A key way that renewable polyesters are prepared is through ring-opening transesterification polymerization (ROTEP) catalyzed by metal-alkoxide complexes. While a mechanism involving coordination of the lactone monomer followed by ring-opening by the alkoxide is generally accepted, a detailed understanding of individual reaction steps and catalyst structural influences on reaction rates that would be potentially useful for future catalyst development is lacking. In research aimed at gaining insight into ligand structural effects on the mechanism of ROTEP, synergistic experimental and theoretical studies of \( \varepsilon \)-caprolactone (CL) polymerization by aluminum-alkoxide complexes 1 and 2 were performed. In the most recent work reported by an interdisciplinary team led by Center for Sustainable Polymers (CSP) Principal Investigators William B. Tolman, Marc A. Hillmyer, and Christopher J. Cramer, and including postdoctoral researchers Elodie E. Marlier and Christine R. Dunbar, graduate students Maria Miranda, Benjamin D. Neisen, Daniel J. Marell and Joahanna A. Macaranas, and undergraduate students Michelle A. Johnson and Yvonne DePorre, detailed kinetic studies of ROTEP of CL by 2 (comprising a longer ligand linker than in 1) were performed in conjunction with computational evaluation of the reaction mechanism. Trigonal bipyramidal catalyst precursor 2 was found to react significantly faster than distorted square pyramidal 1, with measured second order rate constants that varied as a function of the \( \text{para-R} \) group in a similar way for the two catalysts. Computational studies revealed similar octahedral transition state geometries for 1 and 2, suggesting that the observed reaction rate differences arose from the energetics of required ligand distortions associated with proceeding from educt to transition-state structures. This realization led to the invention of a simple computational method that rationalized known rate differences as a function of supporting ligand geometries and that moreover has potential utility for predictive design of new, more effective ROTEP catalysts. The close, synergistic collaboration among experimental and theoretical scientists supported by the CSP was critical for success in this project, and has resulted in a new and detailed understanding of the mechanism of ROTEP by metal-alkoxide species.