

Controlling Regioselectivity of Polymerization in Silyl Ketenes using Computational Methods

Ian S. Baxter and Daniel S. Lambrecht*

Florida Gulf Coast University, Department of Chemistry & Physics

Silyl ketenes, $R_3SiC=C=O$, can polymerize using both the C=C and the C=O functionality, providing access to a range of products, including desirable targets such as conjugated or potentially degradable polymers. To synthesize a specific desirable target polymer, one needs to control the regioselectivity of the chain propagation. *This work* investigates how the reaction can be steered toward propagation via the oxygen functionality to yield products such as potentially degradable esters. Specifically, computational studies were performed to predict the reaction pathways of silyl ketenes with nucleophiles to initiate the chain propagation. Depending on the nature of the nucleophile, the silyl ketene either deprotonates - leading to here undesired propagation via the carbon functionality - or undergoes nucleophilic addition - leading to here desired propagation via the oxygen functionality. The relative preference for nucleophilic addition versus deprotonation is investigated for molecules representative of a wide range of nucleophilicity. Trends between preference for the nucleophilic addition pathway and simple molecular descriptors are investigated. Several nucleophiles are identified that facilitate the desired propagation via the oxygen functionality.