TÉCNICO LISBOA

LISBOA UNIVERSIDADE DE LISBOA

Metal-Catalyzed Polymerizations

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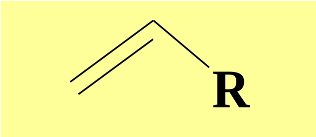
Metal-Catalyzed Polymerizations

(Coordination Polymerization)

- *Polymerization of Olefins (Insertion)* ✓ *Prof. Barbara Milani*
- *Polymerization of Dienes (Insertion)*
- *Polymerization of Alkynes*
- *Ring Opening Metathesis Polymerization (ROMP)*
- *Classical Anionic Polymerization*
- *Ring Opening Polymerization (ROP)*
- *Metal-mediated Radical Polymerization*

POLYMERIZATION OF VINYL MONOMERS



TYPES OF POLYMERIZATION

- **RADICAL** — initiators: ROOR, ROOH, R-N≡N-R
- **CATIONIC** — initiators: Brönsted acids, Lewis acids, stable cations
- **ANIONIC** — initiators: alkyl or aryl lithium or sodium compounds, sodium
- **COORDINATION** — catalysts: Ziegler-Natta, metallocenes, post-metallocenic (the only method that homo- and copolymerizes propylene and α-olefins)

GENERAL MECHANISM

Chain Growth

- **INITIATION**
- **PROPAGATION**

} common to all types

- **CHAIN TRANSFER**
- **TERMINATION**

} they can be suppressed when the polymerization is "controlled"

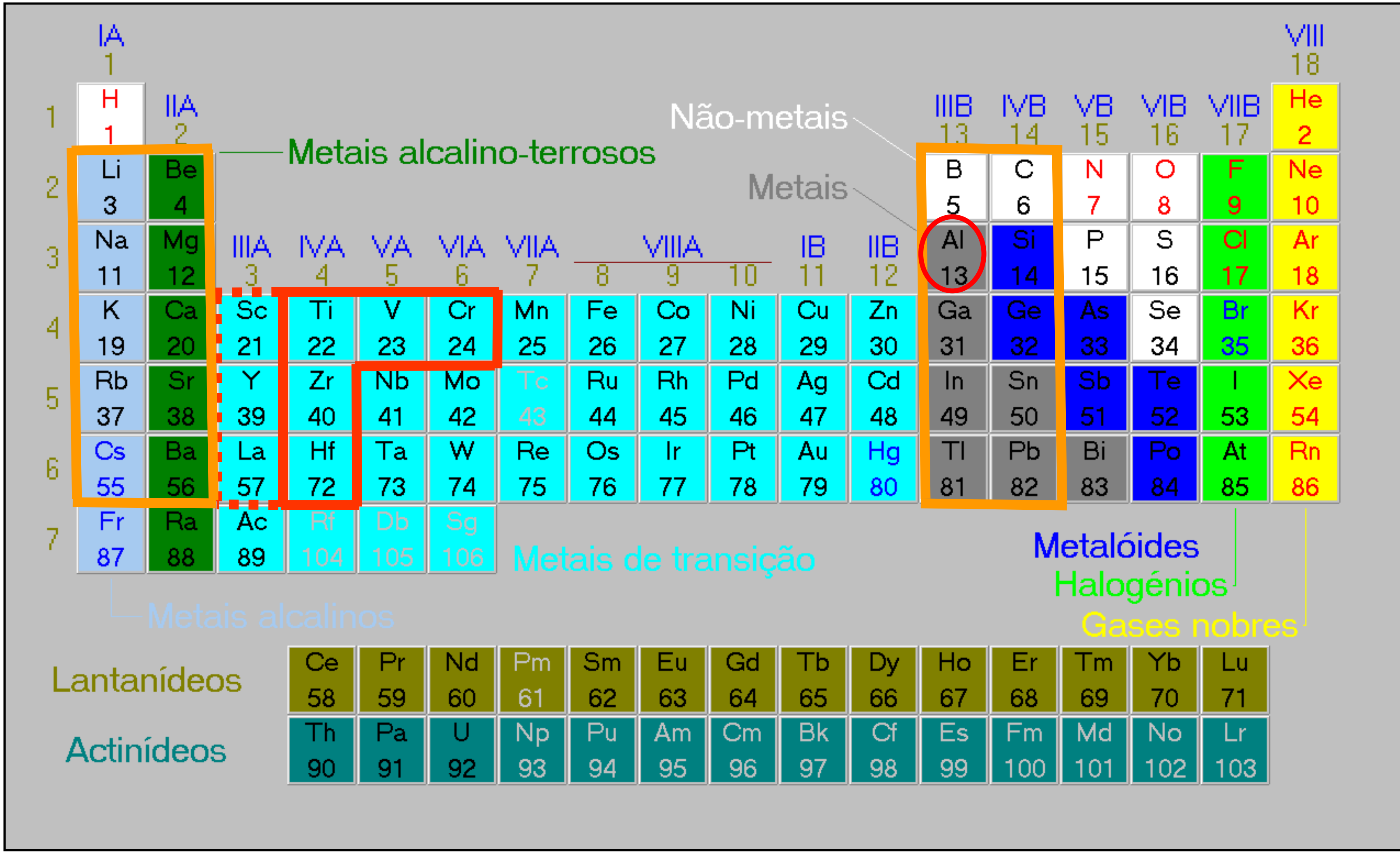
↓

"Living" polymerization

ZIEGLER-NATTA CATALYSTS

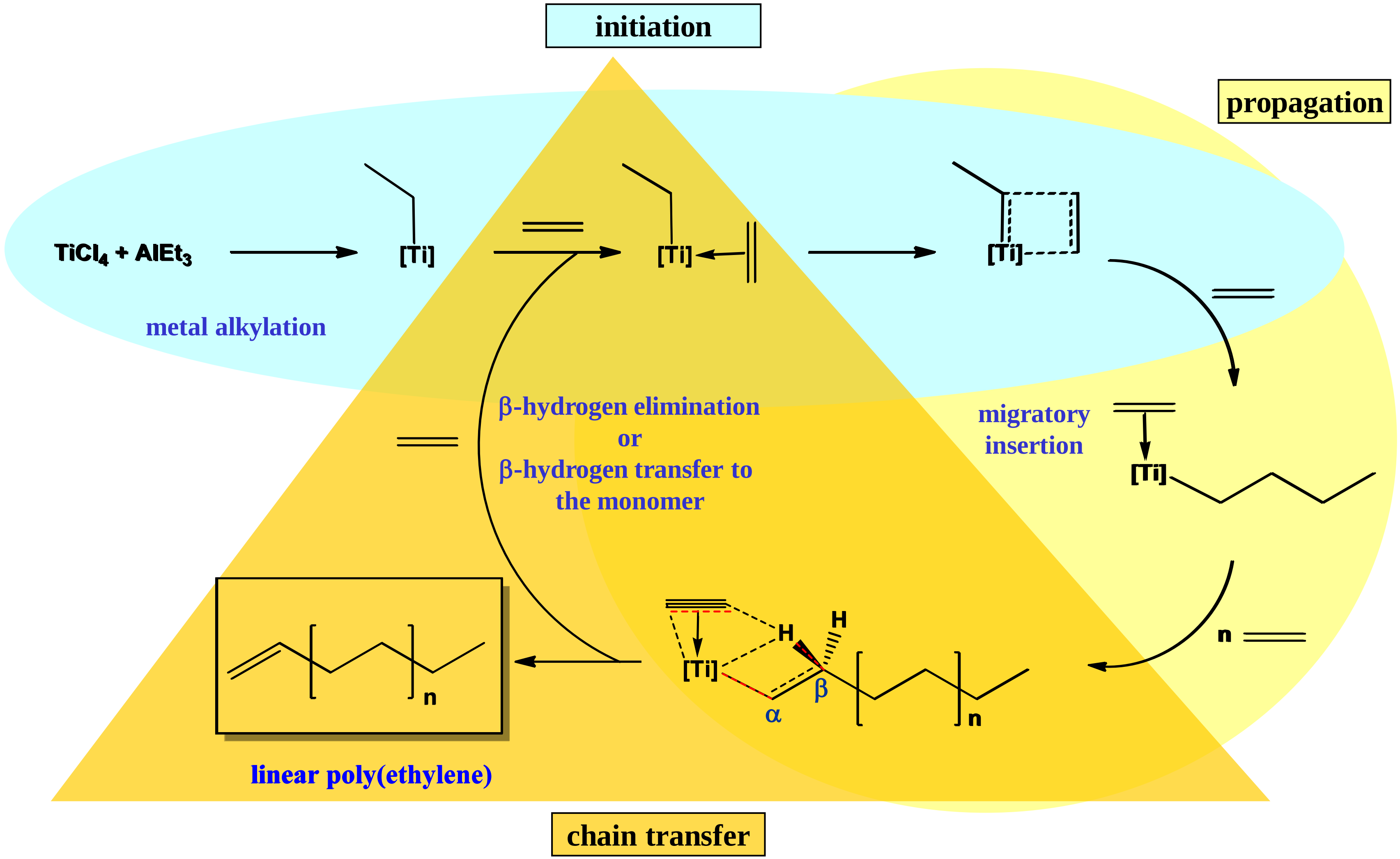
DEFINITION:

Transition Metal Compound	**+**	**Metal Alkyl, Aryl or Hydride**
(groups 4 - 10)		**(groups 1, 2, 13 and 14)**


Metais alcalino-terrosos
Não-metais
Metais
Metais de transição
Metais alcalinos
Metalóides
Halogénios
Gases nobres
Lantanídeos
Actinídeos

By analogy with homogeneous metallocene catalysts

Mechanism of Olefin Polymerization with Ziegler-Natta Catalysts



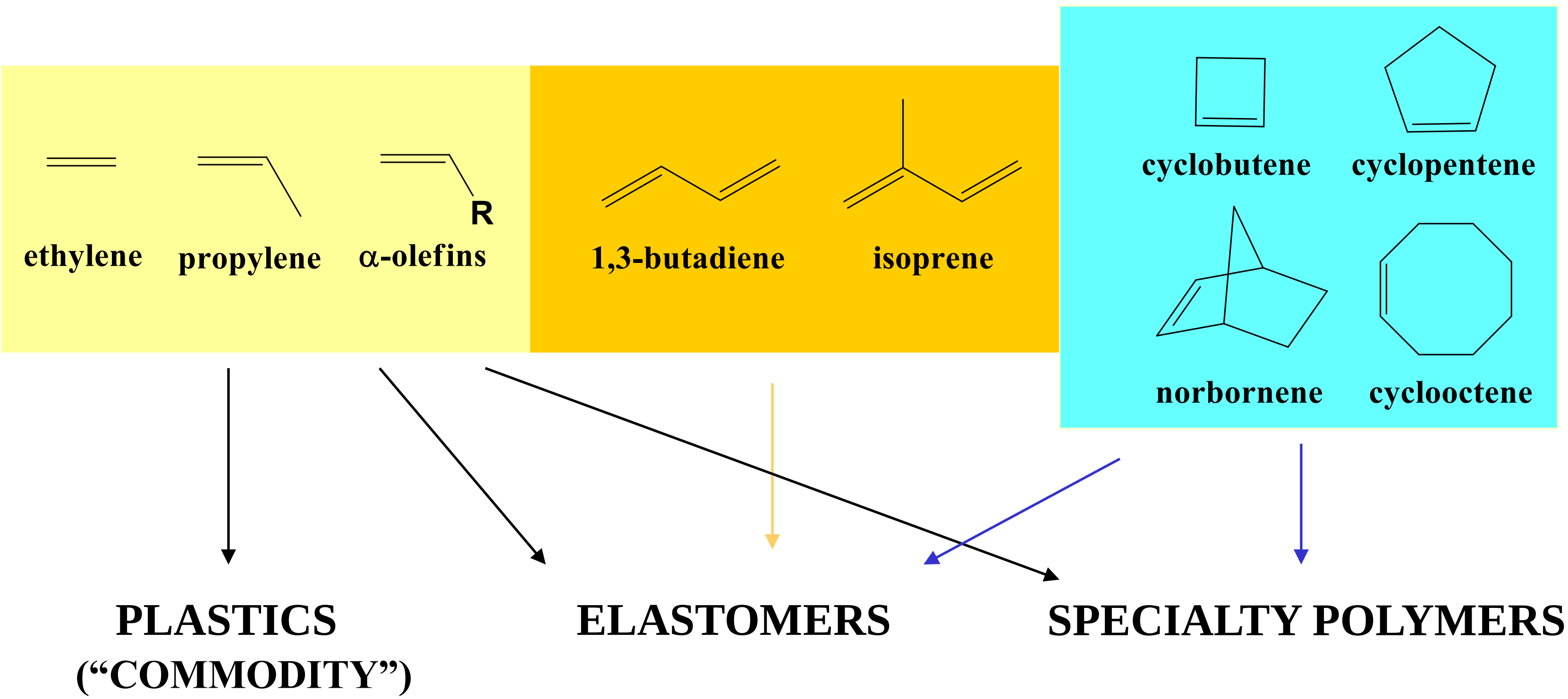
[Ti] ≡ heterogeneous metal site (it can also be a metallocene or a post-metallocene)

POLYOLEFINS

Olefin = unsaturated hydrocarbon = Alkene

Typical Olefin Monomers:

Aliphatic monoolefins (C_nH_{2n}): **Aliphatic diolefins (C_nH_{2n-2}):** **Cycloolefins (C_nH_{2n-2}):**



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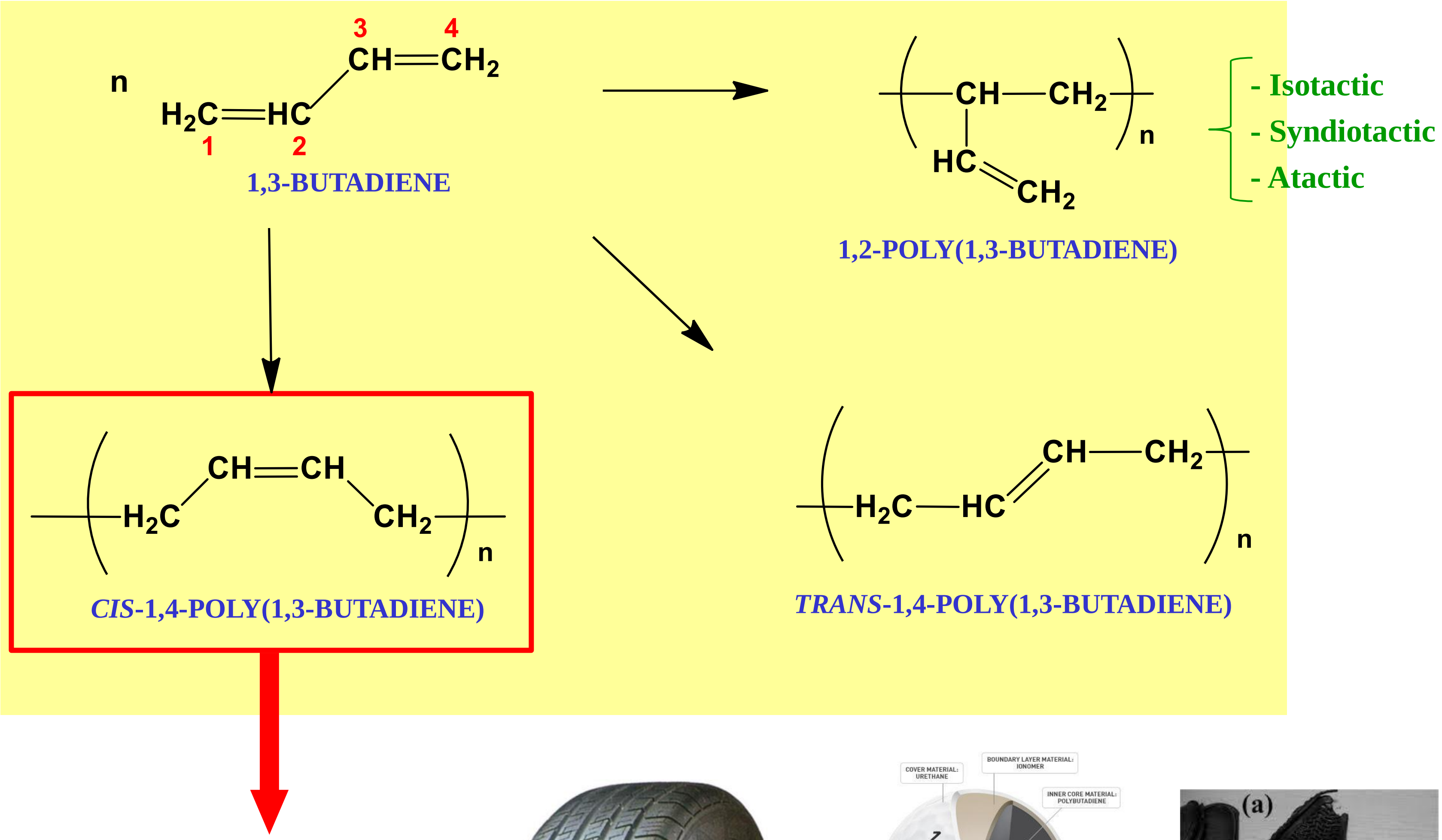
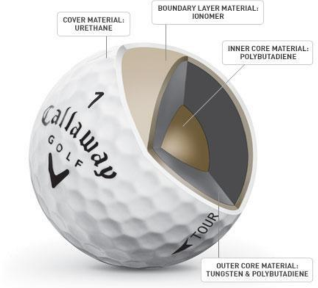
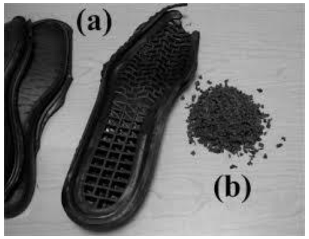
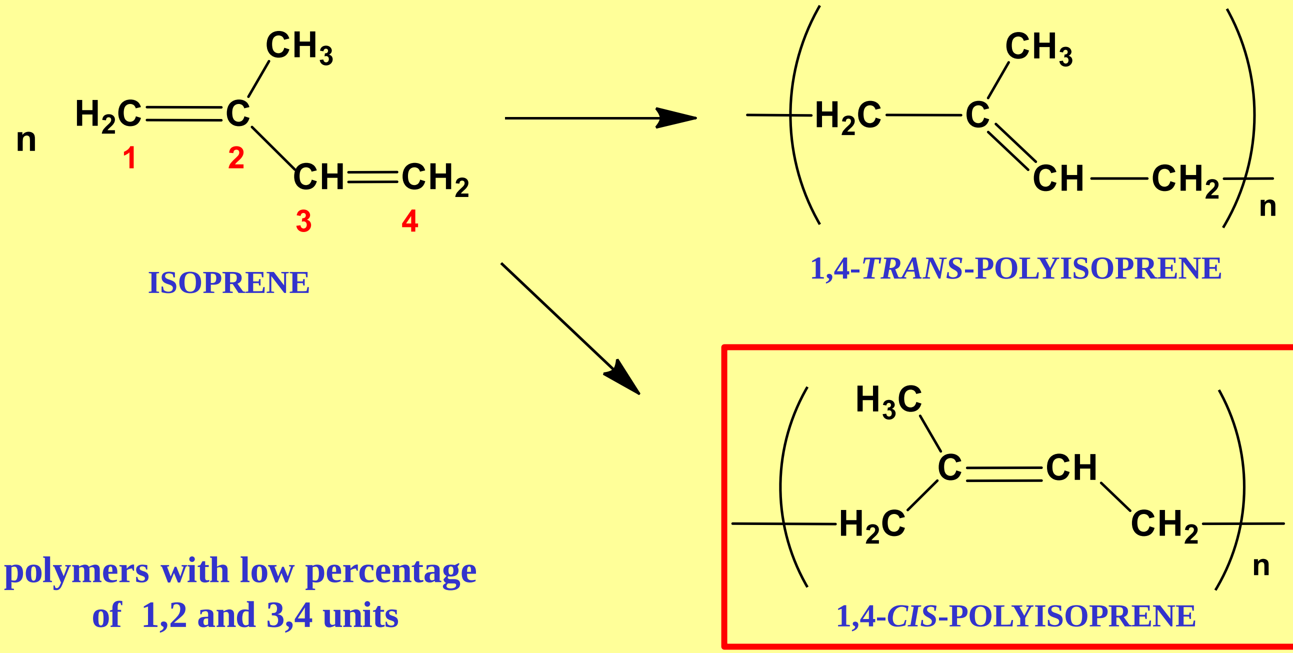
POLYMERIZATION OF DIENES



SYNTHETIC RUBBER







polymers with low percentage of 1,2 and 3,4 units

From natural sources:
GUTTA-PERCHA

Hard material:
- Electrical insulator
- Old golf balls
- Dentistry

THERMOPLASTIC

From natural sources:
NATURAL RUBBER

- *Hevea Brasiliensis*
- *Guayule*

SYNTHETIC NATURAL RUBBER

From natural sources:

NATURAL THERMOPLASTIC
(1,4-*trans*-polyisoprene)

- Gutta-Percha

NATURAL RUBBER
(1,4-*cis*-polyisoprene)

- Hevea Brasiliensis

- Guayule

SYNTHETIC RUBBER MARKET

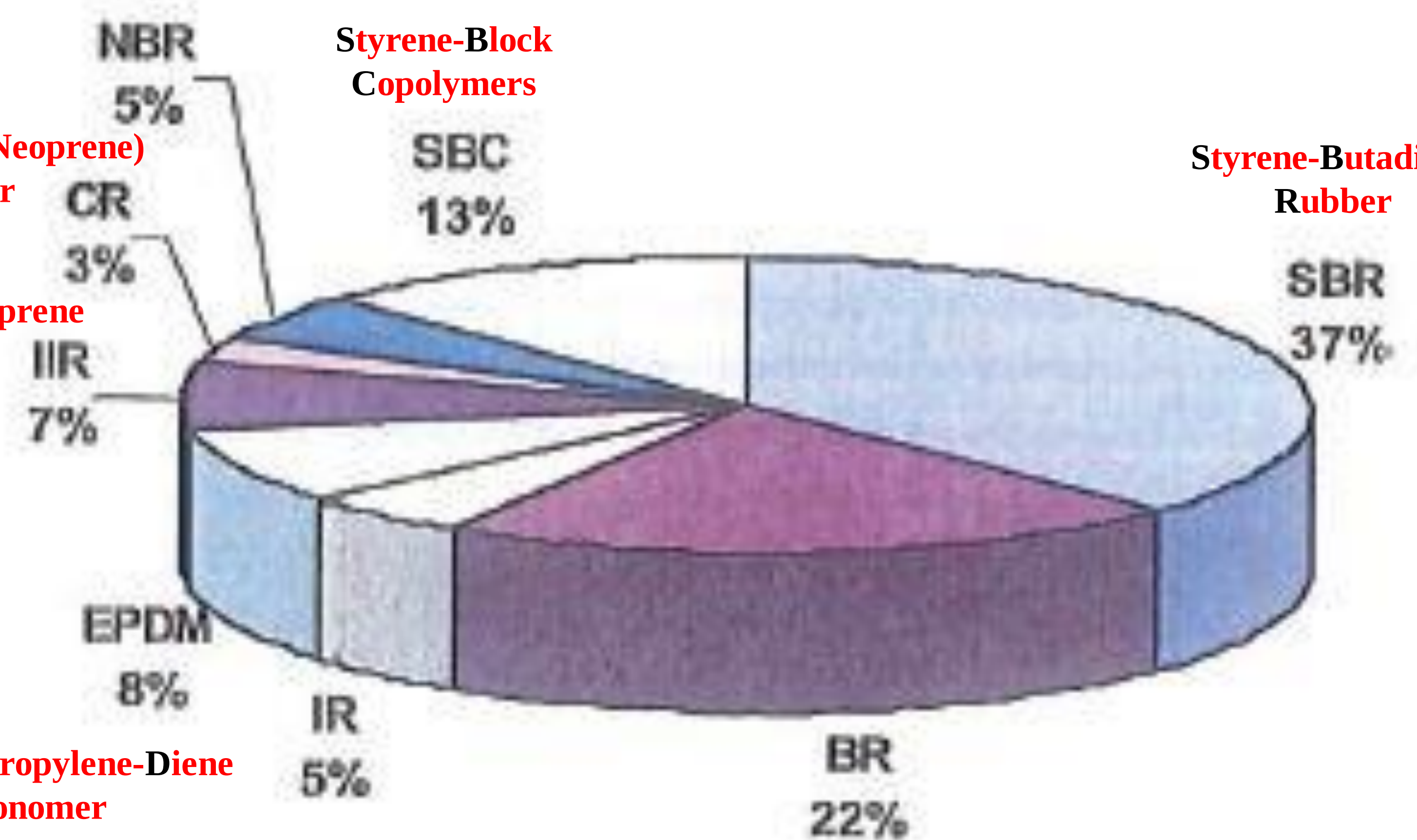
(Acrylo)Nitrile-Butadiene Rubber

Styrene-Block Copolymers

Chloroprene (Neoprene) Rubber

Styrene-Butadiene Rubber

Isobutene-Isoprene Rubber



Ethylene-Propylene-Diene Monomer

Isoprene Rubber

Butadiene Rubber

STEREOREGULAR ELASTOMERS

1,4-*CIS*-POLYBUTADIENE

~3.2 Mton

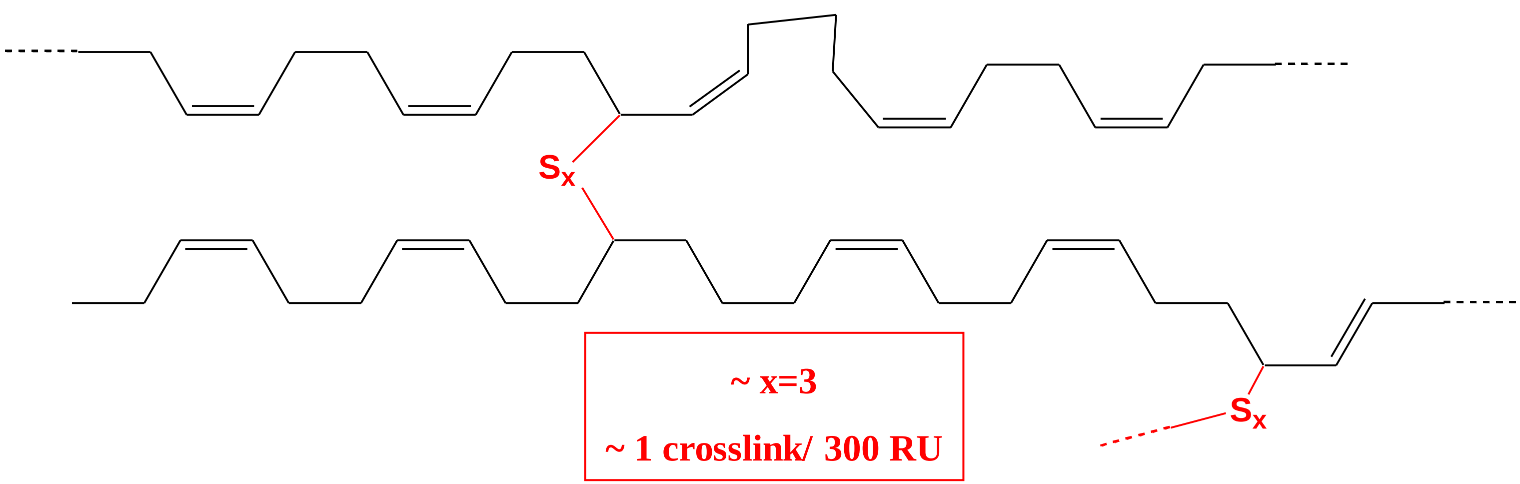
1,4-*CIS*-POLYISOPRENE

~0.75 Mton

Production depends on the NATURAL RUBBER market

~10.3 Mton

S_8 **Vulcanization**



MACROMOLECULAR NETWORK

PolyButadiene Rubber World Producers

Company	Annual Capacity (thousand of metric tons)	% of World Capacity
LANXESS	488	15,4
Sinopec	**390**	**12,3**
Goodyear	265	8,4
Korea Kumho Petrochemicals	222	7,0
UBE Industries	173	5,5
PetroChina	**160**	**5,1**
Polimeri Europa	**160**	**5,1**
Firestone Polymers	150	4,7
Voronezhsynthiezkauchuk	141	4,5
others	1010	32,0
Total	3159	100

North America	Central and South America	Western Europe	Central and Western Europe	Asia*	Middle East/ Africa/Oceania	*Total*
755	93	355	421	**1520**	45	3159

*China, Taiwan, India, Japan, Korea, Thailandia

STEREOSPECIFIC CATALYSTS - POLYBUTADIENE

- **ZIEGLER-NATTA CATALYSTS**

High content (>90%) in:

1,4-cis	**1,4-*trans***	**1,2 (syndiotactic)**
TiI_4 + Al(*i*Bu)$_3$ (1:4-5), 30 ºC	γ-$TiCl_3$ + $AlEt_3$	$Ti(OR)_4$ + $AlEt_3$ (1:7), 15 ºC
$CoCl_2$ + $Al_2Cl_3Et_3$ (1:1000), 5 ºC	VCl_3 + $AlEt_3$ (1:2), 15 ºC	$V(acac)_3$ + $AlEt_3$ (1:6-10), 15°C
$Co(acac)_2$ + $AlEt_2Cl$ + H_2O (branched polymer)	VCl_4 + $AlEt_3$ (1:1.8), 15 ºC	$Cr(C_6H_5CN)$ + $AlEt_3$ (1:2) $Cr(C_6H_5CN)$ + $AlEt_3$ (1:10) (isot.)
$Ni(octanoate)_2$ + $AlEt_3$ + $BF_3{\cdot}OEt_2$ (1:17:15), 50 ºC	$V(acac)_3$ + $AlEt_2Cl$ + Cl_3CCO_2H, 80 ºC	$Co(acac)_3$ + $AlEt_3$ (1:50), 16°C
$U(OR)_4$ + $AlEt_2Cl$	$VOCl_3$ + $AlEt_3$	$Co(acac)_3$ + $AlEt_3$ + H_2O + CS_2
$Nd(neodecanoate)_3$ + AlR_2Cl + AlR_3 , 60 ºC	$V(acac)_3$ + MAO (1:1000)	

ZIEGLER-NATTA CATALYSTS

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(groups 4 - 10)		**(groups 1, 2, 13 and 14)**

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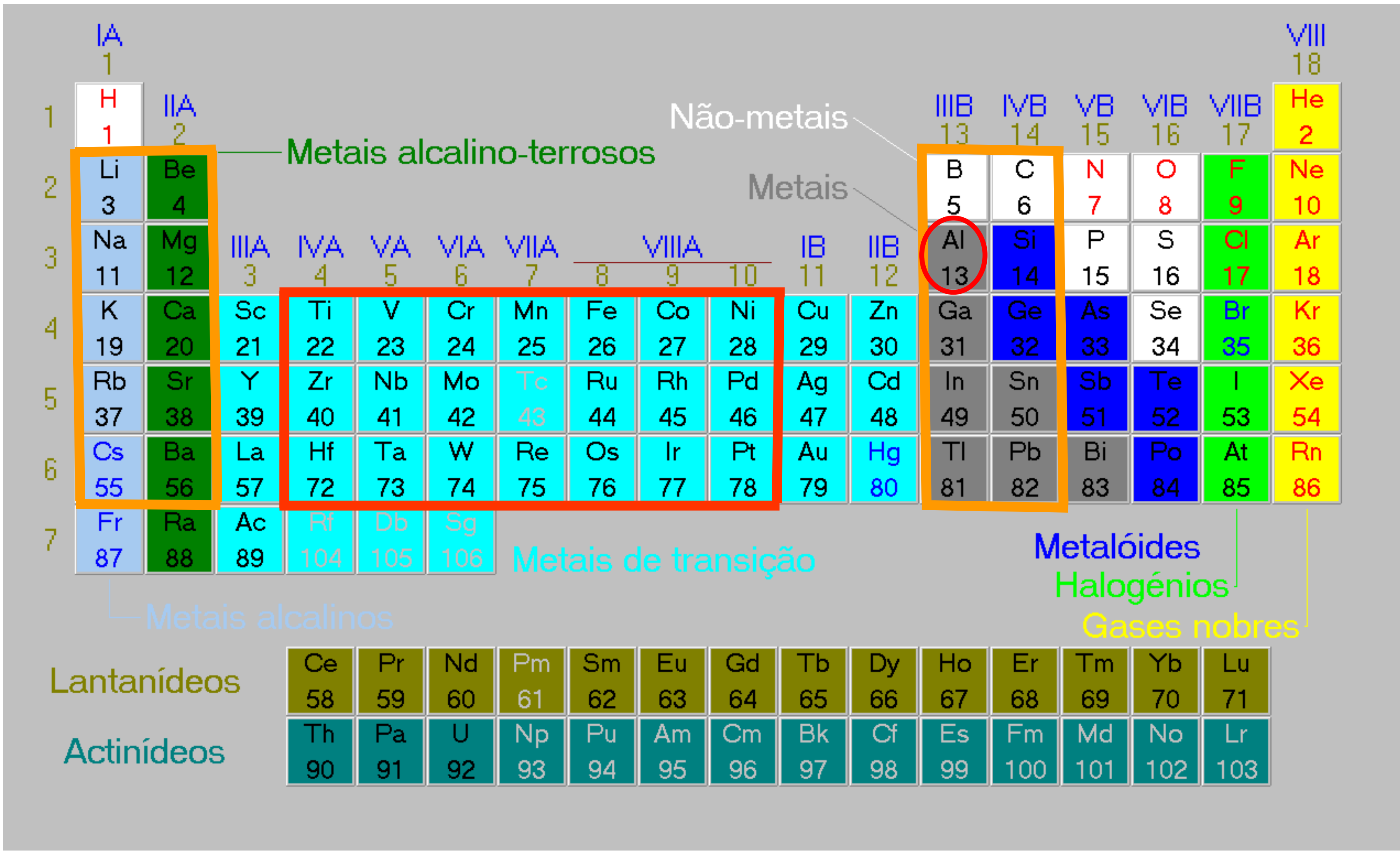

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Ni(octanoate)$_2$ + $AlEt_3$ + $BF_3{\cdot}OEt_2$ (1:17:15), 50 ºC	$V(acac)_3$ + $AlEt_2Cl$ + Cl_3CCO_2H, 80 ºC	$Co(acac)_3$ + $AlEt_3$ (1:50), 16°C
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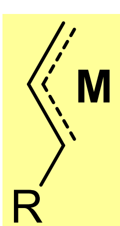
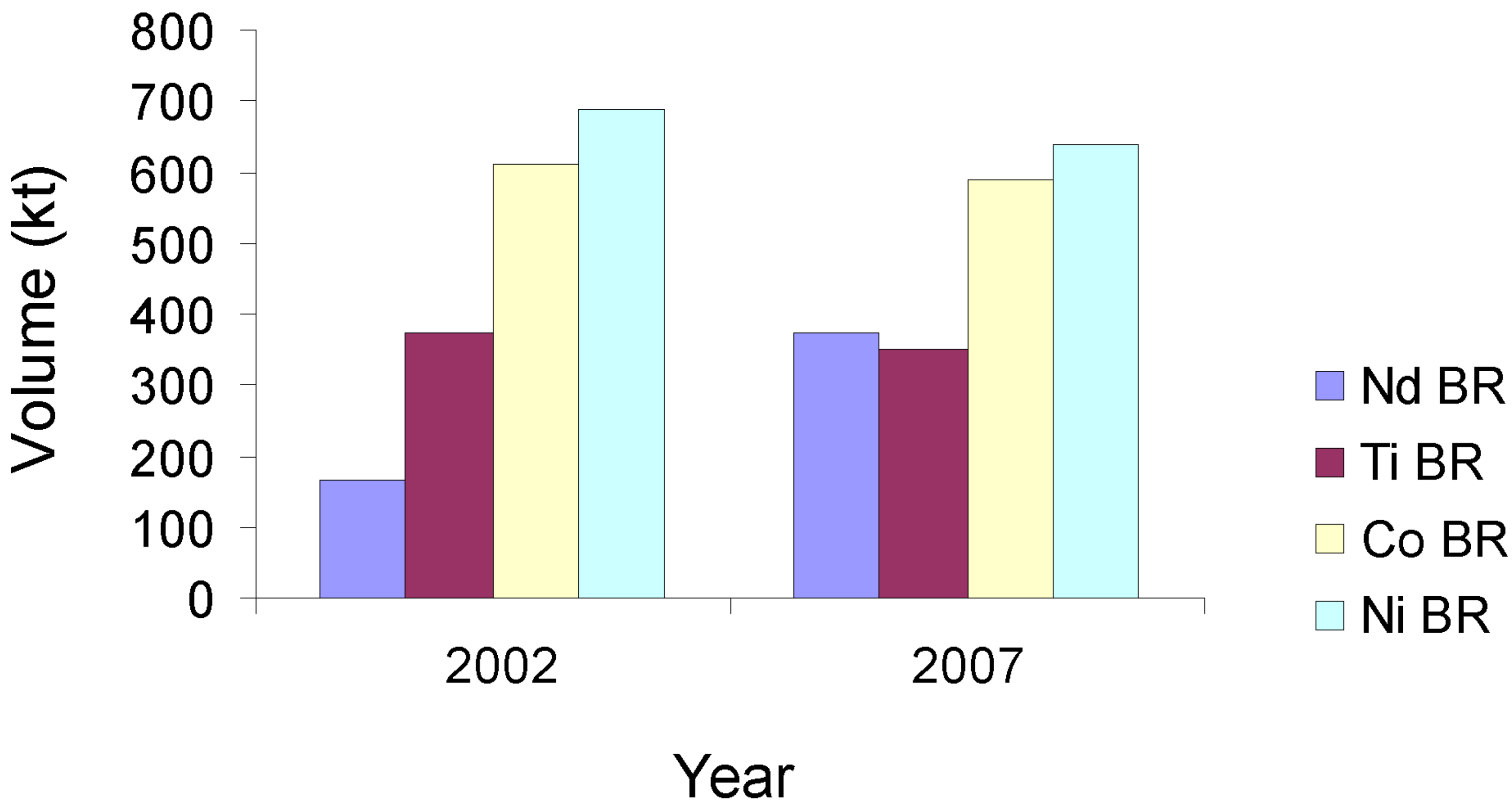
Nd(neodecanoate)$_3$ + AlR_2Cl + AlR_3 , 60 ºC	$V(acac)_3$ + MAO (1:1000)	

• ALLYL METAL CATALYSTS (Aluminium-free catalysts = without Alkyl Aluminium cocatalyst)

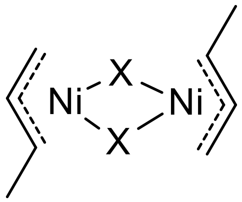


M= Cr, Co, Nb, W, Rh, U, Ni

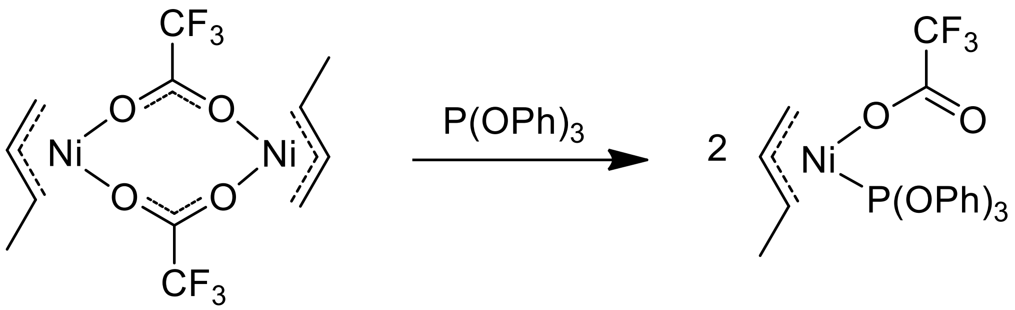
Catalysts for high *cis*-1,4 Polybutadiene



EXAMPLES OF ALLYL NICKEL STEREOSPECIFIC CATALYSTS



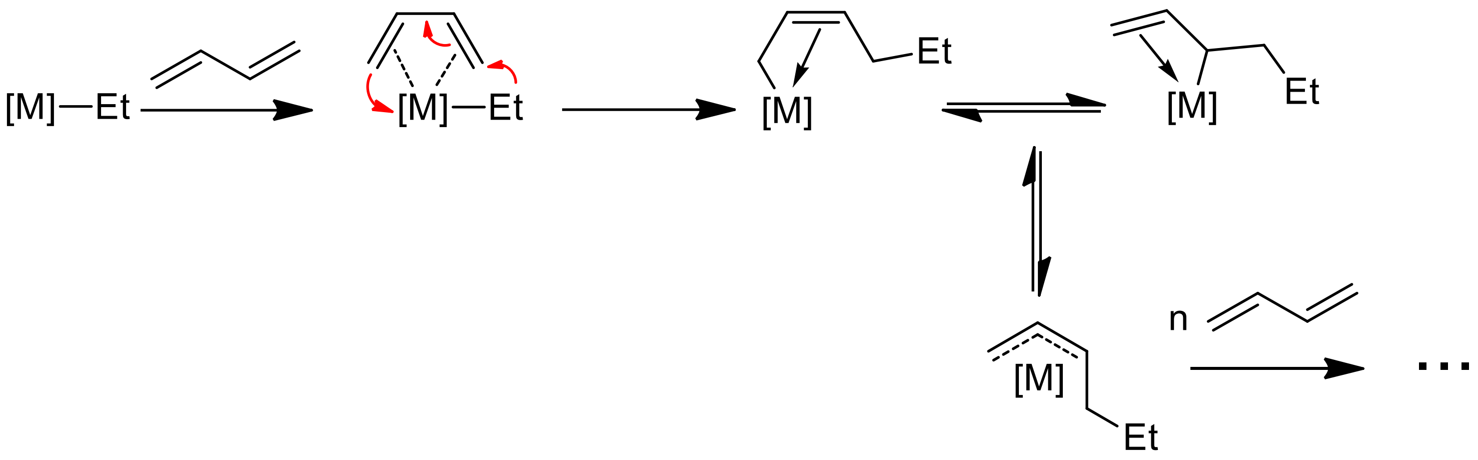
X	1,4-*cis*	1,4-*trans*	1,2
Cl	92	6	2
Br	72	25	3
I	0	97	3



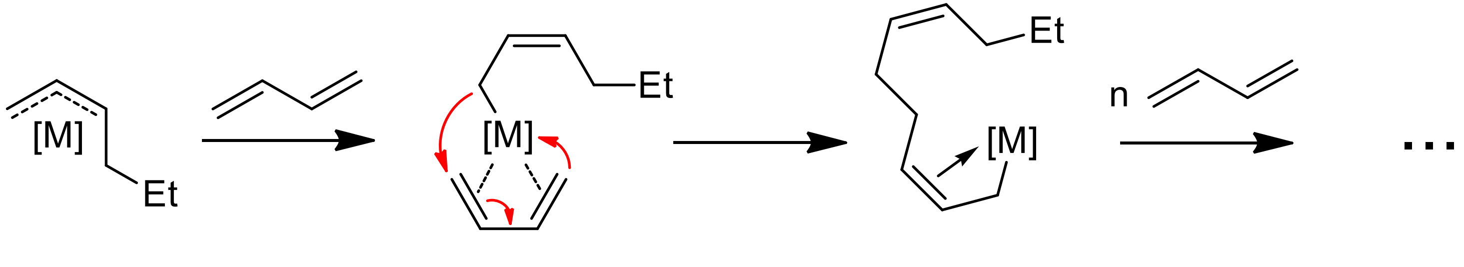
1,4-*cis*	97	0
1,4-*trans*	2	96
1,2	1	4

STEREOREGULATION MECHANISM

- **INITIATION (Z-N CATALYSTS)**



- **PROPAGATION**



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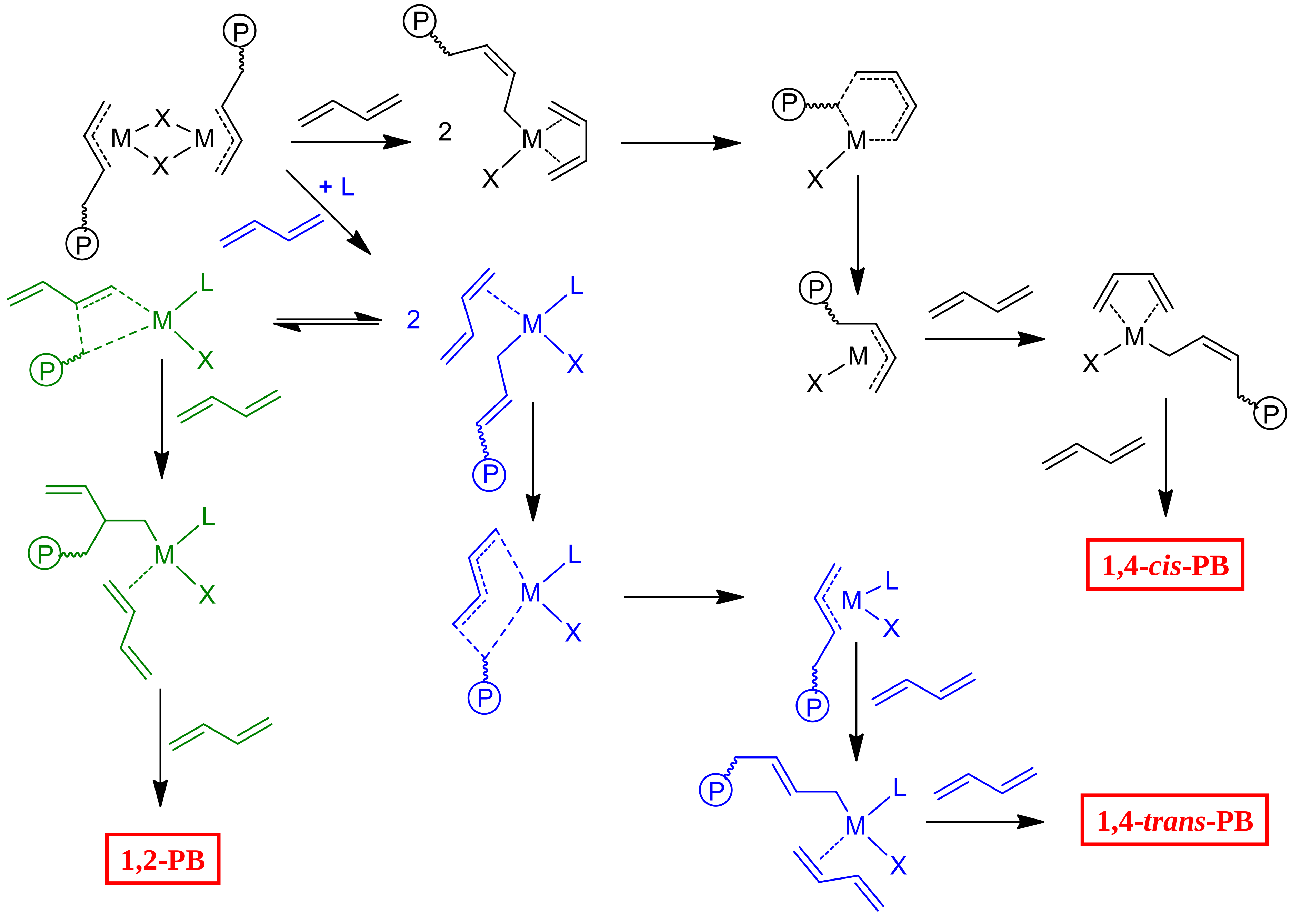

STEREOSPECIFIC CATALYSTS - POLYISOPRENE

- **ZIEGLER-NATTA CATALYSTS**

High content (>90%) in:

1,4-cis	**1,4-*trans***	**3,4**
$TiCl_4 + AlEt_3$ (Al/Ti > 1)	$TiCl_4 + AlEt_3$ (Al/Ti < 1)	$Ti(OR)_4 + AlEt_3$
	α-$TiCl_3 + AlR_3$	
	$VCl_3 + AlEt_3$	

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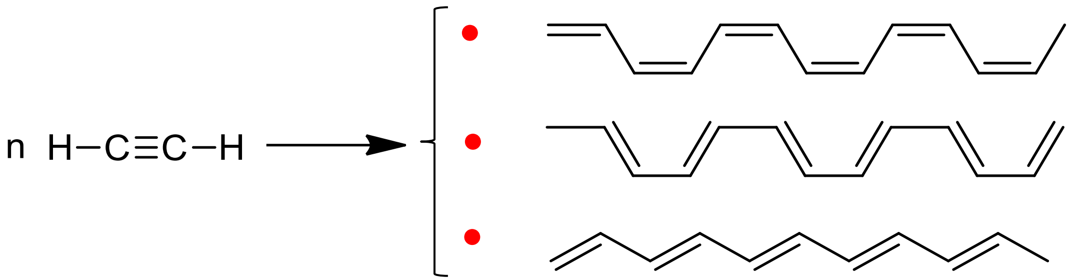
POLYMERIZATION OF ALKYNES

(POLYMERIZATION OF ACETYLENE)



cis-transoid

trans-cisoid

trans-transoid

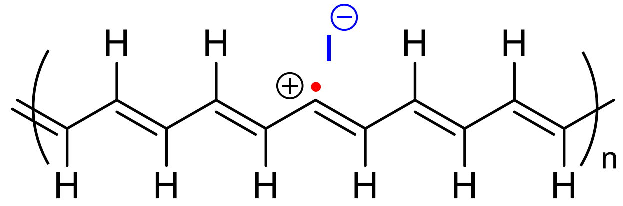
cis
insulator
($\sigma = 4\times10^{-9}\ \Omega^{-1}\ cm^{-1}$)

trans
semiconductor
($\sigma = 9\times10^{-5}\ \Omega^{-1}\ cm^{-1}$)

doped with oxidants (1977)
(ex: I_2)

conductor
$\sigma = 1.5\times10^{3}\ \Omega^{-1}\ cm^{-1}$

Au ($\sigma = 2.4\times10^{4}$)
Cu ($\sigma = 7.2\times10^{4}$)



CONDUCTION (?)

- **Intermolecular**
- **Interchain**
- **Intergrain**

POLYACETYLENE

- **Insoluble (in organic solvents)**
- **Unstable in air (double bonds oxidation)**
- **Bad mechanical properties (poorly processable)**

the objective was to make conducting films

● SYNTHESIS - CATALYSTS

- $Ti(OBu)_4$ + $AlEt_3$ (Natta, 1958)

- $Ti(OBu)_4$ + $AlEt_3$ (Al/Ti ~ 4) (Shirakawa, 1974) **good films when $[Ti] < 10^{-3}$ M**

- $Ti(OBu)_4$ + LiBu (Li/Ti ~ 2) **high *trans* %**

- $MoCl_5$ + $SnPh_4$

- WCl_6 + $SnPh_4$

- $NiX_2(PR_3)_2$ (X= Cl, Br, I) **high *trans* %**

POLYACETYLENE

- **BASF METHOD** (best commercial polyacetylene)

- $Ti(OBu)_4 + AlEt_3$ (Al/Ti ~ 4)
- $Ti(OBu)_4 + LiBu$ (Li/Ti ~ 2)

SOLVENT:

very viscous silicone

↓

Polymers with lower content of *sp*$_3$ defects

↓

Better morphological properties (better oriented fibres)

Films produced on HDPE or PP supports

↓ Stretching 7× the original length

Highly oriented transparent films

↓ Doping with I_2

Ti/Al catalyst: $\sigma = 2\times10^4\ \Omega^{-1}\ cm^{-1}$ (20 μm film)
$\sigma = 8\times10^3\ \Omega^{-1}\ cm^{-1}$ (0.1 μm film)

Ti/Li catalyst: $\sigma \sim 10^5\ \Omega^{-1}\ cm^{-1}$

BASF abandoned this process with the appearance of new conducting polymers (more stable and processable)

POLYMERIZATION OF SUBSTITUTED ACETYLENES

$H-C\equiv C-R$ **or** $R-C\equiv C-R$

POLYMERS:
- **More soluble (in organic solvents)**
- **More stable in air**
- **The majority are electric insulators**

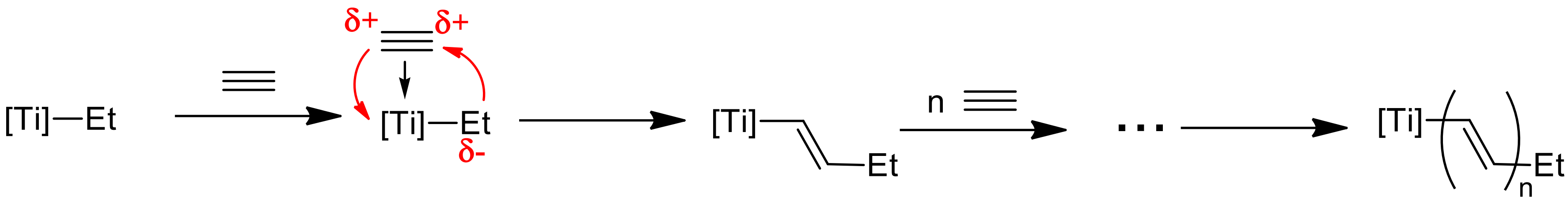
- **CATALYSTS**

- $MoCl_5 + SnPh_4$
- $WCl_6 + SnPh_4$
→ **Small R groups**

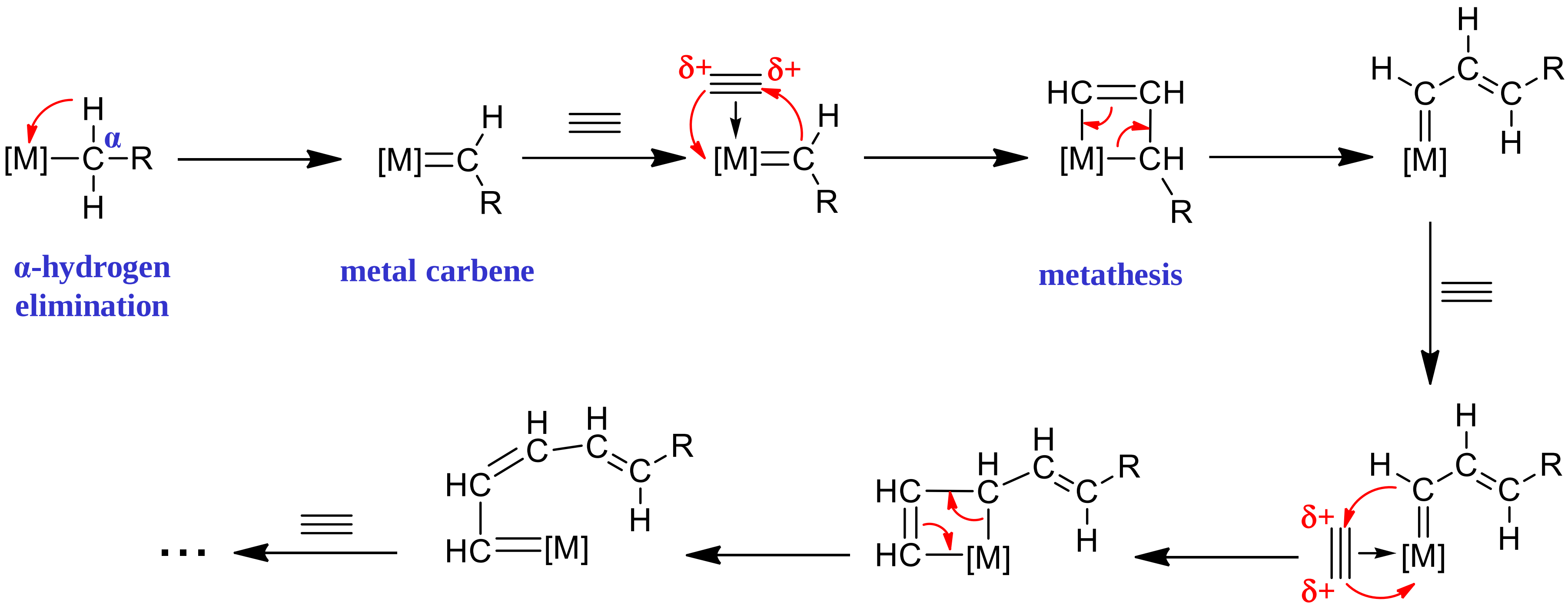
- $NbCl_5 + SnPh_4$
- $TaCl_5 + SnPh_4$
→ **Bulky R groups (ex: $-SiR_3$)**

MECHANISM

- **Ti ZIEGLER-NATTA CATALYSTS (insertion mechanism)**



- **Mo, W, Nb, Ta (Groups 5 and 6) ZIEGLER-NATTA CATALYSTS (metathesis mechanism ??)**



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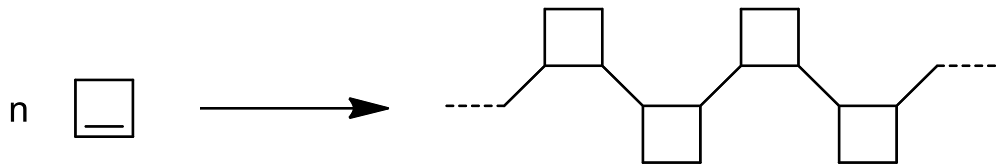
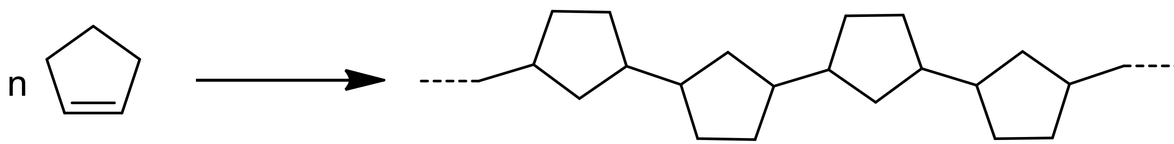
RING-OPENING METATHESIS POLYMERIZATION (ROMP)

MONOMERS: **Cycloolefins and Cycloalkynes**

When <u>Ziegler-Natta</u> or <u>metallocene</u> catalysts based on <u>Group 4 metals</u> (Ti, Zr, Hf) or <u>post-metallocene</u> catalysts are used the polymerization occurs by Insertion (or Vinyl-addition) Polymerization:



cyclobutene — poly(cyclobutene)



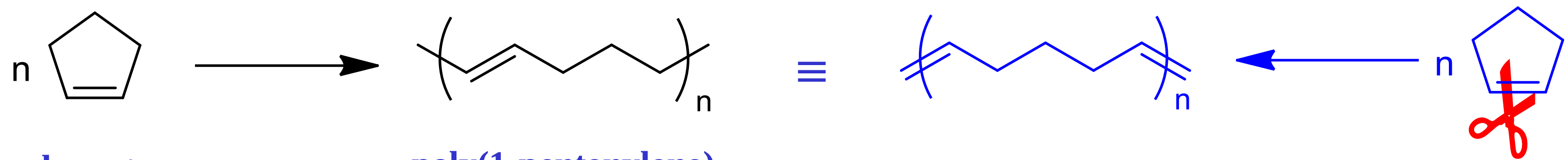
cyclopentene — poly(cyclopentene)

- **The polymers do not have double bonds in the main chain**
- **Very rigid polymers (high melting temperatures)**
- **May copolymerize with linear α-olefins (metallocene catalysts) to give amorphous copolymers**

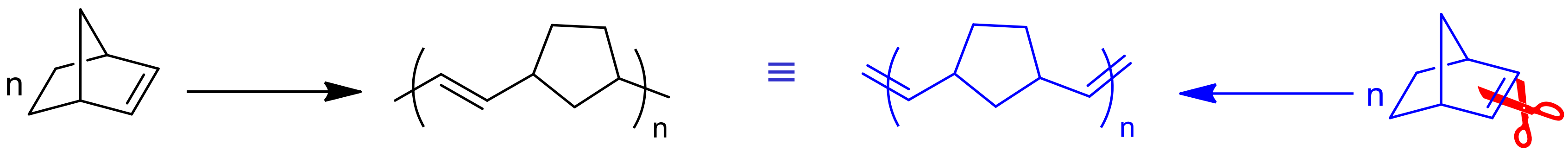
BUT…

RING-OPENING METATHESIS POLYMERIZATION (ROMP)

When Ziegler-Natta catalysts based on Group 6 metal (Mo, W) or metal carbene catalysts are used the polymerization occurs by Ring-Opening Methathesis Polymerization:



cyclopentene **poly(1-pentenylene)**

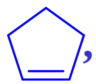


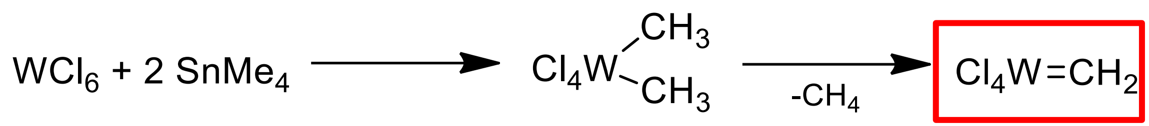
norbornene **poly(cyclopentenylenevinylene)**

- **The monomer double bond is retained in the polymer main chain**
- **The polymerization has a living character**
- **Easy block-copolymerization**
- **Ring tension favours ROMP (thermodynamically)**

ROMP CATALYSTS

• ZIEGLER–NATTA CATALYSTS

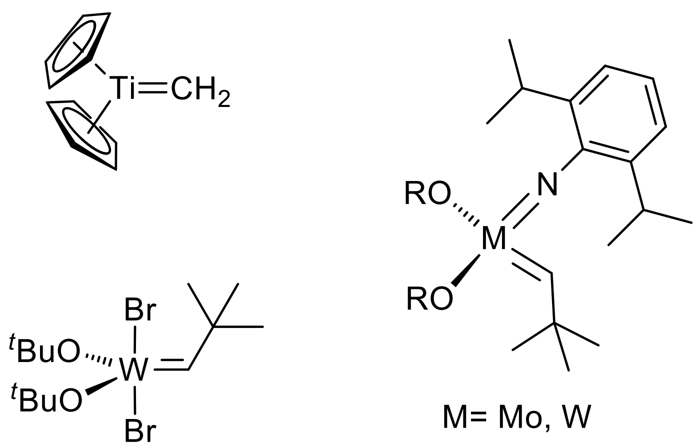
- WCl_6 + $SnMe_4$
- WCl_6 + $ZnMe_2$
- MoO_3 / γ-Al_2O_3
- $MoCl_5$ + $AlEt_3$ ( , Natta, 1964)



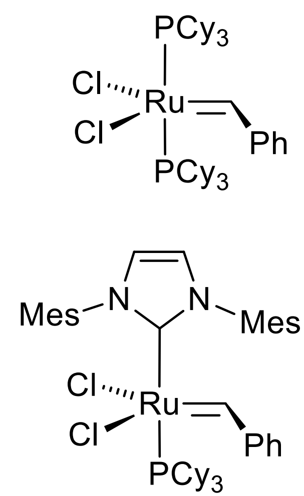
α-hydrogen elimination

carbene

• WELL-DEFINED CARBENE CATALYSTS



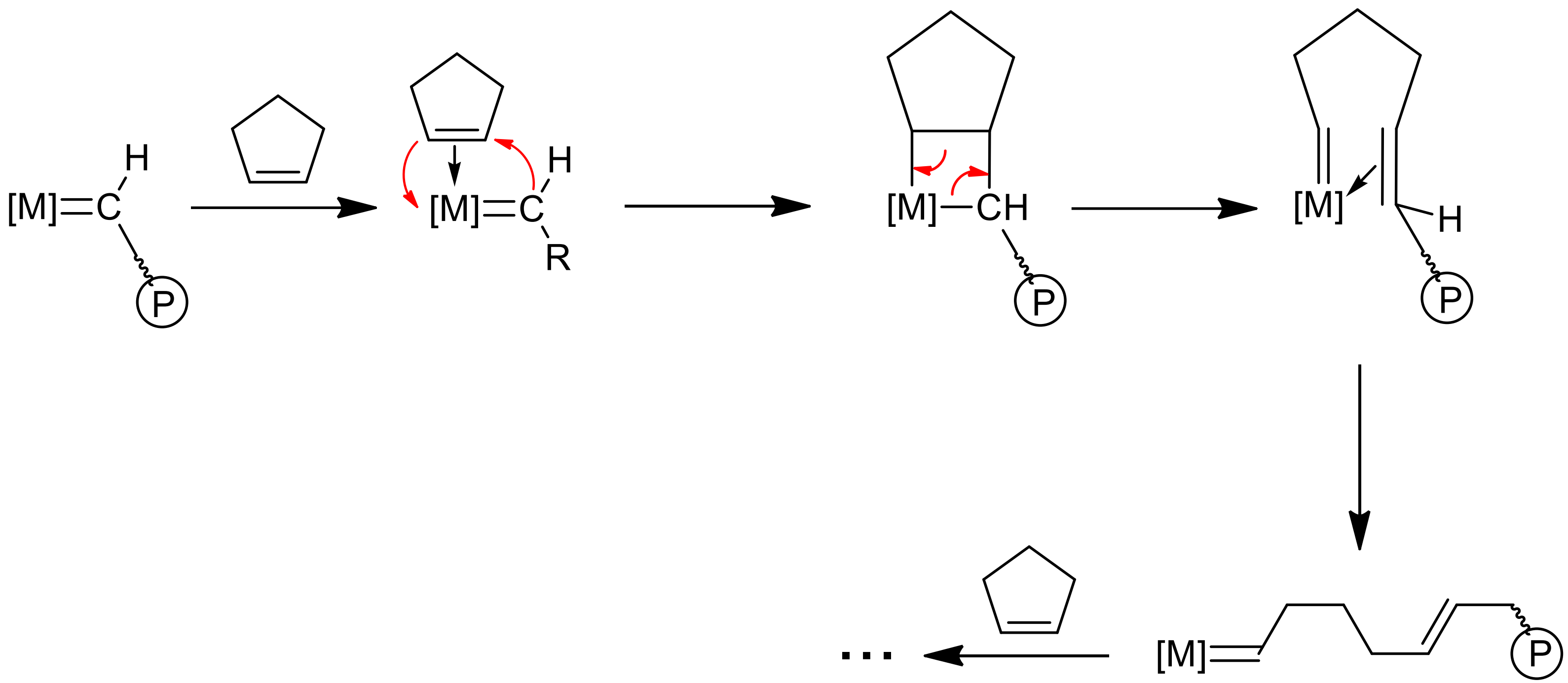
Schrock type catalysts



Grubbs type catalysts

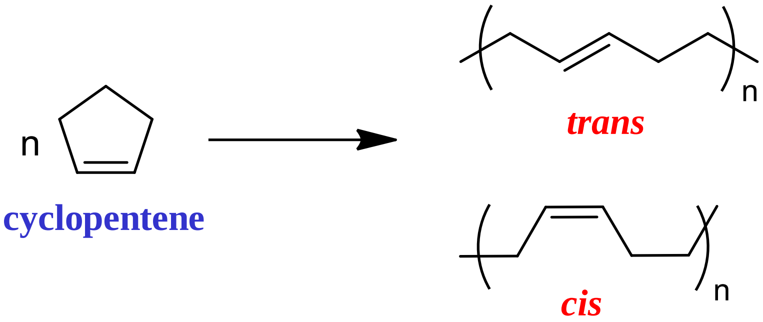
MECHANISM

• PROPAGATION



Living polymerization

ASSORTED EXAMPLES OF ROMP



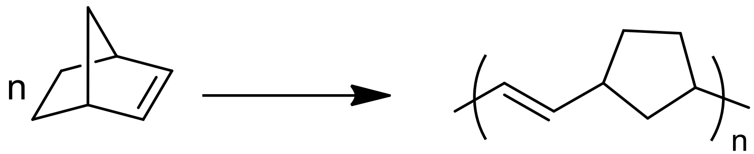
cyclopentene

poly(1-pentenylene)

good elastomer

good elastomer

- Tires

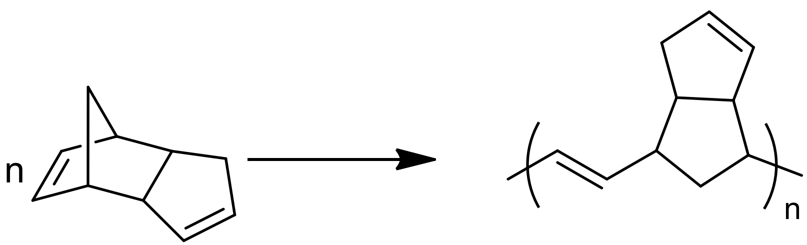


norbornene

poly(cyclopentenylenevinylene)

Norsorex®

- Oil superabsorbent (400% elongation)
- Cleaning up oil spills
- Acoustic insulator
- Gaskets
- Anti-vibration material
- Shock absorption material

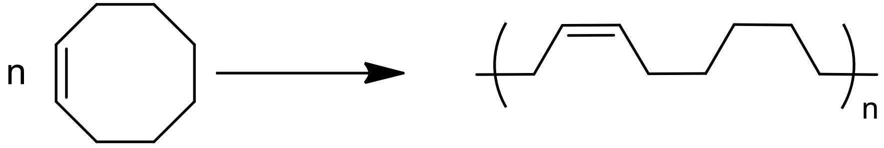


endo-dicyclopentadiene

poly(dicyclopentadiene)

Metton®

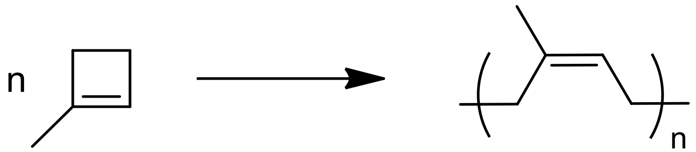
- Commercial engineering plastic for moulding



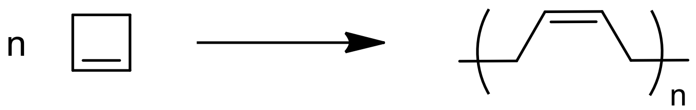
cyclooctene **poly(1-octenylene)**

Vestenamer®

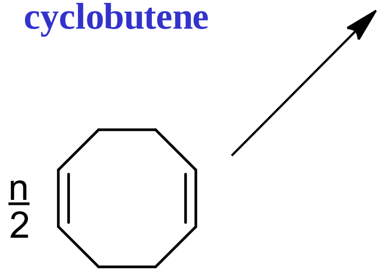
- Minor component in elastomer blends with SBR for gaskets, brake hoses and printing rollers



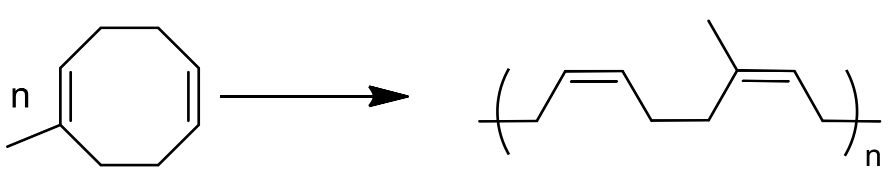
1-methyl-cyclobutene **1,4-*cis*-polyisoprene**



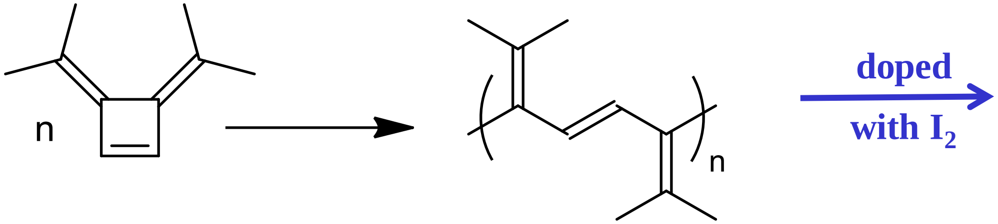
cyclobutene **1,4-*cis*-polybutadiene**



1,5-cyclooctadiene

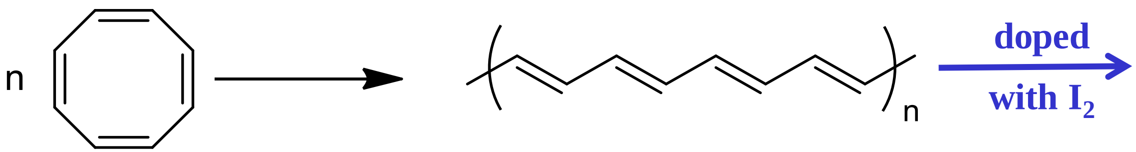


1-methyl-1,5-cyclooctadiene **poly(1,4-*cis*-butadiene)-*alt*-poly(1,4-*cis*-isoprene)**



$\sigma = 2\times10^2\ \Omega^{-1}\ cm^{-1}$

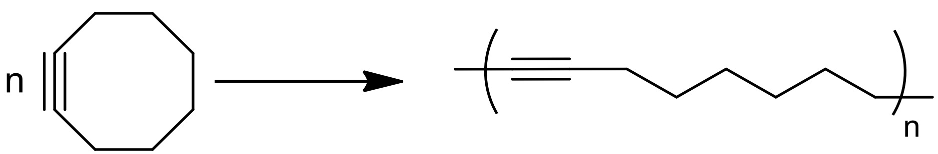
Colourless, soluble, oxidizable



$\sigma = 10^3\ \Omega^{-1}\ cm^{-1}$

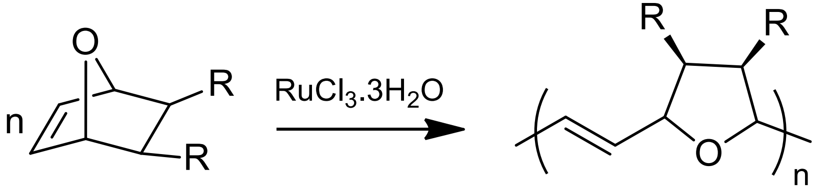
1,3,5,7-cyclooctatetraene

polyacetylene



cyclooctyne

poly(1-octynylene)



7-oxa-2,3-dimethyl norbornene

$M_n = 10^6$

in aqueous solution !!

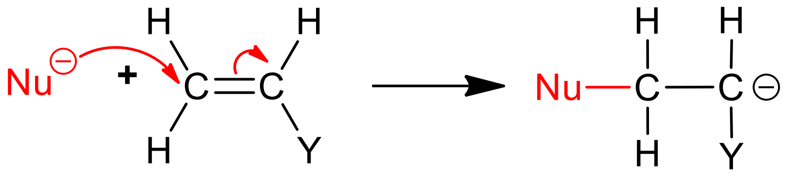
In general, the coordination polymerization experimental conditions impose strict absence of H_2O and O_2

Metal-Catalyzed Polymerization

(Coordination Polymerization)

- *Polymerization of Olefins (Insertion)* ✓ *Prof. Barbara Milani*
- *Polymerization of Dienes (Insertion)*
- *Polymerization of Alkynes*
- *Ring Opening Metathesis Polymerization (ROMP)*
- ***Classical Anionic Polymerization***
- *Ring Opening Polymerization (ROP)*
- *Metal-mediated Radical Polymerization*

ANIONIC POLYMERIZATION



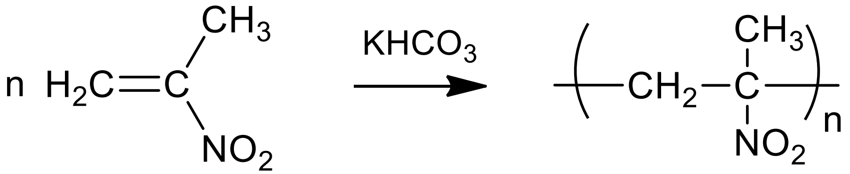
monomer

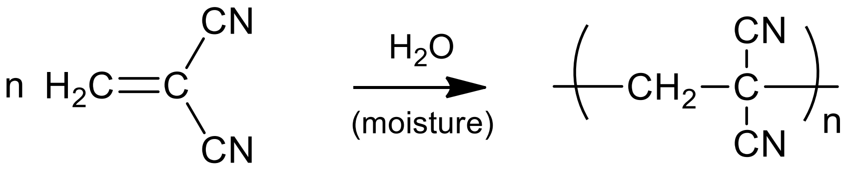
MONOMERS

Most convenient monomers: **those containing Y substituents that stabilize carbanions (electron withdrawing by induction and/or resonance). Exs: nitro, cyano, carboxyl, vinyl, phenyl**

The more electron attractor group Y is, the less need for strong bases in the initiation:

Exs:





ANIONIC INITIATORS

- **ADDITION OF A NEGATIVE ION TO THE MONOMER**
- **ELECTRON TRANSFER TO THE MONOMER**

- **INITIATION BY ADDITION OF A NEGATIVE ION TO THE MONOMER**

  - **Organolithium compounds**

    Exs: $Li\text{-}CH_3$ **(LiMe)**, $Li\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3$ **(LiBu)** **(soluble in inert solvents)**

  - **Organometallic compounds of the higher alkali metals (Na, K, Rb,…)**
    - **higher ionic character than those based on Li**
    - **less soluble (generally heterogeneous)**

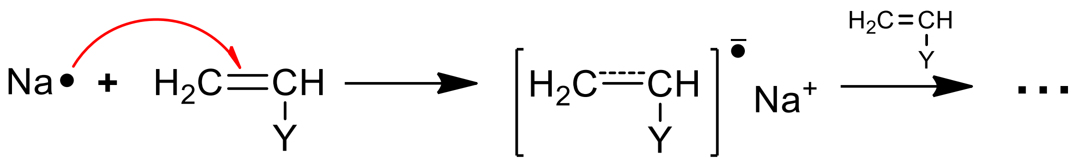
  - **Organometallic compounds of the alkaline earth metals (Ca, Ba)**

  - **Grignard Reagents (RMgX)**

LESS USED

• INITIATION BY ELECTRON TRANSFER TO THE MONOMER

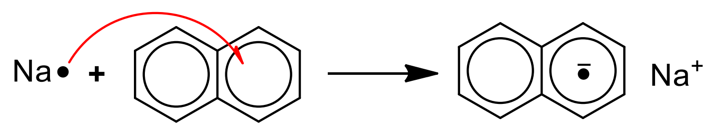
- Alkali Metals
- in solution (of NH_3 or certain ethers)
- in suspension (in inert solvents –"sands")
- supported (in alumina)



radical anion

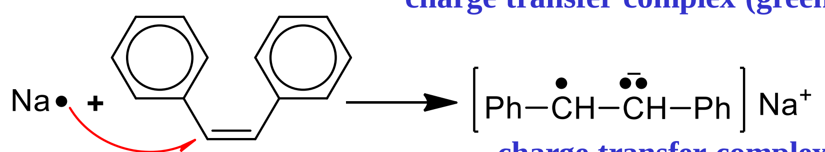
- Alkali Metal Complexes (<u>soluble in inert solvents</u>)

Exs:



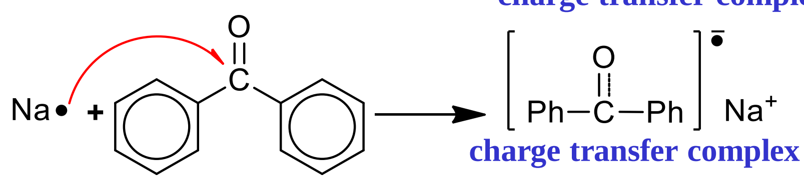
sodium naphthalene

charge transfer complex (green)



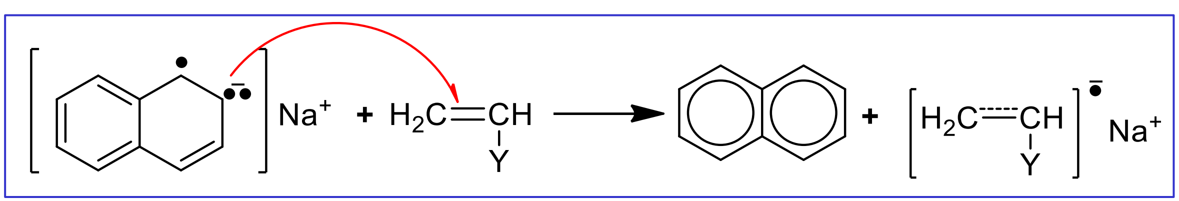
sodium stilbene

charge transfer complex



sodium benzophenone ketyl

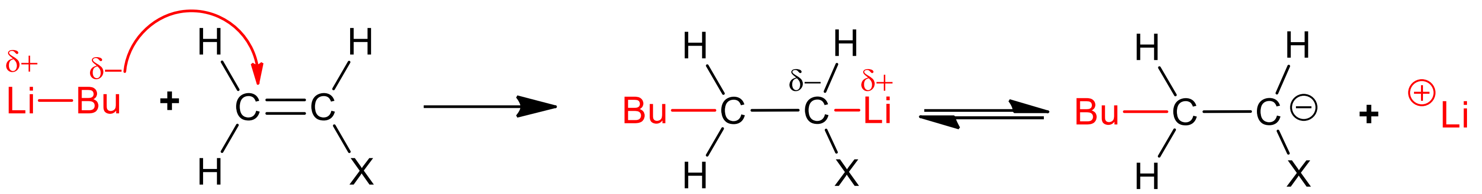
charge transfer complex (blue)



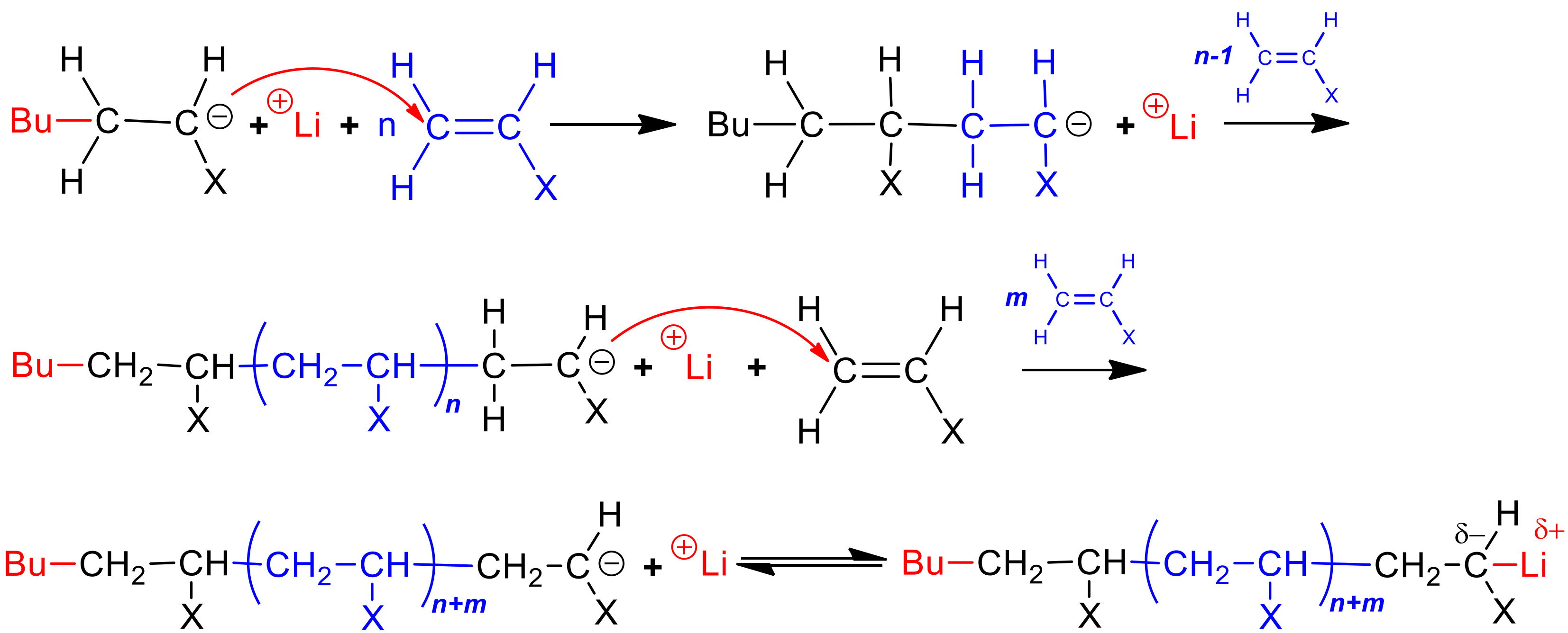
MECHANISM AND KINETICS

- **INITIATION BY ANIONIC SPECIES** **Exs:** **Li-CH_3 (LiMe), Li-CH_2-CH_2-CH_2-CH_3 (LiBu)**

- **Initiation**



- **Propagation**



living polymer **tight ion-pair**

MECHANISM AND KINETICS

• INITIATION BY ANIONIC SPECIES

Exs: $Li\text{-}CH_3$ (LiMe), $Li\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3$ (LiBu)

$$I^{\ominus} + M \xrightarrow{k_i} P_1^{\ominus}$$

$$P_i^{\ominus} + M \xrightarrow{k_p} P_{i+1}^{\ominus}$$

Normally, $r_i >> r_p$ ➡ chains grow all at the same time ➡ $[P_i^{\ominus}]_o = [I]_o$

$$r_p = -\frac{d[M]}{dt} = k_p\,[I]_o[M]$$

$$[M] = [M]_o\, e^{-k_p[I]_o t}$$

M_{RU} = molar mass of the repeating unit

$$\overline{DP}_n = \frac{\overline{M}_n}{M_{RU}}$$

$$\overline{DP}_n = \bar{x} = \frac{[M]_o - [M]}{[I]_o} = \frac{p[M]_o}{[I]_o}$$

$\overline{DP}$ = degree of polymerization

(average number of repeating units per polymer chain)

If the monomer is totally consumed [p = conversion = 1 (*i.e.* 100%)]:

$$\overline{DP}_n = \frac{[M]_o}{[I]_o}$$

$$\frac{\overline{M}_w}{\overline{M}_n} = 1 + \frac{1}{\overline{DP}_n}$$

Poisson distribution

- **If the there are no transfer agents in the reaction medium (including impurities in the solvent):**

↓

LIVING POLYMERIZATION

because there is no chain termination

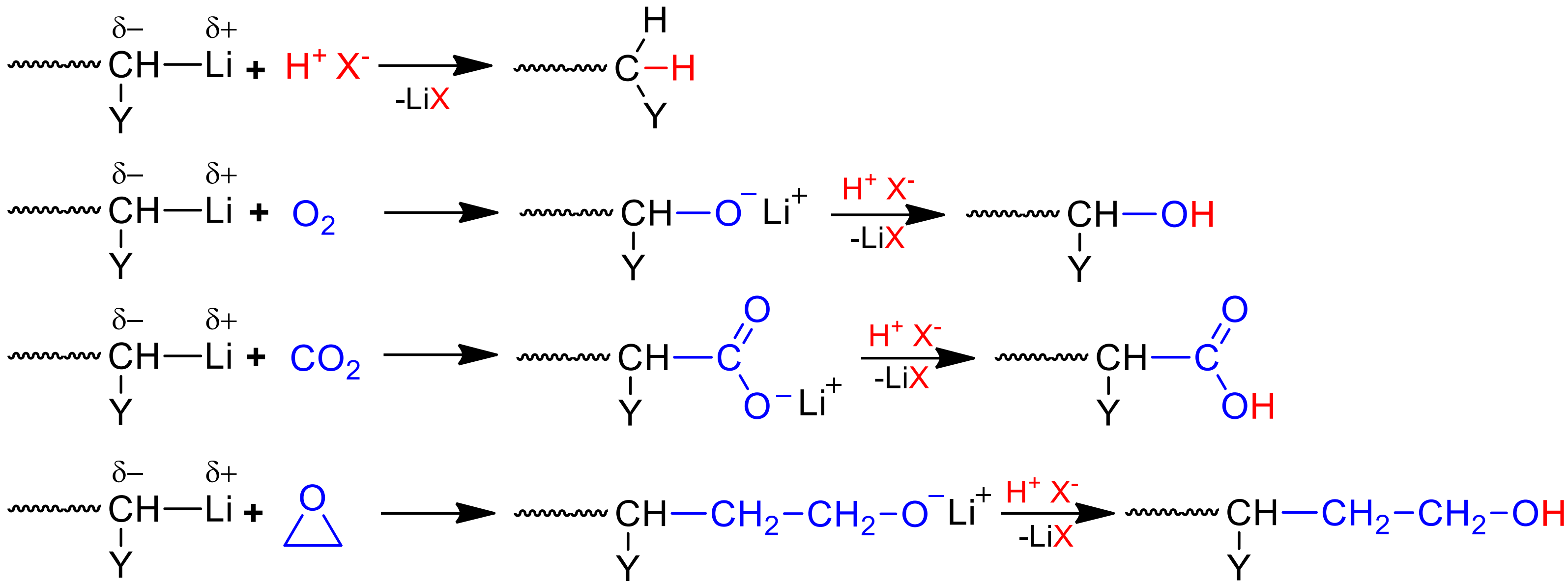
↓

Polymers have a narrow molecular weight distribution i.e. $M_n/M_w \approx 1$

(e.g. GPC/SEC standards)

- **If there is no termination, the chain end is living and can be used for:**

  - **chain end functionalization**
  - **block copolymerization**

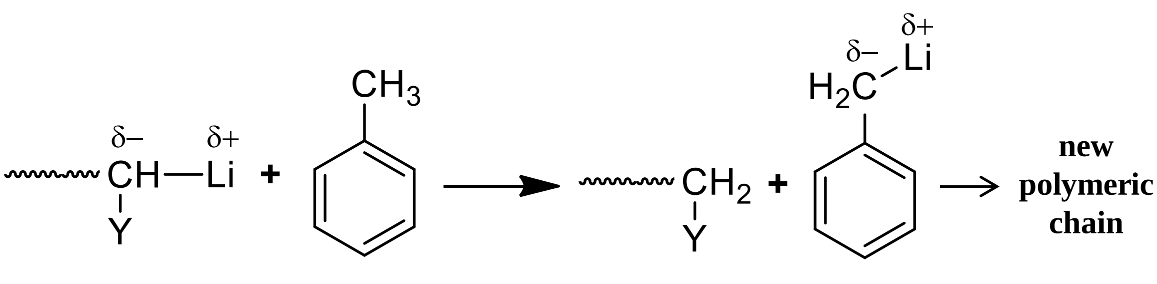


- **Easy control of the molecular weight:**

Routes

- **Stoichiometry** $\left(\overline{DP}_n = \dfrac{[M]_o}{[I]_o}\right)$
- **Termination at time *t* with addition of a terminating agent**
- **Addition of a chain transfer agent** → **to decrease M_n**

Ex:



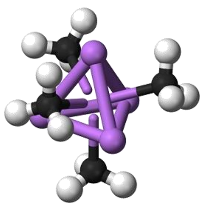
- **The rate of propagation can be influenced by the <u>degree of association</u> between anion and cation, which depends strongly on the SOLVENT:**

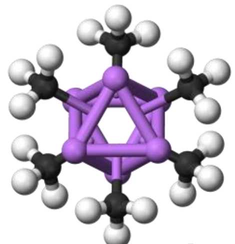
  - **<u>Non-coordinating and weakly polar solvents</u> (*e.g.* hydrocarbons)**

↓

Higher degree of association of the initiator → Lower polymerization rate (r_p)

- Association of the initiator:

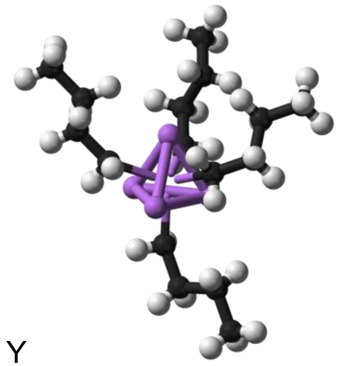


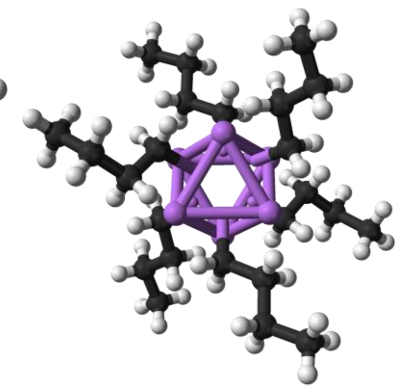


$$n\ LiMe \rightleftharpoons (LiMe)_n$$

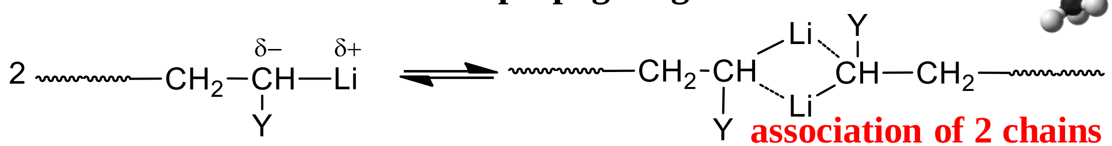
$$n\ LiBu \rightleftharpoons (LiBu)_n$$

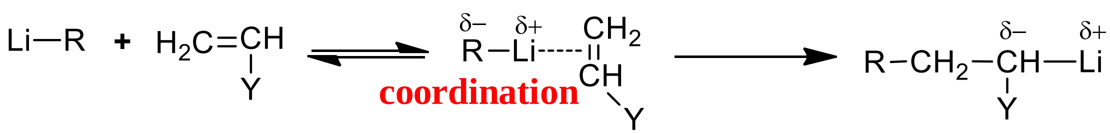
$$n = 1, ..., 4, ..., 6$$





- Association of the propagating chain:

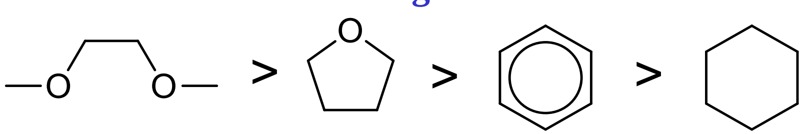




  - **<u>More coordinating and/or more polar solvents</u> (*e.g.* ethers)**

↓

Lower degree of association and higher solvation → Higher polymerization rate (r_p)



DME THF Benzene Cyclohexane

Ex:

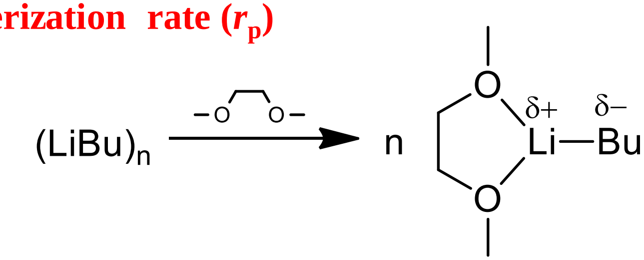


TABLE 7.4. Representative Anionic Propagation Rate Constants, k_p, for Polystyrene[a]

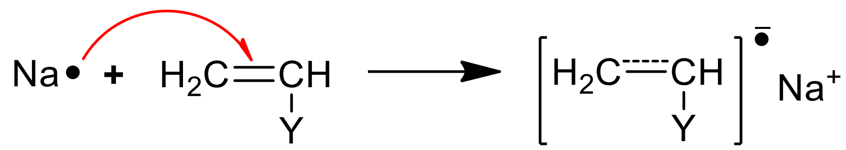
Counterion	*Solvent*	k_p *(L/mol s)*[b]
Na^+	Tetrahydrofuran	80
Na^+	1,2-Dimethoxyethane	3600
Li^+	Tetrahydrofuran	160
Li^+	Benzene	10^{-3}–10^{-1} [c]
Li^+	Cyclohexane	$(5\text{-}100)\times 10^{-5}$ [c]

[a] Data from Morton.[30]

[b] At 25°C unless otherwise noted.

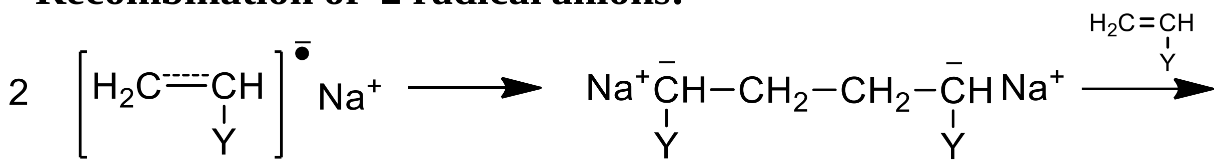
[c] Variable temperature.

• INITIATION BY ELECTRON TRANSFER



radical anion

Recombination of 2 radical anions:



. . . propagation

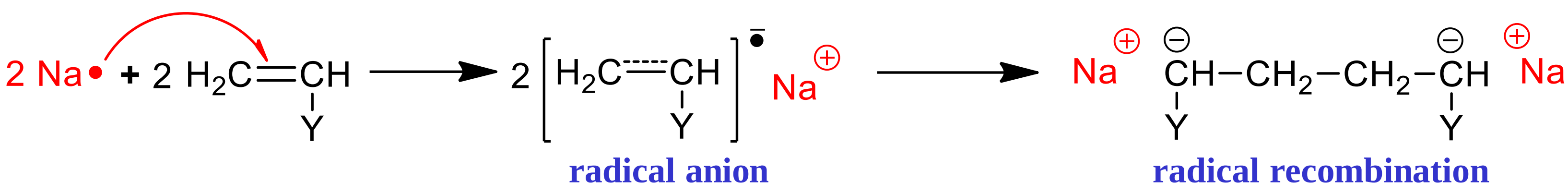
Dianionic chain
with 2 propagation centres

TELECHELIC POLYMERIZATION

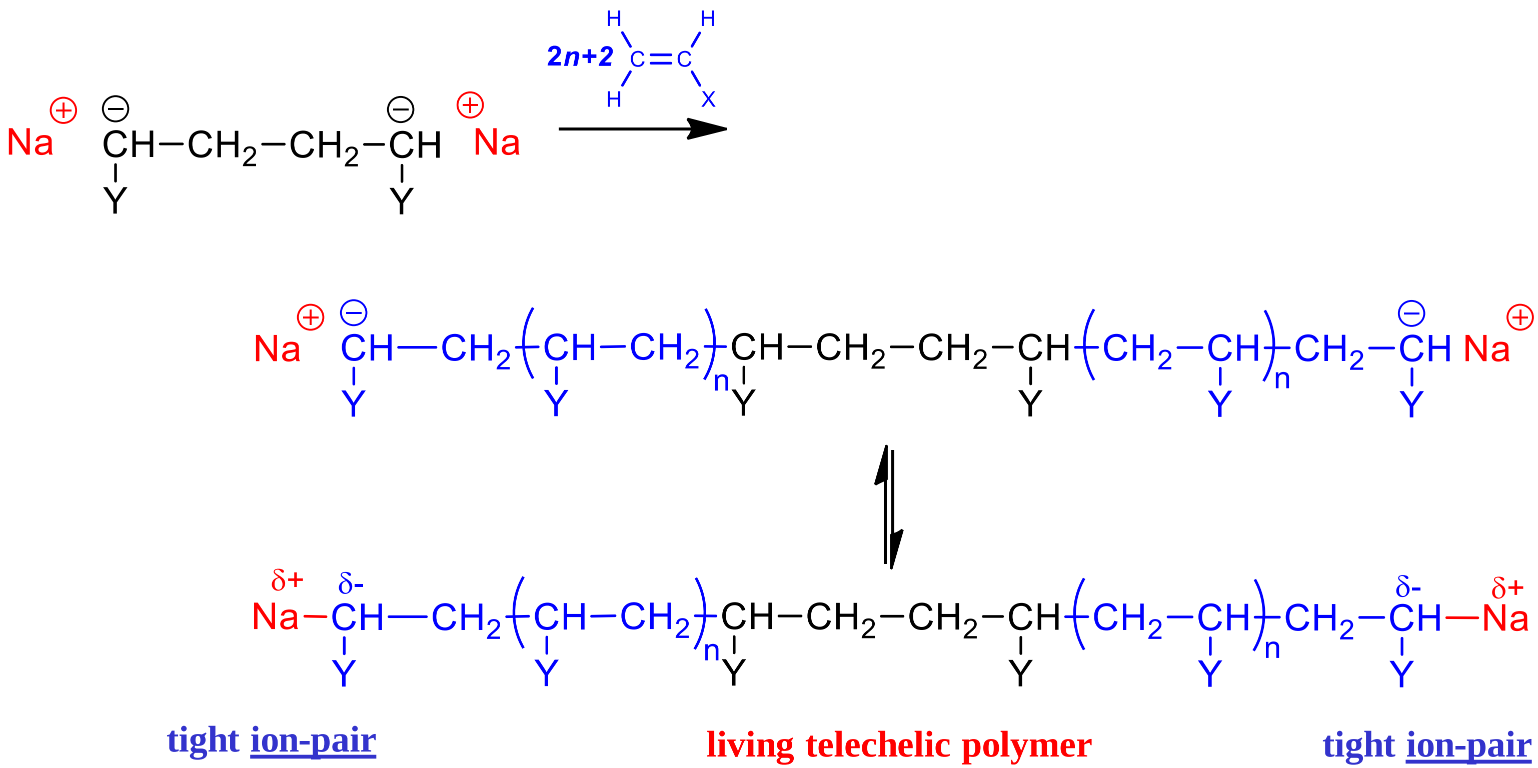
$$\overline{DP}_n = 2\bar{x} = 2\,\frac{[M]_o - [M]}{[I]_o}\,p$$

average kinetic chain length

- **Initiation**

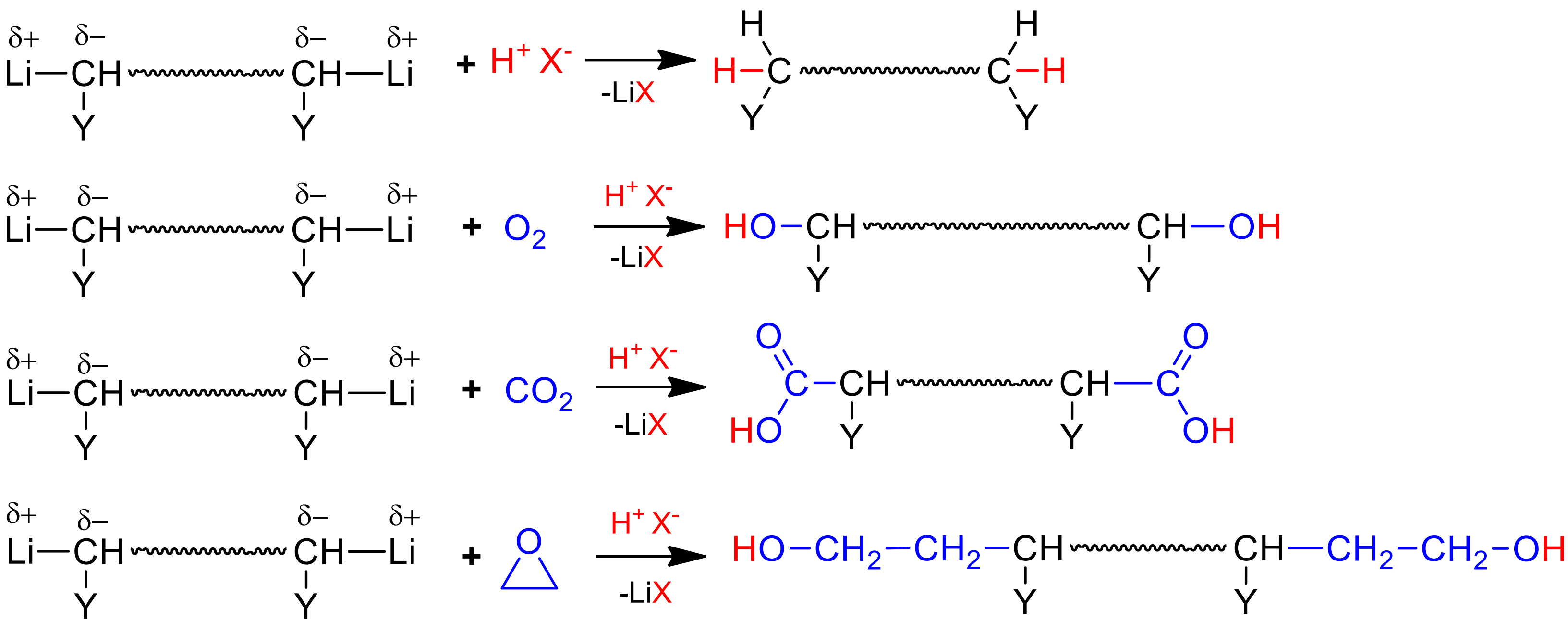


- **Propagation**

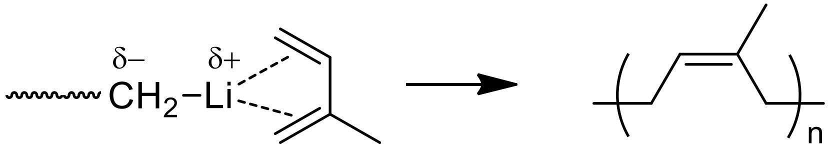


Telechelic chain growth (chain growth at both ends)

- **Functionalization of both chain ends:**

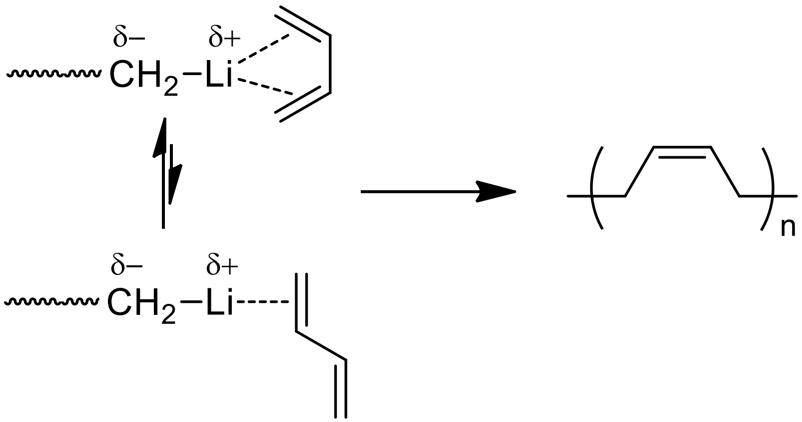


STEREOCHEMISTRY OF PROPAGATION

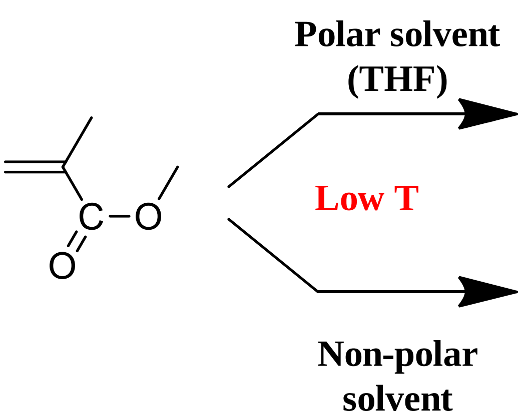


1,4-*cis*-polyisoprene (>95%)

independent of T



1,4-*cis*-polybutadiene (majority)



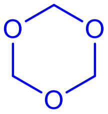
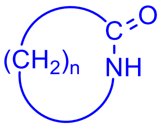
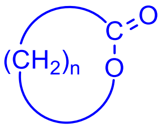
Syndiotactic PMMA

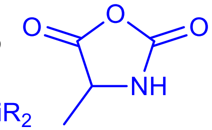
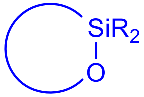
Isotactic PMMA

The Li^+ counter-cation always assists the chain growth by bonding covalently to the chain end, protecting it and avoiding chain termination or chain transfer reactions

ANIONIC RING OPENING POLYMERIZATION

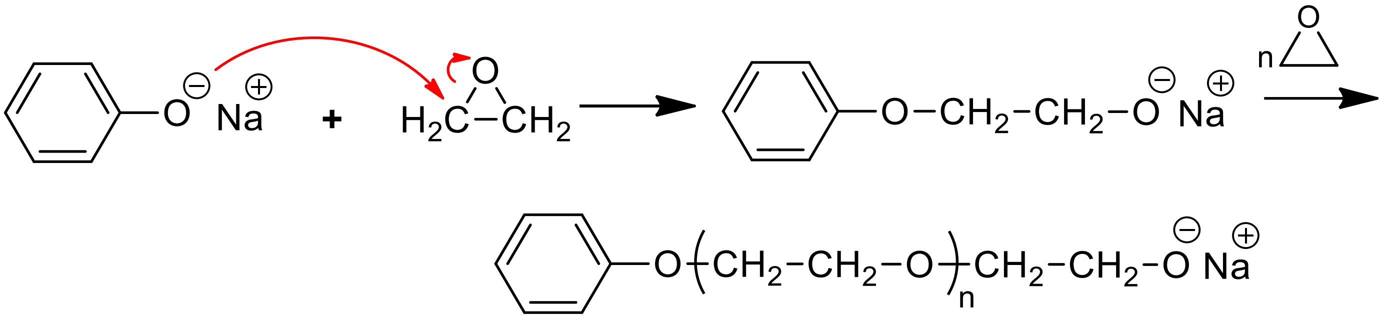
5 Types of Monomers

- **EPOXIDES** 
- **TRIOXANE** 
- **CYCLIC LACTAMS AND LACTONES**  , 

- ***N*-CARBOXYANHYDRIDES** 
- **CYCLIC SILOXANES** 

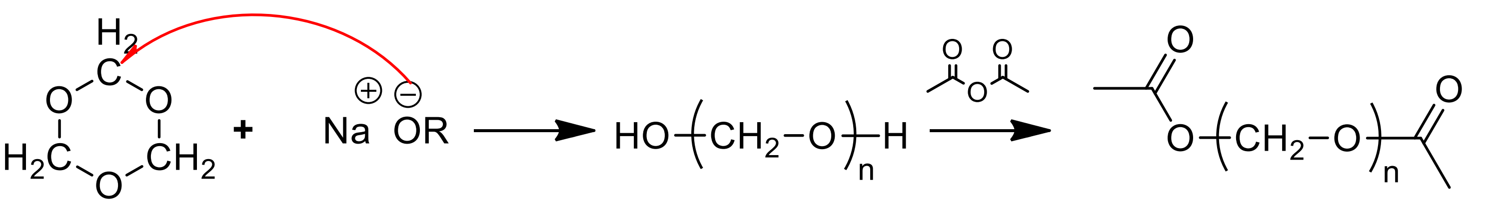
• EPOXIDES

Ex:



Poly(ethylene oxide) (PEO)

• FORMALDEHYDE TRIMER (TRIOXANE)



1,3,5-trioxane (formaldehyde trimer)

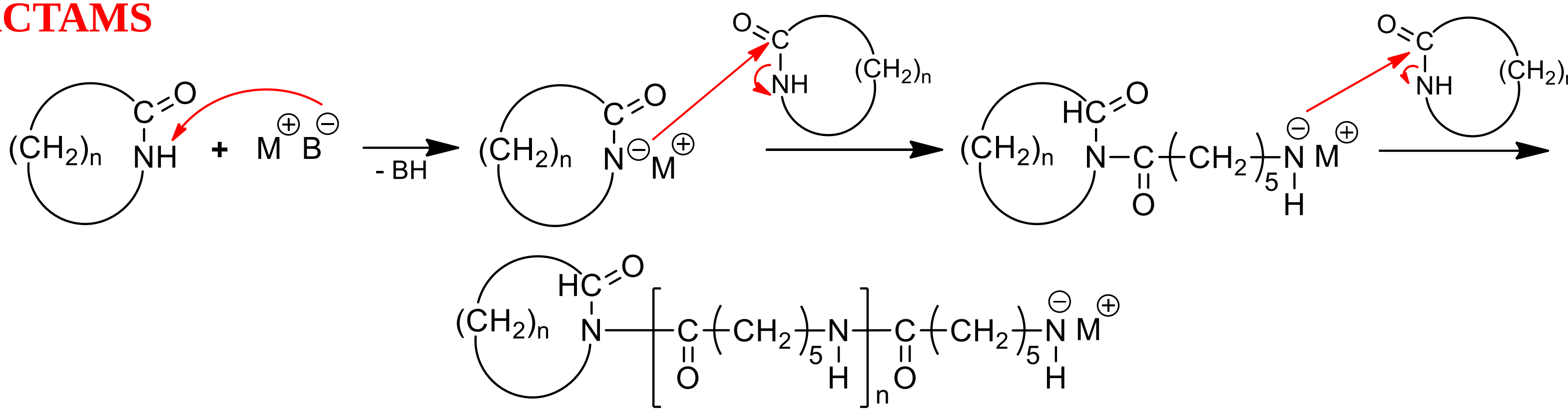
Poly(oxy methylene) (POM) (crystalline, high M_n)

Thermally stable "capped" form of POM

replaces metals in medium duty parts, springs, zipper closures, etc.

• LACTAMS

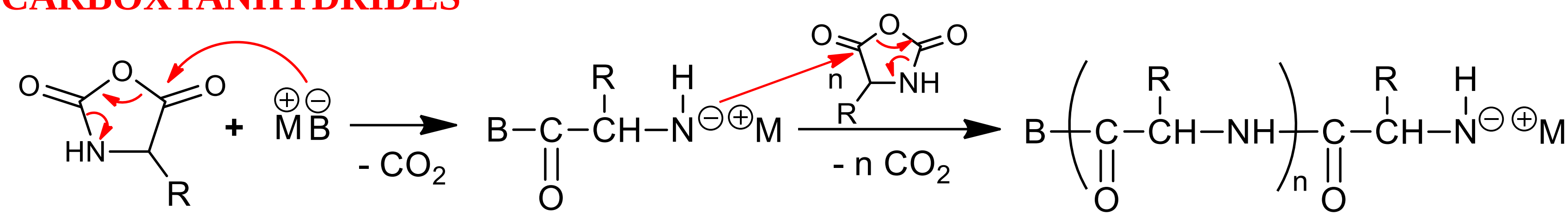
Ex:



Nylon 6

• *N*-CARBOXYANHYDRIDES

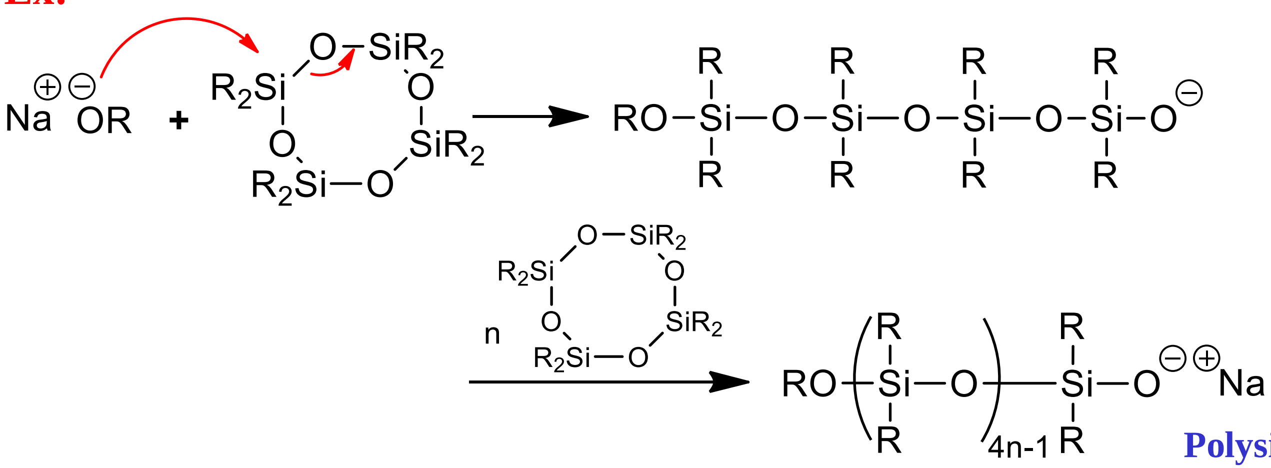
Ex:



Polypeptide (M_n ~10^6)

• CYCLIC SILOXANES

Ex:



Polysiloxane

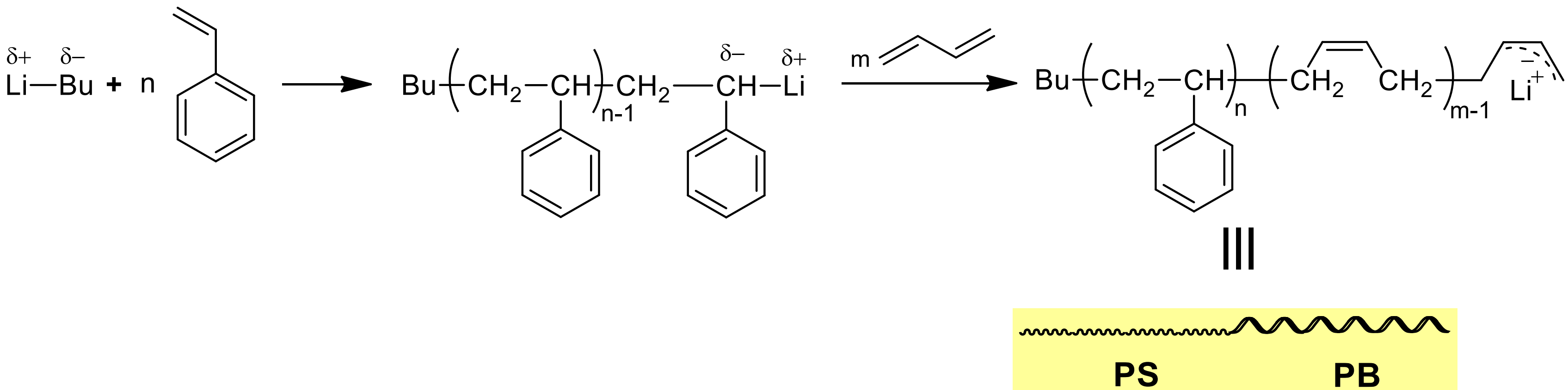
ANIONIC COPOLYMERIZATION

• BLOCK COPOLYMERIZATION (COMONOMERS ADDED SEQUENTIALLY)

Owing to the living nature of anionic polymerization (absence of chain transfer and chain termination reactions) and easy control of molecular weight, this technique is very much used in block copolymerization

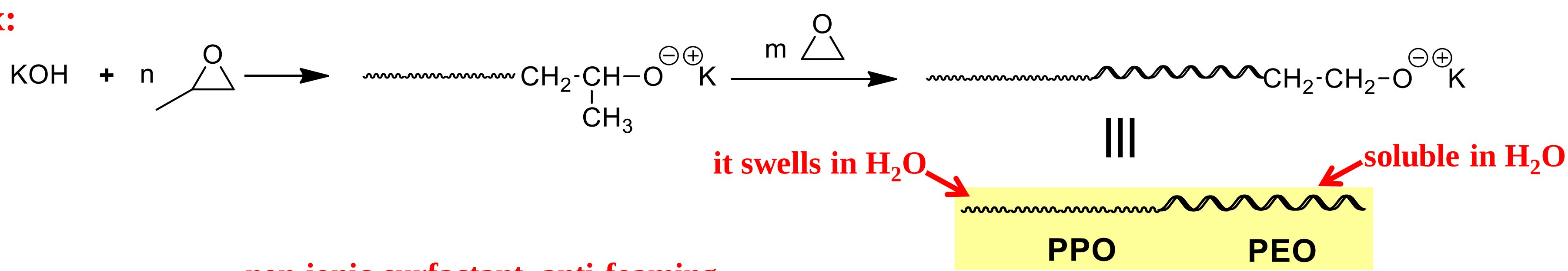
• From mononegative chains

Ex:



Polystyrene-*block*-1,4-*cis*-Polybutadiene

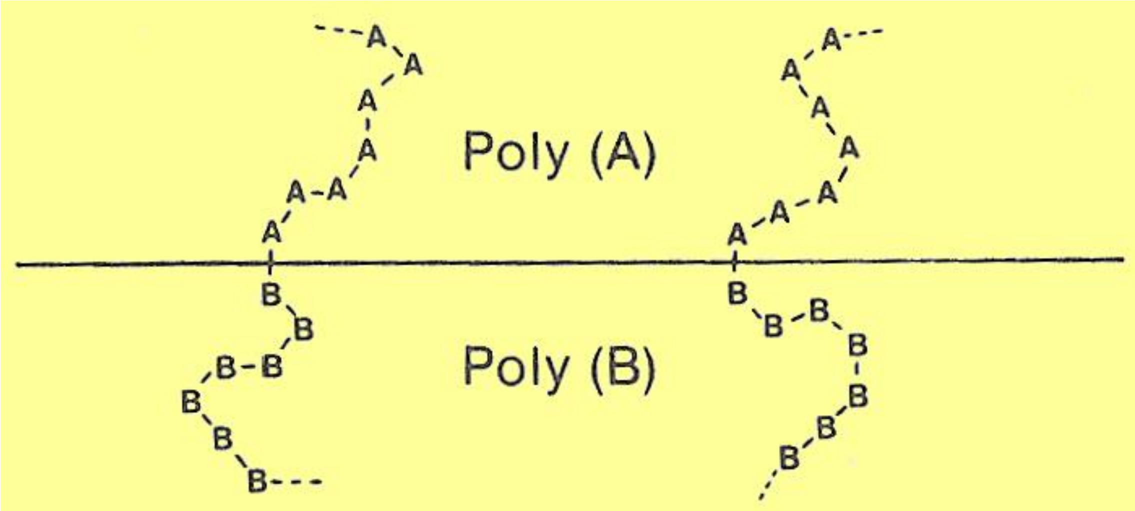
Ex:



non-ionic surfactant, anti-foaming, thickener, wetting agent (Pluronic®)

Poly(propylene oxide)-*block*-Poly(ethylene oxide)

COMPATIBILIZERS OF IMMISCIBLE POLYMER BLENDS



AB BLOCK COPOLYMERS ARE COMPATIBILIZERS

<u>Example</u>: commercial SB (polystyrene-*b*-polybutadiene)

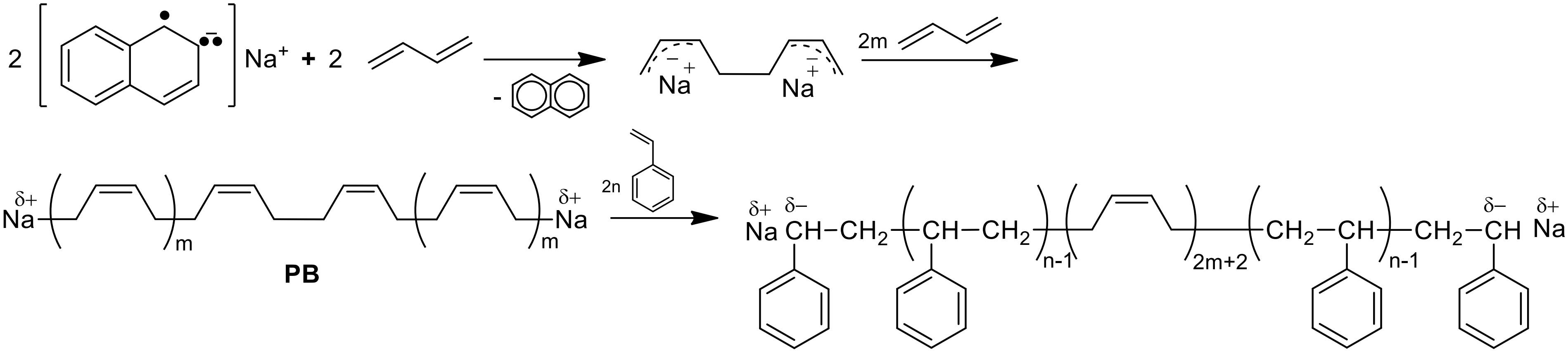
Blends of polybutadiene and polystyrene are immiscible

AB copolymers improve the adhesion between phases and compatibilize them

Sequential polymerization of different monomers (with total monomer consumption) is possible due to the living nature of the polymeric chain end. The preparation of the following types of block copolymers can be performed:

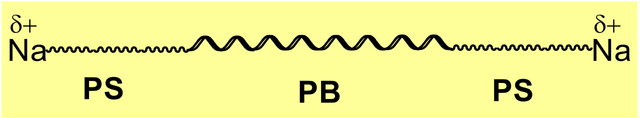
~~AAAAAABBBBBB~~~~	**DIBLOCK AB TYPE**
~~AAAAAABBBB~~~~BBBBCCCCCC~~~~	**TRIBLOCK ABC TYPE**
~~AAAAAABBBB~~~~BBBBAAAAAA~~~~	**TRIBLOCK ABA TYPE**
$[$ ~~~~AAAAAABBBBBB~~~~ $]_n$	**MULTIBLOCK [AB] TYPE**

• From dinegative chains

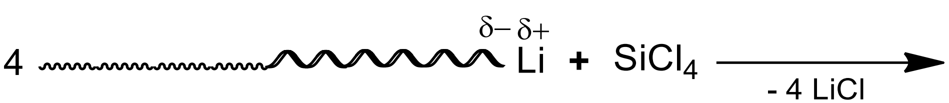


Triblock SBS copolymer

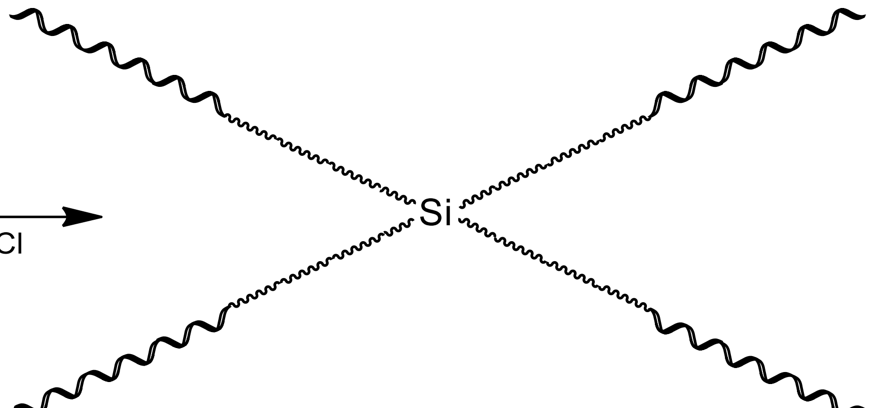
The ABA copolymers are thus obtained in 2 steps whereas from mononegative initiators is obtained in 3 steps



• Star-block copolymers



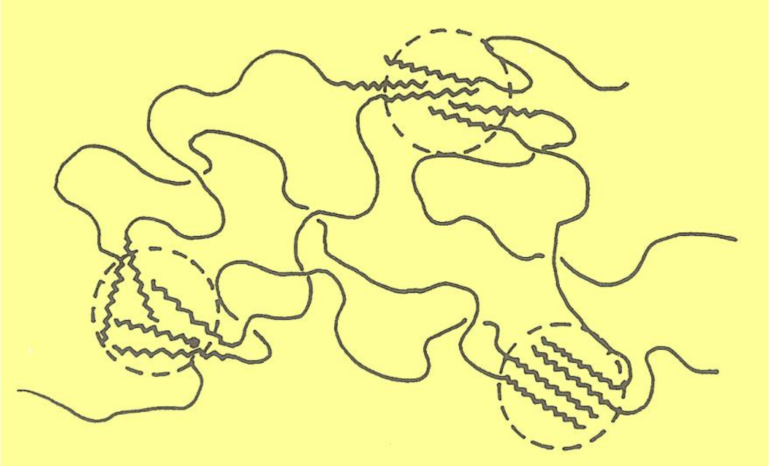
Living AB block copolymer



Star-block copolymer (or radial copolymer)

When melted, star-block copolymers exhibit lower viscosities, even when M_n are high

THERMOPLASTIC ELASTOMERS (TPE)



ABA BLOCK COPOLYMERS ARE THERMOPLASTIC ELASTOMERS
(A= rigid polymer; B= flexible polymer)

<u>Example</u>: commercial SBS (polystyrene-*b*-polybutadiene-*b*-polystyrene)

- PB blocks – *ca.* M_n = 50000 - 70000

- PS blocks – *ca.* M_n = 10000 - 15000

Semicrystalline blocks at the ends (S) tend to aggregate in microdomains, whereas amorphous central blocks (B) form the matrix

Aggregation ≡ elastic behaviour ≡ physical crosslinks

• **NORMAL COPOLYMERIZATION (COMONOMERS MIXED IN THE FEED)**

Relatively few reactivity ratios have been determined for anionic "normal" copolymerization

TABLE 7.5. Representative Anionic Reactivity Ratios (r)[a]

Monomer 1	*Monomer 2*	*Initiator*[b]	*Solvent*[c]	*Temperature*[d] (°C)	r_1	r_2
Styrene	Methyl methacrylate	Na	NH_3		0.12	6.4
		n-BuLi	None		e	e
	Butadiene	*n*-BuLi	None	25	0.04	11.2
		n-BuLi	Hexane	25	0.03	12.5
		n-BuLi	Hexane	50	0.04	11.8
		n-BuLi	THF	25	4.0	0.3
		n-BuLi	THF	−78	11.0	0.4
		EtNa	Benzene		0.96	1.6
	Isoprene	*n*-BuLi	Cyclohexane	40	0.046	16.6
	Acrylonitrile	RLi	None		0.12	12.5
	Vinyl acetate	Na	NH_3		0.01	0.01
Butadiene	Isoprene	*n*-BuLi	Hexane	50	3.38	0.47
Methyl methacrylate	Acrylonitrile	$NaNH_2$	NH_3		0.25	7.9
		RLi	None		0.34	6.7
	Vinyl acetate	$NaNH_2$	NH_3		3.2	0.4

[a]Data from Morton.[30]

[b]Bu = butyl, Et = ethyl, R = alkyl.

[c]THF = tetrahydrofuran.

[d]Temperature not specified in some instances.

[e]No detectable styrene in polymer.

POLYMER ARCHITECTURES ACCESSIBLE BY LIVING POLYMERIZATION

Monofunctionalized polymers

- **Dispersing agents**
- **Synthesis of macromonomers**

Difunctionalized polymers

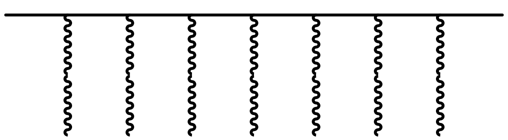
- **Synthesis of elastomers**
- **Crosslinking agents**

AB block copolymers

- **Dispersing agents**
- **Compatibilizers of polymer blends**

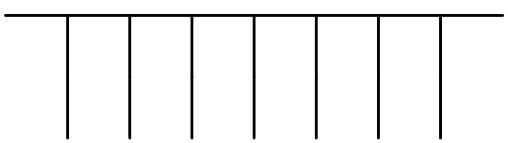
ABA block copolymers

- **Thermoplastic elastomers (TPE)**



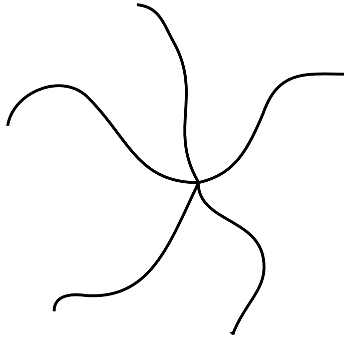
Graft copolymers

- **Elastomers**
- **Adhesives**



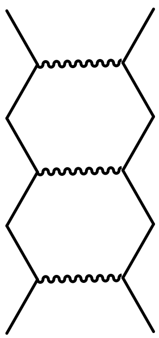
Comb polymers

- **Elastomers**
- **Adhesives**



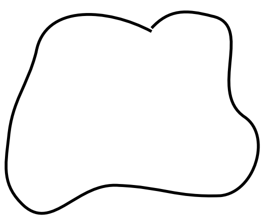
Star polymers/ copolymers

- Rheology control



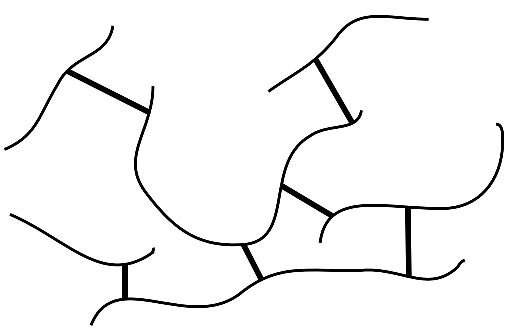
Ladder polymers/ copolymers

- High temperature plastics
- Membranes
- Elastomers



Cyclic polymers

- Rheology control



Amphiphilic networks

- Biocompatible polymers

Metal-Catalyzed Polymerization

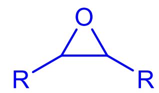
(Coordination Polymerization)

- *Polymerization of Olefins (Insertion)* ✓ ***Prof. Barbara Milani***
- *Polymerization of Dienes (Insertion)*
- *Polymerization of Alkynes*
- *Ring Opening Metathesis Polymerization (ROMP)*
- *Classical Anionic Polymerization*
- ***Ring Opening Polymerization (ROP)***
- *Metal-mediated Radical Polymerization*

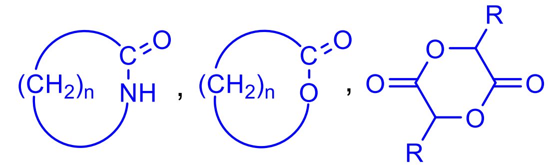
RING-OPENING POLYMERIZATION (ROP)

Types of Monomers (heterocyclic rings)

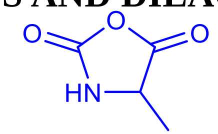
- **EPOXIDES**



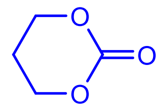
- **CYCLIC LACTAMS, LACTONES AND DILACTONES**



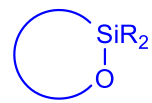
- ***N*-CARBOXYANHYDRIDES**



- **CYCLIC CARBONATES**

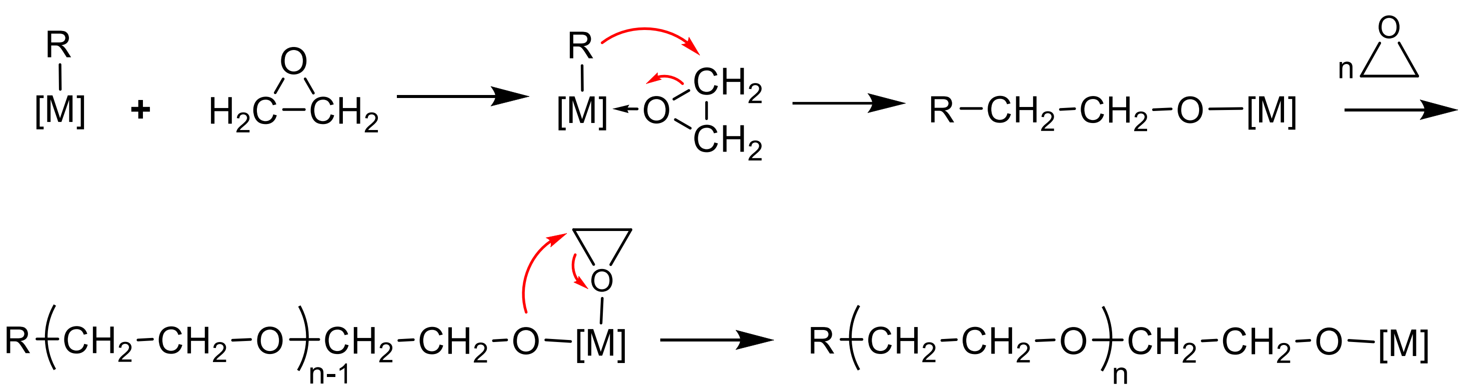


- **CYCLIC SILOXANES**



• EPOXIDES

Ex:



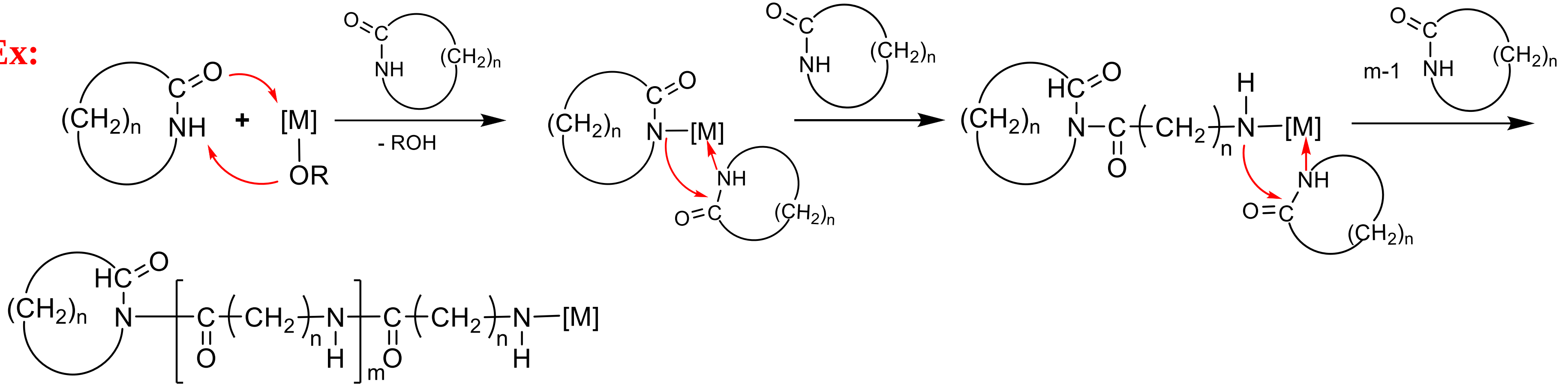
<u>Polyethers</u> [Poly(ethylene oxide) (PEO)]

Main catalytic systems used for the coordination ROP of epoxides

Monomer	*Catalysts*
Methyloxirane	$FeCl_3$/POx, $ZnEt_2/H_2O$, $AlEt_3/H_2O$/pyridine, and others
Phenyloxirane	$ZnEt_2(H_2O)$
(Haloalkyl)oxiranes (e.g., ECH)	$FeCl_3$/POx, $AlEt_3/H_2O$(/pyridine)
Oxiranes substituted with acetal groups	$ZnEt_2$/MeOH, $ZnEt_2$/cyclohexanol
Oxiranes substituted with ester groups	$AlEt_3/H_2O$/acetylacetone
Oxiranes substituted with organosilane or organosiloxane	$ZnEt_2/H_2O$
Oxiranes substituted with nitrile	Al(*i*-Bu)$_3/H_2O$/acetylacetone
2,3-Dimethyloxirane	Al(*i*-Bu)$_3/H_2O$, $ZnEt_2/H_2O$
bis(Chloromethyl)oxirane	Al(*i*-Bu)$_3/H_2O$
1,2-Epoxycyclohexane	$ZnEt_2$, $(EtZnOMe)_4$, Al(*i*-Bu)$_3/H_2O$, $AlEt_3/H_2O$/acetylacetone, and others
Others (ethyl, *tert*-butyl, neopentyl, allyl amines, sulfones, ether, amides)	$ZnEt_2/H_2O$

• LACTAMS

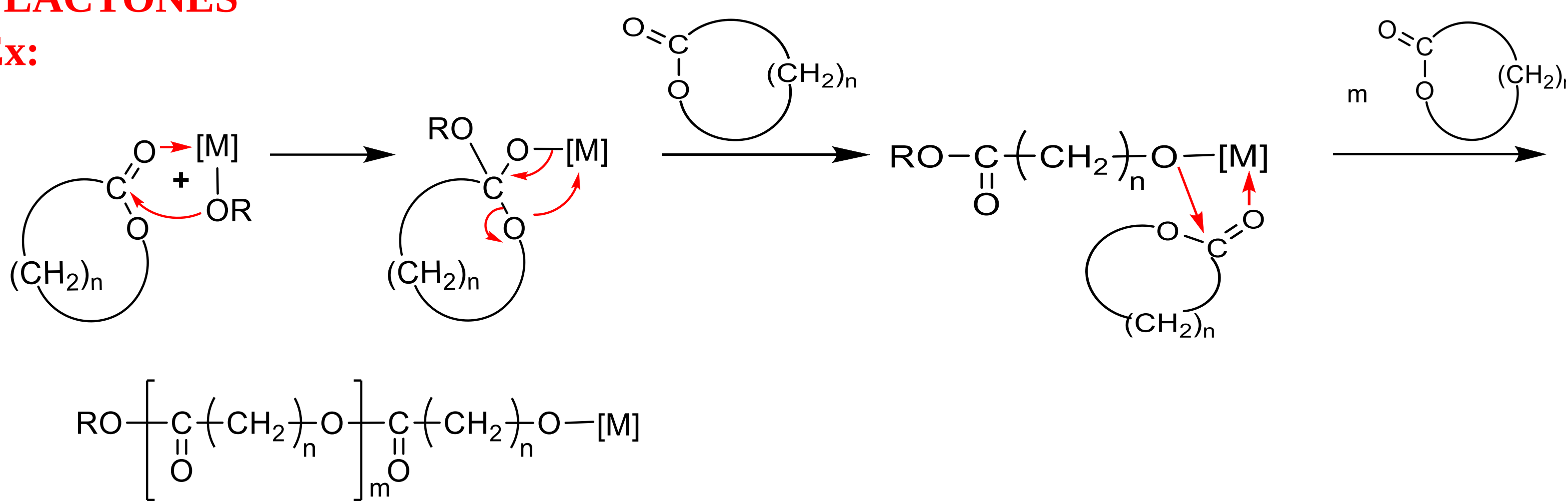
Ex:



Polyamides [nylon 6 or poly(ε-caprolactam) (n=5)]

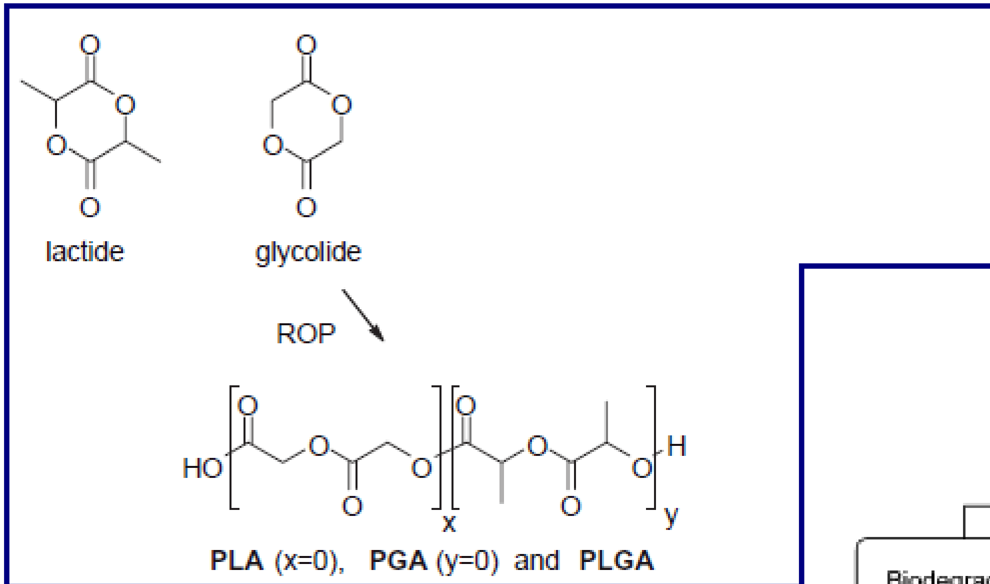
• LACTONES

Ex:



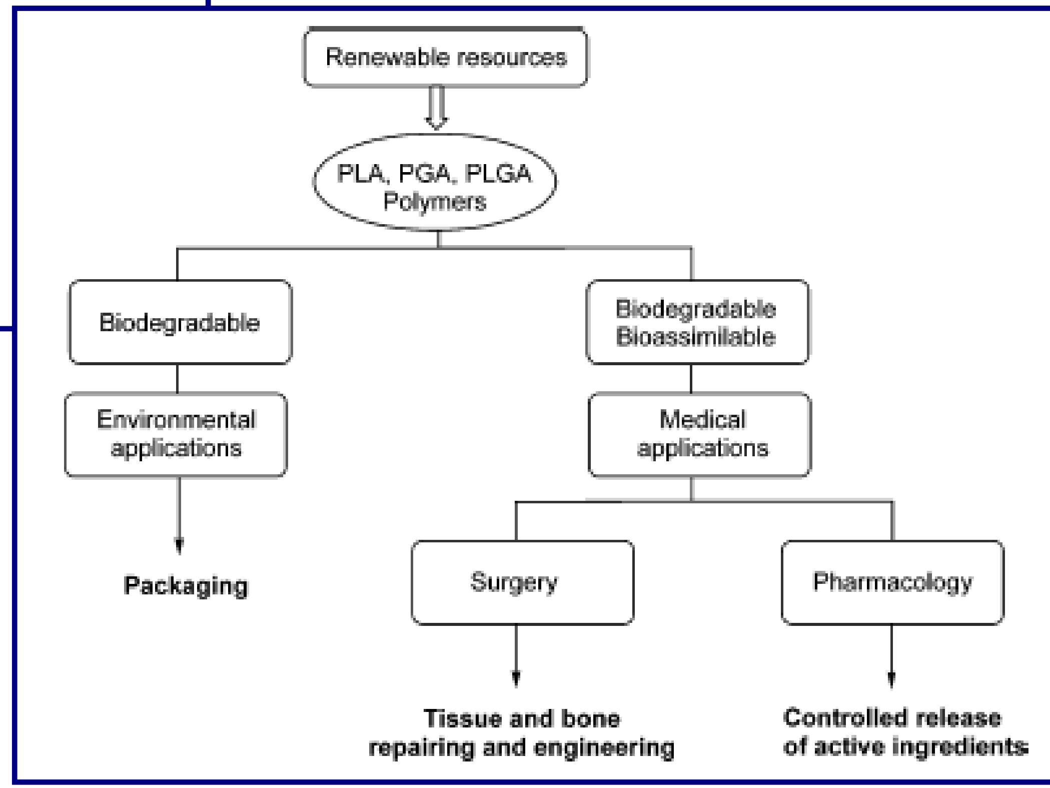
Polyesters [poly(ε-caprolactone)] (n=5)

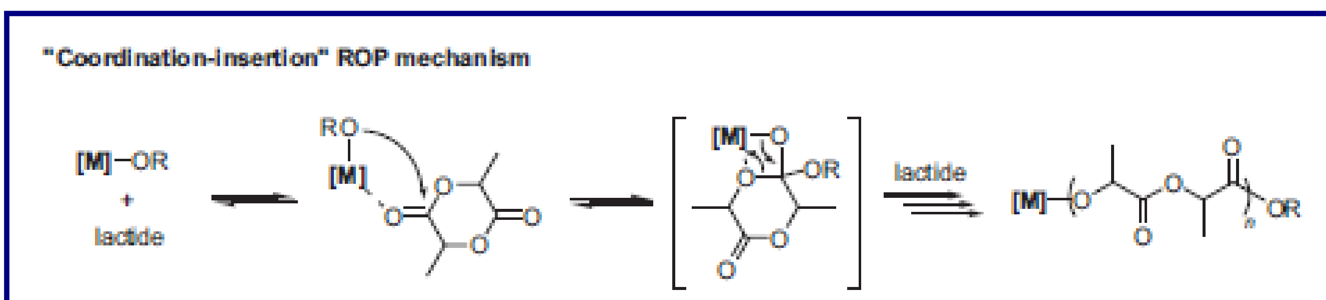
• DILACTONES



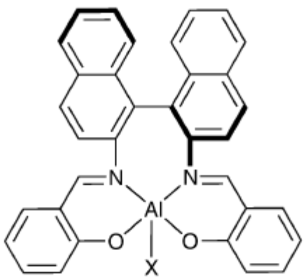
Monomers, polymers and copolymers

Polyesters

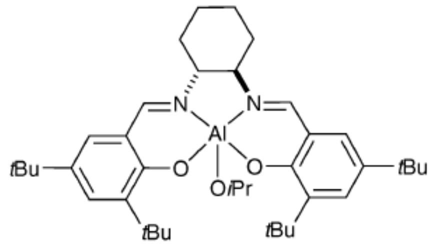




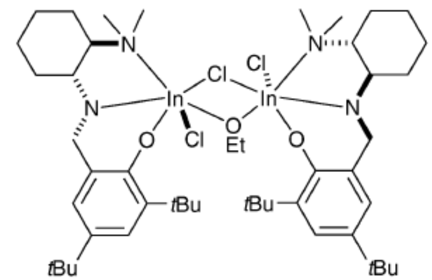
Catalysts used for coordination ROP of lactide



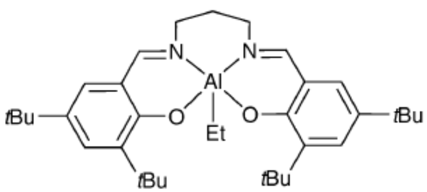
1a: X = O*i*Pr
1b: X = OMe



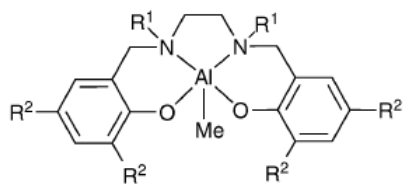
2



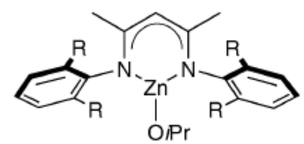
5



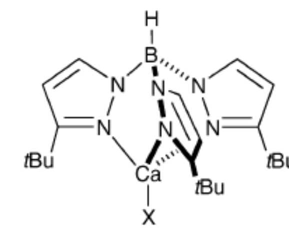
3



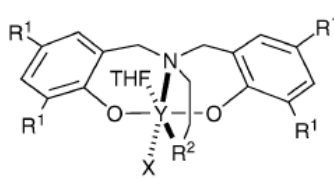
4a: R^1 = Me, R^2 = H
4b: R^1 = CH_2Ph, R^2 = H
4c: R^1 = CH_2Ph, R^2 = Cl
4d: R^1 = Me, R^2 = Me



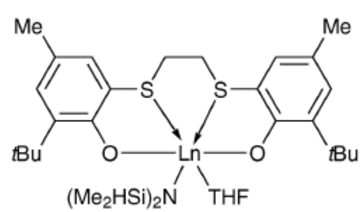
6a: R = Et
6b: R = *n*Pr
6c: R = *i*Pr



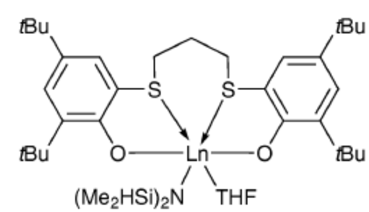
7a: X = $N(SiMe_3)_2$
7b: X = OC_6H_3-2,6-*i*Pr_2



9a: R^1 = CMe_3; R^2 = OMe; X = $N(SiHMe_2)_2$
9b: R^1 = $CPhMe_2$; R^2 = OMe; X = $N(SiHMe_2)_2$
9c: R^1 = $CPhMe_2$; R^2 = OMe; X = O*i*Pr
9d: R^1 = Me; R^2 = OMe; X = $N(SiMe_3)_2$
9e: R^1 = CMe_3; R^2 = NMe_2; X = CH_2SiMe_3
9f: R^1 = CMe_3; R^2 = NEt_2; X = CH_2SiMe_3

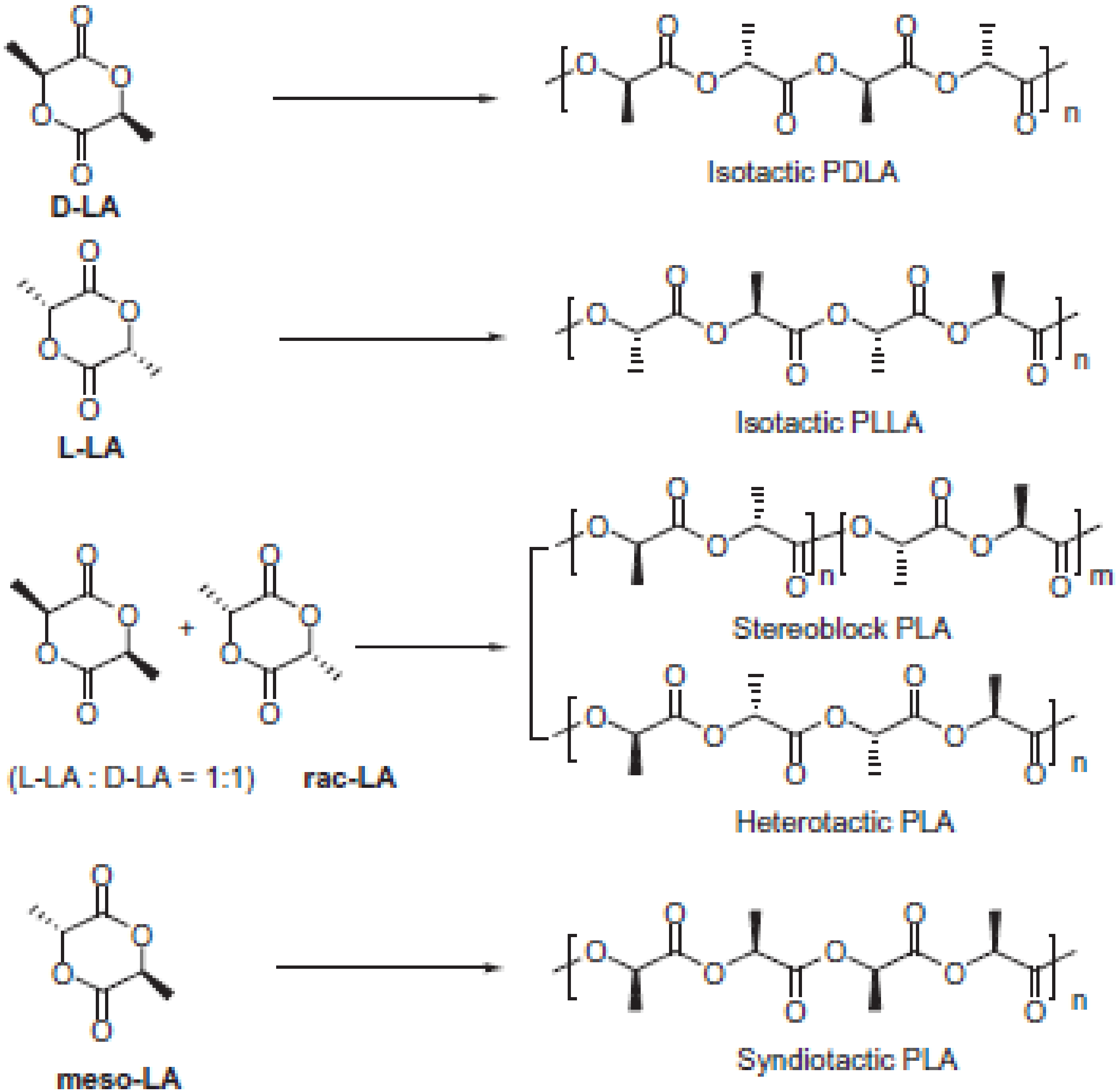


10a: Ln = Sc
10b: Ln = Lu
10c: Ln = Y



11a: Ln = Sc
11b: Ln = Lu
11c: Ln = Y

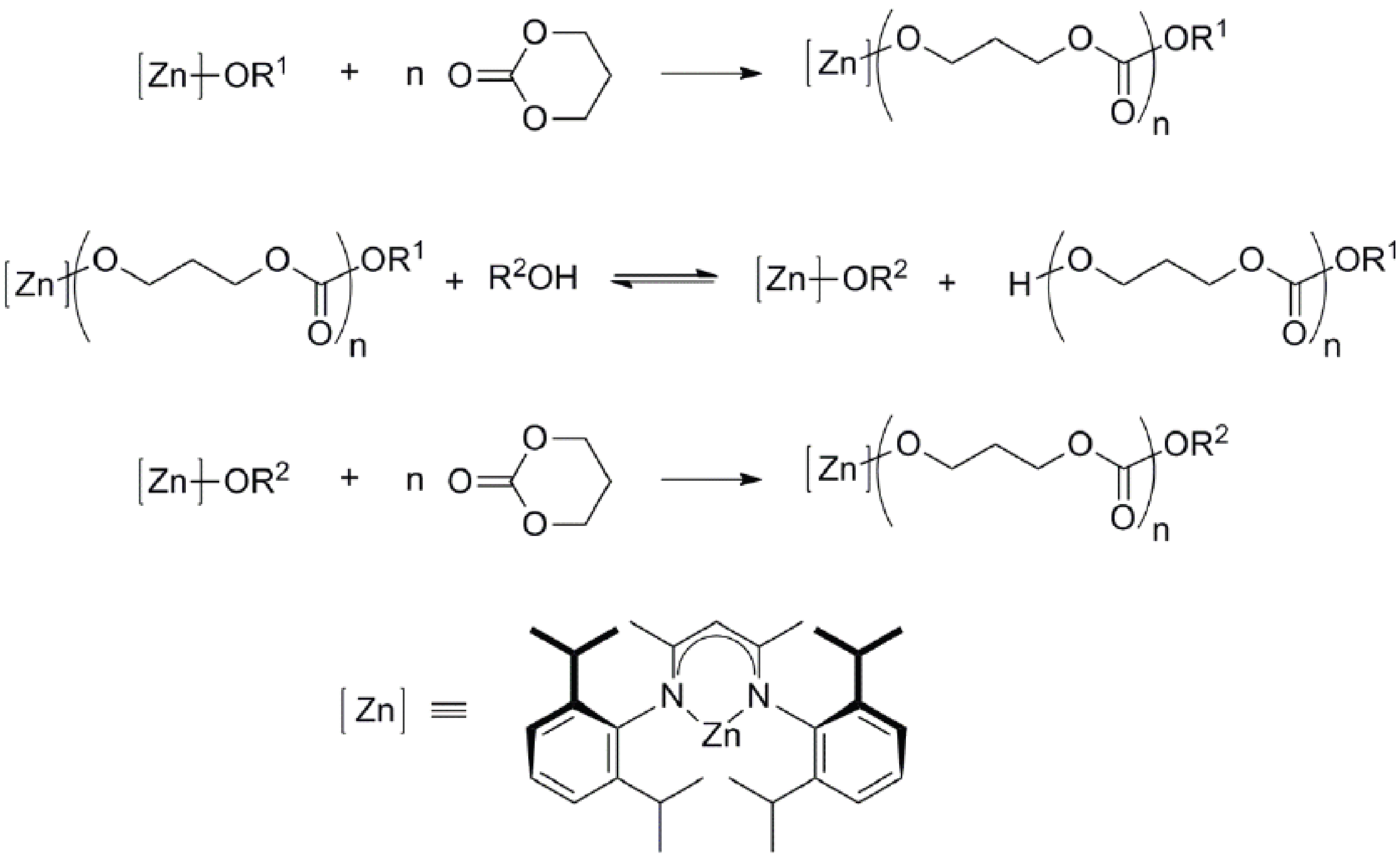
Synthesis of stereoregular PLAs by ROP



Crystalline
T_m = 170-180 ºC

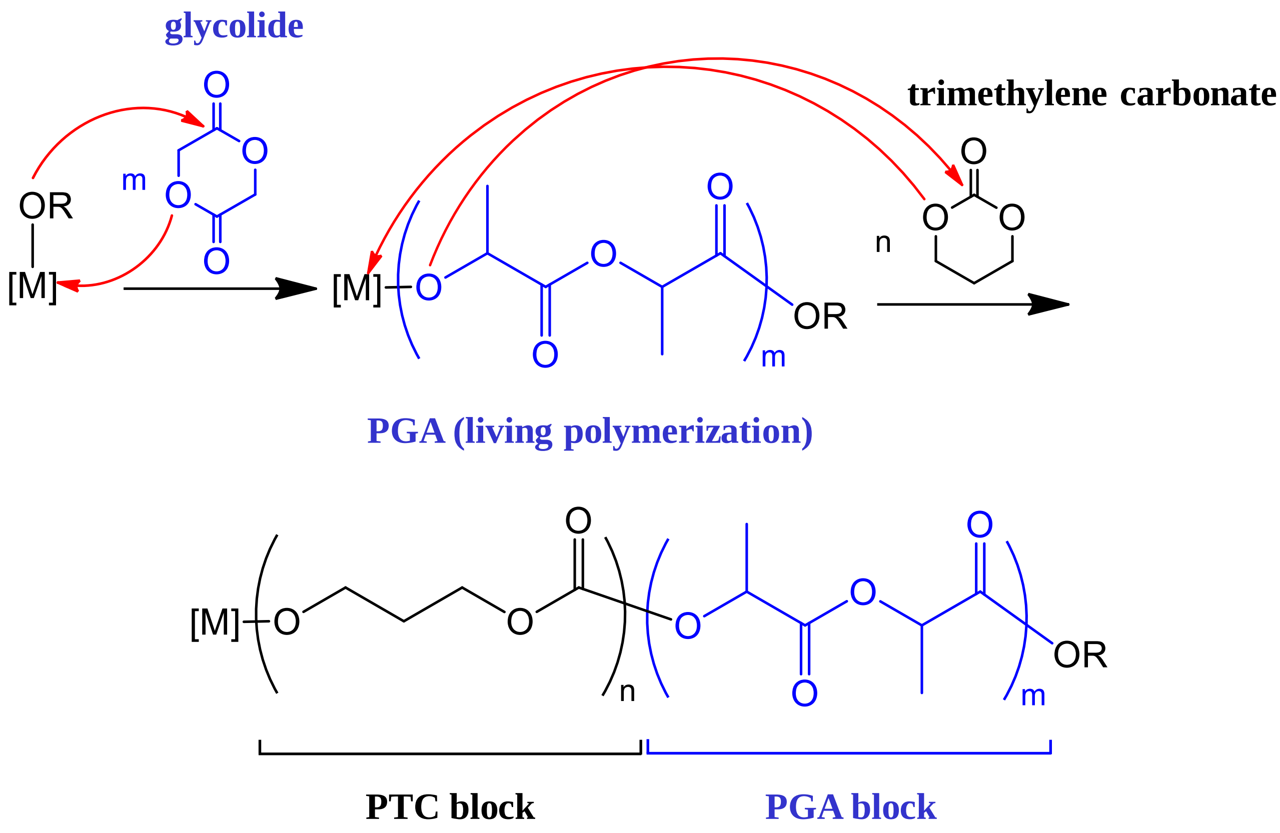
Amorphous

Synthesis of polycarbonates by ROP



[Zn] mediated living ROP of trimethylene carbonate

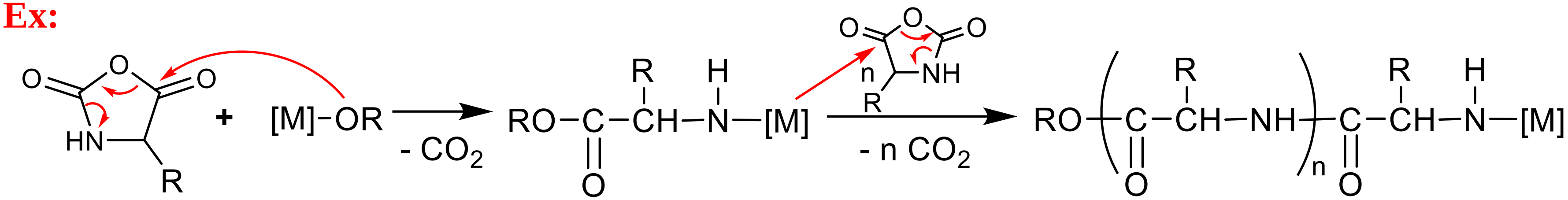
Synthesis of PGA-PTC diblock copolymer by ROP



PGA-PTC diblock copolymer is the material of the <u>Maxon</u>™ suture, a monofilament resorbable suture (also used in other resorbable medical devices)

• *N*-CARBOXYANHYDRIDES

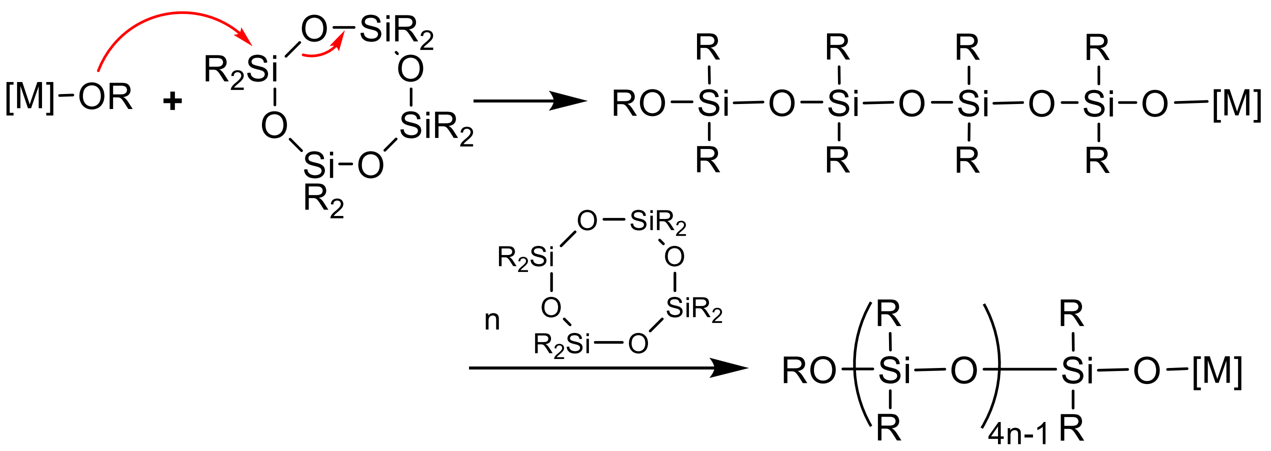
Ex:



Polypeptide (M_n ~10^6)

• CYCLIC SILOXANES

Ex:



Polysiloxane

Metal-Catalyzed Polymerization

(Coordination Polymerization)

- Polymerization of Olefins (Insertion) ✓ **Prof. Barbara Milani**
- Polymerization of Dienes (Insertion)
- Polymerization of Alkynes
- Ring Opening Metathesis Polymerization (ROMP)
- Classical Anionic Polymerization
- Ring Opening Polymerization (ROP)
- **Metal-mediated Radical Polymerization**

FREE RADICAL POLYMERIZATION

It involves:
- Monomer
  +
- Radical Initiator

STEPS
- **INITIATION**
  addition of the radical initiator to the monomer
- **PROPAGATION**
  radical chain growth by sequential addition of monomers
- **CHAIN TERMINATION**
  "death" of the radical propagating species by reaction with other radical species
- **CHAIN TRANSFER**
  growing chain reacts with a neutral molecule and abstracts one of its atoms, the latter becoming a new radical

---

$$I_2 \longrightarrow I\bullet + I\bullet$$
$$I\bullet + M \longrightarrow P_1\bullet$$
INITIATION

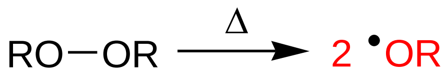
$$P_i\bullet + M \longrightarrow P_{i+1}\bullet$$
PROPAGATION

$$P_i\bullet + P_j\bullet \longrightarrow P_{i+j}$$
$$P_i\bullet + P_j\bullet \longrightarrow P_i + P_j$$
TERMINATION

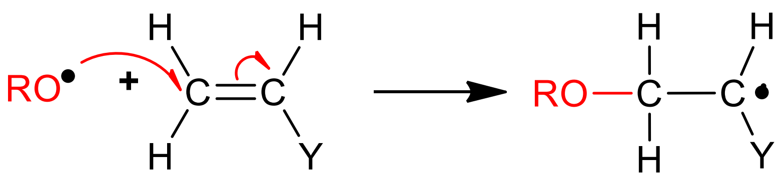
$$P_i\bullet + X \longrightarrow P_i + X\bullet$$
CHAIN TRANSFER

MECHANISM OF CLASSICAL 'FREE RADICAL POLYMERIZATION' (GENERAL)

• INITIATION



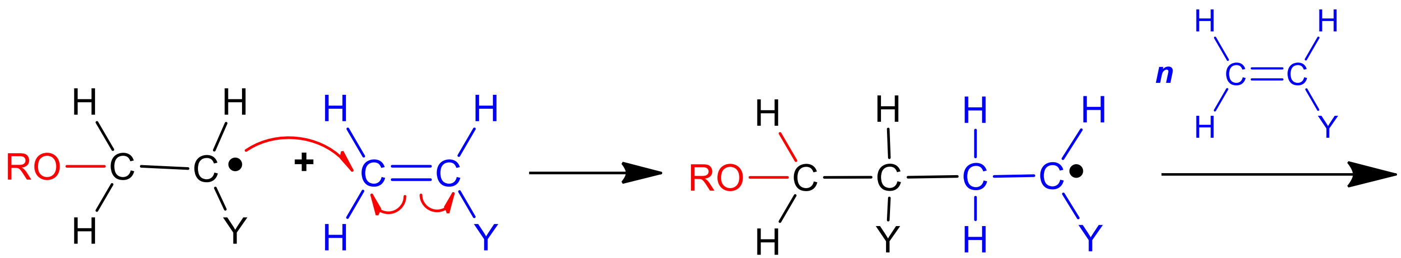
Initiator decomposition

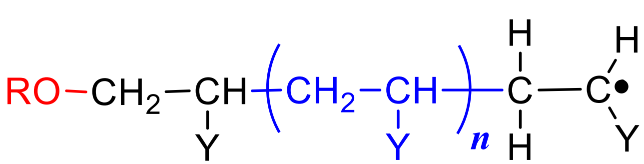


monomer

Addition of initiator radical to monomer

• PROPAGATION





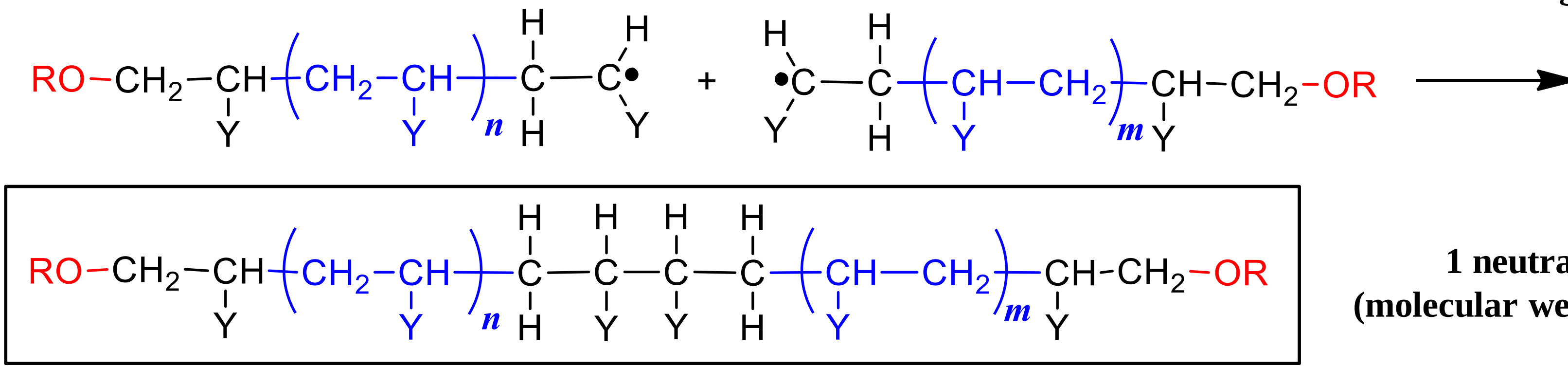
mer

Sequential addition of monomers to radical growing chain → **CHAIN GROWTH**

• TERMINATION

• Recombination (or Coupling) (*low* temperatures)

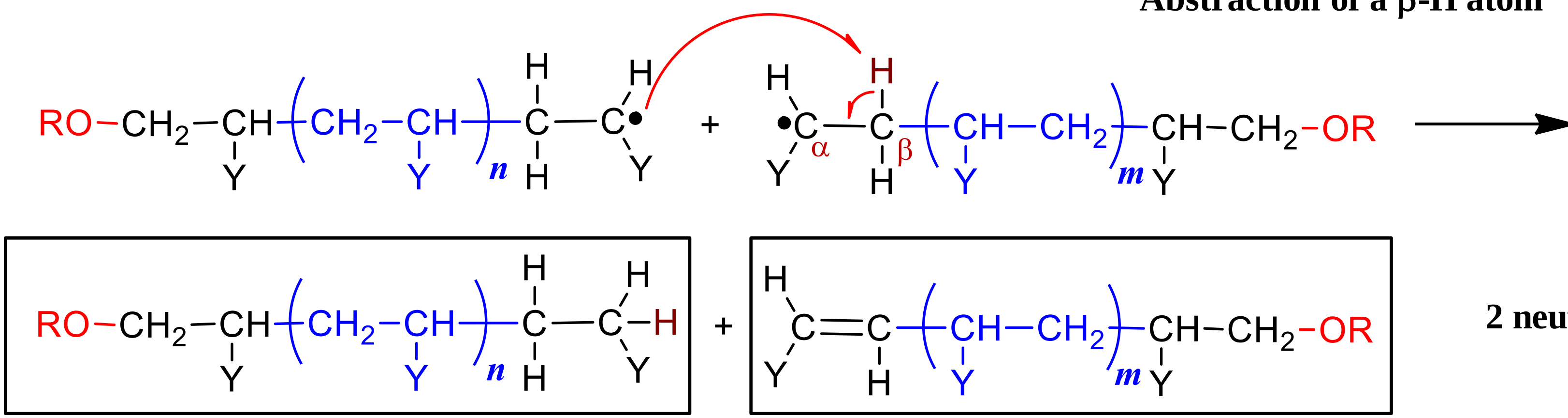
Recombination of 2 radical growing chains



1 neutral chain (molecular weight doubles)

• Disproportionation (*high* temperatures)

Abstraction of a β-H atom

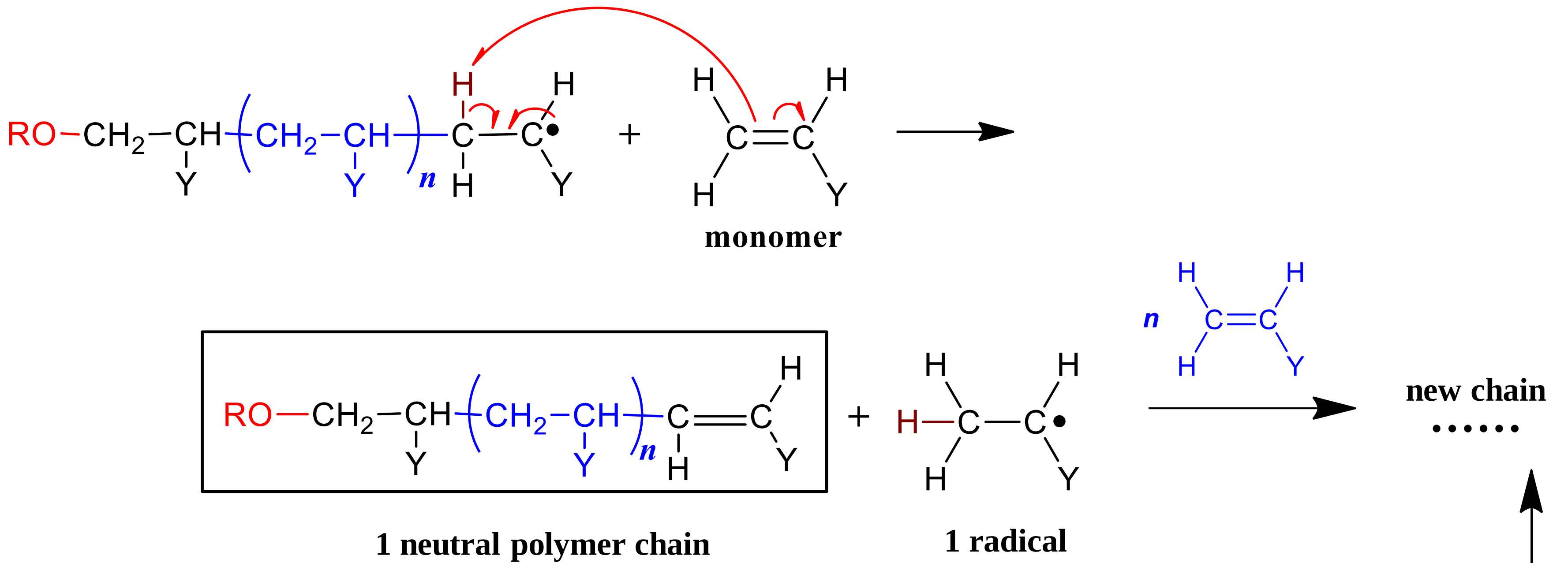


2 neutral polymer chains

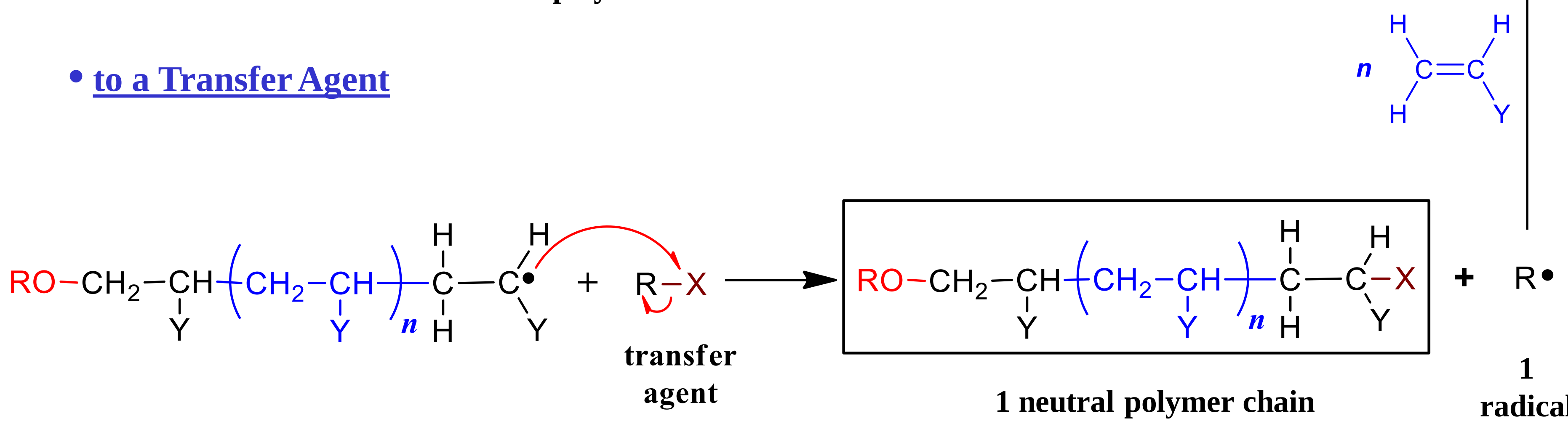
• CHAIN TRANSFER

Step responsible for the decrease in molecular weight and for the broadening of the molecular weight distribution

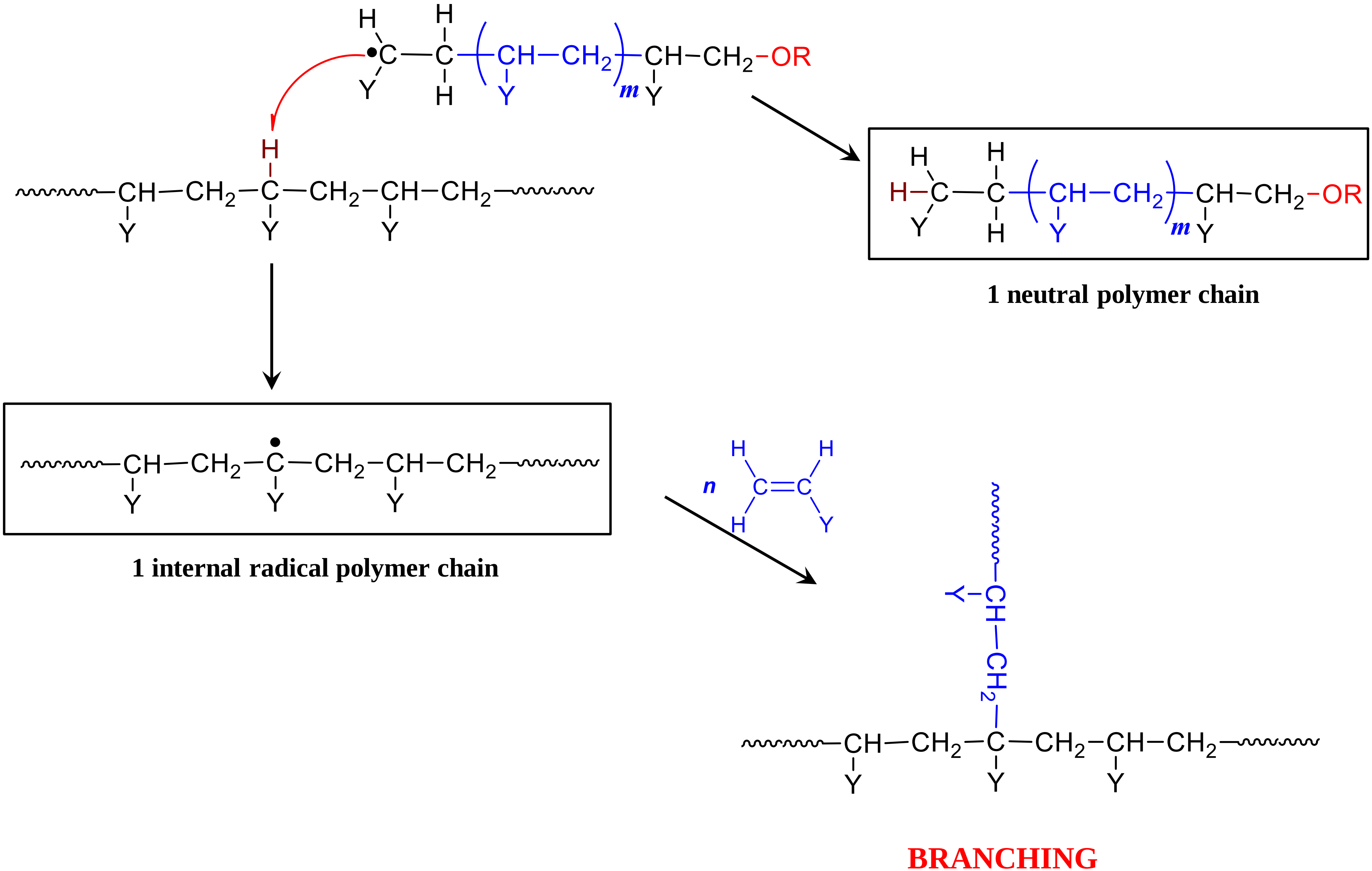
• to the Monomer



• to a Transfer Agent



• **to the Polymer (*very high* temperatures)**



CONTROLLED RADICAL POLYMERIZATION (CRP)

Controlled/Minimized TERMINATION and CHAIN TRANSFER reactions

↓

Quasi-Living Polymers (Controlled Radical Polymerization) → Living Chain Ends

↓

Molecular Weight Control → Narrow Molecular Weight Distribution

↓

Block Copolymers

REVERSIBLE-DEACTIVATION RADICAL POLYMERIZATION (RDRP)

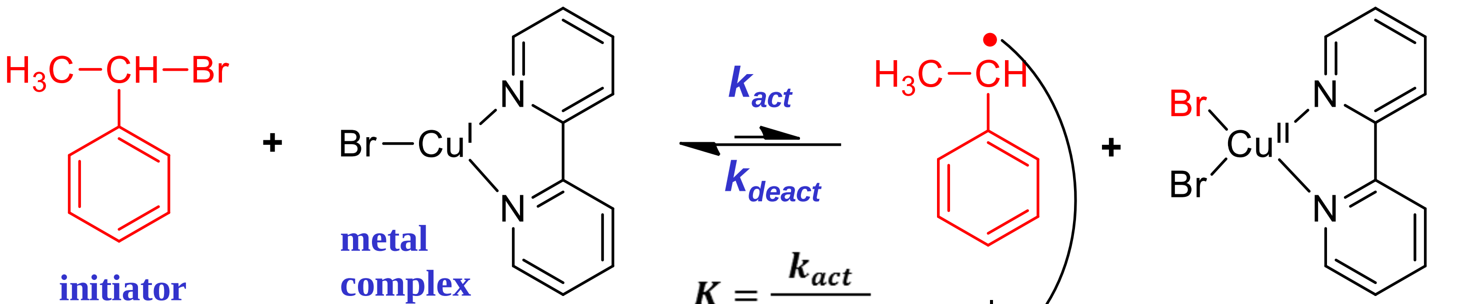
Main Techniques of CRP/RDRP

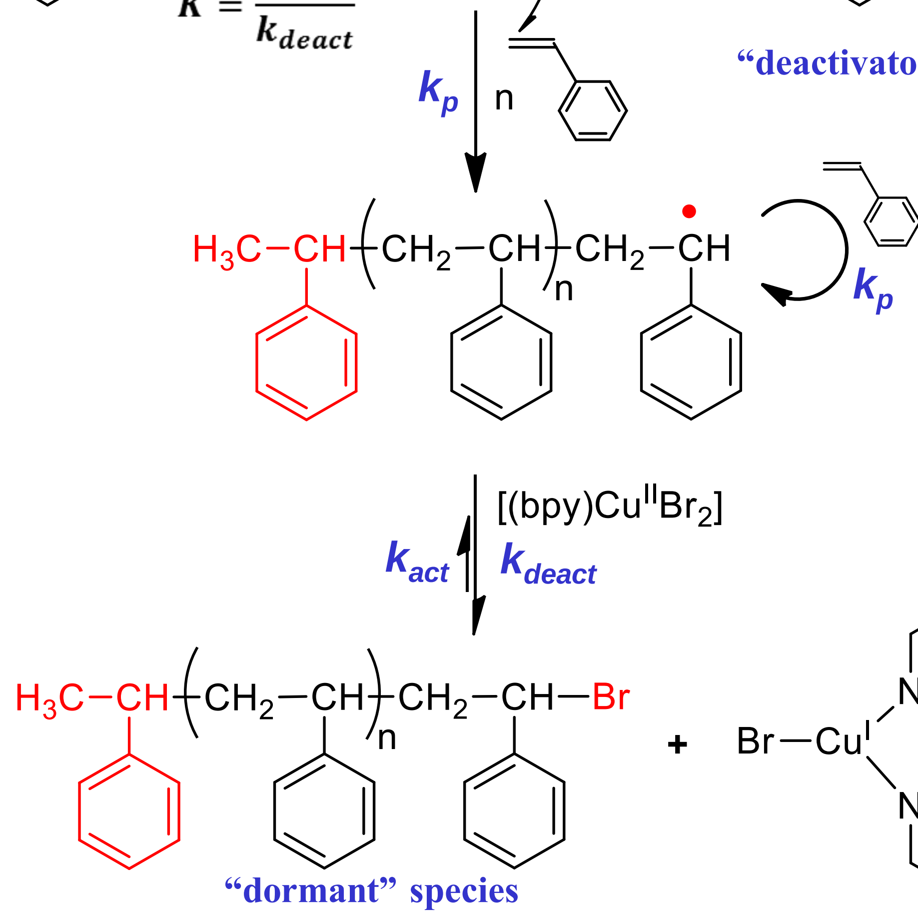
- **SFRP (NMP)**
- **ATRP** → It involves mediation by metals
- **RAFT**

• ATOM-TRANSFER RADICAL POLYMERIZATION (ATRP)

Initiator: Organic halide undergoing a reversible redox catalyzed by a transition-metal complex

Ex:





$$r_p = \frac{k_p K[\mathrm{I}][\mathrm{Cu}^+]}{[\mathrm{Cu}^{2+}]}[\mathrm{M}]$$

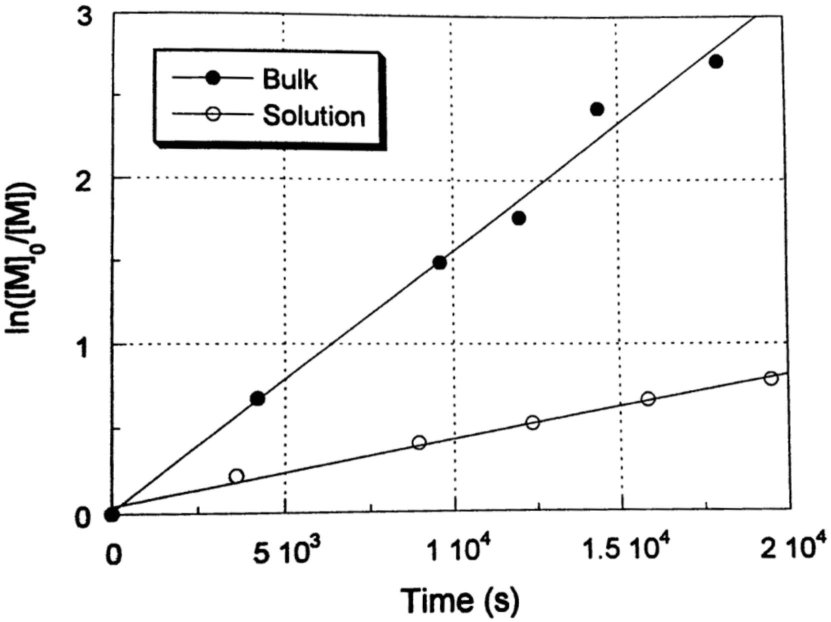
$$\ln\frac{[\mathrm{M}]_o}{[\mathrm{M}]} = \frac{k_p K[\mathrm{I}][\mathrm{Cu}^+]}{[\mathrm{Cu}^{2+}]}t$$

$$\overline{DP}_n = \frac{[\mathrm{M}]_o - [\mathrm{M}]}{[\mathrm{I}]_o} = \frac{p[\mathrm{M}]_o}{[\mathrm{I}]_o}$$

$$\frac{\overline{M}_w}{\overline{M}_n} = 1 + \frac{1}{\overline{DP}_n}$$

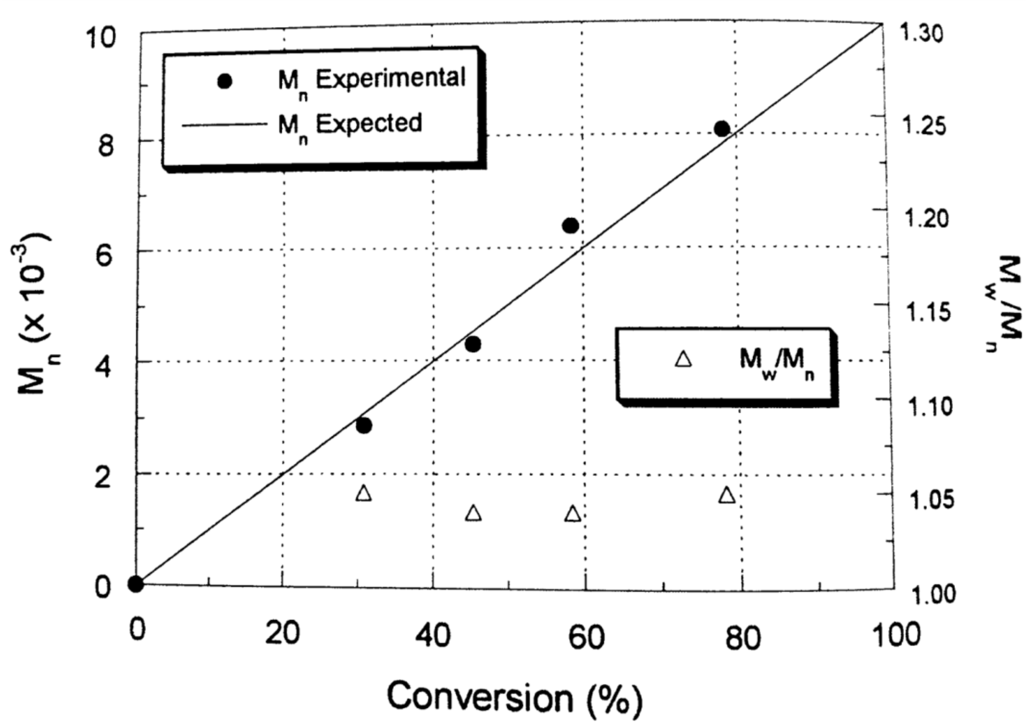
Poisson distribution

1st order kinetics



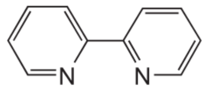
ATRP of Styrene, at 110 ºC,
with CuBr/1-phenylethyl bromide
(bulk and solvent: diphenyl ether)

Linear plot M_n vs p

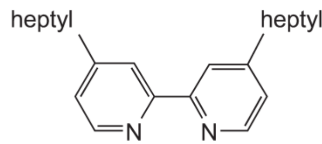


ATRP of Styrene, at 110 ºC,
with CuBr/1-phenylethyl bromide
(bulk)

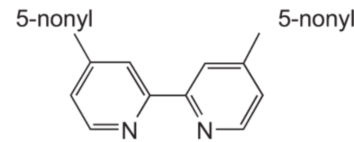
• COMMON LIGANDS (L) OF ATRP



bipy



dHbipy



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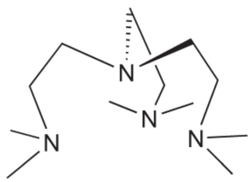
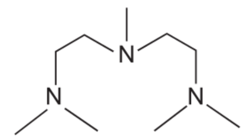
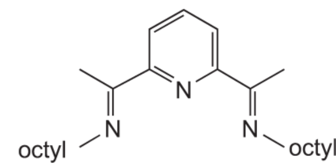


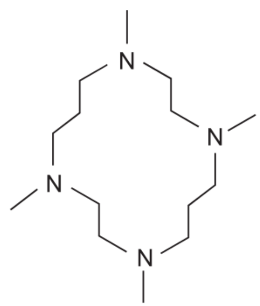
Me_6TREN



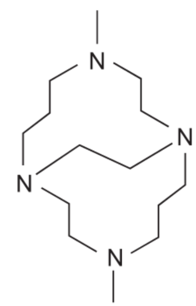
PMDETA



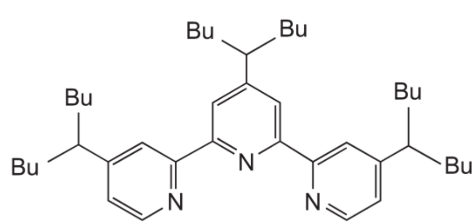
DOIP



Me_4Cyclam

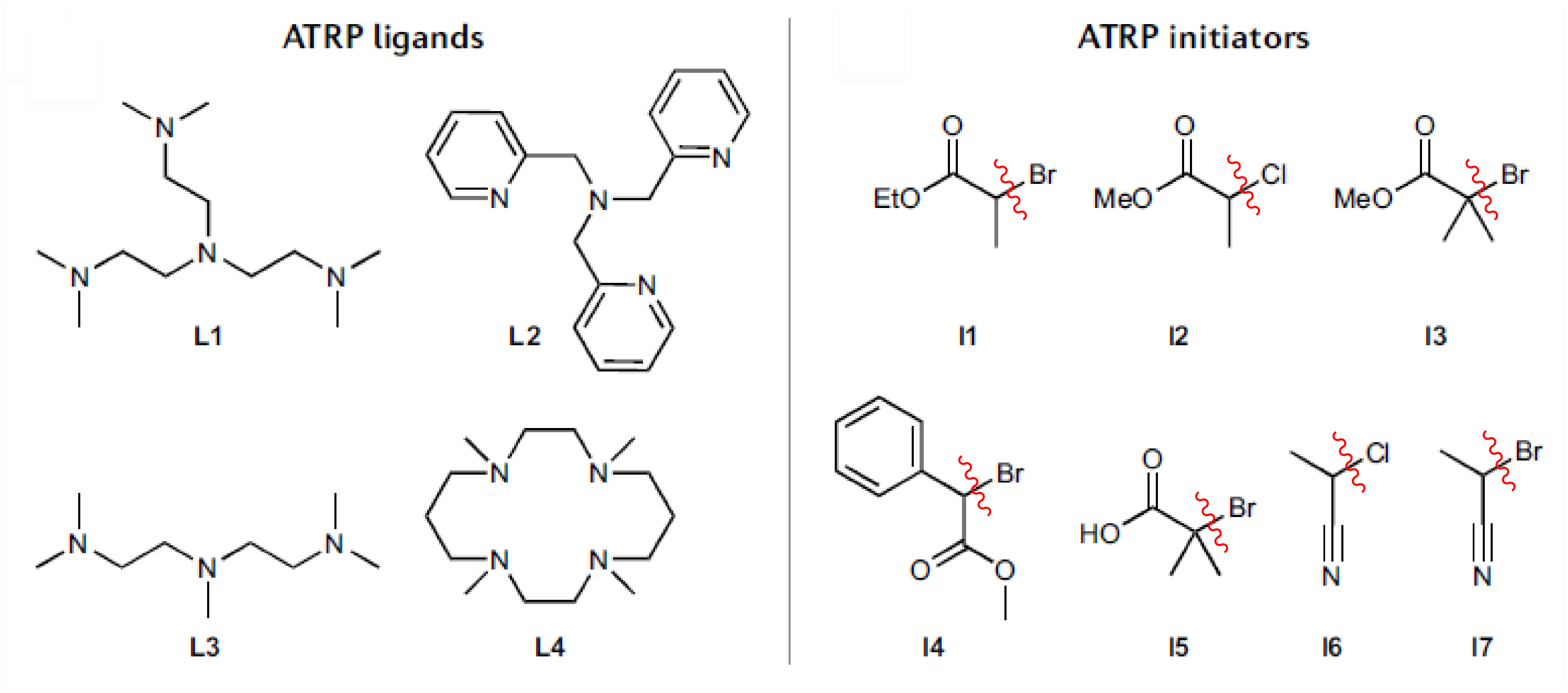


Cyclam-B

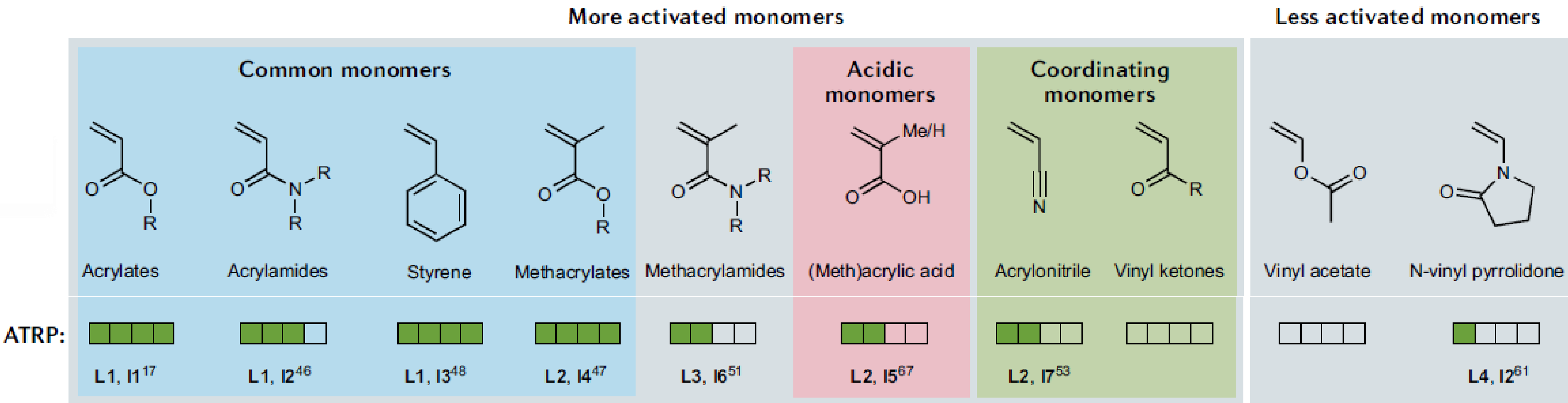


TERPY

• **MOST COMMON LIGANDS (L) AND COMMON INITIATORS OF ATRP**



• **MONOMERS**


More activated monomers
Less activated monomers
Common monomers
Acidic monomers
Coordinating monomers
O
O
R
Acrylates
O
N
R
R
Acrylamides
Styrene
O
O
R
Methacrylates
O
N
R
R
Methacrylamides
Me/H
O
OH
(Meth)acrylic acid
N
Acrylonitrile
O
R
Vinyl ketones
O
O
Vinyl acetate
O
N
N-vinyl pyrrolidone
ATRP:
L1, I1[17]
L1, I2[46]
L1, I3[48]
L2, I4[47]
L3, I6[51]
L2, I5[67]
L2, I7[53]
L4, I2[61]

Comparison of radical polymerization processes			
Property	**Free-radical polymerization**	**Ideal Living polymerization**	**Reversible-deactivation radical polymerization (*e.g.* ATRP)**
Concn. of initiating species	Falls off only slowly	Falls off very rapidly	Falls off very rapidly
Concn. of chain carriers (Number of growing chains)	Instantaneous steady state (Bodenstein approximation applies) decreasing throughout reaction	Constant throughout reaction	Constant throughout reaction
Lifetime of growing chains	~ 10^{-3} s	Same as reaction duration	Same as reaction duration
Main form of termination	Radical combination or radical disproportionation	Termination reactions are precluded	Termination reactions are minimized but **not** precluded
Degree of polymerization	Broad range ($Đ \geq 1.5$) Schulz-Flory distribution	Narrow range ($Đ < 1.5$) Poisson distribution	Narrow range ($Đ < 1.5$) Poisson distribution
Dormant states	None	Rare	Predominant

TABLE 8.1. Commercially Available Polymers Synthesized with Complex Coordination Catalysts

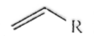
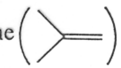
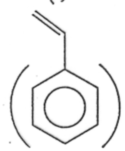
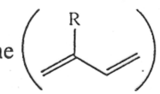
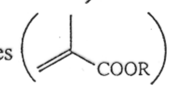
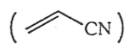
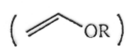
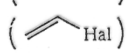
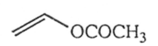
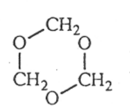
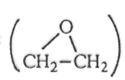
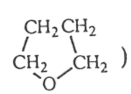
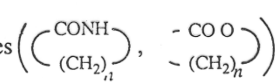
Polymer	Principal Stereochemistry	Typical Uses
Plastics		
Polyethylene, high density (HDPE)	—	Bottles, drums, pipe, conduit, sheet, film, wire and cable insulation
Polyethylene, ultrahigh molecular weight (UHMWPE)	—	Surgical prostheses, machine parts, heavy-duty liners
Polypropylene	Isotactic	Automobile and appliance parts, rope, cordage, webbing, carpeting, film
Poly(1-butene)	Isotactic	Film, pipe
Poly(4-methyl-1-pentene)[a]	Isotactic	Packaging, medical supplies, lighting
Polystyrene	Syndiotactic	Specialty plastics
1,4-Polybutadiene	*trans*	Metal can coatings, potting compounds for transformers
1,4-Polyisoprene	*trans*	Golf ball covers, orthopedic devices
Ethylene-1-alkene[b] copolymer (linear low-density polyethylene, LLDPE)	—	Blending with LDPE, packaging film, bottles
Ethylene-propylene block copolymers (polyallomers)	Isotactic	Food packaging, automotive trim, toys, bottles, film, heat-sterilizable containers
Polydicyclopentadiene[c]	—	Reaction injection molding (RIM) structural plastics
Elastomers		
1,4-Polybutadiene	*cis*	Tires, conveyer belts, wire and cable insulation, footware
1,4-Polyisoprene	*cis*	Tires, footware, adhesives, coated fabrics
Poly(1-octenylene) (polyoctenamer)[c]	*trans*	Blending with other elastomers
Poly(1,3-cyclopentenylenevinylene) (norbornene polymer)[c]	*trans*	Molding compounds, engine mounts, car bumper guards
Polypropylene (amorphous)	—	Asphalt blends, sealants, adhesives, cable coatings
Ethylene–propylene copolymer (EPM, EPR)	—	Impact modifier for polypropylene, car bumper guards
Ethylene–propylene–diene copolymer (EPDM)	—	Wire and cable insulation, weather stripping, tire side walls, hose, seals

[a] Usually copolymerized with small amounts of 1-pentene.

[b] 1-Butene, 1-hexene, and 1-octene.

[c] Synthesized by ring-opening metathesis polymerization of the corresponding cycloalkene.

Table 4.2 Initiation modes of various monomers

Monomer	Initiator: Free radical	Anionic	Cationic	Co-ordination
Ethylene ()	√			√
Propylene (and other α-olefins )				√
Isobutylene ()			√	
Styrene ()	√	√	√	√
Butadiene and isoprene ()	√	√		√
Acrylates and methacrylates ()	√	√		
Acrylonitrile ()	√	√		
Vinyl ethers ()			√	
Vinyl halides ()	√			
Fluorocarbons (e.g. TFE, $CF_2{=}CF_2$)	√			
Vinyl esters (e.g. acetate )	√			
Formaldehyde ($CH_2{=}O$)			√	
Formaldehyde trimer (trioxan )		√		√
Ethylene oxide ()		√		√
Cyclic ethers (e.g. THF )			√	√
Cyclic lactams and lactones ()		√		√
Cyclic siloxanes ($R_2SiO_{3\text{ or }4}$)		√		
Cycloalkenes and cycloalkynes				√
Alkynes ($\equiv$—R)				√

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