PM3 Semi-Empirical Method on the Ring Opening Polymerization of \( \varepsilon \)-Caprolactone Using Bis (Benzoyltrifluoroacetone)Zirconium(IV) Chloride as catalyst

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Abstract. Polycaprolactone (PCL) is an interesting polymer because of its biodegradability, good mechanical properties, and the excellent miscibility with a large range of other polymers. PCL can be obtained via ring opening polymerization (ROP) of \( \varepsilon \)-caprolactone (\( \varepsilon \)-CL) by using Lewis acid as catalyst. The purpose of this study was to focus on the study of the plausible mechanism of the ROP of \( \varepsilon \)-CL using bis-(benzoyltrifluoroacetone)zirconium(IV) chloride as a catalyst. In this research, PM3 semi-empirical method was conducted to optimize the polymer and complex structure. After that, HyperChem 8.0 program package was used to calculate and to visualize the geometry structure. This program run on a personal computer with Windows 07 operating system. The results of the computational calculation indicate that, to obtain PCL using bis(benzoyltrifluoroacetone)zirconium (IV) chloride catalyst needed several reaction steps, that is coordination \( \varepsilon \)-CL on the zirconium complex, deprotonation of \( \varepsilon \)-CL, the \( \varepsilon \)-CL insertion, and the chain propagation.

Keyword: Polycaprolactone (PCL), bis-(benzoyltrifluoroacetone)zirconium(IV) chloride, PM3 semi-empirical method, computational calculation.
1. Introduction
Nowadays, the non-eco-friendly polymer package which is derived from petroleum is disposed in the massive scale. They cannot be biodegradable so it produces negative environmental impact that can be damage the environment. PCL is one of the biodegradable polymers that can be used as packaging to substitute polymer package which is derived from petroleum. The utilization of PCL in packaging material will be able to reduce environmental damage. Besides that, PCL also has other application such as longterm drug delivery systems, orthopedic device, health device, tissue engineering, and agriculture [1][2].

PCL is produced through ROP ε-CL using Lewis acid catalyst or Lewis acid initiators. The catalysts and initiators that have been used include Zn(II) complexes, Cu(II) complexes [1], Co(II) complex [2], Ti/Zr-diphenylpropanedione complexes [3], Sn(Oct)2 [4], Coumarin salen-based zinc complex [5], (Ferrocenylpyrazolyl)zinc(II) acetate complexes [6], Zinc complexes supported by (benzimidazolyl)pyridine [7], Bis(pyrazolylmethyl)pyridine Zn(II) and Cu(II) complexes [8], tetrakis (acetylacetonato)zirconium [9], and bis(β-diketonato)zirconium(IV) chloride [10]. The application of the above catalyst in the ROP ε-CL has proven effective to produce PCL.

In the other hand, some researchers have also proposed the mechanism of ROP of ε-CL using various catalysts and initiators. Grobelny research group has proposed a mechanism of anionic polymerization of ε-CL initiated with t-BuOK. They have also proposed polymerization of ε-CL mediated with KH [11]. Besides that, Dobrinzky research group has also proposed the mechanism of ROP of ε-CL using zirconium tetrakis (acetylacetonato) catalysts. But, they only proposed the mechanism without doing computational calculations [9][11]. The Dobrinzky research group has tried to do computational calculations for complex compounds but without doing the computational calculations for the reaction mechanism [9]. In the previous work, our research group also has doing the computational calculations for the reaction mechanism of ROP of ε-CL using bis(acetylacetone)zirconium(IV) chloride complex as catalyst. While, in this study the calculated complex compound as a catalyst is bis-(benzoyl trifluoroacetone)zirconium(IV) chloride complex [10]. Both of them have a similar metal center and coordination number. But, both of them have a different β-diketonate ligand.

In this research, we performed a computational calculation for the mechanism of ROP of ε-CL using bis(benzoyl trifluoroacetone)zirconium(IV) chloride as catalyst. Every step of the intermediate state will be obtained energy so that the energy profile of each step of the reaction during the ROP ε-CL is known. In the other hand, both substrate and product of this reaction also calculated by using computational calculation.

2. Experimental
2.1 The calculation of the ROP of ε-CL mechanism
The calculation of the ROP of ε-CL mechanism was carried out by using a PM3 semi empirical method in accordance with what was done by the previous research group [9]. PM3 method has a higher calculation speed compared to the ab initio method [12].
Computational calculation of the reaction mechanism was performed by using Hyperchem 8.0 software that is run on Window's 07 [10][13][14][15]. The computational calculation has been done through the following steps, that is: (1) drawing a 3D structure, (2) choosing the pm3 semi-empirical method, (3) optimizing the geometry structure, (4) calculation the energy of substrat, intermediate state, and product. (5) visualizing the molecular structure that produced.
3. Result and discussion
In the Figure 1 below shows the proposed mechanism for ROP \( \varepsilon \)-CL reaction using bis(benzoyltrifluoroacetone)zirconium (IV) chloride as catalyst.

\[
\begin{align*}
\text{Zr-complex} & \quad \text{\( \varepsilon \)-CL} & \quad \text{complex 1} & \quad \text{complex 2} & \quad \text{Hbtfa} \\
\text{complex 1} & \quad \text{Insertion} & \quad \text{complex 2} & \quad \text{Hbtfa} \\
\text{complex 2} & \quad \text{Insertion} & \quad \text{complex 3} & \quad \text{Hbtfa} \\
\text{complex 3} & \quad \text{Insertion} & \quad \text{Hbtfa} & \quad \text{PCL}
\end{align*}
\]

**Figure 1.** ROP of \( \varepsilon \)-CL proposal mechanism using bis(benzoyltrifluoroacetone)zirconium(IV) chloride as catalyst.

ROP of \( \varepsilon \)-CL uses bis(benzoyltrifluoroacetone)zirconium(IV) chloride as a catalyst occur through several steps, that is coordination, deprotonation, \( \varepsilon \)-CL insertion, and \( \varepsilon \)-CL propagation step. The first step was the formation of complex -1. In this step, coordination of the carbonyl oxygen atom of \( \varepsilon \)-CL on the central atom of the complex compound was occurred. This step resulted in the compound which has five-coordination.

The second step was the formation of complex-2. In this step, deprotonation of \( \varepsilon \)-CL occurs followed by the proton transfer on the acac ligands. As a result ligand exchange reactions take place and Hbtfa ligand released. This step resulted in four-coordination compound.

The third step was the formation of complex-3. In this step, the coordination of the zirconium central atom with the second \( \varepsilon \)-CL molecule via the carbonyl oxygen free electron pair (\( \varepsilon \)-CL) occurred. As a consequence, an acyl oxygen-zirconium bond was formed. In this step, the compound which has five-coordination produced. After that, the \( \varepsilon \)-CL monomer change its shape from the closed ring becomes the open ring (linear \( \varepsilon \)-CL).

Last, the formation of dimer \( \varepsilon \)-CL. This step take place through the chain propagation by using \( \varepsilon \)-CL molecule. This process corresponding with the coordination mechanism. To form a longer PCL, the insertion process can be continued after the next \( \varepsilon \)-CL molecule was coordinated on the zirconium central atom. The process like the formation of dimer \( \varepsilon \)-CL repeated again continuously to make the longer PCL. As can be seen, Figure 2 shows the geometry optimization of the structure during the ROP \( \varepsilon \)-CL.
Figure 2. Geometry optimization of the structure during the ROP $\varepsilon$-CL.
In this research, the computational calculation of structure energy also done. The calculation includes for the substrate, intermediate, and product state. But not for transition state. Zr complex as a substrate has energy around 0 kJ/mol. After the complex-1 formed, the energy decrease from 0 kJ/mol to -278.03 kJ/mol. This result derived due to oxygen atom lost of unshared electron as a consequence of coordination of the carbonyl oxygen atom of ε-CL on the central atom of Zr.

Next, the complex-2 has the higher energy than complex-1 due to complex-2 has unshared electron from oxygen atom in the ε-CL molecule. After that, the energy of complex-3 decrease from 207.57 kJ/mol to -123.38 kJ/mol. Like complex-1, this due as a consequence of coordination of the carbonyl oxygen atom of second ε-CL on the central atom of Zr. Then, linear ε-CL has the higher energy (324.57 kJ/mol) compared to complex-3. This fact as an effect from ε-CL molecule has changed from closed to open ring. Last, dimer ε-CL more stable compared to linear ε-CL so that the energy decrease from 324.57 kJ/mol to 226.92 kJ/mol. The profile energy of ROP ε-CL using bis(benzoyl trifluoroacetone)zirconium(IV) chloride catalyst as can be seen in Figure 3.

Figure 3. The profile energy of ROP ε-CL using bis(benzoyl trifluoroacetone)zirconium(IV) chloride catalyst
4. Conclusion
The plausible mechanism of the ROP of $\varepsilon$-CL using bis(benzoyltrifluoroacetone) zirconium (IV) chloride as a catalyst takes place through coordination, deprotonation, insertion, and the chain propagation step. The product energy in this calculation more higher compared to the substrate. Besides that, linear $\varepsilon$-CL has the highest energy compared to all structure according to the results of calculation. This is due to the $\varepsilon$-CL linear molecule has an open ring so it needs a lot of energy to change it from the closed ring.

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