PHYSICS OF SOLID POLYMERS

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Course content

- Which polymers can crystallize and which can not?
- Conformation of polymer chains – why helices? why coils?
- Polymer crystal structure – the atomic scale
- Comparison between synthetic and biopolymers
- Polymer crystals and chain folding – the nanoscale
- Crystallinity in polymers – basics of wide and small-angle X-ray scattering
- Why chains fold? Polymer crystallization – a controversial topic. Case study: "self-poisoning effect in uniform model polymers – the "misled molecules"
- Spherulites and cylindrites – the microscale; basics of birefringence and polarized light microscopy
- Deformation of semicrystalline polymers – microfibrils, yielding, crazing; Synthetic fibers
- Routes to high modulus and strength in flexible polymers: ultradrawing, solid-state extrusion, gel-spinning; the story of *Spectra*
- Routes to high modulus and strength in rigid polymers: thermotropic and lyotropic liquid crystal polymers; the story of *Vectra* and *Kevlar*
- Polymer blends: miscibility, bimodal and spinodal decomposition
- Viscoelasticity and glass transition – why it's difficult to catch "silly putty"?
- Linear and nonlinear viscoelasticity, creep, stress-relaxation; Dynamic Mechanical Spectroscopy, dielectric spectroscopy
- Rubber elasticity; rubber band *vs* metal spring

STRUCTURAL HYERARCHY IN SEMICRYSTALLINE POLYMERS

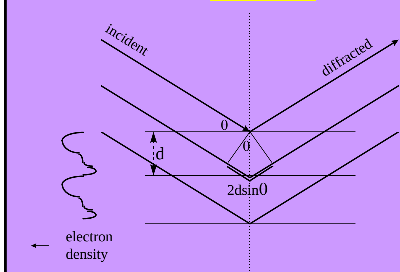
atomic scale - crystal unit cell
- several Angstroms (<1 nm to a few nm)
- detailed crystal structure, conformation of individual bonds
- wide-angle XRD

scale of crystal thickness
-100-500 Å (10 - 50 nm)
- electron microscopy, small-angle XRD

scale of crystal aggregates (spherulites etc.)
-μm scale
- optical microscopy

Bragg equation relating diffraction angle θ to interplanar spacing *d*

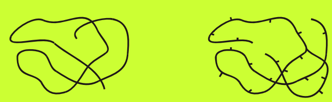
$n\lambda = 2d \sin\theta$



Small *d* - large θ
(wide angle XRD)
when layers are layers of atoms

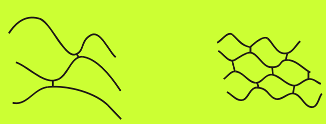
Large *d* - small θ
(small-angle XRD)
when layers are e.g. thin crystals

WHICH POLYMERS CAN CRYSTALLIZE?



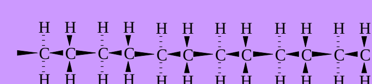
Linear
- thermoplastic (e.g. HDPE)
- potentially crystallizable
(can contain some long branches)

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



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

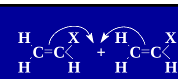
Cross-linked (densely)
- cured thermoset resin
- amorphous (glassy)



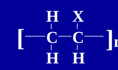
linear polyethylene

Crystallizable polymers must also be:
- homopolymers
- stereoregular
- regioregular

		Can crystallize?
Homopolymer	AAAAAAAAAAAAA	yes
random copolymer	AABABBABBBABA	no
block copolymer	AAAAAAABBBBBB	partially
graft copolymer	AAAAAAAAAAAAA | BBBBBBBBB	partially

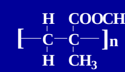


vinyl monomers



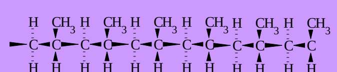
vinyl polyomers:

X = - Cl poly(vinyl cloride) (PV(
- CH3 polypropylene (PP)
- Phenyl polystyrene (PS)
-C≡N polyacrylonitrile (PAN
- COOCH3 poly(methyl acrylate)

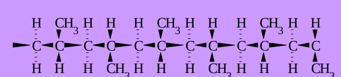


poly(methyl methacryl
(PMMA, Perspex)

SEREOREGULARITY OF POLYMERS

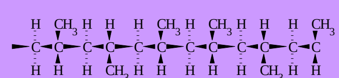


isotactic polypropylene (i-PP)



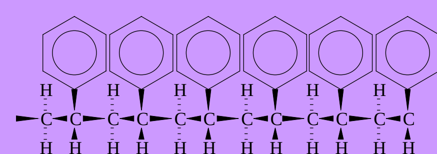
syndiotactic polypropylene (s-PP)

stereoregular



atactic polypropylene

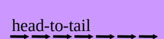
stereo-irregular

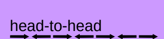


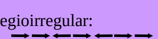
isotactic polystyrene (i-PS)

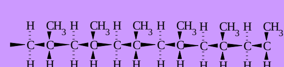
REGIOREGULARITY
= regularity in head-to-tail or head-to-tail orientation of monomers throughout the macromolecule.

regioregular:

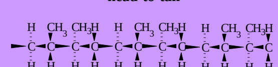
head-to-tail


head-to-head


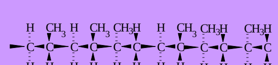
regioirregular:




head-to-tail



head-to-head



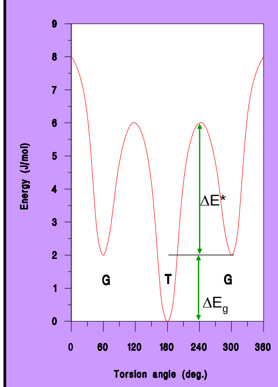
regioirregular

Trans (*anti*) and *gauche* conformations
- hindered rotation about single C-C bond
→ polymers flexible

trans

gauche

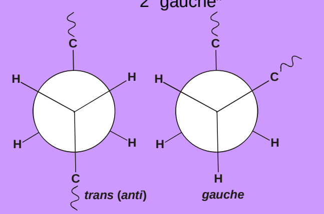
Conformation = shape of a molecule having a degree of flexibility



also **conformation of a bond**

← Potential energy as a function of torsion angle around C-C bond

Minima: 1 "trans" (deepest)
2 "gauche"



Newman projection – view along C-C bond

Rotational Isomeric State Model

- fraction of *gauche* increases with T

$$f_g = \frac{2\exp(-\Delta E_g / kT)}{1 + 2\exp(-\Delta E_g / kT)}$$

- - factor 2 because 2 gauche states (g^+, g^-), only 1 trans
- $\Delta E_g \approx$ 1-2 kJ/mol
  - → at r.t. $f_g \approx 0.5$

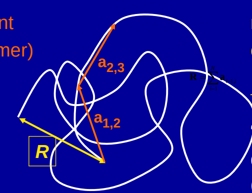
Rotational Isomeric State Model

- RIS model – an approximation
- neglects all dihedral (torsion) angles other than 180º and ±60º (Flory)

Random Coil

- Polymer chain in solution, melt, or amorphous glass

segment (monomer)



root-mean-square end-end distance:

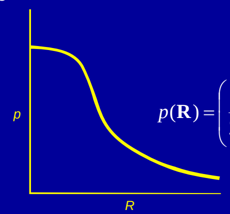
$$R_0 \equiv \langle R^2 \rangle^{1/2} = aN^{1/2}$$

"random walk":
distance ∝ no. of steps
(strictly true only for "ideal chains")

- **End-to-end distance:** $\mathbf{R} = \sum_{i=1}^{N} \mathbf{a}_{i-1,i}$

Gaussian Coil

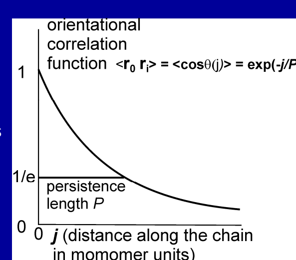
- "ideal chain" = freely-jointed non-self-avoiding chain
  - freely jointed: any angle between a_i and a_{i+1} equally probable
  - non-self-avoiding: chain can overlap with itself
- Distribution of end-to-end distances
  - e.g. for one chain over time – Gaussian distribution



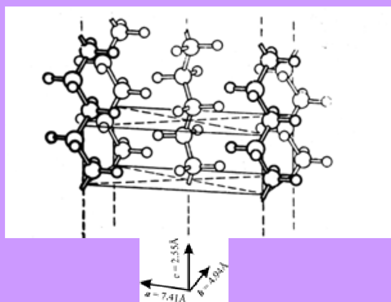
$$p(\mathbf{R}) = \left(\frac{3}{2\pi \langle R^2 \rangle} \right)^{3/2} \exp - \frac{3R^2}{2\langle R^2 \rangle}$$

Persistence Length

- Theory of worm-like chains (Kratky and Porod)
- Persistence length is the distance along the chain at which orientational correlation with the starting segment drops to 1/e.
- Persistence length is a measure of the **rigidity** of a polymer chain

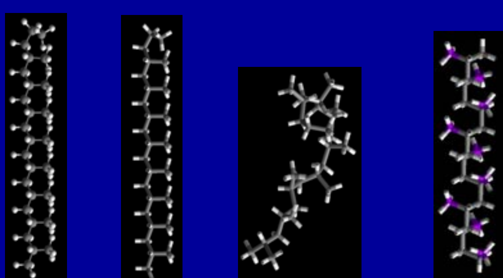


Crystal Structure of Polyethylene



Crystal Structure of Polyethylene

***i*-PP – What conformation in crystal?**



all-*trans* conformation
(severe steric clashes)

relaxed
(energy minimized)
(not crystallizable)

helix
(crystallizable)

***i*-PP – What conformation in crystal?**

helix
(crystallizable)

The three-fold helix of isotactic polypropylene in front of the Giulio Natta Research Center in Ferrara, Italy

Photo of the right-handed helix courtesy of Pr. Galli t(he left-handed one is courtesy of Powerpoint)

Synthetic polymers form regular helices.

- To fit into crystal lattice chains must be:
  - **straight**
  - **periodic**
- 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 crystallographic period (unit cell length)

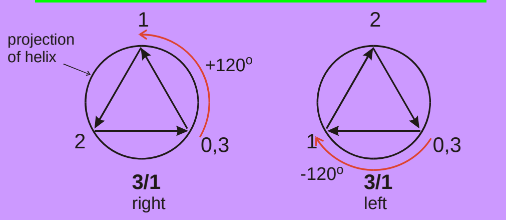
n: number of **turns** of the (continuous) helix per full crystallographic period

Example 1: 3/1 (or 3_1) helix of i-PP:

3 monomers per full repeat

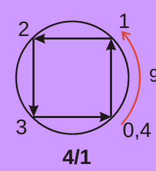
1 turn of a helix per full repeat

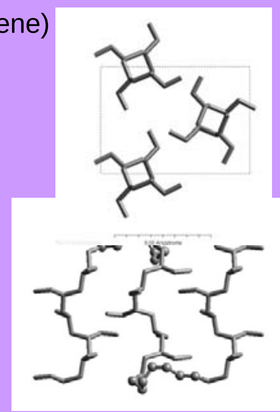
Unit operation of a 3_1 axis: translation by 1/3 repeat period
+ rotation by 1/3 of a circle (120 deg)



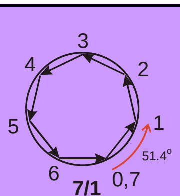
4/1 helix: i-poly(1-butene)

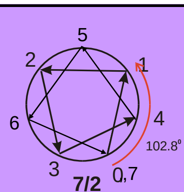
(Form III)





7-fold helices





Poly(ethylene oxide), PEO
[-CH_2-CH_2-O-]n

Per crystallographic repeat:
- 7 monomer repeats,
- 2 helical turns

Rotation between successive repeat units:

360*(n/m)

Translation along helical axis:

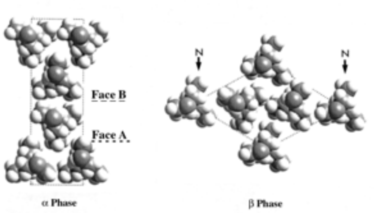
c/m

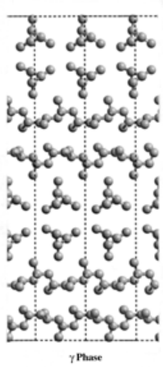
(c = crystal unit cell length)

Problem:

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

Packing of helical chains in crystals
i-PP

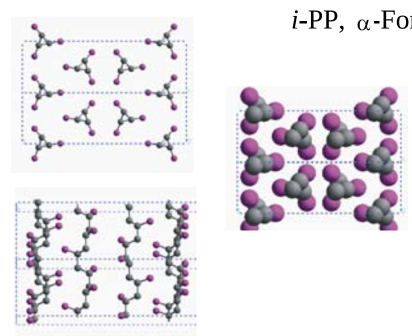




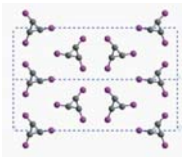
History of the three crystal phases of isotactic polypropylene.

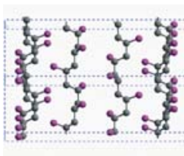
***α* phase**. *Discovered and Solved by Natta and Corradini, 1954*
***β* phase**. *Discovered 1959 (Padden & Keith), Solved 1994 (by Meille, Brückner, Ferro, Lovinger, Padden and by Lotz, Kopp, Dorset). It is a frustrated structure.*
***γ* phase**. *Discovered 1959 (Addink& Beintema), Solved 1989 (Brückner & Meille). Non-parallel chains.*

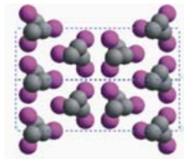
i-PP, α-Form



i-PP, α-Form

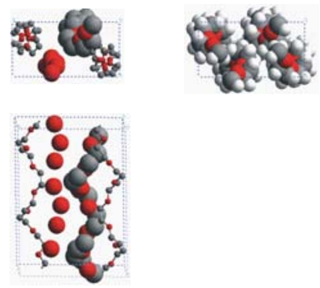




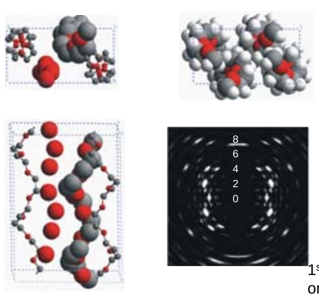


X-ray fibre diffraction pattern
(fibre axis vertical)
- *1st meridional reflection on 3rd layer line*

Poly(ethylene oxide)
Crystal packing of 7_2 helices



Poly(ethylene oxide)
Crystal packing of 7_2 helices



1st meridional reflection on 7th layer line