Metathesis of conjugated polyenes

Author: Turczel Gábor
Supervisor: Tuba Róbert

Throughout my work, the metathesis of different low value conjugated compounds was evaluated. Utilizing Grubbs metathesis catalysts systems, both bio-based and petroleum-based conjugated starting materials were converted to value-added polyurethane and polyester intermediates.

First, the metathesis of conjugated systems was investigated on model compounds, such as 1,6-diphenyl-1,3,5-hexatriene.\(^{(P1)}\) Self- and cross-metathesis (CM) reactions revealed the formation of low solubility polymeric side-products, even at excess of the CM agent. Following the initial model reactions, the metathesis of renewable methyl eleostearate and tung oil was carried out with different ruthenium alkylidene catalysts.\(^{(P2)}\) Applying (Z)-but-2-ene-1,4-diyldiacetate as CM agent formed the expected monomer intermediate hexane-1,6-diyldiacetate after hydrogenation, up to 53% yield. The renewable non-conjugated polyene, methyl linolenate was also utilized in metathesis after its isomerization to a mixture of conjugated fatty acid derivatives.\(^{(P2)}\) This procedure involved subsequent isomerization, metathesis and hydrogenation in one-pot, to yield the value added hexane-1,6-diyldiacetate. Petrochemical-based small cyclic polyenes were also reacted with (Z)-but-2-ene-1,4-diyldiacetate in a subsequent ring-opening cross metathesis/CM fashion, forming the anticipated monomer intermediate, among other diesters. Following the metathesis of different small cyclic polyenes, the CM of cyclopentadiene (CPD) was investigated in detail.\(^{(P3)}\) The CM of CPD was carried out, utilizing (Z)-but-2-ene-1,4-diyldiacetate as CM agent. Catalyst loadings as low as 0.05 mol % showed good conversion (> 90%) and produced the expected polyurethane and polyester intermediates in good yield. Finally, the ethenolysis of CPD was carried out, producing butadiene and 1,4-pentadiene in moderate yield.\(^{(P3)}\)

Publications related to the Thesis: