

Capítulo 06

Estereoquímica de Polímeros

SMM0303 – *Materiais Poliméricos I*

**Horário das aulas: as quartas e quintas
das 08h00 as 10h00 Google Meet**

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Capítulo 6.

Polymer Stereochemistry

Pg. 157 a 167

Architecture

Orientation

Configuration

Geometric Isomerism

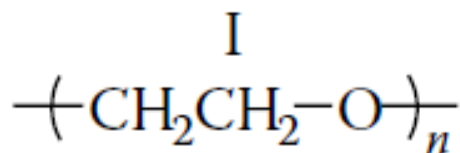
Conformation of Stereoregular Polymers

Factors influencing Stereoregulation

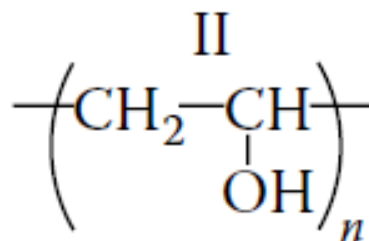
Arquitetura:

Ramificações, estruturas complexas em rede, unidades monoméricas que são isômeros

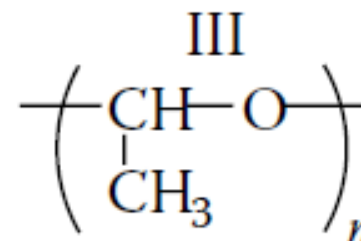
P. ex. C_2H_4O



Poli(óxido de etileno)
 $T_g \sim -67^\circ\text{C}$



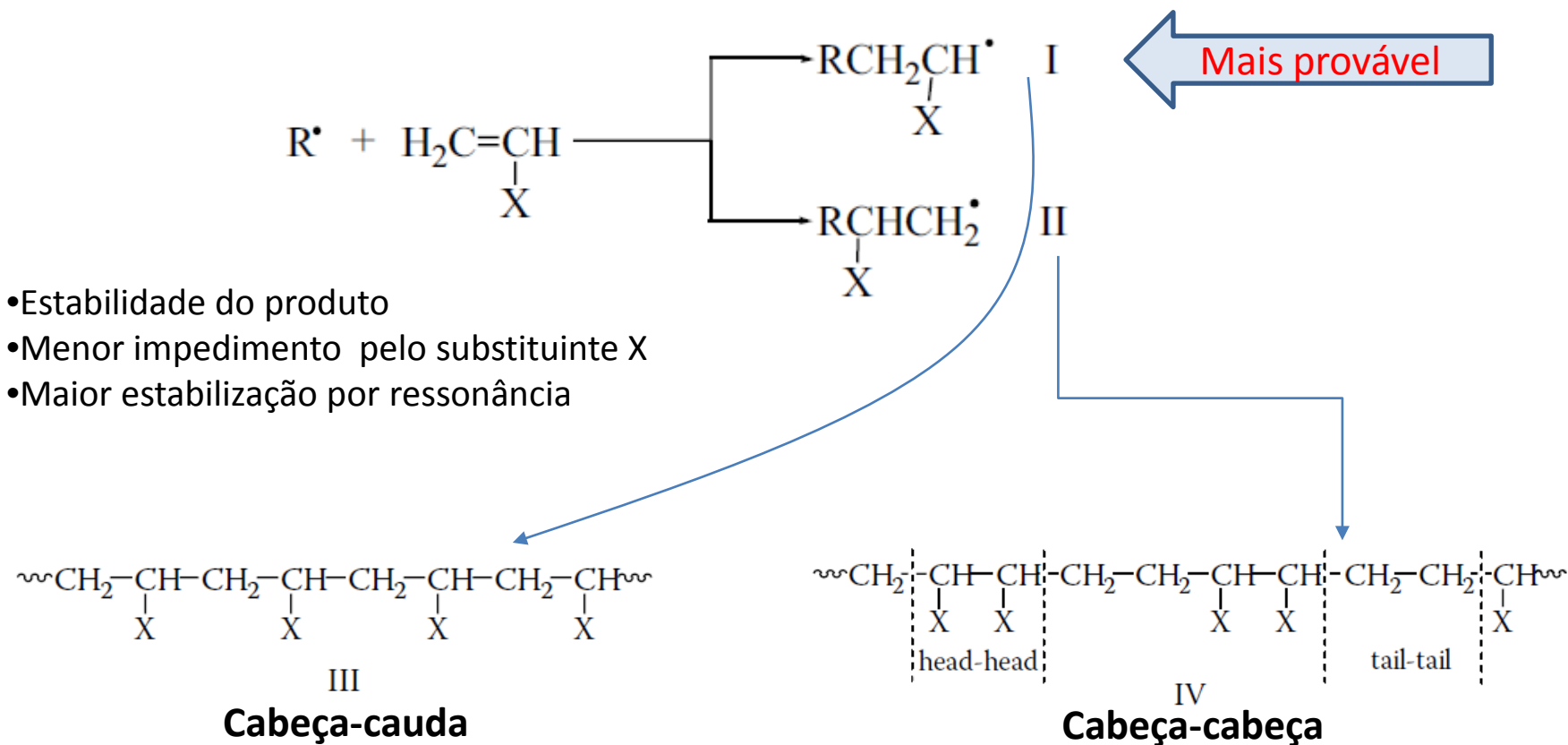
Poli(álcool vinílico)
 $T_g \sim -85^\circ\text{C}$



Poliacetaldeído
 $T_g \sim -30^\circ\text{C}$

Orientação:

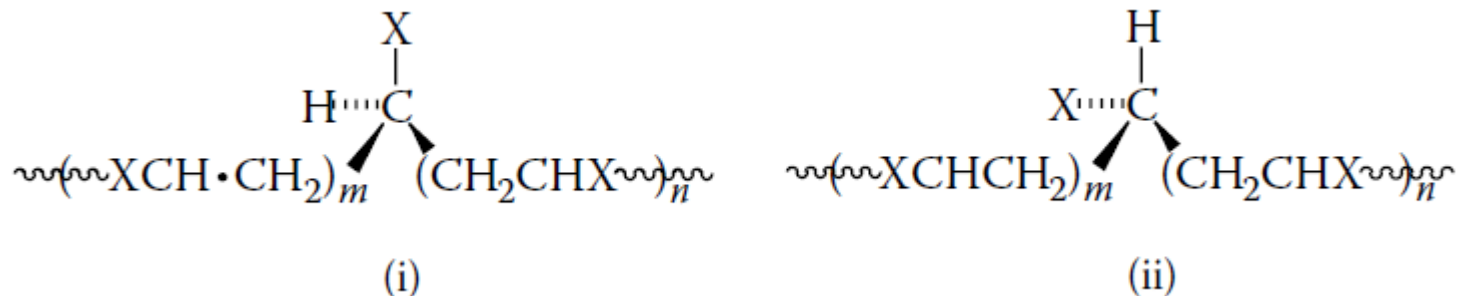
Na reação de um radical com um monômero assimétrico, temos duas possibilidades de adição:



Configuração

$\text{CH}_2=\text{CHX}$

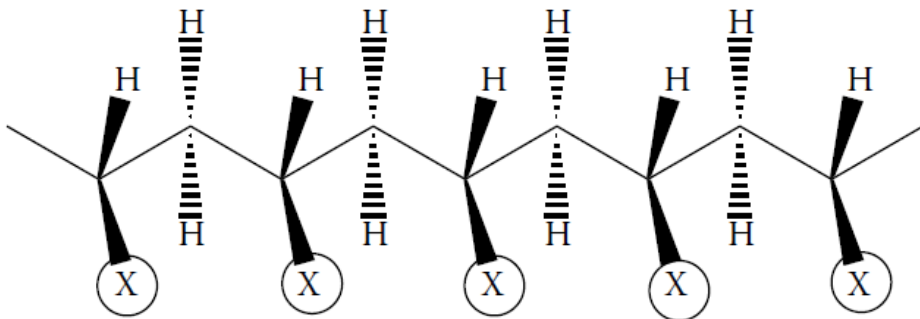
Quando temos um monômero vinílico assimétrico, todos os carbonos terciários podem ser um centro **quiral**, já que as cadeias de cada um dos lados terão m e n diferentes.



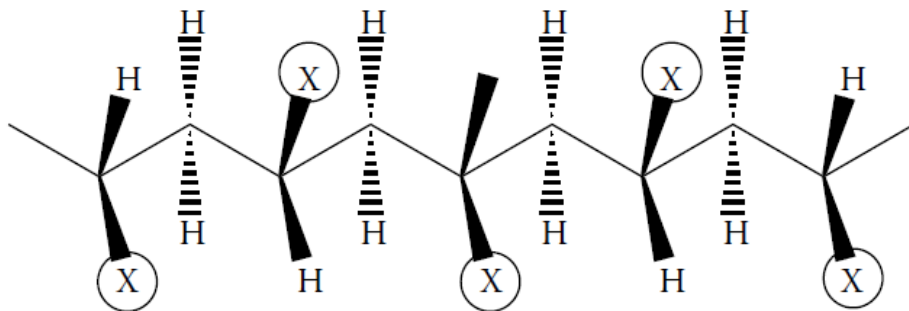
- Como as partes da cadeia correspondente a m e n são grandes e tendem a ficar mais parecidas quanto maiores forem esses polímeros não apresentam atividade óptica. C* é um centro pseudo assimétrico.
- Já no caso de radicais com heteroátomos na cadeia principal os mesmos ($\sim\sim\text{CH}_2\text{C}^*\text{HX-O}\sim\sim$) apresentam atividade óptica baseados em um critério (Cahn-Ingold-Prelo) pois C* nesse caso é um centro assimétrico verdadeiro e nos baseamos em um critério arbitrário como em i e ii.

Polímeros com um carbono quiral na unidade repetitiva na cadeia principal.

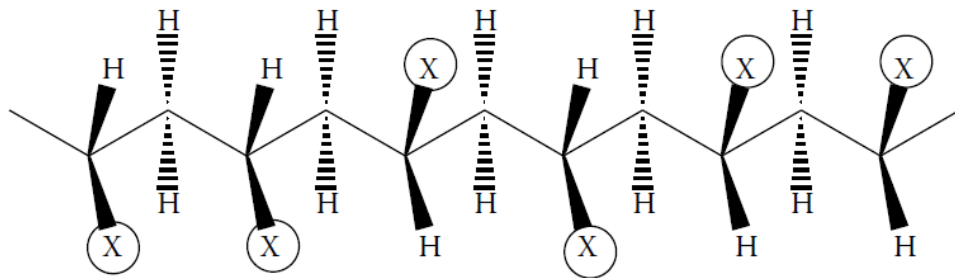
isotático



sindiotático

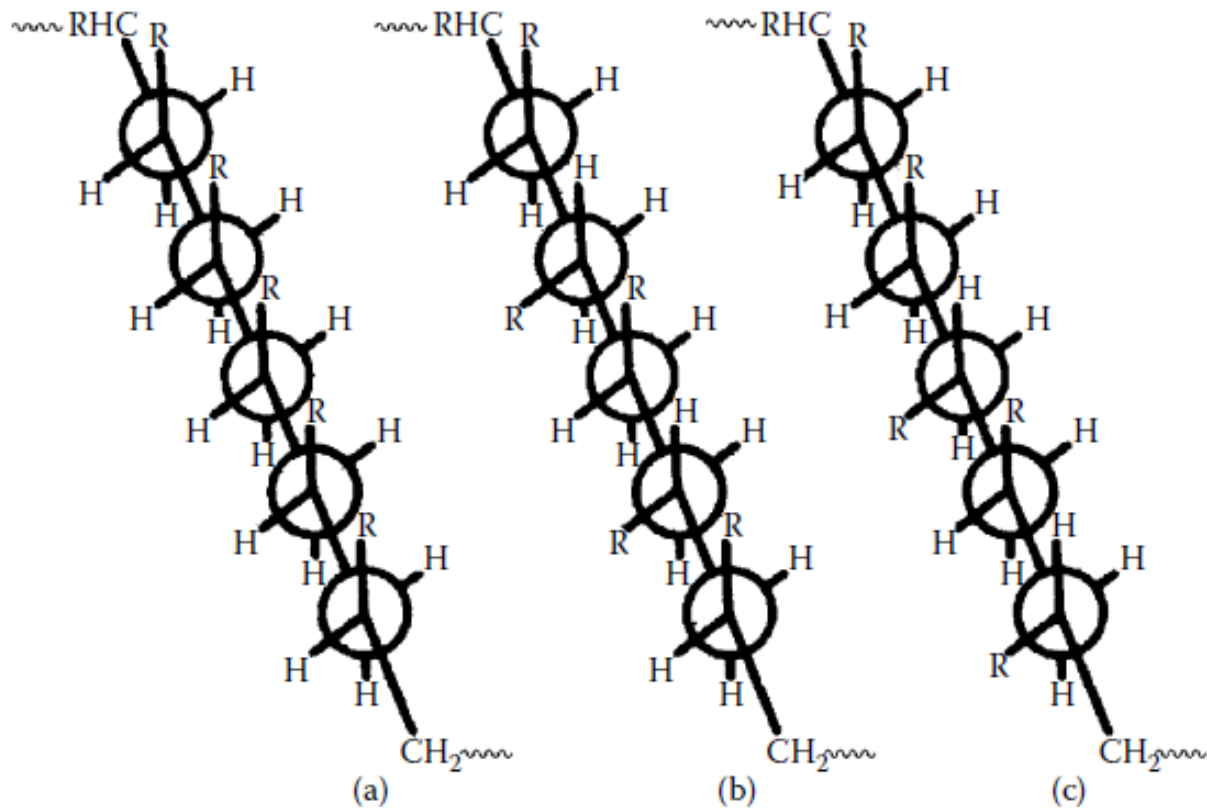


atático



Presença de um carbono assimétrico: $\text{CH}_2=\text{CHR}$

Monotactic



Projeções de Newman:

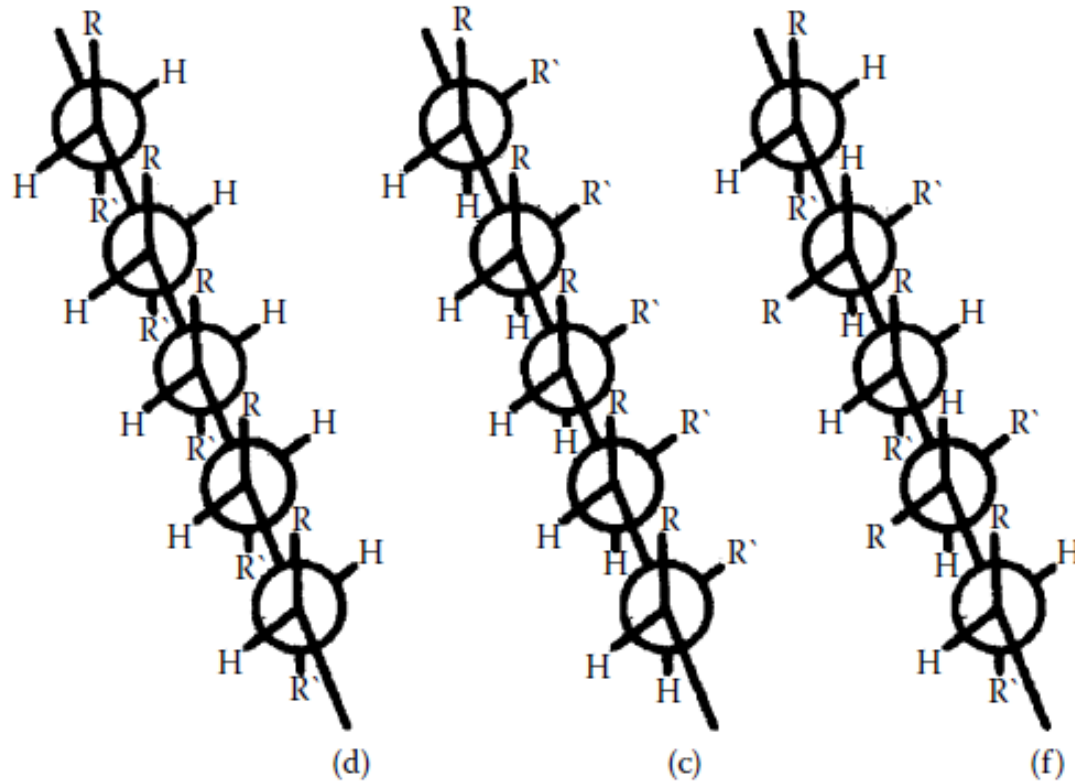
a) Isotático

b) sindiotático

c) atático

Presença de dois carbonos assimétricos: $\text{CHR}=\text{CHR}'$

Ditactic



Projeções de Newman:

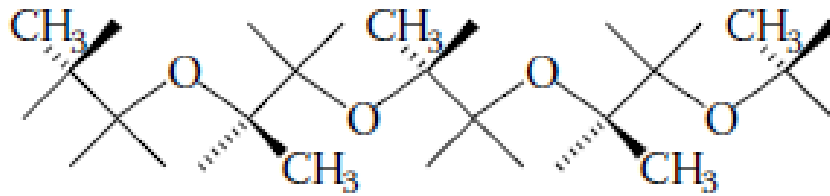
d) eritro-di-isotático

e) tereo-di-isotático

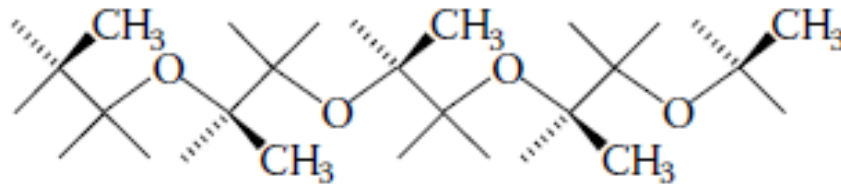
f) di-sindiotático

Configuração de Poliéteres

Isotático

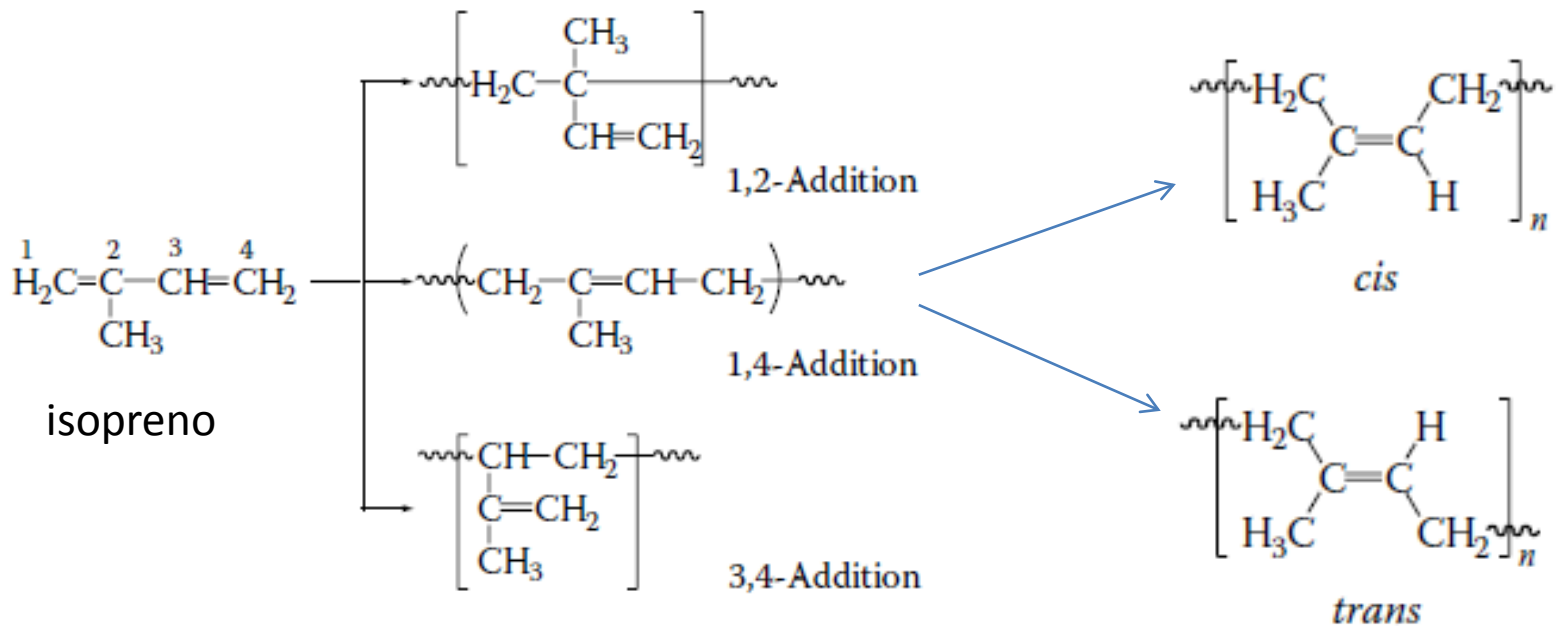


Sindiotático



Isomerismo Geométrico

Polimerização de dienos conjugados: $\text{CH}_2=\text{CX}-\text{CH}=\text{CH}_2$



Conformação de polímeros estereorregulares - Cristalização

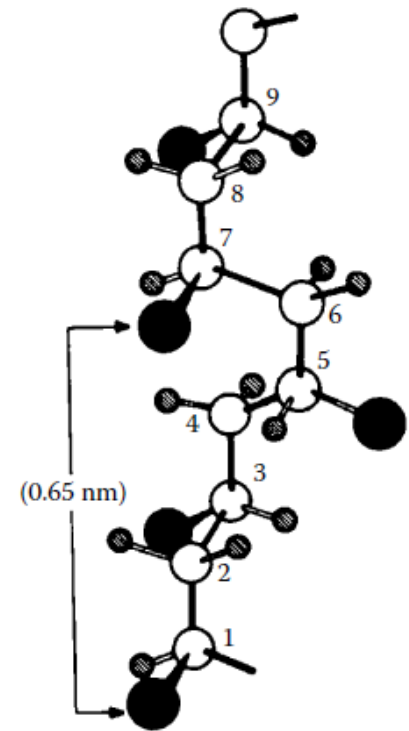
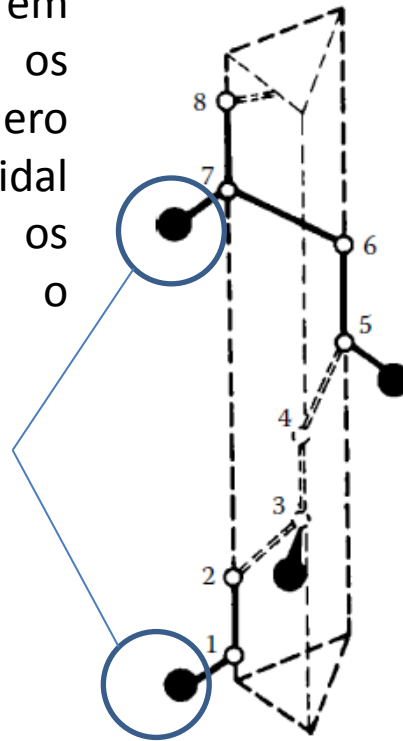
Para o polietileno que não tem um carbono assimétrico a cristalização corre para um arranjo trans zig-zag completo.

Já um polímero sindiotático a conformação zig-zag não é possível em função da curta distância entre os substituintes. Nesse caso o polímero adotará uma conformação helicoidal (maior distância possível entre os substituintes). Ao lado para o polipropileno.

Posição relativa dos carbonos:

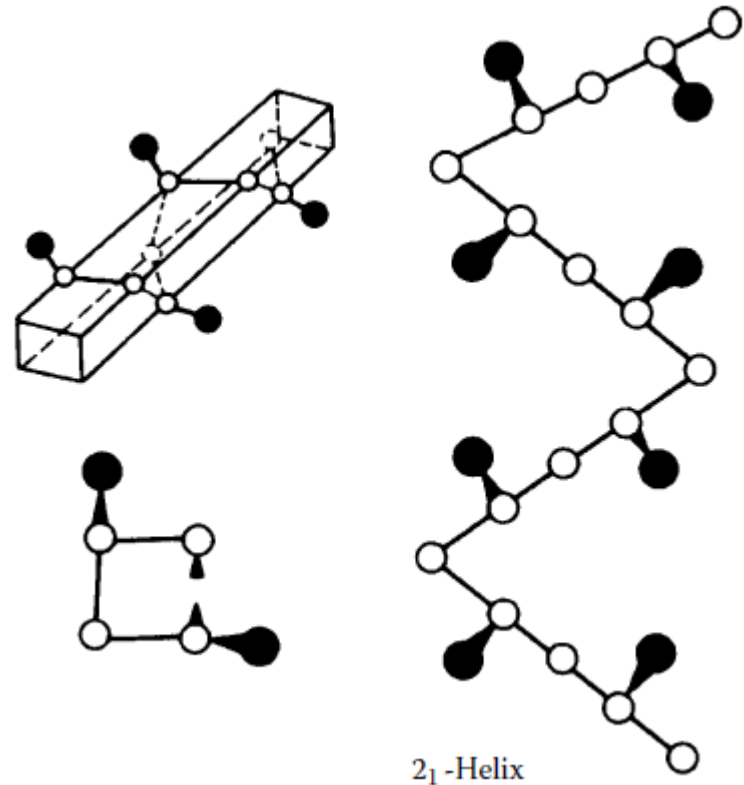
- 1 e 4 trans
- 2 e 5 são gauche
- 3 e 6 são trans
- 4 e 7 gauche

Logo C1 se repete em C7, dando 3 unidades monoméricas por giro completo do hélice (3_1 -hélice)



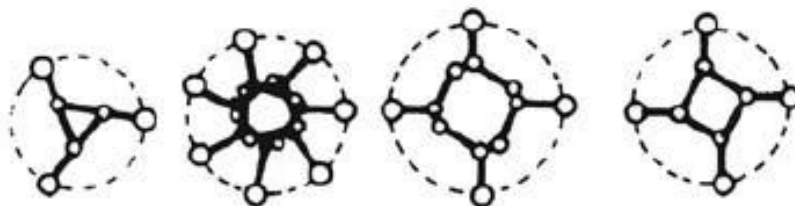
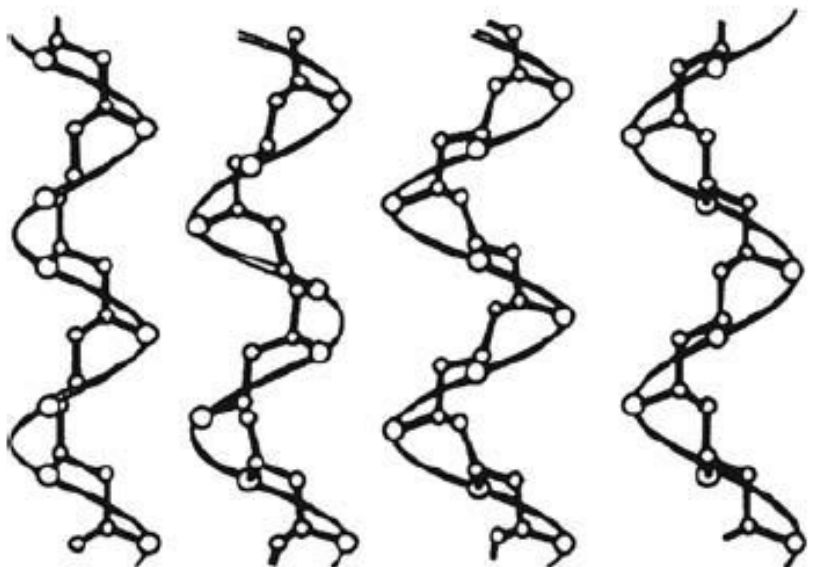
Uma hélice desse tipo com rotação de 120° irá resultar em um período de 0,62 nm (O PP isotático apresenta um período de 0,65 nm). O hélice pode ser no sentido dos ponteiros do relógio (direita) ou contrário (esquerda).

Para um polímero sindiotático a conformação zigzag é muito mais viável, já que os substituintes estão posicionados em orientações opostas. Contudo, uma dupla hélice é possível (ttgg):



Diferentes tipos de hélices podem ser formadas

Depende fundamentalmente do tamanho do substituinte (isotácticos).

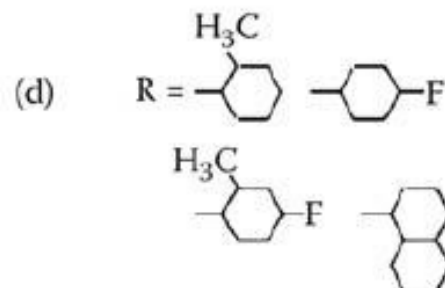
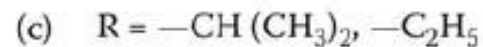
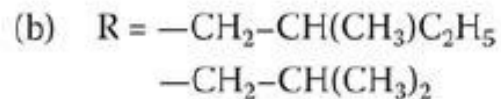
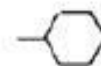
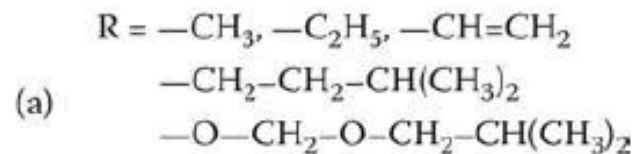


(a)

(b)

(c)

(d)

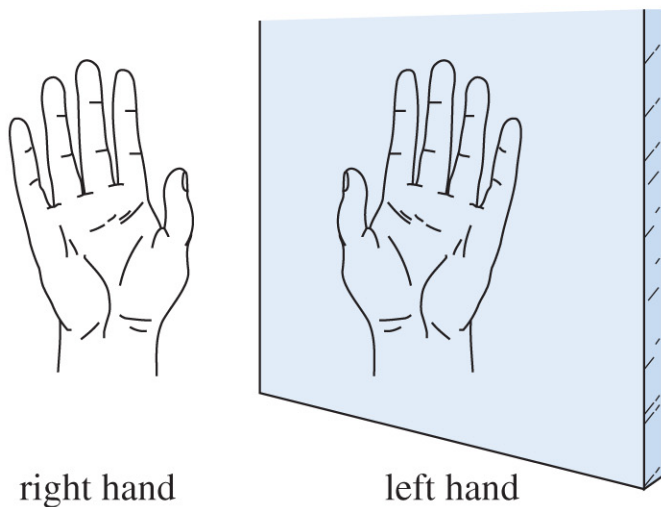


A bit on Stereochemistry

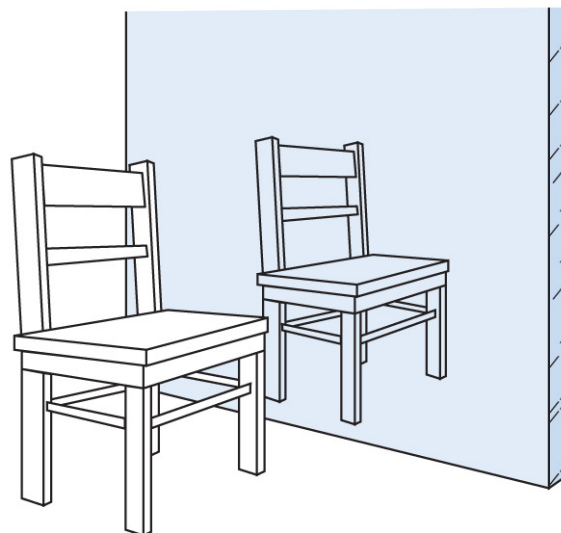
Definitions

- **Stereoisomers** – compounds with the same connectivity, different arrangement in space
- **Enantiomers** – stereoisomers that are non-superimposable mirror images; only properties that differ are direction (+ or -) of optical rotation
- **Chiral compound** – a compound that is optically active (achiral compound will not rotate light)

Chirality



- An object is **chiral** if its mirror image is different from the original object.

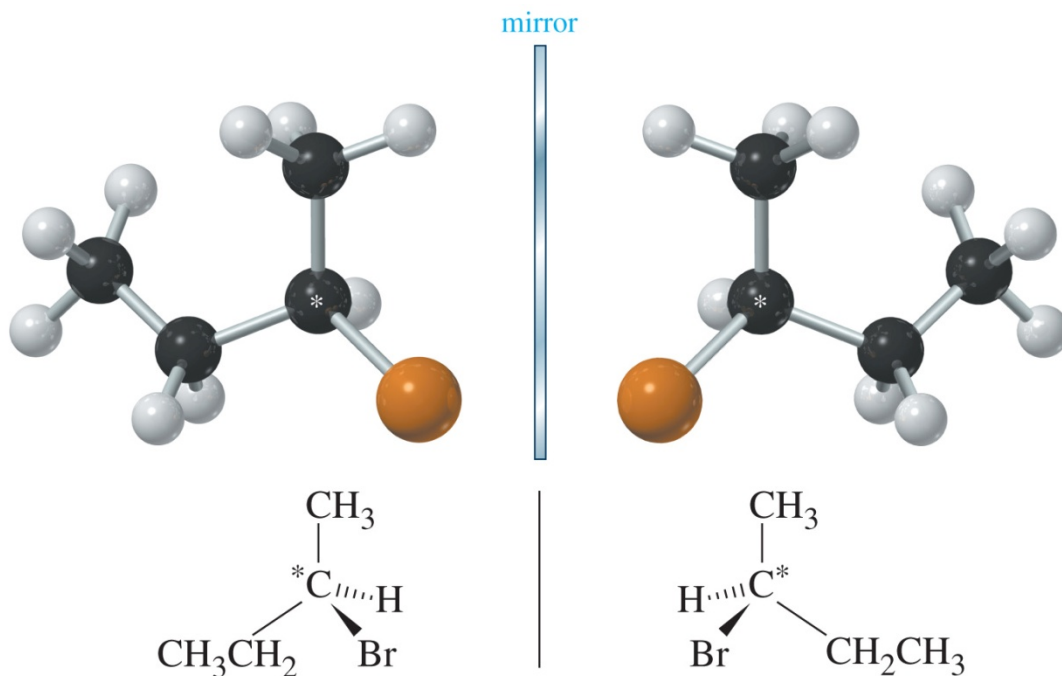


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- Mirror images that can be superposed are **achiral** (not chiral).

Stereoisomers

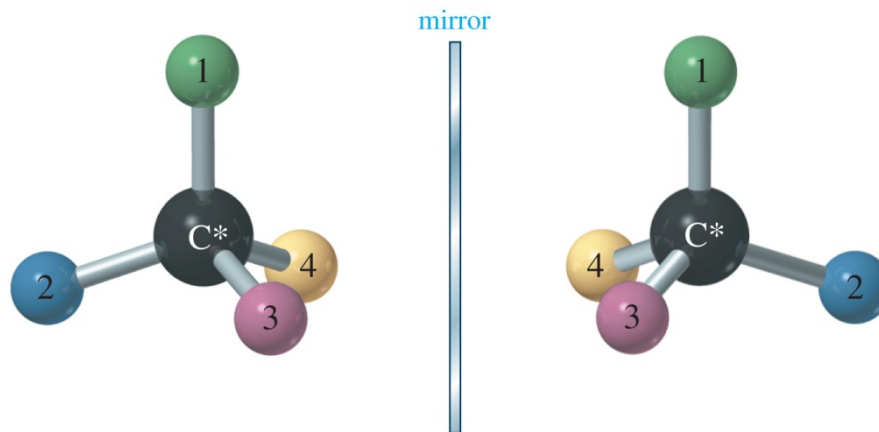
Enantiomers: Compounds that are nonsuperimposable mirror images. Any molecule that is chiral must have an enantiomer.



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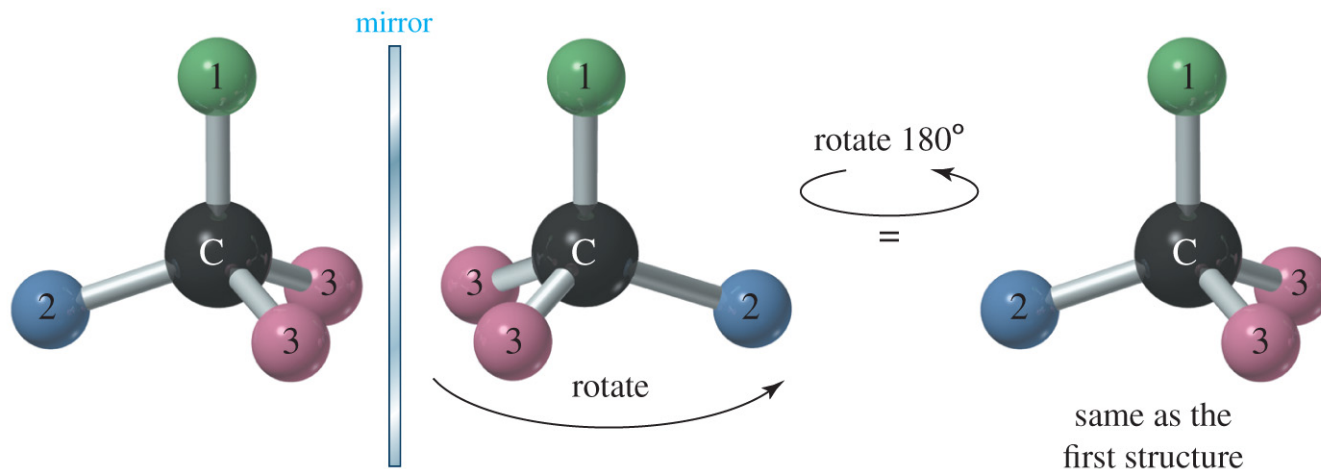
Chiral Carbon Atom

- Also called *asymmetric carbon* atom.
- Carbon atom that is bonded to four different groups is chiral.
- Its mirror image will be a different compound (enantiomer).



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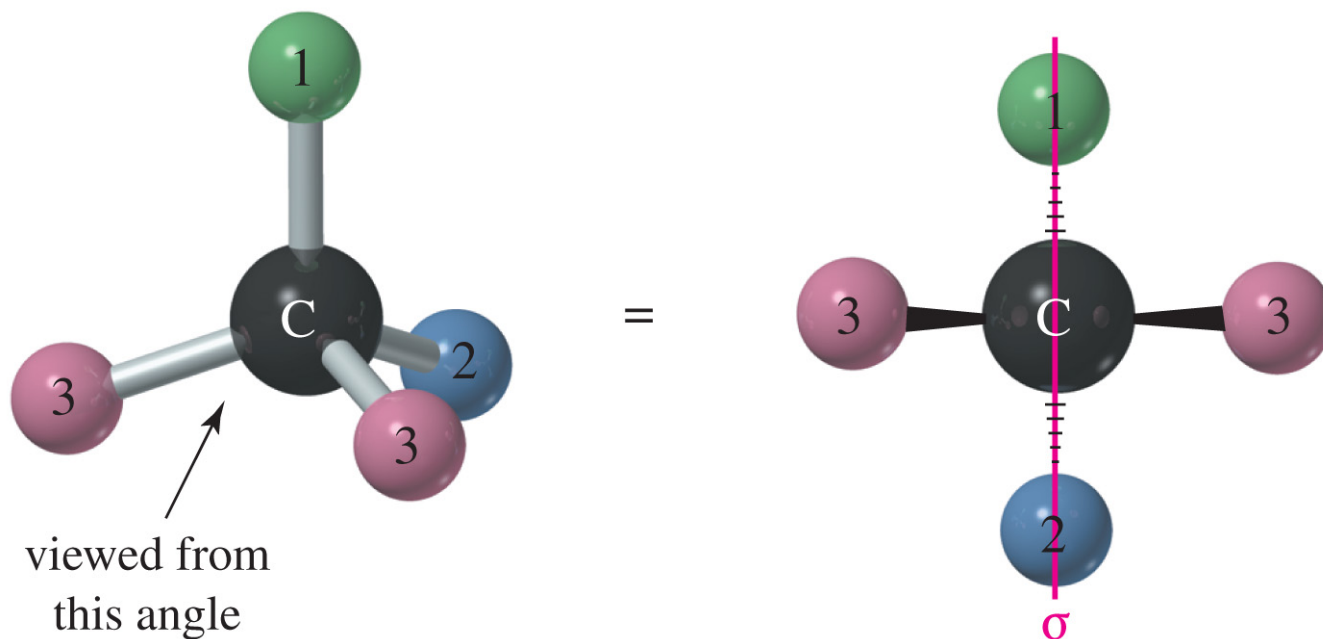
Achiral Compounds



Take this mirror image and try to superimpose it on the one to the left matching all the atoms. Everything will match.

When the images can be superposed, the compound is ***achiral***.

Planes of Symmetry

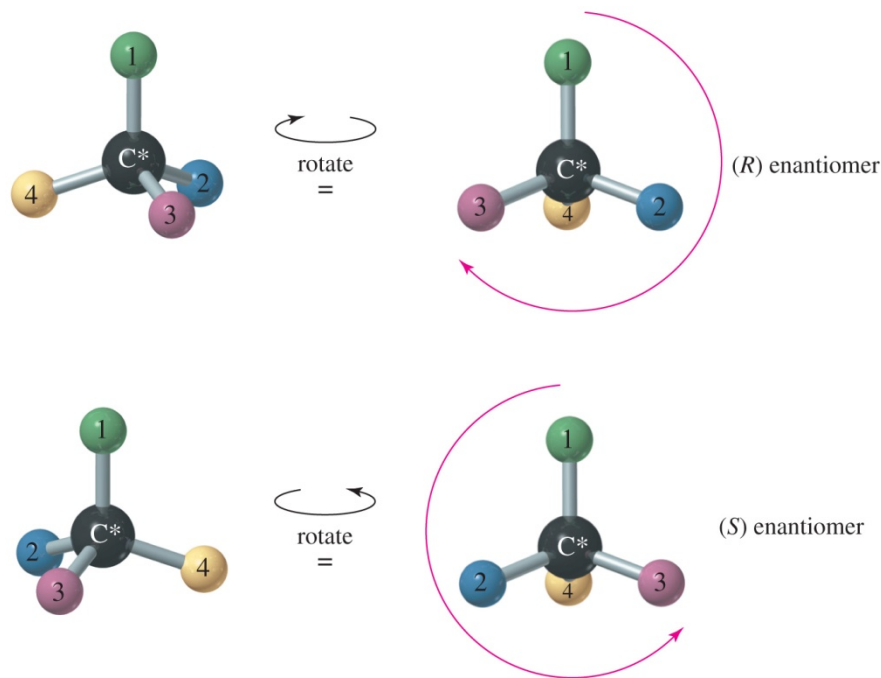


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- A molecule that has a plane of symmetry is ***achiral***.

(R) e (S) Conformations

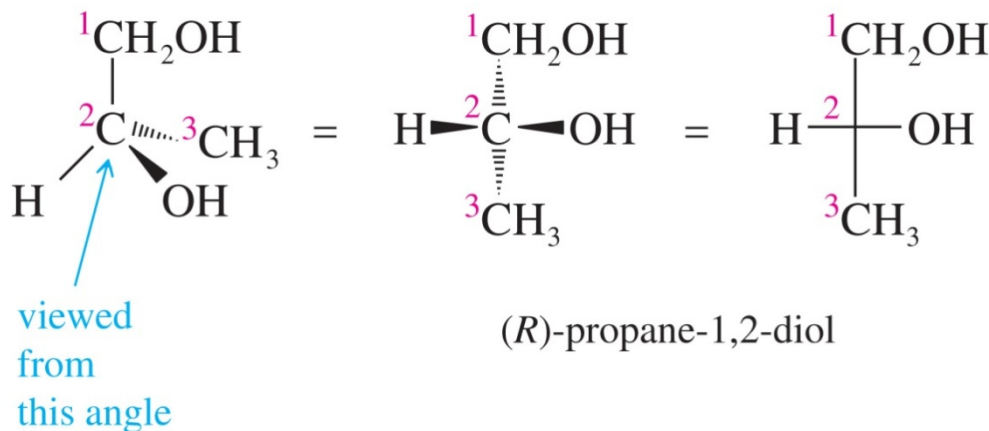
- **Cahn–Ingold–Prelog** convention is the most widely accepted system for naming the configurations of chirality centers.
- Working in 3-D, rotate the molecule so that the lowest priority group is in back.
- Draw an arrow from highest (1) to second highest (2) to lowest (3) priority group.
- Clockwise = (*R*), Counterclockwise = (*S*)



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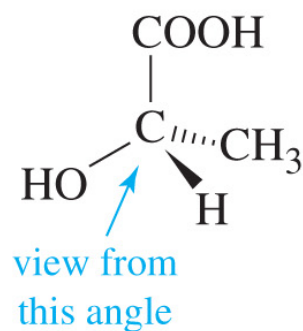
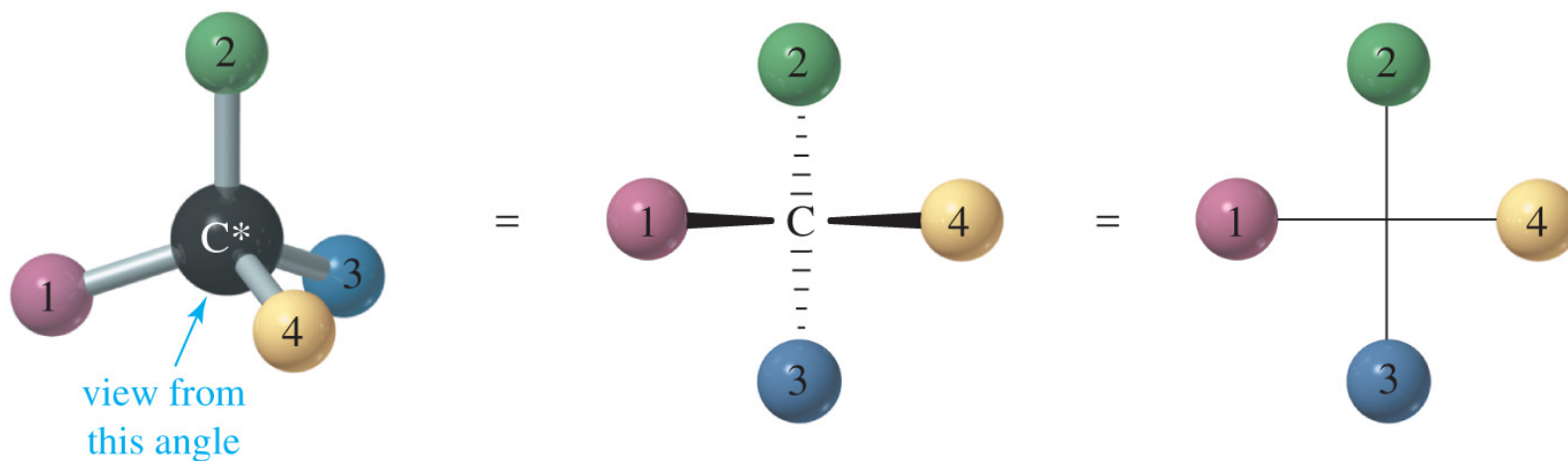
Fischer Projections

- Flat representation of a 3-D molecule.
- A chiral carbon is at the intersection of horizontal and vertical lines.
- Horizontal lines are forward, out of plane.
- Vertical lines are behind the plane.

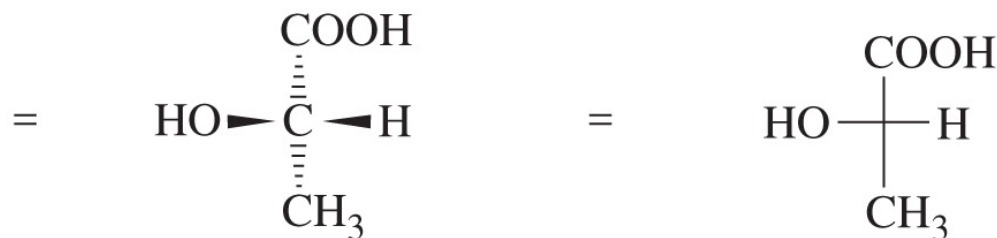


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Fischer Projections (Continued)



(S)-lactic acid
perspective drawing



(S)-lactic acid
Fischer projection

Fischer Rules

- Carbon chain is on the vertical line.
- Highest oxidized carbon is at top.
- Rotation of 180° in plane doesn't change molecule.
- Rotation of 90° is NOT allowed.

Reações de Polimerização iniciadas por catalisadores metálicos – Reações de Transferência

Catalisadores de Ziegler-Natta

Descobertos nos anos 1950 por Ziegler os catalisadores a base de compostos alquil-alumínio e metais de transição permitiam a polimerização do etileno à pressão ambiente e temperatura ambiente sem produzir muitas ramificações, dando origem à um polietileno muito cristalino, que ficou conhecido como Polietileno de Alta Densidade PEAD.

Permite a polimerização de monômeros como propileno, 1-buteno dando origem às α -olefinas.

Metal do grupo I, II ou III/ heterogêneo

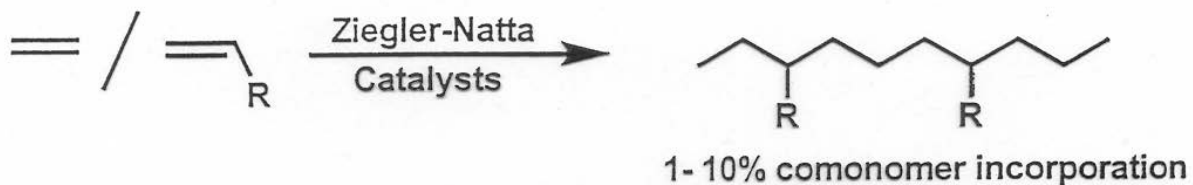
TABLE 7.1**Components of Ziegler–Natta Catalysts****Metal Alkyl or Aryl****Transition Metal Compounds**

Polyethylene



$$T_m = 133-138\text{ }^{\circ}\text{C}$$

High Density
Polyethylene (HDPE)



$$T_m = 115-130\text{ }^{\circ}\text{C}$$

Linear Low Density
Polyethylene (LLDPE)

The Beginnings

- 1953 - K. Ziegler polymerized ethylene at low pressures with binary mixtures of transition metal salts and metal alkyls, e.g., $\text{TiCl}_4 + \text{AlEt}_3$.
- 1954 - G. Natta polymerized propylene with these catalysts and recognized the ability of the catalyst to control stereospecificity. Via the use of $\alpha\text{-TiCl}_3$, highly crystalline propylene 1-butene and styrene polymers were synthesized.
- Hogan, Banks (Phillips Petroleum Co.) disclosed the use of chromium oxide on silica &/or alumina catalysts for polyethylene.
- 1955 - Vandenberg (Hercules) and Bua, Luciani (Montecatini) applied for patents that disclosed the use of H_2 as a chain transfer agent for Ziegler-Natta type catalysts.
- 1962 - Natta, Zambelli & co-workers announced the synthesis of highly syndiotactic PP with $\text{VCl}_4 + \text{AlEt}_2\text{Cl}$ (@-78°C)
- 1963 - K. Ziegler and G. Natta were awarded the Nobel Prize in Chemistry by the Royal Academy of Science of Sweden.

Physical Constants for Polypropylene

<u>Property</u>	<u>Isotactic</u>	<u>Syndiotactic</u>	<u>Atactic</u>
density, g/cm ³	0.92-0.94	0.89-0.91	0.85-0.90
melting point, °C	165	135	
solubility in hydrocarbons at 20°C	none	medium	high
yield strength	high	medium	very low

Giulio Natta

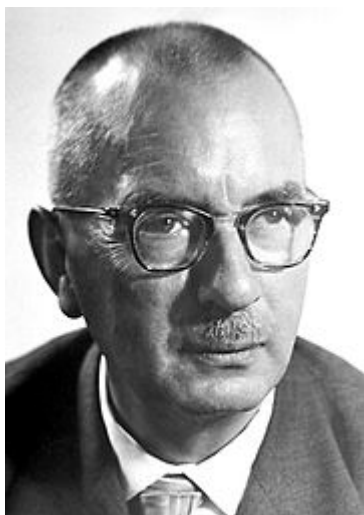
1903 - 1979



Figura 2. Giulio Natta na vigília do Prêmio Nobel em 1963.

Marzo		Marzo	
Giovedì 11	Fatto il polipropilene	s Arrigo	Sabato 13
Venerdì 12	Olivero	s Matilde	Domenica 14
	s Gregorio		

Figura 3. Da agenda de Giulio Natta Março 1954: “fatto il polipropilene” (N.d.T. “feito o polipropileno”).

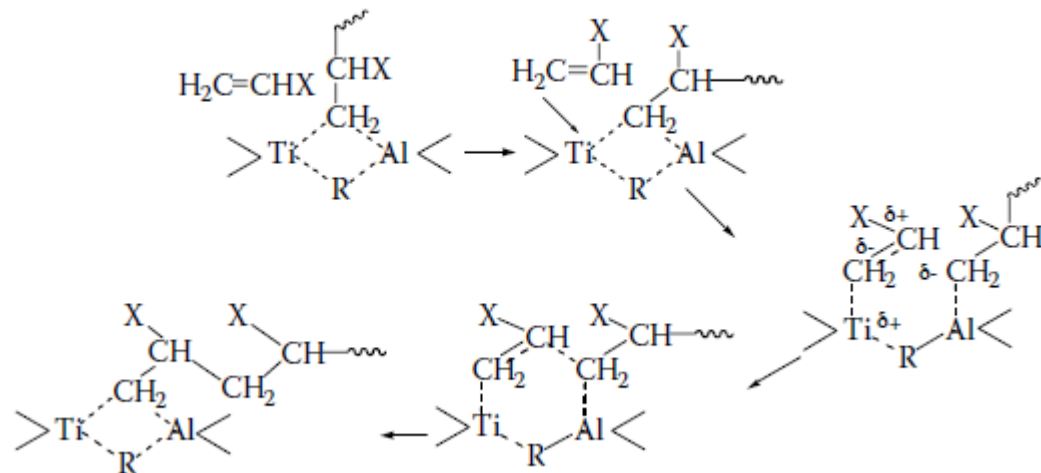
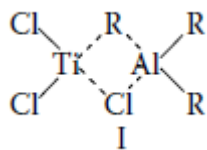


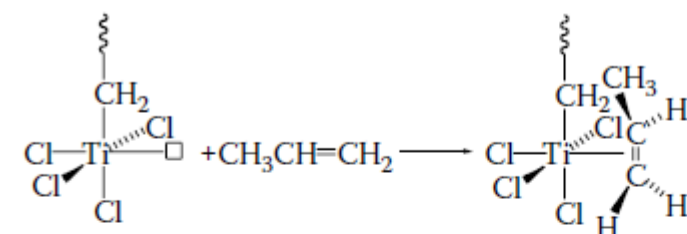
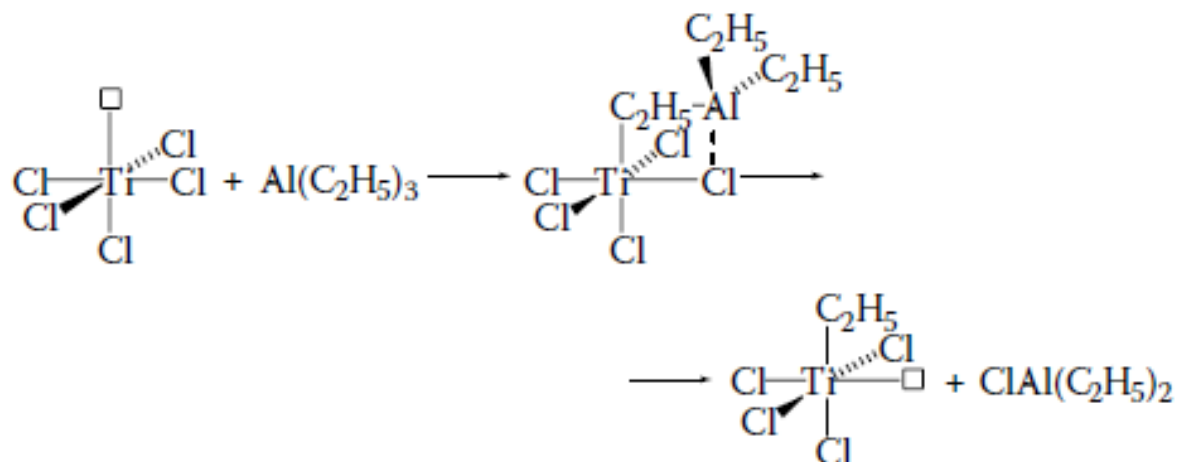
Karl Ziegler
1898 -1973

Os dois mecanismos principais:

-Bimetal - (Natta et al.)

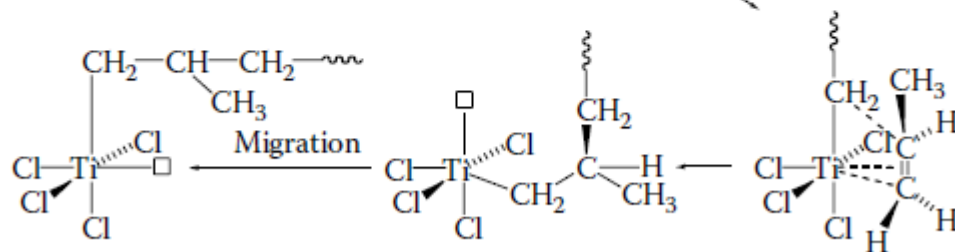
-Monometal (Cossee e Arlman)





Active center (a)

Complex (b)

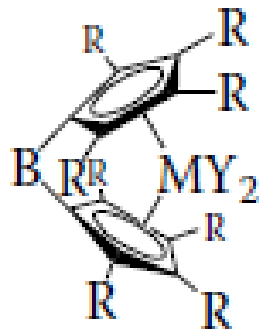


New active center

Active center (d)

Transition state (c)

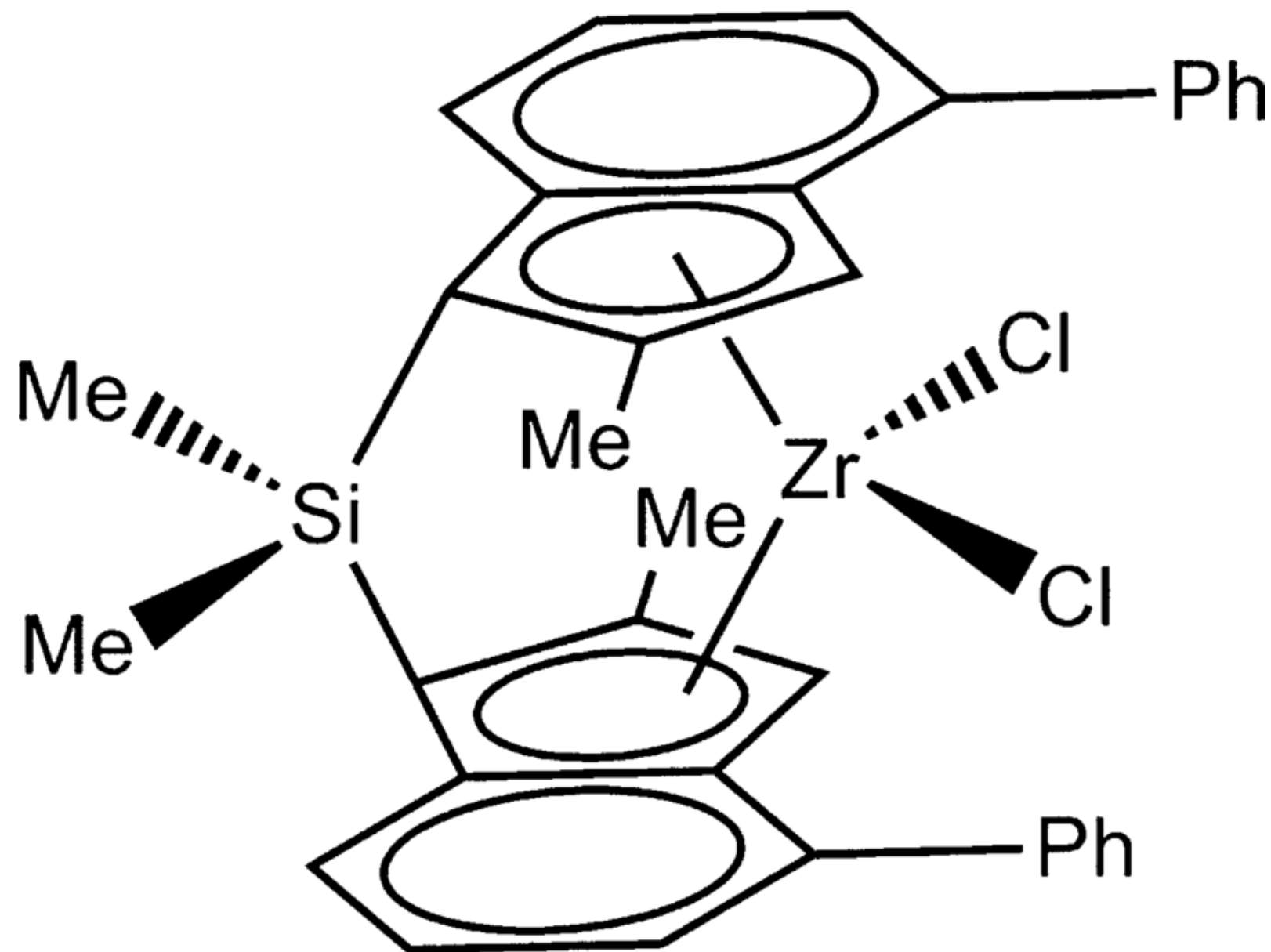
Metalocenos



Y = halogen or alkyl group

R = H, alkyl or fused ring system

M = transition metal from groups 4B, 5B or 6B



Para as próximas Aulas

Capítulo 7. Polymerization Reactions Initiated by metal catalyst and Transfer Reactions

Pg. 157 a 180

Capítulo 8. Polymers in Solution

8.1 Thermodynamics of Polymer Solutions

8.2 Ideal Mixtures of Small Molecules

8.3 Nonideal Solutions

8.4 Flory-Huggins Theory: Entropy of Mixing

8.5 Enthalpy Change of Mixing

8.6 Free energy of Mixing

8.7 limitation of Flory-Huggins Theory

8.8 Phase Equilibria

Da pg. 197 até a pg. 208

8.11 Lower Critical Solution Temperatures pg. 213 a 215

8.12 Solubility and the Cohesive Energy Density pg. 216 a 219

8.13 Polymer-Polymer Mixtures (Blendas Poliméricas) pg. 219 a 223