

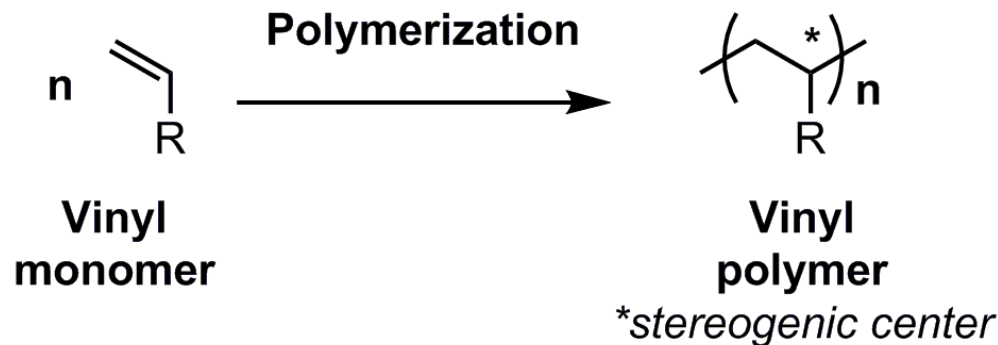
Polymers: Stereochemistry



Contents

- Stereochemistry in vinyl polymers
- Stereoregularity in vinyl polymers
- Stereochemistry in natural polymers:
polypeptides

Vinyl Polymers



- Vinyl polymers often have several thousand repeat units, with each repeating unit having a stereogenic center. *Why not just use R/S to designate each one?*
- Consider a polypropylene chain with a molecular weight of 42,000 Da, which corresponds to ~1,000 repeat units:



Stereoisomers possible = $2^n = 2^{1000}$

> 1×10^{3000} stereoisomers!

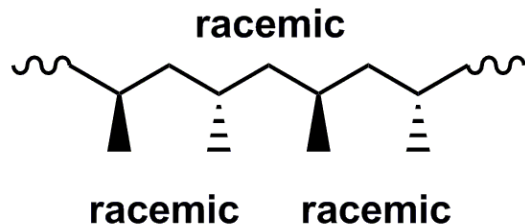
Tacticity

- Rather than assigning R/S to individual stereogenic centers, we compare the relative stereochemistry of neighboring stereogenic centers.
- We use “m” for meso and “r” for racemic as a label comparing adjacent stereocenters.



"mmm tetrad"

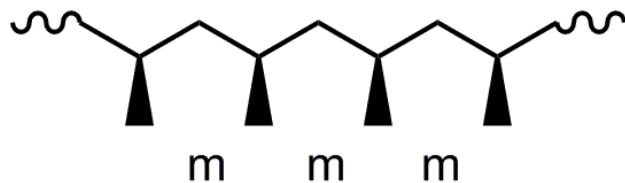
*Polymers with high "m" content are denoted **isotactic***



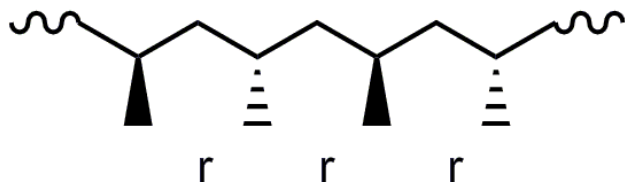
"rrr tetrad"

*Polymers with high "r" content are denoted **syndiotactic***

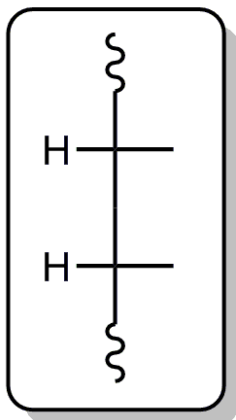
Consequences of Tacticity



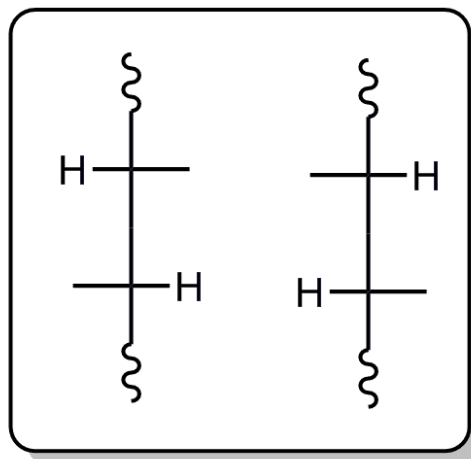
These two structures on the left are diastereomers of each other, and will have different properties.



For example, isotactic polymers will often have higher glass transition temperatures (T_g 's) and show greater crystallinity compared to non-stereoregular polymers.



Meso form



Racemic forms

Why the meso and racemic names?

Consider Fischer projections of the adjacent stereogenic centers on polypropylene. If you envision the polymer chain extending in both directions, you would have either a meso compound or racemic compound.

Synthetic Considerations



- Most vinyl polymerizations result in random mixtures of *r* and *s* adjacent centers. The lack of stereoregularity in a polymer chain makes it **atactic** (lacking tacticity).
- In reality, a polymer sample will be a mixture of different chain lengths (dispersity) but even polymer chains of identical length will be diastereomers of each other.



Synthesis of stereoregular vinyl polymers typically requires a transition metal catalyst

The synthesis of stereoregular vinyl polymers is historically significant, with a *Nobel Prize* awarded to Ziegler and Natta in 1963 in large part because of their work in catalysts that produce stereoregular macromolecules.

Stereogenic Centers in Natural Polymers

- Almost all α -amino acids have a stereogenic carbon
- AB-type monomer capable of a poly-condensation reaction
- The resulting polymer, the familiar polypeptide, possesses stereogenic carbons within the backbone. Because this stereocenter is not involved in the condensation reaction, the stereochemistry on the monomer is retained in the polymer.
- Note that the α -carbons are all stereogenic centers. In most cases, these will have the (S) designation in naturally occurring polypeptides.

