

Metathesis and Polymerization of Olefins

K. Sarath D. Perera

Senior Professor in Chemistry, Department of Chemistry, The Open University of Sri Lanka

Metathesis of simple salts is a double replacement reaction as shown below.



In Greek, "Metathesis" is known as the change of position or transposition. **Olefin metathesis** (OM) is the catalytic **scission** and **regeneration** of C=C bonds as shown in Figure 1. This is a **reversible** process and the reverse reaction is called "**cross metathesis**" of olefins.

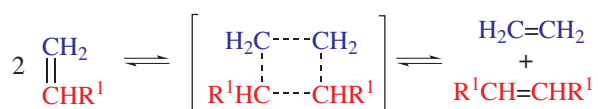


Figure 1: Metathesis of olefins

Ethene is a volatile molecule, thus, metathesis of a

terminal olefin $\text{R}^1\text{CH}=\text{CH}_2$ produces a quantitative amount of $\text{R}^1\text{CH}=\text{CHR}^1$. Using this procedure tetra-substituted alkenes such as $\text{R}_2\text{C}=\text{CR}_2$ are obtained in good yields.

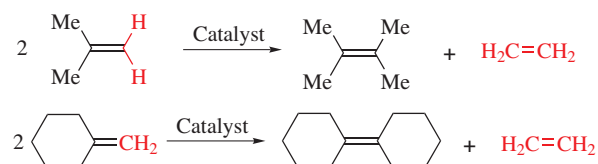


Figure 2: Synthesis of tetra-substituted alkenes

Catalysts for olefin metathesis

Olefin metathesis is normally catalyzed by homogeneous catalysts. Homogeneous catalysis refers to reactions

The steps (a) and (c) involve the formation of the “metallacyclobutane” between $\text{Ru}=\text{CH}_2$ & $\text{R}^1\text{CH}=\text{CH}_2$ and $\text{Ru}=\text{CHR}^1$ & $\text{R}^2\text{CH}=\text{CH}_2$, respectively. In step (b), ethene is released giving $\text{Ru}=\text{CHR}^1$. The step (d) produces $\text{R}^1\text{CH}=\text{CHR}^2$ while generating the active catalyst $\text{Ru}=\text{CH}_2$. This is a random process and this mechanism is known as “Chauvin Mechanism”.

Types of olefin metathesis reactions

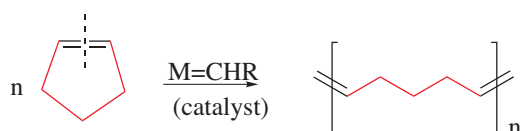
Olefin metathesis can be categorized as (i) **cross** (ii) **ring opening**, and (iii) **ring closing** metathesis reactions. All these reactions proceed *via* a **metallacyclobutane** intermediate.

Cross metathesis reactions

We have already looked at cross metathesis reactions involving terminal olefins. Metathesis of two symmetrical olefins, $\text{R}^1\text{CH}=\text{CHR}^1$ and $\text{R}^2\text{CH}=\text{CHR}^2$ gives a single product $\text{R}^1\text{CH}=\text{CHR}^2$ and vice versa. Metathesis of $\text{R}^1\text{R}^2\text{C}=\text{CR}^1\text{R}^2$ with $\text{CH}_2=\text{CH}_2$ gives a single product $\text{R}^1\text{R}^2\text{C}=\text{CH}_2$. Internal olefins ($\text{R}^1\text{CH}=\text{CHR}^2$) appear to undergo metathesis much faster than terminal ones ($\text{R}^1\text{CH}=\text{CH}_2$).

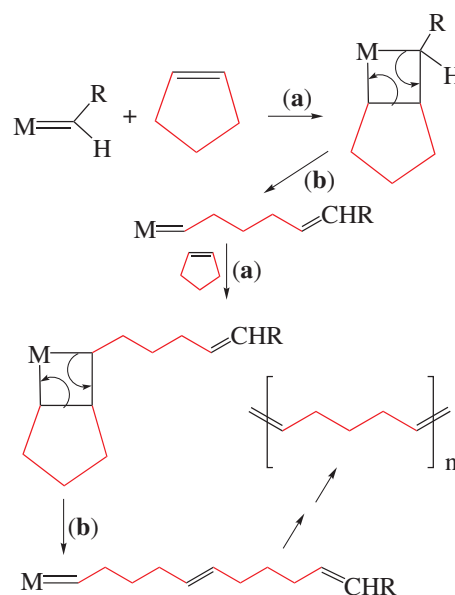
Ring opening metathesis (ROM) reaction

In this case, a cyclic olefin is opened up in the presence of a carbene catalyst to form a polymer, which is called ring opening metathesis polymerization (ROMP).



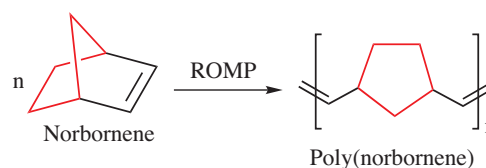
Scheme 3: ROMP of cyclopentene

The mechanism of the above reaction is shown in scheme 4. During step (a), the metallacyclobutane ring is formed. During step (b), the ring is opened up to give a metal carbene with a terminal olefin group. The resulting metal carbene continues to react with cyclopentene molecules leading to a polymer.



Scheme 4: Mechanism for ROMP, coligands on the metal M are not drawn for clarity

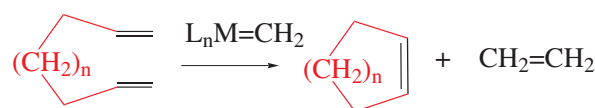
Poly(norbornene) is produced by ROMP of norbornene (scheme 5).



Scheme 5: ROMP of norbornene

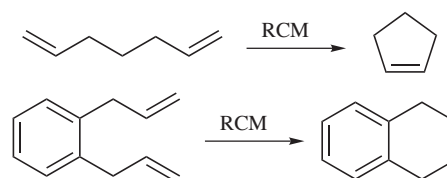
Ring closing metathesis reactions

In a ring closing metathesis (RCM) reaction, a **terminal diene** is converted into a carbocycle and an ethylene molecule is formed as a byproduct (scheme 6).



Scheme 6: Carbocycles from diolefins

Some examples of RCM are shown in scheme 7.

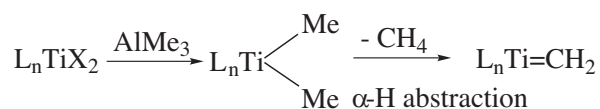


Scheme 7: Examples for RCM

Olefin polymerization with other catalysts

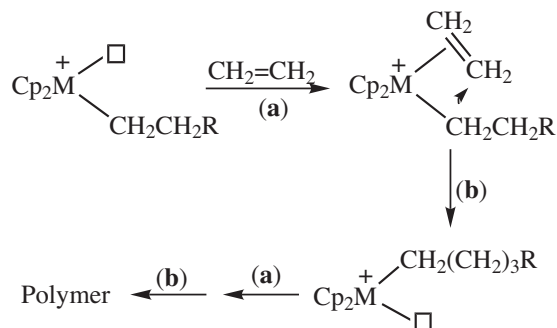
Polyethylene (PE) and polypropylene (PP) are usually prepared using other catalysts. The Ziegler-Natta

catalytic system $\{\text{TiCl}_3 \text{ or } \text{TiCl}_4 \text{ with methylaluminumoxane } (\text{MeAlO})_n, \text{AlEt}_3 \text{ or } \text{AlEt}_2\text{Cl}\}$ was discovered in late 1950s and it operates under mild conditions (at 25 °C and ethene pressure of 1 atm). Ziegler and Natta won the Nobel Prize in 1963 for the discovery of this catalytic system. The active catalyst is formed *in situ* and it could be an intermediate $[\text{L}_n\text{Ti}=\text{CH}_2]$, $[\text{L}_n\text{Ti}=\text{CHR}]$ or $[\text{L}_n\text{TiR}]^+$ as shown below.



Scheme 8: Formation of $[\text{L}_n\text{Ti}=\text{CH}_2]$ from $[\text{L}_n\text{TiMe}_2]$

In the presence of $(\text{MeAlO})_n$, metallocene dihalides (e.g., Cp_2MCl_2 , M = Ti, Zr or Hf) generate highly active homogenous catalysts for the polymerization of simple olefins. They are much better catalysts than Ziegler–Natta catalysts. The active catalyst is believed to be the cationic intermediate $[\text{Cp}_2\text{MR}]^+$ with one alkyl group and a vacant site. Coordination of ethene followed by migration of the R group on to ethene (1,2-insertion) generates $[\text{Cp}_2\text{MCH}_2\text{CH}_2\text{R}]^+$ ion. Propagation and polymerization steps are shown in scheme 9.

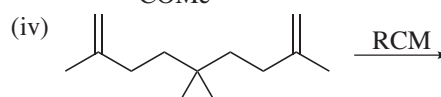
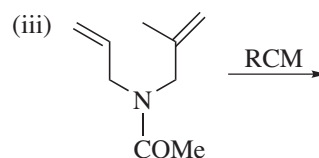
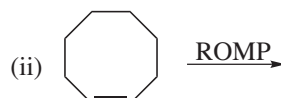
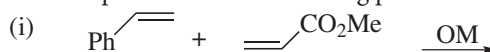


Scheme 9: Polymerization of ethene using the active catalyst $[\text{Cp}_2\text{MR}]^+$

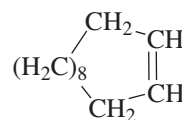
The step (a) refers to coordination of ethene to the vacant site and the step (b) refers to 1,2-insertion of ethene into M-alkyl bond.

Problems

1. Predict the products of the following processes.



2. What is the major product/s formed due to metathesis of



3. Write the mechanism for the polymerization of prop-1-ene using Cp_2ZrCl_2 and $(\text{MeAlO})_n$.