Lecture 33: Ring-Opening Metathesis Polymerization, Oxidative Coupling, Electrochemical Polymerization, Case Study: Electro-Active Polymers

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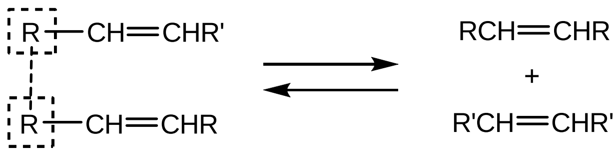
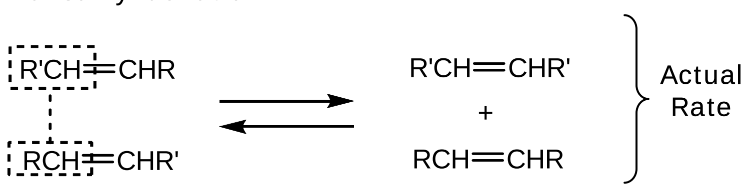
SFRP - Useful for modifying surfaces
- Generation of high adhesive surfaces

Mechanism of Olefin Metathesis (exchange double bonds)

Transalkylation

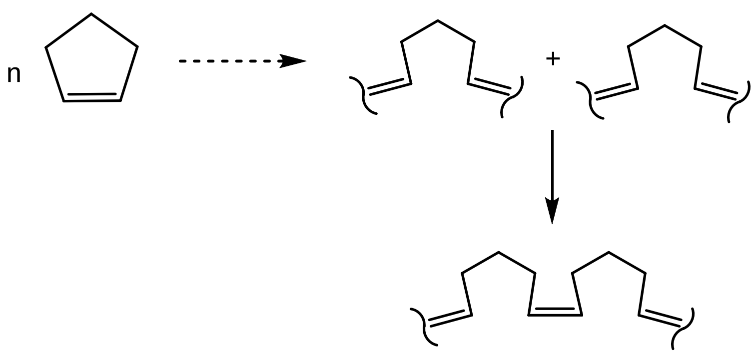


Transalkylidenation



The double bonds exchange

Cyclic Alkene



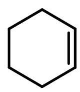
Citation: Professor Paula Hammond, 10.569 Synthesis of Polymers Fall 2006 materials, MIT OpenCourseWare (http://ocw.mit.edu/index.html), Massachusetts Institute of Technology, Date.

Ring Opening Metathesis Polymerization (ROMP)

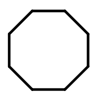
Catalytic Process ⇒ Efficacy of process is dependent on catalyst
Polymer is also dependent on monomer structure

Potential monomers

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

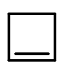


↛ ROMP (no strain)



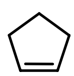
cyclooctane

→ ROMP → 100% conversion far from equilibrium



cyclobutane

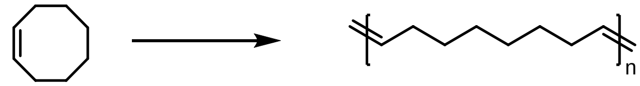
→ ROMP → 100% conversion

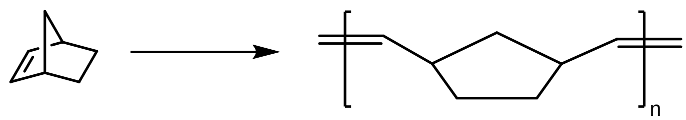


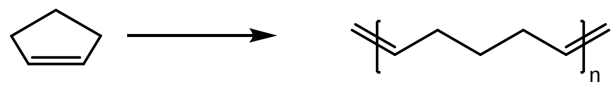
cyclopentane
(not as strained)

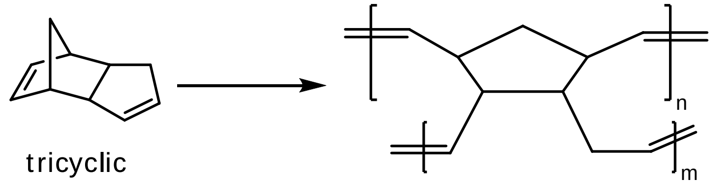
→ ROMP → $[M]_{eq}$

Mono, Bi and Tricyclic ROMP Monomers



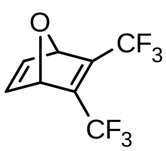




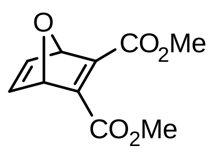


tricyclic

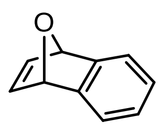
Reactivity of Bi and Tricyclic >> Monocyclic



A



B

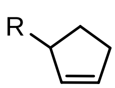


C

Examples of Norbornadienes

↖ oxygen at bridge pinnacle

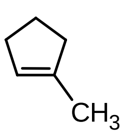
2. For typical monocyclic alkenes:
Substituents available are limited



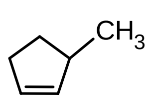
R ≠ NH_2, —C(=O)—OH, -OR' , OH

Must use something less reactive.

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



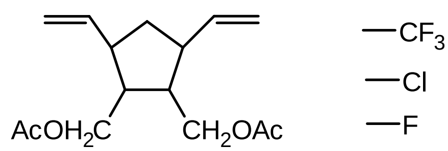
Won't undergo ROMP.

Whereas  will undergo ROMP.

For bicyclics, (and tricyclics)

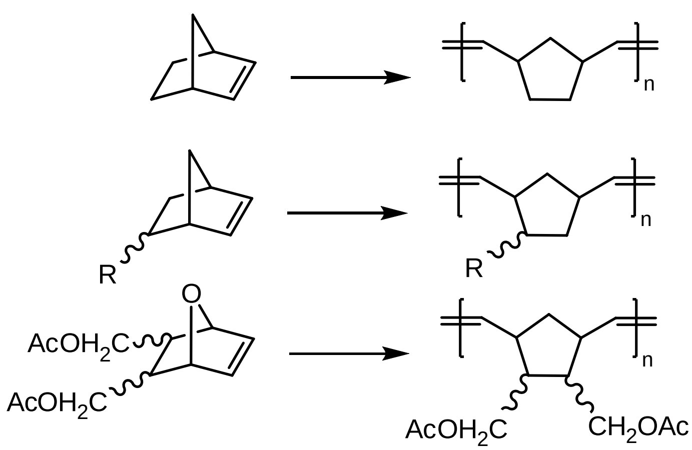
→ much faster rxn rates
→ always get 100% conversion due to high ring strain
→ less prone to secondary rearrangements of backbone (shuffling)
→ side reactions with catalyst are minimized
∴ can introduce some polar substituents

ex

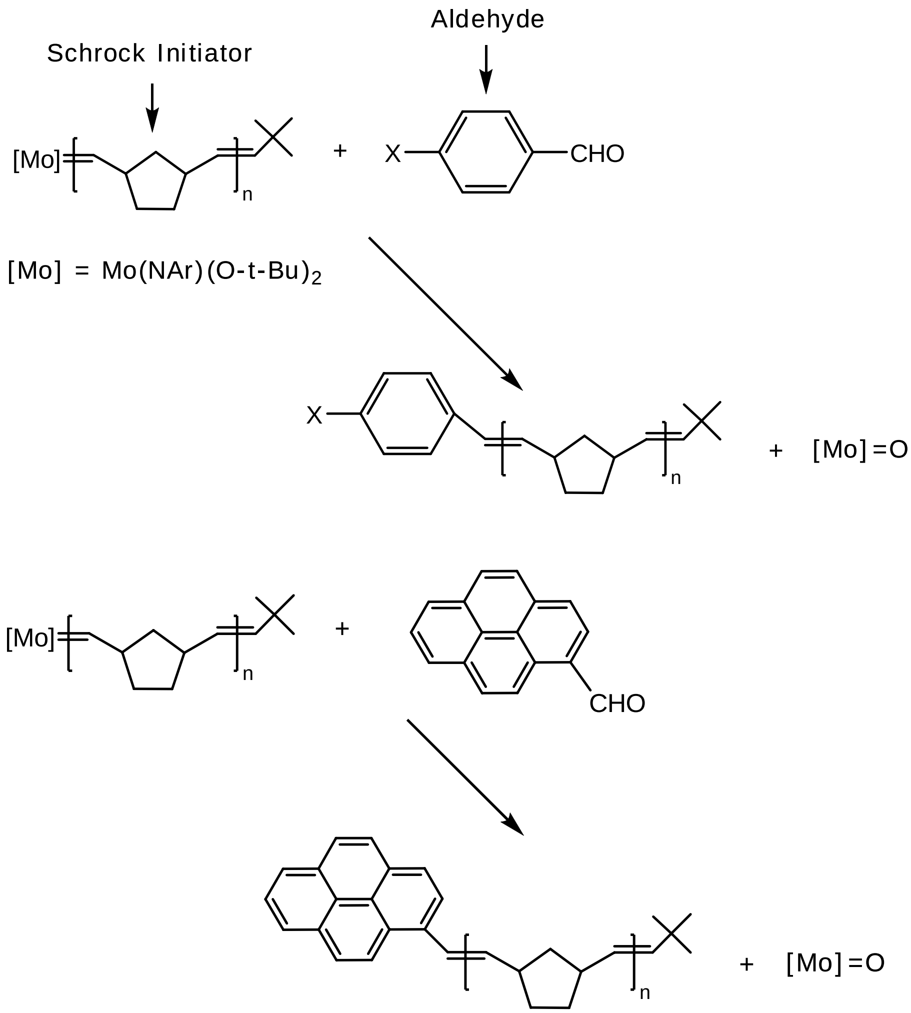


Schrock catalysts: W, Mo
(MIT)
Grubbs catalyst: Ru
(CalTech)

Norbornene will polymerize in its
functionalized forms → functionalized polymers

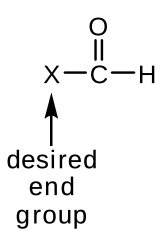


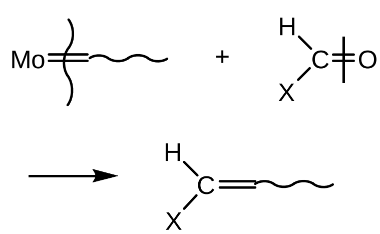
End-Capping Living ROMP – Wittig Reaction



Living ROMP

R_i very rapid with specific catalyst
~ tolerant catalysts for functional groups
→ very low PDI → 1.03 – 1.05
"perfect polymers" almost nature-like

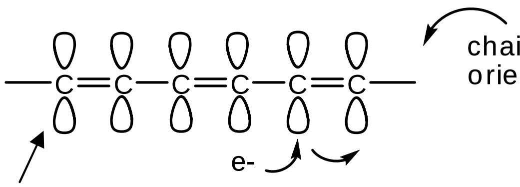




Conducting Polymers

Conjugated polymers that allow e^- transfer along chain.

Polyacetylene



chains should be
oriented macroscopically

π-orbitals overlapping

$\rightarrow$ huge delocalization of e^-

e^- can move back and forth on polymer chain $\Rightarrow$ conjugation

$\Rightarrow$ conjugation

polyacetylene from HC≡CH (gas)

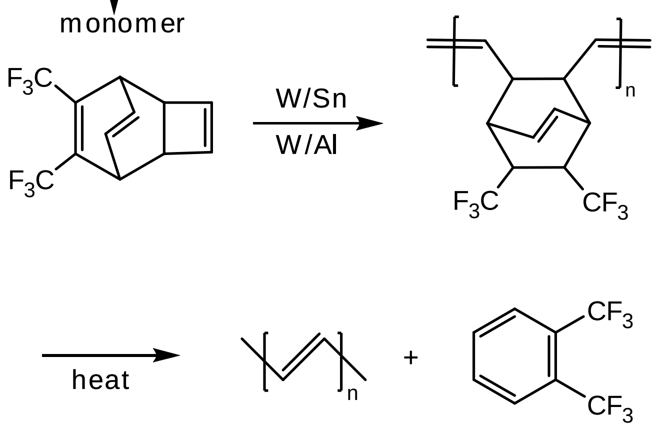
slightly explosive

1st record of polyacetylene $\rightarrow$ 2-N type polym.

(gas bubbled through solvent with solid phase catalyst)

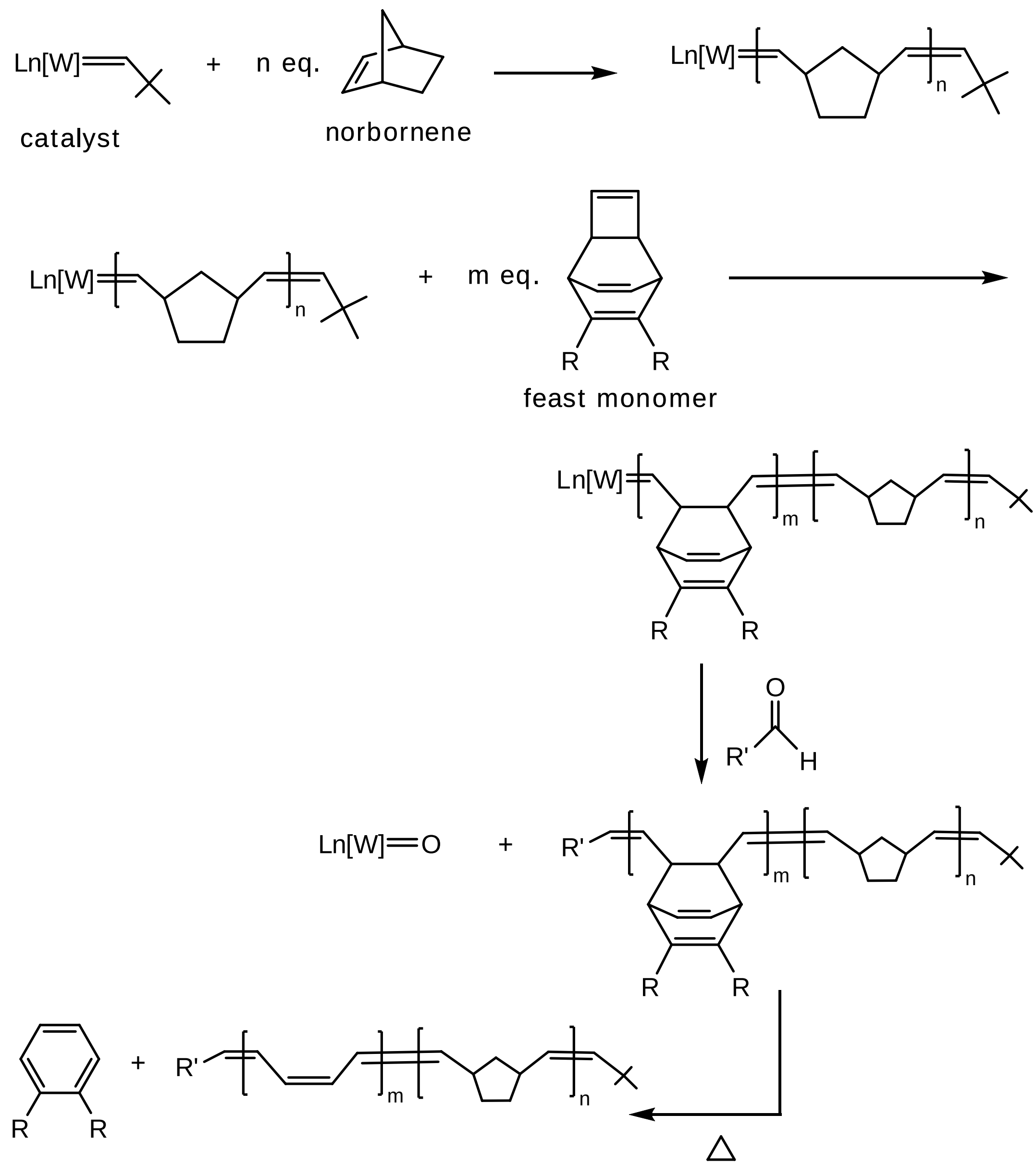
$\Rightarrow$ powder $\Rightarrow$ intractable (T_m too high insoluble)

James Feast
↓
monomer

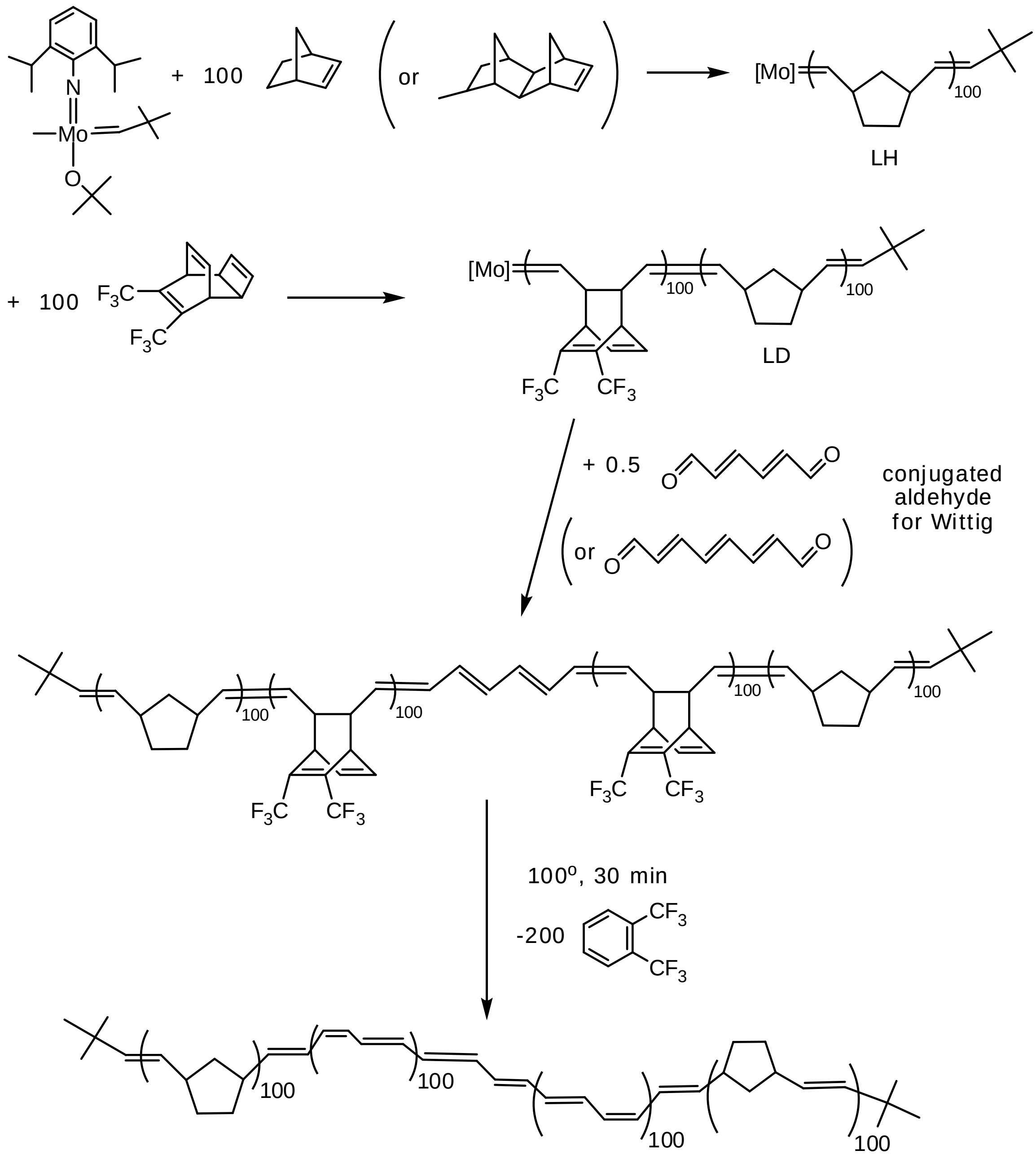


Durham Route

Synthesis of Diblocks



TriBlock Copolymers Containing Durham Polyacteylene



Shirakawa: coated walls of Schlank tube with catalyst, then admitted acetylene gas

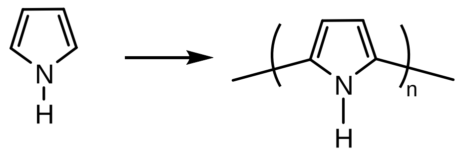
⇒ form a thin film on glass walls
silver, brittle, insoluble, intractable

⇒ confirmed e^- conductivity
~ 0.1 S/cm – 1 S/cm

Difficult to isolate acetylene

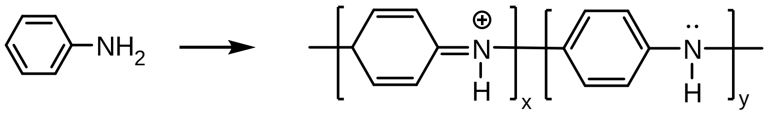
Conjugated Polymers (common) Heeger and MacDiarmid

Pyrrole



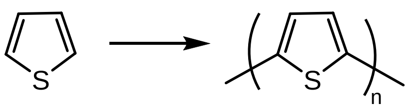
polypyrole

Aniline



polyaniline

Thiophene

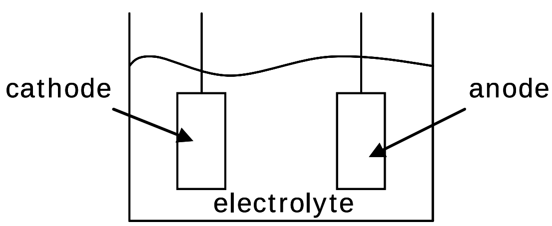


polythiophene

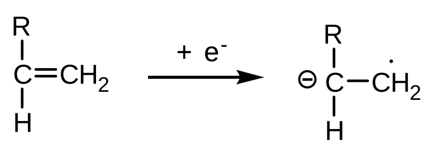
favorable properties in terms of stability
can be functionalized

Oxidation and Reduction Approaches to Polymerization

- Electrochemical
- Chemical (introduction of a reagent)

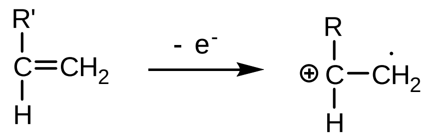


1. Reduction at cathode



radical anion

2. Oxidation at anode



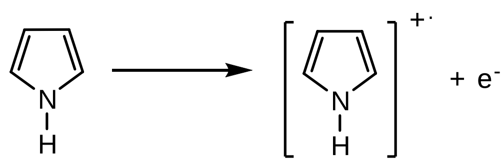
radical cation

Generate combination

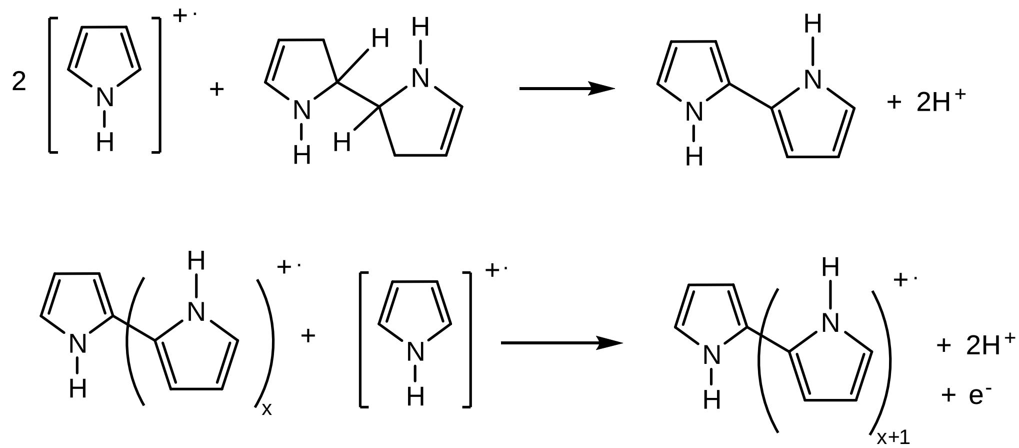
Often radicals combine to generate dionic species.

Electropolymerization of Pyrrole

Initiation



Propagation



Termination