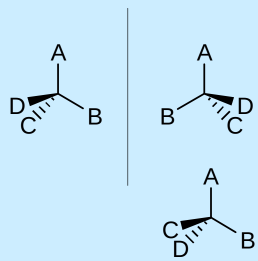
Stereochemistry

Concept

Stereogenicity



Stereochemistry

Types of Tacticity

Tacticity: 1-substituted ethylenes (a-olefins)

Isotactic

Syndiotactic

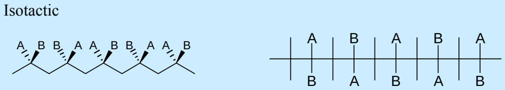
Atactic

Stereochemistry

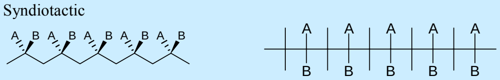
Types of Tacticity

Tacticity of 1,1 Disubstituted Ethylenes

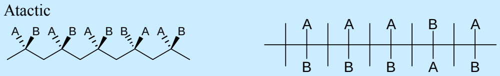
Isotactic



Syndiotactic



Atactic

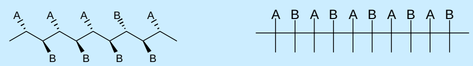


Stereochemistry

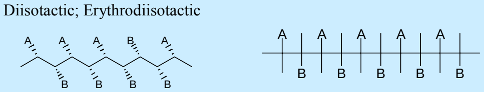
Types of Tacticity

Tacticity of 1,2 Disubstituted Ethylenes: Di-tacticity

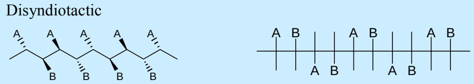
Diisotactic; Erythrodiisotactic



Diisotactic; Erythrodiisotactic



Disyndiotactic

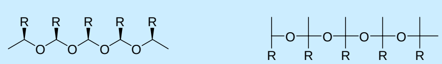


Stereochemistry

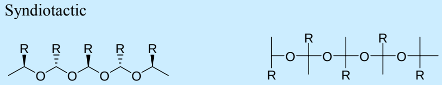
Tacticity

Carbonyls: e.g. polyacetaldehyde

Isotactic



Syndiotactic



Stereochemistry

Tacticity

Carbonyls: e.g. polypropylene oxide

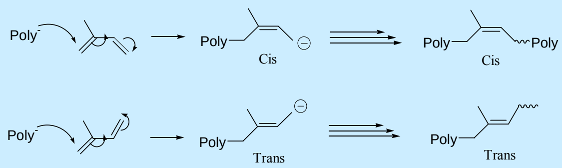
Isotactic

Syndiotactic

Stereochemistry

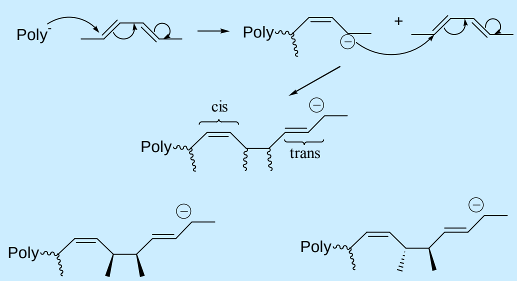
Types of Tacticity

Dienes: 1,4 Polymerization of Dienes (more imp. for practical use)



Stereochemistry

Tacticity of 1,4 Dienes



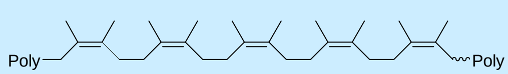
Syn-erythro

Anti-threo

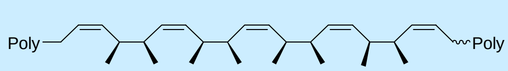
Stereochemistry

Tacticity of 1,4 Dienes

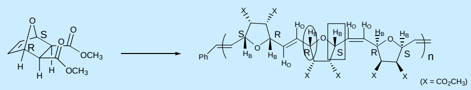
Cistactic 1,4 – (2,3 dimethyl) butadiene

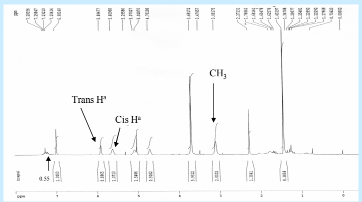


Ciserythrodiisotactic 1,4 dimethyl poly 1,4 butadiene



[1]H NMR of Oligomer from Ring Opening Metathesis Polymerization of Dimethyl 7-oxanorbornene-2,3-dicarboxylate



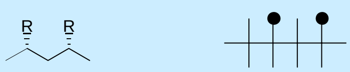


Stereochemistry

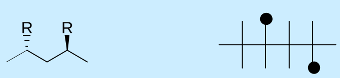
Analysis of Stereoregularity

Diads

Isotactic = Meso = m



Syndiotactic = Racemic = r



Stereochemistry

Analysis of Stereoregularity

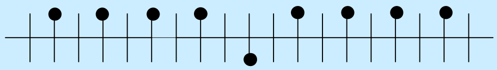
Triads

Isotactic = meso-meso = mm

Syndiotactic = racemic-racemic = rr

Stereochemistry

Analysis of Stereoregularity



Total repeat units: 9 Total diads: 8 Total triads: 7

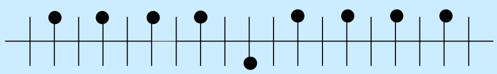
Diads:

- meso = 6
  → fraction meso = (m) = 6/8 = 3/4
- racemic = 2
  → fraction racemic = (r) = 2/8 = 1/4

Total of fractions must = unity: (m) + (r) = 1

Stereochemistry

Analysis of Stereoregularity



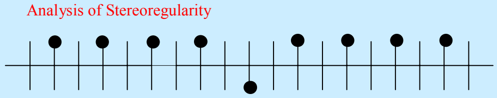
Triads:

- meso = (mm) = 4
  → fraction meso = (mm) = 4/7
- racemic = 1
  → fraction racemic = (rr) = 1/7
- heterotactic = 2
  → fraction heterotactic = (mr) = 2/7

Total of fractions must = unity: (mm) + (mr) + (rr) = 1

Stereochemistry

Analysis of Stereoregularity



Diads and Triads are related by:

$$(m) = (mm) + 0.5(mr)$$

$$(r) = (rr) + 0.5(mr)$$

If these statistics met, then you have random tactic polymers,

Otherwise, stereoblock polymers

NMR Determination of Tacticity for PMMA

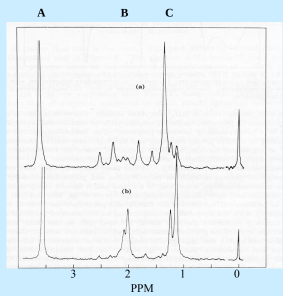
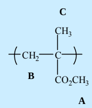


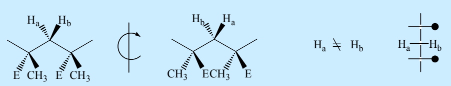
Fig. 14. High-resolution NMR spectra (60 Mc/sec, 15% in chlorobenzene, observed at 150°C) of polymers of methyl methacrylate prepared with (**a**) phenylmagnesium bromide initiator and (**b**) a free-radical initiator (benzoyl peroxide) (13a). Courtesy *Chemical and Engineering News*.



Predominantly Isotactic (anionic)

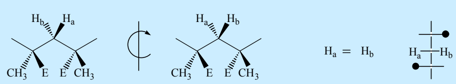
Predominantly Syndiotactic (radical)

Stereochemical Basis for Tacticity



meso (m) dyad → Pure isotactic polymer → $-CH_2-$

"AB quartet" (nearly 2 doublets)

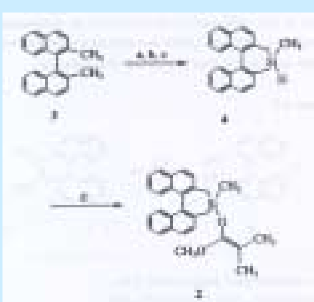


racemic (r) dyad → Pure Syndiotactic polymer → $-CH_2-$

Singlet

Stereochemistry

Analysis of Stereoregularity: Example of Chiral GTP Catalyst



Stereochemistry

Analysis of Stereoregularity

Table 2.16 Stereochemical parameters of poly(tert-butyl acrylate) obtained using the optically pure S-2 under GTP conditions.[a]

Run	Cat	f_{mm}[b]	f_{mr}[b]	f_{rr}[b]	ρ[c]	$P_{m/r}$	$P_{r/m}$	ΣP[d]
30	HgI_2	0.362	0.466	0.172	1.034	0.392	0.575	0.97
31	HgI_2	0.382	0.479	0.139	0.982	0.385	0.633	1.02
32	HgI_2	0.393	0.462	0.145	1.016	0.370	0.614	0.98
33	MCB	0.257	0.513	0.230	0.974	0.500	0.527	1.03
34	MCB	0.270	0.488	0.242	1.024	0.475	0.502	0.98

[a]Calculated values for data taken from Table 2.11. [b]Triad tacticity determined by 400 MHz ^1H NMR: $f_m = f_{mm} + (0.5)f_{mr}$; $f_r = f_{rr} + (0.5)f_{mr}$. [c]Persistence length $\rho = 2(f_m)(f_r)/(f_{mr})$. [d]Summation of P(m/r) under Markov probabilities. ΣP = 1.0 for a Bernoullian system.

NMR Determination of Tacticity for PMMA

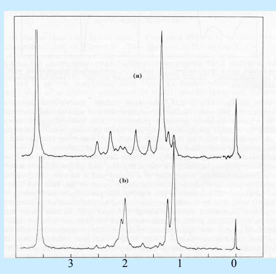
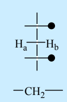
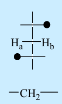


Fig. 14. High-resolution NMR spectra (60 Mc/sec, 15% in chlorobenzene, observed at 150°C) of polymers of methyl methacrylate prepared with (**a**) phenylmagnesium bromide initiator and (**b**) a free-radical initiator (benzoyl peroxide) (13a). Courtesy *Chemical and Engineering News.*

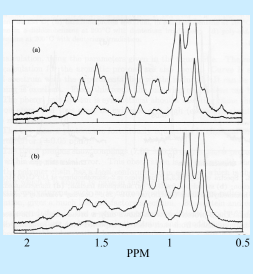


Isotactic - meso

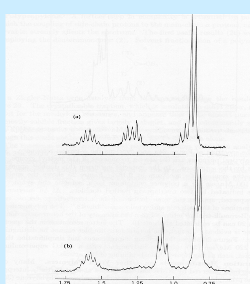


Syndiotactic - racemic

High and Low Resolution NMR of Polypropylene



Low resolution NMR spectrum of polypropylene
(a) Isotactic
(b) Syndiotactic

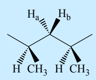


High resolution NMR spectrum of polypropylene
(a) Isotactic
(b) Syndiotactic

Stereochemistry

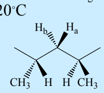
Properties Polypropylene

Isotactic: Crystalline, higher melting, more chemical resistant, fiber and plastic apps.



meso (m) dyad

Syndiotactic: Crystalline (like isotactic), T_g lower by 20°C

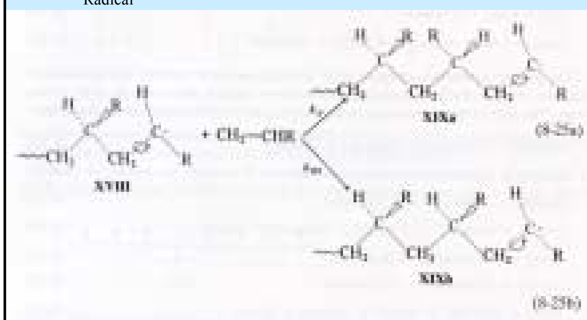


Atactic: Amorphous (non-crystalline), “tacky”, not used much but has uses for adhesives, sealants

Stereochemistry

Forces of Stereoregulation

Radical



Stereochemistry

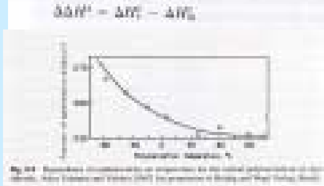
Forces of Stereoregulation

Radical

$$\frac{k_i}{k_s} = \exp\left(\frac{-\Delta\Delta G^{\ddagger}}{RT}\right) = \exp\left\{\left(\frac{\Delta\Delta S^{\ddagger}}{R}\right) - \left(\frac{\Delta\Delta H^{\ddagger}}{RT}\right)\right\}$$

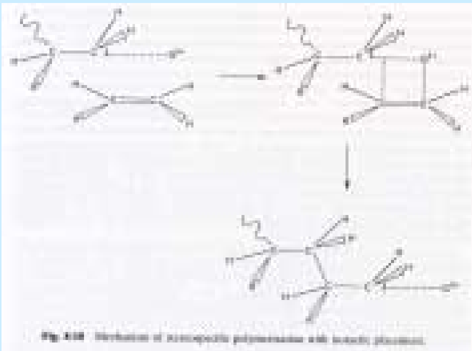
with

$$\Delta\Delta G^{\ddagger} = \Delta G_i^{\ddagger} - \Delta G_s^{\ddagger}$$
$$\Delta\Delta S^{\ddagger} = \Delta S_i^{\ddagger} - \Delta S_s^{\ddagger}$$
$$\Delta\Delta H^{\ddagger} = \Delta H_i^{\ddagger} - \Delta H_s^{\ddagger}$$



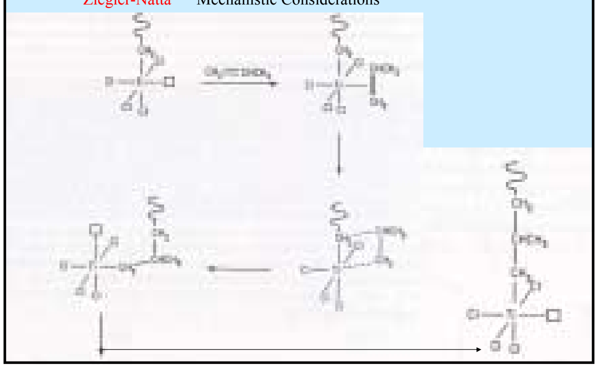
Stereochemistry

Ziegler-Natta Mechanistic Considerations



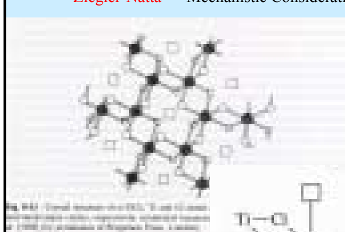
Stereochemistry

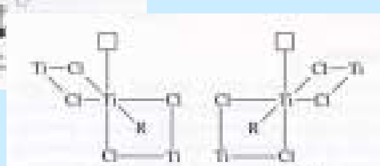
Ziegler-Natta Mechanistic Considerations



Stereochemistry

Ziegler-Natta Mechanistic Considerations





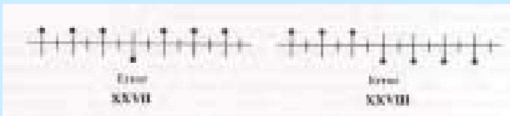
XXV XXVI

Stereochemistry

Ziegler-Natta Mechanistic Considerations

Proof for stereocontrol by the catalyst (as opposed to chirality of the polymer or in particular the penultimate functional group)

This is called “Enantiomorphic” Control = Catalyst Control of Stereochemistry



Pairs of racemic dyads for enantiomorphic control, single dyad for Penultimate control.