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Monomer insertion mechanism of ring-opening polymerization of ε-caprolactone with yttrium alkoxide intermediate: A DFT study

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ABSTRACT

The mechanism of ε-caprolactone (CL) insertion into a Y–OCH_3 bond was investigated using density functional theory (DFT) calculations. The optimized geometries and corresponding Gibbs-free energies of the intermediates were obtained, which confirmed a four-step coordination-insertion mechanism. The coordination of CL onto yttrium center led to a nucleophilic addition of the carbonyl group of CL, followed by an intramolecular alkoxide ligand exchange. A monomer insertion was completed by the CL ring opening via acyl–oxygen bond cleavage. The formation of the five-coordinated yttrium intermediate, **3**, was found to be the rate-determining step. This study could be applicable to ring-opening polymerisation (ROP) of CL initiated by lanthanide metal complexes.

1. Introduction

Biodegradable and biocompatible poly(ε-caprolactone) (PCL) has received much attention for their medical and environmental applications. Since the pioneer researchers developed the aluminum alkoxide initiators and introduced the coordination mechanism [1–4], metal alkoxides have been widely used to initiate ring-opening polymerization (ROP) of ε-caprolactone (CL) [5]. These metals include calcium [6–8], aluminum [9–13], tin [14–19], rare earth and some other transition metals [20,21].

Commercially available yttrium oxo-isopropoxide cluster, $Y_5(\mu\text{-}O)(O^iPr)_{13}$, in which five yttrium atoms were linked to a single central oxygen atom has been extensively studied as initiators of ROP [22]. Feijen and co-workers first reported a living ROP of CL initiated by yttrium isopropoxide prepared by tris(2,6-di-*tert*-butylphenoxy)yttrium and 2-propanol [23,24]. Jérôme and co-workers synthesized yttrium isopropoxide by fast reaction of the commercially available [tris(hexamethyldisilyl)amide]yttrium with 2-propanol [25,26]. Our group studied isopropoxy rare earth diethyl acetoacetate and donor adducts of neodymium isopropoxide for ROP of CL [27,28]. The experimental evidences were reported that propagation proceeds by monomer insertion into rare earth–alkoxide bond via the cleavage of acyl–oxygen bond of CL ring [29–33]. However, to the best of our knowledge, neither theoretical studies nor intermediate species of this process have been described. In this paper we use density functional theory (DFT) to study a chain propagation cycle of CL on yttrium alkoxide active center.

2. Computational details

Geometries and Gibbs-free energies at the standard state (298 K and 1 atm) of all mentioned intermediates were optimized using DFT at the B3LYP level [34] with the Gaussian03 program [35]. This popular and computationally cheap method predicted reliable geometries and quantum chemical results. We used a triple-ζ-contracted basis set 6–31G* for all non-metal atoms and a double-ζ-valence quality basis set LANL2DZ for yttrium. The zero-point vibrational energy corrections were scaled by a factor of 0.9804 [36]. No imaginary frequencies were found in all intermediates by means of frequency calculations.

3. Results and discussion

We optimized the geometry of tris(2,6-di-*tert*-butylphenoxo) yttrium [$Y(OC_6H_3Bu_2{}^t\text{-}2,6)_3$] using DFT method with the basis sets LANL2DZ for yttrium and 6–31G* for carbon, hydrogen and oxygen atoms. The calculated $Y(OC_6H_3Bu_2{}^t\text{-}2,6)_3$ geometry met the X-ray data of its single crystal [37] well (Fig. 1). Some key bond lengths and bond angles were compared in Table 1. The Y atom was in a trigonal planar environment coordinated by three oxygen atoms.

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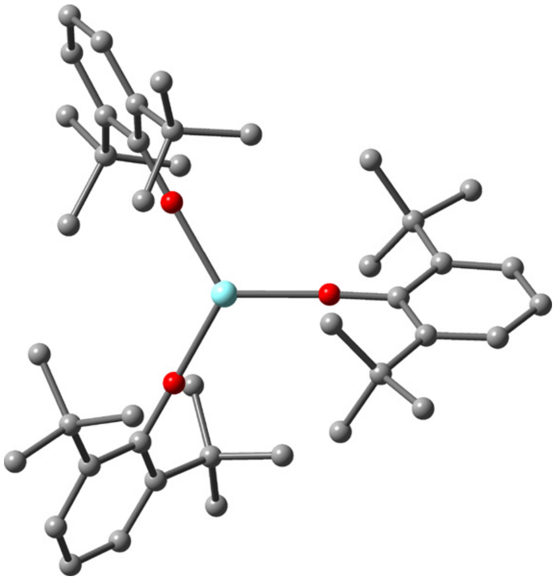


Fig. 1. The molecular geometries of [$Y(OC_6H_3Bu_2{}^t\text{-}2,6)_3$] obtained from DFT calculation. Hydrogen atoms are omitted for clarity.

The distances of Y atom deviated from YO_3 plane were 0.12 Å for DFT results and 0.09 Å for X-ray data. The basis set LANL2DZ was also successfully used for tin and aluminum [15,38].

Rare earth (Ln) alkoxides and other complexes were reported as initiators of ROP of CL including phenolates, thiophenolates, amidates, borohydrides, etc. [30–33,39–51]. They shared the same Ln–oxygen active chain growing center after initiation step. Scheme 1 shows a reported structure of a rare earth phenolate initiated Ln–O–$(CH_2)_5$–CO chain as well as the speculated coordination-insertion mechanism [30]. First, the carbonyl group of the monomer coordinated to rare earth metal to form a complex. Second, the rare earth metal shifted to the oxygen of acyl–oxygen group. Third, the monomer was inserted into the Ln–O bond via the cleavage of acyl–oxygen bond [29–31]. We calculated the monomer insertion mechanism of ROP of CL with yttrium methoxide [$Y(OMe)_3$] intermediate. $Y(OMe)_3$ (compound **1** in Figs. 2 and 3) was applied as a model compound not only for a yttrium alkoxide initiator but also a simplified propagating polymer chain. The DFT-based CL-insertion mechanism is shown in Figs. 2 and 3 and some selected bond lengths and angles are listed in Table 2.

In tetrahydrofuran (THF) solution, the coordination of yttrium compound $Y(OMe)_3$ with the monomer CL and the solvent THF are illustrated in Figs. 2 and 3. Gibbs-free energies of these two coordination reactions were close for the CL (−11.01 kcal/mol) and the THF (−10.09 kcal/mol) cases. Therefore, the equilibrium between $Y(OMe)_3$(THF) (**2T**) and $Y(OMe)_3$(CL) (**2**) was established in the polymerization mixture. The distance of Y–O^2 (2.369 Å) in **2** was shorter than that of Y–O^4 (2.386 Å) in **2T** (Fig. 2 and Table 1). This might be also an evidence for a stronger coordination between yttrium and the *exo*-ring sp^2 hybrid oxygen (O^2) in carbonyl group than that between Y and *endo*-ring sp^3 hybrid oxygen (O^3). It should be mentioned that no stable Y/O^3 coordinating geometry was found in DFT calculation. The O^3 atom in CL ring could not compete with the O^2 atom. The Gibbs-free energy change (ΔG^θ) was −0.11 kcal/mol for the reaction of **2T** → **2**, which means that $Y(OMe)_3$(CL) (**2**) was slightly favored and CL could replace the THF in $Y(OMe)_3$(THF) (**2T**). Similarly, CL coordinated rare earth complexes were reported by Evans and co-workers [52,53]. Guillaume and co-workers [44] found that both trimethylene carbonate (TMC) and diethyl carbonate (DEC) could replace the THF in samarium complex by means of NMR investigation, which was coincidence with our computational conclusions.

After precursor **2** was formed, bond lengths greatly changed during the reaction **2** → **3**. The distance of Y–O^2 decreased while the distance of C^*–O^2 increased (Table 2). Thus the bond Y–O^2 was forming and the double bond C^*–O^2 gradually ruptured. Meanwhile, the distance of C^*–O^1 decreased by 2.783 Å, indicating that the C^*–O^1 bond in intermediate **3** was formed. In intermediate **2**, C^* was coplanar with three adjacent atoms using sp^2 hybrid orbitals while the bond angle O^1–C^*–O^2 was 109.02° in **3** (Fig. 2, Table 2). The C^* atom in **3** became sp^3 hybridization having similar bond distances with three oxygen atoms. With the coordination of Y with CL, the alkoxy group performed a nucleophilic attack at the activated *exo*-ring carbonyl carbon and the addition reaction of the carbonyl double bond was carried out. The energy of this step was +19.15 kcal/mol, suggesting a rate-determining step. Similarly, the addition of carbonyl double bond of lactide was reported by Albertsson as the rate-determining step in tin compound initiated ROP [15]. The single bond of C^*–O^2 allowed the rotation of CL ring round the C–O axis and the approach of O^3 to Y in the next step.

The step **3** → **4** was the actual ring-opening process of CL as the distance of C^*–O^3 increased. The distances of Y–O^3 and Y–O^1 were identical in intermediate **3** while they had 1.561 Å difference in **4** (Fig. 2) as O^3 kept approaching yttrium and O^1 getting away. Meanwhile, the distance of C^*–O^3 was increasing gradually. The carbonyl double bond was recovering in a certain degree as the bond angle O^1–C^*–O^2 changed from 109.02° to 116.78° (Fig. 2 and Table 2). The energy change of this step was −5.05 kcal/mol.

The distance change of C^*–O^3 from 1.615 Å of **4** to 3.602 Å of **5** suggested entirely rupture of C^*–O^3 bond, while bond Y–O^3 formed whose distance (2.081 Å) was similar to that of Y–O^1 (2.048 Å) in **2** as a normal σ bond length. The distance of C^*–O^2 and the bond angle of O^1–C^*–O^2 were 1.238 Å and 121.29°. Thus, a typical C^*–O^2 double bond containing a sp^2 hybrid C^* fully recovered. Intermediate **5** was more stable than **4** since the energy change of step **4** → **5** was −15.32 kcal/mol. A CL insertion cycle then completed, and the coordination of next CL monomer started another cycle from the analogue of intermediate **2**. The Gibbs-free energy changes of a full propagation cycle were shown in Fig. 4.

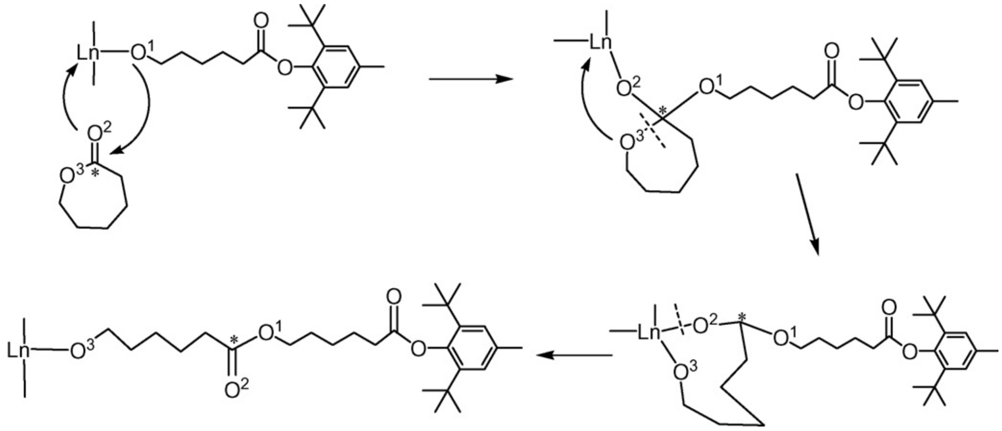
It is well known that molecular dipole moment indicates the separation degree of positive and negative charges in a molecule. We also studied the molecular dipole moments of the intermediates. As shown in Fig. 5, the dipole moments of intermediates **3** and

Table 1
Selected bond lengths (Å) and angles (°) of the geometries of [$Y(OC_6H_3Bu_2{}^t\text{-}2,6)_3$].

Bond length	DFT[a]	Exp[b]	Bond angle	DFT[a]	Exp[b]	Bond angle	DFT[a]	Exp[b]
Y–O(1)	2.07	2.00	O(1)–Y–O(2)	120	119	Y–O(1)–C(1)	177	175
Y–O(2)	2.07	2.00	O(2)–Y–O(3)	120	118	Y–O(2)–C(15)	177	173
Y–O(3)	2.07	2.00	O(1)–Y–O(3)	120	123	Y–O(3)–C(29)	176	171
Average	2.07	2.00	Average	120	120	Average	177	173

[a] Obtained from DFT calculation.

[b] Experimental X-ray data [37].



Scheme 1. The speculated propagation mechanism of ε-caprolactone according to Ref. [30].

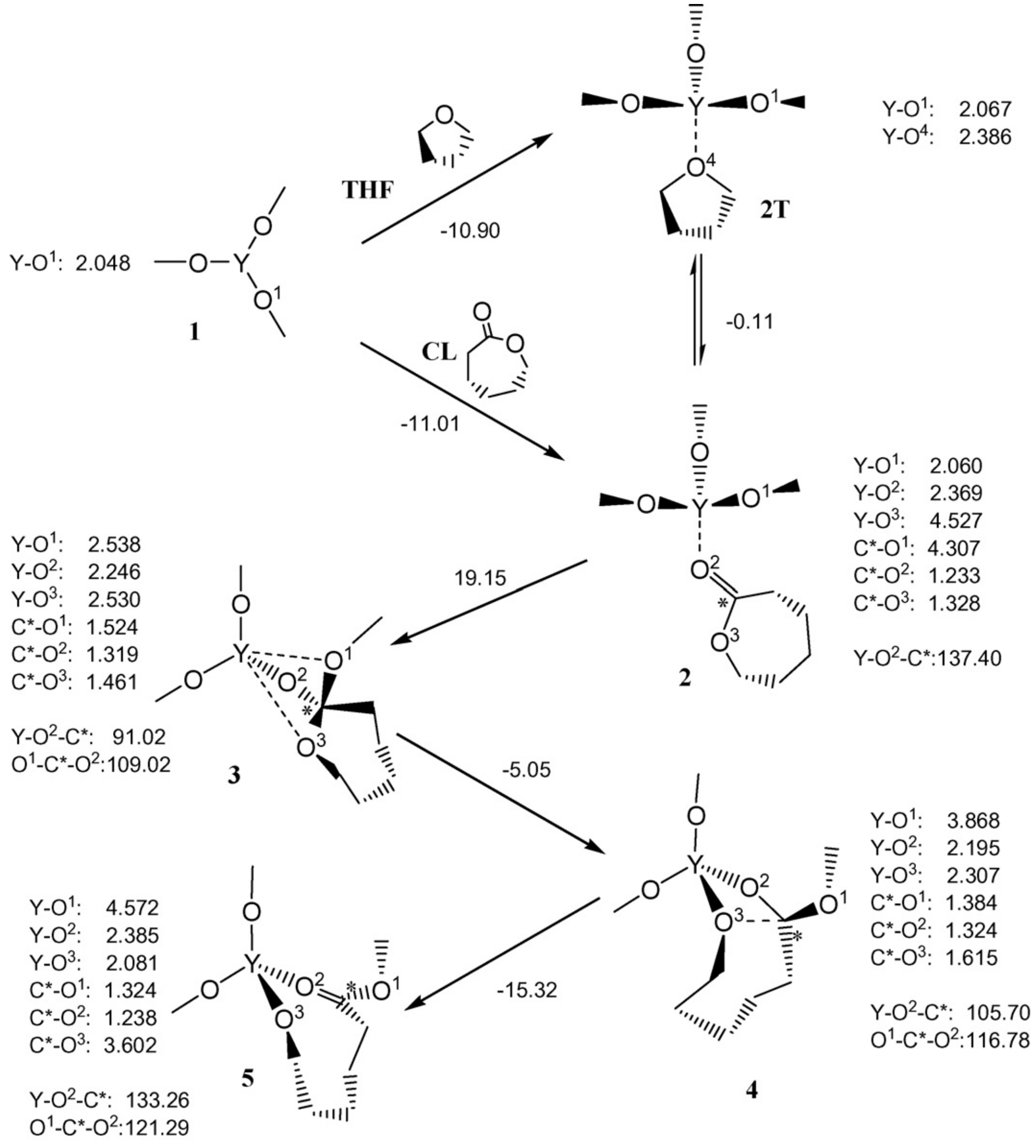


Fig. 2. ε-Caprolactone insertion mechanism of $Y(OCH_3)_3$ mediated ring-opening polymerization. Energy changes, distances and angles are given in kcal/mol, Å and degree, respectively.

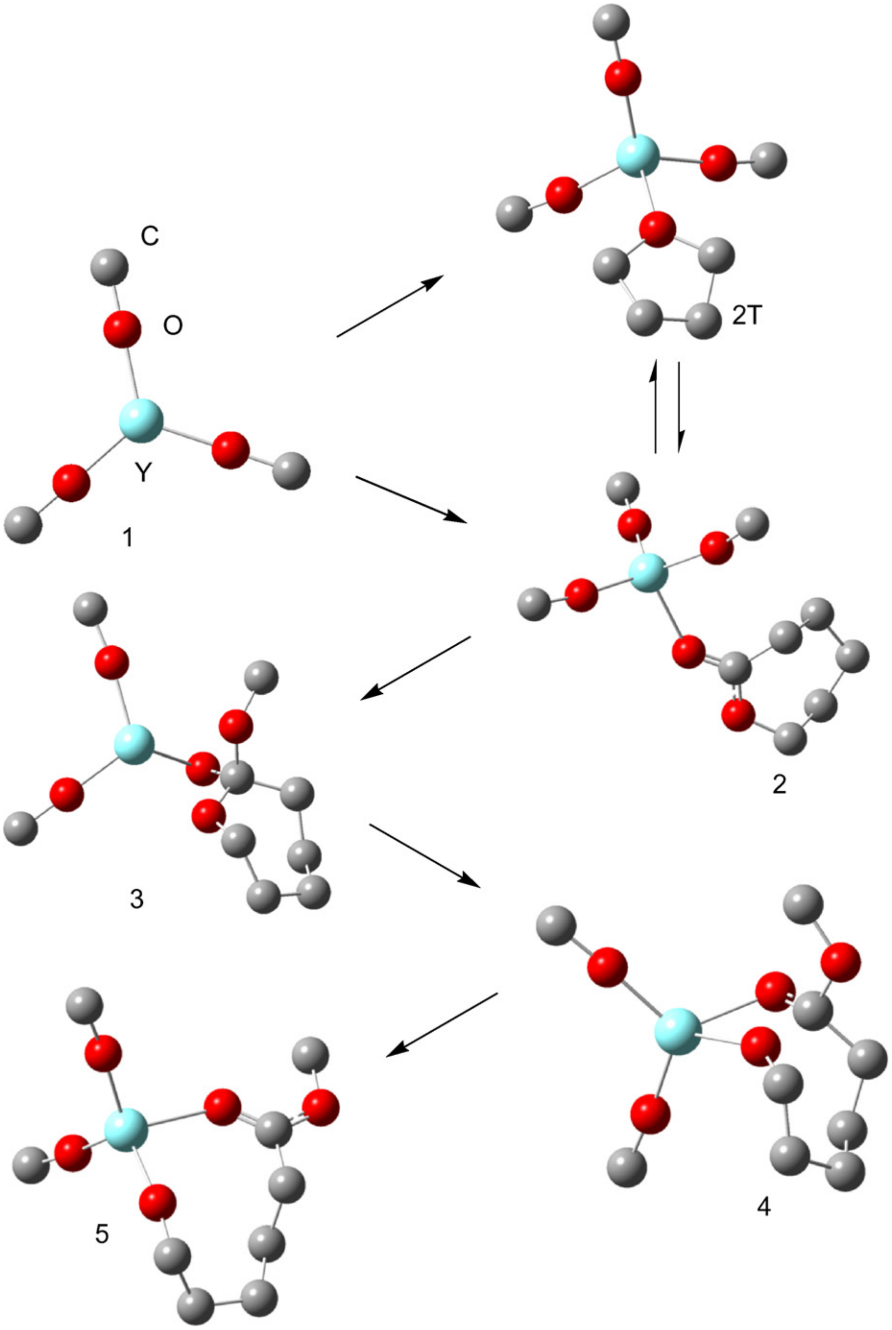


Fig. 3. 3D molecular geometries of the intermediates in Fig. 2. Hydrogen atoms are omitted for clarity. Yttrium, oxygen and carbon atoms are shown in light blue, red and grey, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

Table 2
Selected bond lengths and angles for the intermediates **1**, **2**, **2T**, **3**, **4** and **5**.

Intermediate	Bond lengths (Å)						Bond angles (°)	
	Y–O^1	Y–O^2(O^4)	Y–O^3	C*–O^1	C*–O^2	C*–O^3	Y–O^2–C*	O^1–C*–O^2
1	2.048	–	–	–	–	–	–	–
2	2.060	2.369	4.527	4.307	1.233	1.328	137.40	–
2T	2.067	2.386	–	–	–		–	–
3	2.538	2.246	2.530	1.524	1.319	1.461	91.02	109.02
4	3.868	2.195	2.307	1.384	1.324	1.615	105.70	116.78
5	4.572	2.385	2.081	1.324	1.238	3.602	133.26	121.29

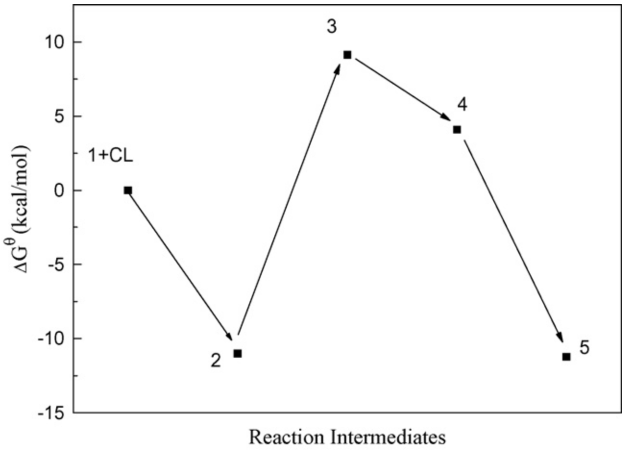


Fig. 4. Relative Gibbs-free energies of the intermediates in the monomer insertion reaction.

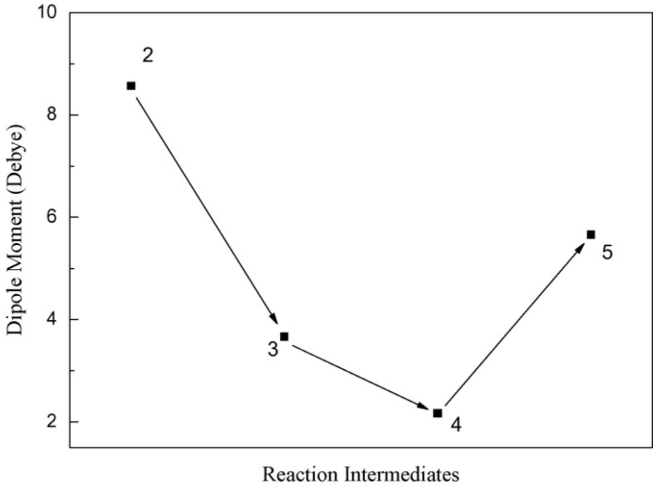


Fig. 5. Dipole moments of the intermediates in the monomer insertion reaction.

4 were smaller than those of reagent **2** and product **5**. Therefore, a solvent with low-polarity stabilized **3** and **4** and a fast CL insertion reaction could be expected, which was proved by experiments [54–58].

In conclusion, a DFT study of a CL insertion into Y–OCH_3 provided evidences for the coordination-insertion mechanism of ROP initiated by yttrium methoxide compounds. The rate-determining step was the nucleophilic attack of the alkoxide on the *exo*-ring carbonyl carbon of the monomer.

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