

Copolymers

Generally homopolymers are produced by addition and ring-opening polymerization of a single monomer. Polycondensation of two bi-functional molecules also results in homopolymers, which are consisting of one type of repeat unit, for example, nylon-4,6 $-\text{[HN(CH}_2)_4\text{NHCO(CH}_2)_4\text{CO]}_n-$ can be considered as a homopolymer made from $\text{H}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ and adipic acid, $\text{HO}_2\text{C(CH}_2)_4\text{CO}_2\text{H}$.

Addition polymerization of two or more monomers (e.g., olefins) in different ratios yields copolymers. SBR is a copolymer $-\text{[(CH}_2\text{CH=CHCH}_2)_x(\text{CH}_2\text{CHPh})_y]-$ made by polymerizing a mixture of styrene (25%) and butadiene (75%), (SBR = Styrene Butadiene Rubber = synthetic rubber). The copolymers are classified into 4 types: (i) **random**, (ii) **block**, (iii) **alternate**, and (iv) **graft** as shown in Figure 11.

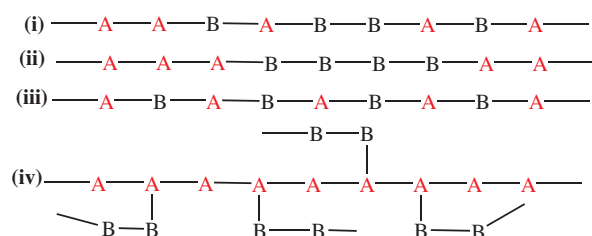


Figure 11: Types of copolymers

Metathesis and Polymerization of Olefins

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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.

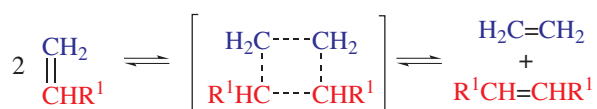


Figure 1: Metathesis of olefins

Ethene is a volatile molecule, thus, metathesis of a

In a random copolymer, the monomers (**A** and **B**) are arranged in a random manner. The polymer $-\text{[(CH}_2\text{CH}_2)_n(\text{CH}_2\text{CHPh})_m]-$ is a block copolymer made from ethene and styrene; **m** and **n** are integers. The polymer $[\text{CH}_2\text{CH}_2\text{CH}_2\text{CHPh}]_n-$ is an alternate copolymer made from ethene and styrene. The polymer $-\text{[HN(CO)NHCH}_2]-$ can be considered as an alternate copolymer made from urea and HCHO. Joining of styrene and maleic anhydride gives an alternate copolymer. Alternate copolymers have one type of repeating unit. The monomer **B** is grafted on to an existing polymer $-(\text{A})_n-$, prepared from monomer **A**. For example, acrylonitrile can be grafted on to polystyrene. Methyl methacrylate can also be grafted on to natural rubber.

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.

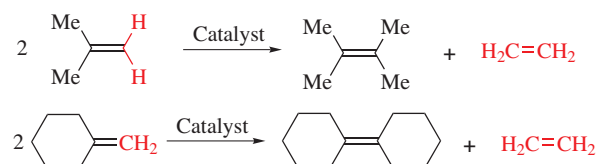


Figure 2: Synthesis of tetra-substituted alkenes

Catalysts for olefin metathesis

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

where the catalyst and the reactants are present in the same phase. Metal carbene or alkylidene complexes with the $M=CR_2$ moiety are used as catalysts.

The well-known metathesis catalysts are $[\{Me(CF_3)_2CO\}_2Mo=CHCMe_2Ph](=NAr)$ (1) (Schrock), $[(PCy_3)_2Cl_2Ru(=CHCH=CPh_2)]$ (2) (Grubbs), $[(PCy_3)_2Cl_2Ru(=CHPh)]$ (3) (Grubbs-1), $[(PCy_3)(L)Cl_2Ru(=CHPh)]$ (4) (Grubbs-2), (L = NitrogenHeteroCarbene). Richard R. Schrock, Robert H. Grubbs and Yves Chauvin shared the Nobel Prize in 2005 for their extensive work on olefin metathesis and polymerization.

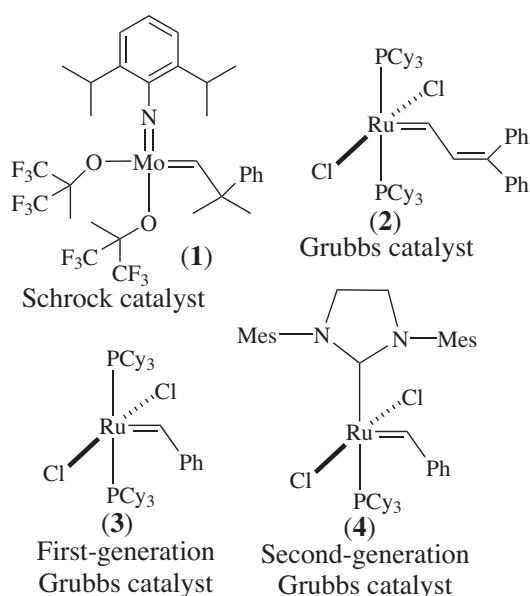
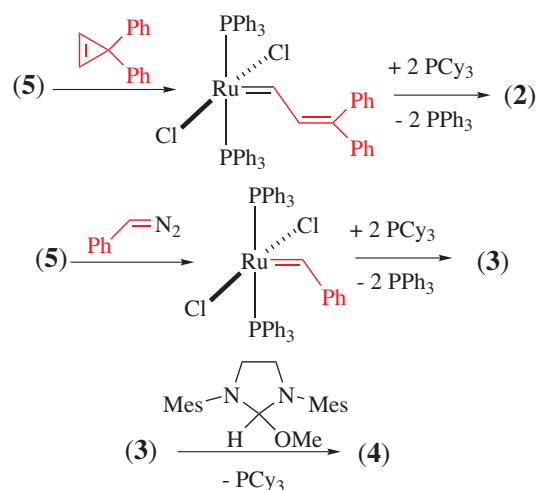


Figure 3: Olefin metathesis catalysts
(Mes = mesityl = $-C_6H_2-2,4,6-Me_3$)

Schrock catalyst (1) has shown high efficiency towards OM but it is extremely unstable in air or in water. The efficiency of Grubbs-1 catalyst (3) is low but it is stable in air and in aqueous media. The Grubbs-2 catalyst (4) has shown increased reactivity, recyclability and stereospecificity. Grubbs catalysts tolerate a wide variety of functional groups.

Synthesis of Grubbs catalysts

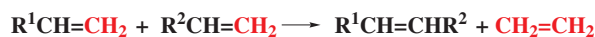
The syntheses of Grubbs catalysts are quite easy from $[RuCl_2(PPh_3)_4]$ (5) as shown in scheme 1.



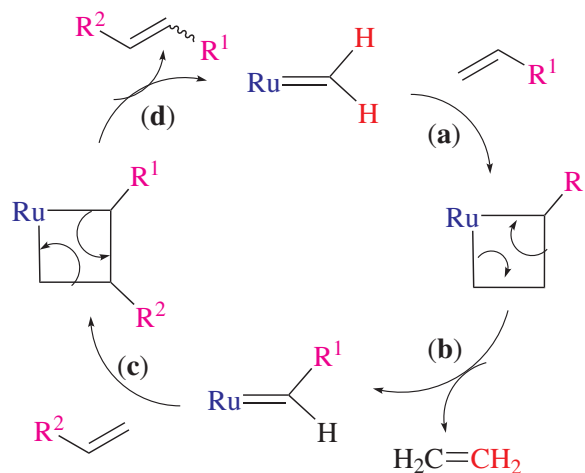
Scheme 1: Syntheses of Grubbs catalysts

Mechanism for cross metathesis

OM was discovered by Robert L. Banks in 1964. He reported the disproportionation of propylene to ethylene and butenes using $[Mo(CO)_6]$ supported on alumina. It is an interesting process because there is no equivalent reaction in traditional organic chemistry. The mechanism for the following cross metathesis reaction using the Grubbs catalyst (3) is given in scheme 2.



The complex $[(PCy_3)_2Cl_2Ru(=CHPh)]$ (3) is an 16e-complex, it loses one PCy_3 ligand to give the reactive intermediate with 14e. One of the olefins joins on to this 14e-complex forming a "ruthenocyclobutane ring" which can generate $Ru=CH_2$ or $Ru=CHR^1$ or $Ru=CHR^2$ moieties as shown in scheme 2. Other ligands on Ru are not drawn for clarity.



Scheme 2: Mechanism for cross metathesis

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

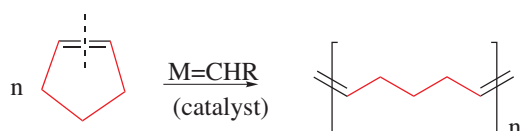
Olefin metathesis can be categorized as (i) **cross** (ii) **ring opening**, and (iii) **ring closing** metathesis reactions. All these reactions proceed *via* a **metallacyclobutane** intermediate.

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 ($\text{R}^1\text{CH}=\text{CH}_2$).

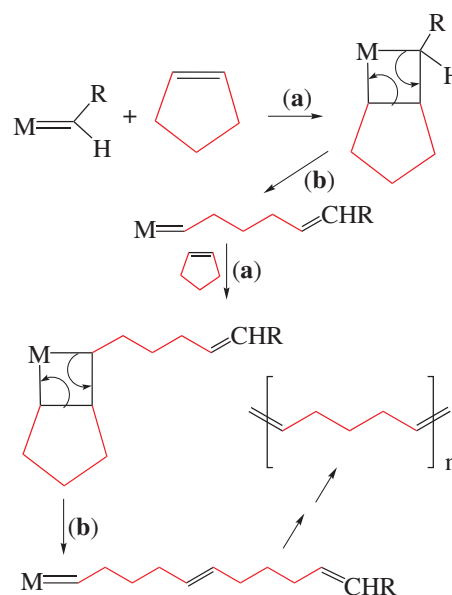
Ring opening metathesis (ROM) reaction

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).



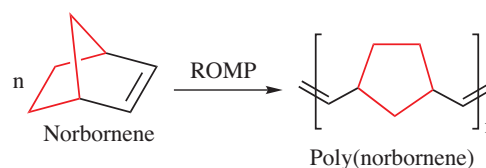
Scheme 3: ROMP of cyclopentene

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

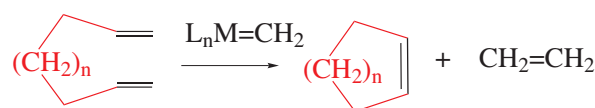
Poly(norbornene) is produced by ROMP of norbornene (scheme 5).



Scheme 5: ROMP of norbornene

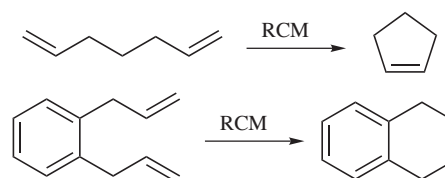
Ring closing metathesis reactions

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.

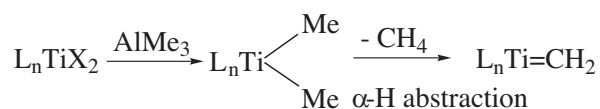


Scheme 7: Examples for RCM

Olefin polymerization with other catalysts

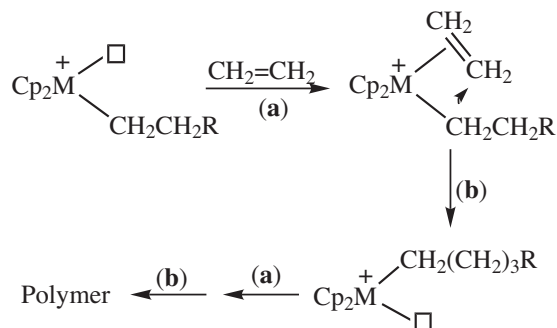
Polyethylene (PE) and polypropylene (PP) are usually prepared using other catalysts. The Ziegler-Natta

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.

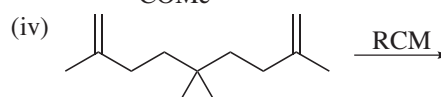
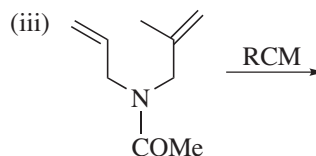
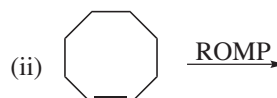
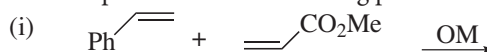


Scheme 9: Polymerization of ethene using the active catalyst $[\text{Cp}_2\text{MR}]^+$

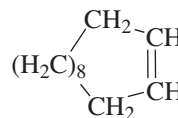
The step (a) refers to coordination of ethene to the vacant site and the step (b) refers to 1,2-insertion of ethene into M-alkyl bond.

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 $(\text{MeAlO})_n$.