

# Theoretical mechanism and kinetics study of the ring-opening polymerization of cyclic esters initiated by tin(II) alkoxides and tin(IV) alkoxides

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## Abstract

In this presentation, the coordination-insertion mechanisms of ring-opening polymerizations (ROP) of important cyclic esters such as  $\epsilon$ -caprolactone ( $\epsilon$ -CL),  $\gamma$ -valerolactone (GVL), *d*-valerolactone (DVL), D-lactide (DL) and L-lactide (LL) initiated by tin(II) alkoxides and tin(IV) alkoxides were theoretically investigated using hybrid density functional theory (DFT) at the B3LYP level with a mixed basis set. DFT calculations along the reaction pathway in the ROP of cyclic esters initiated by both catalyst have provided insight into the detailed mechanisms of their initiation and propagation processes. For example, the ROP mechanism of  $\epsilon$ -CL with tin(II) alkoxide, Sn(OR)<sub>2</sub> initiators (R = *n*-C<sub>4</sub>H<sub>9</sub>, *i*-C<sub>4</sub>H<sub>9</sub>, *t*-C<sub>4</sub>H<sub>9</sub>, *n*-C<sub>6</sub>H<sub>13</sub>, *n*-C<sub>8</sub>H<sub>17</sub>) was studied. A coordination-insertion mechanism was found to occur via two transition states. Starting with a coordination of  $\epsilon$ -CL onto tin center led to a nucleophilic addition of the carbonyl group of  $\epsilon$ -CL, followed by the exchange of alkoxide ligand. The  $\epsilon$ -CL ring opening was completed through classical acyl-oxygen bond cleavage. The reaction barrier heights of  $\epsilon$ -CL with different initiators were calculated using potential energy profiles. The reaction of  $\epsilon$ -CL with Sn(OR)<sub>2</sub> having R = *n*-C<sub>4</sub>H<sub>9</sub> has the least value of barrier height compared to other reactions. The rate constants for each reaction were calculated using the transition state theory with TheRATE program. The rate constants are in good agreement with available experimental data. Moreover, other ROPs of cyclic esters initiated by tin(II) and tin (IV) alkoxides will be discussed and presented.

**Keywords:** ring-opening polymerization, coordination-insertion mechanism, cyclic esters, tin(II)alkoxides, tin(IV) alkoxides, DFT, transition state theory.

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