bzac pm3

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The Reaction Mechanism of Ring-opening Polymerization of *ε*-Caprolactone Using Bis(benzoylacetonato)zirconium(IV) Catalyst With PM3 Semi-Empirical Method

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Abstract. Acknowledged that polycaprolactone (PCL) is one of the prospective polymer category. This is due to PCL has a great mechanical properties, biodegradability, and excellent mixing ability with various other polymers. The effective technique to get PCL is through the ring opening polymerization (ROP) of caprolactone (ε-CL) using metal catalyst. The aims of this research was to determine a reasonable reaction mechanism of the ROP of ε-CL using bis(benzoylacetonato)zirconium(IV) chloride catalyst. In this investigation the PM3 semi-empirical method was assigned to calculate the monomer, intermediate structures, and polymer structure. Then, to compute and visualize geometry structure was employed by using the HyperChem 8.0 program. This software operates on the Windows 07 system. The calculation results imply that to get PCL using bis(benzoylacetonato)zirconium(IV) catalyst required a few steps i.e. coordination ε-CL in metal center, ε-CL deprotonation, the insertion of ε–CL, and propagation of the chain.
Keyword. Bis(benzoylacetonato)zirconium(IV) chloride, PM3 semi-empiris method, Polycaprolactone (PCL).

1. Introduction

In the last few years, non-biodegradable polymers derived from fossil fuels have discarded on a large scale so that it negatively effects the environment. This is caused by the nature of the polymer which cannot be biodegradable. Polycaprolactone (PCL) and the other natural polymers have naturally biodegradable properties, have a high degree of adjustment with other polymer and can be applied as a biodegradable packaging[1-2]. Therefore, by applying PCL in material packaging can reduce environmental pollution. [1], [3].PCL also has some benefits in the health and agriculture sector include as a orthopedic devices, medical devices, long-term drug delivery systems, tissue engineering, and matrix for herbicide.

The method to generate PCL can be done via the ROP ε-CL process by using a catalyst or initiator for instance Lewis acid catalyst. A few catalysts and initiators that have been used consist of the Co(II) complex [4], Sn(Oct)2 [5], Cu(II) and Zn(II) complexes [6], Zn complexes with (benzimidazolyl)pyridine based ligand [7], Ti-/Zr-diphenylpropanedione complexes [8], Zn(II) acetate complexes with (Ferrocenylpyrazolyl) based ligand [9], Zn(II) and Cu(II) complexes with Bis(pyrazolylmethyl)pyridine based ligand [10], bis(*β*-diketonato)zirconium(IV) chloride [1], Zinc complex with type coumarin based ligand [11], and tetrakis (acetylacetonato)zirconium [12]. The utilization of that catalyst in the ROP ε-CL has evident effective to generate PCL as reported in the previous result.

In the previous work, several researchers have presented the ROP ε-CL reaction mechanism by using diverse initiators and catalysts. For example, the Dobrinzky research group recommends the ROP ε-CL reaction mechanism using zirconium tetrakis (acetylacetonato) catalyst. In their research, they presented the reaction mechanism but it were not equipped with the computational calculation results. Besides that, they also have tried to calculation the complex compounds by using Hyperchem software [12-13]. Meanwhile, the other research group has present a reaction mechanism for ε-CL polymerization begins with initiated by t-BuOK [14].

Our research group has also performed calculations for the ε-CL polymerization reaction mechanism using bis(benzoyltrifluoroacetone)zirconium-(IV) chloride catalyst . The ligands used in this study are the same type as the ligands we have reported earlier, namely the β-diketonato ligand type. Meanwhile, the ligands that will be used in this study are also β-diketonato ligands. But, it has different withdrawal and electron donors groups. While the metal center of complex is alike [15].

The purpose of this study was to calculate the ROP ε-CL reaction mechanism by using bis(benzoylacetonato)zirconium(IV) chloride catalyst (bis(bzac)Zr) catalyst. Each stages of the reaction will be calculated including the complex catalyst, several intermediates, and the product. The results will be displayed in the graphical form which is illustrates the energy profile of the ROP ε-CL reaction mechanism using bis(bzac)Zr catalyst.

2. Materials and Method

2.1 Computational calculation of the ε-CL ring opening reaction mechanism

The PM3 method is used for the calculation of the ε-CL ring opening reaction mechanism. This method is appropriate with what we have reported in the previous studies [15]. The reaction mechanism is calculated by computational calculations using Hyperchem 8.0 [16]. The software runs on the Window's 07 operating system [17-18]. The steps taken in computational calculations namely: (1) Drawing 2D and 3D molecules. (2) Choosing the method, charge, and spin. (3) Calculating the energy of complex, several intermediates, and products. (4) The optimized structure is then visualized by using Hyperchem software.

3. Results and Discussion

The detail steps on the ε-CL ring opening reaction mechanism employed bis(bzac)Zr catalyst showed in the Figure **1**.

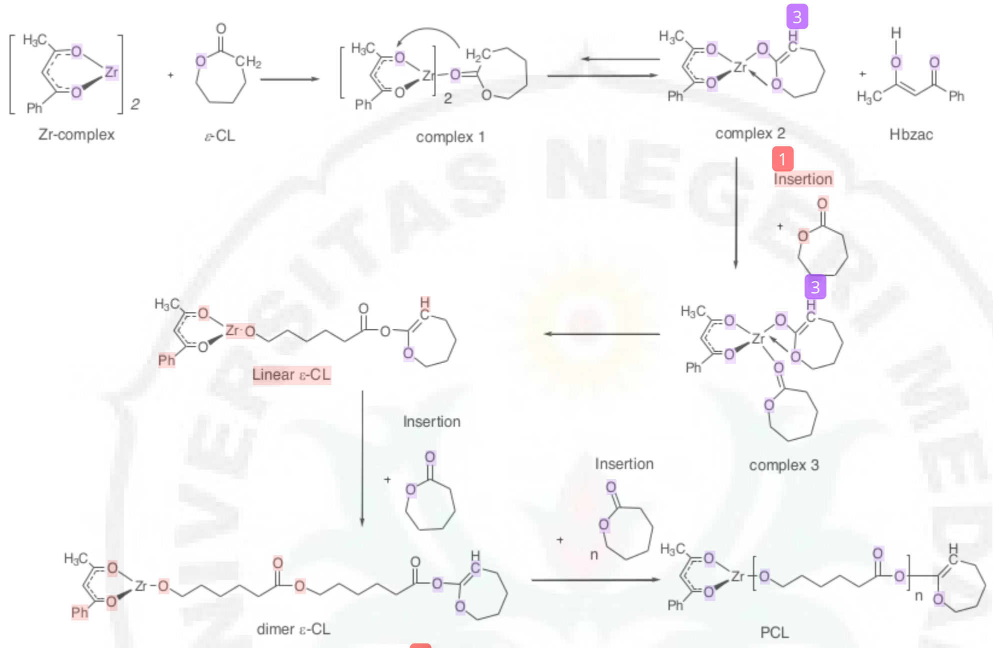


Figure 1. The proposal for a reasonable reaction mechanism of the ROP of ε-CL using bis(bzac)Zr catalyst

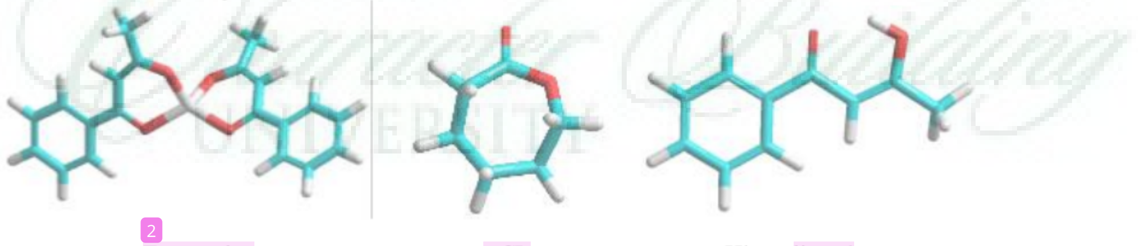
Some of the steps carried out in the ROP ε-CL reaction mechanism using bis(bzac)Zr catalyst consist of several steps:

(1) The five-coordinated complex-1 molecule can be formed by the coordination of the ε-CL monomer with the bis(bzac)Zr complex.

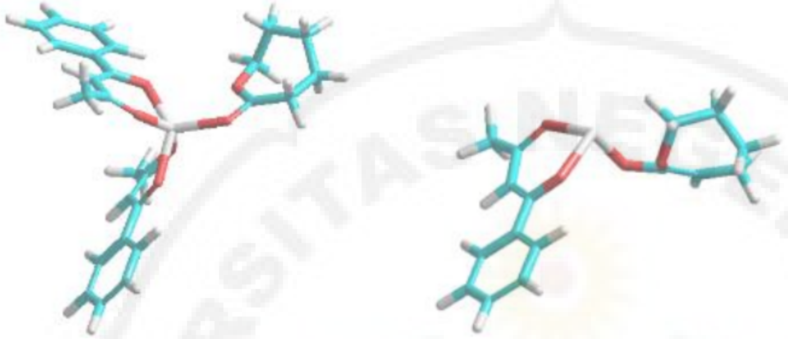
(2) The four-coordinated complex-2 molecule can be formed by the deprotonation of ε-CL. After that the proton transfer on the bzac ligand occurs and Hbzac ligand is freed.

(3) The five-coordinated complex-3 molecule can be formed by coordinating zirconium atom with the other ε-CL monomers so that oxygen-zirconium acyl single bonds are created. Next, the shape of complex-3 molecule can be converted into a linear ε-CL molecule shape.

(4) The final step is the formation of the ε-CL dimer molecule which involves the simple propagation of the ε-CL monomer chain. The propagation steps are done through the ε-CL molecules insertion process on the metal center (Zr). After repeated propagation step several times, this process will be produced PCL [1], [12], [15]. The geometries structures of complex, several intermediates, and products obtained from PM3 method calculation are illustrated in Figure 2.

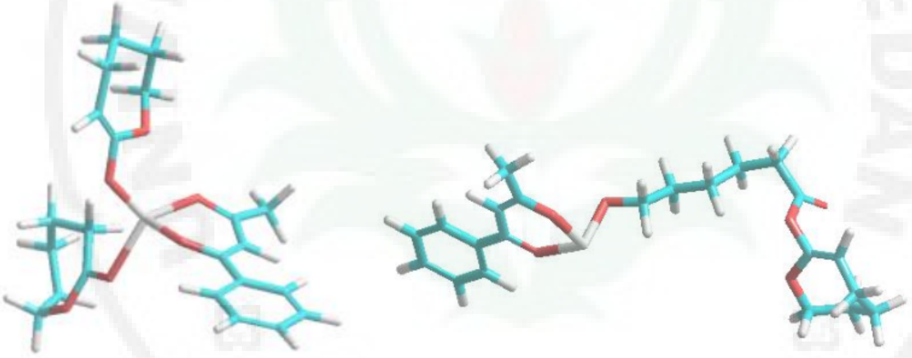


Zr complex ε-CL Hbzac ligand



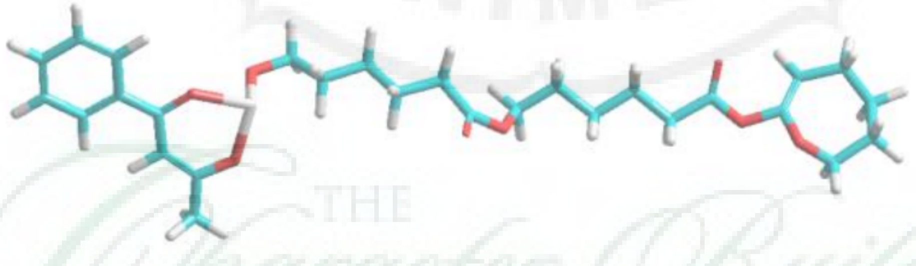
Complex-1

Complex-2



Complex-3

Linear ε-CL



Dimer ε-CL

Figure 2. The geometries structures of complex, several intermediates, and dimer ε-CL obtained from PM3 method calculation

The optimized energy for each step of the reaction mechanism has been obtained using the PM3 Semi-Empirical method as illustrated in Figure 3. The energy of the Zr complex which functions as a catalyst is 0 kJ / mol. The energies of the complex-1 and complex-3 are under Zr complex, respectively. This is because the ε-CL carbonyl group coordinates with the Zr metal of the complex.

As a result, the oxygen atom loses its unshared electrons. The energy required producing complex-1 and complex-3 are -245.68 kJ/mol and -78.14 kJ/mol, respectively.

Meanwhile the energies of the complex-2 and linear ε-CL are above Zr complex, respectively. This is because the oxygen atom in the complex-2 and linear ε-CL doesn't lose its unshared electrons. Apart from that in the linear ε-CL, there has been a change in the ε-CL molecule from a closed ring (complex-3) to an open ring resulting in a linear ε-CL. This process requires high energy. Therefore, the formation energy of the linear ε-CL is higher compared to other compounds. The energy required producing complex-2 and linear ε-CL are 237.31 kJ/mol and 354.52 kJ/mol, respectively. Next, the process of inserting ε-CL molecules in the metal center occurs to produce ε-CL dimer. The energy required to produce ε-CL dimers is lower than to produce a linear ε-CL which is around 254.11 kJ/mol.

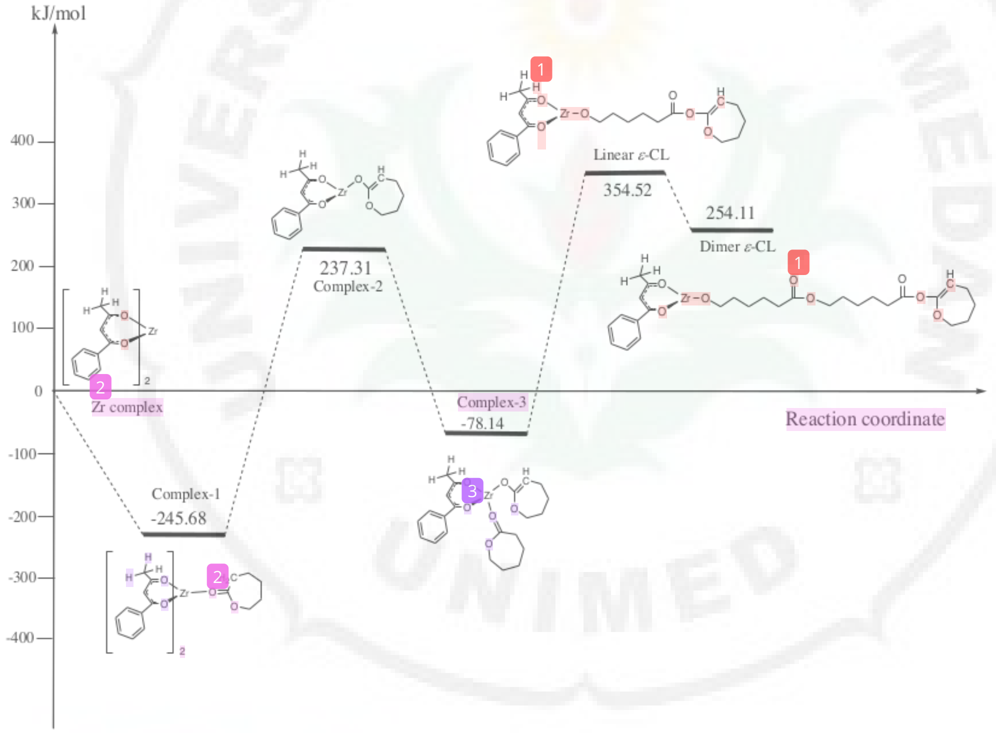


Figure 3. The reasonable reaction mechanism of the ROP of ε-CL using bis(bzac)Zr catalyst. The relative energies are in kJ/mol.

4. Conclusion

The determination of the reasonable reaction mechanism of ROP ε-CL using bis(bzac)Zr catalyst has been investigated using PM3 semi empirical method. The polymerization reaction occurs via a coordinating and insertion mechanism to produce a product. The energy required producing complex-1 and complex-3 are below the Zr complex, namely -245.68 kJ / mol and -78.14 kJ / mol. Meanwhile the energy required producing complex-2, linear ε-Cl and dimer ε-CL are above the Zr complex, namely 237.31 kJ/mol, 354.52 kJ/mol, and 254.11 kJ/mol.

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