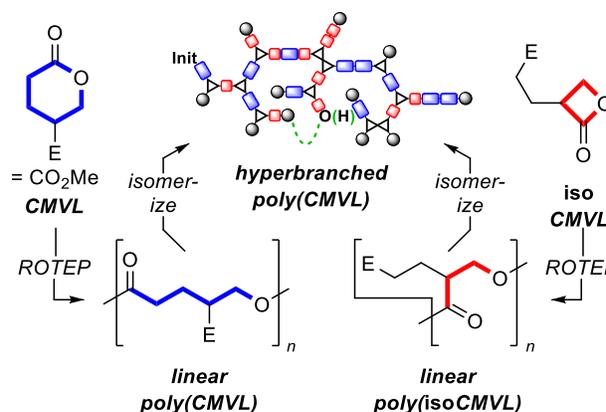


Isomerization of linear to hyperbranched polymers (September 2018)

The Center for Sustainable Polymers (CSP) connects scientists from the University of Minnesota, Cornell University, Northwestern University, the University of California, Berkeley, Washington University in St. Louis, the University of Chicago, and the University of South Dakota in a manner that promotes highly collaborative research. This environment allows partnership across various scientific disciplines, including polymer, organic, biological, inorganic, and theoretical chemistry. As such, CSP researchers have been able to approach challenging problems related to sustainability with a wide range of expertise.

The degree and nature of branching architectures in both synthetic and natural polymers have significant ramifications on material properties. Monomers that can be selectively polymerized to either linear or branched architectures enable the corresponding polymers to be used for a wide array of applications. In nearly all polymers, the linear or branched nature is dictated from the outset of the polymerization. The ability to convert (or isomerize) a polymer with a specific architecture to a new architecture is attractive from both fundamental and practical perspectives.

A team comprising Grant Fahnhorst, Daniel Stasiw, Professor Bill Tolman, and Professor Tom Hoyer demonstrated an unprecedented isomerization pathway by which a preformed linear polymer [**linear poly(CMVL)**] from the monomer **CMVL**] is converted to a highly branched architecture [**hyperbranched poly(CMVL)**] using a metal-alkoxide catalyst. The process is a direct ramification of the use of lactone monomer and/or polyester containing a pendant sidechain ester substituent. The team also demonstrated that the isomeric lactone monomer, **isoCMVL**, and its linear polyester **poly(isoCMVL)**, proceeds through a directly analogous isomerization pathway to give the same polymer as that from **CMVL**, namely the **hyperbranched poly(CMVL)**. The



A scheme showing the polymerization and isomerization of both **CMVL** and **isoCMVL** to the same hyperbranched polymer, **hyperbranched poly(CMVL)**. ROTEP = ring-opening transesterification polymerization.

fundamental concepts exposed through this investigation could also allow for the introduction of branching into other families of degradable polyesters, a potential strategy for management of aliphatic polyester properties.

This collaboration benefitted from combined skillsets from both synthetic organic (Hoyer lab) and inorganic catalyst design (Tolman group). Previously, Fahnhorst and Hoyer were studying the synthesis and polymerization of the biorenewable monomer **CMVL** with other catalysts, while Stasiw and Tolman were designing novel catalysts for ring-opening transesterification polymerization (ROTEP). The idea for using a Tolman-developed catalyst for polymerization of a Hoyer-group monomer arose from a conversation at a monthly CSP meeting between Fahnhorst and Stasiw, another example of how the CSP can foster the initiation of new research and advancements.

Fahnhorst, G. W.; Stasiw, D. E.; Tolman, W. B.; Hoyer, T. R. Isomerization of Linear to Hyperbranched Polymers: Two Isomeric Lactones Converge via Metastable Isostructural Polyesters to a Highly Branched Analogue. *ACS Macro Lett.* **2018**, *7*, 1144–1148.