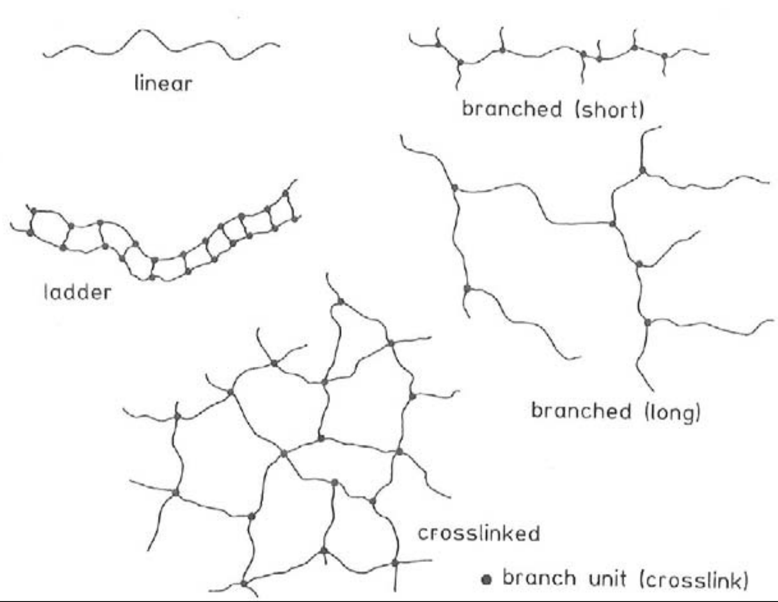
POLYMER SYNTHESIS

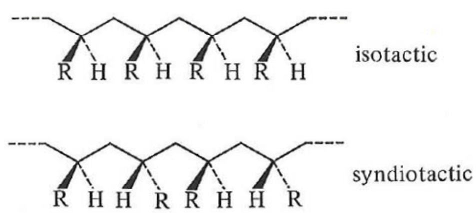
- What are the basic classes of polymer synthesis?
- Which polymers are made which ways?
- Limitations and advantages of different synthetic methods.

P. J. Lutz, P. Rempp & E. W. Merrill, *Polymer Synthesis (3rd ed.)*
Wiley-VCH, New York: 2004

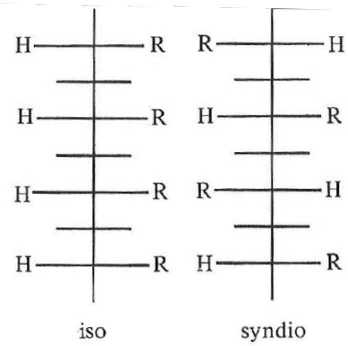
Polymer Types



Polymer Types



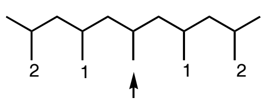
Natta's projection
(Planar zig–zag)



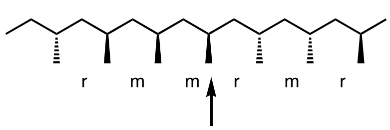
Fischer's projection

How to Determine Microstructure?

^{13}C NMR: powerful method for determination of polymer microstructure.

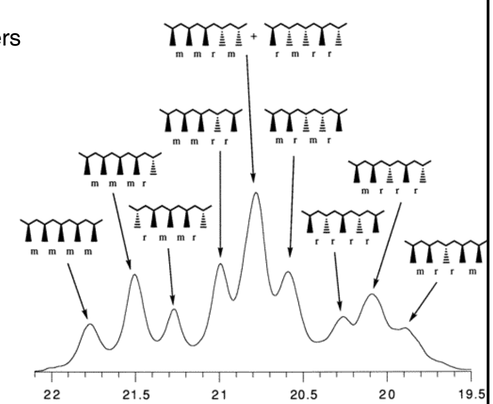


^{13}C NMR shift is sensitive to the two stereocenters on either side on sptectrometers > 300 MHz. This is called pentad resolution.



m = meso (same orientation)
r = racemic (opposite orientation)

^{13}C NMR spectrum of CH_3 region of atactic polypropylene



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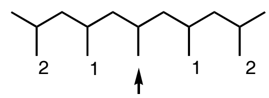

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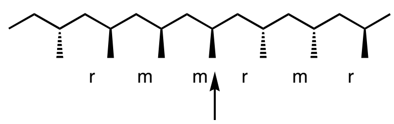

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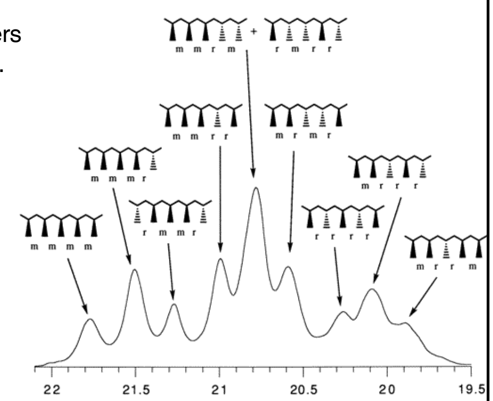
^{13}C NMR spectrum of CH_3 region of atactic polypropylene



Why is this important?

- **Tacticity affects the physical properties**

  Atactic polymers will generally be amorphous, soft, flexible materials.

  Isotactic and syndiotactic polymers will be more crystalline, thus harder and less flexible.

- **Polypropylene (PP) is a good example**

  Atactic PP is a low melting, gooey material.

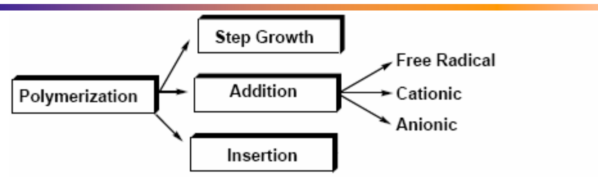
  Isoatactic PP is high melting (176º), crystalline, tough material that is industrially useful.

  Syndiotactic PP has similar properties, but is harder to synthesize.

Polymer Synthesis

- Initiation: Formation of active site on some monomer.
- Propagation: Chain growth, the addition of an active site to a growing polymer chain, restoring the active site at the chain end.
- Termination: Destruction of the active growing site.
- Transfer Reactions: removal of the active site from one chain to another molecule, terminating the first and beginning propagation at the second.

Polymer Synthesis



Condensation or Step-growth Polymerisation
Step growth polymerisation is usually used for monomers with functional groups such as -OH, -COOH etc. It is usually a succession of non-catalysed, chemical condensation reactions associated with the elimination of low-molar-mass side-products, eg., water.

Addition Polymerisation
Usually addition polymerisations involve the polymerisation of olefinic monomers. Polymerisation occurs via a chain reaction. The monomers are converted into polymers by opening of the double bond with a free radical or ionic initiator. The product, then, unlike that obtained from step-growth polymerisation, has the same chemical composition as the starting monomer.

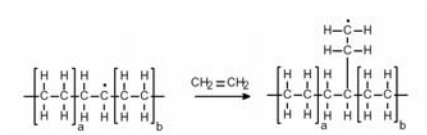
Insertion Polymerisation
Usually addition polymerisations involve the polymerisation of olefinic monomers. Polymerisation occurs via an insertion of a monomer at the end of the growing chain, mediatied by a catalyst. The catalyst stays at the end of the growing chain. Polymers synthesised by insertion polymerisation are typically characterised by a very high stereoregularity. An example for such a polymerisaiton techniques is the Ziegler-Natta polymerisation.

Condensation vs. Addition

- **Addition:**

  Difficult to control molecular weight

  Undesirable branching products



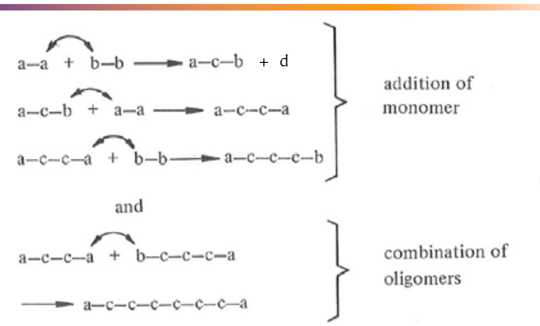
- **Condensation:**

  Molecular weight closely controlled

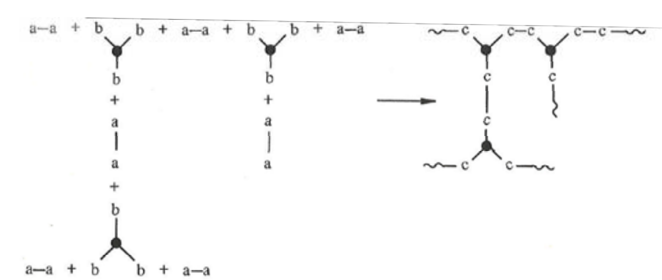
  Polydispersity ratios close to unity can be obtained

Step-Growth or Condensation Synthesis

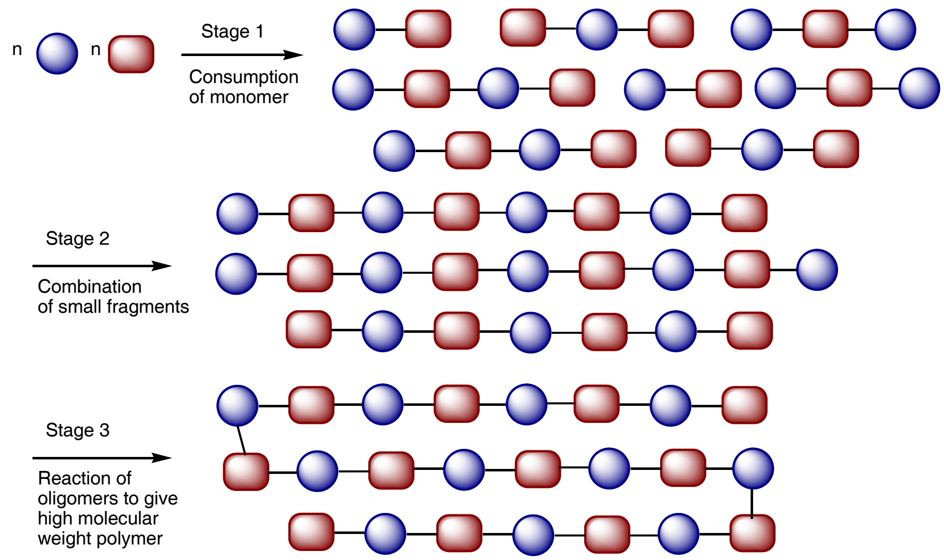
linear:



networks:

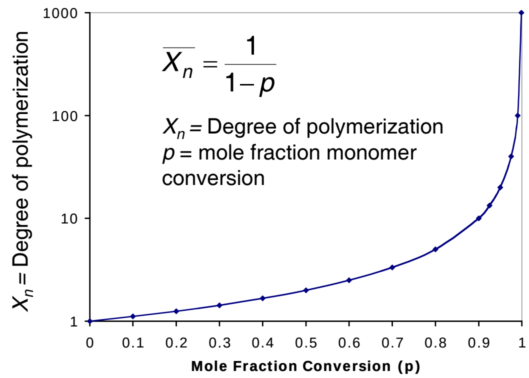


Step-Growth Polymerization

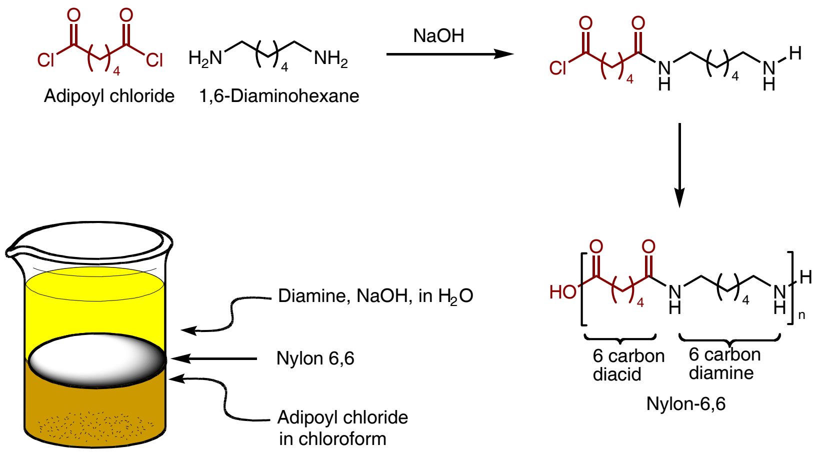


Step-Growth Polymerization

- **Because high polymer does not form until the end of the reaction, high molecular weight polymer is not obtained unless high conversion of monomer is achieved.**

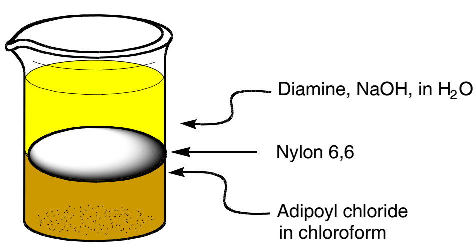


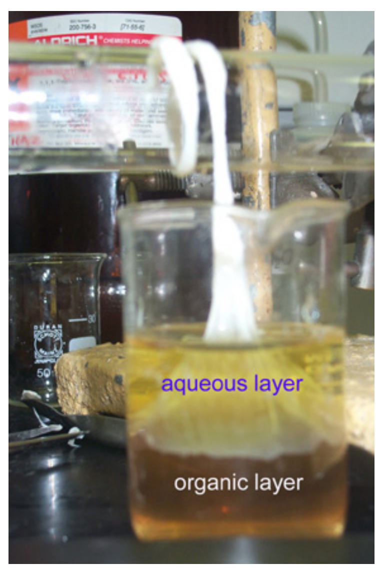
Nylon-6,6



Nylon-6,6

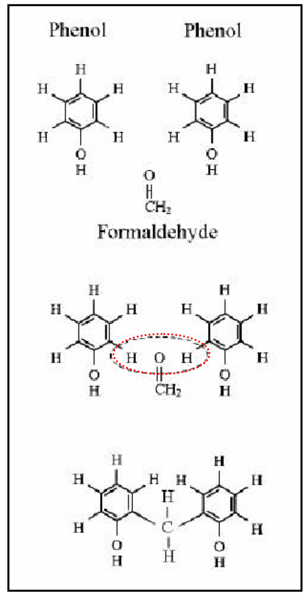
Since the reactants are in different phases, they can only react at the phase boundary. Once a separating layer of polymer forms, the reaction stops. Removing the polymer (e.g., pulling it up as a rope) allows the reaction to continue.





Polymer Synthesis: Condensation

- **phenol-formaldehyde: results in condensation of a water molecule**



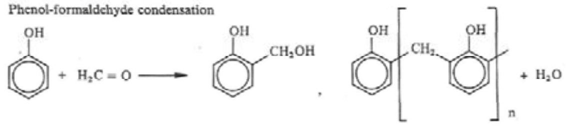
Types of Condensations Polymers

Name of reaction	a	b	c	d
Hydroxyl-carboxylic acid condensation	—OH	—COOH	—C(O)O—	HOH
Hydroxyl-ester interchange	—OH	—C(O)OR	—C(O)O—	HOR
Amine-carboxylic acid condensation	$—NH_2$	—COOH	—NHC(O)—	HOH
Amine-amide interchange	$—NH_2$	—C(O)NHR	—C(O)NH—	H_2NR

II. Irreversible (far from equilibrium) polycondensations

Name of reaction	a	b	c	d
Amine-acid chloride condensation	$—NH_2$	—C(O)Cl	—C(O)NH—	HCl
Hydroxyl-acid chloride condensation	—OH	—C(O)Cl	—C(O)O—	HCl
Isocyanate-hydroxyl condensation *)	—NCO	—OH	—NHC(O)O—	—
Isocyanate-amine condensation *)	—NCO	$—NH_2$	—NHC(O)NH—	—
Oxirane-amine condensation *) ("Epoxy" reaction)	$—CH—CH_2$ (epoxide, —O—)	—NHR	$—C(OH)—CH_2—NR—$	—

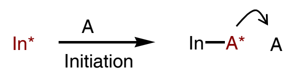
Phenol-formaldehyde condensation



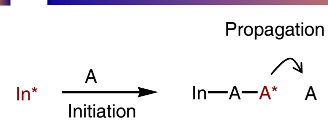
Silane hydrogen-vinyl coupling	—SiH	$CH_2=CH—Si—$	$—Si—CH_2—CH_2—Si—$	—
Silanol-silanol condensation	—Si—OH	HO—Si—	—Si—O—Si—	H_2O
Acetoxysilane condensation	$—Si—OC(O)—CH_3$	HO—Si—	—Si—O—Si—	$CH_3—C(O)—OH$

*) These reactions were sometimes referred to as polyadditions, because in this case there is no formation of low molecular weight by-products.

Addition Polymerization



Addition Polymerization



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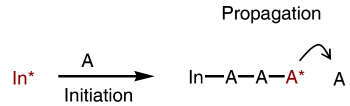
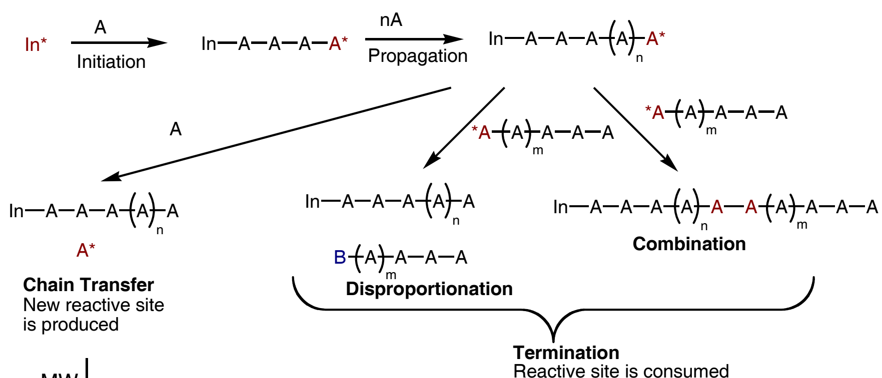
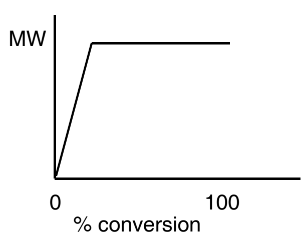


Addition Polymerization

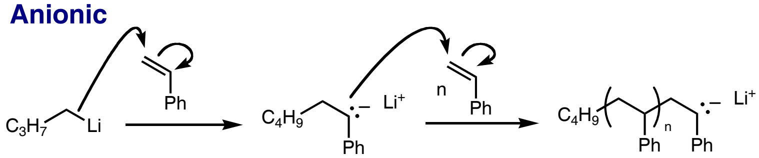




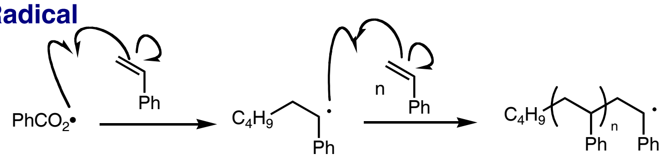
$$MW \propto \frac{k_{propagation}}{k_{termination}}$$

Types of Addition Polymerizations

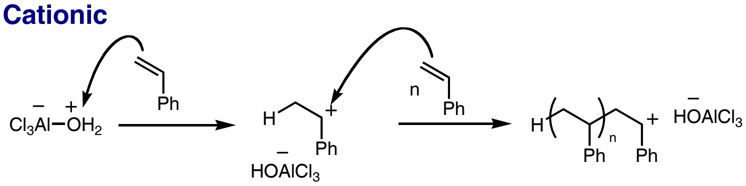
Anionic



Radical



Cationic



Addition: Radical Chain Polymerization

Initiators:

a) Peroxides, organic or inorganic, like dibenzoyl peroxide (which is in fact a peranhydride, $C_6H_5—CO—O—O—CO—C_6H_5$), or potassium peroxodisulfate ($K_2S_2O_8$),
b) Hydroperoxides such as t-butylhydroperoxide: $(CH_3)_3C—O—OH$
c) Peresters like t-butyl perbenzoate: $C_6H_5—CO—O—OtBu$
d) Aliphatic azocompounds, such as azobisisobutyronitrile (AIBN):

$$(CH_3)_2\underset{\displaystyle C\equiv N}{\underset{|}{C}}—N{=}N—\underset{\displaystyle C\equiv N}{\underset{|}{C}}(CH_3)_2$$

Radical Formation:

Decomposition of the initiator to form primary radicals:

$$C_6H_5CO—O—O—CO—C_6H_5 \rightarrow 2\,C_6H_5COO^\bullet$$

$$I \rightarrow 2\,R^\bullet$$

Initiation:

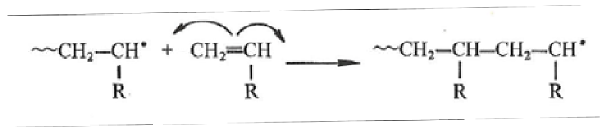
The actual initiation reaction:

$$R^\bullet + CH_2{=}\underset{\displaystyle R'}{\underset{|}{CH}} \rightarrow R—CH_2—\underset{\displaystyle R'}{\underset{|}{CH^\bullet}}$$

$$R^\bullet + M \rightarrow RM^\bullet$$

Addition: Radical Chain Polymerization

Chain Growth:

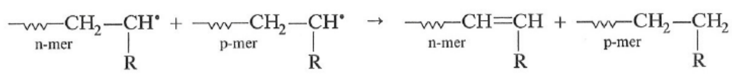


or $RM_n^\bullet + M \rightarrow RM_{n+1}^\bullet$

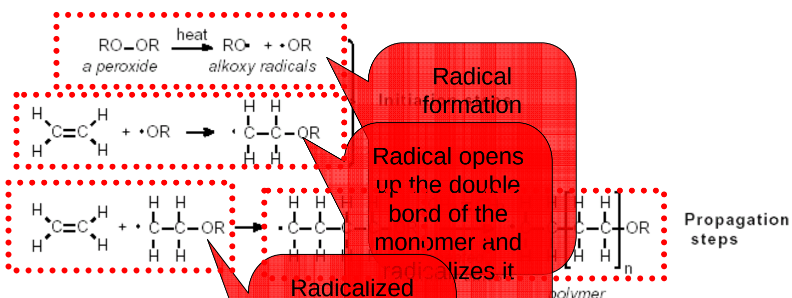
Termination:

Recombination $R - M_n^\bullet + R - M_p^\bullet \rightarrow R - M_{n+p} - R$

Disproportionation



Polymers Synthesis: Addition

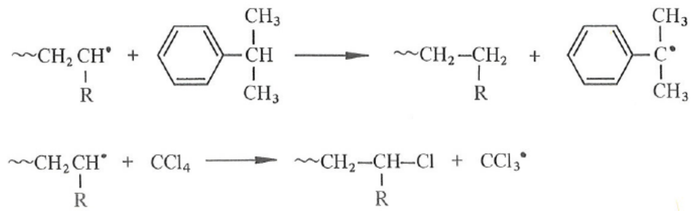


Termination may occur by:

- •two radicalized polymers reacting
- •another radicalized monomer
- •one initiator (alkoxy radical, •OR, in this case)

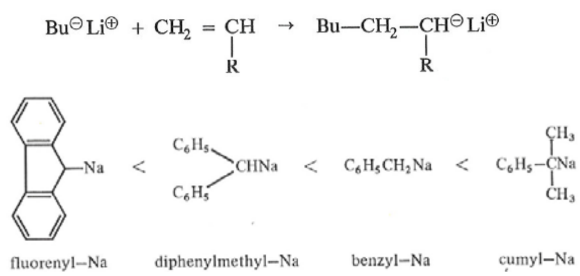
Free Radical Chain Polymerization

Transfers:

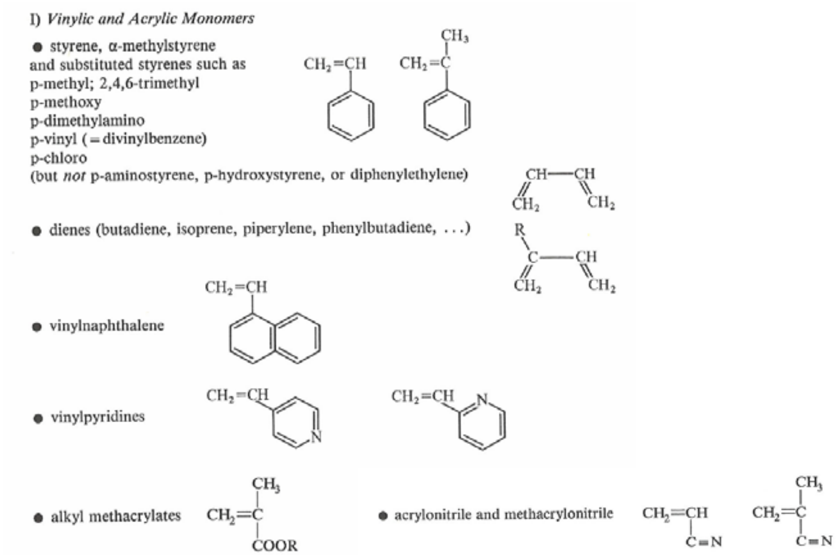


Addition: Anionic Polymerization

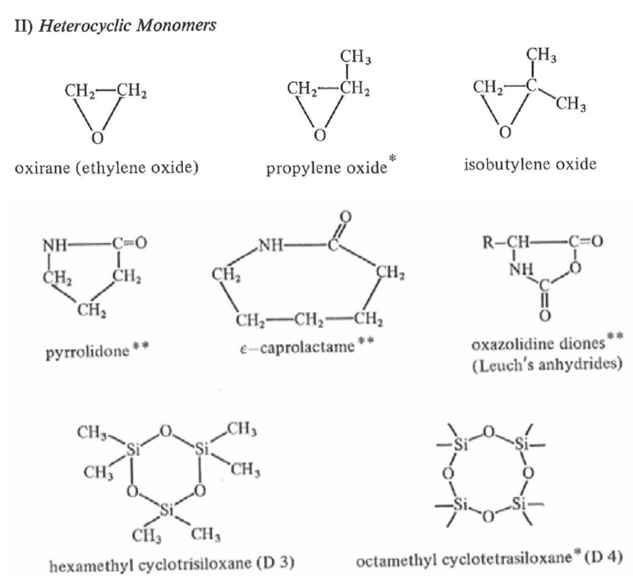
Initiators:



Addition: Anionic Polymerization

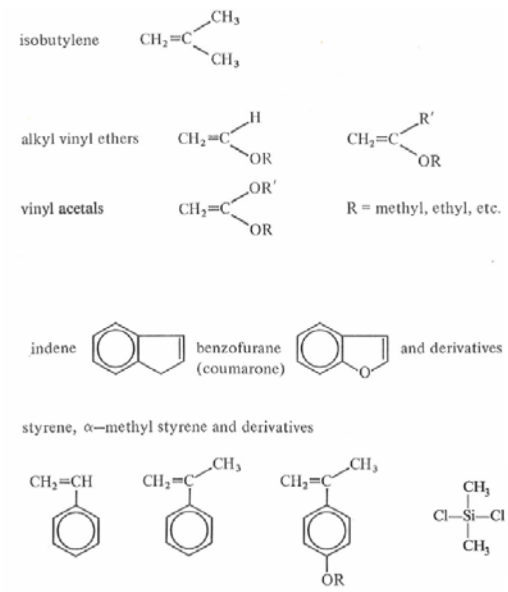


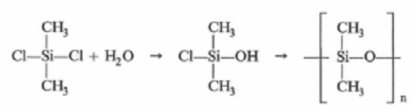
Addition: Anion Polymerization



Addition: Cation Polymerization

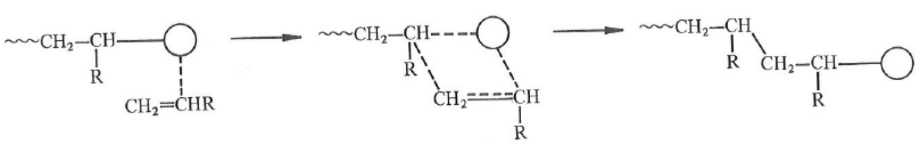
Monomers:





Insertion Polymerization

Insertion Mechanism:



orientation of the incoming monomer with respect to the active site

4–centered transition state

insertion of the monomer into the C–active center bond (implying restoration of the active site at the chain end)

Insertion Polymerization: Ziegler-Natta

Insertion Mechanism:

Insertion (propagation)

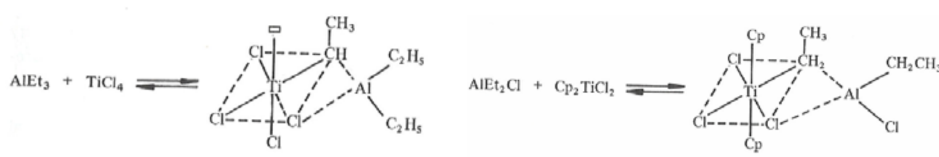
$$R_2Al{-}Et + C_2H_4 \rightarrow R_2Al{-}CH_2CH_2{-}Et$$

$$R_2Al{-}CH_2CH_2{-}Et + (n-1)C_2H_4 \rightarrow R_2Al{-}(CH_2CH_2)_n{-}Et$$

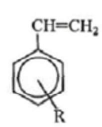
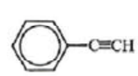
Transfer reactions

$$R_2Al{-}(CH_2CH_2)_n{-}Et \rightarrow R_2AlH + CH_2{=}CH{-}(CH_2CH_2)_{n-1}{-}Et$$

$$R_2Al{-}(CH_2CH_2)_n{-}Et + C_2H_4 \rightarrow R_2AlCH_2CH_3 + CH_2{=}CH{-}(CH_2CH_2)_{n-1}{-}Et$$

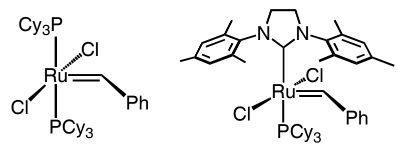


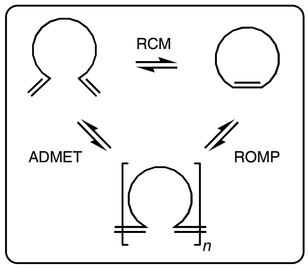
Insertion Polymerization: Ziegler-Natta

ethylene	$H_2C{=}CH_2$
propene	$H_2C{=}CH{-}CH_3$
butene	$H_2C{=}CH{-}CH_2{-}CH_3$
styrene and some substituted styrenes	
vinyl ethers	$CH_2{=}CH{-}OR$
butadiene, isoprene, and various other dienes	$H_2C{=}CH{-}CH{=}CH_2$ $H_2C{=}\overset{CH_3}{C}{-}CH{-}CH_2$
cycloalkenes; C_3 and C_4	
methylene cycloalcanes and spiro [2,2] pentane	
acetylene, phenylacetylene	$CH{\equiv}CH$ 

Insertion Polymerization: ROMP

"Olefin Metathesis" R. H. Grubbs, *Tetrahedron*, **2004**, *60*, 7117-7140.





Metathesis Transformations

Insertion Polymerization: ROMP

2005 Nobel Prize in Chemistry:
Yves Chauvin, Robert H. Grubbs, & Richard R. Schrock
"for the development of the metathesis method in organic synthesis."

In 1971, **Yves Chauvin** was able to explain in detail how metatheses reactions function and what types of metal compound act as catalysts in the reactions.

In 1990, **Richard Schrock** was the first to produce an efficient metal-compound catalyst for metathesis.

Two years later **Robert Grubbs** developed an even better catalyst, stable in air, that has found many applications.

Metathesis Mechanism: Chauvin

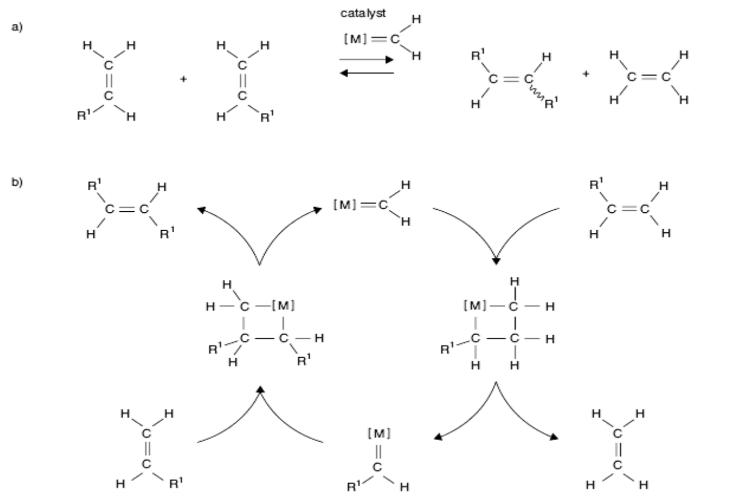


Figure 3. (a) Metathesis of alkenes catalysed by a metal alkylide. The products are two new alkenes – ethene and the alkene with two R' groups – one on each carbon in the double bond. The wavy bond shows that the R' groups can be located on the same side of the double bond or on different sides. (b) Chauvin's mechanism for olefin metathesis. In the catalytic cycle on the way to the products rings with four atoms are formed – three carbons and one metal.

Schrock's catalyst and Grubbs' catalyst

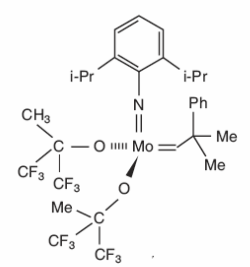


Figure 5. One of Schrock's molybdenum catalysts. High reactivity has been achieved with the specially-selected groups bound to the metal atom (i-Pr=iso-propyl and Ph=Phenyl).

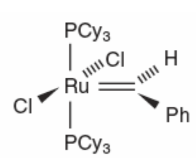
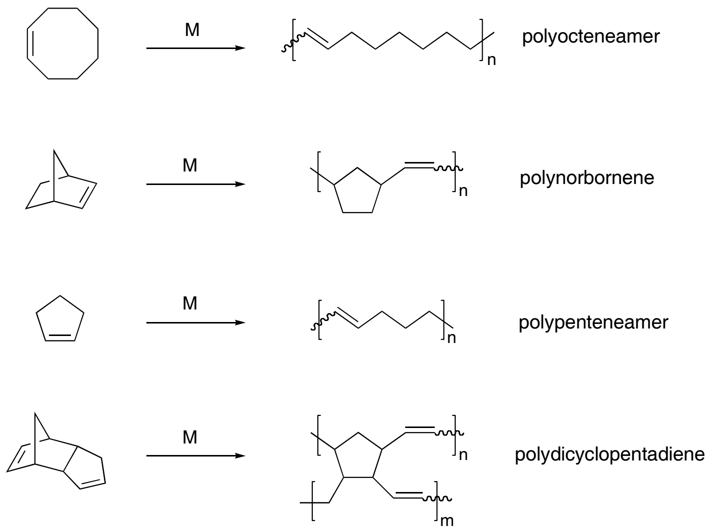


Figure 6. Ruthenium catalyst developed by Grubbs (Ph=phenyl and Cy=cyklohexyl).

Ring-Opening Metathesis Polymerization

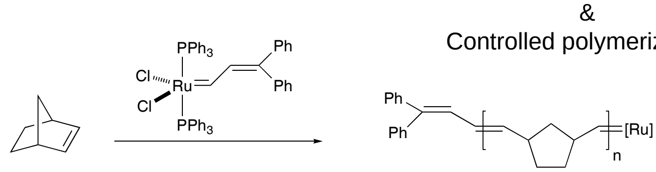
Relief of ring-strain drives the polymerization



Ruthenium-based metathesis catalysts

Ring-opening metathesis polymerization (ROMP) of norbornene in protic media
SonBinh T. Nguyen, Lynda K. Johnson, Robert H. Grubbs, Joseph W. Ziller;
J. Am. Chem. Soc.; 1992; 114(10); 3974-3975

Functional group tolerance
&
Controlled polymerizations

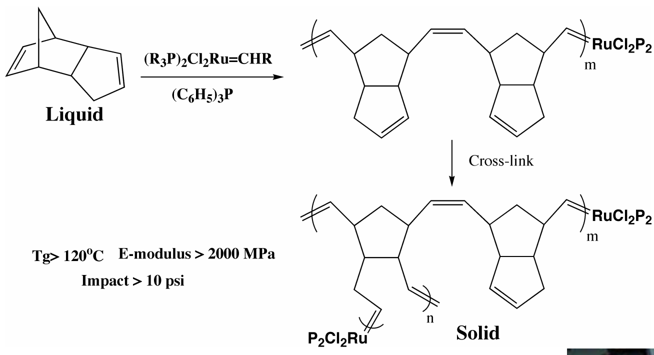


living polymerization

PI = 1.1

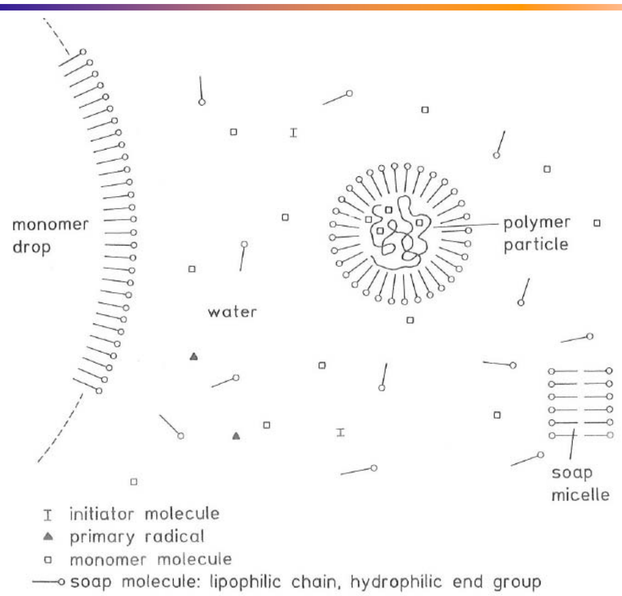
observable propagating species.
stable in the presence of protic solvents.
block copolymers.

Insertion Polymerization: ROMP



a composite wood-ROMP polymer bat that is now commercialized by Easton Sports:

Phases during Polymerization



Phases during Polymerization