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DFT study of the role of substituents in tin(II) bis(amidoethyl)amine complexes used for ε-caprolactone polymerization

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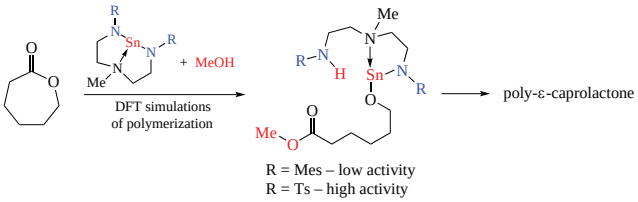
DFT simulations of ring-opening polymerization of ε-caprolactone in the presence of two stannylenes based on bis(2-amidoethyl)amine ligands demonstrated that rate limiting step of the whole process is the nucleophilic attack of a metal initiator with the formation of the tetrahedral carbon from sp^2 carbon atom of the carboxy group. The presence of electron-withdrawing groups at the terminal nitrogen atoms of the ligands leads to decrease in the activation energy of the rate limiting step.



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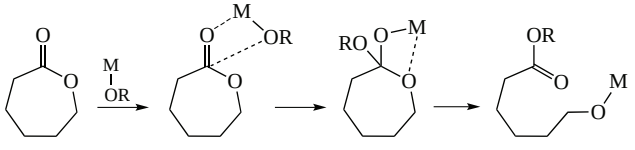
Over the past two decades, one of the most important issues related to large-scale chemical production has been the recycling plastics based on α-olefins (polyethylene, polypropylene, *etc.*). The well-known chemical inertia of these plastics (the degradation time under natural conditions exceeds 300 years) leads to their accumulation in the environment. One of the ways to solve the problem is to use so-called biodegradable polymers where possible. The main area of large-scale use of biodegradable materials is packaging. One of the most promising types of biodegradable polymers is poly(cyclic esters): poly-ε-caprolactone, polylactide, polyglycolide and their co-polymers.[1,2] Their mechanical properties are close to those of polypropylene, and at the same time they are relatively inexpensive. In addition, some of these derivatives can be obtained from renewable sources. The most suitable method for the synthesis of cyclic ester polymers is the polymerization of cyclic monomers in the presence of metal complexes as initiators.[3–11] In general, the mechanism of polymerization of cyclic ester (for example, ε-caprolactone) in the presence of a metal complex as an initiator is reliably established (Scheme 1).

While tin(II) bis(2-ethylhexanoate) is employed in industry, the search for novel more active initiators for this process remains urgent. Despite the importance of the metal atom nature, the design of the ligand system of the complex plays a key role in creating catalytic systems capable of effectively initiating ROP. To date, a significant number of initiators based on various metals have been prepared and tested in polymerization.



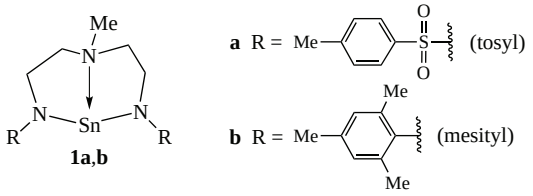
Scheme 1

Unfortunately, not very many patterns of 'ligand structure – activity' have been found during this testing.

The catalytic activity of the initiators is most affected by the steric volume of the substituents in the ligands, which hinder the approach of the cyclic ester, and by the Lewis acidity of the metal center in the complexes, which determines the strength of the binding of the ester to the metal atom. Indirectly electron-donor or acceptor properties of substituents in the ligands of the complex have effect on the rate of the polymerization reaction. However, there is no unambiguous relationship for the electronic properties of substituents in ligands. In some cases, the reaction is accelerated by an initiator with electron-withdrawing substituents, and in others, by those with electron-donating substituents.[12–21] Therefore, the influence of substituents in ligands must be investigated for each initiator independently. It is especially important to use quantum chemical calculations to establish the influence of various structural elements of the ligand on the initiator activity.

One can conclude that Sn^{2+} complexes with transannular bond are promising for polymerization of ε-caprolactone. Very recently we have prepared and tested as initiators of ε-caprolactone two stannylenes based on bis(2-amidoethyl)-amine ligands $PhCH_2N(CH_2CH_2NR)_2Sn$, R = 4-$MeC_6H_4SO_2$ or 2,4,6-$Me_3C_6H_2$.[22] Both are monomeric in solution according to ^{119}Sn NMR data. It was found that compound with tosyl electron-withdrawing groups was much more active (100% conversion, 1 h) in polymerization of ε-caprolactone in mass in the presence of benzyl alcohol (100 °C, [lactone] : [cat] : [BnOH] = 300 : 1 : 1) than the derivative with electron-donating mesityl groups (78% conversion, 24 h).

This result prompted us to investigate in detail the mechanism of catalysis of ε-caprolactone polymerization by complexes **1a** and **1b** with quantum-chemical methods. According to our knowledge, the study of the ROP mechanism



initiated by stannylenes by methods of quantum chemistry is very rare.[23] L-Lactide, γ- and δ-valerolactone, 1,5-dioxepan-2-one, trimethylene carbonate were used as objects of research.[24–27] The only work on polymerization of caprolactone was published in 2013, in which a series of tin(II) bis-alcoholates was studied and a correlation was established between the growth of the activation energy of the rate-limiting stage of reactions and an increase in the size of alkoxy groups.[28] Therefore, the current study is the first quantum-chemical investigation of ROP cyclic esters in the presence of stannylene, SnX_2, where X is not bound to tin *via* oxygen atom, as initiator. All previous reports were devoted to alkoxy and aryloxy derivatives as well as carboxylates. The details of those DFT calculations are presented in Online Supplementary Materials.

The most probable of proposed mechanisms of ROP by tin(II) complexes is the coordination–insertion mechanism,[26] although the activated monomer mechanism was also herein studied (see below). The system considered in this work has a large number of degrees of freedom, so the formation of many isomers and conformers of transition states and stable intermediates is possible. To correctly calculate the energy parameters of the reaction, it is necessary to find the geometries and calculate the energies of as many isomers/conformers as possible; ideally, it is necessary to approach the global minima for each intermediate structure, as well as for complexes of the initial reagents and products. Only then it should be possible to correctly compare activation parameters of individual stages of the process with experimental activation energies and calculated parameters among themselves.[29,30] Therefore, the energy values (Figure 1) are given as intervals corresponding to the range of energy values of isomers/conformers and the energy level itself on the diagram corresponds to the minimum value.

According to the coordination–insertion mechanism, the activation of tin(II) initiator by alcohol is the first stage (Scheme 2 and Figure 1). Methanol, isopropanol and benzyl alcohol are most often used as activators, and the choice of an activator does not affect the reaction mechanism and rate. We used methanol as a simple model activator of polymerization. The low bonding coordination complex of methanol and initiator is the pre-reaction complex (**RC**) for **TS1** and its energy was used as the zero level for calculation of other relative energies.

The addition of methanol to the initial complex (alcoholysis of Sn–N bond) proceeds *via* the four-membered transition state **TS1** with the simultaneous transfer of a proton to the leaving amino group of the ligand with the formation of intermediate **I1**, where coordination number of tin atom is 5 (one equatorial position is occupied by lone electron pair). The minimum transformation barrier corresponds to the axial addition of methanol to the tin complex, and the maximum one should correspond to the equatorial one. The minimum activation energy for **TS1b** with mesitylene substituents is by 2 kcal mol^{-1} lower than that for the transition state with tosyl substituents (**TS1a**), but the transformation barrier at the activation stage is low for both complexes (6.2 kcal mol^{-1} for **1b** and 8.2 kcal mol^{-1} for **1a**). We believe that low energetic barrier for this process is due to the presence of transannular interaction. Due to the weakening or strengthening of such interaction, a

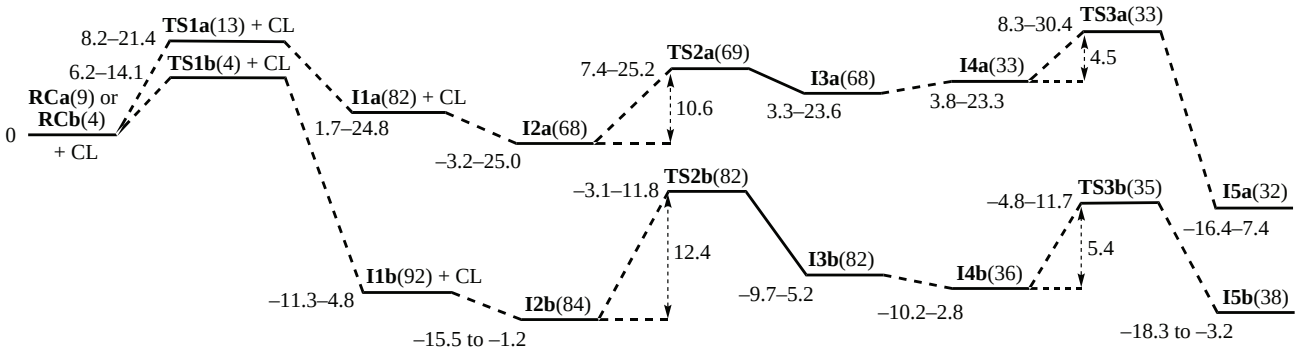
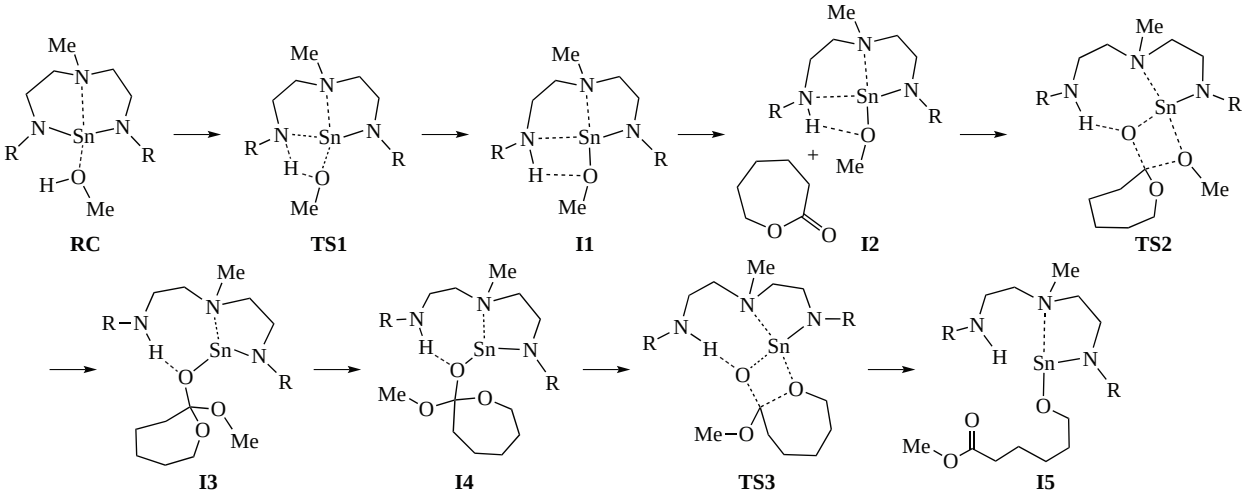


Figure 1 Potential energy surface of ε-caprolactone polymerization reaction catalyzed by tin(II) complexes (**a** R = tosyl, **b** R = mesityl, CL is ε-caprolactone). Energies are given in kcal mol^{-1} by range as they relate to a variety of isomers. The number of isomers is shown in parentheses.



Scheme 2 The first three stages of the mechanism for polymerization of ε-caprolactone in the presence of Sn^{2+} complexes **1a** (R = tosyl) and **1b** (R = mesityl).

redistribution of the electron density in the transition state occurs, which leads to its stabilization.

The structure of the most stable **I1** is similar to the structure of **TS1**. The difference between these structures is in the bond lengths. The weak coordination R(H)N···Sn and hydrogen bond RNH···O of the amino group atoms of the free tail of the ligand remain in **I1**. Of interest, in less stable structures of **I1** these weak bonds [R(H)N···Sn and RNH···O] are broken. The spread of energies of possible structures of **I1** is especially large for complexes with tosyl substituents, reaching 28.2 kcal mol^{-1}. The formation of **I1** leads to a significant decrease in energy relative to **RC**, especially for the complex with the mesityl substituent.

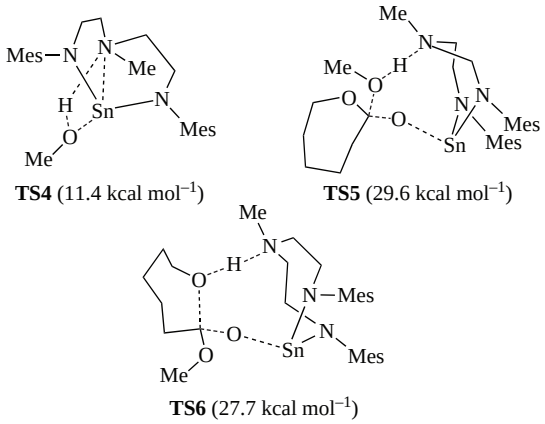
Next, the ε-caprolactone molecule approaches the activated initiator **I1** forming a van der Waals complex **I2**. It should be noted that the complex with caprolactone coordination to tin atom by carbonyl O atom, which was found in previous mechanism calculations,[23] is not formed in our case due to its instability. The addition of ε-caprolactone in **TS2** proceeds through a four-membered transition state. Additional stabilizing factors such as the formation of a hydrogen bond between the free tail of the ligand and the carbonyl O atom of ε-caprolactone, the presence of a transannular bond, weak bonding between the oxygen atom of the SO_2 group and the tin atom, and steric repulsion make a significant contribution to the energy distribution of **TS2** isomers/conformes. The spread of **TS2** energies reaches 23 kcal mol^{-1}. The reaction center in most beneficial structures of **TS2** is a planar four-membered cycle, while in high energy structures of **TS2**, one of the ring atoms is out of the plane. It cannot be argued that the addition of ε-caprolactone in **TS2** occurs axially or equatorially, rather through an intermediate state between the two.

It should be noted that the effective charge in **TS2a** on tin atom is 0.389 eV, while that for **TS2b** is 0.345 eV. It is obviously due to higher electron-withdrawing properties of the substituents at terminal N atoms in ligand in compound **1a**. We believe that tin atom in **I2a** is more attractive for the attack of oxygen atom of ε-caprolactone.

The resulting intermediate **I3** cannot immediately participate in the next stage of the reaction, and some rotation around the C–O bond is required to form intermediate **I4** (see Scheme 1). This rotation has a low barrier of the order of 1–2 kcal mol^{-1} and proceeds without the formation of a transition state on potential energy surface. The formation of a new activated complex **I5** occurs through the four-membered **TS3** which is similar in structure to **TS2**. In **TS3**, the same stabilizing and destabilizing factors act as in **TS2**. The formed alcoholate **I5** can then react with the next ε-caprolactone molecule, thus the polymer chain grows.

In addition to the major coordination–insertion mechanism of polymerization, other paths of the reaction proceeding were considered for mesityl compound **1b**. Calculations were performed using structures of the most favorable isomers of **TS1b**, **TS2b** and **TS3b** without searching for all possible isomers/conformers/rotamers, just to make sure these paths are less beneficial. Thus, the transfer of a proton to the tertiary nitrogen atom rather than the secondary one with the breaking of the transannular bond upon the first stage of activation of the complex has a barrier higher than that of the major mechanism (see **TS4** in Figure 2). The barriers for the next steps, ε-caprolactone addition (**TS5**) and forming next activated complex **TS6**, are even higher and such a mechanism is extremely unlikely.

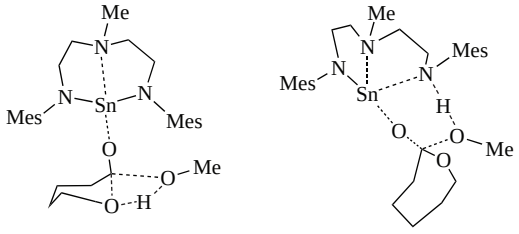
The transesterification of ε-caprolactone with methanol with coordination of the tin complex at the carbonyl O atom, that is, with the activation of ε-caprolactone by the tin complex



TS4 (11.4 kcal mol^{-1}) **TS5** (29.6 kcal mol^{-1})

TS6 (27.7 kcal mol^{-1})

Figure 2 Transition states of alternative ε-caprolactone polymerization mechanism with proton transfer *via* tertiary nitrogen atom. Energies in parentheses are calculated relative to the most stable isomer of **RCb**.



TS7 (36.9 kcal mol^{-1}) **TS8** (15.2 kcal mol^{-1})

Figure 3 Transition states of alternative mechanisms of ε-caprolactone polymerization. Energies in parentheses are calculated relative to the most stable isomer of **RCb**.

(activated monomer mechanism, **TS7** on Figure 3), is also possible and proceeds with a barrier not only higher than that of the major mechanism, but also 4.9 kcal mol^{-1} higher than the transesterification reaction of ε-caprolactone without the participation of a catalyst (E_a = 32.0 kcal mol^{-1}).

The simultaneous addition of methanol and ε-caprolactone molecules to the catalyst is possible, that is, the combination of **TS1b** and **TS2b** into one **TS8** with a six-membered proton transfer cycle (see Figure 3). The transformation barrier along this path is higher than that for the major mechanism because of large steric hindrances. The probability of the reaction proceeding through **TS8** is also lower due to the need for three molecules to approach each other simultaneously, instead of two in **TS1b**.

To sum up, for both complexes under consideration the activation energies are significantly lower compared to that of the reaction without a catalyst, and therefore both catalysts are suitable for the polymerization of ε-caprolactone, which is also confirmed experimentally. According to the experimental data, it follows that the polymerization reaction under catalysis by tin complexes with mesitylene substituents proceeds somewhat more slowly. The DFT calculation showed that the reason for this difference in the kinetics of catalysis is associated with the greater stability of the intermediates **I2b** and **I4b**, compared to the analogous **I2a** and **I4a**. Since the system is not closed, this leads to the need to overcome higher barriers at the stages of chain growth through **TS2b** and **TS3b** and a lower rate of the polymerization reaction in general. The reason for this stability of the intermediates is associated with the higher Lewis acidity of the metal center of the catalyst due to the higher electron-withdrawing properties of the tosyl substituents in the ligand.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2022.07.011.

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