CATALYSTS FOR THE SYNTHESIS OF SUSTAINABLE POLYMERS: MECHANISTIC ANALYSIS AND DESIGN

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At the University of Minnesota, the NSF-funded Center for Sustainable Polymers pursues basic polymer science research aimed at developing new, practical chemistries, polymers, processes, and technologies that embrace sustainability. We carry out our research stressing the principles of green chemistry to help protect the environment and ensure that future generations will be able to meet their societal needs. Theoretical modeling can play an especially critical role in the design cycle of catalysts for the preparation (or degradation) of monomers and polymers in a sustainable fashion, because theory offers in-depth insights into mechanistic details associated with productive and off-cycle reaction pathways, and permits *in silico* testing of next-generation systems having improved characteristics. In combination with collaborating experimental groups, we have been particularly active in pursuing catalysts that (i) generate α-olefins from alkanoic acids,[1] (ii) copolymerize anhydrides and epoxides to prepare designed polyesters,[2] (iii) copolymerize epoxides and carbon dioxide to prepare designed polycarbonates,[3] and (iv) permit redox-switchable homopolymerization of mixed monomers so as to generate block copolymers in a controlled fashion.[4] Selected examples that highlight contributions from theory will be presented.

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2) Fieser, M. E.; Sanford, M. J.; Mitchell, L. A.; Dunbar, C. R.; Mandal, M.; Van Zee, N. J.; Urness, D. M.; Cramer, C. J.; Coates, G. W.; Tolman, W. B. "Mechanistic Insights into the Alternating Copolymerization of Epoxides and Cyclic Anhydrides Using a (Salph)AlCl and Iminium Salt Catalytic System" *J. Am. Chem. Soc.* **2017**, *139*, 15222 (doi:10.1021/jacs.7b09079).
3) Qu, S.; Coates, G. W.; Cramer, C. J. to be published.
4) Ortuño, M. A.; Dereli, B.; Delle Chiaie, K. R.; Biernesser, A. B. ; Byers, J. A.; Cramer, C. J. to be published.