CHAPTER IV

CONCLUSION

The ring-opening polymerization (ROP) of ε-caprolactone (CL) with alkoxide catalysts has been carried out using quantum chemical calculation by mean of density functional method (DFT) at B3LYP level. The reaction proceeds via coordination-insertion mechanism initiated by different tin(II) alkoxide $Sn(OR)_2$ initiators where R = n-C_4H_9, i-C_4H_9, t-C_4H_9, n-C_6H_{13}, and n-C_8H_{17} as a function of reaction progress.

DFT calculations of stationary points along the reaction pathway in the ROP of CL initiated by tin(II) alkoxides give insight into the addition detailed mechanisms of their initiation and propagation processes. Both transition states (**TS1**, **TS2**) having four-membered ring are found in all cases. The apparent energy barriers at **TS1** of initiation step (different energies between **Complex** and **TS1**) of CL with different $Sn(OR)_2$ initiators as R = n-C_4H_9, i-C_4H_9, t-C_4H_9, n-C_6H_{13}, and n-C_8H_{17} are calculated to be 14.58, 14.61, 14.59, 15.04, and 20.04 kcal/mol, respectively. The $Sn(OR)_2$ with R having n-C_4H_9 has the lowest apparent energy barrier resulting in the fastest rate constant under the same condition among all five initiators.

There are two main effects on the initiators. First, the effect of long chain on R group in $Sn(OR)_2$ initiators starting from C_4 (n-But) to C_6 (n-Hex) and C_8 (n-Oct) shows slightly energy change on the **TS1** relative energy, for n-But, n-Hex, and n-Oct going to be 7.05, 7.13 and 8.13 kcal mol^{-1}, respectively. The longer chain on R group slightly destabilizes the **TS1** formation stability. Therefore the shorter R group is more favorable to make the rate of reaction go faster within the same condition as **TS1** is the rate determining step for ROP. The initiators with R group greater than C_4 was considered in our study due to the solubility of initiators based on our experiment study. Second, the effect of branching group on butyl group in $Sn(OR)_2$ initiators from C_4(*n*-But) to *iso*-C_4 (*i*-But) and *tert*-C_4 (*t*-But) reveals significant change on energy of **TS1** formation. Obviously the more steric hindrance of branching C_4, the less stable of **TS1** are observed. The overall reaction of all initiators is found to be exothermic compared with reactants. The calculated rate constants of all initiators by transition state theory are in good agreement with experimental results. Rate constant of tin(II)-*n*-butoxide shows the highest reactivity due to shortest chain length of R group and less steric effect among other initiators.

From our calculation results, it is concluded that, the DFT method at B3LYP level is a powerful tool for describing the reaction mechanism of ROP of cyclic ester monomer. Finally, we hope that the calculation technique and knowledge information in this thesis may be applicable and useful for the other cases such as the ROP of lactide initiated by tin(II) alkoxides and also other cyclic esters initiated by titanium(IV) alkoxide. The understanding of detailed information on ROP mechanism of CL initiated by tin(II) alkoxides studied in this thesis is indispensable to the industry of producing biodegradable polymers.