

PHYSICS OF SOLID POLYMERS

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Recommended texts:

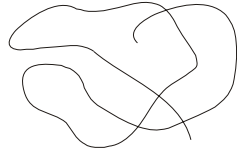
- G. Strobl, The Physics of Polymers, Springer 1996 (emphasis on physics)
- U. Gedde, Polymer Physics, Springer 1995.
- J.M.G. Cowie, Polymers: Chemistry & Physics of Modern Materials, 2nd edn., 1991. (basic)
- R.J. Young, P.A. Lovell, Introduction to Polymers, 2nd edn., 1991. (basic)
- Principles of Polymer Engineering, 2nd edition. N. G. McCrum, C. P. Buckley and C. B. Bucknall, Oxford University Press, 1997. Chap. 1 – 5. (more advanced)
- Wunderlich, Bernhard. - Macromolecular physics. - Vol.1 : Crystal structure, morphology, defects.; Vol. 2: Crystallization; Vol. 3: Melting - New York; London : Academic Press, 1973-74 (highly detailed)

STRUCTURAL HIERARCHY IN SEMICRYSTALLINE POLYMERS

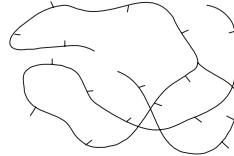
- **atomic scale - crystal unit cell**
 - several Angstroms (<1 nm to a few nm)
 - detailed crystal structure, conformation of individual bonds
 - wide-angle XRD
- **scale of crystal thickness**
 - 100- 500 Å (10 - 50 nm)
 - electron microscopy, small-angle X-ray scattering (SAXS)
($\lambda = 2d \sin\theta$)
- **scale of crystal aggregates (spherulites etc.)**
 - μm scale
 - optical microscopy



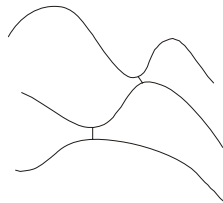
WHICH POLYMERS CAN CRYSTALLIZE?



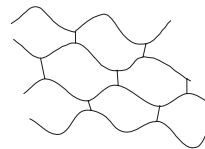
Linear
 - thermoplastic (e.g. HDPE)
 - potentially crystallizable
 (can contain some long branches)



Branched
 (short and long branches)
 - thermoplastic (e.g. LDPE)
 - potentially crystallizable



Cross-linked (lightly)
 - vulcanized rubber
 - may crystallize at low T
 and under stress (unwanted)



Cross-linked (densely)
 - cured thermoset resin
 - does not crystallize
 - amorphous (glassy)

Crystallizable polymers must also be:

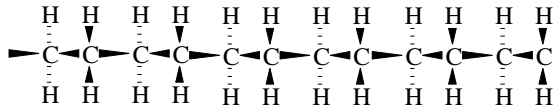
- homopolymers
- stereoregular
- regioregular

		Can crystallize?
homopolymer	AAAAAAAAAAAAA	yes
random copolymer	AABABBABBBABA	no
block copolymer	AAAAAABBBBBB	partially
graft copolymer	AAAAAAAAAAAAAA BBBBBBBBBB	partially

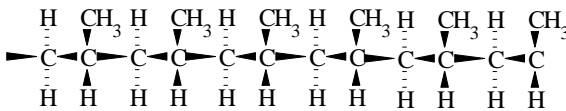
In general, for polymers to be able to crystallize they must be:

- **linear** (or lightly branched)
- **stereoregular**
- **regioregular**

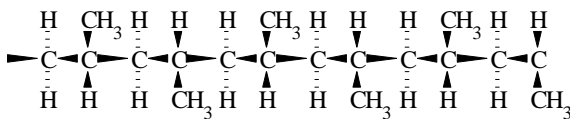
STEREOREGULARITY OF POLYMERS



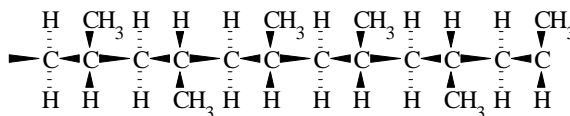
linear polyethylene



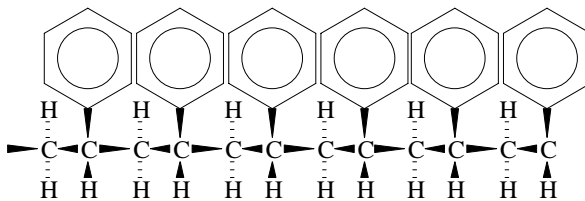
isotactic polypropylene (i-PP)



syndiotactic polypropylene (s-PP)



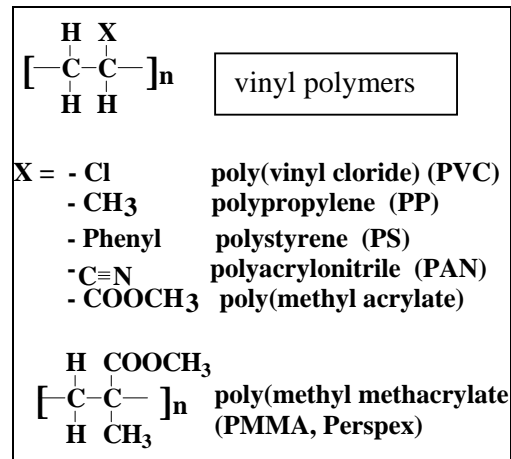
atactic polypropylene



isotactic polystyrene (i-PS)

Polymers are stereoregular when monomer repeat units are incorporated into the chain in a regular steric (i.e. orientational) sequence. Due to high symmetry of a CH₂ group the question of stereoregularity does not arise in polyethylene. However, other vinyl polymers (polypropylene, polystyrene, poly(methyl methacrylate), PVC, ...) can be either stereoregular (isotactic, syndiotactic) or irregular (atactic). Free radical (addition) polymerisation produces atactic polymers. Special catalysts (e.g. Ziegler-Natta) are used to synthesise stereoregular polymers.

Even though they may be linear homopolymers, atactic polymers cannot crystallise. Only stereoregular polymers (including polyethylene) can crystallize.



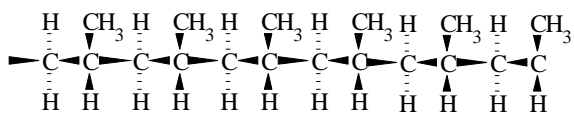
REGIOREGULARITY

= regularity in head-to-tail or head-to-head orientation of successive monomers throughout the macromolecule.

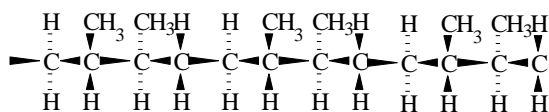
regioregular:



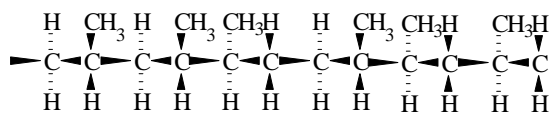
regioirregular: $\rightarrow \rightarrow \leftarrow \rightarrow \leftarrow \rightarrow \rightarrow$



head-to-tail



head-to-head

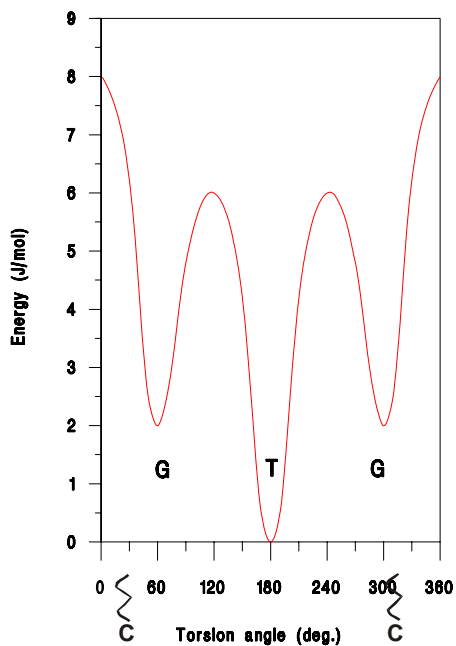


regioirregular

BOND CONFORMATION

- **Conformation** - a particular shape of a molecule having a degree of flexibility
Conversion between conformations takes place without breaking chemical bonds.

- **Bond conformations:**
Torsional Potential Energy for Alkanes

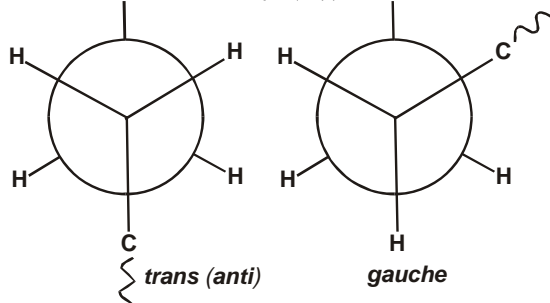


On rotation around a single bond through 360° several potential energy minima are usually encountered, separated by maxima (“energy barriers”). The states corresponding to the minima are “bond conformations”.

A molecule of ethane ($\text{H}_3\text{C}-\text{CH}_3$) passes through 3 potential minima during rotation around the C-C bond. They have equal energy. However if a hydrogen on each of the carbons is substituted for a larger group, the potential energy vs. torsion angle will look as in the diagram on the left.

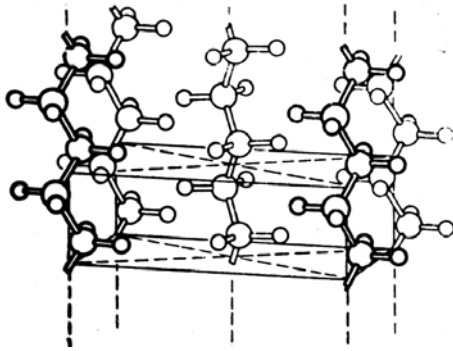
Potential energy as a function of torsion angle

Minima correspond to “trans” (deepest) and “gauche” conformations

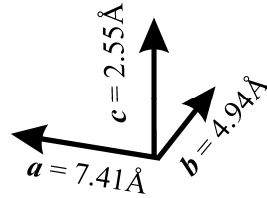


Newman projection along single C-C bond

Here see pages 3 of the “Slides” file for definitions of the random Gaussian coil, end-to-end distance and persistence length.

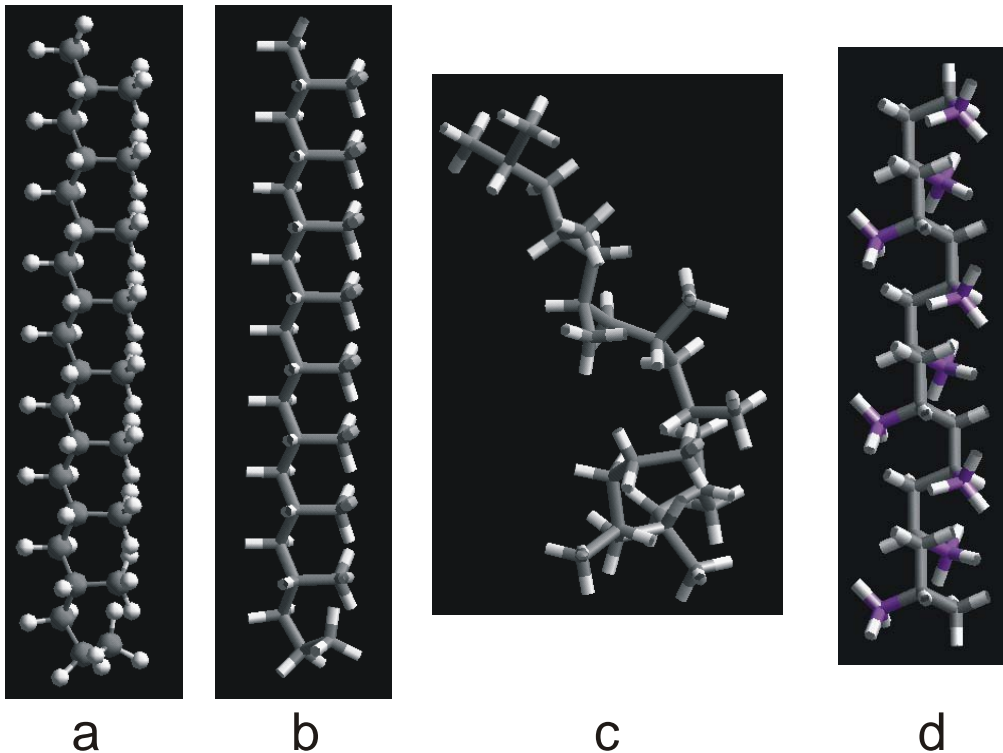


Crystal unit cell of polyethylene - two chains traverse the cell, 2 CH₂ groups per chain, hence 4 CH₂ groups per cell



HELICAL CONFORMATION OF POLYMERS

If i-PP had the same all-*trans* conformation as PE, there would be very severe steric clashes between adjacent methyl groups (Figs. a and b). If the molecule is allowed to relax without



constraint, it would avoid clashes by rotation around C-C bonds, but would not remain straight (Fig. c). There is only one way for the chain to avoid steric clashes *and* remain straight, and this is to form a helix. In i-PP this means that every alternate C-C bond becomes *gauche*, the sequence becoming $tg^+tg^+tg^+...$ for left-handed 3_1 helix (Fig. d) or $tg^-tg^-tg^-...$ for right handed helix. Bond rotation occurs by random fluctuation, but only the correct conformation will fit in the crystal.

- Synthetic polymers form **regular helices** in the process of crystallisation.
 - To fit into crystal lattice chains must be:
 - - **straight**
 - - **periodic**
 - Helix satisfies both conditions.
 - Helix: avoids close contact between side groups.

- **Notation of single-strand helices**

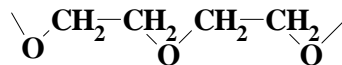
m/n or **m_n**

m: number of **chemical repeat units** (monomers) in a full repeat period

n: number of **turns** of the (continuous) helix per full repeat period

Example 1: 3/1 (or 3₁) helix of i-PP:
 3 monomers per per full repeat
 1 turn of a helix per full repeat

Example 2: 7/2 helix of poly(ethylene oxide) (PEO)



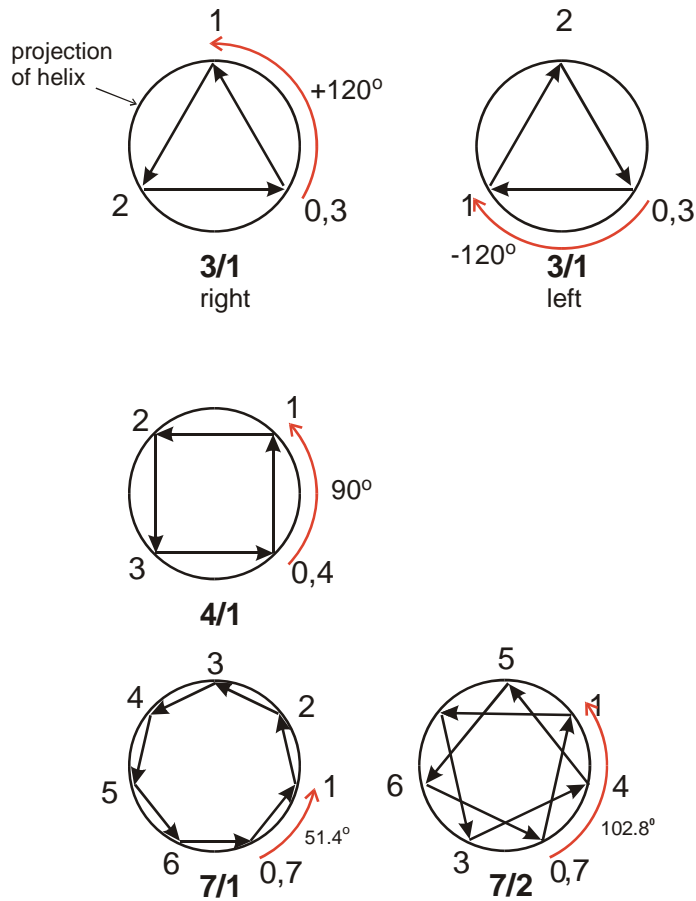
Problem 1: Describe the all-trans planar zig-zag conformation of polyethylene in terms of helical notation.

Problem 2: Show that a 7/2 helix is equivalent to a 7/5 helix, and generally that $m/n = m/(m-n)$.

Example 3: 13/6 helix of poly(tetrafluoroethylene) (PTFE, Teflon)
 - slightly distorted planar zigzag
 - F-atoms are slightly bigger than H-atoms, hence clash and cause distortion

Without the incentive of crystallization synthetic polymer chains would be neither straight nor periodic.





Handedness of helix

- Normally synthetic polymers are **not chiral** - i.e. they have no asymmetric (right- or left-handed) centres. Hence helix has no preferred handedness
- Initial choice of right/left is random; handedness propagates within a crystal according to requirements of close packing.

rotation between successive repeat units:

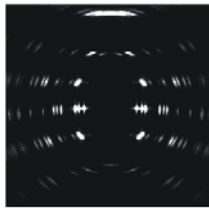
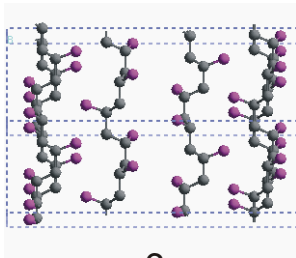
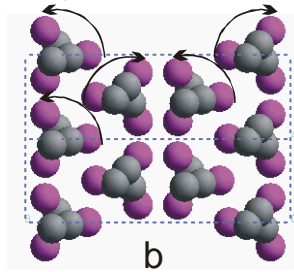
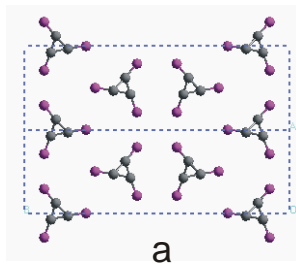
$$360 * \frac{n}{m}$$

translation along helical axis:

$$\frac{c}{m}$$

(c = repeat period; unit cell length along chain axis)

Packing of helical polymers in crystals



Crystal structure of i-PP (α -form)

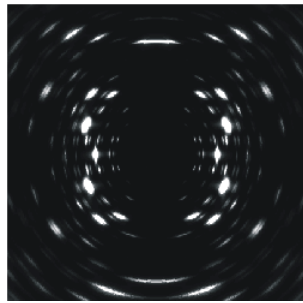
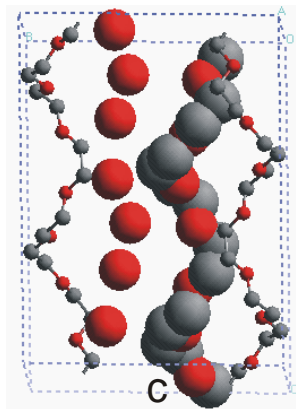
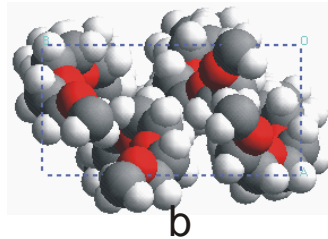
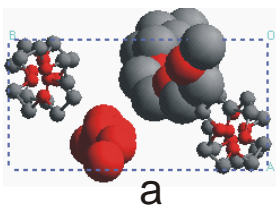
a,b: top view of 2 unit cells (hydrogens not shown)

(4 chains pass through the cell,
2 left-handed and 2 right-handed)

c: side view (2 unit cells)

d: Fibre X-ray diffraction pattern of i-PP

(note: 1st meridional reflection is on 3rd layer line. Hence 3-fold helix.)



Poly(ethylene oxide) (PEO)

a,b: 4 chains (7_2 helices) in a unit cell of PEO (different display styles, hydrogens shown in b)

2 left-handed and 2 right-handed.

c: 7 $\text{CH}_2\text{CH}_2\text{O}$ monomer units and 2 helical turns in 1 unit cell.

d: Fibre X-ray diffraction pattern of PEO

(note: 1st meridional reflection is on 7th layer line. Hence 7-fold helix.

Distance between layer lines smaller than in PP because this distance is $\propto 1/c$, where c is length of unit cell)