SFRP  - Useful for modifying surfaces
- Generation of high adhesive surfaces

**Mechanism of Olefin Metathesis (exchange double bonds)**

**Transalkylation**

\[
\begin{align*}
R & \quad \text{CH} \quad \text{CHR'} \\
\text{R} & \quad \text{CH} \quad \text{CHR} \\
\text{R} & \quad \text{CH} \quad \text{CHR'} \\
\text{R} & \quad \text{CH} \quad \text{CHR}
\end{align*}
\]

**Transalkylidenation**

\[
\begin{align*}
\text{R'CH} & \quad \text{CHR} \\
\text{R'CH} & \quad \text{CHR'} \\
\text{R'CH} & \quad \text{CHR'} \\
\text{R'CH} & \quad \text{CHR}
\end{align*}
\]

Actual Rate

The double bonds exchange

**Cyclic Alkene**

\[
\begin{align*}
n & \quad \text{Cyclic Alkene} \\
n & \quad \text{Cyclic Alkene} \\
n & \quad \text{Cyclic Alkene}
\end{align*}
\]

Citation: Professor Paula Hammond, 10.569 Synthesis of Polymers Fall 2006 materials, MIT OpenCourseWare (http://ocw.mit.edu/index.html), Massachusetts Institute of Technology, Date.
**Ring Opening Metathesis Polymerization (ROMP)**

Catalytic Process $\Rightarrow$ Efficacy of process is dependent on catalyst
Polymer is also dependent on monomer structure

Potential monomers

1. C=C must be in a strained ring system

\[
\text{cyclooctane} \xrightarrow{\text{ROMP}} \text{100\% conversion far from equilibrium}
\]

\[
\text{cyclobutane} \xrightarrow{\text{ROMP}} \text{100\% conversion}
\]

\[
\text{cyclopentane (not as strained)} \xrightarrow{\text{ROMP}} [M]_{eq}
\]

Mono, Bi and Tricyclic ROMP Monomers
Reactivity of Bi and Tricyclic >> Monocyclic

Examples of Norbornadienes

2. For typical monocyclic alkenes:
Substituents available are limited

\[ R \neq \text{NH}_2, \text{C} \text{OH}, -\text{OR}', \text{OH} \]

Must use something less reactive.

3. Can’t polymerize cyclic alkene with R-substituent directly on C=C bond.

For bicyclics, (and tricyclics)
→ much faster rxn rates  
→ always get 100% conversion due to high ring strain  
→ less prone to secondary rearrangements of backbone (shuffling)  
→ side reactions with catalyst are minimized  
∴ can introduce some polar substituents

Schroock catalysts: W, Mo  
(MIT)  
Grubbs catalyst: Ru  
(CalTech)

Norbornene will polymerize in its functionalized forms → functionalized polymers

End-Capping Living ROMP – Wittig Reaction
**Schrock Initiator**

\[ [\text{Mo}] = \text{Mo}(\text{NAr})(\text{O-t-Bu})_2 \]

Living ROMP

- Very rapid with specific catalyst
- Tolerant catalysts for functional groups
- Very low PDI \( \sim 1.03 - 1.05 \)
- "Perfect polymers" almost nature-like

**Conducting Polymers**

Conjugated polymers that allow \( \text{e}^- \) transfer along chain.

Polyacetylene
Chains should be oriented macroscopically

π-orbitals overlapping
→ huge delocalization of $e^-$
$e^-$ can move back and forth on polymer chain ⇒ conjugation

⇒ conjugation
polyacetylene from HC≡CH (gas)
slightly explosive
1st record of polyacetylene → 2-N type polym.
(gas bubbled through solvent with solid phase catalyst)
⇒ powder ⇒ intractable ($T_m$ too high insoluble)

James Feast

monomer

$\text{F}_3\text{C}$

W/Sn

$\text{F}_3\text{C}$

→

$\text{F}_3\text{C}$

$\text{W}/\text{Al}$

heat

$\text{F}_3\text{C}$

Durham Route

Synthesis of Diblocks
TriBlock Copolymers Containing Durham Polyacteylene
Shirakawa: coated walls of Schlank tube with catalyst, then admitted acetylene gas
⇒ form a thin film on glass walls
    silver, brittle, insoluble, intractable
⇒ confirmed e⁻ conductivity
    ~ 0.1 S/cm – 1 S/cm
Difficult to isolate acetylene
**Conjugated Polymers** (common) Heeger and MacDiarmid

**Pyrrole**

\[
\text{H}_2\text{N} - \text{C} = \text{N} - \text{H} \quad \rightarrow \quad \text{H}_n\text{N} - \text{C} = \text{N} - \text{H}
\]

polypyrrole

**Aniline**

\[
\text{H}_2\text{N} - \text{CH}_2\text{NH}_2 \quad \rightarrow \quad \left[ \text{H}_x\text{N} - \text{C} = \text{N} - \text{H} \right]_x \quad \left[ \text{H}_y\text{N} - \text{C} = \text{N} - \text{H} \right]_y
\]

polyaniline

**Thiophene**

\[
\text{H}_2\text{S} \quad \rightarrow \quad \text{H}_n\text{S}
\]

polythiophene

favorable properties in terms of stability can be functionalized

**Oxidation and Reduction Approaches to Polymerization**

- Electrochemical
- Chemical (introduction of a reagent)

1. Reduction at cathode

\[
\text{R} - \text{CH}_2 \quad + \quad e^- \quad \rightarrow \quad \text{R} - \text{CH}_2
\]

radical anion

2. Oxidation at anode

\[
\text{R'} - \text{CH}_2 \quad - \quad e^- \quad \rightarrow \quad \text{R} - \text{CH}_2
\]

radical cation

Generate combination
Often radicals combine to generate dionic species.

**Electropolymerization of Pyrrole**

**Initiation**

\[
\text{Pyrrrole} \rightarrow \text{Pyrrrole}^+ + e^- 
\]

**Propagation**

\[
2 \left[ \text{Pyrrrole}^+ \right] + \text{Pyrrrole} \rightarrow \text{Pyrrrole} + 2H^+ 
\]

\[
\text{Pyrrrole}^+ \left( \text{Pyrrrole} \right)_x + \left[ \text{Pyrrrole} \right]^+ \rightarrow \text{Pyrrrole} \left( \text{Pyrrrole} \right)_{x+1} + 2H^+ + e^- 
\]

**Termination**

\[
\text{Pyrrrole} \left( \text{Pyrrrole} \right)_x + H_2O \rightarrow \text{Pyrrrole} \left( \text{Pyrrrole} \right)_x 
\]