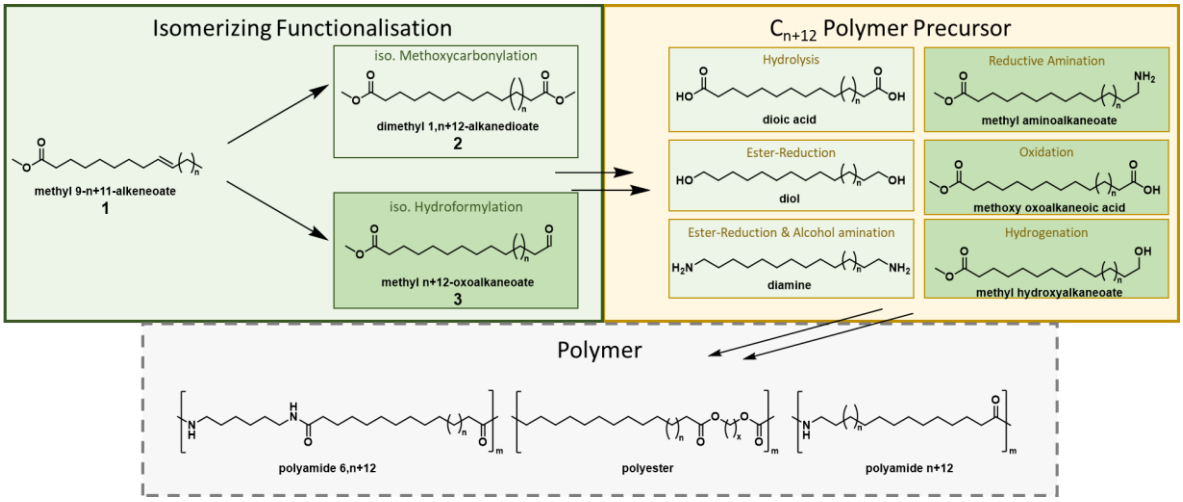
Linear, Aliphatic Polymer Precursors from Local Plant Oils through Cross Metathesis and Isomerizing Functionalisation

J. Hommes, D. Vogt, T. Seidensticker
TU Dortmund University, Laboratory of Industrial Chemistry, Germany

Abstract

The demand for versatile and high-performance polymers, such as polyesters or polyamides, is steadily increasing. To access those polcondensates, a diverse portfolio of C_{n+12} building blocks, such dioic acids, methyl aminoalkaneoates, and diamines, as well as many more, is required. Those building blocks are currently produced based on fossil raw materials.[1] Here, dimethyl 1,n+12-alkanedioate (**2**) and methyl n+12-oxoalkaneoate (**3**) may serve as central platform molecules for those C_{n+12} polycondensates. Those are products of isomerizing functionalization reactions such as the isomerizing methoxycarbonylation or hydroformylation of methyl 9-alkeneoate (**1**). **1** can be produced *via* cross-metathesis of methyl oleate, accessible from local plant oils, and a respective alkene. Scheme 1 illustrates possible C_{n+12} polymer precursors, as well as the polymers that can be produced from **2** and **3**.



*Scheme 1: Isomerizing functionalisation of methyl 9-n+11-alkeneoate (**1**) to dimethyl 1,n+12-alkanedioate (**2**) via isomerizing methoxycarbonylation and to methyl n+12-oxoalkaneoate (**3**) via isomerizing hydroformylation, as a platform for C_{n+12} polymer precursors such as dioic acids, methyl aminoalkaneoates, diamines, etc.*

The internal double bond of **1** requires a preliminary isomerization step before methoxycarbonylation or hydroformylation to obtain **2** or **3**, preferably conducted using an auto-tandem catalytic system. We will primarily investigate the isomerizing hydroformylation of **1** to **3** with rhodium as catalyst metal with bidentate phosphorus ligands and the isomerizing methoxycarbonylation of **1** to **2** with palladium as catalyst metal and 1,2-DTBPMB as ligand.

[1] K. Hares, H. W. Wegener, T. F. H. Roth, R. Reichert, D. Vogt, T. Seidensticker, Catal. Sci. Technol. 2024, DOI: 10.1039/D4CY00368C.