

# Experimental and Computational Electrochemistry to Move Toward Plastic Circularity

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As a society, humans have produced nearly 9 gigatonnes of plastic since plastic production began to accelerate in the 1950s. Traditional plastics are synthesized from petroleum and its derivatives, making it clear that society needs to move away from the traditional linear way in which it uses plastics and move toward plastic circularity. Electroorganic synthesis offers a pathway toward this by allowing for the synthesis of molecules using renewably generated electricity. As a result, this thesis is grounded in the goal of leveraging the potent yet fine-tunable nature of an electrochemical driving force to tackle key issues in augmenting the chemical recyclability of plastics. We demonstrate that electrochemistry – both experimental and computational – have a role to play in the synthesis of novel plastic monomers, in addition to allowing for new potential decomposition pathways for the plastics in use today.

Lactones have the potential to serve as excellent monomers for circular plastics. Currently, they are typically synthesized via the Bayer-Villiger reaction, which transforms cyclic alkanones into their corresponding lactones. This process suffers from drawbacks including the use of dangerous peroxyacids, and in general should be made more sustainable to operate on the scale needed to replace current plastics. In the first part of this thesis, we demonstrate that by using an applied electrochemical potential, platinum catalysts, and water as the oxygen atom source, we can synthesize lactones with selectivity toward branched products, complementing those expected from the Baeyer-Villiger reaction. By collecting electrochemical kinetic data, we propose a mechanism that can explain the observed selectivity in our system. Additionally, we calculate the free energy landscape of our system to investigate whether the thermodynamics of proposed intermediates are also consistent with our observed selectivity.

Hydrogen atom transfer reactions (HATs) are a ubiquitous class of chemical reactions that allow researchers to functionalize inert bonds. When mediated with redox active molecules, HAT reactions have also been shown to be capable of deconstructing common plastics. However, the performance of these redox mediators requires improvement before they can be used on an industrial scale. Previous attempts at utilizing an organic redox mediator to deconstruct plastics suffered from a mismatch of the bond dissociation energy (BDE) of the redox mediator and the target C-H bond. Therefore, in the next part of this thesis, we computationally investigate how well we could modulate mediator energy through functionalization by screening  $> 10^4$  ylide based redox mediators. We used density functional theory to calculate the energies relevant to their catalytic cycle and were able to then identify and synthesize candidate structures with varying bond dissociation energies to investigate how electrochemical performance changed as the bond dissociation energy (BDE) of the redox mediator approached the BDE of the bond in plastic model molecules.

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