

Metal-Catalyzed Polymerizations

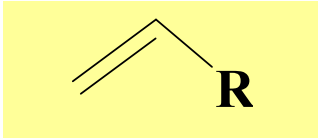
Pedro T. Gomes

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
- CATIONIC
- ANIONIC
- COORDINATION

initiators: ROOR, ROOH, R-N≡N-R

initiators: Brønsted acids, Lewis acids, stable cations

initiators: alkyl or aryl lithium or sodium compounds, sodium

catalysts: Ziegler-Natta, **metallocenes**, **post-metallocenic**
(the only method that homo- and copolymerizes propylene and α -olefins)

GENERAL MECHANISM

Chain Growth

- INITIATION
- PROPAGATION
- CHAIN TRANSFER
- TERMINATION

common to all types

they can be suppressed when the polymerization is “**controlled**”

↓
“**Living**” polymerization

ZIEGLER-NATTA CATALYSTS

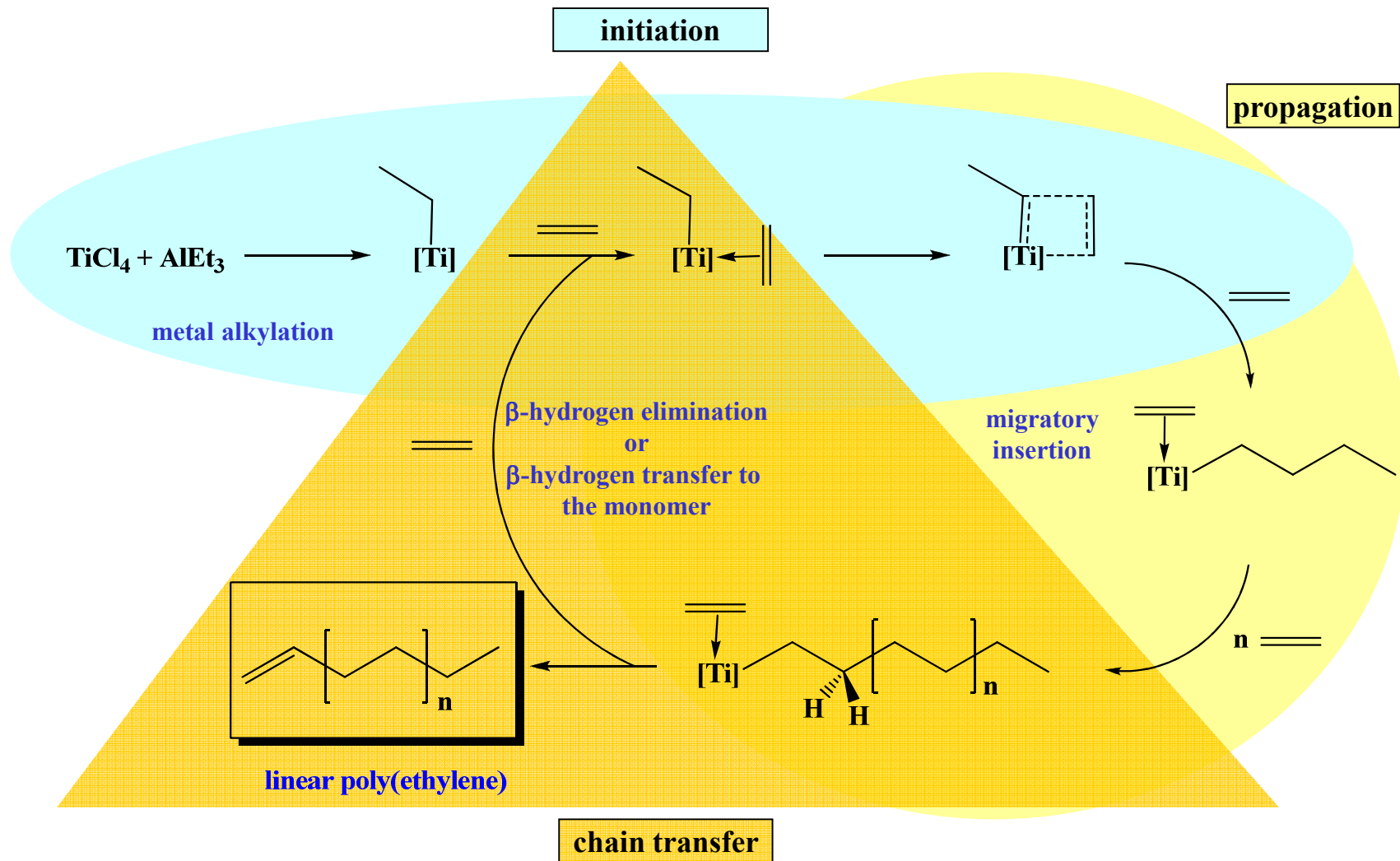
DEFINITION:

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

	IA 1																	VIII 18
1	H 1	IIA 2	Metais alcalino-terrosos										Não-metais					He 2
2	Li 3	Be 4	Metais										B 5	C 6	N 7	O 8	F 9	Ne 10
3	Na 11	Mg 12	IIIA 13	IVA 14	VA 15	VIA 16	VIIA 17	VIIIA 18	VIIIA 19	VIIIA 20	IB 21	IIB 22	Al 13	Si 14	P 15	S 16	Cl 17	Ar 18
4	K 19	Ca 20	Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26	Co 27	Ni 28	Cu 29	Zn 30	Ga 31	Ge 32	As 33	Se 34	Br 35	Kr 36
5	Rb 37	Sr 38	Y 39	Zr 40	Nb 41	Mo 42	Tc 43	Ru 44	Rh 45	Pd 46	Ag 47	Cd 48	In 49	Sn 50	Sb 51	Te 52	I 53	Xe 54
6	Cs 55	Ba 56	La 57	Hf 72	Ta 73	W 74	Re 75	Os 76	Ir 77	Pt 78	Au 79	Hg 80	Tl 81	Pb 82	Bi 83	Po 84	At 85	Rn 86
7	Fr 87	Ra 88	Ac 89	Rf 104	Db 105	Sg 106	Metais de transição					Metalóides						
	Metais alcalinos												Halogénios					
													Gases nobres					
Lantanídeos	Ce 58	Pr 59	Nd 60	Pm 61	Sm 62	Eu 63	Gd 64	Tb 65	Dy 66	Ho 67	Er 68	Tm 69	Yb 70	Lu 71				
Actinídeos	Th 90	Pa 91	U 92	Np 93	Pu 94	Am 95	Cm 96	Bk 97	Cf 98	Es 99	Fm 100	Md 101	No 102	Lr 103				

By analogy with homogeneous metallocene catalysts

Mechanism of Olefin Polymerization with Ziegler-Natta Catalysts



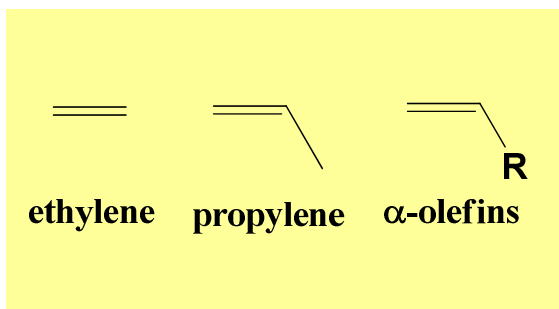
$[\text{Ti}] \equiv$ heterogeneous metal site (it can also be a metallocene or a post-metallocene)

POLYOLEFINS

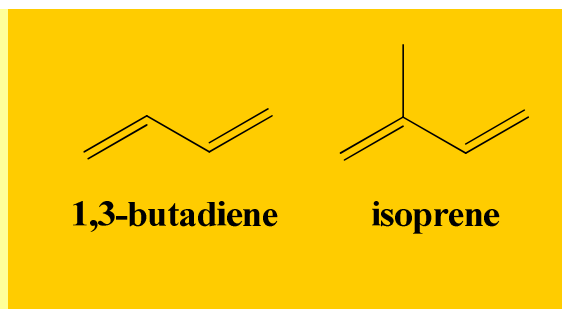
Olefin = unsaturated hydrocarbon = Alkene

Typical Olefin Monomers:

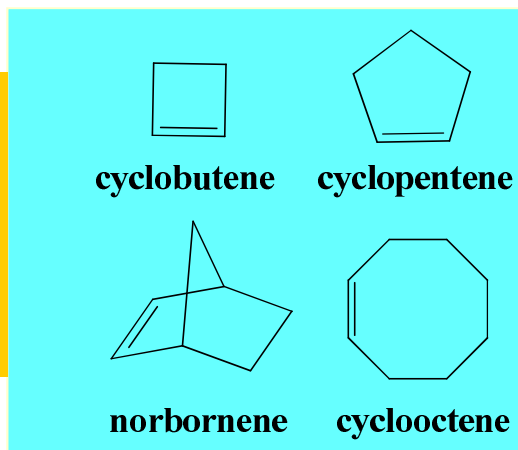
Aliphatic monoolefins (C_nH_{2n}):



Aliphatic diolefins (C_nH_{2n-2}):



Cycloolefins (C_nH_{2n-2}):



PLASTICS
("COMMODITY")

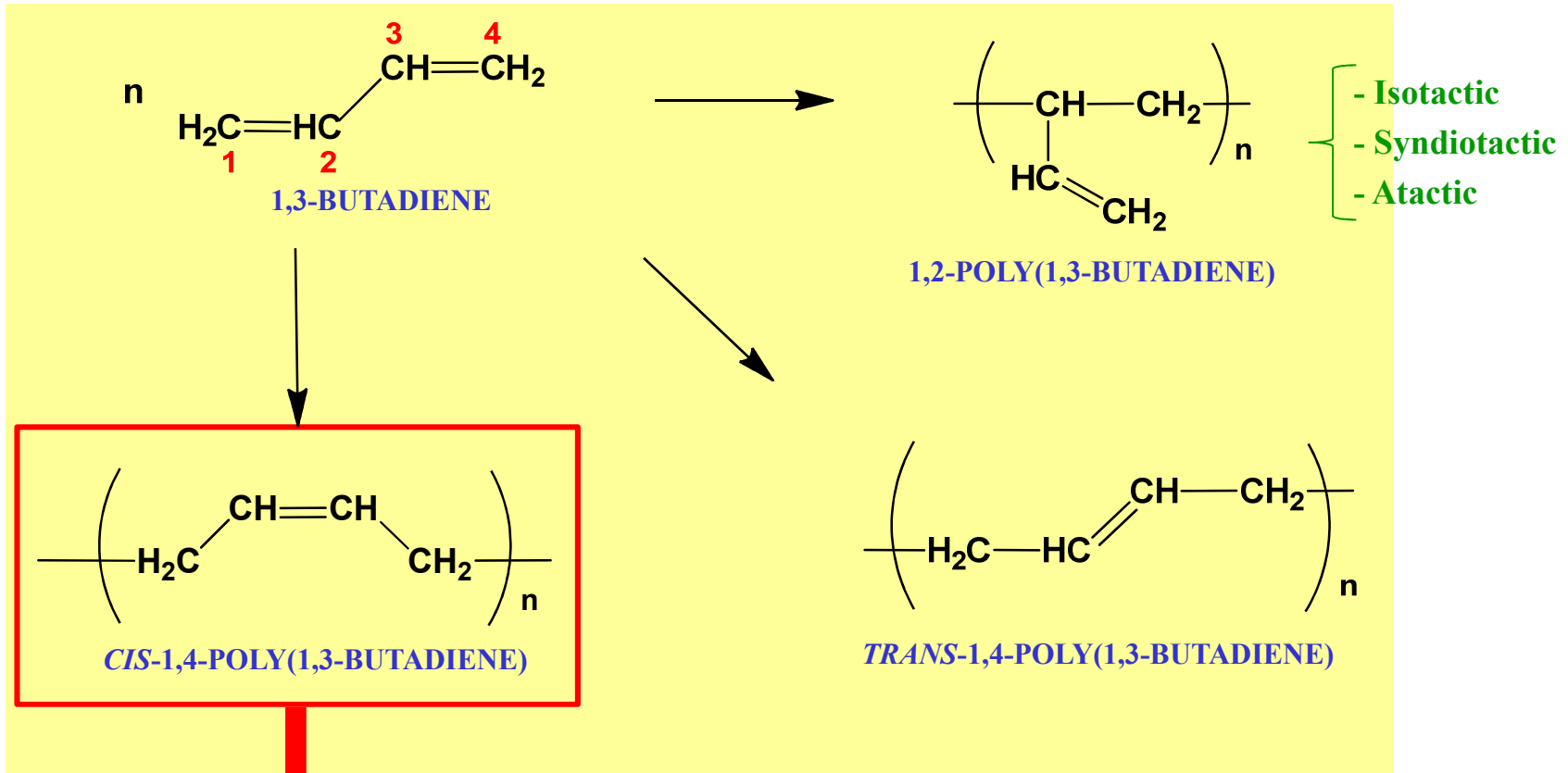
ELASTOMERS

SPECIALTY POLYMERS

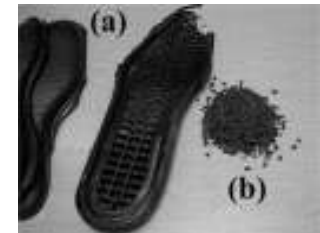
Metal-Catalyzed Polymerization ***(Coordination Polymerization)***

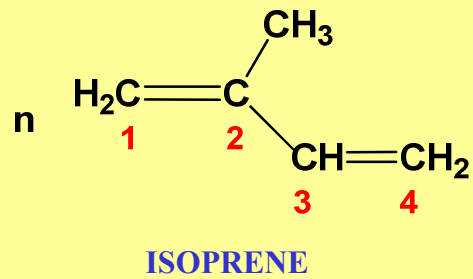
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POLYMERIZATION OF DIENES

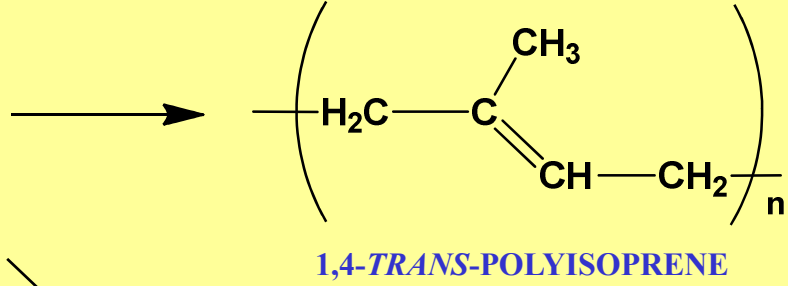


SYNTHETIC RUBBER





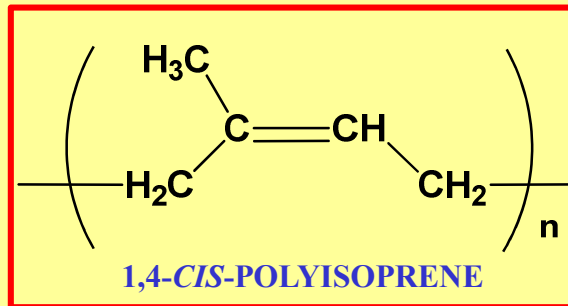
polymers with low percentage of 1,2 and 3,4 units



From natural sources:

GUTTA-PERCHA

- Hard material:
- Insulator
 - Old golf balls



From natural sources:

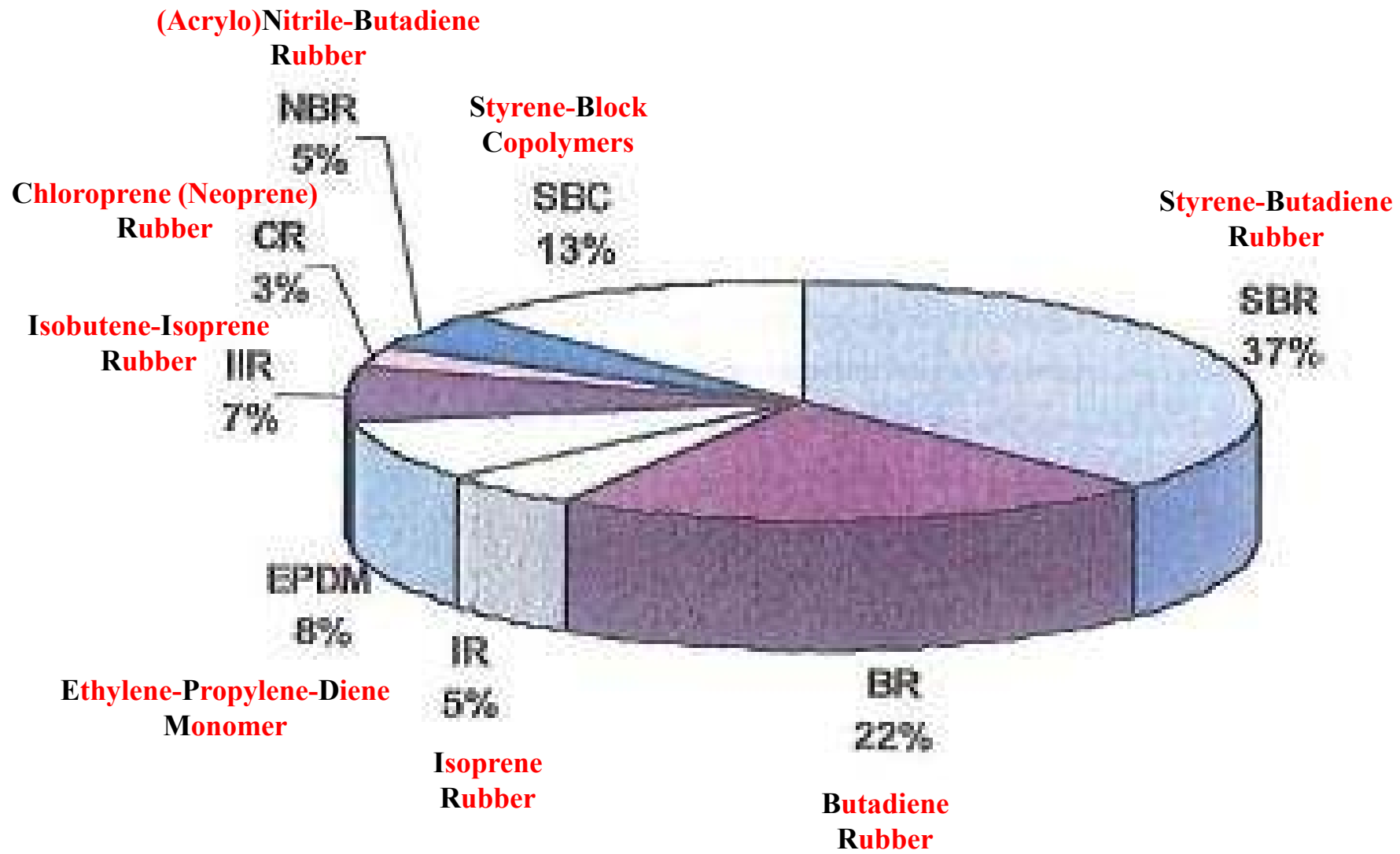
NATURAL RUBBER

- *Hevea Brasiliensis*
- *Guayule*

SYNTHETIC NATURAL RUBBER



SYNTHETIC RUBBER MARKET



STEREOREGULAR ELASTOMERS

1,4-CIS-POLYBUTADIENE

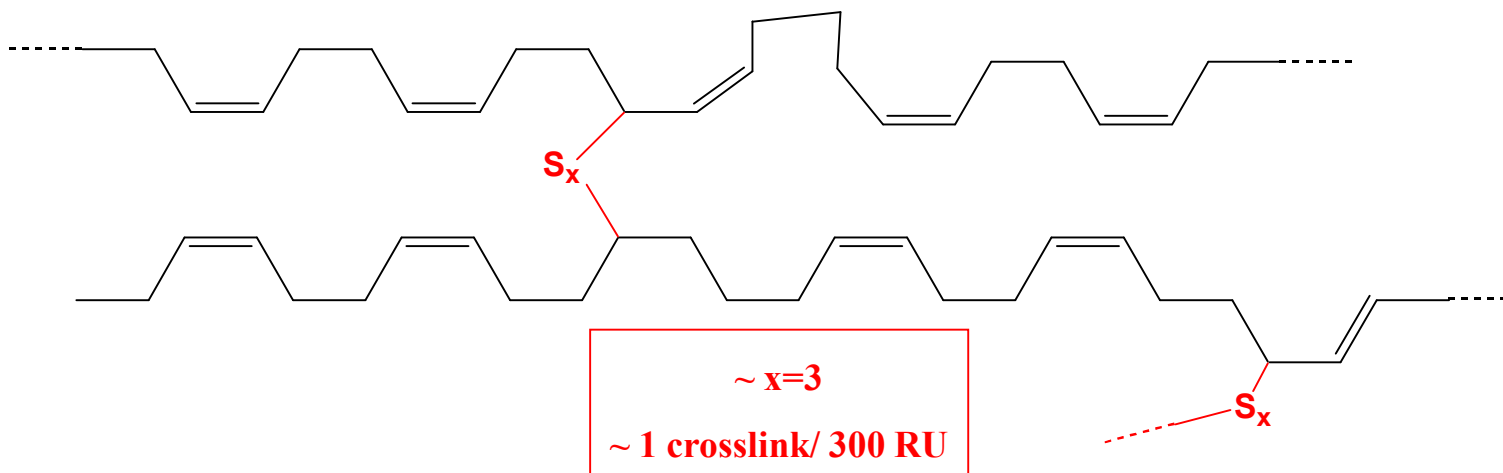
~3.2 Mton

1,4-CIS-POLYISOPRENE

~0.75 Mton

Production depends on the **NATURAL RUBBER** market

~10.3 Mton



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
<i>Total</i>	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

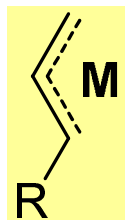
*China, Taiwan, India, Japan, Korea, Thailandia

STEREOSPECIFIC CATALYSTS - POLYBUTADIENE

• ZIEGLER-NATTA CATALYSTS

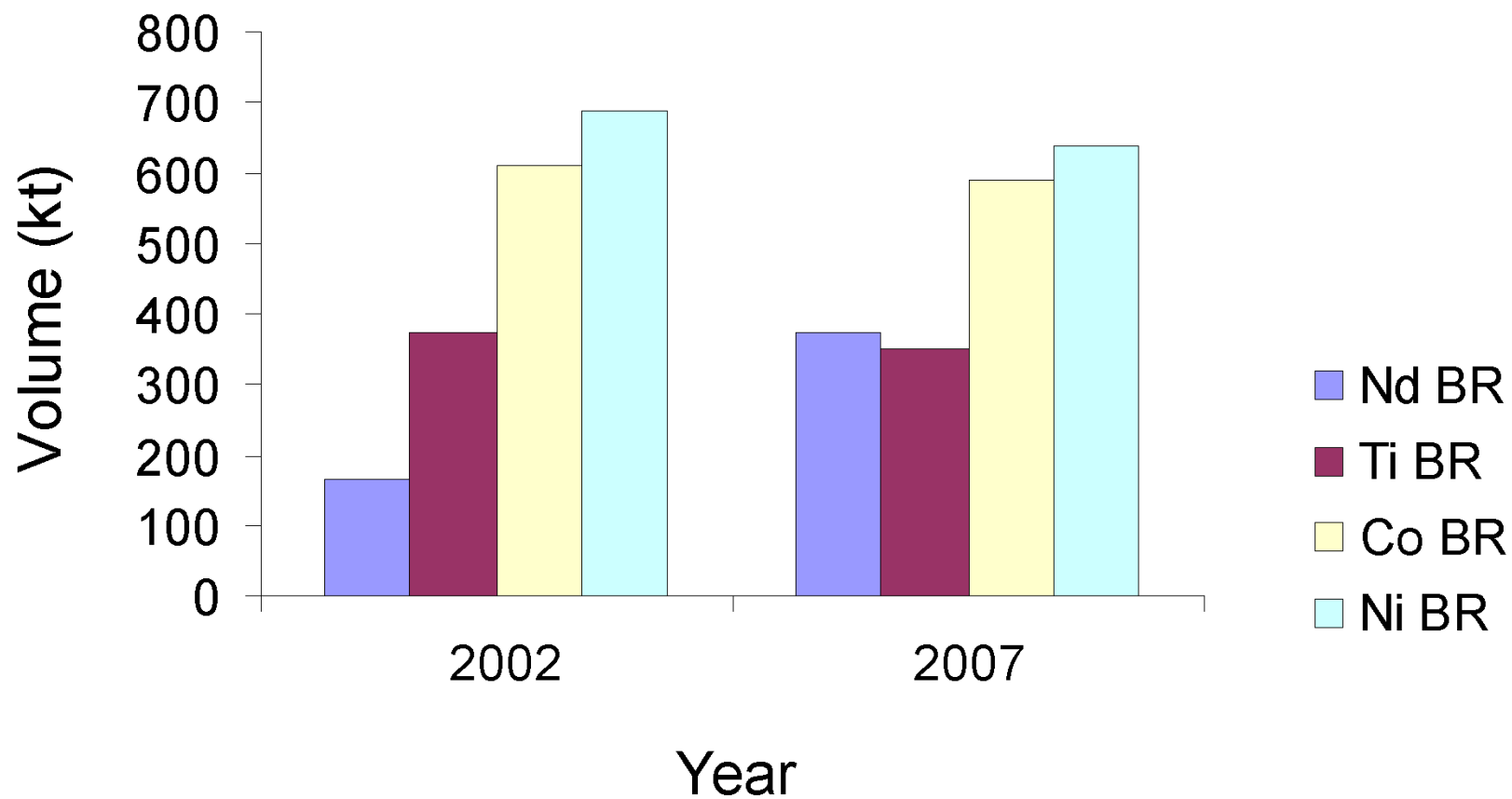
<u>High content (>90%) in:</u>		
1,4-cis	1,4-trans	1,2 (syndiotactic)
TiI ₄ + Al(<i>i</i> Bu) ₃ (1:4-5), 30 °C	γ -TiCl ₃ + AlEt ₃	Ti(OR) ₄ + AlEt ₃ (1:7), 15 °C
CoCl ₂ + Al ₂ Cl ₃ Et ₃ (1:1000), 5 °C	VCl ₃ + AlEt ₃ (1:2), 15 °C	V(acac) ₃ + AlEt ₃ (1:6-10), 15 °C
Co(acac) ₂ + AlEt ₂ Cl + H ₂ O (branched polymer)	VCl ₄ + AlEt ₃ (1:1.8), 15 °C	Cr(C ₆ H ₅ CN) + AlEt ₃ (1:2) Cr(C ₆ H ₅ CN) + AlEt ₃ (1:10) (isot.)
Ni(octanoate) ₂ + AlEt ₃ + BF ₃ ·OEt ₂ (1:17:15), 50 °C	V(acac) ₃ + AlEt ₂ Cl + Cl ₃ CCO ₂ H, 80 °C	Co(acac) ₃ + AlEt ₃ (1:50), 16 °C
U(OR) ₄ + AlEt ₂ Cl	VOCl ₃ + AlEt ₃	Co(acac) ₃ + AlEt ₃ + H ₂ O + CS ₂
Nd(neodecanoate) ₃ + AlR ₂ Cl + AlR ₃ , 60 °C	V(acac) ₃ + MAO (1:1000)	

• ALLYL METAL CATALYSTS (without Alkyl Aluminium cocatalyst)

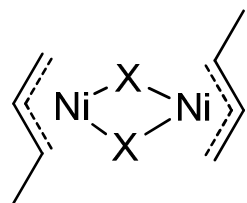


M= Cr, Co, Nb, W, Rh, U, Ni

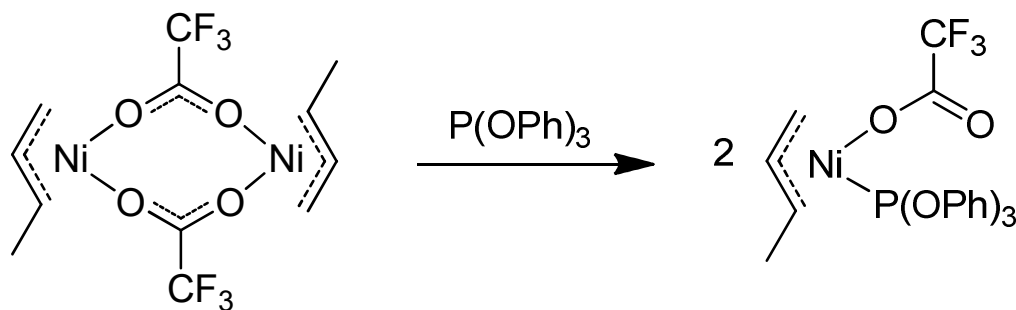
Catalysts for high *cis*-1,4 Polybutadiene



EXAMPLES OF ALLYL NICKEL STEREOSPECIFIC CATALYSTS



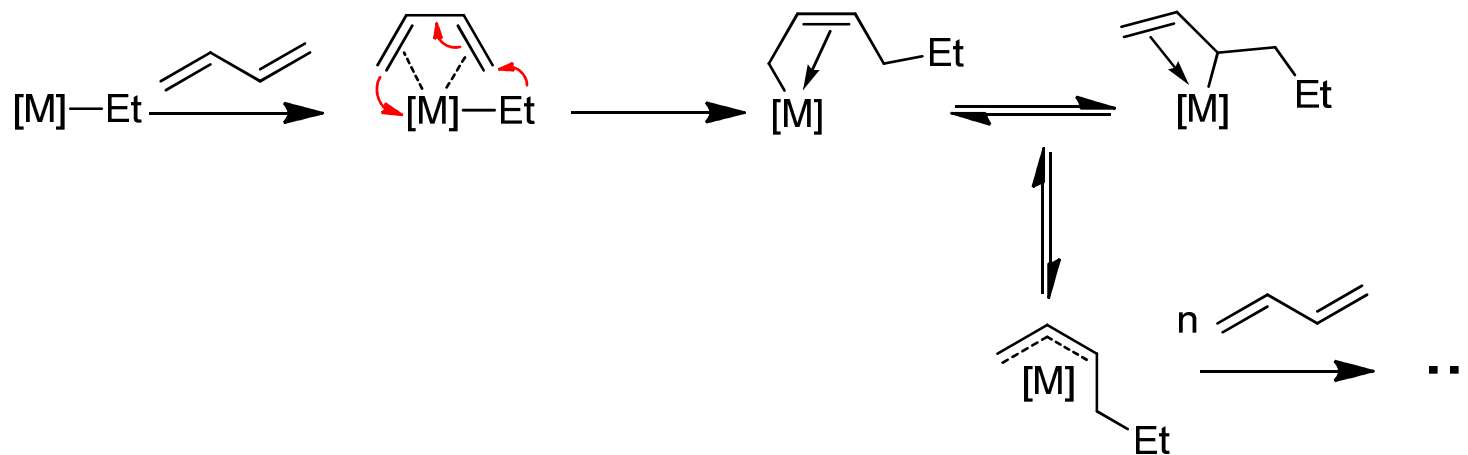
X	1,4-<i>cis</i>	1,4-<i>trans</i>	1,2
Cl	92	6	2
Br	72	25	3
I	0	97	3



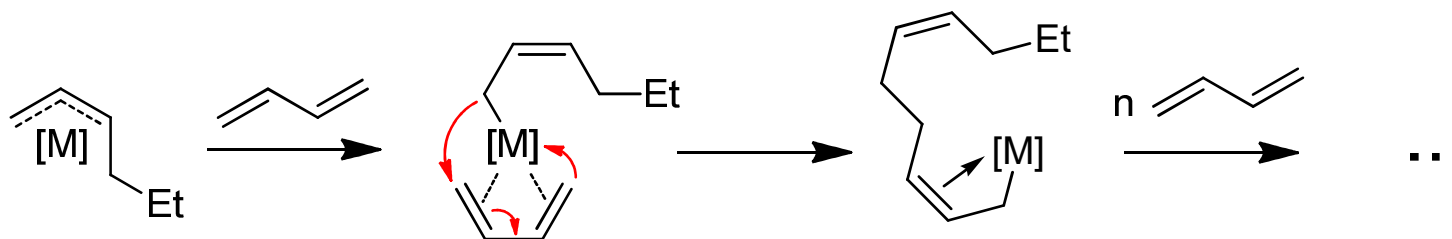
1,4-<i>cis</i>	97	0
1,4-<i>trans</i>	2	96
1,2	1	4

STEREOREGULATION MECHANISM

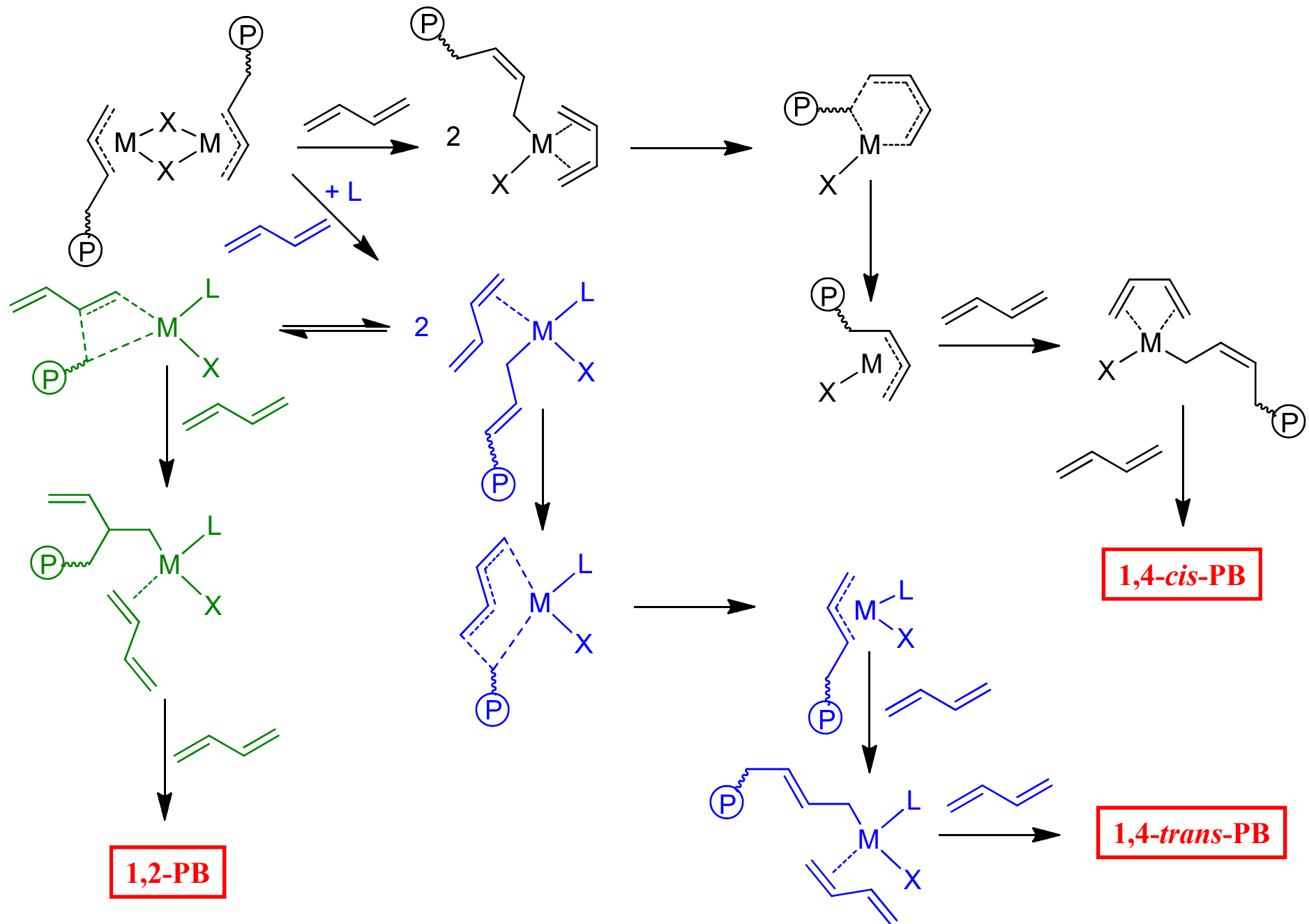
• INITIATION (Z-N CATALYSTS)



• PROPAGATION



STEREOREGULATION MECHANISM



STEREOSPECIFIC CATALYSTS - POLYISOPRENE

• ZIEGLER-NATTA CATALYSTS

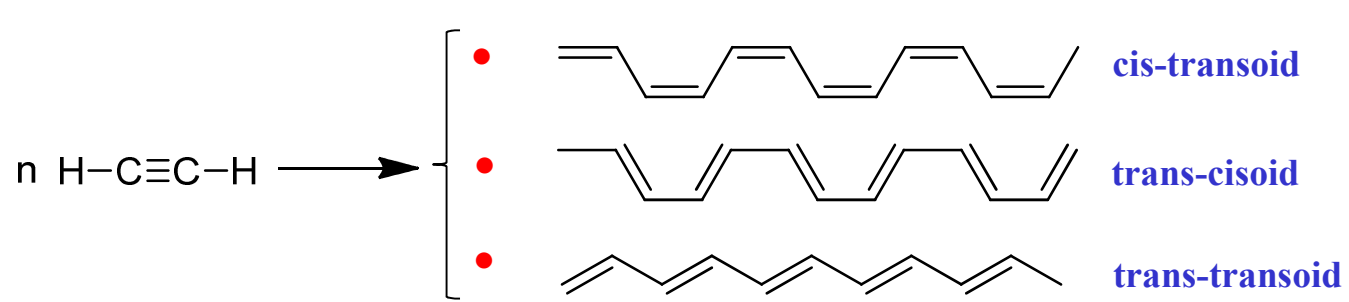
<u>High content (>90%) in:</u>		
1,4-cis	1,4-trans	3,4
$\text{TiCl}_4 + \text{AlEt}_3 \text{ (Al/Ti > 1)}$	$\text{TiCl}_4 + \text{AlEt}_3 \text{ (Al/Ti < 1)}$ $\alpha\text{-TiCl}_3 + \text{AlR}_3$ $\text{VCl}_3 + \text{AlEt}_3$	$\text{Ti(OR)}_4 + \text{AlEt}_3$

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POLYMERIZATION OF ALKYNES

(POLYMERIZATION OF ACETYLENE)



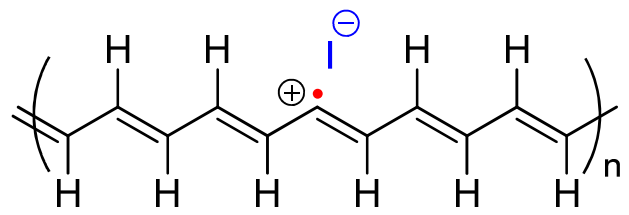
cis
insulator
 $(\sigma = 4 \times 10^{-9} \Omega^{-1} \text{ cm}^{-1})$

trans
semiconductor
 $(\sigma = 9 \times 10^{-5} \Omega^{-1} \text{ cm}^{-1})$

↓
doped with oxidants (1977)
(ex: I_2)

Au ($\sigma = 2.4 \times 10^4$)
Cu ($\sigma = 7.2 \times 10^4$)

conductor
 $\sigma = 1.5 \times 10^3 \Omega^{-1} \text{ cm}^{-1}$



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

- $\text{Ti}(\text{OBu})_4 + \text{AlEt}_3$ (Natta, 1958)
- $\text{Ti}(\text{OBu})_4 + \text{AlEt}_3$ (Al/Ti \sim 4) (Shirakawa, 1974) good films when $[\text{Ti}] < 10^{-3} \text{ M}$
- $\text{Ti}(\text{OBu})_4 + \text{LiBu}$ (Li/Ti \sim 2) high *trans* %
- $\text{MoCl}_5 + \text{SnPh}_4$
- $\text{WCl}_6 + \text{SnPh}_4$
- $\text{NiX}_2(\text{PR}_3)_2$ (X= Cl, Br, I) high *trans* %

POLYACETYLENE

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

- $\text{Ti}(\text{OBu})_4 + \text{AlEt}_3$ (Al/Ti ~ 4)

- $\text{Ti}(\text{OBu})_4 + \text{LiBu}$ (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 $7\times$ the original length

Highly oriented transparent films

↓
Doping with I_2

Ti/Al catalyst: $\sigma = 2 \times 10^4 \Omega^{-1} \text{cm}^{-1}$ (20 μm film)
 $\sigma = 8 \times 10^3 \Omega^{-1} \text{cm}^{-1}$ (0.1 μm film)

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

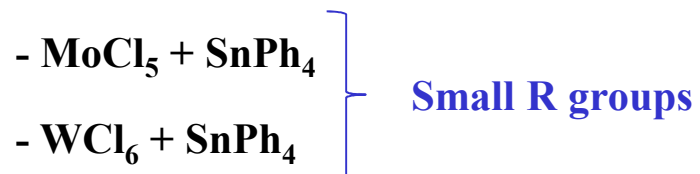
**BASF abandoned
this process with the
appearance of new
conducting polymers
(more stable and
processable)**

POLYMERIZATION OF SUBSTITUTED ACETYLENES



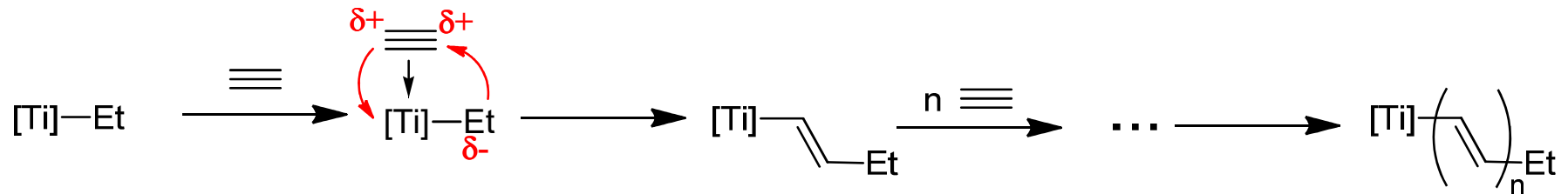
- POLYMERS: {
- More soluble (in organic solvents)
 - More stable in air
 - The majority are electric insulators

• CATALYSTS

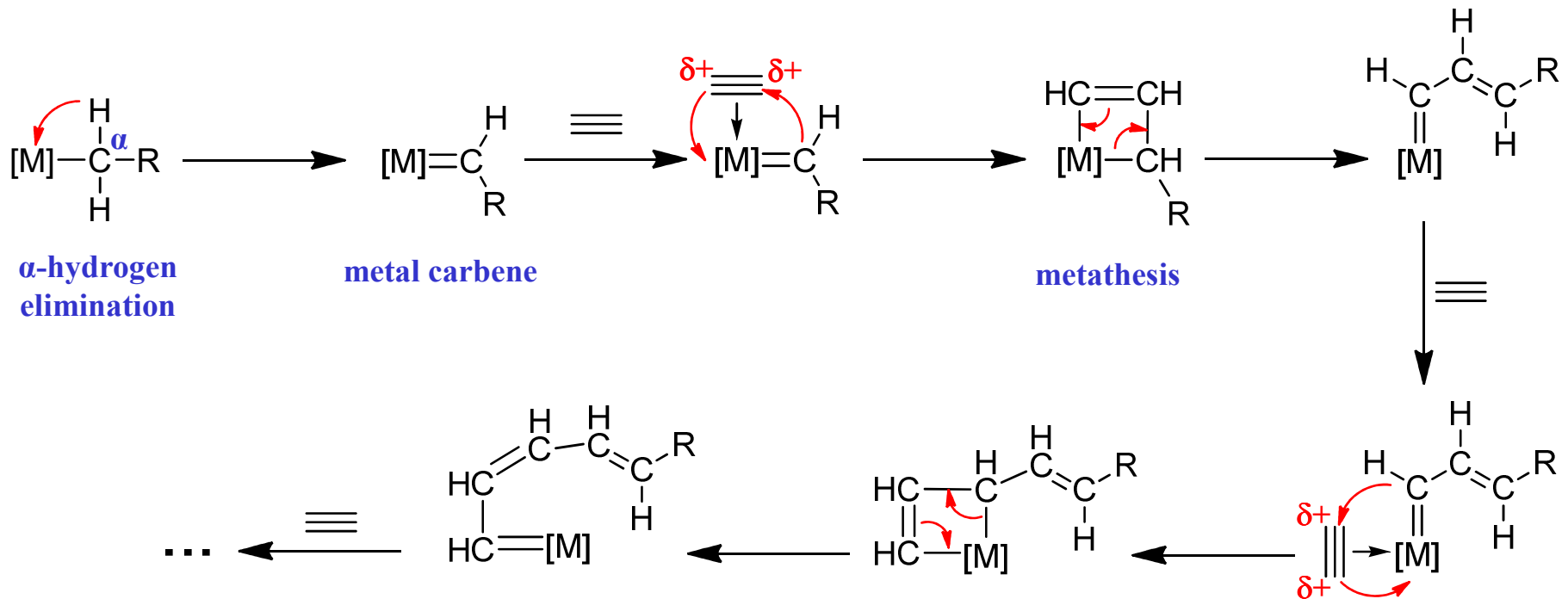


MECHANISM

• Ti ZIEGLER-NATTA CATALYSTS (insertion mechanism)



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



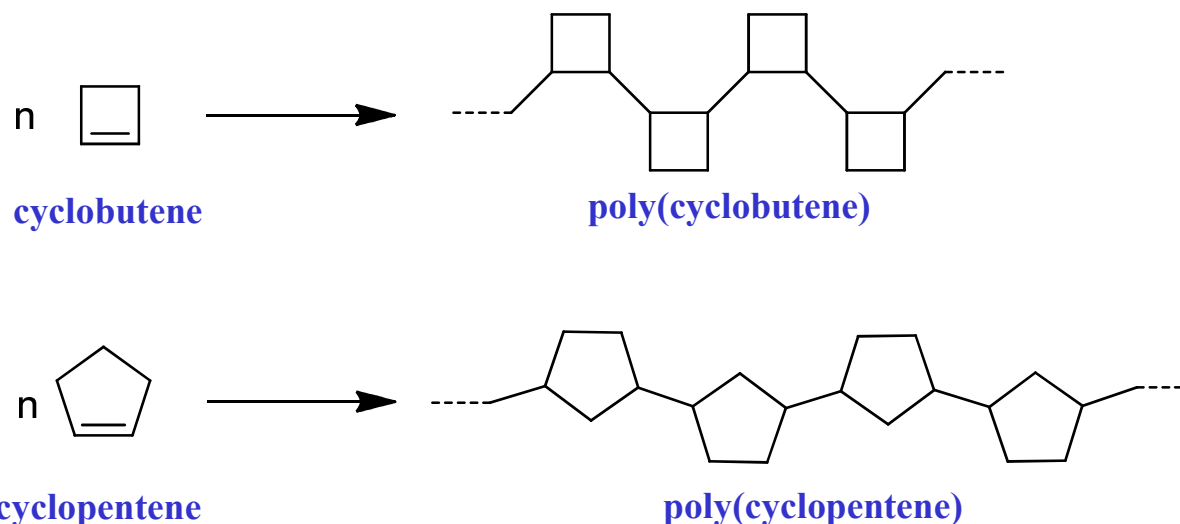
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RING-OPENING METATHESIS POLYMERIZATION (ROMP)

MONOMERS: Cycloolefins and Cycloalkynes

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

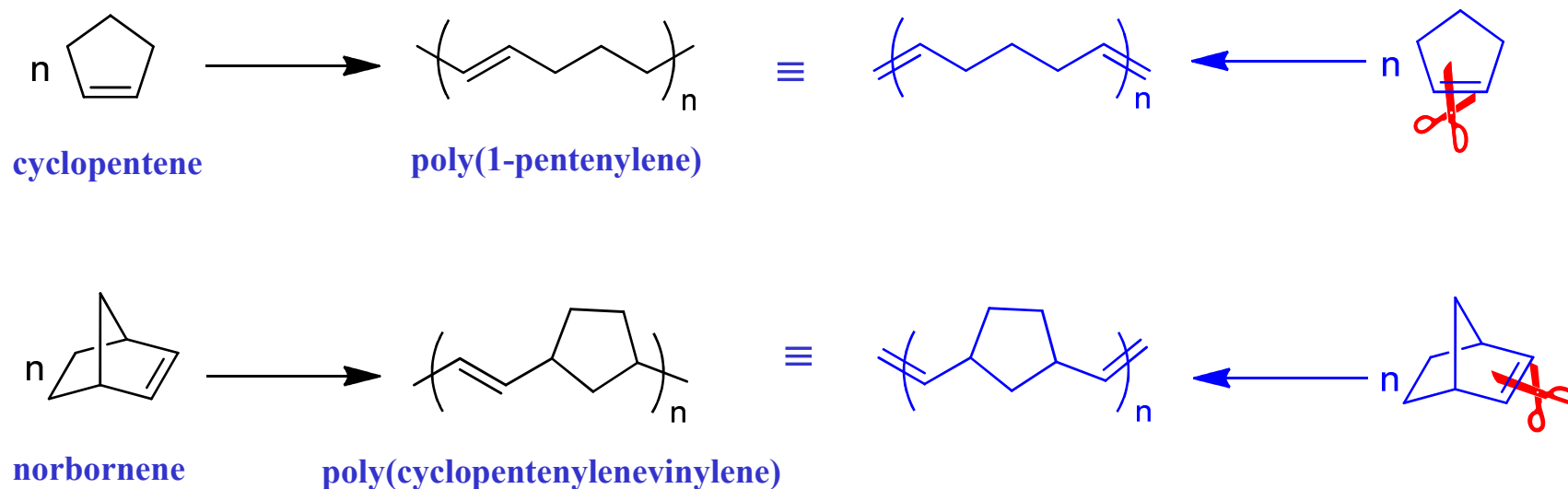


- The polymers do not have double bonds in the main chain
- Very rigid polymers (high melting temperatures)
- May copolymerize with linear α -olefins (metallocene catalysts) to give amorphous copolymers

BUT...

RING-OPENING METATHESIS POLYMERIZATION (ROMP)

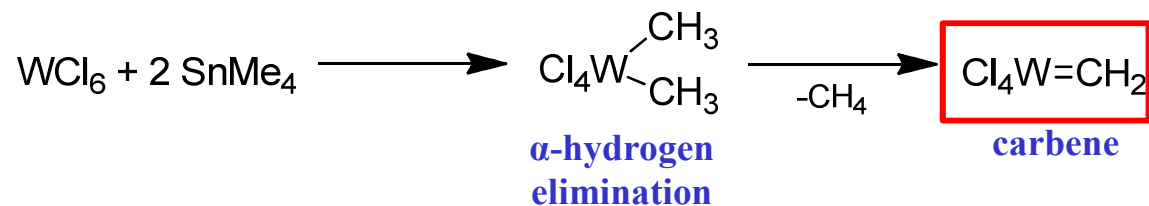
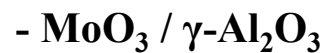
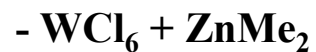
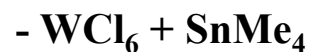
When Ziegler-Natta catalysts based on Group 6 metal (Mo, W) or metal carbene catalysts are used the polymerization occurs by **Ring-Opening Methathesis Polymerization**:



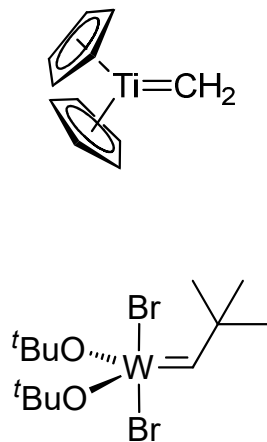
- The **monomer double bond is retained** in the polymer main chain
- The polymerization has a **living** character
- Easy **block-copolymerization**
- **Ring tension favours** ROMP (thermodynamically)

ROMP CATALYSTS

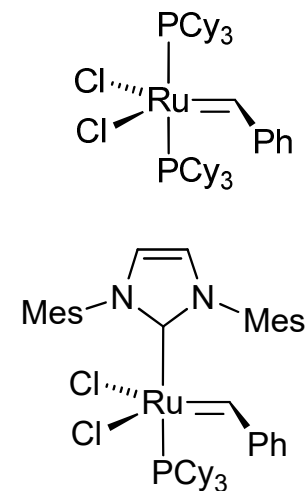
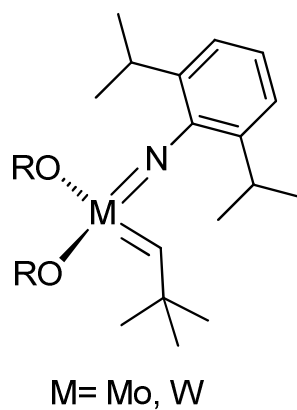
• ZIEGLER-NATTA CATALYSTS



• WELL-DEFINED CARBENE CATALYSTS



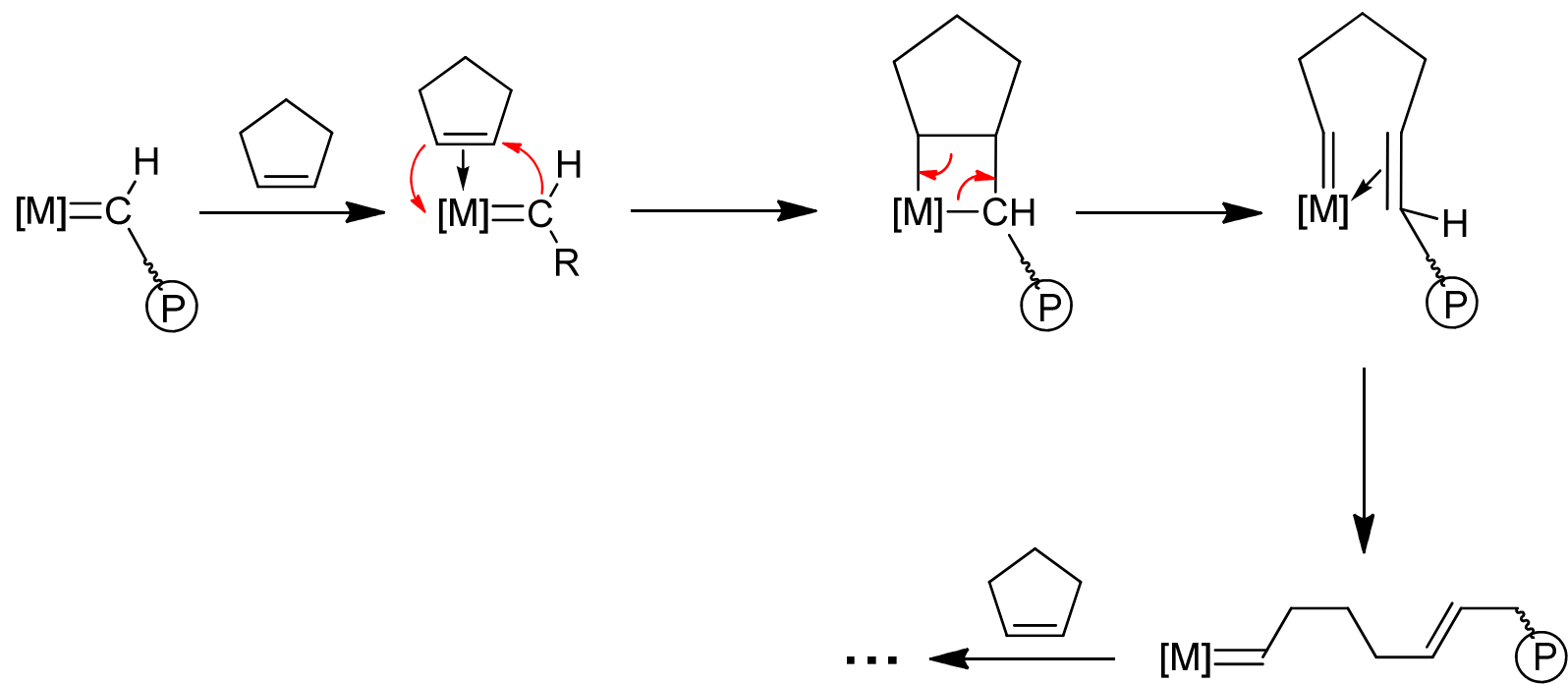
Schrock type catalysts



Grubbs type catalysts

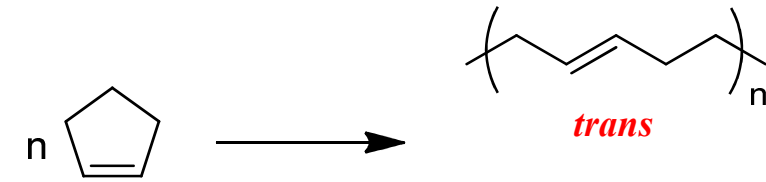
MECHANISM

• PROPAGATION



Living polymerization

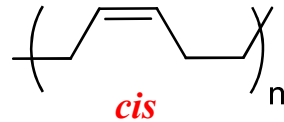
ASSORTED EXAMPLES OF ROMP



cyclopentene

trans

good elastomer

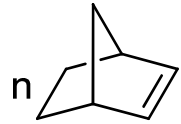


cis

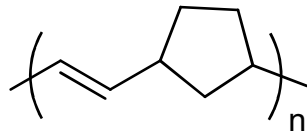
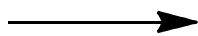
good elastomer

- Tires

poly(1-pentenylene)



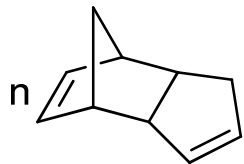
norbornene



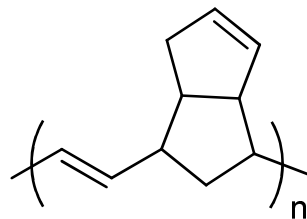
poly(cyclopentenylenevinylene)

Norsorex[®]

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



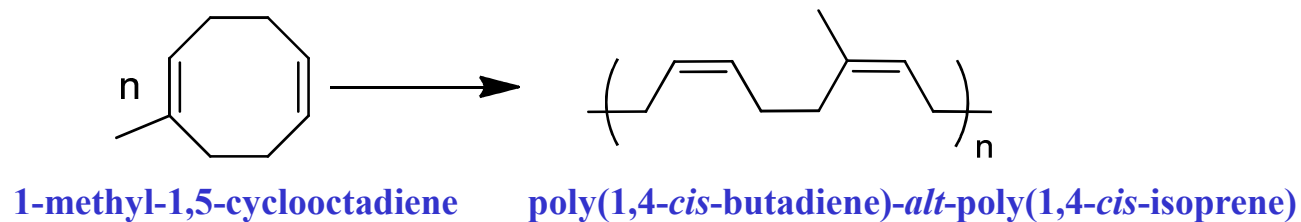
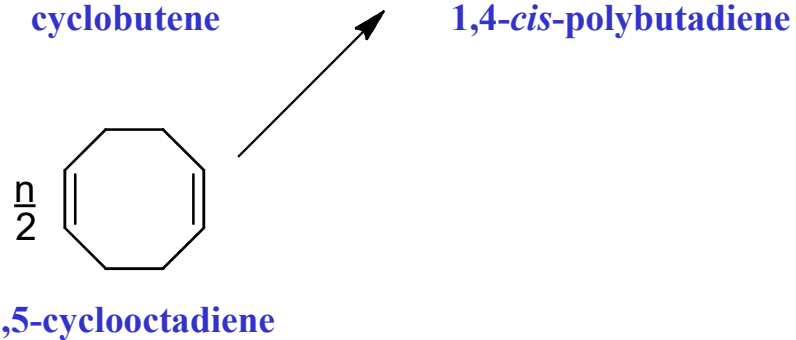
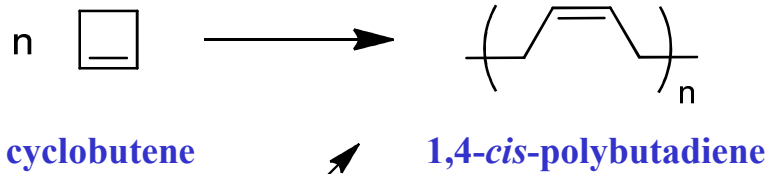
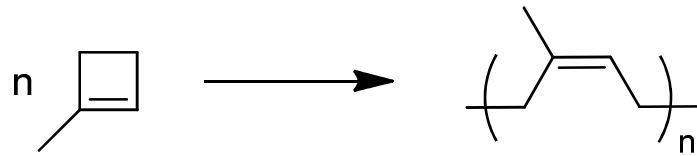
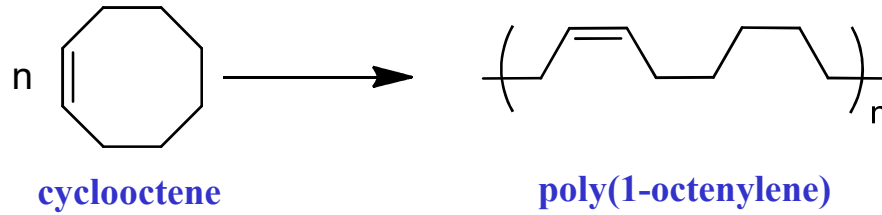
endo-
dicyclopentadiene



poly(dicyclopentadiene)

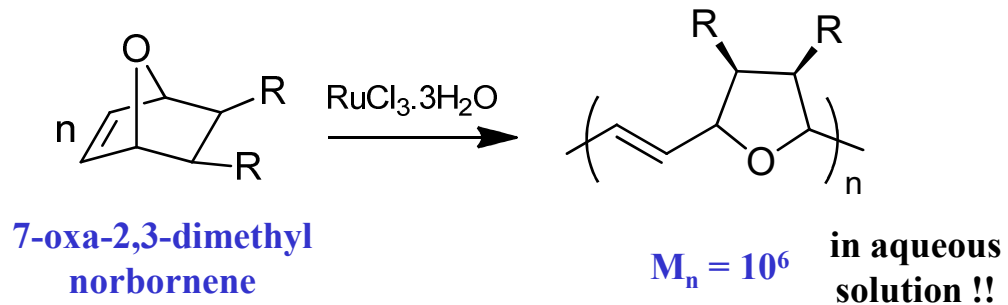
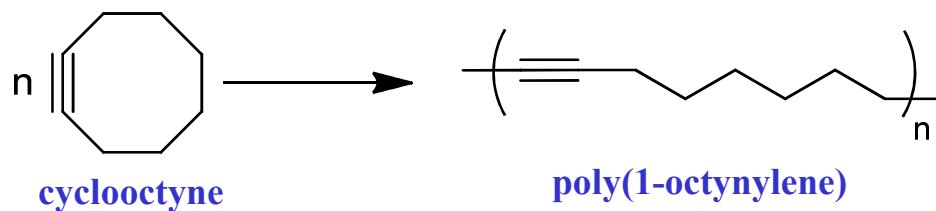
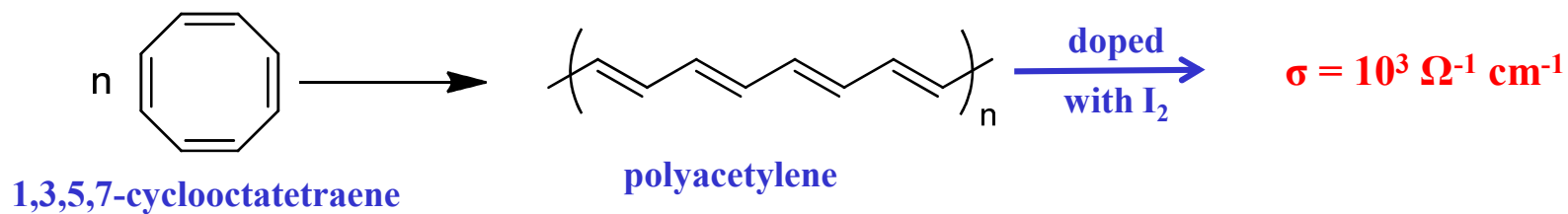
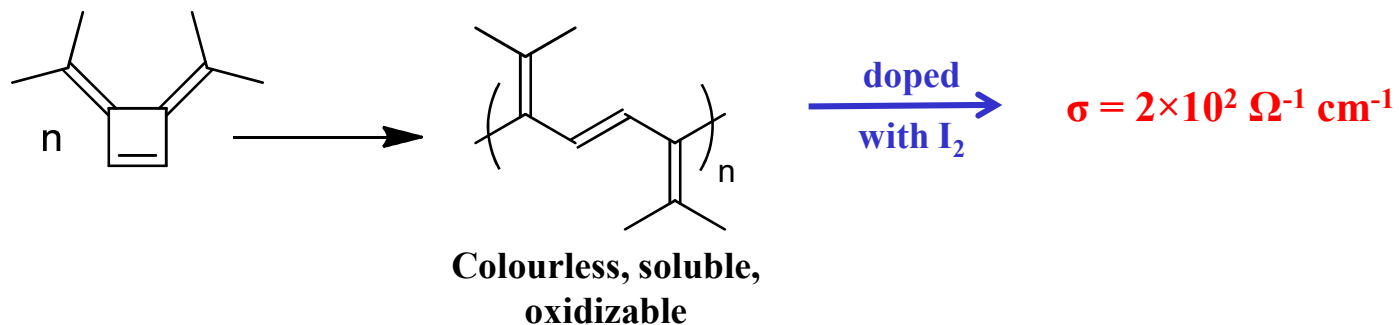
Metton[®]

- Commercial engineering plastic for moulding



Vestenamer[®]

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



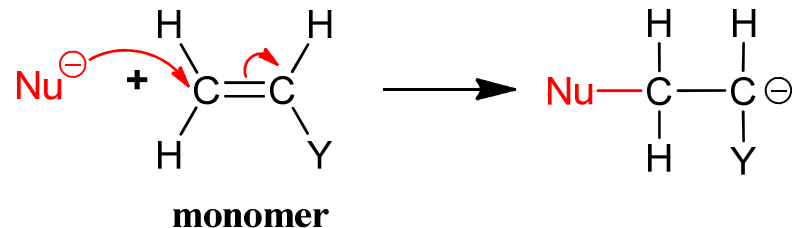
In general, the coordination polymerization experimental conditions impose **strict absence of H_2O and O_2**

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

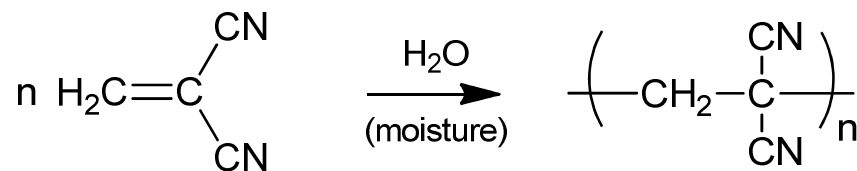
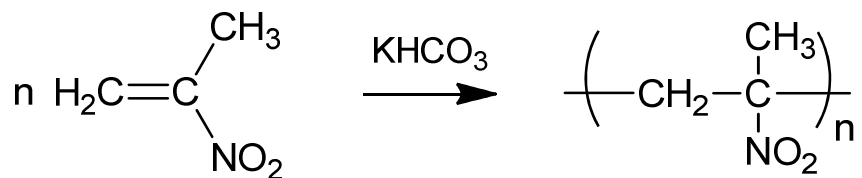


MONOMERS

Most reactive 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-CH₃ (**LiMe**), Li-CH₂-CH₂-CH₂-CH₃ (**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)

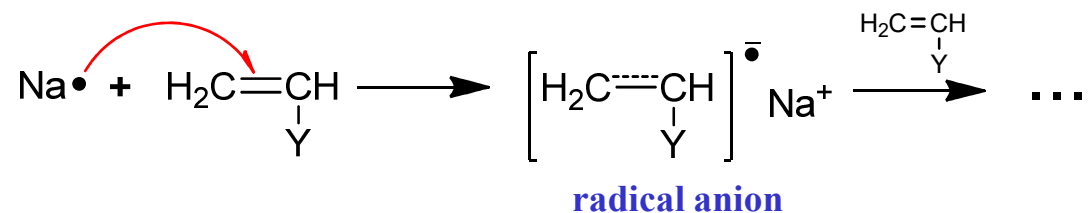
- Organometallic compounds of the alkaline earth metals (Ca, Ba)

- Grignard Reagents (RMgX)

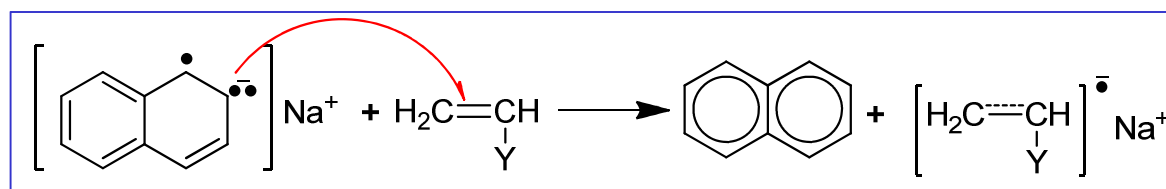
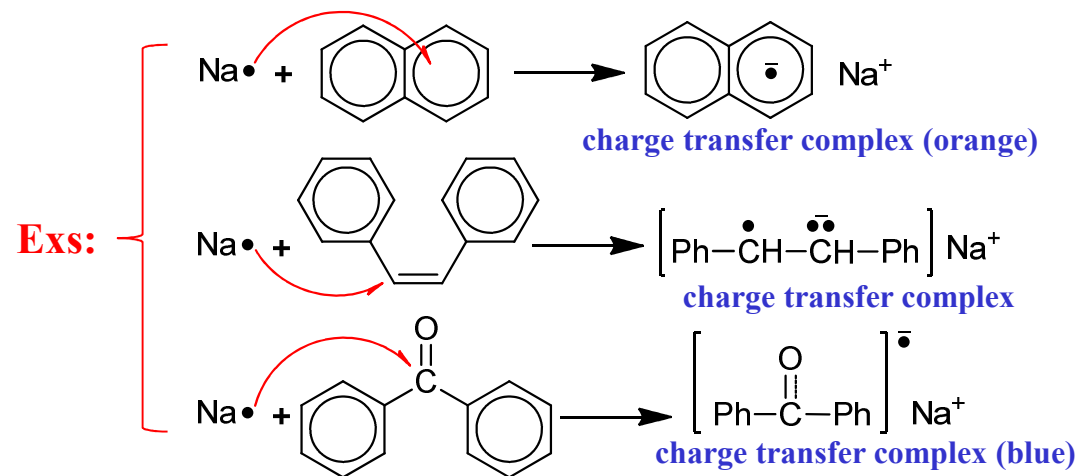
LESS
USED

• **INITIATION BY ELECTRON TRANSFER TO THE MONOMER**

- **Alkali Metals** {
- in solution (of NH₃ or certain ethers)
 - in suspension (in inert solvents –"sands")
 - supported (in alumina)



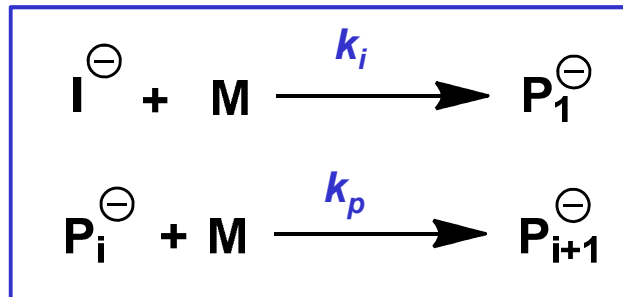
- **Alkali Metal Complexes (soluble in inert solvents)**



MECHANISM AND KINETICS

• INITIATION BY ANIONIC SPECIES

Exs: Li-CH₃ (LiMe), Li-CH₂-CH₂-CH₂-CH₃ (LiBu)



Normally, $r_i \gg r_p$ \longrightarrow chains grow all at the same time \longrightarrow $[\text{P}_i^{\ominus}]_0 = [\text{I}]_0$

$$r_p = -\frac{d[\text{M}]}{dt} = k_p [\text{I}]_0 [\text{M}]$$

$$[\text{M}] = [\text{M}]_0 e^{-k_p [\text{I}]_0 t}$$

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

$$\overline{DP}_n = \bar{x} = \frac{[\text{M}]_0 - [\text{M}]}{[\text{I}]_0} = \frac{p[\text{M}]_0}{[\text{I}]_0}$$

\overline{DP}_n = degree of polymerization

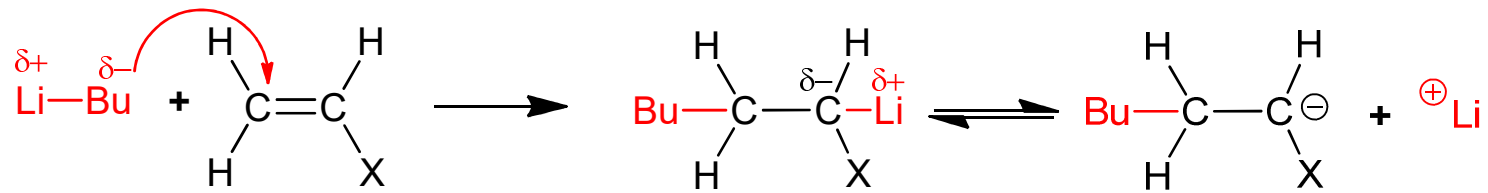
If the monomer is **totally consumed** [$p = \text{conversion} = 1$ (i.e. 100%)]:

$$\overline{DP}_n = \frac{[\text{M}]_0}{[\text{I}]_0}$$

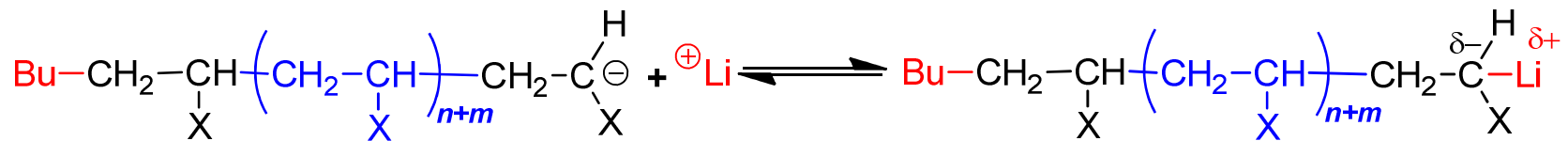
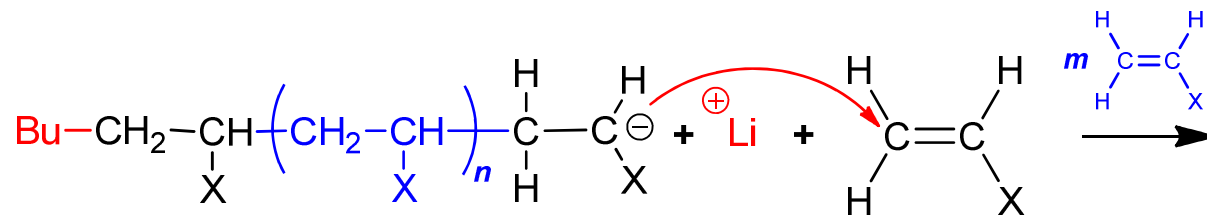
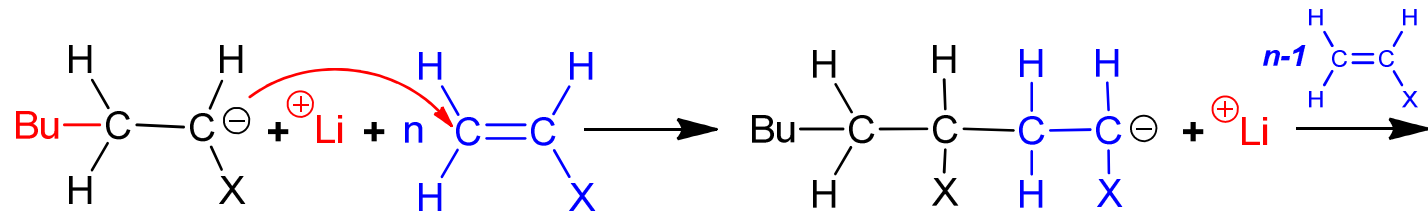
$$\frac{\overline{M}_w}{\overline{M}_n} = 1 + \frac{1}{\overline{DP}_n}$$

Poisson distribution

• Initiation



• Propagation



living polymer

“dormant” species

- If 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

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

- Non-coordinating and weakly polar solvents (e.g. hydrocarbons)

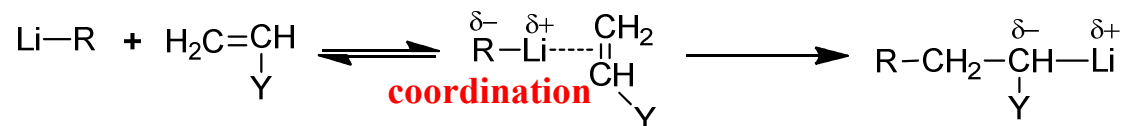
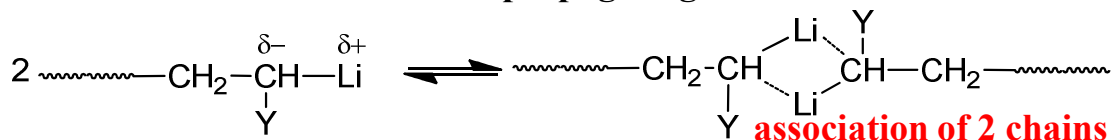


Higher degree of association of the initiator → Lower polymerization rate (r_p)

- Association of the initiator:



- Association of the propagating chain:



- More coordinating and/or more polar solvents (e.g. ethers)



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

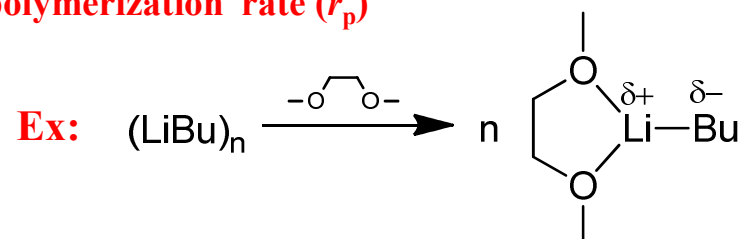
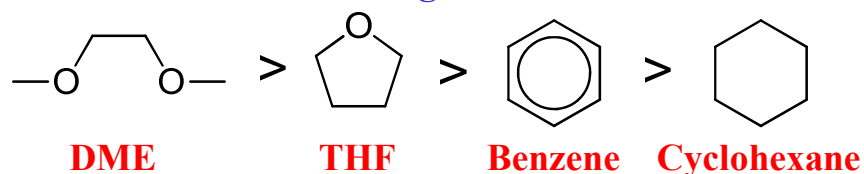


TABLE 7.4. Representative Anionic Propagation Rate Constants, k_p , for Polystyrene^a

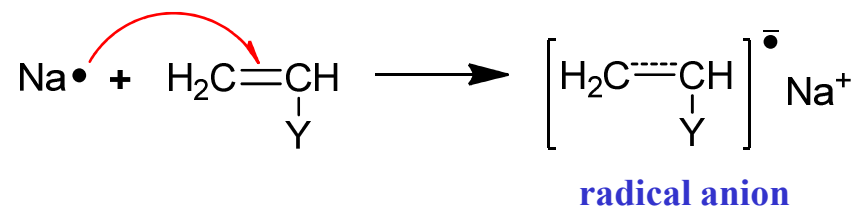
<i>Counterion</i>	<i>Solvent</i>	k_p (L/mol s) ^b
Na ⁺	Tetrahydrofuran	80
Na ⁺	1,2-Dimethoxyethane	3600
Li ⁺	Tetrahydrofuran	160
Li ⁺	Benzene	10^{-3} – 10^{-1} ^c
Li ⁺	Cyclohexane	$(5-100) \times 10^{-5}$ ^c

^aData from Morton.³⁰

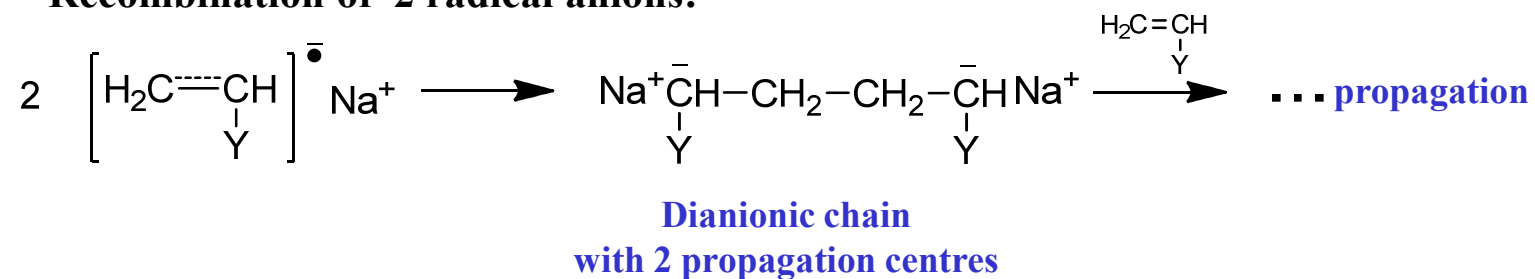
^bAt 25°C unless otherwise noted.

^cVariable temperature.

• **INITIATION BY ELECTRON TRANSFER**



Recombination of 2 radical anions:



TELECHELIC POLYMERIZATION

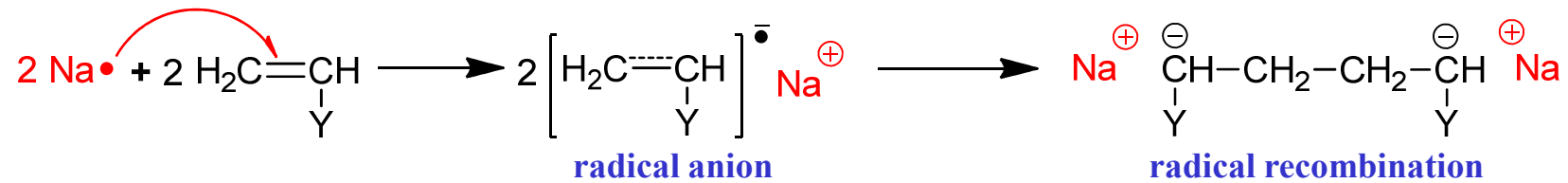


$$\overline{DP}_n = \bar{x} = 2 \frac{[\text{M}]_0 - [\text{M}]}{[\text{I}]_0}$$

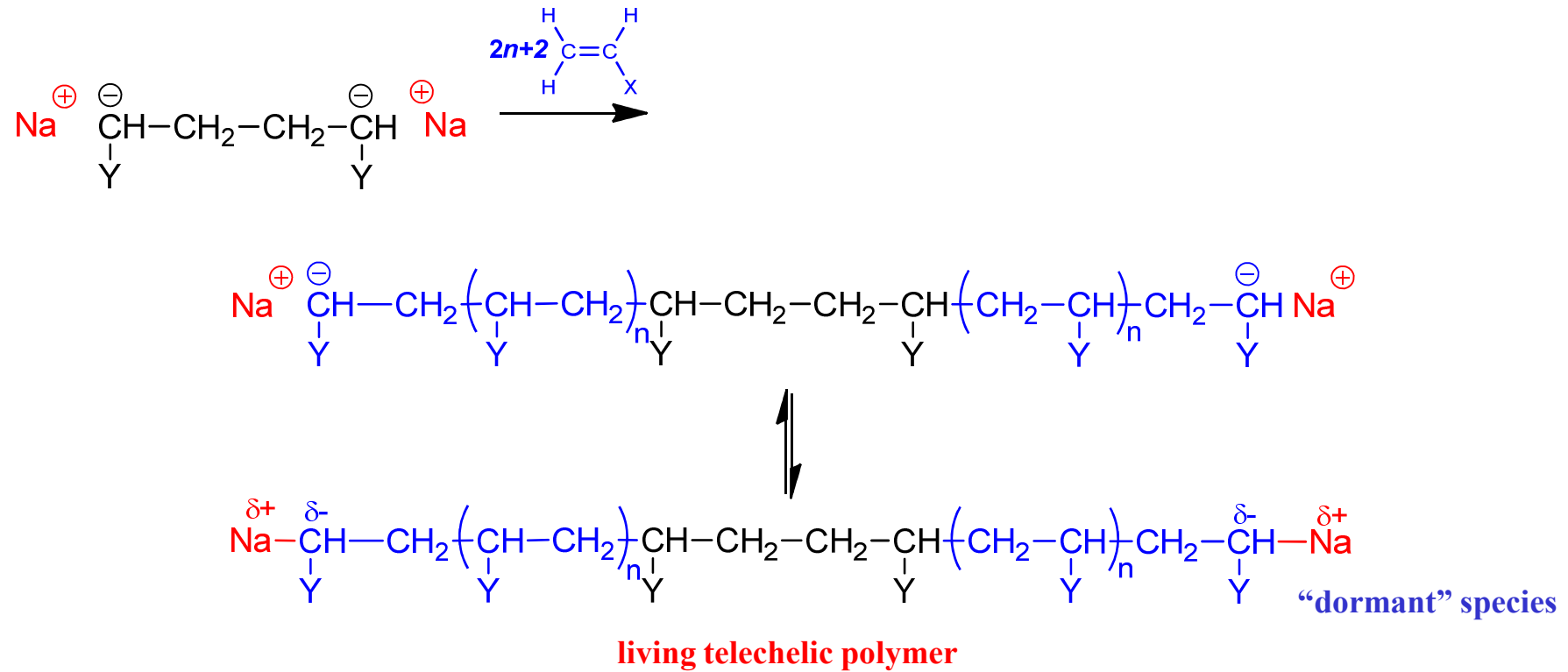


average kinetic chain length

• Initiation

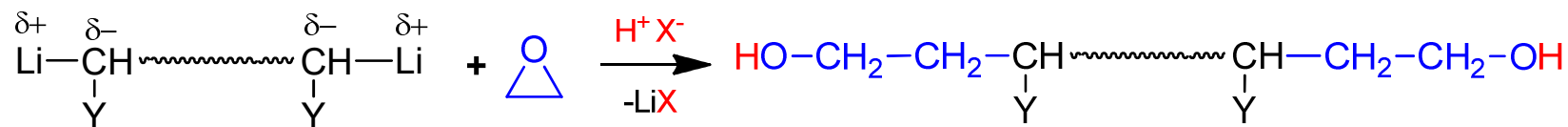
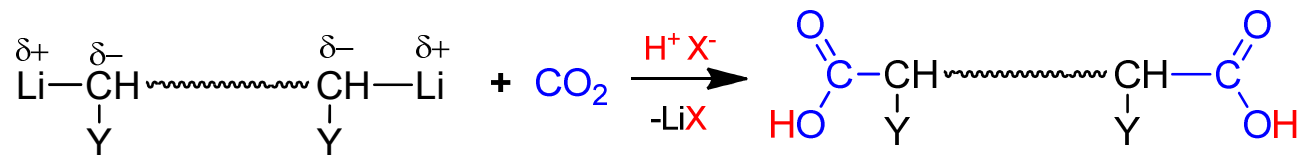
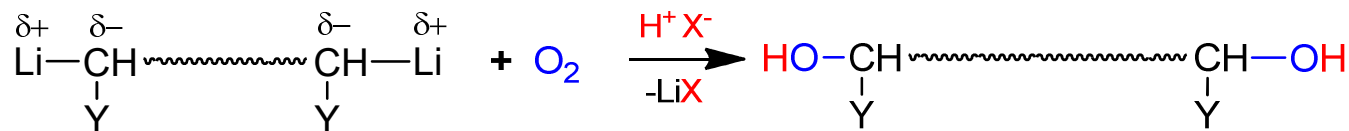
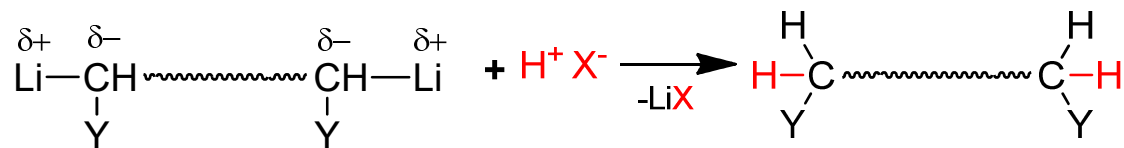


• Propagation

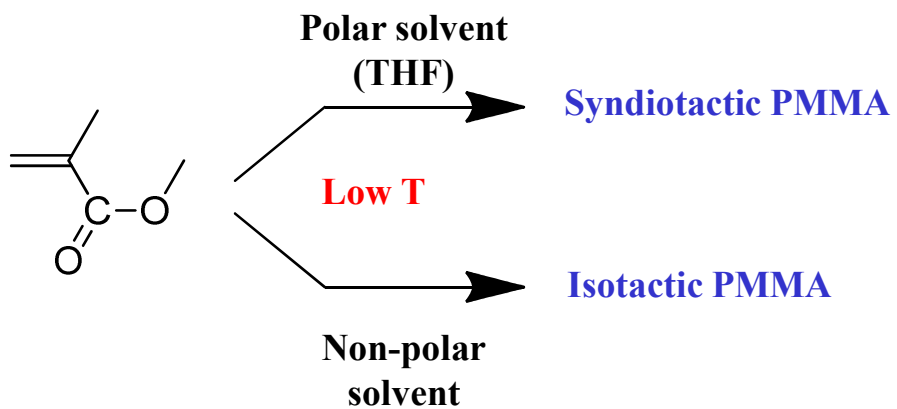
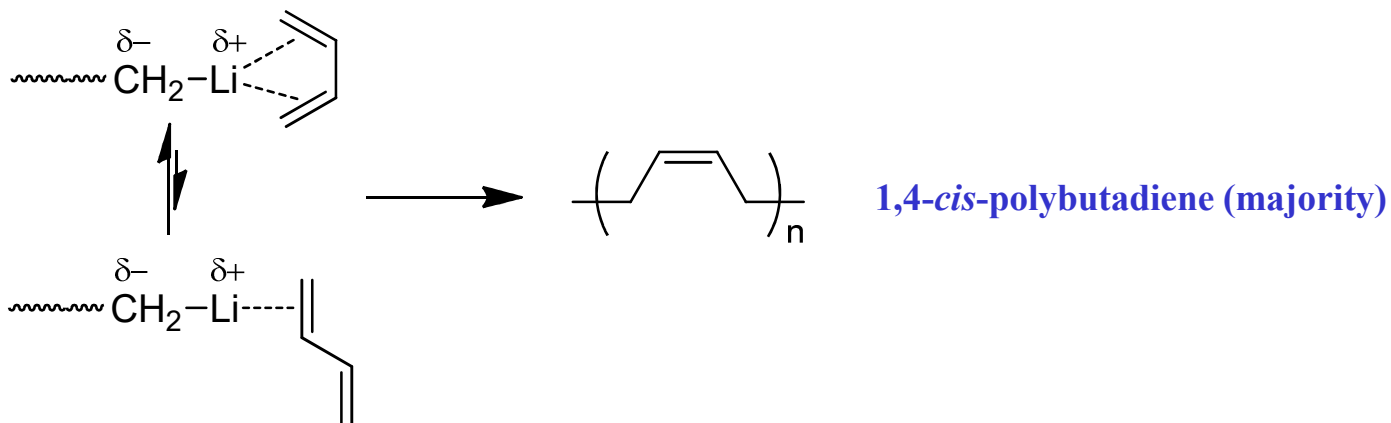
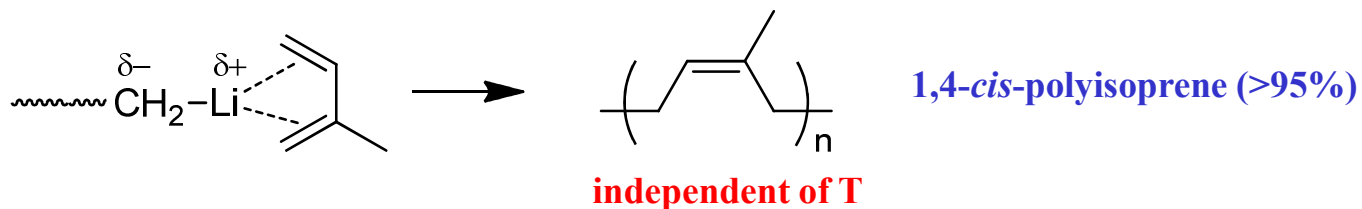


Telechelic chain growth (chain growth at both ends)

• **Functionalization of both chain ends:**



STEREOCHEMISTRY OF PROPAGATION



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

4 Types of Monomers

• **EPOXIDES** 

• **CYCLIC LACTAMS AND LACTONES** $(\text{CH}_2)_n \text{NH}$, $(\text{CH}_2)_n \text{O}$

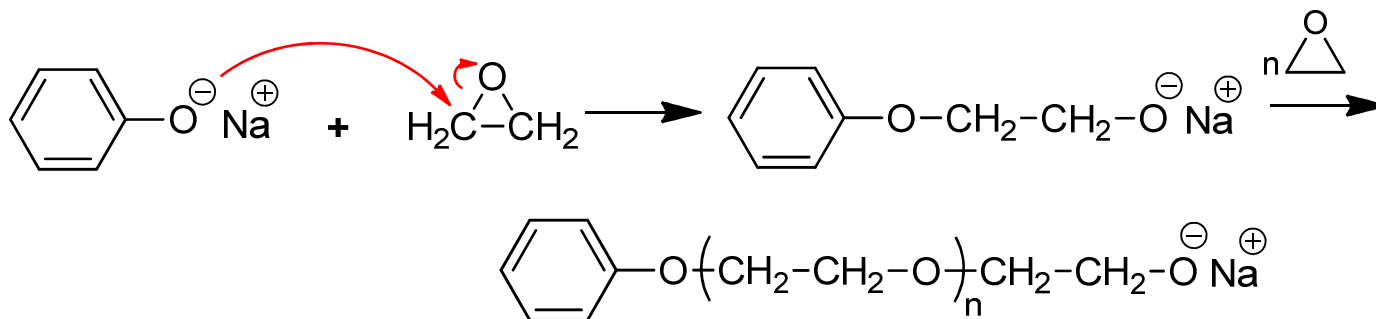
• **N-CARBOXYANHYDRIDES** 

• **CYCLIC SILOXANES** 

Some examples have already been given in the Step-Growth Polymerization

• EPOXIDES

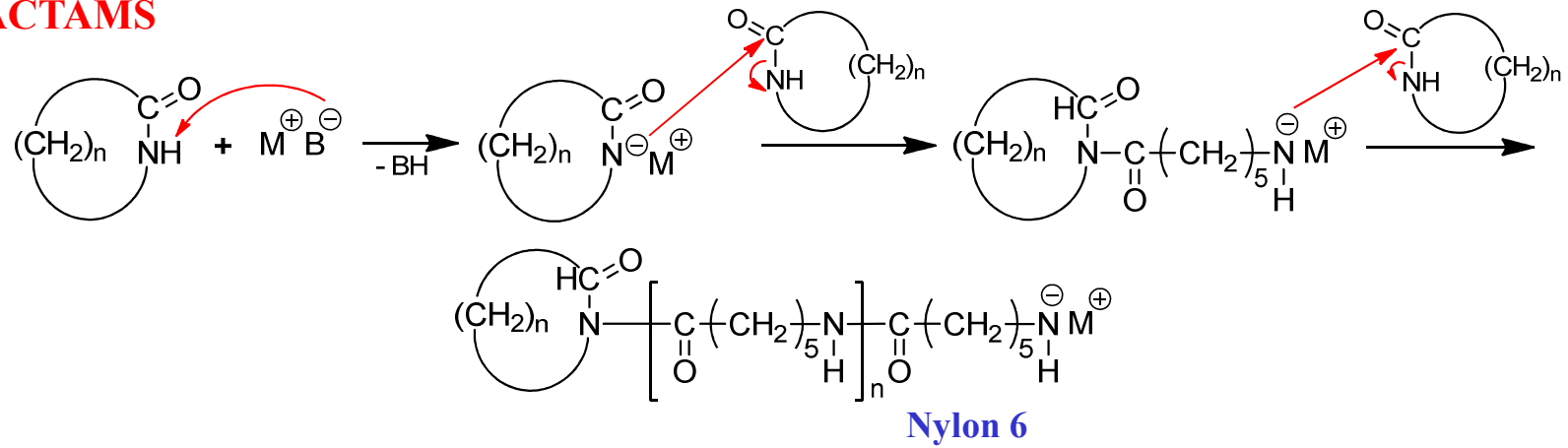
Ex:



Poly(ethylene oxide) (PEO)

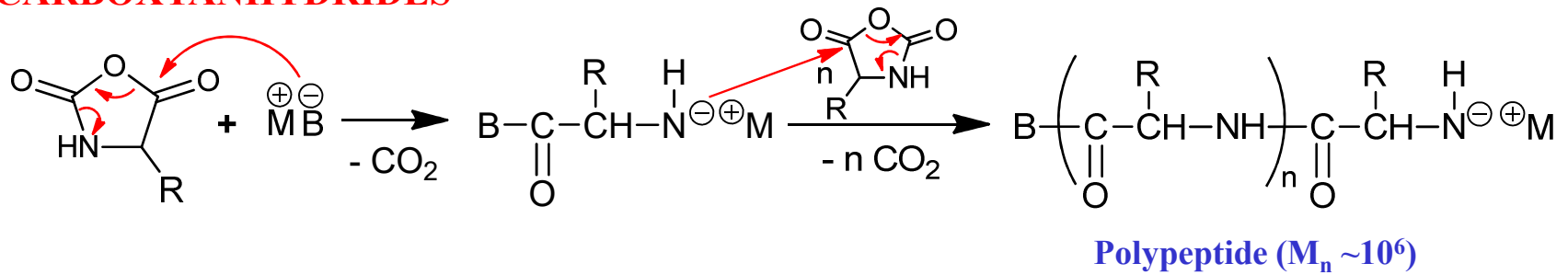
• **LACTAMS**

Ex:



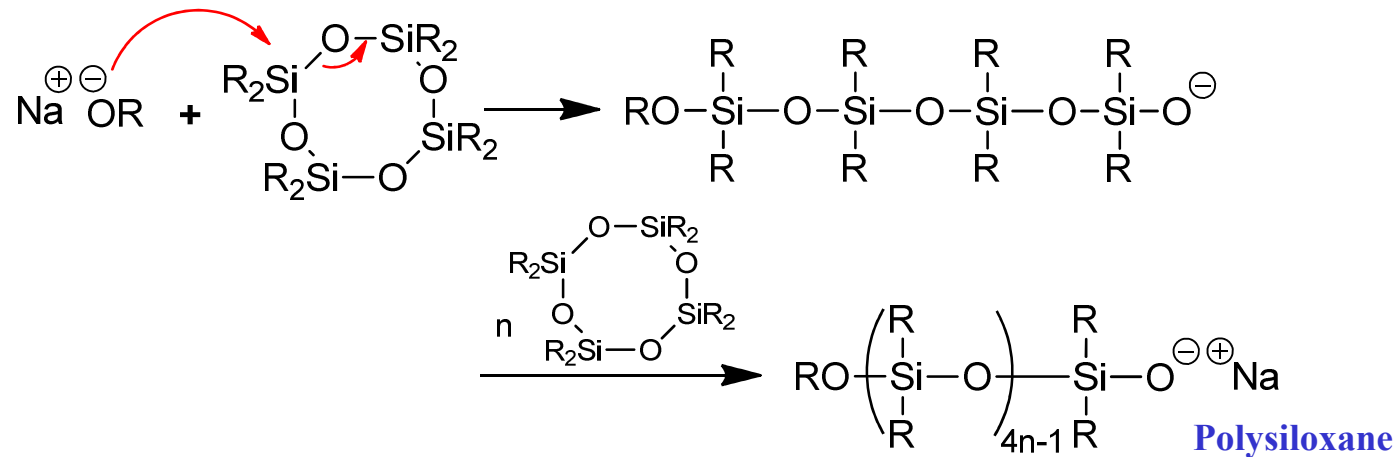
• **N-CARBOXYANHYDRIDES**

Ex:



• **CYCLIC SILOXANES**

Ex:



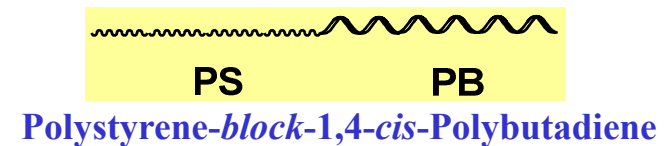
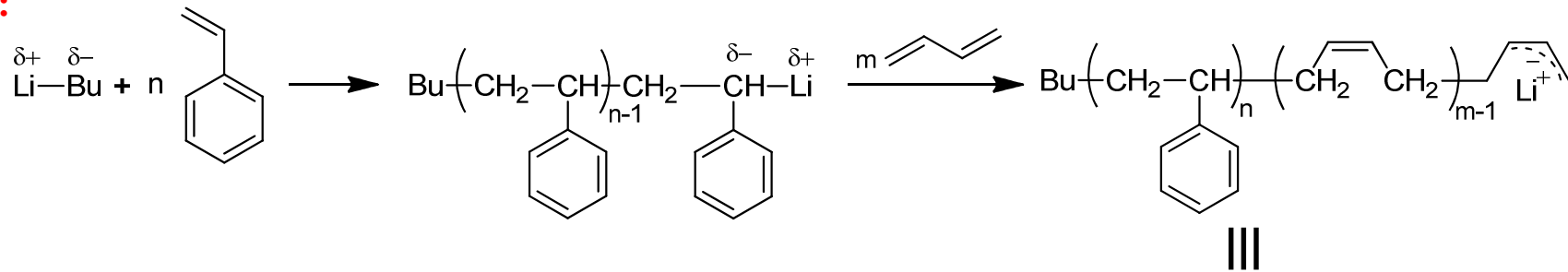
ANIONIC COPOLYMERIZATION

- BLOCK COPOLYMERIZATION (COMONOMERS ADDED SEQUENTIALLY)**

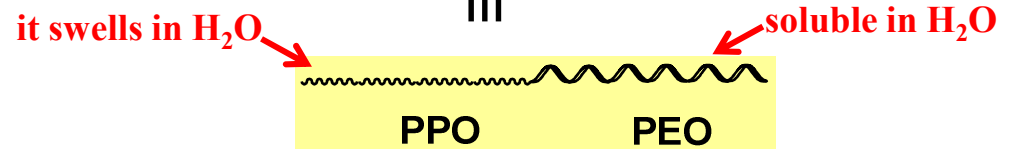
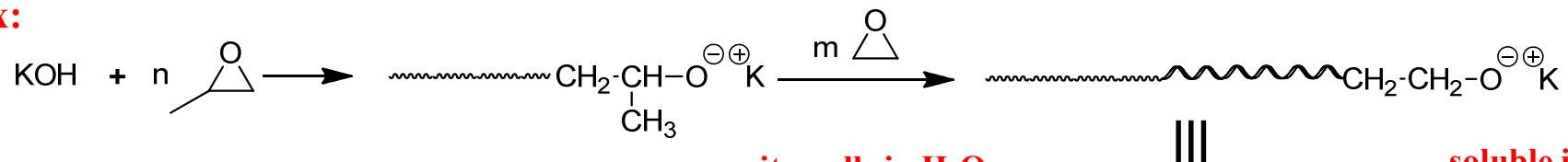
Owing to the living nature of anionic polymerization (absence of chain transfer and chain termination reactions) and easy control of molecular weight, this technique is very much used in block copolymerization

- From mononegative chains

Ex:



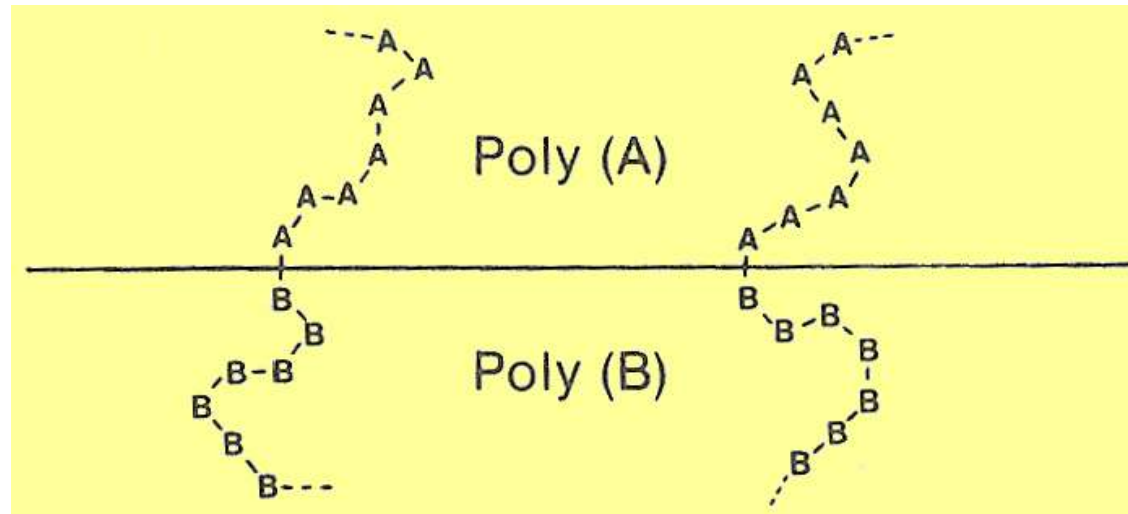
Ex:



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

Example: 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:



DIBLOCK AB TYPE



TRIBLOCK ABC TYPE

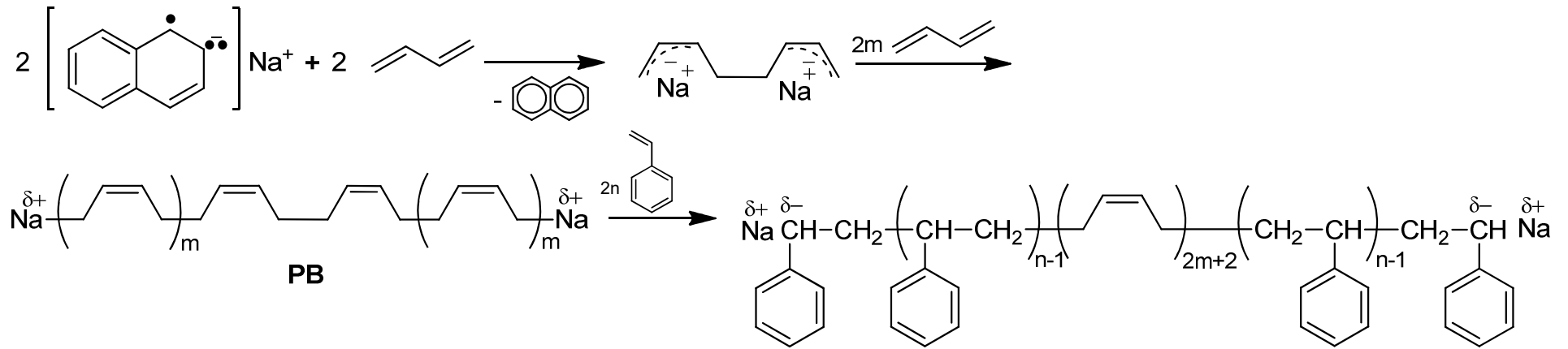


TRIBLOCK ABA TYPE



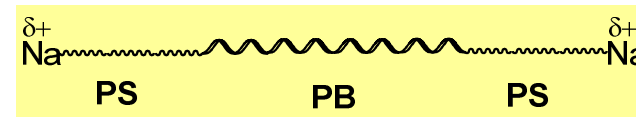
MULTIBLOCK {AB} TYPE

• From dinegative chains

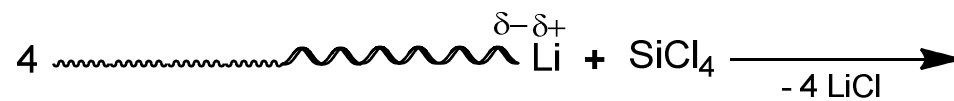


Triblock SBS copolymer

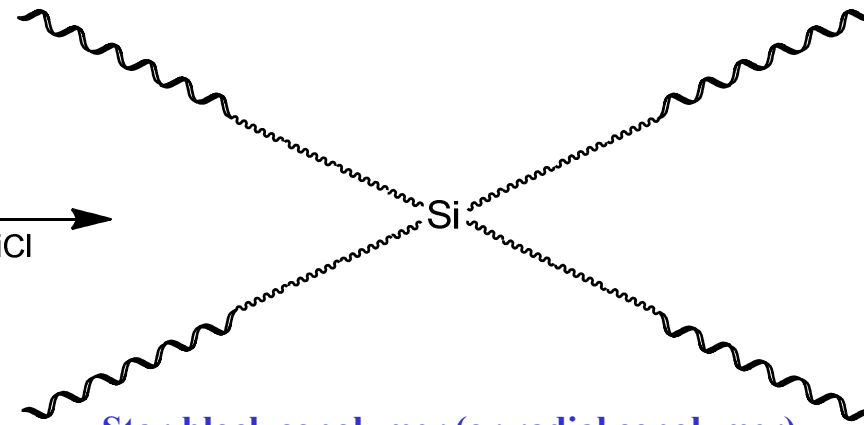
The ABA copolymers are thus obtained in 2 steps whereas from mononegative initiators is obtained in 3 steps



• Star-block copolymers



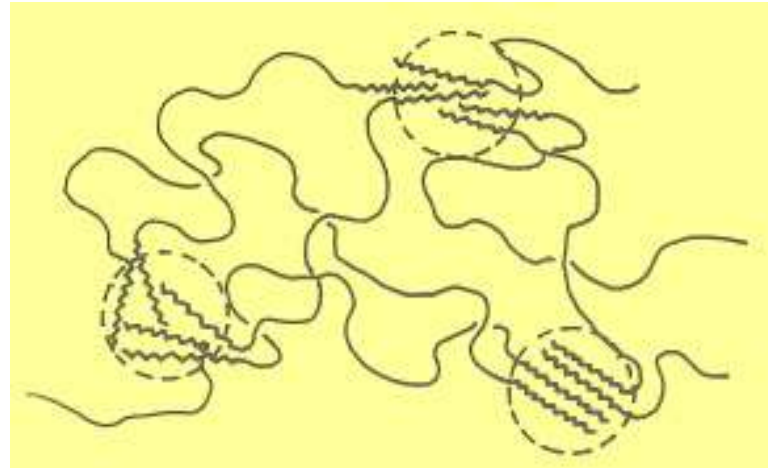
Living AB block copolymer



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)

Example: 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 \equiv elastic behaviour \equiv 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

<i>Monomer 1</i>	<i>Monomer 2</i>	<i>Initiator</i> ^b	<i>Solvent</i> ^c	<i>Temperature</i> ^d (°C)	r_1	r_2	
Styrene	Methyl methacrylate	Na	NH ₃		0.12	6.4	
		<i>n</i> -BuLi	None		^e	^e	
	Butadiene		<i>n</i> -BuLi	None	25	0.04	11.2
			<i>n</i> -BuLi	Hexane	25	0.03	12.5
			<i>n</i> -BuLi	Hexane	50	0.04	11.8
			<i>n</i> -BuLi	THF	25	4.0	0.3
			<i>n</i> -BuLi	THF	-78	11.0	0.4
			EtNa	Benzene		0.96	1.6
			<i>n</i> -BuLi	Cyclohexane	40	0.046	16.6
			RLi	None		0.12	12.5
	Vinyl acetate	Na	NH ₃		0.01	0.01	
Butadiene	Isoprene	<i>n</i> -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	

^aData from Morton.³⁰

^bBu = butyl, Et = ethyl, R = alkyl.

^cTHF = tetrahydrofuran.

^dTemperature not specified in some instances.

^eNo detectable styrene in polymer.

POLYMER ARCHITECTURES ACCESSIBLE BY LIVING POLYMERIZATION



**Monofunctionalized
polymers**

- Dispersing agents
- Synthesis of macromonomers



**Difunctionalized
polymers**

- Synthesis of elastomers
- Crosslinking agents



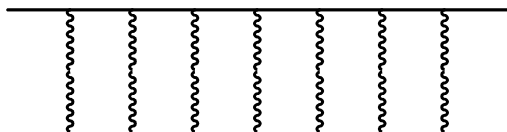
**AB block
copolymers**

- Dispersing agents
- Compatibilizers of polymer blends



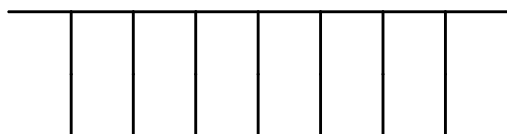
**ABA block
copolymers**

- Thermoplastic elastomers (TPE)



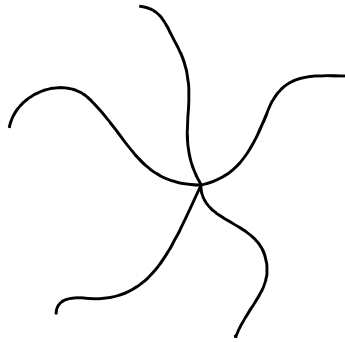
**Graft
copolymers**

- Elastomers
- Adhesives



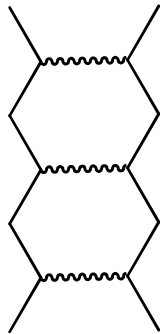
**Comb
polymers**

- Elastomers
- Adhesives



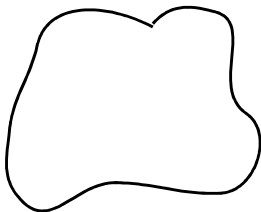
**Star
polymers/
copolymers**

- **Rheology control**



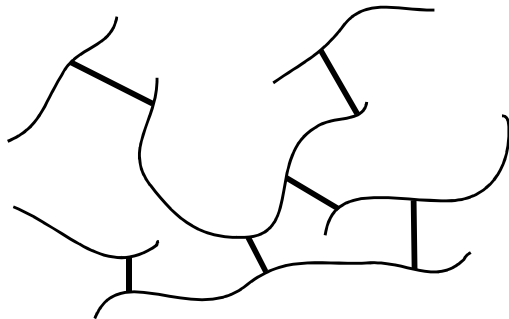
**Ladder
polymers/
copolymers**

- **High temperature plastics**
- **Membranes**
- **Elastomers**



**Cyclic
polymers**

- **Rheology control**



**Amphiphilic
networks**

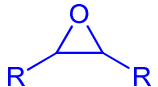
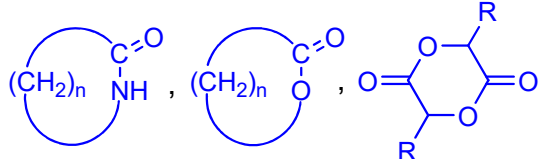
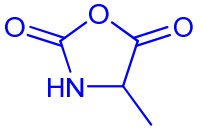
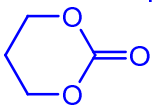
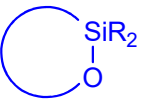
- **Biocompatible polymers**

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*

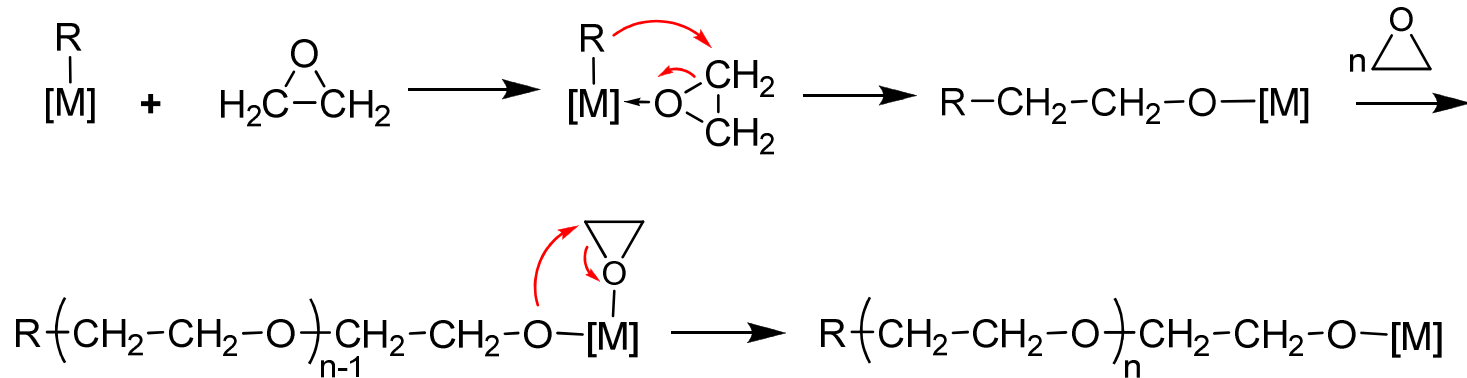
RING-OPENING POLYMERIZATION (ROP)

Types of Monomers (heterocyclic rings)

- EPOXIDES 
- CYCLIC LACTAMS, LACTONES AND DILACTONES 
- N-CARBOXYANHYDRIDES 
- CYCLIC CARBONATES 
- CYCLIC SILOXANES 

• EPOXIDES

Ex:



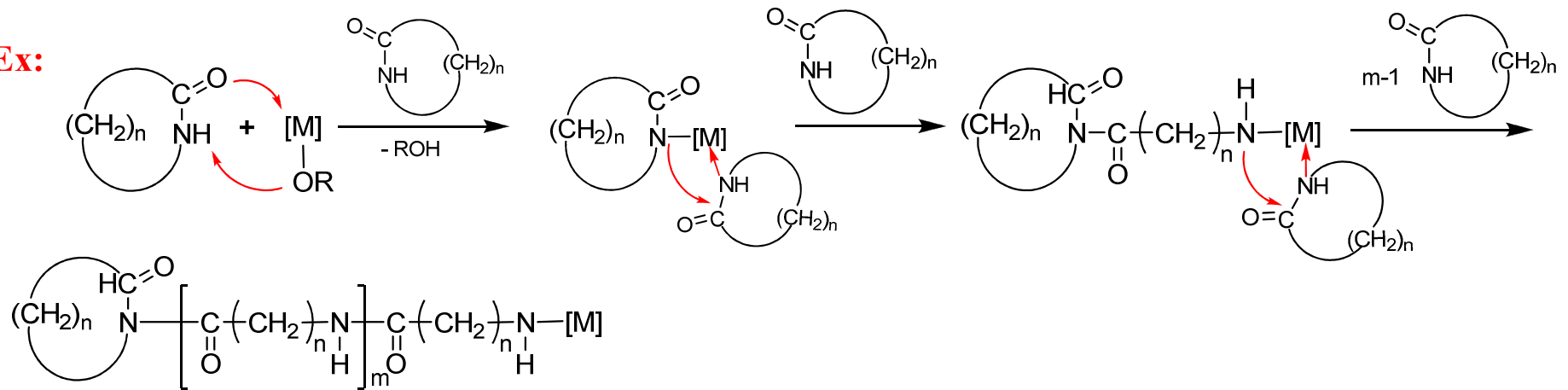
Polyethers [Poly(ethylene oxide) (PEO)]

Main catalytic systems used for the coordination ROP of epoxides

<i>Monomer</i>	<i>Catalysts</i>
Methyloxirane	FeCl ₃ /POx, ZnEt ₂ /H ₂ O, AlEt ₃ /H ₂ O/pyridine, and others
Phenyloxirane	ZnEt ₂ (H ₂ O)
(Haloalkyl)oxiranes (e.g., ECH)	FeCl ₃ /POx, AlEt ₃ /H ₂ O(/pyridine)
Oxiranes substituted with acetal groups	ZnEt ₂ /MeOH, ZnEt ₂ /cyclohexanol
Oxiranes substituted with ester groups	AlEt ₃ /H ₂ O/acetylacetone
Oxiranes substituted with organosilane or organosiloxane	ZnEt ₂ /H ₂ O
Oxiranes substituted with nitrile	Al(<i>i</i> -Bu) ₃ /H ₂ O/acetylacetone
2,3-Dimethyloxirane	Al(<i>i</i> -Bu) ₃ /H ₂ O, ZnEt ₂ /H ₂ O
bis(Chloromethyl)oxirane	Al(<i>i</i> -Bu) ₃ /H ₂ O
1,2-Epoxy cyclohexane	ZnEt ₂ , (EtZnOMe) ₄ , Al(<i>i</i> -Bu) ₃ /H ₂ O, AlEt ₃ /H ₂ O/acetylacetone, and others
Others (ethyl, <i>tert</i> -butyl, neopentyl, allyl amines, sulfones, ether, amides)	ZnEt ₂ /H ₂ O

• **LACTAMS**

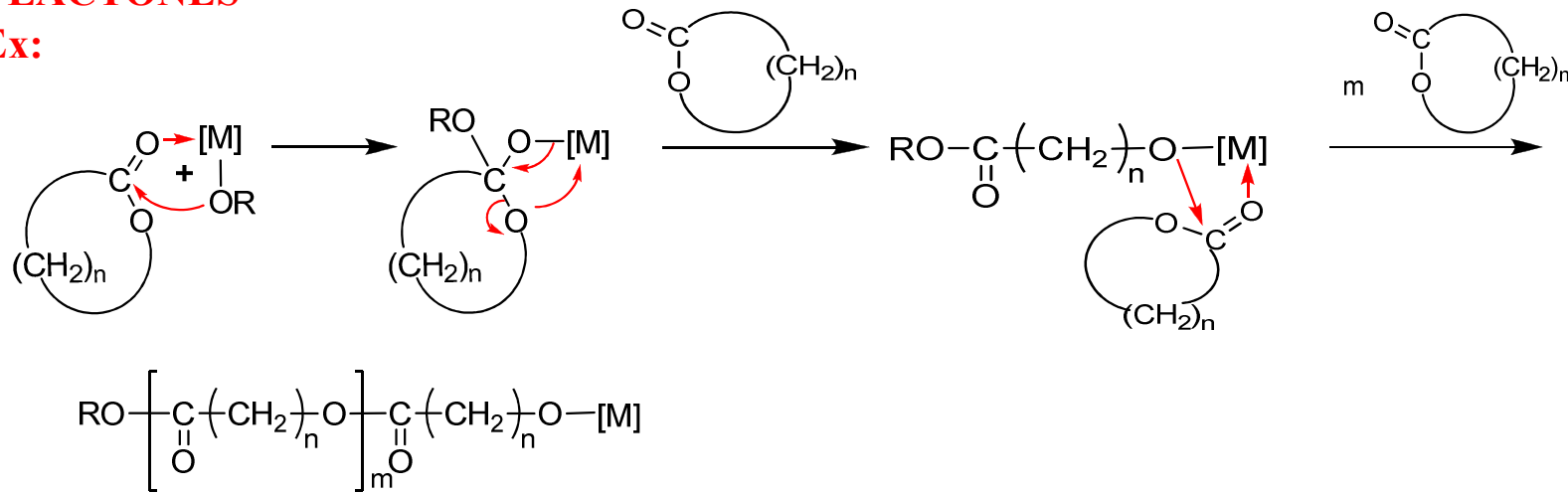
Ex:



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

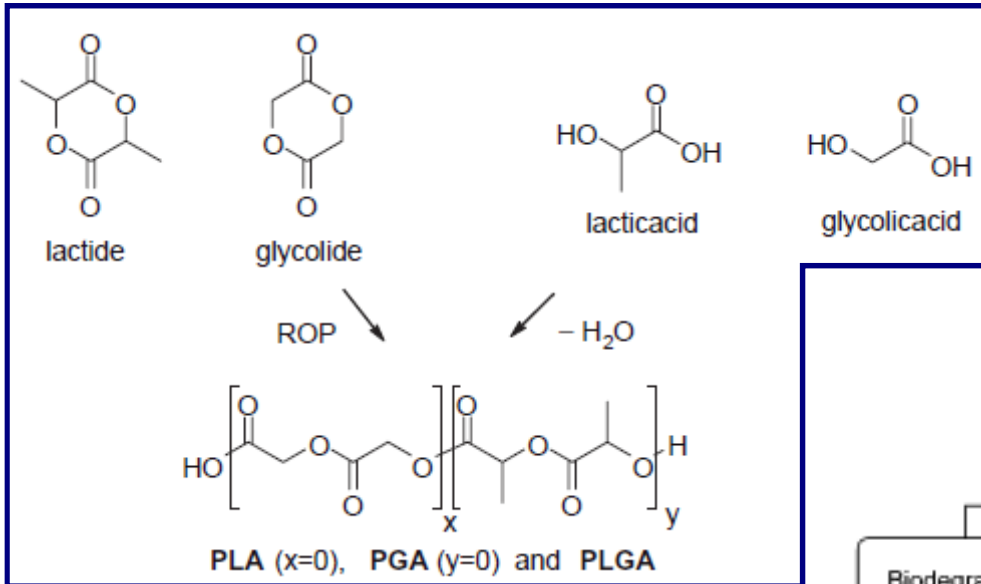
• **LACTONES**

Ex:

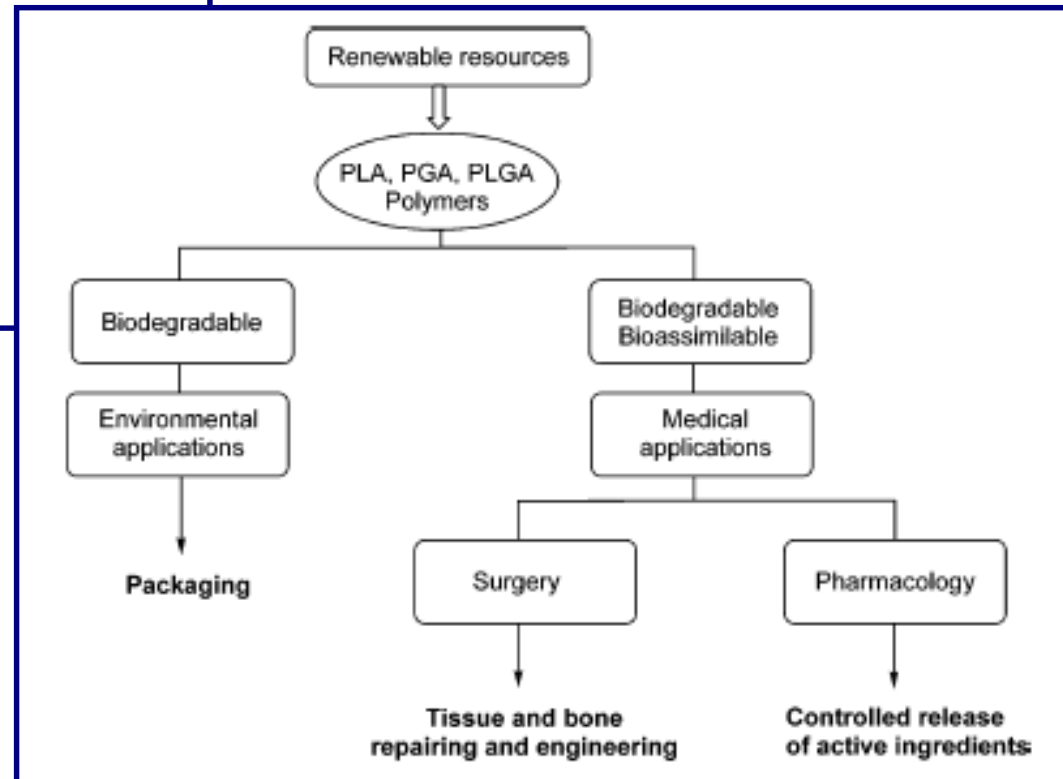


Polyesters [poly(ϵ -caprolactone)] (n=5)

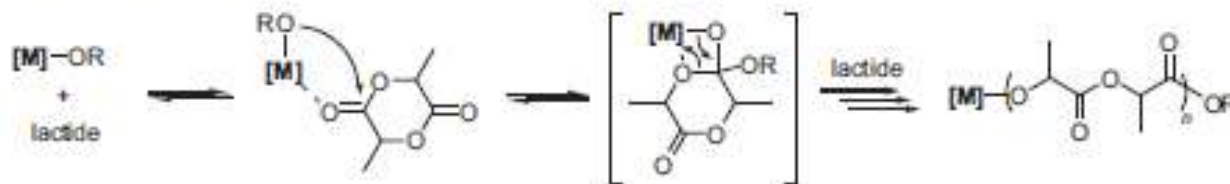
• **DILACTONES**



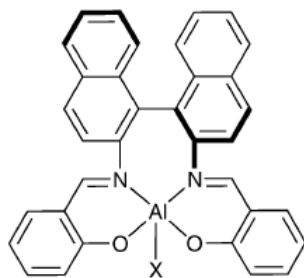
Monomers, polymers and copolymers
Polyesters



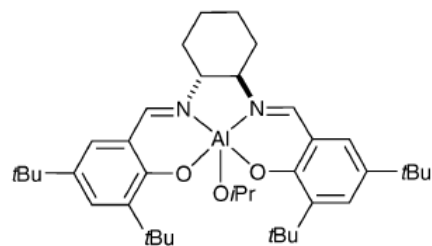
"Coordination-Insertion" ROP mechanism



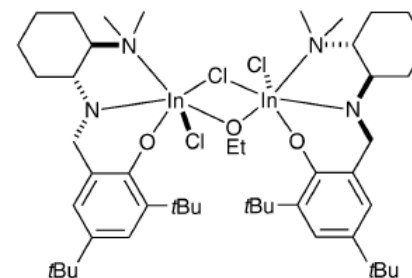
Catalysts used for coordination ROP of lactide



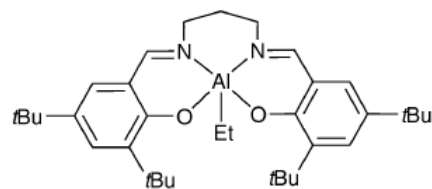
1a: X = O*i*Pr
1b: X = OMe



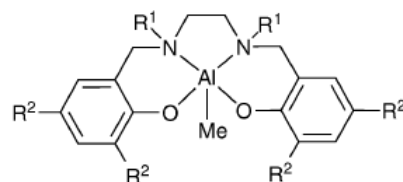
2



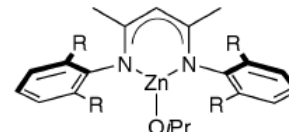
5



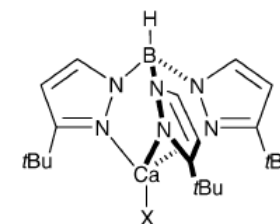
3



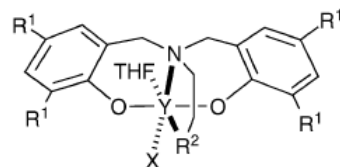
4a: R¹ = Me, R² = H
4b: R¹ = CH₂Ph, R² = H
4c: R¹ = CH₂Ph, R² = Cl
4d: R¹ = Me, R² = Me



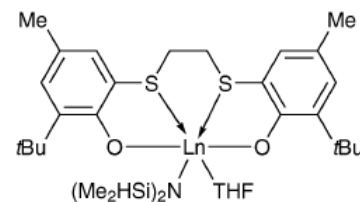
6a: R = Et
6b: R = *n*Pr
6c: R = *i*Pr



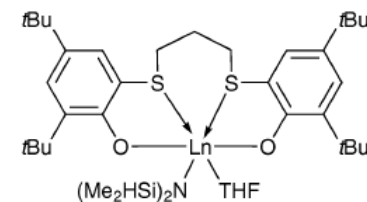
7a: X = N(SiMe₃)₂
7b: X = OC₆H₃-2,6-*i*Pr₂



9a: R¹ = CMe₃; R² = OMe; X = N(SiHMe₂)₂
9b: R¹ = CPhMe₂; R² = OMe; X = N(SiHMe₂)₂
9c: R¹ = CPhMe₂; R² = OMe; X = O*i*Pr
9d: R¹ = Me; R² = OMe; X = N(SiMe₃)₂
9e: R¹ = CMe₃; R² = NMe₂; X = CH₂SiMe₃
9f: R¹ = CMe₃; R² = NEt₂; X = CH₂SiMe₃

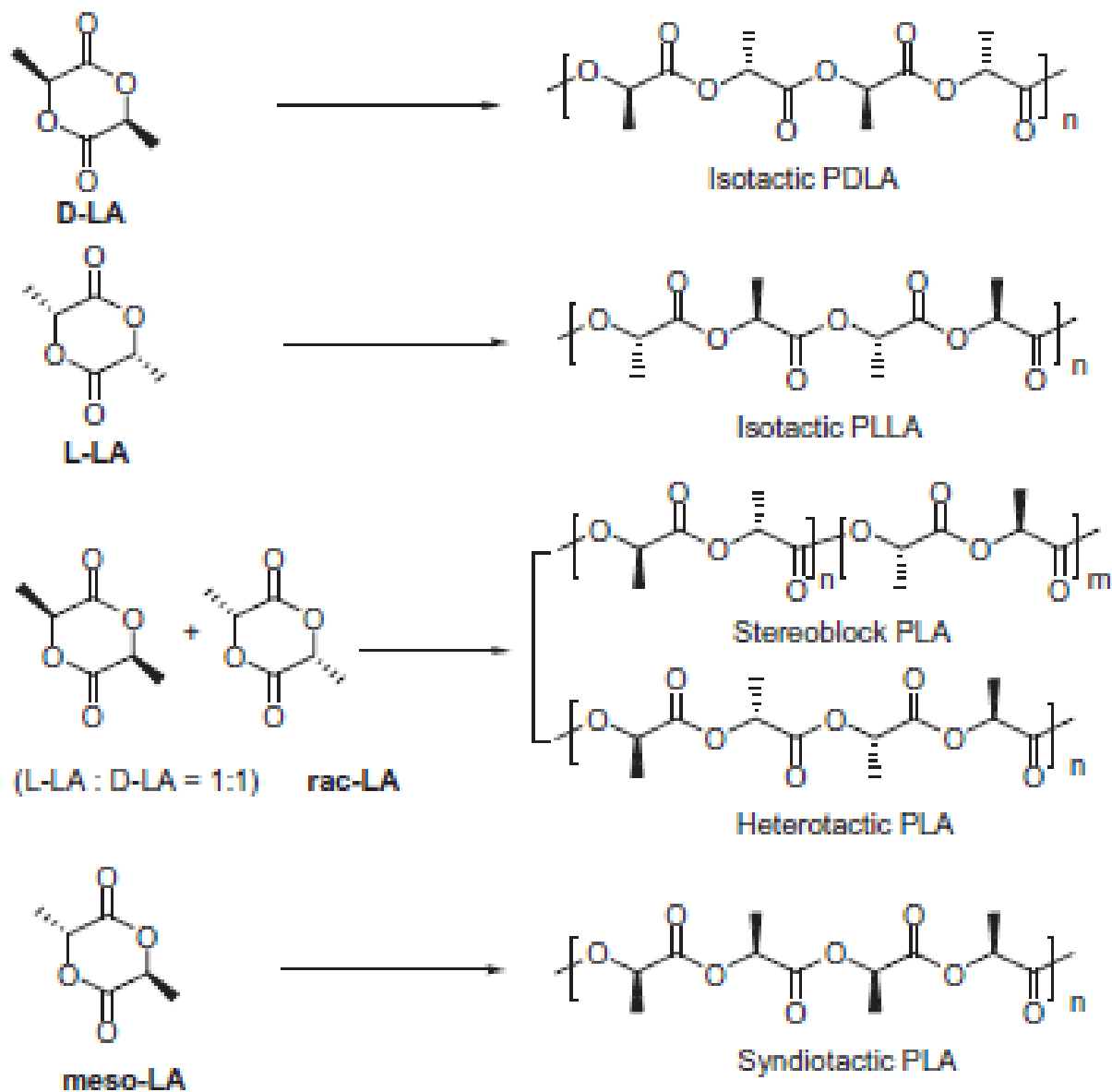


10a: Ln = Sc
10b: Ln = Lu
10c: Ln = Y



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

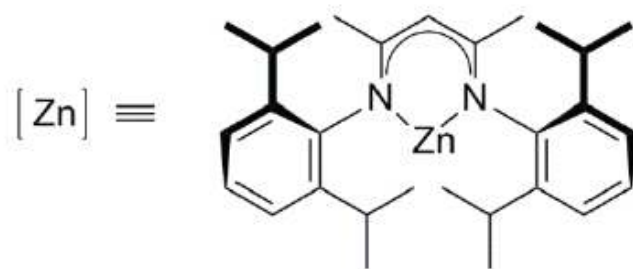
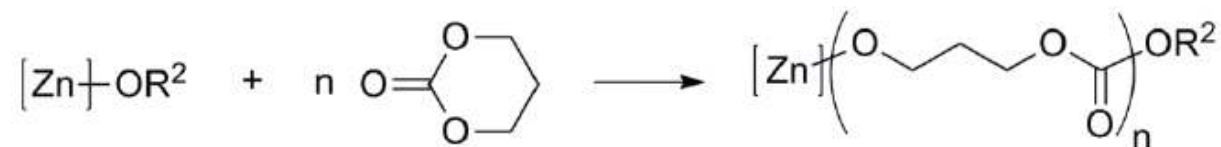
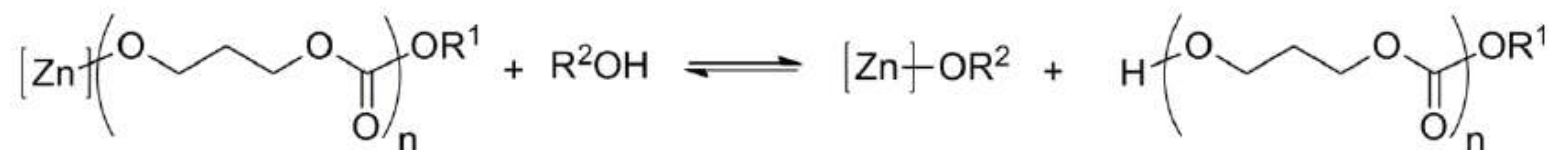
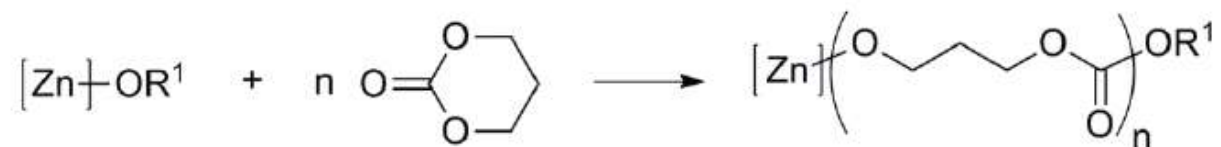
Synthesis of stereoregular PLAs by ROP



Crystalline
 $T_m = 170-180\text{ }^\circ\text{C}$

Amorphous

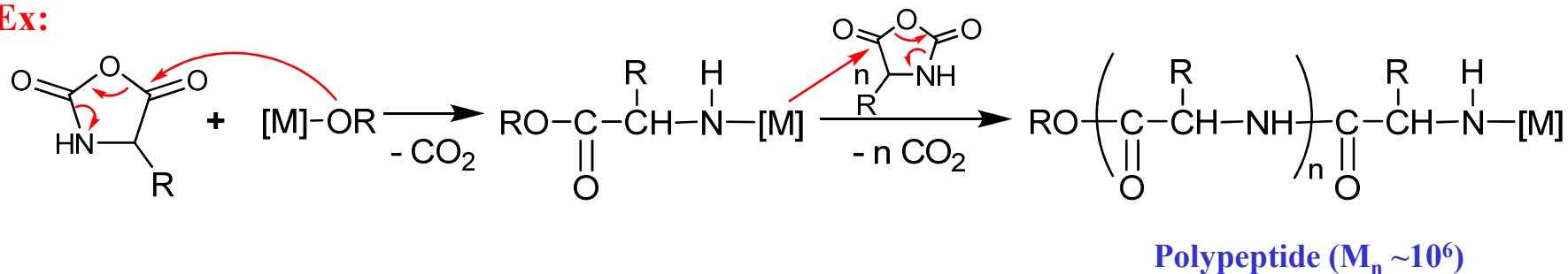
Synthesis of polycarbonates by ROP



[Zn] mediated living ROP of trimethylene carbonate

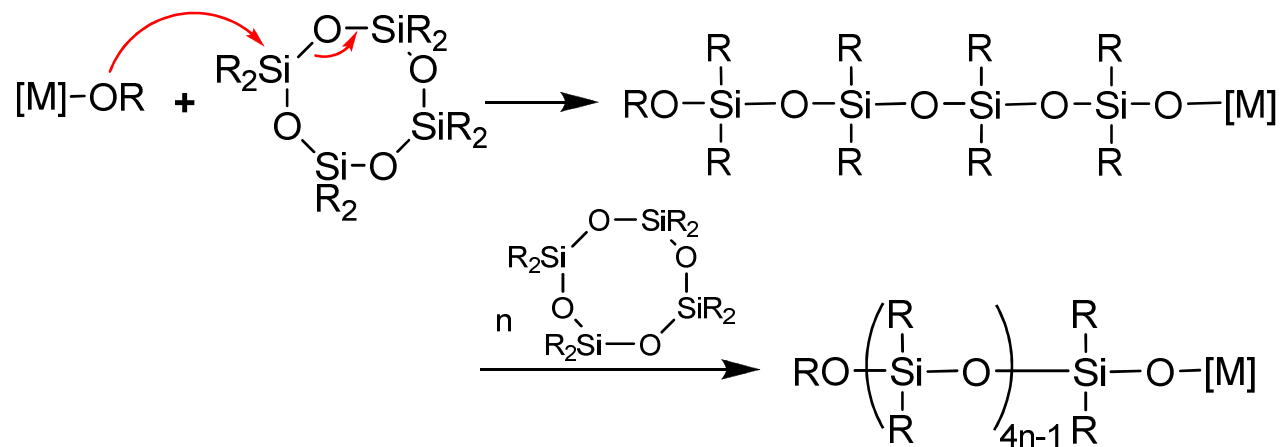
• **N-CARBOXYANHYDRIDES**

Ex:



• **CYCLIC SILOXANES**

Ex:



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***

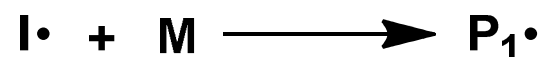
FREE RADICAL POLYMERIZATION

It involves:

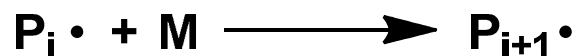
- Monomer
- +
- Radical Initiator

STEPS

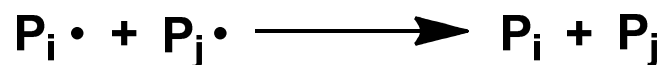
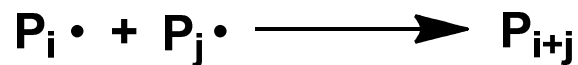
- **INITIATION**
addition of the radical initiator to the monomer
- **PROPAGATION**
radical chain growth by sequential addition of monomers
- **CHAIN TERMINATION**
“death” of the radical propagating species by reaction with other radical species
- **CHAIN TRANSFER**
growing chain reacts with a neutral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



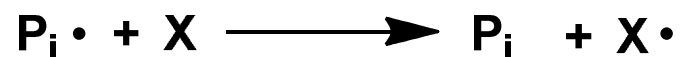
} **INITIATION**



PROPAGATION



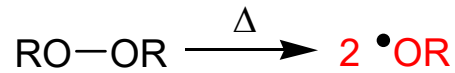
} **TERMINATION**



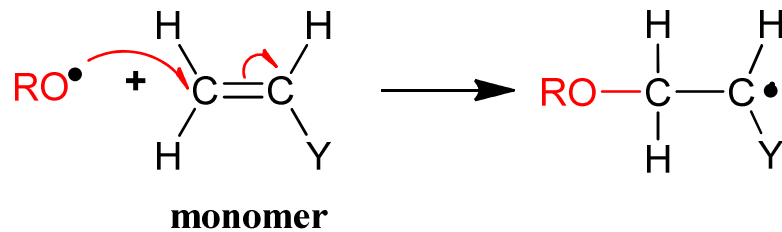
CHAIN TRANSFER

**MECHANISM OF CLASSICAL 'FREE RADICAL POLYMERIZATION'
(GENERAL)**

• INITIATION

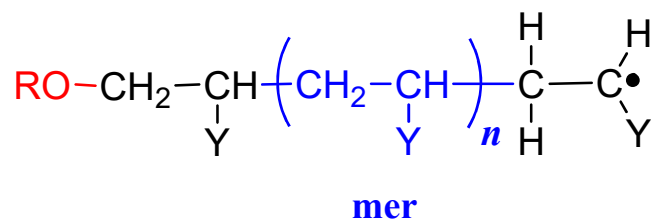
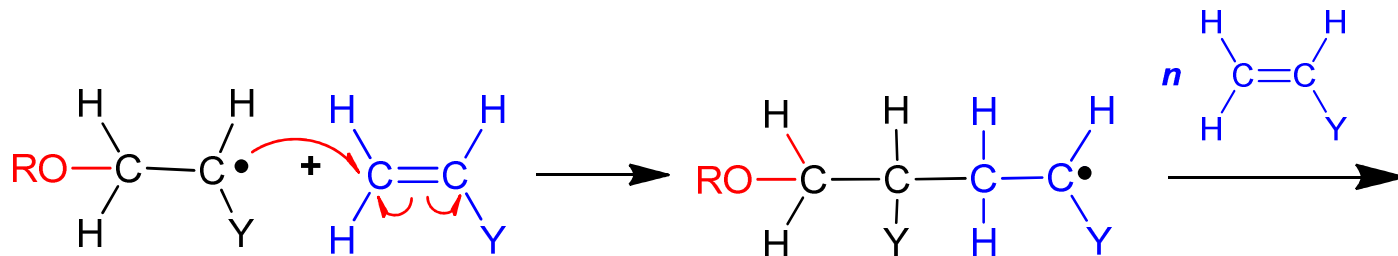


Initiator decomposition



Addition of initiator radical to monomer

• PROPAGATION

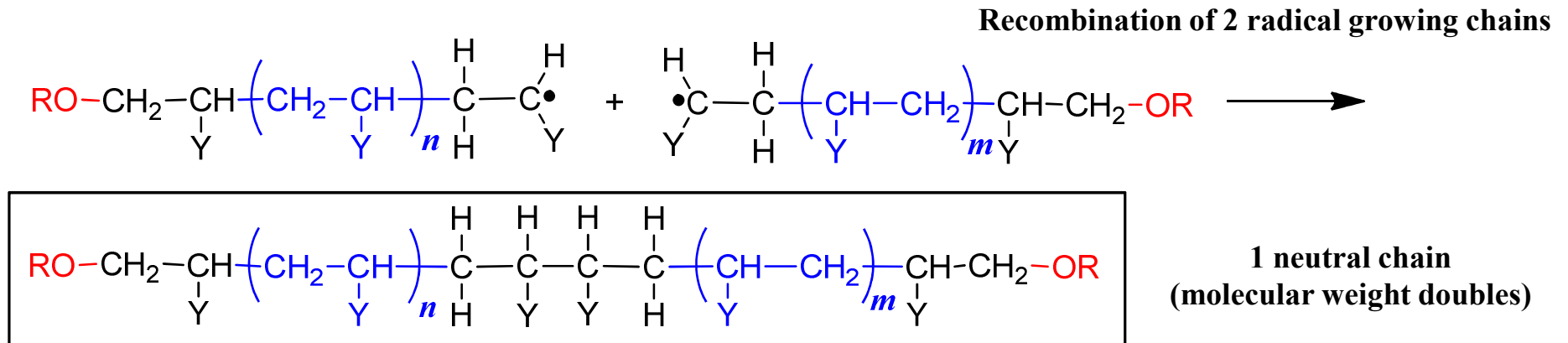


Sequential addition of monomers
to radical growing chain

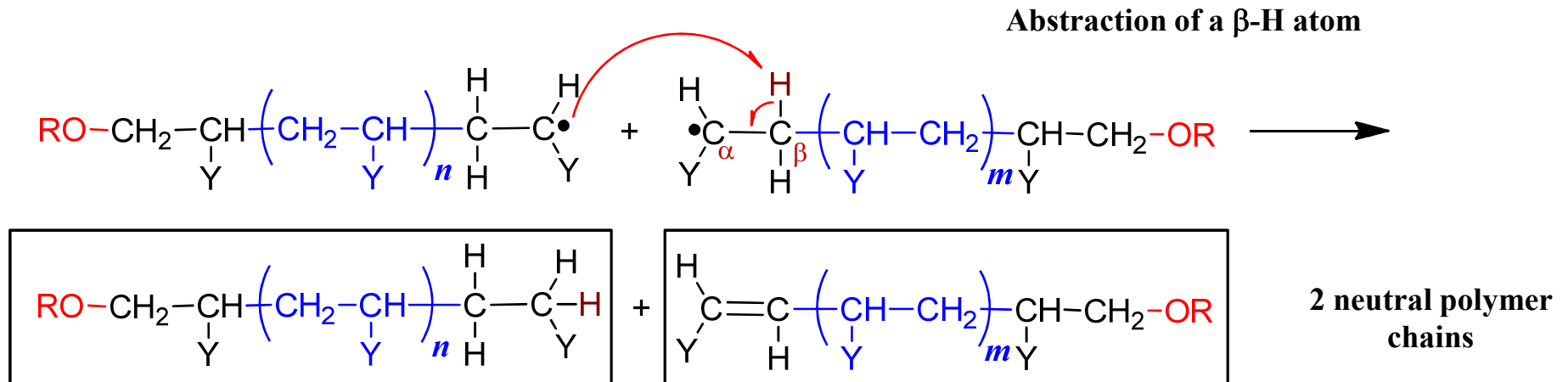
→ **CHAIN
GROWTH**

• **TERMINATION**

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



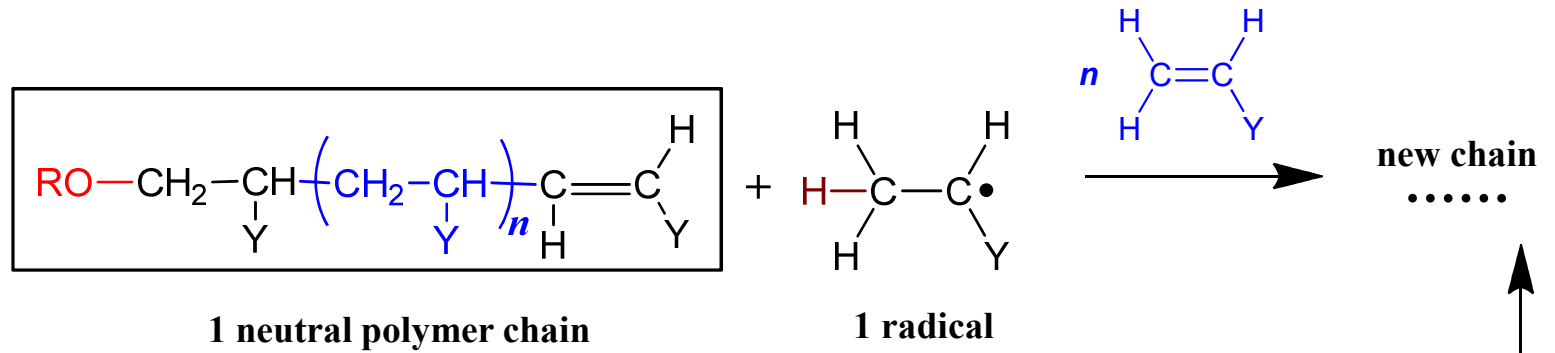
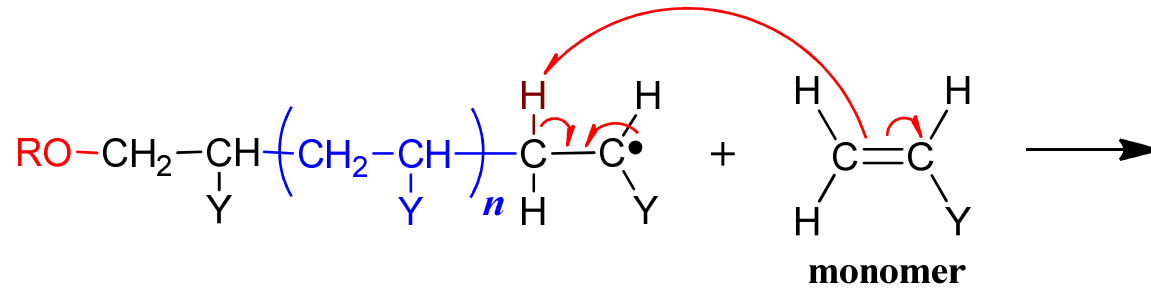
• **Disproportionation** (*high temperatures*)



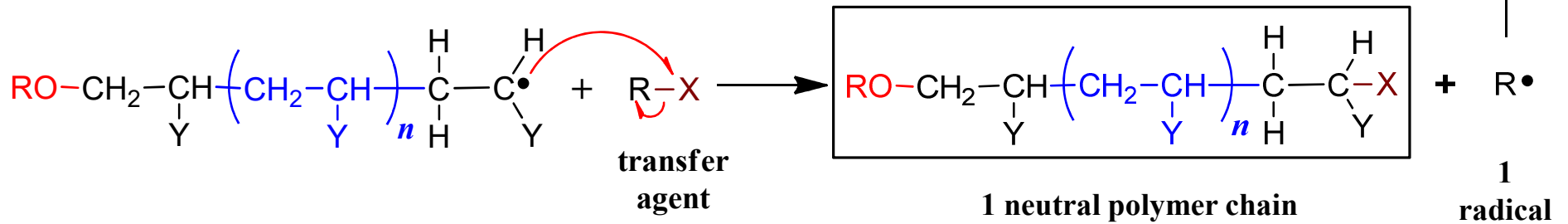
• **CHAIN TRANSFER**

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

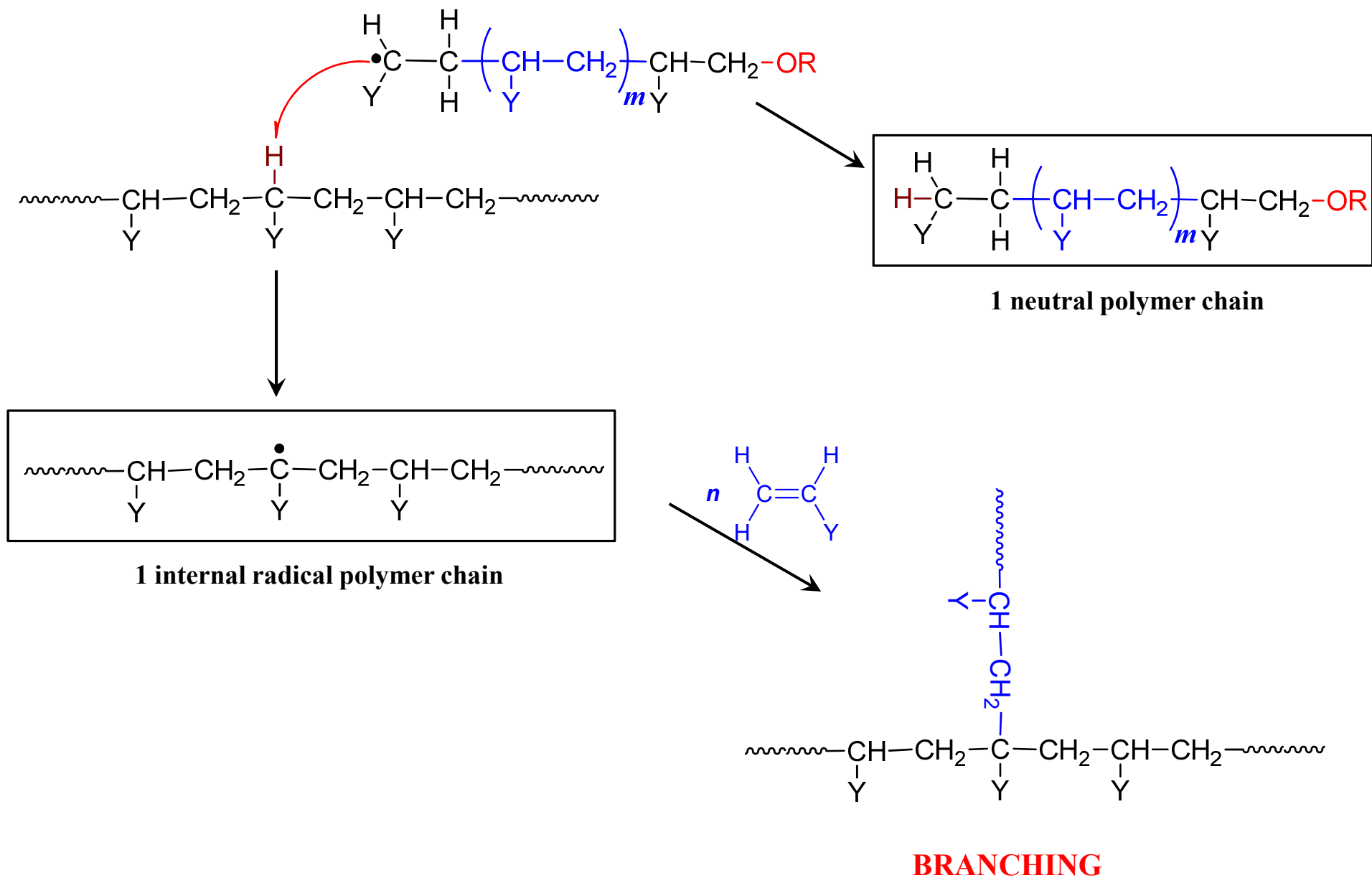
• to the Monomer



• to a Transfer Agent



- to the Polymer (*very high temperatures*)



CONTROLLED RADICAL POLYMERIZATION (CRP)

Absence of **TERMINATION** or **CHAIN TRANSFER**



Living Polymers (Living Polymerization) → Living Chain Ends



Molecular Weight Control → Narrow Molecular Weight Distribution



Block Copolymers

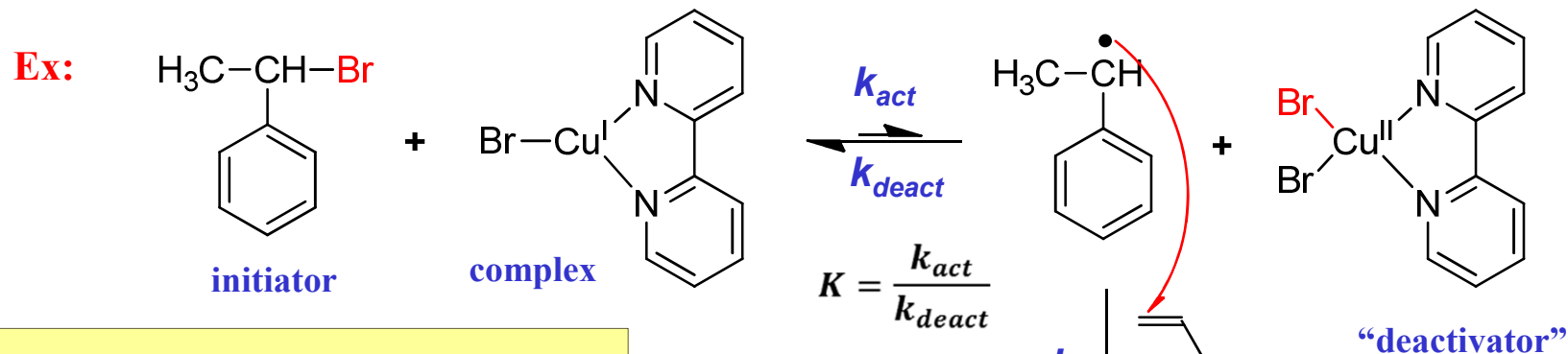
Several
Techniques
of **CRP**
(examples)

- ATRP
 - OMRP
 - NMP
 - RAFT
- } **SFRP**

SFRP = Stable Free Radical Polymerization

ATOM-TRANSFER RADICAL POLYMERIZATION (ATRP)

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



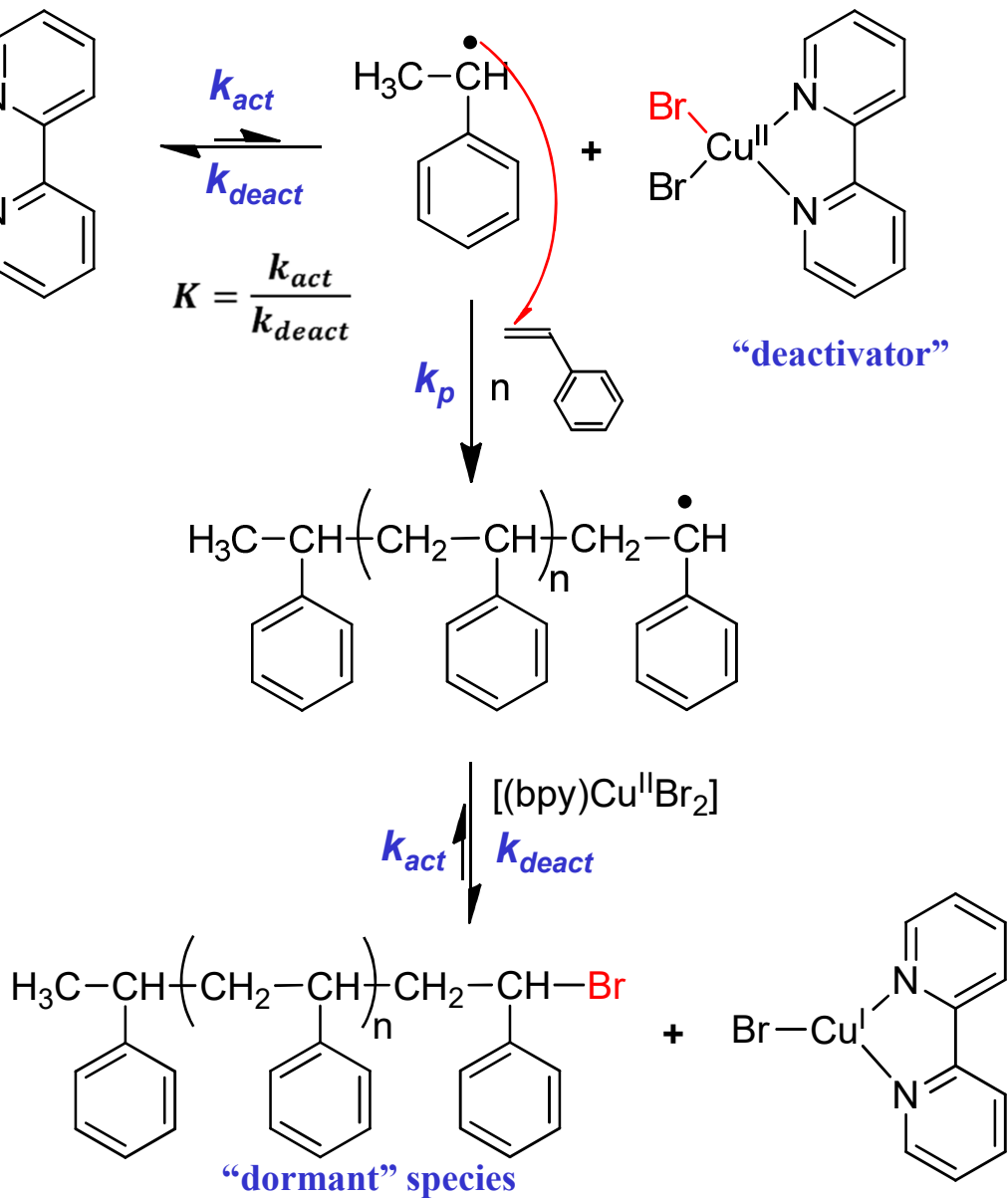
$$r_p = \frac{k_p K [I] [Cu^+]}{[Cu^{2+}]} [M]$$

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

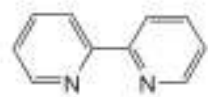
$$\overline{DP}_n = \frac{[M]_o - [M]}{[I]_o} = \frac{p [M]_o}{[I]_o}$$

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

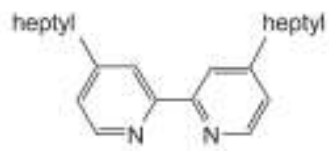
Poisson distribution



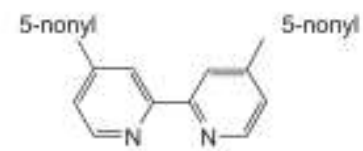
• COMMON LIGANDS (L) OF ATRP



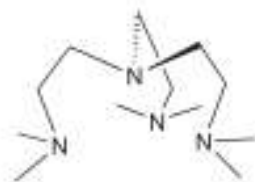
bipy



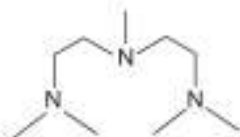
dHbipy



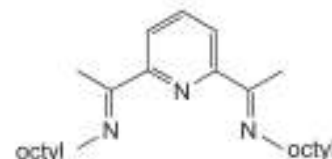
dNbipy



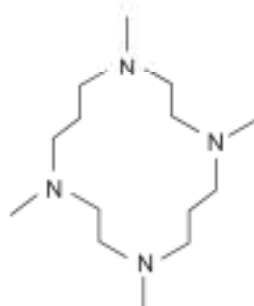
Me₆TREN



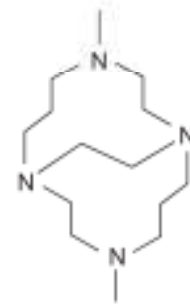
PMDETA



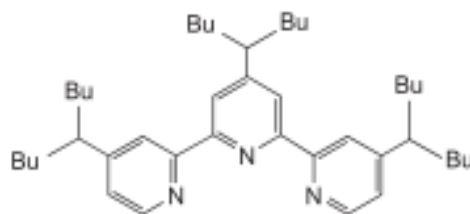
DOIP



Me₆Cyclam



Cyclam-B



TERPY

TABLE 8.1. Commercially Available Polymers Synthesized with Complex Coordination Catalysts

<i>Polymer</i>	<i>Principal Stereochemistry</i>	<i>Typical Uses</i>
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	<i>trans</i>	Metal can coatings, potting compounds for transformers
1,4-Polyisoprene	<i>trans</i>	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	<i>cis</i>	Tires, conveyer belts, wire and cable insulation, footwear
1,4-Polyisoprene	<i>cis</i>	Tires, footwear, adhesives, coated fabrics
Poly(1-octenylene) (polyoctenamer) ^c	<i>trans</i>	Blending with other elastomers
Poly(1,3-cyclopentenylenevinylene) (norbornene polymer) ^c	<i>trans</i>	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

^aUsually copolymerized with small amounts of 1-pentene.

^b1-Butene, 1-hexene, and 1-octene.

^cSynthesized 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 =R)				✓
Isobutylene (=)			✓	
Styrene (=)	✓	✓	✓	✓
Butadiene and isoprene (=)	✓	✓		✓
Acrylates and methacrylates (=COOR)	✓	✓		
Acrylonitrile (=CN)	✓	✓		
Vinyl ethers (=OR)			✓	
Vinyl halides (=Hal)	✓			
Fluorocarbons (e.g. TFE, $\text{CF}_2=\text{CF}_2$)	✓			
Vinyl esters (e.g. acetate =OCOCH_3)	✓			
Formaldehyde ($\text{CH}_2=\text{O}$)			✓	
Formaldehyde trimer (trioxan $\text{CH}_2\text{O-CH}_2\text{O-CH}_2\text{O}$)		✓		✓
Ethylene oxide ($\text{CH}_2\text{-O-CH}_2$)		✓		✓
Cyclic ethers (e.g. THF $\text{CH}_2\text{CH}_2\text{-O-CH}_2\text{CH}_2$)			✓	✓
Cyclic lactams and lactones (-(CONH)_n , -COO , $\text{-(CH}_2)_n$)		✓		✓
Cyclic siloxanes (R_2SiO_3 or 4)		✓		
Cycloalkenes and cycloalkynes				✓
Alkynes (=R)				✓

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- M. Michalovic, K. Anderson, L. Mathias, "The Macrogalleria", Polymer Site Learning Center site of the University of Southern Mississippi) (<http://www.pslc.ws/macrog/>)