# CBE 30361
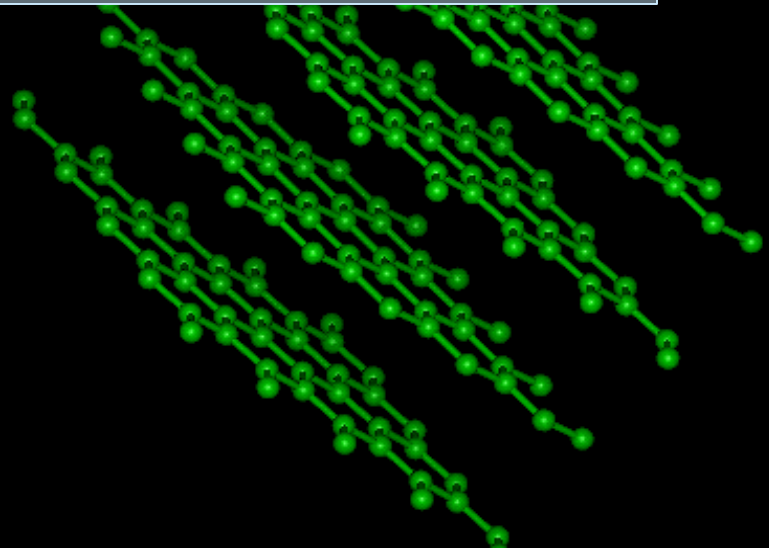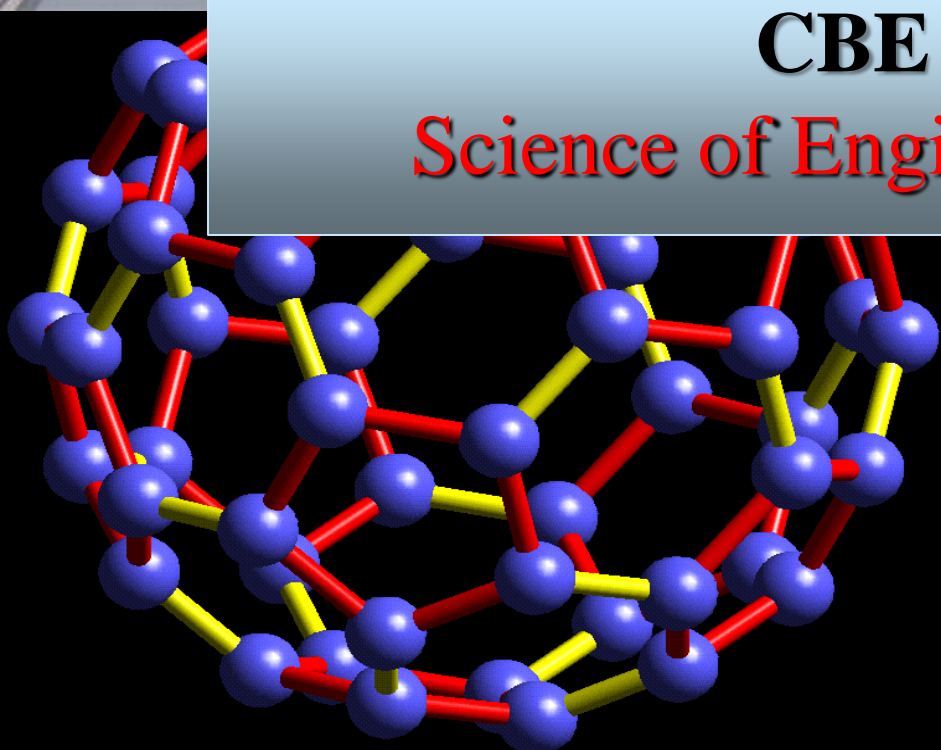## Science of Engineering Materials
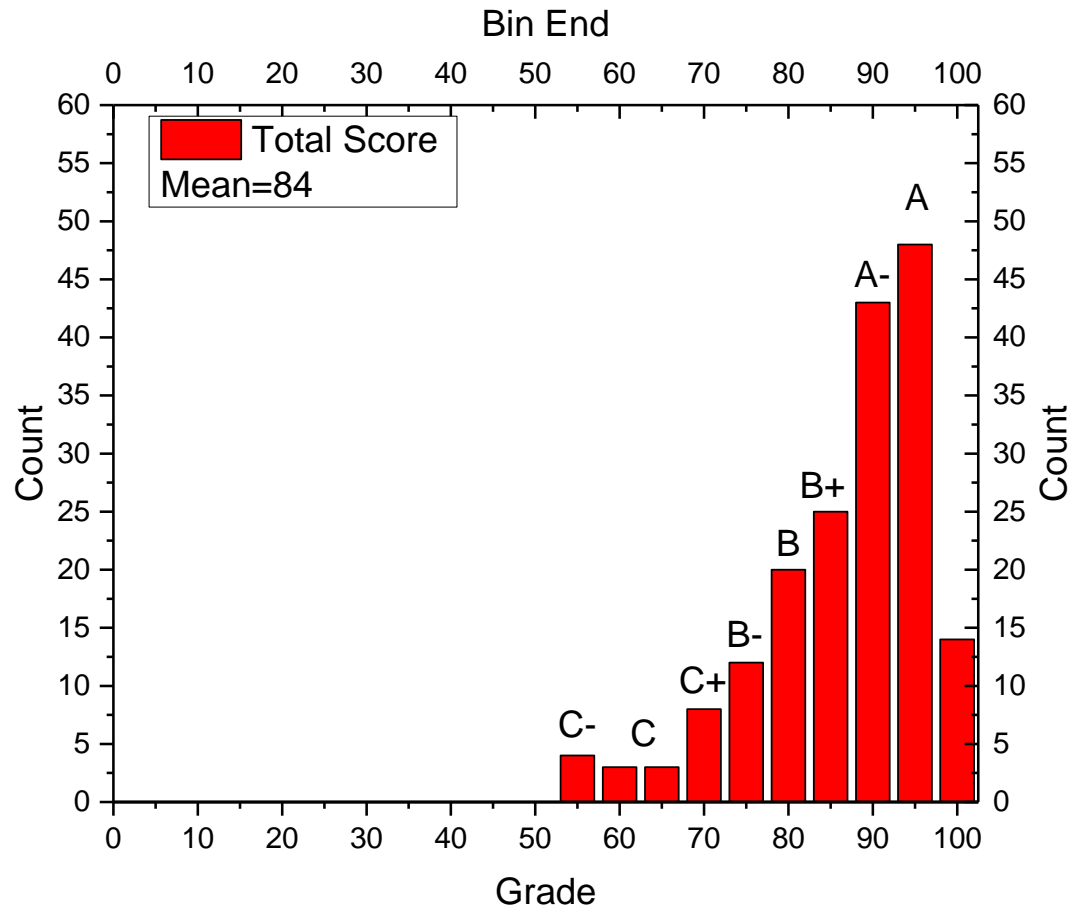
# Assessment

The course will be assessed in the following manner:

- ❑ 1$^{st}$ Midterm Exam      20%
- ❑ 2$^{nd}$ Midterm Exam      20%
- ❑ Final Exam      20%
- ❑ Home works      10%
- ❑ Quizzes      21% (*)
- ❑ Term paper      9%

(*) Seven quizzes total value of 21%

# Overall Standing

# Final Exam Scheme

Friday, December 19, 2014.
8AM to 10 AM
DBRT 101

Two parts:

(a) Set of qualitative questions – similar to those during quizzes
(b) 5 problems similar to those you had during your HWs
- 1 problem on Ceramics (Chapters 12&13)
- 1 problem on Polymers  (Chapters 14&15)
- 3 cumulative problems from the rest of the course

3 cheat sheets are allowed!!!

# Scale of Structure Organization

# TEM
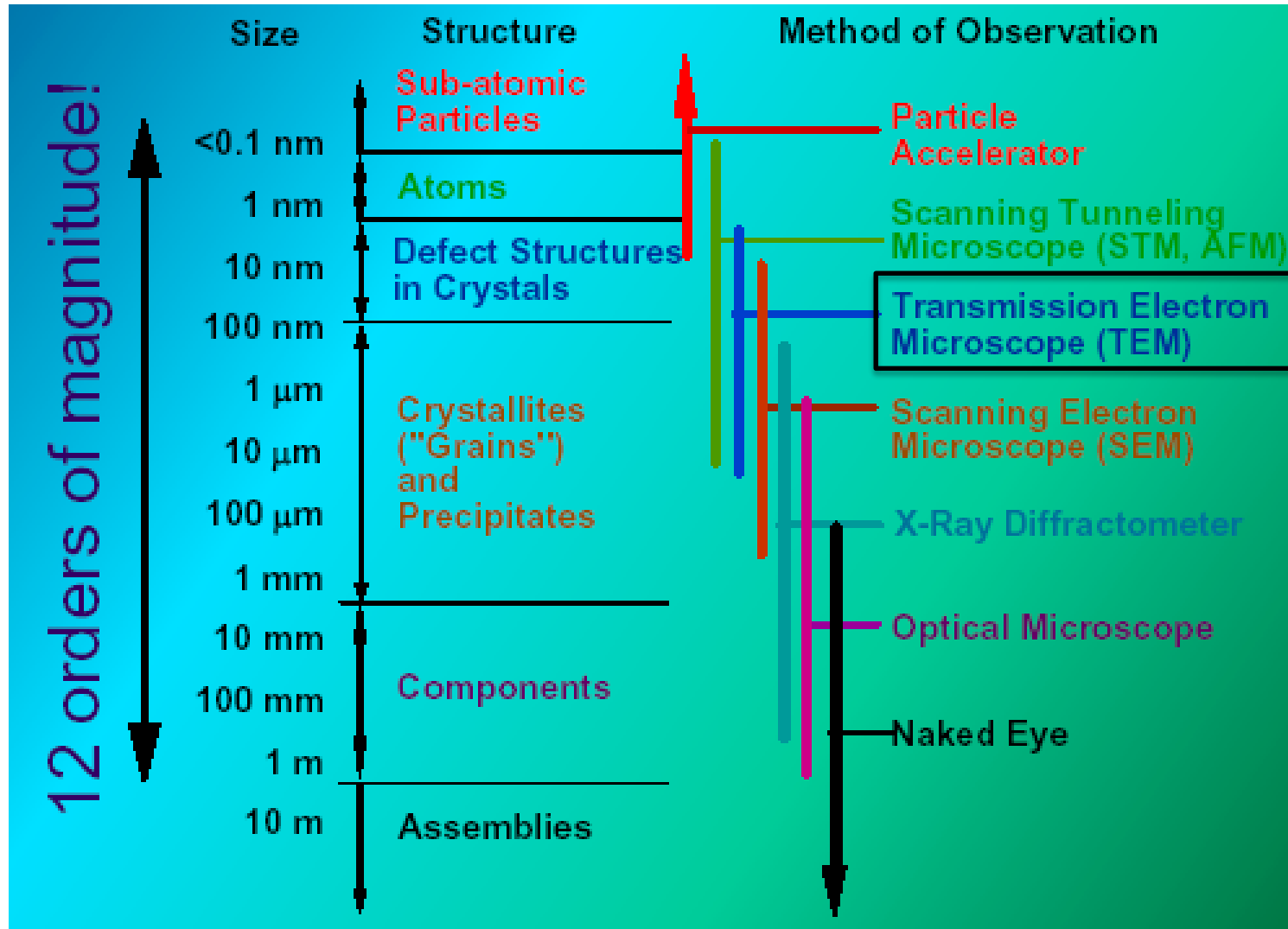
# TEM Imagining

## STANDARD TEM IMAGE MODES

***BRIGHT FIELD (BF) IMAGE:***
Only the transmitted beam is allowed to pass through the objective
aperture.  Image is ∴ <u>bright</u> where <u>diffraction</u> in specimen is <u>weak</u>.

***DARK FIELD (DF) IMAGE:***
Only one diffracted beam passes through objective aperture.
Image is <u>dark</u> where diffraction is weak, bright where diffraction is strong.

***LATTICE IMAGE (High Resolution TEM: HRTEM image):***
Interference of transmitted beam (TB) and diffracted beams (DBs) produces
an image of the crystal lattice.

***DIFFRACTION PATTERN:***
Intermediate lens adjusted to image the diffraction pattern formed in back
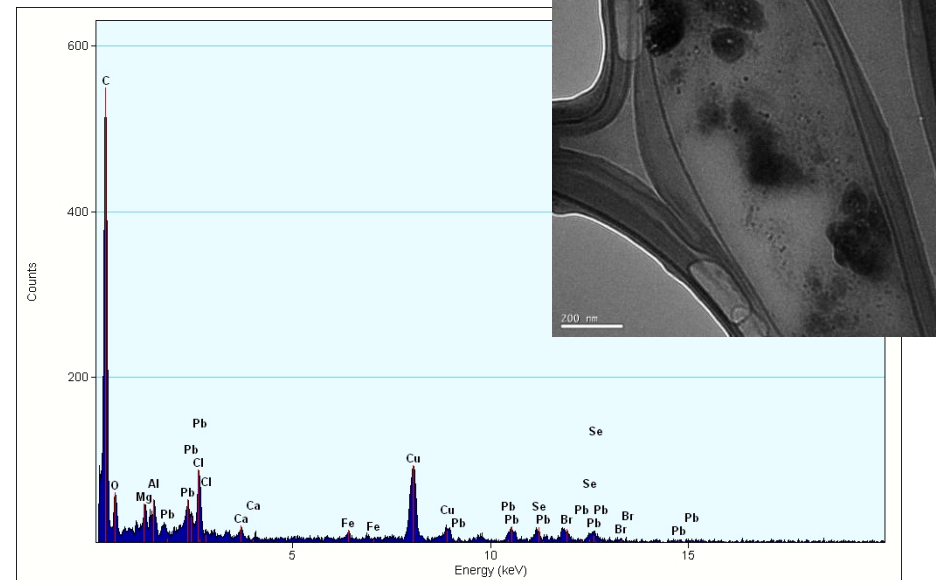focal plane (BFP) of objective lens.

# *Chemical analysis: EDS*

**Energy Dispersive X-ray Spectroscopy (EDS)**
– EDS makes use of the X-ray spectrum emitted by a solid sample bombarded
   with a focused beam of electrons to obtain a localized chemical analysis..
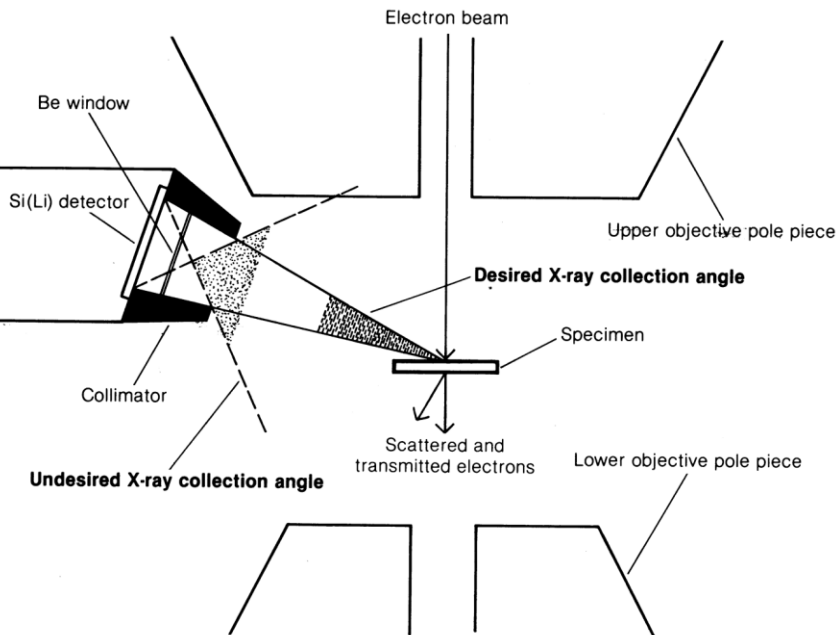
– Spatial resolution - a matter of probe size (can be as low as 0.2Å)



Representative example of ED spectrum obtained
on a ~20 micron grain  of titano maghemite from
submarine basalt. EDAX Phoenix EDS system;15 kV.

# Chemical analysis: EELS

*Electron energy loss spectroscopy (EELS)*

Transmitted electrons lose energy due to plasmon excitation or excitation of atoms by ejecting inner-shell electrons. A bending magnet disperses electrons of different energies to different positions; a slit selects electrons of desired energy loss.
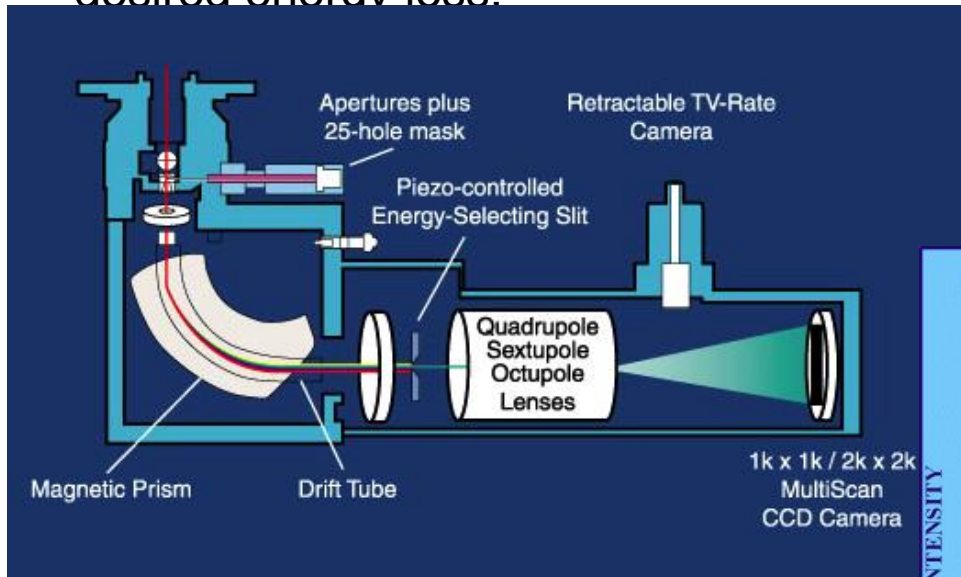


Allows for the determination of *valence,* bond length, nearest neighbor co-ordination and quantification of atomic species in minerals
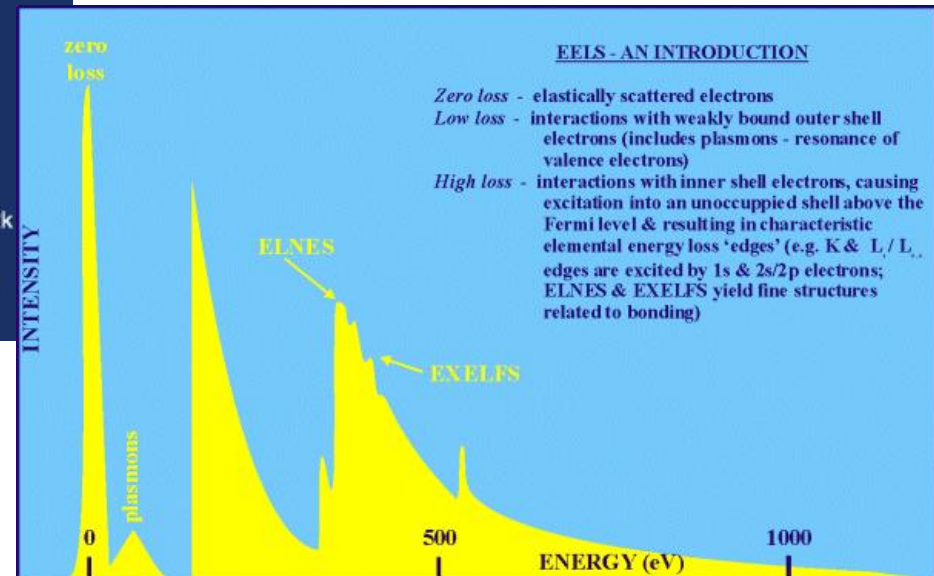
# TYPICAL STRUCTURAL FEATURES STUDIED by TEM

**CRYSTAL STRUCTURE**
Single crystal, polycrystalline or amorphous?
Determine exact orientation of crystal(s).
Identify crystal structure (diffraction).
Evaluate crystal quality (lattice imaging).

**CRYSTAL DEFECTS**
Presence or absence of dislocations, stacking faults, grain boundaries, twins
Dislocation Burgers vectors; nature of stacking faults
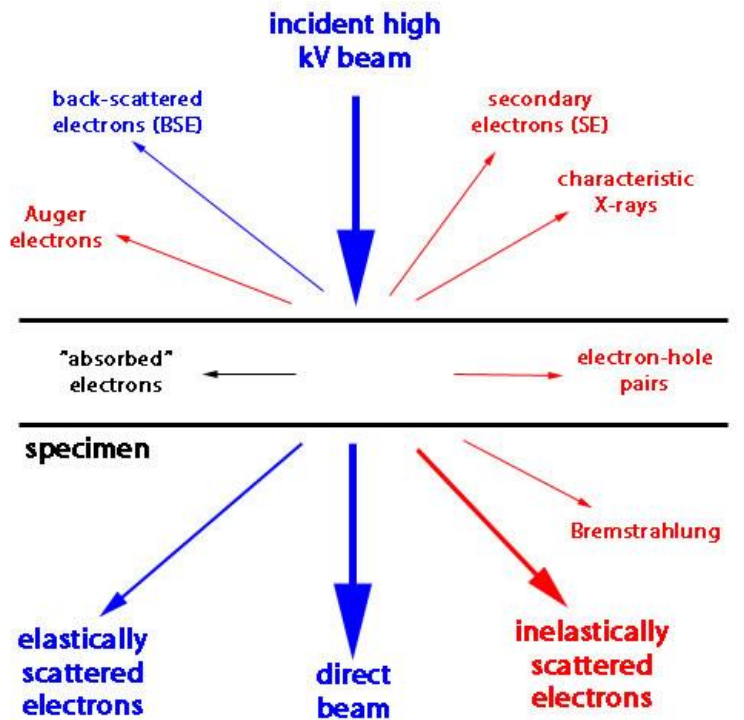
**SECOND-PHASE PARTICLES**
Size, shape, and distribution; crystallographic orientation relative to surrounding "matrix", chemical analysis via analytical attachments (EDXS, EELS)

**NANOPARTICLES, NANOWIRES, NANORODS etc.**
Size distribution, crystal structure and orientation, crystal perfection

# SEM

# *Electron Microscopy: what can be done?*



incident high kV beam

back-scattered electrons (BSE)

secondary electrons (SE)

characteristic X-rays

Auger electrons

"absorbed" electrons

electron-hole pairs

specimen

Bremsstrahlung

elastically scattered electrons

direct beam

inelastically scattered electrons

modified from Williams & Carter (1996) Fig. 1.3

1.  SEM gives *images of the microstructure* of a specimen with the resolution ~ 1nm; the range of the acceleration voltage 50eV - 30 kV.

2.  Two characteristic electrons imaging mode*s:*
    *(a) secondary electron image: contrast  is primarily due to topographical effects;*
    *(b) backscattering electron image:  contrast  is primarily due to average Z-effct effect;*

3.  *Chemical analysis*  is also possible with available analytical attachments (EDS) for x-ray. The space resolution is a function of the acceleration voltage and is in the range of 1 to 5 microns

# *Secondary Electron Imaging*

• The high energy incident electrons can also interact with the loosely-bound conduction **band electrons** in the sample. The amount of energy given to these **secondary** electrons as a result of the interactions is small, and so they have a very limited range in the sample (a few nm). Because of this, only those secondary electrons that are produced within a very short distance of the surface are able to escape from the sample.

• This means that this detection mode boasts high resolution **topographical images**, making this the most widely used of the
SEM modes.

# Back scattered electrons

• When an electron from the beam encounters a nucleus in the sample,
the resultant Coulombic attraction results in the deflection of the electron's path, known as **Rutherford elastic scattering**. A few of these electrons will be completely **backscattered**, re-emerging from the incident surface of the sample.

•Since the scattering angle is strongly dependent on the atomic number of the nucleus involved, the **primary electrons** arriving at a given detector position can be used to yield images containing both topological and compositional information.

# *Energy-Dispersive analysis of X-rays*

• Another possible way in which a beam electron can interact with an atom is by the ***ionization*** of an ***inner shell electron***. The resultant vacancy is filled by an outer electron, which can release it's energy by emitting an X-ray.

•This produces characteristic lines in the X-ray spectrum corresponding to the electronic transitions involved. Since these lines are specific to a given element, the composition of the material can be deduced. This can be used to provide ***quantitative information*** about the ***elements*** present at a given point on the sample, or alternatively it is possible to map the abundance of a particular element as a function of position.
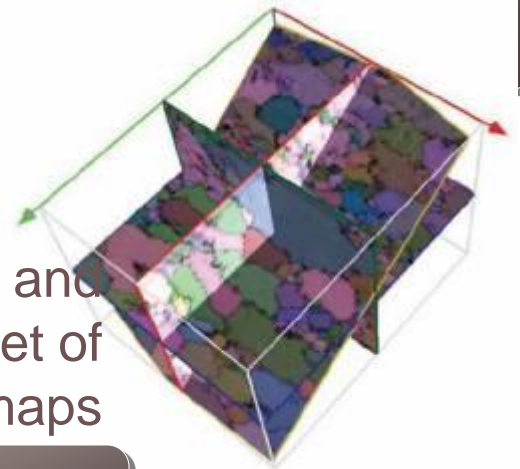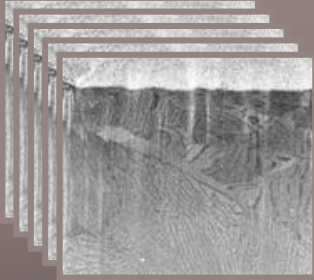
# Helios Nano-Lab 600 Dual-Beam
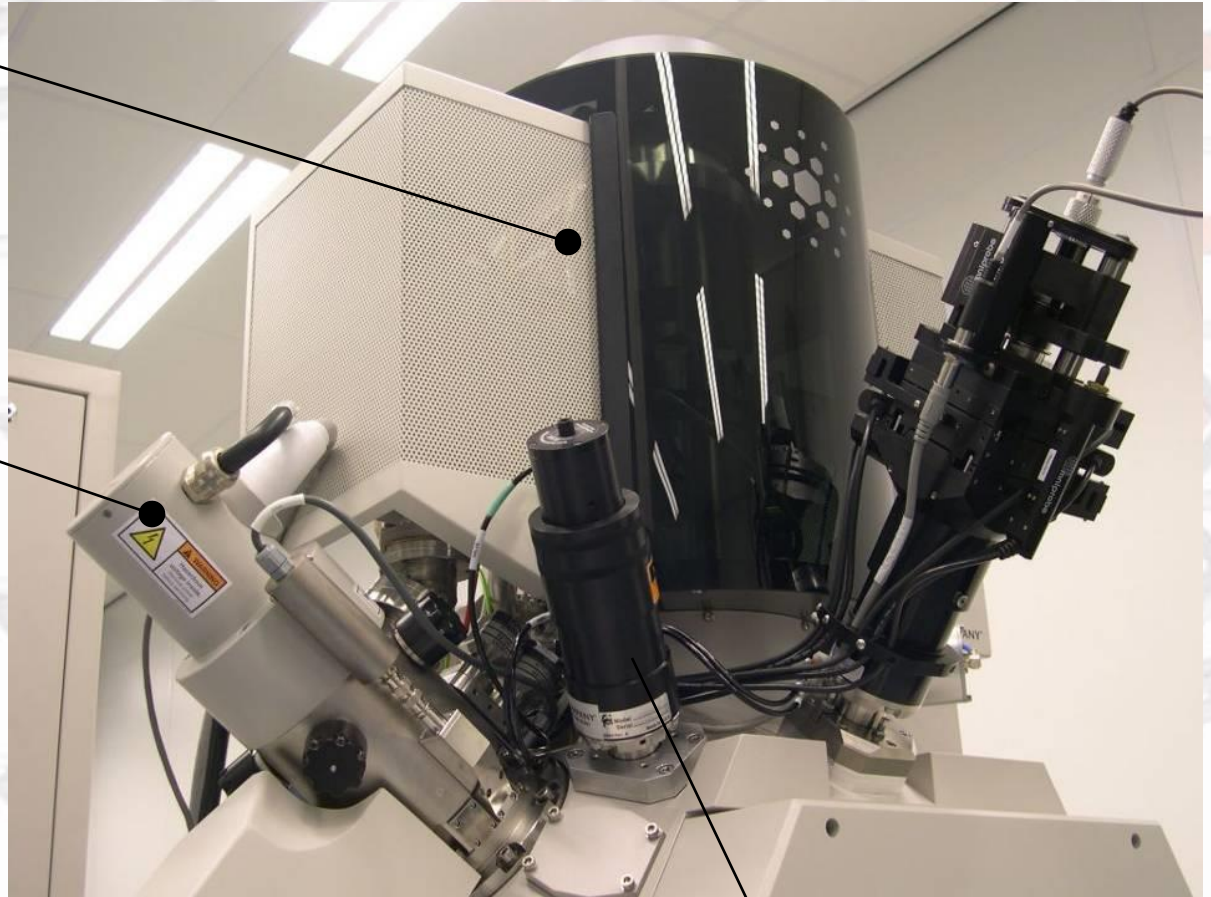
# … Extends to Nano-Analysis in 3D !

Collect your data unattended

- 3D packages handle samples movements and protection to optimize the milling conditions as well as the data acquisition
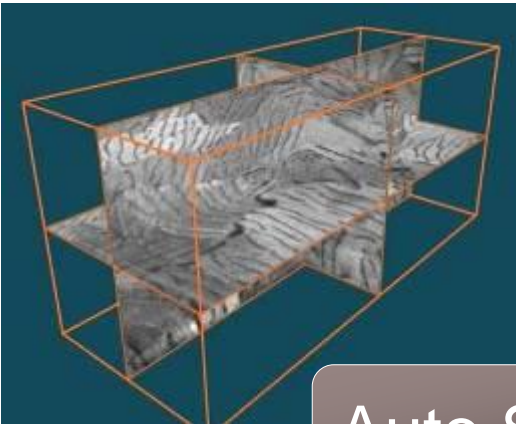- Very large datasets supported

- Reconstruct and explore in 3D a set of EBSD maps
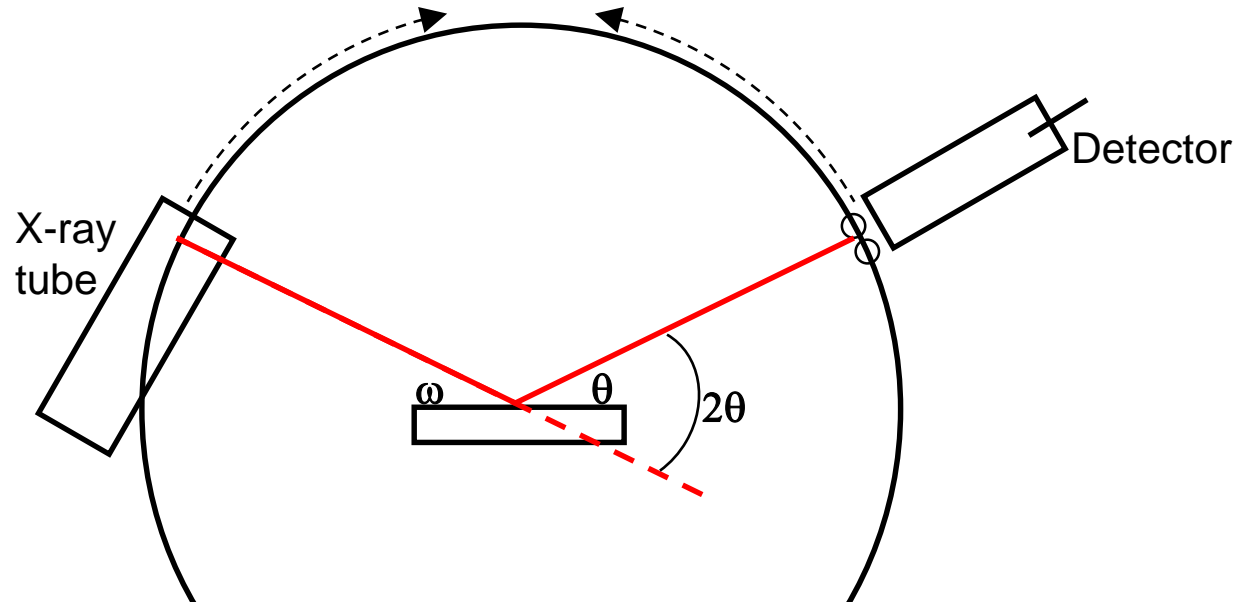
EBS3™

Auto Slice *and View*

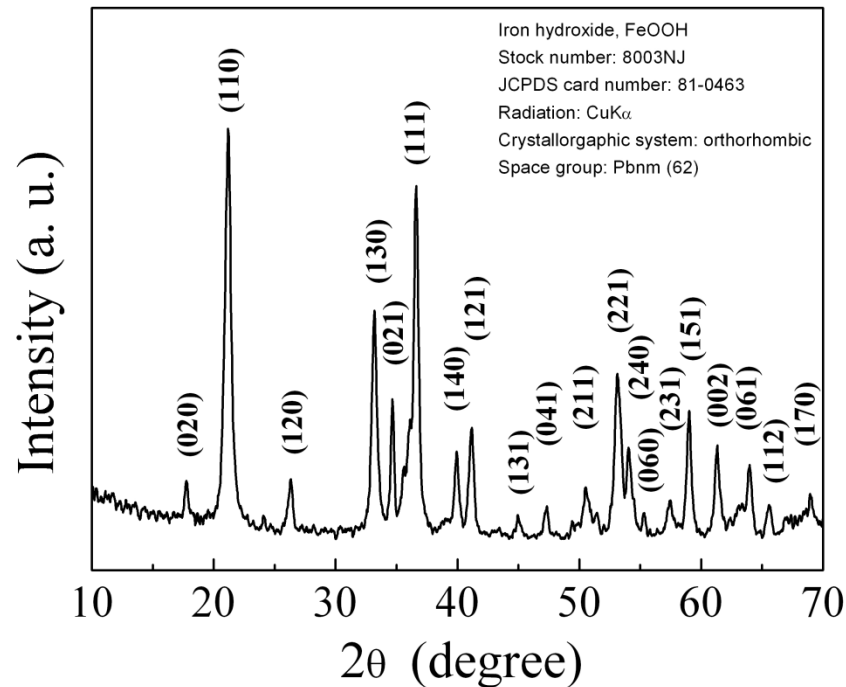explore in 3D a tomographic set of cross-sectional images

**http://www.youtube.com/watch?v=isH0-xCpla8**

# XRD Analysis

# The powder diffractometers typically use the Bragg-Brentano geometry



- The incident angle, $\omega$, is defined between the X-ray source and the sample.
- The diffracted angle, $2\theta$, is defined between the incident beam and the detector angle.
- The incident angle $\omega$ is always ½ of the detector angle $2\theta$ .
- In a $\theta:2\theta$ instrument (e.g. Rigaku RU300), the tube is fixed, the sample rotates at $\theta$ °/min and the detector rotates at $2\theta$ °/min.
- In a $\theta:\theta$ instrument (e.g. PANalytical X'Pert Pro), the sample is fixed and the tube rotates at a rate $-\theta$ °/min and the detector rotates at a rate of $\theta$ °/min.

# Example: Diffraction Patterns

- Each peak represents the solution to Bragg's law for known radiation wavelength ($\lambda = 0.154$ nm)

- The unique relationship between such patterns and crystal structures provide a powerful tool for identification of the phase composition of powders and polycrystalline materials.



Iron hydroxide, FeOOH
Stock number: 8003NJ
JCPDS card number: 81-0463
Radiation: CuK$\alpha$
Crystallorgaphic system: orthorhombic
Space group: Pbnm (62)

# Relationship between diffraction peaks, miller indices and lattice spacings

Simple cubic material $a = 5.0$ Å

| hkl | d(Å) | 2Θ |
|-----|------|-------|
| 100 | 5.00 | 17.72 |
| 110 | 3.54 | 25.15 |
| 111 | 2.89 | 30.94 |

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}$$

Bragg Equation: $n\lambda = 2d\sin\theta$

How many lattice planes are possible?
How many d-spacings?     The number is large but finite.
$n\lambda = 2d\sin\theta$ so if theta = 180, then d = λ/2. For Cu radiation that means that we can only see d-spacings down to 0.77 Å for Mo radiation, down to about 0.35 Å

# d-spacing in different crystal systems

* **Cubic**

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}$$

* **Tetragonal**

$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$$

* **Orthorhombic**

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

* **Hexagonal**

* **Monoclinic**

$$\frac{1}{d^2} = \frac{4}{3}\left(\frac{h^2 + hk + k^2}{a^2}\right) + \frac{l^2}{c^2}$$

* **Triclinic** -

$$\frac{1}{d^2} = \frac{1}{\sin^2 \beta}\left(\frac{h^2}{a^2} + \frac{k^2 \sin^2 \beta}{b^2} + \frac{l^2}{c^2} - \frac{2hl\cos\beta}{ac}\right)$$

# JCPDS Card

**Quality of data**



1.file number 2.three strongest lines 3.lowest-angle line 4.chemical formula and name 5.data on diffraction method used 6.crystallographic data 7.optical and other data 8.data on specimen 9.data on diffraction pattern.

*Joint Committee on Powder Diffraction Standards, JCPDS (1969)*
*Replaced by International Centre for Diffraction Data, ICDF (1978)*

# What Information Do We Get or Can We Get From Powder X-ray Diffraction

*  Lattice parameters
*  Phase identity
*  Phase purity
*  Crystallinity
*  Crystal structure
*  Percent phase composition

# What Information Do We NOT Get From Powder X-ray Diffraction

* Elemental analysis -
  * How much lithium is in this sample?
  * Is there iron in this sample
  * What elements are in this sample
* Tell me what this sample is ????
  * Unless you know something about this sample, powder XRD won't have answers !!!

# Types of Questions:

1.  You need to define the morphology of the nanopowders (size range 1-100 nm). What technique and in what mode you will use?

2.  You applied a thin nano-layered (~1nm) ceramic coating on the metal substrate. You need to verify the average thickness of the coating. What method you will use to get the desired information?

3.  You need to define the phase composition of your powder. What method you will use if the powder is: (a) crystalline; (b) amorphous?

4.  You need to define the distribution of different phases on the micron-scale level. What technique(s) you will use?

5. You need to evaluate the amount of impurities in your nano-sized ceramics. What method(s) you will apply.

# Polymers

# POLYMERS
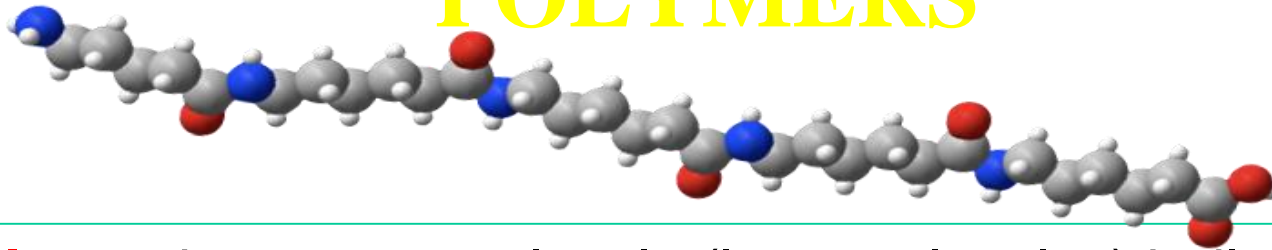


- **A polymer** is a macromolecule (long molecules) built of small **covalently bonded** units called **monomers** ("mer" from the Greek word *meros* meaning part).

- These small units are repeated throughout the macromolecule chain.

- The macromolecules are bonded together by <u>weak Van der Waals</u> and hydrogen (secondary) bonds, or additional covalent cross-links.
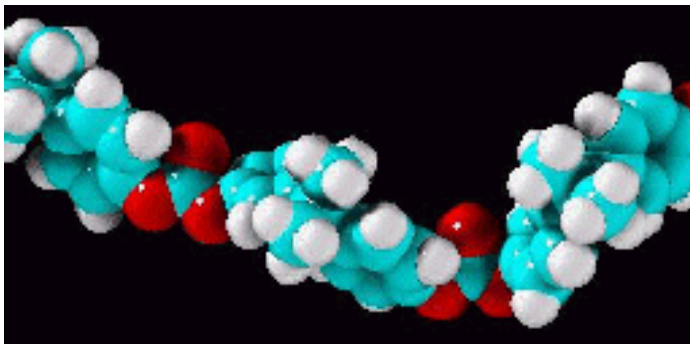
# The Polymers: Classification

The *main classes* of polymers are:

- **Natural polymers**

  <u>Example</u>: *cellulose and protein*, which provide the mechanical basis for most plant and animal life

- **Thermoplastics**, which soften on heating

  <u>Example</u>:  *polyethylene*

- **Thermosets** or **Resins**, which harden when two components  are heated together

  <u>Example</u>: an *epoxy*

- **Elastomers or Rubbers**

# Generic Thermoplastics

| Thermoplastic | Composition | Uses |
|---|---|---|
| Polyethylene, PE | $\left(\begin{array}{c} H \\ | \\ -C- \\ | \\ H \end{array}\right)_n$ Partly crystalline. | Tubing, film, bottles, cups, electrical insulation, packaging. |
| Polypropylene, PP | $\left(\begin{array}{cc} H & H \\ | & | \\ -C-C- \\ | & | \\ H & CH_3 \end{array}\right)_n$ Partly crystalline. | Same uses as PE, but lighter, stiffer, more resistant to sunlight. |
| Polytetrafluoroethylene, PTFE | $\left(\begin{array}{c} F \\ | \\ -C- \\ | \\ F \end{array}\right)_n$ Partly crystalline. | Teflon. Good, high-temperature polymer with very low friction and adhesion characteristics. Non-stick saucepans, bearings, seals. |
| Polystyrene, PS | $\left(\begin{array}{cc} H & H \\ | & | \\ -C-C- \\ | & | \\ H & C_6H_5 \end{array}\right)_n$ Amorphous. | Cheap moulded objects. Toughened with butadiene to make high-impact polystyrene (HIPS). Foamed with $CO_2$ to make common packaging. |
| Polyvinylchloride, PVC | $\left(\begin{array}{cc} H & H \\ | & | \\ -C-C- \\ | & | \\ H & Cl \end{array}\right)_n$ Amorphous. | Architectural uses (window frames, etc.). Plasticised to make artificial leather, hoses, clothing. |
| Polymethylmethacrylate, PMMA | $\left(\begin{array}{cc} H & CH_3 \\ | & | \\ -C-C- \\ | & | \\ H & COOCH_3 \end{array}\right)_n$ Amorphous. | Perspex, lucite. Transparent sheet and mouldings. Aircraft windows, laminated windscreens. |
| Nylon 66 | $(- C_6H_{11}NO -)_n$ Partly crystalline when drawn. | Textiles, rope, mouldings. |

•**Thermoplastics** are made by adding together, i.e. "**polymerizing**", sub-units (monomers) to form long chain. Many of them are made of the unit:
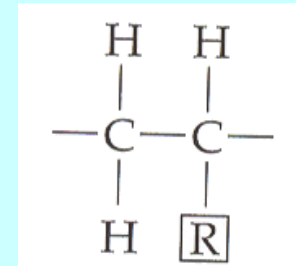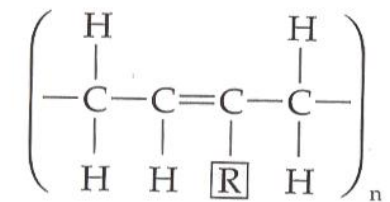


repeated many times.

•The radical R may be hydrogen (PE) or $-CH_3$ (PP) or $-Cl$ (PVC) or more complicated (as for nylon)

# Generic Elastomers (Rubbers)

| Elastomer | Composition | Uses |
|---|---|---|
| Polyisoprene |  Amorphous except at high strains. | Natural rubber. |
| Polybutadiene |  Amorphous except at high strains. | Synthetic rubber, car tyres. |
| Polychloroprene |  Amorphous except at high strains. | Neoprene. An oil-resistant rubber used for seals. |

• Rubbers are almost-**linear polymers** with occasional cross-linked in which at room temperature the secondary bonds have already melted.
• However the cross-linked provide "memory" of the material so that it returns to its original shape on unloading.
• The common rubbers are all based on a **single structure**:

with the position **R** occupied by H, $CH_3$ or Cl.

# Generic Resins

| Thermoset | Composition | Uses |
|---|---|---|
| Epoxy | <br>Amorphous. | Fibreglass, adhesives. Expensive. |
| Polyester | <br>Amorphous. | Fibreglass, laminates. Cheaper than epoxy. |
| Phenol-formaldehyde | <br>Amorphous. | Bakelite, Tufnol, Formica. Rather brittle. |

- Epoxy: an adhesive and a matrix for different composites is a thermoset.

- Thermosets are made by mixing of two components (a resin and a harder) which react and harden, either at room temperature or on heating

- The resulting polymers is usually heavily cross-linked: **network polymer**!!

- The cross-links form during the polymerization of the liquid resin and hardener so the structure is almost **amorphous.**

# Polymer Characteristics
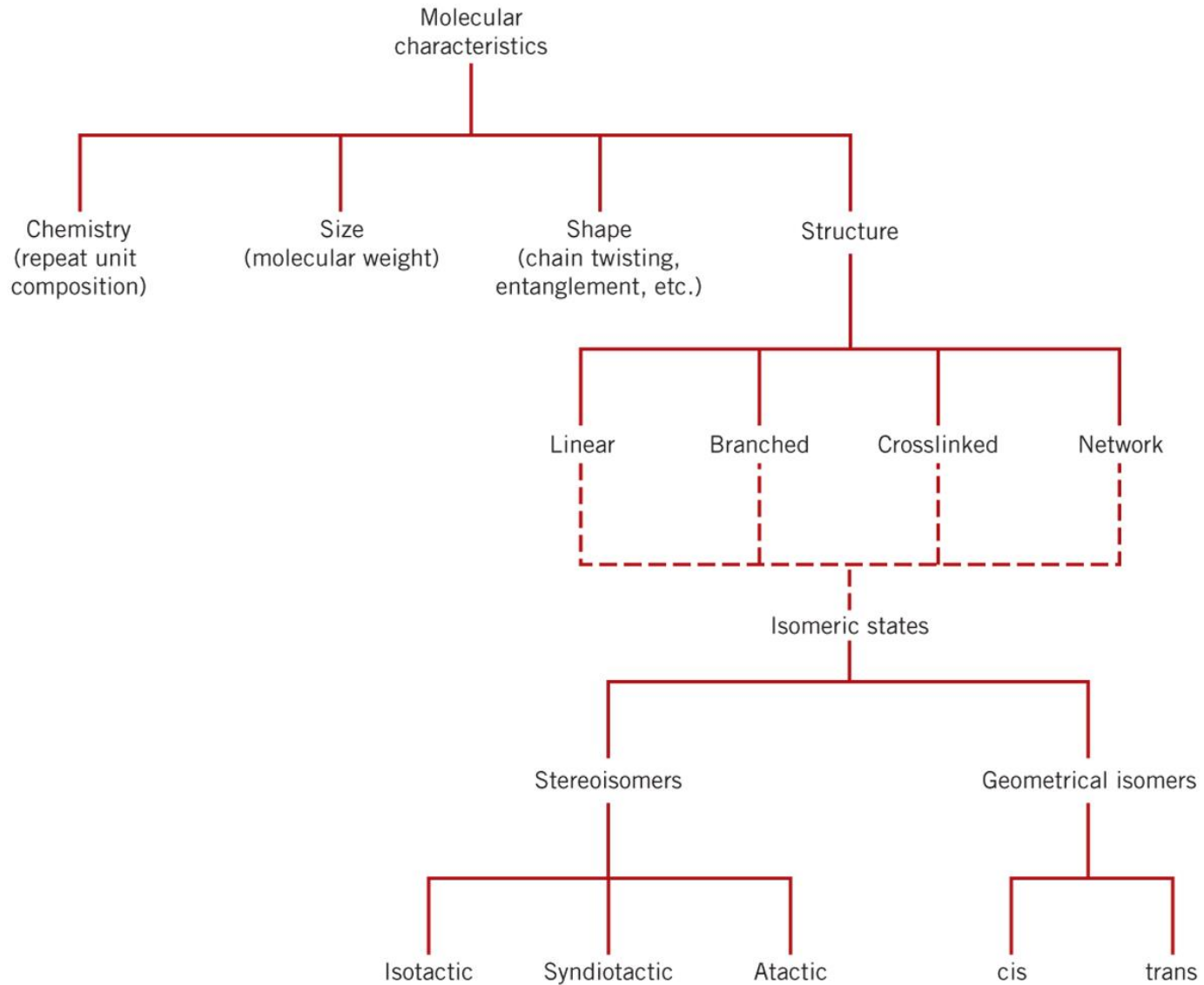
# Degree of Polymerization (2)
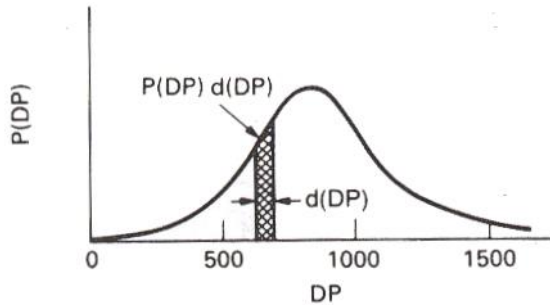
Average **$\overline{DP}$** is simply:
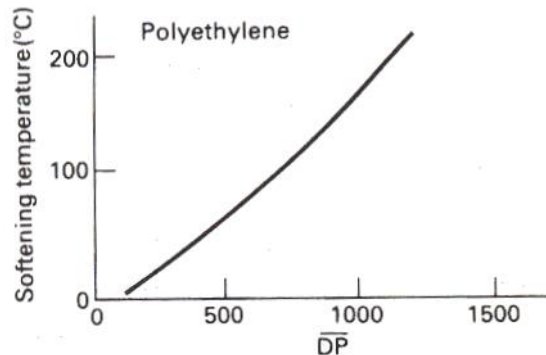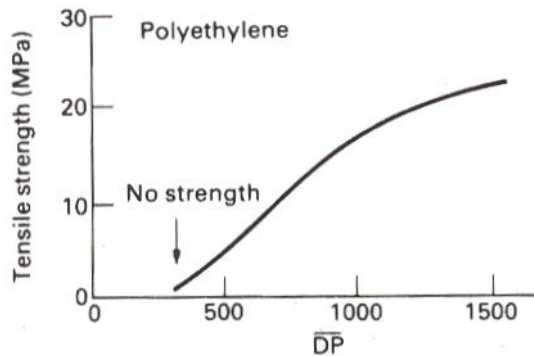
$$\overline{DP} = \int_0^\infty DP \cdot P(DP)d(DP)$$

where P(DP)d(DP) is the fraction of molecules with DP values between DP and DP+d(DP). And the molecular weight, M, is just

**M=m·DP**

where **m** is the molecular weight of monomer

Polymer properties depend on average DP.
Example: higher DP higher **tensile strength** and **melting point**!!
Question: how one can control DP ?!

# Molecular Structure

(a)  **Linear Polymer**: end-to-end joining of mers, single, long flexible chains, van-der-Waals and hydrogen bonds hold chains together (polyethylene etc.)

(b)  **Branched Polymer**: side branch chains connected to main chain, reduced chain packing capability and therefore density

(c)  **Cross-Linked Polymers**: adjacent chains joined by side chains; synthesis at elevated temperatures promotes cross-linking; non-carbon atoms might be involved in cross-linking bond (e.g. sulfur in vulcanization, rubber)

(b)  **Network-Polymers**: highly cross-linked, tri-functional mers can provide three dimensional cross-linking (epoxy resins, phenyl-formaldehyde)
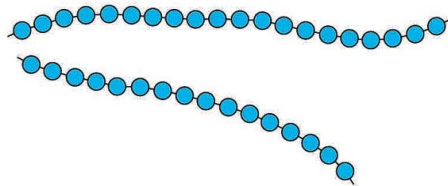


(a)
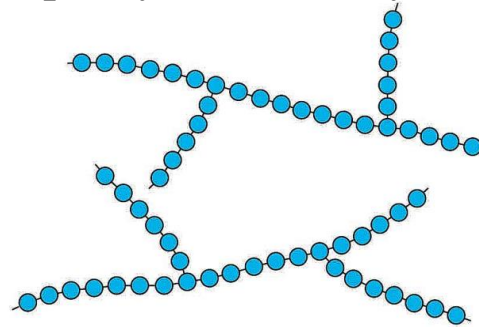
(b)
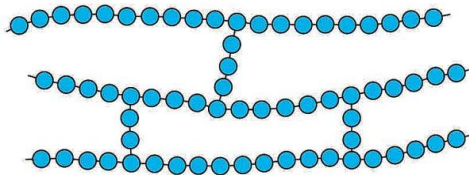
(c)
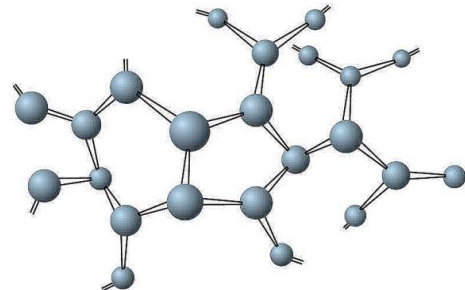
(d)

# Copolymers

**Copolymers** consist of two or more *different mer units*. An idea is similar to this for composites: obtain new polymer properties by combination!!
Depending on the polymerization process and relative fraction of mer types different arrangements are possible.

alternating          graft



random          block
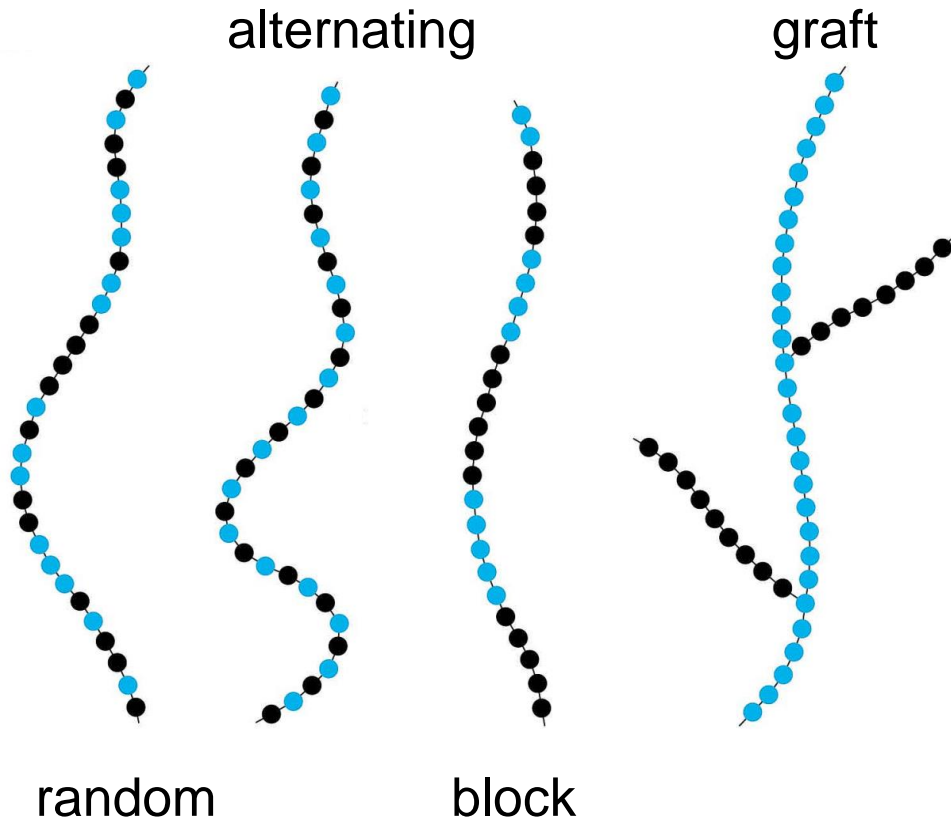
Example: Styrene-butadiene rubber is a common synthetic copolymer
For automobile tires



+          = **SBR**

Styrene          Butadiene
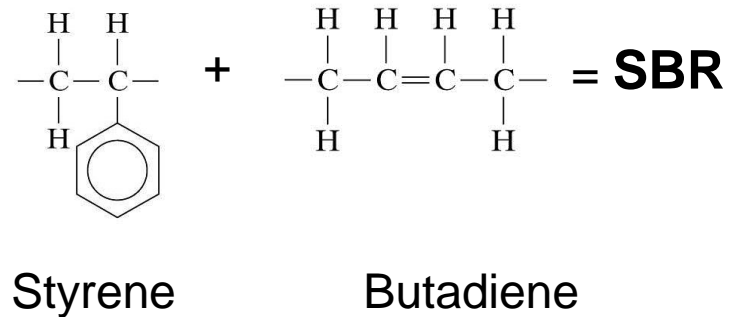
# Stereoisomerism: thermoplastics

- Polyethylene is the simplest linear chain.

By replacing one H atom with a **side-group** or radical **R**→ a <u>vinyl group</u> of polymers

<u>Example: R=Cl (Polyvinyl chloride) or R=CH$_3$ (polypropylene)</u>

**R** gives asymmetry to the repeating units that causes more than one way in which they can be linked to **form** a chain – *stereoisomerism.* Transformation from one in to the other isomer is not possible by bond rotation.


Linear
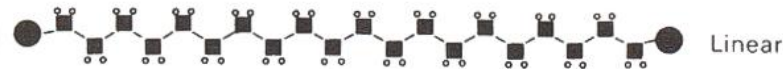

*isotactic configuration*: all R-groups are situated on the same side of the chain
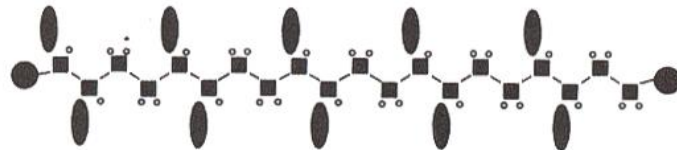

*syndiotactic configuration*: R-groups are situated on alternate sides of the chain
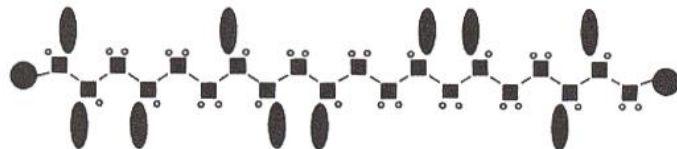

*atactic configuration*: R-groups are arranged in a random position

# POLYMER CRYSTALLINITY (1)

**Reminder:**

• *Crystalline structure:* arrangement of unit cells in a well-defined spatially-ordered manner, which is characterized by translational symmetry

• *Amorphous structures:* random arrangement of units

In polymers the crystalline order can be established by a regular arrangement of the chains. However, since it involves molecules (not atoms) these arrangements are much more complex.



0.255 nm

0.741 nm

0.494 nm

C   H
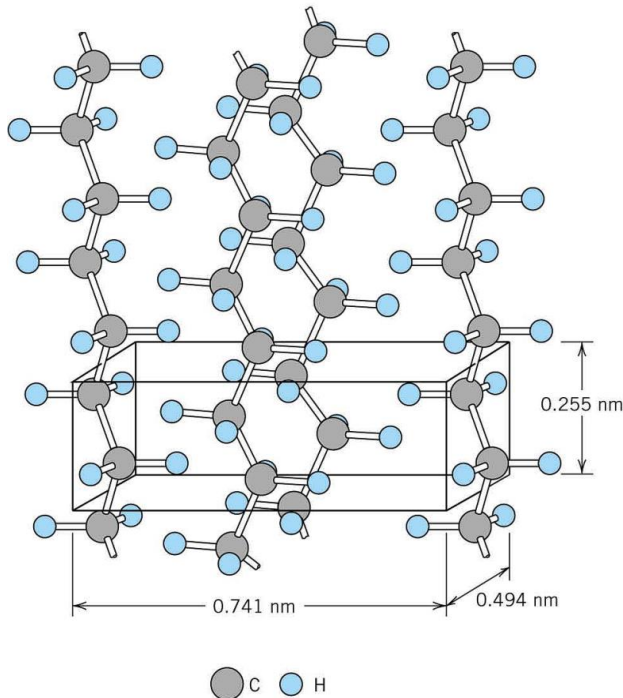
Orthorhombic unit cell (a≠b≠c, $\alpha=\gamma=\beta=90$) of polyethylene. Note that the chain molecules extend beyond the shown unit cell

# Degree of Crystallinity

Degree of crystallinity is determined by:

• **Rate of cooling during solidification**: time is necessary for chains to move and align into a crystal structure

• **Mer complexity**: crystallization less likely in complex structures, simple polymers, such as polyethylene, crystallize relatively easily

• **Chain configuration**: linear polymers crystallize relatively easily; branches inhibit crystallization; network polymers are almost completely amorphous; cross-linked polymers can be both crystalline and amorphous

• **Isomerism**: isotactic, syndiotactic polymers crystallize relatively easily - geometrical regularity allows chains to fit together; atactic difficult to crystallize

• **Copolymerism**: easier to crystallize if mer arrangements are more regular – alternating and block can crystallize more easily as compared to random and graft

More crystallinity: higher density, more strength, higher resistance to dissolution and softening by heating

# Degree of Crystallinity

Thus in polymers crystalline and amorphous regions can coexist. Disturbance of the arrangement of the long chains (twists, kinks...) results in the *local amorphization* of the polymer. Density of the amorphous phase is lower than that of the crystalline Phase. Thus density and can be used to calculate the *degree of crystallinity:*

$$\% \, crystallinity = \frac{\rho_c(\rho_s - \rho_a)}{\rho_s(\rho_c - \rho_a)} \, x100$$

$\rho_c$= density of perfect crystalline polymer
$\rho_a$= density of completely amorphous polymer
$\rho_s$= density of analyzing partially crystalline polymer

# Problem 1

- *For each of the following pairs of polymers, do the following:*
- *(1) state whether it is possible to decide whether one polymer has a **higher tensile** strength than the other;*
- *(2) if this is possible, note which has the higher tensile strength and cite the reason(s) for your choice;*
- *(3) if it is not possible to decide, state why*

- *(a) **Linear and isotactic poly(vinyl chloride)** with a weight-average molecular weight of 100,000 g/mol; **branched and atactic poly(vinyl chloride)** having a weight-average molecular weight of 75,000 g/mol*
- *(b) **Graft acrylonitrile-butadiene copolymer** with 10% of possible sites **crosslinked; alternating acrylonitrile-butadiene** copolymer with 5% of possible sites crosslinked*
- *(c) **Network polyester**; lightly branched **polytetrafluoroethylene***

- (a) **Yes, it is possible**. The linear and isotactic material will have the higher tensile strength. Both linearity and isotacticity favor a higher degree of crystallinity than do branching and atacticity; and tensile strength increases with increasing degree of crystallinity. Furthermore, the molecular weight of the linear/isotactic material is higher (100,000 g/mol versus 75,000 g/mol), and tensile strength increases with increasing molecular weight.

- (b) **No, it is not possible**. Alternating copolymers tend to be more crystalline than graft copolymers, and tensile strength increases with degree of crystallinity. However, the graft material has a higher degree of crosslinking, and tensile strength increases with the percentage of crosslinks.

- (c) **Yes, it is possible**. The network polyester will display a greater tensile strength. Relative chain motion is much more restricted than for the lightly branched polytetra-fluoroethylene since there are many more of the strong covalent bonds for the network structure.

# Problem 2

- *Which of the following would you expect to be **elastomers** and which **thermosetting** polymers at room temperature? Justify each choice.*

- *(a) **Linear and highly crystalline polyethylene***

- *(b) **Phenol-formaldehyde***

- *(c) **Heavily crosslinked polyisoprene** having a glass transition temperature of 50°C (122°F)*

- *(d) **Linear and partially amorphous poly(vinyl chloride)***

- (a) Linear and crystalline polyethylene would be **neither an elastomer nor a thermoset** since it is a linear polymer.

- (b)  Phenol-formaldehyde having a network structure would be **a thermosetting polymer** since it has a network structure.  It would not be an elastomer since it does not have a crosslinked chain structure.

- (c)  Heavily crosslinked polyisoprene having a glass transition temperature of 50°C would be a **thermosetting polymer** because it is heavily crosslinked.  It would not be an elastomer since it is heavily crosslinked and room temperature is below its *Tg*.

- (d)  Linear and partially amorphous poly(vinyl chloride) is **neither an elastomer nor a thermoset**.  In order to be either it must have some crosslinking.

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