

PRF# 63213-DNI6

Project Title: A Computational Approach for Optimizing Metal-Free Synthesis of Conjugated Polymers

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This project aims to establish reaction pathways for the polymerization of β -silyl ketenes, $\text{SiR}_3(\text{H})\text{C}=\text{C}=\text{O}$. Due to their $\text{C}=\text{C}/\text{C}=\text{O}$ bifunctionality, ketenes can polymerize to yield various, previously unrealized architectures, such as poly(silyl ketone) and poly(silyl acetal) [Fig. 1]. Consequently, this project has the potential to facilitate the creation of polymers with new chemical compositions from fossil fuel sources. Moreover, the comparatively high reactivity of ketenes allows for uncatalyzed polymerization, thus having potential to facilitate metal-free polymerization. This could remove costly steps such as product purification.

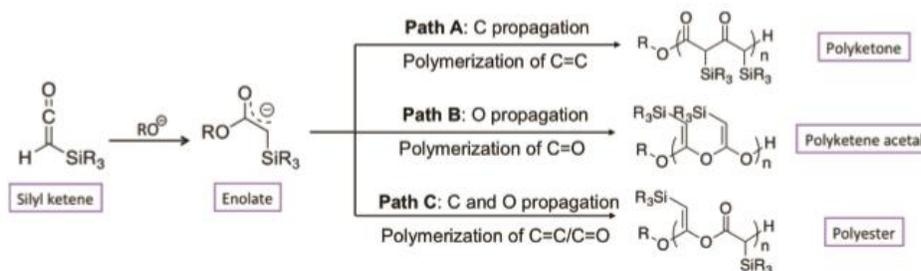


Figure 1: Proposed anionic polymerization of silyl ketenes with alkoxides. Initiation occurs via nucleophilic attack on C_α , yielding an enolate that can propagate both via the O^- and C_β^- functionality. Propagation continues by nucleophilic addition to the C_α on the next silyl ketene monomer, which in turn forms a reactive enolate, etc. Reaction paths A-C illustrate three limiting cases of possible propagation pathways.

Milestones achieved during the previous reporting period include demonstrating the feasibility of β -silyl ketene polymerization and identifying factors that influence the chemical composition of the polymerization product (Fig. 2).

Solvent	ϵ	Thermodynamic preference	Kinetic preference
DMF	38.25	$-\text{O}-\text{C}->-\text{C}-\text{O}>-\text{C}-\text{C}->-\text{O}-\text{O}-$	$-\text{O}-\text{C}->-\text{O}-\text{O}->-\text{C}-\text{O}->-\text{C}-\text{C}-$
Diethyl ether	4.267	$-\text{O}-\text{C}->-\text{C}-\text{O}>-\text{O}-\text{O}->-\text{C}-\text{C}-$	$-\text{O}-\text{O}->-\text{O}-\text{C}->-\text{C}-\text{O}->-\text{C}-\text{C}-$
Dioxane	2.21	$-\text{C}-\text{O}->-\text{C}-\text{C}->-\text{O}-\text{C}->-\text{O}-\text{O}-$	$-\text{C}-\text{O}->-\text{O}-\text{O}->-\text{O}-\text{C}->-\text{C}-\text{C}-$
Vacuum	1	$-\text{C}-\text{O}->-\text{C}-\text{C}->-\text{O}-\text{C}->-\text{O}-\text{O}-$	$-\text{C}-\text{O}->-\text{O}-\text{O}->-\text{O}-\text{C}->-\text{C}-\text{C}-$

Figure 2: Our computations predict that the solvent polarity controls the energetic ordering of products, i.e., the thermodynamics of the polymerization, as well as the relative activation barriers, i.e., the polymerization kinetics. Interestingly, the most significant change occurs in a relatively small window for the dielectric constant, i.e. between $\epsilon = 2.2$ and 4.3. [1]

Milestones achieved during the current reporting period:

1. We have published the findings from reporting period 2016-17 in a collaborative publication together with our experimental collaborator (E. Pentzer, Case Western Reserve University). [1]
2. We found that **poly(silyl ketene)s show potential to form rigid-rod polymers (RRPs)**. This finding is encouraging because of potential applications of RRP to increase e.g. the strength and bulk modulus. Our computational explorations suggest that different backbone architectures accessible via silyl ketene polymerization could lead to the formation of RRP (Fig. 3).

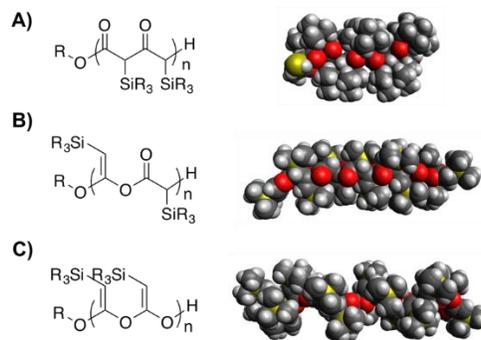


Fig. 3. Space filled models of: A) poly(β -silyl ketone); B) poly(β -silyl enol ester); and C) poly(silylated ketene acetal), from triisopropyl silyl ketene. Structures generated in Avogadro, initial optimizations via MMFF94 force field and optimized structures with OpenBabel's genetic algorithm search. Global minima were subsequently refined using the PM6-DH+ level of theory as implemented in MOPAC.

2. These key results, facilitated by the support from the DNI grant from the American Chemical Society Petroleum Research Fund, enabled us to attract **funding from the National Science Foundation** (award no. CHE-1807683), which will allow us to advance this project with increased resources for a sustained period of time.

Published Results Supported by this Grant:

- [1] Yuanhui Xiang, Daniel J Burrill, Krista K Bullard, Benjamin J Albrecht, Lauren E Tragesser, John McCaffrey, **Daniel S Lambrecht**,* and Emily Pentzer,* "Polymerization of silyl ketenes using alkoxide initiators: a combined computational and experimental study", *Polymer Chemistry* **8**, 5381-5387 (2017). [\[link\]](#)