytic activity would be expected, due to the high oxophilic nature of the early actinides. Hence, oxygen-containing environments will promote the deactivation of the organoactinide complexes or the destruction of the metal−ancillary ligand bonds. Lin et al. have shown this behavior by showing that the use of an alkoxy ligand results in a reduced catalytic activity in the organoactinide-catalyzed hydrogenation of olefins, in comparison to the use of alkyl ligands.[2] In the few last years, in addition to actinides, many main-group[3] and lanthanide[4] metal complexes were found to be good catalysts for the ring-opening polymerization and copolymerization of cyclic esters to form polycaprolactone and poly-L-lactide. These polymers represent a widely researched family of polyesters which are both biodegradable and biocompatible. From a thermodynamic point of view, polymerization of cyclic esters with organoactinides should be a favored reaction. The first step in the polymerization reaction (eq 1 for ϵ-caprolactone) is the

$$(1)$$
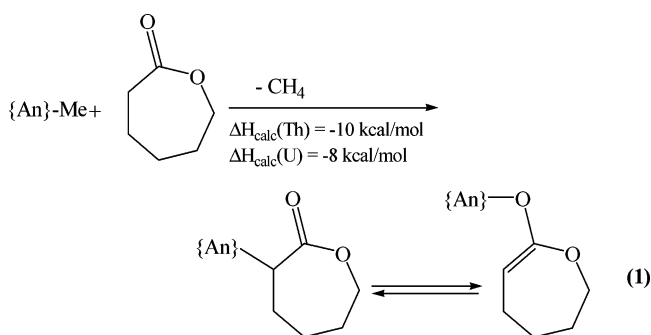
abstraction of the α-hydrogen of the monomer to form the actinide enolate and methane (this step is corroborated by the stoichiometric reaction forming methane, which is detected by ^{1}H NMR).[5] From ligand bond dissociation energies[6] this step was calculated to be exothermic with positive entropy and hence spontaneous. The following steps (eq 2, chain growth) should

$$(2)$$
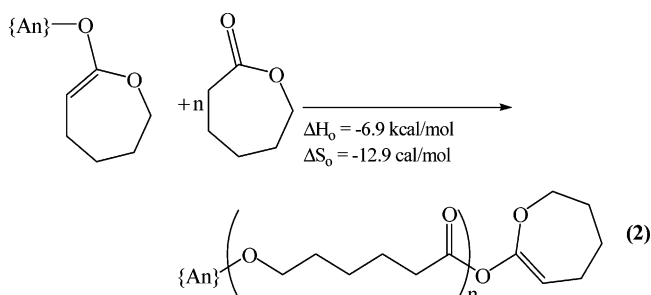
also be exothermic (similar bonds are formed and broken, the monomer ring opens to release ring strain) with a negative entropy (due to the reduction in the number of molecules).[7]

In this contribution we present our results on the highly active polymerization of ϵ-caprolactone (ϵ-CL) and L-lactide (L-LA) by three organoactinide complexes: the neutral complexes $Cp*_2$-

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(1) For recent publications on the chemistry of organoactinide complexes, see: (a) Barnea, E.; Andrea, T.; Kapon, M.; Berthet, J. C.; Ephritikhine, M.; Eisen, M. S. *J. Am. Chem. Soc.* **2004**, *126*, 10860. (b) Stubbert, D. B.; Stern, C. L.; Marks, T. J. *Organometallics* **2003**, *22*, 836. (c) Dash, A. K.; Gourevich, I.; Wang, J. Q.; Wang, J.; Kapon, M.; Eisen, M. S. *Organometallics* **2001**, *20*, 5084.

(2) Lin, Z.; Marks, T. J. *J. Am. Chem. Soc.* **1987**, *109*, 7979.

(3) For recent reviews on polymerization of cyclic mono- and diesters see: (a) Gibson, V. C.; Marshall, E. L. In *Comprehensive Coordination Chemistry II*; Elsevier: Amsterdam, 2004; Vol. 9, p 1. (b) Biela, T.; Duda, A.; Penczek, S. *Macromol. Symp.* **2002**, *183*, 1.

(4) (a) Palard, I.; Soum, A.; Guillaume, S. M. *Chem. Eur. J.* **2004**, *10*, 4054. (b) Nomura, N.; Taira, A.; Tomioka, T.; Okada, M. *Macromolecules* **2000**, *33*, 1497 and references therein.

(5) Using a stoichiometric ratio of complex 1 and ϵ-CL the formation of methane was evident by ^{1}H NMR (300 MHz, toluene-d_8): δ 0.25 (s, CH$_4$). After the tube was opened to vacuum, this signal disappeared.

(6) In step 1 (eq 1) the Th−Me and C−H (α to ester) bonds are broken and Th−CH and Me−H bonds are formed. ΔH calculations were based on the bond dissociation energies as published in: (a) Martinho Simoes, J. A.; Beauchamp, J. L. *Chem. Rev.* **1990**, *90*, 629. (b) Bruno, J. W.; Stecher, H. A.; Morss, L. R.; Sonnenberger, D. C.; Marks, T. J. *Organometallics* **1986**, *5*, 549. (c) Bruno, J. W.; Marks, T. J.; Morss, L. R. *J. Am. Chem. Soc.* **1983**, *105*, 6824. (d) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493.
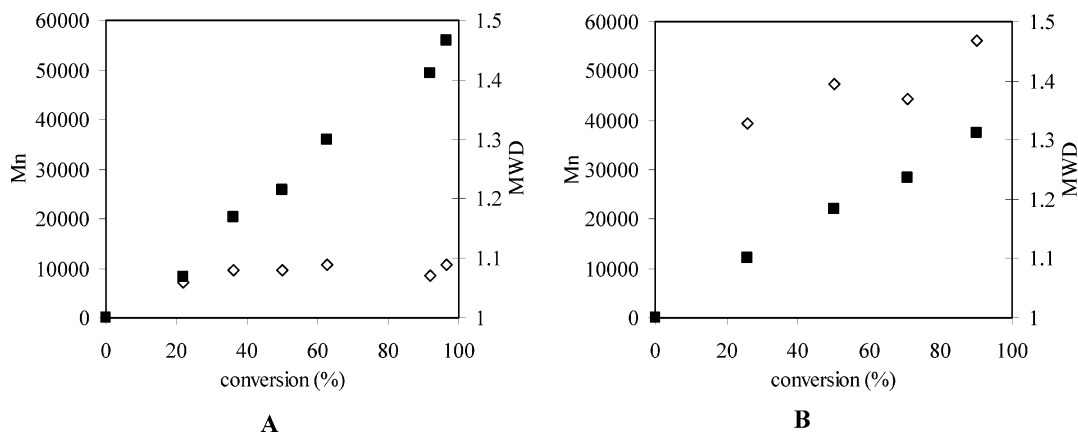
Figure 1. Plots of M_n (■) vs conversion with molecular weight distribution indices (◇) for the polymerization of ϵ-CL with complex **1** at room temperature (catalyst:monomer = 1:600, entries 1 and 2 in Table 1): (A) solvent toluene; (B) solvent THF.

Table 1. Polymerization of ϵ-CL with Complexes 1−3[a]

entry	cat.	solvent	T (°C)	t (min)	conversn (%)	M_n ($\times 10^{-4}$)	MWD
1	**1**	toluene	25	90	92	5.8	1.06
2	**1**	THF	25	90	100	4.5	1.41
3	**1**	toluene	70	10	99	5.0	1.14
4	**1**	THF	70	10	100	6.8	1.35
5	**2**	toluene	25	1440	61	3.0	1.09
6	**2**	toluene	70	120	90	5.5	1.21
7	**2**	THF	70	150	60	3.1	1.29
8	**2**	toluene	110	15	99	5.0	1.49
9	**3**	THF	25	15	100	5.7	1.24
10	**3**	THF	70	5	100	5.9	1.25

[a] Catalyst:monomer = 1:600.

AnMe₂ (**1**, An = Th; **2**, An = U; Cp* = C₅Me₅) and the cationic complex [U(NEt₂)₃][BPh₄] (**3**).
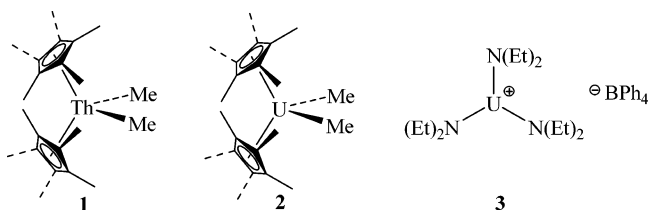
Polymerization of ϵ-CL using complexes **1−3** as initiators was systematically examined. Conversion and reactivity of the complexes were found to be highly affected by temperature, and the results are summarized in Table 1.[8] Comparing the reactivity of complexes **1** and **2** (entries 1 and 5 (room temperature) and **3** and **6** (70 °C) in Table 1) reveals that the thorium complex exhibits the larger activity. These results are in accordance with the higher oxophilic nature of the U complex, which renders complex **2** slightly less active. In addition, and very surprisingly, the use of THF as solvent with complex **1** maintained the conversions and activity but induced only slightly higher molecular weight distributions and slightly lower M_n (due to a possible coordination of the solvent to the active complex, entries 1−4 in Table 1 and Figure 1). For complex **2**, the use of THF had a more profound effect. Both conversion and M_n were lowered, and the molecular weight distribution (MWD) was slightly higher as compared to that with toluene (entries 6 and 7 in Table 1). Monitoring the polymerization over time for complex **1** (Figure 1, entry 1 in Table 1) reveals a linear increase in M_n with increasing conversion, while a low MWD was maintained (values of 1.05−1.10). In addition, a higher monomer to catalyst ratio results in higher M_n (Figure 2). On the basis of the GPC results and the initial catalyst to monomer
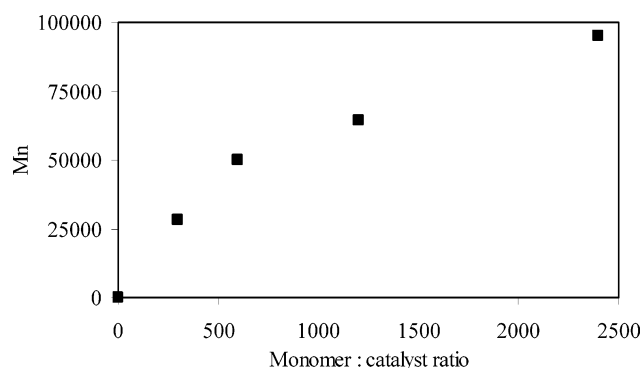

Figure 2. Plot of M_n (■) vs monomer to catalyst ratio for the polymerization of ϵ-CL with complex **1** at 70 °C with toluene as solvent.

ratio, we can suggest that complexes **1** and **2** bear only one active site,[9] which suggests a living polymerization via a coordination−insertion mechanism. Attempts to detect chain end groups by using a low catalyst to monomer ratio and analysis of the reaction mixture by NMR revealed three sets of caprolactone signals which correspond to replacement of the two methyl groups by monomer (eq 1 showing only one replacement) and probably insertion of more monomer units in one of the metal sites (eq 2).

Unexpectedly, the cationic complex **3** shows the highest activity, both at room and elevated temperatures in THF (entries 9 and 10 in Table 1). To distinguish between the possible coordination−insertion and cationic mechanisms, the following test was performed. Complex **3** was mixed with a near-equimolar amount of ϵ-CL and the reaction was quenched with MeOH, resulting in the formation of 6-methoxy-6-oxohexyl 6-hydroxyhexanoate (**4a**)—an open ϵ-CL dimer (eq 3). The

6-methoxy-6-oxohexyl 6-hydroxyhexanoate
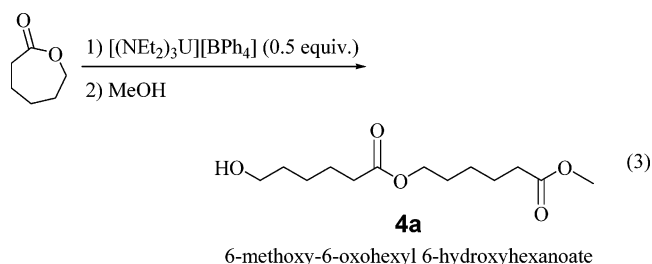
methyl ester chain end suggests a cationic mechanism,[10] since a coordination−insertion mechanism would result in an amide chain end.[11] However, as evident from the high Mn and the
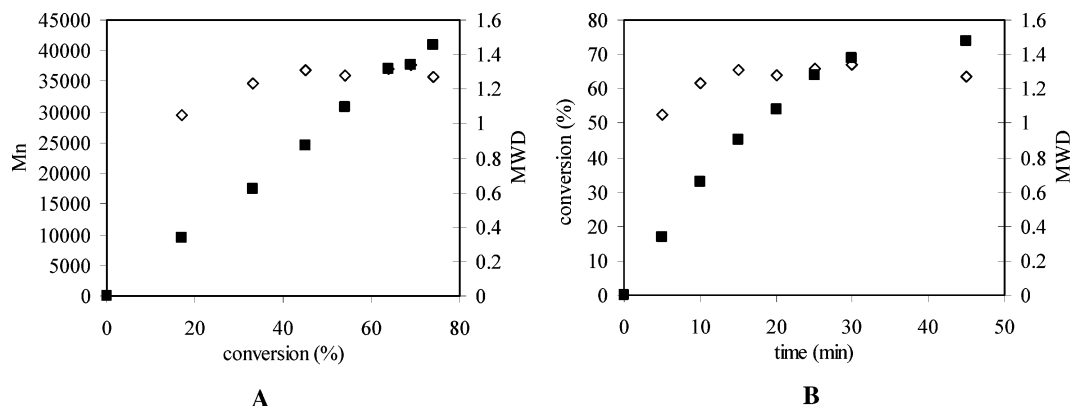
Figure 3. (A) Plot of M_n (■) vs conversion with molecular weight distribution indices (◇) for the polymerization of L-LA with complex **3** in THF at 70 °C (catalyst:monomer = 1:600, entry 9 in Table 2). (B) Plot of conversion (■) vs reaction time with molecular weight distribution indices (◇) for the same reaction.

low polydispersity, we believe that the chain end remains near the metal center (via a weak coordination).[10b] Using perdeuterated methanol resulted in deuterium labeling in the hydroxy and methoxy chain ends to form product **4b** (eq 4). In addition,

6-((D₃-methoxy)-6-oxohexyl 6-deuteroxyhexanoate
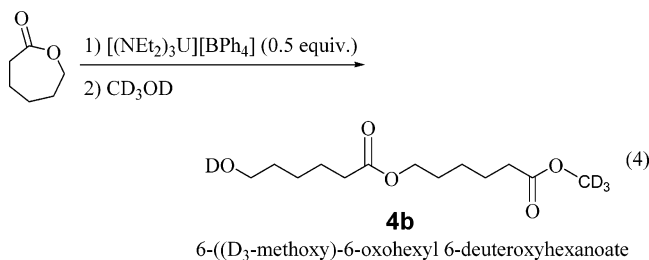
formation of free HNEt₂ was not observed (unlike the formation of CH₄ with complexes **1** and **2**). The higher activity of complex **3** as compared to that of complexes **1** and **2** may be rationalized when considering the monomer approach to the metal center. For complexes **1** and **2** the approach of the monomer is hindered by the two Cp* ancillary ligations, resulting in a slower reaction rate, as compared to that for complex **3**.

   Polymerization of L-lactide (L-LA) was performed with the three complexes, at various temperatures and in distinct solvents, and the results are presented in Table 2. As with ε-CL, the cationic complex **3** showed the highest activity at 70 °C in THF (entries 8 and 9 in Table 2). Figure 3 shows the progress of the polymerization reaction of L-LA with complex **3** in THF over time (entry 9 in Table 2). The linear increase of M_n over

   (7) ΔH_0 and ΔS_0 values for this process (eq 2) have been reported; see: (a) Bechtold, K.; Hillmyer, M. A.; Tolman, W. B. *Macromolecules* **2001**, *34*, 8641. (b) Lebedev, B. V.; Yevstropov, A. A.; Lebedev, N. K.; Karpova, Ye. E.; Lyudvig Ye. B.; Belen'kaya, B. G. *Polym. Sci. USSR* **1979**, *29*, 2219.
   (8) M_n values were received from GPC measurements and calibrated with polystyrene standarts. To correlate with actual PCL values, these results were multiplied by the known factor of 0.58. See: (a) Kowalski, A.; Duda, A.; Penczek, S. *Macromolecules* **1998**, *31*, 2114. (b) Duda, A.; Florjanczyk, Z.; Hofman, A.; Slomkowski, S.; Penczek, S. *Macromolecules* **1990**, *23*, 1640.
   (9) For a 1:600 ratio, living polymerization with one active site should yield a polymer chain with calculated M_n value of 68 400. Comparing this number to that for entry 4 of Table 1 suggests that complex **1** is a single-site catalyst.
   (10) Examples of living cationic polymerization of cyclic esters by organometallic complexes are very rare. See ref 4b and: (a) Sarazin, Y.; Schormann, M.; Bochmann, M. *Organanometallics* **2004**, *23*, 3296. (b) Hayakawa, M.; Mitani, M.; Yamada, T.; Mukaiyama, T. *Macromol. Chem. Phys.* **1997**, *198*, 1305 and references therein.
   (11) Chakraborty, D.; Chen, E. Y. X. *Organometallics* **2002**, *21*, 1438 and references therein.

Table 2. Polymerization of L-LA with Complexes 1−3[a]

entry	cat.	solvent	T (°C)	t (min)	conversn (%)	M_n ($\times 10^{-4}$)	MWD
1[a]	**1**	THF	70	120	98	4.3	1.14
2[b]	**1**	THF	70	210	93	4.5	1.06
3[b]	**1**	toluene	70	90	62	6.2	1.07
4[c]	**1**	toluene	70	180	38	20.5	1.09
5[a]	**1**	toluene	90	60	92	3.2	1.80
6[b]	**2**	toluene	90	90	54	8.1	1.29
7[b]	**2**	toluene	90	270	33	3.0	1.14
8[a]	**3**	THF	25	1080	60	3.9	1.06
9[a]	**3**	THF	70	45	76	4.3	1.21

   [a] Catalyst:monomer = 1:600. *[b]* Catalyst:monomer = 1:1200. *[c]* Catalyst:monomer = 1:2400.

conversion (Figure 3A) and conversion over time (Figure 3B) and low polydispersity suggest that the polymerization proceeds in a living fashion and is zero order in monomer, at least in the early stages of the reaction. At higher conversions (more than 60%), the reaction gradually slows down due to the viscosity and stickiness of the solution. In contrast to complexes **1** and **2** producing only CH₄ at room temperature, complex **3** was found to be active for the polymerization of L-LA at room temperature, yielding living polymer with high M_n and low MWD (entry 8 in Table 2). Considering the initial catalyst to monomer ratio and the GPC results for complexes **1−3**, we may suggest that the polymerization proceeds with only one active site for each complex.

   In conclusion, in this contribution we report the novel reactivity of neutral and cationic organoactinide complexes in the polymerization of ε-caprolactone and L-lactide. The resulting polymers are characterized by high molecular weights and relatively narrow polydispersity. The activity of complex **1** and **3** approaches that of known transition and main-group metals.[3,4] We have also shown the living nature of the polymerization reactions of ε-CL with complexes **1−3**.

   Supporting Information Available: Complete Experimental Section, including the synthesis and characterization of product **4** and detailed procedures for the polymerization reactions. This material is available free of charge via the Internet at http://pubs.acs.org.

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