CHAPTER II

METHODOLOGY: MODEL OF CHEMISTRY

In recent years, there has been increasing number of people using computational chemistry. Many of these newcomers are part-time theoreticians who work on other aspects of chemistry. This increase has been facilitated by the development of computer software that is increasingly easy to use. It is now so easy to do computational chemistry that calculations can be performed with no knowledge of the underlying principles. As a result, many people do not understand even the most basic concepts involved in a calculation.

A term of theoretical chemistry may be defined as the mathematical description of chemistry. The term computational chemistry is generally used when a mathematical method is sufficiently well developed that it can be automated for implementation with a computer. Note that the words "exact" and "perfect" do not appear in these definitions. Very few aspects of chemistry can be computed exactly, but almost every aspect of chemistry has been described in a qualitative or approximately quantitative computational scheme. The biggest mistake a computational chemist can make is to assume that any computed number is exact. However, just as not all spectra are perfectly resolved, often a qualitative or approximate computation can give useful insight into chemistry if the researcher understands what it does and does not predict [49, 50].

Computational chemistry has been used in many ways. One particularly important way is to model a molecular system prior to synthesizing that molecule in the laboratory. Although computational models may not be perfect, they are often good enough to rule out 90% of possible compounds as being unsuitable for their intended use. This is very useful information because synthesizing a single compound could require months of labor and raw materials, and generate toxic waste. A second use of computational chemistry is in understanding a problem more completely. There are some properties of a molecule that can be obtained computationally more easily than by experimental means. There are also insights into molecular bonding, which can be obtained from the results of computations that cannot be obtained from any experimental method. Thus, many experimental chemists are now using computational modeling to gain additional understanding of the compounds being examined in the laboratory. Computational chemistry has become easier to use, professional computational chemists have shifted their attention to more difficult modeling problems. No matter how easy computational chemistry becomes, there will always be problems so difficult that only an expert in the field can tackle them. [49, 51]

Therefore, some background theory related to the method needed to obtain the reaction mechanism and reaction rate of all reactions in ring-opening polymerization (ROP) of ε-caprolactone (CL) initiated by tin(II) alkoxides is presented in brief in this section. The present theory is not exhaustive.

2.1 Quantum chemistry study

2.1.1 Background of quantum chemical calculation

In the late seventeenth century, Isaac Newton discovered "classical mechanics", the laws of motion of macroscopic objects. In the early twentieth century, physicists found that classical mechanics does not correctly describe the behavior of very small particles such as the electrons and nuclei of atoms and molecules. The behavior of such particles is described by a set of laws called quantum mechanics (QM) [52].

Quantum chemistry applies QM to problems in chemistry. The influence of quantum chemistry is evident in all branches of chemistry. Physical chemists use QM to calculate (with the aid of statistical mechanics) thermodynamic properties of gases; to interpret molecular spectra, thereby allowing experimental determination of molecular properties; to calculate molecular properties theoretically; to calculate properties of transition states in chemical reactions, thereby allowing estimation of rate constants; to understand intermolecular forces; and to deal with bonding in solids. Although the large size of biologically important molecules makes QM calculations on them extremely hard, biochemists are beginning to benefit from QM studies of conformations of biological molecules, enzyme-substrate binding, and solvation of biological molecules [52].

QM is a correct mathematical description of the behavior of electrons especially in chemistry. Theoretically, QM can be used to predict any property of an individual atom or molecule exactly. Practically, however, the QM equations have been solved exactly for one electron systems only. The concept of QM is shown in Figure 2.1 below [51].

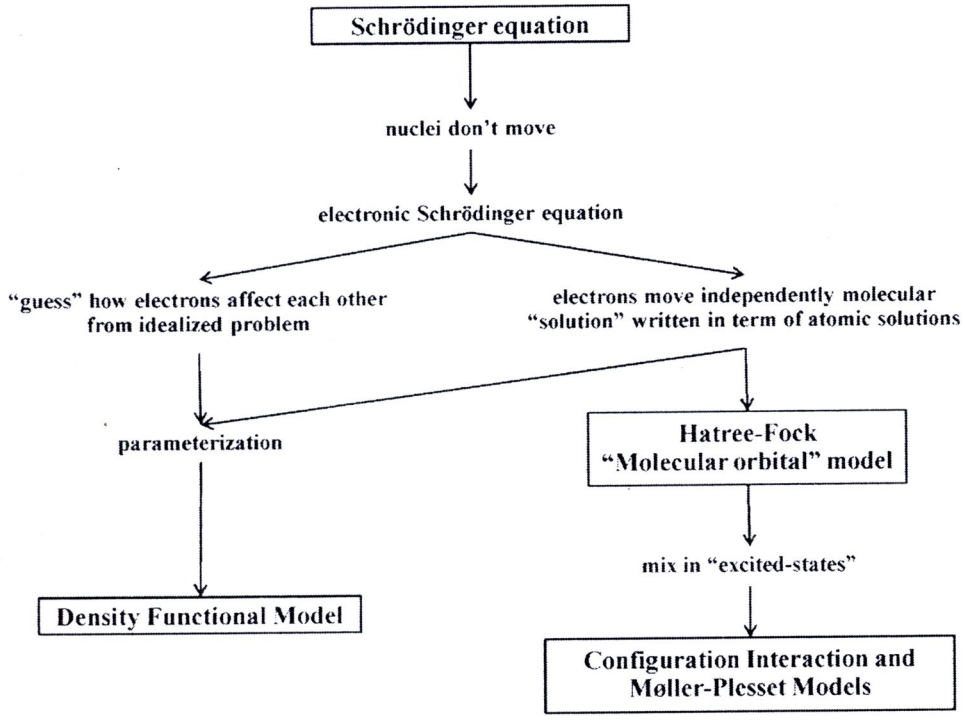

Figure 2.1 Genealogy of quantum chemical models

2.1.1.1 Schrödinger equation

In 1925, Erwin Schrödinger and Werner Heisenberg independently developed the new quantum theory. Schrödinger method involves partial differential equations, whereas Heisenberg's method employs matrices; however, a year later the two methods were shown to be mathematically equivalent. Schrödinger equation seems to have a better physical interpretation via the classical wave equation. Indeed, the Schrödinger equation can be viewed as a form of the wave equation applied to matter waves [53].

There are many descriptions in QM concepts of the motions of particles; one describes the system using a wave function, Ψ. The wave function for an interested system governed by a Hamiltonian, $\hat{H}$ is determined by the Schrödinger equation since it is the basis for most computational chemistry methods.

$$\hat{H}\Psi = E\Psi \tag{2.1}$$

The wave function is found by solving the Schrödinger equation for the system. The Schrödinger equation (2.1) represents a description of a molecular system in terms of a wave function (Ψ), Hamiltonian operator ($\hat{H}$), and the total energy (E). The Schrödinger equation can be solved exactly only for atoms or molecule containing one electron. For this reason, the numerical methods that allow us to approximate wave function have been employed to describe in theoretical approximations such as *ab initio* methods, simiempirical methods, density functional theory, and etc [49].

2.1.1.2 Born-Oppenheimer approximation

The important concept of the Born-Oppenheimer approximation (BOA) is that the electrons are so much lighter than the nuclei that, during any molecular collision, they rearrange their motion instantaneously to respond to changes in the configuration of the nuclei. Consequently, one can calculate the eigenvalues and eigenfunctions of the electronic Hamiltonian (including nuclear repulsion terms) independent of the nuclear motion. These eigenvalue for all nuclear configurations of interest construct the potential energy function that governs the nuclear motion. Thus, the potential energy surface (PES) is a consequence of the BOA. A second consequence of the BOA is that the nuclear motion is adiabatic in that it conserves the quantum numbers associated with the motion of the electrons. Chemical reactions that require the crossing of potential energy surfaces are usually very slow and result in a very slow of their rate constants [54].

The complete nonrelativistic Hamiltonian of a molecule as a sum of kinetic and potential energy terms:

$$\hat{H} = -\frac{\hbar^2}{2m}\sum_i \nabla_i^2 - \sum_A \frac{\hbar^2}{2M_A}\nabla_A^2 - \sum_{A,i}\frac{Z_A e^2}{4\pi\varepsilon_0 r_{iA}} + \sum_{A>B}\frac{Z_A Z_B e^2}{4\pi\varepsilon_0 R_{AB}} + \sum_{i>j}\frac{e^2}{4\pi\varepsilon_0 r_{ij}} \quad (2.2)$$

where Z_A and Z_B are the nuclear charges, M_A is the mass of nucleus A, m is the mass of the electron, R_{AB} is the distance between nuclei A and B, r_{ij} is the distance between electrons i and j, r_{iA} is the distance between election i and nuclei A, ε_0 is the permittivity of free space, and $\hbar$ is the Plank constant. The compact formula could be represented as

$$\hat{H} = T_N(R) + T_e(r) + V_{eN}(r,R) + V_{NN}(R) + V_{ee}(r) \quad (2.3)$$

where $T_N(R)$ = kinetic energy of the nuclei

$T_e(r)$ = kinetic energy of the electrons

$V_{eN}(r,R)$ = electron-nuclei attractive Coulomb potential

$V_{NN}(R)$ = nuclear-nuclear repulsive Coulomb potential and

$V_{ee}(r)$ = electron-electron repulsive Coulomb potential

BOA is the assumption that the electronic motion and the nuclear motion in molecules can be separated. The electronic motion should be the same as if the nuclei are fixed. It notes that the nuclear motion is so much slower than that of electron or the nuclei are very much more massive than the electrons. Thus, leaving $V_{NN}(R)$ out of the electronic Schrödinger equation leads to a similar equation,

$$\hat{H}_{electron} = T_e(r) + V_{eN}(r,R) + V_{ee}(r) \quad (2.4)$$

such that

$$\hat{H}_{electron}\Psi(r;R) = E_{electron}\Psi_{electron}(r;R) \tag{2.5}$$

For most chemical applications, it is a good approximation to assume that the Schrödinger equation can be parametrically separated into a product of electronic and nuclear parts. This leads to an exact solution can be obtained by using an expansion of the form

$$\Psi(r,R) = \psi(r;R)\chi(R) \tag{2.6}$$

where ψ is a wave function associated with solving the electron part of the Schrödinger equation for fixed nuclear coordinates, and χ is a wave function associated with nuclear motion [55].

2.1.2 *Ab initio* method

As implied by the Latin translation, *ab initio* calculations are performed "from the beginning." In essence, *ab initio* calculations originate from first principles and do not rely on known properties of the species being investigated. The basis for *ab initio* calculations is a differential equation known as the Schrödinger equation as shown in previous section. The mathematical approximations are derived from only theoretical principle in order to find an approximate solution with no in conclusion of experimental data [56].

2.1.2.1 Hatree-Fock approximation

The well-known type of *ab initio* calculation is Hartree-Fock (HF) approximation. The HF calculation starts with an initial guess for the orbital coefficients, usually using a semiempirical method. This function is used to calculate

energy and a new set of orbital coefficients, which can then be used to obtain a new set, and so on. This procedure continues iteratively until the energy and orbital coefficient remain constant from one iteration to the next or convergence called a self-consistent field (SCF) [49, 57].

There are several ways in which we can proceed with the derivation of the HF equations. The traditional one is to look for an eigenvalue equation for the HF orbitals:

$$\hat{h}^F \psi_i = \varepsilon_i \psi_i \tag{2.7}$$

where the HF operator $\hat{h}^F$ depends only on the coordinates of any one of the electrons, but allows for the averaging over their interactions.

There are n doubly occupied molecular orbitals, and the number of electrons is $2n$ because we have allocated α and β spin electron. Generally, Hartree model, the many-electron wavefunction was written as a straightforward product of one-electron orbital ψ_A and ψ_B. From Fock's contribution to the field, it shows as a Slater determinant which is satisfied by the Pauli principle. For an N-electron system, the spin-orbital, $\chi_1(x_1)$, where x_1 denotes the position and spin of the singular electron the Slater determinant is defined as

$$\Psi(x_1, x_2, ..., x_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(x_1) & \chi_2(x_1) & \cdots & \chi_N(x_1) \\ \chi_1(x_2) & \chi_2(x_2) & \cdots & \chi_N(x_2) \\ \cdots & \cdots & \cdots & \cdots \\ \chi_1(x_1) & \chi_2(x_N) & \cdots & \chi_N(x_N) \end{vmatrix} \tag{2.8}$$

The linear combination of Hartree products for the two-particle case can clearly be seen as identical with the Slater determinant for $N = 2$. A single Slater determinant is used as an approximation to the electronic wave function in HF theory.

In more accurate theories [49], for example, configuration interaction (CI) and multireference configuration self-consistency field (MCSCF), a linear combination of Slater determinants is needed [57]. In general, *ab initio* calculations give very good qualitative results and can yield increasingly accurate quantitative results as the molecules in question become smaller. The advantage of *ab initio* methods is that they eventually converge to the exact solution once all the approximations are made sufficiently small in magnitude. In general, the relative accuracy of results is

$$\text{HF} << \text{MP2} < \text{CISD} \cong \text{MP4} \cong \text{CCSD} < \text{CCSD(T)} < \text{CCSDT} < \text{Full CI}$$

2.1.3 Density functional theory

Density functional theory (DFT) is one of the most widely used methods based on electron density. This method has become popular in recent years because it is less computational requirement than other methods with similar accuracy such as second order Møller–Plesset perturbation (MP2). The general theoretical framework of DFT was originated by the Hohenberg and Kohn theorem. However, in practical applications, Kohn and Sham developed the theory formulated a method similar in structure of HF method [58-60].

2.1.3.1 Hohenberg-Kohn theorems

Instead of solving the problem using single electron wave function, this method uses one function which represents the entire electron density of the molecule represented as $\rho(r)$. Electronic energy of electron density is represented as

$$E[\rho] = E_T[\rho] + E_V[\rho] + E_U[\rho] \tag{2.9}$$

where $E_T[\rho]$ is kinetic energy, $E_V[\rho]$ is potential energy, and $E_U[\rho]$ is external perturbation and Coulombic repulsive force between pairs of electrons.

2.1.3.2 Kohn-Sham equations

A density functional is used to obtain the energy for the electron density. The advantage of using electron density is that integrals for Coulombic repulsion need to be done only over the electron density which is a three-dimensional function (N^3).

The exact ground-state electron density is given by

$$\rho(r) = \sum_{i=1}^{n} |\psi_i(r)|^2 \tag{2.10}$$

We can write in simple form as

$$E[\rho] = E_T[\rho] + E_V[\rho] + E_{xc}[\rho] \tag{2.11}$$

where the sum is overall energy of the occupied Kohn-Sham orbitals, the first term in the equation 2.11 represent the kinetic energy of the electrons; the second term is potential energy including electron-nucleus attraction and Coulomb repulsive interaction between electrons; and last term is the exchange-correlation energy of the system. E_{xc} term, which is often split the exchange-correlation term into a sum of one part for exchange effects and one part for correlation effects, must be the functional of the electron density.

$$E_{xc}[\rho] = E_x[\rho] + E_c[\rho] \tag{2.12}$$

Therefore, exchange-correlation potential, V_{xc} can be presented as the functional derivatives of the exchange-correlation energy:

$$V_{xc}[\rho] = \frac{\delta E_{xc}[\rho]}{\delta \rho} \tag{2.13}$$

2.1.3.3 B3LYP model

The purpose of including this complex mathematical function (functional) is to suggest the hybrid nature of the mathematics. It notes that various approximations - local density approximation (LDA), Hartree-Fock (HF), Becke-1988 (B88), Lee-Yang-Parr 1988 (LYP88), and Vosko,Wilks, Nusair 1980 (VWN80) – are part of this hybrid functional:

$$E_{hybrid}^{XC}[\rho] = C_{HF} E_{HF}^{XC} + C_{DFT} E_{DFT}^{XC} \tag{2.14}$$

From three parameters of Beck and Lee-Yang-Parr correlation functional (B3LYP), it has been reported that it could give a good results on the organic molecules with various experiments. The hybrid models B3LYP method is expressed in equation:

$$E_{B3LYP}^{XC}[\rho] = E_{LDA}^{X} + c_0(E_{HF}^{X} - E_{LDA}^{X}) + c_X \Delta E_{B88}^{C} + E_{VWN3}^{C} + c(CE_{LYP}^{C} - E_{VWN3}^{C}) \tag{2.15}$$

where HF exchange, E_{HF}^{X}. Local density approximation, E_{LDA}^{X}. Gradient-corrected exchange, E_{B88}^{C}. Lee, Yang, and Parr correlation, E_{LYP}^{C}.

2.1.4 Basis set function

The basis set is the set of mathematical functions from which the wave function is constructed. It uses to describe the electron probability density in molecular orbital which are expanded as a linear combination of such functions with the weights or coefficients to be determined. For this thesis, we chosen two basis set using in the calculation as a function of mixed basis set. For metal atom, a doublet-ζ-valence quality basis set LANL2DZ was assigned for Sn atom. A relativistic electron

core potential (ECP) developed by Hay and Wadt replaced the Sn core electron [61, 62]. For non-metal atom, a valence triple zeta with polarization function (VTZ2P) at cc-pVTZ was assigned for C, H, and O atoms.

About cc-pVTZ basis set, the correlation-consistent basis sets developed by Dunning are popular alternatives [63]. The correlation-consistent basis sets were constructed to extract the maximum electron correlation energy for each atom. The correlation-consistent basis sets are designated as "cc-pVNZ," to be read as correlation-consistent polarized split-valence N-zeta, where N designates the degree to which the valence space is split. As N increases, the number of polarization functions also increases. So, for example, the cc-pVDZ basis set for carbon is double-zeta in the valence space and includes a single set of d functions, and the cc-pVTZ basis set is triple-zeta in the valence space and has two sets of d functions and a set of f functions [60, 64, 65].

About LANL2DZ basis set [66], it is desirable to reduce the amount of computation necessary for heavy atoms. This is done by replacing the core electrons and their basis functions in the wave function by a potential term in the Hamiltonian. These are called core potentials, effective core potentials. This is often the method of choice for heavy atoms, Rb and up. Like as this calculation, there is Sn atom on the molecule of initiator. LANL2DZ was available for H(4s) atom through Pu(7s6p2d2f) atom, this is a collection of double-zeta basis sets, which are all-electron sets prior to Na atom [49, 59].

Basis sets are built into the common computational chemistry programs. A valuable web-enabled database for retrieval of basis sets is available from the

Molecular Science Computing Facility, Environmental and Molecular Sciences Laboratory "EMSL Gaussian Basis Set Order Form" (http://www.emsl.pnl.gov/forms/-basisform.html). However, the basis set functions must be chosen to have a form that is useful in a chemical sense. That is, the functions should have large amplitude in regions of space where the electron probability density (the wave function) is also large, and small amplitudes where the probability density is small. The simultaneous optimization of these three considerations is at the heart of basis set development [60].

2.2 Chemical kinetics study

Kinetics is the study of the rates of chemical processes in an effort to understand what it is that influences these rates and to develop theories which can be used to predict them. Knowledge of reaction rates has many practical applications, for example in designing an industrial process, in understanding the complex dynamics of the atmosphere and in understanding the intricate interplay of the chemical reaction that are the basis of life.

2.2.1 Background of chemical kinetics

Chemical kinetics deals with the experimental determination of reaction rates from which rate laws and rate constants are derived. Relatively simple rate laws exist for zero-order reactions (for which reaction rates are independent of concentration), first-order reactions, and second-order reactions, and can be derived for others. In consecutive reactions, the rate-determining step often determines the kinetics. In consecutive first-order reactions, a steady state approximation can simplify the rate law. The activation energy for a reaction is experimentally determined through the

Arrhenius equation and the Eyring equation. The main factors that influence the reaction rate include: the physical state of the reactants, the concentrations of the reactants, the temperature at which the reaction occurs, and whether or not any catalysts are present in the reaction [60].

In chemical kinetics, a reaction rate constant, k, quantifies the speed of a chemical reaction. For a polymerization reaction where monomers M and initiator I are reacting to produce polymers P, or written as $M + I \rightarrow P$, the reaction rate has the form as equation 2.16.

$$\frac{d[M]}{dt} = k(T)[M]^m[I]^n \tag{2.16}$$

k(T) is the reaction rate constant that depends on temperature. [I] is the concentration of initiator I in moles per volume of solution assuming the reaction is taking place throughout the volume of the solution (for a reaction taking place at a boundary it would denote something like moles of I per area). The components m and n are called orders and depend on the reaction mechanism. They can be determined experimentally.

A single-step reaction can also be written as equation 2.17.

$$\frac{d[M]}{dt} = Ae^{-E_a/RT}[M]^m[I]^n \tag{2.17}$$

E_a is the activation energy and R is the gas constant. Since at temperature T, the molecules have energies according to a Boltzmann distribution, one can expect the proportion of collisions with energy greater than E_a to vary with $e^{-Ea/RT}$. A is the pre-exponential factor or frequency factor. The Arrhenius equation gives the quantitative

basis of the relationship between the activation energy and the reaction rate at which a reaction proceeds [67, 68].

2.2.2 Transition state theory

In the 1930s, Transition state theory (TST) or activated complex theory was developed as a predictive tool for rate constants based on inherently of the potential energy surface with a statistical representation of classical dynamics. TST is a well-known developed formula for obtaining thermal rate constants of chemical reaction. In addition to the born-oppenheimer approximation, TST is based on three assumptions: First, there is a dividing surface existing in a phase space that separates it into a reactant region and a product region. It is assumed that this dividing surface located at the transition state which is assigned as the maximum value on the minimum energy path (MEP) of the potential energy surface that connects the reactant and product. Any trajectory passing through this dividing surface from the reactant side is assumed to cross only once and then forming the product. This is also called the nonrecrossing rule. Second, the reactant is assumed to maintain the equilibrium at the Boltzmann energy distribution. Finally, activated complexes are defined as sumpermolecules having configurations located in the proximity of the transition state [49, 51, 54, 64, 65].

The thermal rate constant, *k(T)*, for a bimolecular reaction is given by equation 2.18 below

$$M + I \leftrightarrow MI \rightarrow P$$

$$k(T) = \frac{k_B T}{h} \frac{Q_{MI}(T)}{Q_M(T) Q_I(T)} e^{\{-\Delta V^{\neq} / k_B T\}} \tag{2.18}$$

Where k_B is Boltzmann's constant, T is the temperature, h is Planck's constant. $\Delta V^{\neq}$ is the classical barrier height; that is, the potential energy difference between the reactants and transition state. Q_M and Q_I are the total partition functions of the reactants M and I, respectively. Q_{MI} is the activated or transition state complex partition function and does not include translational motion along the reaction coordinate because this is treated separately [69].

In general, the partition functions (Q, q) can be calculated from the energy levels, the degeneracy of each level, and temperature of the system. For the rotational and vibrational partition functions, the geometry and vibrational frequencies for a molecule are needed [56, 64].

Translational partition function: The translational partition function for a molecule is dependent on molecular mass (m) and temperature (T). For a given molecular mass and temperature, the translational partition function can be calculated from equation 2.19. In this expression k_B is the Boltzmann constant and the term V, representing volume in m^3, does not need to be considered, as it is canceled out in the final calculation of the rate constant.

$$q_{tran} = \frac{(2\pi m k_B T)^{\frac{3}{2}}}{h^2} V \tag{2.19}$$

Rotational partition function: The rotational partition function for a molecule is dependent on the moments of inertia around the principle axes of rotation (I_A, I_B, I_C) in the molecule and temperature. Two general expressions apply, depending on

whether the molecule is a linear diatomic or nonlinear polyatomic. In the case of a linear diatomic, equation 2.20 is used to determine the rotational partition function. For a nonlinear polyatomic molecule, equation 2.21 is used to determine the rotational partition function. In both cases, the rotational symmetry number (σ) of the rotor must be considered in the final calculation. The rotational symmetry number represents the number of indistinguishable orientations that may be obtained by the rotation of the molecule.

$$q_{rot,1D} = \frac{8\pi^2 I k_B T}{\sigma h^2} \tag{2.20}$$

$$q_{rot,3D} = \frac{8\pi^2 (8\pi^3 I_M I_I I_P)^{1/2} (k_B T)^{3/2}}{\sigma h^3} \tag{2.21}$$

Vibrational partition function: The vibrational partition function can be determined from the vibrational frequencies, ν_i, of each fundamental mode (i) and the temperature. In general, the vibrational partition function can be evaluated from the equation 2.22. The vibrational frequencies for each mode are calculated using the harmonic oscillator (HO) approximation. In the HO approximation, the restoring force of the vibration is proportional to the displacement. Although true vibrational modes are described by anharmonic oscillation, this approximation works fairly well in predicting the frequencies. The zero-point energy of each vibration is normally excluded from this calculation, but rather is included in the energy component in the final calculation of the rate constant.

$$q_{vib} = \prod_i (1 - e^{-h\nu_i / k_B T})^{-1} \tag{2.22}$$

Electronic partition function: The electronic partition can be calculated using equation 2.23. In this expression g_i refers to the degeneracy of the i^{th} electronic state located at energy E_i above the ground state. For nearly all systems, the first electronic state occurs at energy sufficiently high enough, that at room temperature (298 K) only the ground state is populated. In such a case, the electronic partition function is simply equal to the degeneracy of the ground state, equation 2.23.

$$q_{elec} = \sum_i g_i e^{-E_i/k_B T} \tag{2.23}$$

2.2.3 TheRate program

The subjects of computational fluid dynamics, process simulation and design, polymer catalyst, and atmospheric chemistry are just a few of the areas that need accurate rate constants of the underlying elementary chemical reactions. Predicting rate constants is in fact a main purpose of computational chemistry. The TheRate (THEoretical RATEs) program seeks to bring together many of the recent advances in computational chemistry methods in a user-friendly environment to calculate elementary reaction rate constants from first principles, and seeks to bridge the gap between chemistry and chemical engineering [70, 71].

Calculations of rate constants require a delicate balance between the accuracy of the dynamical theory and the efficiency in obtaining accurate potential energy information. In the extreme of rigorous dynamical treatment, accurate quantum dynamics calculations yield detailed state-to-state reactive cross-sections or rate constants with full consideration of quantum effects. However, such calculations are currently limited to four-atom reacting systems with the use of global analytical potential energy functions. In the other extreme, TST has been practical for a wide

range of chemical processes due to its simplicity. The basic model only requires potential energy information at the reactant(s) and transition state, because it treats many dynamical effects only approximately. The major advantage of TST is that such limited potential energy information may be obtained from accurate electronic structure calculations without the need of an analytical potential energy function.

Therefore in this thesis, we decided to calculate the rate constants of all reactions using TheRate code with the TST, that available online at the CSE-Online (http://www.cse-online.net) [70, 71].

2.3 Computational techniques

Computational techniques [49, 50, 52, 53, 59, 60, 64, 65, 72] have been applied to investigate the ROP of CL initiating by tin(II) alkoxides. It is a tool for producing an explanation, and therefore insight into the reactions at the molecular level. The nature of individual species within the chemical systems studied is determined through DFT. These theories can be employed to determine the geometries, fundamental modes of vibration, and energies of molecules in chemical reactions. Intrinsic reaction coordinate (IRC) [49, 64] calculations were performed to confirm all transition states and their corresponding reactants and products. The vibrational frequencies, reaction energies, natural bond orbital charge (NBO) and molecular orbital at all stationary points were then refined at the same level of theory. TST can then be employed to determine the rate constants for the reactions [51, 56].

The calculations associated with density DFT are sufficiently complicated that sophisticated software packages are required. In this research the software packages Gaussian03 [73] were performed on numerous different machines using Intel Core 2

quad processors with Linux operating systems via Chang-noi cluster at computational chemistry laboratory, department of chemistry, Chiang Mai University. The available memories in these machines were up to 4 GB. Meanwhile, the rate constant of all reactions were calculated from the module of TheRate program via University of Utah's web-based [70, 71]. For clearly understanding, the overview of computing step was shown briefly in Figure 2.2.

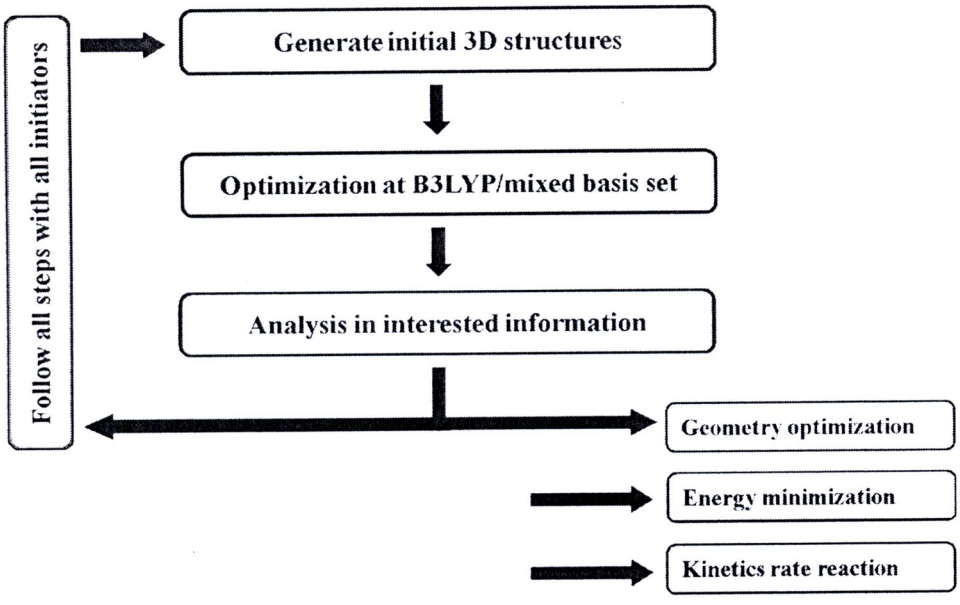

Figure 2.2 Overview of computing step

2.3.1 Method level/basis set calculation

The hybrid DFT, Becke's gradient-corrected exchange-correlation density functionals (B3LYP) with mixed basis set has been selected for locating all stationary points, namely Reactants, Complex, TS1, Int1, TS2, Int2 and Product for the this reactions. In mixed basis set, cc-pVTZ basis set was assigned for C, H and O atom while LANL2DZ basis set was assigned for Sn metal atom as a keyword "B3LYP/Gen Pseudo=read" in route section of input file.

2.3.2 Geometry calculation

Performing a geometry optimization is the primary step in studying a molecule using computational techniques. Geometry optimizations classically attempt to locate a minimum on the potential energy surface in order to foretell the equilibrium structures of molecular systems. They may also be used to locate transition structures or intermediate structures. Moreover, the geometry of a molecule determines many of its physical and chemical properties. We know that the energy of a molecule changes with its structure. Hence, understanding the methods of geometry optimization is the major requirement for energy minimization. It is essential to understand the geometry of a molecule before running computations [53, 59].

The molecular geometries of the five target initiators (Figure 2.3), CL and structures in each stationary point along the reaction pathway follow the purpose mechanism (Figure 1.9) were initially constructed in Gaussview (a visualization tool) and stored in an input file for a geometry optimization. Geometry optimizations were performed with the Berny algorithm by using the "Opt" keyword in the route section of the input files. The geometries were initially optimized using B3LYP/Mixed basis set method at 2.3.1 section. The transition state structure or activated complexes were found by performing a search along the molecular potential energy surface using the Linear Synchronous Transit (LST) and the Synchronous Transit-Guided Quasi Newton (STQN) method. For LST method was defined by keyword Opt=TS. And for the STQN method was initiated by using Opt=QST2 or Opt=QST3 keywords in the route section of the input files. These opt=QST2 or opt=QST3 keywords required either two or three molecular specifications in the input file, respectively [64].

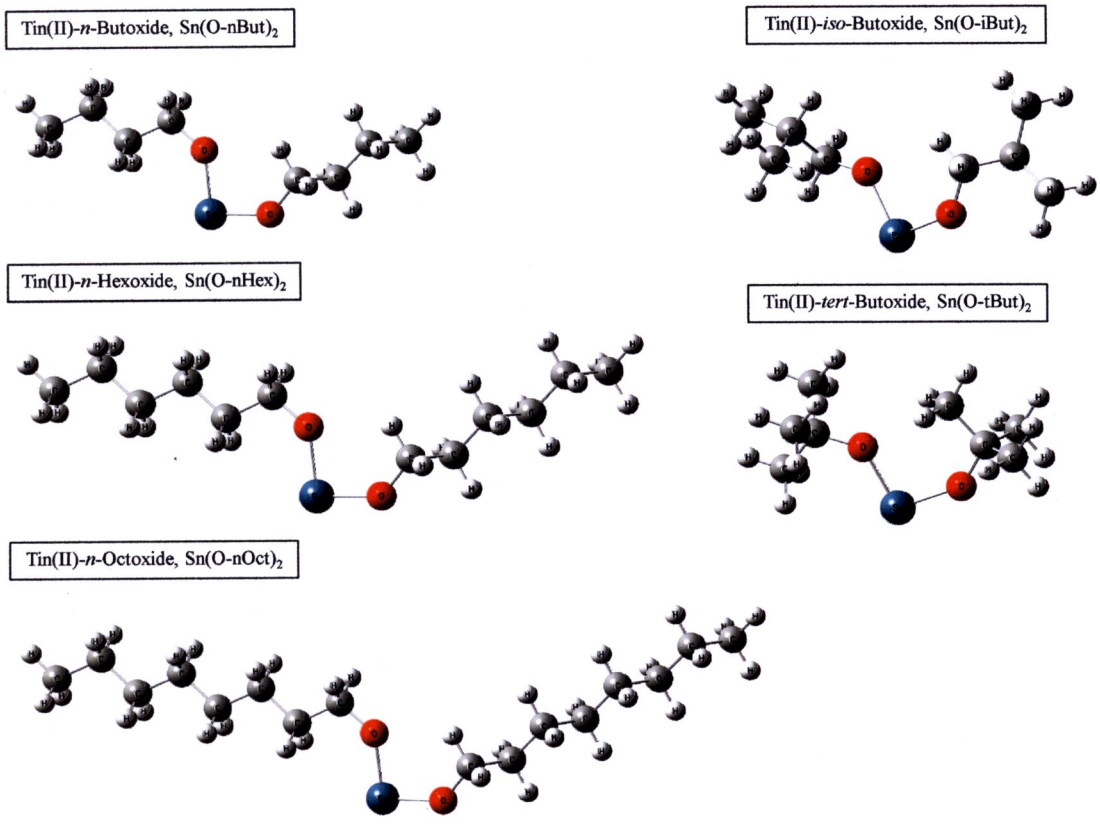

Figure 2.3 The structures of five target initiators used in this study

2.3.3 Vibrational frequency calculation

A geometry optimization alone cannot determine the nature of the stationary point that it attains. In order to characterize a stationary point, it is necessary to perform a frequency calculation on the optimized geometry. Electronic structure programs such as GAUSSIAN are able to carry out such calculations (you can even perform an optimization followed by a frequency calculation at the optimized geometry in a single job) [53]. The vibrational frequencies of all stationary point along reaction profile (Reactants, Complex, TS1, Int1, TS2, Int2 and Product) of the reactions have been calculated with B3LYP/cc-pVTZ. Calculation of the force constants and vibrational frequencies was performed by using the "Freq" keyword in

the route section of the input files. The vibrational frequencies were determined from the second derivatives of the energy with respect to the nuclear coordinates.

The completed frequency calculation will include a variety of results such as frequencies, intensities, the associated normal modes, and the zero point energy (ZPE) of the structure and various thermo-chemical properties. In identifying whether there are any frequency values less than zero, these frequencies are known as imaginary frequencies. The number of imaginary frequencies indicates the sort of stationary point to which the given molecular structure. By definition, a structure which has n imaginary frequencies is an n^{th} order saddle point. Thus, the minimum will have zero imaginary frequencies, and an ordinary transition structure will have one imaginary frequency since it is a first order saddle point [49, 53].

2.3.4 Reaction energy calculation

Energy is one of the most useful concepts in science. The analysis of energetic can predict what molecular processes are likely to occur, or able to occur. All computational chemistry techniques define energy such that the system with the lowest energy is the most stable. Thus, finding the shape of a molecule corresponds to finding the shape with the lowest energy [49].

All energy calculations were performed on the B3LYP/cc-pVTZ. These energy calculations were examined geometry convergence and to determine the reaction barrier height. In formulating a mathematical representation of molecules, it is necessary to define a reference system that is defined as having ZPE. This ZPE is different from one approximation to the next. For DFT methods, which model all the electrons in a system, ZPE corresponds to having all nuclei and electrons at an infinite

distance from one another [49]. For this reason, all calculated energies of this thesis were corrected by ZPE for increases the accuracy of system.

2.3.5 Rate constant calculation

After the calculation completed, the output information such as coordinate structure, energies, frequencies mode at least two molecules of rate determining step are used to calculating the rate constant of reactions (For this thesis used Reactant and TS1 step).

All thermal rate constants for the temperature range 100-120 °C were calculated using the University of Utah's web-based kinetics module within Computational Science and Engineering Online suite (CSEOnline) [70, 71]. The rate constants were calculated using the TST.

2.3.6 Natural bond orbital calculation

Natural bond orbital analysis (NBO) is the name of a whole set of analysis techniques. One of these is the natural population analysis (NPA) for obtaining occupancies (how many electrons are assigned to each atom) and charges. Some researchers use the acronyms NBO and NPA interchangeably. Rather than using the molecular orbitals directly, NBO uses the natural orbitals. Natural orbitals are the eigenfunctions of the first-order reduced density matrix. These are then localized and orthogonalized. The localization procedure allows orbitals to be defined as those centered on atoms and those encompassing pairs of atoms. These can be integrated to obtain charges on the atoms. For this thesis, "NPA" keyword is assigned to calculate the distribution of electron charge in each interested atom for classifying the

nucleophlic and electrophilic property. The obvious mechanism will be improved by this method. In the route section of input file, "Pop=NPA" is assigned. The results in a population analysis scheme that is less basis set dependent than the Mulliken scheme. However, basis set effects are still readily apparent [49, 64].