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Abstract. Polycaprolactone (PCL) is a semi-crystalline polymer and belongs to a biodegradable plastic. PCL also can naturally degraded, has a high degree of adjustment with other polymer, and has great mechanical and thermal properties. By using the Lewis acid catalyst, PCL can be yielded through the ring opening polymerization (ROP) of caprolactone (ε-CL). The objective of this study was to explore the most likely reaction mechanism of the ROP of ε-CL using bis(dibenzoylmethanato) zirconium(IV) chloride as a catalyst. Here, the Hyper Chem 8.0 program was performed to compute the monomer molecule, intermediate molecules, and polymer molecule. The program can be launch on the Windows 07 systems. The method used was the PM3 semi-empirical method. This program also used to show the results of optimized structures. The calculation results show that to generate PCL required bis(dibenzoylmethanato) zirconium (IV) catalyst. The ROP reaction mechanism of ε-CL can be occurs through direct coordination ε-CL on the Zr complex. After that, deprotonation and insertion monomer. Last step was chain propagation of the ε–CL.
Keyword. Bis(dibenzoylmethanato) zirconium(IV) chloride, PM3 semi-empirical method, reaction mechanism, polycaprolactone (PCL).

1. Introduction

Due to its advantages in the medicinal fields and packaging, poly(ε-caprolactone) (PCL) and the other natural polymer has been extensively studied for use in a variety of field [1– 4]. In the biomedical field, PCL can be used as a drug delivery system. In the packaging field, PCL can be used as an environmentally friendly packaging [1– 3].

Ring Opening Polymerization (ROP) technique is commonly used to synthesize polymers and this technique can also be used to synthesize polyester. Ring Opening Polymerization (ROP) of cyclic esters can be performed using cationic, anionic, active monomeric, enzymatic, and organocatalytic methods [1], [2], [5]. Many studies of ROP have been carried out using various catalysts or metal

initiators. The metals are transition [1], [6], aluminum metal [7], and lanthanide [8]. In ROP, the most commonly used catalysts are complex compounds.

In the academia and the catalysts industry, complex compund is still also widely used until today as catalyst for ROP of cyclic esters including for ε-caprolactone (ε-CL). In these complex compounds, transition metals are used as the central atom. Some transition metals that are commonly used as the central atom include zirconium [1], [6], zinc, cuprum [9], copper [10] and titanium [11]. Apart from using transition metals, compounds with the element Sn are also widely used as catalysts in ROP [12-13].

This research will study the mechanism of ε-CL ring opening polymerization reaction using bis(dibenzoylmethanato) zirconium(IV) chloride (bis(dibzm)Zr) catalyst. The method of proof is carried out using computational calculations. The result will be obtained in the form of energy from the optimized structural geometry. The lower the energy obtained, the more likely it is to occur when laboratory experiments are carried out [5]. The results of these calculations will be input for various researchers to conduct further research at the experimental level.

2. Materials and Method

The ROP *ε*-CL mechanism can be predicted using semi empirical method (PM3). The method serves to calculate the geometry, energy, reaction profiles, and some stationary points (reactants, complexes, intermediate and products). These molecules are calculated in the Hyperchem 8.0 software which operated on the Windows operating system [1], [14–16]. Zr atoms are used as metal center in the bis(dibzm)Zr catalyst. Meanwhile, C, H, and O atoms are used as non-metal atoms in the complex compounds. In our previous research the semi empirical method is general and effective in predicting geometry and minimum energy. The procedure is performed using an RMS gradient of 0.1 kcal/(Åmol) with a maximum cycle around 2767. The calculation of the minimum energy confirms the characteristics of the reactant, intermediate and dimer *ε*-CL product [5].

3. Results and Discussion

In the Figure **1**, the ROP mechanism of the cyclic ester using bis(dbzm)Zr as the catalysator has been described. In the diagram, the Zr atom acts as a metal in the complex, while the ε-caprolaktone acts as an ester monomer.

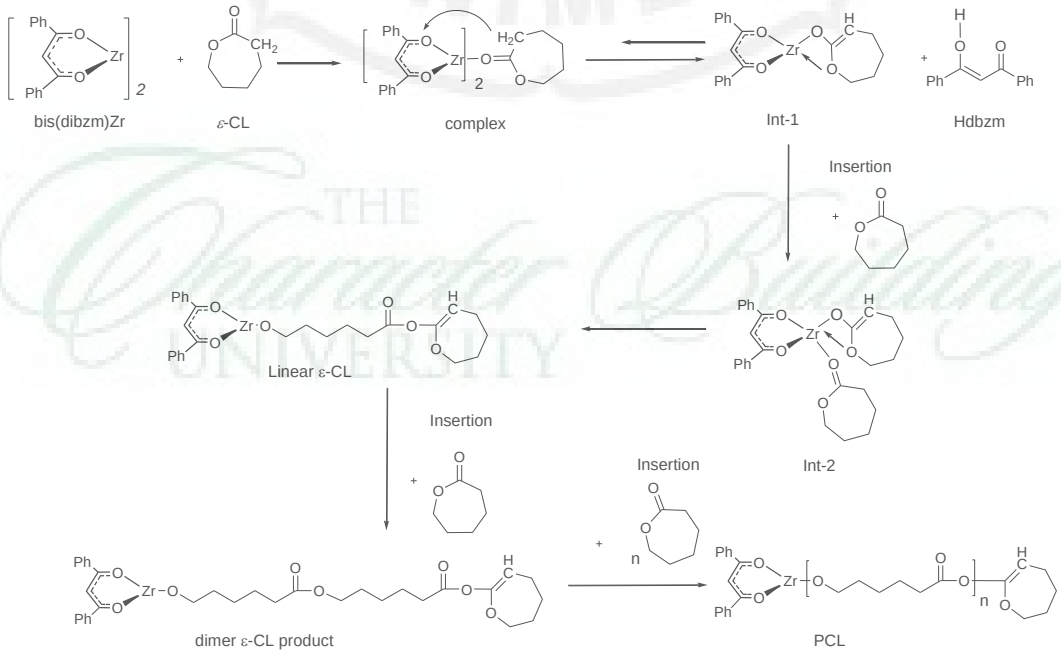


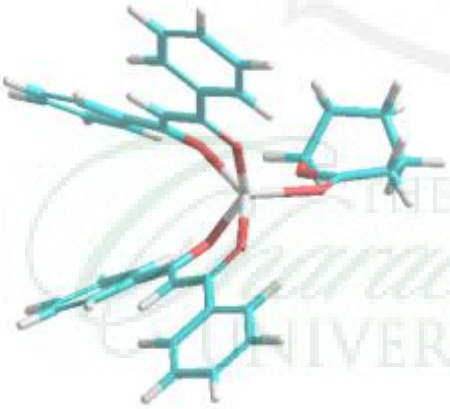
Figure 1. The ROP mechanism of the *ε*-CL using bis(dbzm)Zr as the catalysator

There are four steps for futher explanation of the ROP mechanism from Figure 1:

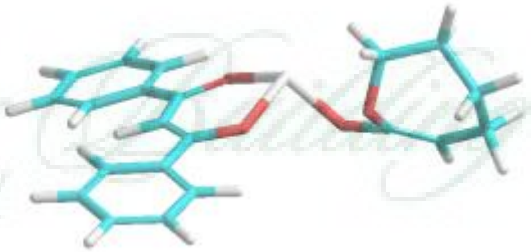
1. Complex: The first stage namely ε-CL monomer and bis(dbzm)Zr complexes perform the weak complexation. The mechanism can be formed due to the coordination interaction among ε-Cl and the catalysator of bis(dbzm)Zr complex. The bis(dbzm)Zr complex undergoes electrophilic attack by the ε-Cl carbonyl group resulting in complex compound.
2. Intermediate1: The second stage is the formation of the four-membered ring intermediate state (Int1). The ε-CL carbonyl group finds a new bond between the Zr atom and the oxygen atom. The monomer deprotonation also occurs so that the Hdbzm ligand becomes free.
3. Intermediate2: The third stage is to form a second intermediate state with five-membered ring (Int2). In this stage, the monomer insertions occur. The Int2 can be reached by making coordination bond of Zr atom (Int1) with the oxygen atom on the carbonyl group of e-CL. Next, Int2 becomes open to form a linear ε-CL.
4. Dimer product: The final step as a result of the ring opening is the formation of the dimer ε-CL product via the monomer insertion. The propagation can occur again and polymerization continues. The optimized molecular structure which involved in the ε-CL polymerization using PM3 calculations described in Figure **2**.

bis(dbzm)Zr

Hdbz



Complex



Int-1

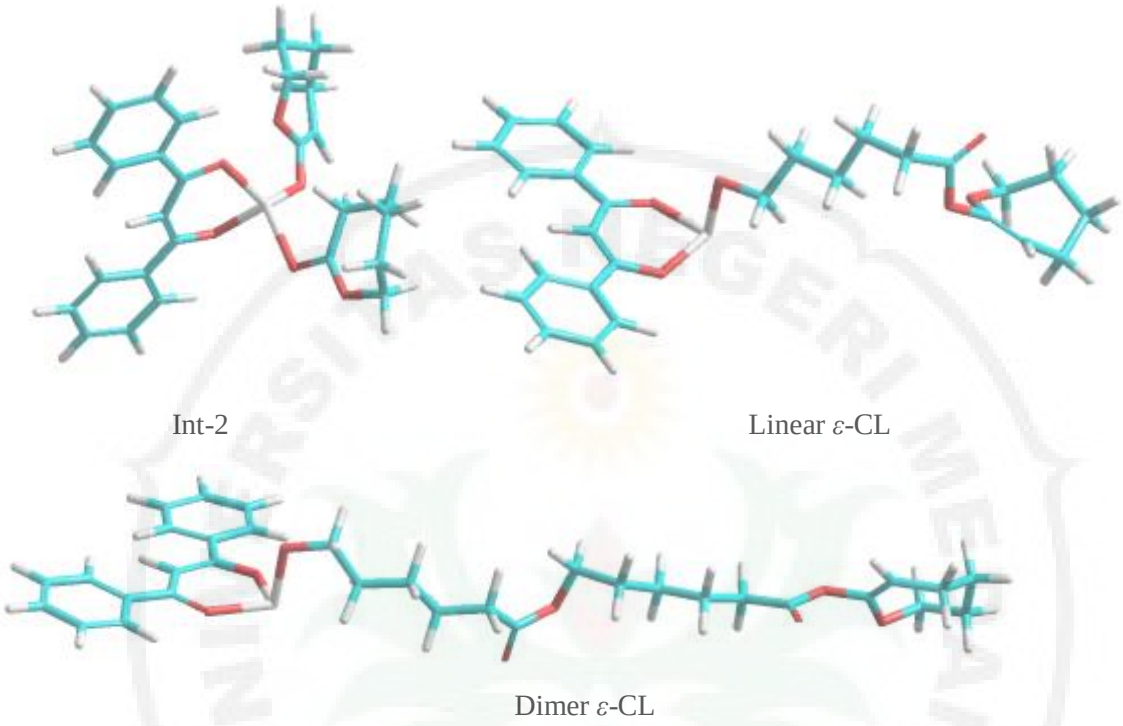


Figure 2. The Optimized molecular structure which involved in the ε-CL polymerization using PM3 calculations

We have observed the energy of complex, intermediate, and dimer using the PM3 Semi-Empirical approach. The energy value at 0 kJ/mol represents the bis(dibzm)Zr energy. Furtheremore, the energy value of int-1, linear ε-CL, and dimer are above of the bis(dibzm)Zr energy i.e 260.52 kJ/mol, 365.08 kJ/mol and 265.28 kJ mol, respectively. Next, the energy value of complex and int-2 are on under the bis(dibzm)Zr energy i.e -225.11 kJ/mol and -54.12 kJ mol, respectively.

The comparisons of energy value between the complex, intermediate state, and product were also discussed in this investigated. We have found that the ε-CL linear has the higher energy value compared with other molecule. It is due to the ε-CL linear has electron lone pair on its oxygen atom. Meanwhile, the dimer has also electron lone pair on its oxygen atom. However, because the open chain is longer, its energy value is more stable. The energy changes of the molecules which involved in the ε-CL polymerization reaction catalyzed by bis (dbzm) Zr describes in the Figure **3**.

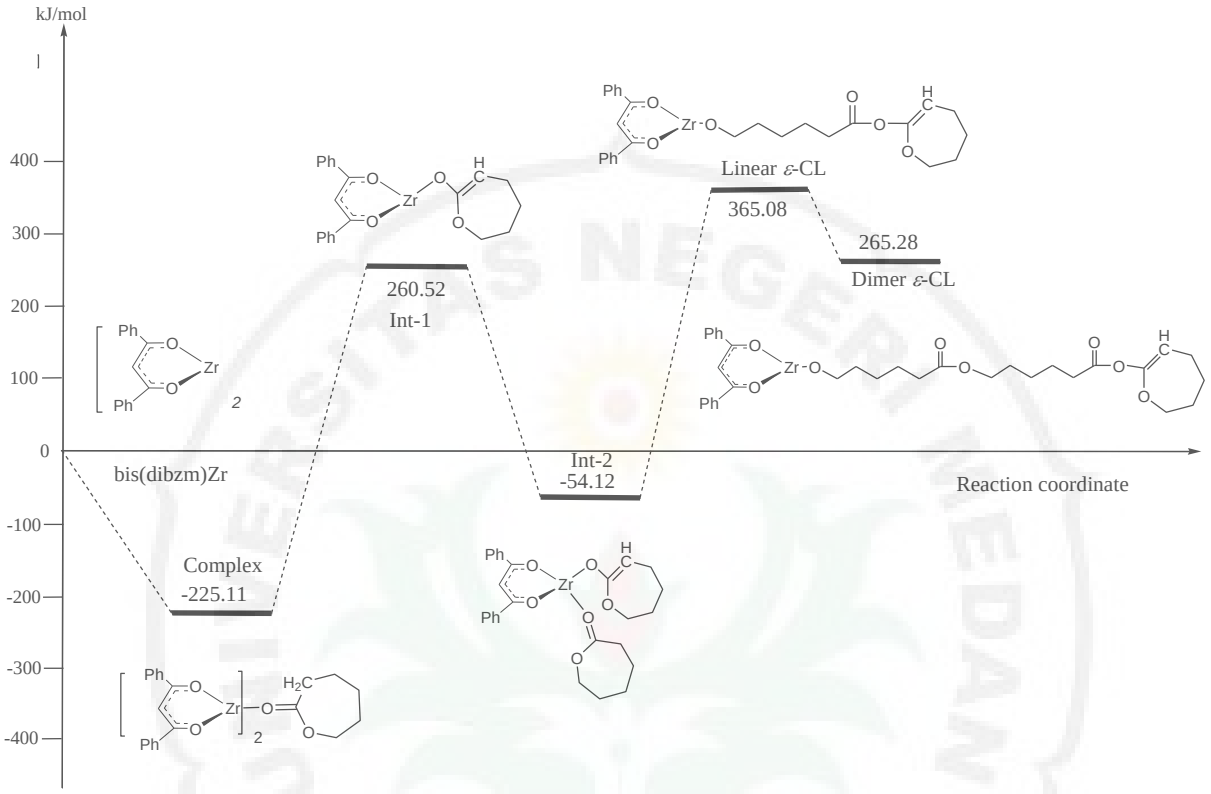


Figure 3. The energy changes of the molecules which involved in the ε-CL polymerization reaction catalyzed by bis(dbzm)Zr

4. Conclusion

The ROP of ε-CL with bis(dibzm)Zr as a catalyst have been investigated using PM3 semi empirical method. The energy of ε-CL linear molecules is higher than other compounds due to the presence of electron lone pairs of oxygen atoms in the ε-CL linear molecules. The same thing with the int1 molecules and dimer product, the energy is higher than bis(dibzm)Zr. In contrast, the energies of int-2 and complex molecules are lower than bis(dibzm)Zr. This is because the ε-CL monomers in the molecule have lost their electron lone pair on the its oxygen atom.

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