Metathesis of conjugated polyenes

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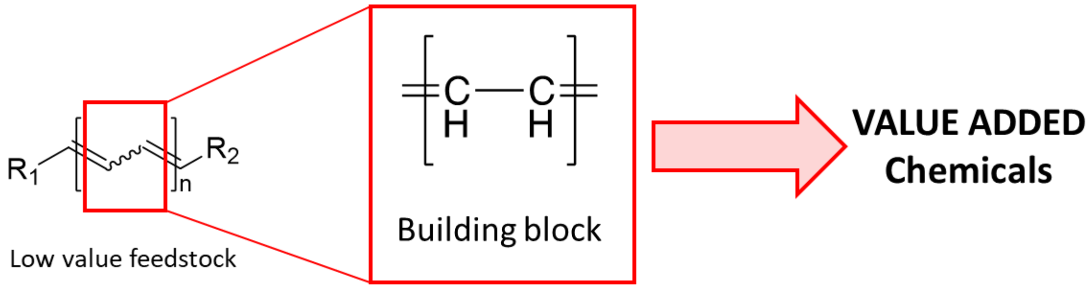
Throughout my work, the metathesis of different low value conjugated compounds was evaluated. Utilizing Grubbs metathesis catalysts systems, both bio-based and petroleum-based conjugated starting materials were converted to value-added polyurethane and polyester intermediates.



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-diyl diacetate as **CM** agent formed the expected monomer intermediate hexane-1,6-diyl diacetate 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-diyl diacetate. Petrochemical-based small cyclic polyenes were also reacted with (*Z*)-but-2-ene-1,4-diyl diacetate 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-diyl diacetate 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:

P1. Kovács E.; Sághy P.; **Turczel G.**; Tóth I.; Lendvay Gy.; Domján A.; Anastas P. T.; Tuba R. *J. Organomet. Chem.* **2017**, *847*, 213–217. [IF (2017): 1.946, independent citation: 1, participation: 100%]

P2. Kovács E.; **Turczel G.**; Szabó L.; Varga R.; Tóth I.; Anastas P. T.; Tuba R. *ACS Sustain. Chem. Eng.* **2017**, *5*, 11215–11220. [IF (2017): 6.140, independent citation: 2, participation: 90%]

P3. **Turczel G.**; Kovács E.; Csizmadia E.; Nagy T.; Tóth I.; Tuba R. *ChemCatChem*, **2018**, *10*, 4884–4891. [IF (2017): 4.674, independent citation: 1, participation: 80%]

P4. **Turczel G.**; Kovács E.; Tuba R. *XL. Kémiai Előadói Napok*, Szeged, **2017.** Conference proceeding, 216-219. [participation: 100%]